Sulphonate Esters as Sources of Sulphonyl Radicals; Ring-closure Reactions of Alk-4- and -5-enesulphonyl Radicals

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Alkyl alkanesulphonates and arenesulphonates were found to be useful sources of sulphonyl radicals, particularly for spectroscopic work, when treated with organotin or organosilyl radicals. Allyl, propynyl and penta-2,4-dienyl methanesulphonates gave, however, allyl, propynyl and pentadienyl radicals, respectively. Sulphonyl radicals generated in this way added efficiently to alk-1-enes with electron-releasing substituents, and the EPR spectra of the adduct radicals were recorded. A variety of radical initiation systems were tried on pent-4-enesulphonyl chloride. The pent-4-enesulphonyl radical cyclised mainly in the *endo* mode to give the six-membered-ring sulphone. Similarly, the hex-5-enesulphonyl radical cyclised to give thiepane 1,1-dioxide, with a seven-membered ring. The cyclohex-2-enylethanesulphonyl radical cyclised mainly in the *exo* mode to give 2-chloro-9-thiabicyclo[4.3.0]nonane 9,9-dioxide. The mechanisms of these reactions are discussed.

Several different types of precursor have been used for the generation of sulphonyl radicals, $RSO_2^{\cdot}$. These include alkane- and arene-sulphinic acids,[1] sulphonyl halides,[2] sulphoxides,[3] and arylmethanesulphonamides.[4] The copper(II) chloride-catalysed decomposition of arenesulphonyl chlorides has frequently been used as a source of sulphonyl radicals for synthetic work,[5] and recently tris(triphenylphosphine)ruthenium(II) chloride has been employed in a similar way.[6] Another important route to sulphonyl radicals is the addition of a carbon- or an oxygen-centred radical to sulphur dioxide.[1,2,7] The reverse of this, *i.e.* α-scission with loss of SO_2, is a rapid reaction for many sulphonyl radicals at temperatures above ambient. Sulphonyl radicals add readily to unsaturated molecules such as alkenes, alkynes, and aromatics, and this is a useful route to sulphones; these processes have been reviewed recently by Chatgilialoglu.[8] Although intermolecular addition of sulphonyl radicals to alkenes has been widely studied, very little is known about the corresponding intramolecular reaction. Johnson and Derenne showed that 6-methylhept-5-en-2-ylcobaloxime reacted with sulphur dioxide to give 1,1-dioxathiacyclohexane-3-sulphonylcobaloxime.[9] The product was formed *via* an alk-5-enesulphonyl radical which cyclised in the *endo* mode to give the six-membered ring. In the reaction of trichloromethanesulphonyl chloride with similar cobaloximes the ring-closed radical intermediate abstracted chlorine from the sulphonyl chloride to give chlorinated cyclic sulphones as the products.[10]

Sulphonate esters are readily prepared and easily handled so we decided to examine them as potential sources of sulphonyl and alkyl radicals. We also generated several unsaturated organosulphonyl radicals from sulphonate esters and sulphonyl chlorides and investigated the regioselectivity of their ring closure to cyclic sulphones. The results of this study are reported in this paper; part of the work has already appeared in preliminary communications.[11]

Results and Discussion

Sulphonate Esters as Radical Sources.—Sulphonate esters, **1** were prepared from the alcohol R′OH and the sulphonyl chloride in the presence of triethylamine. Mixtures of the sulphonate ester, hexamethylditin (or triethylsilane) and di-*tert*-butyl peroxide in *tert*-butylbenzene solvent were photolysed in the cavity of an EPR spectrometer. In most cases the spectrum of the corresponding sulphonyl radical, $RSO_2^{\cdot}$, was observed at 240 K. Thus, the $MeSO_2^{\cdot}$ radical was generated, with EPR parameters identical with those in the literature,[12] from the methanesulphonate esters with R′ = n-C_6H_{13}, Pr^i, c-C_5H_9, Bu^t, C_6H_4OMe-*p*, CH_2Ph, $CH_2CH{=}CH_2$, $CH(C{=}CMe_2)_2$, cyclohex-2-enyl, CH_2COMe and CMe_2COEt. The trichloromethanesulphonyl and propane-2-sulphonyl radicals[12] were also observed from the corresponding sulphonate esters with R′ = Bu^t, CH_2Ph, *etc.* The sulphonyl radical spectra were weak and difficult to observe for aromatic esters $ArSO_2OR'$, but the $4\text{-}MeC_6H_4SO_2^{\cdot}$ radical[13] was successfully identified in the case of R′ = $CH_2CH{=}CH_2$.

It is probable that these sulphonyl radicals are formed in an S_H2 reaction of trimethyltin, or triethylsilyl, radicals with the sulphonate ester [eqns. (1)–(3)].

$$Bu^tOOBu^t \longrightarrow 2\,Bu^tO^{\cdot} \qquad (1)$$

$$Bu^tO^{\cdot} + Me_3SnSnMe_3\ (\text{or } Et_3SiH) \longrightarrow Bu^tOMR^1_3\ (\text{or } Bu^tOH) + R^1_3M^{\cdot} \qquad (2)$$

$$\underset{\mathbf{1}}{RSO_2OR'} + R^1_3M^{\cdot} \longrightarrow RSO_2^{\cdot} + R'OMR^1_3 \qquad (3)$$

The reaction of isopropyl toluene-*p*-sulphonate with tri-*n*-butyltin hydride was carried out on a preparative scale using UV light as initiator. A good yield of toluene-*p*-sulphinic acid, probably formed when the toluene-*p*-sulphonyl radical abstracts hydrogen from the tin hydride, was isolated [eqn. (4)].

$$4\text{-}MeC_6H_4SO_2OPr^i \longrightarrow 4\text{-}MeC_6H_4SO_2^{\cdot} \longrightarrow 4\text{-}MeC_6H_4SO_2H \qquad (4)$$

The cyclic ester, **2**, *i.e.* propane-1,3-sultone, failed to produce spectroscopically observable radicals. This can probably be attributed to the very poor solubility of this compound in hydrocarbon solvents. Trihalogenomethanesulphonyl radicals appeared readily to lose SO_2. Hence, with trichloromethanesulphonate esters, the spectrum showed a build-up of the

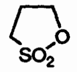

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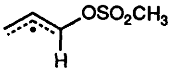
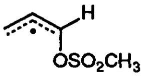
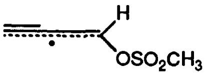
Table 1 EPR data (hfs/mT) for substituted allyl and propynyl radicals

Radical	g-Value	hfs/mT
	2.0026	a(1H) 0.36, a(1H) 1.44, a(1H) 1.55
	2.0026	a(1H) 0.44, a(1H) 1.40, a(1 H) 1.52
		a(1H) 1.16, a(1H) 1.90

trichloromethyl radical as the reaction proceeded. [eqn. (5)].

$$CX_3SO_2OR' + R^1_3M^{\bullet} \longrightarrow R'OMR^1_3 + CX_3SO_2^{\bullet} \longrightarrow CX_3^{\bullet} + SO_2 \quad (5)$$

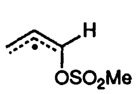
Neither the trifluoromethanesulphonyl radical nor the trifluoromethyl radical was observed during reaction of trifluoromethanesulphonate esters in the temperature range 160–280 K. However, evidence of α-scission was provided by the detection of the *tert*-butoxysulphonyl radical,[2] probably formed by addition of *tert*-butoxyl radicals to the product SO_2 [eqn. (6)].

