ASPECTS OF ORGANOSULPHUR CHEMISTRY

A Thesis submitted to the Board
of the Faculty of Physical Sciences
in partial fulfilment of the
requirements for the Degree of
Doctor of Philosophy in the
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by

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For my parents in thanksgiving.

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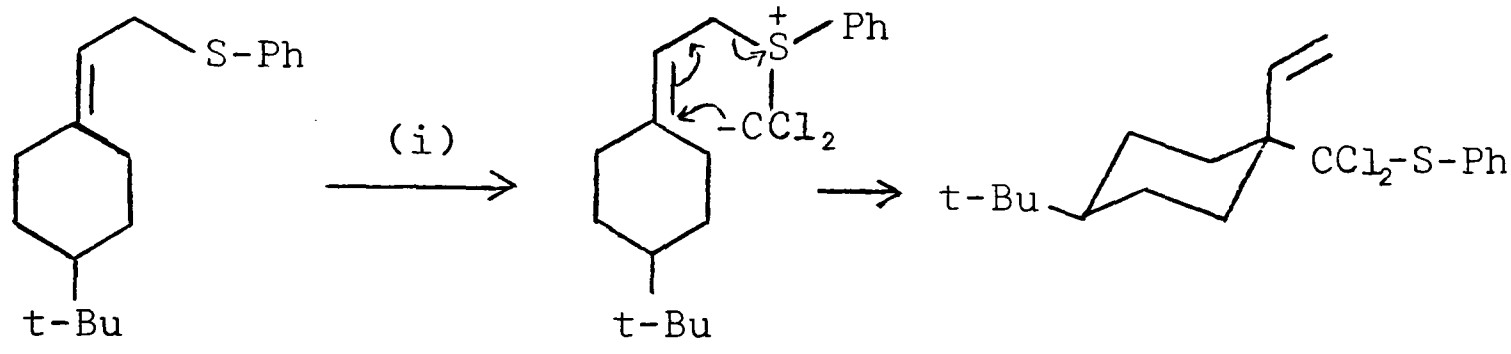
ABSTRACT

INTRODUCTION

INTRODUCTION

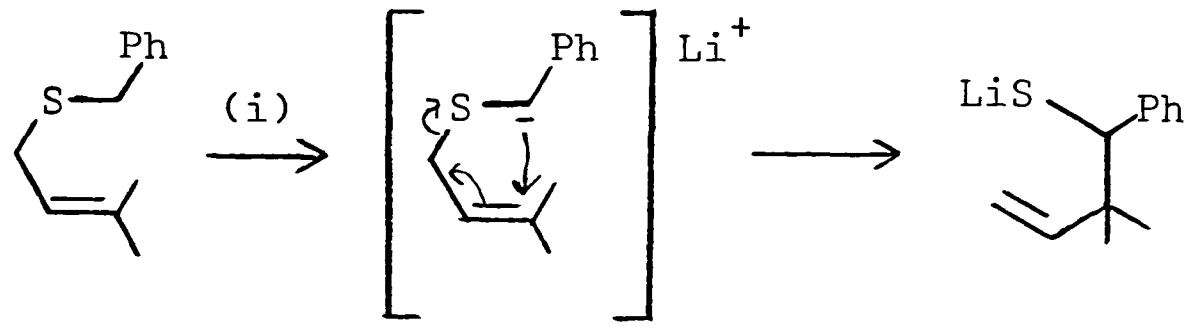
Organosulphur compounds have been much used in synthesis, both because of the wide variety of reactions they undergo and because the sulphone group can finally be removed by elimination, reduction, or hydrolysis. Sulphur-containing carbanions, carbocations and radicals, sulphur ylides, organosulphur carbenes and carbenoids, and the pericyclic reactions of organosulphur compounds have been well reviewed[1,2]. Recent developments in sulphone chemistry have been discussed by Magnus[3], and Stirling[4] has reviewed sulphinate esters. In view of this extensive literature on organosulphur chemistry, only certain aspects which are of relevance to the work presented in this thesis will be highlighted here.

Concerted [2,3] sigmatropic rearrangements of organosulphur compounds will be considered first. In Schemes 1 and 2 (refs. 5 and 6) are shown reactions which probably occur by this [2,3] process.



(i) NaOH, $CHCl_3$.

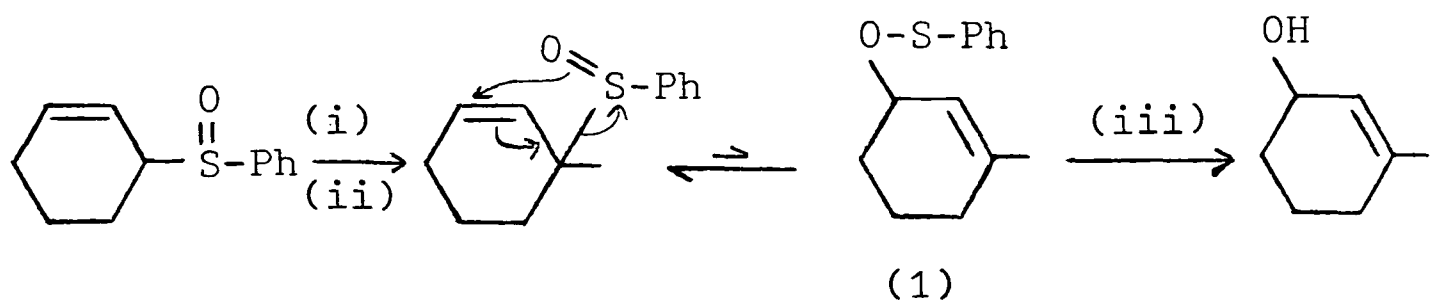
Scheme 1



(i) n-BuLi, THF, -30°C.

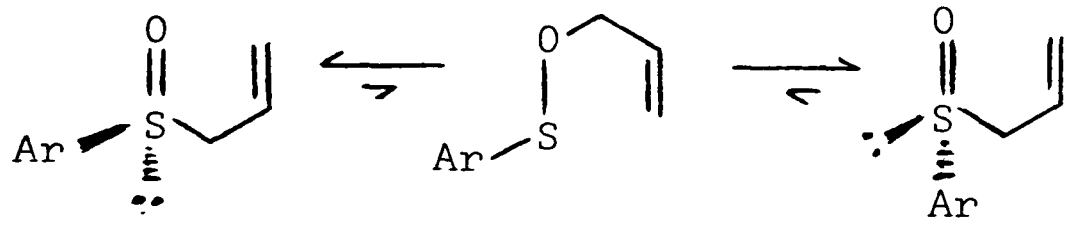
Scheme 2

The equilibrium between an allylic sulphoxide and the corresponding sulphenate ester is also thought to occur by an electrocyclic [2,3] rearrangement[7]. A synthetic application[8] of this reaction involving the trapping of the sulphenate ester (1) with a thiophile is shown in Scheme 3. It has been established[9] that the racemisation of allylic sulphoxides occurs *via* the achiral sulphenate ester (Scheme 4). Such chiral sulphoxides are prepared from sulphinate esters by nucleophilic displacement at sulphur by a Grignard reagent (*e.g.* Scheme 5)[10], this reaction being an important use for sulphinate esters.



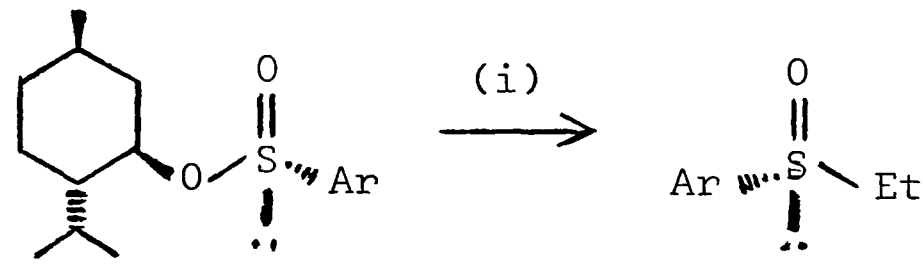
(i) $LiNR_2$
(ii) MeI
(iii) $P(OMe)_3$

Scheme 3



Ar = p-tolyl

Scheme 4

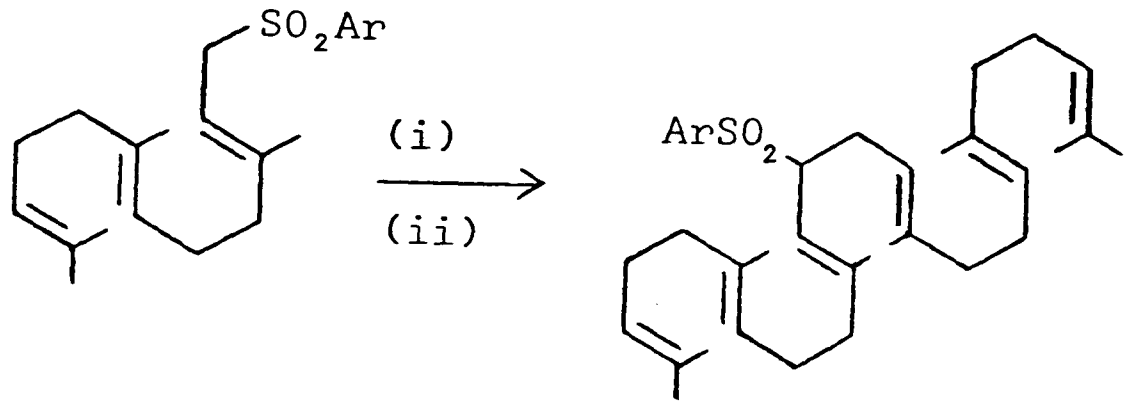


Ar = p-tolyl

(i) EtMgBr (1 mole eq.), ether.

Scheme 5

The second aspect of organosulphur chemistry to be considered is that of α-sulphonyl carbanions. The sulphonyl group is intrinsically electron withdrawing, rendering the protons on the α-carbon acidic. Thus, sulphones can be deprotonated, and the α-metallated species produced can be reacted with an electrophile. Of particular importance in synthesis is alkylation, which occurs exclusively α to the sulphonyl group with metallated allylic sulphones[11] (e.g. Schemes 6 and 7)[12,13].

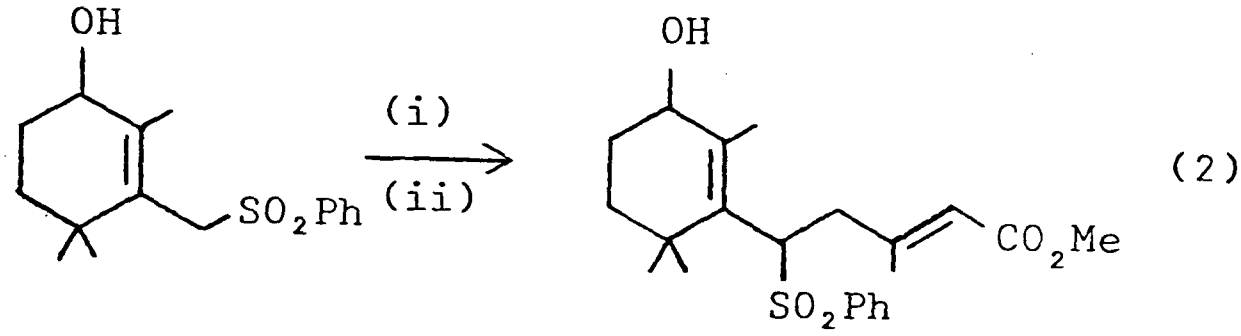


Ar = p-tolyl

(i) n-BuLi, THF-HMPA (4:1 v/v), -20°C.

(ii) trans,trans-farnesyl bromide.

Scheme 6



(2)

(i) $i\text{-Pr}_2NLi$ (2 mole eq.), THF, -78°C.

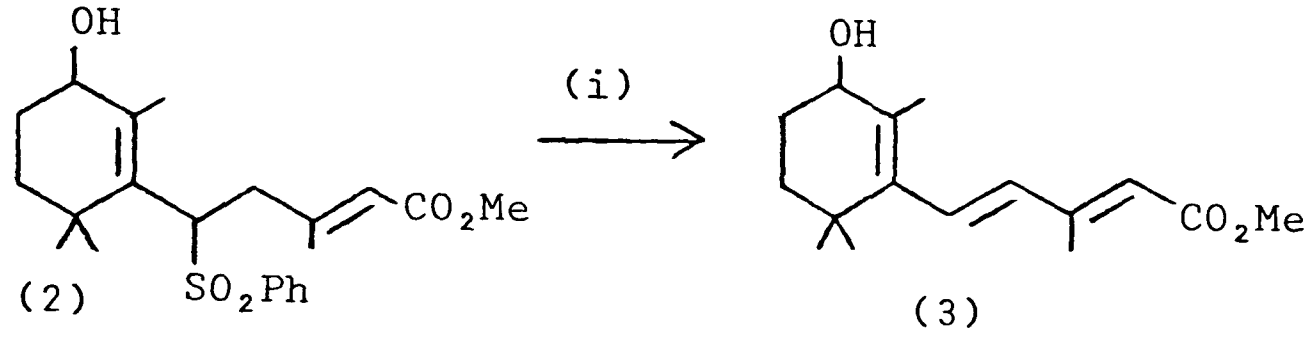
(ii) $Br\text{-}CH_2\text{-}C(Me)=CH\text{-}CO_2Me$.

Scheme 7

Sulphinate is not traditionally considered to be a good leaving group, and this is the third point which is to be discussed here. Many examples are known, however, where a sulphinate group is displaced from a sulphone under favourable circumstances. Generally, if a stable product is formed, and if the displacement of sulphinate can occur by an intramolecular process, then the reaction seems to be favoured.

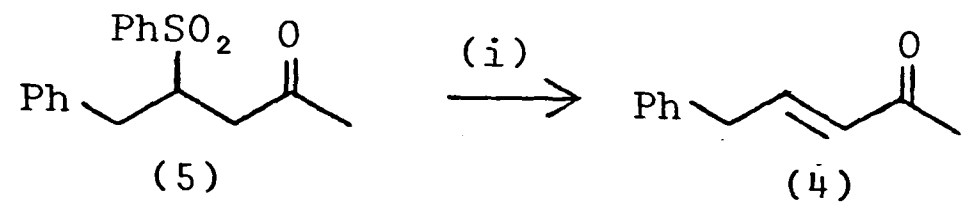
Thus, substituents which stabilise a β-sulphonyl anion promote base-catalysed elimination of sulphinic acid from sulphones by an El_{cb} type mechanism. For example, the

conjugated polyene (3) is formed by mild base treatment of sulphone (2) (Scheme 8)[13], and similar examples are given in ref. 14. Also, the α,β-unsaturated ketone (4) is obtained from sulphone (5) under mild alkaline conditions (Scheme 9)[15], and similar examples are given in ref. 16. In contrast, base-catalysed elimination of sulphinic acid from sulphone (6) requires much more vigorous conditions (Scheme 10)[17].



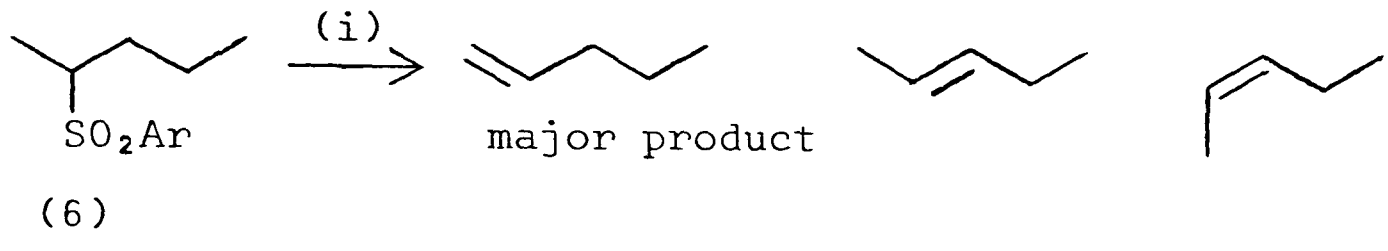
(i) NaOMe, t-BuOH, room temperature.

Scheme 8



(i) aq. NaOH, 30 min, room temperature.

Scheme 9

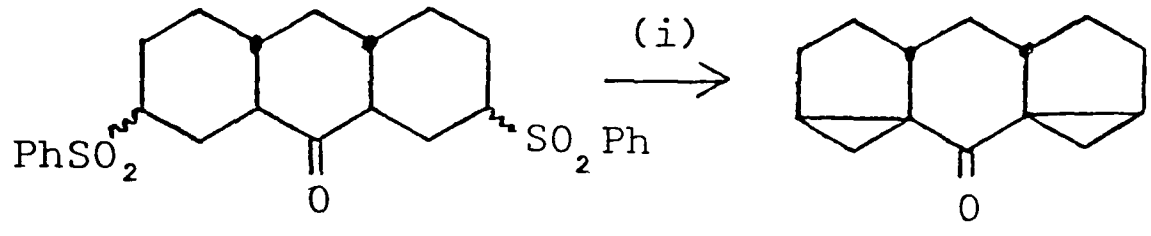


(i) t-BuOK, pyridine, 7h, reflux.

Scheme 10

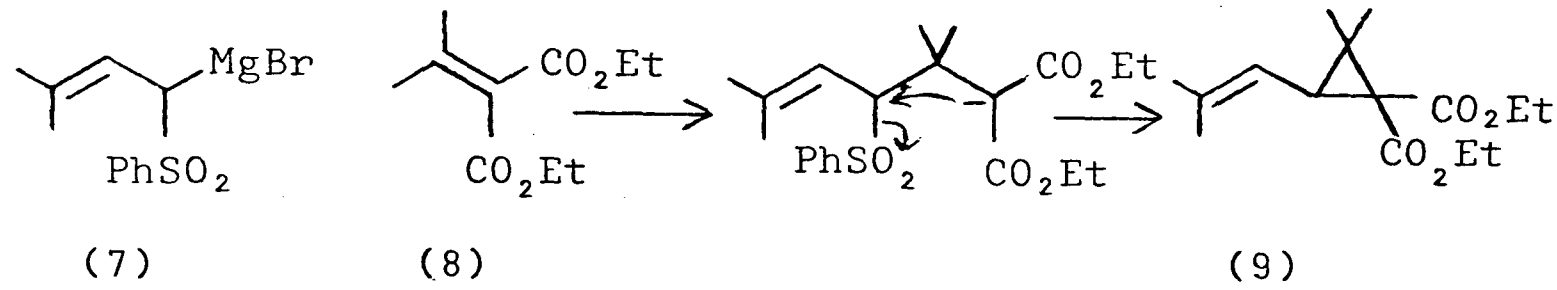
Intramolecular nucleophilic displacement of sulphinate resulting in cyclopropane formation occurs in cases where a γ-sulphonyl anion can be formed. Scheme 11 shows a case[18] in

which the geometry is particularly favourable for this reaction. Michael addition of the metallated sulphone (7) to the α,β-unsaturated ester (8) was followed by 1,3-elimination of sulphinate to give the cyclopropane (9) (Scheme 12)[19], and a similar example is given in ref. 20.



(i) t-BuOK, DMF, 80°C.

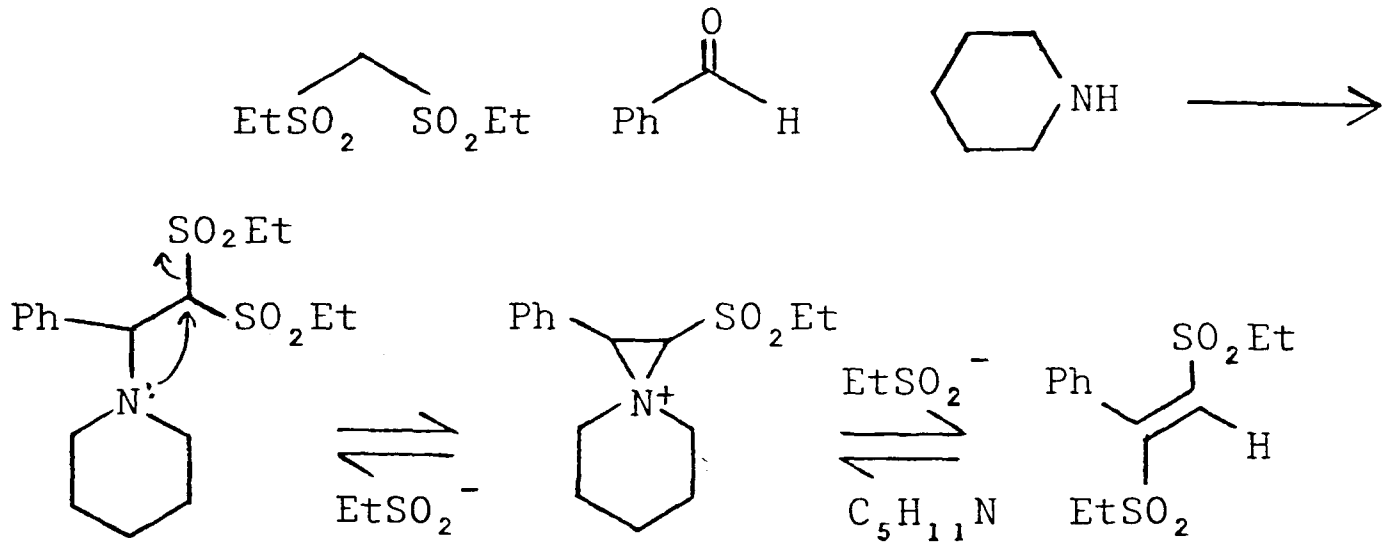
Scheme 11



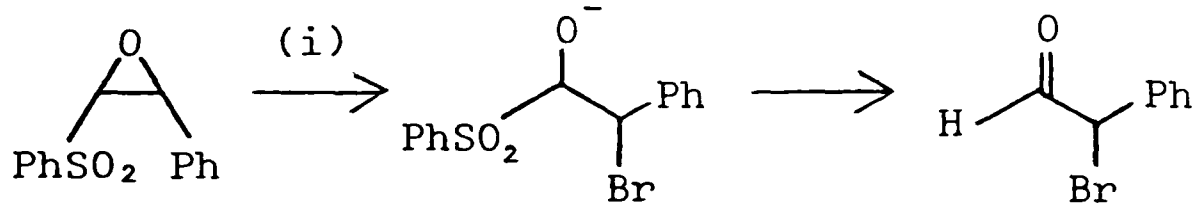
(7) (8) (9)

Scheme 12

Intramolecular displacement of sulphinate by heteroatom nucleophiles occurs in the reactions shown in Schemes 13 and 14 (refs. 21 and 22).



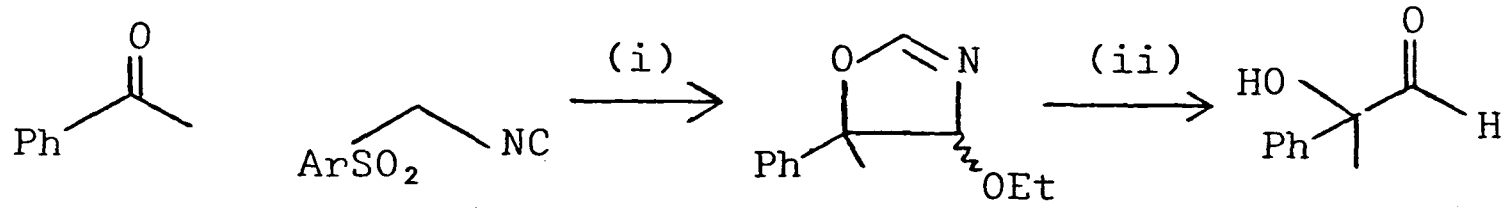
Scheme 13



(i) $MgBr_2$, ether, 15 min, room temperature.

Scheme 14

Schemes 15 to 18 (refs. 23 to 26) show overall reactions in which sulphinate must act as a leaving group at some stage during the course of the reaction.

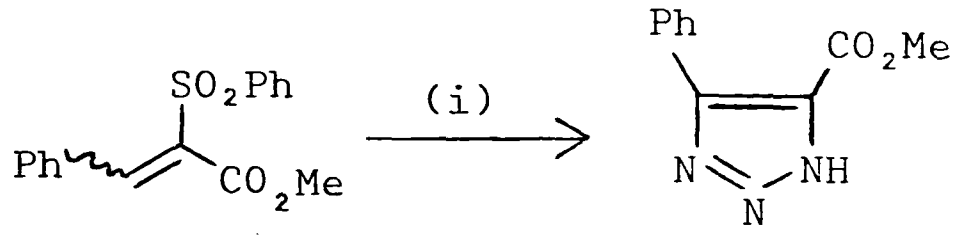


Ar = p-tolyl

(i) EtOTl, EtOH-DME, room temperature.

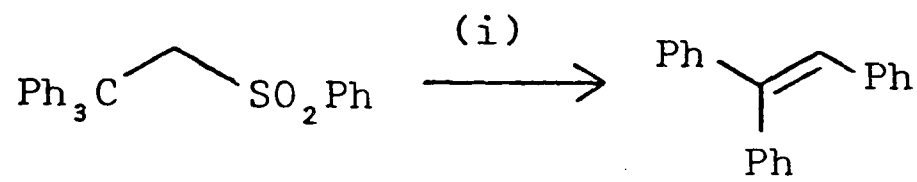
(ii) H^+, room temperature.

Scheme 15



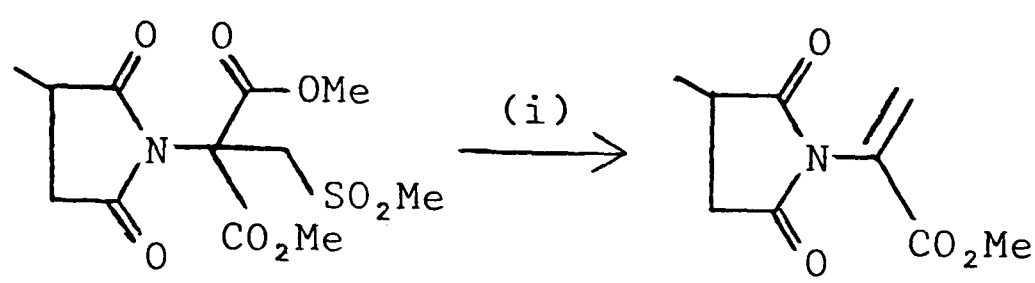
(i) NaN_3, DMF, 100°C.

Scheme 16



(i) Base.

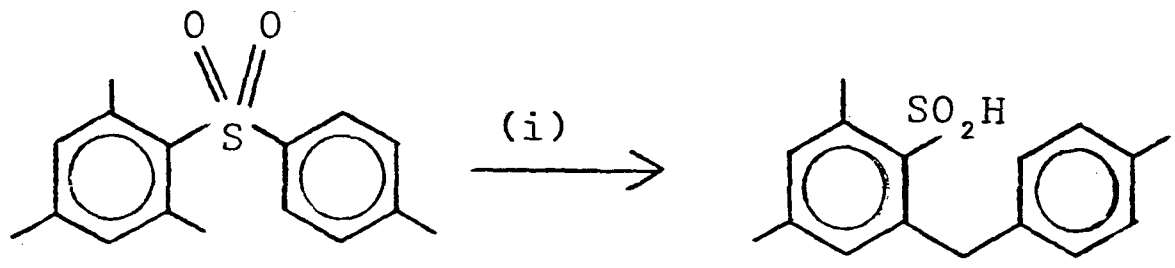
Scheme 17



(i) KI, DMF, 100°C.

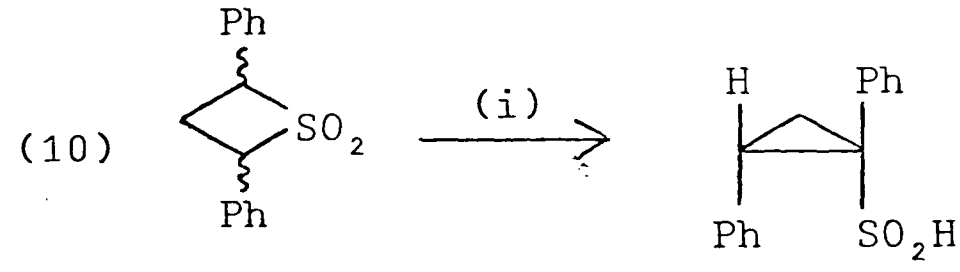
Scheme 18

The Truce-Smiles rearrangement (Scheme 19)[27] and the Stevens rearrangement of sulphone (10) (Scheme 20)[28] are cases where the displaced sulphinate remains attached to the molecule.



(i) n-BuLi, ether, 0°C.

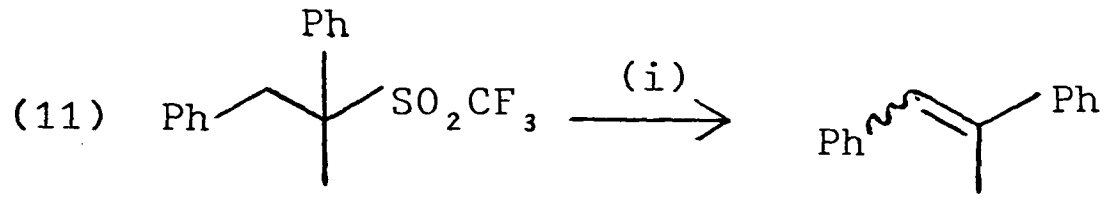
Scheme 19



(i) EtMgBr.

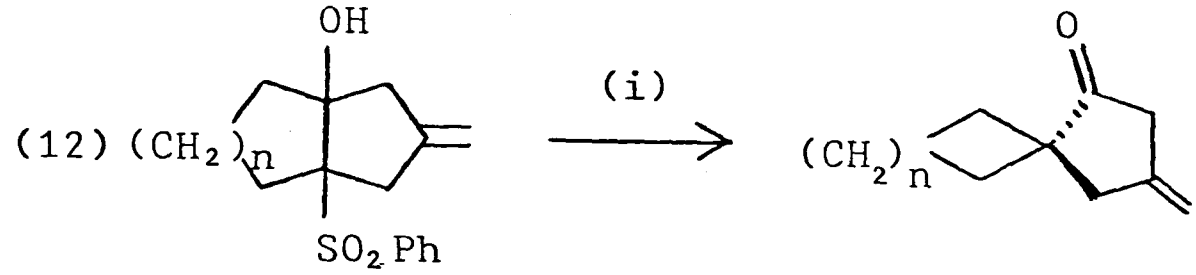
Scheme 20

Thermal elimination of sulphinic acid to give an olefin under non-basic conditions is rare, but has been observed with sulphone (6, Ar = p-C_6H_4-NMe_2) (Scheme 10)[17] and sulphone (11) (Scheme 21)[29]. The pinacol-type rearrangement of sulphone (12) is claimed[30] to be the first example of a reaction in which sulphinate acts as a leaving group in the presence of a Lewis acid (Scheme 22).



(i) 70°C.

Scheme 21

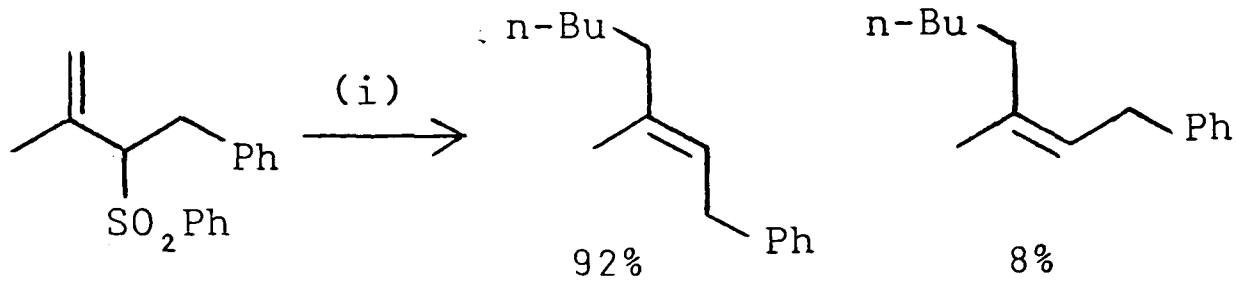


n = 3,4,8.

(i) $EtAlCl_2$ (2 mole eq.), CH_2Cl_2, 3h, reflux.

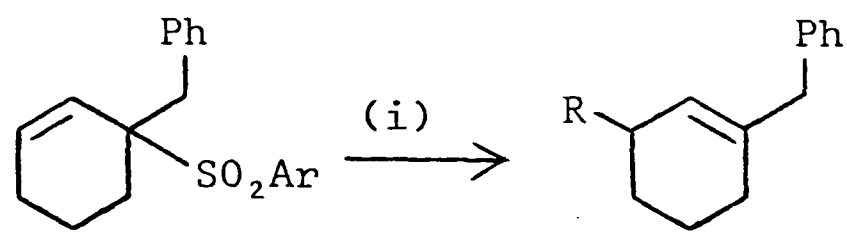
Scheme 22

Recently, displacement of sulphinate has been shown to occur on treatment of allylic sulphones with certain organometallic reagents. Malonate anion in the presence of a palladium phosphine complex[31], organocuprates (Schemes 23 and 24)[32,33], and Grignard reagents in the presence of a copper(II) complex[34] have been used. In addition, an example of intermolecular displacement of sulphinate has been provided by Julia[80]. Treatment of 3-methyl-3-(p-tolylsulphonyl)-1-butene with PhSMgBr or PhSLi in toluene at 100°C gave 3-methyl-1-(phenylthio)-2-butene.



(i) $n\text{-}Bu_2CuLi$, ether, 30 min, $-20^{o}C$.

Scheme 23



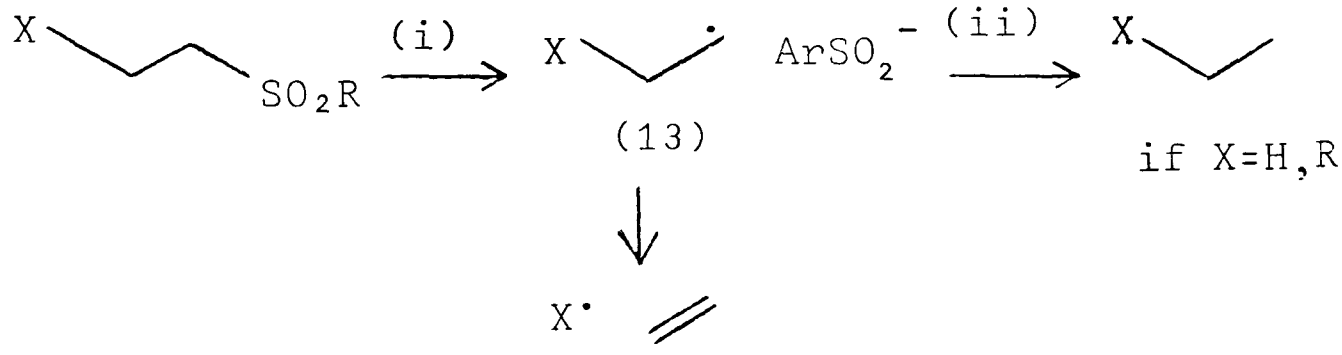
Ar = p-tolyl

R = Me, n-Bu

(i) R_2CuLi, ether, $-20^{o}C$.

Scheme 24

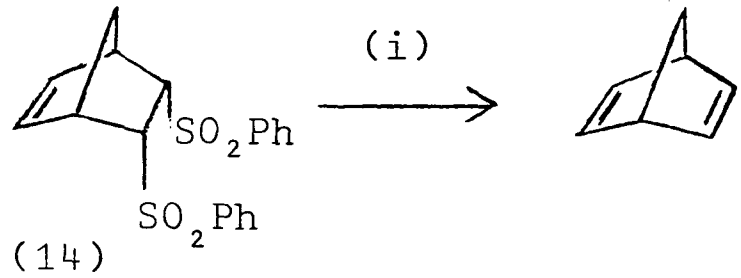
Finally, sulphinate anion probably acts as a leaving group in the desulphonylation of sulphones using dissolving metals[35], lithium in alkylamines and sodium in alcohols often being used. Scheme 25 shows a possible mechanism for this reaction, although it may be the case that the radical (13) is reduced to an anion before it reacts further. An interesting example is provided by the reduction of disulphone (14), in which both sulphone groups are lost (Scheme 26)[36].



(i) Electron from dissolving metal reduction.

(ii) Solvent.

Scheme 25

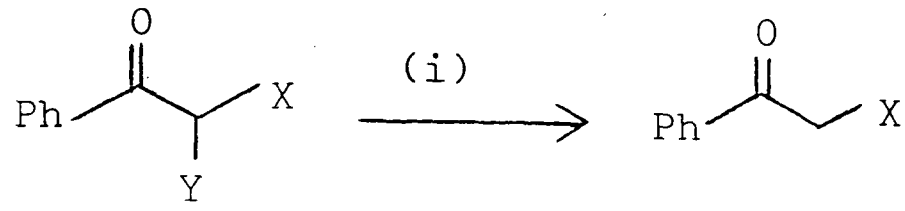


(i) Na(Hg), MeOH, NaH_2PO_4, overnight, room temperature.

Scheme 26

The fourth aspect of organosulphur chemistry to be considered in this Introduction is that of sulphur-centred radicals, a subject which has been well reviewed[1,37]. Evidence has recently been obtained on the relative stabilities of thinyl, sulphinyl, and sulphonyl radicals. Thus, in the partial reduction of compound (15) (Scheme 27)[38], the stability of the eliminated radical ($X^{\bullet}$ or $Y^{\bullet}$) is thought to determine which mode of cleavage occurs, suggesting the ordering of stability is $PhSO^{\bullet} > PhS^{\bullet} > PhSO_2^{\bullet}$. Furthermore, the same ordering of stability is suggested by the relative rates of cleavage of the diradical (16) (Scheme 28)[39], again assuming that the rate is governed by the stability of the sulphur-

centred radicals produced.

(15) 

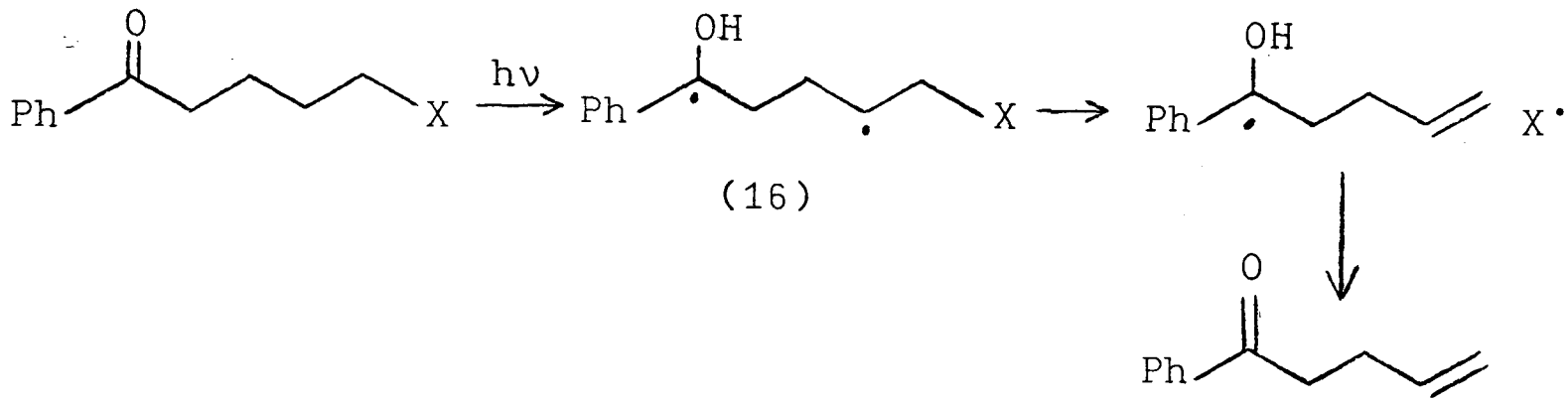
X = $PhSO_2$ Y = PhS

X = $PhSO_2$ Y = PhSO

X = MeS Y = MeSO

(i) n-Bu_3SnH (1 mole eq.), azobisisobutyronitrile (AIBN), 1h, 100°C.

Scheme 27



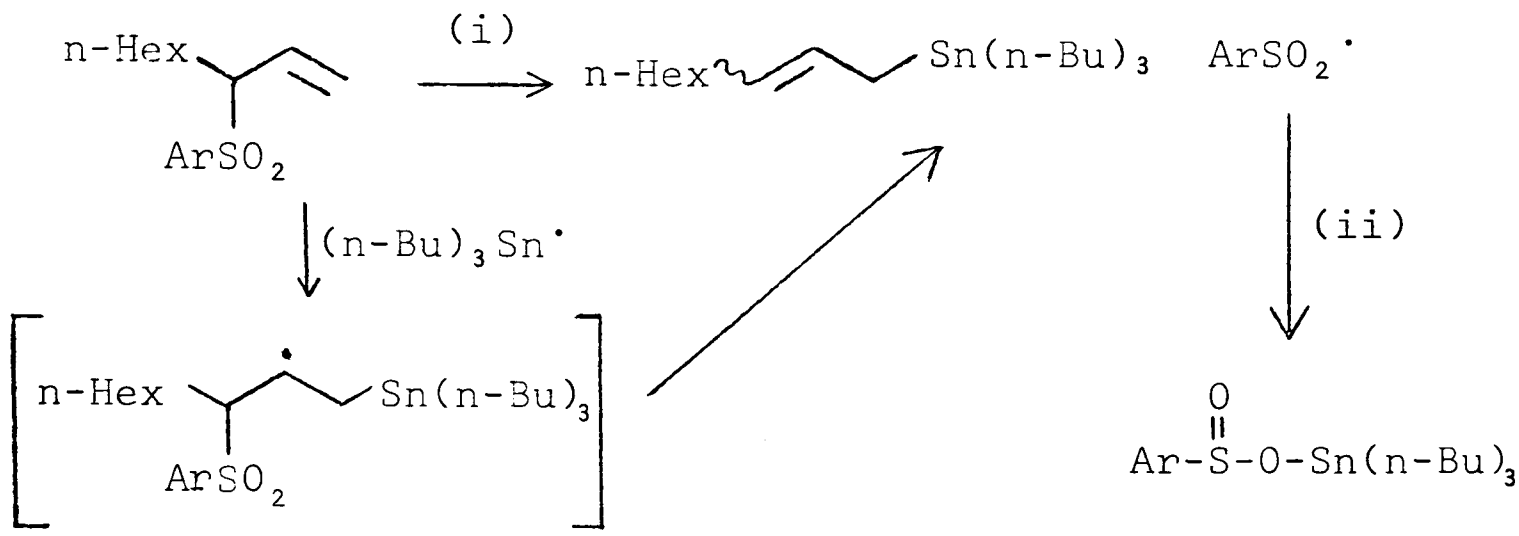
(16)

Relative rates 92.6 : 16.1 : 1

for X = PhSO, PhS, $PhSO_2$

Scheme 28

Sulphonyl radicals have been detected by e.s.r.[40], and they have frequently been postulated as intermediates in various reactions[37], particularly in the addition of sulphonyl halides to carbon-carbon multiple bonds and in the copolymerisation of alkenes with sulphur dioxide. A radical addition-elimination mechanism, with displacement of the aryl sulphonyl radical by n-$Bu_3Sn^{\bullet}$, (Scheme 29) has been proposed for the desulphonylation of allylic sulphones using tin reagents[41].



