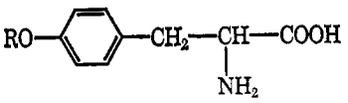
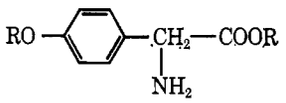
TABLE I
ALKYL ETHERS OF L-TYROSINE



R	Yield, %	Mp, °C	Calcd,[a] % C	H	N	Found, % C	H	N
n-Butyl	40	233.0–233.5	65.79	8.07	5.90	65.90	8.43	5.84
n-Hexyl	72	223.0–224.0	67.89	8.74	5.28	67.25	8.85	5.41
n-Heptyl	82	225.0–227.0	68.79	9.02	5.01	69.15	9.10	4.88
Phenethyl	42	229.0–230.0	71.56	6.71	4.91	71.73	6.84	4.67
n-Decyl	76	218.0–220.0	70.99	9.72	4.35	71.25	9.75	4.27
n-Octadecyl	74	215.0–217.0	74.78	10.92	3.23	74.10	10.72	3.45

[a] See footnote 7.

TABLE II
ALKYL ETHER ESTERS OF L-TYROSINE



R	Yield, %	Mp, °C	Calcd, % C	H	N	S	Found, % C	H	N	S
n-Butyl	31	80.5–82.5	69.24	9.27	4.77		68.89	9.33	5.16	
n-Hexyl	25	81.5–82.0	72.20	10.03	4.01		71.79	10.48	4.14	
a		231.0–232.0	63.31	9.05	3.52	4.02	63.35	8.96	3.62	4.20
n-Heptyl	23	82.0–83.0	73.17	10.41	3.71		73.21	10.10	3.83	
a		222.0–224.0	64.79	9.39	3.29	3.76	64.22	9.22	3.20	3.76
Phenethyl	42	69.5–70.5	77.25	7.04	3.71		77.01	7.10	3.73	
n-Decyl	15	70.0–70.5	75.43	11.13	3.03		74.76	11.17	3.19	
a		221.0–222.0	68.23	10.19	2.75	3.14	68.01	10.05	3.09	3.51
n-Octadecyl	27	68.5–70.0	78.83	12.11	2.04		78.66	12.28	2.12	

[a] For $(p\text{-}ROC_6H_3CH_2CHNH_2COOR)_2 H_2SO_4$.

sodium hydroxide and adding 2 equiv of alkyl halide. The ethers prepared by this method are summarized in Table I, and the ether esters in Table II.

The identity of the compounds prepared by the method of Weiss, *et al.*, with those prepared by the present method can be confirmed by melting points and infrared spectra; this was done in several cases.

Experimental Section[7]

All compounds listed in the tables were prepared by the same two methods. One example will be given for the ethers and one for the ether esters. The starting materials were commercially available reagent grade chemicals. No significant improvement in yield was obtained by further purification.

I. O-*n*-Hexyl-L-tyrosine.—A solution of 9.1 g (0.05 mole) L-tyrosine in 40 g (0.10 mole) 10% aqueous sodium hydroxide was added to 200 ml of dimethyl sulfoxide and heated in a water bath to 80°. To this was added, with stirring, 8.25 g (0.05 mole) 1-bromohexane. Heating and stirring were continued for 2 hr and the reaction mixture was then poured into 250 g of crushed ice. The pH was adjusted to *ca.* 7.5 and the resulting precipitate was filtered off, washed with water, and dried. The crude product was recrystallized from 60% acetic acid to give 9.6 g (71.6% yield) of white leaflets. The melting point and analysis are shown in Table I.

II. Phenethyl Ester of O-Phenethyl-L-tyrosine.—A mixture of 9.1 g (0.5 mole) L-tyrosine in 8.0 g (0.10 mole) of 50% aqueous sodium hydroxide and 500 ml of dimethyl sulfoxide was heated to *ca.* 120° to form a clear solution. The solution was cooled to 60–70° and 20.4 g (0.11 mole) (2-bromoethyl) of benzene was added with stirring. The temperature was raised to 115–125° an heating and stirring were continued for 1 hr. The reaction mixture was then poured into 500 g of crushed ice. The aqueous suspension was extracted with 3–100-ml portions of diethyl ether. The ether solution was dried over anhydrous sodium sulfate, filtered, and evaporated to dryness at reduced pressure. The residue was recrystallized from a large volume of hexane to give 8.1 g (42% yield) of white crystals. The melting point and analysis are shown in Table II.

In some cases it was advantageous to isolate the product as the dibasic salt of sulfuric acid. This could be done by pouring the reaction mixture into ice containing a small excess of sulfuric acid. The salt which precipitated was filtered off and dried. It was then recrystallized from 95% ethanol. The free ether ester could be regenerated in high yield, (>70%) by treating the salt with an aqueous suspension of powdered calcium carbonate. The mixture was then extracted with ether and the solution handled as above.

