A new route to 5- and 6-membered ring sultones

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Reaction of 1,2- or 1,3-alkanedisulfonate esters with one equivalent of *n*-butyllithium in tetrahydrofuran at −78 to 10° affords 5- and 6-membered ring sultones. Similar treatment of alkanesulfonate esters of 1,2-halohydrins gives 5-membered ring sultones. 1,2-Diols and 1,2-halohydrins of known stereochemistry were converted into 5-membered ring sultones in which the stereochemistry at 2 of the 3 ring carbon atoms is uniquely defined. Extension of these reactions to the formation of 7- and 8-membered ring sultones was not successful and products derived from an initial intermolecular reaction were obtained.

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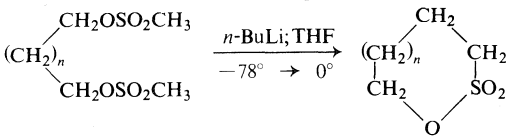
Introduction

The synthesis of sultones is generally carried out either by cyclization of the appropriate halo- or hydroxyalkanesulfonic acid (1) or by sulfonation of olefins with dioxane – sulfur trioxide (1,2). Both of these methods are rather limited; the former suffers from a lack of ready preparation of all but the most simple of the required precursors, while the latter is generally useful only in the synthesis of 3,3-dialkyl-3-hydroxypropanesulfonic acid sultones.

The recent reports of the preparation of α-sulfonate ester carbanions (3–5) have prompted us to investigate their use in the synthesis of sultones according to eq. [1]. Such cyclizations appeared to have considerable potential for the production of a variety of sultones because of the ready availability of the potential precursors i.e. diols or halohydrins.

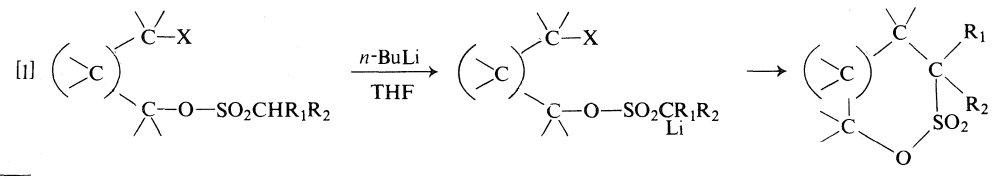
Discussion of Results

Initial experiments were carried out on 1,2-ethylene dimethanesulfonate (**1**) and 1,3-propylene dimethanesulfonate (**2**). Treatment of either **1** or **2** in tetrahydrofuran at −78° with one equivalent of *n*-butyllithium followed by warming to 0° for 30 min yielded the sultones **3** and **4** in 68[1] and 88% yield respectively. The cyclization of the corresponding ethane- and phenylmethanesulfonate esters was carried out similarly except that longer reaction times were required. The crude products from these reactions were generally contaminated with up to 20% of starting materials even when the reaction time was 2 days. The yields of the purified monosubstituted sultones ranged from 47–74% (Table 1). Analytical and spectroscopic properties were in agreement with the assigned structures and are recorded in the Experimental section.



1 $n = 0$ — **3** $n = 0$ (68%)
2 $n = 1$ — **4** $n = 1$ (88%)

Dimethanesulfonate esters of unsymmetrical diols, e.g. 1,2-propane- or 1,3-butanediol, cyclized as expected, with displacement occurring preferentially at the least substituted carbon. Thus the dimesylates **5** and **6** afforded the sultones **7** and **8** in 81 and 75% yield respectively. Nuclear magnetic resonance (n.m.r.) inspection of the total crudes indicated the absence of significant amounts of the isomeric sultones **9** and **10**. Equilibration of the two isomeric lithio derivatives **11***a* and **11***b* is expected to be facile (6) thereby allowing the preferential production of



