

SOME ASPECTS OF
THE CHEMISTRY
OF SULPHUR-HETEROCYCLES
AND
RELATED COMPOUNDS

by
CHRISTOPHER RICHARD HALL

A Thesis
presented for the degree of
Doctor of Philosophy
in the Faculty of Science
of the
University of Leicester
1974

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STUDIES ON
THE CHEMISTRY
OF SULPHUR-ETEROCYCLES
AND
RELATED COMPOUNDS



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University of Leicester
1974

FOR HEATHER, AND MY PARENTS

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 1971 and June 1974.

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

signed

A handwritten signature in black ink, appearing to read 'C.R. Hall', written in a cursive style with a long horizontal stroke at the bottom.

September 1974.

C.R. Hall

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I am extremely grateful to my supervisor, Dr. D.J.H. Smith, for his constant help and encouragement at all stages of this work.

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Many thanks also go to my fellow students, the staff, and the technicians of the Organic Chemistry Department for assistance, for never ending discussions, and for entertainment.

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SUMMARY

3-Substituted thietane 1-oxides have been investigated by proton, carbon-13, and lanthanide induced shift, magnetic resonance studies, and for the two isomers of 3-p-bromophenylthietane 1-oxide, by X-ray crystallography. It has been concluded that it is reasonable to interpret the physical properties of a solution of the cis-isomers in terms of the single conformer in which both substituents occupy equatorial positions, and those of the trans-isomers in terms of approximately equal amounts of both possible conformers.

cis and trans-3-Methylthietane 1-oxide react with toluene-p-sulphonyl isocyanate to give the thietane imides with epimerisation. In polar solvents the reaction involves prior equilibration of the sulphoxides, but in non-polar solvents this does not occur.

Pentamethyl-1-phenylphosphetan 1-oxides react with toluene-p-sulphonyl isocyanate to give the phosphetan imides with retention of configuration. The reaction has been shown to be first order in both reactants. Optically active acyclic phosphine oxides however react to give racemic phosphine imides. The first step of this reaction involves racemisation of the phosphine oxide. Kinetic studies have shown this process to be first order in phosphine oxide and second order in isocyanate.

Investigations suggest that if a reaction involves putting a formal positive charge on sulphur in a thietane or its 1-oxide, and if there is a good nucleophile in solution, then nucleophilic attack will occur at the α -carbon and ring opened products will result.

The photolysis and flash thermolysis of a series of 4π -electron cyclic sulphones have been investigated. These reactions are thought to involve an unsaturated sulphene which rearranges to give a series of cyclic sulphinate esters. In the thermolysis reaction these then fragment.

A number of novel organo-platinum complexes have been prepared and their structures have been determined by n.m.r. and infrared spectroscopy. Attempts to generate stable sulphene-metal complexes by rearrangement of the above complexes induced by thermal, photochemical, and chemical means, have not been successful.

CHAPTER ONE

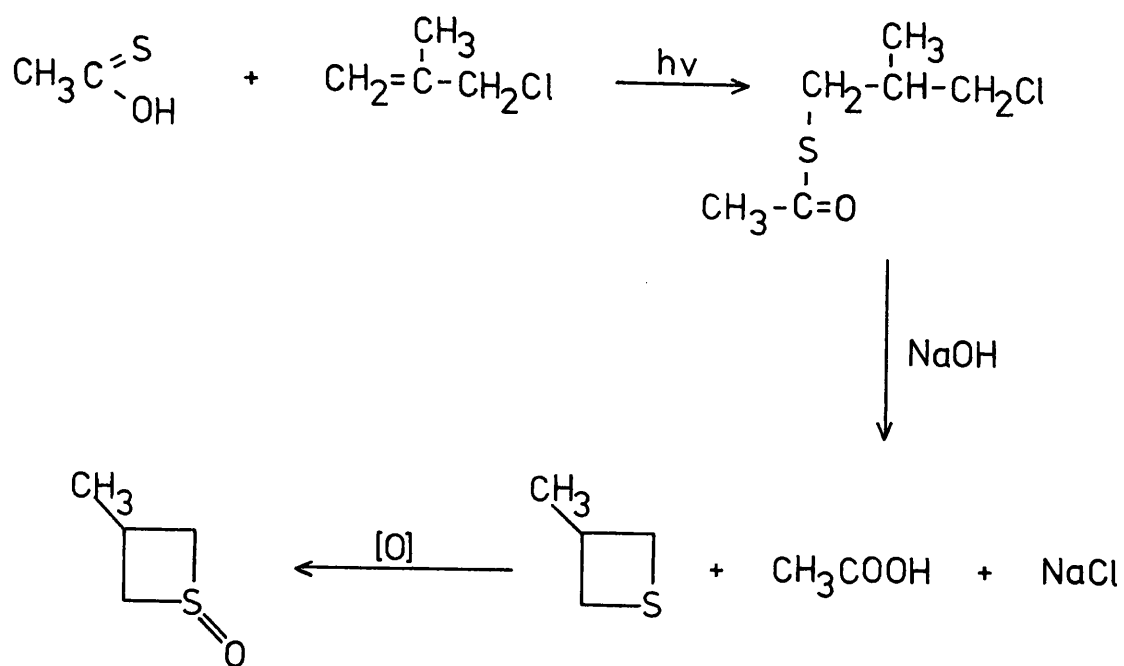
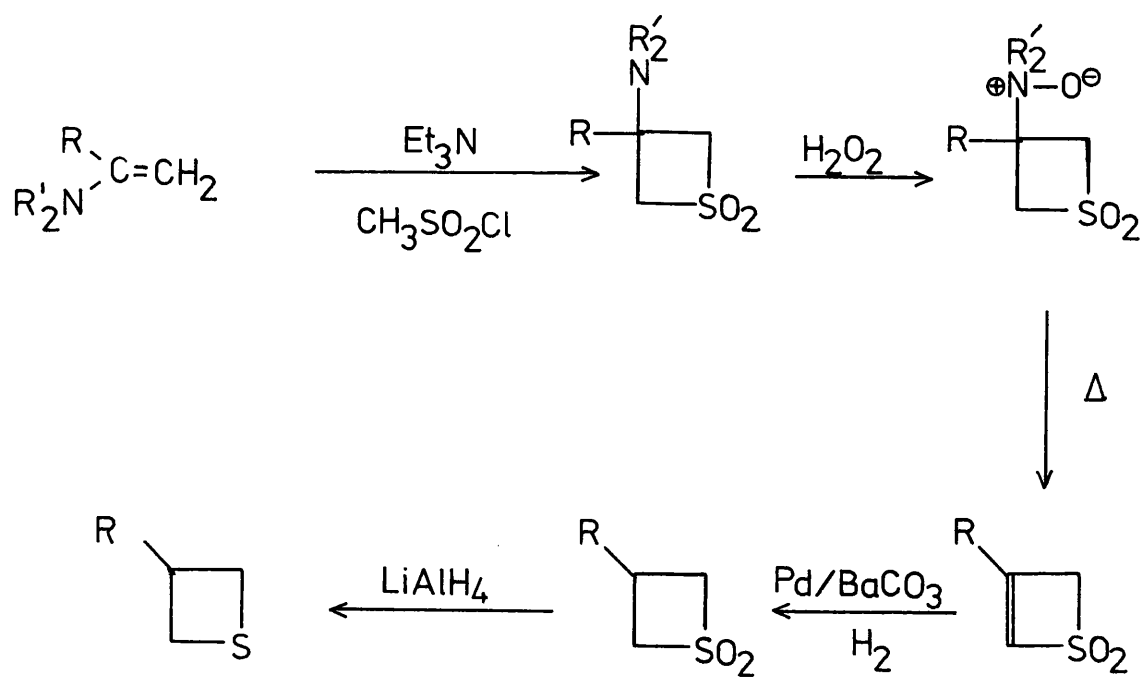
THE PREPARATION AND STRUCTURE OF SOME 3-SUBSTITUTED THIETANE 1-OXIDES.

1.1 Introduction

One of the original aims of this thesis was to use a four-membered ring as a probe to investigate nucleophilic substitution at sulphonyl sulphur. A number of informative stereochemical features have been observed in nucleophilic substitution reactions at phosphorus when phosphorus is constrained in a four-membered ring.¹ It was hoped that equally valuable information might be obtained from a study of the corresponding sulphur-containing heterocycles. The systems chosen for investigation were the 3-substituted thietane 1-oxides. The presence of a 3-substituent means that there are two possible geometric isomers of these molecules; the substituent can either be cis or trans with respect to the sulphonyl oxygen. This allows the stereochemical course of the reactions studied to be determined.

1.2 Preparation

There are at present a number of routes into the 3-substituted thietane system described in the literature.² Probably the simplest is that developed by Bordwell³ (fig. 1). This involves the photolysis of a mixture of thioacetic acid and 2-substituted 3-chloropropene. A free radical addition, via the most stable radical, gives a good yield of the thioester. Basic hydrolysis then leads to the 3-substituted thietane. The major limitation of this method is that it only works for R=Me or Et.

fig.1fig.2

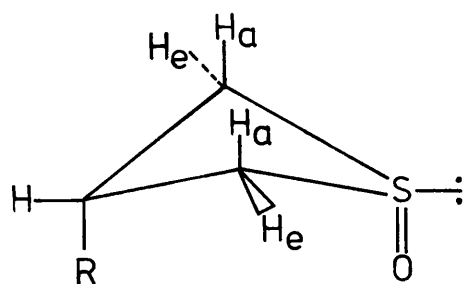
3-Methylthietane was prepared in this way. Controlled oxidation with one mole of hydrogen peroxide, sodium metaperiodate or m-chloroperbenzoic acid gave a mixture of cis and trans-3-methylthietane 1-oxides.⁴ Separation of these isomers, in low yield, was achieved by repeated chromatography on silica and elution with chloroform.

All the other thietanes described in this thesis were prepared by the method due to Johnson⁴ (fig. 2). This route was chosen primarily because it involved initial preparation of the respective 3-substituted thiete 1,1-dioxides, and these were required for thermolysis studies. Johnson reduced the thiete 1,1-dioxides to the corresponding thietane 1,1-dioxides with sodium borohydride. This reaction only proceeds in low yield (~ 30%). Catalytic hydrogenation was therefore investigated as an alternative. Initial experiments using palladium on charcoal as catalyst were unsuccessful due to excessive catalytic poisoning. Use of 10% palladium on barium carbonate however reduced this poisoning to an acceptable degree. Yields of 95% were obtained using 5% of catalyst.

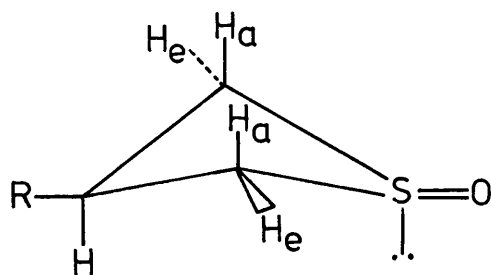
In general it was found that the more bulky the 3-substituent the easier was the separation of the cis and trans sulphoxide isomers.

1.3 Stereochemical Considerations.

The thietane ring has been shown to be puckered by a number of independent studies.⁵ The fact that the ring is not planar means that there are two possible conformations for each geometric isomer. i.e. for the cis isomer.



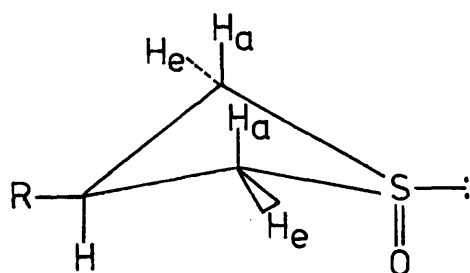
(a)



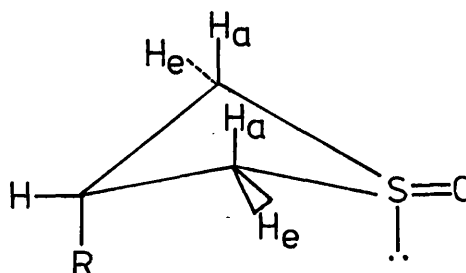
(b)

The difference between these forms is a ring flip. The energy required for this process is not expected to be large⁵ and at room temperature interconversion of conformers is expected to be fast on the n.m.r. time scale. This means that the n.m.r. spectrum should reflect a weighted average of the two conformers. It is probable that if R is a large group then the conformations will be of significantly different energies and one may expect anchoring in the lowest energy form. In the case of the cis isomer this would probably be (b), since (a) would be expected to entail severe 1,3-nonbonded interactions. Conformer interconversion may still be very fast, but if there is a significantly higher population of conformer (b), then the n.m.r. spectrum will approximate to that of (b).

The energy difference between the conformers of the trans isomer should be smaller than for the cis isomer, since in this case only one substituent can occupy an equatorial position.



(c)



(d)

A large R group may be expected to have a greater equatorial preference than oxygen, hence (c) will be the predominant conformer.

Johnson⁶ has investigated the ^1H n.m.r. spectra of a series of 3-substituted thietane 1-oxides and has found a remarkable similarity between them. The four α -protons in one isomer always exhibit two well separated 2H-multiplets, while in the other isomer all four α -protons come up as a broad doublet with a chemical shift approximately midway between the two multiplets. The β -proton in the second isomer is always significantly deshielded with respect to that in the first.

Dipole moment studies^{5b,7} on 3-chloro and 3-*p*-chlorophenylthietane 1-oxides suggest that the α -protons in the cis isomer give rise to the two 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 chromatography. This is expected since in this isomer the polar sulfoxide group is shielded by the 3-substituent on the same side of the ring, thus inhibiting interaction with the solid phase of the column.

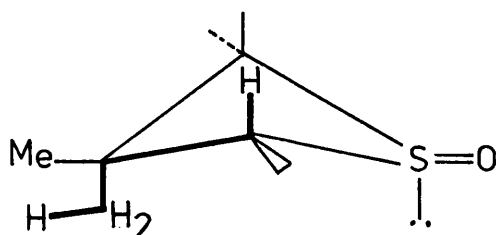
If (b) and (c) are considered as the predominant conformers then the observed ^1H n.m.r. spectra can be explained. In cyclic sulfoxides a large chemical shift difference is observed for the α -methylene protons

when the nonbonded electron pair on sulphur is axial.^{8,9,10} In each case where the configuration has been assigned to the cyclic sulfoxide and the α -protons, the α -protons trans diaxial to the lone pair on sulphur appear at higher field than the equatorial α -protons. A similar effect has been observed and employed for configurational assignment of nitrogen heterocycles.^{11,12} The effect is usually attributed to a selective shielding of the trans co-axial α -protons by the lone pair. This is the case in the cis isomer, the axial α -protons giving rise to the upfield 2H-multiplet. The complexity of these multiplets suggests a degree of cross ring coupling. In the trans isomer the lone pair is no longer axial hence there is no selective shielding and both sets of α -protons have the same chemical shift. The resonance appears as a 4H-doublet due to coupling with the single β -proton (the signal is not sharp because the two sets of protons are not completely equivalent).

The large deshielding of the β -proton in the trans isomer is probably due to an acetylenic type anisotropy of the sulphur-oxygen bond.^{10,13} The effect of this anisotropy on both sets of α -protons in each isomer may be considered to be approximately equivalent. Only when oxygen is axial, however, is the β -proton significantly deshielded. A further contribution to this deshielding may be a cis-axial proximity effect¹³ due to van der Waals interactions.¹⁴

It is somewhat surprising that when R is a small group such as methyl the above features are still observed, because, as the size of the R group decreases, so the energy difference between the two conformers of each isomer [e.g. (c) and (d)] also decreases. As this occurs so the predominance of one conformer over the other decreases and the n.m.r. spectrum is more likely to reflect a time-averaged position which does not relate directly to either conformer.

The ^1H n.m.r. spectrum of 3,3-dimethylthietane 1-oxide^{10,15} exhibits two non-equivalent methyl groups. The high field methyl is observed as a fine doublet ($J \sim 0.8\text{Hz}$). The preferred conformer is assumed to be (e).



(e)

The axial methyl group is expected to resonate at higher field (because of possible shielding by the cis-axial lone pair) and the coupling, which is with the axial α -protons, is attributed to the planar W-configuration of the intervening sigma-bonds.¹⁶ This configuration is only attainable by the axial methyl group.

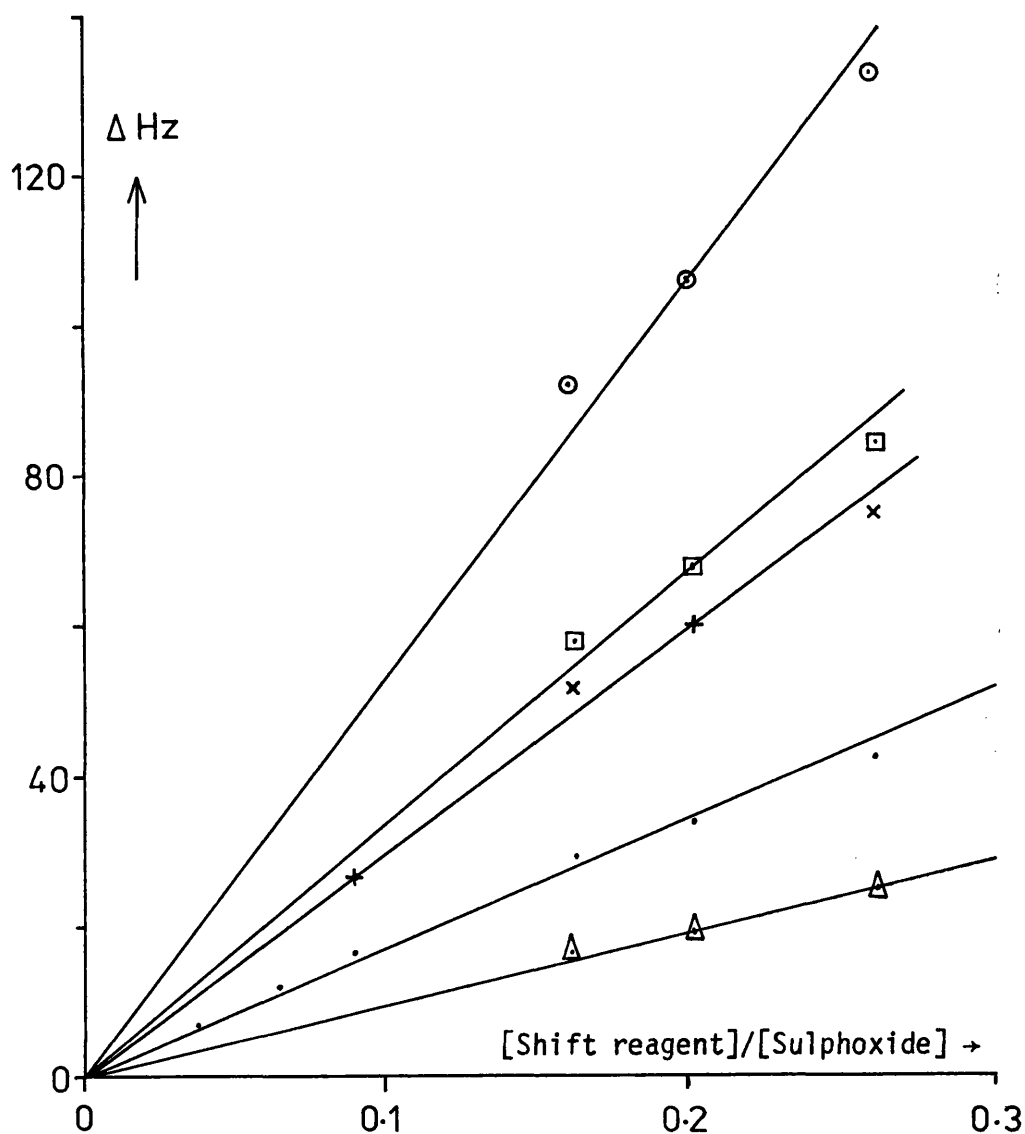
Observation of the methyl group in trans-3-methylthietane 1-oxide as a sharp doublet ($J_{\text{Me}-\beta\text{H}} 7.5\text{Hz}$) with no further long range coupling supports the configurational assignment (c) for this isomer.

1.4 Lanthanide Induced Shift (LIS) Studies.

In order to strengthen the previously made configurational assignments, LIS studies were carried out on the two isomers of 3-methyl

and 3-phenylthietane 1-oxides. The spectra were run at 60 MHz in deuteriochloroform as solvent, using tris(dipivalomethanato)europium (III) as the shift reagent. Since in most cases the spectra consist of a series of overlapping multiplets, it was difficult to measure the shifts accurately. In the cases where it was possible, a plot of shift (ΔHz) against the molar ratio of shift reagent to the sulfoxide gave a straight line.

trans-3-Methylthietane 1-Oxide + Eu(dpm)₃ in CDCl₃.



Δ Me(cis-isomer) • Me(trans-isomer) \times β -H(trans-isomer)
 \square α -H(trans-isomer) \odot α -H(trans-isomer)

Considering first the 3-methyl system, the following qualitative observations were made:

(1) The rate of shift of the methyl group in the trans isomer is greater than in the cis isomer.

(2) The methyl group in the trans isomer remains as a sharp doublet. This suggests that it remains equatorial, and the oxygen predominantly axial as in conformer (c). This is somewhat surprising since one would expect a large bulky group, co-ordinated to the oxygen, to make conformer (d) more favourable.

(3) In the cis isomer, assuming that it adopts conformation (b), 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 (similar to that originally observed for the trans isomer). On addition of further shift reagent the signal is again observed as two 2H-multiplets. The axial α -protons are now responsible for the low field multiplet.

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

(5) In both isomers the rate of shift of the α -protons > β -protons > methyl group.

Other than for the methyl groups it was not possible to compare the relative rates of shift of the same proton in both isomers.

The ring protons in both isomers of 3-phenylthietane 1-oxide show the same behaviour as above. The phenyl group, which in both cases is initially a singlet, is slowly resolved into a complex multiplet.

Lanthanide induced shifts are normally interpreted in terms of the McConnell-Robertson equation.¹⁷ For axially symmetric complexes the spacial dependence of the shifts (S_f) is given by

$$S_i = \frac{\Delta H_i}{H} = k(3\cos^2\theta_i - 1) R_i^{-3}$$

where ΔH_i is the change in field strength at the nucleus i , R_i is the distance between the paramagnetic metal and the nucleus i , and θ_i is the angle between the principal magnetic axis of the complex and the vector R_i . It is common practice to ignore angular dependencies and to analyse the data using the radial term only. In the case of sulfoxides the europium has been shown to co-ordinate to the oxygen,¹⁵ and the principal magnetic axis of the europium is assumed to lie along the sulphur-oxygen-europium bond.^{15,18}

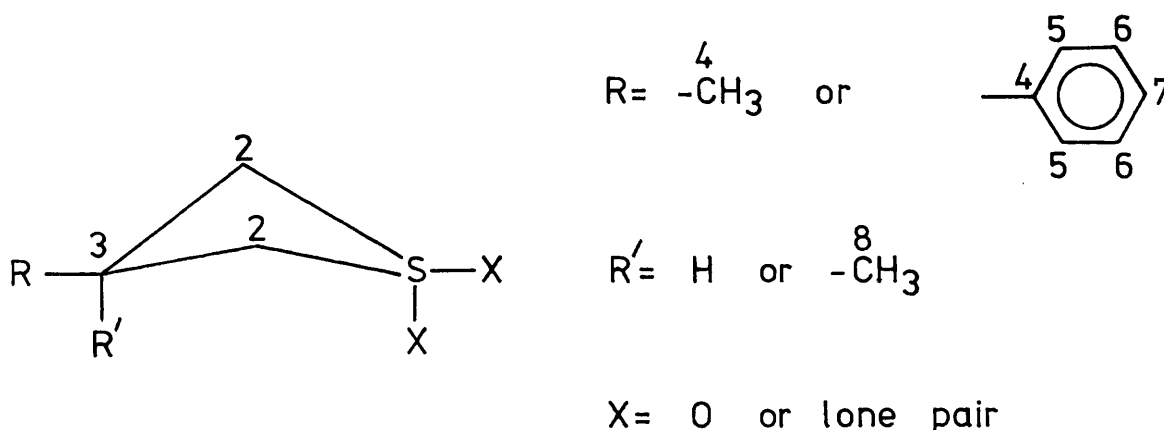
If a static model is used the above observations are consistent with the expected conformers (b) and (c). Previous workers^{15,18,19} however have pointed out the dangers in making these assumptions in a conformationally mobile molecule. Uebel¹⁵ has shown that consideration of a static model only leads to an incorrect assignment in 3,3-dimethylthietane 1-oxide. Consideration and averaging of the rotamer populations about the sulphur-oxygen-europium bond, however, give the correct answer. In our case it is very difficult to predict rotamer populations and the computational requirements are very large. A complete analysis of the data was therefore not attempted, and conclusions drawn from a static model should be treated with care.

1.5 Carbon-13 Magnetic Resonance Spectra.

Further conformational data was sought by examining the ^{13}C n.m.r. spectra of a range of 3-substituted thietanes, their 1-oxides, and 1,1-dioxides. The spectra were run by the Physico-Chemical Measurements Unit, Harwell, Didcot, Berks., in deuteriochloroform as solvent, using

a broad band decoupling technique. All shifts are reported in parts per million (p.p.m.) downfield from tetramethylsilane (TMS). ^{13}C n.m.r. has the advantage that chemical shifts are much greater than in ^1H n.m.r. (the range of carbons paraffin to carbonyl covers approximately 190 p.p.m.). Since a broad band decoupling technique was used each carbon exhibited only a single line. The main disadvantage of ^{13}C n.m.r. is that, because of nuclear Overhauser effects, one cannot integrate carbons in different environments. It is often a reasonable approximation, however, to measure isomer ratios by integration of the same carbon in each isomer.

Numbering System Used to Report Carbon-13 Spectra.



All the samples studied show the same distinct trends:

(1) The chemical shift of the 2-carbon increases in the series sulphide < cis sulfoxide < trans sulfoxide < sulphone. This trend could be predicted on inductive grounds. The order of the cis and trans sulfoxides can be interpreted either in terms of a shielding effect by the axial lone pair in the cis isomer, or a deshielding effect by the axial oxygen in the trans isomer. This observation is consistent with the conformers (b) and (c), but inconsistent with the view that the oxygen

¹³C N.M.R. SPECTRA. Shifts quoted in p.p.m. downfield from TMS for samples in deuteriochloroform.

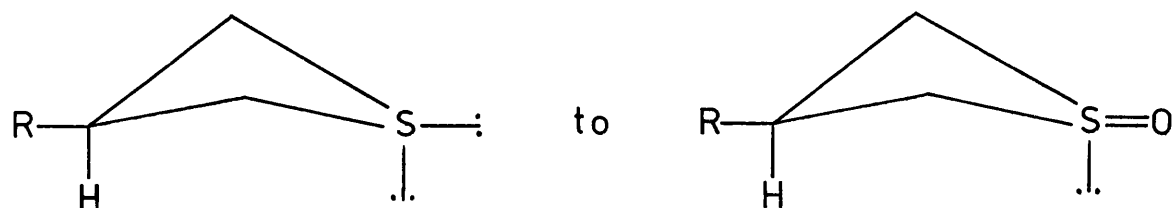
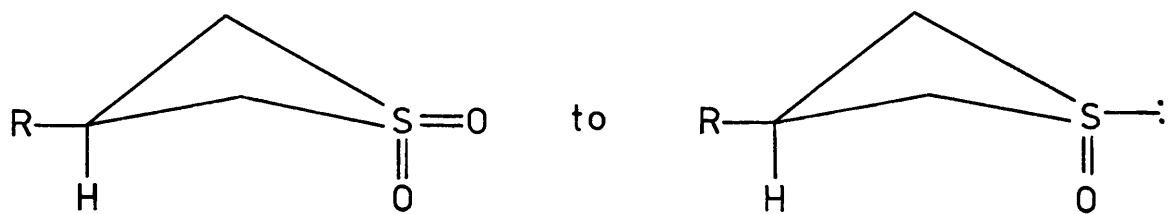
Carbon atom number	2	3	4	5	6	7	8
3-Methylthietane	33.15	36.14	22.62				
<u>trans</u> -3-Methylthietane 1-oxide	57.84	22.94	22.09				
<u>cis</u> -3-Methylthietane 1-oxide	59.72	21.77	18.91				
3-Methylthietane 1,1-dioxide	71.10	20.47	14.75				
<u>trans</u> -3-Phenylthietane 1-oxide	57.00	34.25	141.4	128.9	127.1	126.5	
<u>cis</u> -3-Phenylthietane 1-oxide	59.53	28.01	140.0	128.9	127.6	126.5	
3-Phenylthietane 1,1-dioxide	71.81	24.37	139.4	129.1	127.8	126.6	
<u>trans</u> -3-p-Bromophenylthietane 1-oxide	56.87	33.99	121.1	128.4	132.1	140.4	
<u>cis</u> -3-p-Bromophenylthietane 1-oxide	59.34	27.69	121.5	128.2	132.1	139.1	
3,3-Dimethylthietane 1-oxide	63.78	28.56	31.97				29.21
3-Methyl-3-phenylthietane	38.15	47.44	149.9	128.4	123.7	126.1	30.87
3-Methyl- <u>trans</u> -3-phenylthietane r-1-oxide	62.85	37.17	145.1	128.9	125.1	126.8	34.44
3-Methyl- <u>cis</u> -3-phenylthietane r-1-oxide	63.24	34.44	148.4	128.7	123.7	126.6	30.94
3-Methyl-3-phenylthietane 1,1-dioxide	75.58	29.70	145.4	128.9	125.2	127.2	31.00

is equatorial in the predominant conformer of both isomers.

(2) The 3-carbon exhibits the same trend as the β -proton in the ^1H n.m.r., i.e. the downfield shift increases in the series sulphone < cis sulfoxide < trans sulfoxide < sulphide. The order of the sulfoxides reflects a probable deshielding of the 3-carbon in the trans isomer by the axial oxygen. As in the proton spectrum this is probably an anisotropic effect.

In 3-methyl-trans-3-phenylthietane r-1-oxide both the 3-carbon and the methyl carbon resonate at a lower field than in the corresponding cis isomer.²⁰ This is consistent with conformations (c) and (b) respectively where R = phenyl and H = methyl.

Due to the many similarities in structure, one might expect to be able to relate the spectral properties of the sulphones to those of the trans sulfoxides and the sulphides to the cis sulfoxides.



This relationship is however, not observed. The most probable explanation is that the angle of ring puckering in these systems is not comparable.

1.6 X-ray Crystallographic Investigations.

In general the information gained from the LIS and ^{13}C studies supports the configurations (b) and (c) for the cis and trans sulfoxide isomers respectively. There is however still some room for doubt. The absolute configuration of the whole series of 3-substituted thietane 1-oxides rests on the original dipole moment studies^{5b,7} and a few pieces of supporting evidence. It was therefore considered necessary to undertake an X-ray crystallographic study of at least a cis and a trans isomer and possibly a sulphide and sulphone as well. The only X-ray crystallographic data so far available for these systems is on the complex between 3,3-dimethylthietane 1-oxide and tris(dipivalomethanato)europium-(III),¹⁵ where an equatorial oxygen and a ring puckering angle of 35° are observed, and on trans-(3-carboxylic acid)thietane 1-oxide,²¹ where again the oxygen is approximately equatorial and the ring puckering angle is 27° . Both of these can be considered special cases. The first structure is probably modified by the large europium complex co-ordinated to the oxygen, and in the second, groups of molecules are held together by hydrogen bonds between the carboxyl and sulfoxide groups.

In order to undertake the study it was necessary to prepare a system in which both cis and trans sulfoxide isomers are crystalline (Both 3-methyl isomers are oils and only cis-3-phenylthietane 1-oxide is crystalline). The best possibility seemed to be the 3-p-bromophenylthietane 1-oxide system. The presence of a bromine atom should also

simplify the X-ray determination. A mixture of isomers of the above system was prepared by a method similar to that described by Johnson.⁴ The isomers were separated in good yield by chromatography on silica and elution with ether-methanol (50:1). Both isomers are crystalline and both give essentially the same infra-red spectra in the solid state and in solution (chloroform), suggesting that the solid state structure is the same as that of the predominant conformer in solution.

The crystallographic studies were kindly undertaken by Dr. D.R. Russell and J. Barlow of this University. As yet, however, a complete set of data is available only for the cis isomer. The most relevant geometrical factors are reported in the table and accompanying diagrams.

Geometry of cis-3-p-Bromophenylthietane 1-oxide.

Angles, degree (e.s.d.)		Distances, Å (e.s.d.)	
O,S,C(1)	111.0(0.7)	S-C(1)	1.832(0.014)
O,S,C(3)	112.5(0.7)	S-C(3)	1.849(0.014)
C(1),S,C(3)	76.1(0.6)	S-O	1.482(0.013)
S,C(1),C(2)	89.7(0.9)	C(1)-C(2)	1.538(0.017)
C(1),C(2),C(3)	95.2(1.1)	C(2)-C(3)	1.536(0.026)
C(1),C(2),C(21)	116.1(1.0)	C(2)-C(21)	1.498(0.014)
C(3),C(2),C(21)	118.6(1.6)		
S,C(3),C(2)	89.1(0.9)		
C(3),C(1),H(11)	142.3(1.1)		
C(3),C(1),H(12)	109.1(1.1)		
H(11),C(1),J(12)	107.7(1.2)		
C(1),C(3),H(31)	107.4(1.0)		
C(1),C(3),H(32)	142.3(1.2)		
H(31),C(3),H(32)	109.5(1.5)		
H(2),C(2),C(21)	110.4(1.2)		

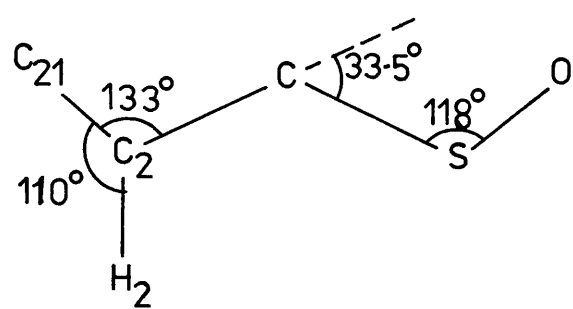
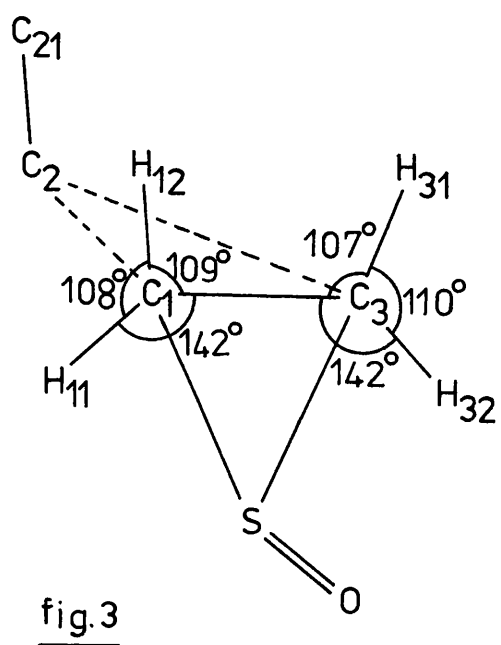
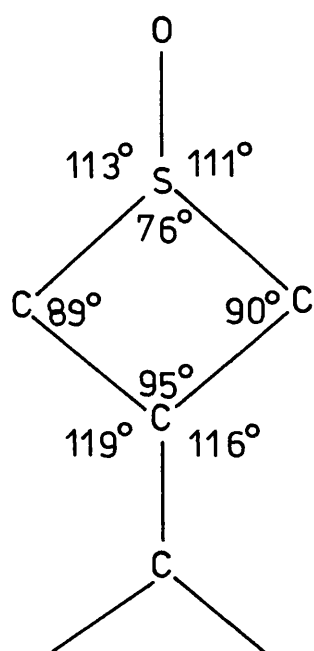
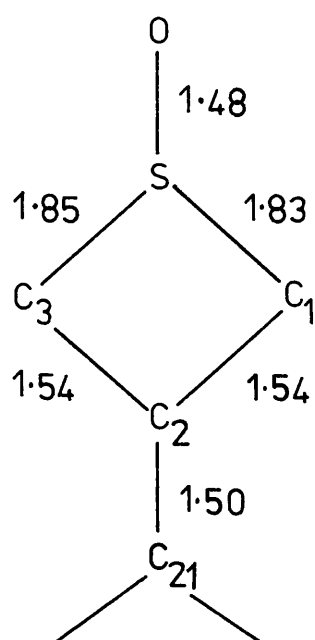


fig. 4

cis-p-Bromophenylthietane 1-oxide.

17.

(Scale drawing)

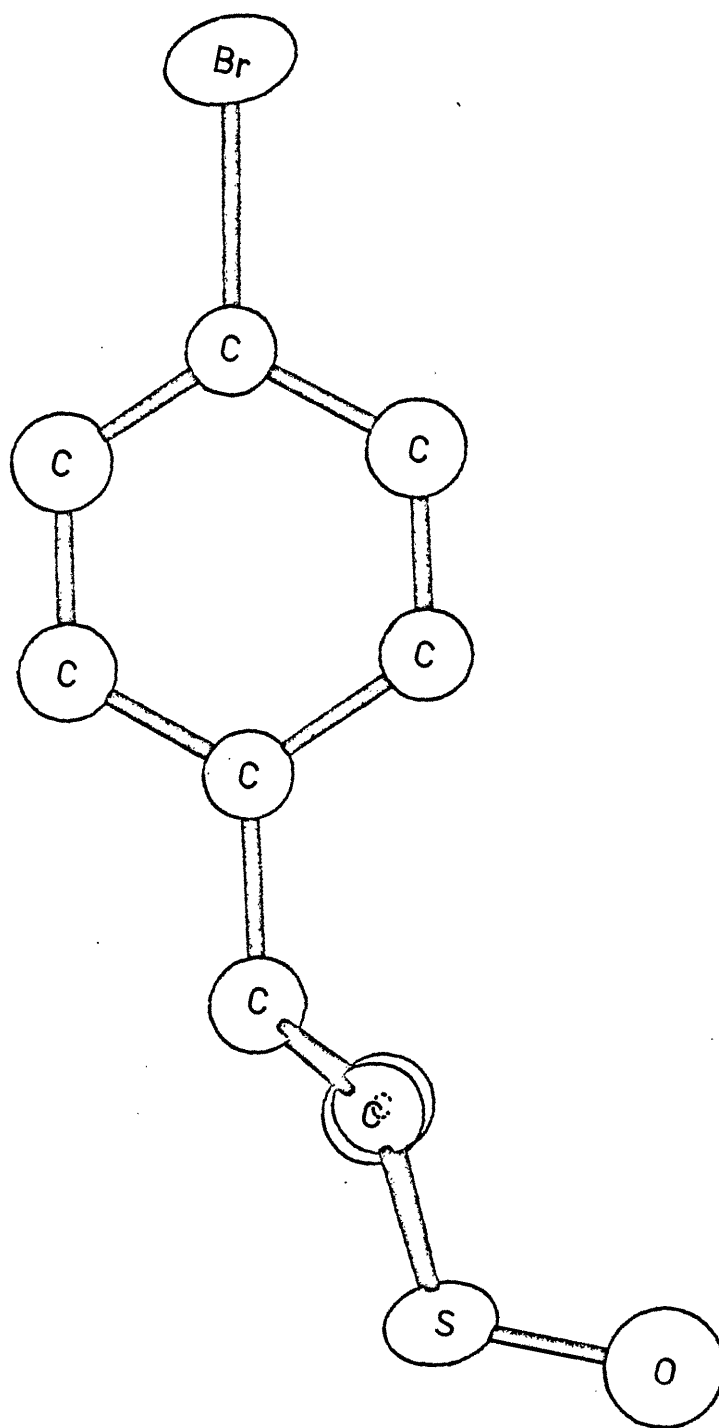


Fig 5

The ring puckering angle is 33.5° . The angle between the plane containing C(1), C(3), and S, and the sulphonyl oxygen bond is 118.1° and that between the plane containing C(1), C(3), and C(2), and the C(2)-C(21) bond is 132.9° . The system therefore approximates very well to the expected conformer (b), i.e. both the oxygen and the 3-substituent occupy equatorial positions (fig. 4).

The difference between the axial [H(12) and H(31)] and the equatorial [H(11) and H(32)] α -protons is illustrated in fig. 3. The bond angles and distances within the thietane ring are very similar to those previously reported^{15,20} and as expected the phenyl ring is at approximately right-angles to the plane containing C(1), C(2), and C(3) (fig. 5).

1.7 Equilibration Studies with Hydrogen Chloride.

A number of workers have investigated the racemisation of optically active sulfoxides with acids,²² and a number of different mechanisms have been proposed.

Contrary to the report by Johnson,⁴ equilibration of the two geometric isomers of 3-methylthietane 1-oxide with hydrogen chloride has been shown to occur in a variety of solvents and with negligible decomposition. The equilibrium mixture contains 85% cis sulfoxide and 15% trans sulfoxide. Assuming that, (i) equilibration occurs through a symmetrical intermediate such as R_2SCl_2 ,^{22a} or that the rate of reaction of hydrogen chloride with both isomers is the same, and that (ii) trans 3-methylthietane 1-oxide exists predominantly in conformation (c), then this isomer ratio reflects the equatorial preference of oxygen in this type of four-membered ring [The cis diequatorial geometry minimises the

1,3 (cross-ring) nonbonded interactions]. The difference in the concentration of each isomer in the equilibrium mixture implies a free energy difference between the two isomers of approximately 1.0 Kcal./mole at 25°.

Recent calculations²³ have suggested that the axial preference exhibited by sulphinyl oxygen in thiane 1-oxides may be due to attractive van der Waals interaction between the oxygen and carbons 3 and 5 or their attached axial hydrogens. No repulsive interactions were calculated. Presumably the different bond lengths and angle of ring puckering in thietane 1-oxides means that these attractive forces are outweighed.

The equilibrium isomer ratio is independent of solvent (within experimental error) and was almost identical to that obtained by Johnson⁷ for 3-t-butyl and 3-p-chlorophenylthietane 1-oxides. Thus, like the n.m.r. spectra, the ratio of isomers in the equilibrium mixture is remarkably insensitive to large changes in the 3-substituent.

CHAPTER TWO

NUCLEOPHILIC SUBSTITUTION AT SULPHINYL SULPHUR

2.1 Introduction.

The majority of reactions involving nucleophilic substitution at sulphonyl sulphur have been shown to go with inversion of configuration. Thus, sulphinic esters react with Grignard reagents stereospecifically to give sulfoxides,²⁴ alkoxysulphonium salts with hydroxide to give sulfoxides,²⁵ sulphinic esters with lithium or magnesium amide to give sulphinamides,^{26,27} and sulphinamides with Grignard reagents to give sulfoxides.^{27,28} In some of these reactions, and in a number of others,²⁹ sulphuranes have been postulated as either transition states or intermediates.

Sulphuranes.

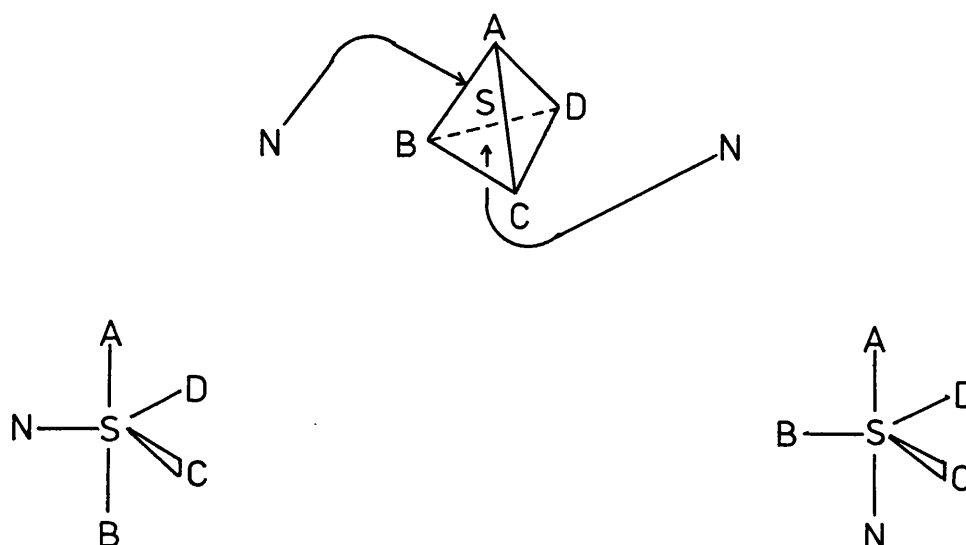
In this thesis the term sulphurane refers to 'pentaco-ordinate' sulphur species in which one of the 'ligands' is considered to be the nonbonding lone pair of electrons.

Several stable sulphuranes have now been prepared and in each case they have been shown to have trigonal-bipyramidal geometry, with the more electronegative ligands preferentially occupying the apical positions.²⁹⁻³²

Formation and Decomposition of Sulphurane Intermediates.

There are two possible modes of attack of a nucleophile on tetrahedral sulphur to form a trigonal bipyramid (TBP); attack on any one of the four faces or on any one of the six edges. Attack on a face is called apical attack because the attacking nucleophile occupies an apical position in the resultant TBP, the equatorial positions being occupied by the three

groups which formed the face being attacked. Attack on an edge is called equatorial attack, as the attacking group occupies an equatorial position in the resultant sulphurane, the two groups forming the edge swinging into apical positions. Similarly, the leaving group can depart from either an apical or an equatorial position.



Structural analyses of several stable sulphuranes²⁹⁻³² have shown that the apical bonds are longer, and therefore weaker and more readily broken, than the equatorial bonds. Theoretical calculations by Van der Voorn and Drago³³ on some corresponding phosphoranes have shown that the increased s character in equatorial bonds gives rise to apical bonds that are weaker and more polar than the equatorial bonds. It has been presumed therefore that electronegative nucleophiles will prefer to enter and depart via these electropositive apical positions.

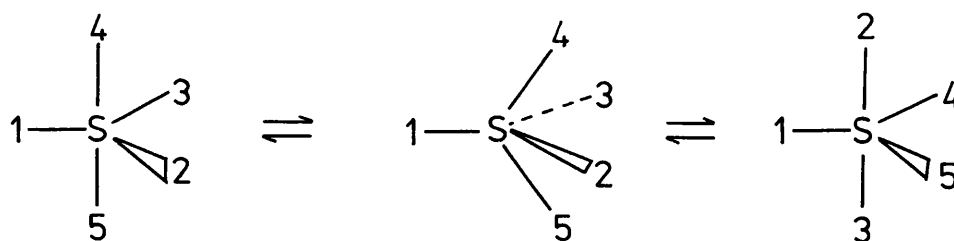
The stereochemistry of the substitution is governed by the position of entry and departure of the groups. The consequences of possible combinations are shown in the following table.

<u>ENTRY</u>	<u>EXIT</u>	<u>STEREOCHEMISTRY</u>
a	a	Inversion
a	e	Retention
e	a	Retention
e	e	Inversion

a = apical, e = equatorial.

Pseudorotation.

In order to account for the observed ^{19}F n.m.r. spectra of pentafluorophosphorane which consists of only one resonance, although electron diffraction studies have shown it to have a trigonal-bipyramidal structure, Berry³⁴ proposed a mechanism whereby exchange of apical and equatorial fluorines could occur. The process suggested, which he called pseudorotation, consisted of simultaneous exchange of a pair of equatorial ligands and a pair of apical ligands by way of a square pyramidal transition state. One ligand remains equatorial and has been designated the pivot.



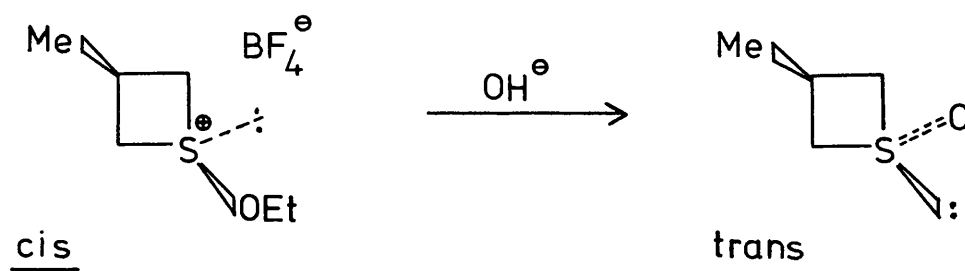
This process has been widely used to account for the n.m.r. spectra of fluorophosphoranes,³⁵ oxyphosphoranes,³⁶ and penta-arylphosphoranes.³⁷

Pseudorotation in sulphuranes has not been reliably demonstrated. In the cases where permutational isomerism does occur, the mechanism has

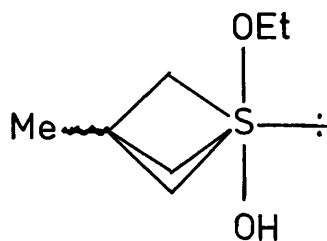
been shown to involve intermolecular ligand exchange.^{29,38} The failure to observe pseudorotation in intermediate sulphuranes has been explained by suggesting that the sulphuranes are very unstable with respect to decomposition, and therefore do not have a sufficiently long lifetime to enable pseudorotation to occur.

Nucleophilic Substitution Reactions.

One of the few reactions investigated where sulphur is constrained in a four-membered ring is the alkaline hydrolysis of thietanium salts. Mislow³⁹ observed sulphoxide formation with almost complete inversion of configuration.