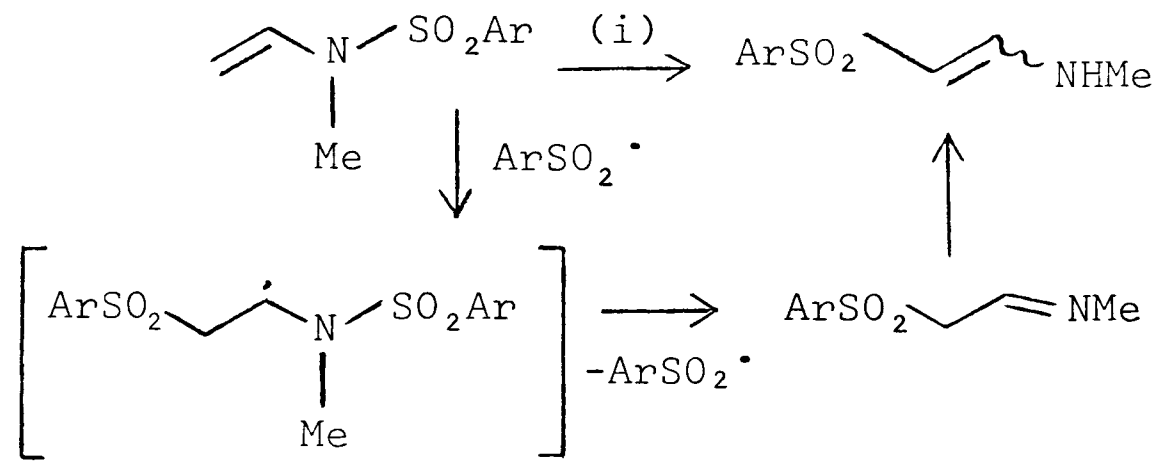
Ar = p-tolyl

(i) $n\text{-}Bu_3SnH$ (2 mole eq.), AIBN, benzene, 2h.

(ii) $n\text{-}Bu_3SnH$.

Scheme 29

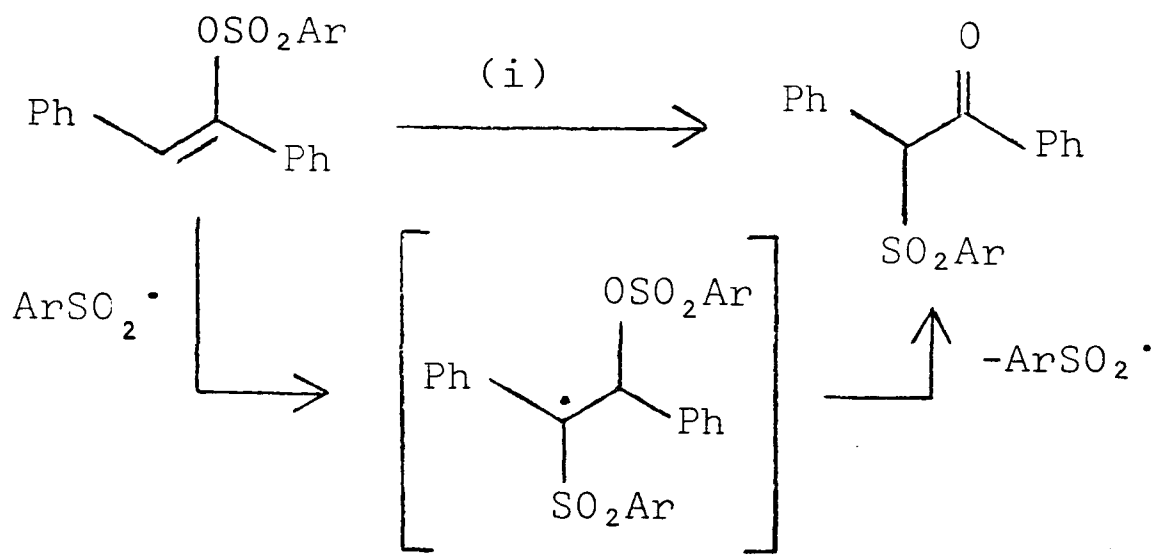
Two examples of a radical chain addition-elimination process with sulphonyl radicals as the chain-carrier are shown in Schemes 30 and 31 (refs. 42 and 43).



Ar = p-tolyl

(i) Bombardment of the solid with electrons.

Scheme 30

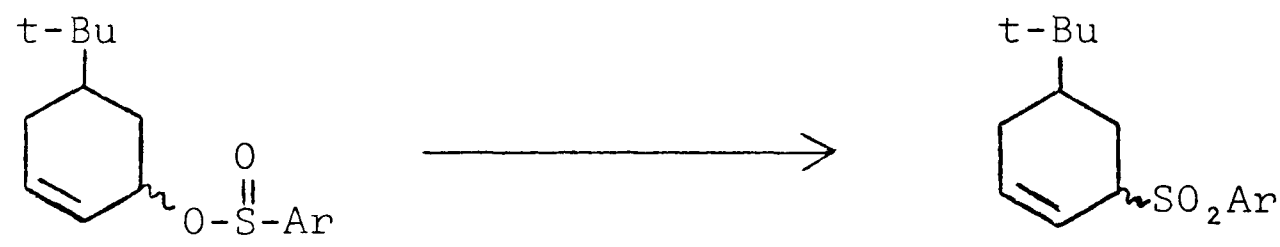


Ar = p-tolyl

(i) Benzoyl peroxide, acetonitrile, ca. 8h, 100°C.

Scheme 31

The main aim of the work presented in Section I of this thesis was to investigate the rearrangement of alicyclic allylic sulphinate esters to allylic sulphones, of particular interest being the reaction of the conformationally biased sulphinates (17) and (18) (Scheme 32). This reaction might provide a convenient route for the preparation of diastereomerically pure sulphones (19) and (20) for Section II.



cis (17)
trans (18)

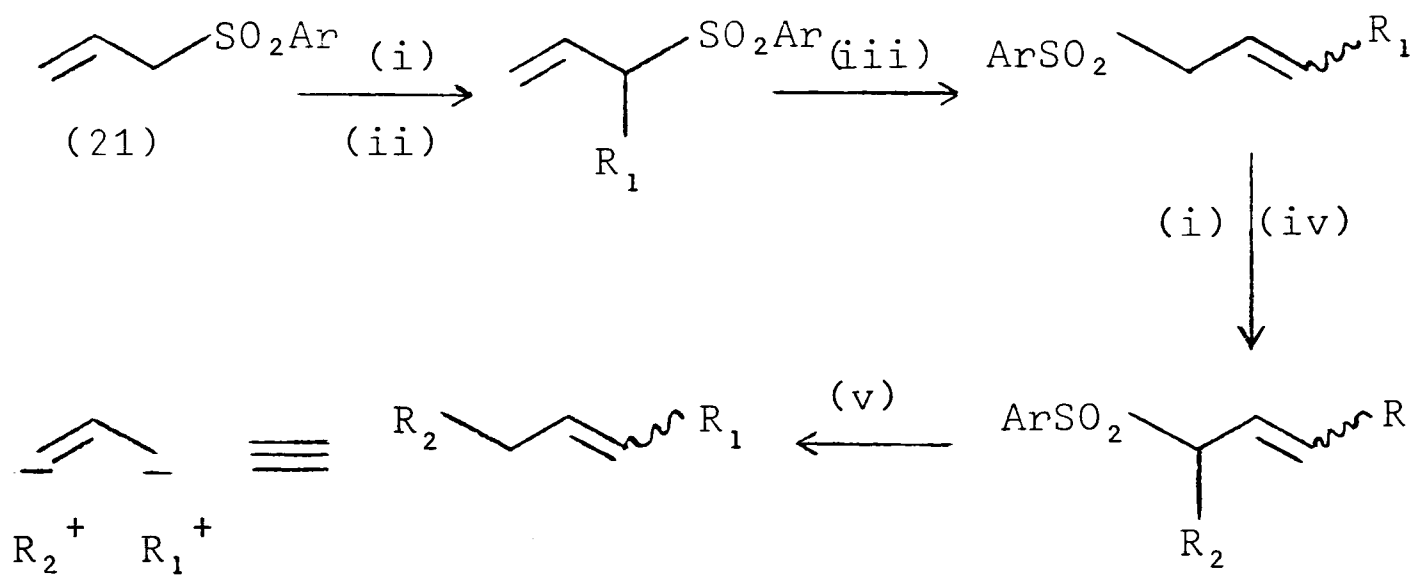
cis (19)
trans (20)

Ar = p-tolyl

Scheme 32

In Section II of this thesis is described an investigation of the [1,3] migration of the sulphonyl group of allylic sulphones. An incentive for this work was that

this [1,3] migration is one of the steps in the proposed[33] synthetic route shown in Scheme 33. Both acyclic and alicyclic systems were studied and attempts were made to elucidate the mechanism of the reaction.



Ar = p-tolyl

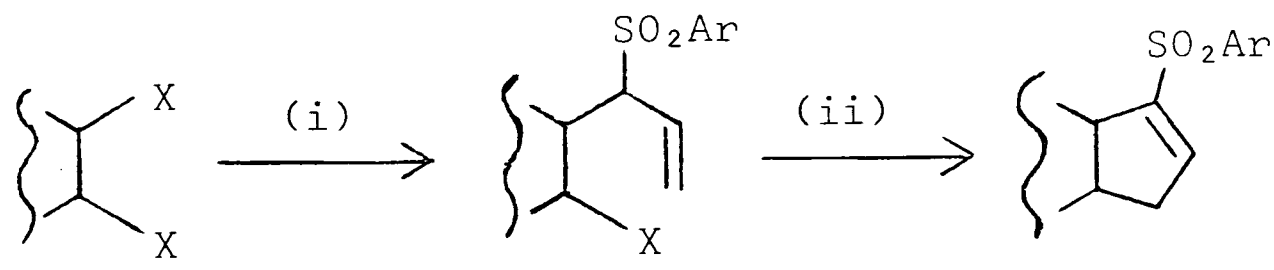
(i) Base. (iv) R_2-Hal.

(ii) R_1-Hal. (v) Desulphonylation.

(iii) [1,3] rearrangement.

Scheme 33

Finally, Section III of this thesis is concerned with attempts to develop a stereoselective 5-ring annulation procedure, involving initial α-alkylation of the allylic sulphone (21) (Scheme 34).



Ar = p-tolyl

X = Br or O

(i) Metallated CH_2=CH-CH_2-SO_2Ar (21).

(ii) Several steps.

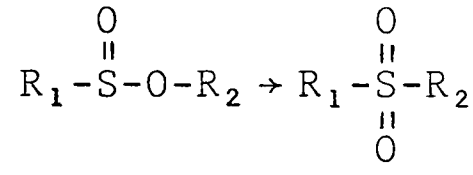
Scheme 34

SECTION I

REARRANGEMENT OF ALICYCLIC ALLYLIC SULPHINATE ESTERS

1. Introduction

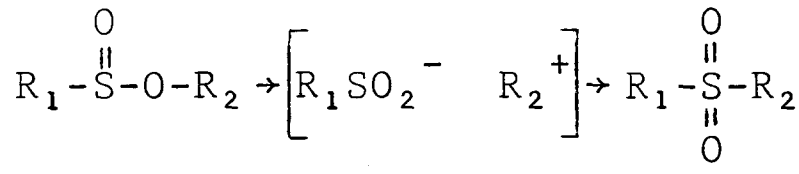
Sulphinate esters (22) can undergo thermal rearrangement to give sulphones (23), Scheme 35. The reaction normally goes to completion, the driving force being the formation of the strong S=O bond[44].



(22) (23)

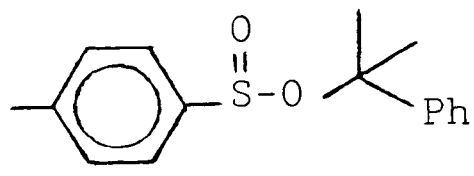
Scheme 35

A dissociative ionic mechanism (Scheme 36) has been fairly well established in certain cases, the rearrangement being promoted by polar solvents[45,46]. Also reaction is favoured for sulphinates which can ionise to give a stable carbocation. For example, sulphinate (24) rearranges to the sulphone on heating in acetic acid or nitromethane, whereas sulphinate (25) is stable under similar conditions[45].

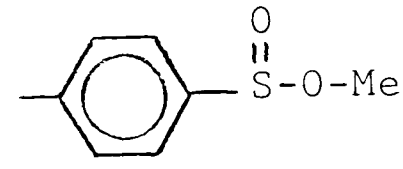


(22) (23)

Scheme 36



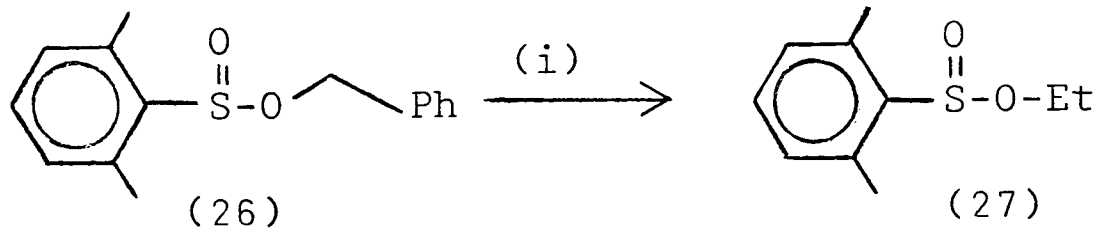
(24)



(25)

In hydroxylic solvents there is sometimes competition between the rearrangement of a sulphinate to a sulphone and

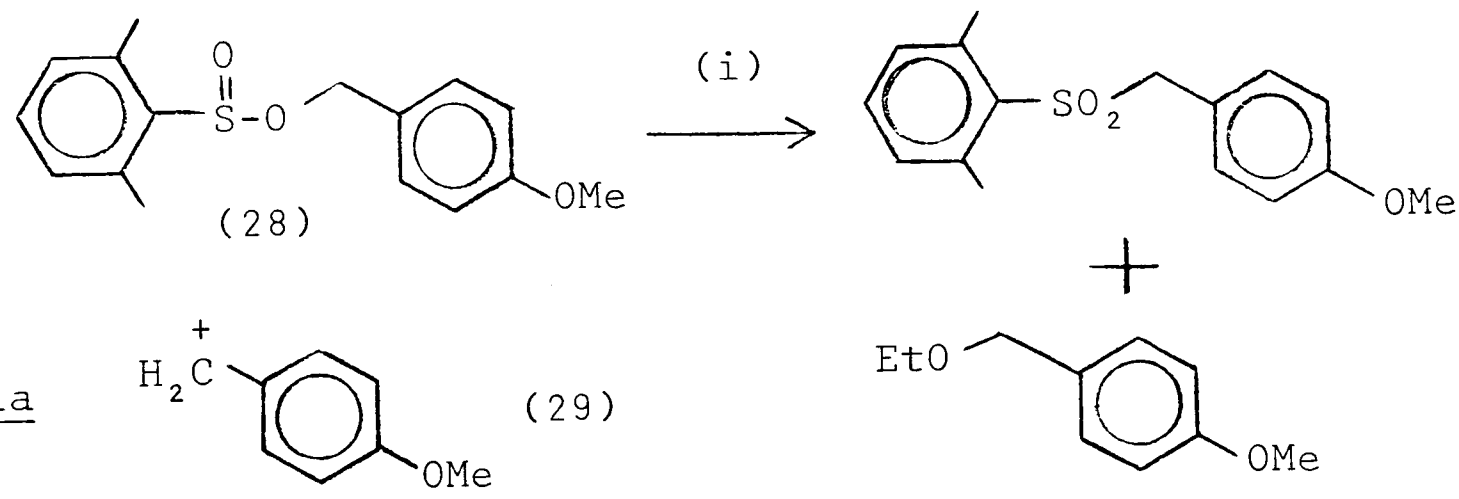
the incorporation of the solvent into the products. For example, sulphinate (26) affords compound (27) by cleavage of the S-O bond promoted by nucleophilic attack at sulphur by the solvent (Scheme 37)[46], a process which is well established[47]. Similar treatment of sulphinate (28), however, results in products derived from the carbocation (29) (Scheme 38)[46], ionisation of sulphinate (28) being favoured by the carbocation-stabilising effect of the methoxy group.



(26) (27)

(i) 2,6-Lutidine, ethanol, 90°C.

Scheme 37

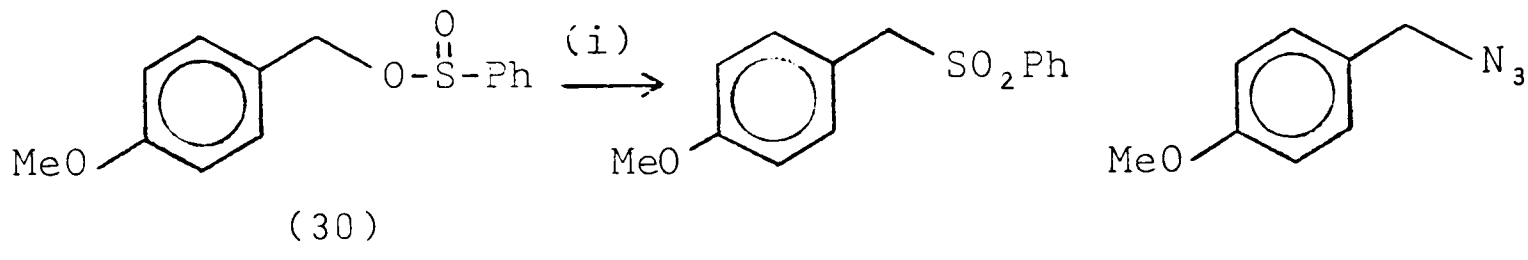


(28) (29)

(i) 2,6-Lutidine, ethanol, 90°C.

Scheme 38

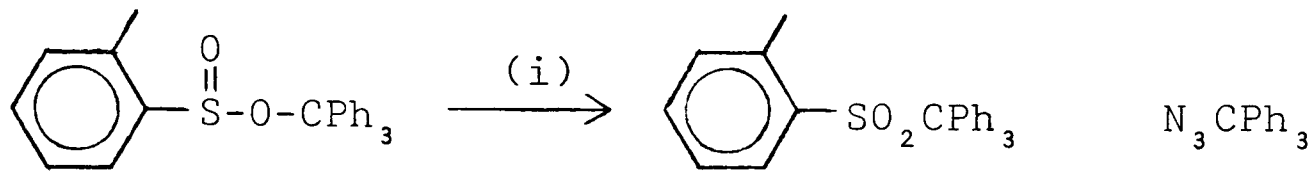
In the case of sulphinate (30) the intermediate carbocation can be trapped by azide ion (Scheme 39)[46]. It has been suggested[48] that the rearrangement of sulphinate (31) involves ion-pairs rather than completely dissociated ions, because there is little incorporation of azide, the major product being the sulphone (32), Scheme 40.



(30)

(i) n-Bu_4NN_3 (5 mole eq.), 2,6-lutidine, formamide, 2h, 100°C.

Scheme 39

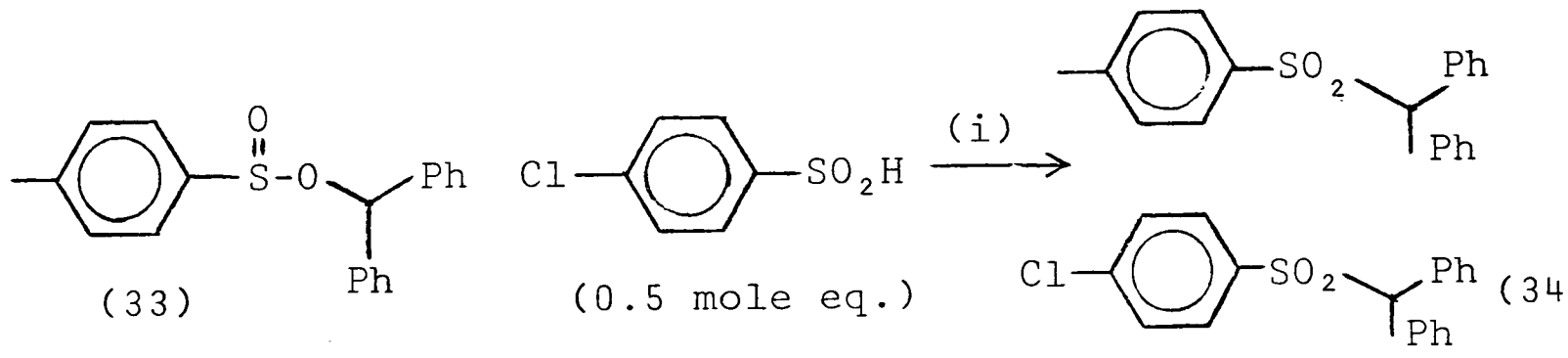


(31) (32) 58% 42%

(i) n-Bu_4NN_3 (2.0 mole eq.), acetonitrile, room temperature.

Scheme 40

Crossover experiments have been performed on sulphinate (33) in which added sulphinic acid is incorporated as the sulphone (34) (Scheme 41)[45]. This suggests that sulphinate (33) rearranges by a dissociative process.

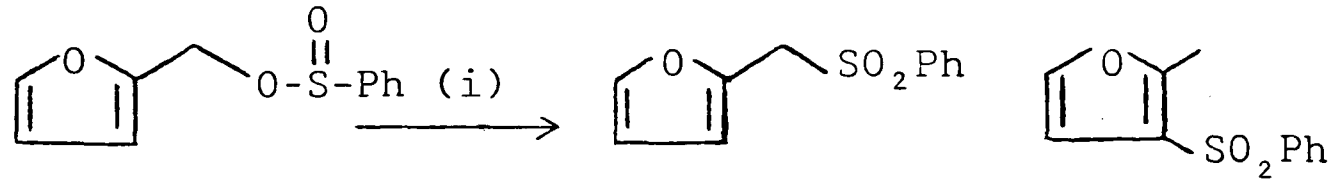


(33) (0.5 mole eq.) (34)

(i) Acetic acid, 15 min, reflux.

Scheme 41

Sulphinate (35) rearranges to give a mixture of sulphones (36) and (37), the proportions of the mixture depending on the solvent used (Scheme 42)[49]. This result has been explained on the basis of ionisation of the sulphinate (35) followed by partial rearrangement of the derived carbocation.

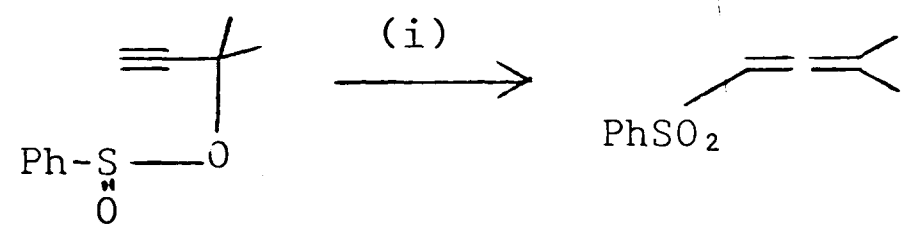


(35) (36) 25% (37) 75%

(i) 2,6-Lutidine, DMF, 1.5h, 153°C.

Scheme 42

Propargyl sulphinates can rearrange to sulphones with a simultaneous acetylene-allene isomerisation (Scheme 43)[50]. This result, the absence of incorporation of hydroxylic solvents[44], and the low sensitivity of the rate of rearrangement to solvent polarity[44], has lead to a suggestion by Braverman[44] that a cyclic intramolecular mechanism is in operation for this rearrangement of propargyl sulphinates.

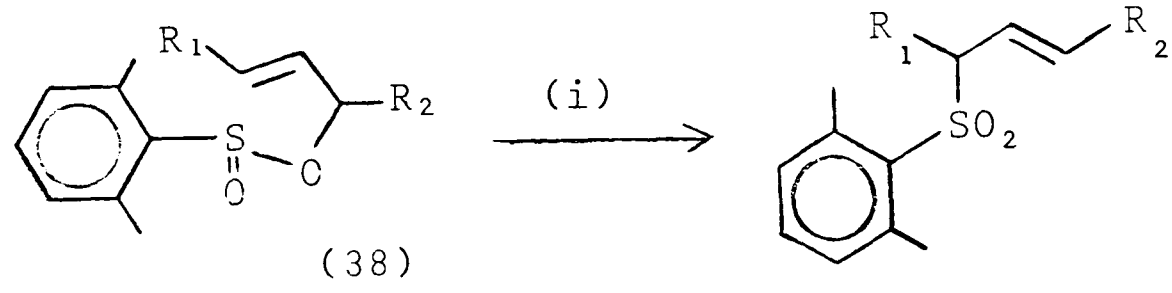


(i) 2,6-Lutidine, aqueous ethanol, 5h, 75°C.

Scheme 43

Braverman[44] claims that rearrangement of unsymmetrically substituted allylic sulphinate esters (38) to sulphones results in simultaneous isomerisation of the allylic group, even if this results in transfer of the migrating group to the more substituted centre, i.e. (38, R_2=H, R_1=Me or Ph), Scheme 44. The report was not in a full paper, however, and few experimental details were given. In other reported examples of the rearrangement of an allylic sulphinate ester to the sulphone accompanied by allylic isomerisation, the migrating group is transferred to the less substituted centre

(e.g. Schemes 45 and 46)[51,52].



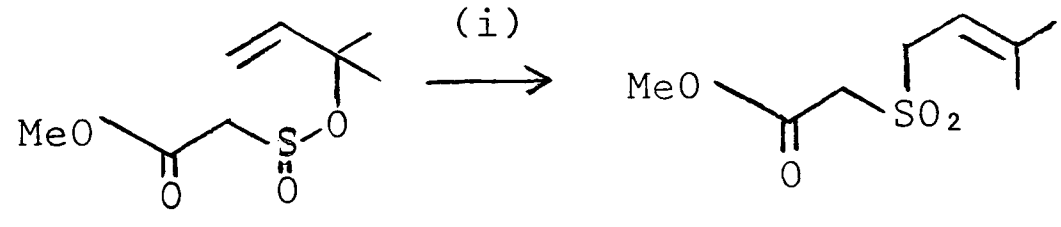
(38)

R_1 = H, Me, H, Ph, H, Me

R_2 = H, H, Me, H, Ph, Me

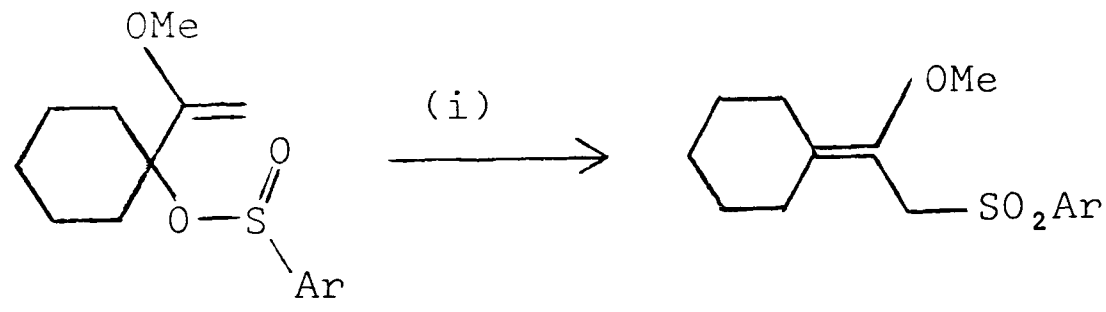
(i) Ethanol-water (3:2 v/v), 90°C.

Scheme 44



(i) Heat or silica gel at room temperature.

Scheme 45

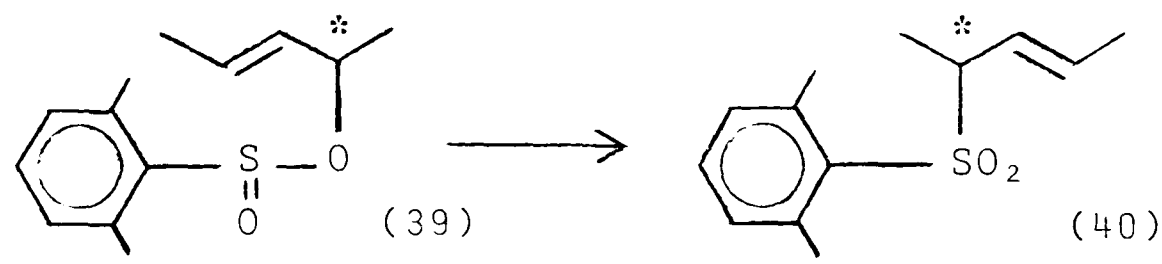


Ar = p-C_6H_4-NO_2

(i) 70 min at 100°C.

Scheme 46

Braverman[44] claimed that optically active sulphinate (39) rearranges with inversion of configuration to the optically active sulphone (40), Scheme 47. However, the report was again not in a full paper, no experimental details were given, and it is not clear how the optical purities of the compounds (39) and (40) were established.

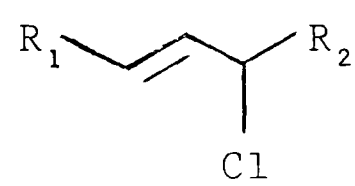


(39) (40)

* chiral centre.

Scheme 47

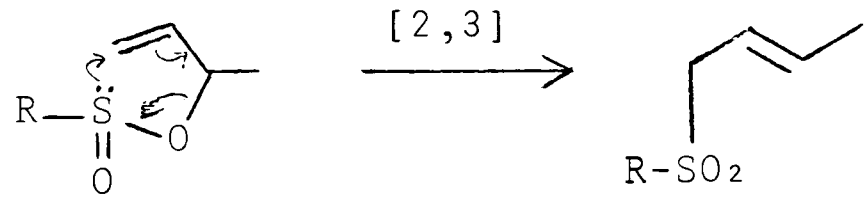
Braverman[44] found that those allylic sulphinates of general structure (38) which are substituted at the α- or γ-position by a methyl or a phenyl group rearrange faster by a factor of between 36 and 2×10^4 than does the non-substituted sulphinate (38, $R_1 = R_2 = H$) (Scheme 44). The allylic chlorides (41), which react by an ionic process, are more sensitive to α- or γ-substitution by a methyl or a phenyl group by a factor of between 10^2 and 10^5 than are the analogous allylic sulphinates (38). Braverman found that the rearrangement of sulphinate (38, R_1 = Ph, $R_2 = H$) exhibited a sensitivity to variation in solvent ionising power similar in magnitude to that observed for the rearrangements of allylic thionbenzoates and allylic azides, which are believed to proceed by a cyclic intramolecular mechanism.



(41)

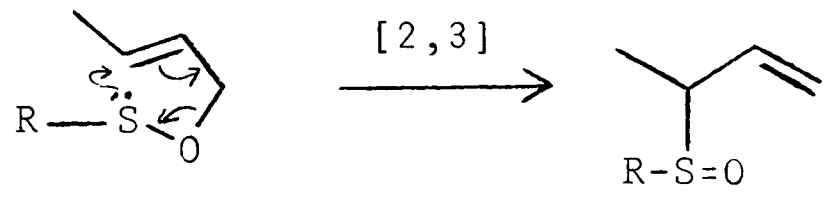
On the basis of the evidence presented above, Braverman[44] suggested that the rearrangement of allylic sulphinates occurs by a cyclic intramolecular mechanism, the degree of polarity of the transition state depending on the particular system and the conditions used. This cyclic process would

be analogous to the [2,3] electrocyclic reaction postulated[7] for the rearrangement of an allylic sulphenate ester (42) to a sulphoxide (43) (Schemes 48 and 49).



Scheme 48

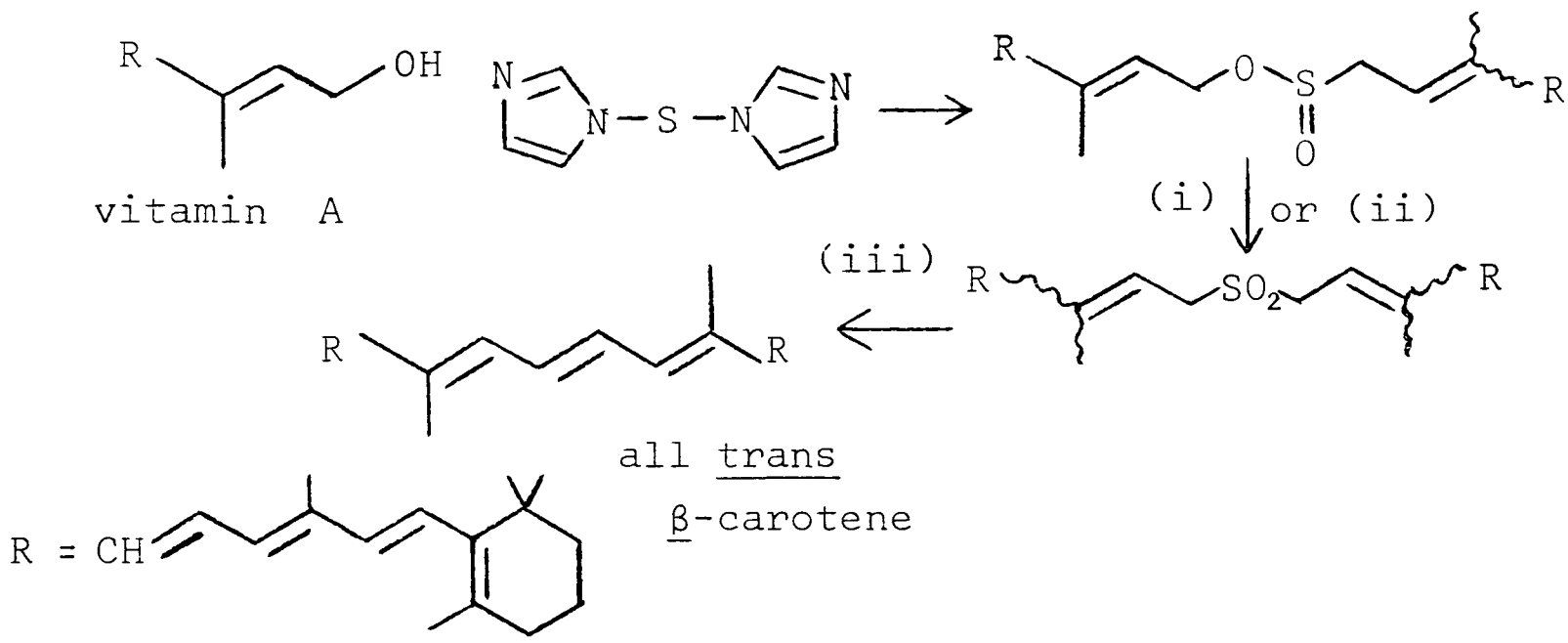
(42)



(43)

Scheme 49

An example of the rearrangement of an allylic sulphinate to a sulphone without simultaneous allylic isomerisation is provided by one of the steps in the conversion of vitamin A to β-carotene[53], Scheme 50. Allylic isomerisation would both require the transfer of the migrating group to the more substituted centre and result in a loss of conjugated double bonds. It is also claimed[53] that the sulphinate (44) rearranges to the sulphone (45) without allylic isomerisation (Scheme 51), although no experimental details are given in the paper.

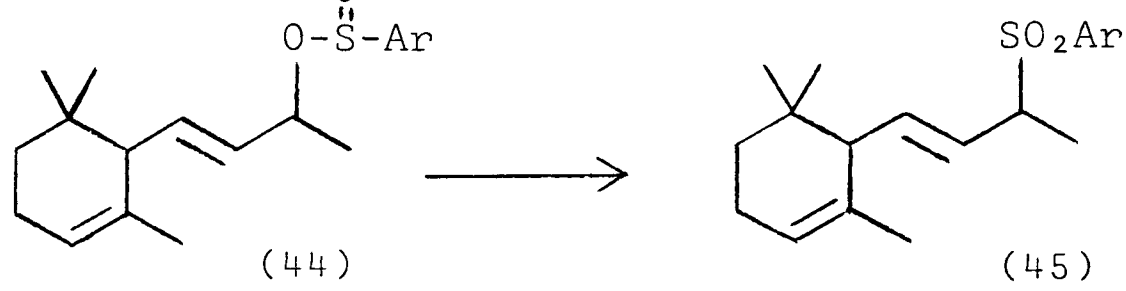


(i) Silica gel, CH_2Cl_2, room temperature.

(ii) K_2CO_3, toluene, 40 min, reflux.

(iii) Several steps.

Scheme 50

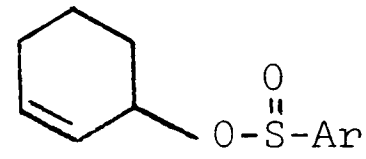


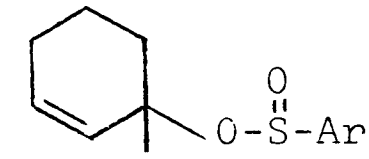
Ar = p-tolyl

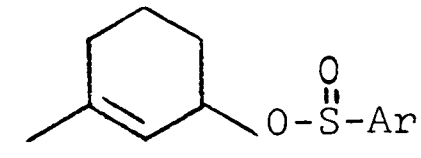
Scheme 51

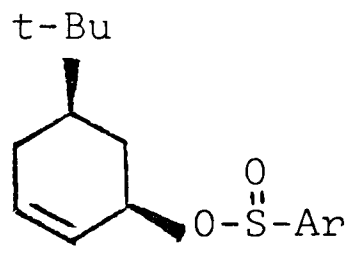
There has been no reported work on the rearrangement of alicyclic allylic sulphinate esters. Therefore it was decided to undertake a study of the rearrangement of sulphinate esters (17), (18), (46), (47), and (48). We had a special interest in the conformationally biased sulphinates (17) and (18), because a completely stereospecific rearrangement would provide a method for the preparation of the conformationally biased sulphones (19) and (20), which were required for experiments to be described in Section II of this thesis. Toluene-p-sulphinate esters were used because

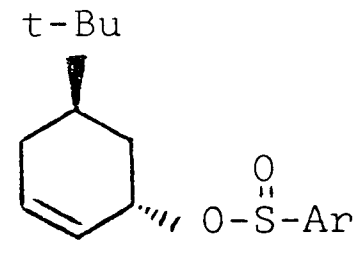
the chemical shifts of the aromatic protons, an AA'BB' system, are affected by the oxidation state of the sulphur atom, which facilitates the interpretation of the n.m.r. spectra.

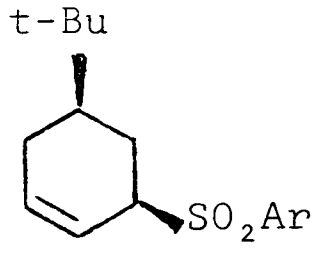

(46)


(47)


(48)


(17)


(18)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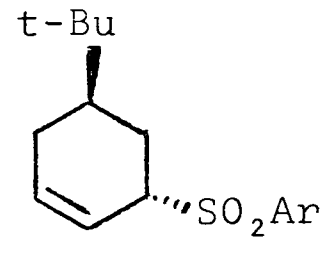
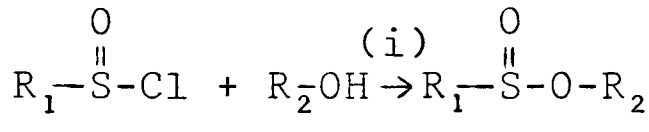

(20)

Ar = p-tolyl

2. Preparation of the Alicyclic Allylic Sulphinate Esters

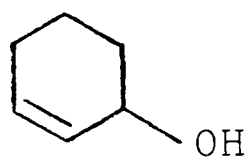
Sulphinate esters can be prepared by esterification of an alcohol by a sulphinyl chloride in the presence of a base, Scheme 52. Pyridine is often used as both solvent and base[45,47,49,50]. Milder conditions involve the use of an inert solvent (ether[54], THF[52], or a halogenated hydrocarbon[55]) with only one mole equivalent of base, often pyridine[54,55], at a low temperature.


(22)

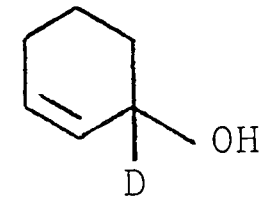
(i) Base.

Scheme 52

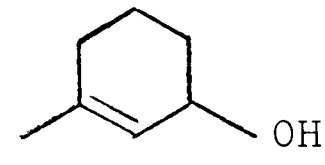
Standard methods were used to prepare the required alcohols (49)[56], (50)[57], (51)[57], and (52)[57]. The conformationally biased alcohols (53) and (54) were prepared by a route based on that developed by Chamberlain[56,58], Scheme 53.



