SOME STUDIES OF SULPHUR CONTAINING HETEROCYCLES

by

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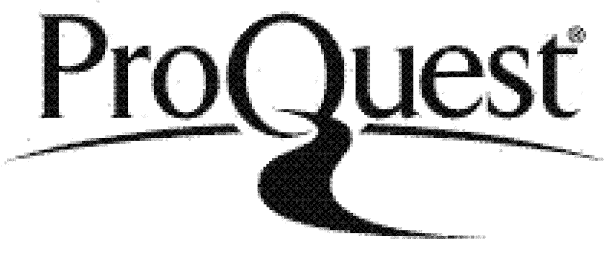
presented for the degree of
Doctor of Philosophy in
the Faculty of Science
of the
University of Leicester

1978



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I would like to thank the S.R.C. for a studentship and Mrs. C. Bennett for typing this thesis and the students, staff and technicians of the Organic Chemistry Department for making my stay here most enjoyable.

STATEMENT

The experimental work described in this thesis has been carried out by the author in the laboratories of the Department of Chemistry of the University of Leicester between October 1974 and June 1977.

No part of this work has been presented or is currently being presented for any other degree.

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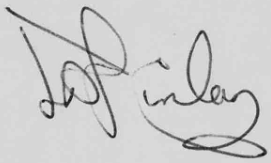

J.D. Finlay

April 1978.

SUMMARY

The flash vacuum thermolysis and photolysis of a number of cyclic sulphones have been studied with a view to developing these reactions as possible synthetic processes. A number of 2-substituted thietan sulphones have been shown to give the appropriately substituted cyclopropanes in high yields. The corresponding reactions of 3-substituted theitan sulphones are not quite so clean however, and a number of products are formed.

Attempts have been made to synthesise sulphoximides based on the thiochroman nucleus ; however, without success.

The flash thermolyses of thiochroman-4-one sulphones have been studied. The products of these reactions are generally α,β-unsaturated ketones, and the mechanism has been probed by deuterium labelling experiments.

The flash thermolyses of some substituted γ-sultines have been studied in detail. Generally, sulphur dioxide is extruded and the products are derived from the remaining biradical species. In one case however, one of the products is derived from a loss of sulphur monoxide from the starting material.

The conformational equilibria of various *cis* and *trans* 3-substituted thietan 1-oxides have been studied using n.m.r. spectroscopy and a lanthanide shift reagent technique. In general it has been found that the oxygen atom prefers to adopt an equatorial position in all of the compounds studied.

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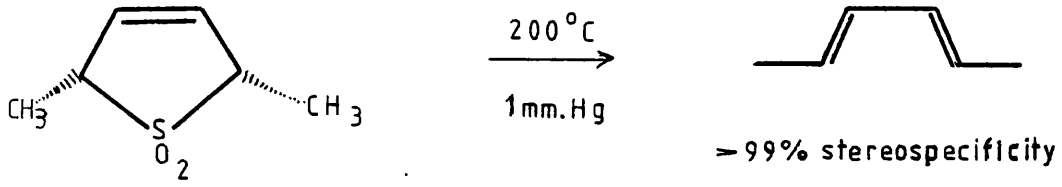
CHAPTER ONE

THE FLASH VACUUM THERMOLYSIS AND PHOTOLYSIS OF SOME THIETAN SULPHONES

1.1 Introduction

Reactions which involve extrusion of a small stable molecule, either thermally or photochemically have been known for many years.[1] The molecules extruded are usually gases at room temperature, such as carbon monoxide, carbon dioxide, nitrogen or sulphur dioxide, and the reaction itself may give rise to novel products, or other compounds previously synthesised only with difficulty. The extrusions may be completely stereospecific in some cases, and although this is uncommon, partial retention of stereochemistry of the system may be observed.

2,5-Dihydrothiophene 1,1-dioxides (1) extrude sulphur dioxide stereospecifically via a concerted disrotatory elimination.[2,4]



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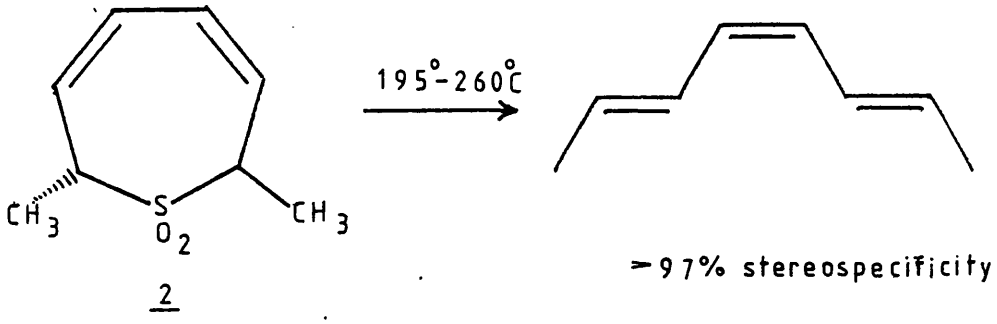
In a similar manner, pyrolysis of 2,7-dimethyl-2,7-dihydrothiepin 1,1-dioxide (2) gives elimination of sulphur dioxide by a stereospecific concerted mechanism.[3,4]



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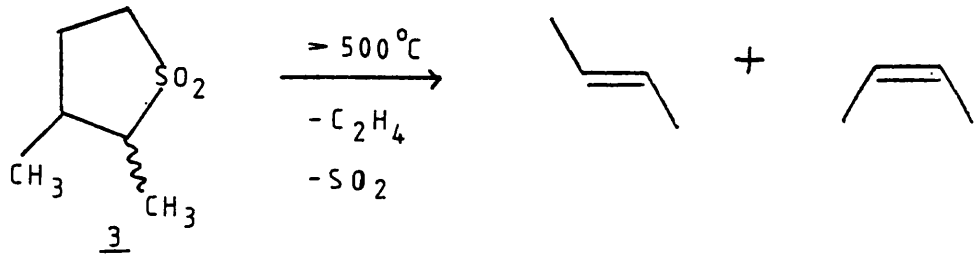
→97% stereospecificity

Tetrahydrothiophene 1,1-dioxides (sulpholans) (3) are pyrolysed to give sulphur dioxide and mixtures of alkenes, and the stereochemistry of this reaction has been examined with a view to detecting possible concertedness,[5] with the following results.



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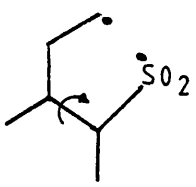
1) 95% cis	36 ± 6 %	53±3%
2) 90% trans	51 ± 6 %	40±3%

The fact that the dissociation did not occur with retention of stereochemistry suggested that the results were best accommodated by a multistep mechanism in which diradical or zwitterionic intermediates existed, and that internal rotation within such an intermediate (4) or (5) was competitive with bond scission.



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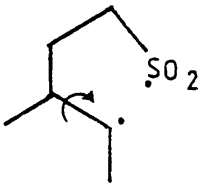

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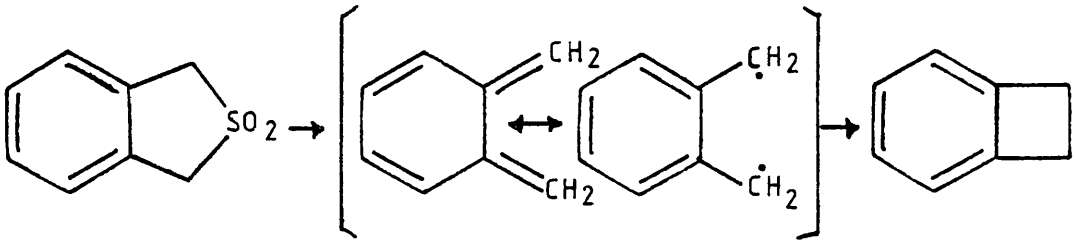
Cava and Deana[6] thermolysed 1,3-dihydroisothionapthene 2,2-dioxide to give benzocyclobutane by direct extrusion of sulphur dioxide.



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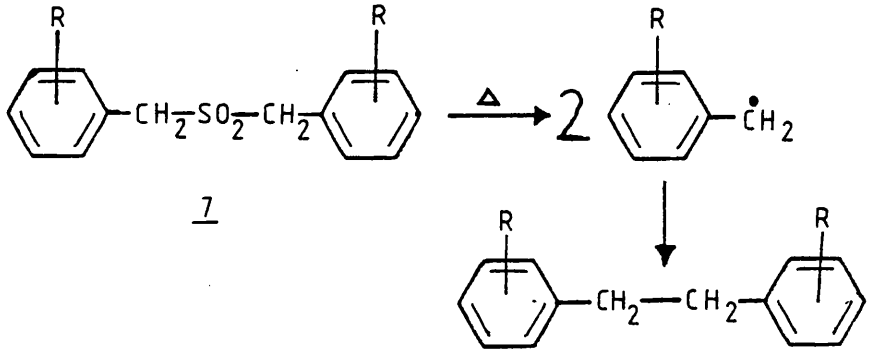
The sulphone vapour was passed at low pressure over a heated wire at various temperatures from 460° to 770°C, and the products trapped out onto a cold finger at -78°C. It was postulated that loss of sulphur dioxide gave o-quinodimethane (6) which rapidly rearranged to give the product. Evidence for the intermediacy of (6) was supplied by trapping experiments with N-phenyl maleimide.

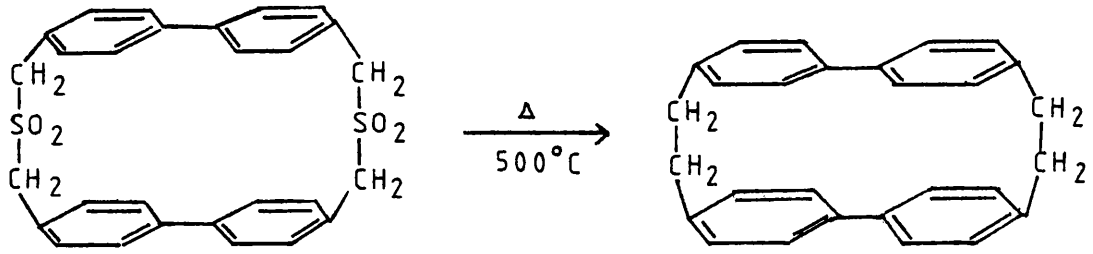
Leonard[7] has studied the flash vacuum thermolysis of a number of dibenzyl sulphones (7) and observed that extrusion of

sulphur dioxide at 600-700°C gave high yields of the corresponding dibenzyls, the mechanism was described as cleavage of the sulphone to benzyl radicals and subsequent coupling.



7

This reaction has found some importance in the synthesis of cyclophanes as described by Staab and Haenel.[8] Vapour phase thermolysis of the disulphones (8) and (9) at 500°C and 0.1 torr gives [2.2](4,4')biphenylophane (10) and 5,6,17,18-tetrahydro[2.2](2.7)phenanthrenophane (11) respectively.



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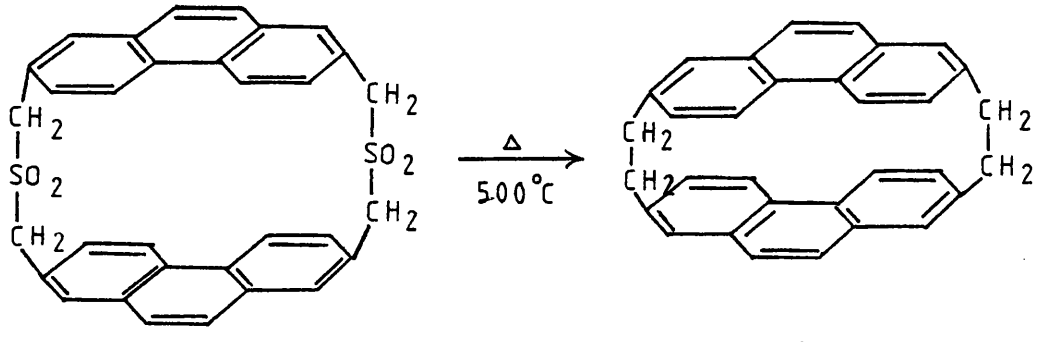

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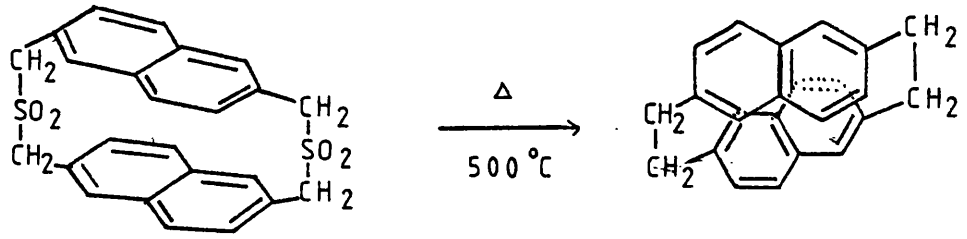
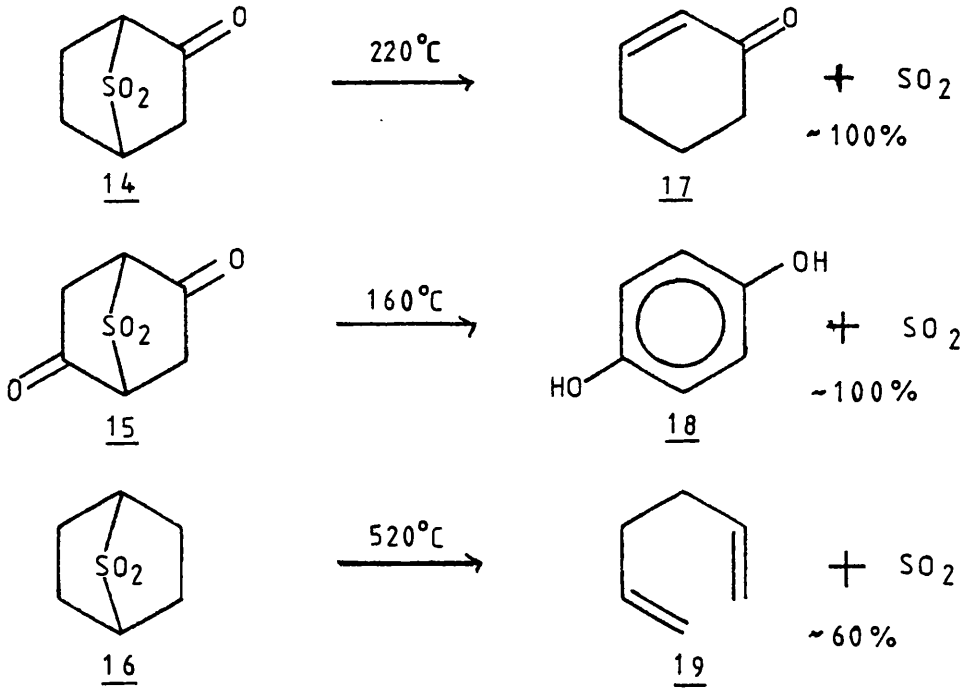
Similarly, vacuum thermolysis of the cyclic disulphone (12), at 500°C gives the chiral cyclophane [2.2] (2,6)naphthalisophane (13).



12 13

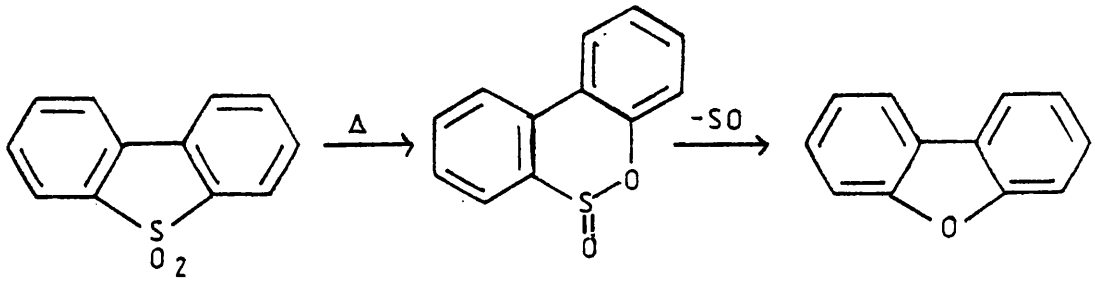
The two step radical mechanism proposed by Leonard was again postulated.

Recently Tabushi[9] has thermolysed a number of strained sulphones (14-16) from which the extrusion of sulphur dioxide is found to be a facile process, leading to the products (17-19).



A number of examples have been cited in the literature[11] which suggest relationships between flash vacuum thermolysis and other high energy processes, such as electron impact fragmentation. There is increasing evidence that in high energy processes such as electron impact, reaction paths with the lowest energy requirement (those favoured in pyrolyses) are likely to be favoured, even when enough energy is available to drive almost any conceivable reaction.

Thermolysis of dibenzothiophene 1,1-dioxide (20) does not lead to the extrusion of sulphur dioxide and formation of biphenylene, but instead, dibenzofuran is observed as the main product.[10] It is postulated that the reaction involves an intermediate cyclic sulphinate ester (a sultine) (21) from which sulphur monoxide can be lost via a biradical mechanism, to give the observed product.

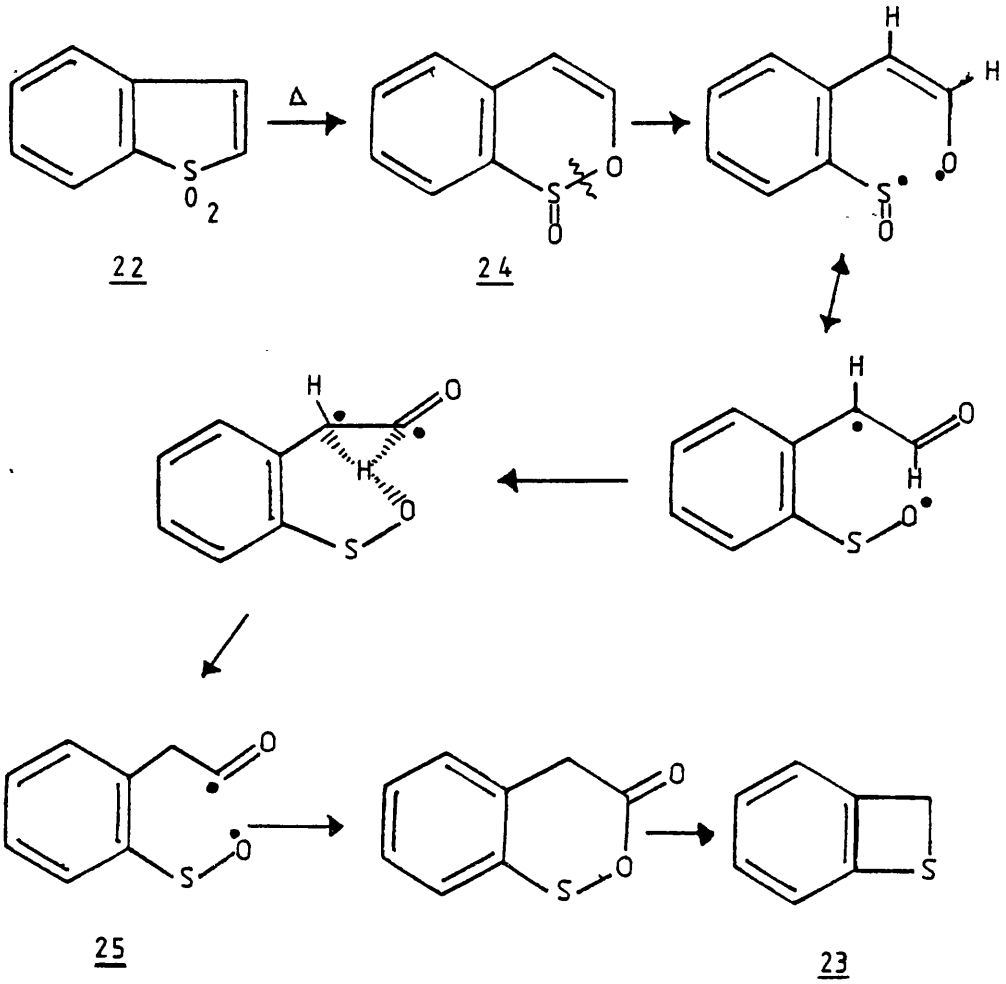


20 21

This decomposition closely parallels the behaviour under electron impact in which the major primary decomposition processes are loss of sulphur monoxide and carbon monoxide. This demands formation

of a C-O bond, i.e. isomerisation to the cyclic ester. This isomerisation parallels the isomerisation of diaryl and alkyl-aryl sulphones under electron impact.[12]

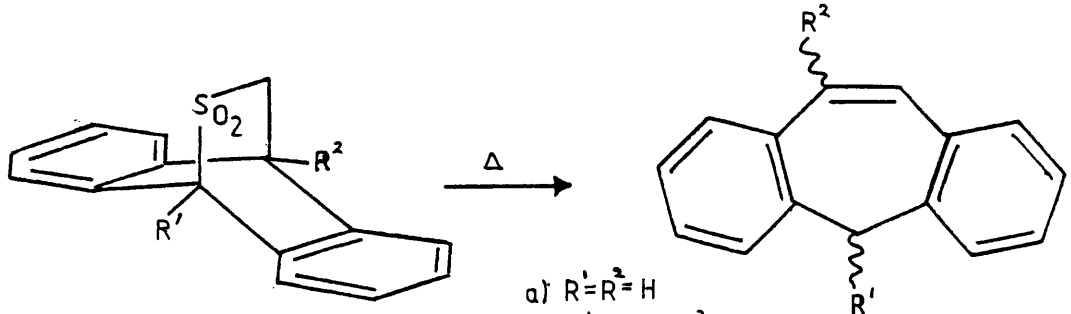
Recently the thermolysis of benzo[b]thiophene 1,1-dioxide (22) has been described.[13] At 1000°C and 5 x 10^{-2} torr, a good yield of benzothiete (23), a hitherto unknown compound, was obtained. The postulated mechanism is as shown in Scheme 1.



Scheme 1

The initial ring expansion to give the sultine (24) followed by rupture of the O-S bond to give the diradical, are the same steps as were outlined for the thermolysis of the dibenzo fused analogue described above. A possible 1-2 hydrogen shift *via* the sulphenoxyl radical to give (25) is described, followed by recombination, and loss of carbon dioxide, to give the observed product (23).

The flash vacuum thermolyses of some 9,10-dihydro-11-thio-9,10-ethanoanthracene-11,11-dioxides have recently been reported by Smith et al.[14] On vacuum thermolysis at 560-610°C the compounds (26) lose sulphur dioxide, and rearrange to give correspondingly substituted 5H-dibenzo[a,d]cycloheptenes (27) in good yields.



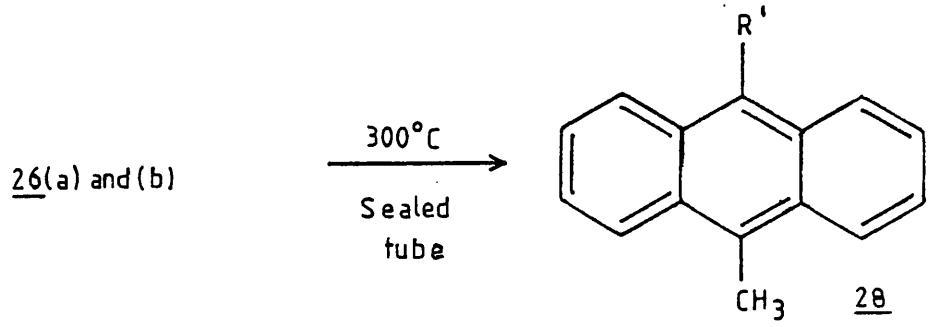
26

a) $R'=R^2=H$
b) $R'=CH_3$, $R^2=H$
c) $R'=R^2=CH_3$

27

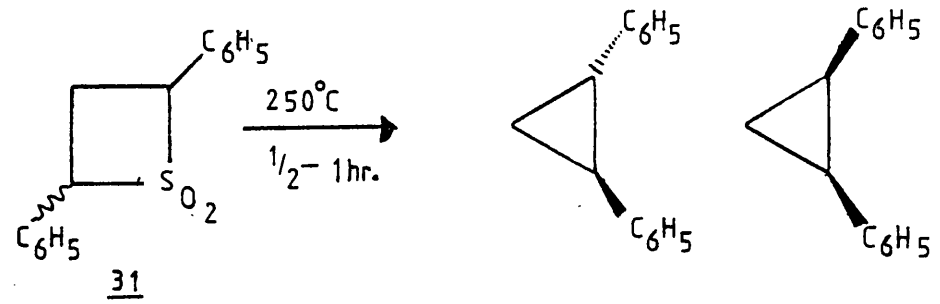
Under pyrolysis conditions in a sealed tube at 300°C however, the compounds (26a) and (26b) give a quantitative yield of the appropriately substituted anthracenes (28), while (26c) is fairly inert under these

conditions. Formation of the anthracene being blocked by the extra methyl group. However the product isolated is the same cycloheptene as is given by the flash thermolysis of (26c).



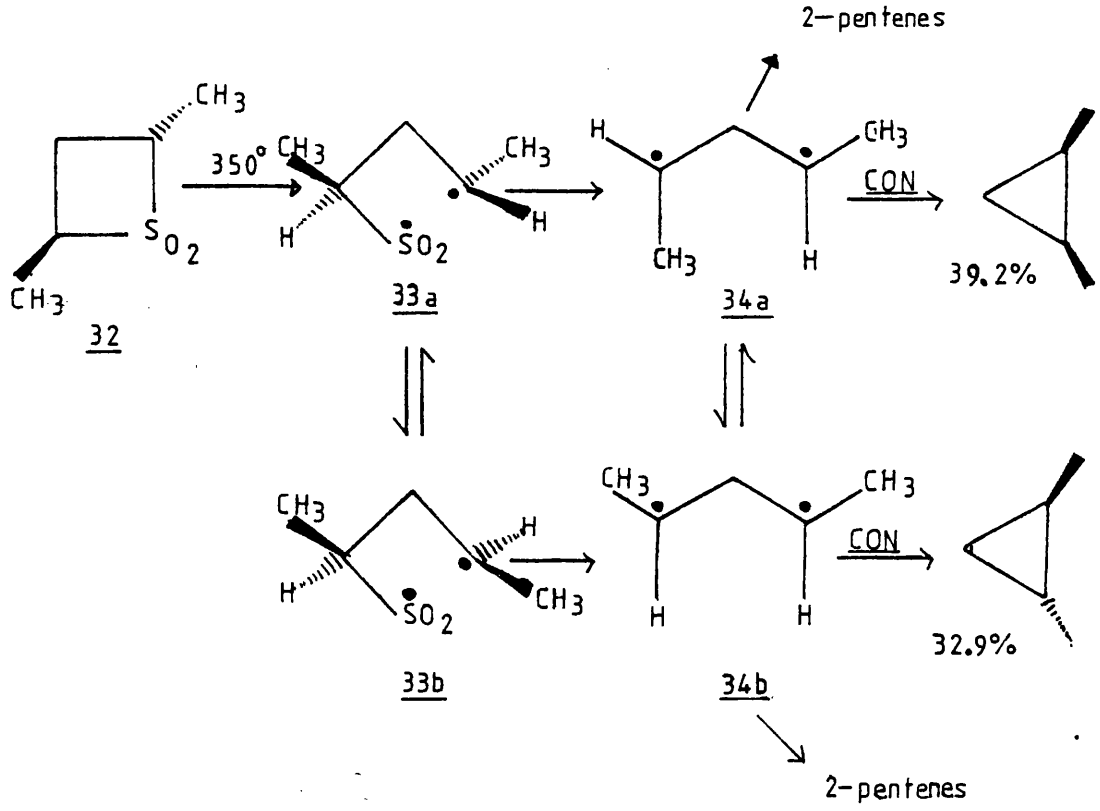
The pyrolyses and gas phase thermolyses of compounds based on the thietan (29) or thiete (30) ring have been described by a number of workers.

Under pyrolytic conditions, thietan 1,1-dioxides have been observed to extrude sulphur dioxide and give mixtures of cyclopropanes, or alkenes, or both. 2,4-Diphenylthietan 1,1-dioxide (31) has been shown to give a mixture of cis and trans 1,2-diphenylcyclopropane on pyrolysis.[15]



31

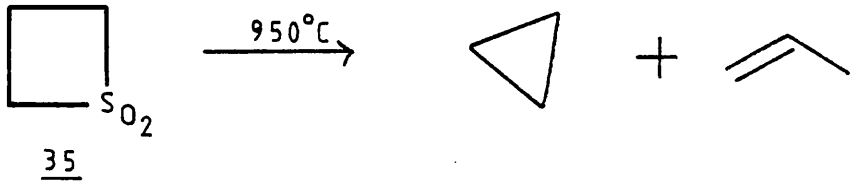
The pyrolysis of 2,4-dimethylthietan 1,1-dioxide (32) has been studied in some detail by Trost et al,[16] and the mechanism investigated. In each case, pyrolysis of either the cis or trans isomer leads to the formation of a mixture of cis and trans 1,2-dimethylcyclopropane in yields of up to 50%, and cis and trans pent-2-enes in yields of up to 12%, the mechanism being postulated for the trans isomer is shown below.



Initial bond homolysis produces the 1,4-diradical (33a) which may either interconvert (33b) or lose sulphur dioxide to give the 1,3-diradical (34a). Interconversion of (33a) to (33b) appears to be slow, relative to its decomposition since there was appreciable "memory" of the stereochemistry in the formation of the cyclopropane products, and there is no loss of stereochemistry in any recovered starting material. It is postulated therefore, that decomposition to π cyclopropane (34) followed by cyclisation, predicts the net stereochemistry obtained. Orbital calculations predict that the 1,3-diradical (34) should close in a predominantly conrotatory manner, to produce a cyclopropane of inverted geometry to that of the original sulphone. This was found to be the case experimentally, although the process is found to be less selective at higher temperatures.

The flash vacuum thermolyses of a number of thietan 1,1-dioxides and thiete 1,1-dioxides have been described by King et al.[17]

Thietan 1,1-dioxide (35) gives a mixture of cyclopropane and propylene while 2,2-dimethylthietan 1,1-dioxide (36) gives a mixture of 3-methyl-1-butene, 2-methyl-2-butene and 2-methyl-1-butene on thermolysis at 950°C, presumably by ring closure or hydrogen migration in the initially formed diradical.



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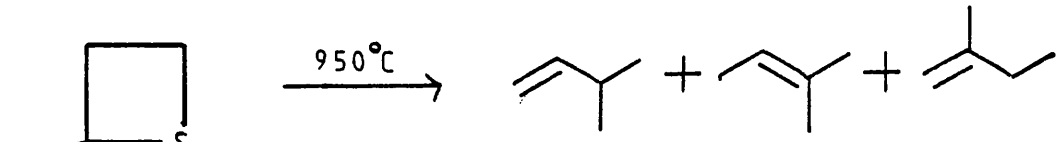

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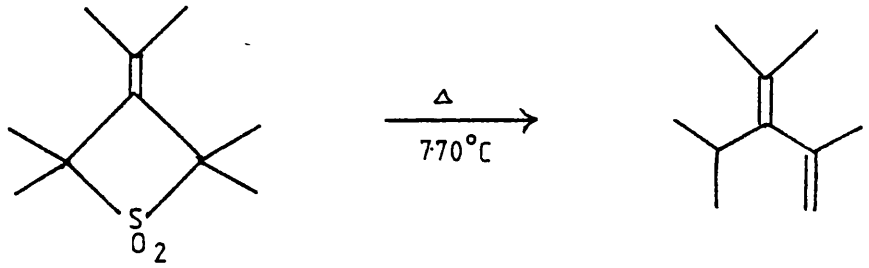
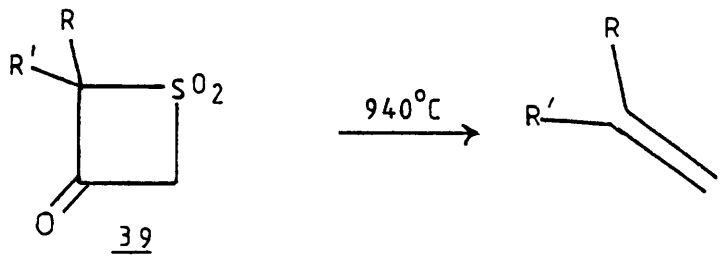
Recently the vacuum thermolysis of 3-isopropylidene-2,2,4,4-tetramethylthietan 1,1-dioxide (37) has been described by Bushby.[18] Thermolysis of (37) at 770°C gives 3-isopropyl-2,4-dimethylpenta-1,3-diene (38) as the only product.



37 38

The thermolyses of some thietanones have also been studied[17] and it was found that in the compounds studied (39) loss of sulphur dioxide is accompanied by loss of carbon monoxide also, presumably sequentially, to leave the olefin.



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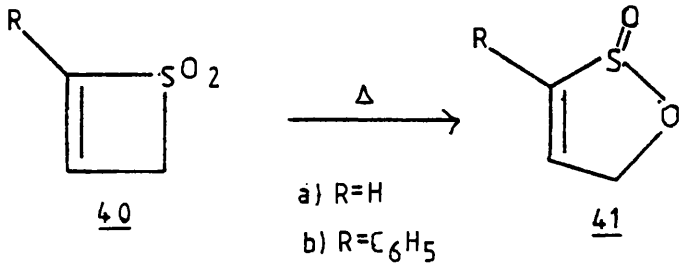
The thiete sulphones (40) are observed to rearrange on either pyrolysis at 220°C or vacuum thermolysis at 390-450°C[17] to give a sultine (41) (a cyclic sulphinate ester).



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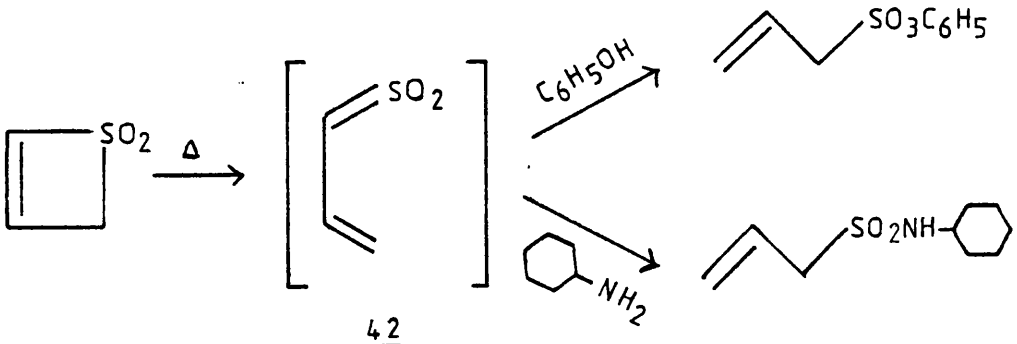
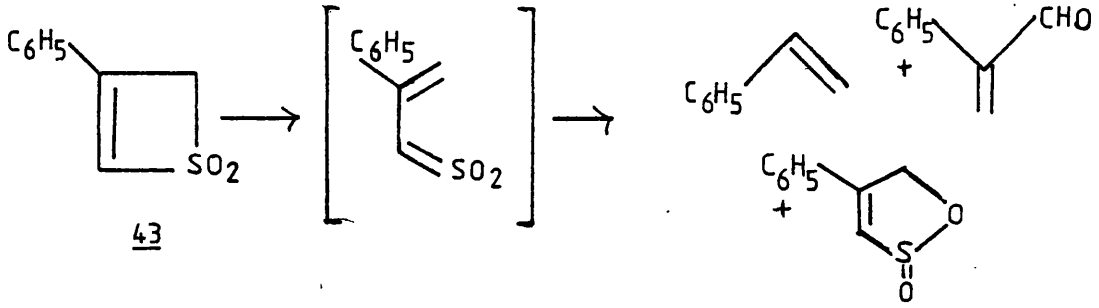
These reactions are postulated to proceed via a vinyl sulphene intermediate (42), evidence for which arises from the formation of trapped products with phenol or cyclohexylamine in liquid pyrolyses.



42

At higher temperatures, fragmentation of the sultine (41) is observed and extrusion of sulphur monoxide takes place.[17,19]

Some 3-substituted thiete 1,1-dioxides (43) and (44) have been studied,[20] and the products obtained are consistent with the mechanism proposed by King et al[17] above.



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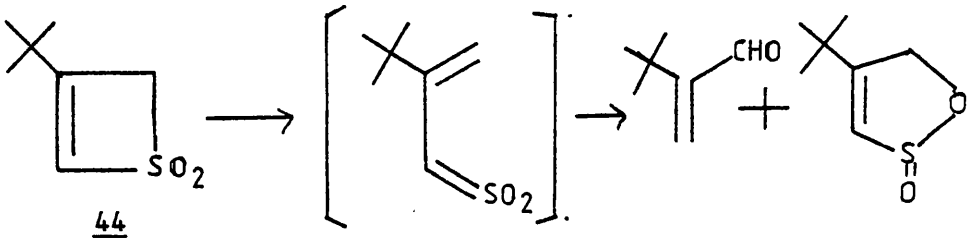
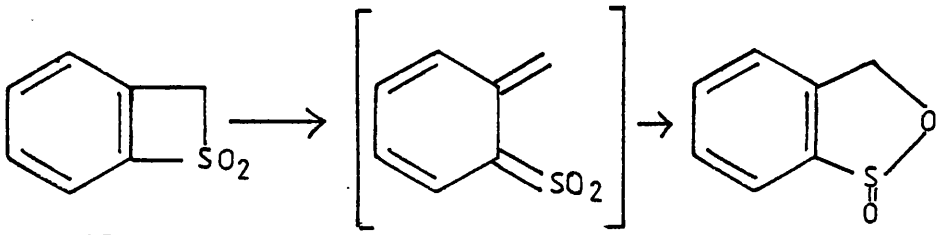


44

Recently, the pyrolysis of benzo[b]thiete 1,1-dioxide (45) has been described by Dittmer and Nelsen.[21] Again, a vinyl sulphene is postulated to explain the observed sultine product.



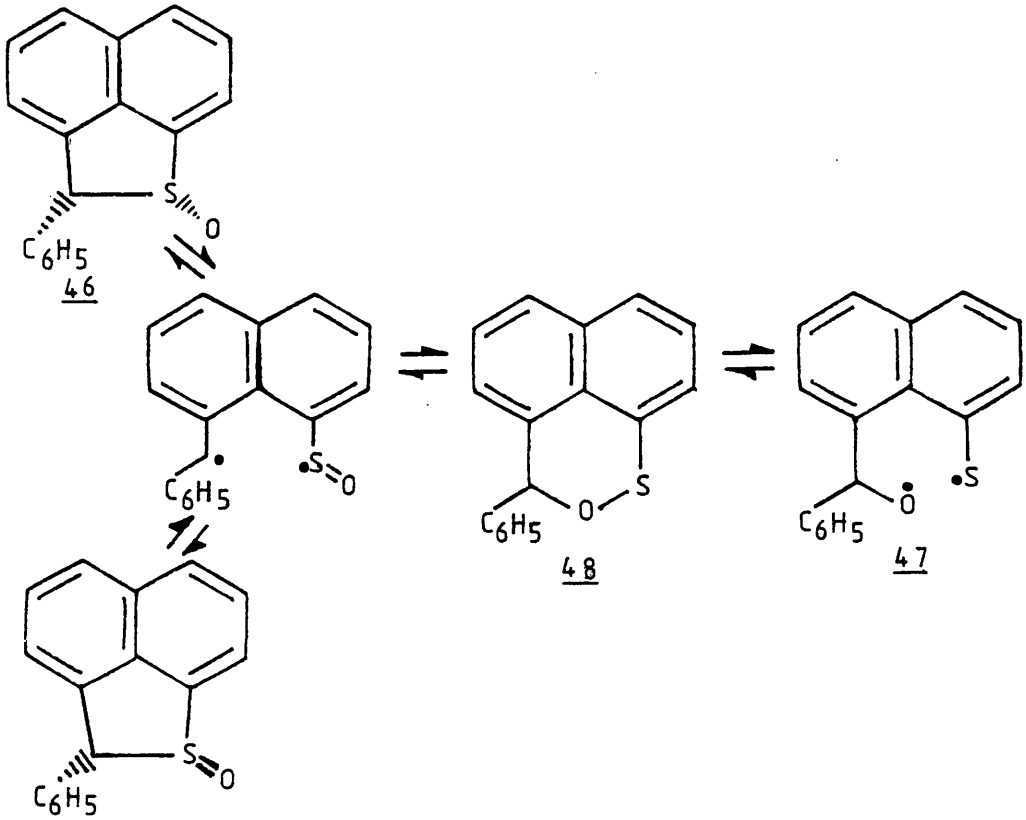
45

1.2 The Photolysis of Sulphoxides and Sulphones

Saturated sulphoxides and sulphones do not absorb strongly within the normally used ultraviolet range (>200 nm), and in order to study their photochemistry, it is necessary to include a strongly

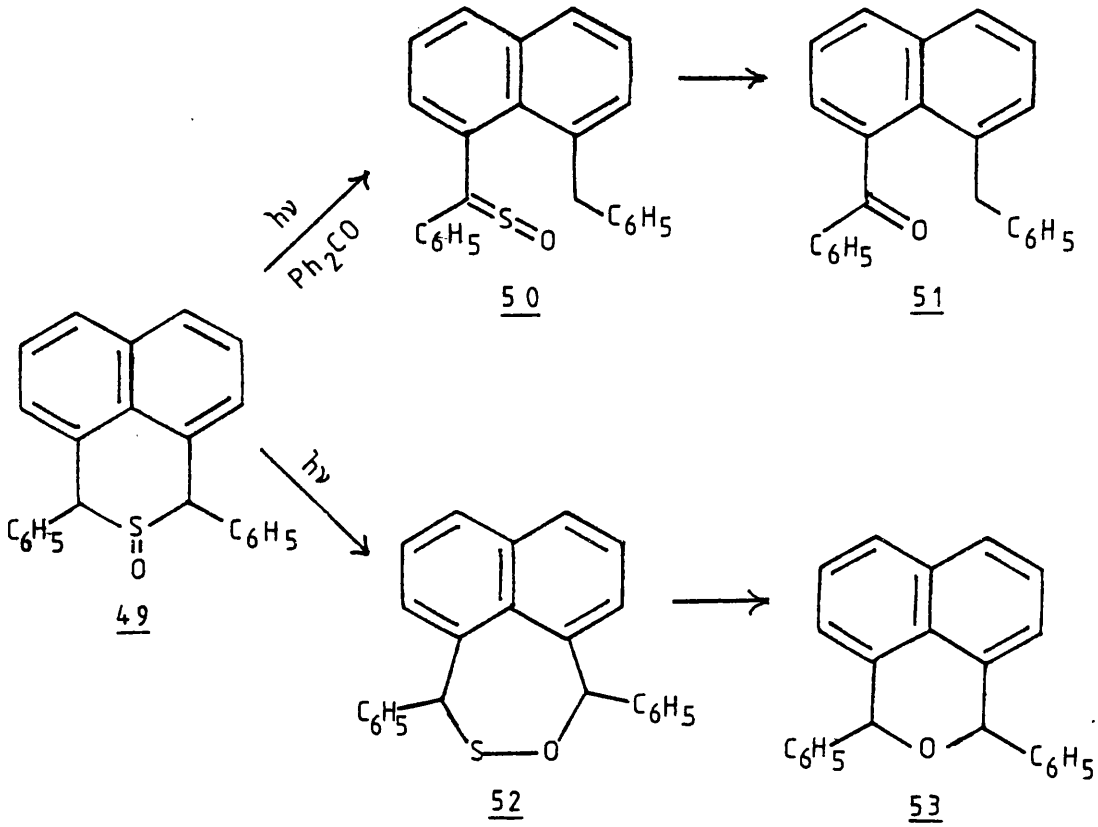
absorbing chromophore in the system. In most of the literature this is either a carbonyl or an aromatic group.

All optically active sulphoxides racemise on irradiation and this has been shown to occur mainly by pyramidal inversion of the sulphur,[22] although there is also evidence for racemisation by the reversible formation of a sulphenate ester, for example in the photolysis of (46).



The reaction is thought to involve α-cleavage to give a biradical, which would lie in equilibrium with a second biradical (47), in which a lone electron is localised on the oxygen. Ring closure would give the observed sulphenate ester (48).

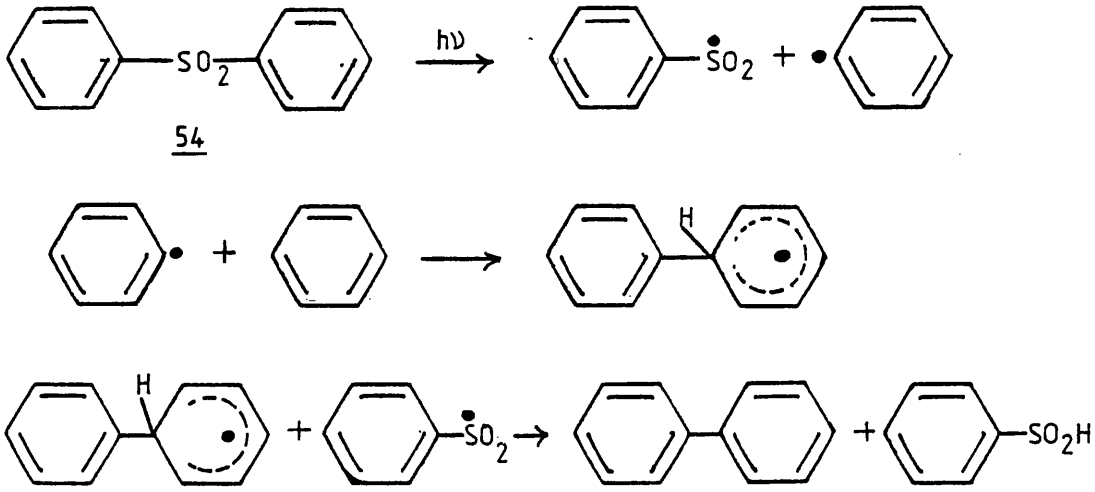
Schultz and Schlessinger[22] have demonstrated the intermediacy of sulphenate esters in the photolysis of (49).



Sensitised irradiation of (49) at 313 nm leads to the ring opened ketone (51) via the sulphine (50), while direct irradiation leads to the pyran (53) via the isolable sulphenate ester (52). In both cases initial C-S cleavage is probably the first step.

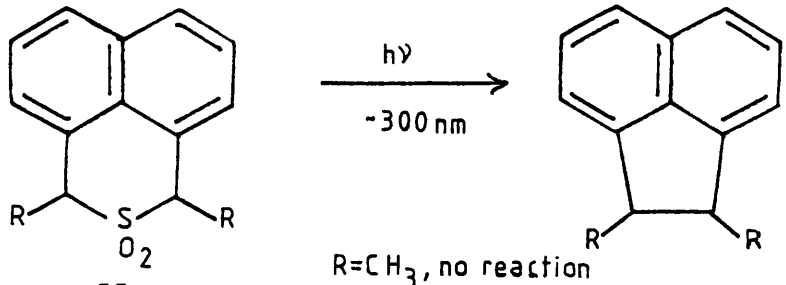
Many sulphones have been observed to lose sulphur dioxide on photolysis, presumably again via an α-cleavage mechanism, since the elimination is much more efficient when stabilised radicals are formed. For example, irradiation of diphenylsulphone (54) at 253 nm in benzene[23] produces biphenyl (71%) and benzenesulphinic

acid (7%) from an α-cleavage followed by attack on the solvent, of the phenyl radical produced.



54

Irradiation of the sulphone (55) however, gives elimination of sulphur dioxide only when the R group is phenyl.[24]

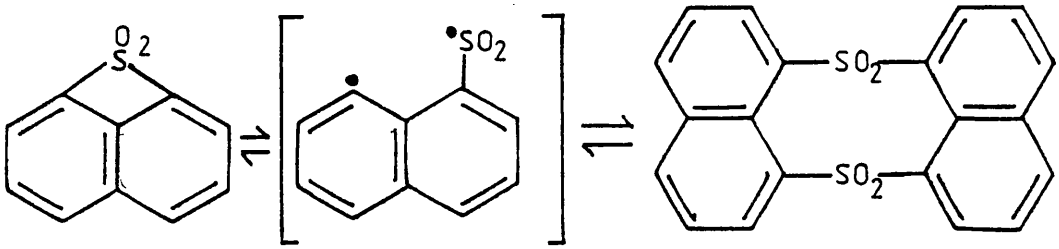


55

R=CH$_3$, no reaction

R=C$_6$H$_5$, efficient reaction

Photolysis of the 1-8 bridged naphthalene derivative (56) gives a dimer (57) which is probably formed from an intermediate biradical (58).[25]



56 58 57

The work in this chapter will be concerned with the synthesis and flash vacuum thermolyses and photolyses of a number of substituted thietan sulphones, to assess their usefulness as a synthesis of substituted cyclopropanes. In conjunction with our thermolytic and photochemical studies, mass spectral data were recorded for all the compounds under study to determine whether any correlation could be made between the modes of fragmentation.

1.3 Description of the Thermolysis Apparatus and Techniques

The technique of flash vacuum thermolysis involves passing a stream, in the gas phase, of the compound under study, at low pressure, through a furnace, and then trapping the products formed.[26] The contact times during which energy is transferred to the system are very short (generally 1-20 ns) and are given by formula 1/1, where P is the pressure, V_r the volume of the hot zone, T_r the reaction temperature (^oK), t is the time of the reaction (s), and m the moles of material passed.

$$T = 0.16 \frac{V_r.p.t}{T_r.m} \qquad \text{——— (1/1)}$$

These low values permit a significant fraction of the intermediates

produced to survive the conditions and emerge from the furnace. Ideally, each molecule strikes the hot surface once only, the reaction takes place, and any excess energy that the products may have is removed by immediate cold trapping. To achieve this experimentally, the pressure must be as low as possible, the hot zone must be small, and the cold trap must come as near as possible to it.

For preparative reactions the temperature of the furnace should be kept as low as possible consistent with a reasonable yield, so that the generated products are as near as possible to their ground state energies, and are therefore less likely to undergo further changes before being trapped.

