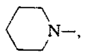
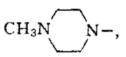


b.p. 99°/14 mm., $n_D^{25}$ 1.4571;



b.p. 116°/15 mm., $n_D^{25}$ 1.4638; n-$C_6H_{13}NH$—, b.p. 129°/14 mm., $n_D^{25}$ 1.4350. Correct elemental analyses were obtained for the four carbamates.

B. *Mercaptoethylation with isobutyl 2-hydroxyethylthiolcarbonate* (IIIb) was conducted on a 0.5-mole basis by a similar procedure.

*Mercaptoethylation with 2-mercaptoethyl acetate* (V). 2-Mercaptoethyl acetate (V) was prepared by the acid-catalyzed acetylation of 2-mercaptoethanol following Miles and Owen[3] and had a b.p. of 49°/8 mm., $n_D^{25}$ 1.4582 (lit. b.p. 55°/13 mm., $n_D^{17}$ 1.4658), with a purity of 98% by iodometric titration. The general mercaptoethylation procedure described for thiolcarbonates IIIa and IIIb was employed with V and piperidine, and with V and di-n-butylamine. The product compositions were analyzed as follows:

A. *Piperidine.* After the reactants had refluxed overnight, the reaction mixture was cooled and the acetate salts of piperidine (VIIc) and possibly some VIIIc separated from solution and were filtered. After removal of solvent and lower boiling fractions, distillation of the filtrate gave three fractions which were analyzed by iodometric titration, infrared spectroscopy, and in one instance by elemental analysis:

(1) B.p. 73–83°/8 mm., $n_D^{25}$ 1.497 (39 g.) and consisted of 87% Ic and 13% VIc;

(2) B.p. 83–91°/8 mm., $n_D^{25}$ 1.487 (11 g.) and consisted of 35% Ic and 65% VIc;

(3) B.p. 91–92°/8 mm., $n_D^{25}$ 1.4801 (31.5 g.) and consisted of 6% Ic and 94% VIc.

*Anal. of Fraction 3.* Calcd. for pure VIc ($C_7H_{13}NO$): C, 66.1; H, 10.0; N, 11.0. Found: C, 66.2; H, 10.4; N, 10.9.

Fractions 1–3 were added to 800 ml. of ether and the 2-piperidinoethanethiol component (Ic) precipitated as its hydrochloride by bubbling in hydrogen chloride. The hydrochloride was filtered, washed with ether, and dried to yield a total of 77 g. (41.5%) of product of 96.6% purity by iodine titration.

B. *Di-n-butylamine.* Unlike the piperidine example, no acetate salts precipitated from solution after the reaction mixture had cooled. Four product fractions were collected upon distillation of this mixture; the analysis by titration and infrared indicated the following compositions: (1) B.p. 82–84°/8 mm., $n_D^{25}$ 1.447 (185 g.) consisting of 43% Id and 57% VIId and VIIId; (2) B.p. 84–100°/8 mm., $n_D^{25}$ 1.454 (9 g.) consisting of 59% Id and 41% VIId and VIIId; (3) B.p. 100–105°/8 mm., $n_D^{25}$ 1.455 (35 g.) consisting of 61% Id and 39% VId; (4) B.p. 105–111°/8 mm., $n_D^{25}$ 1.449 (18 g.) consisting of 21% Id and 79% VId.

From these data a calculated yield of 62% of 2-di-n-butylaminoethanethiol (Id) was obtained.

ROCHESTER, N. Y.

---

[COMMUNICATION NO. 2176 FROM THE KODAK RESEARCH LABORATORIES, EASTMAN KODAK CO.]

# Mercaptoethylation. V. A New Synthesis of Ethylene Monothiolcarbonate

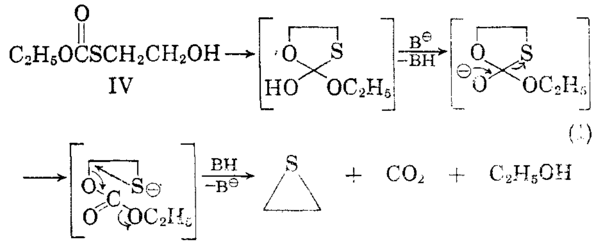
D. D. REYNOLDS, D. L. FIELDS, AND D. L. JOHNSON

*Received May 16, 1961*

**A new synthesis of ethylene monothiolcarbonate by the acid-catalyzed intramolecular transesterification of ethyl 2-hydroxyethylthiolcarbonate is described.**

In a previous paper[1] one of the authors described the preparation of ethylene monothiolcarbonate (I) in a 48% yield by the reaction of phosgene with 2-mercaptoethanol in the presence of pyridine. Investigations of the chemistry of I have since led to several interesting and useful syntheses, as summarized in Chart I. To date, the pyrolysis of I to ethylene sulfide (II)[1] constitutes the most convenient synthesis of pure II, and the preparation of 2-mercaptoethyl carbamates (III) derived from secondary amines represents the only known route to this type of compound.[2]

