

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TEXAS]

## Stereochemistry of Cyclic Sulfides and Sulfones. Relationship to *d*-Orbital Resonance of Sulfur<sup>1</sup>

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The theory that the failure to find the expected number of isomers of the disulfone and trisulfone of trithioacetaldehyde is attributable to the labilizing influence of two sulfonyl groups adjacent to a carbon-hydrogen bond has been tested experimentally. Two series of 4-substituted-1,3-dithiolanes have been synthesized and the members oxidized to the corresponding disulfones. In one series, each 4-substituted-1,3-dithiolane also contained a single substituent in the 2-position, so that the disulfones produced by oxidation of these compounds had two sulfonyl groups adjacent to a carbon-hydrogen bond. In the second series, each 4-substituted-1,3-dithiolane also contained *two different* substituents in the 2-position, so that the same isomerism was possible, but in the disulfones there was *not* a carbon-hydrogen bond adjacent to the two sulfonyl groups. In the latter series, two isomers of each disulfone were isolated. In the former series, no isomeric disulfones were isolated, and it was shown that the same disulfone was produced by oxidation of two isomeric 2,4-disubstituted-1,3-dithiolanes. This demonstrated clearly the significance of the carbon-hydrogen bond. In the disulfones, ionization undoubtedly occurred, and the carbanion did not maintain asymmetry, so that the thermodynamically more stable of the two isomeric disulfones was isolated, regardless of which dithiolane isomer was oxidized. The stabilization of the carbanion by the adjacent sulfonyl groups is attributed to resonance involving the *d*-orbitals of sulfur.

### INTRODUCTION

This research was initiated as a result of the observation by one of the authors that in the case of certain cyclic sulfones the number of stereoisomers expected on the basis of classical structural theory was not found. Although an explanation had been proposed some years earlier, there still was no direct experimental evidence to support it. This paper reports such evidence.

Trithioacetaldehyde was first prepared by Baumann and Fromm<sup>3</sup> and was found to exist in the form of two geometrical isomers (I and II). Later, Chattaway and Kellett<sup>4</sup> showed that the lower-melting isomer could be oxidized (by hydrogen peroxide followed by neutral permanganate) to a mixture of two isomeric monosulfones (III and IV) and the higher-melting isomer to a single monosulfone (V), thus establishing the geometrical structures of I and II. Baumann and Fromm oxidized the two isomers of trithioacetaldehyde separately (with potassium permanganate in sulfuric acid) and found that a single product, which melted above 340° and gave the correct analysis for a trisulfone, was obtained in each case. These products were studied by Lomnitz,<sup>5</sup> who found them to be identical according to all the tests that could be applied at that time. According to classical structural theory, there should be *two geometrical*

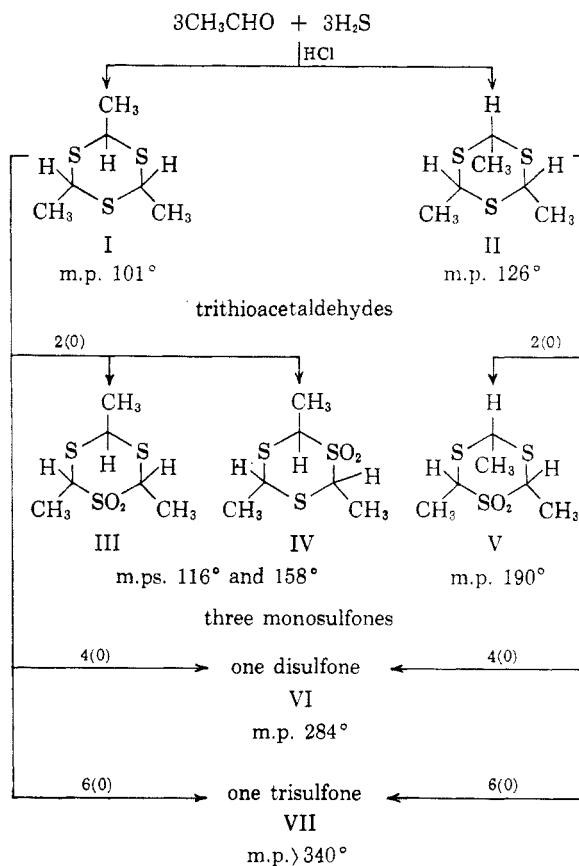


Fig. 1. Oxidation products of trithioacetaldehydes

(1) Presented at the Southwest Regional Meeting of the American Chemical Society, Houston, Tex., December 1, 1954. Taken from the M.A. thesis (1951) and the Ph.D. dissertation (1954) of C. C. Cheng, the University of Texas.

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(3) E. Baumann and E. Fromm, *Ber.*, **22**, 2600 (1889).

(4) F. D. Chattaway and E. G. Kellett, *J. Chem. Soc.*, 1352 (1930).

(5) E. Lomnitz, *Ber.*, **27**, 1673 (1894).

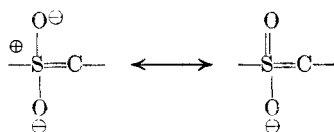
*isomers of the trisulfone*, one corresponding in the relationships of the methyl groups to each of the trithioacetaldehyde isomers. Baumann,<sup>6</sup> using less oxidizing agent (acidic permanganate) prepared a disulfone from each of the trithioacetaldehyde isomers, and again the products were found to be

(6) E. Baumann, *Ber.*, **24**, 2074 (1893).

identical. According to classical structural theory, there should be *three geometrical isomers of the disulfone*, analogous to the three isomeric monosulfones.

