The Preparation of *meso*- and DL-α,α'-Stilbenedithiol, *meso*- and DL-2,3-Butanedithiol, and DL-1,2,3,4-Butanetetrathiol

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The preparation of the *meso* and DL isomers of 2,3-butanedithiol and α,α'-stilbenedithiol are described. The synthetic route employed was the conversion of *cis*- and *trans*-2,3-epoxybutane and *cis*- and *trans*-stilbene oxide to the *trans* and *cis* cyclic trithiocarbonates, respectively, followed by reduction with lithium aluminum hydride to the dithiols. Verification of isomer assignments was obtained by infrared and n.m.r. spectroscopy. The preparation of DL-1,2,3,4-butanetetrathiol by a similar route also is described.

In earlier publications[2] we have described the preparation of a variety of mono- and polyfunctional mercaptans with the aim of studying the effect of structure on the rate of oxidation. As a continuation of this work, we thought it would be of interest to determine if the observed steric effects on the oxidation rates of dithiols[2a,b,d] would appear also in stereoisomeric symmetrical vicinal dithiols. This paper describes the synthesis of the *meso* and DL isomers of α,α'-stilbenedithiol and 2,3-butanedithiol, and DL-1,2,3,4-butanetetrathiol.

Results and Discussion

Iqbal and Owen[3a] prepared DL-2,3-butanedithiol by the following route: *cis*-2,3-epoxybutane reacted with potassium methyl xanthate to give *trans*-4,5-dimethyl-1,3-dithiolane-2-thione (IIIb), which was then reduced with lithium aluminum hydride to the DL dithiol. The isomer assignments were based on the assumption that three Walden inversions occur in going from the *cis* epoxide to the *trans* trithiocarbonate and that the reduction step takes place without racemization. Price and Kirk,[3b] and van Tamelen[4] have shown that the reaction of 1,2-disubstituted epoxides with thiocyanate occurs with two inversions, one at each asymmetric carbon atom. The proposed mechanism considers a *trans* opening of the epoxide ring and a *trans* closing of the episulfide ring. The reaction of 1,2-disubstituted epoxides with other sulfur nucleophiles, such as thiourea,[5] also has been shown to form episulfides *via* the same mechanism.[6] By analogy with these observations, it is reasonable to postulate that the reaction of 1,2-disubstituted epoxides with xanthate proceeds through two inversions, *e.g.*, *racemic* epoxide leads to *racemic* episulfide. The intermediate episulfide is then attacked by a second molecule of xanthate with inversion. Since the closing of the trithiocarbonate ring does not involve the breaking of bonds at the asymmetric centers, the trithiocarbonate of inverted configuration should be obtained; *e.g.*, *cis* epoxide is converted to *trans* trithiocarbonate (Scheme I).

This reaction sequence was used to prepare *meso*-2,3-butanedithiol from *trans*-2,3-epoxybutane, and *meso*- and DL-α-α'-stilbenedithiol from *trans*- and *cis*-stilbene oxide, respectively. Stereoisomer assignments were verified by n.m.r. and infrared spectroscopy.

***cis*- and *trans*-4,5-Dimethyl-1,3-dithiolane-2-thione.**—Trithiocarbonates IIIa and IIIb were prepared in 54% and 72% yields from epoxides Ia and Ib, respectively. The infrared spectra showed typical strong absorption bands in the 1100–1000-cm.$^{-1}$ region, which are due to C=S stretching.[3a] The *cis* isomer showed three high-intensity peaks at 1093, 1069 and 1031 cm.$^{-1}$, whereas the *trans* isomer showed two strong bands at 1088 and 1053 cm.$^{-1}$ and a medium intensity maximum at 1010 cm.$^{-1}$. These values were obtained from the pure liquids. Iqbal and Owen[3a] reported high-intensity maxima at 1093 and 1058 cm.$^{-1}$ for the *trans* isomer in carbon tetrachloride. Since there is sufficient variation in the location of these bands to permit differentiation between isomers, it can be concluded that the xanthate reaction proceeds with little or no racemization; *i.e.*, the *cis* oxide gives the *trans* trithiocarbonate, and vice versa.

Evidence for the indicated isomer assignments was obtained by n.m.r. spectroscopy. Anet[7] reported the spectra of the *cis*- and *trans*-4,5-dimethyl cyclic carbonates, which are the oxygen analogs of trithiocarbonates IIIa and IIIb. The τ-values for the four compounds are shown in Table I. The resonance of the methyl hydrogens is shifted to higher field strengths when the methyl groups are *cis* to each other, as in both the *cis* trithiocarbonate and the *cis* carbonate. This can be

TABLE I

NUCLEAR MAGNETIC RESONANCE SPECTRA OF *cis*- AND *trans*-4,5-DIMETHYL-1,3-DITHIOLANE-2-THIONE AND 4,5-DIMETHYL-1,3-DIOXOLAN-2-ONE

	τ-Values					
	Methyl hydrogens			Ethylenic hydrogen		
Compound	*cis*	*trans*	$c - t$	*cis*	*trans*	$c - t$
4,5-Dimethyl-1,3-dithiolane-2-thione[a]	8.48	8.38	0.10	5.62	5.89	−0.27
4,5-Dimethyl-1,3-dioxolan-2-one[b]	8.63	8.59	0.04	4.16	4.34	−0.18

[a] 10% solution in carbon tetrachloride measured at 60 Mc. in p.p.m. from tetramethylsilane as an internal standard. [b] Ref. 7; 39% solution in carbon tetrachloride measured at 60 Mc. in p.p.m. from tetramethylsilane as an internal standard.

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[1] This paper comprises a portion of a dissertation to be submitted by A. Drucker in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of the Polytechnic Institute of Brooklyn.

[2] (a) C. G. Overberger and J. J. Ferraro, *J. Org. Chem.*, **27**, 3539 (1962); (b) C. G. Overberger, J. J. Ferraro, and F. W. Orttung, *ibid.*, **26**, 3458 (1961); (c) C. G. Overberger and H. Aschkenasy, *ibid.*, **25**, 1648 (1960); *J. Am. Chem. Soc.*, **82**, 4357 (1960); (d) C. G. Overberger and P. V. Bonsignore, *ibid.*, **80**, 5427, 5431 (1958); (e) C. G. Overberger and A Lebovits, *ibid.*, **78**, 4792 (1956).

[3] (a) S. M. Iqbal and L. N. Owen, *J. Chem. Soc.*, 1030 (1960); (b) C. C. Price and P. F. Kirk, *J. Am. Chem. Soc.*, **75**, 2396 (1953).

