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SYNTHESIS AND REACTIVITY OF THE 1,1-DILITHIO DERIVATIVES OF ALKYL PHENYL SULFONES AND *N,N*-DIMETHYL METHANESULFONAMIDE

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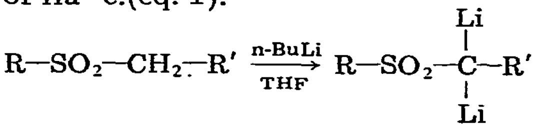
Summary

Alkyl phenyl sulfones Ia,b and *N,N*-dimethyl methanesulfonamide (Ic) are rapidly converted into their 1,1-dilithio salts IIa—c on reaction with n-butyllithium in THF—hexane. The nature of these new organometallic species was confirmed by deuteration and condensation with benzaldehyde. The *gem*-dimetallo derivatives Va—c and VIa, obtained from IIa—c by lithium—magnesium and lithium—boron exchange respectively, react with carbonyl compounds to give α,β-unsaturated sulfones VIIa—c and the corresponding β-hydroxysulfones VIIIa—c.

In the course of synthetic studies on the chemistry of sulfur-stabilized carbanions, we have investigated the possibility of generating dicarbanions such as RSO_2CLi_2R' (IIa—c) as useful intermediates for organic synthesis.

Sulfones and sulfoxides are easily metallated by means of a wide variety of basic reagents to afford monometallo derivatives [1]. On the other hand, only a few 1,1-dicarbanions, probably stabilized by d_π—p_π interaction between the sulfur and carbon atoms and in some cases by other *vicinal* electron-withdrawing groups, have been previously described [2,3]. In this paper we report the preparation of the novel 1,1-dicarbanions of alkylphenylsulfones Ia,b and of *N,N*-dimethyl methanesulfonamide (Ic) and their reactivity towards carbonyl compounds.

Treatment of Ia—c, in dry tetrahydrofuran at room temperature under argon, with 2 mol equivalents of n-butyllithium in hexane gave an insoluble precipitate of IIa—c.(eq. 1).



$$R{-}SO_2{-}CH_2{-}R' \xrightarrow[\text{THF}]{\text{n-BuLi}} R{-}SO_2{-}\overset{\displaystyle Li}{\underset{\displaystyle Li}{C}}{-}R' \qquad (1)$$

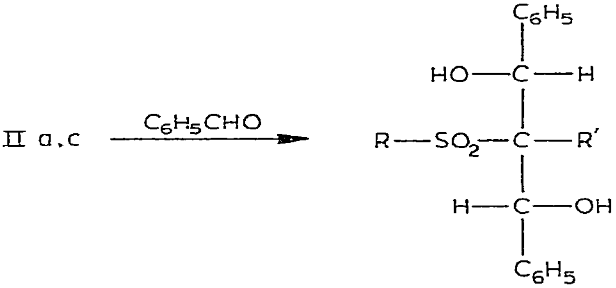
(Ia—c) (IIa—c)

(a: $R = C_6H_5$, $R' = H$; b: $R = C_6H_5$, $R' = CH_3$; c: $R = N(CH_3)_2$, $R' = H$)

The formation of these *gem*-dilithio salts was confirmed by deuteration with DCl/D_2O or condensation reaction with benzaldehyde. The deuteration, involving treatment of IIa in dry THF-hexane at 0°C with a slight excess of DCl/D_2O, afforded the sulfone containing 74% of the dideutero derivative IIIa (eq. 2). Interestingly, the hydrogens of methyl phenyl sulfone (Ia) did not undergo exchange with DCl/D_2O under the same conditions.

$$\mathrm{IIa} \xrightarrow{D_2O/DCl} \underset{\text{(IIIa)}}{R{-}SO_2{-}CD_2{-}R'} \qquad (2)$$

The dilithio salts IIa,c were also condensed with 2 mol equivalents of benzaldehyde to give the diols IVa,c in 60 and 50% yield, respectively (eq. 3). The configurations of IVa and IVc were determined on the basis of their NMR spectra.



