[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, UNION CARBIDE CHEMICALS CO.]

# Synthesis of Ethylene and Propylene Sulfides

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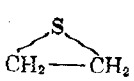
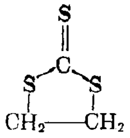
The reaction of carbonyl sulfide with three alkylene oxides has been studied. Ethylene oxide reacted with carbonyl sulfide at 150° under pressure in the presence of trimethylamine catalyst to form a copolymer of ethylene thiocarbonate and ethylene sulfide. Monomeric ethylene sulfide was produced in 40% yield when ethylene oxide and carbonyl sulfide were passed over a lithium phosphate catalyst at 200–220° at atmospheric pressure. This is apparently the first reported synthesis of an episulfide by direct reaction of an alkylene oxide with carbonyl sulfide. Monomeric propylene sulfide was prepared in 23% yield from propylene oxide in an analogous reaction. However, only trace amounts of cyclohexene sulfide were produced from cyclohexene oxide under the conditions studied.

In a previous paper concerned with attempts to prepare ethylene sulfide (I), the reaction between carbon disulfide and ethylene oxide to yield ethylene trithiocarbonate (II) was described.[1] In a further extension of this investigation, the reaction of carbonyl sulfide with ethylene oxide has now been studied. By analogy to the previous work,[1] the supposition was made that carbonyl sulfide would yield ethylene thiocarbonate (III) or ethylene dithiolcarbonate (IV) which could then be pyrolyzed to ethylene sulfide after the method of Reynolds.[2] The latter procedure involves the preparation of III by reaction of phosgene and 2-mercaptoethanol followed by pyrolysis of this ester over solid sodium carbonate to form ethylene sulfide (and carbon dioxide) in excellent yields.


I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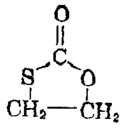
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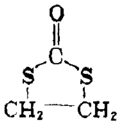
IV

TABLE I

REACTION OF ETHYLENE OXIDE WITH CARBONYL SULFIDE IN HOT TUBE

| Catalyst | Temp. | Nitrogen, Ml./Min. | Moles COS/Min. Moles Oxide/Min. | Reaction Time, Min. | Yield Episulfide, % | Productivity G/L Cat./Hr. |
|---|---|---|---|---|---|---|
| 5 mm. glass beads | 200 | 9.45 | 3 | 65 | Uncertain | — |
| 5 mm. glass beads | 300 | 2.6 | 1.6 | 85 | Uncertain | — |
| 5 mm. glass beads | 385 | 4.5 | 2 | 65 | Uncertain | — |
| Pumice[a] | 200 | 6.1 | 2 | 78 | 0 | 0 |
| Pumice[a] | 300 | 2.6 | 2.1 | 85 | 0 | 0 |
| Pumice[a] | 380 | Slight | 2.4 | 60 | 0 | 0 |
| Iron Pyrites[b] | 200 | 4.5 | 2.8 | 95 | Trace | — |
| Iron Pyrites[b] | 300 | 4.5 | 3 | 45 | Trace | — |
| Iron Pyrites[b] | 380 | 4.5 | 2.9 | 60 | Uncertain | — |
| $K_2CO_3$/SiC[c] | 200 | 4.5 | 2.5 | 120 | 3.6 | Small |
| $K_2CO_3$/SiC[c] | 300 | None | 2.5 | 60 | Trace | Small |
| $K_2SO_3$/SiC[e] | 380 | None | 2.5 | 60 | 3 | Small |
| $Li_3PO_4$[d] | 200 | None | 2.5 | 50 | 40 | 14 |
| $Li_3PO_4$[d] | 300 | None | 2.5 | 60 | 10 | 2.5 |
| $Li_3PO_4$[d] | 100 | None | 2.5 | 85 | 3 | Small |
| $Li_3PO_4$[d] | 380 | None | 2.5 | 60 | Trace | Small |
| $Li_3PO_4$[d,e] | 200–220 | None | 2 | 60 | 10 | 28.2 |

[a] 4 × 5 mm. lumps. [b] Baker Chemical Co., range in size from 3 × 4 mm. to 6 × 7 mm. [c] Carborundum Co., 60% porosity. [d] Harshaw Chemical Co., extruded $^3/_{16}''$ pellet. [e] Catalyst had been heated to 400° and burned off with air.

