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Mercaptoethylation. VII. Preparation of Some Cyclic Sulfides

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A comparison of the behavior of ethylene monothiolcarbonate (I), ethyl 2-hydroxyethylthiolcarbonate (II), ethyl 2-mercaptoethylcarbonate (III), and 2-mercaptoethyl phenylcarbamate (IV) under pyrolytic conditions has been made. It was found that I is a convenient source of pure ethylene sulfide, and II is a more convenient source when the presence of ethanol is not undesirable. Procedures for preparing hydroxymethylethylene sulfide and trimethylene sulfide are discussed.

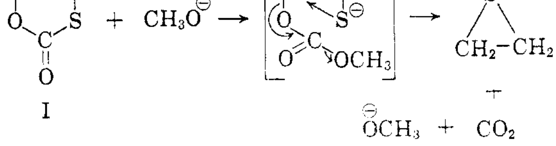
Investigations of four reagents as mercaptoethylating agents have recently been made based upon the tendencies of these reagents to liberate ethylene sulfide under the proper experimental conditions. They are ethylene monothiolcarbonate (I),[1] ethyl 2-hydroxyethylthiolcarbonate (II),[2] ethyl 2-mercaptoethylcarbonate (III),[3] and 2-mercaptoethyl phenylcarbamate (IV)[4] (see Table I). With the exception of I, no attempt was made to isolate the ethylene sulfide derived from these compounds, as it was generated *in situ* in the presence of nucleophiles, thus leading to mercaptoethylated products to the exclusion of the ethylene sulfide.

In an earlier investigation by one of the authors,[5] I was shown to undergo readily a base-catalyzed pyrolytic decomposition to ethylene sulfide and carbon dioxide in 75–85% yields. Since this reaction represents a convenient synthesis of pure ethylene sulfide, it was thought of interest to compare the pyrolytic behaviors of I–IV with respect to their relative thermal stabilities and to the nature and yields of their major decomposition products.

The thermal decompositions of I–IV were effected by heating these compounds, usually in the presence of base catalyst, at atmospheric pressure in a distillation apparatus. The ethylene sulfide, as well as other low-boiling decomposition products, was distilled and trapped out in Dry Ice–acetone-cooled receivers; usually, only polyethylene sulfide was left as pot residue. The results of these experiments are recorded in Table I.

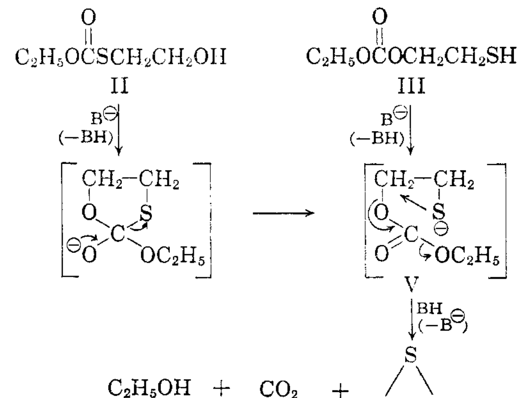
The pyrolysis of I gave ethylene sulfide of high purity, thus allowing the yields to be ascertained by direct weight. An indirect evaluation, however, was necessary with II and III, as the distillate was a mixture of difficultly separable ethylene sulfide and ethanol. In these instances, as with the pyrolyzate of IV, the yields of ethylene sulfide were determined by their quantitative polymerization to the easily isolable polyethylene sulfide.[6] The pyrolysis temperatures recorded in Table I represent the temperatures of the starting materials taken at the point at which condensate was initially observed on the cold finger of the stillhead.

Ethylene monothiolcarbonate (I), which is stable at its atmospheric boiling point—*i.e.*, 237°—both in the absence of catalyst and in the presence of *p*-toluenesulfonic acid, is readily decomposed to ethylene sulfide and carbon dioxide by heating in the presence of sodium methoxide. The reaction mechanism proposed for this decomposition is shown in Equation 1. Increased amounts of base catalyst increase the rate of reaction as evidenced by lower pyrolysis temperatures, but also decrease the yields of isolable ethylene sulfide due to polymerization effected by the additional base.