In a recent investigation concerned with mercaptoethylation reactions, a synthesis of ethyl 2-hydroxyethylthiolcarbonate (IV) was developed in 87–92% yield, by the reaction of ethyl chloroformate with sodium 2-hydroxyethyl mercaptide.[3] Under basic conditions, this thiolcarbonate decomposes primarily to ethylene sulfide, ethanol, and carbon dioxide following the probable reaction path of Equation 1.[3,4]



(1)

We now wish to report that under the action of p-toluenesulfonic acid (PTSA) in refluxing benzene,

---

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

(2) D. D. Reynolds, D. L. Fields, and D. L. Johnson, *J. Org. Chem.*, **26**, 5111 (1961), Part II of this series; D. D. Reynolds, D. L. Fields, and D. L. Johnson, *J. Org. Chem.*, **26**, 5109 (1961), Part I of this series.

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

(4) C. C. Culvenor, W. Davies, and W. E. Savige, *J. Chem. Soc.*, 4480 (1952).

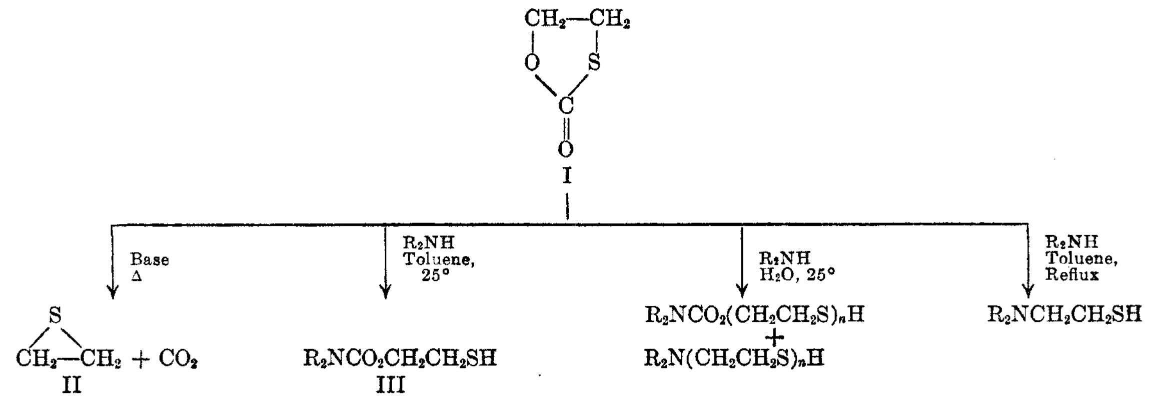
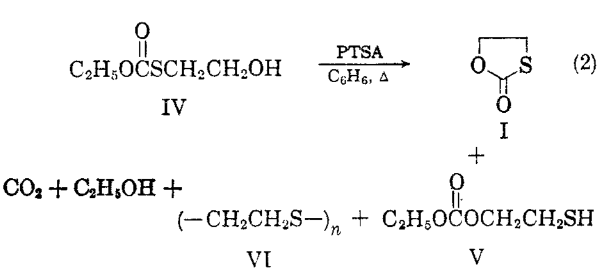


CHART I

thiolcarbonate IV readily undergoes an intramolecular transesterification to yield ethylene monothiolcarbonate (I) in 70–77%, accompanied by the reaction by-products shown in Equation 2.



(2)

By refluxing a mixture of IV with 2 molar % of *p*-toluenesulfonic acid in benzene for nineteen hours, I was obtained in 77% yield and V in 11% yield, in addition to polyethylene sulfide (VI). In an identical experiment conducted over a sixty-hour period, I was again obtained in 77% yield, along with polymer VI. In this case, however, no thiol V was isolated. These comparative experiments would therefore suggest that V might be the actual precursor to VI, and that the extended reaction period allowed the initially formed V to polymerize to VI.

This same conclusion was drawn after considering the iodometric titration data obtained while following the courses of reaction of IV with 2, 4, 8, and 16 molar % of *p*-toluenesulfonic acid (see Fig. 1). While a considerable variation in rates of reaction was observed at these different catalyst levels, all four experiments possessed the common characteristic of having the thiol concentration (presumably thiol V) increase to a maximum and then decrease to a negligible value when given a sufficient reaction time, *i.e.*, four hours with 16% *p*-toluenesulfonic acid, and fifty-six hours with 2% *p*-toluenesulfonic acid. A second factor common to these experiments was that VI and I (70–77% yield) were isolated to the complete exclusion of V.

