tane, b.p. 88–92°, $n^{20}\mathrm{D}$ 1.4223 (reported b.p. 88°, $n^{20}\mathrm{D}$ 1.4131).[19]

3,3-Bis(chloromethyl)thietane.—A solution of 129 g. of potassium hydroxide in 1 l. of 95% ethyl alcohol was saturated with hydrogen sulfide, and 266 g. of pentaerythrityl trichlorobromide[20] in 500 ml. of ethyl alcohol was added with stirring. After being heated on a steam bath for 16 hr. under reflux, the solution was cooled. The potassium bromide was removed by filtration and the ethanol by distillation under reduced pressure. After addition of ether and separation of the water layer, the organic layer was dried over magnesium sulfate. Distillation gave 97 g. (54%) of a mixture of 2,6-dithiaspiro[3.3]heptane (45%) and 3,3-bis(chloromethyl)thietane (55%), b.p. 86–90 (2 mm.), $n^{20}\mathrm{D}$ 1.5690. The components were separated by gas chromatography, using a Ucon polar column. The 2,6-dithiaspiro[3.3]heptane thus obtained had b.p. 87–88° (3.5 mm.), m.p. 28–29° (reported m.p. 31.5°).[21] The other fraction consisted of pure 3,3-bis(chloromethyl)thietane, b.p. 71° (1 mm.), $n^{20}\mathrm{D}$ 1.5439.

Anal. Calcd. for $C_5H_8SCl_2$: C, 35.09; H, 4.71. Found: C, 35.57; H, 4.90.

2-Thiaspiro[3.2]hexane.—The procedure described previously for the corresponding oxaspirohexane was employed. From 58 g. of 3,3-bis(chloromethyl)thietane, added dropwise to a mixture of 131 g. of zinc powder, 53 g. of sodium carbonate, and 75 g. of sodium iodide in 300 g. of molten acetamide, according to procedure previously described for the synthesis of the corresponding oxaspirohexane, 31 g. (10%) of 2-thiaspiro[3.2]hexane, b.p. 141–142°, $n^{20}\mathrm{D}$ 1.5163, was isolated by distillation. The infrared spectrum and retention time in the gas chromatograph were identical to that of the 2-thiaspiro[3.2]hexane obtained by the cyclic carbonate method.

---

[19] N. Kishner, *J. Russ. Phys. Chem. Soc.*, **40**, 1007 (1908).

[20] W. H. Urry and J. R. Eiszner, *J. Am. Chem. Soc.*, **74**, 5822 (1952).

[21] H. J. Backer and K. J. Keuning, *Rec. trav. chim.*, **52**, 499 (1933).

Synthesis of Cyclic Sulfides from Cyclic Carbonate Esters. II. Thiiranes. Mechanism of the Reaction[1]

SCOTT SEARLES, JR., HUGH R. HAYS, AND EUGENE F. LUTZ

Department of Chemistry, Kansas State University, Manhattan, Kansas

Received March 9, 1962

A new synthesis of episulfides by the reaction of thiocyanate salts with cyclic carbonate esters of 1,2-diols is described. The reaction was found to be quite susceptible to steric hindrance. Evidence, stereochemical and otherwise, is presented for a proposed mechanism for the reaction.

The reaction of cyclic carbonate esters of 1,3-diols with alkali thiocyanates has been found to be a good synthesis of thietanes in many cases.[2] The reaction has now been extended to the cyclic carbonate esters of 1,2-diols, to give a new synthesis of episulfides.[3]

This has been found to be a very good method for ethylene sulfide. Gentle heating of commercially available ethylene carbonate with dry potassium thiocyanate at steam-bath temperatures causes a smooth evolution of ethylene sulfide and carbon dioxide. The ethylene sulfide, obtained in about 80% yield, is of very high purity. Contrary to most other preparations, this material can be stored at room temperature for several months without polymerization. The by-product is potassium cyanate. Other thiocyanate salts can be used in place of potassium thiocyanate.

