THE SYNTHESIS AND CHEMISTRY OF CYANOGEN

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I. INTRODUCTION

Cyanogen (dicyan, oxalonitrile), a colorless flammable gas, was first prepared by Gay-Lussac in 1815 by the thermal decomposition of silver cyanide. Until recently, cyanogen was primarily a chemical of academic interest, owing to the absence of economically attractive sources and applications. Many uses to which cyanogen could have been applied were either of no commercial interest or the products of its reactions were obtainable by more feasible or economical means.

Cyanogen has now become of interest to the chemical industry as a high-energy fuel (heat of formation = 73.8 kcal./mole) (98) for use in several applications. For example, a stoichiometric mixture of cyanogen and oxygen produces the hottest flames (*ca.* 4640°K.) known from a chemical reaction (32, 33). Such a flame is useful in welding and cutting new heat-resistant metals. Also, owing to its latent energy, cyanogen is considered to be a promising rocket and missile propellant when mixed with an oxidizing agent such as ozone or fluorine. Because of these and other potential uses of cyanogen, several commercially attractive syntheses have been developed for its preparation.

This review is designed to summarize the methods of preparing cyanogen and to survey its organic chemistry. No attempt is made to summarize in detail any other aspects of the occurrence or chemistry of cyanogen. A large part of the chemistry of cyanogen is described in the older literature; it has been the experience of the authors that yields of products are seldom mentioned and that some discrepancies appear in the earlier reports. It is suggested that the earlier data be verified before being used as a foundation for further experimentation. The material presented herein is taken from the original literature and is assumed to be valid unless data have been presented to the contrary.

II. PROPERTIES OF CYANOGEN

A. PHYSICAL CONSTANTS

Physical constants of cyanogen are listed in table 1. Data on its solubility are given in table 2.

B. STRUCTURE OF CYANOGEN

The structural properties of cyanogen are given below:

Property	Value	Reference
Carbon-carbon bond length	1.37 ± 0.02 A.	(131)
Carbon-nitrogen bond length	1.16 ± 0.02 A.	(131)
C—C—N bond angle	180°	(27)
Carbon-carbon double-bond character	65 per cent	(209)
	40 per cent	(131)

C. TOXICOLOGICAL PROPERTIES

Cyanogen is extremely poisonous, having a toxicity comparable to that of hydrogen cyanide. The maximum allowable vapor concentration is 10 parts per million (46).

TABLE 1

Physical constants of cyanogen

Constant	Value	References	Constant	Value	Reference
Boiling point	−21.17°C.	(34, 136)	Heat of dissociation	120-130 kcal. per mole	(147)
Melting point	−27.9°C.	(34, 136)	Heat of formation (298.1°C., gas)	69.1 kcal. per mole 73.8 kcal. per mole	(169) (98)
Critical pressure	59.6 atm.	(29)	Heat of vaporization (at boiling point)	0.5778 kcal. per mole	(34)
Critical temperature	128.3°C.	(29)	Intermolecular association	None	(34)
Density of gas	2.321 g. per liter	(34)	Mean molecular parachor	117.7 (observed) 125.0 (calculated)	(34) (34)
Density of liquid at boiling point	0.9537 g. per cc.	(34)	Surface tension (at boiling point)	21.98 dynes per centimeter	(34)
Dipole moment	0.38 × 10^{-18} e.s.u.	(24)	Trouton's constant	22.94	(34)
Heat of combustion	261.7 kcal. per mole. 261.94 kcal. per mole	(148) (98)			

Vapor pressure of cyanogen (34, 136, 174)

Solid				Liquid			
Temperature	Pressure	Temperature	Pressure	Temperature	Pressure	Temperature	Pressure
°K.	*mm.* Hg	*°K.*	*mm.* Hg	*°K.*	*mm.* Hg	*°K.*	*mm.* Hg
179.94	1.7	224.08	123.2	245.93	572.6	263.40	1250.7
190.7	5.65	230.27	196.7	247.91	629.8	265.97	1387.4
191.25	6.48	237.82	336.4	251.77	754.0	265.98	1388.4
199.05	12.79	239.92	390.9	255.35	886.4	0°C.	2.42 atm.
203.86	22.29	240.79	412.9	258.26	1007.4	21.15°C.	5.09 atm.
212.41	47.53			260.03	1086.4	75.5°C.	21.4 atm.
				261.82	1171.5		

TABLE 2

Solubility of cyanogen (98)

Solvent	Time	Temperature	$(CN)_2$ per 100 g. water	Solvent	Time	Temperature	$(CN)_2$ per 100 g. water
	hours	*°C.*	*grams*		*hours*	*°C.*	*grams*
Water	2	30	0.73	Chloroform	—	—	19
	97	30	2.03		—	—	29-30
	2		1.1-1.3	Benzene	—	—	28
Ethanol	—	—	26	Turpentine	—	—	9-10
	4	—	39	Ether	—	—	5
	48	—	89	0.01 *N* HCl	—	—	7.9 g. per 100 g. solution
	96	—	223				
Acetic acid	—	—	42				
	72	—	50.5				

III. STABILITY OF CYANOGEN

Cyanogen contains a high latent energy, of the same order as that of acetylene (208), which can be released explosively when the compound reacts with oxidizing agents such as fluorine (120), chlorine monoxide (5), and ozone (178), or when a mixture of cyanogen and air is subjected to a spark (42). Although an explosion hazard exists with cyanogen, the pure material has been stored and shipped in stainless-steel cylinders with no reported mishaps (208). It has also been used safely in numerous reactions other than oxidations.

Monomeric cyanogen polymerizes (see Section V) to a solid material in a manner characteristic of similar nitrile-containing substances, such as cyanogen chloride and hydrogen cyanide. Whereas the latter materials have been known to polymerize explosively in the presence of impurities (119), the polymerization of cyanogen has not been reported to occur in a violent manner.

A comprehensive study was recently made by Welcher, Berets, and Sentz (208) on the stability of pure cyanogen to heat, pressure, chemical additives, and severe mechanical shock. They found that pure cyanogen was unchanged after 18 to 23 days at 65°C. and that it contained only small quantities of solid decomposition products after storage for 100 days under similar conditions. The presence of acids, bases, and salts caused an acceleration in its decomposition. It was concluded that pure cyanogen did not decompose or polymerize rapidly at moderate temperatures and could be stored safely in Monel or stainless-steel cylinders in the absence of a stabilizer.

The shock tests on liquid and solid cyanogen indicated that the material is insensitive to mechanical shock greater than that expected in shipment and laboratory handling. It should not be concluded from these data that all the variables in the stability of cyanogen have been investigated. Until more complete data are available, it has been suggested that the literature on acetylene would be a good guide to the safe handling of cyanogen (208).

IV. Preparation of Cyanogen

During the century following the discovery of cyanogen the thermal decomposition of heavy metal cyanides was the most popular method for its synthesis. In more recent years, numerous additional routes to cyanogen have been devised, but, owing either to the complexity of the reactions or to prohibitive costs of the reactants or equipment, only a few of these methods have been utilized on a laboratory scale, and a more limited number would be of commercial interest. Although cyanogen has been detected in varying quantities in natural gas and in effluent gases from the destructive distillation of coal, these sources are not currently utilized.

Cyanogen has been synthesized by various reactions of metal cyanides, hydrogen cyanide, cyanogen halides, hydrocarbons and nitrogen-containing compounds, glyoxime, and nitrogen-containing derivatives of oxalic acid. A discussion of these methods follows, and a summary is given in table 3.

A. FROM METAL CYANIDES

The formation of cyanogen by the thermal decomposition of cyanides of the noble metals (62, 76, 113, 141, 172, 181) and of copper (101) usually involves heating the dry salt. In most cases an inert gas, such as nitrogen or carbon dioxide, is employed as a carrier gas. The heating of dry metal cyanides in the presence of oxidizing agents, such as chlorine and iron (193), phosphorus pentachloride (10), iron(III) chloride (87, 127), or mercury(II) chloride (95, 112, 143), furnishes higher yields of cyanogen at lower reaction temperatures.

TABLE 3

Preparation of cyanogen

Reactants	Conditions	Products	References
1. From metal cyanides			
Silver or gold cyanide	Heat	$(CN)_2$	(76, 141, 177)
$Hg(CN)_2$	ca. 200°C. >400°C. >800°C.	$(CN)_2$ Paracyanogen $(CN)_2$	(107, 163, 181)
$Hg(CN)_2$, $HgCl_2$	Heat	$(CN)_2$, $HgCl$	(75, 95, 143)
$Cu(CN)_2$	Heat	$CuCN$, $(CN)_2$	(101)
$Cu(CN)_2$, MnO_2, acetic acid	Heat	$(CN)_2$	(87)
$Cu(CN)_2$, $FeCl_3$, H_2O	Heat	$(CN)_2$	(87)
$CuCN$, $FeCl_3$	Heat	$(CN)_2$, $CuCl$, $FeCl_2$	(127)
$CuSO_4$, KCN, H_2O	60–100°C.	$(CN)_2$, CO_2, HCN, $CuCN$, K_2SO_4	(70, 87, 162, 203)
$K_3Fe(CN)_6$, $HgCl_2$, Hg	Ultraviolet light	$(CN)_2$	(160)
$K_3Fe(CN)_5$, H_2O	Ultraviolet light		(160)
KCN, PCl_5	Ultraviolet light	$(CN)_2$, PCl_3, KCl	(10)
KCN, $NaCN$	Electrolysis of fused salt	$(CN)_2$ at anode, K and Na at cathode	(28, 192)
Alkali cyanides, Cl_2, Fe	Heat	$(CN)_2$, alkali chlorides	(193)
$Ba(CN)_2$, N_2	Electrolysis between carbon electrodes	$(CN)_2$ at anode, Ba at cathode	(114)
2. From hydrogen cyanide or cyanogen halides			
HCN	Vapor phase, heat	$(CN)_2$	(152)
HCN, air	Vapor phase, 300–600°C., supported silver catalyst	$(CN)_2$ (yield = 22.8 per cent)	(152)
HCN, Cl_2	Vapor phase, 100–200°C. >200°C.	HCl, $CNCl$ HCl, $(CN)_2$	(100)
$CNCl$, H_2	Vapor phase, 850°C.	HCl, $(CN)_2$ (95 per cent yield)	(43)
$CNCl$, $CH_2{=}CH_2$	Vapor phase, 150–170°C., CuCl catalyst	$(CN)_2$, $ClCH_2CH_2Cl$	(75)
CNI	Vapor phase, 90–123°C.	$(CN)_2$, I_2	(105)
HCN	Electrolysis in water or liquid sulfur dioxide	$(CN)_2$, NH_3, CO_2, H_2, O_2	(85)
3. From hydrocarbons and nitrogen-containing materials			
$CH_2{=}CH_2$, N_2	Vapor phase, electric discharge tube	$(CN)_2$, HCN, CH_4, C_2H_6, $CH{\equiv}CH$	(50, 194)
$CH{\equiv}CH$, NH_3	Vapor phase, 480°C., metal catalyst	$(CN)_2$, HCN	(7)
$CH{\equiv}CH$, N_2	Vapor phase, electric discharge tube	$(CN)_2$, HCN, polymer	(195)
Carbon filament, N_2	Vapor phase, 2200°C.	$(CN)_2$	(56, 137, 151)
CO, N_2	1500–1800°C.	$(CN)_2$	(154, 155, 171, 173)
CO, N_2	Vapor phase, FeO catalyst, 300–525°C., 50 atm. pressure	$(CN)_2$	(165)
Producer gas, air	Vapor phase, Fe, CaO, NaOH catalyst	$(CN)_2$	(168)
Natural gas, air	Vapor phase, Fe, CaO, NaOH catalyst	$(CN)_2$, NH_3	(168)
Hydrocarbons, CO, ionized nitrogen	Vapor phase, high-frequency field	$(CN)_2$	(167)
N_2, CO or N_2, CO, H_2	Vapor phase, passed through molten iron saturated with carbon	$(CN)_2$	(49)
Coal, coal liquors, and slimes	Destructive distillation	$(CN)_2$	(25, 112, 149)

TABLE 3—*Concluded*

Reactants	Conditions	Products	References
4. Miscellaneous procedures			
Paracyanogen	>860°C.	$(CN)_2$	(159, 191)
Calcium cyanamide, carbon disulfide	700–850°C.	$(CN)_2$, CaS, S	(74)
$Cu(CH_3COO)_2$, KSCN, H_2O	Heat	$(CN)_2$	(138)
Tricyanotriazine	Pyrolysis	$(CN)_2$	(166)
Phospham $(PN_2H)_x$, potassium oxalate	Heated to a red glow	$(CN)_2$	(196)
Isocyanato tetrabromide, Ag	Heat	AgCN, AgBr, $(CN)_2$	(179)
Cyanothioformamide, Ag	Heat	Ag_2S	(197)
Dimethyl ester of azodicarbothiamide	110°C.	$(CN)_2$	(3)
Copper, silver, lead, or cadmium cyanamide, air	Heat	$(CN)_2$, CO_2	(23)
5. From the dehydration of glyoxime and nitrogen-containing acid derivatives			
Ammonium oxalate	290°C.	$(CN)_2$	(11, 39, 118, 130, 171)
Oxamide, P_2O_5	130-220°C., vacuum	$(CN)_2$ (86 per cent yield)	(11, 39, 118, 130, 171)
Oxamide, P_2O_6	120-160°C.	$(CN)_2$	(11, 39, 118, 130, 171)
Oxamide, P_2S_5	Heat	$(CN)_2$	(75)
Glyoxime, acetic anhydride	Heat	$(CN)_2$	(99)

The thermal decomposition of metal cyanides is not an attractive method for preparing cyanogen, owing to the inefficiency and hazardous nature of such procedures. Explosions have been known to occur when silver cyanide or mercury cyanide was thermally decomposed, presumably owing to the presence of silver fulminate (AgONC) or mercury fulminate [$Hg(ONC)_2$] as an impurity (47). Also, decompositions of such metal cyanides are usually complicated by the formation of paracyanogen (see Section V).

The reaction of copper sulfate with potassium cyanide in an aqueous medium (70, 87, 162, 203) has been the most widely used procedure for the preparation of cyanogen on the laboratory scale. This procedure involves the addition of an aqueous solution of potassium cyanide to a concentrated solution of copper sulfate at 60–100°C. A mixture of cyanogen (78 per cent), carbon dioxide (20 per cent), and hydrogen cyanide (2 per cent) is evolved concurrently with the production of copper(I) cyanide and potassium sulfate in the reaction kettle (127).

$$2CuSO_4 + 4KCN \rightarrow Cu_2(CN)_2 + 2K_2SO_4 + (CN)_2$$

Pure anhydrous cyanogen is obtained by passing the effluent mixture first through a tower containing dry sodium hydroxide to remove the carbon dioxide, then through silver nitrate solution to remove hydrogen cyanide, and finally through a drying tower of calcium chloride or calcium sulfate. Similarly, aqueous solutions of copper(I) cyanide and iron(III) chloride, or an acetic acid solution of copper(I) cyanide and manganese(IV) oxide, furnish cyanogen on being heated (87).

