[Contribution from the Department of Chemistry, University of Buffalo]

THE REACTION OF CYANOGEN WITH ORGANIC COMPOUNDS
VIII. 2-MERCAPTOETHYLAMINE AND ITS ALKYL DERIVATIVES[1]

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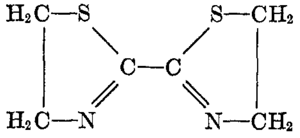
Previous papers in this series (1) have shown that the reactions of cyanogen with unifunctional primary amines, secondary amines, and mercaptans are quite straightforward, but that with ethylenediamines the vicinal amino groups have a mutual effect which makes the course of the reaction difficult to predict (2). This paper reports a continuation of the study of bifunctional compounds, in particular those containing both amino and mercapto groups. Although Hoffman (3) in 1887 reported a reaction between cyanogen and 2-aminothiophenol, no aliphatic aminomercaptans had been investigated previous to this work. The series of reactions here described deals with compounds derived from 2-mercaptoethylamine; the functional groups, in other words, are attached to adjacent carbon atoms.

From *2-mercaptoethylamine*, the only product recovered was bis(Δ^2-2-thiazolinyl) indicating that neither of the functional groups was active enough to capture the cyanogen molecule for itself.

$2\ HSCH_2CH_2NH_2 + (CN)_2 \rightarrow$ 

The structure of the product was assigned on the basis of ultimate analysis, molecular weight, comparison of its infrared absorption with that of known cyanogen derivatives (2), and analogy with the ethylenediamine reaction product (2). Attempts to synthesize the compound from dithioöxamide and 2-mercaptoethylamine [in line with Forsell's preparation (4) of bis(Δ^2-2-imidazolinyl)] failed.

Pure *2-alkylmercaptoethylamines* and their water-alcohol solutions reacted at 0° with cyanogen to give the *sym*-bis(alkylmercaptoethyl)oxamidines.

$$RSCH_2CH_2NH_2 + (CN)_2 \rightarrow RSCH_2CH_2NH\overset{NH}{\overset{\|}{C}}-\overset{NH}{\overset{\|}{C}}NHCH_2CH_2SR$$

A trace of *n*-butylamine appeared to increase the yields (1d), although its presence was not essential to the reaction. This result was in line with expectations since only the amino group was free to react. The methyl, ethyl, *n*-propyl, and *n*-butyl derivatives were isolated.

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[1] From the thesis presented by Bernard G. Pautler in partial fulfillment of the requirements for the Ph.D. degree, February 1953.

Attempts to partially hydrolyze the compounds to substituted oxamides (1b) were unsuccessful, the starting material being recovered in every case. Vigorous hydrolysis with sodium hydroxide resulted in the formation of sodium oxalate.

2-Alkylaminoethyl mercaptans could be cyanogenated successfully only by the addition of a ligroin solution of cyanogen to a ligroin solution of the mercaptan. Under these circumstances white solids precipitated which rapidly darkened and decomposed on filtration. The materials were organic, contained nitrogen and sulfur, and were definitely not the starting compounds; however, accurate analyses were impossible and the structure of these substances cannot be described.

2-Dialkylaminoethyl mercaptans were treated with cyanogen under a variety of conditions (pure, in solvents such as water, alcohol, benzene, or toluene, in an atmosphere of nitrogen, and with *n*-butylamine as catalyst) but without success. Part of the starting material was usually recovered along with disulfide, ammonium salts, and tar.

EXPERIMENTAL

Reagents. Cyanogen. The preparation and purification of cyanogen has been described in Paper IV of this series (1c).

2-Mercaptoethylamine was made from ethylenimine and hydrogen sulfide by the method of Mills and Bogert (5). For good yields it is advisable to use compressed hydrogen sulfide rather than a Kipp generator. It was a white solid melting at 96–97° [Lit. (5) 97–98.5° corr.] Yield, 76.5%.

2-Alkylmercaptoethylamines were made from 2-bromoethylamine hydrobromide, sodium mercaptide, and sodium alkoxide by the method of Brighton and Reid (6).

2-Methylmercaptoethylamine. Yield 81.5%. A colorless liquid boiling at 145–147° [Lit. (7) b.p. 146.8°).

2-Ethylmercaptoethylamine. Yield 55.5%. A colorless liquid boiling at 161–163° [Lit. (7) b.p. 163°).

2-n-Propylmercaptoethylamine. Yield 30%. A colorless liquid boiling at 88–89°/26 mm.; d_4^{25} 0.9280; n_D^{25} 1.4830.

Anal. Calc'd for $C_5H_{13}NS$: N, 11.8; Molar refraction, 36.81; M.W. 119.
Found: N, 11.9; Molar refraction, 36.62; M.W. (ebullioscopic) 122.

2-n-Butylmercaptoethylamine. Yield 35.5%. A colorless liquid boiling at 96–98°/23 mm., 211°/atm. [Lit. (6) b.p. 211°].

