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A Novel Oxidation-Acetylation of Hydroxysulfides[1)]

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A novel oxidative acetylation was found in the oxidation of hydroxyalkyl sulfides (IIIa to VIIIa) with 30% H_2O_2–AcOH. Whereby it was concluded that when the hydroxyl can conformationally approach the sulfur atom the sulfide is prone to acetylation during the oxidation. An oxidation–acetylation mechanism has been proposed for the reaction as summarized in Chart 4.

In the previous papers[3)] the urinary metabolites of thiamine propyl disulfide (TPD) in rats were described, in which the main matabolites of the S-propyl moiety of the compound were identified as methyl propyl sulfone (I), 2-hydroxypropyl methyl sulfone (IVb), 3-methylsulfonylpropanol (Vb), 3-methylsulfonylpropionic acid (II) and inorganic sulfate as summarized in Chart 1.

The present paper deals with the mechanism of the oxidation–acetylation which was encountered in the synthesis of these compounds.

For the preparation of IVb and Vb, we attempted to oxidize the corresponding hydroxysulfides, 2-hydroxypropyl methyl sulfide (IVa)[4)] and 3-methylthiopropanol (Va),[5)] with 30% hydrogen peroxide in acetic acid at 70° for 2 hours. Whereby we found that IVb was obtained in good yield, while Vb was obtained together with about equal amount of the acetate of Vb, the identification of which was carried out by the nuclear magnetic resonance (NMR) and infrared (IR) spectra.

A similar reaction to obtain acetylated sulfones from the sulfides which contain a hydroxyl group has been found and designated as the oxidation–acetylation by Clingman and Richtmeyer,[6)] but no explanation has been given to the mechanism of the reaction.

1) This paper was presented at the 17th Annual Meeting of the Kinki Branch of the Pharmaceutical Society of Japan on November 12, 1967.
2) Location: *Juso–Nishino–cho, Higashiyodogawa–ku, Osaka.*
3) Z. Suzuoki, K. Nishikawa and M. Numata, *J. Biochem.* (Tokyo), **58**, 279 (1965); K. Nishikawa, Z. Suzuoki and M. Numata, *J. Pharmacol. Exptl. Therap.*, **157**, 589 (1967).
4) F.G. Bordwell and H.M. Anderson, *J. Am. Chem. Soc.*, **75**, 4962 (1953).
5) R.M. McCurdy and J.H. Prager, U.S. Patent 2925406 (1960) [*C.A.*, **55**, 11921 (1961)].

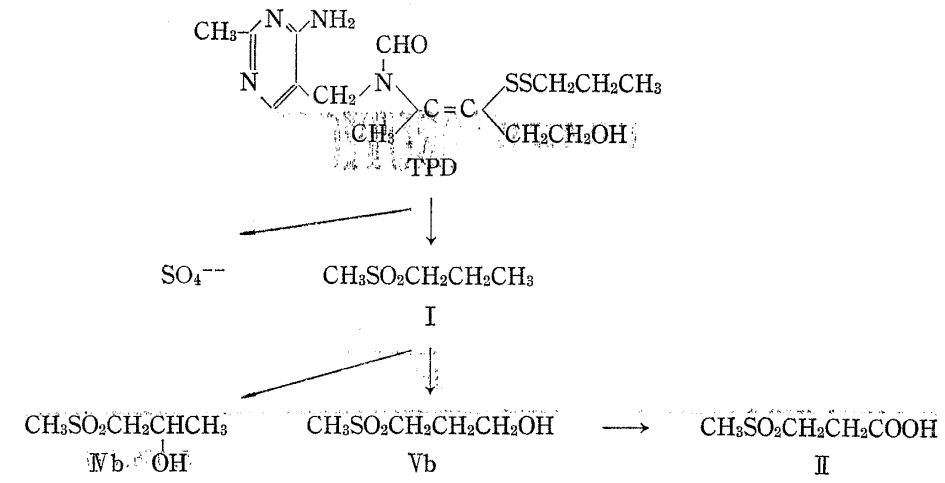
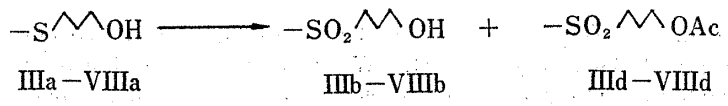


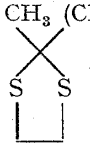
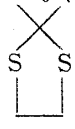
Chart 1. Metabolites of TPD Excreted in the Urine

With the aim of obtaining some clue to the mechanism of the reaction, we have attempted to oxidize several hydroxylsufides (IIIa to VIIIa) under the conditions as described previously and determined the composition and the structures of the products.

