GAS-PHASE PYROLYSES OF 3-THIABICYCLO[3.2.0]-HEPTANE 3,3-DIOXIDE, RING SYSTEMS

by

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Thesis presented for the degree of

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Dedication

To the memory of my parents, Patrick and Margaret McLaughlin.
DECLARATION

I declare that this thesis is my own composition, that the work of which it is a record has been carried out by myself, and that it has not been submitted in any previous application for a Higher Degree.

The thesis describes results of research carried out in the Department of Chemistry, University of Edinburgh, under the supervision of Professor J. I. G. Cadogan since the 1st of October 1977, the date of my admission as a research student.

POST-GRADUATE COURSES

The following is a statement of post-graduate courses attended during the last three years.

Lab 29 Seminars

"Strategy of Organic Synthesis"

"Chemistry at its most Colourful"

"Basic and Advanced Stereochemistry"

"Flash Vacuum Pyrolysis"

"The Bio-Organic Chemistry of Drugs, Toxins and other Xenobiotics"

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L. McLaughlin
ABSTRACT

The flash vacuum pyrolysis of 3, 5-dioxo-4-oxa-9-thiatricyclo-[5.3.0.0_{2,6}]decane 9, 9-dioxide and its derivatives has been extensively investigated. Under these conditions, it is found that cheletropic elimination of SO2 occurs leading to the formation of novel 1, 2-divinylcyclopentane compounds. In all cases the reaction is stereospecific and yielded only cis-isomers which are not prone to Cope rearrangement.

On oxidative bis-decarboxylation 3, 5-dioxo-4-oxa-9-thiatricyclo-[5.3.0.0_{2,6}]decane 9, 9-dioxide is converted into the novel synthon 3-thiabicyclo[3.2.0]hept-6-ene 3, 3-dioxide. It is shown that although the reaction is sluggish epoxidation of this alkene and subsequent pyrolysis provides a worthwhile synthesis to 4, 5-dihydrooxepin in good yield. Attempts to obtain suitable precursors to the carbon and nitrogen analogues of 4, 5-dihydrooxepin by addition of carbenes and nitrenes to 3-thiabicyclo[3.2.0]hept-6-ene 3, 3-dioxide failed as the alkene did not react with these species.

3-Thiabicyclo[3.2.0]hept-6-ene 3, 3-dioxide is also observed to undergo cycloaddition reactions with a variety 1, 3-dipoles including nitrile oxides, nitrones and diazo compounds, to give precursors of other new cis-1, 2-divinyl heterocycles, difficult to prepare by other methods. In the case of the less reactive diphenyl nitrilimine no addition product could be detected. An attempt to prepare the precursor of 1, 4-cycloheptadiene indirectly by addition of diazomethane to the
alkene was also unsuccessful; extrusion of nitrogen by photolysis from the derived adduct gave unidentified products.

$^1$H n.m.r. and $^{13}$C n.m.r. spectroscopy were used extensively to determine the structure of the products and in two cases X-ray analysis was used to confirm assigned structures.
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INTRODUCTION

Preamble

Elemental sulphur has been known since ancient times, yet research on the element and its compounds continues apace. The first organosulphur compound to be prepared was ethanethiol in 1834.1 Sulphones, the major topic of this thesis, were first prepared in 1867.2 3,5-Dioxo-4-oxa-9-thiatricyclo[5.3.0.0^2,6]decane 9,9-dioxide (1) was first reported in the literature in 1972.3 The molecule was recognised to have potential for divinyl synthesis and considered to merit further investigation. This thesis describes the results of the study.

Sections A.1, A.2 and A.3 focus attention on the properties, preparation and reactions of sulphones in general. Cheletropic reactions involving sulphur dioxide formed a major part of the study and will be considered separately in section B. Cope, and to a lesser extent the Claisen, rearrangements, featured in the study and so will be introduced in section C. Finally section D will focus on the programme of research.
A. Sulphones

A.1 General properties of sulphones.

The sulphone group has been known for more than a century but it is only in the last few decades that a more diverse range of chemistry has been discovered. The past fifteen years in particular have witnessed many publications both of a theoretical nature and involving synthetic applications of sulphones. Both these aspects of sulphone chemistry have been reviewed.\(^4,\,^5\)

The sulphone group is represented by the general formula (2) in which the substituents \(R\) and \(R'\) can be any combination of alkyl, vinyl, alkylnyl or aryl.

\[ R-S-R' \]

The sulphur-oxygen bonds are polar giving rise to a large dipole moment relative to the analogous ketones \((\text{CH}_3\text{SO}_2\text{CH}_3, 3.22\text{D}; \text{CH}_3\text{COCH}_3, 2.88\text{D})\).\(^6\) This polarity manifests itself in the physical properties of sulphones. They occur as either solids or high boiling point liquids.

The presence of a sulphone function in a molecule is most easily ascertained by infrared spectroscopy. All sulphones show strong bands in the 1300-1320 and 1140-1160 cm\(^{-1}\) regions due to the asymmetric stretching modes of the \(\text{SO}_2\) group.\(^7,\,^8\) On the other hand proton n.m.r. spectroscopy is of lesser diagnostic value. Aliphatic hydrogens \(\alpha\) to a sulphone function are generally found in the range 2.5-3.15; typical examples being \(\text{CH}_3\text{SO}_2\text{CH}_3, 3.03\text{D}\) and \(\text{CH}_2=\text{CHSO}_2\text{CH}_3, 2.62\text{D}\).\(^9\)

Typically sulphones exhibit high chemical and thermal stability,
and this would tend to suggest a lack of ready manipulation. That this is not the case is testified by recent reviews on sulphone chemistry.\(^4, 5, 10-12\) The sulphone group is fully oxidised and is reduced to the sulphide only with great difficulty.\(^13\) A sulphone group can be removed and replaced by hydrogen using Raney Nickel,\(^14\) Li in diethylamine,\(^15\) or 6% Na/Hg in methanol using Na\(_2\)HPO\(_4\) as buffer.\(^16\)

The chemistry of sulphones can be broadly classified into two areas: (i) those reactions in which the sulphone functional group is a particularly stable unit surviving a large number of transformations, and (ii) those reactions which rely on the disruption and elimination of the sulphone group.

This discussion will focus attention on the latter as these reactions are central to the theme of the thesis.

A. 2 Preparation of sulphones.

a) Oxidation of sulphides and sulfoxides.

The most common method of sulphone preparation is the direct oxidation of sulphides and sulfoxides. A variety of oxidising agents have been utilized to effect these transformations. An extensive tabulation of the experimental results for these processes is available.\(^17\)

The most commonly used oxidant is hydrogen peroxide (30%) in acetic acid (Scheme 1). This method gives excellent yields.\(^18\)

\[
\begin{align*}
\text{C}_6\text{H}_5\text{CH}_2\text{S} & \quad \text{C}_2\text{H}_5 \\
\text{H}_2\text{O}_2 & \quad \text{HOAc} \\
\text{C}_6\text{H}_5\text{CH}_2\text{SO}_2 & \quad \text{C}_2\text{H}_5 \\
80^\circ & \quad 87\%
\end{align*}
\]

Scheme 1

\(m\)-Chloroperbenzoic acid in various organic solvents has also been
used and in general is a very effective reagent giving clean products in high yield. 

b) Aromatic sulphonylation.

The reaction between an arene and a sulphonyl halide in the presence of a suitable Lewis acid constitutes an excellent route to diaryl or alkyl-aryl sulphones (Scheme 2). Sulphonyl chlorides are commonly employed although sulphonyl bromides and fluorides have also been used. Generally, the reaction gives better yields in the case of arenesulphonyl chlorides.

\[
\text{RSO}_2\text{Cl} + \text{C}_6\text{H}_6 \xrightarrow{\text{AlCl}_3} \text{RSO}_2\text{C}_6\text{H}_5
\]

\[
\begin{align*}
\text{R} &= \text{CH}_3 & \text{80\%} \\
\text{R} &= \text{C}_6\text{H}_5 & \text{90\%}
\end{align*}
\]

Scheme 2

been used. Generally, the reaction gives better yields in the case of arenesulphonyl chlorides.

c) Alkylation of sulphinic acids.

This method of preparing sulphones has been known for about eighty years, but has gained importance only relatively recently mainly in connection with the alkylation of the more accessible and stable aromatic sulphinic acids with reactive halides.

d) Cycloaddition reactions of sulphur dioxide with polyenes.

The addition of sulphur dioxide to polyenes as a route to sulphones is only of moderate importance. However, since their classification as \(\pi 4_s + \pi 2_s\) cheletropic transformations, there has been a tremendous upsurge of interest in these reactions. For this reason and since these cycloadditions are central to the theme of this discussion they will be discussed at length in section B.
A. 3 **Reactions of sulphones.**

a) **The Ramberg-Bäcklund reaction**

When an α-halosulphone (3) bearing an α'-hydrogen is treated with base the resultant carbanion (4) is capable of intramolecular 1, 3-elimination to give an alkene (6) in which the position of the double bond is unambiguous (Scheme 3). This extrusion process is known as the Ramberg-Bäcklund reaction after its discoverers. A recent review is available.

\[
\begin{align*}
H-C_{\alpha'}SO_2\alpha \quad + \quad BH & \quad \rightleftharpoons \quad BH + C_{\alpha'}SO_2\alpha \\
(3) \quad & \quad \rightleftharpoons \quad (4) \\
\quad \text{Fast} & \quad \downarrow \quad \text{Slow} \\
\quad \text{Scheme 3} \\
& \quad \Rightarrow \quad \text{C} \quad + \quad X^- \\
& \quad \text{SO}_2 \\
& \quad \text{(6)} \\
& \quad \text{(5)}
\end{align*}
\]

To date the postulated episulphone intermediates (5) have not been isolated although they have been prepared by other routes. When episulphones of the type (5) are treated with base the expected alkene is obtained. The sulphur dioxide loss is markedly stereospecific. Consequently the stereochemistry of the alkene is determined at the ring-closure stage.

The formation of the anion (4) in the proposed reaction mechanism, has been intensively investigated by Paquette and Bordwell and their co-workers. Anion formation occurs at both the α and α' positions in a
reversible manner and does so more rapidly than episulphone formation. This has been demonstrated by the incorporation of deuterium in un-reacted starting material if the reaction is carried out in D$_2$O and by the isolation of deuterated alkenes under similar conditions. This gives the Ramberg-Bäcklund reaction an advantage in alkene synthesis where one wishes to prepare alkenes in which the alkene hydrogens are replaced by deuterium. One simply has to conduct the reaction in deuterated solvents. A typical example is shown in Scheme 4.

![Scheme 4](image)

As other methods of alkene synthesis are now available the importance of the reaction has declined, but it still retains usefulness as a route to stained carbocycles such as (7) (Scheme 5).

![Scheme 5](image)
Meyers et al.\textsuperscript{33} have shown that the need to prepare α-halosulphones in a separate step can be circumvented by treating a sulphone (containing both α and α' hydrogens) with tetrachloromethane in t-butyl alcohol. This gives rise to \textit{in situ} Ramberg-Bäcklund reactions. A typical example is shown (Scheme 6). A drawback to this reaction is that dichlorocarbene is sometimes generated concomitantly and may react subsequently with the desired alkene to form a dichlorocyclopropane.

\begin{equation}
(\text{PhCH}_2)_2 \text{SO}_2 \xrightarrow{\text{KOH, CCl}_4, \text{t-C}_4\text{H}_9\text{OH}} \text{trans-PhCH}=\text{C}=\text{PhH} 100\%
\end{equation}

\textbf{Scheme 6}

b) \textbf{Reduction of sulphones.}

Sulphones are resistant to most reducing agents. In attempts to reduce sulphones using LiAlH\textsubscript{4} Bordwell and McKellin\textsuperscript{13} found that four or five membered ring species gave the corresponding sulphides whereas six-membered rings and acyclic sulphones were either inert or reduced to only a small extent. More recently Gardner and his co-workers\textsuperscript{34} have shown that di-isobutylaluminium hydride (Dibal-H) in ether or THF is an effective reagent for the reduction of sulphones to sulphides. The general reaction is shown in Scheme 7.

\begin{equation}
\text{R R'}\text{SO}_2 + 2(\text{C}_4\text{H}_9)_2\text{AlH} \xrightarrow{\text{PhCH}} \text{R R'}\text{S} + 2(\text{C}_4\text{H}_9)_2\text{AlOH}
\end{equation}

- \text{R=R'=} \ \text{n-propyl} \quad \text{yield} = 77\%
- \text{R=R'=} \ \text{n-butyl} \quad \text{yield} = 68\%
- \text{R=R'=} \ \text{phenyl} \quad \text{yield} = 57\%
- \text{R=Me, R'=} \ \text{phenyl} \quad \text{yield} = 61\%

\textbf{Scheme 7}
Paquette and Photis have reported an interesting reductive elimination of cyclic sulphones (8) and (10) leading to the formation of substituted cyclobutenes (9) and (11) (Scheme 8). This conversion is formally similar to the Ramberg-Bäcklund reaction discussed in the previous section.

\[
\text{Me}_{2}S_{2} \xrightarrow{\text{MeLi, BuLi}} \text{Me}_{2}S_{2} \xrightarrow{\text{LiAlH}_{4}, \text{dioxane}, \Delta} \text{Me}_{2}C_{4}
\]

\[
(8) \quad (9) \quad 20\%
\]

\[
(10) \quad (11) \quad 22\%
\]

**Scheme 8**

c) **Thermal and photochemical extrusion of sulphur dioxide.**

Cyclic sulphones containing structural elements such as aromatic rings, functional groups, heteroatoms and further \(SO_{2}\)-groups as ring members decompose on heating with loss of \(SO_{2}\) and formation of new C-C bonds. The importance of this reaction as synthetic method has recently been reviewed. Cheletropic extrusion of \(SO_{2}\) from sulpholenes are discussed in more detail in section B.

Smith and co-workers have reported that photolysis of the sulphones (12) give 1-substituted phenylcyclopropanes (13) in high yield (Scheme 9).
$R=H, \text{CH}_3, \text{C}_2\text{H}_5, \text{PhCH}_2, \text{or CH}_2=\text{CH-CH}_2$

Scheme 9
B. Cheletropic Reactions

B.1 Introduction

In 1969 Woodward and Hoffmann defined a cheletropic reaction as a process in which two bonds which terminate at a single atom are made or broken in concert. Cheletropic reactions are really a sub-class of cycloadditions, the only difference being that on one of the components both new bonds are being made to the same atom.

The dissociation of (14) to give a molecule Xyz (16) and a polyene containing an m-electron π-system (15) is an example of a cheletropic reaction (Scheme 10). Xyz is usually a small inorganic molecule of high thermodynamic stability, e.g., CO, N₂, SO₂ or N₂O.

Scheme 10

In order to gain insight into the stereochemical features of the cheletropic reaction one must consider the general reaction in which the substrate (17) carries substituents a at the atoms C₁ and Cₘ (Scheme 11). The major stereochemical features of this process

Scheme 11
which require consideration are:

(i) The nature of the concerted rotations that must occur about $C_1$ and $C_m$ in order to bring the substituents $a$ into the 'plane' of the polyene molecule (18) as it is formed.

(ii) The relative dispositions of the polyene (18) and Xyz when the bond breaking process is complete (forward reaction) or bond formation commences (reverse reaction).

(iii) The nature of the orbitals utilized by Xyz.

In case (i) there are only two distinguishable rotation modes viz. conrotation and disrotation. Each mode has two formal possibilities and hence there are four possible polyenic products when the substituents $a$ are all different. However usually the steric constraints imposed by the substituents $a$ dictate that one mode of disrotation or conrotation is preferred over the other and so only one mode operates.

In case (ii) analysis of the pertinent molecular orbital interactions show that two distinct reaction pathways are possible. The pathways have been categorized as either linear (the least motion path) or non-linear (non-least motion path). In this respect Woodward and Hoffmann recognised that there is mechanistic ambiguity for cheletropic reactions, in that the scission (or formation) of a pair of bonds at one atom means that the stereochemical imprint of the transition state for that moiety will be absent in the product. Thus there is no experimental procedure which allows distinction between linear and non-linear cheletropic reactions and so interpretations of this nature are purely theoretical.

In case (iii) the molecule $Xyz$, e.g. $SO_2$, $N_2$, or CO can be
considered to utilize a filled sp\textsuperscript{n} orbital and an empty p-orbital for bonding purposes.

Finally since cheletropic reactions are pericyclic changes they are governed by the general orbital symmetry control rule for such processes which is:

A ground state pericyclic change is symmetry-allowed when the total number of \((4q+2)_s\) and \((4r)_a\) components is odd.

B. 2 Theory of cheletropic extrusion of SO\textsubscript{2} from sulpholenes.

The term sulpholene has been used\textsuperscript{4} generically to describe sulphones which may be considered as cheletropic adducts of SO\textsubscript{2} and a (poly)alkene, e.g. butadiene and hexatriene. Loss of SO\textsubscript{2} from sulpholenes has been analysed from a theoretical viewpoint by workers using a number of different approaches.\textsuperscript{21, 37, 38} The frontier orbital approach of Gilchrist and Storr\textsuperscript{37} will be used in the present discussion.

According to frontier orbital theory, the overriding factor in determining the selection rules for polyene cycloaddition is the symmetry of the HOMO (highest occupied molecular orbital) and the LUMO (lowest unoccupied molecular orbital) of the reactants. This is in turn related to the number of electrons involved in each of the reactants. Any component other than a neutral polyene which can supply the same number of electrons in an orbital of the same symmetry is potentially able to participate in a cycloaddition in place of a polyene. Sulphur dioxide is just such a component.
Sulphur dioxide (19) has a lone pair of electrons in the plane of the molecule and a vacant p orbital orthogonal to it. Thus when considering cheletropic extrusion reactions of sulpholenes one considers the interaction of the HOMO (lone pair orbital) of sulphur dioxide with the LUMO of the alkene as well as the LUMO (vacant p orbital) of sulphur dioxide with the HOMO of the alkene.

Mock\textsuperscript{39} has extensively investigated the family of cheletropic extrusions which are now to be considered (Scheme 12).

\begin{align*}
\text{SO}_2 & \rightarrow \text{HOMO} \rightarrow \text{LUMO} \rightarrow \text{SO}_2 \\
\text{(20)}
\end{align*}

\begin{align*}
\text{SO}_2 & \rightleftharpoons \text{C} + \text{SO}_2 \\
\text{(21)}
\end{align*}

\begin{align*}
\text{SO}_2 & \rightleftharpoons \text{C} + \text{SO}_2 \\
\text{(22)}
\end{align*}

Scheme 12
First consider fragmentation of the episulphone (20), the orbital representations of which are shown in figure 1 and figure 2, for the linear and non-linear reaction pathways respectively.

![Diagram of orbital representations](image)

**Fig. 1.** The linear approach of SO\(_2\) to an alkene

![Diagram of orbital representations](image)

**Fig. 2.** The non-linear approach of SO\(_2\) to an alkene

Thus as shown in Figure 1 a concerted suprafacial, suprafacial \(\pi^2_s + \pi^2_a\) interaction is a disallowed process. For the reaction to be concerted the sulphur dioxide must depart (or approach) in an antarafacial manner as illustrated in Figure 2, an interaction described as a \(\pi^2_s + \pi^2_a\) process.

The best known of this family of reactions is undoubtedly the reversible formation of butadiene sulphone (21) from butadiene and sulphur dioxide. The relevant orbital representation of the reaction is shown in Figure 3.
The reaction proceeds via an allowed linear pathway described as a \( \pi_4^+ + \sigma_2^- \) process (or a \( \pi_2^+ + \sigma_2^+ + \sigma_2^- \) cycloreversion). A point to note is that good overlap of the interacting orbitals requires the terminal carbons on butadiene to rotate in a disrotatory sense.

The concerted fragmentation of 2,7-dihydrothiepin 1,1-dioxide (22) could formally be either a linear or a non-linear cheletropic reaction. Symmetry considerations require that the thermal \( \pi_6^+ + \sigma_2^- \) process be suprafacial, antarafacial. If the sulphur dioxide is the suprafacial component, it is a \( \pi_6^+ + \sigma_2^- \) linear cheletropic reaction and the triene must rotate in a conrotatory sense as illustrated in Figure 4a; if the sulphur dioxide is the antarafacial component, it is a \( \pi_6^+ + \sigma_2^- \) non-linear cheletropic process and the triene must rotate in a disrotatory sense as illustrated in Figure 4b.
Gilchrist and Storr\textsuperscript{37} have summarized the selection rules for cheletropic reactions as follows:

(a) Linear cheletropic reactions in which the polyene is a suprafacial component (i.e., involving distrotatory motion of the terminal carbons) are allowed for a total of $(4n+2)$ electrons.

(b) Linear cheletropic reactions in which the polyene is an antarafacial component (i.e., conrotatory motion of the termini) are allowed for a total of $4n$ electrons. The rules for the non-linear cheletropic reaction are the reverse of these.

The rules for photochemical extrusion are the reverse of those for thermal extrusion.

Fig. 4  
(a) Linear and antarafacial on the triene
(b) Non-linear and suprafacial on the triene.
B. 3 Stereochemistry, kinetics and mechanism of sulpholene and sulpholane extrusion reactions.

This section details the experimental observations which fit the theory discussed in section B. 2.

The decomposition of the substituted episulphone (23) is stereospecific and cleanly suprafacial with respect to the alkene (24) (Scheme 13).\(^{39,40}\) However a \(\pi^2_s\,\pi^2_a\) process is disallowed (see fig. 1) and so if the reaction is to be concerted the sulphur dioxide must depart in an antarafacial manner (see fig. 2) to give a \(\pi^2_s\,\pi^2_a\) process. However this is only a rationalization of the observed stereospecificity, not a proven mechanism.

Mock\(^{39}\) has suggested that the non-linear reaction path for episulphone fragmentation (Scheme 14a), can be readily accommodated by sequential bond cleavage (Scheme 14b). In the two-step mechanism in order to explain the observed stereospecificity it is necessary and sufficient that dissociation of the dipolar intermediate be more rapid than the internal rotation of a bond. It is pertinent to point out that,
on more than one occasion, doubts have been expressed\textsuperscript{4, 41} about the applicability of the selection rules to episulphone fragmentations.

An alternative mechanism involving ring expansion to a four membered ring isomer has also been suggested.\textsuperscript{5}

Kinetic studies involving episulphone fragmentations are not very informative since ring strain plays an important part in the rate of the reaction and thus clouds the effect of orbital symmetry constraints.\textsuperscript{4}

The mechanism of episulphone fragmentation is thus still open to question.

The thermal extrusion of sulphur dioxide from substituted 2, 5-dihydrothiophene 1, 1-dioxides (25) has been extensively investigated\textsuperscript{39, 42-44} and shown to be cleanly suprafacial with respect to the incipient diene (26) (Scheme 15). The reaction has been suggested\textsuperscript{39} to proceed via the transition state (27), a linear concerted process, described as a
Scheme 15

retro-[π4 σπ2 ] process in keeping with the orbital symmetry predictions previously discussed in section B.2. However Mock has alluded to the fact that this is a "nonrisky orbital symmetry prediction" as other possible transition states which have been suggested suffer from unfavourable ring strain considerations. Thus once again the conclusion that one is getting stereoelectronic control is somewhat tentative.

From kinetic studies it has been concluded that substituents in the parent sulphone do not affect the rate as much as might be expected for ionic or radical mechanisms. Aşperger et al. have examined secondary deuterium isotope effect and the primary S isotope effect on the kinetics of thermal decomposition of substituted butadiene sulphones. The results obtained give support to a concerted mechanism.
Recently Hogeveen and co-workers have reported that addition of sulphur dioxide to the diene (28) at or below room temperature led to the formation of the sulphinic ester (29) which immediately rearranged preferentially to an aromatic ester (30) (90%) and to the sulphone (31) (10%) (Scheme 16). The thermal rearrangement to the sulphone was shown to proceed via a retro-Diels-Alder reaction. Thus five-membered ring sulphones and six-membered ring sulphinate esters from the cycloaddition of sulphur dioxide to 1,3-dienes may represent the thermodynamically and kinetically controlled products respectively.

Mock et al. have also investigated the reversible formation of 2,7-dihydrothiepin 1,1-dioxide from $SO_2$ and cis-1,3,5-hexatriene. In contrast to the five-membered ring analogue, decomposition of (32) preferentially proceeded antarafacially with respect to the triene fragment (33) (Scheme 17), the stereochemistry of which is in accord with the reaction pathway being a linear concerted process; this signifies a retro-$\pi^6_a + \omega^2_s$ process, involving a transition state (34).
Scheme 16

\[ \text{SO}_2 + (28) \xrightarrow{20^\circ\text{C}} (29) \]

\[ (28) \xleftrightarrow{20^\circ\text{C}} (29) \]

\[ (29) \xrightarrow{20^\circ\text{C}} (30) \]

\[ (30) \xrightarrow{90\%} \]

\[ (31) \xrightarrow{10\%} \]
Notwithstanding these conclusions it is of interest to note that an analysis of steric considerations\textsuperscript{39, 51} shows that bond-angle deformations and non-bonded interactions are sufficient to explain the observed stereospecificities without the need to invoke orbital symmetry constraints.

Interestingly the sulpholenes (32) could not be prepared by addition of sulphur dioxide to the appropriately substituted triene\textsuperscript{51}. A thorough investigation\textsuperscript{52} of this reaction further established that in some cases 1, 4-addition of sulphur dioxide could compete effectively with 1, 6-addition, depending on the nature of the triene. A typical example is provided by the reaction of SO\textsubscript{2} with the hydrocarbon (35) to give the
sulphone (36) (Scheme 18). 52

Scheme 18

Kinetic data for the extrusion of sulphur dioxide from the parent compound viz. 2, 7-dihydrothiepin 1, 1-dioxide (32, \( R_1, R_2, R_3 = H \))^45 showed that the rate of decomposition was almost identical to that for butadiene sulphone. This observation may offer an explanation as to why the two modes of cycloaddition can effectively compete with each other.

Another classic example of 1, 4-addition of sulphur dioxide is the addition of \( \text{SO}_2 \) to 1, 3, 5-cyclooctatriene (37) to give the sulphone (38) (Scheme 19). \(^{45, 52, 53}\) In this case antarafacial addition to the triene is geometrically impossible and the alternative \( \pi^6_s \pi^2_a \) non-linear addition to the triene does not compete with concerted \( \pi^4_s \pi^2_s \) linear cheletropic addition to the diene component. Mock\(^{53}\) has converted (38) into (40) the formal 1, 6-adduct of 1, 3, 5-cyclooctatriene and sulphur dioxide by the indirect route shown in Scheme 19.

The geometry of (40) is such that the usual retro-\( [\pi^6_s \pi^2_a] \) fragmentation process is impossible. This means that the elimination if concerted would have to be a non-linear cheletropic process \( \text{i.e.} \), retro-\( [\pi^6_s \pi^2_a] \). The extreme unfavourability of the retro-\( [\pi^6_s \pi^2_a] \)
The rate of dissociation of (41a) at 125°C is identical to the rate of dissociation of butadiene sulphone under the same conditions, implying a coupling of the C-S bond scission with opening of the cyclopropane ring.
This conclusion is supported by the stability of the tricyclic sulphone (41c) under similar conditions. This inertness can be readily understood when one considers that fragmentation of (41c) in a manner directly analogous to (41a) or (41b) would produce the impossibly strained trans, trans-1,4-cycloheptadiene.

Finally it is of interest to note that fragmentation of sulfolanes (tetrahydrothiophene 1,1-dioxides) give rise to stereoisomeric mixtures of alkenes indicating that multistep mechanisms are operating in these cases.

