THE Chemistry OF Acrylonitrile

Second Edition

CYANAMID

AMERICAN CYANAMID COMPANY

PETROCHEMICALS DEPARTMENT

30 Rockefeller Plaza

New York 20, N. Y.

FOREWORD

The "CHEMISTRY OF ACRYLONITRILE" *was first published in 1951. Since that time acrylonitrile has continued to grow in importance as an industrial chemical. New applications in the fields of plastics and surface coatings have been developed. The use of acrylonitrile as a basic material in the synthetic fiber industry has shown spectacular growth. Its application as a modifier for natural polymers —cyanoethylation of cellulose, proteins and starch—has introduced many new and promising applications.*

As a result of these increased activities, American Cyanamid has felt it necessary to expand and revise its book, the "CHEMISTRY OF ACRYLONITRILE." *The literature appearing since the publication of the first edition has been examined and a large number of references added, resulting in a twofold increase of the bibliography. A major addition is a new section containing tables of reaction conditions, yields, and literature references for many known reactions of acrylonitrile.*

American Cyanamid invites comments and questions on any phase of acrylonitrile chemistry.

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INTRODUCTION

In his discovery of acrylonitrile (1893) Moureu showed it to be the nitrile of acrylic acid having the structure $CH_2=CHCN$. From its first synthesis until just before World War II, acrylonitrile remained a laboratory curiosity. Because of the need for oil resistant rubber for military purposes, acrylonitrile was then produced commercially in the United States and in Germany for copolymerization with butadiene to form the so-called nitrile rubbers.

At the conclusion of hostilities, nitrile rubber requirements slackened and it became necessary to seek new uses for acrylonitrile. First and foremost of these was the acrylic fibers. This development grew rapidly so that at the present time the manufacture of acrylic fibers represents one of the major consuming industries for acrylonitrile. Additional uses have also developed in the plastics, surface coatings, and adhesives industries. Moreover, a variety of promising applications have been found using acrylonitrile as a chemical intermediate and as a modifier for natural polymers.

Because of its highly polar nitrile group and its activated double bond, acrylonitrile can undergo a wide variety of chemical reactions. For example, practically all compounds having a labile hydrogen atom will add across acrylonitrile's double bond. This permits the introduction of the cyanoethyl group into a large variety of molecules. Moreover, the nitrile group itself can be converted into an acid, ester, amide, or amine.

Perhaps the best known reaction is polymerization. Acrylonitrile can be polymerized or copolymerized with a large number of vinyl monomers using a variety of polymerization techniques. Its introduction into copolymers generally results in greater hardness as well as improved oil, chemical, and heat resistance.

These improvements in copolymer properties are the principal reasons for acrylonitrile's commercial utility in the textile, rubber, and plastics fields previously mentioned. Furthermore, as a chemical intermediate it can be used in the synthesis of antioxidants, pharmaceuticals, dyes, surface active agents, etc.

American Cyanamid invites correspondence concerning the application of acrylonitrile in all fields, and will gladly make available its wealth of experience in the chemistry and applications of this reactive compound.

THE Chemistry OF Acrylonitrile

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SYNTHESES OF ACRYLONITRILE

SYNTHESES

The first synthesis of acrylonitrile (1893) involved the removal of water from (a) ethylene cyanohydrin, or (b) acrylamide, by reaction with phosphorus pentoxide (802):

$$\begin{array}{l} \text{(a)}\quad 3HOCH_2CH_2CN + P_2O_5 \searrow \\ \qquad\qquad\qquad\qquad\qquad\quad 3CH_2{=}CHCN + 2H_3PO_4 \\ \text{(b)}\quad 3CH_2{=}CHCONH_2 + P_2O_5 \nearrow \end{array}$$

Currently acrylonitrile is produced commercially from either ethylene cyanohydrin or acetylene and hydrocyanic acid.

Manufacture from Ethylene Cyanohydrin

To effect the decomposition of ethylene cyanohydrin into acrylonitrile and water it is not necessary to remove the evolved water by the use of a dehydrating agent such as phosphorus pentoxide. The decomposition of the cyanohydrin proceeds spontaneously and rapidly in the presence of suitable catalysts, and under the proper conditions (390). The wet acrylonitrile which is produced may be dried by azeotropic distillation, either by itself (214), or with dichloromethane (146), or chloroform (1080).

Manufacture from Acetylene

An early German patent (92) discloses that acrylonitrile is formed when a mixture of acetylene and hydrocyanic acid is passed over the proper catalysts at 400°C. to 500°C.:

$$C_2H_2 + HCN \longrightarrow CH_2{=}CHCN$$

There have been numerous improvement patents on this process (202, 443, 473, 474, 475, 849, 884, 978, 1013, 1015, 1231, 1232).

The reaction also proceeds readily in an aqueous solution of ammonium chloride and cuprous chloride (511, 992, 993). Excess acetylene is used and the acrylonitrile distills from the reactor. It is recovered and refined, largely by additional fractionation.

Other Methods of Synthesis

		Reference
1	Acetonitrile and Formaldehyde	134, 495
2	Acrolein, Ammonia and Oxygen	103, 104, 331, 332, 333, 334
3	Acrolein Oxime	1101
4	Acrylic Acid and Ammonia	64, 914, 915
5	3-Alkoxypropionamides	975, 976
6	3-Alkoxypropionitriles	599
7	Allylamine	746
8	Lactonitrile	644, 922, 1048, 1450
9	3,3′,3″-Nitrilotrispropionamide	871

(*Other Methods of Synthesis—Continued*)

	Reference
10 Propionitrile	98, 151, 351, 457, 706
11 Vinyl Chloride	352
12 Miscellaneous	

Still other methods reported in the literature include the synthesis of acrylonitrile from various hydrocarbons and hydrocyanic acid (884, 979), from ethylene and cyanogen chloride (35), and from various olefins with ammonia and oxygen (201, 274, 320, 1016).

PHYSICAL PROPERTIES

The important physical properties of acrylonitrile are listed below.

A) *Physical Constants*

Appearance	Colorless liquid
Burning Velocity (1122)	47.0 cm./sec. (in air)
Critical Pressure (1)	34.9 atms.
Critical Temperature (1)	246°C.
Cryoscopic Constant (341, 611, 1164)	2.7 mole %/°C.
Density (1, 312, 341, 641, 1113, 1120)	0.8060 (20°C.) 0.8004 (25°C.) $d = 0.8281 - 0.001106t$ (0-30°C.)
Dielectric Constant (1, 312)	38 (33.5 megacycles)
Dipole Moment (559, 621, 930, 1150)	3.3×10^{-18} e.s.u.-cm. (in CCl_4) 3.51×10^{-18} e.s.u.-cm. (in C_6H_6) 3.88×10^{-18} e.s.u.-cm. (vapor phase)
Explosive Limits (554, 614)	3.05 to $17.0 \pm 0.5\%$ (by volume in air at 25°C.)
Flash Point (Tagliabue Open Cup—1, 312)	0°C. (32°F.)
Freezing Point (341, 611, 1164)	-83.55 ± 0.05°C.
Ignition Temperature (1)	481°C. (898°F.)
Ionization Potential (792)	10.75 electron-volts
Molar Polarization (930)	266.0 cc. (25°C.)
Molar Refraction (341, 930, 1120)	15.67 (D line)
Molecular Weight (theory)	53.06
Odor	Faintly pungent
Parachor (341, 1120)	150.1 (15.1°C.) 151.1 (40.6°C.)
Refractive Index (1, 95, 312, 341, 1120)	$n_D^{25} = 1.3888$
Surface Tension (1, 341, 1120)	27.3 dynes/cm. (24°C.)
Surface Tension of Aqueous Solutions (145)	$C = 0.223d - 0.0018d^2 + 0.00013d^3$ ($C = 0 - 6$ weight percent, d = dynes/cm.)
Vapor Density (theoretical)	1.83 (Air = 1.0)
Vapor Pressure (95, 312, 341, 477, 1038)	See also Figure 1

(*Physical Constants of Acrylonitrile—Continued*)

Pressure, mm. Hg	Temperature, °C.
50	8.7
100	23.6
250	45.5
500	64.7
760	77.3

Vapor Pressure, Partial Water Azeotrope (1, 477)	$\text{Log } p = 7.518 - \frac{1644.7}{T}$
Aqueous Solutions	See Figure 7
Viscosity (1, 341)	0.34 centipoises (25°C.)

B) Azeotropes

	B.P., °C.	Wt. % Acrylonitrile
Benzene (547)	73.3	47
Carbon Tetrachloride (547)	66.2	21
Chlorotrimethylsilane (951)	57	7
Methyl Alcohol (547)	61.4	39
Isopropyl Alcohol (547)	71.7	56
Tetrachlorosilane (950, 951)	51.2	89
Water (1, 126, 312, 547)	71	88

C) Solubilities (1, 312, 341, 403, 611)

	Temp., °C.	% H_2O in Acrylonitrile	% Acrylonitrile in H_2O
Water	0	2.1	7.2
	20	3.1	7.35
	40	4.8	7.9

Organic Solvents	Miscible with most organic solvents including acetone, benzene, carbon tetrachloride, ether, ethyl acetate, ethyl alcohol, ethylene cyanohydrin, liquid carbon dioxide, methyl alcohol, petroleum ether, toluene, xylene, and some kerosenes.

Aqueous Bases and Alkali Salts (1213, 1305)
Three-Component System, Styrene-acrylonitrile-water (585)
Solubility Parameter, 10.5 $[\text{cal./cc.}]^{1/2}$ (972)

D) Spectra

Infrared (1, 82, 315, 459, 1003, 1088, 1095)	See Figure 2
Raman (1, 459, 911, 1091)	See Figure 3
Ultraviolet (1, 312, 930, 1051)	See Figure 4
Microwave (1150)	
Proton Magnetic (769)	

Mass Spectrum (1)

m/e	Intensity*	m/e	Intensity*	m/e	Intensity*
12	7.9	26	94.7	39	2.4
13	3.6	26.5	0.3	40	0.3
14	4.3	27	20.0	50	8.6
15	0.4	28	4.6	51	33.6
24	4.5	36	3.0	52	76.7
25	11.5	37	5.2	53	100.0
25.5	0.3	38	8.1	54	3.6

*Consolidated Model No. 21-103 spectrometer. Relative intensities at 70 ionizing volts and ion-source temperature of 270°C. Only peaks greater than 0.2% of base peak are listed. Ratio of sensitivity of acrylonitrile at mass 53 to sensitivity of *n*-butane at mass 43 is 0.55.

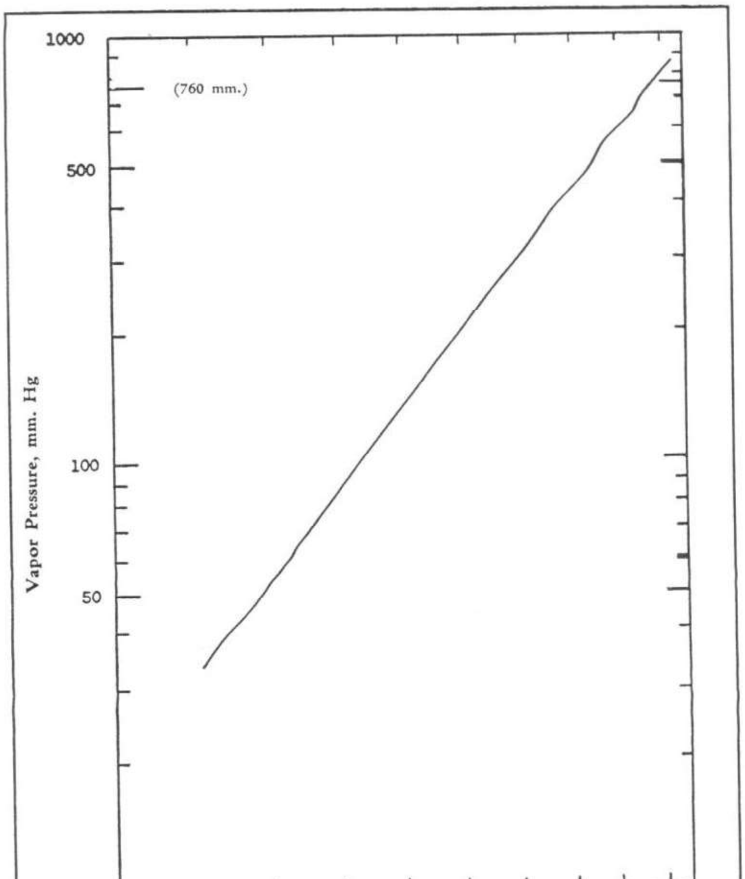


Figure 1 Vapor Pressure of Acrylonitrile.

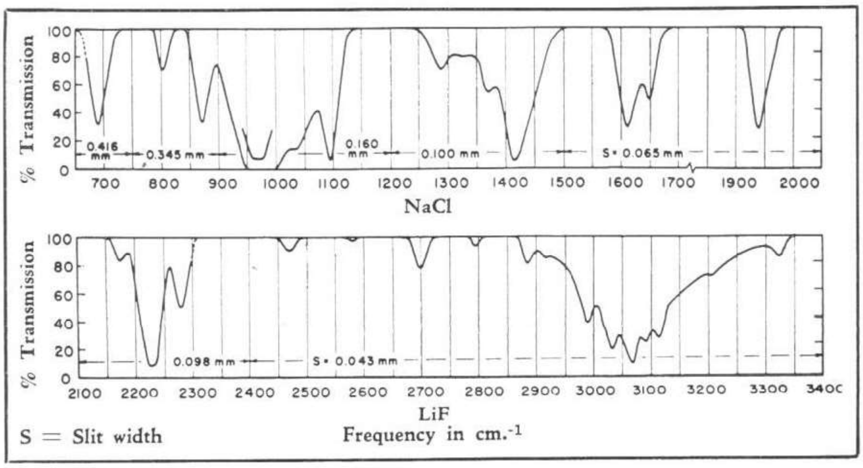


Figure 2 Infrared Spectrum of Liquid Acrylonitrile.

(Cell Length = 0.1 mm.; Temperature = 25°C.)

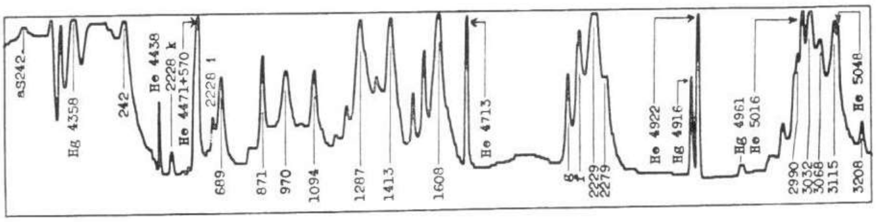


Figure 3 Raman Spectrum of Liquid Acrylonitrile Excited by Hg 4358 Å.

(The strongest lines also appear excited by Hg 4358 Å [f], Hg 4339 Å [g], Hg 4078 Å [i] and Hg 4047 Å [k]. The Raman lines are given in wave-numbers [cm.$^{-1}$].)

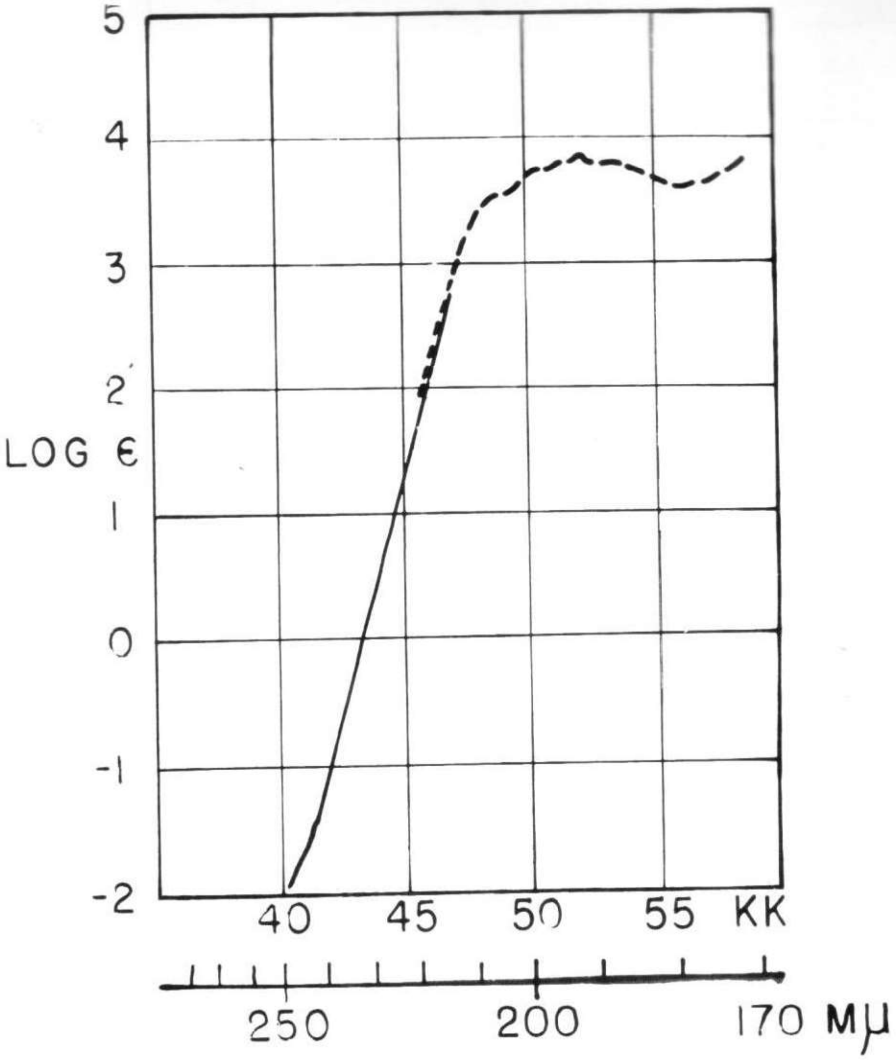


Figure 4 Ultraviolet Absorption Spectrum of Acrylonitrile

The logarithm of the molar absorptivity is plotted against linear energy in kilokaysers (10^3 cm.$^{-1}$) and a non-linear wavelength scale in millimicrons. The molar absorptivity is equal to the absorbance divided by the product of the cell light path length in centimeters and concentration in moles per liter. The solid line represents undiluted liquid acrylonitrile examined in cells of various light path lengths down to 0.05 mm., versus water. The dashed line represents the spectrum of acrylonitrile in solution in heptane, examined with heptane in the comparison cell, and is reproduced from H. B. Klevens and J. R. Platt, "Survey of Vacuum Ultraviolet Spectra of Organic Compounds in Solution," Tech. Report ONR Contract N6ORI-20, Task Order IX, Project NR 019 101 (1954), by permission of the authors.

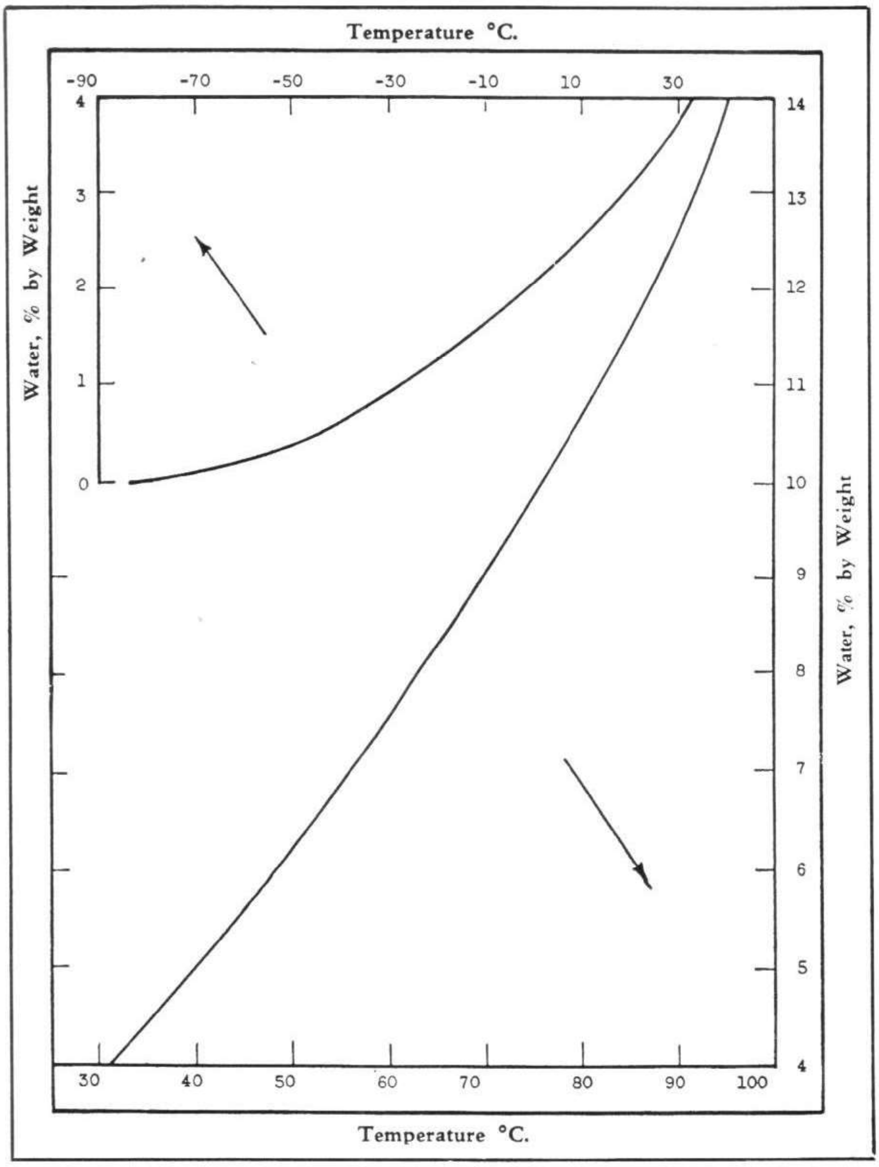


Figure 5 The Solubility of Water in Acrylonitrile.

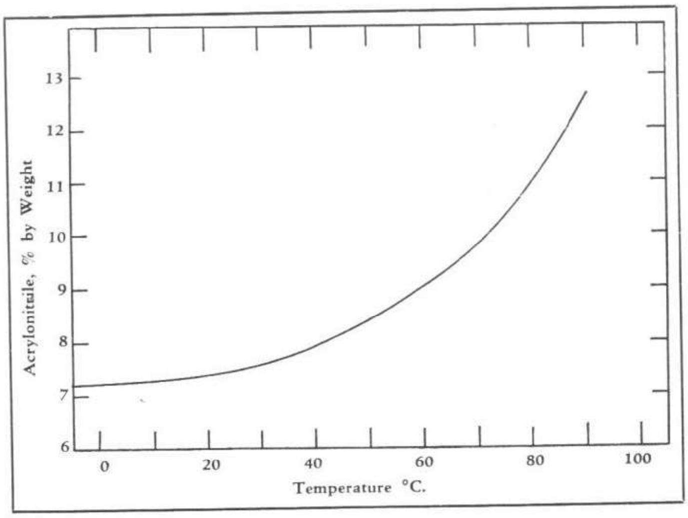


Figure 6 The Solubility of Acrylonitrile in Water.

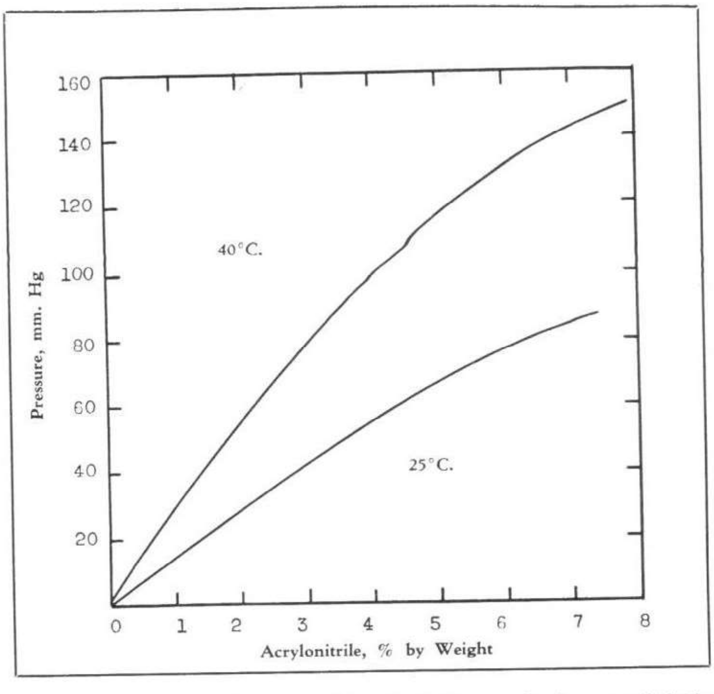


Figure 7 Partial Vapor Pressure of Acrylonitrile over its Aqueous Solutions at 25° and 40°C.

E) *Structure*

The infrared and Raman spectra of liquid acrylonitrile shown in Figures 2 and 3 and the microwave spectra of acrylonitrile vapor (1150) are compatible with a planar structure and the assumed bond distances given in Figure 8 ($\alpha \sim 120°$). Assignments of the vibrational frequencies are available in the literature together with calculations of the thermodynamic functions for the vapor over the temperature range 25-727°C. (459, 647). Combination of these data with the measured heats of vaporization and combustion, assuming perfect gas behavior, yields the thermodynamic data reported in Section F.

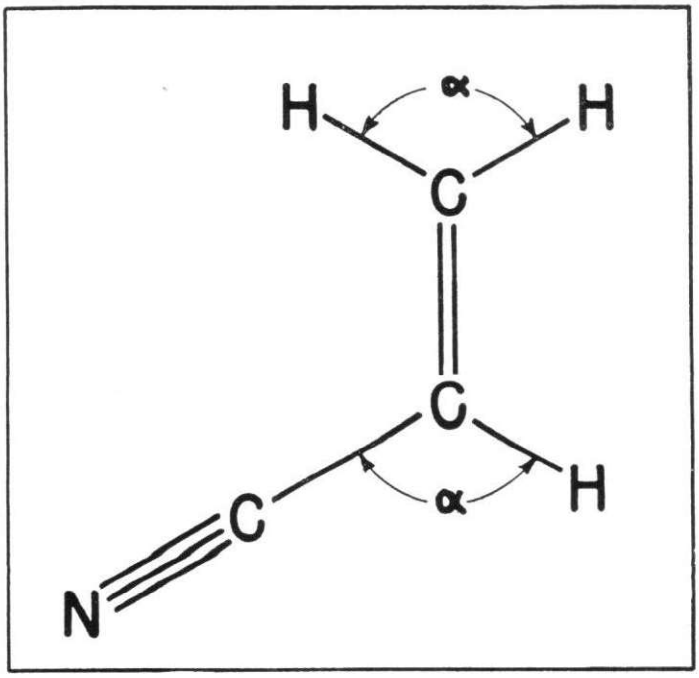


Figure 8 Structure of Acrylonitrile (1150)

$C-C \sim 1.46$ Å
$C=C \sim 1.38$ Å
$C-H \sim 1.09$ Å
$C=N \sim 1.16$ Å
$\alpha \sim 120°$

F) *Thermodynamic Data* (1, 341, 459, 611)

Entropy (vapor), S	65.47 cal./deg./mole (25°C., 1 atm.)
Free Energy of Formation (vapor), ΔF	+45.37 kcal./mole (25°C.)
Heat of Combustion (liquid), ΔH	−420.8 kcal./mole (25°C.)
Heat of Formation (liquid), ΔH	+36.20 ± 0.13 kcal./mole (25°C.)

(*Thermodynamic Data for Acrylonitrile—Continued*)

Heat of Vaporization, ΔH	7.8 kcal./mole (0-77°C.)
Molar Heat Capacity (liquid), Cp.	26.5 ± 1.5 cal./mole/deg.
Molar Heat Capacity (vapor), Cp.	$6.75 + 33.27 \times 10^{-3}$ T -10.91×10^{-6} T^2 cal./mole/deg. (77-1000°C., 1 atm.)
Molar Heat of Fusion	1585 ± kcal./mole

G) Stability

Highly purified acrylonitrile may polymerize spontaneously, particularly in the absence of oxygen or on exposure to visible light. This may be prevented by the incorporation of traces of ammonia, ammonium carbonate, or one of the products resulting from the reaction of ammonia with acrylonitrile (313, 314). Other stabilizing agents have been claimed in the literature (123, 217, 260, 493, 673, 744, 745, 824, 1005, 1119, 1167).

Acrylonitrile polymerizes violently in the presence of concentrated alkali (1). Extreme caution should be exercised if it is found necessary to treat acrylonitrile with strongly alkaline materials. Alkali is used as a catalyst for many of the reactions of acrylonitrile, especially the cyanoethylation reactions, but the amounts involved are small and the cyanoethylation reactions are almost always rapid. It is customary, however, to add the acrylonitrile gradually to the alkaline reaction mixture in order to prevent the accumulation of appreciable amounts of unreacted acrylonitrile. In this manner violent polymerization is avoided.

On standing, acrylonitrile may slowly develop a yellow color particularly after excessive exposure to light. This is prevented by the addition of a small amount of water (36, 213). It is also reported that aluminum, ammonium, cadmium, mercuric and zinc chlorides inhibit color development (749).

H) Handling Precautions (138, 880)

In its technical bulletin entitled, "Handling-Storage-Analyses of Acrylonitrile," American Cyanamid has presented detailed procedures for the proper handling and storage of acrylonitrile. This section summarizes these procedures. For additional details the reader is referred to the above bulletin.

During the time of its large-volume commercial use, acrylonitrile has enjoyed a good record of safe handling. This record has been achieved in spite of the fact that acrylonitrile is explosive, flammable and toxic. It is toxic by ingestion, inhalation, and absorption of vapors or liquids through the skin. It has a low flash point (0°C.), and will form explosive mixtures with air over a range of 3 to 17 volume-percent of acrylonitrile vapor.

Because of these hazards, acrylonitrile should be stored and used in closed systems wherever possible. Work areas should be adequately ventilated, and should be free from open lights, flames, and equipment that is not explosion-proof. Workers should be instructed in the proper handling procedures, and should be provided with the necessary protective clothing and equipment.

CHEMICAL PROPERTIES

Acrylonitrile is an exceptionally versatile chemical intermediate. Its easy introduction into a large variety of compounds affords convenient syntheses of 3-substituted propionitriles, propionamides, propionic acids and esters, and propylamines. Under proper conditions acrylonitrile polymerizes, either by itself or with other monomers.

These chemical properties are discussed briefly in this section. Tables are provided which systematically outline the known reactions of acrylonitrile, giving reaction conditions, yields, and physical properties of products. Where more than one reference describes the same reaction, only the conditions claiming the best yield are listed, although all the pertinent additional references are cited.

REACTIONS OF THE NITRILE GROUP

Hydration and Hydrolysis (*See Table* I)

Acrylonitrile is hydrated rapidly at 100°C. by 84.5% sulfuric acid ($H_2SO_4 \cdot H_2O$) to produce acrylamide sulfate, which upon neutralization yields free acrylamide (9, 30):

$$CH_2{=}CHCN + H_2O + H_2SO_4 \longrightarrow CH_2{=}CHCONH_2 \cdot H_2SO_4$$

$$CH_2{=}CHCONH_2 \cdot H_2SO_4 + CaO \longrightarrow CH_2{=}CHCONH_2 + CaSO_4 + H_2O$$

When acrylonitrile is heated with less concentrated sulfuric acid, or when acrylamide sulfate is heated with additional water, acrylic acid and ammonium bisulfate are formed:

$$CH_2{=}CHCONH_2 \cdot H_2SO_4 \longrightarrow CH_2{=}CHCOOH + NH_4HSO_4$$

The rate of hydrolysis of acrylonitrile with aqueous alkali has been studied (737):

$$CH_2{=}CHCN + 2H_2O \xrightarrow[OH^-]{H^+ \text{ or}} CH_2{=}CHCOOH + NH_3$$

When hydrochloric acid is used to catalyze the hydration- and hydrolysis-reactions, addition of hydrogen chloride also occurs. Good yields of either 3-chloropropionamide or 3-chloropropionic acid may be obtained (80, 580):

$$CH_2{=}CHCN + HCl + H_2O \longrightarrow ClCH_2CH_2CONH_2$$

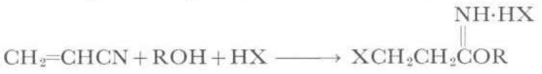
$$CH_2{=}CHCN + HCl + 2H_2O \longrightarrow ClCH_2CH_2COOH + NH_4Cl$$

The reaction of acrylonitrile with alcohols in the presence of concentrated sulfuric acid may be used to prepare esters of acrylic acid (518, 1156). Acrylamide sulfate is formed as the intermediate:

$$CH_2{=}CHCN + H_2SO_4 \cdot H_2O \longrightarrow CH_2{=}CHCONH_2 \cdot H_2SO_4$$

$$CH_2{=}CHCONH_2 \cdot H_2SO_4 + ROH \longrightarrow CH_2{=}CHCOOR + NH_4HSO_4$$

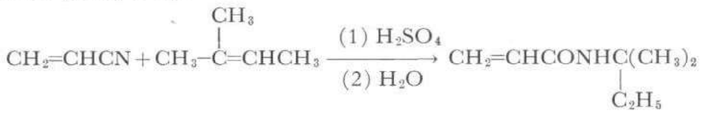
Imido ethers have been prepared by reacting acrylonitrile with alcohols in the presence of anhydrous hydrogen halides (890):



$$CH_2{=}CHCN + ROH + HX \longrightarrow XCH_2CH_2\overset{\overset{\textstyle NH\cdot HX}{\|}}{C}OR$$

Reactions with Olefins and with Alcohols (*See Table* IIa *and* IIb)

Acrylonitrile reacts with olefins in concentrated sulfuric acid to produce N-substituted acrylamides. In a typical example, acrylonitrile is added to a solution of olefin in sulfuric acid. After a short holding period at 30-40°C., the product is precipitated by pouring the reaction mixture into water. Thus 2-methyl-2-butene and acrylonitrile form N-(1,1-dimethylpropyl)-acrylamide (923, 924):



$$CH_2{=}CHCN + CH_3{-}\overset{\overset{\textstyle CH_3}{|}}{C}{=}CHCH_3 \xrightarrow[(2)\ H_2O]{(1)\ H_2SO_4} CH_2{=}CHCONH\underset{\underset{\textstyle C_2H_5}{|}}{C}(CH_3)_2$$

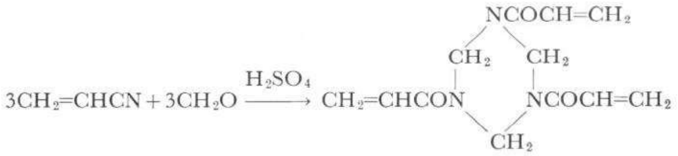
Acrylonitrile will also react with tertiary alcohols to give N-substituted acrylamides. Thus *tert*-butyl alcohol treated with acrylonitrile in sulfuric acid gives excellent yields of N-*tert*-butylacrylamide (879):

$$CH_2{=}CHCN + HOC(CH_3)_3 \xrightarrow{H_2SO_4} CH_2{=}CHCONHC(CH_3)_3$$

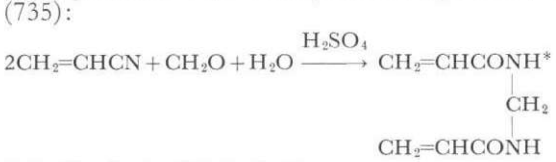
Secondary alcohols such as isopropyl alcohol and cyclohexanol also react to give the corresponding N-substituted acrylamides (879).

Reactions with Aldehydes and Methylol Compounds (*See Table* III)

Anhydrous formaldehyde (meta- or paraformaldehyde) reacts exothermically with acrylonitrile in the presence of catalytic amounts of concentrated sulfuric acid to produce 1,3,5-triacrylylhexahydro-*s*-triazine (1137):



The reaction of acrylonitrile with formaldehyde in the presence of excess 85%-sulfuric acid produces N,N′-methylenebisacrylamide, a good cross linking agent (735):



$$2CH_2{=}CHCN + CH_2O + H_2O \xrightarrow{H_2SO_4} \begin{array}{l} CH_2{=}CHCONH^{*} \\ \qquad\qquad\quad | \\ \qquad\qquad\ CH_2 \\ \qquad\qquad\quad | \\ CH_2{=}CHCONH \end{array}$$

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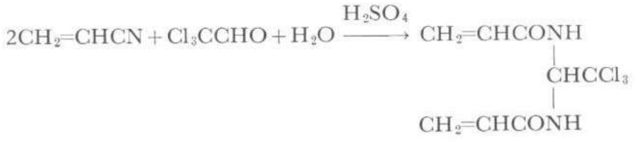
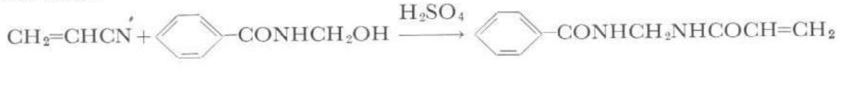
*American Cyanamid Co., New Product Bulletin No. 24

An analogous reaction is observed with chloral (735):



$$2CH_2{=}CHCN + Cl_3CCHO + H_2O \xrightarrow{H_2SO_4} \begin{array}{l} CH_2{=}CHCONH \\ \quad\;\; | \\ \quad\;\; CHCCl_3 \\ \quad\;\; | \\ CH_2{=}CHCONH \end{array}$$

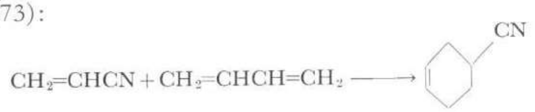
N-Methylol compounds, such as N-methylolbenzamide (804), yield mixed bisamides when allowed to react with acrylonitrile in the presence of sulfuric acid:



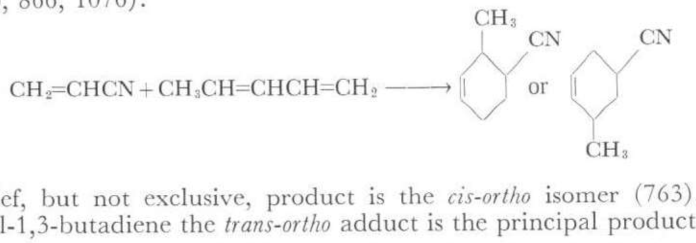
REACTIONS OF THE DOUBLE BOND

Diels-Alder and Related Reactions (*See Table* IV)

Acrylonitrile is a member of a class of organic compounds having activated double bonds which act as dienophiles in the Diels-Alder reaction. Upon heating with aliphatic or alicyclic compounds containing a system of conjugated carbon-to-carbon double bonds, it reacts to form cyclic products. A typical example is the reaction of 1,3-butadiene with acrylonitrile to produce 3-cyclohexene-1-carbonitrile, an intermediate in the synthesis of pimelic acid (873):



The reaction of acrylonitrile with piperylene is particularly interesting because of the possibility of forming two pairs of *cis-trans* isomers (45, 404, 530, 763, 866, 1076):



The chief, but not exclusive, product is the *cis-ortho* isomer (763). With 1-phenyl-1,3-butadiene the *trans-ortho* adduct is the principal product (762).

In most examples of Diels-Alder reactions of acrylonitrile, hydroquinone or another polymerization inhibitor is used. Temperatures of 100-150°C. are commonly maintained from 5 to 24 hours.

Several reactions related to the Diels-Alder reaction have been carried out with acrylonitrile, but with acrylonitrile acting as the diene rather than the dienophile. Prolonged heating of acrylonitrile with tetrafluoroethylene at 125-130°C. produces 2,2,3,3-tetrafluorocyclobutanecarbonitrile (258):

$$CH_2{=}CHCN + F_2C{=}CF_2 \longrightarrow \begin{array}{l} F_2C{-}CH_2 \\ \;\;\,|\quad\;\; | \\ F_2C{-}CHCN \end{array}$$

The dimerization of acrylonitrile at 190-200°C. under pressure is another reaction of this type (284):

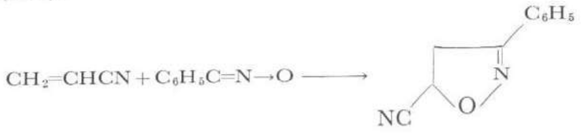
$$2CH_2{=}CHCN \longrightarrow \begin{array}{l} CH_2{-}CHCN \\ | \quad\quad | \\ CH_2{-}CHCN \end{array}$$

Both the *cis*- and *trans*-cyclobutanedicarbonitriles are obtained.

On the other hand, chlorotrifluoroethylene and water react under similar conditions to yield 2,2-difluoroglutaric acid (1202):

$$CH_2{=}CHCN + CF_2{=}CFCl + H_2O \longrightarrow HOOCCF_2CH_2CH_2COOH$$

An interesting cycloaddition-reaction occurs on refluxing acrylonitrile with the N-oxide of benzonitrile in ether, giving 3-phenyl-2-isoxazoline-5-carbonitrile (301):

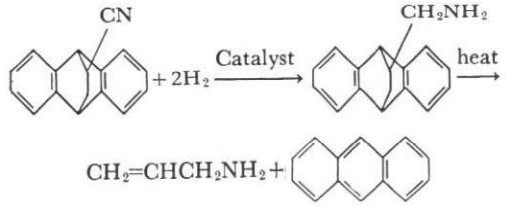


Hydrogenation (*See Table* V)

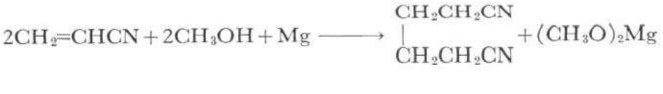
The hydrogenation of acrylonitrile may be accomplished in excellent yields by the use of either copper (913), rhodium (503), or nickel (1, 159) catalysts to give propionitrile. This may be further hydrogenated to propylamine:

$$CH_2{=}CHCN + H_2 \xrightarrow{\text{Catalyst}} CH_3CH_2CN \xrightarrow{2H_2} CH_3CH_2CH_2NH_2$$

The synthesis of allylamine by the hydrogenation of acrylonitrile has not been reported. However, allylamine may be prepared by reduction of the Diels-Alder adduct of acrylonitrile and anthracene, followed by thermal cleavage of the adduct (822):



Chemical reduction under alkaline conditions as, for example, with methyl alcohol and magnesium in an anhydrous medium (687), or with sodium amalgam in aqueous solution (589), produces adiponitrile in low yields. In the latter case, hydrolysis to adipic acid occurs concurrently:



$$2CH_2{=}CHCN + 2CH_3OH + Mg \longrightarrow \begin{array}{l} CH_2CH_2CN \\ | \\ CH_2CH_2CN \end{array} + (CH_3O)_2Mg$$

Halogenation (*See Table* VI)

The halogenation of acrylonitrile at low temperatures proceeds via the addition of a molecule of halogen to produce 2,3-dihalopropionitriles:

$$CH_2{=}CHCN + X_2 \longrightarrow XCH_2CHXCN$$

At elevated temperatures and in the absence of ultraviolet light, the addition reaction is accompanied by evolution of hydrogen halide followed by the addition of a second molecule of halogen to produce 2,2,3-trihalopropionitrile:

$$XCH_2CHXCN \longrightarrow CH_2{=}CXCN + HX$$

$$CH_2{=}CXCN + X_2 \longrightarrow XCH_2CX_2CN$$

In the presence of ultraviolet light both the 2,2,3- and 2,3,3-isomers are obtained.

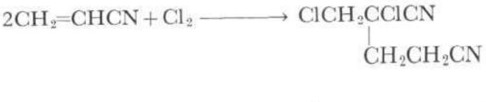
The simple, uncatalyzed addition of a halogen to acrylonitrile is a slow reaction at ordinary temperatures (368, 494, 674). After a considerable induction period the reaction spontaneously accelerates, possibly as a result of catalysis by the hydrogen halide which is formed as a by-product. Rate measurements for the chlorination and bromination of acrylonitrile in dilute acetic acid solution have been reported, and catalysis of bromination by added hydrobromic acid has been demonstrated (368).

A catalyzed reaction involving chlorine and acrylonitrile in pyridine solution has been reported to give almost quantitative yields of 2,3-dichloropropionitrile (140). Reactions illuminated by a 200-watt lamp are also reported to proceed readily (1039).

If acrylonitrile is chlorinated in aqueous solution the hypochlorous acid present reacts to form 2-chlorohydracrylonitrile (324, 1100):

$$CH_2{=}CHCN + HOCl \longrightarrow HOCH_2CHClCN$$

A dichloroglutaronitrile derivative also may be obtained by the action of chlorine on aqueous solutions of acrylonitrile (1121):



$$2CH_2{=}CHCN + Cl_2 \longrightarrow \begin{array}{l} ClCH_2CClCN \\ \quad\;\; | \\ \quad\;\; CH_2CH_2CN \end{array}$$

Simultaneous alcoholysis and chlorination occur to give 2,3-dichloropropionic acid esters when acrylonitrile is reacted with chlorine in aqueous alcoholic solutions containing sulfuric acid (325):

$$CH_2{=}CHCN + Cl_2 + ROH \xrightarrow[H_2O]{H_2SO_4} ClCH_2CHClCOOR + NH_4HSO_4$$

The methyl, ethyl, propyl and isopropyl esters have been prepared in this manner (325).

Formation of 1,2,2,3-tetrachloro-N-2-chloroethylpropylidenimine is observed when a mixture of acrylonitrile and ethylene is reacted with chlorine (200);

$$CH_2{=}CHCN + CH_2{=}CH_2 + 3Cl_2 \longrightarrow ClCH_2CH_2N{=}CClCCl_2CH_2Cl + HCl$$

When nitryl chloride, a pseudohalogen, is added to cold acrylonitrile the principal product is 2-chloro-3-nitropropionitrile (139, 991):

$$CH_2{=}CHCN + NO_2Cl \longrightarrow NO_2CH_2CHClCN$$

When the reaction is carried out in ether, 3-nitroacrylonitrile is the principal product (991).

The various halogenated propionitriles may be dehydrohalogenated by the action of tertiary amines (696, 697, 1014), sodium acetate (1, 140), potassium cyanide (141), phosphorus pentoxide (140), or heat (140, 251, 697, 1160), or dehalogenated by metals (247) to produce a variety of halogen-substituted acrylonitriles.

2-Chloroacrylonitrile may be prepared by simultaneous chlorination and dehydrohalogenation of acrylonitrile. This results when acrylonitrile and chlorine are passed over activated carbon at high temperatures (707).

A particularly interesting reaction of 2,3-dichloroacrylonitrile involves treatment with ammonia or various amines to give 3-amino-2-chloroacrylonitrile or derivatives (363, 781):

$$CHCl{=}CClCN + 2NH_3 \longrightarrow H_2NCH{=}CClCN + NH_4Cl$$

A more detailed description of the reactions of acrylonitrile with halogens is presented in Cyanamid's Petrochemical Department Bulletin PD-5 entitled "The Reaction of Acrylonitrile with Halogens."

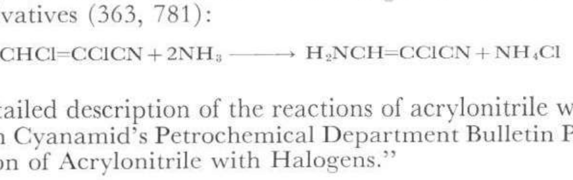
Reactions with Diazo Compounds (*See Table* VII)

2-Halo-3-arylpropionitriles may be prepared by the Meerwein reaction of diazonium chlorides and bromides with acrylonitrile at low temperatures:

$$CH_2{=}CHCN + C_6H_5N_2{}^+Cl^- \xrightarrow[\text{acetone}]{Cu^{++}} C_6H_5CH_2CHClCN + N_2$$

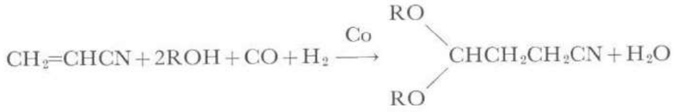
The reaction is conducted in aqueous acetone solutions in which the diazotized amine solution has been neutralized with sodium acetate. Catalytic amounts of cupric chloride are necessary for the reaction (654).

An unusual reaction occurs between 9-diazofluorene and acrylonitrile in the absence of a catalyst to produce a cyanocyclopropane derivative (537, 538):



Reactions with Alcohols and Carbon Monoxide (*See Table* VIII)

A process for the preparation of 3-cyanopropionaldehyde acetals has been reported (86). This reaction involves the treatment of acrylonitrile with an alcohol, carbon monoxide, hydrogen, and a cobalt hydrogenation catalyst at temperatures of 100-200°C. and pressures of 1200 atmospheres:



$$CH_2{=}CHCN + 2ROH + CO + H_2 \xrightarrow{Co} (RO)_2CHCH_2CH_2CN + H_2O$$

When cobalt octacarbonyl is employed (458), a mixture of C_{15} amines is obtained.

Reactions with Miscellaneous Compounds (*See Table* IX)

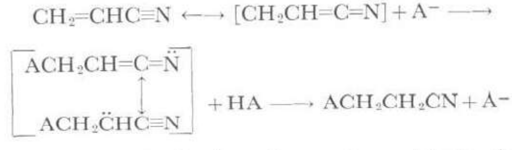
Acrylonitrile is reported to react with ozone to give a product which will catalyze the polymerization of ethylene (721).

Trifluoroiodomethane reacts with acrylonitrile under the influence of ultraviolet light to produce 4,4,4-trifluoro-2-iodobutyronitrile (484):

$$CH_2{=}CHCN + CF_3I \longrightarrow F_3CCH_2CHICN$$

CYANOETHYLATION REACTIONS

There are a great many compounds possessing the grouping HA (wherein H is a reactive hydrogen atom) which add readily to the carbon-carbon double bond of acrylonitrile. In each case a 3(or β)-substituted propionitrile is the primary reaction product. Although little kinetic evidence for the reaction mechanism has been presented, it is reasonable to assume that in most cases this reaction proceeds by attack of the anion of HA on the positively polarized β-carbon atom. This is followed by the transfer of a proton from a neutral HA molecule (or from solvent) to the α-carbon atom:



$$CH_2{=}CHC{\equiv}N \longleftrightarrow [CH_2CH{=}C{=}\ddot{N}] + A^- \longrightarrow$$

$$\left[\begin{array}{c} ACH_2CH{=}C{=}\ddot{N} \\ \updownarrow \\ ACH_2\ddot{C}HC{\equiv}N \end{array}\right] + HA \longrightarrow ACH_2CH_2CN + A^-$$

It has not been determined whether the proton adds to the nitrogen atom (1,4-addition), followed by rearrangement, or whether the proton adds directly to the α-carbon atom (1,2-addition).

The compounds that have been added to acrylonitrile to produce cyanoethyl derivatives may be classified according to the atom attached to the reactive hydrogen. Thus, examples of cyanoethylation of compounds containing As-H, B-H, Br-H, C-H, Cl-H, N-H, O-H, P-H, S-H, Si-H and Sn-H bonds have been reported. Among the specific classes of compounds that readily undergo the cyanoethylation reaction are a variety of alcohols, aldehydes, amines, amides, esters, ketones, mercaptans and inorganic acids and their salts. In nearly every case a strong base is used to catalyze the reaction. However, in the case of most N-H, P-H and As-H compounds, no catalyst is required, while aryl amines (e.g., aniline) require an acidic catalyst.

Carbon-Cyanoethylation

ALDEHYDES (*See Table* X)

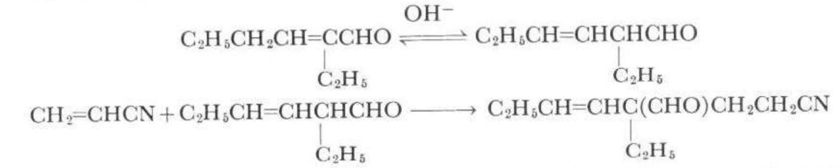
The reaction of acrylonitrile with aldehydes containing at least one hydrogen atom on the 2(or α)-carbon atom leads to formation of derivatives of 4-cyanobutyraldehyde:

$$CH_2{=}CHCN + RR'CHCHO \longrightarrow NCCH_2CH_2CRR'CHO$$

If there is more than one hydrogen atom at the α-position, a mixture of the mono- and di-cyanoethylated derivatives is usually obtained (1124).

Particular care must be taken to prevent aldolization when working with aldehydes such as acetaldehyde, isobutyraldehyde and propionaldehyde (180, 182). Good yields of the cyanoethylated products are obtained, at least in the case of isobutyraldehyde, by the use of alkali cyanide as the condensing agent (587, 916, 1084).

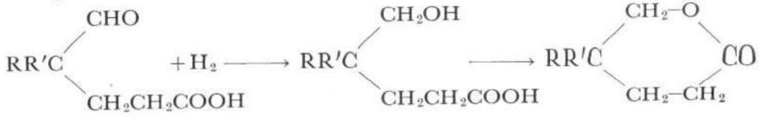
The reaction of acrylonitrile with 2-ethyl-2-hexenal (180, 183) is interesting because no α-hydrogen is immediately available for reaction. The mechanism evidently involves a preliminary allylic rearrangement under the influence of the basic catalyst (180):



$$C_2H_5CH_2CH{=}\underset{\displaystyle C_2H_5}{C}CHO \overset{OH^-}{\rightleftharpoons} C_2H_5CH{=}CH\underset{\displaystyle C_2H_5}{C}HCHO$$

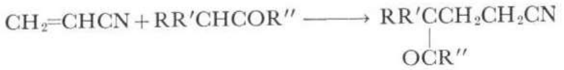
$$CH_2{=}CHCN + C_2H_5CH{=}CH\underset{\displaystyle C_2H_5}{C}HCHO \longrightarrow C_2H_5CH{=}CH\underset{\displaystyle C_2H_5}{C}(CHO)CH_2CH_2CN$$

The 4-cyanobutyraldehyde derivatives obtained by the cyanoethylation of aldehydes are interesting and useful chemical intermediates. They can be converted by hydrolysis to the aldehydo-acids and, by subsequent oxidation, to the glutaric acid derivatives (180), or they may be oxidized directly to 4-cyanobutyric acids (180). By catalytic hydrogenation the aldehydo-acids may be cyclized to δ-lactones (180):



KETONES (*See Table* XI)

Ketones containing at least one α-hydrogen atom can be cyanoethylated by reaction with acrylonitrile in the presence of basic catalysts:



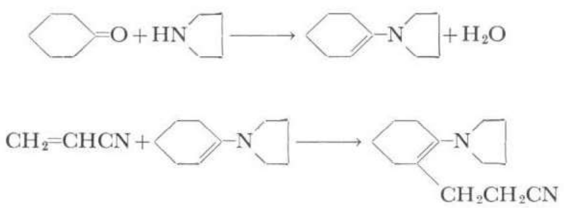
$$CH_2{=}CHCN + RR'CHCOR'' \longrightarrow RR'\underset{\displaystyle OCR''}{C}CH_2CH_2CN$$

In general, where more than one α-hydrogen is present on the same carbon atom, the second cyanoethyl group adds with greater ease than the first, and the third with greater ease than the second:

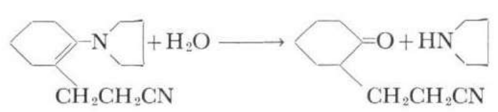
$$CH_2{=}CHCN + RCOCH_3 \longrightarrow RCOCH_2CH_2CH_2CN$$

$$CH_2{=}CHCN + RCOCH_2CH_2CH_2CN \longrightarrow RCOCH(CH_2CH_2CN)_2$$

Use of excess ketone favors the formation of the less highly cyanoethylated products (93). Monocyanoethylation of cyclohexanone in high yield has been accomplished by conversion of the ketone to its pyrrolidine enamine prior to cyanoethylation (1033):



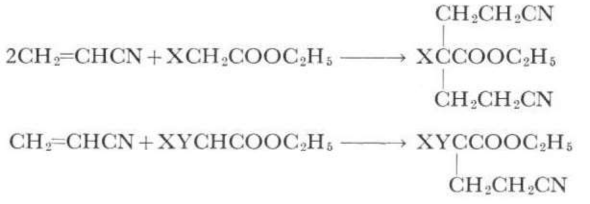
This enamine can be hydrolyzed readily to the ketonitrile:



This product, in turn, can be hydrolyzed readily to the corresponding acid. This method thus presents an excellent path by which to prepare 4-acylbutyric and 4-acylpimelic nitriles or acids. The method is applicable to compounds containing more than one ketone group as indicated in Table XI.

ESTERS AND AMIDES* (*See Table* XII)

Apparently the hydrogen atoms in the α-position of esters and amides are not sufficiently activated by these groups alone to permit cyanoethylation by acrylonitrile. In cases in which the α-position is also activated by one or more other negative groups the reaction proceeds smoothly. The other activating groups may be keto (acetoacetic esters), carbalkoxy (malonic esters), cyano (cyanoacetic esters), aromatic (9-carbalkoxy fluorene) or phosphono (phosphonoacetic esters). The products of these reactions are derivatives of glutaric acid or pimelic acid:



$$2CH_2{=}CHCN + XCH_2COOC_2H_5 \longrightarrow X\underset{\displaystyle CH_2CH_2CN}{\overset{\displaystyle CH_2CH_2CN}{C}}COOC_2H_5$$

$$CH_2{=}CHCN + XYCHCOOC_2H_5 \longrightarrow XY\underset{\displaystyle CH_2CH_2CN}{C}COOC_2H_5$$

(X = negative substituent, Y = any organic group.)

The cyanoethylation of cyanoacetic ester (931) is of particular interest, as it presents evidence that lower temperatures favor polycyanoethylation and higher temperatures favor monocyanoethylation. Thus at 40°C. the dicyano-

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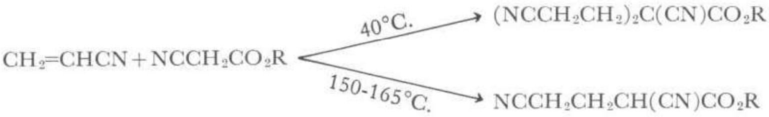
*The Nitrogen-cyanoethylation of amides is discussed on page 24 ethylated cyanoacetic ester is the exclusive product, while at 150-165°C. the monocyanoethylated ester predominates:



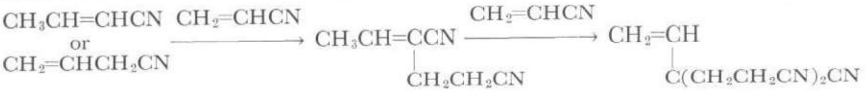
$$CH_2{=}CHCN + NCCH_2CO_2R \begin{cases} \xrightarrow{40°C.} (NCCH_2CH_2)_2C(CN)CO_2R \\ \xrightarrow{150\text{-}165°C.} NCCH_2CH_2CH(CN)CO_2R \end{cases}$$

Nitriles (*See Table* xiii)

The cyano group, like the ester and amide groups, does not by itself exert a sufficient activating influence to cause reaction with acrylonitrile except in the case of hydrocyanic acid. However, if the carbon atom bonded to the cyano group is attached to a second activating group, reaction will occur. Cyanoacetic esters and amides (*Table* xii), phenylacetonitriles, phosphonacetonitriles, and unsaturated nitriles (*Table* xiii) are examples of nitriles which will react with acrylonitrile. The monocyanoethylated products of these reactions are derivatives of glutaronitrile:

$$CH_2{=}CHCN + XYCHCN \longrightarrow \underset{\displaystyle CH_2CH_2CN}{XYCCN}$$

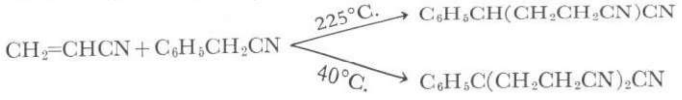
It is interesting to note that 3-butenenitrile and crotononitrile produce the same two products in roughly the same proportions (162, 178). This is evidence for a tautomeric shift of the allylic type:



$$\begin{matrix} CH_3CH{=}CHCN \\ \text{or} \\ CH_2{=}CHCH_2CN \end{matrix} \xrightarrow{CH_2{=}CHCN} \underset{\displaystyle CH_2CH_2CN}{CH_3CH{=}CCN} \xrightarrow{CH_2{=}CHCN} \underset{\displaystyle C(CH_2CH_2CN)_2CN}{CH_2{=}CH}$$

Similar reactions occur with 3-methyl-3-butenenitrile and cyclohexylideneacetonitrile (162, 178).

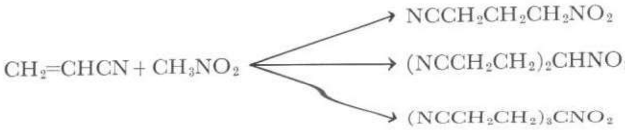
The tendency, mentioned previously (p. 19), of increasing temperature favoring monocyanoethylation over dicyanoethylation has been studied in the case of phenylacetonitrile (931). As the temperature of the reaction is increased from 40°C. to 225°C., the yield of monocyanoethylated product increases from 0% to 80% while that of the dicyanoethylated material decreases from 93% to 0%:



$$CH_2{=}CHCN + C_6H_5CH_2CN \begin{cases} \xrightarrow{225°C.} C_6H_5CH(CH_2CH_2CN)CN \\ \xrightarrow{40°C.} C_6H_5C(CH_2CH_2CN)_2CN \end{cases}$$

Nitro Compounds (*See Table* xiv)

The nitro group is strongly electron-withdrawing, and the hydrogen atom on the adjoining carbon atom will react at moderate temperatures with acrylonitrile. Mono-, di- and tri-cyanoethylated products have been obtained (1089):



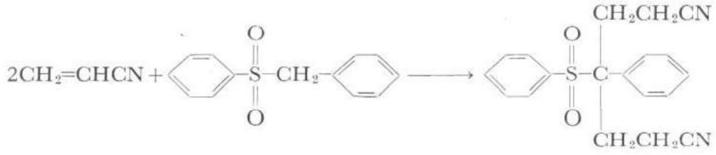
$$CH_2{=}CHCN + CH_3NO_2 \begin{cases} \longrightarrow NCCH_2CH_2CH_2NO_2 \\ \longrightarrow (NCCH_2CH_2)_2CHNO_2 \\ \longrightarrow (NCCH_2CH_2)_3CNO_2 \end{cases}$$

Cyanoethylation of dinitromethane or 2,2-dinitro-1,3-propanediol leads to 4,4-dinitropimelonitrile (383). In the latter case, the loss of formaldehyde to give dinitromethane occurs before reaction with acrylonitrile:

$$2CH_2{=}CHCN + CH_2(NO_2)_2 \longrightarrow (NCCH_2CH_2)_2C(NO_2)_2$$

SULFONES (*See Table* XV)

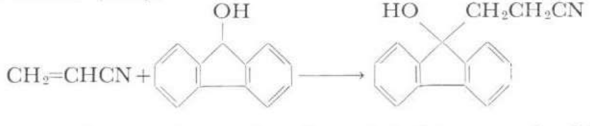
A sulfone group activates the hydrogen on an α-carbon atom sufficiently for cyanoethylation to occur if the α-carbon is also attached to either 1) a second sulfone group, 2) a vinyl group, or 3) a benzene ring. Dicyanoethylation is always observed except with sulfones containing a benzyl moiety which bears an ortho substituent. In this latter case only monocyanoethylation occurs because of the steric interference exerted by the substituent (1300):



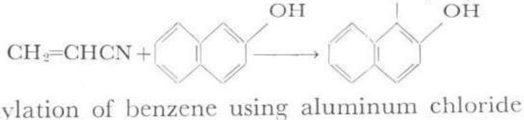
AROMATIC HYDROCARBONS (*See Table* XVI)

Cyclopentadiene and 6,6-dimethylfulvene react with acrylonitrile in the absence of catalyst to form adducts of the Diels-Alder type (*See Table* IV). However, in the presence of a basic catalyst only cyanoethylated products are obtained (158).

Fluorene and substituted fluorenes undergo cyanoethylation at the methylene group. With 9-fluorenol, carbon-cyanoethylation rather than oxygen-cyanoethylation occurs (205):

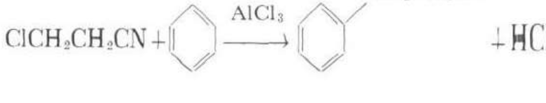


Reaction occurs at the α-carbon when 2-naphthol is treated with acrylonitrile in the presence of an equivalent amount of base (467, 468):

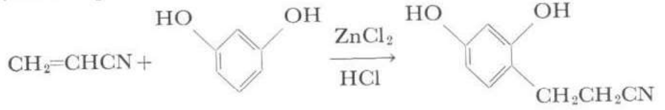


The cyanoethylation of benzene using aluminum chloride as a catalyst has been studied in some detail. Using a large excess of aluminum chloride only a low yield of dihydrocinnamonitrile is obtained. Better yields are obtained by first saturating the reaction mixture with hydrochloric acid to form 3-chloropropionitrile (442):

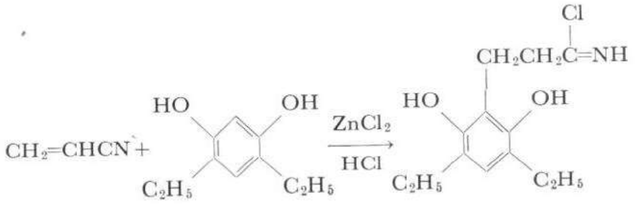
$$CH_2{=}CHCN + HCl \longrightarrow ClCH_2CH_2CN$$



Nuclear cyanoethylation is also observed with various phenols, such as resorcinol, in the presence of zinc chloride and hydrogen chloride (681):



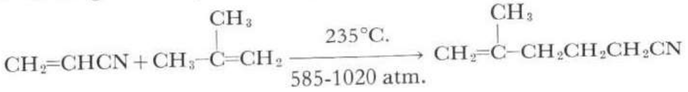
Under the above conditions, 4,6-diethylresorcinol reacts with acrylonitrile to produce a stable compound possessing an unsubstituted imino chloride group:



Aliphatic Hydrocarbons (*See Table* XVII)

Under ordinary conditions of temperature and pressure simple olefins fail to undergo cyanoethylation.

However, it has been reported recently that olefins such as isobutylene will react with acrylonitrile at pressures of 500-1000 atmospheres and 200-300°C. to give fair yields of cyanoethylated products (15, 1194):



$$CH_2=CHCN+CH_3-\overset{CH_3}{\overset{|}{C}}=CH_2 \xrightarrow[585\text{-}1020\text{ atm.}]{235°C.} CH_2=\overset{CH_3}{\overset{|}{C}}-CH_2CH_2CH_2CN$$

Acetylene reacts with acrylonitrile at lower temperatures and pressures in the presence of triphenyl phosphine and nickel-cyanide complex to give 2,4,6-heptatrienenitrile (199, 620):

$$CH_2=CHCN+2HC\equiv CH \xrightarrow[150\text{-}200\text{ p.s.i.}]{65\text{-}70°C.} CH_2=CHCH=CHCH=CHCN$$

Since variation of the mole ratio of acrylonitrile to acetylene produces only the 1:2 adduct, a stepwise-reaction mechanism is considered unlikely (199).

Haloforms (*See Table* XVIII)

Bromoform and chloroform have been cyanoethylated to give 4,4,4-trihalobutyronitriles (175, 827):

$$CH_2=CHCN+X_3CH \longrightarrow X_3CCH_2CH_2CN$$

Under similar conditions, iodoform fails to react (175).

Nitrogen-Cyanoethylation (*See Table* XIX)

The cyanoethylation of amines produces 3-alkylaminopropionitriles. In most cases a catalyst is not required. At low temperatures primary amines react with acrylonitrile to produce the monocyanoethylated product; at higher temperatures a second cyanoethyl group may be added, yielding the tertiary amines, the 3,3′-alkyliminodipropionitriles (173):

$$CH_2{=}CHCN + RNH_2 \longrightarrow RNHCH_2CH_2CN$$

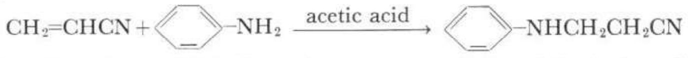
$$CH_2{=}CHCN + RNHCH_2CH_2CN \longrightarrow RN(CH_2CH_2CN)_2$$

The cyanoethylation of ammonia leads to three products:

$$CH_2{=}CHCN + NH_3 \left\{\begin{array}{l} \longrightarrow H_2NCH_2CH_2CN \\ \longrightarrow HN(CH_2CH_2CN)_2 \\ \longrightarrow N(CH_2CH_2CN)_3 \end{array}\right.$$

The relative proportions of the three products are determined by the molar ratio of reactants used (173). The reaction is of most importance in the preparation of β-alanine (207) and 3,3′-iminodipropionitrile (33). Nitrilotrispropylamine is formed in small amounts only.

An aromatic nucleus attached to an amino group tends to hinder cyanoethylation. However, the cyanoethylation of aniline and substituted anilines may be carried out in good yield in the presence of acetic acid, or cupric acetate, yielding 3-anilinopropionitrile (1279):



The list of amines which have been cyanoethylated includes aliphatic, alicyclic, aromatic, and heterocyclic bases. The 3-alkylaminopropionitriles so produced are valuable intermediates (31) for many chemical processes. They may be hydrolyzed, esterified or hydrogenated, or they may be condensed with aromatic systems in the Hoesch synthesis. The diamines obtained through hydrogenation are particularly useful in the synthesis of various pharmaceuticals (31).

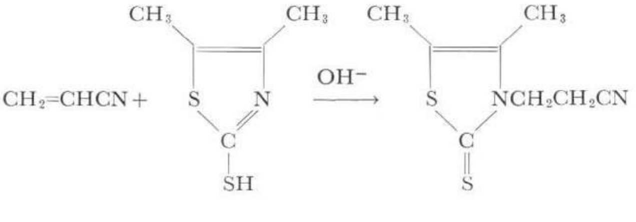
The reaction with cyanamide (485) produces an interesting trinitrile, bis(2-cyanoethyl)cyanamide:

$$2CH_2{=}CHCN + H_2NCN \rightleftharpoons NCN(CH_2CH_2CN)_2$$

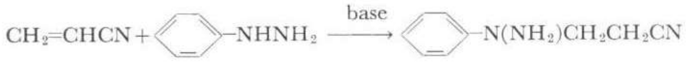
Other amines which have been cyanoethylated include hydrazine (520), hydroxylamine (520) and cyanoguanidine (486).

The cyanoethylation of alkali-metal salts of α-amino acids proceeds smoothly for the acidic or neutral amino acids (728). Histidine and arginine are said to be inert to acrylonitrile under cyanoethylation conditions.

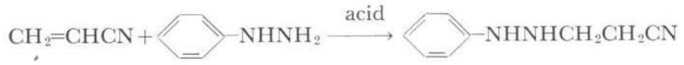
It has been reported that 4,5-dimethyl-2-thiazolethiol reacts with acrylonitrile to effect cyanoethylation of the nitrogen, rather than the sulfur atom (1029):



The cyanoethylation of phenylhydrazine is especially interesting since cyanoethylation with a basic catalyst yields a cyanoethylation product substituted on the α-nitrogen atom:



whereas an acid catalyst yields a product substituted on the β-nitrogen atom (870):



The cyanoethylation of amides is similar to that of amines except that strongly basic catalysts are usually necessary (1135):

$$CH_2{=}CHCN + RCONH_2 \longrightarrow RCONHCH_2CH_2CN$$

$$CH_2{=}CHCN + RCONHCH_2CH_2CN \longrightarrow RCON(CH_2CH_2CN)_2$$

It is interesting that N-methylformamide does not react with acrylonitrile (1135). In general, carboxylic acid amides, imides and lactams, and the aliphatic- and aromatic-sulfonamides will react readily in the presence of basic catalysts.

Oxygen-Cyanoethylation (*See Table* XX)

Alcohols and other hydroxy compounds are cyanoethylated by acrylonitrile, producing 3-alkoxypropionitriles:

$$CH_2{=}CHCN + ROH \rightleftharpoons ROCH_2CH_2CN$$

The reaction has been applied to a large number of aliphatic monohydric and polyhydric alcohols, to alcohols containing ether, tertiary-amino, and other non-reacting groups, and to phenols. The 3-alkoxypropionitriles produced may be hydrolyzed, hydrogenated, esterified or condensed with various reagents (31).

The reaction with primary and secondary alcohols occurs at 20-80°C. in the presence of basic catalysts. Tertiary alcohols require more drastic treatment; in fact, they may be used as solvents for cyanoethylation of primary and secondary alcohols at lower temperatures.

The cyanoethylation of alcohols by acrylonitrile is an equilibrium reaction (173), being more favorable for the cyanoethylation of primary than of secondary or tertiary alcohols. It is probable, therefore, that polyhydric alcohols such as starch, cellulose and viscose are first cyanoethylated at the primary hydroxyl groups.

The cyanoethylation of water produces 3,3′-oxydipropionitrile:

$$2CH_2{=}CHCN + H_2O \rightleftharpoons O(CH_2CH_2CN)_2$$

The reaction probably involves ethylene cyanohydrin as an intermediate, as it has been found that the dipropionitrile is more readily prepared from this intermediate. Aqueous formaldehyde or "methylene glycol" ($HOCH_2OH$) and the higher glycols react in the same manner:

$$2CH_2{=}CHCN + HO(CH_2)_nOH \longrightarrow (CH_2)_n(OCH_2CH_2CN)_2$$

However, if formaldehyde is cyanoethylated in the presence of an alcohol, the reaction occurs as if the first step were hemiformal formation (185):

$$ROH + CH_2O \longrightarrow ROCH_2OH$$

$$CH_2{=}CHCN + ROCH_2OH \longrightarrow ROCH_2OCH_2CH_2CN$$

The reaction of acrylonitrile with phenols requires the use of elevated temperatures (120-140°C.) (58, 268, 1104):

$$CH_2{=}CHCN + C_6H_5OH \longrightarrow C_6H_5OCH_2CH_2CN$$

The cyanoethylation of phenols at the *o*- or *p*-positions has been discussed earlier (page 22).

Aldoximes and ketoximes may be cyanoethylated in excellent yield at room temperature:

$$CH_2{=}CHCN + R_2C{=}NOH \longrightarrow R_2C{=}NOCH_2CH_2CN$$

The cyanoethylation of organic hydroperoxides has been reported (476):

$$CH_2{=}CHCN + C_2H_5OOH \longrightarrow C_2H_5OOCH_2CH_2CN$$

Sulfur-Cyanoethylation (*See Table* XXI)

The reaction of acrylonitrile with sulfhydryl compounds is analogous to that with hydroxy compounds. The products are 3-(alkylthio)propionitriles:

$$CH_2{=}CHCN + RSH \longrightarrow RSCH_2CH_2CN$$

These cyanoethylations proceed readily at temperatures below 50°C., and in the presence of basic catalysts. The reaction has been made the basis for a quantitative analytical method for acrylonitrile (page 61).

