137.5°). The conversion of **5b** to dimethyl sulfone when treated with aqueous hydroxide ion is well documented.[12] Finally, treatment of epichlorohydrin with hydrosulfide ion gives 3-thietanol and *not* hydroxymethyl episulfide.[11,13]

Experimental Section[14]

3-Thietane Carbamate (2b).—To a stirred mixture of 13.0 g (0.20 mole) of sodium cyanate and 9.0 g (0.10 mole) of 3-thietanol in 70 ml of benzene was added dropwise 24.2 g (0.21 mole) of trifluoroacetic acid. The ensuing reaction was mildly exothermic. After completion of the addition (1 hr), the reaction mixture was stirred at room temperature for 18 hr. Water (15 ml) was added, and the organic layer was separated, dried, and evaporated. The resulting gummy solid was recrystallized from absolute ethanol to afford 5.6 g (42%) of white solid, mp 148–150°. Further recrystallization from the same solvent gave pure **2b**: mp 149–150° (lit.[6a] mp 147–147.5°); ν^{KBr} 3410, 2380, 3200, 1615 (NH_2), and 1695 cm^{-1} (C=O).

Anal. Calcd for $C_4H_7NO_2S$: C, 36.04; H, 5.29; N, 10.52. Found: C, 36.31; H, 5.34; N, 10.32.

3-Thietane Carbamate 1,1-Dioxide (3b).—A mixture of 0.50 g (3.8 mmoles) of **2b** and 1.5 ml of 30% hydrogen peroxide was heated on a steam bath for 1 hr with stirring. Upon cooling, the precipitated white solid was filtered and recrystallized from water. There was obtained 390 mg (62%) of colorless needles, mp 224–226° dec. An analytical sample had mp 229–230° dec (lit.[6a] mp 232°); ν^{KBr} 3475 ,3360, 3200, 1630 (NH_2), 1710 (C=O), 1310 and 1155 cm^{-1} (SO_2).

Anal. Calcd for $C_4H_7NO_4S$: C, 29.08; H, 4.27; S, 19.42. Found: C, 29.14; H, 4.29; S, 19.56.

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[12] D. C. Dittmer and M. E. Christy, *J. Am. Chem. Soc.*, **84**, 399 (1962).

[13] B. Sjöberg, *Svensk. Kem. Tidskr.*, **50**, 250 (1938); *Ber.*, **75**, 13 (1941).

[14] Melting points are uncorrected. The infrared spectra were determined with a Perkin-Elmer Infracord spectrophotometer fitted with a sodium chloride prism. The microanalyses were determined by the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

A Study of Aliphatic Sulfonyl Compounds. VII. The Structure of Sultones Derived from Chlorosulfonylated Alkyl Chlorides[1,2]

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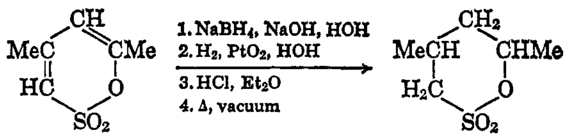
The sultone derived from chlorosulfonylated 4-methyl-2-pentyl chloride was shown to be the δ-sultone of 4-hydroxy-2-methyl-1-pentanesulfonic acid and not the γ-sultone of 4-hydroxy-2-methyl-2-pentanesulfonic acid as reported by Helberger,[4] further substantiating the findings of Asinger[5] concerning the sultone from chlorosulfonylated 3-methyl-1-butyl chloride. This was done by comparison with the authentic γ-sultone[6] from the hydrogenated 1,4-bisulfite addition product of mesityl oxide and the δ-sultone synthesized by reduction of the dienyl δ-sultone[7] from sulfonation of mesityl oxide.