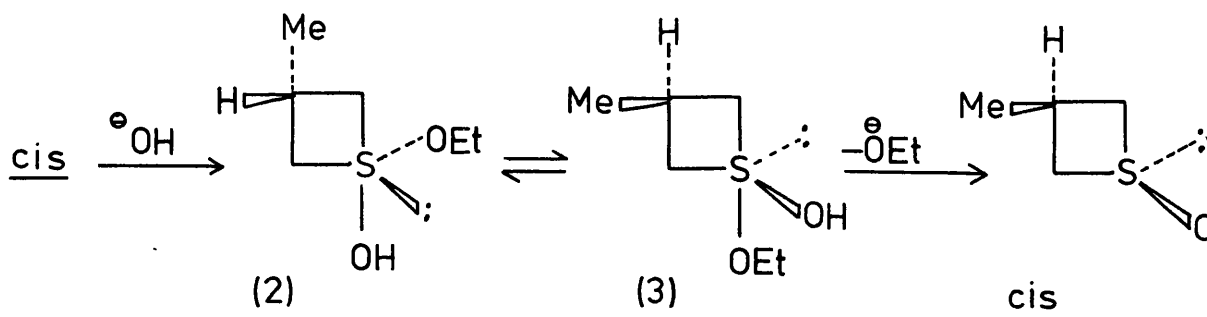


If the reaction proceeds by a direct $\text{S}_\text{N}2$ displacement at sulphur, with the O-S-O angle near 180° , Mislow expects considerable angle strain to be produced by the presence of the four-membered ring (1). The equatorial positions of the TBP transition state, which in an unstrained case have a preferred angle of 120° , are forced to subtend an angle near 90° .

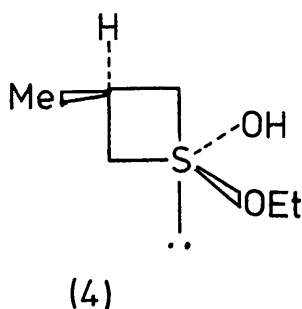


(1)

X-ray crystallography of phosphoranes⁴⁰ has shown that four and five-membered rings prefer to occupy one apical and one equatorial position. In the ideal case the angle between these positions is 90°. It could be assumed that this was also the case in sulphuranes. The expected course of the reaction would therefore be apical attack of hydroxide ion opposite one of the ring ligands to give an intermediate sulphurane (2).



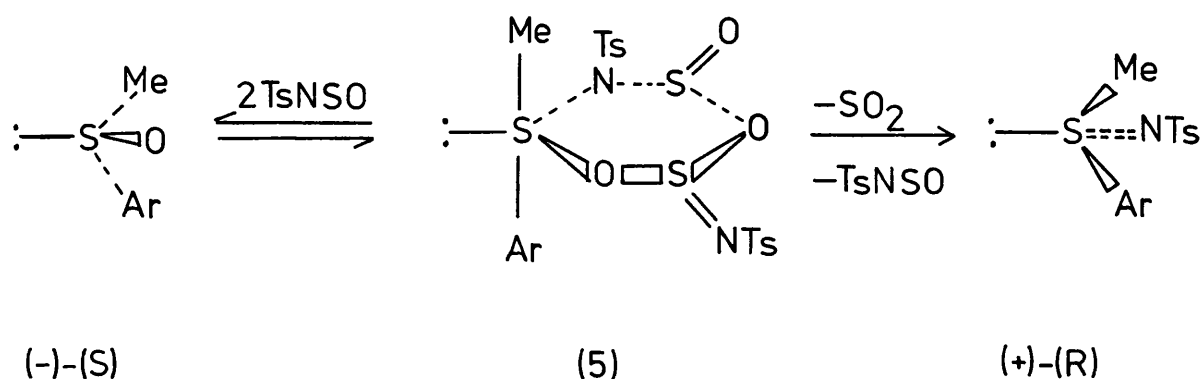
This could then pseudorotate about the lone pair as pivot to give a second TBP (3), from which apical loss of ethoxide ion would lead to sulfoxide formation with retention of configuration. The failure to observe retention of configuration suggests that either the energy barrier to putting the ring diequatorial (1) is low, or that the reaction proceeds by an equatorial attack-equatorial loss mechanism. This type of mechanism does not occur in phosphorus chemistry but it would lead to inversion of configuration. It would involve sulphurane (4) as an intermediate or transition state.



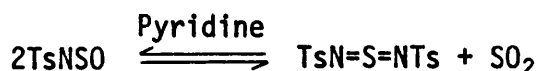
Sulphurane (4) is expected to be of high energy because it has the lone pair in an apical position and this is unfavourable both on steric and electronic grounds.^{30,41,42}

Recent X-ray data³¹ on a sulphurane $\text{Ph}_2\text{S}(\text{OR})_2$ show that, as expected, it has an approximately trigonal-bipyramidal geometry. The two phenyl groups and the lone pair occupy the equatorial positions but the C-S-C angle between the two phenyl groups is 104.4° . The lone pair appears to have a very large steric requirement, repelling the two phenyl groups and contracting the angle between them from the ideal case of 120° . Sulphurane intermediates involving a four-membered diequatorial ring may therefore not be as unfavourable as expected, since the ring may only have to span an angle of approximately 100° .

Cram⁴³ has investigated the reaction of N-sulphinyl-p-toluene sulphonamide⁴⁴ (TsNSO) with optically active methyl-p-tolyl sulphoxide.²⁴ When pyridine was used as solvent, sulphimide was formed with 94% inversion of configuration. When dichloromethane was used as solvent the reaction was less specific (60% inversion). Preliminary kinetic data, and the fact that sulphur dioxide was the only other reaction product, led Cram⁴³ to propose an equatorial attack-equatorial loss mechanism which involved a novel type of intermediate (5).

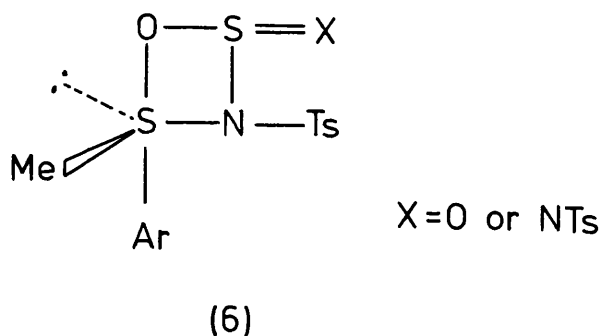


Kresze⁴⁵ has shown that on addition to pyridine, TsNSO reacts rapidly to give N,N'-bis(toluene-p-sulphonyl)sulphur diimide (DIM) and sulphur dioxide.



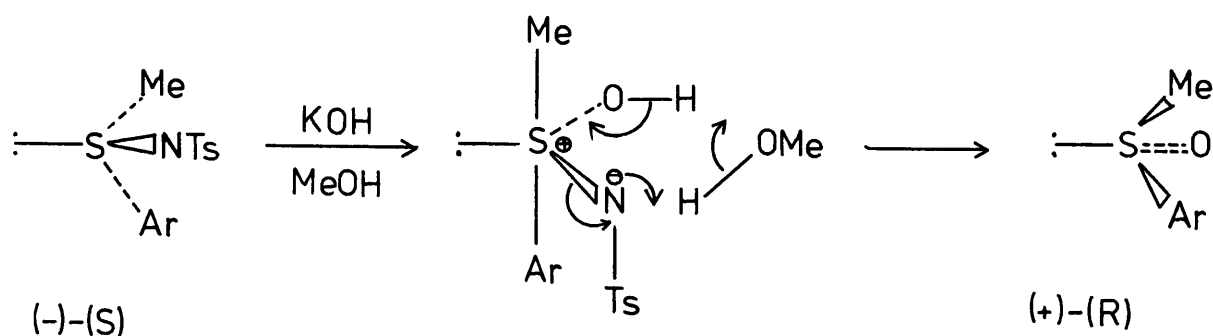
It was suggested that the difference in reaction, when pyridine and dichloromethane are used as solvents, might be due to different reacting species [DIM can be substituted for TsNSO in the intermediate (5)].

In 1971 Christensen⁴⁶ reported the reaction of the same sulfoxide with both TsNSO and DIM in benzene as solvent. In both cases he observed sulphimide formation with complete retention of configuration. This was one of the first examples of a substitution reaction involving retention of configuration at sulphonyl sulphur.⁴⁷ A mechanism involving a Wittig type^{44,48} intermediate (6) was proposed.



Johnson⁴⁹ has reported the reaction of TsNSO and TsNCO with the 4-t-butylthiane 1-oxides. He obtained only very small (~8%) yields of sulphimide, and assumed, on the basis of Cram's results,⁴³ that the reactions went with inversion of configuration.

An equatorial attack-equatorial loss mechanism has also been proposed for the basic hydrolysis of (-)-(s)-methyl-p-tolylsulphimide.⁴³ Sulphoxide is re-formed with inversion of configuration.

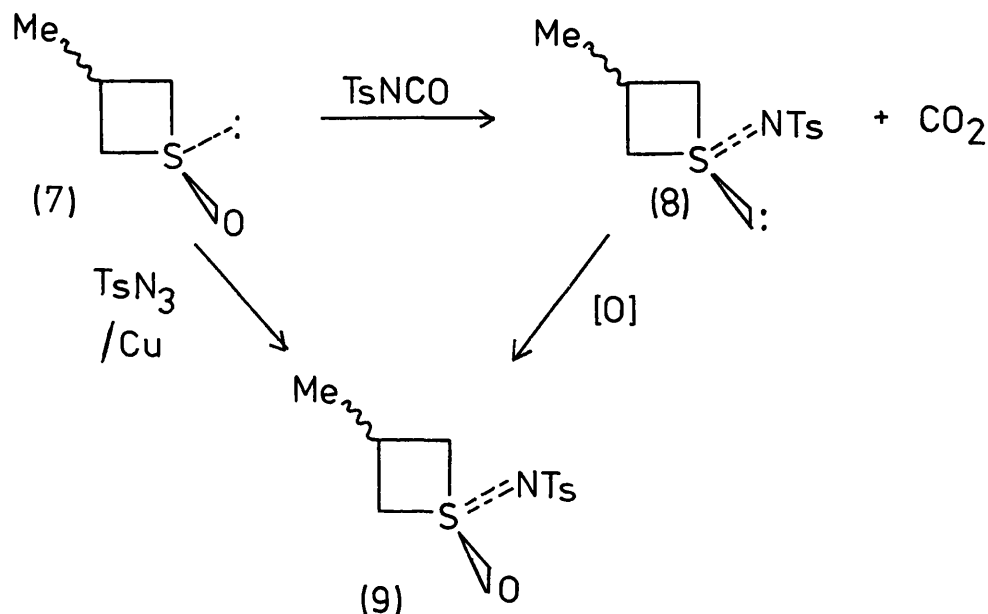


2.2 The Reaction of 3-Methylthietane 1-Oxide with Toluene-p-sulphonyl Isocyanate.

Attempted reaction of both TsNSO and DIM with the 3-methylthietane 1-oxides under a variety of conditions and in a number of solvents led only to the recovery of a quantitative yield of starting material with unchanged configuration. Use of p-tolyl isocyanate and N-sulphonyl aniline gave the same result.

Addition of toluene-p-sulphonyl isocyanate (TsNCO) however, to an ice-cooled solution of the sulphoxide led to the isolation of 3-methylthietane 1-N-(toluene-p-sulphonyl)imide as a mixture of isomers. The same mixture of isomers (in the same ratio) was obtained regardless of the starting material (i.e. cis or trans sulphoxide) and regardless of the solvent (i.e. acetonitrile, benzene, dichloromethane, or chloroform). No sulphimide formation was observed when pyridine was used as solvent.

The isomer ratio in the above mixture was determined by completion of the following reaction cycle:



Sulfoxides react with toluene-*p*-sulphonyl azide in the presence of freshly precipitated copper to give sulfoximides.⁵⁰ Since the reaction involves only simple imidation of the lone pair on sulphur, it is reasonable to assume that it proceeds with retention of configuration. Likewise, oxidation of the lone pair in sulphimides by the sodium salt of *m*-chloroperbenzoic acid^{43,49} can also be assumed to entail retention of configuration. By consideration of the isomer ratio of sulfoximides (9) obtained by oxidation of the crude sulphimide (8) mixture, it was shown that reaction of TsNCO with either isomer of 3-methylthietane 1-oxide (7) gave a mixture of sulphimides (8) containing 84% trans and 16% cis isomer.

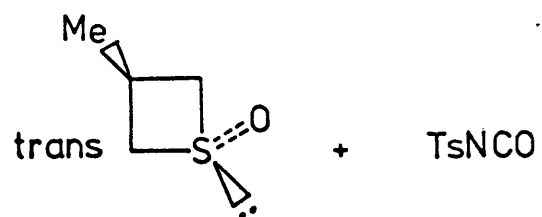
Having previously shown that an equilibrium mixture of sulfoxides (7) contains 85% cis and 15% trans isomer it seemed reasonable to propose that the reaction involves an initial equilibration of the sulfoxide (7) followed by sulphimide (8) formation with inversion of configuration. It

was however surprising that the outcome of the reaction was solvent independent.

By conducting further experiments in the probe of a Jeol PS100 n.m.r. spectrometer at -40° it was shown that when deuterioacetonitrile or deuteriochloroform were used as solvent, there was a prior equilibration of the sulphoxides, followed by a second sulphimide forming reaction. Fig. 6 illustrates the progress of the reaction between trans- (7) and TsNCO in deuterioacetonitrile at -40° (100% excess TsNCO). All five of the reproduced spectra have TMS in the same relative position; the signals due to the five ring protons are shown. As previously described the α -protons in the trans sulphoxide exhibit a broad doublet, while those in the cis isomer give two well separated 2H-multiplets. In this solvent the mixture of sulphimide isomers exhibits a single multiplet. After 1hr the reaction mixture contains trans sulphoxide, cis sulphoxide, and probably a small amount of sulphimide. This does not correspond to an equilibrium mixture of sulphoxides. After 12hr the mixture contains cis sulphoxide and sulphimide, with a smaller amount of trans sulphoxide, and after 24hr sulphimide formation is almost complete.

The fact that most of the signals overlap (the β -proton in the trans sulphoxide must be considered), and that the equilibration and sulphimide formation compete to some degree, means that it is not practical to follow the reaction kinetically. The course of the reaction can also be followed by observation of the methyl doublets. The chemical shift difference is however very small and several of the peaks cannot be completely resolved.

Warming of the product containing solution to room temperature did not affect the n.m.r. spectrum. The use of cis sulphoxide as starting material or deuteriochloroform as solvent does not alter the course of the reaction.

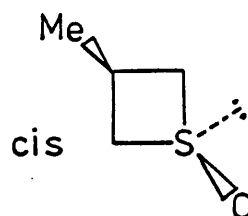
fig. 6

TIME 0 hr

TIME 1 hr

TIME 12 hr

TIME 24 hr

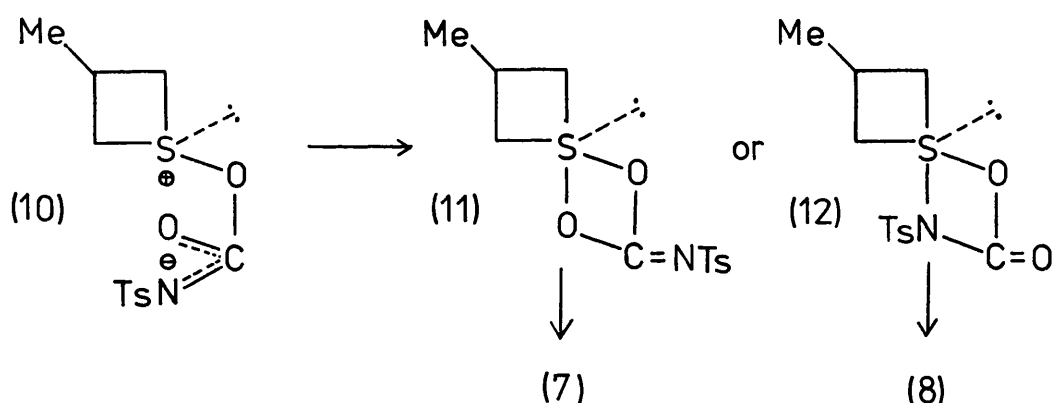


When benzene was used as solvent the reaction was conveniently studied at room temperature. Constant monitoring by n.m.r. showed in this case that there was no prior equilibration of sulfoxides. The spectrum of the crude sulphimide mixture was however identical to that obtained above, and oxidation confirmed that in both cases the isomer ratio was the same (trans:cis, 84:16).

2.3 Mechanistic Considerations.

In Benzene.

The first step of the reaction is probably nucleophilic attack of the sulfoxide oxygen at the carbon of the isocyanate to form a zwitterion (10). This is proposed to be a fast reversible process.

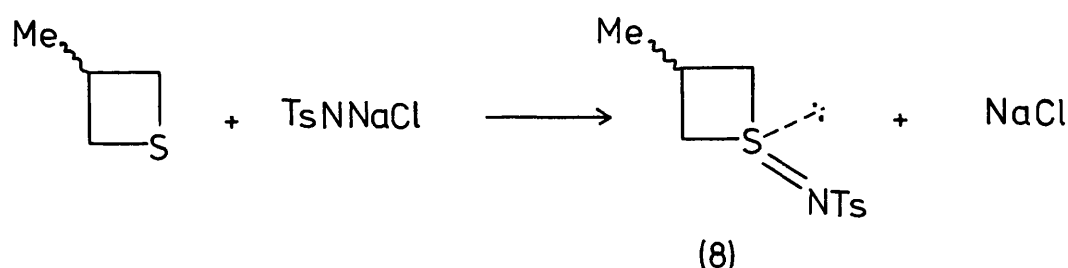


The zwitterion can then ring close by either the oxygen or the nitrogen acting as a nucleophile at sulphur to give intermediates (11) or (12). Pseudorotation of these intermediates is very unlikely (see previous discussion) and therefore their break-up will lead to reformed sulfoxide (7) and sulphimide (8), both with retention of configuration.

Since retention of configuration is not observed, then for the above mechanistic scheme to be correct, the sulphimide (8) must be equilibrated

after it is formed. In order to discover if these sulphimides are subject to equilibration under the reaction conditions it was necessary to prepare a single isomer if possible. Repeated chromatography of the crude mixture of sulphimides previously obtained gave only oils of identical isomer ratio to the starting material.

Preparation of sulphimide (8) by the reaction of 3-methylthietane with chloramine-T⁵¹ again gave the same ratio of isomers. It is possible



that chloramine-T also causes equilibration of the sulphimides. Alternatively cis sulphimide may be converted to the apparently more stable trans isomer by an intramolecular process (i.e. pyramidal inversion or bond cleavage and reformation).

Darwish⁵² has recently shown that optically active acyclic sulphimides can be racemised by pyramidal inversion at sulphur. The activation enthalpy for racemisation is ~ 28 Kcal./mole. Pyramidal inversion of sulphimide (8) would entail putting the four-membered ring diequatorial, but from Mislow's work³⁹ this may not be a high energy process. It seems unlikely however that the activation enthalpy for pyramidal inversion in the cyclic case is substantially lower than in the acyclic case, as it would need to be to explain the above results.

If the mechanism of racemisation entails carbon-sulphur bond cleavage then one would expect the activation enthalpy to be lower for

cyclic sulphimides, since in these cases the bond cleavage involves the relief of ring strain. Darwish⁵² rules out this mechanism in the acyclic case on the failure of one attempted 'cross over' experiment, and the fact that this type of behaviour is not observed for sulfoxides⁵³ and sulphonium salts.⁵⁴ Benzyl-p-tolyl sulfoxide is however racemised by a carbon-sulphur bond cleavage process.⁵³

Johnson⁴⁹ has observed that cis-4-t-butylthiane 1-N-(toluene-p-sulphonyl)imide is entirely converted to the trans isomer on standing at room temperature for two days.

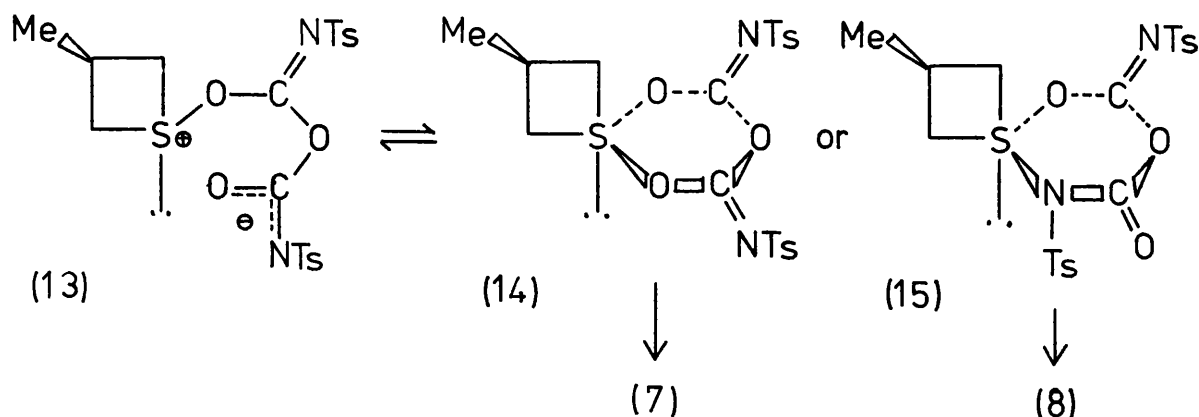
Attempts to prepare 3-phenylthietane 1-N-(toluene-p-sulphonyl)imide by both the reaction of the thietane with chloramine-T and the thietane 1-oxides with TsNCO gave only low yields (~10%) of product, apparently as a mixture of isomers. Repeated chromatography again did not vary the isomer ratio. The previously used reaction cycle could not be completed due to the zero yield in the reaction of the thietane 1-oxides with toluene-p-sulphonyl azide/copper.

Attempts to observe different isomer ratios of the 3-methylthietane imides (7) by conducting the preparation (and monitoring) at varying temperature (-40° to +20°) were not successful.

In Acetonitrile and Chloroform.

In these more polar solvents it is reasonable to assume that the initially formed zwitterion (10) has a longer lifetime. This enables it to react with a second mole of isocyanate to form an extended zwitterion (13), which can then ring close, again by either the oxygen or the nitrogen acting as a nucleophile at sulphur. Ring closure via apical attack at sulphur will, as in the case of benzene as solvent, lead to products initially with retention of configuration. Ring closure via equatorial attack (in a mechanistic scheme analogous to that of Cram⁴³) will lead

to (14) and (15) as intermediates or transition states, which can then



break up to give sulfoxide and sulphimide with inversion of configuration and regenerate at least one mole of TsNCO. The fact that equilibration is observed to be faster than sulphimide formation suggests that, in the zwitterion (13), oxygen is a better nucleophile at sulphur than nitrogen [i.e. formation of (14) is faster than formation of (15)]. This presumably also applies in the mechanism proposed for benzene solution, but in that case oxygen exchange gives only sulfoxide with retention of configuration and there is no observable effect on the course of the reaction.

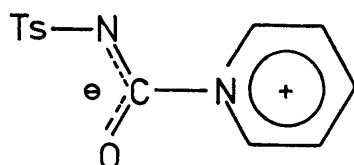
The mechanism for sulphimide formation in acetonitrile could be via the zwitterion (10) or the extended zwitterion (13). The only requirement is that equilibration of the sulfoxide is faster than sulphimide formation. Presumably the sulphimide, once formed, will be subject to any equilibration mechanism that was operating in benzene. Hence the observed isomer ratio of sulphimides will be the same as in the benzene case, and will not be subject to the degree of competition between sulfoxide equilibration and sulphimide formation.

The main difference between intermediates (14) and (15) and Cram's⁴³ diequatorial intermediate (5) is the position of the lone pair. The

presence of the four-membered ring means that the lone pair must occupy an apical position as opposed to the preferred equatorial orientation. This is unfavourable both on electronic and stereochemical grounds.^{30,39,41,42} It is probable that the energy required to put the lone pair apical outweighs that gained from relief of ring strain on going from tetrahedral (109°) to trigonal-bipyramidal (apical-equatorial ring, 90°) geometry. This means that, in polar solvents, the reaction has to go through an intermediate of higher energy than in the acyclic case. This fact could explain the lack of reaction of TsNSO with 3-methylthietane 1-oxide in acetonitrile or chloroform. It does not however explain the lack of reaction in benzene, since in this solvent, the proposed mechanism allows the lone pair to remain in the preferred equatorial orientation. In fact, in benzene, the reaction of the cyclic sulfoxide should be faster than the acyclic one, because in the cyclic case there should be a relief of ring strain on going to the sulphurane (12).

An alternative explanation for the lack of reaction with TsNSO is that the sulphonyl oxygen in the cyclic sulfoxide is a lot less nucleophilic than in the acyclic case, and hence there is no zwitterion formation between TsNSO and 3-methylthietane 1-oxide.

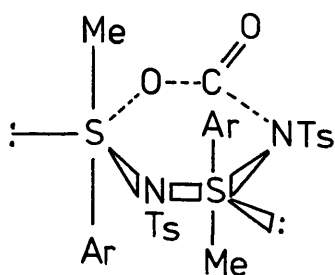
Addition of TsNCO to pyridine results in a rapid reaction to give a red solution and white crystals. These crystals have been shown to be a 1:1 adduct,⁵⁵ probably with a zwitterionic structure (16).



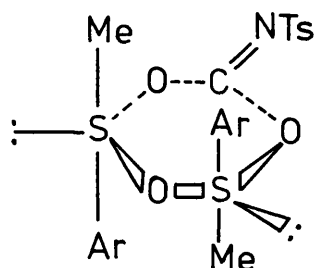
(16)

There is no reaction between (16) and 3-methylthietane 1-oxide.

Since this work was completed Cram⁵⁶ has published the results of an investigation of the reaction between TsNCO and methyl-p-tolyl sulphoxide in acetonitrile. From a series of experiments he concludes that the optically active sulphoxide gives optically active sulphimide with predominant inversion of configuration. The sulphimide then racemises in subsequent reactions, but only in the presence of both sulphoxide and TsNCO. The sulphoxide itself racemises in a competing reaction which depends on the presence of TsNCO. An intermediate, or transition state, such as (17), involving one mole each of sulphoxide, sulphimide and TsNCO is envisaged as being responsible for racemisation of the sulphimide.



(17)



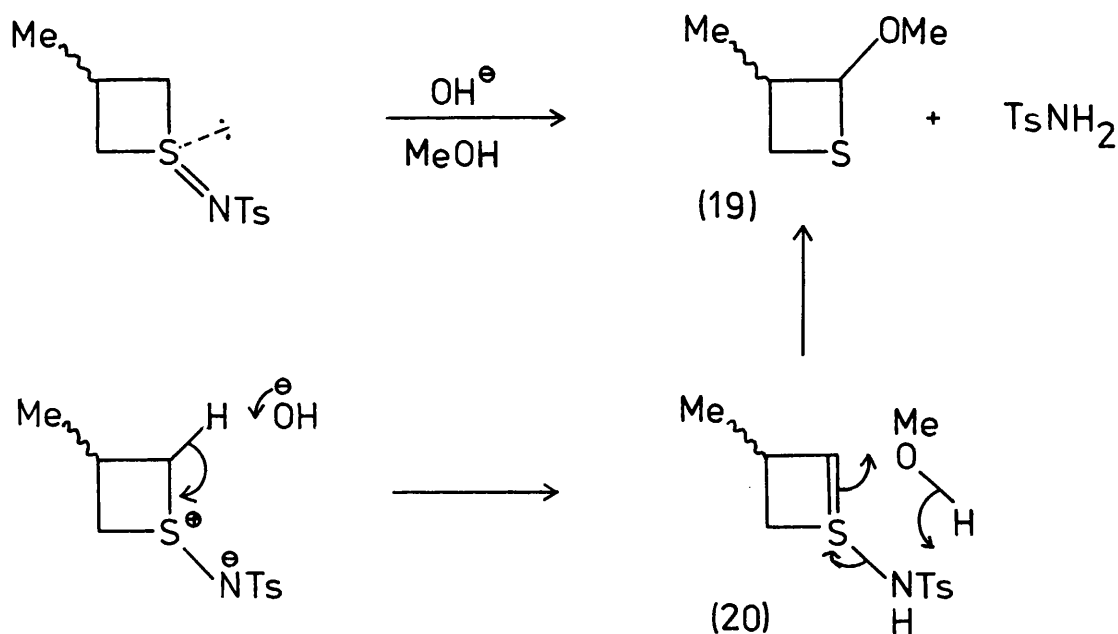
(18)

Break-up of intermediate (17) would lead to racemic sulphimide and carbon dioxide. A similar intermediate (18) involving two moles of sulphoxide and one of TsNCO could be responsible for racemisation of the sulphoxide.

In no case does Cram⁵⁶ observe racemisation of sulphimide without accompanying racemisation of sulphoxide.

2.4 The Hydrolysis of 3-Methylthietane 1-N-(toluene-p-sulphonyl)imide.

Unlike the acyclic case hydrolysis of the sulphimide (8) in potassium hydroxide/methanol does not give the sulfoxide (7) with inversion of configuration.⁴³ The products of the hydrolysis are 2-methoxy-3-methylthietane (19) and toluene-p-sulphonamide. Only one isomer of the disubstituted thietane appears to be produced, even though the starting sulphimide (8) is a mixture of isomers.



A reasonable mechanism for the reaction is proposed in the scheme. The base removes an acidic α -proton from the sulphimide to give an intermediate (20) (which can also be drawn as an ylide). This adds methanol as shown to give the observed products. Attempted oxidation of (19) to the corresponding sulphone with peracetic acid gave only 3-methylthietane 1,1-dioxide. This does however confirm the cyclic structure of the hydrolysis product.

This type of reaction has now also been observed by Oae⁵⁷ for five and six-membered rings.

2.5 Conclusion.

The observed results for the reactions of 3-methylthietane 1-oxide can be explained using modifications of the mechanisms originally proposed by Cram⁴³ and Christensen⁴⁶ for acyclic systems, and by proposing sulphimide equilibration via a carbon-sulphur bond cleaving process. It is not necessary to propose intermediates such as (17) and (18) though they cannot be ruled out.

It is difficult to envisage a mechanism for sulphimide equilibration by TsNCO that does not also equilibrate the sulfoxides, especially since oxygen appears, in the zwitterion, to be the better nucleophile.

No evidence for pseudorotation of sulphurane intermediates has been found.

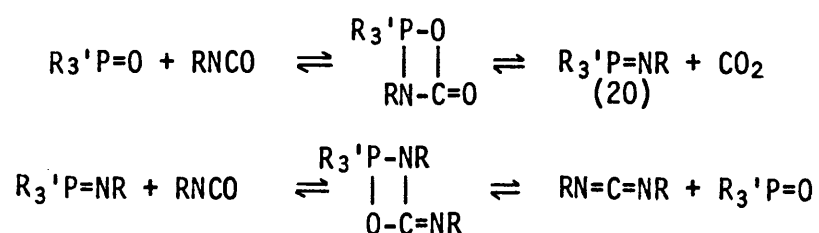
CHAPTER THREE

NUCLEOPHILIC SUBSTITUTION AT PHOSPHORYL PHOSPHORUS

3.1 Introduction.

In order to extend the work described in Chapter Two it was decided to investigate the reaction of toluene-p-sulphonyl isocyanate (TsNCO) with a system in which there were no complications from a lone pair of electrons on the hetero-atom, namely the reaction with phosphine oxides.

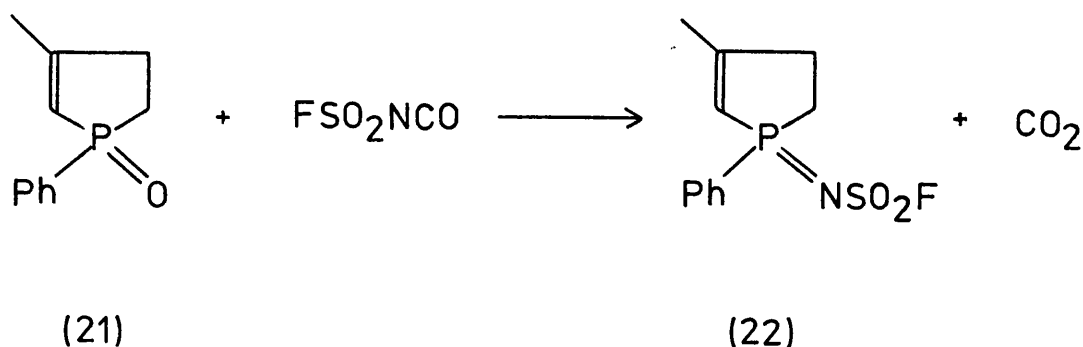
The formation of carbodiimides from isocyanates by the catalytic action of phosphine oxides is a well characterised process.⁵⁸ The reaction involves initial formation of a phosphine imide (20) and carbon dioxide, followed by rapid reaction of the phosphine imide with a second mole of isocyanate to give the carbodiimide and to re-form the phosphine oxide.



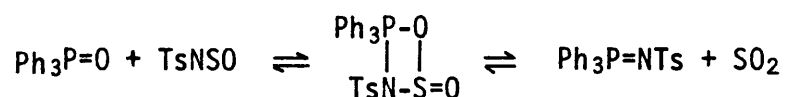
A Wittig type transition state⁴⁸ is envisaged for both steps. Phosphine imide formation is thought to be the rate determining step^{48b} and the best catalyst is the compound now known to be (21).⁵⁹

Hoffman⁶⁰ has more recently described the reaction of (21) with

N-fluorosulphonyl isocyanate. No carbodiimide is obtained in this case because the reaction does not proceed beyond the intermediate N-fluorosulphonylphospholene imide (22).



Senning⁶¹ has found that phosphine oxides also react with N-sulphonyl-toluene-p-sulphonamide (TsNSO). By refluxing a solution of triphenylphosphine oxide and TsNSO in benzene for 14hr he obtained a small yield of triphenylphosphine N-(toluene-p-sulphonyl)imide.



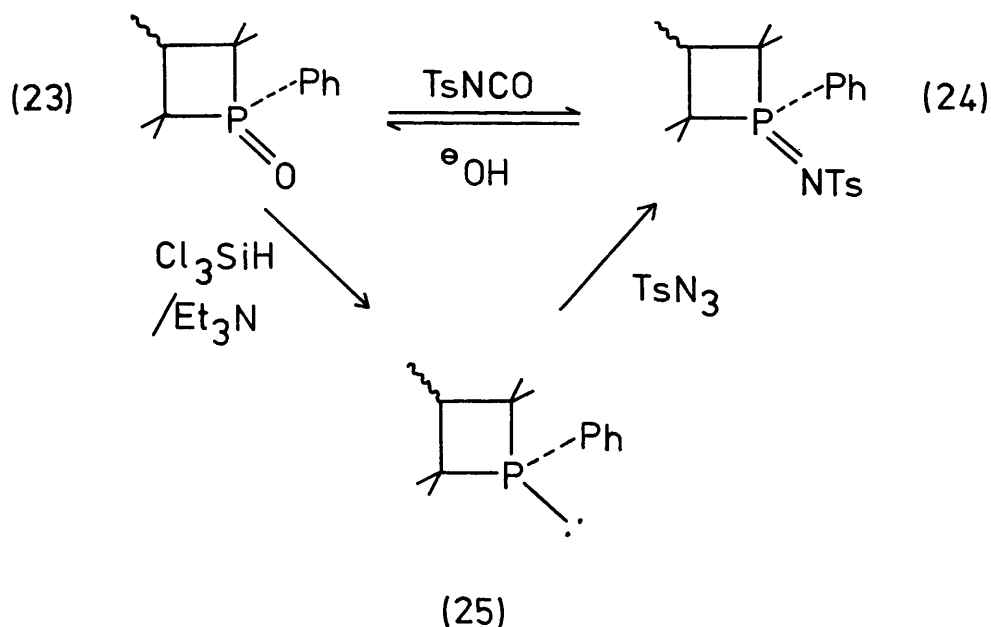
3.2 The Reaction of Pentamethyl-1-phenylphosphetan 1-Oxides with Sulphonyl Isocyanates.

In order to adequately describe the stereochemistry of pentamethyl-phosphetan compounds, Corfield⁶² has suggested the use of the Belstein r-system,⁶³ where the reference group on phosphorus is specified by the symbol r- and the geometrical relationship of this group to the ring 3-methyl is denoted by a cis or trans prefix.

Both isomers of 2,2,3,4,4-pentamethyl-1-phenylphosphetan 1-oxide (23) react with TsNCO remarkably smoothly. Addition of the isocyanate to an ice-cooled solution of a single isomer of the phosphetan oxide in benzene gave a single isomer of the phosphetan imide (24). Identical results were obtained when acetonitrile, dichloromethane or chloroform were used as solvent. In all cases the yield of phosphetan imide was essentially quantitative.

Alkaline hydrolysis of the phosphetan imides in aqueous methanol gave the starting phosphetan oxide, as the same single isomer, again essentially quantitatively.

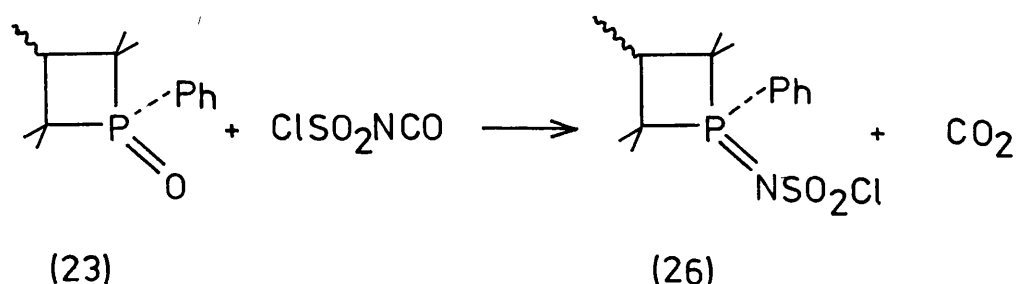
In order to determine the stereochemistry of the above reactions the following reaction cycle was completed:



Phosphetan oxides are known to be reduced by trichlorosilane and triethylamine with retention of configuration.^{64,65} The reaction of the

phosphetan (25) with toluene-*p*-sulphonyl azide in benzene only involves oxidation of the phosphorus lone pair and it is reasonable to assume therefore that it too proceeds with retention of configuration. Since the same phosphetan imide is obtained from both preparative routes, and since two of the reactions in the cycle go with retention of configuration, then both the reaction of phosphetan oxide with TsNCO and the hydrolysis of phosphetan imide must also involve retention of configuration.

Chlorosulphonyl isocyanate (CSI) also reacts with the phosphetan oxides to give the corresponding phosphetan imides (26) as unstable clear oils, again in high yield.



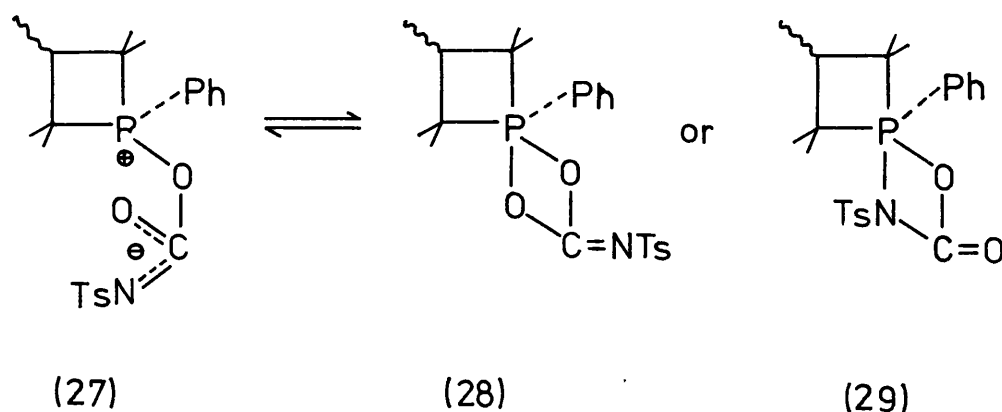
This reaction also gives a single isomer, and by analogy to TsNCO, it probably involves retention of configuration. Alkaline hydrolysis gives the starting phosphetan oxide.

Phosphetan oxides (23) are, as expected from Campbell's⁵⁸ work, very good catalysts for the conversion of *p*-tolyl isocyanate to its carbodiimide, but there is no reaction with *N*-sulphonyl aniline, TsNSO or DIM after refluxing in benzene for two days.

Mechanistic Considerations.

The first step of the reaction of sulphonyl isocyanates with phosphetan oxides is probably nucleophilic attack of the phosphoryl oxygen on the

isocyanate carbon to give a zwitterion (27). This step is proposed to be fast and reversible. The zwitterion can then ring close by either the oxygen or the nitrogen acting as a nucleophile at phosphorus.



It is only reasonable to consider ring closure by apical attack of the nucleophile, since equatorial attack would involve the formation of a phosphorane containing a diequatorial four-membered ring. This is known to be a high energy process.^{41,66,67} Apical attack of the nucleophile opposite one of the ring ligands to give phosphorane (28) or (29) will entail the relief of ring strain within the phosphetane ring [the ideal geometry about the phosphorus changes from tetrahedral (109°) to trigonal-bipyramidal, in which the phosphetane ring occupies one apical and one equatorial position (90°)].

Pseudorotation of intermediate phosphoranes is generally fast with respect to their rate of decomposition.^{36,41,67} In this case however, pseudorotation which alters the stereochemical outcome of the reaction is unlikely to occur because it would entail formation of an intermediate phosphorane in which one of the four-membered rings was diequatorial.

Break-up of the phosphorane (28) regenerates TsNCO and phosphetane

oxide, with retention of configuration, whereas break-up of the phosphorane (29) leads to the observed phosphetan imide, with retention of configuration, and carbon dioxide.

Kinetics.

In order to justify the proposed mechanism the kinetics of the reaction were investigated. This was done by monitoring the reaction at -40° using an n.m.r. spectrometer, as described in the experimental section. The data obtained were substituted into the integrated rate equations for first order, second order (first order in both components), and third order (first order in phosphetan oxide, second order in TsNCO) rate laws. In each case the reaction was followed to $>55\%$ completion. Graphic representation of the results shows a sharp curve for the first order, a shallow curve for the third order and a straight line for the second order rate equation. The rate constants were obtained, for varying concentrations of TsNCO (the phosphetan oxide concentration was kept constant), by measuring the slope of the lines.

Rate Constants for the Reaction of 2,2,trans-3,4,4-Pentamethyl-r-1-phenyl-phosphetan 1-Oxide with Toluene-p-sulphonyl Isocyanate in Deuteriochloroform at -48° .

<u>RUN</u>	<u>A°/B°</u>	<u>K₂(sec⁻¹m⁻¹)</u>	<u>K₃(sec⁻¹m⁻²)</u>
1	1.0	2.4×10^{-4}	5.2×10^{-6}
2	1.75	3.3×10^{-4}	3.3×10^{-4}
3	4.9	2.7×10^{-4}	1.8×10^{-3}
4	1.7	2.9×10^{-4}	-

where A° = the initial concentration of TsNCO, B° = the initial concentration of phosphetan oxide, K₂ is the second order and K₃ is the third order rate constant.

The second order rate constant does in fact remain constant (within experimental error) whereas the third order rate constant varies considerably. This means that the reaction can be at least predominantly represented by the second order rate equation which the proposed mechanism requires.

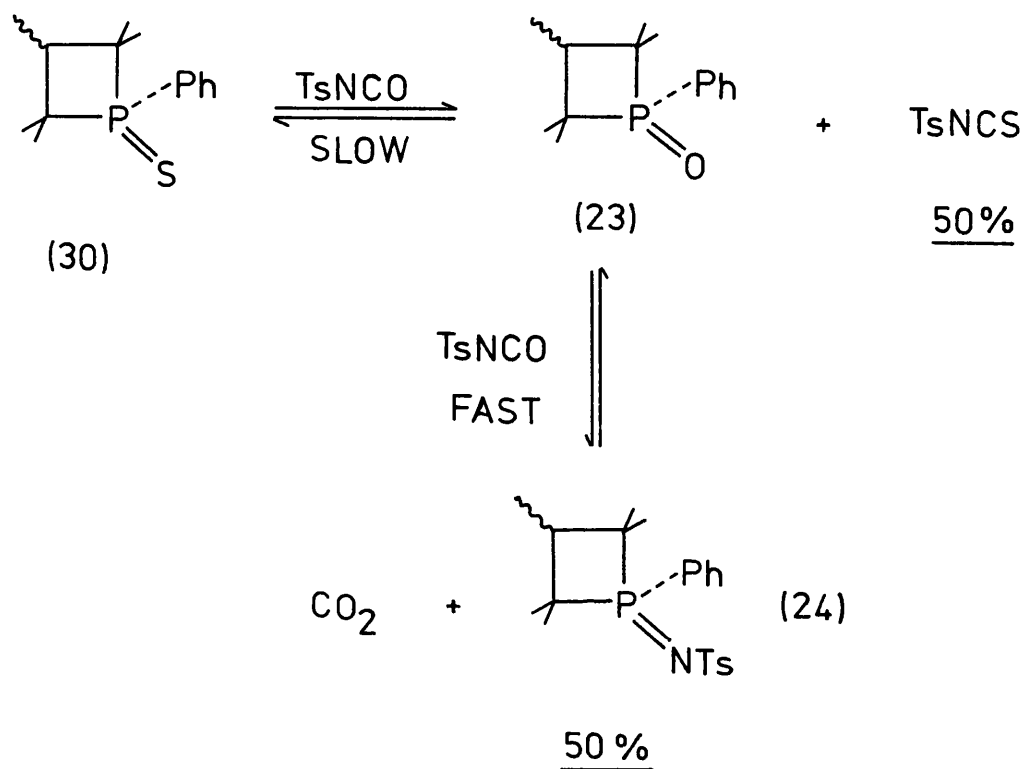
$$K_{OBS} = K_2[\text{Phosphetan oxide}][\text{TsNCO}]$$

The Reaction of Toluene-p-sulphonyl Isocyanate with the Phosphetan Sulphides.

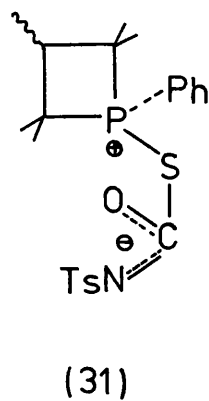
It was suggested above that the reaction between phosphetan oxide (23) and TsNCO involves oxygen exchange with retention of configuration. In order to demonstrate this, the reaction of the corresponding phosphetan sulphides (30) with TsNCO was investigated.

The reaction is very much slower than in the corresponding phosphetan oxide case. Addition of one mole of TsNCO to a solution containing one mole of phosphetan sulphide gives a final product which contains half a mole of phosphetan sulphide (of unchanged configuration) and half a mole of phosphetan imide (24) with retention of configuration. Fifty percent of the tosyl group ends up in the imide and the other fifty percent is recovered as toluene-p-sulphonyl isothiocyanate (TsNCS). This seems to demonstrate that the reaction goes through an intermediate phosphetan oxide (23), which then reacts rapidly with a second mole of TsNCO to give the observed imide (24).

Sulphur nucleophiles are normally better than the corresponding oxygen ones, but in this case it is reasonable to propose that the initial nucleophilic attack of the phosphoryl sulphur on the isocyanate carbon is much slower than by the phosphoryl oxygen of the phosphetan



oxide. The phosphorus-sulphur double bond should be a lot less polarised than the phosphorus-oxygen one, hence the electron rich oxygen should be the better nucleophile.



