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The Reaction of α,α-Dichlorobenzyl Methyl Sulfone with Phenyllithium

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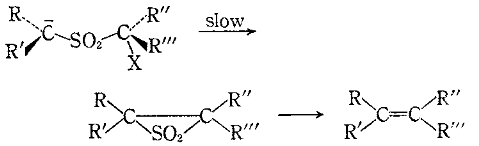
Few studies have been published on the intramolecular nucleophilic substitution of 1-halosulfones. Ramberg and Bäcklund[1] reported on how they formed *cis*-2-butene by reacting 1-bromoethyl ethyl sulfone with potassium hydroxide. Recently, Bordwell and Cooper[2] have elucidated the reaction mechanism as the formation of an episulfone, followed by decomposition to yield an olefin. It is worth noting here the predominant formation of *cis*-olefin:[3]



A similar reaction of 1,1-dihalosulfone with a base has been reported to yield an acetylenic compound and an olefinsulfonic acid, suggesting the

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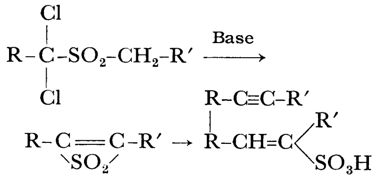
[1] L. Ramberg and B. Bäcklund, *Chem. Abstr.*, **34**, 4725 (1940).

[2] a) F. G. Bordwell and C. D. Cooper, *J. Amer. Chem. Soc.*, **73**, 5187 (1951). b) F. G. Bordwell, *J. Org. Chem.*, **33**, 1182 (1968).

[3] a) L. A. Paquette, *J. Amer. Chem. Soc.*, **86**, 4383 (1964). b) L. A. Paquette, *ibid.*, **90**, 6783 (1968).

formation of thiirene dioxide as the intermediate:[4,5]



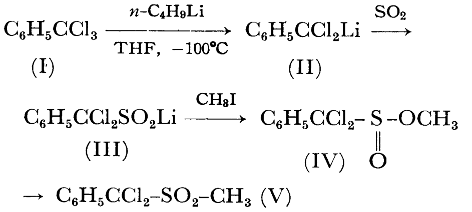
$$R\text{-}\underset{Cl}{\overset{Cl}{C}}\text{-}SO_2\text{-}CH_2\text{-}R' \xrightarrow{\text{Base}} \underset{SO_2}{R\text{-}C{=}C\text{-}R'} \rightarrow \overset{R\text{-}C\equiv C\text{-}R'}{R\text{-}CH{=}C(R')SO_3H} \qquad (2)$$

In the present communication, the results of the reaction of α,α-dichlorobenzyl methyl sulfone with phenylithium in tetrahydrofuran will be reported.

Results and Discussion

α,α-Dichlorobenzyl methyl sulfone (V) has been prepared from benzotrichloride (I). I was treated with *n*-butyllithium in tetrahydrofuran at −100°C to obtain a lithium compound (II). The insertion of sulfur dioxide into II has been found to be very easy, as is the carbon dioxide insertion into a similar compound,[6] which yields the α,α-dichlorobenzylsulfonyl lithium (III).

The reaction of III with methyl iodide resulted in the formation of α,α-dichlorobenzyl methyl sulfone (V) through the rearrangement of IV:



$$\underset{(I)}{C_6H_5CCl_3} \xrightarrow[\text{THF, }-100^\circ C]{n\text{-}C_4H_9Li} \underset{(II)}{C_6H_5CCl_2Li} \xrightarrow{SO_2}$$

$$\underset{(III)}{C_6H_5CCl_2SO_2Li} \xrightarrow{CH_3I} \underset{(IV)}{C_6H_5CCl_2\text{-}\underset{\displaystyle O}{\overset{}{S}}\text{-}OCH_3}$$

$$\rightarrow C_6H_5CCl_2\text{-}SO_2\text{-}CH_3\ (V) \qquad (3)$$

The reaction of the sulfone (V) with phenyllithium has been carried out in diethyl ether at 0°C for 3.5 hr. The products were then separated by alumina column chromatography. Several of the water-soluble products were treated with methyl iodide to convert the lithium salt to the methyl sulfone, and the products were eluted through a silica column in order to separate the methyl sulfones. The identified substances are listed in Table 1.

