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THE REACTION OF BENZYLSULFONYL HALIDES WITH PHENYLLITHIUM

PREPARATION OF SULFONES

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Abstract—The reactions of benzylsulfonyl halides with phenyllithium have been studied. The reaction of benzylsulfonyl chloride with phenyllithium in diethyl ether at 20–25° gave lithiumbenzyl sulfinate as a main product, in addition to other eight products. While the reaction of benzylsulfonyl fluoride with phenyllithium under a similar condition afforded a disulfone, α-benzylsulfonyl-α-benzenesulfonyltoluene, as a major product. On the other hand, the reactions at a low temperature (−80°) yielded a polysulfone which did not form when the reactions were carried out at an ordinary temperature. The differences of reaction courses due to a difference of a halogen content or an experimental condition are discussed, and probable mechanisms of these results are presented.

IT HAS been well known for many years that some arylsulfonyl halides react with a Grignard reagent to form sulfones, sulfoxides or sulfinic acids.[1,2] However, alkanesulfonyl halides have not yet been fully studied. Recently the reactions between alkanesulfonyl chlorides and a weak base, triethylamine, have been discussed in view of the intermediacy of sulfenes.[3] Since alkanesulfonyl halides contain an active hydrogen α to the sulfone group toward organometallic reagents, it appeared to be of much interest to investigate the reaction of alkanesulfonyl halides with organolithium compounds. In a previous communication[4] we reported the products obtained in the reaction of benzylsulfonyl halides with phenyllithium. This paper is concerned with a more detailed description of the reactions above mentioned where different reaction courses have been observed by the difference of the halogen content or experimental conditions, for which possible mechanisms are presented.

RESULTS AND DISCUSSION

By the reaction of benzylsulfonyl chloride (Ia) with a small excess of phenyllithium in diethyl ether at 20–25°, a disulfone, α-benzylsulfonyl-α-benzenesulfonyl toluene (I), α-chlorobenzyl phenyl sulfone (II), chlorobenzene (III), *trans*-stilbene (IV), α,α-dichlorobenzyl phenyl sulfone (V), *trans*-1,2-diphenylvinyl phenyl sulfone (VI), benzyl phenyl sulfone (VII), a trisulfone, α-benzylfonyl-α′-benzenesulfonyl dibenzyl sulfone (VIII) were isolated from the ethereal extract of the reaction mixture and identified respectively. From the aqueous extract the formation of lithiumbenzyl sulfinate (IX) was verified. The reaction products are summarized in Scheme 1.

Characterization of VI as *trans*-1,2-diphenylvinyl phenyl sulfone was evidenced

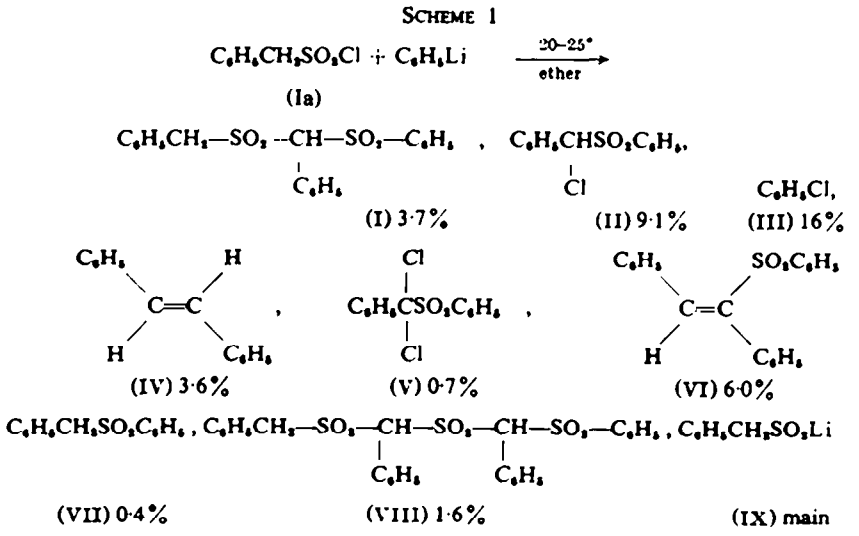
[1] [a] H. Gilman and R. E. Fothergiel, *J. Amer. Chem. Soc.* **51**, 3501 (1929); [b] H. Burton and W. A. Davy, *J. Chem. Soc.* 528 (1948).

[2] [a] D. T. Gibson, *J. Prakt. Chem.* **142**, 218 (1935); [b] H. Fukuda, F. J. Frank and W. E. Truce *J. Org. Chem.* **28**, 1420 (1963).

[3] [a] W. E. Truce and J. R. Norell, *J. Amer. Chem. Soc.* **85**, 3231 (1963); [b] J. F. King and T. Durst, *ibid.* **87**, 5684 (1965).

[4] Y. Shirota, T. Nagai and N. Tokura, *Bull. Chem. Soc. Japan* **39**, 405 (1966).