Thus, in the case of the monosulfone, the expected number of isomers was found, but in the case of the disulfone and the trisulfone, less than the expected number of isomers was found. These results received notice from Richter<sup>7</sup> and Connor<sup>8</sup> independently in 1943. The explanations offered were essentially the same; in the words of the latter author, "This may be attributed to the labilizing influence of the sulfone group upon hydrogen, allowing the formation of an anion which may readily change from one geometric form to the other." It should be observed that, in the case of both the disulfone and the trisulfone, there are *two* sulfonyl groups attached to a single  $-\text{CHCH}_3-$  group, while this is not true of the monosulfone.

The acidifying effect of sulfonyl groups has long been known. Evidence comes from solubility in alkali solutions,<sup>6</sup> titration curves,<sup>9</sup> and hydrogen exchange with deuterium.<sup>10</sup> Comparison of bicyclic and acyclic trisulfones led Doering and Levy<sup>11</sup> to propose that resonance involving the *d*-orbitals of sulfur may contribute to the acidifying effect, and others have interpreted kinetic<sup>12</sup> and equilibrium<sup>13</sup> data as supporting the theory of *d*-orbital resonance in sulfones. Thus there is now considerable agreement that sulfur may expand its octet to a decet or dodecet, and that resonance among such hybrids as



is responsible for stabilization of sulfonyl carbanions.

In the case of carbanions stabilized by carbonyl and nitro groups, a large amount of stereochemical data indicates that the carbanions do not retain optical asymmetry.<sup>14</sup> The stabilization of these carbanions is attributed to resonance among structures in which the original center of asym-

(7) G. H. Richter, *Textbook of Organic Chemistry*, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 269.

(8) R. Connor, in *Gilman's Organic Chemistry*, John Wiley and Sons, Inc., New York, N. Y., 1943, Vol. I, p. 927.

(9) E. Samén, *Arkiv Kemi, Mineral, Geol.*, **24B**, No. 6 (1947).

(10) J. Hochberg and K. F. Bonhoefer, *Z. phys. Chem.*, **184A**, 419 (1939).

(11) W. von E. Doering and L. K. Levy, *J. Am. Chem. Soc.*, **77**, 509 (1955).

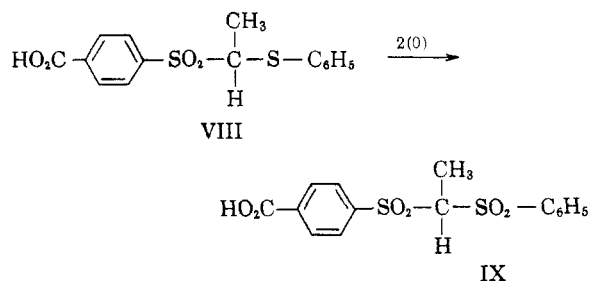
(12) R. L. Heppollette and J. Miller, *J. Chem. Soc.*, 2329 (1956).

(13) H. H. Szmant and G. Suld, *J. Am. Chem. Soc.*, **76**, 3400 (1956).

(14) See, for example, S. K. Hsü, C. K. Ingold, and C. L. Wilson, *J. Chem. Soc.*, 78 (1938); N. Kornblum, N. N. Lichtin, J. T. Patton, and D. C. Iffland, *J. Am. Chem. Soc.*, **69**, 307 (1947).

metry has become planar. Hence, the failure of carbanions stabilized by sulfonyl groups to retain optical asymmetry may be considered as *stereochemical support* of the theory of *d*-orbital resonance.

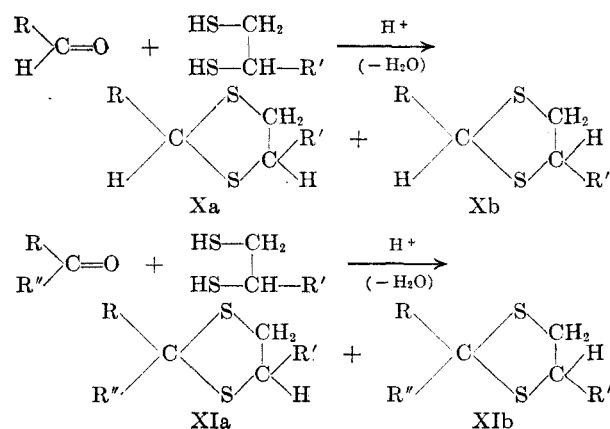
Some information of this type has been available for many years. For example, Kipping<sup>15</sup> found that the monosulfone VIII could be resolved but that its oxidation to the disulfone IX produced a racemic mixture which could not be resolved. Similar di-



sulfones in which the sulfonyl-flanked hydrogen was replaced by an alkyl group were successfully resolved. The results from the oxidation of trithioacetaldehyde appeared to fit into the same general pattern.

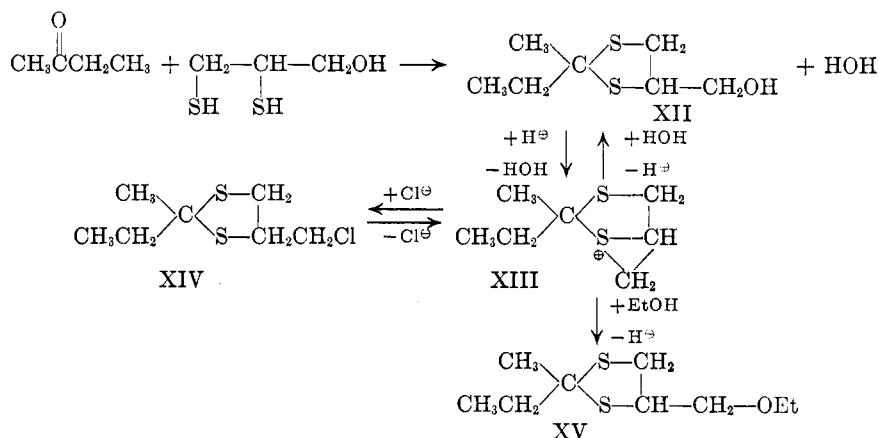
#### DISCUSSION

The most direct way to test the theory that it is the lability of the hydrogen which is responsible for the lack of stereoisomers of trithioacetaldehyde di- and trisulfones would be to synthesize the corresponding trimers of unsymmetrical thioketones and to determine the number of products obtained by oxidizing them to the di- and trisulfone stages. The authors were discouraged from this approach, however, by accounts in the literature of the frightful odor of thioketones<sup>16</sup> and turned to an alternate series of compounds possessing the necessary structural features and less intense odors. These were the 1,3-dithiolanes, which may be obtained from the condensation of 1,2-dithiols with carbonyl compounds. The reaction of an aldehyde or an unsymmetrical ketone with an unsymmetrical dithiol should produce two geometrically<sup>17</sup> isomeric 1,3-dithiolanes such as X and XI.



