Anal. Calcd. for $C_{21}H_{13}ClN_2O_2$: C, 69.8; H, 3.6; N, 7.8. Found: C, 69.4; H, 3.8; N, 7.6.

1,4-Dioxo-3-(3-methylpyridinium)-2-naphthoxide (XXI).—A mixture of 22.7 g. (0.1 *M*) of 2,3-dichloro-1,4-naphthoquinone (II), 18.6 g. (0.2 *M*) of 3-picoline, and 250 ml. of 2-ethoxyethanol was refluxed for 2 hr. and after cooling, the product was isolated by filtration, and crystallized from water to give 26 g. of XXI, m.p. 260°.

Anal. Calcd. for $C_{16}H_{11}NO_3$: C, 72.5; H, 4.1; N, 5.3. Found: C, 72.2; H, 4.4; N, 5.4.

Other naphthoxides prepared in this manner were the following. **1,4-Dioxo-3-(4-styrylpyridinium)-2-naphthoxide (XXII)**, m.p. 370° (from dimethylformamide); yield, 85%.

Anal. Calcd. for $C_{23}H_{15}NO_3$: C, 78.2; H, 4.3; N, 4.0. Found: C, 78.5; H, 4.5; N, 4.0.

1,4-Dioxo-3-isoquinolinium-2-naphthoxide (XXIII), m.p. 330° (from pyridine); yield, 74%.

Anal. Calcd. for $C_{19}H_{11}NO_3$: C, 75.9; H, 3.6; N, 4.6. Found: C, 76.3; H, 3.7; N, 4.7.

2-Anilino-3-chloro-1,4-naphthoquinone (XVII).—This compound has been prepared in a number of ways[6]. We prefer the following method. A mixture of 2,3-dichloro-1,4-naphthoquinone (22.7 g.) (0.1 *M*), 12 ml. (0.13 *M*) of aniline, and 20 ml. of 2-picoline (0.2 *M*) in 100 ml. of 1,2,3-trichloropropane was heated at 95–100° for 3 hr. After cooling, the product, which had separated, was collected by filtration, washed with methanol, and dried; yield, 25 g. (89%); m.p. 210°.

N-(1,4-Dioxo-2-hydroxynaphthyl-3)pyridinium Perchlorate.[2]—A suspension of 5 g. of III in 20 ml. of dimethyl sulfate which contained about 3% of sulfuric acid was heated on the steam bath for 2 hr. or until solution occurred. Methanol (50 ml.) was added, followed by 3 ml. of 70% perchloric acid. The product separated and was collected by filtration, washed with acetone, and dried, yield, 4.7 g.; m.p. 295°.

Anal. Calcd. for $C_{15}H_{10}ClNO_7$: C, 51.2; H, 2.8; N, 3.9; Cl, 10.1. Found: C, 51.3; H, 2.4; N, 4.1; Cl, 10.4.

Alternatively, 5 g. of III was dissolved in 200 ml. of hot 10% hydrochloric acid. The solution was filtered from a small amount of insoluble material and treated with 3 ml. of 70% perchloric acid in 10 ml. of water. The product, which separated immediately, was collected, washed with water, and dried; yield, 5.2 g.; m.p. 295°. The infrared absorption curve was identical with that of the product obtained from dimethyl sulfate and sulfuric acid.

N-Methylpyridinium Perchlorate.—A solution of 2 g. of I and 10 ml. of pyridine was heated on the steam bath for 0.5 hr. An orange solid separated which was collected by filtration and identified as III. The filtrate was evaporated to dryness *in vacuo*. The residue was dissolved in 10 ml. of hot water, a little insoluble material was filtered off, and the filtrate again evaporated to dryness. The residue was taken up in 5 ml. of methanol and 0.5 ml. of 70% perchloric acid was added. On chilling, a solid separated as white needles; yield, 0.8 g.; m.p. 129–130°.

Anal. Calcd. for $C_6H_8ClNO_4$: C, 37.3; H, 4.1; N, 7.3. Found: C, 37.1; H, 4.1; N, 7.3.

The infrared spectrum of this material was identical with that of an authentic sample of N-methylpyridinium perchlorate.

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[6] "Encyclopedia of Organic Chemistry," Vol. 12B, Elsevier Publishing Co., Amsterdam, 1952, p. 2987.

Heterocyclic Vinyl Sulfides. XX. The Reaction of Cyclic Sulfoxides with Acetic Anhydride[1]

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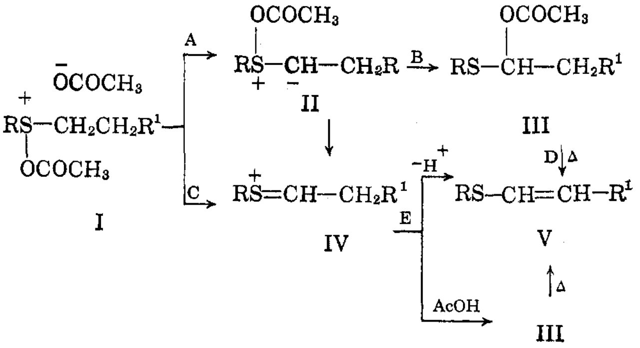
The reactions of 1,4-dithiane 1-oxide and 1,4-dithiane 1,4-dioxide with hot acetic anhydride have been examined, and the structures of the principal products have been established. Evidence has been obtained supporting carbonium ion intermediates in the Pummerer reaction.

