

An α -Sulphonyl Dianion and its *E1cB* Elimination

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The preparation, deuteration, and alkylation of the proposed 1,1-dianion of 9-methyl-6-phenylsulphonylmethyl-7-oxatricyclo[4.3.0.0^{3,6}]nonane (I; R = H), and its subsequent *E1cB* elimination are described.

THE intriguing chiral properties of the α -sulphonyl carbanion have aroused much discussion.¹ We were interested in the possibility that a methylene group adjacent to a bulky chiral system and a sulphonyl group might be asymmetrically alkylated.

The sulphone (I; R = H) was prepared in 95% yield by addition of phenylsulphonylmethylmagnesium iodide² to (+)-6,6-dimethylnorpinan-2-one to give the hydroxy-sulphone (II), followed by irradiating (II) in the presence of mercury(II) oxide and iodine. Treatment of the sulphone (I; R = H) with *n*-butyl-lithium (excess) at -70° in ether, followed by addition of deuterium oxide (at -70°) gave the sulphone (I; R = D) (100%). There was no trace of monodeuteriated sulphone (as judged by n.m.r.). The sulphone (I; R = D) did not exchange the

anion of (I; R = H) failed and only mixtures of (I; R = H) and (I; R = D) were formed. If the supposed dianion of (I; R = H) at -70° was allowed to warm to room temperature, and then quenched with water, the olefin (III; R = H) ($\geq 95\%$) was formed. If the dianion of (I; R = H) was quenched with deuterium oxide at room temperature the olefin (III; R = D) was formed.

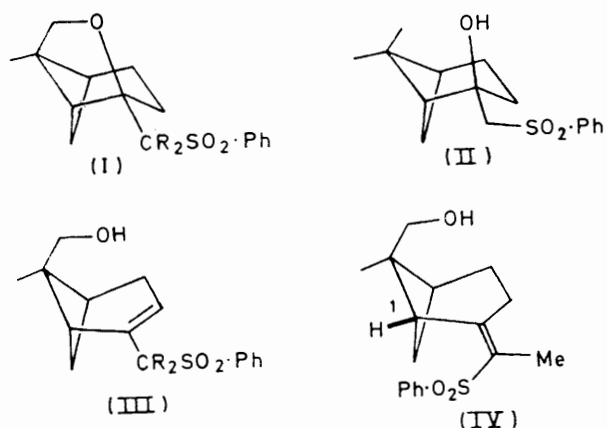
Treatment of the dianion of (I; R = H) at -70° with methyl iodide gave no reaction, but on warming the mixture to room temperature the olefin (IV) was formed. The assignment of geometrical configuration is based on the i.r. and n.m.r. spectra. The i.r. band at 3475 cm^{-1} indicates a hydrogen bonded -OH group, presumably to the sulphonyl group; a situation that can only obtain with the geometric configuration (IV). The n.m.r. spectrum exhibited a triplet at $\tau\ 6.42$ (1H, *J* 2.5 Hz) which can be assigned as the C-1 proton if it is deshielded by the phenylsulphonyl group.[†]

(+)-6,6-Dimethylnorpinan-2-one was treated with 1-phenylsulphonylethylmagnesium iodide to give a mixture of (Va) and (Vb) (arbitrarily assigned configurations) in approximately equal proportions (n.m.r. and t.l.c.). Intramolecular oxidation ($\text{HgO}-\text{I}_2-h\nu$)³ of the mixture gave the corresponding ethers (VIa) and (VIb). The mixture of (VIa) and (VIb) could be separated by p.l.c. Treatment of either (VIa) or (VIb) with *n*-butyl-lithium in ether at -70° gave the same olefin (IV). Quenching at -70° gave only (IV). No isomeric olefin could be detected by n.m.r. on the total product before purification.

Treatment of the olefin (IV) with potassium *t*-butoxide in *t*-butyl alcohol gave a 1 : 1 mixture of the cyclic ethers (VIa) and (VIb) as the only products. Concerted closure of the alkoxide derived from (IV) ought to give (VIb) as the only product. Evidently the ring closure of (IV) to (VIa) and (VIb) must proceed *via* an α -sulphonyl carbanion that inverts before it is protonated from the α -face (opposite the *gem*-dimethyl bridge) (Scheme 1).