In the present case when carbonyl sulfide and ethylene oxide were heated at 150° in a stainless steel bomb in the presence of trimethylamine catalyst under added nitrogen (500 p.s.i.g. at 0°) a gummy, solid product was obtained. A portion of this product was found to be soluble in ethyl acetate and the material was separable into two fractions on this basis. Based on elemental analysis and infrared studies, each fraction was identified as a copolymer of ethylene sulfide and ethylene thiocarbonate containing about two of the former for each one of the latter. Presumably these two fractions differ only in molecular weight.

Since the synthesis of monomeric ethylene sulfide by this procedure was not promising, the re-

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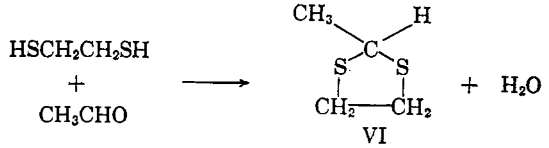
[1] J. A. Durden, H. A. Stansbury, Jr., and W. H. Catlette, *J. Am. Chem. Soc.*, in press.

[2] D. D. Reynolds, *J. Am. Chem. Soc.*, **79**, 4951 (1957).

action of carbonyl sulfide and ethylene oxide in a vapor phase over various potential catalysts at elevated temperatures was investigated. The desired mixture of carbonyl sulfide and ethylene oxide diluted with nitrogen was passed downward through a heated tube packed with the catalyst to be studied. The effluent from the bottom of the tube (collected in a cold trap) was analyzed by means of mass spectrometry, vapor phase chromatography, and infrared spectroscopy. Table I summarizes the results of these experiments.

Iron pyrites, glass beads, and pumice gave no measurable amounts of ethylene sulfide at 200°, 300° or 380°. Over pumice the only products were acetaldehyde (from rearrangement of ethylene oxide,[3] identified as the 2,4-dinitrophenylhydrazone) and low molecular weight poly(ethylene oxide), a colorless, odorless, water-soluble liquid. These results are not surprising since it was shown previously that the reaction of carbon disulfide with ethylene oxide was inhibited by acidic materials.[1]

The use of silicon carbide (60% porosity) impregnated with potassium carbonate enhanced the vapor phase reaction considerably. At 200° ethylene sulfide was formed in 4% yield. Fair yields were also obtained at 300° and 380°, but at 300° a small amount of material tentatively identified as 2-methyl-1,3-dithiolane (VI) was detected together with the desired product. It is known that 2-hydroxymethyl-1,2-dioxolane is formed when ethylene glycol is passed over a dehydrogenation catalyst at elevated temperatures.[4] Compound VI may be produced in a similar manner by the reaction of 1,2-ethanedithiol with acetaldehyde.



VI

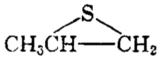
The ethanedithiol can arise by hydrolysis of ethylene dithiol carbonate (IV) (from carbonyl sulfide and ethylene sulfide).

A recent patent[5] has indicated that episulfides upon being heated with acidic catalysts are dimerized to 1,4-dithiane derivatives. The process was exemplified by propylene sulfide which gave 2,5-dimethyl-1,4-dithiane. Comparison of mass spectral properties of 1,4-dithiane with the compound tentatively identified as VI indicated that they were not the same. The mass spectral properties of VI are consistent with proposed structure.

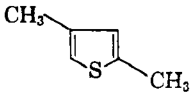
Finally, over lithium phosphate catalyst at 100° the reaction products were ethylene sulfide (3% yield) along with a trace of the dithiolane (VI). (Table I) At 200° the yield of episulfide was raised to 40% and the by-products were acetaldehyde and a trace of carbon disulfide. A complex mixture of at least seven products was obtained at 300°. Ethylene sulfide (I) was shown to be the main product while the material tentatively identified as 2-methyl-1,3-dithiolane (VI) was the next most abundant product along with small amounts of carbon disulfide and acetaldehyde. There was also present small amounts of thiophene which was identified by the means of the mass spectrometer. The mechanism of its formation is being investigated.

Using lithium phosphate as the catalyst, the reaction was extended to homologs of ethylene oxide. The experimental results are summarized in Table II.