$$\mathrm{II\,a,c} \xrightarrow{C_6H_5CHO} R{-}SO_2{-}\overset{\substack{C_6H_5\\ |\\ HO-C-H\\ |}}{\underset{\substack{|\\ H-C-OH\\ |\\ C_6H_5}}{C}}{-}R' \qquad (3)$$

(IVa,c)

The compound IVa showed signals in $CDCl_3/D_2O$ at δ 5.8 ($C\underline{H}OH$, d, J = 3 Hz), 5.3 ($C\underline{H}OH$, d, J = 4Hz) and 3.8 (SO_2CH, dd, J = 3 Hz and 4 Hz) ppm; (IVc) at δ 5.8 ($C\underline{H}OH$, d, J = 3 Hz), 5.1 ($C\underline{H}OH$, d, J = 4 Hz) and 3.7 (SO_2CH, dd, J = 3 Hz and 4 Hz) ppm.

Attention was next directed towards the possible application of the dianions (IIa—c) as starting materials for the preparation of α,β-unsaturated sulfones. Previously we demonstrated that α,α-dilithiobenzyl phenyl sulfone reacted with propionaldehyde to give the expected α,β-unsaturated sulfone in 8% yield, the main product being the β-hydroxysulfone. Exchange of lithium with magnesium in the same dilithio sulfone gave a *gem*-dimetallo derivative which reacted with carbonyl compounds, strongly increasing the yield of α,β-unsaturated sulfones [4].

In the same way we treated (IIa—c) at room temperature with 2 mol equivalents of an ether—benzene solution of magnesium iodide (Method A) to obtain a new organometallic species (Va—c), in which one or both lithium atoms were replaced by magnesium * (Scheme 1).

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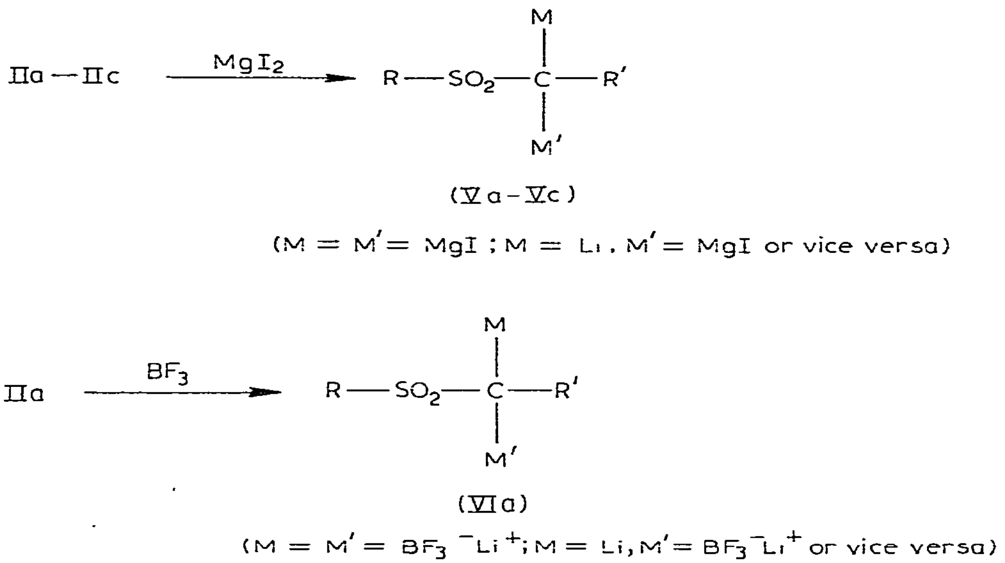
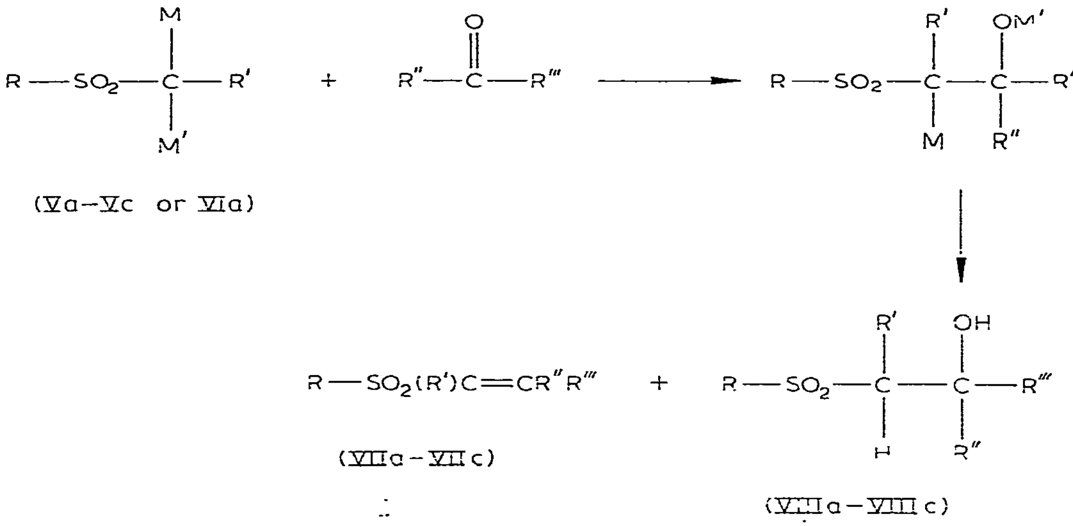
* Although the true structure of the transmetallation product is uncertain, it was established that 2 moles of MgI_2 per mole of dilithio derivative were required in order to obtain a maximum yield of α,β-unsaturated sulfones [4].