(1)

The decompositions of II and III are thought to occur by reaction paths involving a common intermediate (V, Equation 2) of the same general structure as that proposed in Equation 1 for the decomposition of I.



(2)

The notable feature of the pyrolysis of 2-mercap-

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(1) D. D. Reynolds, M. K. Massad, D. L. Fields, and D. L. Johnson, *J. Org. Chem.*, **26**, 5109 (1961), Part I of this series.

(2) D. D. Reynolds, D. L. Fields, and D. L. Johnson, *J. Org. Chem.*, **26**, 5119 (1961), Part IV of this series.

(3) D. D. Reynolds, D. L. Fields, and D. L. Johnson, *J. Org. Chem.*, **26**, 5125 (1961), Part VI of this series.

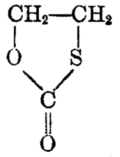
(4) D. D. Reynolds, D. L. Fields, and D. L. Johnson, *J. Org. Chem.*, **26**, 5116 (1961), Part III of this series.

(5) D. D. Reynolds, *J. Am. Chem. Soc.*, **79**, 4951 (1957).

(6) G. I. Braz, *Zhur. Obshcheĭ Khim. S.S.S.R.*, **21**, 688 (1951).

TABLE I

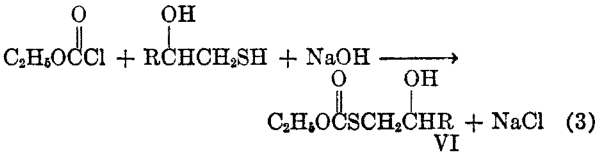
PYROLYSIS DATA

No.	Compound[a]	Mg./Mole $NaOCH_3$	Pyrolysis Temp.	% Yield of Ethylene Sulfide by: Polymerization to polyethylene sulfide	% Yield of Ethylene Sulfide by: Direct weight	Major Isolated By-products
I		0	—[b]	—	0	0
		1.0	189	—	79	0
		20.0	140	—	70	0
II	$C_2H_5OCOSCH_2CH_2OH$	0	224	81	—	C_2H_5OH
		1.0	214	75	—	C_2H_5OH
		20.0	115	67	—	C_2H_5OH
III	$C_2H_5OCO_2CH_2CH_2SH$	0	—[c]	0	—	0
		20.0	153	89	—	C_2H_5OH
IV	$C_6H_5NHCO_2CH_2CH_2SH$	50.0	202	34	—	$(C_6H_5NH)_2CO$, $HOCH_2CH_2SH$

[a] Starting with 1.0 mole of I, II, and III and 0.4 mole of IV. [b] No decomposition. Starting material refluxed at 237°. [c] No decomposition. Starting material refluxed at 203°.

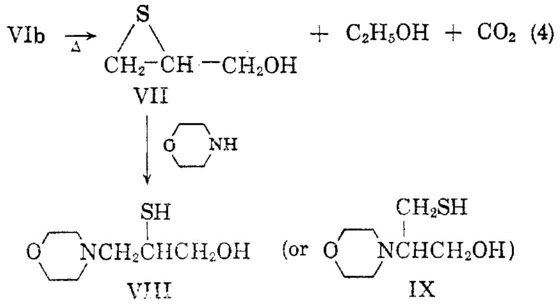
toethyl phenylcarbamate (IV) is its relative stability to base compared to I, II, and III. The single experiment conducted with 0.4 mole of IV in the presence of 20 mg. of sodium methoxide resulted in its very slow degradation at 202° to phenyl isocyanate and 2-mercaptoethanol as well as the expected ethylene sulfide, aniline, and carbon dioxide. The formation of aniline and phenyl isocyanate was substantiated by the isolation of 1,3-diphenylurea from the pot residue. Polyethylene sulfide was obtained by polymerization of the ethylene sulfide in the distillate. Examples of the degradation of carbamates to isocyanates and alcohols, as well as to other products at temperatures above 200°, are well documented in the literature.[7]

