Radical Induced Cyclisations of Some Cyclic Unsaturated Allylic Sulphones

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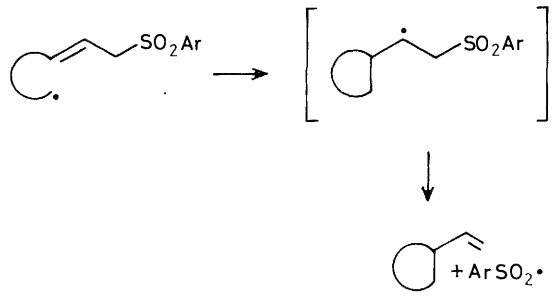
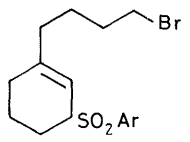
The cyclisations of unsaturated allylic *p*-tolyl sulphones to give ring compounds with adjacent vinyl and *p*-tolylsulphonylmethyl substituents (Scheme 2) is shown to be a feasible process by the conversion, in satisfactory yield, of the allylic ether (**5**; R = Me) into the bicyclic sulphone (**7**), formed as a mixture of diastereoisomers (**8**) and (**9**). The prop-2-ynyl analogue can be similarly cyclised to the vinyl sulphones (**14**) and (**15**), the former predominating. These reactions are considered to occur by a radical chain mechanism involving addition–elimination of $ArSO_2^{\bullet}$ radicals.

In an earlier paper on the 1,3-rearrangement of allylic sulphones,[1] we put forward a mechanism involving addition–elimination of arylsulphonyl radicals to explain, for example, the isomerisation of 1,1-dimethylallyl *p*-tolyl sulphone into prenyl† sulphone under radical induced conditions. There are other examples of S_H2' reactions of allylic sulphones in the literature[2] and in general sulphonyl radical elimination from β-sulphonyl alkyl radicals appears to be well established.[3] It therefore seemed worth investigating the possibility of carrying out cyclisations of the type shown in Scheme 1.‡ The rapidly burgeoning literature on radical cyclisations[4] also provided encouraging precedents.



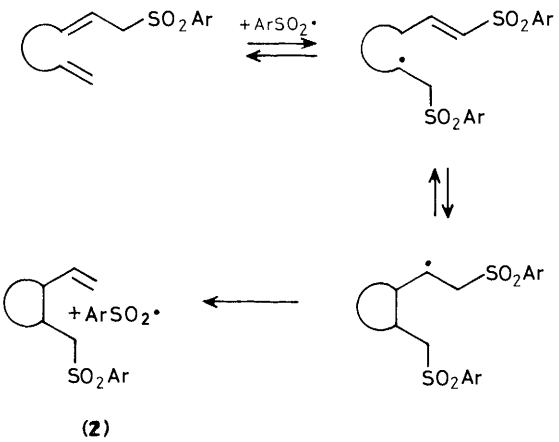
Scheme 1.

After preliminary results on the tributyl tin hydride reduction of the unsaturated bromo sulphone (**1**) had proved unpromising[5] we turned instead to an extension of Scheme 1



(**1**)

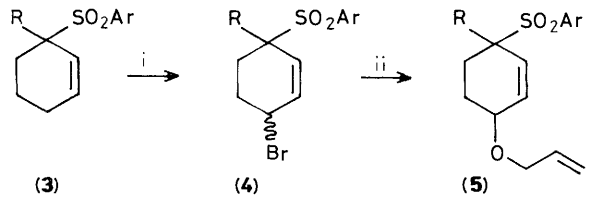
involving a suitably constituted unsaturated allylic sulphone as in Scheme 2. It was envisaged that the moderately electrophilic arene-sulphonyl radical[6] might add preferentially to the isolated terminal double bond, for both steric and electronic reasons, and that the radical formed could undergo an intramolecular S_H2' reaction leading to a cyclic unsaturated sulphone (**2**). The overall isomerisation should be favourable thermodynamically since a σ-bond is formed at the expense of a π-bond. Compounds of type (**2**) could be useful synthetically since they possess two functionalities attached to adjacent atoms of the new ring capable of synthetic manipulation in various ways.