Hydrogen sulfide (421) and sodium sulfide (1, 526) are cyanoethylated to 3,3′-thiodipropionitrile:

$$2CH_2{=}CHCN + H_2S \longrightarrow S(CH_2CH_2CN)_2$$

Acrylonitrile reacts in a similar fashion with sodium polysulfide in aqueous solutions to form 3,3′-dithiodipropionitrile (1037):

$$CH_2{=}CHCN + NaS_x \longrightarrow NCCH_2CH_2SSCH_2CH_2CN$$

Sodium and potassium bisulfites readily add to acrylonitrile to produce the corresponding salts of 3-sulfopropionitrile (209, 958):

$$CH_2{=}CHCN + NaHSO_3 \longrightarrow NaO_3SCH_2CH_2CN$$

Kinetic studies of this reaction in dilute aqueous solution (795) indicate that a bimolecular reaction between sulfite ion and acrylonitrile is the rate-determining step.

The reaction of thioacetic acid with acrylonitrile gives the acetate of 3-mercaptopropionitrile in good yields (288, 289):

$$CH_2{=}CHCN + CH_3\overset{O}{\overset{\|}{C}}SH \longrightarrow CH_3\overset{O}{\overset{\|}{C}}SCH_2CH_2CN$$

The relative susceptibility of sulfhydryl and hydroxyl groups to cyanoethylation is indicated by the reaction of acrylonitrile with 2-mercaptoethanol which forms the sulfur-cyanoethylation product in high yield (422):

$$CH_2{=}CHCN + HOCH_2CH_2SH \longrightarrow HOCH_2CH_2SCH_2CH_2CN$$

The cyanoethylation of diethylphosphorodithioic acid has also been reported (87):

$$CH_2{=}CHCN + (C_2H_5O)_2\overset{S}{\overset{\uparrow}{P}}SH \longrightarrow (C_2H_5O)_2\overset{S}{\overset{\uparrow}{P}}SCH_2CH_2CN$$

The reaction of acrylonitrile with sulfhydryl compounds has also been extended to include a variety of thiazolethiols (557), and thiophenols (557). Alkali-metal salts of dithiocarbamic acids react readily with acrylonitrile to form the corresponding cyanoethyl esters (469):

$$CH_2{=}CHCN + R_2N\overset{S}{\overset{\|}{C}}SNa + H_2O \longrightarrow R_2N\overset{S}{\overset{\|}{C}}SCH_2CH_2CN + NaOH$$

Miscellaneous Cyanoethylations (*See Table* XXII)

ARSINES

Aryl arsines are readily cyanoethylated by reacting them with refluxing acrylonitrile without the use of catalysts (269). Methyl arsine has been reacted with acrylonitrile in the presence of a basic catalyst at room temperature (270):

$$2CH_2{=}CHCN + RAsH_2 \longrightarrow RAs(CH_2CH_2CN)_2$$

PHOSPHINES AND PHOSPHONATES

Organic phosphorus derivatives may be cyanoethylated easily without a catalyst or in the presence of acidic or basic catalysts. With phenyl phosphine the best yields were obtained in the absence of catalyst (739). With alkyl phosphonates good yields were obtained using a basic catalyst (893):

$$2CH_2{=}CHCN + RPH_2 \longrightarrow RP(CH_2CH_2CN)_2$$

BORANES

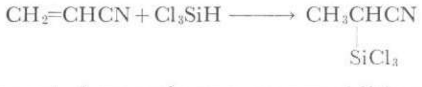
The reaction of diborane with acrylonitrile at room temperature in the absence of a catalyst has been reported (1032) although the structure of the isolated products has not been determined.

SILANES

The cyanoethylation of trichlorosilane has recently been reported (836) to proceed readily at 160°C. in the presence of pyridine, platinum, or benzyltrimethylammonium chloride to give 3-trichlorosilylpropionitrile:

$$CH_2{=}CHCN + Cl_3SiH \longrightarrow Cl_3SiCH_2CH_2CN$$

In the presence of both pyridine and stainless steel however, the only product isolated was 2-trichlorosilylpropionitrile (837):



$$CH_2{=}CHCN + Cl_3SiH \longrightarrow \underset{\displaystyle SiCl_3}{CH_3\underset{|}{C}HCN}$$

This is the only reported case of reverse or α-addition in which hydrogen adds to the β-carbon in acrylonitrile, and the remainder of the molecule adds to the α-carbon.

TIN HYDRIDES

Tri-*n*-butyl- and triphenyltin hydrides react with acrylonitrile in the absence of catalysts to give the 3-substituted propionitriles (1115):

$$CH_2{=}CHCN + R_3SnH \longrightarrow R_3SnCH_2CH_2CN$$

Hydrogen Halide Cyanoethylation (*See Table* XXIII)

Anhydrous hydrogen chloride (800) and hydrogen bromide (803) react exothermically in the cold to give 3-halopropionitriles. This reaction is catalyzed by aliphatic amines, or by quaternary ammonium salts (364, 800) although apparently, good yields can be obtained with no catalyst (388):

$$CH_2{=}CHCN + HX \longrightarrow XCH_2CH_2CN$$

Reaction with Natural and Synthetic Polymers

Many natural and synthetic polymers that contain labile hydrogen atoms react with acrylonitrile under suitable conditions to give cyanoethyl derivatives. In general, aqueous caustic has been used to catalyze these reactions. Since the extent of cyanoethylation of the polymer can be varied by suitable choice of reaction conditions, a variety of products may be obtained from one starting material. Under certain conditions cyanoethylation is accompanied by hydrolysis; in these cases many of the nitrile groups are hydrolyzed to carboxylic acid salts, thereby producing a polyelectrolyte.

As might be expected, the physical properties of polymers change when they are cyanoethylated. Hydrophilic polymers become more hydrophobic, and when cyanoethylated to a high degree, may become soluble in organic solvents.

Cyanoethylation may be carried out either in a homogeneous manner (e.g., on cellulose xanthate as in viscose dope) or in a heterogeneous system (such as on cotton yarn immersed in aqueous caustic solution). For a given polymer, homogeneous-phase cyanoethylation appears to result in the most uniform distribution of cyanoethyl residues.

References to articles and patents describing methods of cyanoethylation of natural and synthetic polymers are given in the accompanying outline. The properties of many of these cyanoethylated products are given in the appropriate parts of the Application Section. The process variables and economics for the commercial-scale cyanoethylation of cotton are described in the industry report "Cyanoethylation of Cotton" (1243).

I. NATURAL POLYMERS
  A. Carbohydrates
    1. Cellulose
      a. Cotton (fabric, staple, yarn) (232, 439, 600, 1018, 1197, 1213, 1237, 1272, 1274, 1294, 1304, 1443, 1446) (for reviews see 261, 310, 1243)
      b. Flax (1394)
      c. Jute (1)
      d. Manila (1)
      e. Pulp (linters, wood cellulose) (127, 414, 551, 561, 776, 1116, 1235, 1451)
      f. Regenerated Cellulose (127, 290, 551, 676, 715, 1018, 1324, 1451)
      g. Sisal (1)
      h. Wood (1)
    2. Dextran (1)
    3. Dextrin (1)
    4. Gums
      a. Galactomannon: guar, locust bean, honey locust, flame tree, tara (783, 784, 785)
      b. Glucomannon: iles mannon (783, 784, 785)
      c. Arabic, tragacanth, karaya (784)
    5. Starch
      a. Corn, potato, tapioca, wheat (1, 126, 427, 549, 719)
    6. Tylose (427)
  B. Lignin (1441)
  C. Proteins (650)
    1. Blood albumen (651)
    2. Casein (279, 651, 1335)
    3. Gelatin (306, 416, 651)
    4. Glue (651)
    5. Gluten (256)
    6. Soybean (279)
      a. Fibers (279)
    7. Wool (732, 1212)
    8. Zein (279, 306, 651)
      a. Fibers (279)

II. MODIFIED NATURAL POLYMERS
   A. Cellulose Xanthate (278, 527, 529, 710, 711, 712, 714, 717, 718, 719)
   B. Dimethylthiourethane of Cellulose (1196)
   C. Ethylcellulose (551)
   D. Ethylthiourethane of Cellulose (1196)
   E. Hydroxyethylcellulose (713, 1117)
   F. Methylcellulose (713)
   G. Phenylthiourethane of Cellulose (1196)

III. SYNTHETIC POLYMERS
   A. Acetone-formaldehyde condensate (1108)
   B. Acetone-isobutyraldehyde condensate (1108)
   C. Methyl ethyl ketone-formaldehyde condensate (1108)
   D. Poly(allyl alcohol) (1143)
   E. Poly(crotyl alcohol) (1145)
   F. Poly(3-chloroallyl alcohol) (1143)
   G. Polyketone from ethylene and carbon monoxide (794)
   H. Polyketone from propylene, ethylene and carbon monoxide (794)
   I. Poly(methallyl alcohol) (1143)
   J. Poly(methyl vinyl ketone) (794)
   K. Poly(vinyl alcohol) (427, 550, 1049, 1098, 1174, 1251, 1319, 1320, 1324)

POLYMERIZATION REACTIONS

The most important property of acrylonitrile is its ability to undergo additional polymerization to form high molecular-weight products. Physical studies (22) indicate that this reactivity is due to the relatively high polarity of the acrylonitrile molecule. These same studies also indicate that acrylonitrile will copolymerize best with other highly active monomers, and that if the comonomer has an electron-rich bond, there will be a tendency toward alternation of monomer units in the chain.

This monomer polarity also gives rise to the unique properties of acrylonitrile polymers. Strong van der Waals forces and close packing of adjacent chains are responsible for high heat distortion temperatures, good resistance to chemicals, excellent outdoor durability, and hard, strong, tough surfaces.

The utilization of these properties is discussed in the Applications Section. The present section discusses polymerization methods, monomer reactivity ratios, chemical modifications, and the physical properties of acrylonitrile polymers.

Homopolymerization

Pure acrylonitrile may be polymerized rapidly and spontaneously at room temperature if inhibitors such as oxygen, water, hydroquinones, and amines are excluded. Less pure monomer exhibits a variable induction period, and may be stable for a long time at fairly high temperatures. Traces of oxygen produce a pronounced inhibiting effect by reacting with active radicals (842, 984, 1005). Acetylene polymers also inhibit the polymerization (539).

Rapid polymerization takes place in the presence of substances capable of producing free radicals. Peroxides such as hydrogen peroxide (995) and benzoyl peroxide (1291), azo compounds such as 2,2′-azobis(isobutyronitrile) (539, 1011, 1190) and 2,2′-azobis(2,4-dimethylvaleronitrile) (1011), and tetra-alkyldiarylethanes (1191) have been used as a source of free radicals for initiation of acrylonitrile polymerization.

Radiation has been employed successfully to bring about acrylonitrile polymerization. Ultraviolet light acting on pure acrylonitrile (610) and on solutions of acrylonitrile containing ferric salts (369, 371, 947, 948), or H_2O_2 (297), will initiate polymerization. Visible light may be used if a dye, a reducing agent, and oxygen are all present (847, 1369). Polymerization by γ-rays (112, 225, 226, 238, 259, 888, 889, 1208, 1209, 1221, 1226, 1380, 1432), X-rays (259, 297, 298, 299, 886, 887, 888), high energy electrons (965, 1268), and ultrasonic vibrations (703) have been reported.

Because of the electron-deficient character of the double bond in acrylonitrile, acid catalysts such as aluminum chloride have very little catalytic effect (455). Silver salts dissolved in acrylonitrile will promote polymerization, but a free radical rather than a cationic mechanism is indicated (945). A variety of basic catalysts such as sodium and sodamide, on the other hand, cause vigorous polymerization of acrylonitrile (367, 536, 862, 1072, 1169).

The polymerization of acrylonitrile is rapid (681) and exothermic [17.3 ± 0.5 k.cal. per mole (1094)], making bulk polymerization difficult to control. Since polyacrylonitrile is insoluble in the monomer, a heterogeneous polymerization with unusual kinetic features results (71, 72, 73, 641, 1087). The polymer insolubility leads to a thick paste from which heat is not easily removed.

It is possible to polymerize acrylonitrile in the vapor phase (596, 615) or, if a suitable solvent is employed, in the homogeneous liquid phase (670, 671, 889, 1036, 1086). The use of concentrated zinc chloride solutions is satisfactory for producing a polymer solution, suitable for direct film casting or fiber spinning (670, 671). Ordinarily, however, the polymer will be insoluble in the reacting medium, and will precipitate as it is formed (1036).

Acrylonitrile is conveniently polymerized in aqueous solution. Advantages of this system are economy, ease of temperature control, and adaptability to certain redox catalyst systems. These allow for rapid polymerization at relatively low temperatures (20-60°C.). Molecular weight is controlled by the catalyst content and the temperature. Chain transfer agents, such as alcohols, also may be used (308, 850). The color of polymer made by low-temperature redox initiation is often better than that obtained by the use of other catalyst systems.

Redox catalyst systems (51, 61, 94, 152, 271, 516, 597, 603, 627, 750, 801, 846, 853, 984, 985) contain at least two components, an oxidizing agent and a reducing agent, and for acrylonitrile, are usually effective only in acid solutions (1). In addition, the ions of certain metals, such as copper, silver and iron, may be employed at very small concentrations (e.g., 5 to 200 p.p.m.) to increase further the rate of initiation (62, 252). However, uncontrolled contamination by metallic ions should be avoided since in many systems polymerization may be retarded or totally inhibited (1). The marked inhibiting effect of oxygen on the polymerization of acrylonitrile by redox systems has been investigated in detail (1005). The catalytic activity of redox systems depends on the fact that some oxidation—reduction reactions progress at a convenient rate via a free-radical mechanism, these radical intermediates being the actual initiators of polymerization. Examples of such systems are ammonium persulfate-sodium bisulfate, and hydrogen peroxide-ferrous sulfate. In the latter system it has been shown that hydroxyl radicals are the chain initiators (94). Many other useful systems have been found, most of them comprising a peroxy compound and an oxidizable sulfoxy compound.

Aqueous solution-polymerization also may be initiated by peroxides alone, by azo compounds, or by radiation. It has been reported that X-rays and gamma rays are effective because of the intermediate formation of hydroxyl radicals (296).

Initially monomer may be present in excess of the solubility limit (152). In the absence of emulsifying agents and with a water-soluble catalyst the reaction appears to occur chiefly in the aqueous phase, while with an organic-solvent soluble catalyst the reaction proceeds in the organic phase (1011).

Acrylonitrile may be polymerized in emulsion (152, 386, 630, 743, 840, 892) using either conventional or redox catalyst systems, and by either batch- or continuous-methods (661). It is somewhat difficult to prepare stable polyacrylonitrile emulsions, particularly with high solids content. However, if the proper concentration of an emulsifier such as lauryl sodium sulfate is used, and if the reaction temperature is kept within certain limits, stable emulsions of 20-25% solids content may be prepared (1). It also has been shown that if the polymerization is effected in the presence of a halogenated hydrocarbon, such as ethylene dichloride, the resulting latex is stable (476). A comparison of the emulsion polymerization of acrylonitrile with that of methyl methacrylate has been made (630).

The ease with which polymerization of acrylonitrile is initiated has led to the use of the monomer as a means of detecting free-radical intermediates in various inorganic and organic reactions (321, 343, 539, 540, 541, 626, 659, 1046, 1390, 1415).

Suitable methods of polymerizing acrylonitrile are indicated more specifically by the following examples. The procedure of Example 1 or some modification of it is ordinarily preferred.

Example 1—Slurry Polymerization with a Redox Catalyst System (61)

The following system is heated at 30°C. under nitrogen with slow stirring:

Water	200	grams
Acrylonitrile	10.0	grams
Potassium persulfate	0.4	gram
Sodium bisulfite	0.15	gram

Polymer begins to form immediately, and after an hour the yield is 86.3%. It is important that the pH be maintained below 5, and it is preferable to operate at about pH 3. The initial pH is 3.6; after an hour it is 3.2.

Example 2—Continuous Slurry Polymerization with a Redox Catalyst (37).

The following system is stirred at 35°C.:

Water	1150 grams
Polyacrylonitrile	450 grams
Sulfuric acid	To give pH 3

A stream of acrylonitrile containing 3.1% water, a stream of catalyst solution containing 2.93 grams of sodium chlorate and 10.5 grams of sodium sulfite per liter of water, and a stream of aqueous sulfuric acid (5 grams per liter) are fed simultaneously to the reactor. Each of the feed streams is run continuously at a rate of 236 ml. per hour. The slurry continuously overflows through a side arm at the 1600 ml. level in the reactor. The average residence time is thus 2.2 hours. After 7.5 hours the pH of the reaction mixture is 2.5 and an 89% yield of polymer having an average molecular weight of about 75,000 is obtained; hence the polymer concentration in the reaction mixture at this time is 24.8% by weight, and the monomer concentration by difference is 3.1%.

Copolymerization

When polymerization is initiated in a mixture of acrylonitrile with another monomer, the two monomers ordinarily enter into the copolymer at different rates. Accordingly, the copolymer is always richer in the more reactive monomer than is the mixture of the monomers from which it is forming. Since the monomers are being used at different rates the composition of the copolymer being formed changes continuously during a batch reaction. For many applications the uniformity of the copolymer composition is not critical. Sometimes, however, it becomes important to prepare an acrylonitrile copolymer with a relatively narrow range of chain compositions, e.g., to improve the strength or clarity of the copolymer (2, 223, 1001) or, in the case of thermoplastic copolymers, to reduce the flow temperature (346, 1056).

Obviously, the composition of the copolymer from a batch-polymerization will be more uniform if the reaction is stopped before the change in the composition of the residual monomer mixture becomes great. However, in practice this involves recovering and recycling a large proportion of the original monomer mixture. This can be avoided if an additional feed of the more reactive monomer (or a mixture of the monomers rich in the more reactive monomer) is continuously fed during the polymerization. The rate should be sufficient to maintain the ratio of concentrations of unreacted monomers substantially constant during the whole period of polymerization. The reflux temperature may be used as an indicator of the relative monomer concentrations (223, 461).

In order to obtain initial production of copolymer of a predetermined composition it is usually necessary to start with a monomer mixture which has a different composition. While the proper composition for the mixture may be determined by trial and error, it can also be calculated from the reactivity ratios r_1 and r_2 for the two monomers (M_1 and M_2) if these ratios are known. The ratios are defined as follows:

$$r_1 = \frac{k_{11}}{k_{12}},\ r_2 = \frac{k_{22}}{k_{21}}$$

k_{11} = rate constant for the reaction between a copolymer chain ending in M_1 and an M_1 monomer

k_{12} = rate constant for the reaction between a copolymer chain ending in M_1 and an M_2 monomer

k_{22} and k_{21} are the rate constants for the reactions of a copolymer chain ending in M_2 with monomers M_2 and M_1, respectively

For a more detailed discussion see reference 759.

Reactivity ratios for the copolymerization of acrylonitrile with various monomers are listed in Table XXIV.

The following is an illustrative calculation of the monomer composition required to make a copolymer of acrylonitrile of definite composition:

Copolymer desired: Acrylonitrile (M_1) 75% by weight
Methyl acrylate (M_2) 25% by weight

One may use the following equation:

$$C = \frac{P-1+\sqrt{(1-P)^2+4Pr_1r_2}}{2r_1}$$

where C = mole ratio of M_1 to M_2 charged

$$P = \text{mole ratio of } M_1 \text{ to } M_2 \text{ in copolymer} = \frac{\frac{75}{53}}{\frac{25}{86}} = 4.84$$

from Table XXIV, $r_1 = 1.26$ and $r_2 = 0.67$

$$\text{Substituting, } C = \frac{(4.84-1)+\sqrt{(1-4.84)^2+4(4.84)\,(1.26)\,(0.67)}}{2(1.26)}$$

$$C = 3.7 \text{ moles } M_1 \text{ per mole } M_2$$

In terms of weight, this means that the monomer mixture should consist of 70% acrylonitrile and 30% methyl acrylate.

It should be emphasized that with this monomer charge, only the initial copolymer will have the desired composition. If, however, the calculated charge (i.e., 70:30) is placed in the reactor and polymerization initiated at reflux, one may then begin adding a mixture of monomers having the same composition as that of the polymer first formed (i.e., 75:25). This addition is done at such a rate as to maintain a constant reflux temperature. Thus the monomers are being added at the same rate at which they are being reacted, keeping the concentrations of unreacted monomers constant. As soon as all the feed has been added, the polymerization is stopped and unreacted monomers are recovered for reuse.

TABLE XXIV

Monomer-Reactivity Ratios for Copolymerization with Acrylonitrile (M_1) at ca. 60°C. (unless otherwise noted)

Comonomer (M_2)	r_1	r_2
1-Acetoxy-1,3-butadiene (456)	0.0	0.7
2-Acetoxystyrene (224)	0.08 ± 0.01	0.4 ± 0.05
Acrylamide (904)	0.875	1.357
Allyl alcohol (1369)	3.96 ± 0.53	0.11 ± 0.10
Allyl chloride (224)	3.0 ± 0.2	0.05 ± 0.01
1,1-Bis(*p*-anisyl)ethylene (337)	0.014 ± 0.002	0
1,1-Bis(*p*-chlorophenyl)ethylene (337)	0.024 ± 0.003	0
Bis(trimethylsiloxy)vinylmethylsilane (1376)	8.0	0.1
Butadiene (501)	0.0 ± 0.04	0.35 ± 0.08
Butyl acrylate (809)	1.003 ± 0.012	1.005 ± 0.005
Chloroprene (501)	0.01 ± 0.01	6.07 ± 0.53
Crotonic acid (337)	21 ± 10	0
2,5-Dichlorostyrene (434)	0.19	0.07
Diethyl fumarate (758)	8	0
Diethyl maleate (758)	12	0
Diphenylacetylene (337)	13.6 ± 1.0	0
1,1-Diphenylethylene (337)	0.028 ± 0.003	0
trans-1,2-Di(2-pyridyl)ethylene (1333)	0.95 ± 0.05	0.02 ± 0.05
Ethyl β-ethoxyethylacrylate (1382)	10.5 ± 1.5	0.02 ± 0.02
Ethyl vinyl ether (1382)	0.7 ± 0.2	0.03 ± 0.02
2-Fluorobutadiene (1368)	0.07 ± 0.03	0.59 ± 0.10
1-Hexene (337)	12.2 ± 2.4	0
1-Hexyne (337)	5.4 ± 0.5	0
Isobutylene (841)	1.02	0
Isoprene (501)	0.03 ± 0.03	0.45 ± 0.05
Maleic anhydride (758)	6	0
Methacrolein (456)	0.06	2.0
Methacrylonitrile (841)	0.32	2.68
Methacryloxymethylpentamethyldisiloxane (1340)	0.19 ± 0.04	1.44 ± 0.15
Methyl acrylate (1) (30°)	1.26 ± 0.1	0.67 ± 0.1
Methyl 2-chloroacrylate (21)	0.15	2.0
Methyl cinnamate (300, 337)	6 ± 2	0
Methyl methacrylate (693)	0.15 ± 0.07	1.2 ± 0.14
α-Methylstyrene (400)	0.06 ± 0.02	0.1 ± 0.02
(460)	0.06 ± 0.02	0.055 ± 0.005
o-Methylstyrene (1)	0.06 ± 0.05	0.33 ± 0.1
m-Methylstyrene (1)	0.07 ± 0.04	0.43 ± 0.1
p-Methylstyrene (1)	0.05 ± 0.02	0.33 ± 0.1
Methyl vinyl ketone (694)	0.61 ± 0.04	1.78 ± 0.22
Phenylacetylene (337)	0.26 ± 0.03	0.33 ± 0.05
Styrene (619)	0.04 ± 0.04	0.41 ± 0.08
Tetrachloroethylene (336)	470	0
Trichloroethylene (758)	67	0
3,3,3-Trichloropropene (337)	12.2 ± 1.2	0.10 ± 0.015
Trimethyl aconitate (1332)	5.50 ± 0.5	0
Trimethylsiloxyvinyldimethylsilane (1376)	8.0	0.1
Tris(trimethylsiloxy)vinylsilane (1376)	8.0	0.1
Vinyl acetate (760)	4.05 ± 0.3	0.061 ± 0.013
(102)	6.0	0.07
Vinyl benzoate (224)	5.0 ± 0.05	0.05 ± 0.005
Vinyl chloride (694)	3.28 ± 0.06	0.02 ± 0.02
Vinyl ethyl ether (758)	5	0
Vinyl 2-ethylhexoate (224)	12 ± 2	0.01 ± 0.01
Vinyl formate (224)	3.03 ± 0.05	0.04 ± 0.005
Vinylidene chloride (693)	0.91 ± 0.1	0.37 ± 0.1
Vinyltrimethoxysilane (1427)	6.0	0
Vinyl stearate (1448)	4.3	0.03

In Table xxv there are listed reactivity values of a somewhat different nature, reported in the earlier literature (833). In these experiments, equimolar quantities of acrylonitrile and a second monomer were copolymerized. The mole ratios of monomers in the resulting polymers are given:

TABLE XXV

Reactivity of Monomers with Acrylonitrile (M_1) (833)

Comonomer (M_2)	Mole Ratio M_1/M_2 in Copolymer
Allyl acetate	9.63
1,1-Diphenylethylene	0.662
Methyl acrylate	1.06
Methyl 2-chloroacrylate	0.345
Indene	1.20
Stilbene	2.53

The arrangement of monomer units in acrylonitrile copolymers will vary with the comonomer used. A random arrangement of the two units appears to be most common. If the product of the monomer reactivity ratios $r_1r_2=1$, the two types of monomer units are arranged completely at random in the chain. If r_1r_2 is less than 1, the structure deviates from the random in the direction of regular alternation. It is seldom if ever found that r_1r_2 is greater than 1 (759).

Special techniques may be used to achieve "block" copolymers of acrylonitrile wherein a substantial number of acrylonitrile units occur in succession, and are followed by a substantial number of comonomer units (513, 514, 515, 834, 835, 1200, 1290, 1343).

Another structural variation may be achieved by grafting branches onto a preformed polymer (1200, 1227, 1290, 1342, 1434). For example, when acrylonitrile is polymerized in the presence of natural rubber polymer, a portion of the polyacrylonitrile formed attaches to mid-chain sites on the rubber giving it increased solvent resistance (685, 1299).

Graft copolymers of acrylonitrile and poly(N-acrylylmorpholine) have been prepared by heating an aqueous mixture of acrylonitrile and the preformed polymer with potassium persulfate (1239).

Vinyl acetate polymer has been grafted onto polyacrylonitrile by heating polyacrylonitrile latex with vinyl acetate monomer and potassium persulfate (483). Solubility studies indicated that about 50% of the vinyl acetate had become grafted onto the polyacrylonitrile.

Flame resistant, spinnable polymers have been produced by grafting acrylonitrile onto poly(vinyl chloride) or poly(vinylidene chloride) (1238).

A different type of graft copolymer is presumably formed when acrylonitrile is copolymerized with poly(vinylsiloxanes) (556, 558), since here the preformed polymer has vinyl groups which may enter either at the end, or in the middle of the polyacrylonitrile chains.

Radiation has been used successfully as an initiator in the preparation of block and graft copolymers (1200, 1201, 1210, 1275, 1342, 1343, 1378, 1411). Irradiation of polymers produces free radical sites which are capable of initiating vinyl polymerizations. Whether a block- or graft-copolymer is formed depends on the location of the radical site.

Several excellent reviews have been published on the techniques employed in block- and graft-polymerization (1267, 1290, 1377, 1378).

Acrylonitrile has been copolymerized with more than 400 different comonomers. A tabulation of these copolymers, together with a summary of properties, uses and typical laboratory procedures is given in an American Cyanamid Company technical bulletin entitled "Polymers and Copolymers of Acrylonitrile."

Modification of Acrylonitrile Polymers

Polymers and copolymers of acrylonitrile are capable of undergoing further transformation through chemical reactions of the nitrile group. For example, polyamines are said to be obtained when polyacrylonitrile (257, 602, 851) and its copolymers (257, 639, 734, 1142) are hydrogenated.

Polymers and copolymers of acrylonitrile can be hydrolyzed by aqueous alkali to give water-soluble materials containing carboxylate groupings (563, 628, 737, 788, 1203). If polyacrylonitrile is heated above about 80°C. with concentrated alkali, the pasty mixture passes through a thick, red stage and eventually becomes clear, viscous, yellow and water-soluble (628). The product is chiefly the salt of polyacrylic acid.

Solutions of hydrolyzed polyacrylonitrile are interesting for a number of applications (1). They may be stored at elevated temperatures without change in viscosity, and they are apparently not susceptible to the action of molds or bacteria. The solutions are stable from about pH 4 to 12, or higher. At lower pH's coagulation tends to occur. Solutions of hydrolyzed polyacrylonitrile have good tolerance for both anions and cations, and for hydrophilic solvents.

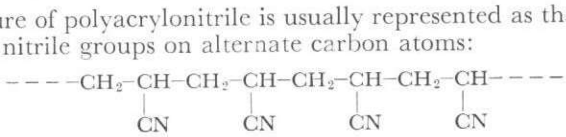
Partial hydration of polyacrylonitrile with concentrated sulfuric acid has been reported to give a solution from which fibers may be spun (883). Reaction of polyacrylonitrile with hydroxylamine introduces amidoxime groups (969, 1400) and hydroxamic acid groups (1399). The resulting polymer is said to have increased dye affinity (969).

Polyacrylonitrile in dilute solutions in dimethylformamide undergoes extremely rapid random chain scission if a strong base such as sodium hydroxide is added (723). The intrinsic viscosity may be reduced to 5 to 10% of its original value. Polymethacrylonitrile does not behave in this way indicating that the α-hydrogen atoms of polyacrylonitrile appear to be involved in the chain cleavage.

Butadiene-acrylonitrile and styrene-acrylonitrile copolymers are reported to become cross-linked when irradiated with high-energy electrons (684).

Properties of Acrylonitrile Polymers

The structure of polyacrylonitrile is usually represented as that of a linear paraffin with nitrile groups on alternate carbon atoms:



$$----\mathrm{CH_2{-}\underset{\underset{CN}{|}}{CH}{-}CH_2{-}\underset{\underset{CN}{|}}{CH}{-}CH_2{-}\underset{\underset{CN}{|}}{CH}{-}CH_2{-}\underset{\underset{CN}{|}}{CH}}----$$

The infrared spectrum of the polymer indicates that by far the major portion of the polymer possesses this head-to-tail structure (552). The absence of ketene-imine absorption, in the infrared spectrum of the polymer, indicates that 1-4 addition does not occur to an appreciable extent, as it does in the polymerization of methacrylonitrile (1050). The extent of chain branching which occurs depends upon the method of polymerization, with high temperatures leading to more branching.

Polyacrylonitrile from bulk polymerization contains trapped-free radicals (75, 76). These radicals are destroyed in a matter of minutes after contact with air.

The unique properties of polyacrylonitrile are attributed to its strong, compact $-CN$ dipoles. Close packing of adjacent chains produces a crystalline structure with powerful intermolecular forces. The specific gravity of the polymer is 1.17, corresponding to a 31% shrinkage on polymerization (641, 825). Only specific, and highly polar liquids are able to solvate the nitrile dipoles, separate the chains and effect solution (197, 409, 552, 869, 1044, 1125). By way of contrast, polymethacrylonitrile, which has the bulky methyl group in place of hydrogen, softens at 115°C., and dissolves in a variety of solvents.

Fractionations of solutions of acrylonitrile polymers (119, 504, 552, 1307) and copolymers (219) by solvent precipitation have been reported. The crystalline nature of the polymer is unfavorable for good fractionation (119). A relationship between viscosity average molecular weight and intrinsic viscosity has been developed by Cleland and Stockmayer (246):

$$[\eta]=2.43 \times 10^{-4} M_2^{0.75}$$

where $[\eta]$ is the intrinsic viscosity in deciliters per gram. This equation, based on light-scattering measurements of unfractionated samples, is in good agreement with similar measurements of other investigators (1). Other equations have been given by Houtz (552), Bisschops (119) and Onyon (1367). In the case of copolymers of acrylonitrile some anomalous effects have been noted; for example, certain liquids dissolve copolymers having a limited range of composition, but will not dissolve either homopolymer (95).

Concentrated solutions of polyacrylonitrile (such as a 20% solution in dimethylformamide) will undergo reversible gelation. The phenomenon is strongly dependent on temperature and concentration, and has been ascribed to the formation of crystalline nuclei (118, 120).

When polyacrylonitrile is heated it softens somewhat, but does not flow except under high pressure. At temperatures above about 130°C. the polymer yellows slowly. Between 200°C. and 300°C. rapid decomposition occurs. Ammonium cyanide, hydrocyanic acid and acrylonitrile are formed in small amounts as a result of pyrolysis between 175°C. and 300°C. (534). The thermal degradation of copolymers of acrylonitrile has been studied (440, 675).

Polyacrylonitrile fibers have been reported to retain more than half their strength after heating 16 hours at 200°C. at which time they are said to be jet black (552). Additives that inhibit color development in heated acrylonitrile polymers have been discovered (982). The exact cause of such color development is unknown, although formation of condensed heterocyclic rings has been postulated (552, 646). The color stability of polyacrylonitrile varies with the method of preparation. The initiating system chosen is particularly important (1). This suggests that color may develop only at special points such as end groups or double bonds, rather than randomly in the molecule.

The second-order transition-temperature of polyacrylonitrile has been given as >100°C. based on dielectric measurements (1177), and as 130°C. from extrapolation of dilatometer measurements (420). This transition temperature has also been determined for several copolymers of acrylotrile (420, 498, 1153).

Because of the difficulties encountered in obtaining perfect molded specimens from polyacrylonitrile, data on mechanical properties are very limited (964). Numerous reports on mechanical properties of polyacrylonitrile fibers (198, 463, 489, 552, 960, 1043) and of copolymers (389, 829, 1092) have appeared.

Some of the electrical properties of polyacrylonitrile (505, 959, 1177, 1178) and acrylonitrile copolymers (190, 357, 358, 505, 959) have been determined.

The permeabilities of polyacrylonitrile films to water vapor (789) and organic vapors (999) have been studied. The diffusion rates of hydrogen and nitrogen through butadiene-acrylonitrile rubber have also been reported (83).

Polyacrylonitrile cannot be spread at an air-water interface to form a monomolecular film, but is said to give a film of the "condensed type" at an oil-water interface (548).

At 25°C. and 50% relative humidity, polyacrylonitrile is stated to absorb only 0.8% water (624). However, Houtz reports that polyacrylonitrile absorbs 1.5 to 2% moisture very rapidly at moderate humidities (552).

The crystallinity of polyacrylonitrile is reported to be evident from X-ray studies of the polymer and of the drawn fibers (552). The presence of 3-mole percent vinyl acetate is said to reduce crystallinity (623).

When examined under the electron microscope, an emulsion or latex of polyacrylonitrile appears to consist of spheroidal particles ranging from 500 to 1000 Ångstroms in diameter (927). These particles are frequently aggregated or joined by fibrous connectors. This appears to be a manifestation of fibrillation. A peculiar property of polyacrylonitrile is this tendency of the "latex" or emulsion particle to persist after molding. An electron micrograph of a fractured surface of molded polyacrylonitrile (Figure 11) shows the presence of particles corresponding in size and shape to the particles of the powder from which it was molded.

Polyacrylonitrile has been studied with regard to its macromolecular texture. Thin films were cast on glass from a 0.5% solution in ethylene carbonate. They were metalized at an angle to improve photographic contrast of the top surface of the film, and were subsequently examined in the electron microscope. Electron micrographs (Figure 11) showed a still finer particulate texture than was observed in the fracture surface. These are probably the ultimate particles, i.e., the macromolecules. Not only are they pictured in size and shape, about 20 to 100 Ångstroms in diameter, but it is possible to estimate their molecular weight from their measured sizes (926). Figure 11 also shows the tendency of the macromolecules to aggregate (appearing as raised areas in picture). This can better be appreciated when depicted at lower magnification, as in Figure 12, which, for maximum effect, should be viewed at arm's length. These aggregates correspond approximately in size and shape with the spheroidal particles shown in Figures 9 and 10. A typical aggregate is indicated in Figure 12 by the arrow.

Secondary aggregates, visible with the optical microscope (1), usually appear spherical or oval (Figure 13); but under some conditions the structure is that of a dried gel (Figure 14). These secondary aggregates usually can be broken down mechanically and are probably dependent on such factors as rate of agitation, kind and quantity of electrolyte, and the presence of copolymers and dispersing agents.

SUMMARY

Acrylonitrile is a monomer capable of imparting unique properties to polymeric materials, both by polymerization and copolymerization. Special characteristics of polyacrylonitrile include:

- Hardness
- Heat resistance and slow burning
- Resistance to most solvents and chemicals
- Resistance to sunlight and exposure
- Ability to form oriented fibers and films
- Reactivity toward nitrile group reagents
- Compatibility with certain polar substances

Some of the more important commercial developments in which these properties have been utilized are summarized in the next section of this book.

APPLICATIONS

This section is based, for the most part, on numerous references to the patent literature. While the information contained in these references is thought to be accurate and reliable, American Cyanamid is not in a position to refute or support their claims. This section merely presents the data, claims, and statements of the literature cited. For additional details on specific items, it is recommended that the reader consult the original sources.

Adhesives

Acrylonitrile-butadiene rubbers can be formulated into adhesives with characteristically high strength, excellent aging properties, and good chemical resistance, including resistance to aliphatic and aromatic solvents, and to most plasticizers that cause bond failure of other adhesives. These adhesives are especially suited to bonding synthetic rubber stocks to metal (555).

Acrylonitrile-butadiene rubber and phenolic resins can be dissolved together in solvents, such as methyl ethyl ketone, to form extremely useful cements (43, 286, 339, 354, 392, 431, 436, 821, 872, 905, 961, 1158). These cements have the flexibility of nitrile rubber and the cured adhesive strength of phenolic resins. Metals, plastics, rubber, leather, wood, fabrics, glass fiber, Nylon and resin-coated materials may be cemented to themselves, and to each other (392, 1407).

Among the other modifying ingredients in reported adhesive formulations based on nitrile rubber are various vinyl polymers and copolymers (372, 401, 560, 799, 863, 905, 986, 1061), wood rosin products (96, 239, 339, 393, 479, 499, 757), polychloroprene (393), chlorinated rubbers (179, 415, 609), butadiene-styrene rubber (104), natural rubber (105, 609), and coumarone resins (372).

Treating acrylonitrile-butadiene resins with dilute sulfuric acid (949) or with concentrated phosphoric acid (330) gives oil-resistant rubber cements. Another modification of the copolymer is achieved by heating with maleic anhydride. This product, compounded with polychloroprene and dehydroabietic acid, is particularly useful in bonding polymer films to metal surfaces (393).

An acrylonitrile-butadiene emulsion, prepared in the presence of dodecyl mercaptan, provides a pressure-sensitive adhesive film with excellent aging characteristics (1247).

Among the specific applications mentioned for the various rubber-based adhesives are: joining leather parts in shoe manufacture (328, 431, 757, 863), bonding an abrasive coating to foam rubber (354), adhesive for resealable waxed paper wrappings (479), subcoat for adhesive tapes (105, 361, 499), adhesives for waterproof plywood lamination (401), bonding glass fibers into insulating board (436), attaching magnetic tape to flexible backing (961), bonding brake linings to brake shoe (43), joining pile fibers to fabric backing (372), attaching patches to plastic film (986), and bonding abrasive materials to form grinding wheels (1379).

Other copolymers of acrylonitrile which have been found useful in adhesive applications are acrylonitrile-ethyl acrylate copolymers for pigment coating of paper (810); acrylonitrile-vinylidene chloride copolymers in conjunction with casein for book binding (1184); and acrylonitrile-acrylic acid -alkyl acrylate terpolymers as coatings for fabric and paper, undercoatings for poly(vinyl chloride) top coats, and as pigment binders for leather (1328).

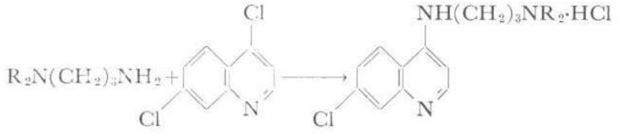
Antioxidants

3-Thiopropionic acids and esters of the type $RSCH_2CH_2COOR'$ are effective antioxidants for edible oils, fats, waxes, and soap (448, 449). These esters may be prepared by esterification of the nitriles resulting from the cyanoethylation of mercaptans. Thiodipropionic acid, the product of hydrolysis of 3,3′-thiodipropionitrile (33), is useful in preventing the rancidification of fats and edible oils (448).

Chemotherapy

Acrylonitrile has been employed in two multi-step syntheses of an antimalarial Hydrangea alkaloid (69) as well as in the synthesis of adrenal cortical hormones (1171, 1172).

Several 3-alkylaminopropylamines, which are prepared by hydrogenation of the alkylamine-acrylonitrile adduct, have been condensed with heterocyclic compounds to yield antimalarials (41, 195, 272, 293, 525, 632, 1000, 1023, 1055, 1105):

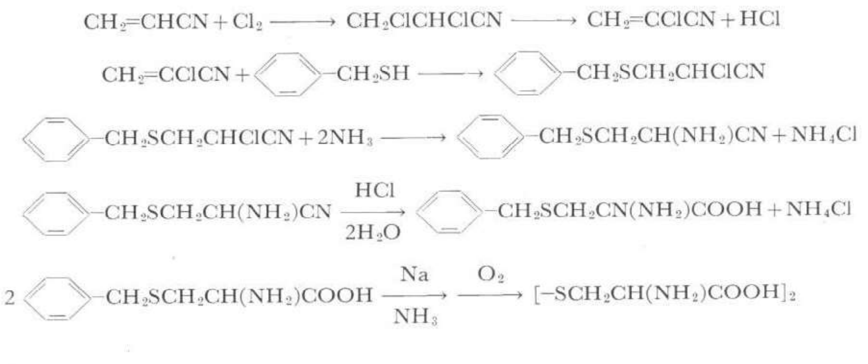


Derivatives of dialkylaminopropylamines, for example N-(3-diethylaminopropyl)-1,8-naphtholimide, have shown activity as local anesthetics, but in most cases their toxicities are relatively high (101, 751).

The synthesis of the pellagra-preventive factor, pantothenic acid, usually involves β-alanine. This intermediate may be prepared in one step from acrylonitrile, ammonia and water (207). Alternatively, β-alanine may be synthesized by hydrolyzing the reaction product from phthalimide and acrylonitrile (412), or from acetamide and acrylonitrile (843).

Ethyl 3-ethoxypropionate, prepared by alcoholysis of 3-ethoxypropionitrile, can be used in the preparation of vitamin B_1 (1012). Among the amino acids which have been synthesized from acrylonitrile are dl-cystine (454), dl-glutamic acid (254), and dl-ornithine (14):

CYSTINE:

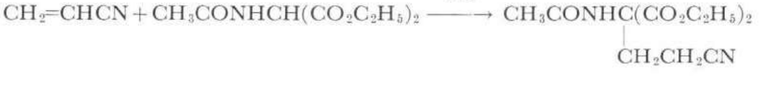


GLUTAMIC ACID:

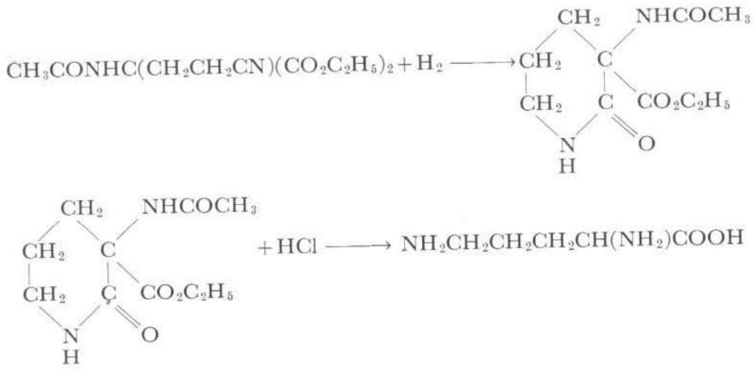
$$CH_2{=}CHCN + NH_2CH(CO_2C_2H_5)_2 \xrightarrow{KOH} NCCH_2CH_2C(NH_2)(CO_2C_2H_5)_2$$

$$NCCH_2CH_2C(NH_2)(CO_2C_2H_5)_2 + H_2O \xrightarrow{H_2SO_4} HO_2CCH_2CH(NH_2)COOH$$

ORNITHINE:



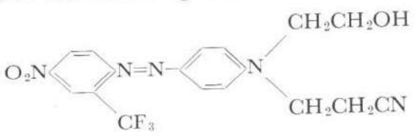
$$CH_2{=}CHCN + CH_3CONHCH(CO_2C_2H_5)_2 \xrightarrow{Na} CH_3CONH\underset{\displaystyle CH_2CH_2CN}{\underset{|}{C}}(CO_2C_2H_5)_2$$

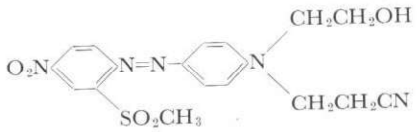


Dyes

Many of the various nitriles, amides, acids, and esters prepared via cyanoethylation reactions may prove useful as intermediates in the synthesis of dyes (664, 1078). Scarlet dyes, which are particularly useful for the dyeing of cellulose acetate fibers, and which are exceptionally fast to the action of light and gas, may be prepared from the product of the cyanoethylation of N-(2-hydroxyethyl)aniline (327).

Two such dyes have the following structures:





Compounds made by the intramolecular condensation of aromatic aminopropionitriles are also of interest in the dye industry (571). Compounds of the type, RCH_2CH_2CN, where R is phenylmethylamino, 1-carbazolyl or 1-(1,2,3,4-tetrahydro)quinolyl residues, can be used for these syntheses.

Electrical Industries

Cable and wire insulation can be made from acrylonitrile-alkyl acrylate copolymers (1393) as well as from acrylonitrile-butadiene rubbers alone (725, 831), or blended with poly(vinyl chloride) (3, 65), poly(vinylidene chloride) (425), poly(isobutylene) (144), or vinyl chloride-vinyl acetate copolymer (1127). Insulating materials can be obtained from polyacrylonitrile blended with polyacrylates, from acrylonitrile-halogenated styrene copolymers (150), from acrylonitrile-vinyl ester copolymers after treatment with an aldehyde or ketone (302), from a heated mixture of a polyacrylate and polyacrylonitrile (832), or from a heated mixture of a polyacrylate, polyacrylonitrile, and an alkyd or phenol-aldehyde resin.

An acrylonitrile-butyl acrylate-methacrylic acid terpolymer, blended with a urea- or melamine-formaldehyde resin, is useful as an insulating coating for magnetic wire (1396).

A styrene-based thermoplastic casting composition, for the potting of electrical components, is improved by incorporating from 1 to 30% acrylonitrile (686). The electrical properties of the resin have been reported for 5% acrylonitrile content (358).

A dielectric paper, made of cyanoethylated wood cellulose, can be used in capacitors (776). Highly cyanoethylated cellulose, an amorphous, thermoplastic material, has an unusually high dielectric constant (13.3 at 60 cycles and 25°C.) (1324). Polyacrylonitrile fibers are finding use for electrical insulation (349).

An electrically conductive rubber can be prepared by incorporating a conductive carbon black into a solution of acrylonitrile-butadiene copolymer in methyl ethyl ketone, evaporating the ketone, and curing (653).

Emulsifying Agents

The cyanoethyl ethers obtained by the reaction of cellulose (127), starch (126) or gums (784) with acrylonitrile are useful as thickening, emulsifying and dispersing agents. Their use in textile sizes and insecticidal sprays has been recommended (126, 127). Oxidized cyanoethylated casein can be used as a substitute for gelatin in peptizing silver-halide dispersions (1325). The use of cyanoethylated proteins as emulsion stabilizers for butadiene-styrene coating compositions has been reported (1335).

The preparation of quaternary ammonium compounds, having the general structure $RCONH(CH_2)_3NR_3Cl$, involves the cyanoethylation of a dialkylamine as an intermediate step in their synthesis. They have excellent wetting, emulsifying and germicidal properties (265).

Polyacrylonitrile is useful as a thickening agent for organic detergents (858).

It has been discovered (32) that 3-methoxypropylamine, which is prepared by hydrogenation of the methyl alcohol-acrylonitrile addition product, is useful in preparing soaps from fatty acids in which the amine serves as the basic constituent. These soaps show excellent emulsifying and dispersing action for certain natural and synthetic resins and waxes. Such emulsions and dispersions are useful in floor finishes, water paints, textile finishes and in similar fields of application. The use of this amine is particularly advantageous for these purposes because its aqueous solutions do not change greatly in composition on evaporation. Approximately constant alkalinity is thus maintained as films containing these materials are allowed to dry.

Fibers

ACRYLIC FIBERS

The importance of acrylonitrile in the synthetic fiber industry is indicated by the fact that approximately 100 million pounds were consumed in 1957. Outstanding physical properties together with moderate cost, have enabled these fibers to find increasingly broader application.

A list of properties and an outline of the uses these properties suggest follow (895, 910, 1336):

Properties

- Resistance to stretch
- Resistance to heat
- Resistance to sunlight and outdoor exposure
- Resistance to microorganisms
- Resistance to insects
- Resistance to chemical attack
- High strength
- Dimensional stability to dry- and wet-cleaning
- Low moisture absorption
- Rapid drying
- High flex life
- Good recovery from wrinkling
- Silk-like luster, hand, and drape
- Warm feel or "hand"
- Adaptability to standard equipment
- Excellent bonding to rubber and resins
- Good electrical properties
- Ability to be set by heat
- High covering power and bulk

Uses

- Acid resistant clothing
- Anode bags
- Aprons
- Auto tops
- Awnings
- Bags for chemicals
- Bathing suits
- Blankets
- Blouses
- Bristles
- Carpets
- Conveyor aprons
- Electrical insulation
- Felts
- Filtration cloths
- Fish nets
- Hosiery
- Jersey fabrics
- Laundry nets
- Lingerie
- Linings
- Outdoor furniture
- Overcoats
- Paint-roller covers
- Pile fabrics
- Pipe covering
- Rainwear
- Sewing thread
- Sheets for hospital beds
- Shirts
- Shock-resistant rope
- Shower curtains
- Suits and dresses
- Sweaters
- Tarpaulins
- Tire cords
- Tropical clothing
- Umbrellas
- Uniforms
- Upholstery
- Yacht sails

Polyacrylonitrile itself does not dissolve in the usual spinning solvents. Therefore, some of its more soluble copolymers were first used, e.g., those with a high proportion of vinyl chloride, which are soluble in acetone. The resulting fibers are better than the older vinyl chloride-vinyl acetate fibers with respect to resistance to solvents, dye affinity, and shrinking and softening temperatures (161, 941).

In the form of staple fibers the vinyl chloride-acrylonitrile copolymers have many advantages over wool. They are strong and resilient, warm, dyeable, and resistant to combustion. Moreover, they are unattacked by moths or mildew, are non-shrinkable, and are resistant to solvents, acids and alkalis.

With the discovery of solvents suitable for spinning polyacrylonitrile and its copolymers, the development of a number of commercial fibers of high acrylonitrile content has taken place. A great many patents have issued within the past few years on new copolymers containing about 85-90% acrylonitrile. The comonomers have usually been added to increase dye or moisture affinity of the fiber. In general, the copolymers retain the desirable physical properties of polyacrylonitrile. Several excellent reviews have covered this rapidly expanding acrylic fiber field (462, 648, 649, 1083).

It has been reported that mixtures of acrylonitrile copolymers and fully cyanoethylated cellulose can be spun from a common solvent (1365).

NATURAL FIBERS

An important chemical modification of cotton may be achieved by cyanoethylation of the hydroxyl groups to such an extent that a nitrogen content of 3 to 4% is obtained (261). Fiber appearance, tensile strength, and elongation are not appreciably changed. However, a marked improvement in resistance to microorganisms, heat degradation and acid degradation is obtained. In general, the affinity for most direct dyes decreases as the nitrogen content of cyanoethylated cotton increases, whereas the affinity for acetate and acid dyes increases (261, 1261).

It is expected that cyanoethylated cotton will find uses in thread, cord, rope, nets and textiles where its improved chemical, physical, and biological properties are needed (1236, 1243). Some of the end uses which are being considered for this modified cotton are:

Enameling duck
Filter fabrics
Fishing lines and nets
Industrial belting
Ironing-board covers
Sand bags
Tents and tarpaulins
Tobacco shade-cloth

Other cellulosic fibers such as manila, sisal and jute can be made rot resistant by cyanoethylation, and may find applications in marine uses (1, 1228, 1236).

Cyanoethylation increases the affinity of wool for cationic and direct dyes (1212).

Graphic Arts

Copolymers of acrylamide, acrylic acid, and the acrylates with acrylonitrile can be used as gelatin replacements in making photographic emulsions (97, 570, 708). A copolymer of acrylonitrile with vinylidene chloride and itaconic acid is useful as a layer between gelatin-silver halide emulsions and the paper-film backing (1045). In addition, a black, opaque, paper backing for film is obtained, by coating with an acrylonitrile-vinylidene chloride copolymer in which carbon black is dispersed (652).

Terpolymers of acrylonitrile, acrylic esters, and vinylpyridines or vinyl quinolines are reported to be useful mordants for acid-photographic dyes. The terpolymers are used in layers or coatings to prevent diffusion of the dyes (1263). Acrylonitrile-butyl acrylate-N-methyl methacrylamide terpolymers can be used as protective coatings on the viewing surface of photographic elements such as prints, negatives and positive transparencies (1404, 1406).

A process for printing designs on fabric by a decalcomania technique employs an emulsion of polyacrylonitrile on the fabric to be printed (1173).

Mixtures of polyacrylonitrile and polystyrene (510), as well as copolymers of acrylonitrile and styrene (509), are reported to be useful for making solvent-resistant printing plates. Acrylonitrile-butadiene rubber has been suggested as a facing for offset printing blankets (618) and other rolls or plates subjected to the action of printing inks (619).

An acrylonitrile-styrene emulsion which has been subjected to alkaline hydrolysis is useful as a thickener for printing pastes (535).

A resin vehicle for fast-drying printing inks can be obtained by heating an esterified mixture of tall oil and polycarboxylic acid with styrene and acrylonitrile monomers (967). Acrylonitrile-butadiene (752) or acrylonitrile-styrene copolymers (968) can be incorporated into printing ink compositions (752).

Insecticides

Acrylonitrile and several of its derivatives are excellent fumigants for use against a variety of insects (356, 631, 771, 1052). Either alone, or mixed with carbon tetrachloride, acrylonitrile gives high penetration and kill against the tobacco moth and cigarette beetle in stored tobacco (78, 79, 1052, 1060), and against the confused flour beetle in stored grain (275, 276, 429, 701, 920, 1004, 1052). Acrylonitrile is also an effective fumigant for combatting rice weevil (275, 771). It is reportedly useful for Aphis rumicis (771), citrus red spider (771), resistant California red scale (771), citrus mealy bug (771), southern army worm (771), oriental fruit fly (70, 700), and the common household insects (428, 429, 771) such as the carpet beetle, cockroach and clothes moth. However, it should be noted that there was some damage to the plants involved in these experiments. A mixture of acrylonitrile and carbon tetrachloride also is valuable in the fumigation of stored seeds. The fumigant appears to kill effectively without any injurious effect upon the germination (430).

The cyanoethyl ester of diethylphosphorodithioic acid is an effective insecticide for the German roach, the milkweed bug, the American roach and the common housefly (87). A large number of halogenated derivatives of acrylonitrile, such as 2-chloroacrylonitrile, have been tested and found to be effective as fumigants for grain-infesting- and household-insects (311). Polyacrylonitrile, 3,3′-oxydipropionitrile (from water and acrylonitrile), and 4-acetyl-4-(2-cyanoethyl)pimelonitrile (from acetone and acrylonitrile) are said to be effective against pea aphids (756).

Leather

Leather-like sheets can be prepared from a blend of acrylonitrile-butadiene copolymer, clay and polyvinyl chloride (973); from a mat of non-woven fibers such as polyacrylonitrile fibers plus a binder, such as an acrylonitrile copolymer (439); or from a blend of phenol-formaldehyde resin and butadiene-acrylonitrile copolymer (1183). Acrylonitrile-butadiene rubber, after heating with a blowing agent and then leaching, gives a moisture- and vapor-permeable leather substitute (845).

Acrylonitrile-butadiene latex is claimed to be a useful finishing agent (115, 374) for natural leather.

Paper

Acrylonitrile rubbers are useful for imparting water and oil resistance to paper, and for providing paper with increased burst factors, tensile strength, elongation, stiffness and sizing resistance. Porosity is decreased (844). Acrylonitrile-butadiene latices can be incorporated into paper, either before sheet formation (28, 55, 115, 121, 683, 854, 1093, 1401) or afterwards (115, 282, 292, 1093, 1109). In the former case, treatment may be effected by the use of alum, or by some other means of precipitation of the latex, so that the rubber particles adhere firmly to the cellulose filaments. Sheets produced from the paper treated in this way are hard and tough and have high density. Incorporation of a mixture of acrylonitrile-butadiene latex and phenol-aldehyde resin, before sheet formation, is said to produce a paper with exceptional stiffness (1401). Paper sheets impregnated by either dry- or wet-web saturation techniques are soft and possess high edge tear resistance, excellent wet strength, low density, high elongation and good fold and drape properties (115). The BARDAC Process can be used for stock addition of synthetic rubber latices to paper and paperboard (28). Mineral pigments and clays can be dispersed in the latex when coating paper sheet (747, 1031).

Papers containing acrylonitrile rubber are very useful as gasket material (1093), protective wrappings, shelf coverings, imitation leather bases, tape backing and other specialized uses (115). A further advantage lies in their compatibility with other vinyl resins. Coatings of these vinyl latices can, therefore, be applied to paper saturated with acrylonitrile-butadiene rubber without the use of additional adhesives (115).

Paper made from polyacrylonitrile fibers is three to ten times as strong as paper made from pulp or rags and may, therefore, find specialized uses (839).

Paper which possesses valuable dielectric properties for capacitor construction (776) has been made from cyanoethylated wood pulp. Cyanoethylation also improves the dimensional stability (1228) and printability (1235) of paper, and renders it rotproof (1).

Acrylonitrile can be polymerized on the surface of paper to impart a beneficial polyacrylonitrile coating (227).

Plastics

Polyacrylonitrile itself is difficult to mold because of its lack of flow. Copolymers of acrylonitrile, on the other hand, have been prepared with good molding characteristics. In general, introduction of acrylonitrile into copolymers increases hardness, solvent resistance and softening temperature. Lack of flow in the high-nitrile copolymers may be overcome by the use of plasticizers.

COPOLYMERS WITH ACRYLATES

Copolymers of acrylonitrile with ethyl acrylate have been suggested for impregnating filling material for upholstery (510), and for covering gloves for amputees (291, 689, 828), while those with methyl methacrylate are useful in oilcloth, linoleum, wall panels, etc. (564).

The bulk copolymerization of acrylonitrile and methyl methacrylate gives a thermoplastic product with unusual mechanical endurance. This property makes it outstandingly useful, for example, in arch supports, or in shuttles (566).

A three-component copolymer of acrylonitrile, butyl acrylate and vinyl acetate, blended by milling with vinyl acetate-butyl acrylate copolymer, produces flexible films particularly suited for rainwear, shoe soles, and food wrapping. Reportedly, the blend has good stiffness-temperature characteristics (222). A product of similar properties and applications results from ternary copolymerization of acrylonitrile, 2-ethylhexyl acrylate and vinyl chloride (955).

Blends of acrylonitrile-ethyl acrylate copolymers with melamine-formaldehyde resins yield tough, dimensionally-stable molded products resistant to crazing and possessing good electrical properties. Low mold shrinkage (e.g., 5.1 mils per inch) and low water absorption also are claimed (1165).

A three-component copolymer of acrylonitrile, methyl methacrylate and methacrylamide has excellent tensile and impact strength as well as good solvent resistance (91).

COPOLYMERS WITH BUTADIENE

The rubbery acrylonitrile-butadiene copolymers have proved to be highly valuable modifying ingredients in both thermoplastic and thermosetting resins.

Acrylonitrile-butadiene copolymers containing larger amounts of acrylonitrile than are used in synthetic rubbers are tough, leathery and oil resistant (496, 983). By blending these copolymers with acrylonitrile-styrene copolymers, a thermoplastic product of considerable versatility is produced (286, 304, 305, 1112, 1129, 1269). This material can be pigmented, molded, cemented, riveted, drilled, sawed, turned, cold-punched, buffed and polished. It has high-impact strength and is resistant to solvents and to most alkalis and acids. It is waterproof, mildew-proof, vermin-proof, odorless, washable, and light in weight, and it is warm to the touch even at low temperatures. Its use in golf-club heads, luggage, radio and typewriter cases, molded cams, gears, pipe fittings, door knobs, golf-bag bottoms, sun helmets, instrument cases, refrigerator strips, panels and food trays has been recommended (286, 1112, 1129). When natural rubber (Hevea) is added to the above blend of copolymers the resulting ternary blend is particularly useful in relatively heavy, semi-rigid sheetings. These can be used as flat panels, or post-formed into curved panellings for automotive interiors, automotive wheel housings and formed luggage shells, as well as sinks, drainboards and counter tops. The finished articles are tough, dimensionally stable and impact resistant (907).

When an acrylonitrile-butadiene elastomer is blended with polystyrene the product exhibits low acid- and water-absorption and high impact strength. Storage-battery containers molded from this blend withstand cycles of hot-and-cold exposure well, and have an impact strength ten times that of containers made from polystyrene alone (335). The addition of a peroxide during the blending of the elastomer with the polystyrene improves the tensile- and impact-strength of the product (329). Instead of blending polystyrene with acrylonitrile-butadiene elastomer, the latter can be dissolved in monomeric styrene and the mixture polymerized. The product is a homogenous interpolymer which can easily be molded (40).

A lower-density thermoplastic copolymer of acrylonitrile, butadiene, and styrene has high tensile and impact strength (782).

Improved mechanical properties of films and molded articles of poly(vinyl chloride) are obtained when butadiene-acrylonitrile copolymers are used as plasticizers (855, 919, 996, 1262). Films of such a blend are eminently suitable for food wrapping (996). The insolubility and inertness of the elastomer are particularly advantageous in this application (688). Suitable food-wrapping films are also obtained with a ternary blend of acrylonitrile-butadiene copolymer, acrylonitrile-vinyl chloride copolymer and polychloroprene (997), and with a blend of acrylonitrile-butadiene copolymer with vinyl chloride-vinylidene chloride copolymer (212). When acrylonitrile-butadiene elastomer is compounded with vinyl chloride-vinyl acetate copolymer, and other additives, a long-wearing phonograph-record composition results (852). A tear-resistant porous-sheet material, used in shoe inner soles, is obtained with a blend of acrylonitrile-butadiene elastomer and poly(vinyl chloride) (1262).

A blend of rubber hydrochloride, butadiene-acrylonitrile rubber and a plasticizer is said to be particularly useful for preparing packaging film for oily foodstuffs, such as lard or margarine (1118).

Molded parts made with phenolic resins, although strong, are inherently brittle. Nitrile rubbers, unlike most other rubbers, are compatible with phenolic resins. Blends of acrylonitrile-butadiene rubber (containing about 90% acrylonitrile) with highly modified phenolic resins have found many commercial uses (286, 724, 823, 1163, 1199). Low-cost, "low-impact" fillers, such as wood flour and asbestos, can be used to give high-impact moldings using these phenolic-rubber blends. The use of mineral fillers permits manufacture of parts with exceptionally good electrical and other physical properties (286). Employment of the nitrile rubber permits phenolic moldings of greater hardness than can usually be obtained without excessive pigment loading (392). The products are more resistant to the effects of high temperature and oxidation, and have much better low-temperature flexibility than the highly loaded compounds of equivalent hardness. Other properties, such as impact strength and water absorption, are also improved (392, 1199). The use of these blends in pipe and pipe fittings is growing. The material can be cut and threaded using standard equipment (724).

High-density molded articles can be formed from blends of nitrile rubber and cork (245, 1155). A joint-sealing composition composed of coal-tar pitch, nitrile rubber and polymerized castor oil has high resistance to jet fuels, as well as high solvent resistance generally (773).

COPOLYMERS WITH ISOBUTYLENE

Copolymerization of acrylonitrile with isobutylene gives products containing 70% acrylonitrile having a flow temperature of 105°C. These copolymers are suitable for molding, and for the impregnation and coating of textiles (346, 1107).

A three-component copolymer of acrylonitrile, isobutylene and vinylidene chloride is extrudable at 150°C. under 50 pounds pressure. With a plasticizer, this copolymer may be pressed at 180°C. to give a clear disk which does not become brittle on prolonged storage (1022). Acrylonitrile-isobutylene copolymers can be plasticized with ketone-aldehyde condensation products, thereby reducing the flow temperature. Other physical properties are unimpaired (1056).

COPOLYMERS WITH STYRENE AND SUBSTITUTED STYRENES

Acrylonitrile-styrene copolymers are easily molded (67) to give products which have much better tensile strength than ordinary polystyrene (221, 223, 303, 451, 524, 742). The flexural and impact strengths are also improved. These copolymers possess improved resistance to abrasion and heat, greater outdoor durability and better resistance to oils and solvents. They also exhibit less after-crazing due to unrelieved molding stresses, and improved insert reduction (1140). Printing plates prepared from acrylonitrile-styrene copolymers show good hardness, great toughness, complete insolubility in benzene, and good stability to motor fuel (509).

Cyanamid's Cymac* 201 methylstyrene and acrylonitrile copolymer is reported to give moldings with high tensile and flexural strengths, high heat-distortion temperature, and good craze-, abrasion-, and chemical-resistance (223, 1338, 1339).

Acrylonitrile-isopropenyltoluene copolymers have also been reported to be desirable molding materials (669).

A third monomer such as *p*-vinylbiphenyl (987), maleic anhydride (988), acrylic acid (1217), or acenaphthylene (1225), can be included to produce thermoplastic molding compositions. A thermosetting material, useful as a binder for mica, results from the four-component copolymerization of acrylonitrile, styrene, maleic anhydride and diallyl phthalate (777).

COPOLYMERS WITH OTHER MONOMERS

Thermoplastic molding compounds may be prepared from copolymers of acrylonitrile with vinyl acetate (461), vinyl acetate plus methacrylonitrile (896), vinyl chloride (417), vinylidene chloride (379, 480, 616, 790, 908), allyl isocyanate (955) and α-methylstyrene (1111).

Copolymers of acrylonitrile and N-2-norcamphanylacrylamide are useful in the preparation of tough, high melting films, sheets and molded products (1220).

CYANOETHYLATED CELLULOSE

With the introduction of two or more cyanoethyl groups per anhydroglucose unit, cellulose is converted into an amorphous, thermoplastic prod-

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*Reg. U. S. Pat. Off.

uct. This material is soluble in organic solvents such as acetone, acrylonitrile, dimethylformamide and pyridine. It can be molded, spun into fibers and cast into films (1, 551, 714, 1324, 1365). It has an unusually high dielectric constant (1324).

Plasticizers

Acrylonitrile-butadiene elastomers are plasticizers for polyvinyl and polyvinylidene chlorides and other vinyl polymers (3, 131, 340, 384, 392, 423, 613, 899, 918, 919, 977, 1182). Problems of staining, plasticizer bloom, and of evaporation or lacquer lifting are avoided when this plasticizer is used (392). Nitrile rubber is also useful as a modifier for phenol-, urea-, and melamine-formaldehyde resins (574). Polyacrylonitrile also can be used as a modifier for these same resins (348, 466, 672). Other copolymers of acrylonitrile reportedly useful in plasticizing vinyl polymers are: acrylonitrile-butadiene-isobutylene terpolymer (77), acrylonitrile-ethyl acrylate copolymer (901), and a three-component polymer of acrylonitrile, butyl acrylate and nitropropane (385).

Acrylonitrile and succinonitrile have been suggested as flow promoters for a blend of epoxy resin and poly(vinyl acetate) (1151). Alkoxypropionitriles plasticize vinyl chloride-vinylidene chloride copolymers (377, 378), and the esters derived from these nitriles also have plasticizing properties. 4-Acylbutyric esters, made by the cyanoethylation of various ketones (130, 176, 395, 898), are particularly useful as plasticizers for vinyl resins such as poly(vinyl chloride). Plasticizers also result from esterification of cyanoethylated alcohols of various types (31). The cyanoethylation products of substituted malonic esters can be used to plasticize vinyl resins (397), while cyanoethylated rosin amines plasticize synthetic rubbers (625). The product of cyanoethylation of ketone-aldehyde condensates can be used to plasticize acrylonitrile-isobutylene copolymers (1056). The reaction products of acrylonitrile with α- and β-tung oil fatty acids are secondary plasticizers for vinyl chloride-vinyl acetate copolymers (1286).

Rubber

Production of rubber goods from acrylonitrile-butadiene copolymers constitutes one of the most important end uses for acrylonitrile. Methods of compounding such rubbers, and descriptions of their properties and uses, are detailed at great length in the patent literature, and are summarized in a number of books and articles (114, 191, 362, 392, 741, 819, 939, 1144).

The rubbers are usually made from acrylonitrile-butadiene copolymers which contain 15-55% by weight acrylonitrile. These rubbers possess high resistance to the swelling action of solvents, oils and greases, far surpassing natural rubber or GR-S products in this respect. In addition, they possess excellent resistance to heat, aging and sunlight (392). Depending upon the methods of compounding, a great variety of rubbers characterized by high tensile strength, excellent elongation, and low-compression set can be produced. Certain formulations provide a combination of low-temperature flexibility and oil resistance, and so are particularly useful for rubber parts operating in coolants. Acrylonitrile rubbers also can be made to have high abrasion resistance, low coefficients of friction, non-corrosiveness to metals, non-adherence to metals, good electrical conductivity and compatibility with vinyl and phenolic resins. It is not possible to have maximum values for all of these properties in one single rubber; but, by proper mixing and compounding, many valuable combinations of these properties can be achieved.

Acrylonitrile-butadiene rubbers are suitable for use at temperatures as high as 250°F., and, if operation in the presence of oxygen is not required, they may be used at temperatures above 300°F. However, elevated temperatures combined with long exposure tend to harden the rubber and reduce its elongation. Low temperatures cause nitrile rubber to become brittle. However, by using certain plasticizers, such as dioctyl adipate, the freeze point can be extended down to as low as −60°F. Long immersion in oil, gasoline, vegetable- and animal-fats and oils, paint- and ink-driers, alcohol or glycol, even at 250°F. or higher, causes little or no change in volume, or in other physical properties of the rubber. For these reasons the acrylonitrile rubbers have found extensive use in parts exposed to petroleum products, coolants, hydraulic fluids and similar liquids. They have been found to be particularly useful for (392):

- Gaskets
- Grommets
- Industrial hose of all kinds
- Mountings for machinery
- Vibration-damping equipment mountings and couplings
- Shock-absorbing equipment
- Adhesives
- Jackets for electric cables, connectors and terminal fittings
- Conveyor belting
- Non-slip, non-marking soles and heels
- Creamery equipment
- Rubber-covered rolls for textile, leather, printing, paper industries
- Printing blankets and mats
- Special parts for machinery requiring resistance to oils or fats
- Pump and valve linings
- Kitchen and plumbing accessories
- Protective clothing

Acrylonitrile-butadiene copolymers can be compounded into either hard- or sponge-rubbers. It is even possible to produce a rubber which is both hard and cellular, and which possesses some very unusual properties (392). This material weighs only 6-8 pounds per cubic foot, yet it has a compressive strength of several hundred pounds per square inch. Water, oil, gasoline and many other liquids are not absorbed, and it will withstand temperatures of 200°F. Its strength-to-weight ratio is one of the highest among commercial materials. It is particularly valuable as insulation against heat, sound, and electricity (392).

Compounding an acrylonitrile-butadiene rubber with a vinyl chloride-vinyl acetate copolymer results in a unicellular foam-rubber with excellent shock-absorbing properties (1381).

Acrylonitrile-butadiene rubbers with special chemical or physical properties may be obtained by polymerizing vinyl monomers within the rubber during cold mastication (1198). Free radicals produced by chain rupture during mastication act as initiators for the polymerization.

The properties of acrylonitrile-butadiene rubbers can be modified by blending the copolymers with natural or synthetic polymers before vulcanization. For example, blending with an equal weight of ethoxyethylcellulose gives vulcanizates with excellent oil and sunlight resistance (424).

Chloroprene and fluoroprene produce rubbery, vulcanizable products when copolymerized with acrylonitrile. The freeze resistance and resilience of the fluoroprene vulcanizate is superior to the corresponding chloroprene formulation (780).

Vulcanizable copolymers of acrylonitrile and acrylic esters also have been obtained. While the tensile strengths of the vulcanizates are lower than those from acrylonitrile-butadiene copolymers, the strengths are still well above the serviceable minimum. The heat resistance of several of these compositions is good, judging from the fact that only small changes in the brittle point take place on aging 72 hours at 350°F. (389).

Rubbery materials which resist swelling in fluorinated (as well as non-fluorinated) solvents can be prepared by copolymerization of acrylonitrile with 1,1-dihydroperfluorobutyl acrylate (10).

A number of rubbery three-component polymers have been prepared which are said to possess advantages over acrylonitrile-butadiene copolymers. A terpolymer of acrylonitrile, butadiene and vinylidene chloride has a better combination of tensile- and elongation-characteristics and lower permanent-set values than acrylonitrile-butadiene rubbers. This three-component polymer also has good resistance to aromatic hydrocarbons, good tear strength and desirable electrical properties (1020). A mixture of vinyl esters of soya-bean-oil acids has been used as a modifying third monomer in acrylonitrile-butadiene rubber compositions (1130). Acrylonitrile-butadiene rubber copolymers of controlled gel content (as indicated by the portion insoluble in methyl ethyl ketone) can be prepared by adding small amounts of divinylbenzene to the partially polymerized mixture of monomers. The rubbery product is particularly suitable for blending with thermoplastic polymers, such as polystyrene or styrene-acrylonitrile copolymer, to improve the impact strength (936). Cross-linking is prevented or retarded during the copolymerization of acrylates with dienes by the addition of small amounts of acrylonitrile which acts as a polymerization regulator. The products can be vulcanized to give synthetic rubbers (394). A three-component copolymer of acrylonitrile, butadiene and 2-methyl-5-vinylpyridine, quaternized during vulcanization, is said to possess better oil- and chemical-resistance and better tensile strength characteristics than acrylonitrile-butadiene copolymers (1414).