The decomposition of sulfoxides in hot acetic anhydride, a reaction analogous to that originally reported by Pummerer,[2] has been shown to be an attractive preparative route[3] to certain α,β-unsaturated sulfides. While the details of the mechanism of this reaction were unknown, the related pathways outlined in the accompanying equations have been implied or suggested.[2–4] Step B could involve an intramolecular rearrangement of II, or a substitution–elimination process involving acetate ion. The formation of ethers,[4a] when related reactions of sulfoxides are carried out in the presence of alcohols, suggest either the substitution–elimination process at step B, or the presence of the intermediate IV. That the olefin V can be formed by thermal decomposition of III has been established.[3b]



The purpose of this study was to determine whether this reaction could be extended successfully to heterocyclic compounds containing more than one sulfur atom, and to determine whether such a study would furnish additional information related to the mechanism of the process.

Preliminary studies were made using 1,4-dithiane 1-oxide (VI). The reaction proceeded smoothly at steam bath temperature, and 1,4-dithiene (VII) was obtained in 53% yield.

Of greater interest was the reaction of 1,4-dithiane 1,4-dioxide (VIII), and for this study the *trans* isomer[5]

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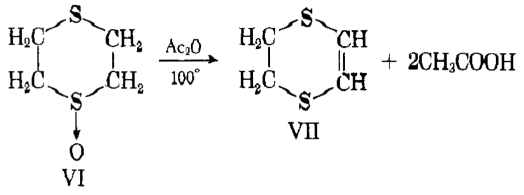
[1] This work was supported by the Office of Ordnance Research, U. S. Army, contract no. DA-ORD-31-124-61-G13.

[2] R. Pummerer, *Ber.*, **43**, 1401 (1910).

[3] (a) L. Horner and P. Kaiser, *Ann.*, **626**, 19 (1959); (b) W. E. Parham and R. Koncos, *J. Am. Chem. Soc.*, **83**, 4034 (1961).

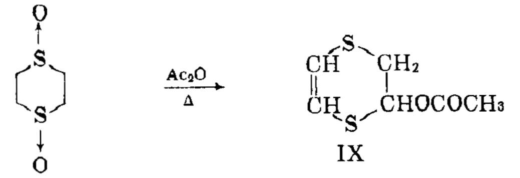
[4] (a) E. F. Schroeder and R. M. Dodson, *ibid.*, **84**, 1904 (1962); (b) W. R. Sorenson, *J. Org. Chem.*, **24**, 978 (1959); (c) D. Walker and J. Leib, *Can. J. Chem.*, **40**, 1242 (1962); (d) W. J. Kenney, J. A. Walsh, and D. A. Davenport, *J. Am. Chem. Soc.*, **83**, 4019 (1961), contains additional references to related reactions.

[5] (a) E. V. Bell and G. M. Bennett, *J. Chem. Soc.*, 1798, (1927); (b) H. M. M. Shearer, *ibid.*, 1394 (1959); (c) P. B. D. DeLaMare, D. J. Millen, J. G. Tillett, and D. Watson, *ibid.*, 1619 (1963).

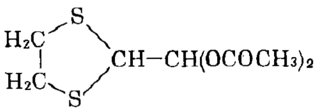


VI VII

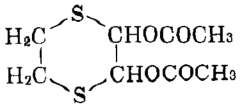
was employed. The products isolated from this reaction were 2-acetoxy-1,4-dithiene-5 (IX, 16.8%), a constant boiling mixture (53.5% yield) containing 1,3-dithiolane-2-methanediol diacetate (X) and 2,3-diacetoxy-1,4-dithiane (XI, *cis* and *trans*), 1,3-dithiolane-2-aldehyde (XII, *ca* 4.8%), and a trace of material considered to be 2-acetoxy-1,4-dithiane 4,4-dioxide.



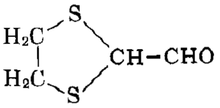
VIII IX



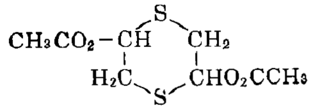
X



XI



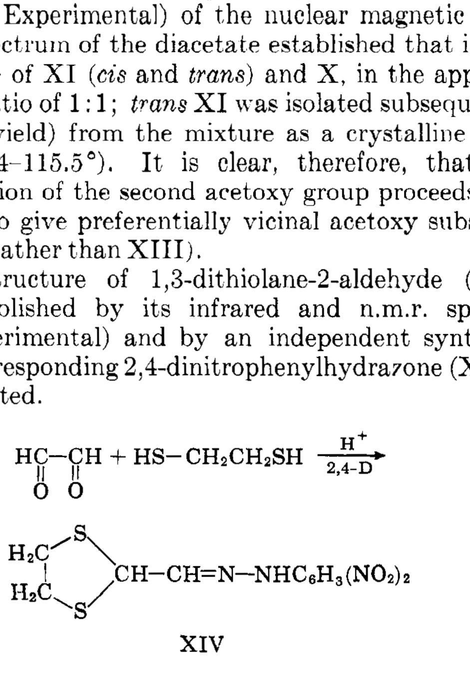
XII



XIII (not detected)