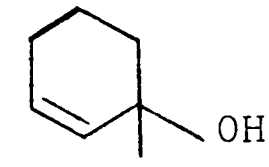
(49)



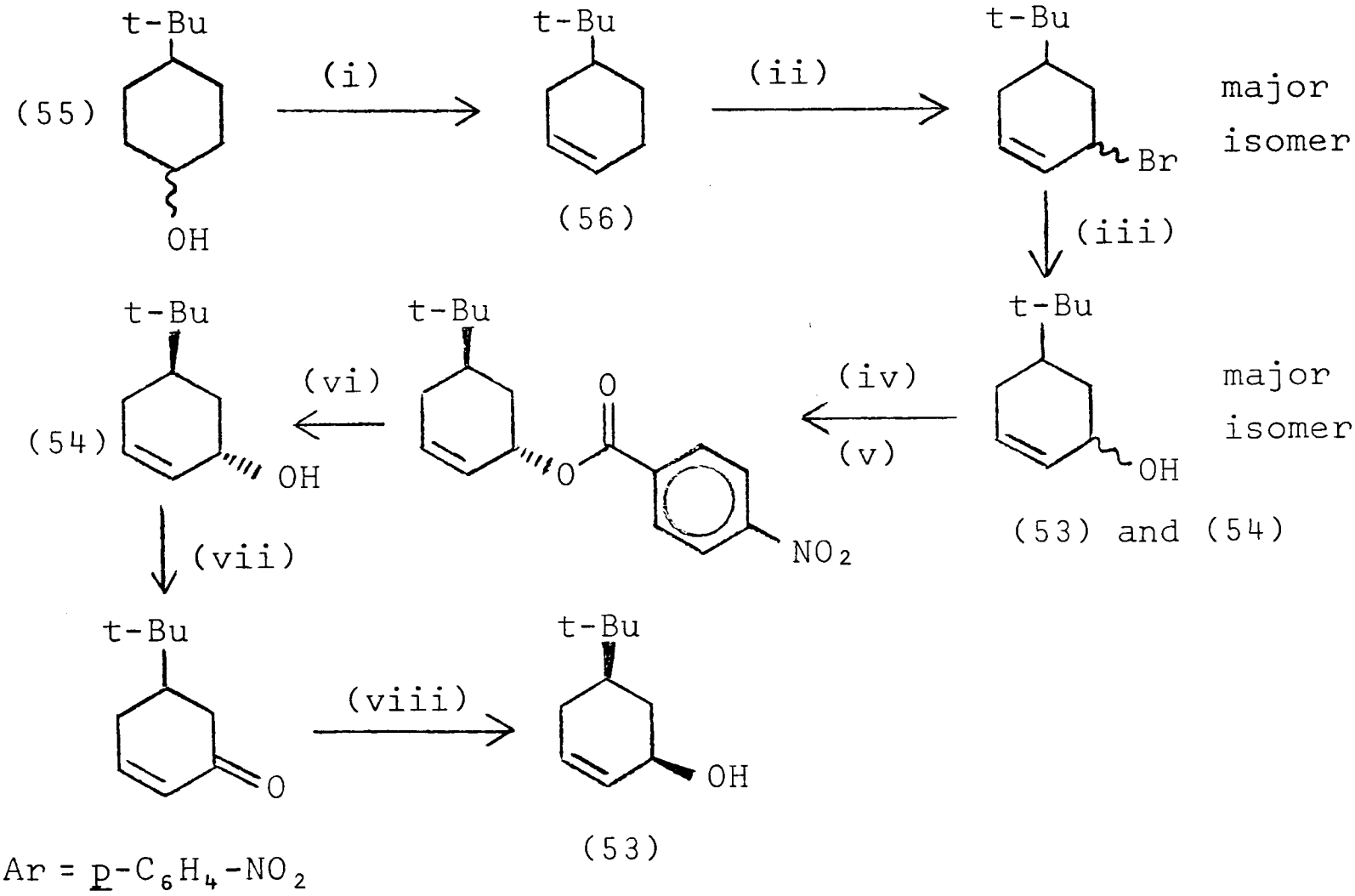
(50)



(51)



(52)

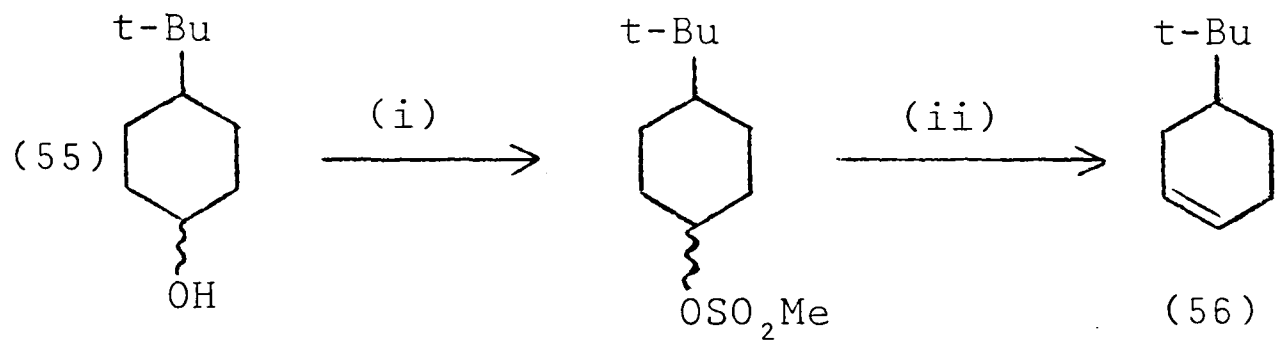


Ar = p-C_6H_4-NO_2

(i) Reflux over $KHSO_4$.
(ii) NBS, benzoyl peroxide, CCl_4, reflux.
(iii) $NaHCO_3$, aq. acetone, 1h, reflux.
(iv) ArCOCl, pyridine, 1h, room temperature.
(v) Recrystallise.
(vi) NaOH, aq. methanol, 30 min, reflux.
(vii) H_2CrO_4, acetone, 2h, room temperature.
(viii) $LiAlH_4$, ether, 10h, $-70^{o}C$.

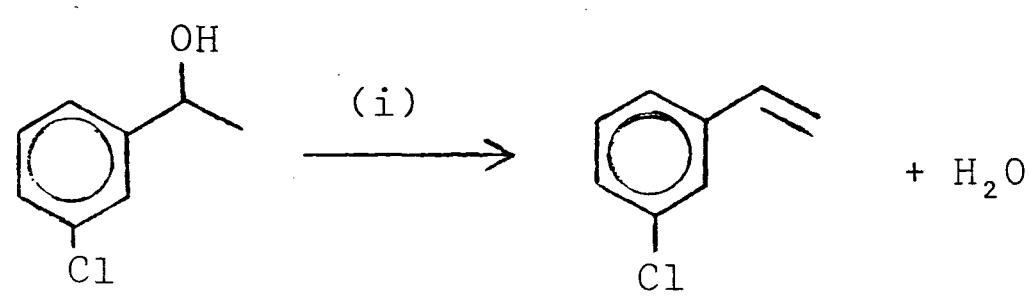
Scheme 53

Chamberlain[56] prepared the alkene (56) from the alcohol mixture (55) by the two-step sequence shown in Scheme 54. A more convenient one-stage procedure was developed, based on the method described by Overberger and Saunders[59] for the preparation of m-chlorostyrene (Scheme 55).



(i) $MeSO_2Cl$, pyridine, overnight at room temperature.
(ii) 2,4,6-Collidine, 2h, reflux.

Scheme 54



(i) Reflux over $KHSO_4$.

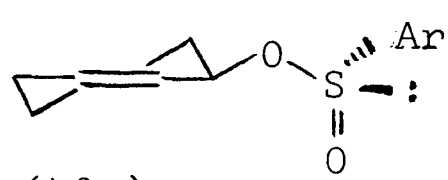
Scheme 55

The alcohols (49) and (51) were esterified at room temperature with toluene-p-sulphinyl chloride (57) to give the sulphinates (46) and (48) using pyridine as both solvent and base. Sulphinate (46) could be purified by column chromatography, but sulphinate (48) was unstable to silica gel.

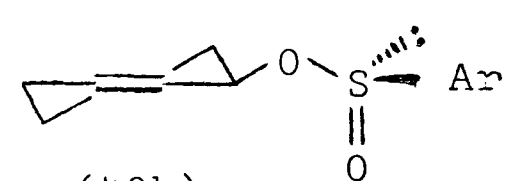
The alcohols (50), (53), and (54) were esterified with sulphinyl chloride (57) to give the sulphinates (47), (17), and (18) using a milder procedure. Dichloromethane was used as solvent, only one mole equivalent of pyridine

was present, and the reaction mixture was cooled on an acetone-dry ice bath.

The sulphinate esters (17), (18), (46), (47), and (48) were each shown by 300 MHz n.m.r. to be a 1:1 mixture of the two possible diastereoisomers. Each diastereoisomer had a different chemical shift for the olefinic protons, the difference being most marked for 2-H. Scheme 56 shows one enantiomer of each of the two diastereoisomers of sulphinate (46). It is not known which structure corresponds to which n.m.r. spectrum.



(46a)

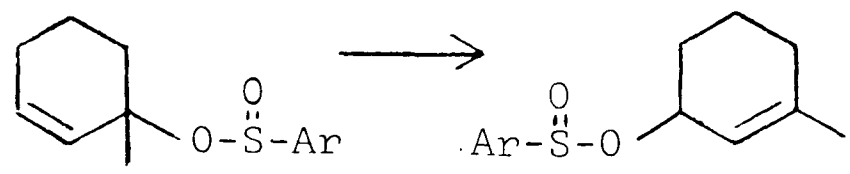


(46b)

Ar = p-tolyl

Scheme 56

Attempts to esterify alcohol (52) with sulphinyl chloride (57) using pyridine (1 mole eq.) in carbon tetrachloride resulted in mixtures of the desired sulphinate (58), sulphinate (48), and unchanged alcohol (52), see Experimental Section. A sample of sulphinate (58) was obtained, however, using the conditions with pyridine as solvent, but rearrangement to sulphinate (48) occurred within a few minutes at room temperature (Scheme 57).

(58) 

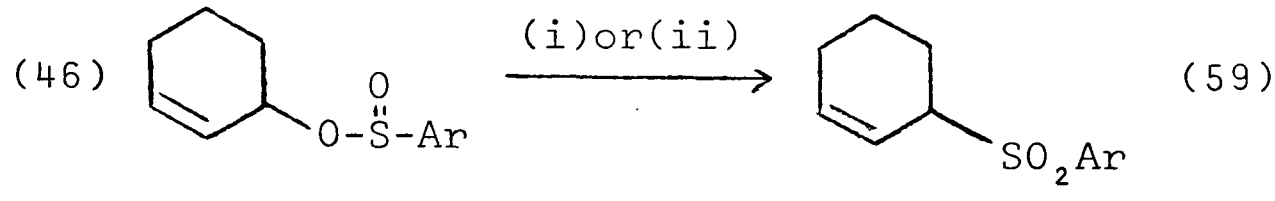
(48)

Ar = p-tolyl

Scheme 57

3. Rearrangement of the Alicyclic Allylic Sulphinate Esters in Dipolar Aprotic and Hydroxylic Solvents

Sulphinate (46) rearranged to sulphone (59) on heating in solution in either DMF or formamide, Scheme 58. In DMF the presence of 2,4,6-collidine was required to prevent side reactions, whereas in formamide the rearrangement proceeded cleanly in the absence of base.



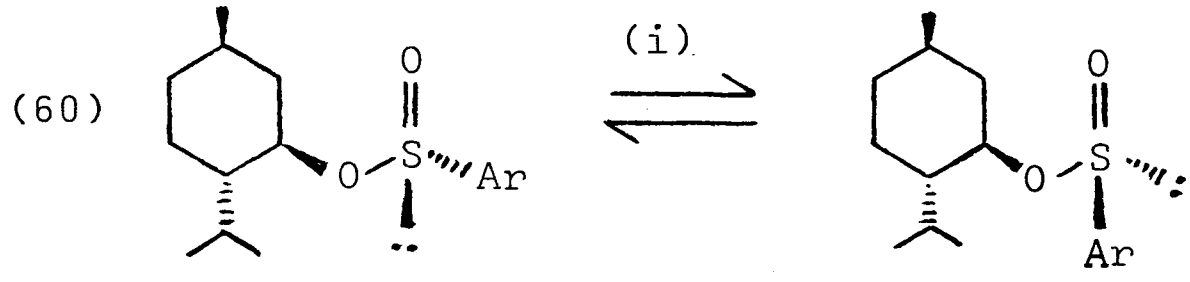
Ar = p-tolyl

(i) Formamide, 3.5h, ca. 80°C.
(ii) 2,4,6-Collidine (1 mole eq.), DMF, 49h, ca.80°C.

Scheme 58

Under mild conditions in formamide, the 1:1 mixture of diastereoisomers of sulphinate (46) was allowed to rearrange partially to the sulphone (59). The unreacted sulphinate (46) was still a 1:1 mixture of diastereoisomers. It is unlikely that sulphinate (46) epimerises *via* the sulphone (59) or by inversion at C-3, as discussed on p. 29. Furthermore, by analogy with the case of sulphinate (60) which epimerises by inversion at sulphur only in the presence of acid and chloride ion[60] (Scheme 59), it is unlikely that sulphinate (46) epimerises by inversion at sulphur. Therefore, since it may be assumed that sulphinate (46) does not epimerise under these formamide conditions, both diastereoisomers of the sulphinate (46) must rearrange to the sulphone at the same rate. In contrast, the analogous

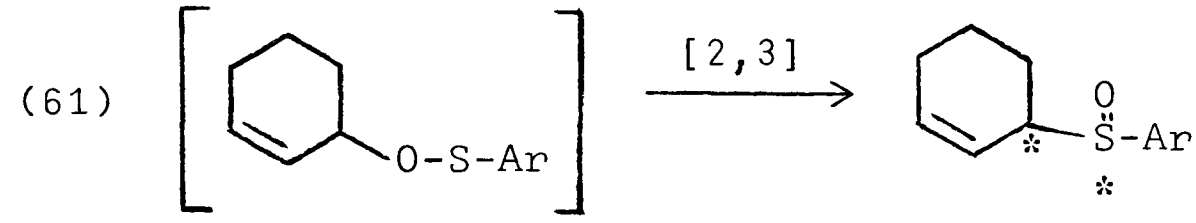
sulphenate ester (61) rearranges stereoselectively to give only one diastereoisomer of the sulphoxide (62) (Scheme 60), because there is a difference in stability between the diastereomeric transition states leading to the two diastereoisomers of the sulphoxide (62) (see p. 36 and 47).



Ar = p-C_6H_4-I

(i) HCl, NH_4Cl, nitrobenzene, 25°C.

Scheme 59



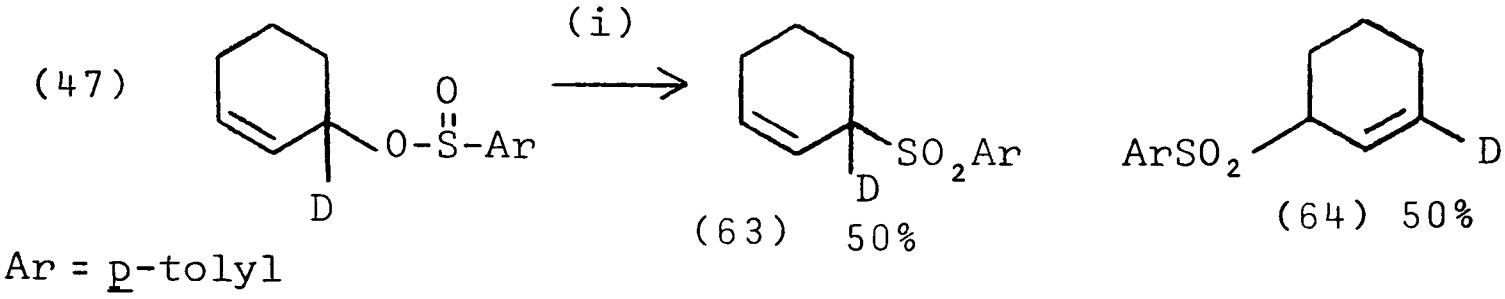
* chiral centre

Ar = p-tolyl

Scheme 60

On heating in formamide, sulphinate (47) rearranged to give an equilibrium mixture of sulphones (63) and (64), Scheme 61. Treatment of sulphinate (47) under milder formamide conditions gave a mixture of recovered sulphinate (47) and the sulphones (63) and (64). Since there was no deuterium scrambling between C-3 and C-1 starting with sulphinate (47), the rearrangement of sulphinate ester to sulphone is irreversible, which shows that epimerisation of the non-deuteriated sulphinate (46) via the allylic sulphone (59) does not occur. Since no sulphinate (65)

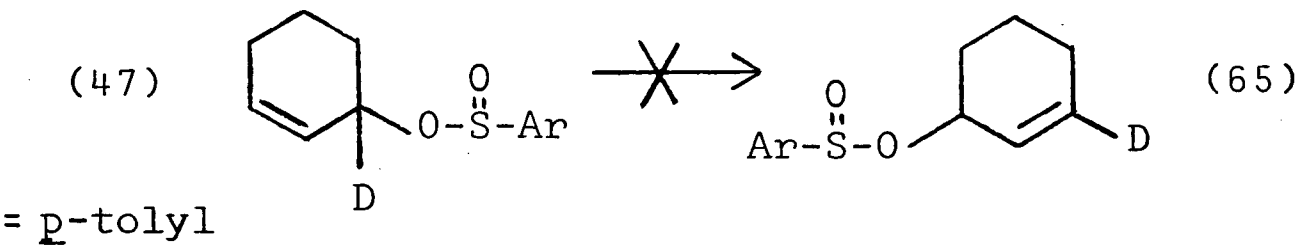
was detected (Scheme 62), this shows that sulphinate (46) does not epimerise at C-3 by a [3,3] rearrangement.



Ar = p-tolyl

(i) Formamide, 5h, 75°C.

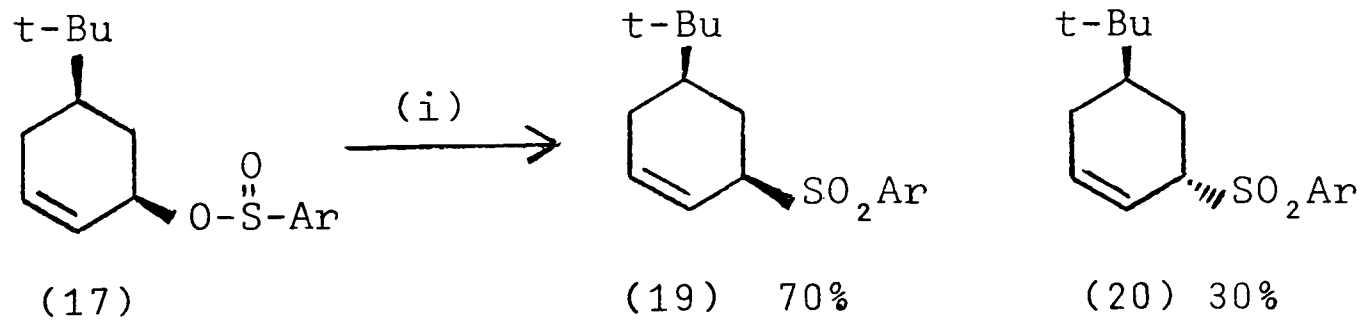
Scheme 61



Ar = p-tolyl

Scheme 62

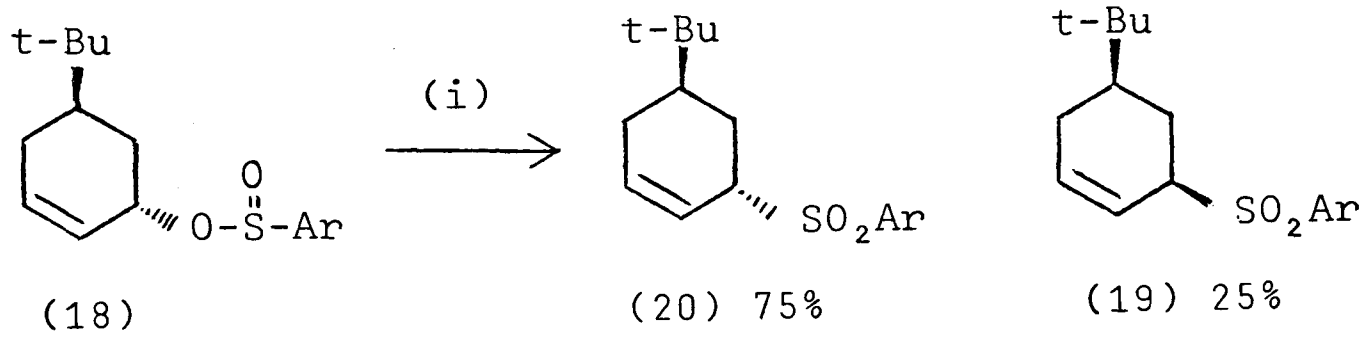
The conformationally biased allylic sulphinates (17) and (18) rearranged to the sulphones (19) and (20) with low stereospecificity on heating in formamide, Schemes 63 and 64. This approach therefore is not suitable for the preparation of diastereomerically pure sulphones (19) and (20). It was confirmed that the sulphones (19) and (20) did not epimerise under these conditions of formation.



Ar = p-tolyl

(i) Formamide, 5h, 80°C.

Scheme 63



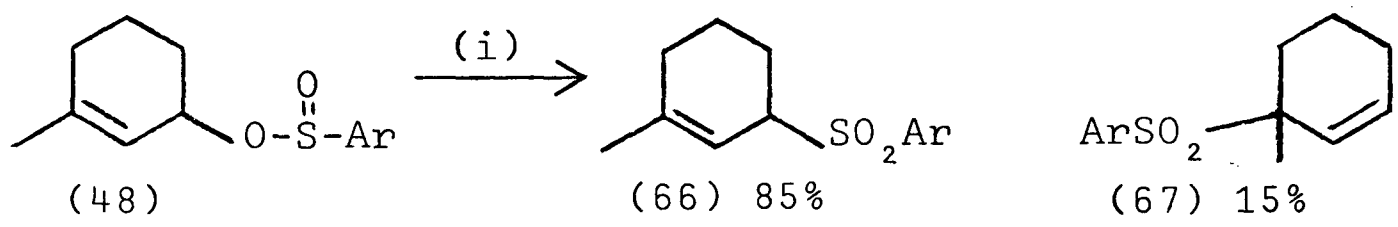
(18) (20) 75% (19) 25%

Ar = p-tolyl

(i) Formamide, 5h, 80°C.

Scheme 64

Heating sulphinate (48) in formamide resulted in a mixture of sulphones (66) and (67) (Scheme 65), the rate of reaction not being appreciably affected by the presence of hydroquinone. This rearrangement was faster than that of sulphinate (46) (Scheme 58). Thus, under conditions where sulphinate (48) had undergone 80% rearrangement, sulphinate (46) was unchanged. It was confirmed that sulphone (67) did not isomerise under these formamide conditions.



(48) (66) 85% (67) 15%

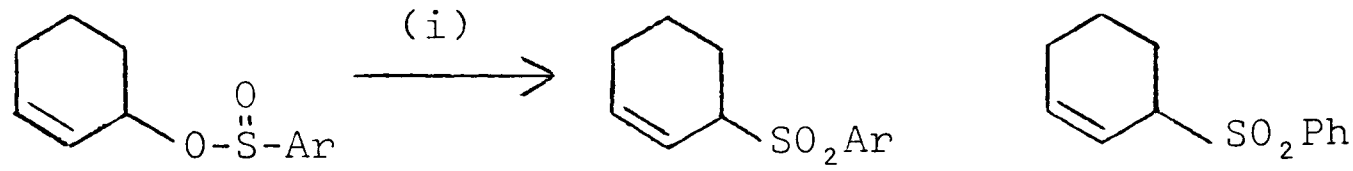
Ar = p-tolyl

(i) Formamide, 55°C.

Scheme 65

Scheme 66 shows the result of a crossover experiment in which sulphinate (46) was heated in formamide with sodium benzenesulphinate, less benzenesulphinate being incorporated than might be expected on a purely statistical basis. It was shown that benzenesulphinate was not incorporated into sulphone (59)

under these formamide conditions (c.f. Scheme 123, p. 69), which shows that the kinetic products were obtained in Scheme 66. Treatment of sulphinate (46) with sodium benzenesulphinate (1 mole eq.) in formamide for 45 min at 55°C lead to the recovery of unchanged sulphinate (46), no benzenesulphinate being incorporated as the sulphinate ester (69).

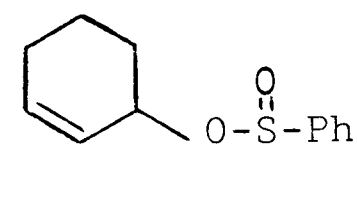


(46) (59) 65% (68) 35%

Ar = p-tolyl

(i) $PhSO_2Na$ (1 mole eq.), formamide, 3h, 105°C.

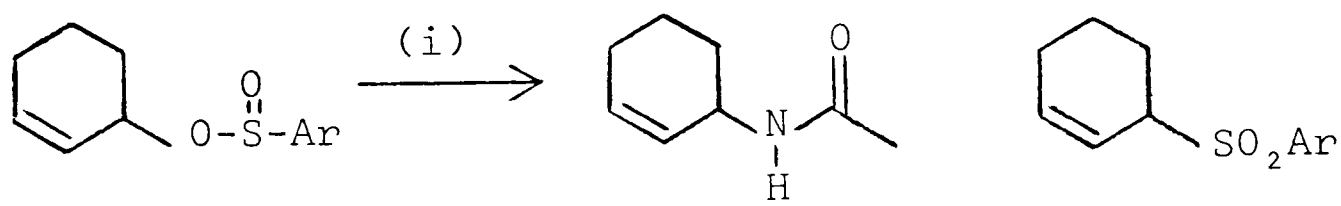
Scheme 66



(69)

Similar crossover experiments were performed with sulphinate (48) and sodium benzenesulphinate, the benzenesulphinate again being incorporated into the sulphone products.

Scheme 67 shows the result of heating sulphinate (46) in acetonitrile. The amide (70), which is a major product, could be produced by trapping of a carbocation by the solvent, such reactions being well established (Scheme 68)[61].

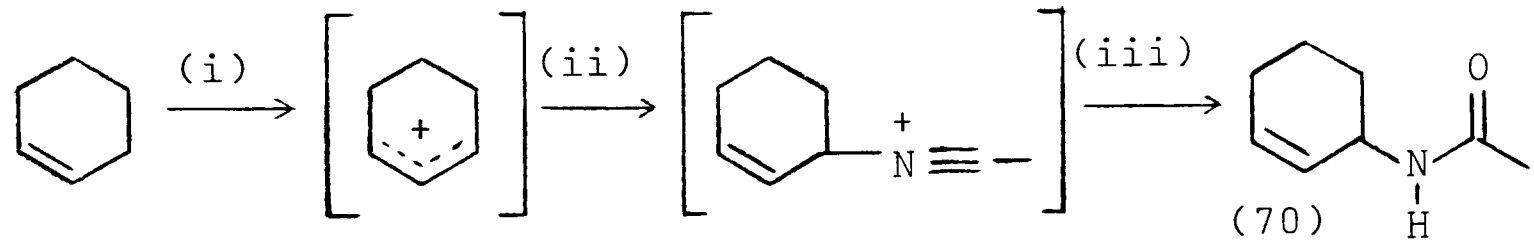


(46) (70) 35% (59) 15%

Ar = p-tolyl

(i) MeCN, 1.5h, 60°C.

Scheme 67

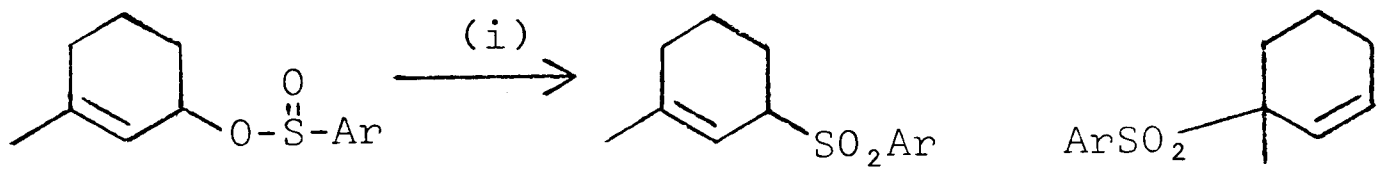


(70)

(i) Anodic oxidation.
(ii) MeCN.
(iii) Water.

Scheme 68

In the treatment of sulphinate esters with hydroxylic solvents, there is the possibility of a reaction competing with rearrangement to sulphone in which S-O bond cleavage occurs and the solvent is incorporated into the products (see p. 16). Treatment of sulphinate (48) with aqueous acetic acid gave a mixture of sulphones (66) and (67) (Scheme 69), no hydrolysis products being formed. Thus in this case, the rate of rearrangement to sulphones must be greater than the rate of hydrolysis.



(48) (66) ca.85% (67) ca.15%

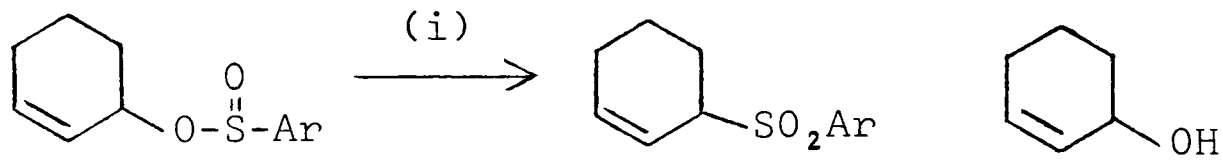
Ar = p-tolyl

(i) AcOH - water (3:2 v/v), 30 min, 50°C.

Scheme 69

Similar treatment of sulphinate (46), however, gave a mixture of sulphone (59) and alcohol (49) (Scheme 70), any toluene-p-sulphinic acid also produced being lost in the work up. Reactions via the carbocation formed from sulphinate (48)

by C-O bond cleavage should occur more readily than those via the less stable carbocation derived from sulphinate (46). Since hydrolysis of sulphinate (46) is favoured, sulphinate (48) giving only sulphones in aqueous acetic acid, hydrolysis must occur by S-O rather than C-O bond cleavage. Assuming the rates of solvent promoted S-O bond cleavage of sulphinates (46) and (48) are comparable, it may be concluded that sulphinate (48) rearranges to sulphones more rapidly in aqueous acetic acid than sulphinate (46) does, as is the case for rearrangement in formamide.



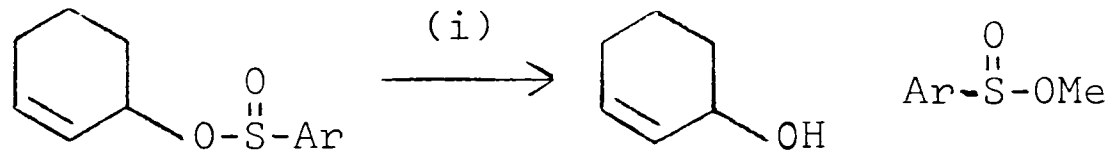
(46) (59) 55% (49) 35%

Ar = p-tolyl

(i) AcOH - water (3:2 v/v), 45 min, 105°C.

Scheme 70

Treatment of sulphinate (46) with methanol gave no sulphone (59), but only products resulting from S-O bond cleavage and solvent incorporation, Scheme 71.



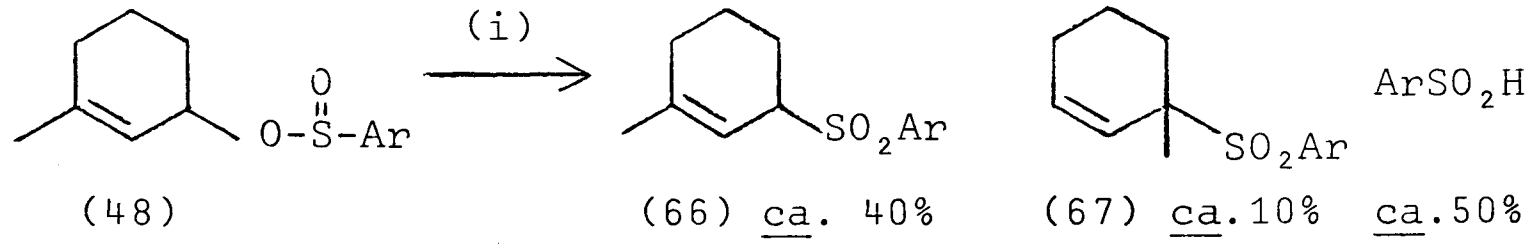
(46) (49) 40% 60%

Ar = p-tolyl

(i) Methanol, 68h, room temperature.

Scheme 71

In contrast, treatment of sulphinate (48) with methanol afforded a mixture of toluene-p-sulphinic acid and sulphones (66) and (67), Scheme 72. It is possible in this particular case that the reaction competing with rearrangement to sulphones is not methanolysis resulting in S-O bond cleavage, but rather elimination of toluene-p-sulphinic acid to give dienes which are lost on work up (see p. 39).



(48) (66) ca. 40% (67) ca. 10% ca. 50%

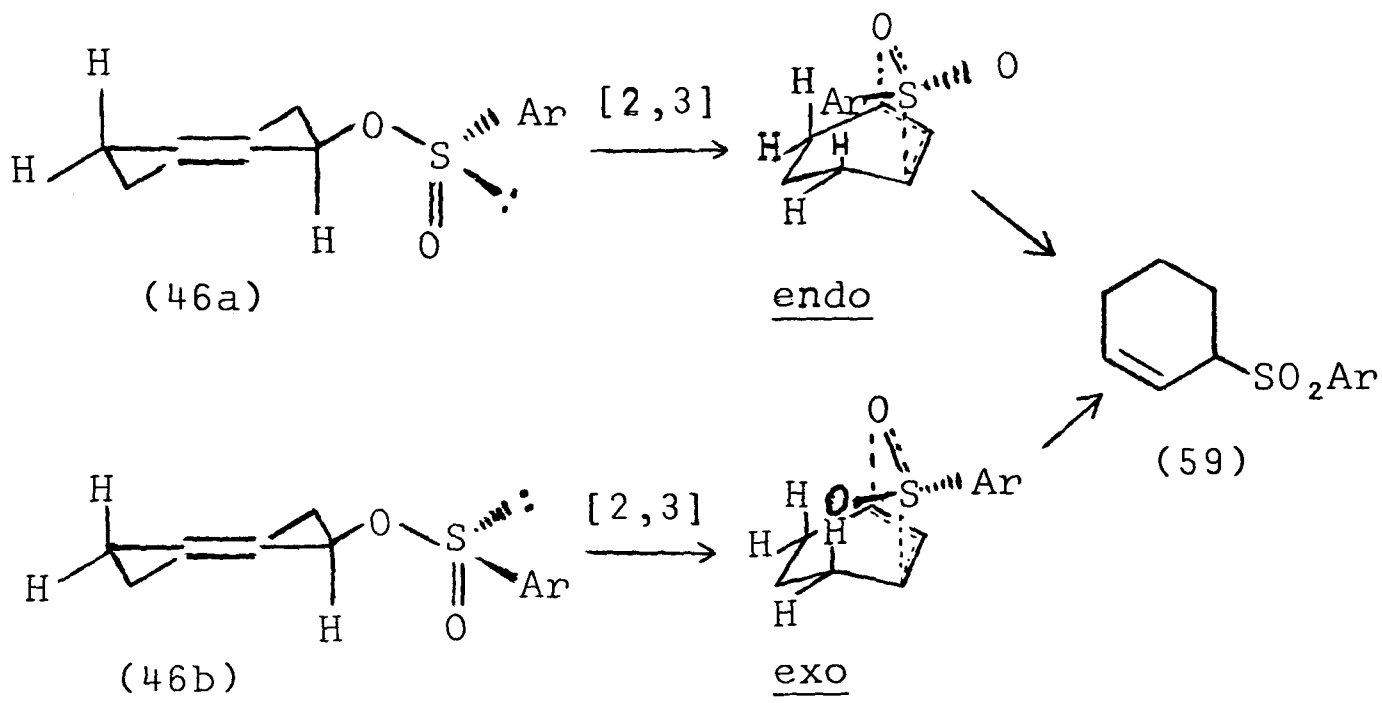
Ar = p-tolyl

(i) Methanol, 30 min, reflux.

Scheme 72

Considering the results presented in this Section, it may be concluded that the rearrangement of the alicyclic allylic sulphinate esters (17), (18), (46), (47), and (48) to the sulphones in polar solvents does not occur by the concerted electrocyclic [2,3] process shown in Scheme 48. Such a concerted process would be stereospecific, whereas scrambling occurs (Schemes 61, 63, 64, and 65). Also, incorporation of benzenesulphinate (Scheme 66) and acetonitrile (Scheme 67) would not occur. Furthermore, by analogy with the [2,3] rearrangement of sulphenate ester (61) (Scheme 60), in which there is a difference in stability between the diastereomeric transition states leading to the two diastereoisomers of sulphoxide (62) (see p. 47), it is to be expected that similar effects occur in the

diastereomeric transition states for a [2,3] rearrangement of the two diastereoisomers of sulphinate (46). Scheme 73 shows the cause of steric destabilisation in the endo transition state, the aromatic ring coming into close proximity to 4-H and 6-H (c.f. p. 48). Since within experimental error the diastereoisomers of sulphinate (46) rearrange at the same rate, a [2,3] electrocyclic process cannot be in operation.

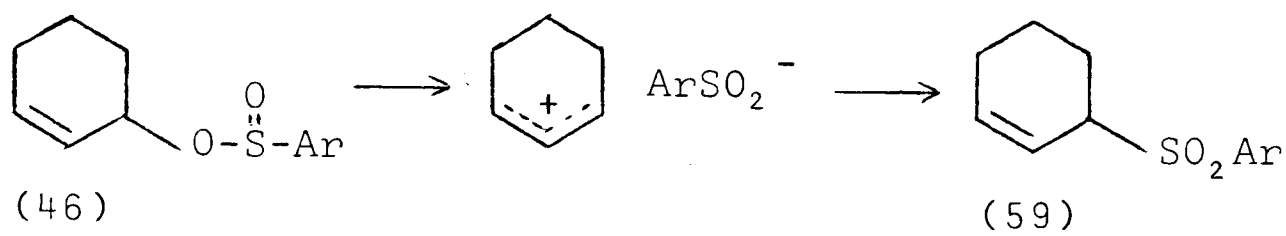


Ar = p-tolyl

Only one enantiomer is drawn.

Scheme 73

Clearly a dissociative rather than a concerted process is occurring. It is unlikely that a radical chain reaction is operating since the rearrangement of sulphinate (48) in formamide is not quenched by hydroquinone. The dissociative process is more likely to involve ions (Scheme 74) than free radicals, both because polar solvents favour the reaction, and because sulphinate (48), which would form the more stable carbocation, rearranges faster than sulphinate (46).



(46) (59)

Ar = p-tolyl

Scheme 74

It seems unlikely that the ions are fully dissociated, both because the conformationally biased sulphinates (17) and (18) do rearrange with some measure of stereospecificity (Schemes 63 and 64), and because the degree of incorporation of benzenesulphinate shown in Scheme 66 is less than 50%. The rearrangement probably occurs *via* an ion-pair, the degree of intimacy depending on the particular sulphinate ester and the solvent used. It is possible, however, that a different mechanism operates for rearrangement in low polarity solvents.

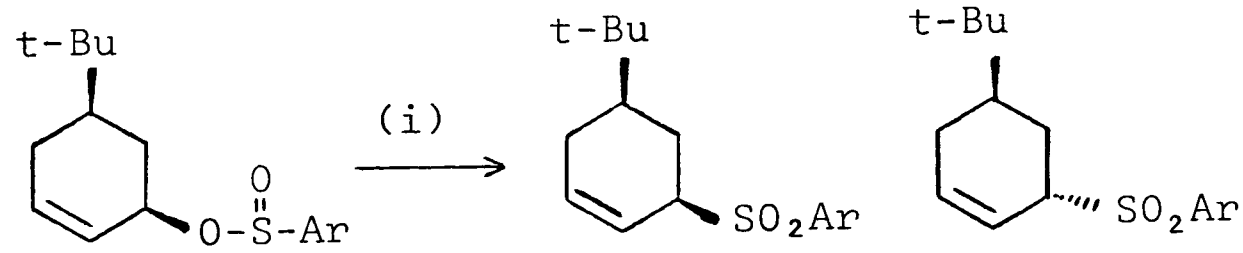
This conclusion, that allylic sulphinate esters (17), (18), (46), (47), and (48) rearrange in polar solvents by a dissociative ionic mechanism similar to that proposed for the rearrangement of benzylic sulphinates (see p. 16), should be contrasted with the suggestion by Braverman[44] that allylic sulphinates of general structure (38) rearrange by a cyclic intramolecular mechanism (Scheme 44).

4. Rearrangement of the Alicyclic Allylic Sulphinate Esters in Low Polarity Solvents

The rearrangement of the sulphinate esters (17), (18), (46), (47), and (48) to the sulphones was somewhat capricious

when it occurred in solution in toluene, chloroform, or carbon tetrachloride. Often an induction period was required before any rearrangement was observed, the duration of which was greatly affected by the purity of the sulphinate ester. Both toluene-p-sulphonic acid and zinc chloride increased the rate of reaction, whereas the bases 2,4,6-collidine and DBU stabilised the sulphinates to such an extent that in some experiments rearrangement was completely prevented.

Sulphinate (46) rearranged to sulphone (59) under these conditions, but the deuteriated analogue (47) was stable in chloroform, requiring the presence of toluene-p-sulphonic acid to promote rearrangement to give a mixture of sulphones (63) and (64). The conformationally biased sulphinates (17) and (18) each gave a 1:1 mixture of the sulphones (19) and (20) on rearrangement in carbon tetrachloride (Schemes 75 and 76), a result which should be compared with the partially stereospecific rearrangement which occurs in formamide (Schemes 63 and 64). Scrambling also occurred on rearrangement of sulphinate (48) in chloroform or carbon tetrachloride (Scheme 77).

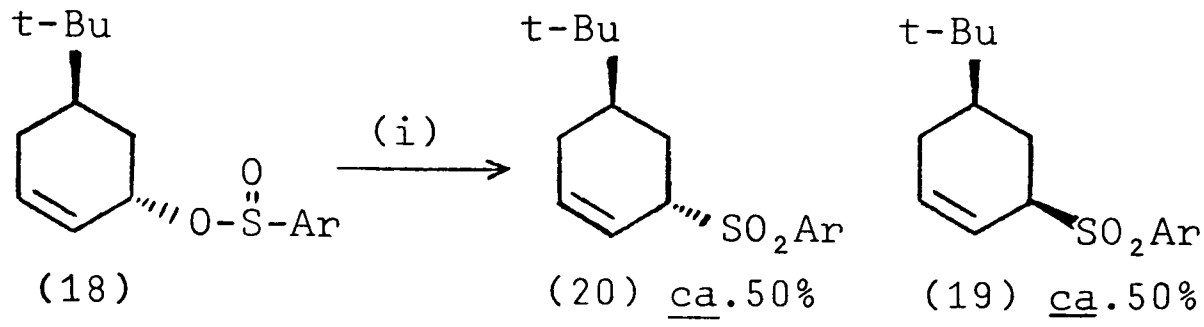


(17) (19) ca.50% (20) ca.50%

Ar = p-tolyl

(i) CCl_4, 18 weeks, room temperature.

Scheme 75

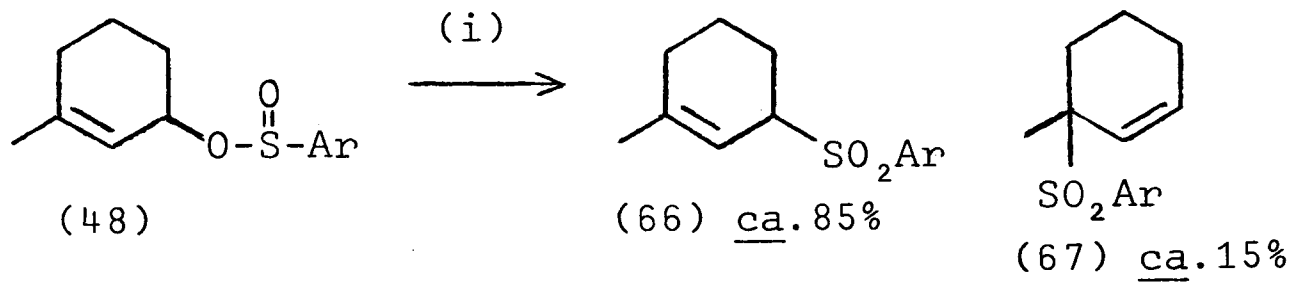


(18) (20) ca.50% (19) ca.50%

Ar = p-tolyl

(i) CCl_4, 17 days, room temperature.

