Scope and Stereochemistry of an Olefin Synthesis from β-Hydroxy-sulphones

By **Philip J. Kocienski,* Basil Lythgoe,*** and **Steven Ruston,** Department of Organic Chemistry, The University, Leeds LS2 9JT

The synthesis of olefins from β-acyloxy-sulphones by reduction with sodium amalgam in methanol–ethyl acetate can be applied to the preparation of a wide variety of conjugated dienes. When used for the synthesis of 1,2-disubstituted olefins in which the new double bond is either isolated or conjugated, the reaction is highly stereoselective, and leads to the *trans*-isomers.

THE ready availability of β-hydroxy-sulphones and their derivatives from reaction [1] of metallated alkyl aryl sulphones with aldehydes and ketones makes them attractive as intermediates for the regiospecific synthesis of olefins. Our first experiments on this theme made use of the observation [2] that β-chloro-sulphones react with bis(ethylenediamine)chromium(II) in dimethylformamide [3] with the elimination of both functional groups to give the olefin. Thus the lithio-derivative of cyclohexyl phenyl sulphone (1) reacted with cyclohexylideneacetaldehyde (2) to give the β-hydroxy-sulphone (3); † treatment with thionyl chloride and *s*-collidine in ether gave the β-chloro-sulphone (4), which was converted into dicyclohexylidene-ethane (7). More recently, we have found [4] that the *S*-methyl dithiocarbonates or the thiobenzoates of β-hydroxy-sulphones react smoothly with tributyltin hydride to give the olefins. Thus the magnesium bromide derivative of n-octyl phenyl sulphone (17) and the aldehyde (14) gave diastereoisomeric β-hydroxy-sulphones from which the thiobenzoates (19) † were obtained; on treatment with tributyltin hydride both were converted exclusively into the *trans*-disubstituted olefin (20). This highly stereoselective method is also applicable to the synthesis of conjugated olefins.[5]

A very simple method of converting β-hydroxy-sulphones into olefins was described by M. Julia [6] in a preliminary communication in 1973; treatment of the methanesulphonates, tosylates, or (in one example) the acetate, with sodium amalgam in ethanol at room temperature caused elimination to the olefin. Mono-, di-, and tetra-substituted olefins were shown to be accessible by this method, but its stereochemical consequences, and the question whether it was applicable to the synthesis of conjugated dienes were not examined. With the aim of evaluating Julia's elimination method for use in synthesis we have made some experiments on these aspects, and now report the results.

Whereas in Julia's experiments methanesulphonates or tosylates were the usual intermediates, many of the β-hydroxy-sulphones in the present work contain an allylic hydroxy group. We therefore preferred to use in the reductive elimination step β-acetoxy- or β-benzoyloxy-sulphones. The latter have the advantage of greater stability. Many of our acetoxy-compounds were prepared in good yield by reaction of the lithio-derivative of a sulphone at −70 °C with a carbonyl compound, followed by treatment of the cold product with acetic anhydride. In some cases, however, this procedure resulted in a mixture of the β-acetoxy-sulphone with the β-hydroxy-sulphone. It was then preferable to use benzoyl chloride in place of acetic anhydride. In general, it was convenient to conduct the condensation phase of the process with the lithio-derivatives of the sulphones, which were particularly appropriate for reaction with αβ-unsaturated carbonyl compounds. However, with easily enolisable carbonyl compounds, for example, n-heptanal (14), use of the lithio-sulphone gave