Soil Aggregating Agents

Partial alkaline hydrolysis of polyacrylonitrile produces a polyelectrolyte which is predominantly a salt of polyacrylic acid. When the sodium, ammonium or calcium salts of hydrolyzed polyacrylonitrile are added to certain soils of poor structure, aggregation of soil particles occurs. Such additives are said to improve soil aeration, moisture retention, rate of germination of seeds and yield of crops (88, 132, 228, 410, 490, 491, 492, 748, 805, 806, 1010, 1058, 1204, 1353, 1444). In addition, erosion of soil during run-off of rainfall is greatly reduced (229, 1010, 1132).

Outdoor piles of finely-divided mineral matter frequently create a dust problem. This can be avoided by spraying the piles with a solution of hydrolyzed polyacrylonitrile. A thin crust is formed which is resistant to erosion by wind and rainfall (38). Aqueous suspensions of mineral fines may be flocculated by the same product (770).

Calcium acrylate, which can be prepared from acrylonitrile via acrylic acid, has been polymerized in soil to improve load-bearing characteristics (236).

Solvents

The solubilizing characteristics of the nitrile and ester groups, either of which can be introduced into a molecule by cyanoethylation, make acrylonitrile a particularly valuable intermediate for the preparation of solvents. Acrylonitrile itself is a polar solvent, largely water-insoluble, and should be considered for the extraction of polar molecules from aqueous solutions. Propene and propane can be separated by a solvent composed of acetonitrile, acrylonitrile and water (1082). The alkoxypropionitriles and alkylaminopropionitriles, obtained by the cyanoethylation of alcohols and amines, possess excellent solvent properties (31, 716). They are miscible with all the common organic solvents. Alkoxypropionitriles will dissolve poly(vinyl acetate), poly(vinyl chloride), polymethacrylates and vinyl chloride-vinyl acetate copolymers, as well as other polymeric materials. Cyanoethylated ethanolamines dissolve nitrocellulose and similar substances (521).

3,3′-Oxydipropionitrile, 3,3′-iminodipropionitrile and 3,3′-thiodipropionitrile are particularly useful solvents (953). They have the property of selectively dissolving aromatic or other highly unsaturated materials in the presence of aliphatics. The use of the thio- and oxydipropionitriles in this application has been investigated in detail, and their superiority to diethylene glycol has been demonstrated in several systems (1002).

Surface Coatings

Acrylonitrile will copolymerize in emulsion with a wide variety of other monomers to produce film-forming resins, useful in surface-coating compositions. The properties which the introduction of acrylonitrile exerts upon the film characteristics of polymers and copolymers are the following (294):

Tack freeness
Hardness and toughness
Very high tensile strength
Very low elongation
Very low water absorption
High resistance to saponification

Many applications in the surface-coatings field have been found for copolymers of acrylonitrile with a few specific comonomers, as discussed below.

COPOLYMERS WITH BUTADIENE

Coating Compositions for Fabrics

A blend of an acrylonitrile-butadiene copolymer with a chlorinated polyethylene and polychloroprene is the essential ingredient in a coating composition for upholstery fabrics. The coating is flexible at low temperatures, shows good abrasion resistance and does not exhibit tackiness at elevated temperatures (380). A composition similar to the above is suitable for coating one side of a flexible base (350).

Compositions recommended for coating glass fibers contain an acrylonitrile-butadiene copolymer alone (208) or combined with poly(tetrafluoroethylene) (1223). The coated fibers are heated to set the copolymer, and then are treated with a water-repellent. Fabric made from these fibers can be washed, dry-cleaned and handled similarly to common fabrics.

Acrylonitrile-butadiene copolymers are useful in making printing pastes for glass fabrics (682).

Acrylonitrile-butadiene latex, following reaction with sulfur dioxide, is useful as a coating resin for textiles, paper and wood (553).

Thermoplastic binders containing copolymers of acrylonitrile and butadiene find use in a surface coating applied by a specifically designed roller-coating apparatus (793).

Synthetic fabrics of a leather-like nature can be prepared from glass fibers, butadiene-acrylonitrile copolymer, a phenolic resin and methyl phenyl-polysiloxane (116).

Coating Compositions for Metals

Water suspensions of a vinyl chloride polymer and an acrylonitrile-butadiene rubber form strong films on many materials when dried at room temperature. Their use as protective coatings for non-ferrous metals and alloys has been suggested (401).

Metal surfaces are protected from corrosive attack and abrasion by a strippable coating comprising an inner rubbery layer 0.002-0.1 inch thick (such as acrylonitrile-butadiene copolymer) and a thicker outer layer of asphaltic material (981).

Coatings for Miscellaneous Surfaces

A coating composition for use on floors and similar surfaces is made from shellac, a terpene phenolic resin, butadiene-acrylonitrile copolymer and a dispersing agent (66).

Non-porous films can be made self-sealing by applying a blend of butadiene-acrylonitrile elastomer and natural rubber (488).

Cracking problems associated with poly(tetrafluoroethylene) dispersion coatings disappear when butadiene-acrylonitrile copolymer is added to the dispersion (518).

An enamel composition having a uniform drying rate is obtained with acrylonitrile-butadiene copolymer, a dispersed pigment, a heavy metal soap dryer and calcium oxide (658).

Acrylonitrile-butadiene copolymers are reportedly useful for mixing with proteins for coatings which are set with ammonia (612).

Priming coats for various surfaces can be formulated by mixing acrylonitrile-butadiene elastomer, another vinyl copolymer and a protein (1141).

Acrylonitrile and butadiene, polymerized in the presence of large mercaptan concentrations, give viscous liquid or semisolid sulfur-containing products useful as drying oils or binding agents (977).

COPOLYMERS WITH STYRENE

Acrylonitrile can be used as a partial replacement for styrene or methylstyrene in styrenated alkyds. The following effects have been shown to result from this replacement: a marked improvement in the resistance of films to mineral spirits and an increased speed of drying. Furthermore, film clarity is better, bronzing and chalking (in pigmented films) is less and resin viscosity is increased (307, 865). Resins of this type are commercially available from American Cyanamid Company under the trademark Cycopol* 320-5.

Three-component polymers of acrylonitrile, styrene and a conjugated diolefin have been incorporated into a recipe for coating paper and fabrics and for blending with asphalts and waxes (1114). These terpolymers are also useful in lacquers and enamels and for coating metal tanks to prevent corrosion.

Coating compositions prepared from a three-component polymer of acrylonitrile, α-methylstyrene and ethyl acrylate have good adhesion to rubber articles, dry tack-free, are flexible and are not rapidly deteriorated by sunlight, ozone or weathering (956).

Nylon fabrics coated with a formulation containing styrene-acrylonitrile copolymer have good gloss, flexibility, surface hardness and wearing ability (856).

When tall oil is heated with a polybasic acid (e.g. maleic or fumaric acid), a polyhydric alcohol (e.g., pentaerythritol), and acrylonitrile- and styrene-monomers, resins are obtained. These resins are useful in paints, lacquers and printing inks (966).

A dispersion of styrene-acrylonitrile copolymer blended with a dispersion of rubbery butadiene-acrylonitrile copolymer gives a highly effective grease-proofing finish to paper. These are applied over a priming coat of a different copolymer (280, 281).

COPOLYMERS WITH VINYLIDENE CHLORIDE

Acrylonitrile-vinylidene chloride resins have a low transfer rate for water and a very low transfer rate for gases such as CO_2 and O_2. Their chemical resistance is, in general, good. When sprayed they form tough, semi-elastomeric, non-flammable films with good hydrocarbon resistance. These coatings have been virtually unaffected in more than two years' service on the interiors and exteriors of oil refinery equipment, including tanks and pipes (810, 909).

Copolymers of acrylonitrile and vinylidene chloride are used in latex paints, and are outstanding for their resistance to a great variety of chemicals and for their toughness. Paints containing these copolymers, plasticized by dibutyl phthalate, exhibit excellent wear. The paints are outstanding for

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*Reg. U. S. Pat. Off.

brushability, levelling, and absence of foam. They show promise for use in industrial maintenance and in food processing plants and dairies where grease and food acids cause trouble (7, 502).

A three-component polymer of acrylonitrile, vinylidene chloride and ethyl acrylate has valuable film-forming properties. The films are tough, flexible, moisture-impervious and greaseproof. The lattices may be used to form coatings by electrodeposition in a manner similar to that employed with rubber latex (1021).

Fuel-Resistant Coatings

A Saran-type coating of acrylonitrile-vinylidene chloride copolymer in methyl ethyl ketone was tested for preventing corrosion of the steel cargo tanks of Navy carriers when successive cargoes of gasoline were carried. The coating was brushed on in several coats to a thickness of 0.008 inch. The coatings were estimated from test data to be adequate protection against the corrosion caused by moisture, salt-water ballast, and gasoline for four years, and it was estimated that life expectancy could be extended indefinitely by touch-ups at four-year intervals (285). Other authors have also reported (283, 811, 906) that acrylonitrile-vinylidene chloride copolymers are acceptable as linings for fuel tanks. The copolymers may be applied as such to steel. In lining concrete, it is best utilized as an overcoating for a more extensible material such as polysulfide rubber.

Moistureproof Coatings

Coatings of acrylonitrile-vinylidene chloride copolymers on rubber hydrochloride film increase the resistance to passage of gases such as oxygen, nitrogen and carbon dioxide. This coated film is especially suitable for packaging coffee, milk powder, egg powder, dried yeast, dried fruits, smoked meat and tobacco wherein low oxygen-permeability is desired (215).

Acrylonitrile-vinylidene chloride copolymer, when applied to regenerated cellulose film, gives an excellent moisture-resistant, heat-sealable, durable, flexible, transparent coating (110, 111, 143, 482, 523, 877). The cellulose film can be given a curable base coating before application of the acrylonitrile copolymer (472).

Other similar coating compositions are described as follows:

(a) A water-sensitive, non-fibrous organic material is waterproofed by an aqueous dispersion of a copolymer of vinylidene chloride and acrylonitrile (848).

(b) A moistureproof, heat-sealable, flexible, transparent film is produced by treating regenerated cellulose with a coating of a three-component polymer of acrylonitrile, vinylidene chloride and itaconic acid (876).

(c) A hydrolyzed three-component polymer of acrylonitrile, vinylidene chloride and vinyl acetate gives a strongly adhering coating on regenerated cellulose film without the use of an anchoring subcoat (875).

An acrylonitrile-vinylidene chloride copolymer, formulated with a halogenated hydrocarbon and methyl ethyl ketone, produces film with good heat-sealability at moderately low temperatures (481).

When a vinyl chloride-vinyl acetate copolymer is modified with an acrylonitrile-vinylidene chloride copolymer and a plasticizer, the product is reported to give a sprayable, webbable, strippable and moisture-impervious coating for metals, woods, plastics, rubbers, glass, etc.(531).

Fire-Retardant Coatings

Fire-retardant, intumescent, abrasion-resistant coating compositions have been described. They consist of a latex-like dispersion of an acrylonitrile-vinylidene chloride copolymer, a non-resinous carbon-containing compound, a foaming agent and a urea-formaldehyde resin (1030) or a non-resinous organic nitrogen compound (1408).

COPOLYMERS WITH MISCELLANEOUS MONOMERS

An interior, white, wall paint containing acrylonitrile-ethyl acrylate copolymer gives a film with superior scrub resistance, film hardness, resistance to blistering in water and resistance to solvents (1).

Copolymers of acrylonitrile and maleic anhydride, on reaction with oxazoline and thiazoline compounds, give resinous imido esters useful as coatings (938).

Coating and impregnating compositions prepared from acrylonitrile-trichloroethylene copolymers are suggested for application to wood, textiles, leather, metals, glass, etc. (50).

Coatings and films of acrylonitrile-isobutylene copolymers are said to be tough, resilient, impervious to acids and alkalis and resistant to weathering. These films are further claimed to be dimensionally stable, not shrinking appreciably even in boiling water (355, 709).

Waterproof coatings can be obtained by blending methylenedistearamide with polyamines prepared by reduction of butadiene-acrylonitrile copolymer (734).

Water-based surface coatings resistant to outdoor exposure have been reported. They are prepared from interpolymer latices of acrylonitrile, alkyl acrylates, styrene and acrylic or methacrylic acid (1413).

A three-component polymer of acrylonitrile, butyl acrylate and N-methylmethacrylamide is useful as a protective coating for photographic prints (1404).

An aqueous wire-enamel composition having good abrasion-, heat- and solvent-resistance is obtained by blending an acrylonitrile-butyl acrylate-methacrylic acid interpolymer with a water-dilutable, heat-reactive synthetic resin (1395, 1396).

Cyanoethylated proteins are said to be useful as emulsion stabilizers for butadiene-styrene coating compositions (1335).

Textiles

Acrylonitrile and its polymers are useful in the treating of fabrics. Wool can be made shrink-resistant by polymerizing acrylonitrile within the fibers (704, 1110, 1434), or by treating with acrylonitrile-vinylaryl isocyanate

(838), acrylonitrile-glycidyl methacrylate (365), acrylonitrile-chloroprene (942, 943) or acrylonitrile-butadiene (944, 1373) copolymers. Although polychloroprene or polybutadiene alone will give this shrinkage control, the presence of up to 20% of copolymerized acrylonitrile improves the feel of the treated wool (942, 943).

Fabrics can be rendered crease-resistant by using a blend of urea-formaldehyde resin with butadiene-acrylonitrile latex (5, 1402) or a blend of melamine-formaldehyde resin with acrylonitrile-alkyl acrylate copolymer (398). Fabrics can be stiffened by polymerizing acrylonitrile on the fabric (227). A similar effect is obtained by impregnating the fabric with a copolymer of acrylonitrile and vinyl chloride or styrene (322, 323). Acrylonitrile-vinyl ester copolymers have also been used to give rigidity to fabrics (645).

Cellulose fabrics can be provided with increased abrasion resistance and a soft, pleasant hand by the application of nitrile latices (4, 517, 1402). Felting resistance is imparted to woolen fabrics by impregnating with a mixture of polybutadiene and acrylonitrile-butadiene copolymer (382). The latter copolymer can also be used to impart run resistance to hosiery (585). Improved adhesion of cloth to rubber (263, 793) and vinyl coatings (820) is imparted by pretreatment of the cloth with nitrile rubber. Sizing properties are claimed for copolymers of acrylonitrile with maleic and fumaric acids (565), for mixtures of polyacrylonitrile and hexamethylenediethylurea (590), for water-soluble cellulose derivatives prepared by cyanoethylation of cellulose xanthate (714) and cellulose esters (713), and for cyanoethylated starch and poly(vinyl alcohol) (714).

Cotton can be rendered mildewproof and, at the same time, more heat-resistant, dyeable and less hygroscopic by cyanoethylation (230, 231, 235, 262, 1019, 1236). The deposition of polyacrylonitrile on and within cotton fibers also renders cotton mildewproof (1229). The acrylonitrile is reported to polymerize and deposit preferentially at the carboxyl groups in the cotton.

Cellulosic fabrics can be made flameproof by treatment with a polymer of cyanoethylated diallyl phosphonate (1438). Alkali-soluble fabrics can be obtained by treating cyanoethylated cotton with chromic acid (1446). Non-woven fabrics are produced by rendering cyanoethylated cellulose fibers adhesive with a suitable solvent (715).

Compositions for printing of textiles include acrylonitrile-butadiene copolymer (115, 413, 419, 441), polyacrylonitrile (1173) and acrylonitrile-vinylidene chloride copolymer (48).

Water-insoluble, alkali-soluble cyanoethyl ethers of cellulose offer possibilities as "scaffolding" threads for cellulosic yarns such as cotton (714, 718). These ethers dissolved in dilute sodium hydroxide can be used for the fixation of pigments, as permanent finishing agents for textiles, as thickeners for printing pastes, for the production of novelty print effects and for the manufacture of non-woven fabrics (277, 714). Water-soluble cyanoethyl ethers of cellulose are useful as sizes for textile yarns since they are more easily removed than starch from woven fabrics in the scouring process.

The addition of copolymers of acrylonitrile and an acrylamide to anionic or nonionic detergents prevents redeposition of soil on textile fabrics during laundering (1428).

Viscosity Modifiers

As described in the Polymerization Section under "Modification of Acrylonitrile Polymers," polyacrylonitrile may be converted by aqueous alkaline hydrolysis into water-soluble polymers. Cyanamid's Cypan* drilling mud conditioner is one such polymer. The viscosity of these resulting polymer solutions is controlled by the molecular weight of the polyacrylonitrile chosen and the degree of hydrolysis obtained.

These water-soluble polymers have found use as additives to control water loss in oil-well drilling muds (392, 1128, 1366). The muds assist in lubricating the bit and in removing cuttings, but the unmodified mud may fail due to water loss and subsequent solidification. Small amounts (about one pound per barrel of mud) of hydrolyzed polyacrylonitrile are effective in retaining the water and in improving wall-building characteristics. A particular advantage of this polymer over some other common additives is its stability at high pH and temperature (1128). A related polymer which performs similarly is the sodium salt of a copolymer of acrylonitrile and acrylic acid (391).

Copolymers of dodecyl methacrylate and acrylonitrile can be added to lubricating oils to improve the temperature-viscosity characteristics (218, 1432). Copolymers of dodecyl fumarate or dodecyl maleate and acrylonitrile are useful as pour-point depressants in lubricating oils (1432).

Miscellaneous

Acrylonitrile has been added as a third component to *separate binary azeotropes*. For example it can be used to recover toluene (444) or benzene (445) from non-aromatics. Tetrachlorosilane (b.p. 57.6°C.) and trimethyl chlorosilane (b.p. 57.5°C.) form an azeotrope (b.p. 54.5°C.) and so cannot be separated by simple distillation. They can be separated, however, by azeotropic distillation with acrylonitrile (145, 950, 951). Acrylonitrile may also be used to dry propionitrile since the acrylonitrile-water azeotrope boils at a lower temperature than does propionitrile (1081).

Tubes knit from polyacrylonitrile fibers have been successfully used as *artery substitutes* in surgery on animals and humans (39, 635).

Asphalt additives which improve the bonding to gravel in roads may be made by reacting fatty amines with acrylonitrile (233). Asphalts reacted with acrylonitrile are claimed to have improved properties and softening-point relationships (720).

A mixture of acetylene black with an acrylonitrile-diolefin copolymer is useful either as a *lubricant* or a *hydraulic fluid* which is oil-insoluble (798). When branched-chain mercaptans are cyanoethylated the sodium salt obtained by hydrolysis of the nitrile is useful as a component of *high-temperature greases* (797). High-temperature greases can also be prepared by reaction of lithium hydroxide and acrylonitrile in a mixture of fatty acids and mineral oil (796).

Aqueous alkaline hydrolysis of polyacrylonitrile produces a water-soluble polymer which is useful in *froth flotation* (1193) and *cyanidation* (1216) of ores.

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*Reg. U. S. Pat. Off.

Low-toxicity hardeners for epoxide-resin systems may be obtained by reacting aliphatic polyfunctional amines with acrylonitrile (1195).

Copolymers of acrylonitrile and vinyl acetate can be employed in *quenching baths* for steel (861). Trichloroethylene stabilized by acrylonitrile is suggested for the *degreasing of iron and aluminum* (637).

A copolymer of acrylonitrile and isobutylene can be converted into cellular microspheres by dropping the polymer particles while still wet with monomer into boiling water. The hollow spheres can be used in life belts or to inhibit surface evaporation in gasoline storage tanks (497).

A matrix for holding particles of cation-exchange resin in the form of a film can be made of acrylonitrile-butadiene copolymer (935). 1,3,5-Triacrylylhexahydro-*s*-triazine, prepared from acrylonitrile and formaldehyde, is useful as a cross-linking agent in the preparation of cation-exchange resins (375).

Pretreating Raney nickel catalyst with acrylonitrile is said to prevent nuclear hydrogenation in the catalytic reduction of anthraquinones (1433). Cyanoethylated ethanolamines are reported to be especially useful as activators in the preparation of acrylonitrile-butadiene copolymers (1264).

METHODS OF ANALYSIS

The qualitative detection of acrylonitrile in samples containing at least 1% acrylonitrile may be accomplished by conversion to 3-piperidinopropionitrile picrate (147). Methods have been devised for the quantitative determination of bound acrylonitrile in copolymers and polymerization systems (81, 373, 946, 1415), in air (138, 478, 864) and in aqueous industrial streams (1245, 1345). Polarographic reduction of acrylonitrile is a rapid, accurate method of assaying very dilute solutions of acrylonitrile (117, 1245). The purity of acrylonitrile can also be determined cryoscopically (1). Other procedures involve oxidative titration of the double bond (830), or addition of an amino- (1064, 1241) or sulfhydryl- (180) compound to the double bond. The latter method is based on the addition of standard dodecyl mercaptan followed by titration of the excess mercaptan with bromate-iodide solution to a yellow end point. In a variation of this method, useful in colored solutions, mercaptan is titrated potentiometrically with silver nitrate (605).

The following procedure presently is employed at the Stamford Laboratories of the American Cyanamid Company. It is a modification of the published mercaptan method (99).

PRINCIPLE OF THE METHOD

The acrylonitrile sample is added to a measured excess of dodecyl mercaptan in isopropyl alcohol. The cyanoethylation of the mercaptan is quantitative within two minutes in the presence of a basic catalyst, and the excess mercaptan is back-titrated with standard bromate-iodide reagent in acid solution.

Reagents

Mercaptan Reagent—Dissolve 35 g. (41 ml.) of crude *n*-dodecyl mercaptan in one liter of isopropyl alcohol (99%). Let stand for 1-2 days before using.

Basic Catalyst—Dissolve 28 g. of KOH in one liter of ethanol to make a 0.5 N solution.

Standard Bromate-Iodide Solution (0.125 N)—Dissolve 3.479 g. of reagent grade $KBrO_3$ and 30 g. of KI in water to make one liter. Standardize by acidifying a 25-ml. sample with 1-2 ml. of conc. HCl and immediately titrating with 0.1 N sodium thiosulfate which has been standardized by any of the familiar methods (660).

Acid Stop Solution—Add 16 ml. of conc. HCl to enough isopropyl alcohol to make one liter.

Procedure

Using a fast-flowing pipette, transfer accurately 25 ml. of mercaptan reagent into an iodine flask, and stopper the flask immediately. Prepare similar flasks for each sample and one for the blank. By means of a medicine dropper, transfer 9-12 drops (0.15-0.20 g.) of sample to a weighed vial, stopper quickly and weigh. Loosen the stopper and let the vial and then the stopper slide down the inside of the flask. Stopper the flask and swirl to effect thorough mixing.

Add 2 ml. of the basic catalyst, stopper again, and mix well by swirling. Start a stop-watch when the catalyst is added. At 20-30-second intervals, add catalyst solution to the other samples being run, last of all to the blank. At the end of two minutes stop the reaction in the first sample by adding 125 ml. of the acid stop-solution, then likewise with each flask at the end of its two-minute reaction period, the blank last of all. Immediately titrate the blank with standard bromate-iodide solution until one drop produces a faint yellow color which is permanent for 30 seconds of swirling. Titrate the samples in the order in which they were started.

Calculation

$$\% \text{ Acrylonitrile} = \frac{(\text{Blank Titer} - \text{Sample Titer}) \text{ x N Bromate-Iodide}}{\text{Grams of sample}} \text{ x } 5.306$$

Notes

1. In view of the volatility of acrylonitrile and of the reagent, speed is essential in all weighing and transfer operations.
2. One-dram vials with polythene (*not* cork) stoppers have been found to be the most satisfactory. Fragile ampules also may be used.
3. The blank loses titer slowly but steadily after adding the stop solution. It is therefore important to titrate the blank immediately after adding the stop solution. The blank may be run simultaneously with the sample, or before or after. If the mercaptan solution has been properly aged, the blank will change only very slowly with time and may be run only once a day if time is scarce.

4. In the original procedure (99) the use of ethyl or isopropyl alcohol was recommended. However, the end point in the titration of the blank has been found to be sharper in isopropyl or *n*-butyl alcohol than in ethyl alcohol.

5. The amount of sample specified above applies to relatively pure acrylonitrile. For the analysis of dilute solutions the quantity of sample taken should be increased accordingly. For aqueous solutions, sample size is limited by the fact that a maximum of 25% water may be tolerated in the reaction solution.

6. Compounds of similar structure will interfere, i.e., those containing the $-CH=CHCN$ structure. α, β-Unsaturated aldehydes react similarly but not appreciably within the two-minute period specified.

TOXICITY

Although acrylonitrile is a highly toxic substance by ingestion, by absorption through the intact skin and by inhalation of vapor, industrial experience and studies* in small animals indicate that it is not as hazardous as has been previously supposed. Several reports published prior to 1950 compared the hazard of acrylonitrile with that of HCN. It is now known that, while the toxic effects of the two substances are qualitatively similar, quantitatively they differ greatly.

Because the vapor pressure of this compound at room temperature is high, the hazard of intoxication by inhalation is greater than by other routes of exposure. The American Conference of Governmental Industrial Hygienists has established a level of 20 ppm as the maximum allowable concentration in the workroom atmosphere for 8-hour exposures. This hazard, together with others commonly encountered in the use of low-boiling organic compounds, requires that acrylonitrile be handled and processed in closed systems.

The manifestations of systemic intoxication in experimental animals resemble those of HCN. Blood cyanide and thiocyanate determinations, as well as other findings, suggest that the toxic action of acrylonitrile is due to the liberation of cyanide ion in vivo. However, the onset and development of symptoms are considerably slower than with HCN. This further suggests that the biological breakdown of acrylonitrile to cyanide ion is a rather slow, gradual process, thus permitting physiological detoxification to proceed apace. There is no evidence to indicate that repeated exposures produce a cumulative effect.

Acrylonitrile is readily absorbed through the intact skin and may with prolonged or repeated exposure produce systemic intoxication by this route. In addition, it is a low-grade primary irritant to the skin. Repeated or prolonged contact may produce a local cutaneous reaction with blistering, particularly if the exposure occurs inside shoes or under clothing that will retard its vaporization. The onset of dermatitis following such an exposure may be delayed for several hours.

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*"Toxicology of Acrylonitrile," Petrochemicals Department Bulletin—American Cyanamid Company.

Industrial experience with acrylonitrile has been uniformly good. To date no case of human fatality or serious systemic poisoning through occupational exposure has come to our attention. Such a remarkable record may be attributed in large measure to the care with which the compound has been handled. Symptoms of poisoning that have been observed include headache, weakness, nausea, vomiting and abdominal cramps. Severe exposures might be expected to produce unconsciousness, convulsions and death through the action of the cyanide ion.

In mild cases of systemic poisoning, the victim should be kept under medical observation for 24 hours. No specific therapy is usually required and a prompt and complete spontaneous recovery may be anticipated. In more serious cases, especially when respiratory difficulty or unconsciousness has occurred, treatment with the nitrite-thiosulfate method* recommended by Chen for HCN poisoning may be expected to be effective. If the exposure has been by inhalation, irritation of the lower respiratory tract may warrant the institution of non-specific treatment usually employed in such cases.

First Aid Instructions *(in order of importance)*

Remove the patient from contact with the poison without delay and call a physician. If exposure has been:

BY INHALATION—Remove patient to fresh air. Rescuer entering contaminated area should wear an oxygen- or fresh-air-supplied gas mask.

BY SKIN CONTACT—Remove contaminated clothing and wash thoroughly with copious quantities of water and soap.

BY SWALLOWING—If conscious, induce vomiting by administration of strong solution of salt water. If unconscious, emptying of the stomach should be left to the physician.

BY EYE CONTACT—Hold eyelids apart and wash eye with continuous gentle stream of water for at least 15 minutes.

If breathing has stopped, give artificial respiration immediately and continuously until arrival of physician, preferably by the Holger-Nielsen method. The Eve rocking method is a satisfactory substitute.

If patient is unconscious, administer amyl nitrite by crushing a pearl (ampule) in a cloth and holding this under patient's nose for 15 seconds in every minute. Artificial respiration must not be interrupted during this procedure. The amyl nitrite pearl should be replaced when its strength is spent. Treatment should be continued until the patient's condition improves or the physician arrives.

BY THE PHYSICIAN

The regimen of treatment recommended for acrylonitrile poisoning is that for cyanide poisoning. It is based upon the administration of nitrites to stimulate methemoglobin formation. Methemoglobin binds the cyanide group as cyanmethemoglobin. Thiosulfate is then administered to facilitate

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*"Toxicology of Acrylonitrile," Petrochemicals Department Bulletin—American Cyanamid Company.

the conversion of cyanide to thiocyanate under the influence of the enzyme rhodanase. This ion is relatively far less toxic than cyanide and is readily excreted in the urine.

This method of treatment has been found to be highly effective in human experience with cyanide poisoning and experimentally in acrylonitrile poisoning. Instances of human intoxication with acrylonitrile of sufficient severity to warrant definitive treatment have been virtually unknown. However, if such cases were encountered, this form of treatment would be expected to be at least as effective as with cyanide poisoning of equal severity. The method, as described by Chen, Rose and Clowes (238A) is quoted as follows:

> "Instruct an assistant how to break, one at a time, pearls of amyl nitrite in a handkerchief and hold the latter over the victim's nose for 15-30 seconds per minute. At the same time the physician quickly loads his syringes, one with a 3 percent solution of sodium nitrite, and the other with a 25 percent solution of sodium thiosulphate.
>
> Stop administration of amyl nitrite and inject intravenously 0.3 g. (10 cc. of a 3 percent solution) of sodium nitrite at the rate of 2.5 to 5.0 cc. per minute.
>
> Inject by the same needle and vein, or by a larger needle and a new vein, 12.5 g. (50 cc. of a 25 percent solution) of sodium thiosulphate.
>
> The patient should be watched for at least 24 to 48 hours."

If signs of poisoning reappear, injection of both sodium nitrite and sodium thiosulphate should be repeated, but each in one-half of the dose. Even if the patient looks perfectly well, the medication may be given for prophylactic purposes two hours after the first injection.

TABLE I—Hydration, Hydrolysis and Alcoholysis

Reactants	Reaction Time (Hr.)	Reaction Temperature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References This Exam.	References See Also:
H_2O water	1.5	100°	$CH_2{=}CHCONH_2$ *acrylamide*	95	M.P. 84-85°	29 30	622, 857, 859, 1250, 934, 1154, 149, 1298, 1139, 578, 579, 29, 1188, 1189, 216, 584, 580
$H_2O + HCl$ *water + hydrochloric acid*	—	0°	$ClCH_2CH_2CONH_2$ *3-chloropropionamide*	85	—	580	1138
$H_2O + HCl$ *water + hydrochloric acid*	6	reflux	$ClCH_2CH_2CO_2H$ *3-chloropropionic acid*	75	B.P. 115-117°/32 mm.	80	388, 387, 1356
CH_3OH *methanol*	—	—	$CH_2{=}CHCO_2CH_3$ *acrylic acid, methyl ester*	96	—	1341	1156, 1278
$CH_3OH + HCl$ *methanol + hydrochloric acid*	48	0°	$ClCH_2CH_2C(NH)OCH_3 \cdot HCl$ *3-chloropropionimidic acid, methyl ester, hydrochloride*	86	M.P. 93-94°	890	
C_2H_5OH *ethyl alcohol*	—	—	$CH_2{=}CHCO_2C_2H_5$ *acrylic acid, ethyl ester*	95	—	1341	1278
$C_2H_5OH + HBr$ *ethyl alcohol + hydrobromic acid*	O.N.	R.T.	$BrCH_2CH_2C(NH)OCH_2CH_3 \cdot HBr$ *3-bromopropionimidic acid, ethyl ester, hydrobromide*	54-56	B.P. 64-65°/5 mm.	20	
$C_2H_5OH + HCl$ *ethyl alcohol + hydrochloric acid*	24	R.T.	$CH_2{=}CHC(NH)OCH_2CH_3 \cdot HCl$ *acrylimidic acid, ethyl ester, hydrochloride*	~100	M.P. 104-104.5°	1051	
$C_2H_5OH + HCl$ *ethyl alcohol + hydrochloric acid*	2.5 2.0 then add water	10-15° 35-40°	$ClCH_2CH_2CO_2C_2H_5$ *3-chloropropionic acid, ethyl ester*	71.7	B.P. 70-75°/30 mm.	1312	
$CH_3CHOHCH_3$ *isopropyl alcohol*	1.0 0.5	100° reflux	$CH_2{=}CHCO_2CH(CH_3)_2$ *acrylic acid, isopropyl ester*	85	—	1278	

Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
$C_9H_{19}OH + HCl$ *nonyl alcohols + hydrochloric acid*	2.0 then add water	—	$ClCH_2CH_2CO_2C_9H_{19}$ *3-chloropropionic acid, nonyl ester*	81.9	B.P. 80-90°/0.3-0.4 mm.	1312	
$C_{13}H_{27}OH + HCl$ *tridecyl alcohols + hydrochloric acid*	2.5 then add water	10-15°	$ClCH_2CH_2CO_2C_{13}H_{27}$ *3-chloropropionic acid, tridecyl ester*	85.0	B.P. 140-145°/0.7 mm.	1312	

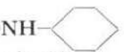
TABLE IIA—Reactions with Alcohols

$HOCH(CH_3)_2$ *isopropyl alcohol*	1.0	<40°	$CH_2{=}CHCONHCH(CH_3)_2$ *N-isopropylacrylamide*	45	B.P. 110-115°/15 mm. M.P. 62°	879	
$HOCH(CH_3)CH_2CH_3$ sec-*butyl alcohol*	1.0	<40°	$CH_2{=}CHCONHCH(CH_3)CH_2CH_3$ *N*-sec-*butylacrylamide*	76	B.P. 125-130°/200 mm. M.P. 26°	879	
$HOC(CH_3)_3$ tert-*butyl alcohol*	1.0	<40°	$CH_2{=}CHCONHC(CH_3)_3$ *N*-tert-*butylacrylamide*	80	M.P. 126-128°	879	1250
$CH_3CH_2C(CH_3)_2OH$ *2-methyl-2-butanol*	0.17	49-51°	$CH_2{=}CHCONHC(CH_3)_2C_2H_5$ *N-(1,1-dimethylpropyl)acrylamide*	93.6	M.P. 92-93°	1	879
–OH *cyclohexanol*	1.0	<40°	$CH_2{=}CHCONH$–  *N-cyclohexylacrylamide*	72	M.P. 112-113°	879	
$HOC(CH_3)_2(CH_2)_2CH_3$ *2-methyl-2-pentanol*	1.0	<40°	$CH_2{=}CHCONHC(CH_3)_2CH_2CH_2CH_3$ *N-(1,1-dimethylbutyl)acrylamide*	71	M.P. 56-57°	879	
$HOC(CH_3)(C_2H_5)_2$ *3-methyl-3-pentanol*	1.0	<40°	$CH_2{=}CHCONHC(CH_3)(C_2H_5)_2$ *N-(1-ethyl-1-methylpropyl)acrylamide*	77	M.P. 63°	879	
$HOC(CH_3)_2CH(CH_3)_2$ *2,3-dimethyl-2-butanol*	1.0	<40°	$CH_2{=}CHCONHC(CH_3)_2CH(CH_3)_2$ *N-(1,1,2-trimethylpropyl)acrylamide*	71	M.P. 91-92°	879	
$HOC(CH_3)_2(CH_2)_3CH_3$ *2-methyl-2-hexanol*	1.0	<40°	$CH_2{=}CHCONHC(CH_3)_2(CH_2)_3CH_3$ *N-(1,1-dimethylpentyl)acrylamide*	90	M.P. 60°	879	

Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
$HOC(CH_3)(C_2H_5)C_3H_7$ *3-methyl-3-hexanol*	1.0	<40°	$CH_2{=}CHCONHC(CH_3)(C_2H_5)C_3H_7$ *N-(1-ethyl-1-methylbutyl)acrylamide*	82	M.P. 71-72°	879	
$C_2H_5C(OH)(CH_3)CH_2CH(CH_3)_2$ *3,5-dimethyl-3-hexanol*	1.0	60°	$CH_2{=}CHCONHC(CH_3)(C_2H_5)CH_2CH(CH_3)_2$ *N-(1-ethyl-1,3-dimethylbutyl)acrylamide*	57	M.P. 88-89°	879	

Additional examples of reactions involving complex alcohols are described in the following references: 878, 879, 1266.

TABLE IIB—Reactions with Olefins

Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	This Exam.	See Also:
$CH_2{=}C(CH_3)CH_2Cl$ *1-chloro-2-methylpropene*	1.0	<40°	$CH_2{=}CHCONHC(CH_3)_2CH_2Cl$ *N-(2-chloro-1,1-dimethylethyl)acrylamide*	92	M.P. 93-94°	879	
$(CH_3)_2C{=}CHCH_3$ *2-methyl-2-butene*	several hours	R.T.	$CH_2{=}CHCONHC(CH_3)_2C_2H_5$ *N-(1,1-dimethylpropyl)acrylamide*	75	M.P. 92-93°	923	924
 *cyclohexene*	1.0	<40°	$CH_2{=}CHCONH-$  *N-cyclohexylacrylamide*	66	—	879	
$(CH_3)_2C{=}CHC(CH_3)_3$ *2,2,4-trimethyl-2-pentene* $+CH_2{=}C(CH_3)CH_2C(CH_3)_3$ *2,2,4-trimethyl-1-pentene*	1.0	<40°	$CH_2{=}CHCONHC(CH_3)_2CH_2C(CH_3)_3$ *N-(1,1,3,3-tetramethylbutyl)acrylamide*	71	M.P. 83° B.P. 140-142°/20 mm.	879	
$CH_2{=}CH(CH_2)_8COOH$ *10-undecenoic acid*	2.0	20-40°	$CH_2{=}CHCONHCH(CH_3)(CH_2)_8CO_2H$ *10-acrylamidoundecanoic acid*	—	M.P. 104-105°	878	1266

Additional examples of reactions involving complex olefins are described in the following references: 807, 878, 929.

TABLE III—Reactions with Aldehydes and Methylol Compounds

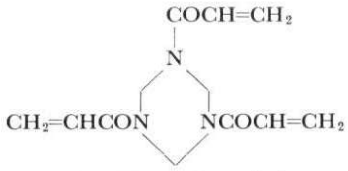
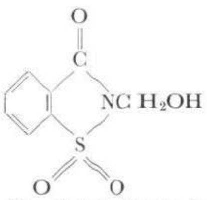
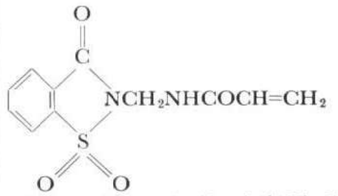
Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
$CH_2O + H_2O$ *formaldehyde + water*	3.0	40-45°	$(CH_2{=}CHCONH)_2CH_2$ *N,N′-methylenebisacrylamide*	86	M.P. 185°	735	220
$-(CH_2O)-_x$ *paraformaldehyde*	—	40-80°	 *1,3,5-triacrylylhexahydro-s-triazine*	70-74	M.P. 155-156°	1137	70, 446, 447, 437, 1186, 1187
$CCl_3CHO + H_2O$ *chloral + water*	2.0	—	$(CH_2{=}CHCONH)_2CHCCl_3$ *N,N′-(2,2,2-trichloroethylidene)bisacrylamide*	18	—	735	
 *N-methylol-o-benzoyl-sulfimide*	dur-ing addn. O.N.	<5° R.T.	 *N-(3-oxo-1,2-benzisothiazol-2(3H)-ylmethyl)-acrylamide,1,1-dioxide*	—	M.P. 167-168°	804	
 *N-methylolbenzamide*	dur-ing addn. 1.0	<5° 5-10°	 *N-acrylamidomethylbenzamide*	83	—	804	

TABLE III—Continued

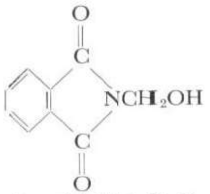
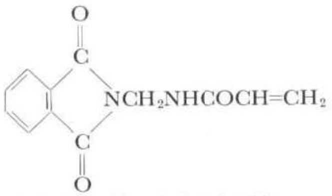
Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 *N-methylolphthalimide*	dur-ing addn. 1.0	33-35° 40°	 *N-phthalimidomethylacrylamide*	95	M.P. 193°	804	

TABLE IV—Diels-Alder and Related Reactions

(A) Diels-Alder

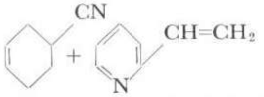
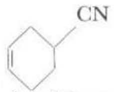
Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	This Exam.	See Also:
$CH_2{=}CBrCH{=}CH_2$ *2-bromo-1,3-butadiene*	18.0	130-135°	 *4-bromo-3-cyclohexene-1-carbonitrile*	31	M.P. 67°	867	
$CH_2{=}CClCH{=}CH_2$ *chloroprene*	12.0	145°	 *4-chloro-3-cyclohexene-1-carbonitrile*	34	B.P. 127-130°/20 mm. M.P. 54°	338	608
$CH_2{=}CHCH{=}CH_2$ *1,3-butadiene*	4 sec.	430°	 *3-cyclohexene-1-carbonitrile + 2-vinylpyridine*	28 1.8	— —	607	3383 606
$CH_2{=}CHCH{=}CH_2$ *1,3-butadiene*	cont.	160-180°	 *3-cyclohexene-1-carbonitrile*	95	B.P. 190-195°/760 mm.	873	338, 867, 606, 607, 108, 1076, 1166, 598, 582, 592, 874

TABLE IV—Continued

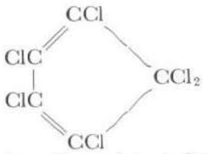
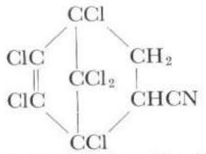
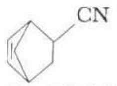
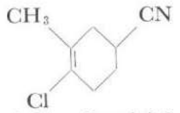
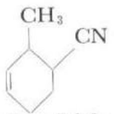
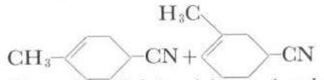
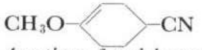
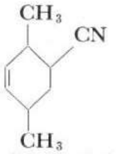
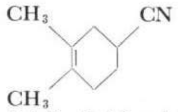
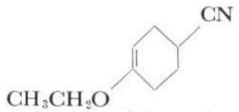
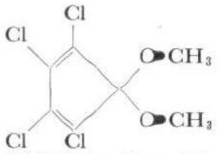
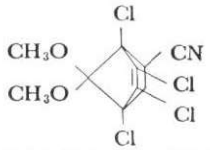
Reactants	Re-action Time (Hr.)	Reaction Temperature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 *hexachlorocyclopentadiene*	24.0	100°	 *1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hept-5-ene-2-carbonitrile*	32.5	—	891	
 *cyclopentadiene*	—	—	 *bicyclo[2.2.1]hept-5-ene-2-carbonitrile*	95	B.P. 84-89°/13 mm.	17	921, 158
$CH_2=C(CH_3)CCl=CH_2$ *3-chloro-2-methyl-1,3-butadiene*	12.0	150°	 *4-chloro-3-methyl-3-cyclohexene-1-carbonitrile*	—	B.P. 122-123°/13 mm.	109	
$CH_3CH=CHCH=CH_2$ *piperylene*	20.0	100°	 *2-methyl-3-cyclohexene-1-carbonitrile*	78	B.P. 202-203°/738 mm.	1076	45, 763, 404, 530, 866
$CH_2=C(CH_3)CH=CH_2$ *isoprene*	18.0	135°	 *3(and 4)-methyl-3-cyclohexene-1-carbonitrile*	92	B.P. 94-95°/20 mm.	866	20, 19, 108

TABLE IV—Continued

(A) Diels-Alder

Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
CH_2=C(OCH_3)CH=CH_2 *2-methoxy-1,3-butadiene*	12.0	145°	 *4-methoxy-3-cyclohexene-1-carbonitrile*	60	B.P. 125.5°/20 mm.	868	
CH_3CH=CHCH=CHCH_3 *2,4-hexadiene*	12.0	120-130°	 *2,5-dimethyl-3-cyclohexene-1-carbonitrile*	40	B.P. 82-83°/8 mm.	46	1076
CH_2=C(CH_3)C(CH_3)=CH_2 *2,3-dimethyl-1,3-butadiene*	—	—	 *3,4-dimethyl-3-cyclohexene-1-carbonitrile*	63	B.P. 94°/7 mm. B.P. 102°/10 mm. B.P. 108-110°/15 mm. B.P. 222-224°/760 mm.	1076	774, 775
CH_2=C(OC_2H_5)CH=CH_2 *2-ethoxy-1,3-butadiene*	12.0	135-140°	 *4-ethoxy-3-cyclohexene-1-carbonitrile*	90	B.P. 125-126°/15 mm.	338	868
 *1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene*	48.0	reflux	 *1,4,5,6-tetrachloro-7,7-dimethoxybicyclo[2.2.1]-hept-5-ene-2-carbonitrile*	70	M.P. 88-89°	722	

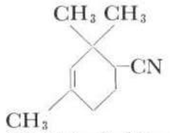
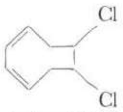
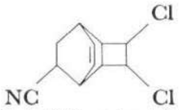
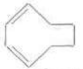
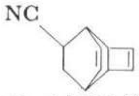
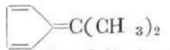
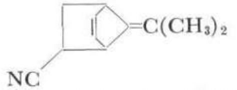
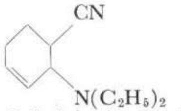
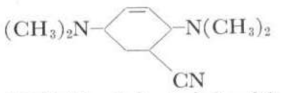
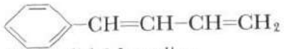
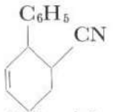
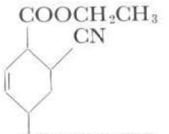
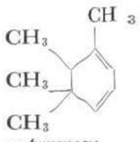
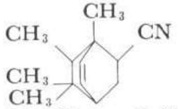
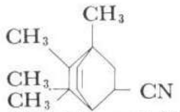
Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
CH_2=CHCH=CHCH=CHCN *2,4,6-heptatrienenitrile*	—	125°	*Mixture of Diels-Alder adducts*	—	—	199	
CH_2=C(CH_3)CH=C(CH_3)$_2$ *2,4-dimethyl-1,3-pentadiene*	38.0	140-145°	 *2,2,4-trimethyl-3-cyclohexene-1-carbonitrile*	71	B.P. 93-97°/10 mm. B.P. 50°/0.2 mm.	1025	
 *cyclooctatetraene dichloride*	6.0	150°	 *3,4-dichlorotricyclo[4.2.2.0^{2,5}]dec-9-ene-7-carbonitrile*	56	B.P. 177-184°/ 3.4-3.9 mm.	107	
 *cyclooctatetraene*	6.0	180°	 *tricyclo[4.2.2.0^{2,5}]deca-3,9-diene-8-carbonitrile*	33	B.P. 68°/0.2 mm. B.P. 103-110°/ 2.0-2.5 mm.	107	
 *6,6-dimethylfulvene*	several hours	reflux	 *7-isopropylidenebicyclo[2.2.1]hept-5-ene-2-carbonitrile*	47	B.P. 95-100°/1 mm. M.P. 87°	158	18
(C_2H_5)$_2$NCH=CHCH=CH$_2$ *N,N-diethyl-1,3-butadienylamine*	48.0	20-30°	 *2-diethylamino-3-cyclohexene-1-carbonitrile*	93	B.P. 125-126°/11 mm.	1288	

TABLE IV—Continued

Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
$(CH_3)_2NCH=CHCH=CHN(CH_3)_2$ *N,N,N′,N′-tetramethyl-1,3-butadiene-1,4-diamine*	—	—	 *2,5-bis(dimethylamino)-3-cyclohexene-1-carbonitrile*	30	B.P. 110-112°/0.5 mm.	1259	
 *1-phenyl-1,3-butadiene*	9.0	reflux	 *2-phenyl-3-cyclohexene-1-carbonitrile*	71	B.P. 150-153°/5 mm. B.P. 119-121°/1 mm.	903	762
$C_2H_5O_2CCH=CHCH=CHCO_2C_2H_5$ *diethyl muconate*	—	150-160°	 *5-cyano-2-cyclohexene-1,4-dicarboxylic acid, diethyl ester*	40-50	B.P. 175-180°	1175	
 *α-pyronene*	20.0	125-140°	 *1,5,5,6-tetramethylbicyclo[2.2.2]oct-7-ene-2-carbonitrile* or  *4,5,6,6-tetramethylbicyclo[2.2.2]oct-7-ene-2-carbonitrile*	36.2	B.P. 128-130°	47	

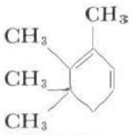
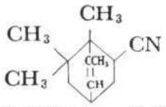
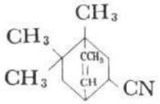
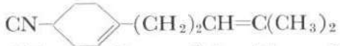
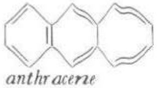
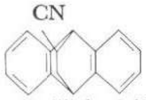
Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 *β-pyronene*	20.0	125-140°	 *1,6,6,7-tetramethylbicyclo[2.2.2]oct-7-ene-2-carbonitrile* or  *4,5,5,8-tetramethylbicyclo[2.2.2]oct-7-ene-2-carbonitrile*	77	M.P. 45-50° B.P. 125-127°/6 mm.	47	
$CH_2{=}CHC({=}CH_2)(CH_2)_2CH{=}C(CH_3)_2$ *myrcene*	4.0	reflux	 $CN-C_6H_8-(CH_2)_2CH{=}C(CH_3)_2$ *4-(4-methyl-3-pentenyl)-3-cyclohexene-1-carbonitrile*	46	B.P. 115-120°/1 mm.	775	
 *anthracene*	—	—	 *9,10-dihydro-9,10-ethanoanthracene-11-carbonitrile*	—	—	818 822	581

TABLE IV—Continued

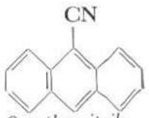
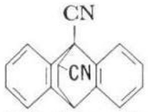
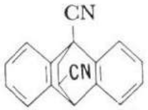
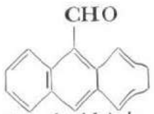
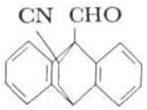
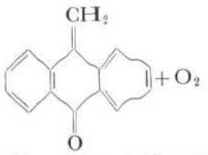
Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 9-anthronitrile	18.0 22.0	135-145° 190-200°	 9,10-ethanoanthracene-9,12(10H)-dicarbonitrile  9,10-ethanoanthracene-9,11(10H)-dicarbonitrile	— —	M.P. 167° M.P. 205°	1337	
 9-anthraldehyde	24.0	125-130°	 12-cyano-9,10-ethanoanthracene-9(10H)-carboxaldehyde	78	M.P. 172° M.P. 181.5-182°	761	
 10-methyleneanthrone + oxygen	—	—	 7-oxo-7H-benz[de]anthracene-3-carbonitrile	—	—	959	

TABLE IV—Continued

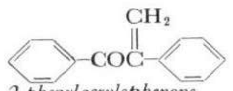
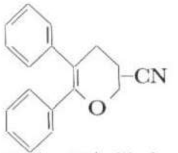
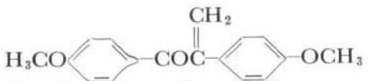
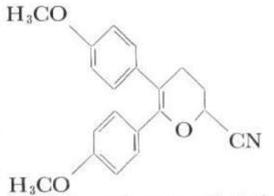
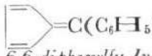
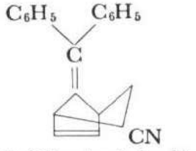
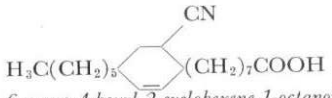
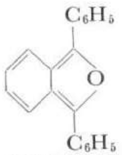
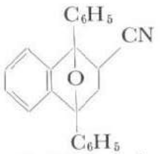
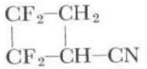
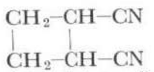
Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 *2-phenylacrylophenone*	3.0	185-205°	 *3,4(or 2,3)-dihydro-5,6-diphenyl-2H(or 4H)-pyran-2(or 3)-carbonitrile*	3.1	M.P. 121-122°	1260	
 *4′-methoxy-2-(p-methoxyphenyl)-acrylophenone*	6.0	190-220°	 *5,6-bis(p-methoxyphenyl)-3,4(or 2,3)-dihydro-2H (or 4H)-pyran-2-carbonitrile*	16.7	B.P. 255-262°/0.3 mm. M.P. 147-148°	1260	
 *6,6-diphenylfulvene*	2 mos.	R.T.	 *7-diphenylmethylenebicyclo[2.2.1]hept-5-ene-2-carbonitrile*	80-90	M.P. 137°	16	
tung oil fatty acids Ⓐ	48.0	reflux	*Mixture of Diels-Alder adducts (4.61% N)*	73	B.P. 240-255°/3 mm.	174	
octadienic acid Ⓑ	4.0	180°	*Mixture of Diels-Alder adducts*	28.2	B.P. 250-260°/4 mm.	174	

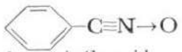
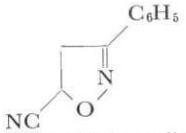
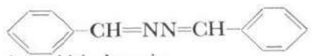
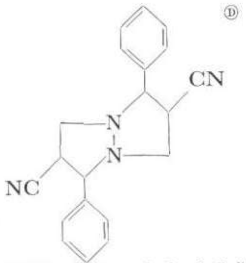
TABLE IV—Continued

Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
$CH_3(CH_2)_5(CH{=}CH)_2(CH_2)_7COOH$ *trans,trans-9,11-octadecadienoic acid*	24.0	200°	 *6-cyano-4-hexyl-2-cyclohexene-1-octanoic acid*	27	M.P. 67-77°	1416	
methyl octadecadienate	13.0	250°	*Mixture of Diels-Alder adducts (3.76% N)*	36.5	B.P. 235-245°/6 mm.	174	
 *1,3-diphenylisobenzofuran*	<1.00	in the shade	 *1,2,3,4-tetrahydro-1,4-diphenyl-1,4-epoxynaphthalene-2-carbonitrile*	88	M.P. 153-154°	366	
"Conjulin" ©	48.0	reflux	*Mixture of Diels-Alder adducts (3.4% N)*	—	B.P. 245-260°/4 mm.	174	

Additional examples of Diels-Alder reactions are described in the following references: 174, 775.

(B) Related Reactions

$CF_2{=}CFCl$ *chlorotrifluoroethylene*	8.0	150°	$HO_2C(CH_2)_2CF_2CO_2H$ *2,2-difluoroglutaric acid*	54.1	M.P. 103-5°	1202	
$CF_2{=}CF_2$ *tetrafluoroethylene*	8.0	150°	$\begin{array}{l} CF_2-CH_2 \\ \vert \quad\;\; \vert \\ CF_2-CH-CN \end{array}$ *2,2,3,3-tetrafluorocyclobutanecarbonitrile*	84	B.P. 148°	258	85, 84
$CH_2{=}CHCN$ *acrylonitrile*	24.0	I 195-200°	$\begin{array}{l} CH_2-CH-CN \\ \vert \quad\;\; \vert \\ CH_2-CH-CN \end{array}$ *1,2-cyclobutanedicarbonitrile*	3.5	cis M.P. <0°, B.P. 108-115°/3-4 mm. trans. M.P. 62°, B.P. 140-145°/3-4 mm.	284	

Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 *benzonitrile oxide*	1.0	reflux	 *3-phenyl-2-isoxazoline-5-carbonitrile*	73	M.P. 66-67°	301	
 *benzaldehyde azine*	36.0	135-142°	Ⓓ  *1,2,3,5,6,7-hexahydro-1,5-diphenylpyrazolo [1,2]-pyrazole-2,6-dicarbonitrile*	2.0	M.P. 223-224°	1277	

NOTES:
- Ⓐ Tung Oil Fatty Acids; mixture of eleostearic acids and oleic acid.
- Ⓑ Octadienic Acid; prepared by the dehydration of castor oil.
- Ⓒ "Conjulin"; linseed oil fatty acid with conjugated double bonds prepared by heating linseed oil fatty acids with caustic soda.
- Ⓓ Structure uncertain.

TABLE V—Reactions with Hydrogen

Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	This Exam.	See Also:
H_2 *hydrogen*	—	120°	CH_3CH_2CN *propionitrile*	91	—	913	1159, 503
			$CH_3CH_2CONH_2$ *propionamide*	2	—		
$Mg+CH_3OH$ *magnesium + methanol*	1.0 + O.N.	reflux	$NCCH_2CH_2CH_2CH_2CN$ *adiponitrile*	Ⓐ 29.3	B.P. 118-128°	687	589
$K(Hg)_x+HCl$ Ⓑ *potassium amalgam + hydrochloric acid*	—	—	$NCCH_2CH_2CH_2CH_2CN$ *adiponitrile*	62.2	B.P. 138-140°/3 mm.	1306	

NOTES: Ⓐ Isolated as adipic acid. Ⓑ Amalgam produced by electrolysis of 40% KOH in a pool of mercury.

TABLE VI—Reactions with Halogens

Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
Cl_2 *chlorine*	—	—	$ClCH_2CCl_2CN$ *2,2,3-trichloropropionitrile*	95	B.P. 61°/13 mm.	140	1, 1039 925
Cl_2 *chlorine*	—	R.T.	$ClCH_2CCl_2CN$ *2,2,3-trichloropropionitrile*	90	B.P. 70-75°/30 mm. 80-81°/63 mm.	695	247, 140
Cl_2 *chlorine*	—	—	$ClCH_2CCl_2CN$ *2,2,3-trichloropropionitrile*	—	B.P. 53°/14 mm.	140	
			$Cl_2CHCHClCN$ *2,3,3-trichloropropionitrile*	—	B.P. 100°/15 mm.		
			Cl_2CHCCl_2CN *2,2,3,3-tetrachloropropionitrile*	—	B.P. 92°/14 mm.		
Cl_2 *chlorine*	—	200-550°	$CH_2{=}CClCN$ *2-chloroacrylonitrile*	—	B.P. 44-45°/150 mm.	707	
$Cl_2 + H_2O$ *chlorine + water*	—	18°	$HOCH_2CHClCN$ *2-chlorohydracrylonitrile*	60	B.P. 92-93°/3 mm.	1100	324
$Cl_2 + H_2O$ *chlorine + water*	—	—	$ClCH_2C(CH_2CH_2CN)ClCN$ *2-chloro-2-chloromethylglutaronitrile*	28	B.P. 133°/115 mm.	1121	
$Cl_2 + H_2C{=}CH_2$ *chlorine + ethylene*	—	—	$ClCH_2CH_2N{=}CClCCl_2CH_2Cl$ *2-chloro-N-(1,2,2,3-tetrachloropropylidene)ethylamine*	34	B.P. 94-95°/4 mm.	200	
Br_2 *bromine*	—	R.T.	$BrCH_2CHBrCN$ *2,3-dibromopropionitrile*	65	B.P. 106-107°/22 mm.	803	
Br_2 *bromine*	—	R.T.	$BrCH_2CHBrCN$ *2,3-dibromopropionitrile*	62	B.P. 120-130°/30 mm.	697	
			$CH_2{=}CBrCN$ *2-bromoacrylonitrile*	17	B.P. 60°/30 mm.		

TABLE VI—Continued

Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
NO_2Cl *nitryl chloride*	—	0°	$O_2NCH_2CHClCN$ *2-chloro-3-nitropropionitrile* $ClCH_2CHClCN$ *2,3-dichloropropionitrile*	76 13.5	B.P. 83°/1 mm. B.P. 61-67°/14-15 mm.	991	139
NO_2Cl *nitryl chloride*	—	0°	$O_2NCH_2CHClCN$ *2-chloro-3-nitropropionitrile* $O_2NCH{=}CHCN$ *3-nitroacrylonitrile* $ClCH_2CHClCN$ *2,3-dichloropropionitrile*	25 48 16	B.P. 83°/1 mm. B.P. 53-59°/3 mm. B.P. 61-67°/14-15 mm.	991	139
dioxane dibromide	24	25°	$BrCH_2CHBrCN$ *2,3-dibromopropionitrile*	95	B.P. 173°	1253	

TABLE VII—Reactions with Diazo Compounds

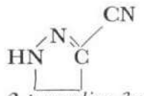
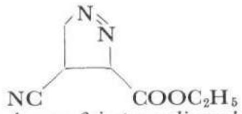
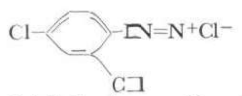
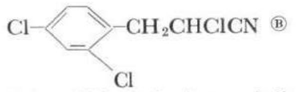
$H_2C{\leftarrow}N{\equiv}N$ *diazomethane*	—	"cooling"	 *2-pyrazoline-3-carbonitrile*	—	B.P. 93-94°/1 mm.	1418	
$CH_3CH_2OO\ CCH_2{\leftarrow}N{\equiv}N$ *ethyl diazoacetate*	24	40° Ⓐ	 *4-cyano-3-isopyrazolinecarboxylic acid, ethyl ester*	65	M.P. 96°	1418	
 *2,4-dichlorobenzenediazonium chloride*	—	30-40°	 Ⓑ *2,4,α-trichlorohydrocinnamonitrile*	>71	B.P. 140°/5 mm. M.P. 45°	595 594	808

TABLE VII—Continued

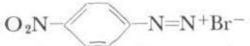
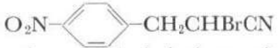
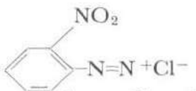
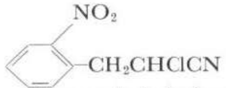
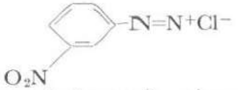
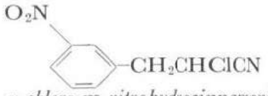
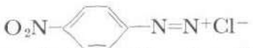
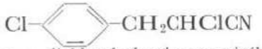
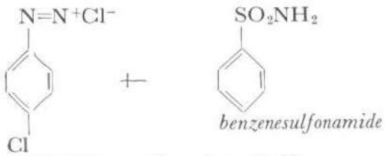
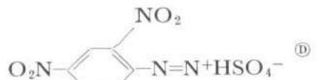
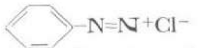
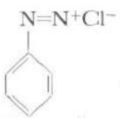
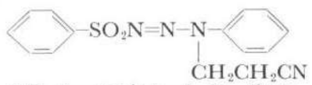
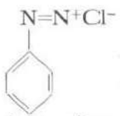
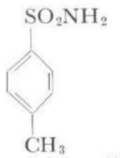
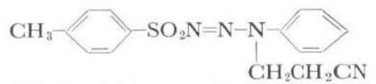
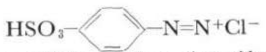
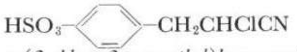
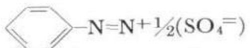
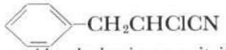
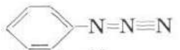
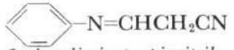
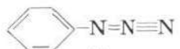
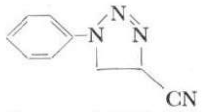
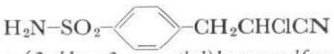
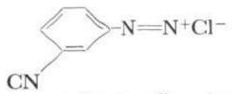
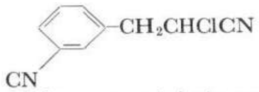
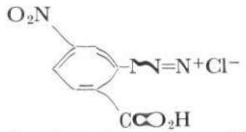
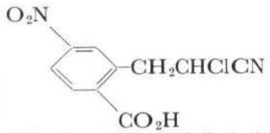
Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 p-*nitrobenzenediazonium bromide*	1.5-2	5°	 α-*bromo*-p-*nitrohydrocinnamonitrile*	54	B.P. 192-194°/2 mm. M.P. 98.5-99°	1254	595, 594
 o-*nitrobenzenediazonium chloride*	1.5-2	5°	 α-*chloro*-o-*nitrohydrocinnamonitrile*	45	B.P. 166-168°/4 mm.	1254	736
 m-*nitrobenzenediazonium chloride*	0.5	18°	 α-*chloro*-m-*nitrohydrocinnamonitrile*	58.5	M.P. 74-76°	153	654, 808, 1254
 p-*nitrobenzenediazonium chloride*	1.5-2	5°	 α-*chloro*-p-*nitrohydrocinnamonitrile*	96.5	M.P. 110-111°	1254	595, 594, 808, 153, 654, 1308
 p-*chlorobenzenediazonium chloride*	0.5	18°	 p,α-*dichlorohydrocinnamonitrile*	85.3	M.P. 56-59° B.P. 153-159°/15 mm.	153	1310, 1309
 *benzenesulfonamide* p-*chlorobenzenediazonium chloride*		5°	 *3-[3-(*p-*chlorophenyl)-1-(phenylsulfonyl)triazen-3-yl]propionitrile*	—	M.P. 127-129°	1276	
 p-*phenylenebis[diazonium chloride]*	18	25°	 α,α′-*dichloro*-p-*benzenedipropionitrile*	40.1	M.P. 184°	1329	

TABLE VII—Continued

Reactants	Re-action Time (Hr.)	Reaction Temperature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 Ⓓ *2,4-dinitrobenzenediazonium bisulfate*	—	10°	Ⓒ	—	M.P. 172°	595 594	
 *benzenediazonium bromide*	2.0	22°	 *α-bromohydrocinnamonitrile*	42.3	—	153	1254
			 *α-chlorohydrocinnamonitrile*	39.5	—		
 *benzenediazonium chloride*	1.5	10-11°	 *α-chlorohydrocinnamonitrile*	81	B.P. 127-128°/12 mm. M.P. 21-22.5°	153	666, 654 1254
 +  *benzenediazonium chloride* *benzenesulfonamide*	—	5°	 *3-[3-phenyl-1-(phenylsulfonyl)triazen-3-yl]-propionitrile*	—	M.P. 109-111°	1276	
 +  *benzenediazonium chloride* p-*toluenesulfonamide*	5 25	—	 *3-[3-phenyl-1-(p-tolylsulfonyl)triazen-3-yl]-propionitrile*	—	M.P. 110°	1276	

Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 p-*sulfobenzenediazonium chloride*	0.5	18°	 p-*(2-chloro-2-cyanoethyl)benzenesulfonic acid*	92.7	M.P. 137-139°	153	
 *benzenediazonium sulfate*	0.5	18°	 *α-chlorohydrocinnamonitrile*	6.0	B.P. 125-135°/14 mm.	153	
 *phenyl azide*	4	steam bath	 *3-phenyliminopropionitrile*	75	B.P. 115°/4 mm.	1418	
 *phenyl azide*	288	R.T. (sealed tube)	 *1-phenyl-$\triangle^2$-1,2,3-triazoline-4-carbonitrile*	91	M.P. 98° (dec.)	1418	
 p-*sulfamidobenzenediazonium chloride*	0.33	36-40°	 p-*(2-chloro-2-cyanoethyl)benzenesulfonamide*	98	—	808	595
 m-*cyanobenzene-diazonium chloride*	—	—	 *α-chloro-*m-*cyanohydrocinnamonitrile*	—	B.P. 159°/1 mm.	808	
 *2-carboxy-4-nitrobenzenediazonium chloride*	8	20°	 *2-(2-chloro-2-cyanoethyl)-4-nitrobenzoic acid*	47	M.P. 137°	736	

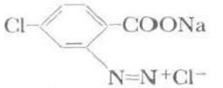
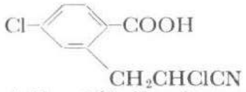
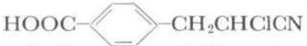
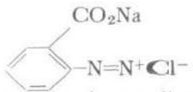
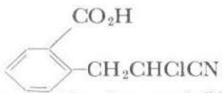
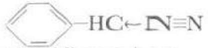
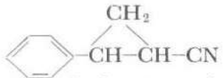
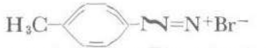
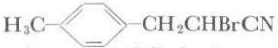
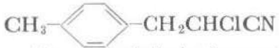
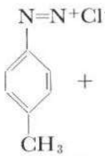
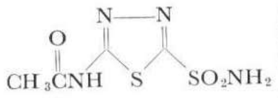
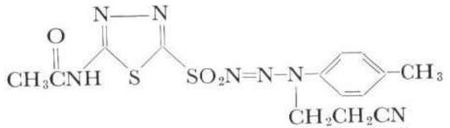
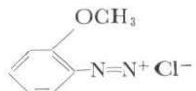
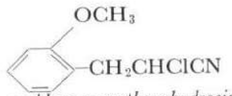
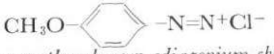
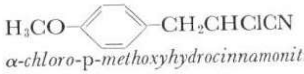
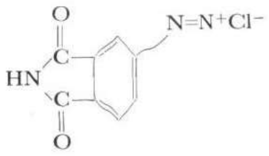
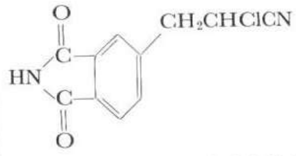
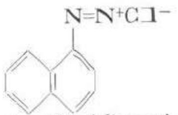
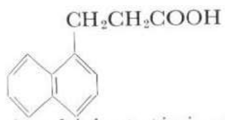
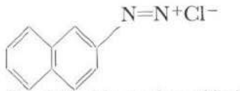
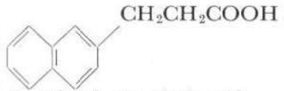
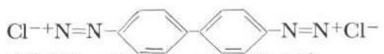
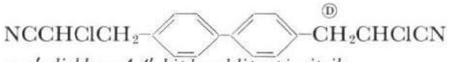
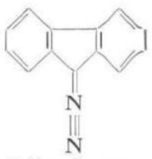
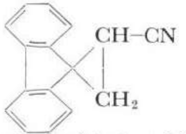
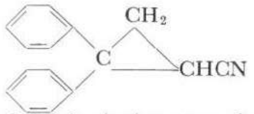
Reactants	Reaction Time (Hr.)	Reaction Temperature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References: This Exam.	References: See Also:
 *2-carboxy-5-chlorobenzenediazonium chloride, sodium salt*	—	40-45°	 *4-chloro-2-(2-chloro-2-cyanoethyl)benzoic acid*	—	M.P. 139°	595 594	
 p-*carboxybenzenediazonium chloride, sodium salt*	0.5	18°	 p-*(2-chloro-2-cyanoethyl)benzoic acid*	88.1	M.P. 108-109°	153	
 o-*carboxybenzenediazonium chloride, sodium salt*	0.5	40°	 o-*(2-chloro-2-cyanoethyl)benzoic acid*	51	M.P. 121-122°	736	
 *phenyldiazomethane*	0.58 18	5° 25°	 *2-phenylcyclopropanecarbonitrile*	65	B.P. 114°/3.2 mm. M.P. 27-30°	1351	
 p-*methylbenzenediazonium bromide*	1.5-2	5°	 *α-bromo-*p*-methylhydrocinnamonitrile*	30.2	B.P. 121-121.5°/2 mm.	1254	
 p-*methylbenzenediazonium chloride*	2.0	35-40°	 *α-chloro-*p*-methylhydrocinnamonitrile*	40	B.P. 140-145°/11 mm.	654	595, 594

TABLE VII—Continued

Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 p-methylbenzenediazonium chloride +  5-acetamido-1,3,4-thiadiazole-2-sulfonamide	5	20-25°	 3-[1-(5-acetamido-1,3,4-thiadiazol-2-ylsulfonyl)-3-p-tolyl]propionitrile	—	—	1276	
 o-methoxybenzenediazonium chloride	4.0	12°	 α-chloro-o-methoxyhydrocinnamonitrile	17.2	B.P. 135-140°/13 mm. M.P. 35-37°	153	
 p-methoxybenzenediazonium chloride	4.0	12°	 α-chloro-p-methoxyhydrocinnamonitrile	76.2	B.P. 174-179°/25 mm. M.P. 41-42°	153	
 1,3-dioxo-5-isoindolinediazonium chloride	—	15-20° exo-thermic	 4-(2-chloro-2-cyanoethyl)phthalimide	—	M.P. 147°	1257	
 1-naphthyldiazonium chloride	2.0	110°	 1-naphthalenepropionic acid	45	M.P. 154-155°	1255	

Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 *2-naphthyldiazonium chloride*	2.0	110°	 *2-naphthalenepropionic acid*	50	M.P. 135°	1255	
 *4,4′-biphenylbis (diazonium chloride)*	—	30-40°	 *α,α′-dichloro-4,4′-biphenyldipropionitrile*		M.P. 126°	595 594	808
 *9-diazofluorene*	24.0	in the cold Ⓔ	 *spiro[cyclopropane-1,9′-fluorene]-2-carbonitrile*	—	M.P. 102°	537	538
 *diphenyldiazomethane*	—	25°	 *2,2-diphenylcyclopropanecarbonitrile*	64	M.P. 106-107°	1439	

NOTES: Ⓐ Cooling necessary, reaction explosive.
Ⓑ This product is incorrectly identified in reference 808.
Ⓒ Product not identified.
Ⓓ Structure uncertain.
Ⓔ The kinetics of this reaction were determined at 50°C.