SCHEME 1



by the elemental analysis, mol. wt. determination, the UV, IR and NMR analyses. The IR spectrum shows the presence of the sulfone group at 1300 and 1140 cm^{-1} and also contains bands at 1620 and 820 cm^{-1}, assignable to a C=C double bond stretching vibration, to a C—H out of plane deformation vibration of trisubstituted ethylene,[5] respectively. The NMR spectrum is in good agreement with the postulated structure, showing a singlet peak at τ 2, assignable to the vinyl proton, and complex peaks centered at τ 2·65, attributable to aromatic protons, the relative areas being 1:15 (Fig. 1). The UV spectrum shows a λ_{max}^{EtOH} at 275 mμ (ε 18,900). The *cis*-isomer

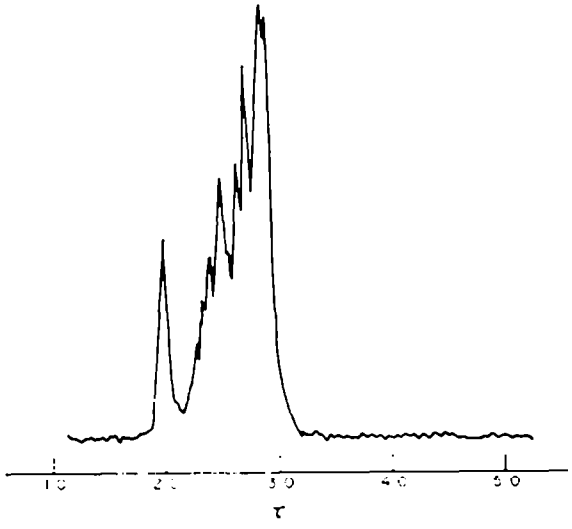


FIG. 1. The NMR spectrum of *trans*-1,2-diphenylvinyl phenyl sulfone in $CDCl_3$.

of VI was isolated only when the reaction was carried out at a low temperature. The assignment of configuration for *cis*- or *trans*-isomer was based on their m.p. and the UV spectra. The *cis*-isomer absorbs at λ_{max}^{EtOH} 272 mμ (ε 13,600) (Fig. 2).

[5] L. J. Bellamy, *The Infrared Spectra of Complex Molecules* p. 51. J. Wiley, New York (1958).

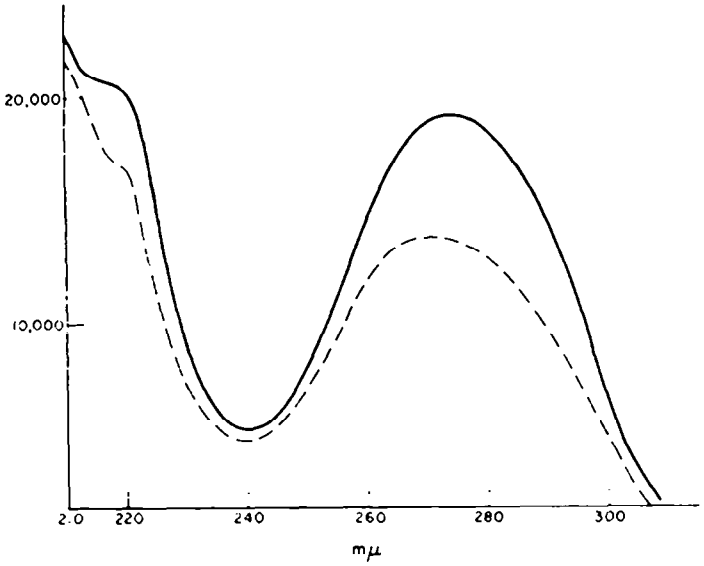
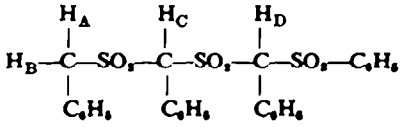


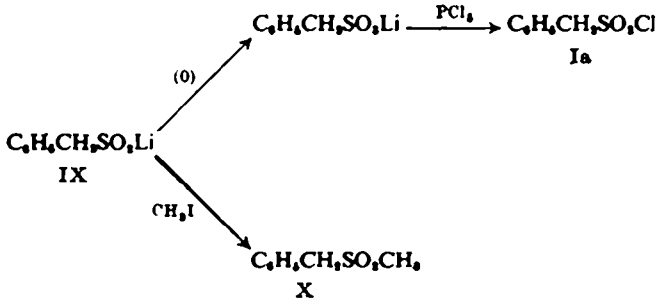
FIG. 2. The UV spectrum of *cis*, *trans*-1.2-diphenylvinyl phenyl sulfone in 95% EtOH.
—— *trans*-isomer
– – – *cis*-isomer

The structure of VIII was identified as



The IR spectrum contains strong bands of the sulfone groups at 1340, 1330, 1320, 1150 and 1120 cm^{-1}. The NMR spectrum shows two non-equivalent hydrogens (H_A and H_B) in a typical AB quartet centered at τ 5·63 with J_{AB} 13·5 c/s, two singlet peaks at τ 3·08 and τ 3·3, assignable to H_D and H_C respectively, and aromatic protons at τ 2·6. The relative areas are 2:1:1:20 (Fig. 3).