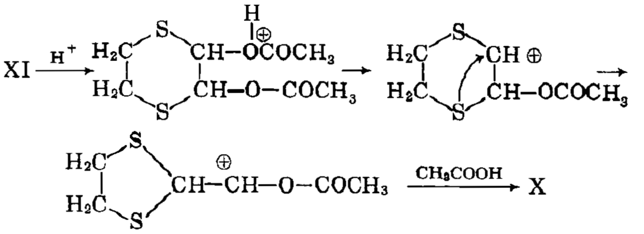
The principal product obtained from VIII (>50% yield) was a high boiling oil with composition and molecular weight consistent with X, XI, or XIII. This product gave an almost quantitative yield of the 2,4-dinitrophenylhydrazone of 1,3-dithiolane-2-aldehyde (XIV) when treated with acid and 2,4-dinitrophenylhydrazine, with only a trace of the glyoxal osazone, an observation which eliminated XIII as a significant component of the mixture. The boiling point and refractive index of samples of this diacetate suggested that it was homogeneous; however, examination (see Experimental) of the nuclear magnetic resonance spectrum of the diacetate established that it was a mixture of XI (*cis* and *trans*) and X, in the approximation ratio of 1:1; *trans* XI was isolated subsequently (4–12% yield) from the mixture as a crystalline solid (m.p. 114–115.5°). It is clear, therefore, that the introduction of the second acetoxy group proceeds in a manner to give preferentially vicinal acetoxy substitution (XI rather than XIII).

The structure of 1,3-dithiolane-2-aldehyde (XII) was established by its infrared and n.m.r. spectra (see Experimental) and by an independent synthesis of the corresponding 2,4-dinitrophenylhydrazone (XIV), as illustrated.

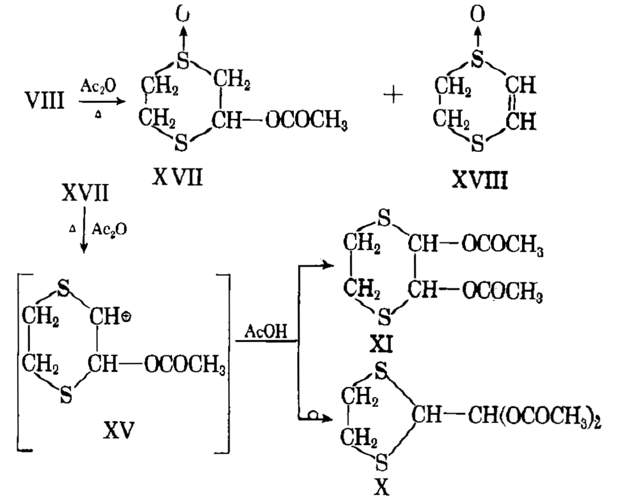


XIV

The rearrangement of XI to X in the presence of strong acid, as evidenced by the formation of XIV from XI, was confirmed in an independent study. A dilute solution containing *cis* and *trans* XI and X in acetic acid and acetic anhydride was treated with a catalytic quantity of sulfuric acid at 10°. The sample was stored at Dry Ice-acetone temperature for one hour, then allowed to warm to approximately 20°. The n.m.r. spectrum of the resulting mixture showed the absence of *cis* and *trans* XI, and an increased concentration of X; there was no evidence for the formation of appreciable quantity of other products. The observed rearrangement of XI to X is analogous to the well known rearrangement of β-halo sulfides,[6a] and may be assisted by the increased ability of oxygen, relative to sulfur, to stabilize an adjacent carbonium ion.[6b]



The observations described in the foregoing can be rationalized in terms of the gross mechanism summarized in equations I–V. Thus, the initial sequence could lead to XVII and/or XVIII. Further reaction of XVII through the intermediate carbonium ion XV could then lead to XI and X.



Similar reactions involving XVIII[7] would lead to IX.

An alternative path for the formation of X would be by rearrangement of XI under the conditions of the original reaction (*i.e.*, hot acetic anhydride and acetic acid). This probability seems unlikely, however, since a sample of *trans* XI and a mixture of X and XI (*cis*

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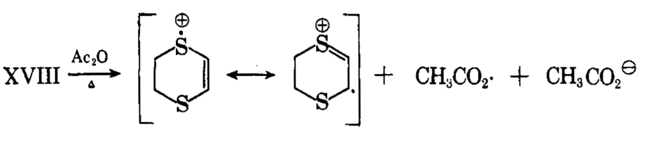
[6] (a) *cf.* W. E. Parham, J. Heberling, and H. Wynberg, *J. Am. Chem. Soc.*, **77**, 1169 (1955); (b) C. C. Price and S. Oae, "Sulfur Bonding," The Ronald Press Co., New York, N. Y., 1962, p. 9–55.

[7] The referee has noted that XVIII could also serve as an intermediate for X and XI through an ion radical.



and *trans*) were recovered unchanged after being treated seventy-two hours with hot acetic anhydride–acetic acid. The formation of significant quantities of X from VIII, therefore, does provide rather convincing evidence for a reaction sequence involving the carbonium ion intermediate XV (IV, path E). While these data do not exclude the possibility of duality of mechanism, for example path B as well as path E, there appears to be no evidence to support this possibility.