The results and the possible minimum distances between sulfur and hydroxyl oxygen in the sulfide molecules which are measured on Dreiding model are summarized in Table I.

Table I. Oxidation of Hydroxyalkylsulfides to Sulfones with 30% H_2O_2–AcOH at 70°[a)]



Starting material a		Products' composition b%	d%	Reaction time hr	Minimum distance between S and O in a Å[f)]
$CH_3S(CH_2)_2OH$	IIIa	100[b)]	0[b)]	0.5	2.60
$CH_3SCH_2CHCH_3$ OH	IVa	100[b)]	0[b)]	0.5	2.60
$CH_3S(CH_2)_3OH$	Va	50[c)]	50[c)]	0.5	1.60
$CH_3S(CH_2)_4OH$	VIa	59[c)]	41[c)]	0.5	0.20
	VIIa	64[c)]	36[c)]	1.5	1.68
	VIIIa	30[d)] 0[b,e)]	70[d)] 100[b,e)]	1.0	0.20

a) 0.01 Mole a was treated with 0.026 mole 30% H_2O_2 in 10 ml AcOH at 70°, unless otherwise stated.
b) Based on TLC evidence. c) Calculated on IR intensity of carbonyl.
d) Calculated on isolated d. e) Oxidation was carried out in 40 ml AcOH.
f) Measured with Dreiding Model.

A comparison of the yield of acetylated sulfones and the minimum distance between sulfur and hydroxyl oxygen apparently indicated that the shorter the distance the higher the yield of acetylation. Typically VIIIa, whose hydroxyl oxygen could be located near sulfur more

6) A.L. Clingman and N.K. Richtmeyer, *J. Org. Chem.*, **29**, 1782 (1964).

closely and frequently than other ones, afforded a highest yield of acetylated sulfone (VIIId). The result thus strongly suggested that a neighbouring group participation mechanism would be operative between sulfur and hydroxyl in the oxidation–acetylation.

When VIIIa was oxidized with 30% hydrogen peroxide in a large quantity of acetic acid, the reaction gave a quantitative yield of acetylated sulfone (VIIId). In order to obtain further information on the mechanism of the reaction, oxidation was carried out with VIIIa and its derivatives as starting materials and in formic and in propionic acid as solvents under the conditions as used for the oxidation of VIIIa in acetic acid.

Thus when VIIIa was oxidized with 30% hydrogen peroxide in formic acid and in propionic acid, the formyl–sulfone (VIIIc) and the propionyl–sulfone (VIIIe) were obtained in a quantitative yield and in 85% yield, respectively (Chart 2).