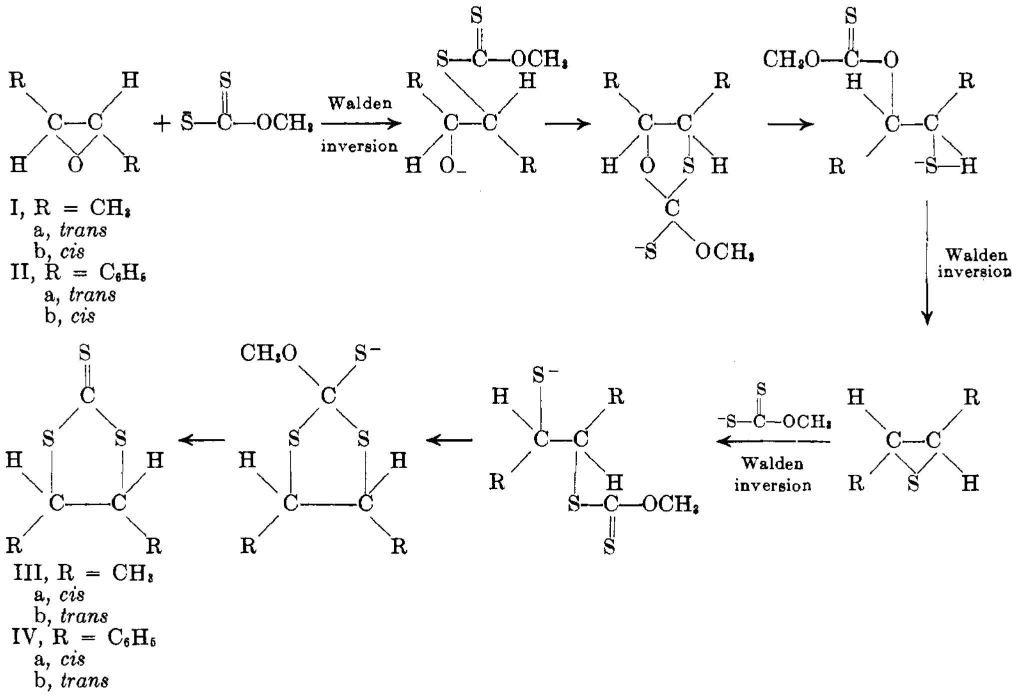
[4] E. E. van Tamelen, *ibid.*, **73**, 3444 (1951).

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

[6] R. Ketcham and V. P. Shah, *J. Org. Chem.* **28**, 229 (1963).

[7] F. A. L. Anet. *J. Am. Chem. Soc.*, **84**, 747 (1962).

SCHEME I



I, R = CH_3
a, *trans*
b, *cis*
II, R = C_6H_5
a, *trans*
b, *cis*

III, R = CH_3
a, *cis*
b, *trans*
IV, R = C_6H_5
a, *cis*
b, *trans*

attributed to the increased shielding of the methyl groups by each other as compared to less shielding of the methyl groups in the *trans* isomers. The chemical shifts for the ethylenic hydrogens occur in the reverse sense. The resonance appears at higher field strengths for both *trans* isomers where the ethylenic hydrogens are shielded by adjacent methyl groups to a greater extent than in the *cis* isomers. Only two peaks appear in the spectra of the trithiocarbonates, a multiplet for the ethylenic hydrogens and a doublet for the methyl hydrogens. The shapes of the respective peaks were essentially identical. The area of the peaks were determined by cutting them from the spectra and weighing them on an analytical balance. The area ratio was found to be 3:1 CH_3:C–H. These observations are consistent with the indicated trithiocarbonate structures.

Further evidence for the isomer assignments was obtained by converting the *cis* and *trans* trithiocarbonates to the corresponding dithiocarbonates (*cis*- and *trans*-4,5-dimethyl-1,3-dithiolan-2-one) and comparing their infrared spectra with the spectrum of L-(−)-4,5-dimethyl-1,3-dithiolan-2-one recently reported by Corey and Mitra.[8] The optically active isomer, m.p. 51–51.5°, is necessarily *trans* and the infrared spectrum should be the same as the *trans* DL isomer, m.p. 41–42.5°, prepared from IIIb. The oxidations to the 2-one derivatives were performed with mercuric acetate in glacial acetic acid according to the general procedure of Challenger, *et al.*[9] The *cis* isomer could not be crystallized. The spectrum discussed later is that from liquid material which was washed and dried free of solvent after isolation from the reaction mixture. Insufficient material was available for further purification. However, its carbon and hydrogen analysis was in close agreement with the theoretical values. The optically active isomer was reported to show strong bands at 6.02, 11.4, and 11.6 μ and a medium-intensity doublet at 5.7 and 5.8 μ (presumably overtones of the 11.4 and 11.6-μ bands).[8] The *trans* DL isomer showed strong bands at 6.10 and 11.40 μ, a shoulder at 11.60 μ, and a medium-intensity doublet at 5.68 and 5.85 μ, whereas the *cis* isomer showed two strong bands at 6.07 and 11.6 μ and only one medium-intensity band at 5.78 μ. The closer correlation of the *trans* DL dithiocarbonate spectrum with the L-(−) isomer is apparent.

Indirect proof of the proposed mechanism was obtained by converting the *cis* oxide (Ib) to *cis*-2-butene episulfide by reaction with thiocyanate,[10a] followed by reaction of the episulfide with xanthate. The resulting trithiocarbonate had the identical infrared spectrum as the *trans* trithiocarbonate (IIIb) prepared directly from the *cis* oxide by reaction with xanthate.

meso- **and** DL-**2,3-Butanedithiol.**—The *cis* trithiocarbonate (IIIa) and the *trans* trithiocarbonate (IIIb) were readily converted to *meso*- and DL-2,3-butanedithiol, respectively, by reduction with lithium aluminum hydride in ether solution at room temperature. Three derivatives of each dithiol were prepared and their melting points are listed in Table II. The *racemic* isomers melt higher than the *meso* isomers in all instances. This trend is the reverse of that found[10b] for a series of derivatives of *meso*- and DL-2,3-butanediol, where the *meso* isomers are higher melting. Two of these derivatives are listed in Table II.

The infrared absorption peaks of *meso*- and DL-2,3-butanedithiol, together with the spectrum of an optically active sample[11] prepared by a different route, are listed in Table III. The spectrum of the *racemic* dithiol is essentially identical with the optically active sample, whereas the *meso* isomer shows some significant

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[8] E. J. Corey and R. B. Mitra, *J. Am. Chem., Soc.*, **84**, 2938 (1962).

[9] F. Challenger, E. A. Mason, E. C. Holdsworth, and R. Emmott, *J. Chem. Soc.*, 292 (1953).

[10] (a) N. P. Neureiter and F. G. Bordwell, *J. Am. Chem. Soc.*, **81**, 578 (1959); (b) F. M. Robertson and A. C. Neish, *Can. J. Res.*, **26B**, 737 (1948).