Scheme 76



(48) (66) ca.85% (67) ca.15%

Ar = p-tolyl

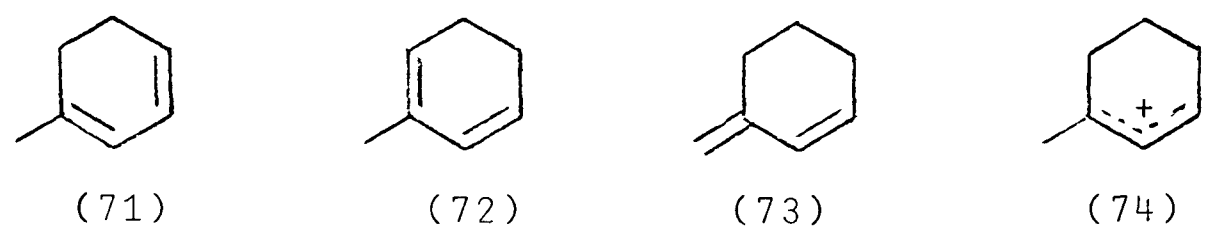
(i) CCl_4 or $CDCl_3$, room temperature.

Scheme 77

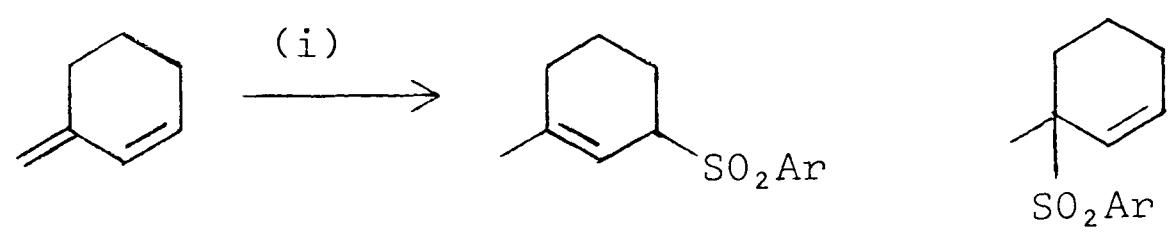
It may be concluded that again a concerted [2,3] mechanism is not occurring, even though these low polarity solvents might be expected to favour such a process. Clearly a dissociative mechanism resulting in scrambling is in operation.

During the rearrangement of sulphinate (48) in solution in chloroform or carbon tetrachloride (Scheme 77), the build up and subsequent decay of diene intermediates was observed by n.m.r. These intermediates were shown to be a mixture of some or all of the dienes (71), (72), and (73) (see Experimental Section), which presumably were formed by deprotonation of the allylic cation (74) derived from

sulphinate (48). Under similar conditions toluene-p-sulphinic acid reacted with diene (73) (Scheme 78), and with a mixture of dienes (71), (72), and (73), to give the sulphones (66) and (67).



(71) (72) (73) (74)



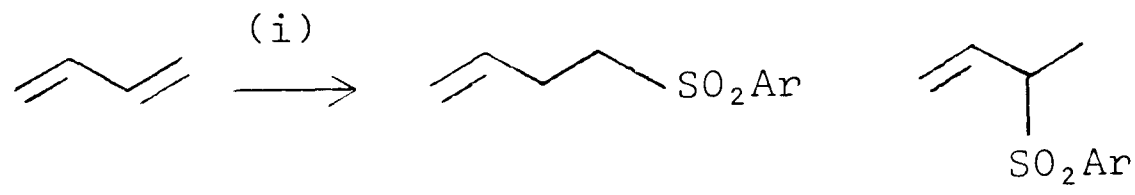
(73) (66) 85% (67) 15%

Ar = p-tolyl

(i) $ArSO_2H$, $CDCl_3$, 18h, room temperature.

Scheme 78

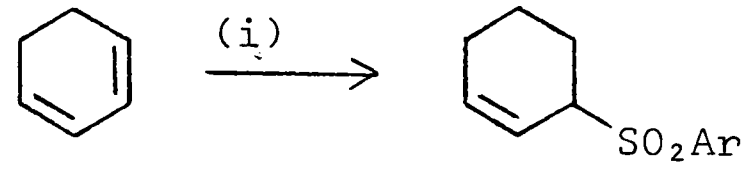
Attempts were made to add toluene-p-sulphinic acid to a variety of alkenes under these conditions (see Experimental Section), but no sulphones were produced. There have been no reports in the literature of such reactions under similar conditions. In the presence of a palladium catalyst, however, sulphinic acids can be added to dienes to give sulphones (Schemes 79 and 80)[62,63].



Ar = Ph or p-tolyl

(i) $ArSO_2H$ (1 mole eq.), $ArSO_2Na$ (0.05 mole eq.), di-π-allylpalladium chloride (0.01 mole eq.), PPh_3 (0.1 mole eq.), THF, 18h, 45°C.

Scheme 79



(59)

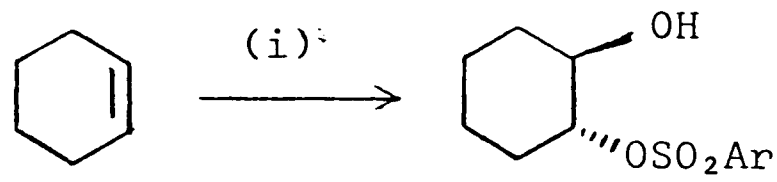
Ar = p-tolyl

(i) $ArSO_2H$ (0.33 mole eq.), palladium acetylacetate reduced with $AlEt_3$, PPh_3, toluene - water (2:1 v/v).

Scheme 80

It seems therefore that both the production of diene intermediates from the sulphinate ester (48) and the addition of toluene-p-sulphinic acid to dienes (71), (72), and (73) is specific to this system, presumably because the allylic cation (74) is exceptionally stable, perhaps because of the pattern of substitution.

Since zinc chloride catalysed the rearrangement of allylic sulphinate esters to sulphones in these low polarity solvents, attempts were made to react toluene-p-sulphinic acid with simple olefins in its presence. No reaction occurred with cyclohexene or styrene in the absence of air, but in air compounds (75), (76), and (77) were formed (Schemes 81 and 82), see Experimental Section. A possible mechanism for this reaction (Scheme 83) involves the intermediacy of a persulphonic acid (78), which is claimed[64] to be an intermediate capable of epoxidising olefins. Ring opening of cyclohexene oxide with toluene-p-sulphonic acid, which is a known reaction[65], gives the product (75).

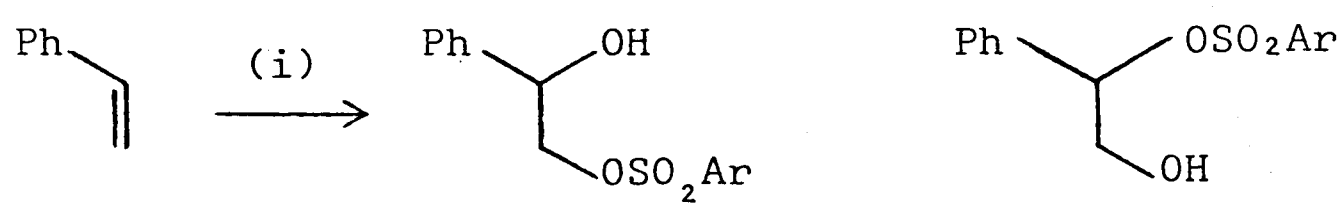


(75)

Ar = p-tolyl

(i) $ArSO_2H$ (1 mole eq.), $ZnCl_2$ (0.1 mole eq.), air, CCl_4-$CHCl_3$ (2:1 v/v), 40h, room temperature.

Scheme 81



(76) 65%

(77) 35%

Ar = p-tolyl

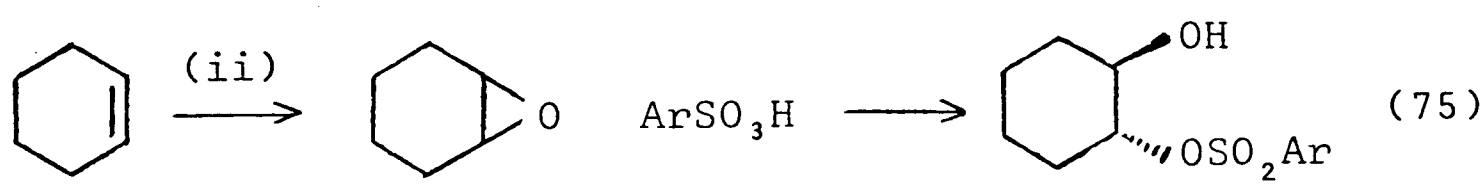
(i) $ArSO_2H$ (1 mole eq.), $ZnCl_2$ (0.1 mole eq.), air, $CHCl_3$, 20h, room temperature.

Scheme 82

(i)

$ArSO_2H \rightarrow ArSO_4H$

(78)



(75)

Ar = p-tolyl

(i) Air, $ZnCl_2$ (?).

(ii) $ArSO_4H$.

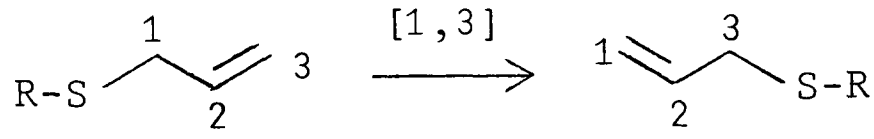
Scheme 83

SECTION II

REARRANGEMENT OF ALLYLIC SULPHONES

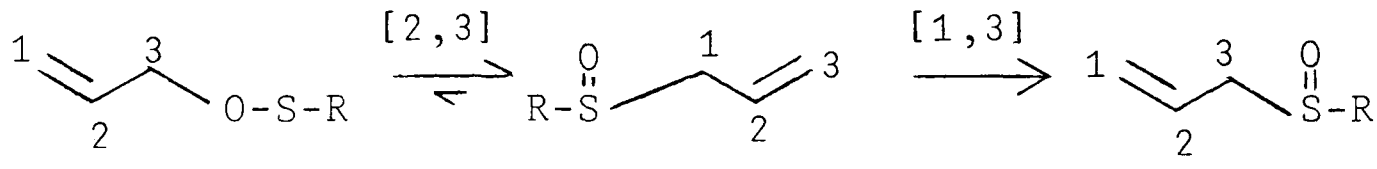
1. Introduction

The thia-allylic shift of allylic sulphides is a [1,3] migration of the thinyl group resulting in allylic reversal, Scheme 84. The rearrangement, which may be induced thermally, photochemically, or by the presence of either a radical source or a Lewis acid, has been reviewed by Lin[33], and access to the literature is provided by ref. 66.



Scheme 84

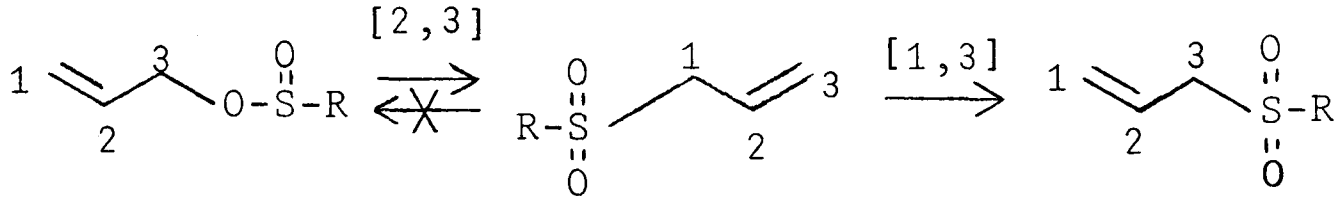
Allylic sulphoxides can undergo two rearrangements, Scheme 85. Firstly, an allylic sulphoxide can participate in a rapid mobile equilibrium with a sulphenate ester *via* a concerted electrocyclic [2,3] process[7,8,9] (Scheme 49). Secondly, allylic sulphoxides may undergo a [1,3] migration of the sulphinyl group resulting in allylic reversal[67,68]. Both of these reactions have been discussed by Lin[33].



Scheme 85

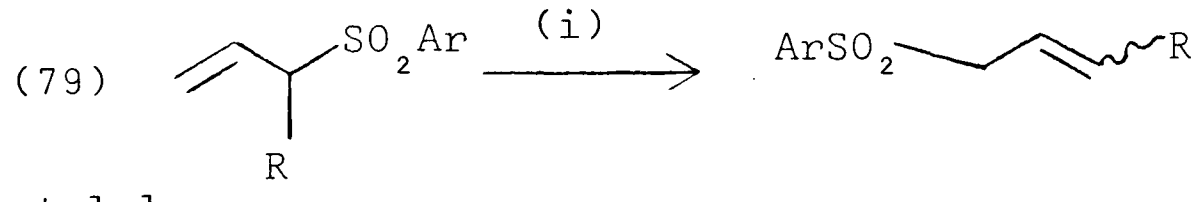
In principle, by analogy with the case of allylic sulphoxides, allylic sulphones could also undergo two possible rearrangements, Scheme 86. There are no reported examples of the [2,3] rearrangement to the sulphinate ester, although the reverse reaction, the isomerisation of an

allylic sulphinate ester to a sulphone, is well established (see Section I). Until recently only a few scattered examples[9,14(c),68,69] were known of [1,3] sulphonyl group migration leading to allylic reversal. The recent report by Kocienski[70] on such [1,3] migrations prompted the publication of a communication[71] summarising the study by Lin[33] which will be discussed below.



Scheme 86

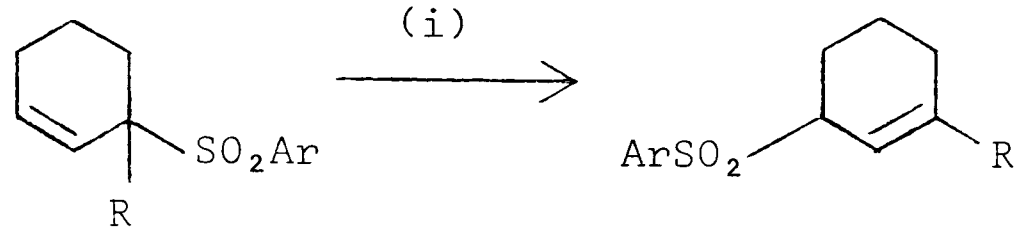
Lin[33] established three types of conditions which could be used to promote [1,3] rearrangement of allylic sulphones, the constitution of the sulphone determining which conditions to use. Radical conditions, treatment with benzoyl peroxide in refluxing carbon tetrachloride, caused sulphones of general structure (79) and (80) to rearrange (Scheme 87). Sulphones of structure (81) rearranged on heating in aqueous acetic acid (Scheme 88). Sulphones of types (79) and (80) were stable to heating in aqueous acetic acid, but rearranged if sodium toluene-p-sulphinate was present (Scheme 89).



Ar = p-tolyl

(i) Benzoyl peroxide, CCl_4, 18h, reflux.

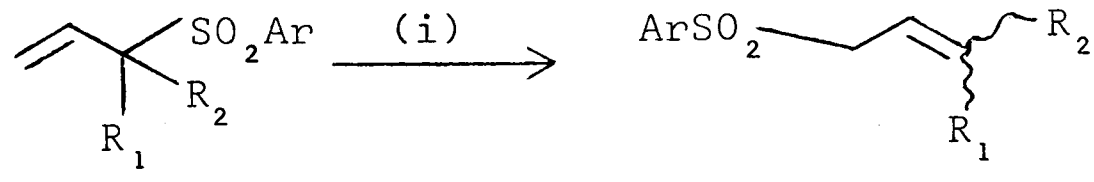
Scheme 87

(81) 

Ar = p-tolyl

(i) AcOH - water (3:2 v/v), 8h, 100°C.

Scheme 88

(80) 

Ar = p-tolyl

(i) $ArSO_2Na$ (0.1 to 7 mole eq.), AcOH - water (3:2 v/v), 8h, 100°C.

Scheme 89

This Section of the thesis is concerned with a continuation of the investigation undertaken by Lin[33] of the [1,3] rearrangement of allylic sulphones in aqueous acetic acid, particularly in the presence of sodium toluene-p-sulphinate. The preparation of the required conformationally biased sulphones (19) and (20) and their α-deuteriated analogues is described first.

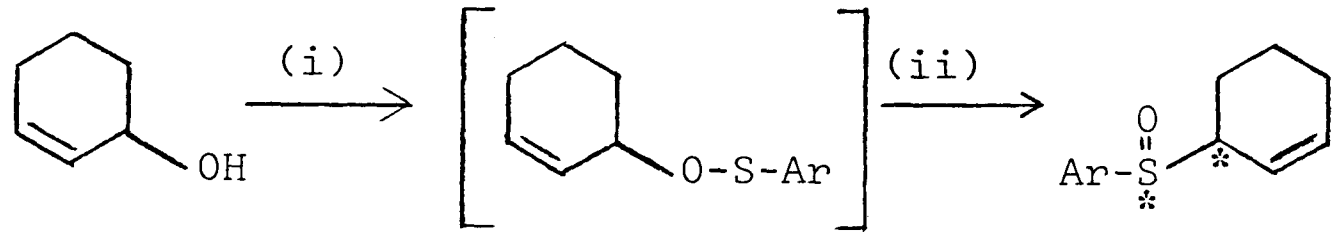
2. Preparation of some Alicyclic Allylic Sulphones

(a) Preparation via the Sulphenate Ester

Since the rearrangement of the conformationally biased sulphinate esters (17) and (18) was not completely stereo-

specific (Schemes 63 and 64), an alternative route to the one originally envisaged had to be developed for the preparation of the sulphones (19) and (20). One possibility was to exploit the well established concerted nature[7,9] of the [2,3] rearrangement of an allylic sulphenate ester to a sulphoxide (Schemes 49 and 60), which often occurs at room temperature[7,72]. The sulphoxide obtained could then be oxidised to the desired sulphone.

As a model for the stereospecific conversion of alcohols (53) and (54) to sulphones (19) and (20), sulphone (59) was prepared *via* the sulphenate ester (61). The base used to promote esterification of alcohol (49) by toluene-*p*-sulphenyl chloride was triethylamine[72] (Scheme 90), rather than the commonly used n-butyl-lithium[7]. The sulphenate ester (61) was not isolated, but underwent rearrangement *in situ* (Scheme 90) to give the sulphoxide (62), which was oxidised to the sulphone (59) by hydrogen peroxide in acetic acid (Scheme 91) using a standard method[33]. Undesired epoxidation of the allylic sulphone (59) occurred if excess oxidant was used.



(49) (61) (62)

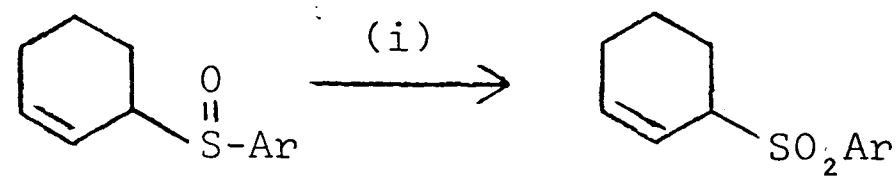
Ar = *p*-tolyl

* chiral centre.

(i) ArSCl (1 mole eq.), NEt_3 (1 mole eq.), CH_2Cl_2, 15 min, room temperature.

(ii) [2,3] rearrangement.

Scheme 90



(62) (59)

Ar = p-tolyl

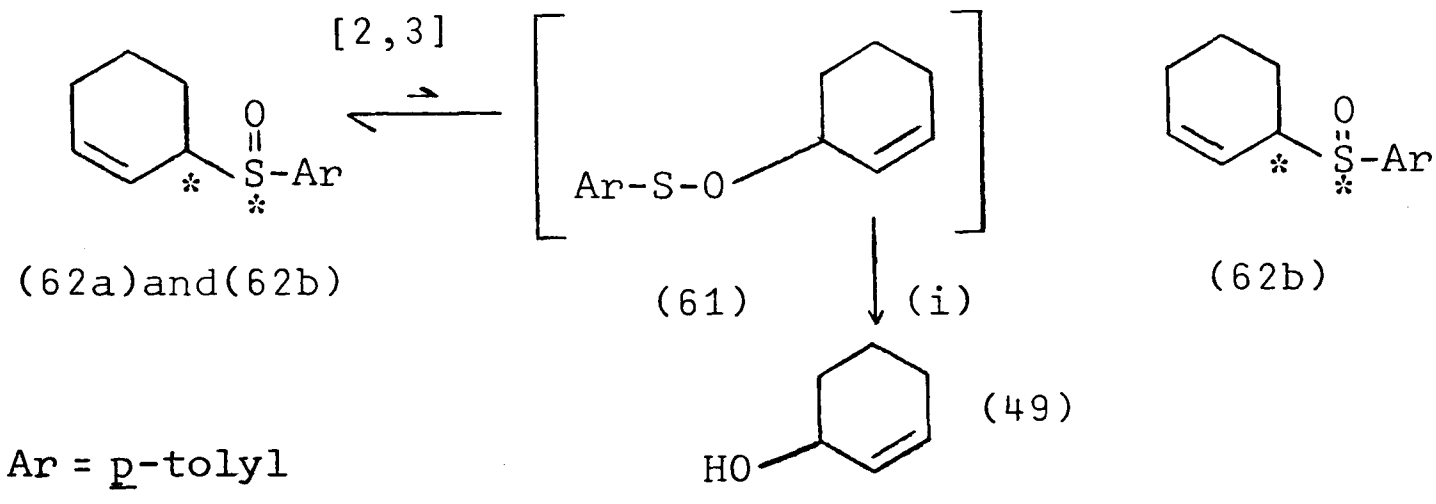
(i) H_2O_2 (2 mole eq.), AcOH, 20h, ca. 30°C.

Scheme 91

A point of interest relating to the [2,3] rearrangement of the sulphenate (61) is that it occurred stereoselectively to produce only one diastereoisomer (62a) of the sulphoxide. Examples of stereoselectivity in the reverse reaction, the rearrangement of an allylic sulphoxide to a sulphenate ester, are given in refs. 7 and 73.

The other diastereoisomer (62b) of the sulphoxide was prepared by Russell[74]. The diastereoisomers (62a) and (62b) could be distinguished by the n.m.r. signals of the olefinic protons. Russell prepared a mixture of diastereoisomers (62a) and (62b) by oxidation of the corresponding sulphide, and treated this mixture with the thiophile trimethylphosphite to intercept any sulphenate ester (61) produced from the sulphoxides[8]. Conditions were established under which the more reactive diastereoisomer (62a) was consumed via the sulphenate ester (61), leaving the less reactive diastereoisomer (62b), Scheme 92. Scheme 93 shows the diastereomeric transition states linking the sulphenate ester (61) and the two diastereoisomers of the sulphoxide (62). Russell suggests that the endo transition state is sterically destabilised by

the aromatic ring coming into close proximity to 4-H and 6-H (<u>c.f.</u> p. 36). Hence the less reactive diastereoisomer (62b) would have the structure shown in Scheme 93.

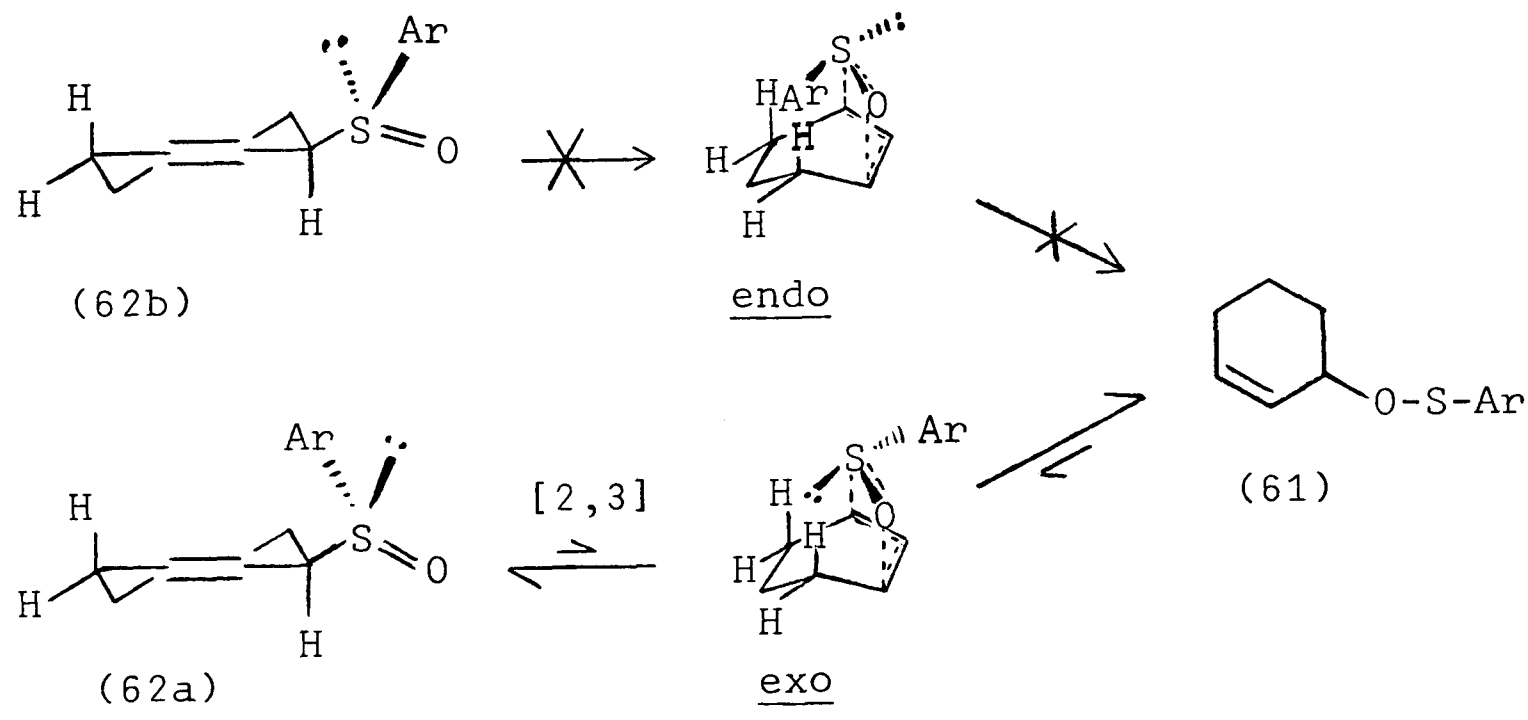


Ar = <u>p</u>-tolyl

* chiral centre

(i) $P(OMe)_3$ (4 mole eq.), MeOH, 20h, reflux.

<u>Scheme 92</u>



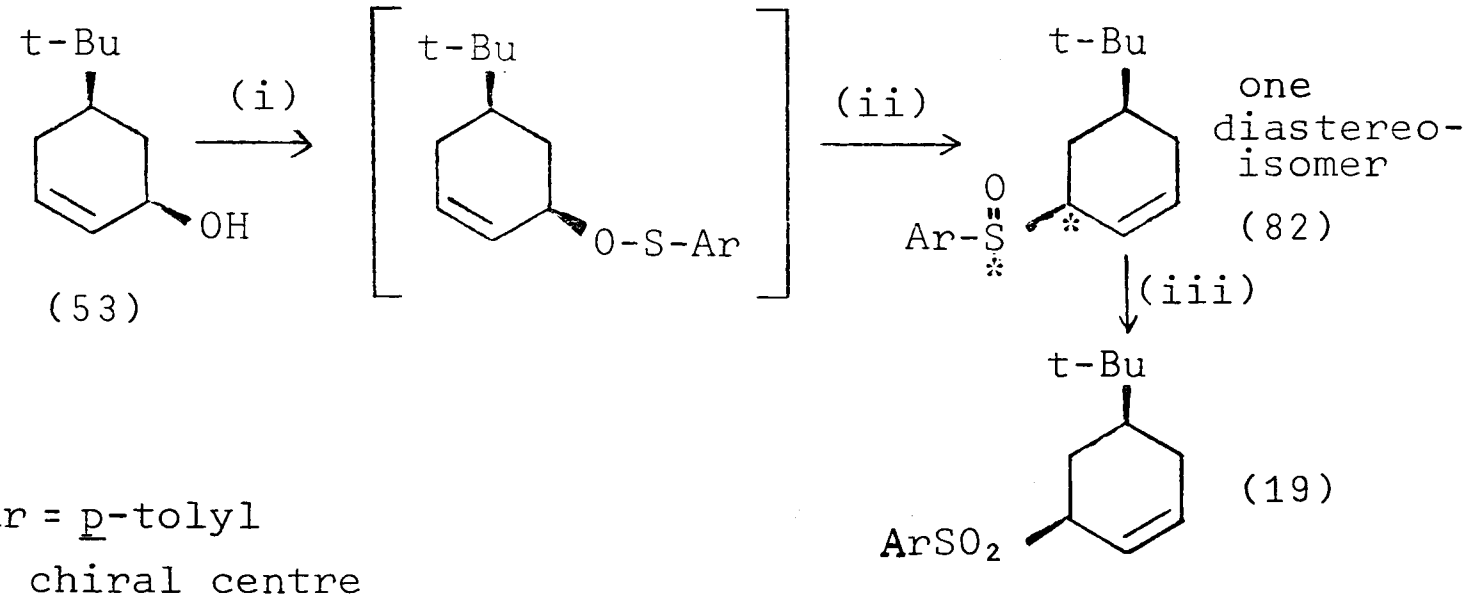
Ar = <u>p</u>-tolyl

Only one enantiomer is drawn.

<u>Scheme 93</u>

Sulphones (19) and (20) were prepared using the route developed with sulphone (59), Schemes 94 and 95. Again the

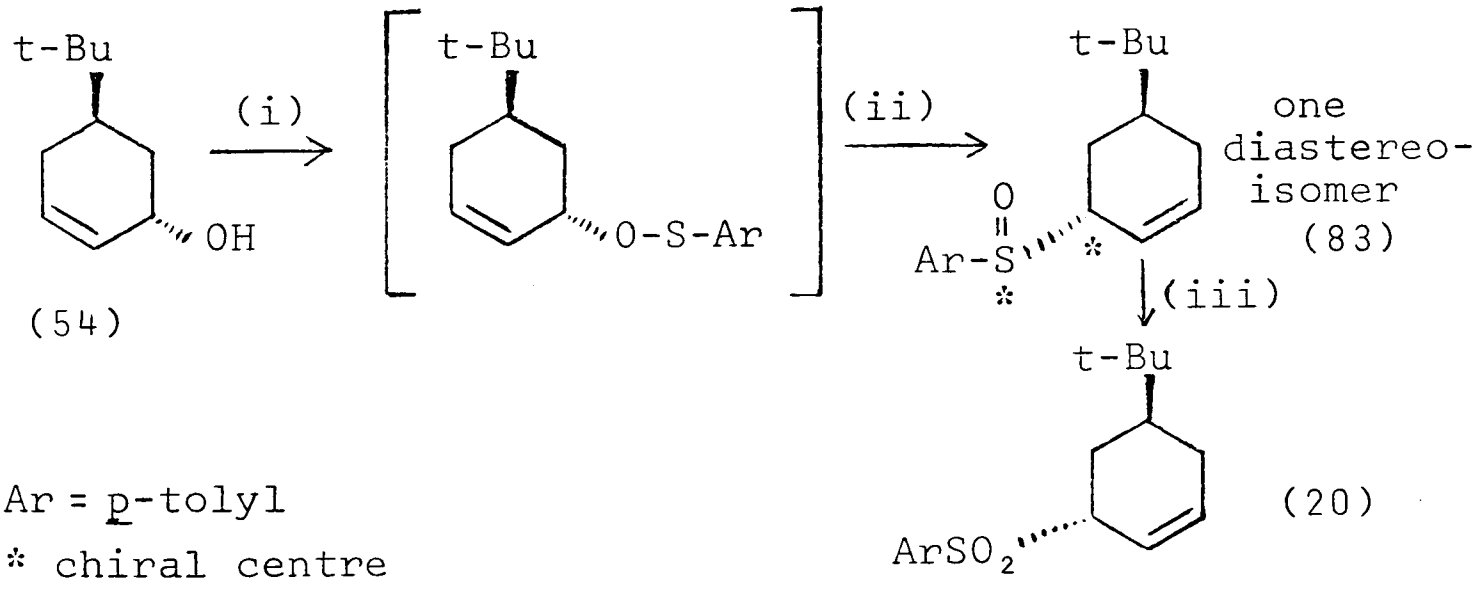
rearrangement of the sulphenate esters was highly stereoselective, only one diastereoisomer of each sulphoxide (82) and (83) being produced. The overall conversion of the conformationally biased alcohols (53) and (54) to the corresponding sulphones (19) and (20) was highly stereospecific.



Ar = p-tolyl
* chiral centre

(i) ArSCl (1 mole eq.), NEt_3 (1 mole eq.), CH_2Cl_2, 15 min, room temperature.
(ii) [2,3] rearrangement.
(iii) H_2O_2 (2 mole eq.), AcOH, 20h, ca. 30°C.

Scheme 94



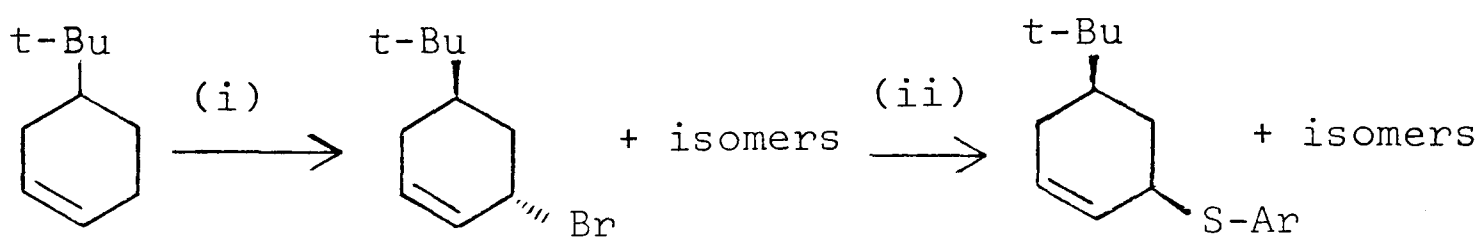
Ar = p-tolyl
* chiral centre

(i) ArSCl (1 mole eq.), NEt_3 (1 mole eq.), CH_2Cl_2, 15 min, room temperature.
(ii) [2,3] rearrangement.
(iii) H_2O_2 (2 mole eq.), AcOH, 20h, ca. 30°C.

Scheme 95

(b) Preparation via the Sulphide

The method described below was used to prepare a 4:1 mixture of the cis- and trans-sulphones (19) and (20). Such a non-equilibrium mixture was suitable for many purposes. Alkene (56) was treated with NBS and benzoyl peroxide to give a mixture of bromo-compounds[58], with isomer (84) expected to be the major product (Scheme 96). This mixture was treated with sodium toluene-p-thiolate using a procedure developed by Russell[74] from that described in ref. 75. Inversion of configuration at C-3 is expected, which would give isomer (85) as the major product (Scheme 96).



(56) (84) (85)

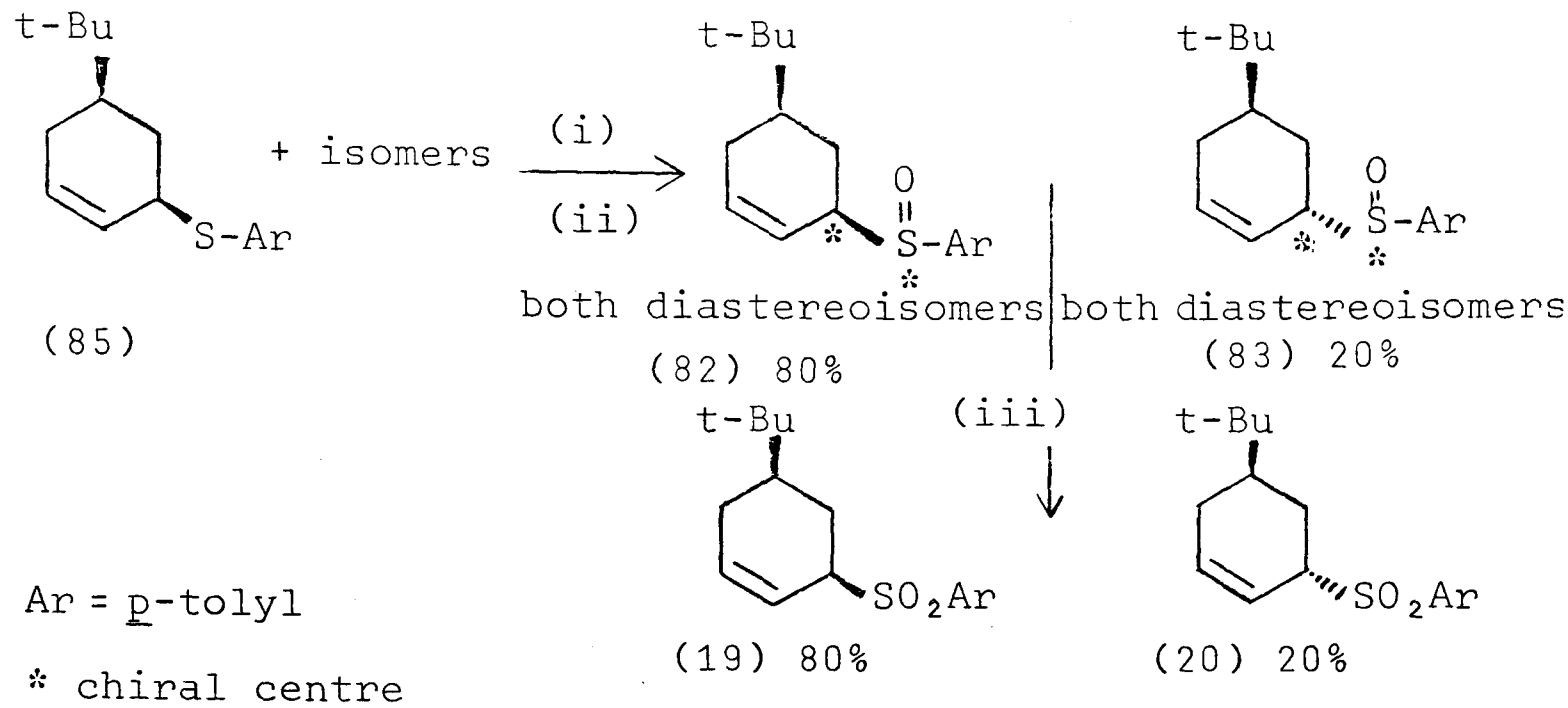
Ar = p-tolyl

(i) NBS (1 mole eq.), benzoyl peroxide, CCl_4, reflux.
(ii) ArSNa (1 mole eq.), MeOH, 30 min, reflux.

Scheme 96

This mixture of sulphides was treated with excess hydrogen peroxide in methanol (Scheme 97), conditions under which a sulphide is converted to a sulphoxide without further oxidation to the sulphone[76]. The material thus obtained was purified by chromatography to give a 4:1 mixture of the cis- and trans-sulphoxides (82) and (83). Both diastereoisomers of each sulphoxide (82) and (83) were shown to be present by 300 MHz n.m.r. (c.f. p. 49). Oxidation with hydrogen peroxide in acetic acid gave a 4:1

mixture of sulphones (19) and (20), Scheme 97. Purification at the sulphoxide stage was more convenient than at the sulphone stage.

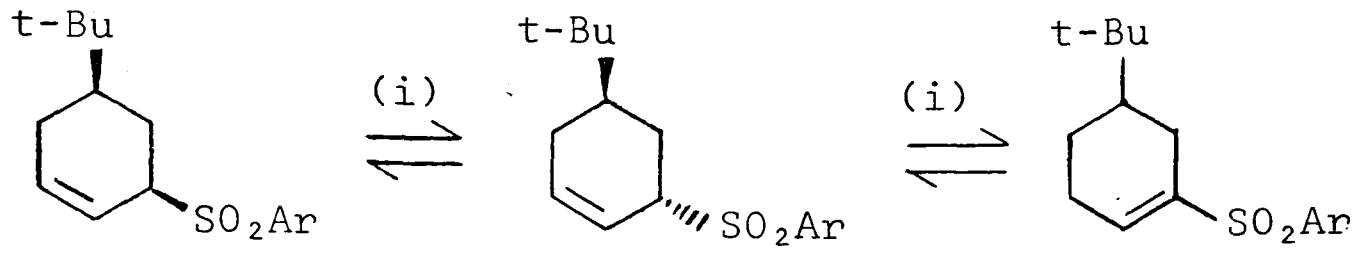


(i) H_2O_2 (4 mole eq.), MeOH, 43h, ca. 30°C.
(ii) Column chromatography.
(iii) H_2O_2 (2 mole eq.), AcOH, 20h, ca. 30°C.

Scheme 97

(c) Preparation of Deuteriated Sulphones

Sulphones (19) and (20) were subjected to treatment with alkali in the course of an investigation to find suitable conditions for their deuteriation. Equilibrium involving the allylic sulphones (19) and (20) and the vinylic sulphone (86) was established (Scheme 98).



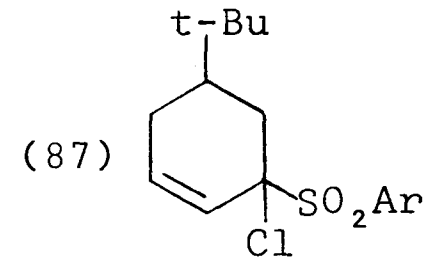
(19) 30% (20) 20% (86) 50%

Ar = p-tolyl

(i) NaOH (0.5M), DMSO - water (1:1 v/v), nitrogen atmosphere, 10 min or 24h, reflux.

Scheme 98

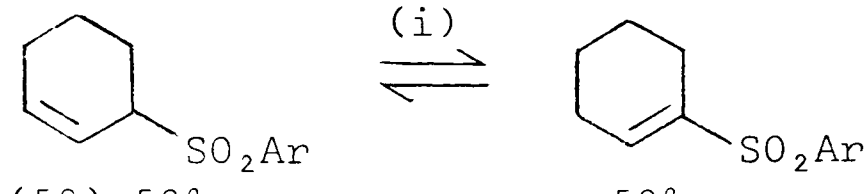
An unexpected product was produced from alkaline treatment of sulphones (19) and (20) in the presence of air. After prolonged treatment, the equilibrium mixture of sulphones (19), (20), and (86) was obtained, but work up after 10 min gave a compound which was tentatively identified as the chloride (87) (see Experimental Section), the chlorine atom presumably being incorporated during work up.