An aspect of value in the synthesis of episulfides becomes apparent upon consideration of the ease and smoothness of the noncatalyzed degradation of II to an 80% yield of ethanolic ethylene sulfide. Such a preparation, being derived from an easily obtained and relatively inexpensive precursor[2] (see Equation 3, R = H), is probably the most convenient source of preformed ethylene sulfide for use in mercaptoethylation reactions that are not affected by the presence of ethanol.



$$C_2H_5O\overset{O}{\overset{\|}{C}}Cl + R\overset{OH}{\overset{|}{C}}HCH_2SH + NaOH \longrightarrow \underset{VI}{C_2H_5O\overset{O}{\overset{\|}{C}}SCH_2\overset{OH}{\overset{|}{C}}HR} + NaCl \qquad (3)$$

VIa. R = H
VIb. R = CH_2OH



The generality of the pyrolysis of ethyl 2-hydroxyalkylthiolcarbonates was examined in one other instance, starting with commercially available monothiolglycerol. The corresponding thiolcarbonate (VIb) was prepared according to Equation 3, and pyrolyzed under reduced pressure to hydroxymethylethylene sulfide (VII), ethanol and carbon dioxide (Equation 4). One redistillation yielded the clear, slightly viscous episulfide, which was characterized by elemental analysis and by reaction with morpholine to yield either VIII or IX, the former being more likely based on the results obtained by Davies and Savige in their study on the direction of ring opening of unsymmetrical ethylene sulfides.[8] Hydroxymethylethylene sulfide has previously been reported in a German patent[9] as obtainable by the reaction of thiourea or potassium thiocyanate with glycidol. Culvenor and coworkers,[10] however, refute this claim and state that only polymeric material results from this reaction. From our own experience with this easily polymerizable episulfide, we also feel that the patent

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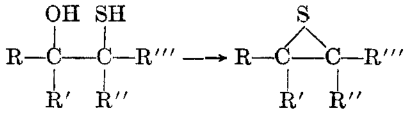
(7) M. Métayer, *Bull. soc. chim. de France*, p. 802 (1951). Elizabeth Dryer and G. E. Newborn, Jr., *J. Am. Chem. Soc.*, **80**, 5495 (1958).

(8) W. Davies and W. E. Savige, *J. Org. Chem.*, **16**, 774 (1951).

(9) K. Dachlauer and L. Jackel, Ger. Patent **636,709** (1936).

(10) C. C. J. Culvenor, W. Davies, and K. H. Pausacker, *J. Chem. Soc.*, 1050 (1946).

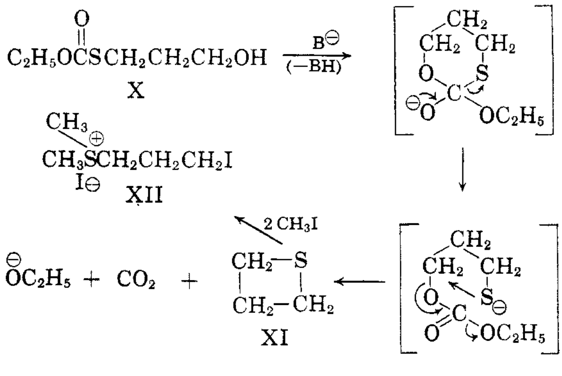
claim is questionable. It therefore appears that this synthesis may provide a general method of converting 1,2-mercaptoalcohols into the corresponding episulfide (Equation 5), and it may be particularly



(5)

useful in affording episulfides of a more sensitive nature that cannot be prepared by the more common procedures.