B.4 Synthetic utility of the sulfolene reaction.

The reaction of 1,3-dienes with sulphur dioxide was first reported in 1914 by de Bruin, who reacted isoprene (43) with liquid sulphur dioxide at room temperature and obtained a pure crystalline monoadduct to which he assigned the structure (44) (Scheme 21).

Today a wide variety of synthetic processes employ the reaction and
Butadiene sulphone (21) rapidly decomposes on heating above 125 °C and can serve as an excellent small scale laboratory source of buta-1, 3-diene. For example it reacts with benzyne (45) to form 1, 4-dihydronaphthalene (46) (Scheme 22).

Since the "sulpholene reaction" is almost always reversible sulpholenes are useful intermediates for the modification, purification and storage of dienes. In general addition of sulphur dioxide to 1, 3-dienes substituted in the 1-position is inhibited. By comparison the addition to 2-substituted dienes is enhanced and it is this difference in reactivity which is exploited in using the reaction as a method of separating diene mixtures.
The main limitation of using sulpholenes as a general synthesis of dienes is that sulpholenes are usually prepared by the reverse of this reaction. This limitation has been largely overcome by the alternative synthesis of 2, 5-dihydrothiephenes (50) by McIntosh et al. from the reaction of a-mercapto ketones (47) with vinyl phosphonium salts (48) the reaction proceeding via the intermediate (49) (Scheme 23). Compounds of the type (50) can be readily oxidized to sulphones (51) which can readily be thermolysed to give dienes (52).

An elegant example of the synthetic utility of the sulpholene reaction has been provided by Nesbitt et al., who separated cis and trans isomers of the red bullworm moth sex pheromone by selective reaction with sulphur dioxide below 0°C (Scheme 24). Since only the trans-isomer reacted, the adduct (53) could be readily separated from the cis-isomer. Subsequent thermolysis of (53) then gave pure trans-diene (54).

\[
\begin{align*}
\text{SO}_2 & \quad \text{cis-diene} \\
\text{-20°C} & \\
\Delta & \quad -\text{SO}_2 \\
\end{align*}
\]

\[R = (\text{CH}_2)_8 \text{OAc}\]

Scheme 24
Scheme 23

R<sup>1</sup> = Me
R<sup>2</sup>, R<sup>3</sup> = H or Me
A synthesis which takes advantage of the ability of sulphones to readily exchange their α-hydrogens for deuterium atoms is the preparation of deuteriobutadienes (55) (Scheme 25).

![Scheme 25](image)

A synthesis which takes advantage of the unreactivity of the α-position of sulphones in free radical halogenations is the preparation of 2-bromomethyl-1,3-butadiene (57) as shown in Scheme 26. Bromination of the methyl group of the sulpholene derivative (44) by N-bromo-succinimide gave (56) thermolysis of which gave the modified diene (57) in good yield (Scheme 26). The complex mixture of bromo derivatives expected from direct bromination of isoprene (43) was thus avoided.

![Scheme 26](image)

Meyers et al. have reported that the method used for the synthesis of homoconjugated dienes (42) is capable of extension to the preparation of divinyl ethers (59) and divinyl carbamates (61) via the
heterocyclic intermediates (58) and (60) (Scheme 27).

\[
\begin{align*}
\text{(58)} & \xrightarrow{\Delta} \text{(59)} \\
\text{(21)} & \xrightarrow{N_3CO_2Et^+} \text{(60)} \xrightarrow{\Delta} \text{(61)}
\end{align*}
\]

Scheme 27

The sulpholene reaction is usually carried out in the 80-150°C temperature range. However in the case of mono or bicyclic sulphones the temperature required may be higher and this can lead to a rearrangement of the products.\textsuperscript{34,65} This problem has been circumvented by Gaoni who has reported,\textsuperscript{66} that sulphones undergo elimination of sulphur dioxide when treated with lithium aluminium hydride in ether to give dienes in good yields. The mechanism of this reaction has not yet been fully investigated.

B. 5 Photochemistry.

The photochemical extrusion of sulphur dioxide from sulpholenes is much less well studied than is the thermal reaction. Bordwell\textsuperscript{67} has reported that ultraviolet light induces decomposition of phenyl-substituted episulphones, however the experiments were not rigorous.
Saltiel and Metts \textsuperscript{68} have studied the photolysis of cis and trans dimethylsulpholene (25a and b) and whilst the reaction was not totally stereospecific, a preference for the antarafacial mode with respect to the diene was observed.
C. **The Cope and Claisen Rearrangements.**

C.1 **Introduction.**

The Cope and Claisen rearrangements both named after their discoverers \(^\text{69, 70}\) have been extensively studied and exploited for their synthetic value. The former, although less valuable than the latter in general is more relevant to the present discussion. Excellent reviews of both reactions are available \(^\text{71, 72}\) and thus attention will focus on example of direct relevance to the present discussion.

The Cope rearrangement is typified by the thermal rearrangement of biallyl compounds (62) to isomeric biallyl compounds (64) via the transition state (63) (Scheme 28). Similarly an example of a typical Claisen rearrangement is the thermal rearrangement of a vinyl allyl ether (65) to the corresponding homoallylic carbonyl compound (66) (Scheme 29).

![Scheme 28](image)

X=C\(_6\)H\(_5\); CN; CO\(_2\)CH\(_3\)

**Scheme 28**

**Scheme 29**
These transformations have been classified as [3, 3] sigmatropic rearrangements by Woodward and Hoffmann. 21

C.2 Mechanism and stereochemistry of the Cope reaction.

Various geometries are possible for the transition state (63), which can be classified according to whether each of the allyl systems interacts with the lobes of the other system on the same side (suprafacially) or on opposite sides (antarafacially). There are two possible geometries for the suprafacial, suprafacial transition states viz. the four-centre "chair-like" overlap (67) or the six centre "boat-like" overlap (68) typified by the 'degenerate' Cope rearrangement of hexa-1,5-diene as shown (Scheme 30). 74

![Diagram of Cope reaction]  
(67)

![Diagram of Cope reaction]  
(68)

Scheme 30

The chair-like arrangement (67) has been deduced to be more favourable than the "boat-like" arrangement (68) by about 25 kJ mol⁻¹. This deduction came from the work of Doering and Roth 75 in which they observed that meso-3,4-dimethyl-1,5-hexadiene (69) rearranged
almost exclusively (99.7%) to cis, trans-2,4-octadiene (70) (Scheme 31).

This stereochemistry is consistent only with a chair conformation for the transition state: as a boat conformation would give either cis, cis or trans, trans-octadiene.

![Scheme 31](Image)

The high stereospecificity and the stereopreference for the "chair-like" transition state has been further confirmed by the work of Hill and Gilman. They reported that the optically active heptal, 5-diene (71) Cope rearranged to give a mixture of two other heptal, 5-dienes (72) and (73) (Scheme 32). In this case the products

![Scheme 32](Image)

possess opposite configurations not only at the double bonds but also at the centres of asymmetry.

Various theoretical interpretations of the rearrangements based on a variety of molecular orbital approaches have been advanced. These approaches vary in elegance and complexity but they do predict
that there should be a stereopreference for the "chair-like" transition state.

One of the simpler ways of arriving at this conclusion is to consider the transition states (67) and (68) as arising from the hypothetical processes in which two allyl radicals approach each other from infinity, in parallel planes, orientated with respect to each other in a "chair-like" or in a "boat-like" fashion.

The relevant orbital interactions for the allowed "chair-like" and "boat" transition states are illustrated in Fig. 5a and Fig. 5b respectively. As will be noted the non-bonding SOMO (singly occupied

![Diagram](image)

**Fig. 5**

a) Chair transition state (suprafacial, suprafacial)

b) Boat transition state (suprafacial, suprafacial)

molecular orbital)-SOMO interaction has nothing to do with this selectivity since these MO's have a node at the central carbon atom.

In order to explain the preference for the "chair-form" transition state one has to consider the NHO (next highest occupied) and NLU (next lowest unoccupied) orbitals, which have interactions between the central p-lobes of the two allyl systems in the "boat-form" (see fig. 6b) but not in the "chair-form" (see fig. 6a). It should be emphasised that the interaction is not all that great and as examples will show the "boat" transition state is often encountered in practice.
It is pertinent to point out that the full details of the mechanism of the Cope rearrangement have not yet been fully resolved as is testified by fairly recent publications. ⁸⁰-⁸²

Finally it should be mentioned that there is a third possible allowed transition state viz, an antarafacial-antarafacial interaction of the diallyl species. Although this is not usually competitive with the other transition states one example does exist viz, the conversion of (74) to (75) (Scheme 33). ⁸³ However attempts to observe the same mechanism operating for the rearrangement of the hydrocarbon (76) failed (Scheme 34). ⁸⁴
C.3 Cope rearrangement of cis-1, 2-divinylcycloalkenes and their analogues.

The general Cope rearrangement for cis-1, 2-divinylcycloalkanes can be represented by the conversion of (77) to (79) via the transition state (78) (Scheme 35). It should be noted that in this case the chair transition state is sterically impossible and so the reaction must go via a boat transition state.

The first member of this series cis-1, 2-divinylcyclopropane (80) (n=1) is interesting in that it undergoes the Cope rearrangement to give cyclohepta-1, 4-diene (81) so readily that for many years this precluded its preparation (Scheme 36). Success was finally achieved by Brown et al. and more recently Schneider and Rau have reported
a general and convenient synthesis for cis-1, 2-dialkenylcyclopropanes.

The ease with which (80) undergoes the Cope reaction has been attributed to release of ring strain in the cyclopropane ring. However Schneider and Rau\textsuperscript{88} have reported that methyl substituents on terminal carbons of the vinyl groups have a dramatic effect on the rate of the isomerization. Indeed in the case of the hydrocarbon (82) there was no Cope rearrangement only cis-trans isomerization.

The thermal rearrangements of the heteroanalogues of divinylcyclopropane (83) to give 4, 5-dihydroheteroepins (84) have also been studied (Scheme 37). The Cope rearrangements of cis-2, 3-divinyl-oxirane (X=O),\textsuperscript{89} cis-2, 3-divinylaziridine (X=NH)\textsuperscript{90} and cis-2, 3-divinylthiirane (X=S)\textsuperscript{91} have been investigated in detail. The intermediacy of cis-2, 3-divinylthiirane 1, 1-dioxides (X=SO\textsubscript{2})\textsuperscript{92} in the synthesis of 4, 5-dihydrothiepin 1, 1-dioxides has also been reported but they have not been isolated or characterized.
The temperature necessary to induce the ring expansion of (83) to (84) increases in the order carbon, nitrogen, oxygen and sulphur. In the case of cis-2, 3-divinylthiirane sulphur extrusion, to give hexatrienes, competes with the Cope rearrangement.

Rearrangement of the corresponding trans-divinyl derivatives has also been studied and they require more vigorous conditions to rearrange apparently via diradical processes or by isomerization to the more labile cis-isomers.

Additional interest in the rearrangement of divinylcyclopropanes has arisen from the suggestion that they are possible precursors in the biosynthesis of natural products from brown algae.

The second member of the series viz. cis-1, 2-divinylcyclobutane (85) rearranges similarly to give cis-cycloocta-1, 5-diene (86) (Scheme 38), first reported by Vogel and later more fully investigated by others. The fact that the rearrangement (85) to (86) requires more vigorous conditions than for cis-1, 2-divinylcyclopropane has been suggested to be due to the lesser ring strain in the cyclobutane ring. Also it has been found by Berson and Dervan that substituents on the terminal carbons of the vinyl groups retard the rearrangement.

In contrast to the small strained ring (n=1, 2) cis-1, 2-divinylcycloalkanes the position of the equilibrium for the medium ring systems (n=3, 4, 5) is determined more by the strain energy of the Cope
rearranged product viz. the cyclic 1, 5-hexadiene systems (79) (Scheme 35), than by the strain energy of the smaller rings.

Vogel and co-workers have reported that cis, cis-1, 5-cyclo-
nonadiene (87) and cis-1, 2-divinyl cyclopentane (88) equilibrate at 220°C to form a mixture in which (88) is strongly favoured (Scheme 39).

Similarly, cis, trans-1, 5-cyclononadiene (89), which is more strained than (87), isomerizes to (88) when heated in the gas phase at 130°C (Scheme 40). The first of these reactions, i.e. (87) to (88), proceeds via the "boat" transition state while the latter goes via the "chair" transition state. It is known that at temperatures above 300°C (88) undergoes reversible cis-trans-isomerization.

The situation for the next higher homolog (n=4) viz. 1, 5-cyclo-
decadienes is similar to that just described for the 1, 5-cyclononadienes. Thus cis, trans-1, 5-cyclooctadiene (90) isomerizes quantitatively at 150°C to cis-1, 2-divinylcyclohexane (91) (Scheme 41) via a "chair" transition state. Similarly trans, trans-1, 5-cyclooctadiene (92)
isomerizes completely, via a "chair" transition state to give trans-1, 2-
divinylcyclohexane (93) (Scheme 42). This reaction has importance in the field of natural products.

An example of the rearrangement of a yet higher homolog (n=5) is provided by Subba Rao et al. Thus (94) is readily converted into (95) (Scheme 43) which as will be noted contains the trans-divinyl system.

The thermal rearrangement of trans and cis-5, 6-divinyl-cis-
cyclooctenes (96) and (98) has also been studied. It has been found that the trans-isomer (96) gives rise to trans-1, trans-5, cis-9-cyclo-
dodecatriene (97) whereas the cis-isomer (98) yields trans-1, cis-5, -
cis-9-cyclooctatriene (99) (Scheme 44). Both these processes have been attributed to Cope rearrangements involving "chair" transition states.
Thus it would appear that a crossover point has been reached (n=6) where the strain energy incurred by incorporation of the 1,5-hexadiene system in a cyclic product does not preclude the reaction taking place.

Finally it should be mentioned that there are several systems which undergo Cope rearrangement very readily and in which the products have the same structure as the starting material. The best example of multiple degeneracy is the molecule tricyclo[3.3.2.0^4,6]deca-2,7,9-triene (100) better known as bullvalene. Doering and Roth\(^{103}\) predicted that this system to be capable of a 1,209,600-fold degenerate rearrangement, the cyclopropane unit being at any three adjacent carbons (Scheme 45).
This system was first synthesized by Schröder and it was found that its $^1$H n.m.r. spectrum collapses to a sharp singlet above 100°C, indicating that under these conditions the degenerate rearrangement is sufficiently rapid for all of the C-H units in the \((\text{CH})_{10}\) system to be essentially equivalent, and they may be considered to move independently on the surface of a sphere.

C.4 Tandem Cope-Claisen rearrangement.

The only example of a Claisen rearrangement relevant to the present discussion is the recently reported first example of a tandem Cope-Claisen rearrangement. As shown in Scheme 46 (101) rearranges to (102). Here the Cope rearrangement triggers the Claisen and as the Claisen rearrangement is irreversible this serves to shift the unfavourable Cope equilibrium.

\[\begin{align*}
\text{(101)} & \xrightarrow{290°C} \text{(102)} \\
\end{align*}\]

Scheme 46
D. **Programme of Research.**

The preparation of 3, 5-dioxo-4-oxa-9-thiatricyclo[5.3.0.0^2,6]-decane 9, 9-dioxide (1) was first reported by Shaikrazieva et al.\(^3\)

It should be noted that Scharf and Korte\(^106\) had briefly reported the preparation of a very similar type of compound much earlier.

![Chemical Structure](image)

(1)

The initial publication gave details of a few chemical transformations of (1) but a notable failure was their attempt to desulphurize it.

It was against this background that the present work began. It was recognised that if the sulphur dioxide was extruded from (1) and its derivatives then this would provide a vehicle for the synthesis of various divinyl compounds. Flash vacuum pyrolysis was the technique chosen for the extrusion and as will be described this proved to be very effective and also general.

A further object of the research was to transform the anhydride moiety into a variety of heterocyclic rings and study the pyrolysis of the products. It was also recognised that conversion of (1) to its dicarboxylic acid derivative, followed by oxidative bis-decarboxylation of this diacid would give the highly interesting molecule 3-thiabicyclo-[3.2.0]hept-6-ene 3, 3-dioxide. A programme designed to investigate the reactions of this alkene with various reactive intermediate species was considered worthwhile as this was a potential route to further heterocycles.
EXPERIMENTAL

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E.1 4-Oxa-9-thiatricyclo[5.3.0.0^2,6]decane 9,9-dioxide  
   a) Dimethyl-3-thiabicyclo[3.2.0]heptane-6,7-dicarboxylate 3,3-dioxide  
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   b) 6,7-Dihydroxymethyl-3-thiabicyclo[3.2.0]-heptane 3,3-dioxide  
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   c) 4-Oxa-9-thiatricyclo[5.3.0.0^2,6]decane 9,9-dioxide  
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E.2 4,9-Dithiatricyclo[5.3.0.0^2,6]decane 4,4-dioxide  
   a) 6,7-Dimesylmethyl-3-thiabicyclo[3.2.0]-heptane 3,3-dioxide  
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   b) 4,9-Dithiatricyclo[5.3.0.0^2,6]decane 4,4-dioxide  
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E.3 9-Benzyl-4-thia-9-azatricyclo[5.3.0.0^{2,6}]decane 4,4-dioxide.
   
a) 6,7-Ditosylmethyl-3-thiabicyclo[3.2.0]-heptane 3,3-dioxide
b) 9-Benzyl-4-thia-9-azatricyclo[5.3.0.0^{2,6}]decane 4,4-dioxide

E.4 9-Phenyl-4-thia-9-azatricyclo[5.3.0.0^{2,6}]decane 4,4-dioxide.
   
a) 7-Phenylcarbamoyl-3-thiabicyclo[3.2.0]-heptane-6-carboxylic acid 3,3-dioxide
b) 9-Phenyl-8,10-dioxo-4-thia-9-azatricyclo-[5.3.0.0^{2,6}]decane 4,4-dioxide
c) 9-Phenyl-4-thia-9-azatricyclo[5.3.0.0^{2,6}]decane 4,4-dioxide.

E.5 Attempted preparation of 9-methyl-4-thia-9-azatricyclo[5.3.0.0^{2,6}]decane 4,4-dioxide
   
a) 7-Methylcarbamoyl-3-thiabicyclo[3.2.0]-heptane-6-carboxylic acid 3,3-dioxide
b) 9-Methyl-8,10-dioxo-4-thia-9-azatricyclo-[5.3.0.0^{2,6}]decane 4,4-dioxide
c) Attempted lithium aluminium hydride reduction of 9-methyl-8,10-dioxo-4-thia-9-azatricyclo-[5.3.0.0^{2,6}]decane 4,4-dioxide.
Preparation and Reactions of 3-Thiabicyclo[3.2.0]hept-6-ene 3, 3-dioxide

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

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

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

F.2 8-Oxa-4-thiatricyclo[5.1.0.0²,6]octane 4,4-dioxide

F.3 Attempted addition of carbenes to 3-thiabicyclo[3.2.0]hept-6-ene 3, 3-dioxide

F.4 Attempted addition of nitrenes to 3-thiabicyclo[3.2.0]hept-6-ene 3, 3-dioxide

a) Ethoxycarbonylnitrene

b) N-Phthalimidonitrene

F.5 Addition of 1,3-dipole to 3-thiabicyclo[3.2.0]hept-6-ene 3, 3-dioxide

a) Preparation of 1,3-dipole precursors

i) C,N-Diphenylnitrone

ii) Anisohydroxamic chloride

iii) Benzhydroxamic chloride

iv) α-Chlorobenzoylphenylhydrazone

b) 4,5-Diphenyl-3-oxa-9-thia-4-azatricyclo[5.3.0.0²,6]decane 9,9-dioxide

c) 5-(p-Methoxyphenyl)-3-oxa-9-thia-4-azatricyclo[5.3.0.0²,6]dec-4-ene 9,9-dioxide

d) 5-Phenyl-3-oxa-9-thia-4-azatricyclo[5.3.0.0²,6]dec-4-ene 9,9-dioxide
e) 4-Thia-9, 10-diazatricyclo[5. 3. 0. 0², 6]dec-9-ene 4, 4-dioxide

f) Attempted addition of diphenylnitrilimine to 3-thiabicyclo[3. 2. 0]hept-6-ene 3, 3-dioxide

G. Preparation of Divinylcyclopentane Analogues by Flash Vacuum Pyrolysis (F.V.P.)

G.1 General procedure

G.2 Pyrolysis of 3, 5-dioxo-4-oxa-9-thiatricyclo-[5. 3. 0. 0², 6]decane 9, 9-dioxide

G.3 Pyrolysis of 4-oxa-9-thiatricyclo[5. 3. 0. 0², 6]-decane 9, 9-dioxide and an alternative synthesis of the product

a) Pyrolysis

b) Alternative synthesis of cis-3, 4-divinyltetrahydrofuran

G.4 Pyrolysis of 4, 9-dithiatricyclo[5. 3. 0. 0², 6]-decane 4, 4-dioxide

G.5 Pyrolysis of 9-benzyl-4-thia-9-azatricyclo-[5. 3. 0. 0², 6]decane 4, 4-dioxide

G.6 Pyrolysis of 9-phenyl-8, 10-dioxo-4-thia-9-azatricyclo[5. 3. 0. 0², 6]decane 4, 4-dioxide

G.7 Pyrolysis of 9-phenyl-4-thia-9-azatricyclo-[5. 3. 0. 0², 6]decane 4, 4-dioxide

G.8 Pyrolysis of 9-methyl-8, 10-dioxo-4-thia-9-azatricyclo[5. 3. 0. 0², 6]decane 4, 4-dioxide
H. Pyrolysis of 3-Thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide and its Adducts

H.1 Pyrolysis of 3-thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide

H.2 Lithium aluminium hydride extrusion of sulphur dioxide from 3-thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide

H.3 Pyrolysis of 8-oxa-4-thiatricyclo[5.1.0.02,6]octane 4,4-dioxide

H.4 Pyrolysis of 5-(p-methoxyphenyl)-3-oxa-9-thia-4-azatricyclo[5.3.0.02,6]dec-4-ene 9,9-dioxide

H.5 High temperature pyrolysis of 5-(p-methoxyphenyl)-3-oxa-9-thia-4-azatricyclo[5.3.0.02,6]dec-4-ene 9,9-dioxide

H.6 Pyrolysis of 5-phenyl-3-oxa-9-thia-4-azatricyclo[5.3.0.02,6]dec-4-ene 9,9-dioxide

H.7 4-Thia-9,10-diazatricyclo[5.3.0.02,6]dec-9-ene 4,4-dioxide
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I. Miscellaneous Preparations and Pyrolyses

I. 1 Preparation of meso-1,5-hexadiene-3,4-dicarboxylic acid

I. 2 Preparation of 7-ethoxycarbonyl-3-thiabicyclo[3.2.0]heptane-1-carboxylic acid 3,3-dioxide

I. 3 Attempted vinylation of 6,7-dihydroxymethyl-3-thiabicyclo[3.2.0]heptane 3,3-dioxide

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J. X-Ray Structures and Other Structural Investigations

J. 1 Structure of 1,5-hexadiene-3,4-dicarboxylic acid

J. 2 X-Ray structure of 9-phenyl-8,10-dioxo-4-thia-9-azatricyclo[5.3.0.0\textsuperscript{2,6}]decane 4,4-dioxide

J. 3 X-Ray structure of 1-phenyl-3,4-divinylsuccinimide
A. Symbols and Abbreviations.

b. p. boiling point
m. p. melting point
I. R. infra-red
n. m. r. nuclear magnetic resonance
s; d; t; singlet; doublet; triplet;
q; m; c quartet; multiplet; complex
br. broad
J spin-spin coupling constant
δ chemical shift,
T. M. S. tetramethylsilane
M⁺ mass of molecular ion
m/e mass to charge ratio
t. l. c. thin layer chromatography
w/v weight per unit volume
w/w weight per unit weight
p. s. i. pounds per square inch
u. v. ultra violet
T. H. F. tetrahydrofuran
F. V. P. Flash vacuum pyrolysis
h; min; s; hours; minutes; seconds
mmol millimoles
B. Instrumentation and General Techniques.

Nuclear Magnetic Resonance Spectroscopy (n.m.r.).

a) Proton H n.m.r. spectra of routine samples were obtained on a Varian EM-360 (60MHz) n.m.r. spectrometer at a probe temperature of 33°C. Spectra of new compounds and decoupling studies were obtained using a Varian HA 100 (100 MHz) n.m.r. spectrometer at a probe temperature of 28°C. The HA 100 instrument was operated by Mr. J.R.A. Millar. High resolution spectra were obtained on a Varian XL-100 (100 MHz) spectrometer equipped with pulse and Fourier transform accessory and was operated by Dr. A. S. F. Boyd. 360 MHz spectra were obtained on a Bruker WH-360 n.m.r. spectrometer which was operated by Mr. L. H. Bell. Chemical shifts were recorded as delta (δ) values in parts per million from tetramethylsilane (δ = 0.00) which was used as internal reference. In a few cases where deuterated dimethyl sulphoxide was used as the n.m.r. solvent an external capillary lock of tetramethylsilane was used.

b) Carbon thirteen $^{13}$C n.m.r. spectra were obtained on a Varian CFT 20 n.m.r. spectrometer which was operated by Mr. J. R. A. Millar. The operating frequency was 25.2 MHz. The deuterium signal from the solvent was used for frequency lock, and chemical shift values were recorded in parts per million from tetramethylsilane. For all types of n.m.r. spectroscopy used, positive δ values are to low field relative to the reference.
Mass Spectrometry

Mass spectra and accurate mass measurements were obtained using an Associated Electrical Industries MS902 double focussing instrument (70eV) using a direct insertion probe. This instrument was operated by Mr. D. J. A. Thomas.

Infrared spectroscopy (i.r.)

Liquid samples were examined as thin films and solid samples as nujol mulls, both on polished sodium chloride plates, using a Perkin-Elmer 157G grating spectrometer.

Elemental Analyses

Microanalyses were carried out on a Perkin Elmer 240 Elemental Analyser by Mr. J. Grunbaum, University of Edinburgh.

Melting Points

The melting points of all new compounds were determined using a Kofler hot stage instrument and are uncorrected.

Medium Pressure Liquid Absorption Chromatography

This is a relatively new technique and a full description has been given.

The pump used was a series II micrometering pump with a mechanically activated diaphragm head, supplied by Metering Pumps Ltd., Ealing. The diaphragm was constructed of nitrile rubber faced with Teflon. The pressure was monitored using a Budenburg gauge equipped with a Nupro pressure relief valve set to open at about 80
pounds per square inch. Glass high performance liquid chromatography columns and Teflon tubing and connections were supplied by Jobling. For small separations (1 g) 1000 x 15 mm columns and 250 x 15 mm pre-columns were used and for longer separations (ca 10 g) 1000 x 25 mm columns and 250 x 25 mm pre-columns were used. Teflon to metal connections at the pump, pressure gauge and detector were made using Swagelok fittings. Columns were packed with Merck aluminium oxide ("90 active, neutral for column chromatography") or silica gel ("60, 40-60mm for column chromatography").

In most cases detection of the products was by t.l.c. but in a few cases use of a u.v. detector was possible.

A model 1521 LUV monitor, Model II detector and chart recorder, manufactured by Laboratory Data Control, Florida U.S.A., was used, the u.v. absorbance of the effluent being observed at 280 nm. The effluent was collected using a central automatic fraction collector equipped with 25 or 50 ml syphons.

Flow rates were generally adjusted to about 5 ml min⁻¹. When the alumina columns were used the solvents were 50% water saturated. This was achieved by saturating a given amount of solvent with water and then mixing this with an equivalent amount of dry solvent.

