

THE PREPARATION AND PYROLYSIS OF
SOME CYCLIC SULPHONES

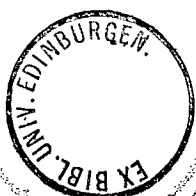
by

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DOCTOR OF PHILOSOPHY

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Dedication

To Professor J.I.G. Cadogan - a great teacher

Acknowledgements

I would like to thank Dr. Ian Gosney for suggesting the topic of research and for his excellent supervision over the three years. I also wish to express my gratitude to Professor J.I.G.Cadogan, the originator of this area of research, for his continued interest. Thanks also go to my colleagues in Lab 29, past and present, for many helpful discussions and advice on various practical techniques.

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Finally, thanks are due to the Science Research Council for financial support.

A B S T R A C T

The addition of 1,3-dipoles and mononuclear electrophilic species to the double bond of 3-thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide, a masked form of *cis*-1,3,5-hexatriene, has been studied. Flash vacuum pyrolysis of the cyclopropyl compound, formed by photolysis of the diazomethane adduct, leads to loss of SO₂ to give 1,4-cycloheptadiene, presumably via a Cope Rearrangement of *cis*-1,2-divinylcyclopropane. The aziridines formed by reaction with azidoformates undergo a similar transformation on pyrolysis to provide a useful synthesis of N-alkoxycarbonyl-4,5-dihydroazepines. In the case of its tetrachlorothiophen dioxide adduct the compound behaves differently, acting as a dienophilic acetylene equivalent by loss of SO₂ and butadiene on pyrolysis.

8-Thiabicyclo[4.3.0]non-3-ene 8,8-dioxide and its 2,5-bridged analogues have been prepared and their pyrolysis studied. Epoxidation of the double bond of these compounds leads to a change in the route of thermal decomposition and provides a synthesis of novel divinylepoxides. The corresponding N-ethoxycarbonyl aziridines have also been prepared but their pyrolysis does not give any useful products.

The isomeric 7-thiabicyclo[4.3.0]non-3-ene 7,7-dioxide and its 2,5-bridged analogues have also been prepared and are found to decompose on pyrolysis either with loss of SO₂ and ethylene or by a retro Diels-Alder reaction, depending on the degree of strain present. The epoxides of these compounds

break down, exclusively by loss of SO₂ and ethylene, to give products which can also be obtained by pyrolytic loss of CO₂ and CO from the corresponding anhydrides.

The first ionisation energies of a number of the sulphones have been determined and the values obtained are discussed in terms of a possible through-space interaction between the sulphone group and the double bond. The correlation between ionisation energy and ease of epoxidation and aziridine formation for these compounds is also considered.

Photochemical [2+2] cycloaddition between maleic anhydride and 2,3-dihydrothiophen dioxide gives 3,5-dioxo-4-oxa-8-thiatricyclo[5.3.0.0^{2,6}]decane 8,8-dioxide. By simple modification of the anhydride function, a large number of compounds with the novel 2-thiabicyclo[3.2.0]heptane ring-system have been prepared and their pyrolysis studied. 2-Thiabicyclo[3.2.0]hept-6-ene has also been obtained and preliminary studies indicate that it acts as a cyclobutadiene equivalent on pyrolysis. Selective decoupling studies in the high resolution NMR spectra of these compounds have been used to confirm their structure and stereochemistry in two cases.

C O N T E N T S

Page No

INTRODUCTION

A. <u>Extrusion reactions</u>	1
B. <u>Extrusion of sulphur dioxide from cyclic molecules</u>	
1. Three-membered rings	
a. Thiirane dioxides	8
b. Thiirene dioxides	10
c. Three-membered rings containing hetero-atoms	11
2. Four-membered rings	
a. Thietane dioxides	12
b. Thiete dioxides	14
c. Four-membered rings containing hetero-atoms	15
3. Five-membered rings	
a. Sulpholanes	16
b. Sulpholenes	17
c. Bicyclo[3.1.0] and [3.2.0] systems	20
d. Benzo- and other aromatic fused sulpholenes	22
e. Thiophen dioxides	27
f. Five-membered rings containing nitrogen	29
g. Five-membered rings containing oxygen or sulphur	32
h. 1,8-Naphtho systems	35

	Page No
4. Six-membered rings	
a. Sulphones	36
b. Sultines and sulphites	38
c. Sultones, thiosultones and sultams	40
5. Seven- and eight-membered rings	
a. Thiopine dioxides	43
b. Seven- and eight-membered rings containing hetero-atoms	44
6. Bridged ring systems	
a. 7-Thiabicyclo[2.2.1] structures	46
b. Bicyclo[2.2.2] structures	49
c. Sulphone-bridged seven-membered rings	50
d. Sulphone-bridged eight-membered rings	51
e. Propellanes	53
7. Cyclophanes	54
C. <u>Programme of Research</u>	57

EXPERIMENTAL

A. <u>Symbols and Abbreviations</u>	60
B. <u>Instrumentation and General Techniques</u>	61
C. <u>Preparation and reactions of 3-Thiabicyclo- [3.2.0]hept-6-ene 3,3-dioxide</u>	
1. Preparation	68
2. Reaction with 1,3-dipoles	69
3. Pyrolysis of 1,3-dipole adducts	75
4. Preparation of the 3-Thiatricyclo- [3.3.0.0 ^{6,8}]octane 3,3-dioxide ring system	77
5. Pyrolysis of 3-Thiatricyclo[3.3.0.0 ^{6,8}]- octane 3,3-dioxide and derivatives	85
6. Diels-Alder reactions	86
D. <u>The 8-Thiabicyclo[4.3.0]non-3-ene 8,8-dioxide ring system</u>	
1. Preparation and pyrolysis of 8-Thiabicyclo- [4.3.0]non-3-ene 8,8-dioxide and bridged analogues	89
2. Preparation and pyrolysis of sulphone epoxides	101
3. Preparation and pyrolysis of sulphone aziridines	106

- E. The 7-Thiabicyclo[4.3.0]non-3-ene 7,7-dioxide ring system
1. Preparation and pyrolysis of 7-Thiabicyclo-
[4.3.0]non-3-ene 7,7-dioxide and bridged
analogues 115
 2. Preparation and pyrolysis of sulphone
epoxides 120
 3. Preparation of sulphone aziridines 126
- F. Preparation and pyrolysis of bicyclic anhydrides and derivatives
1. Preparation and pyrolysis of bicyclic
anhydrides 132
 2. Preparation and pyrolysis of anhydride
epoxides 134
 3. Preparation and pyrolysis of anhydride
aziridines 138
- G. Preparation and pyrolysis of 3,5-Dioxo-4-oxa-
8-thiatricyclo[5.3.0.0^{2,6}]decane 8,8-dioxide
and derivatives
1. Preparation and pyrolysis of 3,5-Dioxo-4-oxa
-8-thiatricyclo[5.3.0.0^{2,6}]decane 8,8-
dioxide 144
 2. Preparation and pyrolysis of 2-Thiabi-
cyclo[3.2.0]heptane-6,7-dicarboxylic
acid and its diesters 145

	Page No
3. Preparation of some mono-amides and the dihydrazide of 2-Thiabicyclo[3.2.0]heptane-6,7-dicarboxylic acid 2,2-dioxide	151
4. Preparation and pyrolysis of cyclic imides of 2-Thiabicyclo[3.2.0]heptane-6,7-dicarboxylic acid 2,2-dioxide	155
5. Reduction of 3,5-Dioxo-4-oxa-8-thiatricyclo[5.3.0.0 ^{2,6}]decane 8,8-dioxide	159
6. Preparation and pyrolysis of 2-Thiabicyclo[3.2.0]hept-6-ene 2,2-dioxide and derivatives	162

DISCUSSION

A. <u>Preparation and pyrolysis of some derivatives of 3-thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide</u>	
1. General background	165
2. Addition of 1,3-dipoles	167
3. Pyrolysis of 1,3-dipole adducts	170
4. Preparation of the 3-thiatricyclo[3.3.0.0 ^{6,8}]octane 3,3-dioxide ring system	172
5. Pyrolysis of these compounds	178
6. Other addition reactions of 3-thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide	179

B.	<u>Preparation and pyrolysis of 8-thiabicyclo-</u> <u>[4.3.0]non-3-ene 8,8-dioxide and related</u> <u>systems</u>	
1.	Preparation of unsaturated sulphones	182
2.	Pyrolysis of unsaturated sulphones	184
3.	Use of the retro Diels-Alder reaction in synthesis	187
4.	Preparation and pyrolysis of sulphone epoxides	190
5.	Preparation and pyrolysis of sulphone aziridines	193
C.	<u>Preparation and pyrolysis of 7-thiabicyclo-</u> <u>[4.3.0]non-3-ene 7,7-dioxide and related</u> <u>systems</u>	
1.	Preparation of unsaturated sulphones	197
2.	Pyrolysis of unsaturated sulphones	200
3.	Preparation and pyrolysis of sulphone epoxides	203
D.	<u>Sulphone reactivity in relation to orbital</u> <u>interactions through space</u>	
1.	Orbital interactions through space	207
2.	Ionisation energies of unsaturated sulphones	211
3.	Correlation between reactivity and ionisation energy	213

E. <u>Preparation and pyrolysis of some bicyclic anhydrides and derivatives</u>	
1. General background	220
2. Preparation and pyrolysis of bicyclic anhydrides	221
3. Preparation and pyrolysis of anhydride epoxides	222
4. Preparation and pyrolysis of anhydride aziridines	227
F. <u>Preparation and pyrolysis of some derivatives of 2-thiabicyclo[3.2.0]heptane 2,2-dioxide</u>	
1. General background	230
2. Preparation, structure and pyrolysis of the 2,3-dihydrothiophen dioxide/maleic anhydride adduct	231
3. Preparation and pyrolysis of diacid and diesters	238
4. Preparation of mono-amides and the dihydrazide of 2-thiabicyclo[3.2.0]-heptane-6,7-dicarboxylic acid 2,2-dioxide	244
5. Preparation and pyrolysis of cyclic imides	247
6. Reduction of the 2,3-dihydrothiophen dioxide/maleic anhydride adduct	249
7. Preparation and pyrolysis of 2-thiabicyclo[3.2.0]hept-6-ene 2,2-dioxide and derivatives	252

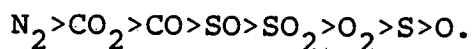
Appendix A - Photoelectron Spectra 264

REFERENCES 265

I N T R O D U C T I O N

A. Extrusion reactions

Extrusion reactions - reactions in which a small stable molecule is expelled from a cyclic structure either thermally or photochemically - are well known in organic chemistry and have been the subject of several reviews^{1,2}. When the extrusion takes place, the termini of the ring may either recombine to regenerate a smaller ring or undergo other reactions to give acyclic products. Among the commoner fragments which can be extruded are nitrogen, carbon monoxide and carbon dioxide, sulphur monoxide and sulphur dioxide, and elemental oxygen, sulphur, selenium and even tellurium³, together with small organic molecules such as acetone, acetonitrile, ethylene, acetylene and certain organophosphorus species. Stark and Duke¹ give an approximate order for the ease of extrusion of these fragments as follows:



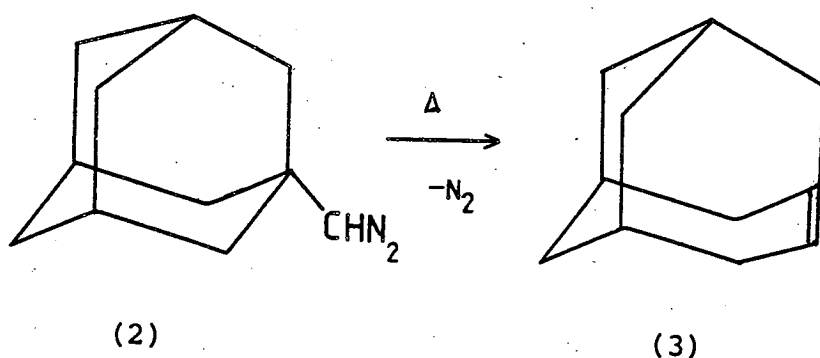
A number of techniques have been used to bring about extrusion reactions. These include thermolysis* of substrate, either neat or in solution, and pyrolysis, particularly under flash vacuum conditions, as well as photochemical extrusion.

* The terms "thermolysis" and "pyrolysis" have often been used interchangeably to describe thermal extrusion reactions and Brown has discussed this point⁴. In the present discussion "thermolysis" is used for reactions which involve heating, either neat or in solution, at temperatures up to 400°C, whereas the use of higher temperatures and all reactions carried out under flash vacuum conditions are denoted by "pyrolysis".

In addition a number of novel techniques such as radio frequency plasma extrusion have been reported recently. The examples which follow serve to illustrate the wide range of extrusion reactions found in organic chemistry, as well as some of the typical conditions used.

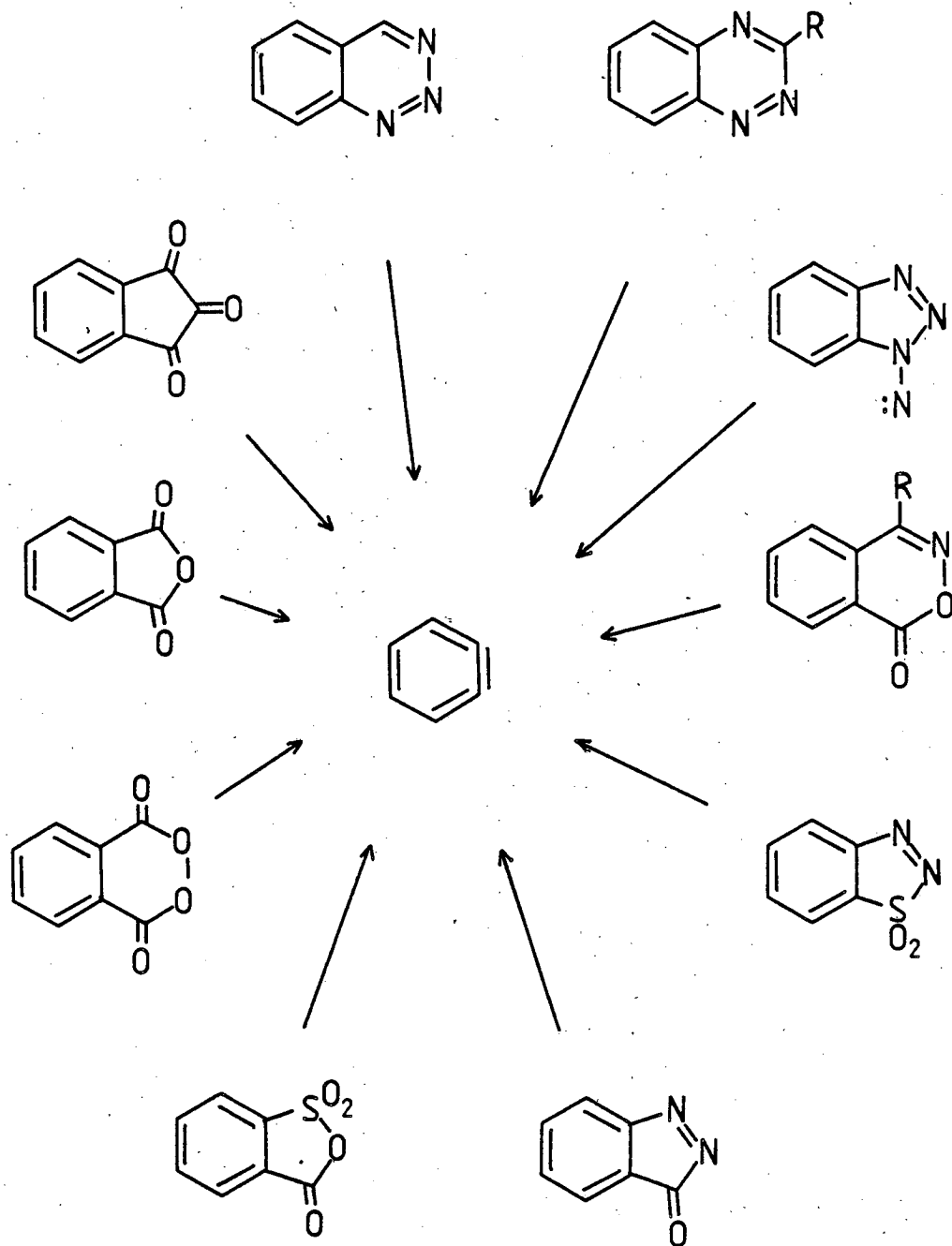
The diversity of possible fragmentation processes can be seen in Schemes 1 and 2 which show the breakdown of several benzo-fused five- and six-membered ring heterocycles with loss of either one, two or three fragments to give benzyne and the fulvenallene derivatives (1), respectively.

In recent years the technique of flash vacuum pyrolysis, with its unique conditions of low pressure and short contact time, has proved to be ideally suited to the study of extrusion reactions and is now the standard technique in many research groups². One of the best methods available for carbene generation, for example, is the flash vacuum pyrolysis of diazoalkanes⁵. Thus extrusion of N_2 from 1-adamantyldiazomethane (2) by pyrolysis at $350^\circ C$ and 10^{-3} mmHg⁶ affords homo-



adamant-3-ene (3) via intramolecular trapping of the intermediate carbene.

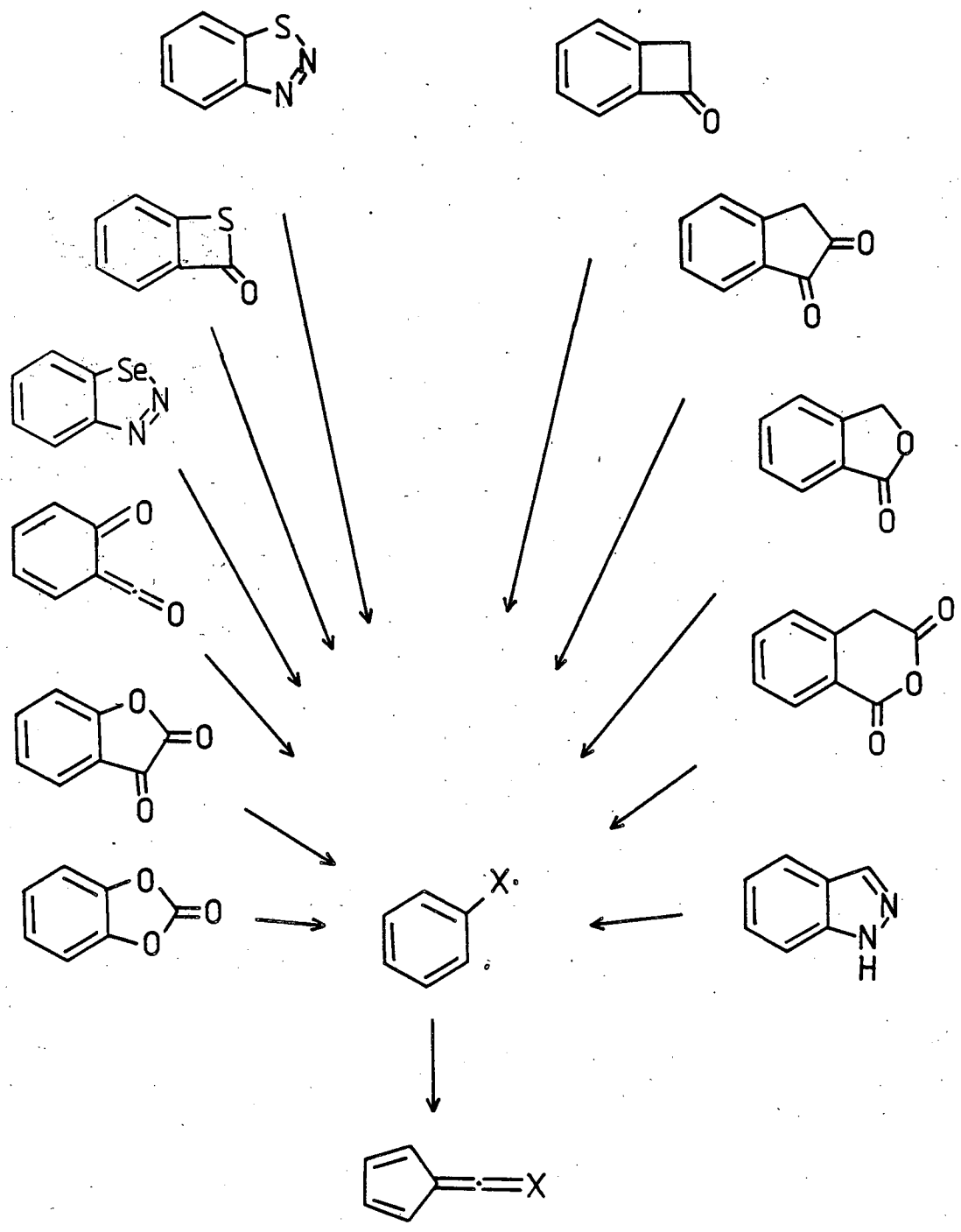
Derivatives of 2,2-dimethyl-1,3-dioxane-4,6-dione (Meldrum's Acid) have also been used to generate carbenes by extrusion of



Scheme 1

X = O, S, Se

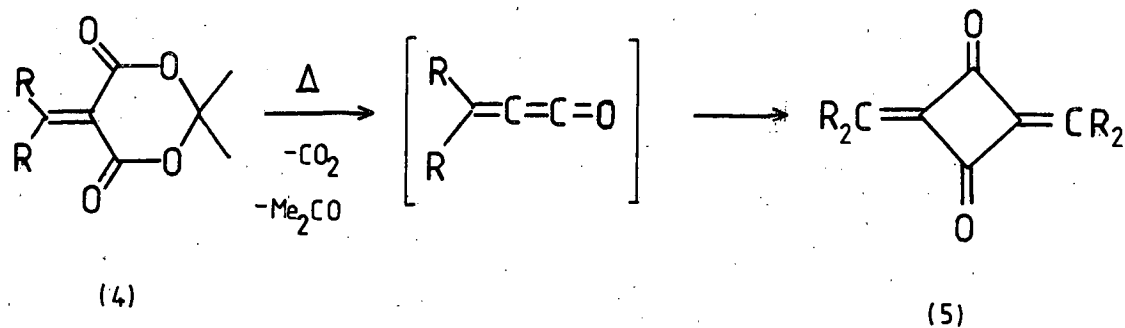
X = CH₂



(1)

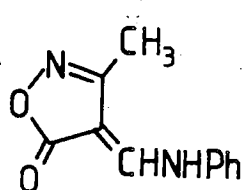
Scheme 2

CO, CO₂ and acetone⁵, while the 5-alkylidene derivatives (4) extruded only CO₂ and acetone on pyrolysis to produce an

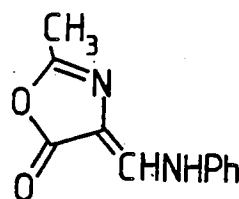


alkylidene ketene which was isolated as its dimer (5).⁷

It can be difficult to predict which fragments will be lost from a given molecule and in some cases the extrusion processes for two apparently similar systems are entirely different. For example, Wentrup found that the isoxazolone (6) lost acetonitrile and CO₂ at 650°C to give products derived



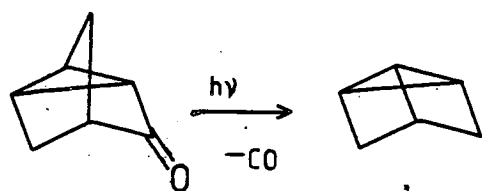
(6)



(7)

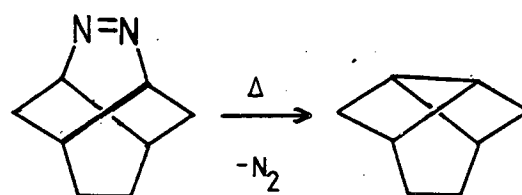
from PhNHCH=C:⁸ while the isomeric oxazolone (7) lost only CO to give the N-acetylketenimine⁹.

Low temperature photochemical extrusion of carbon monoxide has been used in a number of cases to prepare highly strained products. Thus, photolysis of the ketone (8) at -78°C gave



(8)

(9)

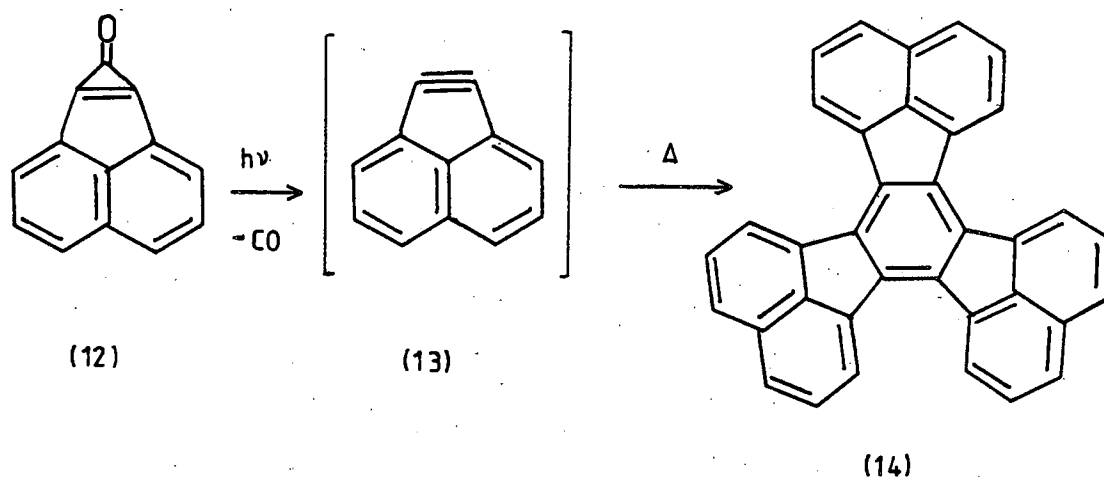


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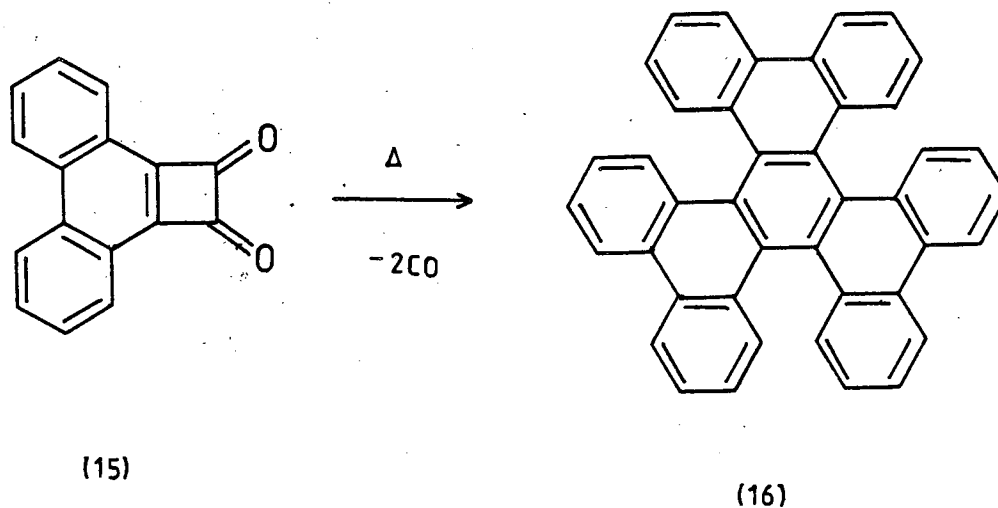
(11)

a low yield of tricyclo[2.2.0.0^{2,6}]hexane (9)¹⁰. Paquette found that thermal extrusion of nitrogen from (10) by heating in a sealed tube at 230°C produced the very similar compound (11)¹¹.

Low temperature photochemical extrusion of CO was also used by Chapman in the first preparation of acenaphthene. Thus, irradiation of the cyclopropanone (12) in an argon matrix

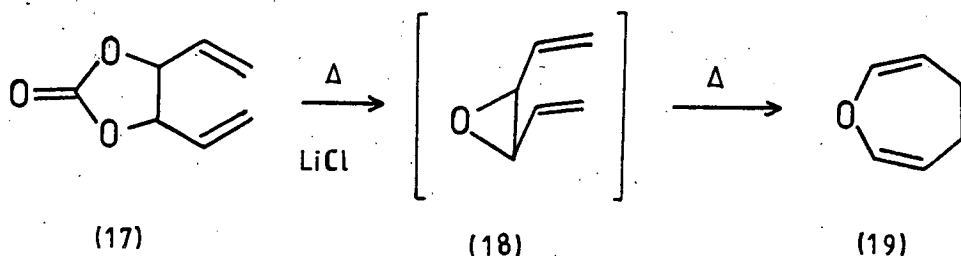


at 15K gave acenaphthene (13) which formed the trimer (14) on warming to room temperature¹². Thermal extrusion of two molecules of CO from the diketone (15) by flash vacuum pyrolysis



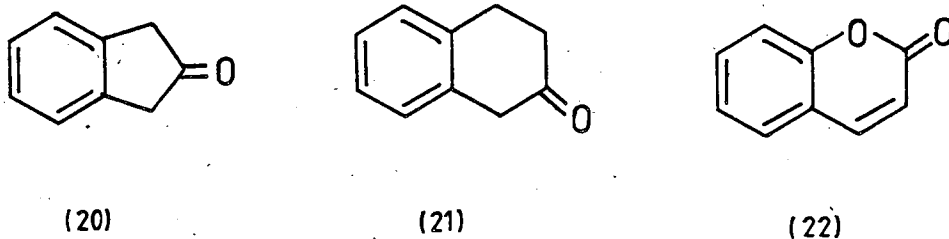
similarly gave the trimer - hexabenzotriphenylene (16)¹³.

Besides the standard methods of thermal and photochemical extrusion several other methods have been used to a limited extent. In some cases thermolysis in the presence of a catalyst can give improved yields and this method was used by Braun¹⁴ who heated divinylethylene carbonate (17) at



200°C, in the presence of lithium chloride, to produce 4,5-dihydro-oxepine (19) via extrusion of CO₂ followed by Cope Rearrangement of the resulting *cis*-1,2-divinyloxirane (18).

A recent novel method for bringing about an extrusion process is reaction in a radio frequency plasma. Miller¹⁵ found that both 2-indanone (20) and 2-tetralone (21) lose



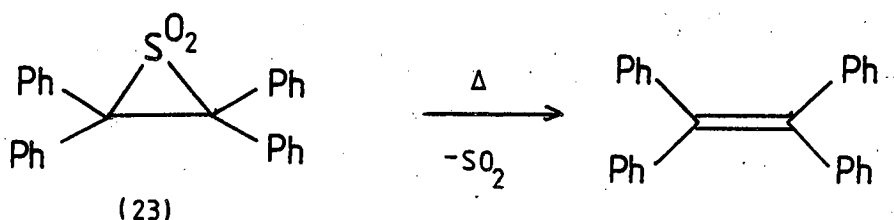
CO on exposure to a 13.56MHz discharge to give reasonable yields of benzocyclobutene and indane, respectively, while coumarin (22) extrudes both CO and CO₂ to give a mixture of benzofuran and styrene.

B. Extrusion of sulphur dioxide from cyclic molecules

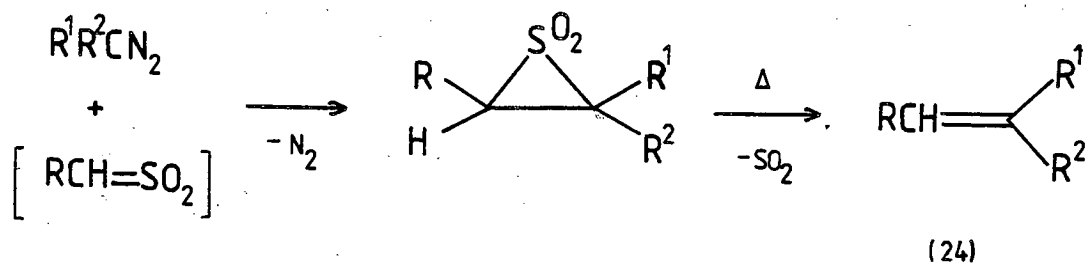
1. Three-membered rings

a. Thiirane dioxides

The first observation of SO_2 extrusion from a three-membered ring was made by Staudinger and Pfenninger in 1916¹⁶. They found that the thiirane dioxide (23), prepared from diphenyldiazomethane and SO_2 , lost SO_2 on heating above its melting point to give tetraphenylethylene. Less highly



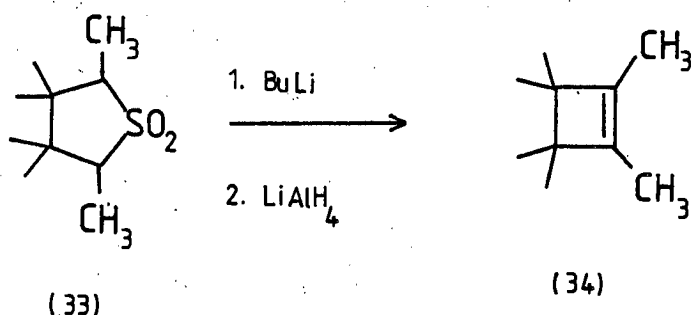
substituted thiirane dioxides are more unstable and decompose slowly at room temperature. Thermolysis of thiirane dioxides as a synthetic route to alkenes has been reviewed by Fischer¹⁷ and gives good yields of unsymmetrically substituted alkenes (24) by the route shown¹⁸.



The thiirane dioxide (25) was assumed to be an intermediate in the reaction of benzyne with divinyl sulphone¹⁹ but decomposed under the reaction conditions to give a mixture of 1,4-dihydronaphthalene and naphthalene. The thiirane dioxide (26) is unusual in that it does not give any of the expected

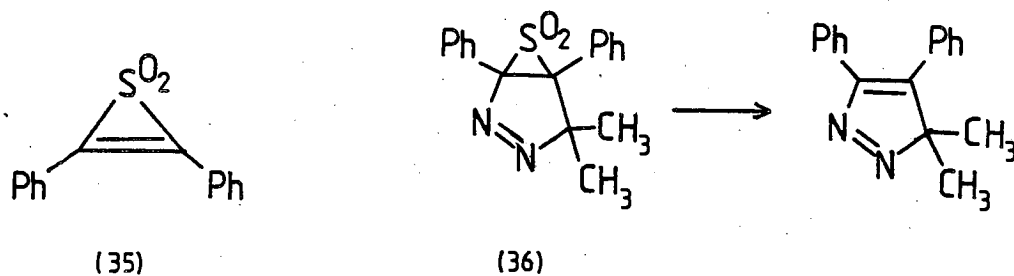
with aqueous potassium hydroxide to give an 80% yield of the bicyclooctene (32) via the thiirane dioxide (31)²².

Paquette has also shown that reaction of the unhalogenated sulphones (33) with *n*-butyl lithium followed by lithium aluminium hydride provides a synthesis of the dimethylcyclobutenes (34)²³.



b. Thiirene dioxides

Carpino obtained the first thiirene dioxide (35) by treating α,α' -dibromodibenzylsulphone with triethylamine²⁴. and a similar method has since been used²⁵ to prepare these compounds from the α,α -dichlorodibenzyl sulphone.



The thiirene dioxides are generally much more stable than their saturated analogues but they undergo decomposition cleanly on heating to give an acetylene and SO_2 . Philips²⁶ has obtained kinetic evidence that this extrusion is stepwise rather than concerted. The thiirene dioxides also lose SO_2

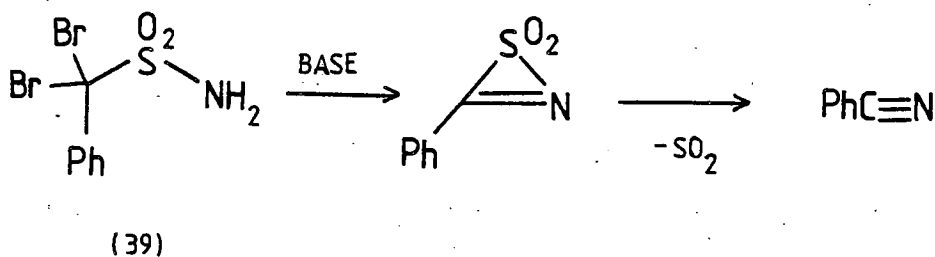
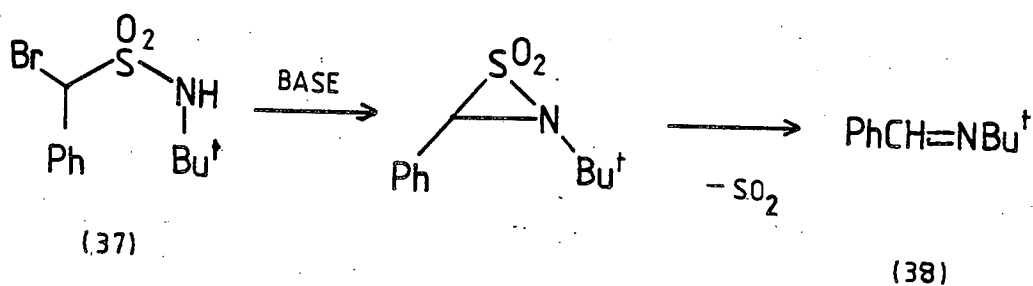
readily in the mass spectrometer so that only the peak for the resulting acetylene is seen under normal conditions²⁷.

Treatment of (35) with a diazoalkane provides a useful synthesis of pyrazoles²⁸ by loss of SO₂ from intermediates such as (36). A triazole has been prepared albeit in low yield, by a related reaction of (35) with lithium azide²⁹.

c. Three-membered rings containing hetero-atoms

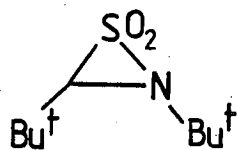
A number of hetero-thiirane and -thiirene dioxides are known, both as intermediates and stable compounds and these have been reviewed by Quast³⁰.

Reaction of the substituted α -halosulphonamide (37) with base resulted in a Ramberg-Bäcklund type reaction to give the imine (38) via a thiazirane dioxide, and the dihalosulphon-

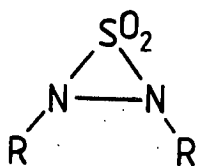


amide (39) similarly gave benzonitrile via a thiazirene dioxide³¹. The compound (40) has been isolated³² and loses

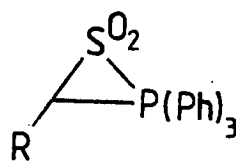
SO₂ at room temperature to give the imine. The thiadiazirane dioxides (41) have also been postulated as reaction intermediates³³, and when isolated they did extrude SO₂³⁴, although



(40)



(41)



(42)

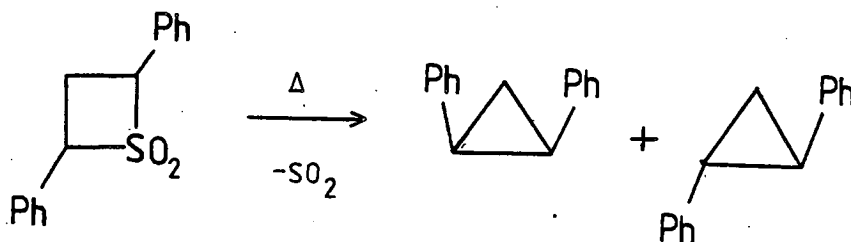
there was competing cleavage of the N-N bond in some cases³⁵.

Treatment of a sulphene with triphenylphosphine gave a phosphorus ylide which was isolated as the quaternary phosphonium salt, presumably via the thiaphosphirane dioxide (42)³⁶.

2. Four-membered rings

a. Thietane dioxides

The first report of SO₂ extrusion from a four-membered ring appeared in 1963 when Dodson and Klose³⁷ prepared the diphenylthietane dioxide (43). This compound loses SO₂, on heating at 250°C for 1 hour, to give a mixture of isomeric diphenyl cyclopropanes (44). The extrusion is likely to be

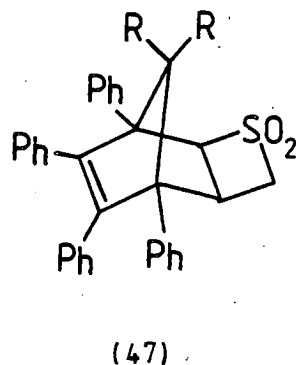
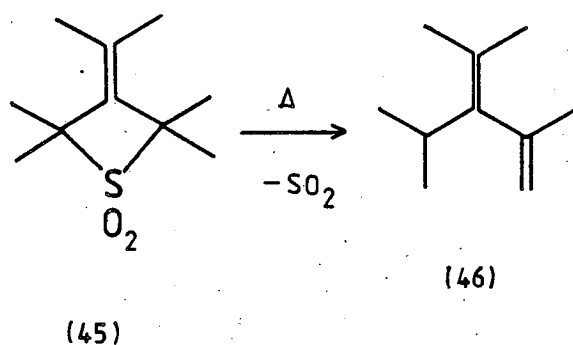


(43)

(44)

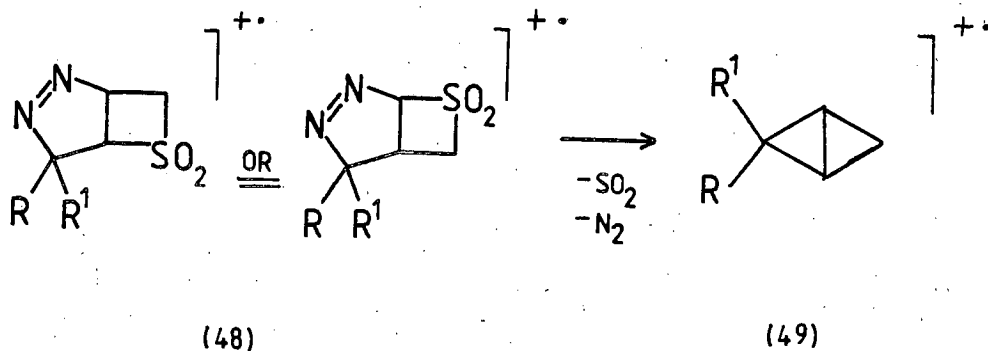
radical in nature since both *cis*- and *trans*-diphenylthietane dioxide give the same mixture of *cis*- and *trans*-diphenylcyclopropanes. Despite this lack of stereospecificity, the utility of this extrusion as a synthetic route to substituted cyclopropanes both by thermolysis³⁸ and photolysis³⁹ has been reported. In the case of 3,3-diethoxy-2-phenylthietane dioxide the cyclopropane formed on pyrolysis was unstable and lost ethanol to give ethyl cinnamate as the final product.⁴⁰

Bushby⁴¹ used the thietane dioxide (45) as a source of the substituted "2-methylenetrimesitylene" diradical which isomerised to the product (46).



Reaction of thiete dioxide with tetracyclone gave tetraphenylcycloheptatriene as the main product⁴² via loss of CO and SO₂ from the intermediate tricyclic thietane dioxide (47; R₂=O). With tetraphenylcyclopentadiene the adduct (47; R=H) was isolated but on heating it underwent a retro Diels-Alder reaction to give tetraphenylcyclopentadiene and a tar derived from the thiete dioxide.

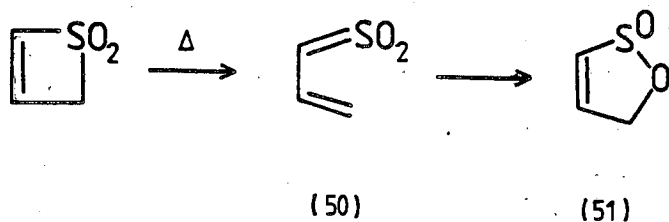
Under mass spectral conditions the bicyclic thietane dioxides (48), formed by addition of a diazoalkane to the double



bond of thiete dioxides, lose both N₂ and SO₂ to give the bicyclo[1.1.0]butane molecular ion (49)⁴³.

b. Thiete dioxides

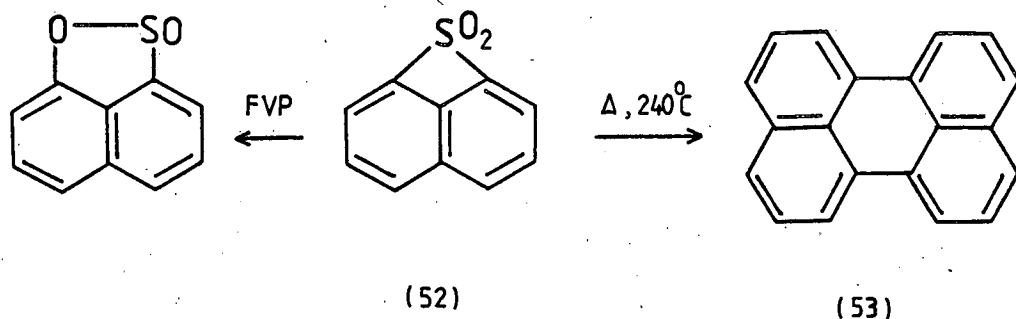
In contrast to their saturated analogues the thiete dioxides do not usually lose SO₂. Instead they undergo a ring expansion on heating to give the five-membered cyclic sultines (51), probably via a vinyl sulphene (50). This



transformation has been reported for the parent compound⁴⁴ as well as for the benzo-,⁴⁵ 2,3-naphtho-,⁴⁶ and 1,8-naphtho-fused analogues⁴⁷. On further pyrolysis the parent sultine (51) loses sulphur monoxide to give a good yield of acrolein. Loss of SO to form carbonyl compounds has also been observed on photolysis of 2-phenylthiete dioxides⁴⁸ and on thermolysis of 2,4-diphenylthiete dioxide⁴⁹.

While flash vacuum pyrolysis of the 1,8-naphthosulphone

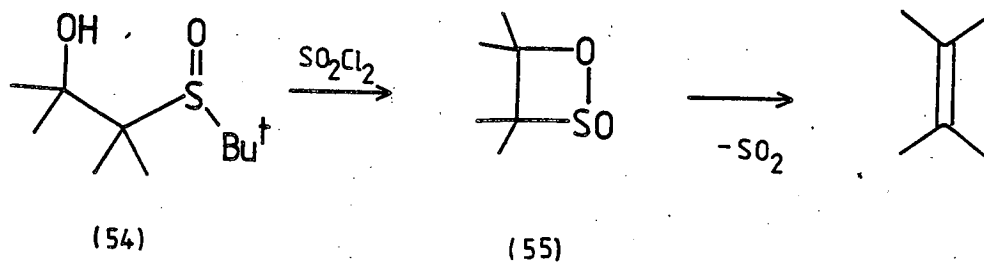
(52) caused mainly ring expansion to the sulfone, heating



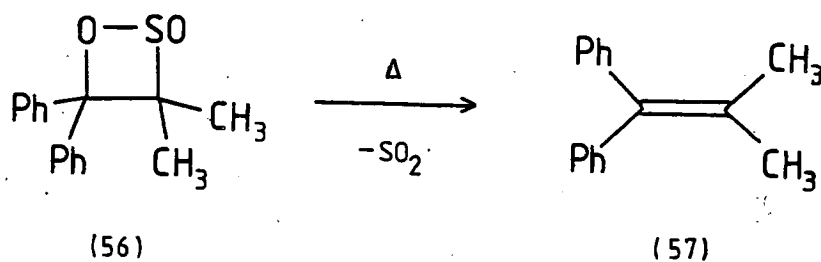
the compound to 240°C led to SO_2 loss and dimerisation of the resulting diradicals to produce perylene (53)⁴⁷.

c. Four-membered rings containing hetero-atoms

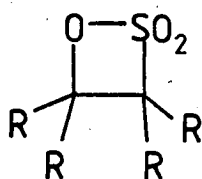
The extrusion of SO_2 from 1,2-oxathietane oxides (55), isomers of the thirane dioxides, has been observed. These compounds were postulated as intermediates in the reaction of



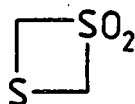
β -hydroxyalkyl-*t*-butyl sulfoxides (54) with sulphuryl chloride to produce alkenes⁵⁰, as well as in other related reactions⁵¹. The stable oxathietane oxide (56) has been prepared⁵² and loses SO_2 at 30°C to give the alkene (57).



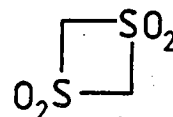
Sulphur trioxide adds to styrene⁵³ and to polyhaloalkenes⁵⁴ to produce the 1,2-oxathietane dioxides (58). On heating, however, these do not lose SO_2 . The carbon to sulphur bond remains intact to give, in the former case, 2-phenylethanesulphonic acid, and in the latter, a β -keto-



(58)



(59)



(60)

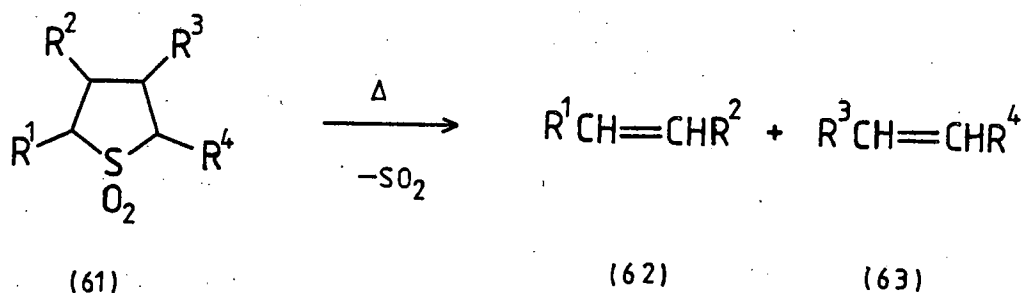
sulphonyl halide.

Block⁵⁵ has recently reported the first synthesis of 1,3-dithietane and its oxides. The thermal decomposition of the sulphones (59) and (60) was examined by photoelectron spectroscopy. The monosulphone (59) was found to lose SO_2 cleanly at 470°C and 10^{-2} mmHg to give thiirane. In the case of the disulphone (60), SO_2 was again lost, at 600°C , to give ethylene and formaldehyde among the products.

3. Five-membered rings

a. Sulpholanes

Solution pyrolysis of the saturated sulphones (61) at 500°C gives SO_2 and the two alkenes (62) and (63)⁵⁶. Mock has shown⁵⁷ that the fragmentation is unlikely to be concerted. The driving force for this reaction is much less than for most other SO_2 containing molecules since there is little ring strain

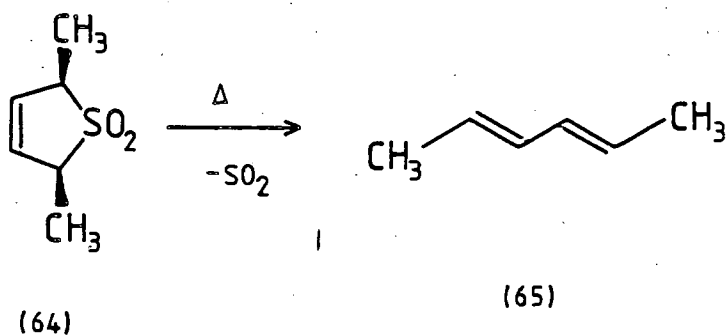


to be relieved by extrusion and no concerted pathway for it to occur. This is reflected in the very high temperature needed to carry out the reaction.

Raasch⁵⁸ has discovered an exception to this behaviour in the case of octachloro- and 3,4-dichlorohexafluorosulpholane. These compounds lose SO₂ to give mainly octachlorocyclobutane and 1,2-dichlorohexafluorocyclobutane respectively.

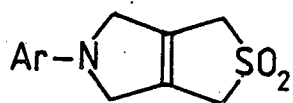
b. Sulpholenes

The reaction of SO₂ with 1,3-dienes, the so called "sulpholene reaction", has been extensively studied, particularly from the stereochemical viewpoint, and is the subject of a comprehensive review⁵⁹. Both this and the reverse reaction: SO₂ extrusion from sulpholenes, have been shown to be specifically suprafacial (disrotatory) processes^{60,61}. Thus for example the *cis*-2,5-dimethylsulpholene (64) gave only the *trans,trans*-hexa-2,4-diene (65), on thermolysis at 100°C while the *trans*-dimethyl

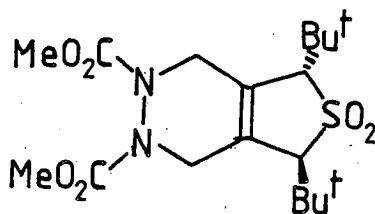


Manipulation of 1,3-dienes using their reaction with SO_2 has proved useful in natural product chemistry. Thus Nesbitt⁶⁹ has separated the *cis* and *trans* isomers of the red bullworm moth pheromone, 12-acetoxydodeca-1,3-diene, by reacting the mixture with liquid SO_2 at -20°C , separating the *cis* isomer which did not react and then heating the sulphone to liberate the pure *trans* isomer. Both Zbiral⁷⁰ and Yamada⁷¹ have achieved isomerisation about the 5,6-double bond of vitamin D derivatives by the addition of SO_2 across the 1,3-diene function and subsequent heating in ethanol to regenerate the isomerised vitamin.

A number of bicyclic sulpholenes have been prepared such as (71) and (72). On heating to 120°C these lose SO_2 to



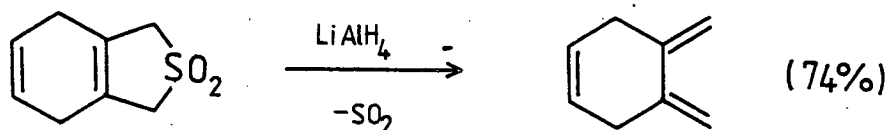
(71)



(72)

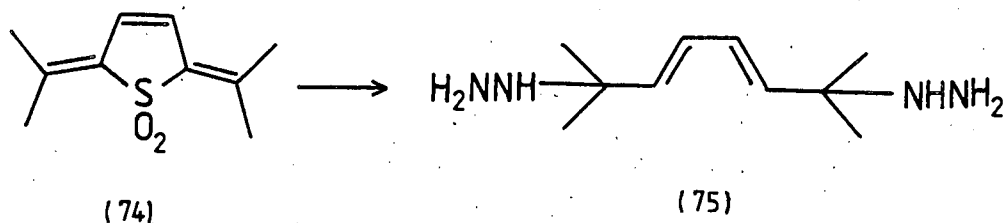
produce 3,4-dimethylenepyrrolidines⁷² and the *cis,trans*-di-*t*-butyldiene⁷³.

In addition to thermolysis and photolysis, the extrusion of SO_2 from sulpholenes has been achieved by various chemical means. The most notable of these is the method of Gaoni⁷⁴ which involves treating the sulpholene with lithium aluminium hydride in boiling ether. This technique gives good yields of the corresponding diene as shown in the example (73).



(73)

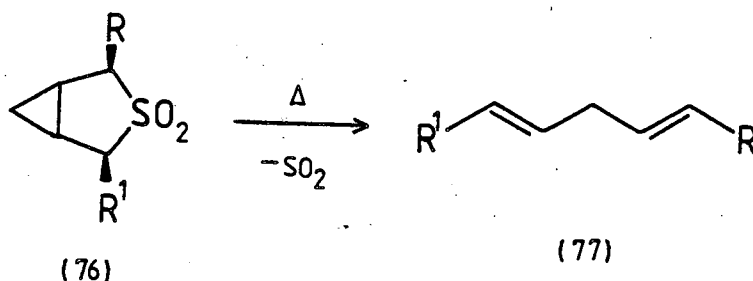
Another example of chemical extrusion is provided by the 2,5-diisopropylidene sulpholene (74) which lost SO_2 on treatment



with hydrazine hydrate to give the addition compound (75)⁷⁵. In both cases the reagent used is a strong reducing agent and the SO_2 is converted into H_2S .

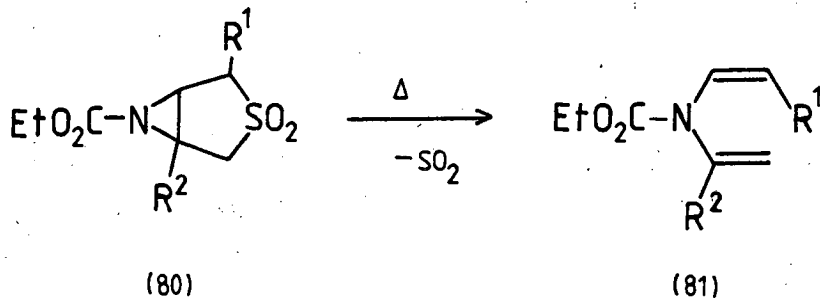
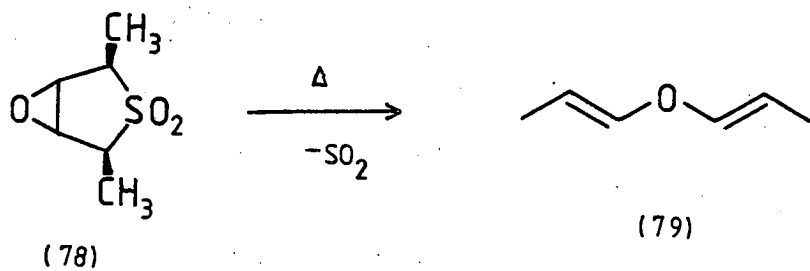
c. Bicyclo[3.1.0] and [3.2.0] systems

Mock has prepared the cyclopropane fused sulpholanes (76; $\text{R}, \text{R}^1 = \text{H}, \text{CH}_3$)⁷⁶ by photolysis of the adduct from the reaction



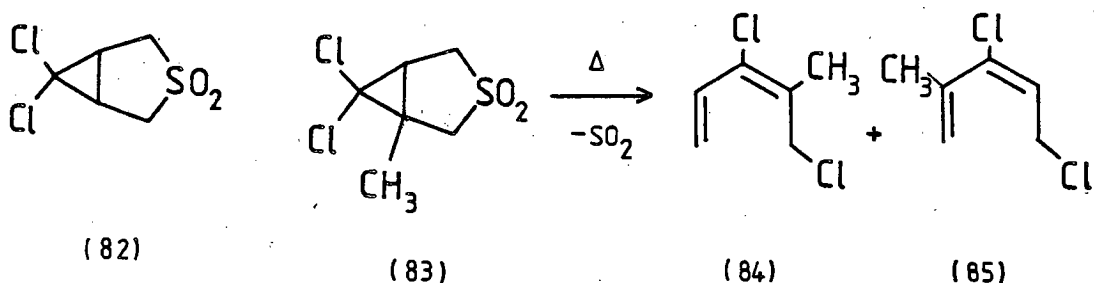
of diazomethane with the corresponding sulpholenes. On heating to 150°C these compounds lose SO_2 to give the 1,4-dienes (77). An exception is the compound (76; $\text{R}, \text{R}^1 = -\text{CH}_2\text{CH}_2\text{CH}_2-$) which failed to extrude SO_2 even at 300°C .

In a related study, Mock observed that the *cis*-dimethyl epoxide (78) and its *trans* isomer decomposed stereospecifically on thermolysis⁷⁶ to give *trans,trans*-dipropenyl ether (79) and the *cis,trans* isomer respectively. This method was used by



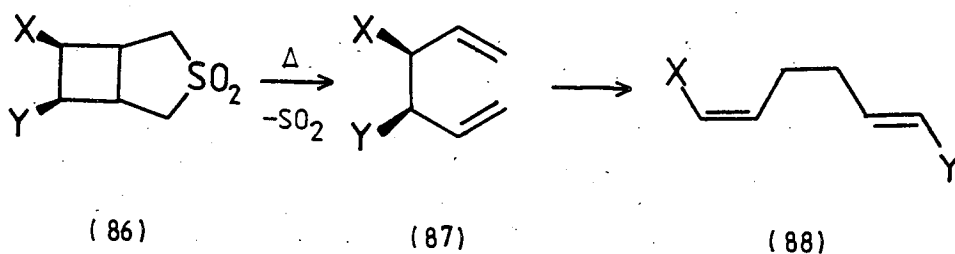
Meyers⁷⁷ for the synthesis of substituted divinyl ethers and also divinyl carbamates (81) from the aziridines (80). In this case rapid heating of the compounds to 250°C brought about the extrusion reaction in good yield.

The compound (82) was prepared by Mock⁷⁶ and similar



dichlorocarbene adducts have since been the subject of a detailed study by Gaoni⁷⁸. The methyl derivative (83), for example, was found to extrude SO₂ on distillation at 140-170°C to give a mixture of dienes (84) and (85), formed via a [1,3] chlorine shift, in 72% yield.

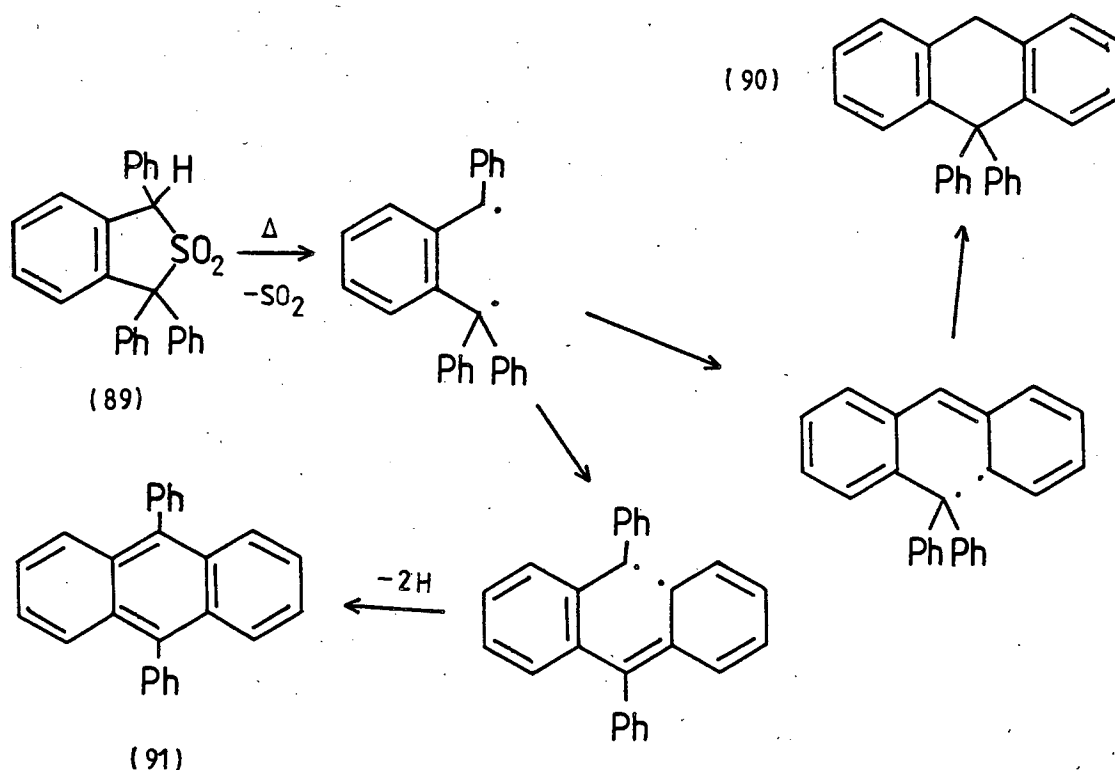
Recent work from this laboratory^{79,80} has utilised the thermal extrusion of SO₂ from the cyclobutasulpholane derivatives (86), readily obtained from the sulpholene-maleic anhydride photoadduct, to provide a synthesis of the *cis*-1,2-divinyl



compounds (87). In the case where X,Y was acyclic these underwent a Cope Rearrangement to provide a stereospecific synthesis of *cis,trans*-1,5-hexadienes (88). Thus flash vacuum pyrolysis of (86; X,Y = $-\text{CH}_2\text{OCH}_2-$) at 625°C and 10^{-3} mmHg gave the divinyl compound in 62% yield while similar pyrolysis of the diester (86; X=Y= CO_2Me) at 550°C gave an 87% yield of *cis,trans*-dimethyl octa-2,6-diene-1,8-dioate via the Cope Rearrangement.

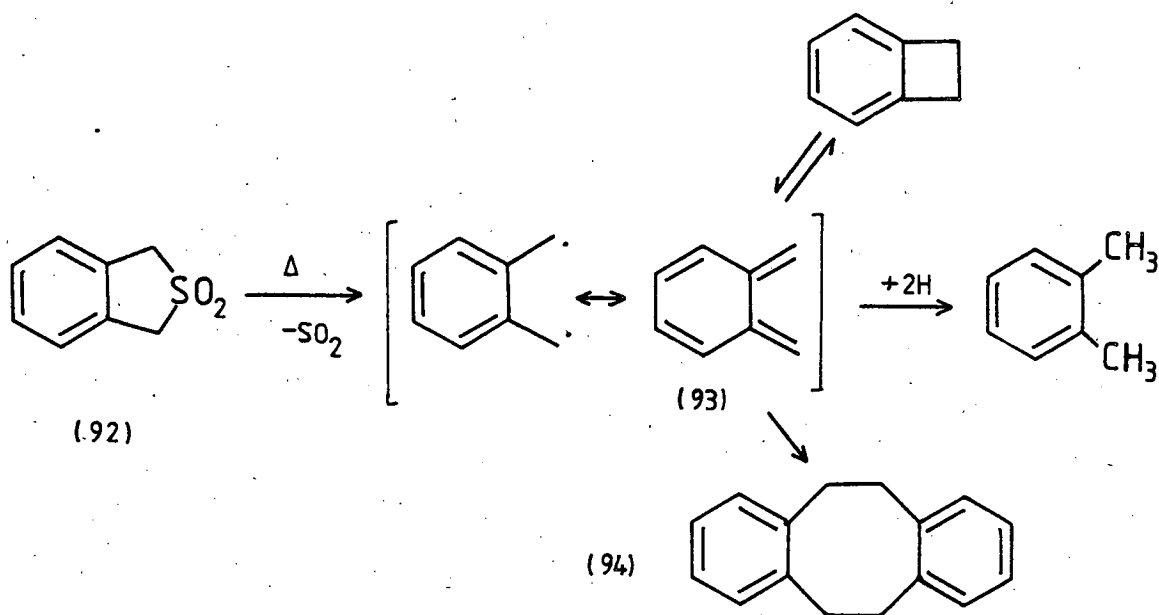
d. Benzo- and other aromatic fused sulpholenes

In 1916 Staudinger and Pfenninger¹⁶ observed that the triphenyl benzo-sulpholene (89), formed by base catalysed rearrangement of tetraphenylthiirane dioxide (23), lost SO_2



on heating to give a mixture of two hydrocarbons. These were later identified by Backer⁸¹ as 9,9-diphenyl-10,10-dihydroanthracene (90) and 9,10-diphenyl anthracene (91) formed via a diradical mechanism.

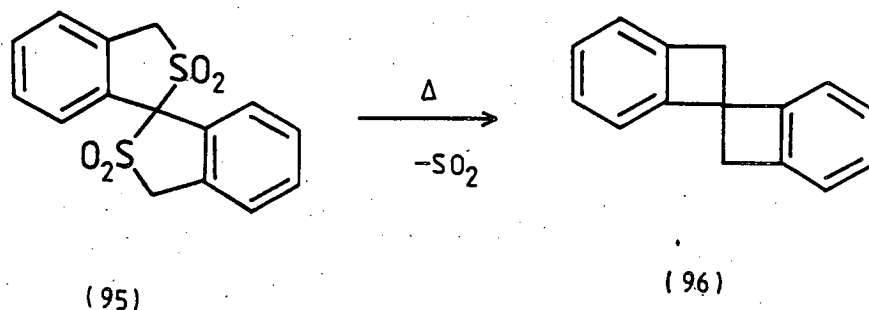
The parent system, 1,3-dihydrobenzo(c)thiophen dioxide (92), was first investigated by Cava and Deana in 1959⁸².



(92) extruded SO_2 on heating but the products depended on the conditions used. Thus thermolysis of the neat sulphone at 280°C gave benzocyclobutene in 13% yield together with 3% of *o*-xylene, and 4% of the dibenzocyclooctadiene (94). Solution thermolysis in boiling diethyl phthalate on the other hand gave the coupling product (94) in 48% yield while flash vacuum pyrolysis at 500°C gave 60% of benzocyclobutene. By using deuterated derivatives of (92), King⁸³ showed that the extrusion proceeds in accordance with the Woodward-Hoffmann rules by disrotatory loss of SO_2 followed by conrotatory ring closure of

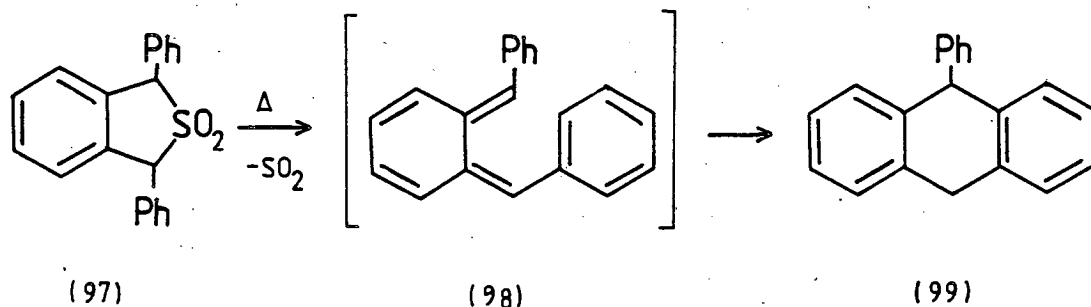
the *o*-xylylene intermediate (93).

The decomposition of aromatic fused sulpholenes to the corresponding cyclobutenes is quite general and this method has been used to prepare naphtho[a]cyclobutene⁸⁴, naphtho[b]-cyclobutene⁸⁵, benzo[1.2:4.5]dicyclobutene⁸⁶, and benzo-[1.2:3.4]dicyclobutene⁸⁷. A particularly elegant example of this reaction is Cava's synthesis⁸⁸ of the spiro compound



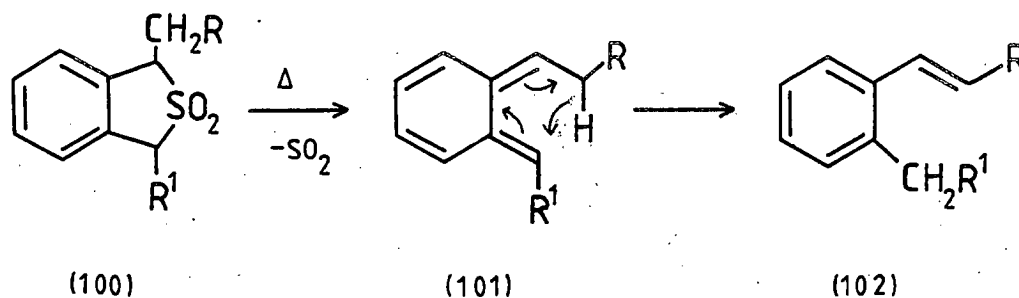
(96) by pyrolysis of the disulphone (95) at 700°C.