The aqueous layer after the extraction with ether was evaporated to dryness to leave solids including inorganic materials. When the solids after drying were treated with PCl_5, there was obtained benzylsulfonyl chloride (Ia) in an unspecified yield. It is interpreted as a result that lithiumbenzyl sulfinate (IX) formed in the reaction was oxidized with air to lithiumbenzyl sulfonate,[6] which gave Ia by the interaction with PCl_5. Moreover, the formation of lithiumbenzyl sulfinate (IX) was confirmed by converting it to benzyl methyl sulfone (X). IX formed in an overwhelming yield in the reaction.



[6] E. Fromm and J. de S. Palme, *Ber Dtsch. Chem. Ges.* **39**, 3308 (1906).

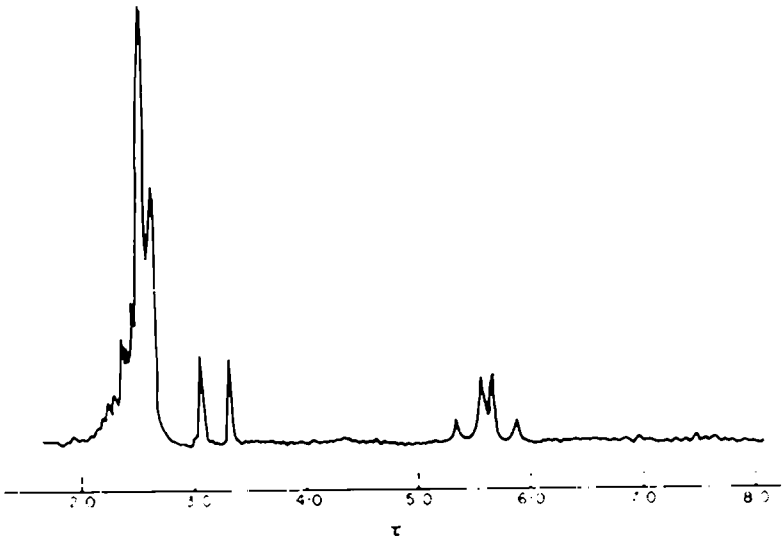


FIG. 3. The NMR spectrum of α-benzylsulfonyl-α′-benzenesulfonyl dibenzyl sulfone in $CDCl_3$.

The similar treatment of benzylsulfonyl fluoride (Ib) with phenyllithium in diethyl ether gave the disulfone, α-benzylsulfonyl-α-benzenesulfonyl toluene (I), *trans*-stilbene (IV), benzyl phenyl sulfone (VII), the trisulfone, α-benzylsulfonyl-α′-benzenesulfonyl dibenzyl sulfone (VIII) and lithiumbenzyl sulfinate (IX). In this case the major product was the disulfone (I) in contrast to the result by benzylsulfonyl chloride, where IX was the main product. It is also to be noted that the corresponding fluorocompounds of II, V and 1,2-diphenylvinyl phenyl sulfone (VI) were not found. When the order of addition was reversed, almost the same result was obtained except the formation of phenylbenzyl sulfonate (XI), as shown in Table 1.

TABLE 1. YIELDS OF THE PRODUCTS (%) FORMED IN THE REACTION OF $C_6H_5CH_2SO_2F$ WITH C_6H_5Li

	I	IV	VII	VIII	IX	$C_6H_5CH_2SO_2OC_6H_5$ (XI)
A	59·1	3·9	1·8	4·0	3·0	none
B	64·8	3·4	0·43	3·6	—	1·5

A: C_6H_5Li was slowly added to ethereal solution of $C_6H_5CH_2SO_2F$
B: $C_6H_5CH_2SO_2F$ was slowly added to ethereal solution of C_6H_5Li

Probable reaction paths

The following competing reactions are assumed to take place simultaneously at an early stage of the reaction.

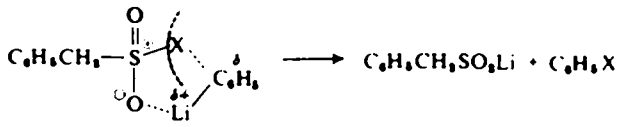
$$C_6H_5CH_2SO_2X + C_6H_5Li \longrightarrow \underset{\text{VII}}{C_6H_5CH_2SO_2C_6H_5} + LiX \qquad (1)$$

$$C_6H_5CH_2SO_2X + C_6H_5Li \longrightarrow \underset{\text{Li XII}}{C_6H_5CHSO_2X} + C_6H_6 \qquad (2)$$