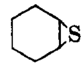
At 300° propylene oxide and carbonyl sulfide reacted to give a 23% yield of propylene sulfide (VII). At 380° the yield of VII was greatly decreased and there was formed a small amount of a dimethyl thiophene which was identified by mass spectrometric analyses. This has been tentatively designated as the 2,4-isomer (VIII).[6]



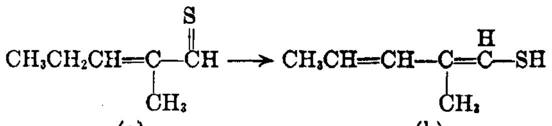
VII



VIII



IX

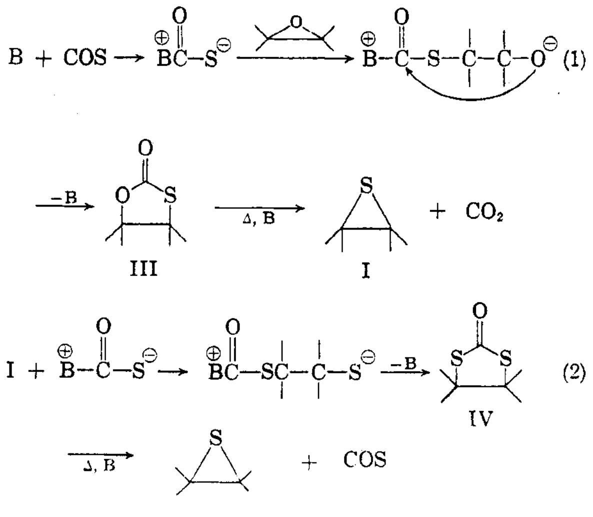


$$CH_3CH_2CH{=}\underset{CH_3}{C}{-}\overset{\overset{S}{\|}}{C}H \longrightarrow CH_3CH{=}CH{-}\underset{CH_3}{C}{=}\overset{H}{C}{-}SH$$

(a) (b)

At 200° cyclohexene oxide did not react to give detectable amounts of cyclohexene sulfide (IX); but at 300° and 380° small amounts of this sulfide were formed in the complex reaction mixtures.

On the basis of this work it appears that the reaction is base-catalyzed and the mechanism may be generalized as follows:



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[3] W. Ipatieff and W. Leontawitsch, *Ber.*, 36, 2016 (1903).

[4] R. W. McNamee and Charles M. Blair, U. S. Patent 2,140,938 (1938).

[5] N. L. Remcs and W. A. Krewer, U. S. Patent 2,891,072 (1959).

TABLE II

REACTION OF CARBONYL SULFIDE WITH PROPYLENE OXIDE AND CYCLOHEXENE OXIDE OVER LITHIUM PHOSPHATE CATALYST

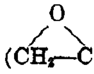
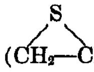
| Oxide Used | Temp. | Moles Oxide Added (Wt., g.) | Rate of Oxide Addition, Ml./Min. | Moles of COS (Wt., g.) | Rate of Addition COS (Ml./Min.) | Wt. of Total Effluent (g.) | Wt. of Residue, G. | Recovered Oxide, Moles | Sulfide Formed, Moles (% Yield) | Total Carbonylic Material, (Moles) | Productivity of Sulfide (g./L. Cat./Hr.) | Reaction Time, Min. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Cyclohexene | 203 | 0.2 (19.6) | 0.39 (liq.) | 0.51 (30.42) | 196 | 43 | 12 | 0.12 | 0 | 0 | 0 | 58 |
| Cyclohexene | 309 | 0.2 (19.6) | 0.40 (liq.) | 0.61 (36.7) | 196 | 36 | 10 | Indeterminate | Indeterminate | Indeterminate | Indeterminate | 70 |
| Cyclohexene | 380 | 0.2 (19.6) | 0.40 (liq.) | 0.61 (36.7) | 196 | 25 | 14 | Indeterminate | Indeterminate | Indeterminate | Indeterminate | 70 |
| Propylene | 200 | 0.2 (11.6) | 0.2 (liq.) | 0.63 (37.9) | 187 | 45 | 7 | 0.108 | 0.001 (1) | 0 | 0.33 | 75 |
| Propylene | 302 | 0.2 (11.6) | 0.33 (liq.) | 0.44 (26.2) | 196 | 34 | 6 | 0.06 | 0.022 (10.8) | 0.014 | 9.65 | 50 |
| Propylene | 304 | 0.2 (11.6) | 0.25 (liq.) | 0.53 (31.5) | 196 | 30 | 6 | 0.046 | 0.0416 (22.8) | 0 | 19.05 | 60 |
| Propylene | 378 | 0.2 (11.6) | 0.25 (liq.) | 0.53 (31.5) | 196 | 34 | 4 | 0.011 | 0.0018 (0.14) | 0.037 | 0.82 | 60 |