The thermolysis apparatus used in our studies is shown in Figure 1/1 The whole of the apparatus is made of quartz glass except for the cold finger insert. Fitted to the ball joint on the bottom, is an n.m.r. tube with a corresponding socket. The hot zone is 10 cm long, the end of which is approximately 13 mm away from the surface of the cold finger, which was generally cooled with liquid nitrogen except when the thermolysis was performed at temperatures greater than 850°C, when a dry ice-acetone mixture was used.

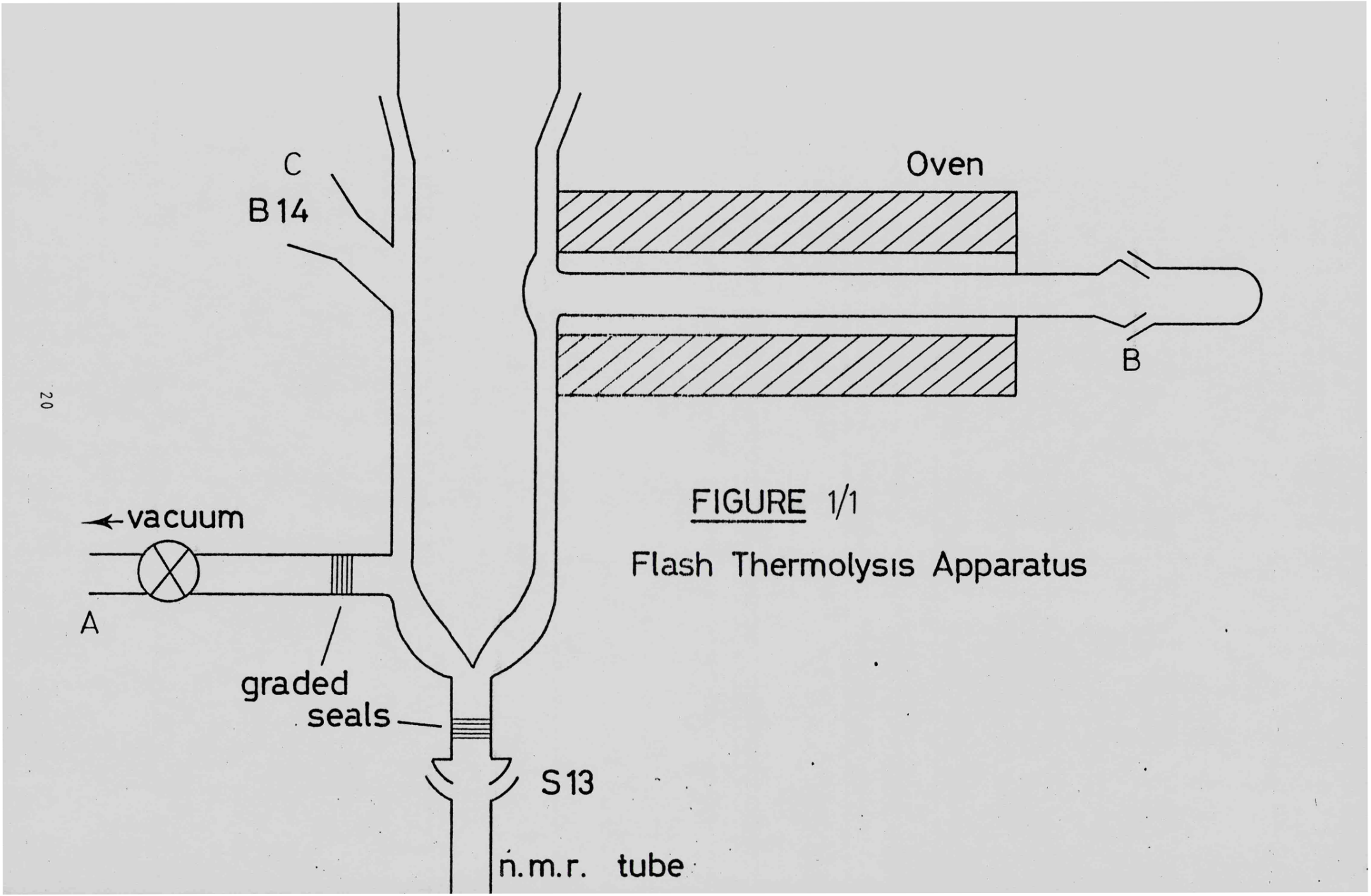


FIGURE 1/1

Flash Thermolysis Apparatus

In a typical run, the apparatus was connected to an oil diffusion pump at 'A', and evacuated to around 1 x 10^{-3} torr as read by a McLeod gauge positioned between the trap and the pump (this was therefore not the same pressure as that in the apparatus, and was used for comparison purposes only). The sample (typically 120 mg) was contained in a round bottomed flask (10 ml) fixed at 'B', or, in the case of a volatile liquid, was put into a U-tube and trapped in a cold bath, until the furnace had reached the desired temperature. The temperature of the hot zone was controlled with a variac, and continuously monitored using a thermocouple connected to a digital thermometer. The thermocouple was inserted between the wall of the furnace and the hot tube, so that it lay in the middle of the hot zone. The sample was slowly sublimed through the apparatus at a rate of about 0.4 g hr^{-1}, by the use of a kugel oven placed externally over the flask, in the case of a solid sample or, if the sample was a volatile liquid, the U-tube was slowly allowed to warm up and the sublimation regulated by a cold bath. The products generally appeared as a glass in the dimple of the cold finger.

When the sublimation had finished, the furnace was switched off, and the system flushed with dry nitrogen. The cold finger was turned in its joint so that the dimple was now facing the inlet port C. When the trap had nearly warmed to room temperature, an n.m.r. solvent was introduced through this port to dissolve the

products and wash them into the n.m.r. tube below, from which the spectrum was obtained.

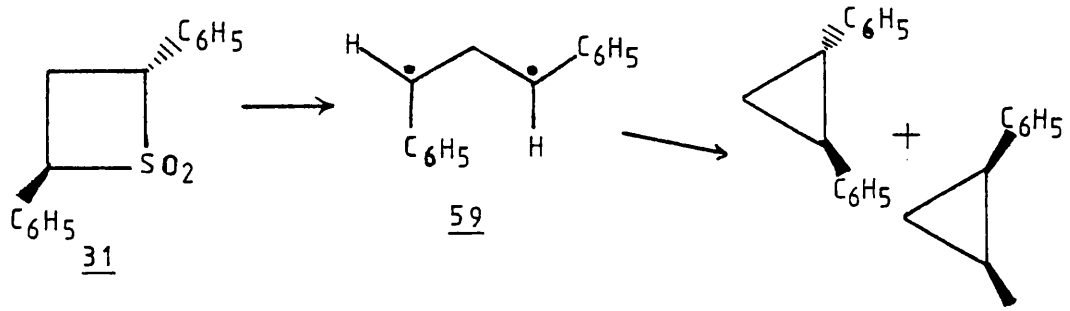
In order to prove the usefulness of our new apparatus, a sample of trans-2,4-diphenylthietan 1,1-dioxide was prepared, and subjected to flash vacuum thermolysis to see if the result was comparable to the pyrolysis products obtained by Dodson and Klose.[15]

1.4 The Thermolysis of Trans-2,4-Diphenylthietan 1,1-Dioxide at 0.003 mm Pressure

PRODUCT	FURNACE TEMPERATURE		
	300°C	400°C	500°C
Starting material	100%	26%	-
cis-1,2-diphenylcyclo-propane	-	19%	23%
trans-1,2-diphenylcyclo-propane	-	55%	77%

The products obtained in this experiment were fairly similar to those obtained by Dodson and Klose[15] where they quote a cis/trans ratio of 0.134. Our results show a cis/trans ratio of 0.34 at 400°C and 0.30 at 500°C. The relative proportion of isomers obtained is opposite to the trend described by Trost et al[16] for 2,4-dimethylthietan 1,1-dioxide, where pyrolysis of the trans isomer led to the predominant formation of the cis cyclo-

propane for the reasons described in the introduction. This probably stems from the greater lifetime of the fairly stable 1,3-diradical formed (59) and consequent diminishing of the importance of orbital symmetry considerations. The reaction is therefore probably thermodynamically controlled, with the thermodynamically more stable isomer preferentially formed.



1.5 The Photolysis of 2,4-Diphenylthietan 1,1-Dioxide

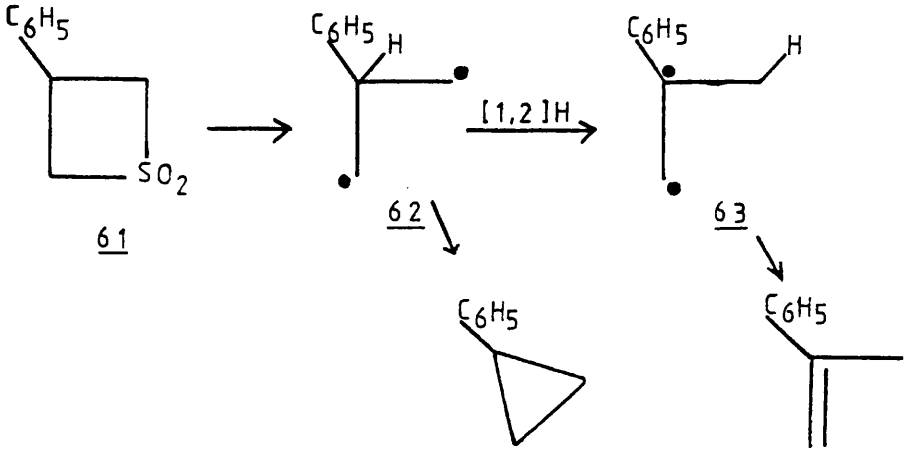
Irradiation of a solution of a mixture of cis and trans 2,4-diphenylthietan 1,1-dioxide (31) in acetonitrile at 253 nm for 12 hours gave a mixture of cis and trans 1,2-diphenylcyclopropane in a ratio of cis (59%) to trans (41%) as estimated by the n.m.r. spectrum of the crude reaction mixture.

The ratio of cyclopropane isomers formed cannot be taken to indicate any particular process, since it was not possible to ascertain the original proportion of cis and trans isomers of the theitan sulphones from n.m.r. spectroscopy.

Attempted synthesis of 2-methyl-4-phenylthietan 1,1-dioxide and 2-phenyl-4-p-methoxyphenylthietan 1,1-dioxide following the same method as for the 2,4-diphenyl analogue described above, using benzylidene acetone and 4-methoxychalcone respectively as the starting materials failed. Some evidence was obtained for the isolation of 2-phenyl-4-p-methoxyphenylthietan, however.

Having effectively tested our thermolysis apparatus, it was decided to subject a sample of 2-phenylthietan 1,1-dioxide (60) to flash vacuum thermolysis.

The thermolysis of 3-phenylthietan 1,1-dioxide (61) at 800°C has been described by Hall[20] to give a mixture of starting material (49%), phenylcyclopropane (30%) and α-methylstyrene (15%).



The mechanism proposed is initial formation of the 1,3-diradical (62) followed either by ring closure to give the cyclopropane or

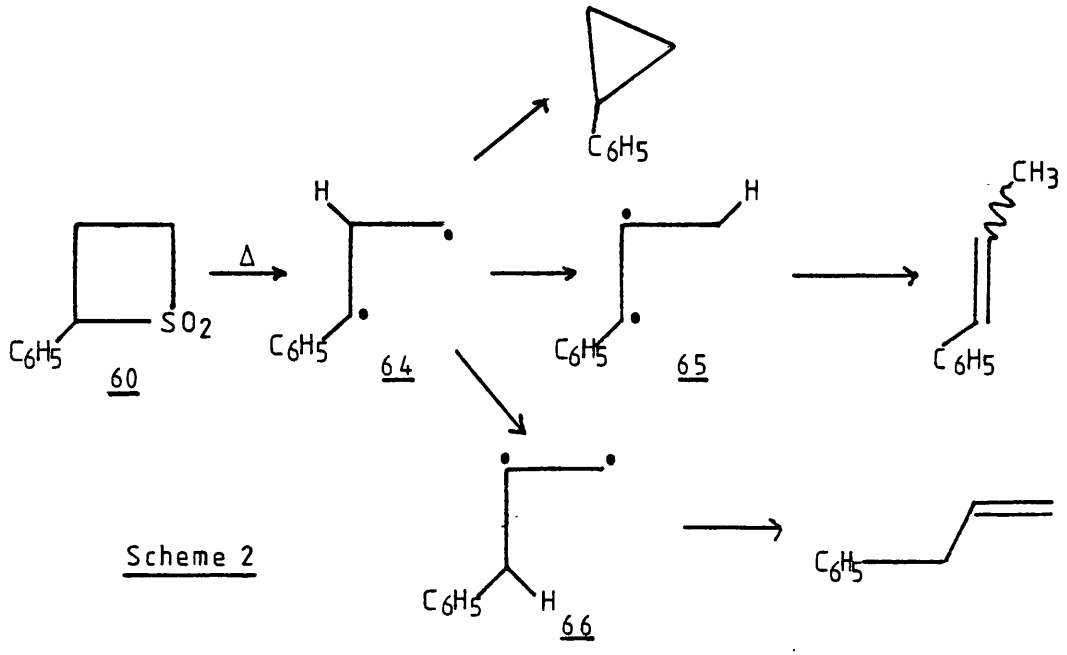
rearrangement to (63) followed by collapse to give the styrene. A possibility also described was that the styrene may have been formed from phenylcyclopropane which had ring opened because of a possible second contact with the hot surface.

The thermolysis of 2-phenylthietan 1,1-dioxide was carried out at a number of temperatures to see any possible changes in product that might indicate a diversity of mechanism.

1.6 The Thermolysis of 2-Phenylthietan 1,1-Dioxide at 0.015 mm Pressure

PRODUCT	FURNACE TEMPERATURE		
	450°C	600°C	750°C
Phenylcyclopropane	95%	70%	-
β-Methylstyrene	-	19%	49%
Allylbenzene	-	11%	49%
Starting material	5%	-	-

The products in this reaction can all be explained from an initial 1,3-diradical (64), as shown in Scheme 2.



Scheme 2

The diradical (64) may either ring close to give the observed cyclopropane, or rearrange in two ways:

(a) a 1-2 migration to (65) followed by collapse to give the styrene,

(b) a 1-2 migration to (66) followed by collapse to give allyl benzene.

The appearance of allylbenzene at higher temperatures reflects the high energy needed to form the fairly unstable diradical (66).

A separate thermolysis of a commercial sample of phenyl cyclopropane at 750°C failed to produce anything except unreacted starting material and hence it must be assumed that the alkenes are not produced from fragmentation of initially produced "high energy" phenylcyclopropane.

1.7 The Photolysis of 2-Phenylthietan 1,1-Dioxide

Irradiation of a solution of (60) in methanol at 253 nm for 20 hours gave phenylcyclopropane identified by the n.m.r. spectrum, as the only product. It is assumed that this product stems from the diradical (64) which does not contain enough energy to rearrange and therefore can only ring close.

As the photolysis productsof (31) and (60) seem to closely parallel those obtained under thermolysis, it was decided to attempt the photolysis of 3-phenylthietan 1,1-dioxide (61) to see if any further correlation could be made between the two processes.

1.8 Photolysis of 3-Phenylthietan 1,1-Dioxide

Irradiation of a solution of (61) in either acetonitrile or methanol with light of wavelength 253 nm for a period of 15 hours resulted only in the recovery of starting material on removal of the solvent. Irradiation for 109 hours under the same conditions gave a yellow oil containing some solid. Chromatography succeeded in separating unreacted starting material with a small amount of an orange oil. The n.m.r. spectrum of this oil was fairly featureless except that it did not contain any resonances in the aromatic region whatsoever.

Irradiation of (61) for 1 week under the same conditions gave, on removal of the solvent, a dark yellow oil. The n.m.r. spectrum of this oil contained no resonances in the aromatic region and otherwise consisted only of broad envelope resonances; at no time in all of these reactions was any indication given of any products resembling those obtained from the thermolysis.

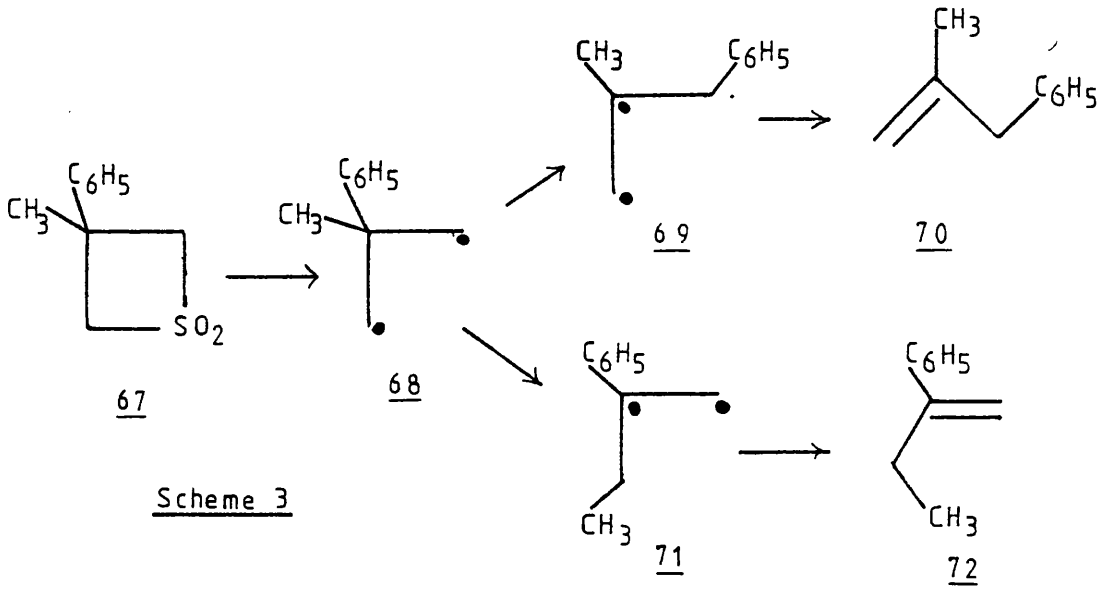
The stability of this molecule to photochemical change is surprising when compared with the 2-phenyl substituted analogue above. It seems that in order to induce photolytic extrusion of sulphur dioxide from a sulphone, the chromophore must be α to the heteroatom. This is reflected in the photolysis of (55) where no reaction was observed when R = Me even though there was a strong naphthyl

chromophore in the β-position. The observation that there was a loss of the aromatic residue of the molecule tends to suggest that the molecule fragmented with a breaking of the C(aryl)-C(alkyl) bond under forcing conditions, to leave a phenyl radical, which could abstract a proton from the solvent, and be taken off as benzene with the reduced pressure removal of the solvent.

As the thermolysis of the 3-phenylthietan 1,1-dioxide (61) had given a fairly clean product mixture it was decided to study the thermolysis of 3-methyl-3-phenylthietan 1,1-dioxide (67).

1.9 Thermolysis of 3-Methyl-3-Phenylthietan 1,1-Dioxide

Thermolysis of (67) at 750°C did not turn out to be as clean as expected from the analogous thermolysis of 3-phenylthietan 1,1-dioxide described above. Apart from unreacted starting material, the main product formed was 1-phenyl-1-methylcyclopropane. Also identified was α-methylstyrene which was a surprising result since this suggests a fragmentation of some kind.

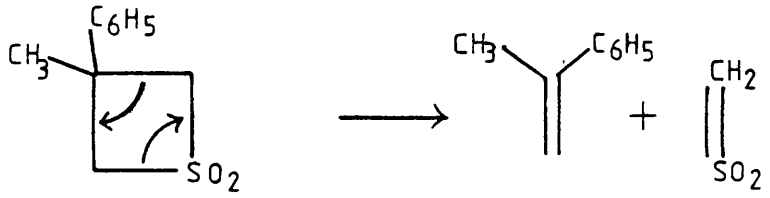


Scheme 3

If we assume formation of the 1,3-diradical (68) then it can be seen that no [1.2]hydride shifts are possible and that ring closure to give the observed cyclopropane is the major process by default.

Possible rearrangements of (68) may involve either a [1,2] aryl transfer to give (69) which would ultimately collapse to 2-methylallylbenzene (70) or a [1,2]methyl shift to give diradical (71) which would collapse to 2-phenylbut-1-ene (72) as shown in Scheme 3. Comparison of the n.m.r. spectrum of the product mixture with the published spectra for 2-methylallylbenzene[27] and 2-phenylbut-1-ene[28] showed that these compounds were absent.

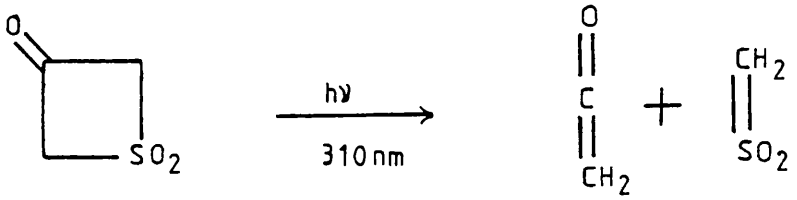
It is difficult to envisage the fragmentation of (68) in a way to produce the precursor of α-methylstyrene which necessitates the formal loss of carbene. Instead an alternative mechanism might be a retro[2.2] cyclisation to give the styrene and sulphene, as shown in Scheme 4.



Scheme 4

If this process is concerted then Woodward-Hoffmann rules predict that the process would be a σ2s + σ2a involving considerable

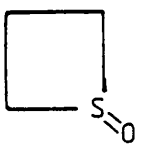
twisting of the four membered ring. Such retro processes take place where the reverse additions are concerted, however this is probably not the case because the orthogonal π^* orbital of sulphene needed to stabilise the transition state in order for the addition to be concerted is probably of too high an energy for efficient interaction with the highest occupied molecular orbital of the olefin. There is a photochemical analogue of this process involving the cycloreversion of 3-thietanone[29] (73). Irradiation of (73) in acetonitrile or in a 90:10 (v/v) mixture of acetonitrile-methanol at 310 nm results in the formation of ketene and sulphene.



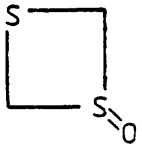
73

The intermediacy of the sulphene was proved by trapping with alcohols and by infrared spectroscopy at low temperatures.

A thermochemical analogue of this process is described by Block et al[30] who have studied the flash vacuum thermolysis of thietan 1-oxide (74) and 1,3-dithietan 1-oxide (75).



74



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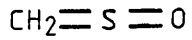
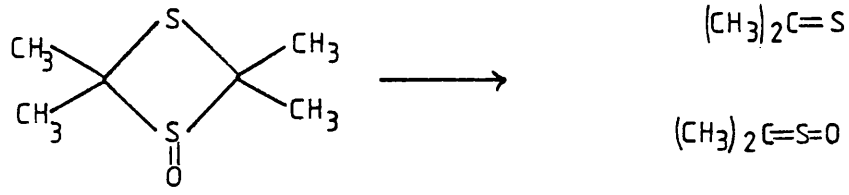


76

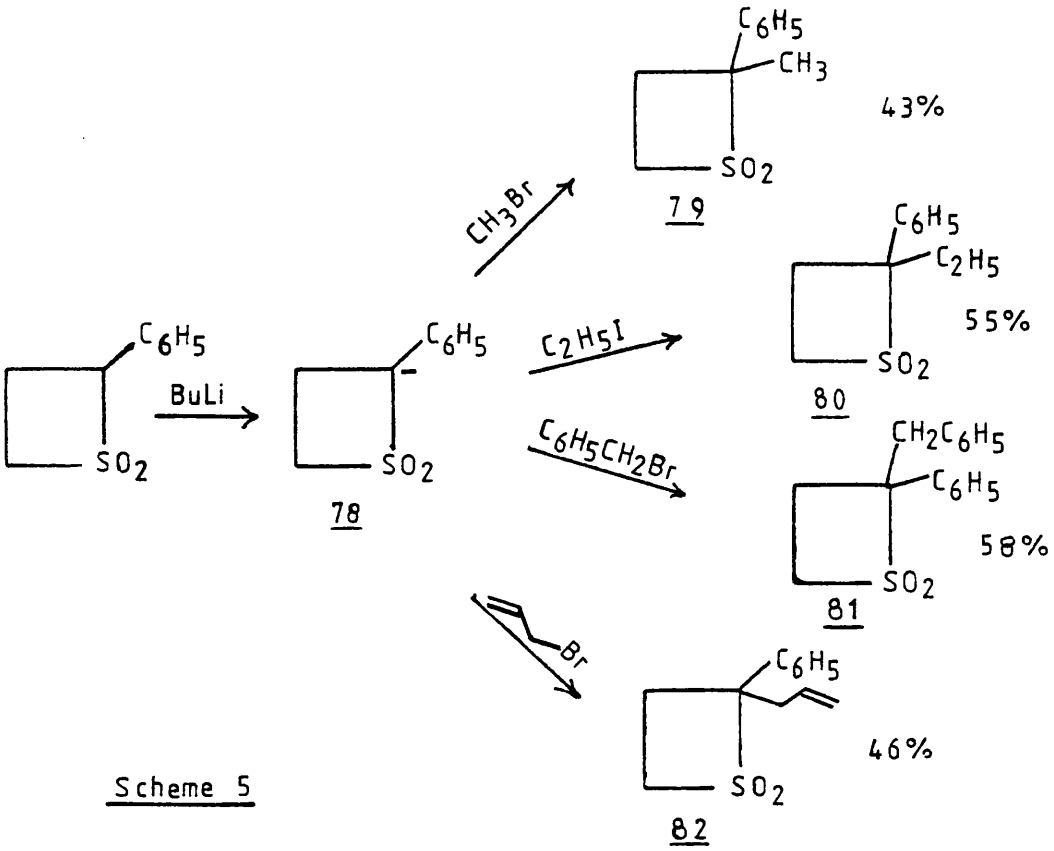
These compounds decompose cleanly in the gas phase to give sulphine (76) at temperatures from 300-600°C. This process may involve radicals, although the flash vacuum pyrolysis of 2,2,4,4-tetramethyl-1,3-dithietan 1-oxide (77) to give thioacetone and dimethyl sulphine is thought to occur from a cycloreversion.



77

In the light of the clean thermolysis product of (60), particularly at relatively low temperatures, it was decided to prepare some further derivatives of 2-phenylthietan 1,1-dioxide, and to study their thermolytic behaviour at 600°C, and their photolytic behaviour to assess their potential as a new synthesis of cyclopropanes.

The new derivatives were all 2,2-disubstituted thietan sulphones, and were prepared by the addition of an alkyl halide to a solution of the anion of 2-phenylthietan 1,1-dioxide (78) generated from the addition of a solution of butyl-lithium to the sulphone. Reactions of the anion (78) with methyl bromide, ethyl iodide, benzyl bromide, and allyl bromide all gave the appropriately substituted thietan 1,1-dioxides (79-82) as shown in Scheme 5.

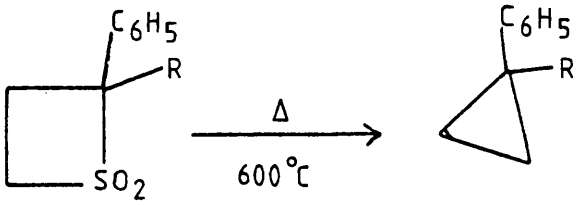


Scheme 5

All compounds gave satisfactory physical and analytical data. Attempted reaction of the anion with epibromohydrin, ethyl chloroformate or propylene oxide failed to produce any of the expected products.

1.10 Thermolysis and Photolysis of 2,2-Disubstituted Thietan Sulphones

Thermolysis of these thietan sulphones (79-82) at 600°C gave the correspondingly substituted cyclopropanes in the yields indicated.



	%
R = CH_3	87
= C_2H_5	88
= $CH_2C_6H_5$	83
= $CH_2CH{=}CH_2$	92

All cyclopropanes gave satisfactory physical and analytical data except in the case of R = CH_3, which was identified by comparison with a known n.m.r. spectrum.[30]

The relatively low temperature (600°C) needed to thermolyse the 2-substituted thietan sulphones, compared to the examples of the 3-substituted analogues described above, reflects the stability and therefore ease of formation of the diradical species.

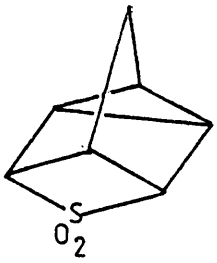
It was observed that thermolysis of 2,4-diphenylthietan 1,1-dioxide gave a complete reaction (i.e. no starting materials remaining) at 500°C while the temperature needed for the 2-substituted or 2,2-disubstituted analogues was at least 600°C. In the case of the 3-substituted analogues, an appreciable amount of starting material was found to remain even after thermolysis at 750°C.

Irradiation of solutions of (79-82) in methanol with light of wavelength 253 nm for periods of 3-4 hours gave in all cases the appropriately substituted cyclopropanes as were afforded by the

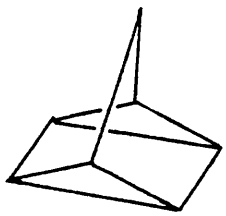
thermolyses. Determination of the yields was not possible since it was felt that any attempt at removal of the solvent under reduced pressure would result in loss of product. All of the photolysis products were pure by g.l.c. analysis.

It seems that the thermolytic extrusion of sulphur dioxide from 2-substituted thietan 1,1-dioxides is a facile process and, that by suitably adjusting the temperature of the furnace, cyclopropanes can be obtained in high yields from the reaction.

To see how far this process could be adapted, the thermolysis of 8-thiatetracyclo[2.2.1.1.0]octane-8,8-dioxide (83) (see Chapter 5) was attempted at various temperatures in order to see if any possible diradical formed would ring close to tetracyclo[3.2.0.0.0]heptane (84) or rearrange.



83



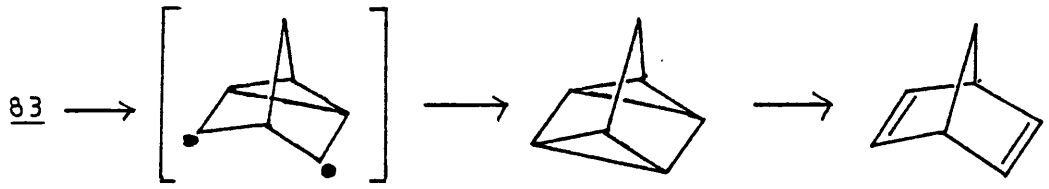
84

1.11 The Thermolysis of 8-Thiatetracyclo[2.2.1.1.0]octane-8,8-dioxide

PRODUCT	FURNACE TEMPERATURE		
	300°C	400°C	700°C
Starting material	86%	-	-
Norbornadiene	14%	98%	80%
Cycloheptatriene	-	-	trace
Toluene	-	-	16%

From the low temperatures needed to produce a reaction it must be assumed that the loss of sulphur dioxide from (83) is a very facile process. This is undoubtedly due to the strain imposed upon the carbon framework by the heteroatom bridging across the 2-5 positions and consequent release of this strain with the expulsion of sulphur dioxide. No trace of tetracyclo[3.2.0.0.0]heptane was observed in any of the products although this does not preclude its existence as an intermediate. A possible mechanism (Scheme 6) might involve initial formation of a diradical species (85) followed by ring closure to (84), which would be generated in an excited state.

The excess energy contained within (84) might cause isomerisation to norbornadiene (86).



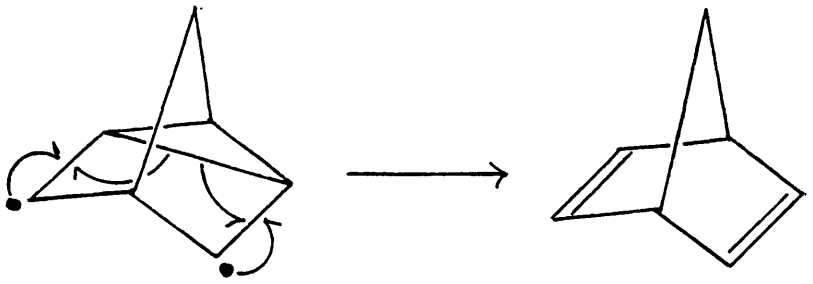
83 → [85] → 84 → 86

Scheme 6

The thermal isomerisation of (84) to (86) at 140°C in the gas phase at pressures of 1-18 mm has been described by Frey.[32]

The complete absence of (84) in the product mixture would be surprising if this was the mechanism operating and another

possibility is the direct formation of (86) from (85) as shown below.



85 86

The formation of cycloheptatriene and toluene at higher temperatures probably stems from a rearrangement of "high energy" norbornadiene since the thermal isomerisation of norbornadiene and a number of norbornadiene based compounds to cycloheptatrienes followed by subsequent isomerisations to toluene or fused analogues has been described by a number of workers.[33]

Flash vacuum thermolysis of a sample of norbornadiene at 720°C using our apparatus, yielded a mixture of starting material (66%), cycloheptatriene (22%) and toluene (12%).

1.12 Mass Spectral Studies

The mass spectrum of 2-phenylthietan 1,1-dioxide (60) at 70 eV is shown in Figure 1/2.

Figure 1/2 Mass spectrum of 2-phenylthietan 1,1-dioxide

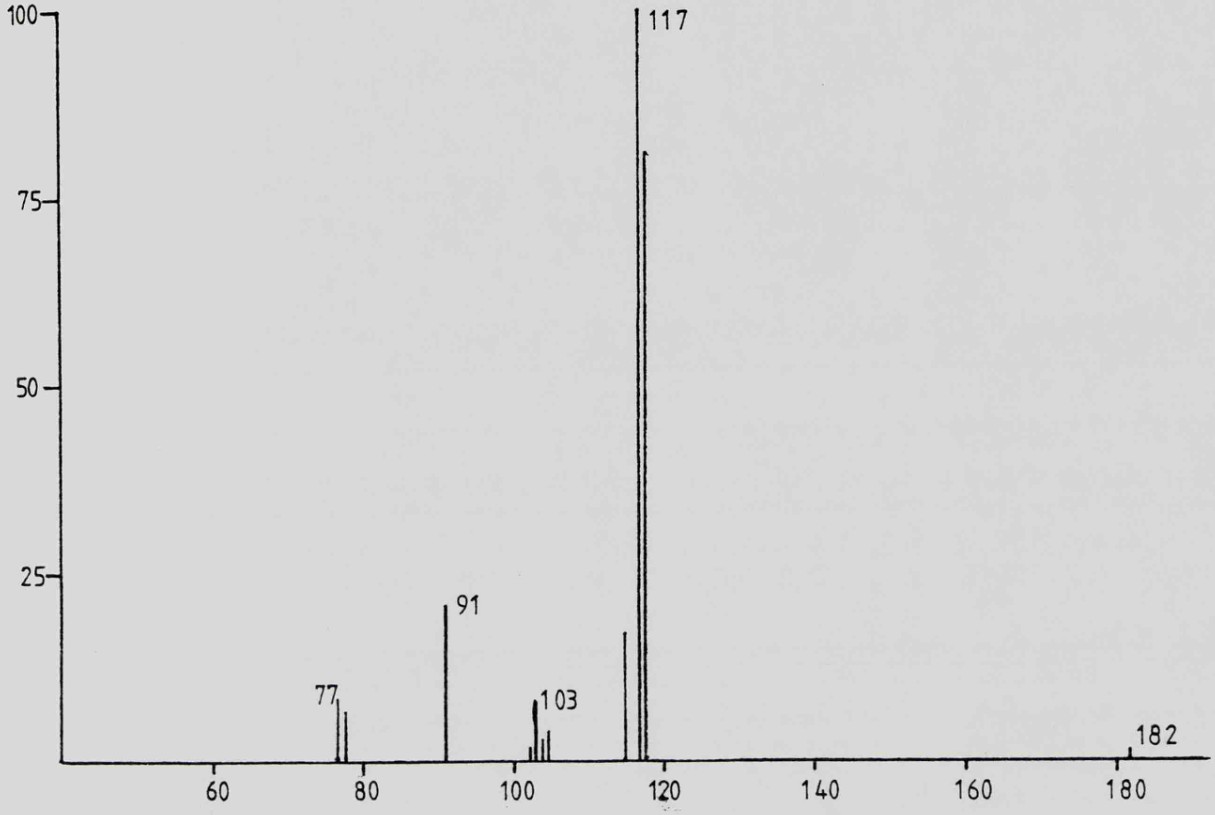
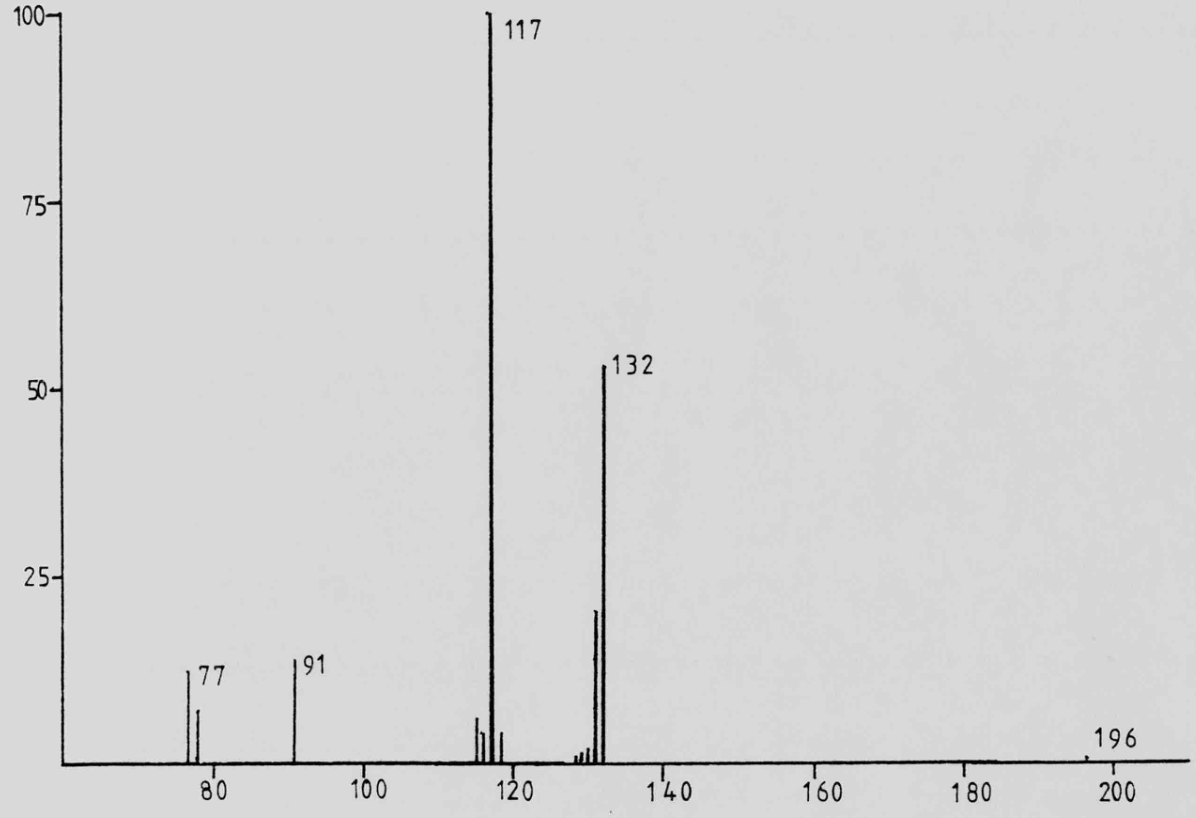


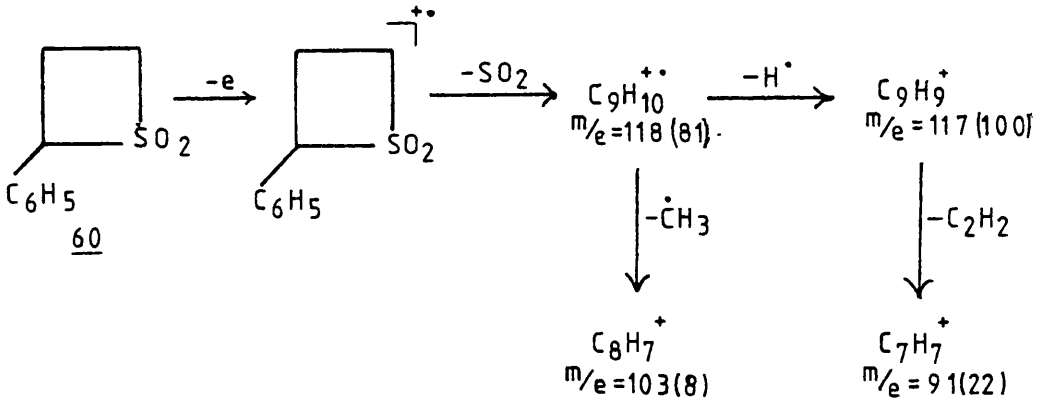
Figure 1/3 Mass spectrum of 2-phenyl-2-methylthietan 1,1-dioxide



The spectrum was quite simple, although the molecular ion was very small even when the spectrum was recorded at 16 eV.

The molecular ion (m/e = 182) appeared to decompose (Scheme 7) by loss of sulphur dioxide to give m/e = 118 from which H$^{\bullet}$ can be expelled to yield the base peak at m/e = 117 ($C_9H_9^{+\bullet}$); a metastable peak at m/e = 117 indicates this is the process, and not a direct loss of SO_2H from the molecular ion. The peak at m/e = 103 could arise from loss of $\dot{C}H_3$ from m/e = 118 and that of m/e = 91 from loss of acetylene from m/e = 117. The peak at m/e = 91 may be considered either as a benzyl cation or a tropylium ion.

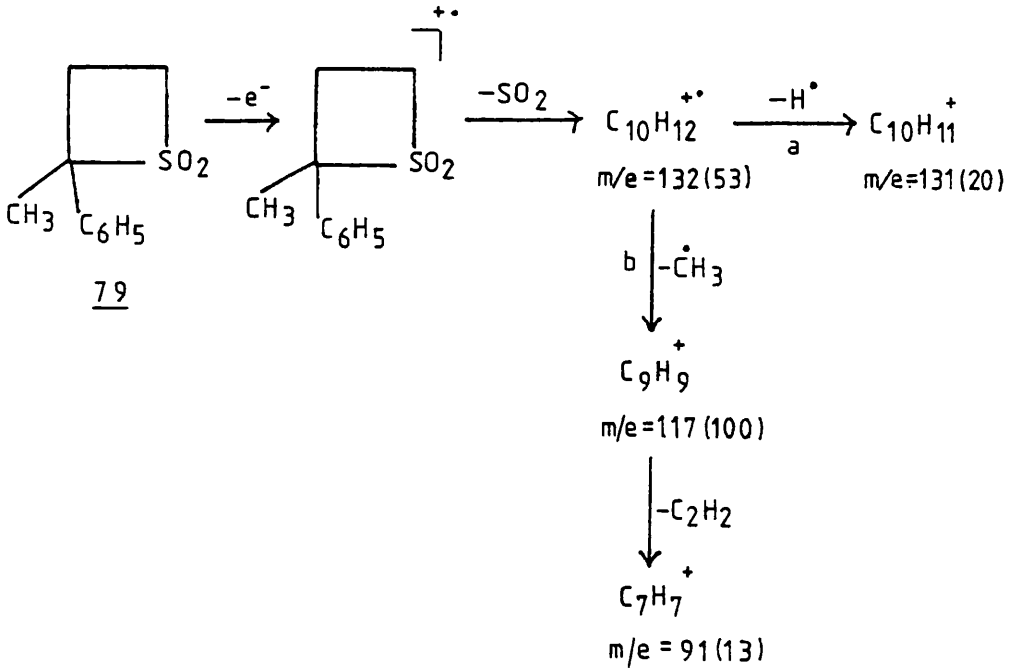
Scheme 7



The mass spectrum of 2-phenyl-2-methylthietan 1,1-dioxide (79) is shown in Figure1/3. This spectrum shows many similarities to that of (60) and can be explained in much the same way (Scheme 8).

Initial loss of sulphur dioxide from the molecular ion (m/e = 196) gives m/e = 132 from which may decompose in one of two ways. Either a) expulsion of H$^{\bullet}$ to give m/e = 131 or b) loss of $\dot{C}H_3$ to give the base peak at m/e = 117 as shown by a metastable peak at 103.7. Loss of acetylene from the base ion gives m/e = 91 as shown by a metastable peak at 70.8. These fragmentations are summarised below (Scheme 8).

Scheme 8



In the case of 2-phenyl-2-ethylthietan 1,1-dioxide (80) the fragmentations are similar - loss of sulphur dioxide from the molecular ion is an important process followed either by loss of

a proton to give an (M-65) peak or fragmentation to the stable m/e = 117 peak which is the base ion.

The mass spectrum of 2-phenyl-2-allylthietan 1,1-dioxide (82) is shown in Figure 1/4.

The molecular ion (m/e = 222) appears to fragment in two ways (Scheme 9) either a) loss of an allyl radical to give m/e = 181 followed by loss of sulphur dioxide to give the base ion at m/e = 117, or b) loss of sulphur dioxide to give m/e = 158 which may itself fragment in a number of ways by either loosing an allyl radical to give m/e = 117, losing a methyl radical to give m/e = 143 (this is substantiated by a metastable peak at m/e = 129.5) or by loss of an ethyl radical leading to m/e = 129. These processes are detailed below.