The following chart will account for the reaction paths for the various products from dichlorobenzyl methyl sulfone (V). (Chart 1).

The formation of *cis*- and *trans*-stilbenes (VI and VII), and the predominance of the *trans* compound over the *cis*, can be well reconciled with the fact that the addition of phenyllithium to 1-chloro-1-phenyl episulfone was followed by the elimination of sulfur dioxide. 1,1-Diphenyl episulfone was not found in the product. The difficulty of adding phenyl to the 1-position can be adequately explained by the steric reason and by the chlorine-lithium interaction.

The cleavage of 1-chloro-1-phenyl episulfone by phenyllithium leads to 1-chloro-1,2-diphenylethylsulfonyllithium, which then gives compound VIII by OLi-phenyl exchange and compound IX by the reaction with methyl iodide.

Experimental

α,α-Dichlorobenzyl Methyl Sulfone (V). To a solution of 58.7 g (0.3 mol) of benzotrichloride (I) in 600 m*l* of dehydrated tetrahydrofuran cooled at −100°C, freshly-prepared *n*-butyllithium (0.3 mol) in 150 m*l* of ether was slowly added under a nitrogen atmosphere for one hour, after which the mixture was stirred further at the same temperature for an additional half hour.

Sulfur dioxide (20 g) gas was streamed into the mixture at −100°C for 30 min, and then the solution was stirred for an additional hour and 50 m*l* of methyl iodide were added. The mixture was then slowly warmed and refluxed for fourteen hours.

After the mixture had been condensed to 1/3 its volume, water was added to the mixture and then it was extracted with ether. The ethereal solution was dried with sodium sulfate, condensed, and treated with 50 m*l* of petroleum ether to yield white crystals, which were then filtered and washed with chilled ether. Yield, 11.6 g (16.2%); mp 134.5—135.0°C. $\nu_{\text{max}}^{\text{Nujol}}$ 1155 and 1335 cm^{-1} (SO_2); 635 cm^{-1} (C–Cl). $\tau_{\text{TMS}}^{\text{CCl}_4}$, 6.80 (3$\underline{H}$ simple peak, SO_2CH_3), 2.4—2.7 (5$\underline{H}$ multiplet, phenyl).

Found: C, 39.96; H, 3.52%. Calcd for $C_8H_8Cl_2O_2S$: C, 40.18; H, 3.37%.

Reaction of α,α-Dichlorobenzyl Methyl Sulfone (V) with Phenyllithium. In a four-necked flask with

TABLE 1. THE REACTION OF α,α-DICHLOROBENZYL METHYL SULFONE WITH PHENYLLITHIUM

Product	Yield %
cis-Stilbene (VI)	2.7
trans-Stilbene (VII)	6.2
1,2-Diphenylethyl phenyl sulfoxide (VIII)	4.7
1,2-Diphenylethyl methyl sulfone (IX)	12.2
$C_6H_5CH{=}\underset{SO_2CH_3}{C}HC(C_6H_5)CH_2C(C_6H_5)(OH)\text{—}CH_2SO_2CH_3$ (X)	8.3
Phenyl methyl sulfone (XI)	24.6

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[4] a) L. A. Paquette, *J. Amer. Chem. Soc.* **86**, 4089 (1964). b) L. A. Paquette and L. S. Wittenbrook, *ibid.*, **89**, 4483 (1967).

[5] L. A. Paquette, L. S. Wittenbrook and V. V. Kane, *ibid.*, **89**, 4487 (1967); *ibid.*, **90**, 5211 (1968).

[6] D. F. Hoeg, D. I. Lusk and A. L. Crumbliss, *ibid.*, **87**, 4147 (1965).

