

Selective Alkylation of Allyl Phenyl Sulphone. A Novel Synthesis of Alk-2-enes

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Treatment of the lithium salt of allyl phenyl sulphone (1) with a variety of alkyl halides affords exclusively α -alkylated products (2a—d), which are easily isomerized to (*E*)- $\alpha\beta$ -unsaturated phenyl sulphones (4a—d) with catalytic amounts of *t*-butoxide. A new, simple method of reductive cleavage of the carbon-sulphur bonds of compounds (2)—(4) with potassium-graphite (C_8K) is described, providing a general route to alk-2-enes [(5) and (6)] in satisfactory yields.

We recently developed two general methods for the synthesis of $\alpha\beta$ -unsaturated sulphones. One involves the reaction of $\alpha\alpha$ -dimetallo-sulphones with carbonyl compounds,¹ and the other phase-transfer-catalysed condensation of sulphones with aldehydes in a two-phase system.²

Sulphur-stabilized allylic anions of sulphides and sulphoxides are assuming an increasingly important role in synthetic chemistry, since they represent useful reagents for extending a carbon chain. In fact, allyl sulphides and sulphoxides are readily α - and γ -alkylated, the relative amounts of products being system-dependent.³

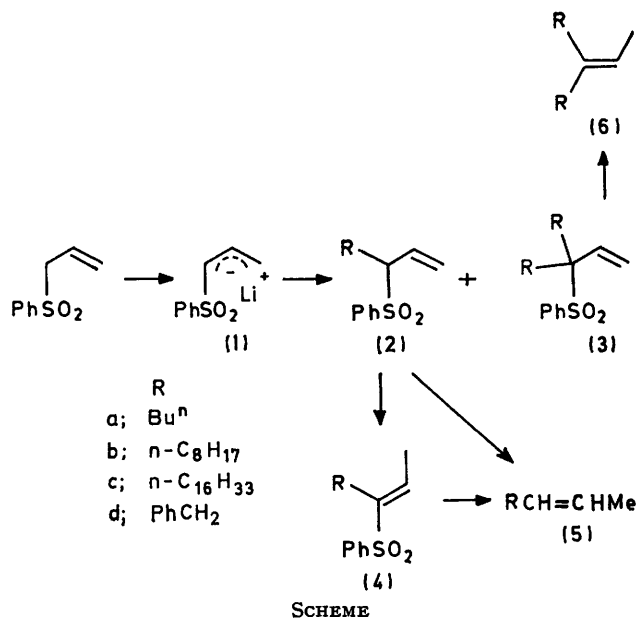
No examples are reported of regioselective alkylation of allyl sulphoxides, but isopropylthioallylcopper⁴ and vinylthioallyl-lithium⁵ are known to undergo exclusive attack at the positions γ and α to sulphur, respectively.

We have now found that a novel stereospecific synthesis of $\alpha\beta$ -unsaturated sulphones may be accomplished from the lithium salt of allyl phenyl sulphone (1). Allyl phenyl sulphone is easily metallated with *n*-butyllithium in tetrahydrofuran-tetramethylethylenediamine at -60°C , and the product (1) is regioselectively alkylated by alkyl halides in the α -position to give $\beta\gamma$ -unsaturated sulphones (2) as major product, with small amounts of dialkylated sulphones (3).

Upon treatment with catalytic amounts of potassium *t*-butoxide in dry tetrahydrofuran at 0°C , the $\beta\gamma$ -unsaturated sulphones (2) are converted completely into the $\alpha\beta$ -unsaturated sulphones (4), with the *E* configuration, as demonstrated by the chemical shifts of vinylic and methyl protons in their n.m.r. spectra. In fact the isomers (4) show the vinylic proton signal at δ 7.0 and that of the methyl protons at δ 1.8.⁶

$\alpha\beta$ -Unsaturated sulphones can be reductively cleaved to the corresponding alkenes by treatment with a reagent such as aluminium amalgam^{7,8} or lithium-ethylamine,⁹ the overall alkylation-desulphuration process providing a useful route to olefins from sulphones. We therefore carried out a series of experiments in order to establish

whether these methods could be applied to our sulphones (2) and (4). In fact alk-2-enes (5) were obtained in satisfactory yields by using lithium-ethylamine at low temperature (method A). No reaction was observed with aluminium amalgam.