An extension of this synthesis to the preparation of 4-membered cyclic sulfides was attempted by the pyrolysis of ethyl 3-hydroxypropylthiolcarbonate (X) as depicted in Equation 6. An ethanolic solution of trimethylene sulfide (XI) was obtained and characterized by conversion to the sulfonium iodide (XII),[11] but only under much more drastic conditions employing base catalyst. The ease of formation of a three- compared to a four-membered cyclic sulfide ring is not unexpected, having analogies in the greater ease of preparation of ethylene sulfide compared to trimethylene sulfide through the reaction of potassium thiocyanate with the cyclic carbonates of 1,2- and 1,3-diols,[12] as well as other examples recorded in the literature.



(6)

EXPERIMENTAL

Compounds I–IV, Table I, were prepared by previously described procedures and had the following physical constants: ethylene monothiolcarbonate (I),[1] b.p. 75°/10 mm., n_D^{25} 1.5104; ethyl 2-hydroxyethylthiolcarbonate (II),[2] b.p. 110°/7 mm., n_D^{25} 1.4782; ethyl 2-mercaptoethylcarbonate (III),[3] b.p. 84°/9 mm., n_D^{25} 1.4522; 2-mercaptoethyl phenylcarbamate (IV),[4] m.p. 61–62°.

General pyrolysis procedure for I–IV. One mole of reagent and anhydrous sodium methoxide catalyst, if used, was placed in a round bottomed flask equipped with a thermometer and a 14-in. Vigreux column topped by a variable-rate, take-off stillhead. With agitation supplied by a magnetic stirrer, the mixture was heated above the decomposition point of the starting material, and the product was collected in a Dry Ice–acetone-cooled receiver.

The pyrolysis of I afforded pure ethylene sulfide, n_D^{25} 1.4902 ± 0.0002 (lit.[5] n_D^{25} 1.4898), as a distillate in yields tabulated in Table I. The yields of ethylene sulfide obtained from II, III, and IV were determined by conversion to polyethylene sulfide by diluting the distillates with 100 ml. of a 1:1 water-ethanol mixture, followed by treatment with three drops of concentrated ammonium hydroxide. After standing at room temperature for 1 week, the solid polyethylene sulfide was filtered, and then dried over calcium chloride. The yields were also estimated in several instances by reaction of the ethanolic ethylenesulfide from identical experiments with one mole of piperidine in 300 ml. of refluxing benzene, followed by distillation. The yields of 2-piperidinoethanethiol were found to be in good agreement with those obtained by the polyethylene sulfide technique.

The pot residue from the pyrolysis of IV crystallized upon cooling and was recrystallized twice from ethanol, to give 17.5 g. of 1,3-diphenylurea, m.p. 240–242° (lit.[13] m.p. 238–239°), as proved by mixed melting points and by a comparison of the infrared spectra with an authentic sample.

Hydroxymethylethylene sulfide (VII). Thiolcarbonate VIb was synthesized following a previously described general procedure,[2] by adding, over a 20-min. period, a mercaptide solution prepared from monothiolglycerol[14] (540 g., 5.0 moles), sodium hydroxide pellets (200 g., 5.0 moles), and 1 l. of water to a very efficiently agitated solution of ethyl chloroformate (567 g., 5.2 moles) in 1 l. of toluene. The reaction temperature was held between 10–15° during this addition. After an additional 10 min. of agitation, the organic layer was separated, dried over magnesium sulfate, and filtered. The filtrate was concentrated, initially at water-pump vacuum and then at vacuum-pump pressure to remove materials boiling below 100°/5 mm. After some residual sodium chloride had been filtered, 776 g. of clear, viscous thiolcarbonate VIb was obtained.

