

TABLE IX

Sulfone	M.P.	Yield	Calcd.			Found		
			C	H	N	C	H	N
XVIII	108-109°	65	47.97	7.94	7.99	48.00	7.47	7.95
XIX	51.8-53.8°	80
XX	49-50°	70	53.17	8.43	6.89	53.25	8.30	6.92
XXI	58.5-59.5°	79	63.74	10.37	4.65	63.68	10.64	4.61

TABLE X

Cyano-sulfone	β -Keto Sulfone	M.P.	Yield	Calcd.		Found	
				C	H	C	H
XVIII	XXVII	...	0
XIX	XXII	95-96.5°	58	50.50	7.41	50.47	7.43
XX	XXIII	92-94°	90	52.86	7.90	53.18	7.69
XXI	XXXI	...	0

washed with water and the ether stripped. The residue was distilled, giving 22.0 g. (0.20 mole, 67%), b.p. 69-70°/60 mm. of XXIV ($n = 3$); oxime, m.p. 66-68°. Bromine (12.0 g., 0.075 mole) was added to sufficient ether, with cooling, to form a solution, and the etherate dripped into 8.4 g. (0.075 mole) of XXIV, $n = 3$, in 75 ml. ether, with stirring. The resulting product was stripped of ether and 0.15 mole of potassium methylmercaptide in methanol was added with stirring and ice cooling, to give after distillation, 4.8 g. (0.03 mole, 40%) of XXVI ($n = 3$), b.p. 81-84°/8 mm., n_D^{25} 1.4843. On oxidation with 30% hydrogen peroxide in acetic acid solution a 1.2 g. yield of XXII was obtained which gave no mixed m.p. depression with the previously prepared sample.

Structure Proof of 2,2-Dimethyl-6-methylsulfonylcyclohexanone (XXIII).—To 54 g. (0.26 mole) of 6-bromo-2,2-dimethylcyclohexanone (XXV, $n = 4$)⁴¹ was added excess potassium methylmercaptide in methanol. After extraction, stripping of solvents, and distillation, 41.2 g. (0.24 mole, 90%) of XXVI ($n = 4$), b.p. 73-75°/1.0 mm., n_D^{25} 1.5012 was obtained. On oxidation to the sulfone a product was obtained which gave no depression of the m.p. when mixed with the previously prepared sample.

Determination of Acidities (pK_a 's) of β -Keto Sulfones.—

(41) E. J. Corey, T. H. Topsis, and W. A. Wozniak, *J. Am. Chem. Soc.*, **77**, 5415 (1955).

With the exception of XXXVII (described previously), stock solutions of the β -keto sulfones (0.001 *M*) were prepared by dissolving a weighed portion of the compound in carbon dioxide-free water (or in a 50:50 ethanol-water solution) in a volumetric flask. One hundred-milliliter portions of the stock solution were partially neutralized with freshly prepared carbonate-free sodium hydroxide solution, made up from the same solvent as the stock solutions. The pH of the solution was measured at different stages of neutralization at 25°. The pK_a values were calculated from the simple Henderson equation⁴² when the pH was below 10; above this value the more accurate form⁴³ was used. The average of five to seven determinations from 20-80% neutralization for each compound is given in Tables I and II; the spread in pK_a values was generally 0.01 to 0.03.

Acknowledgment.—The authors are indebted to the Standard Oil Company of Ohio and the National Institutes of Health (grant CY-4536) for financial assistance.

(42) S. Glasstone, "Textbook of Physical Chemistry," 2nd ed., D. Van Nostrand Co., Inc., New York, 1946, p. 1002.

(43) In the case of 50% ethanol solutions above a pH of 10, the K_w for the solvent was taken to be 1.5×10^{-15} , as given by D. L. Tabroff, G. E. K. Branch, and B. Betlman, *J. Am. Chem. Soc.*, **56**, 1850 (1934).

Synthesis of Cyclic Sulfides from Cyclic Carbonate Esters. I. Thietanes¹

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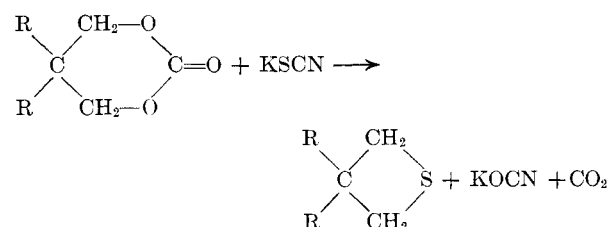
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A new synthesis of thietanes by the reaction of a thiocyanate salt with the cyclic carbonate esters of 1,3-diols is described. The scope of the reaction and the nature of side reactions has been investigated.