TABLE I

SIGNIFICANT ABSORBANCES OF SOME SULTONES, SULFONATES, AND RELATED COMPOUNDS IN THE 6.5–10-μ RANGE

Compd	Absorbance, μ[a]		
Sultone from chlorosulfonylated 3-methyl-1-butyl chloride	7.28 s	7.95 w	
	7.36 s	8.57[b] s	
	7.50 i	8.76 w	
		9.77 s	
Sultone from chlorosulfonylated 4-methyl-2-pentyl chloride and sultone of 4-hydroxy-2-methyl-1-pentanesulfonic acid	7.32 s	7.98 w	
	7.50 i	8.56[b] s	
		8.82 w	
Ethyl 2,3-dimethyl-1-butanesulfonate	6.78 w	7.48 i	
	6.86 w	8.58[b] s	
	7.32 i	9.96 i	
Ethyl 2,2-dimethyl-1-propanesulfonate	7.47 s	8.55[b] s	
		9.95 w	
Sultone of 3-hydroxy-1-propanesulfonic acid	7.36 s	8.57[b] s	
	7.88 w		
	8.39 w	10.29 s	
Sultone of 3-hydroxy-2-methyl-1-propanesulfonic acid	7.32 s	8.52[b] s	
	8.06 w	10.28 i	
Sultone of 3-hydroxy-2,2-dimethyl-1-propanesulfonic acid	6.82 w	8.33[b] s	av
	7.38 s	8.67[b] s	8.50
	7.97 w	10.05 w	
Sultone of 4-hydroxy-2-methyl-2-pentanesulfonic acid	7.44 s	8.45 i	
	8.38 i	8.78[b] s	
Ethyl 2-methyl-2-propanesulfonate	6.78 w	8.74[b] s	
	7.53 s	9.98 s	
2-Methyl-2-propanesulfonyl chloride	6.80 i	7.35 s	
	6.90 i	8.36 i	
	7.13 w	8.73[b] s	
	7.26 s	9.78 w	
N-Cyclohexyl-2-methyl-2-propanesulfonamide	7.16 i	7.90 w	
	7.32 i	8.03 w	
	7.55 s	8.25 w	
	7.58 s	8.85[b] s	
	7.64 s	9.24 s	
Methyl 2-methyl-2-propyl sulfone	7.29 w	8.85[b] s	
	7.61 s		

[a] Strong, intermediate, and weak absorbances are represented by s, i, and w, respectively. [b] Diagnostic absorption for tertiary or nontertiary sulfonyl grouping.



A mixture of the sultone from chlorosulfonylated 4-methyl-2-pentyl chloride, mp 46.5–47°, and the γ-sultone, mp 49.5–50°, was liquified at room temperature and the infrared spectra for the two were significantly different, whereas there was no depression in the melting point of a mixture of it and the δ-sultone and the infrared spectra of these two were identical.

From the infrared spectra of a number of sulfonyl compounds it was concluded that the strong infrared absorbance in the 8.8-μ region for the γ-sultone of 4-

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[1] Principally from the 1955 dissertation presented by M. S. Heller in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Alabama. Presented at the American Chemical Society Southwide Chemical Conference, Memphis, Tenn., Session 22, Paper 1, Dec. 7, 1956.

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[3] To whom inquiries should be addressed: Department of Chemistry, The University of Mississippi, University, Miss.

[4] J. H. Helberger, G. Manecke, and H. M. Fischer, *Ann.*, **562**, 23 (1949).

[5] F. Asinger, G. Geiseler, and M. Hoppe, *Chem. Ber.*, **91**, 2130 (1958).

[6] J. Willems, *Comp. Rend. Congr. Intern. Chim. Ind. 27e, Brussels*, **3** (1954); *Chim. Ind. (Belg)*, **3**, 666 (1954); *Ind. Chim. Belg.*, **20**, 666 (1955); *Bull. Soc. Chim. Belg.*, **64**, 409 (1955).

[7] (a) R. H. Eastman and D. Gallup, *J. Am. Chem. Soc.*, **70**, 864 (1948). (b) T. Morel and P. E. Verkade, *Rec. Trav. Chim.*, **67**, 539 (1948); **68**, 619 (1949); **70**, 35 (1951).

hydroxy-2-methyl-2-pentanesulfonic acid and that at 8.5–8.6 μ for the δ-sultones of 4-hydroxy-2-methyl-1-butane- and -pentanesulfonic acids are not attributable to ring size. Thus, the γ-sultones of 3-hydroxy-1-propanesulfonic acid,[8] 3-hydroxy-2-methyl-1-propanesulfonic acid,[8,9] and 3-hydroxy-2,2-dimethyl-1-propanesulfonic acid[10] do not absorb strongly in the 8.8-μ region. Instead of ring size, the significant attribute is whether the sulfonate grouping is that of a primary or tertiary sulfonic acid. In Table I are compared these and other sultones, several acyclic sulfonates, and some other tertiary sulfonyl compounds.[11]