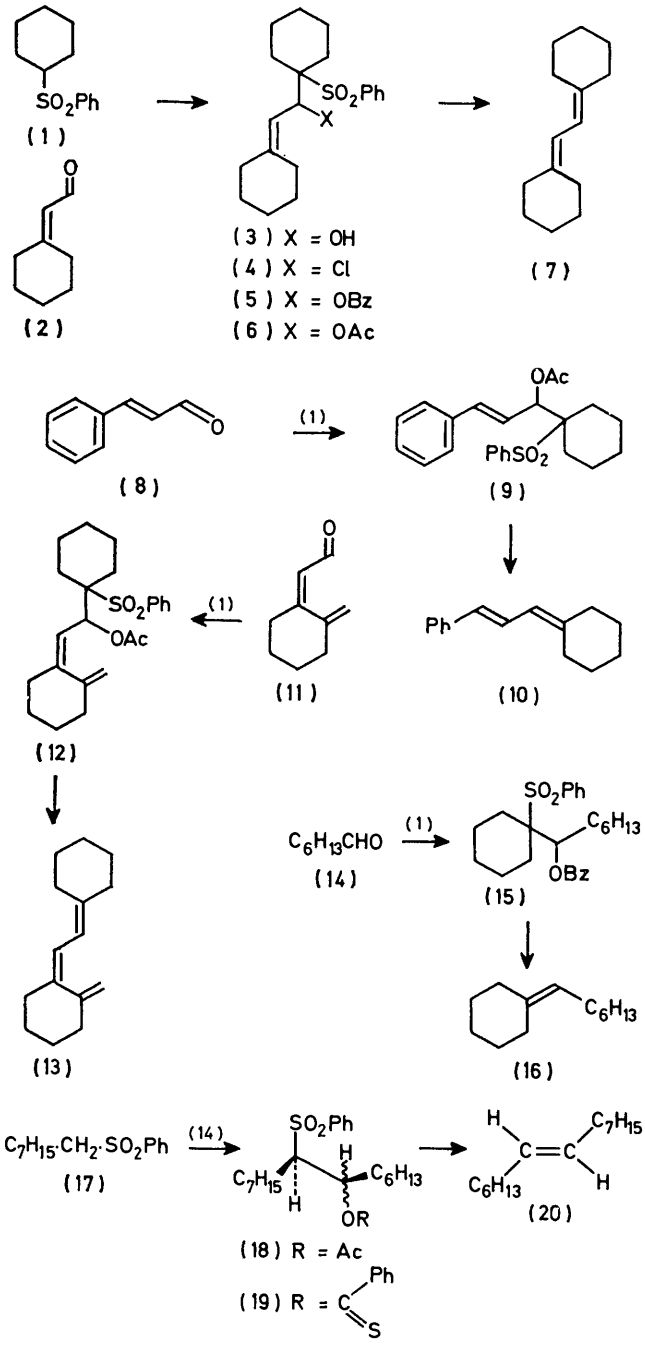
† All the structures in this paper capable of dissymmetry represent racemates.

[1] L. Field, *J. Amer. Chem. Soc.*, 1952, **74**, 3919.
[2] P. W. Wright, Ph.D. Thesis, Leeds, 1974.
[3] J. K. Kochi, D. Singleton, and L. Andrews, *Tetrahedron*, 1968, **24**, 3505; J. K. Kochi and D. Singleton, *J. Amer. Chem. Soc.*, 1968, **90**, 1582.
[4] B. Lythgoe and I. Waterhouse, *Tetrahedron Letters*, 1977, 4223.
[5] B. Lythgoe and I. Waterhouse, to be published.
[6] M. Julia and J.-M. Paris, *Tetrahedron Letters*, 1973, 4833.

poor yields or none of the desired product; the magnesium bromide derivatives of the sulphone were then used successfully. The ensuing reaction of the product with acetic anhydride or benzoyl chloride then took longer than when lithio-derivatives were used. We think that it may occasionally be an advantage to isolate the β-hydroxy-sulphone from a magnesium bromide reaction, convert it at low temperature into the lithio-derivative, and bring this into reaction with benzoyl chloride. Finally, it should be noted that our conditions for the reductive elimination phase of the synthesis depart from those of Julia (reduction in ethanol at room temperature) since it was found that these could cause de-acylation and in some cases β-elimination of acetic acid. Methanol was found preferable to ethanol or propan-2-ol, and a temperature of −20 °C was useful in suppressing the unwanted side-reactions. Use of ethyl acetate–methanol (1 : 2) was an advantage in keeping the starting sulphone dissolved.

We feared at the outset that reactions designed to lead to conjugated olefins might be complicated by reduction of the conjugated system by the reagent, but this side-reaction was encountered on only one occasion, *viz.* during the formation of stilbene from the diastereoisomeric β-benzoyloxy-sulphones (31) and (32), when some 1,2-diphenylethane was obtained also (see Experimental section). In general, the preparation of conjugated dienes proceeded satisfactorily; for example, reduction of the crystalline acetate (6) gave the diene (7) in 71% yield. Reaction of the lithio-derivative of the sulphone (1) with the aldehyde (2), followed by reaction with benzoyl chloride, gave the β-benzoyloxy-sulphone (5); reduction of this afforded the diene (7) in 71% overall yield from the starting components. Similarly, the sulphone (1) and cinnamaldehyde (8) gave the β-acetoxy-sulphone (9), from which the crystalline diene (10), $\nu_{max.}$ 965 cm^{-1}, was obtained in 53% overall yield, the *trans*-geometry of the starting aldehyde being preserved in the final product. Geometry was also preserved during the formation from the *Z*-dienal (11) first of the β-acetoxy-sulphone (12) and then of the *Z*-triene [7] (13) which was obtained in *ca.* 40% overall yield. The aldehyde (11) was obtained by oxidation of the corresponding alcohol.[8]