[11] The authors are indebted to Professor E. J. Corey, Harvard University, for providing the infrared spectrum of the optically active isomer; see ref. 8 for the general method of preparation.

TABLE II

DERIVATIVES OF *meso*- AND DL-2,3-BUTANEDITHIOL AND 2,3-BUTANEDIOL

2,3-Butanedithiol derivatives	Melting point, °C.	
	meso	DL
Bis-*p*-nitrobenzoate	154–156	185–186.5
Bisphenylurethane	208–210	229–231[a]
Bis-α-naphthylurethane	230–232	236–238
2,3-Butanediol derivatives		
Bis-*p*-nitrobenzoate	193–193.5	128–128.5
Bis-3,5-dinitrobenzoate	247–247.5	185–186

[a] Iqbal and Owen[3a] reported m.p. 208–209° for this derivative of DL-2,3-butanedithiol. The apparent discrepancy is due to a typographical error; the actual value they obtained was 228–229° (private correspondence).

TABLE III

INFRARED ABSORPTION PEAKS OF OPTICALLY ACTIVE, DL- AND *meso*-2,3-BUTANEDITHIOL IN THE 6.5- TO 11.5-μ REGION

Optically active[a]	DL	*meso*
6.90 (s)	6.89 (s)	6.91 (s)
7.25 (s)	7.26 (s)	7.27 (s)
7.62 (sh)	7.65 (sh)	7.59 (m)
7.70 (m)	7.71 (m)	7.73 (m)
		8.00 (sh)
8.05 (m)	8.00 (w)	8.09 (m)
8.23 (m)	8.23 (m)	8.23 (m)
		8.33 (sh)
8.50 (w)		
8.72 (sh)		8.74 (w)
8.82 (w–m)	8.85 (w–m)	
9.05 (m)	9.00 (w–m)	
9.24 (sh)	9.28 (sh)	9.20 (sh)
9.40 (m)	9.40 (m)	9.35 (m–s)
		9.51 (sh)
9.80 (w–m)	9.82 (w–m)	9.95 (w–m)
10.00 (w–m)	10.02 (m)	10.15 (m)
10.13 (sh)	10.19 (w)	10.37 (m)
10.43 (w)	10.46 (w)	
11.47 (m)	11.49 (m)	11.50 (m)

[a] See ref. 11.

differences. Thus, the reduction of the trithiocarbonates occurred without racemization.

cis- **and** ***trans*-4,5-Diphenyl-1,3-dithiolane-2-thione.**—*trans*- and *cis*-Stilbene oxide were converted to the *cis* trithiocorbonate (IVa) and the *trans* trithiocarbonate (IVb), respectively, by reaction with potassium methyl xanthate in methanol solution at room temperature for five days. The reaction proceeded without difficulty in the case of the *cis* oxide; a 67% yield was obtained with m.p. 156.5–157.5°. However, xanthate reaction with the *trans* oxide gave only an 18% yield of *cis* trithiocarbonate and chromatographic separation on alumina followed by recrystallization from large volumes of *n*-hexane were required to isolate pure product, m.p. 123.5–124.5°. Although the yield of *cis* isomer was low, no *trans* isomer was formed since all of the yellow material in the crude solids isolated from the reaction mixture was accounted for in the chromatography (all trithiocarbonates are bright yellow compounds). The low yield of the *cis* trithiocarbonate may be due to the instability of the intermediate *trans* stilbene episulfide. Culvenor and co-workers[12] were unsuccessful in their attempt to prepare stilbene sulfide by the reaction of stilbene oxide, presumably the *trans* isomer, with thiourea. The only products obtained were stilbene, sulfur, and urea. Ketcham and Shah[6] were able to prepare *trans*-stilbene sulfide, but it slowly decomposed when stored at room temperature unprotected from light. The xanthate reaction with *trans*-stilbene oxide was carried out at room temperature in daylight. If the ring opening of the intermediate *trans*-stilbene sulfide by xanthate is slow, the possibility of decomposition must be considered. Another possible explanation is based on the steric factor. It was found that the reaction of *trans*-2,3-epoxybutane with xanthate was considerably slower than with the *cis* isomer and the yield of trithiocarbonate was lower (see Experimental section). Backside attack of xanthate in the reactions in which the epoxide and episulfide rings are opened may be more difficult in the case of the *trans* isomer because of greater steric hindrance provided by the ring substituents. This effect would be more pronounced when the bulkier phenyl groups are involved.

The *cis–trans* assignments were verified by a comparison of the n.m.r. spectra of the trithiocarbonates with the spectra of related 1,2-diphenyl five-membered ring compounds. It was felt that the most interesting model compounds for this study would be the oxygen analogs, *i.e.*, *cis*- and *trans*-4,5-diphenyl-1,3-dioxolan-2-one. The *cis*- and *trans* cyclic carbonates were prepared by the condensation of *meso*- and DL-hydrobenzoin, respectively, with diethyl carbonate, according to the procedure of Sarel.[13] The *cis* isomer melted at 126.5–128° and the *trans* isomer melted a 110–111.5°. Sarel, *et al.*,[14] reported the preparation of a 4,5-diphenyl-

TABLE IV

NUCLEAR MAGNETIC RESONANCE SPECTRA OF *cis*- AND *trans*-1,2-DIPHENYL ISOMERS

Compound	τ-Values					
	cis	*trans*	*c − t*	*cis*	*trans*	*c − t*
4,5-Diphenyl-1,3-dithiolane-2-thione[a]	2.97	2.76	0.21	4.33	4.35	−0.02
4,5-Diphenyl-1,3-dioxolan-2-one[a]	3.15	2.73	0.42	4.23	4.69	−0.46
1,2-Diphenylcyclopentane[b]	3.22	3.01	0.21	6.68	7.00	−0.32
3,4-Diphenylcyclopentanone[c]	3.10	2.83	0.27	6.17	6.52	−0.35
1,2-Diphenylcyclopropane[d]	3.04	2.87	0.17	7.55	7.87	−0.32
1,2-Bis(*p*-chlorophenyl)cyclopropane[e]	3.08	2.73	0.35	7.63	7.90	0.27
Stilbene oxide[f]	2.81	2.61	0.20	5.63	6.12	−0.49
Stilbene sulfide[f]	2.85	2.64	0.21	5.60	6.02	−0.42

[a] *Ca.* 8% solution in deuteriochloroform measured at 60 Mc. in p.p.m. from tetramethylsilane (TMS) as an internal standard. [b] Ref. 15; in carbon tetrachloride solution measured from TMS as an internal standard at 60 Mc. [c] Ref. 15; value of 5% solution in deuteriochloroform with TMS. [d] Ref. 15; calculated from value obtained from extrapolation of infinite dilution in carbon tetrachloride at 40 Mc. in p.p.m. relative to water. [e] C. G. Overberger and J. P. Anselme, unpublished results; in carbon tetrachloride solution measured in p.p.m. from TMS. [f] Ref. 6, measured in deuteriochloroform at 60 Mc. with TMS.