Scheme 9

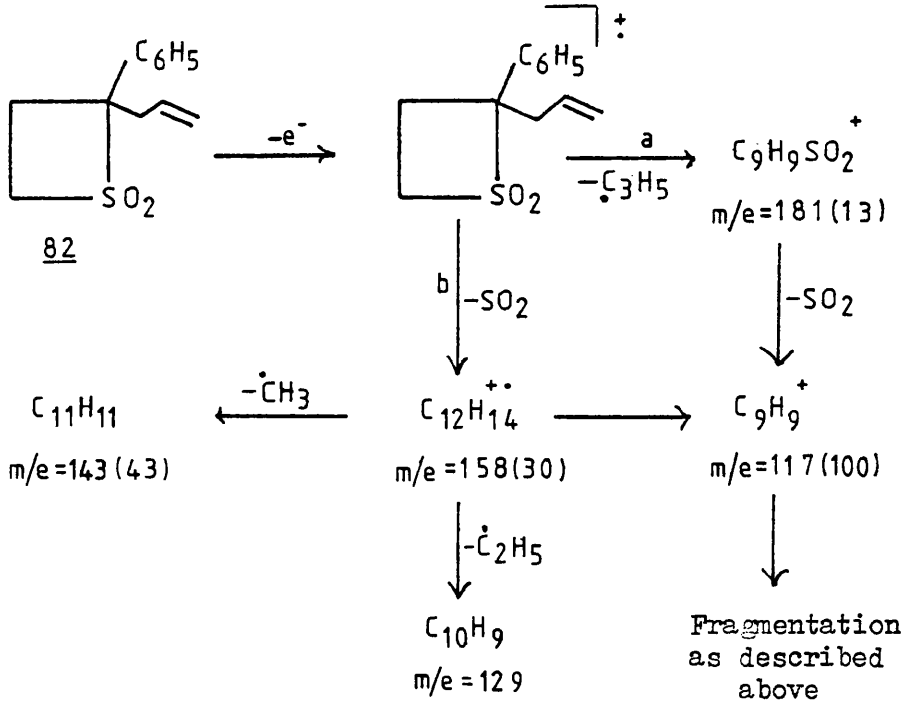


Figure 1/4 Mass spectrum of 2-phenyl-2-allylthietan 1,1-dioxide

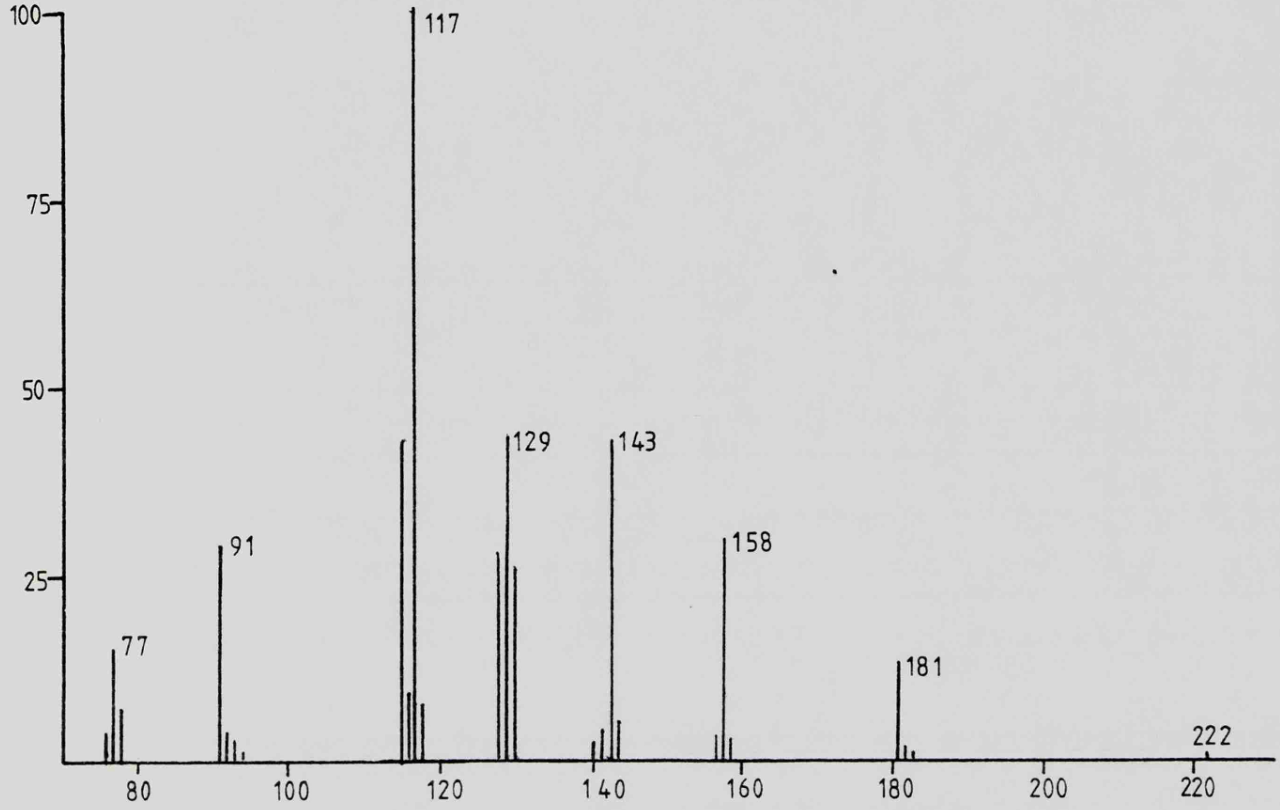
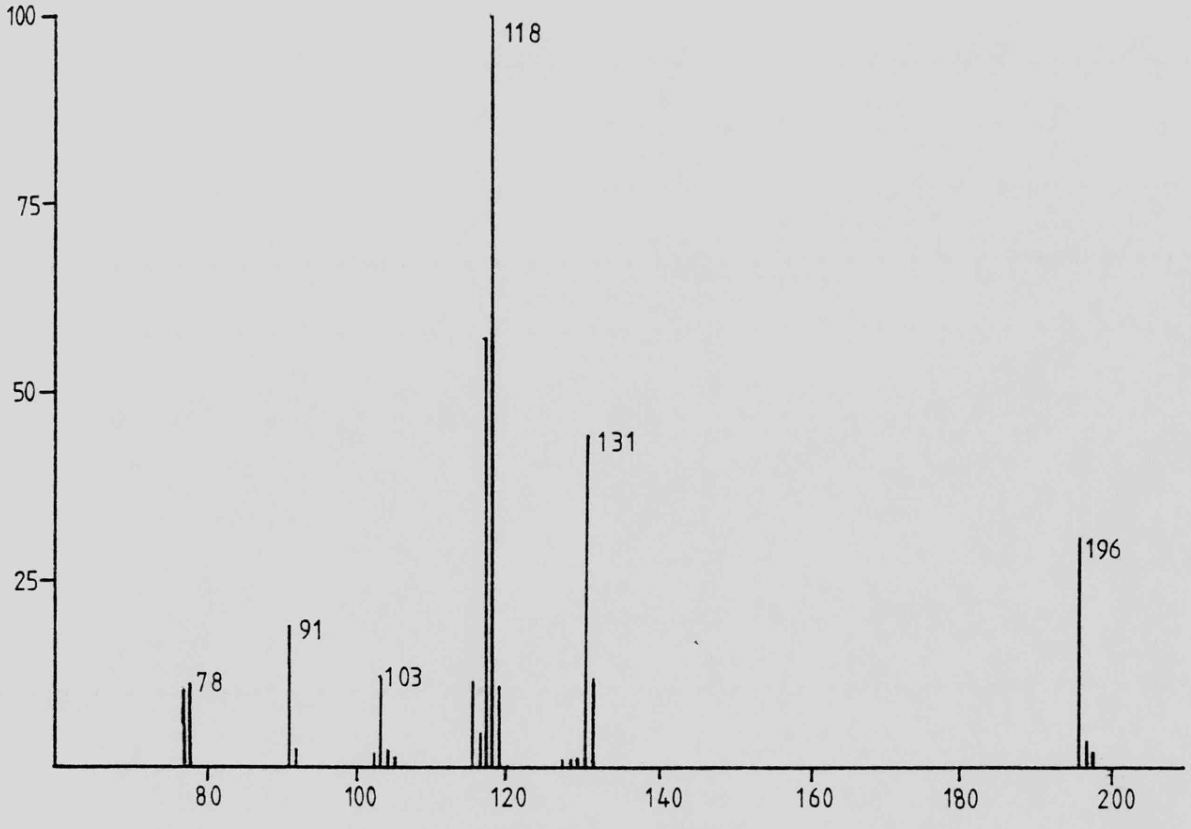


Figure 1/5 Mass spectrum of 3-methyl-3-phenylthietan 1,1-dioxide

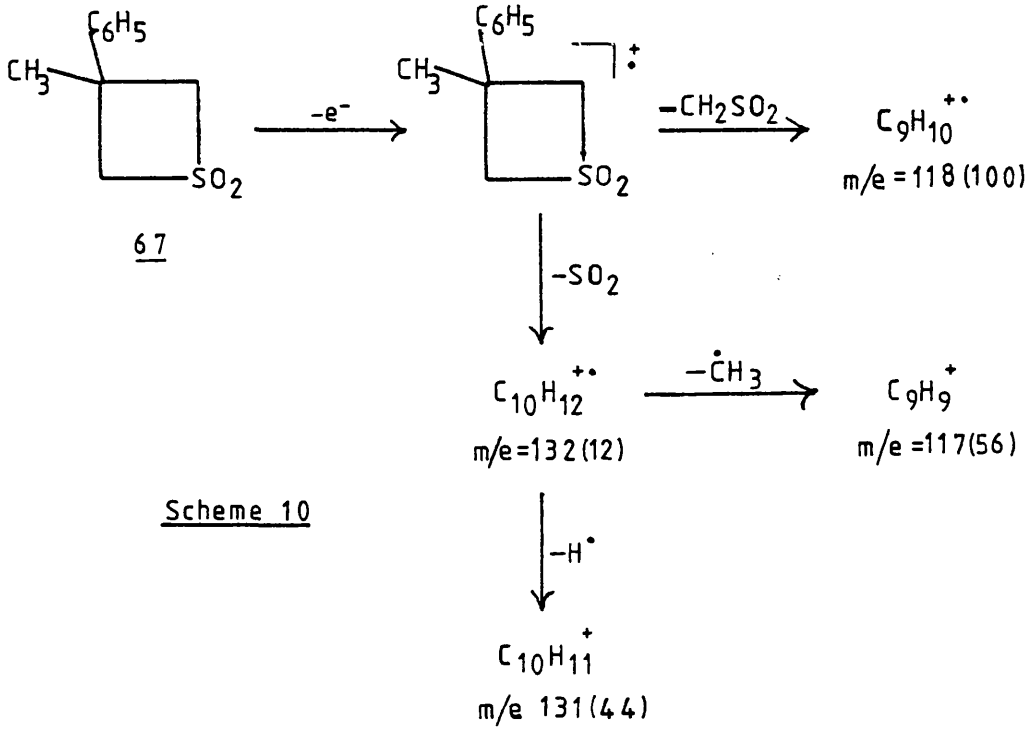


The breakdown pattern for 2-phenyl-2-benzylthietan 1,1-dioxide (81) is similar. The molecular ion may either a) extrude sulphur dioxide to give m/e = 208, followed by loss of a benzyl radical to give the base peak at m/e = 117 or b) lose a benzyl radical to give m/e = 181 followed by loss of sulphur dioxide to give m/e = 117.

The trend in fragmentation of all of these 2-substituted compounds seems to be loss of sulphur dioxide and any other neutral species to form a stable $C_9H_9^{+\cdot}$ allylic radical ion, which always appears as the base peak. This trend partly follows that observed in the photolytic and thermolytic breakdown, but the loss of other stable species, in some cases before the extrusion of sulphur dioxide, tends to indicate that this process is not as important under electron impact conditions.

The mass spectrum of 3-methyl-3-phenylthietan 1,1-dioxide is shown in Figure 1/5. The molecular ion peak is unusually large compared with the previous examples and this is attributed to the lack of stability of the initial diradical formed by loss of sulphur dioxide. This seems to correlate well with its behaviour under thermolysis. There is a small (M-64) peak at m/e = 132, and a larger (M-65) peak. The base peak is at m/e = 118 which corresponds to (M-78). No other thietan sulphone described above has shown an (M-78) peak, and it is thought that this must come from

a cycloreversion reaction leading to the loss of sulphene (Scheme 10) to give m/e = 118. The peak at m/e = 117 is analogous to the previously described examples above, and stems from the loss of a methyl radical from m/e = 132. These fragmentations can be summarised as shown below.



67

Scheme 10

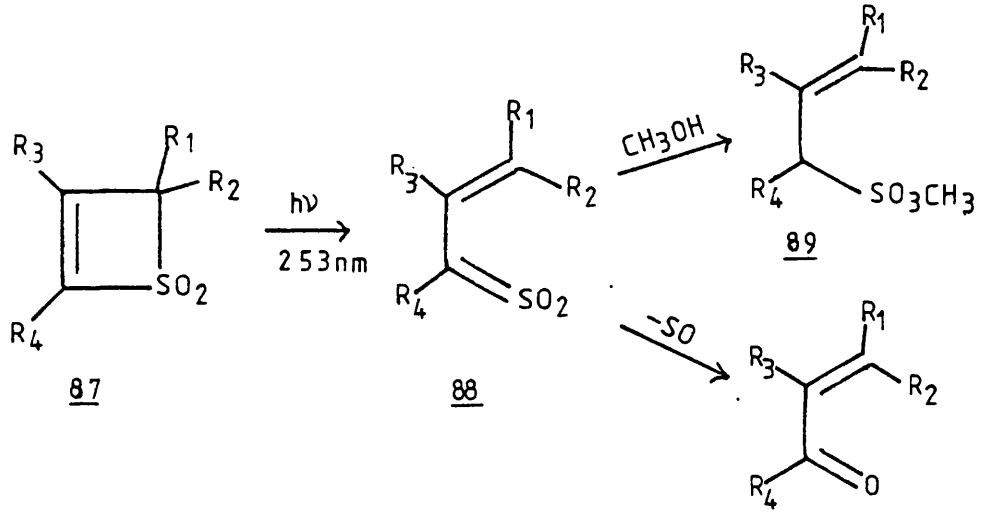
There seems to be a very good correlation between thermolytic and electron impact fragmentation in this example with regard to the possible cycloreversion in the thermolytic breakdown.

CHAPTER TWO

THE FLASH VACUUM THERMOLYSIS OF SOME OXYGEN AND SULPHUR HETEROCYCLES AND ATTEMPTED PREPARATION OF SOME CORRESPONDING SULPHOXIMIDES

2.1 Introduction

A number of people have suggested the generation of sulphene intermediates in the photochemical and thermolytic fragmentation of cyclic sulphones.[17,21,38] A study of the photochemical behaviour of some thiete 1,1-dioxides (87) has been made by DeSchryver and Langendries.[39] Photolysis of these molecules with light of wavelength 253 nm gives vinyl sulphene intermediates (88) which in methanol are trapped to give the sulphonate ester (89). In an inert solvent however, fragmentation occurs to give a vinyl aldehyde or ketone, and sulphur monoxide.

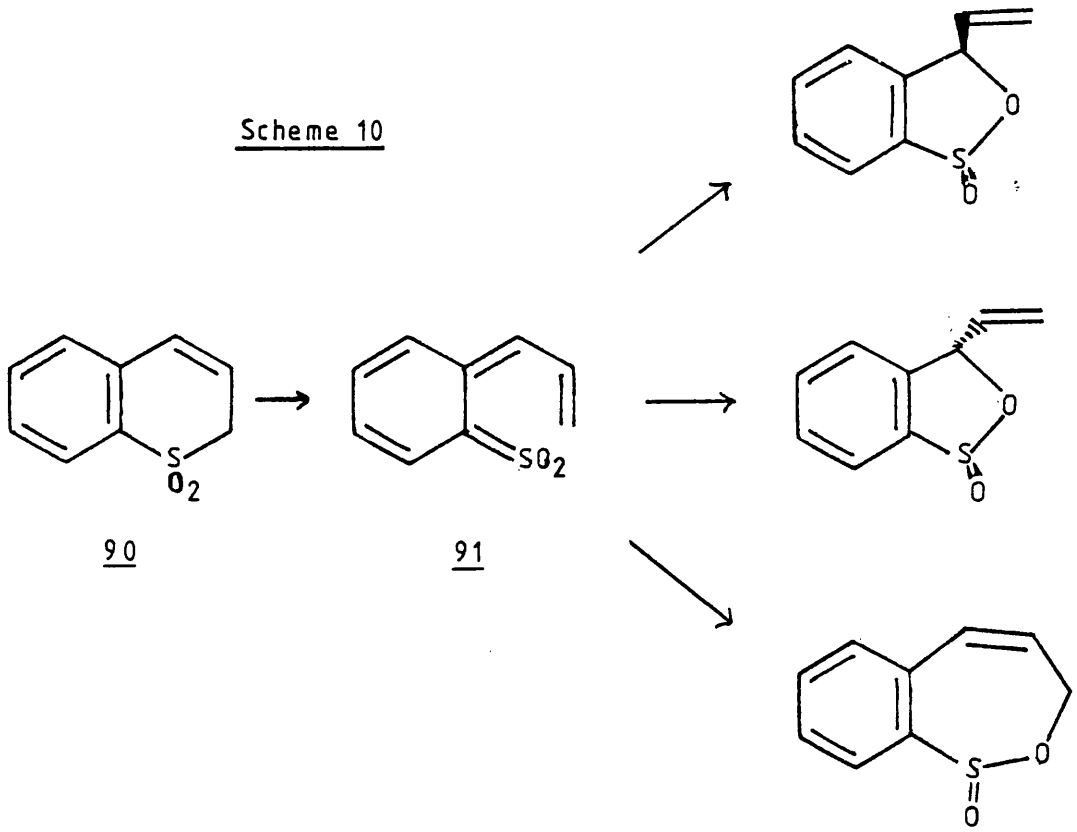


87 88 89

A study of the photolysis and thermolysis of a number of 4π electron cyclic sulphones has been described by Hall and Smith[40] in the search for sulphene intermediates.

Photolysis of 2H-1-benzothiopyran (90) in dichloromethane or methanol (with light of wavelength 253 nm) gives a mixture of sultines which possibly originate from an initially formed unsaturated sulphene intermediate (91) as shown in Scheme 10.

Scheme 10

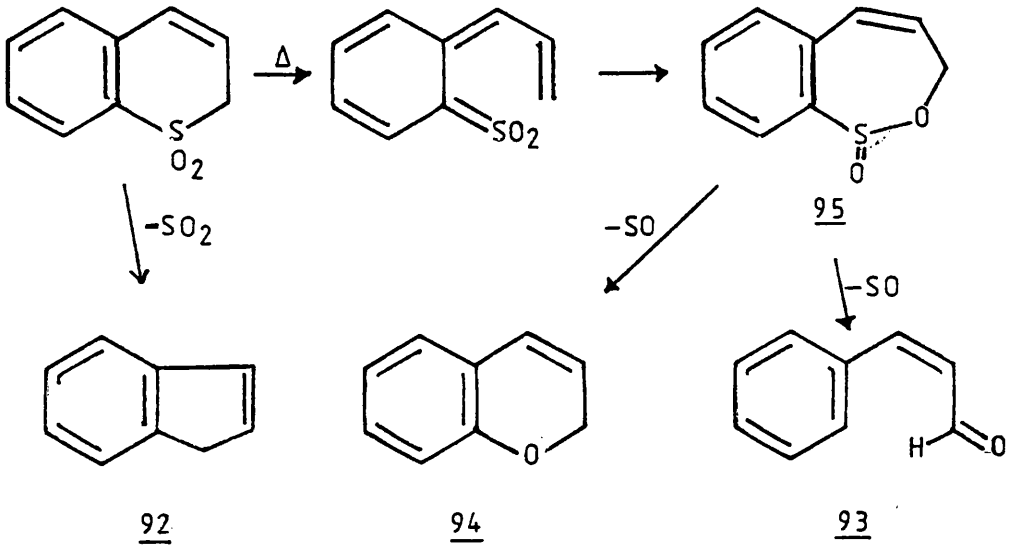


90 91

Attempted trapping of (91) with either methanol or reactive dienophiles failed to isolate any addition product, and it was presumed that the lifetime of the sulphene intermediate was very short because of rapid rearrangement to restore aromaticity.

Flash vacuum thermolysis of (90) at 775°C (Scheme 11) produces indene (92), cinnamaldehyde (93) and 2H-1-benzopyran (94) which

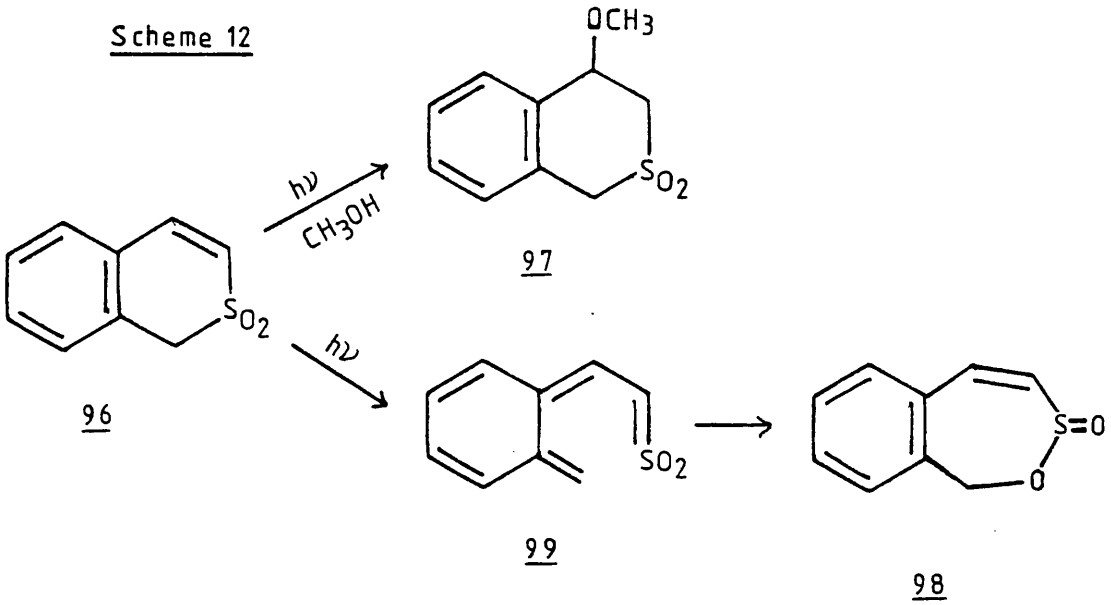
possibly result from direct extrusion of sulphur dioxide or rearrangement to the sultine (95) followed by loss of sulphur monoxide.



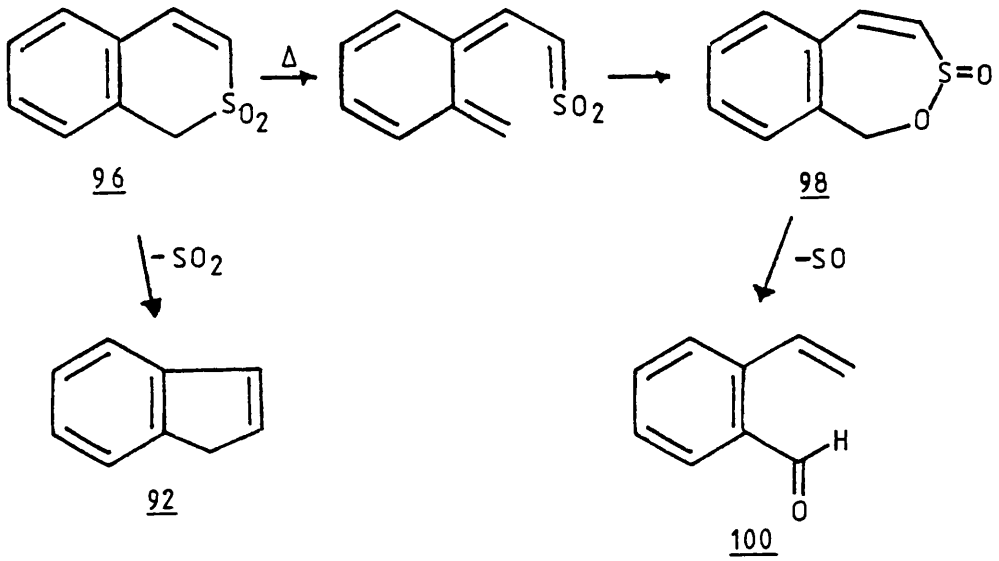
Scheme 11

The photolysis of 1H-2-benzothiopyran 2,2-dioxide (96) in methanol (Scheme 12) gave mainly the addition product (97) and some of the sultine (98), the genesis of which was rationalised via the sulphene intermediate (99).

Scheme 12



Conversely, thermolysis of (96) at 775°C (Scheme 13) gives indene (92) from a possible direct extrusion of sulphur dioxide, and o-vinylbenzaldehyde (100) which may be derived from the sultine intermediate (98).

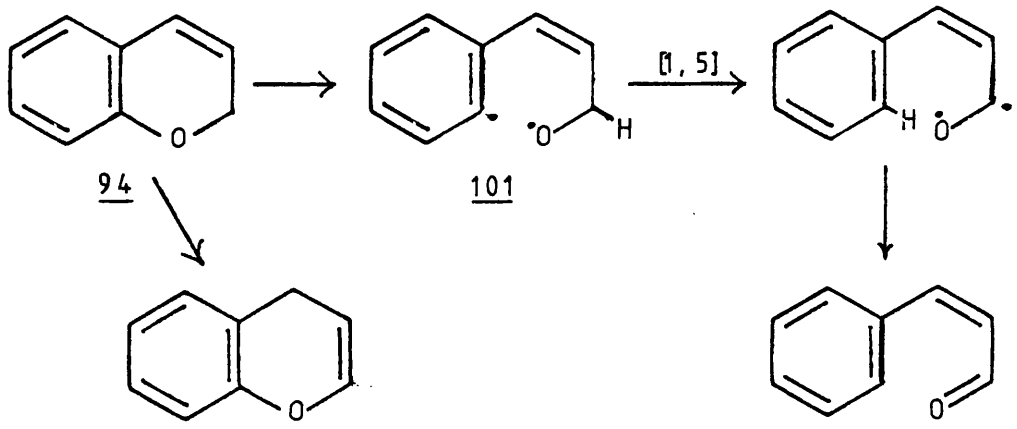


Scheme 13

Since cinnamaldehyde produced from the thermolysis of (90) could have resulted from a rearrangement of 2H-1-benzopyran (94) under the reaction conditions, a sample of (94) was thermolysed in order to see if any cinnamaldehyde was produced.

Thermolysis of (94) at 850°C gave a mixture containing cinnamaldehyde (13%), 4H-1-benzopyran (34%) and unchanged starting material (52%). A possible route for this reaction (Scheme 14) could be formation of an initial diradical (101) by cleavage of the C(aryl)-O bond followed by a [1.5] hydrogen migration and collapse of the resulting diradical. The 4H-1-benzopyran presumably results from

a [1.3] hydrogen transfer although a suprafacial migration would be thermally forbidden under orbital symmetry rules.

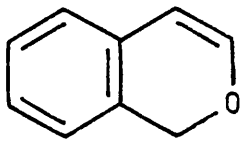


Scheme 14

In order to verify the proposed mechanism (Scheme 13) for the thermolysis of (96), a pure sample of the sultine, 5,6-dibenzo-7H-1,2-oxathiepin-2-oxide (98) was prepared from the photolysis of (96) in acetonitrile, and its behaviour under flash vacuum thermolysis was studied.

Thermolysis of (98) at 750°C gave a dark oil containing o-vinylbenzaldehyde (100) as the only identifiable product. Significantly, there was no trace of indene in this material and this seems to be good evidence to suggest that indene resulting from the thermolysis of (96) arises from the direct extrusion of sulphur dioxide from the starting material, and that (98) is an intermediate in the formation of o-vinylbenzaldehyde in this process.

In an attempt to probe deeper into this scheme, the thermolysis of 1H-2-benzopyran (102) was studied; since this compound might also be an intermediate species in the conversion of (98) to (100). Thermolysis of (102) at 750°C however gave a thick polymeric material of an unknown nature. No trace of (100) was observed in this material from n.m.r. spectroscopy.

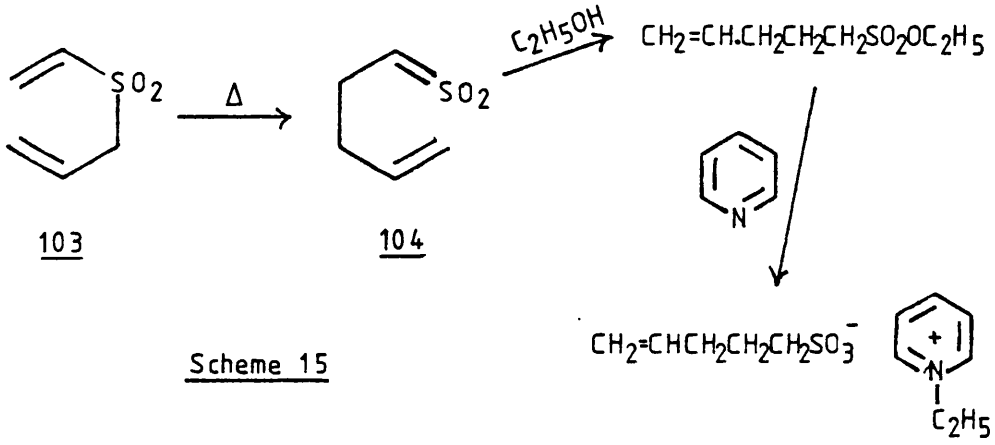


102

This result seems to rule out the intermediacy of (102) in the thermolysis of (96).

The stereochemical course of the ring opening and closure reactions of (90) and (96) (Schemes 10-13) are of some interest since, if this process is a concerted electrocyclic ring opening, then a disrotatory process is implied under Woodward-Hoffmann rules. In the case of these molecules however, the presence of a heteroatom in the system may be a major perturbation of orbital symmetry, and this process cannot be justified in the absence of further evidence, especially since all of the observed products can be explained in terms of biradical intermediates.[20]

Many authors have however reported electrocyclic reactions involving sulphur in all of its oxidation states. The sulphur analogue of the Cope rearrangement has been reported by King and Harding.[41] Allyl vinyl sulphone (103) has been shown to rearrange on pyrolysis or under flash vacuum thermolysis to give a sulphene intermediate (104), which in an ethanol-pyridine solution gives the N-ethylpyridinium salt of the corresponding sulphonic acid (Scheme 15).



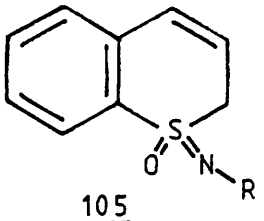
103 104

Scheme 15

Deuterium labelling α to the sulphinyl group has clearly shown the rearrangement to be of the order [3.3] either in the gas or the liquid phase. Sulphur analogues of the Claisen rearrangement have also been described for sulphides,[42] sulphoxides,[43] and sulphonium salts.[44]

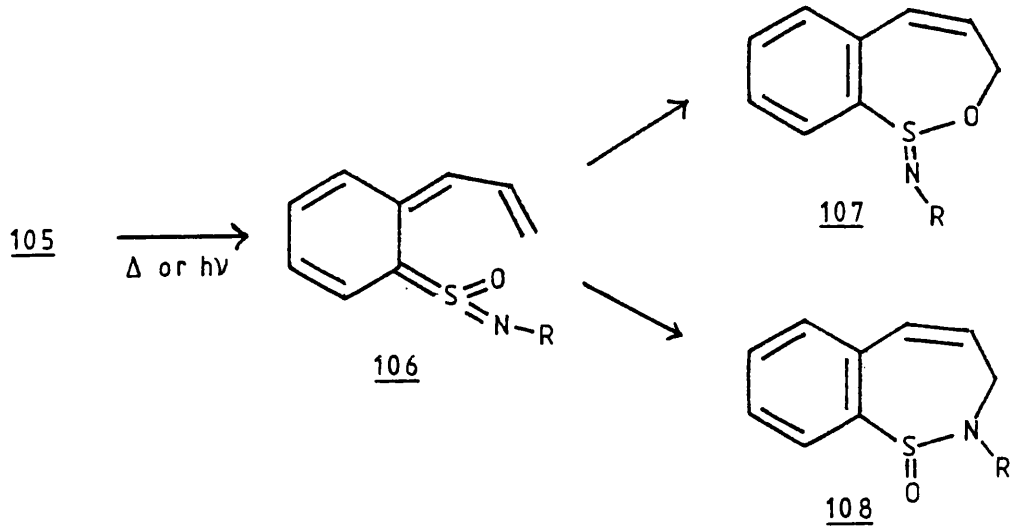
2.2 Attempted Preparations of Some Sulphoximides

To extend this work further, the synthesis of a number of sulphoximides of the type (105) were attempted.



105

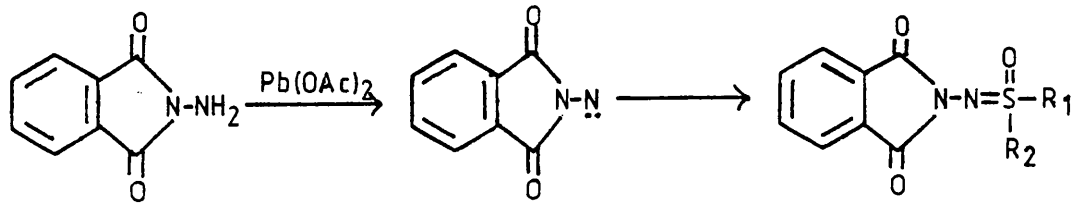
On thermolysis (105) may react in an analogous manner to (90) to give an intermediate (106). There is now the possibility of ring closure either onto oxygen or nitrogen to give (107) or (108) respectively.



A study of the thermolysis or photolysis of such molecules with a suitable label in the 2-position may yield some information about the stereochemistry of this reaction.

Many syntheses of sulphoximides have been described in the literature,[45] either by amination of a sulphoxide (usually by a nitrene intermediate), or oxidation of a sulphimide using potassium permanganate or a per-acid. The reaction of sulphoxides with the

nitrene (109) formed by oxidation of N-aminophthalimide with lead tetraacetate has been described by Rees et al.[46a] This method is quoted as being quite general for dialkyl, diaryl, and alkyl, aryl sulphoxides.



109

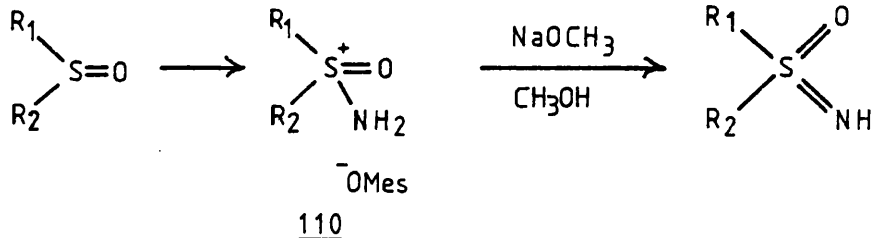
$R_1=R_2=CH_3$

$R_1=R_2=C_6H_5$

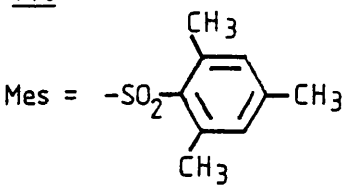
$R_1=CH_3, R_2=C_6H_5$

$R_1=R_2=CH_2C_6H_5$

Another method has been described by Tamura et al[47] which involves the amination of sulphoxides under mild conditions with O-mesitylenesulphonylhydroxylamine to give (110).

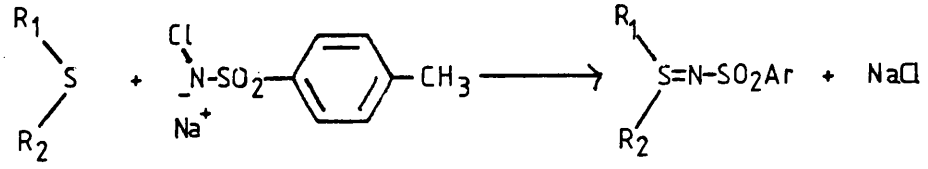


110



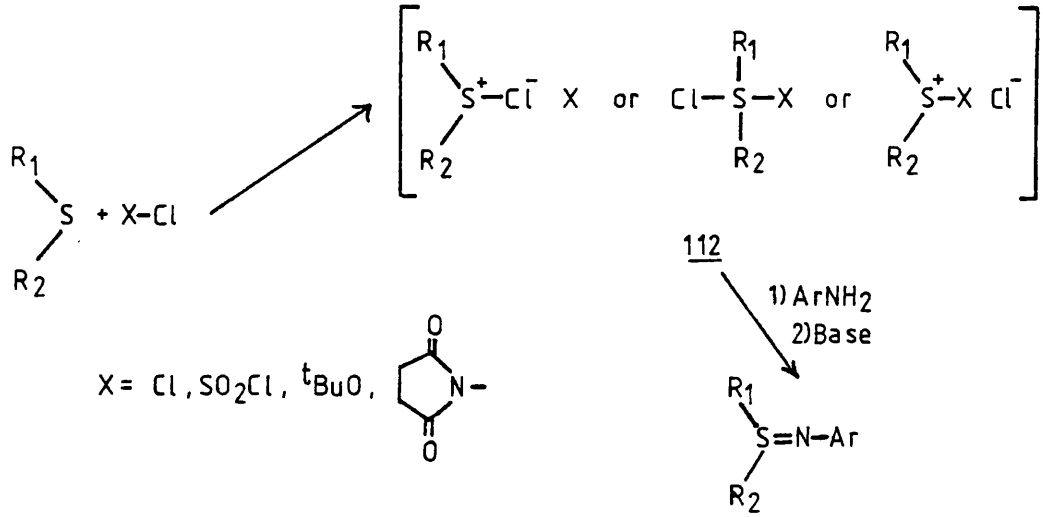
Many cyclic sulphoximides have been prepared using this route, although the main restriction seems to be the limited stability of (110) even at room temperature, and this prevents the use of more forcing conditions.

Sulphimides have been known for many years; the most common procedure for preparing them is the reaction of sulphides with sodium N-p-toluenesulphonylchloramine (chloramine T)[48] (111).



111

Recently, new methods to synthesise N-aryl sulphimides have been described by Claus et al.[49] One of these involves the reaction of anilines with sulphides and N-chlorosuccinimide. The mechanistic details of the reaction are unclear, it may be the reaction of a sulphide with an N-chloroaniline, or the reaction of a chloro-sulphonium salt (112) with the amine.

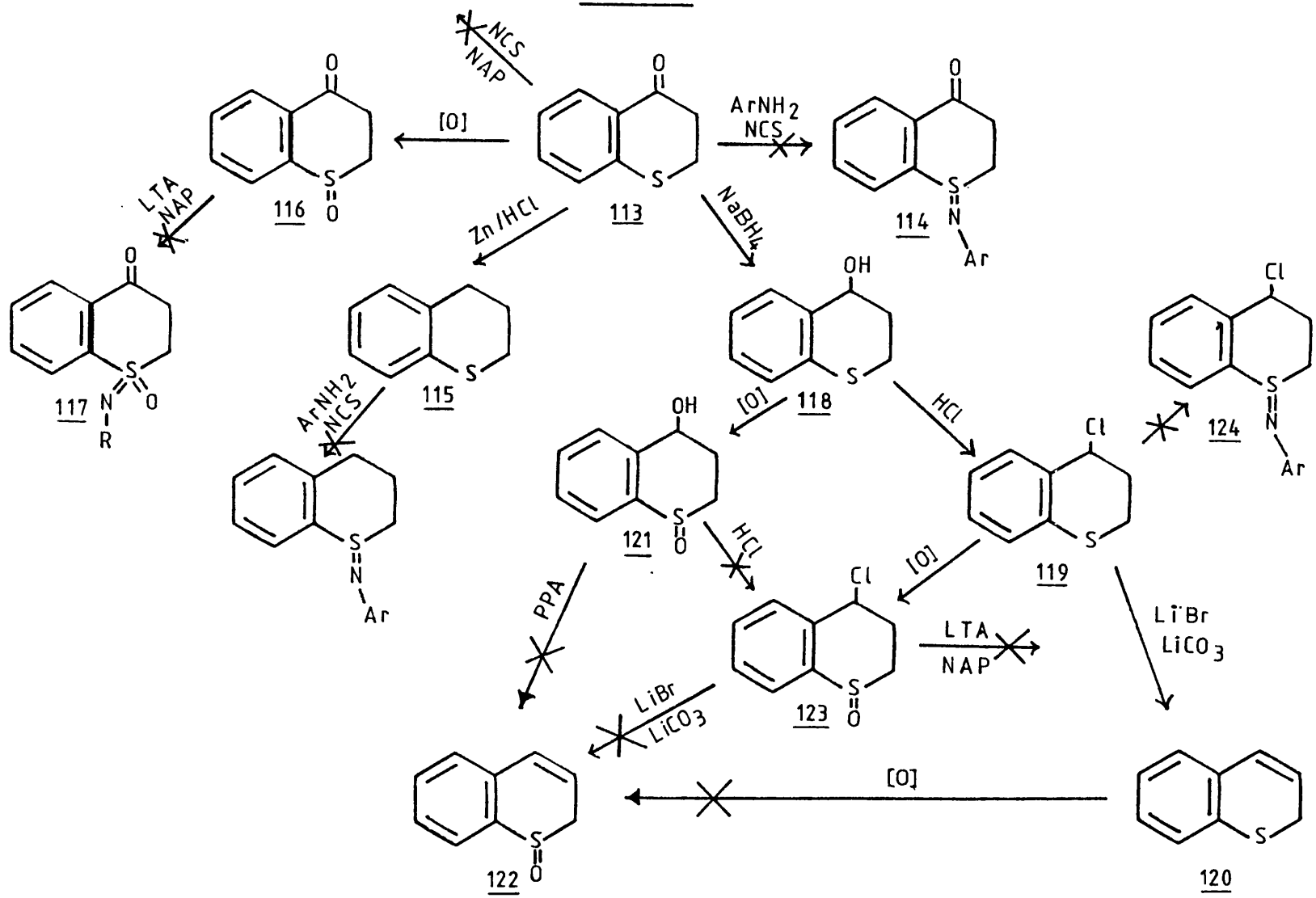


The variety of groups R^1 and R^2 used, indicate that this method is fairly general. Oxidation of the sulphimide formed, using potassium permanganate, gives the corresponding sulphoximides in yields of mostly greater than 65%.

The reactions attempted to synthesise sulphoximides based on the method of Rees et al[46] or sulphimides based on the methods of Claus et al[49] are shown in Scheme 16.

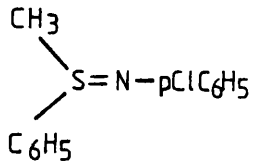
Reaction of thiochroman-4-one (113) with p-anisidene and N-chlorosuccinimide failed to give any of the expected sulphimide (114), and neither did the reaction of (113) with N-chlorosuccinimide and N-aminophthalimide following the method described by Gilchrist et al.[51] Reduction of (113) to thiochroman (115) followed by another attempt at amination using p-anisidene and N-chlorosuccinimide was also unsuccessful. Oxidation of (113) to the sulphoxide (116) followed by attempted amination using N-phthalimido nitrene failed to give the sulphoximide (117). Reduction of (113) with sodium borohydride gave the alcohol (118), which on reaction with dry hydrogen chloride in benzene solution gave an almost quantitative yield of 4-chloro-thiochroman (119). This was surprising since we had expected elimination to give 2H-1-benzothiopyran (120). Attempted elimination of (119) with triethylamine was unsuccessful however reaction with a mixture of lithium bromide and lithium carbonate in D.M.F.[65b] gave a good yield of the eliminated product (120). The combined yields of the chlorination, followed by the elimination reaction were slightly greater than the one step dehydration of (118) using polyphosphoric acid as described by Pagani.[50] Attempted reaction of (119) with N-chlorosuccinimide and aniline or p-anisidine failed to give the sulphimide (124). Oxidation of (118) gave the sulphoxide (121) but attempted dehydration of this compound using polyphosphoric acid failed to give 2H-1-benzothiopyran-1-oxide (122). Attempted reaction

Scheme 16

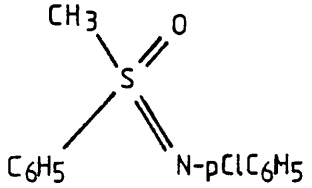

NCS
NAP
[O]
ArNH2
NCS
LTA
NAP
Zn/HCl
NaBH4
116
113
114
117
115
118
ArNH2
NCS
HCl
124
121
HCl
[O]
119
PPA
LTA
NAP
LiBr
LiCO3
123
LiBr
LiCO3
[O]
122
120

of (121) with hydrogen chloride failed to give 4-chlorothiochroman 1-oxide (123) although partial oxidation of (119) with m-chloroperoxybenzoic acid to give (123) as an unstable solid appears to have succeeded. Attempted elimination of (123) using a non-nucleophilic base or a lithium bromide-lithium carbonate mixture also failed to give (122) as did attempted partial oxidation of (120) with m-chloroperoxybenzoic acid or sodium meta-periodate. Reaction of (123) with N-phthalimido nitrene did not succeed in producing the sulphoximide.

The failure of these amination reactions is surprising since the simplest model for this system, phenyl methyl sulphide, has been used as a substrate for the preparation of many sulphimides,[52] and Claus et al have prepared the N-p-chlorophenyl sulphimide (125) using the same route as we have tried.[49] This has been further oxidised to the sulphoximide (126) using potassium permanganate.



125

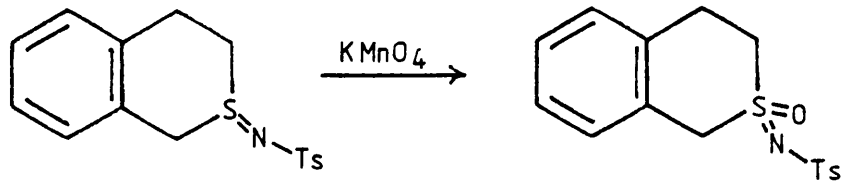


126

The reaction of phenyl methyl sulphoxide with N-phthalimido nitrene to give the sulphoximide has also been described by Rees et al.[46a] In some instances the failure of the amination may be rationalised as being caused by the interception of the aminating

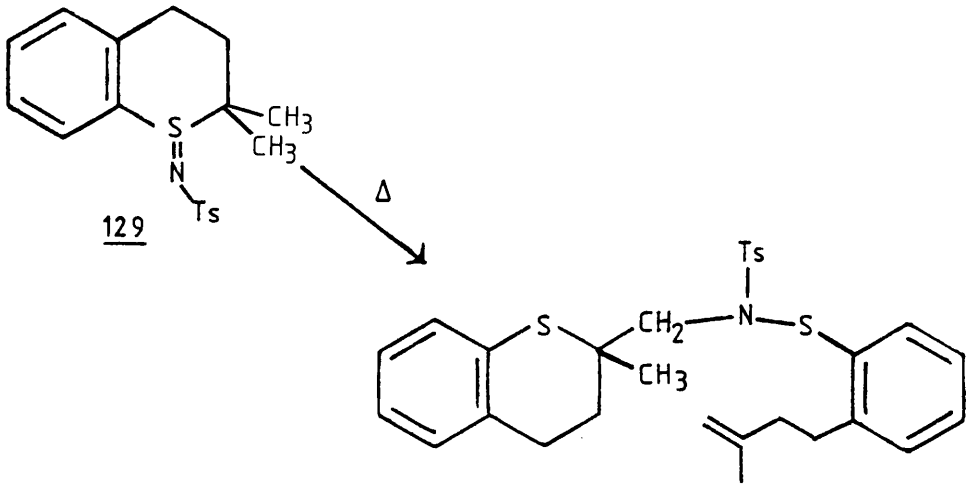
reagent by some other functional group on the molecule, for example, possible reaction of the carbonyl group of (116) with N-phthalimido nitrene.

Recent work in these laboratories[53] has succeeded in synthesising the N-tosyl sulphimide of isothiochroman (127) from the reaction of the sulphide with chloramine-T in the anhydrous state in a D.M.F. solution. Oxidation with potassium permanganate has yielded the sulphoximide (128).



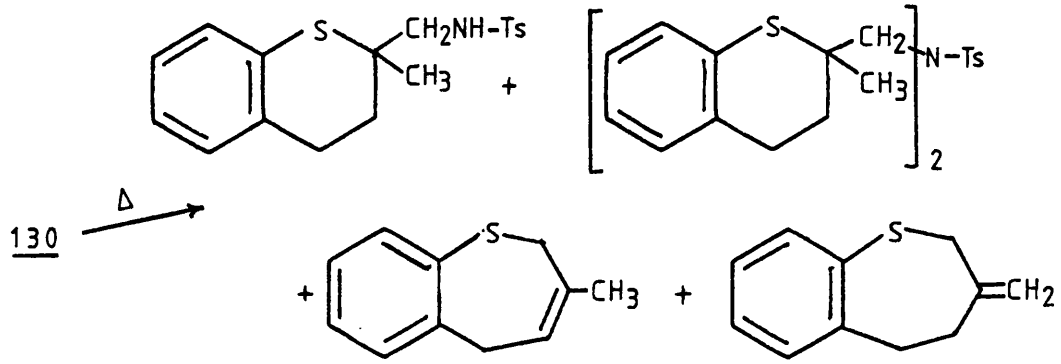
127 128

Recently a sulphimide (129) based on the thiochroman nucleus has been described by Kise et al[54] although no synthetic details were given.

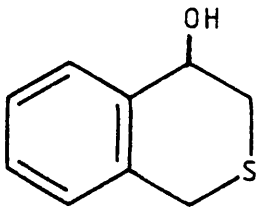


129 130

Solvent pyrolysis of (129) in benzene gives a quantitative yield of (130) which on further pyrolysis in refluxing toluene gives the products shown below.

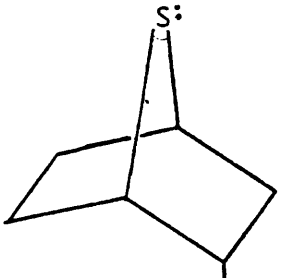


One interesting point resulting from the reactions of Scheme 16 was the observation of the facile halogenation of thiochroman-4-ol (118) to 4-chlorothiochroman (119) using hydrogen chloride in benzene. When this reaction was attempted with the analogous sulphone under the same conditions only starting material was recovered. Reaction of (118) in a sealed tube at 150°C for 15 hr also failed to give any 4-chlorothiochroman 1,1-dioxide. The same pattern was repeated for isothiochroman 4-ol (131), which gave the chlorinated compound although the reaction with the sulphone analogue failed.



131

These results suggest a degree of participation by the lone electron pairs on the sulphur atom, which are not available when the sulphur is oxidised. Neighbouring group participation involving sulphur lone pairs has been well described in the literature.[55] For example, a study of the acetolysis of 2-endo- and 2-exo-7-thiabicyclo[2.2.1]heptanes (132) and (133) has found that the relative rate for the endo-isomer is greater than 4.7 x 10^9 faster than that of the exo-isomer.[56] A sulphonium intermediate of the type (134) is postulated to account for this.



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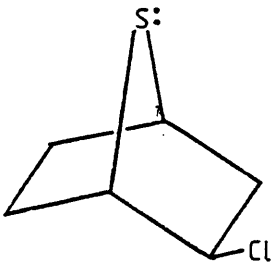

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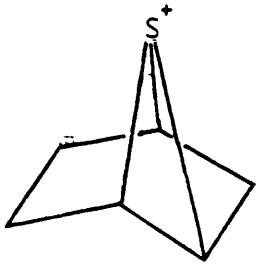
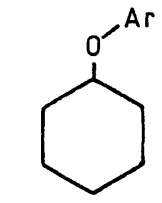


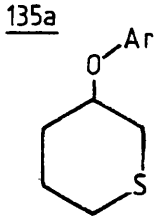
134

Work has also been described on the solvolysis of a number of p-nitrobenzoate esters 135a-c).[57] The relative rates of solvolysis are shown in Table 2.1.

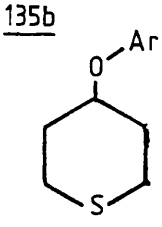
Table 2.1 Relative solvolysis rates of some S-heterocyclic esters in 80% aqueous acetone.



135a — 1.0



135b — 5.8×10^6



135c — 0.10

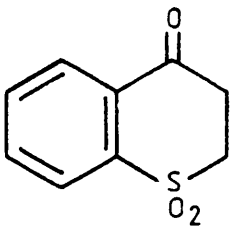
There is a strong assistance to solvolysis when the hetero-atom is β to the substituent although the γ-S contribution is not important and in fact solvolysed slower than the all carbon analogues. Although γ-S contributions are described as being very small, the ease of substitution of (118) in our case seems to question this.

CHAPTER THREE

THE FLASH VACUUM THERMOLYSIS OF SOME THIOCHROMANONE DERIVATIVES

3.1 Introduction

As a continuation of the study of compounds based on the thiochroman-4-one or benzothiopyran nucleus, the flash vacuum thermolyses of the parent sulphones, thiochroman-4-one 1,1-dioxide (136) and isothiochroman-4-one 2,2-dioxide (137) were studied.