Without further purification, VIb (77 g., 0.4 mole) was placed in a distillation apparatus equipped with a 3-in. Vigreux column leading to a receiver submerged in a Dry-Ice–acetone bath, and was heated by an oil bath under reduced pressure of a vacuum pump. The decomposition began at 128°/0.04 mm. and was accompanied by a loss of vacuum due to the evolution of carbon dioxide. A total of 48.7 g. of distillate was collected over a boiling-point range of 52–69°/2.2–3.2 mm., leaving 8.2 g. of polymeric residue.

One redistillation of the distillate through a 14-in. Vigreux column gave 27.7 g. (77%) of hydroxymethylethylene sulfide, b.p. 45–49°/1.0 mm., n_D^{25} 1.5201.

Anal. Calcd. for C_3H_6OS: C, 40.0; H, 6.7. Found: C, 39.5; H, 6.8.

A portion (23.3 g., 0.26 mole) of the episulfide was added to a refluxing mixture of morpholine (87 g., 1.0 mole) and toluene (250 ml.) and the mixture refluxed for 21 hr. Distillation yielded 28.3 g. (62%) of VIII or IX, b.p. 106–107°/0.04 mm., n_D^{25} 1.5183, with a purity of 98.8% as determined by iodometric titration.

Anal. Calcd. for $C_7H_{15}NO_2S$: C, 47.5; H, 8.5; N, 7.9. Found: C, 47.7; H, 8.6; N, 7.6.

It should be mentioned that there was often a considerable variation in the yields of hydroxymethylethylene sulfide obtained from run to run, especially when different lots of starting monothiolglycerol were employed. This may be attributed to the presence of an impurity in some of the starting monothiolglycerol (assay — 90–93% pure) which promoted the polymerization of the episulfide prior to its isolation.

Trimethylene sulfide (XI). Ethyl 3-hydroxypropylthiolcarbonate (X), b.p. 85°/0.05 mm., n_D^{25} 1.4780 was prepared

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[11] G. M. Bennett and A. L. Hock, *J. Chem. Soc.*, 2496 (1927).

[12] S. Searles and E. Lutz, *J. Am. Chem. Soc.*, **80**, 3168 (1958).

[13] W. J. Hickinbottom, *Chemistry of Carbon Compounds*, Vol. 3A, E. H. Rodd, ed., Elsevier, Amsterdam, Holland (1954), p. 192.

[14] Purchased from Evans Chemetics, Inc., Waterloo, N. Y., and sold under the trade name of "Thiovanol."

in 80% yield from ethyl chloroformate and sodium 3-hydroxypropyl mercaptide following a previously described general procedure.[3]

Anal. Calcd. for $C_6H_{12}O_3S$: C, 43.9; H, 7.3. Found: C, 43.6; H, 7.4.

Thiolcarbonate X (60.6 g., 0.37 mole), which was only slowly decomposed at 224° in the presence of 0.1 g. of sodium carbonate, was smoothly pyrolyzed at 192–204°/13 mm. in the presence of one pellet of sodium hydroxide. The resulting distillate (25 g.) had a boiling point of 72–75° upon redistillation. Seventeen grams of this mixture, when placed in 40 ml. of methyl iodide and allowed to stand overnight at room temperature, gave 24.2 g. of the sulfonium iodide (XII) as white needles, with a m.p. 97–98° (lit.[11] m.p. 97–98°).

ROCHESTER, N. Y.

[CONTRIBUTION FROM THE CHEMICAL RESEARCH DEPARTMENT, CENTRAL RESEARCH DIVISION, AMERICAN CYANAMID CO.]

The Preparation of Dithiophosphinates from Secondary Phosphines and Sulfur under Alkaline Conditions

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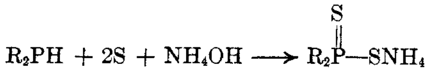
An improved synthesis for the preparation of dialkyldithiophosphinate salts is described. Dialkylphosphines react with sulfur in dilute aqueous ammonium hydroxide or sodium hydroxide to give dialkyldithiophosphinate salts in 25 to 91% yields. A number of new ammonium and nickel dithiophosphinates are reported. Dicyclohexylphosphine sulfide was isolated as an intermediate in the reaction of dicyclohexylphosphine with sulfur.