The possibility that some nonvicinal diacetate XIII was formed in the reaction of VIII with hot acetic anhydride, which decomposed thermally to IX, was considered as an alternative pathway for the formation of the monoene IX. In order to test this possibility *cis*- and *trans*-2,5-diacetoxy-1,4-dithiane (XIII) were prepared by methods previously described, and their conversion into 2-acetoxy-1,4-dithiene-5 (IX) was reexamined.[8,9] It was confirmed that both *cis* and *trans* XIII are converted to IX by pyrolysis, but only the *trans* isomer[10] is converted to the olefin IX by action of hot acetic anhydride. It was concluded, therefore, that if the diacetate XIII is an intermediate in the conversion of VIII to IX then the *trans* isomer of XIII must be formed preferentially, a possibility that cannot be excluded at this time.

It was assumed initially that the low yield of the aldehyde XII (*ca.* 4%) resulted from thermal decomposition of X, since hot acetic anhydride would not provide suitable conditions for hydrolysis. However, experimental support for this assumption was not obtained. A mixture of X and XI was heated under nitrogen at 175° for two and one-half hours and an infrared spectrum of an aliquot taken after one and one-half hours of heating showed no evidence of absorption at 1712 cm.$^{-1}$ characteristic of the aldehyde. An n.m.r. spectrum taken of the residue after two and one-half hours of heating was identical to that of the starting mixture, and showed no evidence for aldehyde. Similar results were observed when a mixture of X and XI was heated seventy-two hours in acetic anhydride–acetic acid.

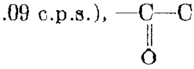
Since very small quantities of the aldehyde could have escaped detection in these control experiments, the possibility that XII was formed by thermal decomposition of X cannot be rigorously excluded. However, we consider it more likely that the aldehyde is formed by some other process—possibly by decomposition of the proposed carbonium ion precursor of X.

Experimental

2-Acetoxy-1,4-dithiene-5(IX) from 2,5-Diacetoxy-1,4-dithiane (XIII). 1. By Pyrolysis in Xylene.—2-Acetoxy-1,4-dithiene-5 [10.8% yield, b.p. 87–91° (0.85 mm.), n^{26}D 1.5750] was prepared from *trans*-2,5-diacetoxy-1,4-dithiane (XIII, m.p. 174–175°, prepared from 2,5-dihydroxy-1,4-dithiane[9]) by the method of Hesse and Jorder.[8]

The ultraviolet spectrum of IX showed $\lambda_{\max}^{95\%\text{ alc}}$ 270 mμ (log ε 3.63), $\lambda_{\min}$ 245 (log 3.33); infrared spectrum (neat liquid) 3400 w, 3000 w, 2900 w, 1735 s, 1630 w, 1552 m, 1417 w, 1377 s, 1322 w, shoulder 1275 w, broad 1230 s, with inflections at 1195 s and 1170 s, 1042 s, inflection 1022 s, 965 s, 935 m, 895 w, 820 s, 750 m, inflection 690 m, shoulder 675 s, shoulder 670 s, and broad 657 s cm.$^{-1}$.

The n.m.r. spectrum[11] (carbon tetrachloride) showed –CH- (triplet at 347.55 c.p.s.), =CH—(345.0), CH_2 (doublet 174.07, J = 3.09 c.p.s.),



$-\underset{\underset{O}{\|}}{C}-CH_3$(119.95).

cis-**2,5-Diacetoxy-1,4-dithiane**[8,9] (**XIII**) (1 g., m.p. 109°) was heated in a flask provided with an air-cooled condenser for an hour at 210–235°. Distillation of the residue gave IX [b.p. 92–95° (0.8 mm.), $n^{25.5}$D 1.5736; 0.27 g., 36.4%]. The ultraviolet and infrared spectrum of this product were identical to those described in the preceding section.

2. **By Action of Acetic Anhydride.**—*trans*-2,5-Diacetoxy-1,4-dithiane (XIII) (1.0 g.) was heated with acetic anhydride (2.0 ml.) on a steam bath until a clear, pale brown solution was obtained (6 days), and the heating was then continued for an additional 24 hr. During the heating period occasional mixing of solid and liquid was required. Distillation of the residue gave almost colorless IX [0.32 g., 43.2%, b.p. 88–92 (0.8 mm.), n^{26}D 1.5738], which was identical (ultraviolet, infrared) to that described in method 1.

cis-**2,5-Diacetoxy-1,4-dithiane** was recovered unchanged after being heated in acetic anhydride, as described for the *trans* isomer, for 88 hr.