It should be noted however, that thermolysis of benzo-sulpholenes does not always produce the cyclobutene. The intermediate *o*-quinodimethane, commonly called an *o*-xylylene, exists in equilibrium with the benzocyclobutene and may for example be trapped by an intramolecular Diels-Alder reaction. This happens in the case of the diphenyl compound (97) which



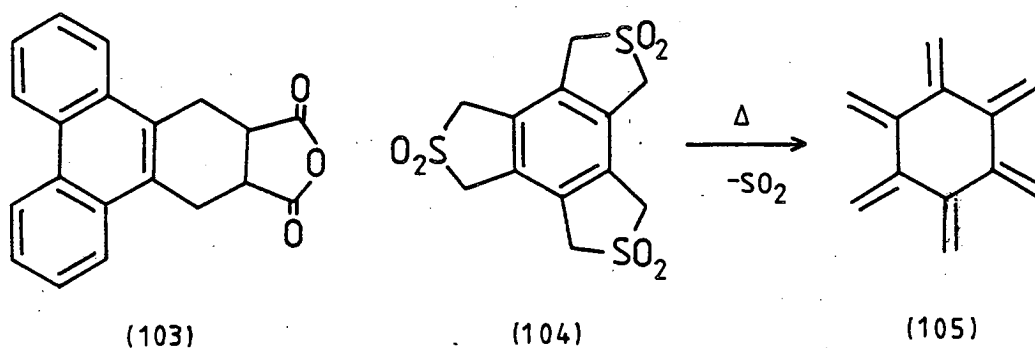
gave 9-phenyl-9,10-dihydroanthracene (99) in 94% yield when thermolysed in solution at 250°C.⁸⁹ By comparison photolysis of (97) gave the expected cyclobutene in low yield¹⁶⁸ but it

readily isomerised by way of (98) to give (99) on heating.⁹⁰
Other reactions of the intermediate are also possible. For



example, compounds of the type (100) give the expected cyclobutene on low temperature pyrolysis, but increasing the temperature affords only the styrene (102) via a [1,5] hydrogen shift in the intermediate *cis,trans*-*o*-xylylene (101).⁹¹

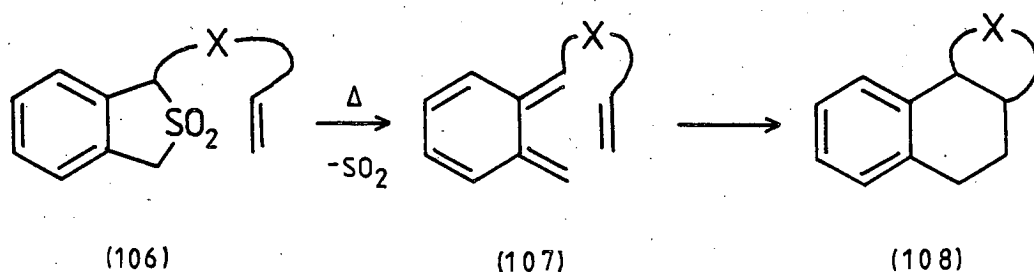
The *o*-xylylene intermediate (93) obtained from the decomposition of (92) exists in equilibrium with benzocyclobutene and can be trapped as a Diels-Alder adduct simply by thermolysing the sulphone in the presence of a dienophile such as *N*-phenylmaleimide⁸². Similar derivatives of other *o*-xylylenes



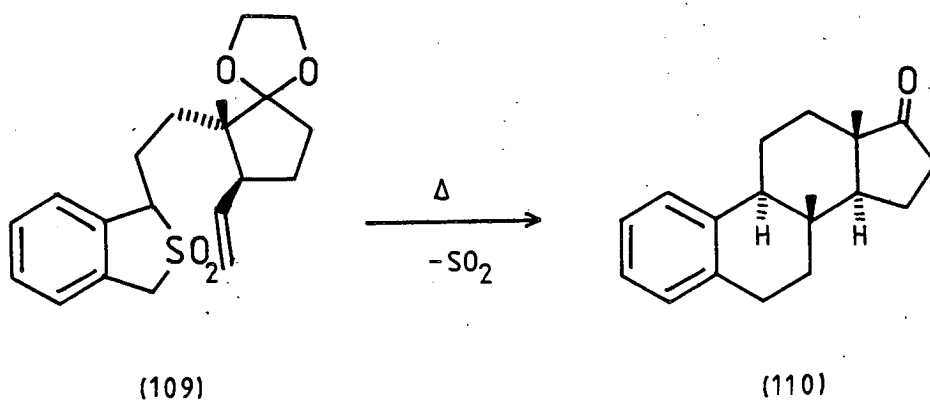
have also been prepared; for example the product (103) was prepared in 90% yield by heating the phenanthrene fused sulpholene in diethyl phthalate at 300°C in the presence of maleic anhydride⁹². A notable example of a system in which the

o-xylylene is more stable than the benzocyclobutene form is [6]-radialene (105) obtained by Boekelheide from flash vacuum pyrolysis of the tris-sulphone (104) at 900°C⁹³.

Generation of *o*-xylylenes using a variety of methods, and their intramolecular trapping by dienophiles, has been widely employed as a synthetic method for the preparation of polycyclic hydrocarbons⁹⁴. More recently Oppolzer⁹⁵ and Nicolaou⁹⁶ have used derivatives of the benzosulphone (92) as a source of *o*-xylylenes in the synthesis of several natural products. The general procedure involves alkylation of (92) with a side-chain containing a double bond to obtain the



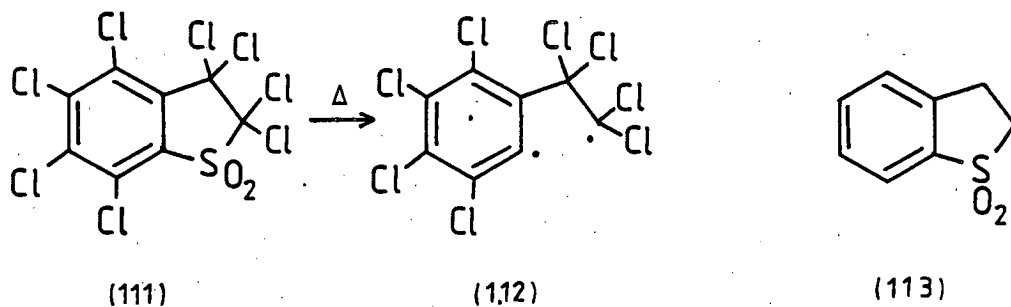
sulphone (106) which on thermolysis loses SO₂ to give the product (108) via the intramolecular Diels-Alder reaction of the *o*-xylylene intermediate (107). For example in Nicolaou's synthesis⁹⁶ of the steroid *estra-1,3,5(10)-trien-17-one* (110) the key step was effected in 85% yield by heating the precursor



(109) at 210°C in di-*n*-butylphthalate for 8 hours.

The extrusion of SO₂ from the isomeric 2,3-dihydrobenzo-
[b]thiophen dioxides has been studied only in one case.

Thus pyrolysis of the perchlorinated benzo[b]sulpholene (111)



afforded an 84% yield of octachlorostyrene⁵⁸, apparently by a [1,3] chlorine shift in the initially formed diradical (112). Under mass spectral conditions the parent compound (113) breaks down both by loss of SO from a sulphinate form, and by loss of SO₂ to give the benzocyclobutene molecular ion.⁹⁷

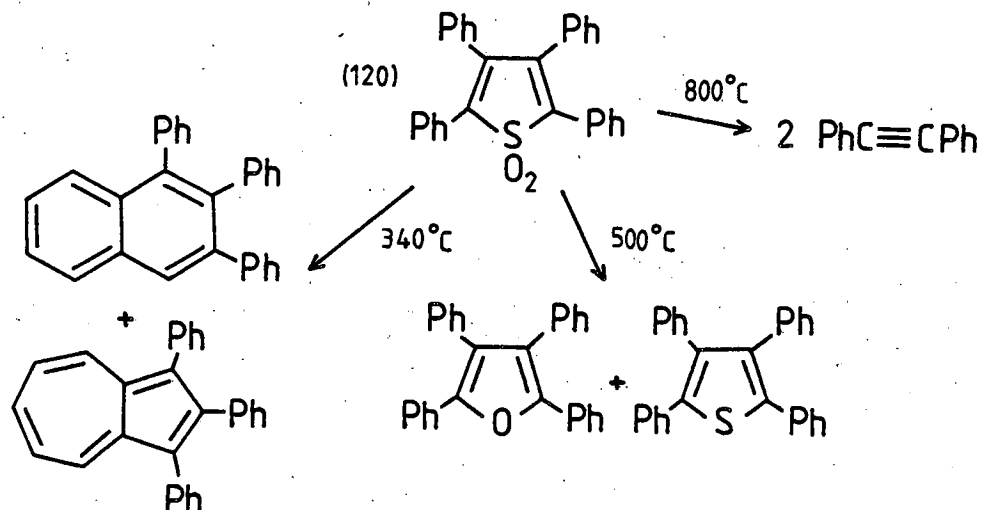
e. Thiophen dioxides

In general the unimolecular loss of SO₂ from thiophen dioxides does not occur although these compounds do readily undergo Diels-Alder reactions, with loss of SO₂ from the bicyclic intermediates. Details are given in Section 6.

Just as with the thiete dioxides, the preferred process on heating is ring expansion to a sultine, followed by loss of sulphur monoxide. For the parent thiophendioxide⁹⁸ the Diels-Alder dimerisation is so rapid that the study of any alternative thermal process is impossible. However flash vacuum pyrolysis of dibenzothiophen dioxide (114) at 700°C gave an 80% yield of dibenzofuran (116) via SO loss from the

conditions to give perchlorobutenyne and perchlorophenylacetylene, respectively, by means of a rearrangement of the initially formed diradical.

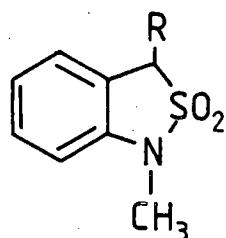
An interesting case is that of tetraphenylthiophen dioxide (120) which, depending on the conditions, can break down by three distinct routes^{101,105}. Thus, solution thermolysis



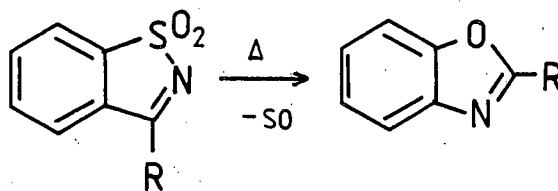
at 340°C leads via a [1,5] shift followed by SO_2 loss, to 1,2,3-triphenylnaphthalene and 1,2,3-triphenylazulene. In contrast neat pyrolysis at 500°C gives SO loss from the sultine to produce tetraphenylfuran as the main product, whereas flash vacuum pyrolysis results in simple extrusion of SO_2 to give diphenylacetylene. These results have been rationalised by van Tilborg¹⁰¹ in terms of radical stabilities.

f. Five-membered rings containing nitrogen

Extrusion of SO_2 from several five-membered ring systems containing nitrogen has been reported. Smith has shown¹⁰⁶ that photolysis of the sultam (121; $\text{R}=\text{H}$) produces N-methylbenzazetidine while under the same conditions (121; $\text{R}=\text{CH}_3$)



(121)



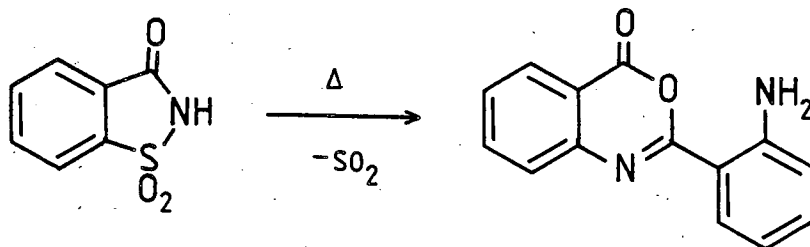
(122)

(123)

gives *o*-(methylamino)styrene via a [1,5] hydrogen shift in an intermediate *o*-quinomethane imine. This type of intermediate was trapped as a Diels-Alder adduct in the reaction of (121; R=H). On the other hand flash vacuum pyrolysis of (121; R=CH₃) produced the expected benzazetidone in good yield.

Abramovitch found¹⁰⁷ that pyrolysis of the 1,2-benzothiazole dioxides (122) gave mainly the benzoxazoles (123) in cases where R = aryl, together with a low yield of the benzonitrile, RCN, formed by complete fragmentation of the ring. Similar pyrolysis of (122; R=CH₃) gave *o*-cyanophenol as the main product. The mechanism of these reactions is uncertain.

Solution thermolysis of benzo-1,2-isothiazol-3-one 1,1-dioxide (124) gave a low yield of compound (125)¹⁰⁸, which is

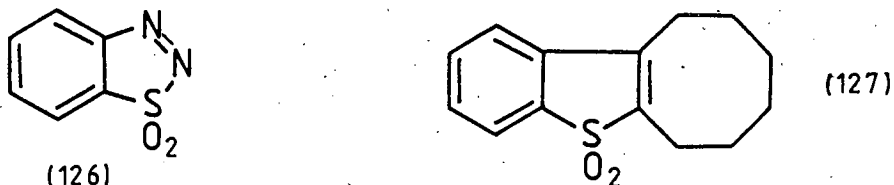


(124)

(125)

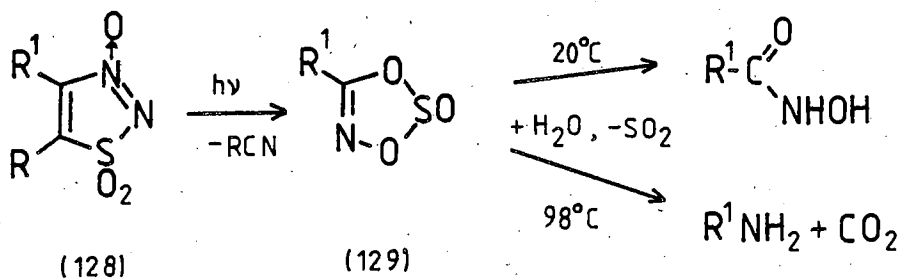
presumably formed by loss of SO₂, followed by dimerisation of the ketene-imine isomer of the resulting benzazetidone. If the reaction was carried out in liquid paraffin however, the initially formed diradical picked up hydrogen from the solvent to give benzamide.

1,2,3-Benzothiadiazole dioxide (126) was found by Wittig¹⁰⁹ to be a convenient source of benzyne. It decomposed in solution below room temperature to give benzyne which could be trapped as a variety of Diels-Alder adducts. The behaviour



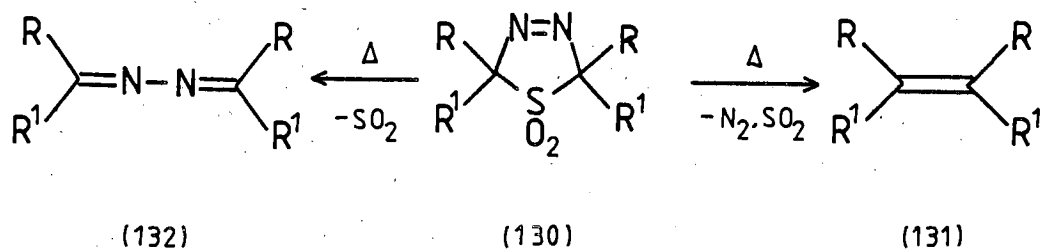
of (126) is anomalous when it is allowed to decompose in the presence of cyclooctyne¹¹⁰. Only nitrogen is lost, to give the annelated benzo[b]thiophen dioxide (127).

The 1,2,3-thiadiazole-1,1,3-trioxides (128) with $R=R^1$ =aryl were found by Meier¹¹¹ to break down on photolysis via loss of



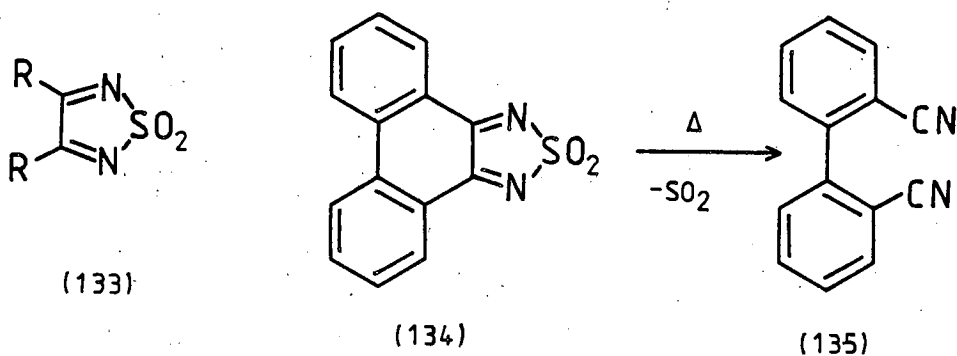
N_2 , SO_2 and O to give the acetylene, $\text{RC}\equiv\text{CR}^1$ in only 5% yield. The major process was breakdown to the nitrile, RCN , and a compound identified as (129) which, on treatment with water, loses SO_2 to give the hydroxamic acid or, in boiling water, the corresponding aniline. No mechanism was proposed for these reactions.

Thermolysis of the 1,3,4-thiadiazoline dioxides (130) was first reported by Hesse and Reichold¹¹². They thermolysed the neat thia-diazoline dioxide (130, $R=\text{Et}$, $R^1=\text{cyclohexyl}$) at 240°C and obtained



the alkene (131) in 10% yield, together with the azine (132) resulting from loss of only SO_2 in 30% yield. This method has since been used to prepare other substituted alkenes¹¹³ although the yields are poor.

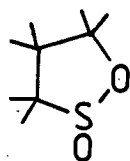
Pyrolysis of the aromatic fused 1,2,5-thiadiazole dioxides (133) provides a good synthesis of aromatic dinitriles¹¹⁴.



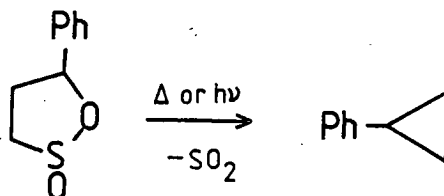
For example, pyrolysis of (134) in a sealed tube at $450^\circ C$ gives the biphenyldinitrile (135) in 84% yield.

g. Five-membered rings containing oxygen or sulphur

As mentioned in an earlier section, the five-membered sultines (51), which are formed by thermal isomerisation of the thiete dioxides, do not lose SO_2 but prefer in general to extrude SO . However, Smith has found that their saturated analogues: the 1,2-oxathiolan-2-oxides (136) are an alternative to the thietane dioxides as starting materials in the synthesis of cyclopropanes by either photolysis¹¹⁵ or pyrolysis¹¹⁶. For



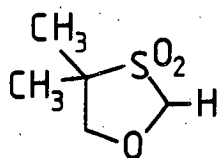
(136)



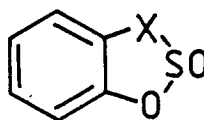
(137)

example, the phenyl sultine (137) can be converted into phenylcyclopropane either by irradiation in benzene solution or by flash vacuum pyrolysis at 750°C , the yield in each case exceeding 90%.

The 1,3-oxathiolan dioxide (138) has been used as a carbonyl anion equivalent¹¹⁷. The parent compound was first



(138)



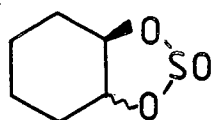
(139)

alkylated in the 2-position by treatment with butyl lithium followed by addition of an alkyl halide, RX . Pyrolysis of the product either under flash vacuum conditions or in boiling benzene, then resulted in loss of SO_2 and isobutene to produce the aldehyde, RCHO , in excellent yield.

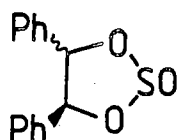
Schulz and Schweig¹¹⁸ recently found that 1,2,3-benzoxathiole-2-oxide (139; $\text{X}=\text{S}$) does not lose SO_2 on pyrolysis but instead loses SO and CO to provide the first synthesis of cyclopentadienethione. De Jongh had already shown that pyrolysis of benzodioxathiole oxide (139; $\text{X}=\text{O}$) produced cyclopentadienone as its dimer 15 years earlier¹¹⁹.

In contrast, the fully saturated cyclohexane-1,2-diol

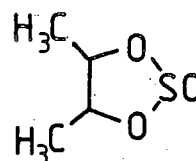
sulphites (140) did lose SO_2 on heating to $250\text{-}300^\circ\text{C}$ ¹²⁰.



(140)



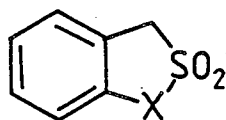
(141)



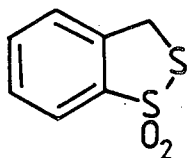
(142)

The *cis* isomer gave cyclohexanone while the *trans* isomer gave cyclopentane carboxaldehyde. The two isomers of the dihydrobenzoin sulphite (141) behaved similarly, giving rise to benzyl phenyl ketone and diphenylacetaldehyde respectively ¹²⁰. The dimethyl compound (142) extruded SO_2 on heating at 275°C with calcium oxide to give butan-2-one and 1,2-dimethyl-oxirane ¹²¹.

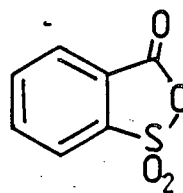
Chapman ¹²² obtained *o*-quinonemethide by photochemical extrusion of SO_2 from the benzoxathiol dioxide (143; $\text{X}=\text{O}$).



(143)



(144)



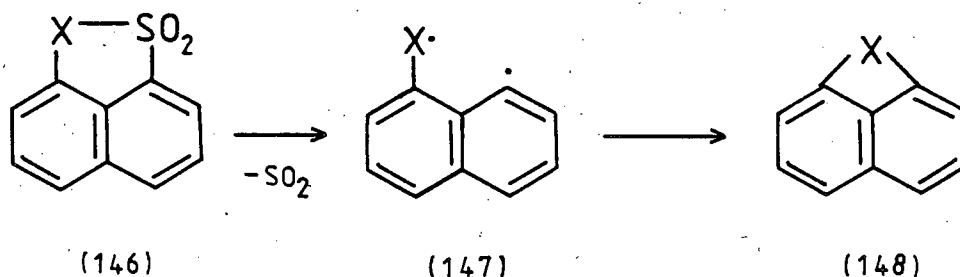
(145)

In the same way the thio-derivative (143; $\text{X}=\text{S}$) gave *o*-thio-benzoquinone methide, which was trapped as an adduct with *N*-phenylmaleimide ¹²³. In contrast, the isomeric compound (144) remained unchanged on irradiation.

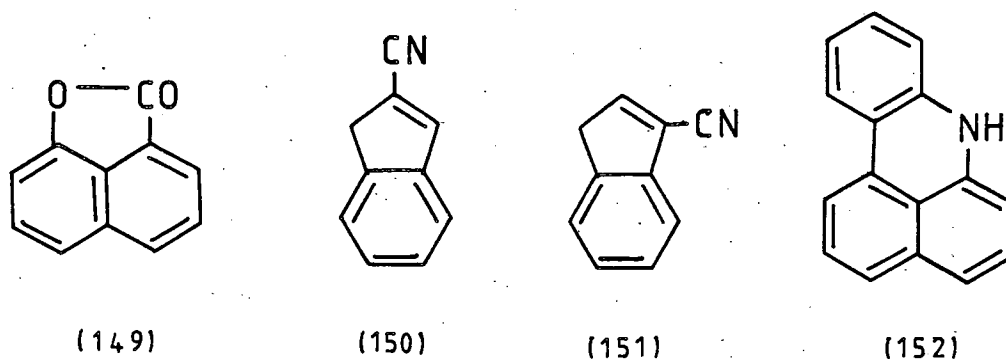
Flash vacuum pyrolysis of 1,2-benzoxathiol-5-one dioxide (145) provides yet another route to benzyne ¹²⁴.

h. 1,8-Naphtho systems

The pyrolysis of several compounds with the general structure (146) has been reported. De Jongh¹²⁵ obtained a 7.5% yield of 1-naphthol by flash vacuum pyrolysis of the sultone (146; X=O) at 650°C; in the presence of methanol vapour this increased to 22%. It was argued that this resulted



from the abstraction of two hydrogen atoms by an intermediate such as (148; X=O) which could be trapped in high yield as the lactone (149) by carrying out the pyrolysis in the presence of CO.



Flash vacuum pyrolysis of the sultam (146; X=NH) at 730°C¹²⁶ gave a mixture of isomeric cyanoindenes, (150) and (151). These are formed by a rearrangement of 1-naphthyl nitrene which results from isomerisation of the initially formed diradical (147; X=NH). Pyrolysis of the N-phenyl sultam (146; X=NPh) gave a 40% yield of the benzacridine (152),¹²⁶

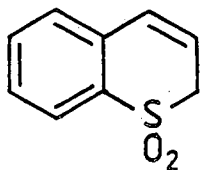
again via an intermediate diradical of the type (147).

The thiosultone (146; X=S) was used by Meinwald¹²⁷ as a source of naphthothiete (148; X=S). Irradiation of (146; X=S) in benzene solution resulted in SO₂ extrusion to give the product in quantitative yield.

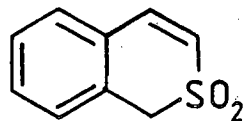
4. Six-membered rings

a. Sulphones

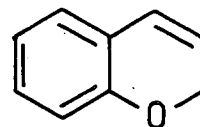
Just as was observed for the thiete dioxides and the thiophen dioxides, the characteristic reaction of the benzo-thiopyran dioxides (153) and (154) is ring expansion to a seven-membered sultine intermediate which then loses SO to give



(153)



(154)



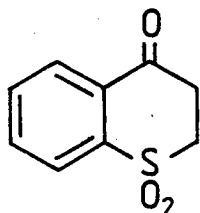
(155)

the products. Thus, Smith¹²⁸ found that on pyrolysis of (153), the main products were cinnamaldehyde and benzopyran (155), with some indene formed via SO₂ loss. Similarly, (154) gave a mixture of indene and *o*-vinyl benzaldehyde. Photolysis of (153)¹²⁹ gave low yields of indene and (155) and three new products: the ring expanded sultine and two isomers of a five-membered sultine. With (154), the major process on irradiation in methanol was addition of methanol across the double bond,

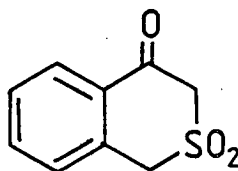
while the seven-membered sultine was obtained in 10% yield.

The thiochromanone dioxides (156) and (157) have been prepared, but the sulphone group is photochemically inert¹³⁰.

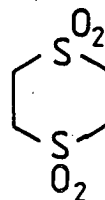
In general, SO_2 extrusion from six-membered sulphones is not an easy process. However it can be achieved when ring strain



(156)

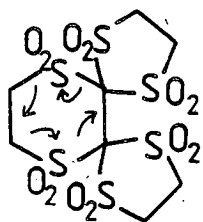


(157)

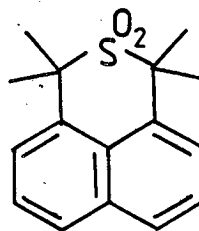


(158)

is present. Thus, while 1,4-dithiane dioxide (158) is stable at 300°C , the hexasulphone (159) could not be isolated from the oxidation of the hexasulphide¹³¹. Breakdown occurred in the manner shown to give an intermediate which underwent further fragmentation to produce two molecules of 1,3-dithiolan tetroxide. Thermolysis of six-membered ring sulphones has been used preparatively in a few cases. For example, Stothers¹³² obtained



(159)

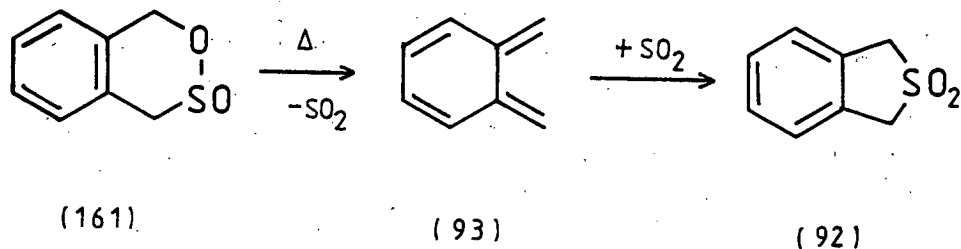


(160)

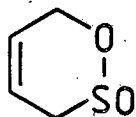
tetramethylacenaphthene in 20% yield by boiling the neat sulphone (160) at 400°C .

b. Sultines and sulphites

The aromatic sultines (161) lose SO_2 much more readily than their benzosulpholene isomers. Thus, either thermal¹³³



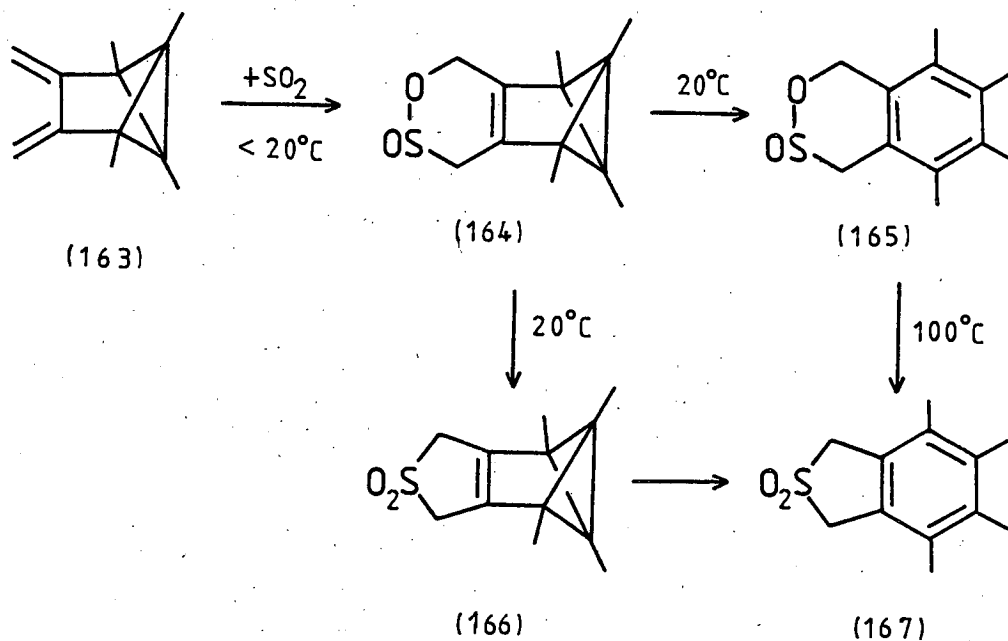
or photochemical¹¹⁵ decomposition produces the *o*-xylylene intermediate (93) which can be trapped either by reaction with a dienophile or with SO_2 to reform the isomeric sulphone (92). The thermal process proceeds rapidly in boiling benzene and the parent sultine (162) is even more unstable,



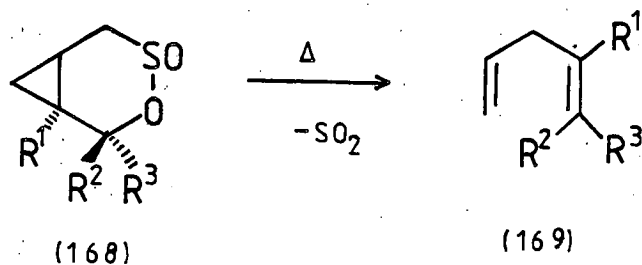
(162)

breaking down below 0°C with quantitative evolution of butadiene and SO_2 ¹³³.

The unusually strained diene (163) provides a useful insight into the processes involved in these systems. Addition of SO_2 to a solution of (163) initially gave the sultine (164)¹³⁴. This kinetic product was unstable and isomerised at room temperature, mainly to the benzosultine (165) but also, via loss of SO_2 and recombination, to form the thermodynamically more stable sulphone (166) which then rearranged to (167). At 100°C the sultine (165) isomerised, again via an *o*-xylylene intermediate, to (167).

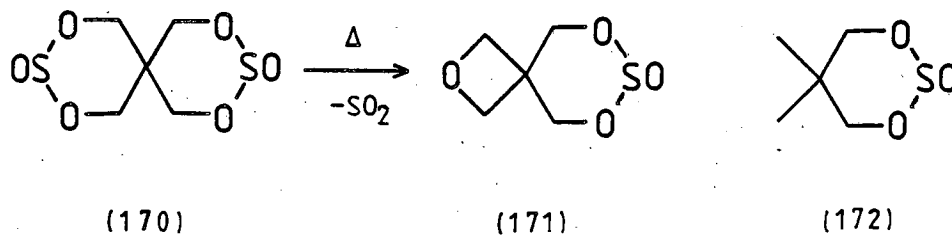


Thermolysis of the cyclopropyl compounds (168) takes place in boiling chloroform to give an excellent yield of the



isomerically pure 1,4-diene (169)¹³⁵.

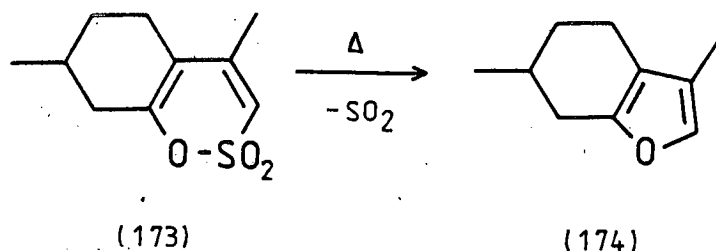
The disulphite of pentaerythritol (170) lost one molecule



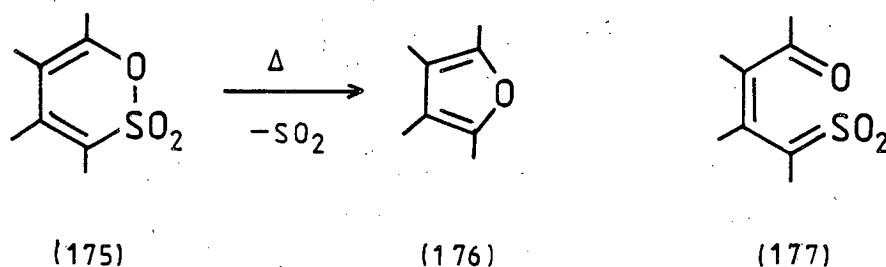
of SO_2 on heating at 270°C to give the spiro oxetane derivative (171)¹³⁶. Under the same conditions the sulphite of 2,2-dimethylpropane-1,3-diol (172) remained unchanged.

c. Sultones, thiosultones and sultams

The thermal extrusion of SO_2 from a six-membered ring sultone was first achieved in 1937 when Treibs¹³⁷ heated equal

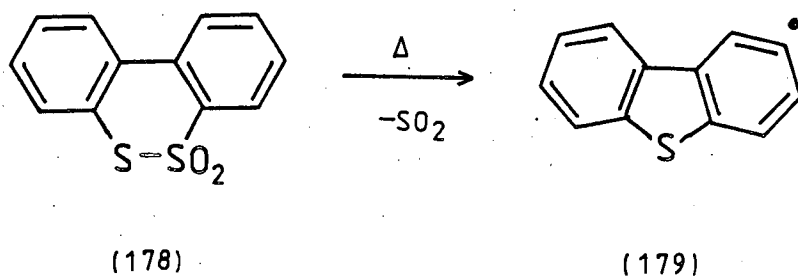


weights of the sultone (173) and zinc oxide and obtained menthofuran (174). Morel and Verkade¹³⁸ later developed this procedure into a general synthetic method for substituted furans. By heating an equal weight of the sultone (175) and

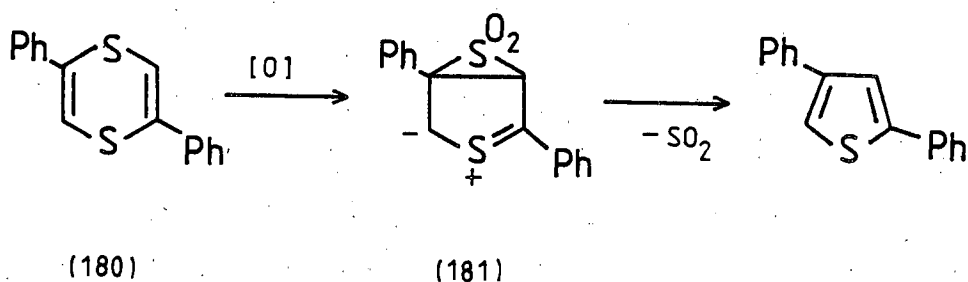


calcium oxide in the presence of a catalytic quantity of quinoline,^{se} the substituted furan (176) is produced in reasonable yield. The absence of calcium oxide and quinoline results in side-reactions and lower yields. In contrast, photolysis of the sultones (175) gave no loss of SO_2 but instead produced products derived from the reaction of the 4-oxosulphene isomer (177) with the solvent¹³⁹.

The corresponding reaction of the thiosultones has been observed in a few cases. For example, thermolysis of (178) or a substituted derivative with copper bronze at 250°C resulted in the formation of dibenzothiophen (179) in good yield¹⁴⁰.

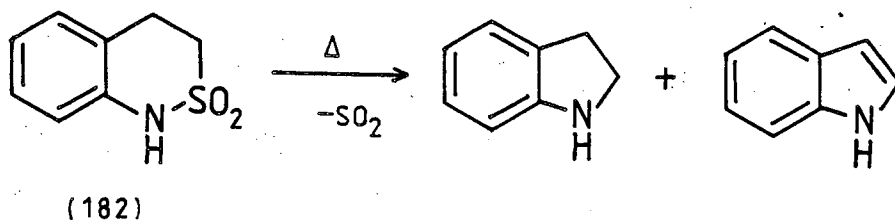


Attempted oxidation of 1,4-dithiins such as (180)



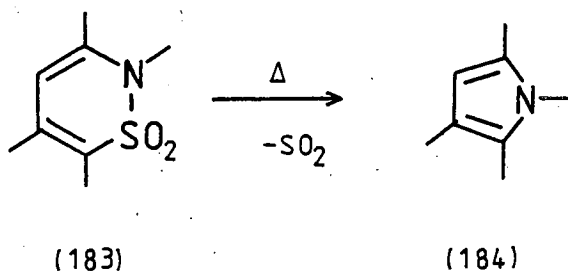
leads to the loss of SO_2 and formation of 2,4-diphenylthiophen¹⁴¹. This reaction probably involves elimination of SO_2 from the intermediate (181).

Abramovitch¹⁴² has shown that under flash vacuum pyrolytic conditions the saturated benzo sultam (182) loses SO_2 at 650°C

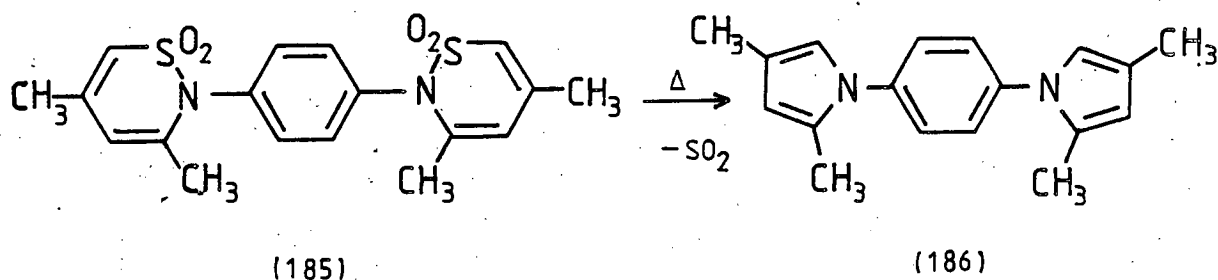


to give a 75% yield of indoline with 7% of indole formed by aromatisation.

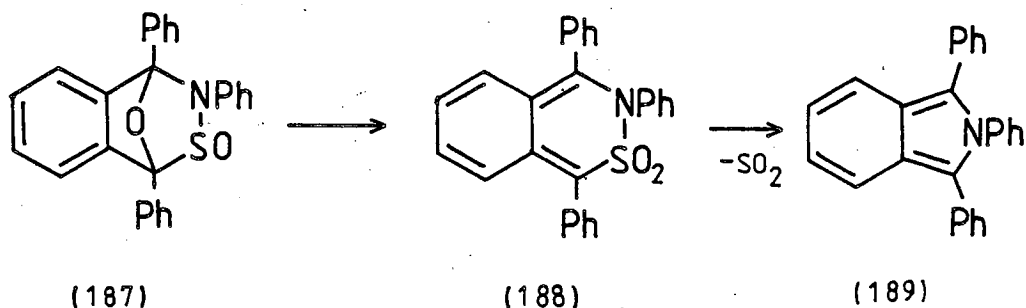
The thermolysis of unsaturated six-membered ring sultams (183) results in SO_2 extrusion to give the pyrroles (184) in good yield¹⁴³. In a typical experiment the bis-sultam (185)



was heated with lead monoxide at 280°C to give the dipyrrolyl-

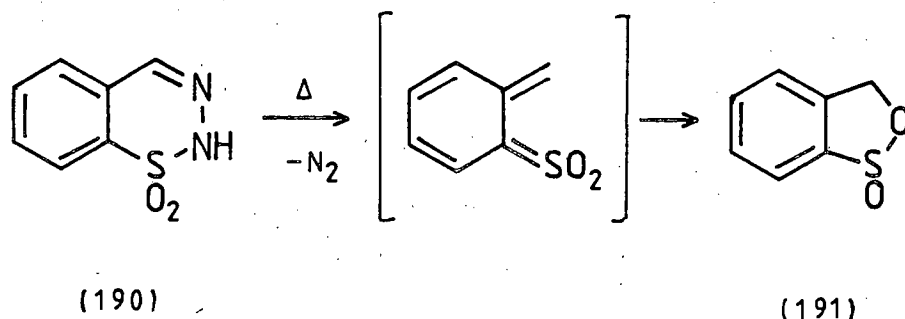


benzene (186) in 78% yield¹⁴⁴. This type of reaction has also been carried out photochemically¹⁴⁵. The same type of extrusion has been postulated in the reaction of 1,3-diphenylisobenzofuran with N-thionylaniline¹⁴⁶, whereby the initial



adduct (187) rearranged to (188) which then lost SO₂ to give the isoindole (189) in 80% yield.

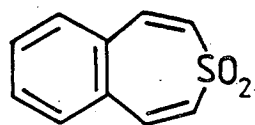
Pyrolysis of the benzothiadiazine dioxide (190) resulted in loss of only nitrogen to produce a good yield of the sultine (191) via a sulphene intermediate¹⁴⁷.



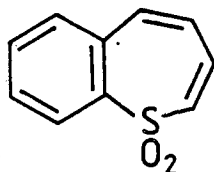
5. Seven- and eight-membered rings

a. Thiepine dioxides

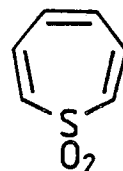
The first extrusion of SO₂ from a seven-membered sulphone ring was observed by Truce¹⁴⁸ who thermolysed benzo[d]thiepine dioxide (192) to produce naphthalene. In contrast, the



(192)



(193)



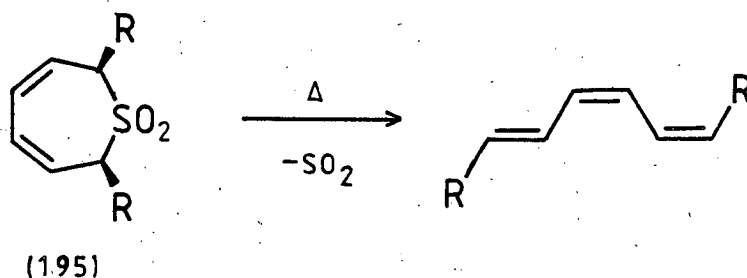
(194)

isomeric benzo[b]thiepine dioxide (193) remained unchanged at 250°C and, on prolonged heating, it underwent polymerisation¹⁴⁹. In 1967 Mock reported the first preparation of thiepine dioxide (194)¹⁵⁰ which gradually decomposed above its melting point, or in solution at 100°C, to give benzene and SO₂. The 2,4,5,7-tetraphenyl derivative behaved similarly, giving 1,2,4,5-tetraphenylbenzene in 70% yield on solution thermolysis¹⁵¹.

The starting point for Mock's synthesis of thiepine dioxide

(194) was the addition of SO_2 to *cis*-1,3,5-hexatriene.

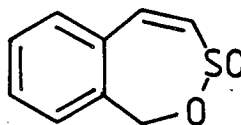
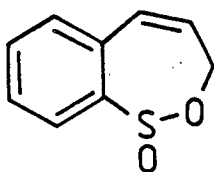
The reverse reaction, elimination of SO_2 , has been the subject of detailed studies, largely because it represents a higher homologue of the sulpholene reaction of dienes. According to the Woodward-Hoffmann rules the extrusion from 2,7-dihydrothiepine dioxides (195) should be stereospecifically antarafacial (conrotatory). By decomposing the dimethyl compound (195; $\text{R}=\text{CH}_3$) and the corresponding *trans* isomer under g.l.c. conditions, Mock^{61,152} showed that this was indeed the case. No thermal decomposition study of the isomeric 4,5-dihydrothiepine dioxide has been reported, although it readily isomerises in the presence of base to the apparently more stable 2,7-dihydroisomer¹⁵³, and the thermal decomposition might also follow this course.



facial (conrotatory). By decomposing the dimethyl compound (195; $\text{R}=\text{CH}_3$) and the corresponding *trans* isomer under g.l.c. conditions, Mock^{61,152} showed that this was indeed the case. No thermal decomposition study of the isomeric 4,5-dihydrothiepine dioxide has been reported, although it readily isomerises in the presence of base to the apparently more stable 2,7-dihydroisomer¹⁵³, and the thermal decomposition might also follow this course.

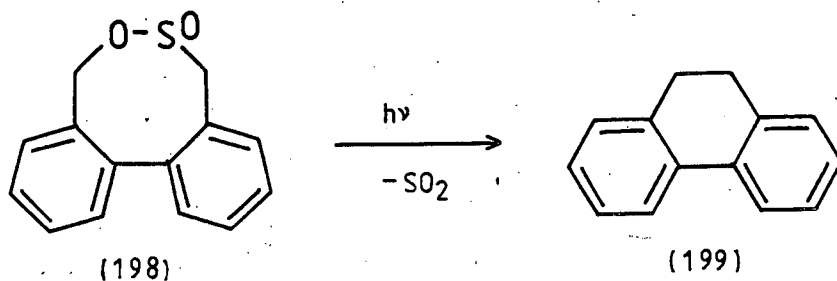
b. Seven- and eight-membered rings containing hetero-atoms

The seven-membered ring sultines (196) and (197) have already been mentioned as probable intermediates in the pyrolysis of the sulphones (153) and (154). Extrusion of SO



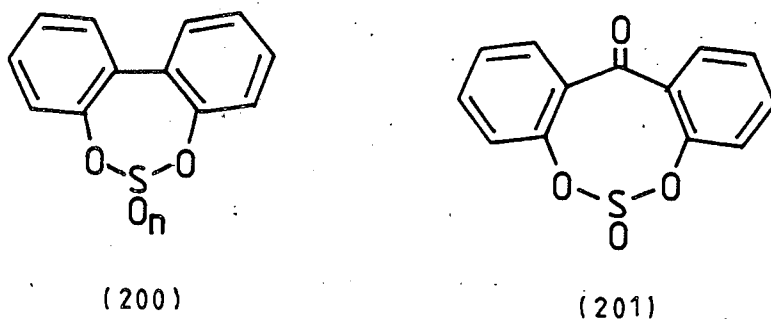
from (196) and (197) would account for the observed products, but, although the sultines could be isolated from the photolysis of (153) and (154)¹²⁹, their direct thermolysis has not been reported.

The eight-membered ring sultine (198) was found to lose



SO₂ on irradiation in methanol to give 9,10-dihydrophenanthrene (199)¹¹⁵.

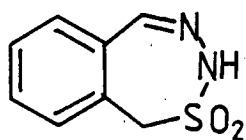
Pyrolysis of the seven-membered ring sulphite (200; n=1) resulted in competitive loss of SO₂ and SO to give respectively,



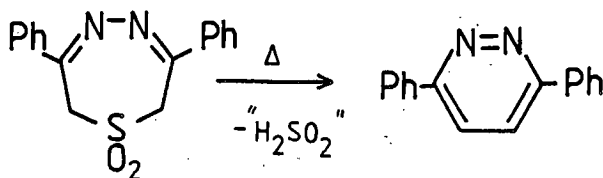
dibenzofuran in 20% yield and 1-hydroxydibenzofuran in 50% yield¹⁵⁴. Flash vacuum pyrolysis of the corresponding sulphate (200, n=2) caused exclusive loss of SO₂ to form 1-hydroxydibenzofuran (90% yield). In contrast, the closely related sulphite (201) gave loss of SO₂ and partial loss of CO under the same conditions to give a mixture of dibenzofuran (30%), 9-xanthenone (10%) and 3,4-benzocoumarin (20%). The saturated tetramethylene sulphite was found to lose SO₂ on

heating at 180°C in the presence of triethylamine to give a high yield of tetrahydrofuran¹⁵⁵.

Extrusion of SO₂ from seven-membered rings containing nitrogen has been reported in a few cases. King found¹⁵⁶ that the compound (202) lost only nitrogen on heating above



(202)



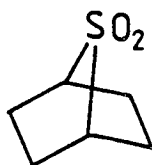
(203)

the melting point to give the benzosulpholene (92) in good yield. However, the thiadiazepine dioxide (203) on heating in ethanol or acetic acid underwent loss of "H₂SO₂" to give 3,6-diphenylpyridazine in high yield¹⁵⁷. This reaction is believed to proceed via a sulphinic acid intermediate.

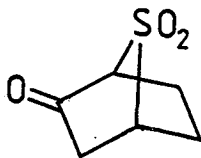
6. Bridged ring systems

a. 7-Thiabicyclo[2.2.1] structures

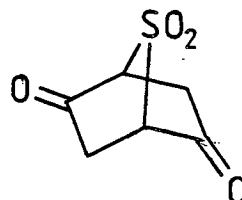
By pyrolysing the simplest bicyclo[2.2.1] structure: 7-thiabicyclo[2.2.1]heptane 7,7-dioxide (204) under flash vacuum conditions at 520°C, Corey obtained a 60% yield of



(204)



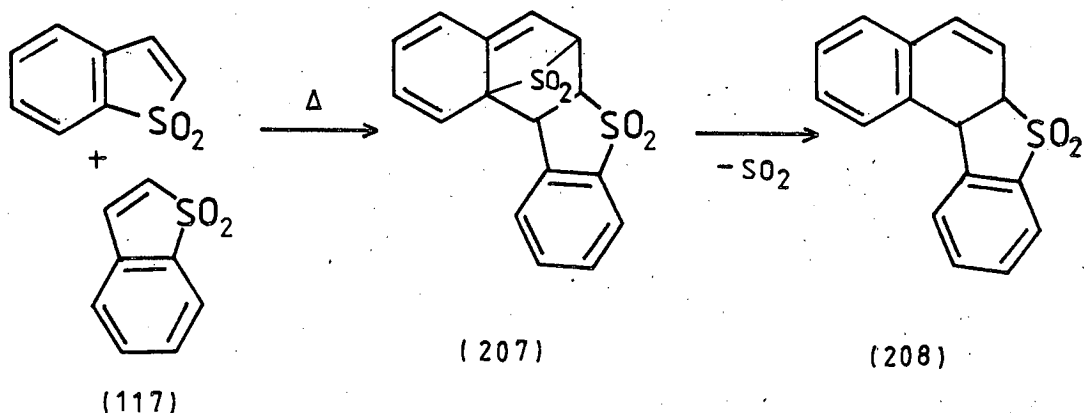
(205)



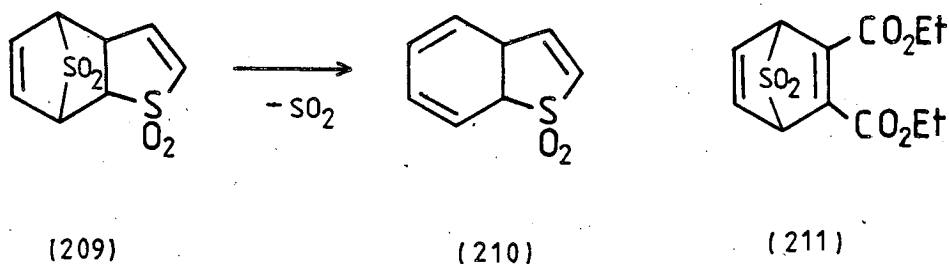
(206)

1,5-hexadiene²². The carbonyl derivatives (205) and (206) decompose in solution at 220°C and 160°C to give quantitative yields of cyclohexen-3-one and hydroquinone, respectively¹⁵⁸.

The vast majority of extrusions from bicyclo[2.2.1] systems however, occur in the Diels-Alder reaction of thiophen dioxides with dienophiles. This particular process was first observed¹⁵⁹ when benzo[b]thiophen dioxide (117) was



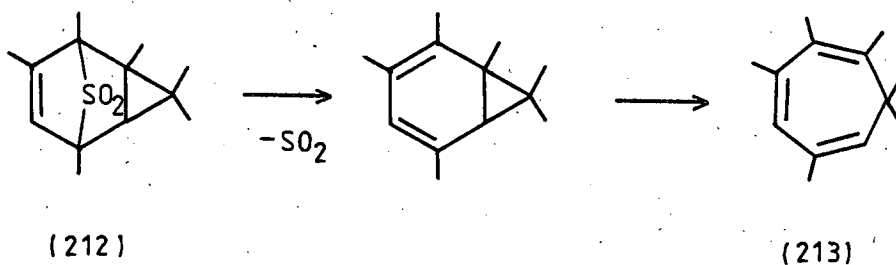
found to dimerise on heating above 200°C to give (207) which immediately lost SO_2 to form the benzo-naphthothiophen dioxide (208). When thiophen dioxide itself was prepared it was found to undergo Diels-Alder reactions much more readily.



Dimerisation occurred in solution below room temperature to give the dihydrobenzothiophen dioxide (210) via (209)⁹⁸. The compound also reacted with other double and triple bonds with

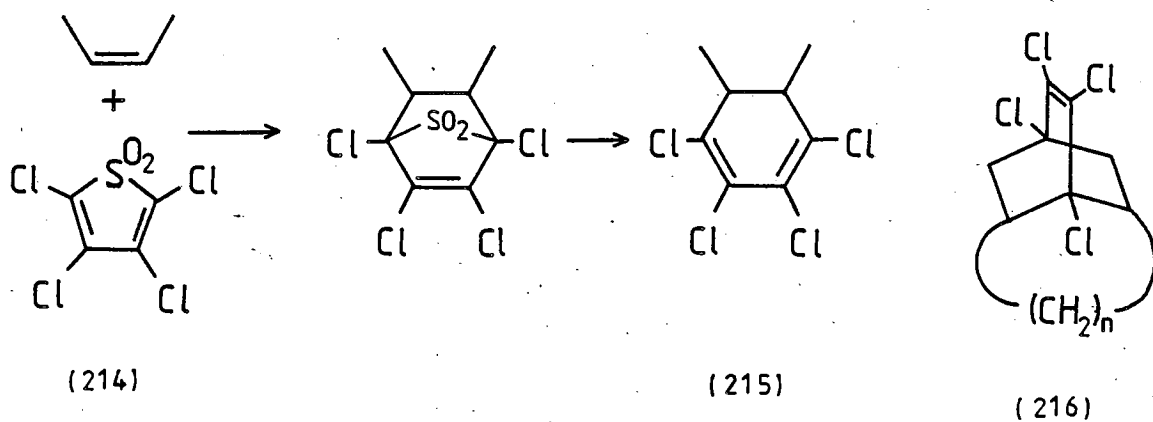
loss of SO_2 to give the expected products in low yield¹⁶⁰. Thus reaction with indene gave a 3% yield of fluorene while reaction with diethyl acetylenedicarboxylate yielded diethyl phthalate in 18% yield by SO_2 loss from the intermediate (211).

van Tilborg and Reinhoudt¹⁶¹ have used the reaction of substituted thiophen dioxides with cyclopropenes to prepare



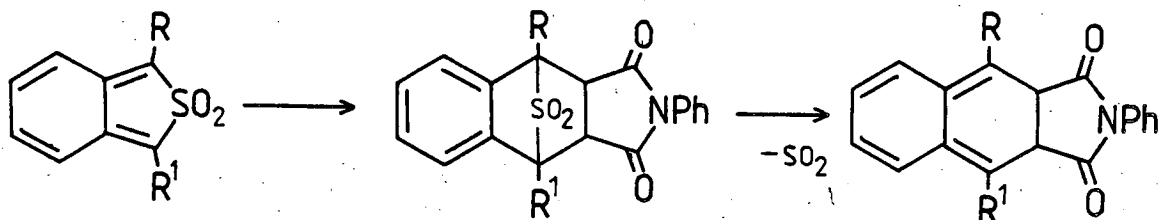
the substituted cycloheptatrienes (213). The initially formed adducts (212) were unstable well below room temperature, rapidly losing SO_2 to form cyclopropabenzenes which ring expanded to give the cycloheptatrienes in quantitative yield.

Raasch¹⁰³ has used the reaction of tetrachlorothiophen dioxide (214) with a large range of unsaturated systems to prepare annelated products in good to excellent yield. The reactions proceed readily in solution between 0°C and 100°C



with loss of SO_2 to give the product (215). Reaction with α,ω -dienes provides a convenient route to isotwistenes (216) via an intramolecular Diels-Alder reaction of the initial adduct.

Cava¹⁶² has recently reported the Diels-Alder reaction of the unstable benzo(c)thiophen dioxides (217a-c). These



(217) a. $\text{R} = \text{Br}, \text{R}^1 = \text{H}$

b. $\text{R} = \text{R}^1 = \text{Br}$

c. $\text{R} = \text{R}^1 = \text{Ph}$

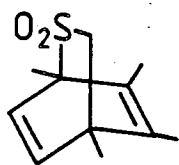
(218)

(219)

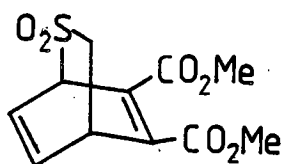
react immediately with N-phenylmaleimide at room temperature to give a high yield of the product (219) arising by elimination of SO_2 from (218).

b. Bicyclo[2.2.2] structures

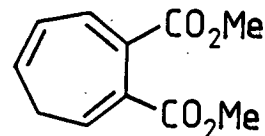
King has shown¹⁶³ that the bicyclic compounds (220) generally fragment to a sulphene and an aromatic ring on thermolysis. However, Fischer¹⁶⁴ discovered that in the case



(220)

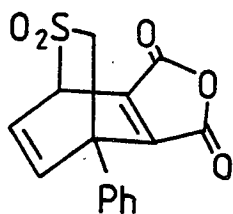


(221)

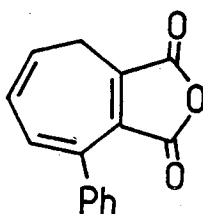


(222)

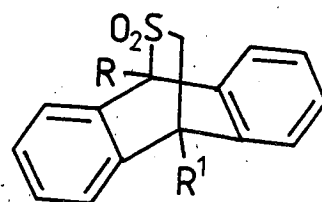
of the diester (221), the loss of sulphene is only a minor pathway and that thermolysis in solution at 200°C results mainly in elimination of SO₂ and rearrangement to give the cycloheptatriene diester (222) and its isomers. King later observed the competing processes himself in the anhydride (223)¹⁶⁵



(223)



(224)

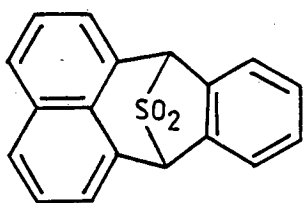


(225)

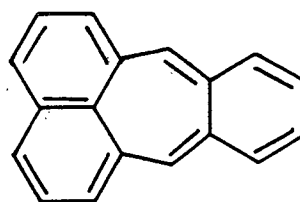
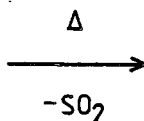
which extruded sulphene and SO₂ to an equal extent to give respectively, 3-phenylphthalic anhydride and the cycloheptatriene (224). Smith has recently shown¹⁶⁶ that the dibenzo compounds (225) undergo exclusive loss of SO₂ to give either the dibenzocycloheptatriene or the 9-methylanthracene depending on the conditions used.

c. Sulphone-bridged seven-membered rings

In 1963 Cava obtained the resonance-stabilised *o*-xylylene compound, pleiadene (227), by heating the corresponding bridged sulphone (226) at 210°C¹⁶⁷. The product could be isolated as



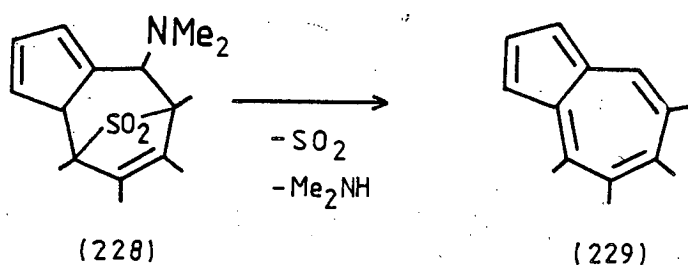
(226)



(227)

the dimer or trapped as an adduct with N-phenylmaleimide. A year later¹⁶⁸ he reported the realisation of the same reaction photochemically and this was indeed the first example of photochemical extrusion of SO₂ from a sulphone.

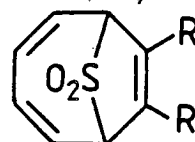
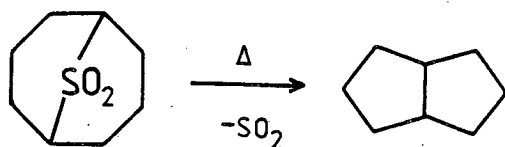
Extrusion of a bridging SO₂ group is the key step in the azulene synthesis reported simultaneously by both Leaver¹⁶⁹ and Houk¹⁷⁰ in 1977. Reaction of a thiophen dioxide with



dimethylaminofulvalene gave the adduct (228) which readily lost SO₂ and dimethylamine to give the azulene (229) in low yield. A similar approach has been used recently by Kanematsu¹⁷¹ to prepare 5,6-diaza-azulenes from a substituted thiadiazole dioxide.

d. Sulphone-bridged eight-membered rings

Corey²² prepared the saturated bicyclo[3.3.1] system (230) and found that it loses SO₂ on flash vacuum pyrolysis at 710°C



a. R = CH₃

b. R₂ = -(CH₂)₄-

c. R₂ = -(CH₂)₅-

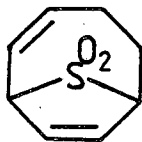
d. R₂ =



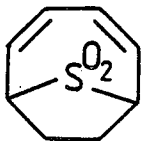
to give a 50% yield of bicyclo[3.3.0]octane in addition to a small quantity of cyclooctene.

In contrast to this radical process, extrusion of SO_2 from unsaturated analogues of (230) can in some cases be concerted and proceed more readily. For example, Paquette has prepared the compounds (231a-d)¹⁷² from an unusual rearrangement of α -chlorosulphones under Ramberg-Bäcklund conditions and found that they readily lose SO_2 , either on flash vacuum pyrolysis at 400°C , or by photolysis in acetone, to give the cyclooctatetraenes. Hydrogenation of (231b) occurred only at the two conjugated double bonds and the product - effectively a bridged sulpholene - again readily lost SO_2 on pyrolysis.

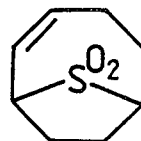
The thermal decomposition of the bridged sulphones (232) - (234) has been studied by Mock¹⁷³ in relation to the orbital symmetry constraints which apply to these systems. (232)



(232)



(233)

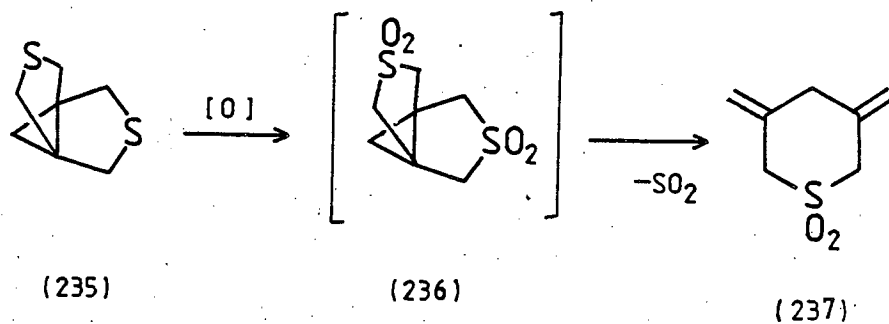


(234)

dissociates readily above 100°C by an allowed 1,4-extrusion of SO_2 to give 1,3,5-cyclo-octatriene. The isomeric sulphone (233) on the other hand only extrudes SO_2 above 200°C and the rate is 60,000 times slower than for (232). This was attributed to the fact that the symmetry-allowed antarafacial (conrotatory) 1,6-extrusion is sterically impossible. The compound (234) with no possible concerted fragmentation pathway is even more stable.

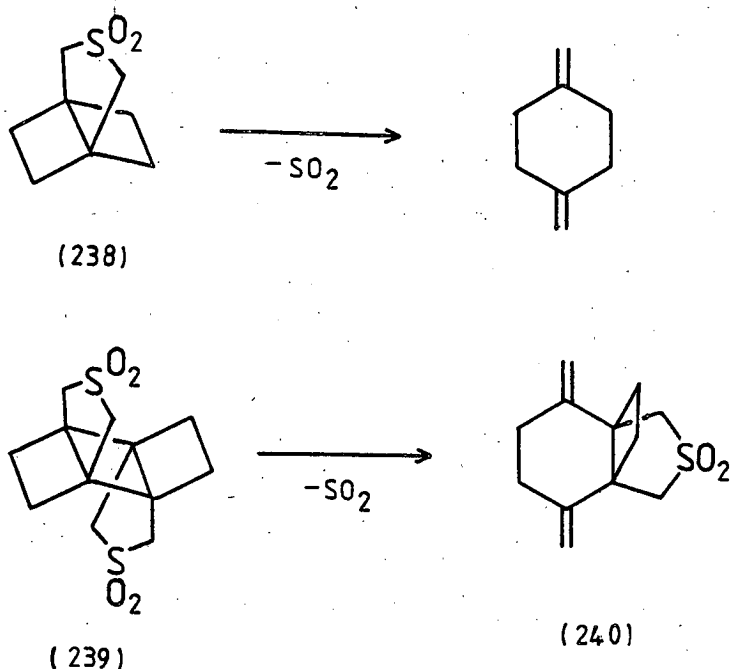
e. Propellanes

Extrusion of SO_2 from tricyclo[1,m,n,0] systems, using the Ramberg-Bäcklund reaction provides a convenient route to propellanes i.e. tricyclo[1,m,n,0] hydrocarbons¹⁷⁴. In a few cases, however, unsuccessful attempts have been made to prepare propellanes by direct extrusion of SO_2 from the parent sulphone. For example, Weinges¹⁷⁵ found that the highly



strained sulphone (236) could not be formed by oxidising the corresponding sulphide (235), since it immediately lost one molecule of SO_2 under the conditions used and formed the monosulphone (237).

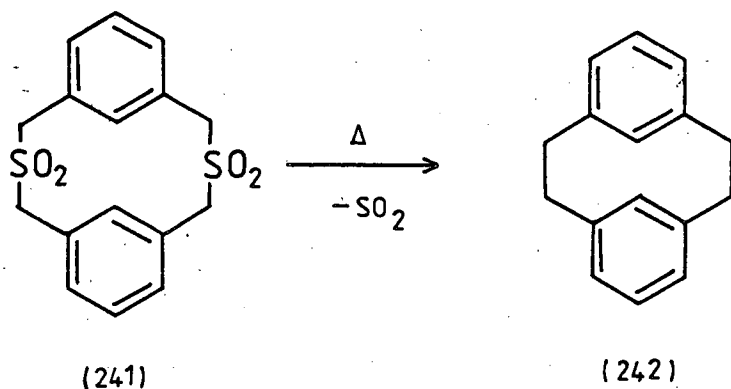
Likewise an attempt by Ginsburg to prepare [2.2.2] propellane proved unsuccessful¹⁷⁶. Although the sulphones (238) and (239) could not be prepared from the corresponding sulphides under normal conditions, they were obtained by low temperature ozonolysis. On warming to room temperature loss of one molecule of SO_2 occurred to give 1,4-dimethylenecyclohexane from (238) and the monosulphone (240) from (239).



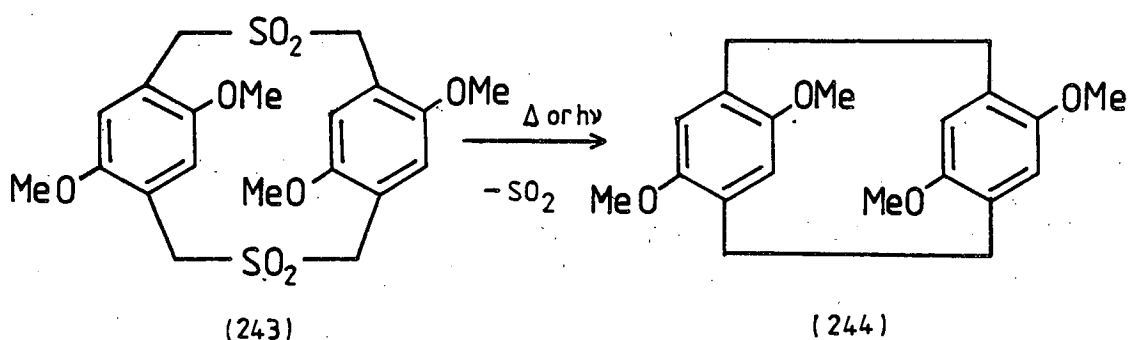
7. Cyclophanes

In recent years there has been intense interest in the chemistry of cyclophanes, i.e. molecules in which two or more aromatic nuclei are joined by two or more saturated carbon chains. Many of the early cyclophane-forming reactions relied on elimination of halogen atoms to form the bridges, but more recently extrusion of SO₂ from the sulphones of thiacyclophanes has emerged as an important method for their preparation. The synthesis of cyclophanes has been the subject of several reviews¹⁷⁷.