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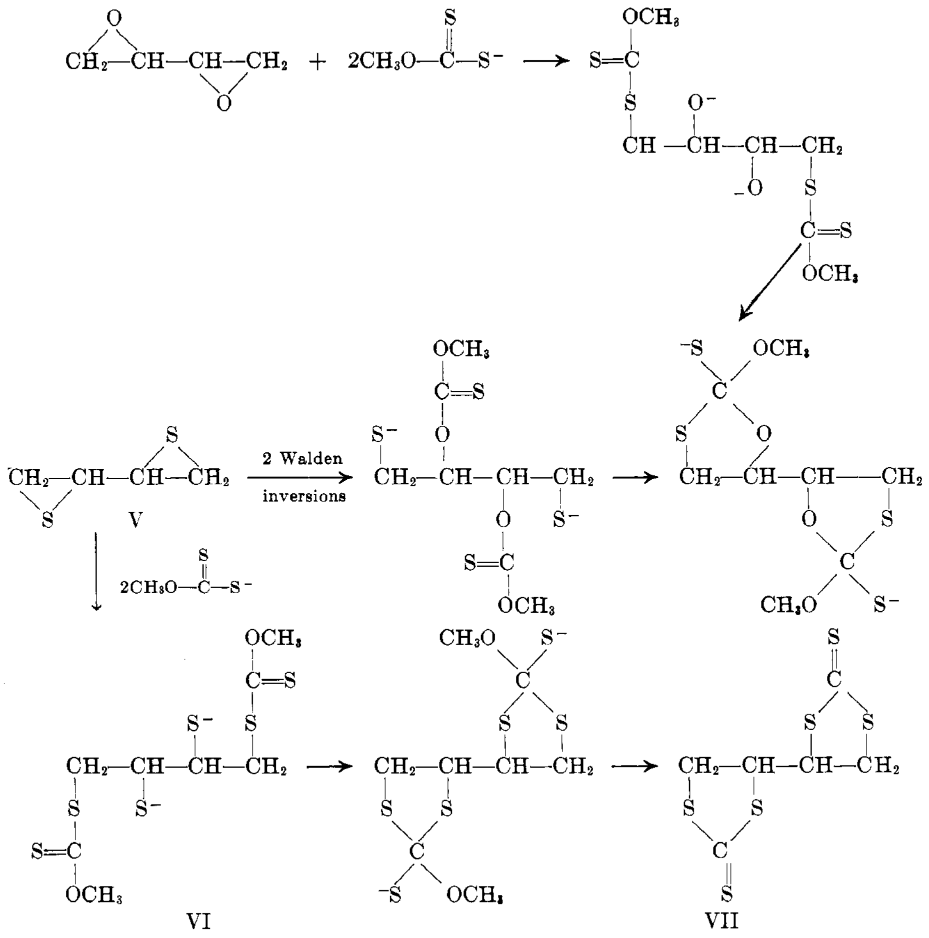
(12) C. C. J. Culvenor, W. Davies, and N. S. Heath, *J. Chem. Soc.*, 278 (1949).

(13) S. Sarel and L. A. Pohoryles, *J. Am. Chem. Soc.*, **80**, 4596 (1958).

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

SCHEME II



1,3-dioxolan-2-one, m.p. 127°, from hydrobenzoin. This evidently was the *cis* isomer.

The chemical shifts observed in the n.m.r. spectra of the isomeric pairs of trithiocarbonates and carbonates are shown in Table IV. A significant aspect of the spectra is the appearance of the aromatic hydrogen resonance as sharp singlets in both *trans* isomers and as unsymmetrical complex multiplets in both *cis* isomers. Similar results were obtained by Curtin, *et al.*[15] for the *cis* and *trans* isomers of 1,2-diphenylcyclopentane and 3,4-diphenylcyclopentanone.

The resonance of the phenyl groups of all the *cis* isomers mentioned before are shifted to higher field strengths relative to the *trans* compounds (Table IV). This is due to the closer proximity of the phenyl groups to each other in the *cis* compounds, where phenyl–phenyl shielding occurs to a greater extent than in the *trans* isomers.

The α-hydrogen spectra of the *cis* and *trans* trithiocarbonates and carbonates were sharp singlets. Curtin[16] reported that the α-hydrogen resonances for both *cis* and *trans* diphenylcyclopentane appeared as multiplets. These differences can be attributed to the splitting of the α-hydrogens by the ring methylene hydrogens in the cyclopentane cases, since these protons are not present in the trithiocarbonates and carbonates.

The α-hydrogen resonance of all the *trans* isomers are shifted to higher field strengths. Again, this can be attributed to increased phenyl–α-proton shielding in the *trans* isomers relative to the *cis* isomers. The low value of τ-*cis*–τ-*trans* for the trithiocarbonates is difficult to explain.

Data for four *cis–trans* isomeric pairs of 1,2-diphenyl three-membered ring compounds are included in Table IV. The trends in chemical shifts discussed earlier, *i.e.*, a positive value for τ-*cis*–τ-*trans* for the phenyl proton resonance and a negative value for the α-proton resonance, appear to be general in nature.

***meso*- and DL-α,α′-Stilbenedithiol.**—Reduction of trithiocarbonates IVa and IVb with lithium aluminum hydride in tetrahydrofuran at reflux gave the *meso*- and DL-α,α′-stilbenedithiols in 49% and 40% yields, respectively. When the reductions were carried out at room temperature in ether solution, the *meso* dithiol was formed in low yield and the *trans* trithiocarbonate gave a mixture of products from which any DL dithiol which may have formed could not be isolated.

The *meso* dithiol, identified as the diacetate and bisphenylurethane derivatives, melted at 220.5–222.5° and the DL dithiol, identified as the diacetate, melted at 70–71°. The melting points of the isomers did not change on standing in air at room temperature for several weeks, indicating that oxidation to disulfide products did not occur.

DL-1,2,3,4-Butanetetrathiol.—The reaction of DL-butadiene dioxide with potassium methyl xanthate afforded DL-butadiene-1,2:3,4-bis(trithiocarbonate) (VII) in 54% yield. The product was soluble in concentrated sulfuric acid, and it was recovered unchanged

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(15) D. Y. Curtin, H. Gruen, Y. G. Hendrickson, and H. E. Knipmeyer, *J. Am. Chem. Soc.*, **83**, 4838 (1961); **84**, 863 (1962).