As a further verification of the apparent stability of I and the instability of IV and V in the presence of *p*-toluenesulfonic acid, V polymerized completely to VI in less than five hours when refluxed with 16 molar % of *p*-toluenesulfonic acid. Under identical conditions, an equimolar mixture of I and ethanol was recovered unchanged. These results, along with the data gathered in a similar experiment with IV, are graphically illustrated in Fig. 2.

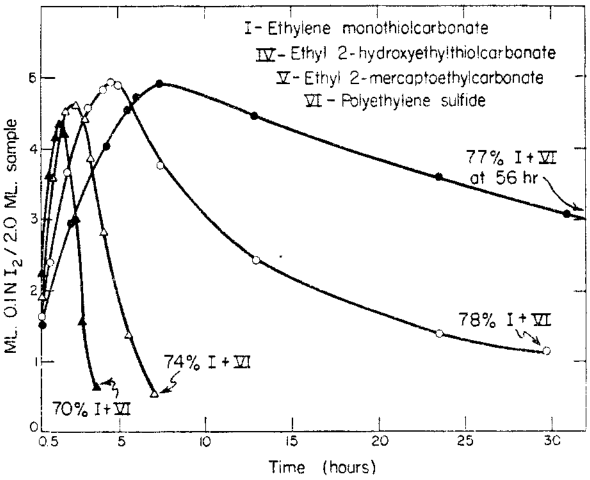


Fig. 1. Results of iodometric titrations of V, illustrating the effect of 2, 4, 8, and 16 molar % of *p*-toluenesulfonic acid on IV in refluxing benzene. Starting materials: IV (1.0 mole), *p*-toluenesulfonic acid (*x* mole), and 500 ml. of benzene. *x* = 0.02 (●), 0.04 (○), 0.08 (△), and 0.16 (▲).

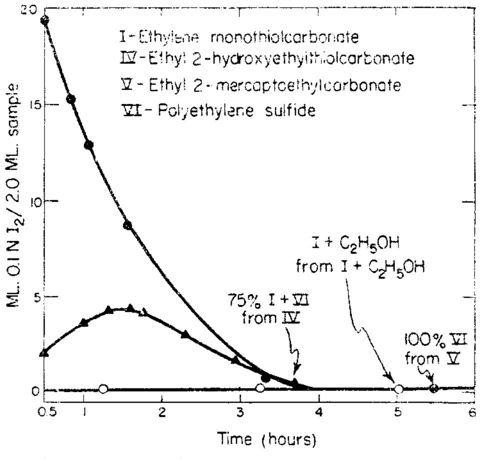


Fig. 2 Results of iodometric titrations of V, illustrating the effect of 16 molar % (0.16 mole) of *p*-toluenesulfonic acid with 1.0 mole each of IV (▲), V (●), and an equimolar mixture of I and ethanol (○) in 500 ml. of refluxing benzene.

As an interpretation of these experimental observations, a reaction mechanism is suggested in Chart II. This mechanism serves as a basis for postulations regarding the relative rates of reaction governing the composition of the reaction mixtures.

Thus, I and V are thought to be derived from a common 1,3-oxathiolane intermediate (VII). Since I and ethanol are recovered unchanged after reaction with *p*-toluenesulfonic acid, the rate of *a* is much greater than that of *a'*. Similarly, since V is polymerized completely to VI under the same conditions, rate *b* is much greater than that of *b'*. Therefore, based on the 75% yields of I to 25% yields of VI isolated in these experiments, it would follow that the rate of *a* must be approximately three times the rate of *b*. Finally, since a rise and decline of V were observed, the rate of *b* must exceed the rate of *c*.

From these findings a method for preparing ethylene monothiolcarbonate has been devised which is more convenient and gives higher yields of I than the previously reported preparation employing phosgene and 2-mercaptoethanol. Thus, 20 molar % of *p*-toluenesulfonic acid in refluxing benzene will completely convert IV to ethylene monothiolcarbonate and polymer in a four-hour period. After the solid polymer has been filtered, and the acid catalyst washed out with aqueous sodium carbonate, pure I may be obtained in 70–75% yield by distillation. It is also possible to obtain I in 55–60% yield by starting with ethyl chloroformate and 2-mercaptoethanol and omitting the isolation of the intermediate IV.