## EXPERIMENTAL

*The reaction of carbonyl sulfide and ethylene oxide under pressure.* A cold mixture of 44 g. (1.0 mole) of ethylene oxide, 150 g. (2.5 moles) of carbonyl sulfide and 2 g. of trimethylamine catalyst was charged to a 3-l., stainless steel pressure vessel. After sufficient nitrogen was added to give 500 p.s.i.g. at 0°, the vessel was shaken while it was heated at 150° for 30 min. The vessel was cooled and discharged to obtain 69 g. of crude, gummy solid. The latter was extracted twice with 400-ml. portions of boiling ethyl acetate and filtered. There remained 17 g. of insoluble product which is designated No. 2 in Table III. The hot ethyl acetate filtrates were combined and cooled to 0° to obtain 13 g. of product which is designated No. 1 in Table III. The infrared absorption spectra of No. 1 and No. 2 were nearly identical and showed the presence of carbonyl groups and ether linkages. The properties of No. 1 and No. 2 indicated that each essentially was a copolymer of ethylene sulfide and ethylene thiocarbonate. Elemental analysis indicated that copolymers No. 1 and No. 2 were each about two thirds ethylene sulfide units and about one third ethylene thiolcarbonate units.

TABLE III

REACTION OF CARBONYL SULFIDE AND ETHYLENE OXIDE

| Product | M.P. | %C | %H | %S | %O |
|---|---|---|---|---|---|
| No. 1 | 82–85 | 38.72 | 6.17 | 44.41 | 10.70[a] |
| No. 2 | 135–137 | 38.25 | 6.31 | 45.08 | 10.36[a] |
| [b] | | 54.53 | 9.15 | 0.00 | 36.32 |
| [b] | | 40.00 | 6.70 | 53.50 | 0.00 |
|  $\overset{O}{\overset{\Vert}{—C}}—SCH_2CH_2O—$[b] | | 34.60 | 3.87 | 30.80 | 30.73 |

[a] By difference. [b] Calculated values.

*The hot tube reaction of carbonyl sulfide with alkylene oxides.* The following example is described to illustrate the general procedure involved in the reactions described in Tables I and II.

A one-inch (I. D.) by 16-inch stainless steel, "Dowtherm"-jacketed tube was packed with about 170 ml. of silicon carbide impregnated with potassium carbonate. This catalyst was prepared by soaking silicon carbide (Carborundum Company, 60% porosity) in a 2% aqueous solution of potassium carbonate. The carborundum was then washed with distilled water to pH 8–9 and was dried in a vacuum oven. The catalyst was charged to the tube and heated at 300 to 350° in a stream (4 ml. per min.) of dry nitrogen. After the temperature was reduced to 200° a mixture of ethylene oxide (56.5 ml. per min.) and carbonyl sulfide (158.5 ml./min.) was passed over the catalyst for 2 hr. The effluent from the tube was collected in a Dry Ice–acetone trap. The total effluent weighed 60 g. The gaseous portion was allowed to volatilize at room temperature leaving a residue of 1 g. This sample was submitted for mass spectrometric analysis and found to be 74.3% ethylene sylfide and 25.7% ethylene oxide. The sulfide was formed in 3.6% yield based on ethylene oxide.

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(6) The authors wish to thank the referee for pointing out the following possible route to the thiophene derivative which by mechanistic considerations would be the 2,4-dimethyl isomer. Under pyrolytic conditions the propylene oxide is isomerized to propionaldehyde which subsequently reacts to form 2-methyl-2-pentenethiol (a) which is tautomeric with the enol form (b). This structure then leads to 2,4-dimethylthiophene (VIII), *cf.* [*J. Org. Chem.*, **21**, 39 (1956)].

In the cases where propylene oxide or cyclohexene oxide were used in this procedure, they were added at a controlled rate dropwise at the top of the tube and the reaction was continued until addition was complete.

In the cases where tentatively identified dithiolane or thiophene derivatives were present, the crude reaction product was partitioned through vapor phase chromatography and various portions were analyzed by mass spectrophotometer and infrared spectroscopy. Since authentic samples of the materials were not available the identification is, at the present time, tentative.

*Acknowledgments.* The authors gratefully acknowledge the mass spectrometric analyses performed by Mr. H. R. Harless and the infrared absorption studies conducted by Dr. H. F. White and Mr. C. M. Lovell. They also wish to thank Dr. Harry Wasserman of Yale University for his helpful advice in the preparation of this paper

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE AMERICAN UNIVERSITY OF BEIRUT]

# Unsaturated Bile Acid Derivatives. II. Desulfurizations with Raney Nickel[1]

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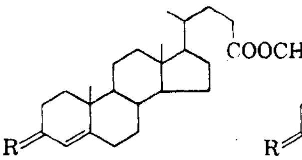
*Received June 15, 1960*

The preparation of methyl $\Delta^4$-cholenate, methyl 3-keto-$\Delta^1$-cholenate, and a compound tentatively regarded as methyl $\Delta^1$-cholenate is described.