Oxidation of the isomeric 1,3-dithiolanes (X) from aldehydes would be expected to give only one disulfone because of the labile hydrogen, while oxidation of the isomeric 1,3-dithiolanes (XI) from unsymmetrical ketones would be expected to give the corresponding two isomeric disulfones, since these compounds would not contain a labile hydrogen on the carbon between the two sulfonyl groups.

Although a number of 1,3-dithiolanes have been prepared previously, most of these were derived from symmetrical reagents, so that no isomerism was possible. The ones capable of isomerism<sup>18,19</sup> were all of the type X and the only one of which



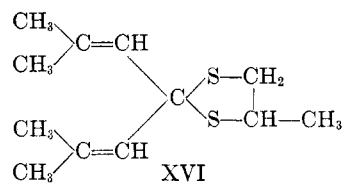
isomers were reported<sup>19</sup> had R = C<sub>6</sub>H<sub>5</sub>, R' = CH<sub>2</sub>OH. None of the corresponding sulfones have been reported.

All of the 1,3-dithiolanes which we synthesized were prepared from two dithiols, 1,2-propanedithiol and 2,3-dimercapto-1-propanol (BAL, British Anti-Lewisite). These were condensed with aldehydes and ketones to give the products listed in Tables I and II. The reaction was carried out conveniently by dissolving the carbonyl compounds and the dithiol in benzene or chloroform and passing gaseous hydrogen chloride into the mixture. In order to avoid replacing the hydroxyl group of BAL by chloride, however, it was necessary to use a modified procedure. The primary product from the condensation of BAL with carbonyl compounds is a β-thioalcohol (XII), and these are known to be extremely reactive toward nucleophilic reagents by virtue of stabilization of an intermediate cation as a sulfonium ion (XIII). Thus it was not surprising that when the condensation was effected by passing gaseous hydrogen chloride into a mixture of methyl ethyl ketone and BAL that the main product isolated was the chloromethyl compound,

XIV. Water was produced in the condensation reaction and was then converted into concentrated hydrochloric acid by the hydrogen chloride.

When the chloromethyl compound XIV was treated with alkali in water-ethanol-dioxane solution, the major product was XV, resulting from alcoholysis, along with some of the hydrolysis product, XII. It was more convenient to obtain XII and the other hydroxymethyl-1,3-dithiolanes, however, by carrying out the condensation with a drop or two of concentrated hydrochloric acid as catalyst rather than by passing hydrogen chloride into the mixture.

The product from the condensation of acetone with 1,2-propanedithiol was light yellow and its carbon analysis was about 2% high. The expected product was apparently contaminated with about 13.5% of the condensation product XVI from the dithiol and phorone, formed by self-condensation of the acetone.



The 1,3-dithiolanes prepared from ketones were all liquids, despite the fact that one of them contained the undecyl group as a substituent. In only two instances was it possible to separate the isomers by distillation (Nos. 3 and 4, Table I). The compounds concerned both contained phenyl groups as substituents and the isomers had boiling points 10 to 13° apart. Apparently the flexibility of alkyl groups allows the molecules of the geometrical isomers containing them as substituents to assume very similar shapes (e.g., XVII and XVIII) and hence to have very similar physical properties, but this is not true of isomers containing aryl groups (XIX and XX). Support for this explanation may be found in the properties of geometrical isomers of analogously substituted alkenes. For example, *cis*- and *trans*-3-methyl-2-pentene have

(15) F. B. Kipping, *J. Chem. Soc.*, 18 (1935).

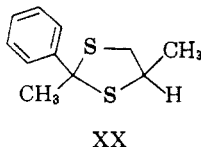
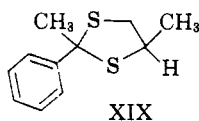
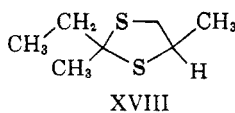
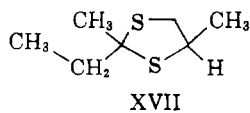
(16) E. Baumann and E. Fromm, *Ber.*, 22, 2592 (1889).

(17) It is recognized that each of the geometrical isomers actually consists of a pair of enantiomorphs, but it was not necessary for our purpose to resolve the optical isomers and no attempt was made to do so.

(18) L. A. Stocken, *J. Chem. Soc.*, 592 (1947).

(19) L. W. C. Miles and L. N. Owen, *J. Chem. Soc.*, 2938 (1950).

boiling points less than 3° apart, but *cis*- and *trans*-2-phenyl-2-butene boil 20° apart.<sup>20</sup>



Another approach was also used to separate the isomeric 1,3-dithiolanes. The product from methyl ethyl ketone and BAL, a liquid, was converted to the 3,5-dinitrobenzoate, which was a solid, and the isomers were separated by fractional crystallization (Nos. 8A and 8B, Table I).