$$Bu^tO^{\bullet} + SO_2 \longrightarrow Bu^tOSO_2^{\bullet} \quad (6)$$

The trimethylsilylmethanesulphonyl radical **4** [a(2H) = 0.34, a(9H) = 0.064 mT] was generated from trimethylsilylmethanesulphonyl chloride, **3**, using photochemically generated trimethyltin radicals. 1,2-Migration of the trimethylsilyl group from carbon to oxygen, and from carbon to nitrogen, has been observed in several free radicals.[14] Migration of Me_3Si from carbon to sulphur in species **4** would produce radical **5** [eqn.(7)], but radical **5** was not spectroscopically detected in the range 160–320 K.

$$\underset{\mathbf{3}}{Me_3SiCH_2SO_2Cl} \longrightarrow \underset{\mathbf{4}}{Me_3SiCH_2SO_2^{\bullet}} \longrightarrow \underset{\mathbf{5}}{Me_3SiSO_2CH_2^{\bullet}} \quad (7)$$

Rather different behaviour was observed with allyl, propynyl, and penta-2,4-dienylmethanesulphonates. Direct photolysis of these esters gave very weak spectra of the $MeSO_2^{\bullet}$ radical. In the presence of di-*tert*-butyl peroxide the preferred mode of reaction was hydrogen abstraction by the *tert*-butoxyl radical to give substituted allyl, propynyl, *etc.* radicals. The EPR parameters of the *syn*- **6**, and *anti*-substituted allyl radicals **7**, and of the substituted propynyl radical, are given in Table 1. The hyperfine splittings (hfs) are very similar to those of other allyl-type radicals.[15]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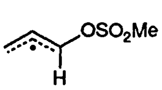
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When hexamethylditin (but not triethylsilane) was included in the reaction mixture the EPR spectrum of the *parent* allyl, propynyl, or pentadienyl radical was observed from the corresponding methanesulphonate ester. That is, the observed radical was generated from the alcohol-derived portion of the ester. In each case the hfs of the parent delocalised radical were essentially identical with those given in the literature.[15] Similar behaviour was observed for isopropylsulphonate esters, but not for trichloromethanesulphonates or toluene-p-sulphonates. That the driving force for this reaction is not the high thermodynamic stability of the delocalised radicals was shown by the fact that benzyl-type radicals were not observed with benzyl methanesulphonate, or with 4-methoxybenzyl methanesulphonate.

Organotin alkoxides such as **8** are formed in the initial reaction of the tin-centred radical with the sulphonate ester. It

$$\underset{\mathbf{8}}{Me_3SnOCH_2CH{=}CH_2}$$

seemed possible that the allyl (or other delocalised radical) could be displaced from the stannane **8** by a second trimethyltin radical. However, an authentic sample of allyl trimethyltin alkoxide did not produce any spectroscopically observable allyl radicals on reaction with trimethyltin radicals, or on direct photolysis. An alternative mechanism involved sulphonyl radical addition to the organotin alkoxide, followed by β-scission to give the sulphone **9**, which then either directly fragments, or reacts with $Me_3Sn^{\bullet}$ radicals to give allyl radicals [eqn. (8)].

$$\mathbf{8} + RSO_2^{\bullet} \longrightarrow Me_3SnOCH_2\dot{C}HCH_2O_2SR \longrightarrow Me_3SnO^{\bullet} + \underset{\mathbf{9}}{RSO_2CH_2CH{=}CH_2} \quad (8)$$

$$RSO_2CH_2CH{=}CH_2 \longrightarrow RSO_2^{\bullet} + \overline{CH_2\text{–}\dot{C}H\text{–}CH_2}$$

This mechanism explains why sulphonate esters with terminal unsaturation give delocalised radicals but benzyl sulphonates do not, *i.e.* because unsaturation is required for the addition step. Other evidence in support of this mechanism was, first, that $MeSO_2^{\bullet}$ radicals, generated from isopropyl methanesulphonate in the presence of the organotin alkoxide **8**, gave rise to the spectrum of the allyl radical. Secondly, it is known already that allyl and benzyl sulphones can decompose to give allyl and benzyl radicals.[16] Allyl methyl sulphone **9** (R = Me) was prepared by oxidation of allyl methyl sulphide with hydrogen peroxide but, surprisingly, no allyl radicals were detected under the conditions of the EPR experiments. The sulphone was very insoluble at low temperatures; a possible explanation of this negative result is that the correct proportions of reactants may not have been found.

Sulphonyl Radical Addition Reactions.—The addition of methanesulphonyl radicals, generated from the isopropyl methanesulphonate–hexamethylditin system, to a variety of alkenes was examined by EPR spectroscopy [eqn. (9)]. Simple alkenes such as hex-1-ene and *tert*-butylethylene gave weak spectra, suggesting that the reaction is inefficient. However, strong spectra of the adduct radicals **10** were observed for alkenes with electron-releasing substitutents. For example, butyl vinyl ether and methyl vinyl ether gave good quality spectra which were easily analysed. The greater efficiency of the

$$MeSO_2^{\bullet} + CH_2{=}CHOR \longrightarrow \underset{\mathbf{10}}{MeSO_2CH_2\dot{C}HOR} \quad (9)$$

addition is probably due to a favourable polar effect in the transition state, between the electrophilic sulphonyl radical and the electron-releasing substituent. These reactions showed the considerable advantage of using sulphonate esters as sulphonyl radical sources for spectroscopic work. When we tried to use methanesulphonyl chloride as the radical source, a black tar was produced in seconds after mixing it with the vinyl ether. That the observed adduct radicals were really due to sulphonyl radical addition was confirmed by photolysing the ether with di-*tert*-butyl peroxide alone, and with hexamethylditin. Spectra

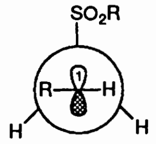
Table 2 EPR data (hfs/mT) for adduct radicals, $\mathrm{MeSO_2CH_2\dot{C}HR}$

R	T/K	$a(\mathrm{H}^{\alpha})$	$a(2\mathrm{H}^{\beta})$	a(Other)
OBu	235	1.71	1.12	0.22 (2H)
OMe	235	1.74	1.10	0.20 (3H)
Bu^t	235	2.24	1.84	
SPh	235	1.70	1.14	
$\mathrm{SiMe_3}$	235	2.27	1.78	
$\mathrm{C_4H_9^n}$ [a]	215	2.20	1.36	2.80 (2H)

[a] Tentative analysis.

were observed under these conditions, but they were much weaker and the hfs were different. The hfs of the adduct radicals obtained from $\mathrm{MeSO_2^{\bullet}}$ radical addition are collected in Table 2.