(7) Elemental analyses were performed by Berkeley Analytical Laboratories, Berkeley, Calif. Melting points are corrected. Infrared spectra were determined on a Perkin-Elmer Model 521 grating spectrophotometer.

The Alleged Functionalized Episulfones of Etlis[1]

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Episulfones have been prepared by the reaction of diazomethane and its derivatives with sulfur dioxide[3] or sulfenes.[4a] In contrast, numerous attempts to

(1) This study was supported in part by the National Science Foundation.

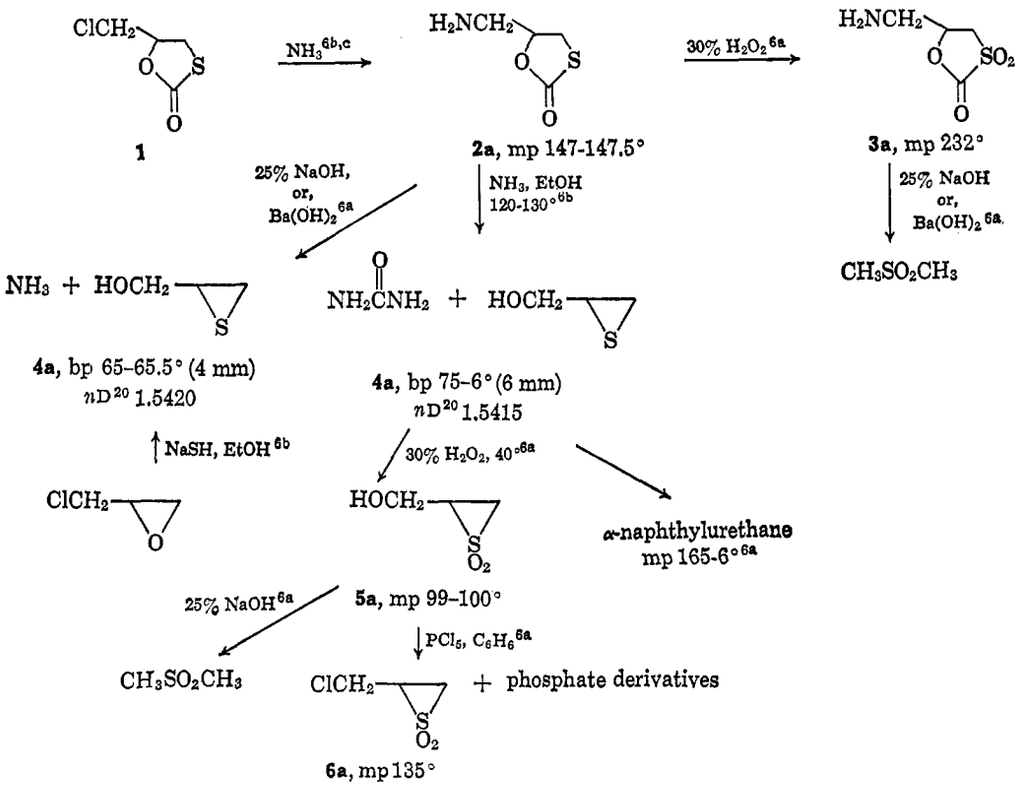
(2) Alfred P. Sloan Foundation Research Fellow.

(3) H. Staudinger and F. Pfenninger, *Ber.*, **49**, 1941 (1916); L. v. Vargha and E. Kovacs, *ibid.*, **75**, 794 (1942); G. Hesse, E. Reichold, and S. Majmudar, *ibid.*, **90**, 2106 (1957); G. Hesse and S. Majmudar, *ibid.*, **93**, 1129 (1960); N. P. Neureiter and F. G. Bordwell, *J. Am. Chem. Soc.*, **85**, 1209 (1963); N. Tokura, T. Nagai, and S. Matsumura, *J. Org. Chem.*, **31**, 349 (1966).

(4) (a) G. Opitz and K. Fischer, *Angew. Chem.*, **77**, 41 (1965); S. Rossi and S. Mairona, *Tetrahedron Letters*, 263 (1966); (b) H. Staudinger and J. Siegwart, *Helv. Chim. Acta*, **3**, 833 (1920); C. C. J. Culvenor, W. Davies, and N. S. Heath, *J. Chem. Soc.*, 282 (1949); for the lone exception to this rule, see D. C. Dittmer and G. C. Levy, *J. Org. Chem.*, **30**, 636 (1965).