Column Chromatography

The alumina used was Laporte industries, Grade H, 100/200 mesh. B. D. H. silica gel for chromatography, 80-200 mesh was also used.

Thin-layer Chromatography (t.l.c.)

Thin layer chromatograms were obtained on 0.3 mm layers of alumina (Merck, aluminium oxide C, type 60/E) or silica gel.
(Merck, silica gel G, type 60) containing fluorescent indicator.

Components in the developed chromatograms were detected by observing the plate under u.v. light, or by reaction with iodine.

**Gas Liquid Chromatography**

A Pye 104 chromatograph with flame ionisation detector was used; all columns were 2m x 2.2mm in diameter. The carrier gas was nitrogen and the flow rates were those recommended by the manufacturer. The following stationary phases, supported on 80-100 mesh celite were employed: silicone elastomer (SE 30) and polyethylene-glycoladipate. '80-100 Chromosorb W' was used to support 30% β,β'-oxydipropionitrile.

**Flash Vacuum Pyrolysis (F.V.P.)**

The type of apparatus used was the conventional horizontal flow reactor a diagram of which is shown in Figure 7.

The inlet consisted of a pyrex tube (30 cm long x 25 mm) closed at one end and a B-24 ground glass joint at the other. The inlet tube was attached via the ground glass joint to a silica tube (30 cm x 25 mm) which was surrounded by a furnace. The products were trapped in a 'U'-tube which was surrounded by liquid nitrogen and was connected to the silica tube at the exit point of the furnace. The pressure was measured by either a McLeod or a Pirani gauge situated between the trap and the pump.

The heat required for the inlet was supplied by either a metal or glass Buchi Kugelrohr. The furnace and control box were supplied
Thermolysis tube containing silica rods

Product trap

Inlet tube

Furnace

Liquid $N_2$

Release tap

To gauge

Release tap

Pump

Fig. 7 Flash vacuum pyrolysis apparatus
by Stanton Redcroft London. The high vacuum pump and vacuum
gauge were supplied by Edwards of Crawley.

**Photolysis**

Photolysis were carried out using either 100 or 400W medium
pressure mercury lamps supplied by Applied Photophysics Ltd. London.
The filters used were either quartz or pyrex insertion wells also
supplied by Applied Photophysics. Similarly power was supplied by
an Applied Photophysics power pack of the appropriate rating depending
on the lamp being used.

The reactions were carried out under dry nitrogen and the reaction
mixture was stirred continuously.

**Solvents**

Anhydrous acetone was prepared by standing analar acetone
(2.5 litres) over anhydrous magnesium sulphate (30 g) for a minimum
of three hours. The acetone was filtered through a glass sinter and
used directly. Benzene was distilled, dried and stored over sodium
wire. Toluene was washed with sulphuric acid, sodium carbonate
solution and water, dried over magnesium sulphate, then distilled
and dried and stored over sodium wire. Pyridine was heated under
reflux over potassium hydroxide pellets for 5 h and then distilled onto
molecular sieve.

Tetrahydrofuran was dried over sodium wire, then boiled under
reflux for 5 h over calcium hydride and distilled onto molecular sieve.
The whole process was carried out under dry nitrogen.
X-Ray Crystallography

X-Ray studies were carried out by G. W. Smith, X-ray analytical laboratory B.P. Research Centre, Sunbury.
C. Nomenclature

All compounds are named in accordance with the principles laid down in the "I. U. P. A. C. 1957 and 1965 Rules." All compounds of the type (103) are named as derivatives of tricyclo[5.3.0.0^2,6]decane. The locant 1 is assigned to the bridge-head which allows the heteroatom of highest priority to be assigned the lowest number, while adhering to the principal that numbering must begin at the point which gives the longest path between bridge-heads the lowest numbers. The order of priority of the heteroatoms is O>S>N.

According to the same rules (104) and (105) are named as derivatives of bicyclo[3,2.0]heptanes and divinylcyclopentanes respectively.

\[ W=O, N, C \]
\[ X=O, S, N \]
D. Preparation of 3, 5-Dioxo-4-oxa-9-thiatricyclo[5. 3. 0. 0^2, 6]-decane 9, 9-dioxide.

This was prepared by the method of Shaikrazieva et al.\textsuperscript{3}

Irradiation of butadiene sulphone (19.0 g, 160 mmol) and maleic anhydride (20.0 g, 200 mmol) in anhydrous acetone (360 ml), at 20-25°C for 24 h, with a 400 W medium pressure mercury lamp, in a cylindrical water cooled quartz reactor gave a colourless crystalline precipitate. The precipitate was filtered off, washed with anhydrous acetone and dried in vacuo to yield 3, 5-dioxo-4-oxa-9-thiatricyclo[5. 3. 0. 0^2, 6]-decane 9, 9-dioxide (17.7 g, 51%) m. p. 292-293°C (lit.,\textsuperscript{3} 292-293°C).

\textsuperscript{1}H n. m. r. δ [(CD\textsubscript{3})\textsubscript{2}SO] 3.49-3.26 (8H, cm, 1-H, 2-H, 6-H, 7-H, 8 and 8'-H, 10 and 10'-H);

\textsuperscript{13}C n. m. r. δ [(CD\textsubscript{3})\textsubscript{2}SO] 172.98 (C=O), 52.67 (C\textsubscript{8} and C\textsubscript{10}'), 43.35 (C\textsubscript{2} and C\textsubscript{6}), 35.03 (C\textsubscript{1} and C\textsubscript{7});

Mass spectrum m/e 216 (0.6%), 198 (2), 172 (6), 108 (50), 80 (100).
E. Preparation of Precursors of 3,4-Divinylcyclopentane Analogues.

E.1 4-Oxa-9-thiatricyclo[5.3.0.0²,6]decan 9,9-dioxide.

a) Dimethyl-3-thiabicyclo[3.2.0]heptane-6,7-dicarboxylate 3,3-dioxide.

3,5-Dioxo-4-oxa-9-thiatricyclo[5.3.0.0²,6]decan 9,9-dioxide (15.0 g, 69 mmol) in analar methanol (150 ml) to which a few drops of concentrated sulphuric acid had been added, was boiled for 3 h. When cooled this solution gave a colourless crystalline product. The precipitate was filtered off and dried in vacuo to yield dimethyl-3-thiabicyclo[3.2.0]heptane-6,7-dicarboxylate 3,3-dioxide (16.4 g, 90%) m.p. 126-127°C (lit. 3 126-127°C).

¹H n.m.r. δ (CDCl₃) 3.7 (6H, s, -Me), 3.6 (4H, m, 1-H, 5-H, 6-H, 7-H), 3.2-3.1 (4H, m, 2 and 2'-H, 4 and 4'-H);
¹³C n.m.r. δ [(CD₃)₂SO] 171.92 (C=O), 53.17 (C₂ and C₄), 51.88 (-OMe), 43.00 (C₆ and C₇), 33.29 (C₁ and C₅);
Mass spectrum m/e 262 (1.4%), 231 (62), 138 (66), 99 (100).

b) 6,7-Dihydroxymethyl-3-thiabicyclo[3.2.0]heptane 3,3-dioxide.

To a suspension of lithium aluminium hydride (5.8 g, 150 mmol) in anhydrous T.H.F. (120 ml) was added dimethyl-3-thiabicyclo[3.2.0]-heptane-6,7-dicarboxylate 3,3-dioxide (10 g, 38 mmol) over a period of ½ h with stirring (mechanical). The mixture was stirred for a further 1 h at room temperature, then heated under reflux for 1 h and cooled to room temperature. The excess lithium aluminium hydride was destroyed by dropwise addition of water (7 ml), 15% sodium hydroxide solution (7 ml) and then water (21 ml). The mixture was stirred for ½ h and was then filtered to remove the inorganic salts. Removal of solvent from
the filtrate gave a yellow oil (4 g) which crystallised. The solid inorganic residue was extracted using T. H. F. (500 ml) in a Soxlet apparatus over a period of 48 h. Removal of solvent in vacuo gave a further amount of yellow oil (3.3 g) which crystallised. The two solid fractions were combined and recrystallised from T. H. F. to give a colourless crystalline solid (5.4 g, 69%) m. p. 98-100°C (lit., 75-82°C). In view of the discrepancy with the literature value the compound was characterized and shown to be the title compound.

I. r. \( \nu_{\text{max}} \) (nujol) 3500-3100 (associated-OH), 1310 (SO\(_2\)), 1255, 1150, 1050 (-OH) cm\(^{-1}\);

\(^1\)H n. m. r. \( \delta \) (TFA) 4.75-4.65 (2H, m, -OH), 4.14-4.04 (4H, m, -CH\(_2\)O-), 3.5-2.9 (8H, m, 1-H, 2 and 2'-H, 4 and 4'-H, 5-H, 6-H, 7-H);

\(^13\)C n. m. r. \( \delta \) [(CD\(_3\))\(_2\)SO] 60.50 (-CH\(_2\)O-), 54.66 (C\(_2\) and C\(_4\)), 41.56 (C\(_6\) and C\(_7\)), 33.29 (C\(_1\) and C\(_5\));

Mass spectrum m/e 170 (6.8%), 79 (79), 70 (100); (Found: C, 46.6; H, 6.8; calc. for C\(_8\)H\(_{14}\)O\(_4\)S: C, 46.6; H, 6.8%).

c) 4-Oxa-9-thiatricyclo[5.3.0.0\(^2,6\)]decane 9,9-dioxide.

Method (i)

This was prepared by the method of Culberson et al. \(^{108}\) P-Toluenesulphonyl chloride (1.5 g, 8 mmol) and 6,7-dihydroxymethyl-3-thiabicyclo[3.2.0]heptane 3,3-dioxide (1.5 g, 7 mmol) were dissolved in anhydrous pyridine (12 ml) and the mixture was stirred for 19 h. The mixture was then heated on a steam bath for 1 h and then poured onto crushed ice (50 g). The resultant mixture was neutralized with 10% hydrochloric acid. This mixture was extracted with dichloromethane (3 x 100 ml) and the extract was dried over magnesium sulphate. The
solvent was removed under reduced pressure to leave an oily liquid (5 g) which smelt strongly of pyridine. The pyridine was removed under high vacuum to leave the crude product (0.79 g). The product was purified by use of medium pressure chromatography with alumina as the packing material and dichloromethane as the eluent. A colourless crystalline compound (0.39 g) was eluted and recrystallized from dichloromethane/hexane to yield 4-oxa-9-thiatricyclo[5.3.0.0²,6]decan-9,9-dioxide (0.34 g, 26%) m.p. 129-130°C.

I.R. ν max (nujol) 1302, 1287, 1179, 1134 (SO₂), 1107, 1073 (C-O-C), 690 cm⁻¹;

¹H n.m.r. δ (CDCl₃) 3.9 (2H, d J 9.5 Hz, 3-H, 5-H), 3.45 (2H, diffuse d of d J 9.5 Hz, 4.5 Hz, 3'-H, 5'-H), 3.1 (4H, m, 1-H, 2-H, 6-H, 7-H), 2.9 (2H, m, 8-H, 10-H), 2.8 (2H, m, 8'-H, 10'-H);

¹³C n.m.r. δ (CDCl₃) 73.24 (C₃ and C₅), 54.59 (C₈ and C₁₀), 43.05 (C₂ and C₆), 36.20 (C₁ and C₇);

Mass spectrum m/e 188 (8%), 94 (60), 79 (100), 54 (78);
(Found: C, 50.80; H, 6.2; C₈H₁₂O₃S requires C, 51.05; H, 6.4%).

Method (ii)

This alternative method gave a high yield on one occasion but subsequent attempts to repeat the preparation failed.

6,7-Dihydroxymethyl-3-thiabicyclo[3.2.0]heptane 3,3-dioxide (1g, 4.9 mmol) was dissolved in dimethyl sulphoxide (10 g) and the mixture was heated at 156-166°C for 16 h. The mixture was allowed to cool, water (30 ml) was added to it, and then was extracted with dichloromethane (2 x 70 ml). The extract was washed with water (2 x 70 ml)
to remove any remaining dimethyl sulphoxide and then dried over magnesium sulphate. The solvent was removed under reduced pressure to give a colourless solid. Purification by chromatography on alumina with dichloromethane as eluent gave 4-oxa-9-thiatricyclo[5.3.0.0²,6]-decane 9,9-dioxide (0.62 g, 71%) m. p. 130°C (benzene).

Method (iii)

6,7-Dihydroxymethyl-3-thiabicyclo[3.2.0]heptane 3,3-dioxide (1 g, 4.9 mmol) was dissolved in acetone and a few drops of concentrated sulphuric acid added. The mixture was boiled under reflux for 48 h during which time it became reddish brown in colour, solvent was removed in vacuo to leave a dark brown oil which was swirled with ether to remove soluble material. The dark brown oil was then chromatographed on silica with dichloromethane:acetone 5:1 as eluent gave 4-oxa-9-thiatricyclo[5.3.0.0²,6]-decane 9,9-dioxide (0.5 g, 55%) m. p. 129-130°C.

E. 2 4,9-Dithiatricyclo[5.3.0.0²,6]-decane 4,4-dioxide.

a) 6,7-Dimesylmethyl-3-thiabicyclo[3.2.0]heptane 3,3-dioxide.

This was made by the method described in Organic Synthesis. A solution of 6,7-dihydroxymethyl-3-thiabicyclo[3.2.0]heptane 3,3-dioxide (6.54 g, 31.7 mmol) in pyridine (25 ml) was introduced to a solution of methanesulphonyl chloride (11.1 g, 97 mmol) in dry pyridine (120 ml) at such a rate that the temperature did not exceed 0°C. The mixture was stirred (mechanical) throughout the addition and then for a further 2 h during which time the temperature was kept at -5 -0°C. Then, cold, 10% hydrochloric acid (200 ml), was introduced at such a rate that the temperature of the mixture remained below 20°C. The
solid which separated was recovered by filtration and washed sequentially 
with dilute hydrochloric acid (100 ml), water (200 ml) and was then 
dried in vacuo to give a colourless crystalline solid (11.09 g). This 
solid was recrystallized from water:ethanol 1:10 to yield 6, 7-dimesyl-
methyl-3-thiabicyclo[3.2.0]heptane 3,3-dioxide (8.65 g, 75%) m. p. 190-
191.5 °C.

\[ \text{L.R.} \nu_{\text{max}} \text{(nujol)} 1333, 1295, 1175, 1141, 1105, 980, 858, 833 \]
\[ 750 \text{ cm}^{-1}; \]

\[ ^1H \text{n.m.r.} \delta [(\text{CD}_3)_2\text{SO}] 4.4-4.3 (4H, m -\text{CH}_2\text{O}^-) 3.2-2.8 (14H, \]
\[ \text{m}, 1-\text{H}, 2 \text{ and } 2'-\text{H}, 4 \text{ and } 4'-\text{H}, 5-\text{H}, 6-\text{H}, 7-\text{H}, -\text{Me}); \]

\[ ^{13}C \text{n.m.r.} \delta [(\text{CD}_3)_2\text{SO}] 69.14 (-\text{CH}_2\text{O}^-), 53.68 (\text{C}_2 \text{ and C}_4), \]
\[ 37.82 (\text{C}_6 \text{ and C}_7), 36.75 (\text{C}_1 \text{ and C}_5), 32.99 (-\text{Me}); \]

Mass spectrum m/e M+ not observed;

(Found: C, 33.24; H, 5.07; C_{10}H_{18}O_5 requires C, 33.14; H, 5.01%).

b) 4, 9-Dithiatricyclo[5.3.0.2,6]decane 4,4-dioxide.

This was prepared by a modification of the method of Auret et al. 111

6,7-Dimesylmethyl-3-thiabicyclo[3.2.0]heptane 3,3-dioxide (5 g, 13.8 
mmol) and sodium sulphide nonahydrate (9.92 g, 41.4 mmol) were 
dissolved in 1:1 aqueous ethanol (150 ml) and heated under reflux for 
4 h. The ethanol was removed under reduced pressure and the aqueous 
residue was extracted with dichloromethane (2 x 100 ml) and the extract 
was dried over anhydrous magnesium sulphate. The solvent was removed 
under vacuum to give a colourless crystalline solid (2.25 g). This was 
recrystallized from trichloromethane (precipitated with petrol) to yield 
4,9-dithiatricyclo[5.3.0.2,6]decane 4,4-dioxide (1.73 g, 62%) m. p. 
195-196 °C.
E. 3 9-Benzyl-4-thia-9-azatricyclo[5.3.0.0^2,6]decane 4,4-dioxide.

a) 6,7-Ditosylmethyl-3-thiabicyclo[3.2.0]heptane 3,3-dioxide

This was prepared by the method of Mundy et al. 6,7-Dihydroxymethyl-3-thiabicyclo[3.2.0]heptane 3,3-dioxide (5 g, 24.3 mmol) was dissolved in pyridine (38 ml) and the solution added dropwise to a suspension of p-toluenesulphonyl chloride (29.7 g, 156 mmol) in pyridine (38 ml) stirred at 0°C. The mixture was stirred for a further 3 h at 0°C and then it was poured into water (300 ml) and the product crystallised as a colourless solid. This was filtered off (11.61 g), washed with water and dried in vacuo. The solid was recrystallised from ethanol to yield colourless needles of 6,7-ditosylmethyl-3-thiabicyclo[3.2.0]heptane 3,3-dioxide (6.39 g, 51%) m.p. 127-128°C.

I.R. ν max (nujol) 1600, 1315, 1175, 1097, 956, 899, 858, 812, 696, 668 cm⁻¹;
1H n.m.r. δ (CDCl₃) 7.8-7.3 (8H, AB system, aromatic H), 4.15-4.05 (4H, m -CH₂O-), 3.1-2.8 (8H, m, 1-H, 2 and 2'-H, 4 and 4'-H, 5-H, 6-H, 7-H), 2.46 (6H, s, -Me);
$^{13}$C n.m.r. $\delta$ (CDCl$_3$) 145.27 (Ar), 132.24 (Ar), 130.02 (Ar), 127.71 (Ar), 68.74 (-CH$_2$O-), 54.14 ($C_2$ and $C_4$), 38.00 ($C_6$ and $C_7$), 33.35 ($C_1$ and $C_5$), 21.54 (-Me);

Mass spectrum m/e 514 (0.2%), 343 (14.2), 172 (35.7), 155 (100), 124 (3.6), 91 (100);

(Found: C 51.13; H, 5.09%)

$C_{22}H_{26}O_8S_3$ requires C, 51.34; H, 5.09%.

b) 9-Benzyl-4-thia-9-azatricyclo[5.3.0.2,6]decane 4,4-dioxide.

A solution of 6,7-ditosylmethyl-3-thiabicyclo[3.2.0]heptane 3,3-dioxide (5 g, 3.88 mmol) and benzylamine (3.1 g, 29 mmol) in ethanol (50 ml) was heated under reflux for 48 h. The solvent was removed in vacuo to leave a colourless solid which was leached with dichloromethane (100 ml). The mixture was filtered and solvent removed under reduced pressure to give a clear oil (3.0 g) which crystallised to give a colourless solid. This was purified by recrystallisation from ethanol to give 9-benzyl-4-thia-9-azatricyclo[5.3.0.2,6]decane 4,4-dioxide (1.5 g, 55.7%) m.p. 132-135°C.

I.R. $\nu_{\text{max}}$ (nujol) 2780, 1603, 1300 (SO$_2$), 1247, 1140 (SO$_2$),

$^1$H n.m.r. $\delta$ (CDCl$_3$) 7.4-7.2 (5H, m, PhH), 3.65 (2H, s, -CH$_2$Ph),

3.1-2.6 (1OH, m, 2-H, 3 and 3′-H, 5 and 5′-H, 6-H, 8 and 8′-H, 10 and 10′H), 2.2-2.0 (2H, m, 1-H, 7-H);

$^{13}$C n.m.r. $\delta$ (CDCl$_3$) 139.11 (Ph), 128.34 (Ph), 128.04 (Ph),

125.76 (Ph), 59.09 ($C_8$, $C_10$ and -CH$_2$Ph) 54.98 ($C_3$ and $C_5$), 41.80 ($C_1$ and $C_7$), 36.71 ($C_2$ and $C_6$);
Mass spectrum m/e 277 (47.4%), 200 (26.3), 186 (47.4), 91 (100);  
(Found: C, 64.84; H, 6.63; N, 4.97; C₁₅H₁₉NO₂S requires C, 64.95; 
H, 6.90; N, 5.05%).

E.4 9-Phenyl-4-thia-9-azatricyclo[5.3.0.0²,6]decane 4,4-dioxide.

This preparation of the title compound proved to be largely unsuccessful.

a) 7-Phenylcarbamoyl-3-thiabicyclo[3.2.0]heptane-6-carboxylic acid 3,3-dioxide.

This was prepared by the method of Shaikrazieva et al.³

3,5-Dioxo-4-oxa-9-thiatricyclo[5.3.0.0²,6]decane 9,9-dioxide (20 g, 
93 mmol) was stirred (mechanical) with absolute methanol (250 ml). 
Aniline (8 ml) was added and the mixture stirred for a further 3 h.
The colourless solid which formed was filtered off and dried to yield 
7-phenylcarbamoyl-3-thiabicyclo[3.2.0]heptane-6-carboxylic acid 3,3-
dioxide (20.2 g, 58%) m.p. 217-220°C (lit.³ 220°C).

b) 9-Phenyl-8,10-dioxo-4-thia-9-azatricyclo[5.3.0.0²,6]decane 4,4-dioxide.

This was prepared by the method of Shaikrazieva et al.³ A mixture of 7-phenylcarbamoyl-3-thiabicyclo[3.2.0]heptane-6-carboxylic acid 
3,3-dioxide (6.3 g, 20.3 mmol), acetic anhydride (28 ml) and sodium 
acetate (0.6 g) was heated and stirred vigorously for 4 h. The precipitate 
was filtered off, washed with methanol and dried in vacuo to give 9-
phenyl-8,10-dioxo-4-thia-9-azatricyclo[5.3.0.0²,6]decane 4,4-dioxide 
(5.0 g, 84%) m.p. 308-314°C (lit.³ 310-315°C) as a colourless crystal-
line solid.
$^1$H n.m.r. δ (T. F. A.) 7.6-7.5 (3H, m, m and p-PhH), 7.3-
7.15 (2H, m, o-PhH), 3.9-3.5 (8H, m, 1-H, 2-H, 3 and 3'-H, 5 and
5'-H, 6-H, 7-H).

$^{13}$C n.m.r. δ [(CD$_3$)$_2$SO] 176.93 (C=O), 132.64 (Ph), 128.76 (Ph),
128.36 (Ph), 127.28 (Ph), 53.01 (C$_3$ and C$_5$), 42.62 (C$_1$ and C$_7$),
35.22 (C$_2$ and C$_6$);

Mass spectrum m/e 291 (69.4%), 119 (11.1), 80 (100).

c) 9-Phenyl-4-thia-9-azatricyclo[5.3.0.0$^{2,6}$]decane 4,4-dioxide.
The method used for this reduction is that of Otzenberger et al.$^{113}$

To a suspension of lithium aluminium hydride (1.4 g, 36.2 mmol) in
dry tetrahydrofuran (100 ml) was added 9-phenyl-8,10-dioxo-4-thia-
9-azatricyclo[5.3.0.0$^{2,6}$]decane 4,4-dioxide (4.5 g, 15.5 mmol) over a
period of fifteen minutes. The mixture was boiled under reflux for 5 h
and then left to stir for a further hour. The excess lithium aluminium
hydride was destroyed by the dropwise addition of water (2 ml) in
tetrahydrofuran (20 ml), followed by 4M sodium hydroxide (2 ml) and
then water (6 ml). The mixture was stirred for fifteen minutes and
then was filtered to remove inorganic salts to give a yellow filtrate.
The solvent was removed under reduced pressure to give a brown oil
which was taken up in dichloromethane (100 ml) and dried over anhydrous
magnesium sulphate. The solvent was removed under reduced pressure
to give a brown gum which was chromatographed on silica with dichloro-
methane as eluent. The eluent polarity was gradually increased by
using first ether then ethanol and finally methanol as the eluent. Four
fractions were obtained but all proved to be intractable gums except
the second which on trituration with ether gave brown crystals (0. 587 g). Recrystallisation from ethanol gave 9-phenyl-4-thia-9-azatricyclo[5. 3. 0. 2, 6]decane 4, 4-dioxide (0. 129 g, 3. 2%) m. p. 200-204°C as reddish crystals.

I. R. \( \nu \) _max (nujol) 1602, 1302, 1141, 760, 795 cm\(^{-1}\);

\( ^1 H \) n. m. r. \( \delta (\text{CDCl}_3) 7. 5-7. 25 (2H, \text{ m, o-PhH}), 6. 94-6. 7 (3H, \text{ m, m and p-PhH}), 3. 8-3. 5 (4H, \text{ m, 8 and 8'-H, 10 and 10'-H}), 3. 25-2. 9 (8H, \text{ m, 1-H, 2-H, 3 and 3'-H, 5 and 5'-H, 6-H, 7-H});

Mass spectrum m/e 263 (100%), 144 (14), 119 (33), 91 (57),

(Found: C, 63. 64; H, 6. 65; N, 5. 15. \( C_{14}H_{17}NO_2S \) requires C, 63. 88; H, 6. 51; N, 5. 32%).

E. 5 Attempted preparation of 9-methyl-4-thia-9-azatricyclo[5. 3. 0. 2, 6]-decane 4, 4-dioxide.

The following route to 9-methyl-4-thia-9-azatricyclo[5. 3. 0. 2, 6]-decane 4, 4-dioxide proved unsuccessful owing to the failure of the final step.

a) 7-Methylcarbamoyl-3-thiabicyclo[3. 2. 0]heptane-6-carboxylic acid 3, 3-dioxide.

This was prepared by the method of Shaikrazieva et al. 3

3, 5-Dioxo-4-oxa-9-thiatricyclo[5. 3. 0. 2, 6]decane 9, 9-dioxide (50 g, 230 mmol) was suspended in methanol (300 ml) and a 25% w/v solution of methylamine [135 ml 31. 38 g of \( \text{CH}_3\text{NH}_2 \) (338 mmol)] in water was added to this suspension. The mixture became warm and a pale yellow solution formed. This solution was stirred for 3 h and then the solvent was removed \textit{in vacuo} to give a gummy yellow solid (68. 31 g). This
was recrystallised from 10:1 ethanol:water to yield 7-methylcarbamoyl-
3-thiabicyclo[3.2.0]heptane-6-carboxylic acid 3,3-dioxide (44.09 g,
77%) m.p. 121-123°C as a colourless crystalline solid.

I.R. \( \nu_{\text{max}} \) (nujol) 1640, 1570, 1140 cm\(^{-1}\);
\( ^1\)H n.m.r. 8.1-7.9 (1H, m, -CO\(_2\)H), 3.4-2.9 (8H, m, 1-H, 2 and
2'-H, 4 and 4'-H, 5-H, 6-H, 7-H), 3.15 (3H, s, -Me);

\( ^13\)C n.m.r. 175.68 (CON), 172.70 (C=O), 54.63 (C\(_2\)), 54.10 (C\(_4\)),
46.38 (C\(_7\)), 45.26 (C\(_6\)), 34.41 (C\(_1\)), 32.40 (C\(_5\)), 24.44 (-Me)
(Found: M\(^+\), 247. C\(_9\)H\(_{13}\)N\(_2\)O\(_5\)S requires 247).

b) 9-Methyl-8, 10-dioxo-4-thia-9-azatricyclo[5.3.0.0\(^2,6\)]dodecane
4,4-dioxide.