(16) D. Y. Curtin, H. Gruen, and B. A. Shoulders, *Chem. Ind.* (London), 1205 (1958).

from the solution as shown by the constancy of the infrared spectrum. However, it was insoluble in a variety of refluxing organic solvents. It did not melt, but rather passed through a series of color changes with increasing temperature, going from the original yellow to orange to red and finally decomposing to a black tar at 225–235°. Elemental analysis, which was performed on the precipitate from the reaction mixture (since the product could not be purified by recrystallization or distillation), was in agreement with the calculated values.

The reaction of xanthate with monosubstituted epoxides has been shown to give the trithiocarbonate of inverted configuration.[17] Initial attack by xanthate occurs at the unsubstituted carbon atom and the only inversion which takes place is in the closing of the episulfide ring. It is reasonable to predict a similar mechanism for the reaction of DL-butadiene dioxide with xanthate. The two epoxide rings are opened *via* xanthate attack at positions 1 and 4, followed by closing of the episulfide rings with inversions at the asymmetric centers 2 and 3. These steps do not necessarily occur simultaneously and the mechanism (Scheme II) is written in this manner for convenience. The over-all effect of the two inversions is the formation of *racemic* episulfide (V). Since further attack by xanthate occurs at the nonasymmetric positions 1 and 4 and the closing of the trithiocarbonate rings does not involve the asymmetric centers, the resulting bistrithiocarbonate is the *racemic* form.

The infusibility and poor solubility of the reaction product (VI) raises the question of polymer formation. Intermolecular reactions which could lead to polymer would have to occur beyond the episulfide (V) stage. Reactions of this nature in earlier steps would give products containing oxygen atoms, which is in conflict with the element analysis for $C_6H_6S_6$. A sulfur anion of intermediate VI could conceivably attack the carbon atom of a thione group in another molecule followed by elimination of methoxide to form noncyclic trithiocarbonate (although intramolecular cyclization would be strongly favored). The infrared spectrum of the product showed only one strong absorption peak in the C=S stretching region at 1052 cm.$^{-1}$. The spectrum in this region is sensitive to the structural environment, and the presence of cyclic and linear trithiocarbonate functions would be expected to show more than one band. In any event, assuming the slight possibility of polymerization, the product obtained on reduction of the trithiocarbonate would be the *racemic* tetrathiol since the bonds of the asymmetric carbon atoms 2 and 3 would not be affected. The contention that only one isomer of the tetrathiol formed is supported by the formation of a sharp melting tetraacetate derivative in high yield.

The reduction of the *dl*-bistrithiocarbonate (VII) to *dl*-1,2,3,4-butanetetrathiol was carried out by adding it as the solid to lithium aluminum hydride in ether at room temperature. By analogy with the conversion of trithiocarbonates IIIa and IIIb to *meso*- and *dl*-2,3-butanedithiol, the reduction in this instance also proceeds without racemization, and the tetrathiol is the *racemic* isomer. The –SH infrared absorption band at 2550 cm.$^{-1}$ is usually of weak to medium intensity, as was found for the four dithiols previously discussed. The *dl* tetrathiol, however, had a very strong absorption band at 2550 cm.$^{-1}$.

Experimental

***trans*-4,5-Dimethyl-1,3-dithiolane-2-thione.**—A slightly modified procedure of Iqbal and Owen[3a] was used. A solution of potassium methyl xanthate was prepared by dissolving 35.1 g. (0.625 mole) of potassium hydroxide and 57.0 g. (0.75 mole) of carbon disulfide in 150 ml. of methanol. To this solution was added 18.0 g. (0.25 mole) of *cis*-2,3-epoxybutane,[18] $n^{20}\text{D}$ 1.3834 (lit.[19] $n^{20}\text{D}$ 1.3828), in small portions with shaking at room temperature. The solution was allowed to stand at room temperature for 4 days. The solid precipitate, most of which formed over the first 12 hr., was filtered and washed with several portions of water until the filtrate was colorless. After drying *in vacuo* at room temperature, 13.8 g. of a yellow solid was obtained, m.p. 41.5–42.5°. More product was isolated by evaporating the solvent from the reaction filtrate, stirring the residual solids with water for several hours, filtering the undissolved solids, washing with water as before, and drying. The recovery was 15.7 g., m.p. 41–42°. The total yield was 72%. An analytical sample was obtained by recrystallization from petroleum ether (75 ml./1 g.) as long yellow needles, m.p. 42.5–43.2° (lit.[3a] m.p. 40–41°). Infrared analysis revealed C=S absorption at 1088 (s), 1053 (s), and 1010 (m) cm.$^{-1}$ (pure liquid); lit.[3a] 1093 (s) and 1058 (s) cm.$^{-1}$ (in carbon tetrachloride).

Anal. Calcd. for $C_5H_8S_3$: C, 36.55; H, 4.91; S, 58.54. Found: C, 36.66; H, 5.17; S, 58.72.

***cis*-4,5-Dimethyl-1,3-dithiolane-2-thione.**—To a solution of potassium methyl xanthate prepared by dissolving 41.9 g. (0.75 mole) of potassium hydroxide and 68.1 g. (0.9 mole) of carbon disulfide in 190 ml. of methanol was added 21.5 g. (0.3 mole) of *trans*-2,3-epoxybutane,[18] $n^{30}\text{D}$ 1.3677 (lit.[19] $n^{25}\text{D}$ 1.3705), in small portions with shaking at room temperature. The reaction mixture was allowed to stand at room temperature for 13 days. The formation of a precipitate was slower than in the reaction of *cis*-2,3-epoxybutane. About 3 to 4 days were required for the formation of a precipitate comparable in quantity to that formed after 12 hr. in the xanthate reaction of the *cis* isomer. Since the *cis* trithiocarbonate existed as an oil prior to purification, isolation of the product required a modification of the prior procedure. Solvent was removed *in vacuo* at 30° and to the residual solids were added 250 ml. of ether and 150 ml. of water. The ether layer was separated, washed with water, dried over anhydrous sodium sulfate, and filtered. The ether was removed *in vacuo* at room temperature. The residual cloudy oil, 37.0 g., was distilled at 101° (0.18 mm.) to give 26.2 g. (53%) of a bright yellow oil which crystallized immediately when touched to Dry Ice. The crystals had m.p. 37–39.5°. The C=S absorption occurred at 1093 (s), 1053 (s), and 1031 (s) cm.$^{-1}$ (pure liquid).

Anal. Found: C, 36.89; H, 5.24; S, 58.72.

***meso*- and *dl*-2,3-Butanedithiol.**—*cis*- and *trans*-4,5-Dimethyl-1,3-dithiolane-2-thione were reduced to the *meso* and *dl* dithiols, respectively, with lithium aluminum hydride in ether solution according to the procedure of Iqbal and Owen.[3a] The *meso* isomer, obtained in 42% yield, had b.p. 62–64° (35 mm.), $n^{25}\text{D}$ 1.5171; lit.[20] b.p. 67° (29 mm.), $n^{25}\text{D}$ 1.5173.