(**2**)

Scheme 2.

As first candidate for a cyclisation according to Scheme 2 we chose the allylic ether (**5**; R = H) since it seemed that it might be readily prepared from cyclohex-2-enyl *p*-tolyl sulphone (**3**; R = H)[7] as in Scheme 3. A further incentive to trying the oxygenated precursor was provided by Beckwith's finding[8] of the favourable cyclisation of 3-oxahex-5-enyl radicals. The allylic bromination to give (**4**; R = H) went in good yield but attempts to prepare the ether (**5**; R = H) or indeed to persuade (**4**; R = H) to undergo direct substitution with a range of different nucleophiles, consistently failed, giving instead the



(**3**) (**4**) (**5**)

Scheme 3. *Reagents:* i, NBS–CCl_4; ii, CH_2=$CHCH_2OH$–base

† Prenyl = Me_2C=$CHCH_2$.

‡ Unless otherwise stated in this paper, Ar = *p*-tolyl.

dienyl sulphone (**6**). Perhaps not surprisingly in retrospect, *E*1cB elimination was the favoured reaction pathway. To obviate the undesired elimination, 1-methylcyclohex-2-enyl *p*-tolyl sulphone (**3**; R = Me)[7] was used as starting material, Scheme 3. Allylic bromination again proceeded satisfactorily and, in this case, the product (**4**; R = Me) underwent substitution to give compound (**5**; R = Me) on treatment with allyl alcohol in the presence of triethylamine (reflux). Although the allylic bromide (**4**; R = Me) was a mixture of diastereoisomers, the ether (**5**; R = Me) was obtained predominantly as one diastereoisomer as shown by ^1H and ^{13}C n.m.r.

The allylic ether (**5**; R = Me) possesses the appropriate disposition of double bond and allylic sulphone for cyclisation according to Scheme 2, and since 1-alkylcyclohex-2-enyl aryl sulphones do not readily undergo 1,3-rearrangement under radical induced conditions,[1] this favourable relationship should be maintained prior to cyclisation. The reaction of the allylic ether (**5**; R = Me) initiated by dibenzoyl peroxide (BPO) (5 mol%) in CCl_4 at 80 °C was monitored by ^1H n.m.r. After 30 min, considerable change had occurred and after 3 h the n.m.r. signals attributable to the five olefinic protons in the starting material had disappeared and a broad peak at δ 5.22, assignable to the single hydrogen of a substituted 1-methylcyclohexene, had appeared.

The product, isolated by chromatography in 63% yield, showed ^1H and ^{13}C n.m.r. data consistent with a mixture of two diastereoisomers of (**7**) in the ratio 5:2. The presence of the CH_2SO_2Ar unit in the structure was corroborated by the presence of a series of double doublets in the δ 3.0—3.3 region in the ^1H n.m.r. spectrum which disappeared after deuterium exchange (0.01M NaOD, D_2O, 100 °C, 16 h).

The two diastereoisomers of (**7**) are considered to be (**8**) and (**9**), differing in configuration of the CH_2SO_2Ar side-chain, since previous precedents[9] for such radical cyclisations leading to substituted bicyclo[4.3.0]nonanes have all given products with a *cis*-fused ring junction. Models indicate that in the transition state (**10**) for cyclisation *via* intramolecular axial attack on the double bond, with a pseudo-axial $ArSO_2$ leaving group, the CH_2SO_2Ar group is either pointing away from (**10**; R^1 = CH_2SO_2Ar, R^2 = H) or under (**10**; R^1 = H, R^2 = CH_2SO_2Ar) the cyclohexene ring. Since the former, leading to (**8**), might be expected to be less sterically demanding than the latter, we tentatively assign structure (**8**) to the major diastereoisomer and (**9**) to the minor one.