The thermal decomposition of carbonate esters of 1,3-diols, forming oxetanes or allylic alcohols, with loss of carbon dioxide, has been observed to be markedly catalyzed by bases and by certain salts.^{2,3} During the course of that study it was observed that the action of potassium thiocyanate led to a different type of reaction, in which a thietane, rather

than an oxetane, was produced.⁴ Potassium thiocyanate was consumed in equimolar quantities, and potassium cyanate was identified as a product:



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

(3) D. B. Pattison, U. S. Patent 2,924,607 (February 9, 1960).

TABLE I
 REACTION OF 1,3-DIOXAN-2-ONES WITH POTASSIUM THIOCYANATE

Substituents	Reaction Temp., °C.	Products	Yield, %
None	140	Thietane	3
4-Methyl	170-180	2-Methylthietane	16
5,5-Dimethyl	175-185	3,3-Dimethylthietane	56
5,5-Diethyl	190-195	3,3-Diethylthietane	63
5-Hydroxymethyl-5-methyl	170-180	3-Hydroxymethyl-3-methylthietane	50
	(130-140 mm.)		
5,5-Dibenzyl	220-240	3,3-Dibenzylthietane	29
	(20-35 mm.)	3,3-Dibenzylthietane	12
4-Isopropyl-5,5-dimethyl	240-250	2-Isopropyl-3,3-dimethylthietane	13
		2-Isopropyl-3,3-dimethylthietane	35
4,6-Dimethyl	180-200	<i>cis</i> -2,4-Dimethylthietane	4
		<i>trans</i> -2,4-Dimethylthietane	3
		2-Penten-4-ol	9
4-Propyl-5-ethyl	210-220	<i>cis</i> -2-Propyl-3-ethylthietane	9
		<i>trans</i> -2-Propyl-3-ethylthietane	7
		Unsatd. alcohols (unidentified)	
4,4,6-Trimethyl	190-200	2-Methyl-2-penten-4-ol	63
		4-Methyl-2-penten-4-ol	8
5-Phenyl-5-ethyl	170-180	α -Ethylstyrene	20
5,5-Pentamethylene	220-230	2-Thiaspiro[3.5]nonane	57
5,5-Tetramethylene	220-230	2-Thiaspiro[3.4]octane	50
5,5-Trimethylene	210-220	2-Thiaspiro[3.3]heptane	33
5,5-Ethylene	170-180	2-Thiaspiro[3.2]hexane	8
5-Methylene	150-160	Polymer	

The simplicity of the method and the easy availability of the starting materials gives this reaction interest as a practical synthesis of thietanes. In order to test its generality we have studied sixteen examples representing considerable variation of structure. The 1,3-dioxan-2-ones used were prepared readily from the corresponding 1,3-diols by ester interchange with ethyl carbonate and were merely heated with dry potassium thiocyanate in the absence of solvent. At temperatures near the unusually low melting point of this salt, carbon dioxide evolution occurred, attended by distillation of the thietane (and other products frequently) from the reaction mixture. The reagent is not limited to potassium thiocyanate, as the higher melting sodium and lithium thiocyanates gave the same reaction. No reaction, however, was observed between the cyclic carbonates and thiourea.

The results, listed in Table I, show that the reaction has a generality resembling that found in the synthesis of oxetanes from carbonate esters of 1,3-diols.² For 3,3-dialkylthietanes, including cycloalkylspirothietanes, it provides an attractive method of synthesis, usually characterized by good yields and a high degree of purity. Worthwhile advantages over the method employing the reaction of 1,3-dibromides with sodium sulfide⁵ are the greater convenience and yields in converting 1,3-diols into carbonate esters rather than 1,3-dibromides.