Vogtle¹⁷⁸ was the first to prepare a cyclophane by sulphone thermolysis, when, in 1969, he obtained a 20% yield of [2.2]metacyclophane (242) by heating the disulphone (241) at 350°C. It was later discovered by Staab¹⁷⁹ that photolytic

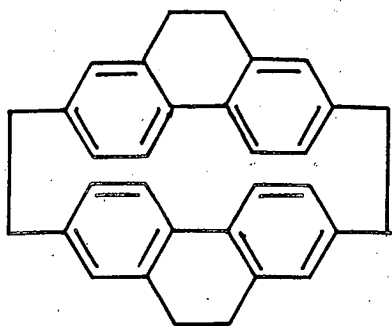


removal of SO_2 could also be used to prepare cyclophanes.

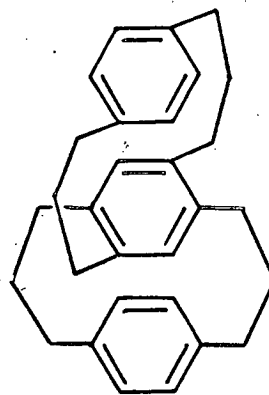


The disulphone (243), for example, could be converted into the cyclophane (244) either by flash vacuum pyrolysis at 440°C or by photolysis in benzene.

Sulphone pyrolysis has since been used to prepare a huge number of cyclophanes. An advantage is that the thiacyclophanes are readily accessible in good yields, either by reaction of two bromoalkylaromatic fragments with sodium sulphide or by reaction of a bromoalkylaromatic with a thioalkyl aromatic. Some typical examples of cyclophanes which have been prepared by vapour phase pyrolysis of disulphones are (245)¹⁸⁰, and the triple-layered compound (246), which was obtained by Otsubo¹⁸¹ by a reaction sequence involving initial sulphone pyrolysis to form the first ring, followed by a further sequence



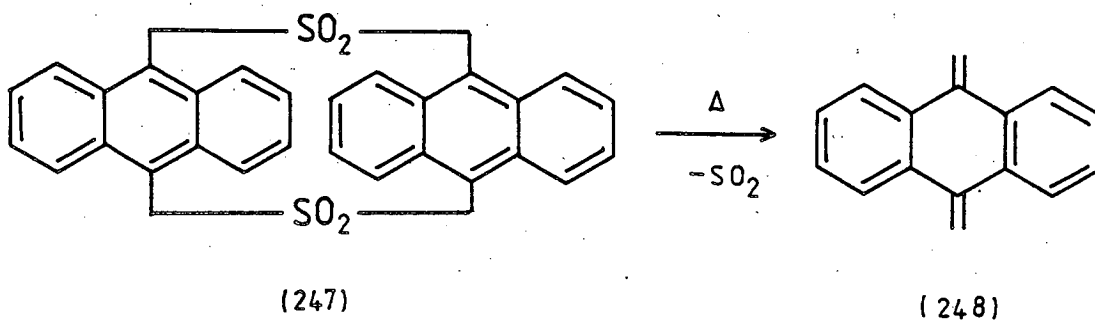
(245)



(246)

of thiacyclophane building, oxidation and pyrolysis to attach the second cyclophane ring.

Finally, it should be noted that when the cyclophane to be formed is too strained, the pyrolysis may lead to products from the two separate diradicals. As long ago as 1964 Millar and Wilson¹⁸² thermolysed the disulphone (247) in



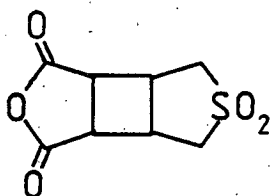
(247)

(248)

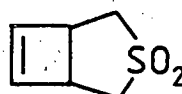
diethylphthalate and obtained 9,10-anthraquinodimethane (248) which could be trapped as its maleic anhydride adduct in 70% yield.

C. Programme of Research

In 1972 Shaikhraieva et al.¹⁸³ reported the preparation and some simple reactions of the tricyclic sulphone (249), but no attempt was made to extrude the SO₂. Subsequent work



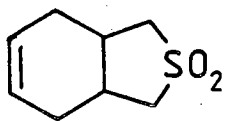
(249)



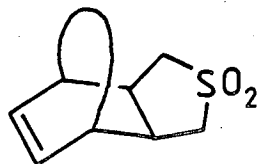
(250)

in these laboratories¹⁸⁴ showed that loss of SO₂ from (249) and its derivatives occurred cleanly under flash vacuum pyrolytic conditions to provide a simple stereospecific synthesis of *cis*-1,2-divinyl compounds⁷⁹ and via a Cope Rearrangement, *cis,trans*-1,5-hexadienes⁸⁰ (see p.21). The initial aim of the present work was to extend the scope of these reactions by investigating the pyrolytic fragmentation of new systems generated by the addition of 1,3-dipoles and mononuclear electrophilic species such as carbenes and nitrenes to the double bond of the alkene (250), which was obtained from the diacid of (249) by oxidative bis-decarboxylation¹⁸⁵.

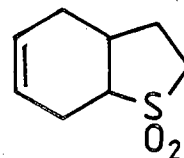
8-Thiabicyclo[4.3.0]non-3-ene 8,8-dioxide (251), a higher homologue of (250), together with its 2,5-bridged analogues (252) was also considered to be of interest in this connection. Pyrolytic removal of SO₂ might produce a 1,4,7-triene system and again, prior functionalisation of its double bond, could provide access to novel divinyl compounds. Although extrusion



(251)



(252)

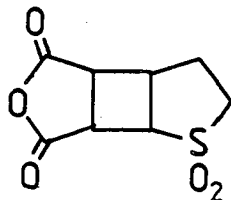


(253)

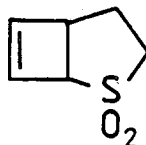
of SO_2 from the aromatic benzo(c)thiophen dioxide (92) is well known⁸², no similar reactions of partly hydrogenated derivatives have been recorded.

The isomeric 7-thia- compound (253) was first prepared in 1938 by Alder¹⁸⁶ from the reaction of 1,3-butadiene with 2,3-dihydrothiophen 1,1-dioxide but since then its chemistry has received little attention. In particular, the extrusion of SO_2 from this system has never been reported. A study was instigated therefore, into the behaviour of (253), its 2,5-bridged derivatives, and the compounds obtained from them by double bond modification, under flash vacuum pyrolysis conditions.

The relationship between (251) and (253) led to the realisation that the novel compound (254), an isomer of (249), might be prepared by the [2+2]cycloaddition of maleic anhydride and 2,3-dihydrothiophen 1,1-dioxide. Preparation of (254) would then open the way to a large number of derivatives whose



(254)


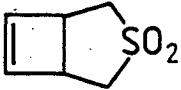
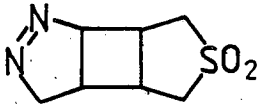
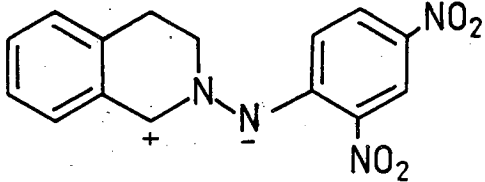
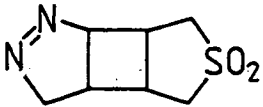


(255)

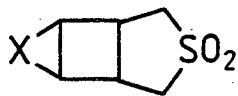
behaviour on pyrolysis would provide an interesting comparison with those of (249), and possibly lead to some new useful syntheses. The alkene (255), isomeric with (250), could again play a key role in extending the scope of these reactions through addition of 1,3-dipoles and mononuclear electrophilic species to its double bond. In particular, it was recognised that (255) could act as a cyclobutadiene synthon by thermal extrusion of SO_2 and ethylene.

EXPERIMENTAL

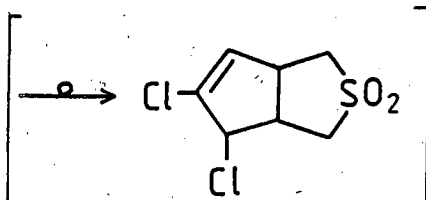
C O N T E N T S

	Page No
A. <u>Symbols and Abbreviations</u>	60
B. <u>Instrumentation and General Techniques</u>	61
C. <u>Preparation and reactions of</u> 	
1. Preparation of 	68
2. Reaction with 1,3-dipoles	
a. Preparation of 	69
b. Attempted reaction with PhCHN ₂	69
c. Attempted reaction with Ph ₂ CN ₂	71
d. Attempted reaction with EtO ₂ CCHN ₂	72
e. Attempted reaction with PhN ₃	73
f. Attempted reaction with <i>p</i> -MeO-C ₆ H ₄ ⁺ C=N-S ⁻	73
g. Attempted reaction with 	74
h. Attempted reaction with Ph ⁺ CH=N-N ⁻ Ph (phase transfer)	74
3. FVP of 1,3-dipole adducts	
a. FVP of 	75

4. Preparation of

a. $\text{X}=\text{CH}_2$

77

b. $\text{X}=\text{CCl}_2$ 

78

c. $\text{X}=\text{CF}_2$ (attempted)

80

d. $\text{X}=\text{EtO}_2\text{CN}$

81

e. $\text{X}=\text{MeO}_2\text{CN}$

83

f. $\text{X}=\text{PhO}_2\text{CN}$ (attempted)

84

5. FVP of

a. $\text{X}=\text{CH}_2$

85

b. $\text{X}=\text{EtO}_2\text{CN}$

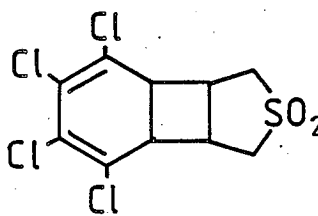
85

c. $\text{X}=\text{MeO}_2\text{CN}$

85

6. Diels-Alder Reactions

a. Preparation of



86

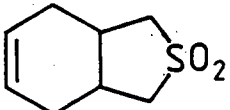
b. FVP of

"

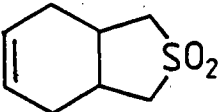
87

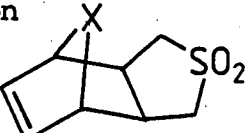
c. Attempted reaction with thiophen
dioxide

87

D. The  ring system

1. Preparation and FVP of sulphones

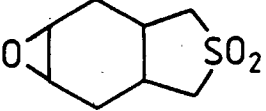
a. Preparation of  89

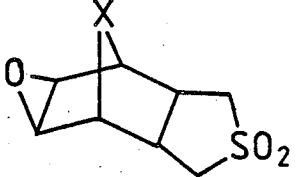
b.-d. Preparation of 
 of
 b. X=CH₂ 91
 c. X=CH₂CH₂ 93
 d. X=O 95

e. Attempted preparation by direct Diels-Alder reaction 98

f. FVP of sulphones 99

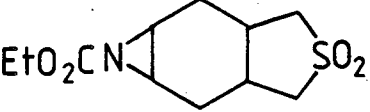
2. Preparation and FVP of sulphone epoxides

a. Preparation of  101

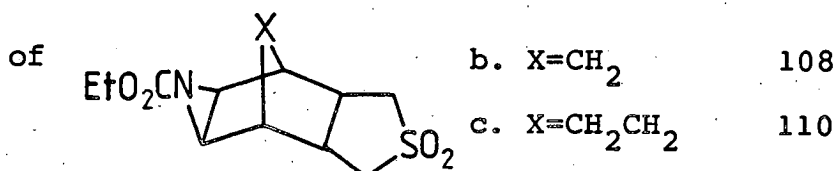

 X=CH₂ 102
 X=CH₂CH₂ 103
 X=O 103

b. FVP of epoxides 104

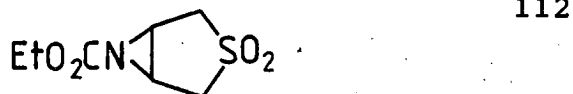
3. Preparation and FVP of sulphone aziridines

a. Preparation of  106

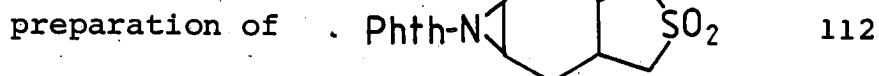
b.-c. Preparation



d. Preparation of



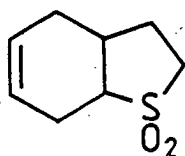
e. Attempted



f. FVP of aziridines

113

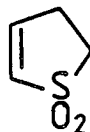
E. The



ring system

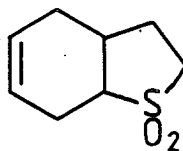
1. Preparation and FVP of sulphones

a. Preparation of

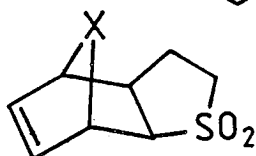


115

b. Preparation of



115

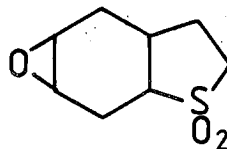
 $X=CH_2$ 116 $X=CH_2CH_2$ 117 $X=CH_2CH_2CH_2$ 117

c. FVP of sulphones

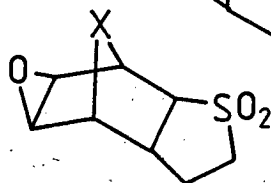
118

2. Preparation and FVP of sulphone epoxides

a. Preparation of



120

X=CH₂

121

X=CH₂CH₂

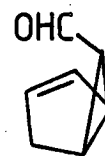
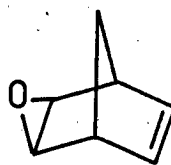
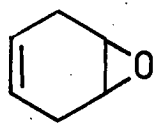
122

b. FVP of epoxides

122

incl. prepn.+FVP

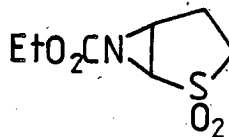
of



3. Preparation of sulphone aziridines

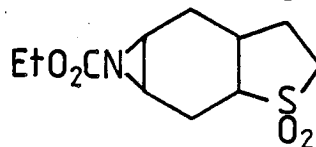
a. Attempted preparation

of



126

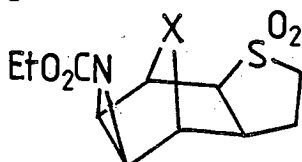
b. Preparation of



128

c.,d. Preparation

of

X=CH₂

129

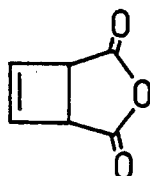
(attempted) X=CH₂CH₂

130

F. Preparation and FVP of some bicyclic anhydrides and derivatives

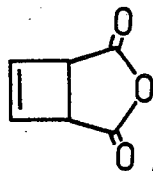
1. Preparation and FVP of anhydrides

a. Preparation of

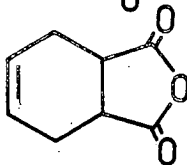


132

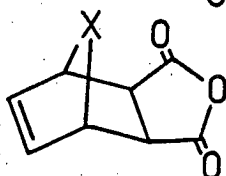
b. FVP of



132



132

X=CH₂

133

X=CH₂CH₂

133

X=O

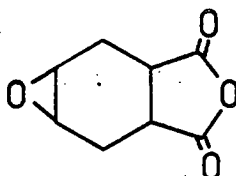
133

maleic anhydride

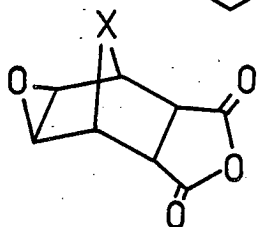
134

2. Preparation and FVP of anhydride epoxides

a. Preparation of



134

X=CH₂

134

X=CH₂CH₂

135

X=O

135

b. FVP of anhydride epoxides

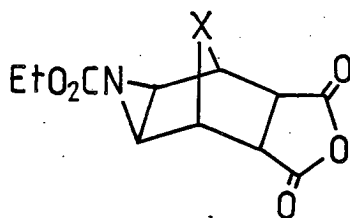
136

(incl. FVP of acrolein)

3. Preparation and FVP of anhydride aziridines

a.-d. Preparation

of

a. X=CH₂

138

b. X=CH₂CH₂

139

c. (MeO₂CN)X=CH₂CH₂

140

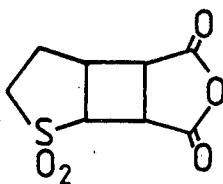
d. X=O

141

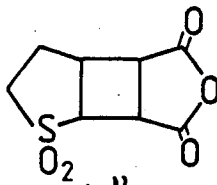
e. FVP of anhydride aziridines

142

G. Preparation and FVP of
and derivatives



1.a. Preparation of



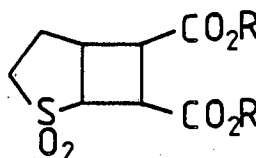
144

b. FVP of

”

144

2. Preparation and FVP
of



a. Preparation of diacid;

R=H

145

b. Preparation of diesters;

R=CH₃

145

R=C₂H₅

146

R=i-C₃H₇

147

R=CH₂Ph

147

R=t-C₄H₉

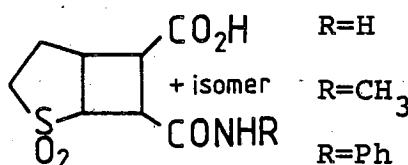
148

(attempted)

c. FVP of compounds

149

3.a. Preparation of



R=H

152

+ isomer

R=CH₃

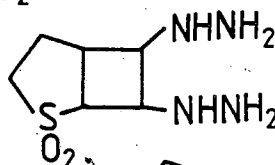
152

CONHR

R=Ph

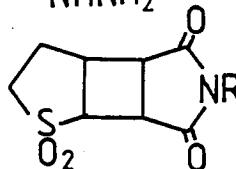
153

b. Preparation of

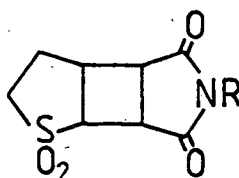


154

4. Preparation and FVP of



a. Preparation of



R=H

155

R=CH₃

156

R=Ph

156

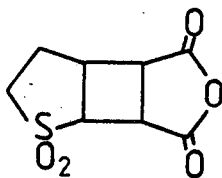
R=NH₂

157

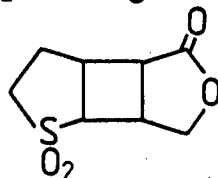
b. FVP of compounds

157

5. Reduction of



a. Preparation of



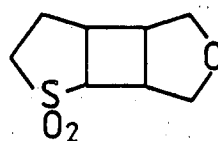
+ isomer

159

FVP of lactone

160

b. Preparation of



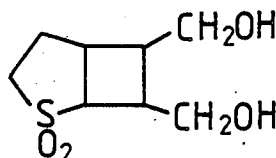
160

FVP of ether

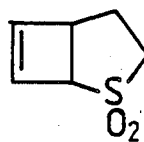
161

Attempted

preparation of



161

6. Preparation and FVP of
and derivatives

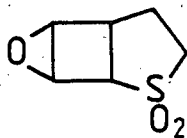
a. Preparation of the alkene

162

b. FVP and solution pyrolysis of the
alkene

163

c. Preparation of



163

d. FVP of epoxide

164

A. Symbols and Abbreviations

mmol	millimoles
M	mol dm^{-3}
h, min	hours, minutes
GC	gas liquid chromatography
TLC	thin layer chromatography
IR	infrared
ν	wave number
NMR	nuclear magnetic resonance
δ	chemical shift
J	spin-spin coupling constant
s,d,t,q,m	singlet, doublet, triplet, quartet, multiplet
MS	mass spectroscopy
m/e	mass to charge ratio
M^+	mass of molecular ion
FVP	flash vacuum pyrolysis
m.p.	melting point
b.p.	boiling point

B. Instrumentation and General Techniques

1. NMR Spectroscopy

a. ^1H NMR

Routine spectra were obtained at 60MHz on a Varian EM-360 spectrometer. Spectra of new compounds were obtained at 100MHz on a Varian HA-100 spectrometer operated by Mr. J.R.A. Millar. High resolution and selectively decoupled spectra were obtained at 360MHz on a Bruker WH-360 spectrometer operated by Dr. I.H. Sadler and Dr. D. Reed.

b. ^{13}C NMR

Routine spectra were obtained at 25MHz on a Varian CFT-20 spectrometer operated by Mr. J.R.A. Millar. Spectra of small samples were obtained at 90MHz on a Bruker WH-360 spectrometer operated by Dr. I.H. Sadler and Dr. D. Reed.

All spectra were obtained from solutions in deuteriochloroform unless otherwise stated and chemical shifts are expressed in parts per million to high frequency of tetramethylsilane.

2. Infrared Spectroscopy

Spectra were obtained on a Perkin-Elmer 157 G grating spectrometer. Unless otherwise stated, solids were run as nujol mulls and liquids as thin films, both on sodium chloride plates. Solution spectra were run in chloroform using matched sodium chloride cells of path length 0.1 mm. Spectra were calibrated with the polystyrene peak at 1603 cm^{-1} .

3. Mass Spectroscopy

Mass spectra and accurate mass measurements were obtained on an A.E.I. ms-902 instrument operated by Mr. D.J.A. Thomas.

4. Gas Chromatography-Mass Spectroscopy

GC-MS measurements were obtained on a Pye series 104 chromatograph coupled to a V.G. Micromass 12 spectrometer and operated by Miss E. Stevenson.

5. Elemental Analyses

Microanalyses for carbon, hydrogen and nitrogen were carried out on a Perkin-Elmer 240 Elemental Analyser by Mr. J. Grunbaum, University of Edinburgh.

6. Melting Points

Routine melting points were determined using an Electro-thermal melting point apparatus while melting points of new compounds were determined on a Reichert hot-stage microscope. All melting points are uncorrected.

7. Gas Liquid Chromatography

A Pye 104 chromatograph with a flame ionisation detector was used with nitrogen as carrier gas and a 2m x 4.5 mm glass column. The columns used were 10% polyethyleneglycoladipate (PEGA), 2% neopentylglycolsuccinate (NPGS) and 5% carbowax 20M, all on Chromosorb W (80-100 mesh).

8. Preparative Gas Chromatography

Preparative GC was carried out using a Carlo Erba Strumentazione Fractovap 2450 instrument. A 0.85m x 12mm column of 30% PEGA on Chromosorb A (40-60 mesh) was used and the products were collected in traps cooled in dry ice/acetone.

9. Thin Layer Chromatography

This was carried out using 0.3 mm layers of alumina (Merck, neutral aluminium oxide 60G, Type E) or silica (Merck, Kieselgel 60G), containing 0.5% Woelm fluorescent green indicator, on glass plates. The components were observed under ultraviolet light or by their reaction with iodine vapour.

10. Preparative Thin Layer Chromatography

This was carried out using 1.0mm layers of the supports mentioned above. After locating the components with iodine or UV light, the bands were scraped off and the products removed from the support by soaking with 5% A.R. methanol in chloroform for 3 h.

11. Column Chromatography

Alumina was Laporte Industries Alumina H (100-200 mesh), deactivated by addition of 6% water. Silica was Fisons Scientific Apparatus - Silica Gel for chromatography (60-120 mesh) and was 10% deactivated.

12. Drying and Evaporation of Organic Solutions

Organic solutions were dried by standing over anhydrous magnesium sulphate for several hours and were evaporated under reduced pressure on a rotary evaporator.

13. Photochemical Reactions

The lamps used were 125W and 400W medium pressure water cooled mercury lamps supplied by Applied Photophysics Ltd., London. Large scale reactions were carried out by inserting the quartz or pyrex reactor well in a vessel containing the reaction mixture. Small scale reactions could be performed by attaching a quartz tube containing the reaction mixture to the side of the reactor well.

14. Drying and Purification of Solvents

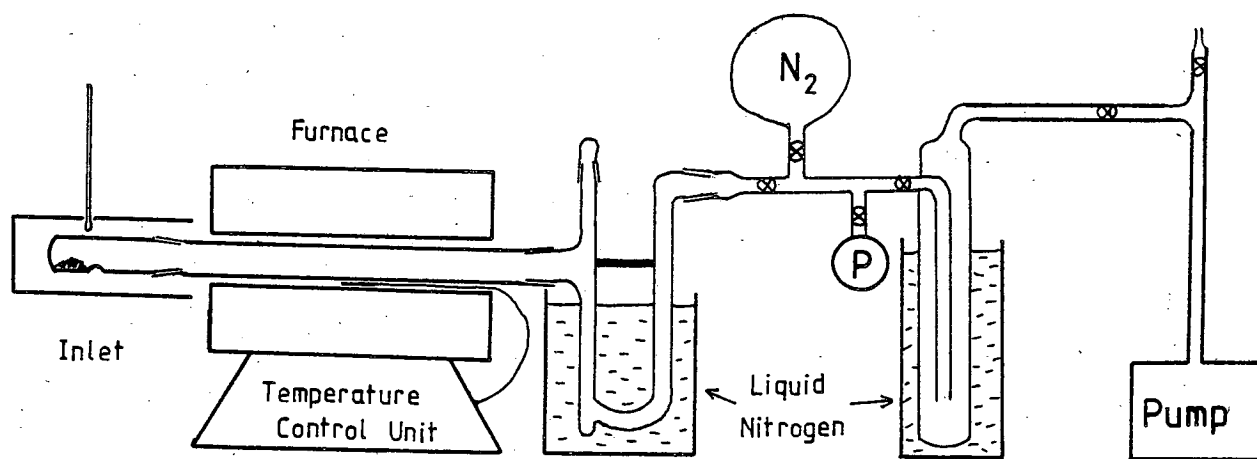
Commercially available solvents were used without further purification unless otherwise indicated. Where pure methanol, chloroform or toluene were required the commercial Analytical Reagent (A.R.) grade solvent was used. Dry acetonitrile was prepared by storing over freshly activated molecular sieve. Dry ether was prepared by addition of sodium wire and dry benzene was prepared by addition of sodium wire to the A.R. grade solvent. Dry methylene chloride and carbontetrachloride (b.p. 77.5°C) were distilled from phosphorus pentoxide and stored over molecular sieve. Pyridine was dried by heating under reflux with KOH for 2 h and then distilling (b.p. $114-117^{\circ}\text{C}$) on to molecular sieve. Dry tetrahydrofuran, dimethoxy-

ethane and dimethylformamide were prepared by heating the solvent under reflux with calcium hydride in an atmosphere of dry nitrogen for 2 h and then distilling onto molecular sieve. Ethyl acetate was dried by the method of Vogel¹⁸⁷ (b.p. 77-79°C) and was stored over molecular sieve. "Pet. ether" refers to light petroleum, the redistilled 40-60°C boiling fraction being used as a reaction solvent and for chromatography, and the 60-80°C fraction being used for recrystallisation.

15. Flash Vacuum Pyrolysis

The apparatus used was based on the design of W.D. Crow, Australian National University. A similar set-up is illustrated in the recent monograph by Brown¹⁸⁸.

The essential features of the apparatus are shown in Scheme 3. The sample was volatilised from a horizontal inlet



Scheme 3

tube, heated in a Büchi Kugelrohr oven, through a 30 x 2.5 cm silica tube. This was heated at temperatures in the range 350-

900°C by a Stanton Redcroft laboratory tube furnace LM8100, the temperature being measured by a Pt/Pt-13%Rh thermocouple situated at the centre of the furnace. The products were collected in a U-shaped trap cooled in liquid nitrogen. The whole system was maintained at a pressure of 10^{-2} - 10^{-3} mmHg by an Edwards Model ED100 high capacity rotary oil pump, the pressure being measured by a Pirani gauge situated between the trap and the pump. Under these conditions the contact time in the hot zone was estimated to be in the range 1-10 milliseconds. In some cases it was desirable to increase the contact time and this was achieved by packing the furnace tube with 5 cm lengths of silica tubing or a plug of silica wool.

The pyrolysis conditions are quoted as follows: "(weight of material volatilised, furnace temperature, average pressure during the pyrolysis, inlet temperature)".

Small scale pyrolyses were generally carried out using 25-100 mg of material. After the pyrolysis the system was isolated from the pump and filled with nitrogen gas. The product was then dissolved out of the trap in deuteriochloroform and analysed directly by NMR. By adding the chloroform while the trap was still frozen and keeping the solution cold, volatile or unstable products could be isolated in high yield. Yields were estimated by adding 5-10 mg of a solvent such as methylene chloride and comparing the NMR integrals. This calibration was estimated to be accurate to $\pm 10\%$.

In large scale pyrolyses 0.2-1.0 g of material was used and after filling the system with nitrogen the product was dissolved out and purified by the normal methods.

16. Photoelectron Spectroscopy

Photoelectron spectra were obtained on a Perkin Elmer PS 16 UV photoelectron spectrometer by Miss I. Simpson and Dr. M.H. Palmer. The results are given in Appendix A.

C. Preparation and reactions of 3-Thiabicyclo[3.2.0]-
hept-6-ene 3,3-dioxide

1. Preparation of 3-Thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide

(i) 3,5-Dioxo-4-oxa-9-thiatricyclo[5.3.0.0^{2,6}]decane 9,9-dioxide.

This was prepared by a modification of the method of Shaikrazieva *et al.*¹⁸³. A solution of butadiene sulphone (50 g, 424 mmol) and maleic anhydride (50 g, 510 mmol) in acetone (750 ml) was irradiated at 400W for 24 h. The crystals were filtered off and washed well with ether. By allowing the filtrate to stand and partly evaporate for several days further crops were obtained to give 3,5-Dioxo-4-oxa-9-thiatricyclo[5.3.0.0^{2,6}]decane 9,9-dioxide (55 g, 60%) as colourless crystals, m.p. 292-293°C (lit.,¹⁸³ 292-293°C).

(ii) 3-Thiabicyclo[3.2.0]heptane-6,7-dicarboxylic acid 3,3-dioxide

3,5-Dioxo-4-oxa-9-thiatricyclo[5.3.0.0^{2,6}]decane 9,9-dioxide (50 g, 231 mmol) was dissolved completely in boiling water (200 ml). The solution was evaporated to dryness and the solid residue washed well with ether to give 3-Thiabicyclo[3.2.0]heptane-6,7-dicarboxylic acid 3,3-dioxide (45 g, 83%) as colourless crystals, m.p. 188-190°C (lit.,¹⁸³ 194-195°C).

(iii) 3-Thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide

3-Thiabicyclo[3.2.0]heptane-6,7-dicarboxylic acid 3,3-dioxide (5.0 g, 21.4 mmol) was dissolved in dry pyridine (50 ml) and oxygen gas was bubbled through the solution for 15 min.

Lead tetraacetate (vacuum dried, 14.2 g, 32.0 mmol) was then added in one portion and the mixture heated to 70°C. After 20 min evolution of CO₂ was complete and the clear dark brown solution was poured into 5% nitric acid (1000 ml). Extraction with methylene chloride (3x250 ml) followed by drying and evaporation gave a clear brown oil. Kugelrohr distillation of this at 0.1 mmHg and 150-200°C, followed by recrystallisation from diisopropyl ether gave 3-Thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide (0.75 g, 24%) as long colourless flakes, m.p. 72-74°C (lit.,¹⁸⁴ 71-75°C).

2. Reaction of 3-Thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide with 1,3-dipoles

a. Reaction with diazomethane

An ether solution containing diazomethane (0.40 g, 9.5 mmol) prepared according to Vogel's Handbook¹⁸⁹ was added to a solution of 3-Thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide (0.35 g, 2.43 mmol) in dry ether (20 ml). After standing at room temperature for 120 h the diazomethane was allowed to evaporate and the solution cooled at 0°C overnight. The product was filtered off to give 4-Thia-8,9-diazatricyclo[5.3.0.0^{2,6}]dec-8-ene 4,4-dioxide (0.125 g, 28%) as colourless crystals, m.p. 149-150°C (lit.,¹⁸⁴ 152-154°C).

b. Attempted reaction with phenyldiazomethane

(i) Benzal hydrazine

This was prepared in 50% yield by the method of Curtius et al.¹⁹⁰ as a colourless liquid, b.p. (oven temperature) 180-200°C at 4 mmHg (lit.,¹⁹⁰ 140° at 14 mmHg).

(ii) Phenyldiazomethane

This was prepared by a modification of the method of Staudinger¹⁹¹. A suspension of benzal hydrazine (9.0 g, 75 mmol) and yellow mercuric oxide (15.0 g, 69.2 mmol) in pet. ether (50 ml) was shaken vigorously at 0°C for 3 h. A further portion of mercuric oxide (5.0 g, 23.1 mmol) was added and shaking continued for 3 h. The deep red solution was filtered and evaporated. Kugelrohr distillation of the residue gave Phenyldiazomethane (5.3 g, 60%) as a clear red oil, b.p. (oven temperature) 40-50°C at 0.1 mmHg (lit.¹⁹¹ 37-43°C at 1.5 mmHg); ν_{\max} 2060 cm^{-1} (diazo). The compound was stored at -30°C in the dark.

(iii) Attempted thermal reaction with phenyldiazomethane

A solution of 3-Thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide (0.17 g, 1.18 mmol) and phenyldiazomethane (0.28 g, 2.33 mmol) in dry ether (25 ml) was allowed to stand at room temperature for 2 weeks. TLC (alumina, Et₂O) showed only the starting materials to be present. The solution was evaporated and the residue taken up in A.R. chloroform (10 ml). Heating under reflux resulted in evolution of nitrogen and after 35 h the red colour of the diazoalkane had disappeared. TLC still showed the presence of the starting sulphone. This was confirmed by the NMR which also showed several aromatic products including benzaldehyde. Chromatography on alumina (Et₂O) gave recovered starting sulphone (0.14 g).

(iv) Attempted photochemical reaction with phenyldiazomethane

A solution of 3-Thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide (7.2 mg, 0.05 mmol) and phenyl diazomethane (12.0 mg, 0.10 mmol):

in deuteriochloroform (0.5 ml) was irradiated in a quartz NMR tube at 400W for 3 h. After this time the red colour of the diazoalkane had changed to brown. The NMR again showed the presence of the starting sulphone and aromatic byproducts including in this case benzal azine ($\text{PhCHN}_2\text{CHPh}$).

c. Attempted reaction with diphenyldiazomethane

(i) Benzophenone hydrazone

This was prepared in 83% yield by the method of Curtius et al.¹⁹² as pale yellow flakes, m.p. $97-99^\circ\text{C}$ (lit.¹⁹² 98°C).

(ii) Diphenyldiazomethane

This was prepared by a modification of the method of Miller¹⁹³. A mixture of benzophenonehydrazone (5.0 g, 25.5 mmol), anhydrous sodium sulphate (5.8 g), ethanol saturated with potassium hydroxide (2 ml) and yellow mercuric oxide (13.5 g, 62.3 mmol) was shaken in dry ether (75 ml) for 2 h. The mixture was filtered and the residue washed well with ether. Evaporation of the combined filtrate at room temperature gave a red oil which was dissolved in pet. ether (200 ml). The white solid which crystallised out on standing was filtered off and the filtrate evaporated at room temperature. Further dissolution in pet. ether and filtration gave, on final evaporation a red oil which crystallised on cooling to long dark red needles of Diphenyldiazomethane (4.43 g, 90%), m.p. $25-27^\circ\text{C}$ (lit.¹⁹³ $29-32^\circ\text{C}$). The compound was stored at -30°C in the dark.

(iii) Attempted thermal reaction with Diphenyldiazomethane

A solution of 3-Thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide

(0.25 g, 1.74 mmol) and diphenyldiazomethane (0.35 g, 1.80 mmol) in dry ether (10 ml) was allowed to stand at room temperature for 65 h. TLC (alumina, Et₂O) showed only the starting materials to be present. After heating under reflux for 6 h there was no change in the TLC. The solution was evaporated and the residue taken up in A.R. toluene (50 ml). On heating at 90°C for 6 h the red colour of the diazoalkane changed to yellow but the TLC still showed the sulphone unreacted. Chromatography on alumina (Et₂O) gave aromatic products (0.37 g) and recovered starting sulphone (0.23 g).

(iv) Attempted photochemical reaction with diphenyldiazomethane

A solution of 3-Thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide (0.20 g, 1.39 mmol) and diphenyldiazomethane (0.30 g, 1.55 mmol) in dry ether (10 ml) was irradiated at 400W for 1.5 h. After this time the red colour had disappeared and a white precipitate formed. Evaporation of the ether followed by chromatography of the residue on alumina (Et₂O) gave the unreacted starting sulphone (0.10 g) and an oil (0.19 g) whose NMR showed only aromatics.

d. Attempted reaction with ethyl diazoacetate

(i) Attempted thermal reaction with ethyl diazoacetate

A solution of 3-Thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide (22.6 mg, 0.16 mmol) in ethyl diazoacetate (0.5 g, 4.4 mmol) was allowed to stand at room temperature for 3 weeks. The NMR showed only the starting materials to be present. After heating at 60°C for 36 h the NMR showed four ethyl containing products but no change in the pattern due to the sulphone.

(ii) Attempted photochemical reaction with ethyl diazoacetate

A solution of 3-Thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide (32.7 mg, 0.23 mmol) in ethyl diazoacetate (0.5 g, 4.4 mmol) was irradiated at 400W for 16 h, by which time evolution of nitrogen had ceased. The NMR of the thick brown oil showed several ethyl containing byproducts and the unreacted sulphone. TLC (alumina, Et₂O) showed only starting sulphone and fast moving byproducts.

e. Attempted photochemical reaction with phenyl azide

(i) A solution of 3-Thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide (0.45 g, 3.1 mmol) in phenyl azide (1.0 g, 8.4 mmol) was irradiated at 125W for 75 h. The NMR and TLC (alumina, Et₂O) showed the presence of many aromatic products and the unchanged starting sulphone.

(ii) Irradiation of a solution of 3-Thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide (30 mg, 0.21 mmol) and phenyl azide (40 mg, 0.34 mmol) in dry ether (0.5 ml) at 400W for 6 h gave a similar result - no change in the starting sulphone.

f. Attempted reaction with *p*-anisonitrile sulphide

A solution of 3-Thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide (0.30 g, 2.1 mmol) and 5-(*p*-methoxyphenyl)-[1,3,4]-oxathiazol-2-one¹⁹⁴ (0.50 g, 2.4 mmol) in A.R. toluene (10 ml) was heated under reflux for 85 h. TLC showed that all the oxathiazolone had been used up to give mainly *p*-anisonitrile and that most of the sulphone was unchanged. A further 0.50 g of oxathiazolone was added and heating continued for 50 h. There was

no change in the TLC so a final 0.50 g of oxathiazolone was added and the mixture heated for 25 h. The residue on evaporation was chromatographed on alumina (Et₂O) to give sulphur (0.13 g), *p*-anisonitrile (0.71 g) and a yellow solid (22 mg). The mass spectrum of this showed none of the desired product to be present. The starting sulphone had apparently been destroyed under the severe conditions.

g. Attempted reaction with an azomethine imine

(i) 1-Ethoxy-2-(2,4-dinitroanilino)-1,2,3,4-tetrahydroisoquinoline

This was prepared in four steps (38% overall yield) by the method of Schmitz¹⁹⁵ as orange flakes, m.p. 136-138°C (lit.¹⁹⁵ 137-140°C).

(ii) Attempted reaction with the azomethine imine

A solution of 3-Thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide (0.20 g, 1.39 mmol) and 1-ethoxy-2-(2,4-dinitroanilino)-1,2,3,4-tetrahydroisoquinoline (0.50 g, 1.39 mmol) in A.R. toluene (25 ml) was heated at 80°C for 40 h. TLC (alumina, Et₂O) showed most of the sulphone unreacted. After heating under reflux for 35 h crystals were formed on cooling which were filtered off to give the hexahyrotetrazine formed by dimerisation of the 1,3-dipole (0.20 g), m.p. 154-155°C (lit.¹⁹⁶ 151-152°C). Evaporation of the filtrate gave a brown solid (0.33 g) whose NMR showed only the dipole dimer and the starting sulphone to be present.

h. Attempted reaction with a nitrile imine under phase transfer conditions

A solution of 3-Thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide

(0.10 g, 0.69 mmol), N-(α -chlorobenzylidene)-N'-phenylhydrazine (0.17 g, 0.69 mmol) and benzyltriethylammonium chloride (16 mg, 0.07 mmol) in chloroform (10 ml) was stirred vigorously with 1M aqueous sodium bicarbonate solution (2 ml) for 30 h. Water (10 ml) was added and the organic layer separated. After washing with water (2x5 ml) this was dried and evaporated to give a yellow crystalline solid (0.25 g). Chromatography of this on alumina (Et₂O/hexane, 2:1) gave a brown oil (110 mg), fluorescent yellow crystals (40 mg) and finally the recovered starting sulphone (90 mg). The yellow crystals proved to be 1,3,4,6-tetraphenyl-1,4-dihydro-s-tetrazine, m.p. 212-214°C (lit.¹⁹⁷ 205-207°C), formed by dimerisation of the nitrile imine. Preparative TLC of the brown oil on alumina (Et₂O/hexane, 2:1) gave a pink solid (50 mg), a yellow gum (5 mg) and finally a brown oil (50 mg) whose mass spectra showed them to contain respectively the starting α -chlorobenzylidene phenylhydrazine, a hydrate of the nitrile imine and the dihydrotetrazine. There was no trace of the desired product.

3. Flash vacuum pyrolysis of 3-thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide/1,3-dipole adducts

a. FVP of 4-thia-8,9-diazatricyclo[5.3.0.0^{2,6}]dec-8-ene 4,4-dioxide

(i) Preparation of 1,3-cycloheptadiene and 1,4-cycloheptadiene

Reaction of cycloheptatriene (18 g) with sodium in liquid ammonia by the method of Rettig et al.¹⁹⁸ followed by Kugelrohr distillation of the product gave a colourless liquid (8.47 g, 47%). GC of this (10% PEGA, 50°C) showed the presence of three

components. These were separated by preparative GC on 30% PEGA (45°C) to give cycloheptene (0.51 g); δ 5.8-5.7 (2H,m), 2.2-2.05 (4H,m) and 1.8-1.4 (6H,m), followed by 1,4-cycloheptadiene (0.85 g); δ 5.75-5.6 (4H,m), 2.85 (2H,m) and 2.24 (4H,m), and finally 1,3-cycloheptadiene (2.54 g); δ 5.72 (4H,s), 2.32 (4H,m) and 1.94-1.7 (2H,m). NMR and GC showed each diene to contain less than 5% of the other isomer.

(ii) FVP of 4-thia-8,9-diazatricyclo[5,3,0.0^{2,6}]dec-8-ene 4,4-dioxide

FVP of the title compound (40 mg, 475°C, 2×10^{-3} mmHg, inlet 140-160°C) gave a yellow oil. NMR of this showed a complex pattern of peaks, δ 6-5 and 4-1. GC (10% PEGA, 55°C) showed the presence of ten components. GC-MS showed eight of these to have m/e 94 and the other two m/e 92. The largest single m/e 94 peak was due to 1,4-cycloheptadiene (identical retention time and MS breakdown pattern to authentic). None of the other isomers could be identified. By comparison with a standard solution of 1,4-cycloheptadiene the yield of hydrocarbons from the sulphone was 72%, made up of 1,4-cycloheptadiene (27%), other C₇H₁₀ isomers (39%) and C₇H₈ isomers (6%). FVP at temperatures from 400°C to 575°C gave essentially the same products.

(iii) FVP of 1,4-cycloheptadiene

FVP of the title compound (25 mg, 750°C, 50×10^{-3} mmHg, inlet 25°C) with silica rods packing the furnace tube to increase the contact time gave a yellow oil whose GC (10% PEGA, 55°C) showed the presence of 7 components. GC-MS and

comparison with authentics showed these to be cyclopentadiene, unreacted 1,4-cycloheptadiene, 1,3-cycloheptadiene, two isomers of m/e 94 and two isomers of m/e 80 (which were not 1,3- or 1,4-cyclohexadiene). By standardisation with a solution of 1,4-cycloheptadiene the overall yield of hydrocarbons was 70% made up of cyclopentadiene (7%), 1,4-cycloheptadiene (3%), 1,3-cycloheptadiene (15%), two C_7H_{10} isomers (18%) and two C_6H_8 isomers (27%).

(iv) FVP of 1,3-cycloheptadiene

FVP of the title compound (30 mg, $750^{\circ}C$, 50×10^{-3} mmHg, inlet $25^{\circ}C$) with silica rods packing the furnace tube gave a yellow liquid whose GC (10% PEGA, $55^{\circ}C$) showed the presence of 4 components. By GC-MS and comparison with authentics these were found to be cyclopentadiene, a compound of m/e 98, benzene and the unreacted starting material. Standardisation with a solution of 1,3-cycloheptadiene gave the overall yield of hydrocarbons as 76%, made up of cyclopentadiene (8%), C_7H_{14} isomer (3%), benzene (46%) and 1,3-cycloheptadiene (19%).

4. Preparation of the 3-Thiatricyclo[3.3.0.0^{6,8}]octane ring system.

a. 3-Thiatricyclo[3.3.0.0^{6,8}]octane 3,3-dioxide

A solution of 4-thia-8,9-diazatricyclo[5.3.0.0^{2,6}]dec-8-ene 4,4-dioxide (196 mg, 1.05 mmol) in dry acetonitrile (5 ml) was irradiated at 125W for 60 h. After this time evolution of nitrogen had stopped and the TLC (alumina, Et_2O) showed no starting material left. Preparative TLC on alumina (Et_2O)

gave byproducts (20 mg) followed by the desired product.

Recrystallisation of this from hexane/ether (3:1) gave 3-Thia-tricyclo[3.3.0.0^{6,8}]octane 3,3-dioxide (80 mg, 48%) as colourless needles, m.p. 94-95°C. (Found: C, 52.9; H, 6.4. C₇H₁₀O₂S requires C, 53.1; H, 6.4%); ν_{\max} 1302, 1290, 1250, 1197, 1169, 1122, 1094, 955, 920, 893 and 713 cm⁻¹; δ 3.24-3.12 (4H, m), 2.6 (2H, m), 1.71 (2H, d, J 5.5 Hz) and 0.96-0.76 (2H, m); m/e 158 (0.6%, M⁺), 94 (18), 93 (63), 92 (36), 91 (37), 80 (13), 79 (100), 78 (25) and 77 (67).

(b) Reaction with dichlorocarbene

(i) Bromodichloromethyl phenyl mercury

This was prepared in 50% yield by reaction of phenyl mercuric chloride and bromodichloromethane with potassium tert-butoxide according to the method of Seyferth et al.¹⁹⁹. The colourless crystals had m.p. 107-109°C (lit., 108-110°C).

(ii) Reaction with dichlorocarbene from the organomercury reagent

This was carried out by the method of Mock⁷⁶. A solution of 3-Thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide (0.10 g, 0.69 mmol) and bromodichloromethyl phenyl mercury (0.60 g, 1.36 mmol) in dry benzene (10 ml) was heated under reflux for 55 h. The solution was evaporated and the residue leached with hot chloroform (5x10 ml). Hydrogen sulphide gas was passed through the solution for 2 min and the resulting precipitate filtered off. Evaporation of the filtrate gave a yellow solid (0.31 g). The NMR of this showed the presence of the starting sulphone and new peaks at δ 5.9 and 4.7. Preparative TLC on silica (CH₂Cl₂)

gave brown crystals (30 mg) and the recovered starting sulphone (70 mg). Recrystallisation of the brown crystals from ether gave 7,8-dichloro-3-thiabicyclo[3.3.0]oct-6-ene 3,3-dioxide (6.2 mg, 4%) as colourless needles, m.p. 143-144°C. (Found: 37.0; H, 3.5. $C_7H_8Cl_2O_2S$ requires C, 37.0; H, 3.5%); ν_{max} 1310, 1253, 1225, 1148, 1111, 938, 875, 821, 792 and 730 cm^{-1} ; δ 5.89 (1H, d, J2Hz), 4.74 (1H, s), 3.8 (1H, m) and 3.46-2.77 (5H, m); ^{13}C δ (90MHz) 135.46 (C_7), 131.41 (C_6), 68.25 (C_8), 52.58 (C_4), 51.93 (C_2), 46.70 (C_5) and 41.89 (C_1); m/e 230, 228, 226 (2.1, 11, 16%, M^+), 193, 191 (2.0, 4.8), 163 (11), 161 (19), 127, 125 (34, 100) and 91 (73).

(iii) Reaction with dichlorocarbene under phase transfer conditions

This was carried out by the method of Gaoni⁷⁸. A solution of 3-Thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide (216 mg, 1.5 mmol) in A.R. chloroform (5 ml) was stirred with a 50% aqueous solution of sodium hydroxide (10 ml) containing benzyl triethylammonium chloride (50 mg) at 50°C for 4 h. Ice (15 g) was added and the mixture extracted with methylene chloride (4x25 ml). Drying and evaporation gave a yellow oil (0.25 g) whose NMR showed mainly the starting sulphone but also peaks at δ 1.1-1.5 corresponding to the expected cyclopropane. Preparative TLC on silica (CH_2Cl_2) gave oily yellow crystals (25 mg) followed by recovered starting sulphone (150 mg). The NMR at this stage showed roughly equal proportions of 7,8-dichloro-3-thiabicyclo[3.3.0]oct-6-ene 3,3-dioxide and the cyclopropyl isomer 7,7-dichloro-3-thiatricyclo[3.3.0.0^{6,8}]-octane 3,3-dioxide; δ 3.7-2.7 (6H, m) and 1.29-1.18 (2H, m).

Recrystallisation from ether resulted in complete isomerisation to give 7,8-dichloro-3-thiabicyclo[3.3.0]oct-6-ene 3,3-dioxide (15 mg, 4.4%) as colourless needles, m.p.143-144°C.

c. Attempted reaction with difluorocarbene

(i) The first method used was that of Burton and Nae²⁰⁰. Dibromodifluoromethane (146 mg, 0.69 mmol) was added to a solution of triphenylphosphine (182 mg, 0.69 mmol) in dry dimethoxyethane (10 ml) stirred under nitrogen. After 30 min a white precipitate had formed and 3-Thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide (100 mg, 0.69 mmol) was added followed by anhydrous potassium fluoride (161 mg, 2.76 mmol). The mixture was stirred at room temperature under nitrogen for 48 h. The solution was evaporated and the residue taken up in methylene chloride (10 ml) which was then washed with water (3x10 ml), dried and evaporated to give a colourless crystalline solid (0.22 g). The NMR of this showed mainly aromatics and the starting sulphone but with small signals at δ 1.3-1.1 possibly corresponding to the desired product. Preparative TLC on silica (Et₂O) gave triphenylphosphine oxide (110 mg) and the recovered starting sulphone (95 mg) with none of the desired product.

(ii) The other method used was that of Seyferth²⁰¹. Phenyl trifluoromethyl mercury was prepared by the method of Seyferth (82% yield, m.p.134-136°C, lit. 141-143°C).

A solution of 3-Thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide (0.10 g, 0.69 mmol) and phenyl trifluoromethyl mercury (0.24 g, 0.69 mmol) in dry benzene (10 ml) containing anhydrous sodium

iodide (0.26 g, 1.73 mmol) was heated under reflux for 36 h. The solid was filtered off, washed with benzene (10 ml) and the combined filtrate evaporated to give a white solid (0.26 g). Preparative TLC on alumina (Et₂O) gave only fast-moving organomercury compounds (0.15 g) and the recovered starting sulphone (0.08 g). A repeat reaction using two equivalents of the organomercury compound gave a similar result; only organomercury compounds and the starting sulphone could be detected by TLC (alumina, Et₂O) or NMR.

d. 7-Ethoxycarbonyl-3-thia-7-azatricyclo[3.3.0.0^{6,8}]octane 3,3-dioxide.

(i) Ethyl azidoformate

This was prepared in 85% yield by the method of Lwowski et al.²⁰² as a colourless liquid, n_D^{15} 1.4187 (lit., n_D^{15} 1.4180), which was stored at -30°C in the dark.

(ii) Photochemical reaction with ethyl azidoformate

The method used was based on that of Meyers et al.⁷⁷. A mixture of 3-Thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide (0.50 g, 3.5 mmol) and ethyl azidoformate (1.25 g, 10.9 mmol) was irradiated at 400W for 15 h. Chromatography of the resulting yellow solid on alumina (Et₂O) gave azide byproducts as a yellow oil (0.85 g) followed by the desired product as oily crystals (0.53 g). Recrystallisation from ether/methylene chloride (4:1) gave 7-Ethoxycarbonyl-3-thia-7-azatricyclo-[3.3.0.0^{6,8}]octane 3,3-dioxide (0.25 g, 31%) as colourless needles, m.p. 142-143°C. (Found: C, 46.8; H, 5.7; N, 6.1. C₉H₁₃NO₄S requires C, 46.7; H, 5.7; N, 6.1%); ν_{\max} 1708,

1309, 1273, 1242, 1140, 1099, 1039, 900, 865, 812, 768 and 721 cm^{-1} ; δ 4.25 (2H, q, J7Hz), 3.26-3.20 (6H,m), 3.0-2.88 (2H,m), 1.31 (3H, t, J7Hz); m/e 231 (0.3%, M^+), 186 (12), 159 (5), 108 (23), 94 (32) and 80 (100).

(iii) Thermal reaction with ethyl azidoformate

A solution of 3-Thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide (40 mg, 0.28 mmol) and ethyl azidoformate (35 mg, 0.31 mmol) in dry carbon tetrachloride (5 ml) was heated under reflux for 40 h. Evaporation gave a yellow solid whose TLC (alumina, Et_2O) and NMR showed the presence of azide byproducts, unreacted starting sulphone (32 mg) and 7-Ethoxycarbonyl-3-thia-7-azatricyclo[3.3.0.0^{6,8}]octane 3,3-dioxide (14 mg, 21%). [Yields estimated from NMR].

(iv) Homogeneous reaction with ethoxycarbonyl nitrene from α -elimination

To a solution of 3-Thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide (50 mg, 0.35 mmol) and ethyl *p*-nitrobenzenesulphonoxycarbamate (110 mg, 0.38 mmol) in dry methylene chloride (10 ml) was added a solution of triethylamine (100 mg, 0.99 mmol) in dry methylene chloride (5 ml) over 10 min. After stirring at room temperature for 12 h, the solution was washed with water (4x15 ml), dried and evaporated to give a yellow oil (0.10 g). The NMR and TLC (alumina, Et_2O) of this showed the presence only of nitrene byproducts and the starting sulphone with no trace of the expected aziridine.

(v) Reaction with ethoxycarbonyl nitrene from α -elimination under phase transfer conditions.

The method used was based on that of Seno et al.²⁰³.

A solution of 3-Thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide (72 mg, 0.5 mmol), ethyl *p*-nitrobenzenesulphoxycarbamate (145 mg, 0.5 mmol) and benzyl triethylammonium chloride (12 mg, 0.05 mmol) in methylene chloride (10 ml) was stirred vigorously with 1M aqueous sodium bicarbonate solution (2 ml) for 4 h. Water (25 ml) was then added and the organic layer separated. After washing with water (10 ml) this was dried and evaporated to give an orange oil (0.12 g). The NMR and TLC (alumina, Et₂O/*i*-PrOH, 20:1) of this showed the presence of nitrene by-products, unreacted starting sulphone (40 mg) and 7-Ethoxycarbonyl-3-thia-7-azatricyclo[3.3.0.0^{6,8}]octane 3,3-dioxide (50 mg, 43%). [Yields estimated from NMR].

e. 7-Methoxycarbonyl-3-thia-7-azatricyclo[3.3.0.0^{6,8}]octane 3,3-dioxide

(i) Methyl azidoformate

This was prepared in 80% yield in an analogous manner to ethyl azidoformate. The colourless liquid had n_D^{25} 1.4146 and δ 3.87 (3H,s).

(ii) Photochemical reaction with methyl azidoformate

A mixture of 3-thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide (0.50 g, 3.5 mmol) and methyl azidoformate (1.5 g, 15 mmol) was irradiated at 400W for 18 h. Chromatography of the resulting brown oil on alumina (Et₂O) gave azide byproducts as a yellow oil (0.24 g) followed by recovered starting sulphone (0.15 g) and finally a white solid (0.49 g). Recrystallisation of this from diisopropyl ether/methanol, (5:1) gave 7-Methoxy-

carbonyl-3-thia-7-azatricyclo[3.3.0.0^{6,8}]octane 3,3-dioxide
 (0.22 g, 30%) as colourless crystals, m.p. 175-177°C. (Found:
 C, 44.2; H, 5.1; N, 6.2. C₈H₁₁NO₄S requires C, 44.2;
 H, 5.1; N, 6.4%); ν_{\max} 1716, 1305, 1280, 1140, 1102, 949,
 928, 890, 862, 811, 806, 775 and 720 cm⁻¹; δ 3.81 (3H, s),
 3.3-3.2 (6H, m) and 2.98-2.88 (2H, m); m/e 217 (0.1%, M⁺),
 186 (14), 152 (3), 151 (8), 139 (32), 138 (100), 95 (10), 94
 (89), 67 (93) and 59 (50).

f. Attempted reaction with phenyl azidoformate

(i) Phenyl azidoformate

This was prepared in 86% yield in a manner analogous to ethyl azidoformate. Kugelrohr distillation of the product gave a colourless liquid, b.p. (oven temperature) 65-69°C at 0.7 mmHg, n_D^{20} 1.5289 (lit.²⁰⁴ 63-67°C at 0.9 mmHg, n_D^{25} 1.5290-2).

(ii) Photochemical reaction with phenyl azidoformate

A solution of 3-Thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide (0.10 g, 0.69 mmol) in phenyl azidoformate (1.0 g, 6 mmol) was irradiated at 400W for 9 h. Chromatography of the resulting dark oil on alumina (Et₂O/hexane, 2:1) gave a single fraction as a clear yellow oil (0.37 g). The NMR of this showed the presence of phenyl carbamate, diphenyldiazodicarboxylate and possibly the benzoxazolone formed by intramolecular reaction of the azide. The sulphone function appeared to have been completely destroyed.

5. Flash vacuum pyrolysis of 3-thiatricyclo[3.3.0.0^{6,8}]-octane 3,3-dioxide and derivatives

a. FVP of 3-thiatricyclo[3.3.0.0^{6,8}]octane 3,3-dioxide

FVP of the title compound (17 mg, 475°C, 2×10^{-3} mmHg, inlet 70-100°C) gave a colourless liquid. There was only one major peak in the GC (10% PEGA, 55°C) with about 12 very small peaks, many of them corresponding to the C₇H₁₀ and C₇H₈ isomers produced in the pyrolysis of the diazo compound (section 3a(ii)). The major product was found to be 1,4-cycloheptadiene and comparison with a standard solution gave the yields as 1,4-cycloheptadiene (80%) and twelve unknown hydrocarbons (total 5%).

b. FVP of 7-Ethoxycarbonyl-3-thia-7-azatricyclo[3.3.0.0^{6,8}]octane 3,3-dioxide

FVP of the title compound (85 mg, 575°C, 10^{-3} mmHg, inlet 120-140°C) with silica rods in the furnace tube gave a brown oil which after preparative TLC on silica (Et₂O/pet.ether, 1:1) gave 1-Ethoxycarbonyl-4,5-dihydroazepine (6.1 mg, 10%) as a colourless liquid. (Found: M⁺ 167.094279. C₉H₁₃NO₂ requires 167.094623); ν_{\max} (CDCl₃) 1715, 1367, 1323, 1224, 1190 and 1144 cm⁻¹; δ 6.67 (2H, d, J10Hz), 5.10 (2H, m), 4.23 (2H, q, J7Hz), 2.30 (4H, t, J3Hz) and 1.31 (3H, t, J7Hz). m/e 167 (100%, M⁺), 149 (23), 105 (44) and 94 (90).

c. FVP of 7-Methoxycarbonyl-3-thia-7-azatricyclo[3.3.0.0^{6,8}]octane 3,3-dioxide

FVP of the title compound (60 mg, 550°C, 2×10^{-3} mmHg, inlet

150-180°C) with silica rods in the furnace tube gave a brown oil which after preparative TLC on silica (Et₂O) gave a colourless oil consisting mainly of 1-Methoxycarbonyl-4,5-dihydroazepine (6 mg, 14%). (Found: M⁺ 153.078113.

C₈H₁₁NO₂ requires 153.078973.); ν_{\max} (CDCl₃) 1704, 1450, 1380, 1317, 1232 and 1198 cm⁻¹; δ 6.65 (2H, d, J10Hz), 5.2-5.0 (2H, m), 3.79 (3H, s) and 2.30 (4H, t, J3Hz); m/e 153 (100%, M⁺), 138 (20), 126 (22), 114 (32), 94 (53) and 79 (32).

6. Diels-Alder reactions of 3-thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide

a. Reaction with tetrachlorothiophen 1,1-dioxide

(i) Tetrachlorothiophen 1,1-dioxide

Reaction of hexachloro-1,3-butadiene with sulphur followed by oxidation of the resulting tetrachlorothiophen with *m*-chloroperoxybenzoic acid in 1,2-dichloroethane according to the method of Raasch¹⁰³, gave Tetrachlorothiophen 1,1-dioxide (30% overall yield) as pale yellow crystals, m.p. 86-87°C (lit., 90-91°C).

(ii) Preparation of 8,9,10,11-Tetrachloro-4-thiatricyclo-[5,4,0.0^{2,6}]undeca-8,10-diene 4,4-dioxide

A solution of 3-Thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide (100 mg, 0.69 mmol) and tetrachlorothiophen 1,1-dioxide (194 mg, 0.76 mmol) in dry benzene (10 ml) was heated under reflux for 48 h. Preparative TLC of the residue after evaporation, on alumina (Et₂O), gave the unreacted thiophen dioxide (80 mg) followed by the desired product. This was recrystallised from

chloroform/hexane (1:1) to give 8,9,10,11-Tetrachloro-4-thiatricyclo[5.4.0.0^{2,6}]undeca-8,10-diene 4,4-dioxide (78 mg, 34%) as colourless needles, m.p.180-181°C.

(Found: C, 36.1; H, 2.4; M⁺, 331.901160, 333.896833, 335.894463 and 337.891440. C₁₀H₈Cl₄O₂S requires C, 36.0; H, 2.4%; M⁺, 331.899912, 333.896962, 335.894012 and 337.891062); ν_{\max} 1617, 1319, 1305, 1233, 1207, 1143, 1101, 900, 750 and 719 cm⁻¹; δ 3.73 (2H, m), 3.55 (2H, m) and 3.18 (4H, m); m/e (only ³⁵Cl peaks listed) 332 (11%, M⁺), 232 (7); 214 (100, tetrachlorobenzene), 179 (9), 162 (10) and 54 (14, butadiene).

b. Flash vacuum pyrolysis of 8,9,10,11-tetrachloro-4-thiatricyclo[5.4.0.0^{2,6}]undeca-8,10-diene 4,4-dioxide

FVP of the title compound (25 mg, 550°C, 2x10⁻³ mmHg, inlet 130-150°C) gave a yellow oil whose NMR showed weak signals at δ 5-6 due to 1,3-butadiene and a singlet at δ 7.23. This proved to be due to 1,2,3,4-tetrachlorobenzene and the product was identical to the authentic material on GC (10% PEGA, 175°C). Preparative TLC on alumina (Et₂O) gave 1,2,3,4-tetrachlorobenzene (5 mg), m.p.43-45°C (lit., ²⁰⁵ 45-46°C). IR spectrum identical to that of the authentic material.

c. Attempted reaction with thiophen 1,1-dioxide

(i) 3,4-Dibromosulpholane

This was prepared by addition of bromine to butadiene sulphone in carbon tetrachloride according to the literature method ²⁰⁶ to give trans-3,4-Dibromosulpholane (88%), m.p.141-

142°C (lit.,²⁰⁶ 139-141°C).

(ii) Reaction with thiophen 1,1-dioxide

The method of Leaver et al.^{169,207} was used. Powdered sodium hydroxide (2.5 g, 62.5 mmol) was added to a solution of 3,4-dibromosulpholane (1.0 g, 3.6 mmol) in dry tetrahydrofuran (75 ml) stirred at 0°C under nitrogen. After 2 h a further portion of sodium hydroxide (2.5 g) was added and the stirring continued for a further 1.5 h. The solution was filtered through celite under nitrogen and 3-Thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide (50 mg, 0.35 mmol) was added. After stirring for 18 h at room temperature, the solution was evaporated to give a pale yellow oily solid. NMR of this showed broad peaks at δ 4-3 and 2, due to thiophen dioxide polymerisation and the singlet at δ 6.2 due to the unreacted bicyclic sulphone. TLC (alumina, Et₂O) confirmed the presence of the unchanged starting material.

D. The 8-Thiabicyclo[4.3.0]non-3-ene 8,8-dioxide ring system

1. Preparation and FVP of 8-Thiabicyclo[4.3.0]non-3-ene 8,8-dioxide and bridged analogues.

a. *cis*-8-Thiabicyclo[4.3.0]non-3-ene 8,8-dioxide

(i) *cis*-4,5-Di(hydroxymethyl)cyclohexene

7,9-Dioxo-8-oxabicyclo[4.3.0]non-3-ene (36.0 g, 240 mmol) was dissolved in dry tetrahydrofuran (400 ml) and the solution was added dropwise to a stirred suspension of lithium aluminium hydride (10.0 g, 264 mmol) in dry tetrahydrofuran (100 ml) under nitrogen. After the addition the mixture was heated under reflux for 2 h and then allowed to cool. The excess^{of} lithium aluminium hydride was destroyed by careful addition of water (10 ml) in tetrahydrofuran (70 ml) followed by 15% sodium hydroxide solution (10 ml) and finally water (30 ml). The inorganic solids were filtered off and washed with acetone (250 ml). Evaporation of the combined filtrates gave a clear colourless oil which was dissolved in ether. Drying and evaporation gave *cis*-4,5-di(hydroxymethyl)cyclohexene (27.2 g, 81%) as a colourless oil, b.p. 288-289°C at 760 mmHg (lit.,²⁰⁸ 169-170°C at 11 mmHg).

(ii) *cis*-4,5-Di(*p*-toluenesulphonoxymethyl)cyclohexene

cis-4,5-Di(hydroxymethyl)cyclohexene (13.3 g, 94 mmol) was dissolved in pyridine (40 ml) and the solution was added dropwise to a suspension of *p*-toluene sulphonyl chloride (59.4 g, 310 mmol) in pyridine at 0°C. The mixture was stirred at 0°C for 3 h and then poured into 10% sulphuric acid (750 ml). Extraction

with methylene chloride (3x250 ml) followed by drying and evaporation gave cis-4,5-di(p-toluene sulphonoxymethyl)cyclohexene (35.2 g, 83%) as colourless crystals, m.p. 86-88°C (lit.²⁰⁸, 94.5°C).

(iii) cis 8-Thiabicyclo[4.3.0]non-3-ene

A solution of *cis*-4,5-Di(*p*-toluene sulphonoxymethyl)cyclohexene (27.7 g, 61.6 mmol) and sodium sulphide nonahydrate (46.2 g, 190 mmol) in ethanol (160 ml) and water (160 ml) was heated under reflux for 12 h. After removal of the ethanol under reduced pressure the residue was extracted with methylene chloride (3x200 ml). Drying and evaporation gave cis-8-thiabicyclo[4.3.0]non-3-ene (5.78 g, 67%) as a colourless oil, b.p. 83-84°C at 0.6 mmHg (lit.²⁰⁹, 121-125°C at 10 mmHg). (Found: C, 68.7; H, 8.6. C₈H₁₂S requires C, 68.5; H, 8.5%).

(iv) cis-8-Thiabicyclo[4.3.0]non-3-ene 8,8-dioxide

A solution of *cis*-8-Thiabicyclo[4.3.0]non-3-ene (4.48 g, 32 mmol) in dry ether (50 ml) was stirred at 0°C while a cold solution of *m*-chloroperoxybenzoic acid ('85%', 13.0 g, contains 64 mmol peracid) in dry ether (200 ml) was added dropwise. After stirring at room temperature for 60 h, the reaction mixture was washed with sodium carbonate solution, dried and evaporated. Recrystallisation of the residue from ether gave cis-8-Thiabicyclo[4.3.0]non-3-ene 8,8-dioxide (4.11 g, 75%) as colourless needles, m.p. 73-74°C. (Found: C, 55.95; H, 7.05.

C₈H₁₂O₂S requires C, 55.8; H, 7.0%); ν_{\max} 1290, 1110, 953, 890, 831, 780, 751 and 728 cm⁻¹; δ 5.66 (2H, t, J2Hz), 3.28-2.88 (4H, m), 2.70 (2H, m) and 2.26 (4H, m); m/e 172 (50%, M⁺), 155 (13), 107 (35), 106 (62), 105 (23), 92 (23), 91 (90), 79 (100), 78 (32) and 77 (32).

b. endo-4-Thiatricyclo[5.2.1.0^{2,6}]dec-8-ene 4,4-dioxide

(i) endo-3,5-Dioxo-4-oxatricyclo[5.2.1.0^{2,6}]dec-8-ene

This was prepared in 90% yield by the method of Diels and Alder²¹⁰ as colourless needles, m.p. 159-162°C (lit.,²¹⁰ 164-165°C).

(ii) endo-2,3-Di(hydroxymethyl)bicyclo[2.2.1]hept-5-ene

A solution of *endo*-3,5-Dioxo-4-oxatricyclo[5.2.1.0^{2,6}]-dec-8-ene (25.0 g, 152 mmol) in dry tetrahydrofuran (320 ml) was added dropwise to a stirred suspension of lithium aluminium hydride (7.90 g, 208 mmol) in dry tetrahydrofuran (160 ml) under nitrogen. After the addition the mixture was heated under reflux for 3 h and allowed to cool. The excess of lithium aluminium hydride was destroyed by addition of water (8 ml) in tetrahydrofuran (50 ml) followed by 15% sodium hydroxide solution (8 ml) and finally water (15 ml). The inorganic solids were filtered off and washed with acetone (250 ml). Evaporation of the filtrate gave a colourless oil which was dissolved in methylene chloride (250 ml) and the solution dried. Evaporation followed by recrystallisation from ether/methylene chloride gave endo-2,3-Di(hydroxymethyl)bicyclo[2.2.1]-hept-5-ene (17.6 g, 75%) as colourless needles, m.p. 86-87°C (lit.,²¹¹ 86°C).

(iii) endo-2,3-Di(p-toluene sulphonoxymethyl)bicyclo[2.2.1]-hept-5-ene

A solution of *endo*-2,3-Di(hydroxymethyl)bicyclo[2.2.1]hept-5-ene (16.5 g, 107 mmol) in pyridine (55 ml) was added dropwise to a suspension of *p*-toluene sulphonyl chloride (71.5 g, 375 mmol) in pyridine (110 ml) at 0°C. After stirring at 0°C for

3 h the mixture was poured into 10% sulphuric acid (750 ml). Extraction with methylene chloride (3x250 ml) followed by drying and evaporation gave endo-2,3-Di(p-toluene sulphonylmethyl)bicyclo[2.2.1]hept-5-ene (35.1 g, 71%) as colourless prisms, m.p. 86-88°C (lit.,²¹¹ 90-91°C).