The mass spectrum of the γ-sultone of 4-hydroxy-2-methyl-2-pentanesulfonic acid indicates considerable methyl group fragmentation consistent with the extensive substitution at the tertiary carbon atom to which the sulfur atom is bonded. On the other hand, the sultone from chlorosulfonylated 3-methyl-1-butyl chloride shows relatively little methyl group fragmentation, thus indicating less extensive methyl substitution, consistent with a primary sulfonate grouping. The relative degree of shattering of the two compounds is shown in Table II.

TABLE II

RELATIVE DEGREE OF METHYL GROUP SHATTERING[a] IN THE MASS SPECTROMETER

Compd	$\frac{\text{P-Me}}{\text{P}}$[a]
Sultone of 4-hydroxy-2-methyl-2-pentanesulfonic acid	24.
Sultone of 4-hydroxy-2-methyl-1-butanesulfonic acid	0.4

[a] Determined by calculating the ratio of material with mass showing loss of one methyl group to that of unshattered material; P = parent mass, Me = methyl mass.

Experimental Section

The γ-sultone from chlorosulfonylated 1-propyl chloride was prepared according to Asinger[8] and the sultones from chlorosulfonylated 3-methyl-1-butyl and 4-methyl-2-pentyl chlorides were prepared as described by Helberger.[4]

The γ-sultone of 4-hydroxy-2-methyl-2-pentanesulfonic acid was prepared according to Willems[6] and characterized as the hemihydrate of the pyridine adduct, mp 232–232.5°.

Anal. Calcd for $C_{11}H_{17}NO_3S\cdot 0.5H_2O$: C, 52.36; H, 7.19. Found: C, 52.18; H, 7.23.

The δ-Sultone of 4-Hydroxy-2-methyl-1-pentanesulfonic Acid.—The δ-sultone of 4-hydroxy-2-methyl-1,3-pentadiene-1-sulfonic acid, prepared by sulfonation of mesityl oxide with chlorosulfonic acid in acetic anhydride according to Eastman[7a] and Morel,[7b] melted at 70–70.5°. A solution of 34.4 g (0.21 mole) of this and 4.6 g (0.11 mole) of sodium hydroxide in 70 ml of water was heated to 70° and a warm solution of 4.0 g (0.11 mole) of sodium borohydride in 80 ml of water was added with stirring during 0.5 hr. The mixture was allowed to cool for 1.5 hr, then was neutralized with dilute hydrochloric acid, and dried *in vacuo*. Upon evaporation of a hot ethanol extract of the residue, 15.0 g (0.07 mole) of hygroscopic sodium 4-hydroxy-2-methyl-1-pentene-1-sulfonate was obtaned. A solution of 6.5 g (0.03 mole) of this salt was hydrogenated in 80 ml of water in the presence of 0.1 g of platinum oxide with an initial pressure of 515-psi gauge at 75° for 3 hr and then cooled to room temperature overnight. The dry sodium 4-hydroxy-2-methyl-1-pentanesulfonate resulting on evaporation of the aqueous filtrate from the hydrogenated product was slurried in 75 ml of ether and treated with gaseous hydrogen chloride over a period of 4 hr. The ether solution then was filtered and evaporated to give 4.6 g (0.02 mole) of dark brown 4-hydroxy-2-methyl-1-pentanesulfonic acid, which then was heated at 180°–195° *in vacuo* to distil over 1.2 g (0.007 mole) of crude sultone, bp 135–142° (4 mm), which solidified after standing. Recrystallization from 2,2,4-trimethylpentane containing some carbon tetrachloride produced needles of the pure δ-sultone, mp 46.5–47°. A mixture of this sultone and that derived from chlorosulfonylated 4-chloro-2-methylpentane showed no depression in melting point, whereas a mixture with the γ-sultone of 4-hydroxy-2-methyl-2-pentanesulfonic acid was a liquid at room temperature.