A number of factors may be recognized as detrimental to the yield of thietanes. Decreasing ring size of the cycloalkane ring in 2-thiaspiro[3.*n*]-

alkanes results in decreased yields and in formation of unsaturated alcohol by-products, probably due to ring enlargement rearrangements, similar to those observed in the corresponding synthesis of 2-oxaspiro[3.3]heptane.⁶

The effect of steric hindrance at the α -carbon atoms is evident in several of the cases studied, including 5,5-dibenzyl- and 4-isopropyl-5,5-dimethyl-1,3-dioxan-2-ones. It was notable that higher temperatures were required for the reaction of these compounds with potassium thiocyanate and that the expected thietane products were accompanied by considerable amounts of the corresponding oxetanes. Molecular models of these carbonate esters indicate some shielding of the α -carbon atoms, evidently causing thiocyanate ion to attack the carbonyl carbon atom to a considerable extent, with resulting oxetane formation.² These results suggest that the mechanism of thietane formation involves attack of the thiocyanate ion on the α -carbon atom of the carbonate ester, similar to the mechanism proposed for the reaction of epoxides with thiocyanates.⁷ Further discussion of the mechanism and stereochemical evidence for it are presented in the accompanying article.⁸

The presence of β -hydrogen atoms in the 1,3-dioxan-2-one is quite detrimental to the yields of thietanes, due to the ease of the β -elimination process leading to unsaturated alcohols. A similar situation exists when these dioxanones are heated with bases such as potassium carbonate, and the mechanism has been discussed.² In spite of this,

(6) S. Searles, E. F. Lutz, and M. Tamres, *J. Am. Chem. Soc.*, **82**, 2932 (1960).

(7) E. E. van Tamelen, *ibid.*, **73**, 3444 (1951); C. C. Price and P. F. Kirk, *ibid.*, **75**, 2396 (1953).

(8) S. Searles, H. R. Hays, and E. F. Lutz, *J. Org. Chem.*, **27**, 2832 (1962).

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

(5) E.g., H. J. Backer and K. J. Keuning, *Rec. trav. chim.*, **53**, 808 (1934).

TABLE II
 1,3-DIOXAN-2-ONES

Substituents	Yield, %	B.p., °C. (mm.)		M.p., °C. (or n_D^{20})	
		Obs.	Lit.	Obs.	Lit.
None	50	90-110 (0.2)	123 (1) ^a	47-48	45 ^a
5,5-Dimethyl	80	110-120 (1)	120-125 (0.2) ^b	100-104	110-111 ^c
5,5-Diethyl	67	135-140 (1)	117-120 (1) ^a	42-44	45-46 ^c
5-Hydroxymethyl-5-methyl ^d	81			90-110	
5,5-Dibenzyl	73			227-229	227-229 ^b
4-Isopropyl-5,5-dimethyl	72	108-110 (0.3)	132 (2)	(1.4591)	
4,6-Dimethyl	71	145-160 (6)	116-117 (2.5)	(1.4458)	(1.4453) ^d
4-Propyl-5-ethyl ^e	84	130-135 (0.7)		(1.4580)	
4,4,6-Trimethyl	55			96-98	97-98 ^b
5-Phenyl-5-ethyl	23			98-100	99-100 ^b
5,5-Pentamethylene ^f	74	135-140 (0.2)		92-93	
5,5-Tetramethylene ^g	71	117-119 (0.1)	130-163 (0.3-9) ^h	94-96	
5,5-Trimethylene	73	150-160 (1)	130-163 (0.3-9) ^h	67-68	66-68 ^h
5,5-Ethylene ⁱ	53	135-140 (1.5)		72-73	
5-Methylene ^j	70	106-108 (1)		54-55	

^a S. Sarel, L. A. Pohoryles, and R. Ben-Shoskan, *J. Org. Chem.*, **24**, 1873 (1959). ^b Ref. 2. ^c B. J. Ludwig and E. C. Piech, *J. Am. Chem. Soc.*, **73**, 5779 (1951). ^d This compound was not analyzed, due to its apparent instability on standing. ^e *Anal.* Calcd. for C₉H₁₆O₂: C, 62.76; H, 9.37. Found: C, 62.94; H, 9.48. ^f *Anal.* Calcd. for C₉H₁₄O₂: C, 63.51; H, 8.29. Found: C, 63.56; H, 8.59. ^g *Anal.* Calcd. for C₈H₁₂O₂: C, 61.52; H, 7.75. Found: C, 51.45; H, 8.21. ^h Ref. 6. ⁱ *Anal.* Calcd. for C₈H₈O₂: C, 56.24; H, 6.29. Found: C, 56.19; H, 6.42. ^j *Anal.* Calcd. for C₆H₈O₂: C, 52.63; H, 5.30. Found: C, 51.19; H, 5.34.

the expected thietanes were obtained in such cases in yields usually comparable to those obtained by less convenient methods.^{9,10} As there has been little or no attempt in this work to determine optimum conditions for each compound, undoubtedly the yields could be improved. In the case of 4,4,6-trimethyl-1,3-dioxan-2-one, however, no thietane formation whatever was detected; the three α -methyl groups and eleven β -hydrogen atoms provide a situation very favorable for β -elimination processes.