(iv) endo-4-Thiatricyclo[5.2.1.0^{2,6}]dec-8-ene

A solution of *endo*-2,3-Di(p-toluene sulphonylmethyl)-bicyclo[2.2.1]hept-5-ene (24.0 g, 52 mmol) and sodium sulphide nonahydrate (35.0 g, 146 mmol) in ethanol (125 ml) and water (125 ml) was heated under reflux for 20 h. After removal of the ethanol under reduced pressure, the residue was extracted with methylene chloride (3x125 ml). Drying and evaporation followed by Kugelrohr distillation gave endo-4-Thiatricyclo[5.2.1.0^{2,6}]dec-8-ene (6.31 g, 80%) as a colourless oil, b.p. 228-229°C and 760 mmHg, n_D^{20} 1.5490 (lit.,²¹² b.p. 57°C at 0.45 mmHg, n_D^{26} 1.5546). (Found: C, 70.8; H, 8.1. $C_9H_{12}S$ requires C, 71.0; H, 7.95%).

(v) endo-4-Thiatricyclo[5.2.1.0^{2,6}]dec-8-ene 4,4-dioxide

A solution of *endo*-4-Thiatricyclo[5.2.1.0^{2,6}]dec-8-ene (5.50 g, 36.2 mmol) in dry ether (125 ml) was stirred at 0°C while a cold solution of *m*-chloroperoxybenzoic acid ('85%', 14.91 g, contains 73.5 mmol peracid) in dry ether (400 ml) was added dropwise. After stirring at room temperature for 75 h the solution was washed with aqueous sodium carbonate, dried and evaporated. Recrystallisation of the residue from ethanol gave endo-4-Thiatricyclo[5.2.1.0^{2,6}]dec-8-ene 4,4-dioxide (3.16 g, 48%) as colourless flakes, m.p. 124-126°C (lit.,²¹³ m.p. 114-116°C [not characterised]). (Found: C, 58.95; H, 6.65. $C_9H_{12}O_2S$

requires C, 58.7, H, 6.6%); ν_{\max} 1312, 1257, 1228, 1150, 1108, 942, 910, 854, 849, 791 and 762 cm^{-1} ; δ 6.23 (2H, t, J2Hz), 3.04 (4H, s), 3.3-2.8 (2H, m), 2.4-2.2 (2H, m), 1.76 and 1.47 (2H, AB pattern, J9Hz); m/e 184 (1.5%, M^+), 156 (18), 139 (1.5), 105 (7), 103 (1.5), 91 (8), 79 (6), 77 (7) and 66 (100, cyclopentadiene).

c. endo-4-Thiatricyclo[5.2.2.0^{2,6}]undec-8-ene 4,4-dioxide

(i) endo-3,5-Dioxo-4-oxatricyclo[5.2.2.0^{2,6}]undec-8-ene

A solution of maleic anhydride (6.0 g, 61.2 mmol) and 1,3-cyclohexadiene (5.0 g, 62.5 mmol) in benzene (50 ml) was heated at 40°C for 8 h. Evaporation followed by recrystallisation of the residue from pet.ether gave endo-3,5-Dioxo-4-oxatricyclo[5.2.2.0^{2,6}]undec-8-ene (9.80 g, 90%) as colourless needles, m.p. 141-143°C (lit.,²¹⁰ 147°C).

(ii) endo-2,3-Di(hydroxymethyl)bicyclo[2.2.2]oct-5-ene

A solution of endo-3,5-Dioxo-4-oxatricyclo[5.2.2.0^{2,6}]undec-8-ene (9.0 g, 50.6 mmol) in dry tetrahydrofuran (100 ml) was added dropwise to a stirred suspension of lithium aluminium hydride (2.10 g, 55.3 mmol) in dry tetrahydrofuran (50 ml) under nitrogen. After the addition the mixture was heated under reflux for 2 h and then the excess^{of} lithium aluminium hydride was destroyed by addition of water (2 ml) in tetrahydrofuran (15 ml) followed by 15% sodium hydroxide solution (2 ml) and finally water (10 ml). The inorganic solids were filtered off and washed with acetone (150 ml). Evaporation of the filtrate gave an oil which was dissolved in ether (150 ml). Drying and evaporation, followed by recrystallisation from ether/

methylene chloride, gave endo-2,3-Di(hydroxymethyl)bicyclo[2.2.2]oct-5-ene (5.24 g, 62%) as colourless crystals, m.p. 95-96°C (lit.,²¹³ 104-106°C).

(iii) endo-2,3-Di(p-toluene sulphonoxymethyl)bicyclo[2.2.2]oct-5-ene

A solution of *endo*-2,3-Di(hydroxymethyl)bicyclo[2.2.2]oct-5-ene (4.60 g, 27.4 mmol) in pyridine (15 ml) was added dropwise to a suspension of *p*-toluene sulphonyl chloride (17.4 g, 91.3 mmol) in pyridine (30 ml) at 0°C. After stirring at 0°C for 3 h the solution was poured into 10% sulphuric acid (400 ml). This was extracted with methylene chloride (3x150 ml) and the solution dried and evaporated. Recrystallisation from chloroform/hexane gave endo-2,3-Di(p-toluene sulphonoxymethyl)bicyclo[2.2.2]oct-5-ene (10.3 g, 87%) as colourless crystals, m.p. 99-100°C (lit.,²¹⁴ 101-102°C).

(iv) endo-4-Thiatricyclo[5.2.2.0^{2,6}]undec-8-ene

A solution of *endo*-2,3-Di(*p*-toluene sulphonoxymethyl)-bicyclo[2.2.2]oct-5-ene (10.27 g, 21.6 mmol) and sodium sulphide nonahydrate (15.5 g, 64.6 mmol) in ethanol (50 ml) and water (50 ml) was heated under reflux for 12 h. After removal of the ethanol under reduced pressure the residue was extracted with methylene chloride (3x50 ml). Drying and evaporation followed by Kugelrohr distillation gave endo-4-Thiatricyclo[5.2.2.0^{2,6}]undec-8-ene (2.46 g, 69%) as a colourless oil, b.p. 246-248°C at 760 mmHg, n_D^{25} 1.5350. (Found: C, 72.25; H, 8.5. C₁₀H₁₄S requires C, 72.2; H, 8.5%); ν_{\max} 3040, 2930, 2860, 1460, 1435, 1375, 1250, 1200, 915, 850, 817, 732 and 710 cm⁻¹; δ 6.13 (2H, t, J4Hz), 2.50 (6H, s), 1.48 and 1.28 (4H, A₂B₂

pattern, J10Hz), and 1.25 (2H, s); m/e 166 (90%, M⁺), 119 (15), 92 (18), 91 (48), 87 (38), 85 (21), 84 (81), 83 (15), 80 (100) and 79 (75).

(v) endo-4-Thiatricyclo[5.2.2.0^{2,6}]undec-8-ene 4,4-dioxide

A solution of *endo*-4-Thiatricyclo[5.2.2.0^{2,6}]undec-8-ene (2.20 g, 13.25 mmol) in dry ether was stirred at 0°C while a solution of *m*-chloroperoxybenzoic acid ('85%', 5.46 g, contains 26.9 mmol peracid) in dry ether (150 ml) was added dropwise. After stirring at room temperature for 60 h the solution was washed with aqueous sodium carbonate, dried and evaporated. Recrystallisation of the residue from ether gave endo-4-Thiatricyclo[5.2.2.0^{2,6}]undec-8-ene 4,4-dioxide (1.98 g, 76%) as colourless crystals, m.p. 112-113°C. (Found: C, 60.9; H, 7.3. C₁₀H₁₄O₂S requires C, 60.6, H, 7.1%); ν_{\max} 1377, 1317, 1293, 1247, 1197, 1148, 1096, 890, 739, 730 and 714 cm⁻¹; δ 6.30 (2H, t, J4Hz), 3.08-2.97 (2H, m), 2.61 (6H, m), 1.61 and 1.38 (4H, A₂B₂ pattern, J11Hz); m/e 198 (14%, M⁺), 105 (6), 104 (3), 91 (16), 80 (100) and 79 (18).

d. exo-10-Oxa-4-thiatricyclo[5.2.1.0^{2,6}]dec-8-ene 4,4-dioxide.

(i) exo-3,5-Dioxo-4,10-dioxatricyclo[5.2.1.0^{2,6}]dec-8-ene

Maleic anhydride (20.0 g, 204 mmol) was dissolved in benzene (200 ml) and the solution was stirred at room temperature while furan (15.0 g, 221 mmol) was added dropwise. After the addition the solution was stirred at room temperature for 40 h. The precipitate was filtered off to give exo-3,5-Dioxo-4,10-dioxatricyclo[5.2.1.0^{2,6}]dec-8-ene (26.5 g, 78%)

as colourless needles, m.p. 105-106°C (lit.,²¹⁵ 125°C).

(ii) exo-2,3-Di(hydroxymethyl)-7-oxabicyclo[2.2.1]hept-5-ene

A solution of *exo*-3,5-Dioxo-4,10-dioxatricyclo[5.2.1.0^{2,6}]-dec-8-ene (15.0 g, 90.4 mmol) in dry tetrahydrofuran (150 ml) was added dropwise to a stirred suspension of lithium aluminium hydride (3.75 g, 99 mmol) in dry tetrahydrofuran (50 ml) under nitrogen. The mixture was heated under reflux for 2 h and then the excess^{of} lithium aluminium hydride was destroyed by addition of water (4 ml) in tetrahydrofuran (30 ml) followed by 15% sodium hydroxide solution (5 ml). The inorganic solids were filtered off and washed with acetone (200 ml). The filtrate was evaporated to give a colourless oil which was dissolved in methylene chloride (200 ml). Drying and evaporation gave exo-2,3-Di(hydroxymethyl)-7-oxabicyclo[2.2.1]-hept-5-ene (8.8 g, 63%) as a colourless oil. As reported in the literature²¹⁶ this decomposed on heating so it was not possible to take a boiling point.

δ 6.26 (2H, s), 4.70 (2H, s), 4.30 (2H, s, OH), 3.80-3.65 (4H; m) and 1.93 (2H, m); m/e 156 (0.08%, M⁺), 138 (0.75) and 68 (100, furan).

(iii) exo-2,3-Di(p-toluene sulphonoxymethyl)-7-oxabicyclo-[2.2.1]hept-5-ene.

A solution of *exo*-2,3-Di(hydroxymethyl)-7-oxabicyclo-[2.2.1]hept-5-ene (8.20 g, 52.6 mmol) in pyridine (50 ml) was added slowly to a stirred suspension of *p*-toluene sulphonyl chloride (32.6 g, 169 mmol) in pyridine (50 ml) at 0°C. After stirring at 0°C for 3 h the mixture was poured into water

(250 ml). The thick white precipitate was filtered off, washed well with dilute sulphuric acid and then water and dried. Recrystallisation from chloroform/hexane gave exo-2,3-Di(p-toluene sulphonoxymethyl)-7-oxabicyclo[2.2.1]hept-5-ene (20.3 g, 83%) as colourless needles, m.p. 145-146°C (decomposition). (Found: C, 57.0; H, 5.2. $C_{22}H_{24}O_7S_2$ requires C, 56.9; H, 5.2%); ν_{\max} 1597, 1355, 1170, 1098, 950, 885, 862, 820, 689 and 668 cm^{-1} ; δ 7.75 and 7.34 (8H, A_2B_2 pattern, J8Hz), 6.30 (2H, s), 4.68 (2H, s), 4.2-3.8 (4H, m), 2.45 (6H, s) and 2.15-1.95 (2H, m); m/e no peaks above 172 (27%, TsOH), 155 (4), 120 (4), 108 (22), 107 (33), 92 (10) and 91 (100).

(iv) exo-10-Oxa-4-thiatricyclo[5.2.1.0^{2,6}]dec-8-ene

A solution of exo-2,3-Di(p-toluene sulphonoxymethyl)-7-oxabicyclo[2.2.1]hept-5-ene (21.0 g, 45.3 mmol) and sodium sulphide nonahydrate (32.6 g, 136 mmol) in ethanol (125 ml) and water (125 ml) was heated under reflux for 60 h. After removal of the ethanol under reduced pressure the residue was extracted with methylene chloride (3x100 ml). Drying and evaporation gave the crude product (4.33 g, 62%) as a low melting solid. Sublimation of a sample (1.0 g) at 0.05 mmHg, 50-70°C gave the pure exo-10-Oxa-4-thiatricyclo[5.2.1.0^{2,6}]dec-8-ene (0.38 g) as colourless needles, m.p. 45-47°C. (Found: C, 62.05; H, 6.6. $C_8H_{10}OS$ requires C, 62.3; H, 6.5%); ν_{\max} (melt) 2980, 2960, 2910, 1437, 1304, 1267, 1255, 1235, 1120, 1090, 1043, 991, 939, 897, 803, 789 and 688 cm^{-1} ; δ 6.34 (2H, s), 4.58 (2H, s) and 2.95-2.6 (6H, m); m/e 154 (26%, M^+),

88 (5), 87 (8), 86 (100), 85 (57), 79 (5), 77 (6), 69 (8) and 68 (21, furan).

(v) *exo*-10-Oxa-4-thiatricyclo[5.2.1.0^{2,6}]dec-8-ene 4,4-dioxide

Crude *exo*-10-Oxa-4-thiatricyclo[5.2.1.0^{2,6}]dec-8-ene (3.33 g, 21.6 mmol) was dissolved in dry methylene chloride (75 ml) and the solution was stirred at 0°C while a cold solution of *m*-chloroperoxybenzoic acid ('85%', 8.90 g, contains 43.9 mmol peracid) was added dropwise. After the addition the mixture was stirred at room temperature for 18 h. The solution was filtered and then washed well with aqueous sodium carbonate. Drying and evaporation followed by recrystallisation of the residue from ethanol gave *exo*-10-Oxa-4-thiatricyclo[5.2.1.0^{2,6}]dec-8-ene 4,4-dioxide (1.95 g, 49%) as colourless crystals, m.p. 168-169°C. (Found: C, 51.8; H, 5.45. $C_8H_{10}O_3S$ requires C, 51.6; H, 5.4); ν_{max} 1313, 1296, 1214, 1167, 1135, 1110, 1050, 990, 945, 911, 898, 801, 791, 770, 726 and 714 cm^{-1} ; δ 6.37 (2H, d, J1Hz), 4.73 (2H, d, J1Hz), 3.4-3.2 (2H, m) and 2.85-2.4 (4H, m); m/e 187 (0.05%, M⁺), 121 (0.7), 120 (1.4), 107 (1.1), 91 (2), 79 (1.5), 77 (3), 69 (5) and 68 (100, furan).

e. Attempted preparation of sulphones by direct Diels-Alder reaction

(i) Diels-Alder reaction of butadiene with butadiene sulphone

A solution of butadiene sulphone (2,5-dihydrothiophen 1,1-dioxide) (10.0 g, 85 mmol) and 1,3-butadiene (5.8 g, 107 mmol) in benzene (25 ml) was heated in an autoclave at 100°C

for 17 h. This gave a clear solution and a brown oil. Evaporation of the clear solution gave the unchanged sulphone (3.9 g) while NMR of the oil showed the presence of unchanged butadiene sulphone and hydrocarbon products, δ 6-5 and 2-1. There was no sign of the expected 8-thiabicyclo[4.3.0]non-3-ene 8,8-dioxide.

(ii) Lewis acid catalysed reaction of butadiene with butadiene sulphone

The method used was based on that of Robinson²¹⁷ using stannic chloride as the catalyst. A solution of butadiene sulphone (5.0 g, 42 mmol), 1,3-butadiene (4.05 g, 75 mmol) and stannic chloride (2.26 g, 8.7 mmol) in dry benzene (50 ml) was kept in a sealed container for 170 h. The solution was evaporated and the residue shaken with water (100 ml) to destroy the residual stannic chloride. Extraction of the aqueous suspension with methylene chloride (2x50 ml) followed by drying and evaporation gave a clear brown oil (5.8 g). TLC (alumina, Et₂O) showed a large proportion of butadiene sulphone and none of the desired product. MS of the hydrocarbons left after the butadiene sulphone had crystallised out, showed peaks at m/e 132 and 186 possibly due to adducts of benzene with one or two molecules of butadiene. GC (10% PEGA, 170°C) showed the presence of at least eight components.

f. Flash vacuum pyrolysis of 8-thiabicyclo[4.3.0]non-3-ene 8,8-dioxide and bridged analogues.

(i) FVP of *cis*-8-thiabicyclo[4.3.0]non-3-ene 8,8-dioxide
FVP of the title compound at temperatures below 750°C

gave recovery of the unchanged starting material. FVP of the title compound (45 mg, 850°C, 5×10^{-3} mmHg, inlet 50-80°C) gave unchanged starting material (5 mg) and a yellow oil. This partly polymerised on warming to room temperature to give an insoluble white solid (6 mg) but the remainder was taken up in deuteriochloroform. The NMR showed the presence of benzene and toluene as well as other minor products. This was confirmed by the GC (10% PEGA, 55°C). Comparison with a standard benzene solution gave the overall yield of hydrocarbons as 70% made up of benzene (33%), toluene (29%) and five minor components (8%). Pyrolysis at 875°C gave the same mixture of products but less unreacted starting material.

(ii) FVP of *endo*-4-thiatricyclo[5.2.1.0^{2,6}]dec-8-ene 4,4-dioxide

FVP of the title compound (92 mg, 675°C, 1×10^{-3} mmHg, inlet 60-120°C) gave unreacted starting material (5 mg) and a yellow oil. On warming to room temperature this partly polymerised to give a cyclopentadiene/SO₂ copolymer (25 mg) (Found: C, 45.0; H, 4.7, expected for cyclopentadiene/SO₂, 1:1. C₅H₆O₂S; C, 46.1; H, 4.65%). The NMR of the chloroform soluble fraction showed the presence of cyclopentadiene and 1,3-butadiene. Calibration with acetone gave the yields, allowing for the cyclopentadiene in the polymer, as cyclopentadiene (42%) and 1,3-butadiene (34%).

(iii) FVP of *endo*-4-thiatricyclo[5.2.2.0^{2,6}]undec-8-ene 4,4-dioxide

Pyrolysis at 675°C gave mainly the unchanged starting material. FVP of the title compound (98 mg, 725°C, 3×10^{-3} mmHg,

inlet 60-70°C) gave unchanged starting material (12 mg) and a yellow oil. A white polymer (15 mg) was formed on warming and NMR of the soluble fraction of the product showed the presence of 1,3-cyclohexadiene and benzene.

FVP of the title compound (120 mg, 750°C, 2×10^{-3} mmHg, inlet 50-100°C) gave unchanged starting material (5 mg), a white copolymer of 1,3-cyclohexadiene and SO₂ (Found: C, 49.1; H, 5.1, expected for C₆H₈O₂S C, 50.0; H, 5.6%), and an NMR solution which contained benzene and 1,3-cyclohexadiene. Calibration with methylene chloride gave the yields, allowing for the cyclohexadiene in the polymer as 1,3-cyclohexadiene (60%) and benzene (20%).

(iv) FVP of *exo*-10-oxa-4-thiatricyclo[5.2.1.0^{2,6}]dec-8-ene 4,4-dioxide

FVP of the title compound (50 mg, 675°C, 5×10^{-3} mmHg, inlet 70-100°C) gave a yellow oil. This was shown by NMR to contain furan and 1,3-butadiene. Calibration with acetone gave the yields as furan (72%) and 1,3-butadiene (51%). A small amount of white polymer (2 mg) was also formed.

2. Preparation and FVP of sulphone epoxides

a. Preparation of 4-Oxa-9-thiatricyclo[5.3.0.0^{3,5}]decane 9,9-dioxide and bridged analogues

(i) 4-Oxa-9-thiatricyclo[5.3.0.0^{3,5}]decane 9,9-dioxide

A solution of 8-thiabicyclo[4.3.0]non-3-ene 8,8-dioxide (0.40 g, 2.3 mmol) and *m*-chloroperoxybenzoic acid ('85%',

0.70 g, contains 3.4 mmol peracid) in dry ethyl acetate (12 ml) was heated under reflux for 7 h. The solution was evaporated and the residue dissolved in methylene chloride (25 ml). This was washed thoroughly with aqueous sodium carbonate solution, dried and evaporated. Recrystallisation of the residue from ethanol gave 4-Oxa-9-thiatricyclo[5.3.0.0^{3,5}]-decane 9,9-dioxide (0.20 g, 46%) as colourless crystals, m.p. 93-95°C. (Found: C, 50.9; H, 6.4. C₈H₁₂O₃S requires C, 51.0; H, 6.4%); ν_{\max} 1300, 1253, 1118, 1084, 894, 889, 835, 810, 772 and 724 cm⁻¹; δ 3.19 (2H, s), 3.12-2.82 (4H, m), 2.70 (2H, m) and 2.22-2.06 (4H, m); m/e 188 (1.4%, M⁺), 187 (1), 171 (1), 123 (24), 109 (36), 105 (17), 96 (12), 93 (28), 91 (27), 83 (65), 79 (50) and 41 (100).

(ii) 9-Oxa-4-thiatetracyclo[5.3.1.0^{2,6}.0^{8,10}]-undecane 4,4-dioxide

A solution of 4-thiatricyclo[5.2.1.0^{2,6}]-dec-8-ene 4,4-dioxide (0.50 g, 2.7 mmol) in acetic acid (10 ml) containing 30% hydrogen peroxide solution (2.0 ml, 18 mmol) was heated at 50-60°C for 70 h. Water (100 ml) was added and the acid neutralised by addition of excess solid sodium bicarbonate. Extraction with methylene chloride followed by drying and evaporation gave a white solid which on recrystallisation from ethanol/methylene chloride gave 9-Oxa-4-thiatetracyclo[5.3.1.0^{2,6}.0^{8,10}]-undecane 4,4-dioxide (0.40 g, 74%) as colourless needles, m.p. 238-240°C. (Found: C, 54.1; H, 5.9. C₉H₁₂O₃S requires C, 54.0; H, 6.0%); ν_{\max} 1412, 1350, 1315, 1263, 1222, 1149, 1108, 940, 850 and 827 cm⁻¹; δ 3.26 (2H, s), 3.1-2.7 (8H, m), 1.60 and 0.92 (2H, AB pattern, J11Hz);

^{13}C 848.81 ($\text{C}_{3,5}$), 48.59 ($\text{C}_{8,10}$), 38.62 and 38.06 ($\text{C}_{1,2,6,7}$) and 27.68 (C_{11}); m/e 200 (0.1%, M^+), 183 (0.4), 172 (0.4), 155 (1), 135 (5), 106 (14), 91 (20), 82 (100) and 81 (64).

(iii) 9-Oxa-4-thiatetracyclo[5.3.2.0^{2,6}.0^{8,10}]dodecane
4,4-dioxide

A solution of 4-thiatriacyclo[5.2.2.0^{2,6}]undec-8-ene 4,4-dioxide (0.25 g, 1.26 mmol) and *m*-chloroperoxybenzoic acid ('85%', 0.50 g, contains 2.5 mmol peracid) in dry ethyl acetate (10 ml) was heated under reflux for 18 h. After washing well with aqueous sodium carbonate solution, drying and evaporation gave a white solid which was recrystallised from ethanol to give 9-Oxa-4-thiatetracyclo[5.3.2.0^{2,6}.0^{8,10}]-dodecane 4,4-dioxide (0.14 g, 52%) as colourless crystals, m.p. 162-164°C. (Found: C, 55.8; H, 6.6. $\text{C}_{10}\text{H}_{14}\text{O}_3\text{S}$ requires C, 56.1; H, 6.6%); ν_{max} 1410, 1300, 1256, 1199, 1140, 1100, 878, 852, 800 and 720 cm^{-1} ; δ 3.33 (2H, s), 3.2-2.7 (6H, m), 2.29 (2H, s), 1.82 and 1.26 (4H, A_2B_2 pattern, J7Hz); m/e 214 (1.0%, M^+), 151 (10), 150 (17), 149 (21), 148 (18), 135 (23), 131 (20), 106 (55), 96 (71), 95 (66), 79 (80) and 67 (100).

(iv) 9,11-Dioxa-4-thiatetracyclo[5.3.1.0^{2,6}.0^{8,10}]undecane
4,4-dioxide

A solution of 10-Oxa-4-thiatriacyclo[5.2.1.0^{2,6}]undecane 4,4-dioxide (0.40 g, 2.14 mmol) in acetic acid (10 ml) containing 30% hydrogen peroxide solution (1.6 ml, 14 mmol) was heated at 50-60°C for 42 h. Water (100 ml) was added and the acid neutralised by addition of solid sodium bicarbonate. Extraction with methylene chloride (3x100 ml) followed by

drying and evaporation gave a white solid which on recrystallisation from ethanol/methylene chloride gave 9,11-Dioxa-4-thiatetracyclo[5.3.1.0^{2,6},0^{8,10}]undecane 4,4-dioxide (0.25 g, 58%) as colourless needles, m.p. 268-269°C. (Found, C, 47.65; H, 5.0. C₈H₁₀O₄S requires C, 47.5; H, 5.0%); ν_{\max} 1378, 1316, 1181, 1150, 1135, 1098, 995, 954, 917, 861 and 800 cm⁻¹; δ (CF₃CO₂H) 4.71 (2H, s), 3.86 (2H, s), 3.63-3.53 (2H, m) and 3.14-3.04 (4H, m); m/e 202 (2%, M⁺), 173 (7), 137 (3), 136 (4), 123 (3), 109 (52), 108 (21), 95 (26), 91 (24), 84 (40), 81 (100) and 79 (80).

b. Flash Vacuum Pyrolysis of 4-Oxa-9-thiatricyclo[5.3.0.0^{3,5}]decane 9,9-dioxide and bridged analogues.

(i) FVP of 4-Oxa-9-thiatricyclo[5.3.0.0^{3,5}]decane 9,9-dioxide

FVP of the title compound (20 mg, 725°C, 10⁻³ mmHg, inlet 70-100°C) gave a colourless oil whose NMR showed signals in the vinyl region. GC and GC-MS (10% PEGA, 100°C and 5% Carbowax, 55-175°C) showed the presence of seven components of which only styrene and *o*-xylene were positively identified. Two of the later peaks might have been due to the *cis* and *trans* isomers of diallyloxirane (1,4,7-octatriene-4,5-epoxide).

FVP of the compound (0.5 g) as above, gave after microdistillation a colourless liquid whose NMR spectra suggested that it contained some 1,2-diallyloxirane. δ 6.1-5.5 (2H, m), 5.3-4.9 (4H, m), 3.16 (2H, d, J6Hz) and 2.6-2.2 (4H, m); ¹³C δ (90 MHz) 136.90, 133.42, 130.45, 118.66, 117.13 and 115.15 (3 vinyl species), 55.67 (CH), 47.67, 41.26, 32.15 and 27.52 (all CH₂).

(ii) FVP of 9-Oxa-4-thiatetracyclo[5.3.1.0^{2,6},0^{8,10}]undecane 4,4-dioxide

FVP of the title compound (0.50 g, 700°C, 4x10⁻³ mmHg, inlet 150-160°C) gave a brown oil which on microdistillation yielded a colourless liquid consisting mainly of 2,4-divinyl-6-oxabicyclo[3.1.0]hexane (0.13 g, 39%), (Found: M⁺ 136.087992. C₉H₁₂O requires 136.088810); ν_{\max} 3085, 1745 (C=O impurity), 1640, 995, 917 and 844 cm⁻¹; δ 5.9-5.6 (2H, m), 5.2-4.9 (4H, m), 3.42 (2H, s), 3.0-2.8 (2H, m) and 2.0-1.3 (2H, m); ¹³C δ (90MHz) 138.72, 115.59, 60.38, 42.90 and 33.60; m/e 136 (21%, M⁺), 121 (10), 118 (10), 107 (16), 100 (29), 94 (39) and 79 (100).

(iii) FVP of 9-Oxa-4-thiatetracyclo[5.3.2.0^{2,6},0^{8,10}]dodecane 4,4-dioxide

FVP of the title compound (94 mg, 700°C, 2x10⁻³ mmHg, inlet 140-160°C) gave a colourless oil which after microdistillation gave a colourless liquid (24.0 mg), containing some of the expected 2,5-divinyl-7-oxabicyclo[4.1.0]heptane. δ 6.1-5.6 (2H, m), 5.25-4.85 (4H, m), 3.1-2.4 (4H, m) and 2.0-1.8 (4H, m); ¹³C δ (90MHz) 210.25 (C=O impurity), 140.52, 138.82, 137.77, 135.56, 116.77, 115.64, 115.56 and 114.46 (4 vinyl species), 55.40, 53.71, 47.11, 41.26 and 37.24 (all CH), 44.60, 29.43, 29.19, 27.86 and 22.14 (all CH₂).

(iv) FVP of 9,11-Dioxa-4-thiatetracyclo[5.3.1.0^{2,6},0^{8,10}]-undecane 4,4-dioxide

FVP of the title compound (0.5 g, 700°C, 2x10⁻³ mmHg, inlet 150-200°C) gave a brown liquid. On microdistillation this yielded 2,4-divinyl-3,6-dioxabicyclo[3.1.0]hexane (0.21 g, 61%) as a colourless liquid. (Found: M⁺ 138.067543.

$C_8H_{10}O_2$ requires 138.068075); ν_{\max} 1423, 1054, 1036, 935, 866, 832 and 762 cm^{-1} ; δ 6.0-5.5 (2H, m), 5.5-5.2 (4H, m), 4.59 (2H, d, J7Hz) and 3.66 (2H, s); ^{13}C δ (90MHz) 135.40, 118.21, 79.42 and 59.45; m/e 138 (1.1%, M^+), 137 (1.0), 109 (8), 100 (44), 81 (45) and 55 (100).

3. Preparation and FVP of sulphone aziridines

a. Preparation of 4-Ethoxycarbonyl-9-thia-4-azatricyclo-[5.3.0.0^{3,5}]decane 9,9-dioxide

(i) Photochemical reaction with ethyl azidoformate

A mixture of 8-thiabicyclo[4.3.0]non-3-ene 8,8-dioxide (0.50 g, 2.9 mmol) and ethyl azidoformate (1.5 g, 13 mmol) was irradiated at 400W for 36 h. Chromatography of the resulting yellow oil on alumina (Et_2O) gave the unreacted azide (0.28 g) followed by ethyl carbamate (0.14 g) and finally the desired product (0.55 g). Recrystallisation from ether/methylene chloride gave 4-Ethoxycarbonyl-9-thia-4-azatricyclo-[5.3.0.0^{3,5}]decane 9,9-dioxide (0.30 g, 40%) as colourless needles, m.p. 126-128°C. (Found: C, 50.9; H, 6.4; N, 5.1. $C_{11}H_{17}NO_4S$ requires C, 50.9; H, 6.6; N, 5.4%); ν_{\max} 1712, 1296, 1233, 1209, 1119, 790, 760 and 723 cm^{-1} ; δ 4.135 and 4.125 (2H, q, J7Hz, *syn* and *anti* isomers), 3.3-2.9 (4H, m), 2.72 and 2.70 (2H, s, $H_{3,5}$ *syn* and *anti* isomers), 2.8-2.4 (2H, m), 2.2-2.0 (4H, m) and 1.24 (3H, t, J7Hz); m/e 259 (38%, M^+), 214 (22), 193 (32), 180 (38), 166 (75), 154 (55), 141 (40), 120 (85), and 80 (100).

(ii) Attempted thermal reaction with ethyl azidoformate

A solution of 8-thiabicyclo[4.3.0]non-3-ene 8,8-dioxide (0.50 g, 2.9 mmol) and ethyl azidoformate (0.40 g, 3.5 mmol) in dry carbon tetrachloride (5 ml) was heated under reflux for 18 h. Evaporation gave a brown solid (0.72 g) whose NMR showed the presence of two azide byproducts and the unchanged starting sulphone. There was no sign of the expected aziridine.

(iii) Attempted homogeneous reaction with ethoxycarbonyl nitrene from α -elimination

To a solution of 8-thiabicyclo[4.3.0]non-3-ene 8,8-dioxide (0.50 g, 2.9 mmol) and ethyl *p*-nitrobenzenesulphoxycarbamate (0.90 g, 3.1 mmol) in dry methylene chloride (20 ml), was added a solution of triethylamine (0.35 g, 3.5 mmol) in dry methylene chloride (10 ml). After stirring for 3 h the solution was washed with water (3x25 ml), dried and evaporated. NMR and TLC (alumina, Et₂O) of the resulting yellow oil (0.72 g) showed nitrene byproducts and the unchanged starting sulphone with none of the expected aziridine.

(iv) Reaction with ethoxycarbonyl nitrene from α -elimination under phase transfer conditions

A solution of 8-thiabicyclo[4.3.0]non-3-ene 8,8-dioxide (100 mg, 0.58 mmol), ethyl *p*-nitrobenzenesulphoxycarbamate (170 mg, 0.59 mmol) and benzyl triethylammonium chloride (13 mg, 0.058 mmol) in methylene chloride (10 ml) was stirred vigorously with 1M sodium bicarbonate solution (2 ml) for 14 h. Water (25 ml) was added and the organic layer separated. Washing with water (10 ml) followed by drying and evaporation gave a yellow oil (0.20 g). The NMR and TLC (alumina, Et₂O/*i*-PrOH,

10:1) showed the presence of the unreacted sulphone (40 mg) and 4-Ethoxycarbonyl-9-thia-4-azatricyclo[5.3.0.0^{3,5}]decane 9,9-dioxide (60 mg, 40%). [Yields estimated from NMR].

b. Preparation of 9-Ethoxycarbonyl-4-thia-9-azatetracyclo[5.3.1.0^{2,6}.0^{8,10}]undecane 4,4-dioxide

(i) Photochemical reaction with ethyl azidoformate

A mixture of 4-thiatricyclo[5.2.1.0^{2,6}]dec-8-ene 4,4-dioxide (48 mg, 0.26 mmol) and ethyl azidoformate (0.5 g, 4.3 mmol) was irradiated at 400W for 21 h. The NMR and TLC (alumina, Et₂O/i-PrOH, 10:1) showed the presence of azide by-products and 9-Ethoxycarbonyl-4-thia-9-azatetracyclo[5.3.1.0^{2,6}.0^{8,10}]undecane 4,4-dioxide (53 mg, 75%). [Yield estimated from NMR].

(ii) Thermal reaction with ethyl azidoformate

A solution of 4-thiatricyclo[5.2.1.0^{2,6}]dec-8-ene 4,4-dioxide (0.50 g, 2.72 mmol) and ethyl azidoformate (0.35 g, 3.04 mmol) in dry carbon tetrachloride (5 ml) was heated under reflux for 18 h. Evaporation gave a brown solid which was recrystallised from ether/methylene chloride to give 9-Ethoxycarbonyl-4-thia-9-azatetracyclo[5.3.1.0^{2,6}.0^{8,10}]undecane 4,4-dioxide (0.28 g, 38%) as colourless crystals, m.p. 153-155°C. (Found: C, 52.9; H, 6.0; N, 4.9. C₁₂H₁₇NO₄S requires C, 53.1; H, 6.3; N, 5.2%); ν_{\max} 1710, 1302, 1289, 1228, 1200, 1148, 1102, 1023, 828, and 789 cm⁻¹; δ 4.13 (2H, q, J7Hz), 3.1-2.7 (10H, m), 1.75 and 1.04 (2H, AB pattern, J10Hz), and 1.26 (3H, t, J7Hz); m/e 271 (2.5%, M⁺), 226 (5), 153 (60), 152 (60), 81 (58), 80 (91) and 66 (100).

(iii) Attempted homogeneous reaction with ethoxycarbonyl nitrene from α -elimination

To a solution of 4-thiatricyclo[5.2.1.0^{2,6}]dec-8-ene 4,4-dioxide (0.10 g, 0.54 mmol) and ethyl *p*-nitrobenzenesulphonoxy-carbamate (0.17 g, 0.59 mmol) in dry methylene chloride (10 ml), was added a solution of triethylamine (0.10 g, 0.99 mmol) in dry methylene chloride (5 ml) over 5 min. After stirring for 18 h the solution was washed with water (2x10 ml), dried and evaporated to give a yellow solid (0.25 g). The NMR and TLC (alumina, Et₂O) showed the presence of the unchanged starting sulphone and nitrene byproducts with none of the expected aziridine.

(iv) Reaction with ethoxycarbonyl nitrene from α -elimination under phase transfer conditions

A solution of 4-thiatricyclo[5.2.1.0^{2,6}]dec-8-ene 4,4-dioxide (0.10 g, 0.54 mmol), ethyl *p*-nitrobenzenesulphonoxy-carbamate (0.16 g, 0.54 mmol) and benzyl triethylammonium chloride (12 mg, 0.054 mmol) in methylene chloride (10 ml) was stirred vigorously with 1M sodium bicarbonate solution (2 ml) for 14 h. Water (25 ml) was added and the organic layer separated. This was washed with water (10 ml), dried and evaporated to give a yellow oil (0.18 g). The NMR and TLC (alumina, Et₂O/*i*-PrOH, 10:1) of this showed the presence of the unreacted starting sulphone (60 mg) and 9-Ethoxycarbonyl-4-thia-9-azatetracyclo[5.3.1.0^{2,6}.0^{8,10}]undecane 4,4-dioxide (45 mg, 30%). [Yields estimated from NMR].

c. Preparation of 9-Ethoxycarbonyl-4-thia-9-azatetracyclo-
[5.3.2.0^{2,6}.0^{8,10}]dodecane 4,4-dioxide

(i) Photochemical reaction with ethyl azidoformate

A mixture of 4-thiatricyclo[5.2.2.0^{2,6}]undec-8-ene 4,4-dioxide (0.50 g, 2.5 mmol) and ethyl azidoformate (1.0 g, 8.7 mmol) was irradiated at 400W for 18 h. Chromatography of the resulting yellow oil on alumina (Et₂O) gave azide byproducts as a clear liquid (0.38 g) followed by a white solid. Recrystallisation of this from ether/methylene chloride gave 9-Ethoxycarbonyl-4-thia-9-azatetracyclo[5.3.2.0^{2,6}.0^{8,10}]dodecane 4,4-dioxide (0.16 g, 22%) as colourless crystals, m.p.172-174°C.

(Found: C, 54.5; H, 6.8; N, 4.8. C₁₃H₁₉NO₄S requires C, 54.7; H, 6.7; N, 4.9%); ν_{\max} 1712, 1402, 1300, 1260, 1145, 1100, 1017, 981, 928, 883, 843, 790 and 780 cm⁻¹; δ 4.17 (2H, q, J7Hz), 3.2-3.0 (4H, m), 2.9-2.7 (4H, m), 2.30 (2H, m), 1.88 (2H, half of A₂B₂ pattern, J8Hz) and 1.27 (5H, t and superimposed A₂B₂ pattern, J (t)7Hz); m/e 285 (17%, M⁺), 240 (9), 213 (10), 212 (8), 167 (28), 152 (25), 119 (22) and 95 (100).

(ii) Thermal reaction with ethyl azidoformate

A solution of 4-thiatricyclo[5.2.2.0^{2,6}]undec-8-ene 4,4-dioxide (50 mg, 0.25 mmol) and ethyl azidoformate (32 mg, 0.28 mmol) in dry carbon tetrachloride (10 ml) was heated under reflux for 40 h. Evaporation gave a brown solid whose NMR and TLC (alumina, Et₂O) showed the presence of azide byproducts, unreacted starting sulphone (45 mg) and 9-Ethoxycarbonyl-4-thia-9-azatetracyclo[5.3.2.0^{2,6}.0^{8,10}]dodecane 4,4-dioxide (6 mg, 8%).

[Yields estimated from NMR].

(iii) Attempted homogeneous reaction with ethoxycarbonyl nitrene from α -elimination

To a solution of 4-thiatricyclo[5.2.2.0^{2,6}]undec-8-ene 4,4-dioxide (0.10 g, 0.51 mmol) and ethyl *p*-nitrobenzenesulphoxycarbamate (0.16 g, 0.55 mmol) in dry methylene chloride (10 ml), was added a solution of triethylamine (0.1 g, 0.99 mmol) in dry methylene chloride (5 ml) over 5 min. After stirring for 18 h the solution was washed with water (2x10 ml), dried and evaporated. NMR and TLC (alumina, Et₂O) of the residue showed only nitrene byproducts and the unreacted starting sulphone with none of the expected aziridine.

(iv) Reaction with ethoxycarbonyl nitrene from α -elimination under phase transfer conditions

A solution of 4-thiatricyclo[5.2.2.0^{2,6}]undec-8-ene 4,4-dioxide (0.10, 0.51 mmol), ethyl *p*-nitrobenzenesulphoxycarbamate (0.15 g, 0.52 mmol) and benzyl triethylammonium chloride (12 mg, 0.05 mmol) in dry methylene chloride (10 ml) was stirred vigorously with 1M sodium bicarbonate solution (2 ml) for 14 h. Water (25 ml) was added and the organic layer separated. It was then washed with water (10 ml), dried and evaporated to give a yellow oil (0.18 g). NMR and TLC (alumina, Et₂O/*i*-PrOH, 10:1) of this showed the presence of nitrene byproducts, the unreacted starting sulphone (80 mg) and 9-Ethoxycarbonyl-4-thia-9-azatetracyclo[5.3.2.0^{2,6}.0^{8,10}]dodecane 4,4-dioxide (29 mg, 20%). [Yields estimated from NMR].

d. Preparation of 6-Ethoxycarbonyl-3-thia-6-azabicyclo-
[3.1.0]hexane 3,3-dioxide

(i) Thermal reaction with ethyl azidoformate

A solution of butadiene sulphone (0.10 g, 0.85 mmol) and ethyl azidoformate (0.11 g, 0.96 mmol) in dry carbon tetrachloride (10 ml) was heated under reflux for 40 h. NMR and TLC (alumina, Et₂O) of the residue on evaporation showed only the unchanged sulphone and azide byproducts to be present.

(ii) Reaction with ethoxycarbonyl nitrene from α -elimination under phase transfer conditions.

A solution of butadiene sulphone (0.10 g, 0.85 mmol), ethyl *p*-nitrobenzenesulphonoxycarbamate (0.25 g, 0.85 mmol) and benzyl triethylammonium chloride (20 mg, 0.085 mmol) in methylene chloride (10 ml) was stirred vigorously with 1M sodium bicarbonate solution (2 ml) for 20 h. Water (10 ml) was added and the organic layer separated and washed with water (10 ml). Drying and evaporation gave a yellow oil (0.23 g). NMR and TLC (alumina, Et₂O) of this showed the presence of unreacted starting sulphone (80 mg) and also 6-Ethoxycarbonyl-3-thia-6-azabicyclo[3.1.0]hexane 3,3-dioxide (28 mg, 16%), identical on TLC to the authentic material prepared by the method of Meyers⁷⁷. [Yields estimated from NMR].

e. Attempted preparation of 4-Phthalimido-9-thia-4-azatri-
cyclo[5.3.0.0^{3,5}]decane 9,9-dioxide

A solution of N-amino phthalimide (0.50 g, 3.1 mmol) and 8-thiabicyclo[4.3.0]non-3-ene 8,8-dioxide (0.50 g, 2.9 mmol) in

dry methylene chloride (25 ml) was stirred at 0°C while dry lead tetraacetate (1.37 g, 3.1 mmol) was added over 5 min. After stirring at room temperature for 18 h, the lead salts were filtered off, washed with methylene chloride (25 ml) and the filtrate evaporated. Pumping for 3 h removed the acetic acid to leave a yellow crystalline solid (1.19 g). The mass spectrum of this did show a small peak at m/e 332 corresponding to the desired product but this could not be detected in the NMR or TLC (alumina, Et₂O/hexane, 1:1) which showed only the starting sulphone and nitrene byproducts. Chromatography on alumina (Et₂O/hexane, 1:1) gave the recovered starting sulphone (0.45 g).

f. Flash Vacuum Pyrolysis of 4-Ethoxycarbonyl-9-thia-4-azatricyclo[5.3.0.0^{3,5}]decane 9,9-dioxide and bridged analogues

(i) FVP of 4-Ethoxycarbonyl-9-thia-4-azatricyclo[5.3.0.0^{3,5}]decane 9,9-dioxide

FVP of the title compound (34 mg, 725°C, 2x10⁻³ mmHg, inlet 100-120°C) resulted in extensive decomposition in the inlet tube with 12 mg residual tar. NMR of the volatile components showed ethanol and many small peaks at δ6-5 and 4-2. GC (10% PEGA, 55°C) showed ethanol to be the only volatile component and none of the other products could be identified.

(ii) FVP of 9-Ethoxycarbonyl-4-thia-9-azatetracyclo[5.3.1.0^{2,6}.0^{8,10}]undecane 4,4-dioxide

FVP of the title compound (37 mg, 675°C, 2x10⁻³ mmHg, inlet 140-150°C) gave a yellow oil whose NMR showed a complex pattern. GC (10% PEGA, 55°C) showed only ethanol while at 150°C five

main components were detected with about seven minor ones. GC-MS showed three of the main components to be indene, *o*-xylene and ethyl carbamate and this was confirmed with the authentics. Other peaks might have been due to indane, *o*-methyl styrene or 1,4-dihydropyridine but the authentic materials were not available to test this. From the NMR there was a considerable degree of polymerisation and radical reactions and the yields of the components which were identified were very low.

(iii) FVP of 9-Ethoxycarbonyl-4-thia-9-azatetracyclo[5.3.2.0^{2,6}.0^{8,10}]dodecane 4,4-dioxide

FVP of the title compound (29 mg, 725°C, 5×10^{-3} mmHg, inlet 160-190°C) gave an oil whose NMR showed the presence of benzene, ethanol, another ethyl component and vinylic species. GC and GC-MS (10% PEGA) showed the presence of benzene and ethanol at 55°C and at 150°C styrene and ethyl carbamate. Again the yields were not high and no other components were positively identified.

E. The 7-Thiabicyclo[4.3.0]non-3-ene 7,7-dioxide ring system

1. Preparation and FVP of 7-Thiabicyclo[4.3.0]non-3-ene 7,7-dioxide and bridged analogues

a. Preparation of 2,3-dihydrothiophen 1,1-dioxide (2-sulpholene)

The method used was based on that of Bailey and Cummins²¹⁸.

A solution of butadiene sulphone (50 g, 424 mmol) and potassium hydroxide (28 g, 500 mmol) in water (1000 ml) was allowed to stand for 36 h. Acidification with 36% hydrochloric acid followed by extraction with methylene chloride (3x350 ml) drying and evaporation gave a colourless oil (39.7 g). This was heated at 150°C for 3 h to decompose the butadiene sulphone and the residue was recrystallised from benzene to give 2,3-dihydrothiophen 1,1-dioxide (13.7 g, 27%) as colourless prisms, m.p. 47-49°C (lit., 48-49°C).

b. Preparation of 7-Thiabicyclo[4.3.0]non-3-ene 7,7-dioxide and bridged analogues

(i) 7-Thiabicyclo[4.3.0]non-3-ene 7,7-dioxide

This was prepared by a modification of Alder's method¹⁸⁶.

A solution of 2,3-dihydrothiophen 1,1-dioxide (4.0 g, 34 mmol) and 1,3-butadiene (3.2 g, 59 mmol) in dry benzene (40 ml) was heated in an autoclave at 180°C for 66 h. Evaporation of the product gave a brown oil (5.85 g). Chromatography of this on alumina (Et₂O) gave hydrocarbons as a brown oil (0.88 g) followed by the desired product (1.72 g) and finally recovered 2,3-

dihydrothiophen 1,1-dioxide (2.68 g). Recrystallisation from ethanol gave 7-Thiabicyclo[4.3.0]non-3-ene 7,7-dioxide (1.56 g, 27%) as colourless needles, m.p. 93-94°C (lit., 94-95°C). (Found: C, 55.7; H, 6.8. $C_8H_{12}O_2S$ requires C, 55.8; H, 7.0%); ν_{max} 1295, 1228, 1135, 1100, 953, 935, 920, 868, 765 and 659 cm^{-1} ; δ 5.69 (2H, s), 3.25-3.05 (3H, m); 2.9-2.5 (1H, m), 2.45-2.35 (2H, m) and 2.2-1.85 (4H, m); m/e 172 (1.7%, M^+), 107 (15), 106 (85), 105 (10), 91 (25) and 79 (100).

(ii) 3-Thiatricyclo[5.2.1.0^{2,6}]dec-8-ene 3,3-dioxide

The method used was again based on that of Alder¹⁸⁶. A solution of 2,3-dihydrothiophen 1,1-dioxide (5.0 g, 42 mmol) and freshly prepared cyclopentadiene (3.2 g, 59 mmol) in dry benzene was heated in an autoclave at 150°C for 20 h. Evaporation gave a brown oil (9.22 g). Chromatography on alumina (Et₂O) gave hydrocarbon oil (3.03 g) followed by the desired product (3.76 g) and finally recovered 2,3-dihydrothiophen 1,1-dioxide (1.96 g). Vacuum sublimation at 100°C and 0.2 mmHg gave 3-Thiatricyclo[5.2.1.0^{2,6}]dec-8-ene 3,3-dioxide (2.85 g, 36%) as a colourless non-crystalline solid, m.p. 141-143°C (lit., 141-142°C). (Found: C, 58.55; H, 6.6. $C_9H_{12}O_2S$ requires C, 58.7; H, 6.6%); ν_{max} (CHCl₃), 2978, 1450, 1410, 1347, 1305, 1220, 1172, 1135, 1104, 955, 909, 901 and 811 cm^{-1} ; δ 6.36 (2H, s), 3.68-3.55 (1H, m), 3.4-1.8 (7H, m), 1.60 and 1.42 (2H, AB pattern, J8Hz); m/e 184 (10%, M^+), 119 (18), 118 (26), 105 (8), 92 (7), 91 (17), 79 (12) and 66 (100).

(iii) 3-Thiatricyclo[5.2.2.0^{2,6}]undec-8-ene 3,3-dioxide

A solution of 2,3-dihydrothiophen 1,1-dioxide (8.0 g, 68 mmol) and 1,3-cyclohexadiene (5.0 g, 62 mmol) in dry benzene (30 ml) was heated in an autoclave at 190°C for 110 h.

Chromatography of the residue after evaporation, on alumina (Et₂O) gave hydrocarbons (1.2 g) followed by the desired product and finally recovered 2,3-dihydrothiophen 1,1-dioxide (5.5 g).

Recrystallisation from ethanol gave 3-Thiatricyclo[5.2.2.0^{2,6}]-undec-8-ene 3,3-dioxide (2.16 g, 18%) as colourless needles,

m.p. 88-89°C. (Found: C, 60.8; H, 7.2. C₁₀H₁₄O₂S requires C, 60.5; H, 7.1%); ν_{\max} 1414, 1305, 1210, 1169, 1120, 956, 927, 890, 844, 720 and 672 cm⁻¹; δ 6.32 (2H, m), 3.3-3.16 (2H, m), 2.88-2.68 (4H, m), 2.4-2.1 (1H, m), 2.0-1.8 (1H, m) and 1.58 and 1.35 (4H, superimposed AB patterns, J10Hz); m/e 198 (32%, M⁺), 134 (14), 119 (25), 105 (41), 92 (49), 91 (68), 80 (96), 79 (50) and 78 (100).

(iv) 1,3-Cycloheptadiene

This was prepared by the method of Dirkzwager *et al.*²¹⁹

Reduction of cycloheptatriene (18 g, 217 mmol) with sodium (10 g, 435 mmol) in liquid ammonia at -78°C, followed by quenching with aniline (40.5 g, 435 mmol), gave an oil which, on Kugelrohr distillation at 100-130°C and 760 mmHg, afforded 1,3-Cycloheptadiene (6.9 g, 34%). GC (10% PEGA, 55°C) showed this to be 90% pure.

(v) 3-Thiatricyclo[5.3.2.0^{2,6}]dodec-11-ene 3,3-dioxide

A solution of 2,3-dihydrothiophen 1,1-dioxide (5.3 g, 45.2 mmol) and 1,3-cycloheptadiene (4.0 g, 42.6 mmol) in benzene

(25 ml) was heated in an autoclave at 150°C for 48 h.

Chromatography of the residue after evaporation, on alumina (Et₂O) gave hydrocarbon oil (0.25 g), the desired product (0.4 g) and finally recovered 2,3-dihydrothiophen 1,1-dioxide (4.8 g). Preparative TLC on alumina (Et₂O) gave 3-Thiatri-cyclo[5.3.2.0^{2,6}]dodec-11-ene 3,3-dioxide (0.33 g, 4%) as a sweet smelling colourless oil. (Found: M⁺ 212.086374.

C₁₁H₁₆O₂S requires 212.087096); ν_{\max} 1500, 1445, 1300, 1127, 1105 and 750 cm⁻¹; δ 6.45-6.25 and 6.2-6.1 (2H, *exo* and *endo* isomers), 3.7-2.7 (6H, m) and 2.4-1.4 (8H, m); ¹³C δ (90MHz) 136.87, 134.81, 132.85 and 132.05 (C₁₁ and C₁₂ - *exo* and *endo*). 65.98 and 64.34 (C₂), 51.58 (2C), 51.39 (2C), 50.16, 47.53, 46.02, 43.08, 41.92, 37.81, 31.18, 28.29 (2C), 27.05, 23.46 and 22.81; m/e 212 (1.4%, M⁺), 184 (2), 146 (1.2), 133 (1), 118 (15), 105 (16), 91 (62) and 66 (100).

c. Flash Vacuum Pyrolysis of 7-Thiabicyclo[4.3.0]non-3-ene 7,7-dioxide and bridged analogues

(i) FVP of 7-Thiabicyclo[4.3.0]non-3-ene 7,7-dioxide

FVP of the title compound (78 mg, 675°C, 2x10⁻³ mmHg, inlet 40-80°C) gave largely the unchanged starting material (73 mg) but also a small quantity of yellow oil whose NMR and GC (10% PEGA, 55°C) showed it to consist only of benzene and 1,4-cyclohexadiene. Calibration of the NMR with acetone indicated a combined yield (on the reacted sulphone) of 60% made up of benzene (43%) and 1,4-cyclohexadiene (17%).

FVP of the title compound (80 mg, 750°C, 3x10⁻³ mmHg, inlet 40-90°C) gave a small amount of white polymer (5 mg) and a

colourless liquid whose calibrated NMR and GC showed a 90% yield made up of benzene (82%) and 1,4-cyclohexadiene (8%).

(ii) FVP of 3-Thiatricyclo[5.2.1.0^{2,6}]dec-8-ene 3,3-dioxide

FVP of the title compound (54 mg, 750°C, 2×10^{-3} mmHg, inlet 40-80°C) gave a liquid and a solid which were taken up in deuteriochloroform. The NMR showed the presence of cyclopentadiene and 2,3-dihydrothiophen 1,1-dioxide only.

Calibration with methylene chloride gave the yields as 70% and 85% respectively.

Pyrolysis at 625°C and 675°C gave similar results.

(iii) FVP of 3-Thiatricyclo[5.2.2.0^{2,6}]undec-8-ene 3,3-dioxide

FVP of the title compound (42 mg, 675°C, 4×10^{-3} mmHg, inlet 40-90°C) gave a white polymer (3 mg) and a colourless oil. NMR of this showed the presence of four components: the unreacted starting material (22 mg), benzene (4.6 mg), 1,3-cyclohexadiene (1.8 mg) and 2,3-dihydrothiophen 1,1-dioxide (5.2 mg) [calibrated with CH₂Cl₂]. The benzene to 1,3-cyclohexadiene ratio was confirmed by the GC (10% PEGA, 55°C). These weights imply a ratio of retro Diels-Alder reaction to stepwise loss of SO₂ and two molecules of ethylene of 45:55. FVP of the title compound (53 mg, 725°C) gave the same products: polymer (1 mg), starting material (9.3 mg), benzene (9.2 mg), 1,3-cyclohexadiene (2.3 mg) and 2,3-dihydrothiophen 1,1-dioxide (7.3 mg) indicating 35% retro Diels-Alder reaction.

FVP (53 mg, 750°C) gave no unreacted starting material and the other products: polymer (2 mg), benzene (8.9 mg), 1,3-cyclohexadiene (2.0 mg) and 2,3-dihydrothiophen 1,1-dioxide

(5.4 mg), implied 30% retro Diels-Alder reaction with 70% stepwise loss of SO_2 and $2\times\text{C}_2\text{H}_4$.

(iv) FVP of 3-Thiatricyclo[5.3.2.0^{2,6}]dodec-11-ene 3,3-dioxide

FVP at 700°C gave the recovered starting material. FVP of the title compound (27 mg, 800°C , 3×10^{-3} mmHg, inlet $150\text{--}200^\circ\text{C}$) gave a brown oil near the furnace exit. NMR showed peaks in the right region for the expected compound but many impurities. GC (10% PEGA, 100°C) showed only one main component and GC-MS indicated this to have m/e 120 corresponding to the expected bicyclo[3.2.2]nona-6,8-diene. The minor components included toluene and ethylbenzene.

(v) FVP of 2,3-dihydrothiophen 1,1-dioxide

FVP of the title compound (46 mg, 725°C , 2×10^{-3} mmHg, inlet $25\text{--}50^\circ\text{C}$) gave the recovered unreacted starting material (39 mg) and a white polymer (2 mg) formed by reaction of the gaseous products: SO_2 , C_2H_4 and C_2H_2 . This indicates 15% decomposition under these conditions.

2. Preparation and FVP of sulphone epoxides

a. Preparation of 4-Oxa-8-thiatricyclo[5.3.0.0^{3,5}]decane 8,8-dioxide and bridged analogues

(i) 4-Oxa-8-thiatricyclo[5.3.0.0^{3,5}]decane 8,8-dioxide

A solution of 7-thiabicyclo[4.3.0]non-3-ene 7,7-dioxide (0.50 g, 2.9 mmol) and *m*-chloroperoxybenzoic acid (85%, 1.20 g, contains 5.9 mmol peracid) in dry ether (25 ml) was stirred for

130 h. The solution was washed thoroughly with aqueous sodium carbonate, dried and evaporated to give a white solid which, after preparative TLC on alumina (CH_2Cl_2), gave 4-Oxa-8-thiatricyclo[5.3.0.0^{3,5}]decane 8,8-dioxide (0.13 g, 24%) as colourless crystals, m.p. 45-47°C. (Found: C, 51.2; H, 6.45. $\text{C}_8\text{H}_{12}\text{O}_3\text{S}$ requires C, 51.0; H, 6.4%); ν_{max} 1296, 990, 940, 916, 838, 810, 785, 762 and 728 cm^{-1} ; δ 3.23 (2H, s), 3.25-3.05 (3H, m) and 2.9-1.8 (7H, m); m/e 188 (0.3%, M^+), 171 (0.3), 139 (0.4), 132 (0.5), 124 (25), 122 (17), 109 (13), 96 (100) and 95 (40).

(ii) 9-Oxa-3-thiatetracyclo[5.3.1.0^{2,6}.0^{8,10}]undecane 3,3-dioxide

A solution of 3-thiatricyclo[5.2.1.0^{2,6}]dec-8-ene 3,3-dioxide (0.50 g, 2.72 mmol) in acetic acid (10 ml) containing 30% hydrogen peroxide solution (2.0 ml, 18 mmol) was stirred at 50-60°C for 24 h. Water (100 ml) was added and the acid neutralised by addition of excess solid sodium bicarbonate. Extraction with methylene chloride (3x25 ml) followed by drying and evaporation gave a colourless oil (0.30 g) which after preparative TLC on alumina (CH_2Cl_2) gave 9-Oxa-3-thiatetracyclo[5.3.1.0^{2,6}.0^{8,10}]undecane 3,3-dioxide (0.20 g, 37%) as colourless crystals, m.p. 122-124°C. (Found: C, 53.9; H, 6.1. $\text{C}_9\text{H}_{12}\text{O}_3\text{S}$ requires C, 54.0; H, 6.0%); ν_{max} 1423, 1208, 978, 920, 855, 840, 790, 715, 688 and 630 cm^{-1} ; δ 3.87 (1H, d, J4Hz), 3.40 (2H, m), 3.18 (1H, m), 3.08 (2H, s), 2.83 (1H, m), 2.25 (2H, m), 1.72 (1H, s), 1.54 and 0.93 (2H, AB pattern, J10Hz); m/e 200 (4%, M^+), 136 (9), 119 (15), 118 (12), 107 (31), 105 (21), 91 (24) and 82 (100).

(iii) 9-Oxa-3-thiatetracyclo[5.3.2.0^{2,6}.0^{8,10}]dodecane 3,3-dioxide

A solution of 3-thiatriacyclo[5.2.2.0^{2,6}]undec-8-ene 3,3-dioxide (0.50 g, 2.53 mmol) and *m*-chloroperoxybenzoic acid ('85%', 1.03 g, contains 5.08 mmol peracid) in dry ethyl acetate (15 ml) was heated under reflux for 72 h. The solution was evaporated and the residue dissolved in methylene chloride (25 ml) which was then washed well with aqueous sodium carbonate, dried and evaporated to give a yellow solid (0.5 g). Recrystallisation from ethanol gave 9-Oxa-3-thiatetracyclo[5.3.2.0^{2,6}.0^{8,10}]dodecane 3,3-dioxide (0.30 g, 56%) as colourless needles, m.p. 132-133°C. (Found: C, 55.8; H, 6.5.

$C_{10}H_{14}O_3S$ requires C, 56.1; H, 6.6%); ν_{\max} 1378, 1305, 1295, 1169, 1122, 1078, 957, 892, 874, 856, 806, 728 and 637 cm^{-1} ; δ 3.60 (1H, t, J4Hz), 3.4-3.2 (2H, m), 3.0-1.9 (7H, m), 1.82 and 1.16 (4H, A_2B_2 pattern, J8Hz); m/e 214 (1.2%, M^+), 150 (41), 119 (28), 106 (35), 96 (48), 94 (54), 93 (67), 91 (70) and 79 (100).

b. Flash Vacuum Pyrolysis of 4-Oxa-8-thiatriacyclo[5.3.0.0^{3,5}]decane 8,8-dioxide and bridged analogues

(i) Preparation of 7-Oxabicyclo[4.1.0]hept-3-ene

An approximately 1M solution of peracetic acid in anhydrous acetic acid was prepared by stirring a mixture of acetic anhydride (45 ml) and 30% hydrogen peroxide solution (15 ml) at 50°C for 4 h. The solution was stored at 0°C.

The peracetic acid solution (7.5 ml, 7.5 mmol) was added dropwise to a solution of 1,4-cyclohexadiene (1.0 g, 12.5 mmol)

in dry methylene chloride (30 ml) containing anhydrous sodium carbonate (6 g). The solution was then stirred for 27 h, filtered and evaporated. Chromatography of the residue on alumina (Et₂O) gave 7-Oxabicyclo[4.1.0]hept-3-ene (1.09 g, 88%) as a colourless liquid, n_D^{20} 1.4740 (lit., n_D^{20} 1.4810); δ 5.45 (2H, s), 3.23 (2H, s) and 2.50 (4H, s). A second product was also obtained, which proved to be the *trans*-diepoxide (0.10 g, 8%), as colourless crystals, m.p. 106-107°C (lit., n_D^{21} 106.5-107°C).

(ii) FVP of 4-Oxa-8-thiatricyclo[5.3.0.0^{3,5}]decane 8,8-dioxide

Pyrolysis below 725°C gave the unchanged starting material.

FVP of the title compound (25 mg, 750°C, 10⁻³ mmHg, inlet 25-50°C) gave a small quantity of white polymer (1 mg) and a colourless oil. NMR and GC (10% PEGA, 55°C) of this showed the presence of benzene. GC on 2% NPGS (150°C) showed the presence of phenol and benzene in the ratio 7:93. By calibration of the NMR with methylene chloride the yields were determined to be benzene (72%) and phenol (5%).

(iii) FVP of 7-Oxabicyclo[4.1.0]hept-3-ene

FVP of the title compound (60 mg, 750°C, 10⁻² mmHg, inlet 20°C) gave a small quantity of polymer (2 mg) and a colourless liquid whose NMR and GC (2% NPGS, 150°C) showed the presence of benzene, phenol, unreacted starting material and other minor components. Calibration of the NMR with 1,4-dioxan gave the yields as benzene (39%), phenol (10%) and starting material (6%). GC confirmed the benzene to phenol ratio and TLC (alumina, Et₂O) showed the presence of phenol and starting material.

(iv) Preparation of 3-Oxatricyclo[3.2.1.0^{2,4}]oct-6-ene

A solution of anhydrous peracetic acid, prepared as in section (i), (50 ml, approx. 50 mmol) was added dropwise to a stirred solution of bicyclo[2.2.1]hepta-2.5-diene (8.0 g, 87 mmol) in methylene chloride (500 ml) containing anhydrous sodium carbonate (75 g). After stirring for 12 h the solution was filtered and evaporated to give a yellow oil (8.32 g).

Kugelrohr distillation gave a colourless liquid (7.71 g) whose NMR showed the presence of 3-Oxatricyclo[3.2.1.0^{2,4}]oct-6-ene (70%); δ 6.47 (2H, t, J2Hz), 3.40 (2H, s), 2.95 (2H, s), 1.68 and 1.26 (2H, AB pattern, J9Hz), (lit.,²²² (CCl₄) 6.4, 3.2, 2.8, 1.6 and 1.2) as well as the isomeric Bicyclo[3.1.0]hex-2-ene-6-carboxaldehyde (20%) and acetic anhydride (10%). All attempts at further purification of the epoxide resulted in isomerisation to the aldehyde.

(v) Preparation of Bicyclo[3.1.0]hex-2-ene-6-carboxaldehyde

A solution of the crude 3-Oxatricyclo[3.2.1.0^{2,4}]oct-6-ene (2.0 g, 18.5 mmol) in methylene chloride (15 ml) was stirred vigorously with 5% sodium hydroxide solution (25 ml) for 12 h. The organic layer was separated, dried and evaporated to give Bicyclo[3.1.0]hex-2-ene-6-carboxaldehyde (0.26 g, 14%) as a clear yellow liquid, n_D^{20} 1.4985, ν_{\max} 1695 cm⁻¹ (lit.,²²³ 1.4965, 1689).

(vi) FVP of 9-Oxa-3-thiatetracyclo[5.3.1.0^{2,6}.0^{8,19}]undecane3,3-dioxide

Pyrolysis of the title compound at 675°C gave the unchanged starting material.

FVP of the title compound (40 mg, 725°C, 2×10^{-3} mmHg, inlet 70-120°C) gave some starting material (16.5 mg) but also a yellow oil. On warming up this partly formed an insoluble polymer (2.5 mg) but the remainder was dissolved in deuteriochloroform. GC (10% PEGA, 55°C) and NMR of this showed the presence of a large proportion of benzene with small peaks in the δ 3-1 range.

FVP of the title compound (35 mg, 750°C, 2×10^{-3} mmHg, inlet 70-120°C) gave no starting material and a yellow liquid whose GC and NMR showed it to be similar to the product at 725°C. Calibration of the NMR with cyclohexane gave the yield of benzene as 33%.

(vii) FVP of 3-Oxatricyclo[3.2.1.0^{2,4}]oct-6-ene

FVP of the product from section (iv) (74 mg) containing 49 mg of the title compound and 8 mg of its aldehyde isomer (750°C, 5×10^{-3} mmHg, inlet 25-50°C) gave a colourless liquid whose NMR showed the presence of benzene and minor components at δ 7-6 and 3-1.5. GC (10% PEGA, 55°C) showed the presence of benzene and 1,3-cyclohexadiene with three other minor components. By calibration of the NMR with methylene chloride the yields were determined to be: benzene (42%), 1,3-cyclohexadiene (5%) and other components (total 22%).

(viii) FVP of Bicyclo[3.1.0]hex-2-ene-6-carboxaldehyde

FVP of the title compound (58 mg, 750°C, 20×10^{-3} mmHg, inlet 25°C) gave a yellow liquid whose NMR showed the presence of benzene and signals at δ 10, 7-6 and 3-2. GC (10% PEGA, 55°C) showed the presence of benzene, 1,3-cyclohexadiene, the unreacted starting material and two other components.

Calibration of the NMR with methylene chloride and comparison of GC peaks gave the yields as: benzene (32%), 1,3-cyclohexadiene (6%), unreacted starting material (6%) and unidentified components (12%).

(ix) FVP of 9-Oxa-3-thiatetracyclo[5.3.2.0^{2,6}.0^{8,10}]dodecane
3,3-dioxide

Pyrolysis at 700°C and 725°C gave 20% and 5% unreacted starting material respectively and volatile products essentially the same as at 750°C.

FVP of the title compound (28 mg, 750°C, 2×10^{-3} mmHg, inlet 120-140°C) gave a white solid whose NMR showed it to be phenol. This was confirmed by comparison with authentic phenol on TLC (alumina and silica, Et₂O/pet.ether, 1:1) and GC (2% NPGS, 150°C). The GC showed the presence of one other minor product. Calibration of the NMR with methylene chloride gave the yield of phenol as 73% with the unknown product in the GC present in 2% yield.

3. Preparation of sulphone aziridines

a. Attempted preparation of 6-Ethoxycarbonyl-2-thia-6-azabicyclo[3.1.0]hexane 2,2-dioxide

(i) Photochemical reaction with ethyl azidoformate

A mixture of 2,3-dihydrothiophen 1,1-dioxide (1.0 g, 8.5 mmol) and ethyl azidoformate (1.0 g, 8.7 mmol) was irradiated at 400W for 100 h. TLC (alumina, Et₂O) showed a large proportion of the starting sulphone present. A further 0.3 g

(2.6 mmol) of ethyl azidoformate was added and the irradiation continued for 85 h. TLC showed only the starting sulphone and fast moving products. Chromatography on alumina (Et_2O) gave azide byproducts (0.21 g) and recovered starting sulphone (0.88 g).

(ii) Thermal reaction with ethyl azidoformate

A solution of 2,3-dihydrothiophen 1,1-dioxide (0.10 g, 0.85 mmol) and ethyl azidoformate (0.11 g, 0.96 mmol) in dry carbon tetrachloride (10 ml) was heated under reflux for 40 h. The solution was evaporated and both NMR and TLC (alumina, Et_2O) of the residue showed only the presence of the starting sulphone and azide byproducts.