2-Alkylaminoethyl mercaptans were prepared by adapting the method described by Reppe and Nicolai (8) to low molecular weight compounds. A solution of 1.0 mole of amine and 0.5 mole of ethylene sulfide in 200 ml. of benzene, was heated for six hours in a stainless steel autoclave at a temperature (internal) of 150–200° and a pressure of 40–70 pounds/in.^{2} Benzene was stripped off at atmospheric pressure and the products were recovered under a vacuum.

2-Ethylaminoethyl mercaptan. Yield, 38% of a colorless liquid boiling at 51.5°/21 mm.; d_4^{25} 0.9195. n_D^{25} 1.4750.

Anal. Calc'd for $C_4H_{11}NS$: C, 45.7; H, 10.5; N, 13.3; Molar refraction, 32.11; M.W. 103.
Found: C, 45.6; H, 10.7; N, 13.0; Molar refraction, 32.15; M.W. (cryoscopic), 103.

2-n-Propylaminoethyl mercaptan. Yield 52% of a colorless liquid boiling at 70°/22 mm.; d_4^{25} 0.9083. n_D^{25} 1.4710.

Anal. Calc'd for $C_5H_{13}NS$: C, 50.4; H, 10.9; N, 11.9; Molar refraction, 36.73; M.W., 119.
Found: C, 50.2; H, 11.0; N, 11.6; Molar refraction, 36.62; M.W. (cryoscopic), 119.

2-n-Butylaminoethyl mercaptan. Yield 57% of a colorless liquid boiling at 84–85°/19 mm.; d_4^{25} 0.9007. n_D^{25} 1.4694.

Anal. Calc'd for $C_6H_{15}NS$: C, 54.1; H, 11.3; N, 10.5; Molar refraction, 41.25; M.W., 133.
Found: C, 54.3; H, 11.6; N, 10.3; Molar refraction, 41.16; M.W. (cryoscopic), 135.

2-Diethylaminoethyl mercaptan was made by the method of Albertson and Clinton (9). Yield, 46% of a colorless liquid boiling at 71–72°/28 mm. [Lit. (9) b.p. 74°/32 mm.].

2-Di-n-butylaminoethyl mercaptan was prepared in poor yield (26%) by the modified method of Reppe and Nicolai (8) described above. A colorless liquid boiling at 95.5°/5 mm. [Lit. (8) b.p. 73–74°/2 mm.].[2]

REACTION OF CYANOGEN WITH 2-MERCAPTOETHYLAMINE

Bis(Δ^2-2-thiazolinyl). The reaction conditions described here were selected from a large number of experiments in which the relative proportions of the reactants and the nature and quantity of the solvent were varied.

2-Mercaptoethylamine (15 g., 0.19 mole) was dissolved in 400 ml. of distilled water, placed in a gas absorption bottle, and cooled to 0°. At that temperature cyanogen was bubbled through the solution until it became very cloudy, the increase in weight indicating that 2.4 g. (0.05 mole) of the gas had been absorbed.

The reaction mixture was kept in an ice chest overnight, after which the brown precipitate was filtered off and washed with distilled water. The yield of crude product was 4.4 g., 25.4% based on the mercaptoamine used.

The crude material was purified by dissolving in the minimum amount of boiling ethyl alcohol, decolorizing with Norit, and filtering. Distilled water was then added to the hot filtrate until it turned faintly cloudy and the solution cooled, finally in an ice-bath. The product was a white solid melting at 127–129°.

Anal. Calc'd for $C_6H_8N_2S_2$: C, 41.8; H, 4.6; N, 16.3; S, 37.1; M.W., 172.
Found: C, 41.5; H, 4.6; N, 16.3; S, 36.9; M.W. (cryoscopic), 175.

REACTIONS OF CYANOGEN WITH 2-ALKYLMERCAPTOETHYLAMINES

(*a*). *sym-Bis(2-methylmercaptoethyl)oxamidine.* Pure, dry cyanogen was passed into 19.6 g. (0.215 mole) of 2-methylmercaptoethylamine, previously cooled to 0°, until it was dark yellow. Increase in weight indicated the absorption of 3.8 g. (0.073 mole) of the gas. The reaction mixture was kept in an ice chest for several days during which time it partially crystallized. Fltration yielded 4.9 g. of solid, a yield of crude product of 19.4%.

The crude material was dissolved in boiling benzene and decolorized with Norit. Ligroin was then added to the warm solution until it was faintly cloudy. Cooling, finally in an ice bath, gave a pure white solid melting at 89–90°.

Anal. Calc'd for $C_8H_{18}N_4S_2$: C, 41.0; H, 7.7; N, 23.9; M.W., 234.
Found: C, 40.8; H, 7.9; N, 23.5; M.W. (cryoscopic), 236.