Two other cases which gave no isolable yields of thietanes were 5-ethyl-5-phenyl-1,3-dioxan-2-one and 5-methylene-1,3-dioxan-2-one. The former underwent decomposition in other ways, including conjugate elimination to α -ethylstyrene, formaldehyde, and carbon dioxide, as observed previously when the compound was heated with potassium carbonate.² The latter gave a nonvolatile, polymeric material. In view of the formation of methacrolein when this carbonate ester was heated with potassium carbonate,² it is believed that thio-methacrolein may have formed and polymerized.

Several of the thietanes obtained in this work were previously known and identified by comparison of physical properties with those reported. The remainder were characterized by elemental analyses and by infrared absorption bands at $8.5 \pm 0.1 \mu$, which we have found to be characteristic of these other thietanes.¹¹

As further proof of structure, reductive desulfurization with Raney nickel was carried out on 3,3-

benzylthietane, 2-thiaspiro[3.4]octane, 3-methyl-3-hydroxymethylthietane, and the phenylurethane of the latter, to give high yields of the expected products, 2,2-dimethyl-1,3-diphenylpropane, 1,1-dimethylcyclopentane, neopentyl alcohol, and its phenylurethane. Incidentally, this route appears to be of synthetic interest for neopentyl alcohol.

Confirmation of the structure of 2-thiaspiro[3.2]hexane, obtained from the reaction of 5,5-ethylene-1,3-dioxan-2-one with potassium thiocyanate, was obtained by an independent synthesis. Analogous to the synthesis of 2-oxaspiro[3.2]hexane,¹² the reaction of 3,3-bis(chloromethyl)thietane with zinc dust gave a product which was identical in all respects, including infrared spectrum, to the 2-thiaspiro[3.2]hexane obtained by the cyclic carbonate route.

Experimental

1,3-Diols.—The 1,3-diols employed were obtained from commercial sources, except 1,1-dimethylolcyclopropane, 1,1-dimethylolcyclobutane, 1,1-dimethylolcyclopentane, 1,1-dimethylolcyclohexane, and 2,2-dibenzyl-1,3-propanediol, which were obtained by lithium aluminum hydride reduction of the corresponding malonic esters¹³ and 2,4-pentanediol, which was obtained by hydrogenation of acetylacetone.¹⁴ These materials were purified by distillation or recrystallization and had boiling or melting points in agreement with the reported values.

1,3-Dioxan-2-ones.—The general procedure previously described² was followed. The properties of these cyclic carbonate esters are summarized in Table II.

Reaction of 1,3-Dioxan-2-ones with Thiocyanate Salts.—The general procedure was to heat 0.1 mole of the 1,3-dioxan-2-one with 0.15 mole of anhydrous potassium thiocyanate¹⁵

(12) S. Searles and E. F. Lutz, *J. Am. Chem. Soc.*, **81**, 3679 (1959).

(13) S. Searles, R. G. Nickerson, and W. K. Witsiepe, *J. Org. Chem.*, **24**, 1839 (1959).

(14) W. Ipatjew, *Ber.*, **45**, 3223 (1912).

(15) The potassium thiocyanate was dried immediately before use by heating in the reaction apparatus for 15 min. at 165° under oil pump vacuum.

(9) Thietane itself is an exception, a good synthesis for which has been reported by F. G. Bordwell and B. M. Pitt, *J. Am. Chem. Soc.*, **77**, 575 (1955).

(10) E.g., E. Grischkevitch-Trochimovski, *J. Russ. Phys. Chem. Soc.*, **48**, 880 (1916); *J. Chem. Soc.*, 112, Abs. A I, 153 (1917).

(11) S. Searles, H. R. Hays, and E. R. Lippincott, manuscript in preparation.

