Preparation of some Allylic Sulphones; Base-catalysed Isomerisation and Deuteriation of Cyclohex-2-enyl *p*-Tolyl Sulphones

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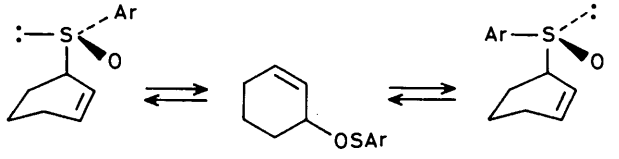
A summary of the methods used in the preparation of a range of allylic sulphones is given. In the case of the conformationally biased sulphones (**5**) and (**6**) stereospecific preparation from the *cis*- and *trans*-5-t-butylcyclohex-2-en-1-ols was achieved by rearrangement of the respective sulphenate esters, which occurred with high diastereoselectivity, followed by oxidation of the resulting sulphoxides. Base-catalysed equilibration and deuteriation studies on the six-membered cyclic allylic sulphones have been carried out.

For an investigation of the 1,3-rearrangement of allylic sulphones to be described in the following paper it was necessary to prepare a range of such sulphones. Although many were known compounds, it is convenient to indicate here the methods used for preparation of those which are new. It is also an opportunity to describe briefly some base-catalysed isomerisations and deuteriation studies which we carried out in the case of the six-membered cyclic allylic sulphones.

The simplest procedure for the preparation of aryl alkyl sulphones consists of alkylation of a sodium arenesulphinate with an alkyl halide.[1] We found this method somewhat limited in scope for the preparation of allylic sulphones, partly because it is not generally applicable to 'unsymmetrical' allylic halides where the possible products of S_N2 and S_N2' reactions are different and also because the less reactive cyclohex-2-enyl halides do not give good yields of crystalline products. In the latter cases it was better to prepare first the allylic sulphide *via* displacement using the more nucleophilic arenethiolate ion and then oxidise to sulphone. A number of ways of carrying out this oxidation have been recommended;[2] we find hydrogen peroxide in acetic acid to be satisfactory if sodium acetate is added. It is possible that the addition of sodium acetate avoids production of peracetic acid; peracids are known slowly to epoxidise allylic sulphones.[3]

The rearrangement of allylic sulphinate esters to allylic sulphones[4,5] is a good way of preparing lightly substituted acyclic allylic sulphones, *e.g.* (*E*)-but-2-enyl *p*-tolyl sulphone from but-3-en-2-ol. However, rearrangement of the toluene-*p*-sulphinate ester of either *cis*- or *trans*-5-t-butylcyclohex-2-en-1-ol on heating in formamide gave a mixture of the diastereoisomeric 5-t-butylcyclohex-2-enyl *p*-tolyl sulphones.[5] Since we needed unambiguously identifiable samples of these sulphones for our later work, we explored their preparation from the corresponding sulphoxides.

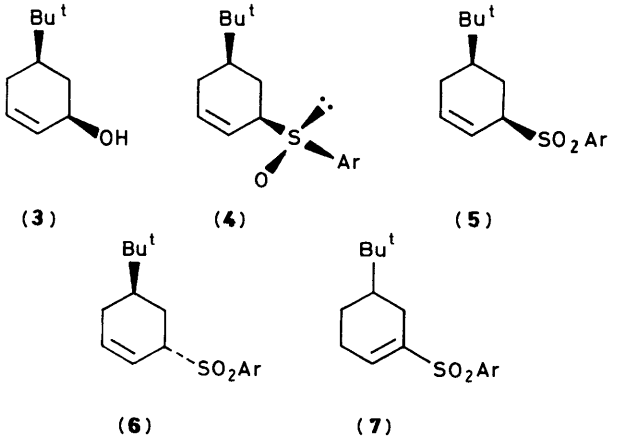
It is well known that allylic sulphenate esters rapidly rearrange to allylic sulphoxides[6,7] and cyclohex-2-en-1-ol is readily converted to cyclohex-2-en-1-yl *p*-tolyl sulphoxide on treatment with toluene-*p*-sulphenyl chloride in the presence of triethylamine. What does not seem to have been reported before is that only one diastereoisomer of the sulphoxide is formed, though it is in line with related findings by Hoffmann[7] for certain other allylic alcohols. We consider that the diastereoisomer formed is the (*RS,RS*)-isomer (**1**) which would have the aryl group away from the ring ('*exo*') in the transition state for rearrangement. In agreement it is found that when cyclohex-2-enyl *p*-tolyl sulphoxide is prepared by oxidation (H_2O_2–MeOH) of the corresponding sulphide it is obtained as a mixture (*ca.* 1:1) of diastereoisomers. Treatment of the latter mixture with trimethyl phosphite[6,7] led to removal of the more reactive '*exo*'-isomer as the allylic alcohol (*via* the allylic sulphenate) and the recovered sulphoxide was predominantly the less reactive (*RS,SR*)-isomer (**2**), see Scheme.



(**1**) (**2**)

Scheme.

