A 1,3-Rearrangement of Allylic Sulphones Caused by *m*-Chloroperbenzoic Acid and Sodium Hydrogen Carbonate

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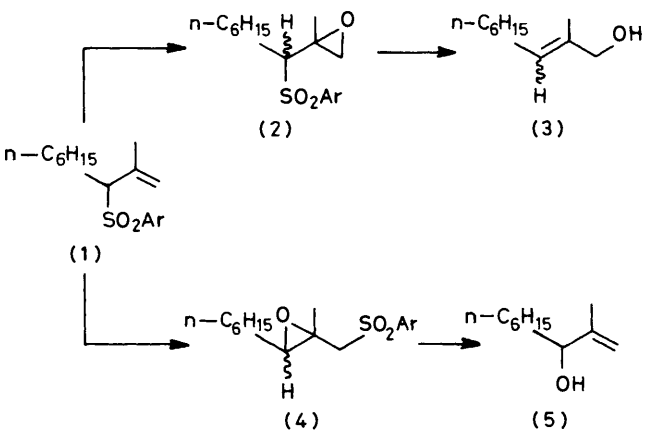
The reaction of allylic sulphones with *m*-chloroperbenzoic in the presence of aqueous sodium hydrogen carbonate can result in 1,3-allylic rearrangement or isomerisation of the double bond depending on the structure of the allylic sulphone. Subsequent epoxidation then gives β,γ-epoxy-sulphones. Epoxidation of allylic sulphones in the absence of sodium hydrogen carbonate gives, β-γ-epoxy-sulphones in which the position and stereochemistry of the double bond is retained. A radical-chain mechanism is proposed for the rearrangement reactions.

The reductive elimination of a variety of β-substituted sulphones is a useful procedure for preparing some di- and tri-substituted olefins.[1,2] For example, treatment of the β,γ-epoxy-sulphone (2) (Scheme 1) with Na–Hg in THF–MeOH (THF = tetrahydrofuran) gave a stereoisomeric mixture of the allylic alcohols (3).[3] The β,γ-epoxy-sulphones (2) were prepared by epoxidation of the allylic sulphone (1) with *m*-chloroperbenzoic acid (*m*-CPBA) in dichloromethane at room temperature (condition A). However, epoxidation of compound (1) with 1.25 equiv. of *m*-CPBA in the presence of 2.50 equiv. of sodium hydrogen carbonate in aqueous dichloromethane at room temperature (condition B) gave a 74% yield of a different β,γ-epoxy-sulphone whose ^{1}H n.m.r. spectrum [1 H-doublets at δ 3.61 and 3.00 (*J* 14 Hz)] indicated an isolated methylene group adjacent to a sulphone group, consistent with structure (4). Control experiments established that the rearranged epoxy-sulphone was formed in the dark and its formation was not catalysed by *m*-chlorobenzoic acid. The rearrangement required the presence of both sodium hydrogencarbonate and *m*-CPBA; t-butyl hydroperoxide gave no reaction. The structure of the β,γ-epoxy-sulphone (4) was verified by reductive elimination[3] to the known[4] allylic alcohol (5) in 78% yield. Thus, by a minor modification of the reaction conditions, the allylic sulphone (1) could be converted into either of the β,γ-epoxy-sulphones (2) or (4). That the rearrangement was general within well defined structural limitations was established by examining the epoxidation of the allylic sulphones (6)—(15) under both conditions A and B as summarized in the Table.

