polymeric by-products also took place. The presence of a photosensitizer, such as benzophenone,[41] appeared to retard the isomerization. When olefin-free petroleum ether (b.p. 35–40°) was used as solvent, the rate of isomerization decreased markedly, while much more polymeric material was produced. The photochemical reaction appeared to take a different course in the presence of a Vycor (No. 7913) filter, since, after 10 hr. of irradiation, only unidentifiable products, which darkened rapidly in air and did not show the presence of olefinic protons in the n.m.r. spectrum, could be isolated. On the other hand, when a Pyrex tube was placed around the light source, no isomerization could be detected after 5 hr. of irradiation.

C. **_m_-Di-_t_-butylbenzene.**—An ether solution (1 l.) of this hydrocarbon (1.00 g.) was irradiated in a similar manner. The photostationary state with the same *para* to *meta* isomer ratio of 4 to 1 was reached after approximately 128 hr.

D. **_p_-Di-_t_-butylbenzene.**—The same photostationary phase was established after 50 hr. of irradiation of an ether solution of this hydrocarbon (200 mg. in 1 l. of ether). The formation of yellow colored, polymeric materials was also observed during the irradiation of *m*- and *p*-di-*t*-butylbenzene.

E. **_o_-_t_-Butyltoluene.**—The photoisomerization of this hydrocarbon (1.00 g.) was also conducted in ether solution (1 l.) and was found to be much slower than that of I. After 104 hr. of irradiation only half of this compound had been converted into its *meta* and *para* isomer, as estimated by the n.m.r. spectrum. However, the *para* isomer did not appear to undergo any appreciable isomerization under the same conditions after 22 hr.

F. **1,3,5-Tri-_t_-butylbenzene (II)**, 1.00 g., was also irradiated in ether solution (1 l.). There was practically no change after 23 hr. The irradiation was continued for 24 more hr. after addition of 1.00 g. of *t*-butylbenzene, but there was still no detectable isomerization or disproportionation.

G. **_o_-Xylene.**—No isomerization of this hydrocarbon could be detected by infrared or n.m.r. analysis after it had been irradiated in dilute ether solution for as long as 90 hr.[54] However, some yellow polymeric materials were formed.

H. **_m_-Xylene[54] and _o_-Terphenyl.**—Under similar conditions, no evidence of isomerization was detected after 32 hr. of irradiation.

I. **3,4-Di-_t_-butylacetophenone (XV), 1,2-Di-_t_-butyl-4-nitrobenzene (VIIa), and 3,4-Di-_t_-butylphenol Methyl Ether (VIIe).**—There was essentially no significant change in the *o*-di-*t*-butylbenzene system after these derivatives had been irradiated separately for 24 hr. in ether solution. On further irradiation (12 hr.), changes were observed in the aromatic proton signals in the n.m.r. spectra, but the signal attributed to the *o*-di-*t*-butyl groups was still essentially unchanged.

Ozonolysis of _m_- and _p_-Di-_t_-butylbenzene.—In a series of preliminary experiments for future C^{14} tracer studies, the oxidative ozonolysis of a mixture of *m*- and *p*-di-*t*-butylbenzene, in 1-g. quantities according to the general procedure of Criegee, *et al.*,[55] resulted in the production of pivalic acid in 20–30% yield.

Acknowledgment.—We are indebted to Professor Earl S. Huyser for the loan of the quartz irradiation apparatus and lamp and to Professor Melvin S. Newman for helpful suggestions and counsel. We also thank John N. Marx for technical assistance. Portions of this investigation were supported by grants from the National Science Foundation (NSF-G 19936), the Petroleum Research Fund administered by the American Chemical Society (462-A), and the University of Kansas Center for Research in Engineering Sciences (CRES-40B).

---

[54] For contrasting results under higher intensity irradiation, see ref. 42.

[55] R. Criegee and H. Höver, *Chem. Ber.*, **93**, 2521 (1960); R. Criegee and W. Funke, *ibid.*, **94**, 2358 (1961).

[CONTRIBUTION FROM THE BOUND BROOK LABORATORIES, AMERICAN CYANAMID CO., BOUND BROOK, N. J.]

The 1,3-Dithiolium Cation and Some Related Dithioles[1]

BY ERWIN KLINGSBERG

RECEIVED AUGUST 5, 1964

The synthesis and properties of the 1,3-dithiolium cation, 1,3-dithiole-2-thione, and related 1,3-dithioles are described.

