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

THE REACTION OF CYANOGEN WITH ORGANIC COMPOUNDS. V. MERCAPTANS^{1,2}

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Received October 15, 1951

Considerable attention has been devoted over the years to the reaction of cyanogen with alcohols and phenols (1). Alcohols produce, depending on conditions, compounds of the types ROC(=NH)CN and ROC(=NH)C(=NH)OR. Monophenols apparently do not react, while the type of product from a polyphenol is determined by the orientation of the groups (2, 3). Thus catechol yields OC(=NH)C(=NH)O whereas resorcinol gives a high OH HO OH HO OH. HO

Only two references to the study of the sulfur analogs of alcohols and phenols have been found.

Sakurada (4) reacted cyanogen with ethyl mercaptan but did not isolate the product. Because further treatment with hydrogen sulfide resulted in diethyl tetrathioöxalate, he assumed the initial formation of an imidic ester.

$$\begin{array}{cccc} & & & & & & \\ HN & & & & \\ HN & & & & \\ 2 & C_2H_5SH + (CN)_2 \rightarrow C_2H_5SC \\ C_2H_5SC \\ -CSC_2H_5 + 2 & H_2S \rightarrow C_2H_5SC \\ -CSC_2H_5 + 2 & H_3S \\ HN & NH \\ \end{array}$$

From 2-aminothiophenol Hoffman (5) isolated two products to which he assigned the structures for *bis*-benzothiazole (I), and for benzothiazole 2-carboxamidine (II).



The research described in this paper was undertaken to establish the true nature of the reaction between cyanogen and mercaptans. Since previous work in this laboratory had indicated that hydrogen activity was an important prop-

¹ From the thesis submitted by C. E. Sroog in partial fulfillment of the requirements for the Ph.D. degree, June 1950.

² This work was supported by the Office of Naval Research under Contract N8-onr-69200.

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erty of organic substances reacting with cyanogen (6) it was of interest to work with mercaptans of varying acidity. Accordingly, not only a series of aliphatic mercaptans, but also thiophenol, certain *para*-substituted thiophenols (chloro, methyl, and nitro), and thiophenethiol were investigated. Thiophenol is more acidic than an aliphatic mercaptan (7) and *para*-substitution of the kind indicated would vary the hydrogen activity without introducing the complicating effects that might result from *ortho*-substitution.

All the compounds investigated, including thiophenol, reacted easily with cyanogen *providing there was present a basic catalyst*. No reaction occurred in the absence of the catalyst. The pure liquid mercaptan or a solution of the solid in an anhydrous solvent was used, the temperature being maintained close to 0° during the reaction.

Dithioöxaldiimidic esters, RSC(=NH)C(=NH)SR were formed in every case. Thus, a change in the hydrogen activity caused no change in the nature of the product. The esters were all solids possessing, when pure, a not unpleasant

EFFECTIVE	NOT EFFECTIVE	
Ethylamine	Aniline	
Diethylamine	Pyridine	
Triethylamine	Aqueous sodium hydroxide, 10%	
n-Butylamine	Di-n-butyloxamidine	
Di-n-butylamine	Aqueous hydrochloric acid	
Sodium methoxide Ammonia	Anhydrous hydrogen chloride	

 TABLE I

 Catalytic Activity of Substances in the Cyanogen-mercaptan Reaction

musty odor. On standing in air they darkened gradually, liberating the odor of mercaptan. All were unstable in the presence of aqueous acid or alkali. A detailed study of the hydrolytic decomposition products was made with the *n*amyl derivative. Solubilities allowed recrystallization from 95% ethanol or benzene. They were insoluble in water.

Numerous compounds were investigated for catalytic activity in an effort to discover the nature of the effect. From Table I it will be noted that the effective compounds were uniformly basic and generally amines. This hinted that the mechanism might be by way of a preliminary action of the amine with cyanogen. However, di-n-butyloxamidine, the reaction product of cyanogen and n-butyl-amine (8), did not function as a catalyst whereas triethylamine, which does not react with cyanogen (9), had a catalytic effect. Evidently it is unnecessary that the catalyst react with cyanogen; consequently, without a more detailed study we subscribe to the view that the reaction proceeds by temporary salt formation and attack on the cyanogen by the nucleophilic mercaptide ion (6). The formation of such an ion was evidenced with p-nitrophenyl mercaptan by the immediate appearance of a red color upon addition of the catalyst.