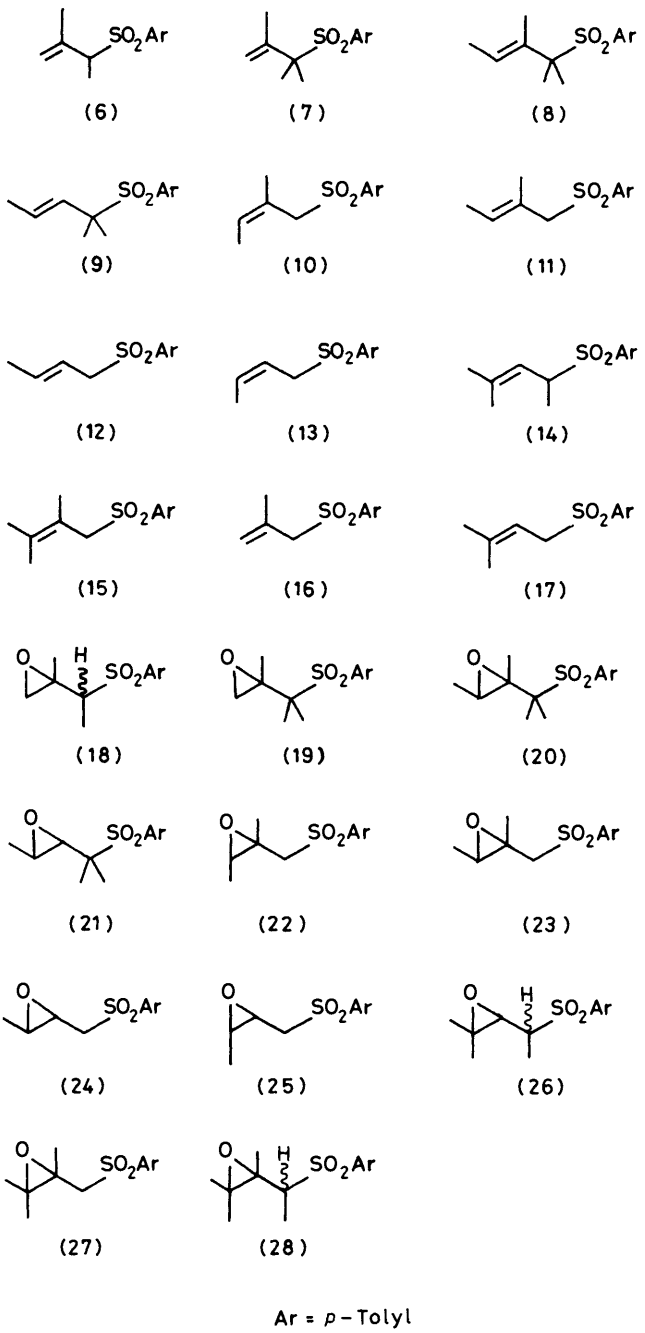
Under condition A, all the allylic sulphones (6)—(15) behaved normally and no 1,3-rearrangement products were observed. Furthermore, epoxidation was stereospecific in cases (9)—(13) and a single isomer was obtained which retained the position and stereochemistry of the initial double bond. However, clear differences in behaviour were observed under condition B. Sulphones (6) and (7) gave exclusively the products of 1,3-rearrangement and the sulphone (8) gave a mixture of the rearranged epoxy-sulphone (28) and the unrearranged product (20) in which the rearranged product was predominant. In these three cases the arylsulphonyl group migrated from a more to a less substituted carbon. From compound (9), which lacks a methyl group at C-2 of the allylic framework, a mixture of the 1,3-rearranged epoxy-sulphone (26) and the normal product (21) was obtained in which the normal product was predominant. Epoxidation of the sulphones (10)—(15) under condition B gave no 1,3-rearrangement products despite the presence of the methyl group at C-2 of the allylic framework in the sulphones (10), (11), and (15). However, epoxidation of compounds (10)—(13) was *not* stereospecific and mixtures of stereoisomeric β,γ-epoxy-sulphones were obtained.



Scheme 1. Ar = *p*-tolyl

We suggest that sodium *m*-chloroperbenzoate can catalyse two related rearrangement reactions of allylic sulphones: 1,3-allylic rearrangement and double-bond isomerisation. A 1,3-migration of an arylsulphonyl group can occur efficiently only when migration can proceed from a more to a less substituted carbon of an allylic framework which bears a substituent at the central carbon (C-2). In allylic sulphones in which the arylsulphonyl group is located on the less substituted carbon atom, stereochemical integrity of the double bond may be lost. Thus the rearranged β,γ-epoxy-sulphones were derived from a sequence of reactions in which the starting allylic sulphones first rearrange and then suffer epoxidation. Evidence in support of this view was derived from the reaction of the sulphones (7) and (10) with 0.3 equiv. of *m*-CPBA in the presence of aqueous sodium hydrogen carbonate. The starting sulphones (7) and (10) were not recovered intact: sulphone (7) had rearranged completely to compound (15) which was isolated in 48% yield along with a 22% yield of the epoxy-sulphone (27), and compound (10) had isomerised to a 4 : 1 mixture of compounds (10) and (11) which was isolated in 51% yield along with a 27% yield of a 3 : 1 mixture of the epoxy-sulphones (22) and (23).