Thus, in contrast to our observations on the six-membered cyclic allylic sulphinate esters[5] the corresponding sulphenates undergo rearrangement by a stereospecific, presumably [2,3]-sigmatropic shift mechanism. The allylic sulphoxide can then be oxidised to sulphone using hydrogen peroxide in acetic acid. By starting with *cis*-5-t-butylcyclohex-2-en-1-ol (**3**), a single sulphoxide (**4**) (stereochemistry assigned on the basis of the above considerations) was obtained by rearrangement of the sulphenate ester. Oxidation of sulphoxide (**4**) gave the *cis*-sulphone (**5**). The *trans*-sulphone (**6**) was obtained similarly from *trans*-5-t-butylcyclohex-2-en-1-ol.



(**3**) (**4**) (**5**) (**6**) (**7**)

The other method used in the preparation of substituted allylic sulphones was alkylation of a simpler allylic sulphone by treatment with an alkyl-lithium followed by the appropriate alkyl halide. This approach, which relies on the high α-selectivity of attack on the metallated intermediate, has often been used.[8] In practice some experimentation was required to

find the appropriate alkyl-lithium–solvent–additive [*e.g.*, hexamethylphosphoric triamide (HMPA)] combination in each case but we were usually able to get respectable yields of substituted acyclic and cyclic allylic sulphones.

For our subsequent work we required some α-deuteriated allylic sulphones. The effect of base, both in the absence and presence of D_2O, on cyclohex-2-enyl *p*-tolyl sulphone and the conformationally biased sulphones (**5**) and (**6**) was therefore briefly explored. Under relatively vigorous conditions (0.5M-NaOH; Me_2SO–H_2O; reflux) equilibrium was established between cyclohex-2-enyl and cyclohex-1-enyl *p*-tolyl sulphones. The equilibrium mixture contained equal amounts of the two isomers. Although the general observation has been made that β,γ-unsaturated sulphones are more stable than the α,β-isomer[9] the arenesulphonyl group in acyclic α,β-unsaturated sulphones does seem to have a small stabilising effect in terms of its overall influence on the position of equilibrium with the β,γ-isomer.[10] Our result for the cyclohexenyl sulphones implies that the effect is small, however, comparisons between cyclic and acyclic systems are notoriously difficult to make with regard to double bond shift equilibria.

H/D Exchange at C-1 in cylohex-2-enyl *p*-tolyl sulphone occurred under much milder conditions than the above β,γ⇌α,β equilibration. Thus treatment with NaOD (0.017M) in Me_2SO–H_2O (2:1) at 50 °C gave virtually complete α-deuteriation without formation of the α,β-isomer. Clearly the anionic intermediate undergoes very predominant α-attack.[8]

Related studies on the t-butyl substituted cyclohexenyl sulphones (**5**) and (**6**) showed that under mildly basic conditions [0.01M-NaOH; Me_2SO–H_2O (2:1); 50 °C] epimerisation occurred, without double bond shift, to give an equilibration mixture of the two sulphones (**5**) and (**6**) in the ratio 6:4. In D_2O, under analogous conditions, a similar ratio of the two α-deuteriated sulphones was obtained. Thus at equilibrium the *cis*-sulphone (**5**) with the pseudoequatorial arenesulphonyl group predominates slightly over the *trans*-isomer (a similar equilibrium mixture is obtained in aqueous acetic acid[11]). The result is what might be expected conformationally on simple steric grounds and it contrasts with the view of Trost and Schmuff[12] that in cyclohex-2-enyl phenyl sulphones the pseudoaxial is more stable than the pseudoequatorial conformer. Since their suggestion is based on two examples, one containing a 2-methyl substituent ($A_{1,2}$ strain) and the other with an ester group at C-5 as the conformational biasing group (polar effects) where the special factors noted in parenthesis might be operative, we consider their proposal that there is a π–σ* stabilising effect in the pseudoaxial form to be debatable.

Under more vigorous conditions [0.5M-NaOH; Me_2SO–H_2O (1:1); reflux] the conformationally biased sulphones (**5**) and (**6**) were partially converted into the vinyl sulphone (**7**). At equilibrium, a mixture containing *ca.* 50% of the vinyl sulphone (**7**) and 50% of the allylic sulphones (**5**) and (**6**) in a 3:2 ratio was obtained. Comparison with the previous result for the simple cyclohexenyl *p*-tolyl sulphones shows that the t-butyl group does not perturb the position of equilibrium in the case of (**5**) + (**6**) ⇌ (**7**). This could be taken as evidence that the t-butyl group does not have a significant polar effect in these compounds.

Experimental

^1H N.m.r. spectra were recorded on Perkin-Elmer R24 (60 MHz) or Bruker WH 300 (300 MHz) instruments using Me_4Si as an internal standard except for Me_3Si-containing compounds when $CHCl_3$ was used. ^{13}C N.m.r. spectra were recorded on Bruker WH 90 (22.63 MHz) or WH 300 (75.43 MHz) instruments using $CDCl_3$ (δ_C 77.0) as the solvent and internal standard.