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The analytical data for the substances formed from cyanogen and various mercaptans would fit any of the three possible structures:



Structure C was ruled out by the 20° difference in the melting points of our methyl derivative and that of N,N'-dimethyldithioöxamide and by the actual synthesis of N,N'-diethyldithioöxamide and comparison by mixed melting point technique with our ethyl product. The result indicated a lack of identity.

The instability at room temperature in the presence of aqueous acid and alkali, and their inability to form sulfonium salts indicated that a sulfide structure (B) was probably not present in our compounds.

Positive evidence for structure A was obtained in two ways. First, our methyl derivative was reacted under various conditions with hydrogen sulfide. From a substance of this structure one could expect as product only dithioöxamide or dimethyl tetrathioöxalate.

$$\begin{array}{ccccc} & \mathrm{HN} & \mathrm{NH} \\ & \parallel & \parallel \\ \mathrm{CH}_3\mathrm{SC} - \mathrm{CSCH}_3 & + & 2 & \mathrm{H}_2\mathrm{S} & \rightarrow & \mathrm{HSC} - \mathrm{CSH} & + & 2 & \mathrm{CH}_3\mathrm{SH} \\ & & \parallel & \parallel \\ & \mathrm{HN} & \mathrm{NH} \\ & & \mathrm{or} & \mathrm{CH}_3\mathrm{SC} - \mathrm{CSCH}_3 & + & 2 & \mathrm{NH}_3 \\ & & \parallel & \parallel \\ & & \mathrm{S} & \mathrm{S} \end{array}$$

Dithioöxamide was proved by analysis and by preparation of N,N'-dimethyl-dithioöxamide from methylamine and the product of the hydrogen sulfide reaction.

Additional support for the oxaldiimidate structure resulted from hydrolysis of the n-amyl derivative with cold, dilute aqueous HCl. The principal hydrolysis products were n-amyl mercaptan, oxalate ion, and ammonium chloride, but in addition, n-amyl thioöxamate and di-n-amyl dithioöxalate were isolated.

$$\begin{array}{cccc} C_{5}H_{11}SC - CSC_{5}H_{11} & + & 2 \ HCl & + & 4 \ H_{2}O & \rightarrow & 2 \ C_{5}H_{11}SH & + & (COOH)_{2} & + & 2 \ NH_{4}Cl \\ & \parallel & \parallel \\ HN & NH \\ \hline C_{5}H_{11}SC - CSC_{5}H_{11} & + \ HCl & + & H_{2}O & \rightarrow & C_{5}H_{11}SC - CNH_{2} & + & C_{5}H_{11}SH & + \ NH_{4}Cl \\ & \parallel & \parallel & \parallel \\ HN & NH & & O & O \\ \hline C_{5}H_{11}SC - CSC_{5}H_{11} & + & 2 \ HCl & + & 2 \ H_{2}O & \rightarrow & C_{5}H_{11}SC - CSC_{5}H_{11} & + & 2 \ NH_{4}Cl \\ & \parallel & \parallel \\ HN & NH & & O & O \end{array}$$

These two organic products could be formed only from a substance possessing structure A. The thioöxamate, previously unreported, was confirmed by analysis for nitrogen, and by a mixed melting point with a sample of the compound, synthesized from di-*n*-amyl dithioöxalate and ammonia according to the method of Gattermann (10).

$$\begin{array}{cccc} C_{5}H_{11}SC - CSC_{5}H_{11} & + & NH_{3} & \rightarrow & C_{5}H_{11}SC - CNH_{2} & + & C_{5}H_{11}SH \\ & & \parallel & \parallel \\ & & 0 & 0 & & 0 & 0 \end{array}$$

The thioöxalate was isolated from the hydrolysis mixture in very small quantities, the total yield amounting to less than 1%.