Conversion of the allyl ether (**5**; R = Me) into the cyclic sulphones (**8**) and (**9**) was also effected in 78% yield using sodium toluene-*p*-sulphinate in 60% aq. acetic acid at 100 °C (16 h). We had previously used this procedure for initiating the 1,3-rearrangement of allylic sulphones.[1]

Attempts to extend the cyclisation to the but-2-enyl ether (**11**), prepared from the allylic bromide (**4**; R = Me), were not very successful. Use of BPO–CCl_4 conditions gave low recovery of unidentified materials and the NaTs–aq. AcOH procedure gave a complex mixture containing *ca.* 40% of (**12**) as judged by the n.m.r. spectrum of the crude material. Apparently attack of $ArSO_2^{\bullet}$ on the disubstituted double bond of (**11**) is relatively unfavourable. We did not pursue this variant since it was apparent, from the point of view of synthetic utility, that compounds of type (**12**) should be readily obtainable by further alkylation (*e.g.* BuLi, R Hal) of the simpler precursor (**7**).

Experiments involving the prop-2-ynyl ether (**13**) were more successful. Using BPO–CCl_4 (74%) or $ArSO_2Na$–aq. AcOH

(83%), the cyclised vinyl sulphones (**14**) and (**15**) were obtained in the yields quoted in parentheses. The diastereoisomeric sulphones were formed in the ratio 10:1 and we consider the major one to be the *Z*-isomer (**14**) by analogy with the known radical chain predominant *trans*-addition of toluene-*p*-sulphonyl iodide to monosubstituted acetylenes.[10] Presumably the small amount of *E*-isomer (**15**) reflects the extent to which radical inversion has occurred at the intermediate vinyl radical stage prior to cyclisation.

One attractive possible extension of the above cyclisations would be conversion of the acrylate ester (**16**) into the lactone (**17**), since (**17**) should be convertible into the α-methylene γ-lactone (**18**) by elimination of toluene-*p*-sulphinic acid.

Unfortunately, however, the ester (**16**) prepared from the allylic bromide (**4**; R = Me) gave either polymeric material, under the BPO–CCl_4 conditions, or the bis-sulphone (**19**) *via* nucleophilic addition of $ArSO_2H$ using $ArSO_2Na$–aq. AcOH. Substitution of a silicon containing group at the α-position of an α,β-unsaturated ester or ketone renders it less prone to radical polymerisation[11] and it was hoped that the α-trimethylsilylester (**20**), again prepared from the bromo sulphone (**4**; R = Me), might cyclise successfully under BPO catalysis. The product (**21**), if formed, should be readily convertible into the α-methylene lactone (**18**). Ester (**20**) was, however, recovered unchanged after prolonged treatment under BPO–CCl_4 conditions. Presumably either the ε-deficient double bond of (**20**) is too unreactive towards the electrophilic arylsulphonyl radicals and/or the first formed adduct radical from (**20**) is insufficiently reactive for electronic and/or steric reasons to add efficiently to the double bond of the allylic sulphone. Treatment of (**20**) with $ArSO_2Na$–aq. AcOH again gave the bis-sulphone (**19**).

The following paper describes further extensions of the cyclisation of unsaturated allylic sulphones.

Experimental

^1H N.m.r. spectra were recorded on Perkin-Elmer R24 (60 MHz) or Bruker WH300 (300 MHz) instruments using Me_4Si as an internal standard. ^{13}C N.m.r. spectra were obtained on a Bruker AM250 instrument (62.86 MHz) using $CDCl_3$ as solvent. Mass spectra were recorded on a VG Analytical 30F, 16F, or ZAB 1F instrument operating at 70 eV.