Ricca and Pirrone (143) found that varying quantities of hydrogen cyanide

TABLE 4

Preparation of cyanogen by the oxidation of cyanide-containing compounds in an acidic aqueous medium (143)

Compound	HCN: $(CN)_2$ (Molar Ratio)						
	$Na_2S_2O_8$	H_2O_2	$KMnO_4$	$K_2Cr_2O_7$	MnO_2	PbO_2	SO_2
HCN	9.39	—	—	180.8	13.14	5.59	8.10
KCN	1.95	7.17	10.57	20.7	13.34	0.78	8.00
$K_4Fe(CN)_6$	0.65	0.97	5.06	8.8	1.75	0.90	5.75
$K_3Fe(CN)_6$	0.13	0.95	0.19	—	1.49	0.73	2.66

and cyanogen were produced when aqueous acidic solutions of hydrogen cyanide, potassium cyanide, or potassium hexacyanoferrate(II) or (III) were treated with a variety of oxidizing agents (see table 4). Ultraviolet irradiation of an aqueous solution of potassium hexacyanoferrate(III) yielded cyanogen, presumably owing to the oxidation of the metal cyanide with hydrogen peroxide which was prepared *in situ* (160).

The preparation of cyanogen by the electrolysis of molten cyanides has not been extensively investigated. The electrolysis of molten barium cyanide, under a nitrogen atmosphere, with carbon electrodes yields cyanogen at the anode and barium at the cathode (114). Cyanogen and metallic sodium or potassium are produced by electrolysis of the corresponding metal cyanides (28, 192). The latter process produces pure alkali metals, with the evolved cyanogen being further used to convert alkali metal carbonates into the corresponding cyanides for recycle.

B. FROM HYDROGEN CYANIDE OR CYANOGEN HALIDES

The preparation of cyanogen from hydrogen cyanide was first demonstrated in 1863 by Deville and Trast, who passed hydrogen cyanide through a porcelain tube heated to redness (152). Carbon, hydrogen, and nitrogen were also produced as by-products. More recently, several efficient and economically attractive routes have been developed for the synthesis of cyanogen from hydrogen cyanide.

The air-oxidation of hydrogen cyanide over a silver catalyst at temperatures between 300° and 600°C. yields cyanogen and polymeric by-products (121). The maximum yield of cyanogen (22.8 per cent) is obtained at about 550°C Hydrogen cyanide and water are condensed from the gas stream and cyanogen is then isolated by cooling the remaining gas stream below −20°C.

$$4HCN + O_2 \text{ (air)} \rightarrow 2(CN)_2 + 2H_2O$$

The formation of cyanogen from hydrogen cyanide is also accomplished by passing the latter substance into a mixture of water and copper(II) oxide at ambient temperatures (52). Cyanogen is evolved with the concurrent precipitation of a complex metal cyanide. By heating the precipitated cyanide above 100°C. an additional quantity of cyanogen is evolved.

$$8HCN + 4CuO \rightarrow (CN)_2 + 2Cu[Cu(CN)_3] + 4H_2O$$

$$2Cu[Cu(CN)_3] \xrightarrow{\text{heat}} 4CuCN + (CN)_2$$

The vapor-phase reaction of hydrogen cyanide with chlorine over a surface-active material, such as activated carbon, furnishes cyanogen chloride (equation 1), which can be isolated or allowed to react *in situ* at higher temperatures with additional hydrogen cyanide to produce cyanogen (equation 2) (100). Reaction 1 prevails at 30–200°C., and reaction 2 at 400–700°C.

$$\mathrm{HCN + Cl_2 \rightarrow ClCN + HCl} \qquad (1)$$

$$\mathrm{CNCl + HCN \rightarrow (CN)_2 + HCl} \qquad (2)$$

Cyanogen is obtained in substantially quantitative yield by this process at temperatures exceeding 700°C. There are no polymers or undesirable by-products produced in this reaction, and the cyanogen may be isolated in a pure form by passing the effluent gases through a water-scrubbing tower.

Cyanogen chloride is also converted into cyanogen when mixed with hydrogen at elevated temperatures. A 95 per cent yield of cyanogen is obtained when a mixture of cyanogen chloride and hydrogen in a mole ratio of 3:1 is passed through a hot (850°C.) quartz tube (43).

$$\mathrm{2CNCl + H_2 \xrightarrow{850°C.} (CN)_2 + 2HCl}$$

At more moderate temperatures cyanogen iodide is converted into cyanogen and iodine (105).

$$\mathrm{2CNI \rightarrow (CN)_2 + I_2}$$

Good yields of cyanogen are realized from the reaction of cyanogen chloride with lower alkenes in the vapor phase over a metal halide catalyst (84). For example, a 70 per cent yield of cyanogen and ethylene chloride is obtained when a mixture of ethylene and cyanogen chloride is passed over a copper(I) chloride catalyst at 200–225°C. Vinyl chloride is the organic chloride realized at a reaction temperature above 300°C.

$$\mathrm{2CNCl + CH_2{=}CH_2 \rightarrow (CN)_2 + ClCH_2CH_2Cl\ (or\ CH_2{=}CHCl + HCl)}$$

Cyanogen is also obtained from hydrogen cyanide by electrolysis of the latter in an aqueous or liquid sulfur dioxide medium (85).

$$\mathrm{2HCN \rightarrow H_2 + (CN)_2}$$

C. FROM HYDROCARBONS AND NITROGEN-CONTAINING MATERIALS

Cyanogen has been produced in varying degrees of success by the reaction of a carbon-containing substance with a nitrogenous material in the presence of a source of extremely high energy. Under the influence of an electrical discharge, active nitrogen and ethylene react to yield a mixture of cyanogen (2 per cent), acetylene (3 per cent), methane (9 per cent), ethane (10 per cent), and hydrogen cyanide (75 per cent) (50, 194). Under similar conditions, acetylene and active nitrogen react to form hydrogen cyanide, polymer, and a small quantity of cyanogen (195). A mixture of acetylene and ammonia is converted into cyanogen on contact with a network of wire formed from silver, gold, iridium, palladium, cobalt, rhodium, chromium, copper, iron, manganese, or an alloy of copper and zinc at 480°C. (7).

A 0.1 per cent yield of cyanogen is obtained by subjecting a mixture of nitrogen and carbon dioxide to a carbon arc discharge (137). By continually recycling the unreacted starting materials, a quantitative yield of cyanogen is eventually realized.

Cyanogen is produced in detectable quantities by heating a carbon filament to about 2200°C. in a nitrogen atmosphere (151, 154, 155, 171, 173). It has been calculated that cyanogen could be formed from carbon and nitrogen at an arc temperature of 3500°C. to an extent of 44 per cent (204). The following expression was derived by Fink and Wroughton (56) for the cyanogen equilibrium in the vicinity of 2200°C.

$$\log \frac{[(\mathrm{CN})_2]}{[\mathrm{N}_2]} = \frac{-15.530}{T} + 0.855 \log T + 7.65 \times 10^{-5}\, T - 9.18 \times 10^{-9}\, T^2 - 0.50$$

Cyanogen is also produced by treating various simple compounds, such as carbon monoxide and ethylene, with ionized nitrogen and subjecting the resulting spray to a high-frequency field (167).

Cyanogen is produced by passing nitrogen, a mixture of nitrogen and carbon monoxide, or a mixture of nitrogen, carbon monoxide, and hydrogen through a molten mixture of iron saturated with carbon, maintained at the highest possible temperatures obtainable with an oxyhydrogen flame (*ca.* 1500–1800°C.) (49). Cyanogen is also obtained by heating charcoal in stick or powder form in an electrical furnace with nitrogen or a nitrogen and inert gas mixture (155).

Small quantities of cyanogen result from the destructive distillation of coal (112), coal liquors (25), and slimes (149). A mixture of synthesis gas (CO, H_2) and nitrogen, or a mixture of carbon monoxide and nitrogen, is converted into cyanogen on being passed over a metal oxide catalyst, such as iron(II) oxide, at 300–500°C. and a pressure of 50 atm. (165). At atmospheric pressure and at temperatures ranging from 500° to 800°C. mixtures of producer gas and air or natural gas and air react in the presence of a catalyst, which consists of metals from the transition and alkali metal groups, to produce cyanogen (168).

D. FROM OXALIC ACID AND GLYOXAL DERIVATIVES

Cyanogen is produced by the dehydration of ammonium oxalate and oxamide with phosphorus pentoxide (11, 39, 118, 130, 171) or phosphorus pentasulfide (75) at temperatures ranging from 100° to 290°C. under reduced pressures. Similarly, cyanogen is produced when glyoxime is heated with an excess of acetic anhydride (99).

$$\mathrm{H_2NCOCONH_2} \xrightarrow{-2\mathrm{H_2O}} (\mathrm{CN})_2$$

$$\mathrm{HON{=}CHCH{=}NOH} \xrightarrow{-2\mathrm{H_2O}} (\mathrm{CN})_2$$

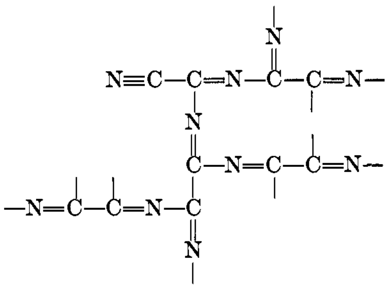
E. BY MISCELLANEOUS PROCEDURES

Cyanogen is formed in the reaction of calcium cyanamide with carbon disulfide at 700–750°C. (74), by treatment of potassium thiocyanate with copper-

(II) acetate in an aqueous medium (138), by thermal decomposition of tricyanotriazine (166), by thermal decomposition of a mixture of phospham [$(PN_2H)_x$] and potassium oxalate (196), by treatment of isocyanato tetrabromide ($Br_2C{=}NN{=}CBr_2$) (179) or cyanothioformamide ($NCCSNH_2$) (197) with a solution containing a silver salt, and by heating the dimethyl ester of azodicarbothiamide, $[({=}NC(SCH_3){=}NH)]_2$, at 110°C. (31). Copper, silver, lead, or cadmium cyanamide is converted into cyanogen, nitrogen, and carbon dioxide on being heated in the presence of air (23).

V. PARACYANOGEN

Paracyanogen, the solid polymeric form of cyanogen, is often a troublesome by-product which forms during reactions of cyanogen, particularly at elevated temperatures. The structure of the material has not been elucidated, but owing to its chemical inertness and insolubility, it is presumed to be either a three-dimensional system (I) or a fused-ring system (II) (164):



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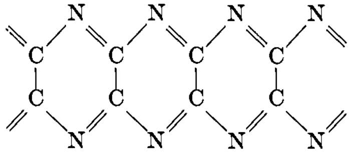


II

Paracyanogen is formed when cyanogen is heated to 300–400°C. at atmospheric pressure or to lower temperatures at higher pressures (26, 191). At about 860°C. in the presence of an inert carrier gas, such as carbon dioxide or nitrogen, paracyanogen depolymerizes to monomeric cyanogen (130, 159, 175, 191). There is little decomposition to elemental carbon and nitrogen at this temperature, but at 1200°C. there is appreciable degradation to the elements (117). If hydrogen is used as the carrier gas, the products formed are hydrogen cyanide, ammonia, and carbon. A mixture of paracyanogen and cyanogen is formed when either silver or mercury(II) cyanide is heated at 350–440°C. (191). 2,4,6-Tricyanotriazine is converted to paracyanogen when heated at 90–100°C. (130). The thermal decomposition of cyanogen iodide yields paracyanogen and iodine (96).

Paracyanogen is also produced when cyanogen vapors are subjected to ultraviolet radiation (12, 18) or to high-voltage electric discharges (163). Similarly, ions of inert gases, such as helium, argon, neon, nitrogen, krypton, and xenon (106, 107, 205), produced from α-particles emitted by radon, accelerate the polymerization of cyanogen.

The chemical properties of paracyanogen have not been defined, and few data are available as to its physical properties. This dark brownish-black material is insoluble in water, liquid cyanogen, and alcohol, partially soluble in caustic solution, and soluble in concentrated sulfuric and hydrochloric acids. Dilution of a concentrated sulfuric acid solution of paracyanogen causes precipitation of the polymer (40, 93, 132).

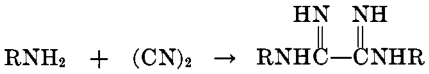
VI. The Reaction of Cyanogen with Amines

The reaction of cyanogen with amines is one of the most extensively investigated areas of cyanogen chemistry. Aromatic amines and ammonia were found by earlier workers to react readily with cyanogen to give oxamidines and numerous unidentified by-products, the identities of which have still not been determined. The reactions of aliphatic and heterocyclic amines with cyanogen, which had not been reported prior to 1950, have recently been studied in a comprehensive manner by Woodburn and associates (215, 216, 218, 219, 221, 222).

A. REACTION WITH MONOAMINES

1. *Aliphatic primary amines*

Cyanogen reacts with primary aliphatic monoamines to produce dialkyloxamidines (III). These are white crystalline solids or colorless liquids, which slowly decompose on standing (219). The free oxamidines are obtained by saturating an aqueous solution of an amine with cyanogen at 0°C. By saturating an anhydrous alcohol solution of an amine, first with cyanogen and then with anhydrous hydrogen chloride, the oxamidine hydrochloride is obtained (see table 5).