Although compounds of unequivocal 1,2-dithiolium structure were first reported in 1960,[2,3] the 1,3-dithiolium system, in the form of benzo derivatives, has been known since 1926.[4] More recently aryl derivatives of the monocyclic cation have been obtained by the cyclization of β-ketoalkyl esters of dithiocarboxylic acids.[5] This method fails in the absence of aryl groups, and the existence of the unsubstituted parent cation thus remained an open question, although LCAO–MO calculations gave favorable indications.[6] With the discovery of the formation of 1,2-dithiolium salts by the peracetic acid oxidation of 1,2-dithiole-3-thiones, the question naturally arose whether 1,3-dithiole-2-thiones can be converted in this way to 1,3-dithiolium salts, including the parent compound. A positive answer was soon given by Leaver, Robertson, and McKinnon,[5] and a different approach to the problem is reported herewith.[7]

Although it is now fairly readily prepared,[8] 1,3-dithiole-2-thione (VIII) had been obtained in only minute amounts at the inception of this investigation, which accordingly took as its starting point the readily accessible 4,5-dicyano derivative II. This is obtained by the action of thiophosgene on disodium dimercaptomaleonitrile (I), itself prepared from sodium cyanide and carbon disulfide.[9] The reaction of peracetic acid with II did not give a cationic product, but a neutral, highly pruritic, brick-red solid. Since analysis shows the presence of one more oxygen atom than in the starting material, the product is evidently a sulfoxide; a strong new infrared absorption band at 993 cm.$^{-1}$ is close to the normal range for sulfoxides.[10] The structure is in all

---

[1] Presented in part at the 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April 8, 1964.

[2] (a) D. Leaver and W. A. H. Robertson, *Proc. Chem. Soc.*, 252 (1960); (b) E. Klingsberg, *Chem. Ind.* (London), 1568 (1960).

[3] Earlier known cationoid 1,2-dithioles were substituted by one or more basic groups capable of accepting the entire positive charge. These include the "trithionium salts" [J. Teste and N. Lozac'h, *Bull. soc. chim. France*, 437 (1955); A. Lüttringhaus and U. Schmidt, *Chem.-Ztg.*, **77**, 135 (1953)] and the cyclization product of dithiomalonamide [U. Schmidt, *Chem. Ber.*, **92**, 1171 (1959)].

[4] W. R. H. Hurtley and S. Smiles, *J. Chem. Soc.*, 1821 (1926); 534 (1927).

[5] D. Leaver, W. A. H. Robertson, and D. M. McKinnon, *ibid.*, 5104 (1962).

[6] J. Koutecký, J. Paldus, and R. Zahradník, *Collection Czech. Chem. Commun.*, **25**, 617 (1960); *cf.* R. Zahradník and J. Koutecký, *Tetrahedron Letters*, 632 (1961).

[7] A preliminary report has been published: E. Klingsberg, *J. Am. Chem. Soc.*, **84**, 3410 (1962).

[8] R. Mayer and B. Gebhardt, *Chem. Ber.*, **97**, 1298 (1964).

[9] G. Bähr and G. Schleitzer, *ibid.*, **90**, 438 (1957).

[10] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 359.

probability III, since there is almost no sign of the thiocarbonyl absorption at 1047 cm.$^{-1}$ which is very strong in II; *cf.* the strong thiocarbonyl absorption at 1053 cm.$^{-1}$ in VIII.[11] S-Oxides of certain thioacid derivatives are known, and recently the S-oxide of 9-fluorenethione has been reported.[12]