SCHEME 1



Addition of carbonyl compounds to Va—c in THF gave, after chromatography on silica gel, the α,β-unsaturated sulfones VIIa—c and the corresponding β-hydroxy sulfones VIIIa—c, in accord with the reported Scheme 2.

SCHEME 2



The low yield of olefins Va—c and the formation of the hydroxy compounds VIIIa—c (Table 1) can be explained by the fact that dilithio derivatives IIa—c were insoluble in the reaction mixture and did not transmetallate completely with MgI$_2$. We therefore attempted an alternative procedure (method B) treating

TABLE 1

CONVERSION OF CARBONYL COMPOUNDS INTO α,β-UNSATURATED SULFONES AND β-HYDROXY SULFONES

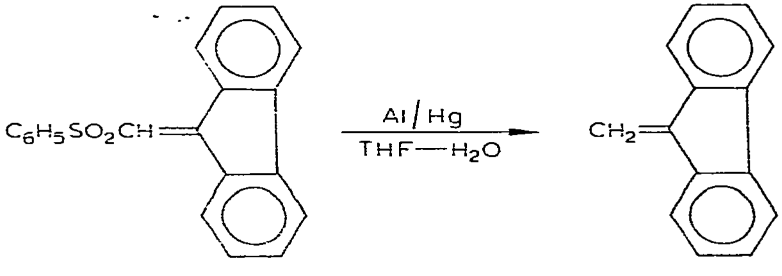
fones	Carbonyl compounds	Yield of α,β-unsaturated sulfones (%) [a]	Yield of β-hydroxysulfones (%)[a]	Method [d]
Methylphenylsulfone	Cyclohexanone	35 [b]	30	A
Methylphenylsulfone	Fluorenone	35	32	A
Methylphenylsulfone	Benzophenone	40 [e]	40	A, B
Methylphenylsulfone	*p*-Chlorobenzaldehyde	35 [c]	40	B
Methylphenylsulfone	Butanal	35 [c]	-	B
N,N-Dimethyl methanesulfonamide	Benzophenone	35 [f]	40 [f]	A
N,N-Dimethyl methanesulfonamide	*p*-Chlorobenzaldehyde	32 [c]	36	A
N,N-Dimethyl methanesulfonamide	Benzaldehyde	30 [c]	35	A
Ethylphenylsulfone	Benzophenone	30	38	A

[a] The yield indicated refers to pure isolated compound. [b] β,γ-Unsaturated sulfone is obtained [8]. [c] *E*-Isomer is isolated. [d] Method A: 2 mol equivalents of MgI_2 are added to 1,1-dilithiosulfone; Method B: 2 mol equivalents of BF_3 are added to 1,1-dilithiumsulfone. [e] Ref. 6. [f] Ref. 7.

dilithiomethyl phenyl sulfone (IIa) with 2 mol equivalents of $BF_3 \cdot (C_2H_5)_2O$ to obtain an "ate complex" VIa **, as shown in scheme 1. This alternative procedure did not give better results in the condensation with carbonyl compounds: VIa, for instance, reacted with benzophenone to afford the expected products with the same yield of product as that obtained from Va.