EXPERIMENTAL

Reagents. Mercaptans. The aliphatic mercaptans and thiophenol were Eastman "white label" products and were used as received. p-Chloro- and p-methyl-thiophenol were prepared by reduction of the appropriate sulfonyl chloride with zinc and sulfuric acid. p-Nitrophenyl mercaptan was prepared by reaction of p-nitrochlorobenzene with sodium sulfide and neutralization of the sodium mercaptide salt with hydrochloric acid. 3-Thiophenethiol was supplied by the Socony-Vacuum Laboratories as a mixture containing, in addition to the thiol, thiophene, and materials boiling between 84° and 171°. The crude material was shaken with aqueous sodium hydroxide and the mercaptide solution separated from the undissolved oil. After washing to remove suspended oil droplets the thiol was regenerated by acidification with acetic acid. Fractional distillation of the dark organic layer gave pale yellow thiophenethiol at 171°.

Oxalyl chloride was prepared from oxalic acid and phosphorus pentachloride.

Dithioöxamide was prepared by the method first described by Formanek (11) in which hydrogen sulfide is bubbled through an aqueous solution of potassium cyanide and a cupric tetrammino complex.

Cyanogen was prepared and purified as described in Paper IV of this series (6). Quantities of reagents resulting in the production of about 0.4 mole of cyanogen were used for each reaction unless otherwise noted.

REACTIONS OF CYANOGEN WITH MERCAPTANS

The mercaptans investigated divided themselves roughly into groups according to the conditions necessary for successful reaction or satisfactory isolation of the product. Details are given only for those reactions which had some distinctive feature.

(a) Di-n-amyl dithioöxaldiimidate. In an 8×1 inch test tube surrounded by ice and water 25.1 g. (0.25 mole) of n-amyl mercaptan and one drop of n-butylamine were allowed to cool to 3°. Purified cyanogen was then bubbled through with no apparent change except a slight yellowing for about ten minutes. At that time the temperature increased to 40° during the period of one minute and a few white crystals appeared on the surface. Precipitation continued for 15 minutes at the end of which time the reaction mixture was semi-solid and the temperature commenced to decrease.

Cyanogenation was stopped and the reaction mixture allowed to remain in the ice-bath for 30 minutes. Upon filtration there resulted 26.5 g. of a white solid which, after recrystallization from ethanol, melted at 96-97°. The yield based on the mercaptan used was 82%.

Anal. Cale'd for C12H24N2S2: C, 55.33; H, 9.28; N, 10.75; M. W., 260.

Found: C, 55.25; H, 9.23; N, 10.88; M. W., 258.

(b) Di-n-butyl dithioöxaldiimidate. A 52% yield of white crystals melting at 105-106° was obtained by the procedure described in (a).

Anal. Calc'd for C10H20N2S2: C, 51.68; H, 8.68; N, 12.06.

Found: C, 51.54; H, 8.61; N, 12.00.

(c) Di-n-propyl dithioöxaldiimidate. A 32% yield of white crystals melting at 104-105° was obtained by the procedure described in (a).

Anal. Cale'd for C₈H₁₆N₂S₂: C, 47.01; H, 7.89; N, 13.71.

Found: C, 46.87; H, 7.98; N, 13.64.

(d) Di-isopropyl dithioöxaldiimidate. Conditions had to be very carefully controlled to insure recovery of this compound in a reproducible manner. In particular the temperature had to be maintained below 10° and an excess of cyanogen avoided. Otherwise tarring became very troublesome. Isopropyl mercaptan (15.2 g., 0.2 mole) was placed in an 8×1 inch test tube and cooled to 0°. One drop of *n*-butylamine was added and cyanogen was bubbled through at the rate of one bubble every five seconds. After 30 minutes, when approximately 0.2 mole of cyanogen had been introduced, the reaction mixture was pale yellow and a few crystals had formed. Cyanogenation was continued at the same rate, the temperature being maintained below 10°, for an additional 45 minutes and was stopped when the mixture was deep orange. Approximately 0.4 mole of cyanogen had been used. Only a few white crystals were present on the bottom of the test tube.