The method used is that of Shaikrazieva et al.\(^3\) A mixture of
7-methylcarbamoyl-3-thiabicyclo[3.2.0]heptane-6-carboxylic acid 3,3-
dioxide (30 g, 120 mmol), acetic anhydride (107 ml) and anhydrous sodium
acetate was heated and stirred on a water bath for 4 h. The solution
was left to stand overnight and a white solid precipitated. This was recovered
by filtration and washed with methanol (50 ml) and ether (50 ml) and dried
in vacuo to yield 9-methyl-8, 10-dioxo-4-thia-9-azatricyclo[5.3.0.0\(^2,6\)]-
decane 4,4-dioxide (26.8 g, 96%) m.p. 235-237°C as a colourless crystal-
line solid.

I.R. \( \nu_{\text{max}} \) (nujol), 1694, 1433, 1390 (SO\(_2\)), 1283, 1160, 1137, 1100,
959, 753, 745 cm\(^{-1}\);
\( ^1\)H n.m.r. \( \delta \) (CDCl\(_3\)) 3.4 (2H, s, 1-H, 7-H), 3.26 (6H, s, 2-H,
3 and 3'-H, 5 and 5'-H, 6-H), 3.04 (3H, s, -Me);

\( ^13\)C n.m.r. \( \delta \) [(CD\(_3\))\(_2\)SO] 177.79 (C=O), 53.05 (C\(_3\) and C\(_5\)), 42.35
(C₁ and C₇), 35.04 (C₂ and C₆), 24.90 (-Me);
Mass spectrum m/e 229 (35%), 165 (57.5), 98 (20), 80 (100), 79 (100);
(Found: C, 47.38; H, 4.81; N, 6.08; C₉H₁₁NO₄S requires C, 47.15; H, 4.84; N, 6.11%).

c) Attempted lithium aluminium hydride reduction of 9-methyl-
8, 10-dioxo-4-thia-9-azатricyclo[5. 3. 0. o₂, 6]dodecane 4, 4-dioxide.
The method that was used was that of Otzenberger et al. 113 To a
suspension of lithium aluminium hydride (2 g, 5.24 mmol) in dry tetra-
hydrofuran (500 ml) was added 9-methyl-8, 10-dioxo-4-thia-9-aza-
tricyclo[5. 3. 0. o₂, 6]decane 4, 4-dioxide (6 g, 26.2 mmol) over a period
of five minutes. The mixture was stirred and boiled under reflux for
3 h and left to stir for a further hour. The excess lithium aluminium
hydride was destroyed by the dropwise addition of water (2 ml) in
tetrahydrofuran (20 ml), followed by 4M sodium hydroxide (2 ml) and
then water (6 ml). The mixture was stirred for fifteen minutes and
then was filtered to remove inorganic salts and gave a pale yellow
filtrate. The solvent was removed under reduced pressure to give a
yellow oil which was kept under high vacuum for 5 h. A sample of
the oil (1.63 g) was distilled in a glass Kugelrohr at 100°C/0.01mmHg
and gave a semi-crystalline pale yellow oil (0.45 g) which was un-
identified.
F. Preparation and Reactions of 3-Thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide.

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

a) 3-Thiabicyclo[3.2.0]heptane-6,7-dicarboxylic acid 3,3-dioxide.

3,5-Dioxo-4-oxa-9-thiatricyclo[5.3.0]2,6-decane 9,9-dioxide (50 g, 230 mmol) was suspended in water (450 ml) and the mixture was heated under reflux for 1 h and gave a clear solution. The water was removed under reduced pressure to give a colourless solid residue (57.68 g). This was dissolved in the minimum amount of wet acetone (acetone:water 50:1) and the product was precipitated using ether. The precipitate was recovered by filtration and dried in vacuo to yield 3-thiabicyclo[3.2.0]heptane-6,7-dicarboxylic acid 3,3-dioxide (42.3 g, 78%) m.p. 188-191°C (lit., 194-195°C) as a colourless crystalline solid.

I.R. $\nu_{\text{max}}$ 1700 (CO$_2$H), 1125 (SO$_2$) cm$^{-1}$;

$^1$H n.m.r. $\delta$ [(CD$_3$)$_2$CO] 9-7 (2H, V. br., -CO$_2$H), 3.6-3.4 (4H, m, 1-H, 5-H, 6-H, 7-H), 3.3-3.2 (4H, m, 2 and 2'-H, 4 and 4'-H);

$^{13}$C n.m.r. $\delta$ [(CD$_3$)$_2$SO] 173.66 (-CO$_2$H), 54.00 (C$_2$ and C$_4$),

43.87 (C$_6$ and C$_7$), 33.79 (C$_1$ and C$_5$);

Mass spectrum m/e 234 (-), 216 (2.3%), 198 (2.5), 172 (8), 108 (65), 108 (65), 80 (100), 79 (100).

b) 3-Thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide.

This was prepared by the method of Jefford et al. 114

3-Thiabicyclo[3.2.0]heptane-6,7-dicarboxylic acid 3,3-dioxide (9.9 g, 42 mmol) and lead tetraacetate (37.3 g, 84 mmol) were intimately mixed and dissolved in dry dioxane (130 ml). The mixture was purged with dry nitrogen for fifteen minutes and then placed in a water bath at
12-15°C. The mixture was vigorously stirred (mechanical) while nitrogen continued to be passed through it and dry pyridine (250 ml) was next admixed. The mixture was placed in a water bath at 60°C for twenty minutes during which time there was rapid evolution of carbon dioxide. The mixture was rapidly cooled and poured into 2N nitric acid (800 ml). This mixture was extracted using dichloromethane (8 x 100 ml) and the extract was washed in turn with water (1 x 100 ml), saturated sodium hydrogen carbonate solution (2 x 100 ml) and saturated sodium chloride solution (1 x 100 ml). The extract was dried over anhydrous magnesium sulphate and the solvent removed in vacuo to leave the crude product (3.92 g). This was purified by medium pressure chromatography on silica with ether as the eluent. 3-Thia-bicyclo[3.2.0]hept-6-ene 3,3-dioxide was eluted as a colourless crystalline solid (1.14 g, 18.8%) m.p. 71-75°C.

\[ \text{l.r. } \nu_{\text{max}} \text{ (nujol) } 1410, 1287, 1229, 1167, 1110, 942, 852, 728 \text{ cm}^{-1}; \]

\[ ^1\text{H n.m.r. } \delta \text{ (CDCl}_3\text{)} \ 6.18 \text{ (2H, s, alkenyl), 3.7-3.6 (2H, m, 1-H, 4-H), 3.2-2.9 (4H, m, 2 and } 2'-\text{H, 4 and } 4'-\text{H),} \]

\[ ^{13}\text{C n.m.r. } \delta \text{ (CDCl}_3\text{)} \ 139.00 \text{ (olefinic), 51.96 (C}_2\text{ and C}_4\text{), 41.04 (C}_1\text{ and C}_5\text{);} \]

Mass spectrum m/e 144 (3%), 81 (5), 80 (55), 79 (100), 77 (30);

(Found: C, 50.10; H, 5.35; C\textsubscript{6}H\textsubscript{8}O\textsubscript{2}S requires C, 50.0; H, 5.5%).

F.2 8-Oxa-4-thiatricyclo[5.1.0.2\textsuperscript{6}]octane 4,4-dioxide

Method (i)

The method that was used is that of Bianchi et al.\textsuperscript{115} To a stirred mixture of hydrogen peroxide 30% (10 ml) and formic acid 90% (40 ml)
was added 3-thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide (0.6 g, 4.2 mmol) in small portions over a period of twenty minutes at room temperature. The mixture was stirred for 48 h at 50°C and for a further 48 h at room temperature. The solvent was removed in vacuo and the oil which remained was taken up in a small amount of ethanol and 8-oxa-4-thia-tricyclo[5.1.0.0\(^2,6\)]octane 4,4-dioxide was precipitated as a colourless crystalline solid (0.26 g, 39%) m.p. 118-119°C.

I.R. \(\nu\) max (nujol) 3080, 1325, 1290, 1240, 1130, 855, 835, 715 cm\(^{-1}\);

\(^1\)H n.m.r. \(\delta\) (CDCl\(_3\)) 4.0-3.9 (2H, \(d J 1.5\) Hz, 1-H, 7-H), 3.3-3.1 (4H, \(m\), 3 and 3'-H, 5 and 5'-H), 3.05-2.9 (2H, \(m\), 2-H, 6-H).

\(^13\)C n.m.r. \(\delta\) (CDCl\(_3\)) 56.51 (C\(_1\) and C\(_7\)), 49.69 (C\(_3\) and C\(_5\)), 40.85 (C\(_2\) and C\(_6\));

Mass spectrum m/e 160 (0.13%), 131 (0.35), 104 (2.9), 95 (44), 94 (100); (Found: C, 45.15, H, 5.00; C\(_6\)H\(_8\)O\(_3\)S requires C, 45.0; H, 5.00%).

Method (ii) via 6-chloro-7-hydroxy-3-thiabicyclo[3.2.0]heptane 3,3-dioxide.

a) 6-Chloro-7-hydroxy-3-thiabicyclo[3.2.0]heptane 3,3-dioxide.

This was prepared by the method of Sorenson.\(^{116}\) To a stirred ice-cooled solution of 3-thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide (360 mg, 2.5 mmol) in water (2.5 ml) was added a solution of HOCl, as prepared in Organic Synthesis,\(^{117}\) until no more HOCl was taken up (KI-HCl test). Water (100 ml) was added to the reaction mixture to increase its volume and this mixture was then extracted with dichloromethane (4 x 50 ml). The extract was dried over magnesium sulphate and solvent was removed under vacuum to leave a solid (223 mg).
Recrystallisation of the solid from ethanol gave 6-chloro-7-hydroxy-3-thiabicyclo[3.2.0]heptane 3,3-dioxide (141 mg, 29%) m.p. 146-148°C as colourless crystals.

\[ \text{I.R. } \nu_{\text{max}} \text{ (nujol) } 3440 (-\text{OH}), 1275, 1118, 857, 802 \text{ cm}^{-1}; \]

Mass spectrum m/e \( M^+ \) not observed;

(Found: C, 36.19; H, 4.53; \( C_6H_9ClO_3S \) requires C, 36.65; H, 4.61%).

b) Attempted dehydrohalogenation of 6-chloro-7-hydroxy-3-thiabicyclo[3.2.0]heptane 3,3-dioxide.

The method used was that of McClure. 6-Chloro-7-hydroxy-3-thiabicyclo[3.2.0]heptane 3,3-dioxide (165 mg, 0.84 mmol) was dissolved in dimethoxyethane (25 ml) with silver (I) oxide (195 mg, 1.68 mmol) and the mixture was boiled under reflux for 24 h. The solids were removed by filtration and extensively washed with hot acetone. The filtrate was dried over magnesium sulphate and solvent removed under reduced pressure to give an oil (260 mg). This was triturated with ether and cooled in an acetone carbon dioxide (-70°C) bath and the product crystallised and was recovered by filtration. However I.R. showed that this solid was unchanged starting material.

F.3 Attempted addition of carbenes to 3-thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide.

a) Ethoxycarbonyl carbene.

Method (i)

3-Thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide (105 mg, 0.73 mmol) was stirred in dry benzene (10 ml) with 3-diazo-2-oxopropionate (105 mg, 0.73 mmol) in the presence of a pinch (1 mg) of rhodium (IV) acetate.
as catalyst. After a short induction period (5 minutes) nitrogen gas was evolved. The mixture was stirred for 21 h and the benzene was removed under vacuum and gave a clear oil. On examination by n.m.r. it was apparent that this oil was a mixture of unchanged alkene, diethyl-maleate, diethyl fumarate and 1-ethoxycarbonyl-cycloheptatrienyliadiene. The mixture was analysed by gas chromatography using a 2½% SE30 column three peaks were observed and the presence of diethyl fumarate and diethyl maleate confirmed by peak enhancement experiments using authentic samples. Thus the experiment was a failure as the carbenes preferred to dimerize or add to benzene rather than add to the alkene.

Method (ii)

The experiment was repeated as before with the modification that this time the 3-diazo-2-oxo-propionate (105 mg, 0.73 mmol) in benzene (5 ml) was added slowly to 3-thiabicyclo[3.2.0]hept-6-ene 3, 3-dioxide (105 mg, 0.73 mmol) dissolved in benzene (5 ml) to which rhodium (IV) acetate (1 mg) had been added. The addition took place over a period of ½ h and nitrogen was slowly evolved. However work up as before revealed that the products were exactly the same and none of the desired carbene addition compound to the alkene had been formed.

Control experiment

A control experiment was carried out in which the experiment was carried out exactly as in method (ii) except that this time no 3-thiabicyclo[3.2.0]hept-6-ene 3, 3-dioxide was added. On removal of the benzene in vacuo the residue was distilled in a glass Kugelrohr (100°C/16 mmHg) and gave a clear liquid. Spectral analysis showed
that this liquid was a mixture of diethylmaleate, diethyl fumarate and 1-ethoxycarbonylcycloheptatrienyladiene as before.

**Method (iii)**

3-Thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide (140 mg, 6.97 mmol) was intimately mixed with copper bronze and placed in a Dreschel tube and a flow of nitrogen passed over it. The tube was placed in an oil bath at 110°C and 3-diazo-2-oxo-propionate (100 mg, 0.70 mmol) added to it. There followed a vigorous reaction and after 10 minutes the Dreschel tube was removed from the oil bath and trichloromethane (200 ml) was added to the reaction mixture. The copper bronze was removed by filtration and removal of solvent in vacuo gave a clear oil. Spectroscopic analysis (n.m.r.) show that this consisted of diethyl maleate, diethyl fumarate and unchanged alkene. Thus 3-thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide is very unreactive toward carbenes.

F.4 **Attempted addition of nitrenes to 3-thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide.**

a) **Ethoxycarbonylnitrene.**

The method used to generate ethoxycarbonylnitrene was that of Cadogan et al. 120 3-Thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide (240 mg, 1.6 mmol) and p-nitrophenylsulphonyloxyurethane (500 mg, 1.7 mmol) were dissolved in anhydrous dichloromethane (25 ml) and a solution of triethylamine (200 mg, 1.98 mmol) in dichloromethane (15 ml) was added dropwise to the reaction mixture over a period of ten minutes. The mixture was stirred for 3 h, the reaction being monitored by the
disappearance of nitrene precursor by t. l. c. (alumina, ether).

Dichloromethane (75 ml) was added to the reaction mixture and this mixture was washed with water (3 x 25 ml) to remove excess amine. The solution was dried over anhydrous magnesium sulphate and solvent removed in vacuo to leave an oil (310 mg). It was shown spectroscopically (n. m. r.) that the alkene was unchanged and that the only other species present was the ethoxycarbonyl nitrene dimer. The mixture was chromatographed on alumina. Elution with dichloromethane and the dichloromethane:ether 9:1 gave recovered alkene (0.2 g).

b) N-Phthalimidonitrene.

The method used was that of Anderson et al. To a stirred mixture of N-aminophthalimide (263 mg, 1.62 mmol) and 3-thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide (900 mg, 6.25 mmol) in dichloromethane (20 ml), was added lead tetraacetate (690 mg, 1.56 mmol) in small portions, over a period of ten minutes. The mixture was stirred for an additional thirty minutes and then the precipitated inorganic salts were removed by filtration. The solvent was removed under reduced pressure to leave a yellow oil (1.21 g) which crystallised. This was purified by medium pressure chromatography on silica. Elution with petroleum ether (40-60): acetone 3:1 gave a colourless crystalline compound (29.9 mg) m. p. 180-181°C which was probably the nitrene addition product but this was not confirmed.

I.R. \( \nu_{\text{max}} \) (nujol) 1775, 1719, 1310, 1247, 1179, 1107, 708, 658 cm\(^{-1}\);

Mass spectrum m/e 304 (16.7%), 240 (13.9), 225 (100), 160 (9.3), 132 (16.7).
Addition of 1, 3-dipoles to 3-thiabicyclo[3.2.0]hept-6-ene 3, 3-dioxide.

a) Preparation of 1, 3-dipole precursors.

i) C, N-Diphenylnitrone.

This was prepared by the method of Wheeler et al. Equimolar amounts of phenylhydroxylamine and benzaldehyde were condensed in ethanol and the product crystallized as a colourless solid. Recrystallization from ethanol gave C, N-diphenylnitrone (88%) as a colourless solid m. p. 109-111°C (lit 114°C).

ii) Anisohydroxamic chloride

Stage (i) Anisaldehyde bisulphate.

This was prepared by the method outlined in Vogel's handbook. Equimolar amounts of sodium metabisulphite and anisaldehyde were condensed in aqueous ethanol and the product was precipitated immediately, and was recovered by filtration (99% yield). It was dried in vacuo and used in the next stage without purification.

Stage (ii) Anisaldoxime

This was prepared by a modification of the method given in Vogel's handbook. Anisaldehyde bisulphite (160 g, 0.67 mol) was dissolved in water (900 ml) and to this was added a solution of sodium hydroxide (100 g of NaOH in 300 ml of water). Hydroxylamine hydrochloride (48 g, 0.7 mol) was added in small portions, the mixture being stirred continuously. Solid carbon dioxide was added to the resulting pale yellow solution and a colourless solid precipitated. The solid was recovered by filtration and dissolved in dichloromethane (600 ml). This solution was washed with water (2 x 200 ml) and then dried over magnesium
sulphate. Removal of solvent under reduced pressure gave an oil (84.8 g) which crystallised. This solid was recrystallised from toluene/pentane to give anisaldoxime (75 g, 73%).

Stage (iii) Anisohydroxamic Chloride.

This was prepared by the method of Rheinboldt et al. 126 Anisaldehyde oxime (18.6 g, 0.12 mol) was dissolved in dry ether (160 ml) and the solution was cooled to between -10 -0°C. An ether solution of nitrosyl chloride (20% w/v 81 ml, 16.2 g, 0.25 mol) 127 was added carefully with constant stirring. The solution was stirred for a further hour at room temperature. The solvent was removed in vacuo to leave a brown oil which was taken up in trichloromethane. Addition of petroleum ether (40-60) gave a colourless precipitate. This was recovered by filtration and dried in vacuo to yield anisohydroxamic chloride (14.06 g, 61%) m.p. 74-75°C (lit., 126 88-89°C).

iii) Benzhydroxamic chloride.

Stage (i) and (ii)

The preparation of benzaldoxime was achieved in two stages by procedures analogous to those used for anisaldoxime. The bisulphite addition compound was obtained in 97% yield and the oxime in 94% yield.

Stage (iii) Benzhydroxamic Chloride.

This was prepared by the method of Perold et al. 128 Benzaldoxime (20 ml) was added to 8.3N hydrochloric acid (120 ml) and the reaction vessel was placed in an ice salt bath and when the temperature of the mixture had dropped to 0°C chlorine was passed through it for 20 minutes. The mixture was extracted with dichloromethane (5 x 200 ml) to give a green solution which was washed with water (8 x 100 ml) to
remove any residual chlorine. The solution was dried over magnesium sulphate and solvent was removed in vacuo to give an oily residue. This was taken up in trichloromethane (20 ml) and the product was precipitated by addition of petroleum ether (40-60). The colourless solid was recovered by filtration and dried in vacuo to yield benzhydroxamic chloride (6.12 g) m.p. 44-48°C (Lit., 42-48°C).

iv) α-Chlorobenzoylphenylhydrazone.

Stage (i) β-Benzoylphenylhydrazone.

This was prepared by the method of Tinley. Phenylhydrazine (10 g, 93 mmol) in pyridine (50 ml) was stirred in an ice-water bath during the addition of benzoyl chloride (108 ml, 13 g; 93 mmol). This mixture was shaken for fifteen minutes before being poured into water (350 ml). An orange coloured solid was washed with water and re-crystallized from ethanol to yield β-benzoylphenylhydrazine as colourless crystals (11.82 g, 60%) m.p. 165-167°C (lit., 168°C).

Stage (ii) α-Chlorobenzoylphenylhydrazone.

This was prepared by the method of Huisgen et al. Finely divided β-benzoylphenylhydrazine (5 g, 21.7 mmol) and phosphorous pentachloride (6 g) were suspended in dry ether (15 ml) and boiled under reflux in dry conditions for 16 h. The solution was cooled and filtered. Then phenol (10 g) dissolved in ether (8 ml) and methanol (10 ml) was added with cooling. The ether was removed in vacuo and the resultant suspension was cooled in fridge. The solid was filtered off, washed with ice-cold methanol and dried in vacuo to give α-chlorobenzoylphenylhydrazone (1.37 g, 25%) m.p. 127-129°C (lit., 129.5-130.5°C) as pale green crystals.
b) **4, 5-Diphenyl-3-oxa-9-thia-4-azatricyclic[5. 3. 0. 2, 6]decane 9, 9-dioxide.**

A solution of 3-thiabicyclo[3. 2. 0]hept-6-ene 3, 3-dioxide (150 mg, 1.04 mmol) and C, N-diphenylnitrone (205 mg, 1.04 mmol) in dry toluene was heated under reflux for 72 h. The reaction progress was monitored by t.l.c. (alumina, petroleum ether (40-60) : trichloromethane 1:1). The solvent was removed under reduced pressure and gave a brown solid (0.5 g). Recrystallization of this solid from ethanol gave **4, 5-diphenyl-3-oxa-9-thia-4-azatricyclic[5. 3. 0. 2, 6]decane-9, 9-dioxide** (0.1 g, 28%) m.p. 185-186°C as a light brown crystalline solid.

I.R. νmax (nujol) 1598, 1490, 1309, 1132, 768, 742, 709, 701 cm⁻¹; ¹H n.m.r. (CDCl₃) 7.5-7.0 (10H, m, Ph), 4.8 (1H, d of d, J 7Hz, 2Hz, 2-H), 4.5 (1H, d J 7Hz, 5-H), 3.5-2.6 (7H, cm, 1-H, 6-H, 7-H, 8 and 8'-H, 10 and 10'-H);

Mass spectrum m/e 341 (50%), 180 (17), 91 (100), 77 (36); (Found: C, 66.60; H, 5.65; N, 3.95; C₁₉H₁₉NO₃S requires C, 66.85; H, 5.60; N, 4.10%).

c) **5-(p-Methoxyphenyl)-3-oxa-9-thia-4-azatricyclic[5. 3. 0. 2, 6]-dec-4-ene 9, 9-dioxide.**

A solution of 3-thiabicyclo[3. 2. 0]hept-6-ene 3, 3-dioxide (260 mg, 1.8 mmol) and anisohydroxamic chloride (310 mg, 1.8 mmol) in dry toluene (20 ml) was boiled under reflux for 48 h. The reaction progress was monitored by evolution of hydrogen chloride gas. When the mixture was cooled to room temperature a brown solid precipitated which was recovered by filtration (0.39 g). This solid was recrystallized from ethanol to give colourless crystals of **5-(p-methoxyphenyl)-3-oxa-9-**
thia-4-azatricyclo[5.3.0.02,6]dec-4-ene 9,9-dioxide (0.24 g, 45%)
m.p. 182-184°C
I.R. νmax (nujol) 1302, 1246, 1125, 872, 835 cm⁻¹.

1 H n.m.r. δ (CDCl₃) 7.2 (4H, AB pattern, aromatic), 5.2 (1H, d of d,
J 8Hz, 4Hz, 2-H), 4.3 (1H, d, J 8Hz, 6-H), 3.8 (3H, s, -OMe),
3.6-3.1 (6H, c m, 1-H, 7-H, 8 and 8'-H, 10 and 10'-H).

13 C n.m.r. δ (CDCl₃) 161.34 (aromatic carbon adjacent to -OMe),
157.61 (C₅), 128.36 (Ar), 119.76 (Ar), 114.44 (Ar), 81.91 (C₂),
55.28 (-OMe), 53.46 (C₁₀), 53.10 (C₈), 41.54 (C₆), 37.30 (C₁ and C₇);
Mass spectrum m/e 293 (30%), 175 (100);
(Found: C, 57.10; H, 5.15; N, 4.70; C₁₄H₁₅N⁰₃S requires C, 57.30;
H, 5.15; N, 4.80%).

d) 5-Phenyl-3-oxa-9-thia-4-azatricyclo[5.3.0.02,6]dec-4-ene
9,9-dioxide.

A solution of 3-thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide (1.1 g,
7.6 mmol) and benzhydroxamic chloride (1.19 g, 7.6 mmol) in dry
toluene (100 ml) was boiled under reflux for 64 h. The reaction progress
was monitored by the evolution of hydrogen chloride gas. The solvent
was removed in vacuo to leave a brown oil (0.93 g). This was purified
by medium pressure chromatography on an alumina column. Elution
with at first petroleum ether (40-60) and later with dichloromethane
gave a colourless crystalline solid (0.74 g). Recrystallization from
ethanol gave 5-phenyl-3-oxa-9-thia-4-azatricyclo[5.3.0.02,6]dec-4-
enoe 9,9-dioxide (0.37 g, 18.5%) m.p. 175-176°C as colourless crystals.
I.R. νmax (nujol) 1308, 1128, 878, 768, 691, 666 cm⁻¹.
The diazomethane was prepared by the method outlined in Vogel's handbook. Diazald \([\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{N(CH}_3\text{)}\text{NO}]\) (4.3 g, 20 mmol) was dissolved in dry ether (60 ml) and an alcoholic solution of potassium hydroxide (0.8 g in 20 ml of 96% aqueous ethanol). This solution was stood in an ice bath for fifteen minutes and then the resultant ethanol solution of diazomethane was distilled off into cold dry ether (50 ml). 3-Thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide (500 mg, 3.5 mmol) was added to this solution and stood in a cold room for 42 days during which time there precipitated a pale yellow solid. The excess diazomethane was destroyed by addition of glacial acetic acid and the solid was recovered by filtration and dried in vacuo to yield 4-thia-9,10-diazatricyclo[5.3.0.0\(^2,6\)]dec-9-ene-4,4-dioxide (500 mg, 82%) m.p. 157-158°C as pale yellow needles.

I.R. v\(_{\text{max}}\) (nujol) 1535, 1295, 1137, 888, 686 cm\(^{-1}\);

\(^1\)H n.m.r. \((\text{CDCl}_3)\) 7.6-7.4 (5H, m, Ph), 5.3-5.1 (1H, d of d J 7.5Hz 2.5Hz, 2-H), 4.4-4.2 (1H, m, 6-H), 3.5-3.2 (6H, c m, 1-H, 7-H, 8 and 8'-H, 10 and 10'-H);

\(^{13}\)C n.m.r. \([\text{CD}_3\text{)}_2\text{SO}\] 158.43 (C\(_5\)), 130.36 (Ph), 129.06 (Ph), 127.66 (Ph), 127.01 (Ph), 82.11 (C\(_2\)), 52.49 (C\(_{10}\)), 52.28 (C\(_8\)), 41.54 (C\(_6\)), 37.40 (C\(_1\) and C\(_7\));

Mass spectrum m/e 263 (8.7%), 145 (100), 144 (57), 117 (13), 77 (22);

(Found: C, 59.15; H, 5.00; N, 5.10; \(\text{C}_{13}\text{H}_{13}\text{NO}_3\) requires C, 59.30; H, 5.00; N, 5.30%).

e) 4-Thia-9,10-diazatricyclo[5.3.0.0\(^2,6\)]dec-9-ene-4,4-dioxide.
5 and 5'-H) 2.82-2.5 (2H, q, 6-H, 7-H);

$^{13}$C n.m.r. $\delta$(CDCl$_3$) 90.05 (C$_1$), 84.03 (C$_8$), 54.10 (C$_3$), 53.18 (C$_5$),
 38.09 (C$_4$), 37.95 (C$_2$), 32.72 (C$_6$);

Mass spectrum m/e 187 (0.8%), 186 (0.04), 93 (16.6), 91 (21),
 79 (100), 77 (50);

(Found: C, 45.26; H, 5.38; N, 14.87; C$_{7}$H$_{10}$N$_{2}$O$_{2}$S requires
  C, 45.15; H, 5.4; N, 15.04%).

f) Attempts to add diphenylnitrilimine to 3-thiabicyclo[3.2.0]-
  hept-6-ene 3, 3-dioxide.