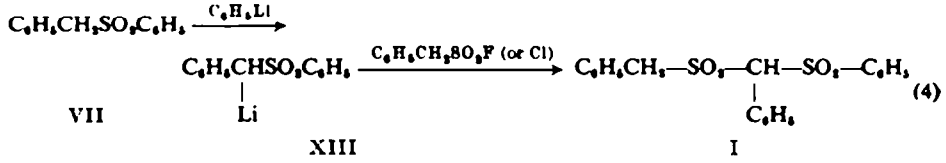
$$C_6H_5CH_2SO_2X + C_6H_5Li \longrightarrow \underset{\text{IX}}{C_6H_5CH_2SO_2Li} + C_6H_5X \qquad (3)$$
$$X = Cl, F$$

Eq. 1 is a S_N2-like substitution reaction by phenyllithium on sulfur (coupling reaction), thus phenyllithium acts as a nucleophile, and in Eq. 2 it acts as a base, abstracting an

α hydrogen to give α-lithiumbenzylsulfonyl halide (XII). Eq. 3 is a halogen–lithium interconversion reaction between benzylsulfonyl halide and phenyllithium possibly via the following process.

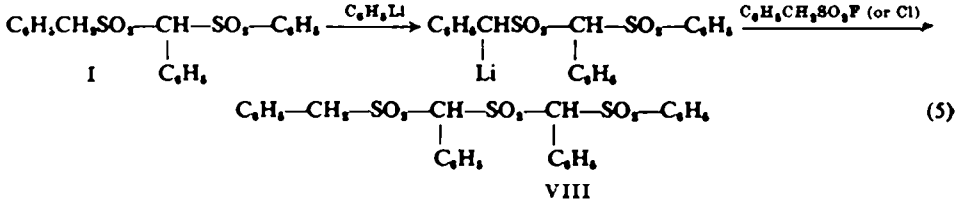


In the reaction of benzylsulfonyl fluoride (Ib) Eq. 1 is the exclusive reaction course, and initially formed benzyl phenyl sulfone (VII) is further metalated by phenyllithium, followed by its S_N2-like substitution reaction (coupling reaction) on Ib to yield the disulfone (I).



(4)

The trisulfone is also presumed to arise in a similar fashion from the disulfone (I) above formed in the reaction.



(5)

From the above observations it is indicated that the metalation on benzyl phenyl sulfone (VII) occurrs preferentially to the metalation on Ib or Ia.

The formation of lithiumbenzyl sulfinate (IX) in the reaction of Ib, though very small, suggests that the fluorine of S—F bond can be replaced by lithium of organolithium reagents, although the F–Li interconversion reaction of a C—F bond has not yet been reported.

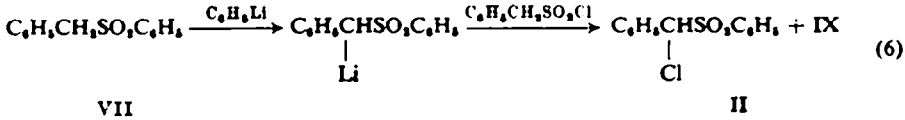
That the Eqs. 1 and 4 are predominant courses with the reaction of benzylsulfonyl fluoride (Ib) was indicated by the method of reversing the order of addition (B method). In this case, in contrast to A method, a bright yellow color resulting from $C_6H_5{\cdot}CH(Li){\cdot}SO_2{\cdot}C_6H_5$ (XIII) developed during the slow addition of Ib and after approximately a half volume of the ethereal solution of Ib was added the color gradually disappeared to form the disulfone by the reaction of XIII with Ib. Furthermore, this was confirmed by the following experiment. Independently synthesized benzyl phenyl sulfone was metalated with phenyllithium[7] and was treated with benzylsulfonyl fluoride to give 61% yield of the disulfone and 3·6% yield of the trisulfone, together with a small amount of *trans*-stilbene. A one-step formation of the disulfone and trisulfone is a result that the starting sulfonyl fluoride possesses

[7] E. A. Lehto and D. A. Schirly, *J. Org. Chem.* 22, 989 (1957).

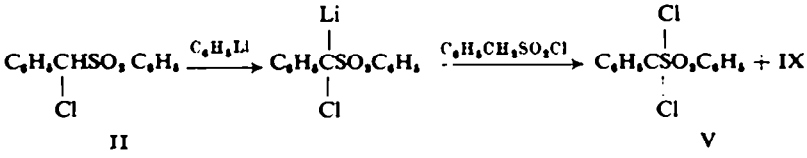
α hydrogens to the sulfone group. Since the reaction here investigated produces a high yield of the disulfone (I), it serves as a good preparatory method.[8] Moreover, it is also anticipated that alkanesulfonyl fluorides generally serve as starting substances for the preparation of such types of unsymmetrical disulfones[10] as $(SO_2Ar)\cdot RCH\cdot(SO_2CH_2R)$ and hitherto unknown trisulfones. Further work is in progress.

On the other hand, the principal reaction of benzylsulfonyl chloride (Ia) is Eq. 3. Moreover the reaction of Ia is different from that of Ib in that II, V and VI form.

The following mechanisms are postulated for the formation of II and V.