Better results under milder reaction conditions have been achieved by the use in dry diethyl ether at room temperature of potassium-graphite,¹⁰ an easily prepared new solid state reagent (method B). Results are summarized in the Table. The reaction seems quite general, leading in good yield to the expected alk-2-enes (5) in all cases studied.

Cleavage of 3-phenylsulphonylundec-1-ene (2b) by Method B did not afford undec-1-ene, but the corresponding alk-2-ene (5b). The same rearrangement of the double bond was also observed in the reduction of 3-octyl-3-phenylsulphonylundec-1-ene (3b).

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⁶ C. Y. Meyers and I. Sataty, *Tetrahedron Letters*, 1972, 42, 4323.

⁷ E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, 1965, 87, 1345.

⁸ V. Pascali and A. Umani-Ronchi, *J.C.S. Chem. Comm.*, 1973, 351.

⁹ J. F. Biellmann and J. B. Ducep, *Tetrahedron*, 1971, 27, 5861.

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However all desulphuration methods have the disadvantage of inducing partial *Z*/*E*-isomerization. The ratio of *Z* to *E*-isomers is temperature-dependent, the *E*-isomer being the major product.

Cleavage of sulphones; synthesis of alk-2-enes

Starting sulphone	Method ^a	Alkene	Yield (%) ^b	<i>Z</i> : <i>E</i> Ratio ^c
(2b)	B	Undec-2-ene	77	35 : 65
(3b)	B	3-Octylundec-2-ene	81	
(4a)	A	Hept-2-ene	60	40 : 60
(4a)	B	Hept-2-ene	61	30 : 70
(4b)	A	Undec-2-ene	62	40 : 60
(4b)	B	Undec-2-ene	65	35 : 65
(4b)	B ^d	Undec-2-ene	55	65 : 35
(4c)	A	Nonadec-2-ene	65	45 : 55
(4c)	B	Nonadec-2-ene	55	35 : 65
(4d)	A	1-Phenylbut-2-ene	24	45 : 55
(4d)	B	1-Phenylbut-2-ene	26	40 : 60

^a See Experimental section. ^b Of pure isolated compounds; the yield of hept-2-ene was determined by g.l.c. with an internal standard. ^c *Z* : *E* Ratio determined by g.l.c. on a Carbowax 20M column ($\frac{1}{4}$ in \times 6 ft; 10% on 80–100 mesh Chromosorb G) (W. E. Falconer and L. G. Walker, *J. Chromatog. Sci.*, 1971, 9, 184). ^d This reaction was performed with lithium-methylamine at -110°C for 10 min.

When performing the cleavage with (*E*)-3-phenylsulphonylundec-2-ene (4b) and lithium-methylamine at -110°C , we observed the greatest retention of configuration in the alkene (*Z* : *E* ratio 65 : 35); when the reaction is conducted at room temperature with potassium-graphite the ratio is inverted.

EXPERIMENTAL

I.r. spectra were determined with a double-beam Leitz Spectrograph, n.m.r. spectra with a Perkin-Elmer R12B instrument (solvent CDCl_3 ; Me_4Si as internal standard), and mass spectra with a Hitachi-Perkin-Elmer RMU6D (single focus) spectrometer (at 70 eV). T.l.c. was performed on silica gel HF₂₅₄ (Merck) and column chromatography on Merck silica gel (0.05–0.20 mesh) with hexane-ether as a solvent. Tetrahydrofuran was obtained dry and oxygen-free by distillation over sodium and lithium aluminium hydride under argon. Tetramethylethylenediamine was distilled from calcium hydride under argon. *n*-Butyllithium was purchased from Schuchardt (Munich) as a 1.8M-solution in *n*-heptane. Graphite was used as supplied from Carlo Erba, and contained 99% carbon.

Alkylation of Allyl Phenyl Sulphone.—In a three-necked flask equipped with stirrer and dropping funnel, dry tetrahydrofuran (50 ml), tetramethylethylenediamine (3.05 ml, 20 mmol), and allyl phenyl sulphone (3.65 g, 20 mmol) were placed under argon. To the stirred solution *n*-butyllithium (1.8M; 11.2 ml, 20 mmol) was added over 15 min at -60°C . After 1 h the alkyl halide (20 mmol) was added and stirring continued at -60°C for 3 h. The temperature was raised to 0°C , then the mixture was poured into ice-water and extracted with ether. After washing with water, drying, and evaporating, the products were isolated by chromatography on silica gel.