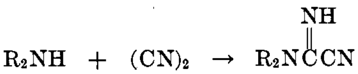


$$RNH_2 + (CN)_2 \rightarrow RNH\overset{HN}{\overset{\|}{C}}-\overset{NH}{\overset{\|}{C}}NHR$$

III

2. *Aliphatic secondary amines*

Cyanogen and secondary aliphatic amines react in organic media such as ethyl acetate, benzene, toluene, and xylene at 0°C. to form the corresponding *N*,*N*-dialkylcyanoformamidines (IV) in good yields (table 6) (218). These materials are colorless liquids, which are stable when pure but decompose to tars when impure. Oxamidines, which are formed from the reaction of primary amines with cyanogen, are not obtained from the reaction of secondary amines with cyanogen, presumably owing to steric effects.



$$R_2NH + (CN)_2 \rightarrow R_2N\overset{NH}{\overset{\|}{C}}CN$$

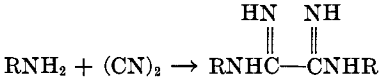
IV

3. *Aromatic amines*

The reaction of primary aromatic amines with cyanogen generally yields oxamidines (table 5); however, 3,5-dinitro-4-hydroxyaniline reacts with cyanogen in an alcoholic medium to produce 3-(3′,5′-dinitro-4′-hydroxyphenyl)-2-ethylpseudourea (V) (67). The *o*- and *p*-aminobenzoic acids react with cyanogen in an aqueous medium, presumably forming 2-cyano-4-hydroxyquinazoline (VI)

TABLE 5

Sym-disubstituted oxamidines

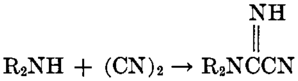


$$RNH_2 + (CN)_2 \rightarrow RNH\overset{\overset{HN}{\|}}{C}-\overset{\overset{NH}{\|}}{C}NHR$$

R	Yield	Melting Point	Boiling Point	References
	per cent	°C.	°C.	
CH_3—	8.5	103-104		(219)
C_2H_5—	35	53		(219)
n-C_3H_7—	22		95 (d.)	(219)
iso-C_3H_7—	22		80	(219)
$CH_2=CHCH_2$—	39	65-75		(219)
		260 (d.) hydrochloride		
n-C_4H_9—	30	63		(219)
iso-C_4H_9—	11	79		(219)
tert-C_4H_9—	—	No product		(219)
$C_2H_5(CH_3)CH$—	13		140	(219)
C_5H_{11}—	27	>100 (d.)		(219)
$C_6H_5CH_2$—		140		(172)
C_6H_5—		210-220		(78)
p-BrC_6H_4—				(161)
p-$NO_2C_6H_4$—				(161)
o,m,p-$CH_3C_6H_4$—				(17, 78, 198)
Pyridyl-2-	16	215-216		(222)
6-Methylpyridyl-2-	16	189-190		(222)
$CH_3OCH_2CH_2$—	46	73-75		(64)
		194-195 (d.) (hydrochloride)		(216)
$C_2H_5OCH_2CH_2$—	52	87-89		(64)
		197-198 (d.) (hydrochloride)		(216)
n-$C_3H_7OCH_2CH_2$—	35	219-220 (hydrochloride)		(64, 216)
$CH_3SCH_2CH_2$—	19.4	89-90		(133, 221)
$C_2H_5SCH_2CH_2$—	16	234-236 (hydrochloride)		(133, 221)
n-$C_3H_7SCH_2CH_2$—	22	74-76		(133, 221)
n-$C_4H_9SCH_2CH_2$—	24.8	78.9		(133, 221)

TABLE 6

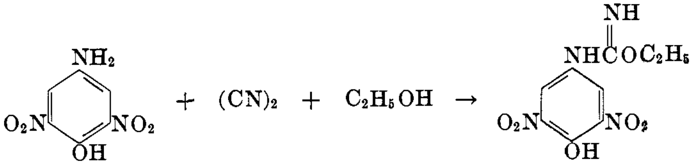
N,N-Dialkylcyanoformamidines (218)



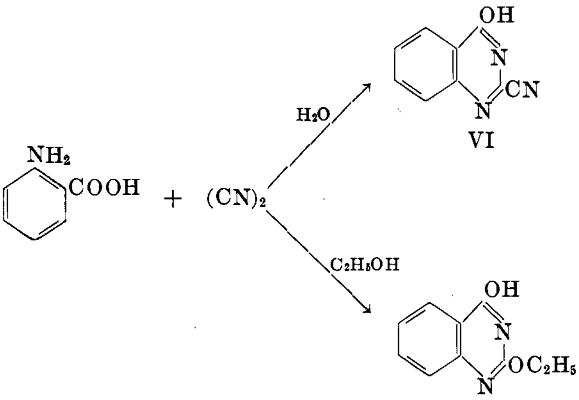
$$R_2NH + (CN)_2 \rightarrow R_2N\overset{\overset{NH}{\|}}{C}CN$$

R	Yield	Boiling Point	Melting Points of Derivatives
	per cent	°C.	°C.
CH_3—	38	80/26 mm.	136-137 (nitrate)
			197-198 (hydrochloride)
C_2H_5—	70	85/15 mm.	123 (nitrate)
			130-135 (hydrochloride)
n-C_3H_7—	60	120/34 mm.	
$CH_2=CHCH_2$—	66.9	102-104/16 mm.	136-138 (hydrochloride)
n-C_4H_9—	70	85/1 mm.	
n-C_5H_{11}—	60	124/4 mm.	

and 3-(3′-carboxyphenyl)cyanoformamidine (VIII), respectively; in an alcoholic solvent they form 2-ethoxy-4-hydroxyquinazoline (VII) and 3-(3′-carboxyphenyl)-2-ethylpseudourea (IX) (53, 65), respectively, in addition to other unidentified products.

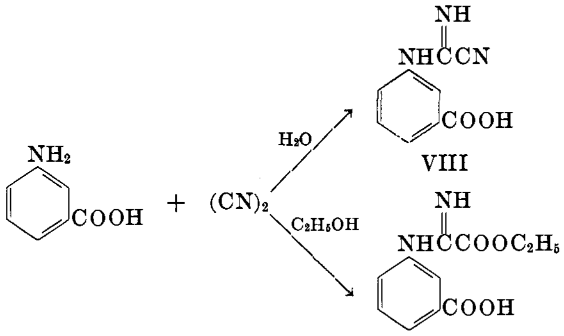


V



VI

VII



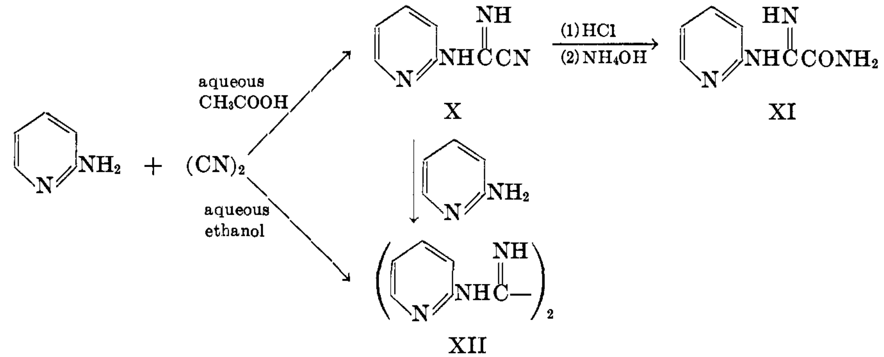
VIII

IX

No reaction was detected between cyanogen and the secondary aromatic amines diphenylamine and *N*-methylaniline (161).

4. Heterocyclic amines

2-Amino-, 2-amino-3-methyl-, 2-amino-4-methyl-, and 2-amino-5-methylpyridine react with cyanogen in an acetic acid–water solution at 0°C. to form the corresponding cyanoformamidines (X) (table 7). In a water–ethanol reaction medium the corresponding oxamidines (XII) are realized. These bispyridyloxamidines can also be obtained from pyridylcyanoformamidines and aminopyridines. The pyridylcyanoformamidines can be converted into carbamylformamidines (XI) (table 8) on reaction with hydrochloric acid followed by neutralization with ammonium hydroxide (222).



XII

Pyrrolidine, piperidine, 2-methylpiperidine, 2,4-dimethylpiperidine, and morpholine react with cyanogen to yield the corresponding cyanoformamidines (225) (table 9). Pyrrole and pyrroline are unreactive with cyanogen.

5. *Mercaptoamines*

2-Aminothiophenol and cyanogen react in an alcoholic medium to give either bis(Δ^2-2-benzothiazolinyl) (XIII) or benzothiazolinylformamidine (XIV) (82) depending upon the ratio of reactants. More recently, it has been found that a similar reaction of mercaptoethylamine and cyanogen at 0°C. in an aqueous medium furnishes bis(Δ^2-thiazolinyl) (XV) in 25.4 per cent yield (132, 221). No additional products were isolated. Using similar procedures, no identifiable products were isolated from the reaction of *N*-alkyl- and *N*,*N*-dialkyl-2-mercaptoethylamine with cyanogen (132, 221).

TABLE 7

Pyridylcyanoformamidines (222)

$$\mathrm{RNH}\overset{\overset{\mathrm{NH}}{\|}}{\mathrm{C}}\mathrm{CN}$$

R	Yield	Melting point	R	Yield	Melting Point
	per cent	°*C.*		*per cent*	°*C.*
Pyridyl-2-	13	125-126 (d.)	4-Methylpyridyl-2-	16	116.5-117 (d.)
3-Methylpyridyl-2-	25	99.5-96 (d.)	5-Methylpyridyl-2-	16	143-144 (d.)

TABLE 8

Carbamylformamidines (222)

$$\mathrm{RNH}\overset{\overset{\mathrm{HN}}{\|}}{\mathrm{C}}\mathrm{CONH_2}$$

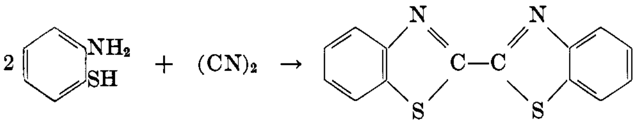
R	Melting Point	R	Melting Point
	°*C.*		°*C.*
Pyridyl-2-	148-149	4-Methylpyridyl-2-	149-151 (approx.)
3-Methylpyridyl-2-	127-127.5	5-Methylpyridyl-2-	196-197

TABLE 9

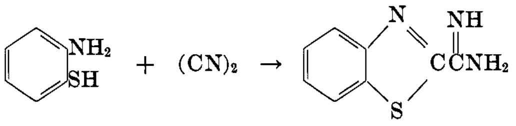
Heterocyclic cyanoformamidines (225)

$R_2N\overset{NH}{\overset{\|}{C}}CN$

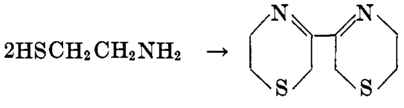
R_2N	Melting Point	Boiling Point	Melting Point of Derivative
	°C.	°C.	°C.
Pyrrolidine	55-56		
Piperidine		79-80/3 mm.	156 (d.) (hydrochloride)
2-Methylpiperidine		88/3 mm.	134-135 (d.) (nitrate)
2,4-Dimethylpiperidine		84/1 mm.	188-189 (d.) (hydrochloride)
Morpholine	90-92		



XIII



XIV



XV

6. *Alkanolamines*

The types of products derived from the reaction of cyanogen with primary aminoalcohols depend on the reaction medium employed. In an aqueous solvent the hydroxyl group is the site of attack with bis(2-aminoalkyl) oxaldiimidates (XVI) the resulting products (table 10). If an alcoholic medium is employed, the amino group is the site of attack with bis(2-hydroxyalkyl)oxamidines (XVII) the resulting products (table 11) (64, 216). There were no products isolated which would suggest cyclization of the type realized from mercaptoethylamines and cyanogen.

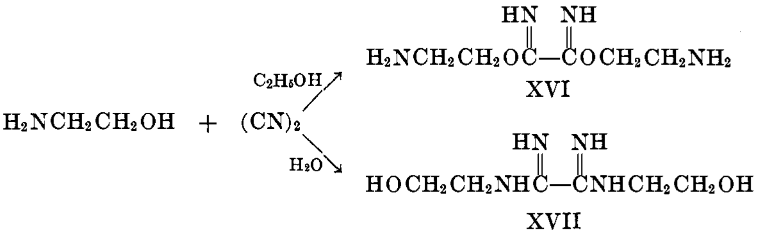
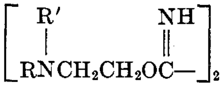


TABLE 10

Bis(2-aminoethyl) oxaldiimidates (64, 216)

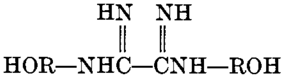


$$\left[\overset{\displaystyle R'}{\overset{|}{RN}}CH_2CH_2O\overset{\displaystyle NH}{\overset{\|}{C}}—\right]_2$$

R	R'	Yield	Melting Point of Derivative
		per cent	°C.
H	H	20	185-187 (picrate)
CH_3—	H	45	165-166 (hydrochloride)
C_2H_5—	H	56	169-170 (hydrochloride)
n-C_3H_7—	H		180-225 (hydrochloride)
$CH_3OCH_2CH_2CH_2$—	H	64.4	89-91 227-228 (d.) (hydrochloride)
C_2H_5—	C_2H_5—		195-198 (picrate)

TABLE 11

Bis(hydroxyalkyl)oxamidines (64, 216)



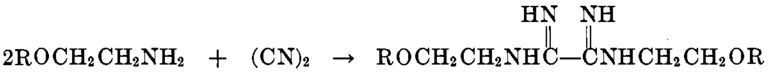
$$HOR—NH\overset{\displaystyle HN}{\overset{\|}{C}}—\overset{\displaystyle NH}{\overset{\|}{C}}NH—ROH$$

H—OR—NH_2	Yield	Melting Point	H—OR—NH_2	Yield	Melting Point
	per cent	°C.		*per cent*	°C.
$HOCH_2CH_2NH_2$..........	29	126-127 (hydrochloride)	$HO(CH_2)_3NH_2$..........		145-148 (d.) (hydrochloride)
$HOCH(CH_3)CH_2NH_2$.....	20	143-144	$HOCH_2C(CH_3)_2NH_2$....		Dark oily residue

Regardless of the reaction medium, mono- and di-*N*-alkylethanolamines and cyanogen produce oxaldiimidates. Attempts to prepare cyanoformamidates from *N*-alkylethanolamines and cyanogen were unsuccessful (64, 216).