² L. Field, *J. Amer. Chem. Soc.*, 1952, **74**, 3919; W. M. Ziegler and R. Conner, *ibid.*, 1940, **62**, 2596.

³ N. Bosworth and P. D. Magnus, *J.C.S. Perkin I*, 1972, 943, and references therein.



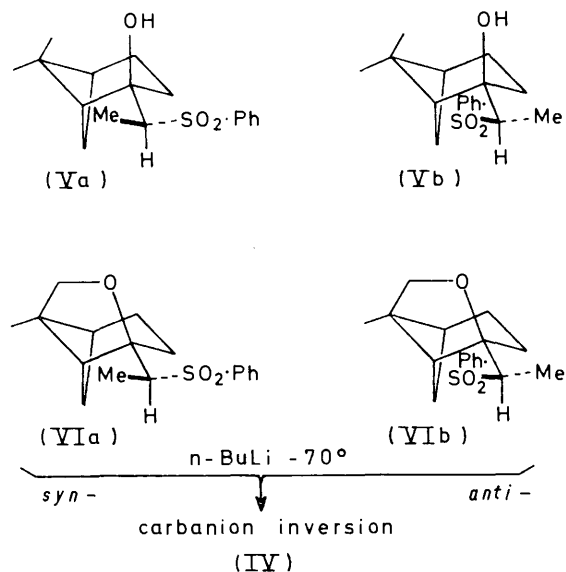
deuterium atoms on treatment with aqueous lithium hydroxide, sodium hydroxide, or potassium *t*-butoxide in *t*-butyl alcohol. All attempts to prepare the mono-

[†] Attempts to prepare the geometrical isomer were unsuccessful.

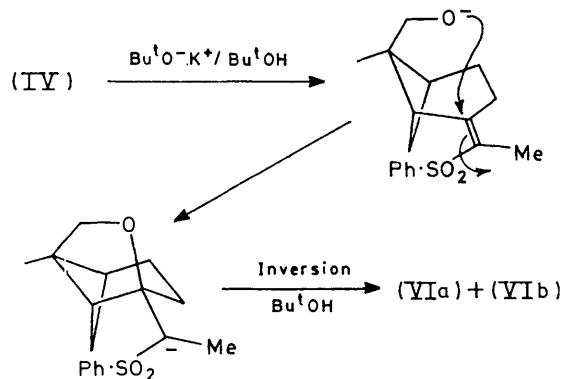
¹ D. J. Cram, 'Fundamentals of Carbanion Chemistry,' Academic Press, New York, 1965; S. Wolfe, A. Rank, and I. G. Csizmadia, *J. Amer. Chem. Soc.*, 1969, **91**, 1567, and references cited therein; D. J. Cram, R. D. Trepka, and P. St. Janiak, *ibid.*, 1966, **88**, 2749; E. J. Corey and T. H. Lowry, *Tetrahedron Letters*, 1965, 793, 803; E. J. Corey, H. König, and T. H. Lowry, *ibid.*, 1962, 515.

A suggested mechanistic rationalisation of these observations is as follows.

The diastereoisomeric sulphones (VIa) and (VIb) undergo irreversible carbanion elimination at -70° either *via syn*- and *anti*-processes to give the same olefin (IV), or the initially formed carbanion first undergoes inversion in one case, followed by elimination. In general, bimolecular elimination processes from diastereoisomeric sulphonate



esters lead by *trans*-elimination to isomeric olefins.⁴ A few cases of so-called stereoconvergent eliminations are known.⁵ The reverse process, conjugate addition to an



SCHEME 1

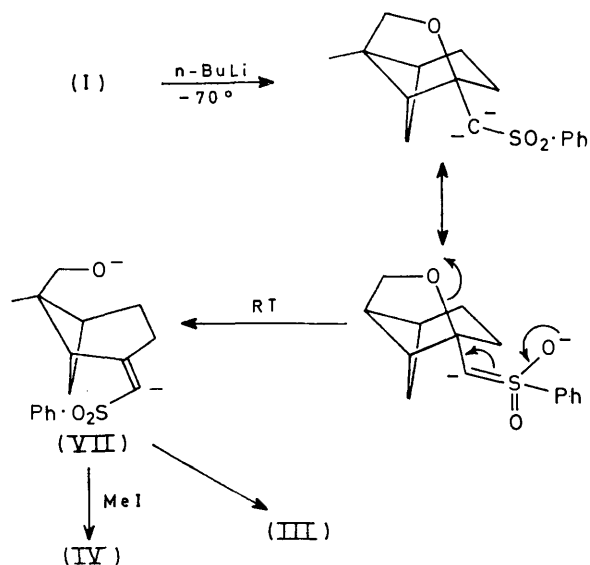
$\alpha\beta$ -unsaturated sulphone (IV) to give both diastereoisomers (VIa) and (VIb) must be non-concerted and proceed with α -sulphonyl carbanion inversion. This result implies that the forward process proceeds *via* α -sulphonyl carbanion inversion rather than *syn*- and *anti*-elimination: a distinction hitherto not observed.