(iii) Reaction with ethoxycarbonyl nitrene from α -elimination under phase transfer conditions

A solution of 2,3-dihydrothiophen 1,1-dioxide (0.10 g, 0.85 mmol), ethyl *p*-nitrobenzenesulphonoxycarbamate (0.25 g, 0.85 mmol) and benzyl triethylammonium chloride (20 mg, 0.085 mmol) in methylene chloride (10 ml) was stirred vigorously with 1M sodium bicarbonate solution (2 ml) for 20 h. Water (10 ml) was added and the organic layer separated and washed with water (10 ml). Drying and evaporation gave a yellow oil (0.17 g) whose NMR and TLC (alumina, Et_2O) showed only the presence of nitrene byproducts and the unreacted starting sulphone.

b. Attempted preparation of 4-Ethoxycarbonyl-8-thia-4-azatricyclo[5.3.0.0^{3,5}]decane 8,8-dioxide

(i) Photochemical reaction with ethyl azidoformate

A mixture of 7-Thiabicyclo[4.3.0]non-3-ene 7,7-dioxide (30 mg, 0.17 mmol) and ethyl azidoformate (0.50 g, 4.3 mmol) was irradiated at 400W for 20 h. Chromatography on alumina (Et₂O) gave some unreacted starting sulphone, ethyl carbamate and the desired aziridine. Preparative TLC of the latter on alumina (Et₂O) gave 4-Ethoxycarbonyl-8-thia-4-azatricyclo[5.3.0.0^{3,5}]decane 8,8-dioxide (18 mg, 40%) as a colourless liquid, identical on NMR and TLC to the compound prepared below.

(ii) Reaction with ethoxycarbonyl nitrene from α -elimination under phase transfer conditions

A solution of 7-Thiabicyclo[4.3.0]non-3-ene 7,7-dioxide (100 mg, 0.58 mmol), ethyl *p*-nitrobenzenesulphonoxycarbamate (169 mg, 0.58 mmol) and benzyl triethylammonium chloride (13 mg, 0.06 mmol) in methylene chloride (10 ml) was stirred vigorously with 1M sodium bicarbonate solution (2 ml) for 40 h. Water (10 ml) was added and the organic layer separated, washed with water (2x5 ml), dried and evaporated to give a clear oil (0.13 g). Preparative TLC on alumina (Et₂O) gave the starting sulphone (30 mg) followed by 4-Ethoxycarbonyl-8-thia-4-azatricyclo[5.3.0.0^{3,5}]decane 8,8-dioxide (26 mg, 17%) as a colourless oil. (Found: M^+ 259.088763. $C_{11}H_{17}NO_4S$ requires 259.087822); ν_{max} 1718, 1425, 1372, 1290, 1231, 1185, 1120, 1040, 795 and 734 cm^{-1} ; δ 4.13 (2H, q, J7Hz), 3.2-1.7 (12H, m) and 1.26 (3H, t, J7Hz); m/e 259 (1.8%, M^+), 214 (12),

193 (19), 167 (81), 120 (70), 106 (41) and 93 (100).

c. Preparation of 9-Ethoxycarbonyl-3-thia-9-azatetracyclo[5.3.1.0^{2,6}.0^{8,10}]undecane 3,3-dioxide

(i) Photochemical reaction with ethyl azidoformate

A mixture of 3-thiatricyclo[5.2.1.0^{2,6}]dec-8-ene 3,3-dioxide (65 mg, 0.35 mmol) and ethyl azidoformate (500 mg, 4 mmol) was irradiated at 400W for 18 h. Chromatography of the resulting yellow oil on alumina (Et₂O) followed by preparative TLC on alumina (Et₂O) gave an oil whose NMR showed it to contain 9-Ethoxycarbonyl-3-thia-9-azatetracyclo[5.3.1.0^{2,6}.0^{8,10}]undecane 3,3-dioxide (12 mg, 12%) [Yield estimated from NMR]. This was confirmed by TLC (alumina, Et₂O) against the product obtained below.

(ii) Reaction with ethoxycarbonyl nitrene from α -elimination under phase transfer conditions

A solution of 3-thiatricyclo[5.2.1.0^{2,6}]dec-8-ene 3,3-dioxide (50 mg, 0.27 mmol), ethyl *p*-nitrobenzenesulphonoxycarbamate (79 mg, 0.27 mmol) and benzyl triethylammonium chloride (6 mg, 0.03 mmol) in methylene chloride (5 ml) was stirred vigorously with 1M sodium bicarbonate solution (1 ml) for 40 h. Water (5 ml) was added and the organic layer separated and washed with water (5 ml). Drying and evaporation gave a clear yellow oil (100 mg). Preparative TLC on alumina (Et₂O) gave byproducts (30 mg) followed by 9-Ethoxycarbonyl-3-thia-9-azatetracyclo[5.2.1.0^{2,6}.0^{8,10}]decane 3,3-dioxide (40 mg, 54%) as colourless crystals, m.p.134-136°C. (Found: C, 52.9; H, 6.4; N, 4.9. C₁₂H₁₇NO₄S requires C, 53.1; H, 6.3;

N, 5.2%); ν_{\max} 1708, 1285, 1094, 1020, 828, 818, 777 and 719 cm^{-1} ; δ 4.13 (2H, q, J7Hz), 3.5-3.3 (2H, m), 3.15-2.7 (6H, m), 2.3-2.1 (2H, m), 1.77 and 0.99 (2H, AB pattern, J10Hz), and 1.27 (3H, t, J7Hz); m/e 271 (2%, M^+), 216 (14), 207 (16), 206 (19), 153 (36), 152 (59), 134 (36), 105 (32), 91 (35) and 80 (100).

d. Attempted preparation of 9-Ethoxycarbonyl-3-thia-9-azatetracyclo[5.3.2.0^{2,6}.0^{8,10}]dodecane 3,3-dioxide

(i) Photochemical reaction with ethyl azidoformate

A solution of 3-thiatriacyclo[5.2.2.0^{2,6}]undec-8-ene 3,3-dioxide (0.22 g, 1.1 mmol) and ethyl azidoformate (0.27 g, 2.3 mmol) in dry carbon tetrachloride (1.0 ml) was irradiated at 400W for 120 h. Evaporation gave a yellow oil (0.36 g) whose NMR and TLC (alumina, Et_2O) showed only the starting sulphone and azide byproducts. Chromatography on alumina (Et_2O) gave azide byproducts (0.09 g) and the recovered starting sulphone (0.19 g). A repeat reaction in the absence of solvent gave a similar result.

(ii) Thermal reaction with ethyl azidoformate

A solution of 3-thiatriacyclo[5.2.2.0^{2,6}]undec-8-ene 3,3-dioxide (0.40 g, 2.02 mmol) and ethyl azidoformate (0.30 g, 2.61 mmol) in dry carbon tetrachloride (5 ml) was heated under reflux for 60 h. Evaporation gave a yellow oil whose NMR and TLC (alumina, Et_2O) showed only azide byproducts and the starting sulphone to be present. Chromatography on alumina (Et_2O) gave the recovered starting sulphone (0.25 g).

(iii) Reaction with ethoxycarbonyl nitrene from α -elimination under phase transfer conditions

A solution of 3-thiatricyclo[5.2.2.0^{2,6}]undec-8-ene 3,3-dioxide (50 mg, 0.25 mmol), ethyl *p*-nitrobenzenesulphonoxy-carbamate (73 mg, 0.25 mmol) and benzyl triethylammonium chloride (6 mg, 0.025 mmol) in methylene chloride (5 ml) was stirred vigorously with 1M sodium bicarbonate solution (1 ml) for 40 h. Water (5 ml) was added and the organic layer separated and washed with water (5 ml). Drying and evaporation gave a clear oil (70 mg). Preparative TLC on alumina (Et₂O) gave only the recovered starting sulphone (20 mg) and nitrene byproducts (10 mg) with no trace of the desired aziridine.

F. Preparation and FVP of some bicyclic anhydrides and derivatives

1. Preparation and flash vacuum pyrolysis of bicyclic anhydrides

a. Preparation of 2,4-Dioxo-3-oxabicyclo[3.2.0]hept-6-ene

The method used was based on that of Bloomfield et al.²²⁴ Acetylene gas was passed through a solution of maleic anhydride (25 g, 255 mmol) and benzophenone (10 g, 54 mmol) in dry ethyl acetate (500 ml) at -78°C while it was irradiated at 400W for 30 h. The solution was evaporated and the residue distilled at 2mmHg to give unreacted maleic anhydride followed by the desired product boiling at $120-135^{\circ}\text{C}$. On recrystallisation from diisopropyl ether this gave 2,4-Dioxo-3-oxabicyclo[3.2.0]hept-6-ene (15.8 g, 49%) as colourless needles, m.p. $86-87^{\circ}\text{C}$ (lit.²²⁵ 89°C).

b. FVP of bicyclic anhydrides

(i) FVP of 2,4-Dioxo-3-oxabicyclo[3.2.0]hept-6-ene

FVP of the title compound (33 mg, 800°C , 5×10^{-3} mmHg, inlet $100-120^{\circ}\text{C}$) gave a white solid whose NMR showed it to be pure maleic anhydride.

Pyrolysis at 650°C gave 15% unchanged starting material and 85% maleic anhydride by NMR.

(ii) FVP of 7,9-Dioxo-8-oxabicyclo[4.3.0]non-3-ene

FVP of the title compound (115 mg, 650°C , 10^{-3} mmHg, inlet $100-120^{\circ}\text{C}$) gave a white solid whose NMR showed it to consist

mainly of the unchanged starting material but also maleic anhydride and 1,3-butadiene. From the integrals the extent of reaction was 20%. Pyrolysis at 700°C and 750°C gave the same products in ratios indicating 40% and 94% reaction respectively.

(iii) FVP of 3,5-Dioxo-4-oxatricyclo[5.2.1.0^{2,6}]dec-8-ene

FVP of the title compound (61 mg, 600°C, 5×10^{-3} mmHg, inlet 50-100°C) gave a product in the cold part of the trap with nothing in the warmer region corresponding to the starting material (m.p. 160°C). When this was dissolved out in deuteriochloroform the NMR showed that the starting anhydride had been reformed in solution from the cyclopentadiene and maleic anhydride.

(iv) FVP of 3,5-Dioxo-4-oxatricyclo[5.2.2.0^{2,6}]undec-8-ene

FVP of the title compound (100 mg, 600°C, 2×10^{-3} mmHg, inlet 50-100°C) gave some unchanged starting material near the furnace exit but also volatile products whose NMR showed the presence of maleic anhydride and 1,3-cyclohexadiene. Comparison of integrals indicated 35% reaction.

Pyrolysis at 650°C and 700°C gave the same products in ratios indicating 72% and 92% reaction respectively.

(v) FVP of 3,5-Dioxo-4,10-dioxatricyclo[5.2.1.0^{2,6}]dec-8-ene

FVP of the title compound (62 mg, 600°C, 5×10^{-3} mmHg, inlet 50-90°C) gave a product whose NMR showed the presence of furan and maleic anhydride. Calibration with acetone gave the yields as 92% and 99% respectively.

(vi) FVP of Maleic anhydride

FVP of the title compound (98 mg, 800°C, 5×10^{-3} mmHg, inlet 25°C) gave partial decomposition to acetylene, CO and CO₂. Calibration of the NMR of the product with methylene chloride indicated 40% loss of maleic anhydride and there was a small peak at $\delta 2.06$ due to acetylene.

NMR of the pyrolysate at 900°C showed over 80% decomposition, again with a small peak for acetylene.

2. Preparation and FVP of anhydride epoxidesa. Preparation of 8,10-Dioxo-4,9-dioxatricyclo[5.3.0.0^{3,5}]-decane and analogues(i) 8,10-Dioxo-4,9-dioxatricyclo[5.3.0.0^{3,5}]decane

The method used was based on that of Gill and Munro²²⁶. A solution of peracetic acid in acetic acid was prepared by stirring a mixture of acetic anhydride (12.9 g, 126 mmol) with 30% hydrogen peroxide solution (2.6 ml, 23.4 mmol) at 40°C for 4 h. 7,9-Dioxo-8-oxabicyclo[4.3.0]non-3-ene (2.0 g, 13.2 mmol) was then added and the solution stirred at room temperature for 18 h. The solid was filtered off and recrystallised from ethyl acetate to give 8,10-Dioxo-4,9-dioxatricyclo[5.3.0.0^{3,5}]-decane (0.70 g, 32%) as colourless needles, m.p. 205-206°C (lit.²²⁶ 204-205°C).

(ii) 3,5-Dioxo-4,9-dioxatetracyclo[5.3.1.0^{2,6}.0^{8,10}]undecane

A solution of 3,5-Dioxo-4-oxatricyclo[5.2.1.0^{2,6}]dec-8-ene (1.0 g, 6.1 mmol) and *m*-chloroperoxybenzoic acid ('85%',

2.5 g, contains 12.3 mmol peracid) in dry ethyl acetate (25 ml) was heated under reflux for 8 h. The solution was cooled and on standing the product crystallised out. It was filtered off and recrystallised from pet.ether/acetone (1:1) to give 3,5-Dioxo-4,9-dioxatetracyclo[5.3.1.0^{2,6}.0^{8,10}]undecane (0.50 g, 46%) as colourless flakes, m.p. 235-237°C (lit.²²⁷ 233-235°C).

(iii) 3,5-Dioxo-4,9-dioxatetracyclo[5.3.2.0^{2,6}.0^{8,10}]dodecane

A solution of 3,5-Dioxo-4-oxatricyclo[5.2.2.0^{2,6}]undec-8-ene (1.0 g, 5.6 mmol) and *m*-chloroperoxybenzoic acid ('85%', 2.5 g, contains 12.3 mmol peracid) in dry ethyl acetate (25 ml) was heated under reflux for 15 h. On cooling at 0°C for 12 h the product crystallised out and was filtered off to give 3,5-Dioxo-4,9-dioxatetracyclo[5.3.2.0^{2,6}.0^{8,10}]dodecane (0.36 g, 33%) as colourless crystals, m.p. 209-211°C (lit.²²⁸ 207-208°C).

(iv) 3,5-Dioxo-4,9,11-trioxatetracyclo[5.3.1.0^{2,6}.0^{8,10}]undecane

This was prepared by a variation of the literature method²²⁹ A solution of 3,5-Dioxo-4,10-dioxatricyclo[5.2.1.0^{2,6}]dec-8-ene (1.0 g, 6.0 mmol) in formic acid (20 ml) containing 30% hydrogen peroxide solution (4.0 ml, 36 mmol) was stirred at room temperature for 64 h. The solution was evaporated to give the epoxy diacid as a white solid (1.19 g), m.p. 182-184°C.

This was then heated with acetyl chloride (10 ml) under reflux for 12 h. The residue on evaporation was a brown solid (0.83 g) which was sublimed onto a cold finger at 220°C.

and 0.03 mmHg to give 3,5-Dioxo-4,9,11-trioxatetracyclo-
[5.3.1.0^{2,6}.0^{8,10}]undecane (0.66 g, 72%) as colourless
 crystals, m.p. 252-253°C (lit.²²⁹ 247-253°C). (Found: C,
 52.5; H, 3.4. C₈H₆O₅ requires C, 52.8; H, 3.3%).

b. FVP of anhydride epoxides

(i) FVP of 8,10-Dioxo-4,9-dioxatricyclo[5.3.0.0^{3,5}]decane

FVP of the title compound (40 mg, 800°C, 5x10⁻³ mmHg,
 inlet 160-180°C) gave a white solid whose NMR showed the
 presence of starting material (2 mg), benzene, phenol and
 other components. GC confirmed the presence of benzene (10%
 PEGA, 55°C) and phenol (2% NPGS, 150°C). By calibration of
 the NMR with cyclohexane and comparison of GC integrals the
 yields were determined as: benzene (30%) and phenol (12%).

Pyrolysis at 750°C gave the same products but with more
 starting material.

(ii) FVP of 3,5-Dioxo-4,9-dioxatetracyclo[5.3.1.0^{2,6}.0^{8,10}]-
decane

Pyrolysis at temperatures below 750°C gave the unchanged
 starting material.

FVP of the title compound (30 mg, 775°C, 2x10⁻³ mmHg,
 inlet 100-130°C) gave a colourless liquid whose NMR showed
 it to be mainly benzene with small peaks in the δ7-6 and 3-15
 regions. GC (10% PEGA, 55°C) showed the presence of benzene,
 1,3-cyclohexadiene and two other unidentified components.
 Calibration of the NMR and comparison of GC integrals gave
 the yields as: benzene (41%), 1,3-cyclohexadiene (11%) and
 minor components (4 and 1.5%).

(iii) FVP of 3,5-Dioxo-4,9-dioxatetracyclo[5.3.2.0^{2,6}.0^{8,10}]-undecane

FVP of the title compound (31 mg, 850°C, 5x10⁻³ mmHg, inlet 110-130°C) gave a small quantity of starting material (2 mg) and a colourless solid whose NMR showed it to be pure phenol. This was confirmed by GC (2% NPGS, 150°C) and TLC (silica, Et₂O/pet.ether, 1:1) against authentic phenol. Calibration of the NMR with acetone gave the yield as 72%.

Pyrolysis at 750°C and 800°C gave mainly the unreacted starting material with increasing yields of phenol.

(iv) FVP of 3,5-Dioxo-4,9,11-trioxatetracyclo[5.3.1.0^{2,6}.0^{8,10}]-undecane

Pyrolysis at temperatures below 700°C gave the unchanged starting material.

FVP of the title compound (1.0 g, 725°C, 3x10⁻³ mmHg, inlet 140-180°C) gave the unreacted anhydride (0.2 g) at the furnace exit and a colourless liquid in the trap. NMR of this showed the presence of maleic anhydride, *p*-dioxin and acrolein. Calibration with acetone gave the yield of maleic anhydride as 40%. Preparative GC (10% PEGA, 55°C) gave acrolein (62 mg, 20%) and *p*-Dioxin (69 mg, 15%); ν_{\max} (CDCl₃) 3125, 1986, 1680, 1642, 1585, 1450, 1280, 1045, 1012 and 988 cm⁻¹ [good agreement with literature spectrum²³⁰]; δ 5.55 (4H, s); ¹³C δ 127.28 (fully coupled: dd, J197.2Hz and 16.4Hz); m/e 84 (100%, M⁺), 56 (9), 55 (54), 54 (16), 42 (8) and 40 (8).

Pyrolysis of the title compound at 850°C gave no starting material and little maleic anhydride or dioxin. The main

product was acrolein with a small proportion of benzene [NMR, GC]. NMR of the 900°C pyrolysate showed acrolein (40% yield) and benzene (5%) as the main components [yields by calibration with cyclohexane].

(v) FVP of acrolein

FVP of acrolein (100 mg, 850°C, 5×10^{-2} mmHg, inlet 25°C) with silica rods in the furnace tube gave a liquid which was shown by GC (10% PEGA, 55°C) and NMR to consist of unchanged acrolein and benzene. Calibration of the GC gave the yield of benzene as 19 mg.

3. Preparation and flash vacuum pyrolysis of anhydride aziridines

a. Preparation of 3,5-Dioxo-9-ethoxycarbonyl-4-oxa-9-azatetracyclo[5.3.1.0^{2,6}.0^{8,10}]undecane

(i) Photochemical reaction with ethyl azidoformate

A mixture of 3,5-Dioxo-4-oxatricyclo[5.2.1.0^{2,6}]dec-8-ene (0.50 g, 3.0 mmol) and ethyl azidoformate (1.0 g, 8.7 mmol) was irradiated at 400W for 18 h. Ether (10 ml) was added to the oily solid and trituration gave a white solid. This was filtered off and washed with ether to give 3,5-Dioxo-9-ethoxycarbonyl-4-oxa-9-azatetracyclo[5.3.1.0^{2,6}.0^{8,10}]undecane (0.49 g, 64%) as colourless crystals, m.p. 184-185°C. (Found: C, 57.4; H, 5.3; N, 5.4. $C_{12}H_{13}NO_5$ requires C, 57.4; H, 5.2; N, 5.6%); ν_{\max} 1861, 1790, 1714, 1293, 1270, 1224, 1192, 1087, 1022, 950, 916, 793 and 721 cm^{-1} ; δ 4.11 (2H, q, J7Hz),

3.44 (2H, m), 3.13 (2H, m), 2.86 (2H, s), 1.85 and 1.18 (2H, AB pattern, J11Hz) and 1.25 (3H, t, J7Hz); m/e 251 (2.4%, M⁺), 223 (10), 206 (6), 179 (25), 153 (52), 152 (83), 127 (45), 108 (46), 106 (38), 96 (60) and 79 (100).

b. Preparation of 3,5-Dioxo-9-ethoxycarbonyl-4-oxa-9-azatetracyclo[5.3.2.0^{2,6}.0^{8,10}]dodecane

(i) Photochemical reaction with ethyl azidoformate

A mixture of 3,5-dioxo-4-oxatricyclo[5.2.2.0^{2,6}]undec-8-ene (0.50 g, 2.81 mmol) and ethyl azidoformate (1.0 g, 8.7 mmol) was irradiated at 400W for 18 h. Ether (10 ml) was added to the resulting yellow oil and the product filtered off and washed with ether. Vacuum sublimation at 10⁻³ mmHg and 150°C gave 3,5-Dioxo-9-ethoxycarbonyl-4-oxa-9-azatetracyclo[5.3.2.0^{2,6}.0^{8,10}]dodecane (0.17 g, 23%) as colourless crystals, m.p. 208-209°C. (Found: C, 58.6; H, 5.7; N, 5.2.

C₁₃H₁₅NO₅ requires C, 58.9; H, 5.7; N, 5.3%); ν_{\max} 1848, 1773, 1725, 1408, 1287, 1212, 1100, 1083, 1020, 948, 913 and 784 cm⁻¹; δ 4.12 (2H, q, J7Hz), 3.12 (2H, s), 2.84 (2H, m), 2.78 (2H, s), 1.90 and 1.27 (4H, A₂B₂ pattern, J8Hz) and 1.24 (3H, t, J7Hz): m/e 265 (11%, M⁺), 220 (9), 193 (30), 165 (37), 120 (56), 99 (27), 95 (40), 93 (74) and 80 (100).

(iii) Thermal reaction with ethyl azidoformate

A solution of 3,5-Dioxo-4-oxatricyclo[5.2.2.0^{2,6}]undec-8-ene (0.10 g, 0.56 mmol) and ethyl azidoformate (0.07 g, 0.61 mmol) in dry carbon tetrachloride (10 ml) was heated under reflux for 40 h. Evaporation gave a brown solid whose NMR and TLC (alumina, Et₂O) showed the presence of azide byproducts

the starting anhydride (86 mg) and 3,5-Dioxo-9-ethoxycarbonyl-4-oxa-9-azatetracyclo[5.3.2.0^{2,6}.0^{8,10}]dodecane (21 mg, 14%). [Yields estimated from NMR].

(iii) Attempted homogeneous reaction with ethoxycarbonyl nitrene from α -elimination

To a solution of 3,5-Dioxo-4-oxatricyclo[5.2.2.0^{2,6}]undec-8-ene (0.50 g, 2.81 mmol) and ethyl *p*-nitrobenzenesulphonoxycarbamate (0.86 g, 2.96 mmol) in dry methylene chloride (10 ml), was added a solution of triethylamine (0.40 g, 3.96 mmol) in dry methylene chloride (5 ml) over 5 min. After stirring for 3 h the solution was washed with water (2x10 ml), dried and evaporated. NMR and TLC (alumina, Et₂O) of the residue showed only nitrene byproducts and the unreacted starting anhydride with none of the expected aziridine.

c. Preparation of 3,5-Dioxo-9-methoxycarbonyl-4-oxa-9-azatetracyclo[5.3.2.0^{2,6}.0^{8,10}]dodecane

A mixture of 3,5-dioxo-4-oxatricyclo[5.2.2.0^{2,6}]undec-8-ene (0.50 g, 2.8 mmol) and methyl azidoformate (1.0 g, 8.7 mmol) was irradiated at 400W for 18 h. Addition of ether (10 ml) to the resulting yellow oil gave a white solid which was recrystallised from chloroform/ether (1:3) to give 3,5-Dioxo-9-methoxycarbonyl-4-oxa-9-azatetracyclo[5.3.2.0^{2,6}.0^{8,10}]dodecane (0.10 g, 15%) as colourless needles, m.p. 221-223°C.

(Found: M^+ 251.080686. C₁₂H₁₃NO₅ requires 251.079365);
 ν_{\max} 1840, 1765, 1710, 1444, 1292, 1209, 1148, 1082, 1010, 942, 909, 825 and 783 cm⁻¹; δ (CDCl₃/CD₃COCD₃, 3:1) 3.68 (3H, s), 3.25 (2H, s), 2.81 (4H, s) and 1.89 and 1.33 (4H, A₂B₂

pattern, J8Hz); m/e 251 (24%, M⁺), 223 (3), 220 (8), 179 (45) and 153 (100).

d. Preparation of 3,5-Dioxo-9-ethoxycarbonyl-4,11-dioxo-9-azatetracyclo[5.3.1.0^{2,6}.0^{8,10}]undecane

(i) Photochemical reaction with ethyl azidoformate

A mixture of 3,5-dioxo-4,10-dioxatricyclo[5.2.1.0^{2,6}]dec-8-ene (0.50 g, 3.01 mmol) and ethyl azidoformate (2.0 g, 17.4 mmol) was irradiated at 125W for 72 h. Addition of ether (10 ml) gave a white solid which was filtered off and washed with ether. Vacuum sublimation at 10⁻³ mmHg and 140°C gave 3,5-Dioxo-9-ethoxycarbonyl-4,11-dioxo-9-azatetracyclo[5.3.1.0^{2,6}.0^{8,10}]undecane (0.20 g, 26%) as a white powder, m.p. 178-179°C. (Found: C, 52.0; H, 4.4; N, 5.4. C₁₁H₁₁NO₆ requires C, 52.2; H, 4.4; N, 5.5%); ν_{\max} 1868, 1788, 1740, 1327, 1300, 1223, 1188, 1090, 1025, 942, 927, 908, 840, 820, 799, 740 and 690 cm⁻¹; δ 5.05 (2H, s), 4.13 (2H, q, J7Hz), 3.36 (2H, s), 2.91 (2H, s) and 1.24 (3H, t, J7Hz); m/e 253 (1%, M⁺), 208 (9), 180 (5), 155 (100), 111 (31) and 83 (91).

(ii) Thermal reaction with ethyl azidoformate

A solution of 3,5-dioxo-4,10-dioxatricyclo[5.2.1.0^{2,6}]dec-8-ene (0.50 g, 3.01 mmol) and ethyl azidoformate (0.40 g, 3.48 mmol) in dry carbon tetrachloride (10 ml) was heated under reflux for 18 h. Evaporation gave a brown oil (0.61 g) whose NMR showed the presence of azide byproducts and maleic anhydride from the retro Diels-Alder reaction of the starting anhydride. There was none of the starting anhydride or of the expected aziridine.

(iii) Attempted homogeneous reaction with ethoxycarbonyl nitrene from α -elimination

To a solution of 3,5-dioxo-4,10-dioxatricyclo[5.2.1.0^{2,6}]-dec-8-ene (0.50 g, 3.01 mmol) and ethyl *p*-nitrobenzenesulphonoxycarbamate (0.92 g, 3.17 mmol) in dry methylene chloride (20 ml), was added a solution of triethylamine (0.34 g, 3.37 mmol) in dry methylene chloride (10 ml) over 10 min. After stirring for 8 h the solution was washed with water (3x50 ml), dried and evaporated to give a yellow oil (0.72 g). The NMR showed the presence of the starting anhydride, furan and maleic anhydride from the retro Diels-Alder reaction and nitrene byproducts. There was none of the expected aziridine.

e. FVP of anhydride aziridines

(i) 3,5-Dioxo-9-ethoxycarbonyl-4-oxa-9-azatetrahydro-[5.3.1.0^{2,6,8,10}]undecane

FVP of the title compound (50 mg, 675°C, 2×10^{-3} mmHg, inlet 140-160°C) gave a dark red oil. On warming up this formed an orange polymer (10 mg) similar to that reported in the preparation of 1,4-dihydropyridine²³¹. NMR of the soluble products (C₆D₆) showed the presence of maleic anhydride (48% yield), pyridine (10%) and ethanol (8%).

FVP of the title compound (52 mg, 725°C, 2×10^{-3} mmHg, inlet 140-160°C) again gave a red oil which formed less of the dihydropyridine polymer. Calibration of the NMR showed the products to be maleic anhydride (46%) and pyridine (46%). GC (10% PEGA, 100°C) confirmed the presence of pyridine.

(ii) 3,5-Dioxo-9-ethoxycarbonyl-4-oxa-9-azatetracyclo-
[5.3.2.0^{2,6}.0^{8,10}]dodecane

FVP of the title compound (39 mg, 725°C, 2x10⁻³ mmHg, inlet 160-180°C) gave a yellow oil whose GC (10% PEGA, 55°C) and NMR showed the presence of maleic anhydride (20% yield), benzene (18%) and ethanol (48%) with a large singlet at δ5.43 in the NMR. The identity of this last component was unknown.

(iii) 3,5-Dioxo-9-ethoxycarbonyl-4,11-dioxa-9-azatetracyclo-
[5.3.1.0^{2,6}.0^{8,10}]undecane

FVP of the title compound (23 mg, 725°C, 2x10⁻³ mmHg, inlet 140-150°C) gave a yellow oil. GC (10% PEGA, 55°C) showed the presence of furan and ethanol. The calibrated NMR gave the products as: maleic anhydride (20% yield), furan (17%) and ethanol (10%). No other products could be identified.

G. Preparation and FVP of 3,5-Dioxo-4-oxa-8-thiatricyclo-
[5.3.0.0^{2,6}]decane 8,8-dioxide and derivatives

1. Preparation and FVP of 3,5-Dioxo-4-oxa-8-thiatricyclo-
[5.3.0.0^{2,6}]decane 8,8-dioxide

a. Photochemical reaction of 2,3-dihydrothiophen 1,1-dioxide
with maleic anhydride in acetone

A solution of 2,3-dihydrothiophen 1,1-dioxide (10.0 g, 85 mmol) and maleic anhydride (10.0 g, 102 mmol) in acetone (250 ml) was irradiated at 400W for 40 h. The resulting white solid was filtered off and washed well with ether. By allowing the filtrate to stand and partly evaporate for several days further crops were obtained to give 3,5-Dioxo-4-oxa-8-thiatricyclo-
[5.3.0.0^{2,6}]decane 8,8-dioxide (6.6 g, 36%) as colourless crystals, m.p. 258-260°C. (Found: C, 44.2; H, 3.65.

C₈H₈O₅S requires C, 44.4; H, 3.7%); ν_{\max} 1862, 1790, 1315, 1307, 1175, 1145, 1125, 1068, 996, 921, 903, 857, 718 and 669 cm⁻¹; δ (CD₃SOCD₃) 3.9 (1H, m), 3.6-3.3 (5H, m) and 2.3-2.0 (2H, m); m/e 216 (3.5%, M⁺), 172 (5), 152 (4), 108 (51), 95 (10), 80 (93), and 79 (100).

b. Flash Vacuum Pyrolysis of 3,5-Dioxo-4-oxa-8-thiatricyclo-
[5.3.0.0^{2,6}]decane 8,8-dioxide

Pyrolysis at temperatures below 700°C led mainly to recovery of unchanged starting material.

FVP of the title compound (67 mg, 750°C, 10⁻³ mmHg, inlet 160-180°C) gave a small quantity of starting material at the furnace exit (10 mg) but the bulk of the product was shown by NMR to be 2,3-dihydrothiophen 1,1-dioxide and maleic anhydride.

FVP of the title compound (80 mg, 800°C) gave unreacted starting material (5 mg), insoluble polymer (2 mg) and a large proportion of 2,3-dihydrothiophen 1,1-dioxide and maleic anhydride. Calibration of the NMR with methylene chloride gave the yields of these as 69% and 62% respectively, on the reacted starting material.

2. Preparation and FVP of the diacid and diesters from 3,5-Dioxo-4-oxa-8-thiatricyclo[5.3.0.0^{2,6}]decane 8,8-dioxide

a. Preparation of 2-Thiabicyclo[3.2.0]heptane-6,7-dicarboxylic acid 2,2-dioxide

A mixture of 3,5-dioxo-4-oxa-8-thiatricyclo[5.3.0.0^{2,6}]decane 8,8-dioxide (4.5 g, 21 mmol) and water (40 ml) was heated under reflux for 2 h. The clear solution was cooled to 0°C and the resulting crystals filtered off, washed with ether and vacuum dried to give 2-Thiabicyclo[3.2.0]heptane-6,7-dicarboxylic acid 2,2-dioxide (4.2 g, 86%) as colourless crystals, m.p. 198-200°C. (Found: C, 41.1; H, 4.3. C₈H₁₀O₆S requires C, 41.0; H, 4.3%); ν_{\max} 1722, 1708, 1410, 1293, 1265, 1241, 1228, 1188, 1120, 1090 and 850 cm⁻³; δ (CD₃SOCD₃) 11.25 (2H, br s), 3.7-3.2 (6H, m) and 2.2-2.0 (2H, m); m/e 235 (0.2%, M+1⁺), 234 (0.03), 217 (0.9), 216 (1.8), 170 (6), 152 (14), 108 (49), 80 (90) and 79 (100).

b. Preparation of diesters

(i) 6,7-Dimethoxycarbonyl-2-thiabicyclo[3.2.0]heptane 2,2-dioxide

A mixture of 3,5-dioxo-4-oxa-8-thiatricyclo[5.3.0.0^{2,6}]decane

decane 8,8-dioxide (1.0 g, 4.6 mmol) and AR methanol (15 ml) containing sulphuric acid (0.05 ml) was heated under reflux for 2 h. The product crystallised out on cooling and was filtered off to give 6,7-Dimethoxycarbonyl-2-thiabicyclo[3.2.0]heptane 2,2-dioxide (0.92 g, 76%) as colourless needles, m.p. 154-155°C. (Found: C, 45.7; H, 5.3. $C_{10}H_{14}O_6S$ requires C, 45.8; H, 5.4%); ν_{\max} 1746, 1732, 1324, 1301, 1253, 1232, 1148, 1126, 1098, 1075, 1015, 949, 848, 835 and 728 cm^{-1} ; δ (360MHz) 3.82 (1H, dd, C_1 -H), 3.73 (1H, ddd, C_7 -H), 3.71 (3H, s, C_7 -CO₂CH₃), 3.68 (3H, s, C_6 -CO₂CH₃), 3.60 (1H, m, C_5 -H), 3.27 (1H, dd, C_6 -H), 3.16 (2H, dd, C_3 -H₂), 2.38 (1H, m, C_4 -H) and 2.08 (1H, m, C_4 -H); m/e 262 (0.2%, M⁺), 231 (54), 198 (45), 171 (12), 166 (77), 139 (58), 138 (35) and 79 (100).

(ii) 6,7-Diethoxycarbonyl-2-thiabicyclo[3.2.0]heptane 2,2-dioxide

A mixture of 3,5-dioxo-4-oxa-8-thiatricyclo[5.3.0.0^{2,6}]-decane 8,8-dioxide (0.50 g, 2.3 mmol) and ethanol (10 ml) containing sulphuric acid (0.05 ml) was heated under reflux for 2 h. On cooling the product crystallised out and was filtered off, washed with ether and dried to give 6,7-Diethoxycarbonyl-2-thiabicyclo[3.2.0]heptane 2,2-dioxide (0.55 g, 82%) as colourless needles, m.p. 126-128°C. (Found: C, 49.5; H, 6.05. $C_{12}H_{18}O_6S$ requires C, 49.6; H, 6.2%); ν_{\max} 1738, 1305, 1270, 1250, 1231, 1124, 1096, 1072, 1019, 916, 858, 753, 725 and 690 cm^{-1} ; δ 4.17 (2H, q, J7Hz), 4.15 (2H, q, J7Hz), 3.85-3.5 (3H, m), 3.4-3.1 (3H, m), 2.6-2.0 (2H, m), 1.27 (3H, t, J7Hz) and 1.26 (3H, t, J7Hz); m/e 290 (4%, M⁺), 245 (100), 226 (15), 217 (30), 180 (65), 171 (18), 153 (51) and 79 (95).

(iii) 6,7-Diisopropyloxycarbonyl-2-thiabicyclo[3.2.0]heptane
2,2-dioxide

A mixture of 3,5-dioxo-4-oxa-8-thiatricyclo[5.3.0.0^{2,6}]-decane 8,8-dioxide (0.50 g, 2.3 mmol) and isopropanol (10 ml) containing sulphuric acid (0.05 ml) was heated under reflux for 4 h. The solution was evaporated and the colourless oil subjected to chromatography (alumina, Et₂O). This gave a crystalline solid, which was recrystallised from diisopropyl ether to give 6,7-Diisopropyloxycarbonyl-2-thiabicyclo[3.2.0]-heptane 2,2-dioxide (0.27 g, 37%) as colourless needles, m.p. 86-87°C. (Found: C, 52.9; H, 7.05. C₁₄H₂₂O₆S requires C, 52.8; H, 7.0%); ν_{\max} 1738, 1725, 1300, 1270, 1242, 1213, 1180, 1148, 1112, 1048, 901 and 719 cm⁻¹; δ 5.017 (1H, septet, J6Hz), 5.011 (1H, septet, J6Hz), 3.9-3.5 (3H, m), 3.3-3.1 (3H, m), 2.6-1.9 (2H, m), 1.253 (6H, d, J6Hz) and 1.247 (6H, d, J6Hz); m/e 318 (0.5%, M⁺), 277 (83), 259 (57), 235 (59), 217 (100), 168 (39), 152 (35), and 126 (81).

(iv) 6,7-Dibenzyloxycarbonyl-2-thiabicyclo[3.2.0]heptane
2,2-dioxide

A mixture of 3,5-Dioxo-4-oxa-8-thiatricyclo[5.3.0.0^{2,6}]-decane 8,8-dioxide (1.0 g, 4.6 mmol) and benzyl alcohol (10 ml) containing sulphuric acid (0.05 ml) was heated under reflux for 2.5 h. Ether (50 ml) was added and the resulting precipitate filtered off, washed with ether and dried to give 6,7-Dibenzyloxy-carbonyl-2-thiabicyclo[3.2.0]heptane 2,2-dioxide (0.81 g, 42%) as colourless needles, m.p. 123-125°C. (Found: C, 63.5; H, 5.2. C₂₂H₂₂O₆S requires C, 63.8; H, 5.4%); ν_{\max} 1740, 1500, 1302, 1273, 1217, 1198, 1178, 1138, 1122, 1095, 1060, 1020,

932, 744 and 696 cm^{-1} ; δ (360MHz) 7.36-7.24 (10H, m), 5.04 and 4.94 (2H, AB pattern, J12Hz), 5.00 and 4.90 (2H, AB pattern, J12Hz), 3.855 (1H, dd, $\text{C}_1\text{-H}$), 3.79 (1H, ddd, $\text{C}_7\text{-H}$), 3.65 (1H, m, $\text{C}_5\text{-H}$), 3.30 (1H, ddd, $\text{C}_6\text{-H}$), 3.18-3.12 (2H, m, $\text{C}_3\text{-H}_2$), 2.44-2.33 (1H, m, $\text{C}_4\text{-H}$) and 2.11-2.05 (1H, m, $\text{C}_4\text{-H}$); m/e 414 (1.2%, M^+), 323 (6), 217 (27), 197 (34), 180 (57), 123 (27), 108 (96), 107 (98), 92 (97) and 91 (100).

(v) Attempted preparation of 6,7-Di-t-butyloxycarbonyl-2-thiabicyclo[3.2.0]heptane 2,2-dioxide

Heating the anhydride in t-butanol gave only the diacid via elimination of isobutene.

The next method tried was that of Organic Synthesis²³². A mixture of 2-thiabicyclo[3.2.0]heptane-6,7-dicarboxylic acid 2,2-dioxide (0.50 g, 2.14 mmol), isobutene (1.7 g, 30.4 mmol), sulphuric acid (0.4 ml) and dry ether (5 ml) was shaken in a sealed flask for 36 h. The solid was filtered off to give the starting diacid (0.25 g) and the filtrate evaporated. Chromatography of the residue on alumina (Et_2O) gave colourless crystals which proved to be the pure dimethyl ester: 6,7-dimethoxycarbonyl-2-thiabicyclo[3.2.0]heptane 2,2-dioxide (0.20 g, 70%), m.p. 154-155°C.

The method of Tsuji²³³, starting from the dihydrazide was also tried. Sodium (0.23 g, 10 mmol) was dissolved in warm t-butanol (20 ml) by stirring for 3 h and the solution was evaporated. The residue was dissolved in dry tetrahydrofuran (10 ml) and dry cupric chloride (1.34 g, 10 mmol) was then added. After stirring vigorously for 30 min the solution of CuClO_4 was ready for use. 6,7-Dihydrazido-

carbonyl-2-thiabicyclo[3.2.0]heptane 2,2-dioxide (0.26 g, 1 mmol) was added and the solution stirred for 18 h. 10% Hydrochloric acid (5 ml) was carefully added and the tetrahydrofuran was evaporated off. The residue was diluted with water (10 ml) and extracted with methylene chloride (3x25 ml). Drying and evaporation gave a white solid (0.10 g) whose IR and NMR showed it to be 6,7-dimethoxycarbonyl-2-thiabicyclo[3.2.0]heptane 2,2-dioxide (yield 38%).

c. Flash Vacuum Pyrolysis of 2-Thiabicyclo[3.2.0]heptane-6,7-dicarboxylic acid 2,2-dioxide and its diesters

(i) FVP of 2-thiabicyclo[3.2.0]heptane-6,7-dicarboxylic acid 2,2-dioxide

FVP of the title compound (53 mg, 750°C, 5×10^{-3} mmHg, inlet 170-190°C) gave a yellow oil whose NMR showed it to consist of 2,3-dihydrothiophen 1,1-dioxide, maleic anhydride, a small proportion of benzene and other minor components in the δ 7.5-5.5 range. The presence of 2,3-dihydrothiophen 1,1-dioxide was confirmed by TLC (alumina, Et₂O) and benzene by GC (10% PEGA, 55°C). Calibration of the NMR gave the yields as: 2,3-dihydrothiophen 1,1-dioxide (62%), maleic anhydride (77%) and benzene (6%).

FVP of the title compound (57 mg, 850°C, 3×10^{-3} mmHg, inlet 170-200°C) gave less 2,3-dihydrothiophen 1,1-dioxide and maleic anhydride, more benzene and several new products of which crotonaldehyde was the most abundant. The product was identical to authentic crotonaldehyde on GC and NMR and was conclusively identified by GC-MS. Calibration of the NMR

gave the yields as: 2,3-dihydrothiophen 1,1-dioxide (22%), maleic anhydride (18%), benzene (14%) and crotonaldehyde (18%, assuming one molecule produced per molecule diacid). These four products accounted for 75% of the protons in the condensed product.

(ii) FVP of 6,7-Dimethoxycarbonyl-2-thiabicyclo[3.2.0]-heptane 2,2-dioxide

FVP of the title compound (250 mg, 775°C, 10⁻³ mmHg, inlet 120-150°C) gave a white oily solid whose NMR showed a complex pattern with several methyl signals at δ3.8 and a forest of peaks in the δ7.4-5.4 region. The only products which were identified by comparison with authentics on GC (2% NPGS, 150°C) were dimethyl fumarate and *trans,trans*-dimethyl^{*}hexa-2,4-dienedioate ("dimethyl muconate"). The corresponding *cis* isomers were not present. Preparative TLC on alumina (Et₂O) gave colourless crystals (15 mg) which proved to be a 1:1 mixture of dimethyl fumarate (5% yield) and *trans,trans*-dimethyl muconate (5%) [NMR, TLC].

Preparation of authentic dimethyl muconates

2,4-Dioxo-3-oxabicyclo[3.2.0]hept-6-ene was heated under reflux in methanol with a trace of sulphuric acid to give *cis*-dimethyl^{*}cyclobutene-3,4-dicarboxylate in 70% yield after distillation.

FVP of this compound (75 mg, 500°C, 10⁻² mmHg, inlet 25°C) gave pure *cis,trans*-dimethyl^{*}muconate (54 mg, 74%) as colourless crystals, m.p. 74-75°C (lit.²³⁴ 75°C).

FVP of the same compound (72 mg, 900°C, 10⁻² mmHg, inlet

25°C) gave pure trans,trans-dimethylmuconate (49 mg, 68%) as colourless crystals, m.p. 145-150°C (lit.²³⁴ 156-157°C).

(iii) FVP of 6,7-Diethoxycarbonyl-2-thiabicyclo[3.2.0]-heptane 2,2-dioxide

FVP of the title compound (40 mg, 750°C, 2×10^{-3} mmHg, inlet 110-130°C) gave a brown oil whose NMR showed the presence of 2,3-dihydrothiophen 1,1-dioxide (1.9 mg, 12%) and maleic anhydride (0.5 mg, 4%) as well as many other components with peaks in the δ 7.5-5.5 region. The ethyl groups had been almost entirely lost and there was a broad OH signal at δ 7.9. Apart from 2,3-dihydrothiophen 1,1-dioxide there were no other TLC mobile components and no other component could be identified. Pyrolysis at 800°C gave almost complete loss of ethyl groups with the other products unchanged.

(iv) FVP of 6,7-Diisopropylloxycarbonyl-2-thiabicyclo[3.2.0]-heptane 2,2-dioxide

FVP of the title compound (45 mg, 700°C, 2×10^{-3} mmHg, inlet 120-150°C) gave products almost identical to those obtained from the diethyl ester above. There were low yields of 2,3-dihydrothiophen 1,1-dioxide and maleic anhydride, very little isopropyl group left and an identical pattern between δ 7.5 and 5.5. None of these products could be identified.

3. Preparation of some mono-amides and the dihydrazide of 2-thiabicyclo[3.2.0]heptane-6,7-dicarboxylic acid 2,2-dioxide

a. Preparation of Monoamides

(i) 2-Thiabicyclo[3.2.0]heptane-6,7-dicarboxylic acid monoamide 2,2-dioxide

A mixture of 3,5-Dioxo-4-oxa-8-thiatricyclo[5.3.0.0^{2,6}]-decane 8,8-dioxide (5.0 g, 23.1 mmol) and 0.88 ammonia solution (25 ml) was stirred for 12 h. Evaporation gave a white solid (5.49 g). This was purified by precipitation by ether from aqueous methanol to give 2-Thiabicyclo[3.2.0]heptane-6,7-dicarboxylic acid monoamide 2,2-dioxide (2.5 g, 46%) as colourless crystals, m.p.198-200°C. (Found: M^+ 233.036310. $C_8H_{11}NO_5S$ requires 233.035789); ν_{max} 3570, 3420, 3160, 1680, 1558, 1292, 1263, 1138, 1126, 1098, 910 and 767 cm^{-1} ; δ 8.85 (0.3H, br s), 6.85 (0.7H, br s), 5.90 (2H, br s), 3.5-3.0 (6H, m) and 2.1-1.9 (2H, m). m/e 233 (0.2%, M^+), 215 (30, M^+-H_2O), 172 (6), 151 (8), 136 (7), 123 (35) and 108 (100).

(ii) 2-Thiabicyclo[3.2.0]heptane-6,7-dicarboxylic acid monomethylamide 2,2-dioxide

Aqueous methylamine solution (25%, 2.7 ml, 22 mmol) was added to a suspension of 3,5-Dioxo-4-oxa-8-thiatricyclo[5.3.0.0^{2,6}]-decane 8,8-dioxide (1.0 g, 4.6 mmol) in AR methanol (15 ml). After stirring for 24 h the solution was evaporated to give a white solid which was dried to give 2-Thiabicyclo[3.2.0]heptane-6,7-dicarboxylic acid monoamide (0.93 g, 81%) as a mixture of isomers, m.p.95-105°C. (Found: M^+ 247.050769. $C_9H_{13}NO_5S$ requires 247.051438); ν_{max} 1650, 1564, 1295, 1262, 1116, 970, 907, 770 and 721 cm^{-1} ; δ 8.16 (1H, br s), 5.97 (1H, br s), 3.6-2.9 (6H, m), 2.58 and 2.54

(3H, s for each isomer) and 1.2-0.9 (2H, m); m/e 247 (0.3%, M^+), 229 (100, $M^+ - H_2O$), 172 (5), 165 (19), 150 (8), 137 (23) and 108 (100).

(iii) 2-Thiabicyclo[3.2.0]heptane-6,7-dicarboxylic acid monoanilide 2,2-dioxide

This was based on the literature method for the 3-Thia-isomer¹⁸³. Aniline (0.44 g, 4.7 mmol) was added to a suspension of 3,5-Dioxo-4-oxa-8-thiatricyclo[5.3.0.0^{2,6}]decane 8,8-dioxide (1.0 g, 4.6 mmol) in AR methanol (15 ml) and the mixture was stirred for 3 h. Partial evaporation gave a white solid which was filtered off and washed with methanol. Recrystallisation from methanol gave a mixture of the two isomers of 2-Thiabicyclo[3.2.0]heptane-6,7-dicarboxylic acid monoanilide 2,2-dioxide (1.06 g, 74%) as colourless crystals which decomposed with loss of water at 250-300°C to the imine which then melted at 322-324°C. The NMR showed a 3:2 ratio of the 7-anilide to the 6-anilide: δ ($CD_3SOCD_3/CDCl_3$) 9.79 (0.6H, s), 9.56 (0.4H, s), 7.65-7.5 (2H, m), 7.4-7.0 (3H, m), 4.0-3.5 (3H, m), 3.4-3.15 (3H, m) and 2.5-2.0 (2H, m), [acid OH not apparent].

In a repeat preparation the solution was not evaporated down after 3 h but the solid filtered off to give the pure 7-anilide isomer: 2-Thiabicyclo[3.2.0]heptane-6,7-dicarboxylic acid-7-N-phenyl amide 2,2-dioxide (0.78 g, 54%) as colourless crystals, m.p. as above. (Found: M^+ 309.067813. $C_{14}H_{15}NO_5$ requires 309.067087); ν_{max} 3450 (OH), 3330 (NH), 1740, 1674, 1598, 1538, 1499, 1290, 1035, 761, 721 and 708 cm^{-1} ; δ ($CD_3SOCD_3/CDCl_3$) 12.4 (1H, br s, OH), 10.18 (1H, s, NH),

7.6-7.0 (5H, m), 3.8-3.2 (6H, m) and 2.3-1.95 (2H, m);
m/e 309 (2%, M⁺), 291 (100), 119 (22), 108 (16), 93 (21),
80 (34) and 79 (45).

On standing for 2 days the other isomer crystallised out to give colourless needles (0.52 g, 36%) consisting of the 7-anilide isomer (15%) and 85% of the 6-anilide: 2-Thia-bicyclo[3.2.0]heptane-6,7-dicarboxylic acid-6-N-phenylamide 2,2-dioxide. ν_{\max} 3240, 1732, 1679, 1606, 1446, 1298, 1158, 1118, 920, 745 and 690 cm⁻¹.

b. Preparation of 6,7-Dihydrazidocarbonyl-2-thiabicyclo-[3.2.0]heptane 2,2-dioxide

This was again based on the literature method for the 3-thia isomer¹⁸³. A solution of 6,7-dimethoxycarbonyl-2-thiatricyclo[3.2.0]heptane 2,2-dioxide (0.50 g, 1.9 mmol) and hydrazine hydrate (0.21 g, 4.2 mmol) in AR methanol (10 ml) was heated under reflux for 2 h. The resulting precipitate was filtered off, washed with methanol and dried. Recrystallisation from aqueous methanol/ether gave 6,7-Dihydrazido-carbonyl-2-thiabicyclo[3.2.0]heptane 2,2-dioxide (0.26 g, 52%) as colourless flakes, m.p. 194-195°C. (Found: 36.7; H, 5.4; N, 21.25. C₈H₁₄N₄O₄S requires C, 36.6; H, 5.4; N, 21.4%); ν_{\max} 3380, 3345, 3310, 3165 (NH), 1743, 1731, 1680, 1663, 1596, 1297, 1268, 1138, 1093, 1028, 961 and 725 cm⁻¹; δ (CD₃SOCD₃) 8.93 (1H, br s, C₇-NH), 8.78 (1H, br s, C₆-NH), 4.17 (4H, br s, NH₂), 3.7-3.1 (6H, m) and 2.2-1.9 (2H, m); m/e 262 (0.03%, M⁺), 230 (82), 171 (7), 137 (17), 135 (13), 112 (100), 107 (26) and 97 (15).

4. Preparation and FVP of cyclic imides of 2-Thiabicyclo-
[3.2.0]heptane-6,7-dicarboxylic acid 2,2-dioxide

a. Preparation of 8,10-Dioxo-3-thia-9-azatricyclo-
[5.3.0.0^{2,6}]decane 3,3-dioxide and derivatives

(i) 8,10-Dioxo-3-thia-9-azatricyclo[5.3.0.0^{2,6}]decane
3,3-dioxide

The first method used was based on the literature method for the 4-thia isomer¹⁸³. A solution of maleimide (0.82 g), 8.5 mmol), 2,3-dihydrothiophen 1,1-dioxide (3.0 g, 25.4 mmol) and acetophenone (0.4 ml) in acetone (10 ml) was irradiated at 400W for 40 h. The resulting solid was filtered off and washed well with ether. It was taken up in hot methanol (25 ml) and the insoluble maleimide dimer filtered off. Cooling the filtrate gave 8,10-Dioxo-3-thia-9-azatricyclo-
[3.2.0.0^{2,6}]decane 3,3-dioxide (0.31 g, 16%) as colourless crystals, m.p. 255-256°C. (Found: C, 44.85; H, 4.2; N, 6.7. C₈H₉NO₄S requires C, 44.6; H, 4.2; N, 6.5%); ν_{\max} 3160, 3080, 1780, 1690, 1360, 1312, 1250, 1202, 1181, 1160, 1141, 1096, 910, 826 and 720 cm⁻¹; δ (CD₃SOCD₃) 11.25 (1H, s), 3.7-3.1 (6H, m) and 2.3-2.1 (2H, m, C₅-H₂); m/e 215 (33%, M⁺), 123 (24), 108 (48), 80 (48) and 79 (100).

The compound could be obtained more easily and in better yield by subliming the diacid monoamide with loss of water. Thus when the product from treating 3,5-Dioxo-4-oxa-8-thiatricyclo[5.3.0.0^{2,6}]decane 8,8-dioxide (1.0 g, 4.6 mmol) with excess ammonia solution and evaporating, was sublimed at 220-250°C and 10⁻² mmHg it gave 8,10-Dioxo-3-thia-9-

azatricyclo[5.3.0.0^{2,6}]decane 3,3-dioxide (0.60 g, 56%) as colourless crystals, m.p. 255-256°C.

(ii) 8,10-Dioxo-9-methyl-3-thia-9-azatricyclo[5.3.0.0^{2,6}]-decane 3,3-dioxide

2-Thiabicyclo[3.2.0]heptane-6,7-dicarboxylic acid monomethylamide 2,2-dioxide (mixture of isomers, 0.50 g, 2.02 mmol) was heated at 130°C and 5×10^{-3} mmHg for 2 h. The solid melted, gas was evolved and finally the product resolidified. Sublimation at 170°C and 5×10^{-3} mmHg followed by recrystallisation from AR methanol gave 8,10-Dioxo-9-methyl-3-thia-9-azatricyclo[5.3.0.0^{2,6}]decane 3,3-dioxide (0.20 g, 43%) as colourless needles, m.p. 190-192°C. (Found: C, 47.4; H, 4.9; N, 6.1. $C_9H_{11}NO_4S$ requires C, 47.2; H, 4.8; N, 6.1%); ν_{\max} 1780, 1690, 1312, 1301, 1290, 1254, 1134, 1096, 961, 915, 725 and 665 cm^{-1} ; $\delta(CD_3SOCD_3)$ 3.7-3.2 (6H, m), 2.86 (3H, s) and 2.3-2.1 (2H, m); m/e 229 (25%, M^+), 165 (8), 137 (15), 108 (22), 80 (58) and 79 (100).

(iii) 8,10-Dioxo-9-phenyl-3-thia-9-azatricyclo[5.3.0.0^{2,6}]-decane 3,3-dioxide

2-Thiabicyclo[3.2.0]heptane-6,7-dicarboxylic acid monoanilide 2,2-dioxide (mixture of isomers, 0.30 g) was heated at 320°C and 5×10^{-3} mmHg. This led to loss of water and sublimation of the product to give 8,10-Dioxo-9-phenyl-3-thia-9-azatricyclo[5.3.0.0^{2,6}]decane 3,3-dioxide (0.22 g, 81%) as colourless crystals, m.p. 322-325°C. (Found: C, 57.5; H, 4.45; N, 4.75. $C_{14}H_{13}NO_4S$ requires C, 57.7; H, 4.5; N, 4.8%); ν_{\max} 1861, 1788, 1704, 1492, 1310, 1297, 1165, 1138,

1098, 920, 767, 745, 722 and 697 cm^{-1} ; $\delta(\text{CD}_3\text{SOCD}_3)$ 7.6-7.2 (5H, m), 3.8-3.2 (6H, m) and 2.4-2.2 (2H, m); m/e 291 (47%, M^+), 198 (2.6), 173 (2.9), 119 (10), 108 (29), 80 (56) and 79 (100).

(iv) 9-Amino-8,10-dioxo-3-thia-9-azatricyclo[5.3.0.0^{2,6}]-decane 3,3-dioxide

A solution of 8,10-dioxo-3-thia-9-azatricyclo[5.3.0.0^{2,6}]-decane 3,3-dioxide (200 mg, 0.93 mmol) and hydrazine hydrate (47 mg, 0.94 mmol) in methanol (5 ml) was heated under reflux for 12 h. The solid was filtered off and sublimed at 220-250°C and 10^{-2} mmHg to give 9-Amino-8,10-dioxo-3-thia-9-azatricyclo[5.3.0.0^{2,6}]-decane 3,3-dioxide (90 mg, 42%) as colourless crystals, m.p. 225-228°C. (Found: C, 41.8; H, 4.4; N, 12.2. $\text{C}_8\text{H}_{10}\text{N}_2\text{O}_4\text{S}$ requires C, 41.7; H, 4.4; N, 12.2%); ν_{max} 3342, 3280, 1787, 1700, 1610, 1304, 1220, 1131, 1103, 920, 727 and 670 cm^{-1} ; $\delta(\text{CD}_3\text{SOCD}_3)$ 5.01 (2H, s, NH), 3.65-3.2 (6H, m) and 2.3-2.1 (2H, m); m/e 230 (100%, M^+), 171 (6), 137 (12), 135 (11), 112 (98), 107 (22) and 79 (38).

b. Flash Vacuum Pyrolysis of cyclic imides of 2-Thiabicyclo[3.2.0]heptane-6,7-dicarboxylic acid 2,2-dioxide

(i) FVP of 8,10-Dioxo-3-thia-9-azatricyclo[5.3.0.0^{2,6}]-decane 3,3-dioxide

FVP of the title compound (60 mg, 675°C, 5×10^{-3} mmHg, inlet 220-230°C) gave largely the unreacted starting material (52 mg) but also volatile products which proved to be a 1:1 mixture of maleimide and 2,3-dihydrothiophen 1,1-dioxide [NMR, TLC].

FVP of the title compound (48 mg, 750°C, 5×10^{-3} mmHg, inlet 220-230°C) gave only 5 mg starting material and a high yield of the retro-[2+2] products. Calibration of the NMR with methylene chloride gave the yields as: maleimide (82%) and 2,3-dihydrothiophen 1,1-dioxide (75%).

(ii) FVP of 8,10-Dioxo-9-methyl-3-thia-9-azatricyclo-
[5.3.0.0^{2,6}]decane 3,3-dioxide

FVP of the title compound (62 mg, 750°C, 5×10^{-3} mmHg, inlet 180-200°C) gave 2 mg starting material and a 1:1 mixture of N-methylmaleimide and 2,3-dihydrothiophen 1,1-dioxide [NMR, TLC]. Calibration of the NMR with methylene chloride gave the yields as 60% and 64% respectively. Pyrolysis at 700°C gave a similar result but with 10% unreacted starting material.

(iii) FVP of 8,10-Dioxo-9-phenyl-3-thia-9-azatricyclo-
[5.3.0.0^{2,6}]decane 3,3-dioxide

FVP of the title compound (46 mg, 750°C, 3×10^{-3} mmHg, inlet 280-300°C) gave a small quantity (5 mg) of unreacted starting material but the bulk of the product consisted of a 1:1 mixture of N-phenylmaleimide and 2,3-dihydrothiophen 1,1-dioxide [NMR, TLC].

(iv) FVP of 9-Amino-8,10-dioxo-3-thia-9-azatricyclo[5.3.0.0^{2,6}]-
decane 3,3-dioxide

FVP of the title compound (39 mg, 750°C, 5×10^{-3} mmHg, inlet 180-200°C) gave 2,3-dihydrothiophen 1,1-dioxide in the colder part of the trap [NMR, TLC] and 3,6-dihydroxypyridazine near the furnace exit; IR and NMR [δ (CD₃SOCD₃) 11.33 (1H, br s) and 6.98 (2H, s)] in good agreement with literature spectra²³⁵.

5. Reduction of 3,5-Dioxo-4-oxa-8-thiatricyclo[5.3.0.0^{2,6}]-decane 8,8-dioxide

a. Reduction with sodium borohydride

(i) Preparation of 3- and 5-Oxo-4-oxa-8-thiatricyclo[5.3.0.0^{2,6}]-decane 8,8-dioxide

A solution of 3,5-Dioxo-4-oxa-8-thiatricyclo[5.3.0.0^{2,6}]-decane 8,8-dioxide (2.0 g, 9.26 mmol) in dry dimethylformamide (8 ml) was stirred at 0°C while a solution of sodium borohydride (0.40 g, 10.6 mmol) in dry dimethylformamide (5 ml) was added over 5 min. After stirring for two hours at room temperature the solution was cooled in ice and 6M hydrochloric acid (4 ml) was carefully added. The mixture was extracted with methylene chloride (3x20 ml) which was then washed with water (6x50 ml), dried and evaporated to give a white solid. Recrystallisation of this from ethyl acetate gave an isomeric mixture of 3-Oxo- and 5-Oxo-4-oxa-8-thiatricyclo[5.3.0.0^{2,6}]-decane 8,8-dioxide (0.35 g, 19%) as colourless crystals, m.p. 155-170°C. (Found: C, 47.5; H, 5.0. C₈H₁₀O₄S requires C, 47.5; H, 5.0%); ν_{\max} 1760, 1305, 1276, 1180, 1140, 1118, 997, 951, 779, 702, 676 and 655 cm⁻¹; δ (CDCl₃/CD₃SOCD₃, 4:1) 4.48 (2H, m), 3.7-3.0 (6H, m) and 2.4-2.1 (2H, m); ¹³C δ (CD₃SOCD₃) 178.24, 176.44, 73.45, 71.94, 57.51, 56.30, 47.00, 46.42, 41.63, 39.72 (2C), 38.22, 36.35, 35.05, 26.25 and 25.74; m/e 202 (29%, M⁺), 184 (1), 153 (1), 119 (4), 107 (5), 93 (18) and 79 (100).

(ii) FVP of 3- and 5-Oxo-4-oxa-8-thiatricyclo[5.3.0.0^{2,6}]-decane 8,8-dioxide

FVP of the title compounds (isomeric mixture, 36 mg, 750°C, 5×10^{-3} mmHg, inlet 140-160°C) gave complete reaction to a 1:1 mixture of 2,3-dihydrothiophen 1,1-dioxide [NMR, TLC] and 2-oxo-2,5-dihydrofuran ("butenolide") [NMR identical to authentic sample prepared by the method of Takano et al.²³⁶].

b. Reduction with lithium aluminium hydride

(i) Preparation of 4-Oxa-8-thiatricyclo[5.3.0.0^{2,6}]decane 8,8-dioxide

3,5-Dioxo-4-oxa-8-thiatricyclo[5.3.0.0^{2,6}]decane 8,8-dioxide (10.0 g, 46 mmol) was added slowly to a suspension of lithium aluminium hydride (2.0 g, 53 mmol) in dry tetrahydrofuran (100 ml) stirred under nitrogen. After heating under reflux for 8 h the excess lithium aluminium hydride was destroyed by successive addition of water (2 ml) in tetrahydrofuran (10 ml), 15% sodium hydroxide solution (2 ml) and finally water (2 ml). The inorganic solids were filtered off and washed with acetone (250 ml). The filtrate was evaporated and the residue distilled in the Kugelrohr at 200-220°C and 0.4 mmHg to give a colourless oil which crystallised on standing. Recrystallisation from ethanol gave 4-Oxa-8-thiatricyclo[5.3.0.0^{2,6}]decane 8,8-dioxide (0.50 g, 6%) as colourless needles, m.p. 129-131°C. (Found: C, 50.9; H, 6.4. $C_8H_{12}O_3S$ requires C, 51.0; H, 6.4%); ν_{max} 1294, 1273, 1124, 1097, 1068, 1025, 917, 908, 889, 840, 768, 701

and 690 cm^{-1} ; δ 4.0 (2H, m), 3.6-3.4 (2H, m), 3.3-3.0 (4H, m), 2.9-2.6 (2H, m) and 2.5-1.9 (2H, m); m/e 188 (22%, M^+), 134 (18), 129 (21), 119 (12), 95 (37), 94 (70), 81 (40) and 79 (100).

(ii) Attempted preparation of 6,7-Di(hydroxymethyl)-2-thiabicyclo[3.2.0]heptane 2,2-dioxide

6,7-Dimethoxycarbonyl-2-thiabicyclo[3.2.0]heptane 2,2-dioxide (10.0 g, 38 mmol) was added in portions to a suspension of lithium aluminium hydride (2.0 g, 53 mmol) in dry tetrahydrofuran (100 ml) stirred under nitrogen. The mixture was heated under reflux for 10 h and then the lithium aluminium hydride was destroyed by addition of water (2 ml) in tetrahydrofuran (10 ml) followed by 15% NaOH (2 ml) and finally water (2 ml). The inorganic solids were filtered off and washed with acetone (250 ml). Evaporation of the filtrate gave a colourless oil (10.5 g). Chromatography on alumina (EtOAc) gave only a colourless oil (1.89 g) which crystallised on cooling and proved to be the recovered starting diester [IR, NMR].

(iii) FVP of 4-Oxa-8-thiatricyclo[5.3.0.0^{2,6}]decane 8,8-dioxide

Pyrolysis at 750°C gave mainly the unchanged starting material. FVP of the title compound (35 mg, 800°C , 3×10^{-3} mmHg, inlet $100\text{-}130^\circ\text{C}$) gave little starting material (2 mg), a small quantity of polymer (1 mg) and a colourless oil. NMR of this showed many peaks in the region δ 7.5-4.5 and 3.5-1.5. None of these could be identified. GC (2% NPGS, 200°C) showed a single component which proved by GC-MS to be

a trace of the starting material. 2,3-Dihydrothiophen 1,1-dioxide and 2,5-dihydrofuran were not present, nor was 3-oxabicyclo[3.2.0]hept-6-ene or its ring expanded isomer 2,7-dihydrooxepine.

6. Preparation and FVP of 2-Thiabicyclo[3.2.0]hept-6-ene 2,2-dioxide and derivatives

a. 2-Thiabicyclo[3.2.0]hept-6-ene 2,2-dioxide

2-Thiabicyclo[3.2.0]heptane-6,7-dicarboxylic acid (5.0 g, 21.4 mmol) was dissolved in dry pyridine (50 ml) and oxygen gas was bubbled through the solution for 15 min. Dry lead tetraacetate (14.2 g, 32 mmol) was then added in one portion and the mixture heated to 70°C. Vigorous gas evolution took place to give finally a clear dark brown solution. After stirring for 10 min at 70-80°C this was poured into 1.5M nitric acid (800 ml). Extraction with methylene chloride followed by drying and evaporation gave a yellow oil. Preparative TLC on alumina (Et₂O/hexane, 4:1) gave 2-Thiabicyclo[3.2.0]-hept-6-ene 2,2-dioxide (0.16 g, 5%) as a colourless oil, n_D^{25} 1.5105. (Found: M^+ 144.024237. C₆H₈O₂S requires 144.024499); ν_{\max} 1415, 1303, 1270, 1225, 1125, 1105, 924, 867, 799, 722 and 688 cm⁻¹; δ (360MHz) 6.33 and 6.22 (2H, AB pattern, J2Hz, H_{6,7}), 3.92 (1H, dd, J4, 2Hz, H₁), 3.74 (1H, dd, J7, 4Hz, H₅), 3.49 (1H, dt, J14, 14, 7Hz, H_{3a}), 2.92 (1H, ddd, J14, 7, 2Hz, H_{3b}), 2.23 (1H, 7 lines, J14, 14, 7, 7Hz, H_{4a}) and 2.06 (1H, dd, J14, 7Hz, H_{4b}); ¹³C δ (90MHz) 143.09

(C₇), 134.05 (C₆), 60.87 (C₁), 46.13 (C₅), 44.52 (C₃) and 21.93 (C₄); m/e 144 (12%, M⁺), 119 (5), 95 (31), 88 (14), 79 (100) and 77 (31).

b(i) Flash Vacuum Pyrolysis of 2-Thiabicyclo[3.2.0]hept-6-ene 2,2-dioxide

Pyrolysis at 350°C gave no reaction. FVP of the title compound (17 mg, 450°C, 5x10⁻³ mmHg, inlet 30-80°C) gave a yellow oil whose NMR showed the main component to be 1,3-cyclohexadiene with a small proportion of benzene. GC (10% PEGA, 55°C) confirmed the presence of these two products. Calibration of the NMR with methylene chloride gave the yields as 30% and 5% respectively.

(ii) Attempted solution pyrolysis

A solution of 2-Thiabicyclo[3.2.0]hept-6-ene 2,2-dioxide in deuteriochloroform showed no change after heating in a sealed NMR tube in boiling toluene for 120 h and in boiling hexachlorobutadiene (b.p. 210-220°C) for 120 h. Addition of silver perchlorate and heating at 210-220°C for a further 36 h gave no change.

A solution of the sulphone in hexachlorobutadiene also remained unchanged after prolonged heating at 210-220°C, even on addition of silver perchlorate or 10% palladium on charcoal.

c. 3-Oxa-6-thiatricyclo[3.3.0.0^{2,4}]octane 6,6-dioxide

A solution of 2-thiabicyclo[3.2.0]hept-6-ene 2,2-dioxide (50 mg, 0.35 mmol) and 30% hydrogen peroxide (1.0 ml, 9 mmol) in formic acid (5 ml) was stirred at 60°C for 50 h.