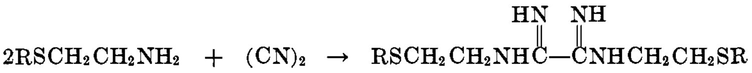
7. *Alkoxyethylamines and 2-alkylmercaptoethylamines*

2-Alkoxyethylamines (64, 216) and 2-alkylmercaptoethylamines (132, 221) react with cyanogen in aqueous or alcoholic media to form the corresponding oxamidines (XVIII; XIX) (table 5).



$$2ROCH_2CH_2NH_2 + (CN)_2 \rightarrow ROCH_2CH_2NH\overset{\displaystyle HN}{\overset{\|}{C}}—\overset{\displaystyle NH}{\overset{\|}{C}}NHCH_2CH_2OR$$

XVIII



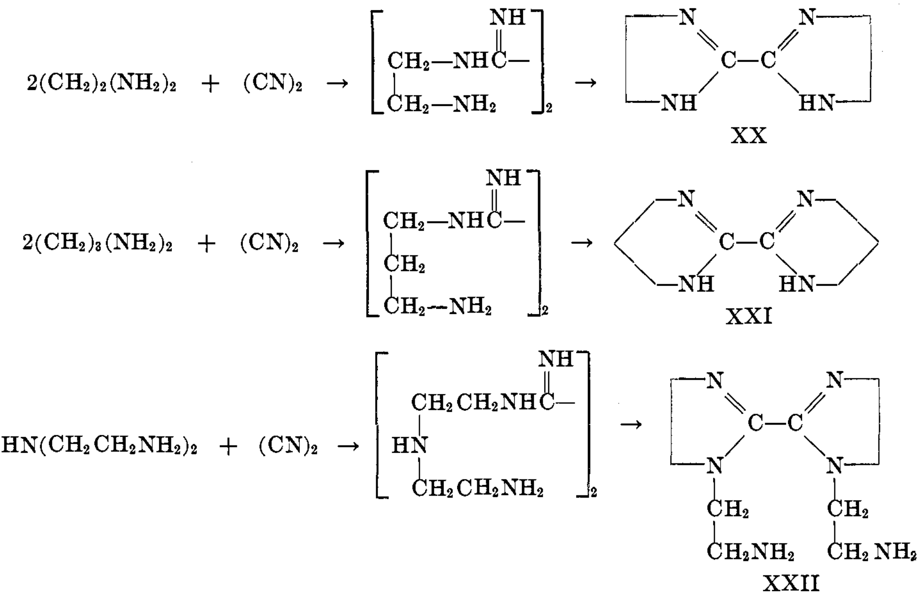
$$2RSCH_2CH_2NH_2 + (CN)_2 \rightarrow RSCH_2CH_2NH\overset{\displaystyle HN}{\overset{\|}{C}}—\overset{\displaystyle NH}{\overset{\|}{C}}NHCH_2CH_2SR$$

XIX

B. REACTION WITH DIAMINES

1. *Aliphatic diamines*

The products derived from primary aliphatic diamines and cyanogen seem to depend on the number of atoms separating the amino groups. When two or three methylene groups separate the two amino groups the aminoalkyloxamidines, which are first formed at low temperatures, decompose at room temperature to give five- and six-membered ring compounds. Thus, 1,2-ethanediamine and 1,3-propanediamine react with cyanogen to form bis(Δ^2-2-imidazolinyl) (XX) and bis(Δ^2-2-pyrimidinyl) (XXI), respectively. Similarly, bis(2-aminoethyl)amine reacts with cyanogen to give bis[Δ^2-1-(2′-aminoethyl)-2-imidazolinyl)] (XXII) (128, 220) (table 12).

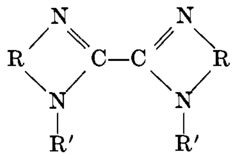

XX

XXI

XXII

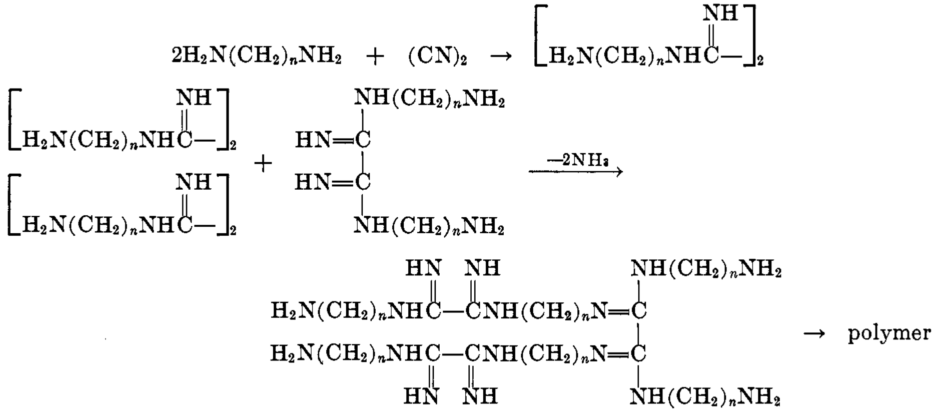
TABLE 12

Bis(Δ^2-2-imidazolinyls) and bis(Δ^2-2-pyrimidinyls) from cyanogen and diamines (60, 77, 128 215, 220)



Amine	R	R'	Yield	Melting Point	Melting Point of Derivative
			per cent	°*C*.	°*C*.
Ethylenediamine	—CH_2CH_2—	H		289–291	
1,3-Propanediamine	—$CH_2CH_2CH_2$—	H	17	129–132	281–284 (d.) (hydrochloride)
1,2-Propanediamine	$CH_3\underset{\vert}{C}HCH_2$—	H	22	246–249	
Bis(2-aminoethyl)amine	—CH_2CH_2—	$H_2NCH_2CH_2$—	12		200–202 (d.) (hydrochloride)
3,3′-Iminobispropylamine	—$CH_2CH_2CH_2$—	$H_2NCH_2CH_2CH_2$—	30		266–268 (d.) (hydrochloride)

When four, five, or six methylene groups separate the amino groups, aminoamidines (table 13) are also obtained, but the ultimate products are polymeric amidines and ammonia. These polymers are assumed to be formed via an intermolecular condensation (60, 128, 215).



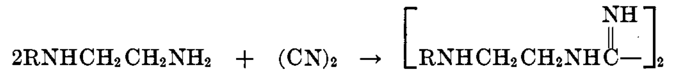
$$2H_2N(CH_2)_nNH_2 + (CN)_2 \rightarrow \left[H_2N(CH_2)_nNH\overset{NH}{\overset{\|}{C}}-\right]_2$$

$$\begin{array}{l}\left[H_2N(CH_2)_nNH\overset{NH}{\overset{\|}{C}}-\right]_2\\ \left[H_2N(CH_2)_nNH\overset{NH}{\overset{\|}{C}}-\right]_2\end{array} + \begin{array}{l}NH(CH_2)_nNH_2\\ \;|\\ HN{=}C\\ \;|\\ HN{=}C\\ \;|\\ NH(CH_2)_nNH_2\end{array} \xrightarrow{-2NH_3}$$

$$\begin{array}{l} H_2N(CH_2)_nNH\overset{HN}{\overset{\|}{C}}-\overset{NH}{\overset{\|}{C}}NH(CH_2)_nN{=}\overset{NH(CH_2)_nNH_2}{\overset{|}{C}} \\ H_2N(CH_2)_nNH\underset{HN}{\underset{\|}{C}}-\underset{NH}{\underset{\|}{C}}NH(CH_2)_nN{=}\underset{NH(CH_2)_nNH_2}{\underset{|}{C}}\end{array} \rightarrow \text{polymer}$$

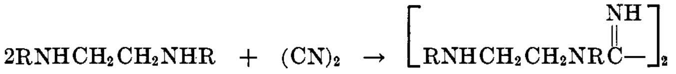
$n = 4, 5, 6.$

N-Alkyl- and *N*,*N*′-dialkylethylenediamines react with cyanogen to give stable bis(2-alkylaminoethyl)oxamidines (XXIII) and *N*,*N*′-dialkyl-*N*,*N*′-bis(2-alkylaminoethyl)oxamidines (XXIV), respectively (table 14), void of any cyclic products (128, 220). These materials are colorless, viscous, fuming liquids which are soluble in water, ethanol, and ether and have a strong ammoniacal odor.



$$2RNHCH_2CH_2NH_2 + (CN)_2 \rightarrow \left[RNHCH_2CH_2NH\overset{NH}{\overset{\|}{C}}-\right]_2$$

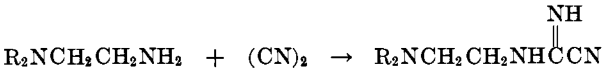
XXIII



$$2RNHCH_2CH_2NHR + (CN)_2 \rightarrow \left[RNHCH_2CH_2NR\overset{NH}{\overset{\|}{C}}-\right]_2$$

XXIV

N,*N*-Dialkylethylenediamines react with cyanogen to form *N*,*N*-dialkylaminoethylcyanoformamidines (XXV) (table 15) (128, 220).



$$R_2NCH_2CH_2NH_2 + (CN)_2 \rightarrow R_2NCH_2CH_2NH\overset{NH}{\overset{\|}{C}}CN$$

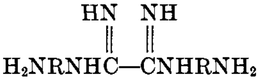
XXV

2. Aromatic diamines

The reaction of aromatic diamines with cyanogen has not been examined in detail; however, *o*-phenylenediamine reacts with cyanogen to produce 2,3-diaminoquinoxaline (XXVI) (77), whereas *p*-phenylenediamine yields a polymeric substance (60). 4,4′-Diaminobiphenyl and cyanogen react to give, first a cyanoformamidine derivative, and then an oxamidine (XXVII) (60, 215).

TABLE 13

Sym-ω-aminoalkyloxamidines or sym-aminoaryloxamidines from cyanogen and diamines (60, 77, 128, 215)

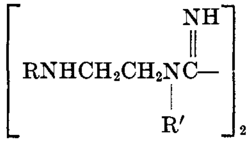


$$H_2NRNH\overset{\overset{HN}{\|}}{C}-\overset{\overset{NH}{\|}}{C}NHRNH_2$$

Amine	R	Yield	Melting Point	Boiling Point	Melting Point of Derivative
		per cent	°C.	°C.	°C.
1,2-Ethanediamine	$-(CH_2)_2-$				207 (hydrochloride)
1,3-Propanediamine	$-(CH_2)_3-$	11			298 (hydrochloride)
1,2-Propanediamine	$-CH_2\underset{\vert}{C}HCH_3$	3.3		166/16mm.	218–222 (hydrochloride)
1,4-Butanediamine	$-(CH_2)_4-$		97-101		258-261 (hydrochloride)
1,5-Pentanediamine	$-(CH_2)_5-$			154-156/4 mm.	273-275 (hydrochloride)
1,6-Hexanediamine	$-(CH_2)_6-$	38	106-110 (d.)		205 (hydrochloride)
p-Phenylenediamine	p-C_6H_4	28			Hydrochloride decomposes on drying
4,4'-Diaminobiphenyl	$-C_6H_4C_6H_4-$	38	181-182 (d.)		>320 (hydrochloride)

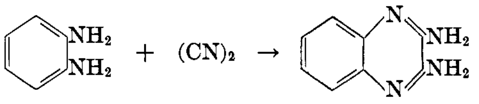
TABLE 14

Bis(2-alkylaminoethyl)oxamidines (128, 220)

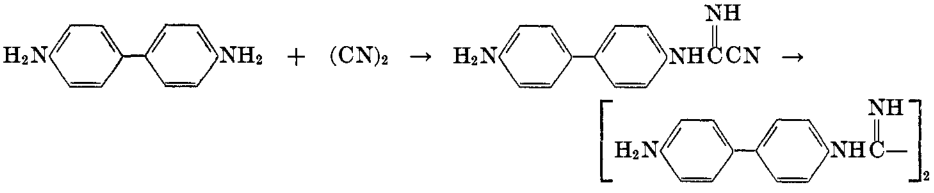


$$\left[RNHCH_2CH_2N\underset{\underset{R'}{|}}{\overset{\overset{NH}{\|}}{C}}-\right]_2$$

R	R'	Yield	Boiling Point	Melting Point of Picrate
		per cent	°C.	°C.
CH_3-	H	32	149/5 mm.	144-145 (d.)
C_2H_5-	H	40	166–167/5 mm.	81 (d.)
n-C_3H_7-	H	63	135-137/4 mm.	148 (d.)
iso-C_3H_7-	H	41	133-134/4 mm.	153-154 (d.)
n-C_4H_9-	H	67	135/4 mm.	150
CH_3-	CH_3-	55	84-85/5 mm.	181
C_2H_5-	C_2H_5-	48	125-126/4 mm.	138-139
n-C_3H_7-	n-C_3H_7-	52	117/5 mm.	84-85
iso-C_3H_7-	iso-C_3H_7-	27	109-110/4 mm.	134
n-C_4H_9-	n-C_4H_9-	33	134-135/4 mm.	>200 (d.)



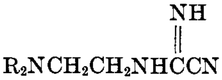
XXVI



XXVII

TABLE 15

N,N-Dialkylaminoethylcyanoformamidines (128, 220)



$R_2NCH_2CH_2NH\overset{NH}{\overset{\|}{C}}CN$

R	Yield	Melting Point	R	Yield	Melting Point
	per cent	°C.		*per cent*	°C.
CH₃—..................	22	116 (d.)	C₂H₅—...............	45	105 (d.)

TABLE 16

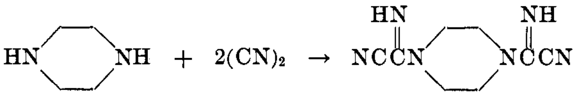
Biscyanoformamidines (225)

$NC\overset{NH}{\overset{\|}{C}}NRN\overset{NH}{\overset{\|}{C}}CN$

—NRN—	Melting Point	—NRN—	Melting Point
	°C.		°C.
Piperazine..............................	187.5-188	*cis*-2,5-Dimethylpiperazine.............	124-125
2-Methylpiperazine.....................	113-113.5	*trans*-2,5-Dimethylpiperazine...........	166-167

3. Heterocyclic diamines

Cyanogen and heterocyclic diamines, such as piperazine, 2-methylpiperazine, *cis*-2,5-dimethylpiperazine, and *trans*-2,5-dimethylpiperazine react in the manner expected for secondary amines to form crystalline biscyanoformamidines: for example, XXVIII (table 16) (225).



XXVIII

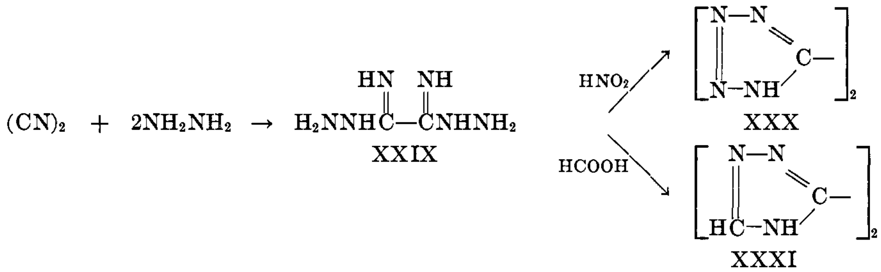
C. REACTION WITH AMMONIA

The reaction of cyanogen with anhydrous ammonia and with aqueous ammonia is reported only once in the very early literature. The products isolated were not characterized further than by their empirical formulas (86). An excess of cyanogen reacts with anhydrous ammonia to form a black solid, hydrazulmin ($C_4H_6N_6$), which is converted into paracyanogen on being heated in the absence of water. When paracyanogen is heated in the presence of water, azulminic acid ($C_4H_5N_5O$), oxamide, and ammonium oxalate are formed. Azulminic acid can also be prepared by passing cyanogen into a concentrated solution of ammonia. The resulting solution fluoresces violet when neutral, and green when acidified with sulfuric acid. Azulminic acid is converted into mykomelinic acid ($C_4H_4N_4O_2$) on being heated in the presence of water, and into azoxulmin ($C_4H_3NO_2$) when treated with either potassium permanganate or nitrous acid. This latter material is insoluble in water but forms a fluorescent solution with sulfuric acid.