Ethyl 2-Methyl-2-propanesulfonate.—The ethyl ester of 2-methyl-2-propanesulfonic acid was prepared by treating an ether solution of the sulfonic acid with diazoethane[12] and also by ethylating the silver salt of the acid.[13] The ester is a liquid,[14] bp 51° (1 mm), $n^{25}\text{D}$ 1.4241, $d^{25}{}_4$ 1.0670, MD 39.3.

Anal. Calcd for $C_6H_{14}O_3S$: C, 43.37; H, 8.43; sapon equiv, 164. Found: C, 43.28; H, 8.46; sapon equiv, 164.

Other Sulfonyl Compounds in the Infrared Comparison.—The γ-sultone[10] of 3-hydroxy-2,2-dimethyl-1-propanesulfonic acid, ethyl 2,2-dimethyl-1-propanesulfonate,[10] and ethyl 2,3-dimethyl-1-butanesulfonate[15] were prepared in earlier work already reported.

2-Methyl-2-propanesulfonyl chloride[16] was prepared by a modification of the Cherbuliez process,[17] N-cyclohexyl-2-methyl-2-propanesulfonamide[16] by oxidation of the corresponding sulfenamide, and methyl 2-methyl-2-propyl sulfone[16] by oxidation of the corresponding sulfide.

Infrared absorption data for the sultone[9a] of 3-hydroxy-2-methyl-1-propanesulfonic acid was obtained from a private source.[9b]

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[8] F. Asinger, H. Eckoldt, and F. Ebeneder, *U. S. Dept. Comm., Office Tech. Serv., PB Rept.*, **70**, **183**, 892 (1943).

[9] (a) C. W. Smith, D. G. Norton, and S. A. Ballard, *J. Am. Chem. Soc.*, **75**, 748 (1953); (b) C. W. Smith, private communication, 1957.

[10] R. B. Scott, Jr., and H. L. McLeod, *J. Org. Chem.*, **21**, 388 (1956).

[11] Much of the previously published information concerning derivatives of 2-methyl-2-propanesulfonic acid is in error. One part of that is corrected in this paper, the rest is part of the subject of a paper in preparation.

[12] M. K. Frye, unpublished post-masters research, University of Alabama, 1951.

[13] H. L. McLeod. Ph.D. Dissertation, University of Alabama, 1956.

[14] H. Rheinboldt, F. Mott, and E. Motzkus, *J. Prakt. Chem.*, **134**, 257 (1932), obtained a solid, mp 114.5°, having the proper sulfur content for the ethyl ester. They also reported a similar preparation of the methyl ester, mp 116°. Each ester was reported to have been recrystallized from chloroform, in which we find the ethyl ester is freely soluble. According to H. J. Backer and P. L. Stedhouder [*Rec. Trav. Chim.*, **52**, 437 (1933)], 2-methyl-2-propanesulfonic acid is a solid which forms a monohydrate melting at 114–116°. Consideration of the symmetry of the acid and of the esters suggests that the acid should be a solid and the simple esters liquids. It seems likely that Rheinboldt may have obtained alcoholates of the acid, particularly if moisture was not meticulously excluded from the reactants and the solvent. However, this does not seem compatible with his statement that the solid methyl ester is soluble in the usual organic solvents and insoluble in water.

[15] R. B. Scott, Jr., and M. S. Heller, *J. Org. Chem.*, **20**, 1159 (1955).

[16] R. B. Scott, Jr., and co-workers, paper in preparation.

[17] R. B. Scott, Jr., J. B. Gayle, M. S. Heller, and R. E. Lutz, *J. Org. Chem.*, **20**, 1165 (1955).

Cyclopropylcarbinyl *p*-Toluenesulfonate Solvolysis. II.[1] 1-Methyl-Substituent Effect

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In previous studies[1,2] it was shown that the SN1 solvolytic reactivity of cyclopropylcarbinyl arenesulfonate derivatives was markedly insensitive to 1-ring substitution. On the basis of the experimental evidence, it was proposed[1] that resonance interaction between the delocalized carbonium ion and the phenyl group was hindered owing to the geometrical requirements of the involved orbitals.

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[1] Paper I: D. D. Roberts, *J. Org. Chem.*, **30**, 23 (1965).

[2] D. D. Roberts, *ibid.*, **29**, 294 (1964).