[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF BUFFALO]

Reaction of Cyanogen with Organic Compounds. X. Aliphatic and Aromatic Diamines[1]

HENRY M. WOODBURN AND JOHN R. FISHER[2]

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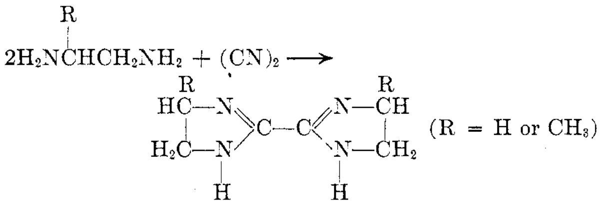
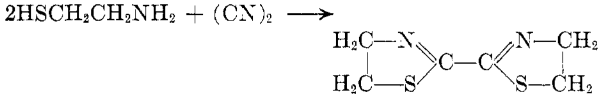
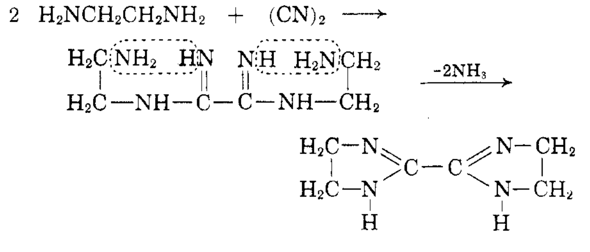
The cyanogenation of aliphatic and *para*-oriented aromatic diamines proceeds through an unstable oxamidine intermediate. This is followed by intramolecular loss of ammonia with the formation of a bicyclic product in those cases where the potential ring contains five or six members, and by intermolecular loss of ammonia to form a condensation polymer when the potential ring contains more than six members.

Several years ago, in the first papers resulting from a series of researches on the behavior of bifunctional compounds with cyanogen[3,4] we reported the formation of bicyclic products from ethylenediamine, 1,2-propanediamine and 2-mercaptoethylamine:

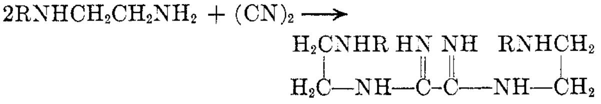




Since, with cyanogen, primary amines and mercaptans normally form oxamidines[5] and dithiooxaldiimidates[6] it seemed reasonable that the reaction might have proceeded by way of such an intermediate which then lost ammonia:



Support for this view was found in the fact that *N*-alkylethylenediamines produced symmetrically disubstituted oxamidines.[3] Here the structure precludes the loss of ammonia:



If this hypothesis is correct, from the series $H_2N(CH_2)_nNH_2$ only those compounds in which n is 2 or 3 should form bicyclic products since from that point on all rings would exceed the stable five- or six-member type.

With the object of establishing the mechanism of the reaction we have, therefore, studied, or restudied, the reaction of cyanogen with the following compounds: ethylenediamine, 1,2-propanediamine, 1,3-propanediamine, 1,4-butanediamine, 1,5-pentanediamine, and 1,6-hexanediamine, and have established these facts:

(1) The formation of a bicyclic product from the cyanogenation of a diamine proceeds by the mechanism of an oxamidine intermediate.

(2) These intermediates are, in general, unstable as free bases but can be isolated as hydrochloride salts.

(3) When the oxamidine intermediate is such that the potential cyclic structure would have more than six atoms per ring, the reaction proceeds by intermolecular loss of ammonia with the formation of an insoluble polymer.

To facilitate isolation of the intermediate, the reaction conditions used by Woodburn and O'Gee[3] were altered to include a solvent for the diamine in which the potential oxamidine would probably be insoluble (usually ethyl ether or an ether-methanol mixture). As cyanogen was passed through the cold solution, an oil or white solid formed which settled to the bottom of the reaction flask. This was the oxamidine. The reaction could be terminated at this point by adding a solvent which would dissolve the oxamidine and passing in dry hydrogen chloride to precipitate the stable salt.

If the oxamidine was isolated as the free base, or if the original reaction mixture was allowed to stand, ammonia was evolved and either a bicyclic endproduct or a condensation polymer resulted.

A summary of the reactions and products follows:

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[1] From the thesis submitted by John R. Fisher in partial fulfillment of the requirements for the Ph.D. degree, June 1956.