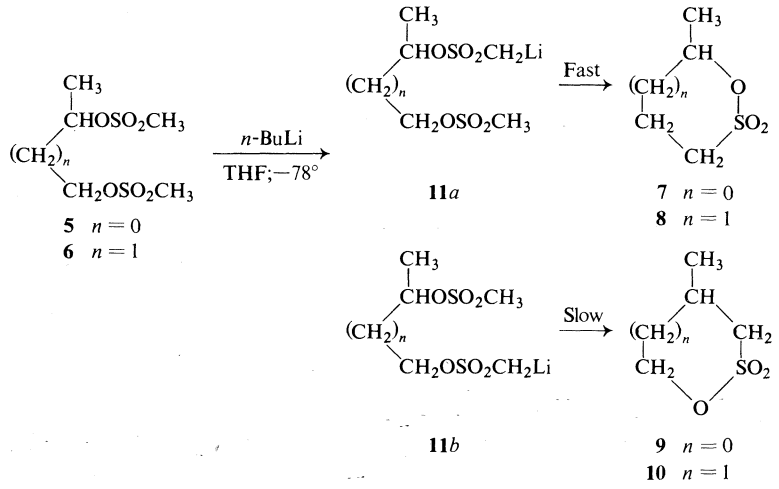
[1]The lower yield of **3** was probably due to its ease of hydrolysis. It was found that only about 70% of a sample of **3** could be recovered when put through the workup conditions (5).

TABLE 1

Formation of 5- and 6-membered ring sultones

Precursor	Sultone	Yield (%)
1,2-Ethylene dimethanesulfonate	Propane-1,3-sultone	68
1,3-Propylene dimethanesulfonate	Butane-1,4-sultone	88
1,2-Ethylene diphenylmethanesulfonate	3-Hydroxy-1-phenylpropanesulfonic acid 1,3-sultone	47
1,3-Propylene diphenylmethanesulfonate	4-Hydroxy-1-phenylbutanesulfonic acid 1,4-sultone	51
1,3-Propylene diethanesulfonate	4-Hydroxy-1-methylbutanesulfonic acid 1,4-sultone	74
1,2-Propylene dimethanesulfonate	3-Hydroxy-3-methylpropanesulfonic acid 1,3-sultone	81
1,3-Butylene dimethanesulfonate	4-Hydroxy-4-methylbutanesulfonic acid 1,4-sultone	75
β-Chloroethyl methanesulfonate	Propane-1,3-sultone	19
β-Chloroethyl phenylmethanesulfonate	3-Hydroxy-1-phenylpropanesulfonic acid 1,3-sultone	30*
trans-2-Bromocyclohexyl methanesulfonate	**15**	33,39†
trans-2-Bromocyclooctyl methanesulfonate	**17**	36,64†
cis-1,2-Cyclooctenyl dimethanesulfonate	**19**	17,48†

*Yield determined by n.m.r.
†Yield based on consumed starting material.

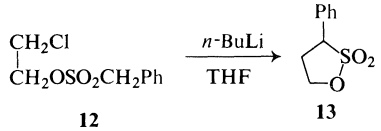


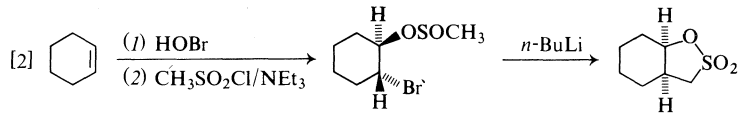
SCHEME 1

the isomer resulting from the faster cyclization (Scheme 1). Although the experimental data is to date very limited it seems reasonable to expect high selectivity in the cyclization of mono-lithio derivatives of other unsymmetrically substituted 1,2- and 1,3-disulfonate esters.

Alkanesulfonate esters of 1,2-halohydrins have also been used for the synthesis of 5-membered ring sultones. The yields of cyclized product from these compounds were considerably lower than those obtained from the disulfonate esters (Table 1); in general they roughly parallel the ease of displacement of the leaving group ($^-OSO_2R > Br^- > Cl^-$). For instance, β-chloroethyl phenylmethanesulfonate (**12**) gave the sultone **13** in 30% yield, while the mesylate of *trans*-2-bromocyclohexanol (**14**) afforded a 33% yield of the *cis*-bicyclic sultone (**15**). The structural assignment of **15** rests on its mode of synthesis, analytical and spectroscopic data. The infrared (i.r.) spectrum showed strong bands at 1340, 1150, 908, and 810 cm^{-1}; n.m.r. absorption occurred at δ = 4.8–5.0 (*m*, 1H, *H*—C—O), an 8-line multiplet from δ = 3.0–3.8 (2H) due to CH—CH_2SO_2— with J_{gem} = 13 c.p.s. and J_{vic} 7.0 and 3.0 c.p.s., and multiplets at δ = 2.5–2.9 (1H) and 1.2–2.4 (8H).