2,4-Dinitrophenylhydrazone of 1,3-Dithiolane-2-aldehyde.—A mixture of ethanedithiol (0.47 g., 0.005 mole), glyoxal (0.29 g., 0.005 mole as 30% aqueous solution), alcohol (10 ml.), and a drop of concentrated hydrochloric acid was heated at the reflux temperature for 30 min. The turbid solution was cooled and the alcohol solution was decanted from the insoluble oil. The alcohol solution was added to a hot mixture prepared from 2,4-dinitrophenylhydrazine (0.99 g., 0.005 mole) and alcohol (60 ml.). The resulting mixture was heated at reflux for 1 hr. and the orange-yellow solid (0.55 g., m.p. 200–223°) which had separated was collected. The solid was added to boiling ethyl acetate (50 ml.), and the insoluble solid (0.2 g., 9.5% yield) identified as the 2,4-dinitrophenylosazone of glyoxal (m.p. and m.m.p. 328°[12]) was separated from the cooled mixture. The 2,4-dinitrophenylhydrazone of 1,3-dithiolane-2-aldehyde (orange-yellow needles, 0.22 g., 14% yield, m.p. 212–214° dec., from ethyl acetate) was recovered by concentration of the ethyl acetate solution.

Anal. Calcd. for $C_{10}H_{10}N_4O_4S_2$: C, 38.21; H, 3.18; N, 17.83; S, 20.38. mol. wt., 314. Found: C, 38.61; H, 3.54; N, 17.64; S, 20.51; mol. wt. (ebullioscopic in benzene), 294.

1-4-Dithiane 1-Oxide (VI).—The reported method[13] was modified. A solution of 30% hydrogen peroxide (4 ml., 0.042 mole) in glacial acetic acid (125 ml.) was added dropwise (7 hr.) to a solution prepared from 1,4-dithiane[14] (10.0 g., 0.083 mole) in glacial acetic acid (250 ml.). The temperature of the reaction mixture was maintained at 23–25° and the mixture was stirred for 15 hr. after addition was complete. The mixture was distilled with steam to remove acetic acid and unchanged 1,4-dithiane. The aqueous residue was evaporated, water was added, and the water was again evaporated. The white solid (5.2 g.) was added to boiling alcohol (40 ml.), and the insoluble disulfoxide was separated from the cooled mixture. The monosulfoxide (2.50 g., 22.1% yield, m.p. 125°, lit.[13] m.p. 125°) was obtained by concentrating the alcohol extract. Benzene was found superior to di-*n*-butyl ether[13] as a solvent for recrystallization of this product.

Action of Acetic Anhydride on 1,4-Dithiane 1-Oxide (VI). Preparation of 1,4-Dithiene (VII).—A mixture of the monosulfoxide VI (2.0 g., 0.0147 mole) and acetic anhydride (4 ml.) was heated on a steam bath for 65 hr. A clear solution resulted after 1.5 hr. which turned yellow, and then brown. 1,4-Dithiene (VII) [0.92 g., 53% yield, b.p. 128–132° (44 mm.), $n^{25.5}$D 1.628, reported[6a] n^{25}D 1.6295] was collected by distillation.

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[8] G. Hesse and I. Jorder, *Ber.*, **85**, 924 (1952).

[9] O. Hromatka and R. Haberl, *Monatsh.*, **85**, 1088 (1954).

[10] The *trans* structure was originally assigned to the higher melting least soluble isomer. The n.m.r. spectrum of this material (deuteriochloroform) determined on a Varian V 4302 at 56.44 Mc. showed: O=C—CH_3 (123.1 c.p.s.); CH_2 an ABX system $J_{1,2}$ = 14.9, $J_{1,3}$ = 2.21, $J_{2,3}$ = 4.42 c.p.s. at 150.7, 165.7, 202.1, and 217.0 c.p.s.; –C–H (multiplet at 329.1 c.p.s.), which is consistent only with the absorption expected for the *trans* configuration. This observation confirms the original assignment given to the *cis–trans* pair.

[11] The n.m.r. spectra were determined on a Varian V 4302 at 56.44 Mc.

[12] R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1960, p. 283.

[13] E. V. Bell and G. M. Bennett, *J. Chem. Soc.*, 86 (1928).

[14] R. C. Fuson, R. D. Lipscomb, B. C. McKusick, and L. J. Reed, *J. Org. Chem.*, **11**, 513 (1946).

Anal. Calcd. for $C_4H_6S_2$: C, 40.67; H, 5.08. Found: C, 40.36; H, 5.34.

The ultraviolet spectrum of this product showed $\lambda_{max}^{95\%\ alc.}$ 281 mμ (log ϵ 3.61), λ_{min} 252 (log 3.22); reported[6a] λ_{max} 282 mμ (ϵ 3.64), λ_{min} 253 (3.22).

1,4-Dithiene was further characterized by conversion to the corresponding monsulfilimine derivative (m.p. 128–129°, lit.[6a] 128.5–129°).

1,4-Dithiane 1,1-Dioxide (VIII).—The reported[5] method was modified. A solution of hydrogen peroxide (20.5 ml., 0.2 mole, 30% in water) in glacial acetic acid (20 ml.) was added during 30 min. to a suspension of 1,4-dithiane[14] (12.0 g., 0.1 mole) in glacial acetic acid (240 ml.). The temperature of the reaction mixture was maintained at 10–15°. The clear solution was stirred at 5–18° for 6 hr. and allowed to stand in a refrigerator for 18 hr. The mixture was distilled with steam, and the aqueous residue was evaporated. The solid (15.0 g.) was recrystallized from ethanol (900 ml.), and the white crystalline solid (8.8 g.) thus obtained, was recrystallized from 50% alcohol (45 ml.) to give pure α-(*trans*)[5]-1,4-dithiane 1,1-dioxide (5.5 g., 36.6% yield, m.p. 263°, lit.[5] m.p. 263°).