1-*Bromo*-4-p-*tolylsulphonylcyclohex*-2-*ene* (**4**; R = H).—*N*-Bromosuccinimide (0.76 g, 4.27 mmol) was added to a stirred solution of 3-*p*-tolylsulphonylcyclohexene (**3**)[7] (1.0 g, 4.23 mmol) in carbon tetrachloride (50 ml). The inhomogeneous mixture was heated under reflux and dibenzoyl peroxide (*ca.* 100 mg) was added at this temperature. The mixture was maintained at reflux until reaction was judged to be complete (4 h) by t.l.c. The mixture was cooled and the succinimide filtered off. The filtrate and washings were washed with dilute aqueous sodium hydroxide (50 ml) and dried ($MgSO_4$). The solvent was removed under reduced pressure to give a pale yellow solid (1.6 g) which was recrystallised to give the *sulphone* as needles (1.25 g, 93%), m.p. 128—130 °C (from light petroleum–CH_2Cl_2) (Found: C, 49.6; H, 5.0. $C_{13}H_{15}BrO_2S$ requires C, 49.50; H, 4.8%); $\delta_H(CDCl_3)$ 1.93—2.41 (4 H, complex, CH_2), 2.46 (3 H, s, MeAr), 3.80 (1 H, m, 4-H), 4.70 (1 H, m, 1-H), 5.77 (1 H, m, C=CH), 6.27 (1 H, m, C=CH), 7.35 (2 H, d, ArH), and 7.75 (2 H, d, ArH); $\delta_C(CDCl_3)$ (two stereoisomers) 21.62 (q), 18.98/19.09 (t), 27.82/30.13 (t), 43.82/44.36 (d) (CHBr), 59.88/62.06 (d) (*C*HSO$_2$Ar), 121.02/122.14 (d), 128.90/129.84 (d), 129.13 (d), 129.62 (d), 134.33/135.75 (s), and 144.96/145.02 (s).

Various conditions were used in an attempt to substitute bromine by oxygen in the allylic bromide (**4**; R = H). In every case the product obtained was 1-*p*-tolylsulphonylcyclohexa-1,3-diene (**6**) obtained as an unstable solid, m.p. 41—43 °C, which rapidly decomposed to unidentified products; $\delta_H(CDCl_3)$ 2.30 (4 H, br s, CH_2CH_2), 2.45 (3 H, s, MeAr), 6.10 (2 H, m, 3- and 4-H), 7.00 (1 H, m, 2-H), 7.3 (2 H, d, ArH), and 7.75 (2 H, d, ArH); *m/z* (NH_3 c.i.) 252 (100%, $M^+ + 18$).

1-*Bromo*-4-*methyl*-4-p-*tolylsulphonylcyclohex*-2-*ene* (**4**; R = Me).—Prepared from 1-methyl-1-*p*-tolylsulphonylcyclohex-2-ene[7] as in the previous preparation giving the *bromo sulphone* as needles (95%), m.p. 96—97/106—108 °C (from light petroleum) (Found: C, 50.95; H, 5.3. $C_{14}H_{17}BrO_2S$ requires C, 51.05; H, 5.20%); $\delta_H(CDCl_3)$ 1.40 (3 H, s, 4-Me, major isomer), 1.56 (3 H, s, 4-Me, minor isomer), 1.66—2.41 (6 H, complex CH_2), 2.45 (3 H, s, MeAr), 4.56 (1 H, m, 1-H, minor isomer), 4.70 (1 H, m, 1-H, major isomer), 5.65 (1 H, d, *J* 10 Hz, 3-H, major isomer), 5.92 (1 H, d, *J* 10 Hz, 3-H, minor isomer), 6.02 (1 H, dd, *J* 10 and 4.5 Hz, 2-H, minor isomer), 6.25 (1 H, dd, *J* 10 and 4.5 Hz, 2-H, major isomer), and 7.26—7.80 (4 H, complex, ArH).