Ar = p-tolyl

Base-catalysed equilibration of sulphone (59) also produced a 1:1 mixture of the allylic and vinylic sulphones, Scheme 99. Similar treatment of sulphone (88)(see p. 76) gave the products shown in Scheme 100. The equilibrium between allylic and vinylic sulphones is discussed in refs. 77 and 78, and one example[79] is given in Scheme 101. In acyclic systems a sulphonyl substituent destabilises a double

bond[78], favouring the allylic sulphone at equilibrium, whereas in these alicyclic systems the allylic and vinylic sulphones are apparently of similar stability.

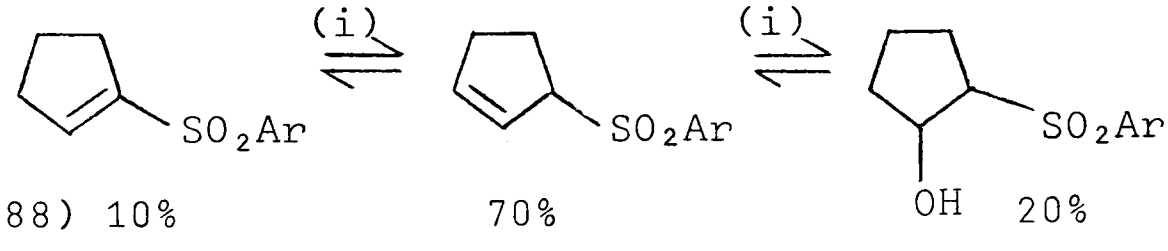


(59) 50% 50%

Ar = p-tolyl

(i) NaOH (0.5M), DMSO - water (1:1 v/v), 10 min, reflux.

Scheme 99

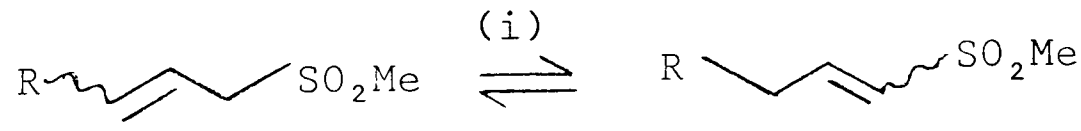


(88) 10% 70% 20%

Ar = p-tolyl

(i) NaOH (0.5M), DMSO - water (1:1 v/v), 10 min, reflux.

Scheme 100



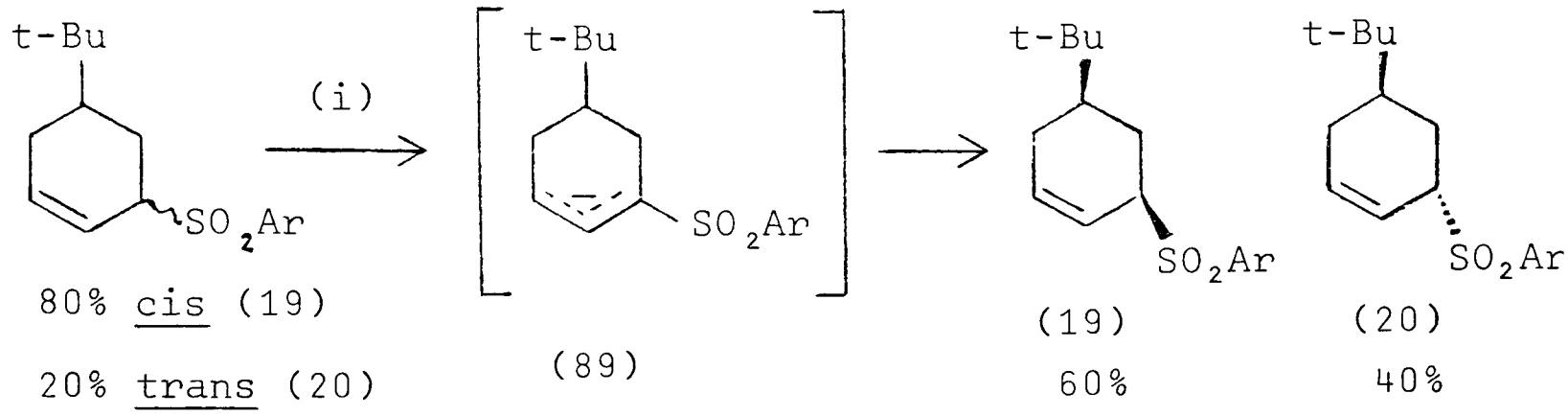
R = n-C_9H_{19} 99% 1%

(i) Base.

Scheme 101

Treatment with alkali under mild conditions resulted in epimerisation of sulphones (19) and (20) to give a 3:2 mixture, no vinylic sulphone (86) being formed, Scheme 102. This reaction presumably occurs because α-protonation of the anion (89) is more rapid than γ-protonation. That electrophilic attack on the anion derived from an allylic sulphone

occurs almost invariably at the α-position is well established[11], the particular case of deuteriation being discussed by Broaddus[77].



80% cis (19)

20% trans (20)

(89)

(19) 60%

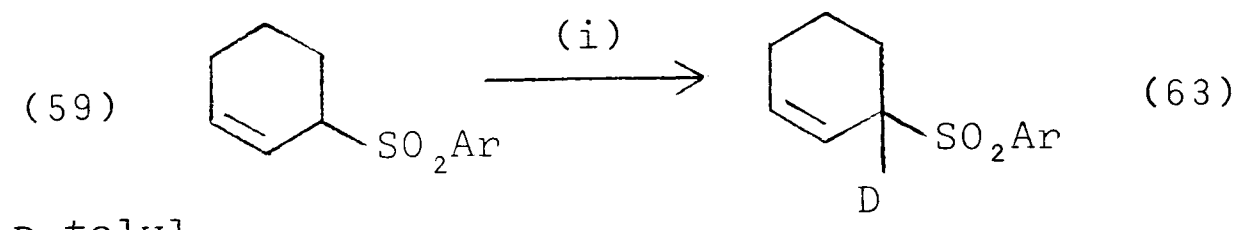
(20) 40%

Ar = p-tolyl

(i) NaOH (0.01M), DMSO - water (2:1 v/v), nitrogen atmosphere, 5 min, 50°C.

Scheme 102

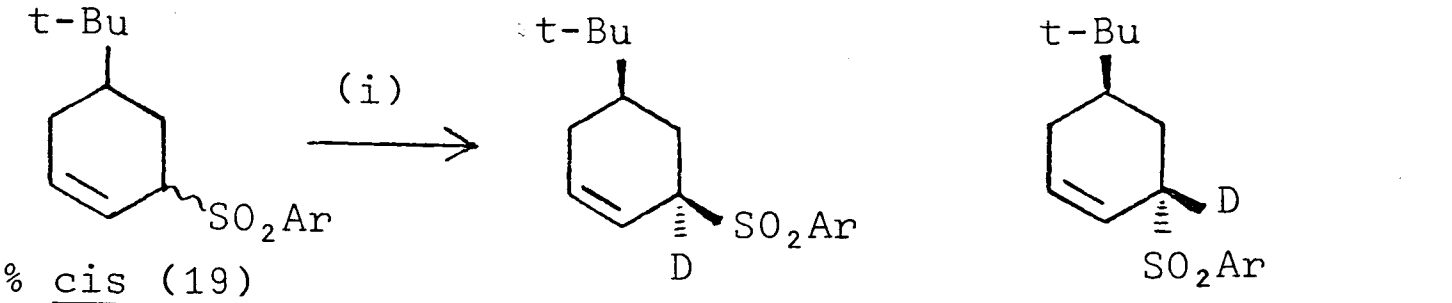
The use of deuterium oxide instead of water lead to α-deuteriation of sulphones (59), (19), and (20) under these mild alkaline conditions (Schemes 103 and 104).



Ar = p-tolyl

(i) NaOD (0.017M), DMSO-D_2O (2:1 v/v), nitrogen atmosphere, 10 min, 50°C.

Scheme 103



80% cis (19)
20% trans (20)

60% (3RS,5RS) (90)

40% (3SR,5RS) (91)

Ar = p-tolyl

(i) NaOD (0.01M), DMSO-D_2O (2:1 v/v), nitrogen atmosphere, 5 min, 50°C.

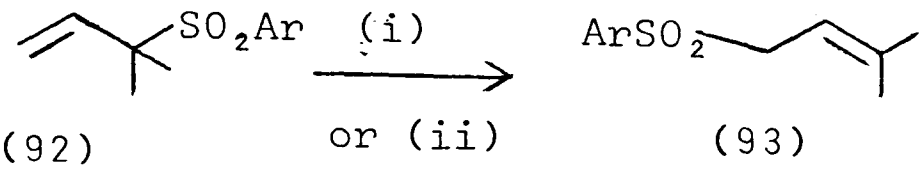
Scheme 104

The procedure used by Lin[33] to deuteriate sulphone (59), treatment with n-butyl-lithium followed by deuterium oxide quench, was used on the 4:1 mixture of sulphones (19) and (20). A 3:2 mixture of deuteriated sulphones (90) and (91) was produced, but since the reaction proved difficult to scale up, it was not used preparatively.

3. Rearrangement of some Allylic Sulphones

(a) Rearrangement of 3-Methyl-3-(p-tolylsulphonyl)-1-butene

The rearrangement of sulphone (92) to the more stable isomer (93) occurred on heating with benzoyl peroxide in carbon tetrachloride[33], Scheme 105. A radical chain addition-elimination process was proposed[33] to account for the reaction, Scheme 106.



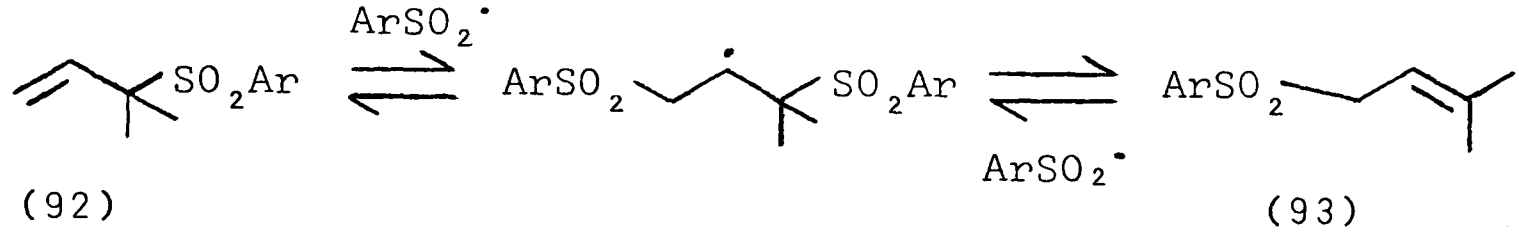
(92) (93)

Ar = p-tolyl

(i) Benzoyl peroxide, CCl_4, 18h, reflux.

(ii) $ArSO_2Na$ (1 mole eq.), AcOH - water (3:2 v/v), 8h, 110°C.

Scheme 105

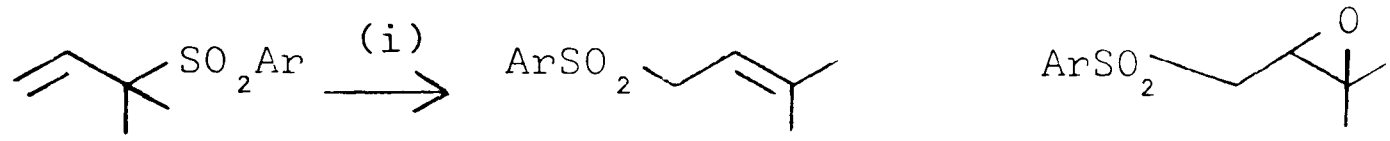


(92) (93)

Ar = p-tolyl

Scheme 106

Lin found[33] that sulphone (92) was stable to heating in aqueous acetic acid, but in the present work it was shown that partial rearrangement did occur under apparently similar conditions. The rate of reaction was very sensitive to temperature and to the state of purity of the solvent (see Table 12, p. 123), which made it difficult to reproduce exactly the conditions used by Lin. It seemed possible that the spontaneous rearrangement of sulphone (92) was promoted by peroxide impurities in the aqueous acetic acid. This hypothesis was supported by the finding that addition of peracetic acid increased the rate of rearrangement, the isomerised sulphone (93) being partially oxidised *in situ* to give the epoxy-sulphone (94), Scheme 107.



(92) (93) 60% (94) 40%

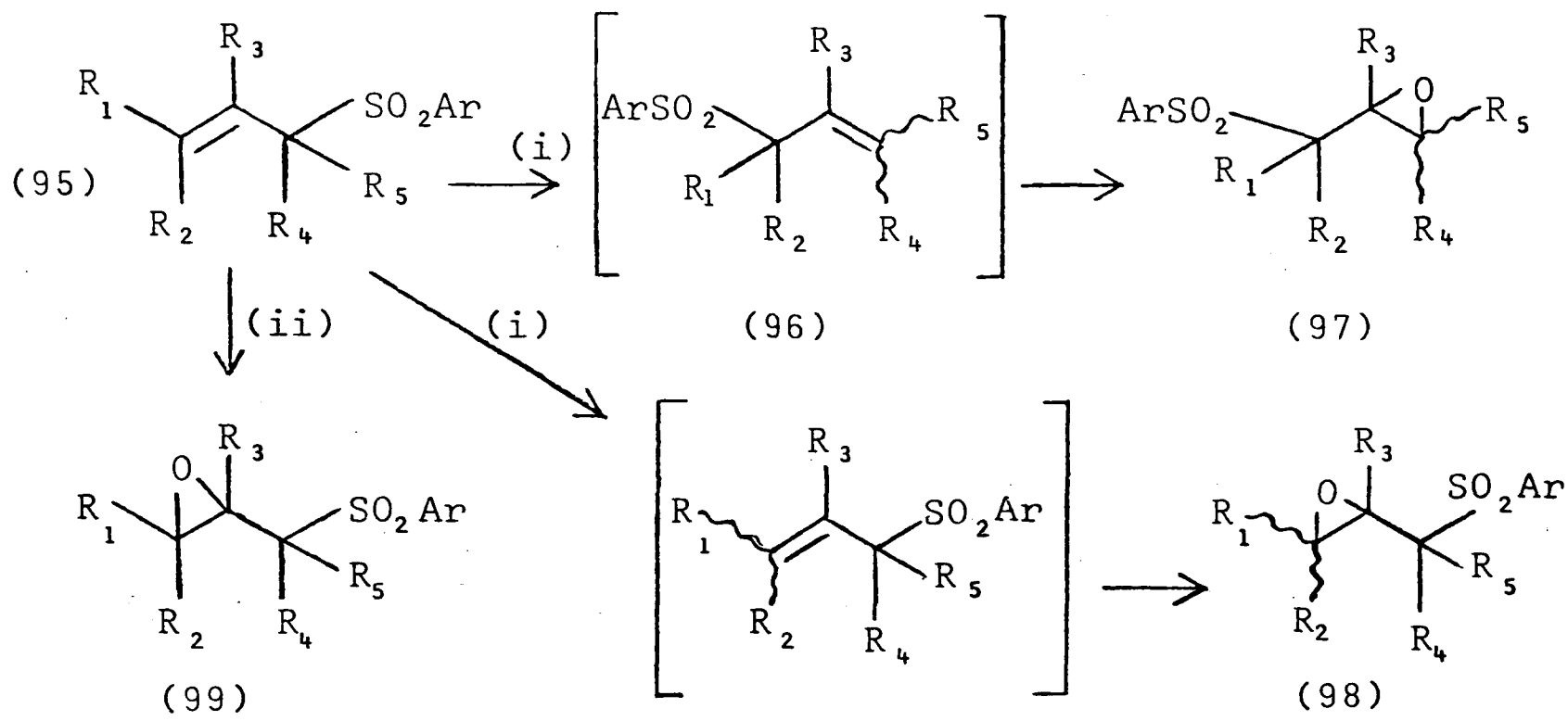
Ar = p-tolyl

(i) $MeCO_3H$ (1.5 mole eq.), AcOH - water (3:2 v/v), 8h, 110°C.

Scheme 107

Kocienski[70] has found that m-CPBA in the presence of sodium hydrogen carbonate can induce a [1,3] rearrangement of certain allylic sulphones (95) at room temperature, the rearranged sulphone (96) being oxidised *in situ* to give the epoxy-sulphone (97), Scheme 108. This [1,3] rearrangement occurred efficiently only in those cases in which the sulphonyl group migrated to a less substituted carbon atom. In the case of allylic sulphones (95) in which the sulphonyl group was already located on the less substituted carbon atom, there was no [1,3] rearrangement, but isomerisation about the double bond occurred before epoxidation, mixtures of stereo-isomers of the epoxy-sulphone (98) being obtained (Scheme 108). The mechanism proposed by Kocienski[70] to account for both the [1,3] allylic rearrangement and the isomerisation about the double bond (Scheme 109) is a radical chain process, which has the same chain-carrying step *via* the sulphonyl radical as that shown in Scheme 106. It is more likely, however, that the radical anion dissociates to give an aryl-sulphinate anion and a carbon radical than as shown in Scheme 109, because then the negative charge would be on an oxygen rather than a carbon atom, which could lead to a $S_{RN}1$

process (Scheme 112). In the absence of sodium hydrogen carbonate, epoxidation of the allylic sulphones (95) occurred without rearrangement, giving a single isomer (99), Scheme 108.



Ar = p-tolyl

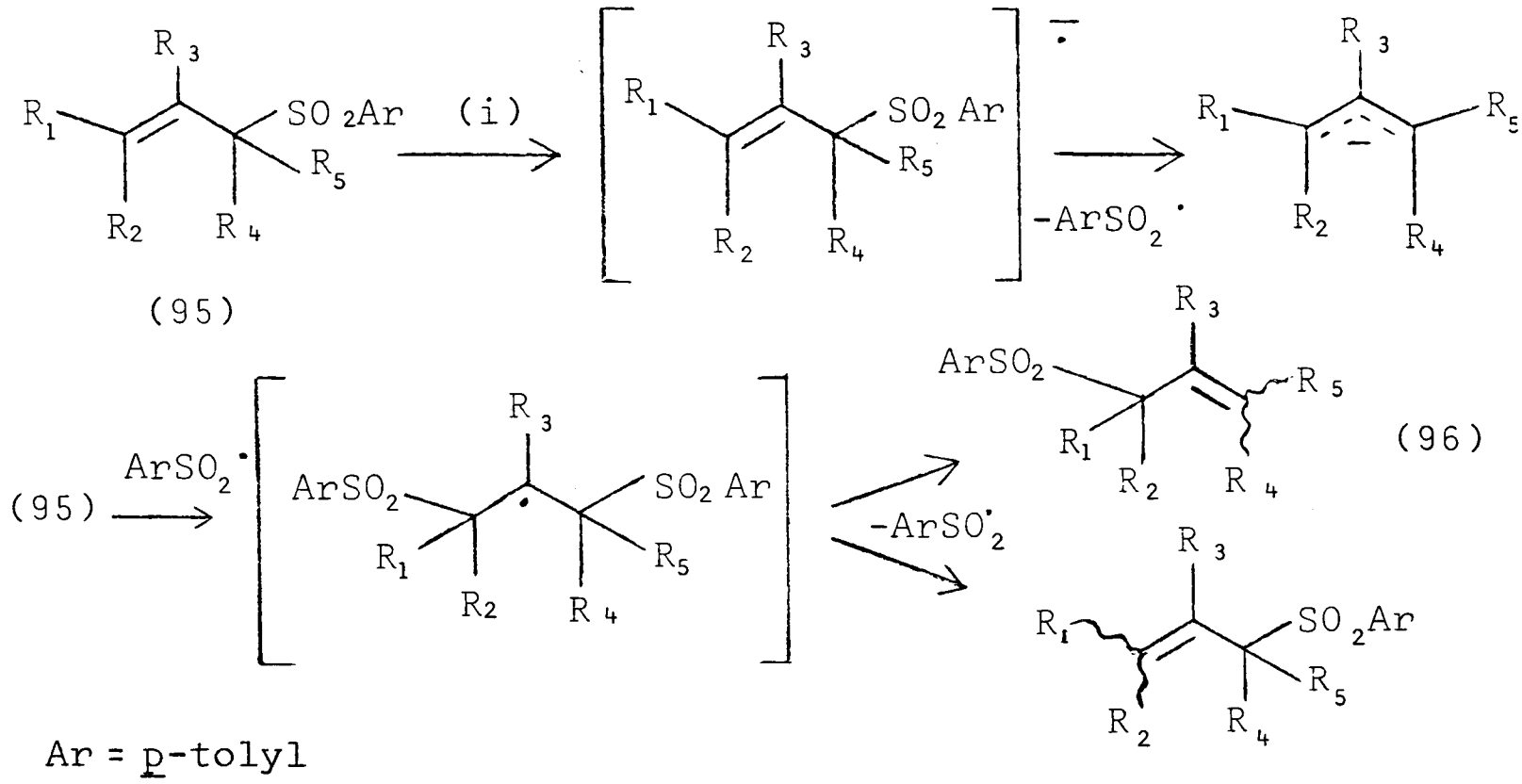
(97) has $R_1 = R_2 = R_4 = H$, $R_3 = Me$, $R_5 = Me$ or n-Bu
and $R_1 = R_2 = H$, $R_3 = R_4 = R_5 = Me$

(98) has $R_1 = R_4 = R_5 = H$, $R_2 = Me$, $R_3 = H$ or Me
and $R_2 = R_4 = R_5 = H$, $R_1 = Me$, $R_3 = H$ or Me

(99) has the substitution patterns for (97) and (98)
and $R_1 = R_4 = R_5 = Me$, $R_2 = H$, $R_3 = H$ or Me
and $R_1 = R_2 = R_4 = Me$, $R_3 = R_5 = H$
and $R_1 = R_2 = R_3 = Me$, $R_4 = R_5 = H$

(i) m-CPBA (1.25 mole eq.), $NaHCO_3$ (2.5 mole eq.), CH_2Cl_2-water, room temperature.
(ii) m-CPBA (1.1 mole eq.), CH_2Cl_2, room temperature.

Scheme 108



Ar = p-tolyl

(i) m-$ClC_6H_4CO_3Na$.

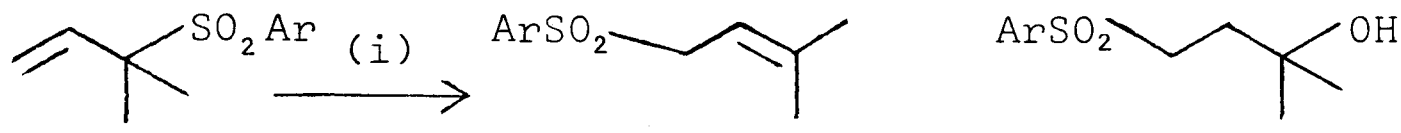
Scheme 109

It seems likely that the spontaneous rearrangement of sulphone (92) in aqueous acetic acid occurs by a radical chain mechanism (Scheme 106), the radical inhibitors hydroquinone and iodine both quenching the reaction. The effect of hydriodic and hydrobromic acids in preventing rearrangement may be caused by the presence of iodine and bromine impurities. Furthermore, the radical source benzoyl peroxide promotes the reaction.

The rate of spontaneous rearrangement is relatively unaffected by the polarity of the reaction medium, which suggests that a free radical rather than an ionic mechanism is in operation. Thus, the addition of salts (sodium acetate, sodium bromide, or sodium metabisulphite) or the use of neat rather than aqueous acetic acid as solvent, has only a small effect on the rate of reaction. Lin also found[33] that added

nucleophiles did not promote the isomerisation of sulphone (92).

Toluene-p-sulphonic acid increases the rate of rearrangement of sulphone (92) in aqueous acetic acid (see Table 12, p.123), but catalyses the hydration of the isomerised sulphone (93) to give the equilibrium mixture shown in Scheme 110. Sulphuric acid, however, does not appreciably affect the rate of isomerisation of sulphone (92), although it does promote hydration to give hydroxy-sulphone (100).



(92) (93) 60% (100) 40%

Ar = p-tolyl

(i) $ArSO_3H$ (1 mole eq.), AcOH - water (3:2 v/v), 8h, 110°C.

Scheme 110

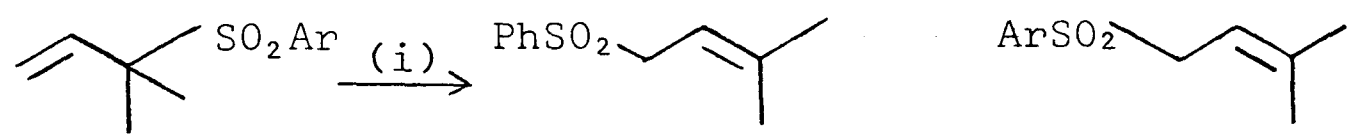
Lin[33] found that the rearrangement of sulphone (92) was catalysed by sodium toluene-p-sulphinate (0.1-7 mole eq.), Scheme 105. Acetic acid has a pK_a of 4.76 and toluene-p-sulphinic acid should have a similar pK_a to benzenesulphinic acid [pK_a 1.29, p.612 of ref. 2(a)]. Therefore, the sodium salt of toluene-p-sulphinic acid is probably partially protonated in aqueous acetic acid, and it was shown that toluene-p-sulphinic acid was indeed present by extracting it into chloroform.

It was found that toluene-p-sulphinic acid was more effective at promoting the rearrangement of sulphone (92)

than was the sodium salt, and that the amount used had little effect on the rate of reaction (see Table 12, p.123). The rearrangement of sulphone (92) in the presence of sodium toluene-p-sulphinate (0.1 mole eq.) was suppressed by hydroquinone. That Lin[33] detected no such inhibition by hydroquinone may be because he used an excess of sodium toluene-p-sulphinate (7 mole eq.).

The use of neat rather than aqueous acetic acid as solvent had little effect on the rate of rearrangement. Since the present work was begun, Julia[80] has confirmed that sulphone (92) can be isomerised to sulphone (93) by heating to 100°C in acetic acid with sodium toluene-p-sulphinate.

Crossover experiments have shown[33] that benzenesulphinate is incorporated as sulphone (92) rearranges, but to a less than statistical extent, Scheme 111.



(92) 75% 25% (93)

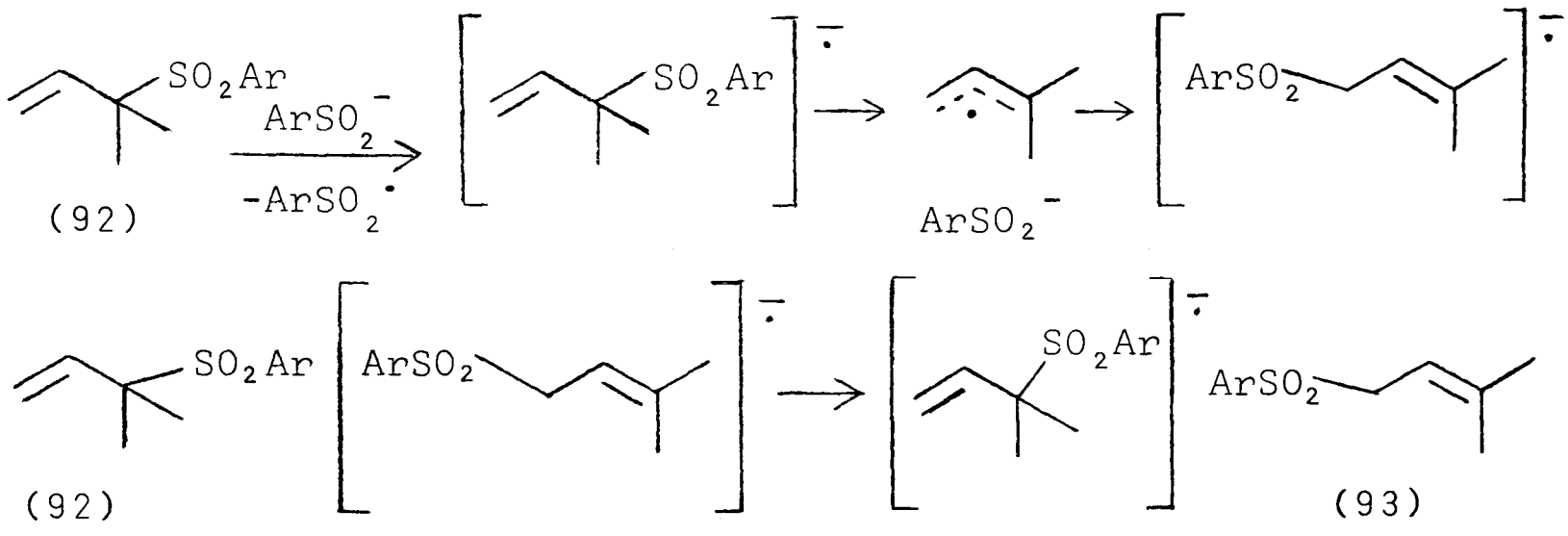
Ar = p-tolyl

(i) $PhSO_2Na$ (7 mole eq.), AcOH - water (3:2 v/v), 8h, 100°C.

Scheme 111

It was tentatively concluded[33] that the toluene-p-sulphinate-induced rearrangement of sulphone (92) may occur either by an anion assisted ion-pair process or by an $S_{RN}1$ reaction[81,82] (Scheme 112), even though the known radical anion trap m-dinitrobenzene[81] did not suppress the reaction. On the basis of the results described in the present work, however, in particular the effect of hydroquinone in

quenching the reaction, the possibility cannot be eliminated of the occurrence of a radical chain addition-elimination process (Scheme 106) initiated by toluene-p-sulphinic acid and/or its sodium salt.

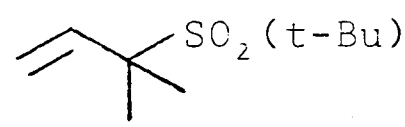


Ar = p-tolyl

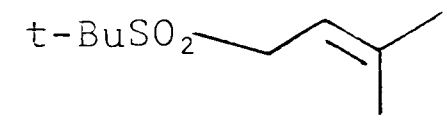
Scheme 112

(b) Rearrangement of 3-Methyl-3-(t-butylsulphonyl)-1-butene

The rearrangement of sulphone (101) to the more stable isomer (102) occurred less readily than was the case for the analogous sulphone (92). Lin[33] found that sulphone (101) was stable to treatment with benzoyl peroxide in refluxing carbon tetrachloride. In the present work, however, it was shown that 40% rearrangement occurred on treatment with benzoyl peroxide in aqueous acetic acid at 100°C for 8h. Lin reported that sulphone (101) was stable to heating in aqueous acetic acid at 100°C for 8h, whereas in the present work it was found that 10% isomerisation to sulphone (102) occurred under these conditions, but that the reaction was quenched by hydroquinone.

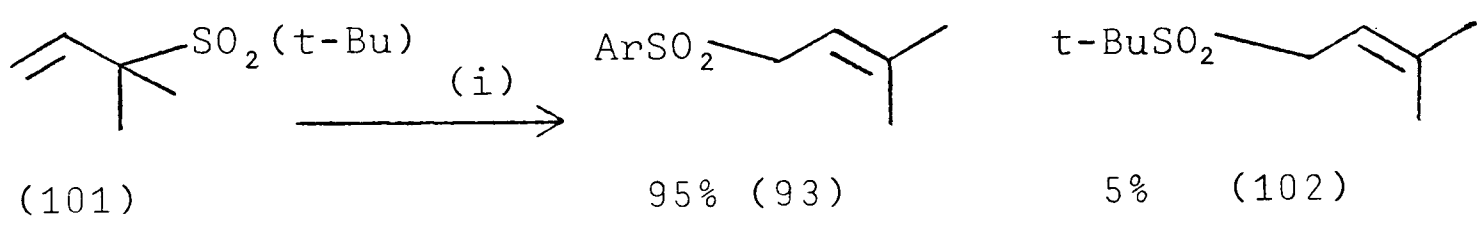


(101)



(102)

Lin[33] showed that reaction of sulphone (101) in aqueous acetic acid could be induced by sodium toluene-p-sulphinate, the arylsulphinate being incorporated into the products, Scheme 113. By using less sodium toluene-p-sulphinate, conditions were established under which sulphone (101) reacted incompletely, and hence it was shown that the presence of hydroquinone had little effect on the rate of reaction (see Table 11, p.122).



(101) 95% (93) 5% (102)

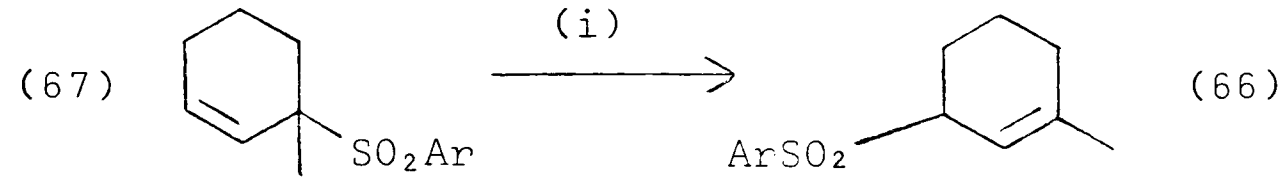
Ar = p-tolyl

(i) $ArSO_2Na$ (7 mole eq.), AcOH - water (3:2 v/v), 8h, 100°C.

Scheme 113

(c) Rearrangement of 3-Methyl-3-(p-tolylsulphonyl)cyclohexene

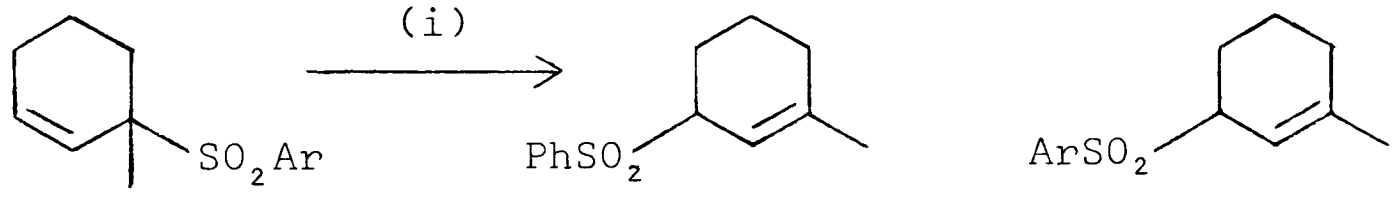
Lin[33] found that sulphone (67) rearranged to the more stable isomer (66) on heating in aqueous acetic acid even in the absence of sodium toluene-p-sulphinate, Scheme 114 (c.f. Scheme 65). Rearrangement also occurred in other solvents, those of high polarity increasing the rate of reaction. A crossover experiment (Scheme 115) lead to incorporation of benzene-sulphinate, but to a less than statistical extent.



Ar = p-tolyl

(i) AcOH - water (3:2 v/v), 8h, 100°C.

Scheme 114

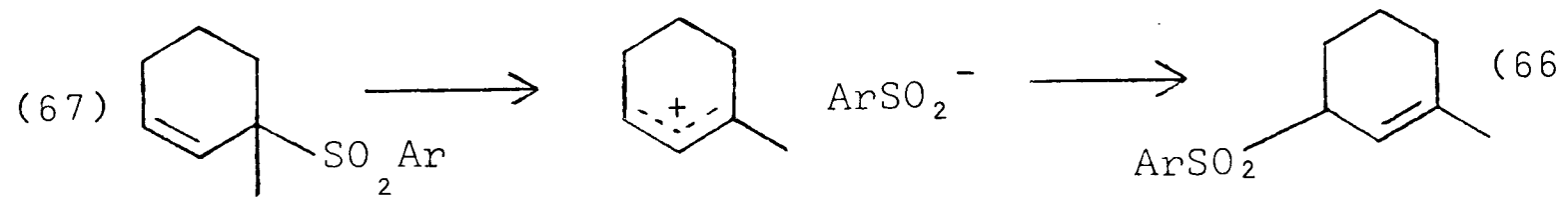


Ar = p-tolyl

(i) $PhSO_2Na$ (7 mole eq.), AcOH - water (3:2 v/v), 8h, 100°C.

Scheme 115

In the present work, aqueous acetic acid conditions have been established under which only partial rearrangement of sulphone (67) occurred, and hence it has been shown that the rate of reaction is not appreciably affected by the presence of hydroquinone. This supports the conclusion [33,71] that the rearrangement of sulphone (67) occurs by a dissociative mechanism involving a fairly tight ion-pair, Scheme 116.

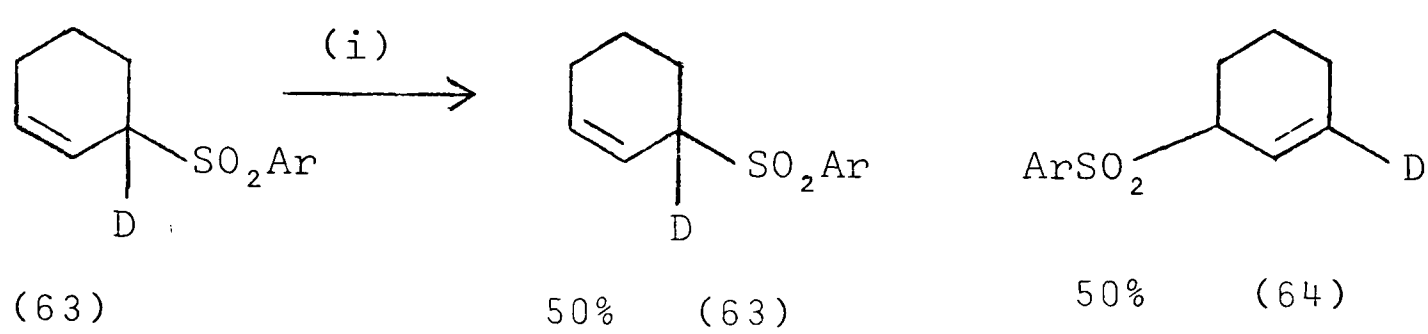


Ar = p-tolyl

Scheme 116

(d) Rearrangement of 3-[^{2}H]-3-(p-Tolylsulphonyl)cyclohexene

Lin[33] found that sulphone (63) was stable to heating in aqueous acetic acid, a finding confirmed in the present work, but that the presence of sodium toluene-p-sulphinate promoted rearrangement to give a 1:1 equilibrium mixture of the sulphones (63) and (64), Scheme 117 (c.f. Scheme 61). In the present work, conditions have been established under which sulphone (63) rearranged only partially in the presence of sodium toluene-p-sulphinate, and hence it has been shown that hydroquinone completely quenches the reaction (see Table 10, p.121).



Ar = p-tolyl

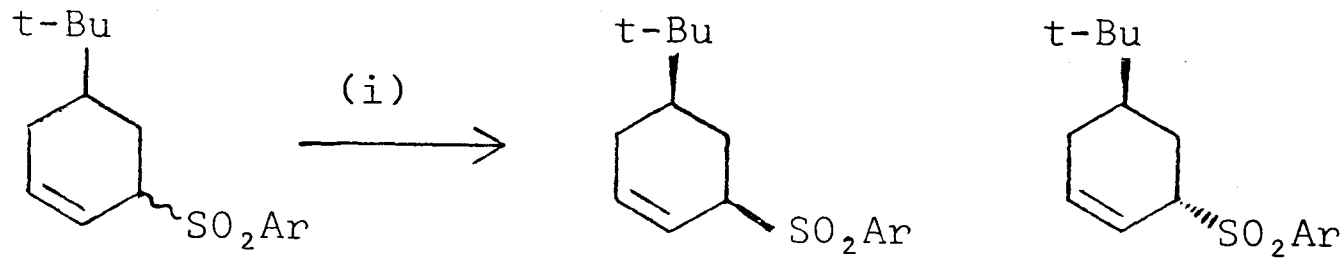
(i) $ArSO_2Na$ (7 mole eq.), AcOH - water (3:2 v/v), 8h, 100°C.

Scheme 117

Treatment of sulphone (63) with benzoyl peroxide, either in aqueous acetic acid at 100°C or in refluxing carbon tetrachloride, caused the equilibrium between sulphones (63) and (64) to be established. A radical chain addition-elimination process (Scheme 106) is probably in operation for this benzoyl peroxide-initiated reaction. Either a similar radical chain process or an $S_{RN}1$ reaction (Scheme 112) could be occurring for the toluene-p-sulphinate induced reaction (see p. 69).

(e) Rearrangement of some Conformationally Biased Alicyclic Allylic Sulphones

The allylic sulphones were rearranged by heating in aqueous acetic acid with sodium toluene-p-sulphinate. Scheme 118 shows the epimerisation of sulphones (19) and (20) to the 3:2 equilibrium mixture. The deuteriated sulphones (90) and (91) underwent deuterium scrambling, resulting from a [1,3] migration of the sulphonyl group, to give the equilibrium mixture shown in Scheme 119. A similar result had been obtained with sulphone (63), Scheme 117.



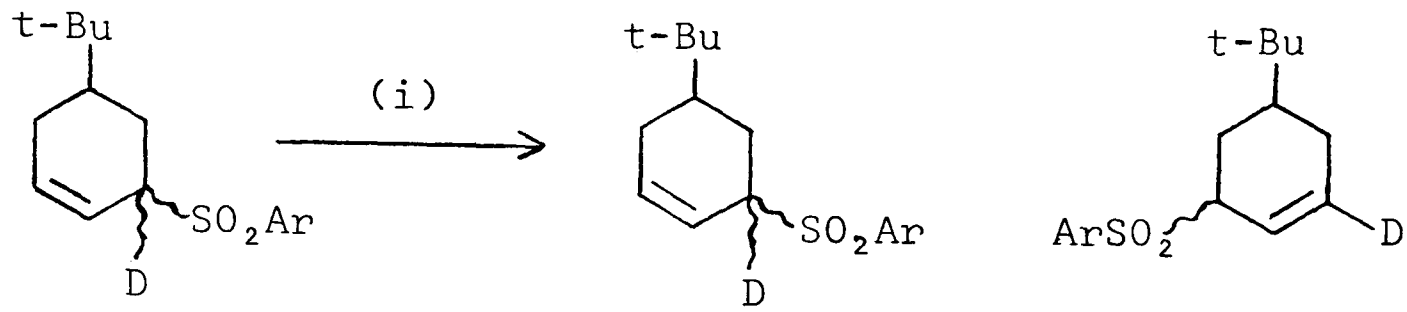
60% (19) 40% (20)

	cis (19),	trans (20)
either	80%,	20%
or	100%,	0
or	0 ,	100%

Ar = p-tolyl

(i) $ArSO_2Na$ (10 mole eq.), AcOH - water (3:2 v/v), 11.5h, 110°C.