Evaporation gave a colourless oil (70 mg) which on preparative TLC (alumina, Et₂O) followed by recrystallisation from diisopropyl ether/hexane (1:1) gave 3-Oxa-6-thiatricyclo-[3.3.0.0^{2,4}]octane 6,6-dioxide (16 mg, 30%) as colourless crystals, m.p. 135-136°C. (Found: C, 45.2; H, 4.9. C₆H₈O₃S requires C, 45.0; H, 5.0%); ν_{\max} (CHCl₃) 1320, 1185, 1140, 1130, 1102 and 978 cm⁻¹; δ (360MHz) 4.23 (1H, m), 3.93 (1H, m), 3.44 (1H, m), 3.28 (1H, t of d, J₁₄ and 7Hz), 3.19 (1H, m), 3.09 (1H, m), 2.43 (1H, 7 lines, J₁₄, 14, 7 and 7Hz) and 2.26 (1H, m); m/e (M⁺ not apparent), 119 (7%), 95 (9), 84 (15), 81 (17), 79 (13) and 68 (100, furan).

d. Flash Vacuum Pyrolysis of 3-Oxa-6-thiatricyclo-[3.3.0.0^{2,4}]octane 6,6-dioxide

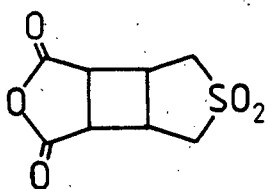
FVP of the title compound (8.5 mg, 550°C, 2x10⁻³ mmHg, inlet 120-140°C) gave a colourless liquid whose GC (10% PEGA, 55°C) showed it to contain furan. The NMR (360MHz) confirmed this and also showed a large proportion of the unreacted starting material. The yield of furan was estimated to be about 10%.

DISCUSSION

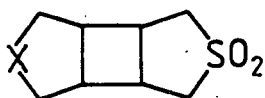
A. Preparation and pyrolysis of some derivatives of
3-Thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide

1. General background

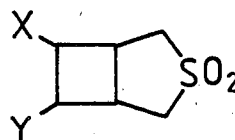
As described in the Introduction, the extrusion of SO_2 from cyclic molecules has found widespread use in the synthesis of a variety of hetero- and carbocyclic systems. In particular, work in these laboratories by McLaughlin¹⁸⁴ showed that cyclobutane-fused sulpholanes derived from the anhydride (249) formed



(249)



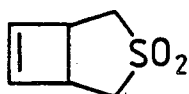
(256)



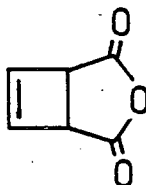
(86)

the basis of useful synthetic methods for obtaining *cis*-1,2-divinylcyclopentanes⁷⁹ from the pyrolysis of (256), and *cis*, *trans*-1,5-hexadiene derivatives from the pyrolysis of (86)⁸⁰.

As part of these studies McLaughlin also investigated the utility of the novel synthon, 3-thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide (250) which was obtained by two different routes,



(250)

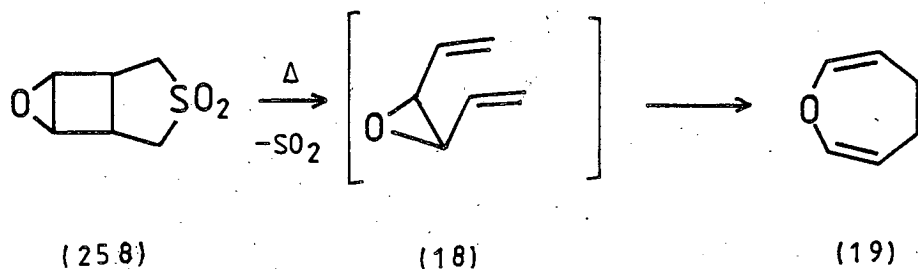


(257)

one involving oxidative bis-decarboxylation of the diacid derived from anhydride (249) either with lead tetraacetate²³⁷ or by electrolysis²³⁸, and the other from cyclobutene-3,4-dicarboxylic anhydride (257) using known methods²³⁹.

Preliminary investigations showed that pyrolysis of (250) under flash vacuum conditions afforded a ca. 1:1 mixture of *cis*-1,3,5-hexatriene and its electrocyclised product, 1,3-cyclohexadiene, in quantitative yield¹⁸⁵. Longer contact times by pyrolysis through a packed silica tube, gave the latter compound as the sole product.

It was realised that functionalization of the double bond of (250) followed by flash vacuum pyrolysis might provide access to a wider range of novel divinyl compounds and their Cope-derived products. One notable reaction already studied by McLaughlin¹⁸⁴ involved epoxidation of (250) to give the tricyclic compound (258). On pyrolysis at 580°C and 10⁻³ mmHg this gave

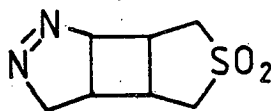


dihydrooxepine (19), apparently via the Cope Rearrangement of *cis*-divinyloxirane (18). This transformation served to illustrate the ability of (250) to act as a masked form of *cis*-1,3,5-hexatriene in which reaction occurs regiospecifically on the central double bond. A very similar approach, using sulpholenes as a masked form of 1,3-dienes which allowed addition to the central double bond, was used by Meyers⁷⁷ in

his synthesis of divinyl ethers and divinyl carbamates (see p.21).

2. Addition of 1,3-dipoles to 3-Thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide

McLaughlin¹⁸⁴ had previously prepared the diazomethane adduct (259) but did not investigate its behaviour on pyrolysis. As part of the present studies an attempt was made to extend this work by examining the corresponding reactions with phenyldiazo-



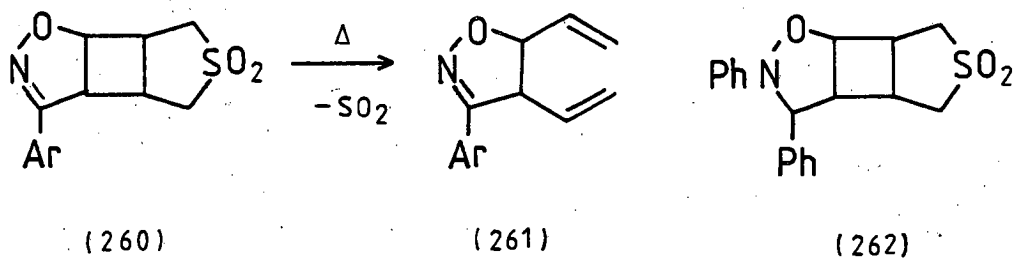
(259)

methane and diphenyldiazomethane. However, the alkene remained unchanged even after prolonged contact with the diazoalkanes in solution at room temperature while, on heating or irradiation, the diazoalkanes underwent side reactions but did not form any of the desired products. Ethyl diazoacetate also failed to react thermally or photochemically. In each case the starting alkene was recovered unchanged. This lack of reactivity is not surprising since it is known²⁴⁰ that introduction of a phenyl group into diazomethane reduces its reactivity and that ethyl diazoacetate is even less reactive²⁴⁰.

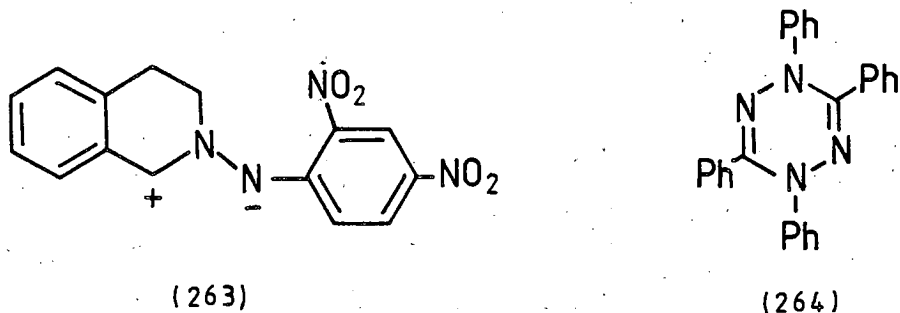
More surprising was the failure of phenyl azide to form an adduct with (250) either thermally or on photolysis. Again the alkene was recovered unchanged even after prolonged reaction. This result contrasts markedly with the ready reaction of the compound with ethyl azidoformate to form an

aziridine which will be dealt with in Section 4.

Previous studies¹⁸⁴ had revealed that (250) reacted with the 1,3-dipole, *p*-anisonitrile oxide, to form the expected



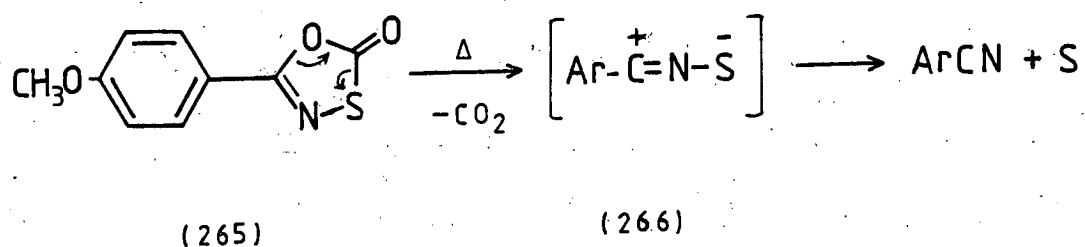
cycloadduct (260) which on pyrolysis yielded the novel *cis*-4,5-divinylisoxazole (261). The adduct (262) was also prepared, by reaction of (250) with diphenyl nitron. In the course of the present study attempts were made to extend the cycloaddition to nitrile imines and nitrile sulphides. The reaction with an azomethine imine (263) was also carried out but in all instances no adducts could be detected in the reaction mixtures.



The reaction of the alkene (250) with diphenylnitrile imine was attempted under phase transfer conditions. The alkene failed to react and was recovered unchanged together with a number of nitrile imine by-products including the dimer (264). The failure of (250) to react with this nitrile imine, generated either by thermal or homogenous base induced

elimination of HCl from the precursor, has already been noted¹⁸⁴. Likewise the azomethine imine (263) did not add to the alkene (250), but instead dimerised to an *s*-tetrazine derivative.

In an additional experiment *p*-anisonitrile sulphide (266) was generated in the presence of (250) by thermolysis of the



oxathiazolone (265)^{194,241} in boiling toluene but even by using a large excess of oxathiazolone and prolonged reaction times none of the desired cycloadduct was formed. It is worth noting that cycloaddition reactions of nitrile sulphides are complicated by a facile competitive degradation to nitriles and sulphur and the lack of reactivity in this instance is not really surprising in view of the foregoing failures.

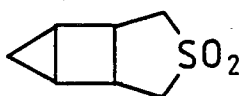
It is possible to explain the pattern of reactivity of (250) with 1,3-dipoles by using molecular orbital theory, and the frontier orbital approach of Houk²⁴² accounts for the results quite well. For a dipole LUMO controlled process, such as might be expected here, the key value is the energy gap between the LUMO of the 1,3-dipole and the HOMO of the dipolarophile. If this gap is small then the transition state will be significantly stabilised and the reaction is likely to take place. Thus for any given dipolarophile, those dipoles with the lowest LUMO energy will react most readily in a LUMO controlled process.

Houk²⁴² gives LUMO energies for many of the 1,3-dipoles used in this study and the values are in good agreement with the observed reactivity. Thus benzonitrile oxide with a LUMO energy of -1.0eV does react with alkene (250) while diphenylnitrile imine (-0.5eV), phenyl azide (-0.2eV) and benzonitrile sulphide ($\sim 0\text{eV}$)²⁴¹ would be expected to be less reactive. The reaction with diazomethane is likely to proceed in a dipole HOMO controlled fashion because of its high LUMO level ($+1.8\text{eV}$) and for this different criteria apply. The exception to this pattern is the azomethine imine (263) which, with a LUMO energy of -1.4eV ²⁴², might be expected to react readily with (250). The reason for the failure of this reaction is unclear since the azomethine imines with low LUMO and high HOMO energy levels are known to react readily with all types of alkenes²⁴⁰.

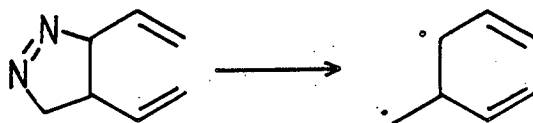
The HOMO energy of the alkene (250) was found by photoelectron spectroscopy to be -10.25eV (see Appendix A). This unusually high ionisation energy for a cyclobutene double bond, which is consistent with its low general reactivity, is thought to be due to a through-space interaction with the sulphone group. This will be discussed more fully in Section D.

3. Flash vacuum pyrolysis of the diazomethane adduct of 3-Thiabicyclo[3.2.0]heptane 3,3-dioxide

Pyrolysis of the adduct (259) might be expected to result either in loss of nitrogen to give the cyclopropyl sulphone (267) or in loss of SO_2 to give the 3,4-divinylpyrazoline (268), or, more likely, loss of both SO_2 and N_2 to give a C_7H_{10} hydrocarbon.



(267)



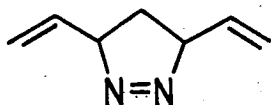
(268)

(269)

In fact pyrolysis at 475°C did result in loss of SO₂ and N₂ to give a mixture of hydrocarbons. GC-MS analysis showed the presence of ten components of which eight had m/e 94 (C₇H₁₀) and the other two, m/e 92 (C₇H₈). The largest component and the only one positively identified was 1,4-cycloheptadiene, obtained in 27% yield presumably via the well documented²⁴³⁻⁵ Cope Rearrangement of *cis*-divinylcyclopropane. The formation of such a large number of products is in marked contrast to the pyrolysis of (267) under similar conditions (see Section 5) which gave almost pure 1,4-cycloheptadiene. The explanation for this is that the diradical (269) formed by loss of SO₂ and N₂ has many other reaction pathways open to it besides ring closure to the divinylcyclopropane. The alternative explanation, that the C₇H₁₀ isomers are secondary pyrolysis products of 1,4-cycloheptadiene, was discounted by pyrolysing it separately. At 475°C it passed through the furnace unchanged, while on pyrolysis at 750°C it gave a mixture of hydrocarbons which was completely different from that obtained from the diazo compound. The largest single product, identified by GC as 1,3-cycloheptadiene, was likewise pyrolysed to give a different set of products again. Thus we can conclude that the C₇H₁₀ isomers are not formed from 1,4-cycloheptadiene but rather that they are produced

concomitantly from the diradical (269).

It is interesting to note here that the extrusion of nitrogen from 3,5-divinylpyrazoline (270), an isomer of (268) has been studied in detail. Schneider found that extrusion



(270)

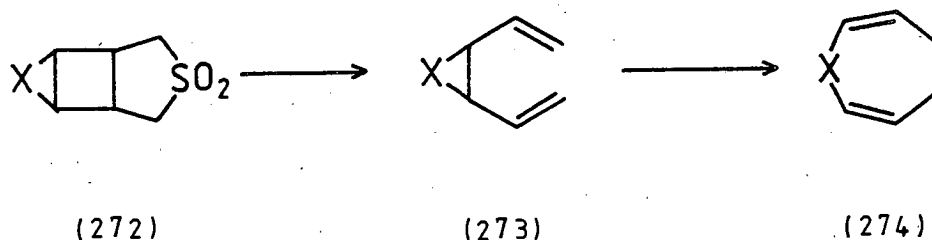


(271)

of N_2 from (270), formed as a mixture of *cis* and *trans* isomers by cycloaddition of 3-diazopropene to 1,3-butadiene, could be achieved either by gas phase pyrolysis or by photolysis.^{244,245} The product in each case was a mixture of *trans*-1,2-divinylcyclopropane and 1,4-cycloheptadiene formed by the Cope Rearrangement of the *cis* isomer. By carrying out the photolysis at low temperature a mixture of the divinylcyclopropane isomers could be obtained²⁴⁴ but the *cis* isomer rearranged on warming to 20°C. In this system there were no isomeric products and the diradical (271) apparently undergoes ring closure to the divinylcyclopropanes very readily.

4. Preparation of the 3-Thiatricyclo[3.3.0.0^{6,8}]octane 3,3-dioxide ring system

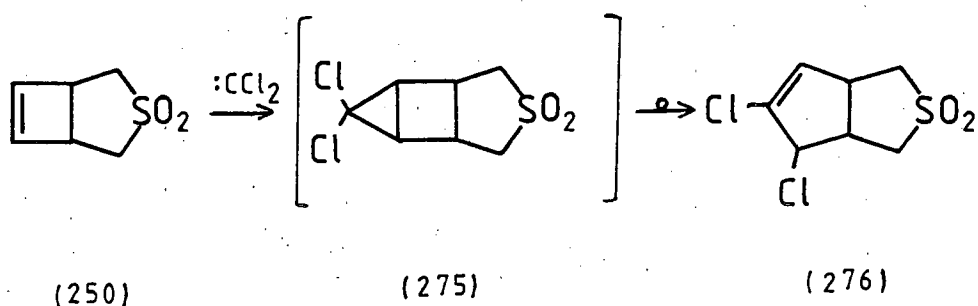
By direct analogy with Meyers' synthesis of divinyl ethers and divinyl carbamates mentioned in Section 1, the 3-thiatricyclo[3.3.0.0^{6,8}]octane system (272), prepared by electrophilic addition to the double bond of (250), might be expected on



pyrolysis to provide a new synthesis of the seven membered ring compounds (274) via a Cope Rearrangement of the intermediate divinyl compound (273). This had already been confirmed in the case of the epoxide (272; X=O) which on pyrolysis¹⁸⁴ gave a good yield of 4,5-dihydro-oxepine (274; X=O) by the well known^{13,246,247} Cope Rearrangement of divinylloxiran (273; X=O). The extension of this to cyclopropanes, aziridines and thiiranes was now studied.

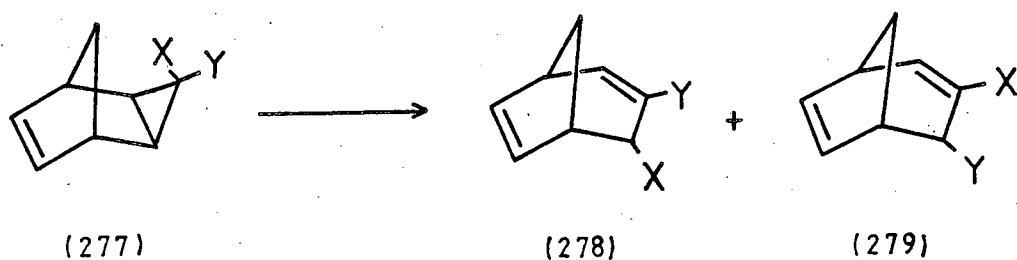
The parent cyclopropyl compound (267) was prepared by photochemical extrusion of nitrogen from the diazomethane adduct (259). Irradiation of (259) in acetonitrile gave a 50% yield of the desired cyclopropyl compound as colourless crystals. The compound showed the expected analytical and spectroscopic data including ¹H NMR signals at δ1.71 and δ0.96-0.76 due to the cyclopropyl CH and CH₂ protons respectively.

As described in Section 2, none of the other diazo compounds which were tried reacted with (250) so this approach could not be applied any further. Instead direct carbene addition to the double bond was used to prepare the dichlorocarbene adduct (275). It was soon discovered that this compound underwent a facile rearrangement at room temperature to give an isomeric product whose spectroscopic data [¹H NMR signals at δ5.89 and δ4.74, ¹³C NMR δ135.46 (quaternary), 131.41



(CH) and 68.25 (CH)] were consistent with the bicyclo[3.3.0] structure (276). Thus reaction with dichlorocarbene under phase transfer conditions ($\text{CHCl}_3/\text{NaOH}$) gave a crude product whose NMR showed equal proportions of (276) and (275) [^1H NMR δ 1.3-1.2] but, on purification by TLC, only (276) could be isolated. Attempts to obtain (275) by reaction of (250) with bromodichloromethyl phenyl mercury in boiling benzene resulted in the formation of only (276).

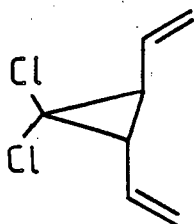
This type of rearrangement is well known. It was found for example that the dihalocarbene adducts of norbornene and norbornadiene (277) rearrange very readily to the ring



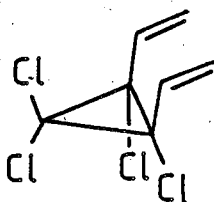
expanded products (278) and (279) for $\text{X}, \text{Y} = \text{Cl}$ ²⁴⁸ and $\text{X}, \text{Y} = \text{Br}$ ²⁴⁹. Jefford later found²⁵⁰ that with (277; $\text{X} = \text{Cl}, \text{Y} = \text{F}$) only the chlorine migrated to give (278) with none of the fluorine migration product (279) and that with (277; $\text{X}, \text{Y} = \text{F}$) this type of rearrangement did not occur. This observation suggested that the difluorocarbene adduct of the alkene (250) would be

stable to rearrangement. However attempts to prepare it using either phenyl trifluoromethyl mercury/sodium iodide²⁰¹ or $\text{CBr}_2\text{F}_2/\text{Ph}_3\text{P}/\text{KF}$ ²⁰⁰ were unsuccessful, the compound (250) being recovered unreacted in each case. This result might have been expected as $:\text{CF}_2$ is known to be less electrophilic than $:\text{CCl}_2$ ²⁵¹.

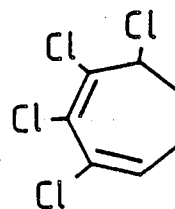
A report has very recently appeared²⁵² describing the preparation, by an entirely different route, of dichlorodivinylcyclopropanes of the type which might have been expected from pyrolysis of (275). The *trans*-divinyl compound (280) was found to be thermally stable, while attempted preparation



(280)



(281)



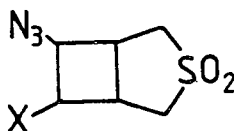
(282)

of the *cis*-divinyl compound (281) gave only the tetrachlorocycloheptadiene (282) formed by Cope Rearrangement of (281) followed by a [1,3] chlorine shift.

Since the Cope Rearrangement of 2,3-divinylaziridines to give 4,5-dihydroazepines has been reported, albeit in a few cases^{253,254}, it seemed reasonable to assume that the corresponding aziridines (283) might provide a new source of



(283)



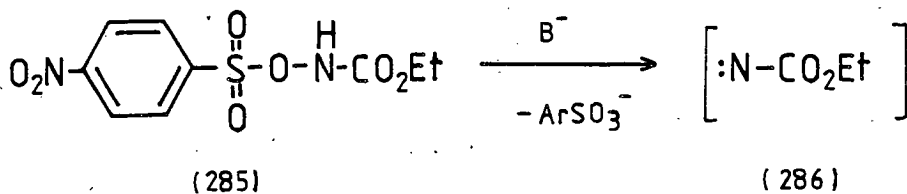
(284)

dihydroazepines.

Several different attempts to prepare the parent aziridine (283; R=H)* all met with no success²⁵⁵. The approaches tried included treatment of the azido-alcohol (284; X=OH) with tri-*n*-butylphosphine, triphenylphosphine, including polymer bound triphenylphosphine²⁵⁶, and lithium aluminium hydride reduction of the iodo-azide (284; X=I)²⁵⁷.

In contrast, the ethoxycarbonyl aziridine (283; R=CO₂Et) was readily prepared using the method of Meyers⁷⁷. Thus irradiation of a homogeneous mixture of the alkene (250) and ethyl azidoformate resulted in vigorous evolution of nitrogen and, after 15 hours, work up gave the desired aziridine in 30% yield. The same product could also be obtained, in somewhat lower yield, by the thermal reaction of (250) with ethyl azidoformate in boiling carbon tetrachloride. The methoxycarbonyl aziridine (283; R=CO₂Me) was similarly prepared by photochemical addition of methyl azidoformate. Phenyl azidoformate was found not to add to (250) under these conditions, preferring to undergo other reactions.

An interesting alternative route to (283; R=CO₂Et) involves the direct electrophilic addition of ethoxycarbonyl nitrene (286), generated by base induced α -elimination from Lwowski's Salt (285)²⁵⁸, to (250).



* These experiments were carried out by Dr. B. J. Hamill, University of Edinburgh.

However a previous study²⁵⁹ has shown that the nitrene might well not react with an alkene having such a high ionisation energy as (250). When the reaction was carried out in the usual way it was found that this was indeed the case and that the alkene (250) is recovered unreacted. On the other hand when the α -elimination was carried out using phase transfer conditions as described by Seno²⁰³ the aziridine was formed in 35% yield.

This appears to be the first case in which the phase transfer reaction has been successful when the homogeneous reaction failed. The explanation for this is uncertain but it may be that the more bulky counter ion (BzNEt_3^+ vs. HNEt_3^+) to $\text{EtO}_2\text{C}\bar{\text{N}}\text{OSO}_2\text{Ar}$ in the phase transfer reaction results in the formation of the nitrene in a more activated state, or it may favour a "nitrenoid" rather than a true nitrene mechanism.

The reactivity of (250) and other sulphone-containing alkenes towards various azide and nitrene species in relation to the ionisation energy of their double bonds will be discussed fully in Section D.

cis-2,3-Divinylthiirane (273; X=S) has been isolated by several groups and shown to rearrange readily on heating to 4,5-dihydrothiepine (274; X=S)²⁶⁰. The corresponding sulphone (273; X=SO₂) was proposed as an intermediate in the preparation of 4,5-dihydrothiepine dioxide from the reaction of 3-diazo-propene with SO₂^{153,261}. Direct entry into these systems via the episulphide of (250) was frustrated, however, since all attempts to prepare it by reaction of the epoxide with potassium thiocyanate, either in solution or supported on silica

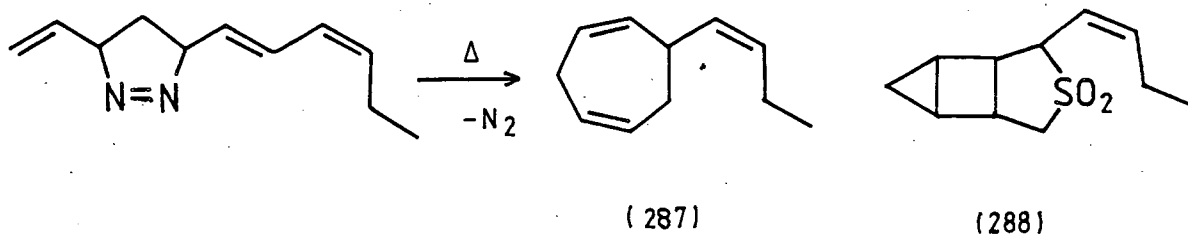
gel²⁶², or with triphenylphosphine sulphide were unsuccessful, as was the attempted reaction of the alkene (250) with $\text{Pb}(\text{CNS})_2/\text{Br}_2/\text{I}_2$.

5. Flash Vacuum Pyrolysis of 3-Thiatricyclo[3.3.0.0^{6,8}]-octane 3,3-dioxide ring systems.

Three examples of this ring system were available for pyrolysis: the cyclopropyl compound (267) and the aziridines (283; $\text{R}=\text{CO}_2\text{Et}$ and CO_2Me). In each case the pyrolysis took the expected course with loss of SO_2 to form the product derived from the Cope Rearrangement of a *cis*-1,2-divinyl intermediate.

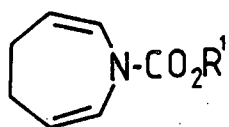
On FVP at 475°C , the cyclopropyl compound (267) gave an 80% yield of 1,4-cycloheptadiene which was identified by GC comparison with an authentic sample¹⁹⁸. Twelve other hydrocarbons were also formed, amounting in total to 5% yield. Many of these compounds were identical to the products obtained from the pyrolysis of the diazomethane adduct (Section 3), and they presumably arise from side reactions of the intermediate divinylcyclopropane.

The Cope Rearrangement of *cis*-1,2-divinylcyclopropanes to 1,4-cycloheptadienes is a well known reaction²⁴³⁻⁵ which in a few cases has been used synthetically to prepare naturally occurring compounds. For example, Schneider²⁶³ used an

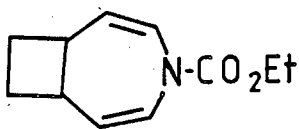


alkylated derivative of the pyrazoline (270) to prepare the pheromone Dicytopterene D¹ (287) which occurs in a marine alga. An alternative route to (287) would of course be the pyrolysis of the sulphone (288) obtained from (267) by alkylation in the α -position and this will be the subject of future work in these laboratories.

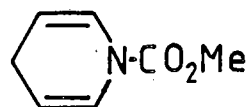
Pyrolysis of the aziridines (283; R=CO₂Et and CO₂Me) at 575°C gave the new dihydroazepines (289) in low yield.



(289)



(290)



(291)

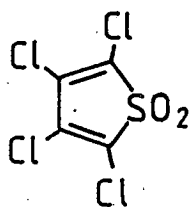
Because of the small scale of operations, these were not obtained analytically pure but their spectroscopic data were fully consistent with the proposed structure. In particular, the characteristic ¹H NMR pattern, including a 10Hz doublet at δ 6.7 due to H₂ and H₇, and an apparent triplet at δ 2.3 due to H₄ and H₅, was in excellent agreement with the published spectra of N-methyl-4,5-dihydroazepine²⁵⁴, the bicyclic dihydroazepine (290)²⁶⁴, the dihydropyridine (291)²⁶⁵, and 4,5-dihydro-oxepine²⁴⁶.

6. Other addition reactions of 3-Thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide

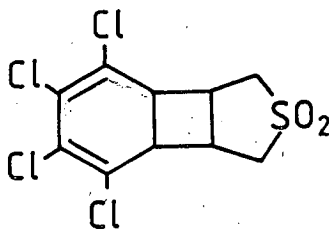
The failure of the alkene (250) to react with many of the reagents in the previous sections was attributed to the fact that the double bond is relatively electron-poor. In certain reactions involving the addition of electron-rich species

however this can be an advantage and an attempt was made to carry out some of these reactions with the compound.

Raasch has shown that tetrachlorothiophen 1,1-dioxide (214) undergoes Diels-Alder addition with a wide variety of alkenes including both electron-rich and electron-poor ones¹⁰³. The course of this reaction was discussed briefly in the Introduction. Reaction of the alkene (250) with tetra-



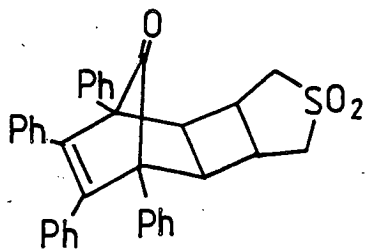
(214)



(292)

chlorothiophen dioxide under standard conditions furnished the expected adduct (292) in 34% yield. An attempt to prepare the unchlorinated adduct by reaction of (250) with thiophen dioxide^{169,207} failed.

The pyrolysis of the adduct (292) gave an unexpected result. Instead of the usual loss of SO₂ to produce a divinyl compound, the reaction proceeded by cleavage across the four membered ring to give 1,2,3,4-tetrachlorobenzene, butadiene and SO₂. This agrees well with the recent finding in these laboratories²⁶⁶ that the tetracyclone adduct (293)



(293)

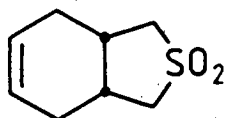
breaks down on pyrolysis with loss of CO, SO₂ and butadiene, to give 1,2,3,4-tetraphenylbenzene. In both cases the driving force is obviously the formation of the stable aromatic product. In these reactions (250) is behaving as an acetylene synthon. There is considerable current interest in finding equivalents to acetylene in the Diels-Alder reaction and compounds which have been used in this way include phenyl vinyl sulphoxide²⁶⁷, fumaroyl chloride²⁶⁸, ethynyl *p*-tolyl sulphone²⁶⁹, and 1-benzenesulphonyl-2-(trimethylsilyl)ethylene²⁷⁰.

Reaction of (250) with benzyne, generated by the action of amyl nitrite on anthranilic acid²⁷¹, was surprisingly unsuccessful, the alkene being recovered unchanged along with several aromatic byproducts.

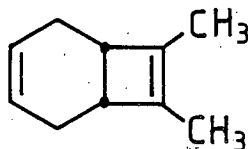
B. Preparation and pyrolysis of 8-Thiabicyclo[4.3.0]non-3-ene 8,8-dioxide and related systems

1. Preparation of unsaturated sulphones

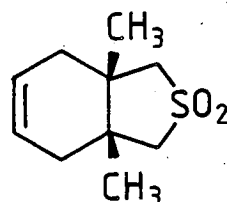
Although the pyrolysis of bicyclic sulphones related to *cis*-8-thiabicyclo[4.3.0]non-3-ene 8,8-dioxide (251) has not been studied, these systems are by no means unknown. Paquette²³



(251)



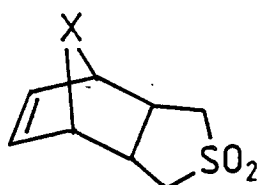
(294)



(295)

used (251) itself to prepare the cyclobutene (294) using the method described on p.10, although no details of the preparation or properties of (251) were given. The same reaction of the 1-methyl derivative has been reported²⁷², while the 1,6-dimethyl compound (295) was prepared in connection with studies of the Ramberg-Bäcklund reaction²⁷³. The *trans*-isomer of (251) has also been prepared, both by chemical and microbial oxidation of the corresponding sulphide²⁷⁴.

The bridged sulphone (296; X=CH₂) has also been prepared by Paquette²³, although this compound and several saturated analogues were first prepared 20 years earlier by Birch as a means of characterising the corresponding sulphides which occur in crude petroleum²¹³. It is interesting to note here that, as



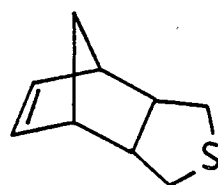
(296)



+



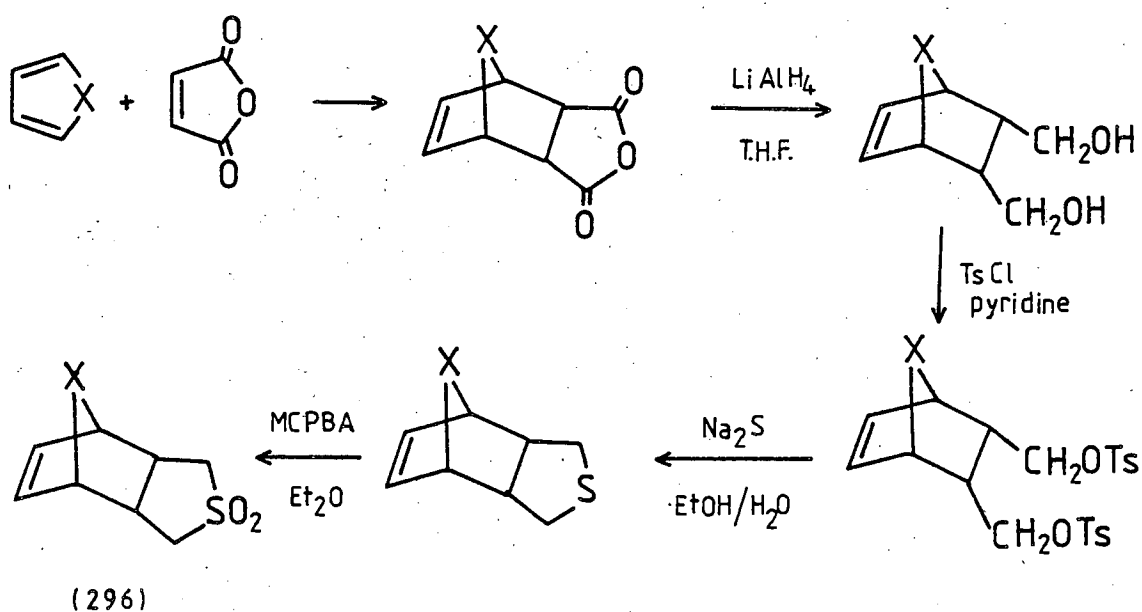
→



(297)

well as preparing the sulphide (297) by the conventional route, shown in Scheme 4 below, Birch also obtained it in 25% yield by the direct Diels-Alder reaction of cyclopentadiene with dihydrothiophen.

The standard procedure for preparing the sulphones (296) involves five steps, beginning with the Diels-Alder reaction of the appropriate 1,3-diene with maleic anhydride. This is then followed by reduction, tosylation, reaction with sodium sulphide and peracid oxidation, as shown in Scheme 4.



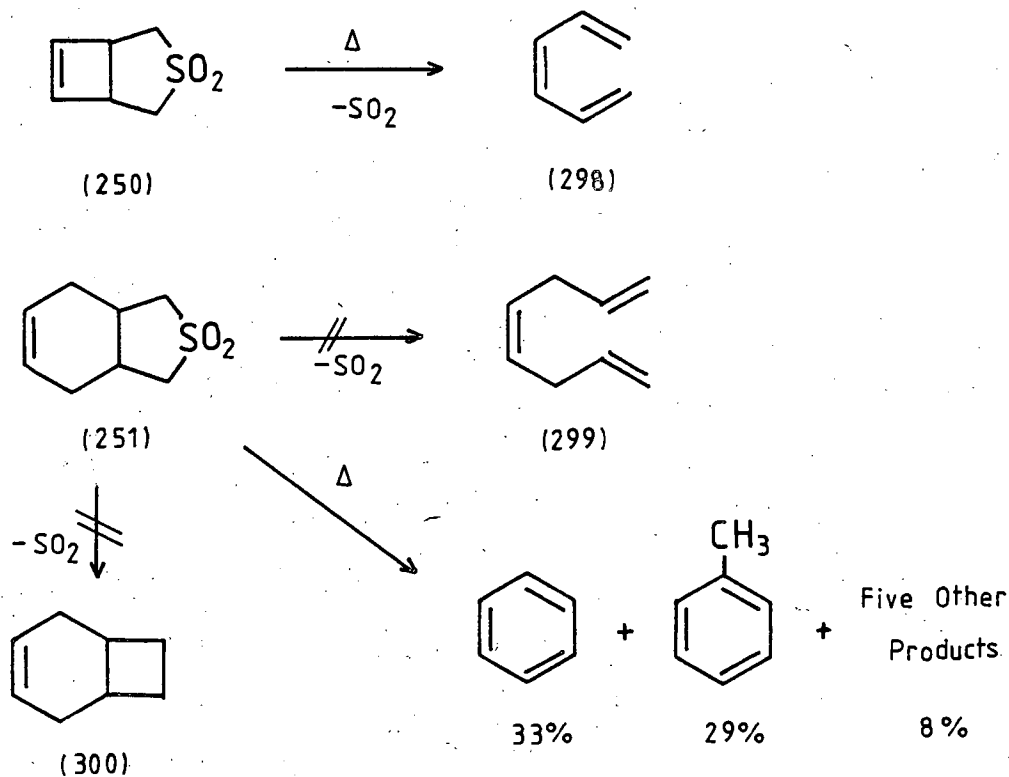
The four sulphones (251) and (296; $X=CH_2$; CH_2CH_2 , and O) were prepared in good yield by the sequence of reactions shown in Scheme 4, starting from the maleic anhydride adducts of 1,3-butadiene, cyclopentadiene, 1,3-cyclohexadiene and furan, respectively. The sulphones are sweet-smelling highly crystalline solids showing all the expected analytical and spectral properties including IR absorption at 1300 and 1150-1100 cm^{-1} due to the sulphone group²⁷⁵. Since no change in stereochemistry

is likely to occur during the reactions of Scheme 4, the sulphones will have the same configuration as the starting anhydrides. Thus (251) is *cis* and (296; X=CH₂ and CH₂CH₂) are *endo*, while the furan/maleic anhydride adduct, which has been shown to be *exo*,²⁷⁶ gives rise to the *exo* configuration for (296; X=O).

Following the successful use of the Diels-Alder reaction to prepare (297), an attempt was made to prepare the sulphones (251) and (296; X=CH₂) directly. However, prolonged reaction of 1,3-butadiene with butadiene sulphone at 100°C, or in the presence of stannic chloride as catalyst²¹⁷, produced only complex hydrocarbon mixtures and unchanged butadiene sulphone. The reaction of cyclopentadiene and butadiene sulphone under similar conditions resulted in polymerisation of the cyclopentadiene.

2. Pyrolysis of unsaturated sulphones

As discussed in the Introduction, the only sulphone similar to (251) whose thermal decomposition has received any attention is the fully aromatic compound (92), which lost SO₂ on flash vacuum pyrolysis to give benzocyclobutene⁸². By analogy with the pyrolysis of (250) which gave *cis*-1,3,5-hexatriene (298)¹⁸⁵, the compound (251), a higher homologue of (250), might be expected to lose SO₂ in a similar way to produce *cis*-1,4,7-octatriene (299) as shown in Scheme 5. Alternatively, reaction along the lines of the aromatic compound (92) would be expected to give rise to bicyclo[4.2.0]-oct-3-ene (300).



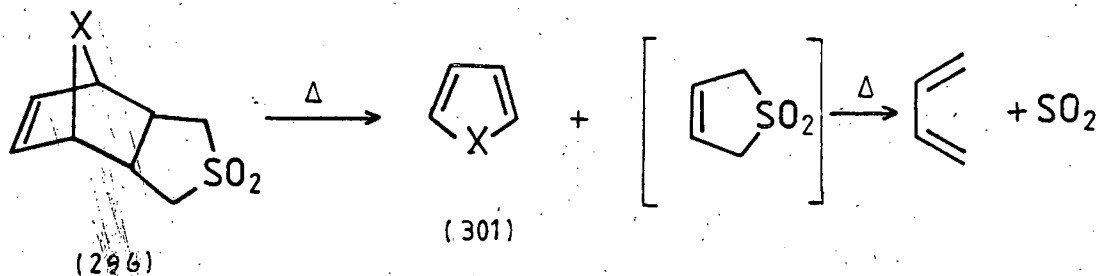
Scheme 5

In fact, the sulphone (251) undergoes neither of these processes. At temperatures below 750°C it is completely unchanged while at 850°C the only products isolated are benzene (33% yield), toluene (29%) and five minor components (8% total), -Scheme 5.

It appears that the high thermal stability of (251) is due to the fact that, in contrast to (92) or (250), the fused five and six-membered rings allow it to adopt a conformation in which the sulpholane ring is under very little strain. When decomposition does occur, the severity of the conditions results in partial breakdown of the carbon skeleton with concomitant dehydrogenation to form the highly stable aromatic products.

The bridged compounds (296) are also less strained than for example (250), but in this case there is a facile pathway

for decomposition: the retro Diels-Alder reaction. With all three compounds this occurred as shown in Scheme 6 to give



Scheme 6

a high yield of the diene (301) together with butadiene and SO₂ from the breakdown of butadiene sulphone. The relative ease of this process apparently depends on the degree of strain imposed on the structure by the bridge. Thus (296; X=CH₂ and O) broke down on pyrolysis at 675°C while (296; X=CH₂CH₂) with less strain due to the longer bridge required a temperature of 750°C.

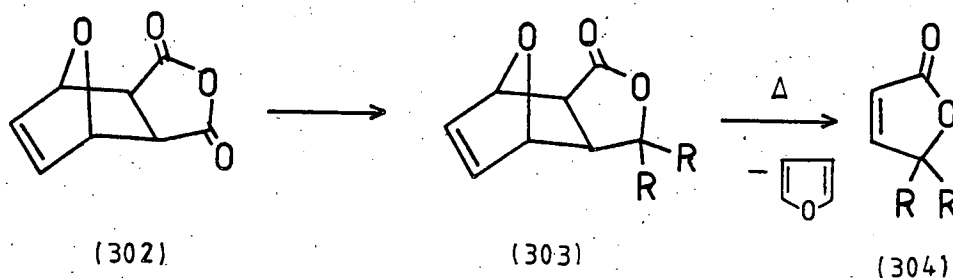
In the pyrolysis of (296; X=CH₂ and CH₂CH₂) there was considerable loss of the products due to the formation of an insoluble white polymer in the trap. A report has appeared in the literature²⁷⁷ that 1,3-cyclohexadiene rapidly forms a 1:1 copolymer with sulphur dioxide at temperatures as low as -50°C. Elemental analysis of the solid from the pyrolysis of (296; X=CH₂CH₂) indicated that it was a 1:1 copolymer to a good approximation. Similarly, the solid from pyrolysis of (296; X=CH₂) gave analysis figures in good agreement with those expected for C₅H₆O₂S, a 1:1 copolymer of cyclopentadiene and SO₂.

The pyrolysis of alkylated derivatives of (296; X=CH₂) forms the basis of a recently reported synthesis of 1,3-dienes -

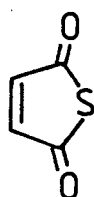
see p.188 .

3. Use of the retro Diels-Alder reaction in synthesis

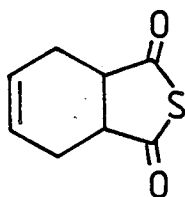
The retro Diels-Alder reaction has been much used in recent years to generate a number of novel compounds²⁷⁸. In particular, the technique of modifying a Diels-Alder adduct and then carrying out the retro reaction to obtain a derivative of one of the original components has proved very useful. For example, the butenolides (304) can be prepared in good yield by reductive alkylation of the furan/maleic anhydride adduct (302) to form (303) which then loses furan on heating^{236,279}.



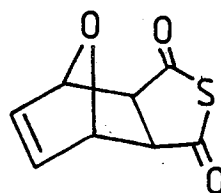
In a related study, thiomaleic anhydride (305) has been prepared in good yield by pyrolysis of either (306)²⁸⁰ or (307)²⁸¹ which are obtained from the maleic anhydride adducts of butadiene and furan respectively, by treatment with sodium



(305)



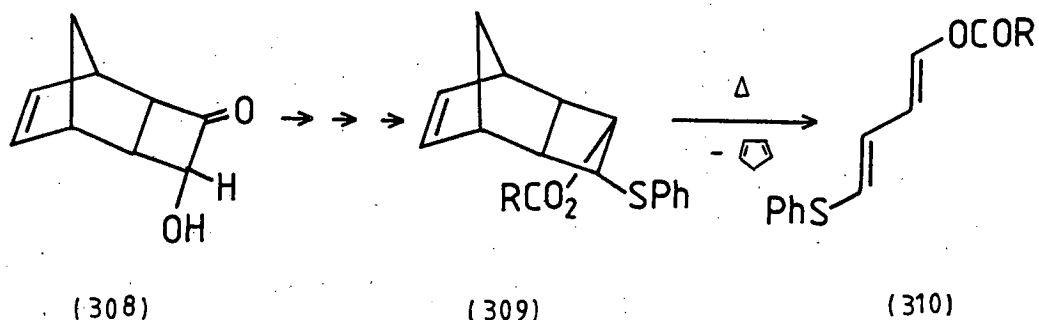
(306)



(307)

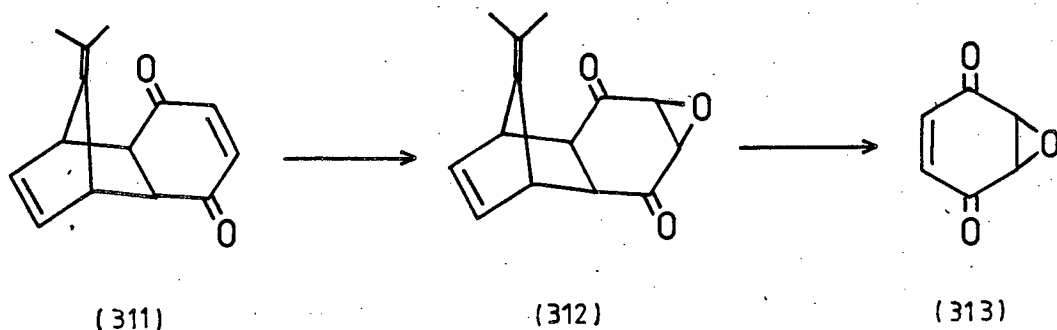
sulphide.

Trost has reported a synthesis of 1,3-dienes which involves conversion of the cyclopentadiene/maleic anhydride adduct, by the acyloin reaction, to the compound (308)²⁸².



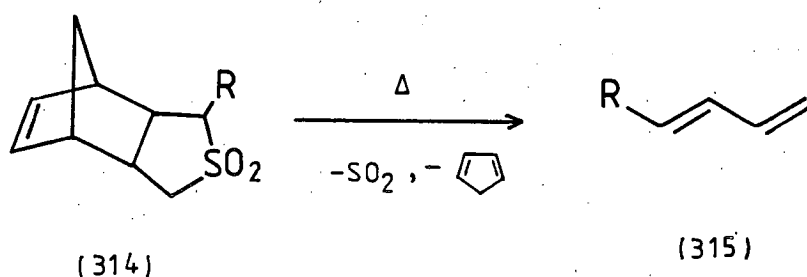
This was then converted in several steps to (309), which on pyrolysis afforded the diene (310) in excellent yield.

A similar approach has been used to prepare benzoquinone monoepoxides (313)²⁸³. Epoxidation of the dimethylfulvene/benzoquinone adduct (311) gave the compound (312) which



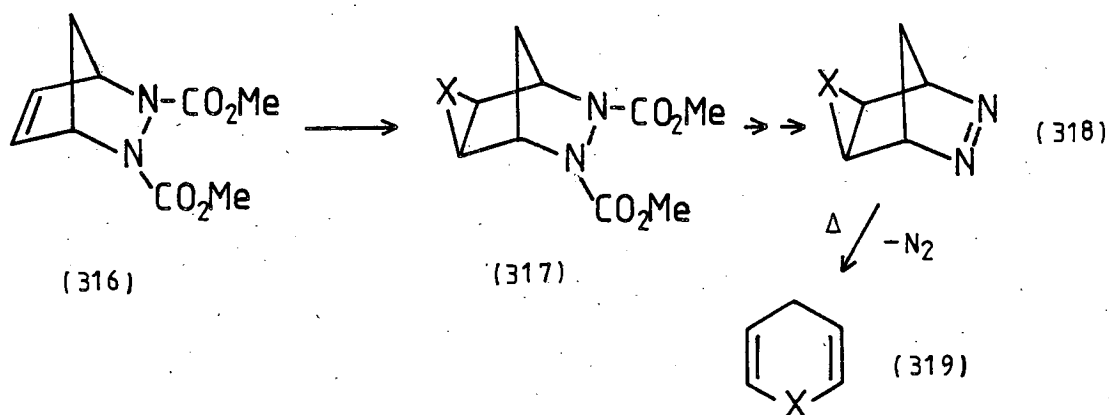
decomposed on heating at 180°C to give the benzoquinone epoxide (313) in quantitative yield.

Very recently this approach has been used for the preparation of 1-alkylated butadienes²⁸⁴. Alkylation of butadiene sulphone in the α -position is unsuccessful but, by alkylating the bicyclic sulphone (296; $X=CH_2$), the product (314) was



obtained which on flash vacuum pyrolysis at 650°C afforded the dienes (315) in good yield via loss of cyclopentadiene and SO₂.

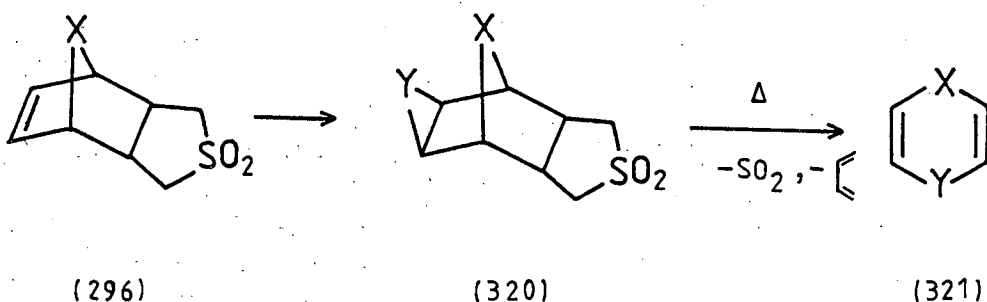
Reactions in which the diene component of the Diels-Alder adduct is modified are less common and all those reported appear to involve elimination of nitrogen in the retro reaction. This is probably because disruption of the diene function removes much of the driving force for the retro reaction and only very high stability in the other product allows the reaction to take place. Thus, the Diels-Alder adduct of cyclopentadiene with dimethylazodicarboxylate (316) can be converted into (317; X=CH₂) via addition of diazomethane



followed by photolytic removal of nitrogen. Hydrolysis, decarboxylation and oxidation then leads to the diazo-compound (318; X=CH₂) which readily loses nitrogen to give 1,4-cyclo-

hexadiene²⁸⁵. The same sequence of reactions involving addition of an azide to (316) to form the aziridine (317; X=PhN, PhSO₂N and EtO₂CN) has been used to provide a synthesis of 1,4-dihydropyridines (319; X=RN)²⁸⁶.

It was realised that the bridged sulphones (296) might provide access to heterocycles of the general type (321) via modification of the double bond followed by pyrolysis of the



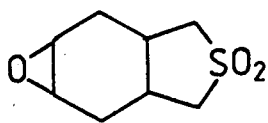
resulting compound (320). For example, epoxidation or addition of nitrenes and carbenes to the double bond would produce (321; Y=O, RN or R₂C).

4. Preparation and pyrolysis of sulphone epoxides

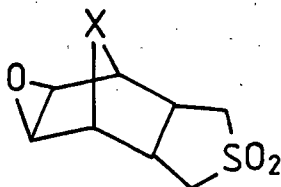
The epoxides of (251) and (296; X=CH₂, CH₂CH₂, and O) were prepared by reaction with peracetic acid for (296; X=CH₂ and O) and with *m*-chloroperoxybenzoic acid in boiling ethyl acetate for (251) and (296; X=CH₂CH₂). The choice of oxidising agent was found to be important as, for example, treatment of (251) and (296; X=CH₂CH₂) with peracetic acid or (296; X=CH₂ and CH₂CH₂) with performic acid resulted in cleavage of the epoxide to give a diol monoester, while (296; X=CH₂ and CH₂CH₂) did not react with *m*-chloroperoxybenzoic acid at room temperature. The implications of this pattern of reactivity

in relation to the ionisation energy of the double bond of the sulphones will be discussed in more detail in Section D.

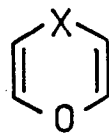
The ^1H NMR spectra of (322) and (323) showed a characteristic sharp singlet at $\delta 3.4-3.2$ due to the epoxide protons,



(322)



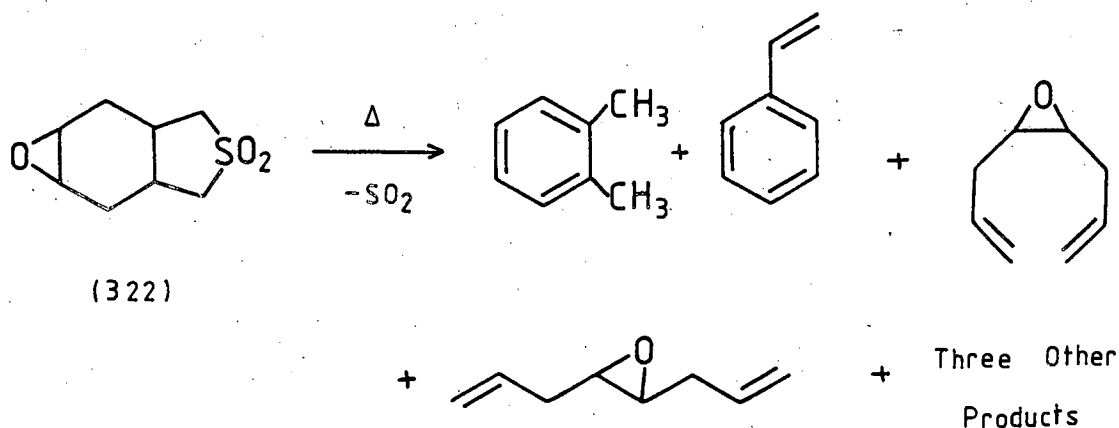
(323)



(324)

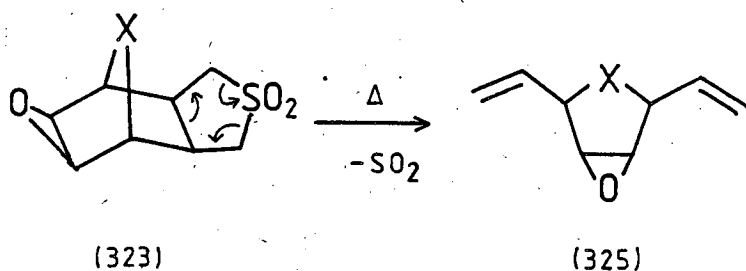
while the mass spectra of (323) all showed prominent peaks at $M^+ - 118$ corresponding to the loss of SO_2 and butadiene to form the heterocycles (324).

Flash vacuum pyrolysis of (322) at 725°C gave a pungent colourless liquid whose GC showed the presence of seven components. Two of these were positively identified as styrene and *o*-xylene while the GC-MS suggested that the two least volatile components might be the *cis* and *trans* isomers of diallyloxirane (1,4,7-octatriene-4,5-epoxide). Further evidence in support of this supposition was provided by the fact that distillation of the product from a larger scale pyrolysis gave a sample which showed ^1H and ^{13}C NMR signals corresponding to the pattern expected for diallyloxirane, although substantial impurities were present. The result of the pyrolysis is summarised in Scheme 7. The formation of styrene is interesting since it implies ring closure after extrusion of SO_2 to form a cyclobutane intermediate.



Scheme 7

Pyrolysis of (323) at 700°C resulted, in all three cases, in loss of SO₂ to produce the novel *cis*-divinylepoxides (325) as shown in Scheme 8. In the case of the methylene and oxygen



Scheme 8

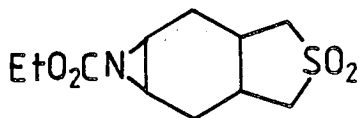
bridged compounds, microdistillation of the pyrolysate gave the products (325; X=CH₂ and O) in good yield and high purity as determined by their ¹³C NMR spectra. Each compound was present as a single isomer and from the stereochemistry of the starting materials the vinyl groups would be expected to be *trans* to the epoxide function in (325; X=CH₂) and *cis* to the epoxide in (325; X=O). In the pyrolysis of (323; X=CH₂CH₂) there were significant side reactions and the ¹³C NMR of the distilled product showed four vinyl signals as well as a

carbonyl group. The greater flexibility in this system possibly provides a greater opportunity for other processes leading to a mixture of products.

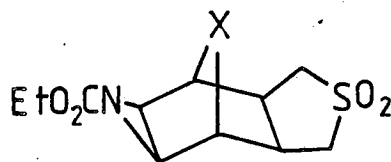
5. Preparation and pyrolysis of sulphone aziridines

The irradiation of a mixture of an alkene and ethyl azidoformate in the absence of solvent provides a particularly convenient one-step route to N-ethoxycarbonyl aziridines and this method has been used successfully in several different systems^{77,287}.

Reaction of (251) and (296; X=CH₂ and CH₂CH₂) under these conditions gave a good yield of the expected aziridines (326) and (327; X=CH₂ and CH₂CH₂). These compounds could also be prepared by reaction of the respective alkenes with ethoxycarbonyl nitrene under phase transfer conditions, using the



(326)



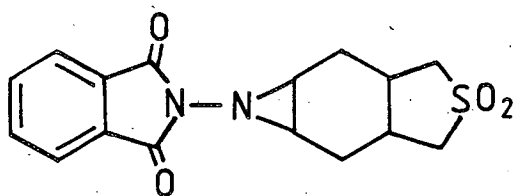
(327)

method of Seno²⁰³ but not under the normal homogeneous conditions²⁵⁸. In addition, (327; X=CH₂ and CH₂CH₂) were also formed albeit in lower yield by thermal reaction of the corresponding alkenes with ethyl azidoformate in boiling carbon tetrachloride. Attempts to prepare (327; X=O) using the same methods were unsuccessful. This pattern of reactivity

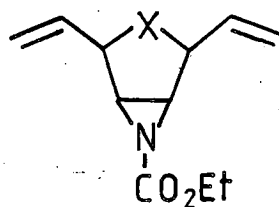
under the different reaction conditions will be discussed in relation to the ionisation energies of the starting alkenes in Section D.

The aziridines are colourless solids with the expected analytical and spectroscopic properties. In the case of (326) the ^1H NMR spectrum revealed the presence of the *syn* and *anti* isomers in roughly equal proportions. These differed by 0.01 ppm in the chemical shift of the methylene protons of the ethyl group and by 0.02 ppm in the position of the aziridine protons. No such effect was observed with (327; $\text{X}=\text{CH}_2$ and CH_2CH_2) and these compounds are assumed to exist as the *exo* aziridine isomers entirely.

An attempt was also made to prepare the phthalimido-nitrene adduct of (251), *viz.* the aziridine (328), by addition of lead tetraacetate to a solution of (251) and N-amino-phthalimide in methylene chloride. However despite the acclaimed electrophilicity of the nitrene²⁸⁸ this reaction was



(328)



(329)

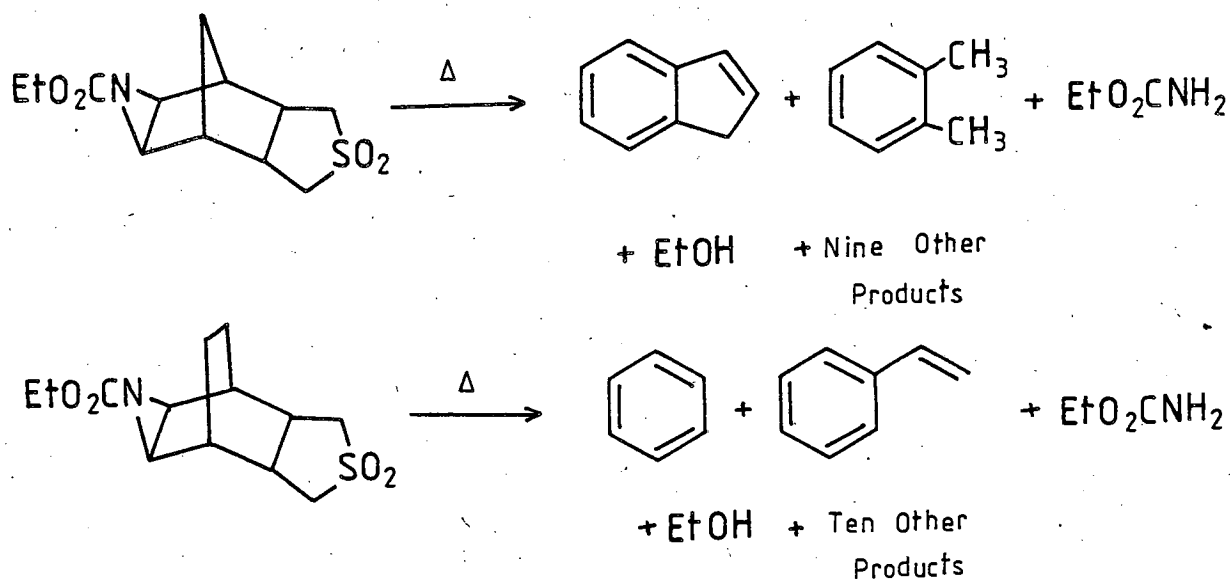
unsuccessful, sulphone being largely recovered unchanged.

Pyrolysis of the aziridines (326) and (327) was expected to proceed in the same way as for the epoxides to give a diallylaziridine and the divinylaziridines (329), respectively.

In fact, pyrolysis of (326) and (327) did not give any useful products. Instead, the compounds underwent extensive decomposition in the inlet of the pyrolysis system, and the volatile products which were isolated were complex mixtures resulting from complete fragmentation of the starting materials.

Ethanol was the only product identified from pyrolysis of (326) at 725°C. A quarter of the sample was left as tar in the inlet tube and NMR analysis of the products showed a complex mixture to be present.

Pyrolysis of (327; X=CH₂ and CH₂CH₂) again produced a large number of products, most of which were not identified. GC-MS did however allow identification of indene, *o*-xylene, ethyl carbamate and ethanol in the pyrolysate from (327; X=CH₂), and benzene, styrene, ethyl carbamate and ethanol in the case of (327; X=CH₂CH₂). The results are summarised



Scheme 9

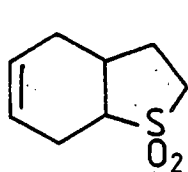
in Scheme 9. The reason for such extensive fragmentation is not clear but it appears that the EtO₂CN group is unstable

under the conditions used, giving rise to ethanol and ethyl carbamate by abstraction of hydrogen atoms by the appropriate radicals. The formation of species such as $\text{EtO}\cdot$ in the inlet of the FVP apparatus may initiate the processes which eventually lead to the aromatic products.

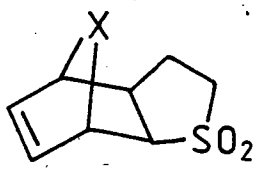
C. Preparation and pyrolysis of 7-Thiabicyclo[4.3.0]non-3-ene 7,7-dioxide and related systems

1. Preparation of unsaturated sulphones

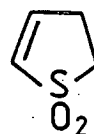
In 1938 Alder reported the formation of (253) and (330; $X=CH_2$)¹⁸⁶ by the cycloaddition reaction of butadiene and cyclopentadiene with 2,3-dihydrothiophen 1,1-dioxide (2-sulpholene) (331) which is readily prepared by base catalysed isomerisation of the commercially available butadiene sulphone²¹⁸.



(253)



(330)



(331)

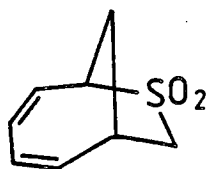
Birch also prepared (253) in 1955²⁸⁹ in connection with studies of the sulphides occurring in crude petroleum, but the chemistry of (253) and (330) has never been investigated and, in particular extrusion of SO_2 from such systems is unknown. It was realised that the behaviour of these compounds and their derivatives, on pyrolysis might provide a useful comparison with the isomeric compounds discussed in the preceding section.

The sulphones (253) and (330; $X=CH_2$, CH_2CH_2 , and $CH_2CH_2CH_2$) were prepared by heating a benzene solution of the appropriate 1,3-diene and 2,3-dihydrothiophen 1,1-dioxide in an autoclave at 150-200°C for an extended period. The yields were not high, ranging from 36% for (330; $X=CH_2$) to only 4% for (330; $X=CH_2CH_2CH_2$) and in each case much of the 2,3-dihydrothiophen dioxide was recovered unreacted. From these findings 2,3-

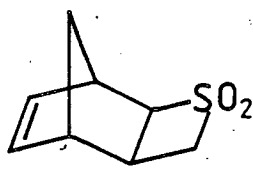
dihydrothiophen dioxide is obviously a poor dienophile; nonetheless it is perhaps surprising that it reacts at all, since the isomeric butadiene sulphone fails to do so under similar conditions. An attempt to increase the yield of (253), by adding stannic chloride as a catalyst²¹⁷, resulted in none of the desired product being formed at all. Instead a mixture of hydrocarbons was produced, including 1,4-cyclohexadiene.

While (253) and (330; $X=CH_2CH_2$) are crystalline, (330; $X=CH_2$) is a waxy solid¹⁸⁶ and (330; $X=CH_2CH_2CH_2$) was obtained as an oil. In the latter case at least, this is due to the presence of the *exo* and *endo* isomers which is obvious from the ^{13}C NMR spectrum which contains 22 lines for the two C_{11} isomers.

The 1H NMR spectra of all these compounds are particularly complex as can be seen from the spectrum of (330; $X=CH_2$) shown in Figure 1. This is because all the protons in the molecule are non-equivalent and there is ample opportunity for coupling between them. The spectra of two very similar



(332)



(333)

molecules (332) and (333) have been published^{290,291} and these too show highly complex patterns with complete assignment of the coupling constants only being possible at 360MHz.