⁴ S. J. Cristol and R. S. Bly, jun., *J. Amer. Chem. Soc.*, 1960, **82**, 142.

⁵ S. J. Cristol and P. Pappas, *J. Org. Chem.*, 1963, **28**, 2066.

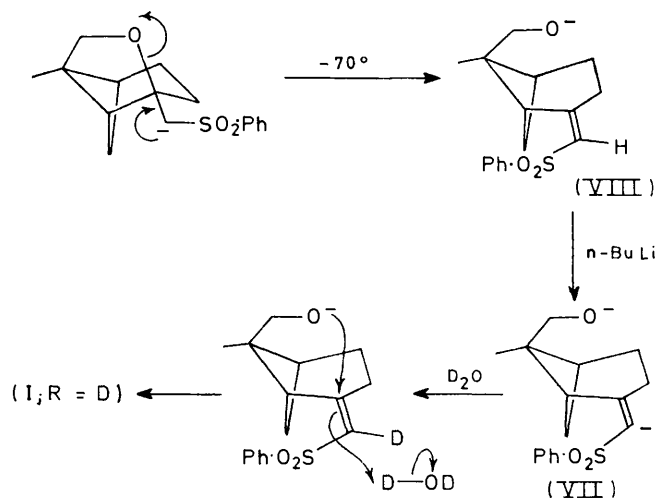
⁶ W. E. Truce and L. W. Christiansen *Chem. Comm.*, 1971, 588; E. M. Kaiser and C. R. Hauser, *J. Amer. Chem. Soc.*, 1966, **88**, 2348; *Tetrahedron Letters*, 1967, 3341; E. M. Kaiser, L. E. Solter, R. A. Schwarz, R. D. Beard, and C. R. Hauser, *J. Amer. Chem. Soc.*, 1971, **93**, 4237.

There are a number of reports of 1,1-dianions.⁶ The results described for compound (I; R = H) can be rationalised as shown in Scheme 2. The dianion remains



SCHEME 2

in the closed ether form at -70° . At room temperature it undergoes irreversible carbanion elimination (*E1cb*),⁷ followed by isomerisation⁸ to the $\beta\gamma$ -unsaturated sulphone (III). In the presence of methyl iodide the vinylsulphonylcarbanion (VII) is trapped to give (IV). An alternative explanation is that the monoanion (Scheme 3) readily undergoes irreversible *E1cb* elimination to give (VIII) which reacts with *n*-butyl-lithium to give the vinylsulphonylcarbanion (VII). This species on work-up with deuterium oxide gives (I; R = D). Whilst there



SCHEME 3

is no diagnostic evidence to distinguish between these two alternatives we feel that the former picture is more

⁷ F. G. Bordwell, M. M. Vestling, and K. C. Lee, *J. Amer. Chem. Soc.*, 1970, **92**, 5950.

⁸ C. J. M. Stirling, *J. Chem. Soc.*, 1964, 5863.

likely. The formation of (III; R = D) must involve a 1,1-dianion. Apparently methylation of (VII) keeps the substrate in the ring-opened form presumably because the lithium alkoxide is not sufficiently nucleophilic to add conjugatively to give (VIa) and (VIb), whereas the potassium alkoxide, being more nucleophilic gives (VIa) and (VIb). If (VII) were an intermediate at low temperature, subsequently quenched with deuterium oxide to give (I; R = D), it must be present as the lithium alkoxide which does not close to give the ether (I; R = H). Consequently we favour the formation of a 1,1-dianion of (I; R = H) at low temperature rather than the alternative vinylsulphonylcarbanion explanation. Furthermore if the supposed 1,1-dianion of (I; R = H) is allowed to open to the isomeric olefin form by warming to room temperature, and then re-cooled to -70° only the olefin (III) is isolated.