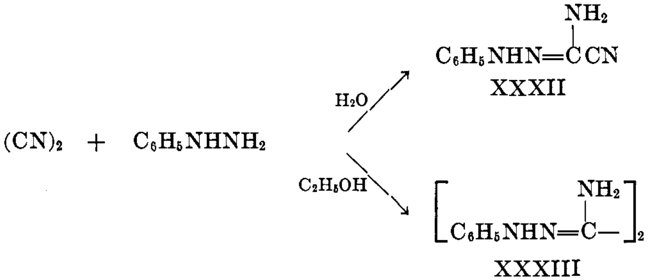
VII. OTHER REACTIONS OF CYANOGEN

A. REACTION WITH HYDRAZINE AND DERIVATIVES

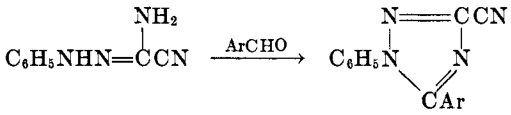
Cyanogen reacts with hydrazine in a cold aqueous solution to form oxaldiimidic acid dihydrazide (XXIX) (27, 36, 38), which can react further with nitrous acid to yield bis(1,2,3,4-tetrazol-5-yl) (XXX) (144). When a mixture of oxaldiimidic acid dihydrazide and formic acid is heated, bis(1,2,4-triazol-3-yl) (XXXI) is formed (144).



Phenylhydrazine reacts with one mole of cyanogen in aqueous solution to form cyanoformimidic acid phenylhydrazide (XXXII) (6, 18, 57). In alcoholic or benzene solution, one mole of cyanogen condenses with two moles of phenylhydrazine to form oxaldiimidic acid phenylhydrazide (XXXIII) (6, 116, 144).

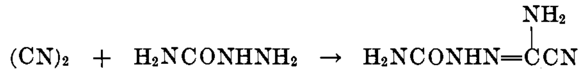


Cyanoformimidic acid phenylhydrazide is converted into a 3-substituted-2-phenyl-5-cyanotriazole (XXXIV) on reaction with an aryl aldehyde followed by mild oxidation (19, 20).



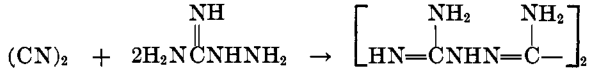
XXXIV

Semicarbazide and aminoguanidine react with cyanogen in an alcoholic medium to form cyanoformimidic acid semicarbazone (XXXV) and 2,5,6,9-tetramino-1,3,4,7,8,10-hexaazadeca-1,4,6,9-tetraene (XXXVI), respectively (180).



$$(CN)_2 + H_2NCONHNH_2 \rightarrow H_2NCONHN{=}\overset{NH_2}{\overset{|}{C}}CN$$

Semicarbazide XXXV

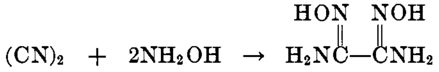


$$(CN)_2 + 2H_2N\overset{NH}{\overset{\|}{C}}NHNH_2 \rightarrow \left[HN{=}\overset{NH_2}{\overset{|}{C}}NHN{=}\overset{NH_2}{\overset{|}{C}}-\right]_2$$

Aminoguanidine XXXVI

B. REACTION WITH HYDROXYLAMINE AND DERIVATIVES

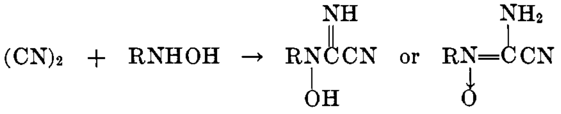
Cyanogen and hydroxylamine condense in a cold aqueous medium to form oxaldihydroxamide (XXXVII) (31, 58, 182) in a yield of 40 per cent. This material is useful as a chelating agent in the separation of small quantities of nickel from zinc, manganese, or cobalt. It is also used for the determination of nickel in minute quantities (31).



$$(CN)_2 + 2NH_2OH \rightarrow H_2N\overset{HON}{\overset{\|}{C}}-\overset{NOH}{\overset{\|}{C}}NH_2$$

XXXVII

Phenyl- and tolylhydroxylamines react with cyanogen in cold ether to form weakly basic products in about 75 per cent yields. These materials are believed to have one of the following tautomeric forms (XXXVIII or XXXIX) (201).

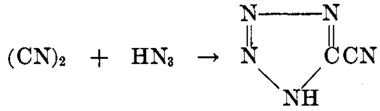


$$(CN)_2 + RNHOH \rightarrow R\underset{OH}{\underset{|}{N}}\overset{NH}{\overset{\|}{C}}CN \text{ or } R\underset{O}{\underset{\downarrow}{N}}{=}\overset{NH_2}{\overset{|}{C}}CN$$

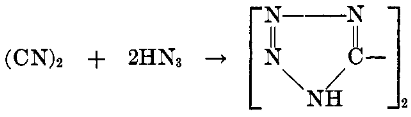
XXXVIII XXXIX

C. REACTION WITH HYDRAZOIC ACID AND DIAZOALKANES

Molar equivalent quantities of cyanogen and hydrazoic acid condense in water to form 5-cyanotetrazole (XL). In a similar manner, cyanogen and an excess of hydrazoic acid react to form bis(1,2,3,4-tetrazol-5-yl) (XLI) (129).

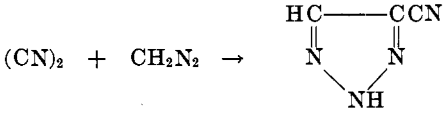


XL

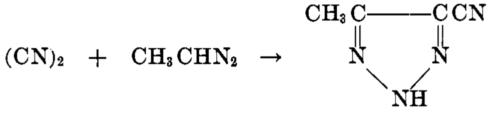


XLI

Diazomethane and diazoethane react with cyanogen in ether to form 4-cyano-2,1,3-triazole (XLII) and 4-cyano-5-methyl-2,1,3-triazole (XLIII), respectively (134). Unless a large excess of cyanogen and a very dilute solution is used in the reaction with diazomethane, the *N*-methyl derivative is the major product.



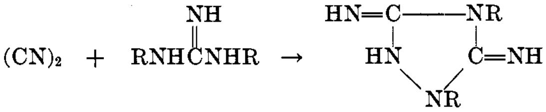
XLII



XLIII

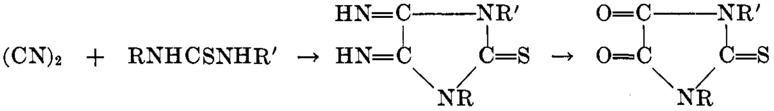
D. REACTION WITH SUBSTITUTED GUANIDINES AND THIOUREAS

1,3-Disubstituted-2,4,5-triiminoimidazolidines (XLIV) are formed (9, 79, 80, 81, 102) when cyanogen is passed into a cold alcoholic solution of diphenyl- and ditolylguanidines. Triphenyl- and tritolylguanidines react with cyanogen in a similar manner.



XLIV

Similarly, substituted thioureas and cyanogen react to form 1,3-disubstituted-2-thio-4,5-diiminoimidazolidines (XLV) (1, 170). These substances can be hydrolyzed with dilute hydrochloric acid to 1,3-disubstituted-2-thio-4,5-dioxoimidazolidines (XLVI).



XLV XLVI

E. REACTION WITH OLEFINS AND HYDROCARBONS

There is little resemblance of cyanogen to pseudo-halogens, such as thiocyanogen and the cyanogen halides, in reactions with olefins and hydrocarbons. Whereas the latter usually react with olefins and hydrocarbons in a facile manner characteristic of halogens, cyanogen reacts only under rigorous conditions.

In the absence of a catalyst, mixtures of methane and cyanogen and of ethane and cyanogen react at temperatures above 700°C. to furnish modest yields of acetonitrile (66) and acrylonitrile (55), respectively. Similarly, ethylene and cyanogen yield acrylonitrile and hydrogen cyanide (54).

$$(CN)_2 + CH_4 \rightarrow CH_3CN + HCN$$

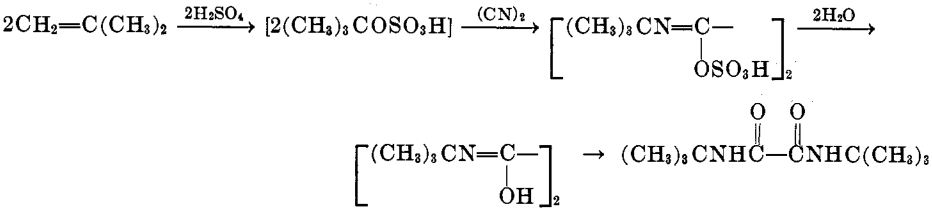
$$(CN)_2 + CH_3CH_3 \rightarrow CH_2{=}CHCN + CH_2{=}CH_2 + HCN$$

$$(CN)_2 + CH_2{=}CH_2 \rightarrow CH_2{=}CHCN + HCN$$

In the presence of an alloy catalyst composed primarily of nickel and chromium and at temperatures of about 1500°C., cyanogen and ethylene or propylene react to yield the corresponding succinonitriles in low conversions (4).

$$(CN)_2 + CH_2{=}CH_2 \xrightarrow{\text{catalyst}} NCCH_2CH_2CN$$

Cyanogen reacts with certain olefins and sulfuric acid (Ritter reaction) to yield substituted oxamides (145). For example, when a mixture of isobutylene and cyanogen is passed into concentrated sulfuric acid and the resulting mixture is subsequently treated with water, a 45 per cent yield of *N*,*N*-di-*t*-butyloxamide is obtained. The reaction is considered to occur via a carbonium-ion type of intermediate.



$$2CH_2{=}C(CH_3)_2 \xrightarrow{2H_2SO_4} [2(CH_3)_3COSO_3H] \xrightarrow{(CN)_2} \left[(CH_3)_3CN{=}\underset{OSO_3H}{\underset{|}{C}}{-}\right]_2 \xrightarrow{2H_2O}$$

$$\left[(CH_3)_3CN{=}\underset{OH}{\underset{|}{C}}{-}\right]_2 \rightarrow (CH_3)_3CNH\overset{O}{\overset{\|}{C}}{-}\overset{O}{\overset{\|}{C}}NHC(CH_3)_3$$

The noncatalytic vapor-phase reaction of cyanogen with a conjugated diolefin, such as butadiene, at about 500°C. does not give the expected addition product, 1,4-dicyano-2-butene, but the Diels–Alder product, 2-cyanopyridine, and smaller amounts of 2,2′-dipyridyl (91). Similarly, isoprene, chloroprene, and 2-methylpentadiene give with cyanogen products of the Diels–Alder type. However, 1-chlorobutadiene, 2,3-dichlorobutadiene, and perchlorobutadiene are unreactive with cyanogen (91) (table 17). These reactions are assumed to occur via a 2-cyano-3,6-dihydropyridine with a subsequent dehydrogenation to 2-cyanopyridine.

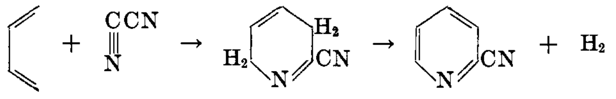


TABLE 17

Diels–Alder reactions with cyanogen (92)

Diene	Product	Combined Yield
		per cent
Butadiene	2-Cyanopyridine	*ca.* 18
Chloroprene	4-Chloro-2-cyanopyridine 5-Chloro-2-cyanopyridine	
2-Methylpentadiene	3,5-Dimethyl-2-cyanopyridine 4,6-Dimethyl-2-cyanopyridine	30
	4-Methyl-2-cyanopyridine 5-Methyl-2-cyanopyridine	18
1-Chlorobutadiene, 2,3-dichlorobutadiene, and perchlorobutadiene	No reaction	

The use of a supported metal oxide catalyst enhances this reaction (73). No products are isolated which would suggest that cyanogen reacts as a diene in the Diels–Alder reaction.

The Diels–Alder reaction of cyanogen with butadiene between 320° and 450°C. at constant pressure and continuous flow is a second-order reaction; it is first order with respect to each reactant (72).

Thermodynamic properties of the cyanogen–butadiene reaction have been calculated (71, 89). The heat of formation of 2-cyanopyridine is 60.59 kcal. per mole, and its entropy is 77.09 cal./degree/mole.

The vapor-phase reaction with benzene with a slight excess of cyanogen at a temperature of about 745°C. and a contact time of 2–3 sec. furnishes benzonitrile in 42 per cent yield and 46 per cent conversion and also a 1–5 per cent yield of phthalonitriles (90). A mixture of benzonitrile and cyanogen is converted into a mixture of phthalonitriles in 26 per cent yield and 63 per cent conversion when passed through a reactor at a temperature of 720°C. and for a contact time of about 18 sec. (90). Naphthalene and cyanogen similarly react to give 1-cyanonaphthalene (115).

$$C_6H_6 + (CN)_2 \rightarrow C_6H_5CN + C_6H_4(CN)_2$$

$$C_{10}H_8 + (CN)_2 \rightarrow 1\text{-}C_{10}H_7CN$$

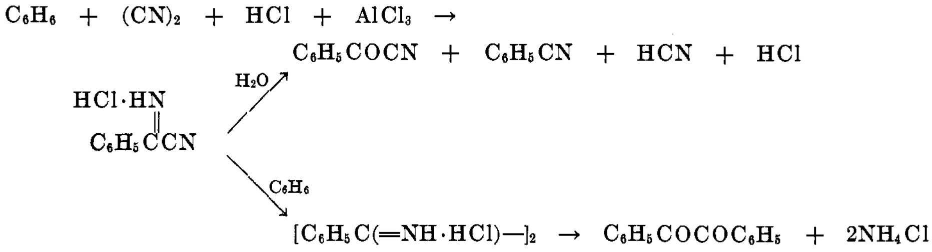
Desgrez (41) originally discovered that aromatic hydrocarbons, such as benzene, toluene, xylene, and mesitylene, reacted with cyanogen in the presence of hydrogen chloride and aluminum chloride to produce the corresponding nitriles in yields of about 12 per cent. Vorländer (199) later discovered that, in addition to the nitriles, benzoyl cyanides and benzils were formed. By passing a mixture of cyanogen and hydrogen chloride through a slurry of aluminum chloride in benzene at 40°C. and subsequently treating the reaction mixture with dilute hydrochloric acid, benzoyl cyanide and benzonitrile were produced in 24 and 26 per cent yields, respectively, together with traces of benzil. Lower yields of these products were obtained when the reaction temperature was maintained at the boiling point of benzene and at ice temperatures. The composition of the product mixture varied with the hydrocarbon used (see table 18).