Action of Acetic Anhydride on 1,4-Dithiane 1,1-Dioxide.—A mixture of *trans*-1,4-dithiane 1,1-dioxide (VIII) (8.36 g., m.p. 263°) and acetic anhydride (17 ml.) was heated on a steam bath for 71 hr.; a brown solution resulted. The acetic anhydride was removed under vacuum, and the liquid residue was diluted with ether. The ether extract was kept in a refrigerator overnight, and a small amount (0.2 g.) of solid, subsequently tentatively identified as 2-acetoxy-1,4-dithiane 4,4-dioxide, was removed. The ether extract containing 10.27 g. of liquid was distilled, and three fractions were collected: (1) through a 12-in. spiral wire column, 0.36 g., b.p. 63–73° (0.4 mm.); (2) no column, 1.62 g., b.p. 108–114° (0.75 mm.); and (3) no column, 6.93 g., b.p. 126–129° (0.75 mm.). A dark brown residue (*ca.* 1 g.) remained.

Identification of 1,3-Dithiolane-2-aldehyde (XII).—Fraction 1 (0.36 g., 4.8% yield) was redistilled [pale yellow liquid, 0.2 g., 2.7% yield as XII, b.p. 77–80° (1.3 mm.), $n^{25.9}$D 1.5946]. This product was not stable at room temperature but could be stored in a refrigerator.

The infrared spectrum (neat liquid) showed 3400 w, 2935 m, 2820 m, 2705 w, 1712 s, 1532 w, broad 1432 m, broad 1380 w, 1285 w, 1250 w, 1212 w, 1152 w, 1053 m, 982 w, shoulder 960 w, 887 w, 855 m, 817 w, 792 w, 680 w, shoulder 655 w cm.$^{-1}$. That an aldehyde was present as a major component was evidenced by the absorption in the 2700–3000-cm.$^{-1}$ region, corresponding to aldehyde stretching,[15] and carbonyl absorption at 1712 cm.$^{-1}$.

The n.m.r. spectrum (carbon tetrachloride) showed $-\overset{\overset{\text{H}}{|}}{\text{C}}{=}\text{O}$ (doublet 499.35 c.p.s., *J* = 6.1 c.p.s.), (RS)$_2$-*CH*-CHO (doublet 254.97, *J* = 6.1), and CH_2 (185.0). These values were consistent with those expected for 1,3-dithiolane-2-aldehyde. There was also weak absorption at 346.15 c.p.s. which was assumed to be an impurity. This value corresponds to the olefin peak found in fraction 2.

The remaining aldehyde was treated with an equivalent of 2,4-dinitrophenylhydrazine in alcohol containing a trace of hydrochloric acid. An essentially quantitative yield of the dinitrophenylhydrazone of 1,3-dithiolane-2-aldehyde (m.p. and m.m.p. 212–214°) resulted.

Anal. Calcd. for $C_{10}H_{10}N_4O_4S_2$: C, 38.21; H, 3.18; N, 17.83; S, 20.38. Found: C, 38.46; H, 3.34; N, 18.07; S, 20.51.

Identification of 2-Acetoxy-1,4-dithiene-5 (IX).—Fraction 2 [1.62 g., 16.8% yield, b.p. 108–114° (0.75 mm.)] was redistilled several times and an almost colorless sample [0.42 g., 4.3%, b.p. 90–92° (0.85 mm.), $n^{25.9}$D 1.5756] found for authentic IX [b.p. 87–91° (0.85 mm.), n^{26}D 1.5750] was obtained.

Anal. Calcd. for $C_6H_8O_2S_2$: C, 40.90; H, 4.54. Found: C, 41.06; H, 4.84.

The ultraviolet spectrum had $\lambda_{max}^{95\%\ alc}$ 270 mμ log ϵ 3.60), λ_{min} 245 (log 3.26); authentic IX showed λ_{max} 270 mμ (ϵ 3.63), λ_{min} 245 (3.33).

Slightly low value for ϵ in the ultraviolet spectrum, one additional weak peak (183.5 c.p.s.) in the n.m.r. spectrum, and a few additional bands (shoulder 1707 s, shoulder 1080 m, and 855 w) in the infrared spectrum as compared to authentic IX are most probably due to the presence of traces of aldehyde not completely removed during distillation.

Identification of 1,3-Dithiolane-2-methanediol Diacetate (X) and 2,3-Diacetoxy-1,4-dithiane (XI).—Fraction 3 [6.93 g. 53.5% yield, b.p. 126–129° (0.75 mm.)] was distilled several times; however, in addition to a small amount of higher boiling residue obtained on the first distillation little separation was achieved as indicated by boiling point and refractive index. The sample obtained weighed 4.08 g. [31.5%, b.p. 122–124° (0.55 mm.), $n^{25.5}$D 1.5213].