The reaction tube was stoppered and placed on Dry Ice, a white solid separating overnight under these conditions. This was filtered off and recrystallized from ligroin. A 7%yield, 1.5 g., of material melting at 57-57.5° was obtained. The filtrate on distillation gave unreacted mercaptan and tar.

Anal. Calc'd for C₈H₁₆N₂S₂: C, 47.01; H, 7.89; N, 13.71.

Found: C, 47.02; H, 8.00; N, 13.71.

(e) Diethyl dithioöxaldiimidate. A 28% yield of white crystals melting at $52-53^{\circ}$ was obtained by the procedure described in (d).

Anal. Calc'd for C₆H₁₂N₂S₂: C, 40.88; H, 6.86; N, 15.90.

Found: C, 40.44; H, 6.63; N, 15.63.

(f) Dimethyl dithioöxaldiimidate. The usual amine catalyst was used in this procedure. Since methyl mercaptan has a boiling point about 15° below room temperature a Dry Icecarbon tetrachloride mixture was used as a cooling medium throughout the cyanogenation. Nevertheless, the mercaptan proved to be so reactive that it was necessary to introduce the cyanogen very slowly in order to hold the temperature down. A solid product began precipitating shortly after cyanogenation was begun and at the end of the reaction the mixture was a semi-solid mass of yellow crystals. These upon recrystallization from carbon tetrachloride or ethanol were recovered as white crystals melting at 118–119°. The yield of product from 9.6 g. (0.2 mole) of mercaptan and approximately 0.4 mole of cyanogen was 10.5 g. or 71%.

Anal. Calc'd for C4H3N2S2: C, 32.39; H, 5.43; N, 18.89.

Found: C, 32.61; H, 5.60; N, 18.62.

(g) Diphenyl dithioöxaldiimidate. This reaction like (f) was highly exothermic and required ice-bath cooling and a very slow rate of cyanogenation. The product precipitated as cyanogenation proceeded. From 11 g. (0.1 mole) of phenyl mercaptan and 1 drop of a butylamine catalyst there was recovered 7 g. of product, a yield of 59%. After recrystallization from ethanol the white solid melted at 127-128°.

Anal. Calc'd for C₁₄H₁₂N₂S₂: C, 61.71; H, 4.44; N, 10.29; M. W., 272.

Found: C, 61.64; H, 4.61; N, 10.24; M. W., 266.

(h) Di-p-chlorophenyl dithioöxaldiimidate. Since p-chlorophenyl mercaptan is a solid (m.p. 53-54°), it was cyanogenated in solution. A solution of 14.4 g. (0.1 mole) of the mercaptan in 155 g. of ligroin (60-90° fraction) was cooled in ice and water. The addition of one drop of n-butylamine caused the precipitation of a small amount of white solid, presumably a mercaptide-amine salt. Additional material precipitated as soon as cyanogenation was begun and continued throughout the reaction period. Cyanogenation was stopped when about 0.5 mole of gas had been passed in. After standing in ice for 30 minutes the mixture was filtered. The filtrate, kept in a Dry Ice chest overnight, yielded additional solid, the total from the two filtrations being 9 g., a 53% yield. Recrystallization from ethanol gave a white solid melting at 155-155.5°.

Anal. Calc'd for $C_{14}H_{10}Cl_2N_2S_2$: C, 49.25; H. 2.95; N, 8.21.

Found: C, 49.41; H, 3.02; N, 8.14.

(i) Di-p-tolyl dithioöxaldiimidate. Under conditions similar to those described in (h), p-methylthiophenol (m.p. 43-44°) gave an 83% yield of a white solid which, after recrystallization from ethanol, had m.p. 152-152.5°.

Anal. Calc'd for C₁₆H₁₆N₂S₂: C, 63.98; H, 5.37; N, 9.33.