The H^{β} hfs of all the adduct radicals are comparatively small in magnitude and they increased with increasing temperature. This indicates that the preferred conformation about the C^{α}–C^{β} bond is that shown in structure **11** in which the sulphonyl substituent eclipses the SOMO. This is normal for radicals of this type in which the leading atom of the substituent is from the second row of the periodic table.[17]



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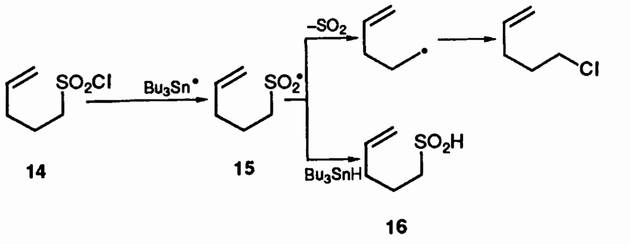
The spectra showed additional line-broadening effects at lower temperature due to restricted rotation about the C^{α}–C^{β} bond, but in no case was the slow-exchange-limit spectrum obtainable. In the case of $\mathrm{CH_2{=}CHSiMe_3}$ the spectrum of the initial adduct was replaced after a few minutes of photolysis by that of a new radical having $a(1\mathrm{H}) = 1.86$, $a(1\mathrm{H}) = 0.45$ mT. On prolonged photolysis a third radical appeared [$a(1\mathrm{H})$ 1.73 mT] which persisted in the dark. We attribute these spectra to radicals **12** and **13**, where R = $\mathrm{MeSO_2}$ or possibly $\mathrm{Bu}^t\mathrm{O}$, which

$\mathrm{MeSO_2\dot{C}HCH(R)SiMe_3}$ **12** $\qquad$ $\mathrm{MeSO_2CH(R)\dot{C}(R)SiMe_3}$ **13**

are formed by a succession of combination and abstraction reactions. The persistence of radical **13** is due to the high extent of steric shielding.

When non-terminal alkenes were used, or dienes such as penta-1,4-diene, thiophene, furan, pyrrole, or *N*-methylpyrrole, no adduct radicals were detected by EPR spectroscopy. Although the sulphonate esters were useful for the spectroscopic observation of sulphonyl radical adducts, when the hexamethylditin was replaced by trimethyltin hydride in preparative-scale work efficient chain reactions were not set up and none of the adducts could be isolated.

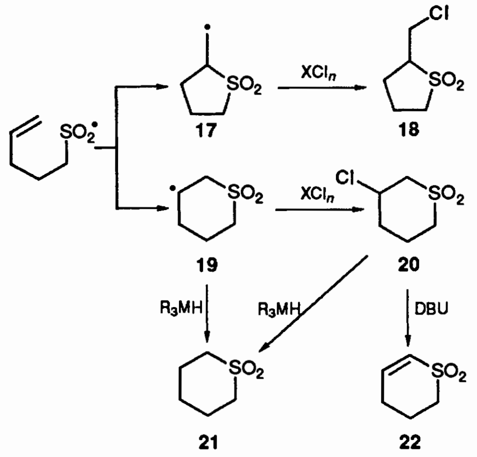
Ring-closure Reactions of Sulphonyl Radicals.—The archetype pent-4-enesulphonyl radical, **15**, was generated, in the cavity of the EPR spectrometer, by chlorine abstraction from pentenesulphonyl chloride, **14**, with photochemically produced trimethyltin radicals. The EPR spectrum of radical **15** [$a(2\mathrm{H}^{\alpha})$ 0.05, $a(2\mathrm{H}^{\beta})$ 0.25 mT] was observed in the temperature range 240–370 K. No cyclised radicals were detected in this range or at higher temperatures. Reduction of compound **14** with tributyltin hydride using photochemical initiation at temperatures between 105 and 170 °C gave pentenesulphinic acid **16** as the only detectable product (Scheme 1).



Scheme 1

It is likely that loss of $\mathrm{SO_2}$ from radical **15** also occurred, but the volatile products derived from the pentenyl radical were not observed. Treatment of compound **14** with several alternative radical initiator systems did lead to the formation of ring-closed products and the results are summarised in Table 3.

The copper chloride-catalysed reaction gave 3-chlorotetrahydropyran 1,1-dioxide **20** and 2-(chloromethyl)tetrahydrothiophene 1,1-dioxide **18** (Scheme 2). The overall yields were low, partly because a good deal of black solid (probably polymer) accompanied the cyclised products, and partly because $\mathrm{SO_2}$ loss was important, particularly at 150 °C, and this led to volatile chloropentene which was detected as a major product in the 75 °C reaction, but which largely escaped at higher temperatures. The reaction was also initiated with dichlorotris(triphenylphosphine)ruthenium(II), but higher temperatures were needed and therefore yields of the 6-membered-ring sulphone **20** were again low. The identity of sulphone **20** was confirmed by dehydrochlorination with 1,8-diazabicyclo-[5.4.0]undec-7-ene (DBU) to give dihydrothiopyran 1,1-dioxide **22**.



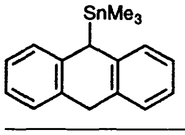
X = $\mathrm{RSO_2}$, Cu, $\mathrm{Ru(PPh_3)_3}$

Scheme 2

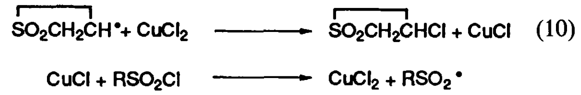
Cyclised products were obtained from the reduction of substrate **14** with tributyltin hydride when the reaction was thermally inititated with 2,2′-azoisobutyronitrile (AIBN). In this case the 3-chloro sulphone **20** was accompanied by tetrahydrothiopyran 1,1-dioxide **21**. This is formed when the intermediate radical **19** abstracts hydrogen from the tin hydride *and* also from reduction of the chloride **20** by the tin hydride. This latter route was confirmed by a separate experiment in which isolated compound **20** was converted by $\mathrm{Bu_3SnH}$, under similar reaction conditions, exclusively into compound **21**. In all the cyclised products addition had occurred with formation of a C–S bond, *i.e.* no reaction of the sulphonyl radicals at oxygen was observed. This behaviour is analogous to the corresponding intermolecular addition.[8]

The mechanism of the $\mathrm{Cu^{II}}$-catalysed reactions is believed to involve chlorine-atom transfer from $\mathrm{CuCl_2}$ by the intermediate radicals **17** and **19**, eqn. (10).[5]

Table 3 Products of radical reactions of pent-4-ene-1-sulphonyl chloride **14**

Initiator system	T/°C	Total yield (mol %)[a]	Rel. yields (%) **20**	**21**	**18**
$CuCl_2$–AIBN	170	17	100		
$CuCl_2$–AIBN	75	nd	88		12
$RuCl_2(Ph_3P)_3$	170	15	100		
Bu_3SnH–AIBN	80	nd	74	26	
Bu_3SnH–AIBN	45	nd	20[b]	80[b]	
Bu_3SnH–ultrasound	20	nd		100	
$(Bu^n{}_3Sn)_2$–AIBN–PhMe	45	nd	77	12	11
Ph_3SiH–$h\nu$	170	nd	78	14	8
 $h\nu$	170	18	91		9

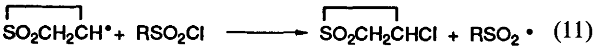
[a] Yield of cyclised products after PLC. nd = not determined [b] Very approximate.



$$\overline{SO_2CH_2CH}{}^{\bullet} + CuCl_2 \longrightarrow \overline{SO_2CH_2CHCl} + CuCl \quad (10)$$

$$CuCl + RSO_2Cl \longrightarrow CuCl_2 + RSO_2{}^{\bullet}$$

In the Ru^{II}-catalysed process chlorine-atom transfer occurs from Ru^{III} chloride.[6] The observation of the 3-chloro sulphone **20** as the major product from the reactions with Bu_3SnH and Ph_3SiH indicates that chlorine-atom transfer must occur very rapidly from the sulphonyl chloride, eqn. (11), *i.e.* reaction



$$\overline{SO_2CH_2CH}{}^{\bullet} + RSO_2Cl \longrightarrow \overline{SO_2CH_2CHCl} + RSO_2{}^{\bullet} \quad (11)$$

(11) must compete effectively with hydrogen-atom transfer from Bu_3SnH, which is known to be very fast.[18] The higher relative yield of sulphone **21** at lower temperatures (Table 3) shows that reaction (11) is a less effective pathway at lower temperatures. Although quantification of the cyclised product was not carried out in the reaction initiated ultrasonically, the overall yield was considerably higher, and this was the best technique for preparative work.