Cyclohex-2-enyl p-*Tolyl Sulphone.**—Hydrogen peroxide (100 vol 30% solution; 5.3 ml, 0.042 mol) was added dropwise to a stirred solution of 3-(*p*-tolylthio)cyclohexene[13] (4.0 g, 0.019 mol) in acetic acid (50 ml) containing sodium acetate (7.8 g, 0.095 mol) heated to 50 °C. The mixture was maintained at 50 °C overnight and then cooled. The mixture was extracted with ether (2 × 50 ml) and washed with dilute sodium hydroxide solution until the aqueous phase was neutral. The extracts were dried ($MgSO_4$) and the solvent removed under reduced pressure to give a pale oil. Trituration of the crude oil with light petroleum afforded the sulphone as a solid (3.62 g). Recrystallisation of this gave needles, m.p. 61 °C (lit.,[13] 61—61.5 °C (from hexane), $\delta_H(CDCl_3)$ 1.35—2.10 (6 H, complex, CH_2), 2.44 (3 H, s, MeC_6H_4), 3.74 (1 H, m, $CHSO_2Ar$), 5.76 (1 H, m, C=CH), 6.07 (1 H, m, C=CH), 7.34 (2 H, d, *J* 8 Hz, ArH), and 7.75 (2 H, d, *J* 8 Hz, ArH); $\delta_C(CDCl_3)$ 19.47 (t), 21.52 (q), 24.33 (t), 61.66 (d), 118.67 (d), 129.03 (d), 129.62 (d), 135.02 (d), and 144.56 (s).

Cyclohex-2-enyl p-*Tolyl Sulphoxide.*—A solution of toluene-*p*-sulphenyl chloride[14] (0.53 g, 3.3 mmol) in dichloromethane (3 ml) was added over 15 min to a stirred solution of cyclohex-2-en-1-ol (0.30 g, 3.1 mmol) and triethylamine (0.5 ml, 3.6 mmol) in dichloromethane (5 ml) at 20 °C. After a further 30 min at 20 °C, the solution was filtered, washed with dilute HCl, aqueous Na_2CO_3, water, and brine, dried ($CaCl_2$), and evaporated to give (*RS,RS*) *cyclohex-2-enyl* p-*tolyl sulphoxide* (0.7 g) as a yellow oil, δ (300 MHz; $CDCl_3$) 1.5—2.15 (6 H, m), 2.45 (3 H, s, Me), 3.3—3.4 (1 H, m, 1-H), 5.65—5.75 (1 H, m, 2-H), 6.1—6.2 (1 H, m, 3-H), 7.3 (2 H, d, ArH), and 7.55 (2 H, d, ArH).

Reaction of Mixed Diastereoisomers of 3-(p-*Tolylsulphinyl*)-*cyclohexene with Trimethyl Phosphite.*—Trimethyl phosphite (dist. from sodium; 3 ml, 4 equiv.) and 3-(*p*-tolylsulphinyl)cyclohexene [1.0 g; obtained by oxidation of 3-(*p*-tolylthio)cyclohexene[13] using hydrogen peroxide in methanol as described below for *cis*-and *trans*-5-t-butyl-3-(*p*-tolylthio)cyclohexene] in dry methanol (30 ml) was heated under reflux for 20 h. The cooled reaction mixture was treated with aqueous $NaHCO_3$ (100 ml) and the product was isolated with ether to give an oil (0.9 g) which was chromatographed on silica gel (24 g). Elution with ether–light petroleum mixtures yielded relatively non-polar components while elution with ether gave a polar fraction (350 mg) as single spot on t.l.c., shown by n.m.r. to be a 1:1 mixture of *O,O*-dimethyl *S*-*p*-tolyl thiophosphate (spectrum identical with that of an authentic specimen) and (*RS,SR*)-cyclohex-2-enyl *p*-tolyl sulphoxide: $\delta_H(CDCl_3)$ 1.6—2.2 (6 H, m), 2.5 (3 H, s, Me), 3.3 (1 H, br s, 3-H), 5.1 (1 H, m, 2-H), 6.0 (1 H, m, 1-H), 7.3 (2 H, d, ArH), and 7.6 (2 H, d, ArH).

After the latter material had been heated in methanol under reflux for 18 h, the n.m.r. spectrum showed the presence of the (*RS,RS*)-sulphoxide (*ca.* 20%).

trans-5-*t-Butylcyclohex-2-enyl* p-*Tolyl Sulphoxide.*—*trans*-5-t-Butylcyclohex-2-enol[15] (0.80 g) was treated with toluene-*p*-sulphenyl chloride as for cyclohex-2-en-1-ol to obtain one of the diastereoisomers of the *trans*-sulphoxide (1.5 g) as a yellow oil, δ (300 MHz; $CDCl_3$) 0.85 (9 H, s, Bu^t), 1.62—2.2 (5 H, m), 2.4 (3 H, s, Me), 3.35—3.45 (1 H, m, 1-H), 5.7—5.75 (1 H, m, 2-H), 6.15—6.25 (1 H, m, 3-H), 7.3 (2 H, d, ArH), and 7.55 (2 H, d, ArH).

trans-5-*t-Butylcyclohex-2-enyl* p-*Tolyl Sulphone* (**6**).—Crude *trans*-5-t-butyl-3-(*p*-tolylsulphinyl)cyclohexene (1.4 g, 5 mmol) in glacial acetic acid (10 ml) was oxidised with aqueous hydrogen peroxide (*ca.* 25% v/v; 1.2 ml, *ca.* 10 mmol) at 30 °C

* We thank Dr. T. A. K. Smith for these experimental details.