The foregoing experiments suggest a radical-chain mechanism for both the 1,3-allylic rearrangement and the double-bond isomerisation. One possibility is shown in Scheme 2. The precise details of the mechanism require further scrutiny; nonetheless the radical nature of the reaction was corroborated by the reaction of the sulphones (7) and (10) with 0.3 equiv. of *m*-CPBA as described above but in the presence of 0.15 equiv. of the radical inhibitor 4,4′-thiobis-(2-t-butyl-6-methylphenol). Both the 1,3-allylic rearrangement of compound (7)



and the double-bond isomerisation of compound (10) were suppressed.

Thermal and photochemically induced thioallylic rearrangements of allylic aryl thioethers are easy.[5,6] By contrast the corresponding sulphones are photochemically stable and undergo thermal 1,3-rearrangement slowly only at elevated temperatures.[7] The experiments reported herein provide a mild and potentially useful rearrangement of allylic sulphones in which a peracid is functioning in an unfamiliar role.

Experimental

Light petroleum refers to the fraction of b.p. 60—80 °C. Commercial 85% *m*-chloroperbenzoic acid was used without further purification. T.l.c. (thin-layer chromatography) was carried out using Kieselgel GF_{254} with 20% EtOAc in light petroleum as developer. Compounds were visualized with 5% H_2SO_4 in ethanol. Column chromatography was carried out on Kieselgel 60 with 10% EtOAc in light petroleum as eluant. ^1H N.m.r. data refer to solutions in $CDCl_3$ at 90 MHz with Me_4Si as an internal standard.

Table

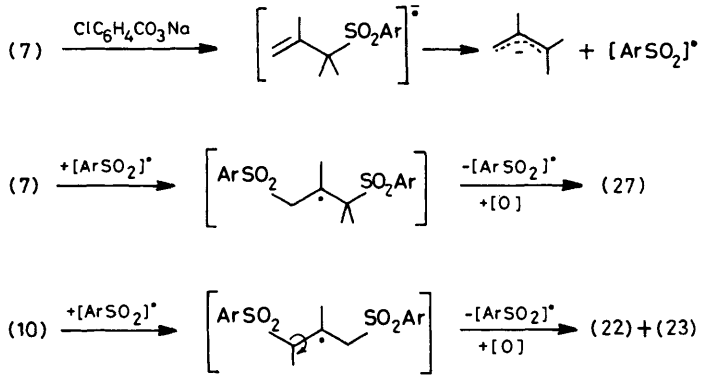
Allylic sulphone	Reaction conditions	Oxiran products	Yield (%)
(1)	A	(2)	87
	B	(4)	74
(6)	A	(18)	92
	B	(23) (67%) + (22) (33%)	55
(7)	A	(19)	77
	B	(27)	85
(8)	A	(20)	86
	B	(28) (75%) + (20) (25%)	90
(9)	A	(21)	77
	B	(21) (83%) + (26) (17%)	73
(10)	A	(22)	83
	B	(22) (50%) + (23) (50%)	84
(11)	A	(23)	72
	B	(23) (75%) + (22) (25%)	90
(12)	A	(24)	82
	B	(24) (85%) + (25) (15%)	52
(13)	A	(25)	71
	B	(24) (67%) + (25) (23%)	65
(14)	A	(26)	71
	B	(26)	69
(15)	A	(27)	85
	B	(27)	81

Synthesis of the Allylic Sulphones.—The allylic sulphones (10) and (11),[8] (16),[9] and (17)[10] were prepared by reaction of the corresponding allylic chlorides with sodium toluene-*p*-sulphinate in dimethylformamide. The sulphones (12) [11] and (13) were similarly prepared from commerical crotyl bromide (*E*:*Z* 3 : 1) using the general procedure described in reference 8. The (*E*)-isomer (12) was obtained directly by crystallization from light petroleum; the (*Z*)-isomer (13) was isolated by high-pressure liquid chromatography of the mother liquors. The (*Z*)-isomer (13) * had m.p. 56—58 °C; $\nu_{max.}$ (CCl_4) 1 665w, 1 330s, 1 305m, 1 145s, 1 090m, 910s, and 685s cm^{-1}; δ 7.75 and 7.3 (each 2 H, d, *J* 9 Hz), 5.82 (1 H, dq, *J* 10.5, *J'* 7, and *J''* 1.1 Hz), 5.43 (1 H, dq, *J* 10.5, *J'* 8, and *J''* 1.8 Hz), 3.82 (2 H, d, *J* 8 Hz), 2.43 (3 H, s), and 1.37 (3 H, dm, *J* 7 Hz with long-range coupling).