TABLE 18

*Reaction of cyanogen with aromatic compounds in the presence of aluminum chloride (41, 199)**

Hydrocarbon	Product Mixture	Yield	Hydrocarbon	Product Mixture	Yield
		per cent			*per cent*
Benzene............	Benzoyl cyanide	24	Anisole...........	4-Methoxybenzoyl cyanide	22.5
	Benzonitrile	6	Phenetole..........	4-Ethoxybenzoyl cyanide	
	Benzil				
Toluene............	4-Methylbenzoyl cyanide	7.2	Biphenyl..........	4-Phenylbenzoyl cyanide	
	4-Methylbenzonitrile	8	Xylene............		
	4,4'-Dimethylbenzil	10	Mesitylene.........		
	p-Toluic acid	3.4			

* See also Section VII,H.



F. REACTION WITH HYDROGEN

The pseudo-halogen behavior characteristic of cyanogen is exemplified by the high-temperature, uncatalyzed reaction of cyanogen with hydrogen. At 550–675°C. the equilibrium lies far to the right, with hydrogen cyanide being formed in yields of 98 per cent in 48 hr. at 625°C. (146, 147) and 86 per cent at 550°C. (16). Polymer, presumably paracyanogen, is also formed as a by-product.

$$(CN)_2 + H_2 \rightleftarrows 2HCN$$

Robertson and Pease (146, 147) concluded, following a kinetic study, that hydrogen cyanide is formed from cyanogen and hydrogen via a radical-chain mechanism in the same manner that hydrogen bromide is produced from hydrogen and bromine under similar conditions.

$$(CN)_2 \rightarrow 2CN\bullet \qquad (1)$$

$$CN\bullet + H_2 \rightarrow HCN + H\bullet \qquad (2)$$

$$H\bullet + (CN)_2 \rightarrow HCN + CN\bullet \qquad (3)$$

$$H\bullet + HCN \rightarrow CN\bullet + H_2 \qquad (4)$$

$$\bullet CN + \bullet CN \rightarrow (CN)_2 \qquad (5)$$

Steady-state assumptions lead to a rate expression identical with that for the bromine + hydrogen ⇄ hydrogen bromide reaction.

$$\frac{d[HCN]}{dt} = \frac{2k_2\left\{\frac{k_1}{k_5}[H_2][(CN)_2]\right\}^{1/2}}{1 + \frac{k_4[HCN]}{k_3[(CN)_2]}}$$

Hydrogen cyanide is also formed when a mixture of hydrogen and cyanogen is subjected to an electron discharge (22). At extremely low temperatures (about −190°C.), a cyanogen–hydrogen mixture is converted into a black polymeric material whose structure approaches that of paracyanogen (63). In the presence of α-irradiation of radon at 25°C., a solid of the formula $C_6H_6N_4$ is isolated (108).

A very early report (51), which has not been verified, suggests that ethylenediamine is produced when a hydrochloric acid solution of cyanogen is treated with metallic tin.

$$(CN)_2 + \underset{(Sn\,+\,HCl)}{H_2} \rightarrow H_2NCH_2CH_2NH_2$$

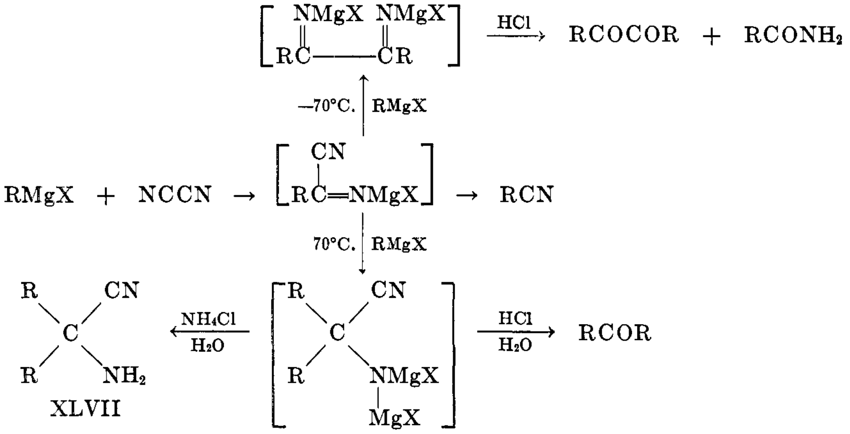
G. REACTION WITH GRIGNARD AND RELATED REAGENTS

The results of Grignard reactions involving cyanogen have, until recently, been confused by contradictory reports where, in one case (68), nitriles were claimed as the products and in another instance monoketones (199) were the end-products. This dilemma was recently resolved in an elegant manner by Woodburn and Lathroum (104, 217), who showed that, by proper choice of reaction conditions and stoichiometry, either nitriles, ketones, or the previously unknown glycinonitriles could be realized. By employing still another procedure, an α-diketone and an amide were obtained as the end-products (109).

The reaction of cyanogen with an excess of a Grignard reagent at temperatures above 0°C. produces a salt which may be hydrolyzed with hydrochloric acid to produce ketones (199), or with ammonium chloride solution to produce glycinonitriles (XLVII) (104, 217) (table 19). Using a similar procedure, but at −70°C., and with subsequent treatment with hydrochloric acid, an α-diketone and an amide are formed (109).

The formation of nitriles (table 20) occurs when an equimolar ratio of Grignard reagent and cyanogen is allowed to react in an ether solution over a broad range of temperatures.

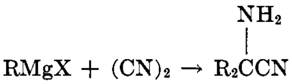
The following mechanism explains the various reactions of cyanogen with a Grignard reagent.



XLVII

TABLE 19

Glycinonitriles from the reaction of cyanogen with Grignard reagents (104, 217)



$$RMgX + (CN)_2 \rightarrow R_2C(NH_2)CN$$

R	Yield	Melting Point	R	Yield	Melting Point
	per cent	°C.		*per cent*	°C.
C_6H_5—..................	33	98-99	n-C_4H_9—..............	12*	
m-$CH_3C_6H_4$—...........	34	95-96	$tert$-C_4H_9—............	15	43-44
Cyclohexyl..............	6	83-84			

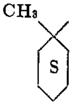
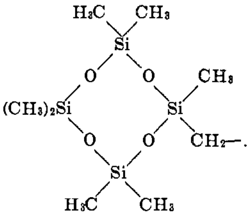
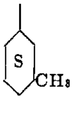
---

* Isolated as the benzoyl derivative.

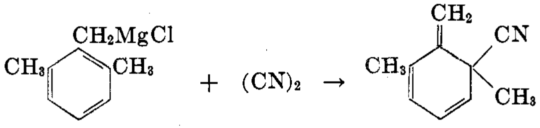
TABLE 20

Nitriles from the reaction of cyanogen with Grignard reagents

$RMgX + (CN)_2 \rightarrow RCN + MgXCN$

R	Yield	Reference	R	Yield	References
	per cent			*per cent*	
C_6H_5—		(68)		30	(68)
o-$CH_3C_6H_4$—	34	(68)			
$C_6H_5(CH_2)_3$—	69	(68)			
$C_6H_5C{\equiv}C$—	61	(68)			
	50	(68)	n-C_4H_9—	12	(104, 117)
			tert-C_4H_9—	15	(104, 217)
			iso-C_5H_{11}—	62	(68, 104, 217)
			$(CH_3)_3SiCH_2$—	54	(140)
			$(CH_3)_3SiOSi(CH_3)_2CH_2$—	38	(140)
	40	(68)			
				52	(140)
	60	(68)			
	40	(68)			

Grignard reagents of the benzyl type react with cyanogen in ether to give o-cyano derivatives, rather than the substituted acetonitriles that might be expected. The Grignard reagents of benzyl chloride, 2-methylbenzyl bromide, and 1-bromonaphthalene thus react with cyanogen to produce 2-methylbenzonitrile, 2,3-dimethylbenzonitrile, and 1-methyl-2-naphthonitrile, respectively, in 40–60 per cent yields. Similarly, 2,6-dimethylbenzylmagnesium chloride, which has both ortho positions blocked, reacts with cyanogen to form 5-cyano-1,5-dimethyl-6-methylene-1,3-cyclohexadiene (XLVIII) (45).



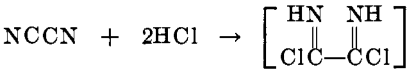
XLVIII

Diethylzinc and cyanogen react to form propionitrile (61).

H. REACTION WITH PHENOLS

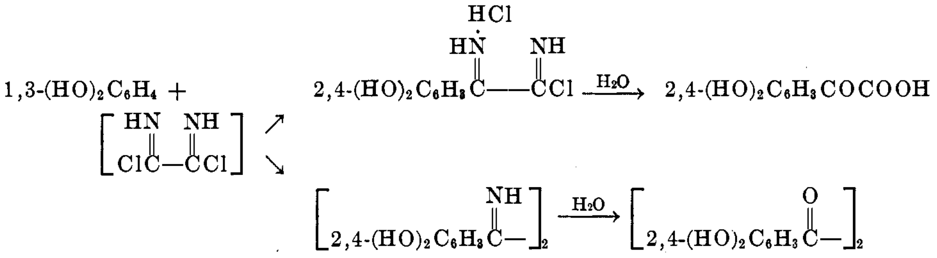
The reaction of cyanogen with phenolic-type materials in the presence of hydrogen chloride or condensing agents of the Lewis acid type has been extensively investigated. There are no reports concerning base-catalyzed reactions of cyanogen with phenols.

Karrer and Fela (94) first disclosed that resorcil and phenylglyoxylic acid were produced in low yields by passing a mixture of cyanogen and hydrogen chloride into a cold ether solution of resorcinol and subsequently hydrolyzing the intermediate imino compounds. The addition product of cyanogen and hydrogen chloride, oxaldiimidyl chloride (XLIX), is probably an intermediate.



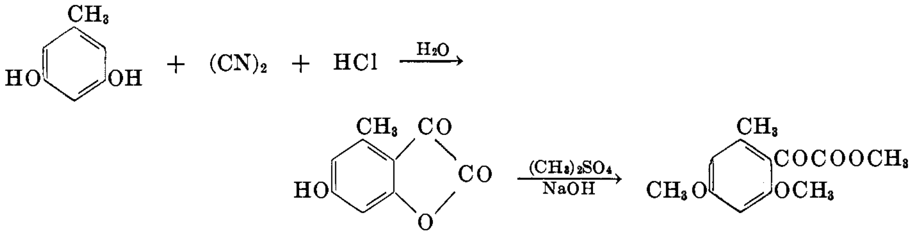
$$\mathrm{NCCN} + 2\mathrm{HCl} \rightarrow \left[\mathrm{Cl}\overset{\mathrm{HN}}{\overset{\|}{\mathrm{C}}}{-}\overset{\mathrm{NH}}{\overset{\|}{\mathrm{C}}}\mathrm{Cl}\right]$$

XLIX



$$1,3\text{-}(\mathrm{HO})_2\mathrm{C_6H_4} + \left[\mathrm{Cl}\overset{\mathrm{HN}}{\overset{\|}{\mathrm{C}}}{-}\overset{\mathrm{NH}}{\overset{\|}{\mathrm{C}}}\mathrm{Cl}\right] \begin{array}{l} \nearrow\ 2,4\text{-}(\mathrm{HO})_2\mathrm{C_6H_3}\overset{\overset{\mathrm{HCl}}{\mathrm{H\dot{N}}}}{\overset{\|}{\mathrm{C}}}{-\!-}\overset{\mathrm{NH}}{\overset{\|}{\mathrm{C}}}\mathrm{Cl} \xrightarrow{\mathrm{H_2O}} 2,4\text{-}(\mathrm{HO})_2\mathrm{C_6H_3COCOOH} \\ \searrow\ \left[2,4\text{-}(\mathrm{HO})_2\mathrm{C_6H_3}\overset{\mathrm{NH}}{\overset{\|}{\mathrm{C}}}{-}\right]_2 \xrightarrow{\mathrm{H_2O}} \left[2,4\text{-}(\mathrm{HO})_2\mathrm{C_6H_3}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}{-}\right]_2 \end{array}$$

Under similar reaction conditions 3,5-dihydroxytoluene and cyanogen did not yield the corresponding benzil but gave the lactone of 2,4-dihydroxy-6-methylglyoxylic acid. The structure of the acid was determined by its conversion to methyl 2,4-dimethoxy-6-methylglyoxylate with dimethyl sulfate.

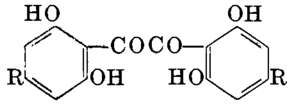


More recently, an extensive study was made of the reaction of cyanogen with various phenolic materials in the presence of hydrogen chloride and a condensing agent such as aluminum chloride or zinc chloride (97, 158). The general procedure employed involved the treatment of a mixture of a phenolic substance and a stoichiometric quantity of a condensing agent in ether with a mixture of cyanogen and hydrogen chloride. The resulting mixture was poured into 10 per cent hydrochloric acid solution, from which the products were then isolated. The monohydric phenols and their derivatives (phenol, anisole, *o*-, *m*-, and *p*-cresols, thymol, *p*-bromophenol, *p*-carboxymethylphenol) and the dihydric phenols (pyrocatechol, hydroquinone, and their mono- or diether derivatives) did not furnish benzils under these conditions. However, resorcinol and 5-alkylresorcinol reacted with cyanogen to furnish good yields of the corresponding 2-resorcil diketimino dihydrochlorides and, subsequently, resorcils (table 21).

The monomethyl and monoethyl ethers of resorcinol yielded a mixture of

TABLE 21

Resorcils from cyanogen and resorcinols with aluminum chloride as the condensing agent (158)

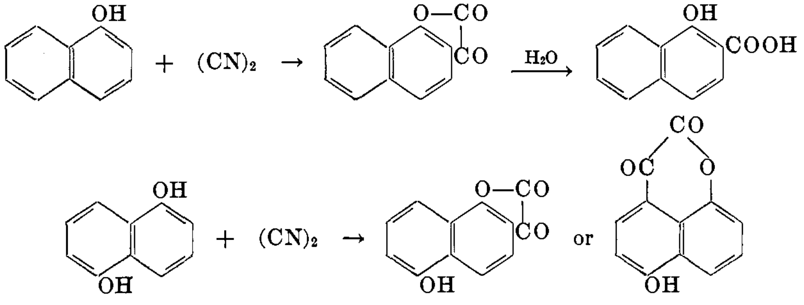


R	Yield	R	Yield	R	Yield
	per cent		*per cent*		*per cent*
H	74	n-C_3H_7—	59	n-C_6H_{13}—	56
C_2H_5—	64	iso-C_5H_{11}—	30	n-$C_{10}H_{11}$—	24

isomeric resorcils and carboxylic acids (97). Although the dimethyl ether of resorcinol was converted into tetramethoxybenzil, the diethyl ether of resorcinol did not give a benzil, presumably owing to steric hindrance by the more bulky ethoxy group (97).