for 20 h. Aqueous NaOH was added and the mixture was extracted with ether. The ethereal solution was washed with aqueous Na_2CO_3, water, and brine, dried (Na_2SO_4), and evaporated. Flash column chromatography eluting with ether–light petroleum (1:2 v/v) gave the trans-*sulphone* (**6**) (0.66 g, 45%) as a solid, m.p. 100 °C (from ether–light petroleum) (Found: C, 69.9; H, 8.2; S, 10.8. $C_{17}H_{24}O_2S$ requires C, 69.8; H, 8.25; S, 10.95%); δ (300 MHz; $CDCl_3$) 0.85 (9 H, s, Bu^t), 1.35—2.3 (5 H, m), 2.45 (3 H, s, Me), 3.75—3.8 (1 H, m, 1-H), 5.75—5.85 (1 H, m, 2-H), 6.2—6.25 (1 H, m, 3-H), 7.35 (2 H, d, ArH), and 7.75 (2 H, d, ArH); δ_C($CDCl_3$) 21.5 (q), 23.1 (t), 26.7 (q), 31.9 (s), 37.3 (d), 62.1 (d), 117.4 (d), 128.9 (d), 129.5 (d), 135.2 (s), 136.5 (d), and 144.4 (s).

cis-5-*t-Butylcyclohex*-2-*enyl* p-*Tolyl Sulphoxide* (**4**).—*cis*-5-t-Butylcyclohex-2-enol[15] (0.85 g) was treated as for the *trans*-isomer to give the *cis*-sulphoxide (**4**) (*ca.* 2 g) as a yellow oil, δ (300 MHz; $CDCl_3$) 0.85 (9 H, s, Bu^t), 1.7—2.2 (5 H, m), 2.45 (3 H, s, Me), 3.35—3.5 (1 H, m, 1-H), 5.55—5.6 (1 H, m, 2-H), 6.05—6.15 (1 H, m, 3-H), 7.35 (2 H, d, ArH), and 7.5 (2 H, d, ArH).

cis-5-*t-Butyl-cyclohex*-2-*enyl* p-*Tolyl Sulphone* (**5**).—Crude *cis*-5-t-butylcyclohex-2-enyl *p*-tolyl sulphoxide (*ca.* 2 g) was oxidised in the same manner as the *trans*-isomer. Flash column chromatography eluting with ether–light petroleum (1:2 v/v) gave the cis-*sulphone* (**5**) (0.8 g, *ca.* 40%), a portion of which was purified by preparative t.l.c. eluting with ethyl acetate–light petroleum (1:9 v/v) to give the *cis*-sulphone (**5**) as an oil (Found: C, 69.35; H, 8.05; S, 10.35. $C_{17}H_{24}O_2S$ requires C, 69.8; H, 8.25; S, 10.95%); δ (300 MHz; $CDCl_3$) 0.85 (9 H, s, Bu^t), 1.25—2.25 (5 H, m), 2.45 (3 H, s, Me), 3.8—3.9 (1 H, m, 1-H), 5.7—5.8 (1 H, m, 2-H), 6.0—6.1 (1 H, m, 3-H), 7.35 (2 H, d, ArH), and 7.75 (2 H, d, ArH); δ_C($CDCl_3$) 21.6 (q), 24.2 (t), 26.3 (t), 26.9 (q), 32.3 (s), 42.9 (d), 64.3 (d), 118.9 (d), 129.1 (d), 129.5 (d), 134.5 (d), and 144.5 (s).

cis- *and* trans-5-*t-Butylcyclohex*-2-*enyl* p-*Tolyl Sulphide*.—4-t-Butylcyclohexene (5.44 g, 0.039 mol) was brominated with *N*-bromosuccinimide.[15] Sodium (0.85 g, 0.037 mol) was dissolved in methanol (30 ml) and 20 °C under a nitrogen atmosphere. First toluene-*p*-thiol (4.64 g, 0.037 mol), then the crude mixture of bromo compounds was added dropwise to the stirred solution. After having been stirred for 1.5 h at 20 °C under nitrogen, the mixture was refluxed for 30 min, then filtered. The filtrate was extracted with light petroleum. The petroleum solution was washed with aqueous NaOH, dilute HCl, water, and brine, dried (Na_2SO_4), and evaporated. Distillation of the residue gave a mixture of *cis*- and *trans*-5-t-butylcyclohex-2-enyl *p*-tolyl sulphide (4.3 g, 41%) as a pale yellow liquid, b.p. 128—134 °C at 0.8 mmHg; δ (300 MHz; $CDCl_3$) 0.9 (9 H, s, Bu^t), 1.35—2.25 (5 H, m), 2.35 (3 H, s, Me), 3.7—3.9 (1 H, m, 1-H), 5.65—5.95 (2 H, m, =CH), 7.15 (2 H, d, ArH), and 7.35 (2 H, d, ArH).