The magnesium bromide derivative of the sulphone (1) reacted with n-heptanal (14) to give, after treatment with benzoyl chloride, the β-benzoyloxy-sulphone (15), reduction of which afforded the trisubstituted olefin (16) in 49% overall yield. The magnesium bromide derivative of n-octyl phenyl sulphone and n-heptanal reacted to give a product which was treated with acetic anhydride, and then afforded a mixture (*ca.* 3 : 2) of two diastereoisomeric β-acetoxy-sulphones (18), as was apparent from the ^1H n.m.r. spectrum, which showed acetoxy singlets at τ 8.03 and 8.22. This mixture was reduced to give in 70% yield (62% from the starting components) the *trans*-disubstituted olefin (20), $\nu_{max.}$ 965 cm^{-1}, which was essentially free (g.l.c.) from the *cis*-isomer. Clearly both diastereoisomers (18) were converted into the same *trans*-olefin (20).



It was of interest to examine the reactions of metallated βγ-unsaturated sulphones with aldehydes and ketones, since here reaction can in principle occur at either the α- or the γ-position of the sulphone. With primary sulphones having two substituents at C_γ, *e.g.* 2-cyclohexylidene-ethyl phenyl sulphone [5] (21), and with those having one substituent at C_γ, *e.g.* cyclohexenylmethyl phenyl sulphone (22), reaction took place ex-

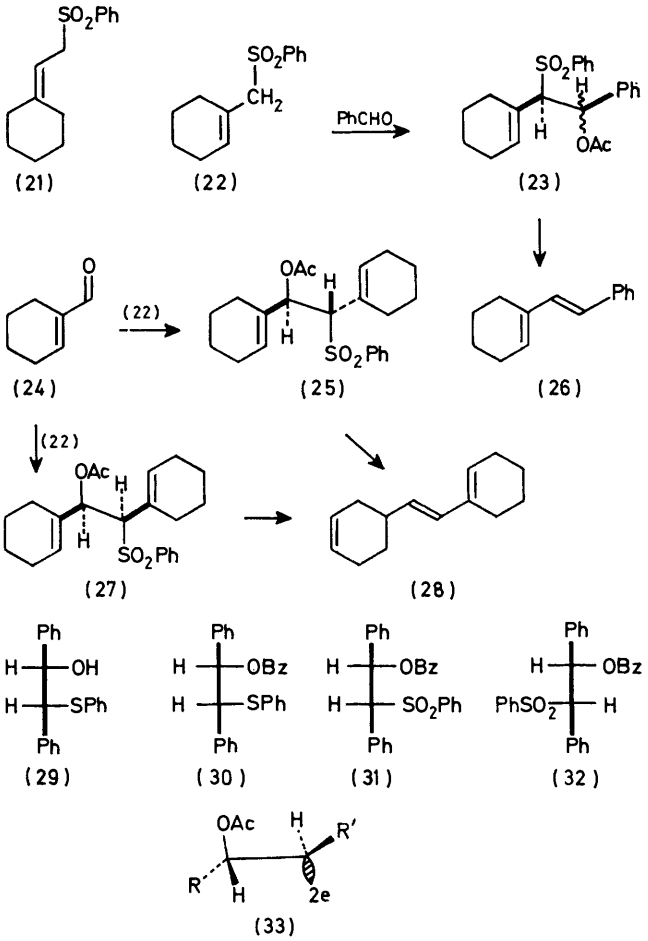
[7] I. T. Harrison and B. Lythgoe, *J. Chem. Soc.*, 1958, 837.
[8] J. V. Frosch, I. T. Harrison, B. Lythgoe, and A. K. Saksena, *J.C.S. Perkin I*, 1974, 2005.

clusively at the α-position, yielding β-hydroxy-sulphones. Thus the lithio-derivative of the sulphone (22) reacted with benzaldehyde to give, after acetylation, a crystalline mixture (*ca.* 1 : 1 by ^{1}H n.m.r.) of the diastereoisomeric β-acetoxy-sulphones (23). On reduction this afforded, in 93% yield, a single olefin (26), $\nu_{max.}$ 965 cm^{-1}, $\lambda_{max.}$ 288 nm (ε 28 800) from which it is apparent that both diastereoisomers (23) gave this *trans*-diene. An olefin to which the structure (26) was assigned has been obtained previously,[9] but its $\lambda_{max.}$ value [255 nm (log ε 4.18)], together with the observation [10] that 1-phenyl-3-methylpenta-1,3-diene has $\lambda_{max.}$ 286 nm (ε 29 500), makes it probable that the assignment was erroneous.