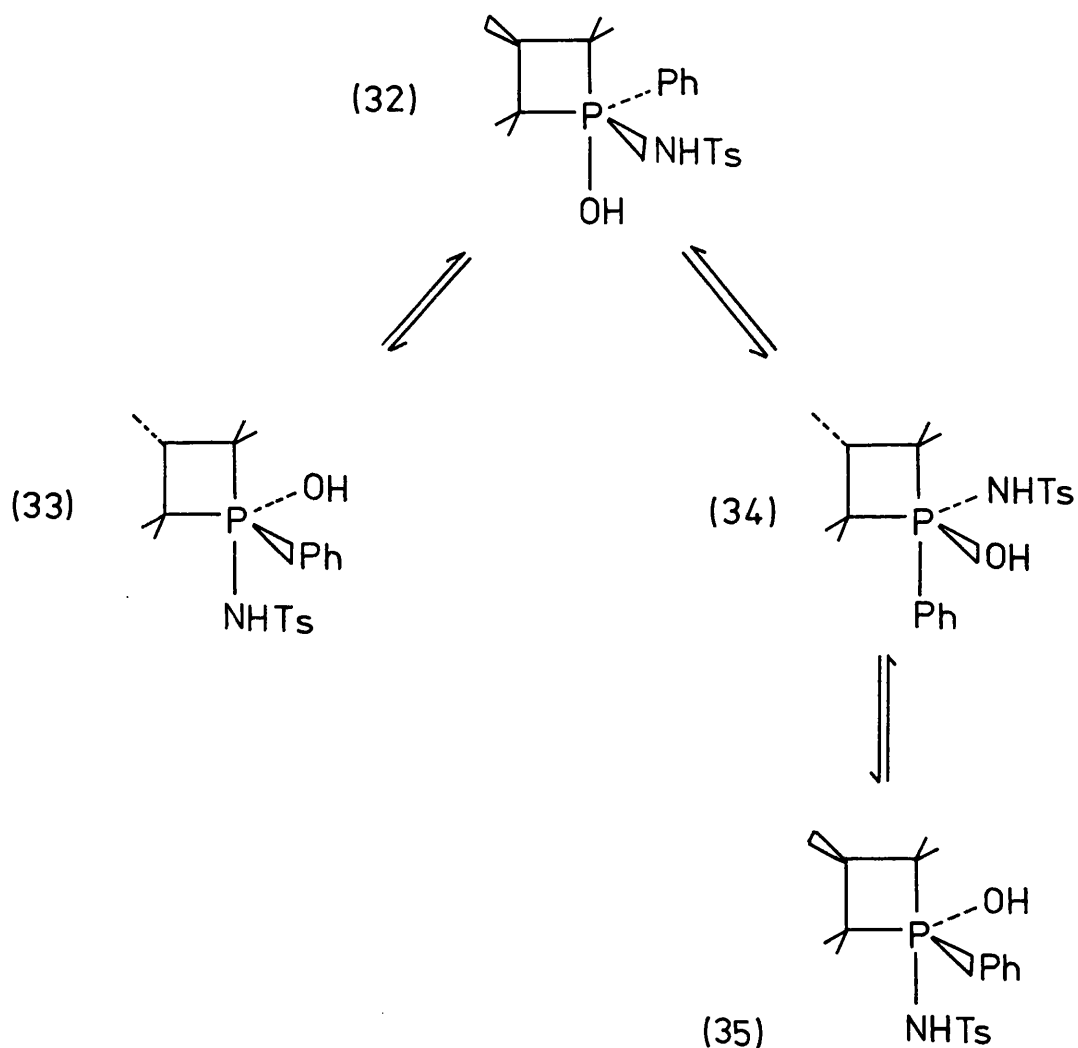
Ring closure of the initially formed zwitterion (31) by nucleophilic attack of the oxygen will lead to phosphetan oxide with retention of configuration and TsNCS. The phosphetan oxide will then react rapidly with a second mole of TsNCO to give phosphetan imide with retention of configuration and carbon dioxide. Since two moles of TsNCO are needed to convert each mole of phosphetan sulphide to phosphetan imide then the reaction reaches only 50% completion. TsNCS, once formed, does not react further.

Ring closure of the zwitterion (31) by nucleophilic attack of the nitrogen will give phosphetan imide with retention of configuration and carbonyl sulphide. In order for this to lead to the observed products in the observed yields, the carbonyl sulphide must react rapidly and quantitatively with TsNCO to give TsNCS and carbon dioxide.

Hydrolysis of the Phosphetan Imides.

Alkaline hydrolysis in aqueous methanol can be reasonably assumed to involve apical attack of a hydroxide ion opposite one of the ring ligands to give an intermediate phosphorane such as (32).⁶⁸ Assuming that pseudorotation to put the phosphetan ring diequatorial does not occur, then (32) can pseudorotate via one of two pathways to put the leaving group apical.

Apical loss of the leaving group from phosphorane (33) leads to product formation with retention of configuration, while that via phosphorane (35) leads to inversion of configuration. The fact that a quantitative yield of phosphetan oxide with retention of configuration is obtained suggests that pseudorotation of (32) to (34) does not compete with phosphorane decomposition whereas pseudorotation of (32) to (33) competes very favourably. This can be explained in terms of



the previously observed low apicophilicity⁶⁹ of the phenyl group.⁷⁰

The Reaction of Phosphetan N-(Toluene-p-sulphonyl)imides with Chlorosulphonyl Isocyanate.

Addition of one mole of CSI to a solution containing one mole of the N-(toluene-p-sulphonyl)imide (24) leads to the formation of one mole of the N-(sulphonyl chloride)imide (26) with retention of configuration and one mole of TsNCO. This reaction reflects the relative nucleophilicities

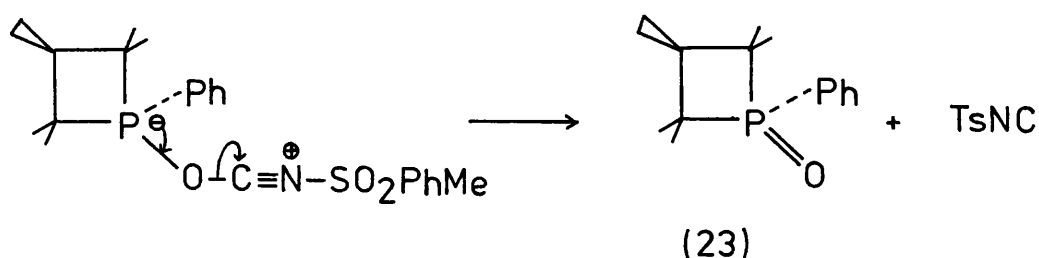
of the phosphetan imide nitrogens and the corresponding electrophilicities of the isocyanate carbons.

Unlike the catalytic conversion of isocyanates to carbodiimides by phosphine oxides,⁵⁸ N-sulphonyl phosphine imides do not react with a second mole of sulphonyl isocyanate. This is because the nitrogen of an N-sulphonyl phosphine imide is much less nucleophilic than that of an N-alkyl or aryl phosphine imide. The phosphorus-nitrogen double bond is in both cases highly polarised but in N-sulphonyl phosphine imides the resultant negative charge on nitrogen can be delocalised on to the strongly polar sulphonyl group, thus making the nitrogen less nucleophilic in this case.

3.3 The Reaction of Pentamethyl-1-phenylphosphetans with Sulphonyl Isocyanates.

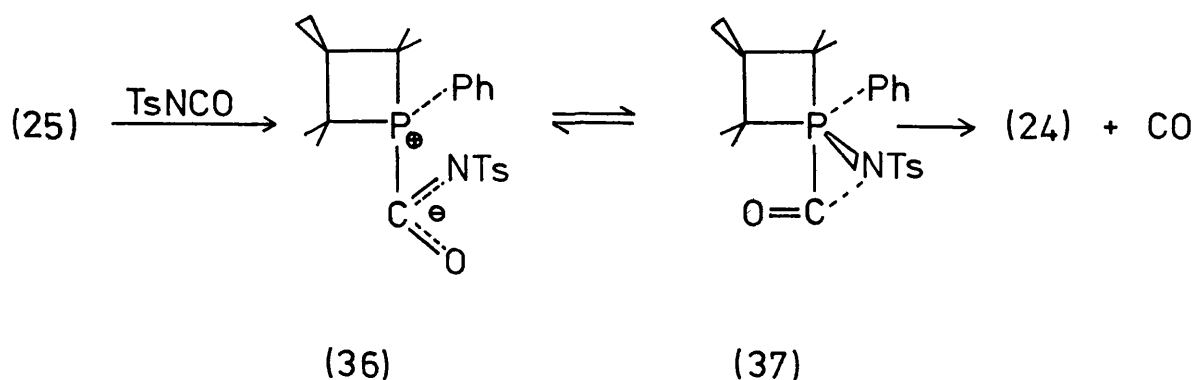
Both TsNCO and CSI react with the phosphetans (25) in degassed benzene solution to give the respective phosphetan imides (24) and (26) with retention of configuration.

Two possible reaction pathways can be considered, i.e. for TsNCO, either the phosphetan is oxidised to the phosphetan oxide which then reacts with a second mole of TsNCO to generate the product and carbon



dioxide, or there is direct phosphetan imide formation with loss of carbon monoxide. Mukaiyama⁷¹ and Hudson⁷² have proposed direct oxidation of a cyclic phosphoramidite by phenyl isocyanate. A similar process in this case would generate toluene-*p*-sulphonyl isocyanide, this is however not observed in the infra-red spectrum of the crude reaction product. Further evidence against an intermediate phosphetan oxide is that the reaction proceeds in yields of up to 85% for equimolar concentrations of starting materials, whereas a process involving two moles of TsNCO for each mole of phosphetan imide formed would not give yields of greater than 50%.

Nucleophilic attack of one of the phosphorus lone pairs on the isocyanate carbon would give a zwitterion (36), this could then ring



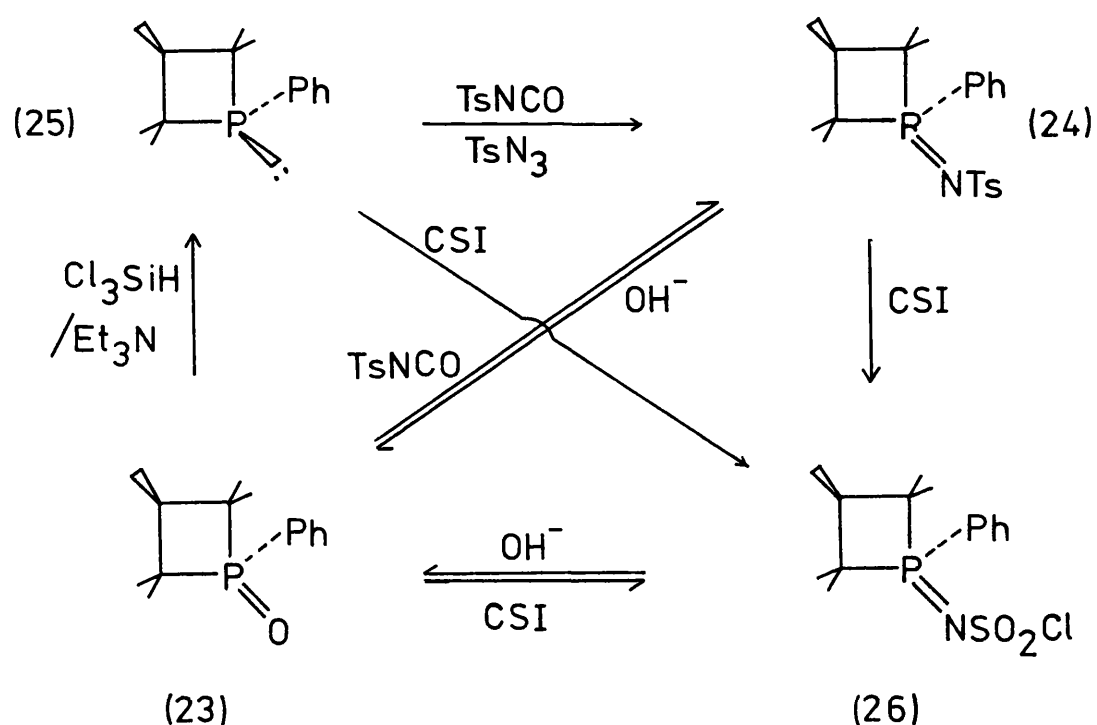
close by nucleophilic attack of the nitrogen at phosphorus to give the phosphorane (37). Fragmentation of this would lead to the observed product and carbon monoxide. Ring closure of (36) via the oxygen would lead to phosphetan oxide with retention of configuration and toluene-*p*-sulphonyl isocyanide.

Control experiments showed that the phosphetan was not being

oxidised by residual atmospheric or dissolved oxygen, i.e. the phosphetans were stable under the reaction conditions in the absence of TsNCO.

3.4 Conclusion.

All of the reactions investigated between phosphetan containing systems and sulphonyl isocyanates have been shown to proceed with retention of configuration. The mechanism probably involves a phosphorane intermediate in which the phosphetan ring occupies one apical and one equatorial position.



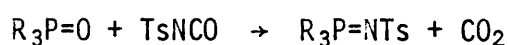
It appears that the corresponding thietane systems only react through such intermediates in non-polar solvents like benzene. In more polar solvents the rate of ring closure of the initially formed

zwitterion is slower than its reaction with a second mole of sulphonyl isocyanate. This difference in reaction between the two systems is probably a reflection of the different amounts of ring strain released on going from an approximately tetrahedral geometry (109°) to a trigonal-bipyramidal one in which the ring spans one apical and one equatorial position (90°). It is reasonable to propose that this is less in the thietane case, especially in view of recent X-ray data on a sulphurane³¹ which shows a fairly large distortion from ideality due to large lone-pair-bond pair repulsions.

The lack of reaction of the phosphetan oxides with the sulphur-containing cumulenes is probably due to the absence of initial zwitterion formation. This is because the sulphur in these systems is less electrophilic than the corresponding carbons. The greater electronegativity of sulphur, and the possibility of back donation of charge from oxygen to the 3d-orbitals on sulphur are both consistent with its lower electrophilicity.

3.5 The Reaction of Acyclic Phosphine Oxides with Toluene-p-sulphonyl Isocyanate.

In order to make a complete comparison with the reactions discussed in Chapter Two, the reaction of TsNCO with a series of acyclic phosphine oxides was investigated. In general the rate of phosphine imide formation is very slow compared to the phosphetan case. Variation of the R groups on phosphorus did not appear to have much effect on the rate, except when either two phenyl or two *t*-butyl groups were used. In these cases the reaction effectively stopped. The same results were observed in a range of solvents, but the rate was much faster in the more polar media.



In order to determine the stereochemistry of the reaction, (+)-(R)-benzylmethylphenylphosphine oxide⁷³ was used. When the reaction was monitored polarimetrically in acetonitrile as solvent, the rotation was observed to drop fairly rapidly to zero. If at this point the TsNCO was quenched with water or methanol a quantitative yield of racemic phosphine oxide could be recovered. If the reaction was allowed to continue, phosphine imide was slowly formed. For a molar ratio of phosphine oxide (0.020g/ml) to TsNCO of 1:4 in acetonitrile at 25°C the half life of racemisation was 40 min while that of phosphine imide formation was 36hr.

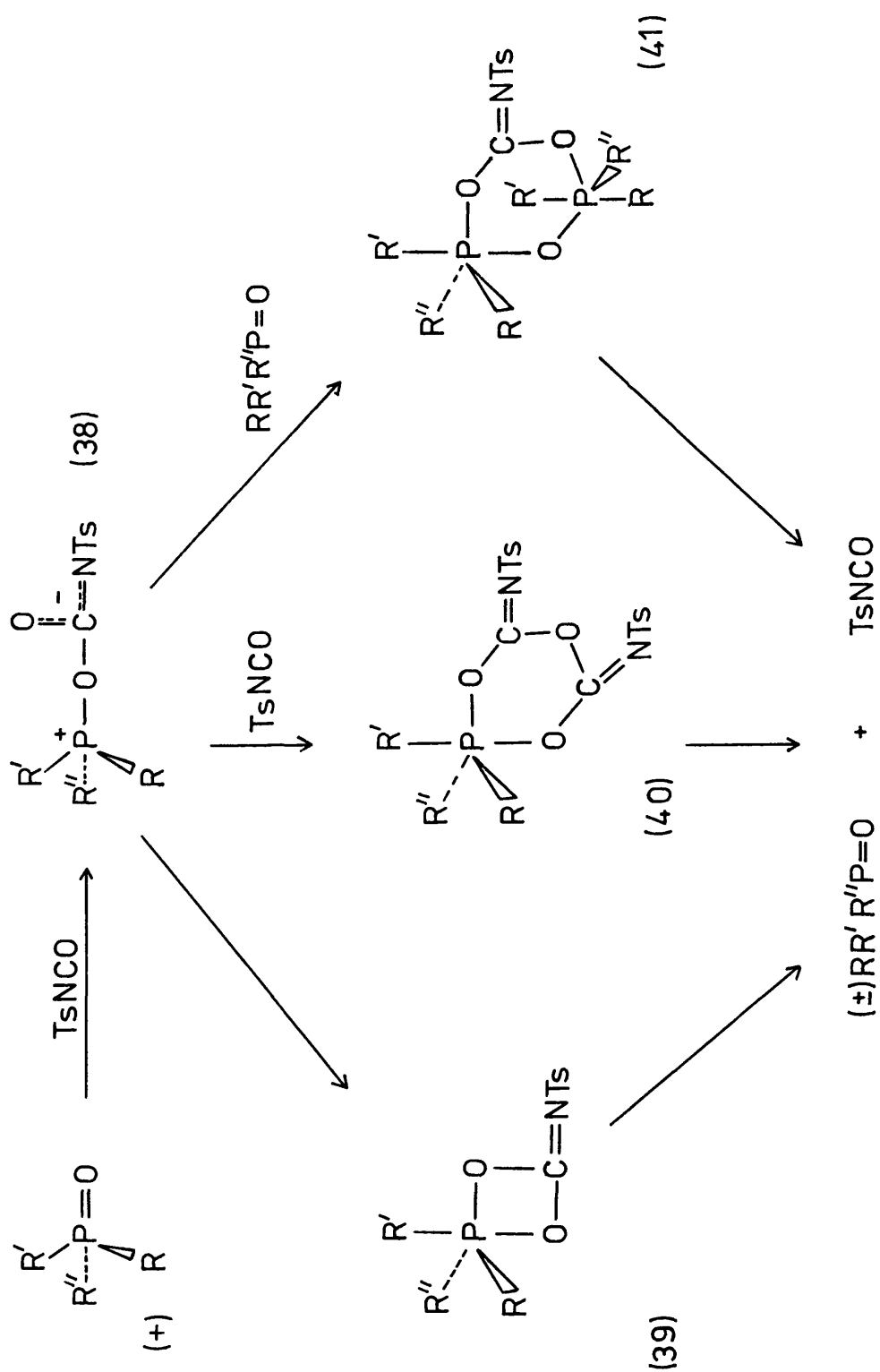
Mechanistic Considerations.

The first step of the racemisation reaction is again assumed to be nucleophilic attack of the phosphoryl oxygen on the isocyanate carbon to give the zwitterion (38). Unlike the phosphetan oxide case this zwitterion cannot ring close with relief of ring strain, hence it may be a longer lived species than zwitterion (27). If this is so, then other reactions have a chance to compete with ring closure. The increase in the rate of phosphine imide formation in more polar solvents is probably a reflection of the longer lifetime of this dipolar species, assuming as previously, that zwitterion formation is not the rate determining step.

Three alternative reactions of the zwitterion (38) are considered:

(1) Ring closure by nucleophilic attack of the oxygen at phosphorus. For reasons previously discussed it is only necessary to consider apical attack to give a phosphorane (39). In order for this intermediate to lead to racemisation either:

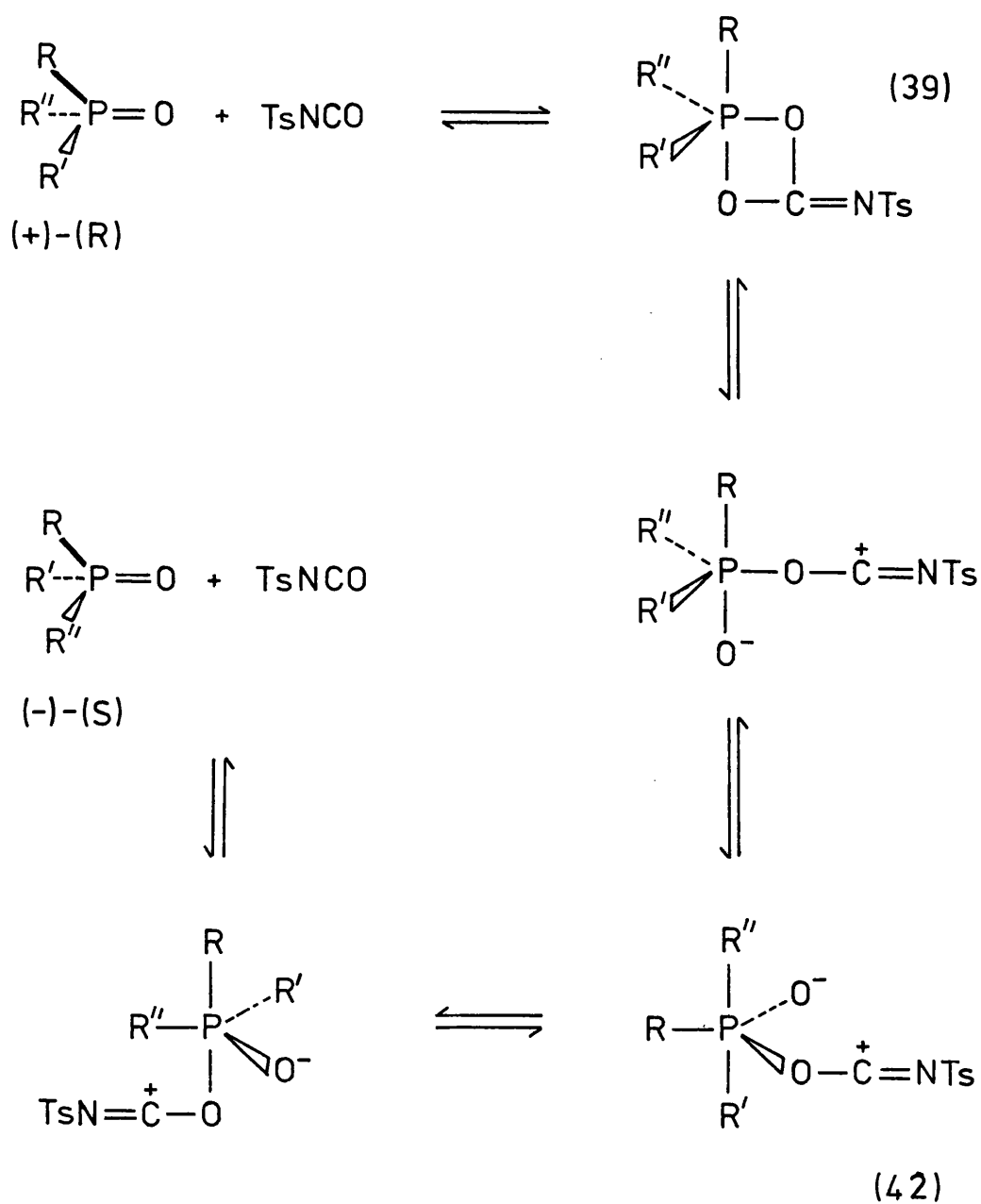
(a) it must pseudorotate to put the four-membered ring diequatorial.



This is a very unlikely process because it not only involves a considerable degree of ring strain,^{66,67,70} but also the two most electronegative ligands must occupy equatorial sites.

or

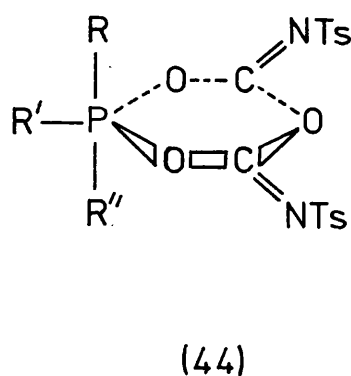
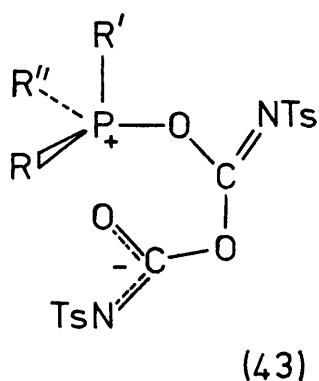
(b) bond cleavage may occur to give racemisation in a way



analogous to that proposed for the formation of racemic phosphates from optically active phosphites via their 1:1 ozone adducts.⁷⁴ This process involves cleavage of either phosphorus-oxygen bond in phosphorane (39), followed by a series of pseudorotations with final apical loss of TsNCO.

The bond cleavage removes the ring strain constraint on pseudorotation, it is still however necessary to go through a phosphorane (41) where the two most electronegative groups occupy equatorial positions.

(2) The zwitterion (38) can react with a second mole of TsNCO to give the extended zwitterion (43), which can then ring close by nucleophilic attack of the oxygen at phosphorus. In this case both apical attack and equatorial attack should be considered. The actual racemisation is assumed to occur by formation of the phosphorane (44) which has a



plane of symmetry. This intermediate could be formed in one of two ways:

(a) by direct equatorial attack. In this case equatorial loss would lead to phosphine oxide with inversion of configuration and hence racemisation.

(b) by apical attack to give phosphorane (40). This intermediate

must then pseudorotate to put the six-membered ring diequatorial.

Phosphorane (44) can then pseudorotate back to (40) or to its mirror image, and apical loss will lead to racemic product.

Equatorial attack-equatorial loss mechanisms have not yet been demonstrated in phosphorus chemistry and calculations^{33,75} suggest that apical attack involves less energy. It is therefore reasonable to assume that racemisation occurs via apical attack to give phosphorane (40) which then racemises by a series of pseudorotations. No ring strain should be involved in making the six-membered ring span two equatorial positions.

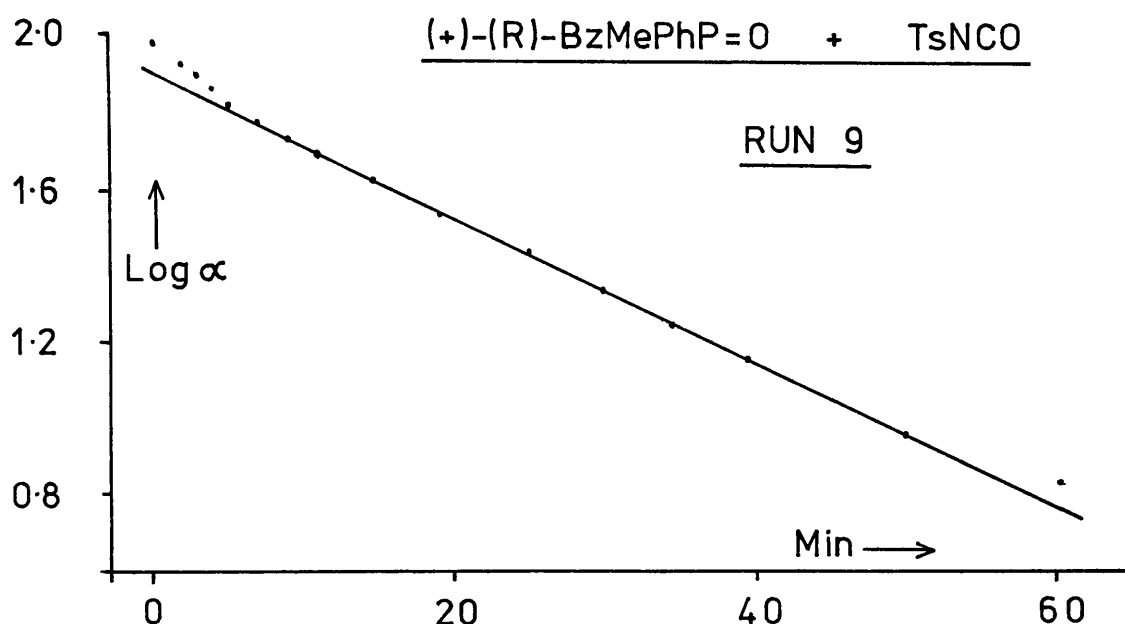
(3) The zwitterion (38) can react with a second mole of phosphine oxide. Ring closure to give an intermediate such as (41) could then lead to racemisation.

Kinetics.

It should be possible to distinguish between the above three racemisation mechanisms by a consideration of the kinetics of the reaction. From a simple view-point the mechanism described in (1) above, should involve a rate law that is overall second order (i.e. first order in both reactants), mechanism (2) above, one that is overall third order (i.e. first order in phosphine oxide and second order in TsNCO), and mechanism (3) above, again a third order rate law (i.e. first order in TsNCO and second order in phosphine oxide).

Since in all cases TsNCO is regenerated, then provided that the concentration of any intermediates is negligible, the concentration of TsNCO should remain constant throughout the reaction. If this assumption is valid, a plot of the logarithm of the observed rotation against time will give a straight line only if the reaction is first order in phosphine oxide. This is in fact observed over a range of concentrations

of TsNCO, the concentration of phosphine oxide being kept constant.



The reaction can therefore be represented by a rate equation:

$$K_{\text{OBSERVED}} = K[\text{phosphine oxide}][\text{TsNCO}]^n$$

where K is the rate constant and n is the order of the reaction in TsNCO.

By taking logarithms of both sides of the equation this becomes:

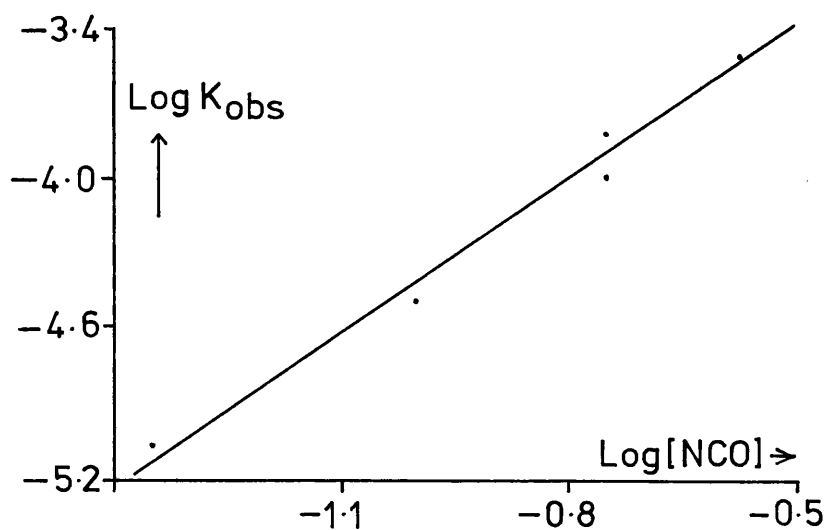
$$\log_{10} K_{\text{OBS}} = \log_{10} K + \log_{10} [\text{phosphine oxide}] + n \log_{10} [\text{TsNCO}]$$

Since the concentration of the phosphine oxide is kept constant, a plot of $\log_{10} K_{\text{OBS}}$ against $\log_{10} [\text{TsNCO}]$ should give a straight line with a slope equal to the order of the reaction in TsNCO (n).

A good straight line is obtained, and a least squares analysis gives a value for n of 1.998 with a standard deviation of 0.149.

Observed Rate Constants for the Reaction of (+)-(R)-Benzylmethylphenyl-phosphine Oxide with Toluene-p-sulphonyl Isocyanate in Acetonitrile at 26°.

<u>RUN</u>	<u>[TsNCO]</u>	<u>[TsNCO]/[Phosphine Oxide]</u>	<u>K_{obs} sec⁻¹</u>
5	0.176N	2	1.60 x 10 ⁻⁴
6	0.089N	1	3.20 x 10 ⁻⁵
7	0.044N	0.5	8.75 x 10 ⁻⁶
8	0.176N	2	9.82 x 10 ⁻⁵
9	0.266N	3	3.25 x 10 ⁻⁴



This result suggests that the reaction can be at least predominantly represented by the following rate law:

$$K_3 = [\text{Phosphine Oxide}][\text{TsNCO}]^2$$

This rate law is consistent only with the mechanism proposed in section (2) above.

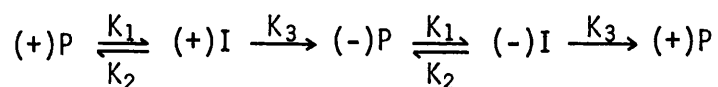
At a later date it was possible, in conjunction with Dr. P. Watts of the Chemical Defence Establishment, Porton Down, Wiltshire, to investigate the kinetic data more thoroughly.

It had been noticed that in each kinetic run the initial loss in rotation was faster than it should be. This is shown up in the non-linearity of the \log_{10}/time plots, over the first few percent of the reaction. There is also a second deviation from linearity at $> 80\%$ reaction. The overall shape of the plots indicates the likelihood of a classic reversible formation of an intermediate followed by its irreversible break-down. The reversibly formed intermediate must have a lower rotation than the original phosphine oxide (or it must be different in sign) or otherwise the rapid initial drop in rotation would not show. It cannot however be optically inactive, i.e. racemised, as its formation would not then be reversible.

The reaction was defined in terms of differential equations which were solved by using an analogue computer.

Two closely related models were considered:

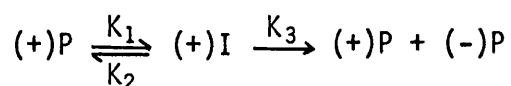
A An inversion scheme:

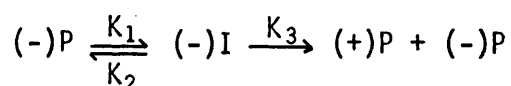


where P is the phosphine oxide, I is an intermediate and (\pm) represents the sign of the rotation.

In this scheme break-up of the intermediate leads to inverted phosphine oxide.

B A racemisation scheme:





In this scheme break-up of the intermediate leads to racemic product.

The two major assumptions were:

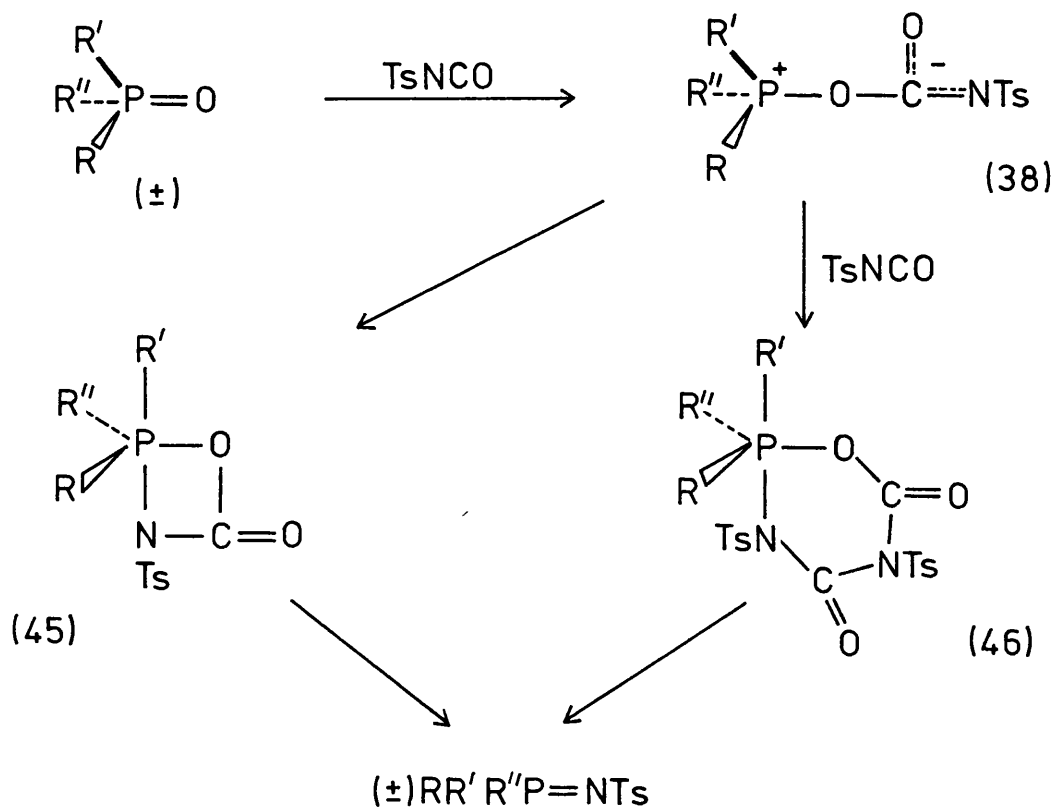
- (i) That the specific rotation of the intermediate is such that it does not contribute to the observed rotation and
- (ii) that the concentration of TsNCO remains constant throughout the reaction. Since we expect detectable quantities of the intermediate to be formed this assumption is introducing an error.

The values of the rate coefficients used in the computation, the derived rate constants and the total percentage of phosphine oxide in the form of the intermediate are given in the experimental section. During preliminary simulations, K_1 , K_2 , and K_3 were allowed to vary. Later a value of K_2 of $38 \times 10^{-4} \text{ sec}^{-1}$ was established and this was kept constant throughout the computations.

The observed kinetic data are consistent with those calculated for the inversion and the racemisation schemes. The computer simulation suggests that the reaction proceeds with the reversible reaction of one molecule of phosphine oxide with one molecule of TsNCO to form an optically active intermediate. This can react irreversibly with a further molecule of TsNCO to regenerate either inverted or racemised phosphine oxide. The model does not require the formation of an intermediate containing one molecule of phosphine oxide and two of isocyanate, and if one is formed then its break-down is very much faster than its formation.

Both the simple and the more complex treatment of the kinetic data suggest that the reaction follows a rate law that is consistent with the mechanism proposed in section (2) above.

Phosphine imide formation could be via intermediates or transition states (45 or 46).



These species are the same as those proposed for the racemisation reaction, except here, ring closure of the intermediate zwitterions (38 and 43) occurs by nucleophilic attack of the nitrogen at phosphorus. The relative rates of racemisation and phosphine imide formation can be correlated to the relative nucleophilicities of oxygen and nitrogen (in the zwitterion) at phosphorus. It is obviously not possible to consider the stereochemistry of the phosphine imide forming reaction because, since the rate of racemisation is much faster than the rate of phosphine imide formation, the reaction effectively starts from racemic phosphine oxide.

A number of phosphorane intermediates have been isolated or observed at low temperature.^{36,41,74} Since isolation of such an intermediate would unequivocally establish the mechanism of the reaction under study, both the reaction of the phosphetan oxide and the acyclic phosphine oxide with TsNCO were carried out at low temperature ($\sim -65^\circ$). The reactions were constantly monitored by n.m.r., but no peaks due to possible intermediates were observed. This is perhaps not surprising in view of the results from the interpretation of the kinetic data.

Electron withdrawing groups are known to stabilise phosphoranes.^{41,74} Replacement of the alkyl groups on phosphorus with alkoxy groups might therefore be expected to stabilise any intermediate phosphoranes. Attempted reaction of TsNCO with trimethylphosphate, trimethylphosphonate and (-)-menthyl methylphenylphosphonate [chirality at phosphorus (s)] led to a quantitative recovery of starting material. It is likely that the same factors which stabilise phosphoranes will make the starting phosphoryl oxygen less nucleophilic, and hence in these cases there is no zwitterion formation (the presence of electron withdrawing substituents on the phosphorus will tend to reduce the dipolar character of the phosphorus-oxygen double bond, thus as the oxygen becomes more covalent so it will become less nucleophilic).

The Reaction of Benzylethylphenylphosphine Sulphide with Toluene-p-sulphonyl Isocyanate.

As in the phosphine oxide case the reaction is very much slower than for the corresponding phosphetan sulphide. If a solution of the acyclic phosphine sulphide and TsNCO (1:1) is refluxed for two weeks in acetonitrile, the solution then contains phosphine sulphide, phosphine imide, phosphine oxide, TsNCO and TsNCS. This is consistent with what would be expected for the mechanisms so far proposed.

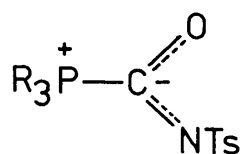
Hydrolysis of Acyclic Phosphine Imides.

Alkaline hydrolysis yielded in all cases a quantitative yield of phosphine oxide. The stereochemistry of the reaction could not be investigated because all the phosphine imides hydrolysed were racemic.

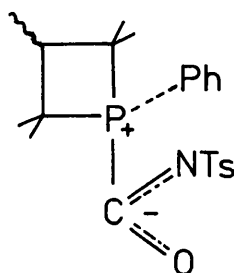
3.6 The Reaction of Acyclic Trivalent Phosphorus Compounds with Toluene-p-sulphonyl Isocyanate.

The Reaction of t-Butylmethylphenylphosphine.

Addition of TsNCO to a degassed solution of the phosphine in dichloromethane or benzene gave phosphine oxide (5%) phosphine imide (5%) and a 1:1 adduct (90%). Control experiments showed that the phosphine is stable under the reaction conditions in the absence of TsNCO. The phosphine imide could either be formed by direct reaction of the phosphine with TsNCO, or by way of the phosphine oxide. It is however most likely that a direct reaction is responsible for the majority of the product because of the short duration of the reaction and the known sluggishness of the imide forming reaction between the phosphine oxide and TsNCO. The adduct, by analogy to the work of Hoffmann,⁶⁰ has a zwitterion structure (47). The negative value of the ^{31}P chemical shift, with respect to phosphoric acid, confirms that the adduct is not a phosphorane. Both



(47)



(36)

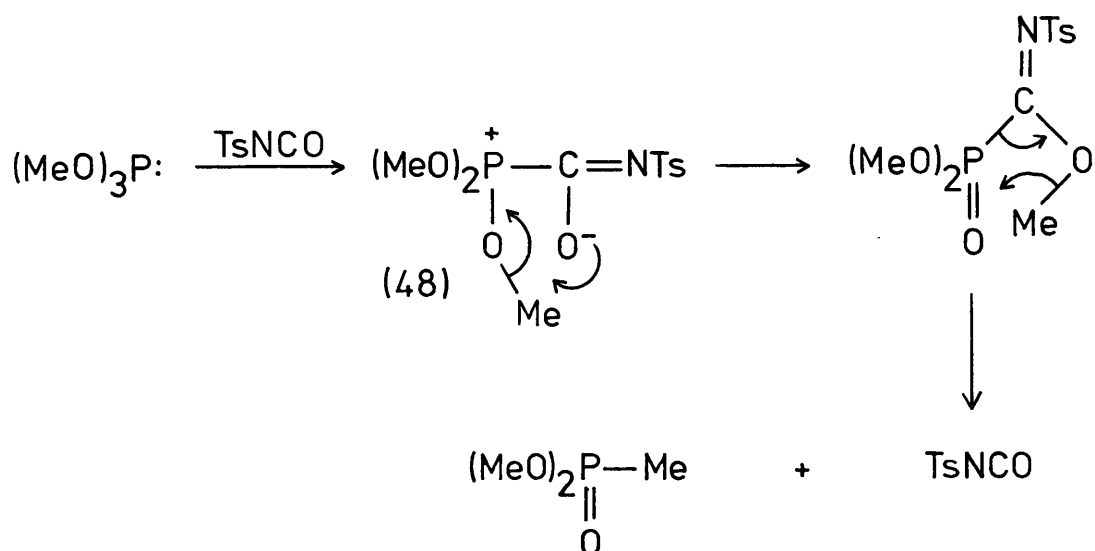
tertiary amines⁵⁵ and acyclic tertiary phosphines therefore react with TsNCO to give 1:1 adducts of zwitterionic structure. Sulphides (both cyclic and acyclic) however do not react with TsNCO even after prolonged refluxing.

The difference in reaction between the phosphetans and the acyclic phosphine with TsNCO is probably due to the potential relief of ring strain on ring closure of a zwitterion such as (36) which is not available on ring closure of (47). The activation energy of the imide forming reaction is thus lower in the phosphetan case.

The Reaction of Trimethylphosphite.

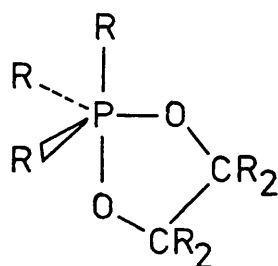
The main products of the reaction are trimethylphosphate (30%) and trimethylphosphonate (55%). Again control experiments showed that the starting material was stable under the reaction conditions in the absence of TsNCO. The phosphate is probably formed by a mechanism similar to those discussed for oxidation of the phosphetans by TsNCO i.e. either a direct oxidation⁷² or via an intermediate zwitterion (48). No product via ring closure by the nitrogen was observed however, and the infra-red spectrum of the crude reaction product did not show any bands characteristic of toluene-*p*-sulphonyl isocyanide.

The trimethylphosphonate is probably formed by an internal Arbuzov

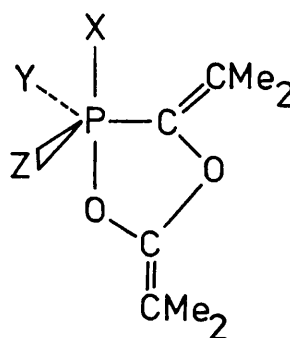


reaction in the zwitterion (48). This reaction regenerates TsNCO and therefore only catalytic amounts of isocyanate should be required. This is however not the case, probably because the phosphate forming reaction consumes TsNCO.

It is somewhat surprising that no stable phosphoranes are formed in the reactions investigated above. The reaction of phosphines and phosphites with ketones and aldehydes has been shown to give oxy-phosphoranes of the general structure (49),³⁶ and Bentrude⁷⁶ has isolated oxy-phosphoranes such as (50) in the reaction of a number of trivalent phosphorus compounds



(49)



(50)

with dimethyl ketene. The structural similarities between isocyanate and ketene especially suggest that oxy-phosphoranes might be expected to be observed in both cases.

3.7 Conclusion.

The reaction of acyclic phosphine oxides with TsNCO resembles the reaction of sulfoxides (both cyclic and acyclic) much more than the corresponding reaction of phosphetan 1-oxides. This supports the previous

conclusion (Section 3.4) that the difference in reaction between thietane 1-oxides and phosphetan 1-oxides is due to differing amounts of ring strain released on assuming trigonal-bipyramidal geometry.

The lowering of the activation energy for a reaction by the relief of ring strain can also explain the differences in the reaction of cyclic and acyclic phosphines with TsNCO .

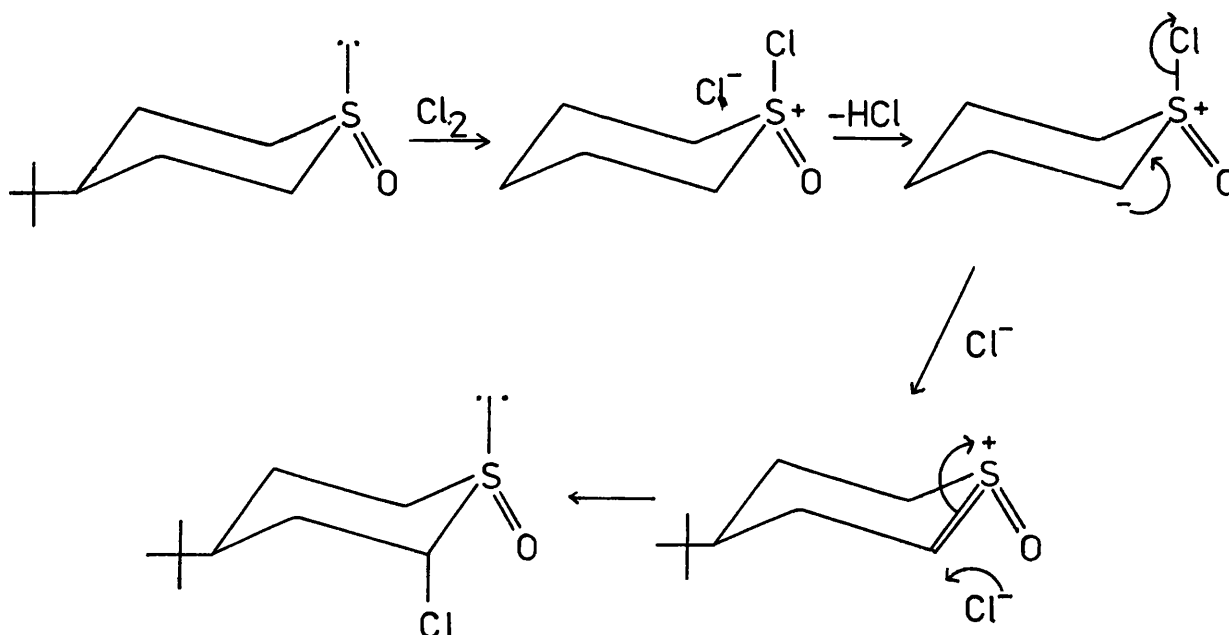
CHAPTER FOUR

RING OPENING REACTIONS OF SMALL SULPHUR-CONTAINING HETEROCYCLES

4.1 Attempted α -Halogenation of the 3-Methylthietane 1-Oxides.

There are a number of methods in the literature that describe the α -halogenation of sulfoxides.^{77,78} Most of these have been shown to work for both five and six-membered cyclic systems, but as yet there is no general method for the preparation of 2-halothietane 1-oxides.

The generally accepted mechanism for this type of reaction is demonstrated by the chlorination of 4-t-butylthiane 1-oxide with chlorine⁷⁸ [Scheme (I)].