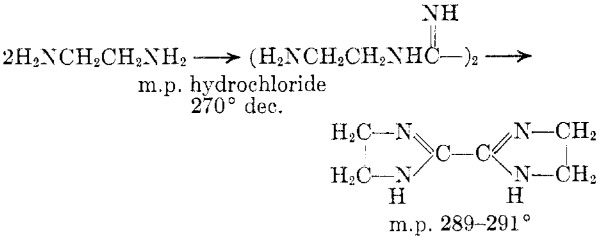
[2] Present address: Film Department, E. I. du Pont de Nemours and Co., Buffalo, N. Y.

[3] H. M. Woodburn and R. C. O'Gee, *J. Org. Chem.*, **17**, 1235 (1952).

[4] H. M. Woodburn and B. G. Pautler, *J. Org. Chem.*, **19**, 863 (1954).

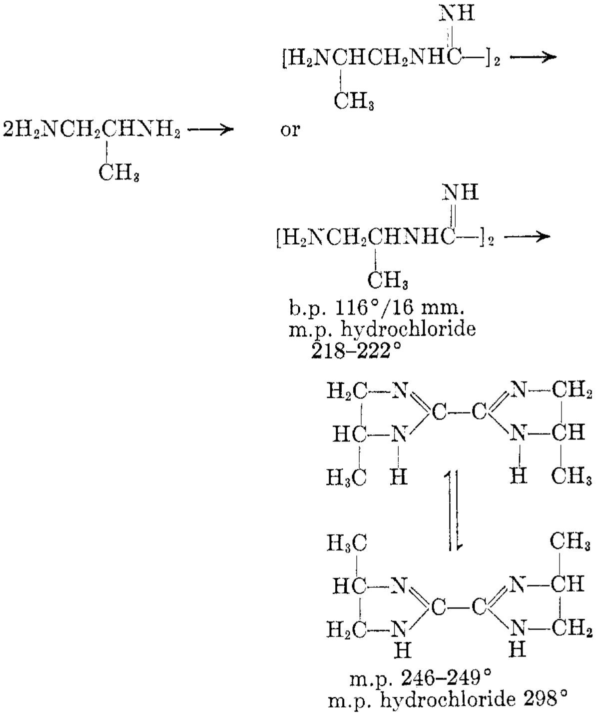
[5] H. M. Woodburn, B. A. Morehead and M. C. Chen, *J. Org. Chem.*, **15**, 535 (1950).

[6] H. M. Woodburn and C. E. Sroog, *J. Org. Chem.*, **17**, 371 (1952).



m.p. hydrochloride 270° dec.

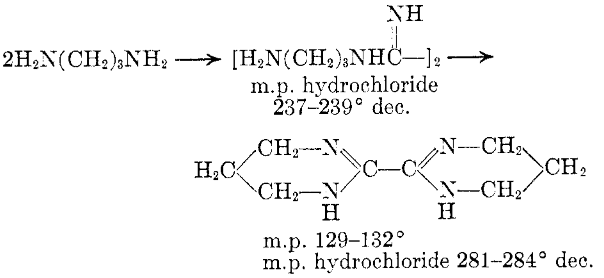
m.p. 289–291°



or

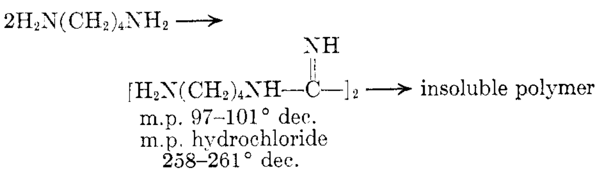
b.p. 116°/16 mm. m.p. hydrochloride 218–222°

m.p. 246–249° m.p. hydrochloride 298°



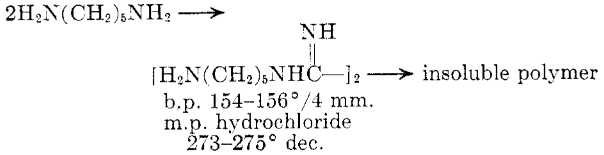
m.p. hydrochloride 237–239° dec.

m.p. 129–132° m.p. hydrochloride 281–284° dec.



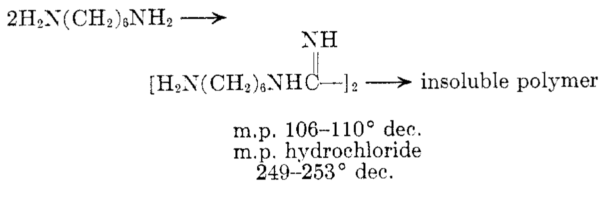
$2H_2N(CH_2)_4NH_2 \longrightarrow [H_2N(CH_2)_4NH-\overset{NH}{\overset{\|}{C}}-]_2 \longrightarrow$ insoluble polymer

m.p. 97–101° dec. m.p. hydrochloride 258–261° dec.



