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THE REACTION OF CYANOGEN WITH ORGANIC COMPOUNDS. I. SECONDARY ALIPHATIC AMINES[1,2,3]

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This paper is the first of a series in which will be reported the results of an extensive study of the reactions of cyanogen with organic compounds. On the basis of its inorganic reactions cyanogen has repeatedly been compared to the halogens (1, 2). Some early work even indicated that a similar comparison could be made in the field of organic chemistry. Merz (3), for example, reported that a mixture of benzene vapor and cyanogen passed through a red hot tube gave benzonitrile, terephthalic acid nitrile, and hydrogen cyanide. Desgrez (4) studied the effect of aluminum chloride and cyanogen on boiling benzene. Decomposition of the reaction products with concentrated hydrochloric acid yielded benzonitrile, benzoyl cyanide, benzil, and unidentified compounds. Vorlander (5) claimed that toluene, diphenyl, ethylbenzene, and phenetole behaved in a similar manner.

However, Machek's report (6) that catechol in aqueous solution reacted with cyanogen to give a 52% yield of 2,3-dihydroxybenzonitrile did not stand up on reexamination, and Hahn and Leopold (7) concluded later that the reaction consisted of condensation between the phenolic and cyano groups and that no nuclear substitution had taken place. Even aniline, which brominates with such extreme ease, produced symmetrical N,N-diphenyloxamidine (8) instead of aminocyanobenzene.

Brief investigation of alcohols, aldehydes, phenylhydrazine, semicarbazide, diphenylguanidine, and benzylamine (9) also showed that comparison with halogens was a poor premise on which to base predictions regarding cyanogen chemistry.

The behavior of each of the amino compounds above could be described as an aminolysis of cyanogen. Under such circumstances the absence from the literature of reactions between cyanogen and aliphatic amines was particularly intriguing. A series of preliminary experiments, consisting in the saturation of a large number of organic liquids and solutions, was, therefore, undertaken and it was quickly indicated that reactions with primary aliphatic amines, secondary aliphatic amines, aliphatic diamines, and mercaptans could be expected once the proper conditions were discovered. The investigation of these reactions has since been actively pursued and the results of one such study are reported in this paper.

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[1] From the thesis submitted by Beachley A. Morehead in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June 1948.

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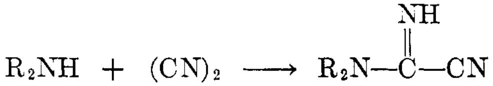
Secondary aliphatic amines react with cyanogen at atmospheric pressure and 0° to give N-substituted cyanoformamidines according to the equation



$$R_2NH + (CN)_2 \longrightarrow R_2N{-}\overset{\overset{\displaystyle NH}{\|}}{C}{-}CN$$

The success of the reaction depends upon the purity of the reagents, the temperature and the nature of the solvent. When pure amine or an aqueous or alcoholic solution is used, tars result from which it is almost impossible to isolate a pure product. Solutions of amines in ethyl acetate, benzene, toluene, or xylene, however, react smoothly and 50–70% yields of the cyanoformamidines are obtained.

Purification of the cyanogen is also important. Unless moisture and carbon dioxide are removed, solid crystals of the carbonic acid salt of the amine separate and the yield of cyanoformamidine is reduced. The reaction of dimethylamine is especially affected by traces of moisture and must be carried out under strictly anhydrous conditions.

TABLE I

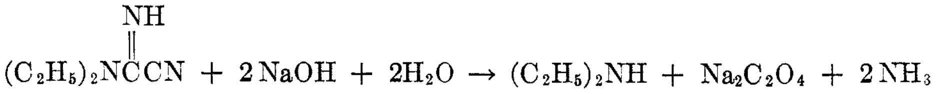
PROPERTIES OF $R_2NC({=}NH)CN$

R	B.P.°C.	n_D^{25}	M.P.°C. HNO_3 SALT	M.P. °C HCl SALT
CH_3	80/26 mm.	$1.4763^{27°}$	136–137	197–198
C_2H_5	85/15 mm.	1.4700	123	130–135
n-C_3H_7	120/34 mm.	1.4670		
n-C_4H_9	85/1 mm.	1.4650		
n-C_5H_{11}	124/4 mm.	1.4645		