The 4-chloro-, 4-bromo-, and 2-nitroresorcinols, and the monoacetate of resorcinol, do not react with cyanogen in the presence of a condensing agent. Of the trihydroxybenzenes, only 1,3,5-trihydroxybenzene does not form a benzil with cyanogen, whereas 1,2,3- and 1,3,5-trihydroxybenzenes yield 2,2′,3,3′,4,4′-hexahydroxybenzil and 2,2′,4,4′,5,5′-hexahydroxybenzil, respectively. 1,4-Dihydroxy-3-methoxybenzene and cyanogen yield 2,2′,4,4′-dihydroxy-3,3′-dimethoxybenzil (table 22). 1,2,3-Trimethoxybenzene and 2-hydroxy-1,3-dimethoxybenzene do not form benzils with cyanogen (97).

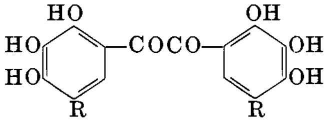
1-Naphthol and 1,5-dihydroxynaphthalene react with cyanogen in the presence of aluminum chloride to produce the lactones of the corresponding hydroxynaphthaleneglyoxylic acids, which can be hydrolyzed to the hydroxy acids (97).



The reaction of cyanogen with pyrocatechol in an aqueous medium was reported by Machek (110) to give 2,3-dihydroxybenzonitrile, but Hahn and Leopold (70) later proved that the product actually obtained was an oxaldiimidate. The oxaldiimidate, which was obtained in 70 per cent yield, could be hydrolyzed to the corresponding oxalate ester. The intermediate cyanoformimidate is, presumably, formed first and then either reacts with the second mole of pyrocatechol to form bis(2-hydroxyphenyl) oxaldiimidate (LI) or cyclizes to give phenylene iminocarbonate (L).

TABLE 22

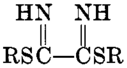
Pyrogallils from cyanogen and pyrogallols with zinc chloride as the condensing agent (158)



R	H	C_2H_5—	*n*-C_3H_7—	*sec*-C_6H_{13}—
Yield (per cent)		50	36	21

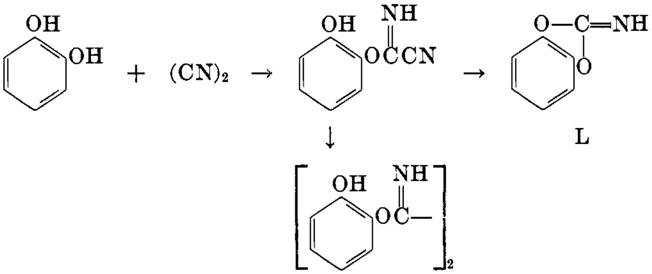
TABLE 23

Dithioöxaldiimidates from cyanogen and thiols or thiophenols (133, 153, 223)



$$RS\overset{\overset{HN}{\|}}{C}—\overset{\overset{NH}{\|}}{C}SR$$

R	Yield	Melting Point	R	Yield	Melting Point
	per cent	*°C.*		*per cent*	*°C.*
CH_3—	71	118-119	*n*-C_5H_{11}—	82	96-97
C_2H_5—	28	52-53	*p*-ClC_6H_4—	53	155-155.5
iso-C_3H_7—	7	57-57.5	*p*-$CH_3C_6H_4$—	83	152-152.5
n-C_3H_7—	32	104-105	*p*-$NO_2C_6H_4$—	62	144-144.5
n-C_4H_9—	52	105-106	3-Thienyl—	51	122.5



L

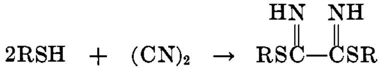
LI

Resorcinol, hydroquinone, pyrogallol, and 2-naphthol do not yield aryl esters on treatment with cyanogen in an aqueous medium; instead, molecular compounds are isolated which melt with decomposition at moderate temperatures. Using similar conditions, no molecular compounds are isolated from phenol, 1,3,5-trihydroxybenzene, 1,4,5-trihydroxybenzene, 1-naphthol, 1,3-dihydroxynaphthalene, or 1,4-dihydroxynaphthalene (111).

I. REACTION WITH THIOLS AND THIOPHENOLS

Cyanogen does not react with either alkanethiols or thiophenols in the absence of a catalyst. In the presence of certain basic catalysts (see table 23), however, the corresponding dithiooxaldiimidates (LII) are formed in good yields. These products are unstable solids which decompose on standing (133, 223). No products could be identified from the reaction of *N*-alkyl- and *N*,*N*-

dialkylaminoethyl mercaptans with cyanogen (223). (See Section VI,A,5 for the reaction of cyanogen with 2-mercaptoethylamine.)



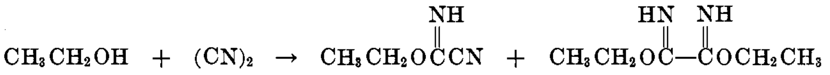
$$2\mathrm{RSH} + (\mathrm{CN})_2 \rightarrow \mathrm{RS}\overset{\mathrm{HN}}{\overset{\|}{\mathrm{C}}}-\overset{\mathrm{NH}}{\overset{\|}{\mathrm{C}}}\mathrm{SR}$$

LII

J. REACTION WITH ALCOHOLS AND GLYCOLS

The reaction of cyanogen with simple alcohols has not been extensively investigated and little is known about these reactions. The data which are currently available, however, indicate that the types of products derived from such reactions are dependent on the solvent, the catalyst, and the alcohols employed (table 24).

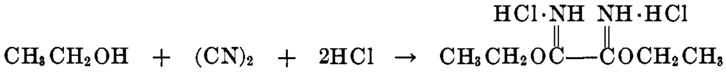
When cyanogen is sparged into a cold aqueous solution of ethyl alcohol containing potassium cyanide, the principal product is ethyl cyanoformimidate (LIII) (125). Diethyl oxaldiimidate (LIV) is also isolated from the reaction, but in smaller quantity. The oxaldiimidate is the major product when cyanogen is passed into an alcoholic solution of sodium ethoxide (125).



$$\mathrm{CH_3CH_2OH} + (\mathrm{CN})_2 \rightarrow \mathrm{CH_3CH_2O}\overset{\mathrm{NH}}{\overset{\|}{\mathrm{C}}}\mathrm{CN} + \mathrm{CH_3CH_2O}\overset{\mathrm{HN}}{\overset{\|}{\mathrm{C}}}-\overset{\mathrm{NH}}{\overset{\|}{\mathrm{C}}}\mathrm{OCH_2CH_3}$$

LIII LIV

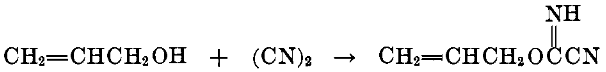
When cyanogen and anhydrous hydrogen chloride are simultaneously passed into ethyl alcohol, a solid product, diethyl oxaldiimidate dihydrochloride (LV), separates from solution (139). Diethyl oxalate and ethyl carbamate, which are also formed, remain in solution.



$$\mathrm{CH_3CH_2OH} + (\mathrm{CN})_2 + 2\mathrm{HCl} \rightarrow \mathrm{CH_3CH_2O}\overset{\mathrm{HCl\cdot NH}}{\overset{\|}{\mathrm{C}}}-\overset{\mathrm{NH\cdot HCl}}{\overset{\|}{\mathrm{C}}}\mathrm{OCH_2CH_3}$$

LV

Allyl alcohol and cyanogen combine in the absence of a catalyst to yield a solid product, which is presumably allyl cyanoformimidate (LVI) (176, 202). This material does not form a stable salt with anhydrous hydrogen chloride, but decomposes to allyl chloride, oxamide, and ammonium chloride.



$$\mathrm{CH_2{=}CHCH_2OH} + (\mathrm{CN})_2 \rightarrow \mathrm{CH_2{=}CHCH_2O}\overset{\mathrm{NH}}{\overset{\|}{\mathrm{C}}}\mathrm{CN}$$

LVI

The reactions of cyanogen with alkoxyethanols (Cellosolves) and dihydroxy-containing materials have recently been investigated in a comprehensive manner by Woodburn and Whitehouse (210, 224).

When cyanogen and hydrogen chloride are simultaneously passed into a solution of a glycol in dimethyl Cellosolve (1,2-dimethoxyethane), the corresponding bis(hydroxyalkyl) oxaldiimidate dihydrochloride is obtained. In this manner, ethylene glycol, 1,3-propanediol, 1,2-propanediol, and 2,3-butanediol were converted into the bis(hydroxyalkyl) oxaldiimidates (LVII, LVIII, LIX,

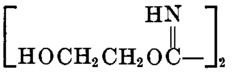
TABLE 24

Reaction of cyanogen with alcohols, glycols, and alkoxyethanols

Alcohol, Glycol, or Alkoxyethanol	Solvent; Catalyst	Yield of Product	Melting Point	Boiling Point	Product	References
		per cent	°*C.*	°*C.*		
C_2H_5OH	C_2H_5OH, H_2O, KCN	—	—		$C_2H_5OC(=NH)CN$	(125)
C_2H_5OH	C_2H_5OH, C_2H_5ONa	—	—		$[C_2H_5OC(=NH)-]_2$	(125)
C_2H_5OH	C_2H_5OH, HCl	—	—		$[C_2H_5OC(=NH \cdot HCl)-]_2$	(139)
$CH_2=CHCH_2OH$	$CH_2=CHCH_2OH$	—	150–151		$CH_2=CHCH_2OC(=NH)CN$	(176)
$HOCH_2CH_2OH$	DMC,* HCl				$[HOCH_2CH_2OC(=NH \cdot HCl)-]_2$	(210, 224)
$HO(CH_2)_3OH$	DMC,* HCl	37	87–88		$[HO(CH_2)_3OC(=NH \cdot HCl)-]_2$	(210, 224)
$HOCH_2CH(CH_3)OH$	DMC,* HCl	74	168–170 (d.)		$[HOCH(CH_3)CH_2OC(=NH \cdot HCl)-]_2$	(210, 224)
$HOCH(CH_3)CH(CH_3)OH$	DMC,* HCl	22	148–152 (d.)		$[HOCH(CH_3)CH(CH_3)OC(=NH \cdot HCl)-]_2$	(210, 224)
$CH_3OCH_2CH_2OH$	DMC,* HCl	9.4	95		$[CH_3OCH_2CH_2OC(=NH \cdot HCl)]_2$	(210, 224)
$CH_3OCH_2CH_2OH$	H_2O, KCN	25		54–55/1.5 mm.	$CH_3OCH_2CH_2OC(=NH)CN$	(210, 224)
$CH_3OCH_2CH_2OH$	Na	6.5	41–43	115/1.5 mm.	$[CH_3OCH_2CH_2OC(=NH)-]_2$	(210, 224)
$C_2H_5OCH_2CH_2OH$	DMC,* HCl	8.3	95		$[C_2H_5OCH_2CH_2OC(=NH \cdot HCl)-]_2$	(210, 224)
$C_2H_5OCH_2CH_2OH$	H_2O, KCN	23		48/1.5 mm.	$C_2H_5OCH_2CH_2OC=(NH)CN$	(210, 224)
$C_2H_5OCH_2CH_2OH$	Na	8.5	30–32	117/1.5 mm.	$[C_2H_5OCH_2CH_2OC(=NH)-]_2$	(210, 224)
$C_4H_9OCH_2CH_2OH$	DMC,* HCl	10.5	85		$[C_4H_9OCH_2CH_2OC(=NH \cdot HCl)-]_2$	(210, 224)
$C_4H_9OCH_2CH_2OH$	H_2O, KCN	28.7		75–77/1.5 mm.	$C_4H_9OCH_2CH_2OC(=NH)CN$	(210, 224)
$C_4H_9OCH_2CH_2OH$	Na	26.8		137–140/1.5 mm.	$[C_4H_9OCH_2CH_2OC=(NH)-]_2$	(210, 224)

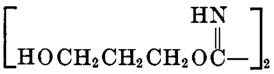
* Dimethyl Cellosolve.

and LX, respectively). 1,2-, 1,3-, and 1,4-Butanediols failed to react with cyanogen under similar conditions. The primary hydroxyl group of 1,2-propanediol is considerably more reactive with cyanogen than the secondary hydroxyl group; thus compound LIX is formed rather than the isomeric product LXI.



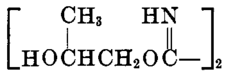
$$\left[\mathrm{HOCH_2CH_2O\overset{HN}{\overset{\|}{C}}-}\right]_2$$

LVII



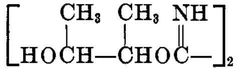
$$\left[\mathrm{HOCH_2CH_2CH_2O\overset{HN}{\overset{\|}{C}}-}\right]_2$$

LVIII



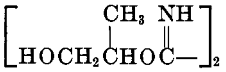
$$\left[\mathrm{HO\overset{CH_3}{\overset{|}{C}}HCH_2O\overset{HN}{\overset{\|}{C}}-}\right]_2$$

LIX



$$\left[\mathrm{HO\overset{CH_3}{\overset{|}{C}}H-\overset{CH_3}{\overset{|}{C}}HO\overset{NH}{\overset{\|}{C}}-}\right]_2$$

LX

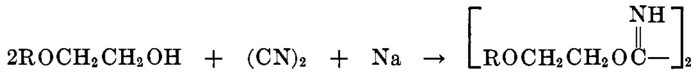


$$\left[\mathrm{HOCH_2\overset{CH_3}{\overset{|}{C}}HO\overset{NH}{\overset{\|}{C}}-}\right]_2$$

LXI

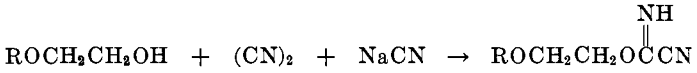
Monoalkyl ethers of ethylene glycol react with cyanogen in the presence of anhydrous hydrogen chloride to yield products which are too unstable to identify. However, the corresponding free oxaldiimidates (LXII) are obtained when cyanogen and the corresponding monoalkyl ether react in the presence of metallic sodium (202, 210, 224). These materials are semistable liquids which can be distilled to yield colorless products. The corresponding stable, crystalline dihydrochlorides are formed when the free oxaldiimidates are treated with anhydrous hydrogen chloride.