Reaction of the lithio-derivative of the βγ-unsaturated sulphone (22) with cyclohexene-1-carbaldehyde (24), followed by acetylation, gave in 86% yield a mixture (*ca.* 1 : 4) of the *erythro*- (25) and the *threo*-isomer (27) of the expected β-acetoxy-sulphone; they were separated, and both were obtained crystalline. Their identification is based on the coupling constants, *J* 6 and 10 Hz, respectively, of the protons attached to the two chiral centres, together with similar data for the authentic *erythro*- (31) and *threo*-[11] (32) forms of 1-benzoyloxy-1,2-diphenyl-2-phenylsulphonylethane, *J* 5 and 11 Hz, respectively. These latter isomers were prepared as shown from the corresponding hydroxy sulphide (29) and its *threo*-isomer [12] by benzoylation and oxidation. When the *erythro*- and *threo*-isomers (25) and (27) were separately reduced, each gave exclusively the crystalline conjugated *trans*-triene [13] (28); it was obtained from the major isomer (27) in 93% yield.

The propensity of Julia's elimination method to give exclusively *trans*-disubstituted olefins is unusual and noteworthy. The same pattern is not followed by other reductive eliminations, for example those of 1,2-dibromoalkanes with zinc and water, or with sodium in ammonia, or those of 2-acetoxy-1-bromoalkanes [14] with zinc and aqueous ethanol. It is possible that reductive removal of the phenylsulphonyl group generates an anion which, whatever may have been its original configuration, is long-lived enough to permit it to assume the low-energy conformation (33), from which the *trans*-olefin is then formed by loss of acylate anion. It is certainly not a question of the initial olefin being equilibrated by a radical mechanism; this would require an equilibrium mixture of the approximate composition 85 *trans* : 15 *cis*, whereas the *trans*-disubstituted olefins obtained in the present paper must have considerably less than 5% *cis*-isomer as contaminants. The method can therefore be regarded as a useful alternative to that of Schlosser [15] for the stereoselective and regioselective synthesis of *trans*-disubstituted olefins. It has been pointed out [16] that the presence in the required olefin of functional groups such as ethoxycarbonyl may make difficult the use of Schlosser's method; the present sequence would then become the method of choice.

There are also reasons, unconnected with questions of stereoselectivity, why the present method should be considered favourably in some cases as an alternative to olefinations based on triphenylphosphonium halides. Secondary alkyltriphenylphosphonium halides are usually difficult to prepare from the corresponding



alcohols or halides, and cyclohexyl derivatives present special difficulties. By contrast, the corresponding sulphones, required for Julia's method, are normally easily prepared,[17] owing to the lower steric requirements of the benzenethiolate anion, its high nucleophilicity, and the ease with which the group is oxidised to the sulphone level, even when double bonds are present.[18] Moreover, allylic sulphones, required for the

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[13] G. N. Burkhardt and N. C. Hindley, *J. Chem. Soc.*, 1938, 987.
[14] W. M. Schubert, B. S. Rabinovitch, N. R. Larson, and V. A. Sims, *J. Amer. Chem. Soc.*, 1952, **74**, 4590; H. O. House, and R. S. Ro, *ibid.*, 1958, **80**, 182.
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[16] R. J. Anderson and C. A. Henrick, *J. Amer. Chem. Soc.*, 1975, **97**, 4327.
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[18] L. Kuhnen, *Angew. Chem. Internat. Edn.*, 1966, **5**, 893.

preparation of conjugated dienes, can frequently be prepared from the allylic alcohol or its acetate by direct reaction with sodium benzenesulphinate.[19]

EXPERIMENTAL

Unless otherwise specified, u.v. data relate to solutions in EtOH, ^{1}H n.m.r. data to solutions in $CDCl_3$, and i.r. data to solutions in CCl_4. Light petroleum refers to the fraction b.p. 60—80 °C. T.l.c. and p.l.c. were performed with Kieselgel GF_{254}. Acetic anhydride was purified by distillation from P_2O_5 and methanol by distillation from magnesium metal activated by iodine. Ethylmagnesium bromide and n-butyl-lithium were assayed by titration in tetrahydrofuran (THF) solution with 1.0M-cyclohexanol in xylene using 1,10-phenanthroline as an indicator.