3-Thiabicyclo[3.2.0]hept-6-ene 3, 3-dioxide (250 mg, 1.7 mmol)
and $\alpha$-chlorobenzoylphenylhydrazone (400 mg, 1.7 mmol) in dry toluene
(30 ml) was boiled under reflux for 90 h the reaction progress was
monitored by the evolution of hydrogen chloride gas. The solvent was
removed under reduced pressure and gave a brown crystalline solid.
This was shown by n.m.r. to consist of unreacted 3-thiabicyclo[3.2.0]hept-6-
ene 3, 3-dioxide and nitrilimine decomposition products. The unreacted
3-thiabicyclo[3.2.0]hept-6-ene 3, 3-dioxide was recovered by chromatography
of the brown solid on silica with ether as the eluent. The
recovery was virtually quantitative showing that the nitrilimine had
not reacted with the alkene.

Method (ii)

This method is that of Huisgen. To a solution of 3-thiabicyclo-
[3,2,0]hept-6-ene 3, 3-dioxide (120 mg, 0.83 mmol) and $\alpha$-chlorobenzoyl-
phenylhydrazone (200 mg, 0.83 mmol) in dry benzene (15 ml) was added
a solution of triethylamine (200 mg, 2 mmol) in benzene (5 ml) over a
period of 1 h. during which time the solution became fluorescent.

The benzene was removed under reduced pressure and gave an almost
colourless crystalline solid. This was shown by n.m.r. to be almost
identical to the product obtained by method (i) and once again the
nitrilimine had failed to react with the alkene.
Preparation of Divinylcyclopentane Analogues by Flash Vacuum Pyrolysis (F.V.P.).

G.1 General procedure.

The pyrolyses were carried out using the apparatus described in section B. The following procedure is typical.

A sample of the substrate was placed in the inlet of the F.V.P. apparatus and the inlet was then attached to the pyrolysis tube. The 'U' shaped trap was attached to the pyrolysis tube exit and the system was sealed by connecting the other end of the trap to the pump. The joints which were subject to high temperatures were sealed with high vacuum silicone grease and the others with L Apiezon grease. When the furnace temperature had reached the required temperature and the system pressure had fallen to approximately $10^{-3}$ mmHg the trap was surrounded by a liquid nitrogen trap and the inlet was surrounded by a Kugelrohr already heated to the required temperature. The substrate was then sublimed into the furnace over a period of between $\frac{1}{2}$ h and 5 h, and the products were trapped in the cold trap. When all of the substrate had sublimed the heat sources were switched off and the system allowed to cool. When the apparatus had cooled it was flooded with dry nitrogen taken apart and the product recovered from the cold trap and purified by standard procedures.

In general each new pyrolysis required a series of small scale (50 mg) experiments in order to find optimum conditions. The two parameters which were of particular importance were (i) the inlet temperature, and (ii) the furnace temperature. The correct inlet temperature was determined by carrying out a pyrolysis in which the
inlet temperature was gradually increased in 10°C intervals from room temperature until a reasonable rate of sublimation was attained. It was desirable to avoid melting the substrate in the inlet and also either very low or very high rates of sublimation. Sometimes however it was impossible to avoid melting the substrate as in these cases inlet temperatures below the melting point of the substrate gave negligible rates of sublimation. The correct furnace temperature had to be found such that the substrate was completely pyrolysed to give the desired products without the products themselves being decomposed. In general furnace temperature was in the range 500-625°C.

Another feature worthy of note is that on some occasions a residue remained in the inlet at the end of the pyrolysis. On these occasions the amount of residue was determined by weighing and taken into account when the yields of the pyrolysis was calculated. One feature which was also of interest was that if one changed the scale of an experiment from small (50 mg) to medium (1 g) scale then one had to increase the furnace temperature by 20-50°C to get the same results as in the lower scale experiment.

In small scale experiments the crude pyrolysate was dissolved in CDCl₃ (0.3 ml) and this solution was analysed directly by n.m.r. [after addition of cyclohexane (5μl) as an integral calibrant]. Absolute yields in these small scale experiments were obtained from the n.m.r. spectra by relating the integral of the various protons to that of cyclohexane. This procedure is estimated to be accurate to ±5%.

In all the pyrolyses optimum conditions are quoted.
G. 2 Pyrolysis of 3, 5-dioxo-4-oxa-9-thiatricyclo[5. 3. 0. 0^2, 6]decane 9, 9-dioxide.

A sample of 3, 5-dioxo-4-oxa-9-thiatricyclo[5. 3. 0. 0^2, 6]decane 9, 9-dioxide (15 g, 69 mmol) was pyrolysed at 630 °C. The inlet temperature was 180 °C, the pressure 6 x 10⁻³ mmHg and time taken was 5 h. At the end of the pyrolysis the pyrolysate was transferred to a Kugelrohr bulb and distilled bulb-to-bulb (65 °C 10.0 mmHg) and gave 2, 5-dioxo-cis-3, 4-divinyltetrahydrofuran as a clear liquid (8.43 g, 80%) nD 1.4835.

I. R. ν max (liquid film) 1900-1700, 1642, 1417, 1206, 1072, 945, 783 cm⁻¹.

H n.m.r. δ(CDCl₃) 5.9-5.5 (2H, m, 6-H, 8-H), 5.4-5.3 (4H, c d of d, 7 and 7'-H, 9 and 9'-H), 3.9-3.4 (2H, d of d J 4.5 Hz 2Hz, 3-H, 4-H)

C n.m.r. δ(CDCl₃) 170.44 (C =O), 127.34 (C₆ and C₈), 122.11 (C₇ and C₉) 48.88 (C₃ and C₄);

Mass spectrum m/e 152 (11.3%), 108 (6.8), 80 (100), 79 (100);
(Found: C, 62.90; H, 5.45; C₈H₆O₃ requires C, 63.15; H, 5.30%).

G. 3 Pyrolysis of 4-oxa-9-thiatricyclo[5. 3. 0. 0^2, 6]decane 9, 9-dioxide and an alternative synthesis of product.

a) Pyrolysis

A sample of 4-oxa-9-thiatricyclo[5. 3. 0. 0^2, 6]decane 9, 9-dioxide (486 mg, 2.59 mmol) was pyrolysed at 625 °C. The inlet temperature was 110 °C, the pressure 10⁻³ mmHg and the time taken was 5 h. The pyrolysate was recovered with a dropping pipette and distilled in a micro distillation apparatus to give cis-3, 4-divinyltetrahydrofuran (197 mg, 61.5%) b.p. 41 °C/41 mmHg, nD 1.465 as a clear liquid.

I. R. ν max (liquid film) 3325, 1638, 1423, 1047, 991, 910 cm⁻¹.
\[^1\] H n.m.r. \(\delta\) (CDCl\(_3\)) 5.9-5.6 (2H, m, 6-H, 8-H), 5.1-5.0 (4H, d of d of d of d 17Hz, 10Hz, 6Hz, 2.5Hz, 2-H, 5-H), 5.3-5.1 (4H, overlapping d of d of d of d 17Hz, 1Hz, 10Hz, 1.5Hz, 10Hz, 1.5Hz, 1 and 1'-H, 6 and 6'-H) 3.62 (6H, s, -Me) 3.5-3.4 (2H, d of d of d 6Hz, 2.5Hz, 3-H, 4-H);

\[^{13}\] C n.m.r. \(\delta\) (CDCl\(_3\)) 171.38 (C=O), 132.61 (C\(_2\) and C\(_5\)), 119.04 (C\(_1\) and C\(_6\)), 52.49 (-OMe), 51.51 (C\(_3\) and C\(_4\));

b) Alternative synthesis of cis-3,4-divinyltetrahydrofuran.

i) meso-Dimethyl-1,5-hexadiene-3,4-dicarboxylate.

2,5-Dioxo-cis-3,4-divinyltetrahydrofuran (8.43 g, 55 mmol) and a few drops of concentrated sulphuric acid were added to methanol (130 ml) and the mixture was boiled under reflux for 24 h. The reaction mixture was filtered and the solvent was removed in vacuo to leave a clear oil (10.76 g) which crystallized and gave a colourless translucent solid. Recrystallization of this solid from petroleum ether (40-60) gave meso-dimethyl-1,5-hexadiene-3,4-dicarboxylate (5.6 g, 51%) m.p. 36-37°C as colourless crystals.

I.R. \(\nu\) \(\text{max}\) (nujol) 1743, 1640, 1315, 1235, 1088, 1000, 892, 787, 695 cm\(^{-1}\);

1 H n.m.r. \(\delta\) (CDCl\(_3\)) 5.9-5.6 (2H, d of d of d of d 17Hz, 10Hz, 6Hz, 2.5Hz, 2-H, 5-H), 5.3-5.1 (4H, overlapping d of d of d of d 17Hz, 1Hz, 10Hz, 1.5Hz, 10Hz, 1.5Hz, 1 and 1'-H, 6 and 6'-H) 3.62 (6H, s, -Me) 3.5-3.4 (2H, d of d of d 6Hz, 2.5Hz, 3-H, 4-H);
Mass spectrum m/e 198 (1%), 167 (18), 139 (23), 138 (27), 99 (100); (Found: C, 60.45; H, 6.90. C_{10}H_{14}O_4 requires C, 60.60; H, 7.10%).

ii) meso-3,4-Dihydroxymethyl-1,5-hexadiene.

To a stirred (mechanical) suspension of lithium aluminium hydride (8.26 g, 220 mmol) in dry tetrahydrofuran (170 ml) was added dropwise a solution of meso-dimethyl-1,5-hexadiene-3,4-dicarboxylate (10.76 g, 54 mmol) in dry tetrahydrofuran (50 ml) over a period of 1 h. The mixture was stirred for 1 h at room temperature and then boiled under reflux for a further 1 h. On cooling the excess lithium aluminium hydride was destroyed by dropwise addition of water (8 ml), 4M sodium hydroxide solution (8 ml) and water (24 ml). The inorganic salts were removed by filtration and the solvent removed from the filtrate in vacuo and gave a clear oil (9.45 g). This oil was dissolved in trichloromethane (60 ml) and this solution was washed with water (10 ml) to remove any residual tetrahydrofuran. The trichloromethane solution was dried over magnesium sulphate and solvent was removed in vacuo to give a clear oil (7.16 g). This oil was distilled in a Kugelrohr (100°C/0.8 mmHg) to give meso-3,4-dihydroxymethyl-1,5-hexadiene (6.7 g, 87%) as a clear oil $^\text{18}_D$ 1.4865.

I.R. v max (liquid film) 3700-3100 (-OH), 1640 (C=C), 1425, 1055, 995, 917 cm$^{-1}$;

$^1$H n.m.r. δ(CDCl$_3$) 5.9-5.5 (2H, d of d of d $\delta$ 16Hz, 11Hz, 8.3Hz, 2-H, 5-H), 5.2-5.0 (4H, overlapping d of d $\delta$ 16Hz, 2.5Hz, 11Hz, 2.5Hz, 1 and 1'-H, 6 and 6'-H), 3.8-3.4 (4H, two sets of d of d $\delta$ 10.5Hz, 4.5Hz, 10.5Hz, 6.5Hz, 7 and 7'-H, 8 and 8'-H), 2.5-2.1 [4H, (2H, when sample
shaken with D$_2$O) br. m, 3-H, 4-H, -OH].

$^{13}$C n.m.r. $\delta$ (CDCl$_3$) 137.46 (C$_2$ and C$_5$), 117.69 (C$_1$ and C$_4$) 63.51 (C$_7$ and C$_8$), 47.84 (C$_3$ and C$_4$);

Mass spectrum m/e 142 (0.3%), 124 (1), 94 (45), 79 (75), 54 (100);

(Found: C, 67.45; H, 10.10. C$_8$H$_{14}$O$_2$ requires C, 67.55; H, 9.90%).

iii) cis-3,4-Divinyltetrahydrofuran.

This was prepared by the method of Corfield et al. A solution of methyl-3,4-dihydroxymethyl-1,5-hexadiene (3.8 g, 27 mmol) and toluene-$p$-sulphonic acid monohydrate (300 mg, 1.58 mmol) in dry benzene (60 ml) was boiled under reflux for 40 h in a flask equipped with a Dean and Stark apparatus. At the end of this period about ½ ml of water had collected below the benzene in the Dean and Stark trap. The benzene was removed from the reaction mixture under reduced pressure at room temperature. The residue was distilled and gave cis-3,4-divinyltetrahydrofuran (2.03 g, 62%) b. p. 41 °C/41 mmHg as a clear liquid.

Analytical and spectroscopic data showed that it was identical in every way to the compound prepared by the pyrolysis of 4-oxa-9-thiatricyclo-[5.3.0.0$^2,6$]decane 9,9-dioxide.

G. 4 Pyrolysis of 4,9-dithiatricyclo[5.3.0.$^2,6$]decane 4,4-dioxide.

A sample of 4,9-dithiatricyclo[5.3.0.$^2,6$]decane 4,4-dioxide (320 mg, 1.55 mmol) was pyrolysed at 620°C. The inlet temperature was 106°C, the pressure was 3 x 10$^{-3}$ mmHg and the time taken for the pyrolysis was 2 h. The pyrolysate a pale yellow liquid was transferred to a microdistillation apparatus and distillation yielded cis-3,4-divinyltetrahydrothiophene (27 mg, 24.6%) b. p. 140°C/16 mmHg as a clear
liquid. As in this case a solid residue (162 mg) remained in the inlet this was taken into account when estimating the yield of the reaction.

$\nu_{\text{max}}$ (liquid film) 1640 (C=C), 1450, 1425, 980, 917 cm$^{-1}$;

$^1\text{H}$ n.m.r. $\delta$ (CDCl$_3$) 6.0-5.0 (6H, divinyl system, 6-H, 7 and 7'-H, 8-H, 9 and 9'-H), 3.1-2.6 (6H, br. m, 2 and 2'-H, 3-H, 4-H, 5 and 5'-H);

$^{13}$C n.m.r. $\delta$ (CDCl$_3$) 136.32 (C$_6$ and C$_8$), 116.29 (C$_7$ and C$_9$), 51.09 (C$_3$ and C$_4$), 34.77 (C$_2$ and C$_5$);

Mass spectrum m/e 140 (30.3%), 86 (100), 85 (75.8);

(Found: C, 68.67; H, 8.59; C$_8$H$_{12}$S requires C, 68.52; H, 8.62%).

G. 5 **Pyrolysis of 9-benzyl-4-thia-9-azatricyclo[5.3.0.0$_2$.6]decane 4,4-dioxide.**

A sample of 9-benzyl-4-thia-9-azatricyclo[5.3.0.0$_2$.6]decane 4,4-dioxide (90 mg, 0.32 mmol) was pyrolysed at 525°C. The inlet temperature was 160°C, the pressure was $1 \times 10^{-3}$ mmHg and the time taken was 1 h. The pyrolysate which was a brown oil was dissolved in trichloromethane (2 ml) and this solution was transferred to a micro distillation apparatus. The trichloromethane was blown off in a stream of dry nitrogen and then distillation of the pyrolysate gave 1-benzyl-cis-3,4-divinylpyrrolidine (40 mg, 58%) b.p. 100°C/10$^{-3}$ mmHg as a light brown oil.

I. R. $\nu_{\text{max}}$ (liquid film) 1642, 1454, 912, 802, 742, 700 cm$^{-1}$;

$^1\text{H}$ n.m.r. $\delta$ (CDCl$_3$) 7.4-7.2 (5H, m, Ph), 6.1-5.8 (6H, divinyl system, 6-H, 7 and 7'-H, 8-H, 9 and 9'-H), 3.6 (2H, s, -CH$_2$Ph) 3.1-2.9 (4H,
m, 2 and 2'-H, 5 and 5'-H), 2.4-2.1 (2H, m, 3-H, 4-H).

Mass spectrum m/e 213 (33%), 133 (28.6), 91 (86), 42 (100);

(Found: C, 84.61; H, 9.08; N, 6.66. C_{15}H_{19}N requires C, 84.46;
H, 8.98; N, 6.57%; M^+, 213.1516. C_{15}H_{19}N requires 213.1517).

G. 6 Pyrolysis of 9-phenyl-8,10-dioxo-4-thia-9-azatricyclo-
[5.3.0.0^2,6]decane 4,4-dioxide.

A sample of 9-phenyl-8,10-dioxo-4-thia-9-azatricyclo[5.3.0.0^2,6]-
decane 4,4-dioxide (283 mg, 6.97 mmol) was pyrolysed at 625°C. The
inlet temperature was 186°C, the pressure 2 x 10^{-3} mmHg and the
time taken was 53 minutes. The pyrolysate collected as a colourless
solid at the entrance to the cold trap. The pyrolysate was dissolved
in trichloromethane (20 ml) and the solution was filtered. The
solvent was removed to leave a colourless crystalline solid (210 mg).
Recrystallisation of this solid from ethanol gave 1-phenyl-cis-3,4-divinyl-
succinimide (120 mg, 52%) m. p. 134-136°C as colourless needles.

\nu_{\text{max}} (\text{nujol}) 1767, 1598, 1496, 1459, 1382, 1264, 1188, 933, 753,
692 \text{ cm}^{-1};

^1H n.m.r. \delta (CDCl_3) 7.5-7.2 (5H, m, Ph) 5.95-5.28 (6H, c divinyl
system, 6-H, 7 and 7'-H, 8-H, 9 and 9'-H), 3.8-3.7 (2H, d of d
J 7Hz, 2Hz, 3-H, 4-H);

^13C n.m.r. \delta (CDCl_3) 175.37 (C=O), 131.72 (Ph), 129.58 (Ph), 128.92
(Ph), 128.41 (Ph), 126.17 (C_6 and C_8), 121.31 (C_7 and C_9), 48.88
(C_3 and C_4);

Mass spectrum m/e 227 (62.5%), 157 (5), 119 (7.5), 108 (7.5), 91
(7.5), 80 (100), 79 (60):
G. 7 Pyrolysis of 9-Phenyl-4-thia-9-azatricyclo[5.3.0.2,6]-decane 4,4-dioxide.

A sample of 9-phenyl-4-thia-9-azatricyclo[5.3.0.2,6]-decane 4,4-dioxide (60 mg, 0.23 mmol) was pyrolysed at 625°C. The inlet temp was 148°C, the pressure was $4 \times 10^{-3}$ mmHg and the time taken was 1.25 h. The pyrolysate was examined by n.m.r. and this was consistent with the product being 1-phenyl-cis-3,4-divinylpyrrolidine. However attempts to pyrolyse larger amounts led to failure on account of the fact that substrate decomposed badly in the inlet. Also since the substrate itself was prepared somewhat fortuitously on only one occasion it was not possible to confirm the pyrolysis result.

$^1$H n.m.r. (60MHz) δ (CDCl₃) 7.45-7.24 (2H, m, o-PhH) 6.82-6.5 (3H, m, m and p-PhH), 6.2-4.9 (6H, c divinyl system, 6-H, 7-H, 8 and 8'-H, 9 and 9'-H), 3.5-2.9 (6H, c m, 2 and 2'-H, 3-H, 4-H, 5 and 5'-H).

G. 8 Pyrolysis of 9-methyl-8,10-dioxo-4-thia-9-azatricyclo-
[5.3.0.2,6]decane 4,4-dioxide.

A sample of 9-methyl-8,10-dioxo-4-thia-9-azatricyclo[5.3.0.2,6]-decane 4,4-dioxide (1 g, 4.4 mmol) was pyrolysed at 625°C. The inlet temperature was 180°C, the pressure was $3 \times 10^{-3}$ mmHg and the time taken was 7 h. There was a solid residue (0.24 g) left in the inlet at the end of the pyrolysis. The pyrolysate was a light brown oil and
this was distilled in a microdistillation apparatus to yield 1-methyl-cis-3,4-divinylsuccinimide (0.32 g, 58%) b. p. 100°/10⁻³ mmHg.

D19 n 1.486 as a pale yellow oil.

I. R. νmax (liquid film) 1690, 1435, 1380, 1290, 980, 930 cm⁻¹;

¹H n. m. r. δ(CDC1₃) 6.1-5.22 (6H, 6 divinyl system, 6-H, 7 and 7'⁻H, 8-H, 9 and 9'⁻H), 3.8-3.6 (2H, m, 3-H, 4-H), 3.05 (3H, s, -Me);

¹³C n. m. r. 176.59 (C=O), 129.64 (C₆ and C₈), 121.15 (C₇ and C₉), 49.75 (C₃ and C₄), 25.00 (-Me);

Mass spectrum m/e 165 (78%), 80 (100), 79 (100), 64 (88), 60 (55).
(Found: M⁺, 165.0778. C₉H₁₁NO₂ requires 165.0790; C, 65.26; H, 6.83, N, 8.65; C₉H₁₁NO₂ requires C, 65.44; H, 6.71; N, 8.48%).
H. **Pyrolysis of 3-Thiabicyclo[3.2.0]hept-6-ene 3, 3-dioxide and its Adducts.**

H. 1 **Pyrolysis of 3-Thiabicyclo[3.2.0]hept-6-ene 3, 3-dioxide.**

A sample of 3-thiabicyclo[3.2.0]hept-6-ene 3, 3-dioxide (50 mg, 0.35 mmol) was pyrolysed at 500°C. The inlet temperature was 70°C, the pressure $5 \times 10^{-3}$ mmHg and the time taken was 1.5 h. Analysis of the pyrolysate by n.m.r. showed that the product was entirely 1,3-cyclohexadiene. This indicates that the first formed product was hexa-1,3,5-triene but the conditions of the pyrolysis were such that it had undergone an electrocyclic reaction to give 1,3-cyclohexadiene.

In an attempt to prevent the hexa-1,3,5-triene isomerizing to 1,3-cyclohexadiene milder conditions for the pyrolysis were employed. It was found that, if the furnace temperature was below 400°C, then unchanged starting material was the "product." At a temperature of 400°C the product consisted of 1,3-cyclohexadiene, cis-hexa-1,3,5-triene and unchanged 3-thiabicyclo[3.2.0]hept-6-ene 3, 3-dioxide.

The presence of cis-hexa-1,3,5-triene was confirmed by comparing the $^1$H n.m.r. of the pyrolysate to that of the published spectra for cis-hexa-1,3,5-triene. Thus it was found impossible to get cis-hexa-1,3,5-triene as the sole product of the pyrolysis.

H. 2 **Lithium aluminium hydride extrusion of sulphur dioxide from 3-thiabicyclo[3.2.0]hept-6-ene 3, 3-dioxide.**

This method used is that of Gaoni. 3-Thiabicyclo[3.2.0]hept-6-ene 3, 3-dioxide (200 mg, 1.4 mmol) was added portionwise to a suspension of lithium aluminium hydride (200 mg, 5.2 mmol) in boiling
ether (50 ml). The mixture was boiled under reflux for 1 h and then samples of the ether solution were withdrawn and analysed by gas chromatography. The column used was 30% β,β'-oxydipropionitrile on '80-100 Chromsorb W' at an oven temperature of 50° C. Two product peaks were observed and these were shown to be due to cis and trans-hexa-1, 3, 5-triene by peak enhancement experiments using an ethereal solution containing authentic samples of cis and trans-hexa-1, 3, 5-triene prepared as described by Hwa et al. Thus the importance of this result is that in this case the extrusion is non-stereospecific.

Control experiment

In order to check that the reaction conditions could not cause isomerization of cis to trans-hexa-1, 3, 5-triene a sample of the authentic mixture of cis and trans hexa-1, 3, 5-triene was dissolved in ether (25 ml). This solution was analysed by gas chromatography and then lithium aluminium hydride (200 mg, 5.2 mmol) was added and the mixture was boiled under reflux for 1 h. The mixture was then analysed again by gas chromatography under the same conditions as before and the traces obtained were identical to those obtained before the reflux period. Thus this confirms that the extrusion of sulphur dioxide by lithium aluminium hydride in this case is non-stereospecific.

H.3 Pyrolysis of 8-oxa-4-thiatricyclo[5.1.0.6]octane 4,4-dioxide.

A sample of 8-oxa-4-thiatricyclo[5.1.0.6]octane 4, 4-dioxide (50 mg, 0.31 mmol) was pyrolysed at 580° C. The inlet temperature was 106° C, the pressure 3 x 10^{-3} mmHg and the time taken was fifteen minutes. The pyrolysate was dissolved in CDCl3 (0.3 ml) and analysed
by $^1$H and $^{13}$C n.m.r. spectroscopy and comparison of the data with known literature values showed that the product was 4, 5-dihydrooxepin (30 mg, 55%).

$^1$H n.m.r. δ (CDCl$_3$) 6.1 (2H, d, $J$ 7.5Hz, 2-H, 7-H), 5.2 (2H, m, 3-H, 6-H), 2.3 (4H, m, 4 and 4'-H, 5 and 5'-H);

$^{13}$C n.m.r. δ (CDCl$_3$) 142.76 (C$_2$ and C$_7$), 108.5 (C$_3$ and C$_6$), 26.91 (C$_4$ and C$_5$),

H. 4 Pyrolysis of 5-(p-Methoxyphenyl)-3-oxa-9-thia-4-azatricyclo-[5.3.0.0$^2$6]dec-4-ene 9,9-dioxide.

A sample 5-(p-methoxyphenyl)-3-oxa-9-thia-4-azatricyclo-[5.3.0.0$^2$6]dec-4-ene 9,9-dioxide (50 mg, 0.17 mmol) was pyrolysed at 500°C. The inlet temperature was 148°C, the pressure was 7 x 10$^{-3}$ mmHg and the time taken was 3 h. The pyrolysate was dissolved in trichloromethane (2 ml) and transferred to a sublimation apparatus. The solvent was blown off in a stream of dry nitrogen and the residue sublimed (100°C/5 x 10$^{-3}$ mmHg) to yield colourless translucent crystals of 4, 5-dihydro-3-(p-methoxyphenyl)-cis-4, 5-divinylisoxazole (13 mg, 33%) m.p. 58-60°C.

I.R. ν max (nujol) 1607, 1512, 1245, 1177, 1043, 837, 810 cm$^{-1}$;

$^1$H n.m.r. δ (CDCl$_3$) 7.8-6.8 (4H, AB pattern, aromatic H) 6.1-4.9 (6H, δ, divinyl system, 6-H, 7 and 7'-H, 8-H, 9 and 9'-H), 4.1 (1H, δ, J Hz, 5-H), 3.66 (3H, s, -OMe), 3.2 (1H, br.s, 4-H);

$^{13}$C n.m.r. δ(CDC$_3$) 160.86 (aromatic carbon adjacent to -OMe), 158.52 (C$_3$), 132.05 (C$_6$), 131.83 (C$_8$), 128.53 (Ar), 121.52 (C$_7$), 120.21 (C$_9$), 119.94 (Ar), 113.91 (Ar), 86.09 (C$_5$), 55.30 (-OMe),
55.16 (C₄).

Mass spectrum m/e 229 (100%), 173 (92);

(Found: C, 73.20; H, 6.50; N, 6.00; C₁₄H₁₅O₂N requires
C, 73.35; H, 6.60; N, 6.10%).