$2H_2N(CH_2)_5NH_2 \longrightarrow [H_2N(CH_2)_5NH\overset{NH}{\overset{\|}{C}}-]_2 \longrightarrow$ insoluble polymer

b.p. 154–156°/4 mm. m.p. hydrochloride 273–275° dec.



$2H_2N(CH_2)_6NH_2 \longrightarrow [H_2N(CH_2)_6NH\overset{NH}{\overset{\|}{C}}-]_2 \longrightarrow$ insoluble polymer

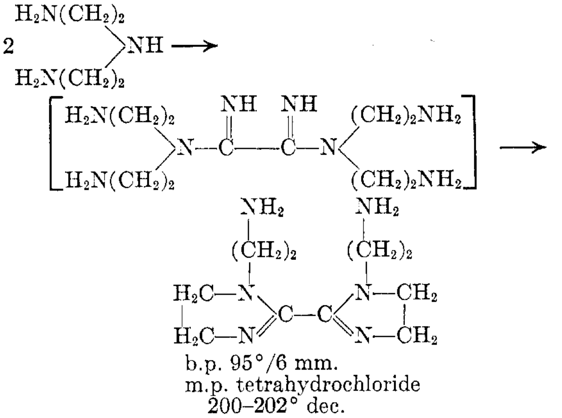
m.p. 106–110° dec. m.p. hydrochloride 249–253° dec.

The insolubility of the polymers suggests that intermolecular loss of ammonia involved the $-NH_2$ group of one molecule and the $=NH$ group of a second since this would lead to crosslinking, rather than only $-NH_2$ groups of separate molecules which should produce a linear polymer.

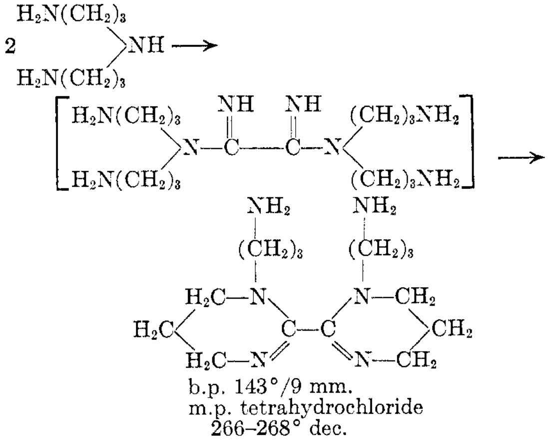
Because of obvious relationships to the series above, four additional amines were investigated:

(a) diethylenetriamine	$H_2N(CH_2)_2NH(CH_2)_2NH_2$
(b) 3,3′-iminobispropylamine	$H_2N(CH_2)_3NH(CH_2)_3NH_2$
(c) *p*-phenylenediamine	$H_2NC_6H_4NH_2$
(d) benzidine	$H_2NC_6H_4C_6H_4NH_2$

While the intermediates were too unstable to isolate, even as hydrochlorides, compounds (a) and (b) produced well defined products whose analyses corresponded to bicyclic structures. The odor of ammonia was noticeable during cyanogenation. Loss of ammonia and the formation of bicyclic compounds with stable rings could come about only by the following mechanism:



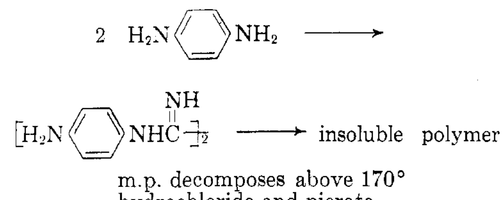
b.p. 95°/6 mm. m.p. tetrahydrochloride 200–202° dec.



b.p. 143°/9 mm. m.p. tetrahydrochloride 266–268° dec.