Scheme 118



(3RS, 5RS) (90) 60%
(3SR, 5RS) (91) 40%

50% (90)and (91) 50%

Ar = p-tolyl

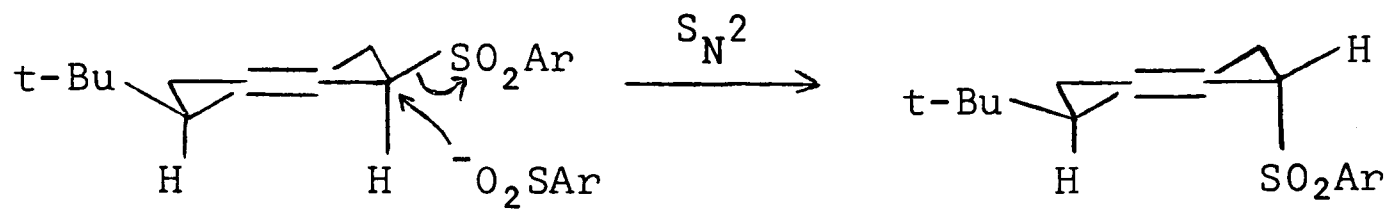
(i) $ArSO_2Na$ (10 mole eq.), AcOH - water (3:2 v/v), 11.5h, 110°C.

Scheme 119

Neither epimerisation nor deuterium scrambling occurred on prolonged heating in aqueous acetic acid in the absence of sodium toluene-p-sulphinate (see Tables 8 and 9, p. 119 and 120). Sulphone (63) is also stable under similar conditions. The presence of sodium bromide did not cause epimerisation to occur, suggesting that sodium toluene-p-sulphinate does not promote reaction by a salt effect.

By establishing conditions under which only partial reaction occurred in the presence of sodium toluene-p-sulphinate, it was shown that within experimental error the rates of epimerisation and deuterium scrambling were the same. This result shows that the major reaction pathway is not an S_N2 process, which would have resulted in epimerisation without deuterium scrambling (Scheme 120). The reaction is probably not an S_N2' process either, for this would have resulted in deuterium scrambling without epimerisation if nucleophilic attack occurs in a syn-manner as has been

suggested[83] (Scheme 121). Furthermore, the cyclic process shown in Scheme 122 suggested by Julia[80], which again would have resulted in deuterium scrambling without epimerisation, is also ruled out.

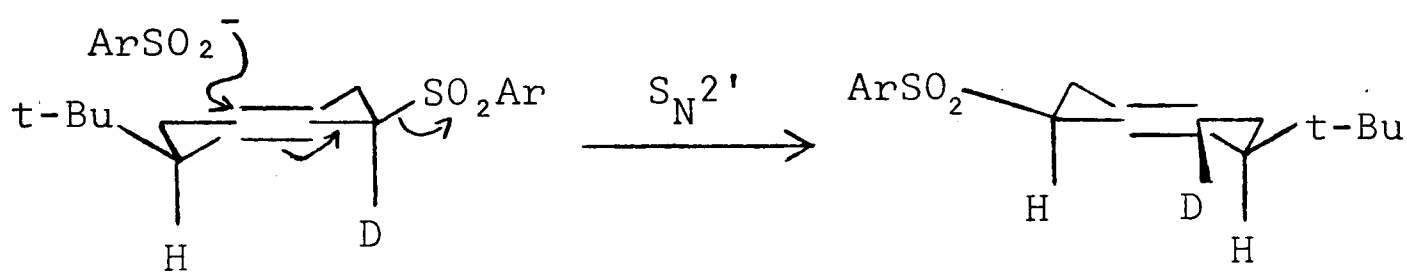


cis (19) trans (20)

Ar = p-tolyl

Only one enantiomer is drawn.

Scheme 120

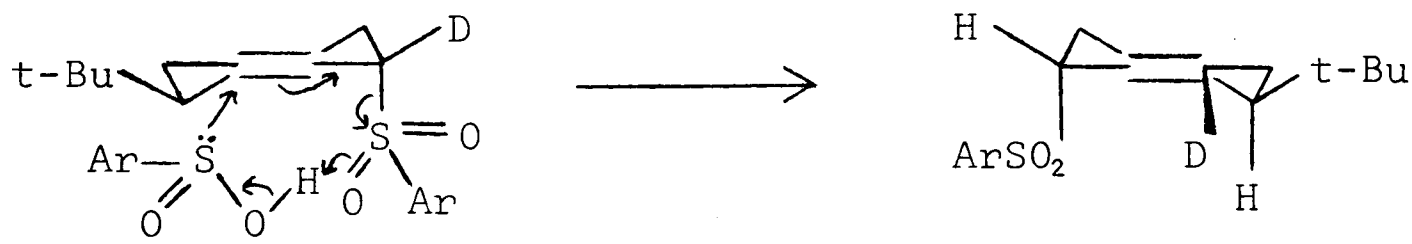


(3RS,5RS) (90) cis

Ar = p-tolyl

Only one enantiomer is drawn.

Scheme 121



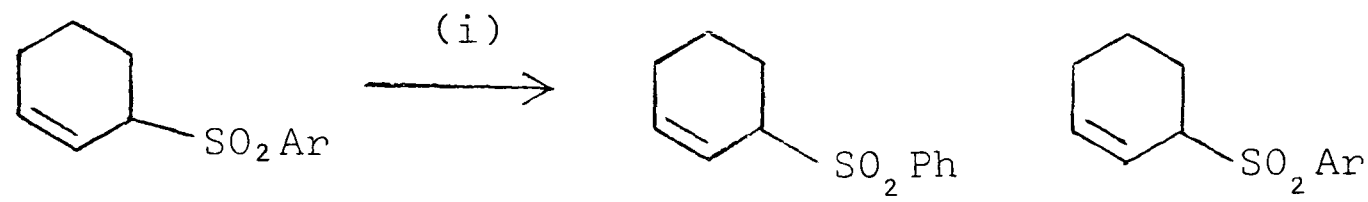
(3SR, 5RS) (91) trans

Ar = p-tolyl

Only one enantiomer is drawn.

Scheme 122

The result of the crossover experiment shown in Scheme 123 (<u>c.f.</u> p. 31) confirms that the major reaction pathway is not by any of the processes shown in Schemes 120, 121, and 122, for the reason that the incorporation of benzenesulphinate would then be 87% or higher.



(59) 70% (68) 30% (59)

Ar = <u>p</u>-tolyl

(i) $PhSO_2Na$ (7 mole eq.), AcOH - water (3:2 v/v), 8h, 100°C.

<u>Scheme 123</u>

Assuming that sulphones (19), (20), and (59) and their <u>α</u>-deuteriated analogues undergo toluene-<u>p</u>-sulphinate-induced rearrangement in aqueous acetic acid by one mechanism, and that reaction occurs by only one major pathway, certain conclusions can be drawn from the results presented in this Section. It is unlikely that the rearrangement occurs by a dissociative mechanism involving ions or free radicals, since this unimolecular process should not be affected by the presence of toluene-<u>p</u>-sulphinate. It is more likely that either a radical chain addition-elimination process (Scheme 106) or an $S_{RN}1$ process[81,82] (Scheme 112) is in operation. Thus, hydroquinone quenches the rearrangement of sulphone (63), as would be expected[81,82] if reaction occurs by either of these chain mechanisms.

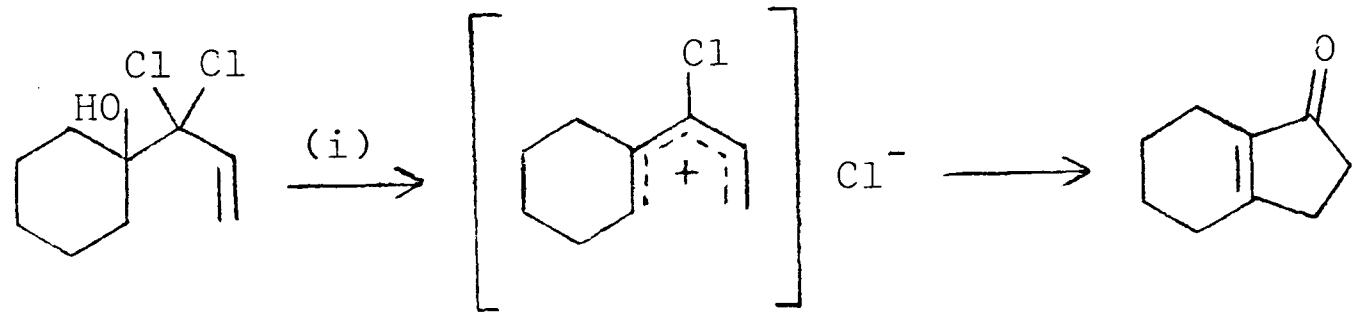
SECTION III

ATTEMPTED DEVELOPMENT OF A 5-MEMBERED RING ANNULATION PROCEDURE

1. Introduction

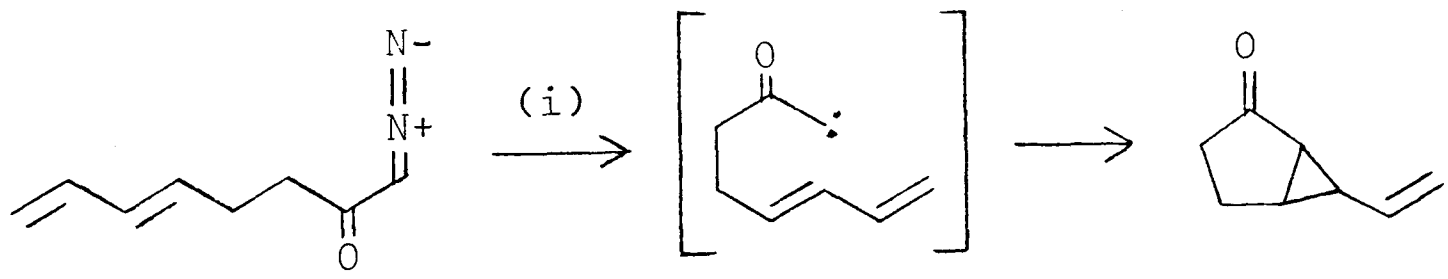
Annulation is the process in which a ring is built onto a pre-existing system, which may or may not be cyclic. Recently much work has been done to develop new methodology for the annulation of 5-membered rings, a summary of which is presented below.

Various methods of ring closure have been used including Claisen[84] and aldol[85] cyclisations, acid-catalysed processes involving rearrangement of carbocations[86] (e.g. Scheme 124)[87], reactions of carbenoids (e.g. Scheme 125)[88], and intramolecular Wittig-type processes (e.g. Scheme 126)[89].



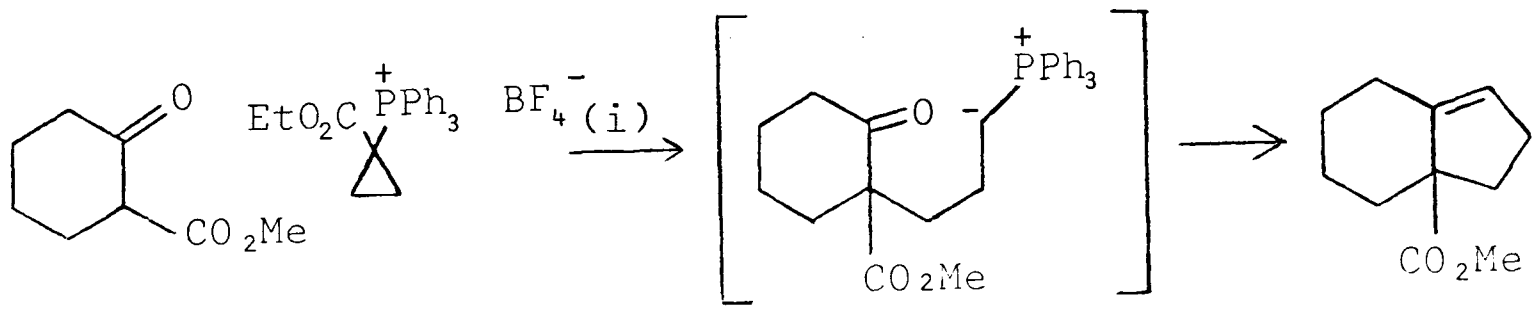
(i) Acid.

Scheme 124



(i) $Cu(acac)_2$.

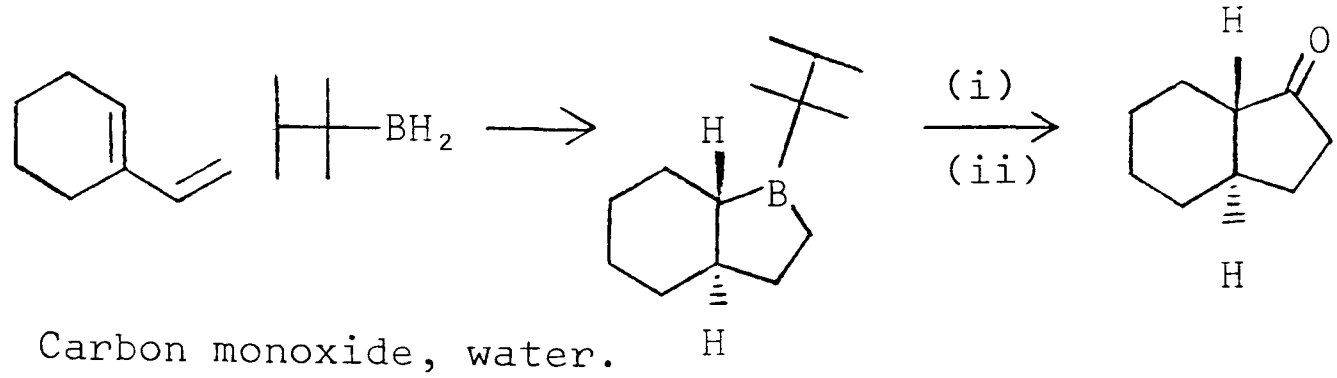
Scheme 125



(i) NaH.

Scheme 126

Stereoselective 5-membered ring annulations can be effected using organoboranes[90] (Scheme 127).

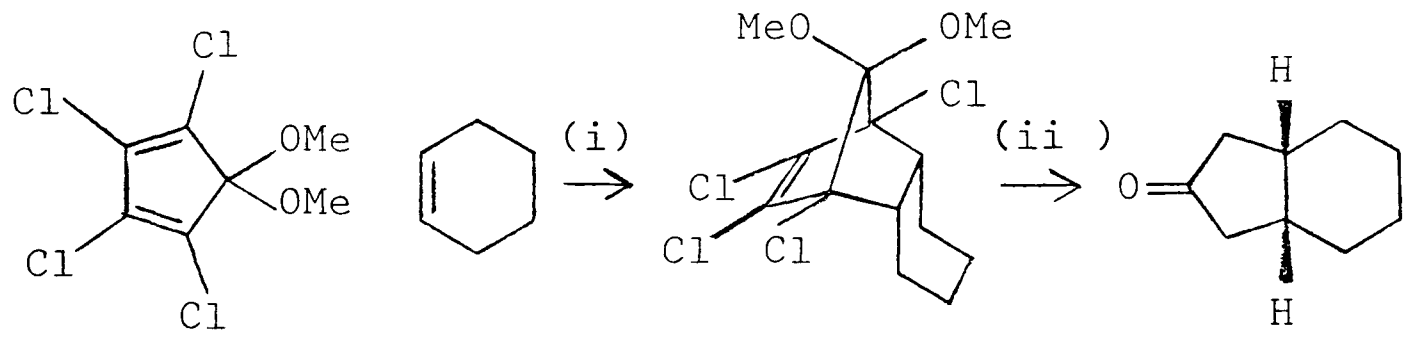


(i) Carbon monoxide, water.

(ii) H_2O_2.

Scheme 127

Examples of the formation of 5-membered carbocyclic rings by a [3+2] cycloaddition process are present in the literature[91]. A synthetic method[92] equivalent to a [3+2] process is shown in Scheme 128.



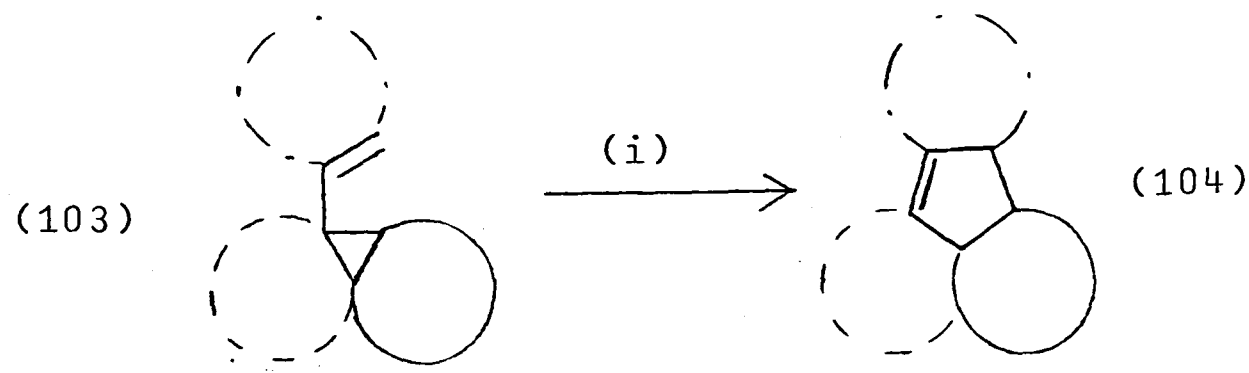
(i) Heat.

(ii) Several steps.

Scheme 128

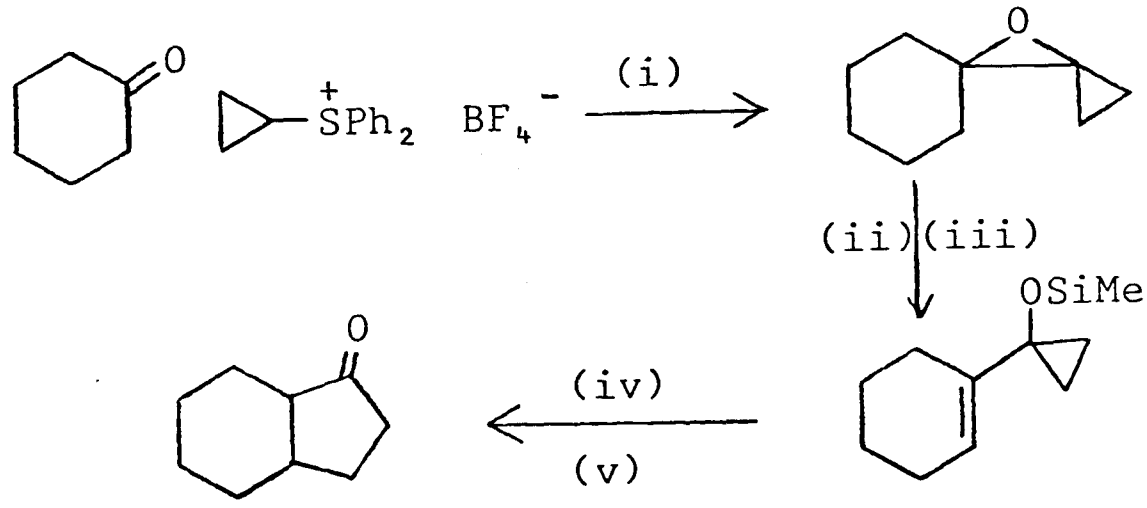
A procedure which has been much used in synthesis exploits the often stereoselective thermal rearrangement of a vinylcyclopropane (103) to a cyclopentene (104) (Scheme 129), perhaps using flow pyrolysis[93]. This reaction is thought to occur by a biradical mechanism[97(a)]. Various methods have been developed for the preparation of the vinylcyclopropane (103)[88,95]. Of interest are the cases in

which a substituent is subsequently converted to a carbonyl group[96] (e.g. Scheme 130)[94]. A recent development is the use of the highly stereoselective alkoxy-accelerated vinylcyclopropane rearrangement, which occurs at room temperature (Scheme 131)[97(b)]



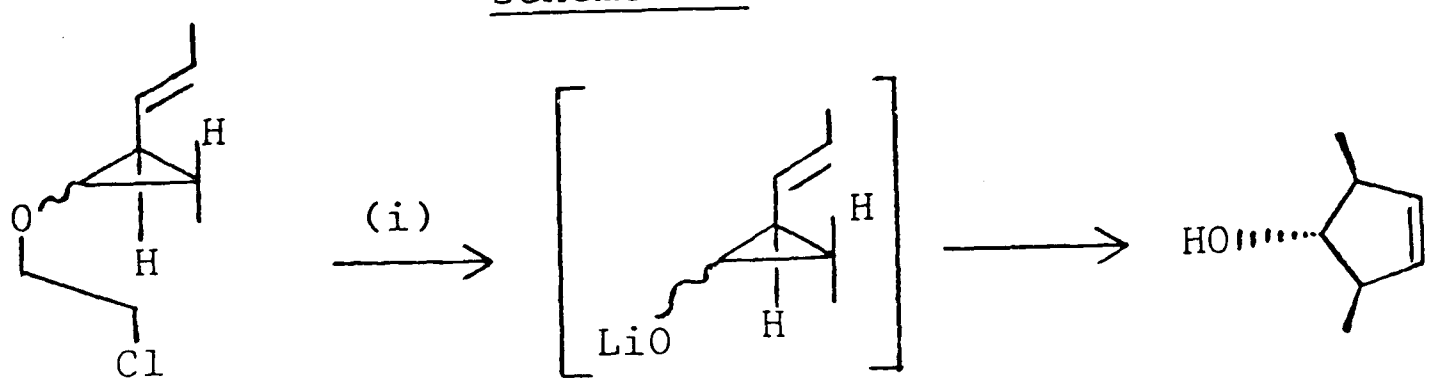
(i) Heat.

Scheme 129



(i) KOH.
(ii) $LiNEt_2$.
(iii) Me_3SiCl.
(iv) Flow pyrolysis.
(v) Acid.

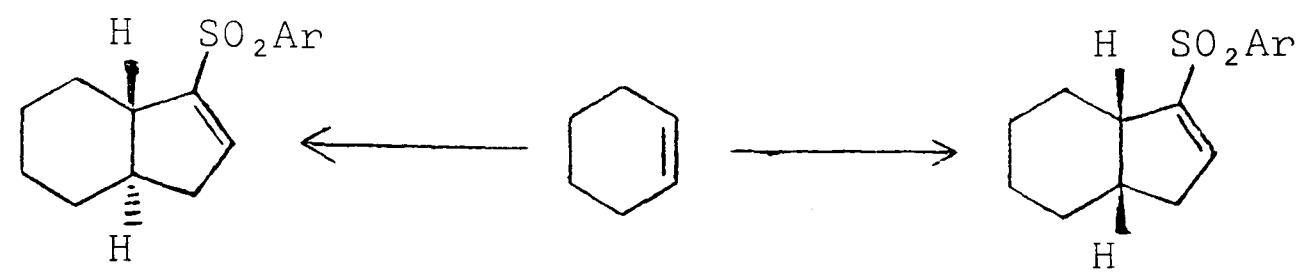
Scheme 130



(i) n-BuLi.

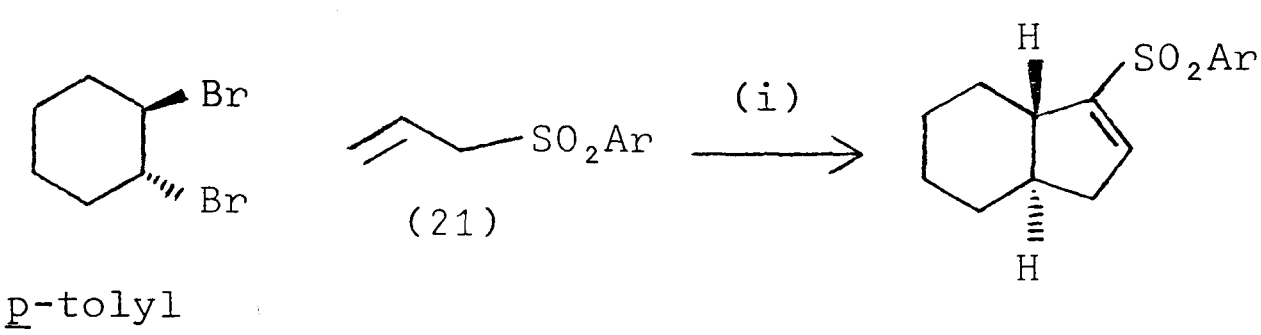
Scheme 131

The aim of the work described in this Section was to develop a synthetic method for the stereoselective 5-membered ring annulation exemplified in Scheme 132. The routes originally proposed are shown in Schemes 133 and 134. Firstly, however, a simple model system was to be investigated.



Ar = p-tolyl

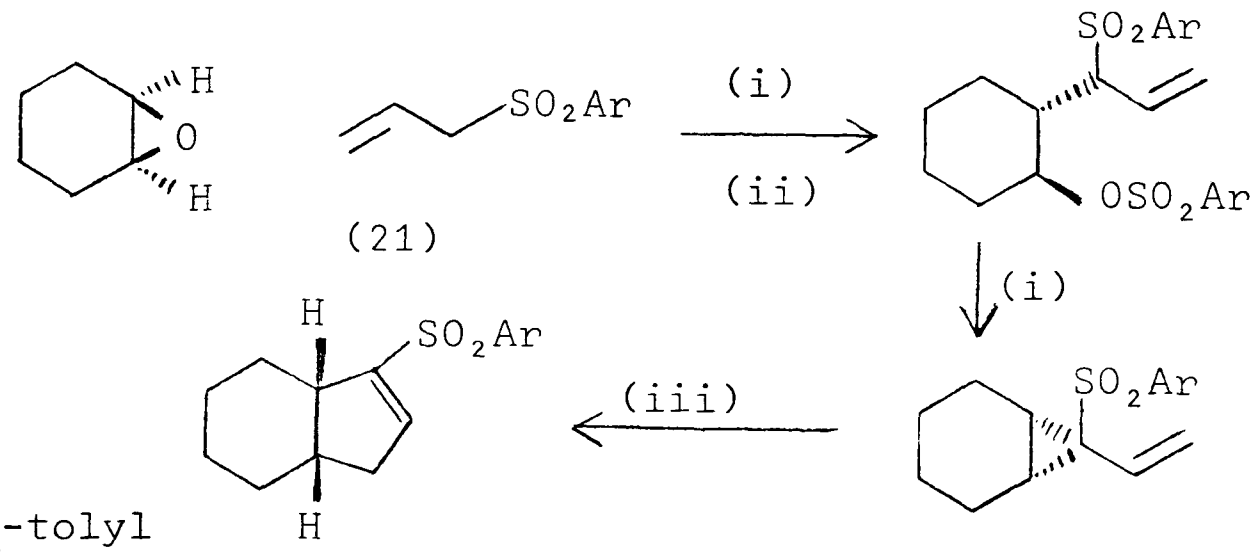
Scheme 132



Ar = p-tolyl

(i) Base (2 mole eq.).

Scheme 133



Ar = p-tolyl

(i) Base (1 mole eq.).

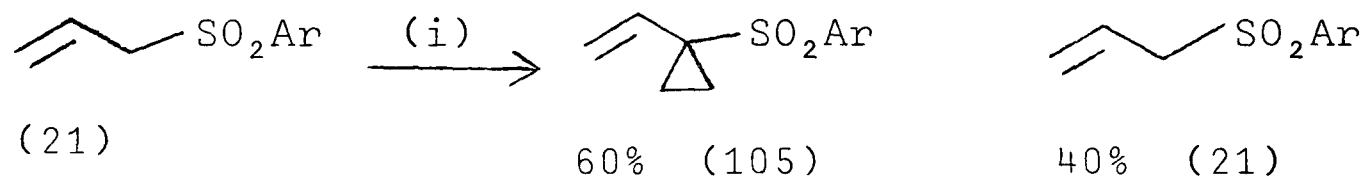
(ii) $ArSO_2Cl$, base.

(iii) Heat.

Scheme 134

2. Preparation of 1-(p-Tolylsulphonyl)cyclopentene

The allylic sulphone (21) was alkylated with 1,2-dibromoethane using a procedure developed by Lin[33], with n-butyl-lithium as the base, α-alkylation occurring as expected[11] (Scheme 135). The mono-alkylated compound (106) was not detected in the products, presumably because it underwent rapid intramolecular alkylation *in situ*. Some starting material (21) was recovered, because the alkyl-lithium was consumed by a competing reaction with 1,2-dibromoethane to produce ethylene[98]. If sodium hydride in DMSO was used instead of n-butyl-lithium, the product was a mixture of starting material (21), cyclopropane (105), and the mono-alkylated compound (107), the latter presumably resulting from base-catalysed isomerisation of the first-formed compound (106). During the course of this investigation, details were published[99] of the preparation of cyclopropane (105) from sulphone (21) and 1,2-dibromoethane using aqueous sodium hydroxide in a two-phase system with a phase-transfer catalyst.



(21) 60% (105) 40% (21)

Ar = p-tolyl

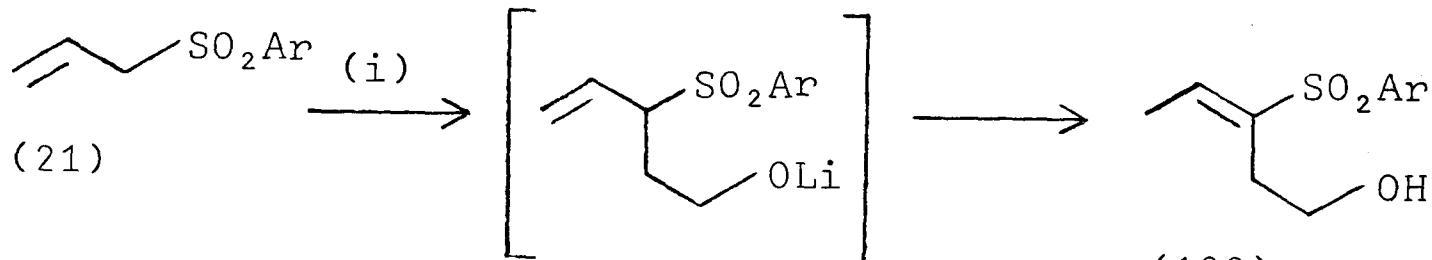
(i) 1,2-Dibromoethane (2 mole eq.), n-BuLi (2 mole eq.), THF-ether (1:1 v/v), 30 min, -60°C.

Scheme 135



Ar = p-tolyl (106) (107)

Alkylation of sulphone (21) with ethylene oxide, using either n-butyl-lithium or methyl-lithium as base, lead to the formation of the (E)-alcohol (109), which presumably resulted from isomerisation of the first-formed compound (108), Scheme 136. The configuration about the double bond was established by tosylating the alcohol (109) by a standard method[100] (Scheme 137), then using the N.O.E. technique on the toluene-p-sulphonate ester (110) (see Experimental Section). The (E)-configuration is to be expected on the basis of the known high steric bulk of the sulphone group.

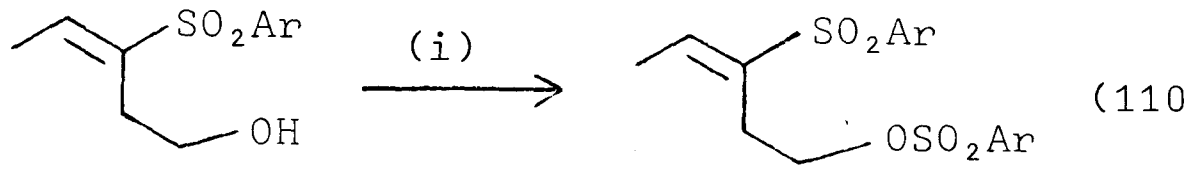


(21) (108) (109)

Ar = p-tolyl

(i) Ethylene oxide (2 mole eq.), n-BuLi (1 mole eq.), THF - ether (1:1 v/v), 30 min, -60°C.

Scheme 136



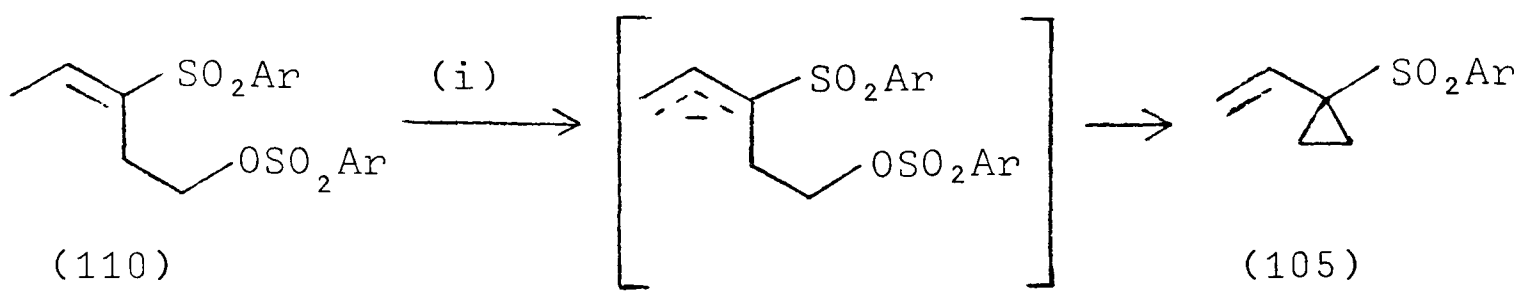
Ar = p-tolyl

(i) $ArSO_2Cl$ (4 mole eq.), pyridine, 12h, ca. 5°C.

Scheme 137

Treatment of tosylate (110) with sodium hydride in DMSO gave cyclopropane (105) (Scheme 138), but the n-butyl-lithium conditions did not induce this reaction. That the cyclo-

propane (105) rather than the cyclopentene (88) was produced again exemplifies the preference for α-electrophilic attack[11] on a sulphonyl-substituted allylic anion.



(110) (105)

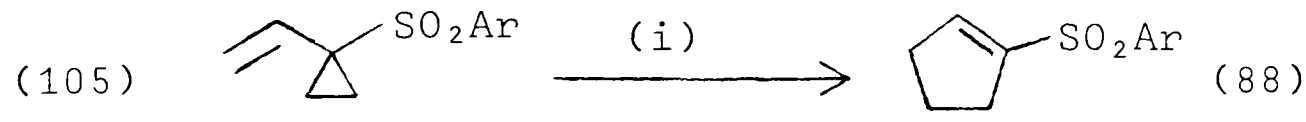
Ar = p-tolyl

(i) NaH (excess), DMSO, 1h, room temperature.

Scheme 138

The allylic sulphone (105) was stable to treatment both with benzoyl peroxide in refluxing carbon tetrachloride and with sodium toluene-p-sulphinate in aqueous acetic acid at 100°C, conditions used in Section II to effect [1,3] rearrangement of allylic sulphones. Such a [1,3]rearrangement of sulphone (105) would produce an unstable cyclopropane with an exocyclic double bond.

Vinylcyclopropane (105) was stable to heating, either in DMSO at 110°C for 72h in the presence of sodium bromide, or in refluxing chlorobenzene for 24h. The rearrangement to the desired cyclopentene (88) (Scheme 139) could be thermally induced, however, by the use of flow pyrolysis[93] (see Experimental Section).



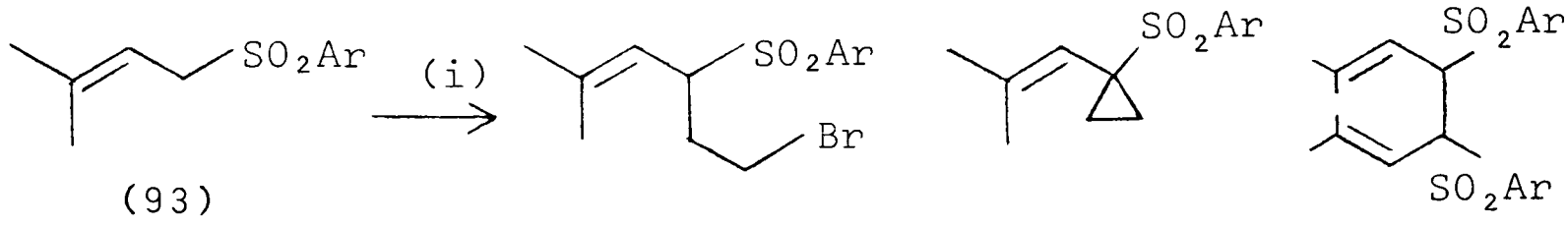
Ar = p-tolyl

(i) Flow pyrolysis.

Scheme 139

3. Attempted Preparation of 5-Membered Ring Compounds

Attempted alkylation of sulphone (93) with 1,2-dibromoethane under the n-butyl-lithium conditions gave a mixture of products, Scheme 140. A possible route for the formation of the dimer (111) is shown in Scheme 141, metal-halogen exchange[98] competing in this case with the alkylation process.

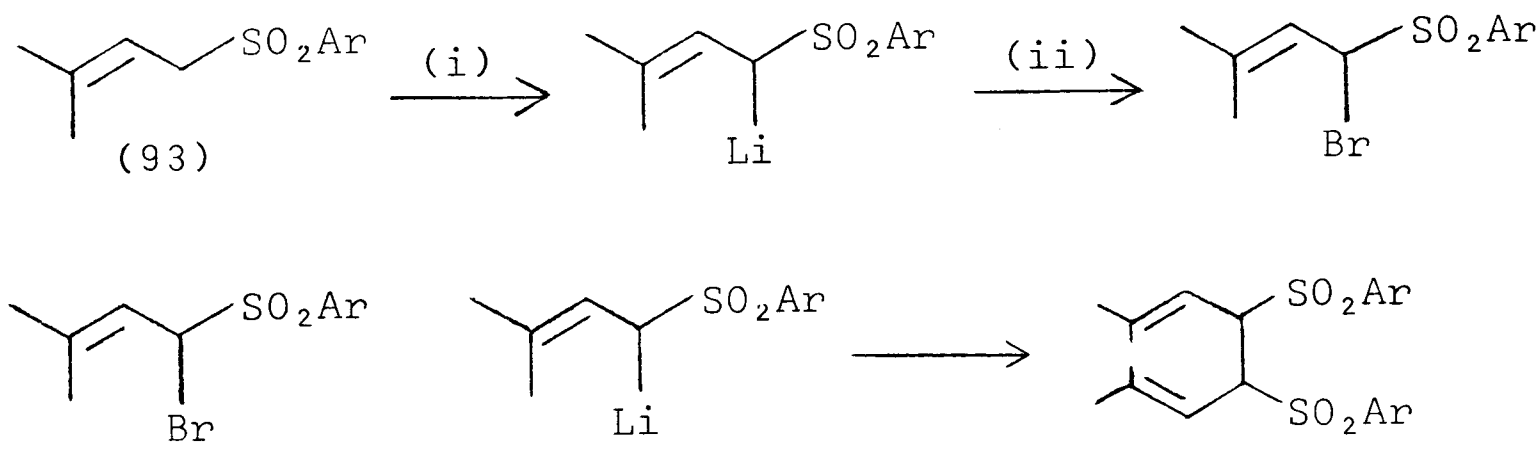


(93) 55% (112) 25% (113) 20% (111)

Ar = p-tolyl

(i) 1,2-Dibromoethane (2 mole eq.), n-BuLi (2 mole eq.), THF - ether (1:1 v/v), 30 min, -60 °C.

Scheme 140



(111)

Ar = p-tolyl

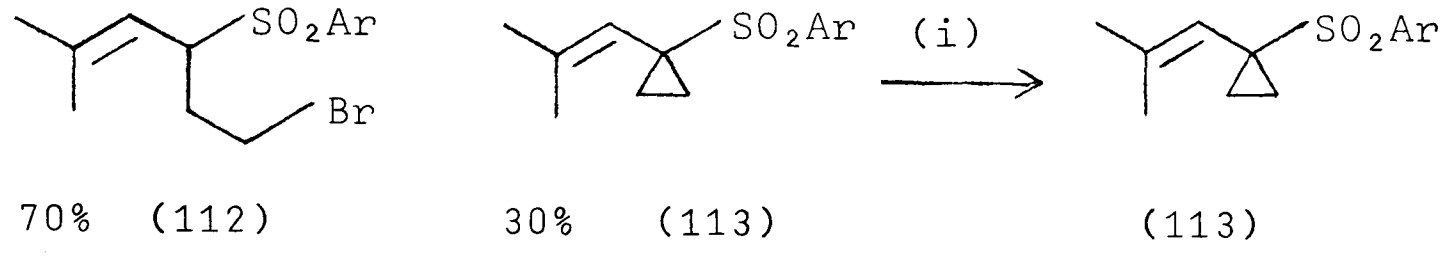
(i) n-BuLi.

(ii) 1,2-Dibromoethane.

Scheme 141

That the mono-alkylated product (112) was isolated contrasts with the case of the less hindered sulphone (21)

(Scheme 135), compound (112) not isomerising to a vinylic sulphone analogous to compound (107). The dimer (111) was removed from the mixture shown in Scheme 140 by crystallisation, leaving the alkylated sulphones (112) and (113). Treatment of this mixture with n-butyl-lithium induced intramolecular alkylation of sulphone (112) to give the cyclopropane (113), Scheme 142.



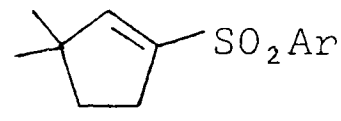
70% (112) 30% (113) (113)

Ar = p-tolyl

(i) n-BuLi, THF - ether (1:1 v/v), 30 min, -60°C.

Scheme 142

Attempts to rearrange the vinylcyclopropane (113) to the desired cyclopentene (114) using flow pyrolysis proved unsuccessful. At temperatures high enough for the reaction to occur, much decomposition took place.



(114)

Ar = p-tolyl

Attempts were made to alkylate sulphone (21) with trans-1,2-dibromocyclohexane or cyclohexene oxide (see Scheme 133 and 134). Various additives (HMPA, TMEDA, and cuprous iodide) were used under the n-butyl-lithium conditions, and a different base-solvent system, sodium hydride in DMSO, was

tried. No products of alkylation were detected, but trans-1,2-dibromocyclohexane or cyclohexene oxide was recovered, along with either sulphone (21) or decomposition products.

Perhaps it is not altogether surprising that nucleophilic attack by the metallated sulphone (21) on cyclohexene oxide or 1,2-dibromocyclohexane did not occur, because alkylation of cyclohexyl systems is known to be difficult[101]. The use of cuprous iodide as additive may have been detrimental rather than beneficial to the chance of the desired reaction occurring[102], since α-sulphonyl organocuprates are unreactive, α-sulphonyl-substituted groups being used as non-transferable ligands for organocopper reagents[103].

Unfortunately it must therefore be concluded that the methodology investigated in this Section is not suitable for 5-membered ring annulation, it being effective only for the preparation of unhindered systems such as cyclopentene (88).

EXPERIMENTAL

GENERAL

Temperatures are quoted in degrees Celsius.

Infra-red spectra were recorded on a Perkin Elmer 257 spectrophotometer either on a chloroform solution or on a liquid film.