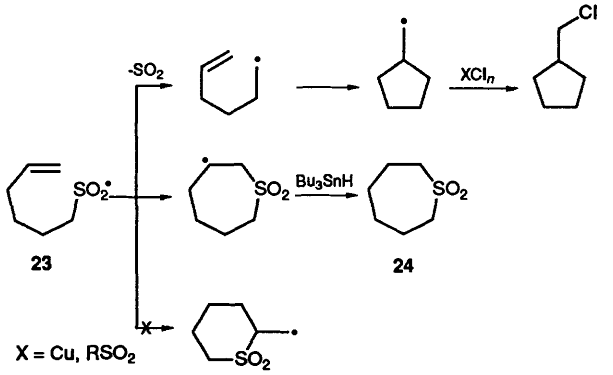
Triphenylsilane has been reported as an alternative to Bu_3SnH in the reduction of organohalides.[19] However, with sulphonyl chloride **14**, this reagent reacted rather slowly, even at 170 °C, and gave a mixture of the same cyclised products in low overall yield. 9-Trimethylstannyl-9,10-dihydroanthracene[20] was also employed as a substitute for Bu_3SnH, but high temperatures were found to be necessary and the overall yields were not significantly improved (Table 3). As expected from the negative result in the intermolecular process (see above), no cyclisation was achieved on treatment of hex-5-enyl methanesulphonate with tributyltin hydride.

The quotients of 6-membered-ring products to 5-membered-ring products, *i.e.* {[**20**] + [**21**]}/[**18**], were:

T/°C	170	75	45
Quotient	10.1	7.3	8.1

Hence we find a preference for *endo* cyclisation which is not strongly temperature dependent. This unusual regioselectivity agrees with the findings of Johnson and co-workers from their cobalamin reactions.[9,10] Radicals centred on carbon, nitrogen and oxygen with pent-4-ene substituents preferentially cyclise in the *exo* mode to give 5-membered-ring products,[21,22] whereas radicals centred on second-row elements generally show lower regioselectivity.[22] Thiyl radicals can ring-close in either the *endo* or the *exo* mode depending on reaction circumstances.[22,23] The preference of the archetype unsaturated sulphonyl radical for *endo* ring closure can be ascribed to the same cause as for other unsaturated radicals centred on second-row elements.[22] That is, the comparatively long C–S bond enables the radical centre to approach the terminal carbon atom of the double bond from directly above; this stereoelectronic factor thus favours the transition state for *endo* cyclisation.

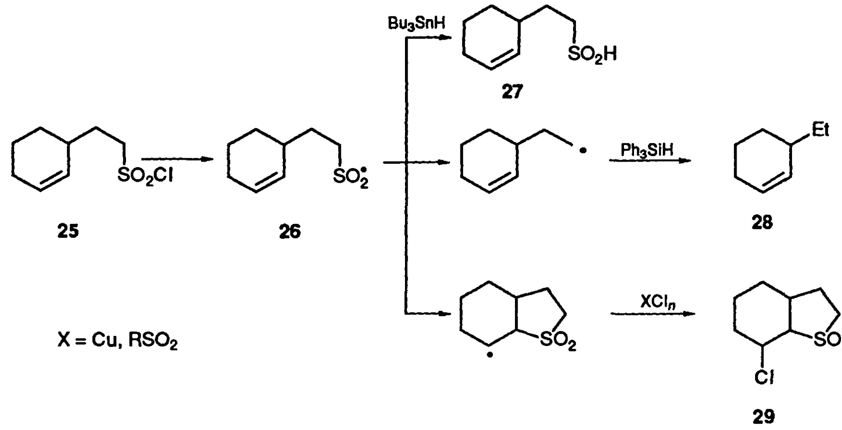
The hex-5-enesulphonyl radical **23** was generated by chlorine abstraction from the corresponding sulphonyl chloride by trimethyltin radicals and was observed by EPR spectroscopy in the range 240–250 K [$a(2H^{\alpha})$ 0.06, $a(2H^{\beta})$ 0.21, $a(2H^{\gamma})$ 0.06 mT]; no cyclised radicals were detected at higher temperatures. Resolved γ-hfs have previously been observed in n-alkanesulphonyl radicals.[2] Reaction of hex-5-enesulphonyl chloride with the Cu^{II} chloride system was investigated, but at the high temperatures required, *i.e.* 160 °C, the only detectable product was (chloromethyl)cyclopentane. It seems clear that this is formed by SO_2 loss from radical **23**; the hex-5-enyl radical thus produced then cyclises and picks up chlorine (Scheme 3).



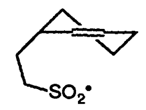
Scheme 3

Reduction of hex-5-enesulphonyl chloride with Bu_3SnH at 45 °C gave, however, a low yield of thiepane 1,1-dioxide **24**; no 2-methyltetrahydrothiopyran 1,1-dioxide, the product of *exo* cyclisation, could be detected (Scheme 3). In this case the use of ultrasound initiation failed to improve the yield. The preference of radical **23** for *endo* cyclisation is not surprising in the light of the preponderant *endo* cyclisation of radical **15**.

The cyclohex-2-enylethanesulphonyl radical, **26**, was formed by chlorine abstraction, by trimethyltin radicals, from cyclohex-2-enylethanesulphonyl chloride, **25**, and was observed by EPR spectroscopy in the range 225–280 K [$a(2H^{\alpha})$ 0.06, $a(2H^{\beta})$ 0.17, $a(2H)$ 0.06 mT]; no cyclised radicals were detected. Reduction of compound **25** with Bu_3SnH gave cyclohex-2-enylethanesulphinic acid, **27**, as the main product. Reduction with triphenylsilane at 170 °C led to the formation of 3-ethylcyclohexene, **28**, probably *via* SO_2 loss from radical **26** (Scheme 4). However, the Cu^{II} chloride-catalysed reaction at 140 °C gave 5-chloro-7-thiabicyclo[4.3.0]nonane 7,7-dioxide **29** in low yield. The unexpected preference of radical **26** for *exo* cyclisation to give the 5-membered ring can be attributed to two factors. The preferred conformation of radical **26** will be as shown in structure **30** where the cyclohexene ring is in the half-chair form with the side-chain in the quasi-equatorial orientation. Molecular models indicate that in this conformation the radical centre cannot easily approach from above the further end of the double bond, as required for *endo* cyclisation, but that *exo* approach is relatively easy. Secondly, it is known that hexenyl radicals with *cis*-substituents on the terminal carbon of the double bond show a greater preference for *exo* cyclisation, probably because of increased steric interaction, in the transition state for 6-membered-ring formation, between the *cis*-substituent and the hydrogens β to the radical centre.[22] A



Scheme 4



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similar effect would be expected for the quasi-equatorial (or quasi-axial) conformation of radical **26**.