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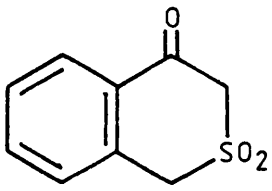
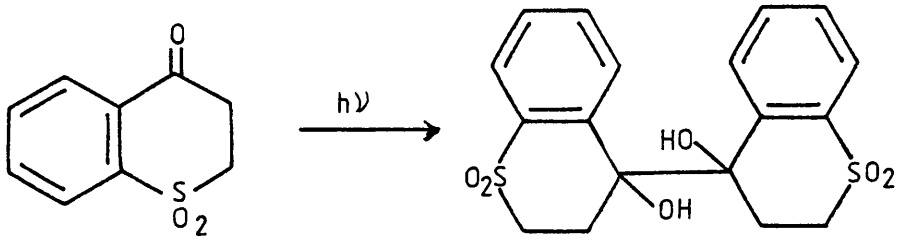


137

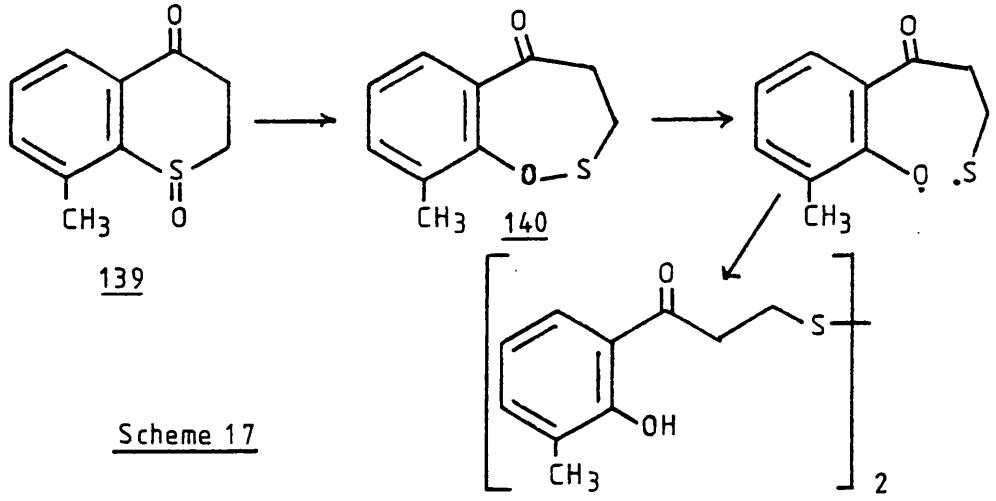
The thermochemical behaviour of these compounds has not been reported previously, although their photochemistry has been described by Still et al.[60] Photolysis of (136) in an inert solvent produces no change after a number of hours, although irradiation in methanol gives a photochemical reduction of the carbonyl group with formation of the corresponding pinacol (138).



138

This reduction was insensitive to the various substitution patterns used, except where the substitution was 5-methyl, or 3-carboxy, when large amounts of starting materials were recovered. This was explained simply as a steric effect of the substituent group in these positions.

The photolysis of a number of substituted thiochromanone sulphoxides has been reported by Still et al.[70] In contrast to the sulphones described above, these sulphoxides undergo a variety of rearrangements and three distinct pathways have been recognised. Those molecules bearing electron withdrawing substituents at the 6- or 8-positions, e.g. (139), tend to give disulphide products *via* initial rearrangement to the sulphenate ester (140), which may or may not be concerted, followed by cleavage and coupling of the thiyl radicals (Scheme 17).

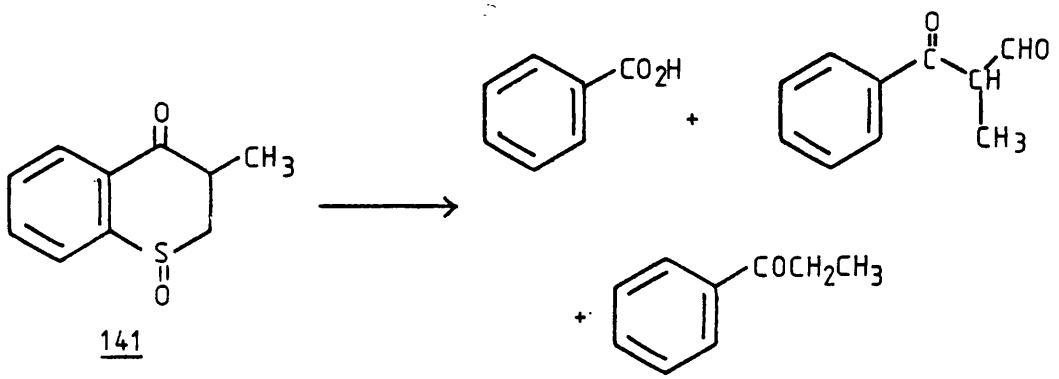


139 140

Scheme 17

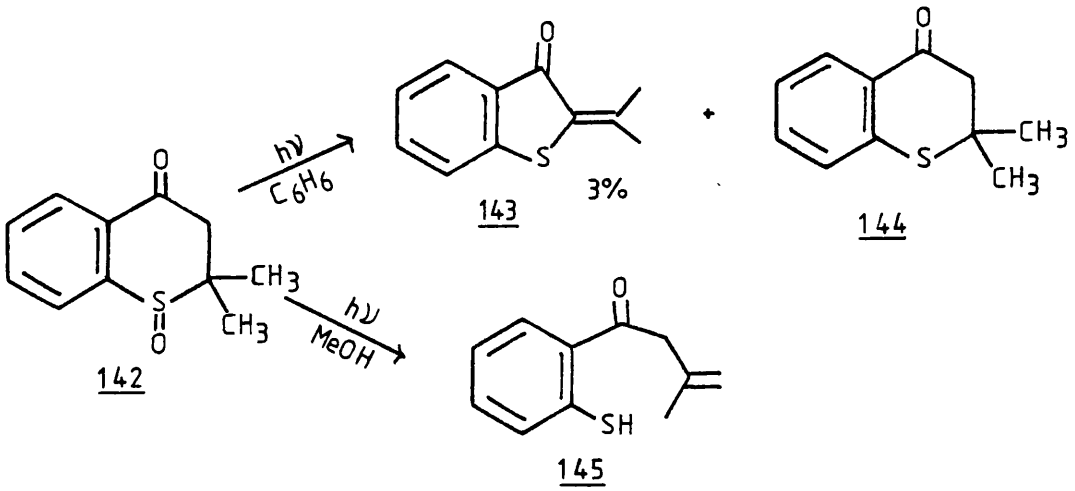
Those molecules with at least one substituent (methyl) in the 3-position tend to give products derived from opening of the hetero-

ring, but from which the sulphur atom is subsequently lost, e.g. irradiation of (141) in benzene was found to give propiophenone, 2-benzoylpropanal, and benzoic acid.



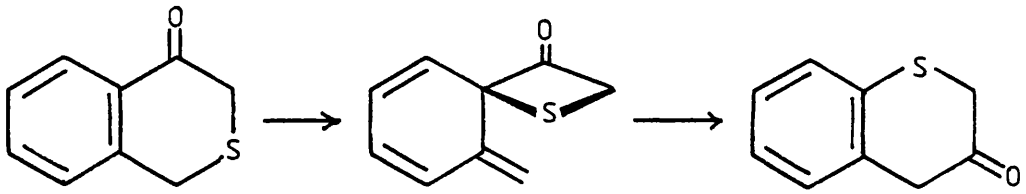
141

Those compounds in which at least one substituent is present in the 2-position (with the 3-position completely unsubstituted) give ring contracted products with more or less deoxygenation on photolysis in an inert solvent. Irradiation in methanol however gives products derived from a formal photoreduction, e.g. photolysis of (142) in benzene gives (143) and (144) while irradiation of (142) in methanol gives (145) only.



142 143 144 145

The photolysis of isothiochroman-4-one (146) has been reported by Berchtold et al.[71] Irradiation of (146) in cyclohexane gives rearrangement to thiochroman-3-one (147), the proposed mechanism being <u>via</u> the triene (148).



146 148 147

Loudon et al[72] have described the pyrolysis of thiochroman (115) and isothiochroman (149) and have compared the results with the mass spectral fragmentations of these molecules.

115 149

For isothiochroman in a static system, the major breakdown is the loss of an $\cdot SH_2$ fragment leading to the formation of indene, while in a flow system, the loss of a $CH_2{=}S$ fragment in a retro-Diels-Alder reaction to give benzocyclobutane, becomes increasingly more important. In the electron impact spectrum of (149) however, the loss of thioformaldehyde is by far the most important fragmentation compared with the loss of $\cdot SH_2$.

For thiochroman (115), the retro-Diels-Alder reaction under electron impact conditions is not so important as in the previous case, probably because of the stability of the molecular ion.[72] Also, no thermal retro-Diels-Alder product (o-thiocresol) is observed in a significant amount using either of the two methods. Instead, the two main products formed result from either expulsion of methane

(to give benzothiophene), or loss of $^{\cdot}SH_2$ (to give indene). The electron impact spectrum of (115) shows a relatively low activation energy for the $(M-15)^+$ peak, while for the $(M-34)^+$ peak, the activation energy was one of the highest measured for this compound. These results suggest that apparent similarities between electron impact spectroscopy and thermal processes should be treated with care.

All of the thermolyses described below were carried out using the apparatus described in Chapter One. The temperatures were recorded using a thermocouple probe as before.

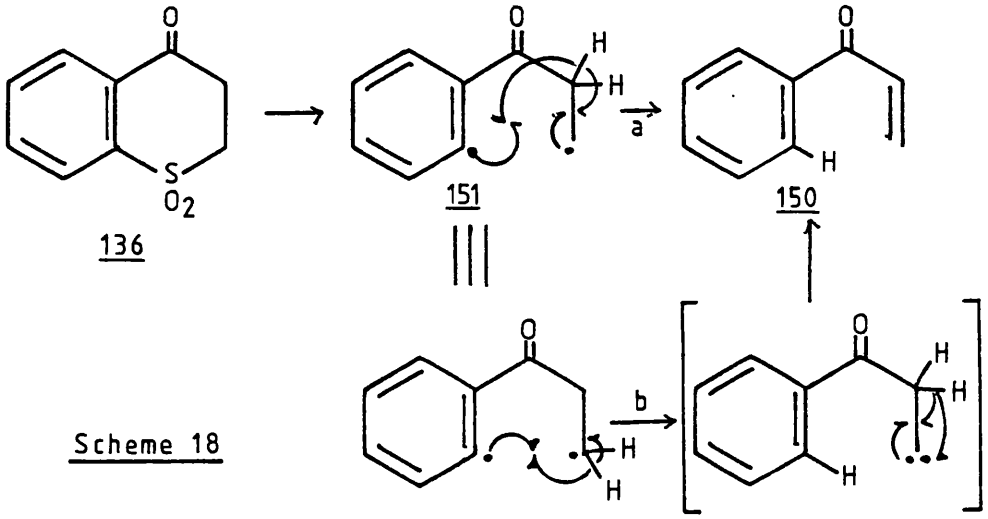
3.2 The Thermolysis of Thiochroman-4-one 1,1-dioxide at 0.05 mm

PRODUCT	FURNACE TEMPERATURE		
	750°C	850°C	900°C
Starting material	100%	✓	-
Acrylophenone	-	✓	∿79%
Phenylacetylene	-	✓	∿21%

The products of this thermolysis were fully identified by n.m.r. spectroscopy and g.l.c. mass spectrometry.

The products obtained were surprising since there was no trace of any product that might have been derived from a loss of sulphur dioxide followed by ring closure (i.e. 1-indanone).

Acrylophenone (150) may be accounted for by a rearrangement of an initially formed diradical (151) either by mechanism a or b (Scheme 18).

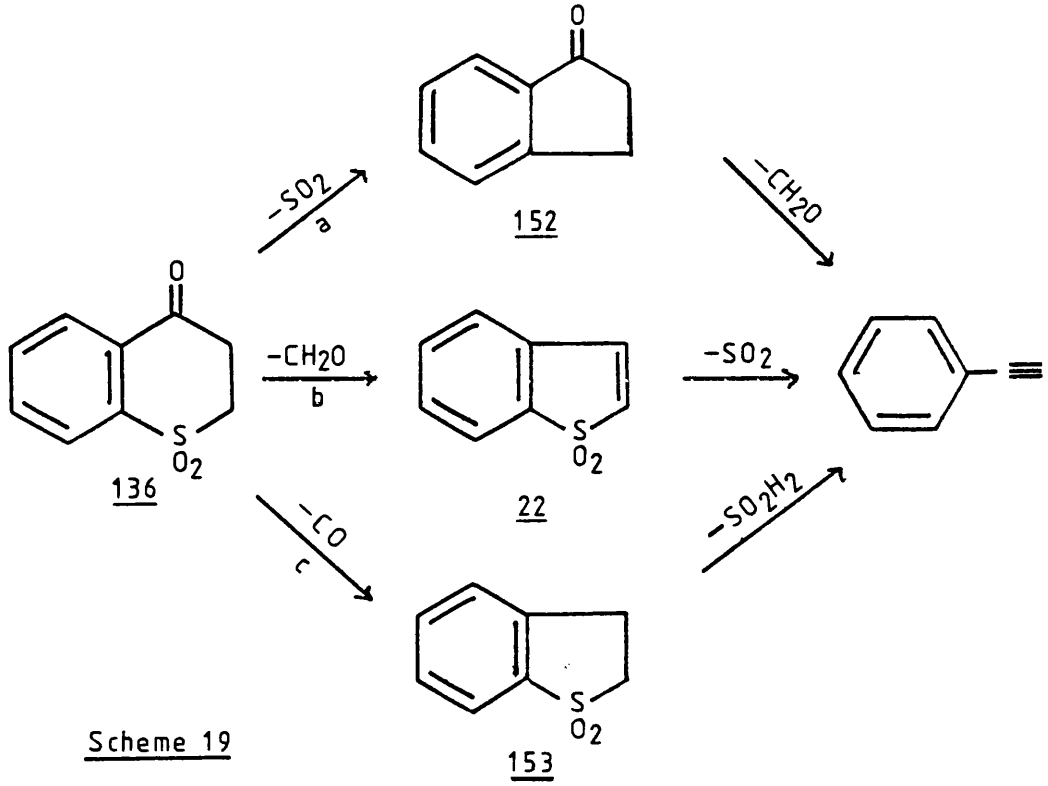


Scheme 18

These mechanisms do not however explain why the diradical (151) prefers to rearrange rather than ring close.

The occurrence of phenyl acetylene in the product demands the loss of CH_2SO_3 from the starting material or possibly the loss of CH_2O from acrylophenone.

Possible routes for the formation of phenyl acetylene are shown below (Scheme 19).



Scheme 19

Sulphone (136) may either:

1) Lose sulphur dioxide, and ring close to give 1-indanone (152) in a high energy state, which could sequentially lose formaldehyde (path a).

2) Lose formaldehyde and ring close to give benzo[b]thiophene 1,1-dioxide (22), which may eliminate sulphur dioxide (path b).

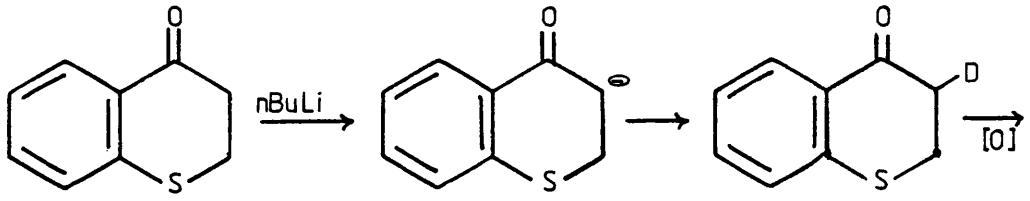
3) Decarbonylate to give (153), which might eliminate an H_2SO_2 fragment (path c).

These processes may be discounted in view of the following results: Thermolysis of (152) at 900°C produced unchanged starting material only. Thermolysis of (22) has been shown to give benzothiete[13] (see Chapter One). Thermolysis of 2,3-dihydrobenzo-

[b]thiophene 1,1-dioxide (153) at 900°C in our apparatus has failed to show any spectral data attributed to phenyl acetylene in the product.

A further possible route for the formation of phenyl acetylene may stem from a second collision of initially formed acrylophenone with the hot surface of the reactor. Thermolysis of a sample of acrylophenone at 900°C gave no trace of phenyl acetylene by g.l.c. or n.m.r. spectroscopy.

In order to study the mechanism of this reaction further, a sample of thiochroman-4-one was deuterated at the 3-position by reacting the anion formed α to the carbonyl group with deuterium oxide (Scheme 20).



Scheme 20

^{13}C n.m.r. spectroscopy showed deuteration specifically α to the carbonyl by the line multiplet centred at 36.36 p.p.m. downfield of T.M.S. caused by ^{13}C-^{2}H coupling. This compared with the singlet given in the proton decoupled spectrum of the undeuterated material. The mass spectrum of this material showed a strong peak at m/e = 197 (corresponding to mono-deuterated material). Some

undeuterated and di-deuterated material was also present however, and the percentages of these materials were calculated from mass spectral data supplied by P.C.M.U., Harwell. The results showed that the material consisted of undeuterated compound (17%); mono-deuterated (51%); and dideuterated (32%). This material was thermolysed at 900°C and the products analysed by g.l.c. mass spectrometry.

The mass spectrum of acrylophenone produced from thermolysis of the undeuterated and deuterated compounds are shown in Figures 3.1 and 3.2.

The fragmentation of acrylophenone is fairly simple. The molecular ion m/e = 132 loses $\dot{C}_2H_3$ to give the benzoyl cation m/e = 105. This further decomposes to the phenyl cation m/e = 77 by loss of CO, and this can lose acetylene to give $C_4H_3^+$ m/e = 51. This behaviour is characteristic of aromatic carbonyl compounds.

In the case of the acrylophenone resulting from thermolysis of the deuterated sample, we have molecular ion peaks at m/e = 132, 133, and 134 resulting from the undeuterated, monodeuterated and di-deuterated compounds respectively. Loss of the side chain then occurs to give a benzoyl cation which appears either unlabelled or monodeuterated at m/e = 106 and 105. In the absence of H/D scrambling, the deuterium atom must lie on the aromatic ring, and this is

Figure 3.1 Mass spectrum of acrylophenone produced from thermolysis of undeuterated (136)

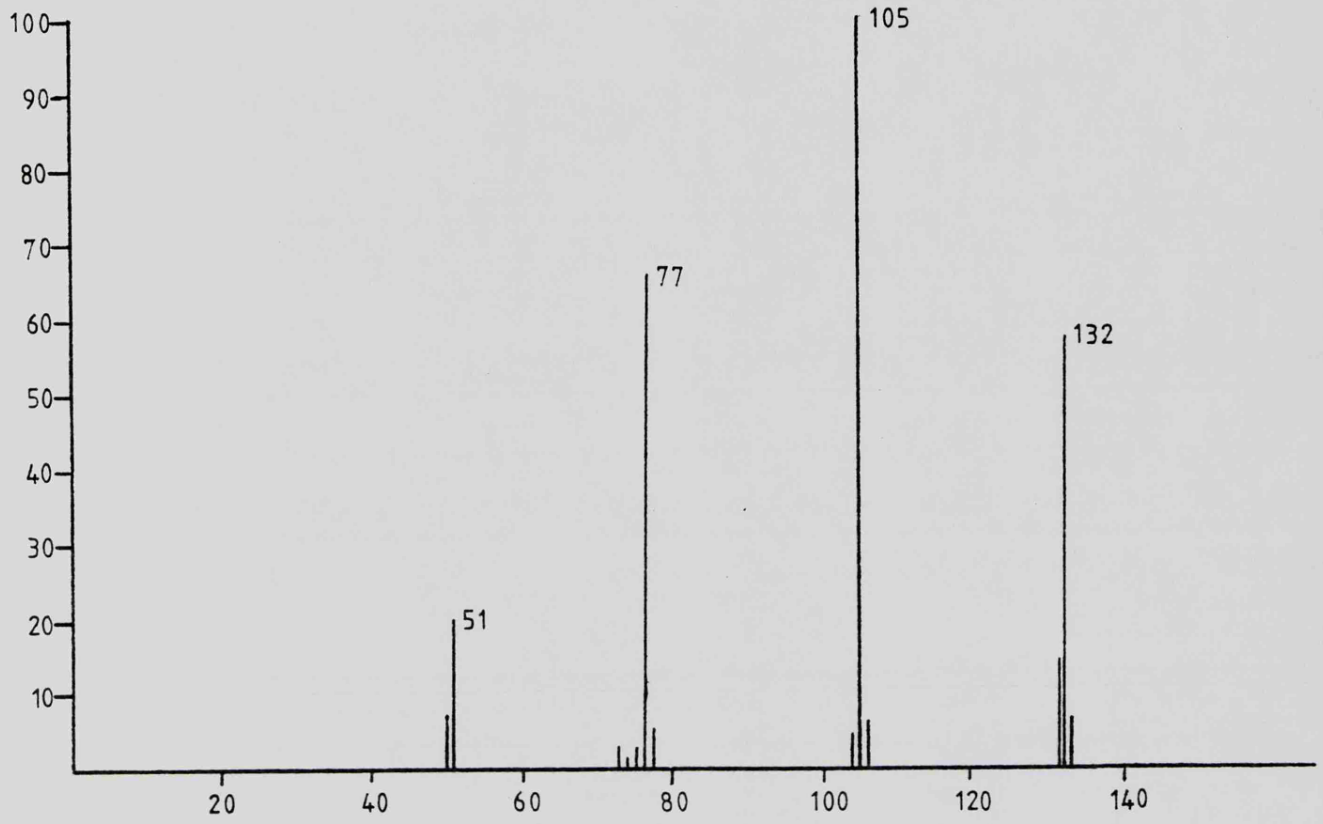
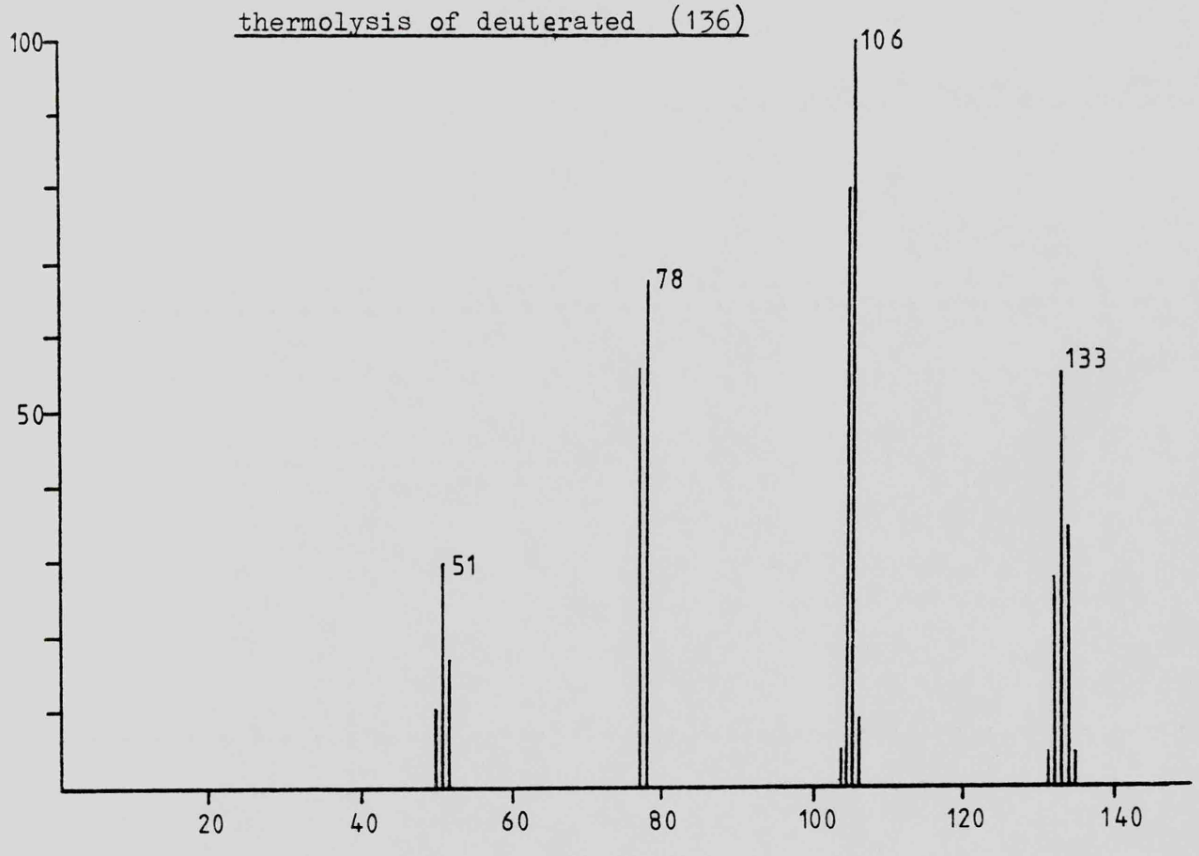


Figure 3,2 Mass spectrum of acrylophenone produced from thermolysis of deuterated (136)



interesting since it is good evidence for believing that the mechanism for the formation of acrylophenone from the thermolysis of thiochroman-4-one 1,1-dioxide must involve the transfer of a hydrogen (or deuterium) atom from a position α to the carbonyl, to the aromatic ring (i.e. mechanism "a" of Scheme 18). Loss of carbon monoxide from the benzoyl cation gives again a phenyl cation, which is undeuterated or monodeuterated, m/e = 77 and 78, with the peaks in more or less the same intensity ratio as for the benzyl cation. Loss of acetylene from the symmetrical phenyl cation takes place indiscriminately with regard to the position of the deuterium isotope, giving rise to a different pattern of intensities around m/e = 51. Further evidence for this mechanism is obtained from the thermolysis of (158).

The mass spectra of the phenyl acetylenes produced from the thermolyses of the deuterated and undeuterated compounds are shown in Figures 3.3 and 3.4.

Apart from the observation that the material contains a high proportion of undeuterated and monodeuterated compound with very little of the dideuterated molecule, no real insight into the position of the isotope can be made, in the light of work reported by Safe,[73] who has shown that the mass spectra of 2H-phenylacetylene shows 100% H/D randomisation in the molecular ion, prior to the

Figure 3.3 Mass spectrum of phenyl acetylene produced from thermolysis of undeuterated (136)

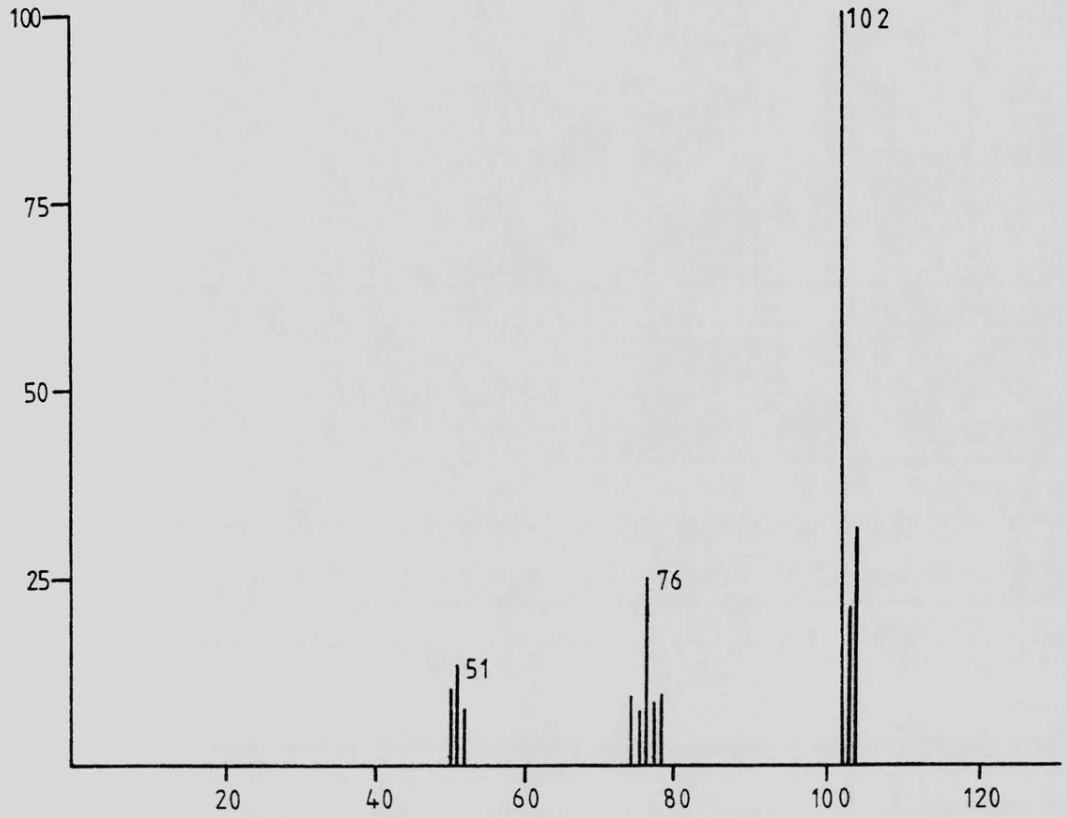
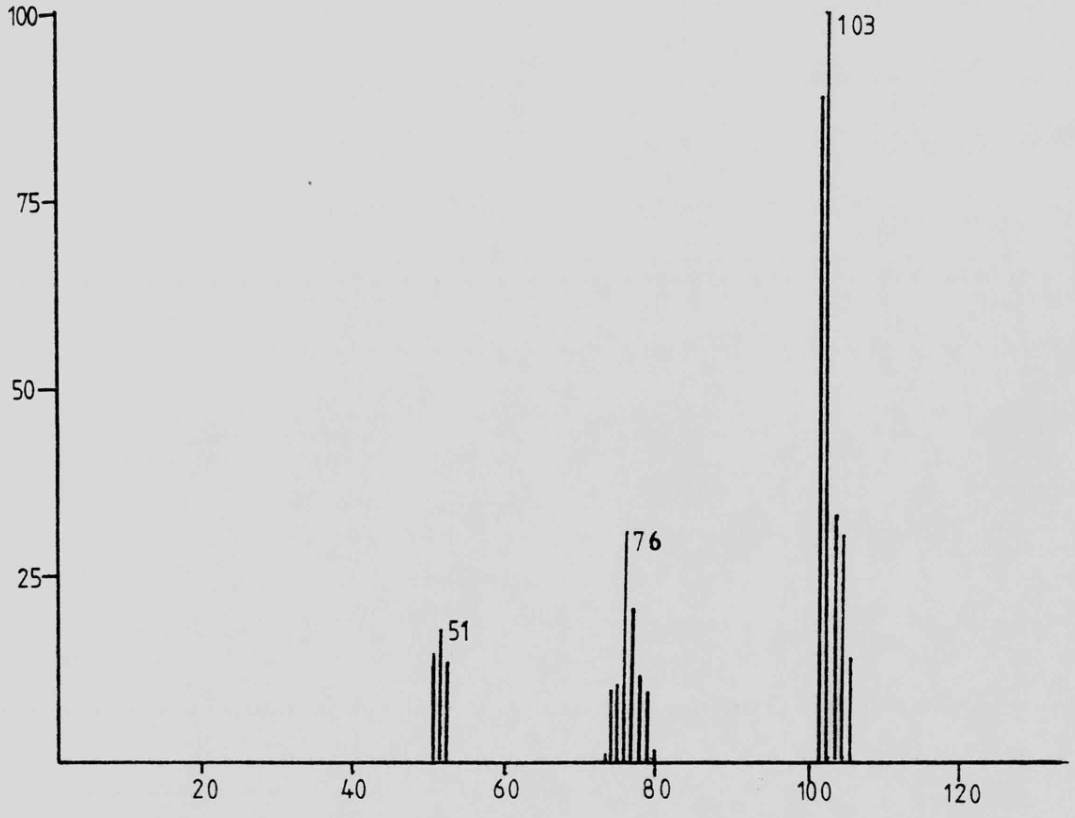
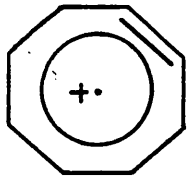


Figure 3.4 Mass spectrum of phenyl acetylene produced from thermolysis of deuterated (136)



expulsion of an acetylene fragment. A symmetrical intermediate of the type (154) is proposed to account for this effect.

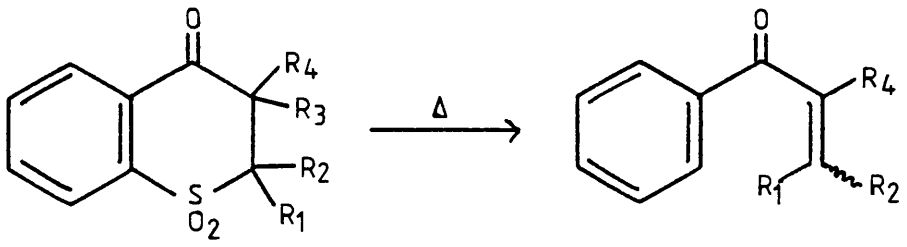


154

Examination of the n.m.r. spectra of the products formed in the two thermolyses, showed a comparable resonance for the acetylenic proton at τ 6.93 in both cases. This tends to indicate that any deuterium incorporated into the acetylene is attached to the aromatic ring, and that in the absence of any rearrangements, the carbon bearing the acetylenic hydrogen was originally the carbon in the 2-position of the thiochromanone sulphone.

3.3 The Thermolyses of Substituted Thiochromanone Sulphones

In order to ascertain how general this reaction was, and to investigate this process or a possible synthesis of α,β-unsaturated ketones as shown in Scheme 21 , a number of substituted analogues were prepared (155-161), and their thermolyses studied.



Scheme 21

155 ; $R^1 = R^2 = R^3 = H$, $R^4 = Me$

156 ; $R^1 = R^3 = R^4 = H$, $R^2 = Me$

157 ; $R^1 = R^3 = H$, $R^2 = R^4 = Me$

158 ; $R^3 = R^4 = H$, $R^1 = R^2 = Me$

159 ; $R^1 = R^2 = H$, $R^3 = R^4 = Me$

160 ; $R^1 = R^3 = R^4 = H$, $R^2 = Ph$

161 ; $R^1 = R^3 = H$, $R^2 = Ph$, $R^4 = Me$

The results of these thermolyses are shown in Table 3.1.

Table 3.1

The Flash Vacuum Thermolyses of Some Substituted Thiochromanone Sulphones

Starting Material	Temperature	Products
(155)	900°C	α-methylacrylophenone (63%)
(156)	850°C	crotonophenone (65%)
(157)	850°C	various products (see discussion)
(158)	800°C	various products (see discussion)
(159)	850°C	starting material only
(160)	750°C	chalcone and starting material
(161)	750°C	unknown (see discussion)

3.4 Discussion

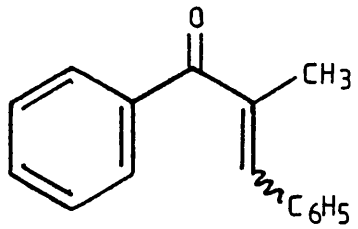
The reaction seems to be fairly general for monosubstituted thiochromanones although other products become increasingly more important as the substitution pattern increases.

In most of these cases the products from the thermolyses were not quite as simple as those obtained from the parent compound.

Thermolysis of (155) at 900°C gave α-methylacrylophenone as the only product in 63% yield based on consumed starting material, while thermolysis of (156) at 850°C gave crotonophenone as the only product, in 65% yield. Both products were identified by n.m.r. and g.l.c. analysis. Thermolysis of (157) at 850°C however yielded six different compounds as indicated by the g.l.c. trace of the crude reaction product. The two main products were analysed by g.l.c. mass spectrometry and were both found to have molecular ions of m/e = 160 followed by similar fragmentation patterns of m/e = 145, 105, and 77. The similarity of these fragmentations to that of acrylophenone described earlier, suggest that the compounds may be the cis and trans isomers of 2-benzoyl-2-butene. Some further evidence is obtained from a comparison of the n.m.r. spectrum of the crude product mixture with that described in the literature for 2-benzoyl-2-butene.[86] Thermolysis of (158) at 800°C gave four compounds as shown by the g.l.c. trace of the crude material although one of the compounds was in large excess. The mass spectrum of this band

showed the molecular ion to be m/e = 160 with fragmentation peaks at m/e = 159, 145, 105, and 77. These fragmentations coupled with the n.m.r. spectrum of the crude material suggest that the compound is 2-methyl-3-benzoyl-2-propene.

The fact that (159) did not give any reaction on thermolysis up to 850°C tends to support the proposed mechanism for the formation of acrylophenone from the thermolysis of (136), since in (159) both of the 3-positions are blocked, and the postulated hydrogen migration cannot occur in this case. Thermolysis of (160) at 750°C gave a mixture containing chalcone as the only product, with some unreacted starting material. The low temperature needed to effect this reaction probably stems from the formation of a benzyl radical after the initial loss of sulphur dioxide. The thermolysis of (161) at 750°C however gave three compounds as shown by g.l.c. analysis along with some unreacted starting material. Mass spectrometry of these three compounds showed them all to have molecular ions of m/e = 222, representing formal loss of sulphur dioxide from the starting material. Working by analogy, the possibility that one of the compounds was either α or β-methylchalcone (162 and 163) was disproved by comparison of the n.m.r. spectrum of the crude thermosylate with that of pure β-methylchalcone (synthesised independently[88]), and with the n.m.r. details of α-methylchalcone described by Fukuoka et al.[87]



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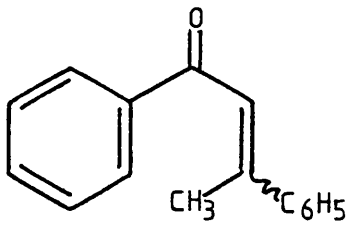
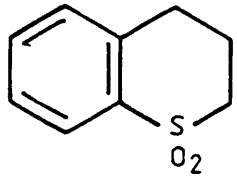


163

In order to study these systems further, the preparation and thermolysis of thiochroman 1,1-dioxide (164), isothiochroman-4-one 2,2-dioxide (165) and the reduced analogue isothiochroman 2,2-dioxide (166) were carried out.



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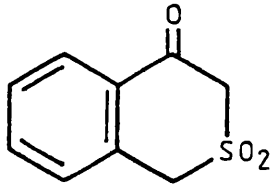

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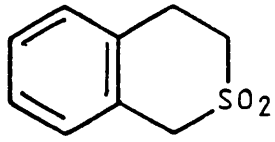
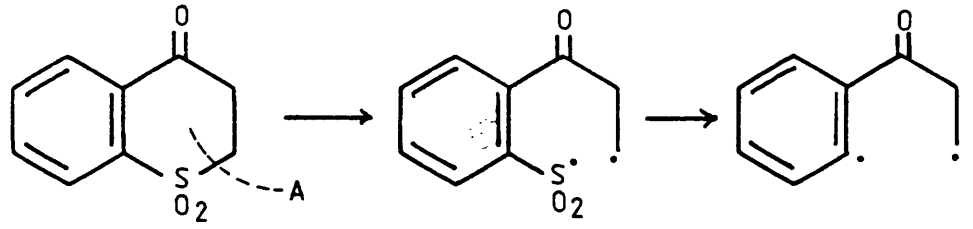


166

Thermolysis of (165) at 750°C gave 1-indanone as the only product in 81% yield while thermolysis of the reduced analogue (166) at 800°C afforded only indan (88%). Both of these products obviously derive from a simple extrusion of sulphur dioxide followed by ring closure of the biradical produced. Thermolysis of (164) at 850°C however yielded a mixture consisting of starting material and indene (18%) with no trace of indan which might have occurred from simple extrusion of sulphur dioxide and ring closure of the biradical. This reaction requires the formal loss of H_2SO_2 from the molecule and an analogy to this process does occur in the thermal breakdown of the corresponding sulphide (115) in which the expulsion

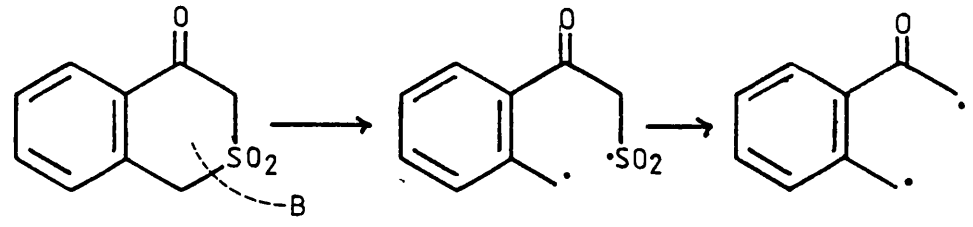
of an $\dot{S}H_2$ fragment is described.[72] To check the possibility of this process being a stepwise reaction, i.e. initial loss of sulphur dioxide followed by ring closure to high energy indan, and a subsequent loss of hydrogen, a sample of indan was thermolysed under the same conditions, however only unreacted starting material was recovered.

The fairly facile elimination of sulphur dioxide from the sulphones (165) and (166) compared with the more unusual reactions of the thiochromanone and thiochroman series of compounds would seem to suggest that the strength of the (aryl)C-S bond may determine the course of the reactions since this is a significant differing factor in the compounds studied. Published values for the dissociation energies of some $C-SO_2$ bonds in aliphatic sulphones has given the following values $D(C_6H_5-SO_2Me)$ = 73 kcal mol^{-1}, $D(C_6H_5CH_2-SO_2Me)$ = 48 kcal mol^{-1}[74] (other workers[75] have given a value of 51.3 kcal mol^{-1}). These calculations were done with the assumption that $D(CH_3-SO_2R) \simeq 60.6$ kcal mol^{-1} independent of the nature of R. If these values can be extended to our examples then it can be seen that in the thermolysis of (136) the weakest C-S bond (and therefore the first bond liable to break) is that given by line A with a difference in dissociation energies of the aryl C-S and alicyclic C-S of the order of 12.4 kcal mol^{-1}.



136

In the case of (165) however the initial scission would be expected to be that given by line B, giving two relatively stable radicals.



165

The lower temperatures needed to effect a complete reaction of (165) and (166) as opposed to (136),(155-161), and (164) may reflect the lower bond dissociation energies of the isomeric sulphones. It can be seen that in the case of (136), the diradical formed after elimination of sulphur dioxide has the capacity for hydrogen transfer (as discussed earlier). The diradical derived from (165) however does not share this capacity since hydrogen transfer in this system involves the formation of an unfavourable carbene intermediate. It is therefore possible that the ring closure reactions of (165) and (166) occur by default.

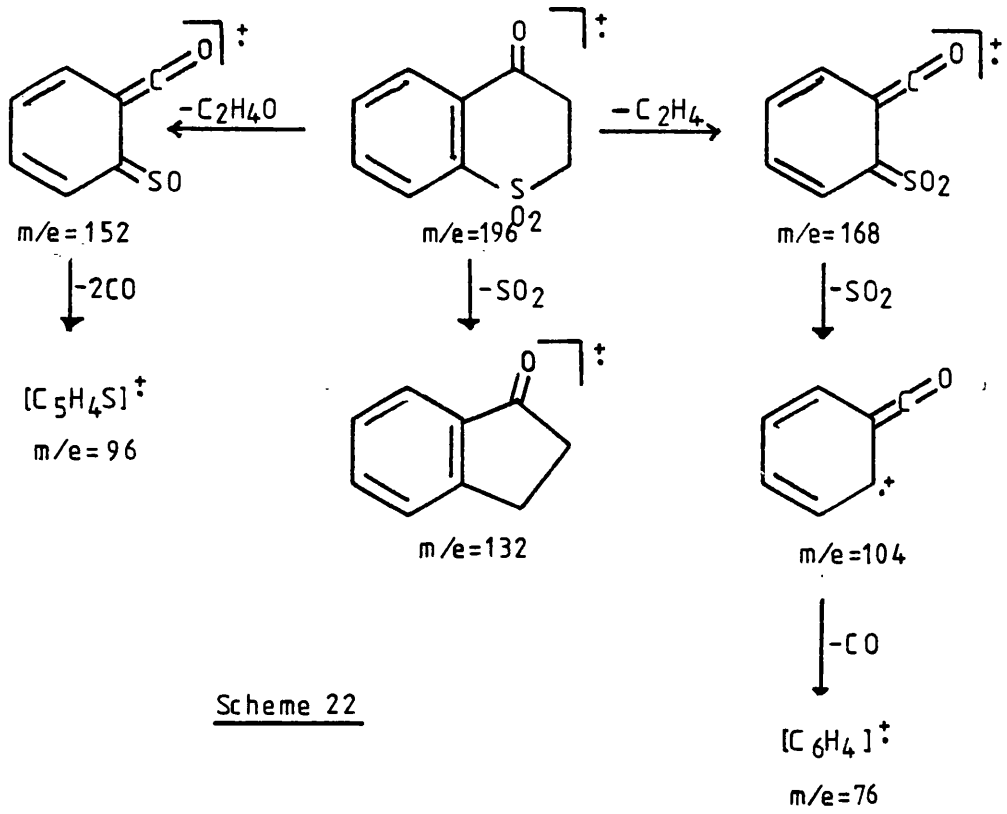
3.5 Mass Spectral Studies

A comparison was made of the thermal breakdown of thiochromanone sulphones with their electron impact fragmentations, in order to ascertain any similarities between the two processes.

The mass spectra of some of these molecules has been described by Still et al[76] in comparison with the analogous sulphoxides and sulphides.

The major fragmentation reaction of thiochromanone 1,1-dioxide (Scheme 22) is a retro-Diels-Alder elimination of ethylene followed by a facile loss of sulphur dioxide to yield $(C_7H_4O)^+$ (M/e = 104) as the base peak. The direct extrusion of sulphur dioxide from the molecular ion is only a very minor process, leading to a peak at m/e = 132 only 1.2% of the base peak. A third (minor) process is the direct loss of C_2H_4O from the molecular ion to give a peak at m/e = 152 (2% of the base peak). This ion further fragments by the sequential loss of two molecules of CO to give a peak at m/e = 96.

The 2-methyl and 3-methyl substituted sulphones show a very similar breakdown. Elimination of C_3H_6 in a retro-Diels-Alder reaction yields m/e = 168 which loses sulphur dioxide to afford the



Scheme 22

base peak at m/e = 104. A new fragmentation route introduced by the presence of the methyl group is a hydrogen transfer followed by the loss of C_3H_5, yielding m/e = 169, which further fragments by loss of OH to give m/e = 152,which loses two molecules of CO as described above to give m/e = 96. The direct loss of sulphur dioxide is again of minor importance giving a peak at m/e = 146 only 1% of the base peak further fragmenting by loss of a methyl radical to give m/e = 131, loss of CO to give m/e = 103 and finally loss of C_2H_2 giving m/e = 77.

The mass spectral fragmentation of the 2,2-dimethyl analogue (Figure 3.5 and Scheme 23) is very similar to those above. There

Figure 3.5 Mass spectrum of 2,2-dimethylthiochroman-4-one 1,1-dioxide.