The attractiveness of the above route is the ready availability of 1,2-halohydrins and 1,2-



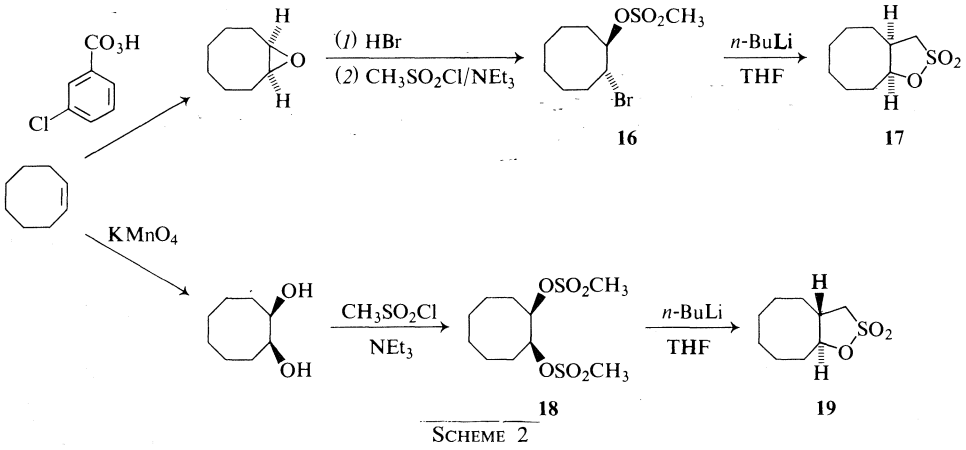


14 **15**

diols of known stereochemistry which in turn can lead to sultones having at least part of their stereochemistry uniquely defined e.g. as in eq. [2].

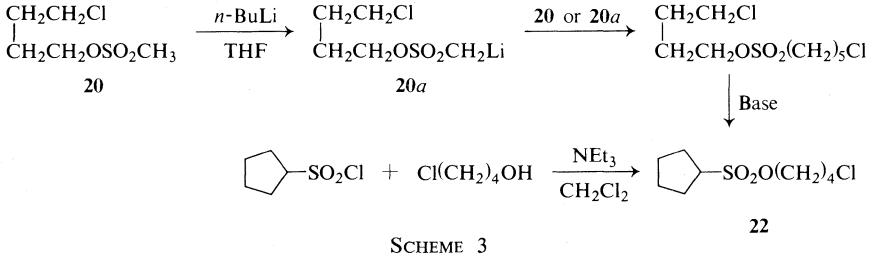
To illustrate the above claim we have synthesized from *cis*-cycloöctene both the *cis*- and *trans*-fused bicyclic sultones **17** and **19**; the final step being the cyclization of the *trans*-2-bromocyclooctyl methanesulfonate (**16**) and *cis*-1,2-cyclooctylene dimesylate (**18**) respectively (Scheme 2). The i.r. and n.m.r. spectra are in agreement with the gross structure of both **17** and **19**. The stereochemical assignment is however based solely on the mode of synthesis and could in these particular cases not be verified by the spectroscopic methods.

The success achieved in the formation of 5- and 6-membered ring sultones could not be duplicated for the 7-membered ring species. Cyclization reactions were attempted with a number of sulfonate esters among them **20** and **21**. The crude reaction mixture from the attempted cyclization of the mesylate of 4-chlorobutanol (**20**) was separated by preparative t.l.c. In addition to significant amounts of starting material, 34% of a colorless oil was obtained which was identified by spectroscopic methods (i.r. peaks at 1330 (s), 1155 (s), and 920 (s) cm^{-1}; n.m.r. absorption δ = 4.2–4.6(m, 2H), 3.4–3.9 (m, 3H), and 1.5–2.4 (12H)) and by independent synthesis as 4-chlorobutyl cyclopentanesulfonate (**22**). The alternate synthesis of **22** and its probable mode of formation from **20** are shown in Scheme 3. The products from the other cyclization attempts were similarly separated. Spectroscopic data in each case indicated that the product was analogous to **22**, i.e. an ester of a cyclopentanesulfonic acid e.g. **23**. The products were not further characterized. A single attempt to obtain an 8-membered ring sultone from **24** was unsuccessful and the starting material was recovered.