cis- *and* trans-5-*t-Butylcyclohex*-2-*enyl* p-*Tolyl Sulphoxide*.—Aqueous hydrogen peroxide (*ca.* 25% v/v; 5.8 ml, *ca.* 0.05 mol) was added dropwise to a stirred solutuion of *cis*- and *trans*-5-t-butylcyclohex-2-enyl *p*-tolyl sulphide (3.11 g, 0.012 mol) in methanol (100 ml). The mixture was stirred for 43 h at *ca.* 30 °C, then diluted with brine and extracted with chloroform. The chloroform solutuion was washed with water and brine, dried ($CaCl_2$), and evaporated. Purification of the residue by column chromatography on silica gel (250 g) eluting with ether gave a mixture of both of the diastereoisomers of *cis*-and both of the diastereoisomers of *trans*-5-t-butylcyclohex-2-enyl *p*-tolyl sulphoxide (*cis*:*trans* 4:1 by n.m.r. spectroscopy; 3.0 g, 90%) as a pale yellow oil, δ (300 MHz; $CDCl_3$) 0.85 (9 H, s, Bu^t), 1.35—2.15 (5 H, m), 2.45 (3 H, s, Me), 3.3—3.5 (1 H, m, 1-H), 5.4—6.3 (2 H, m, =CH), 7.3 (2 H, d, ArH), and 7.55 (2 H, d, ArH).

cis- *and* trans-5-*t-Butylcyclohex*-2-*enyl* p-*Tolyl Sulphones* (**5**) *and*(**6**).—Some of the mixture of *cis*- and *trans*-5-t-butylcyclohex-2-enyl *p*-tolyl sulphoxide (0.58 g) prepared above was oxidised as before to obtain a mixture of the *cis*- and *trans*-sulphones (**5**) and (**6**) (*cis*:*trans* 4:1 by n.m.r. spectroscopy; 0.61 g) as a pale yellow oil. This material was used without further purification.

Cyclohex-2-*enyl t-Butyl Sulphone*.—The *sulphone* was prepared in 64% yield by oxidation of 3-(t-butylthio)cyclohexene[16] with AcOH–water and had m.p. 55 °C (from ether–light petroleum) (Found: C, 59.4; H, 9.15; S, 16.1. $C_{10}H_{18}O_2S$ requires C, 59.4; H, 9.0; S, 15.85%); δ_H 1.35—2.3 (6 H, m, ring CH_2), 1.45 (9 H, s, Bu^t), 3.92 (1 H, m, 1-H), 5.82 (1 H, ddt, *J* 10.5 2.5, 2 Hz, =CH), and 6.13 (1 H, ddt, *J* 10.5, 4, 2.5 Hz, =CH); δ_C 133.80 (d), 119.34 (d), 60.60 (s), 54.56 (d), 23.81 (t), 23.60 (q), 23.38 (t), and 19.55 (t).

Monoalkylation of Sulphones: General Procedure.—The sulphone (5 mmol) dissolved in dry THF–ether (1:1 v/v) (40 ml) was stirred and cooled to *ca.* −50 °C and the required volume of alkyl-lithium added *via* a syringe. The resulting coloured solution was stirred at −70 °C for 30 min and quenched with an alkyl halide either by direct addition of an excess in the case of the cyclic sulphones or by inverse addition for acyclic sulphones at −70 °C over 15 min. After a further 2 h stirring at −70 °C the reaction mixture was allowed to warm to room temperature. Ammonium chloride solution (1 ml) was added and the ether was removed under reduced pressure. The oily residue was partitioned between ether and sodium hydroxide, the organic phase was separated, washed with aqueous hydrochloric acid, water, and brine, dried ($MgSO_4$), and evaporated. The product was isolated by chromatography on silica gel [*ca.* 25 g; eluant ether–light petroleum (6:4)] and crystallisation.

1-*Methylcyclohex*-2-*enyl* p-*tolyl sulphone*.—The *sulphone* was isolated in 82% yield, m.p. 77—77.5 °C (from ether–light petroleum) (Found: C, 67.0: H, 7.3; S, 12.7. $C_{14}H_{18}O_2S$ requires C, 67.2; H, 7.25; S, 12.8%); δ_H 1.42 (3 H, s, Me), 1.4—2.2 (6 H, m, ring CH_2), 2.44 (3 H, s, ArMe), 5.70 (1 H, bd, *J* 10 Hz, =CH), 5.99 (1 H, dt, *J* 10, 4 Hz, =CH), 7.32 (2 H, d, ArH), and 7.72 (2 H, d, ArH); δ_C 144.27 (s), 133.48 (d), 132.83 (s), 130.29 (d), 129.05 (d), 124.85 (d), 63.41 (s), 29.37 (t), 24.19 (t), 22.09 (q), 21.44 (q), and 18.37 (t).

1-*Ethylcyclohex*-2-*enyl* p-*tolyl sulphone*. The *sulphone* obtained in 76% yield had m.p. 58—59 °C (from ether–light petroleum) (Found: C, 68.4; H, 7.45; S, 12.1. $C_{15}H_{20}O_2S$ requires C, 68.4; H, 7.6; S, 12.2%); δ_H 0.93 (3 H, t, *J* 7.5 Hz, Me), 1.3—2.2 (8 H, m, CH_2), 2.44 (3 H, s, ArMe), 5.57 (1 H, br d, *J* 10 Hz, =CH), 6.15 (1 H, dt, *J* 10, 4 Hz, =CH), 7.31 (2 H, d, ArH), and 7.73 (2 H, d, ArH); δ_C 144.16 (s), 135.65 (d), 133.49 (s), 130.34 (d), 129.03 (d), 123.43 (d), 66.34 (t), 27.76 (t), 26.29 (t), 23.86 (t), 21.47 (q), 18.71 (t), and 8.53 (q).