The allylic sulphone (6) was prepared by methylation of compound (16).[9] A second methylation then converted the product (6) into compound (7). A similar tandem alkylation sequence was used to convert compounds (12) and (11) into (9) and (8), respectively. Monoalkylation of compound (17) gave compound (14). The general procedure for all these alkylations is given below.

To a stirred 0.2M solution of the allylic sulphone in THF at −78 °C was added dropwise a solution of n-BuLi (1.1 equiv.) in hexane. After being kept for 15 min at −78 °C the solution was treated wtih MeI (1.5 equiv.; dropwise). The cooling bath was removed and the mixture was allowed to warm to room temperature whereupon brine was added and the organic layer was separated. The aqueous layer was washed with diethyl ether and the combined extracts were washed with

* Although a synthesis of this compound has recently been reported, its physical data were not recorded: M. Julia and L. Saussine, *Eur. Pat. Appl.* 27 421/1981 (*Chem. Abstr.*, 1981, **95**, 204215v).



Scheme 2

brine, dried ($MgSO_4$), and concentrated under reduced pressure. The residue was purified by column chromatography followed by crystallization from light petroleum unless otherwise stated. Yields quoted refer to pure crystalline product.

4-[(1-*Hexyl*-2-*methylprop*-2-*enyl*)*sulphonyl*]*toluene* (1). Alkylation of the sulphone (16) with 1-iodohexane as described above gave compound (1) in 80% yield; m.p. 46—48 °C from aqueous MeOH; $\nu_{max.}$ (neat) 1 640w, 1 315s, 1 305s, 1 290s, 1 145s, 1 085s, and 910 cm^{-1}; δ 7.7 and 7.29 (each 2 H, d, *J* 9 Hz), 4.95br and 4.65br (each 1 H, s), 3.4 (1 H, dd, *J* 10 and *J'* 4 Hz), 2.45 and 1.76 (each 3 H, s), 1.7—2.0 (2 H, m), 1.0—1.4br (8 H), and 0.9 (3 H, distorted t) (Found: C, 68.4; H, 8.9; S, 10.9. $C_{17}H_{26}O_2S$ requires C, 68.6; H, 8.6; S, 10.7%). The following sulphones were similarly prepared. 4-[(1,2-*Dimethylprop*-2-*enyl*)*sulphonyl*]*toluene* (6), 94% from compound (16), m.p. 60—64 °C (lit.,[9] 64 °C). 4-[(1,1,2-*Trimethylprop*-2-*enyl*)*sulphonyl*]*toluene* (7), 75% from compound (16), m.p. 64—67 °C; $\nu_{max.}$ (CCl_4) 1 630w, 1 312s, 1 304s, 1 290s, 1 128s, 1 080s, and 910s cm^{-1}, δ 7.72 and 7.3 (each 2 H, d, *J* 9 Hz), 5.1br and 4.8br (each 1 H, s), and 2.45, 1.95, and 1.52 (each 3 H, s) (Found: C, 65.2; H, 7.6; S, 13.5. $C_{13}H_{18}O_2S$ requires C, 65.5; H, 7.6; S, 13.45%). 4-[(E)-(1,1,2-*Trimethylbut*-2-*enyl*)*sulphonyl*]*toluene* (8), 60% from compound (12), m.p. 50—51 °C; $\nu_{max.}$ (CCl_4) 1 300s, 1 290s, 1 155s, 1 145s, 1 125s, 1 080s, 820m, and 680s cm^{-1}; δ 7.65 and 7.25 (each 2 H, d, *J* 8 Hz), 5.3 (1 H, q with fine splitting, *J* 7 Hz), 2.43 (3 H, s), 1.78 (3 H, q, *J* 1 Hz), 1.55 (3 H, d with fine splitting, *J* 7 Hz), and 1.48 (6 H, s) (Found: C, 66.4; H, 7.7; S, 12.7. $C_{14}H_{20}O_2S$ requires C, 66.63; H, 8.0; S, 12.7%). 4-[(E)-(1,1-*Dimethylbut*-2-*enyl*)*sulphonyl*]*toluene* (9), 80% from compound (12), m.p. 43—45 °C; $\nu_{max.}$ (CCl_4) 1 310s, 1 300s, 1 290m, 1 160s, 1 125s, 1 080s, and 680s cm^{-1}; δ 7.6 and 7.3 (each 2 H, d, *J* 9 Hz), 5.5—5.65 (2 H, m), 2.45 (3 H, s), 1.7 (3 H, d, *J* 6 Hz), and 1.4 (6 H, s) (Found: C, 65.5; H, 7.5; S, 13.2. $C_{13}H_{18}O_2S$ requires C, 65.5; H, 7.6; S, 13.45%). 4-[(1,3-*Dimethylbut*-2-*enyl*)*sulphonyl*]*toluene* (14), 81% from compound (17), m.p. 71.0—71.5 °C; $\nu_{max.}$ (neat) 1 305s, 1 290s, 1 145s, 1 090m, 820m, 725s, and 660s cm^{-1}; δ 7.72 and 7.3 (each 2 H, d, *J* 9 Hz), 5.0 (1 H, dq, *J* 11 and *J'* 1 Hz), 3.85 (1 H, dq, *J* 11 and *J'* 6 Hz), 2.44 (3 H, s), 1.68 (3 H, s), 1.41 (3 H, d, *J* 6 Hz), and 1.3 (3 H, d, *J* 1 Hz) (Found: C, 65.2; H, 7.5; S, 13.3. $C_{13}H_{18}O_2S$ requires C, 65.5; H, 7.6; S, 13.45%). 4-[(2,3-*Dimethylbut*-2-*enyl*)*sulphonyl*]-*toluene* (15), m.p. 63—65 °C, $\nu_{max.}$ (CCl_4) 1 322s, 1 305m, 1 145s, and 1 090m cm^{-1}; δ 7.75 and 7.34 (each 2 H, d *J* 9 Hz), 3.86 (2 H, s) and 2.46, 1.78, 1.66, and 1.33 (each 3 H, s) (Found: C, 65.3; H, 7.6; S, 13.2. $C_{13}H_{18}O_2S$ requires C, 65.5; H, 7.6; S, 13.45%).

General Procedure for Epoxidation.—Condition A. A solution of the allylic sulphone (1.0 mmol) and *m*-CPBA (1.1 mmol) in CH_2Cl_2 (3 cm^3) was stirred at room temperature until t.l.c. indicated complete consumption of starting material. The reaction mixture was diluted with diethyl ether (20 cm^3) and was extracted successively with 10 cm^3 portions of saturated aqueous $NaHSO_4$, $NaHCO_3$, and NaCl. The organic layer was dried ($MgSO_4$) and concentrated under reduced pressure. The crude product in diethyl ether solution was filtered through a 1 cm plug of Kieselgel to remove polar, coloured impurities. The residue obtained on evaporation of the filtrate was crystallized from diethyl ether–light petroleum. Yields quoted in the table refer to recrystallized products unless otherwise stated.

Condition B. To a rapidly stirred mixture of the allylic sulphone (1.0 mmol) in CH_2Cl_2 (3 cm^3) and $NaHCO_3$ (2.5 mmol) in water (3 cm^3) was added, in one portion, *m*-CPBA (1.25 mmol). The mixture was stirred at room temperature until t.l.c. indicated complete consumption of starting material. The residue obtained after aqueous work-up as described above was purified by column chromatography. With the sulphones (1), (6), and (8)—(13) a mixture of epoxy-sulphone products was obtained which could not be resolved by column chromatography; in these cases the isomeric composition was determined by ^1H n.m.r. spectroscopy. In these cases the yields quoted in the Table refer to the chromatographically purified mixture.