Anal. Calcd. for $C_4H_{10}S_2$: C, 39.30; H, 8.25; S, 52.46. Found: C, 39.12; H, 8.09; S, 52.24.

The *dl* isomer, obtained in 34% yield, had b.p. 63–65° (35 mm.), $n^{25}\text{D}$ 1.5179; lit.[3a] b.p. 50–51° (22 mm.), $n^{21}\text{D}$ 1.5315.

Anal. Found: C, 39.45; H, 8.15; S, 52.28.

The bis-*p*-nitrobenzoates of the isomeric dithiols were prepared by heating a mixture of the dithiol with excess *p*-nitrobenzoyl chloride in dry pyridine in a boiling water bath for 1 hr. The *dl* derivative had m.p. 185–186.5° (pale yellow plates from nitro benzene–methanol). The *meso* derivative had m.p. 154–156° (tan needles from acetone).

Anal. Calcd. for $C_{18}H_{16}N_2O_6S_2$: C, 51.42; H, 3.84; N, 6.66; S, 15.25. Found for *dl* isomer: C, 51.48; H, 4.00; N, 6.73; S, 14.96. Found for *meso* isomer: C, 51.63; H, 3.87; N, 6.51.

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(17) A. M. Creighton and L. N. Owen, *J. Chem. Soc.*, 1024 (1960).

(18) The samples of *cis*- and *trans*-2,3-epoxybutane were obtained through the courtesy of Dr. E. J. Vandenberg, Hercules Powder Co., Wilmington, Del.

(19) S. Winstein and H. J. Lucas, *J. Am. Chem. Soc.*, **61**, 1576 (1939).

(20) Reference 2a; the values given are for 2,3-butanedithiol of unspecified isomer composition.

The bisphenylurethane and bis-α-naphthylurethanes were prepared by adding a drop of dry pyridine to a solution of the dithiol in excess phenyl isocyanate and α-naphthyl isocyanate, respectively, and heating in a boiling water bath for 10 min. The α-naphthylurethanes were insoluble in large volumes of several refluxing solvents and, therefore, the analyses were performed on unrecrystallized samples. The phenylurethanes were recrystallized from methanol, in which the *meso* compound was much more soluble.

The bisphenylurethan *dl* isomer had m.p. 229–231°, lit. m.p. 228–229° (see Table II, footnote *a*).

Anal. Calcd. for $C_{18}H_{20}N_2O_2S_2$: C, 59.97; H, 5.59; N, 7.77; S, 17.79. Found: C, 59.46; H, 5.49; N, 7.52.

The bisphenylurethane *meso* isomer had m.p. 208–210°.

Anal. Found: C, 59.77; H, 5.71; N, 7.75; S, 17.52.

The bis-α-naphthylurethane *dl* isomer had m.p. 236–238°.

Anal. Calcd. for $C_{26}H_{24}N_2O_2S_2$: C, 67.79; H, 5.25; N, 6.08. Found: C, 67.28; H, 5.41; N, 6.07.

The bis-α-naphthylurethane *meso* isomer had m.p. 230–232°.

Anal. Found: C, 67.44; H, 5.27; N, 6.07.

***trans*-4,5-Dimethyl-1,3-dithiolane-2-thione from *cis*-2-Butene Episulfide.**—The *cis* episulfide was prepared from *cis*-2,3-epoxybutane by reaction with thiocyanate according to the procedure of Neureiter and Bordwell,[10a] b.p. 41.5–43° (131 mm.), $n^{23.5}D$ 1.4761, infrared bands at 1147 (s) and 1028 (s) cm.$^{-1}$; lit.[10a] b.p. 51–51.5 (130 mm.), $n^{20}D$ 1.4765, infrared at 1146 (s) and 1029 (s) cm.$^{-1}$. To a solution of potassium methyl xanthate prepared by adding 1.79 g. (0.032 mole) of potassium hydroxide and 2.81 g. (0.037 mole) of carbon disulfide in 12 ml. of methanol was added 0.70 g. (0.008 mole) of *cis*-2-butene episulfide. After standing at room temperature for 3 days, half the solvent was evaporated and 20 ml. of water was added with stirring. The yellow solids were filtered and washed with several portions of water. The dry product weighed 1.28 g. (69%), m.p. 40.5–42°. The infrared spectrum was identical with that of the *trans* trithiocarbonate prepared by the reaction of *cis*-2,3-epoxybutane with xanthate.

***cis*- and *trans*-4,5-Dimethyl-1,3-dithiolan-2-one.**—The *cis* and *trans* trithiocarbonates (IIIa and IIIb) were oxidized to the 2-one derivative according to a general procedure of Challenger, *et al.*,[9] for this type of compound. To a solution of 5.0 g. of mercuric acetate in 50 ml. of glacial acetic acid was added dropwise with stirring a solution of 0.50 g. of trithiocarbonate in 6 ml. of chloroform. After standing for 15 hr., the white precipitate was filtered and washed with chloroform. The combined filtrate and chloroform wash was diluted with 70 ml. of water. The acid layer was extracted with several small portions of chloroform. The combined chloroform layers were washed with two 10-ml. portions of water and dried over anhydrous sodium sulfate. After filtration the chloroform was distilled *in vacuo* at room temperature. The residue was an oil in both cases. The *trans* isomer, 0.29 g. (64%), crystallized readily in the cold and had m.p. 41–41.5°, which remained unchanged after two recrystallizations from petroleum ether.

Anal. Calcd. for $C_5H_8OS_2$: C, 40.51; H, 5.44; S, 43.26. Found: C, 40.88; H, 5.49; S, 43.19.

The *cis* isomer could not be crystallized.

Anal. Found: C, 40.51; H, 5.28.

***trans*-4,5-Diphenol-1,3-dithiolane-2-thione.**—*cis*-Stilbene oxide was prepared by the reaction of *cis*-stilbene with perbenzoic acid[21] according to the procedure of Lynch and Pausacker.[22] A solution of potassium methyl xanthate was prepared by dissolving 7.50 g. (0.13 mole) of potassium hydroxide and 12.17 g. (0.16 mole) of carbon disulfide in 35 ml. of methanol. To this solution was added 10.46 g. (0.053 mole) of *cis*-stilbene oxide. The reaction mixture, which never became homogeneous, was stirred at room temperature for 5 days. The yellow solids were filtered, washed with several portions of water until the filtrate was colorless, and dried *in vacuo* at room temperature. The recovery was 11.50 g., m.p. 148–155°. Recrystallization from hexane–benzene yielded 9.07 g. of small lustrous plates, m.p. 156.5–157.5°. A second crop of 1.30 g., m.p. 155–157°, also was obtained. The total yield was 67%. Further recrystallization gave an analytical sample, m.p. 157–158°. The infrared spectrum showed only one strong absorption band in the C=S stretching region at 1068 cm.$^{-1}$ (potassium bromide disk).