1-*Benzylcyclohex*-2-*enyl* p-*tolyl sulphone*. The *sulphone* obtained in 64% yield crystallised from ether–light petroleum and had m.p. 126—127 °C (Found: C, 73.3; H, 6.9; S, 9.95. $C_{20}H_{22}O_2S$ requires C, 73.6; H, 6.8; S, 9.8%); δ_H 0.79 (1 H, br, CH), 1.3—2.2 (5 H, m, 2 × CH_2 and CH), 2.46 (3 H, s, ArMe), 3.11, 3.24 (2 H, AB system, J_{AB} 13 Hz, CH_AH_BPh), 5.78 (1 H, dt, *J* 10, 2 Hz, =CH), 6.10 (1 H, dt, *J* 10, 4 Hz, =CH), and 7.1—7.36 and 7.75—7.92 (9 H, m, ArH).

p-*Tolyl*-1-*trimethylsilylcyclohex*-2-*enyl sulphone*. The *sulphone*, needles from ether–light petroleum, had m.p. 131—132 °C (Found: C, 62.4; H, 7.6; S, 10.1. $C_{16}H_{24}O_2SSi$ requires C, 62.3; H, 7.8; S, 10.4%); *m*/*z* 308 (M^+); δ_H 0.28 (9 H, s, Me_3Si), 0.29 (1 H, br, CH), 1.17 (1 H, m, CH), 1.63 (2 H, m, CH_2), 1.84 (1 H,

ddd, *J* 19.5, 11.5, 4.5 Hz, CH), 2.14 (1 H, dt, *J* 19.5, 4.5, CH), 2.40 (3 H, s, ArMe), 5.90 (1 H, dt, *J* 10, 4 Hz, =CH), 6.01 (1 H, br d, *J* 10 Hz, =CH)), 7.25 (2 H, d, ArH), and 7.65 (2 H, d, ArH); δ_C 143.56 (s), 135.80 (s), 131.32 (d), 129.49 (d), 128.89 (d), 123.23 (d), 59.25 (s), 25.38 (t), 23.38 (t), 21.44 (q), 17.02 (t), and −1.81 (q).

1-*Methylcyclohex-2-enyl t-butyl sulphone.* The sulphone obtained in 60% yield had m.p. 44—44.5 °C (from light petroleum), δ_H 1.51 (3 H, s, Bu^t), 1.54 (3 H, s, Me), 1.4—2.4 (6 H, m, ring CH_2), 5.91 (1 H, dt, *J* 10, 1.5 Hz, =CH), and 5.96 (1 H, dt, *J* 10, 35 Hz, =CH). Satisfactory analytical data were not obtained for this compound.

But-3-en-2-yl p-*tolyl sulphone.* The sulphone was prepared by the addition of methyl lithium–lithium bromide (1.3 mol l^{-1}; 3.85 ml, 5 mmol) to allyl *p*-tolyl sulphone (0.98 g, 5 mmol) according to the standard procedure. The yellow solution was quenched by an inverse addition into methyl iodide (0.5 ml, 1.12 g, 7.9 mmol). The sulphone (58%) had m.p. 68—69 °C (from ethanol) (lit.,[17] 70 °C) (Found: C, 62.9; H, 6.85. Calc. for $C_{11}H_{14}O_2S$: C, 62.85; H, 6.7%); δ_H 1.43 (3 H, d, *J* 7 Hz, Me), 2.45 (3 H, s, ArMe), 3.70 (1 H, t, quintet, *J* 7, 1 Hz, $CHSO_2$), 5.10 (1 H, dt, *J* 17, 1 Hz, =CH), 5.27 (1 H, dt, *J* 9, 1 Hz, =CH, 5.83 (1 H, ddd, *J* 17, 9, 1 Hz, =CH), 7.32 (2 H, d, ArH), and 7.72 (2 H, d, ArH); δ_C 144.43 (s), 133.75 (s), 131.26 (d), 129.37 (d), 129.11 (d), 121.40 (t), 63.95 (d), 21.39 (q), and 12.81 (q).

Pent-1-en-3-yl p-*tolyl sulphone.* The sulphone was prepared from allyl *p*-tolyl sulphone and ethyl iodide and was isolated as needles (68%), m.p. 54—55 °C (from ethanol) (lit.,[17] 54—55 °C) (Found: C, 64.0; H, 7.2; S, 14.1. Calc. for $C_{12}H_{16}O_2S$: C, 64.25; H, 7.2; S, 14.3%); δ_H 0.89 (3 H, t, *J* 7 Hz, CH_2Me), 1.63 and 2.08 (2 H, m, CH_AH_B), 2.4 (3 H, s, ArMe), 3.35 (1 H, dd, *J* 10, 7 Hz, $CHSO_2$), 4.98 (1 H, dd, *J* 17, 1.5 Hz, =CH), 5.23 (1 H, dd, *J* 10, 1.5 Hz, =CH), 5.59 (1 H, ddd, *J* 17, 10, 7 Hz, =CH), 7.30 (2 H, d, ArH), and 7.74 (2 H, d, ArH).