It was possible to separate three of the 1,3-dithiolanes prepared from aldehydes into their geometrical isomers. The product from benzaldehyde and BAL had been prepared and two isomeric forms, m.p. 89° and m.p. 90°, described previously.<sup>19</sup> We found it very difficult to separate the isomers by the methods used by Miles and Owen,<sup>21</sup> but we obtained products with melting points almost the same as those reported by them by converting the crude condensation products to the 3,5-dinitrobenzoates, separating the isomeric esters, and hydrolyzing them separately. The isomeric esters, of course, served as another pair of test compounds, and portions of each isomer were kept and oxidized separately, while the remaining portions were hydrolyzed. The condensation product from BAL and *p*-chlorobenzaldehyde was a liquid, but it was converted to the 3,5-dinitrobenzoate, which was crystalline, and the two isomers were separated by fractional crystallization.

The yields (shown in Tables I and II) were generally higher in the condensations involving ketones rather than aldehydes. (The 91% yield reported for compounds 13A and 13B in Table II refers to the preparation of the 3,5-dinitrobenzoate from the hydroxy-1,3-dithiolane, not to the condensation reaction.)

The first oxidation was carried out with potassium permanganate, but it was found that the products were more conveniently isolated and purified when

(20) D. J. Cram, *J. Am. Chem. Soc.*, **71**, 3883 (1949).

(21) The two isomers were not separated from the same reaction mixture by Miles and Owen. One was obtained by chromatography and recrystallization of the product from condensation of benzaldehyde with BAL, and the other by hydrolysis of the bromide obtained from the condensation product, after recrystallization of the bromide to constant melting point. Apparently it was not possible to obtain both isomers of either the hydroxy or bromo compounds directly by recrystallization. This was confirmed in our hands; *forty-two* systematic crystallizations failed to separate the crude condensation products. When they were converted to the 3,5-dinitrobenzoate, however, the isomers were easily separated.

hydrogen peroxide in a mixture of acetic acid and acetic anhydride was used as the oxidizing agent; this procedure was followed in all subsequent work. The 1,3-dithiolane was usually heated on a steam-cone with excess hydrogen peroxide for about 12 hr. The yields of the disulfones are given in Tables III and IV.

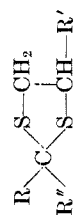
The oxidations of the 1,3-dithiolanes prepared from unsymmetrical ketones without exception resulted in the formation of two isomeric disulfones. One 1,3-dithiolane (No. 9, Tables I and III) prepared from a symmetrical ketone (acetone) was oxidized for comparison, and gave only one disulfone, as expected.<sup>22</sup> Five of the 1,3-dithiolanes from unsymmetrical ketones could not easily be separated into their isomeric forms (Nos. 1, 2, 5, 6, and 7), so the mixture of isomers was oxidized. The disulfones produced were crystalline, and were separated by fractional crystallization into the isomeric forms. The yields reported in Table III refer to the pure isomers. The 1,3-dithiolanes which could be separated into their isomeric forms (Nos. 3, 4, and 8) were oxidized separately and each gave one disulfone, as expected.

The oxidations of the 1,3-dithiolanes prepared from aldehydes without exception resulted in the formation of a single disulfone, whether mixtures of the isomeric 1,3-dithiolanes (Nos. 11, 12, and 13) or the separated isomers (Nos. 14 and 15) were oxidized. The isomeric 1,3-dithiolanes from BAL and benzaldehyde (No. 13) were separated as described previously, but were obtained in such small amounts that they were combined for the oxidation. The products from the oxidations of Nos. 11, 12, and 13 were crystallized with care and the filtrates were searched for isomers, but no evidence of their presence was found. The pure, separated isomers of 1,3-dithiolanes Nos. 14 and 15 were oxidized individually. A single product, m.p. 178–180°, was obtained by oxidation of each of the isomers of No. 14. [This compound was also obtained by treatment of the disulfone from 4-hydroxymethyl-2-phenyl-1,3-dithiolane (m.p. 159–161°) with 3,5-dinitrobenzoyl chloride.] A single product, m.p. 215–217°, was obtained by oxidation of each of the isomers of No. 15.

The fact that isomeric disulfones were obtained from oxidations of all of the 1,3-dithiolanes having two substituents in the 2-position and that isomers were not obtained from oxidations of any of the 1,3-dithiolanes having only one substituent in the 2-position indicates strongly that the lability of the hydrogen in the 2-position of the disulfones allows isomerization to the thermodynamically more stable configuration to occur in these compounds. This is demonstrated unequivocally by the

(22) The small amount of disulfone to be expected from the phorone condensation product which was present as an impurity in the acetone condensation product was not detected.

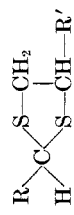
TABLE I  
1,3-DITHIOLANES FROM KETONES



No.	R	R''	R'	Yield, %	Method <sup>a</sup>	B.P., °C. (mm.)	n <sub>D</sub> <sup>20</sup>	d <sub>4</sub> <sup>20</sup>	M.R.		Analyses			
									Calcd. (Sum.)	Found	Calcd.		Found	
1	CH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>	CH <sub>3</sub>	83	A	96-98 (25)	1.5151	1.0229	48.3	47.9	51.79	8.63	51.82	8.66
2	CH <sub>3</sub>	n-C <sub>3</sub> H <sub>7</sub>	CH <sub>3</sub>	91	A	116-117 (30)	1.5115	1.0028	52.9	52.8	54.49	9.15	54.46	9.16
3A	CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	24	B	135-136 (4.4)	1.5935	—	—	—	62.80	6.66	62.76	6.55
3B	CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	26	B	146-149 (4.4)	1.5924	—	—	—	62.80	6.66	62.60	6.53
4A	C <sub>2</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	19	B	112-113 (2)	1.5811	—	—	—	64.23	7.19	64.16	6.98
4B	C <sub>2</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	20	B	122-123 (2)	1.5811	—	—	—	64.23	7.19	64.05	7.36
5	C <sub>2</sub> H <sub>5</sub>	n-C <sub>11</sub> H <sub>23</sub>	CH <sub>3</sub>	74	B	184-185 (3.5)	1.4920	—	—	—	67.48	11.33	67.20	10.91
6	CH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>	CH <sub>2</sub> Cl	76	B	82-84 (1.4)	1.5381	—	—	—	42.90	6.66	43.33	6.44
7	CH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>	CH <sub>2</sub> OC <sub>2</sub> H <sub>5</sub>	76	B, E	102-104.5 (2.8)	—	—	—	—	51.15 <sup>c</sup>	8.59 <sup>c</sup>	51.15	8.57
8A	CH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>	CH <sub>2</sub> ODNB <sup>b</sup>	—	D	94-95 <sup>e</sup>	—	—	—	—	45.30	4.36	45.70	4.34
8B	CH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>	CH <sub>2</sub> ODNB <sup>b</sup>	—	D	81-82 <sup>e</sup>	—	—	—	—	45.30	4.36	45.00	4.44
9	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	—	B	43-45 (3.8)	1.5042	—	—	—	50.54 <sup>d</sup>	8.24 <sup>d</sup>	50.54	8.22
10	CH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>	CH <sub>2</sub> OH	75	C	113-116 (4.1)	1.5328	—	—	—	47.15	7.91	47.70	7.80