(2SR)-2-*Methyl*-2-[(1SR)-1-(p-*tolylsulphonyl*)*heptyl*]*oxiran and* (2SR)-2-*Methyl*-2-[(1RS)-1-(p-*tolylsulphonyl*)*heptyl*]*oxiran* (2). A 2 : 1 mixture of isomers was obtained which was separated by column chromatography. The major isomer had m.p. 58—60 °C; $\nu_{max.}$ (CCl_4) 1 325s, 1 305s, 1 150s, and 1 090s cm^{-1}; δ 7.82 and 7.38 (each 2 H, d, *J* 9 Hz), 2.58 (1 H, dd, *J* 10, *J'* 8 Hz), 2.48 and 1.44 (each 3 H, s), 2.46 and 2.35 (each 1 H, d, *J* 5 Hz), 1.8—2.2 (2 H, m), 1.28br (8 H), and 0.87 (3 H, distorted t) (Found: C, 65.7; H, 8.3; S, 10.0. $C_{17}H_{26}O_3S$ requires C, 65.8; H, 8.4; S, 10.3%). The minor isomer (oil, very similar i.r. spectrum) showed δ 7.75 and 7.3 (each 2 H, d, *J* 9 Hz), 2.83 (2 H, m), 2.61 and 2.41 (each 1 H, d, *J* 5 Hz), and 2.42 and 1.40 (each 3 H, s). The following oxirans were also prepared. cis- *and* trans-3-*Hexyl*-2-*methyl*-2-(p-*tolylsulphonylmethyl*)-*oxiran* (4). An inseparable mixture of *cis* and *trans* isomers was obtained (1 : 4). The major (presumably *trans*) isomer showed δ 7.85 and 7.42 (each 2 H, d, *J* 9 Hz), 3.61 and 3.0 (each 1 H, d, *J* 13.5 Hz, CH_2SO_2), 2.8 (1 H, distorted t, *J* 6 Hz, HCO), 2.45 (3 H, s), 1.45 (3 H, s), 1.1—1.6br (10 H), and 0.88 (3 H, distorted t). The minor isomer showed δ 7.87 and 7.42 (each 2 H, d, *J* 9 Hz), 3.47 and 3.25 (each 1 H, d, *J* 13.5 Hz, CH_2SO_2), 2.45 (3 H, s), and 1.55 (3 H, s). (2SR)-2-*Methyl*-2-[(1SR)-1-(p-*tolylsulphonyl*)*ethyl*]*oxiran and* (2SR)-2-*Methyl*-2-[(1RS)-1(p-*tolylsulphonyl*)*ethyloxiran* (18). A 3 : 1 mixture of isomers was obtained and was separated by column chromatography. The major isomer had m.p. 72—73 °C; $\nu_{max.}$ (CCl_4) 1 325s, 1 305m