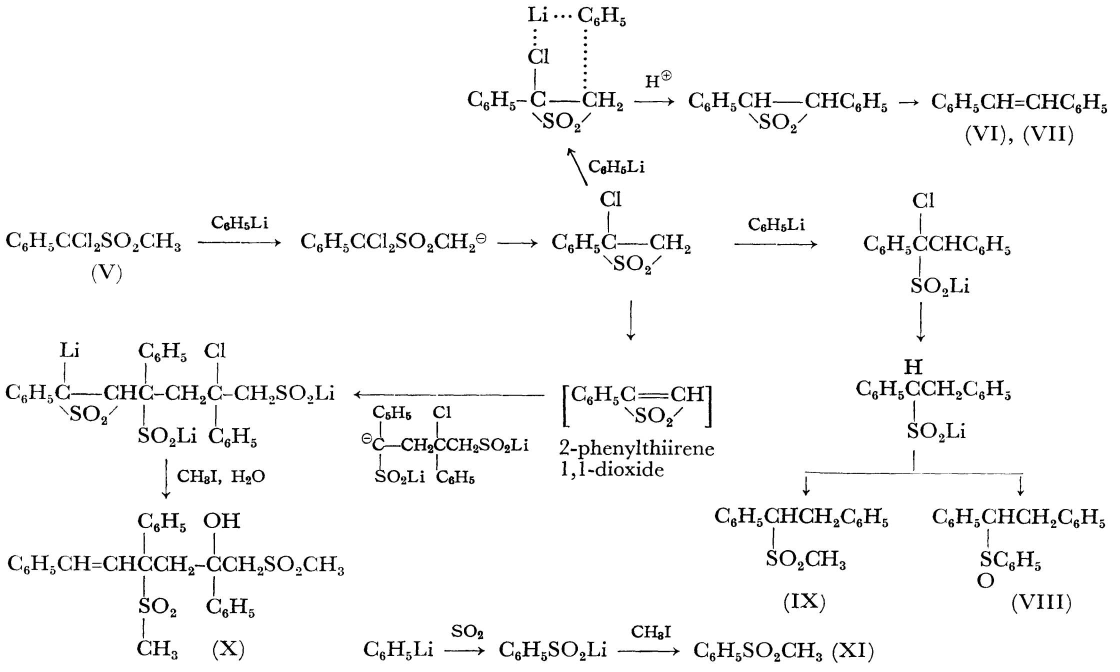


Chart 1

a capacity of 500 m*l*, 0.03 mol of phenyllithium in 70 m*l* of ether was cooled at 0°C; the mixture was stirred and then 2.0 g of α,α-dichlorobenzyl methyl sulfone dissolved in 250 m*l* of ether were added over a 1.5-hr period under a nitrogen atmosphere, with the temperature of the mixture kept at 0°C. The mixture was then stirred for an additional 3.5 hr at the same temperature.

After the reaction was over, the mixture was poured into ice water and the whole mixture was extracted with ether; the ether solution was then dried with sodium sulfate and condensed. The condensate was dissolved in petroleum ether and separated chromatographically using an alumina column. The solvents used as the eluants were in the following order: petroleum ether-benzene-ether-methanol. The aqueous layer was refluxed with 6.0 g of methyl iodide for 15 hr. The reaction mixture was then extracted with ether, and the extract was dried with sodium sulfate and evaporated. The residue was dissolved in benzene and eluted on a silica column.

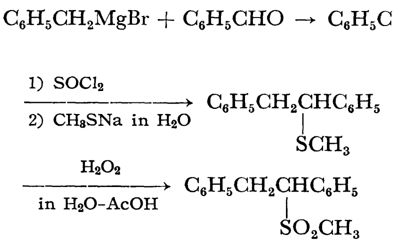
***cis*- and *trans*-Stilbene.** The stilbenes were separated from the alumina column by elution with benzene and were then further separated and purified by preparative g.l.c. (45 m silicone D.C.) to *cis*- and *trans*-stilbenes. *cis*-*S*tilbene (VII), oil; yield 40.7 mg (2.7%); the results of the elemental analysis, the retention time, and the infrared and NMR spectra were consistnt with those of an authentic specimen. *trans*-*S*tilbene (VII), crystal; the mp and mixed mp with an authentic sample were 214—125.0°C; yield 11.28 mg (6.2%); the results of the elemental analysis, the retention time, and the IR and NMR spectra all supported the above identification.