Table 1 shows the results obtained by Methods A and B. The products were identified either by comparison with authentic materials or by spectroscopic data and elemental analyses. The α,β-unsaturated sulfones VIIa,c, derived from aldehydes, possessed the "*E*" configuration, as demonstrated by the NMR coupling constants of the vinyl protons [9].

It is known that sulfones undergo reductive cleavage of the carbon—sulfur bond [7,10]. In fact desulfuration of 9-(benzenesulfonylmethylidene)fluorene (IX) with aluminum amalgam in 10% aqueous THF produced 9-methylenefluorene (X) in 88% yield (eq. 4). Therefore, the overall condensation-desulfuration process provides a synthetic route to olefins from sulfones.



(4)

(IX) (X)

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* It is known that *gem*-organodiboron compounds react with carbonyl compounds yielding olefins [5].

Experimental

IR spectra were determined with a Hilger and Watts H 900 Infrascau Spectrophotometer. NMR spectra were recorded with a Perkin—Elmer R 12B Spectrometer using TMS as an internal standard. Mass spectra were measured on a Perkin—Elmer 270 Mass Spectrometer at 70 eV. TLC was performed on silica gel 0.05—0.20 mm (Merck) with hexane—ether.

Tetrahydrofuran was obtained dry and oxygen-free by distillation over sodium and lithium aluminum hydride under argon. n-Butyllithium was purchased from Schuchardt (München) as a 2.5 *M* solution in n-hexane.

Preparation of 1,1-dimetalsulfones and their reaction with carbonyl compounds

Method A

A dry vessel was flushed with argon and charged with sulfone (7 mmol) and dry THF (20 ml). The mixture under argon was stirred vigorously and n-butyllithium in hexane (6 ml of 2.5 *M* solution, 15 mmol) was added. The mixture was stirred for 1 h at room temperature, and a solution of magnesium iodide (4.17 g, 15 mmol) in dry ether (40 ml) and dry benzene (20 ml) was added over 15 min. After a further 10 min the carbonyl compound (7 mmol) was added. The mixture was stirred for 2 h under reflux, poured into water (100 ml) and extracted with ether. The extracts were washed with water, dried over sodium sulfate, evaporated and the products separated by chromatography on silica gel with hexane—ether.

Method B

The sulfone (7 mmol) was dissolved in dry THF (20 ml) in a dry vessel under argon. The mixture was vigorously stirred and n-butyllithium in hexane (6 ml of 2.5 *M* solution, 15 mmol) was added. Stirring was continued for 1 h at room temperature, and a solution of boron trifluoride—ethyl ether complex (2 ml, 15 mmol) in dry THF (10 ml) was added over 15 min. After a further 10 min the carbonyl compound (7 mmol) was added and the mixture was stirred for 2 h under reflux, poured into water (100 ml) and worked up. The products were isolated by chromatography on silica gel with hexane—ether.

1-(Benzenesulfonylmethyl)cyclohexene (35%, method A) had m.p. 74°C (from hexane); δ ($CDCl_3$) 7.4—7.9 (aromatic, m), 5.4 (vinyl, t), 3.6 (SO_2CH_2, s), 1.3—2.2 (alicyclic, m) ppm; *m/e* 236 (M^+), 143 ($M^+ - C_6H_5O$), 95 ($M^+ - C_6H_5SO$). (Found: C, 66.1; H, 6.8; S, 13.5. $C_{13}H_{16}O_2S$ calcd.: C, 66.1; H, 6.8; S, 13.6%.)