TABLE III
DATA ON NEW THIETANES

Substituents	B.p., °C. (mm.) ^a	<i>n</i> _D ^b	Formula	Calcd.			Found		
				C	H	S	C	H	S
3-Hydroxymethyl-3-methyl-	78-79 (2)	1.5143	(C ₁₅ H ₁₇ NO ₂ S) ^b	66.87	5.96	11.16	67.04	5.82	10.70
<i>cis</i> -2,4-Dimethyl- ^c	113-115 ^d	1.4739	C ₈ H ₁₆ S	58.80	9.80	31.40	59.49	10.16	30.21
<i>trans</i> -2,4-Dimethyl- ^c	113-115 ^d	1.4712	C ₈ H ₁₆ S	58.80	9.80	31.40	60.15	9.95	30.22
<i>cis</i> -2-Propyl-3-ethyl ^c	185-188	1.4804	C ₈ H ₁₆ S	66.59	11.18	22.22	66.99	11.03	22.11
<i>trans</i> -2-Propyl-3-ethyl ^c	185-188	1.4731	C ₈ H ₁₆ S	66.59	11.18	22.22	66.72	10.84	22.50
2-Isopropyl-3,3-dimethyl	173-174	1.4600	C ₈ H ₁₆ S	66.59	11.18	22.22	66.70	10.44	21.51
3,3-Dibenzyl	156 (0.1)	<i>M.p.</i> 57-58°	C ₁₇ H ₁₈ S	80.26	7.13	12.61	79.86	7.40	12.80
3,3-Pentamethylene-									
(2-thiaspiro[3.5]nonane)	105-106	1.5205	C ₈ H ₁₄ S	67.54	9.92	22.54	67.49	9.68	22.70
3,3-Tetramethylene-									
(2-thiaspiro[3.4]octane)	92-93 (23)	1.5191	C ₇ H ₁₂ S	65.56	9.43	25.01	65.85	9.35	25.02
3,3-Trimethylene-									
(2-thiaspiro[3.3]heptane)	149-150	1.5145	C ₆ H ₁₀ S	63.10	8.83	28.07	63.36	9.30	27.21
3,3-Ethylene-									
(2-thiaspiro[3.2]hexane)	141-142	1.5192	C ₅ H ₈ S	59.95	8.05	32.01	59.90	8.05	31.88

^a Pressure about 740 mm. unless specified. ^b 3-Hydroxymethyl-3-methylthietane was characterized as its α -naphthylurethane, m.p. 108-109°, the analysis for which is given. ^c Assignment of configuration made in accordance with the von Auwers-Skita rule, with the isomer with highest boiling point (longest retention time in the gas chromatograph) and density being considered *cis*. The boiling point range given in each case is for the mixture of isomers. ^d E. Grischkevitch-Trochimovski, ref. 10, reported b.p. 112.5-113.5° (757 mm.) and *n*_D¹⁵ 1.4502 for what was probably a mixture of the *cis* and *trans* isomers of 2,4-dimethylthietane.

in a small distillation apparatus until carbon dioxide evolution was complete. A slow stream of nitrogen was bubbled into the reaction mixture, carrying the cyclic sulfide as formed into a received cooled with Dry Ice-acetone. Heating was provided by an oil bath, and the reaction temperature was observed by means of a thermometer in the reaction flask. The products were purified by fractional distillation. In the case of *cis*- and *trans*-2,4-dimethylthietane, additional purification was made by means of gas chromatography, using a Ucon polar column. The assignments of configurations have been made on the basis of the von Auwers-Skita rule.¹⁶

The properties of the thietanes obtained are described in Tables III and IV. The infrared spectra of all the compounds were in agreement with the structures given. Of particular interest was the occurrence in each of a strong, sharp absorption band at $8.5 \pm 0.1 \mu$, which appears to be diagnostic of thietanes. Further details will be published separately.

The nonvolatile products of these reactions generally consisted of a dark liquid boiling at 200° and solidifying at about 100°. In the case of 5,5-dimethyl-1,3-dioxan-2-one, dissolving this material in water and extraction with chloroform gave a 25% yield of a heavy oil, which appeared from its infrared spectrum to be mainly a polymer of the original carbonate ester. Concentration of the aqueous solution gave white needles of an inorganic salt having an infrared spectrum identical to that of authentic potassium cyanate (cf. Sadtler's Standard Spectra, No. 5718).