4-*Methyl*-4-p-*tolylsulphonylcyclohex*-2-*enyl Allyl Ether* (**5**; R = Me).—Dry triethylamine (0.05 ml) was added to a solution of the bromo sulphone (**4**; R = Me) (1.27 g, 4.03 mmol) in allyl alcohol (10 ml) and the resulting mixture heated under reflux for 18 h. Isolation with ether gave the crude product as an oil (1.3 g). Purification on silica gel using 3:1 light petroleum–ether as eluant gave the ether (**5**; R = Me) as a colourless oil (0.82 g, 68%) which rapidly underwent darkening and partial conversion into its isomer (**7**). The ether (**5**; R = Me) could be stored in ether solution in the presence of hydroquinone (*ca.* 5 mg) in the refrigerator; $\delta_H(CDCl_3)$ 1.43 (3 H, s, 4-Me), 1.52—2.31 (4 H, complex CH_2), 2.44 (3 H, s, MeAr), 3.78 (3 H, complex, $CHOCH_2$), 5.17 (2 H, complex, CH=C*H*$_2$), 5.75 (1 H, m, C*H*=CH$_2$), 5.88 (1 H, d, *J* 10.5 Hz, 3-H), 6.04 (1 H, dd, *J* 10.5 and 4.8 Hz, 2-H), 7.30 (2 H, d, ArH), and 7.73 (2 H, d, ArH) $\delta_C(CDCl_3)$ 21.09 (q), 21.54 (q), 24.64 (t), 26.21 (t), 63.23 (s), 68.62 (t), 69.73 (d),116.20 (t), 128.72 (d), 129.16 (d), 129.26 (s), 130.40 (d), 133.11 (d), 134.99 (d), and 144.48 (s); *m/z* (NH_3 c.i.) 324 (100%, $M^+ + 18$), 249 (45, $ArSO_2 - C_7H_{10}^+$), and 139 (35, $ArSO^+$).

4-*Methyl*-4-p-*tolylsulphonylcyclohex*-2-*enyl But*-2-*enyl ether* (**11**).—The ether (**11**) (46%) was obtained similarly using but-2-enyl alcohol; $\delta_H(CDCl_3)$ 1.50 (3 H, s, MeC=), 1.6—2.41 [7 H, complex, $(CH_2)_2$, 4-Me], 2.45 (3 H, s, MeAr), 3.45—4.0 (3 H, complex, $CHOCH_2$), 5.25—6.05 (4 H, complex, 2- and 3-H, HC=CH), 7.30 (2 H, d, ArH), and 7.73 (2 H, d, ArH); *m/z* (NH_3 d.c.i.) 338 (10%, $M^+ + 18$), 321 (18, $M^+ + 1$), and 139 (100, $ArSO^+$).

4-*Methyl*-4-p-*tolylsulphonylcyclohex*-2-*enyl Prop*-2-*ynyl Ether* (**13**).—The ether (**13**) (82%) was similarly obtained using prop-2-ynyl alcohol; $\delta_H(CDCl_3)$ 1.45 (3 H, s, 4-Me), 1.53—2.36 [4 H, complex, $(CH_2)_2$], 2.38 (1 H, t, *J* 2.5 Hz, C≡CH), 2.44 (3 H, s, MeAr), 3.89—4.18 (3 H, complex, $CHOCH_2$), 5.72—6.08 (2 H, complex, HC=CH), 7.32 (2 H, d, ArH), and 7.73 (2 H, d, ArH); *m/z* (NH_3 c.i.) 322 (100%, $M^+ + 18$), 174 (20, $ArSO_2^+ + 1$), and 139 (56, $ArSO^+$).