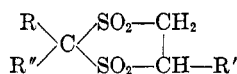
<sup>a</sup> See Exptl. section. <sup>b</sup> DNB = 3,5-dinitrobenzoyl. <sup>c</sup> Calcd. on the basis of containing 6.8% of 4-hydroxymethyl-2-ethyl-1,3-dithiolane (see Exptl. section). <sup>d</sup> Calcd. on the basis of containing 13.5% of the condensation product from phorone (see Exptl. section). <sup>e</sup> Melting point.

TABLE II  
1,3-DITHIOLANES FROM ALDEHYDES



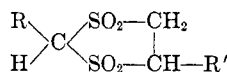
No.	R	R'	Yield, %	Method <sup>a</sup>	B.P., °C. (mm.) or M.P., °C.	n <sub>D</sub> <sup>20</sup>	d <sub>4</sub> <sup>20</sup>	M.R.		Analyses			
								Calcd. (Sum.)	Found	Calcd.		Found	
11	i-C <sub>4</sub> H <sub>9</sub>	CH <sub>3</sub>	40	B	124.5-124.8 (30)	1.5119	1.0045	52.9	52.7	54.49	9.15	54.90	9.26
12	n-C <sub>6</sub> H <sub>13</sub>	CH <sub>3</sub>	87	A	171-172 (40)	1.5030	0.9780	62.1	61.8	58.77	9.86	58.94	9.69
13A	C <sub>6</sub> H <sub>5</sub>	CH <sub>2</sub> OH	56 <sup>c</sup>	C	88.5-89.0 <sup>d</sup>	—	—	—	—	—	—	—	—
13B	C <sub>6</sub> H <sub>5</sub>	CH <sub>2</sub> OH	56 <sup>c</sup>	C	87.5-88.0 <sup>d</sup>	—	—	—	—	—	—	—	—
14A	C <sub>6</sub> H <sub>5</sub>	CH <sub>2</sub> ODNB <sup>b</sup>	91 <sup>c</sup>	D	112-113 <sup>e</sup>	—	—	—	—	50.40	3.48 <sup>f</sup>	50.48	3.20
14B	C <sub>6</sub> H <sub>5</sub>	CH <sub>2</sub> ODNB <sup>b</sup>	91 <sup>c</sup>	D	101-102 <sup>e</sup>	—	—	—	—	50.40	3.48 <sup>g</sup>	50.46	3.23
15A	p-ClC <sub>6</sub> H <sub>4</sub>	CH <sub>2</sub> ODNB <sup>b</sup>	—	C, D	164-165 <sup>h</sup>	—	—	—	—	46.31	2.97	46.10	2.93
15B	p-ClC <sub>6</sub> H <sub>4</sub>	CH <sub>2</sub> ODNB <sup>b</sup>	—	C, D	135-137 <sup>h</sup>	—	—	—	—	46.31	2.97	46.57	3.21

<sup>a</sup> See Exptl. section. <sup>b</sup> DNB = 3,5-dinitrobenzoyl. <sup>c</sup> Yield of crude mixed isomers. See Exptl. section for separation of isomers. <sup>d</sup> Mixture m.p., 69-75°. <sup>e</sup> Mixture m.p., 92-94°. <sup>f</sup> Calcd.: S, 15.82. Found: S, 16.01. <sup>g</sup> Calcd.: S, 15.82. Found: S, 16.17. <sup>h</sup> Mixture m.p., 135-142°.

TABLE III  
 1,3-DITHIOLANE DISULFONES FROM KETONES


Dithiolane No.	Yield, %	Recryst. Solvent	Method <sup>a</sup>	M.P., °C.	Analyses			
					Calcd.		Found	
					C	H	C	H
1	13	EtOH-H <sub>2</sub> O	F	96-97.5	37.15	6.23	37.18	5.97
	31			67-69	37.15	6.23	37.12	6.16
2	15	EtOH-H <sub>2</sub> O	G	96-97	39.98	6.71	40.10	6.50
	30			65-66	39.98	6.71	39.97	6.56
3A	53	MeOH-H <sub>2</sub> O	G	132.5-133.7 <sup>b</sup>	48.20	5.12	48.70	5.22
3B	72	MeOH-H <sub>2</sub> O	G	134.5-136.2 <sup>b</sup>	48.20	5.12	48.00	5.18
4A	50	EtOH, 95% SKB-Bz <sup>e</sup>	G	134-135.5 <sup>c</sup>	49.97	5.59	49.87	5.28
				4B	42	EtOH, 95% SKB-Bz <sup>e</sup>	G	129-130.5 <sup>c</sup>
5	37	EtOH-H <sub>2</sub> O	G	74-74.5 <sup>d</sup>	55.70	9.35	55.93	9.22
	29			70-71 <sup>d</sup>	55.70	9.35	55.77	9.52
6	33	HOAc-H <sub>2</sub> O	G	122.5-124.5	32.25	4.98	32.30	5.22
	17	EtOH-H <sub>2</sub> O	G	104.5-106.5	32.25	4.98	32.74	4.96
7	18	EtOH-H <sub>2</sub> O	G	173-174	40.00	6.71	40.21	6.40
	34			149-150	40.00	6.71	40.17	6.51
8A	45	MeOH-H <sub>2</sub> O SKB-Bz <sup>e</sup>	G	168.5-170.5	38.60	3.71	38.20	3.65
				8B	38	MeOH-H <sub>2</sub> O	G	110-112
9	57	EtOH-H <sub>2</sub> O	G	124-124.5	33.94	5.70	34.30	5.59