TABLE VIII—Reactions with Alcohols and Carbon Monoxide

$CO + H_2 + CH_3OH$ *carbon monoxide, hydrogen and methanol*	—	250°	*an amine mixture (avg.* C_{15}*)*	—	—	458	

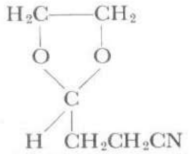
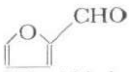
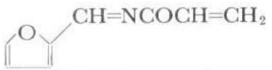
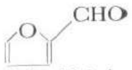
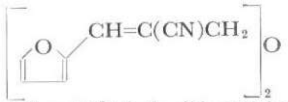
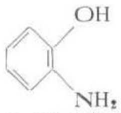
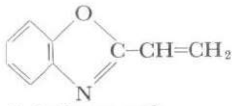
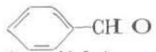
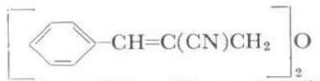
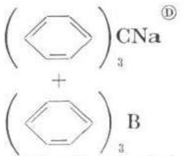
Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
$CO+H_2+CH_3OH$ *carbon monoxide, hydrogen and methanol*	1.0	150°	$(CH_3O)_2CHCH_2CH_2CN$ *3-cyanopropionaldehyde, dimethyl acetal*	31.5	B.P. 90-91°/14 mm.	86	
$CO+H_2+HOCH_2CH_2OH$ *carbon monoxide, hydrogen and ethylene glycol*	1.0	175°	 *1,3-dioxolane-2-propionitrile*	6.7	B.P. 71-75°/6 mm.	86	

TABLE IX—Miscellaneous Reactions

$CHCl_3$ Ⓐ *chloroform*	6.0	190°	$ClCH_2CH_2CN$ *3-chloropropionitrile*	30.5	B.P. 88°/20 mm.	1249	
			$Cl_2CHCH_2CHClCN$ *2,4,4-trichlorobutyronitrile*	5.9	B.P. 90.5°/20 mm.		
CCl_4 Ⓐ *carbon tetrachloride*	6.0	160°	$Cl_3CCH_2CHClCN$ *2,4,4,4-tetrachlorobutyronitrile*	28.6	B.P. 94°/15 mm.		
			$Cl_3CCH_2CH(CN)CH_2CHClCN$ *2-chloro-4-(2,2,2-trichloroethyl)glutaronitrile*	7.3Ⓑ	—	1249	
CF_3I *trifluoroiodomethane*	48	—	CF_3CH_2CHICN *3,3,3-trifluoro-2-iodobutyronitrile*	≥ 72	—	484	
O–O–O *ozone*	—	—	*ozonized product* Ⓒ	—	—	721	
$NaOCOCH_3+CH_3COOH$ *sodium acetate + acetic acid*	267	35°	*polyacrylonitrile* + $C_8H_{12}N_2$	— 1.0	— B.P. 280°/766 mm.	454	
$(CH_3)_2C(OH)CN$ *2-hydroxyisobutyronitrile*	3.0	70-75°	$NCCH_2CH_2CN$ *succinonitrile*	88	B.P. 149-150°/16 mm. M.P. 53-54°	1361	

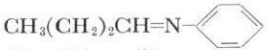
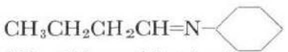
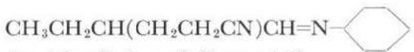
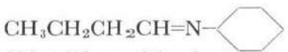
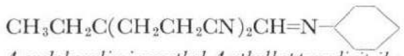
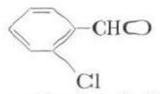
Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 *2-furaldehyde*	5.0	25-30°	 *N-furfurylideneacrylamide*	12.3 cis 20.7 trans	B.P. 139-140°/0.45 mm. B.P. 127-128°/0.4 mm.	1430	
 *2-furaldehyde*	4.0	120-140°	 *2-furfurylidene-3,3′-oxydipropionitrile*	—	B.P. 191-193°/2 mm.	1430	
			 *3,3′-oxybis[2-furfurylidenepropionitrile]*	—	M.P. 85-87°		
 *o-aminophenol*	—	—	 *2-vinylbenzoxazole*	—	—	1403	
 *benzaldehyde*	9.0	30°	 *2-benzylidene-3,3′-oxydipropionitrile*	18.8	B.P. 170°/0.3 mm.	1442	
			 *3,3′-oxybis[2-benzylidenepropionitrile]*	18.1	M.P. 73°		

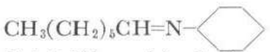
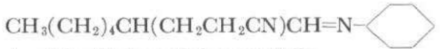
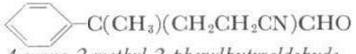
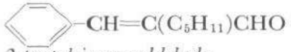
Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 Ⓓ *trityl sodium + triphenylborine*	—	—	 *4,4,4-triphenylbutyronitrile*	70	M.P. 137.5-138°	1449	

NOTES: Ⓐ Hydroquinone employed as an inhibitor.
Ⓑ Mixture of isomers.
Ⓒ Structure not given.
Ⓓ Reaction does not occur with trityl sodium alone.

TABLE X—"C" Cyanoethylation: Aldehydes

Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
CH_3CHO *acetaldehyde*	1.0	—	$CHOCH_2CH_2CH_2CN$ *4-cyanobutyraldehyde* $CHOCH(CH_2CH_2CN)_2$ *4-cyano-2-(2-cyanoethyl)butyraldehyde*	40-50 Ⓐ	B.P. 86-95°/3 mm.	1124	
 *N-ethylidenecyclohexylamine*	—	200°	 *4-cyclohexyliminomethylheptanedinitrile*	40 Ⓑ	M.P. 109-110°	1315 1317	1258
CH_3CH_2CHO *propionaldehyde*	—	—	$CH_3CH(CH_2CH_2CN)CHO$ *4-cyano-2-methylbutyraldehyde* $CH_3C(CH_2CH_2CN)_2CHO$ *4-cyano-2-(2-cyanoethyl)-2-methylbutyraldehyde*	4.9 25.1	B.P. 92-94°/3 mm. B.P. 135.5-137°/3 mm.	1124	
$CH_3CH=CHCHO$ *crotonaldehyde*	8.0	25°	*7.6% N dark red viscous balsam*	—	—	182	
$CH_3CH_2CH_2CHO$ n-*butyraldehyde*	—	reflux	$CH_3CH_2CH_2COCH(CH_3)CN$ *2-methyl-3-oxohexanenitrile*	—	B.P. 60°/15 mm.	1024	
$CH_3(CH_2)_2CH=N-(C_4H_9)$ *N-butylidene-*n-*butylamine*	—	160°	$CH_3CH_2CH[CH=N(C_4H_9)]CH_2CH_2CN$ *4-butyliminomethylhexanenitrile*	69	B.P. 138-142°/10 mm.	1317	

Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 $CH_3(CH_2)_2CH=N-$ *N-butylideneaniline*	—	200°	 $CH_3CH_2CH(CH_2CH_2CN)CH=N-$ *4-phenyliminomethylhexanenitrile*	76	B.P. 116-120°/0.4 mm.	1317	
 $CH_3CH_2CH_2CH=N-$ *N-butylidenecyclohexylamine*	—	150°	 $CH_3CH_2CH(CH_2CH_2CN)CH=N-$ *4-cyclohexyliminomethylhexanenitrile*	80Ⓒ	B.P. 150-153°/10 mm.	1315 1317	1258
 $CH_3CH_2CH_2CH=N-$ *N-butylidenecyclohexylamine*	—	200°	 $CH_3CH_2C(CH_2CH_2CN)_2CH=N-$ *4-cyclohexyliminomethyl-4-ethylheptanedinitrile*	70Ⓓ	M.P. 63-64°	1315 1317	1258
$(CH_3)_2CHCHO$ *isobutyraldehyde*	—	95-105°	$NCCH_2CH_2C(CH_3)_2CHO$ *4-cyano-2,2-dimethylbutyraldehyde*	85	—	916	182, 587, 1084, 1124
$CH_3CHOHCH_2CHO$ *acetaldol*	3.0	25°	*syrup (10.4% N)*	—	—	182	
 *2-furaldehyde*	—	—	—	—	—		Table IX
$(CH_3CH_2)_2CHCHO$ *2-ethylbutyraldehyde*	3.0	25°	$HCOC(CH_2CH_3)_2CH_2CH_2CN$ *4-cyano-2,2-diethylbutyraldehyde*	66	B.P. 124°/4 mm.	182	1334, 180
 o-*chlorobenzaldehyde*	1.5	25°	*(monocyanoethylation product questionable)*	—	M.P. 125°	182	
C_6H_5CHO *benzaldehyde*	8.0	25°	*(dicyanoethylation product questionable)*	—	B.P. 225-230°/5 mm.	182	Table IX

Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 $CH_3(CH_2)_5CH{=}N-$ *N-heptylidenecyclohexylamine*	—	150°	 $CH_3(CH_2)_4CH(CH_2CH_2CN)CH{=}N-$ *4-cyclohexyliminomethylnonanenitrile*	60	B.P. 190-194°/0.4 mm.	1315 1317	1258
$CH_3CH_2CH_2CH{=}C(CH_2CH_3)CHO$ *2-ethylhexenal*	4.5	45-55°	$CH_3CH_2CH{=}CHC(C_2H_5)(CH_2CH_2CN)CHO$ *2-(2-cyanoethyl)-2-ethylhydrosorbaldehyde*	49	B.P. 138-140°/6 mm.	180	183, 182
$CH_3(CH_2)_3CH(C_2H_5)CHO$ *2-ethylhexanal*	4.5	55-58°	$CH_3(CH_2)_3C(C_2H_5)(CH_2CH_2CN)CHO$ *2-(2-cyanoethyl)-2-ethylhexanal*	79.5	B.P. 140-142°/5 mm.	180	182, 1334
 $-CH(CH_3)CHO$ *1-phenylpropionaldehyde*	0.5 1.5	25° 65°	 $-C(CH_3)(CH_2CH_2CN)CHO$ *4-cyano-2-methyl-2-phenylbutyraldehyde*	74	B.P. 135-141°/0.6 mm.	411	182
$C_6H_{13}CH(CH_3)CHO$ *2-methyloctanal*	0.67 3.5	35-38° 25°	$HCOC(CH_3)(C_6H_{13})CH_2CH_2CN$ *2-(2-cyanoethyl)-2-methyloctanal*	—	—	182	
 $-CH{=}C(C_5H_{11})CHO$ *2-pentylcinnamaldehyde*	2.0	25°	*yellow oil* *7.7% N red oil*	— —	B.P. 205-225°/5 mm. B.P. 260-265°/6 mm.	182	

NOTES: Ⓐ Combined yield. Ⓑ Three equivalents of acrylonitrile. Ⓒ One equivalent of acrylonitrile. Ⓓ Two equivalents of acrylonitrile.

TABLE XI—"C" Cyanoethylation: Ketones

(A) Aliphatic Ketones

CH_3COCH_3 *acetone*	1.0	reflux	$CH_3COCH_2CH_2CH_2CN$ *5-oxohexanenitrile*	18	B.P. 108-112°/14 mm.	93	
CH_3COCH_3 *acetone*	2.0	reflux	$CH_3COCH_2CH_2CH_2CN$ *5-oxohexanenitrile*	8	B.P. 93-98°/6 mm.	1066	
			$CH_3COCH(CH_2CH_2CN)_2$ *4-acetylheptanedinitrile*	15	B.P. 196-199°/6 mm.	1067	
			$CH_3COC(CH_2CH_2CN)_3$ *4-acetyl-4-(2-cyanoethyl)heptanedinitrile*	24	M.P. 152°		

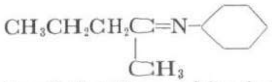
Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
CH_3COCH_3 *acetone*	2.0	0-5°	$CH_3COC(CH_2CH_2CN)_3$ *4-acetyl-4-(2-cyanoethyl)heptanedinitrile*	77	M.P. 154°	177 160	1077, 167, 169, 426, 989
$CH_3COCH_2CH_3$ *methyl ethyl ketone*	0.1	10°	$CH_3COCH(CH_2CH_2CN)CH_3$ *4-acetylvaleronitrile*	29.4	B.P. 114-115°/15 mm.	93	1313
$CH_3COCH_2CH_3$ *methyl ethyl ketone*	5.0	5-10°	$CH_3COC(CH_3)(CH_2CH_2CN)_2$ *4-acetyl-4-methylheptanedinitrile*	89	M.P. 67°	177	998, 1162, 1149, 167, 169, 692, 93, 962
$CH_3COCH_2CH_2CN$ *levulinonitrile*	—	85-90°	$CH_3COC(CH_2CH_2CN)_2CH_2CN$ *4-acetyl-4-cyanomethylheptanedinitrile*	85	M.P. 85-86°	917	
$CH_3COCH_2CH_2CH_3$ *2-pentanone*	50	110°	$CH_3COCH(CH_2CH_3)CH_2CH_2CN$ *4-acetylhexanenitrile*	62	B.P. 85-92°/0.7 mm.	1318	1313
$CH_3COCH_2CH_2CH_3$ *2-pentanone*	1.0	15°	$CH_3COC(CH_2CH_3)(CH_2CH_2CN)_2$ *4-acetyl-4-ethylheptanedinitrile*	43	M.P. 109°	177	
			$NCCH_2CH_2CH_2COC(CH_2CH_2CN)_2CH_2CH_3$ *4-(2-cyanoethyl)-4-ethyl-5-oxononanedinitrile*	9	M.P. 90-91°		
$CH_3CH_2CH_2C(CH_3)=N(C_4H_9)$ *N-(1-methyl)butylidene-n-butylamine*	—	160°	$CH_3CH_2CH(CH_2CH_2CN)C(CH_3)=N(C_4H_9)$ *5-butylimino-4-ethylhexanenitrile*	70	B.P. 98-101°/0.3 mm.		1316
 $CH_3CH_2CH_2\underset{CH_3}{\underset{\vert}{C}}=N-C_6H_{11}$ *1-methylbutylidenecyclohexylamine*	—	150°	 $CH_3CH_2CH(CH_2CH_2CN)C(CH_3)=N-C_6H_{11}$ *4-(1-cyclohexyliminoethyl)hexanenitrile*	68	B.P. 111-114°/0.4 mm.	1315 1316	1258
$CH_3COCH(CH_3)_2$ *3-methyl-2-butanone*	—	—	$CH_3COC(CH_3)_2CH_2CH_2CN$ *4,4-dimethyl-5-oxohexanenitrile*	61	B.P. 134°/18 mm.	204	

TABLE XI—Continued

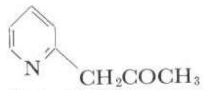
Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
$(CH_3)_2C{=}CHCOCH_3$ *mesityl oxide*	—	5-10°	$(CH_3)_2C{=}C(CH_2CH_2CN)COCH_3$ *4-acetyl-5-methyl-4-hexenenitrile*	10-15	B.P. 110-115°/2 mm.	178	167, 169, 998, 405
			$CH_2{=}C(CH_3)C(CH_2CH_2CN)_2COCH_3$ *4-acetyl-4-isopropenylheptanedinitrile*	73.5	M.P. 116-117°		
$CH_3COCH_2(CH_2)_2CH_3$ *2-hexanone*	3.0 2.0	<5° 5-10°	$CH_3COC(CH_2CH_2CN)_2CH_2CH_2CH_3$ *4-acetyl-4-propylheptanedinitrile*	—	B.P. 205-210°/2 mm. M.P. 63°	177	
$CH_3COCH_2CH(CH_3)_2$ *4-methyl-2-pentanone*	3.0 2.0	<5° 5-10°	$CH_3COC(CH_2CH_2CN)_2CH(CH_3)_2$ *4-acetyl-4-isopropylheptanedinitrile*	20	B.P. 200-205°/1 mm. M.P. 101°	177	178
$CH_3COCH_2CH_2CH_2CH_2CH_3$ *2-heptanone*	3.0 2.0	<5° 5-10°	$CH_3COC(C_4H_9)(CH_2CH_2CN)_2$ *4-acetyl-4-butylheptanedinitrile*	50	B.P. 195-200°/1 mm. M.P. 47° M.P. 63°	177	167, 169
$(CH_3)_2CHCOCH(CH_3)_2$ *2,4-dimethyl-3-pentanone*	4.0	100°	$(CH_3)_2CHCOC(CH_2CH_2CN)(CH_3)_2$ *4,4,6-trimethyl-5-oxoheptanenitrile*	46	B.P. 116-118°/7 mm.	1422 169	167, 1419
			$[(CH_3)_2C(CH_2CH_2CN)]_2C{=}O$ *4,4,6,6-tetramethyl-5-oxononanedinitrile*		B.P. 165-170°/1 mm.		
$CH_3CH_2CH_2COCH_2CH_2CH_3$ *4-heptanone*	5.5 O.N.	50-60° 25°	$CH_3(CH_2)_2COCH(C_2H_5)CH_2CH_2CN$ *4-ethyl-5-oxooctanenitrile*	31	B.P. 101.5-102°/4 mm.	1423	
 *(2-pyridyl)-2-propanone*	— 5 min.	60° reflux	 *γ-acetyl-2-pyridinebutyronitrile*	44.5	M.P. 34°	1211	
 *(2-pyridyl)-2-propanone*	— 5 min.	60° reflux	 *4-acetyl-4-(2-pyridyl)heptanedinitrile*	82	M.P. 111.5°	1211	

TABLE XI—Continued

(A) Aliphatic Ketones

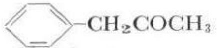
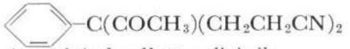
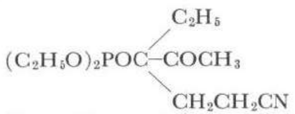
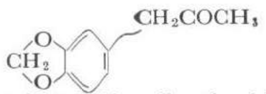
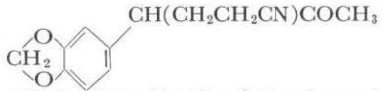
Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
$(CH_3)_2CHCOCH_2CH_2CH_2CH_3$ *2-methyl-3-heptanone*	—	—	$CH_3(CH_2)_3COC(CH_3)_2CH_2CH_2CN$ *4,4-dimethyl-5-oxononanenitrile* $(CH_3)_2CHCOCH(C_3H_7)CH_2CH_2CN$ *6-methyl-5-oxo-4-propylheptanenitrile*	— —	B.P. 132°/5 mm. B.P. 127°/5 mm.	1224	
$CH_3CO(CH_2)_5CH_3$ *2-octanone*	3.0 2.0	<5° 5-10°	$CH_3COC(C_5H_{11})(CH_2CH_2CN)_2$ *4-acetyl-4-pentylheptanedinitrile*	50	—	177	167, 169
 *phenyl-2-propanone*	1.0	20-25°	 *4-acetyl-4-phenylheptanedinitrile*	86	M.P. 109-110°	177	1222
$(CH_3)_2C{=}CH{-}CO{-}CH{=}C(CH_3)_2$ *phorone*	20.0	25°	$(CH_3)_2C{=}CHCOC(CH_2CH_2CN){=}C(CH_3)_2$ *4-isopropylidene-7-methyl-5-oxo-6-octenenitrile* $O{=}C[C(CH_2CH_2CN){=}C(CH_3)_2]_2$ *4,6-diisopropylidene-5-oxononanedinitrile*	59Ⓐ 14	B.P. 120°/1 mm. B.P. 190-200°/1 mm.	167 169	
$C_5H_{11}COCH(CH_3)_2$ *2-methyl-3-octanone*	—	—	$C_5H_{11}COC(CH_3)_2CH_2CH_2CN$ *4,4-dimethyl-5-oxodecanenitrile*	—	B.P. 156-159°/11 mm.	204	
$CH_3COCH(C_2H_5)PO(OC_2H_5)_2$ *3-diethylphosphono-2-pentanone*	4.0	reflux	 $(C_2H_5O)_2PO\overset{C_2H_5}{\underset{CH_2CH_2CN}{C}}{-}COCH_3$ *(1-acetyl-3-cyano-1-ethylpropyl)phosphonic acid, diethyl ester*	70.5	B.P. 185°/5 mm.	1386	
 *1-(3,4-methylenedioxyphenyl-2-propanone*	3.0	50°	 *4-(3,4-methylenedioxyphenyl)-5-oxohexanenitrile*	22.9	B.P. 220-225°/20 mm.	1222	
$CH_3COC(CH_3)(CH_2CH_2CN)_2$ *4-acetyl-4-methylheptanedinitrile*	48.0	25°	$(NCCH_2CH_2)_2CHCOC(CH_3)(CH_2CH_2CN)_2$ *4-methyl-4,4'-carbonyldiheptanedinitrile*	13	B.P. 345-355°/2 mm. M.P. 84-85°	177	

TABLE XI—Continued

(A) Aliphatic Ketones

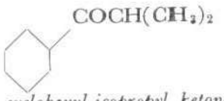
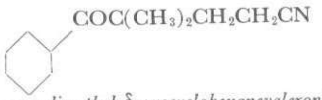
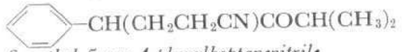
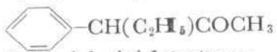
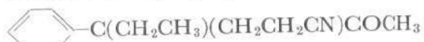
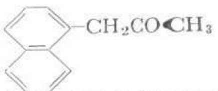
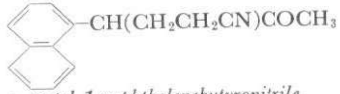
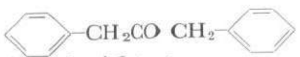
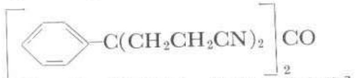
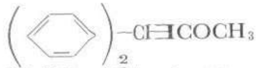
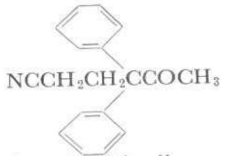
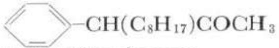
Reactants	Reaction Time (Hr.)	Reaction Temperature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References: This Exam.	References: See Also:
 *cyclohexyl isopropyl ketone*	—	—	 *γ,γ-dimethyl-δ-oxocyclohexanevaleronitrile*	22	M.P. 63°	1423	
 *1-phenyl-3-methyl-2-butanone*	3.0	—	 *6-methyl-5-oxo-4-phenylheptanenitrile*	75	B.P. 218-222°/71 mm.	204	
 *1-phenyl-1-ethyl-2-propanone*	—	—	 *4-acetyl-4-phenylhexanenitrile*	59	B.P. 205-215°/20 mm.	204	
$CH_3COC(CH_2CH_2CN)_3$ *4-acetyl-4-(2-cyanoethyl)heptanedinitrile*	2.0	40°	$NC(CH_2)_3COC(CH_2CH_2CN)_3$ *4,4-bis(2-cyanoethyl)-5-oxononanedinitrile*	13	B.P. 320-340°/1-3 mm. M.P. 121-122°	177	
 *1-(1-naphthyl)-2-propanone*	3.0	50°	 *γ-acetyl-1-naphthalenebutyronitrile*	62.5	B.P. 195-200°/6 mm.	1222	
$C_9H_{19}COCH(CH_3)_2$ *2-methyl-3-dodecanone*	—	—	$C_9H_{19}COC(CH_3)_2CH_2CH_2CN$ *4,4-dimethyl-5-oxotetradecanenitrile*	64	B.P. 210-220°/10 mm.	204	
 *1,3-diphenyl-2-propanone*	18.0	25°	 *4,4′-carbonylbis[4-phenylheptanedinitrile]*	—	—	159	167, 169, 177
 *1,1-diphenyl-2-propanone*	—	—	 *5-oxo-4,4-diphenylhexanenitrile*	—	—	765	

TABLE XI—Continued

(A) Aliphatic Ketones

Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 $-CH(C_8H_{17})COCH_3$ *3-phenyl-2-undecanone*	—	—	 $-C(CH_2CH_2CN)(C_8H_{17})COCH_3$ *4-acetyl-4-phenyldodecanenitrile*	44	B.P. 217°/2-3 mm.	204	

(B) Alkylaryl Ketones

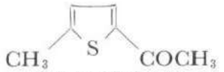
Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 $COCH_3$ *2-thienyl methyl ketone*	2.0	30°	 $COC(CH_2CH_2CN)_3$ *4-(2-cyanoethyl)-4-(2-thenoyl)heptanedinitrile*	89	M.P. 145-146°	1185	184
 $COCH_3$ *2-furyl methyl ketone*	18.0	30°	 $COC(CH_2CH_2CN)_3$ *4-(2-cyanoethyl)-4-(2-furoyl)heptanedinitrile*	90	M.P. 121-122°	184	1185
 COC_2H_5 *2-thienyl ethyl ketone*	24.0	30°	 $COC(CH_2CH_2CN)_2CH_3$ *4-methyl-4-(2-thenoyl)heptanedinitrile*	98	M.P. 81-82°	184	
 CH_3 $COCH_3$ *methyl 5-methyl-2-thienyl ketone*	2.0	25°	 CH_3 $COC(CH_2CH_2CN)_3$ *4-(2-cyanoethyl)-4-(5-methyl-2-thenoyl)heptanedinitrile*	79.6	M.P. 130.5-131.5°	6	
 $COCH_2CH_3$ *2-furyl ethyl ketone*	24.0	30°	 $COC(CH_2CH_2CN)_2CH_3$ *4-(2-furoyl)-4-methylheptanedinitrile*	98	M.P. 49°	184	
 CH_3 $COCH_3$ *methyl 5-methyl-2-furyl ketone*	2.0	25°	 CH_3 $COC(CH_2CH_2CN)_3$ *4-(2-cyanoethyl)-4-(5-methyl-2-furoyl)heptanedinitrile*	70.9	M.P. 177-177.7°	6	

TABLE XI—Continued

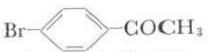
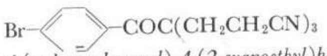
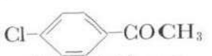
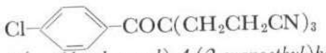
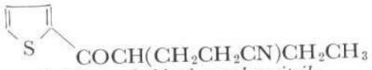
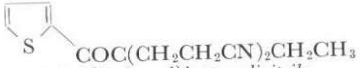
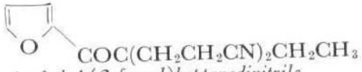
Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 $Br-C_6H_4-COCH_3$ *p-bromoacetophenone*	2-4.0	25-30°	 $Br-C_6H_4-COC(CH_2CH_2CN)_3$ *4-(p-bromobenzoyl)-4-(2-cyanoethyl)heptanedinitrile*	85	M.P. 151-152°	159 177	167, 169
 $Cl-C_6H_4-COCH_3$ *p-chloroacetophenone*	2-4.0	25-30°	 $Cl-C_6H_4-COC(CH_2CH_2CN)_3$ *4-(p-chlorobenzoyl)-4-(2-cyanoethyl)heptanedinitrile*	90	M.P. 141-142°	177 159	167, 169
$C_6H_5COCH_3$ *acetophenone*	26	180°	$C_6H_5CO(CH_2)_3CN$ *4-benzoylbutyronitrile*	75.5	B.P. 128-135°/0.7 mm.	1318	1222
$C_6H_5COCH_3$ *acetophenone*	—	—	$C_6H_5COC(CH_2CH_2CN)_3$ *4-benzoyl-4-(2-cyanoethyl)heptanedinitrile*	—	M.P. 126°	1334	
$C_6H_5COCH_3$ *acetophenone*	0.2	<95°	$C_6H_5COCH(CH_2CH_2CN)_2$ *4-benzoylheptanedinitrile*	90(B)	B.P. 190-240°/2 mm.	407	1077, 159, 11, 1085, 177, 1185, 167, 169
 $C_4H_3S-COCH_2CH_2CH_3$ *2-thienyl propyl ketone*	2.0	25°	 $C_4H_3S-COCH(CH_2CH_2CN)CH_2CH_3$ *γ-ethyl-8-oxo-2-thiophenevaleronitrile*	36	B.P. 154-156°/2.5 mm.	6	
			 $C_4H_3S-COC(CH_2CH_2CN)_2CH_2CH_3$ *4-ethyl-4-(2-thenoyl)heptanedinitrile*	48.3	M.P. 95.5-96°		
 $CH_3-C_4H_2S-COCH_2CH_3$ *ethyl 5-methyl-2—thienyl ketone*	2.0	25°	 $CH_3-C_4H_2S-COC(CH_2CH_2CN)_2CH_3$ *4-methyl-4-(5-methyl-2-thenoyl)heptanedinitrile*	70.4	M.P. 79-80°	6	
 $C_4H_3O-COCH_2CH_2CH_3$ *2-furyl propyl ketone*	24.0	R.T.	 $C_4H_3O-COC(CH_2CH_2CN)_2CH_2CH_3$ *4-ethyl-4-(2-furoyl)heptanedinitrile*	68	M.P. 102°	184	

TABLE XI—Continued

(B) Alkylaryl Ketones

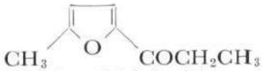
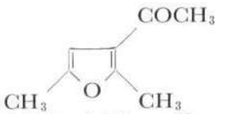
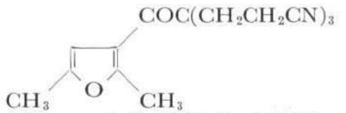
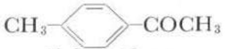
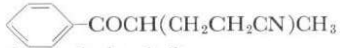
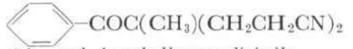
Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 *ethyl 5-methyl-2-furyl ketone*	2.0	25°	 *4-methyl-4-(5-methyl-2-furoyl)heptanedinitrile*	61.5	M.P. 58-59° B.P. 215-218°/3 mm.	6	
 *2,5-dimethyl-3-acetylfuran*	168.0	25°	 *4-(2-cyanoethyl)-4-(2,5-dimethyl-3-furoyl)heptane-dinitrile*	15.7	M.P. 169-170°	6	
 p-*methylacetophenone*	2-4.0	25-30°	 *4-(2-cyanoethyl)-4-*p-*toluoylheptanedinitrile*	90	M.P. 161-162°	177 159	167 169
 *propiophenone*	3.0	50-60°	 *4-benzoylvaleronitrile*	72	B.P. 121-123°/17 mm.	1423	
 *propiophenone*	5.0	25-30°	 *4-benzoyl-4-methylheptanedinitrile*	95	M.P. 66°	159 177 167 169	411
 p′-*methoxyacetophenone*	5.0	25°	 *4-*p-*anisoyl-4-(2-cyanoethyl)heptanedinitrile*	—	M.P. 133°	167 169	159 177
 *propyl 5-methyl-2-thienyl ketone*	3.0	reflux	 *γ-ethyl-5-methyl-δ-oxo-2-thiophenevaleronitrile*	43.2	B.P. 159-160°/2 mm.	6	

TABLE XI—Continued

(B) Alkylaryl Ketones

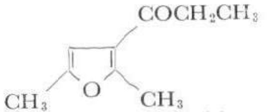
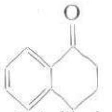
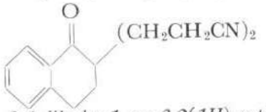
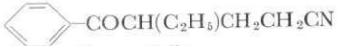
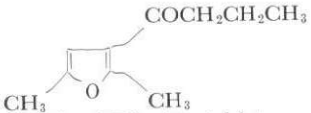
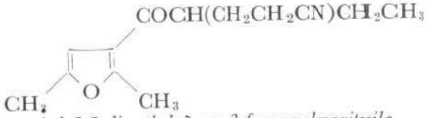
Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 *2,5-dimethylfuryl ethyl ketone*	3.0	reflux	 *2,5,γ-trimethyl-δ-oxo-3-furanvaleronitrile*	56	B.P. 157-158°/8 mm.	6	
 *propyl 5-methyl-2-furyl ketone*	120.0	25°	 *γ-ethyl-5-methyl-δ-oxo-2-furanvaleronitrile*	22.9	B.P. 153-154.5°/5 mm.	6	
			 *4-ethyl-4-(5-methyl-2-furoyl)heptanedinitrile*	47.2	M.P. 93-94°		
 *3,4-dihydro-1[2H]-naphthalenone*	24.0	30°	 *3,4-dihydro-1-oxo-2,2(1H)-naphthalenedipropionitrile*	—	B.P. 250-260°/1 mm. M.P. 80°	177 167 168 169	
 *butyrophenone*	O.N.	25°	 *4-benzoylhexanenitrile*	62	B.P. 153-154°/4 mm.	1314	
 *isobutyrophenone*	1.5	25°	 *4-benzoyl-4-methylvaleronitrile*	62	B.P. 159-162°/4 mm.	1419	1422
 *2,5-dimethylfuryl propyl ketone*	168.0	25°	 *γ-ethyl-2,5-dimethyl-δ-oxo-3-furanvaleronitrile*	54.3	B.P. 137.5-138°/2 mm. M.P. 51-52°	6	

TABLE XI—Continued **(B) Alkylaryl Ketones**

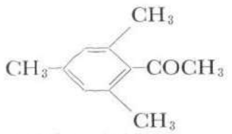
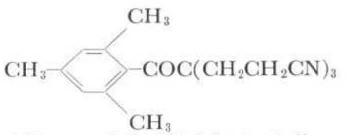
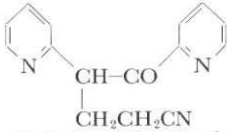
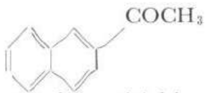
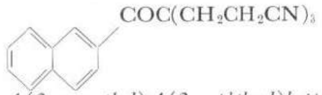
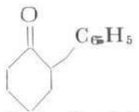
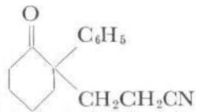
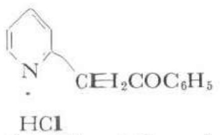
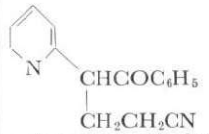
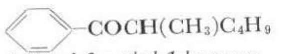
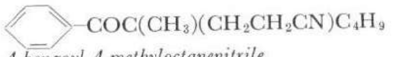
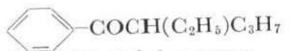
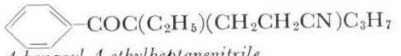
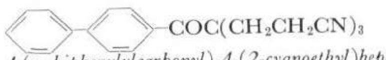
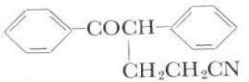
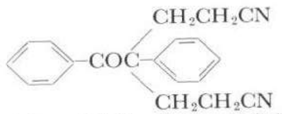
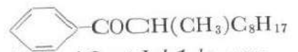
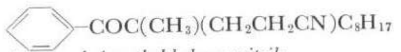
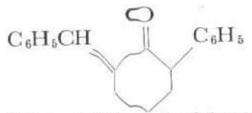
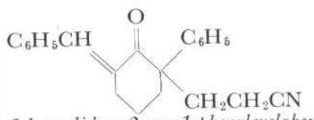
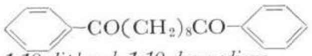
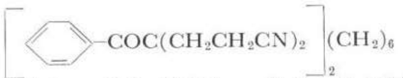
Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 *methyl mesityl ketone*	2-4.0	25-30°	 *4-(2-cyanoethyl)-4-(2,4,6-trimethylbenzoyl)heptane-dinitrile*	30	M.P. 126°	177	
 *desoxypyridoin*	— 5 min.	<60° reflux	 *4,5-di-2-pyridyl-5-oxovaleronitrile*	51	M.P. 72°	1211	
 *methyl 2-naphthyl ketone*	2-4.0	25-30°	 *4-(2-cyanoethyl)-4-(2-naphthoyl)heptanedinitrile*	90	M.P. 122°	159 177 167 169	
 *2 phenylcyclohexanone*	2.0	25-45°	 *2-oxo-1-phenylcyclohexanepropionitrile*	70	B.P. 150-160°/0.4 mm.	60	
 *2 pyridylacetophenone hydrochloride*	— 5 min.	<60° reflux	 *γ-benzoyl-2-pyridinebutyronitrile*	48	M.P. 75°	1211	

TABLE XI—Continued

(B) Alkylaryl Ketones

Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 *1-phenyl-2-methyl-1-hexanone*	—	—	 *4-benzoyl-4-methyloctanenitrile*	47	—	204	
 *1-phenyl-2-ethyl-1-pentanone*	—	—	 *4-benzoyl-4-ethylheptanenitrile*	—	—	204	
 *p-phenylacetophenone*	2-4.0	25-30°	 *4-(p-biphenylylcarbonyl)-4-(2-cyanoethyl)heptane-dinitrile*	90	M.P. 178°	159 177 167 169	
 *desoxybenzoin*	3.0	50°	 *4-benzoyl-4-phenylbutyronitrile*	93.9	M.P. 86.7-87°	1222	
 *desoxybenzoin*	3.0	45°	 *4-benzoyl-4-phenylheptanedinitrile*	95	M.P. 149-150°	159 177	
 *1-phenyl-2-methyl-1-decanone*	—	—	 *4-benzoyl-4-methyldodecanenitrile*	82	B.P. 190-197°/1 mm.	204	
 *6-benzal-1-phenylcyclohexanone*	12.0	25°	 *3-benzylidene-2-oxo-1-phenylcyclohexanepropionitrile*	83	M.P. 82-83.5°	60	

Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 *1,10-diphenyl-1,10-decanedione*	4.0	25-30°	 *4,4′-hexamethylenebis(4-benzoylheptanedinitrile)*	—	—	159 169 167	

(C) Cyclic Ketones

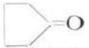
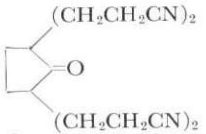
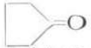
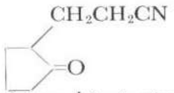
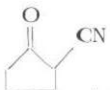
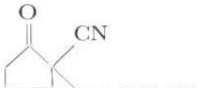
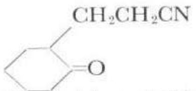
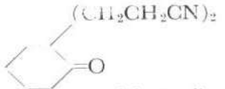
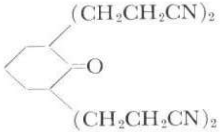
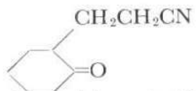
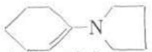
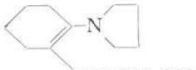
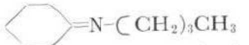
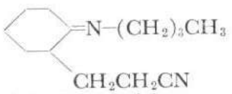
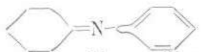
Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	This Exam.	See Also:
 *cyclopentanone*	18.0	25°	 *2-oxo-1,1,3,3-cyclopentanetetrapropionitrile*	97.3	M.P. 175.5°	167 169	1077 168 177
 *cyclopentanone*	2.0	129°	 *2-oxocyclopentanepropionitrile*	73	B.P. 98-105°/0.9 mm.	1318	1230
 *2-cyanocyclopentanone*	—	—	 *1-cyano-2-oxocyclopentanepropionitrile*	90	B.P. 217-218°/21 mm.	1322	1323
 *cyclohexanone*	2.0	180°	 *2-oxocyclohexanepropionitrile*	95	B.P. 109-110°/0.8 mm.	1318	1419, 1423, 1359, 1222

TABLE XI—Continued

(C) Cyclic Ketones

Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 *cyclohexanone*	0.5 1.0	60° 40°	 *2-oxo-1,1-cyclohexanedipropionitrile*	35	M.P. 68°	1423	1359, 1222
 *cyclohexanone*	15.0	25°	 *2-oxo-1,1,3,3-cyclohexanetetrapropionitrile*	88	M.P. 165°	177 168	1362, 167, 426, 169, 691, 1149, 196, 93, 406, 1334, 1423
 *1-(1-cyclohexenyl)pyrrolidine*	—	—	 *2-oxocyclohexanepropionitrile*	80	—	1033	1234
 *1-(1-cyclohexenyl)pyrrolidine*	1.5	105°	 *2-(1-pyrrolidinyl)-1-cyclohexene-1-propionitrile*	87	B.P. 150-172°/10 mm. (pure) 170-172°/10 mm.	1234	
 *cyclohexylidene-n-butylamine*	—	160°	 *2-butyliminocyclohexanepropionitrile*	74	B.P. 116-118°/0.9 mm.	1315 1316	1258
 *cyclohexylideneaniline*	2 3 —	100° 130° 150°	 *2-phenyliminocyclohexanepropionitrile*	63	B.P. 166-168°/0.3 mm.	1315 1316	1258

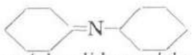
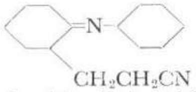
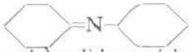
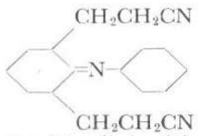
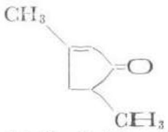
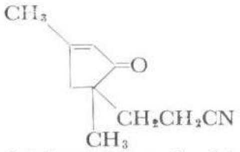
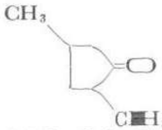
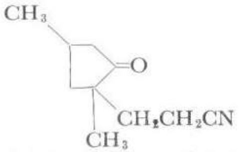
Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 *cyclohexylidenecyclohexylamine*	1.5 —	100° 150°	 *2-cyclohexyliminocyclohexanepropionitrile*	78	B.P. 120-122°/0.2 mm.	1315 1316	1258
 *cyclohexylidenecyclohexylamine*	2.0 2.0	130° 150°	 *2-cyclohexylimino-1,3-cyclohexanedipropionitrile*	79	B.P. 200-205°/0.2 mm.	1315 1316	1258
 *3,5-dimethyl-2-cyclopenten-1-one*	1.0	70-75°	 *1,4-dimethyl-2-oxo-3-cyclopentene-1-propionitrile*	24.2	B.P. 118-122°/5.5 mm.	1359	
 *2,4-dimethylcyclopentanone*	1.0	70-75°	 *1,4-dimethyl-2-oxocyclopropanepropionitrile*	70.6	B.P. 109.5-110°/3 mm.	1359	

TABLE XI—Continued

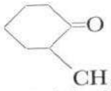
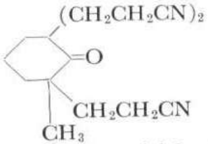
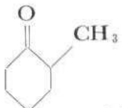
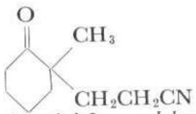
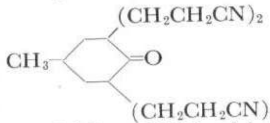
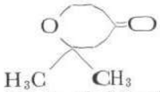
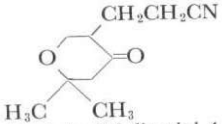
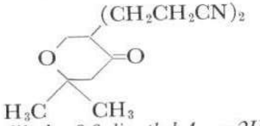
Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 2-methylcyclohexanone	18.0	35-40°	 3-methyl-2-oxo-1,1,3-cyclohexanetripropionitrile	88	B.P. 275-285°/1 mm.	168 177	167 169
 2-methylcyclohexanone	5-16	25°	 1-methyl-2-oxocyclohexanepropionitrile	80	B.P. 131°/1 mm.	406	
 4-methylcyclohexanone	4.0	25°	 5-methyl-2-oxo-1,1,3,3-cyclohexanetetrapropionitrile	91	M.P. 138.5°	168	177, 406
 2,2-dimethyltetrahydro-4-pyrone	—	—	 tetrahydro-6,6-dimethyl-4-oxopyran-3-propionitrile	26	B.P. 132-136°/5 mm.	1359	
			 dihydro-6,6-dimethyl-4-oxo-2H-pyran-3,3(4H)-dipropionitrile	100	M.P. 105.5-106.5°		

TABLE XI—Continued

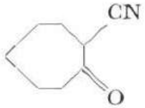
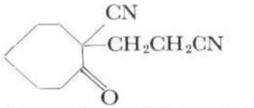
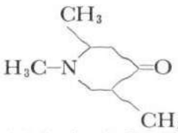
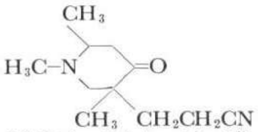
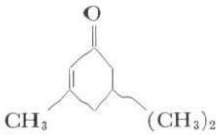
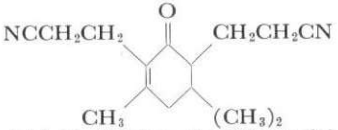
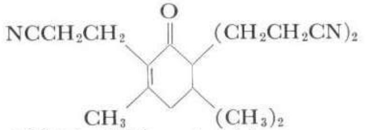
Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 *2-cyanocycloheptanone*	1.0	60-70°	 *1-cyano-2-oxocycloheptanepropionitrile*	65	M.P. 51-52.5°	601	
 *1,2,5-trimethyl-4-piperidone*	54.0	25°	 *1,3,6-trimethyl-4-oxopiperidinepropionitrile*	90.5	M.P. 66.5-67.5°	1359	
 *isophorone*	4.0	30°	 *4,4,6-trimethyl-2-oxo-6-cyclohexene-1,3-dipropionitrile*	22	B.P. 210-220°/1 mm. M.P. 83	186	
			 *4,6,6-trimethyl-2-oxo-3-cyclohexene-1,1,3-tripropionitrile*	2.5	M.P. 120-121°		

TABLE XI—Continued

(C) Cyclic Ketones

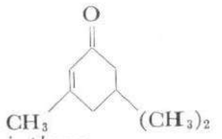
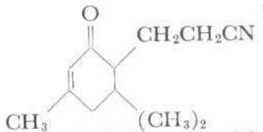
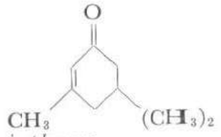
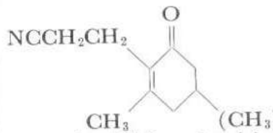
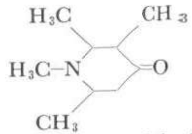
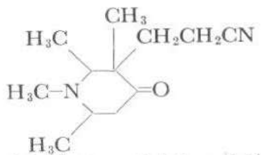
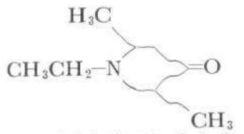
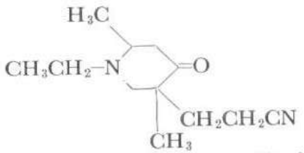
Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 *isophorone*	4.0	26-30°	 Ⓒ *4,6,6-trimethyl-2-oxo-3-cyclohexene-1-propionitrile*	9.2	B.P. 109-111°/0.3 mm. M.P. 23-24°	186	
 *isophorone*	—	—	 Ⓓ *2,4,4-trimethyl-6-oxo-1-cyclohexene-1-propionitrile*	—	B.P. 125°/5 mm.	617	
 *1,2,3,6-tetramethyl-4-piperidone*	1.0	70-75°	 *1,2,3,6-tetramethyl-4-oxo-3-piperidinepropionitrile*	71.4	B.P. 142-145°/1 mm.	1359	
 *1-ethyl-2,5-dimethyl-4-piperidone*	—	—	 *1-ethyl-3,6-dimethyl-4-oxo-3-piperidinepropionitrile*	91.3	B.P. 155-158°/7 mm.	1359	

TABLE XI—Continued

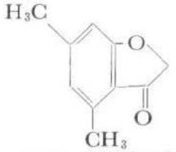
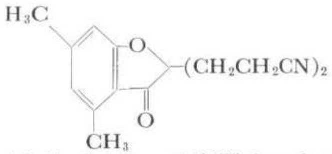
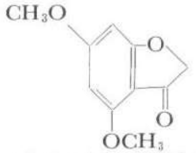
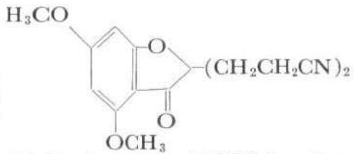
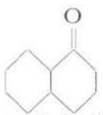
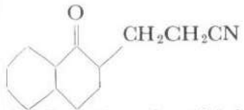
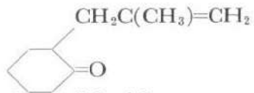
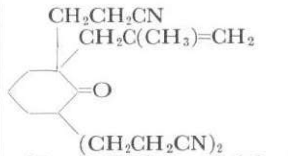
Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 *4,6-dimethyl-3(2H)-benzofuranone*	4.0	<45°	 *4,6-dimethyl-3-oxo-2,2(3H)-benzofurandipropionitrile*	80.2	M.P. 96-97°	1246	
 *4,6-dimethoxy-3(2H)-benzofuranone*	4.0	<45°	 *4,6-dimethoxy-3-oxo-2,2(3H)-benzofurandipropionitrile*	80.7	M.P. 154-155°	1246	
 *octahydro-1(2H)-naphthalenone*	30	190°	 *decahydro-1-oxo-2-naphthalenepropionitrile*	65	B.P. 143-147°/0.9 mm.	1318	
 *2-methallylcyclohexanone*	4.5	25-50°	 *3-(2-methylallyl)-2-oxo-1,1,3-cyclohexanetripropionitrile*	—	B.P. 230-270°/1-3 mm.	168	

TABLE XI—Continued

(C) Cyclic Ketones

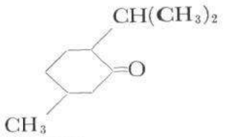
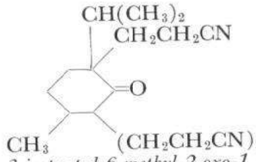
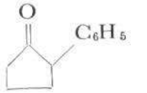
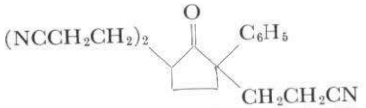
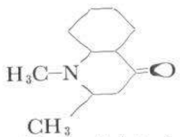
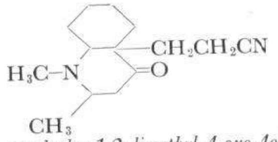
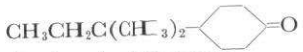
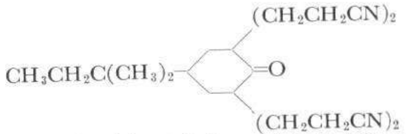
Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 *menthone*	24.0	25°	 *3-isopropyl-6-methyl-2-oxo-1,1,3-cyclohexanetripropionitrile*	—	B.P. 295-300°/1 mm.	168	
 *2-phenylcyclopentanone*	0.5	25-30°	 *2-oxo-3-phenyl-1,1,3-cyclopentanetripropionitrile*	75	M.P. 81.5-83°	52	
 *1,2-dimethyloctahydro-4(1H)-quinolone*	—	—	 *octahydro-1,2-dimethyl-4-oxo-4a(1H)-quinolinepropionitrile*	90.6	B.P. 166-170°/2 mm.	1359	
 4-tert-*amylcyclohexanone*	18.0	35-40°	 *5-(1,1-dimethylpropyl)-2-oxo-1,1,3,3-cyclohexanetetrapropionitrile*	80	M.P. 148°	177	168

TABLE XI—Continued

(C) Cyclic Ketones

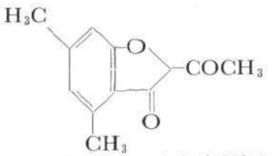
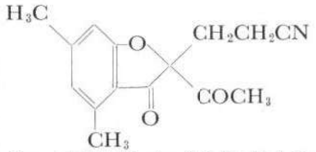
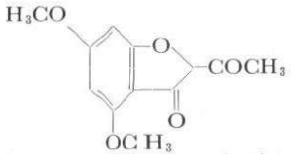
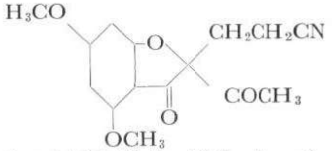
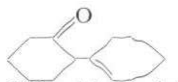
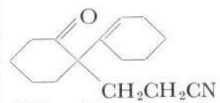
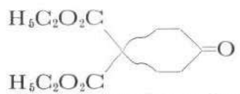
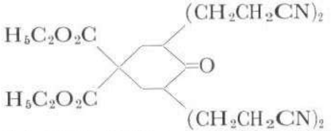
Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 *2-acetyl-4,6-dimethyl-3(2H)-benzofuranone*	4.0	<45°	 *2-acetyl-2,3-dihydro-4,6-dimethyl-3-oxo-2-benzofuranpropionitrile*	39.9	M.P. 108°	1246	
 *2-acetyl-4,6-dimethoxy-3(2H)-benzofuranone*	3.0	—	 *2-acetyl-2,3-dihydro-4,6-dimethoxy-3-oxo-2-benzofuranpropionitrile*	74.9	M.P. 140°	1246	
 *2-(1-cyclohexen-1-yl)cyclohexanone*	2.0	30°	 *1-(1-cyclohexen-1-yl)-2-oxocyclohexanepropionitrile*	47.6	M.P. 61-62°	184	172
 *4-oxo-1,1-cyclohexanedicarboxylic acid, diethyl ester*	—	—	 *3,3,5,5-tetrakis(2-cyanoethyl)-4-oxo-1,1-cyclohexanedicarboxylic acid, diethyl ester*	19	M.P. 205°	1331	

TABLE XI—Continued

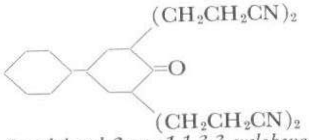
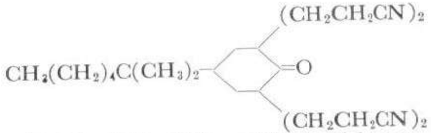
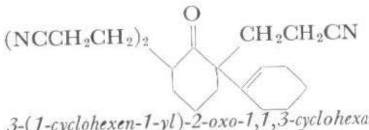
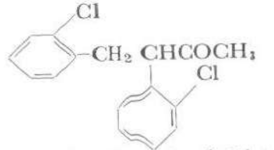
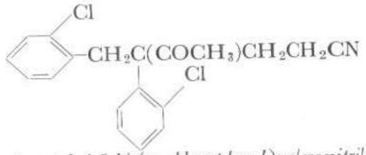
Reactants	Reaction Time (Hr.)	Reaction Temperature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References: This Exam.	References: See Also:
 *4-cyclohexylcyclohexanone*	18.0	35-40°	 *5-cyclohexyl-2-oxo-1,1,3,3-cyclohexanetetrapropionitrile*	80	M.P. 223-224°	177	168
 *4-(1,1-dimethylhexyl)cyclohexanone*	18.0	35-40°	 *5-(1,1-dimethylhexyl)-2-oxo-1,1,3,3-cyclohexane-tetrapropionitrile*	80	M.P. 155-156°	177	
 *2-(2-cyanoethyl)-2-(1-cyclohexen-1-yl)-cyclohexanone*	10.0	30°	 *3-(1-cyclohexen-1-yl)-2-oxo-1,1,3-cyclohexane-tripropionitrile*	54	M.P. 111°	184	
 *3,4-bis(o-chlorophenyl)-2-butanone*	2.0 1.0	25° 45°	 *4-acetyl-4,5-bis(o-chlorophenyl)valeronitrile*	16	B.P. 195-200°/0.1 mm.	1240	

TABLE XI—Continued

(C) Cyclic Ketones

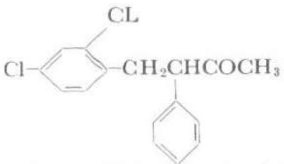
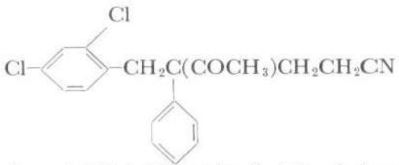
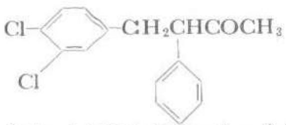
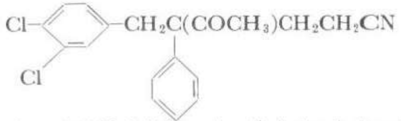
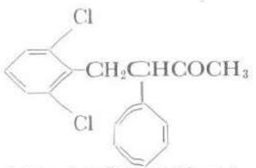
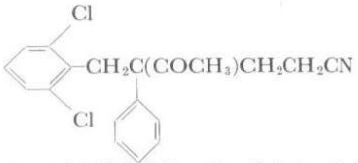
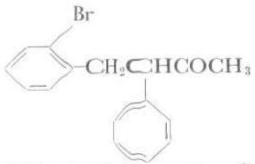
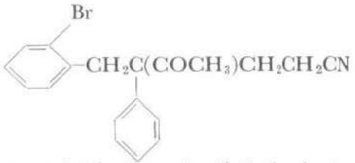
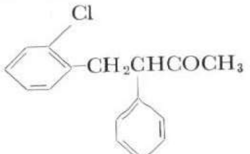
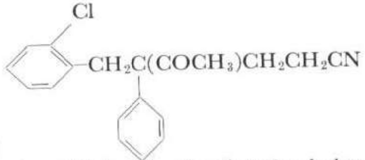
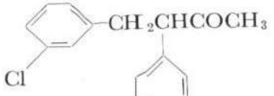
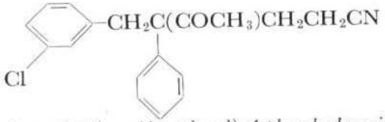
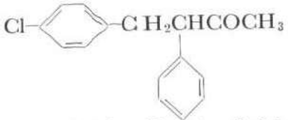
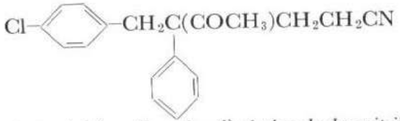
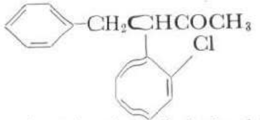
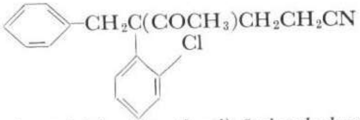
Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 *3-phenyl-4-(2,4-dichlorophenyl)-2-butanone*	3.0	25°	 *4-acetyl-5-(2,4-dichlorophenyl)-4-phenylvaleronitrile*	79	M.P. 89-91°	1240	
 *3-phenyl-4-(3,4-dichlorophenyl)-2-butanone*	2.0 1.0	25° 40°	 *4-acetyl-5-(3,4-dichlorophenyl)-4-phenylvaleronitrile*	87	M.P. 105-107°	1240	
 *3 phenyl-4-(2,6-dichlorophenyl)-2-butanone*	2.0 1.0	25° 82°	 *4-acetyl-5-(2,6-dichlorophenyl)-4-phenylvaleronitrile*	31	M.P. 97.5-99.5°	1240	
 *3-phenyl-4-(o-bromophenyl)-2-butanone*	2.0 1.0	25° 45°	 *4-acetyl-5-(o-bromophenyl)-4-phenylvaleronitrile*	85	M.P. 114-115°	1240	

TABLE XI—Continued

Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 *3-phenyl-4-(o-chlorophenyl)-2-butanone*	3.0	25°	 *4-acetyl-5-(o-chlorophenyl)-4-phenylvaleronitrile*	92	M.P. 106-108°	1240	
 *3-phenyl-4-(m-chlorophenyl)-2-butanone*	2.0 1.0	25° 40°	 *4-acetyl-5-(m-chlorophenyl)-4-phenylvaleronitrile*	81	M.P. 53.5-55.5°	1240	
 *3-phenyl-4-(p-chlorophenyl)-2-butanone*	2.0 1.0	25° 40°	 *4-acetyl-5-(p-chlorophenyl)-4-phenylvaleronitrile*	80	M.P. 86-88°	1240	
 *3-(o-chlorophenyl)-4-phenyl-2-butanone*	2.0 1.0	25° 45°	 *4-acetyl-4-(o-chlorophenyl)-5-phenylvaleronitrile*	30	M.P. 124-126°	1240	

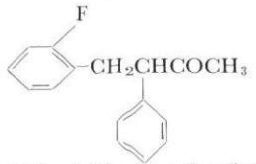
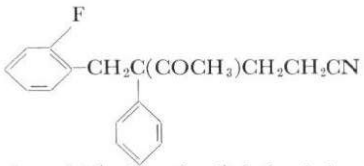
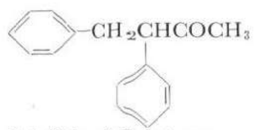
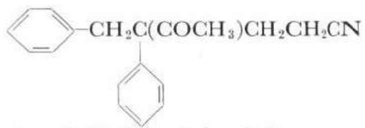
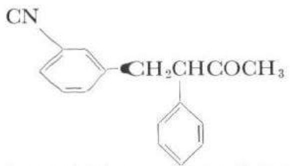
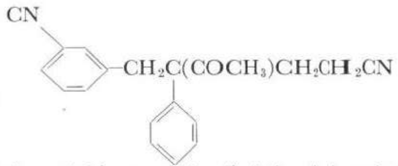
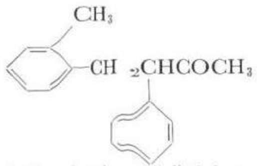
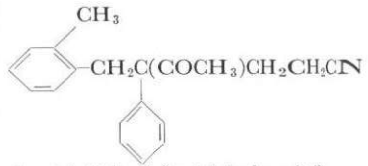
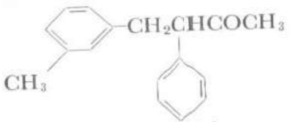
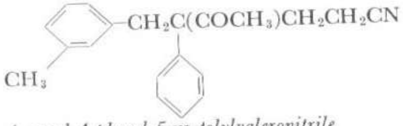
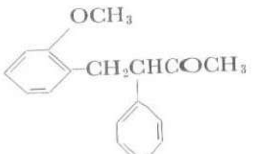
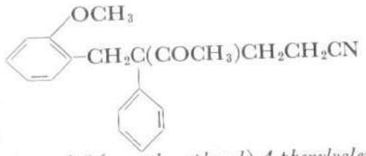
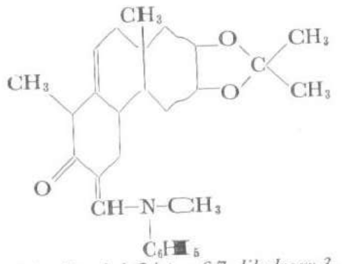
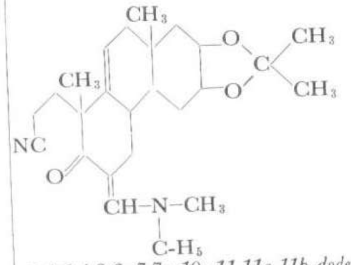
Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 *3-phenyl-4-(o-fluorophenyl)-2-butanone*	2.0 1.0	25° 40°	 *4-acetyl-5-(o-fluorophenyl)-4-phenylvaleronitrile*	95	M.P. 123.5-125.5°	1240	
 *3,4-diphenyl-2-butanone*	3.0	25°	 *4-acetyl-4,5-diphenylvaleronitrile*	95	M.P. 127.5-129°	1240	
 *3-phenyl-4-(m-cyanophenyl)-2-butanone*	2.0 1.0	25° 40°	 *4-acetyl-5-(m-cyanophenyl)-4-phenylvaleronitrile*	83	M.P. 86-88°	1240	
 *3-phenyl-4-(o—tolyl)-2-butanone*	2.0 1.0	25° 40°	 *4-acetyl-4-phenyl-5-o-tolylvaleronitrile*	89	M.P. 89-90°	1240	

TABLE XI—Continued

Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 *3-phenyl-4-(m-tolyl)-2-butanone*	2.0 1.0	25° 40°	 *4-acetyl-4-phenyl-5-m-tolylvaleronitrile*	87	M.P. 94.5-96°	1240	
 *3-phenyl-4-(o-methoxyphenyl)-2-butanone*	2.0 1.0	25° 42°	 *4-acetyl-5-(o-methoxyphenyl)-4-phenylvaleronitrile*	83	M.P. 110-111°	1240	
 *1,8a-dimethyl-2-keto-6,7-dihydroxy-3-(N-methylanilinomethylene)-Δ^{10a}-dodecahydrophenanthrene acetonide*	45.0	50°	 *1,2,3,4,6,6a,7,7a,10a,11,11a,11b-dodecahydro-4,6a,9,9-tetramethyl-2-(N-methylanilinomethylene)-3-oxophenanthro[2,3][1,3]dioxole-4-propionitrile*	—	—	1172 1171	

Additional examples of reactions involving complex cyclic ketones are described in the following references: 167, 168, 169, 353.

Several cyclic ketimines have been included in the table since monocyanoethylation proceeds more readily than with the corresponding cyclic ketones.

TABLE XI—Continued

(D) Diketones

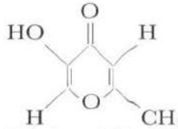
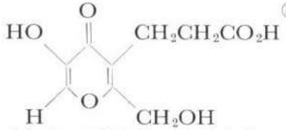
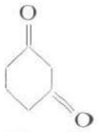
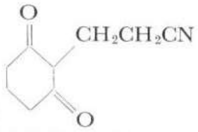
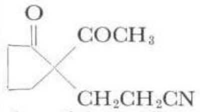
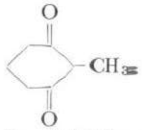
Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
$CH_3COCH_2COCH_3$ *2,4-pentandione*	12.0	25°	$CH_3COC(CH_2CH_2CN)_2COCH_3$ *4,4-diacetylheptanedinitrile*	99	M.P. 181-182°	1349	1185, 130, 1364
 *5-hydroxy-2-(hydroxymethyl)-4H-pyran-4-one (kojic acid)*	19.0	reflux	 Ⓔ *5-hydroxy-2-hydroxymethyl-4-oxo-4H-pyran-3-propionic acid*	—	M.P. 155°	1170	
 *1,3-cyclohexanedione*	7.0	reflux	 *2,6-dioxocyclohexanepropionitrile*	60.5	—	1026	87
 *2-acetylcyclopentanone*	24.0	25°	 *1-acetyl-2-oxocyclopentanepropionitrile*	71	—	898	176
 *2-methyl-1,3-cyclohexanedione*	3.0	reflux	$HO_2C(CH_2)_3COCH(CH_3)CH_2CH_2CN$ *9-cyano-6-methyl-5-oxononanoic acid*	74	B.P. 200-203°/2 mm.	817	

TABLE XI—Continued

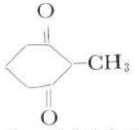
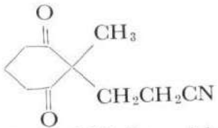
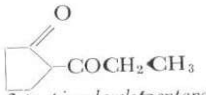
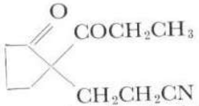
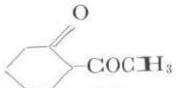
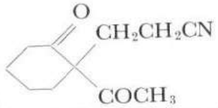
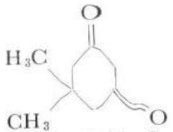
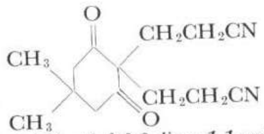
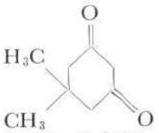
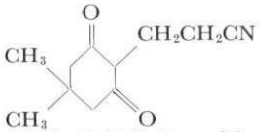
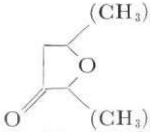
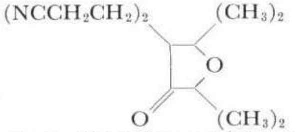
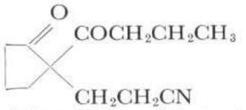
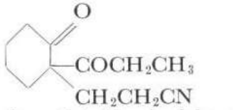
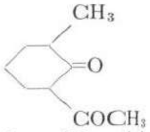
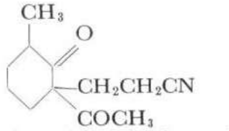
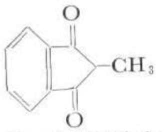
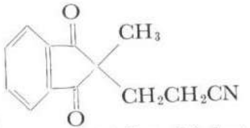
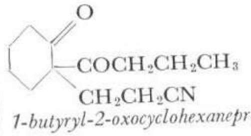
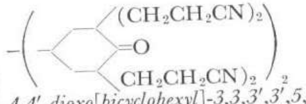
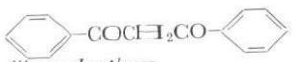
Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 *2-methyl-1,3-cyclohexanedione*	3.0	reflux	 *1-methyl-2,6-dioxocyclohexanepropionitrile*	82	B.P. 142.4°/1 mm.	817	
$CH_3COCH(C_2H_5)COCH_3$ *3-ethyl-2,4-pentanedione*	2.0	reflux	$CH_3COC(CH_2CH_2CN)(C_2H_5)COCH_3$ *4,4-diacetylhexanenitrile*	78	B.P. 134-136°/4 mm. M.P. 54-56°	129	
 *1-(2-thienyl)-1,3-butanedione*	2.0	reflux	 *4-acetyl-4-(2-thenoyl)heptanedinitrile*	40	M.P. 127-127.5°	1185	
 *2-propionylcyclopentanone*	24.0	25°	 *2-oxo-1-propionylcyclopentanepropionitrile*	86	B.P. 140-150°/1 mm.	898	
 *2-acetylcyclohexanone*	24.0	25°	 *1-acetyl-2-oxocyclohexanepropionitrile*	75	—	898	176
 *5,5-dimethyl-1, 3 cyclohexanedione*	3.5	reflux	 *4,4-dimethyl-2,6-dioxo-1,1-cyclohexanedipropionitrile*	81	M.P. 146-147°	817	

TABLE XI—Continued **(D) Diketones**

Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 *5,5-dimethyl-1,3-cyclohexanedione*	5.0	60-70°	 *4,4-dimethyl-2,6-dioxocyclohexanepropionitrile*	56	M.P. 151-152°	817	
 *2,2,5,5-tetramethyltetrahydro-3-furanone*	3.0	25°	 *dihydro-2,2,5,5-tetramethyl-4-oxo-3,3(2H)-furandipropionitrile*	71	M.P. 153°	168 177	
 *2 butyrylcyclopentanone*	—	—	 *1-butyryl-2-oxocyclopentanepropionitrile*	84	B.P. 148-152°/0.6 mm.	898	
 *2 propionylcyclohexanone*	24.0	25°	 *2-oxo-1-propionylcyclohexanepropionitrile*	70	M.P. 58°	898	
 *2-acetyl-6-methylcyclohexanone*	24.0	25°	 *1-acetyl-3-methyl-2-oxocyclohexanepropionitrile*	—	—	898	

(D) Diketones

TABLE XI—Continued

Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References This Exam.	References See Also:
 *2-methyl-1,3-indanedione*	5.0	25°	 *2-methyl-1,3-dioxo-2-indanpropionitrile*	55	M.P. 84-85°	1363	
$C_6H_5COCH_2COCH_3$ *1-phenyl-1,3-butanedione*	2.0	reflux	$CH_3COC(CH_2CH_2CN)_2COC_6H_5$ *4-acetyl-4-benzoylheptanedinitrile*	65	B.P. 175-178°/2.5 mm.	130	1185
 *2-butyrylcyclohexanone*	1.0 48.0	85° 25°	 *1-butyryl-2-oxocyclohexanepropionitrile*	55	B.P. 159-162°/1 mm. M.P. 54°	898	
$CH_3COCH(CH_2C_6H_5)COCH_3$ *3-benzyl-2,4-pentanedione*	—	—	$CH_3COC(CH_2CH_2CN)(CH_2C_6H_5)COCH_3$ *4,4-diacetyl-5-phenylvaleronitrile*	62	—	129	
 *4,4′-diketodicyclohexane*	15.0	25°	 *4,4′-dioxo[bicyclohexyl]-3,3,3′,3′,5,5,5′,5′-octa-propionitrile*	66	M.P. 280-287°	395 957	
 *dibenzoylmethane*	48.0	25°	 *4,4-dibenzoylbutyronitrile*	50	M.P. 117-118°	1349	

Additional examples of reactions involving diketones are described in the following references: 167, 169, 1027, 1185.

NOTES: Ⓐ Based on unrecovered phorone.
Ⓑ Based on unrecovered acetophenone.
Ⓒ Reaction failed if isophorone was not free from acidic impurities.
Ⓓ Structure uncertain.
Ⓔ After hydrolysis with HCl.