Although the reaction of sulfur with dialkylphosphines has been known for ninety years,[1] the processes involved are not well understood. The initial product obtained from diethylphosphine in ether solution has been reported to be a polysulfide, $R_2\overset{S}{\overset{\|}{P}}SS\overset{S}{\overset{\|}{P}}R_2$,[2] or a dithiophosphinic anhydride, $R_2\overset{S}{\overset{\|}{P}}—S—\overset{S}{\overset{\|}{P}}R_2$,[3] which on treatment with ammonium sulfide gives the ammonium dithiophosphinate, $R_2\overset{S}{\overset{\|}{P}}SNH_4$. The over-all yields reported for the dithiophosphinates have been low.[3,4]

We have found that the preparation of dithiophosphinate salts is simplified, and that the yields are considerably improved by treating a secondary phosphine with two equivalents of sulfur in dilute ammonium hydroxide solution.

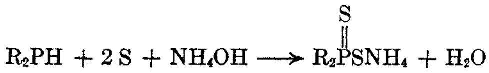


$$R_2PH + 2S + NH_4OH \longrightarrow R_2\overset{S}{\overset{\|}{P}}—SNH_4$$

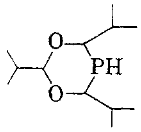
The ammonium salts were obtained by evaporation of the reaction mixture or, less effectively, by extraction with ether. The results are shown in Table I. The ammonium salts of di-*n*-octyldithiophosphinic acid and di-*n*-dodecyldithiophosphinic acid were difficult to crystallize, and products from these reactions were characterized directly as the nickel salts.

Dicyclohexyldithiophosphinic acid and 2,4,6-triisopropyl-1,3-dioxa-5-phosphacyclohexane-5-dithioic acid were conveniently obtained as solids by acidifying solutions of the ammonium salts. The other dithiophosphinic acids, however, separated as oils which did not crystallize.

TABLE I



$$R_2PH + 2\,S + NH_4OH \longrightarrow R_2\overset{S}{\overset{\|}{P}}SNH_4 + H_2O$$

R	Temp.	Time, Min.	Yield, %
n-C_4H_9	25–27	100	91[a]
n-C_8H_{17}	45–50	45	25[b]
n-$C_{12}H_{25}$	60	20	68[b]
C_6H_{11}	60	60	90[c]
$C_6H_5CH_2CH_2$	25–30	180	55[d]
	85	60	85[a]

[a] Ammonium salt. [b] Product isolated as the nickel salt. [c] Product isolated as the free acid. [d] A 26% yield of the ammonium salt was isolated directly. An additional 29% yield was obtained as the nickel salt.

The sodium salt of 2,4,6-triisopropyl-1,3-dioxa-5-phosphacyclohexane-5-dithioic acid was prepared by the reaction of 2,4,6-triisopropyl-1,3-dioxa-5-phosphacyclohexane[5] with two equivalents of sulfur in dilute sodium hydroxide solution. The yield, however, was only 46% compared to the 85% yield of the ammonium salt obtained from the reaction in ammonium hydroxide solution.

In the reaction of dicyclohexylphosphine with sulfur, a dense white solid separated soon after the start of the reaction. This solid was evidently

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(1) A. W. Hofmann, *Ber.*, 4, 430 (1871).

(2) A. W. Hofmann and F. Mahla, *Ber.*, 25, 2436 (1892).

(3) L. Malatesta, *Gazz. Chim. Ital.*, 77, 518 (1947).

(4) L. Malatesta, *Gazz. Chim. Ital.*, 77, 509 (1947).

(5) S. A. Buckler and V. P. Wystrach, *J. Am. Chem. Soc.*, 80, 6454 (1958).