Extension of the reaction to five substituted ethylene carbonates (1,3-dioxol-2-ones) gave results which are summarized in Table I. It is quite evident that increasing substitution by methyl groups resulted in lower yields of episulfides, and in higher temperatures required for a comparable reaction rate. The lower yields may be partly a consequence of the higher temperatures required, as the episulfides tend to polymerize in the hot reaction mixture. Use of a stream of nitrogen or reduced pressure to remove the less volatile episulfides before polymerization occurred was helpful, but the yield of styrene sulfide was greatly diminished by polymerization, nevertheless. The reaction of glycerol carbonate gave only polymeric material, even when carried out *in vacuo*. Similar difficulties have been reported in the attempted preparation of the expected product, 2-hydroxymethylethylene sulfide, from glycidol and potassium thiocyanate.[4]

As in the synthesis of thietanes[2] no rearrangements were observed in the formation of the episulfides. The progressive and marked effect of additional methyl groups on the reaction temperature and yield of episulfide is noteworthy. The completely methylated compound, pinacol carbonate, gave no reaction whatever with potassium thiocyanate even at 280°, at which temperature it distilled out of the reaction vessel unchanged. The susceptibility of the reaction to steric hindrance is, of course, suggestive of a mechanism involving

---

[1] This work was supported by research grants from the National Science Foundation and the Petroleum Research Fund of the American Chemical Society.

[2] S. Searles, H. R. Hays, and E. F. Lutz, *J. Org. Chem.* **27**, 2828 (1962).

[3] A preliminary announcement has been published: S. Searles and E. F. Lutz, *J. Am. Chem. Soc.*, **80**, 3168 (1958).

[4] C. C. J. Culvenor, W. Davies, and N. S. Heath, *J. Chem. Soc.*, 282 (1949).

Table I

Reaction of 1,3-Dioxol-2-ones with Potassium Thiocyanate

Substituent	Reaction Temp., °C.	Products	Yield, %
None	95–100	Ethylene sulfide	80–85
4-Methyl	140–150	Propylene sulfide	51
meso-4,5-Dimethyl	190–200	*cis*-2,3-Butylene episulfide	31[a]
		1-Buten-3-ol	*ca.* 5
4,4,5,5-Tetramethyl	270–280[b]	No reaction	
4-Phenyl	150–160[c]	Styrene sulfide	34
4-Hydroxymethyl	130–150[d]	Polymer	

[a] There was in addition a 1% yield of *trans*-2,3-butylene episulfide, corresponding to the presence of about 3% *dl*-4,5-dimethyl-1,3-dioxol-2-one in the otherwise pure *meso* starting compound. [b] Starting material distilled out unchanged at this temperature (atmospheric pressure). [c] The reaction was carried out at 35–45 mm. pressure. [d] The reaction was carried out at 20–30 mm. pressure.

nucleophilic attack of thiocyanate ion on an alkyl carbon atom.

Further insight into the mechanism of the reaction is given by the observation that the cyclic carbonate ester of *meso*-2,3-butylene glycol was converted cleanly to *cis*-2,3-butylene sulfide. The carbonate ester was obtained by ester interchange of *meso*-2,3-butylene glycol and ethyl carbonate and had properties in agreement with those previously reported for this compound.[5] The 2,3-butylene sulfide was characterized as the *cis* isomer by comparison of the properties and infrared spectrum with those reported by Bordwell and Neureiter.[6] Gas chromatography indicated it to be the pure *cis* episulfide, except for contamination of the *meso* carbonate with about 3% of the *dl* carbonate.

The formation of the *cis* episulfide from the *meso* glycol carbonate indicates that an even number of Walden inversions has taken place. In this respect, the reaction is similar to the well known synthesis of episulfides from epoxides and thiocyanates or thiourea,[7] for which the accepted mechanism involves *trans* opening of the epoxide ring by thiocyanate ion or thiourea, followed by cyclization to an oxathiolane derivative which cleaves, with subsequent *trans* closing of the episulfide ring.[8a,8b;9a,9b] The stereochemical result is two Walden inversions, with net retention of configuration.

It seems reasonable that the reaction of the carbonate esters of 1,2-diols with thiocyanate salts would follow an analogous path with decarboxylation occurring during or immediately after the attack of thiocyanate ion on the α-carbon atom. This also would result in two Walden inversions and the observed net retention of configuration, as shown in Chart I.