Experimental

EPR spectra were recorded with a Bruker ER 200D spectrometer on degassed samples in Spectrosil tubes, irradiated with light from a 500 W super-pressure Hg arc. Unless otherwise noted NMR spectra were obtained with a Bruker A300 instrument for $CDCl_3$ solutions at ambient temperature with Me_4Si internal standard. GCMS analyses were carried out with a Finnegan Incos instrument fitted with an HP17 capillary column. Preparative GLC employed a Pye-Unicam 105 chromatograph with 5 m × 1 cm glass columns packed with Carbowax 20 M.

General Method for the Preparation of Alkane- and Trihalogenoalkane-sulphonate Esters.—To a solution of the alcohol (1 mol equiv.) and triethylamine (1 mol equiv.) in dry methylene dichloride at 0 °C under N_2 was added the corresponding sulphonyl chloride (1.1 mol equiv.) dropwise. The mixture was stirred for 45 min, the organic layer was washed (water, dil. hydrochloric acid, water, sat aq. NaCl), dried (anhyd. $MgSO_4$) and evaporated. The alkanesulphonate esters were used without further purification. This method was used in the preparation of methane-, propane-2-, trifluoromethane-, and trichloromethanesulphonate esters. Confirmation that the sulphonate esters had formed was obtained by IR spectroscopy, which showed absorption bands at 1380–1347 and 1193–1170 cm^{-1}.

*General Method for the Preparation of Toluene-*p*-sulphonate Ester.*—To a solution of the alcohol (1 mol equiv.) and dry pyridine (1 mol equiv.) in dry methylene dichloride at 0 °C under N_2 was added solid toluene-*p*-sulphonyl chloride (1.1 mol equiv.) in small portions. After being stirred for 1 h the mixture was kept at 0 °C for 24 h. The organic layer was washed (water, dil. hydrochloric acid, water, sat. aq. NaCl), dried (anhyd. $MgSO_4$) and evaporated. The toluene-*p*-sulphonate esters were used without further purification.

*Reduction of Isopropyl Toluene-*p*-sulphonate with Tributyltin Hydride.*—To isopropyl toluene-*p*-sulphonate (0.3 g, 1.4 mmol) in *tert*-butylbenzene was added tributyltin hydride (0.37 cm^3, 1.4 mmol). An exothermic reaction began immediately. The solution was heated to 140 °C and photolysed for 2 h, after which the mixture was cooled and diluted with diethyl ether and 2 mol dm^{-3} aq. NaOH. The aq. layer was removed and acidified (conc. HCl; pH paper) before extraction with diethyl ether (× 2). The combined extracts were dried (anhyd. Na_2SO_4) and evaporated to give toluene-*p*-sulphinic acid as a solid, δ_H 2.34 (3 H, s, Me), 6.95–7.58 (4 H, m, ArH) and 10.14 (1 H, s, SO_2H).

Trimethylsilylmethanesulphonyl Chloride 3.[24,25]—Chloromethyl(trimethyl)silane (4.0 g, 32.6 mmol) and thiourea (5.1 g, 67.0 mmol) were refluxed in ethanol (58 cm^3) for 48 h. The solution was evaporated to dryness and pumped at 1 mmHg for 1 h. The isothiouronium salt formed was dissolved in water (70 cm^3) and the solution was cooled to 0 °C. Chlorine gas was bubbled through the stirred solution for 15 min while the temperature was kept below 10 °C. Methylene dichloride was added (50 cm^3) and chlorine was bubbled through for a further 45 min, after which the organic layer was removed and the aq. layer was re-extracted (× 2) with CH_2Cl_2. The combined organic layers were washed (10% aq. $NaHSO_3$, 10% aq. $NaHCO_3$ and water), dried (anhyd. $MgSO_4$) and evaporated. The product was distilled (Kugelrohr), 60–69 °C/1 mmHg (lit.,[24,25] 50–52 °C/0.6 mmHg) (0.6 g, 10%); δ_H 0.32 (9 H, s, Me) and 3.63 (2 H, s, CH_2); δ_C −1.16 (Me) and 59.91 (CH_2); *m/z* 186 (M^+, 1), 171 (2), 141 (4), 137 (9), 123 (6), 93 (15), 73 (100), 58 (7) and 45 (18).

Trimethyl(prop-2-enyloxy)stannane.—Sodium metal (0.25 g, 10.9 mmol) was dissolved (in small pieces) in allyl alcohol (5 cm^3) at 0 °C under N_2. To this was added a solution of trimethyltin chloride (2.17 g, 10.9 mmol) in allyl alcohol (5 cm^3) in small portions. The mixture was stirred for 30 min at 0 °C, then centrifuged. The clear supernatant liquid was carefully removed from the solid deposit of sodium chloride and was then evaporated to give the product, which was distilled (Kugelrohr), 85 °C/14 mmHg, to give a clear liquid (0.9 g, 37%); δ_H 0.44 (9 H, s, $SnMe_3$), 4.17 (2 H, br d, CH_2), 4.99–5.29 (2 H, br dd, CH_2) and 5.86–6.06 (1 H, m, CH); δ_C −1.94 (Me), 65.09 (CH_2), 114.60 (CH_2) and 138.49 (CH). Between 298 and 373 K the ^{13}C NMR spectrum showed line broadening. This was resolved into conventional sharp peaks at 273 and 233 K.

Allyl Methyl Sulphone 9.[26]—A solution of allyl methyl sulphide (6.0 g, 68.0 mmol) in glacial acetic acid (14 cm^3) was chilled in ice. 30% aq. Hydrogen peroxide was added dropwise and the mixture was stirred overnight. The solution was heated at 85 °C for 1 h, then cooled, and diluted with an equal volume of water. The aq. solution was extracted with methylene dichloride (× 2). The combined organic layers were washed (water), dried (anhyd. Na_2SO_4), evaporated under reduced pressure, and distilled (Kugelrohr), 135 °C/1 mmHg (5.45 g, 67%); δ_H 3.00

(3 H, s, Me), 3.82 (2 H, br d, CH_2) and 5.24–6.42 (3 H, m, $CH{=}CH_2$).

Reaction of Methanesulphonyl Radicals with Butyl Vinyl Ether and Tributyltin Hydride under Photolysis Conditions.—To a degassed solution of isopropyl methanesulphonate (0.3 g, 2.17 mmol) and butyl vinyl ether (0.22 g, 2.17 mmol) in *tert*-butylbenzene at 65 °C was added tributyltin hydride during 30 min under photolysis conditions. Photolysis was continued at this temperature for 9 h. Analysis of the mixture showed unchanged isopropyl methanesulphonate ester and none of the expected sulphone.

*Reaction of Methanesulphonyl Radicals with Butyl Vinyl Ether and Hexamethylditin with Di-*tert*-butyl Peroxide as Initiator.*—A degassed solution containing roughly equal volumes of butyl vinyl ether, hexamethylditin, di-*tert*-butyl peroxide, and isopropyl methanesulphonate in toluene was photolysed for 8 h at room temperature. Analysis of the mixture by GCMS showed traces of the adducts formed from *tert*-butoxyl radical addition and methanesulphonyl radical addition.