1-(Benzenesulfonylmethyl)cyclohexanol (30%, method A) had m.p. 62°C (from benzene); δ ($CDCl_3$) 7.5—8.2 (aromatic, m), 3.5 (OH, br, s), 3.3 (SO_2CH_2, s), 1.3—2.0 (alicyclic, m) ppm; *m/e* 254 (M^+), 236 ($M^+ - H_2O$), 141 ($C_6H_5SO_2^+$). (Found: C, 61.1; H, 7.1; S, 12.0. $C_{13}H_{18}O_3S$ calcd.: C, 61.4; H, 7.1; S, 12.5%.)

9-(Benzenesulfonylmethylidene)fluorene (35%, method A) had m.p. 171°C (from ethanol); δ ($CDCl_3$) (7.2—9.0 (aromatic, m), 7.1 (vinyl, s) ppm; *m/e* 318 (M^+), 176 ($M^+ - C_6H_5SO_2H$), 125 ($C_6H_5SO^+$). (Found: C, 75.4; H, 4.6; S, 9.9. $C_{20}H_{14}O_2S$ calcd.: C, 75.5; H, 4.4; S, 10.1%.)

9-(Benzenesulfonylmethyl)-9-hydroxyfluorene (32%, method A) had m.p. 146°C (from ethanol); δ ($CDCl_3$) 7.1—7.7 (aromatic, m), 3.8 (OH, s), 3.7 (SO_2CH_2

s) ppm; *m/e* 336(M^+), 195 ($M^+ - C_6H_5SO_2$). (Found: C, 71.2; H, 4.9; S, 9.4. $C_{20}H_{16}O_3S$ calcd.: C, 71.4; H, 4.8; S, 9.5%.)

1,1-Diphenyl-2-(benzenesulfonyl)ethanol (40%, method A and B) had m.p. 101°C (from ethanol); δ ($CDCl_3$) 7—7.7 (aromatic, m), 5.3 (OH, s), 4.2 (SO_2CH_2) ppm; *m/e* 338 (M^+), 320 ($M^+ - H_2O$) 183 ($M^+ - C_6H_5SO_2CH_2$). (Found: C, 70.8; H, 5.3; S, 9.3. $C_{20}H_{18}O_3S$ calcd.: C. 71.0; H, 5.3; S, 9.5%.)

(E)-β-(Benzenesulfonyl)-p-chlorostyrene (35%, method B) had m.p. 130°C (from benzene); δ ($CDCl_3$) 7.3—8.2 (aromatic, m), 7.7 and 6.9 (vinyl, *AB*, $J = 16$ Hz) ppm; *m/e* 278 (M^+), 137 ($M^+ - C_6H_5SO_2$). (Found: C, 60.2; H, 4.2; Cl, 12.7; S, 11.5. $C_{14}H_{11}ClO_2S$ calcd.: C, 60.4; H, 4.0; Cl, 12.6; S, 11.5%.)

1-(p-Chlorophenyl)-2-(benzenesulfonyl)ethanol (40%, method B) had m.p. 105°C (from benzene); δ ($CDCl_3$) 7.2—8.2 (aromatic, m), 5.3 and 3.4 (SO_2CH_2CH, *ABX*), 3.9 (OH, br, s) ppm; *m/e* 296 (M^+), 278 ($M^+ - H_2O$), 141 ($C_6H_5SO_2^+$). (Found: C, 56.6; H, 4.4; Cl, 11.6; S, 10.7. $C_{14}H_{13}ClO_3S$ calcd.: C, 56.6; H, 4.4; Cl, 12.0; S, 10.8%.)

(E)-1-(Benzenesulfonyl)pent-1-ene (35%, method B) as an oil had δ ($CDCl_3$) 7.4—8.1 (aromatic, m) 7.1 ($SO_2CH{=}C\underline{H}$, dt, $J = 16$ and 7 Hz), 6.4 ($SO_2C\underline{H}{=}CH$, d, $J = 16$ Hz), 2.2 ($C_2H_5C\underline{H}_2$, m), 1.5 ($CH_3C\underline{H}_2$, m) 0.9 (CH_3, t) ppm; *m/e* 210 (M^+), 125 ($C_6H_5{-}SO^+$). (Found: C, 62.2; H, 6.6; S, 15.4. $C_{11}H_{14}O_2S$ calcd.: C, 62.8; H, 6.6; S, 15.3%.)