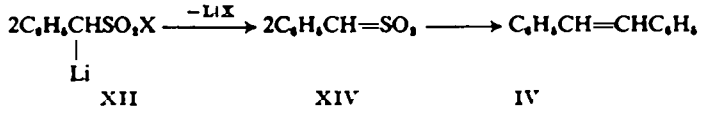
(6)



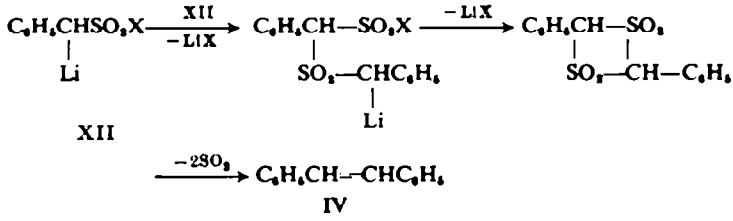
(7)

The Li–Cl interconversion is thus predominant in the case of Ia, therefore the yields of coupling products, I and VIII, are low.

The formation of olefins, IV and VI, is somewhat interesting in view of the possible intermediacy of phenylsulfene. *trans*-Stilbene, which forms in both reactions, results from Eq. 2 and the following two alternative mechanisms are presented.



(8)



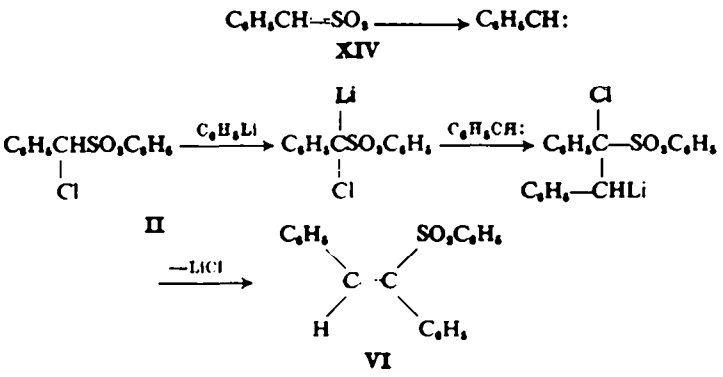
(9)

It is not clear at present whether the reaction involves phenylsulfene as a transient intermediate as shown in Eq. 8, however, the formation of VI can be best rationalized by the assumption of a sulfene intermediate.

[8] α-Benzylsulfonyl-α-benzenesulfonyl toluene has hitherto been prepared by a less attractive route.[9]

[9] T. Posner, *Ber. Dtsch. Chem. Ges.* **36**, 296 (1903); [9] M. M. Campos and H. Hauptmann, *J. Amer. Chem. Soc.* **74**, 2962 (1952).

[10] An analogy exists for the formation of diarylsulfonyl alkanes.[9]



(10)

This mechanism is consistent with the fact that in the reaction of Ib corresponding α-fluorobenzyl phenyl sulfone did not form, hence the formation of VI was not observed.

Of particular interest is that when benzylsulfonyl chloride (Ia) was treated with phenyllithium at −80°, a phenylmethylene polysulfone $(C_6H_5CHSO_2)_n$ (XV) and *cis*-isomer (XVI) of VI, together with other products were obtained, XV was characterized on the basis of IR, NMR spectra and elemental analysis. In the case of benzylsulfonyl fluoride (Ib) only polysulfones with varying mol. wts were obtained under the same condition, whose IR spectra were completely identical with that of XV. Disulfone (I) and trisulfone (VIII) were not detected in both reactions at a low temperature. These findings give an interesting suggestion that reaction courses are substantially different between the reactions at an ordinary temperature and at a very low temperature. The details concerning low temperature reactions are to be reported in a later paper.

EXPERIMENTAL

Materials. Diethyl ether (ether) and tetrahydrofuran (THF) were obtained commercially and of reagent grade. Ether was dried for 1 week over Na and distilled. THF was refluxed with KOH for 2 days, then dried with Na under a reflux and distilled from it immediately before use. Phenyllithium was prepared from Li and bromobenzene in ether according to the method of Gilman.[11] Benzylsulfonyl chloride (Ia) was prepared from benzylmagnesium chloride and sulfuryl chloride according to the method of Cherbuliez and Schnauder,[12] m.p.[13] 91·5–92° (lit. m.p. 92°). Benzylsulfonyl fluoride (Ib) was prepared from the corresponding chloride (Ia) by the method of Tullock and Coffmann,[14] m.p. 92–93° (lit.[15] m.p. 91–92°).

Apparatus. IR spectra were run on a EPI-S2 type Hitachi infrared spectrometer. NMR spectra were obtained with a Varian A-60 spectrometer. UV spectra were taken with a EPS-3 Hitachi recording spectrometer. Vapor phase chromatograms were carried out on a GCG-3DH type Yanagimoto gas chromatograph and on a KGL-S type Hitachi gas chromatograph. Mol. wts were determined with a Mechrolab vapor pressure osmometer.