4-*Methyl*-4-p-*tolylsulphonylcyclohex*-2-*enyl Acrylate* (**16**).—Sodium acrylate (42 mg, 0.45 mmol) was added to a solution of the bromo sulphone (**4**; R = Me) (100 mg, 0.30 mmol) in dry DMF (5 ml). The mixture was heated to 100 °C for 16 h, cooled, and extracted into ether. The ether extracts were washed with dilute aqueous sodium hydroxide, dilute hydrochloric acid, water, and brine. Evaporation of the dried extracts gave the crude ester as an oil (80 mg). Purification on silica gel using 3:1 light petroleum–ether as eluant gave a mixture of isomeric esters (**16**) (27 mg, 29%); $\nu_{max.}(CHCl_3)$ 1 722 cm^{-1} (C=O); $\delta_H(CDCl_3)$

1.51 (3 H, s, 4-Me), 1.54—2.20 (4 H, complex, CH_2), 2.46 (3 H, s, MeAr), 5.40 (1 H, br m, 1-H), 5.80—6.42 (5 H, complex CH=CH_2, C=CH), 7.34 (2 H, d, ArH), and 7.73 (2 H, d, ArH); *m/z* (NH_3 c.i.) 388 (100%, M^+ + 18), 249 (35, $C_{14}H_{17}O_2S^+$), and 139 (35, $ArSO^+$).

4-Methyl-4-p-tolylsulphonylcyclohex-2-enyl 2′-Trimethylsilylacrylate (**20**).—Sodium α-trimethylsilyl acrylate[12] (173 mg, 0.95 mmol) was added to a solution of the bromo sulphone (**4**; R = Me) (207 mg, 0.63 mmol) in dry *N*-methylpyrrolidone (15 ml) and the resulting mixture heated to 100 °C (oil bath temperature). After 16 h the mixture was cooled, diluted with water (10 ml), and the product was isolated with ether to give the crude ester (**20**) as an oil (220 mg). Purification and partial separation of isomers was achieved using 'flash chromatography' on silica gel using 7:1 light petroleum–ether as eluant. The total yield was 77%, and the mixture contained approximately equal amounts of the two isomers.

Isomer A: $\delta_H(CDCl_3)$ 0.15 (9 H, s, Me_3Si), 1.50 (3 H, s, 4-Me), 1.60—2.27 (4 H, complex, CH_2), 2.45 (3 H, s, MeAr), 5.13 (1 H, br m, 1-H), 5.63—6.25 (3 H, complex, HC=CH, H_2C=CSiMe$_3$), 6.77 (1 H, d, *J* 2 Hz, H_2C=CSiMe$_3$), 7.35 (2 H, d, ArH), and 7.75 (2 H, d, ArH).

Isomer B: $\delta_H(CDCl_3)$ 0.17 (9 H, s, Me_3Si), 1.50 (3 H, s, 4-Me), 1.60—2.25 (4 H, complex, CH_2), 2.45 (3 H, s, MeAr), 5.18 (1 H, br m, 1-H), 5.70—6.12 (3 H, complex, HC=CH, H_2C=CSiMe$_3$), 6.58 (1 H, d, *J* 2 Hz, H_2C=CSiMe$_3$), 7.30 (2 H, d, ArH), and 7.73 (2 H, d, ArH).

General Procedure for Radical Cyclisation: (Method A). Using Dibenzoyl Peroxide in Carbon Tetrachloride.—Dibenzoyl peroxide (*ca.* 2 mg) was added to a solution of the substrate (10—100 mg) in carbon tetrachloride (0.5 ml) and the resulting solution transferred to a dry 5.0 mm n.m.r. tube. The tube was stoppered and heated to 80 °C (oil bath temperature). The extent of reaction could then be monitored by n.m.r. If the reaction time exceeded 16 h, the solution was filtered through a plug of silica gel, fresh dibenzoyl peroxide added, and the reaction restarted. When the reaction was complete, the cooled solution was diluted with carbon tetrachloride (10 ml) and washed with dilute aqueous sodium hydroxide (5 ml), water (5 ml), and brine (5 ml). After drying ($MgSO_4$), evaporation gave the product (Table).