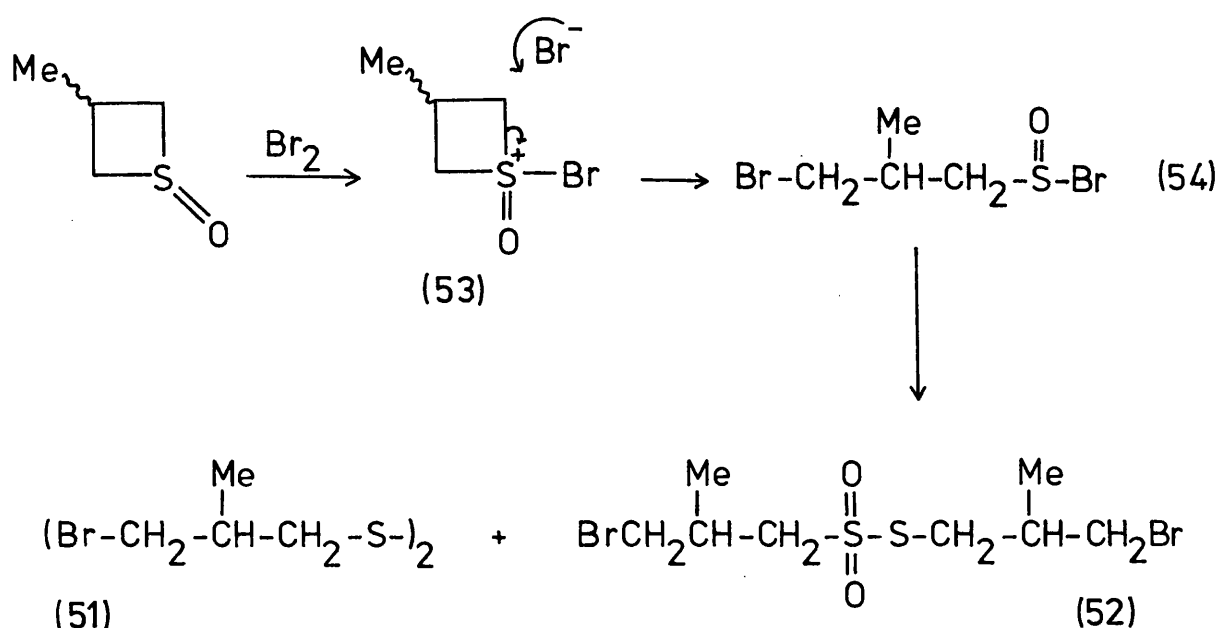


SCHEME I

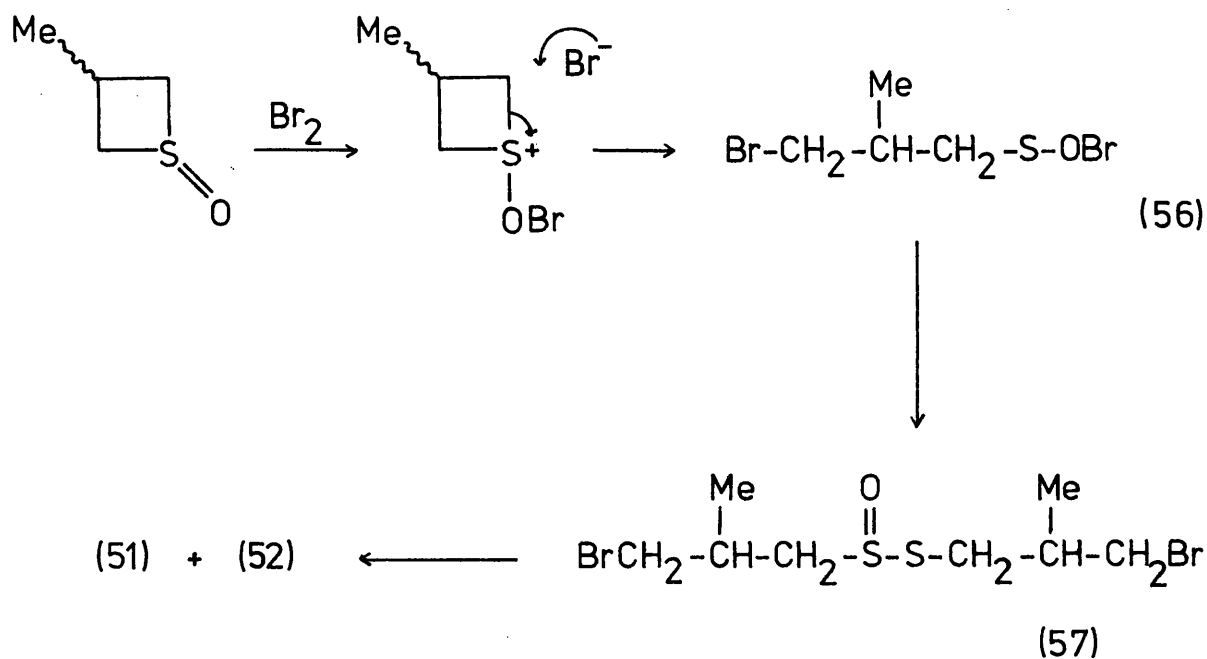
In some cases a base such as pyridine is added to trap the HX formed, which could otherwise cause Pummerer-type rearrangements.

With Bromine.

Addition of bromine to a cooled solution of the thietane 1-oxide, in the presence or absence of pyridine, gave bis(2-methyl-3-bromopropyl)-disulphide (51) (41%) and bis(2-methyl-3-bromopropyl)thiosulphonate (52) (30%). A number of mechanisms can be proposed to explain the products [e.g. (2) and (3)], but no attempt has been made to establish any one of them.



SCHEME 2



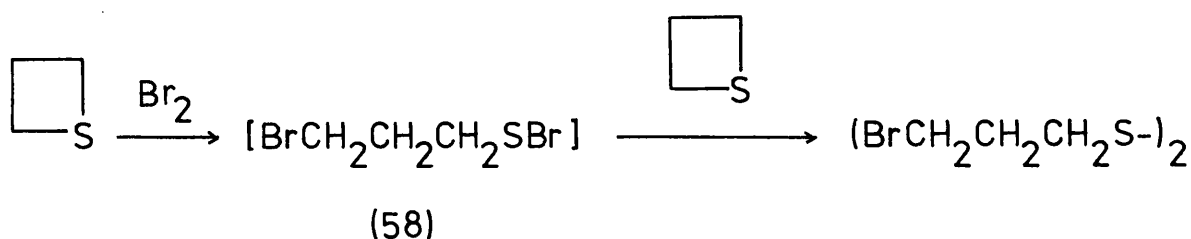
SCHEME 3

The important step in both schemes (2) and (3) is the ring opening of the sulphonium salt intermediate (53) or (55) by nucleophilic attack of the halogen anion of the α -carbon. Relief of ring strain is probably the driving force for this step (It is not present in the reaction of acyclic or larger ring sulfoxides, hence the variation in the reaction).

Sulphonyl bromides, e.g. (54) are known to disproportionate to a mixture of sulphenyl and sulphonyl bromides.⁷⁹ These molecules are not observed, but it is possible that the presence of the thietane 1-oxide alters the course of the disproportionation to give the observed products.

An intermediate such as (56) would be very easily hydrolysed to the corresponding sulphenic acid, and these are known to undergo a condensation and disproportionation similar to that shown.⁸⁰

Stewart⁸¹ has observed that bromine causes the ring opening of thietane itself. It is thought that ring opening initially forms a sulphenyl bromide (58) which then reacts with a second mole of thietane to give the observed disulphide.



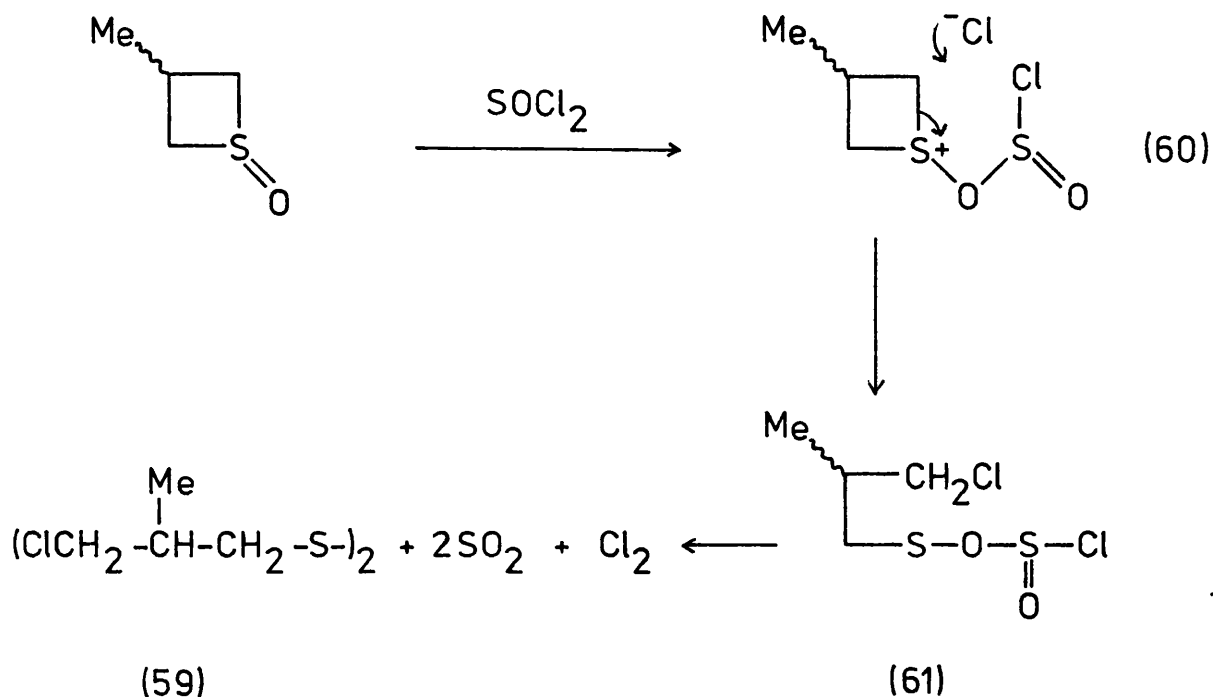
In view of this, and the accepted mechanism for the chlorination of 4-t-butylthiane 1-oxide, it is probable that the ring opening of 3-methyl-thietane 1-oxide occurs by the process outlined in (2) above.

With Thionyl Chloride.

Addition of thionyl chloride to a solution of the thietane 1-oxide

gave bis(2-methyl-3-chloropropyl)disulphide (59) (69%).

The reaction probably occurs by nucleophilic displacement of chlorine by sulphonyl oxygen at the thionyl chloride sulphur to give a sulphonium salt intermediate (60).



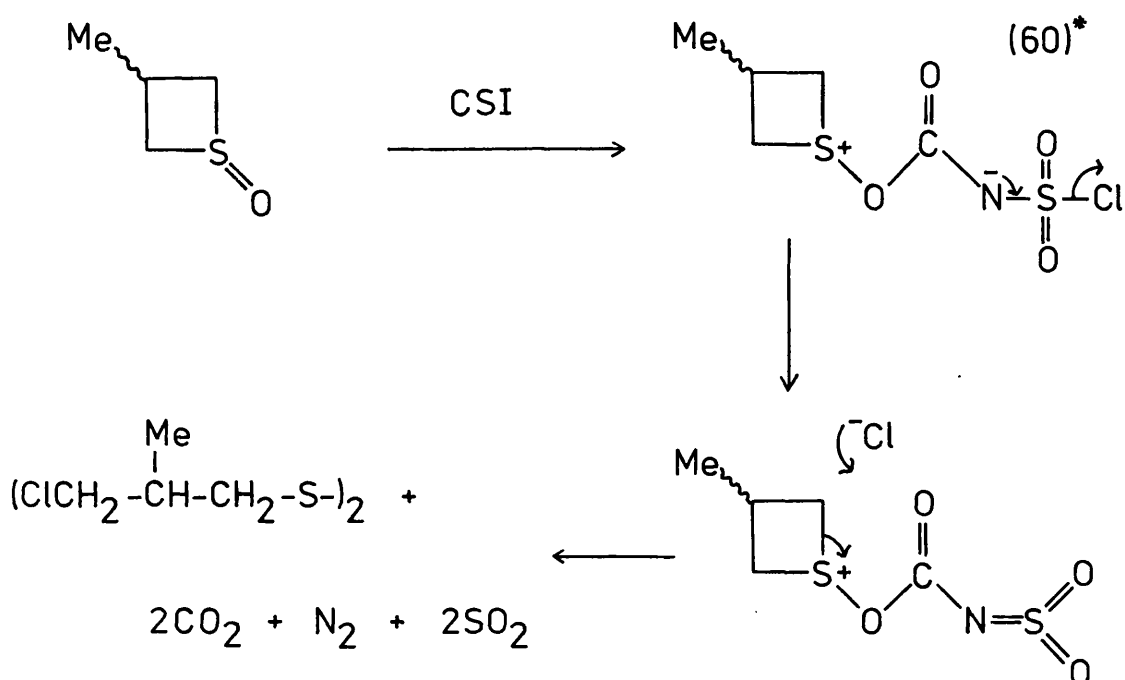
Nucleophilic attack of the chloride ion at the α -carbon again causes ring opening. The resulting compound (61) disproportionates to give the observed disulphide (59).

4.2 The Reaction of the 3-Methylthietane 1-Oxides with Chlorosulphonyl Isocyanate.

It was previously shown in Chapter Two that the 3-methylthietane 1-oxides react with TsNCO to give sulphimides, and in Chapter Three that both cyclic and acyclic phosphine oxides react with TsNCO and CSI to give the respective phosphine imides. The reaction of the thietane 1-oxides

with CSI however leads to the formation of bis(2-methyl-3-chloropropyl)-disulphide (59) (56%).

The initial step of the reaction is probably as in the previous cases, the nucleophilic attack of the sulphanyl oxygen at the isocyanate carbon to give the zwitterion (60)*.



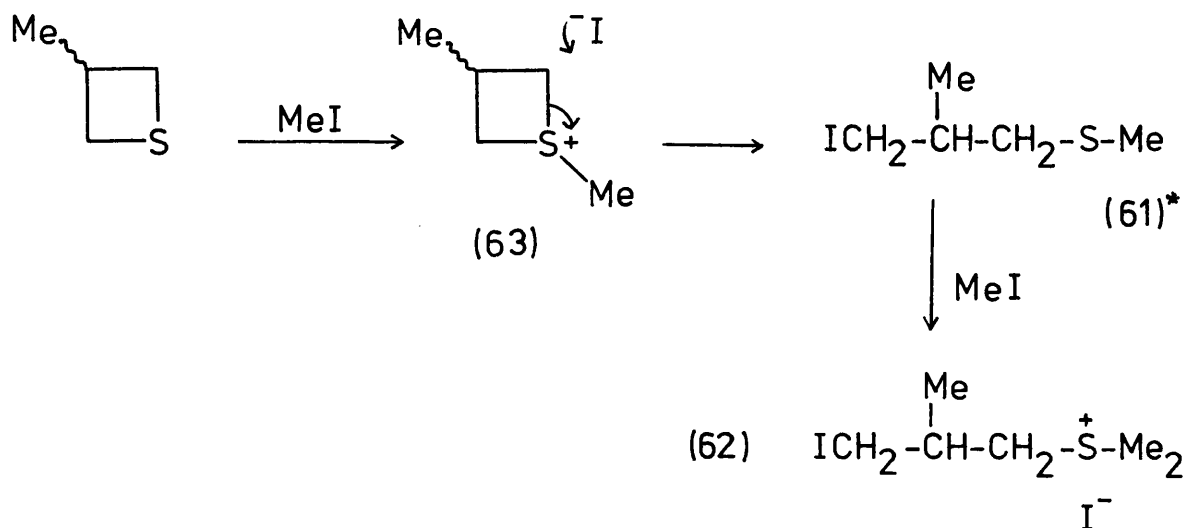
The thietane ring could then be opened by nucleophilic attack of chloride ion at the α-carbon. The molecule thus formed would be expected to disproportionate to give the observed products. One suggestion for the production of chloride ion is illustrated in the scheme. CSI was distilled from potassium carbonate immediately prior to use to remove any hydrogen chloride present.

4.3 The Reaction of 3-Methylthietane with Methyl Iodide.

Bennet and Hock⁸² have previously shown that thietane can be ring

opened with methyl iodide.

3-Methylthietane undergoes a similar reaction. Addition of excess methyl iodide to a solution of thietane gave a mixture of methyl(2-methyl-3-iodopropyl)sulphide (61)* and dimethyl(2-methyl-3-iodopropyl)sulphonium iodide (62).



Again the ring opening is caused by attack of the anion, of the initially formed sulphonium salt (63), at the α -carbon. The sulphonium salt (62) is formed by quaternisation of the ring opened product (61)*.

4.4 Conclusion.

If a reaction involves putting a formal positive charge on the sulphur in a thietane or its 1-oxide, and if there is a good nucleophile in solution, then nucleophilic attack at the α -carbon will occur and ring opened products will result.

An important exception to this conclusion is the hydrogen chloride catalysed epimerisation of 3-methylthietane 1-oxide, mentioned in Section 1.7. This reaction was carried out in anhydrous benzene, in which the chloride

ion is expected to be a good nucleophile, and no ring opened product was obtained. It has however been reported by Johnson⁴ that treatment of the same thietane 1-oxide with hydrogen chloride leads to decomposition. The reaction conditions or the products are not however revealed.

4.5 The Reaction of the 2-Methylthietane 1-Oxides with Hydrogen Azide.

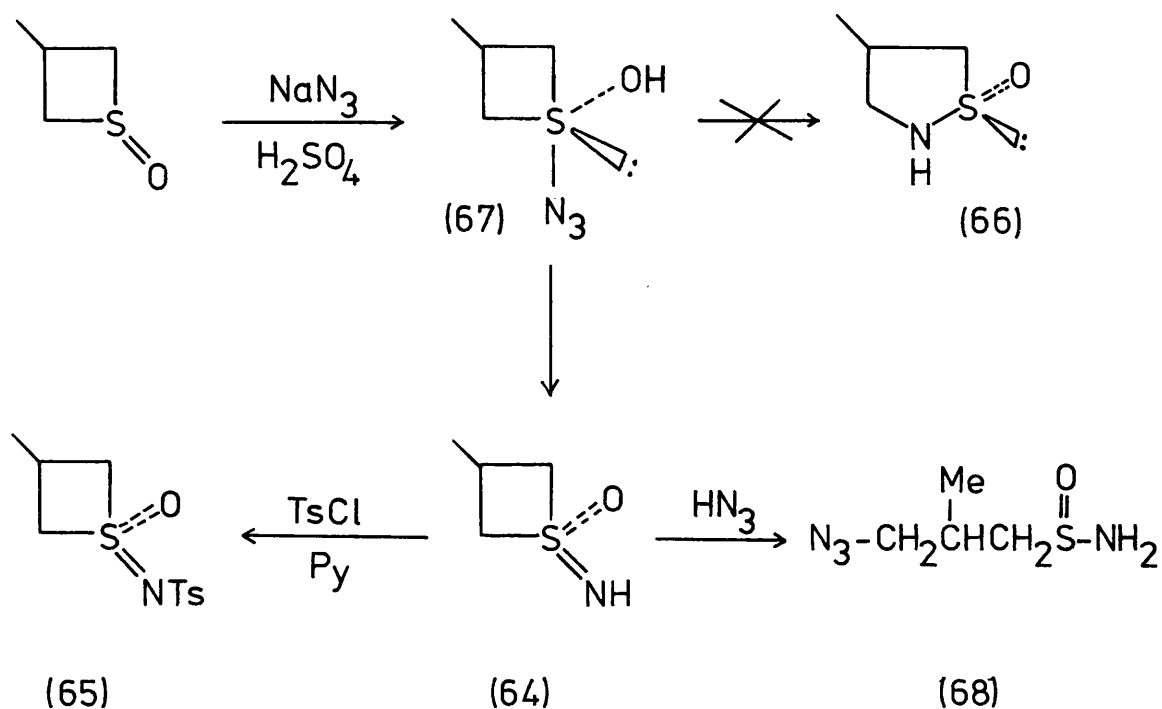
This type of reaction is formally the sulphur analogue of the Schmidt reaction at carbonyl compounds. It has been previously investigated for acyclic⁸³ and six-membered cyclic⁴⁹ sulfoxides and in all cases the product is a sulphoximide, derived from imidation of the sulphur lone pair. There is no evidence for alkyl migration in the intermediate nitrene or azide. It was thought that potential relief of ring strain might provide a driving force for alkyl migration. In the thietane 1-oxide case this would result in ring expansion.

As in the Schmidt reaction excess sulphuric acid is needed as a catalyst and, since sulphuric acid racemises optically active sulfoxides,⁸⁴ it was not possible to investigate the stereochemistry of the reaction.

Under mild conditions the reaction produces the two isomers of 3-methylthietane 1-imide 1-oxide (64) (52%). These isomers can be separated by column chromatography and their structure and stereochemistry were demonstrated by converting them to the previously prepared 3-methylthietane 1-oxide 1-N-(toluene-*p*-sulphonyl)imides (65) (Chapter Two). This reaction, which is brought about by the use of toluene-*p*-sulphonyl chloride and pyridine,^{43,49} does not involve reaction at the sulphoximide sulphur, and can therefore be assumed to occur with retention of configuration.

The sulphuric acid catalyst is probably required for the initial

protonation of the thietane 1-oxide. The second step most likely involves apical attack of the azide anion, at sulphur, to give a sulphurane intermediate such as (67).



This intermediate has the four-membered ring occupying one apical and one equatorial position. No ring strain should therefore be involved and hence it is not surprising that alkyl migration does not occur.

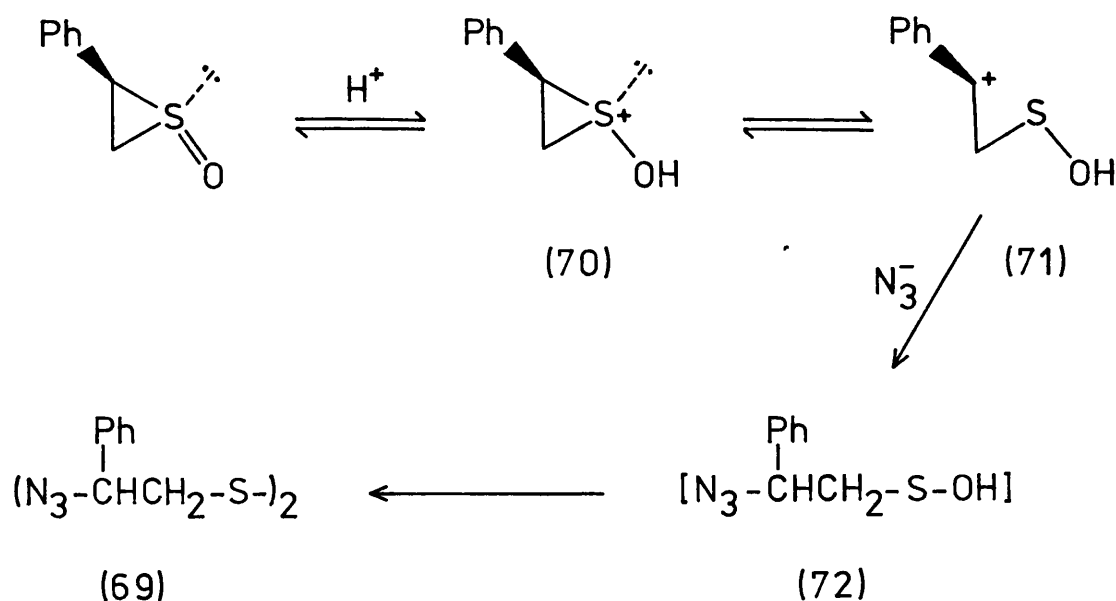
Under more vigorous conditions the sulphoximide (64) reacts with a second mole of hydrogen azide. In this case protonation at either the oxygen or the nitrogen is followed by attack of the azide anion at the α -carbon, thus causing ring opening. The resulting sulphinamide (68) is oxidised during the work-up and is isolated as the corresponding sulphonamide.

4.6 The Reaction of trans-2-Phenylthiirane 1-Oxide with Hydrazoic Acid.

It was hoped that by decreasing the ring size, the increased ring

strain in an intermediate such as (67) would favour alkyl migration from sulphur to nitrogen over sulfoximide formation.

trans-2-Phenylthiirane 1-oxide, formed by the controlled oxidation of 2-phenylthiiran,⁸⁵ is only moderately stable at room temperature with respect to loss of sulphur monoxide and polymerisation.⁸⁶ The reaction with a solution of hydrazoic acid in chloroform (in this case not catalysed by sulphuric acid), is fairly slow at room temperature and the majority of the product is polymeric. The major monomeric product is bis(2-azido-2-phenylethyl)disulphide (69) (30%). The structure was determined by a consideration of the n.m.r. spectrum, and its comparison with that obtained in the next section.

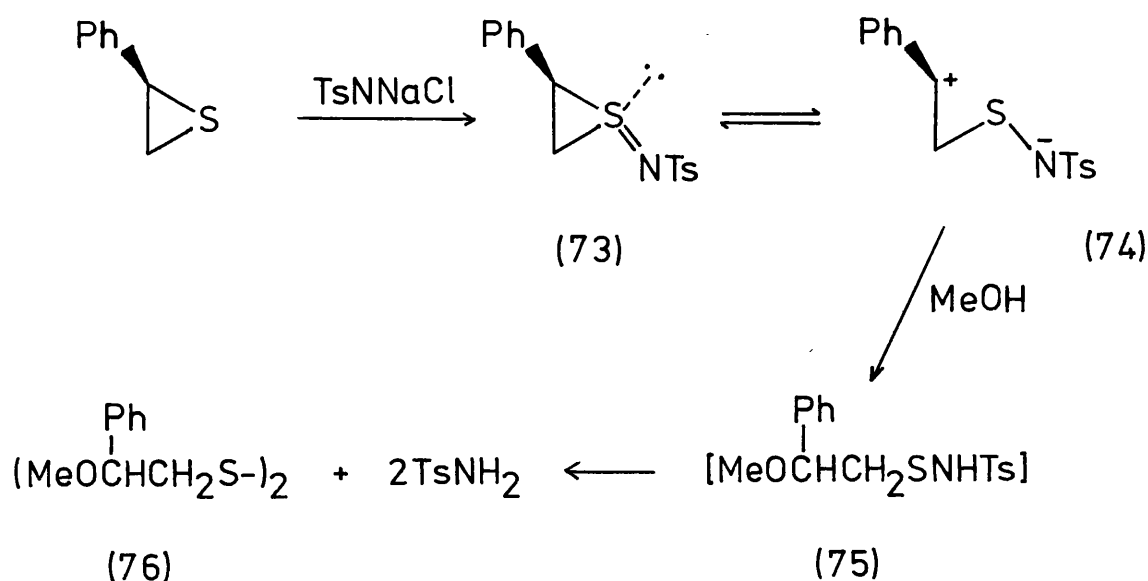


The probable mechanism involves initial protonation of the sulphonyl oxygen. The resulting protonated species (70) is unstable with respect to ring opening, and it does so to form the most stable carbonium ion (71). The carbonium ion is trapped by azide ion from solution to give the sulphenic acid (72). As previously mentioned

sulphenic acids are unstable with respect to self condensation and disproportionation,⁸⁰ but in this case only disulphide (69) and no thiosulphonate was obtained.

This mechanism is favoured over one involving attack of the azide anion at the α -carbon of the protonated species (70) because of the product structure. No bis(2-azido-1-phenylethyl)disulphide is obtained, and this would be the product expected from ring opening by attack of the azide at the least hindered α -carbon.

A similar sort of ring opening was observed during an attempt to make the cyclic sulphimide (73) from the reaction of 2-phenylthiirane⁸⁵ with chloramine-T. When the reaction was carried out at 0° in methanol the major product was bis(2-methoxy-2-phenylethyl)disulphide (76) (60%). This result can be explained by suggesting that the initially formed sulphimide (73) is unstable with respect to ring opening, which occurs to give the most stable zwitterion (74). The zwitterion is then trapped



by methanol and the sulphenamide (75) thus formed disproportionates under the reaction conditions to give the observed disulphide (76) and toluene-*p*-sulphonamide.⁸⁷

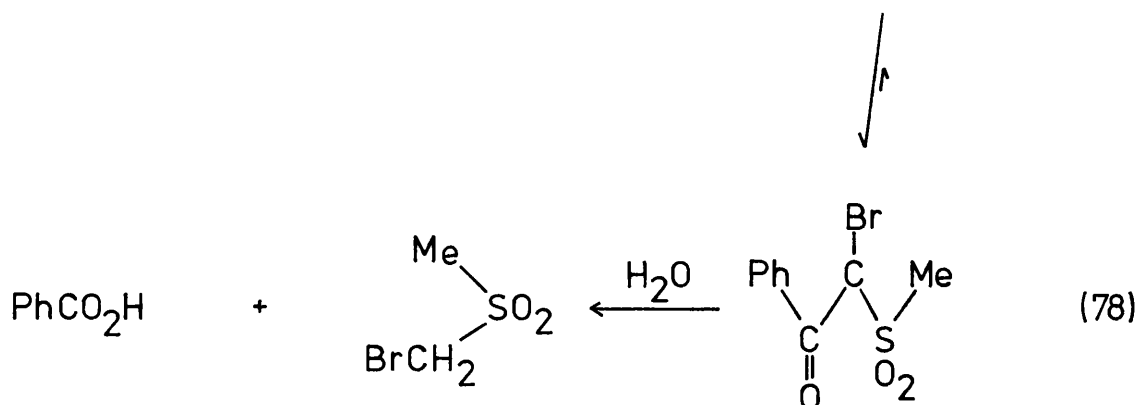
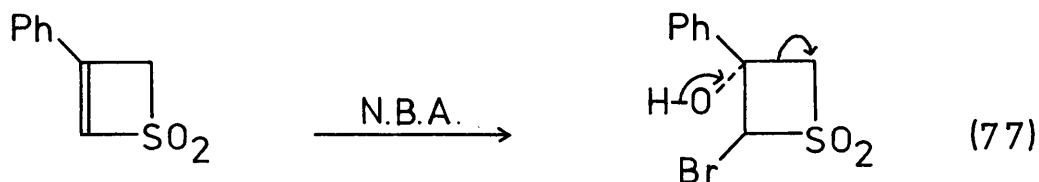
If the reaction is carried out in an inert solvent such as tetrahydrofuran, only polymeric product is obtained. The n.m.r. spectrum of the polymer suggests that it does not contain methyl groups. This is consistent with a polymerisation of the thiirane, initiated by the zwitterion (74).

The majority of the reactions of thiirans and their 1-oxides lead to ring opening.^{88,89} When unsymmetrical systems are involved only one of the two possible isomers is usually⁸⁹ obtained. Which isomer this is depends on the ring opening agent and the ring substituent. As yet no systematic studies have been conducted on this subject.

The single isomer obtained in both of the reactions investigated suggests that the mechanisms involve prior ring opening to give the most stable carbonium ion, as opposed to nucleophilic attack at the least hindered α -carbon.

4.7 Attempted Epoxidation of 3-Phenylthiirane 1,1-Dioxide.

The olefinic bond in 3-phenylthiirane 1,1-dioxide is known to be a lot less reactive than that in the unsubstituted system.^{4,90}



Attempted epoxidation by normal procedures gave only starting material. If, however, the dioxide was heated with N-bromoacetamide in water at 60° for 12hr the ring was cleaved to give benzoic acid and bromomethyl methyl sulphone.

The bromohydrin (77) is probably the initial product, but it is suggested to be unstable with respect to the α -bromo- β -keto sulphone (78), which is then hydrolysed to give the observed products.

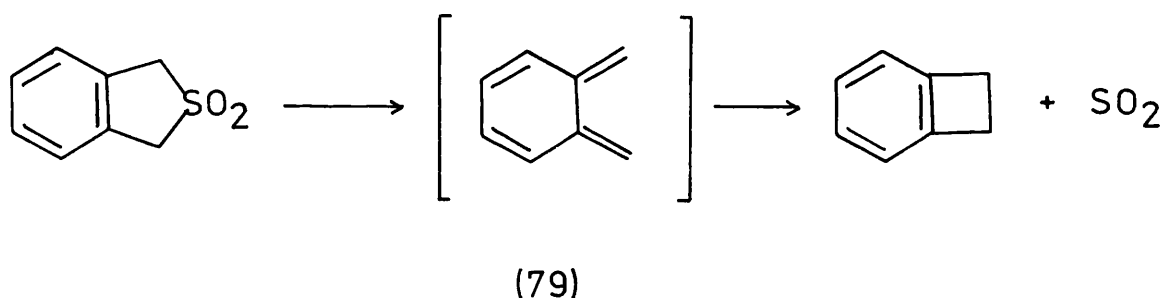
CHAPTER FIVE

THE FLASH THERMOLYSIS OF SOME UNSATURATED CYCLIC SULPHONES.

5.1 Introduction.

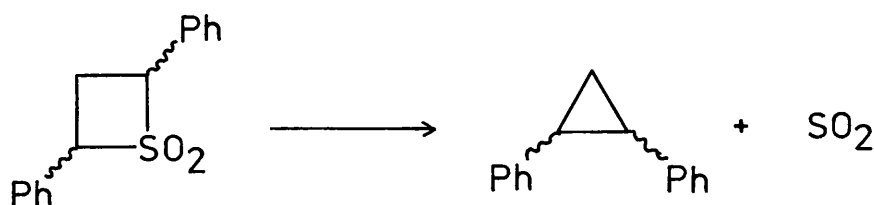
Ring contraction reactions which involve the extrusion of a stable molecule are well known. Some examples where this molecule is sulphur dioxide are reported below.

Cava⁹¹ has synthesised benzocyclobutene by the extrusion of sulphur dioxide from 1,3-dihydroisothianaphthene 2,2-dioxide.



The sulphone was passed in the gas phase, at low pressure, over a heated wire at 450° - 650°. It was proposed that concerted loss of sulphur dioxide gave o-quinodimethane (79) which rapidly rearranged to the product.

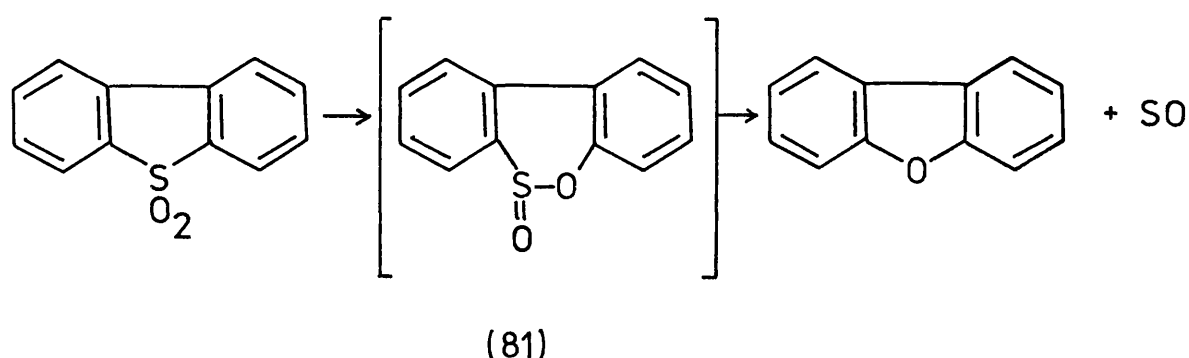
Cyclopropanes have been synthesised by the gas phase thermolysis of



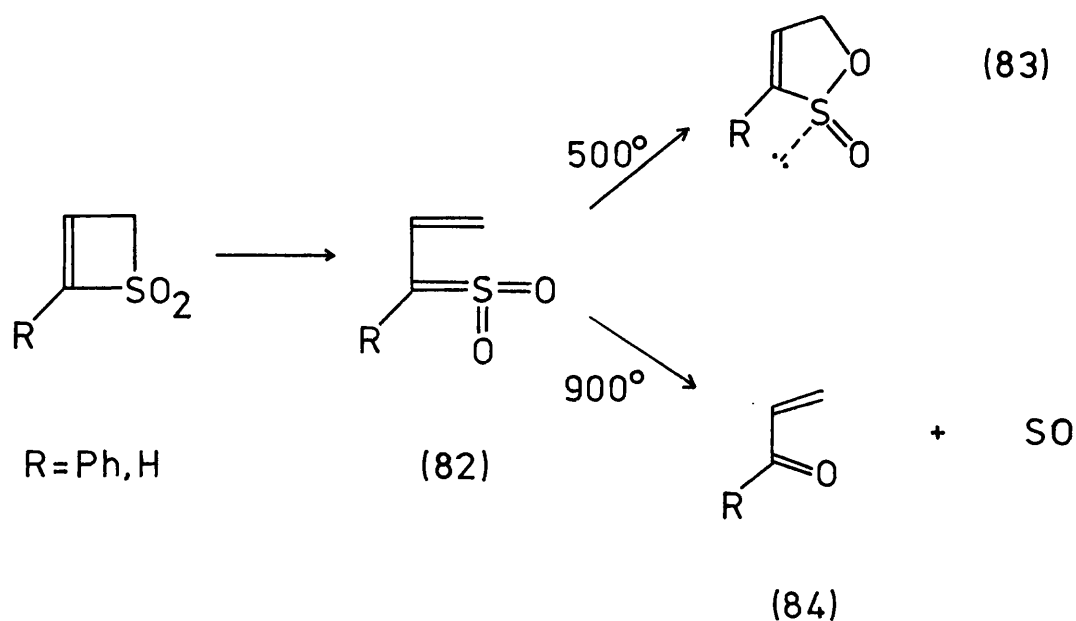
(80)

a number of substituted thietane 1,1-dioxides,⁹²⁻⁹⁴ e.g. 1,2-diphenylcyclopropane (80).

Thermolysis of dibenzothiophene 1,1-dioxide does not however lead to the extrusion of sulphur dioxide and formation of biphenylene. It has been postulated⁹³ that the reaction involves an intermediate cyclic sulphinate ester (sultine) (81), which can then lose sulphur monoxide via a biradical mechanism to give the observed dibenzofuran.



Sulphenes ($R_2C = SO_2$) have been proposed as intermediates in the thermolysis of thiete 1,1-dioxides,⁹⁴ e.g. the 2-substituted systems are thought to undergo electrocyclic ring opening to give the vinyl sulphenes (82). At relatively low temperatures ($\sim 500^\circ$) these sulphenes undergo intramolecular rearrangement to the sultines (83).



At higher temperatures ($\sim 900^\circ$) sulphur monoxide is lost to form the vinyl ketone (84).

Attempts to trap the vinyl sulphene in the gas phase were largely unsuccessful, but a small yield (15%) of the expected sulphonate ester was obtained when phenol was used as the trapping agent. When the sultine (83) was heated with phenol only a brown tar was obtained, suggesting that the sulphonate ester did not arise from (83). Failure of these trapping experiments is attributed to fast intramolecular reactions of the vinyl sulphene.

Loss of sulphur monoxide from the sultine (83) would be expected to give a vinyl aldehyde, hence the vinyl ketone (84) must arise from the rearrangement of the sulphene, and not from the sultine.

To the present date only one sulphene has been directly observed. King⁹⁶ has produced the parent sulphene ($\text{CH}_2 = \text{SO}_2$) by flash thermolysis of chlorosulphonylacetic acid, and has trapped it in a methanol matrix at -196° . At this temperature he observed the infrared spectrum due to the sulphene, and on warming, the sulphene was trapped by the methanol to give methyl methanesulphonate. The same results have recently been obtained from a photochemical generation of the parent sulphene (See Chapter Six).

5.2 The Apparatus and Initial Experiments.

The technique of flash thermolysis involves passing a stream of the vaporised compound under study, at very low pressure, through a furnace and then trapping the reaction products. In the ideal case each molecule only strikes the hot part of the furnace once. Reaction takes place and any excess energy the products may have is removed by immediate

trapping at low temperature. In order to achieve this ideal the mean free path of the molecules must be as long as possible (i.e. the pressure must be as low as possible), the furnace 'hot spot' must be short and the low temperature trap must come as close as possible after it.

The temperature of the furnace should in most cases be kept at the lowest temperature that causes a reasonable percentage reaction, so that the generated products are as near as possible to their ground state energies and are hence less likely to undergo further reaction before being trapped.

The apparatus used in this study (fig. 6)* is of a much simpler design than that used by others.⁹⁴

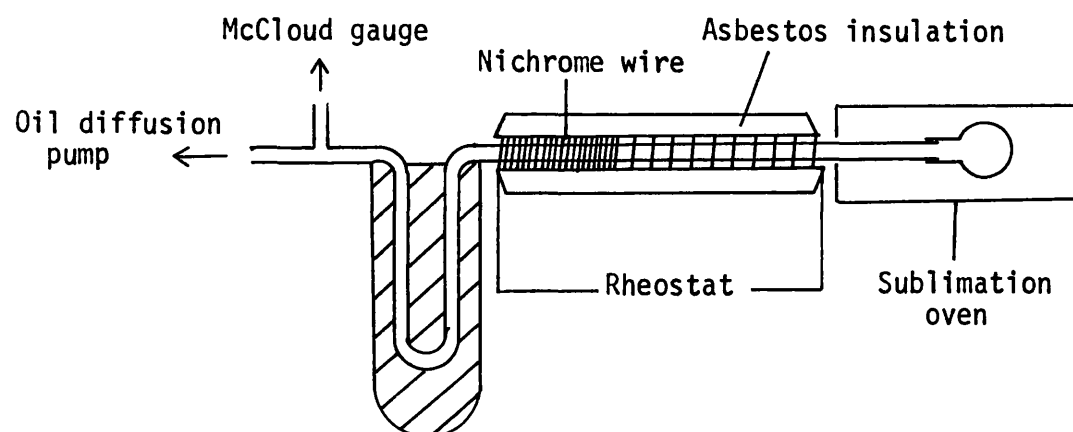


Fig. 6*

The reaction tube itself is made of quartz glass and is bent and drawn out at one end to form a U-tube. At the other end is a ground glass joint to which a flask containing the material under study is attached. The reaction tube passes through the furnace which consists of a second

quartz tube, of slightly larger diameter, and which is bound with turnings of nichrome wire. Over the first six inches these turnings are widely spaced and are intended only to keep the material in the gas phase. (This part of the furnace was originally used to volatilise the sample, but in order that this process could be more conveniently observed the reaction tube was extended as shown in fig. 6). Over the last four inches of the furnace the turnings are close together. This comprises the 'hot spot'. The reaction tube is so positioned that the U-tube, which is immersed in a mixture of solid carbon dioxide and acetone contained in a covered Dewar flask, comes immediately after the exit from the furnace.

The whole system is connected to an oil-diffusion pump. The pressure (usually $\sim 1 \times 10^{-3}$ mm) is read by a McCloud gauge at a position between the cold trap and the pump. (This reading is not therefore the same as that in the reaction tube). The temperature of the 'hot spot' is estimated by suspending a thermocouple within it. The reading obtained is not expected to be the same as that inside the reaction tube, and is only intended to provide a comparison between runs.

Before each reaction the furnace was allowed to equilibrate for at least 1.5 hr, then the sample was slowly sublimed (~ 0.4 g/hr) through it. Separation of products was achieved in many cases by their fortuitous partition within the U-tube, the position of condensation being dependent on the volatility of the particular product. In other cases products were separated by distillation, or by thick-layer chromatography.

In order to prove the usefulness of this relatively simple apparatus design, a number of experiments of a similar nature to those of King⁹⁴ were carried out.

The Thermolysis of 3-Phenylthiete 1,1-Dioxide at 0.05mm Pressure.

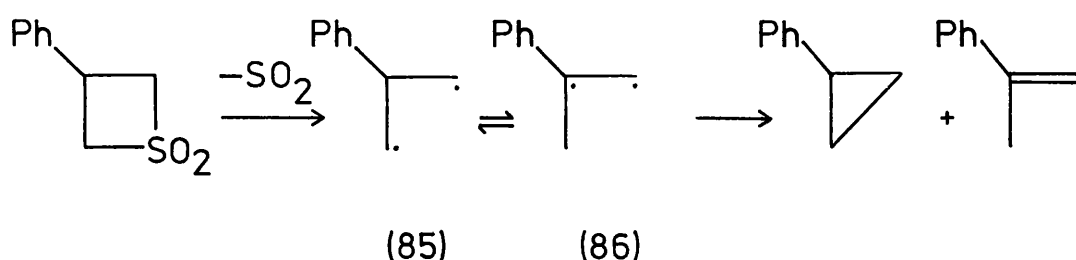
<u>PRODUCT</u>	<u>FURNACE TEMPERATURE</u>	
	<u>460°</u>	<u>680°</u>
Starting material	7%	-
4-Phenyl-5H-1,2-oxathiole 2-oxide	79%	8%
Atropaldehyde	10%	70%
Styrene	-	10%

The atropaldehyde was unstable in solution and was isolated as its cyclic dimer, 3,4-dihydro-2,5-diphenyl-pyran-2-al.

Thermolysis of 3-t-butylthiete 1,1-dioxide at 1×10^{-3} mm pressure and with a furnace temperature of 525° gave, 2-methylene-3,3-dimethyl-butylaldehyde (40%)⁹⁷ and 4-t-butyl-5H-1,2-oxathiole 2-oxide (60%).

The products obtained in both of these experiments are consistent with the mechanism, proposed by King⁹⁴ and described above, for the thermolysis of 2-substituted thiete 1,1-dioxides. It is however not possible in this case to say that the aldehyde is derived from rearrangement of the intermediate vinyl sulphene, since loss of sulphur monoxide from the sultine would be expected to give the same product.

Thermolysis of 3-phenylthietane 1,1-dioxide at 1×10^{-3} mm pressure and with a furnace temperature of 800° gave, starting material (49%), phenylcyclopropane (30%) and α -methylstyrene (15%). These products could be derived from intermediate biradicals such as (85) and (86).



Initial cleavage of sulphur dioxide from the molecule could give the biradical (85), which could then ring close to give the observed cyclopropane or rearrange to the more stable biradical (86) and from there to α -methyl styrene.

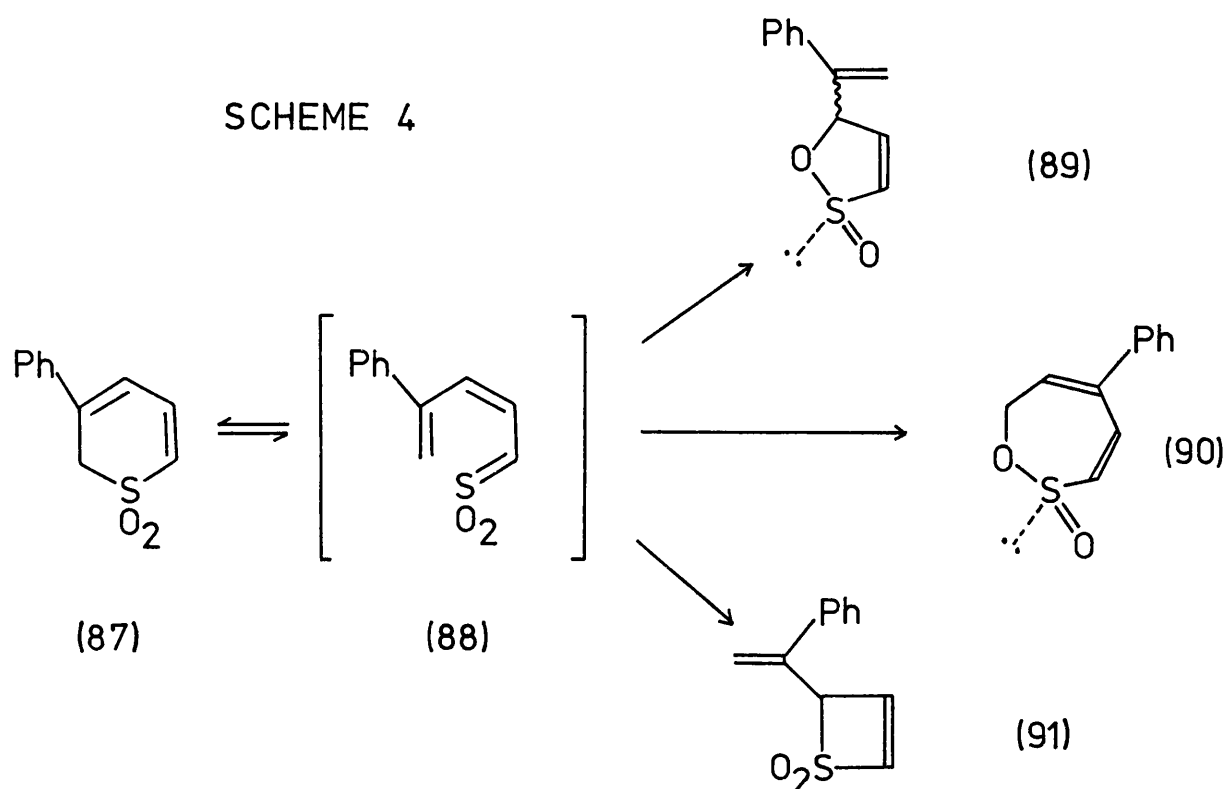
Alternatively loss of sulphur dioxide from the starting material could give phenylcyclopropane directly, followed by a degree of ring opening, either because the cyclopropane is generated with excess energy (i.e. it is formed in an excited state) or on a second contact with the 'hot spot'.

The biradical mechanism is favoured by the lack of stereospecificity of cyclopropane formation observed in the thermolysis of 2,4-di-substituted thietane 1,1-dioxides.^{92,93}

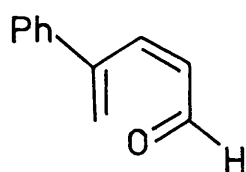
5.3 The Thermolysis of 3-Phenyl-2H-thiopyran 1,1-Dioxide and 2H-1-Benzothiopyran 1,1-Dioxide.

Having demonstrated that the apparatus performed satisfactorily, it was decided to extend the study and investigate the thermolysis of some 4π -electron cyclic sulphones. The systems chosen could potentially undergo electrocyclic ring opening to give unsaturated sulphenes. At relatively low temperature these sulphenes could then ring close via either an oxygen or the sulphur. Scheme 4 shows the expected low temperature products for the thermolysis of 3-phenyl-2H-thiopyran 1,1-dioxide (87).⁹⁸

SCHEME 4

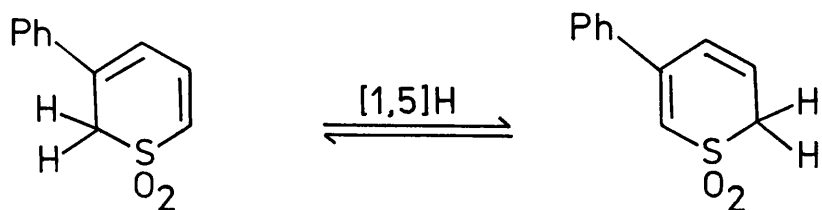


At relatively higher temperatures the products might be expected to be derived from the unsaturated aldehyde (92), formed by oxygen migration in the sulfolene (88).