p-*Tolyl* 1-*trimethylsilylprop-2-enyl sulphone.* The *sulphone* was prepared according to the general monoalkylation procedure from trimethylsilyl chloride and allyl *p*-tolyl sulphone and was isolated as needles (55%), m.p. 87—88 °C (Found: C, 58.45; H, 7.55. $C_{13}H_{20}O_2SSi$ requires C, 58.15; H, 7.5%); *m/z* 268 (M^+); δ_H 0.30 (9 H, s, Me_3Si), 2.39 (3 H, s, ArMe), 3.38 (1 H, d, *J* 10.5 Hz, $CHSO_2$), 4.71 (1 H, d, *J* 17 Hz, =CH), 4.99 (1 H, d, *J* 10 Hz, =CH), 5.78 (1 H, dt, *J* 17, 10 Hz, =CH), 7.26 (2 H, d, ArH), and 7.65 (2 H, d, ArH); δ_C 143.40 (s), 137.69 (s), 129.57 (d), 129.15 (d), 127.98 (d), 119.56 (t), 64.54 (d), 21.50 (q), and −1.39 (q).

1-*Phenylbut-3-en-2-yl* p-*tolyl sulphone.* The sulphone from benzyl bromide and allyl *p*-tolyl sulphone was isolated in 60% yield, m.p. 98—99 °C (from ethanol) (lit.,[18] 95—96 °C) (Found: C, 71.55; H, 6.4; S, 11.3. Calc. for $C_{17}H_{18}O_2S$: C, 71.3; H, 6.35; S, 11.2%); δ_H 2.43 (3 H, s, ArMe), 2.88 (1 H, dd, *J* 13.5, 11.5 Hz, C*H*Ph), 3.55 (1 H, dd, *J* 13.5, 3 Hz, CHPh), 3.74 (1 H, ddd, *J* 11.5, 10, 3 Hz, $CHSO_2$), 4.81 (1 H, dt, *J* 17, 1.5 Hz, =CH), 5.15 (1 H, dt, *J* 10, 1.5 Hz, =CH), 5.65 (1 H, dt, *J* 17, 10 Hz, =CH), 7.05—7.3 (5 H, m, Ph), 7.33 (2 H, d, ArH), and 7.76 (2 H, d, ArH); δ_C 144.73 (s), 136.67 (s), 134.40 (s), 129.72 (d), 129.53 (d), 129.20 (d), 128.49 (d), 126.73 (d), 124.07 (t), 71.10 (d), 33.53 (t), and 21.58 (q).

Hexa-1,5-dien-3-yl p-*tolyl sulphone.* The *sulphone* was prepared (73%) using the standard procedure from allyl *p*-tolyl sulphone and allyl bromide as needles, m.p. 62—63 °C (ether–light petroleum) (Found: C, 65.9; H, 6.65; S, 13.3. $C_{13}H_{16}O_2S$ requires C, 66.1; H, 6.8; S, 13.55%); δ_H 2.43 (1 H, br, CHC=), 2.44 (3 H, s, ArMe), 2.86 (1 H, br, m, CHC=), 3.52 (1 H, ddd, *J* 10, 9.5, 3.5 Hz, $CHSO_2$), 4.95—5.2 (3 H, m, =CH), 5.30 (1 H, dd, *J* 10.5, 1 Hz, =CH), 5.50—5.75 (2 H, m, =CH), 7.33 (2 H, d, ArH), and 7.72 (2 H, d, ArH); δ_C 144.21 (s), 133.85 (s), 132.56 (d), 129.49 (d), 129.00 (d), 128.73 (d), 123.12 (t), 117.7 (t), 68.86 (d), 31.20 (t), and 21.06 (q).

p-*Tolyl* 2-*trimethylsilylbut-3-en-2-yl sulphone.* *p*-Tolyl 1-trimethylsilylprop-2-enyl sulphone was methylated with methyl iodide according to the standard procedure. The *sulphone* was isolated in 85% yield as needles m.p. 89 °C (from light petroleum) (Found: C, 60.1; H, 7.85%; M^+, 282.1109. $C_{14}H_{22}O_2SSi$ requires C, 59.55; H, 7.85%; *M*, 282.1110); δ_H 0.29 (9 H, s, Me_3Si), 1.24 (3 H, s, Me), 2.40 (3 H, s, ArMe), 4.68 (1 H, dd, *J* 17.5, 1 Hz, =CH), 5.11 (1 H, dd, *J* 10.5, 1 Hz, =CH), 6.38 (1 H, dd, *J* 17.5, 10.5 Hz, =CH), 7.26 (2 H, d, ArH), and 7.60 (2 H, d, ArH); δ_C 143.58 (s), 134.81 (d), 133.90 (s), 129.57 (d), 128.63 (d), 115.82 (t), 61.63 (3), 21.42 (q), 14.73 (q), and −2.00 (q).

Table 1. Reactions of cyclohex-2-enyl *p*-tolyl sulphone with sodium hydroxide

Entry	Solvent[a]	[NaOH] (mol l^{-1})	Temp. (°C)	Time[b]	Products (%) Allylic sulphone[c]	Vinylic sulphone[d]
1	2:1		50	10	100	
2	2:1	0.01	50	5	100	
3	2:1[e]	0.017	50	10	100[f]	
4	1:1	0.5	100	10	50	50
5	1:1	0.5	100	4.5 h	50	50

[a] Solvent Me_2SO–water unless otherwise noted. [b] Min unless otherwise specified. [c] Cyclohex-2-enyl *p*-tolyl sulphone. [d] Cyclohex-1-enyl *p*-tolyl sulphone. [e] Me_2SO–D_2O. [f] [1-^{2}H]-cyclohex-2-enyl *p*-tolyl sulphone.