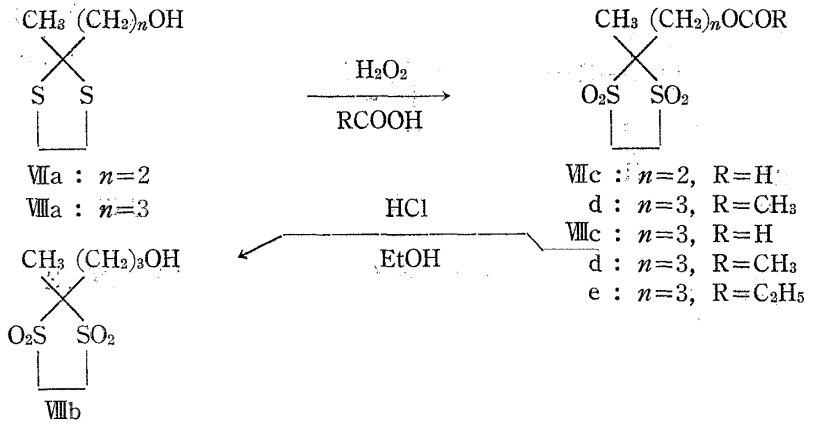


Chart 2

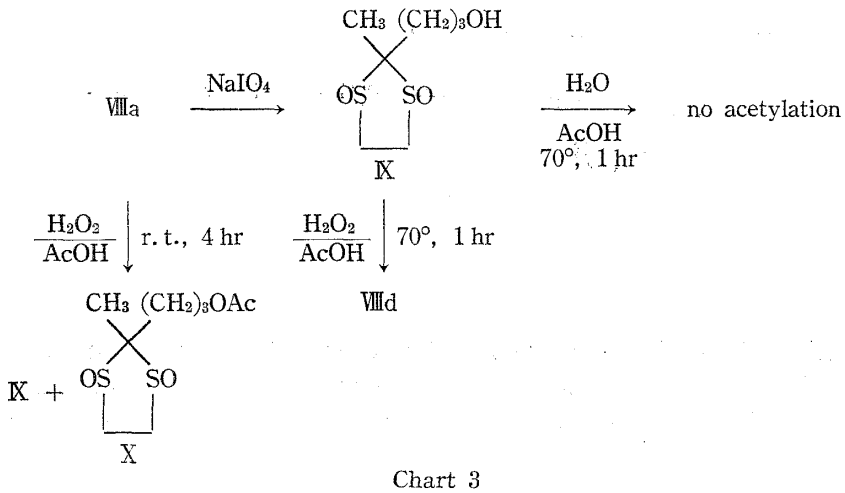
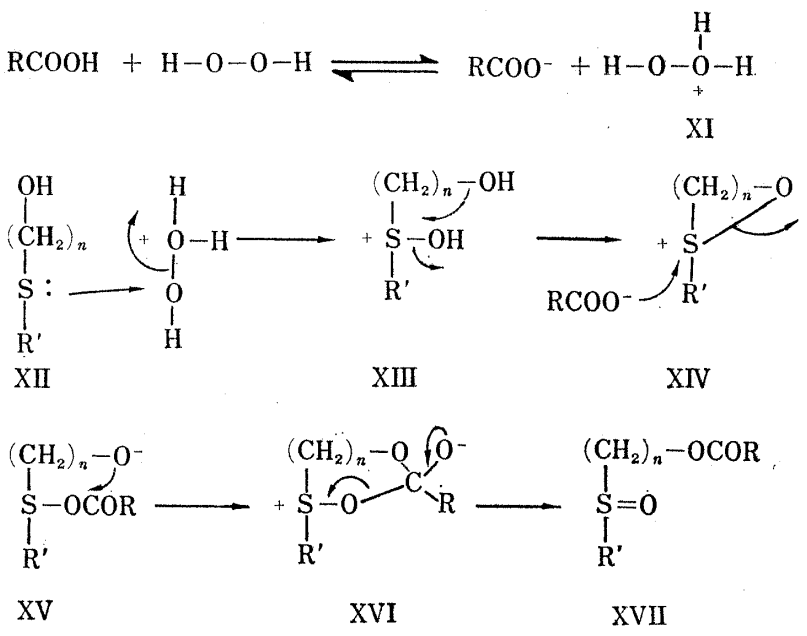


Chart 3

Such acylations of a hydroxyl group with the acids used take place during the both steps of the oxidation, *i.e.*, the oxidation of sulfides to sulfoxides and the oxidation of sulfoxides to sulfones. This is clearly demonstrated by the following experiments (Chart 3). Treatment of VIIIa with 30% hydrogen peroxide in acetic acid at room temperature for 4 hours gave a mixture of hydroxysulfoxide (IX) in major and an acetylated sulfoxide (X) in minor (Fig. 1-a), from which the latter was isolated by column chromatography and the structure was established by the IR absorptions at 1735 cm^{-1} due to the acetyl, and 1040 cm^{-1} due to the sulfoxide group. Treatment of the hydroxysulfoxide (IX) with 30% hydrogen peroxide in acetic acid at 70° for an hour afforded the acetylated sulfone (VIIId) as a sole product. While treatment of hydroxysulfide (VIIIa), hydroxysulfoxide (IX), and hydroxysulfone (VIIIb) with a mixture of acetic acid and water in place of hydrogen peroxide for the oxidation at 70° led to no appreciable amount of the acetylated products.