1,2-*Dicyclohexylidene-ethane* (7).—A solution of cyclohexyl phenyl sulphone [20] (560 mg) in tetrahydrofuran (5 cm^3) was stirred and kept at −78 °C under nitrogen during dropwise addition of 1.3M-n-butyl-lithium in hexane (2.0 cm^3). After a further 10 min cyclohexylidene-acetaldehyde (325 mg) in tetrahydrofuran (2 cm^3) was added dropwise, and after a further 30 min acetic anhydride (300 mg) was added. Stirring was continued at −78 °C for 4 h and then at room temperature for 1 h; saturated aqueous ammonium chloride was then added, and the product was isolated with ether. It was an oil (1.02 g) composed of two major components (t.l.c.). Crystallisation from light petroleum gave the less polar component, 1-(1-*acetoxy*-2-*cyclohexylidene-ethyl*)*cyclohexyl phenyl sulphone* (6) (570 mg, 59%) as prisms, m.p. 112—117°; pure material had m.p. 118.5—120°, $\nu_{max.}$ 1 150, 1 250, 1 310, 1 330, and 1 760 (all s) cm^{-1}, τ 3.86 (1 H, d, J 10 Hz, CH·OAc) and 4.39 (1 H, d, J 10 Hz, =CH) (Found: C, 67.7; H, 7.7; S, 8.2. $C_{22}H_{30}O_4S$ requires C, 67.7; H, 7.7; S, 8.2%).

The more polar component, isolated by p.l.c. (5% ethyl acetate–benzene), separated from light petroleum as prisms, m.p. 94—95°, $\nu_{max.}$ 1 140s, 1 300s, 1 310s, and 3 490m cm^{-1}, τ 4.43 (1 H, d, J 10 Hz, =CH) and 5.20 (1 H, dd, J 6 and 10 Hz, C*H*·OH). It was identified as the hydroxy-sulphone (3) by conversion into the acetate (6) by treatment at −78 °C with n-butyl-lithium, followed by acetic anhydride.

The acetoxy-sulphone (6) (390 mg) in methanol (6 cm^3) and ethyl acetate (3 cm^3) was stirred at −20 °C with 5.65% sodium amalgam. After 10 h, t.l.c. showed the absence of starting material; the mixture was poured into water (50 cm^3), and the product, isolated with light petroleum, was chromatographed on silica gel (20 g) (benzene). Distillation from bulb to bulb at 100 °C (bath) and 0.3 mmHg gave 1,2-dicyclohexylidene-ethane (7) (135 mg, 71%), m.p. 43—45°, $\lambda_{max.}$ 241.5 (ε 31 600), 250 (ε 37 700), and 259 nm (ε 26 000) (lit.,[21] m.p. 45—47°); the i.r. and ^{1}H n.m.r. spectra were identical with those of authentic [22] material.

When the adduct obtained as described above from reaction of phenyl cyclohexyl sulphone (224 mg) and cyclohexylideneacetaldehyde (136 mg) was treated at −78 °C with benzoyl chloride for 5 h, and then at room temperature for 3 h, a product (510 mg) was obtained composed of the benzoyloxy-sulphone (5), $\nu_{max.}$ 1 115, 1 140, 1 280, 1 310, 1 320, and 1 735 (all s) cm^{-1}, τ 3.58 (1 H, d, J 10 Hz, C*H*·OBz) and 4.38 (1 H, d, with fine splitting, J 10 Hz, =CH), contaminated with a little benzoyl chloride. Reduction of this material as described above gave the diene (7) in 71% overall yield from the starting components.

(E)-*Cinnamylidenecyclohexane* (10).—Interaction of cyclohexyl phenyl sulphone (1.12 g) with cinnamaldehyde (660 mg) and acetic anhydride (1.0 g) as described for the acetoxy-sulphone (6) afforded the *acetoxy-sulphone* (9) as prisms (1.05 g, 53%) (from ethanol), m.p. 125—127°, $\nu_{max.}$ 1 145, 1 240, 1 310, and 1 755 (all s) cm^{-1}, τ 2.14 (1 H, d, J 15 Hz, ArC*H*=), 2.38 (1 H, d, J 15 Hz, ArCH=C*H*), 3.98 (1 H, d, with fine splitting, J 7 Hz, C*H*·OAc), and 8.45 (3 H, s, OAc) (Found: C, 69.45; H, 6.75; S, 8.45. $C_{23}H_{26}O_4S$ requires C, 69.3; H, 6.6; S, 8.05%).