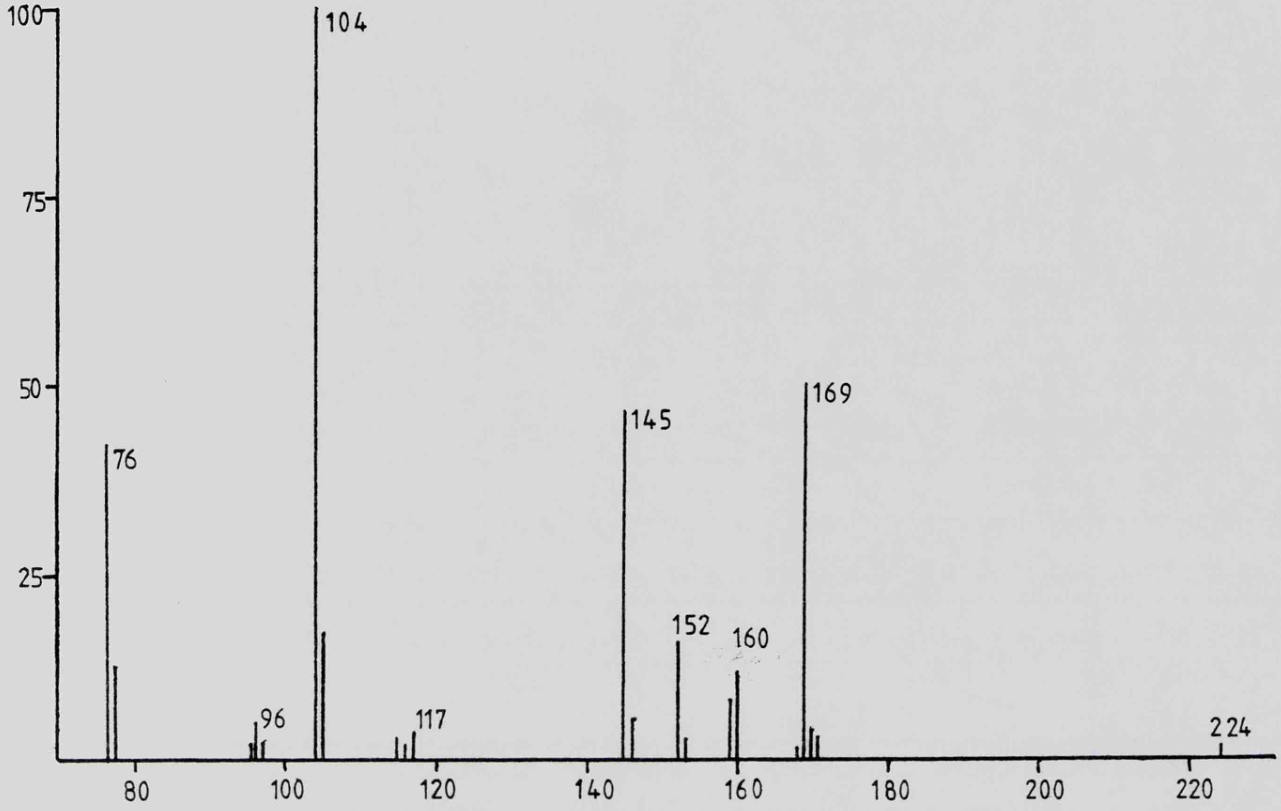
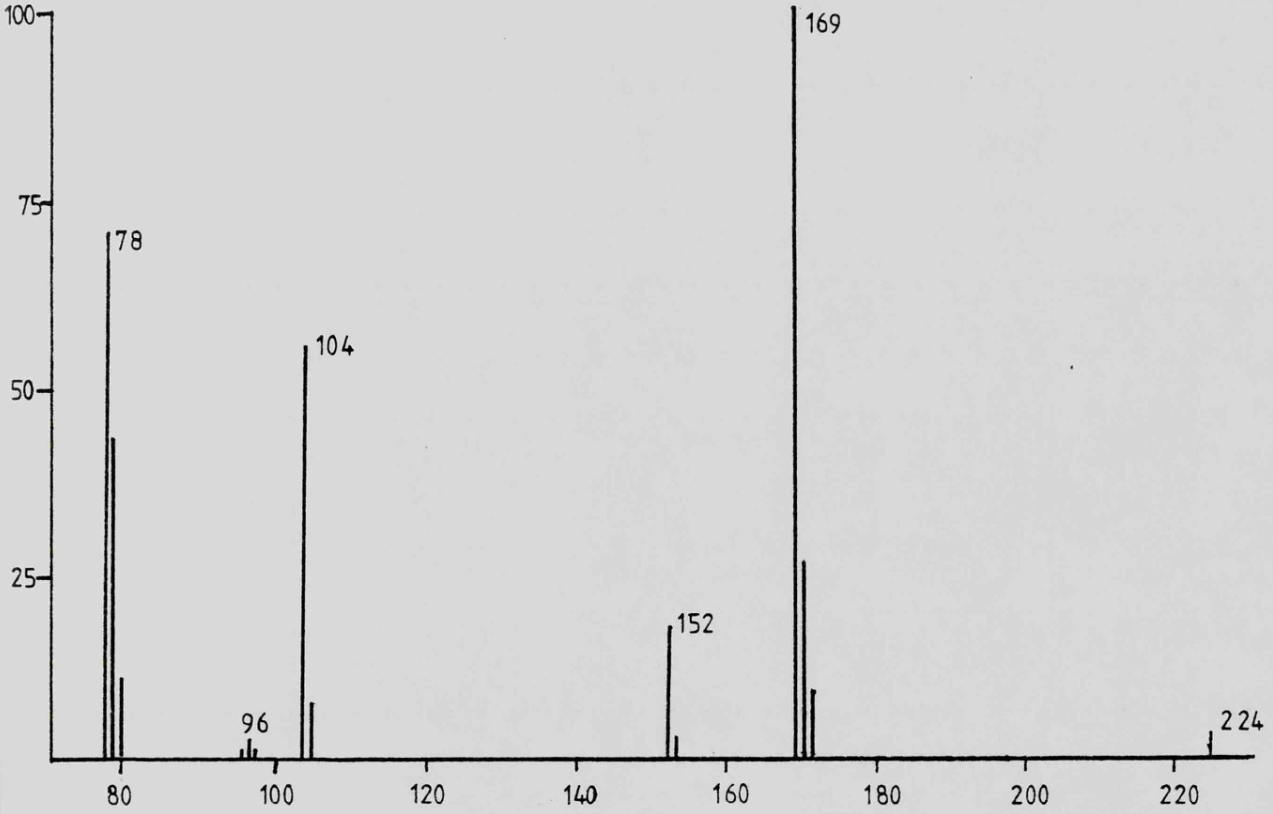
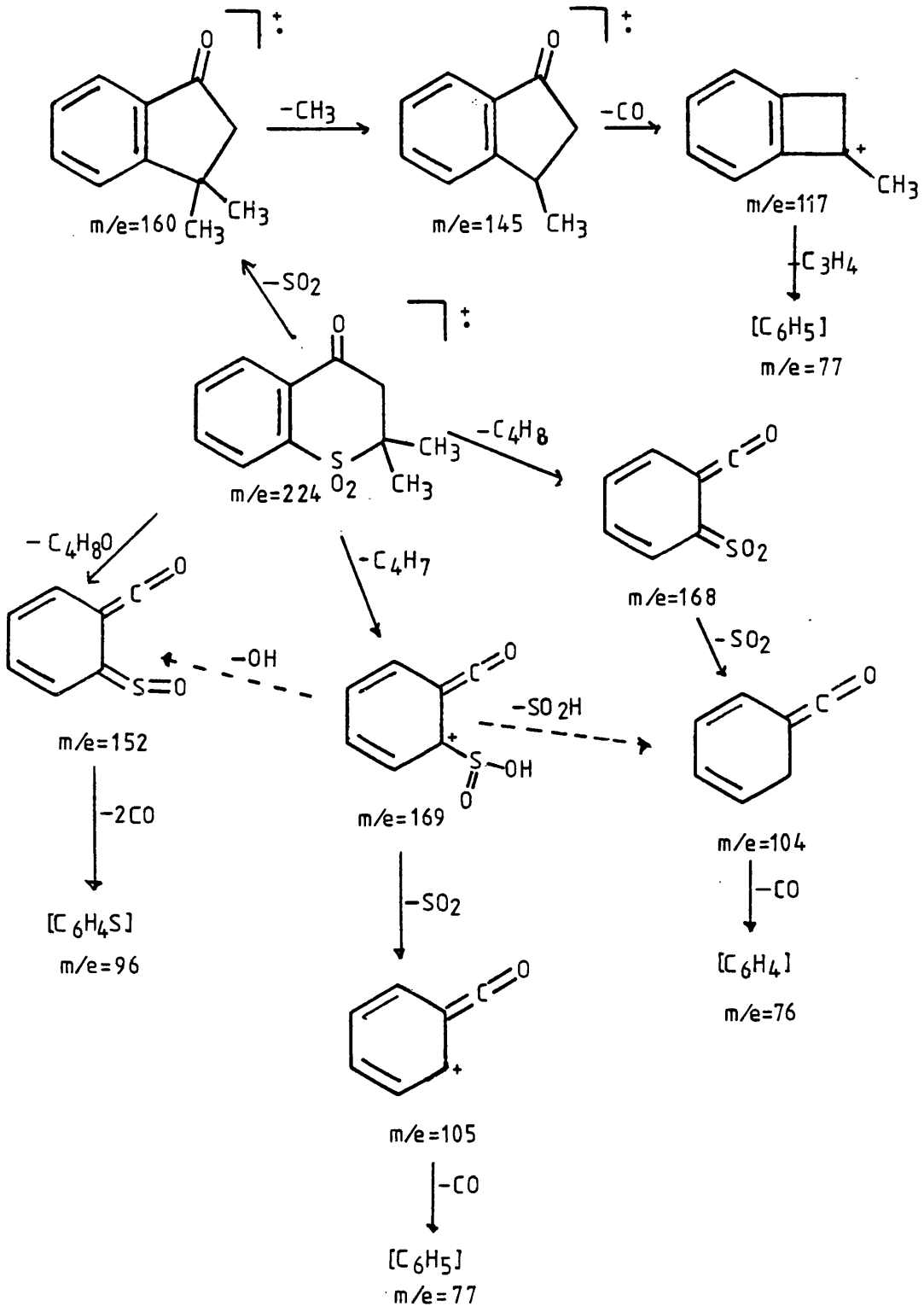


Figure 3.6 Mass spectrum of 2,3-dimethylthiochroman-4-one 1,1-dioxide.



Scheme 23


m/e=160
-CH3
m/e=145
-CO
m/e=117
C3H4
[C6H5]
m/e=77
-SO2
m/e=224
-C4H8
m/e=168
-SO2
-C4H8O
-C4H7
-OH
-SO2H
m/e=152
-2CO
[C6H4S]
m/e=96
m/e=169
-SO2
m/e=104
-CO
[C6H4]
m/e=76
m/e=105
-CO
[C6H5]
m/e=77

is a hydrogen transfer followed by the loss of C_4H_7 from the molecular ion, to give the m/e = 169 ion in far greater abundance than the m/e = 168 ion derived from a retro-Diels-Alder reaction (this pattern was also shown for the 3-methyl analogue). Loss of SO_2 from this species would give m/e = 105 which would further lose CO to give m/e = 77, although possible loss of SO_2H from m/e = 169 to give the base peak at m/e = 104 or loss of OH to give m/e = 152 as described by Still et al[76] cannot be discounted. No metastable peaks were observed for these breakdowns (shown by broken lines in the Scheme). The direct loss of SO_2 from the molecular ion is again a minor process yielding a peak at m/e = 160 only 12% of the base ion. This species then successively loses CH_3 to give m/e = 145 (substantiated by a metastable peak at 131.4) followed by loss of CO to give m/e = 117 (substantiated by a metastable peak at 94.4) and loss of C_3H_4 to give m/e = 77.

A third fragmentation mode of the molecular ion appears to be a direct loss of $[C_4H_8O]$ in some combination, to give a peak at m/e = 152 (this is substantiated by a metastable peak at 103.1). Again, as in the previous example, this loses two molecules of CO to give m/e = 96.

The fragmentation pattern for the 3,3-dimethyl sulphone is very similar in all the essential details.

The mass spectral breakdown of (157) (Figure 3.6) is similar to the examples described above except that the direct loss of SO_2 from the molecular ion seems to be completely suppressed with no ion peaks at m/e = 160, 145, 117, or 77. This also seems to be true of the retro-Diels-Alder reaction since there is no ion at m/e = 168. The base ion at m/e = 169 corresponds to the loss of C_4H_7 from the molecular ion as described above, i.e. hydrogen transfer followed by elimination. This ion then fragments in the manner described above yielding ions at m/e 105 and 77 or it may possibly lose $\dot{S}O_2H$ to yield m/e = 104 although no metastable peaks were observable in order to discriminate between the possible pathways. Loss of C_4H_8O from the molecular ion would give m/e = 152 which would further fragment by the loss of two molecules of CO to give m/e = 96, this latter step having been described by Still et al.[76]

The stability of (164) is reflected in its mass spectrum Figure 3.7) in which the base peak is the molecular ion. The possible direct extrusion of SO_2 to give a peak at m/e = 118 is again suppressed although the loss of H_2SO_2 in an analogous manner to the thermal breakdown to give a peak at m/e = 116 is a possible process. Loss of C_2H_2 from this fragment would yield m/e = 90. The ion at m/e = 165 possibly arises from loss of $\dot{O}H$ and a further loss of C_2H_4 from this fragment gives a peak at m/e = 137 - this transition is substantiated by a metastable peak at m/e = 113.7. A direct loss of C_2H_5O from the molecular ion could also make up some of the intensity

Figure 3.7 Mass spectrum of thiochroman 1,1-dioxide.

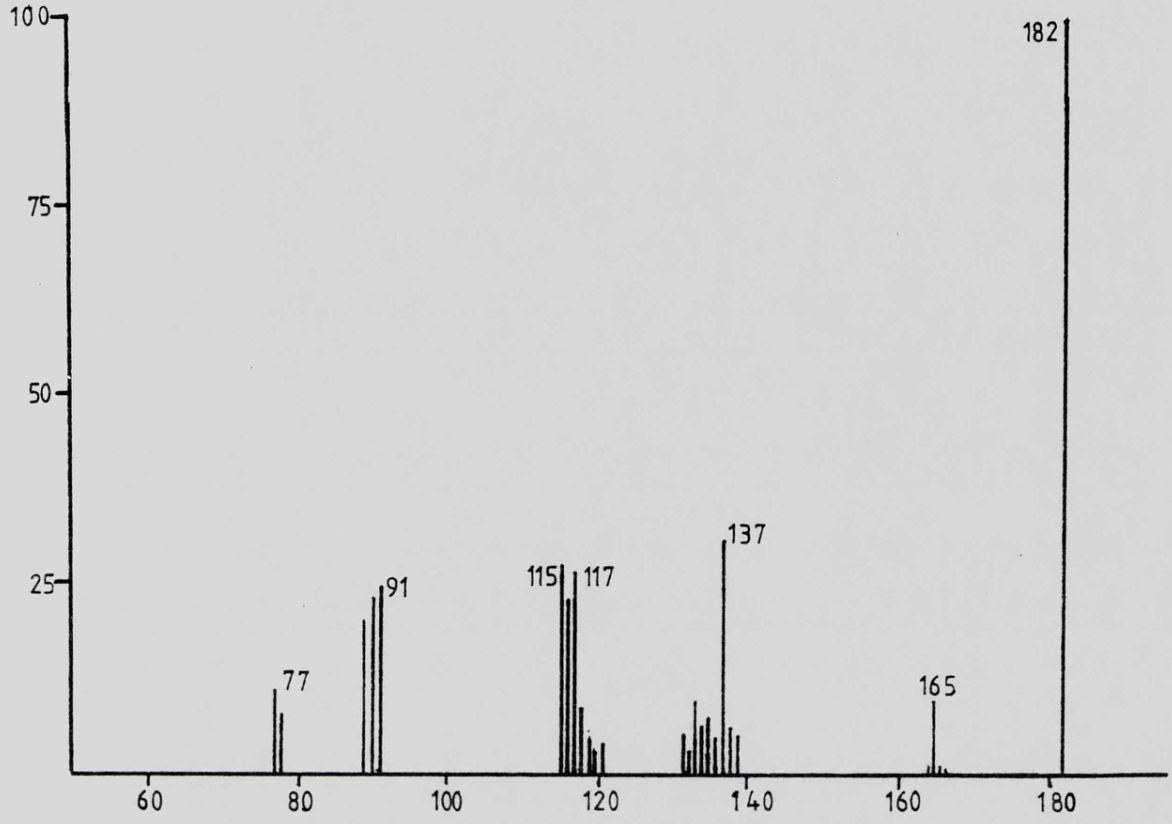
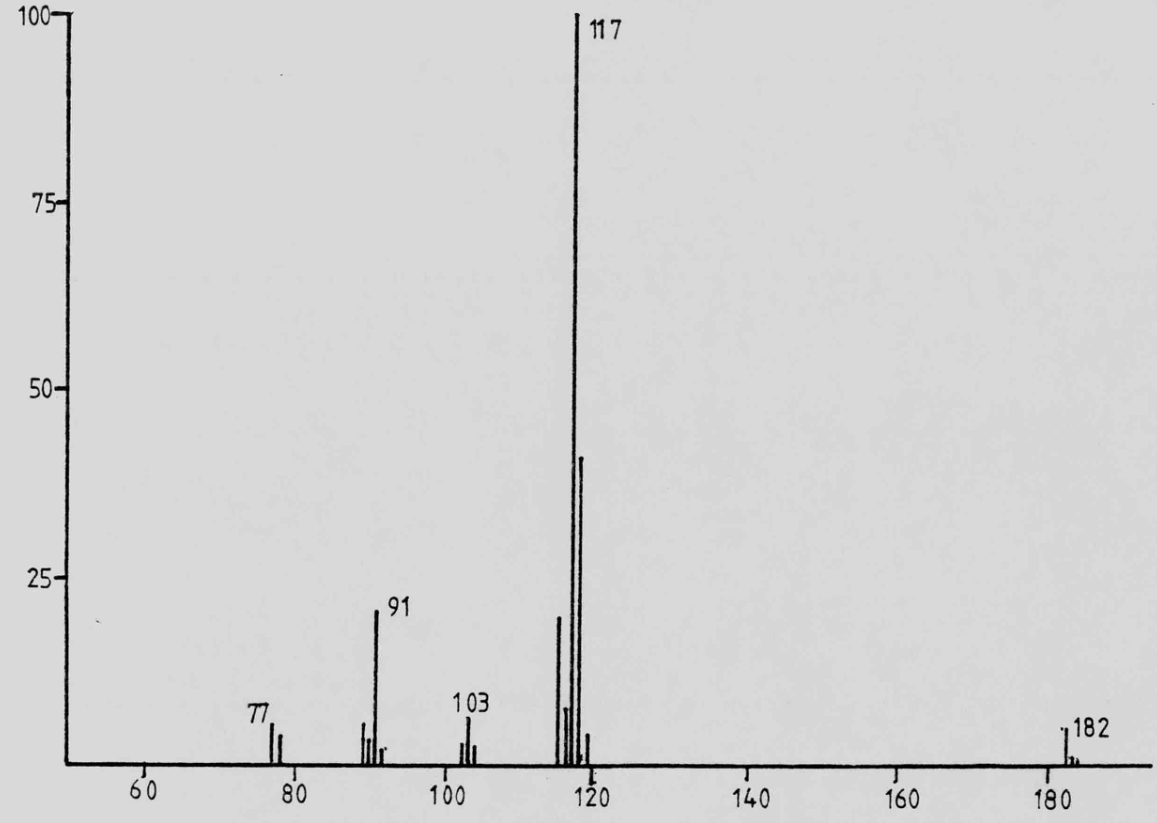


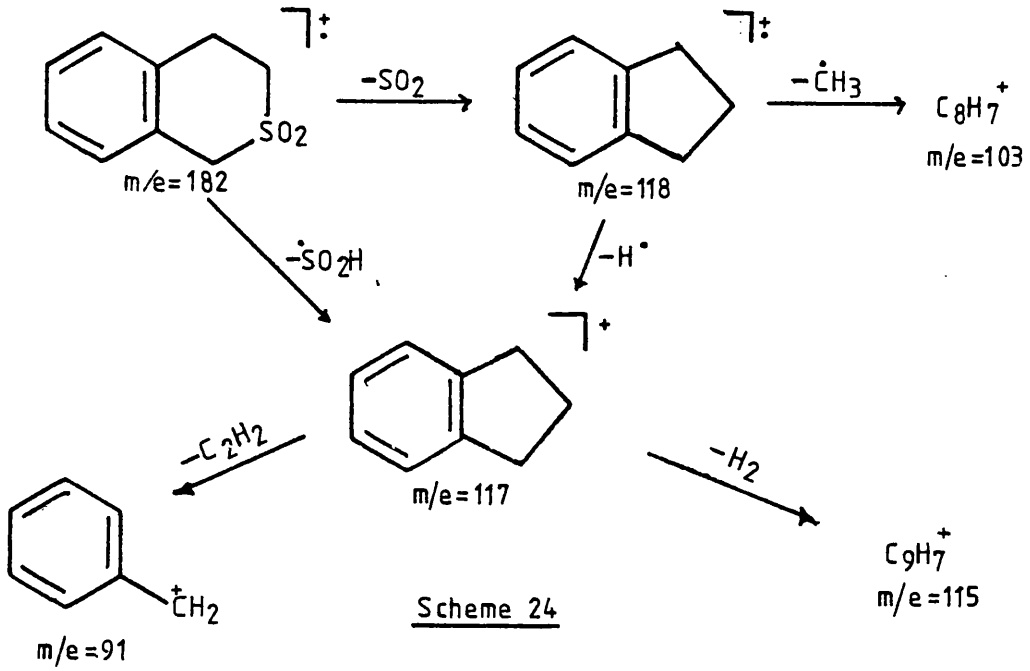
Figure 3.8 Mass spectrum of isothiochroman 2,2-dioxide.



of the m/e = 137 peak - a metastable ion at 103.1 supports this proposition. Loss of SO from m/e = 165 to give m/e = 117 is also a possible fragmentation although there is no metastable ion to confirm this process. Loss of C_2H_2 from this species would give m/e = 91.

For (165)[76] the major fragmentation pathway is the elimination of SO_2 to yield the base ion at m/e = 132. This subsequently fragments by loss of $H^{\bullet}$, CO or C_2H_4. The second fragmentation pathway is the retro-Diels-Alder elimination of $CH_2{=}SO_2$ to give m/e = 118. For the reduced analogue (166) the major fragmentation (Scheme 24 & Fig.3/8) seems to be the loss of SO_2H from the molecular ion to give a peak at m/e = 117. This is corroborated by a metastable ion occurring at m/e = 75.32. The minor fragmentation route is loss of SO_2 to give an M-64 peak at m/e = 118 which may then lose H to give m/e = 117, (isobaric with the direct loss of $\dot{S}O_2H$) or lose CH_3 to yield m/e = 103. The ion at m/e = 117 can then fragment by loss of H_2 to give m/e = 115 (evidence for this process is given by a metastable ion at m/e = 113.0), or it may lose C_2H_2 to yield m/e = 91 (a metastable ion at m/e = 70.77 supports this). There is no M-78 peak at m/e = 104 indicating that there is no retro-Diels-Alder reaction taking place.

The major trend in fragmentation of thiochromanone sulphones of the type described above seems to be a retro-Diels-Alder reaction,



Scheme 24

although increasing substitution tends to emphasise the alternative hydrogen transfer elimination reaction. In contrast, the direct elimination of sulphur dioxide occurs to only a minor extent compared with the isothiochroman and isothiochromanone examples quoted above. The reason given for this is that in the isomeric sulphones, the retro-Diels-Alder reaction involves the expulsion of sulphene $CH_2{=}SO_2$ as a neutral species which is expected to be less stable thermochemically than the olefins derived from the thiochromanone sulphones.[76]

There does not seem to be much correlation between the thermal and electron impact breakdowns of these compounds. None of the thermolysis products of these sulphones result from retro-Diels-Alder reactions although the relative ease with which sulphur dioxide is lost from the molecule is partially reflected in the intensity of the (M-64) peaks in the mass spectra.

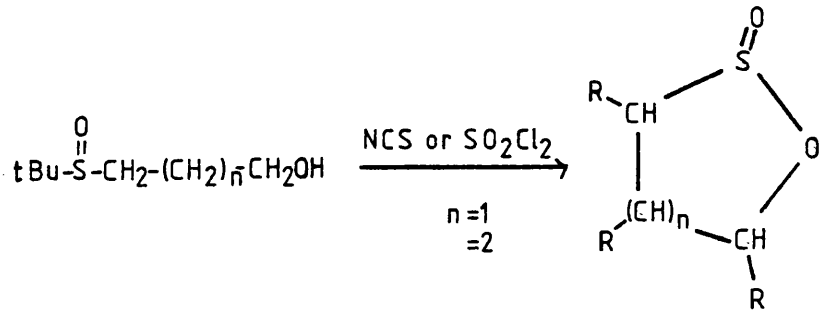
CHAPTER FOUR

THE FLASH VACUUM THERMOLYSES OF SOME SUBSTITUTED γ-SULTINES

4.1 Introduction

Thermolysis studies have also been carried out on various γ-sultines of general formula (167) where n = 1. These compounds were kindly supplied from the laboratory of Professor T. Durst at the University of Ottawa. His novel synthesis of sultines[89] has enabled the preparation of many hitherto unknown β, γ, and δ sultines.

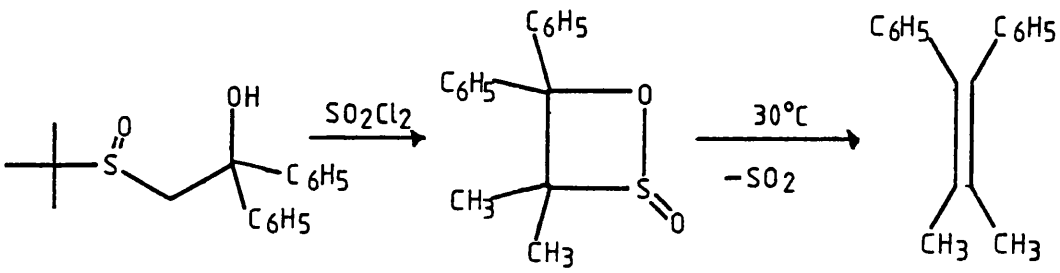
Briefly, his method consists of taking a ^{t}Bu hydroxyalkyl sulphoxide and cyclising from the sulphur atom to the hydroxy oxygen by stirring with an equivalent amount of sulphuryl chloride or N-chlorosuccinimide at low temperatures. To obtain a γ-sultine, a γ-hydroxy sulphoxide is needed.



167

The extrusion of sulphur dioxide from sultines has been previously described. Durst and Gimbarzevsky[90] have described the preparation of a stable β-sultine (168), using the same method as described above.

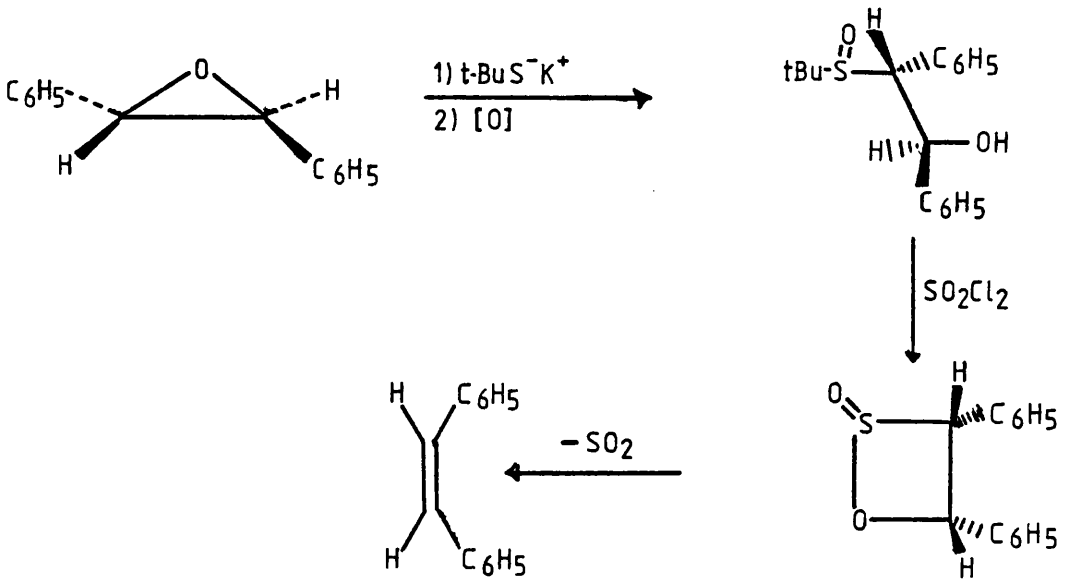
The material was isolated as a white crystalline solid, which, in solution at 30°C, had a half life of about 24 hours, decomposing to give 1,1-diphenyl-2,2-dimethyl ethylene.



168

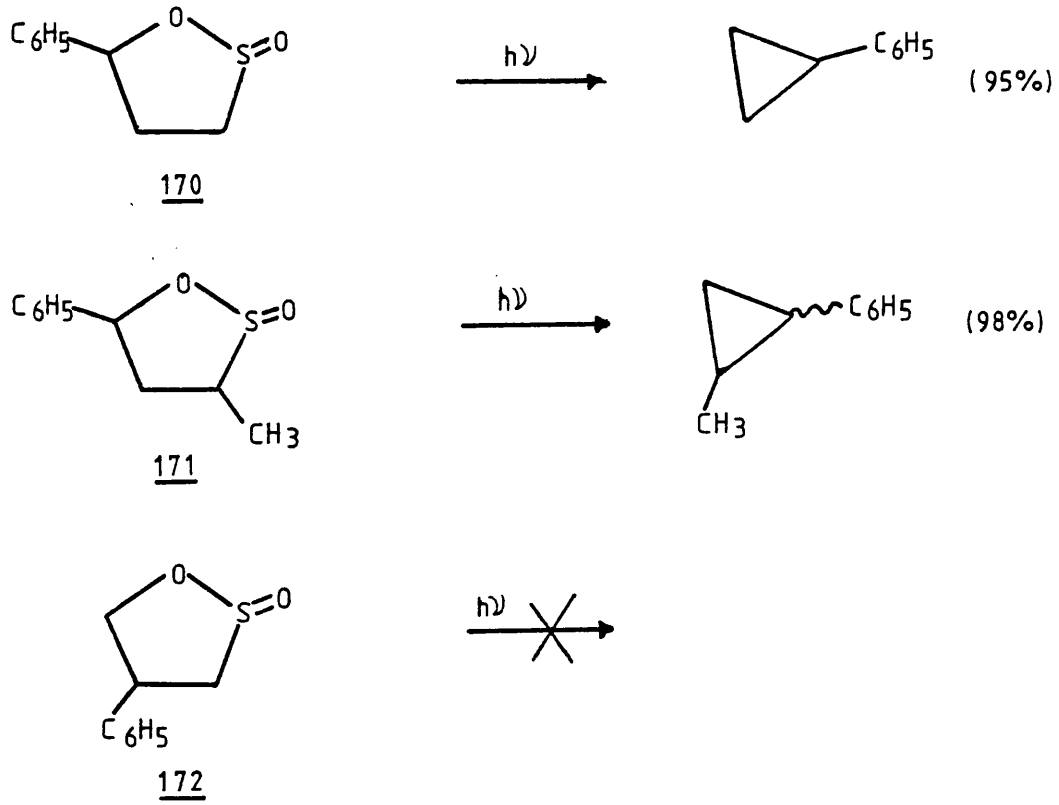
The process was described as a concerted cis elimination since 2,3-diphenyl oxathietan 2-oxide (169) of a known stereochemistry was observed to eliminate sulphur dioxide to afford cis stilbene only.[91]

Loss of sulphur dioxide has also been observed on photolysis of some γ-sultines,[92] although this only occurred where the molecules contained a chromophore in the form of an aryl group, and indeed, where the aryl group was α to the oxygen atom.

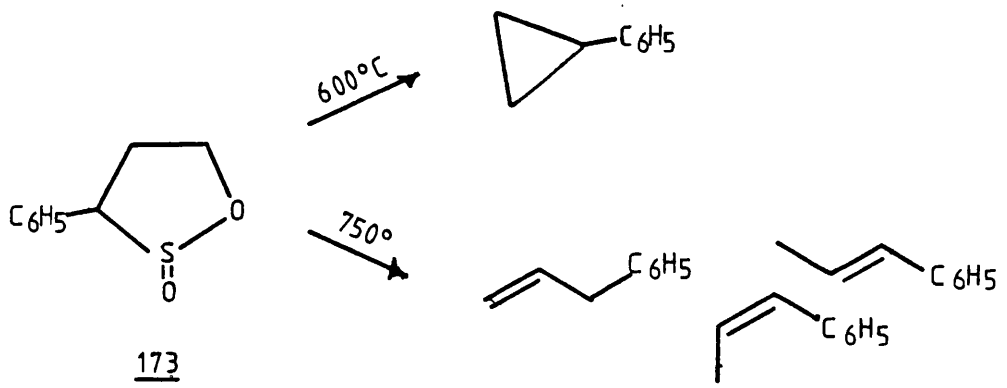


169

Irradiation of 5-phenyl-1,2-oxathiolane-2-oxide (170) gives phenyl_cyclopropane (in 95% yield), similarly 5-phenyl-3-methyl 1,2-oxathiolane 2-oxide (171), gives 1-phenyl-2-methyl_cyclopropane, whereas 4-phenyl-1,2-oxathiolane 2-oxide (172) is recovered unchanged.



3-Phenyl-1,2-oxathiolane-2-oxide (173) has been thermolysed in these laboratories by Hall.[93] Thermolysis of (173) at 600°C gives pure phenyl cyclopropane in quantitative yield whilst at 750°C a mixture of allyl benzene (50%), cis and trans β-methyl styrene (45%) and phenyl cyclopropane (trace amounts) is given.



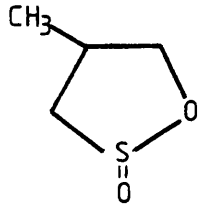
173

In our experiments, the sultines were thermolysed using the apparatus described in Chapter One, and the products were analysed by gas liquid chromatography and ^{1}H n.m.r. spectroscopy by comparison with known materials or published spectra.

The thermolysis products obtained in our experiments were found to differ in some cases, with a change in temperature. In all cases the percentages of the components of a product mixture were determined from the integration values of a 100 MHz n.m.r. spectrum, taken of the product mixture, and therefore cannot be considered to be more accurate than ±2%.

4.2 Results

The thermolysis products of 4-methyl 1,2-oxathiolane 2-oxide (174) at various temperatures are shown in Table 4.1.



174

Table 4.1

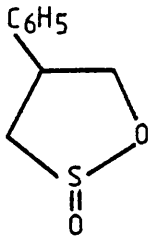
Thermolysis of 4-methyl 1,2-oxathiolane 2-oxide (174)

Product	Furnace Temperature		
	650°C	700°C	750°C
Starting material	87	70	-
Isobutylene	13	30	62
Methylcyclopropane	-	-	37

Isobutylene was identified by comparison with the n.m.r. spectrum of a pure sample obtained from the Matheson Gas Co.

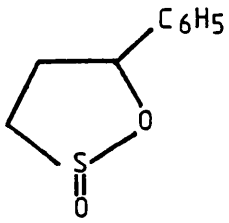
Methylcyclopropane was identified by comparing the n.m.r. spectrum with that of a pure sample obtained by dehalogenation of 1,3-dibromo-2-methyl propane with zinc.[94]

Thermolysis of 4-phenyl-1,2-oxathiolane 2-oxide (172)



172

No products were given below 750°C. At 750°C a mixture of starting material and α-methyl styrene was given. It was impossible to determine the relative amounts of these materials based on the n.m.r. integration values, since many of the starting material and product peaks overlapped. α-Methyl styrene was identified as a product by comparison with a published n.m.r. spectrum.



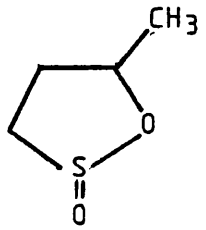
170

Table 4.2

Thermolysis of 5-phenyl 1,2-oxathiolane 2-oxide (170)

Product	Furnace Temperature				
	550°	600°	650°	750°	850° C
Starting material	84	62	24	-	-
Phenylcyclopropane	15	37	75	100	36
Cis/trans β-methylstyrene	-	-	-	-	37
Allylbenzene	-	-	-	-	27

Phenyl cyclopropane, cis and trans β-methylstyrene and allylbenzene were all identified by comparison with authentic n.m.r. spectra.



175

Table 4.3

Thermolysis of 5-methyl 1,2-oxathiolane 2-oxide (175)

Product	Furnace Temperature		
	650°C	700°C	750°C
Starting material	100	✓	-
Acetaldehyde	-	✓	17
Cis/trans but-2-ene	-	✓	35
Methylcyclopropane	-	✓	45

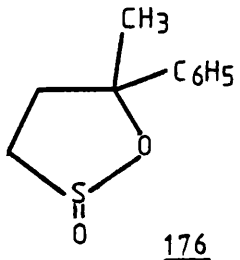
✓ indicates material present

Some white polymeric substance was given at 700°C and 750°C also.

In the product mixture given by thermolysis at 750°C, it was impossible to ascertain the relative percentages of components, because the methyl resonances of the starting material and the olefinic products, were too close to be accurately integrated. The products

were all identified either by comparison with standard samples, or with standard n.m.r. spectra. The polymeric material given at 700° and 750°C may be the result of partial polymerisation of the aldehyde under the reaction conditions.

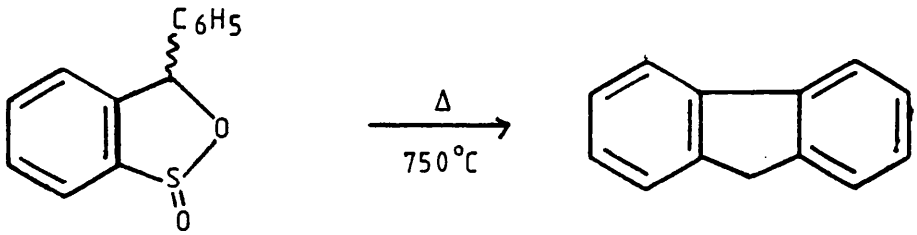
5-Phenyl-5-methyl 1,2-oxathiolane 2-oxide (176)



176

Thermolysis of (176) at 750°C gave 1-phenyl-1-methyl cyclopropane only - this was identified by comparison with the n.m.r. spectrum obtained by Gibert et al.[31]

3-Phenyl-2,1-benzoxathiol-1-oxide (177)



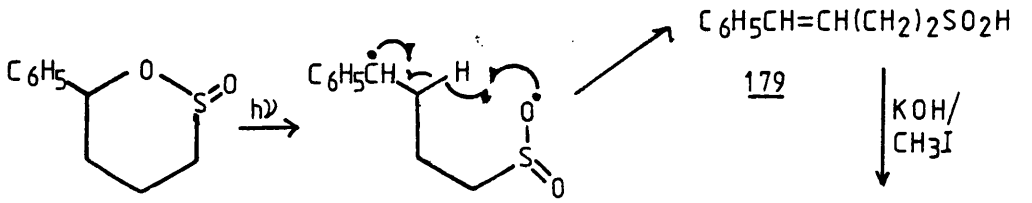
177

No starting material was recovered from the thermolysis of (177) at 750°C with the only identifiable product being fluorene, which

was confirmed by n.m.r. and g.l.c. comparison with a standard sample. There was a much greater integration value for the aromatic signal than was allowed for by the integration of the benzylic signal and it is assumed that any other products given would probably be poly-aromatic compounds, and would therefore have a very long retention time on a g.l.c. apparatus.

4.3 Discussion

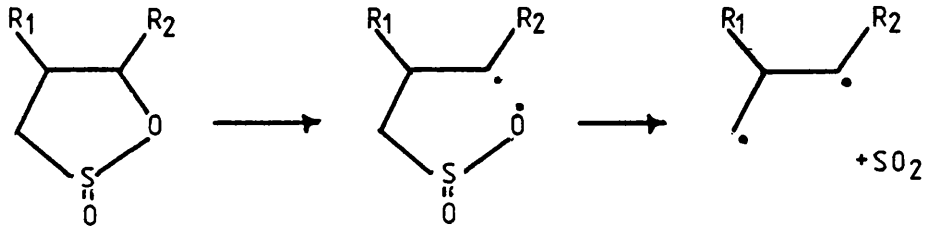
Possible mechanisms for the formation of the products are fairly simple. In general it is not thought that extrusion of sulphur dioxide from γ or δ-sultines is concerted, as it is for β-sultines, since decarboxylation of the structurally similar γ-lactones has been shown to involve radical intermediates[95] and irradiation of the δ-sultines (178) rapidly affords the unsaturated sulphenic acid (179) identified as the methyl sulphone [96] (180).



178 179 180

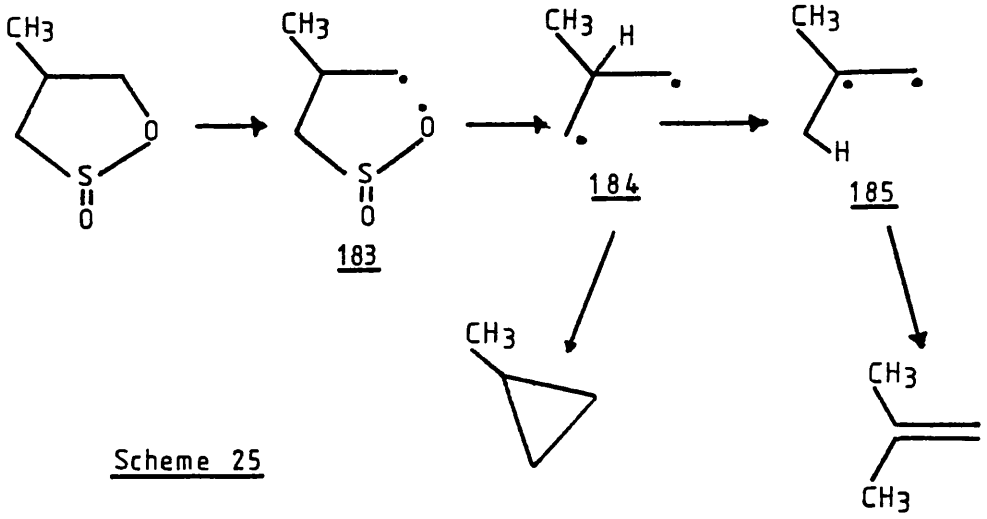
A two step mechanism is therefore postulated, where the initial step is cleavage of the carbon-oxygen bond, the diradical thus formed (181), can lose sulphur dioxide to give the diradical

(182), from which the products may be derived.



181 182

The mechanism for the formation of isobutylene and phenylcyclopropane from the thermolysis of (174) can be postulated as shown in Scheme 25.



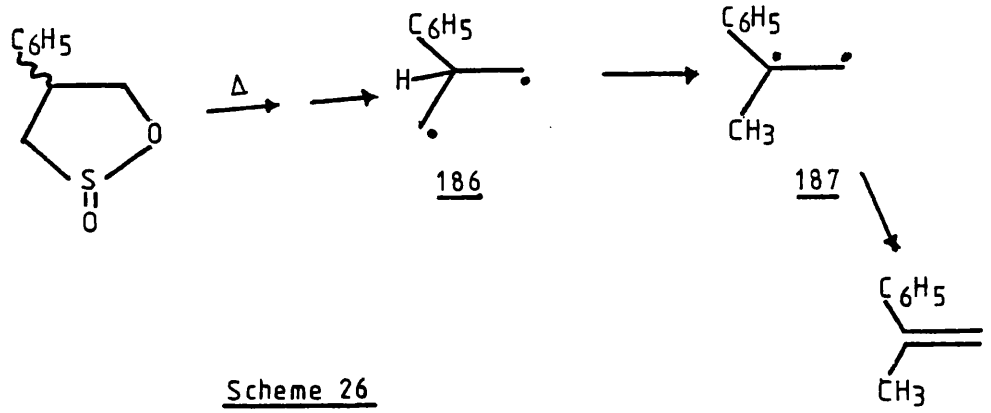
183 184 185

Scheme 25

The formation of isobutylene alone at lower temperatures stems from the rearrangement of diradical (184) to its more stable isomer (185) which can then collapse to give isobutylene. At higher

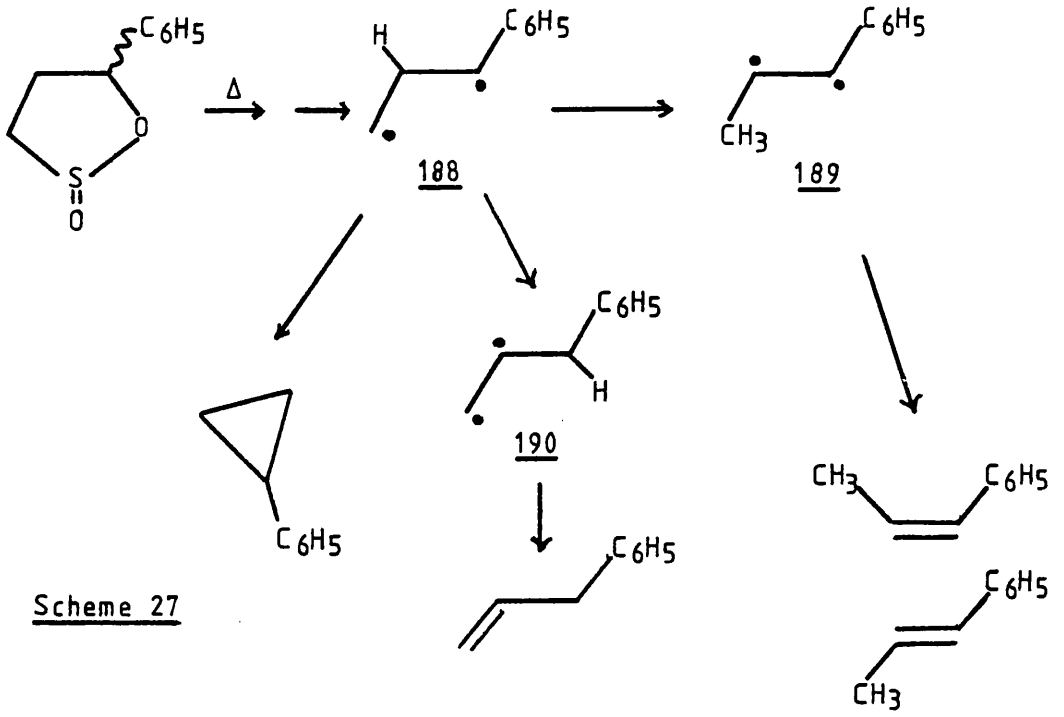
temperatures there is a greater preponderance of the higher energy form (184) which can undergo intramolecular ring closure to give the observed cyclopropane.

The thermolysis of (172) gave α-methyl styrene as the only observed product (Scheme 26), presumably the diradical (186) rearranges totally to the more stable form (187) which involves a benzyl radical and therefore accounts for the absence of phenyl cyclopropane.



Scheme 26

It should be noted that a higher temperature was needed (as compared with (174)), before any products were given, and that in (174) ring closure of the unrearranged diradical (184) became more important as the temperature increased. This may well happen in the case of (172) also, although not enough material was available for closer study. The thermolysis of (170) can be envisaged as shown in Scheme 27.

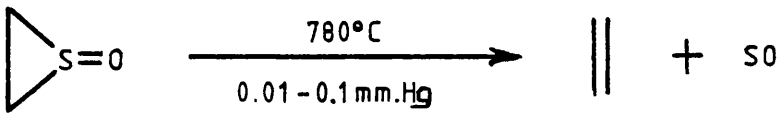


Scheme 27

The diradical (188) may either close to give phenylcyclopropane or, at higher temperatures, rearrange to give (189) which could collapse to give the isomeric styrenes, or rearrange to (190), the least stable form, which would yield allylbenzene. Significantly this product was only observed at high temperatures. It should be noted that products of any kind commence to appear at lower temperatures compared with the two previously discussed examples. This reflects the ease of formation of the initial diradical (188).

The compounds derived from the thermolysis of (175) are interesting because we are faced with the formal loss of sulphur monoxide, to derive one of the products. Examples of the thermolytic elimination

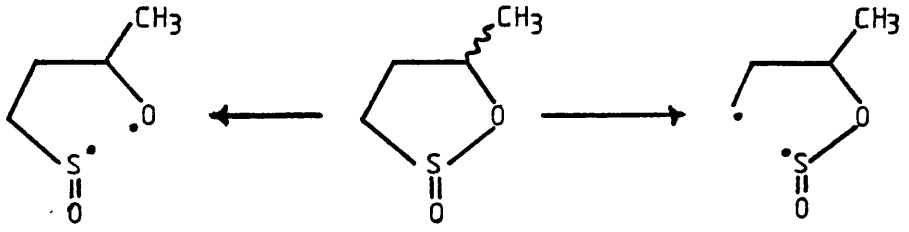
of sulphur monoxide are known, although this is not a common process, e.g. the thermal breakdown of dibenzothiophene 1,1-dioxide (page 6), and in the thermal breakdown of sulphene intermediates on flash thermolysis at temperatures of 700-800°C.[17,38c,97] Thirane sulphoxides (191) also eliminate sulphur monoxide on vacuum thermolysis.[98]



191

The intense red colour of sulphur monoxide is usually observed in those cases where the gas can be condensed onto a cold surface, although this was not seen in our experiment.

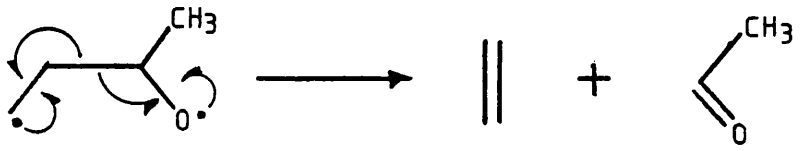
The formation of acetaldehyde implies that to some extent at least, the initial breakdown of the starting material is not cleavage of the carbon-oxygen bond, but may be cleavage of the oxygen-sulphur bond or carbon-sulphur bond (Scheme 28) to give either (192) or (193).



192 175 193

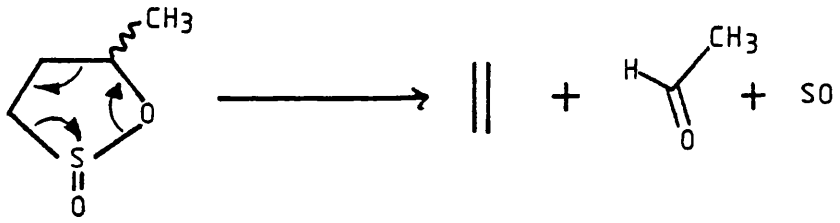
Scheme 28

Of these two processes, the formation of (192) is probably to be preferred. In any event, loss of sulphur monoxide from either species would give (194) which could give acetaldehyde as shown.



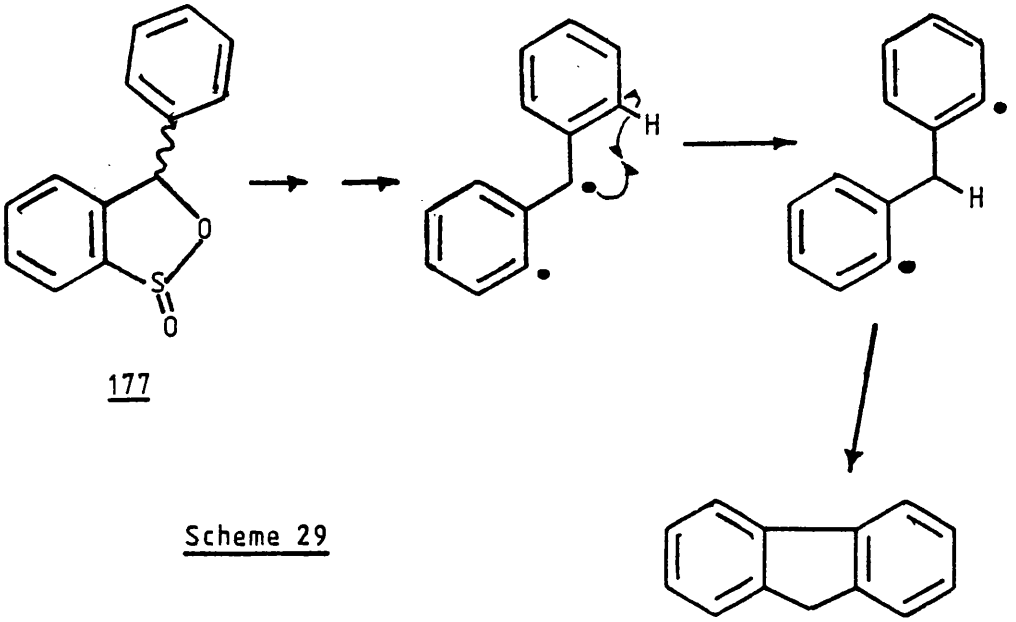
194

An interesting alternative to these processes is that the formation of acetaldehyde may be the consequence of an electrocyclic process as shown below.



No trace of ethylene was seen in the n.m.r. spectrum of the product, but it is unlikely that any would have been trapped, under the conditions of the experiment. The other products are quite simply explained as before.