Taking into account that the mechanism of the oxidation of sulfides to sulfoxides and sulfones is ionic,[7] and that the reaction proceeds by a neighbouring group participation mechanism, the present oxidation–acylation would be most reasonably accounted for by the mechanism as depicted in Chart 4.

neighbouring participation acylation induced by protonation mechanism



concerted mechanism (Barnard, *et al.*)

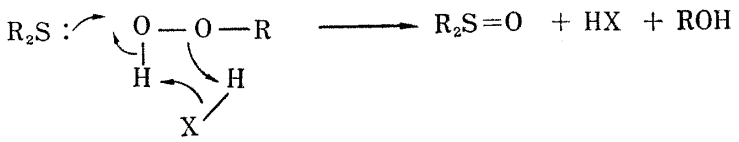


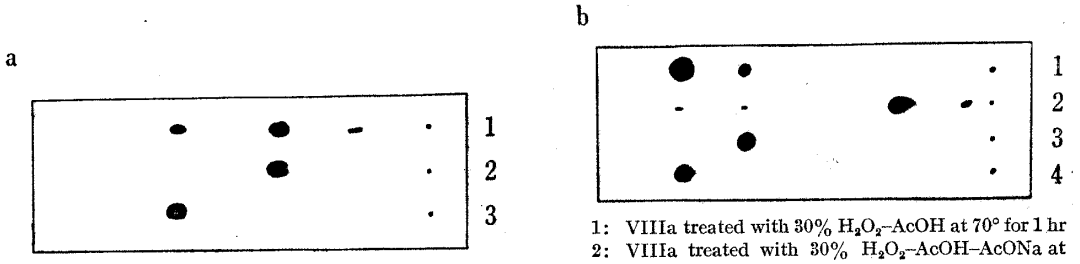
Chart 4

In this regard, it should be mentioned that Barnard, *et al.*[7] preferred a concerted mechanism as depicted in Chart 4 to a protonation mechanism for the oxidation of sulfides. A number of reports which appeared thereafter support the concerted mechanism rather than the protonation mechanism.

However our experiments demonstrate that the protonation mechanism appears more plausible than the concerted mechanism for the oxidation–acylation, because a marked retardation of the oxidation rate was observed by addition of sodium acetate to the reaction medium as is apparently visualized by TLC as shown in Fig. 1—b. Furthermore, the yields of the oxidation–acylation products were proportional to the acid strength of the acids used. Thus the oxidation of VIIa in acetic acid gave the acetyl–sulfone (VIId) in 36% yield (Table I), while the oxidation in formic acid gave the formyl–sulfone (VIIc) in a quantitative yield.

These results would be reasonably explicable on the fact that the present oxidation was carried out in a large excess of an acid, in which a protonation mechanism could possibly overweigh a concerted mechanism.

7) D. Barnard, L. Bateman and J.I. Cuneen, "Organic Sulfur Compound," Vol. 1, N. Kharasch, Ed., Pergamon Press Inc., New York, N. Y., 1961, p. 229.



a: 1: VIIIa treated with 30% H_2O_2–AcOH at r.t. for 4 hr; 2: Authentic IX; 3: Authentic X; solvent: B

b: 1: VIIIa treated with 30% H_2O_2–AcOH at 70° for 1 hr; 2: VIIIa treated with 30% H_2O_2–AcOH–AcONa at 70° for 1 hr; 3: Authentic VIIIb; 4: Authentic VIIId; solvent: A

Fig. 1. Thin-Layer Chromatograms Visualized with conc. H_2SO_4

The possibility of intervention of peracids in the reactions can be ruled out from the fact that the rate of formation of a peracid from the parent acid and 30% hydrogen peroxide under the conditions is much slow.[8]

Concerning the neighbouring participation mechanism as shown in Chart 4, it should be mentioned that Johnson and Philips[9] demonstrated that alkoxysulfonium salts interchange the alkoxy group with solvent alcohols by a S_N2 mechanism on the sulfur atom. Similarly, a 1,7-thioniaoxabicyclo[2,2,1]heptane intermediate, which is structurally related to XIV, has been assumed for the interpretation of the solvolysis rate of *trans*-4-chlorothiane-1-oxide.[10] Moreover Johnson and McCant[11] recognized that a substitution of alkoxysulfonium compounds with a nucleophile takes place predominantly at sulfur rather than at carbon.

Intramolecular acyl migration between hydroxyls is well-known, especially in sugar chemistry, as to need no illustration by examples.