Reduction of compound (9) (398 mg) was carried out as described for the diene (7); after bulb-to-bulb distillation at 130 °C (bath) and 0.3 mmHg (E)-*cinnamylidenecyclohexane* (151 mg, 76%) was obtained, m.p. 52—55°, $\nu_{max.}$ 965s, 1 605w, and 1 650w cm^{-1}, $\lambda_{max.}$ 290 (ε 31 000) and 316 nm (ε 19 000), τ 3.07 (1 H, dd, J 11 and 15 Hz, ArCH=C*H*), 3.65 (1 H, d, J 15 Hz, ArC*H*=), and 4.12 (1 H, d, J 11 Hz, ArCH:CH·C*H*=) (Found: M^+, 198.140 83. $C_{15}H_{18}$ requires M, 198.140 84).

(Z)-1-(2-*Cyclohexylidene-ethylidene*)-2-*methylenecyclohexane* (13).—Reaction of cyclohexyl phenyl sulphone (448 mg) and the dienal (11) (272 mg) and acetylation as described for compound (6) gave the *acetoxy-sulphone* (12) (451 mg, 56%) as prisms, m.p. 126—128.5° (from light petroleum), $\nu_{max.}$ 1 140, 1 230, 1 290, 1 305, and 1 740 (all s) cm^{-1}, τ 3.58 (1 H, d, J 10 Hz, C*H*·OAc), 4.25 (1 H, d, J 10 Hz, =CH), 5.1br (2 H, =CH_2), and 8.48 (3 H, s, OAc) (Found: C, 68.4; H, 7.45; S, 8.2. $C_{23}H_{30}O_4S$ requires C, 68.6; H, 7.5; S, 7.95%).

Reduction of the acetoxy-sulphone (12) (80 mg) by the standard method, and chromatography of the product on neutral alumina (Grade I; 5 g) gave an oil, $\lambda_{max.}$ 261 nm (ε 13 900) (lit.[7] ε 17 000), τ 3.86 (2 H, s, =CH), 5.0 and 5.26 (each 1 H, m, =CH_2). Its spectral properties show this material to contain *ca.* 82% of the triene (13), and to be essentially free from its *E*-isomer.

1-*n-Heptylidenecyclohexane* (16).—Cyclohexyl phenyl sulphone (448 mg) and ethereal 1.1M-ethylmagnesium bromide (2.0 cm^3) were stirred and heated together under reflux in benzene (6.5 cm^3) for 3½ h; the mixture was cooled to 25 °C and n-heptanal (224 mg) in benzene (2 cm^3) was added; the mixture became homogeneous. After 30 min 0.5N-hydrochloric acid was added with rapid stirring; the organic layer was then separated, washed with water, dried, and evaporated, giving the oily hydroxy-sulphone (725 mg), $\nu_{max.}$ 1 140s, 1 300s, and 3 570m cm^{-1}; it was homogeneous to t.l.c. (5% ethyl acetate in benzene).

The hydroxy-sulphone and 1,10-phenanthroline (5 mg), dissolved in tetrahydrofuran (15 cm^3) were stirred and cooled (−78 °C), and n-butyl-lithium in hexane was added dropwise until the red colour persisted. After 10 min benzoyl chloride (600 mg) in tetrahydrofuran (1 cm^3) was added dropwise, and stirring and cooling were continued for 5 h; the mixture was then allowed to gain room temperature, and was diluted with water (15 cm^3). Isolation with ether gave the benzoyloxy-sulphone (15), $\nu_{max.}$ 1 155, 1 280, 1 310, 1 320, and 1 735 (all s) cm^{-1}, contaminated with benzoyl chloride.

[19] A. Fischli and H. Meyer, *Helv. Chim. Acta*, 1975, **58**, 1492, 1585.
[20] J. I. Cunneen, *J. Chem. Soc.*, 1947, 36.
[21] I. T. Harrison, B. Lythgoe, and S. Trippett, *J. Chem. Soc.*, 1955, 4016.
[22] B. Lythgoe, T. A. Moran, M. E. N. Nambudiry, and S. Ruston, *J.C.S. Perkin I*, 1976, 1975.

It was used without purification for reduction by the standard method, using 5.65% sodium amalgam (4.0 g) in methanol (8 cm³) and ethyl acetate (4 cm³). This gave the *olefin* (16) (181 mg, 50% overall) as an oil, b.p. (bath temp.) 120 °C at 25 mmHg, τ 5.0 (1 H, t, *J* 6 Hz, =CH) (Found: M^+, 180.188 2. $C_{13}H_{24}$ requires *M*, 180.187 8). G.l.c. (5 ft of 5% Carbowax 20M) revealed a single component.