SCHEME I

CHEMICAL TRANSFORMATIONS REPORTED BY ETLIS[6]

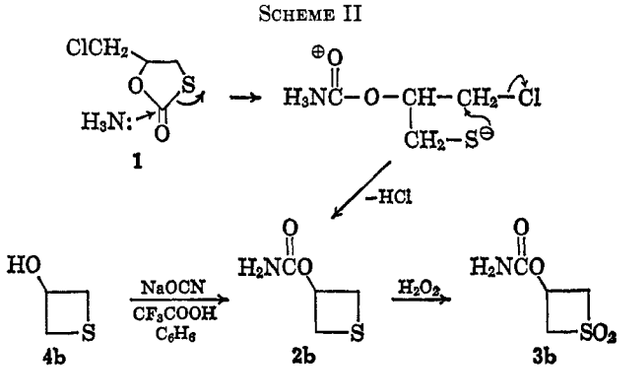


oxidize episulfides to the corresponding three-membered ring sulfones with a variety of oxidizing agents have generally met with failure.[4b] The episulfones readily lose the elements of sulfur dioxide simply on standing at room temperature or upon slight warming; olefins result in stereospecific fashion. Such thermal instability explains the present inability to isolate episulfone intermediates in the Ramberg–Bäcklund rearrangement of α-halosulfones.[5]

In view of the above facts, the recent reports of Etlis[6] concerning the synthesis and successful oxidation of **4a** with 30% hydrogen peroxide to the corresponding sulfone **5a** and its subsequent conversion to **6a** was noted with considerable interest. Such functionalized episulfones could prove of significant utility in a number of mechanistic studies of immediate interest to us. However, these results were suspect not only because of the unprecedented course of certain reactions, but because the properties assigned to **5a** and **6a** (*e.g.*, exceptionally high melting points) did not conform with the properties of episulfones in general (see Scheme I). We offer at this time a correction of Etlis' structural assignments in an attempt to remove any confusion regarding this group of tetravalent sulfur-containing molecules which are of current interest.[3–5,7]

Interaction of monothiolcarbonates such as **1** with nucleophilic reagents is known to proceed by attack at the carbonyl carbon atom.[8] In the special case of **1** (Scheme II), the liberated mercaptide ion would be expected to undergo a 1,4-displacement of chloride ion as shown to afford 3-thietane carbamate (**2b**).[9] In order to test this scheme, 3-thietanol (**4b**) was treated with sodium cyanate in trifluoroacetic acid,[10] and the authentic sample of **2b** thus produced displayed an infrared spectrum superimposable upon that published by Etlis.[6c] Oxidation of **2b** readily afforded **3b** which possessed properties identical with those assigned by Etlis to **3a**.[6a] These results lead to the obvious conclusion (see Scheme I) that **4a** is in reality the well-known 3-thietanol (**4b**) [lit.[11] bp 51–52° (0.9 mm), n^{25}D 1.5408], that **5a** conforms to the 3-thietanol 1,1-dioxide formulation (**5b**) (lit.[11] mp 101–102°), and that **6a** is truly 3-chlorothietane 1,1-dioxide (**6b**) (lit.[11] mp 136.5–

SCHEME II



(5) L. A. Paquette, *J. Am. Chem. Soc.*, **86**, 4085, 4089, 4383 (1964), and references cited therein.

(6) (a) V. S. Etlis, *Zh. Organ. Khim.*, **1**, 730 (1965); *Chem. Abstr.*, **63**, 5621 (1965); (b) V. S. Etlis and G. A. Razuvaev, *Dokl. Akad. Nauk SSSR*, **143**, 633 (1962); (c) V. S. Etlis and G. A. Razuvaev, *ibid.*, **142**, 838 (1962).

(7) L. A. Paquette and L. S. Wittenbrook, Abstracts, 152nd National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966; L. A. Carpino and L. V. McAdams, III, *J. Am. Chem. Soc.*, **87**, 5804 (1965).

(8) D. D. Reynolds, *et al.*, *J. Org. Chem.*, **26**, 5109, 5111 (1961), and subsequent papers in this series.

(9) Throughout this paper the suffix b in a structural designation refers to the correct structure of the identically numbered formulation in Scheme I (which carries suffix a).

(10) B. Loev and M. F. Kormendy, *J. Org. Chem.*, **28**, 3421 (1963).

(11) D. C. Dittmer and M. E. Christy, *ibid.*, **26**, 1324 (1961).

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.

(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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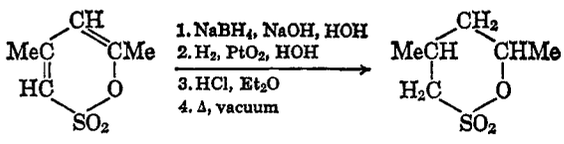
Received November 2, 1965

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.



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-

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.

(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.
(2) The present work was supported in part by the Office of Naval Research. The authors wish to thank the Eastern Laboratory of E. I. du Pont de Nemours and Co. and the Celanese Corporation of America for considerable assistance in the study. Specific thanks are due E. H. Schmorr for infrared spectra, H. T. Thomas for ultimate analyses, and R. M. Guedin for mass spectrographic analyses.
(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).