1,2-Diphenylethyl Phenyl Sulfoxide (VIII). Elution by methanol gave the sulfoxide (VIII); yield, 122 mg (4.7%); mp 126.0—126.5°C. ν_{max}^{Nujol} 1050 cm^{-1} (SO), $\tau_{max}^{CCl_4}$, 2.5—3.4 (15$\underline{H}$ multiplet), 5.9—7.0 (3$\underline{H}$ ABC type multiplet). Found: C, 77.92; H, 5.75%. Calcd for $C_{20}H_{18}OS$: C, 78.39; H, 5.92%.

1,2-Diphenylethyl Methyl Sulfone (IX). An aqueous layer refluxed with methyl iodide was extracted with ether and then separated on a silica column. The fraction eluted with an ether-benzene mixture gave 1,2-diphenylethyl methyl sulfone (IX); yield 269 mg (12.2%); mp 124.5—125°C (from ethanol). ν_{max}^{KBr}, 1295 and 1130 cm^{-1} (SO_2). Mass., parent peak, 260 *m*/*e*, (Calcd 260). $\tau_{TMS}^{CDCl_3}$, 7.39 (3$\underline{H}$, singlet, SO_2-$C\underline{H}_3$), 6.72 (1$\underline{H}$ quartet), 6.18 (1$\underline{H}$ quartet, C_6H_5–$C\underline{H}_A\underline{H}_B$), 5.72 (1$\underline{H}$ quartet, CH_2 - $C\underline{H}_X$), J_{BA}=13.8 Hz, J_{AX}=3.9 Hz, J_{AX}=10.6 Hz.

Found: C, 69.22; H, 6.24%. Calcd for $C_{15}H_{16}O_2S$: C, 69.21; H, 6.20%.

An authentic sample was prepared from benzylmagnesium bromide and benzaldehyde by the following route:



$$C_6H_5CH_2MgBr + C_6H_5CHO \rightarrow C_6H_5CH_2\underset{OH}{CH}C_6H_5$$

$$\xrightarrow[2)\ CH_3SNa\ \text{in}\ H_2O]{1)\ SOCl_2} C_6H_5CH_2\underset{SCH_3}{CH}C_6H_5$$

$$\xrightarrow[\text{in}\ H_2O\text{-}AcOH]{H_2O_2} C_6H_5CH_2\underset{SO_2CH_3}{CH}C_6H_5$$

The mixed melting point of IX with the above specimen was not depressed: 124.5—125.0°C.

Disulfone (X). A fraction obtained from the silica column above mentioned (ether-benzene eluant) was condensed. Recrystallization of the residual substance from ethanol gave crystals of X; mp 182.0—182.5°C; yield 114 mg (8.3%). ν_{max}^{Nujol} 1290 and 1110 cm^{-1},

(=SO_2), 1645 cm^{-1}, (olefin). Mol. Wt. 480 (vapor) pressure osmometry) (calcd 484.5).

Found: C, 64.58; H, 5.97%. Calcd for $C_{26}H_{28}O_5S_2$: C, 64.43; H, 5.82%. $\tau_{max}^{CCl_4}$, 7.32 (3$\underline{H}$ singlet, $SO_2C\underline{H}_3$), 7.41 (3$\underline{H}$ $SO_2C\underline{H}_3$), 8.24 (1$\underline{H}$ singlet, O$\underline{H}$), 5.80—7.00 (4$\underline{H}$ octet, =$C\underline{H}_2$), 4.60 (1$\underline{H}$ doublet), 3.88 (1$\underline{H}$ doublet), 2.10—3.50 (15$\underline{H}$ multiplet).

Phenyl Methyl Sulfone (XI). This substance was obtained from a fraction eluted by benzene on the silica column; after the evaporation of the solvent this substance gave crystals. Yield, 251 mg (24.6%); mp 88.0—89.0°C (from ethanol); mixed mp with an authentic specimen, 88.0—89.0°C; Mass. parent peak, 156 *m/e*, (calcd 156). ν_{max}^{Nujol}, 1295 and 1150 cm^{-1}, (=SO_2). $\tau_{max}^{CCl_4}$, 6.92 (3$\underline{H}$ singlet, $SO_2C\underline{H}_3$), 1.85—2.50 (5$\underline{H}$ multiplet, phenyl protons).