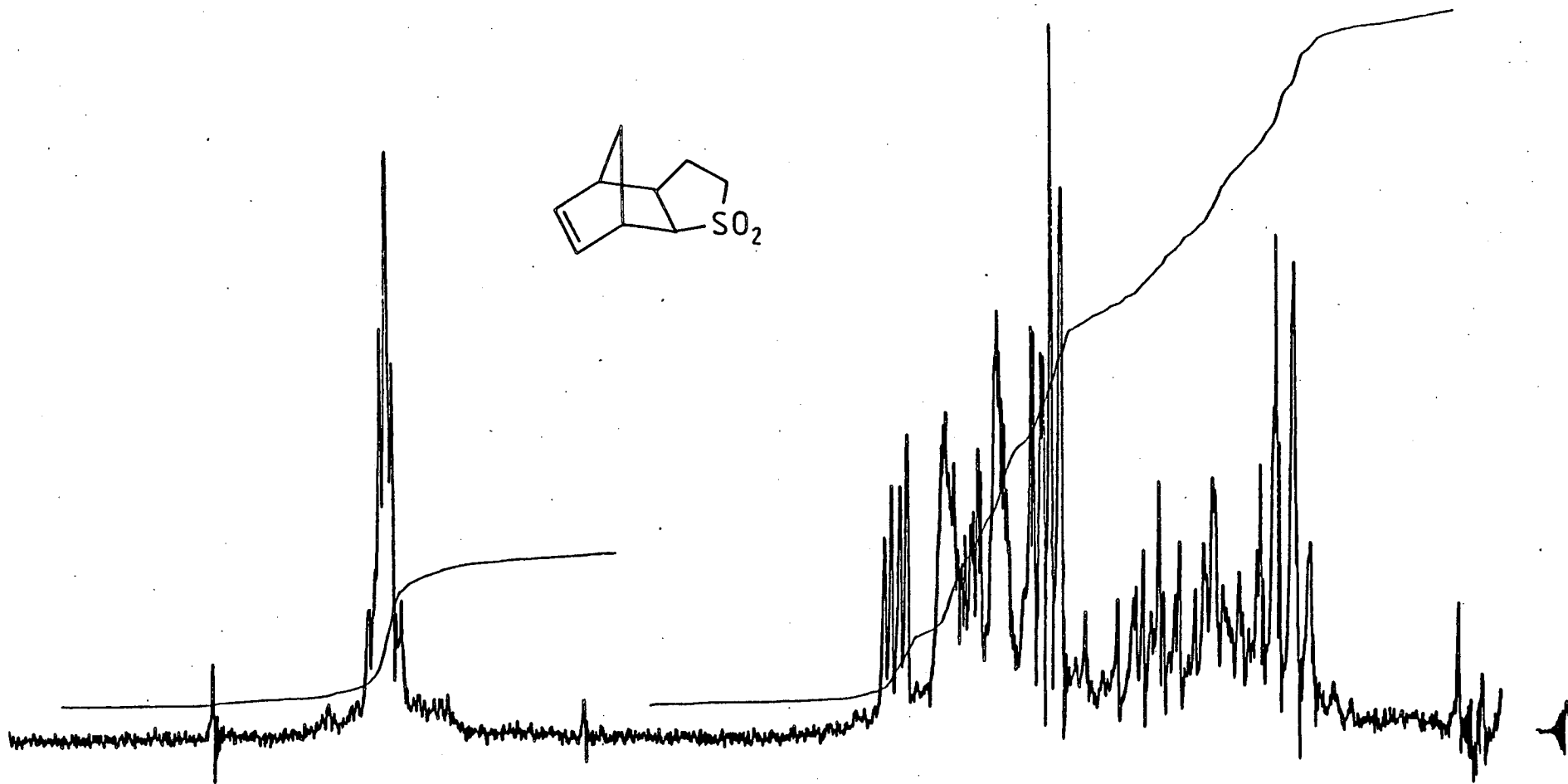
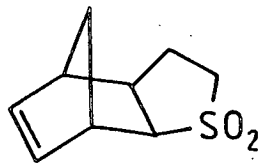
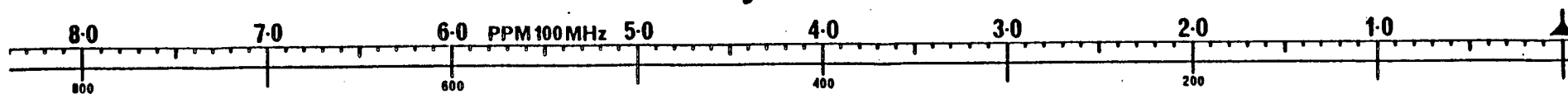
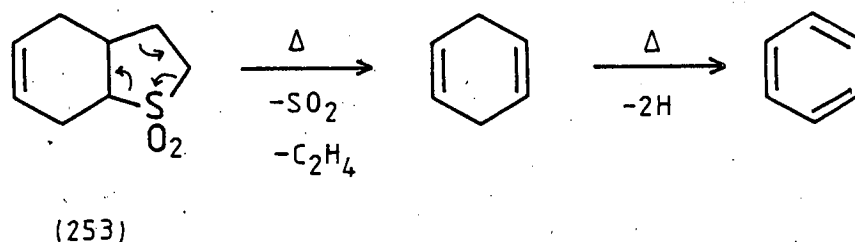


Figure 1

2. Pyrolysis of unsaturated sulphones

Flash vacuum pyrolysis of (253) leads to breakdown as shown in Scheme 10. Loss of SO_2 and ethylene occurs to give



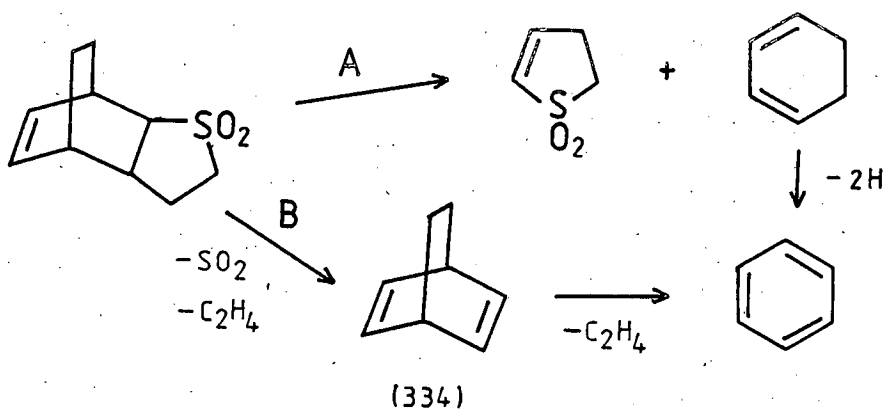
Scheme 10

1,4-cyclohexadiene which is then partly dehydrogenated to benzene under the conditions. Thus, pyrolysis of (253) at 675°C gives mostly the unchanged sulphone with a low yield of hydrocarbons which consists of a 2:5 ratio of 1,4-cyclohexadiene and benzene. At 750°C there is complete reaction to give benzene (82% yield) and 1,4-cyclohexadiene (8%). This fragmentation process is, of course, exactly the same as that observed in the sulpholanes (see Introduction, p.16) but it has never been observed in a bicyclic system before.

An entirely different process occurred in the pyrolysis of (330; $\text{X}=\text{CH}_2$). At temperatures above 650°C this resulted in a retro Diels-Alder reaction to give a high yield of cyclopentadiene and 2,3-dihydrothiophen dioxide. The different pathway followed in this case can be attributed to the release of ring-strain imposed on the structure by the introduction of a methylene bridge.

The lesser degree of ring-strain in the ethylene bridged compound (330; $\text{X}=\text{CH}_2\text{CH}_2$) means that it breaks down by both

types of process as shown in Scheme 11. Pyrolysis at

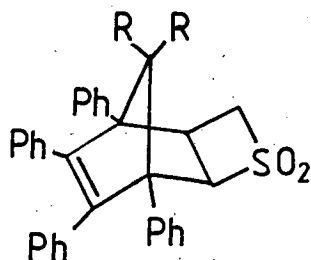


Scheme 11

temperatures between 675°C and 750°C gave a mixture of benzene, 1,3-cyclohexadiene and 2,3-dihydrothiophen 1,1-dioxide, the relative proportion of benzene increasing with temperature. This can be explained in terms of the two reaction pathways shown in Scheme 11. In route A, retro Diels-Alder reaction produces 2,3-dihydrothiophen dioxide and 1,3-cyclohexadiene while in route B loss of SO_2 and ethylene, as with (253), produces the dihydrobarrelene (334), which is known to lose ethylene readily on heating²⁹² to produce benzene. The relative amounts of the three products produced should allow the importance of the two pathways to be calculated at a given temperature but unfortunately there are two complications: some 2,3-dihydrothiophen dioxide may decompose to SO_2 , ethylene and acetylene under the conditions and furthermore the 1,3-cyclohexadiene may be partly dehydrogenated to benzene. These can be allowed for by separate pyrolysis of these two products and, when this is taken into account, the figures show that the "dihydrobarrelene pathway", B, becomes more important with

increasing temperature, accounting for 70% of the total reaction at 750°C compared with only 55% at 675°C.

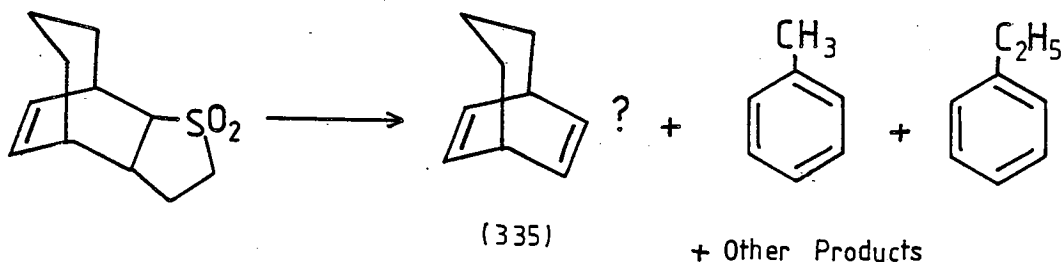
As discussed in the Introduction, the competition between SO₂ extrusion and the retro Diels-Alder reaction has been observed before in a very similar system. Thus, the Diels-



(47)

Alder adduct of tetracyclone with thietane dioxide (47; R₂=O) loses CO and SO₂ to give tetraphenylcycloheptatriene, while (47; R=H) undergoes the retro Diels-Alder reaction on heating to give tetraphenylcyclopentadiene and a polymer derived from thietane dioxide⁴².

With its flexible three carbon bridge, (330; X=CH₂CH₂CH₂) is even less strained and might be expected to decompose only via the loss of ethylene and SO₂. In fact the compound is unchanged at 700°C, and at 800°C it gives an oil which, as well as containing a large proportion of a compound with the correct molecular weight for the expected bicyclo[3.2.2]nona-6,8-diene (335), also includes components resulting from



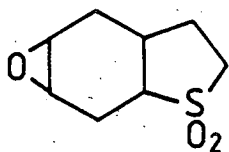
Scheme 12

cleavage of the three-carbon bridge (Scheme 12).

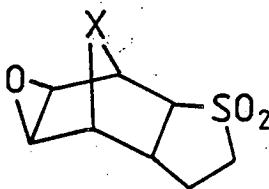
Apparently the lower degree of strain in (330; $X=CH_2CH_2CH_2$) due to the three carbon bridge means that the conditions needed for SO_2 extrusion to occur are so severe that the bridge itself breaks down to give toluene and ethylbenzene, amongst other products.

3. Preparation and pyrolysis of sulphone epoxides

The epoxides (336) and (337; $X=CH_2$ and CH_2CH_2) were prepared by oxidation of the corresponding alkenes. Again,



(336)



(337)

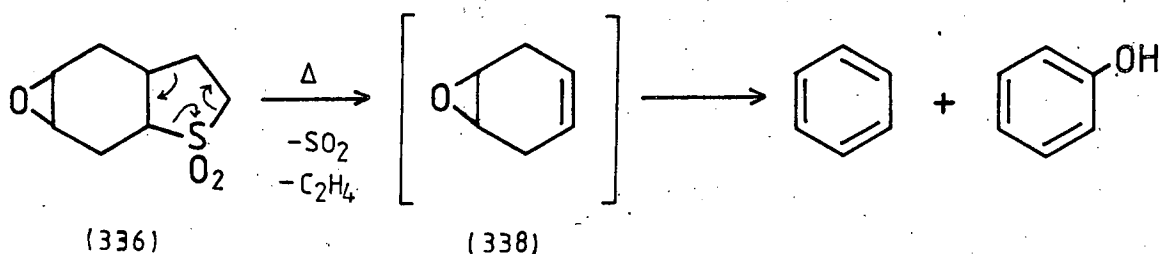
the choice of oxidising agent was found to be important.

The successful reactions involved the use of *m*-chloroperoxybenzoic acid in ether at room temperature, peracetic acid at room temperature and *m*-chloroperoxybenzoic acid in boiling ethyl acetate respectively. For example, treatment of (330; $X=CH_2CH_2$) with *m*-chloroperoxybenzoic acid or peracetic acid at room temperature gave no reaction, while the corresponding reaction with peracetic acid at $50^\circ C$ resulted in cleavage to a diol monoacetate. This is discussed in Section D.

The mass spectra of the epoxides all showed large peaks at M^+-64 corresponding to loss of SO_2 while the base peak in the spectrum of (337) corresponded to loss of SO_2 and ethylene.

Pyrolysis of the epoxides resulted, in each case, in loss

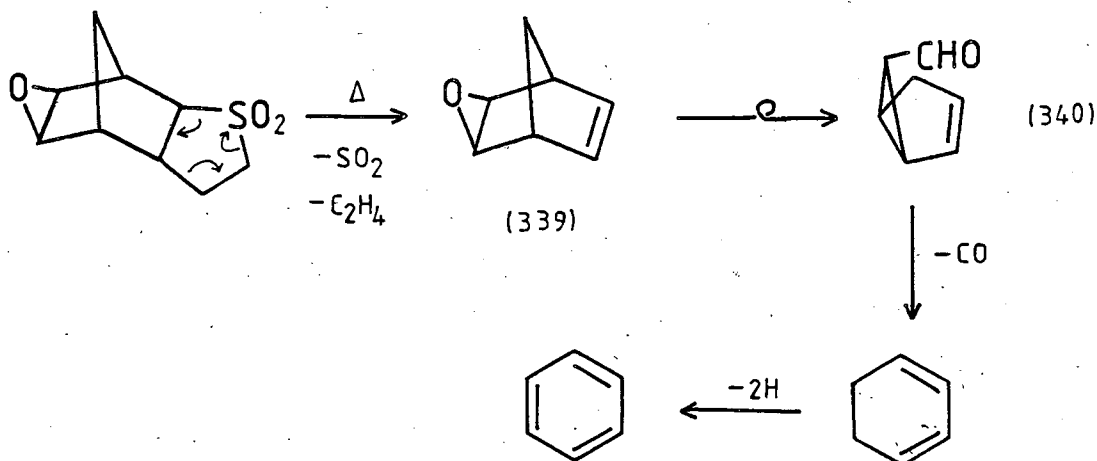
of SO_2 and ethylene to give a diene monoepoxide which then underwent further fragmentation to give the observed products. In the case of (336) the initial product was the monoepoxide of 1,4-cyclohexadiene (338) which then underwent dehydration



Scheme 13

and dehydrogenation to give benzene and phenol (Scheme 13). Thus, pyrolysis of (336) at 750°C gave a mixture of benzene (72% yield) and phenol (5%). In order to confirm the intermediacy of (338), it was prepared by epoxidation of 1,4-cyclohexadiene and pyrolysed at 750°C , when it did indeed give a mixture of benzene and phenol.

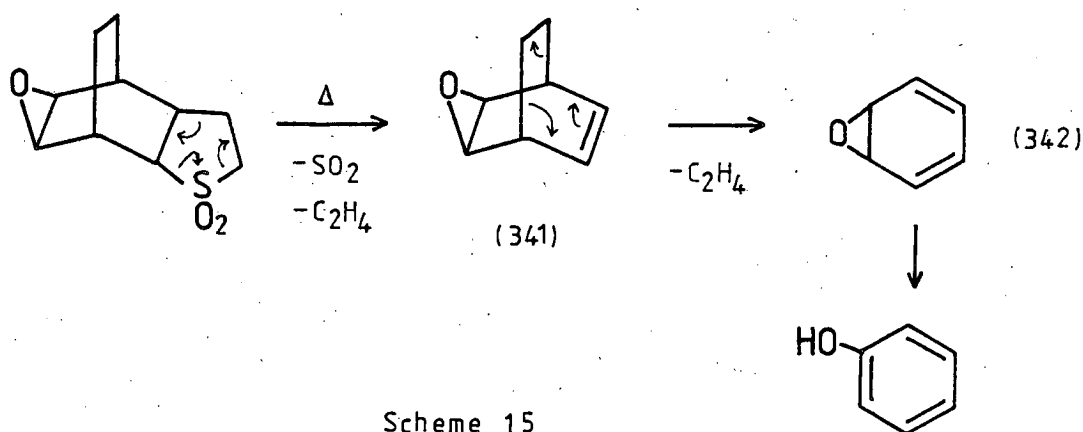
The main product from the pyrolysis of (337; $\text{X}=\text{CH}_2$) at 750°C was benzene and the probable route for its formation is shown in Scheme 14. The initial loss of SO_2 and ethylene



Scheme 14

produces the monoepoxide of norbornadiene (339) which is known^{222,223} to undergo a facile rearrangement to the bicyclic aldehyde (340). Loss of CO from the latter compound produces a cyclohexadiene which is then dehydrogenated to form benzene. Support is given to this proposed pathway by the fact that pyrolysis of both (339) and (340), prepared by epoxidation of norbornadiene, at 750°C gave mainly benzene together with a low yield of 1,3-cyclohexadiene.

Initial loss of SO₂ and ethylene from (337; X=CH₂CH₂) gives the monoepoxide of dihydrobarrelene (341). This then loses ethylene, in a process analogous to that invoked in the



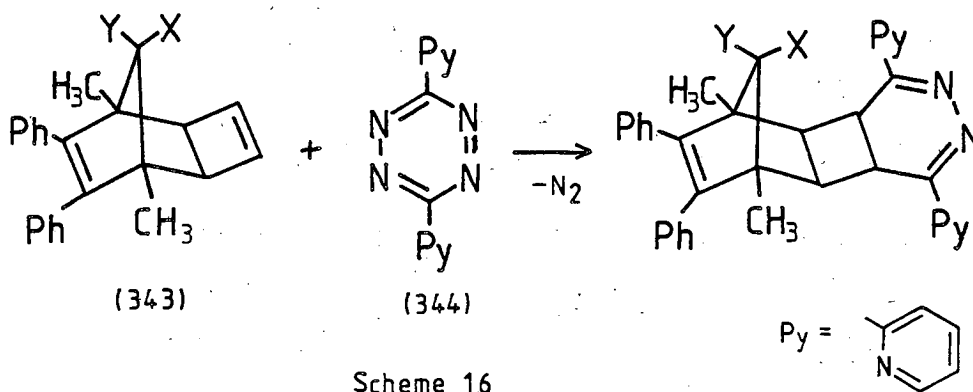
decomposition of the unepoxidised sulphone (Scheme 11), to give benzene epoxide (342) which isomerises to phenol (Scheme 15). Pyrolysis of (337; X=CH₂CH₂) at 750°C gave phenol in 73% yield.

D. Sulphone reactivity in relation to orbital interactions through space

1. Orbital interactions through space

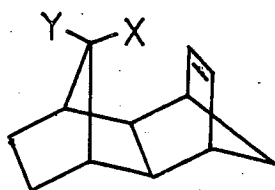
The idea that reactivity can be affected by orbital interactions through space is not a new one²⁹³, but it has become more prominent in recent years, largely due to the work of Paddon-Row and Warrener on the reactivity of systems specially designed to examine this effect.

The first reaction studied by Paddon-Row and Warrener was the Diels-Alder addition of the tetrazine (344) to the cyclobutene double bond of the bridged compounds (343) shown in Scheme 16²⁹⁴. It was found that for (343; X=OCH₃, Y=H)

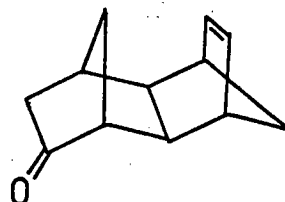


the reaction proceeded 27 times faster than for (343; X=Y=H) while (343; X,Y=O) reacted 22 times slower than the parent compound. These effects were described in terms of a through-space interaction between the groups X and Y and the double bond causing the observed changes in reactivity. The bridged compounds (345) provide an even better opportunity to study

through space effects, the X and Y groups now being one bond further removed from the reaction site, but spatially closer



(345)



(346)

to it. In this system the reaction with the tetrazine (344) was found to be slower for (345; X,Y=O) and (345; X=H, Y=OCH₃) than for the parent compound (345; X=Y=H) while (345; X=OCH₃, Y=H) again gave a faster reaction²⁹⁵.

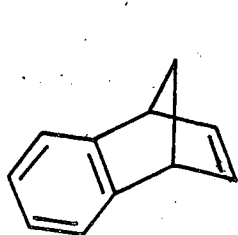
These effects have been rationalised in a perturbational molecular orbital treatment by Paddon-Row^{296,297}. For example, a through-space interaction between the lone-pair electrons of oxygen and the double bond in (343; X=OCH₃, Y=H), results in an increase in the double bond energy, making it more electron rich and thereby causing an increased rate of reaction with an electrophilic species such as the tetrazine (344).

The recently reported photoelectron spectra of (345) show the presence of both through-bond and through-space interactions²⁹⁸. The difference of 0.33eV in the first ionisation energies of (345; X=Y=H) and (345; X,Y=O) was attributed to a combination of through-bond and through-space effects, since the purely through-bond interactions in the isomeric ketone (346) gave a difference of only 0.1eV. The ionisation energy of the *syn*-ether (345; X=OCH₃, Y=H) is 0.36eV lower than that of the *anti*-isomer (345; X=H, Y=OCH₃) and this is due entirely

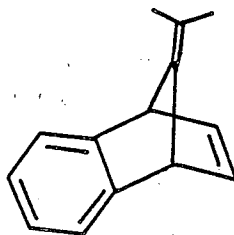
to interactions through space.

Thus, both molecular orbital calculations and the measurement of ionisation energies produce results in good agreement with the observed pattern of reactivity with the tetrazine (344). Similar effects were also observed^{295,297} in the epoxidation of (345) with *m*-chloroperoxybenzoic acid. For example, epoxidation of the *syn* methoxy compound (345; X=OCH₃, Y=H) occurred 40 times faster than its *anti* isomer.

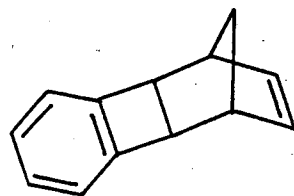
A through-space interaction is also implicated in the Birch reduction of the double bond of norbornadiene and related molecules²⁹⁹. A rate enhancement of the order of 10⁵ is observed in the reduction of norbornadiene and the benzo-derivatives (347) and (348) compared to norbornene.



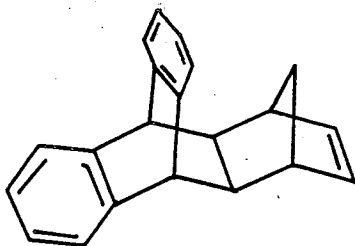
(347)



(348)



(349)

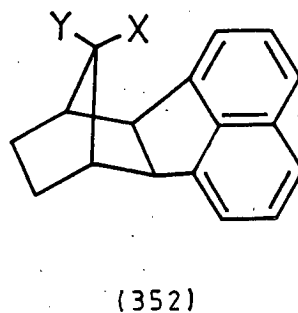
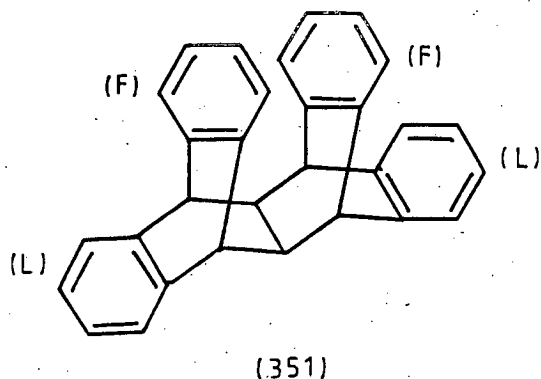


(350)

In contrast, the purely through-bond interactions of (349) and (350) produce rate enhancements of only 10³ and 10², respectively.

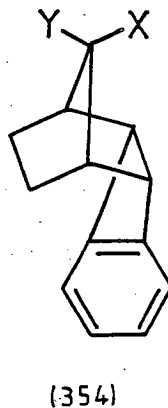
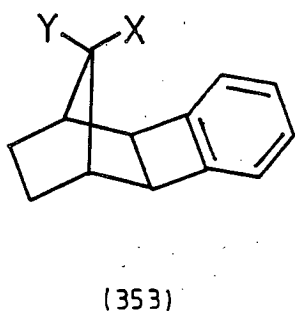
The effect of interactions through space on an electrophilic

aromatic substitution reaction was first observed by Cristol³⁰⁰ who found that the "face" rings (F) were nitrated much more readily than the "lateral" rings (L) in the compound janusene



(351). This was attributed to an interaction through space between the two "face" rings. Paddon-Row found that this conclusion also applied to the nitration of the naphthalene derivatives (352)³⁰¹. While (352; X=Y=H), (352; X,Y=O) and (352; X=H, Y=OCH₃) were all nitrated slightly more slowly than acenaphthene, the reaction with (352; X=OCH₃, Y=H) was 10 times faster.

Electrophilic bromination of the benzene ring in the compounds (353) showed a similar effect³⁰². The through-bond



component could be allowed for by comparing the reactivity of

the *endo* isomers (354). Thus, bromination of (353; X=Y=H) and (354; X=Y=H) occurred at roughly the same rate, but (353; X=OCH₃, Y=H) reacted 170 times faster than (354; X=OCH₃, Y=H). On the other hand, the through-space inductive effect of the carbonyl group in (353; X,Y=O) made it react 100 times slower than (354; X=Y=O). Molecular orbital calculations gave estimated ionisation energies for (353) and (354) in good agreement with the observed reactivity.

To summarise these studies, it appears that whenever a polar group is separated from a π -system by more than two or three σ -bonds but, due to the configuration of the molecule, the two groups lie in close proximity, then the polar group may interact with the π -system by means of an orbital interaction through space and cause some change in its reactivity.

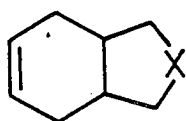
2. Ionisation energies of unsaturated sulphones

It was realised that through-space interactions might well operate in the sulphones discussed in the preceding two sections and in this connection their photoelectron spectra were obtained. In these systems the first ionisation energy, assigned to the double-bond, gives a measure of the extent to which the π -electrons are localised on the double bond and thus their probable ease of reaction with electrophiles. The results³⁰³ are presented in Appendix A (p.264).

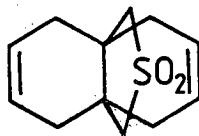
The outstanding feature of these results is that the ionisation energies of the double bonds are all very high. The values of 10.35eV for butadiene sulphone and 10.28eV for 2,3-dihydrothiophen 1,1-dioxide compare with 9.18eV for

cyclopentene³⁰⁴, 9.16eV for 2,5-dihydrofuran³⁰⁵, and 9.86eV for 2,5-dihydrothiophen³⁰⁶. The main effect here is obviously the through-bond inductive influence of the electron withdrawing sulphone group. In compound (250) the ionisation energy of 10.25eV is well above the value of 9.43eV for cyclobutene³⁰⁴ and this may be due to a combination of through-bond and through-space interactions.

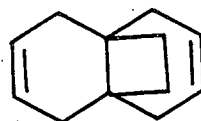
The six-membered ring sulphones (251) and (253) have ionisation energies of 9.69eV and 9.59eV which compare with 9.12eV for cyclohexene³⁰⁴ and the values of 9.10, 9.20, and 9.50eV measured for the bicyclic compounds (355; X=NCH₃), (355; X=S) and (355; X=O)³⁰³. A similar effect has been



(355)



(356)



(357)

observed in the propellane-sulphone (356) which has an ionisation energy of 9.20eV compared to 9.00eV for the hydrocarbon (357)³⁰⁷. In these systems there is a good opportunity for through-space interactions. Molecular models show that (251) can take up a favourable conformation in which the sulphone group is very close to the double bond. The fact that (251) has an ionisation energy 0.1eV higher than (253) tends to support this idea, since its sulphone group is one bond further removed from the double bond but, being better placed for a through-space interaction, it actually has more effect.

The *endo* bridged sulphones (296; X=CH₂ and CH₂CH₂) and

(330; X=CH₂ and CH₂CH₂) provide an even better opportunity for orbital interactions through space with the bridges forcing the sulphone group into close proximity with the double bond. The ionisation energies of 9.60 and 9.55eV for the methylene bridged compounds compare with 8.97eV for norbornene³⁰⁸, while the values of 9.75 and 9.80eV for the ethylene bridged sulphones are much higher than the corresponding hydrocarbon, bicyclo[2.2.2]octene which has a value of 9.05eV³⁰⁸.

The *exo* configuration of (296; X=O) effectively rules out any through-space interaction with the sulphone group and its high ionisation energy of 9.83eV is attributed entirely to the inductive effect of the bridging oxygen.

To summarise, it seems likely that, while the high ionisation energies of the double bonds in butadiene sulphone, 2,3-dihydrothiophen dioxide and (296; X=O) are due to a simple inductive effect, the high values for all the other compounds may be due largely to orbital interactions through space with the sulphone group.

3. Correlation between reactivity and ionisation energy for unsaturated sulphones

In order to investigate the relationship between reactivity and through-space interaction, as measured by the ionisation energy, the behaviour of the sulphones with different reagents is compared. While the yield from these reactions cannot be taken as a measure of their rate, it does provide a rough indication and in particular a very low or zero yield in any

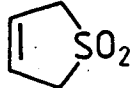
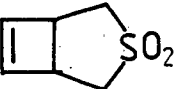
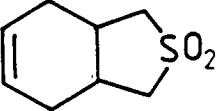
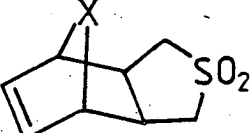
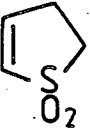
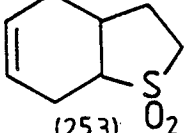
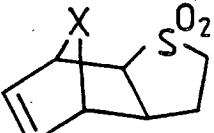
reaction indicates a very slow rate.

The first reaction studied was the conversion of the double bond into the *N*-ethoxycarbonylaziridine. This could be carried out in four different ways: irradiation of the compound in neat ethylazidoformate using the method of Meyers⁷⁷; heating with ethyl azidoformate in boiling carbon tetrachloride; reaction with ethoxycarbonyl nitrene, generated via α -elimination by addition of triethylamine to a methylene chloride solution of ethyl *p*-nitrobenzenesulphoxycarbamate at room temperature²⁵⁸; and finally reaction with ethoxycarbonyl nitrene under phase transfer conditions using the method of Seno²⁰³.

The results are presented in Table 1.

It is immediately obvious from these results that the ease of reaction under the four different sets of conditions used differs widely. For the sulphones which do react, photochemical reaction with the azide and reaction with the nitrene under phase transfer conditions provide reasonable yields of the product, with the thermal azide reaction generally producing a lower yield and the homogeneous nitrene reaction not working at all. This last observation is consistent with previous studies in this laboratory²⁵⁹ which showed that alkenes with a first ionisation energy greater than 9.3-9.4eV do not react with phthalimidonitrene. The implication is that none of the other reactions involve the free nitrene. The azide reactions are likely to proceed by addition of the azide to form a triazoline which then loses nitrogen. The reason for the difference between the phase transfer nitrene reaction and the normal homogeneous conditions has already been discussed.

Table 1 Formation of aziridines from unsaturated sulphones

Compound	I.E. /eV	Reaction with:			
		EtO_2CN_3 hv	EtO_2CN_3 Δ	EtO_2CN : homog.	EtO_2CN : phase transfer
	10.35	41% ⁷⁷	NR	NR ¹⁸⁵	16%
 (250)	10.25	31%	21%	NR	43%
 (251)	9.69	40%	NR	NR	40%
 (296)	X = CH ₂ 9.60	75%	38%	NR	30%
	X = CH ₂ CH ₂ 9.75	22%	8%	NR	20%
	X = O 9.83	NR*	NR*	NR	NR
	10.28	NR	NR	NR	NR
 (253)	9.59	40%	-	-	17%
 (330)	X = CH ₂ 9.55	12%	-	-	54%
	X = CH ₂ CH ₂ 9.80	NR	NR	-	NR

NR = no reaction, - = reaction not carried out,

NR* = unknown product formed - not the aziridine

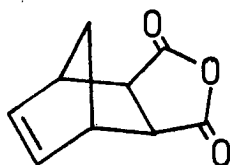
in connection with the reactions of (250) (p.177). The difference may be due to an effect of the more bulky counter-ion in the phase transfer case.

For the three sulphones with the highest ionisation energies there is apparently no correlation between ionisation energy and reactivity. From the results for the other compounds it might have been expected that these three, with ionisation energies above 10eV, would not react at all. In fact butadiene sulphone and (250) give reasonable yields while 2,3-dihydrothiophen dioxide is inert. The reaction of butadiene sulphone and its derivatives with azides and carbenes is discussed in the Introduction (p.20-21).

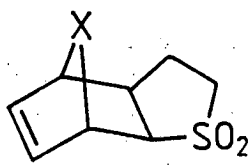
In contrast, the other seven compounds, in which orbital interactions through space are believed to be significant, do show a good correlation between ionisation energy and reactivity. The yields for the compounds with ionisation energy less than 9.7eV: (251) - 40%, (296; X=CH₂) - 75%, (253) - 40%, and (330; X=CH₂) - 54%, are all reasonable while (296; X=CH₂CH₂) with an ionisation energy of 9.75eV gives a lower yield and the two compounds, (330; X=CH₂CH₂) and (296; X=O), with higher ionisation energies fail to react at all.

The pattern of reactivity is also in good agreement with the reactions of similar alkenes studied previously. Lwowski found for example that, with its much lower ionisation energy of 9.12eV, cyclohexene reacted readily with the nitrene under homogeneous conditions²⁵⁸ and with ethyl azidoformate either thermally or photochemically²⁰². Similarly norbornene (I.E. 8.97eV) and norbornadiene (I.E. 8.69eV) react readily with ethoxycarbonyl nitrene¹⁸⁵ and phthalimidonitrene^{185,309}, as well as with several azides including ethyl azidoformate³¹⁰,

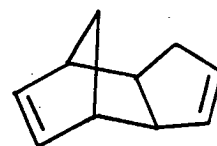
phenyl azide^{311,185}, benzoyl azide²⁴⁰ and benzene sulphonyl azide³¹². On the other hand the more electron deficient bicyclic anhydride (358) does not react with ethoxycarbonyl nitrene¹⁸⁵, but it does react with ethyl azidoformate¹⁸⁵, phenyl azide³¹¹, and benzene sulphonyl azide³¹³. It should



(358)



(330)



(359)

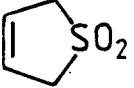
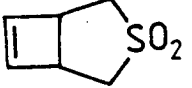
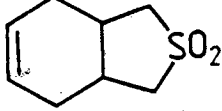
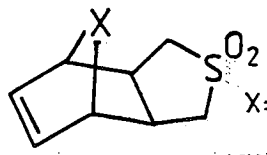
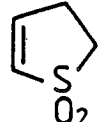
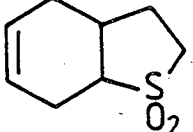
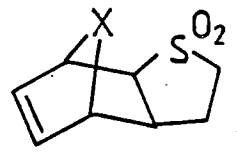
be noted that phenyl azide generally adds much more readily to electron deficient double bonds than ethyl azidoformate. In his original preparation of the sulphone (330; X=CH₂), Alder reported that it readily formed an adduct with phenyl azide at room temperature¹⁸⁶ while dicyclopentadiene (359) also reacts under similar conditions³¹⁴.

The other reaction examined for a correlation with ionisation energies was the epoxidation of the double bond of the sulphones. Again several methods were available for the oxidation including reaction with *m*-chloroperoxybenzoic acid, either at room temperature or in boiling ethyl acetate, and reaction with peracetic acid either at room temperature or at 50-60°C. The results are presented in Table 2.

Here again it is possible to pick out certain patterns although these are less clear cut than in the formation of the aziridines.

The room temperature MCPBA reaction is obviously the least forcing while at the other extreme treatment with peracetic acid at 50-60°C often results in cleavage of the epoxide, a

Table 2. Formation of epoxides from unsaturated sulphones.

Compound	IE /eV	Reaction with:			
		MCPBA R.T.	CH ₃ CO ₃ H R.T.	MCPBA 77°C	CH ₃ CO ₃ H 50-60°C
	10.35	-	70% ⁷⁷	[HCO ₃ H, 50°C: 30% ³¹⁵]	
 (250)	10.25	NR ¹⁸⁴	-	[HCO ₃ H, 50°C: 39% ¹⁸⁴]	
 (251)	9.69	-	NR	46%	CL
 (296)	X=CH ₂ 9.60	NR	-	-	74%
	X=CH ₂ CH ₂ 9.75	NR	-	37%	CL
	X=O 9.83	-	-	-	58%
	10.28	NR	NR	NR	NR
 (253)	9.59	40%	part CL	-	CL
 (330)	X=CH ₂ 9.55	-	40%	-	-
	X=CH ₂ CH ₂ 9.80	NR	NR	56%	CL

NR = no reaction, - = reaction not carried out, CL = epoxide cleaved under conditions.

complication not present for the aziridines.

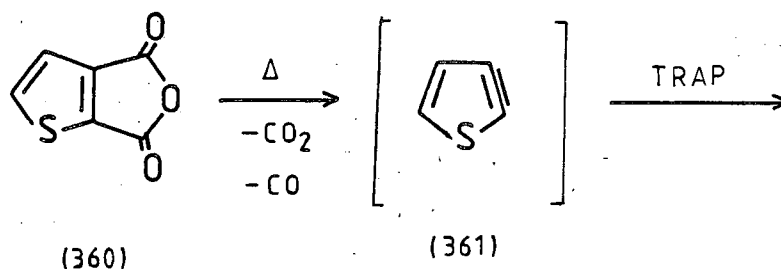
2,3-Dihydrothiophen dioxide is inert to all the reagents shown and attempts to epoxidise it with performic acid at 70° and with t-butyl hydroperoxide/Mo (CO)₆³¹⁶ were also unsuccessful. As with the aziridines the lack of reactivity in this compound bears no relation to the ionisation energy since the other compounds with similar ionisation energies, butadiene sulphone and (250) were readily epoxidised by performic acid.

There is some correlation of reactivity with ionisation energy for the compounds with values below 10eV. For example, the only two compounds to react at room temperature are the two of lowest ionisation energy, (253) and (296; X=CH₂). The others all require more forcing conditions.

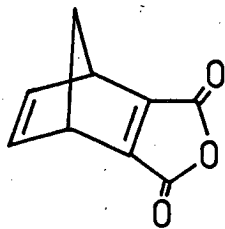
E. Preparation and pyrolysis of some bicyclic anhydrides and derivatives

1. General Background

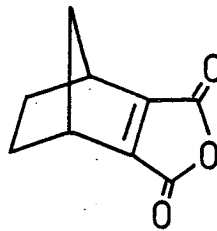
The first study of the thermal fragmentation of acid anhydrides was reported in 1942³¹⁷. Flash vacuum pyrolysis of succinic, maleic and citraconic anhydrides at temperatures of 750-900°C led in each case to loss of CO₂ and CO. The products, formed in high yield, were ethylene, acetylene and propyne, respectively. Similar pyrolysis of fluoromaleic anhydride provided the first synthesis of fluoroacetylene³¹⁸. More recently the pyrolysis of phthalic anhydride³¹⁹ and substituted derivatives³²⁰ has provided a new route for the generation of benzyne and other arynes, again via loss of CO₂ and CO from the anhydride function. Reinecke³²¹ has used this route in the first preparation of thiophyne (361).



At 500°C the anhydride (360) fragmented to give thiophyne which, in the presence of various trapping agents, afforded the expected adducts in good yield. The thermal decomposition of the bridged anhydrides (362) and (363) has also been studied. (362) lost only CO₂ to give benzocyclobutenone at 700°C³²². while (363) lost ethylene and CO₂ to produce the unstable



(362)



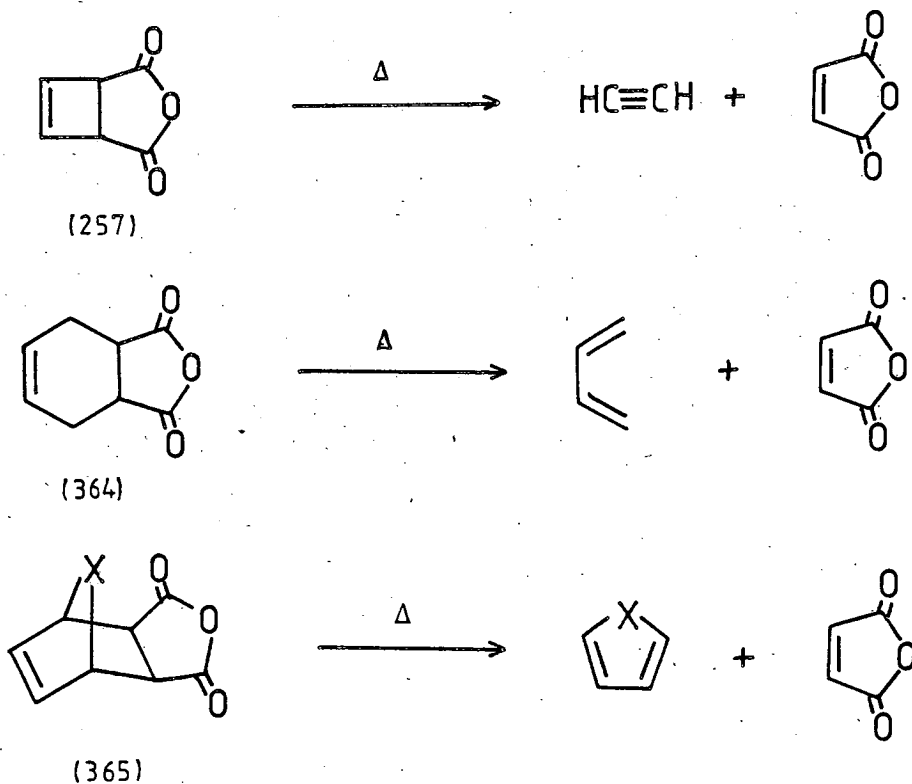
(363)

fulven-6-one³²³.

2. Preparation and pyrolysis of bicyclic anhydrides

As part of the current studies the pyrolyses of several bicyclic anhydrides were investigated, including cyclobutene-3,4-dicarboxylic anhydride (257), tetrahydrophthalic anhydride (364), and the bridged compounds (365; X=CH₂, CH₂CH₂, O), which were all readily prepared by the literature methods.

In all cases pyrolysis at temperatures between 600 and 750°C resulted in the quantitative formation of maleic anhydride, (Scheme 17), by means of a retro-cycloaddition reaction.



Scheme 17

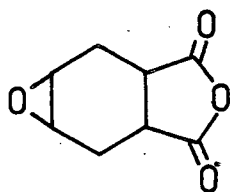
The retro Diels-Alder reaction of (364) and (365) is closely analogous to the decomposition of some of the sulphones discussed in Sections B and C. In these systems it was found that epoxidation of the double bond led to a change in the mode of fragmentation. With this in mind, an attempt was made to prepare the epoxides of anhydrides (257), (364) and (365).

3. Preparation and pyrolysis of anhydride epoxides

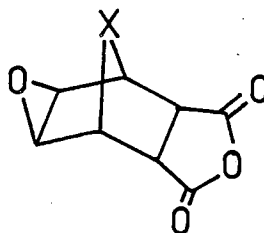
The epoxidation of compounds containing an anhydride function presents practical difficulties since many of the normal epoxidising reagents hydrolyse the anhydride function. This problem may be surmounted in two ways: either by conducting the epoxidation under anhydrous conditions, or by allowing hydrolysis of the anhydride function and then regenerating it.

Cyclobutene anhydride (257) could not be epoxidised by any of the reagents tried. The compound was inert to *m*-chloroperoxybenzoic acid in boiling ethyl acetate and also to *t*-butyl hydroperoxide/Mo (CO)₆³¹⁶ in boiling benzene, while treatment with peracetic or performic acid resulted in cleavage of both the epoxide and the anhydride functions.

The epoxide of tetrahydrophthalic anhydride (364) was prepared in good yield by the literature method²²⁶. Treatment of the anhydride with an anhydrous solution of peracetic acid



(366)

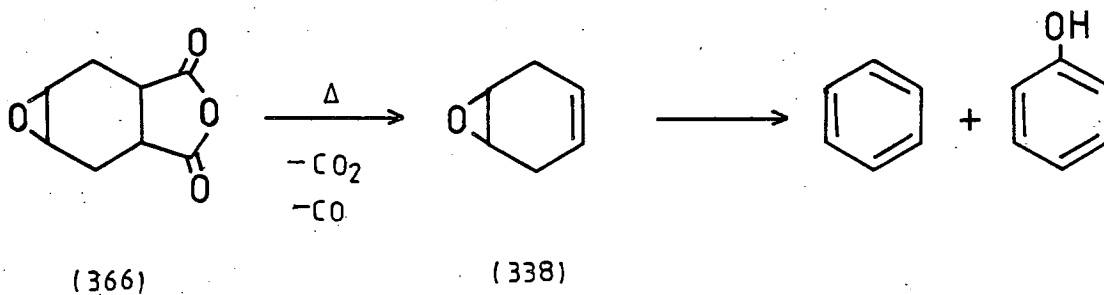


(367)

in acetic acid at 40°C gave the epoxide (366). The epoxides of (365; X=CH₂ and CH₂CH₂) were obtained by treatment with *m*-chloroperoxybenzoic acid in boiling ethyl acetate. The products (367; X=CH₂ and CH₂CH₂) crystallised out on cooling. In the case of the oxygen bridged compound (365; X=O) the literature procedure²²⁹ was followed. This involved treatment with performic acid to produce the epoxy-diacid which could then be dehydrated, either by heating with acetyl chloride or by vacuum sublimation to give the epoxide (367; X=O).

Flash vacuum pyrolysis of the epoxides (366) and (367; X=CH₂ and CH₂CH₂) did not give any maleic anhydride although separate pyrolysis studies showed that the latter compound was quite stable under the conditions used. Instead loss of CO₂ and CO occurred followed by further reaction of the resulting diene monoepoxides to give the same products as before (Section C, p.203-206). The extrusion of CO₂ and CO appears to be more difficult than that of SO₂ and ethylene, requiring a 50-100°C increase in temperature for the corresponding reactions.

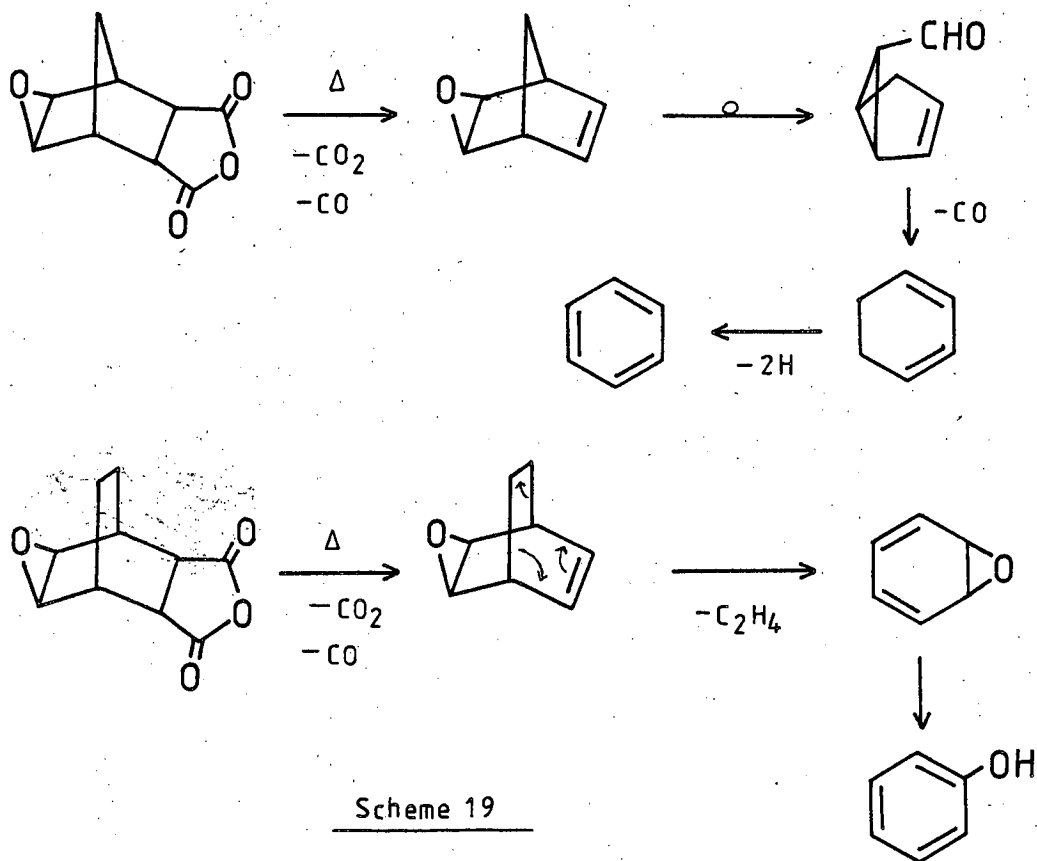
Thus pyrolysis of (366) at 800°C gave a 30% yield of benzene together with 12% of phenol (Scheme 18).



Scheme 18

As mentioned in Section C the pyrolysis of the epoxide (338) also gave a mixture of benzene and phenol.

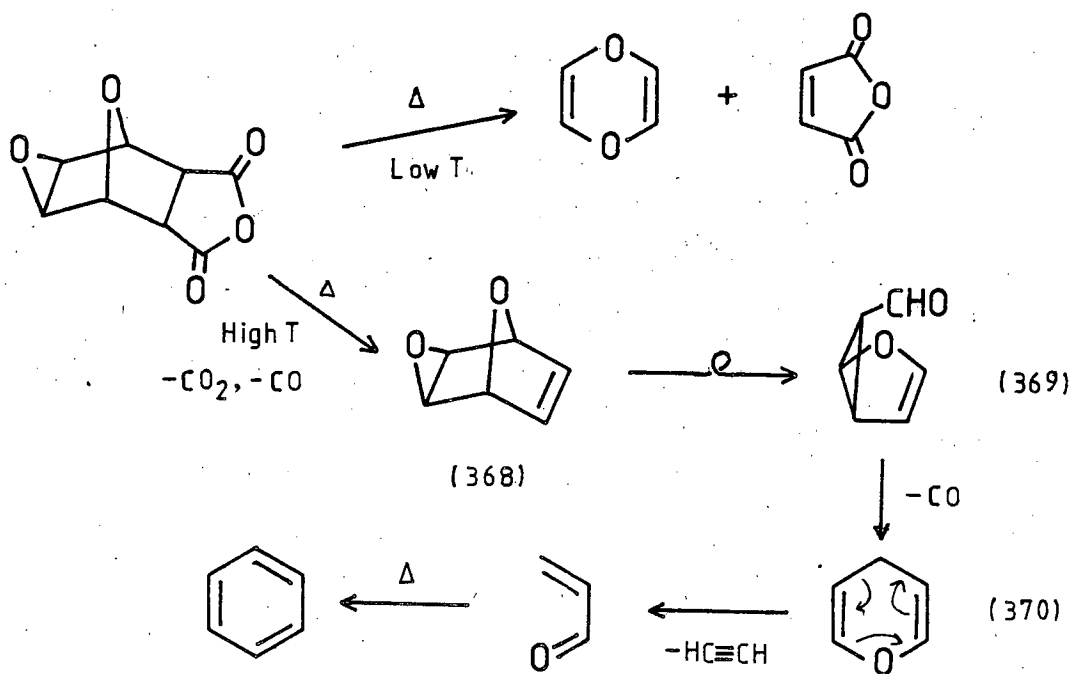
The bridged compounds (367; $X=CH_2$ and CH_2CH_2) behaved similarly (Scheme 19). Pyrolysis of (367; $X=CH_2$) at $775^\circ C$ gave benzene (41%) and 1,3-cyclohexadiene (11%), while (367;



$X=CH_2CH_2$) gave a 72% yield of phenol at $850^\circ C$. The evidence for the pathways shown in Scheme 19 has been discussed already in Section C.

The decomposition of (367; $X=O$) proved to be more interesting since, for the first time, the retro Diels-Alder reaction occurred in competition with loss of CO_2 and CO . Pyrolysis at $725^\circ C$ gave maleic anhydride together with *p*-dioxin whose identity was confirmed by its spectroscopic properties [IR: good agreement with literature²³⁰; 1H NMR

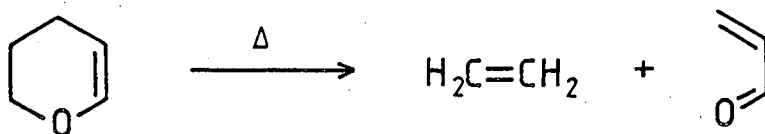
δ 5.55 (s); ^{13}C NMR δ 127.28 ($^1J_{\text{CH}}$ 197.2Hz, $^2J_{\text{CH}}$ 16.4Hz);
 m/e 84 (100%, M^+)]. Even at 725°C a 20% yield of acrolein
 was obtained and on increasing the temperature this became the
 major product. At 850°C there was little maleic anhydride
 or dioxin and at 900°C the only identifiable products were
 acrolein (40%) and benzene (5%). A likely pathway for the
 formation of these products is shown in Scheme 20, whereby



Scheme 20

loss of CO_2 and CO affords the 7-oxabicyclo[2.2.1]heptadiene
 epoxide (368) which rearranges to (369). Subsequent loss of
 CO , as for the CH_2 bridged analogue, then gives γ -pyran (370)
 which could lose acetylene to produce acrolein. The related
 gas phase decomposition of dihydropyran (371) to produce
 ethylene and acrolein is well known.³²⁴

The epoxide (368) has been prepared before³²⁵ but its



(371)

chemistry has not been studied. Pyrolysis of (368) might have substantiated the mechanism for the formation of acrolein but attempts to prepare it by the literature method proved unsuccessful.

The presence of benzene in the high temperature products is surprising but its origin, as a secondary pyrolysis product of acrolein, is unequivocal since flash vacuum pyrolysis of the latter (100 mg) at 850°C gave unreacted acrolein and benzene (19 mg).

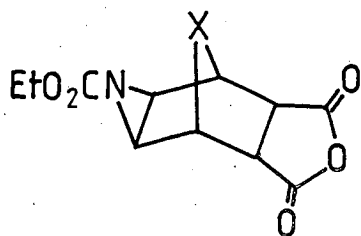
In an attempt to elucidate the mechanism of this apparently novel transformation, several related compounds were subjected to pyrolysis. While methacrolein and acrylonitrile remained unchanged at 850°C, crotonaldehyde broke down completely under the same conditions to yield mainly gaseous products together with a small amount (total 17 mg/100 mg crotonaldehyde) of aromatic products. These were identified by GC-MS as benzene, toluene, naphthalene, indene, 1- and 2-methylnaphthalene, acenaphthene, and other heavier aromatics.

Previous studies on the pyrolysis of acrolein³²⁶ and crotonaldehyde³²⁷ have concentrated on the gaseous products (CO and hydrocarbons) but, in the former case at least, the formation of a non-gaseous residue was noted, accounting for up to 20% of the acrolein reacted.

It might be noted here that very similar mixtures of aromatic hydrocarbons have been obtained by Badger in a series of studies dealing with the mechanism of formation of the carcinogen 3,4-benzopyrene on heating hydrocarbon mixtures such as coal tar and petroleum. Pyrolysis at 700°C resulted in conversion of simple hydrocarbons such as acetylene³²⁸ and 1,3-butadiene³²⁹ into a tar which contained all the products obtained from crotonaldehyde, in very similar proportions, together with up to 30 other, more complex aromatics. These products were thought to be formed by coupling of two, three and four-carbon radical fragments and the aldehyde pyrolyses probably proceed by loss of CO followed by similar radical coupling processes.

4. Preparation and pyrolysis of anhydride aziridines

In the same way as for the unsaturated sulphones discussed in previous sections, the olefinic double bond of the anhydrides could be readily converted into the corresponding N-ethoxy-carbonyl aziridine although the sensitivity of the anhydride function to hydrolysis limited the techniques available for their preparation. For example, irradiation of the anhydrides (257) and (364) with ethyl azidoformate probably did result in aziridine formation but attempted purification of the products by chromatography or by sublimation led to hydrolysis and decomposition respectively. In the case of the bridged anhydrides (365; X=CH₂, CH₂CH₂, and O) on the other hand, the addition of ether to the photolysis mixture led to crystallisation of the aziridines (372) in good yield. The methylene-



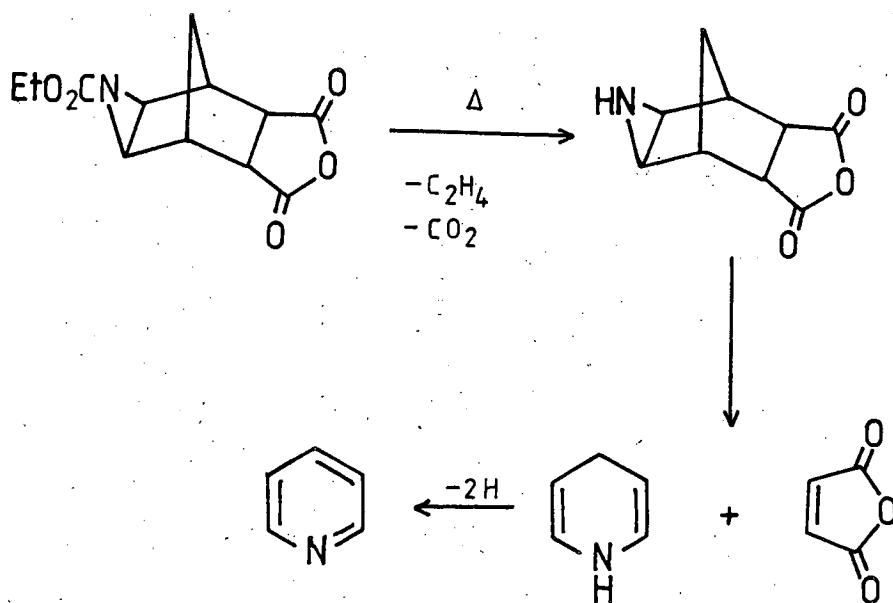
(372)

bridged aziridine (372; $X=CH_2$) had previously been prepared¹⁸⁵ by thermal reaction of the corresponding anhydride with ethyl azidoformate in boiling carbon tetrachloride. The same method also gave a low yield of (372; $X=CH_2CH_2$) but (365; $X=O$), (257) and (364) failed to react under these conditions. None of the anhydrides reacted with ethoxycarbonyl nitrene under homogeneous conditions and the use of the phase transfer method resulted in hydrolysis of the anhydride function.

The anhydrides (372; $X=CH_2$, CH_2CH_2 , and O) were obtained as colourless crystalline solids, readily purified by vacuum sublimation. They showed the expected spectroscopic properties including a characteristic pattern of three carbonyl absorptions, around 1860, 1790 and 1720 cm^{-1} , in the IR spectrum.

Just as with the sulphone aziridines described in Sections B and C, pyrolysis of the anhydrides failed to give the expected products due to the facile fragmentation of the N-ethoxycarbonyl group. Thus, pyrolysis of (372; $X=CH_2$) at 675°C afforded a red oil which formed an orange polymer on warming to room temperature. The other products from the pyrolysis were identified as maleic anhydride (48% yield), pyridine (10%) and ethanol (8%). The formation of pyridine, together with the fact that an orange polymer was reported

in the preparation of 1,4-dihydropyridine²³¹, suggested that the latter might be the initial product in this pyrolysis. A plausible mechanism for the reaction is shown in Scheme 21.



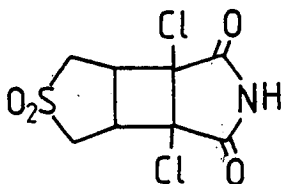
It is supported by the observation that when the temperature of pyrolysis was raised to 725°C, less of the orange polymer was produced while the yield of pyridine increased to 46%. This reaction together with the formation of *p*-dioxin from the anhydride (367; X=O) are the only two cases studied in which a retro Diels-Alder reaction still occurs after modification of the double bond of the sulphones or anhydrides. Clearly the potentially general approach to compounds of the type (321), which was discussed earlier (p.190) is severely limited by competition from other modes of fragmentation.

Pyrolysis of the other aziridines (372; X=CH₂CH₂ and O) did not give any useful products. The only compounds identified were maleic anhydride and ethanol, together with benzene in the former case and furan in the latter, all these being formed in low yield.

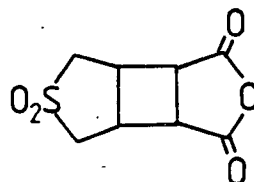
F. Preparation and pyrolysis of some derivatives of
2-Thiabicyclo[3.2.0]heptane 2,2-dioxide

1. General Background

In 1965 Scharf and Korte briefly reported the preparation of the compound (373) by irradiation of a solution of butadiene

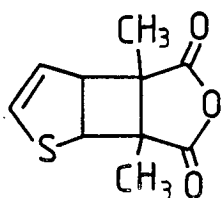


(373)

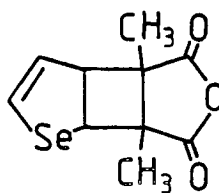


(249)

sulphone and dichloromaleimide³³⁰. The photochemical addition of butadiene sulphone to maleic anhydride has since been carried out by Shaikhrazieva et al.¹⁸³ and the product (249) has been used as the starting material in a number of useful syntheses developed in these laboratories^{79,80} and discussed fully in earlier Sections. In contrast the isomeric 2-thiabicyclo[3.2.0]heptane system derived by cycloaddition with 2,3-dihydrothiophen 1,1-dioxide has never been prepared although related ring systems are known. For example, compounds (374)³³¹ and (375)³³² can be obtained by cycloaddition of thiophen and selenophene to substituted maleic anhydrides.



(374)

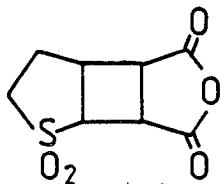


(375)

The corresponding reaction with maleic anhydride itself is unsuccessful.

2. Preparation, structure and pyrolysis of the 2,3-dihydrothiophen dioxide/maleic anhydride adduct

Following the method used for the 3-thia isomer¹⁸³, irradiation of an acetone solution of maleic anhydride and 2,3-dihydrothiophen dioxide gave the adduct (254) in 35% yield. An alternative method which afforded a better yield in the



(254)

case of the 3-thia isomer (249), viz. irradiation in ethyl acetate in the presence of benzophenone, failed to give any (254). This is the first of several instances in which the behaviour of the isomeric systems (249) and (254) was found to differ markedly.

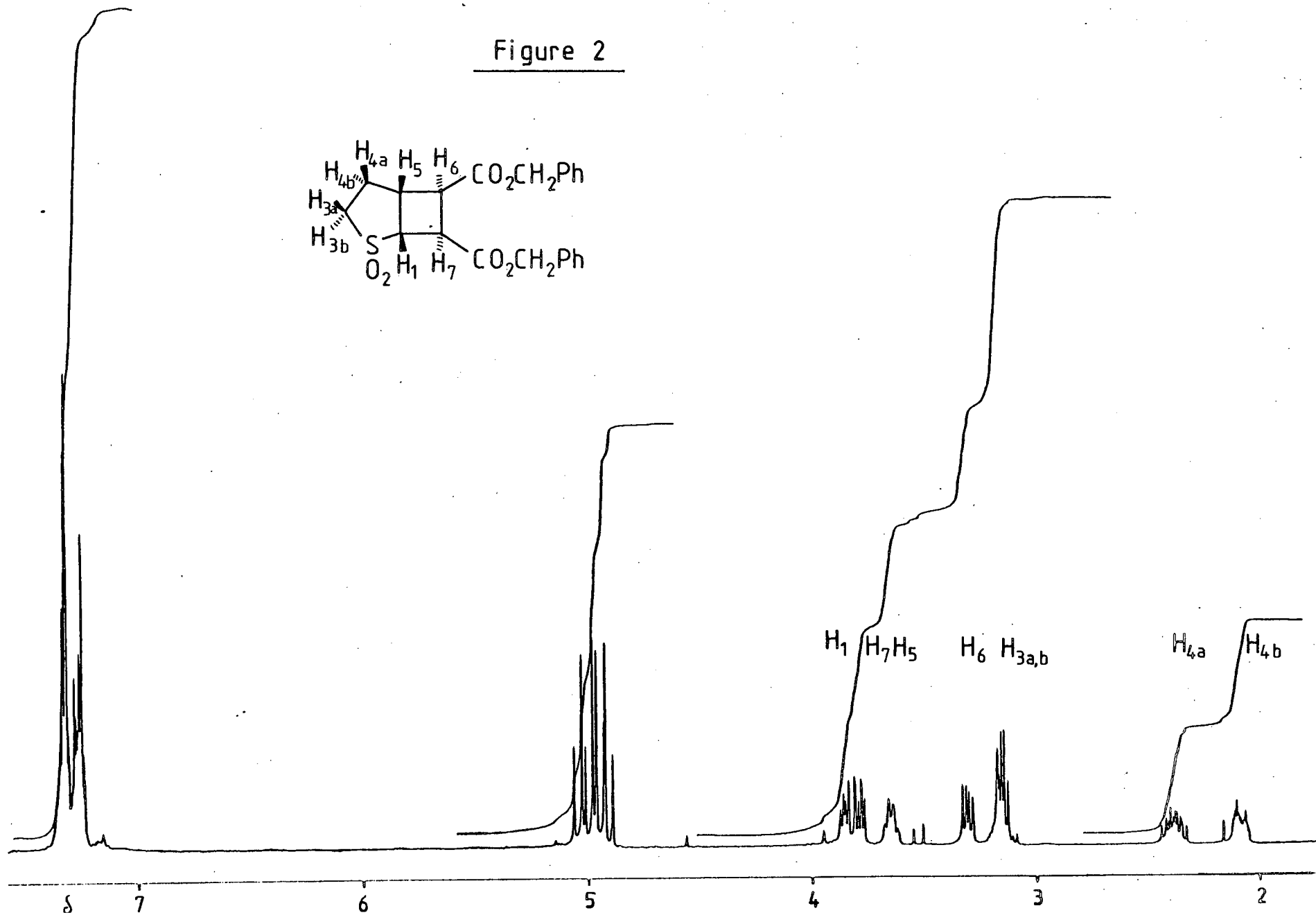
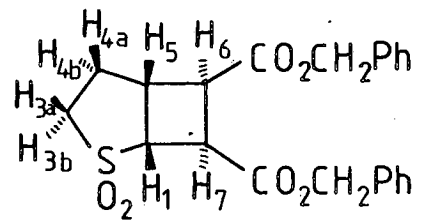
The anhydride (254) is a high-melting colourless solid which exhibits the expected analytical and spectroscopic properties, including IR absorptions at 1862 and 1790 cm^{-1}

due to the anhydride function and at 1307 and 1125 cm^{-1} due to the sulphone group. Due to the insoluble nature of (254), its NMR spectrum could only be obtained in dimethylsulphoxide. The broad multiplets observed in the spectrum prevented access to any detailed structural information although the overall spectrum was in good agreement with the expected pattern. Thus, the cyclobutane proton next to SO_2 resonated at $\delta 3.9$ while the other protons gave rise to signals between $\delta 3.6$ and 3.3, except for the methylene group remote from SO_2 which occurred at $\delta 2.3-2.0$.

In order to overcome the insolubility problem, the anhydride (254) was converted into its more soluble dibenzyl ester, and its NMR spectrum recorded at 360MHz. The spectrum (Figure 2) shows the expected pattern including two slightly non-equivalent AB patterns due to the CH_2 's of the benzyl groups. The pattern between $\delta 4$ and 2, which is due to the protons of the bicyclic ring system, is rather complex, each proton being unique and some of them being coupled to four others, giving a 16-line signal. Despite this complexity a selective decoupling study allowed the assignment of all the signals and the determination of all the coupling constants. The behaviour of the $\delta 4-2$ region on decoupling is shown in Figure 3. The coupling constants are given in Scheme 22.

