# The Reaction Between Benzylsulfonyl Halide and Phenyllithium

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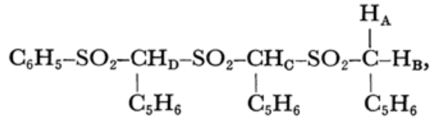
When benzylsulfonyl chloride (Ia) was treated with phenyllithium at 20—25°C, lithium benzylsulfinate (I), $\alpha$-chlorobenzyl phenyl sulfone (II), m. p. 179—180°C, chlorobenzene (III), *trans*-stilbene (IV), m. p. 123°C, $\alpha$, $\alpha$-dichlorobenzyl phenyl sulfone (V), m. p. 151—152°C, *trans*-1, 2-diphenyl vinyl phenyl sulfone (VI), m. p. 182.5—183°C, benzyl phenyl sulfone (VII), m. p. 146°C, $\alpha$ - benzylsulfonyl-$\alpha'$-benzenesulfonyl dibenzyl sulfone (VIII), m. p. 199—201°C and $\alpha$-benzylsulfonyl-$\alpha$-benzenesulfonyl toluene (IX), m. p. 237—242°C (decomp.) were obtained and identified.

(I), $C_6H_5CH_2SO_2Li$, was verified by converting it to benzyl methyl sulfone,[1] m. p. 126°C and to Ia. I was the major product; it was obtained in an overwhelming yield. II, IV and VII were identified by means of mixed melting point methods and by the coincidences of the infrared spectra with those of the respective authentic specimens.[2-4] The yields were 9.1, 3.6 and 0.4% respectively. III was identified by the coincidences of the boiling point, the infrared spectrum and the retention time obtained by V. P. C. with those of the standard sample, the yield being 16%.

V, VI and VIII were identified on the basis of elemental analyses, mol. wt. determinations,[5] and infrared, NMR or ultraviolet spectra. The yields were 0.7, 6.0 and 1.6% respectively. (V), $C_6H_5C(Cl_2)SO_2C_6H_5$, IR: $\nu_{max}^{Nujol}$ 1330 and 1050 $cm^{-1}$ ($SO_2$), NMR: $\tau$ 2.35 (phenyl protons). Found: C, 51.54; H, 3.06; Cl, 23.75: Calcd. for $C_{13}H_{10}Cl_2O_2S$: C, 51.84: H, 3.34; Cl, 23.54%. (VI), $C_6H_5CH{=}C(C_6H_5)SO_2C_6H_5$, IR: $\nu_{max}^{Nujol}$ 1300, 1140 ($SO_2$), 1620(C=C) and 820 $cm^{-1}$ (tri-substituted ethylene), UV: $\lambda_{max}^{EtOH}$ 216 m$\mu$ ($\varepsilon$ 21600) and 275 m$\mu$ ($\varepsilon$ 18900), NMR: $\tau$ 2 (vinyl proton, singlet, 1H) and $\tau$ 2.65 (phenyl protons, 15 H). Found: C, 74.64; H, 5.05; S, 10.09; mol. wt., 316, Calcd. for $C_{20}H_{16}O_2S$: C, 74.97; H, 5.03; S, 10.00%; mol. wt., 320.

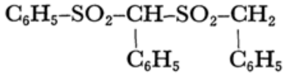
(VIII), 
$$C_6H_5\text{–}SO_2\text{–}\underset{C_5H_6}{CH_D}\text{–}SO_2\text{–}\underset{C_5H_6}{CH_C}\text{–}SO_2\text{–}\underset{C_5H_6}{\overset{H_A}{C}}\text{–}H_B,$$

IR: 1340, 1330, 1320, 1150 and 1120 $cm^{-1}$ ($SO_2$), NMR: $\tau$ 5.63 ($H_A$ snd $H_B$, quartet with $J_{AB}$= 13.5 c.p.s.), $\tau$ 3.3 ($H_C$ singlet), $\tau$ 3.08 ($H_D$, singlet) and $\tau$ 2.6 (phenyl protons). The relative areas were 2 : 1 : 1 : 20. Found: C, 60.01; H, 4.54; S, 17.49; mol. wt., 543, Calcd. for $C_{27}H_{24}O_6S_3$: C, 59.98; H, 4.47; S, 17.78%; mol. wt., 541. (IX), IR; $\nu_{max}^{Nujol}$ 1320, 1310, 1150 and 1135 $cm^{-1}$ ($SO_2$), NMR (in DMSO at 100°C): $\tau$ 2.6 (phenyl protons), $\tau$ 3.5 ($SO_2\text{–}CH(C_6H_5)\text{–}SO_2$) and $\tau$ 5.2 (methylene protons), the relative areas being around 15 : 1 : 1.8. Found: C, 61.99; H, 4.69; S, 16.33; mol. wt., 374. Calcd. for $C_{20}H_{18}O_4S_2$: C, 62.15; H, 4.70; S, 16.59%; mol. wt., 386. Yield: 3.7%.

$C_6H_5CH_2SO_2Cl + C_6H_5Li \rightarrow$

$C_6H_5CH_2SO_2Li$ (I) main product

$C_6H_5CH_2SO_2F + C_6H_5Li \rightarrow$


$$C_6H_5\text{–}SO_2\text{–}\underset{C_6H_5}{CH}\text{–}SO_2\text{–}\underset{C_6H_5}{CH_2}$$
(IX) main product

On the other hand, the similar treatment of benzylsulfonyl fluoride (Ib) with phenyllithium gave the disulfone (IX) with a m. p. of 248—250°C (decomp.) exclusively (60% yield), together with 3.9% of IV, 1.8% of VII, 4.0% of VIII and 3.0% of I. The corresponding fluorocompounds of II, V and VI, however, were not formed.

The results above described indicate that, in the reaction of Ia with phenyllithium, Li–Cl interconversion is the predominant reaction course; it contains both the direct Li–Cl interconversion between Ia and $C_6H_5Li$ and the Li–Cl interconversion after the metalation at the $\alpha$-position to the sulfone group, whereas the reaction of Ib with phenyllithium takes a different course. The formation of IV and VI suggests the possibility of the intermediacy of a phenylsulfene[6] resulting from $\alpha$-lithium benzylsulfonyl halide, followed by the $\beta$-elimination of LiX. The details, including the the formation of a polysulfone, $(C_6H_5CHSO_2)_n$,[7] at a low temperature (−80°C), will be reported in the near future.

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[1] E. Fromm and J. de S. Palma, *Ber.*, **39**, 3308 (1906).

[2] R. Otto, *J. Prakt. Chem.*, (2), **40**, 516 (1889).

[3] L. F. Fieser, "Experiments in Org. Chem.," Heath and Maruzen, Japan (1956), p. 178.

[4] R. Otto and W. Otto, *Ber.*, **21**, 1696 (1885).

[5] The molecular weight was determined with a Mecrolab Vapor Pressure Osmometer.

[6] J. E. King and T. Durst, *Tetrahedron Letters* **1963**, 585.

[7] It has a higher molecular weight than VIII.