*Pent-*4-*ene-*1-*sulphonyl Chloride* **14**.[27]—5-Bromopent-1-ene (10.0 g, 67.1 mmol), sodium sulphite (10.3 g, 81.7 mmol), and water (35 cm^3) were rapidly stirred and refluxed overnight. The solution was allowed to cool and then washed with diethyl ether. The aq. layer was evaporated and the resulting white solid was dried *in vacuo* (130 °C/1 mmHg). Phosphorus trichloride oxide (57 g) was added to the dry solid and the mixture was stirred and heated to 120–140 °C. The solution was cooled and poured carefully onto ice and this mixture was stirred for 20 min to ensure all the phosphoryl trichloride was destroyed. Diethyl ether was added and the solution was extracted (× 3). The combined extracts were washed (water, sat. aq. NaCl) and dried (anhyd. Na_2SO_4). After evaporation, the crude sulphonyl chloride was distilled (Kugelrohr), 98 °C/1 mmHg (lit.,[27] 60–66 °C/0.3 mmHg) to yield a clear colourless liquid (5.0 g, 44%); δ_H 2.11–2.35 (4 H, m), 3.69 (2 H, t, CH_2SO_2Cl), 5.07–5.16 (2 H, m, CH_2) and 5.69–5.82 (1 H, m, CH); *m*/*z* 131 (1), 69 (12), 68 (35), 67 (100), 53 (21), 43 (11), 40 (25) and 39 (40).

*Reduction of Pent-*4-*ene-*1-*sulphonyl Chloride with Tributyltin Hydride.*—Pent-4-ene-1-sulphonyl chloride (0.2 g, 1.2 mmol) was degassed and heated to 105 °C. Tributyltin hydride (0.32 cm^3, 1.2 mmol) was slowly added dropwise, and the mixture was photolysed for 5 h. GCMS analysis of the black intractable tar showed neither cyclised product nor the starting material. The mixture was diluted with diethyl ether and 2 mol dm^{-3} aq. NaOH. The aq. layer was removed and acidified with dil. HCl (pH paper) before re-extraction with diethyl ether (× 2). The latter extracts were dried (anhyd. Na_2SO_4) and evaporated to give a solid which proved to be the sulphinic acid **16**,[28] δ_H 1.77 (2 H, m, CH_2), 2.18 (2 H, m, CH_2), 2.78 (2 H, t, CH_2SO_2H), 5.04 (2 H, m, CH_2), 5.78 (1 H, m, CH) and 8.37 (1 H, br s, SO_2H).

*Photolysis of Pent-*4-*ene-*1-*sulphonyl Chloride.*—Pent-4-ene-1-sulphonyl chloride (0.2 g, 1.19 mmol) was degassed and photolysed at 170 °C for 1 h after which time it had gone black. $CDCl_3$ was added to the dark liquid and the ^1H NMR spectrum showed this to be unchanged pent-4-ene-1-sulphonyl chloride.

*Cyclisation of Pent-*4-*ene-*1-*sulphonyl Chloride by Reaction with Copper*(II) *Chloride.*—To pent-4-ene-1-sulphonyl chloride (0.3 g, 1.8 mmol) was added an equal volume of copper(II) chloride catalyst solution[29] and the mixture was degassed. The temperature was then raised to 170 °C, allowing the acetonitrile to boil off as the temperature increased. The mixture was maintained at 170 °C for 1.5 h. The black viscous residue was purified by preparative TLC (PLC) (× 2) [developer: methylene dichloride–(40–60 °C) light petroleum (4:6)] (35.5 mg, 17%). The product was identified as 3-chlorotetrahydrothiopyran 1,1-dioxide **20**,[10] δ_H 1.73 (4-H, dq), 2.07 (5-H, m), 2.20 (5-H′, d quint), 2.41 (4-H′, m), 2.93 (6-H, dt), 3.05 (6-H′, dq), 3.18 (2-H, q), 3.55 (2-H′, m) and 4.31 (3-H, tt); δ_C 21.72 (CH_2), 34.76 (CH_2), 50.32 (CH_2), 52.23 (CH) and 59.52 (CH_2); *m*/*z* 168 (M^+, 1), 133 (34), 105 (9), 103 (31), 76 (53), 68 (45), 67 (100), 55 (44), 42 (45), 41 (98), 40 (47) and 39 (63).

*Cyclisation of Pent-*4-*ene-*1-*sulphonyl Chloride by Reaction with Tris(triphenylphosphine)ruthenium*(II) *Chloride.*—Pent-4-ene-1-sulphonyl chloride (0.2 g, 1.2 mmol) was heated to 170 °C and degassed. Tris(triphenylphosphine)ruthenium(II) chloride (0.12 g, 1.2 mmol) was added and the mixture was heated at 170 °C for 2.5 h. The mixture was purified by PLC as described above, to give 3-chlorotetrahydrothiopyran 1,1-dioxide[19] as the product (29.7 mg, 15%).

*Cyclisation of Pent-*4-*ene-*1-*sulphonyl Chloride by Reaction with Tributyltin Hydride, and AIBN as Initiator.*—A solution of pent-4-ene-1-sulphonyl chloride (0.2 g, 1.2 mmol) and tributyltin hydride (0.32 cm^3, 1.2 mmol) in dry benzene (2 cm^3) was degassed and heated to 80 °C. A solution of AIBN (0.04 g, 20% mol equiv.) in dry benzene (1 cm^3) was added slowly and the mixture was refluxed under nitrogen for 8 h. After cooling, the mixture was analysed by GCMS and was shown to contain cyclised products; 3-chlorotetrahydrothiopyran 1,1-dioxide **20** (74% rel.) and tetrahydrothiopyran 1,1-dioxide **21** (26% rel.). When this experiment was repeated at 45–50 °C for 24 h, subsequent analysis of the mixture showed that the non-chlorinated sulphone became the major product; 3-chlorotetrahydrothiopyran 1,1-dioxide **20** (20% rel.) and tetrahydrothiopyran 1,1-dioxide **21** (80% rel.).

Reduction of 3-*Chlorotetrahydrothiopyran* 1,1-*Dioxide* **20** *with Tributyltin Hydride.*—To a degassed solution of compound **20** (24.3 mg, 0.14 mmol) in dry benzene (0.5 cm^3) was added tributyltin hydride (43 mm, 0.16 mmol) and the mixture was refluxed under nitrogen for 4 h. Analysis of the reaction mixture by GCMS showed the product to be tetrahydrothipyran 1,1-dioxide.[21] The mixture was purified by preparative TLC using methylene dichloride–(40–60 °C) light petroleum (4:6) as the developer and the identity of the product was confirmed from its NMR spectra (see Ph_3SiH reaction for spectra).

*Cyclisation of Pent-*4-*ene-*1-*sulphonyl Chloride with Tributyltin Hydride with Ultrasound as Initiator.*—To a degassed solution of pent-4-ene-1-sulphonyl chloride in dry benzene (0.5 cm^3) was slowly added tributyltin hydride (0.32 cm^3, 1.2 mmol). No reaction was observable at this stage. The sample tube was then suspended in an ultrasonic bath at ambient temperature and subjected to ultrasonification for 1.75 h. A rapid effervescence was observed as soon as the ultrasonic bath was switched on. Analysis of the mixture by GCMS showed that cyclisation had proceeded in a manner analogous to the low-temperature tributyltin hydride–AIBN reaction to give tetrahydrothiopyran 1,1-dioxide **21** as the only observable product.