(E)-β-(N,N-Dimethylaminosulfonyl)-p-chlorostyrene (32%, method A) had m.p. 126°C (from ethanol); δ ($CDCl_3$) 7.5 (aromatic, m), 7.45 and 6.7 (vinyl, *AB*, $J = 16$ Hz), 2.8 (CH_3, s) ppm; *m/e* 245 (M^+), 137 ($M^+ - (CH_3)_2NSO_2$). (Found: C, 49.1; H, 4.8; Cl, 14.3; N, 5.7; S, 13.0. $C_{10}H_{12}ClNO_2S$ calcd.: C, 48.9; H, 4.9; Cl, 14.5; N, 5.7; S, 13.1%.)

1-(p-Chlorophenyl)-2-(N,N-dimethylaminosulfonyl)ethanol (36%, method A) had m.p. 67°C (from benzene); δ ($CDCl_3$) 7.4 (aromatic, s), 5.25 and 3.2 (SO_2-CH_2CH, *ABX*), 3.7 (OH, s), 2.9 (CH_3, s) ppm; *m/e* 263 (M^+), 245 ($M^+ - H_2O$), 155 ($M^+ - (CH_3)_2NSO_2$). (Found: C, 45.5; H, 5.4; Cl, 13.2; N, 5.5; S, 12.1. $C_{10}H_{14}ClNO_3S$ calcd.: C, 45.6; H, 5.3; Cl, 13.3; N, 5.3; S, 12.2%.)

(E)-β-(N,N-Dimethylaminosulfonyl)-styrene (30%, method A) had m.p. 104°C (from ethanol); δ ($CDCl_3$) 7.4 (aromatic, m), 7.55 and 6.75 (vinyl, *AB*, $J = 16$ Hz), 2.8 (CH_3, s) ppm; *m/e* 211 (M^+), 103 ($M^+ - (CH_3)_2NSO_2$). (Found: C, 56.7; H, 6.3; N, 6.5; S, 15.0. $C_{10}H_{13}NO_2S$ calcd.: C, 56.8; H, 6.2; N, 6.6; S, 12.2%.)

1-Phenyl-2-(N,N-dimethylaminosulfonyl)ethanol (35%, method A) as an oil had δ ($CDCl_3$) 7.4 (aromatic, s), 5.2 and 3.2 (SO_2CH_2CH, *ABX*), 3.7 (OH, br, s), 2.9 (CH_3, s) ppm; *m/e* 229 (M^+), 211 ($M^+ - H_2O$), 120 ($M^+ - (CH_3)_2NSO_2$). (Found: C, 52.6; H, 6.8; N, 5.9; S, 13.8. $C_{10}H_{15}NO_3S$ calcd.: C, 52.4; H, 6.6; N, 6.1; S, 13.9%.)

1,1-Diphenyl-2-(benzenesulfonyl)propene (30%, method A) had m.p. 138°C (from ethanol); δ ($CDCl_3$) 7.1—7.7 (aromatic, m), 2.2 (CH_3, s) ppm; *m/e* 334 (M^+), 193 ($M^+ - C_6H_5SO_2$). (Found: C, 75.4; H, 5.4; S, 9.5. $C_{21}H_{18}O_2S$ calcd.: C, 75.4; H, 5.4; S, 9.6%.)

1,1-Diphenyl-2-(benzenesulfonyl)propan-1-ol (38%, method A) had m.p. 135°C (from benzene); δ ($CDCl_3$) 6.9—7.7 (aromatic, m), 5.15 (OH, s), 4.5 (SO_2CH, q), 1.5 (CH_3, d) ppm; *m/e* 352 (M^+), 334 ($M^+ - H_2O$), 183 (Ph_2COH^+). (Found: C, 71.4; H, 5.7; S, 9.2. $C_{21}H_{20}O_3S$ calcd.: C, 71.6; H, 5.7; S, 9.1%.)