H. 5  High temperature Pyrolysis of 5-(p-methoxyphenyl)-3-oxa-9-thia-4-azatricyclo[5.3.0.0²,6]dec-4-ene-9,9-dioxide.

A sample of 5-(p-methoxyphenyl)-3-oxa-9-thia-4-azatricyclo-
[5.3.0.0²,6]dec-4-ene 9,9-dioxide (79 mg, 0.26 mmol) was pyrolysed
at a furnace temperature of 625°C. The inlet temperature was 144°C,
the pressure was 8 x 10⁻³ mmHg and the time taken for the pyrolysis
was 3 h. The pyrolysate was dissolved in CDCl₃ (0.3 ml) and analysed
by ¹H n.m.r. and then by gas chromatography (2½% SE30 on 80-100
chormsorb) at an oven temperature of 180°C for four minutes and then
an increase of 6°C per minute to 240°C over a period of ten minutes.
The gas chromatograph showed 9 product peaks. Thus due to prolifera-
tion of products this investigation was discontinued.

¹H n.m.r. 6 (CDCl₃) 8-6.7 (aromatic peaks), 3.8 (various types
of -OMe).

H. 6  Pyrolysis of 5-Phenyl-3-oxa-9-thia-4-azatricyclo[5.3.0.0²,6]-
dec-4-ene-9,9-dioxide.

A sample of 5-phenyl-3-oxa-8-thia-4-azatricyclo[5.3.0.0²,6]-
dec-4-ene 9,9-dioxide (50 mg, 0.19 mmol) was pyrolysed at 500°C.
The inlet temperature was 142°C, the pressure was 12 x 10⁻³ mmHg
and the time taken for the pyrolysis was 2 h. Pyrolysate was dissolved
in CDC\textsubscript{3} (0.3 ml) and transferred to a microdistillation apparatus. The solvent was blown off in a stream of dry nitrogen and the residue was distilled and gave 4,5-dihydro-3-phenyl-cis-4,5-divinylisoxazole (7 mg, 19%) b.p. 100°C/0.1 mmHg as a clear liquid.

I.R. ν\textsubscript{max} (liquid film) 1447, 1346, 987, 926, 767, 693 cm\textsuperscript{-1};

\textsuperscript{1}H n.m.r. \delta(CDC\textsubscript{3}) 7.74-7.64 (2H, m, o-ArH), 7.4-7.2 (3H, m, m and p-ArH), 6.1-4.95 (7H, c m, 5-H, 6-H, 7 and 7'-H, 8-H, 9 and 9'-H), 4.14 (1H, t, J=10Hz, 4-H);

Mass spectrum m/e 199 (15%), 143 (100), 117 (70), 115 (25);
(Found: C, 78.07; H, 6.42; N, 7.33; C\textsubscript{13}H\textsubscript{13}NO requires C, 78.36; H, 6.58; N, 7.03%).

H. 7 4-Thia-9,10-diazatricyclo[5.3.0.0\textsuperscript{2,6}]dec-9-ene-4,4-dioxide.

a) Pyrolysis

A sample of 4-thia-9,10-diazatricyclo[5.3.0.0\textsuperscript{2,6}]dec-9-ene-4,4-dioxide (75 mg, 0.47 mmol) was pyrolysed at 450°C. The inlet temperature was 118°C, the pressure was 5 x 10\textsuperscript{-3} mmHg and the time taken for the pyrolysis was 2 h. The pyrolysate was dissolved in CDC\textsubscript{3} (0.3 ml) and examined by \textsuperscript{1}H n.m.r. and by gas chromatography (30% β,β'-oxydipropionitrile on 80-100 Chromsorb W) at a column temperature of 90°C. Five product peaks were observed. The products were not positively identified.

b) Photolysis

4-Thia-9,10-diazatricyclo[5.3.0.0\textsuperscript{2,6}]dec-9-ene 4,4-dioxide (50 mg, 0.3 mmol) was dissolved in deuterated acetonitrile and placed in an n.m.r. tube. The tube was then irradiated with a 100W medium
pressure mercury lamp through a pyrex filter for 58 h. The reaction was monitored by $^1$H n.m.r. The resonances in the region 4-6 $\delta$ almost disappeared while new resonances appeared in the region 0-2 $\delta$. Other more subtle changes took place in the main body of the spectrum. The solvent was removed in vacuo to leave a yellow oil which on trituration with ether gave a brown solid (8 mg). However attempts to identify this solid were unsuccessful.
I. Miscellaneous Preparations and Pyrolyses

I. 1 meso-1, 5-Hexadiene-3,4-dicarboxylic acid.

2, 5-Dioxo-cis-3, 4-divinyltetrahydrofuran (11.6 g, 76 mmol) was suspended in water (50 ml) and boiled for a few minutes. The mixture became homogeneous and when cooled gave a colourless crystalline precipitate. The precipitate was recovered by filtration and dried in vacuo to yield meso-1, 5-hexadiene-3,4-dicarboxylic acid (9.06 g, 70%) m. p. 183-185 °C.

I. R. v max (nujol) 1697 (C=O), 987, 927, 767, 667 cm⁻¹;
1H n.m.r. δ[(CD₃)₂CO] 6.1-5.7 (4H, d of d of d of d and broad signal overlapping J 16.5 Hz, 10 Hz, 6 Hz, 2.5 Hz, 2-H, 5-H), 5.3-5.1 (4H, overlapping d of d, J 16.5 Hz, 2 Hz, 10 Hz, 2 Hz, 1 and 1'-H, 6 and 6'-H), 3.4-3.3 (2H, d of d, J 6 Hz, 2.5 Hz, 3-H, 4-H);
13C n.m.r. δ[(CD₃)₂CO] 172.16 (C=O), 134.06 (C₂ and C₅), 118.59 (C₁ and C₆), 52.82 (C₃ and C₄);
Mass spectrum m/e 157 (28%), 134 (40), 124 (100);
(Found: C, 56.25; H, 5.9. C₈H₁₀O₄ requires C, 56.5; H, 5.9%).

I. 2 7-Ethoxycarbonyl-3-thiabicyclo[3.2.0]heptane-6-carboxylic acid 3,3-dioxide.

3-Thiabicyclo[3.2.0]heptane-6,7-dicarboxylic acid 3,3-dioxide (34 g, 145 mmol) was taken up in boiling ethanol. When the solution cooled a white crystalline solid was obtained. Recovery of the solid by filtration gave 7-ethoxycarbonyl-3-thiabicyclo[3.2.0]heptane-6-carboxylic acid 3,3-dioxide (33.85 g, 89%) m. p. 152-154 °C as colourless crystals.
I. R. 1735 (C=O), 1300 (SO₂), 1188, 1142 cm⁻¹;

¹H n. m. r. δ[(CD₃)₂CO] 6. 5-5. 3 (1H, br. s, -COCH), 3. 7-3. 3 (2H, g. -CH₂ -), 3. 0-2. 5 (8H, m, 1-H, 2 and 2'-H, 4 and 4'-H, 5-H, 6-H, 7-H), 0. 75-0. 55 (3H, t, -Me);

Mass spectrum m/e M⁺ not observed;

(Found: C, 46. 14; H, 5. 46; C₁₀H₁₄O₆S requires C, 46. 17; H, 5. 38%).

1. 3 Attempted Vinylation of 6, 7-dihydroxymethyl-3-thiabicyclo-
[3. 2. 0]heptane 3, 3-dioxide. 137

The general method used in the attempts was that of Watanabe et al. 138

Method (i)

6, 7-Dihydroxymethyl-3-thiabicyclo[3. 2. 0]heptane 3, 3-dioxide
(1 g, 4. 9 mmol) mercuric acetate (0. 2 g, 0. 6 mmol) and one drop of concentrated sulphuric acid was added to ethyl vinyl ether (3. 0 g) and the resultant mixture was boiled under reflux for 2 h and then a further portion of ether (1. 5 g) was added. The mixture was boiled under reflux for a further seven days and the solid residue was removed by filtration. The solvent was removed from the filtrate under reduced pressure to give a colourless solid (193 mg). The solid residue was shown to be a mixture of mercuric acetate and starting material by examination of its I. R. spectrum. Although the colourless solid was not positively identified ¹H n. m. r. showed that it did not contain any vinyl groups and thus was not the desired product.
Method (ii)

Since the main difficulty in the vinylation experiment is the insolubility of the substrate the experiment was carried out using a Soxlet apparatus. This time the diol was placed in the Soxlet and the ether (100 ml) used to extract it. However this also proved unsuccessful.

I.4 Attempted preparation of 5,6-divinyl-3,8-dioxadeca-1,9-diene. meso-3,4-Dihydroxymethyl-1,5-hexadiene (1.02 g, 7.2 mmol), mercuric acetate (0.5 g, 1.6 mmol) and one drop of concentrated sulphuric acid were added to ethyl vinyl ether (25 ml). This mixture was boiled under reflux for 48 h and then mercuric acetate (0.5 g) was added again and this was repeated 24 h later. After 96 h the mixture was filtered and the solvent removed in vacuo to leave an oil. This was distilled bulb-to-bulb in a Kugelrohr and the clear oil (210 mg) distils b. to b. 110°C 10⁻² mmHg was obtained. Although the spectral properties of this oil were consistent with it being the desired compound this was not confirmed by analysis.

\[ \text{H n.m.r. } \delta 6.6-6.2 (2H, \text{ d of } J 14.6\text{Hz} \ 7.3\text{Hz}, \text{ 2-H, 9-H}), \]
\[ 5.9-5.5 (2H, \text{ m, } 11-\text{H, 13-H}), (4H, \text{ m, } 12 \text{ and } 12'-\text{H, 13 and } 13'-\text{H}), \]
\[ 4.2-3.9 (4H, \text{ m, } 1 \text{ and } 1'-\text{H, 10 and } 10'-\text{H}), 3.7 (4H, \text{ d J 4Hz} \ 4 \text{ and } 4'-\text{H, 7 and } 7'-\text{H}), 2.6-2.3 (2H, \text{ m, } 5-\text{H, 6-H}); \]

\[ \text{C n.m.r. } 151.70 (C_2 \text{ and } C_9), 137.27 (C_{11} \text{ and } C_{13}), 117.37 (C_{12} \text{ and } C_{14}), 80.30 (C_1 \text{ and } C_{10}), 69.12 (C_4 \text{ and } C_7), 44.41 (C_5 \text{ and } C_6). \]
I. 5  **Pyrolysis of the product from the attempted preparation of 5, 6-divinyl-3, 8-dioxadecan-1, 9-diene.**

Method (i)

A sample of the clear oil (56. 5 mg, 0. 29 mmol), obtained as described in I. 4, was pyrolysed at a furnace temperature of 500°C. The inlet was at room temperature, the pressure was $6 \times 10^{-3}$ mmHg, and the pyrolysis was five minutes. The pyrolysate was examined by $^1$H n.m.r. but the product was not positively identified.

$^1$H n.m.r. $\delta$ (CDCl$_3$) 9. 6 (br. s), 6. 5-6. 3 (d of d 14Hz 7Hz),
5. 9-5. 4 (c m), 5. 3-4. 9 (c m), 4. 22 (d 1 J 2. 5Hz), 4. 15-3. 9 (c m),
3. 72 (d 1 J 5Hz), 2. 6-2. 3 (c m), 2. 14 (s), 1. 4 (c m).

Method (ii)

A sample of the oil was dissolved in $[^2]$H$_8$ toluene and sealed in an n.m.r. tube. The tube was then placed in a bath of boiling xylene (150°C) for 5 days but during this time no change in the n.m.r. spectrum of the substrate was observed.

I. 6  **Pyrolysis of Dimethyl-3-thiabicyclo[3, 2. 0]heptane-6, 7-dicarboxylate 3, 3-dioxide.**

A sample of dimethyl-3-thiabicyclo[3. 2. 0]heptane-6, 7-dicarboxylate 3, 3-dioxide (1 g, 3. 8 mmol) was pyrolysed at 625°C. The inlet temperature was 180°C, the pressure was $1 \times 10^{-3}$ mmHg, and the time taken for the pyrolysis was 1. 5 h. The pyrolysate, a very volatile pale yellow liquid, was distilled in a micro distillation apparatus at atmospheric pressure and gave cis, trans-octa-2, 6-diene-1, 8-
dicarboxylic acid dimethyl ester (0.574 g, 76%) as a clear liquid. Owing to the very volatile nature of the compound elemental analysis failed but exact mass measurement of the parent peak in the mass spectrum was consistent with the assigned structure. Also the $^1$H n.m.r. and I.R. data were in agreement with published values. I.R. \(\nu_{\text{max}}\) (liquid film) 1725 (C=O), 1660 (C=C) 1440, 1200 cm\(^{-1}\); $^1$H n.m.r. (360 MHz) \(\delta\) (CDCl\(_3\)) 7.010-6.928 (1H, d of t 16Hz 7Hz, 3-H), 6.233-6.160 (1H, d of t 12Hz 7.5Hz, 6-H), 5.895-5.809 (2H m, 2-H, 7-H), 3.727 (3H, s -OMe), 3.715 (3H, s -OMe), 2.874-2.808 (2H m, 4 and 4'-H) 2.403-2.339 (2H, m, 5 and 5'-H); $^{13}$C n.m.r. \(\delta\) (CDCl\(_3\)) 166.58 (C=O), 166.28 (C=O), 147.91 (C\(_2\) or C\(_7\)) 147.54 (C\(_2\) or C\(_7\)), 121.53 (C\(_3\) or C\(_6\)), 120.29 (C\(_3\) or C\(_6\)), 51.15 (C\(_4\)), 50.81 (C\(_5\)), 31.13 (-OMe), 26.98 (-OMe).

Mass spectrum m/e 198 (1%), 167 (43), 166 (33), 138 (100).
(Found: \(M^+\), 198.090244 \(C_{10}H_{14}O_4\) requires 198.089202 error less than 6 ppm).

I.7 Pyrolysis of meso-dimethyl-1,5-hexadiene-3,4-dicarboxylate.

Method (i)
A sample of meso-dimethyl-1,5-hexadiene-3,4-dicarboxylate (100 mg, 0.5 mmol) was pyrolysed at a furnace temperature of 625°C. The inlet temperature was 50°C, the pressure 1 x 10\(^{-3}\) mmHg and the time taken was \(\frac{1}{2}\) h. The pyrolysate was dissolved in CDCl\(_3\) (0.3 ml) and examined $^1$H n.m.r. This showed the presence of cis, trans-octa-2,6-diene-1,8-dicarboxylic acid dimethyl ester which had been prepared in the previous pyrolysis.
Method (ii)

A sample of meso-dimethyl-1, 5-hexadiene-3, 4-dicarboxylate was dissolved in $\text{[}^{2}\text{H}_8\text{]}\text{toluene}$ and placed in an n.m.r. tube. The tube was placed in a bath of boiling toluene and the reaction progress was monitored over a period of 5 days by $^1\text{H}$ n.m.r. At the end of this period all the substrate signals had disappeared to be replaced by those of cis,trans-octa-2, 6-diene-1, 8-dicarboxylic acid dimethyl ester.
J. X-Ray Structures and other Structural Evidence.

J.1 Structure of 1,5-hexadiene-3,4-dicarboxylic acid.

The assigned stereochemistry of 1,5-hexadiene-3,4-dicarboxylic acid (106) was validated, by its essentially quantitative chemical transformation to meso-2,3-diethylsuccinic acid (107) m. p. 190-191°C (dec.) (lit. 192°C; cf. racemic acid, m. p. 129°C), by hydrogenation over 10% palladium-charcoal at room temperature (Scheme 47).

\[
\begin{align*}
\text{H} & \quad \text{CO}_2\text{H} \\
\text{H} & \quad \text{CO}_2\text{H} \\
\text{H} & \quad \text{CO}_2\text{H} \\
\text{H} & \quad \text{CO}_2\text{H} \\
\end{align*}
\]

\[
\begin{align*}
\text{H}_2 & \quad 10\% \text{Pd/C} \\
\end{align*}
\]

\[
\begin{align*}
\text{H} & \quad \text{CO}_2\text{H} \\
\text{H} & \quad \text{CO}_2\text{H} \\
\text{H} & \quad \text{CO}_2\text{H} \\
\text{H} & \quad \text{CO}_2\text{H} \\
\end{align*}
\]

Scheme 47

J.2 X-Ray structure of 9-phenyl-8,10-dioxo-4-thia-9-azatricyclo[5.3.0.0^{2,6}]decane 4,4-dioxide.

9-Phenyl-8,10-dioxo-4-thia-9-azatricyclo[5.3.0.0^{2,6}]decane 4,4-dioxide (108) was recrystallized from glacial acetic acid. The solution was left to stand overnight in a thermos containing hot water, allowing slow crystallization and giving large colourless crystals m. p. 310-315°C.

Crystal data C_{14}H_{13}NO_4S, M = 291, orthorhombic, a = 9.664±0.001, b = 10.510±0.001, c = 25.407±0.003Å, V = 2581Å^3, Z = 8, D_c = 1.498 g cm^{-3}. Space group Pbc\alpha.

Structure was refined to an R factor of 0.072.
The molecular geometry of (108) is shown in Figure 8. The bond lengths (Å) given in Figure 8 have standard deviations ±0.003-0.005Å. Bond angles (°) and standard deviations are given in Table 1. The numbering used for (108) is arbitrary.

**Mean plane displacements**

Cyclobutane ring is nearly planar but slightly saddle shaped:

Perpendicular displacements from least squares plane in Å.

\[
\begin{align*}
(+0.0093) & \quad C_3 & \quad C_2 (-0.0093) \\
(-0.0085) & \quad C_6 & \quad C_5 (+0.0084) \\
\end{align*}
\]

sulphone ring:

\[
\begin{align*}
(+0.3166) & \quad C_1 & \quad C_2 (-0.1242) \\
(-0.0201) & \quad S & \quad C_3 (-0.1070) \\
(+0.3091) & \quad C_4 & \end{align*}
\]
Fig. 8. A computer generated perspective drawing of 9-phenyl-8,10-dioxo-4-thia-9-aza-tricyclo-
[5.3.0.0²,⁶]decane 4,4-dioxide (108) with bond lengths in Å. Hydrogens have been omitted for clarity.
TABLE 1

Bond angles (°) in (108). The e. s. d.'s are given in parenthesis

<table>
<thead>
<tr>
<th>Bond Angle</th>
<th>Value</th>
<th>Bond Angle</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(1)-S-O(2)</td>
<td>118.0(2)</td>
<td>C(3)-C(6)-C(5)</td>
<td>90.7(3)</td>
</tr>
<tr>
<td>O(1)-S-C(1)</td>
<td>108.7(2)</td>
<td>C(3)-C(6)-C(7)</td>
<td>114.0(3)</td>
</tr>
<tr>
<td>O(1)-S-C(4)</td>
<td>108.9(2)</td>
<td>C(3)-C(6)-H(6)</td>
<td>114.6(24)</td>
</tr>
<tr>
<td>O(2)-S-C(1)</td>
<td>111.6(2)</td>
<td>C(5)-C(6)-C(7)</td>
<td>105.5(3)</td>
</tr>
<tr>
<td>O(2)-S-C(4)</td>
<td>111.7(2)</td>
<td>C(5)-C(6)-H(6)</td>
<td>116.0(24)</td>
</tr>
<tr>
<td>C(1)-S-C(4)</td>
<td>95.7(2)</td>
<td>C(7)-C(6)-H(6)</td>
<td>113.8(24)</td>
</tr>
<tr>
<td>C(7)-N-C(8)</td>
<td>113.4(3)</td>
<td>O(3)-C(7)-N</td>
<td>124.5(3)</td>
</tr>
<tr>
<td>C(7)-N-C(9)</td>
<td>123.0(3)</td>
<td>O(3)-C(7)-C(6)</td>
<td>128.1(3)</td>
</tr>
<tr>
<td>C(8)-H-C(9)</td>
<td>123.6(3)</td>
<td>N - C(7)-C(6)</td>
<td>107.4(3)</td>
</tr>
<tr>
<td>S-C(1)-C(2)</td>
<td>105.5(3)</td>
<td>O(4)-C(8)-N</td>
<td>124.3(3)</td>
</tr>
<tr>
<td>S-C(1)-H(101)</td>
<td>107.2(29)</td>
<td>O(4)-C(8)-C(5)</td>
<td>127.5(3)</td>
</tr>
<tr>
<td>S-C(1)-H(201)</td>
<td>101.9(37)</td>
<td>N - C(8) - C(5)</td>
<td>108.2(3)</td>
</tr>
<tr>
<td>C(2)-C(1)-H(101)</td>
<td>110.0(29)</td>
<td>N - C(9) - C(10)</td>
<td>119.4(3)</td>
</tr>
<tr>
<td>C(2)-C(1)-H(201)</td>
<td>117.4(37)</td>
<td>N - C(9) - C(14)</td>
<td>118.6(3)</td>
</tr>
<tr>
<td>R(101)-C(1)-H(201)</td>
<td>113.8(47)</td>
<td>C(10)-C(9)-C(14)</td>
<td>122.0(4)</td>
</tr>
<tr>
<td>C(1)-C(2)-C(3)</td>
<td>110.0(3)</td>
<td>C(9)-C(10)-C(11)</td>
<td>118.1(4)</td>
</tr>
<tr>
<td>C(1)-C(2)-H(101)</td>
<td>116.5(3)</td>
<td>C(9)-C(10)-H(10)</td>
<td>118.5(26)</td>
</tr>
<tr>
<td>C(3)-C(2)-C(5)</td>
<td>109.5(23)</td>
<td>C(11)-C(10)-H(10)</td>
<td>123.4(26)</td>
</tr>
<tr>
<td>C(3)-C(2)-H(102)</td>
<td>89.1(2)</td>
<td>C(11)-C(10)-H(10)</td>
<td>123.4(26)</td>
</tr>
<tr>
<td>C(5)-C(2)-H(102)</td>
<td>116.6(23)</td>
<td>C(10)-C(11)-C(12)</td>
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</tr>
<tr>
<td>C(5)-C(2)-H(102)</td>
<td>114.1(23)</td>
<td>C(10)-C(11)-H(11)</td>
<td>116.8(30)</td>
</tr>
<tr>
<td>C(2)-C(3)-C(4)</td>
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<td>121.6(30)</td>
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<tr>
<td>C(2)-C(3)-C(6)</td>
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<td>C(12)-C(11)-H(11)</td>
<td>121.6(30)</td>
</tr>
<tr>
<td>C(2)-C(3)-H(103)</td>
<td>114.8(2)</td>
<td>C(11)-C(12)-C(13)</td>
<td>118.9(4)</td>
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<td>122.7(29)</td>
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<td>112.1(21)</td>
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<td>112.2(21)</td>
<td>C(13)-C(12)-H(12)</td>
<td>118.3(29)</td>
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<td>C(12)-C(13)-C(14)</td>
<td>121.0(4)</td>
</tr>
<tr>
<td>S-C(4)-H(104)</td>
<td>107.1(22)</td>
<td>C(12)-C(13)-H(13)</td>
<td>123.6(29)</td>
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<td>C(14)-C(13)-H(13)</td>
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<td>C(2)-C(5)-C(8)</td>
<td>111.8(3)</td>
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<td>117.7(25)</td>
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<tr>
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<td>105.5(3)</td>
<td>C(6)-C(5)-H(5)</td>
<td>119.7(26)</td>
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<tr>
<td>C(6)-C(5)-H(5)</td>
<td>119.7(26)</td>
<td>C(8)-C(5)-H(5)</td>
<td>109.7(26)</td>
</tr>
</tbody>
</table>
nitrogen ring:

\begin{center}
\begin{tikzpicture}
  \node (C4) at (0,0) {C4 (+0.0316)};
  \node (C5) at (1,1) {C5 (-0.0097)};
  \node (C8) at (2,0) {C8 (-0.0150)};
  \node (N) at (3,0) {N (-0.0490)};
  \node (C6) at (4,1) {C6 (+0.0059)};
  \node (C7) at (5,0) {C7 (-0.0150)};
  \node (C3) at (6,0) {C3 (+0.0275)};
  \draw (C4) -- (C5) -- (C8) -- (N) -- (C6) -- (C7) -- (C3) -- (C4);
\end{tikzpicture}
\end{center}

Angle between sulphone ring and cyclobutane ring = 100.4°
Angle between cyclobutane ring and nitrogen ring = 113.5°
Angle between nitrogen ring and benzene ring = 64.0°.

J. 3 X-Ray structure of 1-phenyl-3,4-divinylsuccinimide.

1-Phenyl-3,4-divinylsuccinimide (109) was recrystallized from ethyl acetate. The solution was left to stand overnight in a thermos containing hot water, allowing slow crystallization and giving large colourless crystals m.p. 134-136°C.

The structure was refined to an R factor of 0.081.

The molecular geometry of (109) is shown in Figure 9. The bond lengths (Å) given in Figure 9 have standard deviations ±0.015Å. The numbering used for (109) is arbitrary.
**Fig. 9** A perspective drawing of 1-Phenyl-cis-3,4-divinylsuccinimide (109) with bond lengths in Å.
DISCUSSION

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A. 3, 5-Dioxo-4-oxa-9-thiatricyclo[5.3.0.0^2,6]decan-9,9-dioxide.

A.1 Preparation and stereochemistry of 3, 5-dioxo-4-oxa-9-
thiatricyclo[5.3.0.0^2,6]decan-9,9-dioxide.

As mentioned in the introduction, the title compound (1), which possesses some activity as a plant growth inhibitor, has been prepared in 51% yield by photolysis of butadiene sulphone (21) and maleic anhydride for 24 h in anhydrous acetone (Scheme 48).

\[
\begin{align*}
\text{O}_2\text{S} & \quad + \quad \text{O} \quad \text{hv} \\
(21) & \quad \text{qtz, acetone} \quad \text{O}_2\text{S} \\
& \quad \text{(1)} \quad 51\%
\end{align*}
\]

Scheme 48

No details of the absolute stereochemistry of compound (1) were reported at the time, but this is not surprising, since as shown in Figure 10 the 100 MHz proton n.m.r. spectrum is of little use in this respect because the various resonances overlap and preclude unambiguous assignment. Little information can also be obtained from \(^{13}\)C n.m.r. spectroscopy (see figure 11) other than that the spectrum is consistent with either a syn or an anti-structure for which a four line spectrum is expected.

The only absolute way to determine the configuration of (1) is by X-ray analysis but the lack of suitable crystals prevented this approach. However, as shown in scheme 49 the anhydride (1) could
Fig. 10. 100MHz $^1$H n.m.r. spectrum of 3, 5-dioxo-4-oxa-9-thiatricyclo-
[3.5.0.0$^2$,6]decane 9,9-dioxide (1). Inset is an expansion of the complex multiplet in the 3.0-3.5 $\delta$ region.

Fig. 11. 25.2MHz $^{13}$C n.m.r. spectrum of 3, 5-dioxo-4-oxa-9-thiatricyclo-
[5.3.0.$^2$,6]decane 9,9-dioxide (1).
be converted into its imide derivative (108) which on careful recrystal-
lization from glacial acetic acid gave colourless crystals ideal for
X-ray analysis. This showed that the compound possessed an anti-

\[
\begin{align*}
&\text{O}_2\text{S} \quad \text{PhNH}_2 \xrightarrow{\text{MeOH}} \text{O}_2\text{S} \\
&\quad \xrightarrow{\text{Acetic anhydride}} \text{O}_2\text{S} \\
&\quad \xrightarrow{\text{NaOAc}} \text{CONHPh}
\end{align*}
\]

Structure, details of which are shown in Figure 8 (p. 112). As can
be seen, the cyclobutane ring is essentially square planar, whereas
the sulphone ring is puckered and the imide ring is essentially planar
presumably because of the $sp^2$ hybridised carbons at C7 and C8.
The sulphone and the imide rings form dihedral angles of 100.4 and
113.5°, respectively with the mean cyclobutane plane. The bond
lengths and bond angles are within expected limits.