Methyl, ethyl, and butyl Cellosolves react with cyanogen in an aqueous medium which contains alkali metal cyanides or potassium carbonate to produce the corresponding alkoxyalkyl cyanoformimidates (LXIII). The same products were obtained in somewhat better yields by using ether as the reaction medium and ammonia as the basic catalyst. These products are distillable, colorless liquids which slowly decompose on standing (202, 210, 224).



$$\mathrm{2ROCH_2CH_2OH + (CN)_2 + Na \rightarrow \left[ROCH_2CH_2O\overset{NH}{\overset{\|}{C}}-\right]_2}$$

LXII



$$\mathrm{ROCH_2CH_2OH + (CN)_2 + NaCN \rightarrow ROCH_2CH_2O\overset{NH}{\overset{\|}{C}}CN}$$

LXIII

K. REACTION WITH COMPOUNDS HAVING ACTIVE HYDROGEN ON CARBON[1]

The reaction of cyanogen with barbituric acid to form the cyanoformimino derivative (LXIV) was first reported in 1872 (126) and was the first example of the reaction of cyanogen with a compound in which an active hydrogen is attached to a carbon atom. Later, the reaction of cyanogen with compounds in which an α-hydrogen is activated by adjacent carbonyl groups was reported to give either a cyanoformimino [$\mathrm{R_2CHC({=}NH)CN}$] substitution product or an α,β-diimino [$\mathrm{R_2CHC({=}NH)C({=}NH)CHR_2}$] substitution product, depending on the reaction conditions. For example, when cyanogen is passed into a cooled

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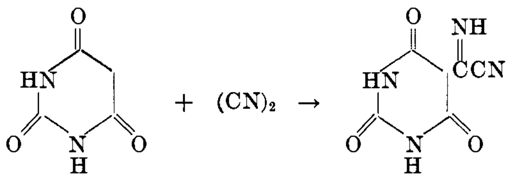
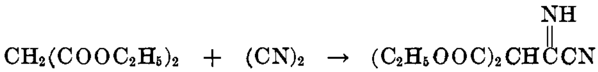
[1] See also Section VII,L.

solution of diethyl malonate in ethanol, a cyanoformiminomalonate (LXV) is the resulting product. If the same procedure is used, but at ambient temperature, tetraethyl 2,3-diimino-1,1,4,4-butanetetracarboxylate (LXVI) is formed. The cyanoimino derivative can be converted into the nitrile (LXVII) by treatment with dilute base (184, 185, 188).

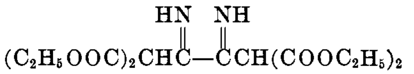


LXIV



$$CH_2(COOC_2H_5)_2 + (CN)_2 \rightarrow (C_2H_5OOC)_2CH\overset{NH}{\overset{\|}{C}}CN$$

LXV



$$(C_2H_5OOC)_2CH\overset{HN}{\overset{\|}{C}}-\overset{NH}{\overset{\|}{C}}CH(COOC_2H_5)_2$$

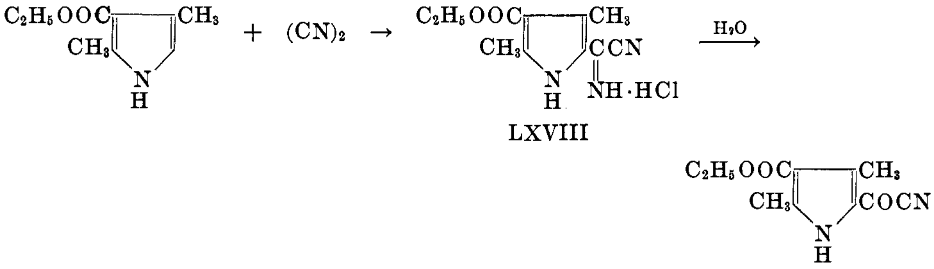
LXVI

$(C_2H_5OOC)_2CHCN$

LXVII

Similarly, ethyl acetoacetate (185, 186, 187), acetylacetone (185, 187), benzoylacetone (190), and ethyl cyanoacetate (44, 190) react with cyanogen in alcoholic medium to give either type of substitution product.

More recently, the reaction of cyanogen with other types of compounds containing active hydrogen atoms has been reported to give substitution products. 3-Carbethoxy-5-cyanoformyl-2,4-dimethylpyrrole (LXIX) is obtained when an ethereal solution of 3-carbethoxy-2,4-dimethylpyrrole is treated with a mixture of cyanogen and hydrogen chloride and, subsequently, with water (59). Presumably, the cyanoformino hydrochloride (LXVIII) is first formed and is then hydrolyzed to the cyanoformyl product. The sodium salt of ethynylbenzene and cyanogen react to form phenylpropargyl cyanide (LXX) (122).



LXVIII

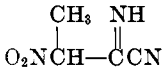
LXIX

$$C_6H_5C{\equiv}CNa + (CN)_2 \rightarrow C_6H_5C{\equiv}CCN + NaCN$$

LXX

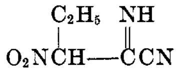
Nitroethane, 1-nitropropane, malononitrile, and acetoacetanilide react with a molar equivalent of cyanogen in the presence of a basic catalyst (44) to form the corresponding cyanoimino derivatives (LXXI, LXXII, LXXIII, and LXXIV, respectively) in low yields. The corresponding α,β-diimino products were not formed by the reaction of the cyanoformimino compounds with a second mole of the substance containing active hydrogen. Substitution of the remaining active hydrogen of the above cyanoformimino derivatives with cyanogen does not occur, presumably because of steric hindrance.

Similarly, no reaction was observed between cyanogen and molecules which contain only one active hydrogen atom, such as diethyl butylmalonate, ethyl α-acetylacetoacetate, 3-chloro-2,4-pentanedione, triphenylmethane, and 4-pyridyldiphenylmethane. 1-Nitrobutane, nitromethane, 2-nitropropane, ethyl chloroacetate, succinonitrile, and phenylacetonitrile are unreactive with cyanogen.



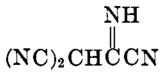
$\mathrm{O_2N\overset{CH_3}{\overset{|}{C}}H{-}\overset{NH}{\overset{\|}{C}}CN}$

LXXI



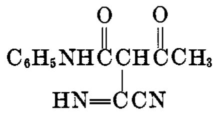
$\mathrm{O_2N\overset{C_2H_5}{\overset{|}{C}}H{-}\overset{NH}{\overset{\|}{C}}CN}$

LXXII



$\mathrm{(NC)_2CH\overset{NH}{\overset{\|}{C}}CN}$

LXXIII



$\mathrm{C_6H_5NH\overset{O}{\overset{\|}{C}}\underset{\underset{HN{=}CCN}{|}}{C}H\overset{O}{\overset{\|}{C}}CH_3}$

LXXIV

Dolce and Woodburn (44) have concluded from these data that the hydrogen in compounds of Group A are sufficiently reactive to react with cyanogen, whereas the hydrogen atoms of compounds of Group B are not sufficiently activated.

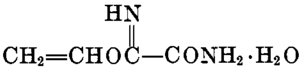
Group A		Group B
$-CH_2NO_2$	$ROOCCH_2CN$	$NCCH_2CH_2CN$
$-COCH_2COOR$	$NCCH_2CN$	$C_6H_5CH_2CN$
$-COCH_2CO-$	$-COCH_2CONH_2$	$=CHCH_2CH=$
$ROOCCH_2COOR$		

L. REACTION WITH ALDEHYDES

Cyanogen and aldehydes which contain hydrogen atoms attached to the α-carbon atom react in a basic aqueous medium to form oxamide. The action of base alone on cyanogen does not yield oxamide but, rather, potassium cyanide and potassium cyanate (124). Thus, the aldehyde is an integral agent in the reaction. Earlier workers (13, 156) suggested that the reaction of cyanogen with acetaldehyde to form oxamide occurred via an ethylidene intermediate (LXXV). More recently, a semistable intermediate was isolated which was suggested to be vinyl oxamimidate (LXXVI) (103). The structure of the intermediate was based on evidence that the material was hydrolyzed with dilute acid to oxamide, oxalic acid, and acetaldehyde, hydrolyzed with base to oxamide and acetaldehyde, and decomposed at 150°C. under vacuum to oxamide. The semistable material isolated from the base-catalyzed reaction of isobutyraldehyde with cyanogen is also assumed to be a vinyl-type ester, isobutenyl oxamimidate (LXXVII) (44).

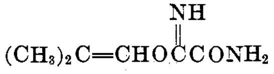
$\mathrm{CH_3CH(NHCOCONH_2)_2}$

LXXV



$\mathrm{CH_2{=}CHO\overset{HN}{\overset{\|}{C}}{-}CONH_2\cdot H_2O}$

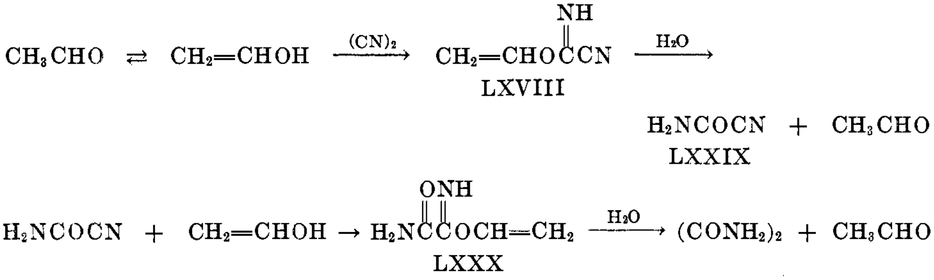
LXXVI



$\mathrm{(CH_3)_2C{=}CHO\overset{NH}{\overset{\|}{C}}CONH_2}$

LXXVII

The reaction of cyanogen with aldehydes is presumed to occur by the combination of the enol form of the aldehyde with cyanogen in a manner characteristic of the reaction of alcohols with cyanogen (see Section VII,J) to form vinyl cyanoformimidate (LXVIII), which is immediately hydrolyzed to cyanoformamide (LXIX). The cyanoformamide subsequently reacts with the enol form of acetaldehyde to yield the semistable vinyl oxamimidate, which is hydrolyzed in the aqueous medium to oxamide.



$$CH_3CHO \rightleftarrows CH_2{=}CHOH \xrightarrow{(CN)_2} \underset{\text{LXVIII}}{CH_2{=}CHO\overset{\overset{NH}{\|}}{C}CN} \xrightarrow{H_2O} \underset{\text{LXXIX}}{H_2NCOCN} + CH_3CHO$$

$$H_2NCOCN + CH_2{=}CHOH \rightarrow \underset{\text{LXXX}}{H_2N\overset{\overset{O}{\|}}{C}\overset{\overset{NH}{\|}}{C}OCH{=}CH_2} \xrightarrow{H_2O} (CONH_2)_2 + CH_3CHO$$

The conclusion that the enol form is the reactive species of the aldehyde is based on the observation that the desired reaction does not occur in the presence of aldehydes which do not have α-hydrogen atoms and thus cannot exist in an enol form (103). For example, no reaction was observed between cyanogen and formaldehyde, benzaldehyde, chloral hydrate, or dextrose.

No products have been obtained from the reaction of aldehydes with cyanogen which would suggest that cyanogenation was occurring at the α-carbon atom, as is characteristic of other active hydrogen-containing materials (44).

M. MISCELLANEOUS REACTIONS OF CYANOGEN

1. Reaction with inorganic and organic acids

Cyanogen is hydrolyzed in concentrated hydrochloric acid (157) or concentrated acetic acid (8) principally to oxamide. In the latter case, urea is also formed. If, however, cyanogen is brought into contact with an aqueous solution of a carboxylic acid or a phosphorus-containing acid at temperatures of 50–90°C. under pressure, cyanoformamide ($NCCONH_2$), is formed (206, 207). Oxamide and ammonium oxalate are obtained in low yields when cyanogen is passed into aqueous solutions of sulfuric or phosphoric acid which contain compounds of zinc, cadmium, magnesium, and mercury (183). Zinc and cadmium salts have a catalytic activity in this reaction and increase the yields of the products. Mercury salts, however, are the most effective catalysts. Almost complete conversion to oxamide is realized when cyanogen is sparged at 40°C. into a 25 per cent sulfuric acid solution containing mercury(II) oxide.

The products obtained from the reaction of cyanogen with reducing acids depend on the acid and the conditions employed. In the absence of air, cyanogen and sulfurous acid react at room temperature to furnish hydrogen cyanide and sulfuric acid (200).

In the presence of refluxing hydriodic acid, cyanogen is converted into glycine, ammonium iodide, and iodine (48).

$$(CN)_2 + 5HI + 2H_2O \rightarrow H_2NCH_2COOH + NH_4I + 2I_2$$

At higher temperatures cyanogen is decomposed by hydriodic acid to the elements and substances such as ethane, carbon dioxide, and ammonia (14, 15).

2. Reaction with inorganic bases

Cyanogen is hydrolyzed in dilute potassium and sodium hydroxide solutions, principally to the corresponding cyanide and cyanate (124).

$$(CN)_2 + 2NaOH \rightarrow NaCN + NaCNO + H_2O$$

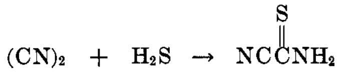
Potassium oxalate is also formed but in smaller amounts. At higher concentrations of base, complex decomposition products are obtained. Similarly, cyanogen reacts with a mixture of potassium carbonate and barium oxide at elevated temperatures to form potassium cyanide, potassium cyanate, barium cyanide, and barium cyanate (212).

The reaction of cyanogen with alkali in liquid ammonia resembles the basic aqueous hydrolysis. Cyanogen reacts with potassium amide in liquid ammonia to form potassium cyanide and potassium cyanamide (35). Sodium cyanamide and ammonium cyanide are the products obtained when sodium amide is used (135).

$$(CN)_2 + 3KNH_2 \rightarrow KCN + K_2NCN + 2NH_3$$

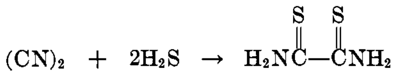
3. Reaction with hydrogen sulfide, sodium hydrogen sulfide, and sodium sulfide

Cyanogen and liquid hydrogen sulfide react in equimolar quantities to form thiocyanoformamide (LXXXI) and in a 2:1 molar ratio to form dithioöxamide (LXXXII) (88). The dithioöxamide is also formed when cyanogen is sparged into an aqueous solution of sodium hydrogen sulfide (37).



$$(CN)_2 + H_2S \rightarrow NC\overset{\overset{\displaystyle S}{\|}}{C}NH_2$$

LXXXI



$$(CN)_2 + 2H_2S \rightarrow H_2N\overset{\overset{\displaystyle S}{\|}}{C}-\overset{\overset{\displaystyle S}{\|}}{C}NH_2$$

LXXXII

Sodium hydrogen sulfide and cyanogen react in an alcoholic medium to form the sodium salt of dithioöxamide (2,13). Sodium cyanide and sodium thiocyanate are the products from the reaction of sodium sulfide with cyanogen (69).

$$(CN)_2 + Na_2S \rightarrow NaCN + NaSCN$$

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