Reaction of benzylsulfonyl chloride (Ia) *with phenyllithium in ether*

To a solution of 26 g (0·14 mole) Ia in 400 ml of anhydrous ether was added slowly 130 ml ethereal solution of phenyllithium (0·15 mole), which was prepared from 29·5 g bromobenzene and

[11] *Organic Reaction*, Ed. by R. Adams, Vol. 6, p. 353. J. Wiley, New York (1951).
[12] F. Cherbuliez and O. Schnauder, *Helv. Chim. Acta* **6**, 256 (1923).
[13] All m.ps are uncorrected.
[14] C. W. Tullock and D. D. Coffman, *J. Org. Chem.* **25**, 2016 (1060).
[15] [a] D. E. Fahrney and A. M. Gold, *J. Amer. Chem. Soc.* **85**, 997 (1963); [b] W. Davis and J. H. Dick, *J. Chem. Soc.* 483 (1932).

2·8 g Li, over a period of 30 min at a bath temp of 20–25° with stirring under N_2. The reaction was slightly exothermic. After the addition was complete, stirring was continued for 4 hr. The reaction mixture was then carefully hydrolysed with cold water and extracted with a large amount of ether. The ethereal extract was dried (Na_2SO_4) and filtered. A white solid (I), 1 g, precipitated upon standing for several hr and subsequently 1·7 g of a white solid (II) separated upon concentration.

I was recrystallized from dimethylformamide, m.p. 248–250°, and identified as α-benzylsulfonyl-α-benzenesulfonyl toluene. The IR spectrum shows strong bands of the sulfone groups at 1320, 1310, 1150 and 1135 cm^{-1}. The NMR spectrum (DMSO, 100°) shows peaks at τ 2·6 (aromatic protons, 15H), at τ 3·5 (—SO_2—CH(C_6H_5)—SO_2, 1H) and at τ 5·2 ($C_6H_5CH_2SO_2$, 2H) relative to TMS as an internal standard. Yield, 3·7%. (Found: C, 61·99; H, 4·69; S, 16·33; mol. wt. 374. Calc. for $C_{26}H_{16}O_4S_2$: C, 62·15; H, 4·70; S, 16·59%; mol. wt. 386.)

II was recrystallized from AcOH to form white needles, m.p. 179–180°, and identified as α-chlorobenzyl phenyl sulfone. The IR spectrum of II was completely identical with that of an authentic sample. No depression of m.p. was observed by admixture with an authentic specimen[16] prepared according to the method of Otto,[16a] mixed m.p. 179–180°. The yield was 9·1%. (Found: C, 58·13; H, 4·34. Calc. for $C_{13}H_{11}ClO_2S$: C, 58·53; H, 4·16%.)

The ethereal extract after removal of the above two products, I and II, was distilled under red. press. to give a colorless liquid, b.p. 62–67°/50 mm, 3·5 g, a lower boiling fraction and a residue.

The colorless liquid was characterized as a mixture of chlorobenzene (III) and a small amount of bromobenzene, the latter being attributable to unreacted bromobenzene used in the preparation of phenyllithium. VPC of the liquid gave peaks of chlorobenzene contaminated with bromobenzene with a relative area of 18 to 7, the retention times being 5·4 and 10·2 min respectively. The coincidence of b.ps, IR spectra, and the retention times with those of the standard samples was confirmed. The lower boiling fraction gave a peak with a retention time, 1·4 min, equal to that of benzene. (The gas chromatography was carried out on a KGL-S type Hitachi gas chromatograph at a column temp of 151° with a 2 m × 4 mm column of T.C.P., at a He flow of *ca.* 35 ml/min.)

The residue, 6·0 g, was dissolved in benzene and separated by column chromatography on alumina (Sumitomo activated alumina KCG 1225, ignited at 200° for 4 hr) to afford 0·45 g (3·6%) of *trans*-stilbene (IV), m.p. 123°, which was eluted with benzene and recrystallized from MeOH, 0·08 g (0·7%) of α,α-dichlorobenzyl phenyl sulfone (V), m.p. 151–152°, which was eluted with benzene and recrystallized from benzene, 0·9 g (6%) of *trans*-1,2-diphenylvinyl phenyl sulfone (VI), m.p. 182·5–183°, which was eluted with ether and recrystallized from ether, 0·1 g (0·4%) of benzyl phenyl sulfone (VII), m.p. 146°, which was eluted with ether and recrystallized from EtOH, and 0·4 g (1·6%) of α-benzylsulfonyl-α′-benzenesulfonyl dibenzylsulfone (VIII), m.p. 199–201°, which was eluted with MeOH, crystallized as a prism from the eluted solution upon standing, respectively.

Identifications of IV as *trans*-stilbene and VII as benzyl phenyl sulfone were based on the mixed m.p. and the coincidence of the IR spectra with those of the authentic samples[17,18] respectively.