16 **17** **18** **19**

SCHEME 2



20 **20*a*** **22**

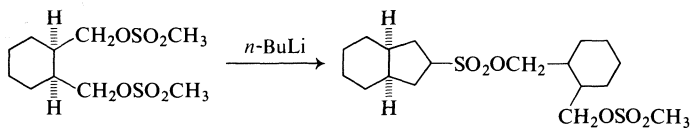
SCHEME 3

TABLE 2

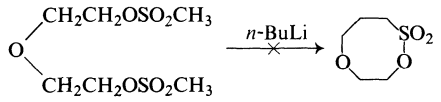
Preparation of alkanesulfonate esters

Ester	Yield (%)	Melting point or boiling point/mm (°C)	Analysis (Found) (%)	Spectroscopic properties	
				n.m.r. (δ)	i.r. (cm^{-1})
1,2-Ethylene diphenylmethanesulfonate	74	141	C, 51.79 H, 4.09	4.23 (s, 2H), 4.40 (s, 2H) 7.40 (s, 5H)	1352 (s), 1160 (s) 905 (s)
1,3-Propylene diethanesulfonate	53	dec.*	C, 32.28 H, 6.17	1.34 (t, 6H), 2.12 (quint., 2H) 3.08 (quart., 4H), 4.28 (t, 4H)	1340 (vs), 1158 (s) 920 (s)
1,3-Propylene diphenylmethanesulfonate	55	109–110	C, 53.08 H, 5.32	1.90 (quint., 2H), 4.05 (s, 2H) 4.32 (s, 2H), 7.37 (s, 5H)	1350 (vs), 1160 (s) 922 (s)
trans-2-Bromocyclohexyl methanesulfonate	50	59	C, 32.71 H, 5.04 S, 12.33 Br, 31.24	1.1–2.7 (m, 8H), 3.10 (s, 3H) 3.9–4.3 (m, 1H), 4.4–4.8 (m, 1H)	1350 (vs), 1160 (s) 960 (s), 940 (m), 895 (s), 867 (s) 817 (s)
trans-2-Bromocyclooctyl methanesulfonate	96†	dec.*		1.2–2.4 (m, 12H), 3.10 (s, 3H) 4.1–4.5 (m, 1H), 4.6–5.1 (m, 1H)	1342 (s), 1160 (s) 908 (s)
cis-1,2-Cyclooctylene dimethanesulfonate	75	69–70	C, 39.76 H, 6.73 S, 20.85	1.2–2.4 (m, 12H), 3.10 (s, 6H) 4.9–5.2 (m, 2H)	1350 (s), 1160 (s) 890 (s)
4-Chlorobutyl methanesulfonate	74	100–103/1.5	C, 32.29 H, 5.96	1.8–2.1 (m, 4H) 3.02 (s, 3H), 3.5–3.7 (m, 2H) 4.2–4.4 (m, 2H)	1340 (vs), 1165 (s) 930 (vs)

*Substance decomposed on attempted distillation at 0.2 mm.
†Crude yield, estimated purity by n.m.r. > 90%.



21 23



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Experimental

Melting points were determined with a Thomas Hoover apparatus and are not corrected; boiling points are also not corrected. Infrared spectra were recorded on a Beckmann IR8 or Beckmann IR20 i.r. spectrophotometers and n.m.r. spectra were obtained on Varian Associates model HA-100 or T-60 spectrophotometers.

Preparation of the Sulfonate Esters

In general the diol was dissolved in dry methylene chloride containing 2.2 equivalents of alkanesulfonyl chloride. The solution was cooled in an acetone – dry ice bath and treated with dropwise addition of 2.2 equivalents of triethylamine in methylene chloride. After the addition of the triethylamine was complete the reaction mixture was allowed to warm to room temperature and poured into water. The methylene chloride layer was separated, dried over magnesium sulfate, and the solvent evaporated. The products were purified either by recrystallization, column chromatography, or distillation under reduced pressure. The yields refer to purified products. The monosulfonate esters of the halohydrins were similarly prepared except that for each equivalent of halohydrin only 1.1 equivalents of sulfonyl chloride and triethylamine were employed.

The following esters have been described in the literature: 1,2-ethylene dimethanesulfonate (7), 1,2-propylene dimethanesulfonate (8), 1,3-propylene dimethanesulfonate (7), 1,3-butylene dimethanesulfonate (9), β-chloroethyl methanesulfonate (10), β-chloroethyl phenylmethanesulfonate (10), and the dimethanesulfonate **22** (11). The physical and spectroscopic properties of the other sulfonate esters are reported in Table 2.