Found: C, 63.82; H, 5.61; N, 9.22.

(j) Di-p-nitrophenyl dithioðxaldiimidate. p-Nitrophenyl mercaptan was so easily converted to disulfide that it was necessary to use strictly anhydrous solvents and an atmosphere of nitrogen in order to recover the cyanogenated product. A solution of 5 g. (0.032 mole) of freshly prepared p-nitrophenyl mercaptan (m.p. 76-77°) in 40 g. of anhydrous toluene was placed in an ice-bath and attached to the cyanogenation train. Dry nitrogen was passed through the entire apparatus for 15 minutes before the generation of cyanogen was begun and during the subsequent reaction. The addition of one drop of n-butylamine caused the formation of a faint red color. Approximately 0.25 mole of cyanogen was admitted after which the tan-colored precipitate was filtered off. It was washed with anhydrous toluene, ethanol, and ether (in that order) to remove unreacted mercaptan. There resulted 3 g. (52% yield) of a pale tan solid, m.p. 144-144.5°.

Anal. Calc'd for C₁₄H₁₀N₄O₄S₂: C, 46.39; H, 2.78; N, 15.46.

Found: C, 46.64; H, 3.02; N, 15.24.

(k) Di-3-thienyl dithioöxaldiimidate.⁴ A solution of 5.8 g. (0.05 mole) of 3-thiophenethiol in 40 cc. of 95% ethanol with one drop of n-butylamine was maintained at a temperature between 5 and 10° while approximately 0.25 mole of cyanogen was passed in. The deep yellow solution was allowed to stand in an ice-bath for 15 minutes at which time a mass of nearly white crystals had precipitated. These were filtered off and the filtrate, left in an ice-bath overnight, yielded an additional small crop of crystals. The product was recrystallized from ethanol; it was pure white, m.p. 122.5°. The yield was 3.6 g. or 51%.

From a similar reaction in which ligroin was the solvent there was obtained a 69% yield of crystals proved by mixed melting point to be identical with the previous product.

Anal. Calc'd for C10H8N2S4: C, 42.23; H, 2.83; N, 9.85.

Found: C, 42.18; H, 2.98; N, 9.59.

EXPERIMENTS RELATED TO PROOF OF STRUCTURE

(1) Synthesis of N, N'-diethyldithioöxamide (12). To 0.2 g. of dithioöxamide in a 25-ml. Erlenmeyer flask was added an excess of 33% aqueous ethylamine and the mixture was heated on a water-bath under reflux. After ten minutes, a vigorous evolution of ammonia took place and the reaction mixture turned a brilliant golden-red. After five more minutes of heating, the mixture was cooled and filtered. The resultant N, N'-diethyldithioöxamide weighed 0.26 g. (88% yield) and after recrystallization from petroleum ether melted at 55°. Its mixture with diethyl dithioöxaldiimidate, m.p. 52-53°, melted at 39°.

(m) Reaction of dimethyl dithioöxaldiimidate with hydrogen sulfde. Hydrogen sulfde was bubbled through a solution of 0.5 g. of dimethyl dithioöxaldiimidate for one hour, the solution changing from colorless to reddish during this period. After concentration of the solution to a slurry under a vacuum at room temperature, filtration gave 0.35 g. (86% yield) of a solid identified as dithioöxamide. Its identity was proved by analysis and by synthesis of the previously reported (12) N,N'-dimethyldithioöxamide as described below (n).

Anal. Calc'd for C₂H₄N₂S₂: C, 19.98; H, 3.35; N, 23.31.

Found: C, 20.42; H, 3.53; N, 23.04.

(n) Synthesis of N, N'-dimethyldithioöxamide. A sample of dithioöxamide (0.04 g.) from the preceding reaction was placed in a 25-ml. Erlenmeyer flask and heated under reflux for a total of 20 minutes with an excess of 25% aqueous methylamine. At the end of ten minutes, a vigorous reaction took place accompanied by the evolution of large quantities of ammonia and the formation of a brilliant yellow color in the reaction mixture. The

⁴ The assistance of Miss Dolores Bogulski in the preparation and analysis of this compound is acknowledged. yellow N,N'-dimethyldithioöxamide recovered upon cooling and filtering weighed 0.035 g. (71% yield) and melted at 140-142°.