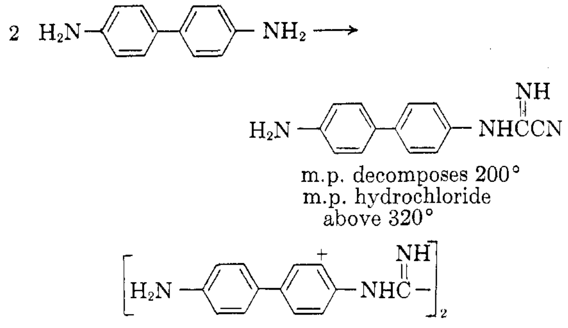
The formation of tetrahydrochlorides is in accord with results obtained previously[3] with bis-[Δ^2-2-imidazolinyl]. Under the more rigorous conditions of heat and prolonged introduction of hydrogen chloride, however, hexachlorides were formed for which we have no plausible explanation although analyses leave no doubt of their composition.

p-Phenylenediamine reacted with cyanogen in the manner of putrescine, cadaverine, and 1,6-hexanediamine. *Sym*-bis(4-aminophenyl)oxamidine was isolated. If the compound or its solution was heated, ammonia was evolved and a dark red solid soluble only in nitric or sulfuric acid resulted.



m.p. decomposes above 170°
hydrochloride and picrate
dec. on drying

Benzidine was unique among the amines investigated, in that both oxamidine and cyanoformamidine could be isolated.



m.p. decomposes 200°
m.p. hydrochloride
above 320°

m.p. decomposes 180°
hydrochloride and picrate
dec. on drying

While the oxamidine appeared to be stable at 105°, a solution in dimethylformamide heated to reflux slowly changed to a tarry mass.

EXPERIMENTAL

Reagents. Cyanogen, prepared and purified by the method of Janz,[7] was frozen to a solid by passing the exit gas through a glass trap immersed in Dry-Ice-acetone mixture. When the trap was removed from the cooling bath the solid melted and vaporized at about the proper rate for cyanogenation. 1,3-Propanediamine and 1,5-pentanediamine (cadaverine) were prepared from the dibromo analogues by the method of Fischer and Koch.[8] 1,4-Butanediamine (putrescine) was prepared by the reduction of succinonitrile supplied by the American Cyanamid Company. Either sodium and ethanol or zinc and hydrochloric acid were used as the reducing mixture.[9] Ethylenediamine, 1,2-propanediamine, 1,6-hexanediamine, *p*-phenylenediamine and benzidine were purchased from Distillation Products Industries and purified by appropriate means. Diethylenetriamine was supplied by Union Carbide Chemicals Co. 3,3′-Iminobispropylamine was supplied by the American Cyanamid Company.

Melting and boiling points are uncorrected. Molecular weight determinations were made cryoscopically in glacial acetic acid, or ebullioscopically in ethanol using a modified Cottrell boiling point apparatus.

Reactions with cyanogen. With a few exceptions noted at the proper place, cyanogenations were carried out as follows: An appropriate weight of diamine, dissolved in ether or ether-methanol mixture was cooled to 0°. Cyanogen, vaporized from the cold trap, was passed through the solution until a cloudy, white mixture resulted which slowly became a light yellow oil layer at the bottom of the reaction vessel. To prevent tar formation, care was taken that the incoming cyanogen did not travel through the oil layer. When it appeared that the volume of oil was no longer increasing, cyanogenation was stopped.

Reaction with ethylenediamine. (a) *sym-Bis(2-aminoethyl)-oxamidine.* Since ethylenediamine is not very soluble in ethyl ether, the compound was first dissolved in methanol, cooled to 0°, and cold ether added until a slight cloudiness persisted. Methanol was then added dropwise until the mixture was again clear.

A solution approximately 20% in strength containing 19 g. of ethylenediamine was thus prepared and cyanogenated at 0°. A cloudy mixture formed immediately which separated into a light yellow oil at the bottom of the reaction vessel. The mixture was allowed to stand for 2 hr. at room temperature during which time a small amount of solid, later identified as bis(Δ^2-2-imidazolinyl), formed. The oil was then isolated by decantation and filtration and diluted to five times its volume with cold methanol. Dry hydrogen chloride was passed into the solution producing a white precipitate immediately.

The precipitated salt was filtered off periodically, six filter cakes of approximately the same size being obtained before salt formation was complete. The first three were combined as product; the last three were discarded because analysis for chlorine indicated an increasing amount of ethylenediamine dihydrochloride in successive filter cakes.

The product was recrystallized twice from ethanol giving white crystals melting at 207° with decomposition. Because of the method of recovery, no estimate of yield was made.

Anal. Calcd. for $C_6H_{16}N_6\cdot 4HCl$: C, 22.7; H, 6.3; N, 26.4; Cl, 44.6. Found: C, 22.9; H, 6.3; N, 26.1; Cl, 44.8.