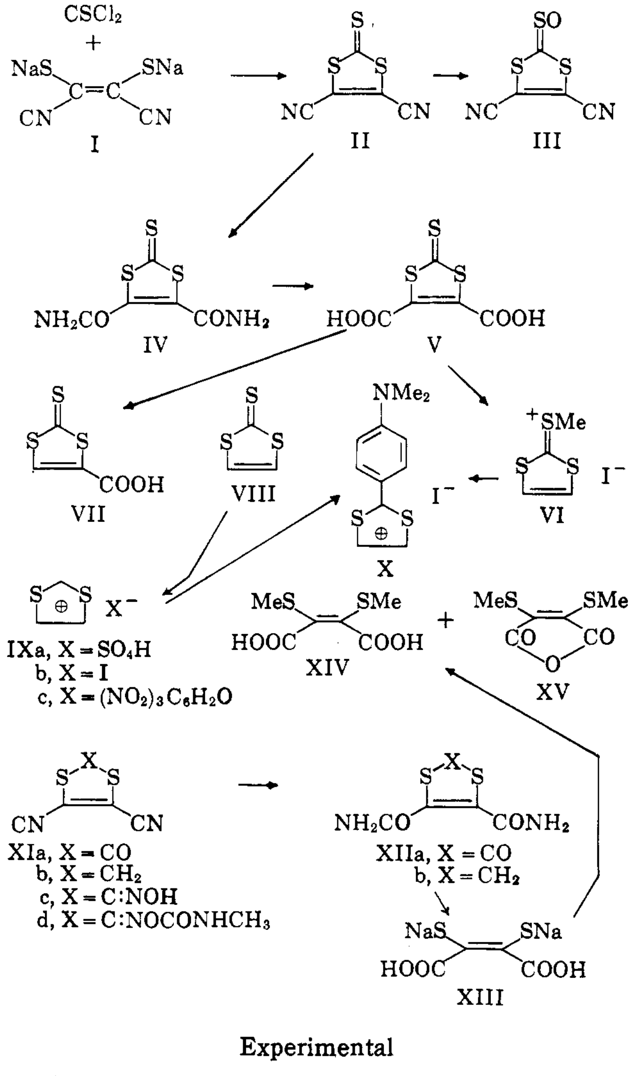
On the supposition that III might represent an intermediate stage in the formation of a dithiolium derivtive, further oxidation was attempted, but without success. The methylation of II also failed even under severe conditions, although VIII, the isomeric 1,2-dithiole-3-thione, and most of their derivatives are known to methylate at the thiocarbonyl group with ease[13]; in the 1,2- series the products are the "trithionium salts."[3]

Upon the failure of these attempts to convert II to a 1,3-dithiolium derivative, the removal of the cyano groups was attempted. This proved to be possible by virtue of the unexpectedly great stability of the ring to mineral acid. Concentrated hydrochloric acid at room temperature effected slow but complete hydrolysis to the corrresponding diamide IV in almost quantitative yield. This could not be deamidated with nitrous acid; presumably oxidation of sulfur interfered. However, constant-boiling hydrochloric acid at reflux effected smooth hydrolysis to the dicarboxylic acid V, again in substantially quantitative yield without ring degradation; V was smoothly decarboxylated to the monocarboxylic acid VII by fusion, but neither V nor VII gave a cationic or indeed identifiable product on reaction with peracetic acid. This result was particularly discouraging in view of the formation under these conditions of the 1,2-dithiolium cation from 5-carboxy-1,2-dithiole-3-thione.[2b] Furthermore, VII resisted decarboxylation to VIII by conventional methods. However, methylation of V with methyl iodide in nitromethane at about 60° was accompanied by smooth elimination of both carboxyl groups despite the mildness of the conditions; the product VI is a known compound obtained by the methylation of VIII itself. The monocarboxylic acid VII, of course, gives the same product under these conditions. Pyridine in refluxing benzene effects smooth demethylation to VIII in 62% over-all yield from the readily prepared II. Peracetic acid in acetone converted VIII in 80% yield to IXa, 1,3-dithiolium hydrogen sulfate, a pale yellow solid that darkened somewhat on standing. The bright yellow iodide IXb is also water soluble; the picrate IXc is insoluble.

Like 1,2-dithiolium and benzo-1,3-dithiolium derivatives, IX substitutes dimethylaniline electrophilically to give a violet dye (X) that is also obtained from VI and dimethylaniline by elimination of methyl mercaptan. With λ_{max} 515 mμ, this is 20 mμ hypsochromic to its 1,2-dithiolium isomer. The 1,2-dithiolium cation[5] and basic dyes derived from it[14] are known to absorb at higher wave length than the 1,3-dithiolium counterparts. Reactions of VI with primary and secondary amines and phenylhydrazine have recently been reported by Mayer and Gebhardt.[8]

Like IV, the dicarboxamides XIIa and XIIb are readily obtained by hydrolysis of the corresponding dinitriles XIa and XIb, which are formed from I and phosgene or methylene iodide, respectively. Alkaline hydrolysis of XIIa opened the ring, giving the deep red disodium salt XIII of dimercaptomaleic acid. Methylation and acidification gave a mixture of bis-(methylthio)maleic acid (XIV) and its anhydride XV. The corresponding imide has recently been reported.[8]

The highly reactive "phosgene oxime," $Cl_2C{:}NOH$, which is readily prepared by reduction of chloropicrin,[15] reacts with I in aqueous solution to give the oxime XIc. This is an interesting example of a reaction in which phosgene oxime resembles phosgene and thiophosgene. Usually it does not, tending instead to eliminate HCl, giving ClCNO followed by dimerization.[16] Reaction of XIc with methyl isocyanate gave the carbamate XId.