Clingman and Richtmeyer[6] carried out the oxidation of thioglucoside (XVIII) by essentially the same technique as in our experiments and found that 6-O-acetyl sulfone (XIX) was obtained as a sole product. Although they recognized that the acetylation could have occurred in the oxidation, they gave no further explanation on the mechanism. Since the Dreiding model of XVIII clearly shows that the hydroxyl at C-6 can take a conformationally nearer position to sulfur than other hydroxyls in the molecule (the minimum distance between S and O is estimated at 0.80 Å in XX), it would be pertinent to assume that the reaction would have proceeded by essentially the same mechanism as in the present oxidation–acylation.

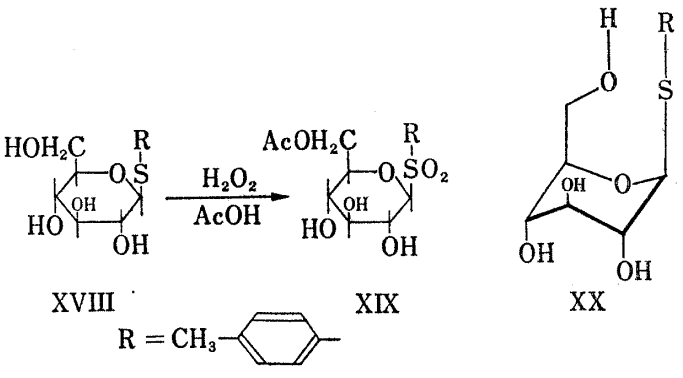


Chart 5

Experimental

Melting points were measured by capillary tubes and uncorrected. Thin-layer chromatography (TLC): Silica Gel GF_{254} (Merck) sprayed with water on the microplates, 26 mm × 76 mm, and activated at 120° for 2 hr; spots were visualized by spraying conc. H_2SO_4 and heating (all sulfur containing compounds) or with 0.1N$KMnO_4$ (sulfide and sulfoxide); solvent system, (A) benzene–acetone (1:1), (B) benzene–acetone–

8) F.P. Greenspan, *J. Am. Chem. Soc.*, **68**, 907 (1946); J. D'Ans and W. Frey, *Z. Anorg. Chem.*, **84**, 145 (1914).
9) C.R. Johnson and W.G. Philips, *Tetrahedron Letters*, **1965**, 2101.
10) J.C. Martin and J.J. Uebel, *J. Am. Chem. Soc.*, **86**, 2936 (1964).
11) C.R. Johnson and D. McCants, Jr., *J. Am. Chem. Soc.*, **87**, 5404 (1965).

methanol (2:2:1). IR spectra were taken on a Hitachi EPI-2. NMR spectra were taken on a Varian A-60.

2-Hydroxypropyl Methyl Sulfone (IVb)——To a solution of 2-hydroxypropyl methyl sulfide[4] (IVa, 21.2 g, 0.2 mole) in AcOH (100 ml) was added dropwise 30% H_2O_2 (50 g, 0.44 mole) under stirring at such a rate that the temperature does not exceed 70°. After 2 hr heating at 70° the mixture revealed a single spot of IVb at *Rf* 0.54 (solvent A) on TLC. The mixture was evaporated under reduced pressure and the residue was dissolved in water. The solution was made alkaline with K_2CO_3 and the excess H_2O_2 was decomposed with Na_2SO_3 until a negative KI–starch test was obtained, and the solution was evaporated to dryness. The residue was extracted with acetone and the extract was evaporated to obtain a colorless oil (26 g). The oil was dissolved in $CHCl_3$ and the solution was cooled with dry ice acetone, whereupon IVb precipitated as a white powdery substance, 18.2 g(66%), mp 47—51°. *Anal.* Calcd. for $C_4H_{10}O_3S$: C, 34.77; H, 7.30; O, 34.73. Found: C, 34.49; H, 7.16; O, 34.25. The IR and NMR spectra were indistinguishable from that of the compound isolated from the urine in the previous paper.[3]