3-Phenylsulphonylhept-1-ene (2a) (78%) had m.p. 46° (from hexane); δ 7.5–8.1 (aromatic, m), 4.8–6.1 (vinylic, m), 3.5 (SO_2CH , dt), and 0.8–2.3 (aliphatic, m); M^+ 238 (Found: C, 65.5; H, 7.5; S, 13.2. $\text{C}_{13}\text{H}_{18}\text{O}_2\text{S}$ requires C, 65.5; H, 7.6; S, 13.4%). 3-Phenylsulphonylundec-1-ene (2b) (71%) had m.p. 71° (from hexane); δ 7.5–8.1 (aromatic, m), 4.8–

6.1 (vinylic, m), 3.5 (SO_2CH , dt), and 0.8–2.2 (aliphatic, m); M^+ 294 (Found: C, 69.1; H, 8.8; S, 10.9. $\text{C}_{17}\text{H}_{26}\text{O}_2\text{S}$ requires C, 69.4; H, 8.9; S, 10.9%). 3-Phenylsulphonylnonadec-1-ene (2c) (70%) had m.p. 91° (from benzene); δ 7.5–8.1 (aromatic, m), 4.8–6.1 (vinylic, m), 3.5 (SO_2CH , dt), and 0.8–2.3 (aliphatic, m); M^+ 406 (Found: C, 73.9; H, 10.4; S, 7.8. $\text{C}_{25}\text{H}_{42}\text{O}_2\text{S}$ requires C, 73.8; H, 10.4; S, 7.9%). 3-Benzyl-3-phenylsulphonylprop-1-ene (2d) (75%) had m.p. 85° (from hexane-benzene); δ 7.5–8.1 ($\text{C}_6\text{H}_5\text{SO}_2$, m), 7.2 ($\text{C}_6\text{H}_5\cdot\text{CH}_2$, m), 4.6–6.1 (vinylic, m), and 2.6–4.0 ($\text{CH}_2\cdot\text{CH}$, m); M^+ 272 (Found: C, 70.6; H, 5.9; S, 11.8. $\text{C}_{16}\text{H}_{18}\text{O}_2\text{S}$ requires C, 70.6; H, 5.9; S, 11.7%). 3-Butyl-3-phenylsulphonylhept-1-ene (3a) (9%) had m.p. 78° (from hexane); δ 7.4–8.0 (aromatic, m), 4.8–6.1 (vinylic, m), and 0.8–2.2 (aliphatic, m); M^+ 294 (Found: C, 69.6; H, 8.8; S, 10.6. $\text{C}_{17}\text{H}_{26}\text{O}_2\text{S}$ requires C, 69.4; H, 8.9; S, 10.9%). 3-Octyl-3-phenylsulphonylundec-1-ene (3b) (8%) was an oil; δ 7.4–8.0 (aromatic, m), 4.8–6.1 (vinylic, m), and 0.8–2.2 (aliphatic, m); M^+ 406 (Found: C, 73.5; H, 10.2; S, 7.7. $\text{C}_{25}\text{H}_{42}\text{O}_2\text{S}$ requires C, 73.8; H, 10.4; S, 7.9%). 3-Hexadecyl-3-phenylsulphonylnonadec-1-ene (3c) (6%) had m.p. 53° (from hexane); δ 7.4–8.0 (aromatic, m), 4.8–6.1 (vinylic, m), and 0.8–2.2 (aliphatic, m); M^+ 630 (Found: C, 78.1; H, 11.3; S, 5.0. $\text{C}_{41}\text{H}_{74}\text{O}_2\text{S}$ requires C, 78.0; H, 11.8; S, 5.1%). 3,3-Dibenzyl-3-phenylsulphonylprop-1-ene (3d) (8%) had m.p. 113° (from ether); δ 7.4–8.0 ($\text{C}_6\text{H}_5\text{SO}_2$, m), 7.2 ($\text{C}_6\text{H}_5\cdot\text{CH}_2$, m), 5.0–6.3 (vinylic, m), and 3.4 (CH_2 , s); M^+ 362 (Found: C, 76.0; H, 6.0; S, 8.5. $\text{C}_{23}\text{H}_{22}\text{O}_2\text{S}$ requires C, 76.2; H, 6.1; S, 8.8%).