Identification of V as α,α-dichlorobenzyl phenyl sulfone was made by the elemental analysis, the IR and NMR spectra. The IR spectrum shows the strong bands at 1330, 1310 and 1150 cm^{-1}, assignable to the sulfone group. The NMR spectrum ($CDCl_3$) exhibits only aromatic protons centered at τ 2·35 relative to TMS. (Found: C, 51·54; H, 3·06; Cl, 23·75. $C_{13}H_{10}Cl_2O_2S$ requires: C, 51·84; H, 3·34; Cl, 23·54%.)

Characterization of VI as *trans*-1,2-diphenylvinyl phenyl sulfone was based on its elemental analysis, mol. wt. determination, UV, IR and NMR spectra. It gives a positive Baeyer's test for unsaturation. UV: $\lambda_{max}^{95\%EtOH}$ 275 mμ (ε 18,900). This indicates the conjugation of the phenyl group with C—C double bond. IR: ν_{max}^{Nujol} cm^{-1} 1300, 1140 (sulfone), 1620 (C=C), 820 (trisubstituted ethylene). NMR: ($CDCl_3$) τ 2 (singlet, 1H, vinyl proton), τ 2·65 (multiplet, 15H, aromatic protons). (Found: C, 74·64; H, 5·05; S, 10·09; mol. wt., 316. $C_{20}H_{16}O_2S$ requires: C, 74·97; H, 5·03; S, 10·00%, mol. wt., 320.)

The identification of the structure of VIII comes from the following evidences. IR: ν_{max}^{Nujol} cm^{-1}: 1340, 1330, 1150, 1120 (SO_2). NMR: ($CDCl_3$) τ 5·63 (quartet; 2H, methylene protons, J 3·5 c/s.).

[16] [a] R. Otto, *J. Prakt. Chem.* **40**, [2] 516 (1889); [b] F. G. Bordwell, *J. Amer. Chem. Soc.* **77**, 572 (1955).
[17] L. F. Fieser, *Experiments in Organic Chemistry* p. 185. Heath and Maruzen, Japan (1956).
[18] R. Otto and W. Otto, *Ber. Dtsch. Chem. Ges.* **21**, 1696 (1885).

τ 3·08 (singlet, 1H methine proton), τ 3·3 (singlet, 1H, methine proton), τ 2·6 multiplet, (20 H, aromatic protons). (Found: C, 60·01; H, 4·54; S, 17·49; mol. wt., 543. $C_{37}H_{34}O_6S_2$ requires: C, 59·98; H, 4·47; S, 17·78; mol. wt., 541.)

The aqueous layer after the extraction with ether was refluxed with 16·2 g (0·14 mole) MeI in the presence of 4 g (0·1 mole) NaOH for about 3·5 hr. After cooling the reaction mixture was extracted twice with 200 ml ether. Evaporation of ether gave approximately 5·0 g benzyl methyl sulfone (X). It melted sharply at 126° after recrystallization from water (lit.[18] m.p. 127°) and was confirmed by the m.p., the IR spectrum, and the elemental analysis. (Found: C, 56·63; H, 6·01. Calc. for $C_8H_{10}O_2S$: C, 56·45; H, 5·92%.)

A small part of the aqueous layer was evaporated to dryness to leave solids including inorganic materials. These solids after drying were mixed with PCl_5, moistened with $POCl_3$ and heated at 70° for about 4 hr. The mixture was then poured into cold water and extracted with ether. On removal of ether benzylsulfonyl chloride (Ia) was separated. After recrystallization from ether it did not depress the mixed m.p. with an authentic specimen,[19] mixed m.p. 91–92°. It showed identical IR spectrum with that of an authentic sample.

Reaction of benzylsulfonyl fluoride with phenyllithium

Method A. 14·8 g (0·085 mole) benzylsulfonyl fluoride (Ib) was dissolved in 250 ml ether and to this solution was slowly added 100 ml ethereal solution of phenyllithium (0·09 mole), prepared from 17·7 g bromobenzene and 1·7 g Li, as was described above. Stirring was continued for 4 hr. The reaction mixture was then hydrolysed with water and extracted with ether. A large amount of a white insoluble product was separated, filtered and collected. It was the disulfone (I), the yield being 9·7 g (59·1%). The ethereal extract gave 0·6 g (4%) of trisulfone (VIII), m.p. 199–201°, and 0·35 g (1·8%) of benzyl phenyl sulfone (VII), m.p. 146°, and 0·3 g (3·9%) of *trans*-stilbene (IV), m.p. 123°, upon concentration followed by a chromatographic separation over alumina. Recrystallization of VIII from AcOH raised the m.p. to 201–203°. The aqueous layer was treated with MeI to give 0·45 g (3%) of benzyl methyl sulfone (X).

Each of these compounds was identified by the method above mentioned. A small amount of benzene was also confirmed in the distillates by VPC on a GCG-3DH type Yanagimoto gas chromatograph at a column temp of 112·5° with a 2 m × 4 mm column of silicone glease at a H_2 flow of *ca.* 100 ml/min, the retention time being identical with that of an authentic sample (0·97 min.)