Proton nuclear magnetic resonance spectra were recorded either on a Perkin Elmer R24 spectrometer, operating at 60 MHz using tetramethylsilane as internal standard, or on a Bruker WH300 spectrometer, operating at 300 MHz using chloroform as internal standard. Coupling constants are quoted in Hertz. For para disubstituted benzene systems, the AA'BB' signals are described as two doublets.

Pulse Fourier transform carbon-13 nuclear magnetic resonance spectra were recorded on a Bruker WH300 spectrometer operating at 75.57 MHz on deuterochloroform solutions, with the central peak of the solvent signal (77.00ppm) as internal standard.

Mass spectra were recorded under the supervision of Dr R.T. Aplin on Varian VG Micromass 16F and ZAB 1F instruments using electron impact or chemical ionisation techniques.

Microanalyses were carried out under the supervision of Dr F.B. Strauss.

Melting points were recorded on a Büchi 510 melting-point apparatus.

Analytical gas liquid chromatography was carried out using a Pye Unicam 104 instrument with a column 5ft long × 4mm bore packed with Embacel coated with OV17 (1.5%) at 195°.

Chromatography. Thin layer chromatography was carried out on plates coated with silica gel HF 254/366 eluted with ether-light petroleum (1:1 v/v), spots being observed by u.v. or iodine treatment. Preparative layer chromatography (p.l.c.) was carried out using 20 × 20cm plates coated with a 1mm layer of silica gel HF 254/366. The plates were pre-eluted with solvent. Bands were detected by their fluorescence. Column chromatography was carried out using silica gel (60-120 mesh), normally eluting with ether-light petroleum (1:1 v/v). For flash column chromatography, Merck 60H t.l.c. silica gel was used.

Solvents. Diethyl ether was dried over sodium wire. Tetrahydrofuran (THF) was dried by distillation under nitrogen from excess benzophenone and sodium wire. Pyridine was dried by refluxing over potassium hydroxide pellets for 2h, followed by distillation. Dimethylformamide (DMF) and dimethyl sulphoxide (DMSO) were dried by refluxing over calcium hydride for 6h, followed by distillation. Hexamethylphosphoramide (HMPA) was dried by distillation from sodium hydride. Light petroleum is of boiling range 40-60° and was redistilled before use. Glacial acetic acid-water (3:2 v/v) is referred to as "aq. AcOH".

n-Butyl-lithium and methyl-lithium were estimated as follows. Equal volumes of the alkyl-lithium solution were added separately to water and 1,2-dibromoethane in ether. The aqueous solution was titrated with 0.1$\underline{M}$ hydrochloric acid, using phenolphthalein as indicator, to determine the total alkali concentration. The organic solution was added to water and similarly titrated to determine the concentration

of alkali other than the alkyl-lithium.

Sodium hydride (50% dispersion in oil) was washed several times with light petroleum immediately before use.

Benzoyl peroxide was obtained from the slurry by dissolving it in the minimum amount of cold chloroform, separating the aqueous phase, and precipitating the benzoyl peroxide with methanol.

The following samples were provided by P. Lin[33]:- sodium toluene-p-sulphinate, 3-(phenylsulphonyl)cyclohexene (68), 3-(p-tolylsulphonyl)cyclohexene (59), 3-[^{2}H]-3-(p-tolylsulphonyl)cyclohexene (63), 3-methyl-3-(p-tolylsulphonyl)-cyclohexene (67), 3-(p-tolylsulphonyl)propene (21), 3-methyl-3-(p-tolylsulphonyl)-1-butene (92), and 3-methyl-3-(t-butyl-sulphonyl)-1-butene (101).

SECTION I

4-t-Butylcyclohexene (56).- cis- and trans-4-t-Butylcyclohexanols (55) (100.5g, 0.643 mol) were refluxed over potassium hydrogen sulphate (10.6g, 0.078 mol) using a 70cm Vigreux column. Liquid (b.p. below 180°) was distilled over and collected. The yellow liquid was separated from the water and distilled to give 4-t-butylcyclohexene (57.6g, 65%), b.p. 69-72° at 28 mm Hg (lit.,[104] 65-66° at 20 mm Hg); δ(60MHz;CCl_4) 0.9(9H, s, t-Bu), 1.0-2.3(7H, m), and 5.6(2H, m, =C-H).

trans-5-t-Butylcyclohex-2-enol (54).[58] - N-Bromosuccinimide (37g, 0.208 mol) and benzoyl peroxide (ca. 0.1g) were added to a solution of 4-t-butylcyclohexene (31.6g, 0.229 mol) in carbon tetrachloride (150 ml). The mixture was refluxed for 1.5h, then filtered and evaporated to give a crude mixture of allylic bromo-compounds. This was dissolved in acetone (40 ml) and the solution was added dropwise over 30 min to a vigorously stirred mixture of sodium hydrogen carbonate (35g, 0.42 mol), water (35 ml) and acetone (75 ml) under reflux. The mixture was stirred under reflux for a further 1h, then filtered and evaporated. Ether was added and the solution was washed with water then brine, dried (Na_2SO_4) and evaporated. Distillation gave the alcohol mixture (14.3g, 45%), b.p. 92-94° at 9 mm Hg (lit.,[58] 100-110° at 20 mm Hg). A portion of this alcohol mixture (11.8g, ca. 77 mmol) was dissolved in pyridine (60 ml), and then distilled p-nitrobenzoyl chloride (16.0g, 86 mmol) was added.

The mixture was shaken for 1h, then water (ca. 1 ml) was added. After further shaking, the mixture was poured into water (ca. 300 ml) and extracted with ether. The ether solution was washed with dilute HCl, aqueous Na_2CO_3, water and brine, dried (Na_2SO_4) and evaporated. The solid was recrystallised from ethanol to give trans-5-t-butylcyclohex-2-enyl p-nitrobenzoate (12.8g, 55%), m.p. 99-101°(lit.,[58] 99-100°). A portion of this ester (6.2g, 20 mmol) was stirred under reflux for 30 min with a solution of sodium hydroxide (4.5g) in methanol (40 ml) and water (20 ml). The reaction mixture was added to water and extracted with ether. After washing with water and brine, drying ($MgSO_4$) and evaporation, distillation gave trans-5-t-butylcyclohex-2-enol (2.6g, 82%), b.p. 115-117° at 20 mm Hg (lit.,[58] 108° at 25 mm Hg); δ(300MHz; $CDCl_3$) 0.9(9H, s, t-Bu), 1.3-2.2(6H, m, 5H after D_2O exch.), 4.25(1H, br s, H-C-OH), and 5.8-6.0(2H, m, =C-H).

cis-5-t-Butylcyclohex-2-enol (53)[56].- 6 N Chromic acid[105] (2 ml) was added dropwise to a stirred solution of trans-5-t-butylcyclohex-2-enol (1.26g, 8.2 mmol) in acetone (5 ml) surrounded by an ice bath. After stirring for 2h at 20°, propan-2-ol (ca. 0.5 ml) was added and the solution was filtered, evaporated, diluted with water and extracted with ether. The ether solution was washed with aqueous Na_2CO_3, water and brine, dried ($MgSO_4$) and evaporated. The crude ketone thus obtained was dissolved in ether (20 ml) and added dropwise over 30 min to a stirred mixture of lithium

aluminium hydride (1.15g, 30 mmol) and ether (10 ml) at -70°. After stirring for 10h at -70°, the mixture was allowed to warm up to 20° over 8h. A slurry of sodium sulphate and water was added and the ether solution was filtered, washed with aqueous Na_2CO_3, water and brine, dried ($MgSO_4$) and evaporated. Distillation gave cis-5-t-butylcyclohex-2-enol (0.465g, 37%), b.p. 114-116° at 13 mm Hg (lit.,[56] 114-116° at 20 mm Hg); δ(300MHz; $CDCl_3$) 0.9(9H, s, t-Bu), 1.3-2.2(6H, m), 4.25-4.35(1H, m, H-C-OH), and 5.6-5.85(2H, m, =C-H).

1-Methylcyclohex-2-enol (52)[57].- Cyclohex-2-enone[56] was prepared from cyclohex-2-enol (49)[106], which had been prepared from cyclohexene. Methyl iodide (14 ml, 0.22 mol) was added dropwise to a stirred mixture of lithium shot (ca. 3.5g, ca. 0.5 mol) in ether (150 ml) under nitrogen. After a 30 min reflux, the mixture was cooled on a CCl_4-dry ice bath and a solution of cyclohex-2-enone (9.9g, 0.10 mol) in ether (50 ml) was added over 30 min. After stirring for 15 min at 20°, first water then dilute HCl were added. Filtration and separation gave an ether solution which was washed with dilute HCl, aqueous Na_2CO_3, water and brine, dried ($MgSO_4$) and evaporated. Distillation gave a mixture of 1-methylcyclohex-2-enol and cyclohex-2-enone (ca. 4:1 by n.m.r.), b.p. 72-76° at 22 mm Hg. The ketone was removed by dissolving the mixture in ether (60 ml) and shaking this solution with saturated aqueous sodium metabisulphite (90 ml) at 20° for 3h. The ether phase was washed with aqueous Na_2CO_3, water and brine, dried ($MgSO_4$) and evaporated to give

1-methylcyclohex-2-enol[57,107], δ(60MHz; CCl_4) 1.2(3H, s, Me), 1.4-2.1(6H, m), 3.3(1H, OH), and 5.3-5.7(2H, m, =C-H).

1-[^{2}H]-Cyclohex-2-enol (50).- A solution of cyclohex-2-enone[56](16.9g, 0.175 mol) in ether (60 ml) was added to lithium aluminium deuteride (1.84g, 0.044 mol) and the mixture was stirred under reflux for 2h. A slurry of sodium sulphate and water was added, and the ether solution was filtered, washed with aqueous Na_2CO_3, water and brine, dried (Na_2SO_4) and evaporated to give a mixture of 1-[^{2}H]-cyclohex-2-enol and cyclohex-2-enone (ca. 1:1 by n.m.r.). This mixture was dissolved in ether (50 ml) and refluxed for 24h with lithium aluminium deuteride (0.67g). After working up as before, the oil was dissolved in ether (30 ml) and shaken at 20° with saturated aqueous sodium metabisulphite solution (30 ml) for 24h. Normal work up and distillation gave 1-[^{2}H]-cyclohex-2-enol (1.37g, 8%), b.p. 68.5-71° at 12 mm Hg; $\nu_{max.}$(neat) 3350br (OH), 3030(=C-H), 2940(C-H), 2130w(C-D), 1645w(C=C), 1170, 1090, 935, and 720cm^{-1}; δ(300MHz; $CDCl_3$) 1.5-2.1(7H, m, C-H and OH), and 5.7-5.9(2H, m, =C-H).

3-Methylcyclohex-2-enol (51)[57].- A solution of 3-methylcyclohex-2-enone[108](9.0g, 82 mmol) in ether (15 ml) was added to lithium aluminium hydride (1.55g, 41 mmol) and the mixture was stirred under reflux for 1h. A slurry of sodium sulphate and water was added, and the ether solution was filtered, dried (Na_2SO_4) and evaporated. Distillation gave 3-methyl-

cyclohex-2-enol (5.2g, 56%), b.p. 75-76° at 10 mm Hg (lit.,[109] 56° at 1 mm Hg); δ(300MHz; $CDCl_3$) 1.5-2.0(10H, m, C-H, Me and OH), 4.2(1H, br s, H-C-OH), and 5.5(1H, m, =C-H).

Cyclohex-2-enyl toluene-p-sulphinate (46).- Cyclohex-2-enol[106] (2.7g, 27.5 mmol) was added over 15 min to a stirred solution of undistilled toluene-p-sulphinyl chloride[110] (5.95g, ca. 34 mmol) in dried pyridine (8.5 ml) on an acetone-dry ice bath. The mixture was stirred for a further 30 min with cooling, then for 30 min at 20°. Ether (100 ml) was added and the solution was washed with dilute HCl, aqueous Na_2CO_3, water and brine, dried (K_2CO_3) and evaporated. Purification by column chromatography on silica gel (120g) gave a 1:1 mixture of the two diastereoisomers of cyclohex-2-enyl toluene-p-sulphinate (5.5g, 85%) as a pale orange oil, $\lambda_{max.}$(cyclohexane) 223 and 257.5 nm (ε28000 and 10600dm^3 mol^{-1} cm^{-1}); $\nu_{max.}$(neat) 3030(=C-H), 2930(C-H), 1645w(C=C), 1595 and 1490(Ar), 1130(S=O)[111], 900, and 700cm^{-1}; δ(300MHz; $CDCl_3$) 1.5-2.1(6H, m), 2.4(3H, s, Me), 4.75-4.85(1H, m, 1-H), 5.45(0.5H, dd, J10,5, 2-H of one diastereoisomer), 5.8(0.5H, dd, J10,5, 2-H of the other diastereoisomer), 5.9(0.5H, dt, J10,5, which collapsed on irradiation at 5.45, 3-H of one diastereoisomer), 5.95(0.5H, dt, J10,5, 3-H of the other diastereoisomer), 7.3 and 7.6(4H, AA'BB', J7.5, p C_6H_4).

3-Methylcyclohex-2-enyl toluene-p-sulphinate (48).- 3-Methylcyclohex-2-enol (2.2g) was esterified in the same

manner as cyclohex-2-enol (p. 87) to give a 1:1 mixture of the two diastereoisomers of 3-methylcyclohex-2-enyl toluene-p-sulphinate (4.5g, 92%) as a pale yellow oil, which was unstable to purification by column chromatography, $\nu_{max.}$(neat) 3040(=C-H), 2930(C-H), 1665(C=C), 1595 and 1490(Ar), 1130(S=O)[111], 900, and 760 cm^{-1}; δ(300MHz; $CDCl_3$) 1.5-2.05 (9H, m, C-H and Me), 2.4(3H, s, $C\underline{H}_3-C_6H_4$), 4.75-4.9(1H, m, 1-H), 5.25(0.5H, br s, 2-H of one diastereoisomer), 5.6(0.5H, br s, 2-H of the other diastereoisomer), 7.3 and 7.6(4H, AA'BB', J7.5, p C_6H_4).

1-[^{2}H]-Cyclohex-2-enyl toluene-p-sulphinate (47).- A solution of 1-[^{2}H]-cyclohex-2-enol (0.30g, 3.0 mmol) in dichloromethane (2 ml) was added dropwise to a stirred solution of undistilled toluene-p-sulphinyl chloride[110](0.59g, ca. 3.4 mmol) and dried pyridine (0.3 ml, 3.7 mmol) in dichloromethane (2 ml) on an acetone-dry ice bath. The mixture was stirred for a further 15 min with cooling, then for 30 min at 20°. Dichloromethane (ca. 10 ml) was added and the solution was washed with dilute HCl, aqueous Na_2CO_3, water and brine, dried ($CaCl_2$) and evaporated to give a 1:1 mixture of the two diastereoisomers of 1-[^{2}H]-cyclohex-2-enyl toluene-p-sulphinate (0.69g, 96%) as a yellow oil, $\nu_{max.}$(neat) 3030(=C-H), 2930(C-H), 1645w(C=C), 1595 and 1490(Ar), 1130(S=O)[111], 900, and 770 cm^{-1}; δ(300MHz; $CDCl_3$) 1.5-2.1(6H, m), 2.4(3H, s, Me), 5.45(0.5H, d, J10, 2-H of one diastereoisomer), 5.8(0.5H, d, J10, 2-H of the other diastereoisomer), 5.9(0.5H, dt, J10,5, 3-H of one diastereoisomer), 5.95(0.5H,

dt, J10,5, 3-H of the other diastereoisomer), 7.3 and 7.6(4H, AA'BB', J7.5, p C_6H_4).

trans-5-t-Butylcyclohex-2-enyl toluene-p-sulphinate (18).- trans-5-t-Butylcyclohex-2-enol (0.96g) was esterified in the same manner as 1-[^{2}H]-cyclohex-2-enol (p. 88) to give a 1:1 mixture of the two diastereoisomers of trans-5-t-butylcyclohex-2-enyl toluene-p-sulphinate (1.8g, ca. 100%) as a yellow oil, $\nu_{max.}$(neat) 3030w(=C-H), 2960(C-H), 1650w(C=C), 1595 and 1490(Ar), 1135(S=O)[111], 900, and 810cm^{-1}; δ(300MHz; $CDCl_3$) 0.8, 0.9(9H, both s, t-Bu of both diastereoisomers), 1.2-2.2(5H, m), 2.4(3H, s, Me), 4.85(1H, br s, 1-H), 5.4-5.45(0.5H, m, 2-H of one diastereoisomer), 5.8-5.9(0.5H, m, 2-H of the other diastereoisomer), 5.95-6.15(1H, m, 3-H of both diastereoisomers), 7.3 and 7.6(4H, AA'BB', J7.5, p C_6H_4).

cis-5-t-Butylcyclohex-2-enyl toluene-p-sulphinate (17).- cis-5-t-Butylcyclohex-2-enol (0.46g) was esterified in the same manner as 1-[^{2}H]-cyclohex-2-enol (p. 88) to give a 1:1 mixture of the two diastereoisomers of cis-5-t-butylcyclohex-2-enyl toluene-p-sulphinate (0.9g, ca. 100%) as a yellow oil, $\nu_{max.}$(neat) 3030w(=C-H), 2960(C-H), 1595 and 1490(Ar), 1135(S=O)[111], 900, and 790cm^{-1}; δ(300MHz; $CDCl_3$) 0.8, 0.9(9H, both s, t-Bu of both diastereoisomers), 1.3-2.1(5H, m), 2.4(3H, s, Me), 4.95-5.05(1H, m, 1-H), 5.45-5.5(0.5H, m, 2-H of one diastereoisomer), 5.7-5.75(0.5H, m, 2-H of the other diastereoisomer), 5.75-5.95(1H, m, 3-H of both diastereo-

isomers), 7.3 and 7.6(4H, AA'BB', J7.5, p C_6H_4).

1-Methylcyclohex-2-enyl toluene-p-sulphinate (58).- 1-Methylcyclohex-2-enol (0.39g) was esterified in the same manner as cyclohex-2-enol (p. 87) to give 1-methylcyclohex-2-enyl toluene-p-sulphinate (0.68g, ca. 80%) as an orange oil, which rearranged on standing and hence could not be purified, $\nu_{max.}$(neat) 3020(=C-H), 2930(C-H), 1595 and 1490(Ar), 1030(S=O)[111], 810, and 770cm^{-1}; δ(60MHz; CCl_4) 1.4-2.3(9H, m, C-H and Me), 2.35(3H, s, CH_3-C_6H_4), 5.2-6.1(2H, m, =C-H), 7.1 and 7.35(4H, AA'BB', J8, p C_6H_4).

Further attempts to prepare 1-methylcyclohex-2-enyl toluene-p-sulphinate (58).- A typical procedure is described. A solution of 1-methylcyclohex-2-enol (0.28g, 2.5 mmol) in carbon tetrachloride containing TMS (2 ml) was added dropwise to a stirred solution of undistilled toluene-p-sulphinyl chloride[110] (0.48g, ca. 2.7 mmol) and dried pyridine (0.25 ml, 3.1 mmol) in carbon tetrachloride (1 ml). After stirring for 10 min at 20°, the solution was filtered and the n.m.r. spectrum was immediately taken. Excess pyridine was removed by washing the solution with dilute HCl, aqueous Na_2CO_3 then water, and drying ($CaCl_2$). Results are listed in Table 1.

Table 1. Attempts to prepare 1-methylcyclohex-2-enyl toluene-p-sulphinate (58).

Time/min	Temperature/°C	Initial products (by n.m.r.)/%		
		1-methyl-sulphinate (58)	3-methyl sulphinate (48)	1-methyl alcohol (52)
ca. 20	ca. 20		100	
10	20	40	40	20
10[a]	20	35	45	20
5	ca. 0	35	55	10

a. Anhydrous sodium carbonate (0.26g) present during the reaction.

Rearrangement of the Allylic Sulphinate Esters.

Four general procedures were used:-

(a) A solution of the sulphinate in CCl_4 or $CDCl_3$ (0.1-0.2M), containing any specified additive, was set aside at the specified temperature. The n.m.r. spectrum was taken periodically.

(b) A solution of the sulphinate in toluene, acetonitrile, or methanol (0.1-0.3M), containing any specified additive, was set aside at the specified temperature and the reaction was followed by t.l.c. After the specified time, the solution was evaporated, toluene solutions having first been washed with dilute HCl, aqueous Na_2CO_3 and water, then dried (Na_2SO_4).

(c) A solution of the sulphinate in either concentrated sulphuric acid or glacial acetic acid-water (3:2 v/v) (0.1-0.3M) was set aside as specified. Aqueous NaOH was added and

the mixture was extracted with ether. The ether solution was washed with aqueous Na_2CO_3, water and brine, dried (Na_2SO_4) and evaporated.

(d) A solution of the sulphinate in DMF or formamide (0.1-0.75M) was set aside as specified and the reaction was followed by t.l.c. Water was added and the mixture was extracted either with toluene or, for some of the formamide solutions, with ether. The organic solution was washed with dilute HCl, aqueous Na_2CO_3, water and brine, dried (Na_2SO_4) and evaporated.

The sulphinate esters were subjected to various conditions as described above. The reaction mixtures thus obtained were analysed by n.m.r. and t.l.c. Only the results from experiments with a weight recovery of higher than 50% are listed in Tables 2 to 5.

Table 2. Rearrangement of Cyclohex-2-enyl Toluene-p-sulphinate (46).

Entry[a]	Solvent	Additive	Temperature	Time	Products[b]			Method of analysis
					Sulphinate(46)	Sulphone(59)	Other[c]	
1	None[d]	None	20°	1 day	✓	×		t.l.c.
	"	"	"	2 days	✓	✓	$ArSO_2H$[e](?)	t.l.c.
	"	"	"	8 days	20%	30%	$ArSO_2H$[e] 40% ROR[f] 10%	n.m.r.,t.l.c.
2	CCl_4	None	ca. 5°	11 months	✓	×	Decomp.	n.m.r.
3	CCl_4	None	Reflux	42h	100%	×		n.m.r.
4	CCl_4	None	20°	3 days	100%	×		n.m.r.
	"	"	"	4 days	100%	Trace		"
	"	"	"	7 days	75%	25%		"
	"	"	"	10 days	55%	45%		"
	"	"	"	12 days	50%	50%		"
	"	"	"	14 days	20%	80%		"
	"	"	"	17 days	×	100%		"

Cont.

Entry[a]	Solvent	Additive	Temperature	Time	Products[b]			Method of analysis
					Sulphinate(46)	Sulphone(59)	Other[c]	
5	CCl_4	2,4,6-Collidine (1 mole eq.)	20°	26 days	✓	×	Decomp.	n.m.r.
6	$CDCl_3$	None	20°	3 days	100%	×		n.m.r.
	"	"	"	4 days	60%	40%		"
	"	"	"	7 days	25%	75%		"
	"	"	"	10 days	Trace	100%		"
7	$CDCl_3$	2,4,6-Collidine (1 mole eq.)	20°	26 days	✓	×	Decomp.	n.m.r.
8	$CDCl_3$	$ZnCl_2$ (ca. 1 mole eq.)	20°	5 min	100%	Trace		n.m.r.
	"	"	"	2h	50%	50%		"
	"	"	"	4h	25%	75%		"
	"	"	"	8h	15%	85%		"
	"	"	"	18h	Trace	100%		"
9	Toluene	None	90°	1h	100%	×		n.m.r., t.l.c.

Cont.

Entry[a]	Solvent	Additive	Temperature	Time	Products[b]			Method of analysis
					Sulphinate(46)	Sulphone(59)	Other[c]	
10	Toluene	None	90°	100 min	×	✓	Decomp. $ArSO_2H$[e] decomposition products(?)	n.m.r.,t.l.c.
11	Toluene	DBU[g] (2 mole eq.)	70°	18h	100%	×		n.m.r.,t.l.c.
12	Toluene	TsOH[h] (saturated soln.)	65°	2h	×	✓	Decomp. $ArSO_2H$[e] decomposition products(?)	n.m.r.,t.l.c.
13	Aceto-nitrile	None	60°	1.5h	Trace	ca. 15%	3-Acetoamido-cyclohexene[i] 35% $ArSO_2H$[e] decomposition products(?) 50%	n.m.r.,t.l.c.
14	Methanol	None	20°	68h	×	×	Cyclohex-2-enol 40% Methyl toluene-p-sulphinate[j] 60% $ArSO_2H$[e](?) trace	n.m.r.,t.l.c.
15	aq.AcOH	None	55°	45 min	45%	20%	Cyclohex-2-enol 35% Decomp.	n.m.r.

Cont.

Entry[a]	Solvent	Additive	Temperature	Time	Products[b]			Method of analysis
					Sulphinate(46)	Sulphone(59)	Other[c]	
16	aq.AcOH	None	105°	45 min	ca. 10%	55%	Cyclohex-2-enol 35% Decomp.	n.m.r.
17	conc. H_2SO_4	None	20°	45 min	Trace	✓	$ArSO_2H$[e] decomposition products(?) Decomp.	n.m.r.,t.l.c.
18	DMF	None	90° then 70°	2.5h for 16h	Trace	60%	ROR[f] 15% $ArSO_2H$[e] decomposition products(?) 25%	n.m.r.,t.l.c.
19	DMF	2,4,6-Collidine (1 mole eq.)	70° then 95°	25h for 24h	Trace	ca. 100%		n.m.r.,t.l.c.
20	Formamide	None	55°	1h	100%	×		n.m.r.
21	Formamide	None	75°	0.5h	[k] 70%	30%		n.m.r. (300MHz)
22	Formamide	None	70° then 95°	1h for 2.5h	Trace	ca. 100%	Decomp.	n.m.r.,t.l.c.
23	Formamide	Sodium benzene-sulphinate (1 mole eq.)	55°	45 min	100%	×		n.m.r.
24[l]	Formamide	Sodium benzene-sulphinate (1 mole eq.)	105°	3h	×	65%	3-(Phenylsulphonyl) cyclohexene 35%	n.m.r.,g.l.c.

a. Each entry is for a separate experiment.

b. The symbols ✓ and × signify respectively the presence or absence of the named compound. Percentages are obtained from the n.m.r. integral and are approximate.

c. A question mark indicates uncertainty in the identification of the named substance. The term "decomp." (for "decomposition products") is used if the material has extra n.m.r. peaks and/or an R_F0 spot on t.l.c.

d. Neat material.

e. $ArSO_2H$ is toluene-p-sulphinic acid.

f. ROR is di-1-cyclohexen-3-yl ether[112](115), see p.103.

g. DBU is 1,8-diazabicyclo[5.4.0]undec-7-ene.

h. TsOH is toluene-p-sulphonic acid.

i. 3-Acetoamidocyclohexene (70) was identified as described on p.103.

j. Peaks for methyl toluene-p-sulphinate[113] were present in the n.m.r. spectrum.

k. The unrearranged sulphinate ester (46) was still a 1:1 mixture of the two diastereoisomers (by 300MHz n.m.r.).

l. 3-(p-Tolylsulphonyl)cyclohexene (59) was recovered unchanged after treatment with sodium benzenesulphinate (1 mole eq.) under these conditions.

Table 3[a]. Rearrangement of 1-[^{2}H]-Cyclohex-2-enyl Toluene-p-sulphinate (47)

Entry	Solvent	Additive	Temperature	Time	Products				Method of analysis
					Sulphinate (47)	1-[^{2}H]-Sulphone (64)	3-[^{2}H]-Sulphone (63)	Other	
1	$CDCl_3$	None	20°	18 days	ca. 100%	×	×	Decomp.	n.m.r.
2	$CDCl_3$	TsOH (ca. 0.1 mole eq.)	20°	88h	✓	✓	✓	Sulphinate (46)[b] or 3-[^{2}H]-cyclohex-2-enyl toluene-p-sulphinate	n.m.r.
3	Formamide	None	75°	0.5h	100%	Trace	Trace		n.m.r.,t.l.c.
4	Formamide	None	75°	1.5h	✓	✓	✓		n.m.r.,t.l.c.
5	Formamide	None	75°	5h	×	ca. 50%	ca. 50%		n.m.r.,t.l.c.

a. Footnotes a, b, and h of Table 2 also apply to this Table.
b. A signal at $\delta(CDCl_3)$ 4.75-4.85(m, 1-H) was present.

Table 4[a]. Rearrangement of cis- and trans-5-t-Butylcyclohex-2-enyl Toluene-p-sulphinate (17) and (18)

Entry	Sulphinate	Solvent	Temperature	Time	Products					Method of analysis
					trans Sulphinate (18)	cis Sulphinate (17)	trans Sulphone (20)	cis Sulphone (19)	Other	
1	trans-(18)	CCl_4	20°	10 weeks	✓		×	×		n.m.r.
	"	"	"	18 weeks	×	×	ca. 50%	ca. 50%		"
2	cis-(17)	CCl_4	20°	5 days		✓	×	×		n.m.r.
	"	"	"	11 days		✓	✓	✓		"
	"	"	"	17 days	×	×	ca. 50%	ca. 50%		"
3	trans-(18)	Formamide[b]	80°	5h	Trace	×	[c] 75%	[c] 25%	$ArSO_2H$ decomposition products(?)[c] Decomp.	n.m.r. t.l.c. i.r.
4	cis-(17)	Formamide[b]	80°	5h	×	[c] Trace	[c] 30%	[c] 70%	$ArSO_2H$ decomposition products(?)[c] Decomp.	n.m.r. t.l.c. i.r.

a. Footnotes a, b, c, and e of Table 2 also apply to this Table.
b. Some of the sulphinate ester did not dissolve.
c. Extracted from the reaction mixture by p.l.c. The ratio of cis- to trans-sulphone, (19) to (20), was estimated by 300MHz n.m.r. Neither cis- nor trans-sulphone (19) and (20) was epimerised under these conditions.

Table 5[a]. Rearrangement of 3-Methylcyclohex-2-enyl Toluene-p-sulphinate (48)

Entry	Solvent	Additive	Temperature	Time	Products			Method of analysis
					Sulphinate (48)	Sulphones[b] (66),(67)	Other	
1	None	None	ca. 0°	18 days	100%	×		n.m.r.
	"	"	"	24 days	×	100%		"
2	CCl_4	None	Reflux	2h	×	100%		n.m.r., i.r.
3	CCl_4	None	20°	0.5h	100%	×	None	n.m.r.
	"	"	"	2.5h	✓	✓	None	"
	"	"	"	7h	×	✓	Dienes[c]	"
	"	"	"	18.5h	×	✓	Dienes[c]	"
	"	"	"	3 days	×	100%	None	"
4	CCl_4	2,4,6-Collidine (0.5 mole eq.)	20°	26 days	✓	×		n.m.r.
5.	$CDCl_3$	None	20°	ca. 15 min	✓	✓	None	n.m.r.
	"	"	"	30 min	✓	✓	Dienes[c]	"
	"	"	"	7h	Trace	✓	Dienes[c]	"

Cont.

6	$CDCl_3$	2,4,6-Collidine (ca. 0.5 mole eq.)	20°	26 days	✓	×	Decomp.	n.m.r.
7	$CDCl_3$	$ZnCl_2$ (ca. 1 mole eq.)	20°	2h	35%	65%		n.m.r.
	"	"	"	4h	20%	80%		"
	"	"	"	18h	Trace	100%		"
8	Methanol	None	Reflux	0.5h	×	ca. 50%	$ArSO_2H$ ca. 50%	n.m.r., t.l.c., i.r.
9	aq. AcOH	None	50°	0.5h	×	100%		n.m.r., i.r.
10	aq. AcOH	Sodium benzene-sulphinate (1 mole eq.)	55°	0.5h	×	✓	1-Methyl-3-(phenylsulphonyl) cyclohexene(?)	n.m.r.
11 [d]	Formamide	None	55°	0.5h	ca. 20%	ca. 80%		n.m.r.
12 [d]	Formamide	Hydroquinone (0.05 mole eq.)	55°	0.5h	ca. 20%	ca. 80%		n.m.r.
13 [d]	Formamide	Sodium benzene-sulphinate (1 mole eq.)	55°	4h	×	✓	1-Methyl-3-(phenylsulphonyl) cyclohexene(?)	n.m.r.

a. Footnotes a, b, c, d, and e of Table 2 also apply to this Table.

b. A small amount (ca. 15%) of 3-methyl-3-(p-tolylsulphonyl)-cyclohexene (67), identified by the $\delta(CDCl_3)$ 1.4 (s, Me-3) peak, was present along with the 1-methyl-3-(p-tolyl-sulphonyl)cyclohexene (66).

c. Some or all of the following dienes were shown to be present (p.103):- 1-methyl-1,3-cyclohexadiene (71), 2-methyl-1,3-cyclohexadiene (72), and 3-methylenecyclohexene (73).

d. Sulphone (67) was stable under these conditions.

di-1-Cyclohexen-3-yl ether (115)[112] was extracted by column chromatography from a sample of distilled cyclohex-2-enol (49) which had partly decomposed to the ether on standing for one month at 20°. The ether (115) was obtained as an oil, $\nu_{max.}$(neat) 3020(=C-H), 2930(C-H), 1645(C=C), 1430, 1385, 1305, 1070 br, 1010, 935, and 720cm^{-1}; $\delta(CCl_4)$ 1.3-2.2(12H, m), 3.7-4.0(2H, m, H-C-O), and 5.65(4H, s, =C-H).

3-Acetoamidocyclohexene (70)[61] was isolated by p.l.c. from the reaction mixture described in entry 13 of Table 2, m.p. 78-79°(lit.,[61] 78°); $\nu_{max.}$(KBr) 3260(NH), 2930 and 2970(C-H), 1635(C=O), 1540, 1370, 1265, and 800cm^{-1} (lit.,[61] 3290, 3070, 3020, 1640, 1550, 1370, and 730cm^{-1}); $\delta(CCl_4)$ 1.45-2.15(9H, m, CH_2 and Me), 4.1-4.55(1H, m, H-C-N), and 5.35-5.95(3H, m, =C-H and NH) [lit.,[114] $\delta(CCl_4)$ 1.98(3H, Me), 4.2(1H), 5.5(2H, =C-H), and 7.6(d, NH)].

Identification of the Diene Intermediates (71), (72), and (73) described in Table 5 (entries 3 and 5). Extra peaks were present at δ(60MHz; CCl_4) 4.65(br s), 5.7(br s), and 7.45(s) or δ(300MHz; $CDCl_3$) 4.75(d, J5), 5.8-5.9(m), and 6.15(d, J10). After ca. 18h, volatile material was flash distilled from the reaction mixture described in entry 5, δ(300MHz; $CDCl_3$) 4.75(d, J5), 5.6-5.7(m), 5.8-5.95(m), and 6.15(d, J10). Material with a similar n.m.r. spectrum was obtained by refluxing 1-methylcyclohex-2-enol (52) over a crystal of iodine for 30 min under a nitrogen atmosphere, then collecting volatile material by distillation at reduced pressure. These n.m.r. signals may be attributed to the

presence of some or all of the dienes:- 1-methyl-1,3-cyclohexadiene (71) [lit.,[115] $\delta(CCl_4)$ 5.40-5.65(2H, m) and 5.65-5.88(2H, m)], 2-methyl-1,3-cyclohexadiene (72) [lit.,[115] $\delta(CCl_4)$ 5.3-5.5(1H, m) and 5.55-5.85(2H, br s)], and 3-methylenecyclohexene (73), an authentic sample of which was prepared as follows. 1-(Diphenylphosphonylmethyl)cyclohex-2-enol, prepared from cyclohex-2-enone[56] using the procedure of Seyferth et al.[116], was treated with sodium hydride in DMF, the method of Bridges and Whitham[117], to give 3-methylene-cyclohexene (73), δ(300MHz; $CDCl_3$) 4.75(d, J7), 5.8-5.9(m), and 6.15(d, J10).

A solution of the 3-methylenecyclohexene (73) and toluene-p-sulphinic acid (ca. 5 mole eq.) in $CDCl_3$ was set aside for 18h at 20°, then washed with aqueous Na_2CO_3 and water, and dried ($CaCl_2$). The 300MHz n.m.r. spectrum of this solution had no signals for the diene (73), but showed the presence of 1-methyl-3-(p-tolylsulphonyl)cyclohexene (66) and 3-methyl-3-(p-tolylsulphonyl)cyclohexene (67) (ca. 85:15). The presence of the sulphones (66) and (67) was confirmed by i.r. and t.l.c. In a similar manner, a mixture of the sulphones (66) and (67), identified by 60MHz n.m.r., i.r., and t.l.c., was obtained from the diene mixture prepared from 1-methylcyclohex-2-enol (52).

Attempts to react Toluene-p-sulphinic Acid with various Alkenes.

The standard conditions are described below. A solution of the alkene (ca. 0.2 mmol) and toluene-p-sulphinic acid

($ArSO_2H$) (ca. 0.2 mmol) in $CDCl_3$ (ca. 0.3 ml), with any specified additive, was set aside at 20° under air for up to 24h, and the n.m.r. spectrum was taken periodically. It had been shown by n.m.r. that $ArSO_2H$ was stable under these conditions for up to 12h, but that by 24h sufficient decomposition had occurred to render it worthless to follow the reaction any further. The decomposition of $ArSO_2H$ was not noticeably accelerated by the addition of $ZnCl_2$ or toluene-p-sulphonic acid (TsOH), but vigorous stirring in air did result in more rapid decomposition. The alkenes were shown by n.m.r. to be stable under these standard conditions.

1,3-Cyclooctadiene, 2,4-hexadienoic acid, cyclohexene, and styrene were treated with $ArSO_2H$ under the standard conditions. In each case the alkene was stable. Styrene was also stable when treated with TsOH (0.2 mole eq.) and $ArSO_2H$. 2,3-Dimethyl-1,3-butadiene, however, was unstable under the standard conditions.

trans-2-Hydroxycyclohexyl toluene-p-sulphonate (75).- A solution of cyclohexene (0.13g, 1.6 mmol) and toluene-p-sulphinic acid (0.24g, 1.6 mmol) in chloroform - carbon tetrachloride (1:2 v/v; 15 ml) was stirred with $ZnCl_2$ (21 mg, 0.15 mmol) at 20° for 40h under air. The solution was washed with dilute HCl, aqueous Na_2CO_3, and water, dried ($CaCl_2$), and evaporated. The residue was purified by p.l.c., eluting with ether - light petroleum (2:1 v/v), to give the sulphonate ester (75) (0.16g, 39%) as an oil, δ(300MHz; $CDCl_3$) 1.15-2.1 (8H, m), 2.45(4H, s, Me and OH), 3.55-3.65(1H, m, 2-H),

4.3-4.4(1H, m, 1-H), 7.4 and 7.85(4H, AA'BB', J7, p C_6H_4). This material was shown by proton and ^{13}C n.m.r., i.r. and t.l.c. to be identical to an authentic sample of the sulphonate ester (75) prepared by the method of Criegee and Stanger[65].

The sulphonate ester (75) was not produced, however, by stirring a chloroform solution of cyclohexene and toluene-p-sulphinic acid with $ZnCl_2$ for 30h at 20° under argon.

Reaction of Styrene with Toluene-p-sulphinic Acid in the presence of Zinc Chloride. A solution of styrene (0.41g, 3.9 mmol) and toluene-p-sulphinic acid (0.62g, 4.0 mmol) in chloroform (7 ml) was stirred with $ZnCl_2$ (50 mg, 0.37 mmol) for 20h at 20° under air. Work up as above followed by flash column chromatography, eluting with ether - light petroleum (1:1 v/v), gave an oil (0.51g), shown to be a mixture of 2-hydroxy-2-phenylethyl toluene-p-sulphonate (76) and 2-hydroxy-1-phenylethyl toluene-p-sulphonate (77) (2:1 by n.m.r.). Recrystallisation of this oil from ether - light petroleum gave the 2-phenyl-isomer (76), m.p. 80-81°; $\nu_{max.}(CHCl_3)$ 3400 br (OH), 1330 br ($-SO_2-O-$), and 1140 br ($-SO_2-O-$)cm^{-1}; δ(300MHz; $CDCl_3$) 1.7(1H, s, OH), 2.45(3H, s, Me), 3.45(1H, dd, J5,15, which collapsed to d, J15 on irradiation at 5.45, 1-H), 3.9(1H, dd, J10,15, which collapsed to d, J15 on irradiation at 5.45, 1-H), 5.45(1H, dd, J5,10, 2-H), 7.3-7.4(7H, m, Ar), and 7.8(2H, m, Ar).

This recrystallised material was proven to be the 2-phenyl-isomer (76) by oxidising it with 6 N chromic acid[105]

and obtaining 2-oxo-2-phenylethyl toluene-p-sulphonate (116), identified by i.r. The carboxylic acid derived from such oxidation of the 1-phenyl-isomer (77) would be lost in the work up. Similar oxidation of the 2:1 mixture of (76) and (77) thus also gave the ketone (116), m.p. 91-92° (from ethanol - light petroleum); $\nu_{max.}$($CHCl_3$) 1680s(C=O), 1330s ($-SO_2-O-$), and 1155s($-SO_2-O-$)cm^{-1}; δ(300MHz; $CDCl_3$) 2.45(3H, s, Me), 4.7(2H, s, $-CH_2-$), 7.3-7.95(9H, m, Ar).

The sulphonate esters (76) and (77) were not produced by stirring a chloroform solution of styrene and toluene-p-sulphinic acid with $ZnCl_2$ for 24h at 20° under argon.

SECTION II

Toluene-p-sulphenyl chloride.- The procedure described in ref. 118 was used. Sulfuryl chloride (7.8 ml, 0.097 mol) was added over 1.5h to a stirred solution of toluene-p-thiol (10.0g, 0.081 mol) in n-pentane (70 ml) on an ice bath. The gas evolved was absorbed by passing it over an aqueous solution of NaOH. After a further 2.5h on an ice bath, the solution was evaporated and the residue was distilled to give toluene-p-sulphenyl chloride (10.2g, 80%) as a red liquid, b.p. 70-74° at 6 mm Hg (lit.,[119] 82-84° at 3.5 mm Hg).

3-(p-Tolylsulphinyl)cyclohexene (62).- This procedure is based on that described in ref. 72. A solution of toluene-p-sulphenyl chloride (0.53g, 3.3 mmol) in dichloromethane (3 ml) was added over 15 min to a stirred solution of cyclohex-2-enol (49) (0.30g, 3.1 mmol) and triethylamine (0.5 ml, 3.6 mmol) in dichloromethane (5 ml) at 20°. After a further 30 min at 20°, the solution was filtered, washed with dilute HCl, aqueous Na_2CO_3, water, and brine, dried ($CaCl_2$), and evaporated to give a quantitative yield of one diastereoisomer of 3-(p-tolylsulphinyl)cyclohexene (62) (0.7g) as a yellow oil, $\nu_{max.}$(neat) 3030(=C-H), 2930(C-H), 1645w(C=C), 1600 and 1495 (Ar), 1450, 1085, 1050br (S=O), and 1015cm^{-1}; δ(300MHz; $CDCl_3$) 1.5-2.15(6H, m), 2.45(3H, s, Me), 3.3-3.4(1H, m, 3-H), 5.65-5.75(1H, m, 2-H), 6.1-6.2(1H, m, 1-H), 7.3 and 7.55(4H, AA'BB', J8, p C_6H_4).