Of particular relevance from a structural point of view are the values of the coupling constants across the cyclobutane ring. It is well known that in systems of this type adjacent protons which are *cis* to each other have a coupling constant generally greater than 6Hz, while *trans* protons have a much smaller coupling constant, i.e. less than 6Hz. For example,

Figure 2



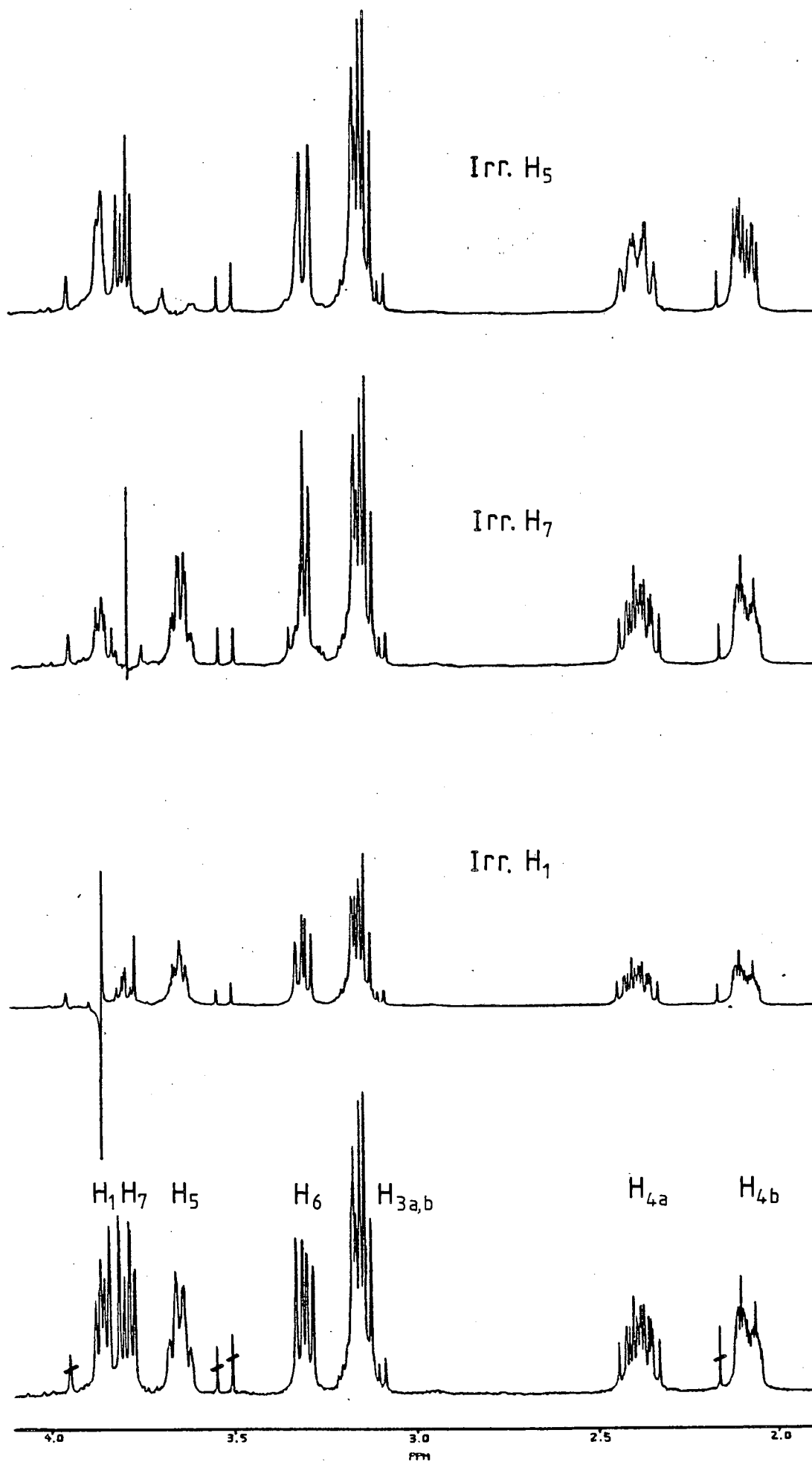


Figure 3

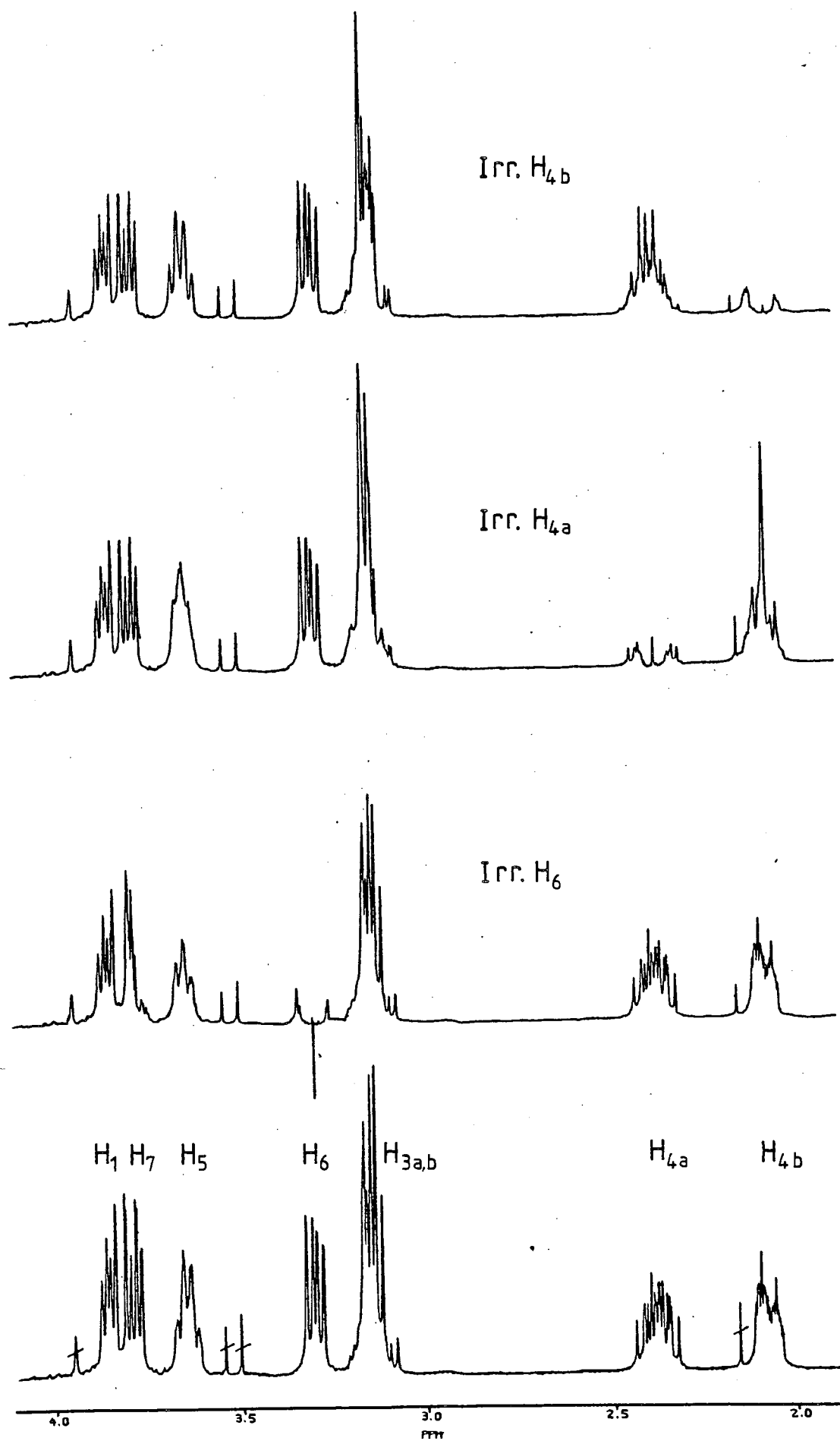
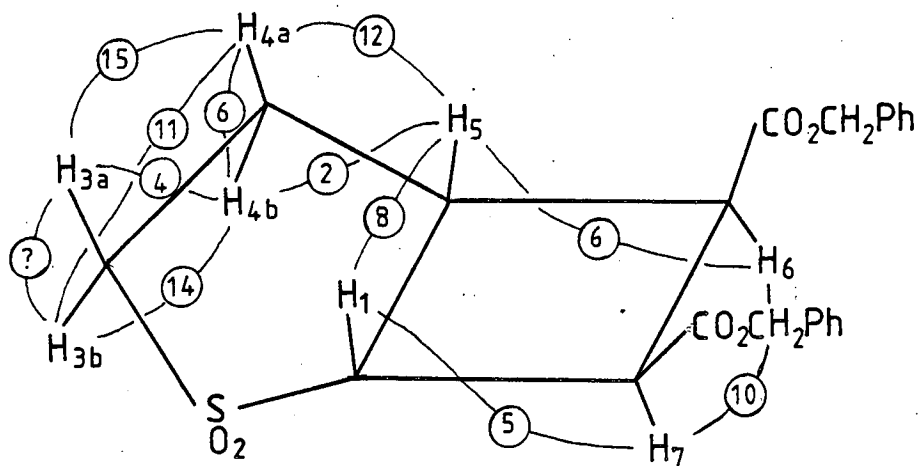


Figure 3

^1H NMR Spectrum of dibenzyl ester (377)

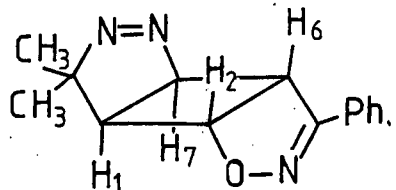
Principal coupling constants in Hertz (to nearest whole number)



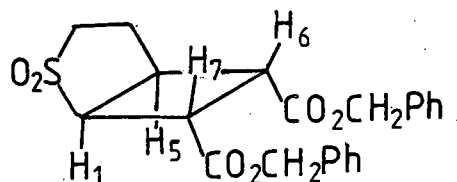
Long range coupling constants: $\text{H}_1\text{-H}_6$ and $\text{H}_5\text{-H}_7 = 1\text{Hz}$.

Scheme 22

Bianchi et al.³³³ found that the *anti* compound (376) possessed the following coupling constants: $J_{1,7}=5.65$



(376)

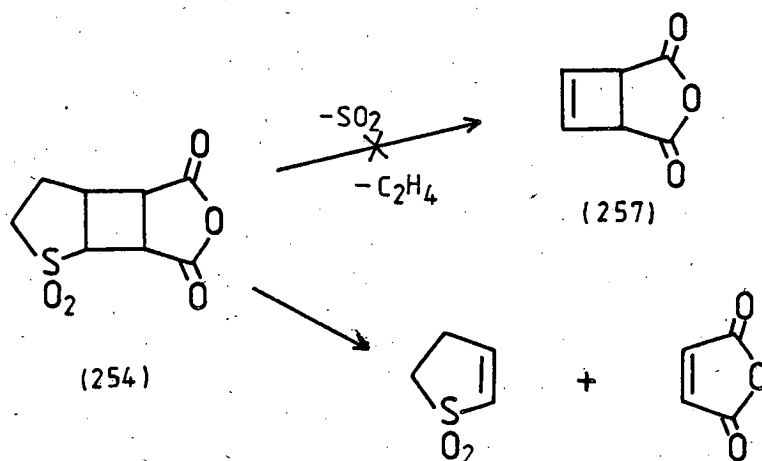


(377)

and $J_{2,6}=7.03$ while $J_{1,2}=2.52$ and $J_{6,7}=2.30$ Hz. By comparison, the *syn* isomer of (376) had values of 7.03, 8.12, 6.13, and 7.34Hz, respectively. In the case of the dibenzyl ester (377) the corresponding values were found to be $J_{1,5}=8.5$, $J_{6,7}=10.3$, $J_{1,7}=4.8$, and $J_{5,6}=6.0$ Hz. Although the $J_{5,6}$ value of 6Hz is rather high for a *trans* coupling constant, it seems likely that the diester (377) and therefore the anhydride (254), possesses an *anti* configuration as shown. This conclusion is also consistent with the fact that the 3-thia isomer (249) was shown to have an *anti* configuration by X-ray diffraction studies on a derivative¹⁸⁴.

The other coupling constants shown in Scheme 22 are also consistent with the proposed structure. Thus the coupling constants between H_{3a} and H_{4b} and between H₅ and H_{4b} are small in keeping with the fact that a Dreiding model shows the dihedral angle in each case to be close to 90°. Small four-bond couplings are also observed across the cyclobutane ring between H₁ and H₆ and between H₅ and H₇.

By analogy with the behaviour of the sulphones described in Section C, the thermal decomposition of the anhydride (254) might be expected to proceed by loss of SO_2 and ethylene to give cyclobutene anhydride (257). In fact this does not occur; instead pyrolysis of the anhydride at 800°C gives rise



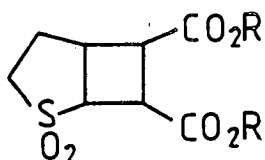
Scheme 23

to a high yield of maleic anhydride and 2,3-dihydrothiophene dioxide, which are formed by a retro[2+2]cycloaddition reaction (Scheme 23). In Section C it was found that ring-strain is an important factor in favouring the retro cycloaddition reaction over loss of SO_2 and ethylene and it was anticipated that conversion of the anhydride function of (254) into acyclic derivatives might similarly result in a change in the mode of fragmentation. With this in mind, an attempt was made to prepare the diacid and diesters from (254).

3. Preparation and pyrolysis of 2-Thiabicyclo[3.2.0]heptane-6,7-dicarboxylic acid 2,2-dioxide and its diesters

The diacid (378; R=H) was obtained analytically pure in

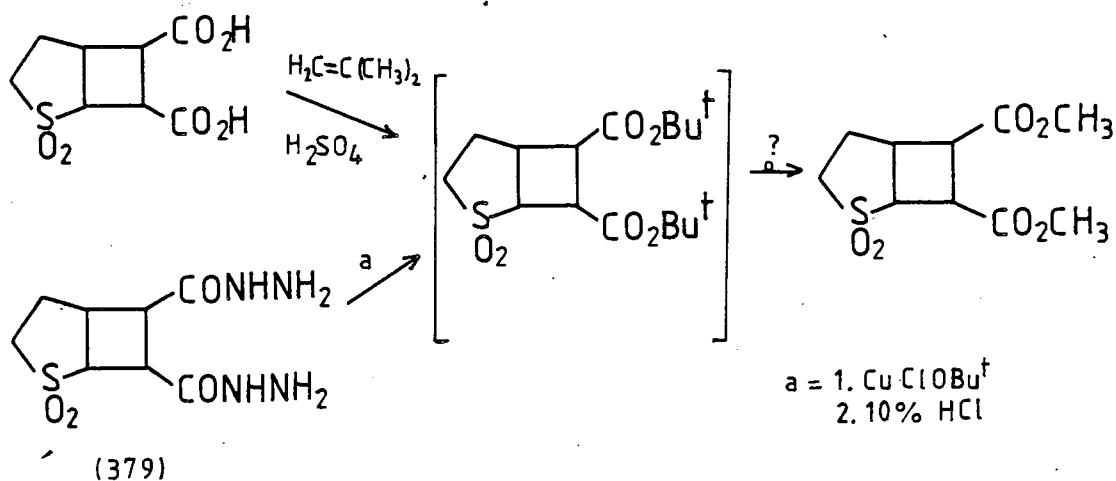
86% yield by heating the anhydride (254) in boiling water. Similar heating of the anhydride (254) in an excess of alcohol



(378)

in the presence of a trace of sulphuric acid likewise gave the corresponding diester. In this way the dimethyl- (378; R=CH₃), diethyl- (378; R=C₂H₅), diisopropyl- (378; R=i-C₃H₇), and dibenzyl (378; R=CH₂Ph) esters were prepared in good yields.

Attempts to prepare the di-*t*-butyl ester (378; R=*t*-Bu) led to the discovery of an apparently novel transformation. Thus reaction of the anhydride (254) with *t*-butanol afforded only the diacid by the well known elimination of isobutene. On the other hand, reaction of the diacid (378; R=H) with isobutene in the presence of sulphuric acid according to the method of Strube²³² gave the dimethyl ester (378; R=CH₃) in 70% yield. This product was also obtained in 38% yield using the recently reported method of Tsuji²³³, whereby the corresponding dihydrazide (379) [see following Section] is treated with a solution of CuCl OBU^t in tetrahydrofuran (Scheme 24).



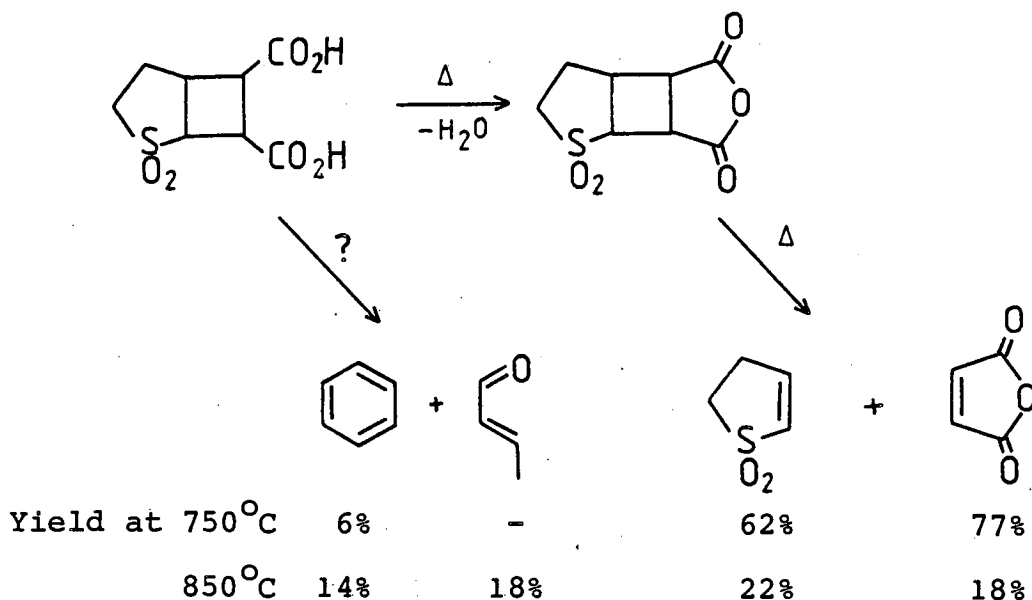
Scheme 24

The mechanism of this transformation, in which there is formal loss of propene, is unclear although in both cases a strong acid was used and the elimination may be acid catalysed. An attempt to prepare the di-*t*-butyl ester from the diacid chloride also failed due to insurmountable difficulties in the latter's preparation. The anhydride (254) was inert to PCl_5 , SOCl_2 , $\text{SOCl}_2/\text{POCl}_3$ and oxalyl chloride, while treatment of the diacid (378; $\text{R}=\text{H}$) with any of these reagents resulted in dehydration to the anhydride (254).

The diacid and diesters (378) are all colourless solids showing the expected analytical and spectroscopic properties. The characteristic feature of the spectra is the slight non-equivalence of the two CO_2R groups. The diacid and the dimethyl- and diisopropyl esters each show two distinct carbonyl absorptions in the IR spectrum. The ester alkyl signals in all the diesters show a slight non-equivalence as follows: dimethyl CH_3 's differ by 0.03 ppm; diethyl CH_2 0.02 ppm, CH_3 0.01 ppm; diisopropyl CH 0.006 ppm, CH_3 0.006 ppm; dibenzyl CH_2 0.04 ppm. As already mentioned, the benzyl CH_2 's in the dibenzyl ester appear as two AB patterns due to restricted rotation caused by the proximity of the two groups. The pattern due to the bicyclic ring-system is the same for all the diesters and has already been completely assigned in the case of the dibenzyl ester (Figures 2 and 3).

The main process observed in the pyrolysis of diacid (378; $\text{R}=\text{H}$) at 750°C was dehydration to the anhydride (254)

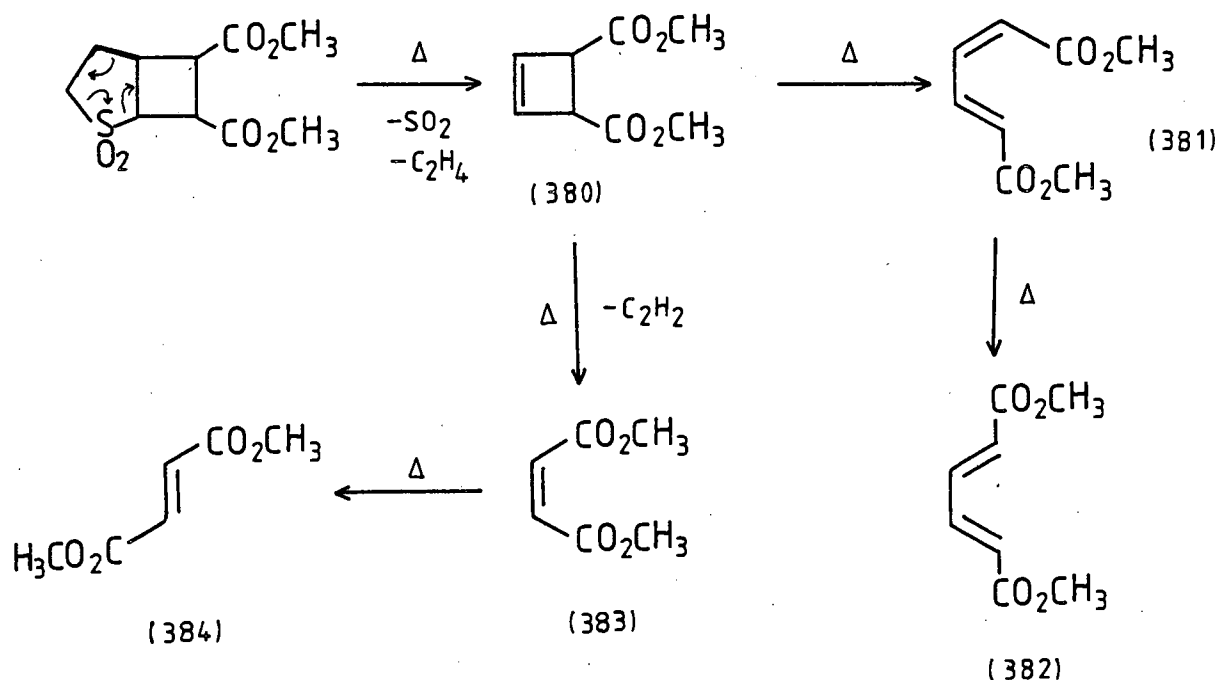
which then fragmented, as described previously, to 2,3-dihydrothiophen dioxide and maleic anhydride. However, other reactions also occurred to give minor products including a 6% yield of benzene. At 850°C these reactions became more important and crotonaldehyde appeared as a major product (Scheme 25). The observation of crotonaldehyde is most



Scheme 25

surprising and the mechanism of its formation is unknown.

Several different pathways are possible in the fragmentation of the dimethyl ester (378; R=CH₃) and some of these are outlined in Scheme 26. Simple loss of SO₂ and ethylene would give the cyclobutene diester (380) which is known to undergo ready electrocyclic ring opening to the *cis,trans*-dimethyl muconate (381)³³⁴. Under the pyrolysis conditions this might be expected to isomerise to the *trans,trans*-dimethyl muconate (382). Alternatively the diester (380)



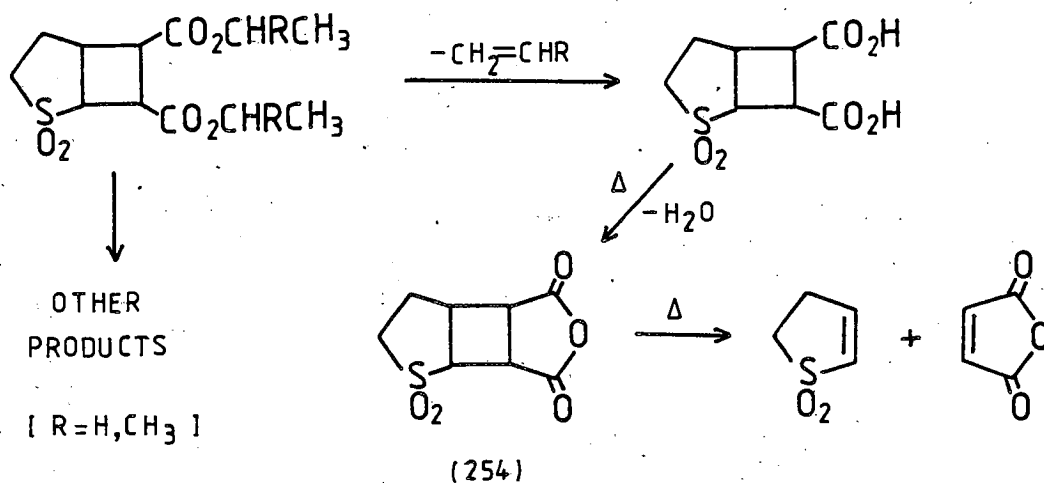
Scheme 26

might lose acetylene to give dimethyl maleate (383) which could likewise isomerise to dimethyl fumarate (384). (384) could also be formed directly from the starting material but in this case 2,3-dihydrothiophen dioxide would also be produced.

When the dimethyl ester (378) was pyrolysed at 775°C it gave a complex mixture of products in which the only recognisable components were the two *trans* diesters (382) and (384). Preparative TLC allowed isolation of each of these compounds in 5% yield. GC comparison with authentic samples showed that neither of the *cis* diesters, (381) or (383), were present. Confirmation of the pathway (380) → (381) → (382) was readily obtained by pyrolysis of (380), a procedure which also allows convenient preparation of the authentic diesters (381) and (382). Thus pyrolysis of (380), readily prepared by reaction of cyclobutene anhydride (257) with methanol, at 500°C gave a good yield of pure (381) while pyrolysis at 900°C gave a good yield of (382). Pyrolysis at

intermediate temperatures produced a mixture of (381) and (382). The fact that no 2,3-dihydrothiophen dioxide was detected among the products from (378; $R=CH_3$) rules out the formation of dimethyl maleate by the direct retro-[2+2] process and it must instead be formed by the stepwise loss of SO_2 , ethylene and acetylene from the starting material. As well as the two products which were identified, several other minor components were also formed.

Pyrolysis of the diethyl and diisopropyl esters was even less productive. There was almost complete loss of ethylene and propene to form diacids and the only products to be identified in each case were 2,3-dihydrothiophen dioxide and maleic anhydride, both of which were formed in low yield, presumably by dehydration of the diacid (378; $R=H$) to the anhydrid (254) which then fragmented (Scheme 27). In this instance also,

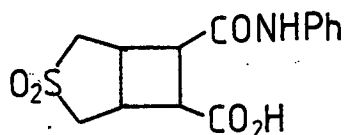


Scheme 27

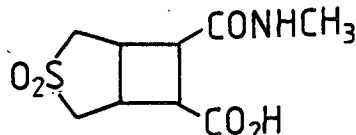
pyrolysis produced many other products with complex NMR signals at $\delta 7.5-5.5$ and a large acid OH signal. None of the isomeric muconic acids or fumaric or maleic acid were present and the identity of these products remains unknown.

4. Preparation of some mono-amides and the dihydrazide of 2-thiabicyclo[3.2.0]heptane-6,7-dicarboxylic acid 2,2-dioxide

In his original paper Shaikhraieva described the reaction of the anhydride (249) with aniline to form the anilide (385)¹⁸³. McLaughlin has similarly prepared the methyl amide (386)¹⁸⁴



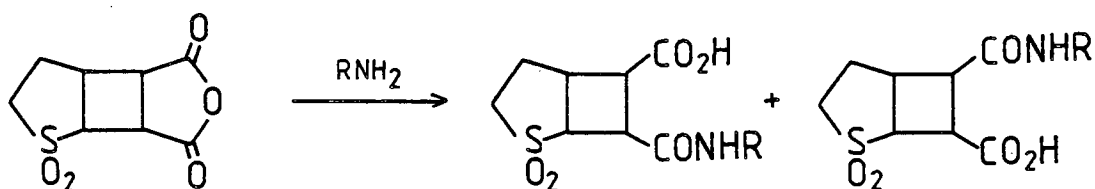
(385)



(386)

and both these compounds have been used to provide access to the cyclic imides by dehydration^{183,184}. As part of the current study, the reaction of the isomeric anhydride (254) with amines and with hydrazine was investigated.

As expected, the anhydride (254) reacts readily with aniline, methylamine and also with aqueous ammonia to form the corresponding amides (387; R=Ph, CH₃, and H) shown in Scheme 28. Problems arise, however, in the handling and



(254)

Scheme 28

(387)

purification of these compounds for two reasons. The first is that they are highly polar, high-melting solids which are soluble only in solvents such as water and dimethyl sulphoxide.

This ruled out the normal chromatographic methods for purification and vacuum sublimation proved useless since it resulted in immediate dehydration to the cyclic imides. The other problem is that here, in contrast to the isomeric 3-thia system, the amides are formed as a mixture of the two isomers shown in Scheme 28 which are very difficult to separate and cause the products to have amorphous properties. Because of these difficulties the amides could not be obtained analytically pure but they did give correct exact-mass measurements, and spectral data in good agreement with the expected pattern.

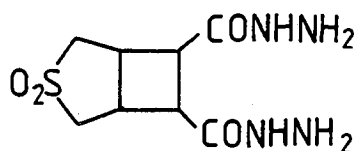
The amide (387; R=H) was obtained by treating the anhydride (254) with 0.88 ammonia solution. After purification by precipitation from aqueous methanol with ether the amide was found to be a 7:3 mixture of the two possible isomers by means of ^1H NMR spectroscopy which showed separate acid-OH signals for each isomer.

The methyl amide (387; R=CH₃), obtained by similar treatment with methylamine¹⁸³, melted over a range of 10°C. Moreover, the N-methyl signals were non equivalent in the NMR, showing an approximately 1:1 ratio of the two isomers.

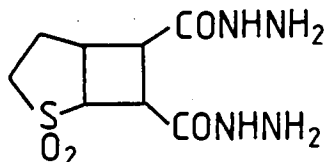
The product obtained by treating the anhydride (254) with aniline showed no distinct melting point, but gradually decomposed between 250 and 300°C with loss of water to give the cyclic imide. The NH protons were non-equivalent in the NMR and indicated a 3:2 mixture of the two isomers. In this case the major isomer could be separated by fractional

crystallisation and its spectra suggested that it was the 7-anilide. The residue consisted mainly of the 6-anilide.

Shaikhrazieva¹⁸³ also described the reaction of the dimethyl ester of anhydride (249) with hydrazine hydrate to produce the dihydrazide (388). The corresponding reaction



(388)



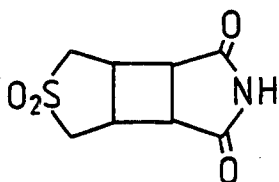
(389)

of the isomeric dimethyl ester (378; $R=CH_3$) produced the dihydrazide (389). Although this compound was also highly polar and insoluble, it had the advantage that it existed as a single isomer and therefore could be obtained analytically pure. Its IR spectrum showed four separate NH absorptions above 3100 cm^{-1} and four absorptions between 1750 and 1650 cm^{-1} . While the NH_2 groups are equivalent in the NMR spectrum, the NH's are separated by 0.15δ .

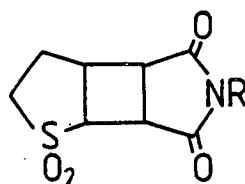
As already mentioned, sublimation of the amides led to immediate loss of water to form the corresponding cyclic imides. Any attempt at pyrolysis, therefore, gave only the products from pyrolysis of the imides which is discussed in the next Section. Although pyrolysis of the isomeric dihydrazide (388) led to loss of hydrazine to form a cyclic hydrazide^{183, 335}, the pyrolysis of (389) resulted in almost complete loss of nitrogen to give an unidentified, possibly polymeric product.

5. Preparation and pyrolysis of some cyclic imides of 2-thiabicyclo[3.2.0]heptane-6,7-dicarboxylic acid 2,2-dioxide

Irradiation of a solution of butadiene sulphone and maleimide in acetone containing acetophenone is known to produce the cyclic imide (390),¹⁸³ whereas the corresponding reaction with N-substituted maleimides is unsuccessful due to the preferential dimerisation of the maleimides. In the present studies it was found that 2,3-dihydrothiophen dioxide



(390)



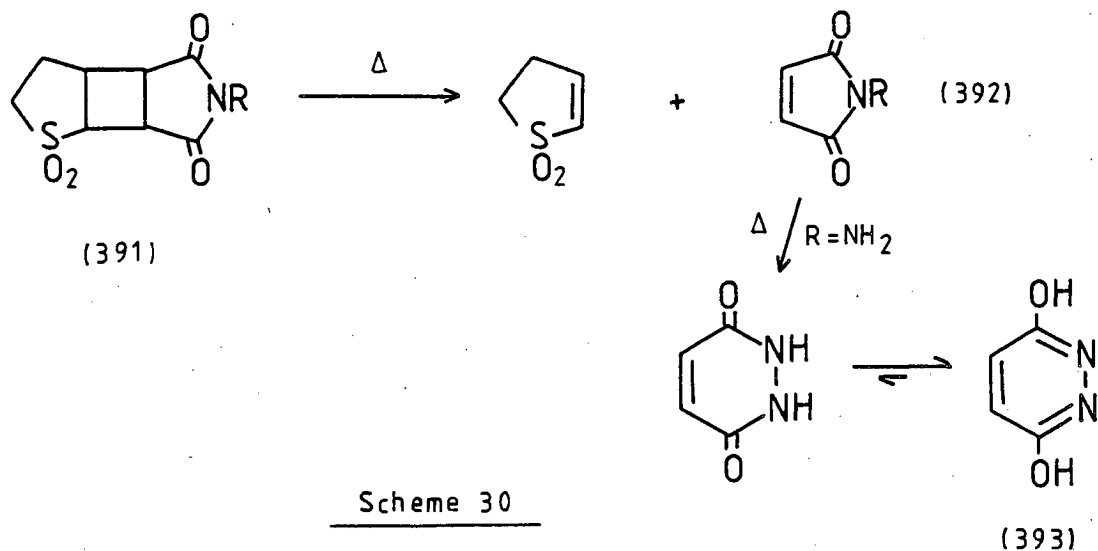
(391)

reacted in the same way to produce a 16% yield of the isomeric imide (391; R=H). Again the reaction with N-phenyl maleimide failed due to dimerisation.

As discussed in the previous section, the products from reaction of the 2,3-dihydrothiophen dioxide/maleic anhydride adduct (254) with amines readily lose water on sublimation, thereby providing a convenient synthesis of the cyclic imides (391) - Scheme 29. Thus, treatment of the anhydride (254) with ammonia solution followed by evaporation, and vacuum sublimation of the product gave the imide (391; R=H) in 56% overall yield. Similar reaction with methylamine and aniline afforded the imides (391; R=CH₃ and Ph) in good yield.

Treatment of (391; R=H) with one equivalent of hydrazine hydrate in methanol gave the N-amino compound (391; R=NH₂).

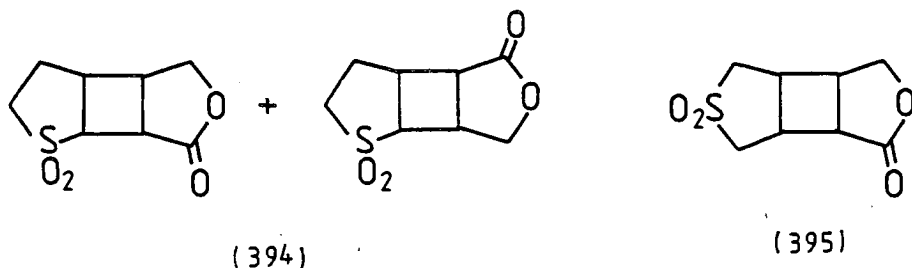
cycloaddition reaction. Thus, the imides (391; R=H, CH₃ and Ph) decomposed at 750°C to give a high yield of 2,3-dihydrothiophen dioxide and the maleimides (392) while, for



the compound with R=NH₂, this rearranged under the conditions to give the more stable dihydroxypyridazine (393) as shown in Scheme 30.

6. Reduction of the 2,3-dihydrothiophen dioxide/maleic anhydride adduct and pyrolysis of the products

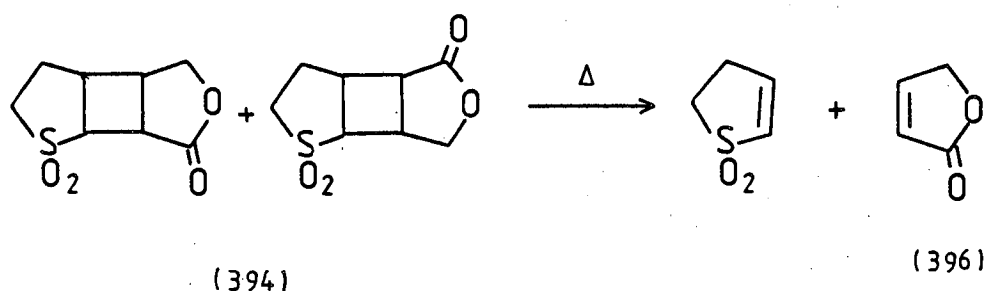
Reduction of the anhydride (254) with sodium borohydride gave the mixture of lactones (394) as a colourless crystalline



solid which melted over a range of 15°C. Similar preparation of the isomeric lactone (395), where only one isomer is possible,

has already been reported⁷⁹. The lactone mixture (394) showed a strong carbonyl absorption at 1760 cm^{-1} and the methylene group of the lactone ring resonated as a sharp NMR signal at $\delta 4.48$. The ^{13}C NMR spectrum of (394) clearly showed the presence of approximately equal amounts of both isomers as evidenced by the observation of eight closely-spaced pairs of lines of roughly equal intensity.

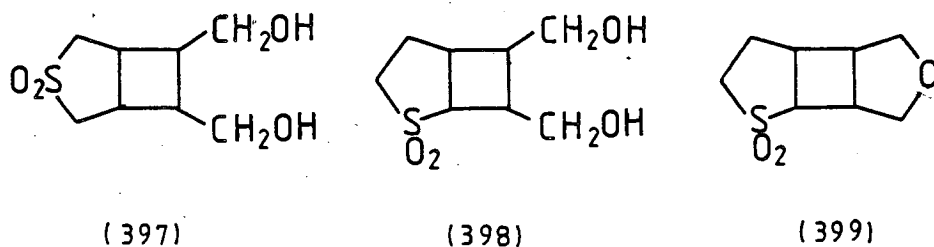
Pyrolysis of (394) resulted, once again, in a retro [2+2] cycloaddition reaction to give a high yield of 2,3-



Scheme 31

dihydrothiophen dioxide and butenolide (396) as shown in Scheme 31.

By treating the butadiene sulphone/maleic anhydride adduct (249) with lithium aluminium hydride, Shaikhrazieva obtained a good yield of the diol (397)¹⁸³. Similar reduction

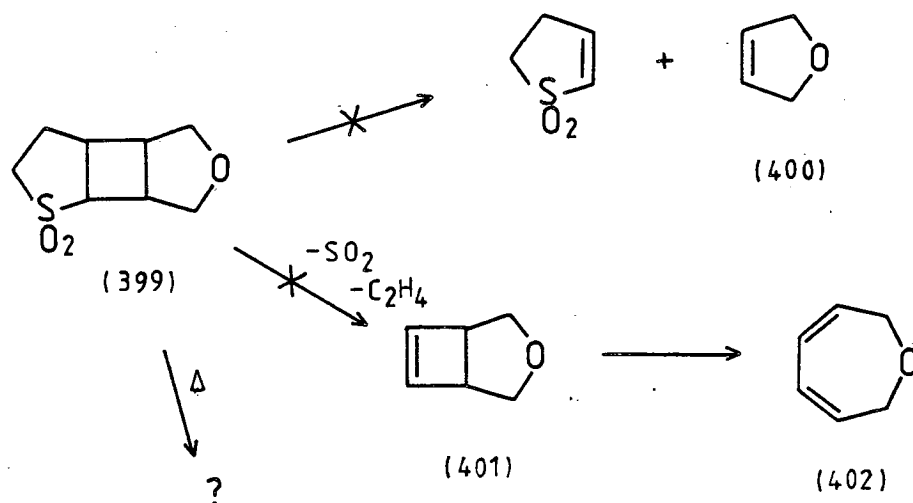


of the dimethyl ester derived from (249) gave the same product

in better yield¹⁸⁴. However, when the isomeric anhydride (254) and its dimethyl ester was treated with this reagent, the expected diol (398) was not produced. Instead, reduction of (254) led to a low yield of the ether (399) as the only isolable product. Even more surprising was the recovery of the diester (378; R=CH₃) unchanged after reaction with lithium aluminium hydride in boiling tetrahydrofuran for 10 hours. The reason for the remarkable difference in reactivity between the isomeric systems is unclear.

The ether (399) was a colourless solid which showed the expected analytical and spectroscopic properties including a characteristic ¹H NMR pattern due to the -CH₂O- protons which is in good agreement with the spectrum of the 3-thia isomer¹⁸⁴.

By analogy with preceding examples, pyrolysis of (399) might be expected to result in a retro [2+2] reaction to give 2,3-dihydrothiophen dioxide and 2,5-dihydrofuran (400) as shown in Scheme 32. Alternatively, the reduction in ring-strain caused by the removal of the carbonyl groups might favour loss of SO₂

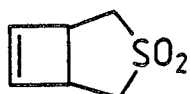


Scheme 32

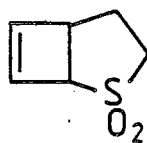
and ethylene to give the bicyclic ether (401) which could then ring open to afford 2,7-dihydrooxepine (402). In fact, pyrolysis of (399) at 800°C gave an oil which contained none of the expected products. Its ¹H NMR spectrum displayed a complex splitting pattern from which no identifiable products could be detected. The only GC volatile product was shown by GC-MS to be a trace of the starting material. The nature of the fragmentation process in this case remains unknown.

7. Preparation and pyrolysis of 2-thiabicyclo[3.2.0]hept-6-ene 2,2-dioxide and derivatives

In Section A the utility of 3-thiabicyclo[3.2.0]hept-6-ene 2,2-dioxide (250) as a masked form of *cis*-1,3,5-hexatriene was described. This involved addition to the double bond of (250) followed by pyrolytic removal of SO₂ leading to a number of useful syntheses. In the same way, the isomeric

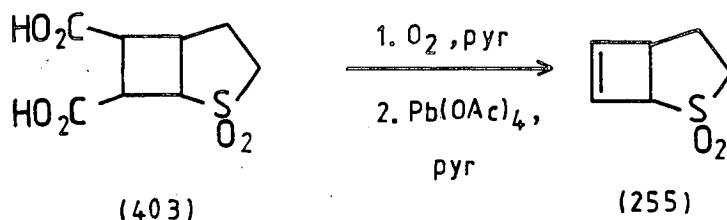


(250)



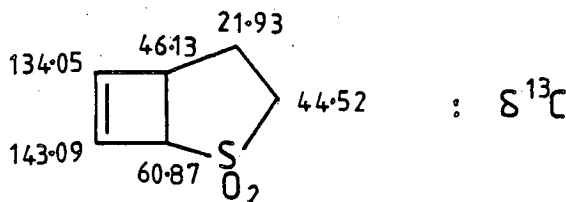
(255)

compound (255) might be expected to act as a cyclobutadiene synthon via electrophilic addition to the double bond followed by pyrolytic elimination of SO₂ and ethylene. With this in mind the compound (255) was prepared in an analogous way to (250) as shown in Scheme 33. Thus, treatment of the diacid (403), in pyridine solution at 60-70°C, with oxygen followed by lead tetraacetate resulted in oxidative bis-decarboxylation to give the expected product (255) in 5% yield as a colourless



Scheme 33

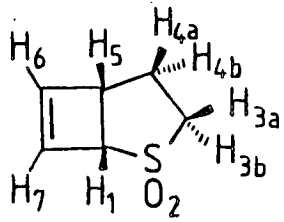
oil which failed to crystallise. Nonetheless (255) gave a correct exact-mass measurement and displayed all the expected spectroscopic properties. In particular the ^{13}C NMR spectrum showed a clean pattern of six lines, which were assigned as shown in Scheme 34. The 360MHz ^1H NMR spectrum of (255)



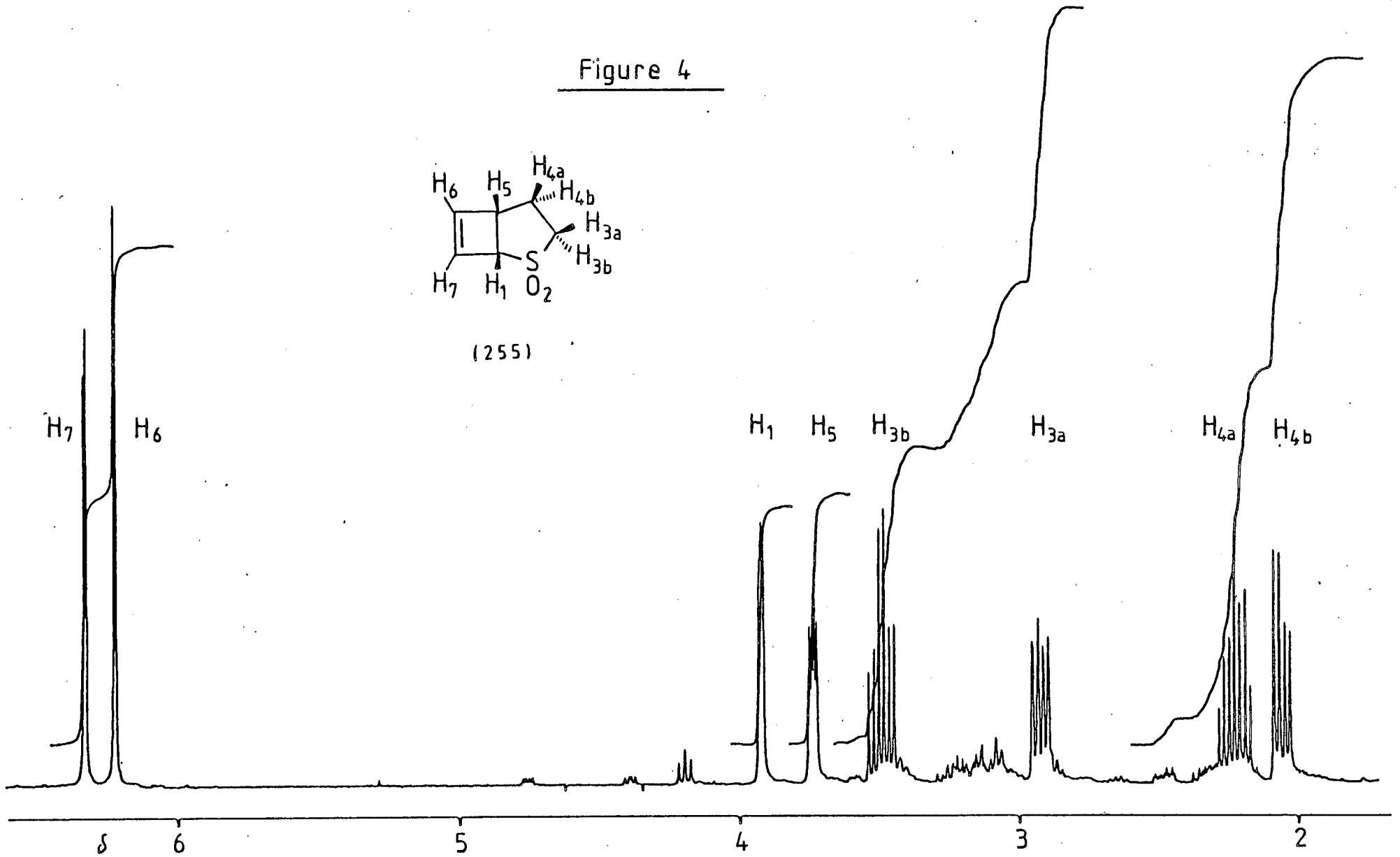
Scheme 34

showed a complex pattern (Figure 4) but selective decoupling studies allowed complete assignment of all the signals and the coupling constants. The behaviour on decoupling is shown in Figure 5 and the coupling constants, which are given in Scheme 35, are consistent with the proposed structure. A Dreiding model of (255) showed that the dihedral angles between H_{3a} and H_{4b} and between H_{4b} and H_5 were very nearly 90° , in agreement with the small coupling constants observed. The

Figure 4



(255)



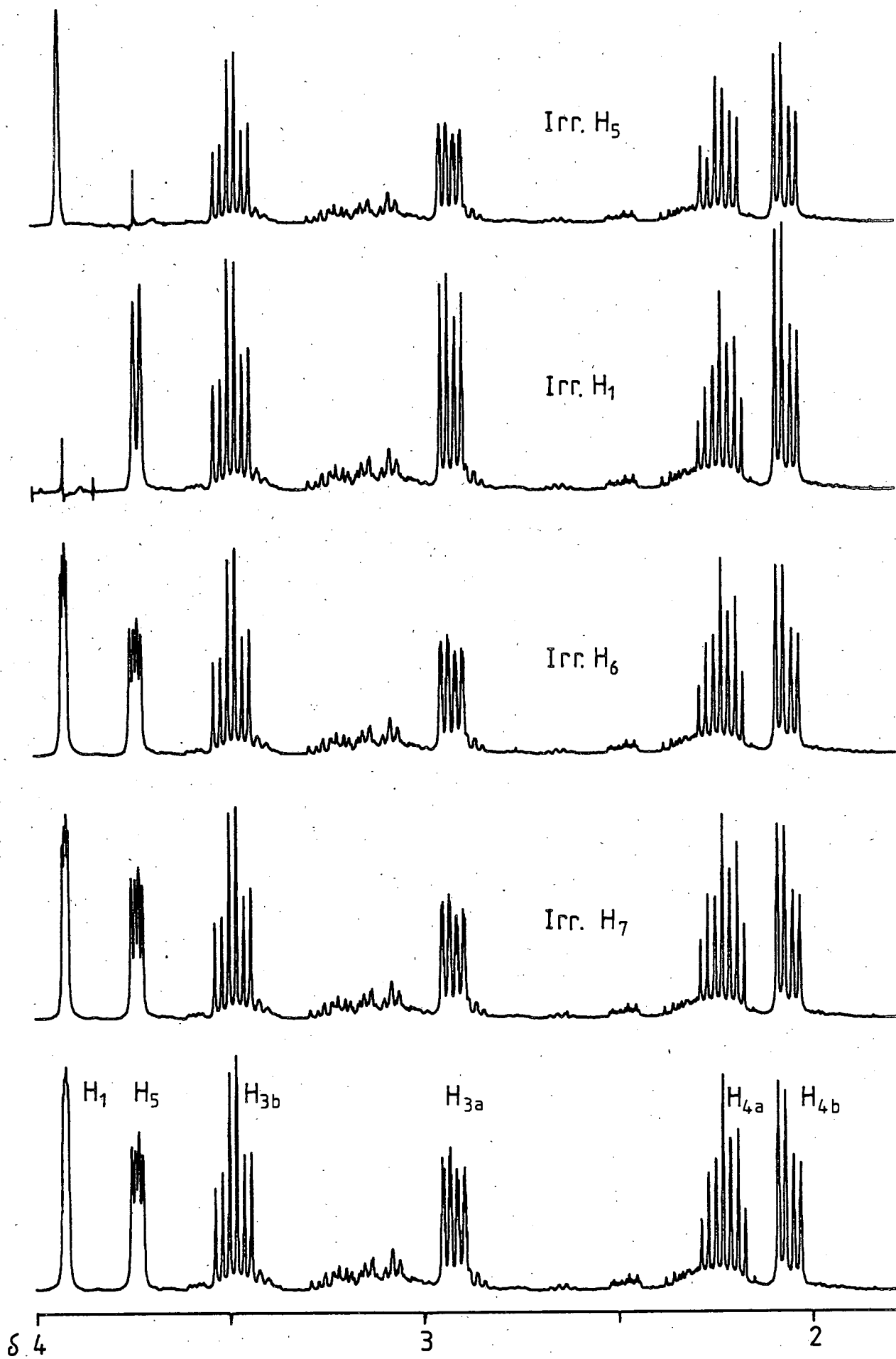


Figure 5

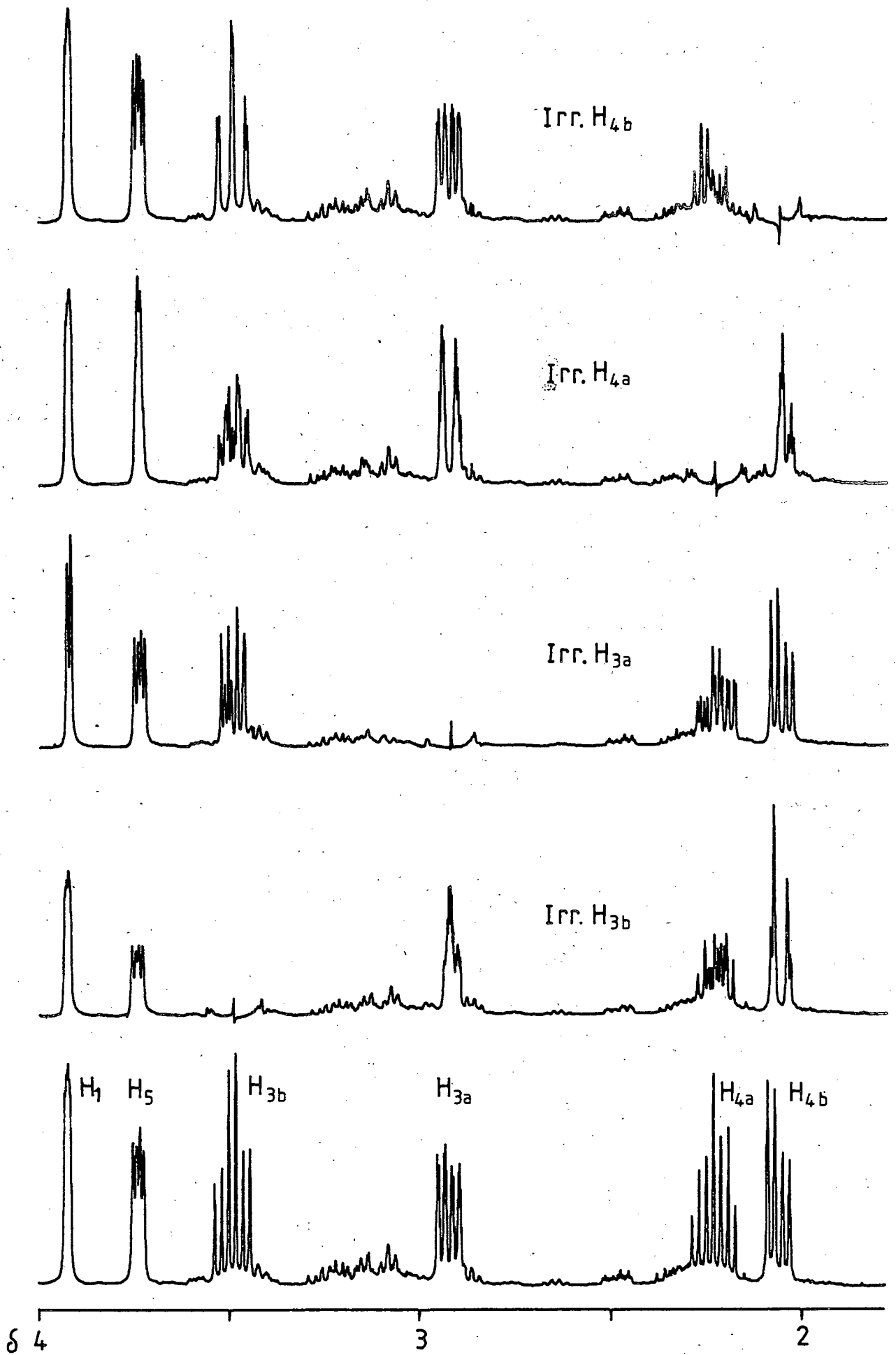
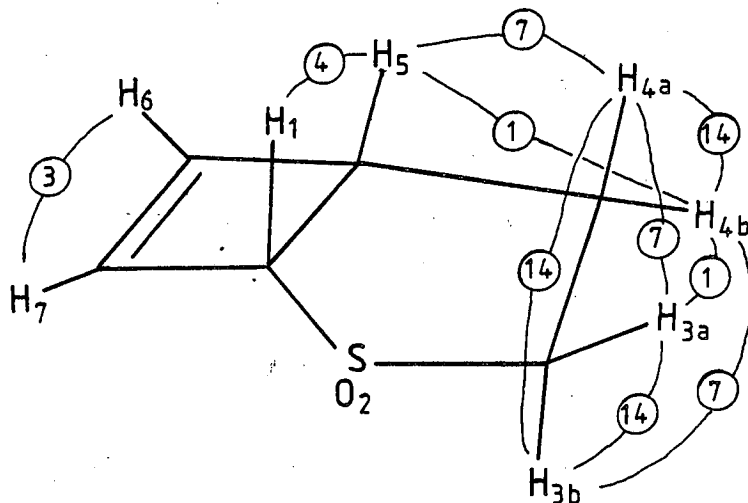


Figure 5

^1H NMR spectrum of alkene (255)

Principal coupling constants in Hertz (to nearest whole number):



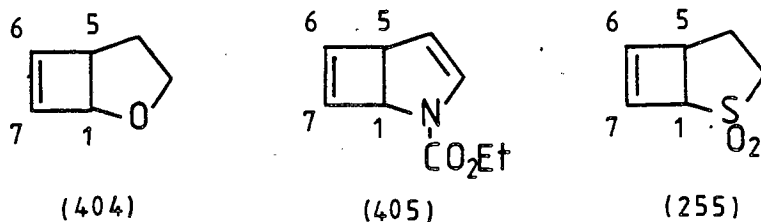
Long range coupling constants:

$\text{H}_1\text{-H}_{3a}$	2Hz
$\text{H}_1\text{-H}_6$	1Hz
$\text{H}_7\text{-H}_5$	1Hz

Scheme 35

dihedral angle between H_{4a} and H_{3b} was nearly 180° giving a large coupling constant of 14Hz. The four-bond coupling of 2Hz between H_1 and H_{3a} is rather large considering that the Dreiding model shows these protons to be widely separated.

The pattern of coupling between the olefinic protons, H_6 and H_7 , and H_1 and H_5 is at first sight surprising. If the downfield olefinic proton signal is assigned to H_7 , then what is observed is not the expected three-bond couplings between H_1 and H_7 and H_5 and H_6 , but rather long-range four-bond couplings diagonally across the four-membered ring. This turns out to be in good agreement with the findings of Paquette^{337,338} on the very similar molecules (404) and (405). In the case of (404) the olefinic protons were unambiguously



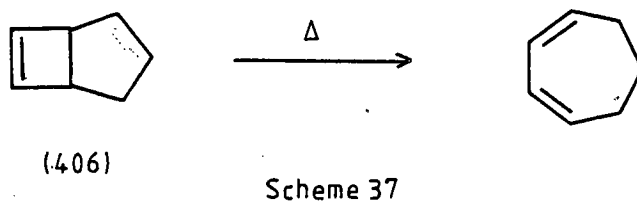
J/Hz	(404)	(405)	(255)
H_1-H_6	2.8	2.8	1
H_5-H_7	1.5	<0.4	1
H_6-H_7	2.8	2.8	3

Scheme 36

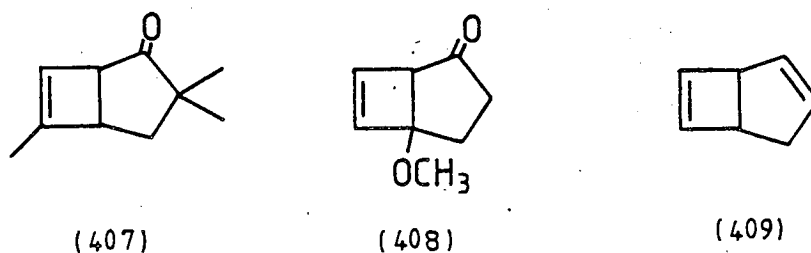
assigned by preparation of (404)-7- 2H . Selective decoupling studies on the latter compound gave the coupling constants shown in Scheme 36. The H_1-H_7 and H_5-H_6 couplings were too small to be observed as is the case with (255). The coupling constants between the two olefinic protons of 2.8Hz are in good

agreement with the value of 3Hz for (255).

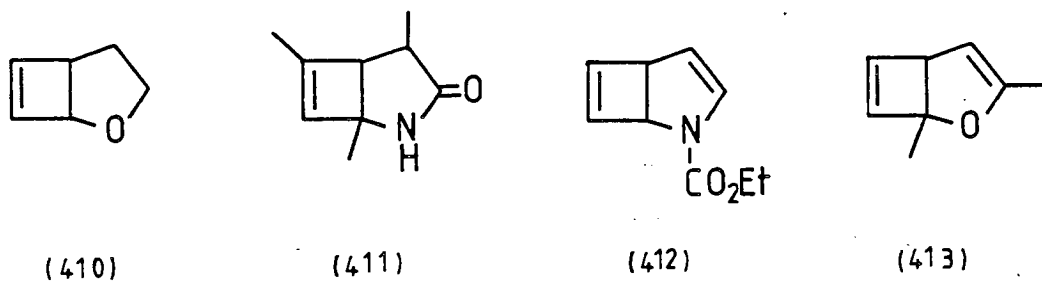
Several compounds possessing the bicyclo[3.2.0]hept-6-ene ring structure have been shown to undergo electrocyclic ring-opening on heating. For example, pyrolysis of the parent hydrocarbon (406) at 400°C resulted in a good yield of 1,3-cycloheptadiene (Scheme 37)³³⁹. Other carbocycles which



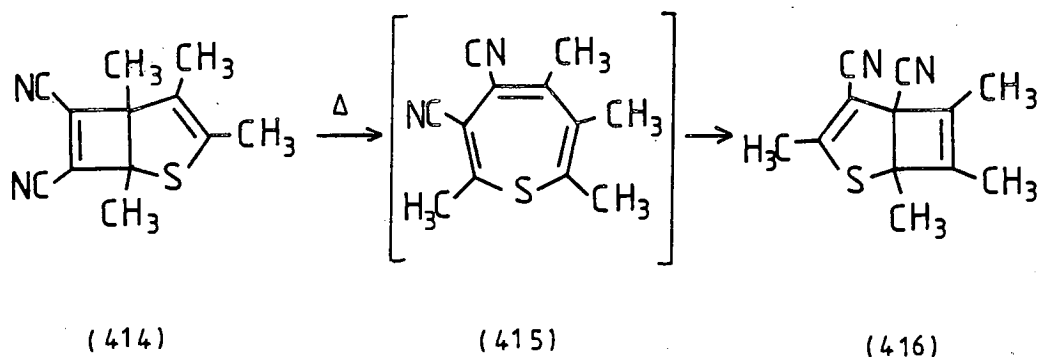
undergo the same reaction are (407) and (408)³⁴⁰ as well as the diene (409)^{339,341}. A variety of 2-hetero-substituted



molecules also undergo thermal ring-opening. These include (410)³³⁷ and (411)³⁴² and also the di-unsaturated compounds (412) and (413)³³⁸. Ring opening has also recently been observed indirectly in the 2-thia system (414)³⁴³ which was found

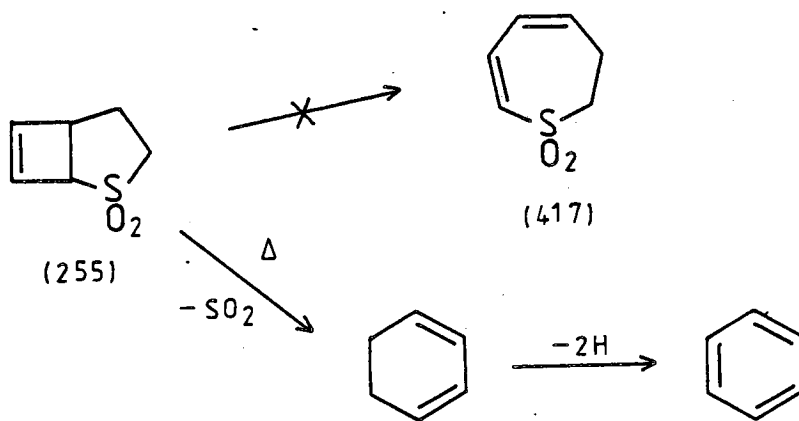


to isomerise in boiling xylene to the product (416), apparently



via the thiopyne (415).

In view of these results it seemed likely that (255) might undergo electrocyclic ring opening to 2,3-dihydrothiopyne dioxide (417), however pyrolysis of (255) at 450°C

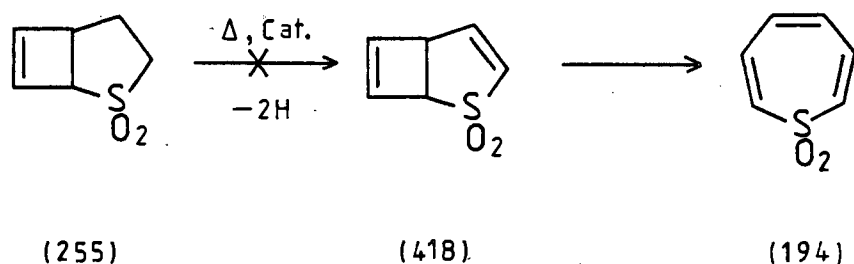


Scheme 38

resulted in loss of SO₂ to give mainly 1,3-cyclohexadiene which under the reaction conditions is partly aromatised to benzene (Scheme 38). It is of course possible that (417) is formed initially, but then loses SO₂ to give cyclohexadiene. However this pathway is unlikely since even the isomeric 2,7-dihydrothiopyne dioxides, which have a concerted pathway for SO₂ loss, require temperatures up to 290°C under g.l.c. conditions for

extrusion to take place¹⁵².

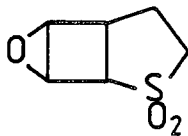
It was envisaged that dehydrogenation of (255) to (418) might facilitate ring-opening and thus produce thiepine dioxide (194) as shown in Scheme 39. However, treatment of



Scheme 39

(255) with 10% Pd/C gave no reaction even on heating at temperatures up to 200°C (solution in hexachlorobutadiene) for many hours. An attempt to bring about ring-expansion by treatment with silver perchlorate was likewise unsuccessful, the starting material being recovered unchanged.

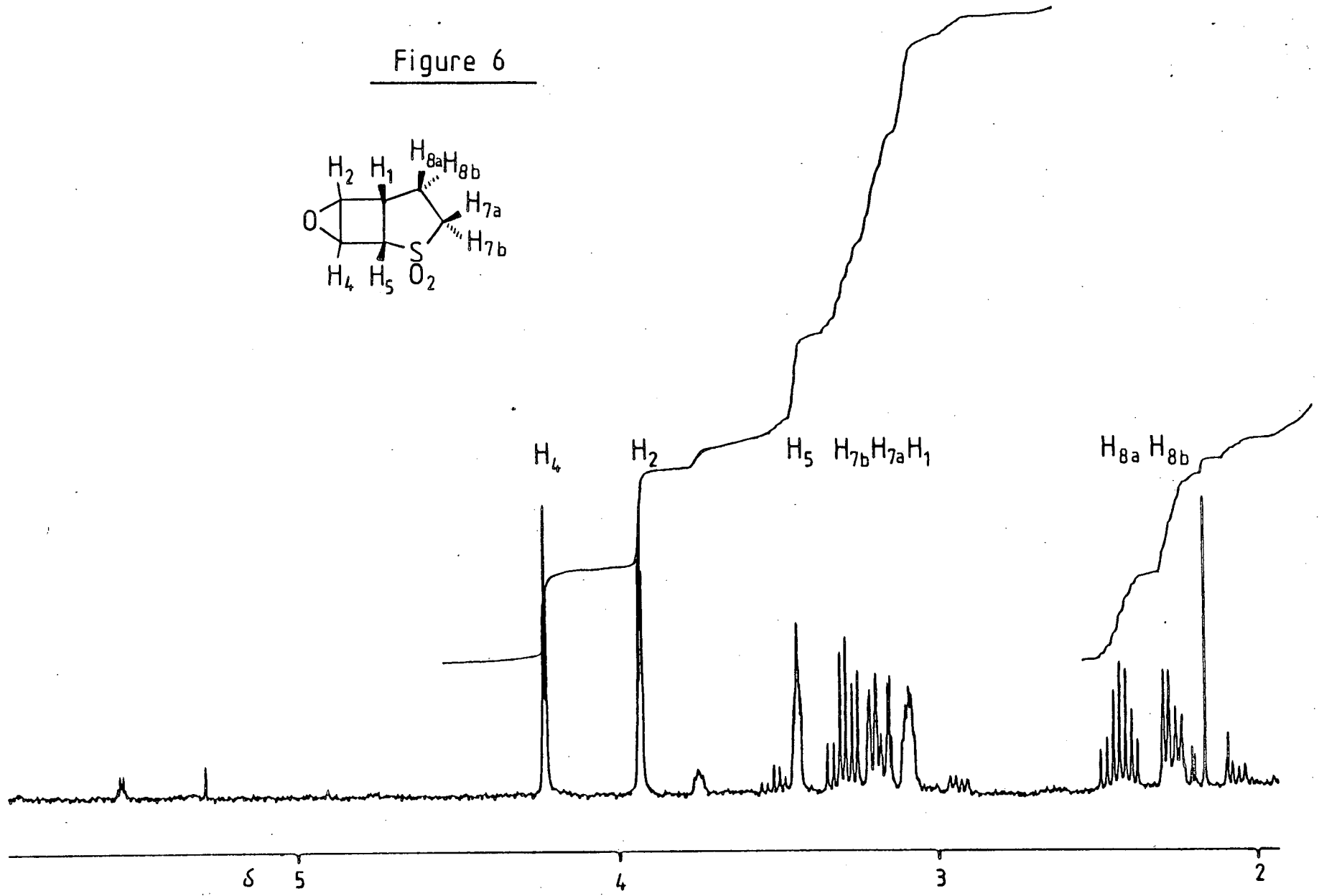
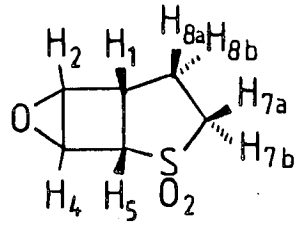
Oxidation of (255) with performic acid at 60°C gave the epoxide (419) in reasonable yield as a colourless solid.



(419)

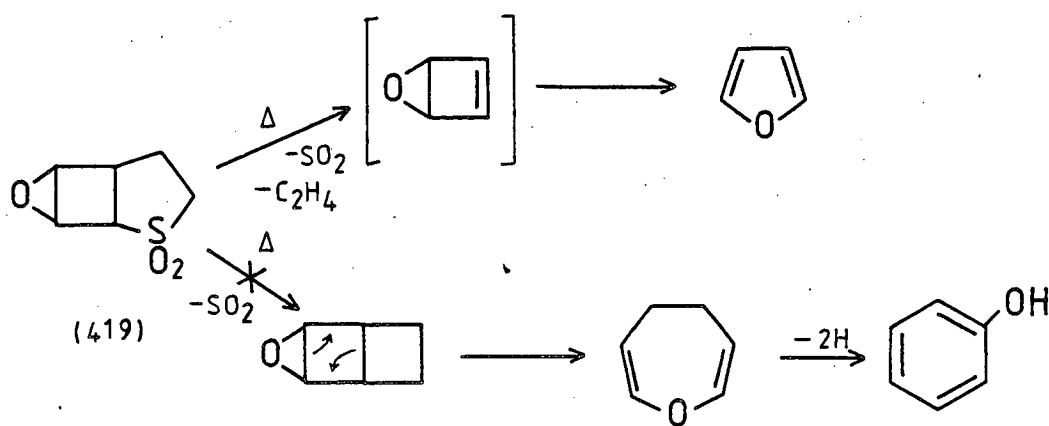
This compound showed the expected analytical and spectroscopic properties including the characteristic IR absorptions at 1320 and 1140 cm^{-1} due to the sulphone group. The ^1H NMR spectrum (Figure 6) showed a pattern which was remarkably similar to

Figure 6



that of the alkene (255), the main difference being that the olefinic protons at δ 6.33 and 6.22 are now replaced by the epoxide protons at δ 4.23 and 3.93 and that the H_1 signal is now upfield of H_{7a} and H_{7b} . Apart from this, many of the coupling constants were identical to those for (255). It is interesting to note that the molecular ion of (419) does not appear in the mass spectrum; the highest peak is at m/e 119 and the base peak is at m/e 68 corresponding to furan.

Pyrolysis of (419) could result in either loss of SO_2 and ethylene to give furan, or in loss of only SO_2 to give eventually phenol (Scheme 40). In fact, it was the former

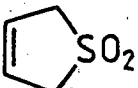
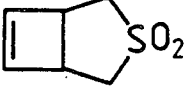
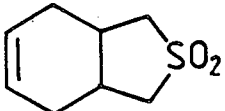
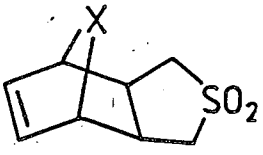
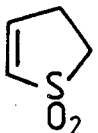
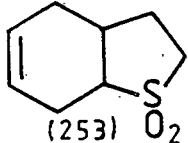
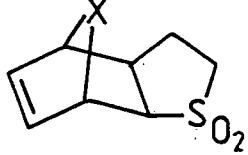


Scheme 40

process which occurred. Thus, at $550^\circ C$, little fragmentation occurred but, based on the reacted starting material, a high yield of furan was obtained and identified by NMR and GC. To date, this is the first example of the novel alkene (255) acting as a cyclobutadiene synthon and it seems reasonable to conclude that the addition of 1,3-dipoles and mononuclear electrophilic species to its double bond followed by extrusion of SO_2 and ethylene might provide a good synthetic method for a wide range of five- and seven-membered heterocycles.

Appendix A - Photoelectron Spectra

The He (I) photoelectron spectra of butadiene sulphone, 2,3-dihydrothiophen 1,1-dioxide and compounds (250), (251), (296; X=CH₂, CH₂CH₂ and O), (253), and (330; X=CH₂ and CH₂CH₂) prepared by the author, were obtained by Dr. M.H.Palmer and Miss I. Simpson. The first three ionisation energies for each compound, assigned in each case to $\pi(\text{C}=\text{C})$, $\pi(\text{SO}_2)$ and $n(\text{SO}_2)$ respectively, are given below³⁰³.

<u>Compound</u>	<u>Ionisation Energy (eV)</u>			
	10.35	10.85	11.32	
 (250)	10.25	10.40	11.25	
 (251)	9.69	10.10	11.20	
 (296)	X=CH ₂	9.60	10.15	11.00
	X=CH ₂ CH ₂	9.75	10.40	10.99
	X=O	9.83	(not determined)	
 (253)	10.28	10.56	11.43	
 (253)	9.59	10.00	11.50	
 (330)	X=CH ₂	9.55	10.00	11.05
	X=CH ₂ CH ₂	9.80	10.40	11.10

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