*Cyclisation of Pent-*4-*ene-*1-*sulphonyl Chloride with Triphenylsilane.*—Pent-4-ene-1-sulphonyl chloride (0.3 g, 1.78 mmol) was heated to 150 °C and degassed. Triphenylsilane (0.46 g, 1.78 mmol) was added and the mixture was stirred. The temperature was raised to 170 °C whilst the sample was photolysed by UV light from a 250 W medium-pressure Hg arc lamp for 30 min. Not all of the sulphonyl chloride had reacted during the experiment so a yield was not recorded. The products obtained were 3-chlorotetrahydrothiopyran 1,1-dioxide **20** (78% rel.);

tetrahydrothiopyran 1,1-dioxide **21**[30] (8% rel.); δ_H 1.65 (2 H, m, 4-H_2), 2.12 (4 H, m, 3- and 5-H_2) and 3.00 (4 H, br t, 2- and 6-H_2); δ_C 23.91 (CH_2), 24.29 (CH_2) and 52.21 (CH_2); *m/z* 134 (M^+, 19), 133 (2), 117 (4), 106 (7), 71 (4), 69 (54), 55 (30), 42 (56), 41 (100) and 39 (22); and 2-(chloromethyl)tetrahydrothiophene 1,1-dioxide **18** (14% rel.). Compounds **20** and **18** could not be separated by preparative TLC, but the NMR spectrum of compound **20** did reveal that some of the five-membered-ring product was present. Those peaks not overlapped, *i.e.* δ_H 3.95, 3.65 (2 H, dd, CH_2Cl); δ_C 19.91 (CH_2), 28.13 (CH_2), 40.68 (CH_2), 52.10 (CH_2Cl) and 61.81 (CH), were in good agreement with the literature;[31] *m/z* 133 [$(M - Cl)^+$, 18], 122 (11), 120 (14), 69 (48), 67 (22), 41 (100) and 39 (34). 5-Chloropentene was also observed in the reaction mixture (by GCMS), *m/z* 104 (M^+, 6), 69 (7), 68 (35), 67 (52), 55 (84), 41 (100) and 39 (80).

Cyclisation of Pent-4-ene-1-sulphonyl Chloride with 9-Trimethylstannyl-9,10-dihydroanthracene.—To pent-4-ene-1-sulphonyl chloride (0.3 g, 1.8 mmol) was added 9-trimethylstannyl-9,10-dihydroanthracene[20] (0.6 g, 1.8 mmol). The mixture was heated to 170 °C, degassed, and photolysed for 2 h. Subsequent analysis by GCMS showed cyclised products to have formed in the ratio of 3-chlorotetrahydrothiopyran 1,1-dioxide **20** (91% rel.) and 2-(chloromethyl)tetrahydrothiophene 1,1-dioxide **18** (9% rel.)

Cyclisation of Pent-4-ene-1-sulphonyl Chloride with Hexabutylditin.—Pent-4-ene-1-sulphonyl chloride (0.2 g, 1.2 mmol) in dry toluene (2 cm^3) was degassed and stirred at 40 °C under N_2. AIBN (0.04 g, 20% mol equiv.) was added and a solution of hexabutylditin (0.12 cm^3) in dry toluene (2 cm^3) was added dropwise. The mixture was stirred at 40 °C for 5 h, after which it was analysed by GCMS. The products of both *endo*- and *exo*-cyclisation were detected in the proportions **20** (77% rel.), **21** (12% rel.) and **18** (11% rel.).

3,4-Dihydro-2H-thiopyran 1,1-Dioxide **22**.—To a solution of 3-chlorotetrahydrothiopyran 1,1-dioxide **20** (28.2 mg, 0.17 mmol) in dry benzene (0.5 cm^3) stirred under N_2 was added dropwise DBU (41 mg, 0.27 mmol). The mixture was then heated to reflux for 1.5 h, before being cooled, and then diluted with dil. HCl. The mixture was extracted with methylene dichloride (× 3) and the combined organics were washed (sat. aq. NaCl), dried (anhyd. $MgSO_4$), and evaporated to give the crude product, δ_H 2.63 (2 H, m, CH_2), 2.97 (2 H, t, CH_2), 3.52 (2 H, m, CH_2) and 5.51–5.76 (2 H, m, CH=CH); δ_C 25.80 (CH_2), 47.43 (CH_2), 50.79 (CH_2), 119.42 (CH) and 126.83 (CH); *m/z* 132 (M^+, 1), 68 (24), 67 (100), 53 (22), 41 (24) and 39 (34).

Attempted Cyclisation of Pent-4-ene-1-sulphonyl Chloride with Triethylsilane, tert-*Dodecanethiol and Dilauroyl Peroxide.*—A degassed solution of pent-4-ene-1-sulphonyl chloride (0.84 g, 5.0 mmol), triethylsilane (1.16 g, 10.0 mmol), dilauroyl peroxide (0.04 g, 2% mol equiv.), and *tert*-dodecanethiol (0.02 g, 2% mol equiv.) in cyclohexane (5 cm^3) was refluxed under nitrogen for 11 h. The mixture was cooled, and diluted to 15 cm^3 with cyclohexane. The solution was then washed successively with water and 6 mol dm^{-3} aq. NaOH (20 cm^3), dried (anhyd. $MgSO_4$) and evaporated. Analysis of the residue by ^1H NMR spectroscopy and GCMS showed no cyclised products.

Attempted Cyclisation of Isopropyl Pent-4-ene-1-sulphonate by Reaction with Tributyltin Hydride.—To isopropyl pent-4-ene-1-sulphonate (0.2 g, 1.04 mmol) was added tributyltin hydride (0.28 cm^3, 1.04 mmol). The mixture was photolysed for 3.5 h at 170 °C. Analysis of the mixture revealed the presence of starting material only. In order to determine whether any of the ester had been reduced to the sulphinic acid the reaction mixture was diluted with diethyl ether and washed with 2 mol dm^{-3} aq. NaOH. The aq. layer was separated, and acidified with conc. hydrochloric acid. The acidified aq. layer was extracted with diethyl ether (× 2), and the extract was dried (anhyd. Na_2SO_4) and evaporated. The mainly inorganic residue contained no sulphinic acid. Similar lack of reaction was found when dibenzoyl peroxide or AIBN was used as initiator at 100 °C.

Hex-5-ene-1-sulphonyl Chloride.—6-Bromohex-1-ene (4.75 g, 29.1 mmol) and sodium sulphite (4.41 g, 35.0 mmol) were refluxed overnight in water (15 cm^3). The solution was cooled, and then washed with diethyl ether, after which the aq. layer was evaporated to dryness to give hex-5-ene-1-sulphinic acid sodium salt as a solid. The solid was dried (130 °C/1 mmHg) before cooling to room temperature and was then carefully treated with phosphoryl trichloride (25 g). The mixture was heated to 120–140 °C for 3.5 h, cooled, and poured onto ice. The mixture was stirred in ice-water for 15 min before being extracted with diethyl ether (× 2). The combined extracts were washed (water, sat. aq. NaCl), dried (anhyd. Na_2SO_4), evaporated and distilled (Kugelrohr), 121 °C/1 mmHg (2.45 g, 46%); δ_H 1.62 (2 H, m, CH_2), 1.97–2.20 (4 H, m, CH_2), 3.79 (2 H, t, CH_2SO_2Cl), 5.06 (2 H, m, CH_2) and 5.70–5.86 (1 H, m, CH); δ_C 23.68 (CH_2), 26.64 (CH_2), 32.87 (CH_2), 65.27 (CH_2SO_2Cl), 115.86 (CH_2) and 137.09 (CH).