Since it is likely that no change occurs in the stereochemistry
about the C2-C6 bond in the conversion of (1) into (108), it seems
reasonable to assume that the anti-configuration can also be assigned
to (1) and to the variety of compounds subsequently derived from it.
Evidence presented in the introduction shows that pyrolysis of sulpholenes provides a useful synthesis of dienes. The present investigation sought to use pyrolysis of compounds of the general type (110) as a preparative route to cis-1, 2-divinyl compounds, e.g. (110) -> (111) (Scheme 50). It was decided to use the flash vacuum pyrolysis (F. V. P.) technique to achieve this objective.

Whilst pyrolysis has long been of great preparative utility in organic chemistry it is only recently that flash vacuum pyrolysis has found widespread application. The principle of this technique is that the substrate is sublimed under high vacuum into a hot zone where it resides for only a short time (10^-3 - 1s), whereupon the products are swept into a trap cooled to very low temperatures (-196°C). Its main advantage over conventional pyrolyses is that the dilute conditions and rapid separation of the primary products from the reaction zone help prevent secondary reactions taking place. As a result it is usually clean, convenient and efficient, and frequently has advantages over other synthetic methods for the preparation of
sensitive or strained compounds.

In this connection it is noteworthy that flash vacuum pyrolysis has been used to great advantage in the field of cyclophane chemistry, cumulating in the recent synthesis of superphane (112) which was once described by Vögtle as the ultimate achievement of work in this area.

Recently Seybold has reviewed the technique in general, while Vögtle and Rossa have focused on its application to sulphones in particular. A very recent monograph by Brown has emphasized that preparative pyrolysis of organic compounds are best run in flow systems.

Upon pyrolysis at 630°C under f.v.p. conditions, the anhydride (1) gave a pale yellow oil which hydrolysed readily on exposure to the atmosphere. Nevertheless, the product could be purified by bulb-to-bulb distillation at 65°C/0.1mmHg to give a clear liquid which on the basis of analytical, spectral and chemical evidence was characterized as 2, 5-dioxo-cis-3, 4-divinyltetrahydrofuran (113) (Scheme 51). Elemental analysis gave percentage composition for carbon and
hydrogen consistent with an empirical formula $C_8H_8O_3$. This was confirmed by observation in the mass spectrum of a peak at m/e 152.

The 100 MHz $^1H$ n.m.r. spectrum of the product is shown in figure 12 and corroborates the structure as 2, 5-dioxo-cis-3, 4-divinyl-tetrahydrofuran (113). Thus, the complex multiplet at 5.9-5.3 δ is ascribed to the cis-divinyl system in (113) and an examination of the fine detail shows that this resonance is very similar to that reported by Brown 87 for cis-divinylcyclopropane. The doublet of doublets ($J$ 4.5 Hz, 2 Hz) can be assigned to the protons 3-H and 4-H. The $^{13}C$ n.m.r. spectrum reproduced in Figure 13 is also consistent with the assigned structure. The anhydride moiety in (113) gives rise to a very broad band at 1900-1700 cm$^{-1}$ in the I.R. spectrum, while the band at 1642 cm$^{-1}$ is due to an olefinic stretch.

The cis-stereochemistry of (113) was validated by its essentially quantitative transformation to meso-2, 3-diethylsuccinic acid (107) m. p. 190-191°C (decomp.) (lit. 141 192°C) (Scheme 52). Thus the possibility of trans-stereochemistry could be ruled out as the trans-isomer would have given a racemic mixture of (+)-2, 3-diethylsuccinic acid (m. p. 129°C 141).
Fig. 12. 100MHz $^1$H n.m.r. spectrum of 2, 5-dioxo-cis-3, 4-divinyl-tetrahydrofuran (113). Insets are expansions of the olefinic and 3.8-4.0δ regions respectively.

Fig. 13. 25.2MHz $^{13}$C n.m.r. spectrum of 2, 5-dioxo-cis-3, 4-divinyl-tetrahydrofuran (113).
A plausible mechanism for formation of the cis-divinyl compound (113) from the anhydride (1) is a $\sigma^2s + \sigma^2s + \sigma^2s$ cheletropic process similar to that postulated for the extrusion of sulphur dioxide from 3-thiabicyclo[3.1.0]hexanes 3,3-dioxides (41a and 41b) (see scheme 20, p. 25). However, one cannot discount the possibility that the fragmentation goes via a radical process or polar mechanism. Distinction between these possibilities would require a stereocchemical investigation involving pyrolysis of an appropriately substituted 3,5-dioxo-4-oxa-9-thiatricyclo[5.3.0.0$^{2,6}$]decane 9,9-dioxide similar to the studies carried out by Mock with 3-thiabicyclo[3.1.0]hexanes (see p. 24). Such a study has not been carried out to date.

In view of the successful preparation of the cis-divinyl compound (113) it was decided to prepare a variety of derivatives of (1) and investigate their pyrolysis as a general route to cis-1,2-divinyl systems. To date, synthetic access to these systems has been difficult and existing methods usually give mixtures of cis and trans isomers which can only be separated by preparative gas chromatography. A typical approach which illustrates some of the problems involved is the preparation of cis-divinylcyclopropane (80) reported by Brown.
in which addition of ethoxycarbonyl carbene to butadiene yielded a mixture of cis and trans-vinylcyclopropanecarboxylic esters (Scheme 53).

![Chemical structure](image)

This mixture was separated by preparative gas chromatography and the cis-isomer then used in the remaining steps of the sequence. It is of interest to note that the final product was still contaminated with 10% of trans-divinylcyclopropane, perhaps due to some epimerisation in the Wittig step.

Other attempts at the preparation of cis-1, 2-divinyl compounds have also led to isomeric mixtures. For example, Stogryn\textsuperscript{89a} prepared
2, 3-divinylloxiranes by the route shown in Scheme 54. Once again isolation of the pure cis and trans isomers required preparative gas chromatography.

\[
\begin{align*}
\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2 & \xrightarrow{\text{AcCl}} \text{CH}_2=\text{CH} \cdot \text{CH}=\text{CH} \cdot \text{CH}=\text{CH}_2 \\
& \xrightarrow{\text{NaOH/KOH} \ \langle 50^\circ \text{C} \rangle} \\
& \text{cis} + \text{trans}
\end{align*}
\]

Scheme 54

A further example is the recently reported preparation of cis-2, 3-divinylthiirane in which treatment of a mixture of cis and trans-divinylloxiranes with a saturated aqueous solution of KSCN gave a mixture of cis and trans-divinylthiirane (Scheme 55). The pure isomers were obtained by preparative gas chromatography.

\[
\begin{align*}
\text{cis} \ & \text{cis} + \text{trans} \\
\text{trans} \ & \text{trans}
\end{align*}
\]

Scheme 55

Finally it is of interest to note that Hammond has reported
that photosensitized dimerization of butadiene leads to a mixture of cis and trans-1, 2-divinylcyclobutane and 4-vinylcyclohexene with the cis-isomer being the minor product (Scheme 56).

\begin{align*}
\text{\textbf{Scheme 56}} \\
\text{One example of a stereo specific synthesis in this area has been reported by Heimbach}^{99} \text{ who utilized a reverse Cope-reaction to prepare cis-1, 2-divinylcyclohexane from cis, trans-1, 5-cyclo-decadiene (90) (see Scheme 41, p. 41). The latter was easily prepared from butadiene and ethylene using nickel-based } \pi \text{-complex catalysts.}^{148}
\end{align*}

To date the only method which gives entirely cis-divinyl compounds is that due to Vogel$^{94}$ but this lengthy route suffers from the fact that it requires different starting materials for each preparation. Scheme 57 shows the typical preparation of cis-1, 2-divinylcyclobutane (85) from cis-1, 2, 3, 6-tetrahydrophthalic anhydride (114) by the methods indicated.
**Scheme 57**

5 Steps

\[
\overset{114}{\text{O}} \quad \overset{5 \text{ Steps}}{\Longrightarrow} \quad \overset{\text{(85) 81\%}}{\text{N(CH}_3\text{)}_3\text{OH}}
\]

\[
\overset{95\%}{\text{CO}_2\text{Me}} \quad \overset{\text{CH}_3\text{N}_2}{\longrightarrow} \quad \overset{50\%}{\text{CO}_2\text{H}}
\]

\[
\overset{87\%}{\text{OH}} \quad \overset{\text{TsCl, pyridine}}{\longrightarrow} \quad \overset{66\%}{\text{OTs}}
\]

\[
\overset{100\%}{\text{N(CH}_3\text{)}_3\text{I}} \quad \overset{\text{Ag}_2\text{O}}{\longrightarrow} \quad \overset{97\%}{\text{I}}
\]
B. Preparation of Precursors of 3,4-Divinylcyclopentane Analogues.

B.1 4-Oxa-9-thiatricyclo[5.3.0.0^2,6]decane 9,9-dioxide.

The preparation of the title compound (117) was carried out in three steps starting from (1) as outlined in Scheme 58. When boiled with a few drops of concentrated sulphuric acid in methanol the anhydride (1) gave a 90% yield of the diester (115) as a white crystalline solid m.p. 126-127°C (lit. 3 126-127°C).

![Scheme 58](image)

In the case of the diol (116) reduction of the diester (115) with lithium aluminium hydride in THF gave a colourless crystalline compound which had a m.p. 98-100°C compared to the literature value of 75-82°C. Nevertheless on the basis of analytical, spectral and chemical evidence the structure of the colourless compound was established as 6,7-dihydroxymethyl-3-thiabicyclo[3.2.0]heptane 3,3-dioxide (116). Elemental analysis gave percentage composition for carbon and hydrogen consistent with an empirical formula C_{8}H_{14}O_{4}S.
Despite its insolubility in most solvents, the diol (116) could be recovered from the inorganic salts after reduction by continuous extraction with THF in a Soxhlet apparatus over a period of 48 h.

Some difficulty was encountered in the third step, viz., the conversion of the diol (116) into 4-oxa-9-thiatricyclo[5.3.0.0^2,6]-decane 9,9-dioxide (117). Initial attempts to dehydrate the diol (116) using dimethyl sulphoxide as the dehydrating agent\(^ {109}\) gave, in one instance, a 71% yield of a colourless crystalline solid m.p. 129-130\(^\circ\)C which on the basis of its analytical and spectral data was identified as the desired tetrahydrofuran (117). However when the method was repeated, the extraction step using dichloromethane did not give any product, presumably because the diol (116) had not reacted. Whilst there is no obvious explanation for this failure it is clear that the dimethyl sulphoxide needs to be super dry and the reaction temperature carefully controlled for this procedure to be successful.

To circumvent this problem an alternative procedure\(^ {108}\) was adopted involving conversion of the diol (116) into its tosylate and cyclisation in pyridine. This procedure proved successful but the work-up required chromatography and gave the cyclic ether (117) in only 26% yield.

In another procedure concentrated sulphuric acid was employed as the dehydrating agent and whilst this method was successful, giving yields of 55\%, it suffered from the drawback that the acid tended to char the reaction mixture.

The n.m.r. data for the ether (117) will be fully discussed in Section B.6.
B. 2 4,9-Dithiatricyclo[5.3.0.0^{2,6}]decane 4,4-dioxide.

Conversion of the diol (116) into the title compound (119) was achieved in two steps as shown in Scheme 59.

Scheme 59

In the first step, reaction of the diol (116) with methane sulphonyl chloride in pyridine gave the dimesyl ester (118) in 75% yield. When boiled under reflux with sodium sulphide nonahydrate in aqueous ethanol the latter gave a colourless crystalline solid in 62% yield. This was identified as 4,9-dithiatricyclo[5.3.0.0^{2,6}]decane 4,4-dioxide (119) on the basis of analytical and spectral evidence. Elemental analysis gave percentage composition for carbon and hydrogen consistent with an empirical formula $C_8H_{12}O_2S_2$. This was verified by observation in the mass spectrum of a parent ion peak at m/e 204.
B.3 Attempted preparation of 9-phenyl and 9-methyl-4-thia-9-azatricyclo[5.3.0.0^2,6]decane 4,4-dioxides by lithium aluminium hydride reduction of the cyclic imides.

Attempts to prepare the 9-phenyl amine (120) by reduction of the cyclic imide (108), as shown in Scheme 60 were largely unsuccessful.

![Scheme 60]

On one occasion a 3% yield of (120) was obtained but it could not be obtained in a pure state due to decomposition on standing. All attempts to work-up the products from the reduction of (108) by chromatography inevitably led to the formation of intractable tarry residues. This is not surprising since (120) is a tertiary aromatic amine which are very susceptible to aerial oxidation. 149

As tertiary alkyl amines are less susceptible to aerial oxidation than are their aromatic counterparts, it was decided to try to prepare the methyl analogue of (120). The 9-methyl analogue of (108) was prepared by a route similar to that used for the preparation of (108) (see Scheme 49, p.121), using methylamine instead of aniline. Reduction of this imide with lithium aluminium hydride in THF gave a pale yellow oil whose $^{13}$C n.m.r. spectrum identified it as the desired amine but showed the presence of large amounts of unidentified
impurities. Attempts to purify this oil, by bulb-to-bulb distillation and by chromatography failed and so a pure sample for elemental analysis could not be obtained. However the mass spectrum of the yellow oil did have a peak at 201 consistent with an empirical formula \( C_9H_{15}NO_2S \).

\[ \text{B.4 9-Benzyl-4-thia-9-azatricyclo[5.3.0.0^2,6]decane 4,4-dioxide.} \]

In view of the failure to prepare amines by the reduction of imides it was decided to adopt a procedure similar to that used for the preparation of the cyclic sulphide (119). Thus treatment of the diol (116) with tosyl chloride in pyridine gave a 51% yield of the ditosylate (121), which on boiling with benzylamine under reflux in ethanol for 48 h gave a 56% yield of a colourless solid (Scheme 61).

\[
\begin{align*}
\text{CH}_2\text{OH} & \quad \text{TsCl} \quad \text{pyridine} \\
\text{O}_2\text{S} & \quad \text{CH}_2\text{OH} \\
\text{(116)} & \quad \text{OTs} \\
\text{CH}_2\text{OH} & \quad \text{OTs} \\
\text{(121)} & \quad 51\% \\
\text{PhCH}_2\text{NH}_2 & \quad \text{EtOH} \\
\text{O}_2\text{S} & \quad \text{N-CH}_2\text{Ph} \\
\text{(122)} & \quad 56\%
\end{align*}
\]

\text{Scheme 61}

Analytical and spectral evidence established the structure of the colourless solid as 9-benzyl-4-thia-9-azatricyclo[5.3.0.0^2,6]-decane 4,4-dioxide (122). Elemental analysis gave percentage
composition for carbon, hydrogen and nitrogen consistent with an empirical formula $\text{C}_{15}\text{H}_{19}\text{NO}_2\text{S}$. This was verified by observation in the mass spectrum of a parent ion peak at m/e 277.

B.5 **Mechanism of formation of 1-heterocyclopentane rings.**

The mechanism for the formation of the 1-heterocyclopentane rings in compounds (116), (119) and (122) is presumably similar in each case. Scheme 62 illustrates the typical conversion of the ditosylate (121) into the cyclic amine (122). Thus nucleophilic attack on one of the $-\text{CH}_2\text{OTs}$ groups by the amine followed by loss of a proton gives an amine which is ideally suited to repeat the process intramolecularly and thus give the observed cyclic amine (122).

\[
\begin{align*}
\text{R} &= -\text{CH}_2\text{Ph} \\
\text{Scheme 62}
\end{align*}
\]

The mechanism for the dehydration of the diol (116) using dimethyl sulphoxide is more difficult to rationalize but it is thought that a cyclic transition state ensues as depicted in Figure 14.
B. 6 Spectroscopic properties of precursors of 3,4-divinylcyclopentane analogues.

The main evidence for the structural assignments given to (116), (119) and (122) comes from their $^1$H and $^{13}$C n.m.r. spectra which show strong similarities for each compound.

These compounds could possibly exist in either syn or anti-configurations but were assigned the anti-structure on the grounds that they are all derived from (1), presumably with retention of configuration.

As can be seen from figure 15 the most striking feature of the $^1$H n.m.r. spectrum of 4-oxa-9-thiatricyclo[5.3.0.0$^{2,6}$]decane 9,9-dioxide (117) is the pair of doublets centred at 3.9 and 3.56. These signals are due to the methylenes adjacent to the ether linkage and since they are pro-chiral centres, the protons are non-equivalent.

This is confirmed by the differences in chemical shift and by the fact that they show geminal coupling (9.5 Hz). The $^{13}$C n.m.r. spectrum of (117) shown in figure 16 further confirms this assignment as it shows only four resonances.
Fig. 15. 100MHz $^1$H n.m.r. spectrum of 4-oxa-9-thiatricyclo[5.3.0.0$^2$.6]-decane 9,9-dioxide (117). Inset is an expansion of the signals in 2.5-4.05 region.

Fig. 16. 25.2MHz $^{13}$C n.m.r. spectrum of 4-oxa-9-thiatricyclo[5.3.0.0$^2$.6]-decane 9,9-dioxide (117). Inset is an expansion of the signals in 30-60 $\delta$ region.
The $^1$H and $^{13}$C n.m.r. spectra of compounds (119) and (122) are similarly consistent with the assigned structures. However in these cases there is more overlap of resonances in the $^1$H n.m.r. spectra and the individual peaks are less easy to assign unambiguously.
C Preparation and Reactions of 3-Thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide.

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

The bicyclic compound, 3-thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide (123) offers considerable scope as a synthon for the preparation of other cis-divinyl derivatives, which might be difficult to obtain by existing methods. A methodology can be envisioned, as illustrated in scheme 63, involving annelation of the strained cyclobutene ring to give (110) which under flash vacuum pyrolytic conditions, might be expected to lose SO$_2$ and form cis-1,2-divinyl compounds (111). It is pertinent to point out that when the ring in (111) is of suitable size, such compounds can readily undergo a Cope rearrangement to give larger rings (see Section C in Introduction).

Several well-documented procedures exist for functionalising the alkene moiety in compounds of type (123). For example Meyers $^{64}$ has used a variety of epoxidation and nitrene addition reactions to prepare precursors to divinyl ethers (59) and divinyl carbamates (61) (see Scheme 27, p. 30).
In an extension of these procedures, Meyers and his co-workers have reported an efficient synthesis of 1,4-dihydropyridines (124) as outlined in Scheme 64.

Other workers have reported the application of similar ring-forming reactions involving cyclobutene and its derivatives. For example, Anderson et al. found that reaction of N-phthalimidonitrene, generated by treatment of N-amino phthalimide with lead tetraacetate, with cyclobutene (125) or cis-3,4-dichlorocyclobutene (127) gave adducts (126) or (128) in 18-22% and 9-12% yields, respectively (Scheme 65).
The facile addition of 1, 3-dipoles to alkenes including cyclobutenes has also found extensive application in the synthesis of five-membered heterocycles. In these circumstances the 1, 3-dipole (129), which can only be represented by zwitterionic octet resonance structures, combines in a concerted fashion with a multiple bond system (130) (the dipolarophile) to form an unchanged five-membered ring (131) (Scheme 66).

Thus, benzonitrile oxide affords an 82% yield of the adduct (132) when added to cis-3, 4-dichlorocyclobutene (127) (Scheme 67). 152

Diazooalkanes and cyclic nitrones have also been reported to react readily with cis-3, 4-dichlorocyclobutene (127) to give the corresponding
adducts in 90% and 70% yields, respectively. More recently nitrilimines have been successfully reacted with cyclobutenes.

The synthetic strategy adopted for the preparation of the bicyclic alkene (123) was to convert the readily available anhydride (1) into its diacid (133) then bis-decarboxylate the latter with either lead tetra-acetate or by electrolysis (Kolbe reaction) (Scheme 68). The oxidative bis-decarboxylation step (133) -> (123) has adequate precedent in that similar decarboxylations have been used with considerable success to prepare cyclobutene derivatives.

For example, treatment of the dibasic acid (134) with lead tetra-acetate gave bicyclo[2.2.0]hex-2-ene (135) in 30-38% yield as shown in Scheme 69. Under similar conditions the anhydride (136) afforded...
bicyclo[2.2.0]hex-2,5-diene (Dewar benzene) in 20% yield, which could be raised 35-40% by carrying out the decarboxylation using electrolysis (Scheme 70). However, in general the electrolytic technique is limited to small scales and is not very convenient.

Hydrolysis of the anhydride (1) was first carried out by treatment with 3M sodium hydroxide solution. This method gave the diacid (133) as a colourless crystalline solid, m. p. 188-191°C (lit. 3 194-195°C) in 70% yield but subsequent experiments showed that the diacid could be obtained quantitatively simply by boiling the anhydride with water for ½ h.

Traditionally oxidative bis-decarboxylation reactions give low yields and the conversion of (133) into (123) was no exception. Thus treatment of the diacid (133) with lead tetraacetate according to the procedure of Jefford et al. produced a brown oil, purification of which by medium pressure chromatography gave only 19% yield of a colourless crystalline solid, m. p. 71-75°C. This was identified as the alkene (123) on the basis of its spectral and analytical properties.

Thus elemental analysis of (123) gave a percentage composition for carbon and hydrogen consistent with the empirical formula C₆H₈O₂S. This was corroborated by observation in the mass spectrum of a parent
ion peak at m/e 144.

The i.r. spectrum of the alkene (123) shows very weak absorptions at 3120 cm$^{-1}$ and 1553 cm$^{-1}$ characteristic of the cyclobutene ring.\footnote{161}

The $^1$H n.m.r. spectrum of (123) is reproduced in Figure 17 and shows that the two olefinic protons in the cyclobutene ring resonate as a singlet at 6.18 $\delta$. Presumably the lack of coupling between the olefinic and bridgehead protons is due to the fact that the dihedral angle between these protons is approximately 90$^\circ$ and thus give zero coupling constants. The multiplet at 3.7-3.6 $\delta$ is due to the bridgehead protons (1-H and 5-H), while the remaining -methylene groups give rise to a multiplet at 3.2-2.9 $\delta$. In keeping with the assigned structure, the $^{13}$C n.m.r. spectrum of the alkene (123) exhibited only three resonances as shown in figure 18.

Attempts to improve the yield of alkene (123) by adopting other methods for the decarboxylation of the diacid (133) gave only mediocre results. Thus use of the alternative procedure of Cimarusti and Wolinsky\footnote{162} whereby oxygen instead of nitrogen is bubbled through the reaction mixture gave only a 16% yield of the alkene (123). Likewise electrolysis (60-100V dc 0.5-0.8 amp) of the diacid (133) in a mixture of 10% pyridine and triethylamine at room temperature gave only a 20% yield of the alkene (123).

In another approach, use was made of bis-triphenylphosphinenickel dicarbonyl as a decarboxylating agent.\footnote{163} This reagent is relatively new but its synthetic utility has been clearly demonstrated by Dauben\footnote{164} who used it with spectacular success in the preparation of barralene (138) as shown in Scheme 71. Its main drawback appears to be the high
Fig. 17. 100MHz $^1$H n.m.r. spectrum of 3-thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide (123).

Fig. 18. 25.2MHz $^{13}$C n.m.r. spectrum of 3-thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide (123).
temperature required for decarboxylation making it unsuitable for products that are thermally labile. Since the alkene (123) decomposes at temperatures above 140°C [vide infra] it was decided to modify the procedure by using dimethoxyethane (b.p. 81°C) instead of diglyme (b.p. 165°C) as the solvent. However, even after several days under reflux, the reaction mixture showed no apparent change in colour and examination by t.l.c. showed the absence of any alkene. When the reaction was repeated with diglyme as solvent decomposition ensued within three hours.

In order to corroborate the structure of the alkene (123) it was also synthesised by the alternative route outlined in Scheme 72. Thus

\[
\text{III} + \text{(139)} \xrightarrow{\text{LiAlH}_4, \text{THF}} \text{(140)} 82\%
\]

\[
\text{(123)} \xrightarrow{[\text{O}]} \text{(142)} 90\%
\]

\[
\text{(142)} \xrightarrow{\text{Na}_2\text{S}, \text{HMPA}} \text{(141)} 70\%
\]
Cyclobutene anhydride (139) was obtained as a colourless crystalline solid in 24% yield by photochemical cycloaddition of acetylene to maleic anhydride in methanol. Reduction of this anhydride with lithium aluminium hydride in tetrahydrofuran gave an 82% yield of the diol (140) as a pale yellow oil which was converted into its dimesylate (141) in 70% yield by treatment with methanesulphonyl chloride in pyridine. Treatment of this diester with sodium sulphide in hexamethylphosphoramide (HMPA) at 50°C according to the procedure of Paquette gave the cyclic sulphide (142) as a yellow oil in 90% yield. Oxidation of this oil with m-chloroperbenzoic acid in dichloromethane gave the alkene (123) together with another compound which was subsequently shown to be the epoxide of (123) (see section C.2).

C.2 8-Oxa-4-thiatricyclo[5.1.0²,6]octane 4,4-dioxide.

The title compound (143) was recognised as a potential precursor to cis-2,3-divinyloxirane (83, X=O) which is known to undergo a facile Cope rearrangement to give 4,5-dihydrooxepin (84, X=O) as outlined in Scheme 73. A potential drawback to this strategy is the possible

\[ \text{O}_2\text{S} \begin{array}{c} \text{[O]} \end{array} \text{O}_2\text{S} \begin{array}{c} \Delta \text{-SO}_2 \end{array} \]

\[ \begin{array}{c} \text{[123]} \end{array} \quad \begin{array}{c} \text{(143)} \end{array} \]

\[ \begin{array}{c} \text{O}_2\text{S} \end{array} \]

\[ \begin{array}{c} \text{(84, X=O)} \end{array} \]

\[ \begin{array}{c} \text{O}_2\text{S} \end{array} \]

\[ \begin{array}{c} \text{(83, X=O)} \end{array} \]

\[ \begin{array}{c} \text{Scheme 73} \end{array} \]
isomerization of the highly strained (143) to (144) prior to cheletropic extrusion of $\text{SO}_2$. This would lead eventually to the formation of cyclohex-1-ene-3-one (145) as depicted in Scheme 74.

Scheme 74

Initial attempts to convert the alkene (123) into the epoxide (143) were carried out using $m$-chloroperbenzoic acid as the oxidant. However the reaction proved to be very slow, an observation consistent with the observation by Cope et al. that epoxidation of the cyclobutene ring in compound (146) with $m$-chloroperbenzoic acid required a reaction time of 400 h. Work-up of the reaction after several days gave 12% yield of a colourless crystalline solid which on the basis of analytical data was established as the desired epoxide (143).
In view of the poor yield of epoxide (143) obtained by direct oxidation of the alkene (123) it was decided to seek a different synthetic approach. One possibility involved the dehydrohalogenation of the appropriate chlorohydrin using silver oxide. This method had been reported to give an efficient synthesis of the epoxide (148) from (147) in 90% yield (Scheme 75).

\[ \text{CH}_2\text{CHOH}\text{SO}_2\text{Cl} \xrightarrow{85^\circ C} \text{Ag}_2\text{O} \rightarrow \text{CH}_2\text{COSO}_2\text{OH} \]

Scheme 75

The preparation of the desired chlorohydrin (149) was carried out as shown in Scheme 76 by addition of hypochlorous acid to the alkene (123) according to the procedure of Sorenson. However, subsequent attempts to dehydrohalogenate compound (149) with silver (I) oxide in dimethoxyethane led to the recovery of starting material. Apparently, in this case, the strain energy incurred in the formation of the epoxide (143) is too high and cyclization is disfavoured.