Conversion of $\beta\gamma$ - into $\alpha\beta$ -Unsaturated Sulphones.—Potassium *t*-butoxide (56 mg, 0.5 mmol) was added to a stirred solution of $\beta\gamma$ -unsaturated sulphone (2) (10 mmol) in dry tetrahydrofuran (20 ml). The mixture was stirred for 3 h, then added to saturated aqueous sodium chloride and extracted with ether. The dried organic layer was evaporated *in vacuo*. The $\alpha\beta$ -unsaturated sulphone was isolated after chromatography on a silica gel column (hexane-ether, 98 : 2).

(*E*)-3-Phenylsulphonylhept-2-ene (4a) (95%) was an oil, δ 7.4–8.1 (aromatic, m), 7.0 (vinylic, q), 1.8 ($=\text{CH}\cdot\text{CH}_3$, d), and 0.8–2.4 (aliphatic, m); M^+ 238. (*E*)-3-Phenylsulphonylundec-2-ene (4b) (96%) was an oil; δ 7.4–8.0 (aromatic, m), 7.0 (vinylic, q), 1.8 ($=\text{CH}\cdot\text{CH}_3$, d), and 0.8–2.4 (aliphatic, m); M^+ 294. (*E*)-3-Phenylsulphonylnonadec-2-ene (4c) (94%) had m.p. 43° (from hexane); δ 7.4–8.0 (aromatic, m), 7.0 (vinylic, q), 1.8 ($=\text{CH}\cdot\text{CH}_3$, d), and 0.8–2.4 (aliphatic, m); M^+ 406. (*E*)-1-Benzyl-1-phenylsulphonylprop-2-ene (4d) (95%) had m.p. 76° (from hexane-benzene); δ 7.3–7.9 ($\text{C}_6\text{H}_5\cdot\text{SO}_2$, m), 7.2 (vinylic, q), 7.1 ($\text{C}_6\text{H}_5\cdot\text{CH}_2$, m), 3.7 (CH_2 , s), and 1.8 (CH_3 , d); M^+ 272.

Cleavage of Sulphones.—*Method A.* By lithium-ethylamine. General procedure. Dry ethylamine (20 ml) was condensed in a three-necked flask equipped with stirrer and cold finger. Lithium (0.25 g, 45 mg atom), previously washed with pentane, was added over 10 min to the stirred amine. After the lithium had completely dissolved, the sulphone (4) (5 mmol) in dry ether (5 ml) was added at -30°C . After 1 h the mixture was quenched with solid ammonium chloride and then allowed to rise to room temperature in order to remove most of the amine. After 30 min water (10 ml) was added and the mixture extracted with ether. Alk-2-enes were isolated as previously reported.⁹

A single reaction was carried out with lithium-methylamine at -110°C on the sulphone (4b) dissolved in methanol.

Method B. By potassium-graphite (C₈K). General procedure. A three-necked flask was flushed with argon and heated with a flame, then charged with graphite (6.0 g, 0.5 mol) and flamed again under argon in order to desorb any oxygen and water from the graphite. A stirrer was then introduced and the system heated at 100 °C (oil-bath). Potassium (2.42 g, 62 mg atom), previously washed with n-pentane, was added in small portions over 10 min with stirring, a bronze-coloured solid being obtained. The sulphone (5 mmol) in dry ether or dry tetrahydrofuran (20 ml) was added dropwise to the potassium-graphite at room temperature. After 1 h ice and ether were added, graphite was filtered off, and the organic phase was separated and evaporated. The residue was chromatographed on silica gel (15

cm column, 1.7 cm diam.; elution with 50 ml of n-pentane) to give the alk-2-ene, identified by i.r., n.m.r., and mass spectral data, or by comparison with an authentic sample; hept-2-ene, M^+ 98; undec-2-ene, M^+ 154, ν_{\max} (film) 695 (CH=CH-*cis*)¹¹ and 965 cm⁻¹ (CH=CH-*trans*), δ (CCl₄) 5.2—5.6 (vinylic, m); nonadec-2-ene, M^+ 266, ν_{\max} (film) 700 (CH=CH-*cis*) and 960 cm⁻¹ (CH=CH-*trans*), δ (CCl₄) 5.2—5.7 (vinylic, m); 3-octylundec-2-ene, M^+ 266, ν_{\max} (film) 845, 970, 1 015, and 1 060 cm⁻¹, δ (CCl₄) 5.3—5.6 (vinylic, m).

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¹¹ F. Näf and P. Degen, *Helv. Chim. Acta*, 1971, **54**, 1939.