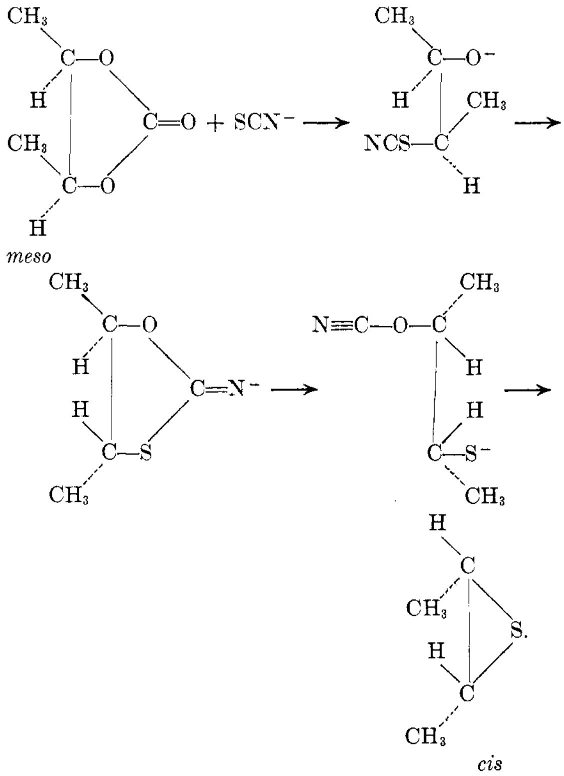

Chart I. Mechanistic Scheme

An alternative mechanism, involving first decarboxylation of the cyclic carbonate to the epoxide, followed by its well known reaction with thiocyanate,[7] can be excluded by several facts. In the first place, the decarboxylation of 4,5-dimethyl-1,3-dioxol-2-one in the presence of the basic catalyst requires a temperature in excess of 240° and gives only about a 10% yield of the epoxide.[10] Furthermore, the epoxide from the *meso*-glycol carbonate is the *trans* isomer, showing that epoxide formation goes with one Walden inversion.[10] This alternative mechanism, therefore, would require three Walden inversions, with a net inversion of configuration. The different experimental conditions used (aqueous solution at low temperature) for the reaction of epoxides with thiocyanates to form episulfides, and the lack of extension of that reaction to form thietanes[11] also weighs against such a mechanism.

The same mechanism is considered to apply to reactions of both 1,2- and 1,3-diol carbonates with thiocyanates, because of the similarity of the reaction in both types of cases. The mechanism proposed explains why this reaction is applicable to the synthesis of both thiiranes and thietanes, while the

---

(5) S. Sarel, L. Pohoryles, and R. Shoskan, *J. Org. Chem.*, **24**, 1873 (1959).

(6) N. P. Neureiter and F. G. Bordwell, *J. Am. Chem. Soc.*, **77**, 578 (1959).

(7) K. Dachlauer and L. Jackel, French Patent 297,621 [*Chem. Abstr.*, **30**, 1122 (1936)].

(8a) M. G. Ettlinger, *J. Am. Chem. Soc.*, **72**, 4792 (1950).

(8b) E. E. van Tamelen, *ibid.*, **73**, 3444 (1951).

(9a) C. C. Price and P. F. Kirk, *ibid.*, **75**, 2396 (1953).

(9b) F. G. Bordwell and H. M. Anderson, *ibid.*, **75**, 4959 (1953).

(10) S. Searles and N. K. Patel, unpublished research.

(11) Unpublished observation in this laboratory.

TABLE II

SUBSTITUTED 1,3-DIOXOL-2-ONES

Substituents	Yield, %	B.p., °C. (mm.) Obs.	B.p., °C. (mm.) Lit.	$n^{20}D$ or m.p. Obs.	$n^{20}D$ or m.p. Lit.
4-Methyl	86	64–66 (0.1)	92.94 (4.5)[a]	1.4212	...
meso-4,5-Dimethyl[b]	89	70–75 (0.1)	93 (3.5)[c]	1.4251	1.4251[c]
4,4,5,5-Tetramethyl	96	...	...	179–181°	180–181°[a]
4-Phenyl[d]	72	152–154 (0.6)	...	55.5–56.5	
4-Hydroxymethyl	...[e]				

[a] Ref. 17. [b] *Anal.* Calcd. for $C_5H_8O_3$: C, 51.71; H, 6.94. Found: C, 51.40; H, 6.90. [c] Ref. 17, for a mixture of the *meso* and *dl* compounds which was "mainly the *meso* form." [d] *Anal.* Calcd. for $C_9H_8O_3$: C, 65.86; H, 4.91. Found: C, 66.21; H, 5.09. [e] Obtained as a viscous liquid which was not purified, due to instability.

epoxide–thiocyanate reaction is not. The strain and reactivity is about the same in the five- and six-membered cyclic carbonates, whereas these are quite different for epoxides and oxetanes. The lack of reactivity of thiourea with the cyclic carbonates is probably due to its nucleophilicity being lower than that for thiocyanate ion[12]; the more reactive epoxides, however, can react with either. Finally, the mechanism accounts for the observed decrease in reactivity with α-substitution, for the first step, as a typical S$_N$2 process, would be very susceptible to steric hindrance.