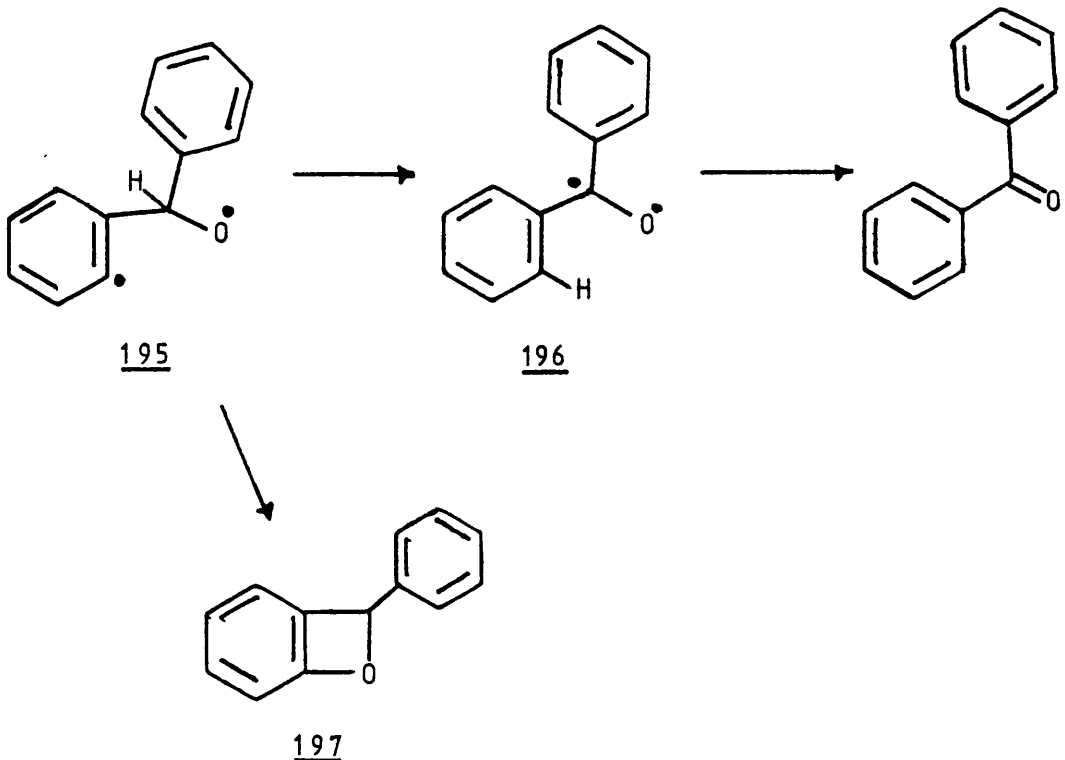
The thermolysis of the benz-fused sultine (177) to give fluorene can be described as in Scheme 29.



177

Scheme 29

As the thermolysis of (177) proceeded, a vivid red colour was noticed on the surface of the cold finger which, on warming, disappeared. This colour could be due either to the trapped bi-radical intermediate at low temperature, or to the presence of sulphur monoxide as an elimination product. If the latter reason is the case then we must consider (195) as a possible biradical intermediate in the reaction scheme.



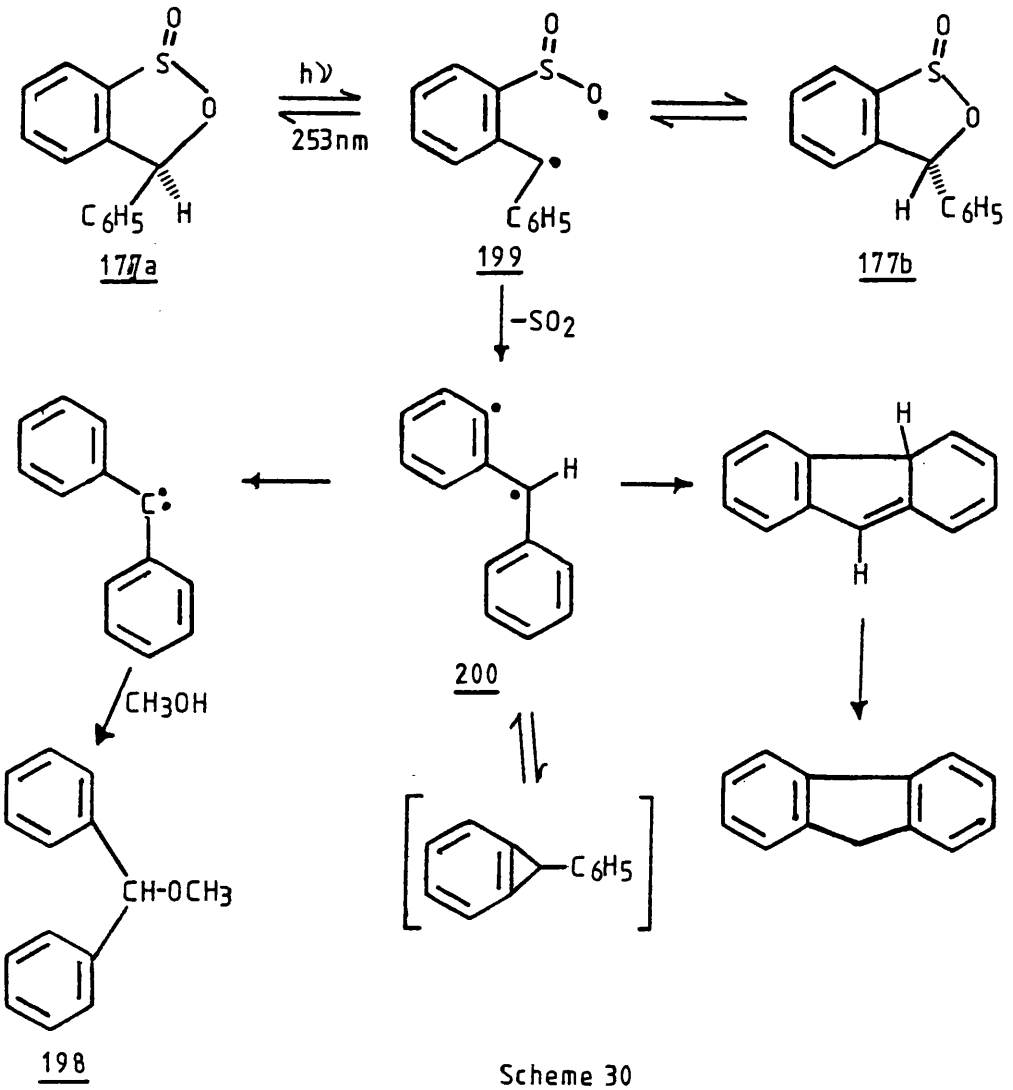
195 196 197

Possible products derived from (195) could be benzophenone formed from rearrangement to (196) followed by collapse , or 2-phenylbenzo[b]oxetan (197) formed by simple ring closure. However, none of these products were detected either by g.l.c. (against a standard sample of benzophenone), or n.m.r. spectroscopy.

A sample of (177) was also photolysed at 253 nm in absolute methanol to see if a cleaner product could be obtained. The n.m.r. spectrum of the resulting brown oil given was similar to that obtained from the thermolysis. The g.l.c. trace recorded under the same conditions as for the thermolysis products showed three products which were fairly volatile, one of them coinciding with the peak ascribed to fluorene from the thermolysis. These peaks were separated and passed into the input of a mass spectrometer. The first peak which was relatively minor, gave a molecular ion at m/e = 168. This corresponds to the molecular formula $C_{12}H_8O$, and may indicate the presence of dibenzofuran. The second peak gave a molecular ion at m/e = 198, which corresponds to the molecular formulae $C_{13}H_{10}S$ or $C_{14}H_{14}O$. The third peak (which coincided with that given by the thermolysis trace) gave a molecular ion at m/e = 166, corresponding to the formula $C_{13}H_{10}$. This indicates the probable presence of fluorene in the product mixture.

The photolysis of (177) has recently been described by Durst et al[96] to give two identifiable materials, fluorene and di-

phenylmethyl ether (198). The proposed mechanism is shown in Scheme 30.

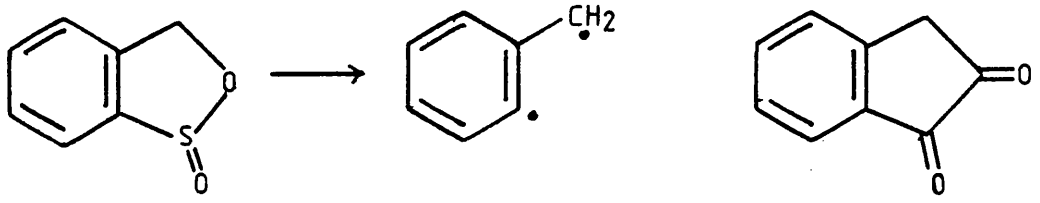


Scheme 30

The initial diradical formed (199) can ring close to give starting material or its isomer (177b), or it may lose sulphur dioxide to give the diradical (200). The presence of (198) in the product mixture implied the intermediacy of diphenylcarbene.

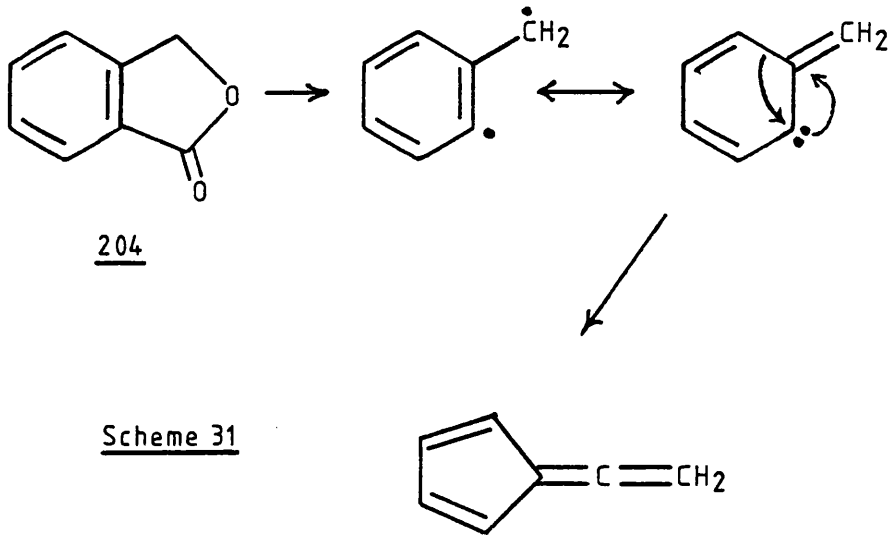
The thermolysis of 2,1,benzoxathiole,1-oxide (201), has also been studied. In this case we had hoped that loss of sulphur dioxide

would give the diradical (202), which has been described previously by



201 202 203

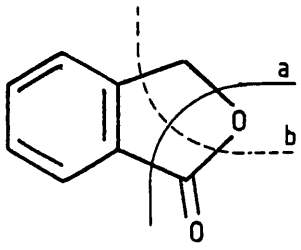
Hedaya et al[99] as an intermediate from the flash vacuum thermolysis of 1,2-indandione (203). Thermolysis of (203) gives a mixture of benzocyclobutanone, benzocyclopropane, fulvenallene, and ethynylcyclopentadiene in various ratios, depending on the temperature of the furnace - the higher the temperature, the greater the proportion of fulvenallene. The thermolysis of the carbon analogue of (201), phthalide (204), has also been described, by Wiersum and Nieuwenhuis.[100] Thermolysis of (204) at 700-750°C gives a liqiud containing fulvenallene with up to 40% benzene also, the mechanism being represented in Scheme 31.



204

Scheme 31

In this case the thermal breakdown (path a) did not parallel the primary fragmentation observed in the mass spectrometer, which was initial loss of a CH_2O fragment (path b).

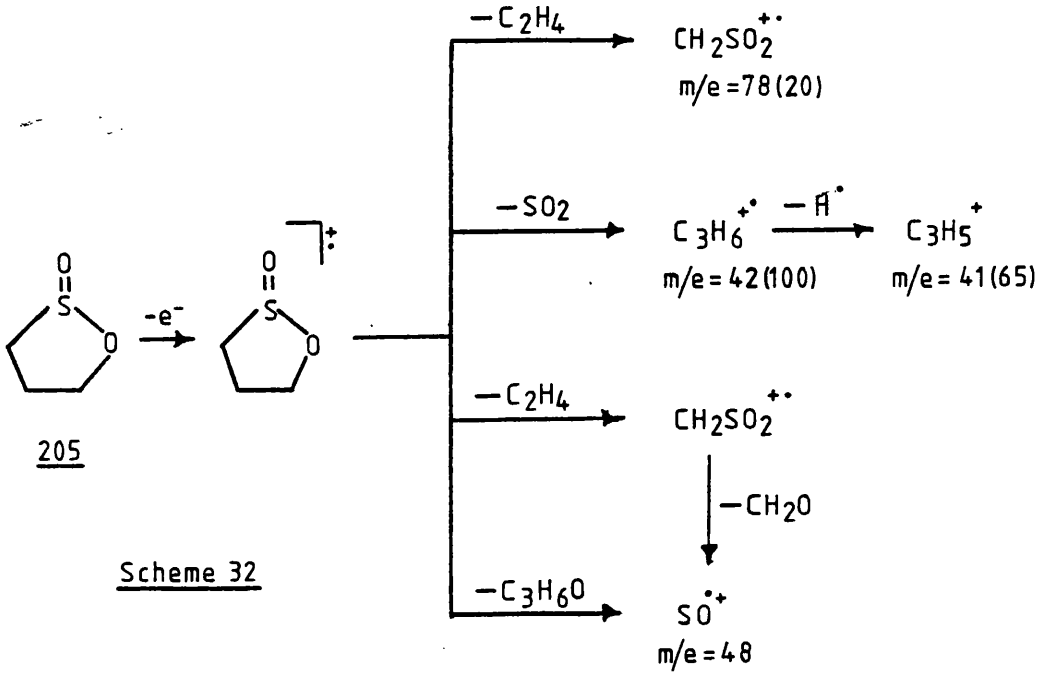


Unfortunately our thermolyses did not give such a clean reaction. Thermolysis of (201) below 700°C gave a recovery of starting material, while at 750°C a mixture of starting material as well as a spreading of the aromatic resonances, and a single resonance at τ 5.31 was observed. This did not fit any of the products derived from the thermolysis of (203).[8] Thin layer chromatography on silica using ether as the developing solvent showed at least six compounds present. An attempt to trap out any possible intermediates on the cold surface using a methanol "sandwich" and thermolysing at 850°C did not give any identifiable products.

Irradiation of (201) at 253 nm in absolute methanol gave a brown oil after 18 hrs. There was still some starting material after this time however, products were indeterminable. A repetition of this experiment by Durst et al[96] has also failed to give any identifiable products after irradiation for 48 hr.

4.4 Mass Spectral Studies

The mass spectral breakdown of some γ-sultines has been studied by Sharma.[92] In general the processes taking place are quite simple, the genesis of each peak being well understood. The breakdown of 1,2-oxathiolane-2-oxide (205) is summarised in Scheme 32.



Scheme 32

The spectrum shows only five peaks at m/e = 106, 78, 48, 42, and 41. Loss of sulphur dioxide gives rise to the base peak at m/e = 42 ($C_3H_6^{+\cdot}$) from which H· can be expelled to give $C_3H_5^+$ at m/e = 41. Elimination of ethylene to form $CH_2SO_2^{+\cdot}$ at m/e = 78 can take place with a further loss of CH_2O to leave $SO^{+\cdot}$ at m/e = 48. An alternative fragmentation to give the m/e = 41 peak may be a direct loss of SO_2H from the molecular ion, however no metastable ions were apparent in the mass spectrum which might have allowed corroboration. The mass spectral fragmentations observed for the two isomeric

monomethyl γ-sultines (174) and (175) are shown in Table 4.4. The fragmentation of these sultines can be explained using the generalised pathway as shown for the unsubstituted parent compound above. Loss of ethylene from the molecule was again observed to give m/e = 92. The significant m/e = 91 peak was probably due to loss of H$^{\cdot}$ from 92. These fragmentations were easily rationalised for the 5-methyl isomer (175) but it was suggested that in (174), a prior reorganisation of the carbon skeleton must have occurred.

The mass spectra for the 4-phenyl derivative (172) and that of the 5-phenyl derivative (170) are detailed in Table 4.5. In each case the (M-65) fragment corresponding to loss of sulphur dioxide, followed by loss of H$^{\cdot}$, was the base peak. Loss of ethylene, as for the previous examples was suppressed, presumably in the case of (170) the weakening of the C_5-O bond, due to the presence of the phenyl group made the (M-65) fragmentation facile, whilst in the case of (172) loss of ethylene would involve a rearrangement.

The mass spectrum of the benzofused sultine (177) was remarkably simple as there were only four peaks in the spectrum. The base ion was the (M-65) peak at m/e = 165 corresponding to loss of sulphur dioxide followed by $^{\cdot}$H, but this peak was only just larger than the (M-64) peak at m/e = 166. There was no (M-48) peak at m/e = 182 corresponding to the loss of sulphur monoxide. The other peak was at m/e = 77 corresponding to $C_6H_5^{+\cdot}$.

The mass spectrum of the benzofused sultine (201) was also

Table 4.4

Mass spectra of monomethyl γ-sultines

Sultine	M^+	M-28	M-29	M-42	M-64	M-65	M-79
174	120(22)	92(10)	91(15)	78(12)	56(37)	55(33)	41(100)
175	120(13)	92(20)	91(34)	78(22)	56(15)	55(100)	41(64)

The numerals in brackets denote the relative abundancies.

Table 4.5

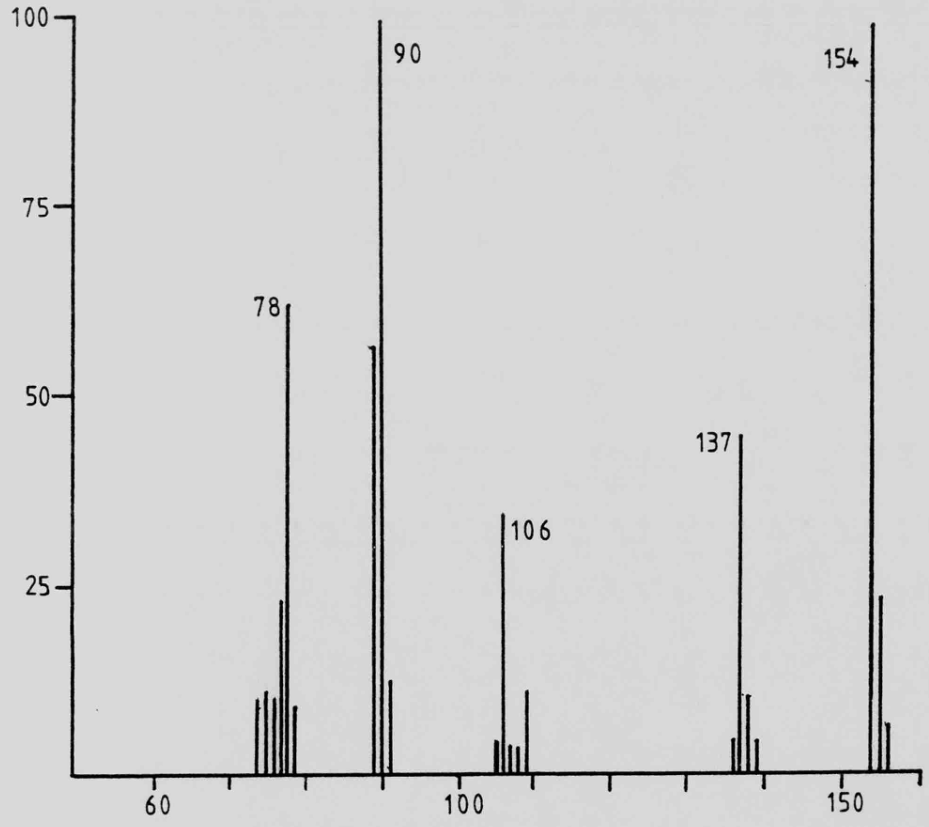
Mass spectra of some monophenyl γ-sultines

Sultine	M^+	M-64	M-65	M-78	M-79
170	182(2)	118(84)	117(100)	-	103(-)
172	182(8)	118(41)	117(100)	104(59)	103(17)

The numerals in brackets indicate the relative abundancies.

fairly simple (Figure 4.1). The stability of this molecule is reflected by a substantial molecular ion at m/e = 154, which is 99% of the base ion at m/e = 90. There is a peak at m/e = 137 which probably represents the loss of OH, since there is a metastable ion at m/e = 121.8 indicating that this is a direct process. There is an (M-48) peak at m/e = 106 indicating the loss of SO from the molecular ion. The base peak at m/e = 90 is the (M-64) peak although it was not possible to determine whether this is a direct loss of SO_2 or a stepwise loss of SO followed by $^{\cdot}O$ because no metastable ions were available in order to substantiate any of these pathways.

Fig. 4.1 Mass spectrum of 2,1,benzoxathiole,1-oxide.



The mass spectral fragmentation trend of the methyl substituted sultines studied seems to be a competition between the loss of sulphur

dioxide and ethylene from the molecular ion, followed by the loss of $^{\cdot}H$ from either of the two fragments formed. In the aryl substituted sultines however, the loss of ethylene is very much suppressed and the expulsion of SO_2 followed by $^{\cdot}H$ is the only process. The thermal decomposition of the monocyclic sultines studied suggests that the loss of SO_2 is the major process occurring and products are generally derived from this fragmentation only, except in the case of (175), where the products may be derived from the loss of ethylene followed by loss of SO_2. In the case of the benzofused sultine (177), both the thermal and photochemical breakdown gave products derived from a loss of SO_2 and this is reflected in the electron impact fragmentation where this breakdown constitutes almost all of the ion current. The breakdown of the benzofused sultine (201) showed both the loss of SO and SO_2 from the molecular ion. It was not possible to determine the major processes occurring in the thermal and photochemical breakdowns of this molecule although if the loss of SO_2 was a major process then products derived from the intermediate biradical (202) might have been expected.

CHAPTER FIVE

THE CONFORMATIONAL ANALYSIS OF SOME 3-SUBSTITUTED THIETAN 1-OXIDES USING LANTHANIDE SHIFT REAGENTS

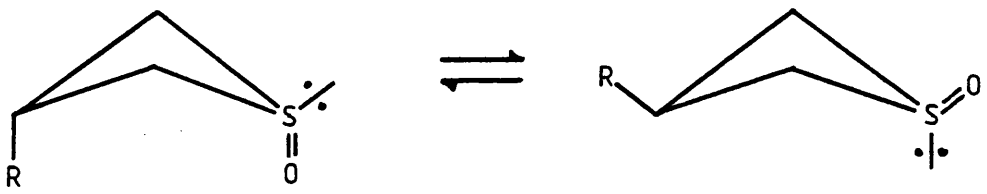
5.1 Introduction

Substituted thietan 1-oxides have been used in the study of intramolecular neighbouring group effects of sulphinyl oxygen, and for studying the competitive stereochemical requirements of sulphinyl oxygen and the non-bonded electron pair on trigonal sulphur, the stereochemical consequences of which have come under scrutiny in recent times.[101] The systems chosen for these studies were the 3-substituted thietan 1-oxides. The presence of a 3-substituent means that there are two possible geometric isomers for these molecules, i.e. the substituent may either be *cis* or *trans* with respect to the sulphinyl oxygen, and this allows the stereochemical course of the reactions to be determined if the isomers can be readily distinguished from one another by a variety of means.

5.2 Stereochemical Considerations

By analogy with the cyclobutane ring system,[102] puckering in thietan ring systems has now been well documented by a number of independent studies.[15,103,107] Because of the energy barrier to planarity, two conformations must be considered for each isomer,

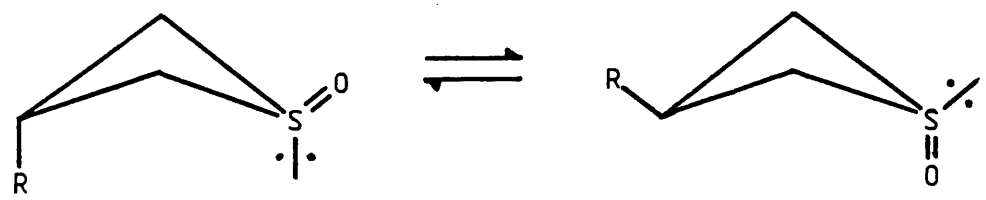
e.g. for the cis isomer (206)



206A 206B

The difference between these two conformers is a ring flip. The energy for this process is not large and interconversion of conformers (206A and 206B) at room temperature is expected to be a fast process on the n.m.r. time scale, and therefore the n.m.r. spectrum at room temperature should reflect the weighted average of the two conformations. Also, by analogy with cyclobutane chemistry,[104] it is reasonable to expect that if R is a large enough group, then the conformers will be of significantly different energies, and that the molecule will adopt its lower energy form predimonantly. In the case of the cis isomer, this would be (B), since (A) would be expected to involve severe 1,3-non-bonded diaxial interactions.[105] Conformer interconversion may still be a very rapid process, but if there is a significantly higher proportion of conformer (B) present then the n.m.r. spectrum will approximate to that expected for (B).

In the trans isomer (207), because one group is always axial, the energy difference between the two conformers is expected to be smaller than that of the cis isomer, however the R group might still be expected to show an equatorial preference[105] and hence (207B) will be the predominant conformer.



207A 207B

Crystal structure,[106] dipole moment,[101,107] and n.m.r. studies[101] have all been used to assign configuration to thietan 1-oxides, although n.m.r. has been found to be the most versatile and most readily available technique. Johnson[108] has investigated the ^{1}H n.m.r. of a series of 3-substituted thietan 1-oxides, and has found a consistent trend apparent. The four α protons in one isomer always exhibit two well separated 2H multiplets, while in the second isomer all four α protons appear as a broad doublet with a chemical shift approximately midway between the multiplets. Also, the β-proton in the second isomer always appears to be significantly deshielded with respect to that of the first.

Dipole moment studies[101,107] on cis and trans 3-chloro- and 3-p-chlorophenylthietan 1-oxides suggest that the α protons in the cis-isomer give rise to the separate 2H multiplets while those in the trans-isomer give the observed broad doublet. This assignment is supported by the fact that the cis-isomer is always eluted first during vapour phase or column chromatography. This is expected since it has been shown that in the absence of complicating effects, the isomer with the more sterically accessible sulphinyl oxygen has the highest retention time.[109] In the cis-isomer, the polar sulphoxide group is slightly shielded by the 3-substituent on the same side of the ring and hence inhibits interaction with the solid phase of the column.

Assuming that (206B) and (207B) are the predominant conformers of the molecules in question, then the ^1H n.m.r. spectra can be easily explained.

In cyclic sulphoxides, a large chemical shift difference is observed for the α protons when the non-bonded electron pair on sulphur is axial.[105,108,110] In each case, where the configuration of the sulphinyl oxygen and α-protons have been determined by other methods, the α-protons trans diaxial to the lone pair on the sulphur atom appear at a higher field than the equatorial α-protons (similar effects have been observed and applied for configurational assignments of nitrogen heterocycles[111]). This effect is attributed to a selective shielding of the trans co-axial protons by the lone

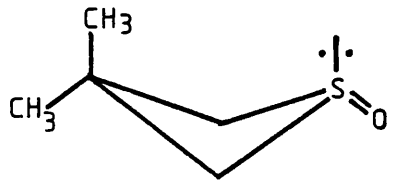
pair on sulphur. This implies that the sulphinyl oxygen (and hence the 3-substituent) are both (predominantly at least) in an equatorial position, since the lone pair must adopt an axial position for the effect to occur. The complexity of these multiplets suggests that there may also be a degree of cross-ring coupling.

In the trans-isomer (assuming a predominance of conformer (207B)), there is no selective shielding of this type because the lone pair is no longer axial, and therefore both sets of protons have the same chemical shift. The signal appears as a doublet due to coupling with the β-proton (the signal is not sharp because the two sets of protons are not completely equivalent).

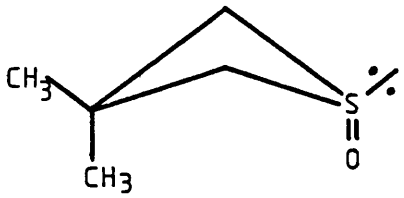
Two factors have been postulated for the large deshielding of the β-proton in the trans-isomer of this system - an acetylenic type anisotropy of the sulphur-oxygen bond, and/or a proximity effect.[110a-c] The effect of this anisotropy on both sets of α-protons may be considered equivalent, however only when the sulphur-oxygen bond is syn-axial to the 3C-β hydrogen bond is it significantly deshielded. The syn axial proximity effect which may or may not be a factor is due to Van der Waals interactions.[110a] These features are still observed when the 3-substituent is a relatively small group such as methyl,[112] and this is surprising becase as the size of the R group decreases, the energy difference between the two conformers for each isomer must decrease, and this should lead to a

decrease in the preference for one conformer over another. The n.m.r. spectrum should reflect a time averaged position not relating directly to any one conformer.

Studies of the ^{1}H n.m.r. spectrum of 3,3-dimethylthietan 1-oxide (208) have been made.[105,113]



208A



208B

The spectrum shows two separate methyl resonances, the one at lower field being a singlet, and the other one a finely split doublet (J = 8 Hz). The large difference in shifts for the methylene protons implies that the major conformer (208A) with the oxygen equatorial for the reasons detailed above. The axial methyl group is expected to resonate at a higher field because of possible anisotropic shielding by the cis co-axial lone pair, and the coupling is to the axial α-protons attributed to the planar W-configuration of the intervening σ bonds.

5.3 Lanthanide Induced Shift Studies

Simplification of n.m.r. spectra by the addition of lanthanide shift reagents has proven to be a significant extension to the usefulness of n.m.r. spectroscopy.[114]

The observed shift is a weighted average reflecting the rapid equilibration of the lanthanide shift reagent, and the organic substrate (equation 5.1).

$$Ln(Y)_3 + RX \rightleftharpoons RX{:}Ln(Y)_3 \qquad (5.1)$$

For this reason, the mean lifetime of the substrate lanthanide complex must be small on the n.m.r. time-scale. The shift of the resonance signal for a given nucleus depends on two main contributions;

1) Fermi-contact interaction - This is a delocalisation of the unpaired electrons of the shift reagent leading to the transfer of electron density and/or spin polarisation *via* covalent bonds from the metal to the binding nucleus. This interaction is dependent on both the ability of the metal ion to transfer electron density and the ability of the binding nucleus to accept such a transfer. This effect is propagated through bonds and declines rapidly when only σ bonds are involved. In lanthanide shift reagents however, the unpaired electrons lie in 4f orbitals which are well shielded by occupied 5s and 5p shells, and for practical purposes, the contribution to the observed shift from this effect is very low.[114b,115]

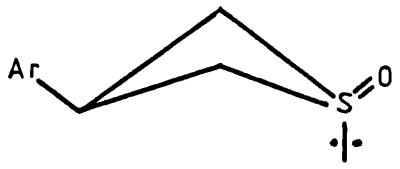
2) Dipolar or pseudocontact interaction - This is a sum term of all the magnetic dipolar interactions of a given nucleus with the anisotropic magnetic field of the valence electron shell of the shift reagent and therefore is a through space interaction determined by a distance factor only.[116]

Apart from this dipolar contribution, several small factors are involved in determining the shift observed, e.g. possible diamagnetic properties of the ligands, and disturbance of the solvation cage of the substrate, by the formation of the substrate-lanthanide complex. Increasing effort is being directed towards a more quantitative treatment of the data available from these studies particularly for elucidating molecular geometries.[117]

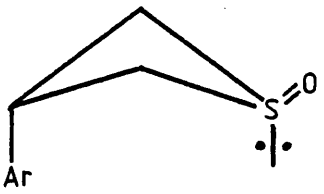
Hall[20] has reported lanthanide induced shift studies on the two isomers of 3-methyl and 3-phenylthietan 1-oxides at 60 MHz using $Eu(dpm)_3$ (dpm = dipivalomethanato) as the shift reagent. The results were applied using a static model, i.e. the assumption was made that any conformational mobility in the system could be adequately described by a single average shift reagent-substrate structure. Previous workers[113,116,118] have however pointed out the dangers of making these assumptions in a conformationally mobile molecule, and in fact this treatment has been shown to lead to an incorrect assignment in the case of 3,3-dimethylthietan 1-oxide.[113] If the rotamer populations about the sulphur-oxygen-europium bond are averaged however, the correct answer is obtained. These

are very difficult to predict however and the computational requirements are generally very large (substitute methods have been published, e.g.[118]), and a complete analysis of the system was not attempted.

The results obtained by Hall were not satisfactorily explained in terms of the predominant conformers described for these systems by Johnson[105] however, and in an attempt to clarify this problem, the syntheses and crystal structure of cis and trans 3-p-bromophenylthietan 1-oxides (209) have been described by Smith et al.[119] The structural determination shows that in the solid state, the cis isomer adopts conformation (209A), i.e. the expected diequatorial configuration, while the trans-isomer adopts configuration (210B) with the aryl group axial and the oxygen equatorial.



209A

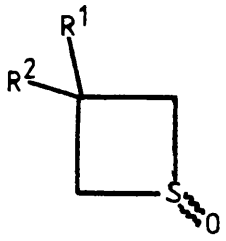


210B

Ar = p-BrC_6H_5

The prediction for the trans isomer in the solid state is opposite to that described by Johnson for these systems in solution, and the study described here is an attempt to treat the shift reagent studies of some of these compounds in a more quantitative fashion

in order to try and determine the relative proportions of each conformer in solution for a given isomer. The compounds chosen for study were (211-214).



211 $R^1=C_6H_5, R^2=H$

212 $R^1=pBrC_6H_5, R^2=H$

213 $R^1=tBu, R^2=H$

214 $R^1=C_6H_5, R^2=CH_3$

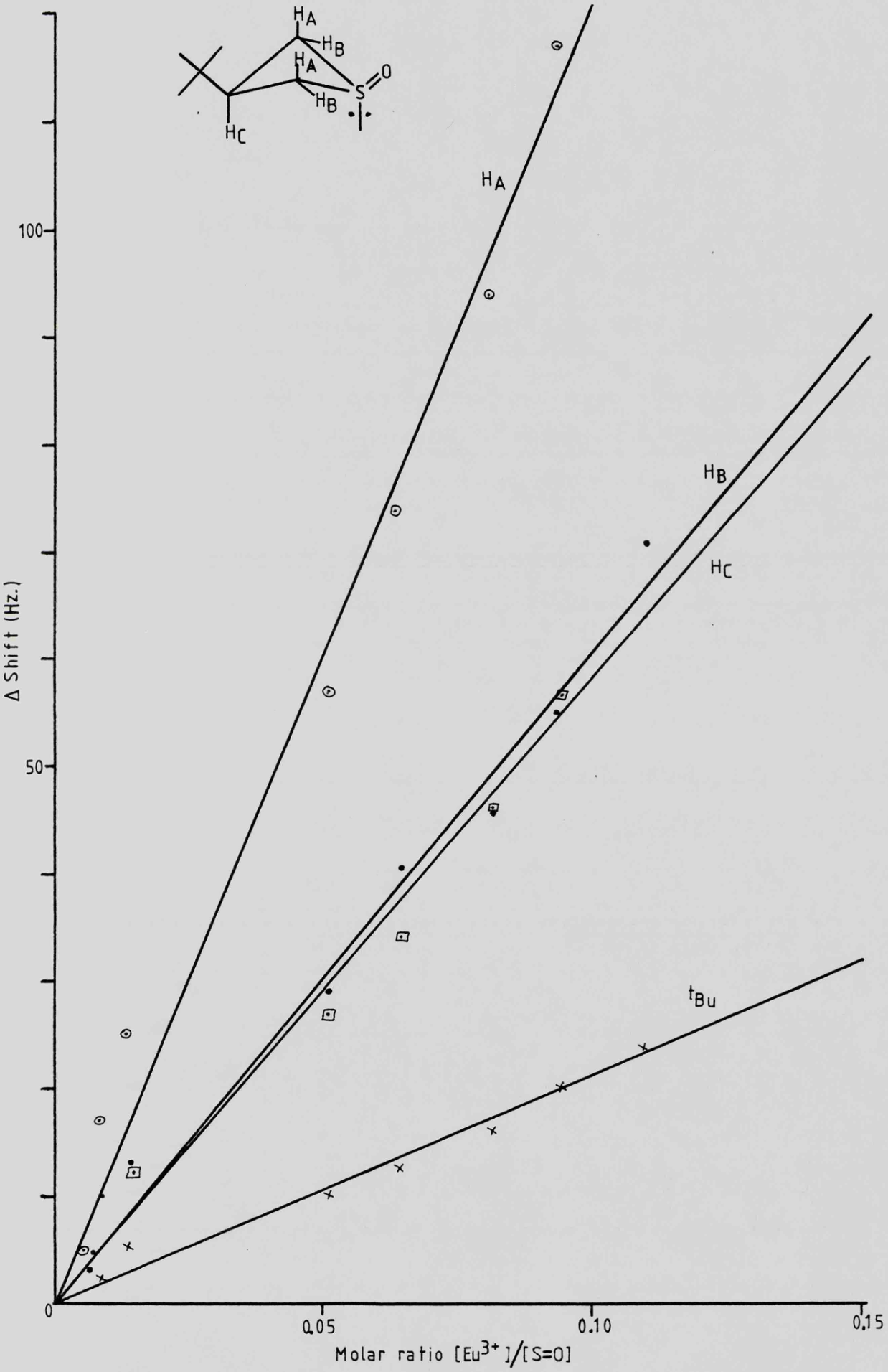
The spectra were run at 100 MHz in deuteriochloroform, using $Eu(dpm)_3$ as the shift reagent, although $Yb(fod)_3$ (fod = 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionate) was later used for reasons of greater solubility and shifting ability. Since in some cases the spectra consisted of a series of overlapping multiplets, it was difficult to measure the shifts accurately, and estimations were made in a few cases. In all cases, a plot of the shift (Δ Hz) against the weight or molar ratio of shift reagent to the sulphoxide gave a straight line as for example, for cis 3-t-butylthietan 1-oxide (fig. 5.1).

All of the data was statistically treated using a linear regression formula in order to fit the best straight line. The angles of slope of these lines were then measured, and the % angularity of each line defined as

$$\frac{\text{(angle measured for the line)}}{\text{(sum of all the angles)}} \times 100$$

was calculated for each line.

Fig 5.1 A plot of the induced shift (Hz) against molar ratio of shift reagent for Cis 3-tButylthietan,1-oxide.



In addition to this, ^{13}C n.m.r. shift work was also carried out on cis and trans 3-phenyl, 3-methylthietan 1-oxide (214) using $Yb(fod)_3$ as the shift reagent. The data was treated as described above.

Generally, the following qualitative observations were made; (1) In the cis isomers, assuming that the diequatorial conformation is adopted, the axial α-protons exhibit a greater rate of shift than the equatorial α-protons. At the point where the two sets of protons become equivalent (i.e. their chemical shifts are the same) the signal becomes a 4H doublet. On addition of further quantities of shift reagent, the signal splits into two 2H-multiplets. The axial α-protons are now responsible for the downfield multiplet.

(2) In the trans isomers, addition of the shift reagent resolves the initial 4H doublet (due to the α-protons) into two 2H multiplets.

(3) In all cases the magnitude of the shifts for the equatorial α-protons and the β-protons (where present) were very similar.

(4) For both of the isomers the rate of shift of the protons was α-protons > β-protons > 3-substituent.

(5) Generally, as the concentration of shift reagent in the mixture increased, the resolution of the spectra became gradually worse. This effect is frequently observed in samples containing unpaired electrons and are caused by intramolecular spin delocalisations and time dependent intermolecular reactions.[120]

In both isomers of 3-phenylthietan 1-oxide (211) and 3-methyl,3-phenylthietan 1-oxide (214) the aromatic ring protons appear as a singlet which is slowly resolved into a complex multiplet as the concentration of shift reagent increases. In the case of the 3p-bromophenyl substituted analogue (212), the initial A_2B_2 pattern slowly moves together to give a singlet. Both of these observations are probably distance effects. The aromatic protons α- to the thietan-C(aryl) bond would be expected to exhibit more of a shift than the other protons on the ring since they lie closer to the shift reagent in the thietan shift reagent complex.

Lanthanide shifts are normally interpreted in terms of the McConnell-Robertson equation.[121] For axially symmetric complexes the special dependence of the shifts (Si) is given by formula 5.2.

$$Si = \frac{\Delta Hi}{H} = \frac{K(3\cos^2\theta i - 1)}{r_i^3} \qquad (5.2)$$

Where ΔHi is the change in field strength at nucleus i, r_i is the distance between the paramagnetic metal and the nucleus i, and θi is the angle between the principal magnetic axis of the complex and the vector r_i. Earlier applications of this equation to structural problems assumed a constant angular term thus taking the observed shift to be proportional to r_i^{-3}; however, improved agreements between calculated and observed shifts are found when the full ex-

pression is used, rather than the radial portion only.[122] The difficulty with this method is that the location of the principal magnetic axis (which is needed to define θi) is generally unknown. In the case of sulphoxides, the lanthanide metal has been shown to coordinate to the oxygen,[116] and the principal magnetic axis is assumed to lie along the lanthanide-substrate axis[113] since for the purposes of computation, the results obtained by placing the principal magnetic axis in this direction are invariably the optimum obtainable.

5.4 Treatment of Results

A calculation of the relative percentage shift is made for each i nucleus under examination from the McConnell-Robertson equation (1) above, using a computer simulation of a Dreiding model, in order to ascertain values for θi and r_i in the lanthanide substrate complex. Then the observed relative percentage shifts are applied to the programme, and the scaling of the calculated shifts to the observed shifts is accomplished by forcing K (of equation 5.2) to be of such a value that

$$\Sigma Si^{c} = \Sigma Si^{o} \qquad (5.3)$$

where Si^{c} is the calculated shift for nucleus i, and Si^{o} is the observed shift.

In the programme, the metal nucleus of the shift reagent is placed at the origin of a right-handed cartesian system, with the donor-substrate bond parallel to the x axis. The Dreiding coordinates of the nucleus in question are then removed from their original position by a coordinate transformation to give a new position with respect to the lanthanide coordinate system. The positions of the substrate and the shift reagent are then optimised until the sum of the square differences between the calculated and the observed shifts is minimised, i.e. the quantity

$$\Sigma(Si^{O}-Si^{C})^{2}$$

At this point the placement is considered to be "correct". An R factor (similar to the crystallographic R factor) is defined as

$$R = \sqrt{\frac{\Sigma(Si^{O}-Si^{C})^{2}}{\Sigma(Si^{O})^{2}}} \qquad (5.4)$$

and is quoted in the results as a measure of the "goodness" of fit. The advantage of treating the calculation in this way (and not orienting the lanthanide molecule with respect to the substrate) is that several torsion angles can be easily introduced into the calculation as adjustable parameters and thus rotomer averaging is readily treated. Both the lanthanide-oxygen distance and the lanthanide-oxygen-sulphur bond angle are adjustable parameters in the programme as are the possible mixtures of conformers. Each of these parameters

were adjusted to obtain the lowest R value although only those calculations which arose from chemically reasonable substrate-shift reagent structures were considered, e.g. any calculations which produced a metal-oxygen distance of <2.0 or >3.0 Å were disregarded.

5.5 Results

All of the cis sulphoxides gave their best correlation in the diequatorial conformation. Any attempts to mix in small amounts of the diaxial conformation always lead to considerably poorer results. The best correlations tended to locate the lanthanide relatively close to the oxygen at ∿2.0 Å (or even less if allowed to do so) with a lanthanide-oxygen-sulphur bond angle of about 170°. This compares with a europium-oxygen bond length of 2.40 Å and a europium-oxygen-sulphur bond angle of 141° as measured by X-ray diffraction for a 1:1 complex of 3,3-dimethylthietan 1-oxide and $Eu(dpm)_3$.[113] Similarly the 3,3-disubstituted compounds preferred the equatorial oxygen conformation very strongly. Once again, the best correlations tended to have the lanthanide located relatively close to the oxygen although the lanthanide-oxygen-sulphur bond angle tended to be more acute (120-150°). Attempts to improve correlations by mixing small amounts of the axial-oxygen conformation were again not very successful. Factors contributing to these variations in the location of the lanthanide are uncertainties in the lanthanide induced shift and the geometry of the ring. The assumption was made that all thietan

rings have the same dihedral angle. This is not a bad assumption at least for the equatorial oxygen sulphoxides, since thietan 1-oxide, 3,3-dimethylthietan 1-oxide and cis and trans p-chlorophenyl-thietan 1-oxides all have ring pucker angles within a few degrees of one another.

Conversely, in the case of the trans isomers, the best correlations for all the compounds studied tended to have a somewhat longer lanthanide-oxygen bond length (2.5-3.0 Å or longer if allowed to do so) with farily acute lanthanide-oxygen-sulphur bond angles (100-125°). All trans isomers preferred the equatorial oxygen conformation to varying degrees as shown in Table 5.1.

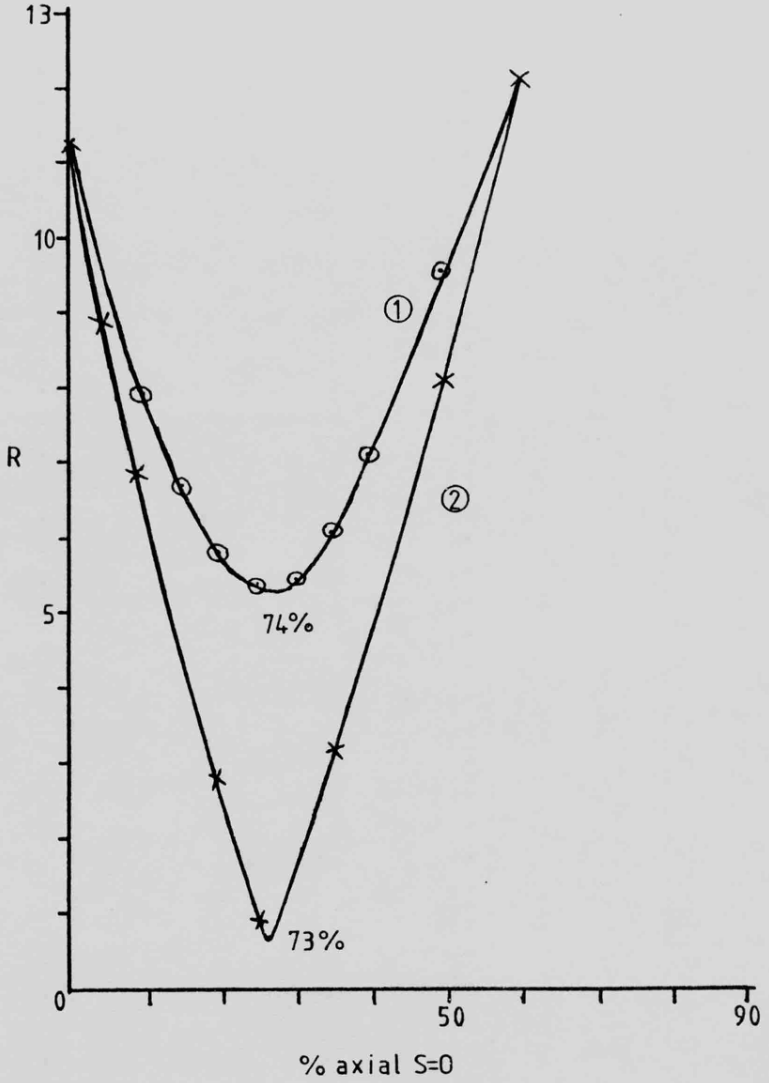
Table 5.1.

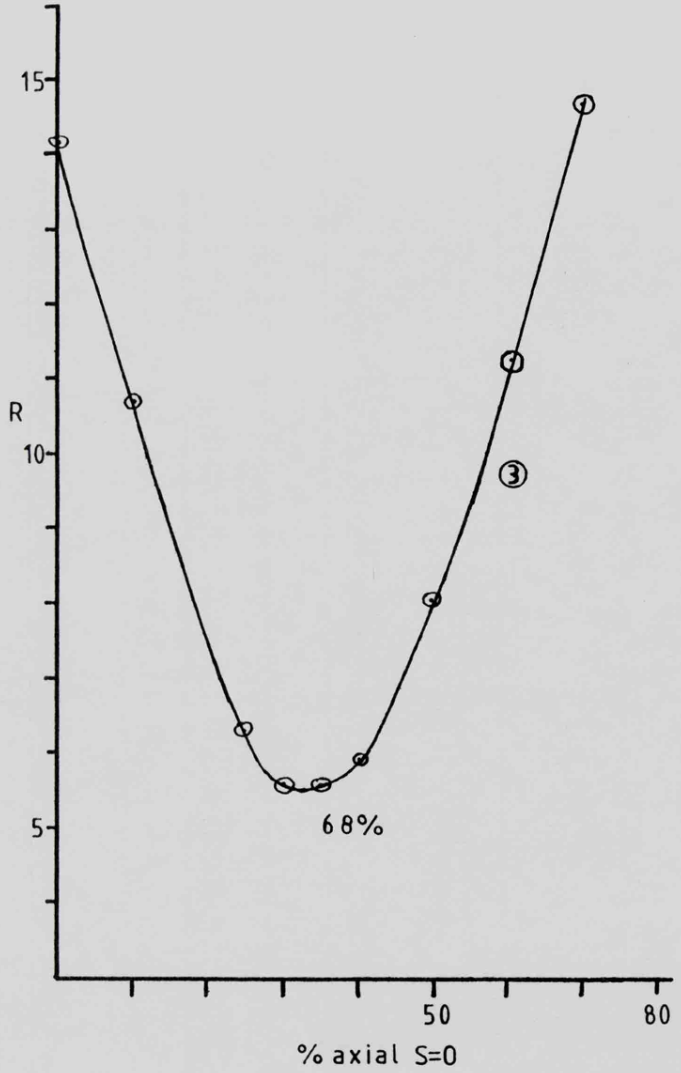
The % Equatorial Oxygen Conformation of Some 3-Substituted Thietan 1-Oxides

R	% Equatorial Oxygen Conformation
C_6H_5	74 ± 20
p-Br-C_6H_4	73 ± 3
t-Bu	65 ± 20

The trends are quite reasonable. The t-butyl group (well known for its ability as a conformational anchor) shows a marked

Figs. 5.2 & 5.3 Plots of the R factor against % equatorial oxygen conformation for 1) trans 3-phenyl thietan 1-oxide, 2) trans 3-p-bromophenylthietan-1-oxide, and 3) 3-t-butylthietan-1-oxide.