The cyanoformamidines are high-boiling, colorless liquids, with faint, not unpleasant odors. Pure samples are stable, but impure samples turn dark and deposit tar on standing. Distillation of the compounds under atmospheric pressure generally results in decomposition. Miscibility with water decreases rapidly as the molecular weight increases, the di-*n*-propyl derivative being already only slightly soluble. Nitric and hydrochloric acid salts of the dimethyl and diethyl derivatives are easily made and being crystalline are suitable compounds for identification, analysis, or storage. Attempts to make similar derivatives of the higher molecular weight compounds have thus far resulted only in oily products difficult to obtain in a pure state.

The nature of the reaction of cyanogen with aliphatic secondary amines and the structure of the product were deduced from a careful study of the diethylamine reaction. Analysis of the product for carbon, hydrogen, and nitrogen indicated the empirical formula $C_6H_{11}N_3$. Titration of the pure substance was impossible but the nitric acid salt, easily prepared and purified, gave an equivalent weight of 190. The calculated value for $C_6H_{11}N_3 \cdot HNO_3$ is 188.

Hydrolysis with 20% sodium hydroxide produced diethylamine, sodium oxalate, and ammonia and indicated that the structure of the substance was $(C_2H_5)_2NC({=}NH)CN$.



$$(C_2H_5)_2N\overset{\overset{NH}{\|}}{C}CN + 2NaOH + 2H_2O \rightarrow (C_2H_5)_2NH + Na_2C_2O_4 + 2NH_3$$

To prove that the reaction had not led to diethylcyanamide, which is likewise a high-boiling liquid and conceivably could result from the reaction of a secondary amine with cyanogen,

$$(C_2H_5)_2NH + (CN)_2 \rightarrow (C_2H_5)_2NCN + HCN$$

that compound was synthesized (10) for a comparison of boiling point and refractive index. There was not the slightest doubt that the cyanamide was absent from the reaction products.

EXPERIMENTAL

Carbon and hydrogen analyses reported below were carried out on a semimicro scale, the removal of interfering nitrogen oxides being accomplished by the method of Elving and McElroy (11). Nitrogen was determined by the semimicro Kjeldahl procedure. Melting and boiling points are uncorrected.

Preparation and purification of cyanogen. Cyanogen was prepared by the familiar reaction of cupric sulfate and sodium or potassium cyanide. Tests indicated that the gas stream contained HCN, CO_2, and water. Consequently, it was passed through a purifying train consisting of two condensers to remove most of the water, a bubbler filled with silver nitrate to remove HCN, a calcium chloride tower followed by a tower containing solid sodium hydroxide to remove CO_2, and a calcium chloride or phosphorus pentoxide tower to remove the last traces of water.

N-dimethylcyanoformamidine. A solution of 25 g. (0.55 mole) of anhydrous dimethylamine in 200 ml. of anhydrous ethyl acetate was saturated with pure cyanogen gas at 0°. The gas was absorbed slowly at first but more rapidly after the reaction began. The straw-colored liquid product was fractionated at reduced pressure yielding 20 g. (38%) of colorless material, b.p. 80° at 26 mm.; n_D^{27} 1.4763.

Since the liquid was quite unstable and hygroscopic, analysis was carried out on the hydrochloric and nitric acid salts. A solution of 16 g. (0.1 mole) of dimethylcyanoformamidine was made in 300 ml. of ether to which was added, slowly and with cooling, 39 ml. (0.1 mole) of concentrated nitric acid. White crystals precipitated which on recrystallization from ethyl alcohol melted at 136–137°.

Anal. Calc'd for $C_4H_7N_3 \cdot HNO_3$: C, 30.0; H, 5.0; Equivalent weight, 160.
Found: C, 30.1; H, 5.2; Equivalent weight, 161.