(92)

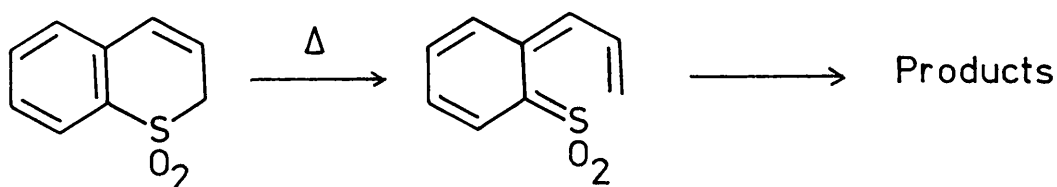
However in practice (87) undergoes a [1,5] hydride shift on simple sublimation. This, according to the Woodward-Hoffmann orbital symmetry rules,⁹⁹ is thermally a suprafacial process and is hence expected to be of relatively low energy.



(87)

This facile hydride shift means that the thermolysis is performed on a mixture of two isomers, and not surprisingly the mixture of products is very complex. Study of this particular system was therefore discontinued.

A [1,5] hydride shift in the thiopyran ring can be prevented by substituting the 2 and 3-positions. This is achieved in 2H-1-benzothiopyran 1,1-dioxide (93).¹⁰⁰ Electrocyclic ring opening of this system could give the sulphene (94), and this should lead to rearrangement products similar to those expected from (88) above.



(93)

(94)

The sulphene (94) might be expected to have a relatively short life time since its formation involves destroying the resonance energy of the aromatic ring.

The Thermolysis of 2H-1-Benzothiopyran 1,1-Dioxide at 1×10^{-3} mm Pressure.

<u>PRODUCT</u>	<u>FURNACE TEMPERATURE</u>		
	<u>650°</u>	<u>675°</u>	<u>775°</u>
Starting material	100%	75%	15%
Indene	-	5%	20%
Cinnamaldehyde	-	10%	30%
2H-1-Benzopyran ¹⁰¹	-	6%	18%

Mechanistic Considerations.

The first step of this reaction is probably cleavage of a carbon-sulphur bond. This can occur in one of two ways:

(1) By a Concerted Process.

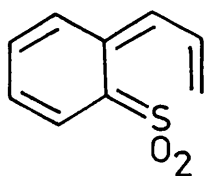
This is the equivalent of an electrocyclic ring opening reaction, i.e. as the carbon-sulphur bond cleaves so the two sigma-bonds flanking it rotate to give a species which is formally a triene [in this case the sulphene (94)]. If this process involved an all carbon system it could be classified under the Woodward-Hoffmann orbital symmetry rules as conrotatory. In this case however the presence of the sulphur atom is a major perturbation of orbital symmetry and such a classification is therefore not justified.

(2) By a Homolytic Bond Cleavage.

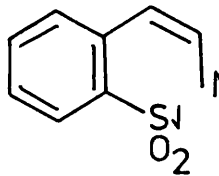
This would lead to the initial formation of a singlet state biradical (95) in which the orbitals containing the unpaired electrons are orthogonal to the molecular π -system. Sigma-bond rotations could now convert this biradical to a completely conjugated system.

Both of these considerations have neglected the geometric and electronic importance of the sulphur-oxygen bonds, and the nature of the

π -overlap between carbon and sulphur. It is very difficult to predict the importance of these terms and hence any difference in energy between the singlet biradical (95) and the sulphene (94). Both of these pictures are probably extremes, but here it will be assumed that the sulphene (94) conveys the best picture of the intermediate. It should however be stressed that there is no definite evidence for the participation of unsaturated sulphenes in thermally induced ring opening processes. All of the results presented here, and those presented in the literature by others⁹⁴ can be explained in terms of biradical intermediates. The sulphene notation is used here mainly for reasons of convenience.



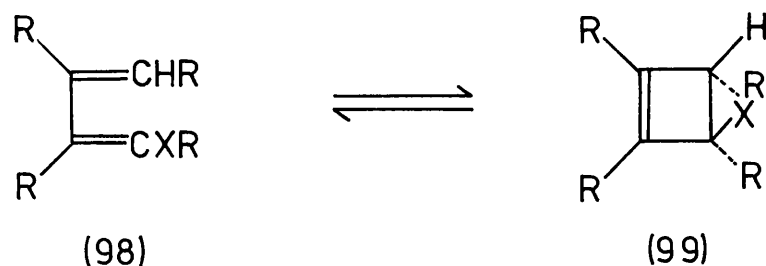
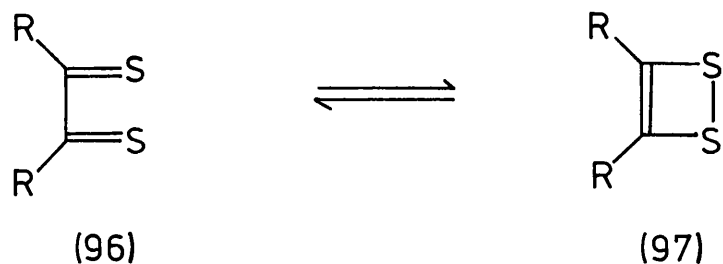
(94)



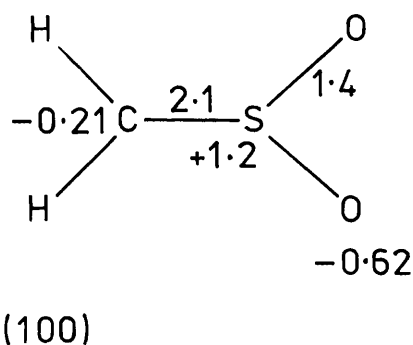
(95)

The difficulty in considering the sulphene (94) formation as a concerted electrocyclic reaction (in the same sense as the all carbon system) is emphasized in some recent work of Snyder.¹⁰¹ He points out that although the conversion of the α -dithione (96) to the dithiete (97) is π -isoelectronic with the corresponding hydrocarbon reaction (98) to (99), and that it proceeds with similar energy requirements, the mechanistic details of ring opening and closure appear to be quite different.

Semi-empirical SCF-MO calculations for a variety of α -dithiones suggest that while the conversion of (96) to (97) is photochemically allowed, both the forward and the reverse processes are thermally forbidden (Allowed and forbidden are used in the sense defined by Woodward and Hoffmann.⁹⁹).

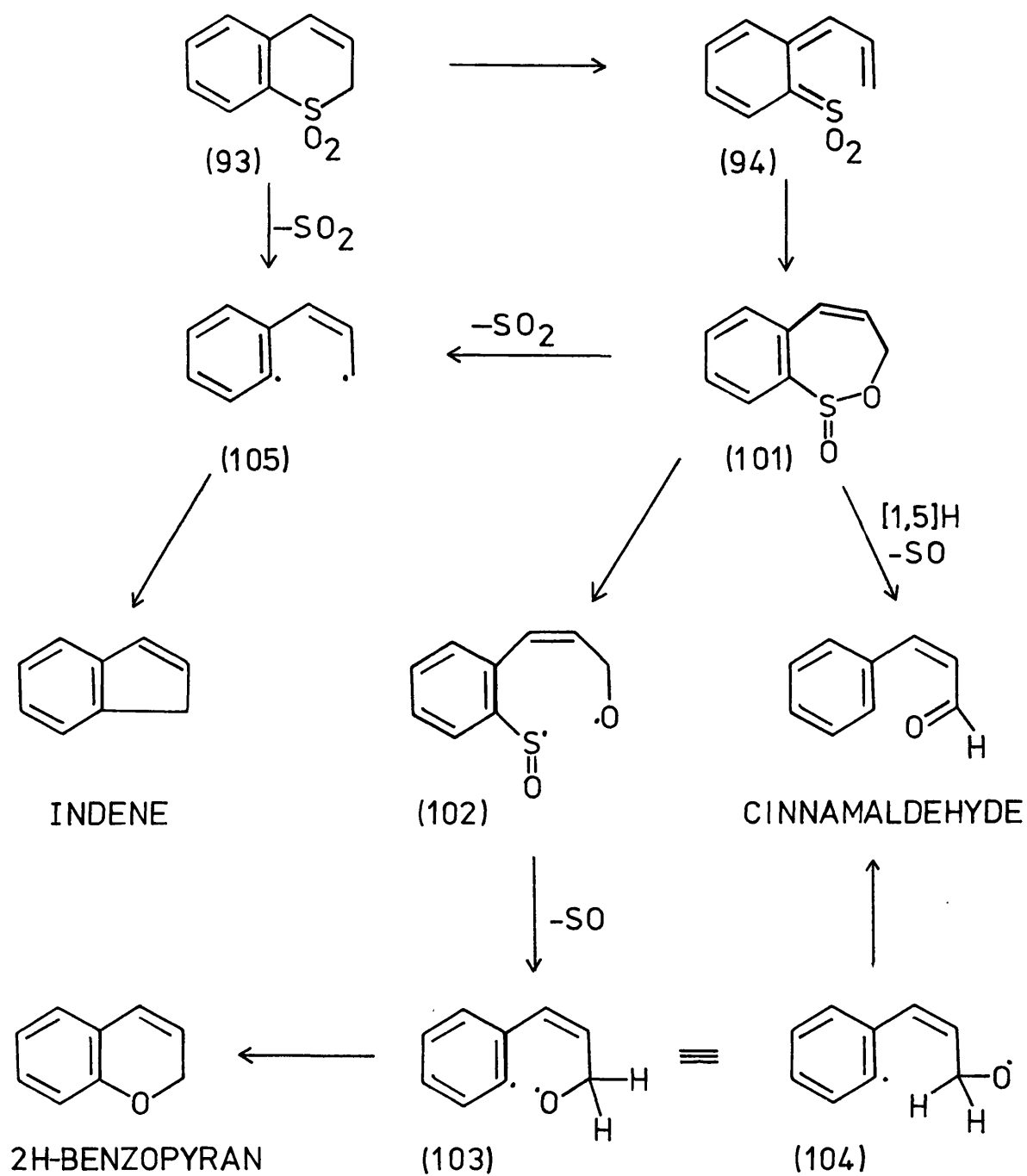


From the results of MO-SCF-CNDO calculations, Snyder¹⁰² predicts that a sulphene contains a full carbon-sulphur double bond and partial sulphur-oxygen double bonds. Computed bond orders and charge densities are shown in (100).



The sulphene (94), once formed, can react in a number of ways outlined in Scheme 5. The fact that no sultines are obtained as reaction products, even under conditions where most of the starting material is recovered, suggests that they are unstable under the conditions in which they are generated and that they rearrange themselves. In order to explain the observed reaction products it is only necessary to consider sulphene cyclisation via the oxygen to give the sultine (101). [Presumably the alternative modes of cyclisation outlined in Scheme 4 do occur, but

the equilibrium lies well over to the sulphene (94)]. Sultine (101) must be assumed to be generated with an energy greater than its dissociation energy.



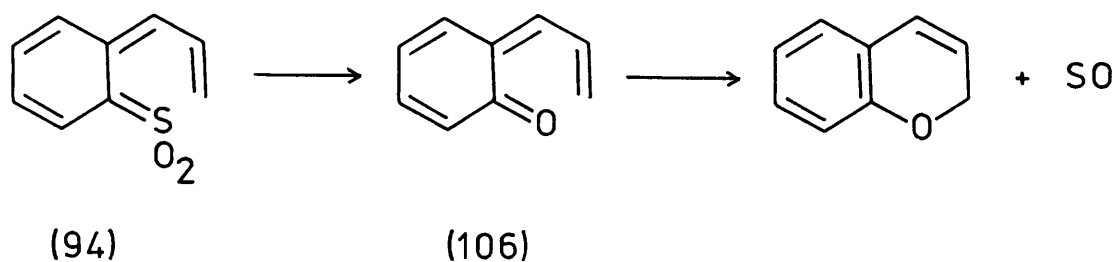
SCHEME 5

One mode of dissociation of (101) is cleavage of the sulphur-oxygen bond to give the biradical (102). Loss of sulphur monoxide from this species forms a further biradical (103), which can ring close to give the observed 2H-1-benzopyran. Alternatively it can undergo a hydrogen radical shift, via a favourable six-membered transition state (104), to give the observed cinnamaldehyde.

The indene is probably formed from ring closure of the biradical (105), which can arise by the direct loss of sulphur dioxide from either (93) or (94).

A second possible route to cinnamaldehyde is a thermally allowed [1,5] hydride shift and concerted loss of sulphur monoxide from sultine (101). (This hydride shift cannot be classified in terms of the Woodward-Hoffmann rules because the orbital to which the hydride moves is orthogonal to the molecular π -system).

It is possible that sulphene (94) could rearrange by migration of an oxygen from sulphur to the α -carbon, with simultaneous loss of sulphur monoxide. The resulting species (106) would be expected to cyclise immediately to give 2H-1-benzopyran. By analogy to the previously discussed results, a higher furnace temperature would be expected to favour this process over cyclisation of the sulphene (94) to the sultine (101). Hence an increase in the reaction temperature should favour the formation of 2H-1-benzopyran over that of cinnamaldehyde. In fact the ratio of these



two products stays the same, suggesting that they are probably both formed from the sultine (101).

The increase in the relative percentage of indene at higher temperature suggests that it is formed by a process with a higher activation energy than for the other products, this is consistent with the reaction pathways proposed in Scheme 5.

5.4 The Thermolysis of 1H-2-Benzothiopyran 2,2-Dioxide.¹⁰⁰

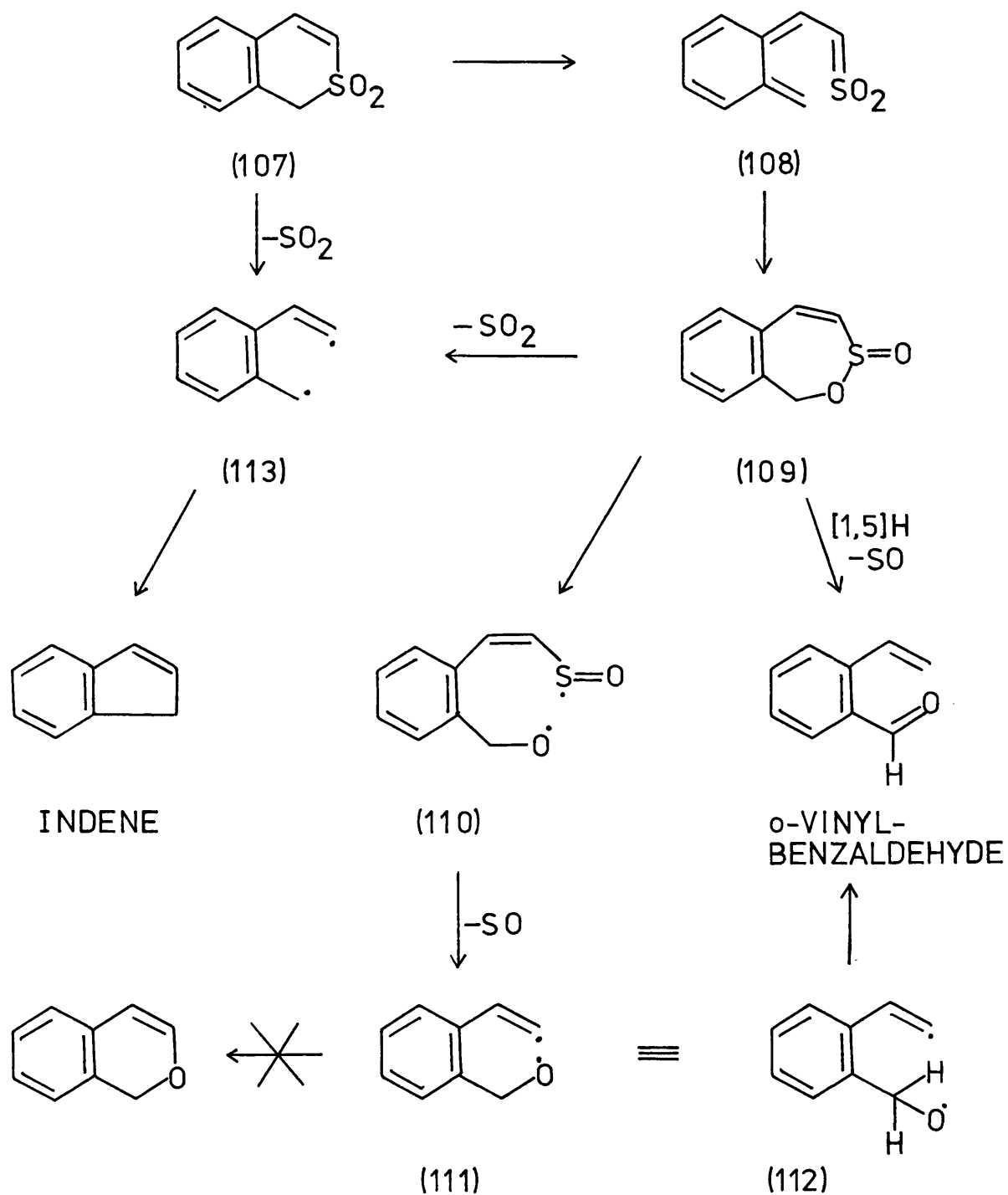
<u>PRODUCT</u>	<u>FURNACE TEMPERATURE</u>	
	<u>700°</u>	<u>775°</u>
Starting material	50%	12%
Indene	23%	42%
o-Vinylbenzaldehyde ¹⁰³	23%	36%

Both experiments were carried out at 1×10^{-3} mm pressure.

The most likely course of the reaction involves the initial formation of the sulphene (108) (as in the previous section the molecule is pictured as a sulphene as opposed to a biradical). The number of rearrangements open to this sulphene (108) is much less than for the sulphene (94). Ring closure via the sulphur can only reasonably be expected to regenerate starting material, and ring closure via an oxygen, only the single sultine (109). Since it is not isolated, it must again be assumed that the sultine (109) is generated with an energy greater than its dissociation energy.

Cleavage of the sulphur-oxygen bond in (109) will lead to the biradical (110), this could then lose sulphur monoxide to give the biradical (111) which is equivalent to (112) and is ideally set up to undergo

a [1,5] hydrogen radical shift, via a favourable six-membered transition state, to form the observed o-vinylbenzaldehyde.



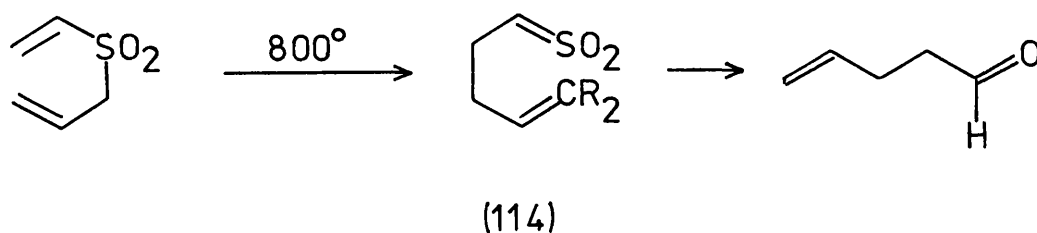
SCHEME 6

As in the previous case, this aldehyde could also be formed by a [1,5] hydride shift and concerted loss of sulphur monoxide from the sultine (109).

Ring closure of the biradical (111) would give 1H-2-benzopyran. The fact that this product was not observed could be taken as evidence in favour of aldehyde formation by the concerted route, i.e. no 1H-2-benzopyran was formed because the biradical (111) was not generated and hence aldehyde formation cannot be via (111). Alternatively the absence of 1H-2-benzopyran could be because ring closure of the biradical (111) is not competitive with hydrogen radical transfer as it was in the previous case for biradical (103). A third possibility is that 1H-2-benzopyran is not stable under the conditions in which it was generated.

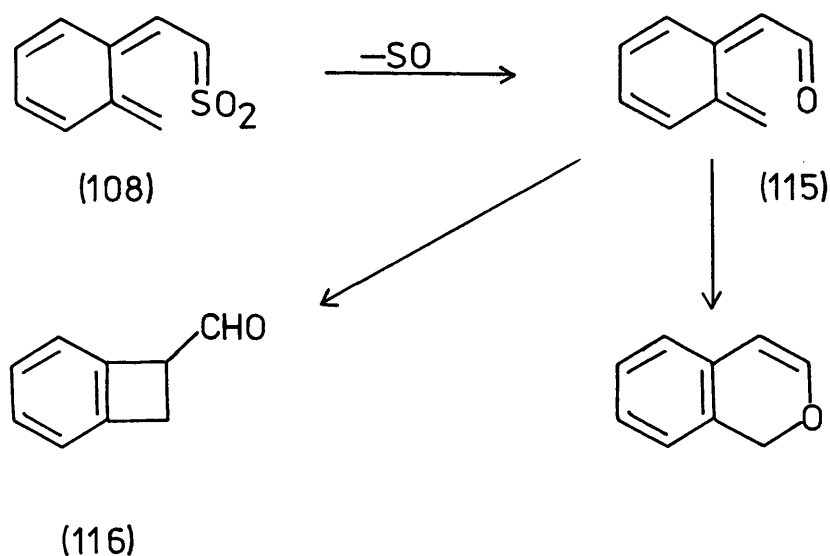
Indene was probably formed by ring closure of the biradical (113), which was formed by the direct loss of sulphur dioxide from (107) or (109). As in the previous case the relative percentage of indene increases with increasing furnace temperature.

The transfer of oxygen from sulphur to carbon and the simultaneous loss of sulphur monoxide is thought to be a characteristic reaction of sulphenes at temperatures in excess of $\sim 700^\circ$.^{94,96,104} Apart from the reactions already discussed, the formation of pent-4-enal on the thermolysis of allyl vinyl sulphone has been taken as evidence for the participation of a sulphene (114) in the reaction.¹⁰⁴



In this case the sulphene (114) can also be trapped by alcohols.

The sulphene (108) generated by the thermolysis of 1H-2-benzothiopyran 2,2-dioxide (107) might be expected to undergo oxygen migration and loss of sulphur monoxide to give the species (115). This could then ring close in one of two ways. 1H-2-Benzopyran is the most likely product, but the aldehyde (116) is also possible.



In fact no trace of either of these products was found, even at relatively high temperature.

The probable reason for the lack of this reaction on thermolysis of both benzothiopyran dioxides is the relatively short life times of the intermediate sulphenes (94) and (108). Recovery of the resonance energy lost in the formation of the sulphenes is the prime concern, and rearrangements that do not immediately achieve this are not competitive.

5.5 Conclusion.

The products from the thermolysis of 2H-1-benzothiopyran 1,1-dioxide

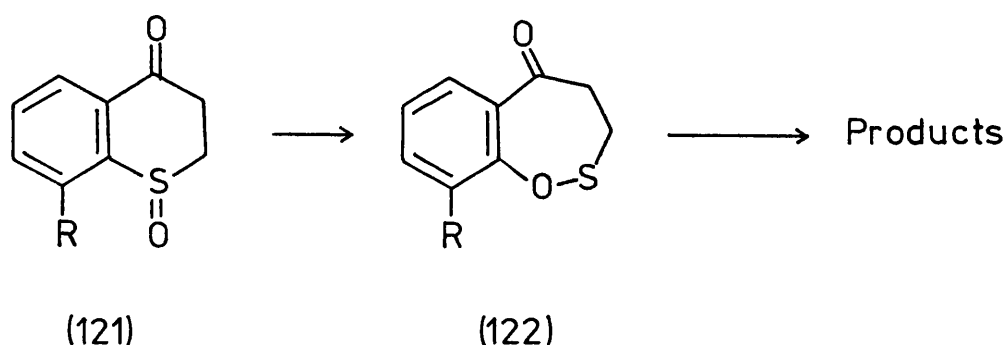
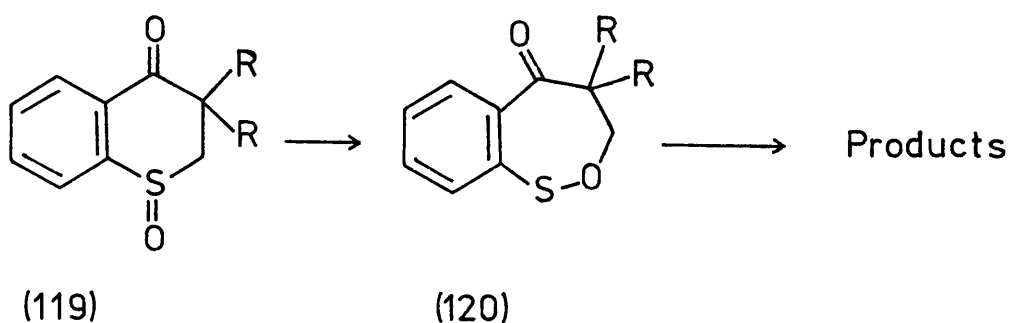
(93) and 1H-2-benzothiopyran 2,2-dioxide (107) have been explained in terms of an initially formed sulphene which ring closes via an oxygen to give the sultine (101) or (109). The instability of these sultines under the conditions in which they are generated leads to further rearrangements.

No evidence for a process involving migration of oxygen from sulphur to carbon in the intermediate sulphenes has been found.

The simplicity of the apparatus design has prevented attempted gas phase trapping experiments, but in view of the suspected short life time of the sulphenes involved it is unlikely that these would be successful. Trapping of biradical intermediates might however be possible.

oxygen. Ring closure would give the observed sulphenate ester (118).

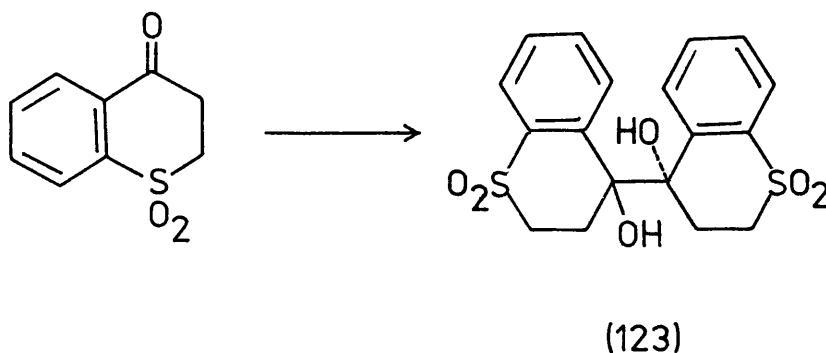
Still¹⁰⁶ has demonstrated the intermediacy of sulphenate esters in the photolysis of thiochromanone sulfoxides.



The sulphenate ester formed (120) or (122) depends on the substituents present in the initial sulfoxide. In both of the cases illustrated extensive polymerisation accompanies sulphenate ester formation. The unusual aryl carbon-sulphur bond cleavage in (121) is explained in terms of an electronic or steric influence of the 8-substituent.¹⁰⁶

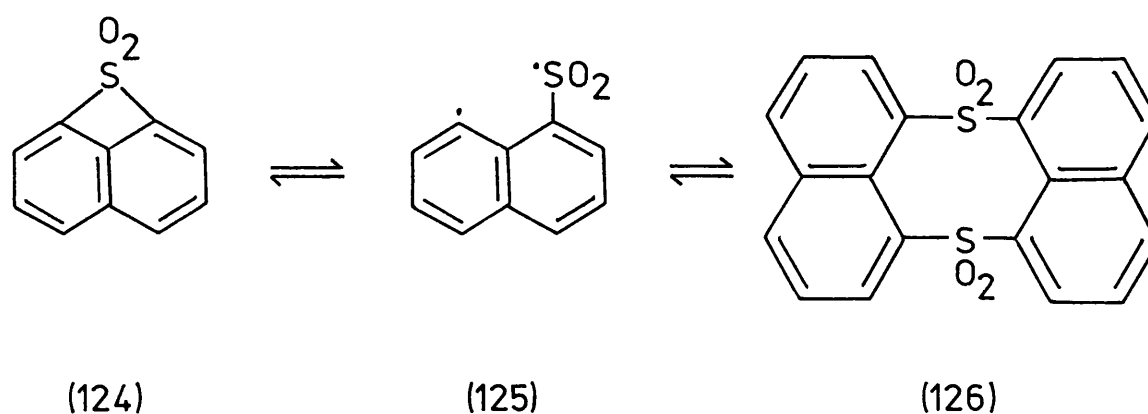
Photolysis of a series of the related thiochromanone sulphones¹⁰⁷ does not however lead to cyclic sulphenate esters either as intermediates or products. In inert solvents such as acetonitrile or benzene, irradiation for three days led only to a quantitative recovery of starting material. In methanol, which can act as a hydrogen donor to the excited carbonyl

group, photochemical reduction takes place to give the pinacol (123).



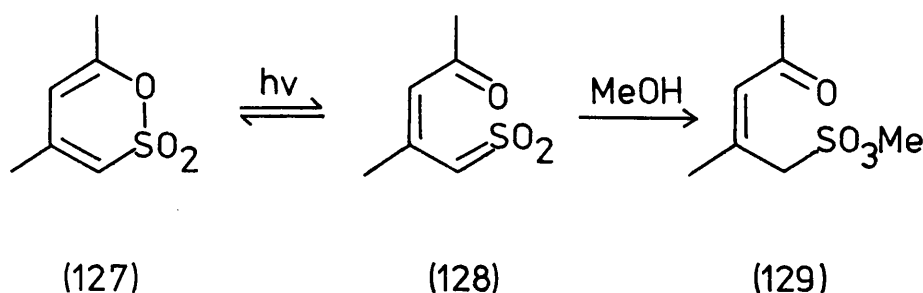
The difference between the reaction of the sulfoxides and the sulphones may be attributable to charge transfer effects in the sulfoxides,¹⁰⁸ which do not occur in the sulphones. There is however no very marked difference between the ultra-violet absorption spectra for each series, which suggests that this explanation is unlikely to be correct.

Photolysis of the 1,8-bridged naphthalene derivative (124) gives a dimer (126) which is probably formed from an intermediate biradical (125).¹⁰⁹

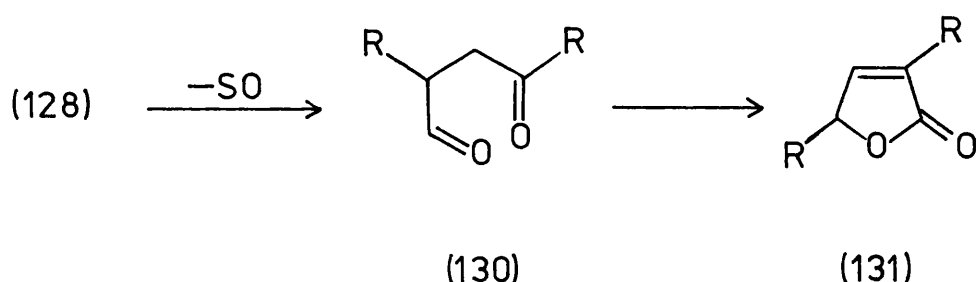


Sulphenes have been postulated as intermediates in several photochemical reactions:

The photolysis of sultones such as (127) in methanol is thought to involve electrocyclic ring opening to give the unsaturated sulphene (128), which is then trapped by the solvent to give the sulphonate ester (129).¹¹⁰

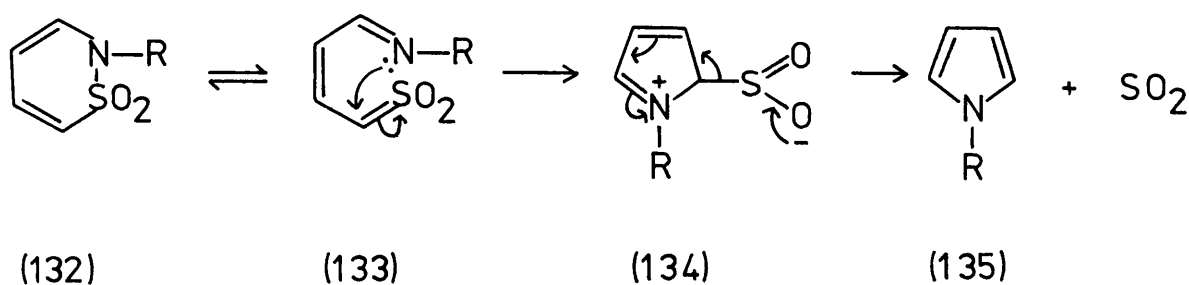


When the reaction is carried out in a non-nucleophilic solvent however the major product is a lactone (131).¹¹¹



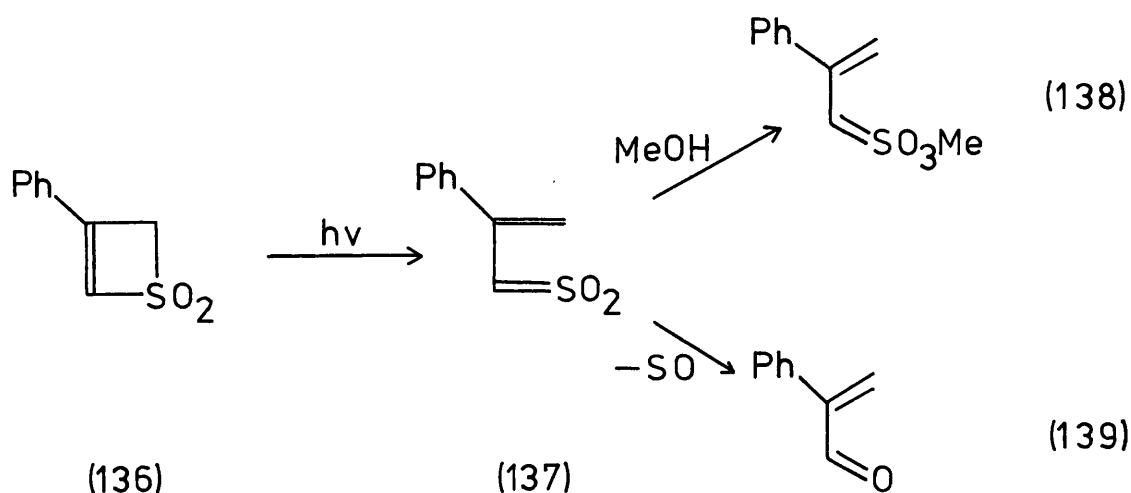
The mechanism suggested¹¹¹ involves oxygen migration from sulphur to the α -carbon in the sulphene (128), to give the dicarbonyl intermediate (130) and sulphur monoxide. This migration is comparable with that observed on the high-temperature thermolysis of thiete 1,1-dioxides (See Chapter Five). The formation of a lactone from an intermediate such as (130) is well documented.^{111,112}

Ring contraction is also the result of photolysing cyclic sultams such as (134).¹¹³ In the absence of other trapping agents, an "abnormal process" occurs.



The normal reaction (i.e. attack of the base at sulphur) leads only to the regeneration of starting material and over a period of time "abnormal attack" of the base at the sulphene carbon competes to give an intermediate (134) which then loses sulphur dioxide to give the observed pyrrole (135).

Langendries and DeSchryver¹¹⁴ have investigated the photolysis of a series of substituted thiete sulphones, e.g. (136).

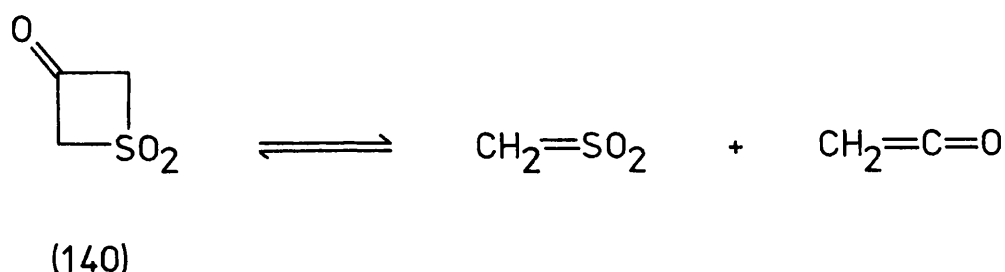


In the presence of methanol the proposed vinyl sulphene intermediate (137) is trapped to give the sulphonate ester (138). In an inert solvent however, it fragments to give the vinyl aldehyde (139), which in many cases

then polymerises, and sulphur monoxide. No sultines were observed or isolated.

The same products in the same yields were obtained on direct irradiation (253nm) or on sensitised irradiation (benzophenone, 350nm).

Recently DeSchryver et al.¹¹⁵ have investigated the photochemistry of 3-thietanone 1,1-dioxide (140). Irradiation in a pentane matrix at -196° with light of wavelength $> 280\text{nm}$ led to the direct observation (infrared spectroscopy) of the parent sulphene and ketene.



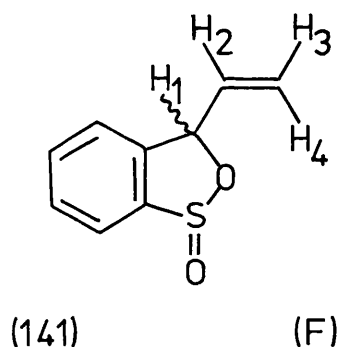
Photochemical kinetics suggest that this reaction occurs through both the triplet and the singlet excited states.

6.2 The Photolysis of 2H-1-Benzothiopyran 1,1-Dioxide.

Irradiation of a solution of 2H-1-benzothiopyran 1,1-dioxide (93) in methanol, dichloromethane or acetonitrile with light of wavelength 253nm, gave the same products, in almost identical yields in each solvent, (as estimated by n.m.r. and g.l.c. of the crude reaction mixture). The reaction was monitored by g.l.c., and when all of the starting material had reacted the solvent was removed under reduced pressure to give a dark oil. Careful chromatography on silica gave indene (5%), 2H-1-benzopyran (5%), starting material (8%), a clear oil F (25%), which was a single compound, and a clear oil GH (55%), which was a mixture.

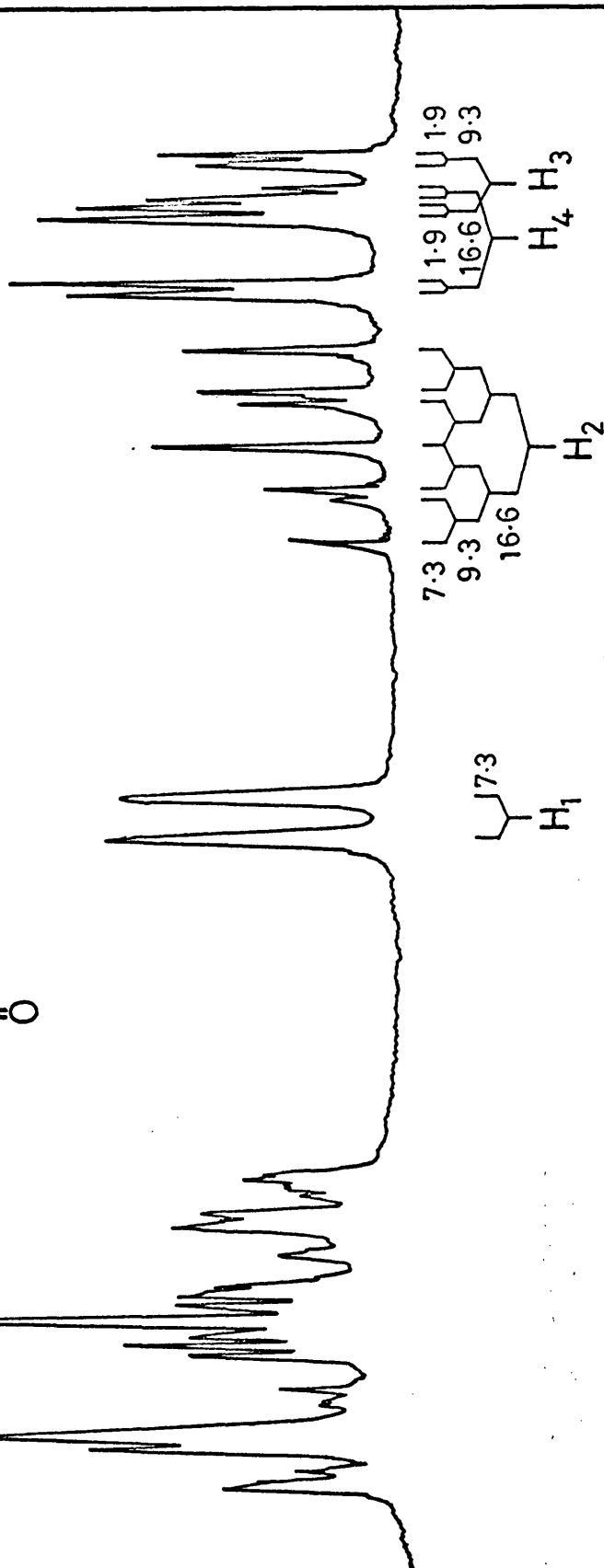
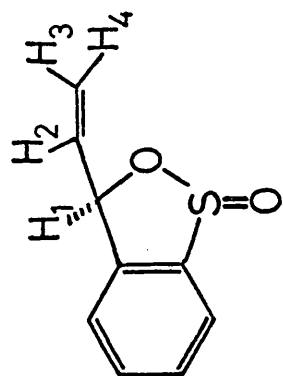
The infrared spectrum of F shows a strong band at 1130 cm^{-1} . This is characteristic of a sulphonate ester.^{94,11b} At 60 MHz, in deuteriochloroform, the n.m.r. spectrum of F shows an aromatic multiplet τ 1.93-2.80 (4H), a one proton doublet τ 3.62 (J 6 Hz), and a three proton multiplet τ 4.17-4.62. This three proton multiplet can however be completely resolved by examining the n.m.r. spectrum at 100 MHz in deuteriobenzene as solvent (fig. 7). The multiplet is shown to be made up of a double doublet of doublets, H_2 , and two doublets of doublets, H_3 and H_4 . INDOR spectroscopy was used to show that the broadness of the doublet, H_1 , is due to a small coupling with the aromatic protons.

On the basis of the above evidence, and the values of the observed coupling constants, F is proposed to be one of the two possible geometric isomers of 3,4-benzo-5-vinyl-1,2-oxathiole 2-oxide (141).



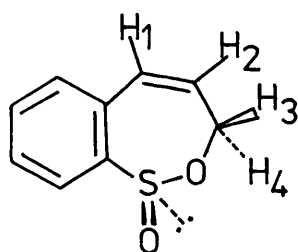
The coupling constants: J_{12} 7.3, J_{24} 16.6, J_{23} 9.3, and J_{34} 1.9 Hz, are all typically those expected from this structure.¹¹⁷ As in the case of cyclic sulfoxides,¹⁰ this molecule would be expected to have a preferential mode of solvation in benzene. The solvent probably co-ordinates to the face of the molecule containing the sulphur lone pair, and thus the benzene anisotropy will shield and deshield each proton to different degrees. The previously complex multiplet is therefore resolved.

Fig 7



Repeated chromatography and distillation of the oil GH did not separate it into its constituent components. The mixture was therefore hydrogenated by stirring an ethanolic solution of GH and 10% palladium-charcoal catalyst under an atmosphere of hydrogen for 12hr. Chromatography of the products gave two further sulphinate esters (as shown by infrared spectroscopy), G(25%) and L (30%). Both yields are quoted with respect to 2H-1-benzothiopyran 1,1-dioxide (93).

The n.m.r. spectrum of G, at 60 MHz in deuteriochloroform, shows an aromatic multiplet τ 2.20-2.90 (4H), a one proton broad doublet that is almost resolved into a doublet of triplets τ 3.53 (J 12 Hz), a one proton doublet of triplets τ 4.10 (J 12 and 3 Hz), and a two proton doublet of doublets τ 5.13 (J 3 and 3 Hz). This evidence, taken with the infrared and mass spectra, suggests that G is 3,4-benzo-7H-1,2-oxathiepin 2-oxide (142).



(142)

(G)

There are two alternative ways of explaining the n.m.r. spectrum of (142).

(i) It must be assumed that protons H_3 and H_4 are accidentally equivalent. (They are potentially non-equivalent because one is cis and the other is trans with respect to the sulphonyl oxygen). The fact that the oxathiepin ring is not planar could explain this accidental equivalence. The coupling constants with H_2 and H_1 must then be assumed to be equal (3Hz). This is in fact very nearly true in the

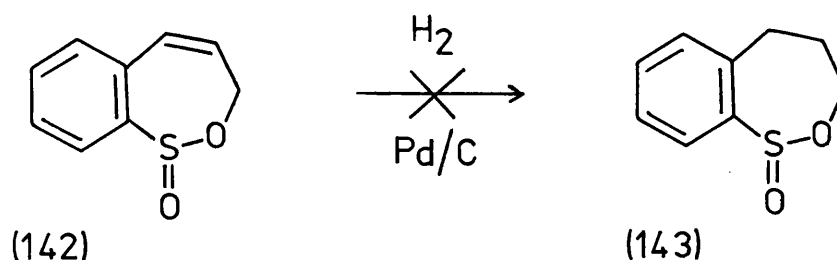
starting material (93) and related compounds, indene and 2H-1-benzopyran.

As required by these assumptions, H_2 exhibits a doublet of triplets (J_{12} 12 Hz, and J_{23} and J_{24} 3 Hz). H_1 gives rise to an almost identical pattern as H_2 , except the expected coupling constant of 3 Hz with H_3 and H_4 cannot be measured due to broadening of the signal, probably caused by a small coupling with the aromatic protons.

(ii) Protons 4,3,2,1 form an ABMX system where the coupling between H_3 and H_4 is very large compared to the chemical shift difference between them, so that only the central bands of the AB system are seen. It must then be considered fortuitous that both H_3 and H_4 show a coupling constant of 3 Hz with H_2 . The structure on the broad doublet due to H_1 must then be wholly explained by a coupling into the aromatic ring, since no allylic coupling to H_3 and H_4 is observed.

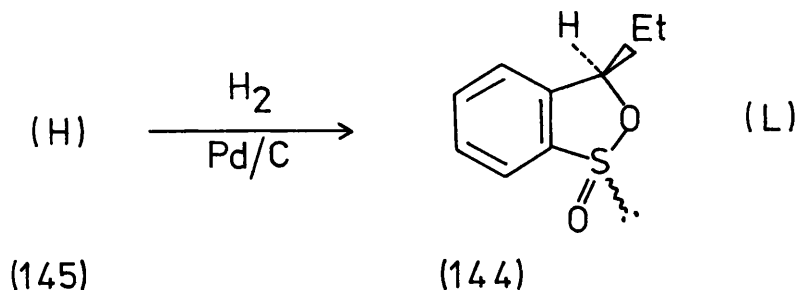
Unfortunately it has not as yet proved possible to prepare (142) by an alternative route, or to undertake decoupling experiments. At present the n.m.r. explanation (i) seems most likely.

It was initially surprising that G (142) was not hydrogenated to the corresponding oxathiepan (143).



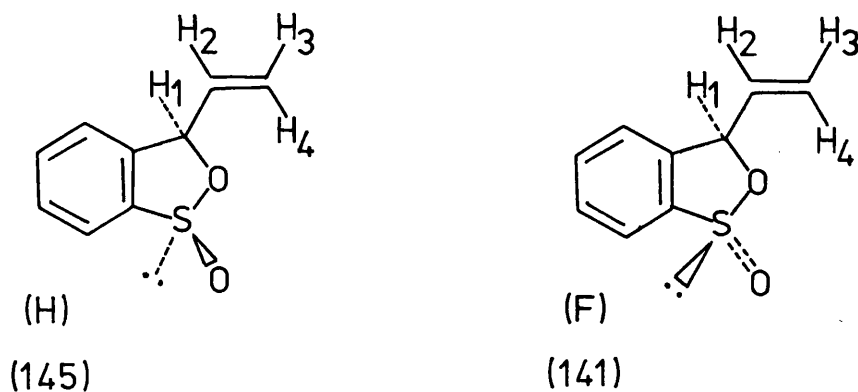
Further experiments under identical conditions showed this to be the general case for sultines having a double bond incorporated in the ring, e.g. 4-phenyl and 4-t-butyl-5H-1,2-oxathiole 2-oxides, and 5,6-benzo-7H-1,2-oxathiepin 2-oxide could not be hydrogenated.

The n.m.r., infrared and mass spectra of oil L are consistent with those expected from 3,4-benzo-5-ethyl-1,2-oxathiole 2-oxide (144).



This product was obviously formed by the hydrogenation of the corresponding 5-vinyl compound, i.e. the second isomer of 3,4-benzo-5-vinyl-1,2-oxathiole 2-oxide, H (145).

By subtracting the n.m.r. spectrum of G from that of the mixture GH it is possible to show that the n.m.r. of H consists of an aromatic multiplet τ 2.17-2.77 (4H), and a four proton multiplet τ 3.90-4.85.