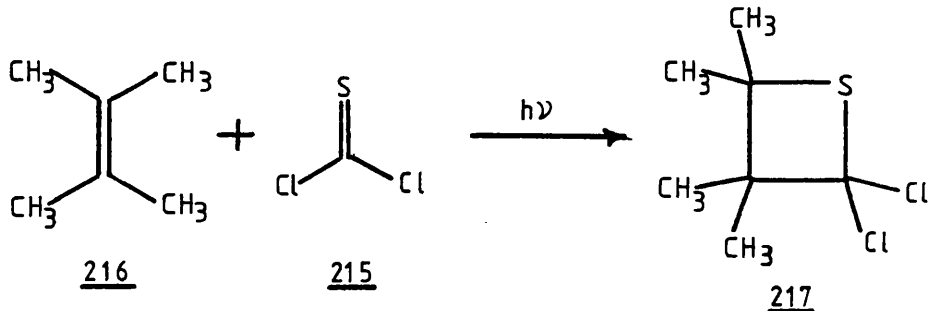


preference for the equatorial position compared with the two aromatic substituents which both show a similar disposition. The ranges arise because various lanthanide locations were explored in an effort to test the sensitivity of the correlation to this parameter. Plots of the R factors against % of conformation (Figures 5.2 and5.3) show the sensitivity of the correlations to this conformational parameter. The ranges given in Table 5.1 represent the amount that the conformational percentage must be changed in order to cause the R-factor to increase by 1.7. A change of this magnitude represents the 95% confidence level for a hypothesis test of order (4,1) using Hamilton statistics.[123] In this method, the lanthanide was placed so as to obtain the best correlation, and the location of the metal was assumed to be the same in both conformations. Models suggested that this was a reasonable approximation.

However, in an effort to test this hypothesis it was necessary to perform the same analysis with conformationally locked thietans since it is possible that the conformational preference of the molecules studied were significantly influenced by the coordination of the shift reagent itself. At the same time these should prove to be useful models in themselves.

The first attempts towards the synthesis of these molecules were based on the attempted photoaddition of thiophosgene to olefins.

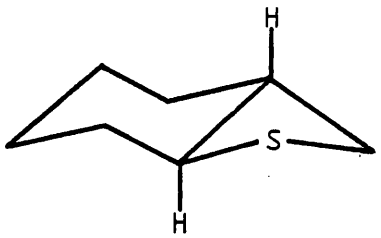
The photochemical addition of thiophosgene (215) to 2,3-dimethylbut-2-ene (216) has been described by Gotthardt.[124]



216 215 217

Irradiation of a mixture of (215) and (216) in benzene with light of wavelength > greater than 455 nm gave the thietan (217) in 51% yield. In the same way 2-methylbut-2-ene and 2,4-dimethylpenta-2,3-diene were also reacted.

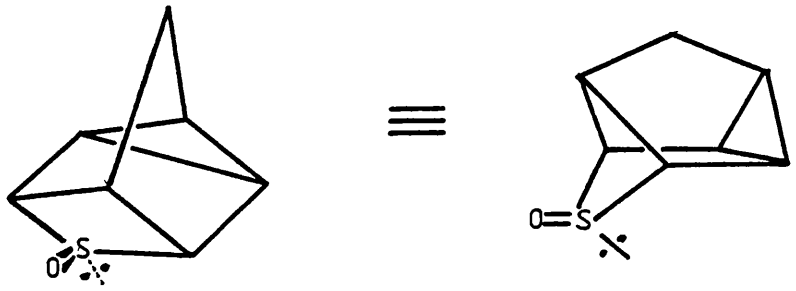
It was found that a thietan ring fused with a cyclohexyl ring (218) in the configuration shown below would be a rigid structure and therefore an attempt was made to photochemically add thiophosgene and cyclohexene using the method described by Gotthardt with cyclohexene used as the solvent.



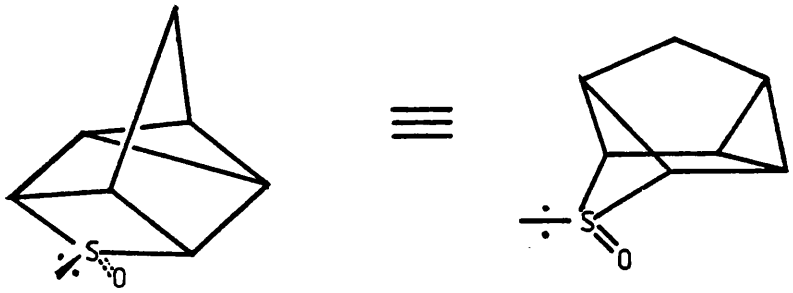
218

Although the Woodward-Hoffmann rules only allow a concerted cis addition, it was thought that the presence of two radical stabilising chlorine atoms would favour a non-concerted radical path. Any isomers formed should be separable by chromatography. In the event however, no reaction had taken place after five days irradiation. An analogous reaction was tried with thiophosgene and norbornylene, however no reaction was observed after irradiation for 18 hours at 589 nm.

The locked thietan 1-oxides (219) and (220) based on examples described by Lautenschlaeger[125] were finally chosen for study.

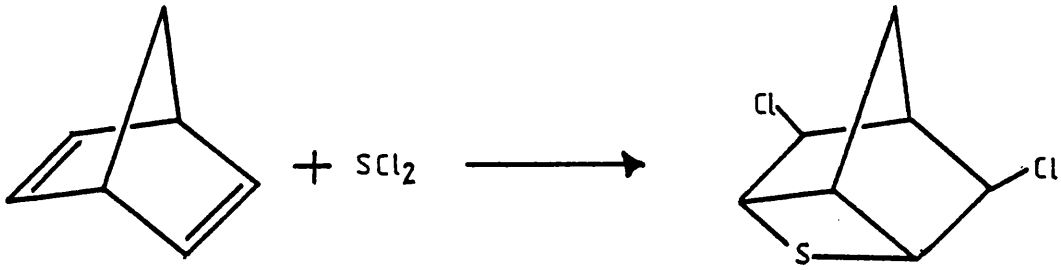


219 exo - axial oxygen



220 endo - equatorial oxygen

The initial skeleton is made by the reaction of sulphur dichloride and bicyclo[2.2.1]hepta-2,5-diene, to give the addition product (221).



221

Reaction of (221) with an aqueous solution of sodium carbonate gave the exo sulphoxide (219) directly.

Reduction of (219) with lithium aluminium hydride was found to give a mixture of starting material and the corresponding sulphide, from an analysis (n.m.r.) of the crude reaction product. Oxidation of this material, without purification, with an excess of sodium metaperiodate gave a mixture of the sulphone (83), and the endo sulphoxide (220) which were separated by column chromatography. There was no trace of any exo isomer present in this mixture. This can be explained if the rate of oxidation of the exo isomer (to give the observed sulphone) is greater than that of the endo isomer. Models show that the endo site of the sulphur atom is more sterically accessible than the exo site and is therefore more likely to undergo further oxidation.

^{1}H and ^{13}C lanthanide shift analysis of these sulphoxides using $Yb(fod)_3$ has confirmed the disposition of the sulphinyl oxygen in the proposed structures and has confirmed shift data obtained by Lemal et al[126] for the exo isomer only. For either compound, the

lanthanide-oxygen distances tend to be somewhat short (2.0-2.3 Å) while the lanthanide-oxygen-sulphur bond angle for the endo isomer is larger (150-160°) than for the exo isomer (120-130°). Larger angles were also calculated for the equatorially locked cis-3-substituted thietan 1-oxides as well as the 3,3-disubstituted compounds. These results support theprevious assumption that the lanthanide is similarly located in either conformation. They also suggest an alternative approach for the conformational analyses of the trans sulphoxides. The lanthanide locations for (219) and (220) could be assumed to hold for the respective conformations of the trans sulphoxides. Using these lanthanide locations the conformational percentages that gave the best fits are listed in Table 5.2.

Table 5.2

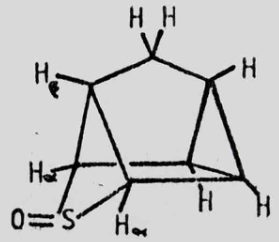
The % Equatorial Oxygen Conformations of Some 3-Substituted Thietan 1-Oxides (2nd Method)

R	% Equatorial Conformation
C_6H_5	76
p-BrC_6H_5	75
t-Bu	74

The results of both methods seem to compare favourably.

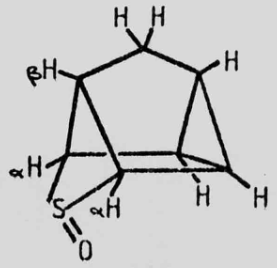
The n.m.r. spectra of (219) and (220) (Figures 5.4 and 5.5)

Fig. 5.4



219

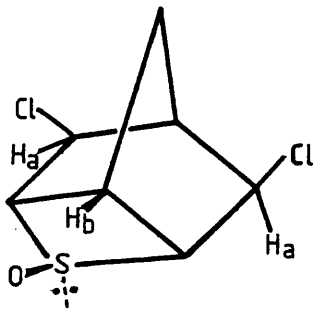
Fig. 5.5



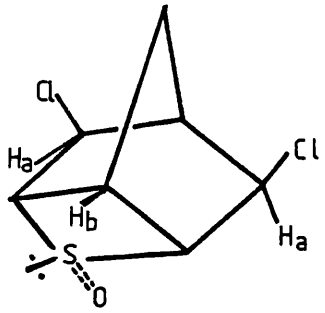
220

are interesting, and show some features in common with the 3-substituted thietan 1-oxides discussed previously. In the endo (equatorial oxygen) isomer, the β-proton of the thietan ring, at the bridgehead position is found to resonate at τ 8.00, whereas the β-proton of the exo (axial oxygen) isomer shows a massive deshielding, and is found to resonate at τ 5.60, a difference of 2.40 p.p.m. This effect is due, as discussed before, to the anisotropy of the sulphur-oxygen bond in a syn axial position, although the magnitude of this deshielding (compared with a difference of 1.06-1.16 p.p.m. in the conformationally mobile molecules described above), must reflect the rigidity of these molecules in which the β-proton and the sulphoxide bond are held in a more nearly diaxial conformation. The observed magnitude of this effect must represent almost the extreme values. It must be said that these rigid systems and the 3-substituted thietan 1-oxides described earlier cannot be strictly compared with one another since the geometry of the thietan rings are slightly different. In the rigid structures the ring pucker angle was measured to be 43° from molecular models, while it was taken to be 35° for all other thietan 1-oxides. The α-protons in the rigid thietan 1-oxides were not found to be much affected by the disposition of the sulphinyl oxygen (τ 6.70 in the exo isomer as opposed to τ 6.40 in the endo isomer), but this is to be expected since in both isomers the α-protons adopt a pseudo-equatorial position w.r.t. the thietan ring and are hence not affected by coaxial lone-pair interactions.

Lautenschlaeger[127] has previously assigned the stereochemistry of two similar sulphoxides (222) and (223) by ^1H n.m.r.



222

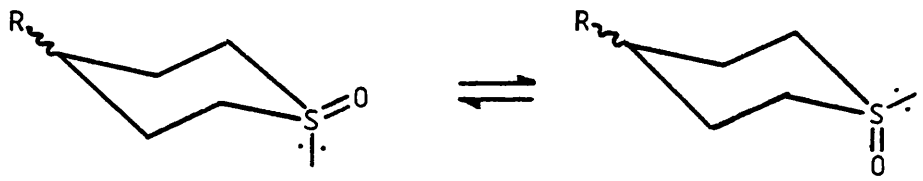


223

Assignment was based on the anisotropic effect of the sulphoxide bond on the β-protons H_a and H_b. The chemical shift difference of the protons H_b in the two isomers was found to be 1.59 p.p.m. and the fact that this value is lower than that obtained for our molecule probably reflects the slightly increased conformational mobility of this structure compared with our examples. Protons H_a also show some anisotropic effects of the sulphoxide bond. In the <u>endo</u> isomer (223) protons H_a are found to be deshielded by 1.53 p.p.m. compared with the <u>exo</u> isomer (222) in which the H_a protons show the same chemical shift as the corresponding sulphide. This effect is also shown in our molecules where the signals for H_a occurs at τ 8.2 in (219) and 7.73 in (220). In this case the difference is smaller than observed for (222) and (223) but this is probably because the protons at this position in (219) and (220) are further away from the sulphoxide bond than in (222) and (223) and are hence less affected by the anisotropic field.

The strong preference for oxygen to go equatorial in conformationally mobile 3-substituted thietan 1-oxides has been supported by oxidation studies[112] and equilibration studies using hydrogen chloride.[20] For 3-methylthietan 1-oxide, an energy difference between the two isomers of approximately 1.0 kcal/mole at 25°C has been calculated from the equilibrium mixture composition, although the assumption was made that the trans isomer existed predominantly in the axial oxygen conformation which we have shown not to be the case.

Conversely, in the case of thietan 1-oxide and cis and trans 3-substituted thietan 1-oxides (224) it has been established that the preferred conformation is a chair in which there is a slight preponderance of the axial oxygen conformer (224B).[110d,128]



224A 224B

Calculations[129] have suggested that this may arise from an attractive Van der Waals interaction between the oxygen atom and carbons 3 and 5 or their attached axial protons. There are no repulsive interactions between the oxygen and carbons 3, 4, and 5 or any of their attached hydrogens for either conformation of the oxygen.

5.6 Conclusion

This study has verified previous work describing the general diequatorial conformational preference of cis-3-substituted thietan 1-oxides although the results obtained suggest that in solution at least, this conformer is exclusive. For the trans substituted sulphoxides however, the correlations consistently point to a preponderance of the equatorial oxygen conformer (i.e. with the substituent axial). This trend is opposite to that described by previous workers[112] who have explained the ^{1}H n.m.r. spectra of these systems on the assumption that the major conformer was that with the substituent equatorial. It is possible that the minor conformer does in fact give rise to the observed phenomena and that the anisotropic effect of the sulphoxide bond may be much greater than has been previously thought.

EXPERIMENTAL

Instrumentation

Infrared spectra were recorded on a Perkin-Elmer 237 grating spectrometer or a Perkin-Elmer 580 grating spectrometer. Mass spectra were determined at 70 eV with an A.E.I. MS9 instrument or a V.G. Micromass 16B instrument, with a gas chromatograph attachment. In each case, the molecular ion is given first, followed by peaks of structural significance.

Nuclear magnetic resonance spectra were recorded on a Varian T60 instrument with a locking facility, using deuteriochloroform as the solvent and tetramethylsilane (TMS) as internal standard unless otherwise stated. Spectra run at 100 MHz were recorded on a JEOL PS100 instrument. ^{13}C n.m.r. spectra were recorded on a JEOL FX60 instrument, at 15 MHz, operating in the fourier transform mode, with TMS as internal standard.

Melting points were determined on a Kofler heating stage, and are uncorrected. Gas-liquid chromatography was carried out on a Pye-Unicam series 104 chromatograph.

General

Solutions in organic solvents were dried over anhydrous magnesium sulphate, and a rotary evaporator was used for reduced pressure solvent removal unless the volatility of the products under

reduced pressure was considered too great. Light petroleum had a boiling point of 40-60°C. Diethyl ether, 40-60°C and 60-80°C petrol, benzene, and toluene were stored over sodium wire. 60-80°C Petrol used for recrystallising, was distilled before use rejecting any fraction that boiled above 80°C. Methanol and ethanol were refluxed over, and distilled from their magnesium alkoxides. Acetonitrile was dried and fractionally distilled from phosphorus pentoxide, through a four foot column of glass helices, to render it free from benzene impurities. The fractions were analysed for benzene using a U.V. spectrometer.

Column chromatography on silica was carried out using Silica M.F.C. or Keiselgel 80 PF_{254}, supplied by E. Merck, for preparative layer chromatography, with the solvent under slight positive pressure. Peracetic acid solution used for oxidation of sulphides to sulphones, was supplied by Laporte Ltd.

Photolyses were carried out in a Rayonet photochemical reactor fitted with lamps emitting light of the required wavelength. The solutions were contained in quartz tubes and all solvents were degassed immediately prior to use.

General method fo oxidising sulphides to sulphones using peracetic acid solution

The sulphide was slowly added in portions to an excess of a solution of peracetic acid (40% supplied by Laporte) and stirred at 0°C.

The mixture was then allowed to stir at room temperature for at least 2 days. The mixture was then poured into 10 volumes of water with stirring, and extracted three times with dichloromethane. The combined organic fractions were washed with an aqueous sodium carbonate solution and dried ($MgSO_4$). Removal of the solvent gave the crude sulphone.

CHAPTER ONE

Preparation of 2-phenylthietan 1,1-dioxide (60)

2-Phenylthietan was prepared using the method described by Schaal[34] except that sodium sulphide was used as the reagent for the cyclisation step, instead of thiourea.

Dry sodium sulphide (19 g) was dissolved in a mixture of water (20 ml) and ethanol (23 ml). A three necked flask (100 ml) was assembled with two dropping funnels and a condenser. Some of the sodium sulphide solution (10 ml) was allowed to heat under reflux in the flask with stirring, while the remainder was held in one of the dropping funnels. The previously prepared 1-phenyl, 1-chloro,3-bromopropane (9.80 g) was held in the second dropping funnel, and simultaneous dropwise addition of each of the contents of the dropping funnels was carried out at reflux temperatures. On completion of the addition, the mixture was heated under reflux for 2 h, after which it was diluted with water (100 ml), and extracted with dichloromethane. Drying and removal of the solvent gave an opalescent oil, which on distillation afforded 2-phenylthietan as a clear oil (4.6 g, 73%), b.p. 90°C at 0.2 mm pressure. The n.m.r. spectrum agreed with that quoted.[34]

The sulphide was oxidised with peracetic acid (20 ml, page 145) to give 2-phenylthietan 1,1-dioxide (60) as a white crystalline material (4.70 g, 84%), m.p. 82-84°C (chloroform-petrol), τ 2.43-2.60 (5H, m), 6.48 (1H, t, J = 9.5 Hz), 5.60-6.08 (2H, m), and 7.14-7.83 (2H, m), ν_{max} (dichloromethane), 1498, 1458, 1322, 1190, and 1130 cm^{-1}.

m/e 182, 118, 117, 103, 91, 78, and 77. (Found: C, 59.43; H, 5.43; S, 17.59. $C_9H_{10}O_2S$ requires C, 59.32; H, 5.53; S, 17.59).

Preparation of cis and trans 2,4-diphenylthietan 1,1-dioxide (31)[15]

Thiol acetic acid (10 g, 0.131 ml) was slowly added to a solution of benzilidene acetophenone (23.2 g, 0.112 mol) in carbon tetrachloride (56 ml) with stirring at room temperature, whilst being illuminated with a 100 W lamp. A rise in temperature to 53°C was observed, which then fell slowly back after a few minutes. After stirring for 1 h, the solvent and excess acid were removed under reduced pressure, to give the addition product as a buff coloured solid, in an almost quantitative yield, τ 1.79-2.09 (2H, m), 2.30-2.84 (8H, m), 4.65 (1H, t, J = 7 Hz), 6.30 (2H, d, J = 7 Hz), and 7.71 (3H, s).

Some of the above compound (10 g) was slowly added in portions to a stirred mixture of lithium aluminium hydride (2 g) in diethyl ether at 0°C. The reaction was warmed to room temperature and, after refluxing for 1 h, the reaction was quenched in the usual way. Normal work-up procedures gave a pale yellow opalescent oil, ν_{max} 3380 cm^{-1}, τ 2.68 (broad s), 5.00-6.02 (m), 6.85-7.21 (broad resonance), and 7.40-8.12 (m).

This product was stirred in concentrated hydrochloric acid (50 ml) for 2 h at room temperature. Dilution with water (120 ml) and

extraction with dichloromethane gave, after work-up, a pale green oil (7.2 g); the infrared spectrum showed a very much reduced hydroxyl band.

This product was stirred and heated in a twice molar excess aqueous solution of sodium hydroxide for 4 h. At the end of this time, the mixture was cooled to room temperature, extracted with ether and dried. Removal of the solvent yielded a brown solid (5 g). This was dissolved in hot petrol, to give a tarry insoluble oil and a clear solution which was decanted. Removal of the solvent gave crude cis and trans 2,4-diphenylthietan. Fractional crystallisation of this mixture from a petrol-chloroform mixture gave pure trans 2,4-diphenyl thietan (0.7 g) after two recrystallisations. The n.m.r. spectrum showed the symmetrical A^2B^2 system expected for that isomer.

Oxidation of the cis and trans mixture or the trans sulphide with peracetic acid (page 145) gave respectively the cis and trans sulphones and the trans sulphone. M.p. of trans sulphone 165-167°C (lit.[15] 166-167°C). m/e 194 (no molecular ion detected), 193, 179, 178, 116, 115, 103, 91, 78, and 77.

Attempted preparation of 2-phenyl-4-p-methoxyphenylthietan 1,1-dioxide

This was prepared by the same method as described for 2,4-diphenylthietan above, using 4-methoxychalcone. Cyclisation of the γ-chlorothiol (8.7 g), resulting from the first three steps, using

the same method, resulted in a viscous opalescent oil (5.2 g). Extraction of this oil with hot petrol gave a slight yellow oil (3.5 g).

Purification of some of this product (1 g) by column chromatography on silica (40 g) eluting with 40% petrol-ether gave 2-phenyl, 4-p-methoxyphenylthietan as a clear oil. ν_{max} 1620, 1250 cm^{-1}. τ 2.18-3.20 (9H, m), 4.86-5.28 (2H, m), 4.19 (3H, s), and 6.40-6.90 (2H, m).

Numerous attempted oxidations of this material with either peracetic acid or m-chloroperoxybenzoic acid gave a breakdown of the starting material to a yellow-red polymeric oil, of an indeterminate nature.

Attempted preparation of 2-methyl-4-phenylthietan 1,1-dioxide

This preparation was attempted using benzylidene acetone as the starting material and using the same methods as described for 2,4-diphenylthietan above. The sequence could not be completed however, because the intermediate γ-hydroxy thiol could not be chlorinated, even after prolonged stirring in concentrated hydrochloric acid, with heating.

3-Methyl-3-phenylthietan 1,1-dioxide[35]

2-Methyl-2-phenylpropane 1,3-diol was prepared by the Tollers condensation of 2-phenylpropionaldehyde (45.2 g) and a 40% aqueous

solution of formaldehyde (105 g) in the presence of anhydrous potassium carbonate (33.7 g), ethanol (100 ml) and water (30 ml). The reactants were refluxed together for 5 h, after which most of the volatile material was removed on a rotary evaporator, and the residues dissolved in dichloromethane.

The insoluble materials were removed by filtration and washed with dichloromethane after which the organic solutions were combined and the solvent removed to give a heavy viscous oil (21 g) which solidified on standing to give a white solid.

Some of this diol (18.5 g) was dissolved in dry pyridine (110 ml) and stirred at $0^{\circ}C$. To this was added dropwise, 2.2 equivalents of benzene sulphonyl chloride, while maintaining the temperature below $12^{\circ}C$ by the use of an ice bath. When the addition was complete, the mixture was allowed to warm to room temperature and stirred overnight. The product was isolated by pouring the resultant mixture into water (370 ml) while stirring vigorously. Filtration of the resultant precipitate yielded the crude dibenzenesulphonate ester as a pink solid, which was washed with water, 2M hydrochloric acid, water, and air dried to give the ester which was considered pure enough for direct use.

Toluene (100 ml) was added to a mixture of crushed sodium sulphide nonohydrate (24.5 g) and dimethyl sulphoxide (200 ml), and the mixture heated under reflux with a Dean-Stark apparatus collecting

the water which began to appear at 120°C. When about 15 ml of water had been azeotroped from the system, the excess of toluene was removed by applying a slight vacuum on the system. The resultant DMSO solution appeared slightly green with small gummy residues inside the flask. The solution was cooled to 90°C, and some of the previously prepared dibenzenesulphonate ester (30.4 g) was added to the stirred solution over a period of 1 h. The mixture was stirred at 90°C for a further 1½ h, after which it was cooled and poured into water (1 litre). The aqueous solution was extracted with light petroleum (5 x 100 ml), and the combined petrol extracts washed with fresh water (2 x 100 ml). Drying and removal of the solvent gave a yellow oil (15 g), which on distillation afforded 3-phenyl-3-methylthietan (12 g) as a yellow oil, b.p. 140-160°C at 15 mm. τ 2.52-3.18 (5H, m), 6.21 (2H, d, J = 9 Hz), 7.01 (2H, d, J = 9 Hz), and 8.22 (3H, s).

Some of this material (2 g) was oxidised with peracetic acid (10 ml) as described on page 145 , to give 3-phenyl-3-methylthietan 1,1-dioxide as a white crystalline solid (2.1 g, 84%), m.p. 48-49°C (chloroform-petrol), τ 2.29-2.88 (5H, m), 5.61 (4H, A'B' quartet), and 8.18 (3H, s), ν_{max} (dichloromethane) 1409, 1330, 1226, 1142, and 1089 cm^{-1}. m/e 196, 132, 118, 117, 103, 91, 78, and 77. Found : C, 61.32; H, 6.36 ; S, 16.30. $C_{10}H_{12}SO_2$ requires C, 61.20; H, 6.16; S, 16.34.

Preparation of 2-phenyl-2-methylthietan 1,1-dioxide (79)

An equivalent amount of n-butyl-lithium solution was added over a period of 20 min to a stirred suspension of 2-phenylthietan 1,1-dioxide (0.5 g, 2.74 mmol) in dry ether (25 ml) at -78°C under an atmosphere of dry nitrogen. The mixture was then stirred at -78°C for 1 h to give a clear yellow solution. An excess amount of methyl bromide (0.5 ml, 4.36 mmol) was dissolved in dry ether (8 ml), and added dropwise to the cooled solution over a period of 10 min. The mixture was then allowed to warm up to room temperature and stirred for a further 2 h. At the end of this time, the reaction was quenched with water (5 ml) and stirred vigorously to dissolve the lithium bromide formed in the reaction. The clear ether layer was separated and dried. Evaporation gave a pale opalescent oil. This could not be crystallised, but chromatography on silica (50 g) eluting with ether gave 2-phenyl-2-methylthietan 1,1-dioxide (79) (0.23 g, 43%). m.p. 77-78°C (chloroform-petrol), ν_{max} (dichloromethane), 1315, 1182 and 1130 cm^{-1}. τ 2.40-2.70 (5H, m), 5.50-6.32 (2H, m), 6.82-6.97 (2H, m), and 8.05 (3H, s). m/e 196, 132, 131, 117, 91, and 77. (Found: C, 60.99; H, 6.12; S, 16.74. $C_{10}H_{12}O_2S$ requires C, 61.19; H, 6.16; S, 16.34). ^{13}C n.m.r. 22.16, 25.89, 60.22, 87.49, 125.97, 128.15, 128.73, and 137.80,(p.p.m.).

Preparation of 2-phenyl-2-ethyl thietan 1,1-dioxide (80)

An equivalent amount of n-butyl-lithium solution was added over a period of 5 min to a stirred suspension of 2-phenylthietan 1,1-dioxide (0.5 g, 2.74 mmol), in dry ether (20 ml) at -78°C, under

an atmosphere of dry nitrogen. The mixture was then stirred at -78°C for 15 min to give a pale yellow solution. An excess solution of ethyl iodide (0.30 ml) dissolved in dry ether (8 ml), was added dropwise over a period of 10 min. The mixture was then allowed to slowly warm up to room temperature and stirred for one hour, during which time a misty precipitate gradually became apparent. After 1 h, the reaction was quenched with water (5 ml) and after vigorous stirring for 1 min, the clear ether solution was separated, dried, and evaporated to give a white opalescent oil. Crystallisation and recrystallisation of this oil gave 2-phenyl-2-ethylthietan 1,1-dioxide (80) (0.32 g, 55%). m.p. 101-102°C (chloroform-petrol), ν_{max} (dichloromethane), 1500, 1450, 1310, 1175, and 800 cm^{-1}, τ 2.32-2.91 (5H, m), 5.60-6.40 (2H, m), 7.10-7.97 (4H, m), and 9.22 (3H, t, J = 7.5 Hz), m/e molecular ion not detected, 146, 117, 91 and 77. (Found: C, 62.83; H, 6.71; S, 15.10. $C_{11}H_{14}O_2S$ requires C, 62.82; H, 6.71; S, 15.24.) ^{13}C n.m.r. 8.60, 19.15, 30.92, 60.06, 92.45, 126.62, 128.08, 128.64, and 135.71,(p.p.m.).

Preparation of 2-phenyl-2-benzylthietan 1,1-dioxide (81)

An equivalent amount of n-butyl-lithium solution was added over a period of 18 min to a stirred suspension of 2-phenylthietan 1,1-dioxide (0.5 g, 2.74 mmol) in dry ether (25 ml) at -78°C under an atmosphere of dry nitrogen. The mixture was stirred for a further 10 min to give a clear, pale yellow solution. An excess of benzyl bromide (0.4 ml) dissolved in dry ether (8 ml) was added

dropwise over a period of 15 min. The mixture was then slowly warmed up to room temperature and was stirred for 24 h. At the end of this time, water (5 ml) was added to quench the reaction, after which the mixture was vigorously stirred for 1 min. Separation of the organic layer, drying, and removal of the solvent gave 2-phenyl-2-benzylthietan 1,1-dioxide (81) (0.43 g, 58%), m.p. 153-155°C, (chloroform-petrol). ν_{max} (dichloromethane) 3060, 1605, 1498, 1457, 1448, 1316, and 1218 cm^{-1}, τ 2.44-3.32 (10H, m), 5.70-6.25 (2H, m), 6.42 (2H, s), 7.33-7.69 (2H, m), m/e 272, 208, 194, 181, 117, 104, 91, and 77. (Found: C, 70.49; H, 6.15; S, 11.84. $C_{16}H_{16}O_2S$ requires C, 70.56; H, 5.92; S, 11.77).

Preparation of 2-phenyl-2-allylthietan 1,1-dioxide (82)

An equivalent amount of n-butyl-lithium solution was added over a period of 20 min to a stirred suspension of 2-phenylthietan 1,1-dioxide (0.5 g, 2.74 mmol), in dry ether (30 ml), at -78°C under an atmosphere of dry nitrogen. The mixture was stirred for 1 h to give a clear yellow solution. An excess of allyl bromide (0.5 ml) dissolved in dry ether (10 ml) was added dropwise over a period of 30 min to the stirred solution. The mixture was allowed to stir for 30 min at -78°C after which it was warmed to room temperature and stirred for a further 48 h. At the end of this time a pale mistiness was observed in the mixture. Water (5 ml) was added to quench the reaction and dissolve the precipitate. The mixture

was vigorously stirred for 1 min, and the clear ether layer was separated and dried. Evaporation of the solvent gave an orange oil. Attempts at crystallisation failed, but chromatography on silica (40 g) using 20% ether in light petroleum gave 2-phenyl-2-allylthietan 1,1-dioxide (82) (0.28 g, 46%), m.p. 61-63°C (chloroform-petrol), ν_{max} (dichloromethane), 3063, 3032, 1642, 1498, 1448, 1317, 1174, and 1125 cm^{-1}. τ 2.40-2.84 (5H, m), 4.32-5.00 (3H, m), 5.72-6.30 (2H, m), 7.01 (2H, d, J = 7 Hz), 7.12-7.88 (2H, m), m/e 222, 181, 158, 143, 129, 117, 115, 91, and 77. (Found: C, 64.89; H, 6.38; S, 14.83. $C_{12}H_{14}O_2S$ requires C, 64.83; H, 6.35; S, 14.42). ^{13}C n.m.r. 18.58, 42.44, 60.22, 90.49, 120.2, 126.53, 128.15, 128.64, 130.99, and 135.78, (p.p.m.).

Attempted reaction of the 2-phenylthietan 1,1-dioxide anion with epibromohydrin

This reaction was attempted using the same method as described for the previous preparations of disubstituted thietan sulphones, with epibromohydrin and the anion of the thietan. The mixture was stirred for 4 h after which work-up gave a pale yellow oil. The n.m.r. showed some starting material present and t.l.c. analysis on silica eluting with ether, showed three spots off the base line.

Chromatography on silica gel (50 g) eluting with a 1:1 ether-petrol mixture rising to 2% methanol in ether led to the isolation of a small amount of a clear oil (50 mg) with an n.m.r. spectrum approx-

imating to that expected for the product, τ 2.32-2.90 (5H, m), 5.65-6.30 (2H, m), and 6.84-7.90 (7H, m), dichloromethane impurity peak at τ 4.72.

Numerous attempts were made to try and improve this yield, however these were unsuccessful.

Attempted reaction of 2-phenylthietan 1,1-dioxide anion with propylene oxide

A slight excess of propylene oxide was added to the anion generated from 2-phenylthietan 1,1-dioxide (0.5 g) and an equivalent amount of butyl-lithium solution as described previously. After stirring for 4 h, normal work-up procedures gave a viscous yellow oil. The t.l.c. plate on silica using ether as the eluent showed at least six different compounds present, and this reaction was abandoned.

Attempted reaction of 2-phenylthietan 1,1-dioxide anion with ethyl chloroformate

A slight excess of ethyl chloroformate was added to a solution of the anion generated from 2-phenylthietan 1,1-dioxide (0.5 g) and butyl-lithium. The reaction was worked-up after stirring overnight to give a slightly yellowish oil. The n.m.r. spectrum showed a mixture of unreacted starting materials only.

Thermolysis of 2-phenylthietan 1,1-dioxide (60)

The sulphone (243 mg) was sublimed through the apparatus at 0.015 mm pressure with the furnace at 450°C to obtain phenylcyclopropane (150 mg, 95%) which was identified by comparison of the n.m.r. spectrum with that of a known sample. The material gave only one peak on g.l.c. analysis (3% OV17 at 110°C, flow rate 60 ml min^{-1}) retention time 3 min.6 sec. Thermolysis of the sulphone under the same conditions with the furnace at 600°C gave a mixture of three compounds as shown by the g.l.c. trace under the same conditions as above; retention times 1 min.51 sec, 2 min.28 sec, and 3 min.6 sec. From known n.m.r. spectra, these were identified as mainly phenylcyclopropane with small amounts of cis and/or trans β-methylstyrene and allylbenzene. G.l.c./mass spectral analysis of the peaks showed them all to have a molecular ion at m/e = 118 (which corresponds to loss of sulphur dioxide) and very similar breakdown patterns. Thermolysis of the sulphone under the same conditions with the furnace at 750°C gave cis and/or trans β-methylstyrene and allylbenzene only, as identified by comparison of the n.m.r. spectrum of the product with that of published spectra. G.l.c. analysis under the same conditions showed three compounds present.

Thermolysis of phenylcyclopropane

Phenylcyclopropane (120 mg) was sublimed through the apparatus at 0.015 mm pressure with the furnace at 750°C. The product was shown to be unchanged starting material by n.m.r. spectroscopy.

Photolysis of 2-phenylthietan 1,1-dioxide

2-Phenylthietan 1,1-dioxide (0.5 g) was dissolved in dry methanol (150 ml) and irradiated at 253 nm for 20 h. The resultant slightly yellowish solution was evaporated using a water pump at room temperature, to give a yellow oil with a slight trace of a precipitate. The n.m.r. spectrum showed phenylcyclopropane which was identified by comparison with a known sample, and a small amount of starting material. The material gave only one peak on g.l.c. analysis (10% E30 at 83°C, flow pressure 12 p.s.i.), retention time 11 min.2 sec.

Thermolysis of trans 2,4-diphenylthietan 1,1-dioxide

The sulphone (100 mg) was sublimed through the apparatus at 0.003 mm pressure with the furnace at 500°C. A mixture of cis and trans 1,2-diphenylcyclopropane in the approximate ratio of 23% cis and 77% trans, was obtained as a yellow oil. The two isomers were identified by comparison of the n.m.r. spectrum with that described by Curtin et al.[36]

Thermolysis under the same conditions with the furnace at 400°C gave a mixture of starting material (26%) and cis and trans 1,2-diphenylcyclopropane, in the ratio of approximately 19% and 55% respectively, while at 300°C unchanged starting material was obtained.

Photolysis of cis and trans 2,4-diphenylthietan 1,1-dioxide (31)

An isomer mixture of cis and trans 2,4-diphenylthietan 1,1-dioxide (100 mg) was dissolved in acetonitrile (25 ml), and irradiated for 2 h.at 253 nm. Removal of the solvent gave a yellow oil which partially crystallised. N.m.r. examination showed this to be a mixture of starting material and 1,2-diphenylcyclopropane. Further irradiation under the same conditions for 12 h. gave a yellow oil after solvent removal. The n.m.r. analysis of this product showed a mixture of cis and trans 1,2-diphenylcyclopropane only, in the ratio of approximately 59% cis and 41% trans.

Thermolysis and photolysis of 2-phenyl-2-methylthietan 1,1-dioxide (79)

The sulphone (105 mg) was sublimed through the apparatus at 0.015 mm pressure with the furnace at 600°C. 1-Phenyl-1-methylcyclopropane was obtained as a colourless oil (61.2 mg, 87%), τ 2.50-2.90 (5H, m), 8.61 (3H, s), and 9.00-9.40 (4H, br, d, J = 7 Hz). This agrees with values quoted by Gibert and Seyden-Penne.[31] The material gave one peak only on g.l.c. analysis (3% OV17 at 150°C, flow pressure 5.5 p.s.i.), retention time 2 min. 2 sec.

The sulphone (20 mg) was dissolved in dry methanol (20 ml) and irradiated at 253 nm for 4 h, after which most of the solvent was removed under reduced pressure using a water pump. G.l.c. analysis of this product under the same conditions as for the therm-

olysis product, showed one main peak with the same retention time as the thermolysis product with three much smaller peaks after; there was not enough sample to carry out any further investigation into this.

Thermolysis and photolysis of 2-phenyl-2-ethylthietan 1,1-dioxide (80)

The sulphone (111 mg) was sublimed through the apparatus at 0.01 mm.pressure with the furnace at 600°C. A very pale yellow oil was obtained, τ 2.44-3.02 (5H, m), 8.42 (2H, q, J = 7.5 Hz), and 8.92-9.44 (7H, m), with a dichloromethane peak at 4.78 τ, ν_{max} (liquid film) 2978, 1460 and 1020 cm^{-1}. Distillation afforded 1-phenyl-1-ethylcyclopropane as a colourless oil (68 mg, 88%), b.p. 130°C at 5 mm. M/e = 146, 117, 105, 91, and 77. G.l.c. analysis showed only one peak (3% OV17 at 150°C, flow pressure 6 p.s.i.), retention time 3 min.4 sec. (Found: C, 89.44; H, 9.81. $C_{11}H_{14}$ requires C, 90.35; H, 9.65).

A further sample of the sulphone (100 mg.) was dissolved in dry methanol (20 ml) and irradiated at 253 nm while monitoring the reaction by g.l.c. under the same conditions as above. After 3 h the solvent was removed under reduced pressure on a water pump to give a clear oil. The n.m.r. spectrum showed the presence of 1-phenyl-1-ethylcyclopropane as was formed in the thermolysis, with possibly a small amount of unreacted starting material. This was

confirmed by g.l.c. analysis under the same conditions as described for the thermolysis; only one peak was given, retention time 3 min. 8 sec.

Thermolysis and photolysis of 2-phenyl-2-benzylthietan 1,1-dioxide (81)

The sulphone (112 mg) was sublimed through the apparatus at 0.015 mm.pressure, with the furnace at 600°C to give a pale yellow oil (76 mg). τ (100 MHz), 2.60-3.18 (10H, m), 7.10 (2H, s), and 9.19 (4H, s). ν_{max} (liquid film) 3030, 1604, 1497, 1453, and 1025 cm^{-1}, m/e 208, 108, 106, 92, and 78. G.l.c. analysis showed only one peak (3% OV17 at 200°C, flow pressure 6 p.s.i.), retention time 8 min.24 sec. Distillation afforded 1-phenyl-1-benzylcyclopropane as a colourless oil (71 mg, 83%), b.p. 160° at 15 mm. (Found: C, 91.97; H, 7.76; $C_{16}H_{16}$ requires C, 92.26; H, 7.74).

The sulphone (100 mg) was dissolved in dry methanol (20 ml) and irradiated at 253 nm for 3 h. Removal of the solvent gave a yellow oil which was confirmed to be 1-phenyl-1-benzylcyclopropane by n.m.r. and g.l.c. analysis as above.

Thermolysis and photolysis of 2-phenyl-2-allylthietan 1,1-dioxide (82)

The sulphone (113 mg) was sublimed through the apparatus at 0.007 mm.pressure, with the furnace at 600°C to give a pale yellow

oil, which on distillation afforded 1-phenyl-1-allylcyclopropane as a colourless oil (74 mg, 92%), b.p. 120°C at 20 mm. τ (100 MHz), 2.52-3.00 (5H, m), 4.00-4.32 (1H, m), 4.80-5.24 (2H, m), 7.64 (2H, d x d, J_1= 8 Hz, J_2= 1.5 Hz), and 9.08-9.40 (1H, m), ν_{max} (liquid film), 3081, 2252, 1642, 1602, 1496, 1445, and 1002 cm^{-1}, m/e 158, 143, 129, 117, 91, and 77. G.l.c. analysis showed only one peak (3% OV17 at 150°C, flow pressure 5 p.s.i.), retention time 3 min. 30 sec. (Found: C, 90.69; H, 9.04. $C_{12}H_{14}$ requires C, 91.08; H, 8.92).

The sulphone (90 mg) was dissolved in dry methanol (20 ml) and irradiated at 253 nm for 2h. while monitoring the change by g.l.c. Removal of the solvent, using a water pump, gave a light brown oil which was confirmed to be 1-phenyl-1-allylcyclopropane only from n.m.r. and g.l.c. analysis using the same conditions as described above.

Thermolysis of 8-thiatetracyclo[2.2.1.1.0]octane 8,8-dioxide

The sulphone prepared as described in Chapter 5 (110 mg) was sublimed through the apparatus at 0.007 mm.pressure, with the furnace at 700°C, to give a pale yellow oil, and a small amount of a white polymeric solid. The n.m.r. spectrum of the oil showed that this was mainly norbornadiene (bicyclo[2.2.1]hepta 2,5-diene) (80%), with some toluene (16%) and a trace amount of cyclohepta-

triene. This was confirmed from authentic n.m.r. spectra and g.l.c. analysis against standard samples (3% OV17 at 50°C, flow rate 42 ml. min^{-1}).

Thermolysis of this sulphone under the same conditions with the furnace at 600°, 508° and 400°C gave norbornadiene as the only product identified by n.m.r. Thermolysis at 300°C gave a mixture of starting material (86%) and norbornadiene (14%). No traces of tetracyclo[3.2.0.0.0]heptane were observed in any of the products although each thermolysis produced small amounts of a white, solid, polymeric material on the surface of the cold finger.

Thermolysis of norbornadiene at 720°C under the same conditions gave a mixture consisting of starting material (66%), toluene (12%) and cycloheptatriene (22%).

Photolysis of 3-phenylthietan 1,1-dioxide

A sample of the sulphone (200 mg), which had been prepared by Hall,[20] was dissolved in dry acetonitrile (30 ml) and irradiated at 253 nm. No change was observed after 15 h. Irradiation of the sulphone (300 mg) in dry methanol (150 ml) for 109 h. gave a yellow oil containing some solid. T.l.c. analysis of this oil on silica, using ether as the developing solvent showed three compounds. Chromatography on silica (45 g) led to the isolation of

a light yellow solid (108 mg) which was shown to be unreacted starting material, and a yellow-orange oil (60 mg). The n.m.r. spectrum of this oil was fairly featureless being composed of unresolved envelopes from τ 3.70 to 9.30, with no absorption in the aromatic region of the spectrum.

A further attempt was made by irradiating the sulphone (1.5 g) in methanol (250 ml) at 253 nm. for one week. Removal of the solvent after this time gave a dark yellow oil, the n.m.r. spectrum showed almost a complete loss of aromatic resonances with multiplets from τ 5.48-7.13 and smaller broad featureless resonances from τ 7.13-9.00. Attempts at separation of the components of this product by chromatography failed to isolate any pure material and the reaction was abandoned.

Thermolysis of 3-phenyl-3-methylthietan 1,1-dioxide

The sulphone (124 mg) was sublimed through the apparatus at 0.005 mm.pressure with the furnace at 750°C. A reddish glass was seen to collect on the surface of the cold trap which on warming gave a light yellow viscous oil. From the n.m.r. spectrum of this product could be identified unchanged starting material, 1-phenyl-1-methylcyclopropane and α-methylstyrene. No trace of α,β-dimethylstyrene was observed from n.m.r. details given by Corbiau and Bruylants.[37] G.l.c. analysis (3% OV17 at 100°C, flow pressure 7 p.s.i.) against standard samples of 1-phenyl-1-methylcyclopropane and α-methylstyrene showed them both to be present, although the cyclopropane was by far the major product, three other minor products were given and these remain unidentified.

CHAPTER TWO

Thiochroman-4-ol and thiochroman-4-ol 1,1-dioxide

Commercially available thiochroman-4-one (113) was reduced with sodium borohydride, using the general method for borohydride reductions outlined by Vogel,[58] except that absolute ethanol was used as the solvent. Yields were generally greater than 92%, m.p. 66-69°C, (lit. m.p.[59] 68-69°C).

Oxidation of this compound with peracetic acid or m-chloroperoxybenzoic acid gave the sulphone, m.p. 94-95°C, (lit. m.p.[50] 94-95°C).

Thiochroman-4-one-1-oxide (116)

Thiochroman-4-one (2 g, 12.1 mmol) was added to a solution of sodium metaperiodate (3.0 g, 14.02 mmol) in water (50 ml) and stirred for 36 h.at room temperature. Extraction of this solution with dichloromethane (3 x 10 ml) and usual work-up procedures gave crude thiochroman-4-one-1-oxide (2.1 g) as an orange oil. ν_{max} 1050 cm^{-1}, τ 1.40-2.55 (4H, m), and 5.95-7.35 (4H, m). This compound was used without further purification.

Thiochroman-4-one 1,1-dioxide

Commercially available thiochroman-4-one was oxidised by the method of Still and Thomas.[60] Crystallisation gave thiochroman-4-one

1,1-dioxide as a white solid, m.p. 134-135°C, (lit. m.p.[6] 130-132°C), τ 1.82-2.46 (4H, m), and 6.12-6.77 (4H, m), m/e 196, 168, 105, 104, and 76.

Isothiochroman-4-one and isothiochroman-4-one 2,2-dioxide

Isothiochroman-4-one was prepared using a method based on that of Kiang and Mann[69] from S-benzylthioglycolic acid. The method used for cyclisation was as follows: a solution of S-benzylthioglycolic acid (20 g) dissolved in chlorobenzene (20 ml) was added to a mechanically stirred mixture of phosphorus pentoxide (43 g), celite (40 g), and chlorobenzene (250 ml) under dry nitrogen. The mixture was stirred at room temperature overnight, and then heated to 100°C for 3 h. After cooling the slurry was filtered under reduced pressure,and the residue washed with chlorobenzene (2 x 50 ml) and dichloromethane (4 x 100 ml). Removal of the solvent under reduced pressure gave a dark oil which on bulb to bulb distillation (110°C at 2 mmHg) afforded isothiochroman-4-one as a yellow oil which solidified on standing (7.1 g, 39%), τ 1.85-2.30 (1H, m), 2.50-3.20 (3H, m), 6.22 (2H, br.s), and 6.59 (2H, br.s).

Some of this sulphide (5 g) was oxidised with a 40% solution of peracetic acid (25 ml) following the general method (page 145) to give isothiochroman-4-one 2,2-dioxide as a white solid (4.5 g, 75%), m.p. 161-163°C (lit. m.p.[60] 163-164°C), insoluble in common n.m.r. solvents. m/e 196, 132, 131, 118, 104, 103, 90, 89, 78, and 77, metastable peaks at 82[132→104], 58.5 [104→78], and 68.8 [118→90].

Isothiochroman-4-ol 2,2-dioxide

This was prepared from the reduction of isothiochroman-4-one 2,2-dioxide, using sodium borohydride and following the method as described by Lotspeich[61] for thiochroman-4-ol. τ 2.42-3.12 (4H, m), 4.83 (1H, t, J_1 = 5 Hz), 5.58-5.91 (1H, m), 6.37 (2H, s), and 6.58 (2H, d, J = 5Hz).

1H-2-Benzothiopyran 2,2-dioxide (96)

This was prepared by dehydration of isothiochroman-4-ol 2,2-dioxide either with polyphosphoric acid as described by Hall[20] or by a phosphoryl chloride/pyridine elimination using the following method. A twice molar excess of phosphoryl chloride was slowly added to a stirred solution of isothiochroman-4-ol 2,2-dioxide (4.3 g, 21.7 mmol) dissolved in dry pyridine (40 ml) at room temperature. The temperature of the mixture was raised to 80°C for 2 h after which time the mixture was cooled and water (3ml) was added dropwise to the dark mixture. The mixture was poured into water (200 ml) and extracted with dichloromethane (3 x 40 ml) to give a dark solid 2.1 g after normal work up procedures. Chromatography on silica (40 g) eluting with ether gave (96) as a pale yellow solid (1.8 g, 46%), m.p. 111-112°C (lit. m.p.[50] 111°C).

Isothiochroman-4-ol

This was prepared by reduction of previously prepared isothiochroman-4-one using the method described for thiochroman-4-ol above. M.p. 48-50°C, (lit. m.p.[62] 50°C).

Thiochroman-4-ol 1-oxide (121)

Thiochroman-4-ol (1 g, 6.01 mmol) was added to a stirred solution of 85% m-chloroperoxybenzoic acid (1.25 g, 6.15 mmol) dissolved in dichloromethane (20 ml) at 0°C. After 3 h. the mixture was shaken with an aqueous solution of sodium carbonate, and normal work up procedures gave a pale opalescent oil after removal of the organic solvent (300 mg). Continuous extraction of the aqueous fraction with dichloromethane gave a further yield of a clear oil (350 mg). τ 2.20-2.95 (4H, m), 5.16-5.81 (2H, m), and 6.45-8.35 (4H, m), ν_{max} 3360 and 1040 cm^{-1}. This compound was used without further purification.