The use of other alkali thiocyanates was investigated. The yields of 2,2-dimethylthietane obtained from heating 5,5-dimethyl-1,3-dioxan-2-one with lithium thiocyanate, with sodium thiocyanate, or with potassium thiocyanate, by the same procedure as described above, were 10, 40, and 59%, respectively. When thiourea was substituted for the thiocyanate salt, no cyclic sulfide was obtained.

Reductive Desulfurization.—The general procedure is

(16) K. von Auwers, *Ann.*, **420**, 84 (1920); A. Skita, *Ber.*, **53**, 1792 (1920); A. Skita and W. Faust, *ibid.*, **64**, 2878 (1931). The application of the rule to the present case seems justified, since in a number of related systems the *cis* isomer has higher boiling point, melting point, and index of refraction than the *trans* isomer: the 2-butene episulfides [N. P. Neureiter and F. G. Bordwell, *J. Am. Chem. Soc.*, **81**, 578 (1959)], the 1,2-cyclobutanedicarboxylic acids [A. I. Vogel, *J. Chem. Soc.*, 1985 (1922)], the 1,2-dibenzoylcyclobutanes [E. Ellinghoe and R. C. Fuson, *J. Am. Chem. Soc.*, **56**, 1774 (1934)], and the 1,3-dialkylcyclopentanes [G. Chiurdoglu, *Bull. soc. chim. Belg.*, **53**, 45 (1944)].

TABLE IV
PREVIOUSLY KNOWN PRODUCTS OBTAINED FROM
1,3-DIOXAN-2-ONES

Compound	B.p., °C. (mm.)		<i>n</i> _D ^b	
	Obs.	Lit.	Obs.	Lit.
Thietane	94-95	95 ^a	1.5096	1.5102 ^a
2-Methylthietane	103-105	105-107 ^a	1.4881	1.4831 ^a
3,3-Dimethylthietane	116	120 ^b	1.4733	1.4731 ^b
3,3-Diethylthietane	172	170-173 ^c	1.4831	1.4833 ^c
3,3-Dibenzyl-oxetane	127-135 (0.1)	135 (0.1) ^d	1.5772	1.5765 ^d
2-Isopropyl-3,3-dimethyl-oxetane	135	135 ^d	1.4157	1.4157 ^d
2-Penten-3-ol	117-122	122 ^e	1.4270	1.4277 ^e
2-Methyl-2-penten-4-ol	119-120	121-122 ^f	1.4300	1.4295 ^f
4-Methyl-2-penten-4-ol	137-138	138 ^g	1.4395	1.4410 ^g
α -Ethylstyrene	160-180	81-82 (20) ^d	1.5362	1.5270 ^d

^a Ref. 9. ^b Ref. 5. ^c Ref. 4. ^d Ref. 2. ^e K. von Auwers and H. Westerman, *Ber.*, **54**, 2996 (1921). ^f Ref. 19. ^g W. Krestinski, *Ber.*, **55**, 2759 (1922).

illustrated by the following example: A mixture of 4.74 g. of the phenylurethane of 3-hydroxymethyl-3-methylthietane and 32 g. of Raney nickel (W-2) in 100 ml. of benzene was refluxed with stirring for 24 hr. After cooling, the mixture was filtered and evaporated to dryness under reduced pressure to give 4 g. (96%) of the phenylurethane of neopentyl alcohol, m.p. 110-112°. After one recrystallization from alcohol, the sample melted at 113-114° (m.p. reported 114°).¹⁷

In like manner, 3,3-dibenzylthietane was reduced in 94% yield to 2,2-dibenzylpropane, b.p. 291-293°, m.p. 68-69° (reported b.p. 293-294°, m.p. 68-69°).¹⁸ Treatment of 2-thiaspiro[3.4]octane with Raney nickel for 5 hr. in refluxing *p*-xylene gave an 81% yield of 1,1-dimethylcyclopent-

(17) A. Richard, *Ann. Chim. Phys.* [8], **21**, 339 (1910).

(18) E. R. Trotman, *J. Chem. Soc.*, **127** 94 (1925).

tane, b.p. 88–92°, n_D^{20} 1.4223 (reported b.p. 88°, n_D^{20} 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 trichlorobromide²⁰ 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_D^{20} 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_D^{20} 1.5439.

Anal. Calcd. for $C_6H_8S_2Cl_2$: 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_D^{20} 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.

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Synthesis of Cyclic Sulfides from Cyclic Carbonate Esters.

II. Thiiranes. Mechanism of the Reaction¹

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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 thietanes² 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

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