(b) *Bis(Δ^2-2-imidazolinyl).* Cyanogenation was carried out as above and the mixture allowed to stand 2 days. The solid which separated represented a 17% yield.

Reaction with 1,2-propanediamine. (a) *sym-Bis(2-aminopropyl)oxamidine* or *sym-bis(1-methyl-2-aminoethyl)oxamidine.* A solution of 20 g. of 1,2-propanediamine dissolved in 100 ml. of diethyl ether was cooled to 0° and cyanogenated as above. When the reaction mixture had stood for 1 day at room temperature, the oil was separated and distilled from a Claisen flask. The fraction boiling at 166°/16 mm. weighed 0.9 g., a 3.3% yield.

Anal. Calcd. for $C_8H_{20}N_6$: C, 48.0; H, 10.1; N, 41.9; mol. wt., 200.3. Found: C, 48.4; H, 9.7; N, 42.2; mol. wt. (Cryoscopic) 194.

The *tetrahydrochloride* was made by cyanogenating as above, dissolving the separated oil in methanol, and saturating with dry hydrogen chloride. The product, recrystallized from ethanol, was a white solid melting at 218–222° with decomposition.

Anal. Calcd. for $C_8H_{20}N_6\cdot 4HCl$: C, 27.7; H, 7.0; N, 24.3; Cl, 41.0. Found: C, 27.4; H, 7.3; N, 24.1; Cl, 40.9.

(b) *Bis[Δ^2-2-(4-methylimidazolinyl)].* Cyanogenation of 1,2-propanediamine was carried out as above and the mixture of the two layers was allowed to stand at room temperature in a closed flask.

At the end of 1 week a small amount of white solid had formed at the layer interface. This was filtered off and recrystallized from ethanol. It melted at 246–249° with decomposition, contained 33.4% nitrogen, and had a molecular weight of 169. Woodburn and O'Gee[3] reported a melting point of 246–250°, nitrogen 33.8%, and molecular weight 166.2 for bis[Δ^2-2-(4-methylimidazolinyl)].

During seven months' standing the white solid which continued to form was filtered off periodically, ultimately representing a yield of 22%. It was converted to the *dihydrochloride* by dissolving it in an ether-ethanol mixture and saturating with dry hydrogen chloride. The white salt darkened at 194° and melted with decomposition at 298°.

Anal. Calcd. for $C_8H_{14}N_4\cdot 2HCl$: C, 40.2; H, 6.7; N, 23.4; Cl, 29.7. Found: C, 40.0; H, 7.2; N, 23.5; Cl, 29.7.

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(7) G. J. Janz, *Inorganic Synthesis*, **V**, in press.
(8) E. Fischer and H. Koch, *Ber.*, **17**, 1799 (1884).
(9) T. Fairley, *Ann.*, **Supplement 3**, 371 (1864).

The pure oxamidine resulting from a cyanogenation similar to (a) was allowed to stand at room temperature for 4 months. A small amount (0.04 g.) of white solid formed which was filtered, recrystallized from methanol, and analyzed for nitrogen. It contained 33.6% (theory, 33.8%) and melted at 244–249°.

Reaction with 1,3-propanediamine. (a) *sym-Bis(3-aminopropyl)oxamidine.* A solution of 20 g. of 1,3-propanediamine in 50 ml. of diethyl ether was cyanogenated as above. The reaction mixture was allowed to stand until a slight cloudiness appeared in the oil layer (25 min.). Hydrogen chloride was then passed in, the white precipitate filtered and recrystallized twice from ethanol. The yield was 11%.

Anal. Calcd. for $C_8H_{20}N_6 \cdot 4HCl$: C, 27.8; H, 7.0; N, 24.3; Cl, 41.0. Found: C, 27.5; H, 6.8; N, 24.5; Cl, 41.3.

(b) *Bis(Δ²-2-pyrimidinyl).* Twenty grams of 1,3-propanediamine in 100 ml. of diethyl ether was cooled to 0° and cyanogenated. The mixture was placed in an ice bath and allowed to warm up slowly overnight. Ammonia was evolved and the lower layer changed from an oil to a light yellow solid. This was filtered and recrystallized from ethanol giving a white product melting at 129–132° with decomposition. The yield was 15%.

Anal. Calcd. for $C_8H_{14}N_4$: C, 57.8; H, 8.5; N, 33.7; mol. wt. 166.2. Found: C, 57.5; H, 8.8; N, 33.5; mol. wt. (ebullioscopic) 169.