Reaction of thiochroman-4-ol with hydrogen chloride in benzene

Dry hydrogen chloride gas was passed through a stirred solution of thiochroman-4-ol (2 g) dissolved in dry benzene (30 ml) for 15 min. at 50°C. Removal of the solvent under reduced pressure gave a dark oil, which was distilled (110°C at 2 mmHg) to give 4-chlorothiochroman (119) (2.1 g, 94%) as a colourless oil that slowly solidified, m.p. 28-30°C. ν_{max} (liquid film) 1225 and 975 cm^{-1}, τ 2.67-3.30 (4H, m), 4.79 (1H, t, J = 4 Hz), 6.20-6.72 (1H, m), and 7.00-8.03 (3H, m). m/e 186, 184, 148, 147, 146, 134, 116, and 115. Found: C, 58.55; H, 4.98; S, 19.3. C_9H_9ClS requires C, 58.53; H, 4.92; S, 19.19.

Thiochroman (115)

Zinc (24 g) was amalgamated by stirring in a solution of mercuric chloride (2.4 g) and dilute hydrochloric acid (concentrated acid (1.2 ml)

in water (30 ml), for 15 min.[63] The solution was decanted and the amalgam added to a mixture of water (15 ml), concentrated hydrochloric acid (35 ml), and toluene (20 ml). Thiochroman-4-one (10.0g.) (113) was added, and the mixture heated under reflux for 24 h, adding further portions of concentrated hydrochloric acid (10 ml) every 6 h.

At the end of this time, the toluene layer was separated, and after cooling, the aqueous layer was diluted and extracted with ether (3 x 20 ml). The organic fractions were combined, dried, and the solvent removed, to give a golden oil (10 g). Distillation afforded thiochroman as a colourless oil (6.5 g, 72%), b.p. 100°C at 1.0 mm. The infrared spectrum showed no carbonyl bond and the n.m.r. spectrum agreed with that quoted in the literature.[64]

Reactions of thiochroman-4-ol 1-oxide with hydrogen chloride

The sulphoxide (350 mg) was azeotroped with benzene (20 ml) using a Dean-Stark apparatus. After cooling to 30°C, dry hydrogen chloride was passed into the resultant stirred solution. The solution turned orange immediately, and then dark purple. Removal of the solvent gave a dark purple oil, t.l.c. analysis on silica, eluting with ether, showed that at least three compounds were present.

Attempted dehydration of thiochroman-4-ol 1-oxide

This reaction was attempted using polyphosphoric acid as the dehydrating reagent, and following the method outlined by Pagani[50]

for thiochroman-4-ol, 1,1-dioxide. On heating the sulphoxide (200 mg) and polyphosphoric acid (7 ml) together however, the mixture was seen to turn very dark. Normal work up procedures gave a black intractable tar from which no product could be isolated.

Attempted elimination of 4-chlorothiochroman

a) Using triethylamine:

A slight excess amount of triethylamine was added to a solution of 4-chlorothiochroman (100 mg) dissolved in dry ether (5 ml). The mixture was examined every few days and when no reaction had been observed after 2 weeks, the reaction was abandoned.

b) Using lithium chloride-lithium carbonate:[65]

A mixture of anhydrous lithium bromide and lithium carbonate (0.52 g) mixed in the ratio of 6:4 by weight, was added to a solution of 4-chlorothiochroman (0.5 g) dissolved in dry dimethylformamide (20 ml). This mixture was heated under reflux in an inert atmosphere for 2 h, after which it was poured into water (100 ml). Usual work-up procedures gave a golden oil, which on distillation afforded 2H-1,benzothiopyran (120) as a colourless oil (0.35 g, 88%), b.p. 110°C at 0.01 mm. The n.m.r. spectrum agreed with that described by Parham et al.[64]

Attempted preparation of 4-chlorothiochroman 1-oxide (123)

A solution of m-chloroperoxybenzoic acid (2.3 g dissolved in dichloromethane (30 ml)) was added dropwise to a solution of 4-chloro-

thiochromanone (2.1 g dissolved in dichloromethane (30 ml)) at 0°C. The mixture was then stirred for 3 h at room temperature after which normal work up procedures gave an orange oil (0.7 g). ν_{max} 1040 cm^{-1} (v.s.). Distillation at 2 mm.gave a clear oil which was found to be starting material by n.m.r. spectroscopy. A black intractable tar was left as a residue of the distillation and attempted purifications of this residue by column chromatography on alumina was unsuccessful. The reaction was repeated in the same way using 1.52 g of sulphide, except that the reactants were refluxed together for 18 h.once the addition had been completed - the result was a pale yellow solid (1.4 g, 84%) with a strong bond in the infrared spectrum at 1040 cm^{-1}. τ 2.19-2.95 (4H, m), 4.57-4.77 (1H, m), and 6.42-7.96 (4H, m). This product was used without further purification.

Attempted elimination of 4-chlorothiochroman 1-oxide

This was attempted in two ways: (a) using a lithium chloride-lithium bromide mixture, and (b) using a non-nucleophilic base-1,5-diazabicyclo[5.4.0]undec-5-ene (D.B.U). Method (a): this reaction was carried out as described above for 4-chlorothiochroman, using 1.0 g of the sulphoxide, and 1.06 g of the lithium bromide-lithium carbonate mixture. On heating however, the mixture was seen to darken considerably and after heating under reflux for 2 h, work-up gave a dark purple oil. T.l.c. analysis on silica, using ether as the developing solvent showed at least six compounds present, and distillation of the material at 0.001 mm pressure, failed to isolate any pure material.

Method (b): D.B.U (0.36 g) was added to a stirred solution of the sulphoxide (400 mg) dissolved in dimethyl sulphoxide (25 ml). The stirred mixture was heated to 80°C and maintained at this temperature for 3 h, after which it was cooled and poured into water (100 ml). Extraction with dichloromethane and normal work-up procedure yielded a black tarry material. The n.m.r. spectrum failed to detect the presence of any olefinic protons in this material, and the reaction was abandoned.

Attempted oxidation of 2H-1-benzothiopyran to 2H-1-benzothiopyran 1-oxide

An equivalent amount of 30% hydrogen peroxide solution was added dropwise to a solution of the sulphide (400 mg) in glacial acetic acid (5 ml) at 0°C. This mixture was stirred at room temperature for 12 h, after which it was poured into water (100 ml). Extraction with dichloromethane (3 x 10 ml) and normal work up procedures gave a light brown oil, τ 2.22-2.97 (m), 3.21 (d x d, J_1 = 10 Hz, J_2 = 2 Hz), 3.82-4.24 (m), 6.05 (d x d, J_3 = 6 Hz, J_4 = 16 Hz), 6.50 (t, J_5 = 3 Hz) and 6.81 (t, J_5 = 3 Hz), ν_{max} 1040 cm^{-1}.

A second attempt at oxidation using an excess of sodium meta-periodate gave the same result. T.l.c. analysis on silica eluting with ether showed a number of compounds present and attempted chromatography on silica or alumina failed to isolate any pure compound.

Reactions of hydrogen chloride in benzene with:

a) Isothiochroman-4-ol

A solution of isothiochroman-4-ol (0.49 g) in dry benzene (20 ml) was saturated with dry hydrogen chloride gas using the same method as described for thiochroman-4-ol above. The solution was observed to turn green and gradually darken after 3 days. Removal of the solvent gave a brown oil. Infrared analysis showed no hydroxyl bond present. Distillation afforded a pale green oil b.p. 80° at 0.001 mm which slowly darkened after 2 days. τ 2.50-7.08 (m), 5.10-5.62 (m), and 5.75-6.40 (m), m/e 186, 184, 168, 167, 147 and 135.

b) Thiochroman-4-ol 1,1-dioxide

Using the same reaction conditions as described for the sulphide (118) above, unchanged starting material was obtained, even after some days.

A solution of the sulphone (150 mg) in benzene (10 ml) was saturated with dry hydrogen chloride, and sealed in a Carius tube. After heating at 150°C for 15 h, the tube was opened and the solvent removed. The n.m.r. spectrum of the resultant material showed mainly starting material, however no trace of any 4-chlorothiochroman-1,1-dioxide was present by comparison with the spectrum of an authentic sample prepared by oxidation of (119) with m-chloroperoxybenzoic acid.

c) Isothiochroman-4-ol 2,2-dioxide

Using the same conditions as described for the sulphide (118) above, after 2 days no trace of 4-chloroisothiochroman was detected in the reaction mixture.

Preparation of 5,6-benzo-7H-1,2-oxathiepin-2-oxide (98)

This compound was prepared as described by Hall,[20] from photolysis of a solution of 1H-2 benzothiopyran 2,2-dioxide (1.5 g) in acetonitrile (200 ml) at 253 nm. Removal of the solvent and careful chromatography of the resulting oil on silica (40 g) eluting with ether, gave the sultine (98) as an orange oil (160 mg, 11%) which solidified after a few hours at room temperature. The n.m.r. spectrum agreed with that described by Hall.[20]

Thermolysis of 5,6-benzo-7H-1,2-oxathiepin-2-oxide (98)

The sultine (160 mg) was sublimed through the apparatus at 0.007 mm pressure with the furnace at 750°C. N.m.r. spectral analysis of the product confirmed the presence of o-vinylbenzaldehyde which was identified by comparison with the spectrum described by Hall.[20] Indene was shown to be completely absent from this material by comparison with the n.m.r. spectrum of a standard sample. Also noticed in the spectrum was a doublet at τ 8.41 (J = 7 Hz) and larger aromatic and olefinic resonances than were allowed for by the integration of the aldehydic proton. These remain unidentified so far.

An identical procedure with the furnace at 450°C gave a mixture of starting material and the products described above.

Attempted reaction of 4-chlorothiochroman with aniline or p-anisidine

Equimolar quantities of aniline (0.93 g) and 4-chlorothiochroman (1.84 g) were dissolved in dichloromethane (20 ml) and the stirred solution cooled to -20°C under dry nitrogen. To this mixture was added an equivalent solution of N-chlorosuccinimide dissolved in dichloromethane (50 ml) over a period of 25 min.

After stirring the mixture at -20°C for one hour, the solution was shaken with a 5% aqueous sodium hydroxide solution. Normal work up procedures gave a dark oil which was not crystallisable from a mixture of chloroform and petroleum. The n.m.r. spectrum indicated the presence of a simple mixture of starting materials. Repetition of this experiment using p-anisidine also failed to produce any product.

Attempted reaction of thiochroman-4-one (113) and thiochroman (115) with p-anisidine

Attempted reaction of either of these two sulphides with p-anisidine, using the method as described for 4-chlorothiochroman above, resulted in a simple mixture of starting materials after the work up, as shown by the n.m.r. spectrum.

Attempted reaction of thiochroman-4-one (113) and N-aminophthalimide

This reaction was attempted using the method of Gilchrist et al[51] in the following way.

A stirred solution of the sulphide (1.8 g, 0.01 m), and freshly prepared N-aminophthalimide (1.62 g, 0.01 m) dissolved in dichloromethane (50 ml) at -25°C was treated with a solution of N-chlorosuccinimide (1.33 g, 0.01 m) in dichloromethane (50 ml) added dropwise over a period of 30 min. Stirring was continued for 30 min. after which the mixture was allowed to warm to room temperature and stirred for a further 45 min. At the end of this time, the solution was washed with a saturated sodium bicarbonate solution (3.50 ml) and water (1 x 30 ml). The aqueous layers were extracted with dichloromethane until no colour was extracted into the organic phase. The organic fractions were combined; drying, and removal of the solvent gave a yellow gummy oil which could not be crystallised. Attempted chromatography on silica failed to isolate any pure compound.

Attempted reaction of thiochroman-4-one 1-oxide with N-phthalimido-nitrene

The sulphoxide (116) (0.5 g, 2.49 mM), and freshly prepared N-aminophthalimide (0.4 g, 2.46 mM) were dissolved in dichloromethane (20 ml). Lead tetracetate (1.5 g) was added to this mixture in small portions to the stirred solution, and the mixture was stirred

for 10 min. A precipitate gradually appeared during this time. The mixture was filtered and the solid was washed with portions of dichloromethane. Removal of the solvent from the filtrate gave a viscous yellow oil. T.l.c. examination on alumina, eluting with ether, showed three spots close to the base line and the oil was seen to turn to a vivid purple colour on application to the plate. Attempted purification by column chromatography on alumina failed to isolate any pure material.

Attempted reaction of 4-chlorothiochroman 1-oxide with N-phthalimdo-nitrene

Using the sulphoxide (123) (0.5 g), N-aminophthalimide (0.4 g) and following the method described above for thiochroman-4-one 1-oxide the reaction afforded a yellow viscous oil after work up. Attempted purification by chromatography on alumina (100 g) using ether as the eluent, failed to isolate any pure material.

Preparation of 2H-1-benzopyran

This was made from commercially obtainable 4-chromanone as described by Parham et al.[66] From 5 g.of starting material-distillation of the crude product gave 2H-1-benzopyran as a colourless oil (2.0 g, 45%) b.p. 60°C at 1.0 mm. The n.m.r. spectrum agreed with that given by Parham et al.[66]

Thermolysis of 2H-1-benzopyran (94)

2H-1-benzopyran (100 mg) was sublimed through the apparatus at 0.008 mm pressure, with the furnace at 800°C. The n.m.r. spectrum of the product showed the following features; τ (100 MHz), 0.45 (d, J = 8 Hz), 2.37-4.00 (m), 4.14-4.44 (m), 5.17-5.28 (m), and 6.56-6.72 (m).

From the g.l.c. trace of the product material (3% OV17 at 150°C) (flow rate 42 ml min^{-1}) there were two main products apart from unconsumed starting material (retention time 8 min.12 sec. and 11 min. 25 sec). Comparison of the n.m.r. spectrum with that of quoted spectra indicated that the products were cinnamaldehyde (13%), 4H-1-benzopyran (35%), and starting material (52%).

Preparation of 1H-2-benzopyran (102)

The diethyl ester of homophthalic acid was prepared by refluxing the acid (10 g) with ethanol (200 ml), and concentrated sulphuric acid (4 ml) for 6 h with the addition of further portions of concentrated sulphuric acid (2 ml) every 2 h. At the end of this time, the mixture was cooled and most of the ethanol removed under reduced pressure. The resultant mixture was added to dichloromethane (35 ml) and the solution was washed with water (2 x 20 ml) and a solution of sodium carbonate until the evolution of carbon dioxide had ceased. Separation of the organic fraction and normal work up procedures gave a pale oil which on distillation afforded diethylhomophthalate

as a colourless oil (11.7 g, 86%), b.p. 138°C at 0.05 mm, τ 1.76-2.05 (1H, m), 2.29-2.84 (3H, m), 5.38-6.09 (6H, m), and 8.40-9.00 (6H, m).

Some of the diester (5 g) was then selectively reduced with diisobutylaluminium hydride as described by Kraiss et al[67] to give 3-hydroxyisochroman (2.2 g, 72%) m.p. 69-70°C (chloroform-petrol), lit m.p. 71-71.5°C.

Some of the 3-hydroxyisochroman was then dehydrated using the method described by Parham et al for 4-chromanal,[66] using the following method. A stirred solution of 3-hydroxyisochroman (1.6 g), and purified dimethylsulphoxide (6.4 mg) was heated at 170-175°C under an atmosphere of nitrogen for 12 h. The resulting yellow solution was cooled and extracted with light petroleum (4 x 8 ml) and the combined extracts washed with a dilute solution of sodium carbonate (2 x 6 ml). Drying and removal of the solvent gave a light brown oil, which on distillation afforded 1H-2-benzopyran as a colourless oil (0.62 g, 44%), b.p. 105°C at 15 mm (lit. m.p. 80°C at 8 mm). The n.m.r. spectrum agreed with that previously described in the literature.[68]

Thermolysis of 1H-2-benzopyran (102)

1H-2-benzopyran (118.2 mg) was sublimed through the apparatus at 0.02 mm pressure, with the furnace at 750°C. The product appeared as a white polymer, much of which was insoluble in $CDCl_3$. The n.m.r. spectrum showed broad envelope resonances at δ 2.51-3.50, and 7.58-8.82. G.l.c. analysis (3% OV17 at 150°C) showed no volatile components in this material.

CHAPTER THREE

3-Methylthiochroman-4-one 1,1-dioxide (155)

3-Methylthiochroman-4-one was prepared following the method described by Petropoulus et al,[77] from cyclisation of the hydrolysed addition product of thiophenol and methyl methacrylate. The product, a pale yellow oil, slowly solidified on standing, and was considered pure enough for direct oxidation, τ 1.61-2.05 (1H, m), 2.31-3.15 (3H, m), 6.56-7.36 (3H, m), and 8.66 (3H, broad d).

The sulphide (3.0 g) was oxidised with peracetic acid solution (25 ml) as described on page 145 to give 3-methylthiochroman-4-one 1,1-dioxide as a white crystalline material, m.p. 145-147°C (lit. m.p.[60] 146-147°C), τ 1.84-2.44 (4H, m), 6.24-6.50 (3H, m), and 8.44-8.64 (3H, m), m/e 210, 169, 168, 152, 105, 104, and 76.

2-Methylthiochroman-4-one 1,1-dioxide (156)

2-Methylthiochroman-4-one was prepared by the method of Petropoulus et al[77] from the sulphuric acid cyclisation of the addition product of thiophenol and crotonic acid, to give a pale yellow oil, (140°C at 5 mmHg), τ 1.66-1.98 (1H, m), 2.32-2.94 (3H, m), 6.02-6.62 (1H, m), 6.67-7.53 (2H, m), and 8.56 (3H, d, J = 6.5 Hz).

Oxidation of the sulphide (3 g) with peracetic acid (25 ml)

using the general method as described on page 145 gave 2-methylthiochroman-4-one 1,1-dioxide (2.22 g, 63%), m.p. 125-127°C (chloroform-petrol), lit. m.p.[60] 127-128°C, τ 1.68-2.30 (4H, m), 5.95-6.81 (3H, m), and 8.42 (3H, d, J = 7 Hz), m/e 210, 169, 168, 152, 105, 104, and 76.

2,3-Dimethylthiochroman-4-one 1,1-dioxide (157)

2,3-Dimethylthiochroman-4-one was prepared by the method of Chauhan and Still[78] using one half of the scale. Cyclisation of the intermediate acid followed by quick chromatography on silica M.F.C. (40 g) eluting with ether, gave the product as an orange oil, the n.m.r. spectrum agreed with that quoted.[78]

Some of this sulphide (2 g) was oxidised with peracetic acid (10 ml) using the general method (page 145). Removal of the solvent gave a white opalescent oil which was crystallised, to give 2,3-dimethylthiochroman-4-one 1,1-dioxide (157) as a white solid (1.58 g, 68%), m.p. 94-96°C (chloroform-petrol). ν_{max} (dichloromethane), 1698, 1305, and 1150 cm^{-1}, τ 1.75-2.42 (4H, m), 5.90-6.95 (2H, m), and 8.25-8.72 (6H, m). Found C, 58.64; H, 5.35; S, 14.10. $C_{11}H_{12}SO_3$ requires C, 58.91; H, 5.39; S, 14.30. M/e 224, 168, 152, 104, and 76.

3,3-Dimethylthiochroman-4-one 1,1-dioxide (159)

3,3-Dimethylthiochroman-4-one was prepared using the method described by Still et al,[79] by methylation of thiochroman-4-one,

on one tenth of the scale described. Distillation of the crude product afforded 3,3-dimethylthiochroman-4-one as a colourless oil (1.4 g, 60%), b.p. 120-122°C at 1.5 mm, τ 1.65-1.89 (1H, m), 2.38-2.96 (3H, m), 6.90 (2H, s), and 8.69 (6H, s).

This was oxidised with peracetic acid (7 ml) using the general method described on page 145 to give a pale opalescent oil. Chromatography on silica M.F.C. (35 g) and eluting with ether gave 3,3-dimethylthiochroman-4-one 1,1-dioxide as a colourless oil whic crystallised on standing (1.23 g, 75%), m.p. 92-94°C (chloroform-petrol), ν_{max} (dichloromethane) 1700, 1320, and 1150 cm^{-1}, τ 1.70-2.30 (4H, m), 6.38 (2H, s), and 8.50 (6H, s). The ^{13}C n.m.r. was identical to that reported by Still et al.[78] M/e 224, 169, 142, 117, 104, 94, and 76.

2,2-Dimethylthiochroman-4-one 1,1-dioxide (158)

2,2-Dimethylthiochroman-4-one was prepared following the method described by Still et al,[78] by polyphosphoric acid cyclisation of the addition product of thiophenol and 3,3-dimethylacrylic acid. The only deviation from the method was that chlorobenzene was used as the solvent in the cyclisation. The dark brown oily crude product was chromatographed on silica M.F.C. (60 g). Elution with ether, gave 2,2-dimethylthiochroman-4-one as a yellow oil which partially solidified. τ 1.70-1.90 (1H, m), 2.38-2.96 (3H, m), 7.12 (2H, s), and 8.54 (6H, s).

A small amount of this sulphide (2 g) was oxidised using peracetic acid (10 ml) using the general method described on page 145 to give 2,2-dimethylthiochroman-4-one 1,1-dioxide as a white solid (1.0 g, 43%) m.p. 105-108°C (chloroform-petrol), ν_{max} (dichloromethane) 1698, 1305, and 1150 cm^{-1}, τ 1.63-2.33 (4H, m), 6.70 (2H, s), and 8.45 (6H, s). The ^{13}C n.m.r. was identical to that reported by Still,[78] m/e 224, 169, 160, 152, 145, 105, 104, and 76.

2-Phenylthiochroman-4-one 1,1-dioxide (160)

2-Phenylthiochroman-4-one (thioflavonone) was prepared according to the method of Arndt,[80] by cyclisation of the addition product of thiophenol and cinnamic acid, with phosphorus oxychloride. Work up gave an oil which was distilled to give 2-phenylthiochroman-4-one as a colourless oil (195°C at 0.015 mmHg), τ 1.66-1.92 (1H, m), 2.35-3.10 (8H, m), 5.39 (1H, d x d, J_1 = 7 Hz, J_2 = 10 Hz), and 6.70-6.98 (2H, m).

Some of this sulphide (2 g) was oxidised by peracetic acid (10 ml) following the general method outlined on page 145 to give crude 2-phenylthiochroman-4-one 1,1-dioxide as an oil which slowly crystallised. Recrystallisation gave the pure material as a white crystalline solid (1.77 g, 78%), m.p. 148-151°C (chloroform-petrol), ν_{max} (dichloromethane), 1705, 1600, 1325, and 1160 cm^{-1}. 1.70-2.34 (5H, m), 2.47 (5H, s), 5.04 (1H, d x d, J_1 = 12 Hz, J_2 = 3.5 Hz), and 5.75-6.86 (2H, m). The ^{13}C n.m.r. agreed with that reported by Still et al.[78] M/e 272, 208, 179, 165, 104, and 76.

3-Methyl-2-phenylthiochroman-4-one 1,1-dioxide (161)

3-Methyl-2-phenylthiochroman-4-one was prepared using the method of Still et al,[70] by cyclisation of the addition product of thiophenol and α-methylcinnamic acid with phosphorus oxychloride. Work up gave crude 3-methyl-2-phenylthiochroman-4-one as a pale yellow oil considered pure enough for direct oxidation, τ 1.64-1.90 (1H, m), 2.30-3.00 (8H, m), 5.10-5.70 (1H, m), 6.40-7.02 (1H, m), 8.63-8.98 (3H, m), small impurity peaks at τ 7.62, 7.80 and 8.10.

Some of this sulphide (2 g) was added dropwise to a peracetic acid solution (10 ml) with stirring at 0°C. After stirring the solution at room temperature for three days, the mixture was poured into water (100 ml). After extraction with methylene chloride, and washing the combined extracts with sodium carbonate solution, the organic fraction was separated and dried. Removal of the solvent gave a pale oil (0.5 g), the n.m.r. spectrum of which showed that product was present. Continuous extraction of the aqueous fractions with dichloromethane gave a further 0.82 g of oil although this was contaminated with acid residues. A quick filtration on silica M.F.C. (30 g) eluting with ether, gave a crystalline fraction which, when combined with the original material and recrystallised, gave 3-methyl-2-phenylthiochroman-4-one 1,1-dioxide (161) as a white solid (1.12 g, 50%), m.p. 141-144°C (chloroform-petrol), ν_{max} (dichloromethane), 1695, 1320, and 1155 cm^{-1}, τ 1.60-2.30 (5H, m), 2.45 (5H, s), 5.33 (1H, d, J_1 = 13 Hz), 5.73-6.40 (1H, m), and 8.78 (3H, d, J_2 = 7 Hz). Found: C, 66.68; H, 4.87; S, 10.97.

$C_{16}H_{14}SO_3$ requires C, 67.11; H, 4.93; S, 11.19. M/e 286, 222, 221, 207, 179, 178, 118, 117, 104, 91, and 76. ^{13}C n.m.r. (chloroform), 13.37, 46.49, 69.73, 123.89, 127.26, 129.08, 128.86, 130.64, 133.37, 134.67, 141.29, and 193.88.P.P.M.

3-Deuteriothiochroman-4-one 1,1-dioxide

One mole equivalent of butyl-lithium in hexane was added to a solution of thiochroman-4-one (1.0 g, 6.1 mmol) with rapid stirring at -78°C under dry nitrogen. An excess of deuterium oxide (0.5 ml, 24 mmol), was added to the resultant pale yellow solution, and the mixture was allowed to warm up to room temperature, and stirred for twelve hours. Work up gave a pale orange oil (1.13 g). This was oxidised with peracetic acid using the general method described above, to give a white solid. Recrystallisation gave predominantly 3-deuteriothiochroman-4-one 1,1-dioxide (0.67 g, 66%), m.p. 128-131°C. The n.m.r. spectrum showed a much diminished multiplet at τ 6.40-6.80, compared with that of undeuterated material.

Thiochroman 1,1-dioxide (164)

Some of the previously prepared thiochroman (see Chapter 2) (1 g) was oxidised by adding a 2.1 equivalent solution of m-chloroperbenzoic acid in dichloromethane (15 ml), to a solution of the sulphide in dichloromethane (10 ml) at 0°C. The stirred mixture

was allowed to warm to room temperature and stirred for a further 24 h. At the end of this time the organic solution was washed with an excess of sodium carbonate solution, separated and dried. Removal of the solvent gave a white solid which was recrystallised to give thiochroman 1,1-dioxide (1.0 g, 82%) m.p. 89-90°C (chloroform-petrol), lit. m.p.[81] 90.5-91.5°C, 1.82-2.23 (1H, m), 2.24-2.89 (3H, m), 6.42-7.21 (4H, m), and 7.23-7.82 (2H, m). M/e 182, 137, 117, 115, 91, 90, and 77.

Isothiochroman 2,2-dioxide (166)[82]

Hydrazine hydrate (4.38 g) was added dropwise to a stirred solution of isothiochroman-4-one (3.5 g) dissolved in diethylene glycol (25 ml). This was then heated under reflux (~170°C) for two hours to give a very dark solution. A condenser and still-head were set onto the flask, and water was taken off until the temperature of the contents of the flask had reached 185°C. After cooling the mixture to room temperature, potassium hydroxide (4.37 g) was added to the stirring mixture, and the temperature increased to 185-190° (care was taken to control the sudden rise in temperature), for a period of one hour. The mixture was cooled to 100°C and poured quickly into cold water (200 ml), with vigorous stirring. Extraction with ether (3 x 20 ml), drying, and removal of the solvent gave an orange oil which was distilled to give a colourless oil (2.5 g, 71%), b.p. 100-110°C at 0.1 mm. The n.m.r. spectrum showed slight impurities because the aromatic area integrated slightly larger than allowed for by the rest of the spectrum. The infrared spectrum

showed no carbonyl band. τ 2.60-3.10 (m), 6.32 (s), and 6.84-7.37 (m).

Some of this sulphide (2 g) was oxidised with peracetic acid (10 ml) following the general method (page 145) to give isothiochroman 2,2-dioxide as a white solid, (1.51 g, 62%), m.p. 161-163°C (chloroform), (lit. m.p.[60] 163-164°C), m/e 182, 118, 117, 115, 103, 91, 78, and 77.

Acrylophenone

Acrylophenone was synthesised following the method of Mannich et al[88] from acetophenone, paraformaldehyde, and dimethylamine hydrochloride. Steam distillation of the product gave a colourless oil which was redistilled (115°C at 10 mm) to give acrylophenone as a colourless oil. The n.m.r. spectrum was comparable to that described by Gutowsky et al.[83]

Flash Vacuum Thermolyses

Thermolysis of thiochroman-4-one 1,1-dioxide

The sulphone (136) (140 mg) was sublimed at 0.05 mm pressure, through the furnace at 900°C. A mixture of acrylophenone and phenyl acetylene was given as a yellow oil (64 mg) on the surface of the trap, which darkened on warming to room temperature, τ 1.85-2.20 (m), 2.35-3.10 (m), 3.60 (d x d, J_1 = 17 Hz, J_2 = 2 Hz), 4.11 (d x d, J_3 = 10 Hz, J_4 = 2 Hz), and 6.93 (s). The products were identified by

comparison with reported n.m.r. spectra[83] and by gas chromatography mass spectra (3% OV 17 at 150°C, nitrogen pressure 5 psi, retention time phenyl acetylene 1 min.40 sec, acrylophenone 5 min.12 sec).

An identical procedure to the above, with the furnace at 850°C, gave a mixture of starting material and the products described above; relative amounts of material were not possible to determine due to overlapping of some of the resonances in the n.m.r. spectrum. Attempted thermolysis with the furnace temperature below 750°C led to the complete recovery of starting material.

Thermolysis of 3-methylthiochroman-4-one 1,1-dioxide

The sulphone (155) (165 mg) was sublimed at 0.005 mm pressure through the furnace at 900°C. Crude α-methylacrylophenone was obtained as a yellow oil on the cold finger, which on warming gave a slightly darker oil (72.5 mg, 63%), τ 2.05-2.90 (m), 3.98-4.15 (m), 4.30-4.42 (m), and 7.70-8.03 with small traces of starting material; this spectrum was comparable with an authentic spectrum recorded by Combaut and Giral.[84] The g.l.c. trace showed only one main compound (3% OV17 at 200°C, nitrogen flow rate 36 ml min^{-1}, retention time 2 min.0 sec). An identical procedure to the above with the furnace at 850°C gave a mixture of starting material (73%) and α-methylacrylophenone (27%), as identified by n.m.r. spectroscopy. Attempted thermolysis with the furnace temperature below 750°C led to a complete recovery of starting material.

Thermolysis of 2-methylthiochroman-4-one 1,1-dioxide

The sulphone (156) (115 mg) was sublimed at 0.03 mm pressure, through the furnace at 850°C. Crude crotonophenone was obtained as a yellow oil, with trace amounts of starting material, (52.5 mg, 65%), τ 1.77-2.90 (m), 3.02 (s), and 8.02 (d, J = 5 Hz), the compound was identified by comparison with an authentic n.m.r. spectrum described by Lowe and Ferguson.[85] Only one main peak was seen in the g.l.c. trace, (3% OV17 at 200°C, flow rate 36 ml $min.^{-1}$, retention time 2 min.48 sec).

An identical procedure to that described above with the furnace at 900°C gave an indeterminate mixture containing some of the product described above but otherwise unresolved. Thermolysis at 800°C yielded a mixture of the product (60%) and starting material (40%), while at 750°C the ratio was product (24%) and starting material (76%).

Thermolysis of 2,3-dimethylthiochroman-4-one 1,1-dioxide

The sulphone (157) (139 mg) was sublimed at 0.025 mm pressure, through the furnace at 850°C. There was no starting material left after this run, and a mixture of products appeared to have been given. The g.l.c. trace (3% OV17 at 200°C with a flow pressure of 6 psi), showed at least six different compounds present.

An identical procedure with the furnace at 750°C gave some recovery of starting material plus two other compounds as shown by g.l.c. (retention time 2 min.24 sec, and 3 min.4 sec under the same conditions as the previous run). The n.m.r. spectrum showed starting material and a spreading of the aromatic resonances plus a new resonance at τ 7.95-8.10. G.l.c./mass spectral analysis of these two peaks under the same conditions as above showed that they both had molecular ions at m/e = 160 followed by identical fragmentation peaks at m/e = 145, 105, and 77. The n.m.r. spectrum obtained was comparable to the values given by DePuy et al[86] for cis and trans 2-benzoyl-2-butene.

Thermolysis of 3,3-dimethylthiochroman-4-one 1,1-dioxide

Thermolysis of the sulphone (159) at 850°C and 0.01 mm pressure gave a yellow oil, which on examination by n.m.r. was unchanged starting material. This was confirmed by g.l.c. analysis (3% OV17 at 200°C, flow pressure 5 psi).

Thermolysis of 2,2-dimethylthiochroman-4-one 1,1-dioxide

The sulphone (158) (128 mg) was sublimed at 0.01 mm pressure through the furnace at 800°C. G.l.c. examination of the yellow oil product (71 mg) (3% OV17 at 200°C, flow rate 37 ml min^{-1}) showed four compounds, one of them in large excess over the others. The g.l.c./mass spectrum of this band showed M^+ = 160 with the following

breakdown, 159, 145, 105, 83, and 77. The n.m.r. spectrum of the crude material showed the following pattern: τ 1.83-2.15 (m), 2.30-2.90 (m), 3.15-3.25 (m), 7.77 (s), and 8.03 (s).

An identical procedure with the furnace at 750°C gave a mixture of starting material and product described above.

Thermolysis of 2-phenylthiochroman-4-one 1,1-dioxide

The sulphone (160) (140 mg) was sublimed at 0.01 mm pressure with the furnace at 750°C. Starting material and benzylidene acetophenone (chalcone) was obtained on the surface of the trap (104 mg). This was identified by comparison of the t.l.c. trace, and n.m.r. spectrum with that of standard samples.

The n.m.r. spectrum indicated an approximate ratio of 10% starting material in the product mixture.

Thermolysis of 3-methyl-2-phenylthiochroman-4-one 1,1-dioxide

The sulphone (161) (119.2 mg) was sublimed at 0.01 mm pressure, with the furnace at 750°C. A yellowish glass was observed on the surface of the cold trap, which on warming gave a dark oil (92.1 mg). The n.m.r. spectrum of this material showed starting material and a doublet of doublets at τ 7.78, J_1 = 7.5 Hz, J_2 = 2 Hz. G.l.c. mass spectral analysis showed three products with starting material (3%

OV17 at 190°C, flow rate 6 psi). Band A (retention time 16 min.36 sec) showed the highest mass peak at m/e = 222 thereafter 207, 179, 114, 105 and 77; Band B (retention time 23 min.12 sec), m/e = 222, 207, 179, 165, 91, and 77; Band C (retention time 30 min, 18 sec), m/e = 222, 207, 179, 165, 145, 115, 105, and 77.

Thermolysis of thiochroman 1,1-dioxide

The sulphone (164) (130 mg) was sublimed at 0.01 pressure, with the furnace temperature at 850°C to give a pale yellow oil (106 mg) consisting of mostly starting material with indene (18%). This was confirmed by comparison with an authentic n.m.r. spectrum and g.l.c. analysis against a standard sample (3% OV17 at 200°C, flow rate 40 ml min^{-1}), retention time for indene 2 min.26 sec.

Thermolysis of indan

Indan (500 mg) was sublimed through the apparatus at 0.001 mm pressure, with the furnace temperature at 850°C. The n.m.r. spectrum of the product showed complete recovery of starting material.

Thermolysis of isothiochroman-4-one 2,2-dioxide

The sulphone (165) (29.2 mg) was sublimed at 0.001 mm pressure with the furance at 750°C. Indan-1-one (19.6 mg, 81%) was obtained, τ 2.18-3.08 (4H, m), 6.70-7.05 (2H, m), and 7.20-7.46 (2H, m), identified by comparison of the n.m.r. spectrum with that of an authentic spectrum.

Thermolysis of isothiochroman 2,2-dioxide

The sulphone (166) (101 mg) was sublimed at 0.03 mm pressure, with the furnace at 800°C. Indan (58 mg, 88%) was obtained as a clear oil, τ 2.56-2.95 (4H, m), 6.85-7.25 (4H, m), and 7.62-8.27 (2H, m). This was identified by comparison of the n.m.r. spectrum with that of an authentic sample.

Thermolysis of 1-indanone

The ketone (120 mg) was sublimed at 0.015 mm pressure, through the furnace at 900°C. The product was found to be unchanged starting material.

Thermolysis of 2,3-dihydrobenzo[b]thiophene 1,1-dioxide

The sulphone (153) (283 mg) was sublimed at 0.01 mm pressure through the furnace at 900°C. The n.m.r. spectrum of the products formed did not show any trace of phenylacetylene or acrylophenone.

Thermolysis of acrylophenone

Acrylophenone (117 mg) was sublimed at 0.03 mm pressure through the furnace at 900°C. The product was found to contain no traces of phenylacetylene, from n.m.r. and g.l.c. analysis.

CHAPTER FOUR

Thermolyses of sultines

Thermolysis of 4-methyl 1,2-oxathiolane 2-oxide (174)

The sultine (270 mg) was sublimed at 0.025 mm pressure through the furnace at 750°C. A crude mixture of methyl cyclopropane and isobutylene was obtained as a clear glass on the surface of the cold trap, which on warming melted to give a clear oil, τ 5.20-5.36 (m), 8.02-8.30 (d, J = 1 Hz), 8.80-9.02 (m), and 9.42-9.75 (m).

Under the same conditions, with the furnace temperature at 700°C and 650°C different mixtures of starting material and isobutylene were obtained, as described in Table 4.1 (page 93).

Thermolysis of 4-phenyl-1,2-oxathiolane 2-oxide (172)

The sultine (150 mg) was sublimed at 0.007 mm pressure, through the furnace at 750°C. A mixture of the starting material and α-methyl styrene was obtained, τ 2.20-2.90 (m), 4.60 (s), 4.88 (s), 5.55-5.80 (m), 6.50-7.10 (m), and 7.84 (s). Under the same conditions, thermolysis below 700°C gave starting material only.

Thermolysis of 5-phenyl 1,2-oxathiolane 2-oxide (170)

The sultine (141 mg) was sublimed at 0.007 mm pressure, through the furnace at 850°C. A crude mixture of phenylcyclopropane, *cis* and/or *trans* β-methylstyrene, and allyl benzene was obtained; τ 2.37-

3.07 (m), 3.29-4.38 (m), 4.66-4.86(m), 4.89-5.12 (m), 6.62 (d, J = 7 Hz), 7.85-8.35 (m), and 8.90-9.47 (m). Under the same conditions with the furnace at 750°C, crude phenylcyclopropane was the only product, τ 2.58-3.18 (m), 7.90-8.46 (m), and 8.90-9.50 (m). Under the same conditions with the furnace below 750°C, mixtures of starting material and phenylcyclopropane were given as described in Table 4.2 (page 94).

Thermolysis of 5-methyl 1,2-oxathiolane 2-oxide (175)

The sultine (190 mg) was sublimed at 0.06 mm pressure, through the furnace at 750°C to obtain a crude mixture of acetaldehyde, cis and/or trans but-2-ene and methylcyclopropane, with some white polymeric material adhering to the surface of the cold trap, τ 0.16-0.36 (m), 4.36-4.64 (m), 7.64-8.02 (m) 8.12-8.54 (m), 8.80-9.06 (m), and 9.06-9.68 (m). Thermolysis under the same conditions with the temperature at 700°C gave a mixture of starting material and the products above as shown in Table 4.3 (page 95).

Thermolysis of 5-phenyl 5-methyl 1,2-oxathiolane 2-oxide (176)

The sultine (50 mg) was sublimed at 0.005 mm pressure through the furnace at 750°C. 1-Phenyl 1-methylcyclopropane was obtained, and identified by comparison with the n.m.r. details reported by Gibert and Seyden-Penne,[31] τ 2.50-3.00 (m), 8.63 (s), and 9.02-9.40 (m).

Thermolysis of 3-phenyl 2,1-benzoxathiole, 1-oxide (177)

The sultine (120 mg) was sublimed at 0.001 mm pressure through the furnace at 750°C. A vivid red glass was seen to gradually form on the surface of the cold trap, the colour of which disappeared on warming, to give a very viscous yellow oil. τ 1.96-3.60 (broad envelope), and 6.10 (s). No starting material was left and the g.l.c. trace (3% OV17 at 200°C, flow pressure 5 psi) showed only one peak (retention time 9 min.35 sec), which was identified as fluorene from the g.l.c./mass spectrum, and comparison with a known sample.

Thermolysis of 2,1-benzoxathiole, 1-oxide (201)

The sultine (∿120 mg) was sublimed at 0.005 mm pressure, through the furnace at 850°C. A dark red-brown glass was seen to form gradually in the cold surface, which on warming, gave a tarry brown oil. τ 2.10-3.30 (m), 5.31 (s), and 5.60-5.77 (m), a t.l.c. plate on silica using ether as the developing solvent showed the presence of at least six compounds.

Thermolysis under the same conditions with the furnace temperature at 750°C gave a mixture of starting material with a broader aromatic resonance and a singlet at τ 5.31. Thermolysis at 650°C yielded starting material only.

Photolysis of 3-phenyl 2,1-benzoxathiole 1-oxide (177)

The sultine (100 mg) was dissolved in dry absolute methanol (25 ml), degassed using dry nitrogen, and irradiated for 15 h at 253 nm to give a slightly yellowish solution with traces of a precipitate. Removal of the solvent under reduced pressure at room temperature gave a brown oil, τ 2.08-3.49 (broad evelope), 4.70 (s), and 6.10 (s). G.l.c./mass spectral analysis of this oil (3% OV17 at 200°C, flow rate 36 ml min^{-1}) separated three products (retention time 4 min.0 sec, 5 min.50 sec, and 7 min. 20 sec) with molecular ions m/e = 168, 190, and 166 respectively. The last peak was identified as fluorene from the retention time of a known sample, and comparison of the n.m.r. spectrum, but no positive identification could be made of the others.

Photolysis of 2,1-benzoxathiole 1-oxide (201)

The sultine (70 mg) was dissolved in dry absolute methanol (25 ml), degassed and irradiated for 21 h at 253 nm. The reaction was monitored by removal of the solvent and n.m.r. spectroscopy every 6 h and at the end of 12 h there was still predominantly starting material. After a further 9 h, removal of the solvent gave a dark brown oil, n.m.r. analysis showed still some starting material with a broadened aromatic region; the nature of the products formed could not be determined.

Preparation of methylcyclopropane[94]

To a stirred mixture of zinc (12 g) and 70% aqueous ethanol (20 g) was added 1,3-dibromobutane (10 g). The mixture was then heated to 60°C when a brisk evolution of gas was observed. This gas was condensed in an ice salt bath to give a clear liquid (3 ml). This liquid was then redistilled at room temperature using an ice salt condenser to give pure methylcyclopropane, as a colourless liquid, τ (100 MHz), 9.00 (d, J = 5 Hz), 9.12-9.68 (m).

CHAPTER FIVE

Preparation of samples for shift reagent studies

Cis and trans 3-phenylthietan 1-oxides, cis and trans 3-p-bromophenylthietan 1-oxides, and cis and trans 3-t-butylthietan-1-oxides were all prepared from available samples of the appropriately substituted thiete sulphones, previously prepared in this laboratory.[20] This was effected using the method described by Johnson and Siegl.[112] Reduction of the thiete sulphones to thietan sulphones was achieved using sodium borohydride (procedure B), except for the 3-t-butyl analogue, which was catalytically hydrogenated to give an almost quantitative yield of the thietan sulphone.

The thietan sulphones were reduced to the sulphides, using lithium aluminium hydride, and reoxidised to the isomeric sulphoxides by stirring overnight with an equivalent amount of m-chloroperoxybenzoic acid dissolved in dichloromethane, at room temperature.

Careful chromatography of this mixture of isomers (typically 1.2 g) on silica (50 g) and eluting with ether, gave the cis isomer first, closely followed by the trans isomer. Confirmation of the stereochemical assignments of these compounds were based on n.m.r. spectradescribed previously.[108]

Cis and trans 3-phenyl-3-methylthietan-1-oxide

3-Phenyl-3-methylthietan (prepared as described in Chapter One (1 g)) was oxidised to the isomeric sulphoxide using m-chloroperoxybenzoic acid as described for the previous examples above. Careful chromatography of this mixture on silica (50 g) using ether as the eluent afforded the cis-isomer as a clear oil (632 mg) followed by the trans-isomer as a white crystalline solid (300 mg).

Preparation of exo 8-thiatetracyclo[2.2.1.1.0]octane 8-oxide[125,127]

The addition product of sulphur dichloride and norbornadiene (20 g) was treated with a hot aqueous sodium carbonate solution.

The reaction was worked up after 30 min and there was found to be no change. Treatment for 3 h however afforded a small amount of the desired sulphoxide after work up (1.93 g, 13.4%), m.p. 72-76°C, lit. m.p.[125] 76-77°C. τ 5.45-5.69 (1H, br.m), 6.56-6.77 (2H, m), 7.78-8.02 (1H, m), and 8.10-8.47 (4H, m), ν_{max} (dichloromethane), 3050, 2939, 2862, 1125, and 1049 cm^{-1}, m/e 140, 123, and 91. ^{13}C n.m.r. (p.p.m. downfield of TMS) 9.82, 21.18, 34.09, 45.13, and 64.36.

Preparation of endo 8-thiatetracyclo[2.2.1.1.0]octane 8-oxide

Some of the previously prepared exo sulphoxide (1.2 g) was suspended-dissolved in dry ether (50 ml) while stirring at 0°C. Lithium aluminium hydride (0.2 g) was slowly added to this mixture over a period of 10 min, while stirring rapidly. The reaction was allowed to warm up to room temperature after which it was stirred for 4 h. Usual work up procedures gave a very smelly colourless oil. The n.m.r. spectrum still showed some traces of the starting material but there were other resonances at τ 6.28-6.47 (m), 6.92-7.19 (m), and 7.51-7.85 which could reasonably be assigned to the sulphide. T.l.c. on silica eluting with ether showed two spots, one of them coincident with the starting material R_f = 0.052, and the other one R_f = 0.84. This material was stirred in an excess aqueous sodium metaperiodate solution (3 g saturated) for 2 days at room temperature, after which extra action with dichloromethane and normal work up gave a white solid (1.0 g). The n.m.r. spectrum showed that none of the exo sulphoxide was present. T.l.c. analysis (silica) eluting with ether showed two spots; R_f 0.032 and 0.26. Careful chromatography of some of this material (0.75 g) on silica (80 g) eluting with pure ether increasing to 2% methanol in ether, succeeded in isolating two compounds as white crystalline solids. The first compound to be eluted (R_f = 0.26) was shown to be 8-thiatetracyclo[2.2.1.1.0]octane 8,8-dioxide (350 mg), m.p. 135°C (dec.) lit. m.p.[125] 130°C (dec.), τ 5.90-6.10 (2H, m), 7.05-7.30 (1H, br.m), 3.63-7.90 (1H, m), 7.90-8.13 and 8.15-8.34 (4H, m). ν_{max} (dichloromethane) 3060, 2950, 2815, 1300, 1175, and 1097. M/e (no molecular

ion) 92, 91, 66 and 65. ^{13}C n.m.r. (p.p.m.) 13.23, 21.34, 31.17, 34.90 and 76.78. The second compound, R_f = 0.032 (101 mg) gave the following data: m.p. 113-115°C, τ 6.21-6.51 (2H, m), 7.20-7.49 (1H, m), 7.58-7.84 (2H, m), and 7.84-8.10 and 8.10-8.38 (3H, m). ν_{max} (dichloromethane) 3051, 2942, 2875, 1138, and 1080 cm^{-1}. M/e 140, 123, and 91. ^{13}C n.m.r. (p.p.m.) 21.02, 27.35, 32.55, 36.36, and 68.01. Found: C, 60.06; H, 5.76; S, 22.54. C_7H_8OS requires C, 59.99; H, 5.75; S, 22.84.

The remainder of the crude oxidation mixture (250 mg) was dissolved in a peracetic acid solution (4 ml) and stirred for 4 days. Work up gave a white solid (200 mg) with the same n.m.r. spectrum as that of the known sulphone.

Attempted photoaddition of thiophosgene with cyclohexene and norbornylene

A mixture of freshly distilled cyclohexene (12.8 ml, 0.126 mol) and thiophosgene (5 ml, 0.043 mol) was irradiated with daylight tubes for five days. G.l.c. analysis against a small portion of the mixture which had been kept in the dark showed that no reaction had taken place.

The reaction was also tried using a solution of norbornylene (0.5 g, 5.31 mmol), and thiophosgene (0.4 ml, 5.31 mmol), dissolved in dichloromethane (15 ml). Irradiation of the solution at 589 nm for 18 h gave no change as indicated by g.l.c. analysis against a control sample of the mixture which had been kept in the dark.

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SUMMARY

The flash vacuum thermolysis and photolysis of a number of cyclic sulphones have been studied with a view to developing these reactions as possible synthetic processes. A number of 2-substituted thietan sulphones have been shown to give the appropriately substituted cyclopropanes in high yields. The corresponding reactions of 3-substituted theitan sulphones are not quite so clean however, and a number of products are formed.

Attempts have been made to synthesise sulphoximides based on the thiochroman nucleus ; however, without success.

The flash thermolyses of thiochroman-4-one sulphones have been studied. The products of these reactions are generally α,β-unsaturated ketones, and the mechanism has been probed by deuterium labelling experiments.

The flash thermolyses of some substituted γ-sultines havebeen studied in detail. Generally, sulphur dioxide is extruded and the products are derived from the remaining biradical species. In one case however, one of the products is derived from a loss of sulphur monoxide from the starting material.

The conformational equilibria of various cis and trans 3-substituted thietan 1-oxides have been studied using n.m.r. spectroscopy and a lanthanide shift reagent technique. In general it has been found that the oxygen atom prefers to adopt an equatorial position in all of the compounds studied.