and 1 150s cm^{-1}; δ 7.75 and 7.35 (each 2 H, d, *J* 9 Hz), 2.66 (1 H, q, *J* 7 Hz), 2.63 and 2.5 (each 1 H, d, *J* 3 Hz), 2.45 (3 H, s), 1.46 (3 H, d, *J* 7 Hz), and 1.44 (3 H, s) (Found: C, 60.0; H, 6.7; S, 13.1. $C_{12}H_{16}O_3S$ requires C, 60.0; H, 6.7; S, 13.3%). The minor isomer (oil) showed $\nu_{max.}$ (CCl_4) 1 320s, 1 305s, 1 290s and 1 150s cm^{-1}; δ 7.75 and 7.35 (each 2 H, d, *J* 8 Hz), 3.08 (1 H, q, *J* 8 Hz), 2.6 and 2.55 (each 1 H, d, *J* 4.5 Hz), 2.44 and 1.51 (each 3 H, s), and 1.28 (3 H, d, *J* 8 Hz). 2-*Methyl*-2-[1-*methyl*-1-(p-*tolylsulphonyl*)*ethyl*]*oxiran* (19), m.p. 60—63 °C; $\nu_{max.}$ (CCl_4) 1 370m, 1 315s, 1 305s, 1 290m, 1 150s, 1 125s, 1 080m, and 1 070m cm^{-1}; δ 7.72 and 7.32 (each 2 H, d, *J* 8 Hz), 2.62 and 2.45 (each 1 H, d, *J* 4 Hz), and 2.42, 1.53, 1.42, and 1.08 (each 3 H, s) (Found: C, 61.1; H, 6.9; S, 12.4. $C_{13}H_{18}O_3S$ requires C, 61.4; H, 7.1; S, 12.6%). trans-2,3-*Dimethyl*-2-[1-*methyl*-1-(p-*tolylsulphonyl*)*ethyl*]*oxiran* (20), m.p. 71—72 °C; $\nu_{max.}$ (CCl_4) 1 315s, 1 305s, 1 290m, 1 135s, and 1 080s cm^{-1}; δ 7.85 and 7.3 (each 2 H, d, *J* 9 Hz), 2.9 (1 H, q, *J* 6 Hz), 2.48 and 1.13 (each 3 H, s), 1.51 (6 H, s), 1.22 (3 H, d, *J* 6 Hz) (Found: C, 62.3; H, 7.2; S, 11.6. $C_{14}H_{20}O_3S$ requires C, 62.65; H, 7.5; S, 11.95%). trans-2-*Methyl*-3-[1-*methyl*-1-(p-*tolylsulphonyl*)*ethyl*]*oxiran* (21), m.p. 63—65 °C; $\nu_{max.}$ (CCl_4) 1 305s, 1 290s, 1 170m, 1 140s, and 1 080s cm^{-1}; δ 7.85 and 7.3 (each 2 H, d, *J* 9 Hz), 3.05 (1 H, d, *J* 2.5 Hz), 2.72 (1 H, dq, *J* 6 and *J'* 2.5 Hz), 2.48, 1.33, and 1.24 (each 3 H, s), and 1.28 (3 H, d, *J* 6 Hz) (Found: C, 61.4; H, 7.0; S, 12.8. $C_{13}H_{18}O_3S$ requires C, 61.4; H, 7.1; S, 12.6%). cis-2,3-*Dimethyl*-2-(p-*tolylsulphonylmethyl*)*oxiran* (22), m.p. 67—68 °C; $\nu_{max.}$ (CCl_4) 1 330s, 1 305m, 1 150s, and 1 090m cm^{-1}; δ 7.8 and 7.35 (each 2 H, d, *J* 9 Hz), 3.42 and 3.18 (each 1 H, d, *J* 14 Hz), 2.88 (1 H, q, *J* 6 Hz), 2.43 and 1.53 (each 3 H, s), and 1.13 (3 H, d, *J* 6 Hz) (Found: C, 59.8; H, 6.5; S, 13.5. $C_{12}H_{16}O_3S$ requires C, 60.0; H, 6.7; S, 13.3%). trans-2,3-*Dimethyl*-2-(p-*tolylsulphonylmethyl*)*oxiran* (23), m.p. 52—54 °C; $\nu_{max.