Table 2. Reactions of 5-t-butylcyclohex-2-enyl *p*-tolyl sulphone[a] with sodium hydroxide

Entry	Solvent[b]	[NaOH] (mol l^{-1})	Temp. (°C)	Time[c]	Products (%) Allylic sulphones[d]	Vinylic sulphone[e]
1	2:1		60	10	100 (4:1)	
2	2:1	0.01	50	5	100 (3:2)	
3	2:1[f]	0.01	50	5	100 (3:2)[g]	
4	1:1	0.5	100	10	50 (3:2)	50
5	1:1	0.5	100	24 h	50 (3:2)	50

[a] *cis*:*trans*, 4:1. [b] Solvent Me_2SO–water unless otherwise stated. [c] Min unless otherwise specified. [d] 5-t-Butylcyclohex-2-enyl *p*-tolyl sulphone, *cis*:*trans* ratio in brackets. [e] 4-t-Butylcyclohexen-2-yl *p*-tolyl sulphone. [f] Me_2SO–D_2O. [g] [1-^{2}H] labelled sulphones.

Dimethylation of Sulphones: General Procedure.—The general procedure for monoalkylation of sulphones was adopted with the following modifications. Methyl lithium–lithium bromide (2.1 equiv.) was added at −50 °C to the solution of the sulphone which contained an excess of methyl iodide (3 equiv.). The following sulphones were prepared.

2-*Methylbut-3-en-2-yl* p-*tolyl sulphone.* The sulphone was prepared from allyl *p*-tolyl sulphone in 80% yield as needles, m.p. 53 °C (from ethanol) (lit.,[17] 51—52 °C) (Found: C, 64.4; H, 7.2; S, 14.3. Calc. for $C_{12}H_{16}O_2S$: C, 64.25; H, 7.2; S, 14.25%); δ_H 1.43 (6 H, s, Me_2C), 2.43 (3 H, s, ArMe), 5.07 (1 H, d, *J* 17 Hz, =CH), 5.26 (1 H, d, *J* 10 Hz, =CH), 6.04 (1 H, dd, *J* 17, 10 Hz, =CH), 7.30 (2 H, d, ArH), and 7.69 (2 H, d, ArH); δ_C 144.10 (s), 136.28 (d), 131.80 (s), 130.08 (d), 128.62 (d), 118.27 (t), 64.05 (s), 21.06 (q), and 20.20 (q).

2-*Methylbut-3-en-2-yl t-butyl sulphone.* The *sulphone* was prepared from allyl t-butyl sulphone (71%) as needles, m.p. 31—31.5 °C (from ether–light petroleum) (Found: C, 56.55; H, 9.35; S, 16.6. $C_9H_{18}O_2S$ requires C, 56.8; H, 9.55; S, 16.8%); δ_H 1.45 (9 H, s, Bu^t), 1.58 (6 H, s, Me_2C), 5.28 (1 H, d, *J* 11 Hz, =CH), 5.29 (1 H, d, *J* 17 Hz, =CH), and 6.30 (1 H, dd, *J* 17, 11 Hz, =CH); δ_C 138.87 (d), 115.62 (t), 67.88 (s), 65.19 (s), 25.49 (q), and 22.52 (q).

(2Z)-2-*Methylpent-3-en-2-yl* p-*tolyl sulphone.* The *sulphone*

was prepared from (2*Z*)-but-2-enyl *p*-tolyl sulphone and methyl iodide in 76% yield, m.p. 62—62.5 °C (from ether–light petroleum) (Found: C, 65.4; H, 7.5. $C_{13}H_{18}O_2S$ requires C, 65.5; H, 7.6%); δ_H 1.55 (6 H, s, Me_2C), 1.57 (3 H, dd, *J* 7.0, 2 Hz, =CMe), 2.45 (3 H, s, ArMe), 5.29 (1 H, dq, *J* 12, 7 Hz, =CH), 5.7 (1 H, d, *J* 12, =CH), 7.32 (2 H, d, ArH), and 7.75 (2 H, d, ArH); δ_C 142.6 (s), 132.71 (s), 131.69 (d), 130.56 (d), 129.00 (d), 128.16 (d), 64.93 (s), 23.32 (q), 21.47 (q), and 14.10 (q).

Reactions of Cyclohex-2-enyl p-*Tolyl Sulphone and of the* cis- *and* trans-5-*t-Butylcyclohex-2-enyl* p-*Tolyl Sulphones with Sodium Hydroxide.*—A solution of the allylic sulphone (0.05—0.15M; 0.3—1.5 mmol) in water–Me_2SO or D_2O–Me_2SO containing NaOH was treated as indicated in Tables 1 and 2. The cooled product was isolated by extraction with benzene. The benzene solution was washed with dilute HCl, water, and brine, dried, and evaporated. Analysis was by 300 MHz ^2H n.m.r. spectroscopy. Only reactions with good mass recovery are reported in the Tables.

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