(Method B) Using Sodium p-Tolylsulphinate in Aqueous Acetic Acid.—Sodium *p*-tolylsulphinate (7.0 equiv.) was added to a stirred solution, or suspension, of the substrate in 60% aqueous acetic acid (*ca.* 25 ml $mmol^{-1}$) and the resulting mixture heated to 100 °C (oil bath temperature). In most cases reaction was complete after 16 h. After cooling, the mixture was diluted with water and extracted into ether. The ether extracts were washed with dilute aqueous sodium hydroxide, water, and brine. Drying ($MgSO_4$) and evaporation gave the product (Table).

3-Methyl-9-p-tolylsulphonylmethyl-7-oxabicyclo[4.3.0]*non-2-ene* (**7**).—The *bicyclic ether* (**7**) (Table, entry 2) was obtained as a colourless oil (78%) after chromatography on silica gel using 1:1 light petroleum–ether as eluant (Found: C, 66.8; H, 7.2. $C_{17}H_{22}O_3S$ requires C, 66.5; H, 7.25%); $\delta_H(CDCl_3)$ 1.65 (3 H, s, 3-Me, major isomer), 1.68 (3 H, s, 3-Me, minor isomer), 1.7—2.4 (4 H, complex, CH_2), 2.46 (3 H, s, MeAr), 2.50 (2 H, br m, 1- and 9-H, major isomer), 2.81 (2 H, br m, 1- and 9-H, minor isomer), 3.01* (1 H, dd, *J* 13 and 7.5 Hz, CH_2SO_2Ar, minor isomer), 3.14* (1 H, dd, *J* 13 and 7.5 Hz, CH_2SO_2Ar, major isomer), 3.27* (1 H, dd, *J* 13 and 5 Hz, CH_2SO_2Ar, both isomers), 3.35 (1 H, dd, *J* 10 and 7 Hz, 8-H, minor isomer), 3.50 (1 H, dd, *J* 9 and 5 Hz, 8-H, major isomer), 3.88 (1 H, br m, 8-H, minor isomer), 3.97 (1 H, dd, *J* 9 and 6 Hz, 8-H, major isomer), 4.12 (**1** H, m, 6-H, major isomer), 4.20 (1 H, br m, 6-H, minor isomer), 5.22 (1 H, br s, 2-H, minor isomer), 5.22 (1 H, br s, 2-H, major isomer), 7.36 (2 H, d, ArH), and 7.80 (2 H, d, ArH); $\delta_C(CDCl_3)$ 21.63 (q), 23.77 (q, major isomer), 24.27 (q, minor isomer), 24.77 (t, minor isomer), 25.48 (t, major isomer), 26.51 (t, major isomer), 26.66 (t, minor isomer), 37.98 (d, minor isomer), 40.80 (d, major isomer), 41.15 (d, minor isomer), 44.39 (d, major isomer), 56.06 (t, minor isomer), 59.44 (t, major isomer), 71.0 (t, minor isomer), 71.82 (t, major isomer), 74.91 (d, major isomer), 75.88 (d, minor isomer), 116.14 (s), 119.96 (d), 127.97 (d), 130.00 (d), 136.49 (s), and 144.84 (s); *m/z* (NH_3 c.i.) 324 (55%, M^+ + 18) and 307 (100, M^+ + 1).

* Absent in the spectrum of the deuteriated material prepared as described below.

Table. Radical cyclisations

Entry	Substrate	Method	Time (h)	Product	Yield (%)
1	(**5**; R = Me)	A	3	(**7**)	75[a,b]
2	(**5**; R = Me)	B	16	(**7**)	78[a,b]
3	(**11**)	B	24	(**12**)	40[c]
4	(**13**)	A	20	(**14**) + (**15**)	74[b,d]
5	(**13**)	B	16	(**14**) + (**15**)	83[b,d]

[a] As a 5:2 mixture of diastereoisomers. [b] Isolated. [c] Estimated by n.m.r. [d] As a 10:1 mixture.