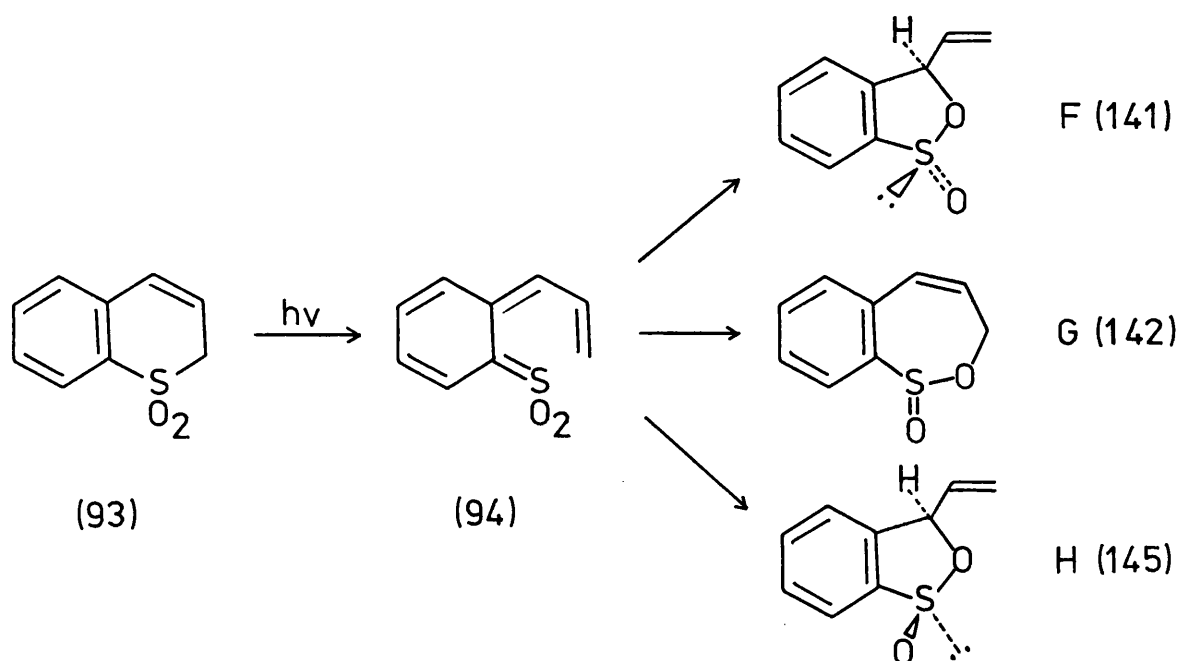


On the basis of work discussed in Chapter One (e.g. refs. 9 and 6), and the work of King,⁹⁴ H_1 in the isomer of 3,4-benzo-5-vinyl-1,2-oxathiole 2-oxide in which H_1 and the sulphonyl oxygen are cis to each other, is expected to be deshielded with respect to H_1 in the isomer where the two groups are mutually trans. H_1 in isomer F (141) exhibits a broad doublet at τ 3.62 while that in isomer H (145) is part of the multiplet τ 3.90-4.85.

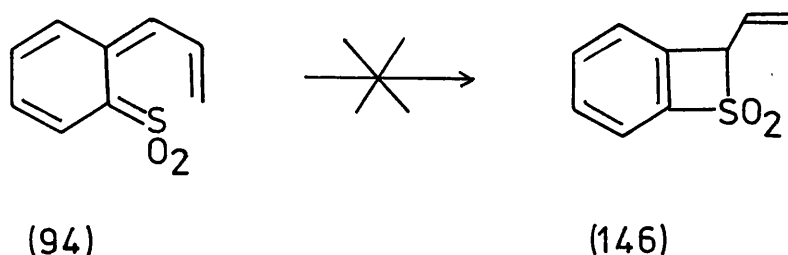
It is therefore reasonably assumed that H₁ and sulphonyl oxygen are cis in isomer F (141) [N.B. thus isomer F (141) is named 3,4-benzo-trans-5-vinyl-1,2-oxathiole r-2-oxide.

Mechanistic Considerations.

It is proposed that the reaction occurs by way of an intermediate sulphene (94). This could be formed by an electrocyclic ring opening process, although presumably the mechanistic details will not be the same as for the corresponding thermally induced ring opening discussed in Chapter Five. Ring closure of the sulphene (94) via an oxygen could give the three observed sulphinate esters.



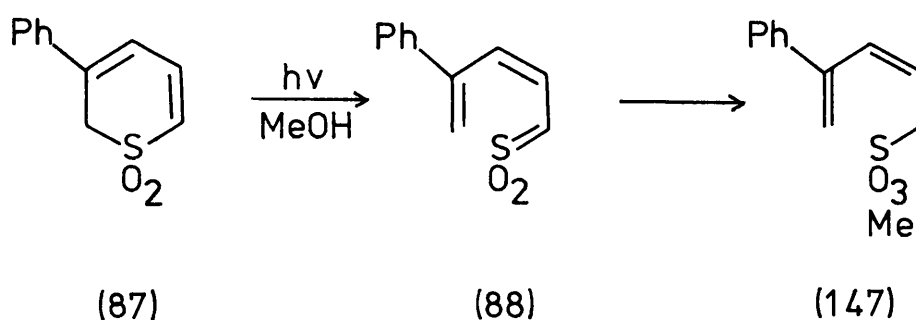
Ring closure of the sulphene (94) via the sulphur to give starting material or the thiete sulphone (146) is either not competitive, or the products are not stable under the reaction conditions.



The small amounts of indene and 2H-1-benzopyran are probably formed by a similar mechanism to that proposed for the thermolysis reaction (See scheme 5 in Chapter Five).

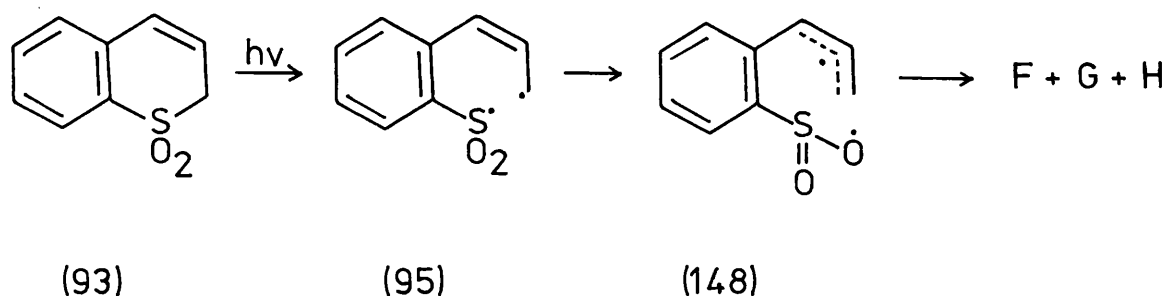
The failure of the solvent methanol to trap the intermediate sulphene (94) is further proof of its previously suggested very short lifetime. Intramolecular rearrangements that directly recover the resonance energy of the aromatic ring are very fast and other intra or intermolecular reactions are not able to compete. As in the thermal reaction, this fact apparently precludes the migration of oxygen to the α -carbon with concomitant loss of sulphur monoxide, although as previously mentioned the small amount of 2H-1-benzopyran formed may be formed by this process.

In a personal communication¹¹⁸ King and Lewars have indicated that preliminary experiments show that a sulphonate ester (147) is obtained on the photolysis of the sulphone (87) in methanol.

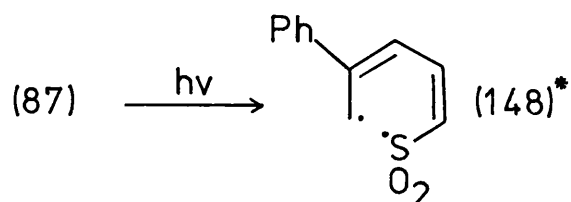


In this case ring closure of the sulphene (88) does not involve a gain in resonance energy. The life time of the sulphene (88) is therefore expected to be longer than that of (94) and it is not surprising that intermolecular reactions, such as trapping by methanol, are in this case able to compete successfully with intramolecular rearrangements.

An alternative mechanistic possibility is that the photolysis of (93) proceeds by initial cleavage of the weakest carbon-sulphur bond to form the biradical (95). This could rearrange to localise a lone electron on an oxygen instead of sulphur. The all carbon part of the biradical (148) is allylic, and therefore ring closure would be expected to give all three of the observed sulphinate esters.



The above process does not require the loss of the aromatic resonance energy and there is therefore no apparent reason why biradical (95) should have a significantly different life time from the biradical (148)*, which would be formed in the corresponding photolysis of (87), and hence why (148)* is trapped by methanol and (95) is not.



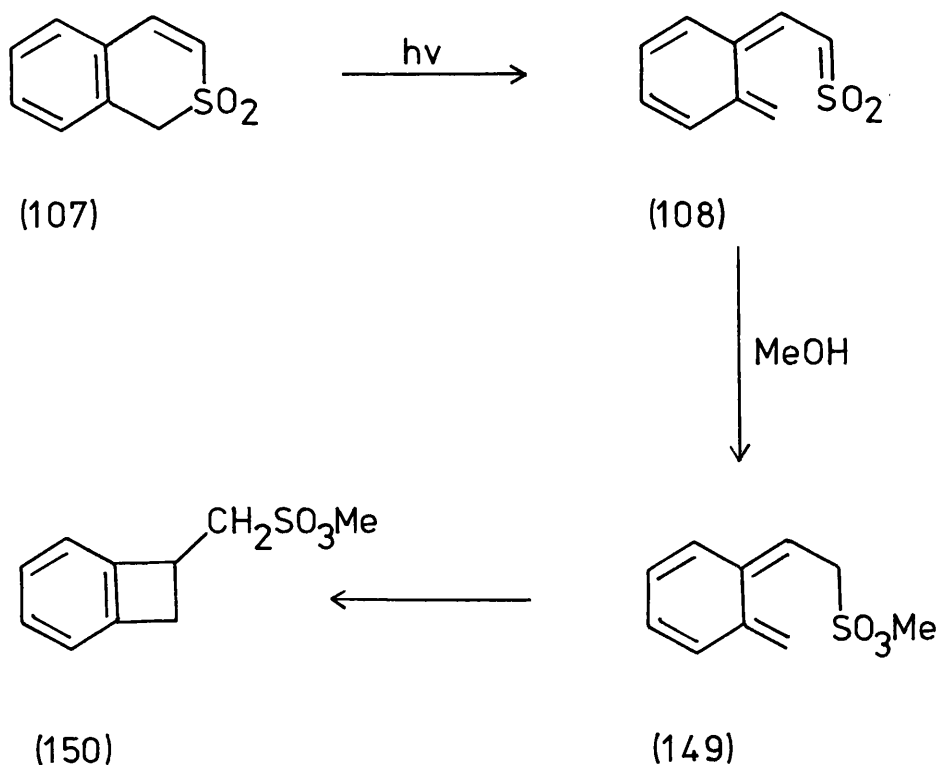
It would therefore seem that the mechanism involving a sulphene intermediate (94) provides the best description of the reaction.

2H-1-Benzothiopyran 1,1-dioxide (93) absorbs light λ_{\max} 259 [ϵ 5400], 294 [ϵ 2600], and 304 [ϵ 1500] nm in acetonitrile. There is no absorption at 350nm at the concentrations used during the photolysis reactions. When irradiations of (93) in acetonitrile or dichloromethane were carried out at 350nm, using benzophenone as a triplet sensitiser (equal concentrations of donor and acceptor), the same products, in the same yields as in the unsensitised reaction, were obtained. This was also the case when cis/trans-1,3-pentadiene (concentration of donor to acceptor 1:2.5) was used as a triplet quencher, with irradiation at 253nm. No kinetic studies have yet been undertaken, but these preliminary results suggest that the reaction is occurring from both the singlet and the triplet excited states.

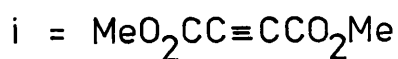
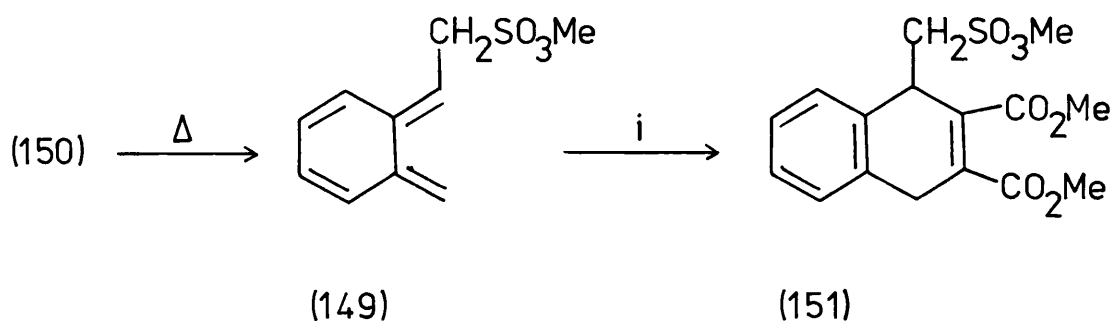
6.3 The Photolysis of 1H-2-Benzothiopyran 2,2-Dioxide.

Irradiation of this molecule (107) in methanol, with light of wavelength 253nm, did give an addition product (75%). This was originally thought to be the benzocyclobutene derivative (150), which could arise by trapping of the initially generated sulphene (108) with methanol, followed by ring closure of the resulting o-quinoid system (149).

The n.m.r. spectrum of the addition product, at 60 MHz in deuteriochloroform, shows a complex multiplet τ 5.23-6.67 (5H) which, when one considers that the exocyclic methylene group is adjacent to a potentially asymmetric centre, is not inconsistent with the structure (150).¹¹⁹

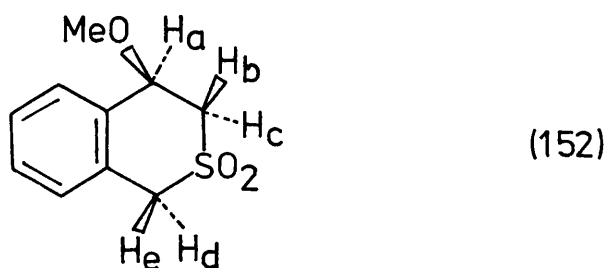


Photolysis of the sulphone (107) in a mixture of methanol and dimethyl acetylenedicarboxylate or maleic anhydride failed to trap the o-quinoid species (149).¹²⁰ There was also no reaction when the addition product was heated at 150° in neat dimethyl acetylenedicarboxylate. By analogy with the work of Jones,¹²¹ the o-quinoid species (149) should be generated by a thermally induced electrocyclic ring opening, and then undergo a Diels Alder addition with the acetylene to give (151).



Investigation of the n.m.r. spectrum of the addition product, in deuteriobenzene at 100 MHz, enabled the five proton multiplet to be completely resolved.

This spectrum (fig. 8) led to a reassignment of the structure to 4-methoxy-isothiochroman 2,2-dioxide (152).

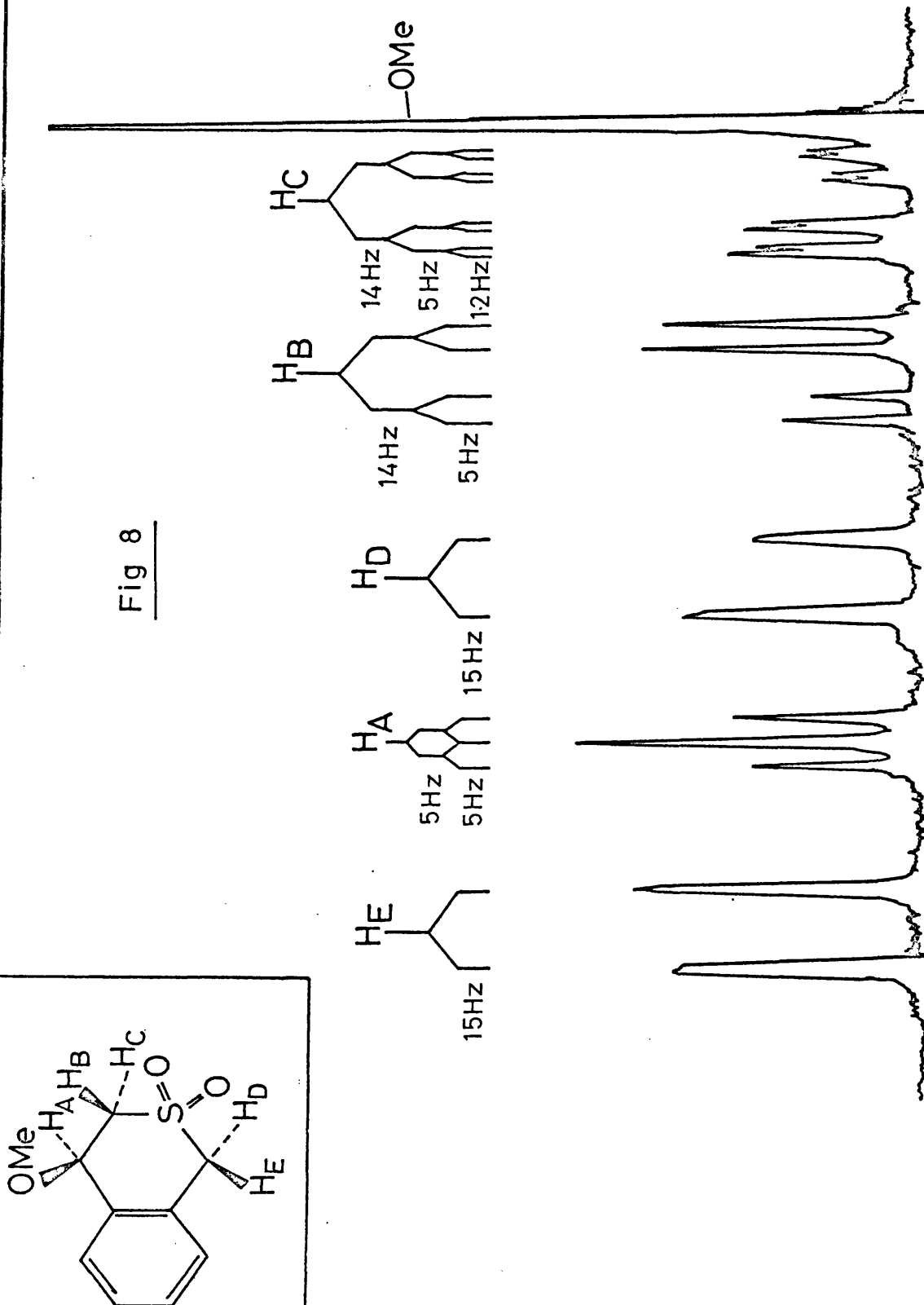


H_A is coupled to H_B and H_C to give a doublet of doublets (the central lines overlap and the signal is observed as a triplet). H_B likewise gives rise to a doublet of doublets. H_C however shows an extra coupling of 1.2 Hz. Decoupling experiments show that this coupling is with H_D . (Irradiation of H_D only causes its collapse). H_D itself exhibits a broad doublet due to coupling with H_E . The broadening is caused by the coupling of H_D with H_C and by a small interaction with the aromatic protons. This interaction also causes broadening of the doublet due to H_E , and it is demonstrated by INDOR experiments.

The spin-spin interaction between H_C and H_D presumably results from the planar W-arrangement of the intervening sigma-bonds.¹⁶ This is a rare example of coupling through a sulphone group.^{16d}

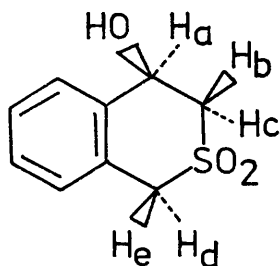
Further evidence for structure (152) comes from its infrared spectrum. The observed sulphur-oxygen stretching frequencies (symmetrical 1119, and asymmetrical 1314 cm^{-1}) are of much lower frequency than those expected for

Fig 8



low field half of its respective AB system.^{6,9,94}

When the photolysis (253 nm) of (107) was carried out in acetonitrile-water (3:1) as solvent the only product was 4-hydroxy-isothiochroman 2,2-dioxide (153).



(153)

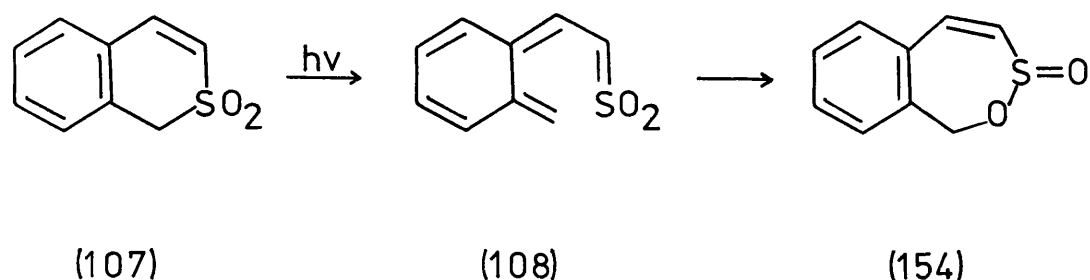
Unlike the corresponding 4-methoxy derivative (152), this molecule does not exhibit any coupling between H_C and H_D . This is presumably because of a slight change in the ring geometry which means that the sigma-bonds between H_C and H_D no longer occupy a planar configuration.

When acetonitrile-diethylamine was used as solvent in the photolysis reaction, no addition product was obtained. When neat acetonitrile was used as solvent the only products were the oxathiepin (154) (20%) and a high molecular weight compound, the n.m.r. spectrum of which suggested it was dimeric starting material.

Control experiments showed that there is no reaction between (107) and either water or methanol in the dark.

Mechanistic Considerations.

The photolysis of 1H-2-benzothiopyran 2,2-dioxide (107) can presumably involve electrocyclic ring opening to give the unsaturated sulphene (108). This can then ring close via an oxygen to give the oxathiepin (154). Unlike the case for sulphene (94) only one sulphinate ester is expected from this reaction.

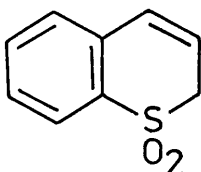


As previously described (Section 5.4) oxygen migration from sulphur to the α -carbon in sulphene (108) would be expected to give 1H-2-benzopyran or the aldehyde (116). Since neither of these products is obtained it is assumed that oxygen migration does not occur. Also as before, generation of this sulphene (108) involves the loss of the aromatic resonance energy. The sulphene is therefore expected to have a very short life time and it is not surprising that it is not trapped by methanol to give a sulphonate ester.

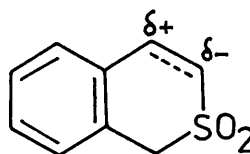
When methanol or acetonitrile-water is used as solvent the formation of sulphene (108) is not very competitive with photoaddition. The photoaddition of methanol to double bonds constrained in a six-membered ring has been explained in terms of facile photoprotonation of the trans-olefin.¹²² There is abundant evidence to suggest that a trans-substituted double bond can be generated in a six or seven-membered ring by a photochemical process involving either the singlet or the triplet excited states.^{122,123} This highly strained system is then very prone to protonation.

It seems unlikely that this is the operative mechanism in the case of (107) since relief of ring strain in the trans-olefin, if it were generated, could easily be attained by ring opening to form the sulphene (108), and there is no apparent reason why 2H-1-benzothiopyran 1,1-dioxide (93) should not also undergo a similar sort of photoaddition.

It is more probable that direct ionic addition to the cis-olefin is involved. A consideration of the ground states of (93) and (107) suggests that the double bond in (107) is more dipolar in nature than that in (93).



(93)

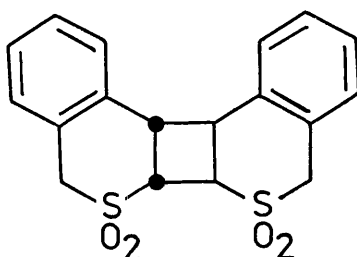


(107)

The negative end of the dipole is stabilised by the sulphonyl group and the positive end by the aromatic system. The lower olefinic bond order in (107) is reflected by a red shift in the ultra-violet spectrum (table 1, below). It is reasonable to assume that the dipolar character of the olefin in (107) is accentuated in the excited state, and hence (107) undergoes ionic addition of water or methanol and (93) does not.

The rate of photoaddition depends on the acidity of the solvent. Thus when acetonitrile-water is used only the addition product is obtained, when methanol is used ring opening to give the sulphene (94) competes to some degree (75% addition product, 10% oxathiepin), and when diethylamine is used no addition product is obtained.

An acetonitrile solution of (107) absorbs light λ_{\max} 271nm. At the concentrations used in the photolysis experiments there is no absorption at 350nm. When the photolysis was carried out using benzophenone or xanthone as a triplet sensitiser (equal concentrations of donor and acceptor) with irradiation at 350nm, a 90% yield of a $2\pi + 2\pi$ dimer was formed. The n.m.r. spectrum suggests that only the cis-dimer (155) was formed.

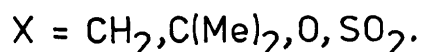
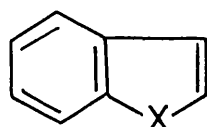


(155)

No oxathiepin (154) was obtained.

When cis/trans-1,3-pentadiene was used as a triplet quencher, with irradiation at 253nm, numerous products were obtained, probably the result of addition reactions.

The photodimerisation of compounds of the general formula (156) has been reported to proceed only in the presence of triplet sensitisers.¹²⁴ Harpp¹²⁵ has shown that when $X = SO_2$ dimerisation occurs on direct irradiation, the mechanism is still however via the triplet state.

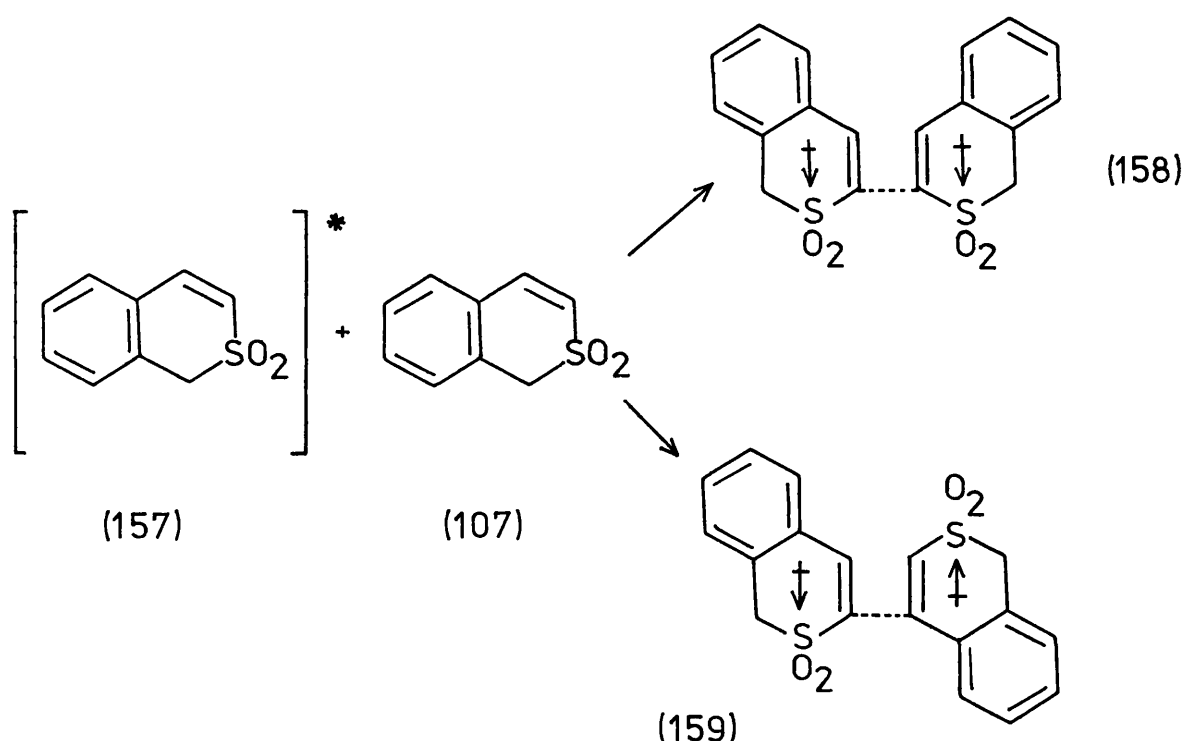


(156)

The ratio of cis to trans dimers was observed to vary with the polarity of the solvent. This fact can be explained by proposing attack of a triplet excited molecule on a ground state one to give an intermediate or a transition state. That intermediate leading to the cis-dimer is more polar than that leading to the trans-dimer. The more polar solvents therefore favour the cis-dimer.

The same mechanism probably applies to the photodimerisation of (107). Attack of the triplet excited state molecule (157) on a ground

state one (107) can give either (158) or (159). The expected dipole moments of the two molecules in (158) are additive while those in (159) tend to negate one another. More polar solvents would therefore be expected to favour (158) over (159) and hence the cis-dimer over the trans.



Thianaphthene 1,1-dioxide was also shown to undergo $2\pi + 2\pi$ additions with other olefins,¹²⁶ and again the mechanism is via the triplet state. Although it has not yet been fully investigated this is probably what happened when cis/trans-1,3-pentadiene was used as an attempted triplet quencher during the photolysis of (107).

The photolytic addition reactions of thianaphthene 1,1-dioxide and 1H-2-benzothiopyran 2,2-dioxide are obviously very similar. This is not surprising due to their very similar structures. One important difference however was found during an investigation of Harpp's experiments in methanol as solvent. Irradiation of a solution of thianaphthene 1,1-dioxide in

methanol at 253nm did not give any methanol addition product, but a 95% yield of the cis-dimer.

This could perhaps be taken as evidence that (107) adds methanol via the highly strained trans-olefin, since cis-trans isomerisation is not thought to be possible in a five-membered ring.¹²² If this is the case then the difference in reaction between (107) and (93) must be explained either by different ring geometries, putting different demands on the formation of the trans-olefin, or by an unfavourable competition with an alternative process in (93).

Alternatively the smaller ring size in thianaphthene 1,1-dioxide could mean that there is less conjugation through the double bond, i.e. less stabilisation of a dipolar olefin is possible. This is not immediately obvious from the ultra-violet spectrum of thianaphthene 1,1-dioxide which consists of a very broad absorption λ_{max} (methanol) 304nm [ϵ , 2080].

The ultra-violet and emission spectra of 3-phenylthiete 1,1-dioxide and 2H-1-benzothiopyran 1,1-dioxide are very similar. This is in line with their related structures and with their apparently similar reaction on initial irradiation (i.e. sulphene formation). The variation in the spectral data for 1H-2-benzothiopyran 2,2-dioxide however, especially the lower triplet energy and lack of fluorescence, reflects the different mode and/or rates of its photochemical reactions.

Preliminary flash photolysis experiments on degassed solutions of 3-phenylthiete 1,1-dioxide in methanol or acetonitrile failed to detect any intermediate with an ultra-violet absorption above 310nm. A photolytic flash, operated from a 10 μ f rapid discharge condenser, was followed by a spectral flash with delay times ranging from 2 μ s to 50ms,

TABLE ONE

COMPOUND	U.V. SPECTRUM	FLUORESCENCE		PHOSPHORESCENCE	
	$\lambda_{\max}[\epsilon]$	$\lambda_{\max}[\Phi_F]$	Onset[E _T]	$\lambda_{\max}[E_T]$	
3-Phenylthiete 1,1-Dioxide	262 [23,000]	355 [0.026]	378 [75.6]	417 [68.6]	
2H-1-Benzothiopyran 1,1-Dioxide	259 [5400] 294 [2600] 304 [1500]	353 [0.021]	373 [76.6]	418 [68.4]	
1H-2-Benzothiopyran 2,2-Dioxide	271 [10,800]	[0]	390 [73.3]	463 [61.7]	

All spectral data quoted are for solutions in ethanol, and wavelengths are in nanometers. Quantum yields of fluorescence (ϕ_F) were measured relative to 1-methyl naphthalene,¹²⁷ all solutions having an optical density of 0.1 at 295nm. Phosphorescence measurements were made in an ethanol glass at -196°. Triplet energies (E_T) are quoted in kcal/mole. λ_{\max} for fluorescence and phosphorescence did not vary with the exciting wavelength in the range 290-310nm.

but no intermediates were observed. Solution strengths ranged from 10^{-5} to 10^{-2} molar, and it is probable that any intermediate sulphene was not formed in sufficient concentration to be observed. Further experiments should therefore be carried out on stronger solutions.

6.4 Conclusion.

Photochemical ring opening of (93) and (107) probably involves the formation of unsaturated sulphenes (94) and (108). These sulphenes must have very short life times because they cannot be trapped by methanol and no evidence for the migration of oxygen to the α -carbon is found. Sulphene formation is apparently through both the singlet and the triplet excited states.

Photoaddition reactions of (107) with protic solvents, and triplet sensitised photodimerisation, compete favourably with sulphene formation. The reasons for the variation in the photochemistry of (93) and (107) have been discussed.

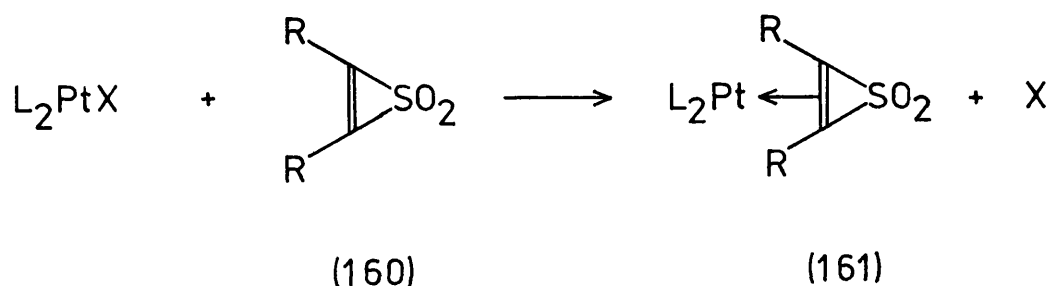
CHAPTER SEVEN

SOME ORGANOPLATINUM CHEMISTRY OF SULPHONYL-CONTAINING MOLECULES.

7.1 Introduction.

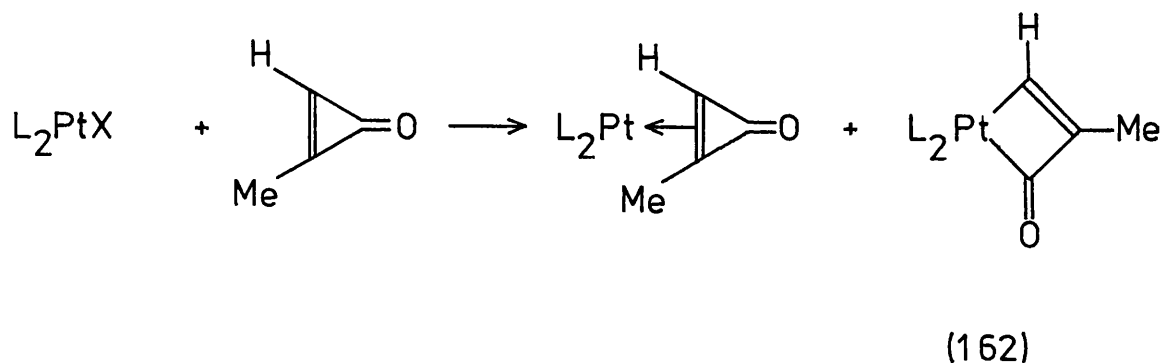
The co-ordination of reactive intermediates or products to transition metals is now a recognised way of increasing their stability. Thus carbenes,¹²⁸ cyclobutadienes,¹²⁹ trimethylene,¹³⁰ cyclopropenes,¹³¹ and vinyl ketenes,¹³² have all been obtained as stable transition metal complexes. It was hoped that a stable adduct between a sulphene and a platinum complex could be prepared.

Visser¹³³ has prepared a number of complexes between thiiren 1,1-dioxides (160) and zerovalent platinum and palladium by ligand exchange reactions. Complexes of the general formula L_2PtX and PdL_4 (where L = triphenylphosphine and X = triphenylphosphine, ethylene or carbon disulphide) undergo ready reaction at ambient temperature in chloroform or toluene as solvent.



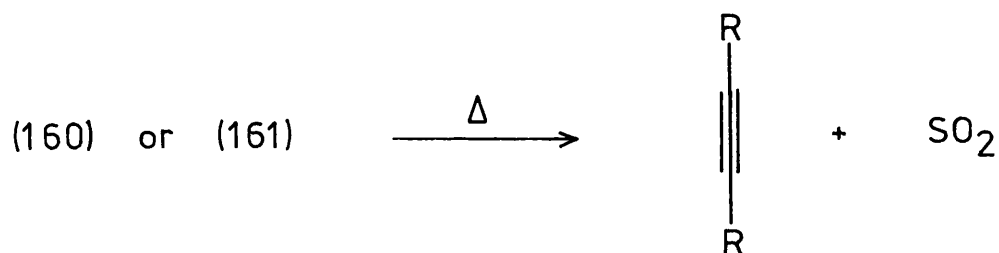
The structure of the resulting complexes (161) was determined by n.m.r. and infrared spectroscopy.

Cyclopropanones undergo similar reactions,¹³⁴ but in this case a ring opened product (162) is also formed.



Both of these structures have been established by X-ray crystallography.

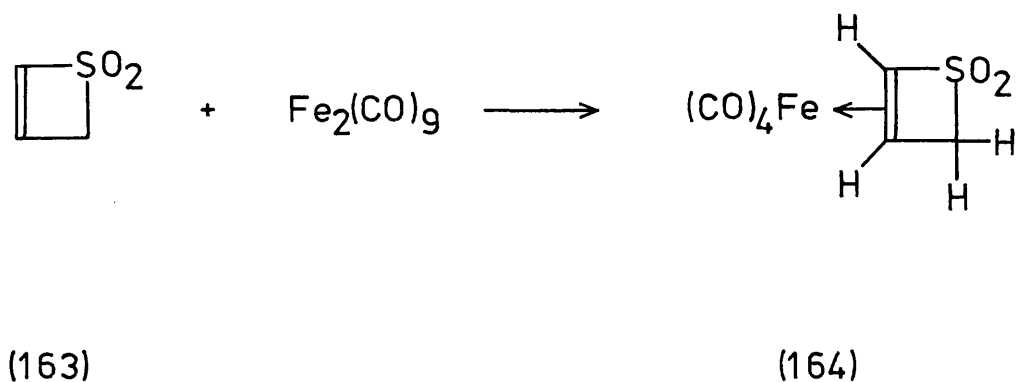
Thermolysis of both the unco-ordinated thiiren 1,1-dioxides (160) and their complexes (161), in the solid state or in solution, yields an acetylene and sulphur dioxide.¹³³



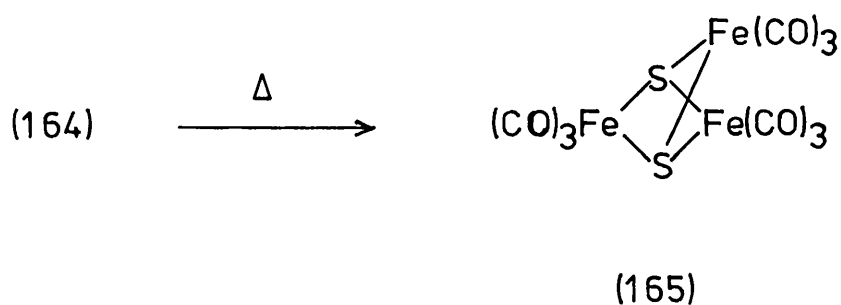
Thus in this case complexing does not fundamentally alter the course of the thermolysis of (160).

Dittmer¹³⁴ has prepared a complex between thiete 1,1-dioxide (163) and iron tetracarbonyl. On the basis of n.m.r. and infrared spectroscopy he has assigned the structure (164).

4-Phenyl-2H-thiete 1,1-dioxide does not give an adduct under similar conditions.



Thermolysis of the complex (164), in the liquid state, led to low yields of the tricyclic complex (165). The product (165) was obtained in higher yield (20%) when equimolar amounts of (164) and thiete 1,1-dioxide were refluxed together in hexane solution. This suggests that an intermediate complex containing two moles of (163) is involved in the reaction.



7.2 Olefin Complexes of Zerovalent Platinum.

A large variety of formally zerovalent platinum-olefin complexes of the type $\text{Pt}(\text{olefin})(\text{PR}_3)_2$ are now known.¹³⁵ X-ray crystallographic data for all of the complexes studied so far show that there is an approximate square planar arrangement of ligands about the metal.¹³⁵

Calculations have shown this to be a more stable arrangement than

a system where the olefin sits perpendicular to the plane containing the platinum and the other ligands.¹³⁶

The bonding in platinum (0) olefin complexes can be explained by the Chatt-Dewar model,¹³⁷ formally used for silver(I) and platinum(II) olefin complexes. In this scheme it is considered that transfer of charge from a filled $2p\pi_z$ molecular orbital of the olefin to a vacant orbital on the metal, and back donation of charge from filled non-bonding d-orbitals of the metal to empty anti-bonding $2p\pi_z^*$ orbitals of the olefin, occurs (fig. 9).

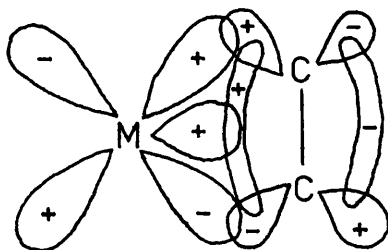


fig. 9

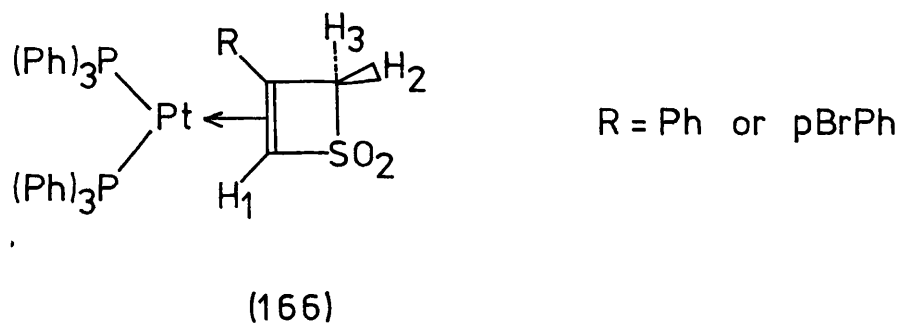
However, since the nodal plane of the $2p\pi$ orbital of the olefin is not a symmetry plane of the molecule, there will be some mixing of the $\sigma 2s$ and $2p\pi$ orbitals, which will result in a rehybridisation of the olefinic carbon atoms so that their s and p character will approach that observed in cyclopropane. Thus on co-ordination double bond character in the olefin is lost and the geometry and the properties of the olefin are expected to approach those of its saturated counterpart. This fact is demonstrated by Visser's¹³³ observation that the thermal stability of (161) is approximately the same as that of thiiran 1,1-dioxide.

Complexes with 3-Substituted Thiete 1,1-Dioxides.

Complexes of 3-phenyl and 3-p-bromophenylthiete 1,1-dioxides were

prepared by ligand displacement from trans-stilbenebis(triphenylphosphine)-platinum¹³⁸ at room temperature in ether solution, trans-stilbene being the displaced ligand. 3-t-Butylthiete 1,1-dioxide did not form a complex under these conditions, probably for steric reasons.

The n.m.r. spectrum of both thiete 1,1-dioxide complexes (166) reveals that on complexing the olefinic proton undergoes a large upfield shift (~ 2.5 p.p.m.). This large shielding is very good evidence for the formation of a π -complex (166).



Such large shifts are not observed for ring opened complexes such as that obtained with the cyclopropanone (162). The methylene protons (H_2 and H_3) exhibit very little shielding ($\sim 0.3 - 0.5$ p.p.m.) on complexing.

The angle between the square plane containing the platinum and its ligands and that containing the thiete ring is expected, in the ideal case, to be approximately 90° , hence the methylene protons (H_2 and H_3) should be non-equivalent (i.e. cis or trans with respect to the platinum). In both complexes (166) they are in fact observed to be equivalent. This accidental equivalence could be explained by a dihedral angle, between the two planes, of substantially larger than the expected 90° . It is probable that the thiete ring is not in fact planar, hence the dihedral between the two 'planes' need not be as great as 180° .

When R = phenyl in complex (166), H_1 exhibits coupling to both of the phosphorus atoms and to the platinum. Platinum-195 has a spin of one half and a natural abundance of 33.8%. The signal due to H_1 is therefore observed as three doublets of doublets in the ratio 1:4:1. (In the Experimental section this type of signal is described as a tdd, J_{PH} 9.8 and 4 Hz, J_{PtH} 40 Hz). The larger phosphorus coupling is expected from that which is trans to H_1 .¹³⁹ The methylene protons are coupled to platinum and only one phosphorus, again probably the one that is trans. When R = p-bromophenyl the only variation in the coupling pattern is a second, very much smaller, methylene-phosphorus coupling (i.e. to the cis phosphorus).

The asymmetrical sulphur-oxygen stretching frequency undergoes a shift to lower energy on complexation, but a very much larger shift of both the asymmetrical and the symmetrical stretching frequencies would be expected if the platinum were directly co-ordinated to sulphur.^{140,141} (Table Two) (See also Section 7.3).

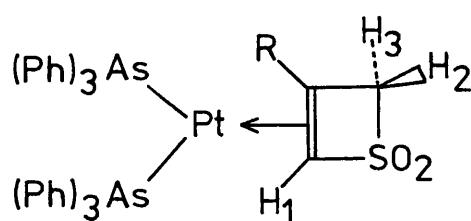
TABLE TWO

	<u>Sulphur-Oxygen Stretching Frequency</u>	
	<u>Symmetrical</u>	<u>Asymmetrical</u>
3- <u>p</u> -Bromophenylthiete 1,1-Dioxide	1130 cm^{-1}	1312 cm^{-1}
Complex (166), R = <u>p</u> BrPh	1132 cm^{-1}	1286 cm^{-1}
3-Phenylthiete 1,1-Dioxide	1130 cm^{-1}	1320 cm^{-1}
Complex (166), R = Ph	1130 cm^{-1}	1276 cm^{-1}
Toluene- <u>p</u> -sulphonyl Chloride	1180 cm^{-1}	1375 cm^{-1}
Toluene- <u>p</u> -sulphonylchlorobis- (triphenylphosphine)platinum(II) ¹⁴¹	1043 cm^{-1}	1205 cm^{-1}

All spectra were run as nujol mulls.

Addition of one mole of tetracyanoethylene to a solution of the complex (166) led to a quantitative recovery of the thiete sulphone. This is further evidence that (166) is a π -complex. Tetracyanoethylene has a larger co-ordinating ability than the thiete sulphones and therefore they are displaced.

Similar π -complexes (167) were obtained when triphenylarsine was the other ligand on platinum.

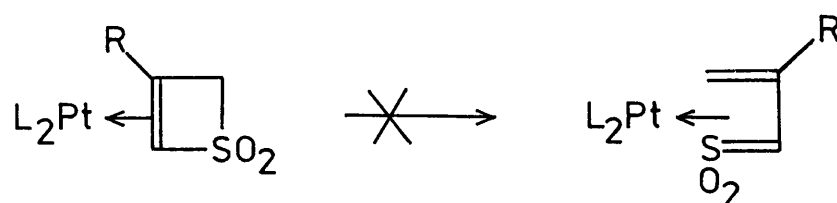


(167)

In this case the two methylene protons (H_2 and H_3) are no longer equivalent. The upfield methylene proton (probably that which is cis to the platinum) exhibits a doublet of doublets (neglecting platinum coupling). The large coupling, 11.8 Hz is with the second methylene proton and the small coupling, 2 Hz is with H_1 . This small coupling is not observed for the low field methylene proton and is probably due to the previously discussed planar W-arrangement of the intervening sigma-bonds. Without further information on the geometry of the complex, and the nature of the bonding to platinum, it is not possible to say whether this is a second example of coupling through a sulphone group. (The W can be drawn in either direction round the ring). This is evidence, however, that the thiete ring is not planar.

It was hoped that, on thermolysis, the thiete sulphone part of

these π -complexes (166) and (167) would behave in a similar manner to the unco-ordinated ligands (Chapter Five). The initially formed vinyl sulphene might form a stable complex with the platinum.



(166) or (167)

The close proximity of the two reactants should overcome the short lifetime of the vinyl sulphene.⁹⁴ Unfortunately none of the complexes is sufficiently volatile for flash thermolysis experiments to be undertaken, and heating them under nitrogen at 300° for 1 - 2hr. led to an uncharacterised black tar.

When a solution of complex (166), R = *p*BrPh, in dichloromethane was irradiated with light of frequency 253nm, a white solid crystallised from solution. Filtration gave a 90% yield of 3-*p*-bromothiote 1,1-dioxide. The inorganic species which remained in solution could not be identified. Recovery of the thiote sulphone was somewhat surprising since it should itself undergo photolysis under these conditions.¹¹⁴

The failure of this experiment to produce a rearranged complex or the expected aldehyde¹¹⁴ could be due to a number of reasons. The main problem is one of solubility. The thiote sulphone is only slightly soluble in solvents in which the complex is soluble.

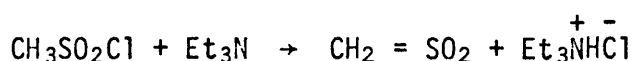
If the photolysis involves an equilibrium between the complex, and bis(triphenylphosphine)platinum and the thiote sulphone, then it will be

drawn over to the right hand side by the crystallisation of the thiete sulphone from solution. It is probable that the small amount of thiete sulphone that remains in solution is not photolysed because the excess of bis(triphenylphosphine)platinum acts as a filter and effectively absorbs all of the light.

This problem should be overcome by using a trialkylphosphine ligand on platinum, and if possible a more polar solvent.

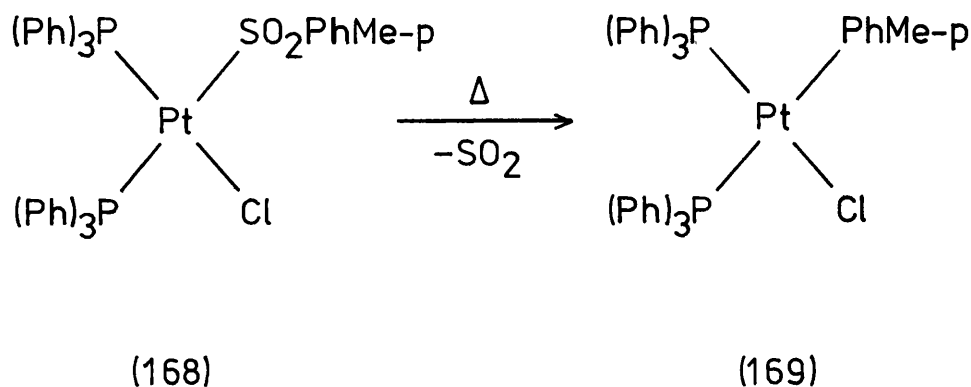
7.3 Platinum(II) - Sulphonyl Chloride Complexes.