3-Methylsulfonylpropanol (Vb) and Its Acetate (Vd)——3-Methylthiopropanol[5] (Va, 21.2 g, 0.2 mole) was treated with 30% H_2O_2 (50 g, 0.44 mole) and AcOH (100 ml) in the same way as mentioned above to obtain a colorless oil (22.8 g). TLC of the oil revealed two spots at *Rf* 0.40 and *Rf* 0.71 (solvent A), which correspond to Vb and Vd, respectively. The oil was dissolved in hot AcOEt and the solution was cooled slowly, whereupon Vb precipitated as colorless rods, 10.5 g (38%), mp 32—37°. *Anal.* Calcd. for $C_4H_{10}O_3S$: C, 34.49; H, 7.16; S, 23.20. Found: C, 34.93; H, 7.05; S, 23.10. The IR and NMR spectra were identical with those of the compound isolated from the urine in the previous paper.[3] Column chromatography of the mother liquor (silica gel as an adsorbent and eluted with benzene–acetone 1:1) yielded the Vd as a colorless oil. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1730 (CO), 1310 and 1135 (SO_2). NMR ($CDCl_3$, inner TMS) τ: 7.93 (3H, singlet, $COCH_3$), 7.06 (3H, singlet, SO_2CH_3), 5.79 (2H, triplet, OCH_2).

2-(2-Hydroxyethyl)-3-methyl-1,3-dithiolane (VIIa)——A solution of 2-ethoxycarbonylmethyl-2-methyl-1,3-dithiolane,[12] bp 116—120° (0.8 mmHg), (24.3 g, 0.12 mole) in ether (40 ml) was added to a stirred suspension of $LiAlH_4$ (6 g) in ether (100 ml) at such a rate as the ether refluxed gently. After 1 hr stirring, 10% H_2SO_4 (40 ml) was added dropwise under ice cooling. The organic layer was separated, washed, dried and evaporated to dryness. The residual oil was distilled to give 15.1 g (77%) of a colorless oil, bp 119—121° (0.4 mmHg). *Anal.* Calcd. for $C_6H_{12}OS_2$: C, 43.86; H, 7.36. Found: C, 43.66; H, 7.37. NMR (CCl_4, inner TMS) τ: 8.23 (3H, singlet, CH_3), 7.84 (2H, triplet, CCH_2C), 6.68 (4H, singlet, SCH_2CH_2S), 6.23 (2H, triplet, CH_2O).

2-(3-Hydroxypropyl)-2-methyl-1,3-dithiolane (VIIIa)——A solution of 2-(2-ethoxycarbonylethyl)-2-methyl-1,3-dithiolane, bp 103—106° (0.1 mmHg), (23.1 g, 0.11 mole), which was prepared by the condensation of ethyl levulate with 1,2-ethanedithiol, was dissolved in ether (40 ml) and added to a stirred suspension of $LiAlH_4$ (7 g) in ether (100 ml) at such a rate as the ether refluxed gently. After 2 hr stirring, 10% H_2SO_4 (40 ml) was added dropwise under ice cooling. The organic layer was separated, washed, dried and evaporated to dryness. The residual oil was distilled to give 10.0 g (51%) of a colorless oil, bp 145—165 (15 mmHg). *Anal.* Calcd. for $C_7H_{14}OS_2$: C, 47.15; H, 7.91; O, 8.97; S, 35.96. Found: C, 47.33; H, 8.01; O, 9.15; S, 35.73. NMR (CCl_4, inner TMS) τ: 8.25 (3H, singlet, CH_3), 7.8—8.3 (4H, broad, CCH_2CH_2C), 6.71 (4H, singlet, SCH_2CH_2S), 6.42 (2H, triplet, CH_2O).

Oxidation of Hydroxyalkyl Sulfides (IIIa to VIIIa) to Sulfones (Table I)——To a stirred solution of a hydroxyalkyl sulfide (0.01 equimole to a sulfur) in acetic acid (10 ml) was added 30% H_2O_2 (3.25 g, 0.026 mole) keeping the temperature not to exceed 70° and the mixture was kept at 70° until the TLC demonstrated no existence of the sulfide and sulfoxide; the time required is listed in Table I. The solution was then evaporated under reduced pressure to dryness, H_2O (5 ml) was added to the residue, and the solution was again evaporated to remove excess H_2O_2. For removing moisture azeotropically, benzene was added to the residue and the mixture was evaporated to dryness. The residue was dissolved in $CHCl_3$ and the solution was dried over $MgSO_4$. The solvent was evaporated to afford a mixture of hydroxyalkylsulfone (IIIb to VIIIb) and the acetylated sulfone (IIId to VIIId). These products were easily identified by the direct comparison with authentic specimens on TLC, in which the latter ran faster than the former. The constitution of the mixture was determined by comparing the relative intensity of the acetyl carbonyl band (near 1730 cm^{-1}) in the IR spectrum with that of an acetoxyalkylsulfones.