Method B. 200 ml ethereal solution of phenyllithium (0·12 mole) was placed in a 1-l. round three-necked flask. 17 g (0·1 mole) benzylsulfonyl fluoride dissolved in 250 ml of ether was added to the above solution over a period of 1 hr at a bath temp of 5–10°. During the addition a bright yellow color developed and after 30 min its color gradually disappeared together with the formation of white precipitate. After completion of the addition, the reaction mixture was stirred for 3 hr and hydrolysed. Disulfone (I), 12·5 g (64·8%), separated and was collected. The ethereal extract was concentrated to give 0·4 g of trisulfone (VIII) and 2·72 g of a residue.

The residue was dissolved in benzene and chromatographed over alumina. Benzene eluted 0·3 g (3·4%) of *trans*-stilbene (IV) and 0·38 g (1·5%) of phenyl benzylsulfonate (XI). Ether eluted 0·1 g (0·43%) of benzyl phenyl sulfone (VII). Ether–MeOH (10:3) eluted 0·25 g of trisulfone (VIII). The total yield of trisulfone (VIII) was 0.65 g (3·6%). Recrystallization of XI from EtOH afforded white needles, m.p. 87–87·5°, and it was identified on the basis of mixed m.p. and comparable IR spectrum with the authentic sample, which was prepared from Ia and phenol in the presence of pyridine.

Reaction of benzylsulfonyl fluoride (Ib) *with α-lithiumbenzyl phenyl sulfone.* The procedure of E. A. Lehto[7] was employed for the preparation of α-lithiumbenzyl phenyl sulfone. 11·6 g (0·05 mole) benzyl phenyl sulfone was suspended in 100 ml dry ether and metalated with 0·055 mole of phenyllithium with stirring at an ice bath temp over a period of 25 min. It was stirred for 1 hr. in an ice bath, then for 2 hr at room temp (15°). The solution is deeply yellow colored. To a solution of 8·7 g (0·05 mole) benzylsulfonyl fluoride in 150 ml dry ether was slowly added the ethereal solution of α-lithiumbenzyl phenyl sulfone above prepared over 20 min at 10°. The yellow color of α-lithiumbenzyl phenyl sulfone solution instantly disappeared and the resulting solution became white cloudy. It was stirred for 3 hr and then allowed to stand overnight. After hydrolysing with water a white insoluble product, disulfone (I), was collected, the yield being 7·0 g. The ethereal extract, which was again shaken with dilute HCl, was dried (Na_2SO_4) and evaporated to give 4·7 g benzyl phenyl sulfone

(VII) and subsequently 0·3 g trisulfone (VIII). From a residue 0·1 g *trans*-stilbene (IV) was obtained. Thus, 59·5% metalation of benzyl phenyl sulfone occurred, and the yields of I and VIII were 61·1%, 3·6% respectively based on unrecovered benzyl phenyl sulfone.

Reactions at a low temperature (−80°)

Phenylmethylene polysulfone ($-CH(C_6H_5)-SO_2-)_n$ (XV). 26·7 g (0·14 mole) benzylsulfonyl chloride (Ia) was dissolved in 400 ml dry THF and the solution was cooled to −80° (bath temp) by means of acetone–Dry Ice bath. To this solution was added 150 ml ethereal solution of phenyllithium (0·16 mole) over a period of 10 min. The solution developed a dark yellow color. The reaction mixture was stirred for 5 hr at −80° and allowed to stand overnight at −80°. Then it was slowly warmed to room temp. After stirring for 2-3 hr at 20–25° it was hydrolysed. Approximately 1·2 g XV was obtained m.p. 230–235° (dec). The IR spectrum shows strong sulfone bands at 1360 and 1150 cm^{-1}. The NMR spectrum (DMF) exhibits a peak at τ 2·5 ~ τ 3·0. (Found: C, 56·05; H, 4·41; S, 17·93. $(C_7H_6O_2S)_n$ requires: C, 54·53; H, 3·92; S, 20·79%.) Benzylsulfonyl fluoride (Ib) was similarly treated to yield XV (approximately 7·0 g from 14·8 g Ib) with varying m.ps, mol. wts and the identical IR spectra. (Found: C, 53·12; H, 4·06. $(C_7H_6O_2S)_n$ requires: C, 54·53; H, 3·92%.) The mol. wts were from 600 to 850.

cis-1,2-*Diphenylvinyl phenyl sulfone* (XIV). This was recrystallized from MeOH as white needles, m.p. 133–134°. IR: ν_{max}^{Nujol} 1635 (C=C), 1590, 1490 (phenyl), 1360, 1150 (SO_2), 820 cm^{-1} ($R_1R_2C{=}CHR_3$). UV $\lambda_{max}^{95\%\,EtOH}$ 272 mμ (ε 13,600). NMR: ($CDCl_3$) τ 2·33 (singlet, vinyl proton, 1H) τ 2·85 (multiplet, aromatic protons, 15H). (Found: C, 74·88; H, 5·12. $C_{26}H_{18}O_2S$ requires: C, 74·97; H, 5·03%.)