Sulphonyl chlorides react with tertiary amines to give sulphenes.¹⁴²



This type of 'saturated' sulphenes has a much longer lifetime than vinyl sulphenes and it is possible to isolate the products of its intermolecular reactions (e.g. page 2). It is not however possible to generate sulphenes by this method in the presence of trans-stilbenebis(triphenylphosphine)platinum, because the sulphonyl chloride itself reacts with the platinum complex.

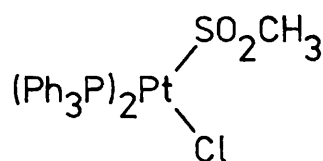
Previous workers¹⁴¹ have shown that toluene-*p*-sulphonyl chloride reacts with a variety of Pt(0) complexes to give the Pt(II) complex (168).



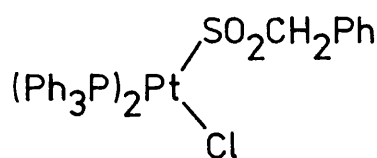
This oxidative addition is presumed to give the cis-isomer.¹⁴¹
On heating sulphur dioxide is evolved and the Pt(II) aryl complex (169) is formed.¹⁴¹

It was hoped that if similar complexes containing α -protons could be prepared they might react with base to eliminate hydrogen chloride and form a stable sulphene complex.

Methane and α -toluene sulphonyl chlorides react rapidly with a benzene solution of trans-stilbenebis(triphenylphosphine)platinum to give complexes which by analogy to Cook's¹⁴¹ work are presumed to be the cis-isomers.



(170)



(171)

The infrared spectra of these complexes show that the bands due to the symmetric and asymmetric stretching modes of the sulphonyl group are displaced to lower frequency by 100 - 150 cm^{-1} on complexing. This is good evidence for the co-ordination of platinum to sulphur.^{140,141}

Sulphonyl absorptions are usually insensitive to conjugative effects.¹¹⁶ The displacement is however probably a reflection of $d\pi - d\pi$ back-bonding from the metal to the sulphur. This would tend to reduce the double bond character of the sulphur-oxygen bonds and hence shift their infrared absorptions to lower energy.

When (170) was heated at 250° for 2hr. under nitrogen, sulphur dioxide was evolved and a high yield of the Pt(II) methyl complex¹⁴¹ was obtained.

Both complexes (170) and (171) were recovered quantitatively after refluxing for two days in dichloromethane containing excess triethylamine. Two possible reasons for the lack of reactivity are:

- (i) The greater strength of the platinum-chlorine bond relative to the sulphur-chlorine bond in the free sulphonyl chloride.
- (ii) The lower acidity of the α -sulphonyl protons in the complexes. This may be caused by the expected $d\pi - d\pi$ back bonding from platinum to sulphur, which would destabilise an adjacent negative charge.

Experiments using the stronger base, butyl-lithium, led to a complex mixture of products. Butyl-lithium is known to react with platinum chlorine bonds to give lithium chloride and a platinum-butyl complex.¹⁴³

7.4 Conclusion.

A number of novel organo-platinum complexes have been prepared and their structures have been determined by a consideration of the infrared and n.m.r. spectra.

Attempts to generate sulphene-metal complexes by rearrangement of the above complexes, induced by thermal, photochemical and chemical means, have not been successful.

EXPERIMENTAL

Instrumentation.

Infrared spectra were recorded on a Perkin-Elmer 237 grating spectrometer. Mass spectra were determined with an A.E.I. MS9 instrument; in each case the molecular ion is given first followed by peaks of structural significance. Ultra-violet spectra were recorded on a Unicam SP 800 spectrophotometer. Emission spectra were obtained using a Baird-Atomic Fluorispec SF 100E. Nuclear magnetic resonance spectra were recorded on a Varian T-60 spectrometer with deuteriochloroform as solvent and tetramethylsilane as internal standard unless otherwise stated; (100 MHz) refers to spectra recorded on a Jeol PS100 instrument. 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 magnesium sulphate and a rotary evaporator was used for reduced pressure solvent removal. All reactions involving air or moisture sensitive reactants or products were carried out under an atmosphere of dry, oxygen free, nitrogen. Light petroleum had a boiling point of 40 - 60°.

Solvents were dried as follows:

Diethyl ether, light petroleum and benzene were stored over sodium wire; when required very dry they were refluxed over, and distilled from, lithium aluminium hydride. Methanol and ethanol were refluxed over, and distilled from, their magnesium alkoxides. Pyridine was refluxed over, and distilled from, potassium hydroxide. Acetonitrile was refluxed over phosphorus pentoxide and fractionally distilled through a four foot column of glass helices.

Small scale distillations were carried out using a Kugelrohr and the boiling points quoted are the oven temperatures at which distillation commenced.

Column chromatography on silica was carried out using Kieselgel 60 PF₂₅₄, supplied by E. Merck for layer chromatography, with the solvent under a slight positive pressure.

Toluene-p-sulphonyl isocyanate was supplied by Fluka AG (Switzerland) and was fractionally distilled before use. Chlorosulphonyl isocyanate was supplied by R.N. Emanuel Ltd. (Wembley) and was distilled from anhydrous potassium carbonate before use. N-Sulphonyl aniline was supplied by R.N. Emanuel Ltd. and was used as received.

CHAPTER ONE

3-Methylthietane 1-Oxides.

3-Methylthietane³ was oxidised by the method of Johnson.⁴

Chromatography on silica and elution with chloroform gave cis-3-methylthietane 1-oxide as a clear oil, τ 6.10-6.43 (2H, m), 6.87-7.32 (2H, m), 7.23-8.13 (1H, m), and 8.74 (3H, d, J 7.5 Hz), and trans-3-methylthietane 1-oxide as a clear oil, τ 6.53-7.20 (1H, m), 6.73 (4H, broad d), and 8.73 (3H, d, J 7.5 Hz).

Equilibration with Hydrogen Chloride.

A solution of hydrogen chloride in anhydrous benzene (0.15M) (0.5ml) was added to a solution of either cis or trans-3-methylthietane 1-oxide (0.1g) in benzene (1ml). The n.m.r. of the solution immediately after mixing showed only sulphoxides (isomer ratio, cis:trans, 85:15). The spectrum did not change over 48hr. The solution was poured into excess water and was extracted with chloroform. Removal of the solvent under reduced pressure gave a clear oil. G.l.c. analysis on a 5ft x 0.15in column of 10% PEG 20M on 100-120 mesh diatomite C at 150° with a nitrogen flow of 50ml/min showed only sulphoxides (cis:trans, 85:15)

Similar experiments using dioxan, aqueous dioxan or benzene, or water as solvent gave the same results.

Preparation of the 3-p-Bromophenylthietane 1-Oxides.

p-Bromo- α -morpholinostyrene.

A mixture of p-bromoacetophenone (80g, 0.4mol), morpholine (52.5g, 0.6mol), toluene-p-sulphonic acid (0.1g), and benzene (250ml) was refluxed

in a water separator until no more water separated (5 days). The solvent was removed under reduced pressure to give p-bromo- α -morpholino-styrene as a yellow oil.

3-Morpholino-3-p-bromophenylthietane 1,1-Dioxide.

Methane sulphonyl chloride (47.6g, 0.4mol) was slowly added to an ice-cooled solution of the crude enamine, above (0.4mol) and triethylamine (41.9g, 0.4mol) in benzene (250ml). The mixture was allowed to warm to room temperature and was stirred overnight. The product was filtered off, washed with water to remove triethylamine hydrochloride, and dried.

3-p-Bromophenylthiete 1,1-Dioxide.

The oxidation of the above crude product and the amine oxide pyrolysis were conducted as described by Johnson⁴ for the preparation of 3-phenylthiete 1,1-dioxide. Recrystallisation of the crude product from ethanol gave 3-p-Bromophenylthiete 1,1-dioxide (62g, 60%) as white crystals. M.p. 228-230° (from ethanol), ν_{max} . (chloroform) 1600, 1312, 1209, 1130, and 785 cm^{-1} , τ 2.47 (2H, d, J 9 Hz), 2.80 (2H, d, J 9 Hz), 3.13 (1H, s), and 5.30 (2H, s), m/e 260, 258, 212, 210, 196, 194, 183, 181, 131, and 115, (Found: C, 41.6; H, 2.75; S, 12.5. $\text{C}_9\text{H}_7\text{BrO}_2\text{S}$ requires C, 41.7; H, 2.7; S, 12.35%).

3-p-Bromophenylthietane 1,1-Dioxide.

Procedure A: The thiete sulphone above (22g, 0.09mol) was added in small portions over 2hr to a mixture of sodium borohydride (15g, 0.4mol) and isopropyl alcohol (50ml) at 60°. The mixture was stirred for 4 days. A further 5gms (0.13mol) of sodium borohydride were added after the first 2 days. The mixture was cooled and made slightly acidic by dropwise

addition of dilute sulphuric acid. The solvent was removed under reduced pressure and the residue was extracted with hot ethyl acetate. Removal of the solvent gave 3-p-Bromophenylthietane 1,1-dioxide (11g, 50%), m.p. 154-155° (from methanol), ν_{max} . (chloroform) 1495, 1325 (s), 1220, 1140 (s), 1015, and 825 cm^{-1} , τ 2.68 (2H, d, J 9 Hz), 3.32 (2H, d, J 9 Hz), and 5.35-6.72 (5H, m), m/e 262, 260, 198, 197, 196, 184, 182, 133, 118, 117, 116, 115, 103, and 102, (Found: C, 41.3; H, 3.5; S, 12.3. $\text{C}_9\text{H}_9\text{BrO}_2\text{S}$ requires C, 41.4; H, 3.45; S, 12.25%).

Procedure B: The thiete sulphone (5g, 0.02mol) and 10% palladium on barium carbonate (1g) were stirred in ethanol (50ml) under an atmosphere of hydrogen overnight. The solution was filtered and the solvent was removed under reduced pressure to give an identical product to the above (4.5g, 90%).

This procedure was also used for the reduction of 3-phenylthiete 1,1-dioxide (yield 95% using 5% catalyst).

3-p-Bromophenylthietane.

3-p-Bromophenylthietane 1,1-dioxide was reduced with lithium aluminium hydride, as described by Johnson⁴ for the preparation of 3-phenylthietane, to give 3-p-Bromophenylthietane (35%).

3-p-Bromophenylthietane 1-Oxides.

A solution of m-chloroperbenzoic acid (1.07g, 5.2mmol) in dichloromethane (30ml) is slowly added to an ice-cooled solution of 3-p-bromophenylthietane (1.1g, 4.8mmol) in dichloromethane (35ml). After 3hr the solution was allowed to warm to room temperature and was filtered. The filtrate was washed with aqueous sodium carbonate. Removal of the solvent under reduced pressure gave a clear oil (1gm). Chromatography on silica (50g)

and elution with ether-methanol (50:1) gave cis-3-p-Bromophenylthietane 1-oxide (0.45g, 38%), m.p. 108-109° (from chloroform-light petroleum) ν_{\max} . (chloroform) 1495, 1142, 1065 (broad), 1012, and 820 cm^{-1} , ν_{\max} . (nujol) 1490, 1138, 1060 (b), 1012, and 823 cm^{-1} , τ 2.63 (2H, d, J 8.5 Hz), 3.02 (2H, d, J 8.5 Hz), and 6.00-6.83 (5H, m), m/e 246, 244, 197, 195, 184, 182, 171, 169, 117, 116, 115, 103, and 77 (Found: C, 43.8; H, 3.65; S, 13.1. $\text{C}_9\text{H}_9\text{BrOS}$ requires C, 44.1; H, 3.65; S, 13.05%) followed by trans-3-p-Bromophenylthietane 1-oxide (0.46g, 39%), m.p. 112-113° (from chloroform-light petroleum), ν_{\max} . (chloroform) 1495, 1095, 1078, 1060 (broad), 1011, and 827 cm^{-1} , ν_{\max} . (nujol) 1495, 1095, 1075, 1059 (b), 1010, and 790 cm^{-1} , τ 2.65 (2H, d, J 8.5 Hz), 3.02 (2H, d, J 8.5 Hz), 5.38-5.93 (1H, m), and 6.45 (4H, d, J 6 Hz), m/e 246, 244, 230, 228, 197, 195, 184, 182, 171, 169, 117, 116, 115, 103, 102, 91, and 77, (Found: C, 44.35; H, 3.8%).

CHAPTER TWOcis-3-Methylthietane r-1-Oxide 1-N-(Toluene-p-sulphonyl)imide.

cis-Sulphoxide (7) (0.46g, 4.3mmol), toluene-p-sulphonyl azide (1.75g, 8.9mmol), and freshly precipitated copper (0.6g, 9.4mmol) were refluxed in methanol (15ml) for 1hr. A further 0.85g (4.3mmol) of azide and 0.5g (7.9mmol) of copper were then added and the mixture was refluxed overnight. The hot solution was filtered and the green residue was extracted repeatedly with hot chloroform. The extracts were combined and the solvent was removed under reduced pressure to give a light green oil. Chromatography on silica (100g), and elution with ether, gave, as the major products: toluene-p-sulphonamide (2.1g), and cis-3-Methylthietane r-1-oxide 1-N-(toluene-p-sulphonyl)imide (0.72g, 69%), m.p. 125-126° (from chloroform-light petroleum), ν_{max} . (nujol) 1315, 1250, 1150, and 1040 cm^{-1} , τ 2.10 (2H, d, \underline{J} 9 Hz), 2.67 (2H, d, \underline{J} 9 Hz), 5.03-5.53 (2H, m), 5.87-6.37 (2H, m), 6.72-7.37 (1H, m), 7.60 (3H, s), and 8.60 (3H, d, \underline{J} 7 Hz), m/e 273, 155, and 91, (Found: C, 48.4; H, 5.65; N, 5.1. $\text{C}_{11}\text{H}_{15}\text{NO}_3\text{S}$ requires C, 48.3; H, 5.5; N, 5.15%).

trans-3-Methylthietane r-1-Oxide 1-N-(Toluene-p-sulphonyl)imide.

trans-Sulphoxide (7) (0.18g, 1.7mmol), toluene-p-sulphonyl azide (0.68g, 3.4mmol), and freshly precipitated copper (0.22g, 3.5mmol) were refluxed in methanol (10ml) for 1hr. A further 0.35g (1.8mmol) of azide and 0.22g (3.5mmol) of copper were then added and the mixture was refluxed overnight. An identical work up to the one above gave trans-3-Methylthietane r-1-oxide 1-N-(toluene-p-sulphonyl)imide (0.17g, 37%), m.p. 114-115° (from chloroform-light petroleum), ν_{max} . (nujol) 1315, 1245, 1157, 1072, and 1030 cm^{-1} , τ 2.05 (2H, d, \underline{J} 9 Hz), 2.65 (2H, d, \underline{J} 9 Hz), 5.40-5.80 (4H, m),

6.67-7.33 (1H, m), 7.58 (3H, s), and 8.53 (3H, d, \underline{J} 7 Hz), m/e 273, 155 and 91, (Found: C, 48.4; H, 5.7; N, 4.9%).

3-Phenylthietane 1-oxide was recovered quantitatively from a reaction with toluene-p-sulphonyl azide under the same conditions.

3-Methylthietane 1-N-(Toluene-p-sulphonyl)imide (8).

A solution of 3-methylthietane (1.0g, 11.4mmol) in absolute ethanol (12ml) was added to a stirred solution of anhydrous chloramine-T (2.7g, 11.8mmol) in absolute ethanol (80ml). Sodium chloride was slowly precipitated. After 20hr the solution was filtered and the solvent was removed under reduced pressure. The sticky solid which remained was extracted with dichloromethane and the undissolved sodium chloride was again filtered off. Removal of the solvent under reduced pressure gave 3-Methylthietane-1-N-(toluene-p-sulphonyl)imide (2.95g, 101%), ν_{\max} . (nujol) 1287, 1140, 1090, 1030, 975 (broad), 825, 747, and 658 cm^{-1} , τ 2.13 (2H, d, \underline{J} 9 Hz), 2.65 (2H, d, \underline{J} 9 Hz), 5.87-7.00 (4H, m), 7.00-8.00 (1H, m), 7.62 (3H, s), and 8.77 (3H, broad d, \underline{J} 6.5 Hz), m/e 257, 155, 139, 102, 91, and 88, as a mixture of isomers.

Repeated chromatography on silica and elution with ethyl acetate or chloroform did not separate the above mixture.

Oxidation of 3-Methylthietane 1-N-(Toluene-p-sulphonyl)imide (8).

Anhydrous sodium carbonate (0.70g, 6.6mmol), and m-chloroperbenzoic acid (1.44g, 8.3mmol) were added in one portion to an ice-cooled solution of the imide (8) (0.42g, 1.64mmol) in acetone (60ml). The suspension was allowed to warm to room temperature and was stirred for 18hr. The mixture was tipped into excess dilute aqueous sodium metabisulphite, and was extracted with dichloromethane. The solvent was removed under reduced

pressure to give a clear oil (0.41g). Chromatography on silica (30g) and elution with ether gave cis-3-methylthietane r-1-oxide 1-N-(toluene-p-sulphonyl)imide (0.03g, 6%), m.p. and mixed m.p. 125-126°, and trans-3-methylthietane r-1-oxide 1-N-(toluene-p-sulphonyl)imide (0.18g, 40%), m.p. and mixed m.p. 114-115°. Further elution with ethyl acetate gave starting material (8) (0.20g, 48%).

Hydrolysis of 3-Methylthietane 1-N-(Toluene-p-sulphonyl)imide.

The sulphimide (3.5g, 13.6mmol) was dissolved in an ice-cooled saturated solution of potassium hydroxide in methanol (100ml). The solution was stirred at room temperature for 20hr, and was then re-cooled and carefully neutralised with dilute sulphuric acid. Extraction with dichloromethane, washing of the organic layer with water, and removal of the solvent at reduced pressure gave a clear oil (3.3g). Chromatography on alumina (120g) and elution with ether-light petroleum (1:4) gave 2-Methoxy-3-methylthietane (19) (1.2g, 75%), b.p. 180°/760mm (with slight decomposition), ν_{max} . (film) 1115 cm^{-1} , τ 6.72 (1H, d, \underline{J} 5 Hz), 6.72 (3H, s), 6.95-8.23 (3H, m), and 9.05 (3H, d, \underline{J} 7 Hz), m/e 118 and 87. Satisfactory analysis could not be obtained owing to the instability of the compound.

Oxidation of 2-Methoxy-3-methylthietane.

A solution of the thietane (19) (0.25g, 2.1mmol) in hydrogen peroxide (30%, 5ml) and glacial acetic acid (1ml) was stirred at 45° overnight. The solution was poured into excess water and was extracted with dichloromethane. The organic fractions were washed with 5% aqueous sodium hydroxide and with water. Removal of the solvent under reduced pressure gave 3-methylthietane 1,1-dioxide (0.25g, 98%).⁴

Reaction of the 3-Methylthietane 1-Oxides (7) with Toluene-p-sulphonyl Isocyanate.

A solution of the isocyanate (0.83g, 4.2mmol) in benzene (10ml) was slowly added to a solution of the cis-sulphoxide (0.22g, 2.1mmol) in benzene (5ml). The reaction was monitored by n.m.r. spectrometry and on its completion excess isocyanate was neutralised with water. Removal of the solvent under reduced pressure gave a clear oil. Chromatography on silica (40g) and elution with ethyl acetate gave toluene-p-sulphonamide and 3-methylthietane 1-N-(toluene-p-sulphonyl)imide (8) (0.5g, 93%) as a mixture of isomers. Oxidation of these sulphimides as previously described gave a mixture of the sulfoximides (9) (cis:trans, 16:84). Alternatively the crude reaction mixture (before neutralisation of excess isocyanate) was directly oxidised. This procedure gave, within experimental error ($\pm 2\%$), an identical result.

When the reaction was carried out in acetonitrile at -40° , chloroform or dichloromethane at room temperature, or when trans-sulphoxide (7) was used as starting material, both of these procedures again gave the same result.

When pyridine was used as solvent there was no reaction.

Attempted Reaction of the 3-Methylthietane 1-Oxides with N-Sulphonyl-sulphonamide.

A solution of cis-3-methylthietane 1-oxide (0.22g, 2.1mmol) and N-sulphonylsulphonamide (TsNSO)⁴⁴ (0.90g, 4.1mmol) in benzene (10ml) was stirred at room temperature for 1 week. The solvent was removed under reduced pressure. The n.m.r. spectrum of the crude oil showed only cis-sulphoxide, TsNSO and a trace of toluene-p-sulphonamide. A similar reaction conducted at 65° for 20 hr gave the same result.

Similar reactions using acetonitrile, chloroform or pyridine as solvent, or N,N'-bis(toluene-p-sulphonyl)sulphur diimide, N-sulphonyl aniline or p-tolyl isocyanate instead of TsNSO, also gave the same result. Use of trans-sulphoxide as starting material gave trans-sulphoxide as the only product.

Reaction of the 3-Phenylthietane 1-Oxides with Toluene-p-sulphonyl Isocyanate.

A solution of either cis- or trans-thietane 1-oxide (0.33g, 2.0mmol) and TsNCO (0.80g, 4.0mmol) in benzene (10ml) was refluxed for 20hr. The solution was cooled, then unreacted isocyanate was neutralised with water. Removal of the solvent under reduced pressure gave a clear oil. Chromatography on silica (50g) and elution with ether-methanol (35:1) gave 3-Phenylthietane 1-N-(toluene-p-sulphonyl)imide (0.065g, 10%) as a mixture of isomers. M.p. 91-97°, ν_{\max} . (chloroform) 1300 (b), 1148, 1090, 1025, 1010, 1000, 965, and 815 cm^{-1} , τ 2.08 (2H, d, J 9 Hz), 2.65 (2H, d, J 9 Hz), 2.55 (5H, s), 5.22-6.62 (5H, m), and 7.58 (3H, s), m/e 319, 164, 155, 139, 118, 117, 104, 91, 90, and 77.

An identical product was obtained when 3-phenylthietane was reacted with chloramine-T (Conditions as for the equivalent reaction of 3-methylthietane).

CHAPTER THREE

Reaction of 2,2,trans-3,4,4-Pentamethyl-r-1-phenylphosphetan 1-Oxide with Toluene-p-sulphonyl.Isocyanate.

The isocyanate (0.65g, 3.2mmol) was slowly added to an ice-cooled solution of the trans-phosphetan oxide⁶² (0.75g, 3.18mmol) in benzene (10ml). A gas was slowly evolved. The reaction was monitored by infrared spectroscopy. The band due to the isocyanate (ν_{\max} . 2240 cm^{-1}) disappeared after 30min. Removal of the solvent under reduced pressure gave 2,2,trans-3,4,4-Pentamethyl-r-1-phenylphosphetan 1-N-(Toluene-p-sulphonyl)imide (1.2g, 97%), m.p. 144°C (from chloroform-light petroleum), ν_{\max} . (nujol) 1265, and 1150 (broad) cm^{-1} , τ 1.75-2.84 (9H, m), 7.45-8.06 (1H, m), 7.68 (3H, s), 8.64 (6H, d, J_{PH} 19 Hz), 8.81 (6H, d, J_{PH} 19 Hz), and 9.02 (3H, dd, J 6 and 1 Hz), m/e 389, 374, 325, 215, and 180, (Found: C, 64.8; H, 7.1; N, 3.8). $\text{C}_{21}\text{H}_{18}\text{NO}_2\text{PS}$ requires C, 64.8; H, 7.2; N, 3.6%). The reaction was also carried out in acetonitrile, dichloromethane and chloroform as solvents. An identical product was obtained.

Reaction of 2,2,cis-3,4,4-Pentamethyl-r-1-phenylphosphetan 1-Oxide with Toluene-p-sulphonyl Isocyanate.

An identical procedure to the above using cis-phosphetan oxide (0.30g, 1.28mmol) and toluene-p-sulphonyl isocyanate (0.26g, 1.30mmol) gave 2,2,cis-3,4,4-Pentamethyl-r-1-phenylphosphetan 1-N-(Toluene-p-sulphonyl)imide (1.16g, 94%), m.p. 179-180° (from chloroform-light petroleum), ν_{\max} . (nujol) 1270, 1140, and 1100 cm^{-1} , τ 2.24-3.10 (9H, m), 7.10-7.65 (1H, m), 7.76 (3H, s), 8.45 (6H, d, J_{PH} 19 Hz), 8.75 (6H, d, J_{PH} 19 Hz), and 9.04 (3H, dd, J 7.5 and 1 Hz), m/e 389, 374, 236, 221, 215, and 180, (Found: C, 64.6; H, 7.05; N, 3.8%).

Hydrolysis of the 2,2,3,4,4-Pentamethyl-1-phenylphosphetan 1-N-(Toluene-p-sulphonyl)imides.

A solution of the trans-phosphetan imide (0.18g, 0.46mmol) in a mixture of methanol (10ml) and aqueous potassium hydroxide (5ml, 10%) was stirred at room temperature for 2hr. The solution was poured into excess water and was extracted with dichloromethane. The organic layer was washed with water. Removal of the solvent under reduced pressure gave trans-phosphetan oxide (23) (0.11g, 98%), m.p. and mixed m.p. 125-126°.

An identical procedure using the cis-phosphetan imide (24) gave the cis-phosphetan oxide (23) (98%), m.p. and mixed m.p. 117-118°.

Reaction of the 2,2,3,4,4-Pentamethyl-1-phenylphosphetans with Toluene-p-sulphonyl Azide.

A solution of toluene-p-sulphonyl azide (0.43g, 2.18mmol) in degassed benzene (10ml) was slowly added to an ice-cooled solution of 2,2,trans-3,4,4-pentamethyl-1-phenylphosphetan^{64,65} (0.32g, 1.46mmol) in degassed benzene (20ml). The solution was stirred at room temperature overnight. Removal of the solvent under reduced pressure gave a clear oil (0.6g). Fractional crystallisation from chloroform-light petroleum gave the trans-phosphetan imide (24) (0.43g, 75%) and the trans-phosphetan oxide (23) (0.07g, 20%).

An identical procedure using 2,2,cis-3,4,4-pentamethyl-1-phenylphosphetan^{64,65} gave the cis-phosphetan imide (24) (65%).

Reaction of the 2,2,3,4,4-Pentamethyl-1-phenylphosphetans with Toluene-p-sulphonyl Isocyanate.

A solution of the isocyanate (0.28g, 1.41mmol) in degassed benzene (15ml) was slowly added to an ice-cooled solution of the trans-phosphetan (25) (0.31g, 1.41mmol) in degassed benzene (10ml). The mixture was stirred at room temperature overnight. Removal of the solvent under

reduced pressure gave the trans-phosphetan imide (24) (0.47g, 85%), m.p. 144° (from chloroform-light petroleum).

An identical procedure using the cis-phosphetan (25) gave the cis-phosphetan imide (24) (75%), m.p. 179-180° (from chloroform-light petroleum).

Reaction of the 2,2,3,4,4-Pentamethyl-1-phenylphosphetan 1-Oxides with Chlorosulphonyl Isocyanate.

Chlorosulphonyl isocyanate (CSI) (0.21g, 1.49mmol) was slowly added to a stirred solution of the trans-phosphetan oxide (23) (0.35g, 1.49mmol) in dichloromethane (10ml) at -40°. The solution was allowed to warm to room temperature and the solvent was removed under reduced pressure to give 2,2,trans-3,4,4-Pentamethyl-r-1-phenylphosphetan 1-N-(chlorosulphonyl)imide (0.49g, 98%) as an unstable, clear oil. ν_{\max} . (dichloromethane) 1470, 1325, 1165 (broad), and 1005 cm^{-1} , τ 1.64-2.17 (5H, m), 7.25-7.78 (1H, m), 8.38 (6H, d, J_{PH} 19 Hz), 8.68 (6H, d, J_{PH} 21 Hz), and 8.93 (3H, dd, J_{PH} 7 Hz, J_{HH} 2 Hz), m/e 335, 333, 298, 236, 221, 168, 166, 164, 119, and 108.

An identical procedure using the cis-phosphetan oxide (23) gave 2,2,cis-3,4,4-Pentamethyl-r-1-phenylphosphetan 1-N-(chlorosulphonyl)imide (98%) as an unstable, clear oil. ν_{\max} . (dichloromethane) 1465, 1322, 1165 (broad), and 1000 cm^{-1} , τ 2.00-2.48 (5H, m), 7.17-7.62 (1H, m), 8.49 (6H, d, J_{PH} 19 Hz), 8.69 (6H, d, J_{PH} 21 Hz), and 9.04 (3H, dd, J_{PH} 7 Hz, J_{HH} 1 Hz), m/e 335, 333, 236, 221, 168, 166, 119, and 108.

Reaction of the 2,2,3,4,4-Pentamethyl-1-phenylphosphetans with Chlorosulphonyl Isocyanate.

Chlorosulphonyl isocyanate (0.28g, 2.0mmol) was slowly added to an ice-cooled solution of the trans-phosphetan (25) (0.43g, 1.95mmol) in degassed benzene (10ml). After 10min the solution was allowed to warm

to room temperature and the solvent was removed under reduced pressure. The n.m.r. spectrum of the resulting clear oil showed that no cis product was present. Tituration with ether-light petroleum gave the trans-phosphetan imide (26) (0.34g, 53%).

An identical procedure using the cis-phosphetan (25) gave the cis-phosphetan imide (26) (55%). The n.m.r. spectrum of the crude reaction mixture showed that no trans product was present.

Hydrolysis of the 2,2,3,4,4-Pentamethyl-1-phenylphosphetan 1-N-(Chloro-sulphonyl)imides.

A solution of the trans-phosphetan imide (26) (0.20g, 0.6mmol) in a mixture of methanol (10ml) and aqueous potassium hydroxide (5ml, 10%) was stirred at room temperature for 2hr. The solution was poured into excess water and was extracted with dichloromethane. The combined organic layers were washed with water. Removal of the solvent under reduced pressure gave the trans-phosphetan oxide (23) (0.14g, 99%).

An identical procedure using the cis-phosphetan imide (26) gave the cis-phosphetan oxide (23) (98%).

Reaction of 2,2,cis-3,4,4-Pentamethyl-r-1-phenylphosphetan 1-Sulphide with Toluene-p-sulphonyl Isocyanate.

The isocyanate (0.074g, 0.38mmol) was slowly added to an ice-cooled solution of the cis-phosphetan sulphide⁶² (30) (0.09g, 0.38mmol) in deuteriochloroform (2ml). The solution was allowed to stand at room temperature overnight. The n.m.r. spectrum of the crude product showed cis-phosphetan sulphide (30) (50%) and cis-phosphetan imide (24) (50%). The infrared spectrum of this solution showed a strong absorption at 1900 cm^{-1} and none at 2240 cm^{-1} .

Reaction of 2,2,cis-3,4,4-Pentamethyl-r-1-phenylphosphetan 1-N-(Toluene-p-sulphonyl)imide with Chlorosulphonyl Isocyanate.

Chlorosulphonyl isocyanate (0.013g, 0.096mmol) was slowly added to an ice-cooled solution of the cis-phosphetan N-(toluene-p-sulphonyl)imide (24) (0.40g, 0.096mmol) in deuteriochloroform (1.5ml). The n.m.r. spectrum of this solution showed the cis-phosphetan N-(chlorosulphonyl)imide (26) (~100%). The infrared spectrum showed a strong absorption at 2240 cm^{-1} and none at 2250 cm^{-1} .

Reaction of 2,2,cis-3,4,4-Pentamethyl-r-1-phenylphosphetan 1-Oxide with p-Tolyl Isocyanate.

p-Tolyl isocyanate (0.3g, 2.3mmol) was slowly added to a solution of the cis-phosphetan oxide (23) (0.1g, 0.4mmol) in benzene (10ml). The solution was allowed to stand overnight. The infrared spectrum showed a strong absorption at 2130 cm^{-1} and none at 2275 cm^{-1} . The n.m.r. spectrum in deuteriochloroform showed only the cis-phosphetan oxide (23) and p-tolylcarbodiimide.¹⁴⁴

Attempted Reaction of 2,2,trans-3,4,4-Pentamethyl-r-1-phenylphosphetan 1-Oxide with N-Sulphinylaniline, N-Sulphinyl-toluene-p-sulphonamide and N,N'-bis(Toluene-p-sulphonyl)sulphur diimide.

N-Sulphinylaniline (0.37g, 2.7mmol) was slowly added to a solution of the cis-phosphetan oxide (23) (0.60g, 2.5mmol) in benzene (5ml). The solution was refluxed for 2 days. The infrared and n.m.r. spectra of the reaction mixture showed only starting materials. Identical results were obtained when dichloromethane or acetonitrile were used as solvent.

An identical procedure using N-sulphinyl-toluene-p-sulphonamide or N,N'-bis(toluene-p-sulphonyl)sulphur diimide also gave only starting materials.

Reaction of Acyclic Phosphine Oxides with Toluene-p-sulphonyl Isocyanate.

General Procedure: Toluene-p-sulphonyl isocyanate (1.3mmol) was slowly added to a stirred solution of the phosphine oxide (0.9mmol) in acetonitrile, benzene, dichloromethane or chloroform (5ml). The reaction was monitored by ^1H n.m.r. spectrometry and was complete in approximately 4 days, at room temperature. The excess isocyanate was then hydrolysed with water and the solvent was removed under reduced pressure to give a clear oil. Chromatography on silica and elution with ethyl acetate gave:

Benzylmethylphenylphosphine N-(Toluene-p-sulphonyl)imide (95%), m.p.

130-131° (from chloroform-light petroleum), ν_{max} . (chloroform) 1495, 1440, 1250, 1140 (broad), 1085 (s), and 900 cm^{-1} , τ 2.00-3.10 (14H, m), 6.38 (2H, dd, J_{PH} 16 Hz, J_{HH} 3 Hz), 7.63 (3H, s), and 8.10 (3H, d, J_{PH} 14 Hz), m/e 383, 349, 306, 293, 292, 276, 229, 228, 214, and 91, (Found:

C, 66.05; H, 5.85; N, 3.75; P, 7.9. $\text{C}_{21}\text{H}_{22}\text{NO}_2\text{PS}$ requires C, 65.8; H, 5.75; N, 3.65; P, 8.1%).

Benzylethylphenylphosphine N-(Toluene-p-sulphonyl)imide (98%), m.p.

106-107° (from chloroform-light petroleum), ν_{max} . (chloroform) 1440, 1260, 1140 (broad), and 1087 cm^{-1} , τ 2.05-3.13 (14H, m), 6.28 (2H, d, J_{PH} 16 Hz), 7.62 (3H, s), 7.28-8.08 (2H, m), and 8.60-9.38 (3H, m), m/e 397. 368, 333, 332, 306, 242, 175, 160, 144, 142, and 112, (Found: C, 66.45; H, 5.95; N, 3.5. $\text{C}_{22}\text{H}_{24}\text{NO}_2\text{PS}$ requires C, 66.5; H, 6.05; N, 3.5%).

Ethylmethylphenylphosphine N-(Toluene-p-sulphonyl)imide (80%), m.p. ambient,

ν_{max} . (chloroform) 1440, 1260, 1140 (broad), and 1090 cm^{-1} , τ 1.98-2.87 (9H, m), 7.65 (3H, s), 7.50-8.17 (2H, m), 8.08 (3H, d, J_{PH} 13.5 Hz) and 8.63-9.30 (3H, m), m/e 321, 293, 275, 268, 265, 257, 230, 228, 214, 139, and 71, (Found: C, 57.7; H, 6.1; N, 4.15; P, 9.4.

$\text{C}_{13}\text{H}_{20}\text{NO}_2\text{PS}$ requires C, 59.8; H, 6.25; N, 4.35; P, 9.65%).

t-Butylmethylphenylphosphine N-(Toluene-p-sulphonyl)imide (75%) as a clear

oil. ν_{max} . (dichloromethane) 1465, 1350, 1170 (broad), 1135 (broad), and 1082 cm^{-1} , τ 2.22-2.90 (9H, m), 7.63 (3H, s), 7.95 (3H, d, J_{PH} 13 Hz), and 8.88 (9H, d, J_{PH} 16.5 Hz), m/e 349, 334, 293, 292, 276, 258, 244, 149, 139, 138, and 91. No analysis could be obtained owing to complete decomposition on attempted distillation.

Hydrolysis.

The above phosphine imides were hydrolysed by stirring in a mixture of methanol - 2N aqueous potassium hydroxide (2:1) overnight. In all cases the only products were the respective phosphine oxide and toluene-*p*-sulphonamide.

Reaction of Benzylethylphenylphosphine Sulphide with Toluene-*p*-sulphonyl Isocyanate.

A solution of the phosphine sulphide¹⁴⁵ (0.17g, 0.66mmol) and the isocyanate (0.13g, 0.66mmol) in acetonitrile (7ml) was refluxed for 2 weeks. The n.m.r. spectrum of the crude product shows the presence of phosphine sulphide, phosphine oxide, and phosphine imide. The infrared spectrum shows the presence of the isocyanate (ν_{max} . 2240 cm^{-1}) and isothiocyanate (ν_{max} . 1900 cm^{-1}).

Reaction of *t*-Butylmethylphenylphosphine with Toluene-*p*-sulphonyl Isocyanate.

The isocyanate (0.37g, 1.9mmol) was slowly added to a solution of the phosphine (0.34g, 1.9mmol) in degassed dichloromethane (12ml) at -78° . The n.m.r. spectrum of the solution, which did not change on warming to room temperature, showed phosphine oxide (5%), phosphine imide (5%), and a 1:1 adduct (90%). Removal of the solvent under reduced

pressure and crystallisation from degassed benzene gave the adduct as sticky crystals. (0.57g, 80%) ν_{\max} . (benzene) 1675 (s), 1640, 1600 (s), 1440, 1400, 1350 (broad), and 1150 (broad) cm^{-1} , τ 1.73-2.83 (9H, m), 7.53 (3H, s), 8.72 (3H, d, J_{PH} 16 Hz), and 8.90 (9H, d, J_{PH} 14 Hz), m/e (No mass peak), 222, 197, 180, 155, 140, 123, 91, 78, 77, and 57, ^{31}P -23.6ppm (rel. H_3PO_4). No analysis could be obtained owing to the instability of the adduct.

The same product was obtained when degassed benzene or chloroform were used as solvent, and when a 100% excess of the isocyanate was used.

Reaction of Trimethylphosphite with Toluene-p-sulphonyl Isocyanate.

The isocyanate (0.21g, 1.1mmol) was slowly added to a solution of trimethylphosphite (0.07g, 0.54mmol) in deuteriochloroform (2ml). The reaction was constantly monitored by n.m.r. and was complete after 60min. The products, trimethylphosphate (30%) and trimethylphosphonate (55%) were characterised by comparison (g.l.c. and n.m.r.) with authentic samples and by heteronuclear decoupling experiments.

Kinetic Measurements.Reaction of 2,2,trans-3,4,4-Pentamethyl-r-1-phenylphosphetan 1-Oxide with Toluene-p-sulphonyl Isocyanate.

The reactions were run in n.m.r. tubes in the thermostated probe compartment ($-48^{\circ} \pm 1^{\circ}$) of a Jeol PS100 spectrometer. The percentage reaction was calculated by comparing the relative intensities of the absorptions due to two equivalent methyl groups in the starting material and the same groups in the product by a cutting and weighing technique. The required amount (1ml) of a stock solution of trans-phosphetan oxide (0.167M), in ethanol free deuteriochloroform, was allowed to equilibrate in the n.m.r. tube at -48° under dry nitrogen. Toluene-p-sulphonyl isocyanate was added neat through an injection septum using a previously standardised micro-syringe, and the solution was rapidly shaken. The reactions were followed to greater than 55% completion and the results obtained were plotted using the integrated rate equations for first, second (first order in both components), and third (first order in trans-phosphetan oxide and second order in isocyanate) order reactions.

RUN 1. $A^{\circ}/B^{\circ} = 1.0$

<u>TIME (Min)</u>	<u>%B</u>	<u>TIME</u>	<u>%B</u>
22	95.7	120	77.4
28	93.9	150	74.8
34	94.6	180	70.8
40	92.5	200	67.8
47	88.0	225	65.8
60	85.6	260	61.4
80	83.5	305	59.3
100	80.3	330	58.8

where A° = the initial concentration of TsNCO and B° = the initial concentration of phosphetan oxide.

RUN 2. $A^\circ/B^\circ = 1.75$

<u>TIME (Min)</u>	<u>%B</u>	<u>TIME</u>	<u>%B</u>
2.5	93.4	42.5	74.1
4.5	93.0	51.5	70.2
6.5	91.1	61.5	67.6
10.5	89.1	66.5	65.5
15.5	87.0	75.5	60.4
18.5	86.2	90.5	56.5
27.5	81.2	105.5	53.7
33.5	79.0	125.5	46.6

RUN 3. $A^\circ/B^\circ = 4.9$

<u>TIME (Min)</u>	<u>%B</u>	<u>TIME</u>	<u>%B</u>
1.25	83.7	18.5	66.0
3.5	79.6	22.5	63.6
5.5	78.0	28.5	58.5
7.5	77.7	36.5	51.3
9.5	75.3	42.5	49.8
11.5	74.1	46.5	47.6
14.5	69.2	56.5	36.7
16.5	70.6		

RUN 4. $A^\circ/B^\circ = 1.7$

<u>TIME (Min)</u>	<u>%B</u>	<u>TIME</u>	<u>%B</u>
7	89.9	54	65.9
9	88.2	64	63.6
11	87.0	85	55.1
18	84.7	98	52.0
24	80.4	113	45.6
30	77.0	128	42.6
36	74.3	140	38.5
49	67.7		

The Racemisation of (+)-(R)-Benzylmethylphenylphosphine Oxide by Toluene-p-sulphonyl Isocyanate.

Rate data were obtained using a Perkin-Elmer 141 polarimeter operating at 589nm. The required amount (5.2ml) of a stock solution of the phosphine oxide⁷³ (0.088M, $[\alpha]_D + 66.3^\circ$) in acetonitrile was thermostated ($26^\circ \pm 0.5^\circ$) in a 1dm pathlength quartz cell. The isocyanate was added neat using a previously standardised micro-syringe and the solution was rapidly shaken. The reactions were followed to greater than 85% loss in rotation and the results were treated as described in the text (3.5).

The phosphine oxide was found to be optically stable for at least six days in acetonitrile or chloroform solution. When the reaction was quenched with water or methanol as soon as the rotation reached zero a quantitative yield of racemic phosphine oxide could be recovered. The corresponding phosphine imide was stable in a solution containing water, methanol, and toluene-p-sulphonamide.

RUN 5. $A^{\circ}/C^{\circ} = 2$

<u>TIME (Min)</u>	<u>ROTATION</u>	<u>TIME</u>	<u>ROTATION</u>
0	100	50	31
2	88.5	60	24.5
4	83.5	70	19.5
6	79	80	15.5
10	72.5	90	12.5
15	65.5	100	10
20	59.5	110	8.5
25	53.5	120	6.5
30	48.5	130	5.5
40	39	140	4.5

where A° = the initial concentration of TsNCO and C° = the initial concentration of (+)-(R)-benzylmethylphenylphosphine oxide. Rotation values are normalised.

RUN 6. $A^{\circ}/C^{\circ} = 1$

<u>TIME (Min)</u>	<u>ROTATION</u>		
	OBS.	CALC. (A)	CALC. (B)
0	100	100	100
2	95	96	96
6	91	92	92.5
10	89	89.5	90
20	85	85.5	86
29	82	82.5	82.5
38	79	79	79
50	74	75	75
65	69	70.5	70
80	65	66.5	65.5
95	61	62	61.5
110	58	58.5	57.5
140	51	51.5	50
170	45	45.5	44
200	39	40	38.5
245	32	33	31.5
290	26	27	25.5
335	21	22.5	20.5
380	17	18.5	17.

RUN 7. $A^{\circ}/C^{\circ} = 0.5$

<u>TIME (Min)</u>	<u>ROTATION</u>		
	OBS.	CALC. (A)	CALC. (B)
0	100	100	100
7	95	96	97
13	94.5	95	96.5
22	93.5	94	95
46	91.5	91.5	92.5
70	89.5	89	90
100	87	86	87
130	84.5	83	84
190	79.5	77	78
250	74	72	72.5
340	67	64.5	65
430	60.5	58	58.5
550	53	50	50.5
700	42	42	42
775	38	38.5	38.5
844	34	35	35
1037	26	28	28
1286	17.5	20.5	20.5

RUN 8. $A^{\circ}/C^{\circ} = 2$

<u>TIME (Min)</u>	<u>ROTATION</u>		
	OBS.	CALC. (A)	CALC. (B)
0	100	100	100
3	89	90	91
6	84	83	84.5
9	80	80	81.5
15	74	72.5	74.5
21	68.5	68	69
30	61	61	61
39	54	54	54
48	48	48	48
57	43	43	43
69	36	37	36
81	31	31.5	31
99	24	25	24
117	19	20	19
153	11.5	12.5	11.5
189	7	8	7

RUN 9. $A^{\circ}/C^{\circ} = 3$

<u>TIME (Min)</u>	<u>ROTATION</u>		
	OBS.	CALC.(A)	CAL.(B)
0	100	100	100
2	84.5	84.5	83
3	78	78.5	77
4	72.5	73	72
5	68	69	68
7	61	61.5	60.5
9	55	56	54.5
11	50	50.5	49.5
15	41.5	42.5	40.5
20	33	34	31.5
25	26.5	27	24.5
30	21	21.5	19
35	17	17.5	15
40	13.5	14	11.5
50	9	9	7
60	6.5	5.5	4.5
70	4.5	3.5	2.5

<u>RUN</u>	<u>A°/C°</u>	<u>SCHEME (A)</u>			<u>SCHEME (B)</u>		
		<u>k₁</u>	<u>k₂</u>	<u>%I</u>	<u>k₁</u>	<u>k₂</u>	<u>%I</u>
6	1	3.8	4.4	8	3.8	10	7
7	0.5	3.4	5.0	4	3.4	12.4	4
8	2	3.8	3.8	15	5.0	7.5	14
9	3	6.8	4	30	7.7	11.3	28

where k_1 and k_2 are the second order rate constants ($\text{sec}^{-1} \text{mol}^{-1}$) derived from the computation. The values of the actual rate coefficients used are equal to the rate constants multiplied by A°/C° . The first order rate constant k_2 was fixed at $38 \times 10^{-4} \text{ sec}^{-1}$. %I refers to the percentage of the phosphine oxide bound up in the intermediate.

CHAPTER FOUR

Reaction of the 3-Methylthietane 1-Oxides with Bromine.

A solution of bromine (1.75g, 10.9mmol) in acetonitrile (10ml) was slowly added to a stirred solution of the sulfoxides (0.57g, 5.5mmol) in acetonitrile (12ml) at -40° . After 1hr the solution was allowed to warm to room temperature and to stir overnight. It was then poured into excess water and extracted with chloroform. The organic layer was washed with dilute aqueous sodium metabisulphite, with water, and was then dried. Removal of the solvent under reduced pressure gave a red oil (0.75g). Chromatography on silica (36g), and elution with ether-light petroleum (1:1) gave bis(2-Methyl-3-bromopropyl)disulphide (0.38g, 41%), b.p. $160^{\circ}/0.1\text{mm}$ (with slight decomposition), τ 6.53 (4H, d, J 5 Hz), 7.00-7.35 (4H, m), 7.50-8.13 (2H, m), and 8.93 (6H, d, J 7 Hz), m/e 338, 336, 334, 169, and 167. No analysis could be obtained owing to the slight decomposition on distillation. Further elution with ether gave bis(2-Methyl-3-bromopropyl)thiosulphonate (0.30g, 30%), ν_{max} . (film) 1325, and 1125 cm^{-1} , m/e 370, 368, 366, 201, 199, 169, and 167. No analysis could be obtained owing to complete decomposition on attempted distillation.

Reaction of the 3-Methylthietane 1-Oxides with Thionyl Chloride.

A solution of thionyl chloride (freshly distilled b.p. $69-70^{\circ}$) (0.52g, 4.4mmol) in dichloromethane (15ml) was slowly added to a stirred solution of the sulfoxides (0.36g, 3.5mmol) in dichloromethane (15ml) at -20° . After 3hr the solution was allowed to warm to room temperature, and the solvent was removed under reduced pressure to give a red oil (0.40g). Chromatography on silica (25g) and elution with ether-light petroleum (1:20) gave bis(2-Methyl-3-chloropropyl)disulphide (0.295g, 69%),

ν_{max} . (film) 735 and 683 cm^{-1} , τ 6.38 (4H, d, \underline{J} 5.5 Hz), 6.88–7.35 (4H, m), 7.42–8.13 (2H, m), and 8.88 (6H, d, \underline{J} 6.5 Hz), m/e 250, 248, 246, 213, 211, 158, 156, 124, and 122, (Found: C, 38.9; H, 6.6; $\text{C}_8\text{H}_{16}\text{Cl}_2\text{S}_2$ requires C, 39.0; H, 6.5%).

Reaction of 3-Methylthietane with Methyl Iodide.