EXPERIMENTAL

M.p.s were determined on a Kofler hot-stage apparatus. I.r. spectra were measured for Nujol mulls or thin films unless otherwise stated. N.m.r. spectra were recorded with Varian A60 and HA100 instruments for solutions in $[^2\text{H}]$ -chloroform with tetramethylsilane as internal standard.

All solvents were purified prior to use by standard techniques. Light petroleum refers to the fraction of b.p. $40-60^\circ\text{C}$.

6,6-Dimethyl-2-phenylsulphonylmethylmorphinan-2- β -ol (II).—To a suspension of phenylsulphonylmethylmagnesium iodide² [prepared from magnesium (0.87 g), methyl iodide (5.55 g), and phenyl methyl sulphone (6.15 g) in ether (30 ml) and benzene (100 ml) refluxed for 2 h] was added (+)-6,6-dimethylnorpinan-2-one (5.0 g) in benzene (10 ml). After stirring overnight the mixture was poured into saturated aqueous ammonium chloride solution. The benzene layer was dried (Na_2SO_4) and evaporated to give the hydroxy-sulphone (II) (70%), m.p. $101-103^\circ$ (from light petroleum), $[\alpha]_{\text{D}}^{24} +27.1^\circ$ (c 2.4 in chloroform), ν_{max} 3500, 1320, and 1170 cm^{-1} , τ^* 8.9 (3H, s), 8.75 (3H, s), 6.6 (2H, s), 2.3 (5H, m), 4.45br (1H, s, exchanged by D_2O) (Found: C, 65.1; H, 7.4; S, 10.9. $\text{C}_{17}\text{H}_{22}\text{O}_3\text{S}$ requires C, 65.3; H, 7.5; S, 10.9%).

9-Methyl-6-phenylsulphonylmethyl-7-oxatricyclo[4.3.0.0^{3,9}]-nonane (I; R = H).—The hydroxy-sulphone (II) (2.0 g) in carbon tetrachloride (20 ml) was treated with mercury(II) oxide (5 g) and iodine (3.52 g). The mixture was stirred and irradiated (tungsten lamp, 500 W) for 2 h at room temperature under nitrogen. After filtering, the solution was washed with aqueous sodium metabisulphite solution, aqueous sodium chloride solution, and dried (Na_2SO_4). Evaporation gave the sulphone (I; R = H) (95%), m.p. 104° (from hexane-ether), $[\alpha]_{\text{D}}^{24} -100^\circ$ (c 0.7 in chloroform), ν_{max} 1340 and 1170 cm^{-1} , λ_{max} (EtOH) 272, 265, 258, and 253 nm (ϵ 1770, 940, 660, and 410), τ 8.7 (3H, s), 6.55br (2H, s), 6.5 (2H, ABq, J 9 Hz), and 2.3 (5H, m) (Found: C, 65.9; H, 6.8; S, 11.0. $\text{C}_{17}\text{H}_{20}\text{O}_3\text{S}$ requires C, 65.7; H, 6.9; S, 11.0%).

Reactions of the Sulphone (I; R = H) with *n*-Butyllithium.—(a) The sulphone (I; R = H) (100 mg) in ether

* The methylene signals occurred at τ 7.9–9.0 and only diagnostic signals are mentioned (similarly for all subsequent n.m.r. data).

(5 ml) at $+70^\circ$ was treated with excess of *n*-butyl-lithium (3 ml; 2M) at -70° . After 0.5 h at -70° the reaction was quenched with deuterium oxide. The sulphone (I; R = D) (100 mg) was isolated in the usual way, m/e 294 (M^+), τ 8.7 (3H, s), 6.5 (2H, ABq, J 9 Hz), 2.3 (5H, m).

(b) The sulphone (I; R = H) (120 mg) in ether (5 ml) at -70° was treated with excess of *n*-butyl-lithium (6 ml; 2M) at -70° . The mixture was allowed to warm to room temperature and quenched with water, and (1R,5S,6S)-10-phenylsulphonylpin-2-en-8-ol (III; R = H) (120 mg) was isolated in the usual way, m.p. 75° (from light petroleum), ν_{max} 3500 and 1585 cm^{-1} , λ_{max} (EtOH) 272, 265, and 258 nm (ϵ 760, 1000, and 1000), τ 8.6 (3H, s), 6.5 (2H, ABq, J 11 Hz), 6.15br (2H, s), 4.4 (1H, m), and 2.3 (5H, m) (Found: C, 65.6; H, 7.2; S, 11.0. $\text{C}_{17}\text{H}_{20}\text{O}_3\text{S}$ requires C, 65.7; H, 6.0; S, 11.0%).