Experimental

Melting points are corrected.

4,5-Dicyano-1,3,-dithiole-2-thione[8] **(II).**—A solution of 15.0 g. (10.0 ml., 0.130 mole) of thiophosgene in 15 ml. of benzene was added during 15 min. to a suspension of 24.0 g. (0.130 mole) of disodium dimercaptomaleonitrile[9] stirred in 200 ml. of benzene with ice cooling. The reaction mixture was then stirred 1.5 hr. at room temperature, filtered, and evaporated. The yield of yellow-brown product, m.p. 119–123°, was 15.9 g. (66%). Crystallization from methylcyclohexane (30 ml./g.) gave a 90–95% recovery of golden-yellow needles, m.p. 122–124°.

---

[11] R. Mecke, R. Mecke, and A. Lüttringhaus, *Z. Naturforsch.*, **10b**, 367 (1955).

[12] W. A. Sheppard and J. Diekmann, *J. Am. Chem. Soc.*, **86**, 1891 (1964).

[13] F. Challenger, E. A. Mason, E. C. Holdsworth, and R. Emmott, *J. Chem. Soc.*, 292 (1953).

[14] E. Klingsberg and A. M. Schreiber, *J. Am. Chem. Soc.*, **84**, 2941 (1962).

[15] E. Gryskiewicz-Trochimowski, K. Dymowski, and E. Schmidt, *Bull. soc. chim. France*, 597 (1948).

[16] A. Seher, *Chem. Ber.*, **83**, 400 (1950).

Anal. Calcd. for $C_5N_2S_3$: C, 32.6; N, 15.2; S, 52.2. Found: C, 32.6; N, 15.2; S, 52.6.

4,5-Dicyano-1,3-dithiole-2-thionoxide (**III**).—A solution of 1.8 g. (0.010 mole) of 4,5-dicyano-1,3-dithiole-2-thione in 30 ml. of acetone was treated during 20 min. with a solution of 2.2 g. (0.010 mole) of 40% peracetic acid in 5 ml. of acetone. The brick-red product was filtered and washed with acetone; yield 1.8 g. (90%), dec. 182°. Dioxane gave purple crystals, dec. 190°. This compound caused intense itching.

Anal. Calcd. for $C_5ON_2S_3$: C, 30.0; N, 14.0; S, 48.0. Found: C, 29.9; N, 14.2; S, 48.1.

1,3-Dithiole-2-thione-4,5-dicarboxamide (**IV**).—Twenty-four grams (0.130 mole) of finely ground 4,5-dicyano-1,3-dithiole-2-thione was stirred at room temperature in 160 ml. of concentrated HCl for 4 to 5 days. Dilution, filtration, and washing gave 27.0 g. (94%) of bright yellow product, dec. *ca*. 230°. (Mayer and Gebhardt[8] report dec. 236°.)

1,3-Dithiole-2-thione-4,5-dicarboxylic Acid (**V**).—A mixture of 7.5 g. (0.034 mole) of 1,3-dithiole-2-thione-4,5-dicarboxamide, 50 ml. of concentrated HCl, and 40 ml. of water was stirred and refluxed for 4 hr. in a 1-l. flask. The large flask was desirable because foaming sometimes occurred. During the last half-hour a clear solution was present, which gave a mass of orange crystals on cooling. These were filtered and dried without washing, because of water solubility; yield 7.2 g. (95%). It crystallized as a bright yellow solid from chlorobenzene and as a yellow-brown solid from nitromethane. The melting point of about 160° dec. was somewhat dependent on the rate of heating. A sample was crystallized from toluene for analysis, m.p. 151–153° dec.

Anal. Calcd. for $C_5H_2O_4S_3$: C, 27.0; H, 0.9; S, 43.2. Found: C, 27.0; H, 1.5; S, 43.7.

Mayer and Gebhardt[8] obtained a somewhat lower yield using 20% H_2SO_4, which is evidently more destructive.

1,3-Dithiole-2-thione-4-carboxylic Acid (**VII**).—1,3-Dithiole-2-thione-4,5-dicarboxylic acid (V, 0.85 g., 3.8 mmoles) was heated for 10 min. in an oil bath at 165°, effervescing and fusing to a black liquid. Cooling and grinding gave 0.62 g. (91%) of yellow solid, m.p. 193–195° dec., soluble in sodium bicarbonate solution and reprecipitated by HCl. Crystallization from toluene raised the m.p. to 201–205°.