The *dihydrochloride* was prepared by passing dry hydrogen chloride through a methanol solution of the free base. Recrystallization from ethanol gave a white solid melting at 281–284° with decomposition.

Anal. Calcd. for $C_8H_{14}N_4 \cdot 2HCl$: C, 40.2; H, 6.7; N, 23.4; Cl, 29.7. Found: C, 40.6; H, 6.8; N, 23.3; Cl, 29.4.

Reaction with 1,4-butanediamine (putrescine). sym-Bis(4-aminobutyl)oxamidine. This material decomposed so rapidly that a special method had to be devised to allow its isolation. An ether solution of cyanogen was prepared at 0° from 100 ml. of ether and 6.4 g. of cyanogen and placed in a cold buret. In a second buret was placed 100 ml. of a 5% ether solution of 1,4-butanediamine which had been cooled to −10° in a Dry-Ice chest. The two burets were arranged so as to deliver drops onto a glass rod which carried the liquid to a Buchner funnel. Where drops from the two solutions met, a white precipitate formed, which by this arrangement was almost immediately filtered from the solution. Throughout the reaction the precipitate was washed constantly with ether cooled to −40°. The entire process took 7 min.

The white solid was recrystallized from methanol, 0.6 g. being recovered (9% yield). It was unstable at room temperature and gave off ammonia. It melted between 97° and 101°.

Anal. Calcd. for $C_{10}H_{24}N_6$: C, 52.6; H, 10.6; N, 36.8. Found: C, 52.9; H, 10.1; N, 36.3.

The *tetrahydrochloride* was prepared by repeating the cyanogenation, dissolving the precipitate in cold methanol, and passing in dry hydrogen chloride. The salt was recrystallized twice from ethanol and melted at 258–261° with decomposition.

Anal. Calcd. for $C_{10}H_{24}N_6 \cdot 4HCl$: C, 32.1; H, 7.5; N, 22.5; Cl, 37.9. Found: C, 32.6; H, 7.8; N, 22.0; Cl, 38.0.

Reactions with 1,5-pentanediamine (cadaverine). sym-Bis-(5-aminoamyl)oxamidine. A solution of 17 g. of 1,5-pentanediamine in 100 ml. of a 65–35 ether-methanol mixture was saturated with cyanogen at 0°. Since the oil layer did not separate after standing overnight, the mixture was distilled. A light yellow oil which boiled at 154–156°/4 mm. was recovered. The yield was only 1%. On standing the product decomposed with the evolution of ammonia.

Anal. Calcd. for $C_{12}H_{28}N_6$: C, 56.2; H, 11.0; N, 32.8; mol. wt. 256.4. Found: C, 55.9; H, 11.4; N, 33.3; mol. wt. (cryoscopic) 248.

The *tetrahydrochloride* was prepared by passing dry hydrogen chloride through the cyanogenation mixture which had stood overnight. The white precipitate was recrystallized from glacial acetic acid. It melted at 273–275° with decomposition.

Anal. Calcd. for $C_{12}H_{28}N_6 \cdot 4HCl$: C, 36.0; H, 8.0; N, 20.9; Cl, 35.3. Found: C, 36.0; H, 8.4; N, 20.5; Cl, 35.7.

Reaction with 1,6-hexanediamine. sym-Bis(6-aminohexyl)-oxamidine. A solution of 50 ml. of 1,6-hexanediamine in 100 ml. of a 65–35 ether-methanol mixture was saturated with cyanogen at room temperature. The reaction mixture contained no oil layer; however, after standing overnight a tan-colored solid had precipitated. The yield was 38%.

Because of the relatively high yield, careful study could be made of the decomposition of this compound. When it was heated above 60° or, in solution, above 50°, it decomposed in a few hours into a reddish, resinous material, insoluble in organic solvents.

Twelve grams of the oxamidine was dissolved in 55 ml. of methanol by heating to boiling for less than 1 min. The solution was cooled, filtered and allowed to stand. After 3 weeks the solution had become a clear, firm gel which did not liquefy when heated.

Placed in an oven at 110° for three weeks, the oxamidine was converted to a shiny, black, very hard solid. The polymer was insoluble in water, methanol, ethanol, dioxane, ethyl acetate, acetonitrile, ligroin, petroleum ether, benzene, toluene, aqueous ammonia, acetic acid, concentrated hydrochloric acid, and strong sodium hydroxide solution. It was attacked by concentrated nitric and concentrated sulfuric acids.