Similarly if the above reaction was quenched with deuterium oxide the olefin (III; R = D) was formed, m/e 294 (M^+), with no signal at τ 6.15 in the n.m.r. spectrum.

(c) The sulphone (I; R = H) (100 mg) in ether (5 ml) at -70° was treated with *n*-butyl lithium (3 ml; 2M) at -70° . Methyl iodide (200 mg) was added to the mixture and the solution was left overnight at room temperature (no reaction took place at -70 to 0°). Work-up in the usual way gave (Z)-(1R,5S,6S)-10-methyl-10-phenylsulphonylpin-2(10)-en-8-ol (IV) (70%), m.p. $134-135^\circ$ (from hexane-ethyl acetate), $[\alpha]_{\text{D}}^{24} +252^\circ$ (c 0.4 in chloroform), ν_{max} 3475 and 1610 cm^{-1} , λ_{max} (EtOH) 272 and 267 nm (ϵ 750 and 1200), τ 8.64 (3H, s), 8.02 (3H, s), 6.8 (2H, ABq, J 5.5 Hz), 6.24 (1H, t, J 2.5 Hz), and 2.5 (5H, m) (Found: C, 66.6; H, 7.1; S, 10.2. $\text{C}_{18}\text{H}_{22}\text{O}_3\text{S}$ requires C, 66.7; H, 7.3; S, 10.4%).

9-Methyl-6-(1-phenylsulphonylethyl)-7-oxatricyclo[4.3.0.0^{3,9}]-nonane (VIa and b).—To a solution of 1-phenylsulphonylethylmagnesium iodide³ in ether was added (+)-6,6-dimethylnorpinan-2-one (3.0 g) in benzene (100 ml). The mixture was heated at 70° for 4 h then worked up in the usual way to give an oil consisting of a mixture of (10R)- and (10S)-10-methyl-10-phenylsulphonylpin-2-ol (Va and b) (3.5 g), ν_{max} 3500 cm^{-1} (Found: C, 66.4; H, 7.6; S, 10.2. $\text{C}_{18}\text{H}_{24}\text{O}_3\text{S}$ requires C, 66.2; H, 7.8; S, 10.4%). Treatment of the mixture of (Va and b) (3.32 g) in carbon tetrachloride (40 ml) with mercury(II) oxide (10 g) and iodine (6 g) followed by irradiation (17 h) gave the sulphones (VIa and b) (2.5 g), as an oil, ν_{max} 1330 and 1175 cm^{-1} , τ (less polar constituent) 8.75 (3H, s), 8.63 (3H, d, J 7.5 Hz), 6.55 (2H, ABq, J 8.5 Hz), 6.6 (1H, q, J 7.5 Hz), and 2.3 (5H, m); (more polar constituent), 8.7 (3H, s), 8.75 (3H, d, J 7 Hz), 6.4 (2H, ABq, J 8.5 Hz), 6.65 (1H, q, J 7 Hz), and 2.3 (5H, m) (Found: C, 66.6; H, 7.1; S, 10.4. $\text{C}_{18}\text{H}_{22}\text{O}_3\text{S}$ requires C, 66.7; H, 7.3; S, 16.4%).

Reaction of the Sulphones (VIa and b) with *n*-Butyllithium.—The two diastereoisomers (VIa and b) (60 mg) were separately treated with excess of *n*-butyl-lithium at -70° and quenched with deuterium oxide. Work-up by extraction with ether and washing gave the olefin (IV) (55 mg) from both (VIa) and (VIb), identical with an authentic sample (t.l.c., i.r., n.m.r., $[\alpha]_{\text{D}}$, and m.p. and mixed m.p.).

Treatment of the olefin (IV) (20 mg) in *t*-butyl alcohol (5 ml) with potassium *t*-butoxide (50 mg) at 30° rapidly gave (5 min) a 1:1 mixture of (VIa) and (VIb) (100%).

The S.R.C. is thanked for a studentship to N. B.