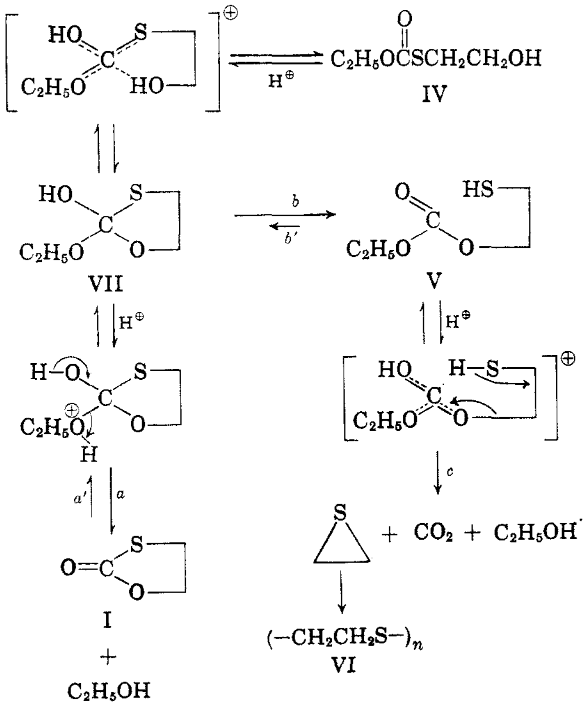


CHART II

EXPERIMENTAL

*Materials.* Ethyl 2-hydroxyethylthiolcarbonate (IV), b.p. 108°/5 mm., $n_{D}^{25}$ 1.4782, was prepared by a previously described procedure.[3] Ethyl 2-mercaptoethylcarbonate (V), b.p. 84°/9 mm., $n_{D}^{25}$ 1.4522, was prepared by a procedure to be described in a forthcoming publication.[5]

*Preparation of ethylene monothiolcarbonate* (I). A mixture of ethyl 2-hydroxyethylthiolcarbonate (IV) (750 g., 5.0 moles), *p*-toluenesulfonic acid monohydrate (190.5 g., 1.0 mole), and 1.5 l. of benzene was refluxed for 4 hr. under an 18-in., glass-helices-packed distillation apparatus. During this period, the benzene-water-alcohol and then the benzene-alcohol azeotropes were continuously distilled at a rate sufficient to maintain a stillhead temperature of 70°.

The reaction mixture was cooled, and the polymer formed during the reaction further precipitated by the addition, with stirring, of 1.5 l. of ether. After the polymer had been filtered, the acidic filtrate was neutralized with an aqueous sodium carbonate solution (62.0 g., 0.5 mole of sodium carbonate in 500 ml. of water), and the *p*H adjusted to about 6 by the addition of 10 ml. of glacial acetic acid. The organic layer was separated, stabilized with 20.0 g. of stearic acid, and distilled under reduced pressure through an 18-in., glass-helices-packed column to yield 384 g. (73.6%) of product, b.p. 75°/1.0 mm., $n_{D}^{25}$ 1.5104 (lit.,[1] b.p. 47–50°/0.08 mm., $n_{D}^{25}$ 1.5102). To prevent possible contamination of product during distillation, it was found necessary to remove a small amount of white crystalline material identified as 1,4-dithiane (m.p. 105°. Calcd.: C, 40.0; H, 6.7. Found: C, 39.5; H, 6.5), from the cold finger just prior to the distillation of the ethylene monothiolcarbonate.

*Iodometric titration procedures.* The data illustrated in Figs. 1 and 2 were obtained by iodometric titration of 2.0-ml. aliquot samples diluted with 100 ml. of absolute ethanol, which had been withdrawn from the reaction mixtures at the time intervals indicated in these respective figures.

Isolation of the ethylene monothiolcarbonate was effected by distillation through a 14-in., glass-helices-packed column after polymer VI had been filtered and the acid catalyst neutralized in the manner described in the preceding section. The refractive index of I isolated in each experiment was $n_{D}^{25}$ 1.5103 ± 0.0003.

*Nineteen-hour reaction of 2% p-toluenesulfonic acid and* IV. A mixture of ethyl 2-hydroxyethylthiolcarbonate (IV) (150 g., 1.0 mole) and *p*-toluenesulfonic acid monohydrate (3.81 g., 0.02 mole) was allowed to react in refluxing 500 ml. of benzene for a 19-hr. period, and the resulting reaction mixture readied for distillation in the manner just described in the general procedure for the preparation of ethylene monothiolcarbonate. Four product fractions, none of which were constant boiling, were collected upon distillation of the mixture through a 14-in., glass-helices-packed column. Analysis of each fraction by iodometric titration and by infrared spectroscopy indicated the following compositions:

(1) B.p. 77–84°/7 mm., $n_{D}^{25}$ 1.467 (9.6 g.) consisting of 74% V and 26% I;

(2) B.p. 84–87°/7 mm., $n_{D}^{25}$ 1.475 (9.7 g.) consisting of 57% V and 43% I;

(3) B.p. 87–93°/7 mm., $n_{D}^{25}$ 1.494 (21.0 g.) consisting of 21% V and 79% I;

(4) B.p. 93–95°/7 mm., $n_{D}^{25}$ 1.504 (56.8 g.) consisting of 2% V and 98% I.

From these data, V and I were obtained in calculated yields of 11% and 77%, respectively. Polyethylene sulfide, constituting the balance of the yield, was left as a pot residue.

ROCHESTER, N. Y.

---

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