Experimental

1,3-Dioxol-2-ones.—Except for ethylene carbonate, which was obtained commercially,[13] (m.p. 35–37°, lit. value,[14] 39°) the cyclic carbonates used in this work were prepared by the same method used for the preparation of 1,3-dioxan-2-ones[15]—that is, a solution of 1.1 moles of ethyl carbonate and 1.0 mole of diol in which 0.5 g. of sodium metal had been dissolved, has heated under reflux for 3 hr., after which the ethanol was removed by slow distillation in order to force the transesterification to completion. Purification was by distillation or recrystallization. The properties of the products are given in Table II.

An exception was 4-hydroxymethyl-1,3-dioxol-2-one, prepared from glycerol and ethylene carbonate by the similar procedure of Bruson and Reiner.[16] Since this material is a viscous liquid reported to decompose to glycidol on distillation[14] and has not been successfully purified before, it was used without purification in the reaction with potassium thiocyanate.

It is noteworthy that pinacol gave a practically quantitative yield of its cyclic carbonate ester, since Sarel, *et al.*,[17] recently reported that pinacol tends to undergo fission to acetone and isopropyl alcohol under these conditions. We were unable to observe any evidence for such fission; our result is in accord with the previous observation that pinacol forms a monoalkoxide, which does not readily cleave in a basic medium.[18]

The *meso*-2,3-butanediol used in preparing *meso*-4,5-dimethyl-1,2-dioxol-2-one was obtained from the Eastman Kodak Co. and was purified by an efficient fractional distillation before being used. Its properties were b.p. 180–181° (745 mm.), m.p. 32–33° (lit. values,[19] b.p. 60–61° (2 mm.), m.p. 33–34°), and gas chromatography indicated it to be 97% pure, the only impurity being the *dl* isomer.

Reaction of 1,3-Dioxol-2-ones with Thiocyanate Salts.—The method employed was essentially the same as that described for the synthesis of thietanes by the reaction of 1,3-dioxan-2-ones with potassium thiocyanate.[2] The reaction temperatures and pressures employed are listed in Table I. An ice trap was used for collection of the products. The time required for the reactions was generally 1 or 2 hr.

Identification of the products was readily made by comparison of their physical properties with those previously reported, as shown in Table III and by their infrared spectra. The infrared spectra were of particular value in establishing the identity of *cis*- and *trans*-2,3-butylene episulfide. The lower boiling product, obtained in about 1% yield, showed absorption bands at 1088 and 1293 cm.$^{-1}$, both weak, characteristic of the *trans* isomer,[6] while the higher boiling sulfide showed strong absorption bands at 1030 and 1149 cm.$^{-1}$, characteristic of the *cis* isomer.[6] The infrared spectrum of the third and highest boiling product in the mixture was consistent with the structure of 1-buten-3-ol.

Generality of the reaction with respect to thiocyanate salts was indicated by isolation of a 71% yield of ethylene sulfide from the reaction of sodium thiocyanate with ethylene carbonate, and a 30% yield of this product from the reaction of calcium thiocyanate with ethylene carbonate. The usual conditions for the reaction were employed. Substitution of thiourea for the thiocyanate salt resulted in the formation of no ethylene sulfide.

---

[12] C. G. Swain and C. B. Scott, *J. Am. Chem. Soc.*, **75**, 141 (1953).

[13] We thank Dr. M. Lichtenwalter and the Jefferson Chemical Co. for a gift of ethylene carbonate.

[14] D. Vorlander, *Ann.*, **280**, 187 (1894).

[15] S. Searles, D. G. Hummel, S. Nukina, and P. E. Throckmorton, *J. Am. Chem. Soc.*, **82**, 2928 (1960).

[16] H. Bruson and R. Reiner, *ibid.*, **74**, 2100 (1952).

[17] S. Sarel, L. A. Pohoryles, and R. Ben-Shoshan, *J. Org. Chem.*, **24**, 1873 (1959).

[18] C. B. Wooster and D. S. Latham, *J. Am. Chem. Soc.*, **58**, 76 (1936).

[19] L. Fishbein, *ibid.*, **79**, 2959 (1957).