3-(p-Tolylsulphonyl)cyclohexene (59)[33,75].- This procedure is based on that described in refs. 33 and 75. Aqueous hydrogen peroxide (ca. 25% v/v; 0.8 ml, ca. 6.7 mmol) was added dropwise to a stirred solution of crude 3-(p-tolylsulphinyl)cyclohexene (62) (0.71g, ca. 3.7 mmol) in glacial acetic acid (5 ml). The solution was stirred at ca. 30° for 20h. Aqueous NaOH was added and the mixture was extracted with ether. The ether solution was washed with aqueous Na_2CO_3, water, and brine, dried (Na_2SO_4), and evaporated to give the sulphone (59) (0.52g, ca. 70%), a portion of which was recrystallised from ether - light petroleum, m.p. 53-54° (lit.,[75] 62-63°), δ(300MHz; $CDCl_3$) 1.45-2.05(6H, m), 2.5(3H, s, Me), 3.7-3.8(1H, m, 3-H), 5.8(1H, dd, J3,13, 2-H), 6.05-6.15 (1H, m, 1-H), 7.35 and 7.8(4H, AA'BB', J10, p C_6H_4) (lit. n.m.r. spectrum[33,120]).

trans-5-t-Butyl-3-(p-tolylsulphinyl)cyclohexene (83).- trans-5-t-Butylcyclohex-2-enol (54) (0.80g) was treated in the same manner as cyclohex-2-enol (p.108) to obtain a quantitative yield of one of the diastereoisomers of the trans-sulphoxide (83) (1.5g) as a yellow oil, $\nu_{max.}$(neat) 3030w (=C-H), 2960(C-H), 1650w(C=C), 1595w and 1495(Ar), 1395 and 1365(t-Bu), 1085, 1040br(S=O), and 1015cm^{-1}; δ(300MHz; $CDCl_3$) 0.85 (9H, s, t-Bu), 1.6-2.2(5H, m), 2.4(3H, s, Me), 3.35-3.45(1H, m, 3-H), 5.7-5.75(1H, m, 2-H), 6.15-6.25(1H, m, 1-H), 7.3 and 7.55(4H, AA'BB', J8, p C_6H_4).

trans-5-t-Butyl-3-(p-tolylsulphonyl)cyclohexene (20).- Crude trans-5-t-butyl-3-(p-tolylsulphinyl)cyclohexene (83) (1.4g) was oxidised in the same manner as 3-(p-tolyl-sulphinyl)cyclohexene (p.109). Flash column chromatography eluting with ether - light petroleum (1:2 v/v) gave the trans-sulphone (20) (0.66g, 45%) as a solid, m.p. 100°(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%); $\nu_{max.}$(neat) 3040w (=C-H), 2970(C-H), 1595(Ar), 1365(t-Bu), 1315, 1300, 1290 and 1145br (all SO_2), and 1085cm^{-1}; δ(300MHz; $CDCl_3$) 0.85(9H, s, t-Bu), 1.35-2.3(5H, m), 2.45(3H, s, Me), 3.75-3.8 (1H, m, 3-H), 5.75-5.85(1H, m, 2-H), 6.2-6.25(1H, m, 1-H), 7.35 and 7.75(4H, AA'BB', J8, p C_6H_4); ^{13}Cδ($CDCl_3$) 21.5(q), 23.4(t), 26.1(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-Butyl-3-(p-tolylsulphinyl)cyclohexene (82).- cis-5-t-Butylcyclohex-2-enol (53) (0.85g) was treated in the same manner as cyclohex-2-enol (p.108) to obtain a quantitative yield of one of the diastereoisomers of the cis-sulphoxide (82) (ca. 2g) as a yellow oil, $\nu_{max.}$ 3030w(=C-H), 2960(C-H), 1650w(C=C), 1595w and 1490(Ar), 1295 and 1270(t-Bu), 1085, 1040br(S=O), and 1015cm^{-1}; δ(300MHz; $CDCl_3$) 0.85(9H, s, t-Bu), 1.7-2.2(5H, m), 2.45(3H, s, Me), 3.35-3.5(1H, m, 3-H), 5.55-5.6(1H, m, 2-H), 6.05-6.15(1H, m, 1-H), 7.35 and 7.5(4H, AA'BB', J8, p C_6H_4).

cis-5-t-Butyl-3-(p-tolylsulphonyl)cyclohexene (19).- Crude cis-5-t-butyl-3-(p-tolylsulphinyl)cyclohexene (82) (ca. 2g) was oxidised in the same manner as 3-(p-tolylsulphinyl)cyclohexene (p.109). Flash column chromatography eluting with ether - light petroleum (1:2 v/v) gave the cis-sulphone (19) (0.8g, ca. 40%), a portion of which was purified by p.l.c. eluting with ethyl acetate - light petroleum (1:9 v/v) to give the cis-sulphone (19) 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%); $\nu_{max.}$($CHCl_3$) 2960(C-H), 1595 and 1495(Ar), 1365(t-Bu), 1310, 1300, 1285 and 1140br (all SO_2), and 1085cm^{-1}; δ(300MHz; $CDCl_3$) 0.85(9H, s, t-Bu), 1.25-2.25(5H, m), 2.45(3H, s, Me), 3.8-3.9(1H, m, 3-H), 5.7-5.8(1H, m, 2-H), 6.0-6.1(1H, m, 1-H), 7.35 and 7.75(4H, AA'BB', J8, p C_6H_4); ^{13}Cδ($CDCl_3$) 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-Butyl-3-(p-tolylthio)cyclohexene.- 4-t-Butylcyclohexene (5.44g, 0.039 mol) was brominated with N-bromosuccinimide as described on p. 83 . The following procedure is based on that developed by Russell[74]. Sodium (0.86g, 0.037 mol) was dissolved in methanol (30 ml) at 20° under a nitrogen atmosphere. First toluene-p-thiol (4.64g, 0.037 mol), then the crude mixture of bromo-compounds (prepared as above) was added dropwise to the stirred solution. After stirring for 1.5h at 20° 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 gave a mixture of cis- and trans-5-t-butyl-3-(p-tolylthio)cyclohexene (4.3g, 41%) as a pale yellow liquid, b.p. 128-134° at 0.8 mm Hg; $\nu_{max.}$(neat) 3020(=C-H), 2950(C-H), 1490(Ar), 1390w and 1365(t-Bu), and 810br cm^{-1}; δ(300MHz; $CDCl_3$) 0.9(9H, s, t-Bu), 1.35-2.25(5H, m), 2.35(3H, s, Me), 3.7-3.9(1H, m, 3-H), 5.65-5.95(2H, m, =C-H), 7.15 and 7.35(4H, AA'BB', J8, p C_6H_4).

cis- and trans-5-t-Butyl-3-(p-tolylsulphinyl)cyclohexene (82) and (83).- This procedure is based on that described in refs. 74 and 76. Aqueous hydrogen peroxide (ca. 25% v/v; 5.8 ml, ca. 0.05 mol) was added dropwise to a stirred solution of cis- and trans-5-t-butyl-3-(p-tolylthio)cyclohexene (3.11g, 0.012 mol) in methanol (100 ml). The mixture was stirred for 43h at ca. 30°, then diluted with brine and extracted with chloroform. The chloroform solution was washed with water and brine, dried ($CaCl_2$), and evaporated. Purification by column chromatography on silica gel (250g) eluting with ether gave a mixture of both of the diastereoisomers of cis- (82) and both of the diastereoisomers of trans-5-t-butyl-3-(p-tolyl-sulphinyl)cyclohexene (83) (cis - trans 4:1 by n.m.r.; 3.0g, 90%) as a pale yellow oil, δ(300MHz; $CDCl_3$) 0.85(9H, s, t-Bu), 1.35-2.15(5H, m), 2.45(3H, s, Me), 3.3-3.5(1H, m, 3-H), 5.4-6.3(2H, m, =C-H), 7.3 and 7.55(4H, AA'BB', J8, p C_6H_4).

cis- and trans-5-t-Butyl-3-(p-tolylsulphonyl)cyclohexene (19) and (20).- Some of the mixture of cis- and trans-5-t-butyl-3-(p-tolylsulphinyl)cyclohexene (82) and (83) (0.58g) prepared above was oxidised in the same manner as 3-(p-tolylsulphinyl)cyclohexene (p. 109) to obtain a quantitative yield of a mixture of the cis- and trans-sulphones (19) and (20) (4:1 by n.m.r.; 0.61g) as a pale yellow oil. This material was used without further purification.

Treatment of Allylic Sulphones with Sodium Hydroxide.- A 0.05 - 0.15 M solution of the allylic sulphone (0.3 - 1.5 mmol) in aqueous DMSO containing NaOH was set aside as specified, Tables 6 and 7. After cooling, the mixture was extracted with benzene. The benzene solution was washed with dilute HCl, water, and brine, dried (Na_2SO_4), and evaporated. The product, obtained in a weight recovery of higher than 50%, was analysed by n.m.r.

Identification of the Chloro-sulphone (87) described in Table 7, entry 6.- The material from this reaction was purified by p.l.c. eluting with ether - light petroleum (1:2 v/v) to obtain 5-t-butyl-3-chloro-3-(p-tolylsulphonyl)-cyclohexene (87) as an oil, $\nu_{max.}$($CHCl_3$) 2960(C-H), 1595(Ar), 1365(t-Bu), 1315, 1300, 1285 and 1145br (all SO_2), and 1080cm^{-1}; δ(300MHz; $CDCl_3$) 0.9(9H, s, t-Bu), 1.7-2.3(5H, m), 2.5(3H, s, Me), 5.75-5.9(1H, m, 2-H), 6.15-6.4(1H, m, 1-H), 7.4 and 7.85(4H, AA'BB', J9, p C_6H_4); $^{13}C\delta(CDCl_3)$ 21.7(q),

Table 6. Treatment of 3-(p-Tolylsulphonyl)cyclohexene (59) with Sodium Hydroxide

Entry	Solvent,[a] DMSO-water	Molarity in NaOH	Temperature	Reaction time	Atmosphere	Products[b]		
						Allylic sulphone (59)	Vinylic sulphone[c]	Other
1	2:1 [d]	0	50°	10 min	Nitrogen	100%	×	
2	2:1	0.01	50°	5 min	Nitrogen	100%	×	
3	2:1 [d]	0.017	50°	10 min	Nitrogen	×	×	3-[^{2}H]-3-(p-Tolylsulphonyl)cyclohexene (63) 100%
4	1:1	0.5	Reflux	10 min	Air	50%	50%	
5	1:1	0.5	Reflux	4.5h	Air	50%	50%	
6	5:1	0.017	50°	5 min	Air	20%	40%	3-Chloro-3-(p-tolylsulphonyl) cyclohexene[e] ? 100%

a. The DMSO - water ratio is quoted on a v/v basis.
b. Percentages are obtained from the n.m.r. integral and are approximate. A cross significes the absence of the named compound.
c. Vinylic sulphone is 1-(p-tolylsulphonyl)cyclohexene.
d. Deuterium oxide was used instead of water.
e. Identified by comparison of the n.m.r. spectrum with that of an authentic sample of sulphone supplied by Lombard[121].

Table 7[a]. Treatment of 5-t-Butyl-3-(p-tolylsulphonyl)cyclohexene[b] with Sodium Hydroxide

Entry	Solvent, DMSO-water	Molarity in NaOH	Temperature	Reaction time	Atmosphere	Products		
						Allylic sulphones (19) and (20)[c]	Vinylic sulphone (86)[d]	Other
1	2:1	0	60°	10 min	Nitrogen	100%(4:1)	×	
2	2:1	0.01	50°	5 min	Nitrogen	100%(3:2)	×	
3	2:1[e]	0.01	50°	5 min	Nitrogen	×	×	3-[^{2}H]-Sulphones[f] 100%
4	1:1	0.5	Reflux	10 min	Nitrogen	50%	50%	
5	ca.1:1	ca.0.5	Reflux	24h	Air	50%(3:2)	50%	
6	1:1	0.5	Reflux	10 min	Air	Trace	Trace	3-Chloro-sulphone (87)[g] ca. 100%

a. Footnotes a and b of Table 6 also apply to this Table.
b. The 4:1 mixture of cis- and trans-sulphones (19) and (20) was used (p.113).
c. The ratio of cis- to trans-sulphone (19) to (20), estimated by 300MHz n.m.r., is quoted in brackets.
d. Vinylic sulphone (86) is 5-t-butyl-1-(p-tolylsulphonyl)cyclohexene.
e. Deuterium oxide was used instead of water.
f. 3-[^{2}H]-Sulphones are (3RS,5RS)- and (3SR,5RS)-5-t-butyl-3-[^{2}H]-3-(p-tolylsulphonyl)cyclohexene (90) and (91) (3:2 by 300MHz n.m.r.). This mixture was used for subsequent reactions.
g. 3-Chloro-sulphone is 5-t-butyl-3-chloro-3-(p-tolylsulphonyl)cyclohexene (87), identified as described on p. 113.

26.6(t), 27.0(q), 31.9(s), 32.8(t), 39.7(d), 84.7(s), 122.0 (d), 129.4(d), 131.4(d), 137.1(d), 138.4(s), and 145.6(s); m/z 173(0.9%, M-$C_7H_7SO_2$), 171(2.3, M-$C_7H_7SO_2$), 91(12, $C_7H_7^+$), and 57(100, $C_4H_9^+$). The chloro-sulphone (87) was not converted to the allylic and vinyl sulphones (19), (20), and (86) by treatment with alkali similar to that described in entry 5 of Table 7.

For comparison, Lombard[121] supplied an authentic sample of 3-chloro-3-(p-tolylsulphonyl)cyclohexene, δ(300MHz; $CDCl_3$) 1.8-2.25(6H, m), 2.5(3H, s, Me), 5.85-5.95(1H, m, 2-H), 6.2-6.3(1H, m, 1-H), 7.4 and 7.9(4H, $AA'BB'$, J9, p C_6H_4); ^{13}Cδ($CDCl_3$) 18.0(t), 21.5(q), 24.2(t), 32.0(t), 82.6(s), 122.0(d), 129.2(d), 130.8(s), 131.1(d), 136.9(d), and 145.4(s); m/z 117(32%, M-$C_7H_7SO_2$), 115(100, M-$C_7H_7SO_2$), and 91(14, $C_7H_7^+$).

(3RS,5RS)- and (3SR,5RS)-5-t-Butyl-3-[^{2}H]-3-(p-tolylsulphonyl)cyclohexene (90) and (91).- This procedure was based on that described in ref. 33. The apparatus was dried before use and the reaction mixture was kept under a positive pressure of dry nitrogen. A solution of n-butyl-lithium in hexane (1.6 M; 0.3 ml, 0.48 mmol) was added dropwise to a stirred solution of the 4:1 mixture of cis- and trans-5-t-butyl-3-(p-tolylsulphonyl)cyclohexene (19) and (20) (0.13g, 0.44 mmol) in THF (8 ml) at -60°. After 5 min, a solution of deuterium oxide (0.5 ml) in THF (2 ml) was added dropwise. After a further 15 min at -60°, aqueous HCl (3 M; 0.5 ml) was added and the solution was allowed to warm up. Brine was

added, the two phases were separated, and the aqueous solution was extracted with ether. The ether and THF solutions were combined and washed with dilute HCl, water, and brine, dried (Na_2SO_4), and evaporated to give a quantitative yield of a mixture of (3RS,5RS)- and (3SR,5RS)-5-t-butyl-3-[^{2}H]-3-(p-tolylsulphonyl)cyclohexene (90) and (91) (ca. 3:2 by 300MHz n.m.r.) as an oil, which had an n.m.r. spectrum similar to that of the undeuteriated sulphones (19) and (20), but without the signal at $\delta(CDCl_3)$ 3.75-3.9(1H, m, 3-H).

Reactions of Allylic Sulphones in Aqueous Acetic Acid.- These reaction conditions were based on those used by Lin[33]. A ca. 0.05 M solution of the allylic sulphone (0.15-0.6 mmol) in aq. AcOH [glacial acetic acid - water (3:2 v/v)], with any specified additive, was set aside as described, under a nitrogen atmosphere, Tables 8 to 12. Aqueous NaOH was added and the mixture was extracted with ether. The ether solution was washed with aqueous Na_2CO_3, water, and brine, dried (Na_2SO_4), and evaporated. The product, obtained with a weight recovery of higher than 50%, was analysed by n.m.r.

Reaction of 3-(p-Tolylsulphonyl)cyclohexene (59) with Sodium Benzenesulphinate.- A solution of 3-(p-tolylsulphonyl)-cyclohexene (59) (0.18g, 0.75 mmol) and sodium benzene-sulphinate (0.87g, 5.3 mmol) in aq. AcOH (1.5 ml) under a nitrogen atmosphere was heated on an oil bath at 100° for 8h,

then left to cool overnight. Work up as described above gave an oil (0.17g), which was shown by n.m.r. and g.l.c. to be a 7:3 mixture of 3-(phenylsulphonyl)cyclohexene (68) and 3-(p-tolylsulphonyl)cyclohexene (59).

Rearrangement of 3-Methyl-3-(p-tolylsulphonyl)cyclohexene (67) in Aqueous Acetic Acid.- An aq. AcOH solution of the sulphone (67) (0.4 M) was heated to 100° for 2h. Work up as described above afforded a mixture of the 3-methyl-sulphone (67) (75%) and the 1-methyl-sulphone (66) (25%). Similar treatment of the sulphone (67) in the presence of hydroquinone (0.1 mole eq.) gave a similar mixture.

Table 8. Reaction of 5-t-Butyl-3-(p-tolylsulphonyl)cyclohexene[a] with Sodium Toluene-p-sulphinate in Aqueous Acetic Acid

Entry	$ArSO_2Na$[b] / mole eq.	Temperature[c]	Time[d] / h	Products[e]	
				cis-Sulphone (19)	trans-Sulphone (20)
1	0	110°	ca. 30	80%	20%
2[f]	0	110°	14	80%	20%
3	1	110°	8	80%	20%
4	1	110°	23	70%	30%
5	ca. 10	110°	11.5	60%	40%
6[g]	1	Reflux	27	60%	40%
7[h]	1	Reflux	24	60%	40%

a. Unless specified otherwise the 4:1 mixture of cis- and trans-sulphone (19) and (20) was used (p. 113).

b. $ArSO_2Na$ is sodium toluene-p-sulphinate.

c. The temperature is of the bath in which the reaction mixture was heated.

d. In some cases the reaction mixture was allowed to cool overnight before being worked up.

e. Products were estimated by 300MHz n.m.r.

f. Sodium bromide (10 mole eq.) was present.

g. trans-Sulphone (20) was used. The solution (0.2 M) was heated under air.

h. cis-Sulphone (19) was used. The solution (0.2 M) was heated under air.

Table 9[a]. Reaction of 5-t-Butyl-3-[^{2}H]-3-(p-tolylsulphonyl)-cyclohexene[b] with Sodium Toluene-p-sulphinate in Aqueous Acetic Acid

Entry	$ArSO_2Na$/ mole eq.	Temperature	Time/h	Products	
				3-[^{2}H]-Sulphones (90) and (91)	1-[^{2}H]-Sulphone[c]
1	0	110°	44	100%	0
2	1.3	110°	8	100%	Trace
3	1.1	110°	23	ca. 65%	ca. 35%
4	ca. 10	110°	11.5	50%	50%

a. Footnotes b, c, d, and e of Table 8 also apply to this Table.

b. A 3:2 mixture of (3RS,5RS)- and (3SR,5RS)-sulphone(90) and (91) was used.

c. 1-[^{2}H]-Sulphone is 5-t-butyl-1-[^{2}H]-3-(p-tolylsulphonyl)-cyclohexene.

Table 10[a]. Reactions of 3-[^{2}H]-3-(p-Tolylsulphonyl)-cyclohexene (63) in Aqueous Acetic Acid

Entry	Additive/mole eq.	Temperature	Time /h	Products[b]	
				3-[^{2}H]-Sulphone (63)	1-[^{2}H]-Sulphone[c] (64)
1[d]	None	100°	8	100%	None
2[d]	0.1 Benzoyl peroxide	100°	8	50%	50%
3[d]	0.1 $ArSO_2Na$	100°	8	ca. 70%	ca. 30%
4[d]	0.1 $ArSO_2Na$ and 0.1 hydroquinone	100°	8	100%	None
5	1 $ArSO_2Na$	110°	26	50%	50%

a. Footnotes b and c of Table 8 also apply to this Table.

b. Products were estimated by 60MHz n.m.r.

c. 1-[^{2}H]-Sulphone is 1-[^{2}H]-3-(p-tolylsulphonyl)cyclohexene (64).

d. The solutions of sulphone (63) were ca. 0.25 M.

Table 11[a]. Reactions of 3-Methyl-3-(t-butylsulphonyl)-1-butene (101) in Aqueous Acetic Acid

Entry	Additive/mole eq.	Temperature	Time /h	Products[b]	
				αα-Dimethyl-sulphone (101)[c]	γγ-Dimethyl-sulphone (102)[d]
1	None	100°	8	90%	10%
2	0.1 Hydroquinone	100°	8	100%	Trace
3	0.1 Benzoyl peroxide	100°	2	60%	40%
4	0.1 Benzoyl peroxide	100°	8	60%	40%
5	0.1 $ArSO_2Na$	100°	8	80%	20%
6	0.1 $ArSO_2Na$ and 0.1 hydroquinone	100°	8	80%	20%

a. Footnotes b and c of Table 8 also apply to this Table. The solutions of sulphone (101) were ca. 0.3 M.

b. Products were estimated by 60MHz n.m.r.

c. αα-Dimethyl-sulphone is 3-methyl-3-(t-butylsulphonyl)-1-butene (101).

d. γγ-Dimethyl-sulphone is 3-methyl-1-(t-butylsulphonyl)-2-butene (102).

Table 12[a]. Reactions of 3-Methyl-3-(p-tolylsulphonyl)-1-butene (92) in Aqueous Acetic Acid

Entry	Additive[b] / mole eq.	Temperature	Time[c] / h	Products[d]		
				αα-Dimethyl-sulphone (92)[e]	γγ-Dimethyl-sulphone (93)[f]	Other
1	None	95°	8	100%	Trace	
2	None	110°	0.5	80%	20%	
3	None	110°	8	50%	50%	
4[g]	None	110°	8	85%	15%	
5[h]	None	110°	8	35%	65%	
6[i]	None	110°	8	20%	80%	
7[i]	1.5 Peracetic acid	110°	8	None	60%	γγ-Dimethyl-sulphone epoxide (94) 40% j
8	0.1 Benzoyl peroxide	110°	8	None	100%	
9	0.1 Hydroquinone	110°	8	100%	None	
10	ca. 0.1 Iodine	110°	8	100%	None	
11	0.6 HI[k]	110°	8	100%	None	
12	1 HBr	110°	8	100%	None	
13	1 NaBr	110°	8	85%	15%	
14	1 Sodium acetate	110°	8	50%	50%	
15	1 Sodium meta-bisulphite	110°	8	15%	85%	

Cont.

16	1 TsOH	110°	0.5	45%	55%	
17	1 TsOH	110°	8	None	60%	2-Methyl-4-(p-tolyl-sulphonyl)butan-2-ol (100) [1] 40%
18	1 H_2SO_4	110°	8	55%	30%	2-Methyl-4-(p-tolyl-sulphonyl)butan-2-ol (100) 15%
19	1 $ArSO_2H$	110°	0.5	None	100%	
20	1 $ArSO_2H$	110°	5 min	10%	90%	
21	1 $ArSO_2H$	70°	0.5	10%	90%	
22	1 $ArSO_2H$	50°	0.5	40%	60%	
23	0.1 $ArSO_2H$	50°	0.5	75%	25%	
24	5.6 $ArSO_2H$	50°	0.5	45%	55%	
25	1 $ArSO_2Na$	50°	0.5	100%	Trace	
26	0.1 $ArSO_2Na$	100°	0.5	30%	70%	
27	7 $ArSO_2Na$	100°	0.5	35%	65%	
28[m]	ca. 7 $ArSO_2Na$	110°	10	None	100%	
29	0.1 $ArSO_2Na$ and 0.1 hydro-quinone	110°	8	85%	15%	
30[n]	None	110°	8	45%	55%	
31[n]	1 $ArSO_2Na$	110°	8	None	100%	

a. Footnotes b and c of Table 8 also apply to this Table. The solutions of sulphone (92) were ca. 0.45 M.

b. $ArSO_2H$ is toluene-p-sulphinic acid and TsOH is toluene-p-sulphonic acid.

c. In some of the cases where the reaction time was 8h, the reaction mixture was allowed to cool overnight before being worked up.

d. Products were estimated by 60MHz n.m.r.

e. αα-Dimethyl-sulphone is 3-methyl-3-(p-tolylsulphonyl)-1-butene (92).

f. γγ-Dimethyl-sulphone is 3-methyl-1-(p-tolylsulphonyl)-2-butene (93).

g. Acetic acid of AR grade was used. In all other cases SLR grade was used.

h. The acetic acid was distilled from $FeSO_4$ before use.

i. The acetic acid was distilled from $KMnO_4$ before use.

j. γγ-Dimethyl-sulphone epoxide is 2,2-dimethyl-3-[(p-tolylsulphonyl)methyl]oxirane (94), which was tentatively identified in the reaction mixture by n.m.r.

k. The HI was coloured with iodine impurity.

l. Characterisation described on p. 126.

m. This reaction was performed on a 15 mmol scale as a preparation of 3-methyl-1-(p-tolylsulphonyl)-2-butene (93), as described in ref. 33.

n. Neat AR grade glacial acetic acid was used as solvent.

2-Methyl-4-(p-tolylsulphonyl)butan-2-ol (100).- The reaction mixture described in entry 17 of Table 12 was separated by column chromatography, eluting with ether, to give 2-methyl-4-(p-tolylsulphonyl)butan-2-ol (100), m.p. 57° (from ether - light petroleum) (Found: C, 59.4; H, 7.55; S, 13.45. $C_{12}H_{18}O_3S$ requires C, 59.45; H, 7.5; S, 13.25%); $\nu_{max.}$($CHCl_3$) 3600 and 3500br (OH), 2970(C-H), 1595(Ar), 1315, 1300, 1285 and 1145br (all SO_2), and 1090cm^{-1}; δ(300MHz; $CDCl_3$) 1.2(6H, s, 2-Me), 1.7(1H, s, OH, peak lost after D_2O exch.), 1.85-1.9(2H, AA'BB', 3-H), 2.45(3H, s, Me-C_6H_4), 3.2-3.25(2H, AA'BB', 4-H), 7.35 and 7.8(4H, AA'BB', J8, p C_6H_4).

Reaction of the alcohol (100) with toluene-p-sulphonic acid (1 mole eq.) in aq. AcOH at 110° for 8h (p. 117) gave a mixture of 3-methyl-1-(p-tolylsulphonyl)-2-butene (93) (60%) and the alcohol (100) (40%).

Hydration of 3-Methyl-1-(p-tolylsulphonyl)-2-butene (93).- The allylic sulphone (93) was treated with toluene-p-sulphonic acid (1 mole eq.) in aq. AcOH at 110° as described on p. 117. Reaction times of 4h, 8h, and ca. 70h each afforded a mixture of the allylic sulphone (93) (ca. 60%) and 2-methyl-4-(p-tolylsulphonyl)butan-2-ol (100) (ca. 40%).

Reaction of 3-[^{2}H]-3-(p-tolylsulphonyl)cyclohexene (63) with Benzoyl Peroxide in Carbon Tetrachloride.- This procedure is based on that used by Lin[33]. The 3-[^{2}H]-sulphone (63) (87mg, 0.37 mmol) and benzoyl peroxide (5 mg, 0.02 mmol) were

heated under reflux in CCl_4 (5 ml) for 18h under an argon atmosphere. After cooling, the solution was washed with aqueous NaOH, dilute HCl, water, and brine, dried ($CaCl_2$), and evaporated to give an oil (0.10g), which was shown by n.m.r. to be a 1:1 mixture of the 3-[^{2}H]-sulphone (63) and the 1-[^{2}H]-sulphone (64).

SECTION III

1-(p-Tolylsulphonyl)-1-vinylcyclopropane (105).- This procedure is based on that described in ref. 33. The apparatus was dried before use and the reaction mixture was kept under a positive pressure of dry nitrogen. A solution of n-butyl-lithium in hexane (1.6 M; 4.6 ml, 7.4 mmol) was added dropwise to a stirred solution of 3-(p-tolylsulphonyl)-propene (21) (0.68g, 3.5 mmol) in THF (10 ml) and ether (10 ml) at -60°. After 10 min, 1,2-dibromoethane (0.6 ml, 7 mmol) was added. After a further 30 min at -60°, the mixture was stirred on an ice bath for 1h, then quenched by dropwise addition of a solution of acetic acid (2 ml) in ether (20 ml). Water was added, the two phases were separated, and the aqueous solution was extracted with ether. The organic solutions were combined and washed with aqueous Na_2CO_3, water, and brine, dried (Na_2SO_4), and evaporated to give a yellow glass (0.79g), which was shown by n.m.r. to be a 3:2 mixture of the cyclopropane (105) and the allylic sulphone (21). Recrystallisation from ether - light petroleum (1:1 v/v) gave 1-(p-tolylsulphonyl)-1-vinylcyclopropane (105) (0.32g, 41%), m.p. 98-99° (lit.,[99] 98.5-99.5°) (Found: C, 64.5; H, 6.15; S, 14.35. Calc. for $C_{12}H_{14}O_2S$: C, 64.85; H, 6.35; S, 14.4%); $\nu_{max.}$($CHCl_3$) 1595(Ar), 1315, 1300, 1285 and 1140 (all SO_2), and 1080cm^{-1}; δ(300MHz; $CDCl_3$) 1.1 and 1.75(4H, AA'BB', ring CH_2), 2.45(3H, s, Me), 5.05(1H, d, J_{trans}17.5, H-CH=), 5.2(1H, d, J_{cis}10, H-CH=), 6.2(1H, dd, J_{cis}10 and J_{trans}17.5, H-C=), 7.35 and 7.7(4H, AA'BB', J8, p C_6H_4).

1-p-(Tolylsulphonyl)cyclopentene (88).- The flow pyrolysis apparatus used for this preparation was based on that described in ref. 94. A quartz column of diameter 50 mm and length 0.7m, surrounded by a furnace, was packed with glass helices which had been washed with trimethylsilyl chloride, diethylamine, and hexane. Over a 30 min period, a solution of 1-(p-tolylsulphonyl)-1-vinylcyclopropane (105) (0.27g, 1.2 mmol) in hexane (50 ml) was run into the column which was maintained at 510-520° under a flow of nitrogen. The vapour was condensed into a flask surrounded by an acetone - dry ice bath. The solution obtained was evaporated and the residue was dissolved in chloroform. The chloroform solution was washed with dilute HCl, aqueous Na_2CO_3, and water, dried ($CaCl_2$), and evaporated to give 1-(p-tolylsulphonyl)cyclopentene (88) (0.22g, 81%), m.p. 115° (from ether) (lit.,[75] 115-116°) (Found: C, 65.0; H, 6.35; S, 14.1. Calc. for $C_{12}H_{14}O_2S$: C, 64.85; H, 6.35; S, 14.4%); $\nu_{max.}$($CHCl_3$) 1615(C=C), 1595(Ar), 1315, 1305, 1290 and 1150br (all SO_2), and 1095cm^{-1}; δ(300MHz; $CDCl_3$) 2.05(2H, quintet, J8, 4-H), 2.45(3H, s, Me), 2.55(4H, t, J8, 3-H and 5-H), 6.75(1H, s, H-C=), 7.35 and 7.8(4H, AA'BB', J8, p C_6H_4).

Treatment of 1-(p-Tolylsulphonyl)cyclopentene (88) with Sodium Hydroxide.- Sulphone (88) was subjected to the conditions described in entry 4 of Table 6 using the general procedure described on p. 113. Analysis by 300MHz n.m.r. of the product showed it to be a mixture of 3-(p-tolylsulphonyl)-cyclopentene[75] (70%), identified by peaks at δ($CDCl_3$)

3.8-3.85(1H, m, 3-H), 5.65(1H, dd, 2-H), and 6.1(1H, dt, 1-H), 2-(p-tolylsulphonyl)cyclopentanol[75] (20%), identified by peaks at δ($CDCl_3$) 3.3-3.4(1H, m, 1-H) and 4.05-4.15(1H, m, 2-H), and 1-(p-tolylsulphonyl)cyclopentene (88) (10%).

(E)-3-(p-Tolylsulphonyl)pent-3-enyl toluene-p-sulphonate (110).- 3-(p-Tolylsulphonyl)propene (0.70g, 3.5 mmol) was treated with n-butyl-lithium in hexane (1.6 M; 2.2 ml, 3.5 mmol) then ethylene oxide (0.35 ml, 6.5 mmol) in a manner analogous to that described on p.128 to give a quantitative yield of (E)-3-(p-tolylsulphonyl)pent-3-enol (109) (0.9g) as a yellow oil, $\nu_{max.}$($CHCl_3$) 3620 and 3500br (OH), 2960(C-H), 1640(C=C), 1595 and 1490(Ar), 1310, 1285br and 1145br (all SO_2), and 1085cm^{-1}; δ(300MHz; $CDCl_3$) 1.9(3H, d, J7, Me-C=), 2.45(4H, s, CH_3-C_6H_4 and OH), 2.5(2H, t, J7, 2-H), 3.7(2H, t, J7, 1-H), 7.05(1H, q, J7, H-C=), 7.3 and 7.75(4H, AA'BB', J8, p C_6H_4).

The following procedure is based on that described in ref. 100. A portion of the alcohol (109) (0.53g, 2.2 mmol) was dissolved in pyridine (5 ml) and toluene-p-sulphonyl chloride (1.7g, 8.8 mmol) was added. The solution was set aside for 12h at ca. 5°, then quenched by adding water (ca. 0.5 ml) and stirring at 20° for 1h. The mixture was poured into cold water and extracted with ether. The ether solution was washed with dilute HCl, water, and brine, dried (Na_2SO_4), and evaporated. Flash column chromatography, eluting with ether - chloroform (3:1 v/v), yielded (E)-3-(p-tolylsulphonyl)-pent-3-enyl toluene-p-sulphonate (110) (0.39g, 45%), a portion

of which was purified by p.l.c. eluting with ether to give the ester (110) as an oil (Found: M^+, 394.0909. $C_{19}H_{22}O_5S_2$ requires M, 394.0908); $\nu_{max.}$($CHCl_3$) 1645w(C=C), 1595 and 1490w (Ar), 1365br (OSO_2), 1310 and 1300 (SO_2), 1190, 1175s (OSO_2), 1150br and 1130 (SO_2), and 1085cm^{-1}; δ(300MHz; $CDCl_3$) 1.9[3H, d, J7, Me-C=, N.O.E. (3 and 2%) on irradiation at 2.6 and 7.1], 2.45 and 2.5(6H, ss, CH_3-C_6H_4), 2.6[2H, t, J7, 2-H, N.O.E. (1.5%) on irradiation at 1.9], 4.05[2H, t, J7, 1-H, N.O.E. (6%) on irradiation at 2.6], 7.1[1H, q, J7, H-C=, N.O.E. (15%) on irradiation at 1.9], 7.3 and 7.7(4H, AA'BB', J10, p C_6H_4), 7.35 and 7.75(4H, AA'BB', J8, p C_6H_4).

Treatment of(E)-3-(p-Tolylsulphonyl)pent-3-enyl toluene-p-sulphonate (110) with Sodium Hydride.- A solution of the sulphonate ester (110) (34 mg, 0.086 mmol) in DMSO (1 ml) was added dropwise to sodium hydride (ca. 1 mmol) and the mixture was stirred for 1h at 20° under a nitrogen atmosphere. Water was added dropwise and the mixture was extracted with toluene. The toluene solution was washed with dilute HCl, water, and brine, dried (Na_2SO_4), and evaporated to give 1-(p-tolylsulphonyl)-1-vinylcyclopropane (105) (10 mg, 52%), which was identified by 300MHz n.m.r. and t.l.c. (only one spot).

Reaction of 3-Methyl-1-(p-tolylsulphonyl)-2-butene (93) and 1,2-Dibromoethane with n-Butyl-lithium.- 3-Methyl-1-(p-tolylsulphonyl)-2-butene (93) (0.75g, 3.3 mmol), prepared as described on p. 125, in THF (20 ml) and ether (20 ml) was

treated with n-butyl-lithium in hexane (1.6 M; 4.4 ml, 7.0 mmol) then 1,2-dibromoethane (0.5 ml, 5.8 mmol) in a manner analogous to that described on p. 128. The product was recrystallised from ether - light petroleum to give 2,7-dimethyl-4,5-di(p-tolylsulphonyl)-2,6-octadiene (111) (0.14g, 20%), m.p. 178-179° (from chloroform - light petroleum) (Found: C, 65.0; H, 6.9. $C_{24}H_{30}O_4S_2$ requires C, 64.55; H, 6.75%); $\nu_{max.}$($CHCl_3$) 1665w (C=C), 1600 and 1490w (Ar), 1310, 1300, 1285 and 1140br (all SO_2), and 1085cm^{-1}; δ(300MHz; $CDCl_3$) 1.1(6H, s, Me-C=), 1.7(6H, s, Me-C=), 2.45(6H, s, CH_3-C_6H_4), 3.6-3.75(2H, m, 4-H and 5-H, collapses on irradiation at 4.9), 4.95(2H, d, J10, 3-H and 6-H, collapses to s on irradiation at 3.65), 7.3 and 7.65(8H, AA'BB', J8, p C_6H_4).

The mother liquor was evaporated to give a yellow oil (0.53g), shown by n.m.r. to be a 1:2 mixture of 1-(2'-methyl-propen-1'-yl)-1-(p-tolylsulphonyl)cyclopropane (113) and 6-bromo-2-methyl-4-(p-tolylsulphonyl)-2-hexene (112), the latter identified by peaks at δ(60MHz; CCl_4) 3.0-4.0(3H, m, 4-H and 6-H) and 4.85(1H, d, J10, 3-H). A portion of this mixture (0.21g) in THF (5 ml) and ether (5 ml) was treated with n-butyl-lithium in hexane (1.6 M; 0.35 ml) in the manner described on p. 128 to give the cyclopropane (113) (0.17g), m.p. 80° (from carbon tetrachloride - light petroleum) (Found: C, 67.4; H, 7.15; S, 12.4. $C_{14}H_{18}O_2S$ requires C, 67.15; H, 7.25; S, 12.8%); $\nu_{max.}$($CHCl_3$) 1660w (C=C), 1595 and 1490w (Ar), 1310, 1300, 1285 and 1140br (all SO_2), and 1085cm^{-1}; δ(300MHz; $CDCl_3$) 0.9(2H, AA'BB', ring CH_2), 1.3(3H, s, Me-C=), 1.65(3H, s, Me-C=), 1.75(2H, AA'BB', ring CH_2),

2.45(3H, s, C<u>H</u>$_3$-C_6H_4), 5.25(1H, s, H-C=), 7.3 and 7.7(4H, AA'BB', J8, <u>p</u> C_6H_4).

<u>Attempts to Rearrange</u> 1-(2'-<u>Methylpropen</u>-1'-<u>yl</u>)-1-(p-<u>tolylsulphonyl)cyclopropane</u> (113).- Using the apparatus described on p.129, the cyclopropane (113) (50 mg) in hexane (10 ml) was subjected to flow pyrolysis at various temperatures:- at 420° cyclopropane (113) was recovered; at 490° cyclopropane (113) and decomposition products were obtained; at 550° as well as peaks for the cyclopropane (113), the 60MHz n.m.r. spectrum had a peak at δ($CDCl_3$) 6.5(s), which may be attributed to 2-H of 3,3-dimethyl-1-(<u>p</u>-tolyl-sulphonyl)cyclopentene (114); and at 590° the recovered material consisted mainly of decomposition products.

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ABSTRACT

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Aspects of Organosulphur Chemistry

Section I of this thesis is concerned with the rearrangement of allylic sulphinate esters to sulphones. Isomerisation of cyclohex-2-enyl toluene-p-sulphinate (1) and several related substituted sulphinates was investigated particularly in ionising solvents such as formamide. The substituted systems, 1-[^{2}H]-cyclohex-2-enyl toluene-p-sulphinate and 3-methylcyclohex-2-enyl toluene-p-sulphinate (2), gave sulphones with the label scrambled between C-1 and C-3. Rearrangement of the conformationally biased esters, cis- and trans-5-t-butylcyclohex-2-enyl toluene-p-sulphinate, was not stereospecific. Sulphinate (1), both diastereoisomers of which reacted at the same rate, rearranged more slowly than did sulphinate (2). Rearrangement of sulphinate (1) in the presence of sodium benzenesulphinate lead to formation of some of the phenyl sulphone. A dissociative mechanism involving ion-pairs is proposed for the rearrangement of the above allylic sulphinates in ionising media.

The [1,3] sulphonyl group migration of some allylic sulphones is discussed in Section II. 3-Methyl-3-(p-tolylsulphonyl)-1-butene rearranged on heating in acetic acid - water (3:2 v/v) containing toluene-p-sulphinic acid or its sodium salt, and in this case slow rearrangement did occur in the absence of such additives. Substituted 3-(p-tolylsulphonyl)cyclohexenes rearranged in hot aqueous acetic acid containing sodium toluene-p-sulphinate, but were stable in the absence of added sulphinate. Under these conditions, epimerisation of cis- and trans-5-t-butyl-3-(p-tolylsulphonyl)-cyclohexene occurred at the same rate as deuterium was scrambled between C-1 and C-3 starting with 5-t-butyl-3-[^{2}H]-3-(p-tolylsulphonyl)cyclohexene. Benzenesulphinate was incorporated in a crossover experiment with 3-(p-tolylsulphonyl)cyclohexene. A chain addition - elimination mechanism involving either radicals or radical anions (an $S_{RN}1$ process) is suggested for the [1,3] rearrangement of the allylic sulphones under the above conditions.

Attempts to develop a stereospecific 5-membered ring annulation procedure involving allylic sulphones are described in Section III. As a model system, 1-(p-tolylsulphonyl)-1-vinylcyclopropane, prepared from 3-(p-tolylsulphonyl)propene, rearranged on flow pyrolysis to 1-(p-tolylsulphonyl)-cyclopentene.