The bicyclic ether (**7**) (14 mg) was heated under reflux with NaOD [from Na (1 mg) in D_2O (5 ml)]. After 1 h the mixture had become turbid and a further portion of D_2O (1 ml) was added. After 16 h under reflux, the deuteriated ether was isolated with ether. The 300 MHz n.m.r. spectrum was very similar to that of the undeuteriated material but without the signals at δ 3.01, 3.14, and 3.27.

3-Methyl-9-p-tolylsulphonylmethylene-7-oxabicyclo[4.3.0]*non-2-ene* (**14**) *and* (**15**).—The bicyclic vinyl sulphones (**14**) and (**15**) (Table, entry 5) were purified by chromatography on silica gel using 3:1 light petroleum–ether as eluant to give the two isomers in a ratio of 10:1.

Crystallisation of the major isomer from light petroleum gave the (*Z*)-*sulphone* (**14**), m.p. 99 °C (Found: C, 67.1; H, 6.75. $C_{17}H_{20}O_3S$ requires C, 67.10; H, 6.60%); $\delta_H(CDCl_3)$ 1.55—2.15 (4 H, complex, CH_2), 1.68 (3 H, s, 3-Me), 2.45 (3 H, s, MeAr), 3.25 (1 H, br s, 1-H), 4.16 (1 H, m, 6-H), 4.76 (1 H, dd, 8-H), 5.05 (2 H, complex, 2- and 8-H), 6.20 (1 H, m, =C*H*SO_2Ar), 7.35 (2 H, d, ArH), and 7.78 (2 H, d, ArH); *m/z* (NH_3 c.i.) 322 (65%, M^+ + 18), 305 (28, M^+, +1), 242 (100), and 139 (50, $ArSO^+$).

The (*E*)-sulphone (**15**) was obtained as a colourless oil; $\delta_H(CDCl_3)$ 1.58—2.28 (4 H, complex, CH_2), 1.71 (3 H, br s, 3-Me), 2.48 (3 H, s, MeAr), 4.18 (2 H, br s, 1- and 6-H), 4.28 (1 H, dd, 8-H), 4.55 (1 H, d, 8-H), 5.36 (1 H, br s, 2-H), 6.11 (1 H, br s, C=CHSO_2Ar), 7.36 (2 H, d, ArH), and 7.83 (2 H, d, ArH).

Reaction of the Esters (**16**) *and* (**20**) *with Sodium p-Tolylsulphinate in Aqueous Acetic Acid.*—The esters (**16**) and (**20**) were treated separately according to Method B. In both cases an oil was obtained, assigned the structure of 4-methyl-4-*p*-tolylsulphonylcyclohex-2-enyl (3′-*p*-tolylsulphonyl)propionate (**19**) (94 and 89%, respectively); $\nu_{max.}$ 1 730 cm^{-1} (C=O); $\delta_H(CDCl_3)$ 1.47 (3 H, s, 4-Me), 1.50—2.20 (4 H, complex, CH_2), 2.47 (3 H, s, MeAr), 2.71, 3.38 (4 H, m, AA′BB′, 2 × t, *J* 7 Hz, $CH_2CH_2SO_2Ar$), 5.05 (1 H, m, 1-H), 5.87 (2 H, br s, 2- and 3-H), and 7.30—7.83 (4 H, complex, Ar); *m/z* (NH_3 d.c.i.) 494 (35%, M^+ + 18) and 139 (100, $ArSO^+$).

A solution of the bis-sulphone (**19**) (*ca.* 10 mg) and potassium hydroxide (0.1 ml of a 1.0M solution in water) in ethanol (15 ml) was stirred at room temperature for 20 h. Dilution with water (15 ml) followed by isolation with ether gave material which had identical t.l.c. behaviour and n.m.r. spectra to 4-methyl-4-*p*-tolylsulphonylcyclohex-2-en-1-ol[5] obtained by alternative means.

Acknowledgements

We thank the S.E.R.C. for a research studentship (to T. A. K. S.) and Dr. A. E. Derome and his associates for n.m.r. spectra.

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Received 26 *May* 1988; *Paper* 8/02105H