Formation of the Lithio Derivatives of the Sulfonate Ester and Subsequent Cyclization. General Procedure

To a tetrahydrofuran solution of disulfonate ester or β-halosulfonate ester at −78° under nitrogen atmosphere was added via syringe 1.05–1.10 equivalent of *n*-butyllithium (Foote Mineral Co., 1.6 *M* in hexane). The reaction mixture was allowed to warm to −20, 0°, or room temperature for the times specified. It was then poured into water and extracted with methylene chloride. The organic extracts were dried over magnesium sulfate and the solvent evaporated. The crude products were usually purified by preparative thin-layer chromatography (t.l.c.); yields refer to purified materials.

1,3-Propane Sultone

(a) From 1,2-Dimethanesulfonate

1,2-Ethylene dimethanesulfonate (1.00 g, 4.6 mmoles) was dissolved in 30 ml of tetrahydrofuran at −78° and then treated with 3.0 ml (4.8 moles) of *n*-butyllithium. The reaction mixture was warmed to −20° for 30 min during which time a colorless precipitate was formed. Workup gave 380 mg (68%) of 1,3-propane sultone, identified by comparison of t.l.c. behavior and i.r. spectrum with authentic commercial material.[2]

(b) From β-Chloroethyl Methanesulfonate

To a solution of 1.28 g (6.6 mmoles) of the ester in 50 ml of tetrahydrofuran at −78° were added dropwise 7.2 mmoles of *n*-butyllithium. The reaction mixture was stored for 2 days. The crude product (316 mg) was separated by preparative t.l.c. and yielded 155 mg (19%) of 1,3-propane sultone.

1,4-Butane Sultone

To a solution of 780 mg (3.36 mmoles) of 1,3-propylene dimethanesulfonate in 30 ml of tetrahydrofuran at −78° were added 2.2 ml (3.5 mmoles) *n*-butyllithium. Workup of the reaction mixture after it had been stored at −20° for 30 min gave 400 mg (88%) of 1,4-butane sultone whose i.r. was identical with that of authentic material.[2]

*3-Hydroxy-1-phenylpropanesulfonic Acid 1,3-Sultone (**13**)*

(a) From 1,2-Ethylene Diphenylmethanesulfonate

1,2-Ethylene diphenylmethanesulfonate (255 mg, 0.69 mmole) was dissolved in 10 ml of tetrahydrofuran at −78° and treated with 0.70 mmole of *n*-butyllithium. The reaction mixture was stored at 0° for 3 days. Workup gave 129 mg of crude material whose n.m.r. spectrum indicated approximately 85% product and 15% starting material; n.m.r. yield approximately 80%. Purification by preparative t.l.c. gave 64 mg (47%) of sultone m.p. 93.5–96° (methylene chloride – pentane). The i.r. spectrum ($CHCl_3$) showed strong bands at 1350, 1160, and 990 cm^{-1}; n.m.r. peaks occurred at δ = 2.6–3.1 (m, 2H), 4.2–4.7 (m, 3H), and 7.40 (s, 5H).

Anal. Calcd. for $C_9H_{10}O_3S$: C, 54.54; H, 5.09; S, 16.15. Found: C, 54.15; H, 5.16; S, 16.19.

[2]Supplied by the Aldrich Chemical Co. Ltd., Milwaukee, Wis.

(b) From β-Chloroethyl Phenylmethanesulfonate

Sulfonate ester (1.50 g, 6.4 mmoles) was converted into its lithio salt in the usual manner at −78°. The reaction mixture was stored at 5° for 3 h. An n.m.r. spectrum of the crude product (674 mg) indicated a 30% yield of the sultone **13**.

3-Hydroxy-3-methylpropanesulfonic Acid 1,3-Sultone

1,2-Propylene dimethanesulfonate (1.57 g, 6.8 mmoles) was dissolved in 40 ml tetrahydrofuran at −78° and reacted with 7.5 mmoles *n*-butyllithium. The reaction mixture was kept at 10° for 12 h during which time a colorless precipitate was formed. Workup, followed by flash distillation of the crude product, gave 0.75 g (81%) of sultone **7**. The n.m.r. spectrum was in agreement with that given by Ohline *et al.* (12).