Anal. Calcd. for $C_8H_{12}O_4S_2$: C, 40.67; H, 5.08; S, 27.11; mol. wt., 236. Found: C, 40.84; H, 5.42; S, 26.66; mol. wt. (ebullioscopic in benzene), 217.

The infrared spectrum (neat) showed absorption at 3460 w, 2930 w, shoulder 2840 w, broad 1750 s, broad 1430 w, 1377 s, shoulder 1320 w, shoulder 1285 w, broad 1210–1235 s flat peak with slight depression in center, inflection 1100 w, shoulder 1050 s, inflection 1035 s, broad 1018 s, shoulder 985 s, inflection 935 s, shoulder 910 m, 858 w, 790 w, 750 w, 690 w, 650 w cm.$^{-1}$.

A sample of this material (0.2 g.) was treated with twice the molar quantity of 2,4-dinitrophenylhydrazine in alcohol containing a trace of hydrochloric acid. The resulting product was recrystallized from ethyl acetate and the trace of insoluble hydrazone was identified as the 2,4-dinitrophenylosazone of glyoxal (m.p. and m.m.p. 328°). The orange-yellow needles obtained from the ethyl acetate solution melted at 212–214° dec., and the derivative was identical to the 2,4-dinitrophenylhydrazone of 1,3-dithiolane-2-aldehyde. The yield was essentially quantitative, and the alcoholic filtrate was found to contain a molar equivalent of unreacted 2,4-dinitrophenylhydrazine.

That fraction 3 was not pure 1,3-dithiolane-2-methanediol diacetate but a mixture of X and *cis* and *trans* XI in the approximate ratio 1:1 was shown by analysis of the n.m.r. spectrum (carbon tetrachloride): CH_3 C=O (116.6, 118.6, 120.9 c.p.s.), CH_2 (complex region with principle peaks at 169.5 assigned to XI, 180.4 assigned to X), (RS)$_2$*CH*-CH(OR)$_2$ (doublet, 247.7 and 255.2, *J* ~ 8 c.p.s.), *cis* and *trans* $CH_3CO_2\mathit{CHCHO}_2CCH_3$ (339 and 310), (RS)$_2$CH-*CH*(OR)$_2$ (doublet 363.8 and 371.3, *J* ~ 8).

Isolation of *trans* XI.—Samples of fraction 3 deposited some crystalline material after standing for several weeks. A small amount of ether was added to seeded samples of fraction 3 cooled in the refrigerator and the solid thus obtained (m.p. 114–115.5° from carbon tetrachloride, 4–12% of fraction 3) was identified as *trans*-2,3-diacetoxy-1,4-dithiane (XI).

Anal. Calcd. for $C_8H_{12}O_4S_2$: C, 40.67; H, 5.08; S, 27.11; mol. wt., 236. Found: C, 40.57; H, 5.1; S, 27.13; mol. wt. (Rast in camphor), 241.

The infrared spectrum of this material was not significantly different from the crude mixture. The n.m.r. spectrum in deuteriochloroform was consistent with that expected for *trans* XI; CH_3CO (123.7 c.p.s.), CH_2 (complex with peaks at 139.5, 149.6, 185.7, and 195.7), CH (317.2).

trans XI gave essentially a quantitative yield of the 2,4-dinitrophenylhydrazone of 1,3-dithiolane-2-aldehyde when treated with acid and 2,4-dinitrophenylhydrazine.

Isolation of Compound Assumed to Be 2-Acetoxy-1,4-dithiane 4,4-Dioxide.—The small residue left after fraction 3 was collected was combined with similar products of several runs and extracted with hot acetone. The extract was decolorized with Norit, and the acetone was allowed to evaporate. The sticky product (0.29 g.), was recrystallized from methanol which afforded (0.1 g.) of white plates melting at 166–168°.

Anal. Calcd. for $C_6H_{10}O_4S_2$: C, 34.28; H, 4.76; S, 30.47; mol. wt., 210. Found: C, 34.95; H, 4.89; S, 30.68; mol. wt. (ebullioscopic in benzene), 179.

Infrared spectrum (Nujol mull): 1740 s, 1325 s, 1300 m, 1275 m, inflection 1250 m, 1230 s, 1203 s, 1170 m, 1145 w, 1132 s, 1122 s, 1042 s, inflection 1030 s, 972 m, 942 w, 923 w, 882 m, 767 w cm.$^{-1}$.

The solid (0.2 g.) which separated when ether was added to the original reaction mixture obtained from 1,4-dithiane disulfoxide and acetic anhydride was recrystallized from methanol. A small quantity of solid (60 mg., m.p. 162–167°) was obtained which seemed to be a slightly impure (infrared and mixture melting point) 2-acetoxy-1,4-dithiane 4,4-dioxide.

Attempted Rearrangement of XI and X in Acetic Anhydride–Acetic Acid.—A mixture containing *trans* XI (60 mg.), acetic anhydride (0.2 ml.), and acetic acid (1 drop) was heated for 72

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[15] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1959, pp. 133, 155–157.

hr. on a steam bath. The solvent was removed and the n.m.r. spectrum of the residue (solid), determined in deuteriochloroform, was found to be identical to *trans* XI.

Similar experiments were carried out using a mixture of XI (*cis* and *trans*) and X. The n.m.r. spectrum of the product was identical to that of the starting mixture.