Measurements were made of the ammonia evolved when the oxamidine was refluxed in methanol solution. The evolution was greatest during the first day, about half of that on the second day and one fourth as much on the third. Insoluble material began to appear on the second day.

To obtain a sample for analysis the crude oxamidine was dissolved in ethanol without allowing the temperature to rise above 40° and precipitated by the addition of acetone. After three reprecipitations it was dried overnight in a vacuum desiccator. The white solid melted at 106–110° with decomposition. A sample closed in a tube for several weeks had developed a distinct odor of ammonia when reopened.

Anal. Calcd. for $C_{14}H_{32}N_6$: C, 59.1; H, 11.3; N, 29.6; mol. wt., 284.4. Found: C, 59.0; H, 11.5; N, 29.2; mol. wt. (cryoscopic), 296.

The *tetrahydrochloride* was prepared by dissolving the free base in methanol and passing in dry hydrogen chloride. The white salt melted with decomposition at 249–253°. It appeared to be completely stable at room temperature.

Anal. Calcd. for $C_{14}H_{32}N_6 \cdot 4HCl$: C, 39.1; H, 8.4; N, 19.5; Cl, 33.0. Found: C, 38.8; H, 9.0; N, 19.0; Cl, 32.5.

Reaction with diethylenetriamine. Bis[Δ³-1-(2-aminoethyl)-2-imidazolinyl]. Twenty grams of diethylenetriamine was dissolved in 100 ml. of diethyl ether and cyanogenated at 0°. A white solid formed immediately and at once began to decompose into a reddish, viscous oil which settled to the bottom of the reaction vessel. Fractionation under reduced pressure gave a 12% yield of almost colorless liquid boiling at 95°/6 mm.

Anal. Calcd. for $C_{10}H_{20}N_6$: C, 53.5; H, 9.0; N, 37.5; mol. wt., 224.3. Found: C, 53.1; H, 9.5; N, 37.3; mol. wt. (ebullioscopic), 231.

The *tetrahydrochloride* was produced by dissolving the oil in 60–40 methanol-ether mixture and passing dry hydrogen chloride into the cooled solution. The white salt melted at 200–202°.

Anal. Calcd. for $C_{10}H_{20}N_6 \cdot 4HCl$: C, 32.4; H, 6.5; N, 22.7; Cl, 38.3. Found: C, 32.4; H, 7.1; N, 22.8; Cl, 38.0.

By dissolving the oil in ethanol and passing in dry hydrogen chloride without cooling, the mixture became very warm and no precipitate formed until the hydrogen chloride had been passed in for 30 min. The white, solid product corresponded in analysis to a *hexahydrochloride.*

Anal. Calcd. for $C_{10}H_{20}N_6 \cdot 6HCl$: C, 27.1; H, 5.9; N, 19.0; Cl, 48.0. Found: C, 27.1; H, 6.3; N, 19.1; Cl, 47.8.

Reaction with 3,3′-iminobispropylamine. (a) *Bis*[Δ^3-*1-(3-aminopropyl)-2-pyrimidinyl*]. A solution of 10 g. of 3,3′-iminobispropylamine in 100 ml. of diethyl ether was cyanogenated at 0°. A white solid immediately formed and at once changed to a viscous oil. Fractionation gave a 30% yield of a liquid boiling at 143°/9 mm. which changed upon cooling to a pale yellow waxy solid.

Anal. Calcd. for $C_{14}H_{28}N_6$: C, 60.0; H, 10.1; N, 30.0; mol. wt. 280.2. Found: C, 59.8; H, 10.4; N, 29.9; mol. wt. (ebullioscopic) 270.

The *tetrahydrochloride* was prepared by dissolving the product from the reaction above in 70–30 methanol-ether mixture and passing in dry hydrogen chloride, keeping the solution in an ice bath during the precipitation. The white solid melted at 266–268° with decomposition.

Anal. Calcd. for $C_{14}H_{28}N_6 \cdot 4HCl$: C, 39.4; H, 7.6; N, 19.7; Cl, 33.3. Found: C, 39.7; H, 7.1; N, 19.2; Cl, 33.4.

By dissolving the bispyrimidinyl in ethanol and allowing the temperature to rise while dry hydrogen chloride was passed in for 30 min., a white solid *hexachloride* was produced.