4-Hydroxy-1-phenylbutanesulfonic Acid 1,4-Sultone

A solution of 2.01 g (5.2 mmoles) of 1,3-propylene diphenylmethanesulfonate in 30 ml of tetrahydrofuran at −78° was treated with 5.5 mmoles of *n*-butyllithium, and then stored at room temperature overnight. Workup gave 1.22 g of crude product from which 0.56 g (51%) of pure sultone, m.p. 157–158.5°, was obtained after two recrystallizations from methylene chloride – pentane. Spectroscopic properties were as follows: i.r. ($CHCl_3$), 1350 (vs), 1162 (s), 1010 (s) and 925 (s) cm^{-1}; n.m.r. peaks ($CDCl_3$), δ = 1.8–2.8 (m, 4H), 4.22 (d of d, J = 4 and 12 c.p.s., 1H), 4.3–4.8 (m, 2H) and 7.3–7.6 (m, 5H).

Anal. Calcd. for $C_{10}H_{12}O_3S$: C, 56.60; H, 5.70; S, 15.08. Found: C, 56.53; H, 5.72; S, 15.24.

4-Hydroxy-1-methylbutanesulfonic Acid 1,4-Sultone

To a solution of 1.74 g (6.7 mmoles) of 1,3-propylene diethanesulfonate in 40 ml of tetrahydrofuran at −78° were added dropwise 7.5 mmoles of *n*-butyllithium. The reaction mixture was stored at 10° for 2 h. Distillation of the crude product gave 0.74 g (74%) of sultone (11).

4-Hydroxy-4-methylbutanesulfonic Acid 1,4-Sultone

n-Butyllithium (6.7 mmoles) was added to a solution of 1.55 g (6.3 mmoles) of 1,3-butylene dimethanesulfonate in 35 ml of tetrahydrofuran at −78°. The reaction mixture was stored at −20° for 2 h (colorless precipitate) then at 5° for a further 12 h. Distillation of the crude product gave 0.71 g (75%) of sultone **10**, n_D^{20} = 1.460, lit. (13) n_D^{25} = 1.4586.

*Sultone **15***

A solution of 1.03 g (4.0 mmoles) of *trans*-2-bromocyclohexyl methanesulfonate in 35 ml tetrahydrofuran was treated with 4.8 mmoles of *n*-butyllithium and then stored at 5° for 2 days. Workup gave 0.672 g of crude material from which was obtained by preparative t.l.c. 0.232 g (33%, 39% based on recovered starting material) of sultone **15**, m.p. 54–55° (methylene chloride – pentane).

Anal. Calcd. for $C_7H_{12}O_3S$: C, 47.72; H, 6.87; S, 18.16. Found: C, 47.73; H, 6.93; S, 18.01.

*cis-Sultone **17***

n-Butyllithium (4.7 mmoles) was added dropwise to a solution of 1.13 g (3.9 mmoles) of *trans*-2-bromocyclooctyl methanesulfonate in 30 ml of tetrahydrofuran which had been cooled to −78°. The reaction mixture was kept at 10° for 18 h. Workup gave 830 mg of crude product as a yellowish oil whose n.m.r. spectrum indicated a 1:1 mixture of starting material and sultone **17**. The sultone was isolated by preparative t.l.c. (3:2 pentane–ether). The yield was 294 mg (36%, 64% based on recovered starting material). Recrystallization from methylene chloride – pentane gave colorless flakes m.p. 56.5–57.5°. The n.m.r. spectrum ($CDCl_3$) showed multiplets from δ = 1.2–2.3 (12H), 2.8–3.6 (3H) and 4.8–5.0 (1H); i.r. peaks ($CHCl_3$), 1340 (vs), 1155 (s), and 910 (s) cm^{-1}.

Anal. Calcd. for $C_9H_{16}O_3S$: C, 52.93; H, 7.90; S, 15.67. Found: C, 53.08; H, 7.89; S, 15.54.

*trans-Sultone **19***

To a solution of 2.80 g (9.0 mmoles) of *cis*-dimesylate **18** in 50 ml of tetrahydrofuran at −78° were added dropwise 9.9 mmoles of *n*-butyllithium. The reaction mixture was kept at 10° overnight. Workup gave 2.30 g of crude product whose n.m.r. spectrum indicated a 3:1 mixture of starting material and product. Separation by preparative t.l.c. (3:2 pentane–ether) gave 304 mg (17%, 48% based on consumed starting material) of the *trans*-sultone **19** as colorless needles m.p. 56–57° (mixed m.p. with the *cis*-sultone **17**, 35–50°). The n.m.r. spectrum ($CDCl_3$) showed multiplets at δ = 1.2–2.4 (12H), 2.6–3.7 (3H), and 4.5–4.8 (1H); i.r. peaks ($CHCl_3$), 1340 (vs), 1155 (s), 905 (m), 880 (m), 848 (m) cm^{-1}.