Attempted Cyclisation of Hex-5-ene-1-sulphonyl Chloride by Reaction with Copper(II) *Chloride.*—Hex-5-ene-1-sulphonyl chloride (0.3 g, 1.6 mmol) and an equal volume of copper(II) chloride catalyst[29] were heated (allowing acetonitrile to evaporate off) at 160 °C for 1.5 h. The reaction mixture was analysed by GCMS but neither chlorinated nor non-chlorinated products of cyclisation were detected. The major product was found to be (chloromethyl)cyclopentane.

Cyclisation of Hex-5-ene-1-sulphonyl Chloride by Reaction with Tributyltin Hydride, with AIBN as Initiator.—Hex-5-ene-1-sulphonyl chloride (0.2 g, 1.1 mmol) in dry benzene (1 cm^3) was degassed, and AIBN (0.04 g, 20% mol equiv.) was added. The mixture was heated to 50 °C under N_2, a solution of tributyltin hydride (0.35 cm^3, 1.3 mmol) in dry benzene (1 cm^3) was added dropwise, and the mixture was stirred for 11 h. Analysis of the mixture by GCMS indicated that the sole product of cyclisation was thiepane 1,1-dioxide,[32] *m/z* 148 (M^+, 4), 131 (4), 120 (5), 83 (24), 67 (10), 56 (60), 55 (100), 41 (87) and 39 (32). Similar results were obtained on ultrasonification.

3-(2-Bromoethyl)cyclohexene.—To a solution of 2-(cyclohex-2-enyl)ethanol[33] (6.0 g, 47.6 mmol) and triethylamine (4.82 g, 47.6 mmol) in methylene dichloride (40 cm^3) at 0 °C under N_2 was added dropwise methanesulphonyl chloride (5.98 g, 52.4 mmol). The solution was stirred for 45 min and was then washed (water, dil. HCl, water, sat. aq. NaCl), dried (anhyd. Na_2SO_4) and evaporated under reduced pressure. The crude mesate was added dropwise to a solution of lithium bromide (8.27 g, 95.2 mmol) in AnalaR acetone (90 cm^3), which was then stirred at room temperature for 30 min before being refluxed overnight. The solution was allowed to cool before being filtered. The filtrate was evaporated under reduced pressure then water and diethyl ether were added. The ether layer was separated and the aq. layer was re-extracted (× 3) with diethyl ether. The combined ether layers were washed (water), dried (anhyd. Na_2SO_4), evaporated under reduced pressure and distilled (Kugelrohr), 95 °C/1 mmHg (lit.,[34] 50–70 °C/0.2 mmHg) (6.8 g, 76%); δ_H 0.86 (9 H, m, 1-H, 4-, 5- and 6-H and CH_2), 3.50 (2 H, t, CH_2Br) and 5.36–5.98 (2 H, m, 2- and 3-H).

2-(*Cyclohex-2-enyl*)*ethanesulphonyl Chloride* **25**.—3-(2-Bromoethyl)cyclohexene (6.0 g, 3.2 mmol) and sodium sulphite (5.07 g, 40.2 mmol) were refluxed overnight in water (16 cm^3). The solution was cooled, and washed with diethyl ether. The aq. layer was evaporated under reduced pressure to yield the solid, white cyclohexenylethanesulphinic acid sodium salt, which was dried (135 °C/1 mmHg). The solid was cooled, phosphoryl trichloride (50 g) was carefully added and the mixture was heated at 130 °C for 2 h. The mixture was cooled and poured onto ice, and the solution was stirred for 15 min. The aq. layer was extracted with diethyl ether (× 3) and the combined extracts were dried (anhyd. Na_2SO_4), evaporated under reduced pressure and distilled (Kugelrohr), 70 °C/1 mmHg (1.65 g, 25%); δ_H 1.28 (1 H, m), 1.57 (1 H, m), 1.78 (2 H, m, CH_2), 1.91–2.20 (4 H, m, CH_2), 2.34 (1 H, m), 3.71 (2 H, t, CH_2SO_2Cl) and 5.44–5.85 (2 H, m, CH=CH); δ_C 21.01 (CH_2), 25.00 (CH_2), 28.28 (CH_2), 30.06 (CH_2), 33.47 (CH), 63.40 (CH_2), 128.70 (CH) and 129.62 (CH).

Attempted Cyclisation of Cyclohexenylethanesulphonyl Chloride by Reaction with Triphenylsilane.—Cyclohexenylethanesulphonyl chloride **25** (0.2 g, 0.96 mmol) was heated to 170 °C and degassed. Triphenylsilane (0.25 g, 0.96 mmol) was added and the mixture was photolysed at 170 °C for 2 h. Analysis of the residue by GCMS indicated that the mixture contained some unchanged sulphonyl chloride, but that the major product was 3-ethylcyclohexene **28**.

Reduction of Cyclohexenylethanesulphonyl Chloride to Cyclohexenylethanesulphinic Acid by Reaction with Tributyltin Hydride.—To a degassed solution of compound **25** (0.2 g, 0.96 mmol) and AIBN (0.032 g, 20% mol equiv.) in dry benzene (1 cm^3) was added dropwise a solution of tributyltin hydride (0.26 cm^3, 0.96 mmol) in benzene (1 cm^3). The mixture was heated at 40 °C under nitrogen for 24 h. Analysis of the mixture by GCMS showed that neither cyclised nor starting material was present. The reaction mixture was diluted with diethyl ether and washed with 2 mol dm^{-3} aq. NaOH. The aq. layer was removed, and acidified with conc. hydrochloric acid. The acidified aq. layer was extracted with diethyl ether (× 2), and the extract was dried (anhyd. $MgSO_4$) and evaporated to give cyclohexenylethanesulphinic acid **27**, δ_H 1.00–2.49 (9 H, m), 2.80 (2 H, br t, CH_2SO_2), 5.26–5.92 (2 H, m, CH) and 8.28 (1 H, br s, SO_2H). A similar result was obtained with ultrasonic initiation.

5-*Chloro*-7-*thiabicyclo*[4.3.0]*nonane* 7,7-*Dioxide* **29**.—A mixture of compound **25** (0.2 g, 0.96 mmol) and copper(II) chloride catalyst solution[29] (an equal volume) was degassed and heated to 110 °C (allowing the acetonitrile to evaporate off). After 3 h at 140 °C, the sample had gone black. The residue was purified by PLC [methylene dichloride–(40–60 °C) light petroleum (4:6)] (31.2 mg, 16%); δ_H 1.48–1.90 (5 H, m), 1.93–2.28 (2 H, m), 2.28–2.45 (1 H, m), 2.78 (1 H, m), 3.24 (2 H, m), 3.43 (1 H, m) and 4.55 (1 H, q); δ_C 19.09 (C-3), 25.76 (C-9), 26.36 (C-2), 31.82 (C-4), 35.00 (C-1), 51.36 (C-8), 53.64 (C-5) and 67.27 (C-6); *m/z* 173 [$(M - Cl)^+$, 2], 143 (4), 142 (6), 116 (13), 107 (38), 93 (34), 91 (16), 81 (62), 80 (46), 79 (100), 77 (27), 67 (49), 65 (15), 53 (22), 41 (30) and 39 (33).

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Paper 1/01109J
Received 8*th March* 1991
Accepted 2*nd April* 1991