Anal. Calcd. for $C_{15}H_{12}S_3$: C, 62.45; H, 4.20; S, 33.35. Found: C, 62.75; H, 4.01; S, 33.60.

***cis*-4,5-Diphenyl-1,3-dithiolane-2-thione.**—To a solution of potassium methyl xanthate prepared by dissolving 11.28 g. (0.20 mole) of potassium hydroxide and 18.24 g. (0.24 mole) of carbon disulfide in 65 ml. of methanol was added 15.68 g. (0.08 mole) of *trans*-stilbene oxide (prepared as before). The mixture was stirred at room temperature for 5 days. The solids were filtered, pulverized, washed with several portions of water, and dried *in vacuo* at room temperature. The recovery was 16.60 g., m.p. 95–121°. Two grams of this solid was purified by chromatography on an alumina column (Fisher Scientific Co., neutral grade, Brockman activity I). Elutions were made with increasing ratios of benzene (solvent)–hexane (nonsolvent). The bright yellow eluents yielded a total of 1 g. of solid, average m.p. 115–120°. Recrystallization from hexane gave 0.50 g. of yellow needles, m.p. 123.5–124.5°. The total yield was 18%. A strong absorption band appeared in the infrared spectrum in the C=S stretching region at 1060 cm.$^{-1}$ and a shoulder at 1075 cm.$^{-1}$ (potassium bromide disk).

Anal. Found: C, 62.54; H, 4.48; S, 33.33.

***meso*- and *dl*-α,α'-Stilbenedithiol.**—The *cis* and *trans* trithiocarbonates (IVa and IVb) were reduced to *meso*- and *dl*-α,α'-stilbenedithiol, respectively, with lithium aluminum hydride. To 0.30 g. (0.0079 mole) of lithium aluminum hydride in 8 ml. of tetrahydrofuran was added a solution of 1.00 g. (0.0035 mole) of the trithiocarbonate in 12 ml. of tetrahydrofuran dropwise over 25 min. with stirring at room temperature. The reaction mixture was heated to reflux for 7 hr. and then it was allowed to stand at room temperature for 11 hr. After cooling to 0°, 3 ml. of water was added dropwise (caution) to decompose the excess hydride and the mixture was then acidified with cold 6 *N* hydrochloric acid. The solution was then extracted with 50 ml. of ether. The acid layer was extracted with 10 ml. of ether and the combined ether layers were washed with saturated aqueous sodium chloride. The *meso* isomer was not completely soluble in ether and 100 ml. of benzene was required to dissolve the residual white solids suspended in the acid layer. The organic layers were dried over anhydrous sodium sulfate. After filtration and removal of solvent *in vacuo* at room temperature, 0.80 g. of crude product was obtained in each case.

Final purification was effected as follows. The crude *dl* isomer, m.p. 53–62°, was recrystallized twice from hexane to give 0.34 g. (40%) of product, m.p. 70–71°.

Anal. Calcd. for $C_{14}H_{14}S_2$: C, 68.24; H, 5.73; S, 26.03. Found: C, 68.31; H, 5.90; S, 26.27.

The diacetate, m.p. 119–121° (methanol), was prepared by adding excess acetic anhydride to the *dl* dithiol in dry pyridine solution.

Anal. Calcd. for $C_{18}H_{15}O_2S_2$: C, 65.42; H, 5.49; S, 19.41. Found: C, 65.18; H, 5.65; S, 19.65.

The crude *meso* isomer, m.p. 205–215°, was recrystallized twice from benzene to give 0.42 g. (49%) of product, m.p. 220.5–222.5°.

Anal. Found: C, 68.57; H, 5.97; S, 26.00.

The diacetate, m.p. 188–190° (methanol), was prepared as before.

Anal. Found: C, 65.17; H, 5.52; S, 19.21.

The bisphenylurethane, m.p. 258–260° dec., from ethyl acetate, was prepared by refluxing a solution of the *meso* dithiol and excess phenyl isocyanate in decalin for 1 hr.

Anal. Calcd. for $C_{28}H_{24}N_2O_2S_2$: C, 69.39; H, 4.99; N, 5.78. Found: C, 68.68; H, 5.10; N, 5.67.

***cis*-4,5-Diphenyl-1,3-dioxolan-2-one.**—The procedure of Sarel, *et. al.*,[13] was used in this preparation. A mixture of 4.29 g. (0.02 mole) of *meso*-hydrobenzoin, which was prepared by the reduction of benzyl with sodium borohydride,[23] 2.98 g. (0.025 mole) of diethyl carbonate and 0.041 g. (0.00075 mole) of sodium methoxide was heated to 130° in an oil bath kept at 150–160°. As ethanol formed, the temperature fell to 107°. The ethanol was removed by distillation and the temperature went to 130° where it was maintained for 1 hr. Excess diethyl carbonate was distilled at reduced pressure. After cooling to room temperature, the residual white solid was dissolved in 75 ml. of benzene, washed with water, dried over anhydrous sodium sulfate, and filtered. The benzene was distilled *in vacuo*. The residue, 4.49 g., m.p. 115–122°, was recrystallized twice from 95% ethanol to give 3.00 g.

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(21) "Organic Syntheses," Coll. Vol. I, H. Gilman and A. H. Blatt, Ed., John Wiley and Sons, Inc., New York, N. Y., 1941, p. 431.

(22) B. M. Lynch and K. H. Pausacker, *J. Chem. Soc.*, 1525 (1955).

(23) L. F. Fieser, "Experiments in Organic Chemistry," 3rd Ed.; Rev., D. C. Heath and Co., Boston, Mass., 1957, p. 175.

(63%) of product, m.p. 126.5–128°. Sarel[14] reports m.p. 126° for the cyclic carbonate prepared from hydrobenzoin.

Anal. Calcd. for $C_{15}H_{12}O_3$: C, 74.98; H, 5.04. Found: C, 75.19; H, 4.88.

***trans*-4,5-Diphenyl-1,3-dioxolan-2-one.**—*dl*-Hydrobenzoin, prepared by the sequence *trans*-stilbene → *meso*-stilbene dibromide (Br_2)[24] → *dl*-hydrobenzoin monoacetate (silver acetate–wet glacial acetic acid) → *dl*-hydrobenzoin (sodium hydroxide–ethanol[25]), was converted in 74% yield by the prior procedure to the *trans* cyclic carbonate, m.p. 110–111.5°.

Anal. Found: C, 75.11; H, 5.11.