Anal. Calcd. for $C_9H_{16}O_3S$: C, 52.93; H, 7.93; S, 15.67. Found: C, 52.79; H, 7.90; S, 15.53.

Reaction of 4-Chlorobutyl Methanesulfonate with n-Butyllithium

n-Butyllithium (7 ml, 11.2 mmoles) was added dropwise to a solution of 2.01 g (10.7 mmoles) of 4-chlorobutyl methanesulfonate in 50 ml of tetrahydrofuran at −78°. The reaction mixture was stored at room temperature for 2 days. The crude product (1.04 g) was purified by preparative t.l.c. and gave 475 mg (34%) of the ester **22** whose n.m.r. and i.r. spectra were identical to those obtained by reacting cyclopentanesulfonyl chloride with 4-chlorobutanol in methylene chloride in the presence of triethylamine (see below).

Reaction of Cyclopentanesulfonyl Chloride with 4-Chlorobutanol

Cyclopentanesulfonyl chloride (14) (5.35 g, 32 mmoles) and 3.8 g (35 mmoles) of 4-chlorobutanol were dissolved in 45 ml of methylene chloride at −78° and treated with dropwise addition of 3.5 g (35 mmoles) of triethylamine. The reaction mixture was warmed to room temperature and worked up in the usual manner. Two distillations of the crude product gave a slightly yellowish oil 4.25 g (57%), b.p. 145–150/0.75 mm.

Anal. Calcd. for $C_9H_{17}ClO_3S$: C, 44.91; H, 7.12; O, 19.92; S, 13.28. Found: C, 44.96; H, 6.91; O, 20.18; S, 13.49.

*Diester **23***

To a solution of 2.04 g (6.7 mmoles) of dimethanesulfonate **21** in 40 ml of tetrahydrofuran at −78° were added dropwise 7.3 mmoles of *n*-butyllithium. Workup gave 1.47 g of crude product from which 0.50 g of starting material was obtained by recrystallization. The remainder was purified by preparative t.l.c. and yielded 311 mg (23%) of the diester **23**. The i.r. and n.m.r. spectra were in agreement with the proposed structural assignment.

The compound tended to decompose and was not analyzed.

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1. D. S. Breslow and H. Skolnik. *In* The chemistry of heterocyclic compounds. Vol. 21. Part I. *Edited by* A. Weissberger. Interscience Publishers Inc., New York, 1966. pp. 79–87; Vol. 21. Part II. pp. 774–780.
2. F. G. Bordwell, R. D. Chapman, and C. E. Osborne. J. Amer. Chem. Soc. **81**, 2002 (1959).
3. E. J. Corey and T. Durst. J. Amer. Chem. Soc. **88**, 5656 (1966); **90**, 5548 (1968).
4. W. E. Truce and D. J. Vrencur. Can. J. Chem. **47**, 860 (1969).
5. T. Durst and J. du Manoir. Can. J. Chem. **47**, 1230 (1969).
6. D. J. Cram. Fundamentals of carbanion chemistry. J. Wiley and Sons Inc., New York, 1965. Chapter II.
7. G. M. Timms. Br. Pat. 700 677; C. A. **49**, 1773 (1955).
8. J. H. Chapman and L. N. Owen. J. Chem. Soc. 579 (1950).
9. A. G. Koslova and L. B. Leont'eva. Zhur. Obshchei Khim. **30**, 3541 (1960); C. A. **55**, 20944 (1961).
10. W. J. C. Ross and W. Davis. J. Chem. Soc. 2420 (1957).
11. G. A. Haggis and L. N. Owen. J. Chem. Soc. 389 (1953).
12. R. W. Ohline, A. L. Allred, and F. G. Bordwell. J. Amer. Chem. Soc. **86**, 4641 (1964).
13. W. E. Truce and F. D. Hoerger. J. Amer. Chem. Soc. **76**, 5357 (1964).
14. C. Ziegler and J. M. Sprague. J. Org. Chem. **16**, 621 (1951).