}$ (CCl_4) 1 330s, 1 305m, 1 160s, 1 140s, and 1 090m cm^{-1}; δ 7.76 and 7.35 (each 2 H, d, *J* 9 Hz), 3.55 and 2.93 (each 1 H, d, *J* 14 Hz), 2.73 (1 H, q, *J* 6 Hz), 2.43 and 1.43 (each 3 H, s), and 1.17 (3 H, d, *J* 6 Hz) (Found: C, 60.2; H, 6.6; S, 13.3. $C_{12}H_{16}O_3S$ requires C, 60.0; H, 6.7; S, 13.3%). trans-2-*Methyl*-3-(p-*tolylsulphonylmethyl*)*oxiran* (24), m.p. 49—53 °C; $\nu_{max.}$ (CCl_4) 1 330s, 1 310m, and 1 155s cm^{-1}; δ 7.82 and 7.35 (each 2 H, d, *J* 9 Hz), 3.2—3.5 (2 H, m, CH_2SO_2), 3.0 (1 H, dd, *J* 6.3, *J'* 4.8, and *J''* 1.8 Hz), 2.65 (1 H, qd, *J* 5.2 and *J'* 1.8 Hz), 2.46 (3 H, s), and 1.24 (3 H, d, *J* 5.2 Hz) (Found: C, 58.0; H, 6.3; S, 13.9. $C_{11}H_{14}O_3S$ requires C, 58.4; H, 6.2; S, 14.2%). cis-2-*Methyl*-3-(p-*tolylsulphonylmethyl*)*oxiran* (25), m.p. 53—56 °C; $\nu_{max.}$ (CCl_4) 1 330s, 1 310m, 1 155s, 1 135m, 1 090m, and 895m cm^{-1}; δ 7.82 and 7.35 (each 2 H, d, *J* 9 Hz), 2.9—3.35 (3 H, m), 2.45 (3 H, s), and 1.08 (3 H, d, *J* 5.4 Hz) (Found: C, 57.9; H, 6.1; S, 14.0. $C_{11}H_{14}O_3S$ requires C, 58.4; H, 6.3; S, 14.2%). 2,2-*Dimethyl*-3-[1-(p-*tolylsulphonyl*)*ethyl*]*oxiran* (26). A single isomer of unknown relative stereochemistry was obtained directly by crystallization, m.p. 67—70 °C; $\nu_{max.}$ (CCl_4) 1 380m, 1 330s, and 1 320s cm^{-1}; δ 7.72 and 7.34 (each 2 H, d, *J* 8 Hz), 2.7—3.05 (2 H, m, OC*H*C*H*Me_3), 2.43 (3 H, s), 1.43—1.6 (3 H, m, OCHCH*Me*), and 1.16 and 0.78 (each 3 H, s) (Found: C, 61.1; H, 7.0; S, 12.5. $C_{13}H_{18}O_3S$ requires C, 61.4; H, 7.1; S, 12.6%). 2,2,3-*Trimethyl*-3-(p-*tolylsulphonylmethyl*)*oxiran* (27), m.p. 60—62 °C; $\nu_{max.}$ (neat) 1 315s, 1 305s, 1 290m, and 1 145s cm^{-1}; δ 7.72 and 7.24 (each 2 H, d, *J* 9 Hz), 3.43 and 3.13 (each 1 H, d, *J* 14 Hz), and 2.38, 1.48, 1.2, and 1.07 (each 3 H, s) (Found: C, 61.3; H, 6.9; S, 12.8. $C_{13}H_{18}O_3S$ requires C, 61.4; H, 7.1; S, 12.6%). 2,2,3-*Trimethyl*-3-[1-(p-*tolylsulphonyl*)-*ethyl*]*oxiran* (28), m.p. 83—85 °C; $\nu_{max.}$ (CCl_4) 1 320s, 1 305s, 1 290m, 1 155s, 1 090m, and 650s cm^{-1}; δ 7.75 and 7.35 (each 2 H, d, *J* 9 Hz), 3.1 (1 H, q, *J* 7 Hz), 1.49, 1.32, and 1.22 (each 3 H, s), and 1.42 (3 H, d, *J* 7 Hz) (Found: C, 62.3; H, 7.7; S, 11.7. $C_{14}H_{20}O_3S$ requires C, 62.65; H, 7.5; S, 11.95%