<sup>a</sup> See Exptl. section. <sup>b</sup> Mixture m.p., 101-110°. <sup>c</sup> Mixture m.p., 110-127°. <sup>d</sup> Mixture m.p., 58-63°. <sup>e</sup> Skellysolve B-benzene.

 TABLE IV  
 1,3-DITHIOLANE DISULFONES FROM ALDEHYDES


Dithiolane No.	Yield, %	Method <sup>a</sup>	Solvent	M.P., °C.	Analyses			
					Calcd.		Found	
					C	H	C	H
11	43	G	EtOH-H <sub>2</sub> O	92.5-93.5	39.98	6.71	40.35	6.36
12	66	G	EtOH-H <sub>2</sub> O	61-62	44.75	7.51	45.00	7.22
13A	43	G	—	159-161	43.46	4.38	43.75	4.52
13B								
14A <sup>b</sup>	72	G	EtOH	178-180 <sup>c</sup>	43.50	3.00	44.20	2.46
							44.04	2.31
14B	61	G	EtOH	178-180 <sup>c</sup>	—	—	—	—
15A	47	G	MeOH-H <sub>2</sub> O	215-217 <sup>d</sup>	—	—	—	—
15B	64	G	MeOH-H <sub>2</sub> O	215-217 <sup>d</sup>	40.44	2.59	40.02	2.06
							40.00	1.93

<sup>a</sup> See Exptl. section. <sup>b</sup> Calcd.: N, 5.96. Found: N, 6.10. <sup>c</sup> Mixture m.p., 178-180°. <sup>d</sup> Mixture m.p., 215-217°.

results from compounds No. 14 and 15. It is noteworthy that these isomerizations occurred in acetic acid solution at temperatures no higher than 100°.

Thus, our results with the 1,3-dithiolanes and their oxidation products are in line with those of Kipping on acyclic sulfides and sulfones, and, owing to the close analogy between the 1,3-dithiolanes and trithioacetaldehyde, there is no doubt that the stereochemistry of all of these compounds is explainable on the same basis. Apparently resonance interaction of one sulfonyl group with a carbanion is not extensive, but two adjacent carbonyl groups

so strongly interact with a carbanion that it fails to retain optical asymmetry. Since this resonance interaction is thought to involve the *d*-orbitals of sulfur, the present stereochemical results provide new and definite evidence of the reality of *d*-orbital resonance in sulfones.

#### EXPERIMENTAL<sup>23,24</sup>

*1,2-Propanedithiol* was prepared from 1,2-dibromopropane by the method of Hagelberg<sup>25</sup> and Auterrieth and Wolff.<sup>26</sup>

(23) All melting points are corrected; boiling points are uncorrected.

*2,3-Dimercapto-1-propanol* (BAL) can be purchased; most of that used in this research was made from 2,3-dibromo-1-propanol, however. Potassium hydrosulfide was prepared by dissolving potassium hydroxide in methanol and saturating the cold solution with hydrogen sulfide; the dibromide was added and the reaction was allowed to proceed at room temperature in stoppered bottles for three days. The product was isolated as described previously.<sup>27,28</sup> Yields of 54–63% were obtained.

*Preparation of 1,3-dithiolanes. Method B* is illustrated by description of the synthesis of the isomeric 2,4-dimethyl-2-phenyl-1,3-dithiolanes (compounds 3A and 3B, Table I). Twenty-eight grams (0.25 mole) of 1,2-propanedithiol was mixed with 30 g. (0.25 mole) of acetophenone in 30 ml. of chloroform. Dry hydrogen chloride was passed through the mixture for three hours; heat was evolved and water separated during this time. The mixture was poured into 500 ml. of water with stirring. After allowing three hours for the layers to separate, the organic layer was removed by means of a separatory funnel. The aqueous layer was extracted once with ether and the extract was combined with the main chloroform solution, which was dried and then distilled through a 12-inch Vigreux column. After the solvents had been removed, the pressure was reduced and two fractions were collected; the first (12 g.) boiled at 131–138° (3.5 mm.) and the second (13 g.) at 145–149° (3.5 mm.). (Both of these fractions had a violet color which turned yellow after one to four days.) The combined yield was 48%. When redistilled carefully, the two fractions boiled at 134.5–136° (4.4 mm.) and 146–149° (4.4 mm.). During the redistillation it was observed that the liquid in the condenser was violet, but turned light yellow by the time it reached the receiver.<sup>29</sup> The refractive indices and the analyses of the isomers are given in Table I.

Benzene was used in place of chloroform as solvent in other condensations with equally good results. The product from propiophenone was easily separated into its isomers as in the example described above but none of the other products gave any indication of being separable by distillation even though an efficient column of at least ten theoretical plates was used.

*Method A* was identical with Method B except that no solvent was used in these early experiments. It was found later that the heat produced by the reaction was dissipated better when a solvent was used.