TABLE XII—"C" Cyanoethylation: Esters and Amides

(A) Malonic Esters

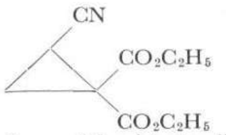
Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
$BrCH(CO_2C_2H_5)_2$ *bromomalonic acid, diethyl ester*	—	—	 *2-cyano-1,1-cyclopentanedicarboxylic acid, diethyl ester*	35	—	1265	
$CH_2(CO_2C_2H_5)_2$ *malonic acid, diethyl ester*	2.0	reflux	$HC(CH_2CH_2CN)(CO_2C_2H_5)_2$ *(2-cyanoethyl)malonic acid, diethyl ester*	57	B.P. 163-173°/15 mm.	507	426, 656 1148, 772
$CH_2(CO_2C_2H_5)_2$ *malonic acid, diethyl ester*	—	100-130°	$(NCCH_2CH_2)_2C(COOC_2H_5)_2$ *bis(2-cyanoethyl)malonic acid, diethyl ester*	83	B.P. 175-180°/.02 mm. M.P. 65°	426	179, 1334, 1148, 772
$(C_2H_5OCO)_2CHNH_2$ *aminomalonic acid, diethyl ester*	4.0 1.25	25° reflux	$(C_2H_5OCO)_2C(NH_2)CH_2CH_2CN$ *amino(2-cyanoethyl)malonic acid, diethyl ester*	47	B.P. 150-154°	254	
$C_2H_5OCOCH(CH_3)CO_2C_2H_5$ *methylmalonic acid, diethyl ester*	3.0	25-35°	$C_2H_5OCOC(CH_3)(CH_2CH_2CN)CO_2C_2H_5$ *(2-cyanoethyl)methylmalonic acid, diethyl ester*	97	B.P. 110°/0.04 mm.	42	
$CH_3CONHCH(COOC_2H_5)_2$ *acetaminomalonic acid, diethyl ester*	1.0	25°	$CH_3CONHC(CH_2CH_2CN)(COOC_2H_5)_2$ *acetamido(2-cyanoethyl)malonic acid, diethyl ester*	95	M.P. 92-94°	13 14	
$C_2H_5CH(COOC_2H_5)_2$ *ethylmalonic acid, diethyl ester*	5.0	25°	$C_2H_5C(CH_2CH_2CN)(COOC_2H_5)_2$ *(2-cyanoethyl)ethylmalonic acid, diethyl ester*	96	M.P. 47°	179	42
$(C_2H_5OCO)_2CHCH_2CH_2CH_3$ n-*propylmalonic acid, diethyl ester*	—	—	$(C_2H_5OCO)_2C(CH_2CH_2CN)CH_2CH_2CH_3$ *(2-cyanoethyl)propylmalonic acid, diethyl ester*	—	M.P. 31-32°	42	
$(C_2H_5OCO)_2CHCH(CH_3)_2$ *isopropylmalonic acid, diethyl ester*	—	—	$(C_2H_5OCO)_2C(CH_2CH_2CN)CH(CH_3)_2$ *(2-cyanoethyl)isopropylmalonic acid, diethyl ester*	—	B.P. 125°/0.035 mm.	42	
$n\text{-}C_4H_9CH(CO_2C_2H_5)_2$ n-*butylmalonic acid, diethyl ester*	—	70°	$n\text{-}C_4H_9C(CH_2CH_2CN)(CO_2C_2H_5)_2$ *butyl(2-cyanoethyl)malonic acid, diethyl ester*	87	B.P. 133-134°/1 mm.	396	179, 772, 42

TABLE XII—Continued

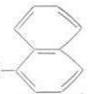
Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
$-CH(CO_2C_2H_5)_2$ *cyclopentylmalonic acid, diethyl ester*	1.0 2.0	35-40° 50°	$-C(CH_2CH_2CN)(CO_2C_2H_5)_2$ *α-(2-cyanoethyl)cyclopentanemalonic acid, diethyl ester*	61	B.P. 162°/2 mm.	705	
$(C_2H_5OCO)_2CHC_6H_5$ *phenylmalonic acid, diethyl ester*	3.0	25-35°	$(C_2H_5OCO)_2C(CH_2CH_2CN)C_6H_5$ *(2-cyanoethyl)phenylmalonic acid, diethyl ester*	93	M.P. 37°	42	1146
$(C_2H_5OCO)_2CH(OC_6H_5)$ *phenoxymalonic acid, diethyl ester*	1.0	reflux	$(C_2H_5OCO)_2C(OC_6H_5)CH_2CH_2CN$ *(2-cyanoethyl)phenoxymalonic acid, diethyl ester*	87	B.P. 158°/0.1 mm.	69	
n-$C_6H_{13}CH(CO_2C_2H_5)_2$ n-*hexylmalonic acid, diethyl ester*	—	70°	n-$C_6H_{13}C(CH_2CH_2CN)(CO_2C_2H_5)_2$ *(2-cyanoethyl)hexylmalonic acid, diethyl ester*	82	B.P. 149-150°/1 mm.	396	
$C_6H_5CH_2CH(COOC_2H_5)_2$ *benzylmalonic acid, diethyl ester*	3.0	25°	$C_6H_5CH_2C(CH_2CH_2CN)(COOC_2H_5)_2$ *benzyl(2-cyanoethyl)malonic acid, diethyl ester*	79	B.P. 175-180°/1 mm. M.P. 47°	179	42
$[CH(CO_2C_2H_5)_2]_2$ *ethanetetracarboxylic acid, tetraethyl ester*	5.0	55-60°	$(C_2H_5OCO)_2CHC(CH_2CH_2CN)(CO_2C_2H_5)_2$ *4-cyano-1,1,2,2-butanetetracarboxylic acid, tetraethyl ester*	77	B.P. 165-170°/0.01 mm.	122	
$(C_2H_5OCO)_2CHCH_2CH_2C_6H_5$ *2-phenylethylmalonic acid, diethyl ester*	3.0	25-35°	$(C_2H_5OCO)_2C(CH_2CH_2CN)CH_2CH_2C_6H_5$ *(2-cyanoethyl)(2-phenethyl)malonic acid, diethyl ester*	97	B.P. 168-170°/0.03 mm.	42	
n-$C_8H_{17}CH(CO_2C_2H_5)_2$ n-*octylmalonic acid, diethyl ester*	—	30-40°	n-$C_8H_{17}C(CH_2CH_2CN)(CO_2C_2H_5)_2$ *(2-cyanoethyl)octylmalonic acid, diethyl ester*	90	B.P. 163-165°/1 mm.	396	
$(C_2H_5OCO)_2CH-$ *1-naphthylmalonic acid, diethyl ester*	3.0	25-35°	$(C_2H_5OCO)_2C(CH_2CH_2CN)-$ *α-(2-cyanoethyl)-1-naphthalenemalonic acid, diethyl ester*	90	M.P. 82.5-83.5°	42	

TABLE XII—Continued

(A) Malonic Esters

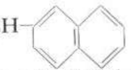
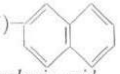
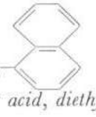
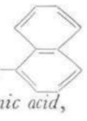
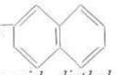
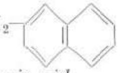
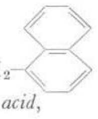
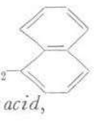
Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
$(C_2H_5OCO)_2CH-$  *2-naphthylmalonic acid, diethyl ester*	3.0	25-40°	$(C_2H_5OCO)_2C(CH_2CH_2CN)-$  *α-(2-cyanoethyl)-2-naphthalenemalonic acid, diethyl ester*	93	B.P. 170-175°/0.03 mm.	42	
$(C_2H_5OCO)_2CHC_{10}H_{21}$ n-*decylmalonic acid, diethyl ester*	1.0	—	$(C_2H_5OCO)_2C(CH_2CH_2CN)C_{10}H_{21}$ *(2-cyanoethyl)decylmalonic acid, diethyl ester*	90	B.P. 145-147°/0.1 mm.	397	396
$(C_2H_5OCO)_2CHCH_2-$  *1-naphthylmethylmalonic acid, diethyl ester*	3.0	25-35°	$(C_2H_5OCO)_2C(CH_2CH_2CN)CH_2-$  *(2-cyanoethyl)(1-naphthylmethyl)malonic acid, diethyl ester*	95	B.P. 156-158°/ 0.003 mm.	42	
$(C_2H_5OCO)_2CHCH_2-$  *2-naphthylmethylmalonic acid, diethyl ester*	3.0	25-40°	$(C_2H_5OCO)_2C(CH_2CH_2CN)CH_2-$  *(2-cyanoethyl)(2-naphthylmethyl)malonic acid, diethyl ester*	94	—	42	
$(C_2H_5OCO)_2CHCH_2CH_2-$  *2-(1'-naphthyl)ethylmalonic acid, diethyl ester*	3.0	25-35°	$(C_2H_5OCO)_2C(CH_2CH_2CN)CH_2CH_2-$  *(2-cyanoethyl)[2-(1-naphthyl)ethyl]malonic acid, diethyl ester*	95	—	42	
$n\text{-}C_{12}H_{25}CH\ (CO_2C_2H_5)_2$ n-*dodecylmalonic acid, diethyl ester*	—	30-40°	$n\text{-}C_{12}H_{25}C(CH_2CH_2CN)(CO_2C_2H_5)_2$ *(2-cyanoethyl)dodecylmalonic acid, diethyl ester*	92	B.P. 182-183°/1 mm.	396 397	
$n\text{-}C_{14}H_{29}CH\ (CO_2C_2H_5)_2$ n-*tetradecylmalonic acid, diethyl ester*	—	60-70°	$n\text{-}C_{14}H_{29}C(CH_2CH_2CN)(CO_2C_2H_5)_2$ *(2-cyanoethyl)tetradecylmalonic acid, diethyl ester*	86	B.P. 189-190°/1 mm.	396	
$n\text{-}C_{16}H_{33}CH\ (CO_2C_2H_5)_2$ n-*hexadecylmalonic acid, ethyl ester*	—	70°	$n\text{-}C_{16}H_{33}C(CH_2CH_2CN)(CO_2C_2H_5)_2$ *(2-cyanoethyl)hexadecylmalonic acid, diethyl ester*	89	M.P. 45°	396	

TABLE XII—Continued

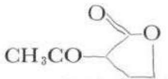
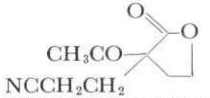
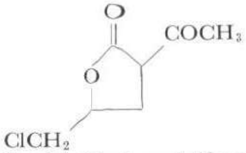
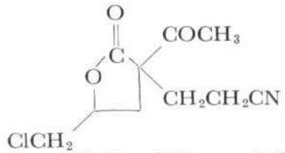
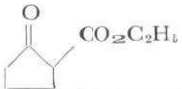
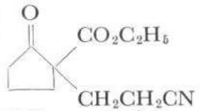
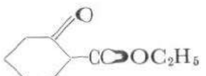
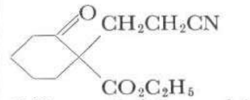
(B) Acylacetic Esters

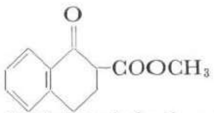
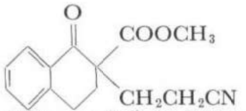
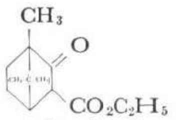
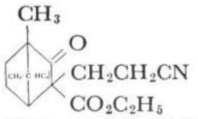
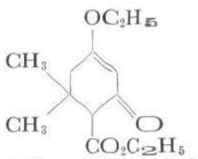
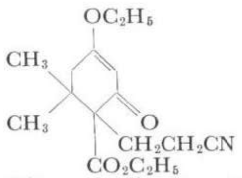
Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
$CH_3OCOCH_2COCH_3$ *acetoacetic acid, methyl ester*	0.5	25°	$CH_3OCOC(CH_2CH_2CN)_2COCH_3$ *2,2-bis(2-cyanoethyl)acetoacetic acid, methyl ester*	>69	M.P. 154°	166	177, 167, 169
$CH_3OCOCH_2COCH_3$ *acetoacetic acid, methyl ester*	20.0	25-40°	$CH_3COCH(CH_2CH_2CN)COOCH_3$ *2-(2-cyanoethyl)acetoacetic acid, methyl ester*	—	B.P. 141-145°/7 mm.	167 169	
$C_2H_5OCOCH_2COCH_3$ *acetoacetic acid, ethyl ester*	—	—	$C_2H_5OCOCH(CH_2CH_2CN)COCH_3$ *2-(2-cyanoethyl)acetoacetic acid, ethyl ester*	63	B.P. 121°/2 mm.	11	1180, 1313
$C_2H_5OCOCH_2COCH_3$ *acetoacetic acid, ethyl ester*	—	20°	$C_2H_5OCOC(CH_2CH_2CN)_2COCH_3$ *2,2-bis(2-cyanoethyl)acetoacetic acid, ethyl ester*	83	M.P. 82°	1077	170, 168, 169, 1185, 583, 962, 177, 1148
$C_2H_5OCOCH(CH_3)COCH_3$ *2-methylacetoacetic acid, ethyl ester*	—	—	$C_2H_5OCOC(CH_3)(CH_2CH_2CN)COCH_3$ *2-(2-cyanoethyl)-2-methylacetoacetic acid, ethyl ester*	59	B.P. 118-118.5°/4 mm.	657	778
$C_2H_5OCOCOCH_2CO_2C_2H_5$ *oxalacetic acid, diethyl ester*	48.0	30-35°	$C_2H_5OCOCOCH(CO_2C_2H_5)CH_2CH_2CN$ *(2-cyanoethyl)oxalacetic acid, diethyl ester*	15	B.P. 215-220°/5 mm.	1349	
$C_2H_5OCOCH_2COCH_2CH_2CH_3$ *3-oxohexanoic acid, ethyl ester*	0.5 0.3	30-35° reflux	$C_2H_5OCOCH(CH_2CH_2CN)COCH_2CH_2CH_3$ *2-(2-cyanoethyl)-3-oxohexanoic acid, ethyl ester*	63.1	B.P. 152-158°/9 mm.	812	1185, 1180
$C_2H_5OCOCH_2COCH(CH_3)_2$ *4-methyl-3-oxopentanoic acid, ethyl ester*	1.0	25-45°	$C_2H_5OCOCH(CH_2CH_2CN)COCH(CH_3)_2$ *2-(2-cyanoethyl)-4-methyl-3-oxovaleric acid, ethyl ester*	53.0	B.P. 134-137°/3 mm.	1180	
$C_2H_5OCOCH(CH_2CH_3)COCH_3$ *2-ethylacetoacetic acid, ethyl ester*	4.0	25°	$C_2H_5OCOC(CH_2CH_2CN)(CH_2CH_3)COCH_3$ *2-(2-cyanoethyl)-2-ethylacetoacetic acid, ethyl ester*	71	B.P. 164-164.5°/11 mm.	1313	778
 $C_2H_5OCOCH_2CO$ *3-(2-thienyl)-3- oxopropanoic acid, ethyl ester*	1.0	25-45°	 $C_2H_5OCOCH(CH_2CH_2CN)CO$ *α-(2-cyanoethyl)-β-oxo-2-thiophenepropionic acid, ethyl ester*	64.0	B.P. 175-176°/1 mm.	1180	1185

Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 $C_2H_5OCOCH_2CO$ *3(2-furyl)-3-oxopropanoic acid, ethyl ester*	1.0	25-45°	 $C_2H_5OCOCH(CH_2CH_2CN)CO$ *α-(2-cyanoethyl)-3-oxo-2-furanpropionic acid, ethyl ester*	37.1	B.P. 180-185°/2.5 mm.	1180	
 $C_2H_5OCOCH_2CO$ *3-(2-furyl)-3-oxopropanoic acid, ethyl ester*	2.0	R.T.	 $C_2H_5OCOC(CH_2CH_2CN)_2CO$ *α,α-bis(2-cyanoethyl)-β-oxo-2-furanpropionic acid, ethyl ester*	25	M.P. 91-91.5°	1185	
$C_2H_5OCOCH(CH_2CH{=}CH_2)COCH_3$ *2-allylacetoacetic acid, ethyl ester*	3.0	30-35°	$C_2H_5OCOC(CH_2CH_2CN)(CH_2CH{=}CH_2)$ $COCH_3$ *2-acetyl-2-(2-cyanoethyl)-4-pentenoic acid, ethyl ester*	76	B.P. 180-181°/10 mm.	778	
$C_2H_5OCOCH_2COCH_2CH(CH_3)_2$ *5-methyl-3-oxohexanoic acid, ethyl ester*	2.0	R.T.	$C_2H_5OCOC(CH_2CH_2CN)_2COCH_2CH(CH_3)_2$ *2,2-bis(2-cyanoethyl)-5-methyl-3-oxohexanoic acid, ethyl ester*	68	M.P. 53.5-54.4°	1185	1180
$C_2H_5OCOCH(CH_2CH_2CH_3)COCH_3$ *2-propylacetoacetic acid, ethyl ester*	5.0	30-35°	$C_2H_5OCOC(CH_2CH_2CN)(CH_2CH_2CH_3)$ $COCH_3$ *2-acetyl-2-(2-cyanoethyl)valeric acid, ethyl ester*	88	B.P. 192°/6 mm.	778	
$C_2H_5OCO\ CH[CH(CH_3)_2]COCH_3$ *2-isopropylacetoacetic acid, ethyl ester*	5.0	30-35°	$C_2H_5OCOC(CH_2CH_2CN)[CH(CH_3)_2]COCH_3$ *2-(2-cyanoethyl)-2-isopropylacetoacetic acid, ethyl ester*	43	B.P. 183-185°/4 mm.	778	11
$C_2H_5OCO\ CH(CH_2CO_2C_2H_5)COCH_3$ *acetosuccinic acid, diethyl ester*	—	—	$C_2H_5OCOC(CH_2CH_2CN)(CH_2CO_2C_2H_5)$ $COCH_3$ Ⓐ *2-acetyl-2-(2-cyanoethyl)succinic acid, diethyl ester*		B.P. 165-166°/1.7 mm.	12	1057
$C_2H_5OCO\ CH_2COC_5H_{11}$ *3-oxooctanoic acid, ethyl ester*	0.5 0.3	30-35° reflux	$C_2H_5OCOCH(CH_2CH_2CN)COC_5H_{11}$ *2-(2-cyanoethyl)-3-oxooctanoic acid, ethyl ester*	66.9	B.P. 170-177°/9 mm.	813	1180
$C_2H_5OCO\ CH(i\text{-}C_4H_9)COCH_3$ *2-isobutylacetoacetic acid, ethyl ester*	—	—	$C_2H_5OCOC(i\text{-}C_4H_9)(CH_2CH_2CN)COCH_3$ *2-acetyl-2-(2-cyanoethyl)-4-methylvaleric acid, ethyl ester*	60	B.P. 125°/0.1 mm.	11	

TABLE XII—Continued

Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
$C_2H_5OCOCH_2COC_6H_5$ *3-phenyl-3-oxopropanoic acid, ethyl ester*	—	—	$C_2H_5OCOCH(CH_2CH_2CN)COC_6H_5$ *2-benzoyl-4-cyanobutyric acid, ethyl ester*	86	B.P. 176°/0.7 mm.	11	1180, 167, 169
$C_2H_5OCOCH_2COC_6H_5$ *3-phenyl-3-oxopropanoic acid, ethyl ester*	2.0	R.T.	$C_2H_5OCOC(CH_2CH_2CN)_2COC_6H_5$ *2-benzoyl-4-cyano-2-(2-cyanoethyl)butyric acid, ethyl ester*	53	M.P. 61.5-62°	1185	
$C_2H_5OCOCH_2CO(n\text{-}C_6H_{13})$ *3-oxononanoic acid, ethyl ester*	1.0	25-45°	$C_2H_5OCOCH(CH_2CH_2CN)CO(n\text{-}C_6H_{13})$ *2-(2-cyanoethyl)-3-oxononanoic acid, ethyl ester*	34.6	B.P. 154-156°/1.3 mm.	1180	
$C_2H_5OCOCH(n\text{-}C_5H_{11})COCH_3$ *2-amylacetoacetic acid, ethyl ester*	5.0	30-35°	$C_2H_5OCOC(CH_2CH_2CN)(n\text{-}C_5H_{11})COCH_3$ *2-acetyl-2-(2-cyanoethyl)heptanoic acid, ethyl ester*	71	B.P. 182°/4 mm.	778	772
$C_2H_5OCOCH(i\text{-}C_5H_{11})COCH_3$ *2-isoamylacetoacetic acid, ethyl ester*	3.0	30-35°	$C_2H_5OCOC(CH_2CH_2CN)(i\text{-}C_5H_{11})COCH_3$ *2-acetyl-2-(2-cyanoethyl)-5-methylhexanoic acid, ethyl ester*	72	B.P. 187-189°/4-6 mm.	778	
$CH_3OCOCH(CH_2C_6H_5)COCH_3$ *2-benzylacetoacetic acid, methyl ester*	—	—	$CH_3OCOC(CH_2C_6H_5)(CH_2CH_2CN)COCH_3$ *α-acetyl-α-(2-cyanoethyl)hydrocinnamic acid, methyl ester*	56	B.P. 163°/0.2 mm.	11	
$C_2H_5OCOCH(C_6H_5)COCH_3$ *2-phenylacetoacetic acid, ethyl ester*	1.0	—	$C_2H_5OCOC(C_6H_5)(CH_2CH_2CN)COCH_3$ *2-(2-cyanoethyl)-2-phenylacetoacetic acid, ethyl ester*	27	B.P. 180-220°/ 0.003 mm.	657	
$C_2H_5OCOCH(n\text{-}C_6H_{13})COCH_3$ *2-n-hexylaceto acetic acid, ethyl ester*	3.0	30-35°	$C_2H_5OCOC(CH_2CH_2CN)(n\text{-}C_6H_{13})COCH_3$ *2-acetyl-2-(2-cyanoethyl)octanoic acid, ethyl ester*	84	B.P. 168°/4 mm.	778	11
$C_2H_5OCOCH(CH_2C_6H_5)COCH_3$ *2-benzylacetoacetic acid, ethyl ester*	0.5	25-35°	$C_2H_5OCOC(CH_2C_6H_5)(CH_2CH_2CN)COCH_3$ *α-acetyl-α-(2-cyanoethyl)hydrocinnamic acid, ethyl ester*	85Ⓑ	B.P. 172°/1.5 mm.	11	12, 778
$C_2H_5OCOCH(n\text{-}C_7H_{15})COCH_3$ *2-n-heptylacetoacetic acid, ethyl ester*	—	—	$C_2H_5OCOC(n\text{-}C_7H_{15})(CH_2CH_2CN)COCH_3$ *2-acetyl-2-(2-cyanoethyl)nonanoic acid, ethyl ester*	81	B.P. 145°/0.9 mm.	11	

Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 *2-acetyl-4-hydroxybutyric acid, γ-lactone*	1.0	—	 *2-(2-cyanoethyl)-2-(2-hydroxyethyl)acetoacetic acid, γ-lactone*	86-92	B.P. 162°/1.5 mm.	11 12	
 *2-acetyl-4-hydroxy-4-chloromethylbutyric acid, γ-lactone*	—	—	 *2-acetyl-5-chloro-2-(2-cyanoethyl)-4-hydroxyvaleric acid, γ-lactone*	61	B.P. 199°/1.6 mm.	11	
 *2-oxocyclopentanecarboxylic acid, ethyl ester*	—	—	 *1-(2-cyanoethyl)-2-oxocyclopentanecarboxylic acid, ethyl ester*	82	B.P. 145°/1.5 mm.	11	1363
 *2-oxocyclohexanecarboxylic acid, ethyl ester*	—	120-125°	 *1-(2-cyanoethyl)-2-oxocyclohexanecarboxylic acid, ethyl ester*	85	B.P. 142°/0.3 mm.	500	1363

Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 *1,2,3,4-tetrahydro-1-oxo-2-naphthoic acid, methyl ester*	2.0	25°	 *2-(2-cyanoethyl)-1,2,3,4-tetrahydro-1-oxo-2-naphthoic acid, methyl ester*	92	M.P. 75-76°	56	
 *camphocarboxylic acid, ethyl ester*	—	110-117°	 *2-(2-cyanoethyl)-4,7,7-trimethyl-3-oxo-2-norcamphanecarboxylic acid, ethyl ester*	78.3	B.P. 160-162°/0.5 mm.	500	
 *4-ethoxy-6,6-dimethyl-2-oxo-3-cyclohexene-1-carboxylic acid, ethyl ester*	—	110°	 *1-(2-cyanoethyl)-4-ethoxy-6,6-dimethyl-2-oxo-3-cyclohexene-1-carboxylic acid, ethyl ester*	60	B.P. 160°/0.05 mm.	500	
(D) Miscellaneous Esters							
CH_3OCOCH_2CN *cyanoacetic acid, methyl ester*	—	80-90°	$CH_3OCOC(CH_2CH_2CN)_2CN$ *2-(2-cyanoethyl)-2,4-dicyanobutyric acid, methyl ester*	68	B.P. 218-225°/3 mm.	426	

Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References This Exam.	References See Also:
$O_2NCH_2CO_2C_2H_5$ *nitroacetic acid, ethyl ester*	4	80-90°	$O_2NCH(CH_2CH_2CN)CO_2C_2H_5$ *4-cyano-2-(2-cyanoethyl)-2-nitrobutyric acid, ethyl ester*	52	B.P. 147-151°/4 mm.	1392	
$O_2NCH_2CO_2C_2H_5$ *nitroacetic acid, ethyl ester*	4	80-90°	$O_2NC(CH_2CH_2CN)_2CO_2C_2H_5$ *4-cyano-2-(2-cyanoethyl)-2-nitrobutyric acid, ethyl ester*	80	M.P. 51.9-52.7°	1392	
$C_2H_5OCOCH_2CN$ *cyanoacetic acid, ethyl ester*	—	150-165°	$C_2H_5OCOCH(CN)CH_2CH_2CN$ *2,4-dicyanobutyric acid, ethyl ester* $C_2H_5OCOC(CN)(CH_2CH_2CN)_2$ *2,4-dicyano-2-(2-cyanoethyl)butyric acid, ethyl ester*	39 26	— —	931	
$C_2H_5OCOCH_2CN$ *cyanoacetic acid, ethyl ester*	1.0	25°	$C_2H_5OCOC(CH_2CH_2CN)_2CN$ *2,4-dicyano-2-(2-cyanoethyl)butyric acid, ethyl ester*	98	M.P. 37°	179	931, 1148
$C_2H_5OCOCH(NHCOCH_3)CN$ *N-acetyl-2-cyanoglycine, ethyl ester*	1.0	<20°	$C_2H_5OCOC(CH_2CH_2CN)(NHCOCH_3)CN$ *2-acetamido-2,4-dicyanobutyric acid, ethyl ester*	86-90	M.P. 101-102°	464	
 $(C_2H_5O)_2\overset{\overset{O}{\Vert}}{P}CH_2CO_2C_2H_5$ *phosphonoacetic acid, triethyl ester*	3.0	25°	 $(C_2H_5O)_2\overset{\overset{O}{\Vert}}{P}C(CH_2CH_2CN)_2CO_2C_2H_5$ *4-cyano-2-(2-cyanoethyl)-2-diethylphosphonobutyric acid, ethyl ester*	88	—	679 680	
 $C_2H_5OOCCH_2\overset{\overset{O}{\Vert}}{P}(OCH_2CH_3)_2$ *phosphonoacetic acid, triethyl ester*	—	—	 $C_2H_5OOCCH(CH_2CH_2CN)\overset{\overset{O}{\Vert}}{P}(OCH_2CH_3)_2$ *4-cyano-2-diethylphosphonobutyric acid, ethyl ester*	27	B.P. 185-186°/4 mm.	894	
			 $C_2H_5OOCC(CH_2CH_2CN)_2\overset{\overset{O}{\Vert}}{P}(OCH_2CH_3)_2$ *4-cyano-2-(2-cyanoethyl)-2-diethylphosphono-butyric acid, ethyl ester*	27			

TABLE XII—Continued

(D) Miscellaneous Esters

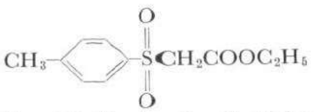
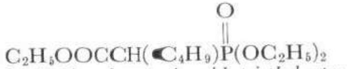
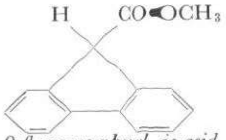
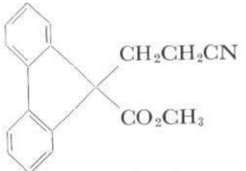
Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 $C_2H_5OOCCH(CH_3)\overset{O}{\overset{\|}{P}}(OCH_2CH_3)_2$ *2-phosphonopropionic acid, triethyl ester*	0.5	R.T.	 $C_2H_5OOCC(CH_2CH_2CN)(CH_3)\overset{O}{\overset{\|}{P}}(OC_2H_5)_2$ *4-cyano-2-diethylphosphono-2-methylbutyric acid, ethyl ester*	59	B.P. 176-178°/5 mm.	894	
$NCCH(C_6H_5)CO_2C_2H_5$ *2-phenyl-2-cyanoacetic acid, ethyl ester*	1.0 18.0	40-45° 25°	$NCC(CH_2CH_2CN)(C_6H_5)CO_2C_2H_5$ *2,4-dicyano-2-phenylbutyric acid, ethyl ester*	83	B.P. 157-167°/ 0.5-1.0 mm.	542	543
 *2-p-tolylsulfonylacetic acid, ethyl ester*	2.0	25°	 *4-cyano-2-(2-cyanoethyl)-2-p-tolylsulfonylbutyric acid, ethyl ester*	—	M.P. 100-106°	171	
 $C_2H_5OOCCH(C_4H_9)\overset{O}{\overset{\|}{P}}(OC_2H_5)_2$ *2-phosphonohexanoic acid, triethyl ester*	0.5	R.T.	 $C_2H_5OCOC(CH_2CH_2CN)(C_4H_9)\overset{O}{\overset{\|}{P}}(OC_2H_5)_2$ *2-(2-cyanoethyl)-2-diethylphosphonohexanoic acid, ethyl ester*	74	B.P. 186-187°/2 mm.	894	
 *9-fluorenecarboxylic acid, methyl ester*	0.25	—	 *9-(2-cyanoethyl)-9-fluorenecarboxylic acid, methyl ester*	94	M.P. 84-86°	206	1099

TABLE XII—Continued

(D) Miscellaneous Esters

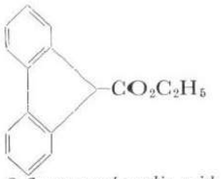
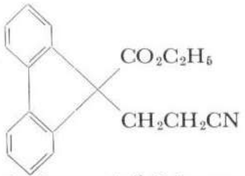
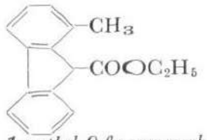
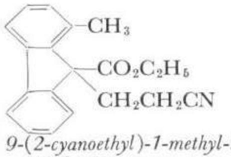
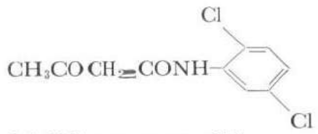
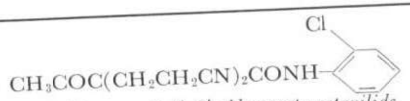
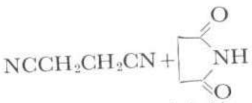
Reactants	Reaction Time (Hr.)	Reaction Temperature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 *9-fluorenecarboxylic acid ethyl ester*	0.5	25°	 *9-(2-cyanoethyl)-9-fluorenecarboxylic acid, ethyl ester*	94	B.P. 210-220°/1-2 mm.	642	206
 *1-methyl-9-fluorenecarboxylic acid, ethyl ester*	0.5	R.T.	 *9-(2-cyanoethyl)-1-methyl-9-fluorenecarboxylic acid, ethyl ester*	78	B.P. 190-196°/1 mm. M.P. 92-93°	643	
(E) Amides							
$NCCH_2CONH_2$ *cyanoacetamide*	1.0	25°	$NCC(CH_2CH_2CN)_2CONH_2$ *2,4-dicyano-2-(2-cyanoethyl)butyramide*	74	M.P. 118°	179	
$CH_2(CONH_2)_2$ *malonamide*	1.0	35-38°	$(NCCH_2CH_2)_2C(CONH_2)_2$ *bis(2-cyanoethyl)malonamide*	13	M.P. 210°	179	
 *2,5-dichloroacetoacetanilide*	2.5	40-45°	 *2,2-bis(2-cyanoethyl)-2′,5′-dichloroacetoacetanilide*	84	M.P. 121°	166 167 169	

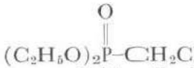
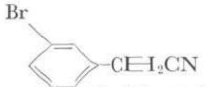
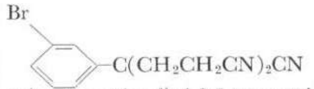
TABLE XII—Continued

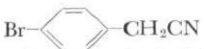
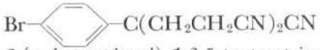
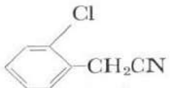
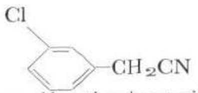
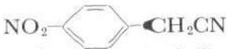
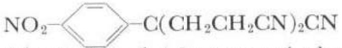
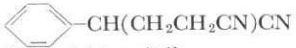
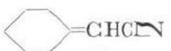
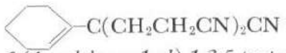
Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 o-chloroacetoacetanilide	3.0	40-50°	 2,2-bis(2-cyanoethyl)-2′-chloroacetoacetanilide	96	M.P. 105°	166 167 167	
$CH_3COCH_2CONHC_6H_5$ aeetoacetanilide	2.5	45-50°	$CH_3COC(CH_2CH_2CN)_2CONHC_6H_5$ 2,2-bis(2-cyanoethyl)acetoacetanilide	—	M.P. 82°	166 167 169	

NOTES Ⓐ Deacetylation occurs when absolute alcohol is used. Ⓑ Based on unrecovered starting material.

TABLE XIII—"C" Cyanoethylation: Nitriles (Including HCN)

Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	This Exam.	See Also:
HCN hydrocyanic acid	5.0	55-60°	$NCCH_2CH_2CN$ succinonitrile	97.2	—	211	962, 787, 678, 677, 342, 1074, 1071, 148
$NaCN + CH_3CO_2H$ sodium cyanide + acetic acid	~2.0	70°	 succinonitrile + succinimide	—	—	244 768 767 766	1168
$NaCN + H_2SO_4$ sodium cyanide + sulfuric acid	—	70°	$HO_2CCH_2CH_2CO_2H$ succinic acid	90	M.P. 182-183°	244 769 768 766	
$NCCH_2CO_2Na$ cyanoacetic acid, sodium salt	21.0	—	$NaO_2CCH(CN)CH_2CH_2CN$ 2,4-dicyanobutyric acid, sodium salt	96	decomposes	1331	
$NCCH_2CN$ malononitrile	—	—	$(NC)_2C(CH_2CH_2CN)_2$ 1,3,3,5-pentanetetracarbonitrile	95	M.P. 92°	1331	

Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
$CH_2{=}CHCH_2CN$ *3-butenenitrile*	1.0 2.0	10° 25°	$CH_3CH{=}C(CN)CH_2CH_2CN$ *2-ethylideneglutaronitrile* $CH_2{=}CHC(CH_2CH_2CN)_2CN$ *3-vinyl-1,3,5-pentanetricarbonitrile*	9 55	B.P. 134-137°/10 mm. B.P. 210-245°/1 mm. M.P. 60-61°	162 178	15
$CH_3CH{=}CHCN$ *cis-and trans-crotononitrile (mixture)*	24.0	25°	$CH_3CH{=}C(CH_2CH_2CN)CN$ *2-ethylideneglutaronitrile* $CH_2{=}CHC(CH_2CH_2CN)_2CN$ *3-vinyl-1,3,5-pentanetricarbonitrile*	14 14	B.P. 134-137°/10 mm. M.P. 60-61°	162 178	
$CH_3CH{=}CHCH_2CN$ + $CH_2{=}CHCH(CH_3)CN$ *3-pentenenitrile + 2-methyl-3-butenenitrile*	18.0	25°	$C_8H_{10}N_2 + C_{11}H_{13}N_3$	—	B.P. 140-150°/10 mm. B.P. 200-210°/1 mm.	162	
$(CH_3)_2C{=}CHCN$ *3-methyl-3-butenenitrile*	2.0	25°	$(CH_3)_2C{=}C(CH_2CH_2CN)CN$ Ⓐ *2-isopropylideneglutaronitrile* $CH_2{=}C(CH_3)C(CH_2CH_2CN)_2CN$ *3-isopropenyl-1,3,5-pentanetricarbonitrile*	4.5 13	B.P. 150°/10 mm. M.P. 67-68°	162 178	
 $(C_2H_5O)_2\overset{O}{\overset{\Vert}{P}}{-}CH_2CN$ *cyanomethylphosphonic acid, diethyl ester*	—	25-50°	 $(C_2H_5O)_2\overset{O}{\overset{\Vert}{P}}C(CH_2CH_2CN)_2CN$ *[1,3-dicyano-1-(2-cyanoethyl)propyl]phosphonic acid, diethyl ester*	92	M.P. 75-76°	679 680	1387
$CH_3CH{=}C(CH_2CH_2CN)CN$ *2-(2'-cyanoethyl)-2-butenenitrile*	24.0	25°	$CH_2{=}CHC(CH_2CH_2CN)_2CN$ *3-vinyl-1,3,5-pentanetricarbonitrile*	79Ⓑ	M.P. 60-61°	162 178	
$CH_2{=}C(CH_3)CH_2CH_2CH_2CN$ *5-methyl-5-hexenenitrile*	4.0	235° (pressure)	$CH_2{=}C(CH_2CH_2CH_2CN)_2$ *5-methylenenonanedinitrile*	71Ⓒ	B.P. 132-137/0.5 mm.	15	
 m-*bromophenylacetonitrile*	2.0	25°	 *3-(*m-*bromophenyl)-1,3,5-pentanetricarbonitrile*	89	M.P. 83°	778	

Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 *p-bromophenylacetonitrile*	2.0	25°	 *3-(p-bromophenyl)-1,3,5-pentanetricarbonitrile*	84	M.P. 132°	778	
 *o-chlorophenylacetonitrile*	2.0	25°	 *3-(o-chlorophenyl)-1,3,5-pentanetricarbonitrile*	47	M.P. 73°	778	
 *m-chlorophenylacetonitrile*	2.0	25°	 *3-(m-chlorophenyl)-1,3,5-pentanetricarbonitrile*	64	M.P. 80°	778	
p-ClC$_6$H$_4$CH$_2$CN *p-chlorophenylacetonitrile*	—	—	 *3-(p-chlorophenyl)-1,3,5-pentanetricarbonitrile*	80	M.P. 124-125°	940	
 *p-nitrophenylacetonitrile*	2.0	25°	 *3-(p-nitrophenyl)-1,3,5-pentanetricarbonitrile*	92	M.P. 147-148°	179 508	
C$_6$H$_5$CH$_2$CN *phenylacetonitrile*	0.5	225°	 *2-phenylglutaronitrile*	80	B.P. 163°/1 mm.	931	203, 666, 1222
C$_6$H$_5$CH$_2$CN *phenylacetonitrile*	—	50-60°	$C_6H_5C(CN)(CH_2CH_2CN)_2$ *3-phenyl-1,3,5-pentanetricarbonitrile*	100	—	1148	179, 1077, 931, 508
 *cyclohexylideneacetonitrile*	2.0	25°	 Ⓐ *3-(1-cyclohexen-1-yl)-1,3,5-pentanetricarbonitrile*	38	M.P. 81-82°	178	162

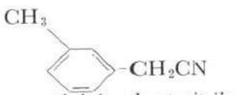
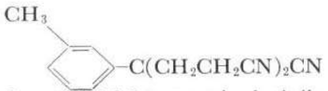
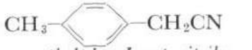
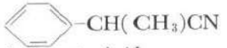
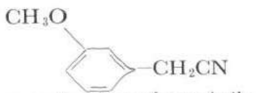
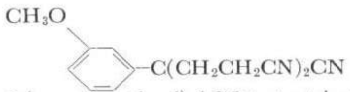
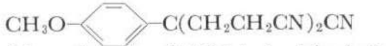
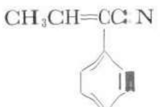
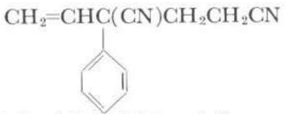
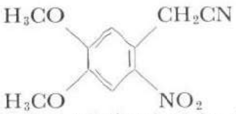
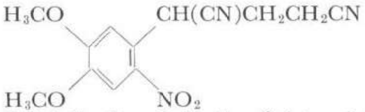
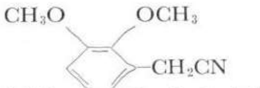
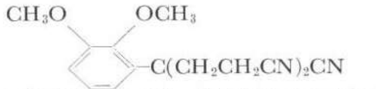
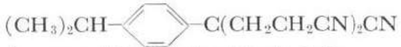
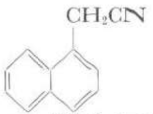
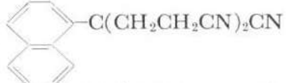
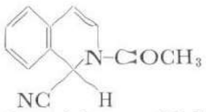
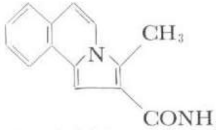
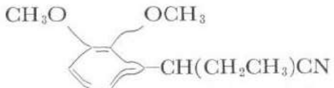
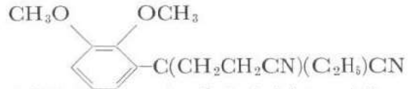
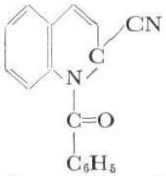
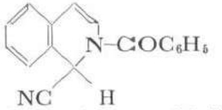
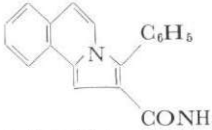
Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 m-*methylphenylacetonitrile*	2.0	25°	 *3-*m*-tolyl-1,3,5-pentanetricarbonitrile*	88	M.P. 67-68°	778	
 p-*methylphenyl acetonitrile*	2.0	25°	 *3-*p*-tolyl-1,3,5-pentanetricarbonitrile*	95	M.P. 104°	778	
 *hydratroponitrile*	2.0	20°	$CH_3C(CH_2CH_2CN)(C_6H_5)CN$ *2-methyl-2-phenylglutaronitrile*	55	B.P. 151°/0.3 mm. B.P. 165°/2 mm.	411	
 m-*methoxyphenylacetonitrile*	24.0	25°	 *3-(*m*-methoxyphenyl)-1,3,5-pentanetricarbonitrile*	77	M.P. 73-74°	512	
 p-*methoxyphenylacetonitrile*	24.0	25°	 *3-(*p*-methoxyphenyl)-1,3,5-pentanetricarbonitrile*	68	M.P. 83-83.5°	512	
 $(C_2H_5O)_2\overset{O}{\overset{\Vert}{P}}CH(CN)CH_2CH{=}CH_2$ *1-cyano-3-butenylphosphonic acid, diethyl ester*	—	90-100°	 $(C_2H_5O)_2\overset{O}{\overset{\Vert}{P}}C(CN)(CH_2CH_2CN)CH_2CH{=}CH_2$ *[1-cyano-1-(2-cyanoethyl)-3-butenyl]phosphonic acid, diethyl ester*	42.6	B.P. 175°/3 mm.	1387	
 *2-phenylcrotononitrile*	1.5 1.0	0-5° 10°	 *2-phenyl-2-vinylglutaronitrile*	30	B.P. 132-135°/0.15 mm.	1287	

TABLE XIII—Continued

"C" Cyanoethylation: Nitriles (Including HCN)

Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 2-nitro-4,5-dimethoxyphenylacetonitrile	1.0	reflux	 2-(4,5-dimethoxy-2-nitrophenyl)glutaronitrile	41	M.P. 140-142°	1440	
 2,3-dimethoxyphenylacetonitrile	2.0	25°	 3-(2,3-dimethoxyphenyl)-1,3,5-pentanetricarbonitrile	96	M.P. 65-66°	545	
 p-isopropylphenylacetonitrile	—	—	 3-p-cumenyl-1,3,5-pentanetricarbonitrile	—	M.P. 58-59°	940	
 α-naphthylacetonitrile	—	—	 3-(1-naphthyl)-1,3,5-pentanetricarbonitrile	—	M.P. 103-104.5°	940	
 2-acetyl-1-cyano-1,2-dihydroisoquinoline	18.0	25°	 3-methyl-2-benzo[g]pyrrocolinecarboxamide	60	M.P. 189-190°	128	
 2-(2,3-dimethoxyphenyl)butyronitrile	1.0 18.0	40-45° 25°	 2-(2,3-dimethoxyphenyl)-2-ethylglutaronitrile	87ⓒ	B.P. 190-191°/2 mm.	544	

Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
$(C_6H_5)_2CHCN$ *diphenylacetonitrile*	3.0	50°	$(C_6H_5)_2C(CN)CH_2CH_2CN$ *2,2-diphenylglutaronitrile*	82	M.P. 71.5-72.5°	228	
 *2-cyano-1-benzoyl-1,2-dihydroquinoline*	18.0	25°	*unidentified red gum*	—	—	128	
 *2-benzoyl-1-cyano-1,2-dihydroisoquinoline*	18.0	25°	 *3-phenyl-2-benzo[g]pyrrocolinecarboxamide*	76	M.P. 168-169°	128	

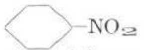
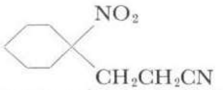
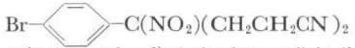
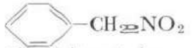
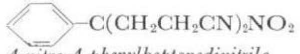
Additional examples involving complex nitriles may be found in the following references: 162 and 546.

NOTES: Ⓐ Structure uncertain. Ⓑ Based on unrecovered starting material. Ⓒ Based on unrecovered hexenenitrile.

TABLE XIV—"C" Cyanoethylation: Nitro Compounds

Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	This Exam.	See Also:
$KCH(NO_2)_2$ *dinitromethane, potassium derivative*	3.0	35-45°	$(NO_2)_2C(CH_2CH_2CN)_2$ *4,4-dinitroheptanedinitrile*	35	M.P. 79°	506	
			$NO_2C(CH_2CH_2CN)_3$ *4-(2-cyanoethyl)-4-nitroheptanedinitrile*	12	M.P. 114.5-116°		
NO_2CH_3 *nitromethane*	25-30	reflux	$NO_2CH_2CH_2CH_2CN$ *4-nitrobutyronitrile*	29	B.P. 123-132°/15 mm.	1089	192

TABLE XIV—Continued

Reactants	Reaction Time (Hr.)	Reaction Temperature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
NO_2CH_3 *nitromethane*	—	—	$NO_2CH(CH_2CH_2CN)_2$ *4-nitroheptanedinitrile*	44	M.P. 65-66°	1089	
NO_2CH_3 *nitromethane*	3.0	50°	$NO_2C(CH_2CH_2CN)_3$ *4-(2-cyanoethyl)-4-nitroheptanedinitrile*	63	M.P. 114°	962	1176, 179, 23, 163, 1334
$NO_2CH_2CH_3$ *nitroethane*	—	R.T.	$CH_3CH(NO_2)CH_2CH_2CN$ *4-nitrovaleronitrile*	31	B.P. 96-101°/1 mm.	1089	163, 192, 194
$NO_2CH_2CH_3$ *nitroethane*	1.0	40°	$CH_3C(NO_2)(CH_2CH_2CN)_2$ *4-methyl-4-nitroheptanedinitrile*	67	—	173	1089
$HOCH_2C(NO_2)_2CH_2OH$ *2,2-dinitro-1,3-propandiol*	9.0	30°	$NCCH_2CH_2C(NO_2)_2CH_2CH_2CN$ *4,4-dinitroheptanedinitrile*	37	M.P. 78°	760	
$CH_3CH_2CH_2NO_2$ *1-nitropropane*	18.0	50°	$CH_3CH_2CH(NO_2)CH_2CH_2CN$ *4-nitrohexanenitrile*	80	B.P. 76°/0.1 mm.	192	163
$CH_3CH(NO_2)CH_3$ *2-nitropropane*	1.0	reflux	$CH_3C(NO_2)(CH_3)CH_2CH_2CN$ *4-methyl-4-nitrovaleronitrile*	79	B.P. 70°/0.09 mm.	192	1089, 163, 193
 *nitrocyclohexane*	1.0	reflux	 *1-nitrocyclohexanepropionitrile*	40	B.P. 98-108°/0.15 mm. M.P. 42°	192 193	
 p-*bromophenyl nitromethane*	24.0	25°	 *4-(*p-*bromophenyl)-4-nitroheptanedinitrile*	32	M.P. 138-139°	192	
 *phenylnitromethane*	48.0	25°	 *4-nitro-4-phenylheptanedinitrile*	42	M.P. 206-207°	1349	

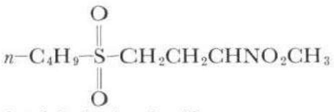
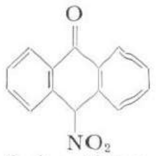
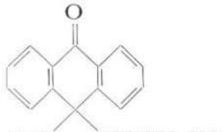
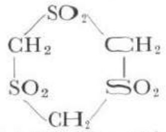
Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 $n\text{-}C_4H_9\text{-}\overset{O}{\underset{O}{S}}\text{-}CH_2CH_2CHNO_2CH_3$ *butyl 3-nitrobutyl sulfone*	3.0	reflux	 $n\text{-}C_4H_9\text{-}\overset{O}{\underset{O}{S}}\text{-}CH_2CH_2C(CH_2CH_2CN)(NO_2)CH_3$ *6-butylsulfonyl-4-methyl-4-nitrohexanenitrile*	—	—	192 193	
$CH_3OCH(C_6H_5)CH(NO_2)CH_3$ *methyl 2-nitro-1-phenylpropyl ether*	18.0	20-25°	$CH_3OCH(C_6H_5)C(CH_2CH_2CN)(NO_2)CH_3$ *5-methoxy-4-methyl-4-nitro-5-phenylvaleronitrile*	82	B.P. 163-167°/0.5 mm.	192 193	
 *9-nitroanthrone*	48.0	25°	 *9,10-dihydro-9-nitro-10-oxo-9-anthracenepropionitrile*	77	M.P. >270°	163	
NO_2 *11-nitro-9,10- dihydro-9,10-ethanoanthracene*	6.0	60°	NO_2 CH_2CH_2CN *9,10-dihydro-11-nitro-9,10-ethanoanthracene-11-propionitrile*	49	M.P. 114-115° M.P. (Pure) 121-122°	638	

TABLE XV—"C" Cyanoethylation: Sulfones

 *1,3,5-tris(dioxide)-s-trithiane*	2.0	0°	*monocyanoethyl derivative*	—	—	532	370

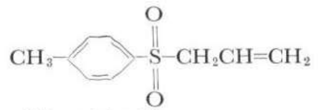
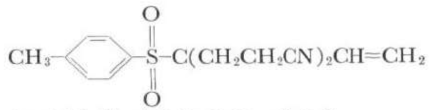
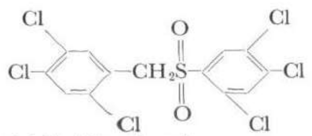
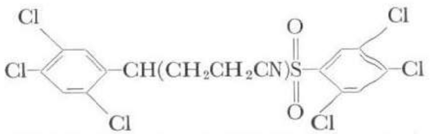
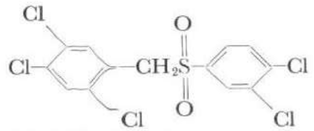
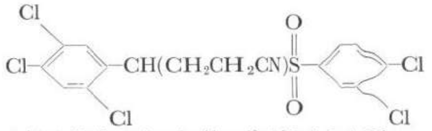
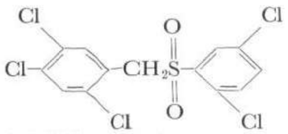
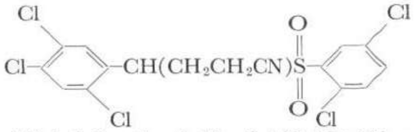
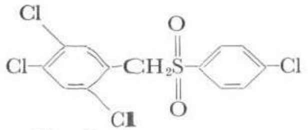
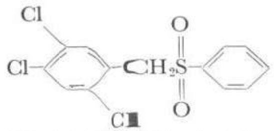
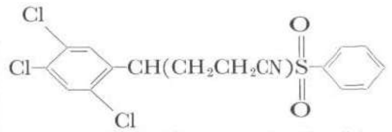
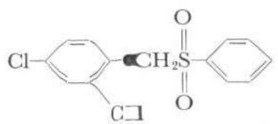
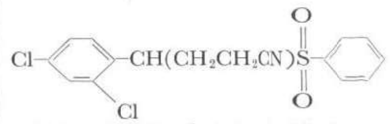
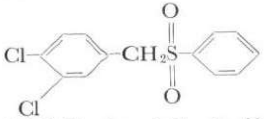
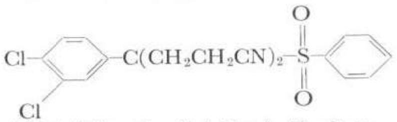
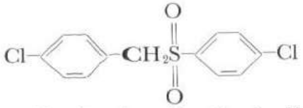
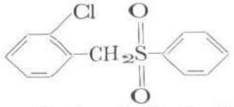
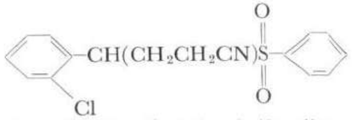
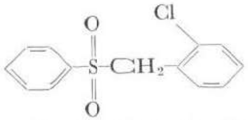
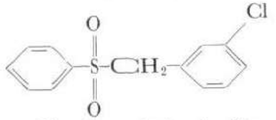
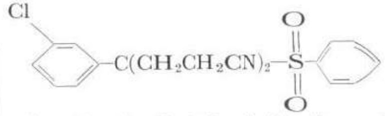
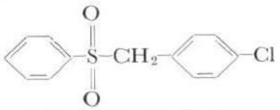
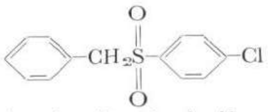
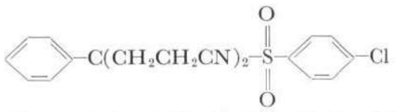
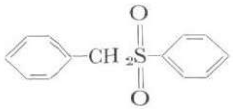
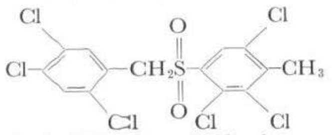
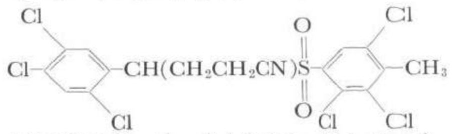
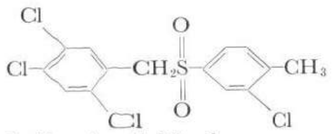
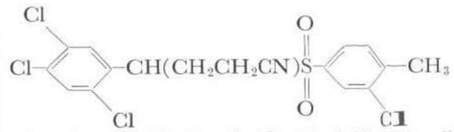
Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 *allyl p-tolyl sulfone*	2.0	25°	 *4-p-tolylsulfonyl-5-hexenenitrile*	—	—	171	
			 *4-p-tolylsulfonyl-4-vinylheptanedinitrile*				
 *2,4,5-trichlorobenzyl 2,4,5-trichlorophenyl sulfone*	20.0	R.T.	 *4-(2,4,5-trichlorophenyl)-4-(2,4,5-trichlorophenylsulfonyl)butyronitrile*	65	M.P. 210-211°	1300	
 *3,4-dichlorophenyl 2,4,5-trichlorobenzyl sulfone*	20.0	R.T.	 *4-(3,4-dichlorophenylsulfonyl)-4-(2,4,5-trichlorophenyl)butyronitrile*	73	M.P. 159-160.5°	1300	

TABLE XV—Continued

Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 2,5-dichlorophenyl 2,4,5-trichlorobenzyl sulfone	20.0	R.T.	 4-(2,5-dichlorophenylsulfonyl)-4-(2,4,5-trichlorophenyl)butyronitrile	58	M.P. 118.5-120°	1300	
 p-chlorophenyl 2,4,5-trichlorobenzyl sulfone	20.0	R.T.	 4-(p-chlorophenylsulfonyl)-4-(2,4,5-trichlorophenyl)butyronitrile	76	M.P. 130-131.5°	1300	
 phenyl 2,4,5-trichlorobenzyl sulfone	20.0	R.T.	 4-phenylsulfonyl-4-(2,4,5-trichlorophenyl)butyronitrile	70	M.P. 130-130.5°	1300	
 2,4-dichlorobenzyl phenyl sulfone	20.0	R.T.	 4-(2,4-dichlorophenyl)-4-phenylsulfonylbutyronitrile	76	M.P. 105-105.5°	1300	

Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 *3,4-dichlorobenzyl phenyl sulfone*	20.0	R.T.	 *4-(3,4-dichlorophenyl)-4-phenylsulfonylheptanedinitrile*	59	M.P. 199.5-201°	1300	
 p-*chlorobenzyl* p-*chlorophenyl sulfone*	48.0	R.T.	 *4-(*p-*chlorophenyl)-4-(*p-*chlorophenylsulfonyl)-heptanedinitrile*	80	M.P. 184-185°	1348	
 o-*chlorobenzyl phenyl sulfone*	20.0	R.T.	 *4-(*o-*chlorophenyl)-4-phenylsulfonylbutyronitrile*	63	M.P. 85-86°	1300	
 o-*chlorobenzyl phenyl sulfone*	48.0	30-35°	 *4-(*o-*chlorophenyl)-4-phenylsulfonylheptanedinitrile*	83.5	M.P. 87-88°	54	
 m-*chlorobenzyl phenyl sulfone*	48.0	30-35°	 *4-(*m-*chlorophenyl)-4-phenylsulfonylheptanedinitrile*	24	M.P. 162-163°	54	

Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 p-*chlorobenzyl phenyl sulfone*	55.0	30-35°	 *4-(*p-*chlorophenyl)-4-phenylsulfonylheptanedinitrile*	60	M.P. 194-195°	54	
 *benzyl* p-*chlorophenyl sulfone*	48.0	25°	 *4-(*p-*chlorophenylsulfonyl)-4-phenylheptanedinitrile*	78	M.P. 179-180°	1348	
 *benzyl phenyl sulfone*	18.0	25°	 *4-phenyl-4-phenylsulfonylheptanedinitrile*	59	M.P. 180°	184 171	
 *2,3,5-trichloro-4-methylphenyl* *2,4,5-trichlorobenzyl sulfone*	20	R.T.	 *4-(2,4,5-trichlorophenyl)-4-(2,3,5-*p-*tolylsulfonyl)-butyronitrile*	20	M.P. 196-200°	1300	
 *3-chloro-4-methylphenyl* *2,4,5-trichlorobenzyl sulfone*	20	R.T.	 *4-(3-chloro-*p-*tolylsulfonyl)-4-(2,4,5-trichlorophenyl)-butyronitrile*	88	M.P. 200-202.5°	1300	

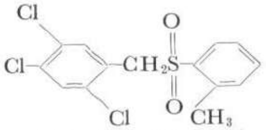
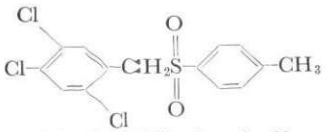
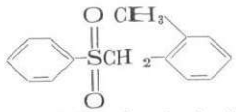
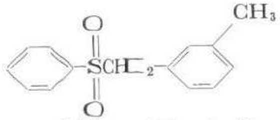
Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 o-tolyl 2,4,5-trichlorobenzyl sulfone	20	R.T.	 4-o-tolylsulfonyl-4-(2,4,5-trichlorophenyl)butyronitrile	94	M.P. 155-156.5°	1300	
 p-tolyl 2,4,5-trichlorobenzyl sulfone	20	R.T.	 4-p-tolylsulfonyl-4-(2,4,5-trichlorophenyl)butyronitrile	96	M.P. 143-144.5°	1300	
 o-methylbenzyl phenyl sulfone	48.0	30-35°	oil	—	—	54	
 m-methylbenzyl phenyl sulfone	48.0	30-35°	oil	—	—	54	

TABLE XVI—"C" Cyanoethylation: Aromatic Hydrocarbons

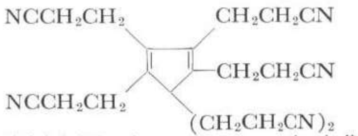
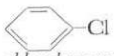
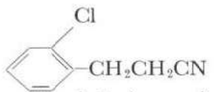
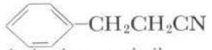
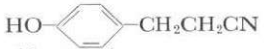
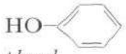
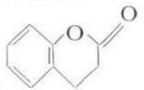
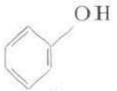
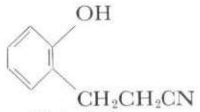
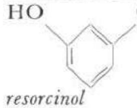
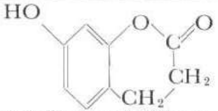
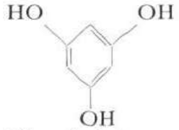
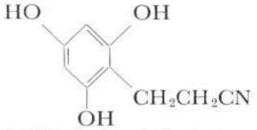
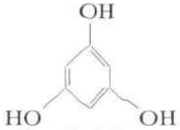
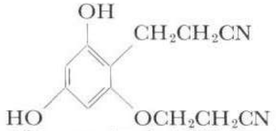
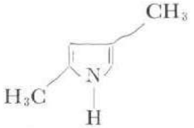
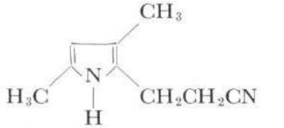
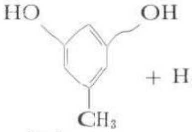
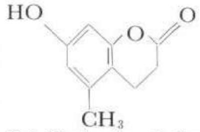
Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 *cyclopentadiene*	3.0	20°	 *1,1,2,3,4,5-cyclopentadienehexacarbonitrile*	27	M.P. 203°	154 158	
 *chlorobenzene*	30.0	140-165°	 o-*chlorohydrocinnamonitrile*	12	B.P. 147-152°/15 mm.	442	
 + HCl *benzene* + *hydrogen chloride*	12-15 30.0	R.T. Ⓐ 84-98°	 *hydrocinnamonitrile*	66	B.P. 125-126°/15 mm.	442	
 *benzene*	10.0	150-160°	 *hydrocinnamonitrile*	27	B.P. 128-130°/16 mm.	442	575
			 *phloretonitrile*	72	M.P. 58-59°	1297	1296
 *phenol*	1.5 1.5	15° 80°	 *hydrocoumarin*	3	B.P. 111-112°/2.5 mm.		
 *phenol*	1 O.N.	18° 25°	 *melilotonitrile*	12	B.P. 153-155°/1 mm.	1296	

TABLE XVI—Continued

Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 + H_2O Ⓑ *resorcinol*	12.0	25°	 *3,4-dihydroumbelliferone*	—	M.P. 133-134°	681	
 *phloroglucinol*	8.0	reflux	 *2,4,6-trihydroxyhydrocinnamonitrile*	78	M.P. 179-180°	1349	681
 *phloroglucinol*	8.0	reflux	 *2-(2-cyanoethoxy)-4,6-dihydroxyhydrocinnamonitrile*	56	M.P. 160-161°	1349	
 *2,4-dimethylpyrrole*	—	—	 *3,5-dimethyl-2-pyrrolepropionitrile*	—	B.P. 128°/1 mm.	1429	
 + H_2O Ⓑ *orcinol*	—	—	 *3,4-dihydro-5-methylumbelliferone*	51	M.P. 140-141.5°	681	

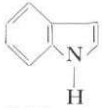
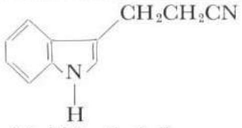
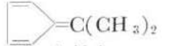
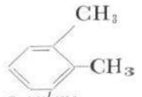
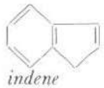
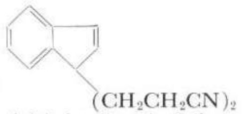
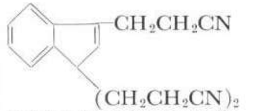
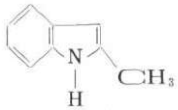
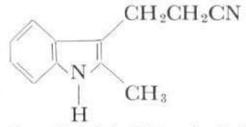
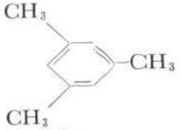
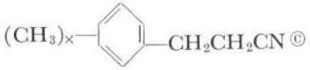
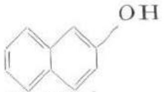
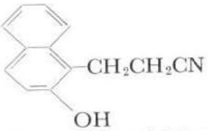
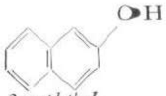
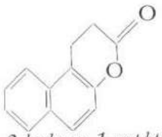
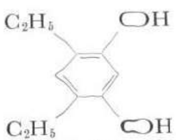
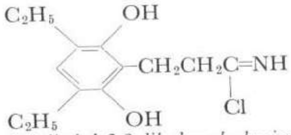
Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 *indole*	6.0	180-190°	 *3-indolepropionitrile*	81.3	M.P. 67-68°	1425	
 *dimethylfulvene*	—	—	*higher cyanoethylation products in impure form*	—	—	158	
 o-*xylene*	9.0	130°		55.4	B.P. 124-160°/15 mm.	442	
 *indene*	1.0	25°	 *1,1-indenedipropionitrile*	14	B.P. 210-220°/2 mm.	154 158	
			 *1,1,3-indenetripropionitrile*	35	B.P. 280-290°/1 mm. M.P. 65°		
 *2-methylindole*	6.0	180-190°	 *2-methyl-3-indolepropionitrile*	81	M.P. 79.5°	1425	572

TABLE XVI—Continued

Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 *mesitylene*	9.5	130-135°		47	B.P. 128-138°/12 mm.	442	
 *2-naphthol*	2.0	reflux	 *2-hydroxy-1-naphthalenepropionitrile*	93	M.P. 142°	467 485	1311
 *2-naphthol*	— 16.0 1.0	0° 25° 100°	 *2-hydroxy-1-naphthalenepropionic acid, δ-lactone*	40.1	M.P. 73-74.5°	1311	
 *4,6-diethylresorcinol*	—	—	 *3,5-diethyl-2,6-dihydroxyhydrocinnamimidyl chloride*	—	M.P. 156°	360	

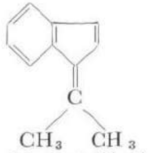
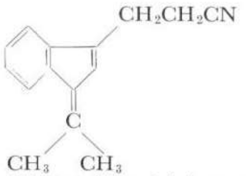
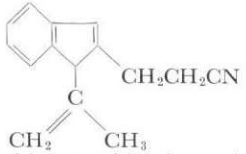
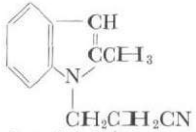
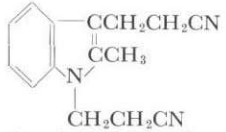
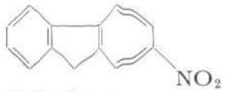
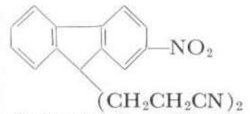
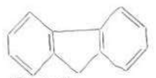
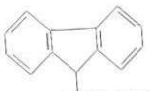
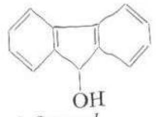
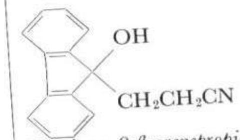
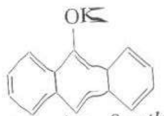
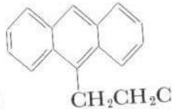
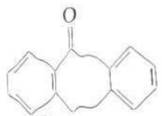
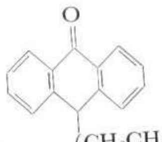
Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 *1-isopropylidenindene*	4.0	25°	 *1-isopropylidene-3-indenepropionitrile*	22	M.P. 121°	158	
			 *1-isopropenyl-2-indenepropionitrile*				
 *2-methyl-N-(2-cyanoethyl)indole*	—	—	 *2-methyl-1,3-indenedipropionitrile*	—	M.P. 138°	572	
 *2-nitrofluorene*	2.0	25°	 *2-nitro-9,9-fluorenedipropionitrile*	70	M.P. 236-237°	154	

TABLE XVI—Continued

Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References: This Exam.	References: See Also:
 *fluorene*	3.0	25°	 $(CH_2CH_2CN)_2$ *9,9-fluorenedipropionitrile*	74	M.P. 121°	158	154, 998
 *9-fluorenol*	3.0	25°	 *9-hydroxy-9-fluorenepropionitrile*	14	M.P. 105-107°	205	
 *potassium 9-anthrolate*	2.0	reflux	 Ⓓ CH_2CH_2COOH *9-anthraceneprop ionic acid*	90	M.P. 190-193°	309	
 *anthrone*	19.0	35°	 $(CH_2CH_2CN)_2$ *10-oxo-9,9(10H)-anthracenedipropionitrile*	89	M.P. 215°	154 158	

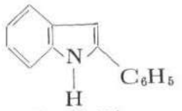
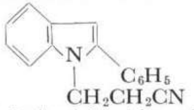
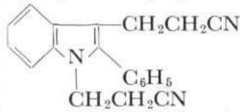
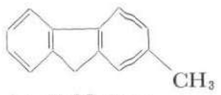
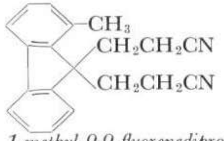
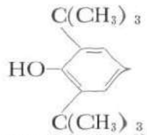
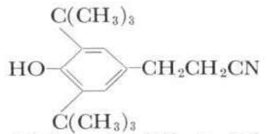
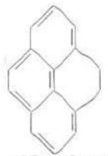
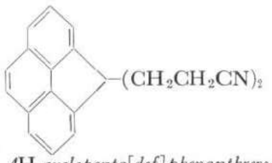
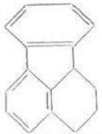
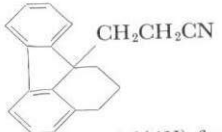
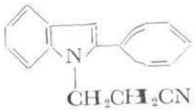
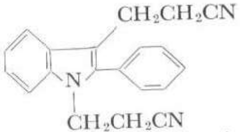
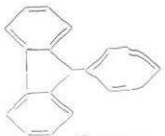
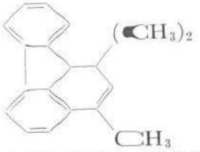
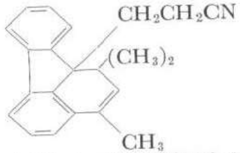
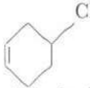
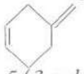
Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 *2-phenylindole*	1-2.0	75°	 *2-phenyl-1-indolepropionitrile*	~100	M.P. 90°	572	
			 *2-phenyl-1,3-indoledipropionitrile*		M.P. 159°		
 *1-methylfluorene*	—	—	 *1-methyl-9,9-fluorenedipropionitrile*	70	M.P. 105-106°	643	
 *2,6-di-*(t-*butyl*)*phenol*	1.0 7.0	55° 85°	 *3,5-di-*tert-*butylphloretonitrile*	13	M.P. 111-113°	1233	255
 *4*H-*cyclopenta[def]phenanthrene*	—	—	 *4*H-*cyclopenta[def]phenanthrene-4,4-dipropionitrile*	—	—	522	

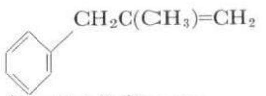
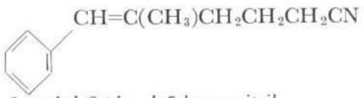
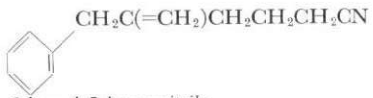
TABLE XVI—Continued

Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 *1,2,3,10b-tetrahydrofluoranthrene*	—	50°	 *2,3-dihydro-10b(1H)-fluoranthrenepropionitrile*	—	M.P. 110°	522	243
 *2-phenyl-N-(2-cyanoethyl)indole*	—	—	 *2-phenyl-1,3-indoledipropionitrile*		M.P. 159°	572	
 *9-phenylfluorene*	2.0	25°	 *9-phenyl-9-fluorenepropionitrile*	74	M.P. 148-149°	205	
 *1,10b-dihydro—1,1,3-trimethyl-fluoranthrene*	1.0	60°	 *1,1,3-trimethyl-10b(1H)-fluoranthrenepropionitrile*	—	B.P. 185-194°/0.1 mm.	522	

NOTES: Ⓐ Before AlCl₃ addition.
Ⓑ Added after the condensation reaction.
Ⓒ 4-Methyl and 2,4-dimethyl isomers were identified in the mixture.
Ⓓ After acid hydrolysis and reduction with zinc dust.

TABLE XVII—"C" Cyanoethylation: Aliphatic Hydrocarbons

Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
$HC\equiv CH$ *acetylene*	—	65-71° 155-200 p.s.i.	$CH_2{=}CHCH{=}CHCH{=}CHCN$ *2,4,6-heptatrienenitrile*	89Ⓐ	B.P. 58-59°/1 mm.	620	199
$CH_3CH{=}CH_2$ *propylene*	4.0	240° (pressure)	$CH_2{=}CHCH_2CH_2CH_2CN$ *5-hexenenitrile*	18	B.P. 162°	1194	
$CH_3CH{=}CHCH_3$ *2-butene*	5.0	245° (pressure)	$CH_2{=}CHCH(CH_3)CH_2CH_2CN$ *4-methyl-5-hexenenitrile*	4	B.P. 174°	1194	
$CH_2{=}C(CH_3)_2$ *2-methylpropene*	4.0	235° (585-1020 atm.)	$CH_2{=}C(CH_3)CH_2CH_2CH_2CN$ *5-methyl-5-hexenenitrile*	56		15	970, 971
$CH_3CH(CH_3)CH_3$ *2-methylpropane*	17 min.	450°F. (4500 p.s.i.)	$CH_3C(CH_3)_2CH_2CH_2CN$Ⓑ *4,4-dimethylvaleronitrile*	38	B.P. 165-178°	1034	
 *cyclohexene*	5.0	250° (pressure)	 CH_2CH_2CN *2-cyclohexene-1-propionitrile*	5	B.P. 230°	1194	15
$(CH_3)_2C{=}C(CH_3)_2$ *2,3-dimethyl-2-butene*	8.0	235° (190 atm.)	$CH_2{=}C(CH_3)C(CH_3)_2CH_2CH_2CN$ *4,4,5-trimethyl-5-hexenenitrile*	16Ⓒ	B.P. 205-209°	15	1194
$CH_2{=}C(CH_3)CH_2CH_2CH_2CN$ *5-methyl-5-hexenenitrile*	0.25	300° (pressure)	$NCCH_2CH_2CH_2C({=}CH_2)CH_2CH_2CH_2CN$ *5-methylenenonanedinitrile*	61	B.P. 152-154°/2.5 mm.	1194	
$CH{=}CH_2$  *4-vinylcyclohexene*	4.0	240° (pressure)	$CHCH_2CH_2CH_2CN$  *5-(3-cyclohexen-1-ylidene)valeronitrile*	3	B.P. 117°/7 mm.	1194	

Reactants	Re-action Time (Hr.)	Reaction Temperature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References: This Exam.	References: See Also:
$CH_3OCOCH_2CH_2CH_2C(CH_3)=CH_2$ *methyl 5-methyl-5-hexenoate*	5.0	230° (pressure)	$CH_3OCO(CH_2)_3C(=CH_2)(CH_2)_3CN$ *8-cyano-5-methyleneoctanoic acid, methyl ester*	19			
$CH_2=C(CH_3)CH_2C(CH_3)_3$ *2,4,4-trimethyl-1-pentene*	4.0	225° (pressure)	$(CH_3)_3CCH_2C(=CH_2)CH_2CH_2CH_2CN$ *7,7-dimethyl-5-methyleneoctanenitrile*	—	—	971	
$CH_2=C(CH_3)CH_2C(CH_3)_3$ *2,4,4-trimethyl-1-pentene* $CH_3C(CH_3)=CHC(CH_3)_3$ *2,4,4-trimethyl-2-pentene*	4.0 2.0	245° 255° (23.8 28.6 atm.)	$C(CH_3)_3C(=CH_2)CH_2CH_2CH_2CN$ *6,6-dimethyl-5-methyleneheptanenitrile* $CH_2=C(CH_3)CH[C(CH_3)_3]CH_2CH_2CN$ *4-tert-butyl-5-methyl-5-hexenenitrile*	17 combined	B.P. 126-134°/30 mm.	15	
 $C_6H_5CH_2C(CH_3)=CH_2$ *(2-methylallyl)benzene*	6.0	240° (pressure)	 $C_6H_5CH=C(CH_3)CH_2CH_2CH_2CN$ *5-methyl-6-phenyl-5-hexenenitrile*  $C_6H_5CH_2C(=CH_2)CH_2CH_2CH_2CN$ *5-benzyl-5-hexenenitrile*	23Ⓓ	B.P. 142°/4 mm.Ⓔ B.P. 151°/4 mm.	1194	

NOTES: Ⓐ Based on unrecovered acrylonitrile.
Ⓑ Possible structure of main component.
Ⓒ Based on unrecovered olefin.
Ⓓ Yield of mixed isomers.
Ⓔ Boiling points not assigned to specific isomers.