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References

1 B. Lythgoe, *Chem. Soc. Rev.*, 1981, **10**, 449.
2 P. J. Kocienski, *Chem. Ind.* (*London*), 1981, 548.
3 P. J. Kocienski, *Tetrahedron Lett.*, 1979, 441.
4 J. A. Katzenellenbogen and K. J. Christy, *J. Org. Chem.*, 1974, **39**, 3315.
5 P. Brownbridge and S. Warren, *J. Chem. Soc., Perkin Trans. 1*, 1976, 2125.
6 A. P. Kozikowski, E. M. Huie, and J. P. Springer, *J. Am. Chem. Soc.*, 1982, **104**, 2059.
7 R. D. Baechler, P. Bentley, L. Deuring, and S. Fisk, *Tetrahedron Lett.*, 1982, **23**, 2269.
8 P. J. Kocienski, B. Lythgoe, and I. Waterhouse, *J. Chem. Soc., Perkin Trans. 1*, 1980, 1045.
9 K. Koosha, J. Berlan, M. L. Capmau, and W. Chodkiewics, *Bull. Soc. Chim. Fr.*, 1975, 1284.
10 F. G. Bordwell and T. G. Mecca, *J. Am. Chem. Soc.*, 1972, **94**, 5829.
11 R. Moreau, Y. Adam, and P. Loiseau, *C. R. Hebd. Séances Acad. Sci., Ser. C*, 1978, **287**(2), 39.

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