Anal. Calcd. for $C_{14}H_{28}N_6 \cdot 6HCl$: C, 33.7; H, 6.9; N, 16.8; Cl, 42.6. Found: C, 33.7; H, 7.2; N, 16.7; Cl, 42.9.

Reaction with p-phenylenediamine. sym-Bis(p-aminophenyl)oxamidine. A solution of 20 g. of *p*-phenylenediamine in 20 ml. of ethanol was cyanogenated at 0° with excess cyanogen. While standing overnight in the ice box a large amount of red, tarry material separated from the reaction mixture. This was filtered off and the filtrate mixed with water until a red precipitate formed. After filtration and drying in a vacuum desiccator, the solid was recrystallized from dimethylformamide, care being taken to keep the temperature below 40°. The yield was 28%. The solid was slightly soluble in ethanol, acetone, chloroform, diethyl ether, ethyl acetate, and dilute hydrochloric acid, very soluble in dimethylformamide, nitrobenzene, and dioxane, and insoluble in water, carbon disulfide, toluene, ligroin, and carbon tetrachloride.

It was kept in a vacuum desiccator for a week to rid it of traces of dimethylformamide before analysis.

Anal. Calcd. for $C_{14}H_{16}N_6$: C, 62.7; H, 6.0; N, 31.3; mol. wt. 268.3. Found: C, 62.8; H, 6.5; N, 31.1; mol. wt. (cryoscopic) 279.

The *hydrochloride* was prepared by dissolving the oxamidine in 1:1 dimethylformamide-ethanol mixture and passing in dry hydrogen chloride. The product decomposed on drying. This was also true of the *picrate.*

Reaction with benzidine. (a) *N-(cyanoformimino)benzidine.* Twenty grams of benzidine was dissolved in 100 ml. of methanol and the solution was cyanogenated at 0° (4.9 g. of cyanogen was absorbed). During 24 hr. standing in the ice chest a large amount of dark red solid had precipitated from the reaction mixture. This was filtered off [see (b) below] and the orange-colored filtrate mixed with water until a solid precipitated. This was recovered, dried in a vacuum desiccator, and recrystallized from methanol. The yield was 34%. The solid was soluble in methanol, ethanol, acetonitrile, dioxane, and dimethylformamide, insoluble in water, ligroin, petroleum ether, and dilute sodium hydroxide solution. It decomposed at about 200°.

Anal. Calcd. for $C_{14}H_{12}N_4$: C, 71.2; H, 5.1; N, 23.7; mol. wt., 236.3. Found: C, 70.9; H, 5.8; N, 23.9; mol. wt. (cryoscopic) 239.

The *dihydrochloride* was prepared by passing dry hydrogen chloride through a methanol solution of the base. It was a red solid melting at 315–317°.

Anal. Calcd. for $C_{14}H_{12}N_4 \cdot 2HCl$: C, 54.4; H, 4.6; N, 18.1; Cl, 22.9. Found: C, 54.0; H, 4.9; N, 18.6; Cl, 22.9.

(b) *sym-Bis-4-(4′-aminobiphenylyl)oxamidine.* The dark red solid filtered off from the original cyanogenation [see (a) above] was recrystallized twice from dimethylformamide without allowing the temperature to rise above 40°. The dark red, solid product was freed of solvent by storing it in a vacuum desiccator. It decomposed at 182°. It was slightly soluble in dilute hydrochloric acid, ethanol, ethyl acetate, acetic acid, acetone, acetonitrile, and dimethylformamide. It was insoluble in water, dilute sodium hydroxide solution, ether, and carbon tetrachloride. The yield of this product was 38%.

Anal. Calcd. for $C_{26}H_{24}N_6$: C, 74.3; H, 5.8; N, 20.0; mol. wt., 420.5. Found: C, 73.5; H, 6.0; N, 20.1; mol. wt. (cryoscopic), 440.

A *hydrochloride* and a *picrate* prepared from the dimethylformamide solution decomposed on drying.

A 5% methanol solution of the cyanoformamidine prepared above (a), was mixed with a 5% solution of benzidine in methanol and allowed to stand at room temperature for 2 weeks. A red-brown precipitate formed which was filtered and recrystallized twice from dimethylformamide without allowing the temperature to rise above 40°. The product corresponded to *sym-bis*-4-(4′-aminobiphenylyl)oxamidine in solubility and nitrogen analysis (19.6% found; 20.0% theory). Its hydrochloride was unstable.

BUFFALO, N. Y.