TABLE XVIII—"C" Cyanoethylation: Haloforms

Br_3CH *bromoform*	3.0 3.0	5-10° 25°	$Br_3CCH_2CH_2CN$ *4,4,4-tribromobutyronitrile*	11	B.P. 126-128°/6 mm. M.P. 98°	827	175
Cl_3CH *cloroform*	—	—	$Cl_3CCH_2CH_2CN$ *4,4,4-trichlorobutyronitrile*	18		1372	175, 485

TABLE XIX—"N" Cyanoethylation

(A) Amino and Primary Aliphatic Amines

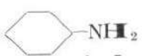
Reactants	Reaction Time (Hr.)	Reaction Temperature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References: This Exam.	References: See Also:
NH_3 Ⓐ *ammonia*	2 min.	112°	$NH_2CH_2CH_2CN$ *3-aminopropionitrile*	82.2	—	188	189, 664, 207, 963, 187, 34, 399, 566, 1145, 579
			$NH(CH_2CH_2CN)_2$ *3,3'iminodipropionitrile*	17.8	—		
NH_3 Ⓑ *ammonia*	—	30°	$NH_2CH_2CH_2CN$ *3-aminopropionitrile*	1.7	—	1147	1135, 1065, 568, 665, 520, 1145
			$NH(CH_2CH_2CN)_2$ *3,3'-iminodipropionitrile*	88.5	—		
			$N(CH_2CH_2CN)_3$ *3,3',3''-nitrilotripropionitrile*	6.0	—		
$NH_3 + HCHO$ *ammonia + formaldehyde*	Ⓣ 8-10	350-400°	$CH_2(NHCH_2CH_2CN)_2$ *3,3'-(methylenediimino)dipropionitrile*	—	B.P. 140°/10 mm.	1437	
CH_3NH_2 *methylamine*	—	—	$CH_3NHCH_2CH_2CN$ *3-methylaminopropionitrile*	85	—	963	815, 702, 267, 1053
			$CH_3N(CH_2CH_2CN)_2$ *3,3'(methylimino)dipropionitrile*	12			
CH_3NH_2 *methylamine*	16	80-90°	$CH_3N(CH_2CH_2CN)_2$ *3,3'-(methylimino)dipropionitrile*	51	B.P. 195-197°/22 mm.	1409	
$CH_3CH_2NH_2$ *ethylamine*	5.0 1.0 16.0	R.T. steam bath R.T.	$CH_3CH_2NHCH_2CH_2CN$ *3-ethylaminopropionitrile*	90.4	B.P. 92-95°/30 mm.	1145	1055, 1120
$CH_3CH_2NH_2 + CS_2$ Ⓒ *ethylamine + carbon disulfide*	—	R.T.	 $CH_3CH_2\overset{+}{N}H_2CH_2CH_2CN\ \overset{-}{S}\overset{\overset{S}{\parallel}}{C}\underset{\underset{CH_2CH_3}{\vert}}{N}CH_2CH_2CN$ *3-ethylaminopropionitrile, compound with (2-cyanoethyl)ethyldithiocarbamic acid*	~100	—	471	
$HOCH_2CH_2NH_2$ *2-aminoethanol*	—	—	$HOCH_2CH_2NHCH_2CH_2CN$ *3-(3-hydroxyethylamino)propionitrile*	100		567 569	521, 1041, 1040, 1364

TABLE XIX—Continued

(A) Amino and Primary Aliphatic Amines

Reactants	Reaction Time (Hr.)	Reaction Temperature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
$HOCH_2CH_2NH_2$ *2-aminoethanol*	—	—	$HOCH_2CH_2N(CH_2CH_2CN)_2$ *3,3′-(2-hydroxyethylimino)dipropionitrile*	—	—	1145	
CH_3COONH_4 *ammonium acetate*	20	68°	$N(CH_2CH_2CN)_3$ *3,3′,3″-nitrilotrispropionitrile*	30	M.P. 55-57°	1352	
$H_2NCH_2CH_2NH_2$ *ethylenediamine*	19.5	25°	$H_2NCH_2CH_2NHCH_2CH_2CN$ *3-(2-aminoethylamino)propionitrile*	59	B.P. 124-127°/10 mm.	1252	
$H_2NCH_2CH_2NH_2$ *ethylenediamine*	2.0 0.25	R.T. 100°	$NCCH_2CH_2HNCH_2CH_2NHCH_2CH_2CN$ *3,3′-(ethylenediimino)dipropionitrile*	93	B.P. 186-192°/0.2 mm.	699	1073, 665, 664, 786
$NH_2CH_2CH_2NH_2+CS_2$Ⓒ *ethylenediamine + carbon disulfide*	—	<60°	 $NC(CH_2)_2-\underset{S=C-S^-}{\underset{\vert}{N}}-CH_2CH_2\overset{+}{N}H_2CH_2CH_2CN$ Ⓓ *(2-cyanoethyl)[2-(2-cyanoethylamino)ethyl] dithiocarbamic acid*	—	—	471	
$CH_2=CHCH_2NH_2$ *allylamine*	5.0	reflux	$CH_2=CHCH_2NHCH_2CH_2CN$ *3-allylaminopropionitrile*	79	B.P. 75°/5 mm.	731	
$CH_3CH_2CH_2NH_2$ n-*propylamine*	—	—	$CH_3CH_2CH_2NHCH_2CH_2CN$ *3-propylaminopropionitrile*	92	B.P. 119-121°/30 mm.	1055	885, 1120
$(CH_3)_2CHNH_2$ *isopropylamine*	O.N.	R.T.	$(CH_3)_2CHNHCH_2CH_2CN$ *3-isopropylaminopropionitrile*	95	B.P. 86-87°/17 mm.	860	
$HOCH(CH_3)CH_2NH_2$ *1-amino-2-propanol*	5.0 0.5 18.0	25° steam bath 25°	$CH_3CH(OH)CH_2NHCH_2CH_2CN$ *3-(2-hydroxypropylamino)propionitrile*	25	B.P. 111-113°/0.6 mm.	1042	
$NH_2CH_2CH_2CH_2NH_2$ *1,3-propanediamine*	— 2.0	40-45° water bath	$NH_2CH_2CH_2CH_2NHCH_2CH_2CN$ *3-(3-aminopropylamino)propionitrile* $NCCH_2CH_2NHCH_2CH_2CH_2NHCH_2CH_2CN$ *3,3′-(trimethylenediimino)dipropionitrile*	80	B.P. 200-210°/3 mm. B.P. 230-270°/3 mm.	1075	

Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
$NCC(CH_3)_2NH_2$ *2-aminoisobutyronitrile*	15 1	R.T. 75°	$NCC(CH_3)_2NHCH_2CH_2CN$ *2-methyl-2,3′-iminodipropionitrile*	40	B.P. 115-116°/15 mm.	1417	
$CH_2{=}C(CH_3)CH_2NH_2$ *2-methylallylamine*	—	30°	$CH_2{=}C(CH_3)CH_2NHCH_2CH_2CN$ *3-(2-methylallylamino)propionitrile* $CH_2{=}C(CH_3)CH_2N(CH_2CH_2CN)_2$ *3,3′-(2-methylallylimino)dipropionitrile*	— —	— —	731	
$CH_3(CH_2)_3NH_2$ n-*butylamine*	— 1.0	10° —	$CH_3CH_2CH_2CH_2NHCH_2CH_2CN$ *3-butylaminopropionitrile*	~100	B.P. 114-116°/20 mm.	520 566 568 519	1055, 963, 408, 1120
$CH_3CH_2CH(CH_3)NH_2$ sec-*butylamine*	—	—	$CH_3CH_2CH(CH_3)NHCH_2CH_2CN$ *3-*sec-*butylaminopropionitrile*	83	B.P. 92-96°/10 mm.	1055	
$(CH_3)_2CHCH_2NH_2$ *isobutylamine*	4.0 1.0 O.N.	R.T. reflux R.T.	$(CH_3)_2CHCH_2NHCH_2CH_2CN$ *3-isobutylaminopropionitrile*	91	B.P. 82-88°/7 mm. B.P. 107°/11 mm.	1053	1023
$(CH_3)_3CNH_2$ tert-*butylamine*	20	reflux	$(CH_3)_3CNHCH_2CH_2CN$ *3-*tert-*butylaminopropionitrile* $(CH_3)_3CN(CH_2CH_2CN)_2$ *3,3′-(*tert-*butylimino)dipropionitrile*	78 8	B.P. 69-71°/1.5 mm. B.P. 121-130°/0.4 mm.	1327	1055
$CH_3CH(OH)CH_2CH_2NH_2$ *1-amino-3-butanol*	—	—	$CH_3CH(OH)CH_2CH_2NHCH_2CH_2CN$ *3-(3-hydroxybutylamino)propionitrile*	74	B.P. 132-135°/0.8 mm.	1042	
$HOCH_2CH(CH_2CH_3)NH_2$ *2-amino-1-butanol*	—	—	$HOCH_2CH(CH_2CH_3)NHCH_2CH_2CN$ *3-(1-hydroxymethylpropylamino)propionitrile*	75	B.P. 120-122°/3 mm.	59	
$HOCH_2C(CH_3)_2NH_2$ *2-amino-2-methyl-1-propanol*	—	40-60°	$HOCH_2C(CH_3)_2NHCH_2CH_2CN$ *3-(2-hydroxy-1,1-dimethylethylamino)propionitrile*	88.5	M.P. 55-56°	59	
$(CH_3)_2C(OH)CH_2NH_2$ *1-amino-2-methyl-2-propanol*	O.N.	R.T.	$(CH_3)_2C(OH)CH_2NHCH_2CH_2CN$ *3-(2-hydroxy-2-methylpropylamino)propionitrile*	86.5	B.P. 94-96°/1 mm.	1023	1054

Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
$H_2N(CH_2)_4NH_2$ *putrescine*	23.0 1.0 1.0	R.T. steam bath R.T.	$NCCH_2CH_2HN(CH_2)_4NHCH_2CH_2CN$ *3,3'(tetramethylenediimino)dipropionitrile*	—	Ⓔ	974	
$CH_3(CH_2)_4NH_2$ n-*amylamine*	O.N.	50° R.T.	$CH_3CH_2CH_2CH_2CH_2NHCH_2CH_2CN$ *3-pentylaminopropionitrile*	88	B.P. 112-113°/10 mm.	195	1120
$HOCH_2C(CH_3)(CH_2CH_3)NH_2$ *2-amino-2-methyl-1-butanol*	—	—	$HOCH_2C(CH_3)(CH_2CH_3)NHCH_2CH_2CN$ *3-(1-hydroxymethyl-1-methylpropylamino)propionitrile*	73	B.P. 125-127°/3 mm. M.P. 35-36°	59	
$(CH_3)_2C(OCH_3)CH_2NH_2$ *2-methoxy-2-methylpropylamine*	2.0 18.0	50° 25°	$(CH_3)_2C(OCH_3)CH_2NHCH_2CH_2CN$ *3-(2-methoxy-2-methylpropylamino)propionitrile*	71	B.P. 85°/1 mm.	1054	
$CH_3OCH_2CH(CH_3)CH_2NH_2$ *3-methoxy-2-methylpropylamine*	— 18.0	50° 25°	$CH_3OCH_2CH(CH_3)CH_2NHCH_2CH_2CN$ *3-(3-methoxy-2-methylpropylamino)propionitrile*	91	B.P. 90-91°/2 mm.	1054	
 $-NH_2$ *cyclohexylamine*	1.0	reflux	 $-NHCH_2CH_2CN$ *3-cyclohexylaminopropionitrile*	~100	B.P. 149-151°/11 mm.	568 520 566 519	1055, 408
 $O\quad NCH_2CH_2NH_2$ *N-(2-aminoethyl)morpholine*	—	—	 $O\quad NCH_2CH_2NHCH_2CH_2CN$ *3-(2-morpholinoethylamino)propionitrile*	81.5	B.P. 183°/20 mm.	1145	
$CH_3COHN(CH_2)_4NH_2 \cdot HCl$ *monoacetylputrescine hydrochloride*	16 1 2	R.T. reflux R.T.	$CH_3COHN(CH_2)_4NHCH_2CH_2CN \cdot HCl$ *3-(4-acetamidobutylamino)propionitrile, hydrochloride*	70	M.P. 143-144°	1293	
$CH_3(CH_2)_4CH_2NH_2$ n-*hexylamine*	1-2.0	100°	$CH_3(CH_2)_4CH_2NHCH_2CH_2CN$ *3-(hexylamino)propionitrile*	77	B.P. 126°/9 mm.	1120	
$H_2N(CH_2)_6NH_2$ *1,6-hexanediamine*	—	—	$NCCH_2CH_2HN(CH_2)_6NHCH_2CH_2CN$ *3,3'-(hexamethylenediimino)dipropionitrile*	85	B.P. 230-238°/2 mm.	699	472

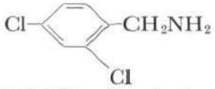
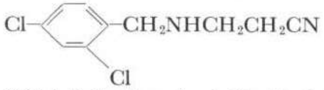
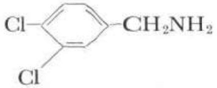
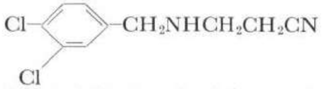
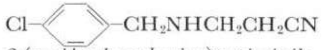
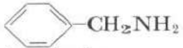
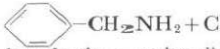
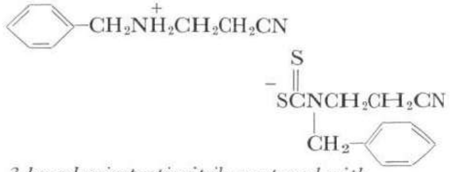
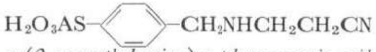
Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 *2,4-dichlorobenzylamine*	—	R.T.	 *3-(2,4-dichlorobenzylamino)propionitrile*	77	B.P. 158°/1 mm.	1412	
 *3,4-dichlorobenzylamine*	—	R.T.	 *3-(3,4-dichlorobenzylamino)propionitrile*	97	B.P. 165°/0.8 mm.	1412	
 p-*chlorobenzylamine*	—	R.T.	 *3-(*p-*chlorobenzylamino)propionitrile*	83	B.P. 120°/0.07 mm.	1412	
 *benzylamine*	—	R.T.	$C_6H_5CH_2NHCH_2CH_2CN$ *3-benzylaminopropionitrile*	100	B.P. 124°/0.9 mm.	1412	633, 408, 1383
 *benzylamine + carbon disulfide*	1.0	100-110°	 *3-benzylaminopropionitrile, compound with benzyl(2-cyanoethyl)dithiocarbamic acid*	~100	—	471	
 *α-amino-*p-*toluene arsonic acid*	1.25	—	 *α-(2-cyanoethylamino)-*p-*toluenearsonic acid*	—	M.P. > 300°	402	
 *N-(3-aminopropyl)morpholine*	—	—	 *3-(3-morpholinopropylamino)propionitrile*	76	B.P. 178-180°/9 mm.	1145	

TABLE XIX—Continued

(A) Amino and Primary Aliphatic Amines

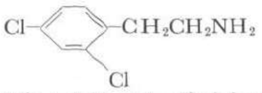
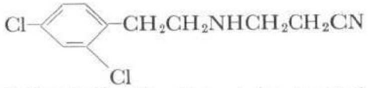
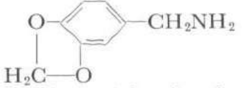
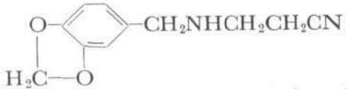
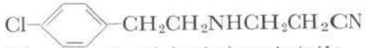
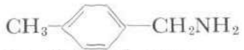
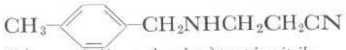
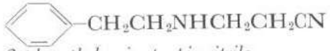
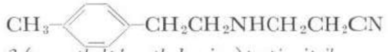
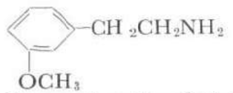
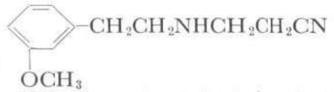
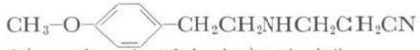
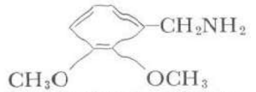
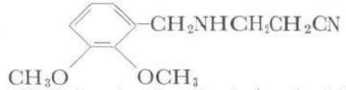
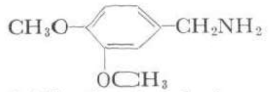
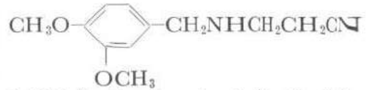
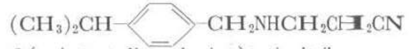
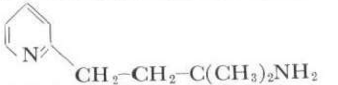
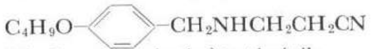
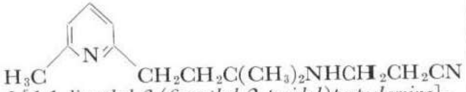
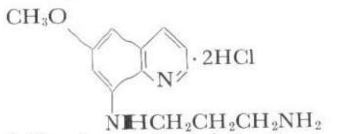
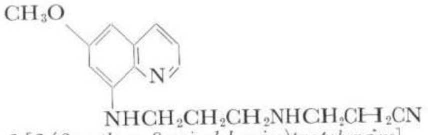
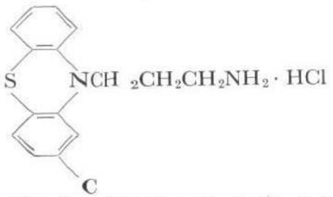
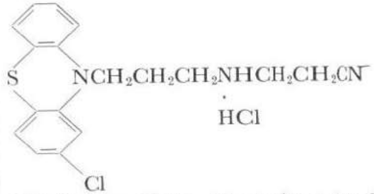
Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
$(CH_3)_2CHNHCH_2C(CH_3)_2NH_2$ *N'-isopropyl-2-methyl-1,2-propanediamine*	—	—	$(CH_3)_2CHNHCH_2C(CH_3)_2NHCH_2CH_2CN$ *3-(2-isopropylamino-1,1-dimethylethylamino)-propionitrile*	56.7	B.P. 104-105°/3 mm.	59	
$(CH_3CH_2)_2NCH_2CH_2CH_2NH_2$ *N,N-diethyl-1,3-propanediamine*	—	—	$(CH_3CH_2)_2NCH_2CH_2CH_2NHCH_2CH_2CN$ *3-(3-diethylaminopropylamino)propionitrile*	79.4	B.P. 163-165°/25 mm.	1145	
$(CH_3CH_2)_2NCH_2CH_2CH_2NH_2$ *N,N-diethyl-1,3-propanediamine*	—	—	$(C_2H_5)_2NCH_2CH_2CH_2N(CH_2CH_2CN)_2$ *3,3'-(3-diethylaminopropylimino)dipropionitrile*	8.8	B.P. 233-235°/25 mm.	1145	
 *2-(2,4-dichlorophenyl)ethylamine*	—	R.T.	 *3-(2,4-dichlorophenethylamino)propionitrile*	65	B.P. 130°/0.3 mm.	1412	
 *3,4-dioxymethylenebenzylamine*	—	R.T.	 *3-(3,4-methylenedioxybenzylamino)propionitrile*	79	B.P. 127°/0.03 mm.	1412	
 2-(p-*chlorophenyl*)*ethylamine*	—	R.T.	 *3-(*p-*chlorophenethylamino)propionitrile*	87	B.P. 110°/0.03 mm.	1412	
 p-*methylbenzylamine*	—	R.T.	 *3-(*p-*methylbenzylamino)propionitrile*	74	B.P. 123°/0.7 mm.	1412	
 *2-phenylethylamine*	—	R.T.	 *3-phenethylaminopropionitrile*	96	B.P. 133°/0.08 mm.	1412	
$(CH_3)_3CCH_2C(CH_3)_2NH_2$ t-*octylamine*	20	reflux	$(CH_3)_3CCH_2C(CH_3)_2NHCH_2CH_2CN$ *3-(1,1,3,3-tetramethylbutylamino)propionitrile*	83	B.P. 100-105°/1.5-2.0 mm.	1327	

TABLE XIX—Continued

Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
$(NH_2CH_2CH_2CH_2OCH_2)_2$ *3,3-(ethylenedioxy)bispropylamine*	18.0 1.0	R.T. steam bath	$(NCCH_2CH_2NHCH_2CH_2CH_2OCH_2)_2$ *3,3′-[ethylenebis(oxytrimethyleneimino)]dipropionitrile*	100	—		
$NH(CH_2CH_2NHCH_2CH_2NH_2)_2$ *tetraethylenepentamine*	0.50	—	Ⓕ	—	—	487	
 *2-(p-tolyl)ethylamine*	—	R.T.	 *3-(p-methylphenethylamino)propionitrile*	92	B.P. 130°/0.5 mm.	1412	
 *2-(m-methoxyphenyl)ethylamine*	—	R.T.	 *3-(m-methoxyphenethylamino)propionitrile*	86	B.P. 128°/0.05 mm.	1412	
 *2-(p-methoxyphenyl)ethylamine*	—	R.T.	 *3-(p-methoxyphenethylamino)propionitrile*	88	B.P. 118°/0.07 mm.	1412	
 *2,3-dimethoxybenzylamine*	—	R.T.	 *3-(2,3-dimethoxybenzylamino)propionitrile*	73	B.P. 125°/0.06 mm.	1412	
 *3,4-dimethoxybenzylamine*	—	R.T.	 *3-(3,4-dimethoxybenzylamino)propionitrile*	79	B.P. 158°/0.05 mm.	1412	1383
 *p-isopropylbenzylamine*	—	R.T.	 *3-(p-isopropylbenzylamino)propionitrile*	91	B.P. 102°/0.07 mm.	1412	

Reactants	Re-action Time (Hr.)	Reaction Temperature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 $CH_2{-}CH_2{-}C(CH_3)_2NH_2$ *1,1-dimethyl-3-(2-pyridyl)propylamine*	1	reflux	 $CH_2CH_2C(CH_3)_2NHCH_2CH_2CN$ *3-[1,1-dimethyl-3-(2-pyridyl)propylamino]propionitrile*	59	B.P. 154-157°/1.2 mm.	1385	
 $C_4H_9O{-}C_6H_4{-}CH_2NH_2$ p-*butoxybenzylamine*	—	R.T.	 $C_4H_9O{-}C_6H_4{-}CH_2NHCH_2CH_2CN$ *3 (p-butoxybenzylamino)propionitrile*	94	B.P. 138°/0.05 mm.	1412	
 H_3C … $CH_2CH_2C(CH_3)_2NH_2$ *1,1-dimethyl-3-(6-methyl-2-pyridyl)-propylamine*	3	reflux	 H_3C … $CH_2CH_2C(CH_3)_2NHCH_2CH_2CN$ *3-[1,1-dimethyl-3-(6-methyl-2-pyridyl)propylamino]-propionitrile*	64	B.P. 147-150°/0.6 mm.	1385	
$CH_3(CH_2)_{10}CH_2NH_2$ n-*dodecylamine*	0.5 1.0	35° reflux	$CH_3(CH_2)_{10}CH_2NHCH_2CH_2CN$ *3-dodecylaminopropionitrile*	95	B.P. 140°/0.5 mm.	344	408, 519, 963
 CH_3O … $\cdot 2HCl$ $NHCH_2CH_2CH_2NH_2$ *8-(3-aminopropylamino)-6-methoxy-quinoline dihydrochloride*	2.0 4.0	R.T. R.T.	 CH_3O … $NHCH_2CH_2CH_2NHCH_2CH_2CN$ *3-[3-(6-methoxy-8-quinolylamino)propylamino]-propionitrile*	31.2	M.P. 217-218°	636	
 $NCH_2CH_2CH_2NH_2 \cdot HCl$ *3-(2-chloro-10-phenothiazinyl)propylamine hydrochloride*	3 0.3	R.T. 70°	 $NCH_2CH_2CH_2NHCH_2CH_2CN \cdot HCl$ *3-[3-(2-chloro-10-phenothiazinyl)propylamino]-propionitrile, hydrochloride*	—	M.P. 194-197° (dec.)	1270	

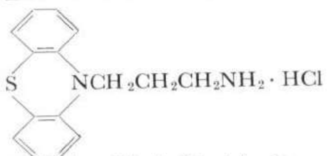
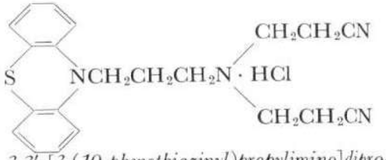
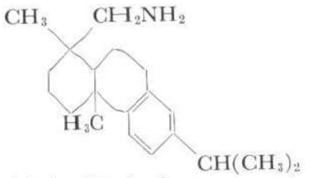
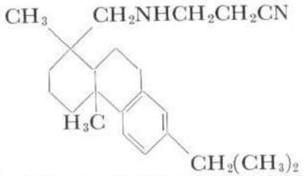
Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 *3-(10-phenothiazinyl)propylamine hydrochloride*	3 0.3	R.T. 70°	 *3,3′-[3-(10-phenothiazinyl)propylimino]dipropionitrile, hydrochloride*	62	M.P. 158-160°	1270	
$CH_3(CH_2)_{17}NH_2$ *octadecylamine*	—	steam bath	$CH_3(CH_2)_{17}NHCH_2CH_2CN$ *3-octadecylaminopropionitrile*	~100	—	963	
 *dehydroabietylamine*	16.0	90° pressure	 *N-(2-cyanoethyl)dehydroabietylamine*	—	—	625	
palm kernel oil amine	—	steam bath	*mono cyanoethyl deriv. of palm kernel oil amine*	—	—	963	
RNH_2ⓐ *tallow amine*	0.5 1.0	35° reflux	$RNHCH_2CH_2CN$		—	344	
coconut oil amine	—	steam bath	*mono cyanoethyl derivative of coconut oil amine*	—	—	963	
(B) Secondary Aliphatic Amines							
$(CH_3)_2NH$ *dimethylamine*	—	—	$(CH_3)_2NCH_2CH_2CN$ *3-dimethylaminopropionitrile*	~100	—	963	815, 265, 664, 801, 1069, 933, 1068, 266, 1065, 1355

TABLE XIX—Continued

Reactants	Reaction Time (Hr.)	Reaction Temperature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
$CH_3NHCH_2CH_2CN$ *3-methylaminopropionitrile*	16.0	90°	$CH_3N(CH_2CH_2CN)_2$ *3,3′-methyliminodipropionitrile*	95	B.P. 159.5-169°/5 mm.	815	
$CH_3CH_2CH_2NHCH_3$ *N-methylpropylamine*	O.N.	95°	$CH_3CH_2CH_2N(CH_3)CH_2CH_2CN$ *3-(methylpropylamino)propionitrile*	93	B.P. 102-106°/26 mm.	272	
$(CH_3)_2CHNHCH_3$ *N-methylisopropylamine*	O.N.	95°	$(CH_3)_2CHN(CH_3)CH_2CH_2CN$ *3-(isopropylmethylamino)propionitrile*	76	B.P. 94-96°/32 mm.	272	
$(C_2H_5)_2NH$ *diethylamine*	—	—	$(C_2H_5)_2NCH_2CH_2CN$ *3-diethylaminopropionitrile*	96-98	B.P. 65°/2 mm. B.P. 76°/9 mm. B.P. 87°/20 mm. B.P. 197.3°/755 mm.	664	1145, 1244, 1068, 1355, 1120
$HOCH_2CH_2NHC_2H_5$ *N-ethylaminoethanol*	O.N.	50° R.T.	$HOCH_2CH_2N(CH_2CH_3)CH_2CH_2CN$ *3-(ethyl-2-hydroxyethylamino)propionitrile*	72	B.P. 133-134°/7 mm.	195	1040
$(HOCH_2CH_2)_2NH$ *2,2′-iminodiethanol*	—	60°	$(HOCH_2CH_2)_2NCH_2CH_2CN$ *3-bis(2-hydroxyethyl)aminopropionitrile*	~100	—	567 569	521, 1145, 266, 249
$CH_3CH_2CH_2CH_2NHCH_3$ *N-methylbutylamine*	O.N.	95°	$CH_3CH_2CH_2CH_2N(CH_3)CH_2CH_2CN$ *3-(butylmethylamino)propionitrile*	83	B.P. 108-112°/40 mm.	272	
$(CH_3)_2CHCH_2NHCH_3$ *N-methyl-2-methylpropylamine*	O.N.	95°	$(CH_3)_2CHCH_2N(CH_3)CH_2CH_2CN$ *3-(isobutylmethylamino)propionitrile*	78	B.P. 103-105°/33 mm.	272	
$C_2H_5CH(CH_3)NHCH_3$ *N-methyl-1-methylpropylamine*	O.N.	95°	$CH_3CH_2CH(CH_3)N(CH_3)CH_2CH_2CN$ *3-(sec-butylmethylamino)propionitrile*	87	B.P. 111-112°/32 mm.	272	
$(CH_3)_2CHNHC_2H_5$ *1-methyldiethylamine*	O.N.	95°	$(CH_3)_2CHN(CH_2CH_3)CH_2CH_2CN$ *3-(ethylisopropylamino)propionitrile*	31	B.P. 98-101°/29 mm.	272	
$HN(CH_2CH_2CN)_2$ *3,3′-iminodipropionitrile*	60	160-180°	$N(CH_2CH_2CN)_3$ *3,3′,3′′-nitrilotripropionitrile*	40	M.P. 57-58°	1065	

TABLE XIX—Continued

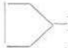
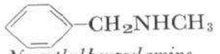
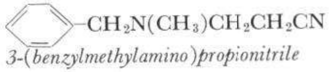
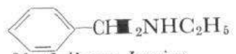
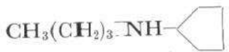
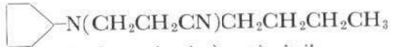
Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 $-NHCH_3$ *N-methylcyclopentylamine*	O.N.	95°	 $-N(CH_3)CH_2CH_2CN$ *3-(cyclopentylmethylamino)propionitrile*	96	B.P. 134-135°/33 mm.	272	
$CH_3CH_2CH_2CH(CH_3)NHCH_3$ *N-methyl-1-methylbutylamine*	O.N.	95°	$CH_3CH_2CH_2CH(CH_3)N(CH_3)CH_2CH_2CN$ *3-(methyl-1-methylbutylamino)propionitrile*	89	B.P. 101-103°/18 mm.	272	
$(C_2H_5)_2CHNHCH_3$ *N-methyl-1-ethylpropylamine*	O.N.	95°	$(C_2H_5)_2CHN(CH_3)CH_2CH_2CN$ *3-[(1-ethylpropyl)methylamino]propionitrile*	81	B.P. 111-114°/17 mm.	272	
$(CH_3)_2CHCH_2NHC_2H_5$ *N-ethyl-2-methylpropylamine*	O.N.	95°	$(CH_3)_2CHCH_2N(CH_2CH_3)CH_2CH_2CN$ *3-(ethylisobutylamino)propionitrile*	56	B.P. 114-115°/35 mm.	272	
$(C_3H_7)_2NH$ *dipropylamine*	O.N.	50° R.T.	$(C_3H_7)_2NCH_2CH_2CN$ *3-dipropylaminopropionitrile*	90	B.P. 104-105°/1 mm.	195	1145, 1120
$(CH_3)_2CHNH(C_3H_7)$ *N-propyl-1-methylethylamine*	O.N.	95°	$(CH_3)_2CHN[(CH_2)_2CH_3]CH_2CH_2CN$ *3-(isopropylpropylamino)propionitrile*	80	B.P. 110-113°/31-32 mm.	272	
$[(CH_3)_2CH]_2NH$ *diisopropylamine*	O.N.	50° R.T.	$[(CH_3)_2CH]_2NCH_2CH_2CN$ *3-diisopropylaminopropionitrile*	12	B.P. 100-102°/13 mm.	195	
$(CH_3)_2CHCH(CH_3)NHCH_3$ *N,1,2-trimethylpropylamine*	O.N.	95°	$(CH_3)_2CHCH(CH_3)N(CH_3)CH_2CH_2CN$ *3-[(1,2-dimethylpropyl)methylamino]propionitrile*	92	B.P. 131-134°/40 mm.	272	
$CH_3(CH_2)_3NHCH_2CH_2OH$ *N-butyl-2-hydroxyethylamine*	O.N.	50° R.T.	$HOCH_2CH_2N[(CH_2)_3CH_3]CH_2CH_2CN$ *3-(butyl-2-hydroxyethylamino)propionitrile*	61	B.P. 147-148°/7 mm.	195	1040
$CH_3CH_2NHCH_2Si(CH_3)_3$ *N-[(trimethylsilyl)methyl]ethylamine*	12	60°	$(CH_3)_3SiCH_2N(CH_2CH_3)CH_2CH_2CN$ *3-[ethyl(trimethylsilylmethyl)amino]propionitrile*	77.4	B.P. 83.5°/3 mm.	1346	
 $-NHCH_3$ *N-methylcyclohexylamine*	O.N.	95°	 $-N(CH_3)CH_2CH_2CN$ *3-(cyclohexylmethylamino)propionitrile*	61	B.P. 145-148°/40 mm.	272	
 $-NHC_2H_5$ *N-ethylcyclopentylamine*	O.N.	95°	 $-N(CH_2CH_3)CH_2CH_2CN$ *3-(cyclopentylethylamino)propionitrile*	48	B.P. 130-133°/20 mm.	272	

TABLE XIX—Continued

(B) Secondary Aliphatic Amines

Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
$CH_3CH_2CH(CH_3)NHC_3H_7$ *1-methyldipropylamine*	O.N.	95°	$CH_3CH_2CH(CH_3)N[(CH_2)_2CH_3]CH_2CH_2CN$ *3-[(1-methylpropyl)propylamino]propionitrile*	34	B.P. 105-111°/22-25 mm.	272	
$n\text{-}C_4H_9NHC_3H_7$ *N-propylbutylamine*	O.N.	95°	$CH_3CH_2CH_2CH_2N[(CH_2)_2CH_3]CH_2CH_2CN$ *3-(butylpropylamino)propionitrile*	61	B.P. 128-129°/35 mm.	272	
$(CH_3)_2CHCH_2NHC_3H_7$ *2-methyldipropylamine*	O.N.	95°	$(CH_3)_2CHCH_2N[(CH_2)_2CH_3]CH_2CH_2CN$ *3-(isobutylpropylamino)propionitrile*	49	B.P. 105-110°/21 mm.	272	
 $-CH_2NHCH_3$ *N-methylbenzylamine*	36.0	steam cone	 $-CH_2N(CH_3)CH_2CH_2CN$ *3-(benzylmethylamino)propionitrile*	75-93	B.P. 163-164°/14 mm.	633	
$(n\text{-}C_3H_7)_2CHNHCH_3$ *N-methyl-1-propylbutylamine*	O.N.	95°	$[CH_3(CH_2)_2]_2CHN(CH_3)CH_2CH_2CN$ *3-(methyl-1-propylbutylamino)propionitrile*	65	B.P. 152-153°/38 mm.	272	
$[CH_3(CH_2)_3]_2NH$ *dibutylamine*	O.N.	50° R.T.	$[CH_3(CH_2)_3]_2NCH_2CH_2CN$ *3-dibutylaminopropionitrile*	96	B.P. 127-131°/11 mm.	195	1145, 568, 963, 566, 579, 1120, 520
$[(CH_3)_2CHCH_2]_2NH$ *diisobutylamine*	O.N.	50° R.T.	$[(CH_3)_2CHCH_2]_2NCH_2CH_2CN$ *3-diisobutylaminopropionitrile*	51	B.P. 116-117°/10 mm.	195	
$(CH_3)_2CHCH_2NHC_4H_9$ *N-butyl-2-methylpropylamine*	O.N.	95°	$(CH_3)_2CHCH_2N[(CH_2)_3CH_3]CH_2CH_2CN$ *3-(butylisobutylamino)propionitrile*	42	B.P. 135-138°/28 mm.	272	
$CH_3CH_2NHSi(CH_2CH_3)_3$ *N,1,1,1-tetraethylsilylamine*	61	77-80°	$(CH_3CH_2)_3SiN(CH_2CH_3)CH_2CH_2CN$ *3-(tetraethylsilylamino)propionitrile*	13.6	B.P. 262-265°/740 mm.	1346	
 $-CH_2NHC_2H_5$ *N-ethylbenzylamine*	10	110°	 $-CH_2N(CH_2CH_3)CH_2CH_2CN$ *3-(benzylethylamino)propionitrile*	94	B.P. 148°/3 mm.	1205	
 $CH_3(CH_2)_3-NH-$ *N-butylcyclopentylamine*	O.N.	95°	 $-N(CH_2CH_2CN)CH_2CH_2CH_2CH_3$ *3-(butylcyclopentylamino)propionitrile*	68	B.P. 142-143°/17 mm.	272	

Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 *N-[(trimethylsilyl)methyl]aniline*	24	130°	 *3-[N-trimethylsilylmethyl)anilino]propionitrile*	68.6	B.P. 199-200°/6 mm.	1346	
$[CH_3(CH_2)_4]_2NH$ *diamylamine*	O.N.	50° R.T.	$[CH_3(CH_2)_4]_2NCH_2CH_2CN$ *3-dipentylaminopropionitrile*	90	B.P. 136°/6 mm.	525	1145, 1120
$[CH_3(CH_2)_5]_2NH$ *dihexylamine*	—	—	$[CH_3(CH_2)_5]_2NCH_2CH_2CN$ *3-dihexylaminopropionitrile*	85	B.P. 145-146°/2 mm.	1145	
$[(C_2H_5)_2NCH_2CH_2CH_2]_2NH$ *3,3′-bis(diethylamino)dipropylamine*	—	—	$[(C_2H_5)_2NCH_2CH_2CH_2]_2NCH_2CH_2CN$ *3-[bis(3-diethylaminopropyl)amino]propionitrile*	70	B.P. 153°/3 mm.	1145	
$[CH_3(CH_2)_7]_2NH$ *dioctylamine*	100.0	steam bath	$[CH_3(CH_2)_7]_2NCH_2CH_2CN$ *3-dioctylaminopropionitrile*	80	B.P. 180-182°/2 mm.	195	
$[CH_3(CH_2)_3CH(C_2H_5)CH_2]_2NH$ *2,2′-diethyldihexylamine*	100.0	steam bath	$[CH_3(CH_2)_3CH(C_2H_5)CH_2]_2NCH_2CH_2CN$ *3-[bis(2-ethylhexyl)amino]propionitrile*	65	B.P. 163-164°/2 mm.	195	

(C) Heterocyclic Amines

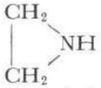
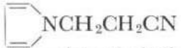
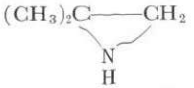
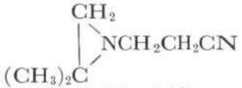
Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	This Exam.	See Also:
 *ethylenimine*	O.N.	R.T.	 *1-aziridinepropionitrile*	90	B.P. 80-82°/10 mm.	113	608
 *pyrrole*	O.N.	steam bath	 *1-pyrrolepropionitrile*	86	B.P. 135-150°/8-10 mm.	273	572, 124, 912
 *2,2-dimethylaziridine*	34.0	reflux	 *2,2-dimethyl-1-aziridinepropionitrile*	66	B.P. 79-83°/8 mm. B.P. 198-199°/752 mm.	1053	

TABLE XIX—Continued

(C) Heterocyclic Amines

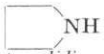
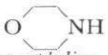
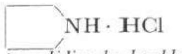
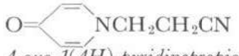
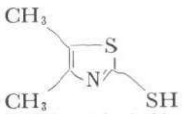
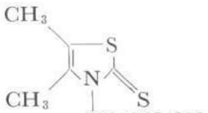
Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 *pyrrolidine*	0.5	100°	 *1-pyrrolidinepropionitrile*	86	B.P. 78-80°/8 mm.	1205	273
 *morpholine*	—	—	 *4-morpholinepropionitrile*	95	B.P. 149°/20 mm.	1145	912
 *pyrrolidine hydrochloride*	72	reflux	 *1-pyrrolidinepropionitrile, hydrochloride*	90	M.P. 168-170°	1280	
 *piperazine*	2.0	40-50°	 *1,4-piperazinedipropionitrile*	—	—	100	912, 572
 *4-pyridone*	5.0	60-65°	 *4-oxo-1(4H)-pyridinepropionitrile*	42.5	M.P. 109-111°	8	
 *4,5-dimethyl-2-thiazolethiol*	11.0	R.T.	 *4,5-dimethyl-2-thioxo-4-thiazoline-3-propionitrile*	22	M.P. 158-159°	1029	
 *piperidine*	4.0	100°	 *1-piperidinepropionitrile*	99	B.P. 114-115°/18 mm.	1069 665	1070, 664, 1079, 1145, 572, 273, 912

TABLE XIX—Continued

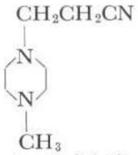
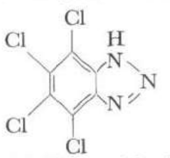
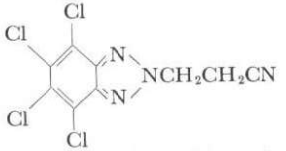
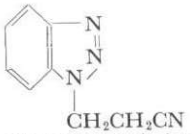
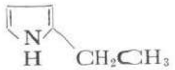
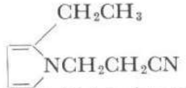
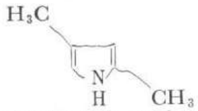
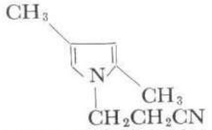
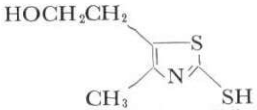
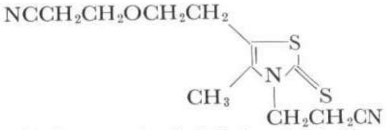
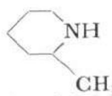
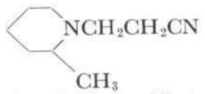
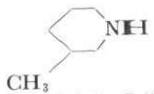
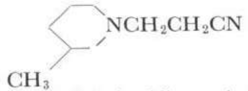
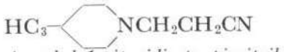
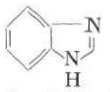
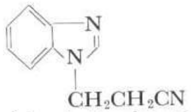
Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 *N-methylpiperazine*	several hours O.N.	reflux 25°	 *4-methyl-1-piperazinepropionitrile*	79.5	B.P. 68-72°/0.3 mm.	1391	
 *4,5,6,7-tetrachlorobenzotriazole*	18	75°	 *4,5,6,7-tetrachloro-2H-benzotriazole-2-propionitrile*	52	M.P. 195-198°	1447	
 *benzotriazole*	5.0	water bath	 *1H-benzotriazole-1-propionitrile*	23-25	M.P. 79-80°	1157	
 *2-ethylpyrrole*	—	—	 *2-ethyl-1-pyrrolepropionitrile*	—	—	912	
 *2,4-dimethylpyrrole*	4.5	40°	 *2,4-dimethyl-1-pyrrolepropionitrile*	58	B.P. 152-153°/18 mm.	1420	

TABLE XIX—Continued

(C) Heterocyclic Amines

Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 *4-methyl-5-(2-hydroxyethyl)-2-thiazolethiol*	10	R.T.	 *5-[2-(2-cyanoethoxy)ethyl]-4-methyl-2-thioxo-4-thiazoline-3-propionitrile*	—	M.P. 62-63°	1181	
 *2-methylpiperidine*	O.N.	steam bath	 *2-methyl-1-piperidinepropionitrile*	99	B.P. 137-140°/30 mm.	273	
 *3-methylpiperidine*	O.N.	steam bath	 *3-methyl-1-piperidinepropionitrile*	97	B.P. 126-128°/28 mm.	273	
 *4-methylpiperidine*	O.N.	steam bath	 *4-methyl-1-piperidinepropionitrile*	87	B.P. 127-130°/27-28 mm.	273	
 *benzimidazole*	2.0 0.5	28-35° 80°	 *1-benzimidazolepropionitrile*	94	M.P. 112°	572	912

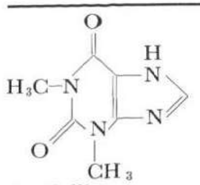
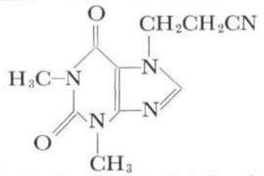
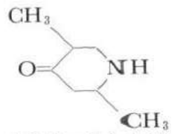
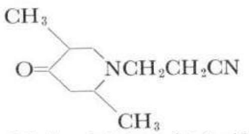
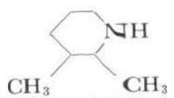
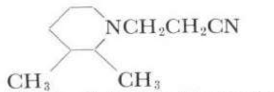
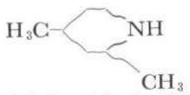
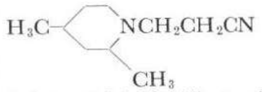
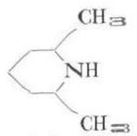
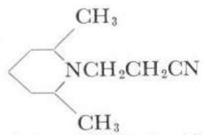
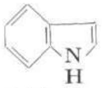
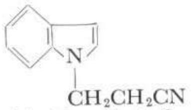
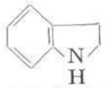
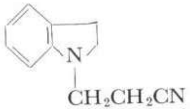
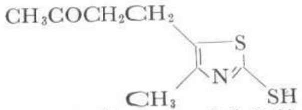
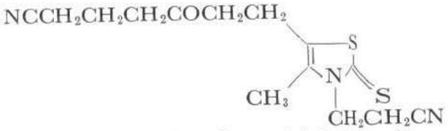
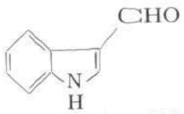
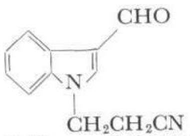
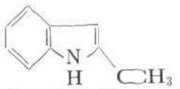
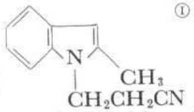
Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References This Exam.	References See Also:
 *theophylline*	—	reflux	 *1,2,3,6-tetrahydro-1,3-dimethyl-2,6-dioxo-7-purinepropionitrile*	~100	M.P. 160°	882	
 *2,5-dimethyl-4-piperidone*	3.0 O.N.	95-97° R.T.	 *2,5-dimethyl-4-oxo-1-piperidinepropionitrile*	96Ⓗ	B.P. 143-145°/5.5 mm.	815	
 *2,3-dimethylpiperidine*	O.N.	steam bath	 *2,3-dimethyl-1-piperidinepropionitrile*	99	B.P. 140-142°/35 mm.	273	
 *2,4-dimethylpiperidine*	O.N.	steam bath	 *2,4-dimethyl-1-piperidinepropionitrile*	68	B.P. 130-133°/29 mm.	273	
 *2,6-dimethylpiperidine*	O.N.	steam bath	 *2,6-dimethyl-1-piperidinepropionitrile*	82	B.P. 121-125°/26-28 mm.	273	

TABLE XIX—Continued

(C) Heterocyclic Amines

Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 *indole*	1-2	exo-thermic	 *1-indolepropionitrile*	95	B.P. 168-180°/3 mm. M.P. 47°	1424	912, 572
 *2,3-dihydroindole*	—	—	 *1-indolinepropionitrile*	—	—	912	
 *4-methyl-5-(2-acetoxyethyl)-2-thiazolethiol*	10.0	R.T.	 *5-[2-(2-cyanoethoxy)ethyl]-4-methyl-2-thioxo-4-thiazoline-3-propionitrile*	20.2	M.P. 62-63°	1181	
 *3-indolecarboxaldehyde*	24.0	R.T.	 *1-(2-cyanoethyl)-3-indolecarboxaldehyde*	68.2	M.P. 127-127.5°	124	
 *2-methylindole*	12	130°	①  *2-methyl-1-indolepropionitrile*	74	B.P. 180-194°/2 mm. M.P. 82°	572	912

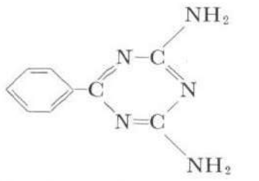
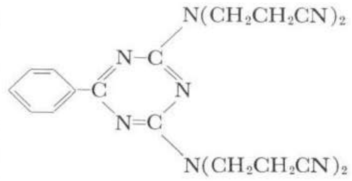
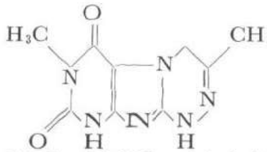
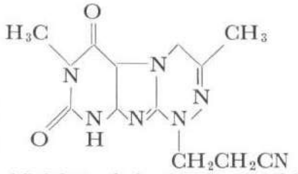
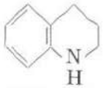
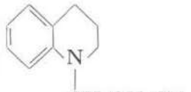
Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 *2,4,diamino-6-phenyl-s-triazine*	1.0	75°	 *2,4-bis[bis(2-cyanoethyl)amino]-6-phenyl-s-triazine*	98	M.P. 162-163°	826	
 *3,7-dimethyl-1H-as-triazino[4,3-f]purine-6,8(7H,9H)-dione*	0.3	reflux	 *6,7,8,9-tetrahydro-3,7-dimethyl-6,8-dioxo-1H-as-triazino[4,3-f]purine-1-propionitrile*	60	M.P. 210-211°	1454	
 *1,2,3,4-tetrahydroquinoline*	3.0 6.0	108-125° reflux	 *3,4-dihydro-1(2H)-quinolinepropionitrile*	75.5	B.P. 192°/10 mm.	1145	740, 573, 912
 *1,2,3,4-tetrahydroisoquinoline*	—	—	 *3,4-dihydro-2(1H)-isoquinolinepropionitrile*	—	—	912	

TABLE XIX—Continued

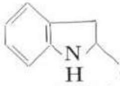
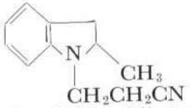
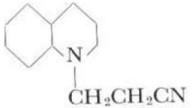
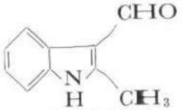
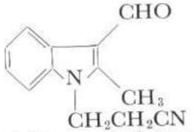
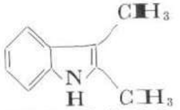
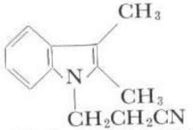
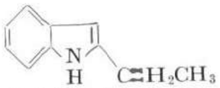
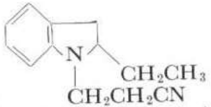
Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 2-methyl-2,3-dihydroindole	—	120-140°	 2-methyl-1-indolinepropionitrile	—	B.P. 140-142°/1 mm.	573	912
 decahydroquinoline	2.0	200°	 octahydro-1(2H)-quinolinepropionitrile	61	B.P. 160-167°/15 mm.	572	912
 2-methyl-3-indolecarboxaldehyde	24.0	R.T.	 1-(2-cyanoethyl)-2-methyl-3-indolecarboxaldehyde	—	M.P. 148-149°	124	
 2,3-dimethylindole	12.0	130-140°	 2,3-dimethyl-1-indolepropionitrile	83.5	M.P. 80°	572	912
 2-ethylindole	—	—	 2-ethyl-1-indolepropionitrile	—	—	912	

TABLE XIX—Continued

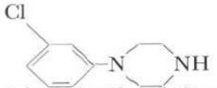
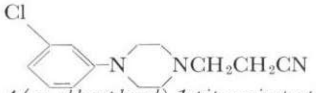
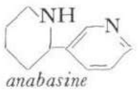
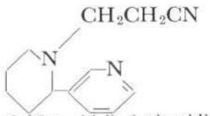
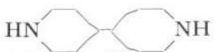
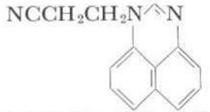
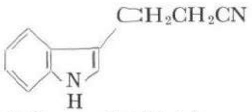
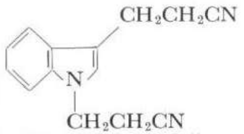
Reactants	Reaction Time (Hr.)	Reaction Temperature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References: This Exam.	References: See Also:
 1-(m-chlorophenyl)piperazine	—	—	 4-(m-chlorophenyl)-1-piperazinepropionitrile	48.7	B.P. 210.6-212.6°/ 1.3 mm.	881	
 1-phenylpiperazine	1.5	55°	 4-phenyl-1-piperazinepropionitrile	86	M.P. 71.3-72.1°	881	
 anabasine	0.5	50-60°	 2-(3-pyridyl)-1-piperidinepropionitrile	95-98	B.P. 163-165°/0.5 mm. B.P. 172-173°/2 mm. B.P. 212-215°/10 mm.	1090	
 4,4′-bipiperidirze	1.75	reflux	 [4,4′-bipiperidine]-1,1′-dipropionitrile	—	M.P. 109°	433	
 perimidine	1.50	reflux	 1-perimidinepropionitrile	—	M.P. 136-139°	572	912
 3-(2-cyanoethyl)indole	1.2	exothermic	 1,3-indoledipropionitrile	97	M.P. 96-97°	1424	912

TABLE XIX—Continued

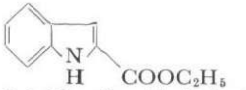
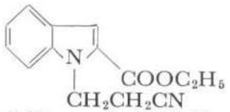
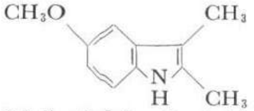
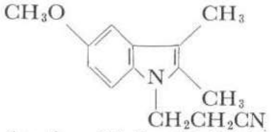
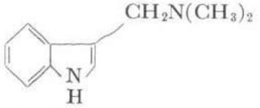
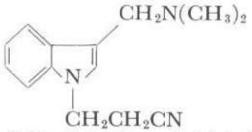
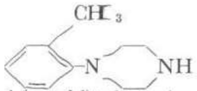
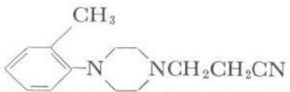
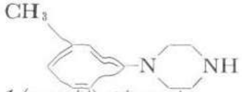
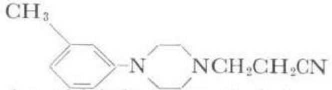
Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 *2-indoleacetic acid, ethyl ester*	O.N.	50°	 *1-(2-cyanoethyl)-2-indolecarboxylic acid, ethyl ester*	90	M.P. 86-87°	102	
 *2,3-dimethyl-5-methoxyindole*	1.0 1.0	120-130° 140°	 *5-methoxy-2,3-dimethyl-1-indolepropionitrile*	81.3	M.P. 93°	572	
 *gramine*	O.N.	50°	 *3-dimethylaminomethyl-1-indolepropionitrile*	90	M.P. of picrate 140-142°	102	
 *1-(o-tolyl)piperazine*	—	—	 *4-o-tolyl-1-piperazinepropionitrile*	~100	M.P. 78.4-79.4°	881	
 *1-(m-tolyl)piperazine*	—	—	 *4-m-tolyl-1-piperazinepropionitrile*	77.5	B.P. 197-199°/1.3 mm.	881	

TABLE XIX—Continued

(C) Heterocyclic Amines

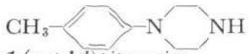
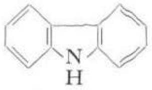
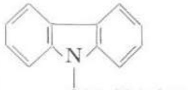
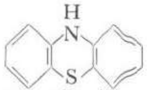
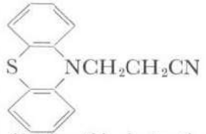
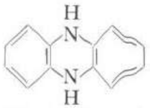
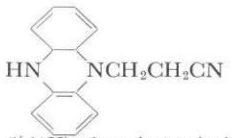
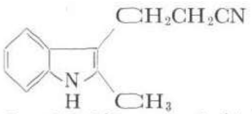
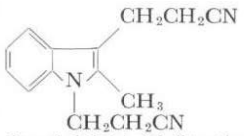
Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 *1-(p-tolyl)piperazine*	—	—	 *4-p-tolyl-1-piperazinepropionitrile*	86.0	M.P. 70.4-71.4°	881	
 *carbazole*	—	0°	 *9-carbazolepropionitrile*	89	M.P. 156.5°	1077	1145, 572, 912
 *phenothiazine*	0.5	0-5° reflux	 *10-phenothiazinepropionitrile*	92	M.P. 156-157°	1270	264
 *dihydrophenazine*	—	—	 *5(10H)-phenazinepropionitrile*	—	—	264	
 *2-methyl-3-(2- cyanoethyl)indole*	—	—	 *2-methyl-1,3-indoledipropionitrile*	—	—	912	

TABLE XIX—Continued

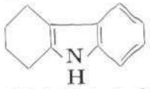
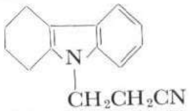
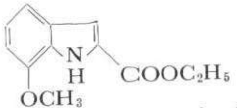
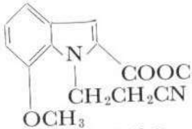
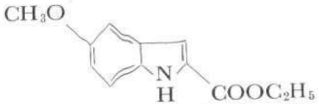
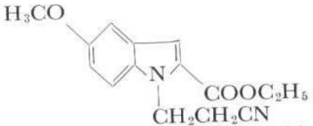
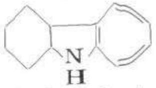
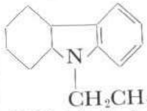
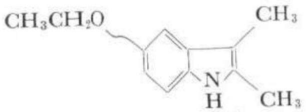
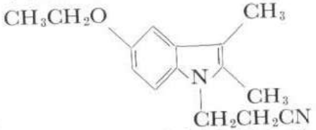
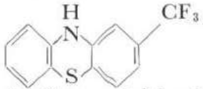
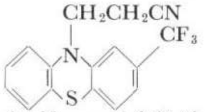
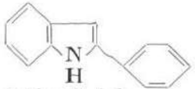
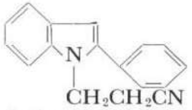
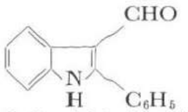
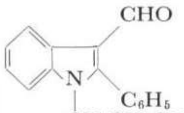
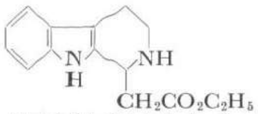
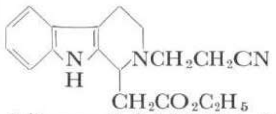
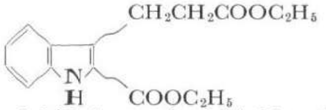
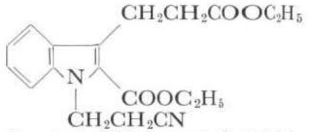
Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References This Exam.	References See Also:
 *1,2,3,4-tetrahydrocarbazole*	1.0	—	 *1,2,3,4-tetrahydro-9-carbazolepropionitrile*	53	M.P. 115-116°	1006	
 *7-methoxy-2-indolecarboxylic acid, ethyl ester*	O.N.	50°	 *1-(2-cyanoethyl)-7-methoxy-2-indolecarboxylic acid, ethyl ester*	72	M.P. 110-112°	102	
 *5-methoxy-2-indolecarboxylic acid, ethyl ester*	O.N.	50°	 *1-(2-cyanoethyl)-5-methoxy-2-indolecarboxylic acid, ethyl ester*	82.7	M.P. 112°	102	
 *1,2,3,4,4a,9a—hexahydrocarbazole*	—	120-140°	 *1,2,3,4,4a,9a-hexahydro-9-carbazolepropionitrile*	—	B.P. 180-200°/2 mm.	573	912
 *2,3-dimethyl—5-ethoxyindole*	—	—	 *5-ethoxy-2,3-dimethyl-1-indolepropionitrile*	—	—	912	

TABLE XIX—Continued

Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 2-trifluoromethylphenothiazine	1.0	steam bath	 2-trifluoromethyl-10-phenothiazinepropionitrile	67	M.P. 159.5-160°	1007	
 2-phenylindole	2-3.0	reflux	 ① 2-phenyl-1-indolepropionitrile	~100	M.P. 90°	572	1077, 124, 912
 2-phenyl-3-indolecarboxaldehyde	3 days	R.T.	 1-(2-cyanoethyl)-2-phenyl-3-indolecarboxaldehyde	90	M.P. 155-156.5°	124	
 ethyl 1,2,3,4-tetrahydro-β-carboline-1-acetate	18.0	reflux	 2-(2-cyanoethyl)-1,2,3,4-tetrahydro-9H-pyrid[3,4-b]-indole-1-acetic acid, ethyl ester	39	M.P. 179.5-180.5°	452	
 ethyl (2-ethoxycarbonyl-3-indolepropionate	10.0	R.T.	 2-carboxy-1-(2-cyanoethyl)-3-indolepropionic acid, diethyl ester	80	M.P. 70-71°	1326	

(C) Heterocyclic Amines

TABLE XIX—Continued

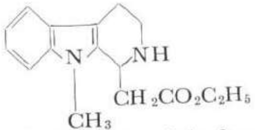
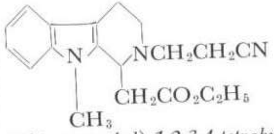
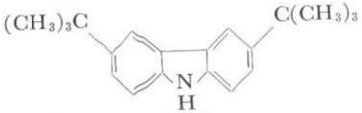
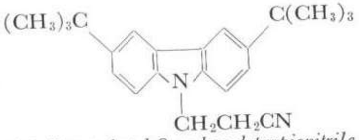
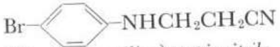
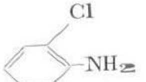
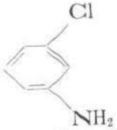
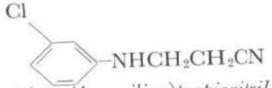
Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 *ethyl 1,2,3,4-tetrahydro-9-methyl-β-carboline-1-acetate*	20.0	115° (sealed tube)	 *2-(2-cyanoethyl)-1,2,3,4-tetrahydro-9-methyl-9H-pyrid-[3,4-b]indole-1-acetic acid, ethyl ester*	8	M.P. 116-117°	452	
 *3,6-di-t-butylcarbazole*	1.0	steam bath	 *3,6-di-*tert-*butyl-9-carbazolepropionitrile*	59	M.P. 190-190.5°	1006	
(D) Aromatic Amines							
 p-*bromoaniline*	1.0	reflux	 3-(p-*bromoanilino*)*propionitrile*	96	M.P. 96.5-97.5°	1279	
 o-*chloroaniline*	3.0	reflux	 3-(o-*chloroanilino*)*propionitrile*	62	B.P. 139-141°/0.3 mm.	1279	1282
 m-*chloroaniline*	2.0	reflux	 3-(m-*chloroanilino*)*propionitrile*	65	B.P. 146-149°/0.3 mm. M.P. 48-49°	1279	

TABLE XIX—Continued

(D) Aromatic Amines

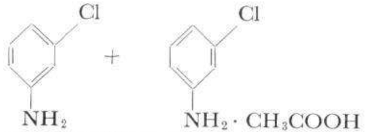
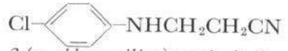
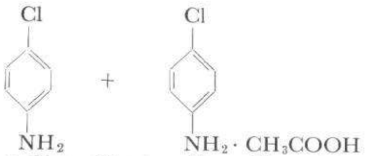
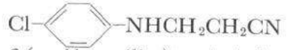
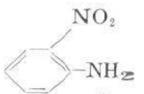
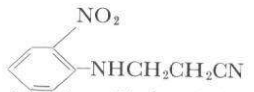
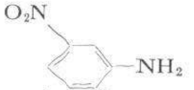
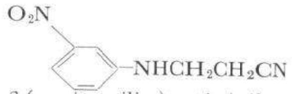
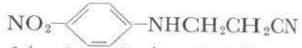
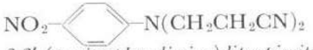
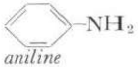
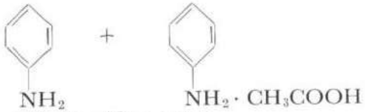
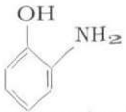
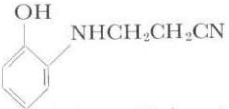
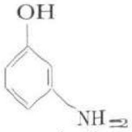
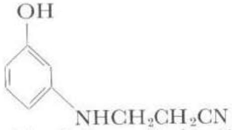
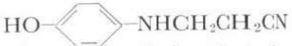
Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 m-*chloroaniline* + m-*chloroaniline acetate*	14.0	130-140°	 *3-(*m-*chloroanilino)propionitrile*	81	B.P. 187-189°/9 mm. M.P. 48°	101	
 p-*chloroaniline*	1.25	reflux	 *3-(*p-*chloroanilino)propionitrile*	78	B.P. 168-169°/1.0 mm. M.P. 73.5-75°	1279	101, 1206
 p-*chloroaniline* + p-*chloroaniline acetate*	14.0	130-140°	 *3 (*p-*chloroanilino)propionitrile*	72	M.P. 72-73° B.P. 182-185°/4 mm.	101	137, 136, 135
 o-*nitroaniline*	12.0	reflux	 *3-(*o-*nitroanilino)propionitrile*	—	—	1279	
 m-*nitroaniline*	12.0	reflux	 *3-(*m-*nitroanilino)propionitrile*	81	M.P. 95-96°	1279	137
 p-*nitroaniline*	12.0	reflux	 *3-(*p-*nitroanilino)propionitrile*	6	M.P. 128-130°	136	1279

TABLE XIX—Continued

Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 p-*nitroaniline*	18.0	40° 25°	 *3,3′-(p-nitrophenylimino)dipropionitrile*	69.7	M.P. 163-164°	1219	
 *aniline*	1.0	reflux	 *3-anilinopropionitrile*	73	B.P. 114-116°/0.3 mm. M.P. 52-53°	1279	1206, 1409
 *aniline + aniline acetate*	14.0	120-140°	 *3-anilinopropionitrile*	98	B.P. 160°/6 mm. M.P. 40°	101	1008, 136, 135, 270, 885, 963, 1418
 o-*aminophenol*	24.0	reflux	 3-(o-*hydroxyanilino)propionitrile*	78	M.P. 110-111°	1279	
 m-*aminophenol*	24.0	reflux	 3-(m-*hydroxyanilino)propionitrile*	69	—	1279	
 p-*aminophenol*	24.0	reflux	 3-(p-*hydroxyanilino)propionitrile*	22	M.P. 86-88°	1279	

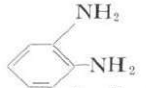
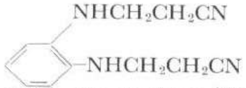
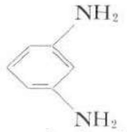
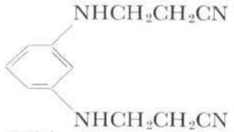
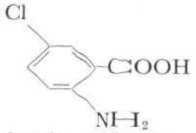
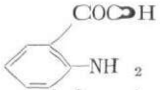
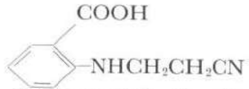
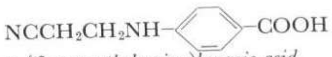
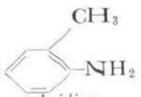
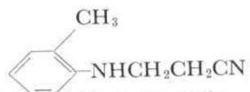
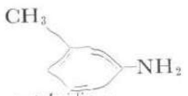
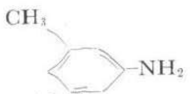
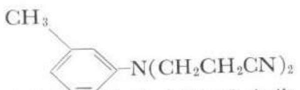
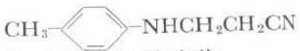
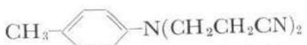
Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 o-*phenylenediamine*	14.0	reflux	 *3,3′-(*o-*phenylenediimino)dipropionitrile*	63	M.P. 115-118°	1279	1205, 136
 m-*phenylenediamine*	0.67	reflux	 *3,3′-(*m-*phenylenediimino)dipropionitrile*	95	—	1279	
 p-*phenylenediamine*	—	—	 *3,3′-(*p-*phenylenediimino)dipropionitrile*	22	M.P. 140°	699	1205
 p-*phenylenediamine*	14.0	120° (pressure)	 *3,3′,3″,3‴-(*p-*phenylenedinitrilo)tetrapropionitrile*	83	M.P. 141-142°	136	699
 *2-amino-5-chlorobenzoic acid*	—	—	 *5-chloro-N-(2-cyanoethyl)anthranilic acid*	89.7	—	1207	
 o-*aminobenzoic acid*	—	—	 *N-(2-cyanoethyl)anthranilic acid*	89.7	M.P. 169.5°	1207	1384

TABLE XIX—Continued

Reactants	Reaction Time (Hr.)	Reaction Temperature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References: This Exam.	References: See Also:
 p-aminobenzoic acid	7.0	150° (pressure)	 p-(2-cyanoethylamino)benzoic acid	35	M.P. 221.5-222.5°	136	
 o-toluidine	12.0	reflux	 3-o-toluidinopropionitrile	65	B.P. 125-126°/0.2 mm.	136	1279
			 3,3'-(o-tolylimino)dipropionitrile	35	B.P. 173°/0.2 mm.		
 m-toluidine	0.33	reflux	 3-m-toluidinopropionitrile	71	B.P. 143-146°/0.5 mm. M.P. 49.5-50.5°	1279	
 m-toluidine	20.0	reflux	 3,3'-(m-tolylimino)dipropionitrile	75	M.P. 87-88°	136	135
 p-toluidine	12.0	reflux	 3 p-toluidinopropionitrile	56	B.P. 148-155°/1.0 mm. M.P. 103.5-105°	1279	135, 136, 1206
			 3,3'-(p-tolylimino)dipropionitrile	36	M.P. 61-62°		

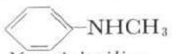
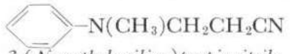
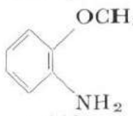
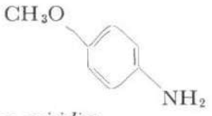
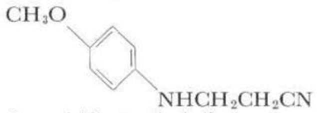
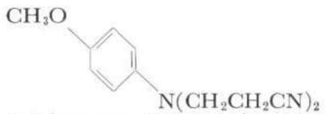
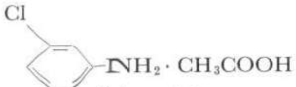
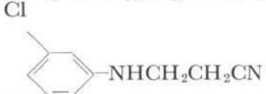
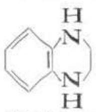
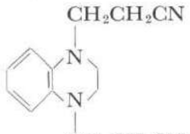
Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 *N-methylaniline*	22.0	reflux	 *3-(N-methylanilino)propionitrile*	84	B.P. 170-171°/19 mm.	1279	1145, 573, 25
 o-*anisidine*	18.0	reflux	 *3-*o*-anisidinopropionitrile*	33	B.P. 140-141°/1.0 mm.	1279	
 p-*anisidine*	15.0	reflux	 *3-*p*-anisidinopropionitrile*	84	B.P. 154-155°/0.8 mm. M.P. 59-61°	1279	135, 136, 359, 1206 1244
			 *3,3′-(*p*-methoxyphenylimino)dipropionitrile*	14	B.P. 210-211°/0.7 mm. M.P. 100-101°		
 m-*chloroaniline acetate*	14.0	120-140°	 *3-(*m*-chloroanilino)propionitrile*	Ⓙ 81	B.P. 187-189°/9 mm. M.P. 48°	101	
 *1,2,3,4-tetrahydroquinoxaline*	7.0	reflux	 *2,3-dihydro-1,4-quinoxalinedipropionitrile*	80	M.P. 88.5-89°	26	

TABLE XIX—Continued

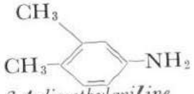
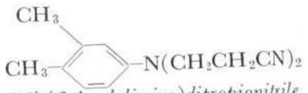
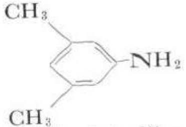
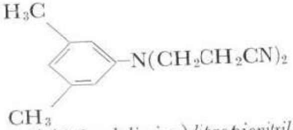
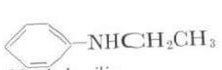
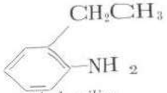
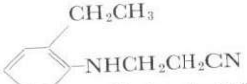
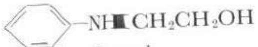
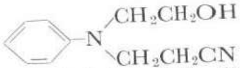
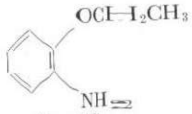
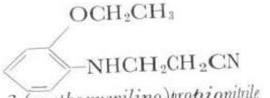
Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References: This Exam.	References: See Also:
 *3,4-dimethylaniline*	12.0	reflux	 *3,3′-(3,4-xylylimino)dipropionitrile*	11	M.P. 84°	136	
 *3,5-dimethylaniline*	4.0	reflux	 *3,3′-(3,5-xylylimino)dipropionitrile*	79	M.P. 130°	1292	
 *N-ethylaniline*	100.0	100°	 *3-(N-ethylanilino)propionitrile*	70	—	664	1078, 1077, 665, 520, 566, 568, 519, 1279
 *o-ethylaniline*	12.0	reflux	 *3-(o-ethylanilino)propionitrile*	53	B.P. 125-132°/0.3 mm.	1279	
 *2-anilinoethanol*	150.0	reflux	 *3-[N-(2-hydroxyethyl)anilino]propionitrile*	91	B.P. 305-307°/8 mm.	327	
 *o-phenetidine*	22.0	reflux	 *3-(o-ethoxyanilino)propionitrile*	45	B.P. 141-143°/0.7 mm.	1279	912

TABLE XIX—Continued

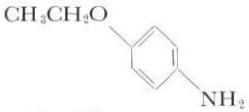
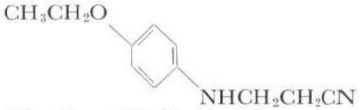
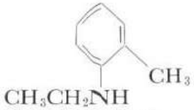
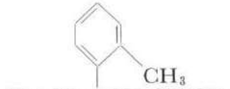
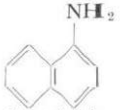
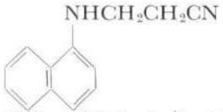
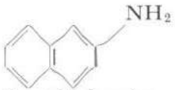
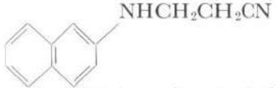
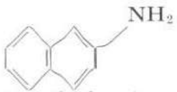
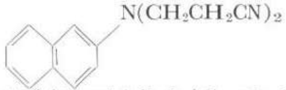
Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 p-*phenetidine*	22.0	reflux	 *3-(*p-*ethoxyanilino)propionitrile*	90	B.P. 165-166°/0.7 mm. M.P. 73-75°	1279	912, 1206
 *N-ethyl-*o-*toluidine*	—	—	 *3-(N-ethyl-*o-*toluidino)propionitrile*	—	—	912	
 *1-naphthylamine*	5.5	reflux	 *3-(1-naphthylamino)propionitrile*	89	B.P. 180-210°/0.5 mm. M.P. 69-70°	1279	
 *2-naphthylamine*	4.0	reflux	 *3-(2-naphthylamino)propionitrile*	—	M.P. 99-100°	137	
 *2-naphthylamine*	12.0	reflux	 *3,3′-(2-naphthylimino)dipropionitrile*	25-35	M.P. 127.5-128.5°	136	136
 *N-*n-*butylaniline*	5.0	reflux	 *3-(N-butylanilino)propionitrile*	68	B.P. 145-148°/0.7 mm.	1279	912

TABLE XIX—Continued

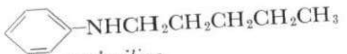
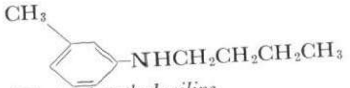
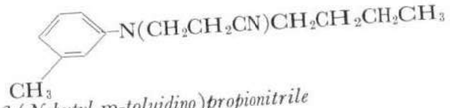
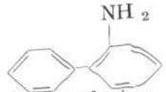
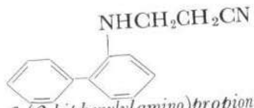
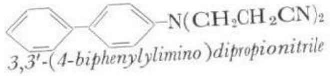
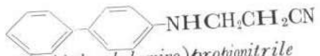
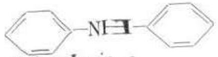
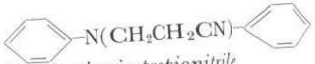
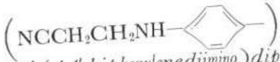
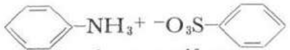
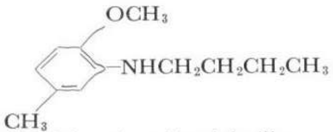
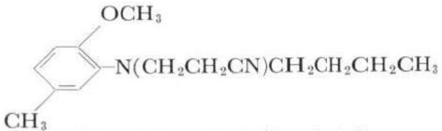
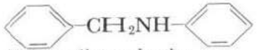
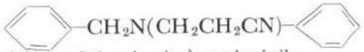
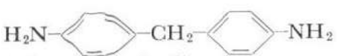
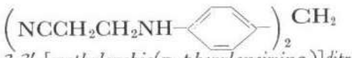
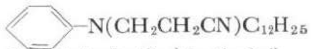
Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 *N*-n-amylaniline	3.0	reflux	 3-(*N*-pentylanilino)propionitrile	66	B.P. 172-180°/0.8 mm.	1279	
 *N*-butyl-3-methylaniline	—	—	 3-(*N*-butyl-m-toluidino)propionitrile	—	—	912	
 2-biphenylamine	12.0	reflux	 3-(2-biphenylylamino)propionitrile	65	M.P. 86°	136	
 4-biphenylamine	12.0	reflux	 3,3′-(4-biphenylylimino)dipropionitrile	80	M.P. 165.5-166°	136	1279
 4-biphenylamine	4.0	150° (sealed tube)	 3-(4-biphenylylamino)propionitrile	13	M.P. 174-177°	90	
 diphenylamine	8.0	150°	 3-diphenylaminopropionitrile	22.8	B.P. 133°/0.05 mm. M.P. 41°	270	
 benzidine	8.0	reflux	 3,3′-(4,4′-biphenylenediimino)dipropionitrile	~100	M.P. 245-245.5°	136	1279

TABLE XIX—Continued

(D) Aromatic Amines

Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 *anilinium benzene sulfonate*	1.0	180°	$(C_2H_5)_2NCH_2CH_2CN$ *3-diethylaminopropionitrile*  *3-anilinopropionitrile*	— 2.5	B.P. 35-40°/0.07 mm. B.P. 120-125°/0.07 mm.	90	
 *N-butyl-2-methoxy-5-methylaniline*	—	120-140°	 *3-(N-butyl-5-methyl-o-anisidino)propionitrile*	—	B.P. 160-165°/2 mm.	573	912
 *N-phenylbenzylamine*	—	—	 *3-(benzylphenylamino)propionitrile*	—	—	912	
 *4,4′-methylenedianiline*	3.0	reflux	 *3,3′-[methylenebis(p-phenyleneimino)]dipropionitrile*	96	M.P. 115-117°	1279	
 *N-dodecylaniline*	3.0	reflux	 *3-(N-dodecylanilino)propionitrile*	64	B.P. 197-202°/0.3 mm.	1279	

(E) Amino Acids and Derivatives

Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	This Exam.	See Also:
$HO_2CCH_2NH_2$ *glycine*	18.0 2.0	25° 50°	$HO_2CCH_2N(CH_2CH_2CN)_2$ *N,N-bis(2-cyanoethyl)glycine*	90	M.P. 77.8-78.8°	729 726	
$HO_2CCH_2NH_2$ *glycine*	O.N.	R.T.	$HO_2CCH_2NHCH_2CH_2CN$ *N-(2-cyanoethyl)glycine*	87	M.P. 190-191° (dec.)	728 726	

TABLE XIX—Continued

Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
$CH_3OCOCH_2NH_2$ *glycine, methyl ester*	72.0 5.0	25° reflux	$CH_3OCOCH_2NHCH_2CH_2CN$ *N-(2-cyanoethyl)glycine, methyl ester*	55.2	B.P. 142-143°/12 mm.	1062	
$CH_3CH(NH_2)COOH$ *dl-alanine*	18.0 4.0	25° 50°	$HOOCCH(CH_3)N(CH_2CH_2CN)_2$ *N,N-bis(2-cyanoethyl)alanine*	97	M.P. 75.5-76.8°	729 726	728
$CH_3CH(NH_2)COOH$ *dl-alanine*	O.N.	R.T.	$HOOCCH(CH_3)NHCH_2CH_2CN$ *N-(2-cyanoethyl)-dl-alanine*	82.5	M.P. 249-250° (dec.)	728 726	
$HOCH_2CH(NH_2)COOH$ *dl-serine*	—	50°	$NCCH_2CH_2OCH_2CH(NHCH_2CH_2CN)COOH$ *3-(2-cyanoethoxy)-N-(2-cyanoethyl)-dl-alanine*	51	M.P. 210-215° (dec.)	1453	
$CH_3OCOCH_2NH_2 \cdot HCl$ *glycine, methyl ester, hydrochloride*	10.0	75°	$CH_3OCOCH_2NHCH_2CH_2CN$ *N-(2-cyanoethyl)glycine, methyl ester*	17.8	—		
			$CH_3OCOCH_2N(CH_2CH_2CN)_2$ *N,N-bis(2-cyanoethyl)glycine, methyl ester*	21.9	B.P. 218-219°/12 mm. M.P. 59.5-60°	1062	
$KO_2CCH_2CH(NH_2)CO_2K$ *dipotassium dl-aspartate*	18.0 2.0	25° 50°	$KO_2CCH_2CH(NHCH_2CH_2CN)CO_2K$ *N-(2-cyanoethyl)-dl-aspartic acid, dipotassium salt*	~100	—	728 726	729
$HO_2CCH(NH_2)CH_2CO_2H$ *dl-aspartic acid*	18.0 4.0	25° reflux	$HO_2CCH[N(CH_2CH_2CN)_2]CH_2CO_2H$ *N,N-bis(2-cyanoethyl)-dl-aspartic acid*	88	M.P. 136-137°	729 726	
$HO_2CCH_2NHCOCH_2NH_2$ *glycylglycine*	18.0	R.T.	$HO_2CCH_2NHCOCH_2NHCH_2CH_2CN$ *N-[N-(2-cyanoethyl)glycyl]glycine*	78.5	M.P. 144°	1063	
$C_2H_5OCOCH_2NH_2$ *glycine, ethyl ester*	72.0 5.0	25° reflux	$C_2H_5OCOCH_2NHCH_2CH_2CN$ *N-(2-cyanoethyl)glycine, ethyl ester*	70.5	B.P. 148-149/12 mm.	1062	254
$C_2H_5OCOCH_2NH_2$ *glycine, ethyl ester*	10.0	75°	$C_2H_5OCOCH_2NHCH_2CH_2CN$ *N-(2-cyanoethyl)glycine, ethyl ester*	23.2	—	1062	
			$C_2H_5OCOCH_2N(CH_2CH_2CN)_2$ *N,N-bis(2-cyanoethyl)glycine, ethyl ester*	29.3	B.P. 221-222°/12 mm.		