*Method C* is illustrated by the condensation of benzaldehyde with BAL; 21.2 g. of the former (redistilled) and 25 g. of the latter were dissolved in 60 ml. of anhydrous benzene. A reflux condenser was attached to the flask, and several drops of concentrated hydrochloric acid were added to the mixture through the condenser. An exothermic reaction developed, and the flask was immersed in ice water with continuous shaking. After 15 min. no more heat was produced, and the flask was heated on a steam bath for 10 min. Water separated from the reaction mixture during this time. The whole mixture was poured into 200 ml. of water and the product was extracted into chloroform. The chloroform solution was washed well with dilute sodium hydroxide

solution and water, dried over magnesium sulfate, and evaporated. The crude product was recrystallized from aqueous ethanol; white needles, m.p. 68–71°, were obtained, weighing 24 g. This amounted to a yield of 56% of 4-hydroxymethyl-2-phenyl-1,3-dithiolane.

The conversion of this hydroxy compound to the ester by means of 3,5-dinitrobenzoyl chloride illustrates *Method D*. Ten grams of 4-hydroxymethyl-2-phenyl-1,3-dithiolane was mixed with 20 g. of 3,5-dinitrobenzoyl chloride in 60 ml. of dry benzene. To the mixture was added dropwise, with shaking, 40 g. of dry pyridine. The mixture was boiled on a steam bath for 25 min. with occasional shaking and then allowed to stand at room temperature overnight. To the reaction mixture was added 150 ml. of water. The organic layer was then shaken with five portions of 5% sodium bicarbonate solution, the aqueous layers being discarded. The benzene solution was then washed with water, dried over magnesium sulfate, and evaporated. The crude product was recrystallized from aqueous methanol; m.p. 91–94°, weight 18.4 g. (91%).

*Anal.* Calcd. for  $C_{17}H_{14}N_2O_6S_2$ : N, 6.91. Found: N, 7.10. The product was crystallized fractionally from a mixture of methanol and water. Two isomers were separated. The less soluble one (Compound 14A, Table II), 8.9 g., melted at 112–113°, and the more soluble one (Compound 14B, Table II), 6.6 g., melted at 101–102°. Both were in the form of light yellow needles. The melting point of a mixture of the two was 92–94°. Analyses are reported in Table II.

The preparation of 4-ethoxymethyl-2-ethyl-2-methyl-1,3-dithiolane (Compound 7, Table I) by solvolysis of the corresponding chloromethyl compound represents *Method E*. The chloromethyl compound (8.6 g., 0.044 mole) was dissolved in a mixture of 90 ml. of dioxane and 210 ml. of 95% ethanol. Two hundred milliliters of 2*N* sodium hydroxide was added. The mixture was shaken for five minutes and allowed to stand at room temperature for 12 hr. It was then diluted with 300 ml. of water and extracted with 10-ml. portions of chloroform five times. The chloroform solution was dried over calcium chloride and distilled; 6.9 g. of colorless liquid distilled at 102.0–104.5° (2.8 mm.) and 1.2 g. of light yellow liquid distilled at 108.0–114.5° (2.8 mm.). The analysis of the main product almost corresponded to the composition of 4-ethoxymethyl-2-ethyl-2-methyl-1,3-dithiolane. The presence of 6.8% of the 4-hydroxy compound would exactly account for the analytical data; the higher-boiling product of the solvolysis was undoubtedly the 4-hydroxymethyl compound. The two products were not separated completely in the distillation.

*Anal.* Calcd. for 93.2%  $C_9H_{13}OS_2$ , 6.8%  $C_7H_{11}OS_2$ : C, 51.15; H, 8.59. Found: C, 51.15; H, 8.57.

*Oxidation of 1,3-dithiolanes. (a) Oxidation of the unseparated isomers of a 2,2-disubstituted-1,3-dithiolane with subsequent isolation of the two isomeric disulfones. Method F* is illustrated by the oxidation of 2-ethyl-2,4-dimethyl-1,3-dithiolane (Compound 1). This compound, 6 g. (0.037 mole) was added to a mixture of 16 g. (0.27 mole) of potassium permanganate and 15 ml. of concd. sulfuric acid in 150 ml. of water. The mixture was stirred at room temperature for 72 hr. An additional 5 g. of potassium permanganate was then added and the mixture was heated on the steam bath for 3 hr. The manganese dioxide was removed by filtration, the excess permanganate was reduced by two grams of sodium nitrite, and the acid was neutralized with potassium carbonate. A white solid separated from the solution after it had stood overnight. Systematic recrystallization from aqueous ethanol separated the isomeric sulfones, m.p. 96–97.5° and m.p. 67–69°. Analyses are given in Table III.

All of the other oxidations were carried out with hydrogen peroxide. Three examples of this, *Method G*, are given below.

(b) *Oxidation of the separated isomers of a 2,2-disubstituted-1,3-dithiolane with subsequent isolation of the two isomeric disulfones.* To a mixture of 8.7 g. of the lower-boiling

(24) Microanalyses were done by (a) Biochemical Institute, the University of Texas, Austin, Tex., (b) Clark Microanalytical Laboratory, Urbana, Ill., and (c) Drs. G. Weiler and F. B. Strauss, Oxford, England.

(25) L. Hagelberg, *Ber.*, **23**, 1085 (1890).

(26) W. Autenrieth and K. Wolff, *Ber.*, **32**, 1369 (1899).

(27) L. A. Stocken, *J. Chem. Soc.*, 592 (1947).

(28) R. A. Peters, *et al.*, U. S. Pat. 2,432,797, Dec. 16, 1947; *Chem. Abstr.*, **42**, 2623 (1948).