Anal. Calcd. for $C_4H_2O_2S_3$: C, 27.0; H, 1.1; S, 53.9. Found: C, 27.3; H, 1.1; S, 54.1.

2-Methylthio-1,3-dithiolium Iodide[13] (**VI**).—Methyl iodide (50 ml.) was carefully added to a solution of 11.1 g. (0.0500 mole) of 1,3-dithiole-2-thione-4,5-dicarboxylic acid in 60 ml. of warm nitromethane. Stirring and refluxing for 8 hr. followed by filtration gave 13.8 g. (100%) of yellow-brown solid, dec. 116–121°. A specimen formed stubby yellow needles, m.p. 120–121° dec., on quick crystallization from a small volume of nitromethane.

Anal. Calcd. for $C_4H_5IS_3$: C, 17.4; H, 1.8; I, 46.0; S, 34.8. Found: C, 17.5; H, 2.0; I, 45.8; S, 34.6.

1,3-Dithiole-2-thione[8] (**VIII**).—Ten grams (0.036 mole) of VI and 6.0 ml. (5.9 g.; 0.075 mole) of pyridine were stirred at reflux for 2 hr. in 150 ml. of benzene, filtered, and evaporated. The residue was dried on a porous plate, yielding 3.35 g. (69%) of yellow-brown solid with a characteristic pungent odor, m.p. 43–46°. Soxhlet extraction with petroleum ether gave a 70% recovery of bright yellow light-sensitive needles, m.p. 50–51°.

Anal. Calcd. for $C_3H_2S_2$: C, 26.9; H, 1.5. Found: C, 27.1; H, 1.5.

1,3-Dithiolium Hydrogen Sulfate (**IXa**).—A solution of 2.00 g. (0.015 mole) of 1,3-dithiole-2-thione in 15 ml. of acetone was stirred in an ice bath and treated during 0.5 hr. with a solution of 9.0 g. (0.047 mole) of 40% peracetic acid in 10 ml. of acetone. Stirring was continued 10 min. longer and the product then filtered and washed with very cold acetone; yield 2.45 g. (82%) of pale yellow water-soluble solid, m.p. *ca*. 125° dec. Without purification it was analyzed.

Anal. Calcd. for $C_3H_4O_4S_3$: C, 18.0; H, 2.0; S, 48.0. Found: C, 18.5; H, 2.3; S, 47.8.

The bright yellow water-soluble light-sensitive iodide IXb was prepared in propyl alcohol and crystallized from acetic acid; m.p. 134–135° dec.

Anal. Calcd. for $C_3H_3IS_2$: C, 15.7; H, 1.3; I, 55.2; S, 27.9. Found: C, 15.9; H, 1.3; I, 55.2; S, 28.1.

The perchlorate exploded at about 250° in the capillary m.p. apparatus. The picrate IXc was prepared from the sulfate in water solution and crystallized from acetonitrile; m.p. 113–115°.

Anal. Calcd. for $C_9H_5N_3O_7S_2$: C, 32.6; H, 1.5; N, 12.7; S, 19.4. Found: C, 32.4; H, 1.6; N, 12.7; S, 19.4.

2-(*p*-Dimethylaminophenyl)-1,3-dithiolium Iodide (**X**).—A mixture of 0.50 g. (0.18 mmole) of 2-methylthio-1,3-dithiolium iodide and 0.50 ml. (0.50 g., 0.42 mmole) of dimethylaniline in 6.0 ml. of acetic acid was heated to boiling and then warmed on a steam bath for 3 hr. After cooling, the deep purple product was filtered and washed with 2–3 drops of acetic acid; yield 0.45 g. (71%), dec. 196–199°. After crystallization from acetic acid or isobutyl alcohol, it decomposed at about 215°; λ_{max} (alcohol) 515 mμ (ϵ 59,000).

Anal. Calcd. for $C_{11}H_{12}INS_2$: C, 37.8; H, 3.4; I, 36.4; N, 4.0; S, 18.3. Found: C, 37.4; H, 3.7; I, 35.6; N, 4.2; S, 18.1.

The same product is obtained under similar conditions from 1,3-dithiolium iodide and dimethylaniline.