***dl*-Butadiene-1,2:3,4-bis(trithiocarbonate) (VII).**—A solution of 21.51 g. (0.25 mole) of *dl*-butadiene dioxide (obtained from the Koppers Co., Pittsburgh, Pa.) in 25 ml. of methanol was added over 10 min. to a stirred solution of 70.13 g. (1.25 moles) of potassium hydroxide and 114.21 g. (1.4 moles) of carbon disulfide in 325 ml. of methanol cooled to 0–5°. After about one-half of the dioxide was added, gentle reflux occurred and a precipitate formed. The mixture was kept at room temperature for 64 hr. The precipitate was filtered, washed with several portions of water, and dried *in vacuo* at room temperature. The product, 36.48 g. (54%), did not melt, but changed from yellow to orange to red to a black tar at 225–235°. It was insoluble in refluxing dimethylformamide, benzene, acetone, ether, and tetrahydrofuran, but dissolved readily in concentrated sulfuric acid at room temperature. The sulfuric acid solution was poured into ice–water and the precipitated product, after washing and drying, had an infrared spectrum which was identical with the original compound. The infrared spectrum showed only one absorption band in the C=S stretching region at 1052 cm.$^{-1}$ (Nujol).

Anal. Calcd. for $C_6H_6S_6$: C, 26.64; H, 2.24; S, 71.12. Found: C, 26.94; H, 2.48; S, 70.82.

***dl*-1,2,3,4-Butanetetrathiol.**—To 3.80 g. (0.1 mole) of lithium aluminum hydride in 175 ml. of anhydrous ether was added 5.41 g. (0.02 mole) of the bistrithiocarbonate (VII) in small portions over 10 min. with stirring. Immediately thereafter the reaction mixture began to reflux vigorously. After 19 hr. at room temperature all of the yellow solid had reacted. The mixture was cooled to 0° and water was added (caution) to decompose the excess hydride. After acidifying with cold 6 *N* hydrochloric acid, the ether layer was separated and washed with two 100-ml. portions of 10% aqueous sodium bicarbonate, two 50-ml. portions of water, dried over anhydrous sodium sulfate, and filtered. The ether was distilled *in vacuo* at room temperature. Fractional distillation of the residual oil, 4.03 g., yielded 1.57 g. (42%) of a water white liquid, b.p. 131–132° (0.6 mm.).

Infrared analysis revealed a high-intensity mercaptan absorption band at 2550 cm.$^{-1}$ (pure liquid).

Anal. Calcd. for $C_4H_{10}S_4$: C, 25.78; H, 5.40; S, 68.82. Found: C, 25.70; H, 5.80; S, 68.41.

The tetraacetate, prepared as before, had m.p. 87–88.5°.

Anal. Calcd. for $C_{12}H_{18}O_4S_4$: C, 40.65; H, 5.12; S, 36.18. Found: C, 40.83; H, 5.31; S, 35.90.

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[24] L. I. Smith and M. M. Falkof, "Organic Synthesis," Coll. Vol. III, E. C. Horning, Ed., John Wiley and Sons, Inc., New York, N. Y., 1955, p. 350.

[25] Reference 23, p. 189.

Seven-Membered Heterocycles. II. The Reactions of Benzo[*b*]thiepin 1,1-Dioxide[1-3]

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The light-catalyzed addition of 1 or 2 moles of bromine to benzo[*b*]thiepin 1,1-dioxide proceeded on the heterocyclic ring, while attempted additions of piperidine and hydrogen bromide failed. Electrophilic nitration of I gave two mononitro derivatives with substitution taking place on the benzene ring. The nitration of 2,3-dihydrobenzo[*b*]thiepin 1,1-dioxide formed an adduct which decomposed to 4-nitrobenzo[*b*]thiepin 1,1-dioxide.

In a previous paper[1] the literature of thiepin chemistry was reviewed and the synthesis of benzo[*b*]thiepin 1,1-dioxide described. This report deals with the chemical properties of that compound, in particular, thermal stability, the addition of bromine, and the effects of electrophilic and nucleophilic reagents.

When benzo[*d*]thiepin-2,4-dicarboxylic acid was placed in refluxing ethanol, sulfur and naphthalene-2,3-dicarboxylic acid resulted,[5,6] while benzo[*d*]thiepin 3,3-dioxide required elevated temperatures for conversion to naphthalene.[7] Unlike these materials benzo[*b*]thiepin 1,1-dioxide, a colorless crystalline solid, was stable in refluxing ethanol and distilled with slight decomposition when inserted into a Wood's metal bath at 250°; however, when it was refluxed in diethylcarbitol for several hours, resinification took place. In no experiment was naphthalene detected.

Thianaphthene sulfone undergoes facile nucleophilic additions with a variety of reagents such as piperidine, diethylamine, and hydrogen bromide to cite a few examples.[8] The product formed in each reaction is the 3-substituted (3-piperidino, 3-diethylamino, 3-bromo) 2,3-dihydrothianaphthene sulfone. When benzo[*b*]thiepin 1,1-dioxide was allowed to react with piperidine or with concentrated hydrobromic acid under conditions which resulted in addition to thianaphthene sulfone,[8] no reaction was observed and good recoveries of starting benzo[*b*]thiepin 1,1-dioxide were made. These observations indicate that the heterocyclic ring of benzo[*b*]thiepin 1,1-dioxide does not behave as an ordinary α,β-unsaturated sulfone.

While 2,3-dihydrobenzo[*b*]thiepin 1,1-dioxide added bromine readily in both warm chloroform or glacial acetic acid, the reaction of benzo[*b*]thiepin 1,1-dioxide (I) with bromine occurred only in the presence of sunlight or ultraviolet light. Addition of 1 mole of bromine produced a dibromide (II) in 71% yield which could add a 2nd mole of bromine to form a tetrabromide (III) (60% yield). Alternately, the tetrabromide was formed by the addition of 2 moles of bromine to I (84% yield).

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[1] For paper I in this series, see V. J. Traynelis and R. F. Love, *J. Org. Chem.*, **26**, 2728 (1961).

[2] Presented in part at the 135th National Meeting of the American Chemical Society, Boston, Mass., April, 1959.

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[4] Socony Mobil Fellow 1956–1957; Eastman Kodak Fellow 1957–1958; abstracted from part of the Ph.D. dissertation of R. F. Love, June, 1960.

[5] G. P. Scott, *J. Am. Chem. Soc.*, **75**, 6332 (1953).

[6] K. Dimroth and G. Lenke, *Ber.*, **89**, 2608 (1956).

[7] W. E. Truce and F. J. Lotspeich, *J. Am. Chem. Soc.*, **78**, 848 (1956).

[8] F. G. Bordwell and W. H. McKellin, *ibid.*, **72**, 1985 (1950).