(o) Hydrolysis of di-n-amyl dithioöxaldiimidate. Di-n-amyl dithioöxaldiimidate (10 g.) and 75 ml. of 1 N aqueous hydrochloric acid were placed in a 200 ml. round-bottom flask. The mixture slowly turned dark brown, and the odor of n-amyl mercaptan could be detected. A mercury-sealed stirrer and reflux condenser were attached and the mixture was stirred for 168 hours at room temperature. At the end of this period a dark colored organic layer smelling strongly of n-amyl mercaptan had been formed. Ether was added and, after several more hours of stirring, the ether layer was separated. After removal of the ether at atmospheric pressure the dark brown organic residue was distilled at 5 mm. The mercaptan (4 g.) came over below 100°. Redistillation of this fraction gave a product boiling at 128° (literature 128.5°). The residue was allowed to cool and was separated by suction filtration into a black liquid, whose volume amounted to 1 ml., and a black tarry solid. Vacuum-distillation of the filtrate gave about 0.5 ml. of yellow, liquid, di-n-amyl dithioöxalate. Qualitative tests proved the absence of nitrogen and the presence of sulfur.

Anal. Cale'd for $C_{12}H_{22}O_2S_2$: C, 54.92; H, 8.45.

Found: C, 55.24; H, 8.53.

The tarry residue obtained by suction filtration hardened on standing and was recrystallized several times from ligroin. This resulted in the isolation of white crystals melting at 117-117.5°. Analysis indicated that the substance was *n*-amyl thioöxamate; consequently, this compound was separately prepared (q), the product of that reaction melting at 117-118°. A mixture of the two melted at 117-118°.

Anal. Calc'd for C₇H₁₃NO₂S: C, 47.99; H, 7.48; N, 8.00.

Found: C, 47.63; H, 7.72; N, 7.84.

(p) Synthesis of di-n-amyl dithioöxalate. To 13 g. of oxalyl chloride contained in a 200ml. round-bottom flask fitted with a reflux condenser and a dropping-funnel and maintained at 70-80° by a water-bath, was added 21 g. (0.2 mole) of n-amyl mercaptan over a period of 30 minutes. A vigorous evolution of hydrogen chloride occurred. After addition of the mercaptan the mixture was heated at 100° for one hour and then vacuum-distilled. The high-boiling ester distilled over at 197-200°/8 mm. It was a strong-smelling, yellow oil, insoluble in water, slightly soluble in alcohol, and soluble in ether. The total recovery was 22 grams or 84%. Refractive index: $n_{\rm D}^{22}$ 1.5001.

Anal. Calc'd for C₁₂H₂₂O₂S₂: C, 54.92; H, 8.45.

Found: C, 54.83; H, 8.32.

(q) Synthesis of n-amyl thioöxamate. To 5 g. of di-n-amyl dithioöxalate (p) in 15 ml. of 95% ethanol was added with continuous stirring and ice-cooling over a three-minute period, 16 ml. of approximately 1.2 M alcoholic ammonia. After ten minutes of stirring, a white solid began to form and at the end of 30 minutes, the reaction mixture was semisolid. Filtration gave 3 g. (91% yield) of the thioöxamate. Recrystallization from petroleum ether gave a solid melting at 117-118°.

Anal. Calc'd for C₇H₁₃NO₂S: N, 8.00. Found: N, 7.82.

SUMMARY

1. Under the influence of a basic catalyst, cyanogen reacts at 5° or below with aliphatic and aromatic mercaptans to yield dithioöxaldiimidic esters, RSC-(=NH)C(=NH)SR.

2. The preparation and properties of six aliphatic esters (C_1-C_5) and five aromatic esters (including 3-thienyl) are described.

3. The conclusion is drawn that under the conditions used the acidity of the thiol hydrogen has no effect on the nature of the product.

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