2-(3-Acyloxypropyl)-2-methyl-1,3-dithiolane-1,1,3,3-tetraoxide (VIIIc, VIIId and VIIIe) (TableII)——To a solution of VIIIa (0.89 g, 0.05 mole) in acid (0.7 mole) was added 30% H_2O_2 (3.25 g, 0.026 mole) and the solution was heated at 70° for 2 hr. The solution was evaporated to dryness and the residue was treated with water to obtain a solid residue. The solid thus obtained was almost a pure corresponding acylalkylsulfone. By this procedure VIIIc and VIIId were obtained in quantitative yields and VIIIe in 85% yield respectively. The specimens for analyses were prepared by recrystallization from aqueous MeOH.

2-(2-Hydroxyethyl)-2-methyl-1,3-dithiolane-1,1,3,3-tetraoxide (VIIb)——VIIa (0.411 g, 0.0025 mole) was treated with 30% H_2O_2 (1.63 g, 0.013 mole) in acetic acid (20 ml) at 70° for 1.5 hr. The TLC of the solution

12) J.F. Harris, Jr., U.S. Patent 2839445 (1958) [*C.A.*, 52, 17290 (1958)].

Table II

Material	mp (°C)	Formula	Analysis (%) Calcd. C	H	O	S	Found C	H	O	S
VIIIc	95— 96.5	$C_8H_{14}O_6S_2$	35.55	5.22	35.51	23.72	35.64	5.22	35.25	23.82
VIIId	91— 93	$C_9H_{16}O_6S_2$	38.02	5.67	33.76	22.55	37.90	5.67	33.85	22.40
VIIIe	112—114	$C_{10}H_{18}O_6S_2$	40.25	6.08	32.17	21.49	40.05	6.12	31.94	21.20

with solvent A revealed two spots at *Rf* 0.80 (minor), corresponding to acetylated sulfone (VIId), and at *Rf* 0.66 (major) of the compound. The solution was evaporated to dryness and the residual oil was treated with ether to result crystallization. Recrystallization of the solid from $CHCl_3$ afforded VIIb, 336 mg (59%) of white leaflets, mp 108—110°. *Anal.* Calcd. for $C_6H_{12}O_5S_2$: C, 31.56; H, 5.30. Found: C, 31.71; H, 5.23. NMR (D_2O, outer TMS) τ: 8.19 (3H, singlet, CH_3), 7.65 (2H, triplet, CCH_2C), 6.08 (2H, triplet, CH_2O), 5.93 (4H, singlet, SCH_2CH_2S).

2-(2-Formyloxyethyl)-2-methyl-1,3-dithiolane-1,1,3,3-tetraoxide (VIIc)——Treatment of VIIa with 30% H_2O_2 in HCOOH by the same procedure as described for the preparation of VIIIc afforded a compound in a quantitative yield. Recrystallization from 20% MeOH gave colorless needles, mp 97—99°. *Rf* 0.62 (solvent A). *Anal.* Calcd. for $C_7H_{12}O_6S_2$: C, 32.80; H, 4.72; O, 37.45. Found: C, 32.58; H, 4.69; O, 37.39. IR ν_{max}^{KBr} cm^{-1}: 1715 (CHO), 1316 and 1136 (SO_2), 1182 (OCHO).

2-(2-Acetoxyethyl)-2-methyl-1,3-dithiolane-1,1,3,3-tetraoxide (VIId)——2-(2-Acetoxyethyl)-2-methyl-1,3-dithiolane (0.856 g, 0.0042 mole), which was prepared by acetylation of VIIa with acetic anhydride, was added to a solution of 30% H_2O_2 (4.7 g) in HCOOH (20 ml) and the mixture was heated at 50—60° for 1 hr. The mixture was evaporated to dryness and the residue was recrystallized from water to afford 0.92 g (81%) of white leaflets, mp 132—134°. *Rf* 0.80 (solvent A). *Anal.* Calcd. for $C_8H_{14}O_6S_2$: C, 35.55; H, 5.22; O, 35.51; S, 23.72. Found: C, 35.42; H, 5.13; O, 35.50; S, 23.72. IR ν_{max}^{KBr} cm^{-1}: 1739 (CO), 1325 and 1130 (SO_2), 1250 (OAc).