Reaction between 1,1-dilithiosulfones and benzaldehyde

A dry vessel was flushed with argon and charged with methylphenylsulfone or *N,N*-dimethyl methanesulfonamide (5 mmol) and dry THF (15 ml). The mixture was vigorously stirred and n-butyllithium in hexane (4 ml of 2.5 M solution, 10 mmol) was added. The mixture was stirred for 1 h at room temperature and then benzaldehyde (10 mmol) was added. Stirring was continued for 1 h; the mixture was poured into water, dried over sodium sulfate, evaporated and the residue eluted through a silica gel column with hexane—ether.

1,3-Diphenyl-2-(benzenesulfonyl)propan-1,3-diol (60%) had m.p. 154°C (from ethanol); δ ($CDCl_3$) 6.7—7.7 (aromatic, m), 5.8 and 5.3 ($C_6H_5C\underline{H}$, 2d), 4.0 (2 OH, 2d), 3.8 (SO_2 CH, dd) ppm; *m/e* 262 ($M^+ - C_6H_5COH$), 244 ($262^+ - H_2O$), 141 ($C_6H_5SO_2^+$). (Found: C, 68.4; H, 5.5; S, 8.7. $C_{21}H_{20}O_4S$ calcd.: C, 68.5; H, 5.5; S, 8.7%.)

1,3-Diphenyl-2-(N,N-dimethylaminosulfonyl)propan-1,3-diol (50%) had m.p. 109°C (from ethanol); δ ($CDCl_3$) 7.1—7.5 (aromatic, m), 5.8 and 5.1 ($C_6H_5C\underline{H}$, 2d), 3.9 (2 OH, 2d), 3.7 (SO_2CH, dd), 2.8 (CH_3, s) ppm; *m/e* 228 ($M^+ - C_6H_5$-CHOH), 208 ($M^+ - H_2O - 2H$). (Found: C, 60.8; H, 6.3; N, 4.2; S, 9.4. $C_{17}H_{21}NO_4S$ calcd.: C, 60.9; H, 6.3; N, 4.2; S, 9.5%.)

Treatment of 1,1-dilithiomethylphenylsulfone with DCl/D_2O

A solution of 1,1-dilithiomethylphenylsulfone (5 mmol), prepared as described above, was vigorously stirred and DCl in D_2O (2.5 ml of 6.4 *N* solution, 16 mmol) was added at 0°C. The solution was poured into water (20 ml) and extracted with ether. The extracts were dried over sodium sulfate and evaporated, and the residue was crystallized from hexane—benzene. The sulfone contained 74% of the dideutero derivative, as calculated from the mass spectrum (70 eV, solid inlet 50°C). The NMR spectrum of the same product (Varian XL-100, lock on internal TMS, solvent $CDCl_3$, sweep width 25 Hz) showed a complex pattern that could be resolved into a singlet at δ 3.033 for the methyl group, a triplet (1 : 1 : 1) at δ 3.019 for the monodeutero derivative and a quintet (1 : 2 : 3 : 2 : 1) at δ 3.005 ppm for the dideutero derivative. From J(H,D) 1.95 Hz we obtained J(H,H) 12.70 Hz according to the inductive and hyperconjugative effects of the sulfonyl group [11]. The mechanical integration of the constituents of the NMR pattern gave quantitative values in good agreement with the mass spectroscopic results.

Desulfuration of 9-(benzenesulfonylmethylidene)fluorene to give 9-methylenefluorene

To a solution of 0.48 g (1.5 mmol) of 9-(benzenesulfonylmethylidene)fluorene in 50 ml of 10% aqueous THF 0.015 g-at. of aluminum amalgam [7] was added under argon. The mixture was refluxed for 3 h and worked up in the usual way. After chromatography of the residue on silica gel, 0.23 g (88% yield) of 9-methylenefluorene [12] was isolated. The NMR spectrum in $CDCl_3$ showed signals at δ 7.1—7.8 (aromatic, m) and 6.0 (methylene, s).

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