A mixture of 3-methylthietane (1g, 0.01mol), methyl iodide (14.2g, 0.10mol) and benzene (30ml) was allowed to stand at room temperature. A light yellow solid slowly crystallised from the solution. After three weeks the solution was filtered. Distillation of the filtrate gave Methyl(2-methyl-3-iodopropyl)sulphide (0.90g, 34%), b.p. 80°/0.2mm, τ 6.75 (2H, d, \underline{J} 5 Hz), 7.43–7.60 (2H, m), 7.95 (3H, s), 8.13–8.53 (1H, m), and 8.93 (3H, d, \underline{J} 6 Hz), m/e 230, 169, 141, 127, 103, 61, 55 and 47. Recrystallisation of the solid gave Dimethyl(2-methyl-3-iodopropyl)sulphonium iodide (2.1g, 50%), m.p. 143° (from water), ν_{max} . (nujol) 1208, 1055, and 1017 cm^{-1} , τ (D_2O) 6.73–6.95 (4H, m), 7.28 (6H, s), 7.82–8.28 (1H, m), and 9.07 (3H, d, \underline{J} 7 Hz), (Found: C, 19.6; H, 3.85. $\text{C}_6\text{H}_{14}\text{I}_2\text{S}$ requires C, 19.35; H, 3.75%).

Reaction of the 3-Methylthietane 1-Oxides with Chlorosulphonyl Isocyanate.

CSI (0.41g, 2.9mmol) was slowly added to a solution of the sulphoxides (cis:trans, 3:1) (0.30g, 2.9mmol) in acetonitrile (5ml) at -23°. The reaction was monitored by infrared spectrometry. The band due to the isocyanate function (ν_{max} . 2250 cm^{-1}) disappeared completely after 30min. Removal of the solvent at reduced pressure gave a yellow oil (0.32g). Chromatography on silica (25g) and elution with ether-light petroleum (1:1) gave bis(2-methyl-3-chloropropyl)disulphide (0.20g, 56%).

Reaction of the 3-Methylthietane 1-Oxides with Hydrazoic Acid.

Sodium azide (2.5g, 33.0mmol) was suspended in a solution of the sulphoxides (cis:trans, 7:3) (1.7g, 16.3mmol) in chloroform (20ml). Concentrated sulphuric acid (2.75ml) was slowly added. The reaction, which was exothermic, was maintained at 45° for 8hr. After cooling, the mixture was filtered to remove the sodium sulphate, and the filtrate was poured into excess water. Extraction of the acid solution with chloroform gave an uncharacterisable oil (0.4g). The aqueous layer was made basic with sodium hydroxide and was again extracted with chloroform. Removal of the solvent at reduced pressure gave a clear oil (1.1g). Chromatography on alumina (100g), and elution with chloroform gave: trans-3-Methylthietane 1-imide r-1-oxide (0.2g, 10%) as a clear oil. ν_{\max} . (chloroform) 3320, 2965, 2225, 1400, 1235 (s), 1205, 1185, 1110, 1020, 965 (s), and 910 (broad) cm^{-1} , τ 5.55-6.47 (4H, m), 6.85-7.57 (1H, m), 6.3-7.5 (1H, s, broad, concentration dependent) and 8.58 (3H, d, J 7 Hz), m/e 119, 104, 77, 63, 56, 55, 41, and 39, (Found: C, 40.0; H, 7.6; N, 11.8. $\text{C}_4\text{H}_9\text{NOS}$ requires C, 40.3; H, 7.55; N, 11.75%), and cis-3-Methylthietane 1-imide r-1-oxide (0.1g, 5%) as a clear oil ν_{\max} . (chloroform) 3320, 2965, 2225, 1400, 1230 (s), 1205, 1185, 1110, 1020, 960 (s), and 910 (broad) cm^{-1} , τ 5.47-6.47 (4H, m), 6.83-7.57 (1H, m), 6.3-7.5 (1H, s, broad, concentration dependent), and 8.57 (3H, d, J 7 Hz), m/e 119, 104, 77, 63, 56, 55, 41, and 39, (Found: C, 39.9; H, 7.5; N, 11.65%). Intermediate fractions contained a mixture of isomers (0.70g, 37%).

Sodium azide (5.7g, 90.0mmol) was suspended in a solution of the sulphoxides (cis:trans, 7:3) (2.6g, 25.0mmol) in chloroform (25ml). Concentrated sulphuric acid (6ml) was slowly added. The reaction was

maintained at 45° for 60hr and was then worked up as above. Chromatography of the basic extract (2.0g) on alumina (75g) and elution with dichloromethane-methanol (50:1) gave 3-Azido-2-methylpropylsulphonamide (1.85g, 42%), b.p. 210°/0.1mm (decomposition), ν_{max} . (film) 3340, 3250, 2105 (s), 1640, 1550, 1460, 1320 (broad), and 900 cm^{-1} , τ 4.72 (2H, s), 6.57 (2H, dd, J 6 Hz and 1 Hz), 6.83 (2H, dd, J 6.5 Hz and 6.5 Hz), 7.32-7.90 (1H, m), and 8.82 (3H, d, J 7 Hz), (Found: C, 27.3; H, 5.7; N, 31.5. $\text{C}_4\text{H}_{10}\text{N}_4\text{O}_2\text{S}$ requires C, 27.0; H, 5.6; N, 31.45%).

Reaction of trans-3-Methylthietane 1-Imide \underline{r} -1-Oxide with Toluene-p-sulphonyl Chloride and Pyridine.

A solution of toluene-p-sulphonyl chloride (0.15g, 0.8mmol) in pyridine (3ml) was added to a solution of the trans-sulphoximide (0.05g, 0.4mmol) in pyridine (3ml). After 4hr the solvent was removed under reduced pressure to give a yellow oil. Thick layer chromatography on alumina, and elution with ether, gave trans-3-methylthietane \underline{r} -1-oxide 1-N-(toluene-p-sulphonyl)imide (0.085g, 81%), m.p. and mixed m.p. 114-115°.

Reaction of cis-3-Methylthietane 1-Imide \underline{r} -1-Oxide with Toluene-p-sulphonyl Chloride and Pyridine.

An identical procedure to the above, using cis-sulphoximide gave cis-3-methylthietane \underline{r} -1-oxide 1-N-(toluene-p-sulphonyl)imide (75%), m.p. and mixed m.p. 125-126°.

Reaction of trans-2-Phenylthiirane 1-Oxide with Hydrazoic Acid.

A solution of 1.54N hydrazoic acid¹⁴⁶ in chloroform (4.6ml, 6.95mmol) was slowly added to a solution of trans-2-Phenylthiirane-1-oxide⁸⁵ (1.07g, 7.0mmol) in chloroform (3ml) at -50°. The solution

was allowed to warm to room temperature. The reaction was monitored by n.m.r. spectrometry and was complete after 3 days. Removal of the solvent under reduced pressure gave a thick red oil (1.35g). Chromatography on silica (35g) and elution with ether-light petroleum (1:9) gave styrene (0.1g, 14%) and bis(2-Azido-2-phenylethyl)disulphide (0.35g, 30%) b.p. 140°/0.01mm (decomposition), ν_{\max} . (chloroform) 2100 (s), 1480, 1455, and 1255 (broad) cm^{-1} , τ 2.75 (10H, m), 5.33 (2H, t, \underline{J} 7 Hz), and 7.05 (4H, d, \underline{J} 7 Hz), m/e 356, 181, 150, 136, 132, 118, 104 and 77. No analysis could be obtained owing to complete decomposition on attempted distillation.

Reaction of 2-Phenylthiirane with Chloramine-T in Methanol.

A solution of 2-phenylthiirane (1.0g, 7.4mmol) in methanol (5ml) was slowly added to an ice-cooled solution of anhydrous chloramine-T (1.68g, 7.4mmol) in methanol (10ml). After 90min the solvent was removed under reduced pressure. The residue was extracted with dichloromethane. Sodium chloride and any unchanged chloramine-T remained undissolved. Removal of the solvent under reduced pressure gave a clear oil (1.7g). Chromatography on silica (50g) and elution with ether gave bis(2-Methoxy-2-phenylethyl)disulphide (0.74g, 60%), b.p. 190°/0.05mm (slight decomposition), ν_{\max} . (chloroform) 1095 cm^{-1} , τ 2.77 (5H, s), 5.67 (2H, dd, \underline{J} 7.5 and 6 Hz), 6.82 (6H, s), and 6.63-7.13 (4H, m), m/e 334, 302, 198, 167, 135, 121, and 77, (Found: C, 63.7; H, 6.45; S, 18.95. $\text{C}_{18}\text{H}_{22}\text{O}_2\text{S}_2$ requires C, 64.6; H, 6.6; S, 19.15%), and toluene-*p*-sulphonamide (0.7g, 56%), m.p. and mixed m.p. 139°.

There was no reaction between 2-phenylthiirane and methanol after 48hr at room temperature.

An identical procedure to the above using tetrahydrofuran as solvent gave a polymeric product. N.m.r. spectrometry suggested that

this polymer did not contain methyl groups.

Attempted Epoxidation of 3-Phenylthiete 1,1-Dioxide.

A 40% solution of peracetic acid (3.6ml, 16.5mmol) was shaken with a little hydrated sodium acetate, then added dropwise to an ice-cooled suspension of anhydrous sodium carbonate (2g) in a solution of the sulphone (1g, 5.6mmol) in dichloromethane (50ml). After 20hr the mixture was tipped into excess water and was extracted with dichloromethane. The organic layer was washed with aqueous sodium metabisulphite and water. Removal of the solvent under reduced pressure gave starting material only (1g).

A similar procedure, using m-chloroperbenzoic acid as oxidant, also gave only starting material.

A suspension of the sulphone (0.75g, 4.2mmol) and N-bromoacetamide (1.74g, 12.6mmol) in water (50ml) was heated at 60° overnight. The mixture was extracted with dichloromethane. Removal of the solvent under reduced pressure gave a white, oily solid (1.0g). Chromatography on silica (50g) and elution with ether gave bromomethyl methyl sulphone (0.44g, 65%), identical to an authentic sample, and benzoic acid (0.32g, 62%) m.p. and mixed m.p. 122°.

A similar procedure using acetone or acetone-water (3:1) as solvent gave only starting material.

CHAPTER FIVE

Flash Vacuum Thermolyses.

Thermolysis of 3-Phenylthiete 1,1-Dioxide.

The sulphone⁴ (0.75g, 4.2mmol) was sublimed at 0.05mm pressure through the furnace at 460°. 4-Phenyl-5H-1,2-oxathiole 2-Oxide collected as a yellow oil in the neck of the trap. B.p. 190°/1.0mm, ν_{\max} . (film) 1603 (s), and 1120 (s) cm^{-1} , τ 2.62 (5H, m), 3.10 (1H, dd, J 2 and 2 Hz), 4.23 (1H, dd, J 15 and 2 Hz), and 4.63 (1H, dd, J 15 and 2 Hz), m/e 180, 163, 151, 135, 132, 115, 104, 103, and 40, (Found: C, 60.15; H, 4.9; $\text{C}_9\text{H}_8\text{O}_2\text{S}$ requires C, 60.0; H, 4.45%), and atropaldehyde¹⁴⁷ (0.06g, 10%) collected as white crystals which melted on warming to room temperature, in the middle of the trap. τ 0.1 (1H, s), 2.5 (5H, s), 3.33 (1H, s), and 3.77 (1H, s).

An identical procedure to the above, with the furnace at 680° gave the cyclic sulphinate (12%), atropaldehyde (70%), and styrene (10%). On standing or on attempted chromatography the atropaldehyde dimerised¹⁴⁸ to give 3,4-Dihydro-2,5-diphenyl-pyran-2-al, ν_{\max} . (film) 3055, 2930, 2805, 1735 (s), 1640 (s), 1165 (broad), 757, 736, and 700 cm^{-1} , τ 0.35 (1H, s), 2.3-2.8 (11H, m), and 7.2-8.0 (4H, m), m/e 264, 235, 234, 132, 115, 105, 104, 103, 91, and 77. No analysis could be obtained owing to the instability of the compound.

Attempted thermolysis with the furnace temperature below 370° led to the complete recovery of starting material.

Thermolysis of 3-t-Butylthiete 1,1-Dioxide.

The sulphone⁴ (0.6g, 3.8mmol) was sublimed at 0.001mm through the furnace at 525°. Distillation of the product gave: 2-methylene-3,3-

-dimethyl-butylaldehyde (0.17g, 40%), b.p. 124-125° (Lit. value⁹⁶ 125-126°), ν_{max} . (chloroform) 2860, 2710, 1690, 1612, and 950 cm^{-1} , τ 0.77 (1H, s), 3.90 (1H, s), 4.28 (1H, s), and 8.85 (9H, s), and 4-t-Butyl-5H-1,2-oxathiole 2-Oxide (0.36g, 60%), b.p. 105-108°/0.2mm, ν_{max} . (chloroform) 1610, 1112 (s), and 962 cm^{-1} , τ 3.83 (1H, dd, J 2 and 2 Hz), 4.60 (1H, dd, J 15 and 2 Hz), 5.05 (1H, dd, J 15 and 2 Hz), and 8.80 (9H, s), m/e 160, 145, 131 and 83 (Found: C, 52.45; H, 7.7; S, 20.15. $\text{C}_7\text{H}_{12}\text{O}_2\text{S}$ requires C, 52.45; H, 7.55; S, 20.0%).

Attempted thermolysis with the furnace temperature below 430° led to the complete recovery of starting material.

Thermolysis of 3-Phenylthietane 1,1-Dioxide.⁴

An identical procedure to the above, using a furnace temperature of 800° gave: starting material (49%), phenylcyclopropane (30%), and α -methyl styrene (15%), identical to authentic samples.

Thermolysis of 3-Phenyl-2H-thiopyran 1,1-Dioxide.⁹⁸

Simple sublimation (150°/0.001mm) yields a mixture of starting material (55%) and 3-phenyl-6H-thiopyran 1,1-dioxide (45%).

Thermolysis with a furnace temperature of 500° and a pressure of 5×10^{-4} mm gave the same mixture of products as simple sublimation.

Thermolysis with a furnace temperature of 750° gave a black oil containing a large number of products. The only identified product was phenyl acetylene (5%). Intermediate temperatures did not give a simpler mixture.

Thermolysis of 2H-1-Benzothiopyran 1,1-Dioxide.¹⁰⁰

The following experiments were carried out at a pressure of

1×10^{-3} mm. The products were separated by chromatography on silica and elution with light petroleum.

<u>PRODUCT</u>	<u>FURNACE TEMPERATURE</u>		
	<u>650°</u>	<u>675°</u>	<u>775°</u>
Starting material	100%	75%	15%
Indene	-	5%	20%
Cinnamaldehyde	-	10%	30%
2H-1-Benzopyran ¹⁰¹	-	6%	18%

Thermolysis of 1H-2-Benzothiopyran 1,1-Dioxide.¹⁰⁰

The following experiments were carried out at a pressure of 1×10^{-3} mm. The products were separated by chromatography on silica and elution with light petroleum. σ -Vinylbenzaldehyde was characterized as its semi-carbazide derivative, m.p. 189-190° (from ethanol) (Lit. value¹⁰³ 190-191°).

<u>PRODUCT</u>	<u>FURNACE TEMPERATURE</u>	
	<u>700°</u>	<u>775°</u>
Starting material	50%	14%
Indene	23%	37%
σ -Vinylbenzaldehyde	23%	43%

CHAPTER SIX

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 unless otherwise stated. All solvents were of spectroscopic grade and were degassed prior to use.

Photolysis of 2H-1-Benzothiopyran 1,1-Dioxide.

A solution of the sulphone (93) (2.0g, 11.1mmol) in methanol (300ml) (0.04M) was irradiated with light of wavelength 253nm. The reaction was monitored by g.l.c. After 2hr no starting material remained. The solvent was removed at room temperature under reduced pressure to give a dark oil. (2.0g). Chromatography on silica (200g) and elution with ether-light petroleum (1:1) gave: indene (0.1g, 5%), identical to an authentic sample, 2H-1-benzopyran (0.11g, 5%), identical to an authentic sample, a clear oil (1.1g, 55%) which contained at least two compounds, and 3,4-Benzo-trans-5-vinyl-1,2-oxathiole r-2-Oxide (141) (0.5g, 25%), b.p. 122°/0.1mm (with slight decomposition), ν_{max} . (chloroform) 1600, 1435 (broad), 1130 (s), 985, 965, 943, and 902 (s) cm^{-1} , τ (100MHz spectrum in deuteriobenzene) 2.72-3.30 (4H, m), 3.89 (1H, d, J 7.3 Hz), 4.54 (1H, ddd, J 16.6, 9.3, and 7.3 Hz), 4.90 (1H, dd, J 16.6 and 1.9 Hz), and 5.00 (1H, dd, J 9.3 and 1.9 Hz), m/e 180, 151, 135, 134, 132, 131, 116, 115, and 77, (Found: C, 60.45; H, 4.8; S, 17.1. $\text{C}_9\text{H}_8\text{O}_2\text{S}$ requires C, 60.0; H, 4.45; S, 17.75%), and starting material (0.16g, 8%).

The photolysis was also carried out in acetonitrile and in dichloromethane as solvent. In both cases, n.m.r. spectrometry and g.l.c. analysis of the crude product showed almost identical results to those obtained above.

Repeated chromatography and distillation of the clear oil obtained above did not enable separation into its constituent components to be achieved.

The clear oil (1.1g) was dissolved in absolute ethanol (100ml) and palladium-charcoal catalyst (10% Pd) (0.1g) was added. The mixture was stirred under an atmosphere of hydrogen for 12hr. The mixture was filtered to remove the catalyst and the solvent was removed at reduced pressure to give a clear oil (1.1g). Chromatography on silica (50g) and elution with ether gave: 3,4-Benzo-cis-5-ethyl-1,2-oxathiole r-2-Oxide (144) (0.6g, 30%), $\nu_{\text{max.}}$ (chloroform) 1467, 1440, 1262, 1122 (s), and 1008 (s) cm^{-1} , τ 2.00-2.30 (1H, m), 2.45-2.83 (3H, m), 5.77-6.50 (1H, m), 7.98-8.43 (2H, m), and 8.45 (3H, t, J 7 Hz), m/e 182, 134, and 118, (Found: C, 59.4; H, 5.5; S, 17.55. $\text{C}_9\text{H}_{10}\text{O}_2\text{S}$ requires C, 59.35; H, 5.5; S, 17.6%), and 3,4-Benzo-7H-1,2-oxathiepin 2-Oxide (142) (0.5g, 25%) as an oil. $\nu_{\text{max.}}$ (chloroform) 1148 (s), 1120, and 1045 cm^{-1} , τ 2.20-2.90 (4H, m), 3.53 (1H, broad d, J 12 Hz), 4.10 (1H, dt, J 12 Hz and 3 Hz), and 5.13 (2H, dd, J 3 and 3 Hz), m/e 180, 151, 137, 125, 134, 132, 131, 117, 116, 115, and 77, (Found: C, 59.45; H, 4.4. $\text{C}_9\text{H}_8\text{O}_2\text{S}$ requires C, 60.0; H, 4.45%).

Triplet Sensitised Photolysis of 2H-1-Benzothiopyran 1,1-Dioxide.

A solution of the sulphone (93) (0.18g, 1.0mmol) and benzophenone (0.18g, 1.0mmol) in acetonitrile (25ml) was irradiated in a pyrex tube with light of wavelength 350nm for 2hr. The solvent was removed under reduced pressure. The n.m.r. spectrum of the crude product was identical to that obtained in the unsensitised reaction above.

An identical procedure to the above using xanthone as sensitiser gave the same mixture of products.

Triplet Quenched Photolysis of 2H-1-Benzothiopyran 1,1-Dioxide.

A solution of the sulphone (93) (0.18g, 1.0mmol) and cis/trans-1,3-pentadiene (0.17g, 2.5mmol) in acetonitrile (25ml) was irradiated with light of wavelength 253nm for 2hr. The volatile materials were removed under reduced pressure at room temperature. The n.m.r. spectrum of the residue was almost identical to that obtained above. There was no unchanged starting material.

Photolysis of 1H-2-Benzothiopyran 2,2-Dioxide.

A solution of the sulphone (107) (1.0g, 5.5mmol) in methanol (150 ml) was irradiated with light of wavelength 253nm. The reaction was monitored by g.l.c. After 2hr no starting material remained. The solvent was removed under reduced pressure to give a yellow oil (1.0g). Chromatography on silica (50g) and elution with ether-light petroleum (1:1) gave 5,6-Benzo-7H-1,2-oxathiepin 2-Oxide (154) (0.10g, 10%), b.p. 140°/0.2mm, ν_{\max} . (chloroform) 1608, 1600, 1570, 1459, and 1110 (s) cm^{-1} , τ 2.67 (4H, s), 2.98 (1H, d, \underline{J} 12 Hz), 3.52 (1H, d, \underline{J} 12 Hz), 4.72 (1H, d, \underline{J} 13.5 Hz), and 5.23 (1H, d, \underline{J} 13.5 Hz), m/e 180, 164, 151, 132, 116, and 115, (Found: C, 60.2; H, 4.55; S, 17.75. $\text{C}_9\text{H}_8\text{O}_2\text{S}$ requires C, 60.0; H, 4.45; S, 17.75%), and 4-Methoxy-isothiochroman 2,2-Dioxide (152) (0.75g, 75%), b.p. 145°/0.005mm, ν_{\max} . (dichloromethane) 1314 (s), 1200, 1144, 1119 (s), and 813 cm^{-1} , τ (100 MHz spectrum in deuteriobenzene) 7.16 (3H, s), 7.00 (1H, ddd, \underline{J} 14, 5 and 1.2 Hz), 6.67 (1H, dd, \underline{J} 14 and 5 Hz), 6.27 (1H, d, \underline{J} 15 Hz), 5.93 (1H, dd, \underline{J} 5 and 5 Hz), 5.56 (1H, d, \underline{J} 15 Hz), and 3.18-2.48 (4H, m), m/e 212, 180, 149, 148, 134, 133, 132, 119, 118, 117, 116, 115, 105, 91, 89, and 77, (Found: C, 56.9; H, 5.7. $\text{C}_{10}\text{H}_{12}\text{O}_3\text{S}$ requires C, 56.6; H, 5.65%).

The sulphone (107) was recovered unchanged from a methanolic

solution after 1 week at room temperature in the dark.

An identical photolysis to the above using acetonitrile as solvent gave, after 2hr, starting material (107) (60%), the oxathiepin (154) (20%), and a high molecular weight compound, apparently dimeric starting material (20%).

A solution of the sulphone (107) (0.18g, 1.0mmol) in acetonitrile-water (3:1) (25ml) was irradiated with light of wavelength 253nm for 2hr. The solution was poured into excess water and extracted with dichloromethane. Removal of the solvent under reduced pressure gave 4-hydroxy-isothiochroman 2,2-dioxide (153)¹⁰⁰ (0.18g, 92%), τ 2.47-3.17 (4H, m), 4.97 (1H, t, \underline{J} 6 Hz), 5.68 (1H, d, \underline{J} 15 Hz), 6.08 (1H, d, \underline{J} 15 Hz), 6.37 (1H, s), and 6.75 (2H, d, \underline{J} 6 Hz).

The sulphone (107) was recovered unchanged from an aqueous acetonitrile solution after 1 week at room temperature in the dark.

A solution of the sulphone (107) (0.18g, 1.0mmol) in acetonitrile-diethylamine (3:1) (25ml) was irradiated with light of wavelength 253nm for 2hr. Removal of the solvent under reduced pressure gave: starting material (70%) and the oxathiepin (154) (30%) as judged by n.m.r. of the crude reaction mixture.

A solution of the sulphone (0.18g, 1.0mmol) and dimethyl acetylenedicarboxylate (0.28g, 2.0mmol) or maleic anhydride (0.2g, 2.0mmol) in methanol (25ml) was irradiated with light of wavelength 253nm for 2hr. The only products were 4-methoxy-isothiochroman 2,2-dioxide (152) (75%) and the oxathiepin (154) (15%).

Triplet Sensitised Photolysis of 1H-2-Benzothiopyran 2,2-Dioxide.

A solution of the sulphone (107) (0.18g, 1.0mmol) and benzophenone (0.18g, 1.0mmol) in acetonitrile (25ml) was irradiated in a pyrex tube with light of wavelength 350nm for 2hr. Removal of the solvent under

reduced pressure gave a clear oil. Crystallisation from acetonitrile gave a $2\pi + 2\pi$ Dimer (158) (0.16g, 89%), m.p. $> 330^\circ$ (from acetonitrile), ν_{max} . (nujol) 1325, 1302, 1120, and 767 cm^{-1} , τ (deuteriodimethyl sulphoxide) 2.60–3.20 (8H, m), 4.97 (2H, d, J 17 Hz), 5.52 (2H, d, J 17 Hz), and 6.67 (4H, s), m/e 360 and 180, (Found: C, 59.85; H, 4.45; S, 17.45. $\text{C}_{18}\text{H}_{16}\text{O}_4\text{S}_2$ requires C, 60.0; H, 4.45; S, 17.75%).

An identical procedure using xanthone as sensitiser gave the same product (90%).

Triplet Quenched Photolysis of 1H-2-Benzothiopyran 2,2-Dioxide.

A solution of the sulphone (107) (0.18g, 1.0mmol) and cis/trans-1,3-pentadiene (0.17g, 2.5mmol) in acetonitrile (25ml) was irradiated with light of wavelength 253nm for 2hr. Removal of the volatile material at reduced pressure gave a black oil. G.l.c., t.l.c., and n.m.r. showed the presence of a large number of products.

Methylation of 4-Hydroxy-isothiochroman 2,2-Dioxide.

A solution of the hydroxy-sulphone (153) (0.4g, 2.0mmol) in dichloromethane (3ml) was slowly added to a suspension of trimethyloxonium fluoroborate (0.6g, 4.0mmol) in dichloromethane (5ml). After 48hr the mixture was poured into excess water and was extracted with dichloromethane. Removal of the solvent under reduced pressure gave a light green oil (0.4g). Chromatography on silica (16g) and elution with ether-light petroleum (1:1) gave: 1H-2-benzothiopyran 2,2-dioxide (107) (0.18g, 50%) and 4-methoxy-isothiochroman 2,2-dioxide (153) (0.21g, 50%).

An identical procedure using trimethyloxonium hexachloroantimonate as methylating agent gave 1H-2-benzothiopyran 2,2-dioxide (107) (85%) and starting material (10%).

Photolysis of Thianaphthene 1,1-Dioxide.

A solution of the sulphone (1.0g, 55mmol) in methanol (250ml) was irradiated with light of wavelength 253nm. A small amount of white solid slowly crystallised from solution. After 4hr the solution was filtered and the solvent was removed under reduced pressure to give further amounts of a white solid identical to that obtained above. Recrystallisation of the combined fractions from methanol gave the cis-dimer (0.95g, 95%) identical to that of Harpp,¹²⁵ m.p. 328-329° (Lit. value¹²⁵ 329-330°).

CHAPTER SEVEN

bis(Triphenylphosphine)platinum (0) Olefin Complexes.

A mixture of trans-stilbenebis(triphenylphosphine)platinum(0)¹³⁸ (0.45g, 0.5mmol) and 3-phenylthiete 1,1-dioxide⁴ (0.09g, 0.5mmol) was stirred in dry ether (25ml). The reactants slowly dissolved to give a yellow solution. After 10min a white solid crystallised and the solution became clear. Filtration gave 3-Phenylthiete 1,1-dioxidebis(triphenylphosphine)platinum(0) (0.35g, 78%), m.p. 172° (from chloroform-light petroleum), ν_{max} . (nujol) 1600, 1588, 1276, 1198, 1130, 1096, 748, and 704 cm^{-1} , τ (100 MHz) 3.10 (30H, m), 4.18 (5H, m), 5.82 (2H, td, J_{PH} 9.8 Hz, J_{PtH} 40 Hz), and 5.68 (1H, tdd, J_{PH} 9.8 and 4 Hz, J_{PtH} 29 Hz), (Found: C, 60.25; H, 4.3; $\text{C}_{45}\text{H}_{38}\text{O}_2\text{P}_2\text{PtS}$ requires C, 60.1; H, 4.25%) (Mol. wt. found: 883, requires 899).

An identical procedure using 3-p-bromophenylthiete 1,1-dioxide gave 3-p-Bromophenylthiete 1,1-dioxide bis(triphenylphosphine)platinum (0) (75%), m.p. 196-197° (from chloroform-light petroleum), ν_{max} . (nujol) 1587, 1286, 1194, 1132, 1101, 746, and 698 cm^{-1} , τ (100 MHz) 3.16 (32H, m), 3.93 (2H, m), 5.69 (1H, tdd, J_{PH} 8.5 and 4.5 Hz, J_{PtH} 29 Hz), and 5.83 (2H, tdd, J_{PH} 9.5 and 3 Hz, J_{PtH} 41 Hz), (Found: C, 54.95; H, 3.75. $\text{C}_{45}\text{H}_{37}\text{BrO}_2\text{P}_2\text{PtS}$ requires C, 55.2; H, 3.8%).

An identical procedure using 3-t-Butylthiete 1,1-dioxide gave only starting materials.

Photolysis of 3-p-Bromophenylthiete 1,1-dioxidebis(triphenylphosphine)-platinum(0).

A solution of the complex (0.15g, 0.15mmol) in dichloromethane (10ml) was irradiated with light of wavelength 253nm for 2hr. A white

solid crystallised from solution. Filtration gave 3-p-bromophenylthiete 1,1-dioxide (0.036g, 90%).

The original complex exhibits a very broad band in the ultra-violet, with a maximum at 265nm.

Displacement of 3-Phenylthiete 1,1-Dioxide with Tetracyanoethylene.

A solution of tetracyanoethylene (0.026g, 0.20mmol) in chloroform (10ml) was slowly added to a solution of the complex (166) (0.20g, 0.20 mmol) in chloroform (10ml). The solution turns dark green. After 20min the solution was filtered and reduced in volume to 5ml. Treatment with light petroleum gave 3-phenylthiete 1,1-dioxide (0.029g, 80%).

bis(Triphenylarsine)platinum(0) Olefin Complexes.

A mixture of tetrakis(triphenylarsine)platinum(0)¹⁴⁹ (0.66g, 0.46 mmol) and 3-phenylthiete 1,1-dioxide (0.087g, 0.48mmol) was stirred in refluxing chloroform (30ml) for 5hr. The solution was cooled, filtered and the solvent was removed under reduced pressure. The residual oil was crystallised from chloroform-light petroleum to give 3-Phenylthiete 1,1-dioxidebis(triphenylarsine)platinum(0) (0.185g, 40%), m.p. 185-186° (decomposition), ν_{\max} . (nujol) 1595, 1587, 1275, 1192, 1128, 737, and 695 cm^{-1} , τ (100 MHz) 2.22-2.88 (33H, m), 5.04 (1H, td, J_{HH} 2 Hz, J_{PtH} 39.3 Hz), 5.36 (1H, d, J_{HH} 11.8 Hz), and 5.56 (1H, dd, J_{HH} 11.8 and 2 Hz), (Found: C, 54.73; H, 3.98. $\text{C}_{45}\text{H}_{38}\text{As}_2\text{O}_2\text{PtS}$ requires C, 54.72; H, 3.88%). (Mol. wt. found: 970, requires 988).

An identical procedure using 3-p-bromophenylthiete 1,1-dioxide gave 3-p-Bromophenylthiete 1,1-dioxidebis(triphenylarsine)platinum(0) (55%), m.p. 184-187° (decomposition) (from chloroform-light petroleum), ν_{\max} . (nujol) 1580, 1282, 1190, 1128, 1075, 740, and 697 cm^{-1} , τ 2.60-3.20 (32H, m), 3.62-3.80 (2H, m), 5.27 (1H, d, J_{HH} 2 Hz), 5.56 (1H, d,

J_{HH} 11.3 Hz), and 5.79 (1H, dd, J_{HH} 11.3 and 2 Hz), (Found: C, 50.97; H, 3.61. $\text{C}_{45}\text{H}_{37}\text{As}_2\text{BrO}_2\text{PtS}$ requires C, 50.67; H, 3.50%) (Mol. wt. found: 1040, requires 1067).

Preparation of Platinum(II) Sulphonyl Chloride Complexes.

A solution of methanesulphonyl chloride (0.06g, 0.5mmol) in benzene (2ml) was slowly added to a stirred solution of trans-stilbenebis(triphenylphosphine)platinum(II) (0.45g, 0.5mmol) in benzene (5ml). A white solid slowly (2hr) crystallised from solution. Filtration gave Methanesulphonyl chlorobis(triphenylphosphine)platinum(II) (0.34g, 82%) as a single isomer presumably cis. M.p. 248-250° (decomposition) (from chloroform-light petroleum), ν_{max} . (nujol) 1218 (s), 1100, and 1070 (s) cm^{-1} , (Found: C, 52.65; H, 3.85. $\text{C}_{37}\text{H}_{31}\text{ClO}_2\text{P}_2\text{PtS}$ requires C, 53.3; H, 3.95%).

An identical procedure using α -toluenesulphonyl chloride gave α -Toluenesulphonylchlorobis(triphenylphosphine)platinum(II) (85%) as a white solid that went yellow on exposure to light. M.p. 188-189° (from chloroform-light petroleum), ν_{max} . (dichloromethane) 1480, 1435, 1209, 1096, and 1054 cm^{-1} , τ 2.33-3.33 (35H, m), and 5.52 (2H, s), (Found: C, 56.3; H, 4.0. $\text{C}_{43}\text{H}_{35}\text{O}_2\text{P}_2\text{PtS}$ requires C, 56.7; H, 4.05%).

Reaction with Base.

A solution of either of the above complexes and triethylamine (400% excess) in dichloromethane was refluxed for 2 days. Removal of the volatile material under reduced pressure gave starting material (100%).

Thermolysis of Methanesulphonylchlorobis(triphenylphosphine)platinum(II).

The complex (0.05g, 0.06mmol) was heated at 250° under nitrogen for 2hr. The resulting oil was crystallised from chloroform-light

petroleum to give methylchlorobis(triphenylphosphine)platinum(II) (0.04g, 87%), m.p. 273-274° (decomposition) (Lit. value¹⁴¹ 273-278° [decomposition]), ν_{max} (dichloromethane) 1480, 1435, and 1095 cm^{-1} ,

APPENDIX

THE CRYSTAL STRUCTURE OF trans-3-p-BROMOPHENYLTHIETANE 1-OXIDE.

Since the major part of this thesis was completed the result of the crystal structure of trans-3-p-bromophenylthietane 1-oxide has been obtained. The facts and their interpretation, presented below, should be read and considered along with those already discussed in Chapter One.

Geometry of trans-3-p-Bromophenylthietane 1-Oxide.

Angles, degree (e.s.d.)		Distances, Å° (e.s.d.)	
O,S,C(1)	114.7(1.0)	S-C(1)	1.865(0.022)
O,S,C(3)	112.5(1.0)	S-C(3)	1.828(0.024)
C(1),S,C(3)	76.4(1.0)	S-O	1.489(0.021)
S,C(1),C(2)	88.1(1.3)	C(1)-C(2)	1.518(0.033)
C(1),C(2),C(3)	97.0(1.8)	C(2)-C(3)	1.529(0.033)
C(1),C(2),C(21)	113.1(1.8)	C(2)-C(21)	1.509(0.033)
C(3),C(2),C(21)	116.9(1.9)		
S,C(3),C(2)	89.1(1.4)		
C(3),C(1),H(11)	141.0(1.7)		
C(3),C(1),H(12)	110.1(1.5)		
H(11), C(1),H(12)	108.6(1.9)		
C(1),C(3),H(31)	108.0(1.6)		
C(1),C(3),H(32)	143.8(1.9)		
H(31), C(3),H(32)	107.2(2.0)		
H(2),C(2),C(21)	105.0(2.0)		

The estimated standard deviations (e.s.d.'s) are slightly larger than those for the cis-isomer because lack of time has prevented as many

refinements being made.

The ring puckering angle is 31.5° . The angle between the planes containing C(1), C(3) and S, and the sulphonyl oxygen bond is 119.4° and that between the plane containing C(1), C(3) and C(2), and the C(2)-C(21) bond is 53.1° . These facts are illustrated (fig. 10) and compared to those for the cis-isomer (fig. 4).

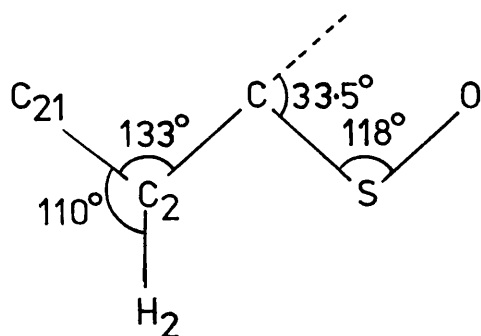


fig. 4

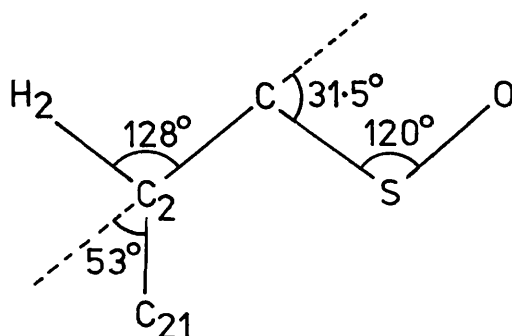
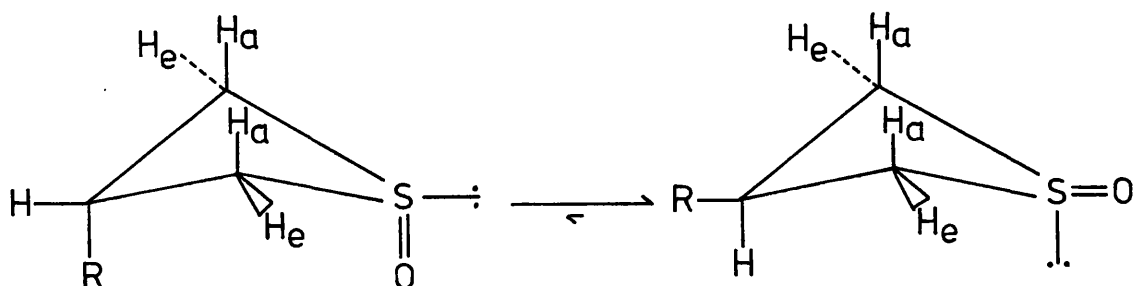


fig.10

Thus in the cis-isomer both ring substituents occupy equatorial positions but in the trans-isomer, the oxygen is equatorial and the p-bromophenyl group is axial. As previously stated (Chapter One) the crystal structure of the cis-isomer approximates very well to that expected of the predominant conformer (b) in solution.

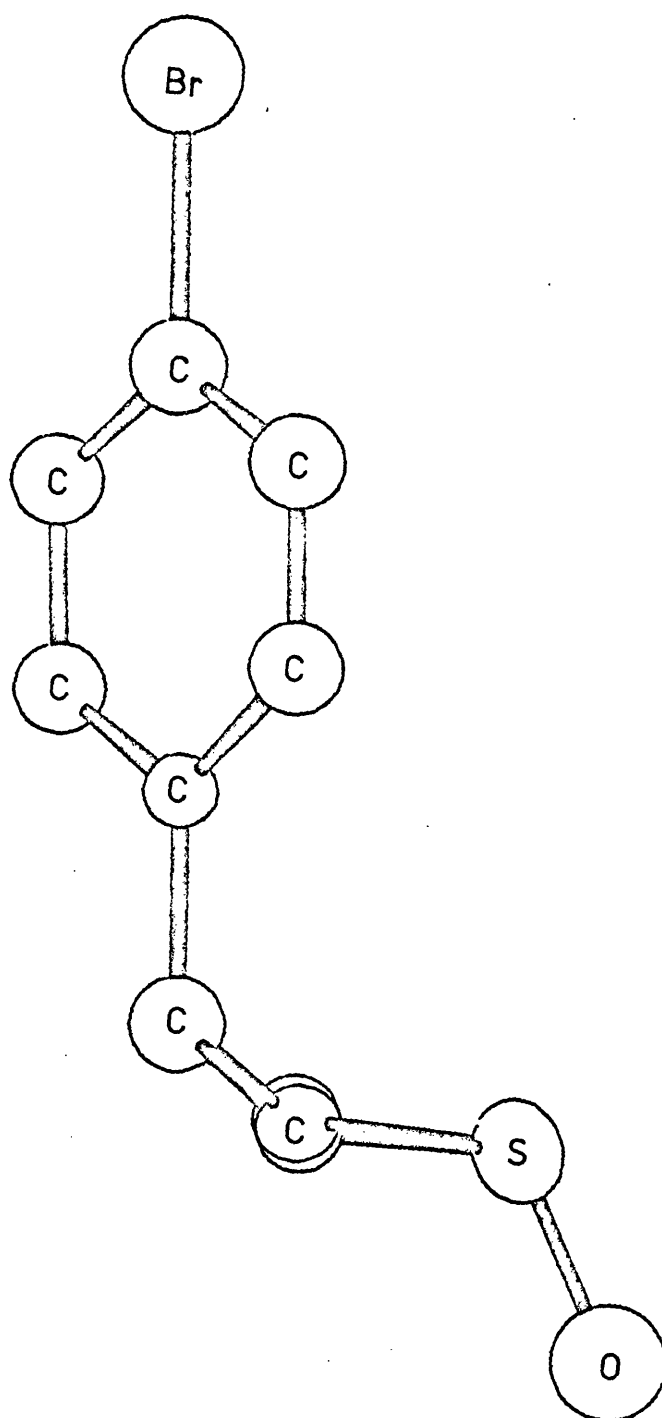


(a)

(b)

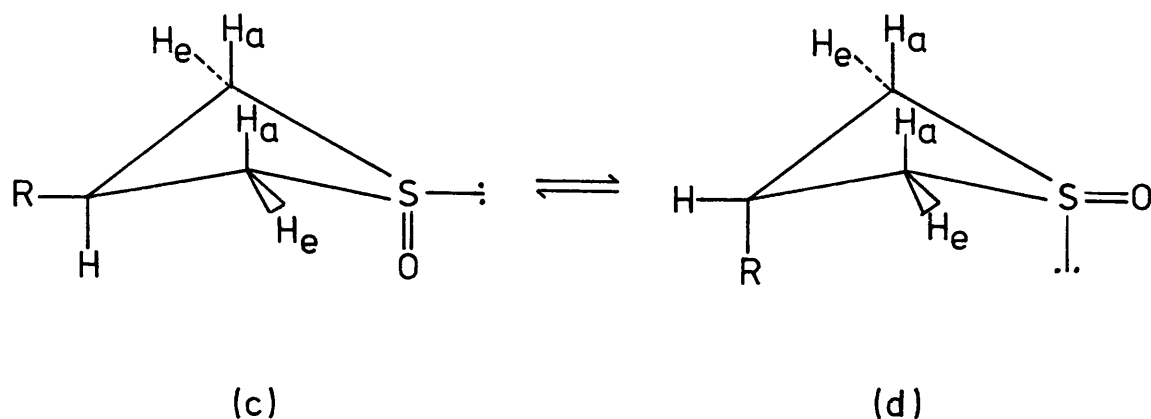
trans-p-Bromophenylthietane 1-Oxide.

(Scale drawing)



The physical properties of the cis-isomer have all been successfully described by considering that the equilibrium between conformers (a) and (b) lies almost completely over to the right hand side and hence that the properties are derived almost entirely from conformer (b).

There is not expected to be as much difference in energy between the two possible conformers of the trans-isomer (p. 4).



Johnson has however concluded, on the basis of dipole moment studies,^{5b,7} the order of elution of the two isomers on chromatography,^{4,10} and his interpretation of the ¹H n.m.r. spectrum,^{6,10} that conformer (c) is predominant in solution and that the observed physical properties can be explained by consideration of conformer (c) only.

The results reported in Chapter One appeared to agree with these previous assignments of conformation, although a number of doubts were expressed, especially in the case of the trans-isomer. It was surprising that when R is a small group such as methyl, conformer (c) still appeared to be predominant (p. 6), and that even when a bulky europium shift reagent was co-ordinated to the sulphonyl oxygen it apparently remained so (p.9).

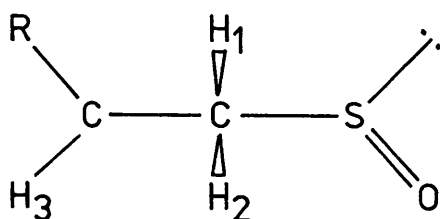
The crystal structure of trans-3-p-bromophenylthietane 1-oxide approximates very well to that expected of conformer (d). This fact

suggests that it is very unlikely that conformation (c) is much more highly populated than (d) in solution, and hence it seems of doubtful value to interpret the physical properties of the trans-isomer in terms of conformer (c) only.

The ^1H n.m.r. spectrum of conformer (d) is expected to be very similar to that exhibited by the cis-isomer [i.e. conformer (b)], since the only difference between (d) and (b) is the position of the R group. The spectra of both cis and trans-isomers have been shown to vary very little with large changes in R. The fact that the n.m.r. spectrum of the trans-isomer is very different from that of the cis-isomer suggests that conformer (d) is not completely predominant in solution.

It therefore seems that the most likely explanation of the observed physical properties of the trans-isomer is that they are due to approximately equal concentrations of both conformers (c) and (d).

The rate of interconversion between the conformers (c) and (d) is expected to be very fast on the n.m.r. time scale,⁵ and if there are approximately equal concentrations of both conformers, then the n.m.r. spectrum observed will be approximately midway between that expected for the two single conformers. The α -protons that are axial in one conformer become equatorial when the ring 'flips' to the other conformation, and hence the average effect is somewhere between the two. This situation can be represented by a planar ring system (172) (drawn sideways on).



(172)

Protons H_1 and H_2 are still not identical (H_2 is always cis with respect to sulphonyl oxygen and H_1 is always trans). The differences between the two sets of protons are however very much reduced and it must be assumed that they are approximately equivalent. The signal derived from the α -protons is a broad doublet, a doublet due to coupling with the single β -proton, with broadening because the α -protons are not completely equivalent.

The fact that the β -proton in the trans-isomer is always deshielded with respect to that in the cis-isomer can still be explained in terms of an acetylenic anisotropy of the sulphur-oxygen bond (p. 6).

This scheme also enables an alternative interpretation of the europium shift reagent data (Section 1.4). As progressively larger amounts of shift reagent are added to a solution of the trans-isomer, so the n.m.r. spectrum gradually changes until it resembles that of the cis-isomer. This is what would be expected, since co-ordination of a bulky group to the sulphonyl oxygen will make the conformation in which the oxygen is equatorial (d) much more favourable than that in which it is axial (c), and as previously explained the n.m.r. of conformer (d) is expected to resemble that of the cis-isomer.

The fact that no W-coupling is observed when $R = \text{methyl}$ suggests that there is a slight difference in geometry between (d) and 3,3-dimethylthietane 1-oxide (e) (p. 7).

All of the solution properties of the trans-isomer will be due to an approximately equal concentration of both conformers (c) and (d). The dipole moment data ^{5b,7} for the trans-isomer should therefore reflect a sulphur-oxygen bond mid-way between axial and equatorial. The fact that it has been interpreted as meaning that the sulphur-oxygen bond is axial⁷ could be due to an insufficiently accurate knowledge of the geometry of the

remainder of the molecule.

There is very little difference between the solid state (nujol) and the solution infrared spectra for the trans-isomer.

Conclusion.

It is reasonable to interpret the physical properties of a solution of cis-3-substituted thietane 1-oxide in terms of its solid state structure only. The corresponding properties of a solution of the trans-3-substituted thietane 1-oxide are more reasonably interpreted by assuming that the solution contains approximately equal amounts of both possible conformers.

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SUMMARY

3-Substituted thietane 1-oxides have been investigated by proton, carbon-13, and lanthanide induced shift, magnetic resonance studies, and for the two isomers of 3-p-bromophenylthietane 1-oxide, by X-ray crystallography. It has been concluded that it is reasonable to interpret the physical properties of a solution of the cis-isomers in terms of the single conformer in which both substituents occupy equatorial positions, and those of the trans-isomers in terms of approximately equal amounts of both possible conformers.

cis and trans-3-Methylthietane 1-oxide react with toluene-p-sulphonyl isocyanate to give the thietane imides with epimerisation. In polar solvents the reaction involves prior equilibration of the sulphoxides, but in non-polar solvents this does not occur.

Pentamethyl-1-phenylphosphetan 1-oxides react with toluene-p-sulphonyl isocyanate to give the phosphetan imides with retention of configuration. The reaction has been shown to be first order in both reactants. Optically active acyclic phosphine oxides however react to give racemic phosphine imides. The first step of this reaction involves racemisation of the phosphine oxide. Kinetic studies have shown this process to be first order in phosphine oxide and second order in isocyanate.

Investigations suggest that if a reaction involves putting a formal positive charge on sulphur in a thietane or its 1-oxide, and if there is a good nucleophile in solution, then nucleophilic attack will occur at the α -carbon and ring opened products will result.

The photolysis and flash thermolysis of a series of 4π -electron cyclic sulphones have been investigated. These reactions are thought to involve an unsaturated sulphene which rearranges to give a series of cyclic sulphinate esters. In the thermolysis reaction these then fragment.

A number of novel organo-platinum complexes have been prepared and their structures have been determined by n.m.r. and infrared spectroscopy. Attempts to generate stable sulphene-metal complexes by rearrangement of the above complexes induced by thermal, photochemical, and chemical means, have not been successful.