(E)-*Pentadec-7-ene* (20).—n-Octyl phenyl sulphone [23] (762 mg) was metallated with ethylmagnesium bromide, and brought into reaction with n-heptanal (342 mg) in essentially the same way as described for the olefin (16); but the product was treated with acetic anhydride (400 mg), and then stirred for 6 h. Addition of saturated aqueous ammonium chloride, and isolation in the usual way, gave a mixture (*ca.* 2 : 3 by ^{1}H n.m.r. and t.l.c.) of diastereoisomers (18) (1.075 g), $\nu_{max.}$ 1 160, 1 250, 1 320, 1 330, and 1 760 (all s) cm^{-1}, τ 4.6—5.1 (1 H, C*H*·OAc), 6.6—7.2 (1 H, CH·SO_2), and 8.03 and 8.22 (two s, total 3 H, OAc).

Reduction of a portion (387 mg) gave (*E*)-pentadec-7-ene [24] (127 mg; 62% overall), $\nu_{max.}$ 965 cm^{-1}, τ 4.7 (2 H, m, =CH) (Found: M^+, 210.234 88. Calc. for $C_{15}H_{30}$: *M*, 210.234 74). G.l.c. (5 ft of Carbowax 20M or DEGS) revealed a single component.

Cyclohex-1-enyl Phenyl Sulphone (22).—Phenylthiomethyl-lithium [25] (20 mmol) in tetrahydrofuran at 0 °C was stirred during dropwise addition of cyclohexanone (1.96 g) in tetrahydrofuran (5 cm³). After a further 1 h at room temperature the mixture was added to cold N-hydrochloric acid, and was extracted with ether (50 cm³). The ether layer was washed successively with dilute hydrochloric acid, aqueous sodium carbonate, and water, and then dried and evaporated, and the residual oil, dissolved in methylene chloride (80 cm³) at 0 °C was treated during 10 min with portions of 85% *m*-chloroperbenzoic acid (7.93 g). The mixture was stirred for 1 h at room temperature and then washed successively with aqueous sodium sulphite, aqueous sodium carbonate, and water, and was then dried and evaporated. Crystallisation from ether–light petroleum gave 1-*hydroxy*-1-*phenylsulphonylmethylcyclohexane* as prisms (3.91 g, 77%), m.p. 62—64°, $\nu_{max.}$ 1 150s, 1 310s, 1 320s, and 3 570m cm^{-1}, τ 6.7 (2 H, s, CH_2·SO_2) (Found: C, 61.7; H, 7.05; S, 12.5. $C_{13}H_{18}O_3S$ requires C, 61.4; H, 7.1; S, 12.6%).

The above hydroxy-sulphone (2.54 g) and phosphoryl chloride (1.60 g) were kept together in pyridine (10 cm³) at room temperature for 8 h. Water (1 cm³) was added, and after 30 min ether (25 cm³) was added, and the mixture was washed with water, dilute hydrochloric acid, and water, and was then dried and evaporated. Crystallisation of the residue from light petroleum gave the sulphone (22) as needles (1.34 g, 57%), m.p. 75—77° (lit.,[26] 76.5—77°), τ 4.58br (1 H, =CH) and 6.3 (2 H, s, CH_2·SO_2).

The mother liquor material contained more of the sulphone (22) together with its αβ-unsaturated isomer, $\nu_{max.}$ 1 630m cm^{-1}, τ 3.82 (=CH·SO_2). The anion derived from this mixture could be used in place of that from the sulphone (22).

(E)-1-*Styrylcyclohexene* (26).—The sulphone (22) (472 mg) was metallated in the usual way with n-butyl-lithium, and, after reaction with benzaldehyde (212 mg), the product was treated with acetic anhydride to give material from which a crystalline mixture of diastereoisomeric acetoxy-sulphones (23) separated as needles (550 mg, 72%) (from ethanol), m.p. 110—166°, $\nu_{max.}$ 1 150, 1 235, 1 315, 1 330, and 1 765 (all s) cm^{-1}. The isomers were not readily separable by t.l.c., but their presence (*ca.* 1 : 1) was apparent from the ^{1}H n.m.r. spectrum: isomer A had τ 2.75 (5 H, s, ArH), 3.41 (1 H, d, *J* 7 Hz, C*H*·OAc), 4.1br (1 H, =CH), 6.17 (1 H, d, *J* 7 Hz, CH·SO_2), and 7.91 (3 H, s, OAc); isomer B had τ 2.70 (5 H, s, ArH), 3.63 (1 H, d, *J* 10 Hz, C*H*·OAc), 4.2br (1 H, =CH), 5.93 (1 H, d, *J* 10 Hz, CH·SO_2), and 8.14 (3 H, s, OAc).