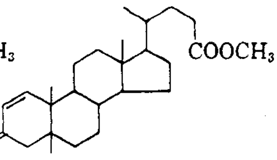
In a previous paper[4] we reported the preparation of methyl 3-keto-$\Delta^4$-cholenate and the epimeric 3-hydroxy-$\Delta^4$-cholenic acids from hyodesoxycholic acid. Extending our work on unsaturated bile acids we would now like to report the preparation of methyl $\Delta^4$-cholenate (Ic), methyl 3-keto-$\Delta^1$-cholenate (IIa) and a compound to which we are assigning tentatively the structure methyl $\Delta^1$-cholenate (IIc).



Ia. R = O

b. R = $\begin{matrix}CH_2-S\diagdown \\ CH_2-S\diagup\end{matrix}$

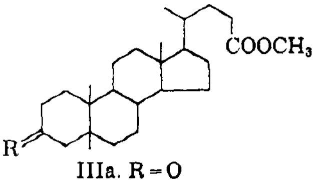
c. R = $H_2$



IIa. R = O

b. R = $\begin{matrix}CH_2-S\diagdown \\ CH_2-S\diagup\end{matrix}$

c. R = $H_2$



IIIa. R = O

b. R = $H_2$

For the preparation of methyl $\Delta^4$-cholenate (Ic), methyl 3-keto-$\Delta^4$-cholenate[4,5] was used as our starting material. Initial attempts to convert Ia to Ib by addition of boron fluoride etherate to an acetic acid solution of the ketone and excess ethanedithiol or by addition of boron fluoride etherate to a solution of the ketone in ethanedithiol[6] led to the formation of oils which solidified only upon prolonged cooling and were difficult to purify. However, crystalline ethylenethioketal (Ib) could be prepared easily and in high yield by treatment of a methanolic solution of the ketone with ethanedithiol and boron fluoride etherate. This procedure gave excellent results also in the preparation of ethylenethioketals from $\Delta^4$-cholestene-3-one and methyl 3-ketocholanate.

The next step in the synthesis was desulfurization with Raney nickel of the ethylenethioketal (Ib) to methyl $\Delta^4$-cholenate. This method, introduced by Hauptmann[7] in the steroid series, has found extensive use in recent years. Desulfurization of unsaturated ethylenethioketals may or may not be accompanied by saturation of the double bond depending on the type of Raney nickel catalyst used and on the position of the double bond in the molecule.[8] In attempting to find out

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[1] Abstracted in part from the M.S. thesis of M.Z.N., American University of Beirut, June 1960.

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[3] To whom requests for reprints should be addressed.

[4] M. J. Haddadin and C. H. Issidorides, *J. Org. Chem.*, 25, 403 (1960).

[5] C. H. Issidorides, M. Fieser, and L. F. Fieser, *J. Am. Chem. Soc.*, **82**, 2002 (1960).

[6] L. F. Fieser, *J. Am. Chem. Soc.*, 76, 1945 (1954).

[7] H. Hauptmann, *J. Am. Chem. Soc.*, 69, 562 (1947).

[8] Some examples reported: (a) $\Delta^4$-cholestene-3-one ethylenethioketal to $\Delta^4$-cholestene, ref. 7; (b) 5-Furosten-3$\beta$-ol acetate 26-ethylenethioketal to 5-furosten-3$\beta$-ol acetate [C. Djerassi, O. Halpern, G. R. Pettit, and G. H. Thomas, *J. Org. Chem.*, **24**, 1 (1959)]; (c) 7,7,10-Trimethyl-$\Delta^{1(9)}$-octal-2-one ethylenethioketal to 7,7,10-trimethyl-$\Delta^{1(9)}$-octalin [F. Sondheimer and S. Wolfe, *Can. J. Chem.*, **37**, 1870 (1959)]; (d) Methyl 12-(ethylenedithio)-3$\alpha$-hydroxy-$\Delta^{9(11)}$-etiocholenate to methyl 3$\alpha$-hydroxy-$\Delta^{9(11)}$-etiocholenate [R. Casanova, C. W. Shoppee, and G. H. R. Summers, *J. Chem. Soc.*, 2983 (1953)]; (e) $\Delta^1$-Cholestene-3-one ethylenethioketal to cholestane [Pl. A. Plattner, A. Fürst, and H. Els, *Helv. Chim. Acta*, **37**, 1399 (1954)]; (f) $\Delta^4$-Cholestene-3,6-dione 3-monoethylenethioketal to cholestane-6-one, ref. 6.