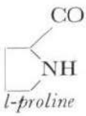
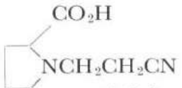
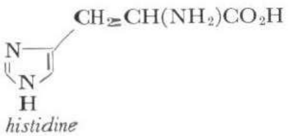
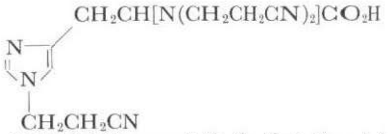
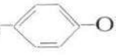
Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
$KO_2CCH_2CH_2CH(NH_2)CO_2K$ *dipotassium l-glutamate*	24.0	25°	$KO_2CCH_2CH_2CH(NHCH_2CH_2CN)COOK$ *N-(2-cyanoethyl)glutamic acid, dipotassium salt*	~100	—	728 726	
 *l-proline*	48.0	25°	 *1-(2-cyanoethyl)-l-proline*	17	M.P. 137-140°	728 726	
$HO_2CCH_2CH_2CH(NH_2)CO_2H$ *glutamic acid*	24.0	25°	$HO_2CCH_2CH_2CH(NHCH_2CH_2CN)CO_2H$® *N-(2-cyanoethyl)glutamic acid*	>97	—	727	
$HO_2CCH(NH_2)CH_2CH_2CO_2H$ *l-glutamic acid*	18.0 20.0	25° 60°	$HO_2CCH[N(CH_2CH_2CN)_2]CH_2CH_2CO_2H$ *N,N-bis(2-cyanoethyl)-l-glutamic acid*	88.4	M.P. 71.5-72.8°	729	728
$HO_2CCH(NH_2)CH(CH_3)_2$ *dl-valine*	18 20	25° reflux	$HO_2CCH[N(CH_2CH_2CN)_2]CH(CH_3)_2$ *N,N-bis(2-cyanoethyl)-dl-valine*	84	M.P. 54-55°	729	
$HO_2CCH(NH_2)CH(CH_3)_2$ *dl-valine*	O.N.	R.T.	$(CH_3)_2CHCH(NHCH_2CH_2CN)COOH$ *N-(2-cyanoethyl)-dl-valine*	—	M.P. 252-253° (dec.)	728	
$HO_2CCH(NH_2)CH_2CH_2SCH_3$ *dl-methionine*	18.0 2.0	25° 50-60°	$HO_2CCH(NHCH_2CH_2CN)CH_2CH_2SCH_3$ *N-(2-cyanoethyl)-dl-methionine*	98	M.P. 246-247° (dec.)	728	
$HO_2CCH(NH_2)CH_2CH_2SCH_3$ *dl-methionine*	18.0 19.0	25° reflux	$HO_2CCH[N(CH_2CH_2CN)_2]CH_2CH_2SCH_3$ *N,N-bis(2-cyanoethyl)-dl-methionine*	91	M.P. 65-66°	729	
$CH_3CH(NH_2)COOC_2H_5 \cdot HCl$ *alanine hydrochloride, ethyl ester*	4-5	65-70°	$CH_3CH(NHCH_2CH_2CN)COOC_2H_5$ *N-(2-cyanoethyl)alanine, ethyl ester*	68	B.P. 157-158°/20 mm.	1417	
 *histidine*	18.0 2.0	25° 50-60°	 *N,N,1-tris(2-cyanoethyl)-4(or 5)-imidazolealanine*	70	M.P. 184-186°	729	728

TABLE XIX—Continued

(E) Amino Acids and Derivatives

Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References This Exam.	References See Also:
$HO_2CCH(NH_2)CH_2CH(CH_3)_2$ *l-leucine*	18.0 12.0	25° reflux	$HO_2CCH[N(CH_2CH_2CN)_2]CH_2CH(CH_3)_2$ *N,N-bis(2-cyanoethyl)-l-leucine*	95	M.P. 64-65°	729	
$HO_2CCH(NH_2)CH_2CH(CH_3)_2$ *l-leucine*	O.N. 2.0	R.T. reflux	$(CH_3)_2CHCH_2CH(NHCH_2CH_2CN)COOH$ *N-(2-cyanoethyl)-l-leucine*	75	M.P. 249-250° (dec.)	728 726	
$CH_3CH_2CH(CH_3)CH(NH_2)COOH$ *dl-isoleucine*	O.N. 2.0	R.T. reflux	$CH_3CH_2CH(CH_3)CH(NHCH_2CH_2CN)COOH$ *N-(2-cyanoethyl)-dl-isoleucine*	86	M.P. 211-212° (dec.)	728	
$NaO_2CCH(NH_2)CH_2$--OH *tyrosine, monosodium salt*	18.0 28.0	25° reflux	$HO_2CCH[N(CH_2CH_2CN)_2]CH_2$--OH *N,N-bis(2-cyanoethyl)tyrosine*	—	M.P. 123-124°	729	
$HO_2CCH(NH_2)CH_2$--OH *l-tyrosine*	O.N. 2.0	R.T. reflux	$HO_2CCH(NHCH_2CH_2CN)CH_2$--OH *N-(2-cyanoethyl)-l-tyrosine*	93	M.P. 238-239° (dec.)	728 726	
-$CH_2CH(NH_2)COOH$ *dl-phenylalanine*	O.N.	R.T.	-$CH_2CH(NHCH_2CH_2CN)COOH$ *N-(2-cyanoethyl)-3-phenyl-dl-alanine*	92	M.P. 228-230° (dec.)	728 726	
$C_2H_5OCOCH(NH_2)CH_2$- *phenylalanine, ethyl ester*	5.0	75°	$C_2H_5OCOCH(NHCH_2CH_2CN)CH_2$- *N-(2-cyanoethyl)-3-phenylalanine, ethyl ester*	78.5	B.P. 191-192°/8 mm.	1062	
R–CH(NH_2)COOH ① *crude mixture of amino acids*	2.0 4.0	R.T. reflux	$RCH(NHCH_2CH_2COOH)COOH$	89	—	730	

(F) Miscellaneous Amino Compounds

Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References This Exam.	References See Also:
$NCNH_2$ *cyanamide*	—	reflux	$NCN(CH_2CH_2CN)_2$ *3,3′-(cyanoimino)dipropionitrile*	98	M.P. 54°	485	
$(NCNH)(NH_2)C{=}NH$ *cyanoguanidine (or dicyandiamide)*	3.0	reflux	*resinous syrup*	—	—	486 487	

TABLE XIX—Continued

(F) Miscellaneous Amino Compounds

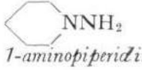
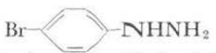
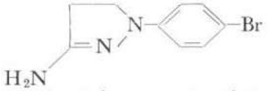
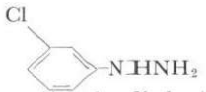
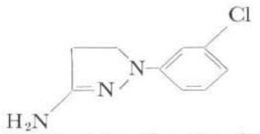
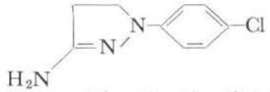
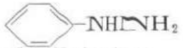
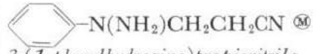
Reactants	Reaction Time (Hr.)	Reaction Temperature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References: This Exam.	References: See Also:
$(CH_3)_2NNH_2$ unsym-*dimethylhydrazine*	2.0	reflux	$(CH_3)_2NNHCH_2CH_2CN$ *3-(2,2-dimethylhydrazino)propionitrile*	87	B.P. 80-90°/3 mm.	1285	
$(CH_3)_2C{=}NNH_2$ *acetone hydrazone*	0.5 24	40-45° reflux	$(CH_3)_2C{=}NNHCH_2CH_2CN$ *acetone, 2-cyanoethylhydrazone*	40.7	B.P. 123-127°/23 mm.	1283	
$(CH_3)_2CHCH{=}NNH_2$ *isobutyraldehyde hydrazone*	0.5 24	40-45° reflux	$(CH_3)_2CHCH{=}NNHCH_2CH_2CN$ *isobutyraldehyde, 2-cyanoethylhydrazone*	—	—	1283	
 *1-aminopiperidine*	—	—	 *3-(piperidinoamino)propionitrile*	—	—	264	
 p-*bromophenylhydrazine*	6.0	reflux	 *3-amino-1-*(p-*bromophenyl)-2-pyrazoline*	—	M.P. 121°	1301	
 m-*chlorophenylhydrazine*	4.0	reflux	 *3-amino-1-*(m-*chlorophenyl)-2-pyrazoline*	—	M.P. 142°	1301	
 p-*chlorophenylhydrazine*	6.0	reflux	 *3-amino-1-*(p-*chlorophenyl)-2-pyrazoline*	42	M.P. 135°	345	1301
 *phenylhydrazine*	1.0	water bath	 *3-(1-phenylhydrazino)propionitrile*	—	—	870	1374

TABLE XIX—Continued

(F) Miscellaneous Amino Compounds

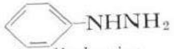
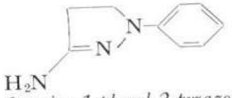
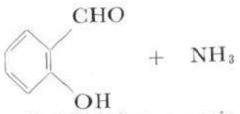
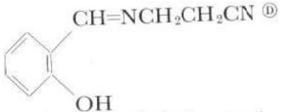
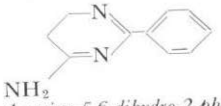
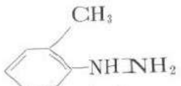
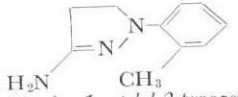
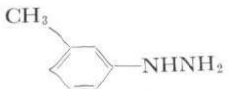
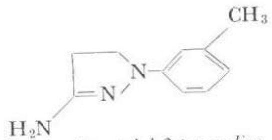
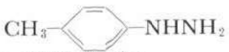
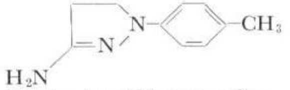
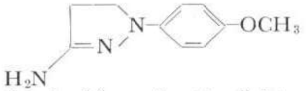
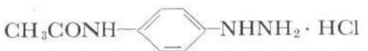
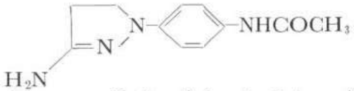
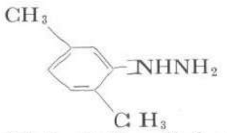
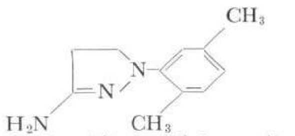
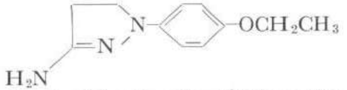
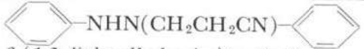
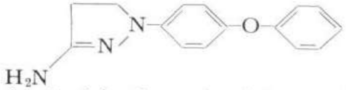
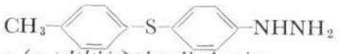
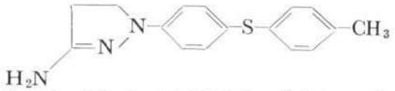
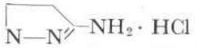
Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 *phenylhydrazine*	2.0	water bath	 *3-(2-phenylhydrazino)propionitrile*	74	B.P. 199°/3 mm.	870	345, 1375, 1281
 *phenylhydrazine*	6.0	reflux	 *3-amino-1-phenyl-2-pyrazoline*	74	M.P. 169°	345	1301
 *salicylaldehyde + ammonia*	0.5 0.5 several days	25° steam bath 25°	 *α-(2-cyanoethylimino)-o-cresol*	6	M.P. 74-75°	1059	
 *benzamidine*	8.0	—	 *4-amino-5,6-dihydro-2-phenylpyrimidine*	55	M.P. 177°	870	1374
 *o-tolylhydrazine*	6.0	reflux	 *3-amino-1-o-tolyl-2-pyrazoline*	8.5	M.P. 74°	345	1301
 *m-tolylhydrazine*	6.0	reflux	 *3-amino-1-m-tolyl-2-pyrazoline*	47	M.P. 110°	345	1301

TABLE XIX—Continued

(F) Miscellaneous Amino Compounds

Reactants	Re-action Time (Hr.)	Reaction Temperature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 p-*tolylhydrazine*	6.0	reflux	 *3-amino-1-*p*-tolyl-2-pyrazoline*	70	M.P. 143°	345	1301
 p-*methoxyphenylhydrazine*	4	reflux	 *3-amino-1-*(p*-methoxyphenyl)-2 pyrazoline*	—	M.P. 179-180°	1301	
 *N'-phenylacetic acid hydrazide*	3.0	water bath	 *acetic acid, 1-(2-cyanoethyl)-2-phenylhydrazide*	25	M.P. 230°	870	
 p-*acetaminophenylhydrazine hydrochloride*	3.5	reflux	 *1-*(p*-acetamidophenyl)-3-amino-2-pyrazoline*	—	M.P. 204°	1301	
 *2,5-dimethylphenylhydrazine*	4.0	reflux	 *3-amino-1-(2,5-xylyl)-2-pyrazoline*	—	M.P. 99°	1301	
 p-*ethoxyphenyl hydrazine*	6.0	reflux	 *3-amino-1-*(p*-ethoxyphenyl)-2-pyrazoline*	—	M.P. 192°	1301	

Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 *hydrazobenzene*	0.5	—	 *3-(1,2-diphenylhydrazino)propionitrile*	73	M.P. 125°	870	1374
 p-*phenoxyphenylhydrazine*	24.0	reflux	 *3-amino-1-(*p*-phenoxyphenyl)-2-pyrazoline*	—	M.P. 147°	1301	
 p-(p-*tolylthio)phenylhydrazine*	24.0	reflux	 *3-amino-1-[*p-(p-*tolylthio)phenyl]-2-pyrazoline*	—	M.P. 123°	1301	
HN_3 *hydrazoic acid*	24- 72.0	25°	$N_3CH_2CH_2CN$ *3-azidopropionitrile*	17.3	B.P. 64°/1 mm.	133	
$HONH_2$ *hydroxylamine*	2.0	10°- R.T.	$HONHCH_2CH_2CN$ *3-hydroxyaminopropionitrile*	~100	— Ⓝ	520 568 566 519	
$H_2NNH_2 \cdot H_2O$ *hydrazine hydrate*	—	R.T.	$H_2NNHCH_2CH_2CN$ *3-hydrazinopropionitrile*			520 568 566 519	
			$H_2NNHCH_2CH_2CONH_2$ *3-hydrazinopropionamide*	90	B.P. 108-112°/4 mm.		
$H_2NNH_2 \cdot H_2O$ *hydrazine hydrate*	2 stored	35°	$H_2NN(CH_2CH_2CN)_2$ *3,3′-hydrazonodipropionitrile*	80	B.P. 125-128°/ 0.1-0.3 mm.	1354	
			$NCCH_2CH_2HNNHCH_2CH_2CN$ *3,3′-hydrazodipropionitrile*	9.1	B.P. 110-125°/ 0.1-0.3 mm.		
$H_2NNH_2 \cdot H_2O$ *hydrazine hydrate*	0.5 4.0	0° reflux	 *3-amino-2-pyrazoline hydrochloride*	—	M.P. 196°	1301	

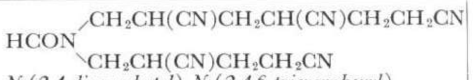
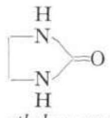
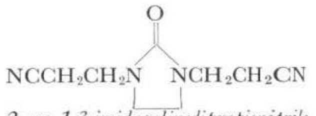
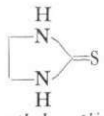
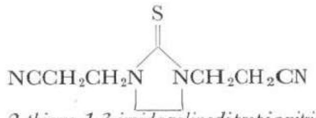
Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
$HCONH_2$ *formamide*	—	110-130°	$HCON\begin{cases}CH_2CH(CN)CH_2CH(CN)CH_2CH_2CN\\CH_2CH(CN)CH_2CH_2CN\end{cases}$ *N-(2,4-dicyanobutyl)-N-(2,4,6-tricyanohexyl) formamide*	—	—	1134	
$HCONH_2$ *formamide*	—	85°	$HCONHCH_2CH_2CN$ Ⓞ *N-(2-cyanoethyl)formamide* $HCON(CH_2CH_2CN)_2$ Ⓟ *N,N-bis(2-cyanoethyl)formamide*	85	B.P. 150°/3 mm.	1135	1133, 63, 1334
NH_2CONH_2 *urea and derivatives*	—	—	*cyanoethylated urea and derivatives* Ⓠ	—	—	1136	
$HCONHCH_3$ *N-methylformamide*	5.0	90-100°	$HCON(CH_3)CH_2CH_2CN$ *N-(2-cyanoethyl)-N-methylformamide*	—	—	63	1133
CH_3CONH_2 *acetamide*	—	—	$CH_3CONHCH_2CH_2CN$ *N-(2-cyanoethyl)acetamide*	84.5	M.P. 62° B.P. 132-135°/0.5-1 mm.	1135	843
CH_3CONH_2 *acetamide*	O.N.	<30°	$CH_3CON(CH_2CH_2CN)_2$ *N,N-bis(2-cyanoethyl)acetamide*	72 Ⓡ	B.P. 210-225°/2 mm.	733	1135
 *ethylene urea*	3.0	40°	 *2-oxo-1,3-imidazolinedipropionitrile*	95	—	1436	
 *ethylene thiourea*	2.5	40°	 *2-thioxo-1,3-imidazolinedipropionitrile*	88.4	M.P. 134°	1436	

TABLE XIX—Continued

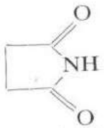
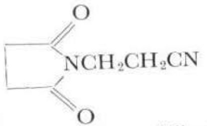
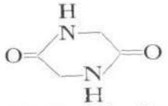
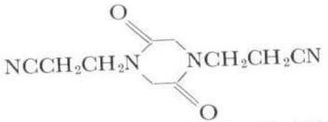
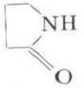
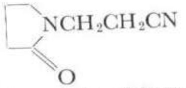
Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
$CH_3CONHCH_3$ *N-methylacetamide*	—	—	$CH_3CON(CH_3)CH_2CH_2CN$ *N-(2-cyanoethyl)-N-methylacetamide*	78	B.P. 112°/1 mm. B.P. 160°/14 mm.	1135	577
$CH_3CH_2CONH_2$ *propionamide*	—	—	$CH_3CH_2CONHCH_2CH_2CN$ *N-(2-cyanoethyl)propionamide* $CH_3CH_2CON(CH_2CH_2CN)_2$ *N,N-bis(2-cyanoethyl)propionamide*	—	—	1135	
 *succinimide*	—	95°	 *2,5-dioxo-1-pyrrolidinepropionitrile*	97	M.P. 120°	1135	
 *2,5-piperazinedione*	1.5	65-70°	 *2,5-dioxo-1,4-piperazinedipropionitrile*	64.9	M.P. 166°	1063	
$CH_3CH=CHCONH_2$ *crotonamide*	2.0	R.T.	$CH_3CH=CHCON(CH_2CH_2CN)_2$ *N,N-bis(2-cyanoethyl)crotonamide*	17.4	M.P. 77°	173	
 *2-pyrrolidinone*	—	—	 *2-oxo-1-pyrrolidinepropionitrile*	86	B.P. 122°/0.7 mm.	1135	577
$HCONHCH_2CH_2CH_3$ *N-propylformamide*	—	—	$HCON(CH_2CH_2CN)CH_2CH_2CH_3$ *N-(2-cyanoethyl)-N-propylformamide*	—	—	1135	

TABLE XIX—Continued

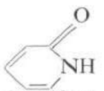
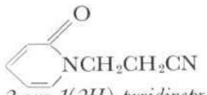
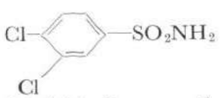
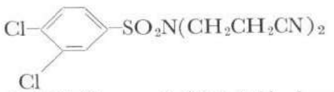
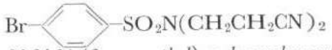
Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
$CH_3CH_2CONHCH_3$ *N-methylpropionamide*	—	—	$CH_3CH_2CON(CH_3)CH_2CH_2CN$ *N-(2-cyanoethyl)-N-methylpropionamide*	66-74	B.P. 114-115°/1 mm.	1135	577
$CH_3CH_2CH_2CH_2SO_2NH_2$ *1-butanesulfonamide*	O.N.	<30°	$CH_3CH_2CH_2CH_2SO_2N(CH_2CH_2CN)_2$ *N,N-bis(2-cyanoethyl)butanesulfonamide*	55	B.P. 225-233°/2 mm. M.P. 46-49°	733	
$CH_3CH_2CH_2CH_2SO_2NH_2$ *1-butanesulfonamide*	O.N.	<30°	$CH_3CH_2CH_2CH_2SO_2NHCH_2CH_2CN$ *N-(2-cyanoethyl)butanesulfonamide*	51	B.P. 195-206°/3 mm.	733	
$CH_3CH_2CH_2SO_2NHCH_3$ *N-methyl-1-propylsulfonamide*	—	—	$CH_3CH_2CH_2SO_2N(CH_3)CH_2CH_2CN$ *N-(2-cyanoethyl)-N-methylpropanesulfonamide*	—	B.P. 146-148°/ 0.7-1.0 mm.	1135	
 *2-pyridone*	0.5	steam cone	 *2-oxo-1(2H)-pyridinepropionitrile*	90	M.P. 93-94°	9	
$HCONH(CH_2)_3CH_3$ *N-butylformamide*	—	—	$HCON(CH_2CH_2CN)CH_2CH_2CH_2CH_3$ *N-butyl-N-(2-cyanoethyl)formamide*	87	B.P. 129-130°/0.5 mm.	1135	1133, 63
$HCONHCH(CH_3)CH_2CH_3$ *N-(1-methylpropyl)formamide*	—	—	$HCON(CH_2CH_2CN)CH(CH_3)CH_2CH_3$ *N-sec.-butyl-N-(2-cyanoethyl)formamide*	—	B.P. 129-130°/0.5 mm.	63	
 *3,4-dichlorobenzenesulfonamide*	—	—	 *N,N-bis(2-cyanoethyl)3,4-dichlorobenzenesulfonamide*	93	M.P. 158°	1135	
 p-*bromobenzenesulfonamide*	48.0	25°	 *N,N-bis(2-cyanoethyl)*-p-*bromobenzenesulfonamide*	66	M.P. 133°	1348	

TABLE XIX—Continued

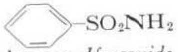
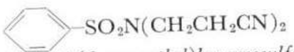
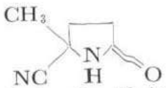
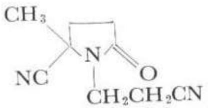
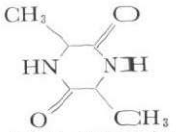
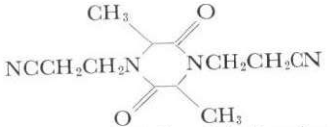
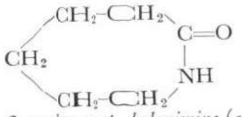
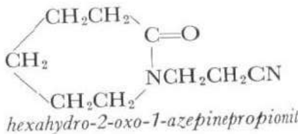
Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 p-*chlorobenzenesulfonamide*	48.0	25°	 *N,N-bis(2-cyanoethyl)*-p-*chlorobenzenesulfonamide*	87	M.P. 132°	1348	
 *benzenesulfonamide*	—	—	 *N,N-bis(2-cyanoethyl)benzenesulfonamide*	87	M.P. 92°	1135	1348
 *5-cyano-5-methyl-2-pyrrolidinone*	0.5	steam bath	 *2-cyano-2-methyl-5-oxo-1-pyrrolidinepropionitrile*	43.9	M.P. 75-77°	432	
 *3,6-dimethyl-2,5-piperazinedione*	1.5	65-70°	 *2,5-dimethyl-3,6-dioxo-1,4-piperazinedipropionitrile*	—	M.P. 185°	1063	
 *2-oxohexamethylenimine (ε-caprolactam)*	2.0 63.0	30-35° R.T.	 *hexahydro-2-oxo-1-azepinepropionitrile*	65	M.P. 32-34° B.P. 153-158°/ 1.5-1.8 mm.	106	577, 1135

TABLE XIX—Continued **(G) Amides**

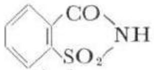
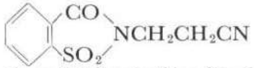
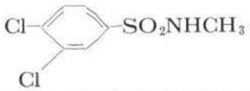
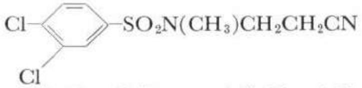
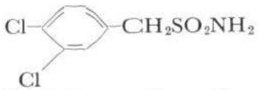
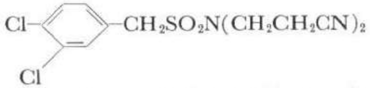
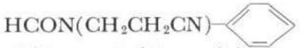
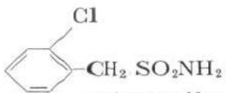
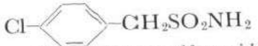
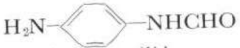
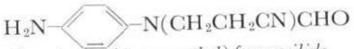
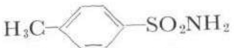
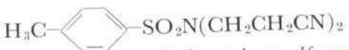
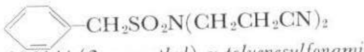
Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 *saccharin*	—	—	 *3-oxo-1,2-benzisothiazoline-2-propionitrile,1,1-dioxide*	—	—	1135	
 *N-methyl-3,4-dichlorobenzenesulfonamide*	—	—	 *3,4-dichloro-N-(2-cyanoethyl)-N-methylbenzenesulfonamide*	88	M.P. 134.5°	1135	
 *3,4-dichloro-α-toluenesulfonamide*	48.0	35° R.T.	 *N,N-bis(2-cyanoethyl)-3,4-dichloro-α-toluenesulfonamide*	75	M.P. 150°	1350	
 *benzamide*	—	—	 *N-(2-cyanoethyl)benzamide*	~50	M.P. 92-93°	1135	577
 *N-phenylformamide*	—	—	 *N-(2-cyanoethyl)formanilide*	88	B.P. 159-161°/2 mm.	1135	63, 1133
 *o-chloro-α-toluenesulfonamide*	48.0	35° R.T.	 *o-chloro-N,N-bis(2-cyanoethyl)-α-toluenesulfonamide*	77	M.P. 92-93°	1350	

TABLE XIX—Continued

Reactants	Reaction Time (Hr.)	Reaction Temperature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 m-*chloro-α-toluenesulfonamide*	48.0	35° R.T.	 m-*chloro-N,N-bis(2-cyanoethyl)-α-toluenesulfonamide*	82.5	M.P. 85-86°	1350	
 p-*chloro-α-toluenesulfonamide*	48.0	R.T.	 p-*chloro-N,N-bis(2-cyanoethyl)-α-toluenesulfonamide*	90	M.P. 121-22°	1350	
 p-*aminoformanilide*	—	—	 *4′-amino-N-(2-cyanoethyl)formanilide*	—	—	1218	
 p-*toluenesulfonamide*	48	25°	 *N,N-bis(2-cyanoethyl)-*p-*toluenesulfonamide*	88	M.P. 105-106°	1348	1303
 *α-toluenesulfonamide*	24.0	R.T.	 *N,N-bis(2-cyanoethyl)-α-toluenesulfonamide*	97.5	M.P. 103-104°	179 184	
 *N-methylbenzenesulfonamide*	—	—	 *N-(2-cyanoethyl)-N-methylbenzenesulfonamide*	85	M.P. 72°	1135	
 *N-cyclohexylformamide*	—	—	*brown oil*	—	—	63	1135
$HCONH(CH_2)_5CH_3$ *N-hexylformamide*	—	—	$HCON(CH_2CH_2CN)CH_2(CH_2)_3CH_2CH_3$ *N-(2-cyanoethyl)-N-hexylformamide*	—	—	1135	

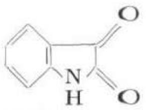
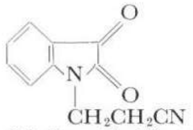
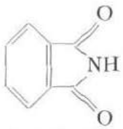
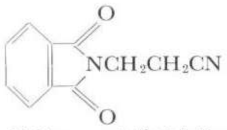
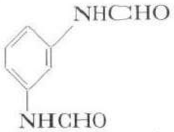
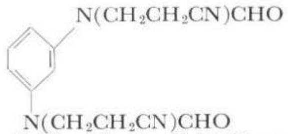
Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
$HCONHCH_2(CH_2)_2CH(CH_3)_2$ *N-(4-methylpentyl)formamide*	—	—	$HCON(CH_2CH_2CN)CH_2(CH_2)_2CH(CH_3)_2$ *N-(2-cyanoethyl)-N-isohexylformamide*	80	B.P. 131°/0.8 mm.	1135	63, 1133
 *isatin*	several days	R.T.	 *2,3-dioxo-1-indolinepropionitrile*	50	M.P. 130-131° M.P. 133°	326	
 *phthalimide*	0.33	reflux	 *N-(2-cyanoethyl)phthalimide*	100	M.P. 154-155.5°	412	1135, 928
 *N,N′-(m-phenylene)bis(formamide)*	O.N.	50° 25°	 *N,N′-m-phenylenebis[N-(2-cyanoethyl)formamide]*	~100	M.P. 114-117°	1218	
 *N,N′-(p-phenylene)bis(formamide)*	O.N.	50° 25°	 *N,N′-p-phenylenebis[N-(2-cyanoethyl)formamide*	87	—	1218	

TABLE XIX—Continued

(G) Amides

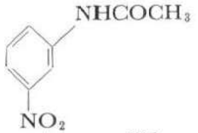
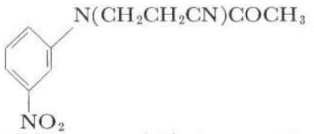
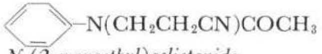
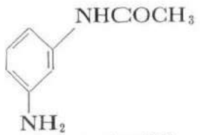
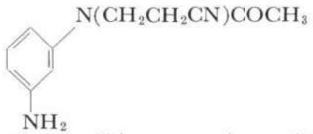
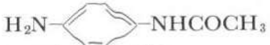
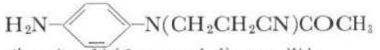
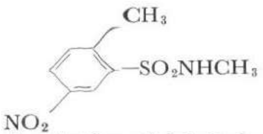
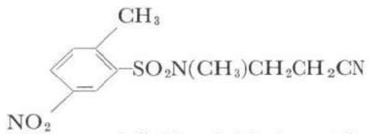
Reactants	Reaction Time (Hr.)	Reaction Temperature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References: This Exam.	References: See Also:
 m-*nitroacetanilide*	16	reflux	 *N-(2-cyanoethyl)-3'-nitroacetanilide*	91	M.P. 81-82.5°	1218	
 *acetanilide*	—	—	 *N-(2-cyanoethyl)aclietanide*	64	M.P. 60-61°	1135	577, 135
 m-*aminoacetanilide*	2.5 O.N.	35° 25°	 *3'-amino-N-(2-cyanoethyl)acetanilide*	81.2	—	1218	
 p-*aminoacetanilide*	24.0	reflux	 *4'-amino-N-(2-cyanoethyl)acetanilide*	95.6	—	1218	
 *N-methyl-2-methyl-5-nitrobenzenesulfonamide*	—	—	 *N-(2-cyanoethyl)-N-methyl-5-nitro-o-toluenesulfonamide*	—	M.P. 119°	1135	

TABLE XIX—Continued

(G) Amides

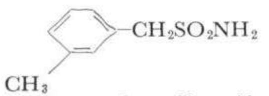
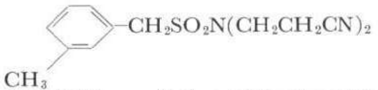
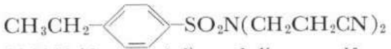
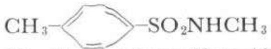
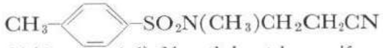
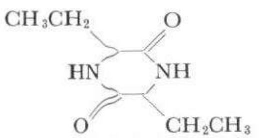
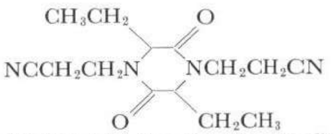
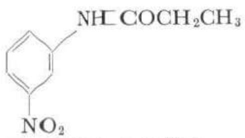
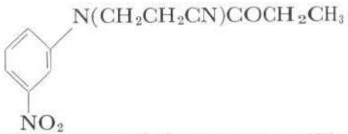
Reactants	Reaction Time (Hr.)	Reaction Temperature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References This Exam.	References See Also:
 m-*toluenemethanesulfonamide*	48.0	35° R.T.	 *N,N-bis(2-cyanoethyl)*-m-*tolylmethanesulfonamide*	80	M.P. 94-95°	1350	
 p-*ethylbenzenesulfonamide*	48.0	25°	 *N,N-bis(2-cyanoethyl)*-p-*ethylbenzenesulfonamide*	80	M.P. 75-76°	1348	
 *N-methyl*-p-*toluenesulfonamide*	48.0	25°	 *N-(2-cyanoethyl)-N-methyl*-p-*toluenesulfonamide*	87	M.P. 105-106°	1348	
 *3,6-diethyl-2,5-piperazinedione*	1.5	65-70°	 *2,5-diethyl-3,6-dioxo-1,4-piperazinedipropionitrile*	—	M.P. 176.5°	1063	
$CH_3NHCO(CH_2)_4CONHCH_3$ *N,N'-dimethylhexanediamide*	—	—	$[NCCH_2CH_2N(CH_3)CO]_2(CH_2)_4$ *N,N'-bis(2-cyanoethyl)-N,N'-dimethylhexanediamide*	—	—	577	
 m-*nitropropionanilide*	—	—	 *N-(2-cyanoethyl)-3'-nitropropionanilide*	—	—	1218	

TABLE XIX—Continued

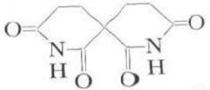
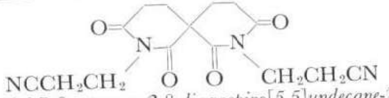
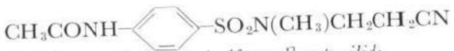
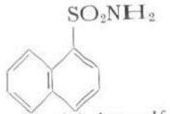
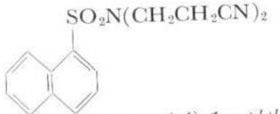
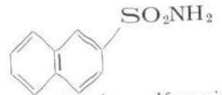
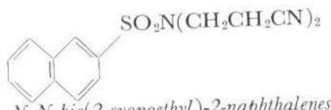
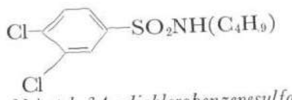
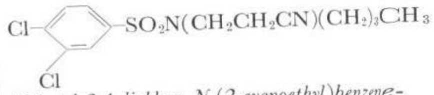
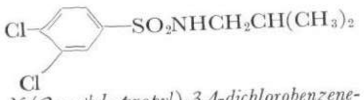
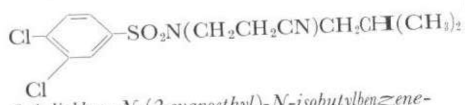
Reactants	Reaction Time (Hr.)	Reaction Temperature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 *1,3,7,9-tetraketo-2,8-diazaspiro[5.5]-hendecane*	—	—	 *1,3,7,9-tetraoxo-2,8-diazaspiro[5.5]undecane-2,8-dipropionitrile*	35	M.P. 122°	1331	
 *4-acetylamino-N-methylbenzenesulfonamide*	—	—	 *4′-[(2-cyanoethyl)methylsulfamoyl]acetanilide*	73	M.P. 142-143°	1135	
 *α-naphthalenesulfonamide*	48.0	25°	 *N,N-bis(2-cyanoethyl)-1-naphthalenesulfonamide*	66	M.P. 120-121°	1348	
 *β-naphthalene sulfonamide*	48.0	25°	 *N,N-bis(2-cyanoethyl)-2-naphthalenesulfonamide*	78	M.P. 109-110°	1348	
 *N-butyl-3,4-dichlorobenzenesulfonamide*	—	—	 *N-butyl-3,4-dichloro-N-(2-cyanoethyl)benzenesulfonamide*	85	M.P. 91°	1135	
 *N-(2-methylpropyl)-3,4-dichlorobenzenesulfonamide*	—	—	 *3,4-dichloro-N-(2-cyanoethyl)-N-isobutylbenzenesulfonamide*	82	M.P. 104°	1135	

TABLE XIX—Continued

(G) Amides

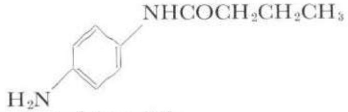
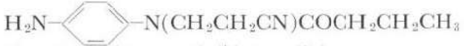
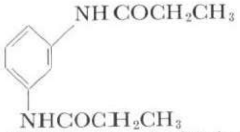
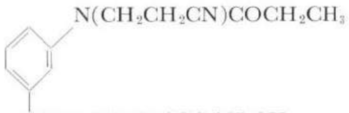
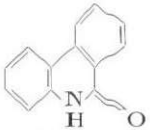
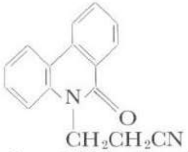
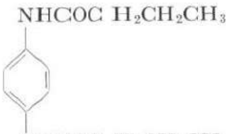
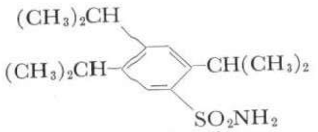
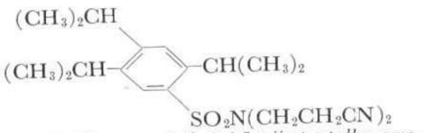
Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 p-*aminobutyranilide*	—	—	 *4′-amino-N-(2-cyanoethyl)butyranilide*	—	—	1218	
 *N,N′-(m-phenylene)bis(propionamide)*	—	—	 *N,N′-m-phenylenebis[N-(2-cyanoethyl)propionamide]*	—	—	1218	
 *6,5H-phenanthridone*	4.0	reflux	 *6-oxo-5(6H)-phenanthridinepropionitrile*	98	M.P. 170-170.5°	89	
 *N,N′-(p-phenylene)bis(butyramide)*	—	—	 *N,N′-p-phenylenebis[N-(2-cyanoethyl)butyramide]*	—	—	1218	

TABLE XIX—Continued

Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 *2,4,5-tris-(1-methylethyl)benzene-sulfonamide*	—	—	 *N,N-bis(2-cyanoethyl)-2,4,5-triisopropylbenzene-sulfonamide*	—	M.P. 140-145°	1135	
$C_{15}H_{31}SO_2NHCH_3$ Ⓢ *mixed N-methylalkanesulfonamides*	—	—	$C_{15}H_{31}SO_2N(CH_3)CH_2CH_2CN$ *mixed N-(2-cyanoethyl)-N-methylalkanesulfonamides*	—	—	1135	

NOTES:

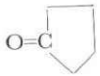
- Ⓐ Mole ratio, ammonia: acrylonitrile = 6:1.
- Ⓑ Mole ratio, ammonia: acrylonitrile = 0.53:1.
- Ⓒ Added after stirring acrylonitrile and amine.
- Ⓓ Structure uncertain.
- Ⓔ Product decomposes on heating—even at 0.01 mm.
- Ⓕ Product not positively identified.
- Ⓖ Mixed alkyl groups derived from tallow fatty acids.
- Ⓗ Based on unrecovered piperidone.
- Ⓘ A small amount of 1,3-cyanoethyl derivative was also produced.
- Ⓙ Yield based on unrecovered aniline.
- Ⓚ Product isolated after refluxing in acetone was— 
- Ⓛ Principally leucine, isoleucine and methionine.
- Ⓜ On heating with HCl, this gives 1-phenyl-3-pyrazolidoneimine.
- Ⓝ Decomposes during attempted distillation.
- Ⓞ Using excess formamide.
- Ⓟ Using excess acrylonitrile.
- Ⓠ Whitmore et al. (ref. 1145) were unable to obtain a reaction between acrylonitrile and urea.
- Ⓡ Based on unrecovered acetamide.
- Ⓢ Mixture of hydrocarbons, from 11-17 carbon atoms obtained from Fischer-Tropsch synthesis.
- Ⓣ Acrylonitrile and formaldehyde dropped into heated reaction chamber over 3-5 hours, then ammonia added over 5 hours at a rate of 25 liters per hour.

TABLE XX—"O" Cyanoethylation

(A) Water and Aliphatic Monohydric Alcohols

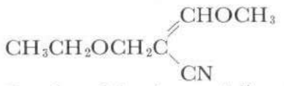
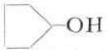
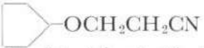
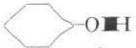
Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
H_2O *water*	3.0	30-40°	$O(CH_2CH_2CN)_2$ *3,3'-oxydipropionitrile*	77	B.P. 119-120°/1 mm.	962	165, 179, 885
CH_3OH *methanol*	—	—	$CH_3OCH_2CH_2CN$ *3-methoxypropionitrile*	90	B.P. 164°	716	1106, 248, 53, 27, 1364, 1103
CH_3CH_2OH *ethyl alcohol*	2.0	20-30°	$CH_3CH_2OCH_2CH_2CN$ *3-ethoxypropionitrile*	95.5	B.P. 167-173°	248	586, 1106, 962, 1012, 716, 1103, 53, 27, 655, 1355
$CH_3CH_2OH + Na$ *ethyl alcohol + sodium*	—	—	$CH_3CH_2OCH_2CH_2CH_2NH_2$ *3-ethoxypropylamine*	30	B.P. 49-50°/30 mm.	1179	668
$CH_3CH_2OH + HCO_2C_2H_5$ *ethyl alcohol + ethyl formate*	—	—	 $CH_3CH_2OCH_2C(=CHOCH_3)CN$ *3-methoxy-2-(methoxymethyl)acrylonitrile*	26.4	B.P. 94-96°/3 mm.	1431	
$CH_2{=}CHCH_2OH$ *allyl alcohol*	1.0 1.0	45° 50-55°	$CH_2{=}CHCH_2OCH_2CH_2CN$ *3-allyloxypropionitrile*	95	B.P. 77-79°/9 mm.	586	242, 155, 240, 27, 53
$HOCH_2CH(NH_2)COOH$ *dl-serine*	—	50°	$NCCH_2CH_2OCH_2CH(NHCH_2CH_2CN)COOH$ *dl-3-(2-cyanoethoxy)-N-(2-cyanoethyl)alanine*	51	M.P. 210-215° (dec.)	1453	
$CH_3CH_2CH_2OH$ *propyl alcohol*	18.0	25°	$CH_3CH_2CH_2OCH_2CH_2CN$ *3-propoxypropionitrile*	95	B.P. 85-89°/24 mm.	1355	690, 27, 1120, 240, 242
$(CH_3)_2CHOH$ *isopropyl alcohol*	2.0	20-30°	$(CH_3)_2CHOCH_2CH_2CN$ *3-isopropoxypropionitrile*	91	B.P. 83-85°/24 mm.	248	716, 1106, 586, 53, 1334

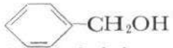
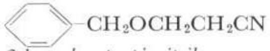
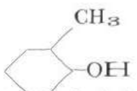
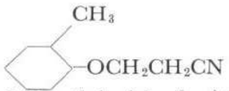
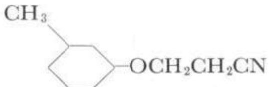
TABLE XX—Continued

Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
$CH_3CHOHC{\equiv}CH$ *3-butyn-2-ol*	O.N.	<30°	$CH_3CH(C{\equiv}CH)OCH_2CH_2CN$ *3-(1-methyl-2-propynyloxy)propionitrile*	—	B.P. 94-96°/16 mm.	1357	
$CH_2{=}C(CH_3)CH_2OH$ *2-methyl-2-propen-1-ol*	6.0	15-25°	$CH_2{=}C(CH_3)CH_2OCH_2CH_2CN$ *3-(2-methylallyloxy)propionitrile*	63.2	B.P. 209-212°	155	15
$CH_3(CH_2)_2CH_2OH$ *butyl alcohol*	—	80°	$CH_3(CH_2)_3OCH_2CH_2CN$ *3-butyloxypropionitrile*	88	B.P. 206°	716	1334, 1355, 903, 1103, 53, 27, 1421
$CH_3CH_2CH_2CH_2OH + Na$ *butyl alcohol + sodium*	—	—	$CH_3CH_2CH_2CH_2OCH_2CH_2CH_2NH_2$ *3-butoxypropylamine*	44.3 59.6	B.P. 78-79°/23 mm. B.P. 71-72°/19 mm.	117	668, 1452
$(CH_3)_2CHCH_2OH$ *isobutyl alcohol*	3.25	<35°	$(CH_3)_2CHCH_2OCH_2CH_2CN$ *3-isobutoxypropionitrile*	90	B.P. 193-195°	248	242, 240
$(CH_3)_2CHCH_2OH + Na$ *isobutyl alcohol + sodium*	—	reflux	$(CH_3)_2CHCH_2O(CH_2)_3NH_2$ *3-isobutoxypropylamine*	63.1	B.P. 72-73°/34 mm.	668	1179
$CH_3CH_2CH(CH_3)OH$ sec-*butyl alcohol*	3 days	22-30°	$CH_3CH_2CH(CH_3)OCH_2CH_2CN$ *3-*sec-*butoxypropionitrile*	86	—	248	242, 240
$(CH_3)_3COH$ tert-*butyl alcohol*	—	—	$(CH_3)_3COCH_2CH_2CN$ *3-*tert-*butoxypropionitrile*	—	B.P. 87°/10 mm.	27	
$(CH_3)_3SiCH_2OH$ *trimethylsilylmethanol*	24.0	<50°	$(CH_3)_3SiCH_2OCH_2CH_2CN$ *3-[(trimethylsilyl)methoxy]propionitrile*	79	B.P. 201.5°	1370	
$HC{\equiv}CC(OH)(CH_3)_2$ *2-methyl-3-butyne-2-ol*	6.0 O.N.	R.T. R.T.	$HC{\equiv}CC(OCH_2CH_2CN)(CH_3)_2$ *3-(1,1-dimethyl-2-propynyloxy)propionitrile*	84	B.P. 96-96.5°/18 mm.	814	155, 1321
$CH_3CH_2CHOHC{\equiv}CH$ *1-pentyn-3-ol*	O.N.	<30°	$C_2H_5CH(C{\equiv}CH)OCH_2CH_2CN$ *3-(1-ethyl-2-propynyloxy)propionitrile*	—	B.P. 104-105°/15 mm.	1357	
$H_2C{=}CHC(OH)(CH_3)_2$ *2-methyl-3-buten-2-ol*	6.0 O.N.	R.T. R.T.	$CH_2{=}CHC(OCH_2CH_2CN)(CH_3)CH_3$ *3-(1,1-dimethylallyloxy)propionitrile*	95 Ⓐ	B.P. 98-100/24 mm.	814	155

TABLE XX—Continued

(A) Water and Aliphatic Monohydric Alcohols

Reactants	Reaction Time (Hr.)	Reaction Temperature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References: This Exam.	References: See Also:
 *cyclopentanol*	— 18.0	20-35° 20-25°	 *3-cyclopentyloxypropionitrile*	81	B.P. 122°/22 mm.	156	
$CH_3(CH_2)_3CH_2OH$ *amyl alcohol*	—	—	$CH_3(CH_2)_4OCH_2CH_2CN$ *3-pentyloxypropionitrile*	92	B.P. 218°	716	27
$(CH_3)_2CHCH_2CH_2OH$ *isopentyl alcohol*	—	—	$(CH_3)_2CHCH_2CH_2OCH_2CH_2CN$ *3-isopentyloxypropionitrile*	82	B.P. 99°/13 mm.	240 242	
$(CH_3)_2CHCH_2CH_2OH + Na$ *isopentyl alcohol + sodium*	—	—	$(CH_3)_2CHCH_2CH_2OCH_2CH_2CH_2NH_2$ *3-isopentyloxypropylamine*	41.4	B.P. 78.5-80°/18 mm.	1179	668
$CH_3CH_2CH_2CH(CH_3)OH$ *1-methyl-1-butanol*	—	—	$CH_3CH_2CH_2CH(CH_3)OCH_2CH_2CN$ *3-(1-methylbutoxy)propionitrile*	70	B.P. 98°/16 mm.	240 242	
$CH_3CH_2C(OH)(CH_3)_2$ *2-methyl-2-butanol*	4.0 O.N.	R.T. R.T.	$CH_3CH_2C(OCH_2CH_2CN)(CH_3)_2$ *3-(1,1-dimethylpropoxy)propionitrile*	10	B.P. 92-97°/18 mm.	814	
$C_2H_5Si(CH_3)_2CH_2OH$ *dimethylethylsilylmethanol*	24.0	<50°	$CH_3CH_2Si(CH_3)_2CH_2OCH_2CH_2CN$ *3-[(ethyldimethylsilyl)methoxy]propionitrile*	82.8	B.P. 225.8°	1370	
$CH_3CH_2CH_2CH(OH)C{\equiv}CH$ *1-hexyn-3-ol*	24.0	R.T.	$CH_3CH_2CH(OCH_2CH_2CN)C{\equiv}CH$ *3-(1-ethyl-2-propynyloxy)propionitrile*	82	B.P. 90-91°/6.5 mm.	816	
$(CH_3)_2CHCH(OH)C{\equiv}CH$ *4-methyl-1-pentyn-3-ol*	24.0	R.T.	$(CH_3)_2CHCH(OCH_2CH_2CN)C{\equiv}CH$ *3-(1-isopropyl-2-propynyloxy)propionitrile*	61	B.P. 83-85°/5.5 mm.	816	
$CH_3CH_2C(CH_3)(OH)C{\equiv}CH$ *3-methyl-1-pentyn-3-ol*	24.0	R.T.	$CH_3CH_2C(CH_3)(OCH_2CH_2CN)C{\equiv}CH$ *3-(1-ethyl-1-methyl-2-propynyloxy)propionitrile*	96	B.P. 67-68°/3.5 mm. B.P. 64°/2.5 mm.	816	
 *cyclohexanol*	6.0 O.N.	R.T. R.T.	 *3-cyclohexyloxypropionitrile*	97 Ⓐ	B.P. 130-132°/20 mm.	815	586, 156, 962
$CH_3(CH_2)_4CH_2OH$ *1-hexanol*	18.0	reflux	$CH_3(CH_2)_4CH_2OCH_2CH_2CN$ *3-hexyloxypropionitrile*	31	B.P. 115.5°/9 mm.	1120	

Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
$(CH_3)_3SiCH_2CH_2CH_2OH$ *3-trimethylsilyl-1-propanol*	24.0	<50°	$(CH_3)_3Si(CH_2)_3OCH_2CH_2CN$ *3-[3-(trimethylsilyl)propoxy] propionitrile*	53.6	B.P. 242°	1370	
 *benzyl alcohol*	—	—	 *3-benzyloxypropionitrile*	94	B.P. 114-116°/0.5 mm.	1106	1334, 586, 53
$H_2C{=}CHC{\equiv}CC(OH)(CH_3)_2$ *2-methyl-5-hexene-3-yn-2-ol*	6.0 O.N.	R.T. R.T.	$H_2C{=}CHC{\equiv}CC(OCH_2CH_2CN)(CH_3)_2$ *3-(1,1-dimethyl-4-penten-2-ynyloxy)propionitrile*	80	B.P. 93-94°/6 mm.	814	1321
$(CH_3CH_2)_2C(OH)C{\equiv}CH$ *3-ethyl-1-pentyn-3-ol*	O.N.	<30°	$(C_2H_5)_2C(C{\equiv}CH)OCH_2CH_2CN$ *3-(1,1-diethyl-2-propynyloxy)propionitrile*	—	B.P. 111-113°/15 mm.	1357	
$CH_3CH_2CH_2C(OH)(CH_3)C{\equiv}CH$ *3-methyl-1-hexyn-3-ol*	O.N.	<30°	$CH_3CH_2CH_2C(C{\equiv}CH)(CH_3)OCH_2CH_2CN$ *3-(1-ethynyl-1-methylbutoxy)propionitrile*	—	B.P. 112-114°/15 mm.	1357	
$(CH_3)_2C(C{\equiv}CH)OCH_2CH_2OH$ *3-(2-hydroxyethoxy)-3-methylbutyne*	3.0	80°	$HC{\equiv}CC(CH_3)_2OCH_2CH_2OCH_2CH_2CN$ *3-[2-(1,1-dimethyl-2-propynyloxy)ethoxy] propionitrile*	65.8	B.P. 144-145.5/25 mm.	1321	
 *2-methylcyclohexanol*	—	R.T.	 *3-(2-methylcyclohexyloxy)propionitrile*	Ⓐ 93	B.P. 134-137°/18 mm.	815	
 *3-methylcyclohexanol*	—	R.T.	 *3-(3-methylcyclohexyloxy)propionitrile*	Ⓐ 98	B.P. 133-136°/16 mm.	815	
$(CH_3)_2CH(CH_2)_3CH_2OH$ *5-methyl-1-hexanol*	—	<50°	$(CH_3)_2CH(CH_2)_3CH_2OCH_2CH_2CN$ *3-(5-methylhexyloxy)propionitrile*	—	B.P. 120°/15 mm.	427	
$CH_3(CH_2)_3C(OH)(CH_3)_2$ *2-methyl-2-hexanol*	2.0	25-45°	$CH_3(CH_2)_3C(OCH_2CH_2CN)(CH_3)_2$ *3-(1,1-dimethylpentyloxy)propionitrile*	20	B.P. 105-107°/11 mm.	814	

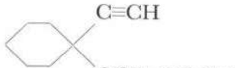
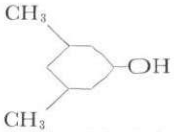
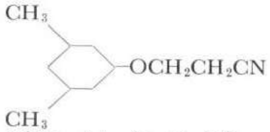
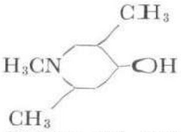
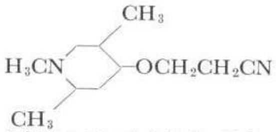
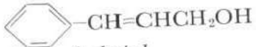
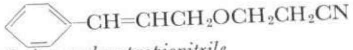
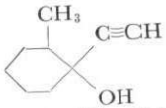
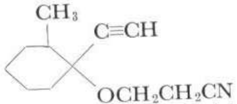
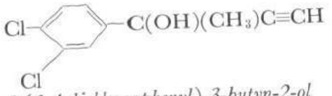
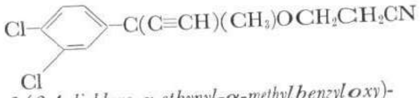
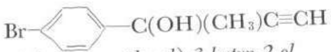
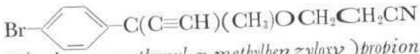
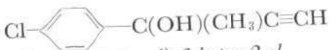
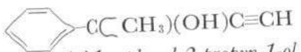
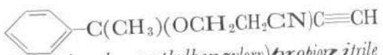
Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
$C_6H_5CHOHCH_3$ *1-phenyl-1-ethanol*	1.5	40-45°	$C_6H_5CH(OCH_2CH_2CN)CH_3$ *3-(α-methylbenzyloxy)propionitrile*	79	B.P. 72-74°/1 mm.	378	
$(CH_3)_2C{=}CHC(CH_3)(OH)C{\equiv}CH$ *3,5-dimethyl-4-hexen-1-yn-3-ol*	24.0	R.T.	$(CH_3)_2C{=}CHC(CH_3)(OCH_2CH_2CN)C{\equiv}CH$ *3-(1-ethynyl-1,3-dimethyl-2-butenyloxy)propionitrile*	73	B.P. 98-100°/5 mm.	816	
 *1-ethynylcyclohexanol*	24.0	R.T.	 *3-(1-ethynylcyclohexyloxy)propionitrile*	93	B.P. 92-95°/3 mm.	816	1357
 *3,5-dimethylcyclohexanol*	—	—	 *3-(3,5-xylyloxy)propionitrile*	51	B.P. 95-96°/0.5 mm.	1106	
 *1,2,5-trimethyl-4-piperidinol*	4.0 O.N.	R.T. R.T.	 *3-(1,2,5-trimethyl-4-piperidyloxy)propionitrile*	68.7	B.P. 117°/4 mm.	815	
$CH_3(CH_2)_6CH_2OH$ *1-octanol*	1.0 —	40° reflux	$CH_3(CH_2)_6CH_2OCH_2CH_2CN$ *3-octyloxypropionitrile*	80	B.P. 150°/20 mm.	716	
$(CH_3)_2CH(CH_2)_4CH_2OH$ *6-methyl-1-heptanol*	—	—	$(CH_3)_2CH(CH_2)_4CH_2OCH_2CH_2CN$ *3-(6-methylheptyloxy)propionitrile*	—	—	413	
$CH_3(CH_2)_3CH(CH_2CH_3)CH_2OH$ *2-ethyl-1-hexanol*	1.0 —	40° reflux	$CH_3(CH_2)_3CH(CH_2CH_3)CH_2OCH_2CH_2CN$ *3-(2-ethylhexyloxy)propionitrile*	88	B.P. 100-110°/2 mm.	716	1106, 27

TABLE XX—Continued

Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 *cinnamyl alcohol*	6.5	25°	 *3-cinnamyloxypropionitrile*	59	B.P. 160-170°/1-2 mm.	155	
 *1-ethynyl-2-methylcyclohexanol*	O.N.	<30°	 *3-(1-ethynyl-2-methylcyclohexyloxy)propionitrile*	—	B.P. 135-136°/10 mm.	1357	
$[(CH_3)_2CH]_2C(OH)C{\equiv}CH$ *3-isopropyl-4-methyl-1-pentyn-3-ol*	O.N.	<30°	$[(CH_3)_2CH]_2C(C{\equiv}CH)OCH_2CH_2CN$ *3-(1,1-diisopropyl-2-propynyloxy)propionitrile*	—	B.P. 126-128°/13 mm.	1357	
$(CH_3CH_2CH_2)_2C(OH)C{\equiv}CH$ *3-propyl-1-hexyn-3-ol*	24.0	R.T.	$(CH_3CH_2CH_2)_2C(OCH_2CH_2CN)C{\equiv}CH$ *3-(1-ethynyl-1-propylbutoxy)propionitrile*	95	B.P. 98-99°/4 mm. B.P. 102-103°/5 mm.	816	
 *2-(3,4-dichlorophenyl)-3-butyn-2-ol*	1.5 O.N.	40-50° R.T.	 *3-(3,4-dichloro-α-ethynyl-α-methylbenzyloxy)-propionitrile*	92	B.P. 158-159°/1 mm.	1358	
 *2-(p-bromophenyl)-3-butyn-2-ol*	1.5 O.N.	40-50° R.T.	 *3-(p-bromo-α-ethynyl-α-methylbenzyloxy)propionitrile*	90	B.P. 153-154°/2 mm.	1358	
 *2-(p-chlorophenyl)-3-butyn-2-ol*	1.5 O.N.	40-50° R.T.	 *3-(p-chloro-α-ethynyl-α-methylbenzyloxy)propionitrile*	93	B.P. 140-141°/1 mm.	1358	
 *1-methyl-1-phenyl-2-propyn-1-ol*	24.0	R.T.	 *3-(α-ethynyl-α-methylbenzyloxy)propionitrile*	97	B.P. 115-118°/3.5 mm.	816	1358

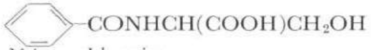
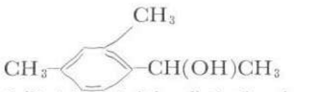
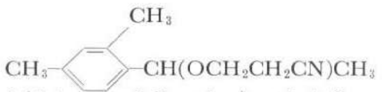
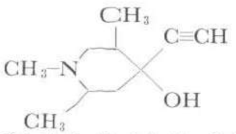
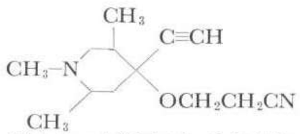
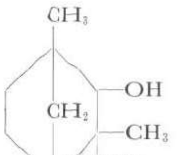
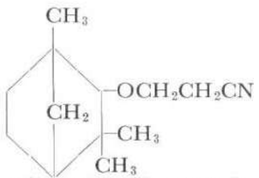
Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 *N-benzoyl-dl-serine*	—	50°	 *N-benzoyl-3-(2-cyanoethoxy)-dl-alanine*	80	M.P. 143°	1453	
 *N-benzoyl-l-serine*	—	50°	 *N-benzoyl-3-(2-cyanoethoxy)-l-alanine*	50	M.P. 95°	1453	
 *1-(2-4-dimethylphenyl)-1-ethanol*	1.5	40-45°	 *3-(2,4,α-trimethylbenzyloxy)propionitrile*	72	B.P. 150-151°/1-2 mm.	378	
 *1,2,5-trimethyl-4-ethynyl-4-piperidinol*	O.N.	<30°	 *3-(4-ethynyl-1,2,5-trimethyl-4-piperidyloxy)-propionitrile*	—	B.P. 135-137°/3 mm.	1357	
$CH_3(CH_2)_5C(CH_3)(OH)C\equiv CH$ *3-methyl-1-nonyn-3-ol*	O.N.	<30°	$CH_3(CH_2)_5C(C\equiv CH)(CH_3)OCH_2CH_2CN$ *3-(1-ethynyl-1-methylheptyloxy)propionitrile*	—	B.P. 115-116°/2.5 mm.	1357	
 *fenchyl alcohol*	— 2.25 2.0	25-35° R.T. 45-50°	 *3-(2-fenchyloxy)propionitrile*	—	B.P. 135-137°/9 mm.	156	

TABLE XX—Continued

(A) Water and Aliphatic Monohydric Alcohols

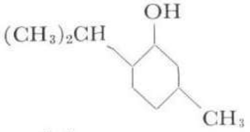
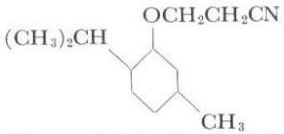
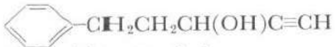
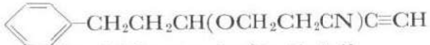
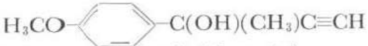
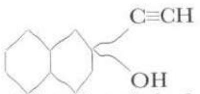
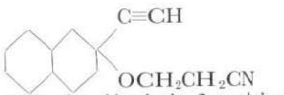
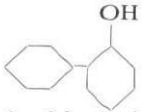
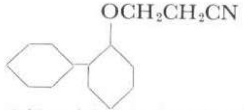
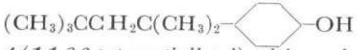
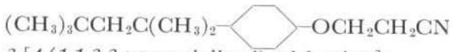
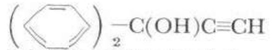
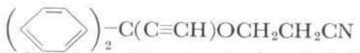
Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References This Exam.	References See Also:
 *menthol*	several hours	30-40°	 3-(p-*menth-3-yloxy)propionitrile*	—	B.P. 149°/10 mm.	156	
$CH_3(CH_2)_8CH_2OH$ *1-decanol*	1.0 —	40° reflux	$CH_3(CH_2)_8CH_2OCH_2CH_2CN$ *3-decyloxypropionitrile*	37	B.P. 283°	716	
 *5-phenyl-1-pentyne-3-ol*	24.0	R.T.	 *3-(1-phenethyl-2-propynyloxy)propionitrile*	80	B.P. 141-143°/3 mm.	816	
 *3-phenyl-1-pentyn-3-ol*	1.5 O.N.	40-50° R.T.	 *3-(α-ethyl-α-ethynylbenzyloxy)propionitrile*	97	B.P. 127-129°/2 mm.	1358	
 *2-*(p-*tolyl)-3-butyn-2-ol*	1.5 O.N.	40-50° R.T.	 *3-(α-ethynyl-*p,*α-dimethylbenzyloxy)propionitrile*	97.4	B.P. 134-136°/2 mm.	1358	
 *2-*(p-*methoxyphenyl)-3-butyn-2-ol*	1.5 O.N.	40-50° R.T.	 *3-(α-ethynyl-*p-*methoxy-α-methylbenzyloxy)-propionitrile*	97	M.P. 65-66°	1358	
 *2-ethynyldecahydro-2-naphthol*	24.0	R.T.	 *3-(2-ethynyldecahydro-2-naphthyloxy)propionitrile*	89	B.P. 150-153°/4.5 mm.	816	

TABLE XX—Continued

(A) Water and Aliphatic Monohydric Alcohols

Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 *2-cyclohexylcyclohexanol*	3.0	30-40°	 *3-(2-cyclohexylcyclohexyloxy)propionitrile*	—	B.P. 154-156°/1 mm.	156	
$CH_3(CH_2)_{10}CH_2OH$ *1-dodecanol*	—	—	$CH_3(CH_2)_{10}CH_2OCH_2CH_2CN$ *3-(dodecyloxy)propionitrile*	—	B.P. 140-143°/1 mm.	27	
$CH_3(CH_2)_8C(OH)(CH_3)C{\equiv}CH$ *3-methyl-1-dodecyn-3-ol*	O.N.	<30°	$CH_3(CH_2)_8C(C{\equiv}CH)(CH_3)OCH_2CH_2CN$ *3-(1-ethynyl-1-methyldecyloxy)propionitrile*	—	B.P. 148-150°/3.5 mm.	1357	
 *4-(1,1,3,3-tetramethylbutyl)cyclohexanol*	— 4.0	25° 40°	 *3-[4-(1,1,3,3-tetramethylbutyl)cyclohexyloxy]-propionitrile*	—	B.P. 165-170°/2 mm.	156	
 *1,1-diphenyl-2-propyn-1-ol*	1.5 O.N.	40-50° R.T.	 *3-(1,1-diphenyl-2-propynyloxy)propionitrile*	99	M.P. 84-85°	1358	816
$CH_3(CH_2)_7CH{=}CH(CH_2)_7CH_2OH$ *9-octadecenol*	2.0	75-80°	$CH_3(CH_2)_7CH{=}CH(CH_2)_7CH_2OCH_2CH_2CN$ *3-(9-octadecenyloxy)propionitrile*	85	M.P. 16°	586	155
$CH_3(CH_2)_{16}CH_2OH$ *1-octadecanol*	—	—	$CH_3(CH_2)_{16}CH_2OCH_2CH_2CN$ *3-octadecyloxypropionitrile*	—	M.P. 50°	27	1103
leuna alcohol Ⓑ	—	50-60°	*cyanoethylated leuna alcohol*	—		427	

Additional examples of reactions involving complex monohydric alcohols are contained in the following references: 155, 156.