Reduction of a portion (384 mg) of the mixture (23) gave after bulb-to-bulb distillation at 140 °C (bath) and 0.3 mmHg the *diene*, (26) as an oil (172 mg, 93%), $\nu_{max.}$ 965s, 1 610w, and 1 640w cm^{-1}, τ 3.3 (1 H, d, *J* 16 Hz, ArCH=), 3.7 (1 H, d, *J* 16 Hz, ArCH·C*H*), and 4.2br (1 H, =CH), $\lambda_{max.}$ 279 (ε 28 200), 288 (ε 28 800), and 314infl nm (Found: M^+, 184.125 16. $C_{14}H_{16}$ requires *M*, 184.125 19).

(E)-1,2-*Di*(*cyclohex*-1-*enyl*)*ethylene* (28).—From treatment of the sulphone (22) (755 mg), as the lithio-derivative, with cyclohex-1-enecarbaldehyde (24) (343 mg), followed by acetylation, a mixture (4 : 1 by ^{1}H n.m.r.) of the diastereoisomeric acetoxy-sulphones (25) and (27) was obtained as an oil (1.036 g, 86%). Crystallisation from ether–light petroleum gave the threo-*isomer* (25) as prisms, m.p. 95—97°, $\nu_{max.}$ 1 155, 1 240, 1 320, 1 330, and 1 760 (all s) cm^{-1}, τ 4.14 (1 H, d, *J* 11 Hz, C*H*·OAc), 4.17br (1 H, =CH), 4.33br (1 H, =CH), 6.05 (1 H, d, *J* 11 Hz, CH·SO_2), and 8.16 (3 H, s, OAc) (Found: C, 67.95; H, 7.35; S, 8.35. $C_{22}H_{48}O_4S$ requires C, 68.0; H, 7.3; S, 8.25%).

P.l.c. of the mother liquor material (benzene) gave the erythro-*isomer* (27) as needles (from benzene–light petroleum), m.p. 127—129°, $\nu_{max.}$ as for the *threo*-isomer, τ 4.1 (1 H, d, *J* 6 Hz, C*H*·OAc), 4.2br (2 H, =CH), 6.3 (1 H, d, *J* 6 Hz, CH·SO_2), and 7.98 (3 H, s, OAc) (Found: C, 67.9; H, 7.25; S, 8.3%).

Reduction of the *threo*-acetoxy-sulphone (25), and bulb-to-bulb distillation at 140 °C (bath) and 0.3 mmHg afforded the *E*-triene (28) (174 mg, 93%), m.p. 27—29°, $\nu_{max.}$ 845s, 920m, 960s, and 1 640w cm^{-1}, $\lambda_{max.}$ 259.5, 269 (ε 42 500), and 281 nm, τ 4.02 (2 H, s, CH=CH) and 4.38br (2 H, =CH) (Found: M^+, 188.156 69. Calc. for $C_{14}H_{20}$: *M*, 188.156 49).

Similar reduction of the *erythro*-acetoxy-sulphone (27) (38.8 mg) gave the same triene (28) (yield 64%).

erythro-1-*Benzoyloxy*-1,2-*diphenyl*-2-*phenylsulphonylethane* (31).—*erythro*-1,2-diphenyl-2-(phenylthio)ethanol (29) was converted into the erythro-*benzoyloxy-sulphone* (31) (85% yield) by the method used [11] for the preparation of the *threo*-isomer (32). Crystallisation from benzene–light petroleum gave the product (31) as needles, m.p. 162—163°, $\nu_{max.}$ 1 155, 1 270, 1 330, and 1 735 (all s) cm^{-1}, τ 2.95 (1 H, d, *J* 5 Hz, C*H*·OBz) and 5.6 (1 H, d, *J* 5 Hz, CH·SO_2) (Found: C, 72.9; H, 4.48; S, 7.15. $C_{27}H_{22}O_4S$ requires C, 73.3; H, 5.0; S, 7.2%).

(E)-*Stilbene*.—Reduction of the *threo*-benzoyloxy-sulphone (32) in the usual way gave a mixture (94 mg, 52%) of *trans*-stilbene, the *cis*-isomer, and 1,2-diphenylethane in the ratio (^{1}H n.m.r.; g.l.c.) 90 : 5 : 5. The *erythro*-isomer (31) afforded the same mixture in 57% yield. The reduction of *trans*- and *cis*-stilbene under the reaction conditions was

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shown to afford 1,2-diphenylethane. The *cis*-stilbene was shown to owe its formation to an elimination of benzoic acid from the isomers (31) and (32), followed by reductive removal of the phenylsulphonyl group.

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