The *hydrochloric acid salt*, prepared in the same manner as the nitric acid salt, was a white crystalline solid melting at 197–198°.

Anal. Calc'd for $C_4H_7N_3 \cdot HCl$: N, 31.4. Found: N, 31.4.

N-diethylcyanoformamidine. A solution of 36 g. (0.5 mole) of diethylamine in 150 ml. of anhydrous ethyl acetate was cooled in an ice-bath and saturated with purified cyanogen. Fractionation of the liquid product gave a 70% yield of a colorless liquid boiling at 85° under 15 mm. pressure, 186° under atmospheric pressure; n_D^{25} 1.4700.

Anal. Calc'd for $C_6H_{11}N_3$: C, 57.6; H, 8.8; N, 33.6.
Found: C, 58.0; H, 8.5; N, 33.5.

The *nitric acid salt* prepared as above was a white crystalline solid melting at 123°.

Equivalent weight. Calc'd for $C_6H_{11}N_3 \cdot HNO_3$: 188. Found: 190.

The *hydrochloric acid salt* melted at 130–135°.

When unpurified cyanogen was used for the saturation of an ethyl acetate solution of diethylamine (made as above), a white crystalline precipitate was present at the end of the reaction instead of a clear liquid. Filtration yielded 4 g. of solid melting at 61° which was proved to be the *carbonic acid salt* of diethylamine by analysis and comparison with a known sample.

Anal. Calc'd for $C_4H_{11}N \cdot H_2CO_3$: C, 44.4; H, 9.6; N, 10.4; Equivalent weight, 135.
Found: C, 44.7; H, 9.2; N, 11.0, Equivalent weight, 131.

Fractionation of the mother liquor under reduced pressure gave a 60% yield of N-diethylcyanoformamidine.

N-dipropylcyanoformamidine. The preparation of N-dipropylcyanoformamidine was accomplished by saturation at 0° of dipropylamine in anhydrous ethyl acetate with purified cyanogen. The colorless liquid product was obtained in a 60% yield, b.p. 120° at 34 mm.; n_D^{25} 1.4670.

Anal. Calc'd for $C_8H_{15}N_3$: C, 62.7; H, 9.8; N, 27.5.
Found: C, 62.4; H, 10.0; N, 27.6.

N-dibutylcyanoformamidine. The product from the saturation of dibutylamine in anhydrous ethyl acetate was sufficiently insoluble in water so that it could be washed before fractionation. This helped to prevent the formation of tar during distillation. Three 50-ml. portions of 10% NaCl were used to minimize the loss of ethyl acetate. After drying over magnesium sulfate, fractionation gave a 70% yield of colorless liquid boiling at 85° under 1 mm. pressure and at 240° with decomposition at atmospheric pressure; n_D^{25} 1.4650.

Anal. Calc'd for $C_{10}H_{19}N_3$: C, 66.3; H, 10.5; N, 23.2.
Found: C, 66.5; H, 10.3; N, 23.8.

N-diamylcyanoformamidine. The procedure for this preparation was that previously used for the dibutyl analog. A 60% yield of a colorless liquid boiling at 124° under 4 mm. pressure was obtained; n_D^{25} 1.4645.

Anal. Calc'd for $C_{12}H_{23}N_3$: C, 68.9; H, 11.0; N, 20.1.
Found: C, 68.8; H, 11.3; N, 20.0.

Diethylcyanamide. This compound was prepared for reference by the method of McKee (10). It was a colorless liquid boiling at 186–188°, with n_D^{25} 1.4126.

Carbonic acid salt of diethylamine. Prepared by saturating a wet solution of diethylamine in ethyl acetate with carbon dioxide. White crystals melting at 62° with decomposition into diethylamine, carbon dioxide, and water.

SUMMARY

1. Cyanogen reacts with secondary aliphatic amines dissolved in anhydrous ethyl acetate, benzene, toluene, or xylene to give reasonable yields of N-disubstituted cyanoformamidines.

2. The methyl, ethyl, *n*-propyl, *n*-butyl, and *n*-amyl derivatives have been prepared and described.

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