Attempted Thermal Decomposition of X and XI.—A mixture (0.25 g.) of X and XI (*cis* and *trans*) was heated in a nitrogen atmosphere for 2.5 hr. at 175–176°. The n.m.r. spectrum of the residue was identical to that of the starting mixture and showed no absorption characteristic for the aldehyde XII. The infrared spectrum of the product was identical to that of the starting mixture and showed no absorption at 1712 cm.$^{-1}$ characteristic for XII.

Isomerization of XI to X.—A mixture (80 mg.) of XI (*cis* and *trans*) and X was dissolved in 0.6 ml. of a cold (10°) solution prepared by mixing acetic anhydride (2 ml.), acetic acid (0.5 ml.), and sulfuric acid (1 drop). The resulting solution was placed in an n.m.r. tube and stored for about 1 hr. at Dry Ice–acetone temperature after sealing under vacuum. A blank solution was prepared in the same manner, but the sulfuric acid was omitted. Each solution was warmed to approximately 20° and the n.m.r. spectra were determined. The blank solution showed absorption bands characteristic for the CH_2 and $-\underset{|}{CH}-OCO-$ groups for all three components (the $O{=}\overset{|}{C}{-}CH_3$ groups were masked by the solvent). The solution containing the acid showed absence of XI (*cis* and *trans*) and increased concentration of X.

Acknowledgment.—Helpful discussions related to this study with Professor R. M. Dodson are gratefully acknowledged.

The Pinacol Rearrangement of Cyclopentylcyclohexane-1,1′-diol

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When cyclopentylcyclohexane-1,1′-diol is heated with dilute acid, the major product is the diene, 1-(1-cyclopentenyl)cyclohexene; spiro[5.5]undecan-1-one and spiro[4.6]undecan-6-one, with the former predominating, are minor products.

The pinacols of several cycloalkanes have been reported and converted to a mixture of a spiro ketone and a diene[1–3] (Table I). The purpose of this investigation was to uncover some of the factors that influence the course of these reactions.

TABLE I

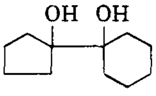
PINACOL REARRANGEMENT OF ALICYCLIC GLYCOLS

Glycol	% Spiro ketone[a]	% Diene
Bicyclobutyl-1,1′-diol	100[b]	
Bicyclopentyl-1,1′-diol (II)	86[c]	10–15[d]
Bicyclohexyl-1,1′-diol (III)	12.7[e]	88[g]
Bicycloheptyl-1,1′-diol	1.25[f]	98.75
Bicyclooctyl-1,1′-diol	1.83[f]	98.17

[a] All per cents represent composition of product mixtures isolated; per cent yields are less. [b] Diene not reported.[1] [c] See ref. 4. [d] Isolated as maleic anhydride adduct.[2] [e] Isolated as semicarbazone.[3] [f] See ref. 2. [g] E. deB. Barnette and C. A. Lawrence, *J. Chem. Soc.*, 1104 (1935).

Cyclopentylcyclohexane-1,1′-diol (I) was chosen for this purpose because it is capable of giving two rearrangement products as well as a diene. Structural features that influence the rearrangement would be indicated by determining which of the two possible rearrangement products is formed in greater quantity.

Preparation of the glycol I was accomplished by pinacol reduction of a mixture of cyclopentanone and cyclohexanone. Since the product proved to be an inseparable mixture of I, II, and III, rearrangement was carried out by refluxing the impure glycol with 25% sulfuric acid. Seven products were obtained (Table II).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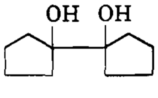
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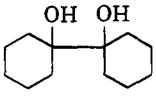
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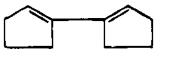
TABLE II

PINACOL REARRANGEMENT OF CYCLOPENTYLCYCLOHEXANE-1,1′-DIOL

	Per cent from			
Product	Impure I[a]	Pure I[b]	Pure II[b,c]	Pure III[b,c]
IV	3.0		15.2	
V	16.8		84.8	
VI	40.3	80.2		
VII	1.3	2.6		
VIII	8.7	17.2		
IX	4.0			13.5
X	25.6			86.5

[a] These per cents represent the composition of the 60 g. of product mixture obtained from 100 g. of the glycol. They were determined by weighing the peaks obtained in the gas chromatographic analysis of the mixture. [b] Calculated from the percentages determined for the impure glycol. [c] The agreement with the reported values in Table I is confirmation of the reliability of the analytical method.

The composition of the product mixture was determined by gas chromatography. The components of the mixture were identified by comparison with authentic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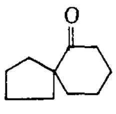
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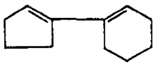
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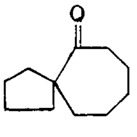
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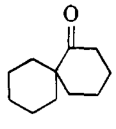
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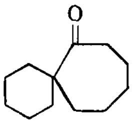
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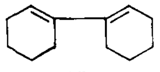
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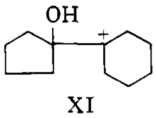
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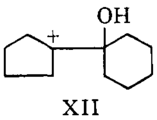
XII

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