2-(3-Hydroxypropyl)-2-methyl-1,3-dithiolane-1,1,3,3-tetraoxide (VIIIb)——VIIIc was dissolved in 3N HCl in EtOH (10 ml) and the solution was allowed to stand at room temperature overnight. The solution was evaporated to dryness and the residue was triturated with ether to effect crystallization. The crystalline solid was collected and recrystallized from EtOAc to give 0.86 g (93%) of colorless prisms, mp 111—112°. *Rf* 0.61 (solvent A). *Anal.* Calcd. for $C_7H_{14}O_5S_2$: C, 34.48; H, 5.82; O, 33.01; S, 26.47. Found: C, 34.48; H, 5.67; O, 33.00; S, 26.46. IR ν_{max}^{KBr} cm^{-1}: 3597 (OH), 1319, 1126 and 1095 (SO_2). NMR (D_2O, outer TMS) τ: 8.12 (3H, singlet, CH_3), 7.5—8.4 (4H, multiplet, CCH_2CH_2C), 6.20 (2H, triplet, CH_2O), 5.86 (4H, singlet, SCH_2CH_2S).

2-(3-Hydroxypropyl)-2-methyl-1,3-dithiolane-1,3-dioxide (IX)——VIIIa (1.78 g, 0.01 mole) was added dropwise to a stirred solution of $NaIO_4$ (4.28 g, 0.02 mole) in H_2O (40 ml) under ice cooling. After 2 hr stirring the solid deposited was filtered and the filtrate was evaporated to dryness and the residue was extracted with acetone. The extract was evaporated and the residue was dissolved in $CHCl_3$ and the solution was dried over $MgSO_4$. The solvent was evaporated and the residual oil was recrystallized from AcOEt to afford 0.63 g (30%) of white powders, mp 48—52°. *Rf* 0.02 (solvent A), *Rf* 0.34 (solvent B). *Anal.* Calcd. for $C_7H_{14}O_3S_2$: C, 39.98; H, 6.71; O, 22.82; S, 30.49. Found: C, 39.75; H, 6.67; O, 22.78; S, 30.27. IR ν_{max}^{KBr} cm^{-1}: 3436 (OH), 1026 (SO). NMR (D_2O, outer TMS) τ: 8.42 (3H, singlet, CH_3), 7.90—8.30 (4H, multiplet, CCH_2CH_2C), 6.1—6.4 (2H, multiplet, CH_2O), 6.10 (3H, singlet, SCH_2CH_2S).

2-(3-Acetoxypropyl)-2-methyl-1,3-dithiolane-1,3-dioxide (X)——To a solution of 2-(3-acetoxypropyl)-2-methyl-1,3-dithiolane (0.22 g, 0.001 mole), which was prepared by acetylation of VIIIa with acetic anhydride, in AcOH (10 ml) was added 30% H_2O_2 (0.227 g, 0.002 mole) and the solution was allowed to stand at room temperature for 3 days. The excess H_2O_2 was decomposed with Na_2SO_3 and the mixture was evaporated to dryness. The residue was dissolved in water and the solution was made alkaline with $NaHCO_3$ and extracted with $CHCl_3$. The organic layer was separated, dried over $MgSO_4$ and evaporated to afford 0.23 g (85%) of colorless oil. *Rf* 0.64 (solvent B). *Anal.* Calcd. for $C_9H_{16}O_4S_2$: C, 42.84; H, 6.39. Found: C, 42.10; H, 6.64. IR ν_{max}^{KBr} cm^{-1}: 1735 (CO), 1040 (SO). NMR (D_2O, outer TMS) τ: 8.40 (3H, singlet, CH_3), 7.8—8.1 (4H, multiplet, CCH_2CH_2C), 7.80 (3H, singlet, CH_3CO), 6.09 (4H, singlet, SCH_2CH_2S), 5.9—5.6 (2H, multiplet, CH_2O).

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