The *hydrochloric acid salt* was prepared by saturating an alcoholic solution of the oxamidine with dry hydrogen chloride. Recrystallization from alcohol gave white crystals which melted at 220–221° dec.

(*b*). *sym-Bis(2-ethylmercaptoethyl)oxamidine.* Attempts to recrystallize the crude material obtained from 2-ethylmercaptoethylamine by the method described above, resulted in an oil which refused to solidify. The mixture (oil, benzene, and ligroin), therefore, was saturated with dry hydrogen chloride and the white solid which formed was recrystallized

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[2] This compound is better prepared by the method of Snyder, *et al.*, *J. Am. Chem. Soc.*, **69**, 2672 (1947).

by dissolving in alcohol and precipitating with ether. The *hydrochloride* had m.p. 234–236° dec. Yield, 16%.

Anal. Calc'd for $C_{10}H_{22}N_4S_2 \cdot 2HCl$: C, 35.9; H, 7.2; N, 16.7; M.W., 335.
Found: C, 35.8; H, 7.3; N, 16.8; M.W. (ebullioscopic), 337.

(*c*). *sym-Bis(2-n-propylmercaptoethyl)oxamidine.* A 22% yield of crude product was obtained by the method described in (*a*). Recrystallization from benzene and ligroin gave white crystals melting at 74–76°.

Anal. Calc'd for $C_{12}H_{26}N_4S_2$: C, 49.7; H, 8.9; N, 19.3; M.W., 290.
Found: C, 49.6; H, 9.1; N, 19.5; M.W. (cryoscopic), 288.

The *hydrochloric acid salt* melted at 228–230° dec.

(*d*). *sym-Bis(2-n-butylmercaptoethyl)oxamidine.* To a solution of 9.5 g. (0.087 mole) of 2-*n*-butylmercaptoethylamine in 170 ml. of water and 44 ml. of ethyl alcohol was added two drops of *n*-butylamine. The mixture was cyanogenated at 0° until it was *just* turbid. After a day in the ice chest 2.8 g. (24.8% yield) of a white solid had precipitated. Recrystallized from benzene and ligroin this melted at 78.9°.

Anal. Calc'd for $C_{14}H_{30}N_4S_2$: C, 52.9; H, 9.5; N, 17.6; M.W., 318.
Found: C, 52.5; H, 9.4; N, 17.7; M.W. (cryoscopic), 322.

The *hydrochloric acid salt* prepared as above melted at 248–250° dec.

Hydrolysis of the free bases by several hours refluxing with 10% aqueous sodium hydroxide produced sodium oxalate, ammonia, and the original amine.

Attempts to bring about partial hydrolysis producing substituted oxamides by allowing the oxamidines to stand in contact with cold aqueous solutions of the corresponding amines (1b) were unsuccessful.

REACTIONS OF CYANOGEN WITH 2-ALKYLAMINOETHYL MERCAPTANS

2-Alkylaminoethyl mercaptans when treated with cyanogen, in the pure state or in various concentrations of solution in water, alcohol, ligroin, benzene, or toluene, with or without *n*-butylamine as catalyst, and blanketed by nitrogen, gave only a black gummy tar from which ammonium chloride could be recovered by treatment with hydrogen chloride. Fractionation as well as severe and prolonged cooling were of no avail in the isolation of a product. Recourse was had, therefore, to the use of a solution of cyanogen added to a solution of the mercaptan. Only when ligroin was used could a product be isolated. It decomposed so rapidly that no reliable analytical data could be obtained.

Reaction with 2-ethylaminoethyl mercaptan. To a solution of 0.5 ml. of the mercaptan in 25 ml. of ligroin was added 10 ml. of a saturated solution of cyanogen in ligroin. The reaction mixture immediately turned cloudy and on immersion in an ice-bath deposited a white solid. Filtration and washing with ethyl alcohol gave a product which melted at 55–56° but immediately began to discolor and decomposed so rapidly that it was impossible to weigh a sample for analysis. Storage under nitrogen did not prevent decomposition.

Reaction with 2-n-propylaminoethyl mercaptan. A white solid obtained as above melted at 56–57°. It decomposed rapidly forming a black tar.

Reaction with 2-n-butylaminoethyl mercaptan. A white product melting at 48–50° dec. was obtained which decomposed very rapidly on standing.

SUMMARY

The reaction of cyanogen with a series of mercaptoethylamines has been studied in an attempt to discover the relative reactivities of the mercapto and amino groups.

From 2-mercaptoethylamine there resulted bis(Δ^2-2-thiazolinyl) by a reaction analogous to that of ethylenediamine (2).

2-Alkylmercaptoethylamines produced *sym*-bis(2-alkylmercaptoethyl)oxamidines.

The products from the reaction of 2-alkylaminoethyl mercaptans and from 2-dialkylaminoethyl mercaptans were too unstable to allow characterization.

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