(B) Monohydric Ether Alcohols

$CH_3OCH_2CH_2OH$ *2-methoxyethanol*	—	—	$CH_3OCH_2CH_2OCH_2CH_2CN$ *3-(2-methoxyethoxy)propionitrile*	87	B.P. 98-100°/9 mm.	1106	157, 53

TABLE XX—Continued

(B) Monohydric Ether Alcohols

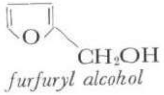
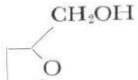
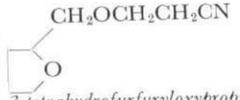
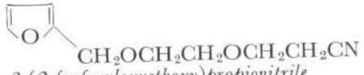
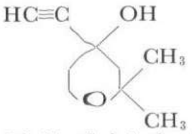
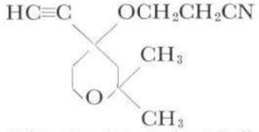
Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
$CH_3CH_2OCH_2CH_2OH$ *2-ethoxyethanol*	0.75 8.0	15° 25°	$CH_3CH_2OCH_2CH_2OCH_2CH_2CN$ *3-(2-ethoxyethoxy)propionitrile*	75	B.P. 128°/26 mm.	157	
 *furfuryl alcohol*	5.0	25-45°	 *3-furfuryloxypropionitrile*	74	B.P. 145-149°/20 mm.	53	155
 *tetrahydrofurfuryl alcohol*	—	—	 *3-tetrahydrofurfuryloxypropionitrile*	80	B.P. 100°/15 mm.	1106	157
$CH_2{=}CHCH_2OCH_2CH_2OH$ *2-(allyloxy)ethanol*	3.0	18-20°	$CH_2{=}CHCH_2OCH_2CH_2OCH_2CH_2CN$ *3-(2-allyloxyethoxy)propionitrile*	80	B.P. 110°/2 mm.	980	
$CH_3OCH_2CH_2OCH_2CH_2OH$ *2-(2-methoxyethoxy)ethanol*	0.75 7.0	25-30° 25°	$CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2CN$ *3-[2-(2-methoxyethoxy)ethoxy]propionitrile*	64	B.P. 145-150°/10 mm.	157	
$(CH_3OCH_2)_2CHOH$ *1,3-dimethoxy-2-propanol*	0.67 6.0	25-35° —	$(CH_3OCH_2)_2CHOCH_2CH_2CN$ *3-[2-methoxy-1-(methoxymethyl)ethoxy]propionitrile*	80.4	B.P. 110°/0.5 mm.	157	
$CH_2{=}CHCH_2OCH_2CH_2CH_2OH$ *3-allyloxy-1–propanol*	3.0 0.5	15-25° 20°	$CH_2{=}CHCH_2O(CH_2)_3OCH_2CH_2CN$ *3-(3-allyloxypropoxy)propionitrile*	78	B.P. 138-142°/12 mm.	980	
$CH_2{=}CHCH_2OCH_2CH(CH_3)OH$ *1-allyloxy-2–propanol*	3.0 0.5	15-25° 20°	$CH_2{=}CHCH_2OCH_2CH(CH_3)OCH_2CH_2CN$ *3-(2-allyloxy-1-methylethoxy)propionitrile*	77	B.P. 140-142°/12 mm.	980	
$CH_3(CH_2)_3OCH_2CH_2OH$ *2-butoxyethanol*	— 1.0	30-45° R.T.	$CH_3(CH_2)_3OCH_2CH_2OCH_2CH_2CN$ *3-(2-butoxyethoxy)propionitrile*	78.3	B.P. 130°/10 mm.	157	
 *2-(2-furfuryloxy)ethanol*	2.0 0.5	<25° 25°	 *3-(2-furfuryloxyethoxy)propionitrile*	52	B.P. 152-154°/1 mm.	980	

TABLE XX—Continued

(B) Monohydric Ether Alcohols

Reactants	Re-action Time (Hr.)	Reaction Temperature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
$-OCH_2CH_2OH$ *2-phenoxyethanol*	1.0 18.0	25-50° 25°	$-OCH_2CH_2OCH_2CH_2CN$ *3-(2-phenoxyethoxy)propionitrile*	77.5	B.P. 160°/1 mm.	157	
$CH_3(CH_2)_3OCH_2CH_2OCH_2CH_2OH$ *2-(2-butoxyethoxy)ethanol*	0.58 8.0	10-15° 25°	$CH_3(CH_2)_3O(CH_2CH_2O)_2CH_2CH_2CN$ *3-[2-(2-butoxyethoxy)ethoxy]propionitrile*	70	B.P. 165-175°/10 mm.	157	
$-CH_2OCH_2CH_2OH$ *2-benzyloxyethanol*	0.5 4.0	25-30° 25-30°	$-CH_2OCH_2CH_2OCH_2CH_2CN$ *3-(2-benzyloxyethoxy)propionitrile*	76	B.P. 146°/1 mm.	157	
 *2,2-dimethyl-4-ethynyltetrahydropyran-4-ol*	24.0	R.T.	 *3-(4-ethynyltetrahydro-2,2-dimethyl-4-pyranyloxy)-propionitrile*	72	B.P. 122-125°/3 mm.	816	
$-CH(CH_3)OCH_2CH_2OH$ *2-(α-methylbenzyloxy)ethanol*	1.5	40-45°	$-CH(CH_3)OCH_2CH_2OCH_2CH_2CN$ *3-[2-(α-methylbenzyloxy)ethoxy]propionitrile*	73	B.P. 102-104°/1 mm.	378	

Additional examples of reactions involving complex monohydric ether alcohols are contained in reference 157.

(C) Hemiformals (ROH + HCHO)

$CH_3OH + CH_2O$ *methanol + formaldehyde*	— 4.0 3.0	25-35° R.T. 45°	$CH_3OCH_2OCH_2CH_2CN$ *3-(methoxymethoxy)propionitrile*	44	B.P. 103-106°/26 mm. B.P. 200°/775 mm.	185	
$CH_3CH_2OH + CH_2O$ *ethyl alcohol + formaldehyde*	5 days	R.T.	$CH_3CH_2OCH_2OCH_2CH_2CN$ *3-(ethoxymethoxy)propionitrile*	65.7	B.P. 94-98°/15 mm.	764	

Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
$CH_2{=}CHCH_2OH + CH_2O$ *allyl alcohol + formaldehyde*	3.0	25-50°	$CH_2{=}CHCH_2OCH_2OCH_2CH_2CN$ *3-(allyloxymethoxy)propionitrile*	32	B.P. 100-110°/ 11-12 mm.	185	
$(CH_3)_3COH + CH_2O$ t-*butyl alcohol + formaldehyde*	0.44 1.5	25-45° 35-40°	$(CH_3)_3COCH_2OCH_2CH_2CN$ 3-(tert.-*butoxymethoxy)propionitrile*	40	B.P. 75-80°/1-3 mm.	185	
 $-CH_2OH + CH_2O$ *benzyl alcohol + formaldehyde*	6.0	R.T.	 $-CH_2OCH_2OCH_2CH_2CN$ *3-(benzyloxymethoxy)propionitrile*	40	B.P. 133-135°/0.5 mm.	185	
$CH_3(CH_2)_5CH(CH_3)OH + CH_2O$ *2-octanol + formaldehyde*	0.33 1.0	30-45° 40-43°	$CH_3(CH_2)_5CH(CH_3)OCH_2OCH_2CH_2CN$ *3-[(1-methylheptyloxy)methoxy]propionitrile*	47	B.P. 160°/10 mm.	185	
(D) Dihydric Alcohols							
$CH_2O \cdot H_2O$ *methylene glycol*	7-8	reflux	$CH_2(OCH_2CH_2CN)_2$ *3,3'-(methylenedioxy)dipropionitrile*	—	B.P. 155-160°/2 mm.	1123	347
$HOCH_2CH_2OH$ *ethylene glycol*	6.0 22.0	30° R.T.	$NCCH_2CH_2OCH_2CH_2OCH_2CH_2CN$ *3,3'-(ethylenedioxy)dipropionitrile*	97.1	—	1360	53, 170, 962, 698, 427, 287, 179, 164, 885, 663, 210, 27, 248, 1097, 1421
$HOCH_2CH_2CH_2OH$ *1,3-propanediol*	— 6.5	20-42° 25°	$NCCH_2CH_2OCH_2CH_2CH_2OCH_2CH_2CN$ *3,3'-(trimethylenedioxy)dipropionitrile*	87.5	B.P. 165-170°/1-2 mm.	170	179, 164
$HOCH_2CH(CH_3)OH$ *1,2-propanediol*	2.0 6.0	25-28° R.T.	$NCCH_2CH_2OCH_2CH(CH_3)OCH_2CH_2CN$ *3,3'-(propylenedioxy)dipropionitrile*	78	B.P. 160-170°/1-2 mm.	170 164	179, 663
$HOCH_2{-}C{\equiv}C{-}CH_2OH$ *2-butyne-1,4-diol*	48.0	R.T.	$NCCH_2CH_2OCH_2C{\equiv}CCH_2OCH_2CH_2CN$ *3,3'-(2-butynylenedioxy)dipropionitrile*	96	B.P. 189-195°/3 mm.	814	

TABLE XX—Continued

(D) Dihydric Alcohols

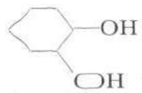
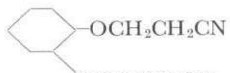
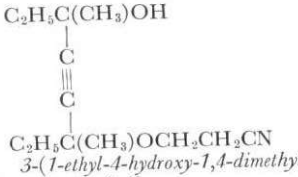
Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
$HO(CH_2)_4OH$ *1,4-butanediol*	1.5 1.0	<50° 50°	$NCCH_2CH_2O(CH_2)_4OCH_2CH_2CN$ *3,3′-(tetramethylenedioxy)dipropionitrile*	85	B.P. 165°/0.2 mm. M.P. 36-39°	586	663, 885, 1097, 1360
$HO(CH_2)_4OH$ *1,4-butanediol*	1.5 1.0	<50° 50°	$HO(CH_2)_4OCH_2CH_2CN$ *3-(4-hydroxybutoxy)propionitrile*	—	B.P. 115°/0.3 mm.	586	
$HOCH_2CH_2CH(CH_3)OH$ *1,3-butanediol*	1.0 7.0	25-40° 25°	$NCCH_2CH_2OCH_2CH_2CH(CH_3)OCH_2CH_2CN$ *3,3′-(1-methyltrimethylenedioxy)dipropionitrile*	68.1	B.P. 170-175°/1 mm.	170	427, 885, 1097, 164, 1360
$HOCH(CH_3)CH(CH_3)OH$ *2,3-butanediol*	— 6.0	10-20° 20-25°	$[NCCH_2CH_2OCH(CH_3)\text{-}]_2$ *3,3′-(1,2-dimethylethylenedioxy)dipropionitrile*	67.2	B.P. 165-175°/2 mm. M.P. 53-54°	170	179, 1161 885
$(CH_3)_2C(OH)CH_2OH$ *2-methyl-1,2-propanediol*	— 5.5	23-35° 25°	$(CH_3)_2C(OCH_2CH_2CN)CH_2OCH_2CH_2CN$ *3,3′-(1,1-dimethylethylenedioxy)dipropionitrile*	71	B.P. 126-130°/10 mm.	170	
$HOCH_2CH_2OCH_2CH_2OH$ *diethylene glycol*	5.0	10-20°	$NCCH_2CH_2(OCH_2CH_2)_2OCH_2CH_2CN$ *3,3′-[oxybis(ethyleneoxy)]dipropionitrile*	92	B.P. 185-195°/1-2 mm.	170	663, 1161, 179, 164, 427, 1146, 1360
$HOCH_2CH_2OCH_2CH_2OH$ *diethylene glycol*	—	—	$HOCH_2CH_2OCH_2CH_2OCH_2CH_2CN$ *3-[2-(2-hydroxyethoxy)ethoxy]propionitrile*	—	B.P. 186°/9 mm.	1161	
$HOCH_2(CH_2)_2CH(OH)CH_3$ *1,4-pentanediol*	—	—	$NCCH_2CH_2O(CH_2)_3CH(CH_3)OCH_2CH_2CN$ *3,3′-(1-methyltetramethylenedioxy)dipropionitrile*	83	B.P. 157°/1 mm.	240 241	
$HOCH_2CH_2CH_2CH_2CH_2OH$ *1,5-pentanediol*	1.0 6.0	18-38° 25°	$NCCH_2CH_2O(CH_2)_5OCH_2CH_2CN$ *3,3′-(pentamethylenedioxy)dipropionitrile*	80	B.P. 180-190°/1-2 mm.	170	179
 *1,2-cyclohexanediol*	0.67 7.0	35-50° 25°	 *3,3′-(o-phenylenedioxy)dipropionitrile*	58	B.P. 180-190°/1 mm.	170	

TABLE XX—Continued

Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 *1,4-cyclohexanediol*	1.5	reflux	 *3,3′-(p-phenylenedioxy)dipropionitrile*	—	M.P. 112°	753 754 755	
$HO(CH_2)_6OH$ *1,6-hexanediol*	—	—	$NCCH_2CH_2O(CH_2)_6OCH_2CH_2CN$ *3,3′-(hexamethylenedioxy)dipropionitrile*	—	B.P. 190-200°/1.5 mm.	663	418, 698
$HOCH(CH_3)CH_2OCH_2CH(CH_3)OH$ *dipropylene glycol*	— 17.0	25-45° 25°	$O[CH_2CH(CH_3)OCH_2CH_2CN]_2$ *3,3′-[oxybis(1,2-propyleneoxy)]dipropionitrile*	73	B.P. 185-195°/1-2 mm.	170	164
$HO(CH_2CH_2O)_2CH_2CH_2OH$ *triethylene glycol*	1.5 16.0	20-30° 25°	$NCCH_2CH_2(OCH_2CH_2)_3OCH_2CH_2CN$ *3,3′-[ethylenebis(oxyethyleneoxy)]dipropionitrile*	77	B.P. 210-220°/1-2 mm.	170	179, 164, 885, 427
$HO(CH_2)_3C(OH)(CH_3)C{\equiv}CH$ *3-methyl-1-hexyne-3,6-diol*	O.N.	<30°	$NC(CH_2)_2O(CH_2)_3C(OH)(CH_3)C{\equiv}CH$ *3-(4-hydroxy-4-methyl-5-hexynyloxy)propionitrile*	—	B.P. 148-150°/3 mm.	1357	
	—	35-50°	$HOC(CH_3)_2C{\equiv}CC(CH_3)_2OCH_2CH_2CN$ *3-(4-hydroxy-1,1,4-trimethyl-2-pentynyloxy)-propionitrile*	48	B.P. 119-121°/0.3 mm.	1284	814, 1321
$HOC(CH_3)_2C{\equiv}CC(CH_3)_2OH$ *1,1,4,4-tetramethyl-2-butyne-1,4-diol*	0.5	105°	$[NCCH_2CH_2OC(CH_3)_2]_2C{\equiv}C$ *3,3′-(1,1,4,4-tetramethyl-2-butynylenedioxy)-dipropionitrile*	37	B.P. 149-152°/0.3 mm.		
$HOCH_2CH_2(OCH_2CH_2)_3OH$ *tetraethylene glycol*	1.5 16.0	20-30° 25°	$NCCH_2CH_2(OCH_2CH_2)_4OCH_2CH_2CN$ *3,3′-[oxybis(ethyleneoxyethyleneoxy)]dipropionitrile*	61	B.P. 220-230°/1-2 mm.	170	
			$C{\equiv}C[C_2H_5C(CH_3)OCH_2CH_2CN]_2$ *3,3′-(1,4-diethyl-1,4-dimethyl-2-butynylenedioxy)-dipropionitrile*	40	B.P. 161-162°/0.5 mm.	1284	
$[C_2H_5C(OH)(CH_3)-]_2C{\equiv}C$ *3,5-dimethyl-4-octyne-3,5-diol*	0.5 O.N.	reflux R.T.	 $\begin{array}{c}C_2H_5C(CH_3)OH\\ \vert\\ C\\ \vert\vert\vert\\ C\\ \vert\\ C_2H_5C(CH_3)OCH_2CH_2CN\end{array}$ *3-(1-ethyl-4-hydroxy-1,4-dimethyl-2-hexynyloxy)-propionitrile*	19.5	B.P. 124-130/0.5 mm.		

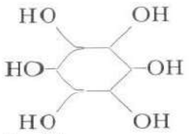
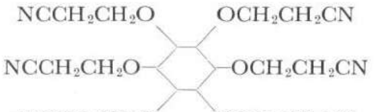
Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
$HO(CH_2)_{10}OH$ *1,10-decanediol*	18.0	25-35°	$NCCH_2CH_2O(CH_2)_{10}OCH_2CH_2CN$ *3,3′-(decamethylenedioxy)dipropionitrile*	—	B.P. 225°/1 mm.	179	170
$(HOCH_2CH_2OCH_2CH_2OCH_2)_2$ *pentaethylene glycol*	—	—	$CH_2OCH_2CH_2OCH_2CH_2OCH_2CH_2CN_2$ *3,3′-[ethylenebis(oxyethyleneoxyethyleneoxy)]-dipropionitrile*	—	B.P. 215-225°/4 mm.	885	
$HOCH_2CH_2(OCH_2CH_2)_5OH$ *hexaethylene glycol*	— 17.0	20-28° 25°	$NCCH_2CH_2(OCH_2CH_2)_6OCH_2CH_2CN$ *3,3′-[oxybis(ethyleneoxyethyleneoxyethyleneoxy)]-dipropionitrile*	94	—	170	
$HOCH_2CH_2(OCH_2CH_2)_xOH$ *polyethylene glycol*	— 5.0	30° 30°	$NCCH_2CH_2(OCH_2CH_2)_xOCH_2CH_2CN$ *3,3′-[oxybis(ethyleneoxy)$_x$]dipropionitrile*	94	—	170	427
(E) Polyhydric Alcohols							
$HOCH_2CH(OH)CH_2OH$ *glycerol*	2.5 6.0	25-30° 25°	$NCCH_2CH_2OCH(CH_2OCH_2CH_2CN)_2$ *3,3′,3″-glyceryltrioxytripropionitrile*	71.3	B.P. 250-260°/1-2 mm.	170	1161, 179, 164
$C(CH_2OH)_4$ *pentaerythritol*	7.0 24.0	40-50° R.T.	$C(CH_2OCH_2CH_2CN)_4$ *3,3′-[2,2-bis(2-cyanoethoxymethyl)trimethylenedioxy]-dipropionitrile*	79	—	170	164
 *inositol*	5.0	40-50°	 *1,2,3,4,5,6-hexakis(2-cyanoethoxy)cyclohexane*	—	—	170	
$O=CH(CHOH)_4CH_2OH$ *glucose*	18.0	—	$O=CH(CHOH)_4CH_2OCH_2CH_2CN$ *6-O-(2-cyanoethyl)glucose*	—	—	427	
$HOCH_2(CHOH)_4CH_2OH$ *mannitol*	10-12	—	$HOCH_2(CHOH)_4CH_2OCH_2CH_2CN$ *3-(2,3,4,5,6-pentahydroxyhexyloxy)propionitrile*	—	—	427	562

TABLE XX—Continued

(E) Polyhydric Alcohols

Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
$HOCH_2(CHOH)_4CH_2OH$ *mannitol*	5.0	40-50°	$CH_2OCH_2CH_2CN$ $(CHOCH_2CH_2CN)_4$ $CH_2OCH_2CH_2CN$ *1,2,3,4,5,6-hexakis(2-cyanoethoxy)hexane*	—	—	170	562, 164
$HOCH_2(CHOH)_4CH_2OH$ *sorbitol*	16-20	—	$HOCH_2(CHOH)_4CH_2OCH_2CH_2CN$ *2-(2,3,4,5,6-pentahydroxyhexyloxy)propionitrile*	—	—	427	
$HOCH_2(CHOH)_4CH_2OH$ *sorbitol*	—	20-30°	$CH_2OCH_2CH_2CN$ $(CHOCH_2CH_2CN)_4$ $CH_2OCH_2CH_2CN$ *1,2,3,4,5,6-hexakis(2-cyanoethoxy)hexane*	—	—	164	
$C_{12}H_{22}O_{11}$ *sucrose*	—	—	*colorless viscous oil*	—	—	234	427
(F) Miscellaneous Aliphatic Alcohols							
$HOCH_2SO_3Na$ *hydroxymethanesulfonic acid, sodium salt*	1.0 2.0	60-70° 70-80°	$NCCH_2CH_2OCH_2SO_3Na$ *(2-cyanoethoxy)methanesulfonic acid, sodium salt*	—	—	591	
$NaHSO_3 + CH_2O$ *sodium bisulfite + formaldehyde*	—	20-25°	Ⓓ	—	—	591	
$HOCH_2CN$ *glycolonitrile*	0.75	80-90°	$NCCH_2OCH_2CH_2CN$ *3-(cyanomethoxy)propionitrile*	—	B.P. 125°/5 mm.	465	
$ClCH_2CH_2OH$ *2-chloroethanol*	10.0	40°	$ClCH_2CH_2OCH_2CH_2CN$ *3-(2-chloroethoxy)propionitrile*	—	B.P. 126-127°/16 mm.	533	
FCH_2CH_2OH *2-fluoroethanol*	—	—	$FCH_2CH_2OCH_2CH_2CN$ *3-(2-fluoroethoxy)propionitrile*	—	—	952	

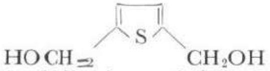
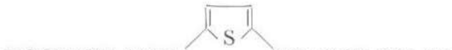
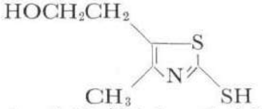
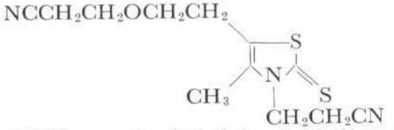
Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
$HOCH_2CH_2SH$ *2-mercaptoethanol*	16.0	25°	$NCCH_2CH_2OCH_2CH_2SCH_2CH_2CN$ *3-[2-(2-cyanoethylthio)ethoxy]propionitrile*	98.3	B.P. 218-219°/7 mm.	557	
$NCCH_2CH_2OH$ *hydracrylonitrile (ethylene cyanohydrin)*	—	—	$O(CH_2CH_2CN)_2$ *3,3′-oxydipropionitrile*	88.7	—	667	165, 662, 465, 1096, 210, 27
$CH_3CHOHCN$ *lactonitrile*	0.5	90°	$CH_3CH(CN)OCH_2CH_2CN$ *2,3′-oxydipropionitrile*	—	B.P. 150-155°/20 mm.	465	
$CH_3CH(OH)COONa$ *lactic acid, sodium salt*	1.0 2.0	50° 50-55°	$CH_3CH(OCH_2CH_2CN)COOH$ *2-(2-cyanoethoxy)propionic acid*	—	B.P. 145-155°/0.6 mm. Ⓔ	586	
$FCH_2CH_2CH_2OH$ *3-fluoro-1-propanol*	—	—	$FCH_2CH_2CH_2OCH_2CH_2CN$ *3-(3-fluoropropoxy)propionitrile*	—	—	952	
$CH_3CH(OH)CO_2CH_3$ *lactic acid, methyl ester*	18.0	25°	$CH_3CH(OCH_2CH_2CN)CO_2CH_3$ *2-(2-cyanoethoxy)propionic acid, methyl ester*	51	B.P. 90°/1.2 mm.	900 902	
$ClCH_2CH_2OCH_2CH_2OH$ *2-(2-chloroethoxy)ethanol*	0.5 2.0	20-25° 25-30°	$ClCH_2CH_2OCH_2CH_2OCH_2CH_2CN$ *3-[2-(2-chloroethoxy)ethoxy]propionitrile*	67.7	B.P. 133-137°/1 mm.	157	
$S(CH_2CH_2OH)_2$ *2,2′-thiodiethanol*	1.0 7.0	20-25° 25°	$S(CH_2CH_2OCH_2CH_2CN)_2$ *3,3′-[thiobis(ethyleneoxy)]dipropionitrile*	92	B.P. 220-230°/1-2 mm.	170	557
$HOCH_2CH_2SCH_2CH_2CN$ *β-(2-hydroxyethylmercapto)propionitrile*	16.0	25°	$NCCH_2CH_2OCH_2CH_2SCH_2CH_2CN$ *3-[2-(2-cyanoethylthio)ethoxy]propionitrile*	88	B.P. 224-225°/9 mm.	557	422
$C_2H_5OCOCH(OH)CH_3$ *lactic acid, ethyl ester*	18.0 1.0	25° 100°	$CH_3CH(OCH_2CH_2CN)CO_2C_2H_5$ *2-(2-cyanoethoxy)propionic acid, ethyl ester*	Ⓕ	B.P. 95°/1 mm.	902	900
$CH_3N(CH_2CH_2OH)_2$ *2,2′-methyliminodiethanol*	—	<50°	$CH_3N(CH_2CH_2OCH_2CH_2CN)_2$ *3,3′-[methyliminobis(ethyleneoxy)]dipropionitrile*	—	—	427	
 *2,5-bis(hydroxymethyl)thiophene*	6.0 16.0	45° R.T.	 *2,5-bis(2-cyanoethoxymethyl)thiophene*	31.8	B.P. 210-212°/0.45 mm.	450	

TABLE XX—Continued

(F) Miscellaneous Aliphatic Alcohols

Reactants	Reaction Time (Hr.)	Reaction Temperature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References: This Exam.	References: See Also:
 *4-methyl-5-(2-hydroxyethyl)-2-thiazolethiol*	10.0	R.T.	 *5-[2-(2-cyanoethoxy)ethyl]-4-methyl-2-thioxo-4-thiazoline-3-propionitrile*	—	M.P. 62-63°	1181	
$HOCH_2CH_2SCH_2CH_2COOCH_3$ *2-hydroxyethylmercaptopropionic acid, methyl ester*	24.0	steam bath	$NCCH_2CH_2OCH_2CH_2SCH_2CH_2COOCH_3$ *3-[2-(2-cyanoethoxy)ethylthio]propionic acid, methyl ester*	29	B.P. 178.5-180°/2 mm.	557	
 *N-2-hydroxyethylmorpholine*	0.33 18.0	25-35° 25°	 *3-(2-morpholinoethoxy)propionitrile*	61	B.P. 140-142°/1-2 mm.	161	
$(CH_3CH_2)_2NCH_2CH_2OH$ *2-(diethylamino)ethanol*	—	—	$(CH_3CH_2)_2NCH_2CH_2OCH_2CH_2CN$ *3-(3-diethylaminoethoxy)propionitrile*	83.5	B.P. 100-101°/5 mm.	59	1146, 161
$(HOCH_2CH_2)_3N$ *2,2′,2″-nitrilotriethanol*	1.0 16.0	20-40° 25°	$N(CH_2CH_2OCH_2CH_2CN)_3$ *3,3′,3″-[nitrilotris(ethyleneoxy)]tripropionitrile*	97.7	—	161	
$C_4H_9OCOCH(OH)CH_3$ *lactic acid, butyl ester*	18.0 1.0	25° 100°	$CH_3CH(OCH_2CH_2CN)CO_2C_4H_9$ *2-(2-cyanoethoxy)propionic acid, butyl ester*	50-80	B.P. 55°/0.04 mm. B.P. 77°/0.2 mm. B.P. 109°/1 mm.	902	900
$(CH_3CH_2)_2NCH_2CH_2CH_2OH$ *3-diethylamino-1-propanol*	—	—	$(CH_3CH_2)_2NCH_2CH_2CH_2OCH_2CH_2CN$ *3-(3-diethylaminopropoxy)propionitrile*	75.4	B.P. 148-150°/25 mm.	1146	
 *1-(4-chlorophenyl)-1-ethanol*	1.5	40-45°	 *3-(p-chloro-α-methylbenzyloxy)propionitrile*	83	B.P. 140-150°/6-7 mm.	378	

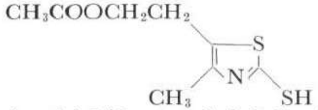
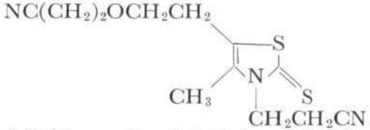
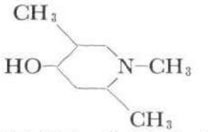
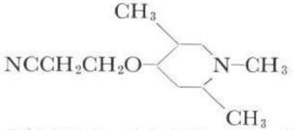
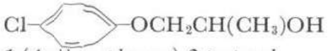
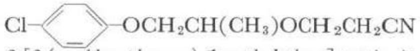
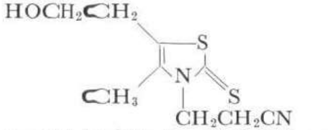
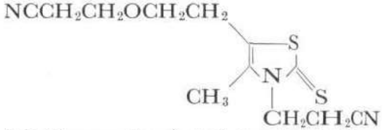
Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 *4-methyl-5-(2-acetoxyethyl)-2-thiazolethiol*	10.0	R.T.	 *5-[2-(2-cyanoethoxy)ethyl]-4-methyl-2-thioxo-4-thiazoline-3-propionitrile*	20.2	M.P. 62-63°	1181	
 *1,2,5-trimethyl-4-piperidinol*	4.0 O.N.	R.T. R.T.	 *3-(1,2,5-trimethyl-4-piperidyloxy)propionitrile*	99	B.P. 117°/4 mm.	815	
$(CH_3CH_2CH_2)_2NCH_2CH_2OH$ *2-dipropylaminoethanol*	2.0	45°	$(CH_3CH_2CH_2)_2NCH_2CH_2OCH_2CH_2CN$ *3-[2-(dipropylamino)ethoxy]propionitrile*	66.9	B.P. 123-125°/3 mm.	59	
$CH_3(CH_2)_2CH_2N(CH_2CH_2OH)_2$ *2,2'-butyliminodiethanol*	—	35-40°	$CH_3CH_2CH_2CH_2N(CH_2CH_2OCH_2CH_2CN)_2$ *3,3'-[butyliminobis(ethyleneoxy)]dipropionitrile*	—	—	427	
 *1-(4-chlorophenoxy)-2-propanol*	0.58 2.0	25-40° 25-30°	 *3-[2-(p-chlorophenoxy)-1-methylethoxy]propionitrile*	72.2	B.P. 170°/1 mm.	157	
 *4-methyl-5-(2-hydroxyethyl)-2-thioxo-4-thiazoline-3-propionitrile*	12.0	R.T.	 *5-[2-(2-cyanoethoxy)ethyl]-4-methyl-2-thioxo-4-thiazoline-3-propionitrile*	—	M.P. 62-63°	1181	

TABLE XX—Continued

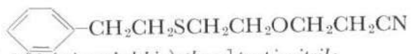
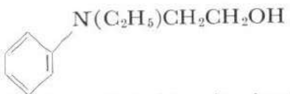
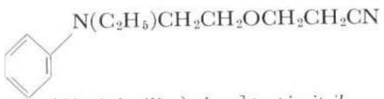
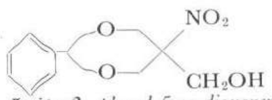
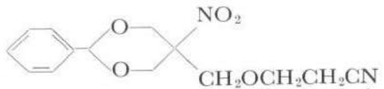
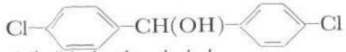
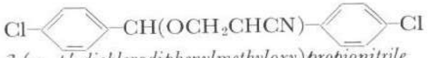
Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References This Exam.	References See Also:
$(CH_3CH_2)_2N(CH_2)_3CH(OH)CH_3$ *1-diethylamino-4-pentanol*	—	—	$(CH_3CH_2)_2N(CH_2)_3CH(CH_3)OCH_2CH_2CN$ *3-[4-(diethylamino)-1-methylbutoxy]propionitrile*	66	B.P. 125-130°/3 mm.	1146	
$[HOCH(CH_3)CH_2]_3N$ *1,1′,1″-nitrilotri-2-propanol*	— 18.0	30-40° 25°	$[NCCH_2CH_2OCH(CH_3)CH_2]_3N$ *3,3′,3″-[nitrilotris(1,2-propyleneoxy)]tripropionitrile*	Ⓖ 100	—	161	
 *S-(2-phenylethyl)-2-mercaptoethanol*	18.0	25°	 *3-[2-(phenethylthio)ethoxy]propionitrile*	86.5	B.P. 177-185°/1-2 mm.	316 317	
 *N-phenyl–N-ethyl-2-aminoethanol*	— 18.0	20-30° 25°	 *3-[2-(N-ethylanilino)ethoxy]propionitrile*	66.6	B.P. 180-185°/4 mm.	161	
$ClCH_2(CH_2)_8CH_2OH$ *10-chloro–1-decanol*	2.0	25°	$ClCH_2(CH_2)_8CH_2OCH_2CH_2CN$ *3-(10-chlorodecyloxy)propionitrile*	70	B.P. 170-174°/5 mm.	24	
$[CH_3CH(CH_3)CH_2]_2NCH_2CH_2OH$ *2-di-(2-methylpropyl)aminoethanol*	—	—	$[CH_3CH(CH_3)CH_2]_2NCH_2CH_2OCH_2CH_2CN$ *3-[2-(diisobutylamino)ethoxy]propionitrile*	61.5	B.P. 129-130°/3 mm.	59	
 *5-nitro-2—phenyl-5-*m*-dioxanemethanol*	O.N.	—	 *3-(5-nitro-2-phenyl-*m*-dioxan-5-ylmethoxy)-propionitrile*	—	M.P. 77.7°	954	
 *4,4′-dichlorobenzhydrol*	—	—	 *3-(p, p′-dichlorodiphenylmethyloxy)propionitrile*	67	M.P. 75-76.5°	453	

TABLE XX—Continued

(G) Phenols

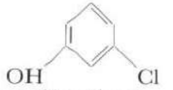
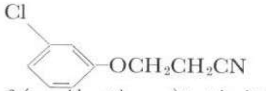
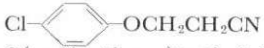
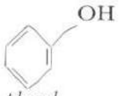
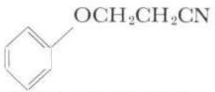
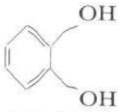
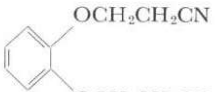
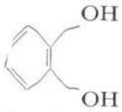
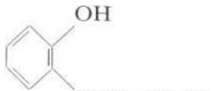
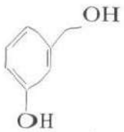
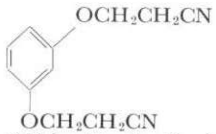
Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 m-*chlorophenol*	3.0	120-130°	 *3-(*m-*chlorophenoxy)propionitrile*	—	—	1104 404	58, 1103
 p-*chlorophenol*	—	reflux	 *3-(*p-*chlorophenoxy)propionitrile*	10	—	58	
 *phenol*	5.0	130-140°	 *3-phenoxypropionitrile*	70	M.P. 61-62°	268	58, 404, 1104, 1103, 1334
 *pyrocatechol*	24.0	85°	 *3,3′-(*o-*phenylenedioxy)dipropionitrile*	24.7	M.P. 123°	268	
 *pyrocatechol*	5.0	130-140°	 *3-(2-hydroxyphenoxy)propionitrile*	—	—	1104 404	
 *resorcinol*	24.0	85°	 *3,3′-(*m-*phenylenedioxy)dipropionitrile*	53	M.P. 112°	268	58

TABLE XX—Continued

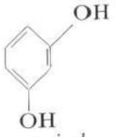
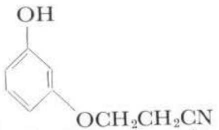
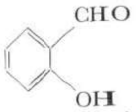
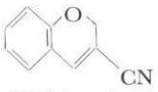
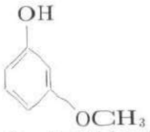
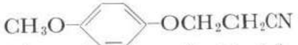
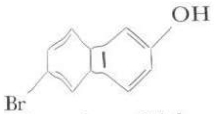
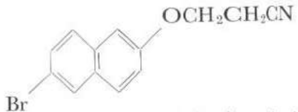
Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 *resorcinol*	—	—	 *3-(m-hydroxyphenoxy)propionitrile*	—	—	1103	
 *hydroquinone*	—	—	 *3,3′-(p-phenylenedioxy)dipropionitrile*	70	—	44	268, 404, 1104, 1103
 *salicylaldehyde*	72.0	—	 *2H-1-benzopyran-3-carbonitrile*	19	M.P. 50°	1059	58
 *3-methoxyphenol*	20.0	reflux	 *3-(m-methoxyphenoxy)propionitrile*	76	B.P. 145-146°/3 mm. M.P. 29.5-30.5°	58	
 *4-methoxyphenol*	—	—	 *3-(p-methoxyphenoxy)propionitrile*	50	M.P. 63-64.5°	879	
 *6-bromo-2-naphthol*	20.0	reflux	 *3-(6-bromo-2-naphthyloxy)propionitrile*	10	—	58	

TABLE XX—Continued

(G) Phenols

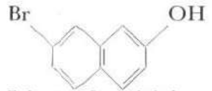
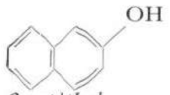
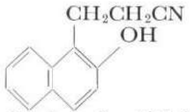
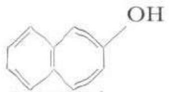
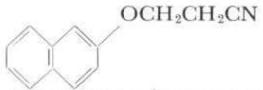
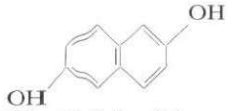
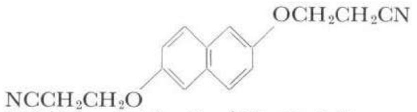
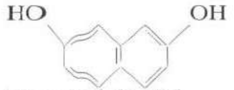
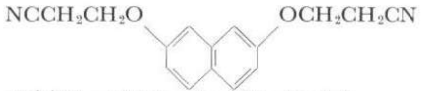
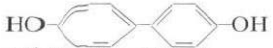
Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 *7-bromo-2-naphthol*	20.0	reflux	 *3-(7-bromo-2-naphthyloxy)propionitrile*	10	M.P. 120°	58	
 *2-naphthol*	2.0	reflux	 *2-hydroxy-1-naphthalenepropionitrile*	94	M.P. 142°	467 485	57, 1103, 1104, 404
 *2-naphthol*	24.0	reflux	 *3-(2-naphthyloxy)propionitrile*	—	M.P. 108-109°	1349	
 *2,6-naphthalenediol*	—	—	 *3,3′-(2,6-naphthylenedioxy)dipropionitrile*	—	M.P. 194°	268	
 *2,7-naphthalenediol*	—	—	 *3,3′-(2,7-naphthylenedioxy)dipropionitrile*	—	M.P. 153°	268	
 *4,4′-dihydroxydiphenyl*	—	—	 *3,3′-(4,4′-biphenylenedioxy)dipropionitrile*	47	M.P. 188-189°	268	

TABLE XX—Continued

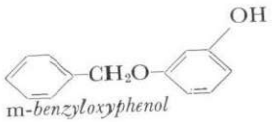
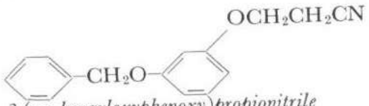
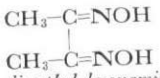
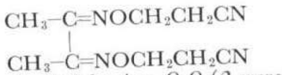
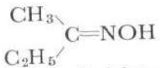
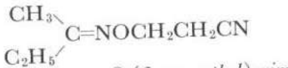
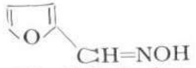
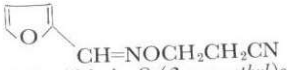
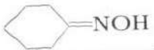
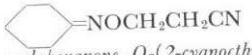
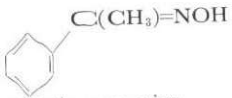
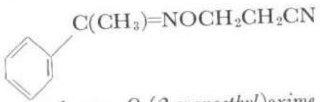
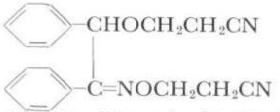
Reactants	Reaction Time (Hr.)	Reaction Temperature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References This Exam.	References See Also:
 m-*benzyloxyphenol*	30.0	95-105°	 *3-(m-benzyloxyphenoxy)propionitrile*	95	M.P. 89-90°	1273	
(H) Oximes							
$(CH_3)_2C{=}NOH$ *acetone oxime*	14.0	25-30°	$(CH_3)_2C{=}NOCH_2CH_2CN$ *acetone, O-(2-cyanoethyl)oxime*	60.5	B.P. 85°/10 mm.	179	181
 $CH_3{-}C{=}NOH$ $CH_3{-}C{=}NOH$ *dimethylglyoxamine*	0.83 24.0	25-38° R.T.	 $CH_3{-}C{=}NOCH_2CH_2CN$ $CH_3{-}C{=}NOCH_2CH_2CN$ *dimethylglyoxime, O,O-(2-cyanoethyl)diether*	60	M.P. 123°	181	179
 $CH_3(C_2H_5)C{=}NOH$ *methyl ethyl ketoxime*	14.0	R.T.	 $CH_3(C_2H_5)C{=}NOCH_2CH_2CN$ *2-butanone, O-(2-cyanoethyl)oxime*	71	B.P. 109°/21 mm.	179	181
 *2-furaldehydeoxime*	0.5 2.0	30-40° R.T.	 *2-furaldehyde, O-(2-cyanoethyl)oxime*	45.7	M.P. 116°	181	179
 *cyclohexanone oxime*	0.25 24.0	25-46° 25°	 *cyclohexanone, O-(2-cyanoethyl)oxime*	—	B.P. 130-135°/8 mm.	181	
 *acetophenone oxime*	2.0 2.0	R.T. 40-50°	 *acetophenone, O-(2-cyanoethyl)oxime*	92	M.P. 44°	179	181

TABLE XX—Continued

(H) Oximes

Reactants	Reaction Time (Hr.)	Reaction Temperature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References: This Exam.	References: See Also:
$CH_3(CH_2)_2CH{=}C(C_2H_5)CH{=}NOH$ *2-ethyl-2-hexenaldoxime*	18.0 0.75	25° 90°	$CH_3(CH_2)_2CH{=}C(C_2H_5)CH{=}NOCH_2CH_2CN$ *2-ethyl-2-hexenal, O-(2-cyanoethyl)oxime*	80.7	B.P. 105-115°/1 mm.	181	
$CH_3(CH_2)_3CH(CH_2CH_3)CH{=}NOH$ *2-ethylhexylaldoxime*	— 4.0	25.57° R.T.	$CH_3(CH_2)_3CH(CH_2CH_3)CH{=}NOCH_2CH_2CN$ *2-ethylhexanal, O-(2-cyanoethyl)oxime*	—	B.P. 90°/0.5 mm.	181	
$CH_3(CH_2)_6C(CH_3){=}NOH$ *2-nonanone oxime*	— 20.0	30-40° 25-30°	$CH_3(CH_2)_6C(CH_3){=}NOCH_2CH_2CN$ *2-nonanone, O-(2-cyanoethyl)oxime*	84.6	B.P. 102-104°/1 mm.	181	
 *benzoin oxime*	24.0	R.T.	 *3-(α-phenylphenacyloxy)propionitrile, O-(2-cyanoethyl)oxime*	96	M.P. 72-73°	179	

(I) Hydroperoxides

Reactants	Reaction Time (Hr.)	Reaction Temperature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References: This Exam.	References: See Also:
CH_3CH_2OOH *ethyl hydroperoxide*	—	20-25°	$CH_3CH_2OOCH_2CH_2CN$ *(2-cyanoethyl) ethyl peroxide*	—	—	470	
$(CH_3)_3COOH$ t-*butyl hydroperoxide*	1.0	30-35°	$(CH_3)_3COOCH_2CH_2CN$ tert-*butyl (2-cyanoethyl) peroxide*	—	—	470	

NOTES:
Ⓐ Based on unrecovered carbinol.
Ⓑ Leuna alcohol—a mixture of medium molecular weight alcohols boiling in the range of 160-220°C.
Ⓒ Condensation product of 9 moles of ethylene oxide and *p-tert*-octyl-o-cresol.
Ⓓ Structure not given.
Ⓔ Boiling point of the free acid.
Ⓕ Yields varied unaccountably.
Ⓖ Yield of crude product.

TABLE XXI—"S" Cyanoethylation

(A) Inorganic Sulfur Compounds

Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
H_2S *hydrogen sulfide*	—	65-70°	$S(CH_2CH_2CN)_2$ *3,3′-thiodipropionitrile*	86-93	B.P. 191-194°/7 mm.	421	629, 142, 576, 698, 526
H_2S *hydrogen sulfide*	—	reflux	$S(CH_2CH_2CSNH_2)_2$ *3,3′-thiobis[thionopropionamide]*	46	—	295	
NaS_x *sodium polysulfide*	1.0	25°	$NCCH_2CH_2SSCH_2CH_2CN$ *3,3′-dithiodipropionitrile*	19 Ⓐ	M.P. 47.6°	1037	
$NaHSO_3$ *sodium bisulfite*	24.0	25°	$NaO_3SCH_2CH_2CN$ *2-cyanoethanesulfonic acid, sodium salt*	96 Ⓑ	—	958	209
$KHSO_3$ *potassium bisulfite*	— 16.0	50° 25°	$KO_3SCH_2CH_2CN$ *2-cyanoethanesulfonic acid, potassium salt*	72	—	209	
$Na_2SO_3 + H_2O$ *sodium sulfite + water*	—	15-45°	$NCCH_2CH_2SO_3Na$ *2-cyanoethanesulfonic acid, sodium salt*	—	—	795	
$Na_2S_2O_3 + H_2O$ *sodium thiosulfate + water*	—	reflux	$(NCCH_2CH_2SSO_3Na)$ © *2-cyanoethanethiosulfonic acid, sodium salt*	—	—	937	
$Na_2CS_3 + H_2O$ *sodium thiocarbonate + water*	—	—	$S(CH_2CH_2CN)_2$ *3,3′-thiodipropionitrile*	—	—	526	

(B) Alkyl Mercaptans

Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	This Exam.	See Also:
CH_3SH *methanethiol*	16.0	R.T.	$CH_3SCH_2CH_2CN$ *3-methylthiopropionitrile*	91	B.P. 97°/15 mm.	557	1047
CH_3CH_2SH *ethanethiol*	18.0	25°	$CH_3CH_2SCH_2CH_2CN$ *3-ethylthiopropionitrile*	95	B.P. 100°/13 mm.	1355	557, 469, 448, 449
$CH_3CH_2CH_2SH$ *1-propanethiol*	1.0	<30°	$CH_3CH_2CH_2SCH_2CH_2CN$ *3-propylthiopropionitrile*	78	B.P. 95-100°/4 mm.	469	

TABLE XXI—Continued

(B) Alkyl Mercaptans

Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
$(CH_3)_2CHSH$ *2-propanethiol*	16.0	R.T.	$(CH_3)_2CHSCH_2CH_2CN$ *3-isopropylthiopropionitrile*	95	B.P. 102.5-103°/12 mm.	557	
$CH_3CH_2CH_2CH_2SH$ *1-butanethiol*	0.5	35-40°	$CH_3CH_2CH_2CH_2SCH_2CH_2CN$ *3-butylthiopropionitrile*	98	B.P. 117°/3 mm.	1131	557, 469
$(CH_3)_2CHCH_2SH$ *2-methyl-1-propanethiol*	1.0	R.T.	$(CH_3)_2CHCH_2SCH_2CH_2CN$ *3-isobutylthiopropionitrile*	85	B.P. 132.5-133°/30 mm. B.P. 106°/6 mm.	557	
$(CH_3)_3CSH$ *2-methyl-2-propanethiol*	—	—	$(CH_3)_3CSCH_2CH_2CN$ *3-tert-butylthiopropionitrile*	95	B.P. 113.5-114°/17 mm.	557	
$(CH_3)_3SiCH_2SH$ *trimethylsilylmethanethiol*	—	—	$(CH_3)_3SiCH_2SCH_2CH_2CN$ *3-(trimethylsilylmethylthio)propionitrile*	88.5	B.P. 250°	1347	
$CH_3Si(C_2H_5)_2CH_2SH$ *diethylmethylsilylmethanethiol*	—	—	$CH_3Si(C_2H_5)_2CH_2SCH_2CH_2CN$ *3-(diethylmethylsilylmethylthio)propionitrile*	79.5	B.P. 100.5°/2 mm.	1347	
$(CH_3)_3SiCH_2CH_2CH_2SH$ *3-trimethylsilyl-1-propanethiol*	—	—	$(CH_3)_3SiCH_2CH_2CH_2SCH_2CH_2CN$ *3-(3-trimethylsilylpropylthio)propionitrile*	71	B.P. 108.5°/1 mm.	1347	
 $-CH_2SH$ *α-toluenethiol*	—	—	 $-CH_2SCH_2CH_2CN$ *benzylthiopropionitrile*	95	B.P. 131°/0.9 mm.	1047	557, 449
$CH_3(CH_2)_7SH$ *1-octanethiol*	1.0 O.N.	40-50° R.T.	$CH_3(CH_2)_7SCH_2CH_2CN$ *3-octylthiopropionitrile*	63	—	897	
octanethiol ⓓ	during addn. 2.0	<50° 50-60°	—	—	—	1009	
$CH_3Si(CH_2CH_2CH_3)_2CH_2SH$ *dipropylmethylsilylmethanethiol*	—	—	$CH_3Si(C_3H_7)_2CH_2SCH_2CH_2CN$ *3-[(methyldipropylsilyl)methylthio]propionitrile*	70.5	B.P. 124-125°/2 mm.	1347	

TABLE XXI—Continued

(B) Alkyl Mercaptans

Reactants	Reaction Time (Hr.)	Reaction Temperature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References: This Exam.	References: See Also:
$CH_3(CH_2)_8SH$ *1-nonanethiol*	1.0 O.N.	40-50° R.T.	$CH_3(CH_2)_8SCH_2CH_2CN$ *3-nonylthiopropionitrile*	48	—	897	
$CH_3(CH_2)_9SH$ *1-decanethiol*	0.5 1.0	40-50° —	$CH_3(CH_2)_9SCH_2CH_2CN$ *3-decylthiopropionitrile*	69	B.P. 154-156°/3 mm.	994	
$CH_3(CH_2)_{10}CH_2SH$ *1-dodecanethiol*	—	—	$CH_3(CH_2)_{10}CH_2SCH_2CH_2CN$ *3-dodecylthiopropionitrile*	81	B.P. 197-198°/4 mm. M.P. 21°	994	897, 469
dodecanethiol Ⓔ	during addn. 2.0	<50° 50-60°	—	—	—	1009	
$CH_3(CH_2)_{17}SH$ *1-octadecanethiol*	—	—	$CH_3(CH_2)_{17}SCH_2CH_2CN$ *3-octadecylthiopropionitrile*	70	M.P. 50-51°	994	

(C) Miscellaneous Mercaptans

Reactants	Reaction Time (Hr.)	Reaction Temperature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References: This Exam.	References: See Also:
CH_3COSH *thioacetic acid*	2.0	38-105°	$CH_3COSCH_2CH_2CN$ *thiolacetic acid, 2-cyanoethyl ester*	88.6	—	289 288	
$HSCH_2COOH$ *thiolacetic acid*	—	—	$HOOCCH_2SCH_2CH_2CN$ *(2-cyanoethylthio)acetic acid*	77	—	1398	791
$HOCH_2CH_2SH$ *2-mercaptoethanol*	0.5 16.0	55-60° R.T.	$HOCH_2CH_2SCH_2CH_2CN$ *3-(2-hydroxyethylthio)propionitrile*	92-94	B.P. 178-180°/14 mm.	422	557, 448, 449
$HSCH_2CH_2SH$ *1,2-ethanedithiol*	1.0 —	— 40-50°	$NCCH_2CH_2SCH_2CH_2SH$ *3-(2-mercaptoethylthio)propionitrile*	26	B.P. 139-141°/6 mm.	449	448
$HSCH_2CH_2SH$ *1,2-ethanedithiol*	1.0 —	— 40-50°	$NCCH_2CH_2SCH_2CH_2SCH_2CH_2CN$ Ⓕ *3,3′-(ethylenedithio)dipropionitrile*	—	M.P. 151°	448	449

TABLE XXI—Continued

(C) Miscellaneous Mercaptans

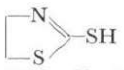
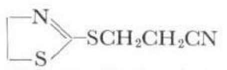
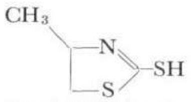
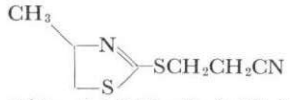
Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 *2-thiazoline-2-thiol*	2.0	<30°	 *3-(2-thiazolin-2-ylthio)propionitrile*	70	—	469	
 *4-methyl-2-thiazoline-2-thiol*	2.0	<30°	 *3-(4-methyl-2-thiazolin-2-ylthio)propionitrile*	—	—	469	
$CH_3CH_2OOCCH_2SH$ *thiolacetic acid, ethyl ester*	0.5	R.T.	$CH_3CH_2OOCCH_2SCH_2CH_2CN$ *(2-cyanoethylthio)acetic acid, ethyl ester*	89	B.P. 169°/16 mm.	557	791
$(C_2H_5O)_2PSSH$ *phosphorodithioic acid, O,O′-diethyl ester*	22.0	R.T.	$(C_2H_5O)_2PSSCH_2CH_2CN$ *phosphorodithioic acid, S-(2-cyanoethyl) O,O-diethyl ester*	—	—	87	
 *2-thiomethylthiophene*	1.0	reflux	 *3-(2-thenylthio)propionitrile*	47	B.P. 127-130°/2.5 mm.	635	
 *S-(2-amino-4-thiazolylmethyl)isothiourea hydrochloride*	3 min.	R.T.	 *3-(2-amino-4-thiazolylmethylthio)propionitrile*	—	M.P. 110-111°	1017	
$(C_2H_5)_2NCH_2CH_2SH$ *2-diethylaminoethanethiol*	O.N.	R.T.	$(C_2H_5)_2NCH_2CH_2SCH_2CH_2CN$ *3-(2-diethylaminoethylthio)propionitrile*	92	B.P. 111°/2.5 mm.	253	

TABLE XXI—Continued

(C) Miscellaneous Mercaptans

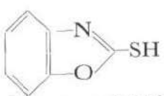
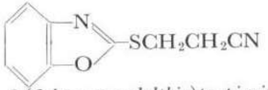
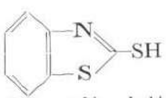
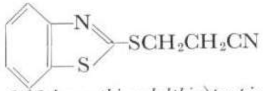
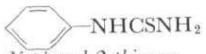
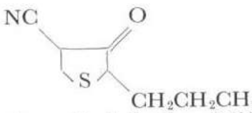
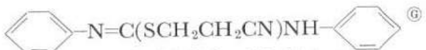
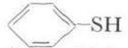
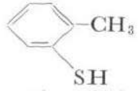
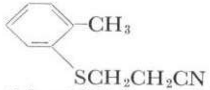
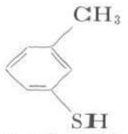
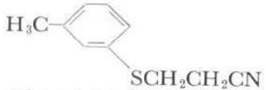
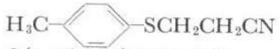
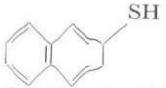
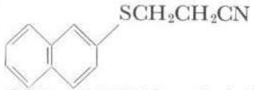
Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 *2-benzoxazolethiol*	45.0	R.T.	 *3-(2-benzoxazolylthio)propionitrile*	88	M.P. 173-173.5°	557	
 *2-benzothiazolethiol*	16.0	R.T.	 *3-(2-benzothiazolylthio)propionitrile*	87	M.P. 167°	557	250, 469
 *N-phenyl-2-thiourea*	—	—	—	—	—	376	
$CH_3OOC(CH_2)_3CH(SH)COOCH_3$ *2-thiol-7,6-hexanedioic acid, dimethyl ester*	2.0	reflux	 *4-cyanotetrahydro-3-oxo-2-thiophenebutyric acid, methyl ester*	81	—	68	
 *thiocarbanilide*	2.0	—	 *2-(2-cyanoethyl)-1,3-diphenyl-2-thiopseudourea*	—	—	469	
HS–R—SH *dimercaptans*	—	—	$NCCH_2CH_2S–R–SCH_2CH_2CN$	—	—	142	

TABLE XXI—Continued

(D) Thiophenols

Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 *benzenethiol*	16.0	R.T.	 *3-phenylthiopropionitrile*	97	B.P. 154°/8 mm.	557	469, 49
 o-*toluenethiol*	16.0	R.T.	 *3-(*o-*tolylthio)propionitrile*	81	B.P. 177.5°/16 mm.	557	
 m-*toluenethiol*	16.0	R.T.	 *3-(*m-*tolylthio)propionitrile*	97	B.P. 177.5°/18 mm.	557	
 p-*toluenethiol*	16.0	R.T.	 *3-(*p-*tolylthio)propionitrile*	95	B.P. 178.5°/17 mm.	557	469
 *2-naphthalenethiol*	1.0	65°	 *3-(2-naphthylthio)propionitrile*	92	B.P. 178-179°	57	469

(E) Thiocarbamates

Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	This Exam.	See Also:
H_2NCSNH_2 *thiourea*	— 3.0	<30° —	$H_2NC(=NH)SCH_2CH_2CN$ Ⓖ *2-(2-cyanoethyl)-2-thiopseudourea*	94	—	469	
$H_2NCSSNH_4$ *ammonium dithiocarbamate*	— —	20-30° 50°	Ⓗ	—	B.P. 150°	604	

TABLE XXI—Continued

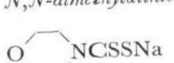
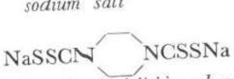
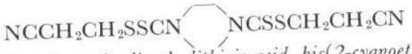
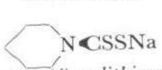
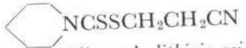
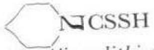
Reactants	Reaction Time (Hr.)	Reaction Temperature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References: This Exam.	References: See Also:
$(CH_3)_2NCSSNa$ *N,N-dimethyldithiocarbamic acid, sodium salt*	—	R.T.	$(CH_3)_2NCSSCH_2CH_2CN$ *dimethyldithiocarbamic acid, 2-cyanoethyl ester*	—	M.P. 37-38°	318	
$(CH_3)_2NCSSH$ *N,N-dimethyldithiocarbamic acid*	3.0	<30°	$(CH_3)_2NCSSCH_2CH_2CN$ *dimethyldithiocarbamic acid, 2-cyanoethyl ester*	—	M.P. 40-42°	469	
 *morpholinodithiocarbamic acid, sodium salt*	—	R.T.	 *4-morpholinecarbodithioic acid, 2-cyanoethyl ester*	—	M.P. 86.5°	318	
$(CH_3CH_2)_2NCSSNa$ *N,N-diethyldithiocarbamic acid, sodium salt*	—	R.T.	$(CH_3CH_2)_2NCSSCH_2CH_2CN$ *diethyldithiocarbamic acid, 2-cyanoethyl ester*	—	—	318	
 *piperazinobis(dithiocarbamic) acid, disodium salt*	—	30°	 *1,4-piperazinedicarbodithioic acid, bis(2-cyanoethyl) ester*	—	M.P. 140°	319	
 *piperidinodithiocarbamic acid, sodium salt*	—	R.T.	 *1-piperidinecarbodithioic acid, 2-cyanoethyl ester*	—	M.P. 79.5°	318	
$(CH_2)_2[N(CH_3)CSSNa]_2$ *N,N′-dimethylethylenediaminebisdithiocarbamic acid, disodium salt*	—	30°	$(CH_2)_2[N(CH_3)CSSCH_2CH_2CN]_2$ *ethylenebis[methyldithiocarbamic acid], bis(2-cyanoethyl) ester*	—	M.P. 151°	319	
 *piperidinodithiocarbamic acid*	3.0	<40°	 *1-piperidinecarbodithioic acid, 2-cyanoethyl ester*	61	M.P. 80-82°	469	
$(CH_2)_3[N(CH_3)CSSNa]_2$ *N,N′-dimethyltrimethylenediaminebisdithiocarbamic acid, disodium salt*	—	30°	$(CH_2)_3[N(CH_3)CSSCH_2CH_2CN]_2$ *trimethylenebis[methyldithiocarbamic acid], bis(2-cyanoethyl) ester*	—	M.P. 93°	319	

TABLE XXI—Continued

(E) Thiocarbamates

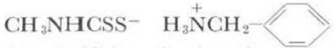
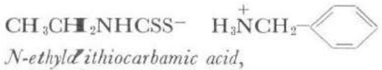
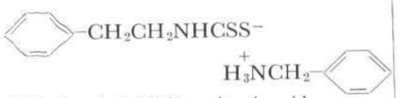
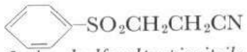
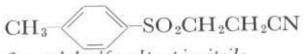
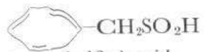
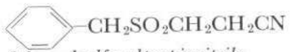
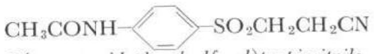
Reactants	Reaction Time (Hr.)	Reaction Temperature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
$(CH_2)_2[N(C_2H_5)CSSNa]_2$ *N,N′-diethylethylenediaminebisdithiocarbamic acid, disodium salt*	—	30°	$(CH_2)_2[N(C_2H_5)CSSCH_2CH_2CN]_2$ *ethylenebis[ethyldithiocarbamic acid], bis(2-cyanoethyl) ester*	—	M.P. 102°	319	
 $CH_3NHCSS^- \quad H_3\overset{+}{N}CH_2-$ *N-methyldithiocarbamic acid, benzylammonium salt*	—	—	$CH_3NHCSSCH_2CH_2CN$ *methyldithiocarbamic acid, 2-cyanoethyl ester*	—	M.P. 38°	1248	
$(CH_2)_3[N(C_2H_5)CSSNa]_2$ *N,N′-diethyltrimethylenediaminebisdithiocarbamic acid, disodium salt*	—	30°	$(CH_2)_3[N(C_2H_5)CSSCH_2CH_2CN]_2$ *trimethylenebis[2-ethyldithiocarbamic acid], bis(2-cyanoethyl) ester*	—	M.P. 56°	319	
$(n\text{-}C_4H_9)_2NCSSH$ *dibutyldithiocarbamic acid*	—	<30°	$(n\text{-}C_4H_9)_2NCSSCH_2CH_2CN$ *dibutyldithiocarbamic acid, 2-cyanoethyl ester*	82.5	—	469	
 $CH_3CH_2NHCSS^- \quad H_3\overset{+}{N}CH_2-$ *N-ethyldithiocarbamic acid, benzylammonium salt*	—	—	$CH_3CH_2NHCSSCH_2CH_2CN$ *ethyldithiocarbamic acid, 2-cyanoethyl ester*	—	M.P. 91°	1248	
$(CH_2)_6[N(CH_3)CSSNa]_2$ *N,N′-dimethylhexamethylenediamine-bisdithiocarbamic acid, disodium salt*	—	30°	$(CH_2)_6[N(CH_3)CSSCH_2CH_2CN]$ *hexamethylenebis[methyldithiocarbamic acid], bis(2-cyanoethyl) ester*	—	M.P. 72.5°	319	
$(CH_2)_6[N(C_2H_5)CSSNa]_2$ *N,N′-diethylhexamethylenediamine-bisdithiocarbamic acid, disodium salt*	—	30°	$(CH_2)_6[N(C_2H_5)CSSCH_2CH_2CN]_2$ *hexamethylenebis[ethyldithiocarbamic acid], bis(2-cyanoethyl) ester*	—	M.P. 93.5°	319	
 $-CH_2NHCSS^- \quad H_3\overset{+}{N}CH_2-$ *N-benzyldithiocarbamic acid, benzylammonium salt*	—	—	 $-CH_2NHCSSCH_2CH_2CN$ *benzyldithiocarbamic acid, 2-cyanoethyl ester*	—	M.P. 54°	1248	

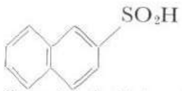
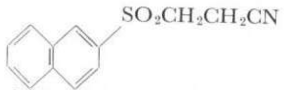
TABLE XXI—Continued

(E) Thiocarbamates

Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 *N-2-phenylethyldithiocarbamic acid, benzylammonium salt*	—	—	 *phenethyldithiocarbamic acid, 2-cyanoethyl ester*	—	M.P. 54°	1248	
$(CH_2)_2[N(CH_2C_6H_5)CSSNa]_2$ *N,N′-dibenzylethylenediaminebisdithiocarbamic acid, disodium salt*	—	30°	$(CH_2)_2[N(CH_2C_6H_5)CSSCH_2CH_2CN]_2$ *ethylenebis[benzyldithiocarbamic acid], bis(2-cyanoethyl) ester*	—	M.P. 119.5°	319	

(F) Sulfinic Acids

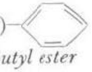
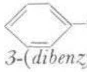
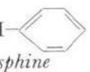
Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
$CH_3CH_2SO_2H$ *ethylsulfinic acid*	—	—	$CH_3CH_2SO_2CH_2CH_2CN$ *3-ethylsulfonylpropionitrile*	—	—	1192	
 *benzenesulfinic acid*	—	—	 *3-phenylsulfonylpropionitrile*	97	M.P. 95-96°	1192	
 p-*toluenesulfinic acid*	—	—	 *3-*p*-tolylsulfonylpropionitrile*	98	M.P. 93.5-94°	1192	
 *benzylsulfinic acid*	—	—	 *3-benzylsulfonylpropionitrile*	84	M.P. 115-116°	1192	
 p-*acetamidobenzenesulfinic acid*	—	—	 *3-(*p*-acetamidophenylsulfonyl)propionitrile*	95	M.P. 208-209°	1192	

Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 SO$_2$H *2-naphthylsulfinic acid*	—	—	 SO$_2$CH$_2$CH$_2$CN *3-(2-naphthylsulfonyl)propionitrile*	90	M.P. 137-138°	1192	

NOTES: Ⓐ Based on unrecovered acrylonitrile.
Ⓑ By analysis an 89% recovery was obtained; HSO_3^- is the reacting species.
Ⓒ Products have not been isolated; structure uncertain.
Ⓓ No structure given; prepared from diisobutylene.
Ⓔ No structure given; prepared from triisobutylene.
Ⓕ Isolated as the dicarboxylic acid.
Ⓖ Structure uncertain.
Ⓗ Product not identified.

TABLE XXII—Boron, Phosphorus, Arsenic, Silicon and Tin Cyanoethylation

B_2H_6 *diborane*	20.0	25°	red solid possibly $B(CH_2CH_2CN)_3$ *tris(2-cyanoethyl)boron*	—	—	1032	
$(CH_3O)_2P(O)H$ *dimethyl phosphonate*	—	60-70°	$(CH_3O)_2P(O)CH_2CH_2CN$ *(2-cyanoethyl)phosphonic acid, dimethyl ester*	86.3	B.P. 158°/11 mm.	893	
$(CH_3CH_2O)_2P(O)H$ *diethyl phosphonate*	—	—	$(CH_3CH_2O)_2P(O)CH_2CH_2CN$ *(2-cyanoethyl)phosphonic acid, diethyl ester*	83	B.P. 159-160°/10 mm.	893	
$[(CH_3)_2CHO]_2P(O)H$ *diisopropyl phosphonate*	—	—	$[(CH_3)_2CHO]_2P(O)CH_2CH_2CN$ *(2-cyanoethyl)phosphonic acid, diisopropyl ester*	46.4	B.P. 160°/13 mm.	893	
$(n\text{-}C_4H_9O)_2P(O)H$ *di-n-butyl phosphonate*	—	20-25°	$(CH_3CH_2CH_2CH_2O)_2P(O)CH_2CH_2CN$ *(2-cyanoethyl)phosphonic acid, dibutyl ester*	84	—	125	893, 1295
$[(CH_3)_2CHCH_2O]_2P(O)H$ *diisobutyl phosphonate*	—	—	$[(CH_3)_2CHCH_2O]_2P(O)CH_2CH_2CN$ *(2-cyanoethyl)phosphonic acid, diisobutyl ester*	71	B.P. 171°/11 mm.	893	
$[(CH_3)_2CHCH_2CH_2O]_2P(O)H$ *diisoamyl phosphonate*	—	—	$[(CH_3)_2CHCH_2CH_2O]_2P(O)CH_2CH_2CN$ *(2-cyanoethyl)phosphonic acid, diisopentyl ester*	55	B.P. 168-170°/3 mm.	1388	

Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
$[CH_3(CH_2)_5O]_2P(O)H$ *di-n-hexyl phosphonate*	—	—	$[CH_3(CH_2)_5O]_2P(O)CH_2CH_2CN$ *(2-cyanoethyl)phosphonic acid, dihexyl ester*	61.1	B.P. 198-200°/1 mm.	1388	
$[CH_3(CH_2)_7O]_2P(O)H$ *di-n-octyl phosphonate*	—	—	$[CH_3(CH_2)_7O]_2P(O)CH_2CH_2CN$ *(2-cyanoethyl)phosphonic acid, dioctyl ester*	63.2	B.P. 218-220°/2 mm.	1388	
$(C_2H_5O)(CH_3CH_2)P(O)H$ *ethyl ethylphosphinate*	0.5	steam bath	$(CH_3CH_2O)(CH_3CH_2)P(O)CH_2CH_2CN$ *(2-cyanoethyl)ethylphosphinic acid, ethyl ester*	67	B.P. 171-171.5°/12 mm.	1389	
$[CH_3(CH_2)_3O](CH_3CH_2)P(O)H$ *butyl ethylphosphinate*	0.5	steam bath	$[CH_3(CH_2)_3O](CH_3CH_2)P(O)CH_2CH_2CN$ *(2-cyanoethyl)ethylphosphinic acid, butyl ester*	53	B.P. 192°/13 mm.	1389	
$CH_3CH_2OP(O)H-$  *ethyl phenylphosphinate*	0.5	steam bath	$(CH_3CH_2O)(NCCH_2CH_2)P(O)-$  *(2-cyanoethyl)phenylphosphinic acid, ethyl ester*	48	B.P. 162-163°/1 mm.	1389	
$CH_3(CH_2)_3OP(O)H-$  *butyl phenylphosphinate*	—	15-18°	$[CH_3(CH_2)_3O](NCCH_2CH_2)P(O)-$  *(2-cyanoethyl)phenylphosphinic acid, butyl ester*	67	B.P. 111-114°/0.01 mm.	1215	
 $-CH_2P(O)HCH_2-$  *dibenzylphosphine oxide*	— 18.0	50-60° 0°	 $-CH_2P(O)(CH_2CH_2CN)CH_2-$  *3-(dibenzylphosphoroso)propionitrile*	66	M.P. 109-110°	1344	
$[CH_3(CH_2)_7]_2P(O)H$ *di-n-octylphosphine oxide*	1-2	—	$[CH_3(CH_2)_7]_2P(O)CH_2CH_2CN$ *3-(dioctylphosphoroso)propionitrile*	39	M.P. 53.4-54.2°	1344	
 $-PH_2$ *phenyl phosphine*	6.0	130-135°	 $-P(CH_2CH_2CN)_2$ *3,3′-(phenylphosphinidene)dipropionitrile*	62	M.P. 72-73° B.P. 195-205°/0.2 mm.	739	
 $-PH-$  *diphenyl phosphine*	7.0	130°	 $-P(CH_2CH_2CN)-$  *3-(diphenylphosphino)propionitrile*	71	M.P. 64-64.5°	739	
$(CH_3O)_2P(S)H$ *dimethyl phosphonothioate*	0.5	steam bath	$(CH_3O)_2P(S)CH_2CH_2CN$ *(2-cyanoethyl)phosphonothioic acid, O,O-dimethyl ester*	59	B.P. 138-139°/14 mm.	1389	

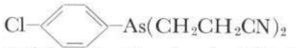
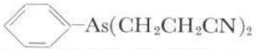
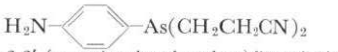
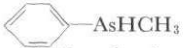
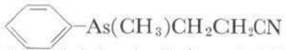
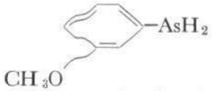
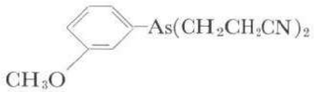
Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
$(CH_3CH_2O)_2P(S)H$ *diethyl phosphonothioate*	0.5	steam bath	$(CH_3CH_2O)_2P(S)CH_2CH_2CN$ *(2-cyanoethyl)phosphonothioic acid, O,O-diethyl ester*	74	B.P. 134-135°/7 mm.	1389	
$[CH_3(CH_2)_3O]_2P(S)H$ *dibutyl phosphonothioate*	0.5	steam bath	$[CH_3(CH_2)_3O]_2P(S)CH_2CH_2CN$ *(2-cyanoethyl)phosphonothioic acid, O,O-dibutyl ester*	68	B.P. 167°/5 mm.	1389	
$[(CH_3)_2CHCH_2O]_2P(S)H$ *diisobutyl phosphonothioate*	0.5	steam bath	$[(CH_3)_2CHCH_2O]_2P(S)CH_2CH_2CN$ *(2-cyanoethyl)phosphonothioic acid, O,O-diisobutyl ester*	67	B.P. 174°/14 mm.	1389	
CH_3AsH_2 *methyl arsine*	2 wks. 2 hrs.	R.T. reflux	$CH_3As(CH_2CH_2CN)_2$ *3,3′-(methylarsylene)dipropionitrile*	53	B.P. 148-149°/0.1 mm.	270	
 p-*chlorophenyl arsine*	2.0	reflux	 *3,3′-(*p-*chlorophenylarsylene)dipropionitrile*	92	M.P. 71-72°	269	
 *phenyl arsine*	5.0	reflux	 *3,3′-(phenylarsylene)dipropionitrile*	77	B.P. 200-210°/0.1 mm. M.P. 59-60°	269	783
 p-*aminophenyl arsine*	1.0 4.0	55° 100°	 *3,3′-(*p-*aminophenylarsylene)dipropionitrile*	96	M.P. 77.5-78.5°	269	
 *methylphenyl arsine*	4.0	reflux	 *3-(methylphenylarsino)propionitrile*	85	B.P. 172-174°/14 mm.	1330	
 m-*methoxyphenyl arsine*	6.0	100°	 *3,3′-(*m-*methoxyphenylarsylene)dipropionitrile*	100	B.P. 206-212°/0.03 mm.	1330	

TABLE XXII—Continued

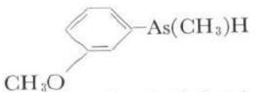
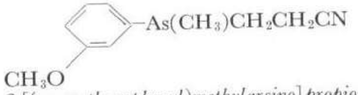
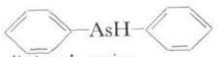
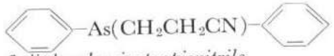
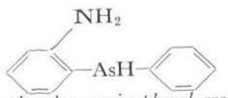
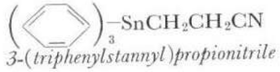
Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
 *m-methoxyphenylmethyl arsine*	6.0	100°	 *3-[(m-methoxyphenyl)methylarsino]propionitrile*	90	B.P. 148-152°/1 mm.	1330	
 *diphenyl arsine*	1.5	reflux	 *3-diphenylarsinopropionitrile*	83	M.P. 37-39°	269	
 *phenyl-o-aminophenyl arsine*	4.0	reflux	 *3-[(o-aminophenyl)phenylarsino]propionitrile*	46	B.P. 197-200°/0.35 mm.	270	
Cl_3SiH *trichloro silane*	20.0	100°	$Cl_3SiCH(CH_3)CN$ *2-(trichlorosilyl)propionitrile*	31	B.P. 70°/8 mm.	1271	837
Cl_3SiH *trichlorosilane*	5.0	160°	$Cl_3SiCH_2CH_2CN$ *3-(trichlorosilyl)propionitrile*	76	M.P. 34.6-35.1° B.P. 109°/30 mm.	836	837, 1371
CH_3SiHCl_2 *methyldichlorosilane*	26.0	75°	$NCCH(CH_3)SiCl_2CH_3$ *2-(dichloromethylsilyl)propionitrile*	26	B.P. 60-62.5°/4 mm.	1271	
$(CH_3CH_2CH_2)_3SnH$ *tripropyltin hydride*	4	100°	$(CH_3CH_2CH_2)_3SnCH_2CH_2CN$ *3-(tripropylstannyl)propionitrile*	70	B.P. 157-160°/12 mm.	1435	
$(CH_3CH_2CH_2CH_2)_3SnH$ *tributyltin hydride*	—	—	$(CH_3CH_2CH_2CH_2)_3SnCH_2CH_2CN$ *3-(tributylstannyl)propionitrile*	70	B.P. 126-134°/0.2 mm.	1115	
 *triphenyltin hydride*	—	80°	 *3-(triphenylstannyl)propionitrile*	94	M.P. 93-94°	1115	1435

TABLE XXIII—"Cl" and "Br" Cyanoethylation

Reactants	Re-action Time (Hr.)	Reaction Tem-perature (°C.)	Products	% Yield	M.P. or B.P. (°C.)	References	
						This Exam.	See Also:
HBr *hydrobromic acid*	—	—	$BrCH_2CH_2CN$ *3-bromopropionitrile*	91	B.P. 92°/25 mm.	803	
HCl *hydrochloric acid*	18.0	25°	$ClCH_2CH_2CN$ *3-chloropropionitrile*	97.2	B.P. 91-93°/41 mm.	800	388, 890, 364, 800, 1028

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