(29) The violet color may be attributable to thioacetophenone, formed in small amounts by decomposition of the dithiolanes during distillation. Thioacetophenone has been reported to be a blue oil, prepared by rapid distillation of its trimer, and very unstable [E. Baumann and E. Fromm, *Ber.*, **28**, 895 (1895)].

isomer (Compound 4A) of 2-ethyl-4-methyl-2-phenyl-1,3-dithiolane in about 50 ml. of glacial acetic acid and 10 ml. of acetic anhydride was added 53 ml. of 30% hydrogen peroxide. After the heat of the initial reaction had been dissipated, the reaction mixture was heated on a steam cone for 12 hr. The solvents were removed by distillation leaving a crude crystalline product which melted at 127–129°. Three recrystallizations from 95% ethanol brought the melting point to 134.0–135.5°. Two more recrystallizations, from ethanol and then from benzene-petroleum ether, did not raise the melting point. The yield of recrystallized product was 4.5 g. (50%).

Oxidation of 8.1 g. of the higher-boiling isomer (Compound 4B) was carried out similarly. The crude product melted at 112–115°, but one recrystallization from 95% ethanol gave crystals, m.p. 129–130.5°, which differed in appearance from those from the lower-boiling isomer. A further recrystallization from benzene-petroleum ether did not raise the melting point; 4.0 g. (42%) of recrystallized product was obtained. The melting point of a mixture of the two disulfones was 110–127°. Analyses are given in Table III.

(c) *Oxidation of the unseparated isomers of a 2-monosubstituted-1,3-dithiolane with subsequent isolation of a single disulfone.* 2-Hexyl-4-methyl-1,3-dithiolane (Compound 12), 21.8 g., was dissolved in 60 ml. of glacial acetic acid and 182 g. of 30% hydrogen peroxide was added with swirling, while the flask was cooled in an ice bath. After several hours at room temperature, the reaction mixture was heated on a steam bath for 40 hr. The disulfone separated as a layer at the bottom and, after it had been separated from the upper layer, it began to crystallize. Recrystallized from aqueous alcohol, it melted at 61–62° and amounted to 19 g. (66%). Analysis is given in Table IV.

(d) *Oxidation of the separated isomers of a 2-monosubstituted-1,3-dithiolane with subsequent isolation of a single disulfone.* To a mixture of 3 g. of the high-melting isomer (Compound 14A) of 4-(3',5'-dinitrobenzoxymethyl)-2-phenyl-1,3-dithiolane, 50 ml. of glacial acetic acid, and 10 ml. of acetic

anhydride was added slowly 50 g. of 30% hydrogen peroxide. After the initial reaction had ceased, the mixture was heated on the steam bath for 12 hr. The solvents were distilled and the residue was recrystallized from ethanol to give 2.5 g. (72%) of white crystals, m.p. 178–180°.

Three grams of the lower-melting isomer (Compound 14B) was oxidized in the same manner; 2.1 g. (61%) of the same disulfone, m.p. 178–180°, was obtained. The melting point of a mixture of these two products was not depressed. Analyses are given in Table IV.

*Hydrolysis of 4-(3',5'-dinitrobenzoxymethyl)-2-phenyl-1,3-dithiolanes.* Five grams of the higher-melting isomer (Compound 14A) was suspended in 200 ml. of water containing 5 g. of potassium hydroxide. The mixture was refluxed for three hours and then cooled. Crystals separated and were collected and washed with water. Recrystallization from aqueous ethanol gave 1.8 g. (70%) of white crystals, m.p. 88.5–89° (Compound 13A).

Similar treatment of 3 g. of the lower-melting isomer (Compound 14B) gave 0.85 g. (54%) of white crystals, m.p. 87.5–88° (Compound 13B). A mixture of these two products melted at 69–75°.

*Oxidation of a mixture of Compounds 13A and 13B with hydrogen peroxide in acetic acid-acetic anhydride gave the disulfone, m.p. 159–161°, after recrystallization.* Two grams of this disulfone was treated with 2 g. of 3,5-dinitrobenzoyl chloride in 30 ml. of dry benzene and 30 g. of dry pyridine. The mixture was stirred for 0.5 hr. and then allowed to stand at room temperature for two days. The reaction mixture was decomposed by addition of 150 ml. of water containing two grams of sodium bicarbonate. The mixture was evaporated slowly to dryness and the residue was extracted with a mixture of benzene and heptane. The crystals obtained by cooling this solution weighed 2.3 g., and melted at 178–180°. This product did not depress the melting point of the product obtained by oxidizing Compounds 14A and 14B.

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[CONTRIBUTION FROM THE DIVISION OF PURE CHEMISTRY, NATIONAL RESEARCH COUNCIL]

## Organic Deuterium Compounds. XX. Synthesis of the Deuterated Propadienes<sup>1</sup>

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Propadiene-*d*<sub>1</sub>, -1,1-*d*<sub>2</sub>, -1,3-*d*<sub>2</sub>, -*d*<sub>3</sub>, -*d*<sub>4</sub> and butadiene-*d*<sub>6</sub> were synthesized by dehalogenation of the appropriate halides. A few new halides and their deuterated analogs are reported. A tentative mechanism for their dehalogenation is proposed.

Several recent spectroscopic investigations have dealt with the geometry of the allene molecule.<sup>2</sup> Since the deuterated forms of allene were expected to provide information not obtainable by other means, syntheses were developed in this laboratory which eventually led to the preparation of all four possible deuterated allenes in moderate yields. This paper reports a number of routes to these compounds which have been rather fully explored.

Only two deuterated allenes have been reported

up to now. The tetradeutero compound was isolated in small quantities from a mixture of allene-*d*<sub>4</sub> and propyne-*d*<sub>4</sub> prepared by the action of deuterium oxide on magnesium sesquicarbide, Mg<sub>2</sub>C<sub>3</sub>,<sup>3</sup> by removing the alkyne as the silver derivative.<sup>4</sup> An indication of the tedious nature of this process can be gained by observing that from sixty-five ml. of liquid hydrocarbons only four ml. of pure allene-*d*<sub>4</sub> was isolated. This method of preparing allene-*d*<sub>4</sub> was quite unsatisfactory for our requirements.

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