4,5-Dicyano-1,3-dithiol-2-on (**XIa**).—During a period of 15 min., a solution of 4.5 g. (0.080 mole) of phosgene in 16 ml. of acetonitrile was added to a suspension of 14.8 g. (0.080 mole) of disodium dimercaptomaleonitrile stirred at 0–5° in 100 ml. of acetonitrile. The mixture was stirred 20 min. longer at 0–5° and then for 2 hr. at room temperature. Filtration of sodium chloride, followed by evaporation to dryness at room temperature and crystallization from carbon tetrachloride, gave a 50% yield of buff product, m.p. 122–124°. A specimen crystallized from methylcyclohexane melted at 123–124°.

Anal. Calcd. for $C_5ON_2S_2$: C, 35.7; N, 16.7; S, 38.1. Found: C, 35.8; N, 16.8; S, 38.4.

Hydrolysis to the dicarboxamide XIIa, dec. 188°, is reported by Mayer and Gebhardt.[8] Our product melted at 217–218° after crystallization from water or dioxane.

Anal. Calcd. for $C_5H_4N_2O_3S_2$: C, 29.4; H, 2.0; N, 13.7; S, 31.4. Found: C, 29.5; H, 2.2; N, 13.7; S, 31.2

Bis(methylthio)maleic Acid (**XIV**) **and Anhydride XV**.—1,3-Dithiol-2-one-4,5-dicarboxamide (XIIa, 2.04 g., 0.0100 mole) was dissolved in 25 ml. of water containing 1.6 g. (0.04 mole) of sodium hydroxide. The red color of the solution changed to yellow-orange on treatment with excess dimethyl sulfate (3–4 ml.). Acidification, ether extraction, and evaporation of the ether gave a yellow solid that was digested with hot petroleum ether. The insoluble portion (17% yield) was XIV, a water-soluble solid, m.p. 122–123°.

Anal. Calcd. for $C_6H_8O_4S_2$: C, 34.6; H, 3.9; S, 30.9. Found: C, 34.7; H, 3.9; S, 30.4.

The anhydride XV crystallized as lemon-yellow needles (58% yield) from petroleum ether; m.p. 35–36°.

Anal. Calcd. for $C_6H_6O_3S_2$: C, 37.9; H, 3.2; S, 33.7. Found: C, 37.8; H, 3.1; S, 33.7. Hot water converts XV to XIV.

1,3-Dithiole-4,5-dicarboxamide (**XIIb**).—Finely ground 4,5-dicyano-1,3-dithiole[8] (3.00 g., 1.95 mmoles) was stirred for 4 days at room temperature in 30 ml. of concentrated HCl. Dilution with 20 g. of ice gave a solution from which the yellow product crystallized and was filtered; yield 2.10 g. (57%), dec. *ca*. 190°. Crystallization from ethanol gave very pale yellow needles, dec. 205–206°.

Anal. Calcd. for $C_5H_6O_2N_2S_2$: C, 31.6; H, 3.2; N, 14.7; S, 33.7. Found: C, 31.7; H, 3.3; N, 14.7; S, 34.1.

4,5-Dicyano-1,3-dithiol-2-oxim (**XIc**).—A solution of 65.0 g. (0.35 mole) of disodium dimercaptomaleonitrile in 1.5 l. of water was stirred vigorously while 38.0 g. (0.33 mole) of freshly distilled phosgene oxime was added (care!). The solution turned red and then deposited an orange-brown solid. After 2 hr. this was filtered, dried, and crystallized from toluene, giving a 50% yield of orange-brown sternutatory crystals, m.p. 156°. A specimen was crystallized twice from benzene for analysis.

Anal. Calcd. for $C_5HON_3S_2$: C, 32.8; H, 0.5; N, 22.9; S, 35.0. Found: C, 32.9; H, 0.5; N, 22.6; S, 35.2.

4,5-Dicyano-1,3-dithiol-2-oxime Carbamate (**XId**).—A solution of 9.0 g. (0.049 mole) of XIc, 6.0 ml. (0.097 mole) of methyl isocyanate, and 12 drops of triethylamine in 250 ml. of anhydrous ether was stirred and refluxed 1 hr. and then filtered. Crystallization from benzene–heptane gave a 59% yield of yellow solid, m.p. 158° dec.

Anal. Calcd. for $C_7H_4O_2N_4S_2$: C, 35.0; H, 1.7; N, 23.3. Found: C, 34.5; H, 1.9; N, 22.6.

Acknowledgment.—The author is indebted to Miss Peggy Hoffman for technical assistance and to John J. Kobliska and his staff for microanalyses.