In a final attempt to obtain (143) by direct oxidation of the alkene (123) performic acid was employed as the oxidising agent. As a rule performic acid is not considered to be a good epoxidation reagent because the high acidity of formic acid (employed either as solvent or
formed in the oxidation) usually leads to epoxide ring opening. Nonetheless its use was prompted by a report by Bianchi et al. describing the successful epoxidation of the alkene (150).

\[ \text{(150)} \]

Treatment of (123) with performic acid did give a 40% yield of the epoxide (143) but the reaction was still slow and required a 96 h reaction period.

As shown below the epoxide (143) can exist in two geometric forms, viz., in either a syn or an anti-configuration. Only one isomer was detected by t.l.c. and by $^{13}$C n.m.r. spectroscopy and this was tentatively assigned the anti-configuration as it has been reported that epoxidation of formally similar cyclobutenes such as (150) give an anti-epoxide as the predominant product (anti:syn 20:1) upon treatment with performic acid. The latter assignments were made from evidence that treatment of the major product with HCl gave a chlorohydrin whose stereochemistry was confirmed by $^1$H n.m.r. spectroscopy and shown to arise from an anti-epoxide.
The stereochemistry of (143) could not be determined by $^1$H n.m.r. spectroscopy since assignment of cis and trans orientations of protons on four-membered rings from vicinal coupling constants gives results that are ambiguous.

The only type of $^1$H n.m.r. analysis which might resolve this stereochemical problem is to utilize the approach adopted by Gamba and Mondelli who reported that the sign of four bond couplings in cyclobutanes is highly stereospecific and much more sensitive to cis-trans orientation of the two interacting protons than to the effects of substituents or to distortions of the ring. However the authors did not elaborate on the details of the experimental methods employed.

C.3 Attempted addition of carbenes and nitrenes to 3-thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide.

a) Attempted addition of carbenes.

The addition of carbenes to the alkene (123) was investigated as a possible route to the carbon analogue of the epoxide (143). It was recognised that pyrolysis of this compound (151) should lead to cis-1,2-divinylcyclopropanes (152) which are known to undergo Cope rearrangement and thus give cyclohepta-1,4-dienes (153) (Scheme 77).

\[ R = \text{CO}_2\text{Et} \]

Scheme 77
All attempts to prepare compound (151) by addition of ethoxy-carbonyl carbene to the alkene (123) failed completely. It was found that reaction occurred preferentially with benzene which was used as solvent or the carbenes dimerized rather than add to the alkene (123).

b) Attempted addition of nitrenes

The addition of nitrenes to the alkene (123) was investigated as a possible route to the nitrogen analogue of the epoxide (143) viz. the aziridine (154) (Scheme 78).

\[
\begin{align*}
\text{Scheme 78} \\
(123) & \xrightarrow{R-N^+} (154) \\
O_2S & \quad N-R
\end{align*}
\]

The first attempt at nitrene addition involved the use of ethoxy-carbonylnitrene generated by treatment of p-nitrophenylsulphonyloxycarbamide with triethylamine and gave only nitrene dimers and unchanged alkene (123) as the product. This failure is hardly surprising in that it has been reported that addition of the same nitrene to cyclobutene (125) gave only a 1.5% yield of the aziridine product (155).

\[
\begin{align*}
\text{Scheme 79} \\
(125) & \xrightarrow{R-N^+} (155) \\
\text{R=CO}_2\text{Et} \\
N-R & 1.5\%
\end{align*}
\]

(Scheme 79). However it has been reported that photolysis of a dichloromethane solution of ethylazidoformate and 1, 2-dimethylcyclo-
butane gave a 65% yield of the desired aziridine product which proved stable. 

In view of the failure of ethoxycarbonylnitrene to add to the alkene (123) it was decided to try the same reaction using the more nucleophilic nitrene \( \text{N-phthalimidinonitrene} \), generated by treatment of \( \text{N-aminophthalimide} \) with lead tetraacetate. \(^{121}\) Work-up of the reaction mixture gave a 6% yield of a colourless crystalline compound which exhibited a parent ion peak at \( m/e \) 304 indicative of the expected structure.

\[
\text{H}_2\text{N}^-\text{N} \quad \text{O} \\
\text{O}_2\text{S} \\
(123) \quad \text{Pb(OAc)}_4 \quad \text{in CHCl}_2 \\
(156) \quad \text{6\%}
\]

Scheme 80

(156) (Scheme 80). Unfortunately, correct analytical data could not be obtained due to the unstability of the compound. In this connection it is worth noting that the corresponding adducts obtained by addition of \( \text{N-phthalimidonitrene} \) to cyclobutene tend to decompose fairly readily. In these instances also the yields of adducts were low (ca. 10-20%). \(^{121,151}\)

The lack of reactivity of the strained alkene (123) toward reactive species is only one of several examples in a much wider study presently.

* Photolysis of the alkene (123) with neat ethyl azidoformate, gave the desired aziridine in 31% yield. The mode of formation is assumed to proceed by way of electronically excited azide with the intermediacy of ethoxycarbonylnitrene.
being carried out by other workers at Edinburgh. They have found that alkenes of the same general type as (123) show a pronounced lack of reactivity toward addition of reactive species such as carbenes and nitrenes.

In an attempt to explain this phenomenon, Simpson has carried out both theoretical and photoelectron spectroscopic studies on (123) and several related compounds. The results showed that the energetic availability of the alkene \( \pi \) electrons was determined by a combination of through space delocalization, inductive and hyperconjugative effects which lead to the stabilization of the \( \pi \) level; this is evidenced by a relatively high ionization potential of the olefinic \( \pi \) electrons as shown in Table 2.

**C.4 The addition of 1, 3-dipoles to 3-thiabicyclo[3.2.0]hept-6-ene 3, 3-dioxide.**

The addition of 1, 3-dipoles of general formula (129) was studied as a possible general route to precursors of cis-divinyl-5-membered heterocycles (158) as depicted in Scheme 81.

![Scheme 81](image-url)
TABLE 2

Magnitude of 1st ionization potential (eV) of unsaturated level.

<table>
<thead>
<tr>
<th>Structure</th>
<th>1st Ionization Potential (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Structure" /> (139)</td>
<td>10.49</td>
</tr>
<tr>
<td><img src="image2" alt="Structure" /> (123)</td>
<td>10.25</td>
</tr>
<tr>
<td><img src="image3" alt="Structure" /> (114)</td>
<td>10.00</td>
</tr>
<tr>
<td><img src="image4" alt="Structure" /> CO₂Me</td>
<td>9.76</td>
</tr>
<tr>
<td><img src="image5" alt="Structure" /> SO₂</td>
<td>9.69</td>
</tr>
<tr>
<td><img src="image6" alt="Structure" /></td>
<td>9.43</td>
</tr>
<tr>
<td><img src="image7" alt="Structure" /> CO₂Me</td>
<td>9.25</td>
</tr>
<tr>
<td><img src="image8" alt="Structure" /></td>
<td>8.94</td>
</tr>
</tbody>
</table>

* Data reproduced from ref. 173.
a) Addition of C, N-diphenylnitrone

The reaction of C, N-diphenylnitrone (159) with the alkene (123) in boiling toluene gave a 28% yield of a light brown solid which on the basis of analytical and spectral evidence was assigned the structure (160) (Scheme 82).

![Scheme 82](image)

Elemental analysis of the solid gave percentage composition for carbon, hydrogen, and nitrogen consistent with an empirical formula C$_{19}$H$_{19}$N$_3$O$_5$. This was corroborated by observation in the mass spectrum of a parent ion peak at m/e 341.

As indicated in Scheme 83 the structure of (160) is of interest

![Scheme 83](image)
not only from the point of view of a syn or anti-configuration, but also with regard to the stereochemistry about the C_5 atom. Only one isomer could be detected by t.l.c. and this was tentatively assigned the anti-structure (a) or (b) from consideration of the steric interactions involved. Further evidence in support of the assigned stereochemistry of (160) was obtained by \textsuperscript{1}H n.m.r. spectroscopy using the technique of double irradiation. An examination of the \textsuperscript{1}H n.m.r. spectrum of (160) (Fig. 19) shows that two of the protons viz. 2-H and 5-H, can easily be assigned to the resonances at 4.85 and 4.56, respectively due to the deshielding effects of the oxygen and nitrogen atoms. Upon irradiation of the large multiplet at 3.66 both these signals collapsed to broad singlets (figure 20) presumably as a result of decoupling of the 6-H proton leading to the disappearance of both 7Hz couplings. This suggests that there is a cis-relationship between the 5-H and 6-H protons because of the large J_{5,6} = 7Hz, compared to the value of <0.5Hz for the coupling between trans orientated protons in the adduct formed by addition of 3,4-dihydroisoquinoline-\textsubscript{N}-oxide to the alkene (139). The smaller coupling constant of 2Hz found in the resonance at 4.86 is most likely to be J_{1,2}. This supports the assignment of (160) as an anti-structure since as already reported \textsuperscript{154} for cyclobutane rings, values of coupling constants lower than 5Hz cannot arise from cis-interactions of adjacent protons.

b) Addition of anisonitrile oxide and benzonitrile oxide.

The nitrile oxides used in these experiments were generated in situ by thermal dehydrohalogenation of the appropriate hydroxamic
Fig. 19. 100MHz $^1$H n.m.r. spectrum of 4, 5-diphenyl-3-oxa-9-thia-4-azatricyclo[5. 3. 0. 0$^2$, 6]decane 9, 9-dioxide (160).

Fig. 20. 100MHz $^1$H n.m.r. spectrum of 4, 5-diphenyl-3-oxa-9-thia-4-azatricyclo[5. 3. 0. 0$^2$, 6]decane 9, 9-dioxide (160) with inset showing effect of irradiating multiplet at 3.6$\delta$. 
chloride. Thus when the alkene (123) was boiled in toluene with
anisohydroxamic chloride (161) for 48 h the reaction gave a 45% yield
of a colourless solid which on the basis of analytical and spectral
evidence was characterized as compound (162) (Scheme 84). Similarly
reaction of the alkene (123) with benzonitrile oxide (163) gave a 19%
yield of an adduct whose structure was established as compound (164).

\[
\begin{align*}
\text{O}_2\text{S} & + \text{X-C}_6\text{H}_4\text{CClNOH} \xrightarrow{\Delta} \text{O}_2\text{S} \\
(123) & \quad (161) \quad (162) \quad 45\%
\end{align*}
\]

\[
\begin{align*}
\text{X} & = \text{OMe} \\
(163) & \quad (164) \quad 19\%
\end{align*}
\]

Scheme 84

The structural assignments of compound (162) and (164) were
mainly based on their \(^1\)H n.m.r. spectra which showed strong
similarities to the \(^1\)H n.m.r. spectrum of the nitrone adduct (160).
As shown in Figure 21 the \(^1\)H n.m.r. spectrum of compound (162)
displays resonances at 5.28 and 4.38 which are assigned to the 2-H
and 6-H protons, respectively. These chemical shift values compare
favourably with those reported for the corresponding protons in the
adducts obtained from the cycloaddition of nitrile oxides to \textit{cis}-3,4-
dichlorocyclobutene.\(^{152}\) The large coupling constant (8Hz) observed
for these two signals is probably \(J_{2,6}\) since these protons are \textit{cis}-
orientated.

The small coupling constant (2Hz) in the resonance at 5.28 is
presumably \(J_{1,2}\) in keeping with the assignment of the stereochemistry
Fig. 21. 100MHz $^1$H n.m.r. spectrum of 5-(p-methoxyphenyl)-3-oxa-9-thia-4-azatricyclo[5.3.0.0$^{2,6}$]dec-4-ene 9,9-dioxide (162).

Fig. 22. 25.2MHz $^{13}$C n.m.r. spectrum of 5-(p-methoxyphenyl)-3-oxa-9-thia-4-azatricyclo[5.3.0.0$^{2,6}$]dec-4-ene 9,9-dioxide (162).
as an anti-structure. This is further supported by the secondary splitting of the doublet at 4.36 which is just visible and is presumably $J_{6,7}$.

Figure 22 shows the $^{13}$C n.m.r. spectrum of (162) and contains eleven lines which is consistent with the assigned structure.

The $^1$H n.m.r. and $^{13}$C n.m.r. spectra of adduct (164) shows strong similarities to the spectra of adduct (162) and a similar analysis to that described above confirms the assigned structure.

c) Addition of diazomethane

The reaction was carried out by standing an etheral solution of the alkene (123) and diazomethane in a cold room (0-5°C) for several weeks during which time a colourless crystalline solid gradually precipitated out of solution in 80% yield. Analytical and spectral evidence established the structure of the compound as the pyrazoline (165) shown in Scheme 85. The slow rate of formation of the adduct (165) accords with a report by Mock who observed that diazomethane only adds to butadiene sulphone in 35% yield over a period of several weeks.

Elemental analysis for (165) gave percentage composition for
carbon, hydrogen and nitrogen consistent with an empirical formula
\[ \text{C}_7\text{H}_{10}\text{N}_2\text{O}_2\text{S} \]. This was verified by observation in the mass spectrum of a peak at m/e 186.

The i.r. spectrum of (165) showed a band at 1535 cm\(^{-1}\) which is characteristic of \(\delta^1\)-pyrazolines.\(^{174}\)

The assigned stereochemistry of (165) is based on its \(^1\)H n.m.r. and \(^{13}\)C n.m.r. spectra and on the results of selective \(^1\)H n.m.r. decoupling experiments. The 360MHz \(^1\)H n.m.r. spectrum of (165) is shown in Figures 23 and 23a and contains five multiplets. Due to the strong deshielding effect of the diazo group on adjacent protons the multiplet at 5.3-5.26 is considered to be due to the bridgehead methine proton 1-H. Similarly the multiplet centred at 4.66 is due to the methylene protons 8-H and 8'-H. The \(\alpha\)-sulphone methylenes are considered to give rise to the multiplet from 3.4-3.16, whilst the bridgehead methine protons 2-H, 7-H, 6-H are assigned to the multiplets at 3.056, 2.76 and 2.66 respectively.

Double resonance experiments helped to confirm these assignments as well as the \underline{anti}-structure. Thus irradiation of the multiplet at 5.26 leads to a simplification in the resonance at 4.66 (Fig. 23b). This shows that there is coupling between 1-H and the methylene at C-8, an effect which has been noted for similar compounds.\(^{174}\) Of the three cyclobutane protons the resonance due to 7-H simplifies to a much greater extent than the other two suggesting the removal of a fairly large coupling constant in this case. This is in keeping with the \underline{anti}-orientation of the sulphone and pyrazoline rings.
Fig. 23. 360MHz $^1$H n.m.r. spectrum of 4-thia-9,10-diazatricyclo-
[5.3.0.0$^2,6$]dec-9-ene 4,4-dioxide (165).

Fig. 24. 25.2MHz $^{13}$C n.m.r. spectrum of 4-thia-9,10-diazatricyclo-
[5.3.0.0$^2,6$]dec-9-ene 4,4-dioxide (165).
Fig. 23a. Expansion of 360MHz $^1$H n.m.r. spectrum of 4-thia-9, 10-diaza-tricyclo[5.3.0.0$^2,6$]dec-9-ene 4,4-dioxide (165).

Fig. 23b. 360MHz $^1$H n.m.r. spectrum of 4-thia-9, 10-diaza-tricyclo[5.3.0.0$^2,6$]dec-9-ene 4,4-dioxide (165) with decoupling of the 1-H proton by irradiation at 5.2$\delta$.

Fig. 23c. 360MHz $^1$H n.m.r. spectrum of 4-thia-9, 10-diaza-tricyclo-[5.3.0.0$^2,6$]dec-9-ene 4,4-dioxide (165) with decoupling of the 6-H proton by irradiation at 2.6$\delta$. 
Fig. 23a. Expansion of 360MHz $^1$H n.m.r. spectrum of 4-thia-9,10-diazatricyclo[5.3.0.0$^2$,6]dec-9-ene 4,4-dioxide (165).

Fig. 23d. 360MHz $^1$H n.m.r. spectrum of 4-thia-9,10-diazatricyclo[5.3.0.0$^2$,6]dec-9-ene 4,4-dioxide (165) with decoupling of the 7-H proton by irradiation at 2.78.

Fig. 23e. 360MHz $^1$H n.m.r. spectrum of 4-thia-9,10-diazatricyclo[5.3.0.0$^2$,6]dec-9-ene 4,4-dioxide (165) with decoupling of the C-3 methylene by irradiation at 3.48.
Similarly, irradiation at 2.6\,\delta, 2.7\,\delta and 3.4\,\delta, respectively
gave results which corroborated these assignments (see figures 23c-e).
Notably irradiation at 2.7\,\delta (7-H) produces major simplification in the
resonances at 5.25\,\delta (1-H) and at 4.6\,\delta (8 and 8'-H) (Figure 23d).
Little simplification is observed in the resonances due to 2-H and 6-H
as would be expected for the removal of a four-bond and a trans-coupling
constant, respectively.

The $^{13}$C n.m.r. spectrum of (165) shown in figure 24 has only
seven lines (2, overlap) and confirms that there is only one isomer present.

d) Attempted addition of diphenylnitrilimine.

Attempts to add diphenylnitrilimine to the alkene (123) led to
failure. The diphenylnitrilimine was generated by two different routes,
one involving thermal elimination of HCl from $\alpha$-chlorophenylhydrazone
in boiling toluene, and the other by addition of triethylamine to the
substrate in benzene. In both cases work-up of the reaction mixtures
by chromatography gave an almost quantitative recovery of unreacted
alkene. This lack of reactivity is presumably due to the lower reactivity
of nitrilimines compared to the nitrile oxides which were investigated
earlier. In this connection it is noteworthy that Tinley\textsuperscript{129} has observed
that the same dipole also failed to react with the structurally similar
cyclobutene anhydride (139).
D. Synthesis of cis-Divinyl Compounds by Flash Vacuum Pyrolysis of Tricyclic Sulphones.

D.1 Preparation of 1-phenyl and 1-methyl-cis-3,4-divinylsuccinimides.

As mentioned in section A.2 of the discussion pyrolysis of the anhydride (1) provides a clean and efficient synthesis of the hitherto unknown 2,5-dioxo-cis-3,4-divinyltetrahydrofuran (113). This initial success prompted a more detailed investigation aimed at evaluating the usefulness of this approach as a general route to cis-divinyl compounds. Since X-ray structure determination of 9-phenyl-8,10-dioxo-4-thia-9-azatricyclo[5.3.0.02,6]decane 4,4-dioxide (108) provided key evidence as to the stereochemistry of the anhydride (1) it was decided to pyrolyse compound (108) in an attempt to prepare the previously unknown 1-phenyl-cis-3,4-divinylsuccinimide (109) as shown in Scheme 86.

Pyrolysis of the imide (108) at 625°C in a flow system gave a 52% yield of a colourless crystalline solid whose analytical and spectroscopic data established its structure as the desired succinimide (109). Thus elemental analysis gave percentage composition for...
carbon, hydrogen and nitrogen consistent with an empirical formula
\( \textbf{C}_{14} \textbf{H}_{13} \textbf{NO}_2 \). This was verified by observation in the mass spectrum
of a parent ion peak at \( m/e \) 227.

The \( \text{\textsuperscript{1}} \text{H n.m.r.} \) spectrum of (109) is reproduced in figure 25 and
is consistent with the assigned structure. Thus the multiplet centred
at 7.35 ppm is attributed to the phenyl protons whilst the complex multiplet
at 5.9-5.3 ppm is typical of a cis-divinyl system. The doublet of
doublets centred at 3.75 ppm is assigned to the 3-H and 4-H protons.

The \( \text{\textsuperscript{13}} \text{C n.m.r.} \) spectrum of (109) is shown in figure 26 and as
expected consists of eight resonances. The carbonyl carbons give rise
to the signal at 175 ppm whilst the signals due to the aromatic carbons
occur in the 132-128 ppm region. The signals at 126 ppm and 121 ppm are due
to the secondary (C_6 and C_8) and terminal vinyl carbons, respectively.
Finally the C_3 and C_4 carbons are represented by the signal at 49 ppm.

Since compound (109) is a crystalline solid it was decided to carry
out an X-ray study to further confirm the assigned stereochemistry.
Careful recrystallization of (109) from ethyl acetate gave colourless
crystals ideal for X-ray studies. This showed that the compound
possessed cis-orientated vinyl groups at the 3 and 4 positions (see
figure 9, p.115). However the quality of the X-ray data was not very
high presumably because there is some disorder in the crystal lattice.
As a consequence the bond geometry obtained from the analysis was
unsatisfactory and no comment can be made on the bond lengths or bond
angles obtained.

Similar pyrolysis of the methyl analogue of (108) viz. compound
Fig. 25. 100MHz $^1$H n.m.r. spectrum of 1-phenyl-cis-3,4-divinyl-succinimide (109).

Fig. 26. 25.2MHz $^{13}$C n.m.r. spectrum of 1-phenyl-cis-3,4-divinyl-succinimide (109).
(166) gave a 58% yield of a light brown oil which was characterized as 1-methyl-cis-3,4-divinylsuccinimide (167) on the basis of its elemental composition and spectral properties which showed strong similarities to those described above for compound (109).

D. 2 Preparation of cis-3,4-divinyl-1-heterocyclopentanes.

Prior to the present study, the heterocyclic analogues of cis-1,2-divinylcyclopentane (88) were unknown although the latter had been the subject of several studies concerned with its Cope rearrangement to cis,cis-1,5-cyclononadiene (87) (see Scheme 39, p.40). Consequently it was of considerable interest to examine the utility of compounds of type (168) previously obtained by chemical modification of the anhydride (1) as precursors to cis-3,4-divinyl-1-heterocyclopentanes (169) under flash vacuum pyrolysis conditions (Scheme 87).
a) cis-3, 4-Divinyltetrahydrofuran.

Pyrolysis of the tetrahydrofuran (117) under f. v. p. conditions at 625°C gave a 62% yield of a clear volatile liquid with a sickly odour and spectroscopic properties typical of the desired cis-3, 4-divinyltetrahydrofuran (170) (Scheme 88).

Elemental analysis of the liquid gave percentage composition for carbon and hydrogen consistent with an empirical formula C₈H₁₂O which was corroborated by observation in the mass spectrum of a parent ion peak at m/e 124.

The ¹H n.m.r. spectrum of (170) was recorded in [²H₆]-acetone at a frequency of 360MHz and this spectrum is reproduced in figure 27. The high frequency used allows a full analysis of this spectrum.

The multiplet centred at 5.756 is assigned to the 6-H and 8-H protons and can be considered as a doublet of doublet of doublets (J₆, 7-trans = 17.5Hz, J₆, 7-cis = 10.5Hz, J₃, 6 = 9.5Hz). The protons 7, 7', 9 and 9'-H give rise to the multiplet centred at ca. 5.056 which may be interpreted as overlapping sets of doublets of doublets with fine splitting due to the allylic couplings to the 3-H proton. The coupling constants for the proton trans to 6-H are (J₆, 7-trans = 17.5Hz, J₇, 7 = 2.5Hz, J₃, 7 = 1Hz) and those due to the proton cis to 6-H are...
Fig. 27. 360 MHz $^1$H n.m.r. spectrum of cis-3,4-divinyltetrahydrofuran (170).

Fig. 28. 25.2 MHz $^{13}$C n.m.r. spectrum of cis-3,4-divinyltetrahydrofuran (170).
The 2 and 5'-H and 2' and 5'-H give rise to the doublet of doublets centred at 3.375 and 3.5(5, respectively with coupling constants $J_{2,2'} = 9.5 \text{Hz}$, $J_{2,3} = 7.5 \text{Hz}$) and $J_{2,2'} = 9.5 \text{Hz}$, $J_{2,3} = 6 \text{Hz}$). The multiplet centred at 2.935 is due to the 3-H and 4-H protons. The shifts and coupling constants for the divinyl system compare very well with those reported for cis-divinylcyclopropane. 87

The $^{13}$C n.m.r. spectrum of (170) is shown in figure 28 and as expected consists of four lines.

The structure of (170) was unambiguously confirmed by its alternative synthesis via the route shown in Scheme 89. Thus pyrolysis of the anhydride (1) gave the cis-3,4-divinyl derivative (113) (see Scheme 51, p.124), which could be converted into the dimethyl ester (171) in 50% yield by boiling in methanol with a few drops of concentrated sulphuric acid. Reduction of this diester with lithium aluminium hydride in tetrahydrofuran followed by dehydration of the resulting
diol (172) yielded the desired product in 62% yield.

In passing it is of interest to note that the diester (171) has been reported but only as a mixture of the meso form and its diastereomers. The proton n.m.r. of (171) compared well with that reported by these workers, whilst the $^{13}$C n.m.r. supported the assigned structure and confirmed the presence of only one isomer.

The fact that cis-3,4-divinyltetrahydrofuran (170) is stable under the pyrolysis conditions indicates that it has little tendency to undergo a Cope rearrangement to the unknown heterocycle 1-oxa-cis, cis-3,7-cyclononadiene (173) as depicted in Scheme 90. This contrasts strongly with cis-1,2-divinylloxirane (83, X=O) which is known to undergo a facile Cope rearrangement but is in keeping with the report by Vogel that the Cope equilibrium of cis-1,2-divinylcyclopentane with its hydrocarbon counterpart strongly favours the former.

b) cis-3,4-Divinyltetrahydrothiophene

The appropriate precursor (119) for the synthesis of the title compound was successfully prepared as discussed in Section B.2. Pyrolysis of (119) under f.v.p. conditions at 620°C gave a 25% yield of a pale yellow liquid which was identified as cis-3,4-divinyltetrahydrothiophene (174) on the basis of analytical and spectral data after
purification by bulb-to-bulb distillation (Scheme 91).

\[
\begin{array}{c}
\text{O}_2\text{S} & \xrightarrow{\Delta} & \text{S} \\
\text{\textit{119}} & \quad \quad & \quad \quad \quad \text{\textit{174}}
\end{array}
\]

\(25\%\)

\textbf{Scheme 91}

A gummy residue remained in the inlet system after pyrolysis indicating that some decomposition of (119) had occurred during sublimation into the furnace. The spectra of the crude product also contained peaks due to unidentified impurities probably formed by extrusion of sulphur. This decomposition might also explain the low yield of (174) obtained.

Elemental analysis of the clear liquid obtained by microdistillation gave percentage composition for carbon and hydrogen consistent with an empirical formula \(\text{C}_8\text{H}_{12}\text{S}\). This was confirmed by observation in the mass spectrum of a parent ion peak at m/e 140. A very strong peak at m/e 86 corresponds to the loss of the two vinyl groups (140 - 2x27 = 86).

The \(^1\text{H n.m.r.}\) and \(^{13}\text{C n.m.r.}\) spectra of (175) were entirely consistent with the assigned structure and showed strong similarities to those described in detail for \textit{cis}-3, 4-divinyltetrahydrofuran (170).

It would seem that compound (174) like compound (170) has little tendency to undergo a Cope rearrangement as no Cope rearranged products were detected.
c) 1-Benzyl-cis-3, 4-divinylpyrroolidine

In an attempt to prepare a nitrogen analogue of (170) and (174), the precursor (122) was prepared as described in Section B. 2. Pyrolysis of (122) at 525°C under f.v.p. conditions gave a 58% yield of light brown oil which was purified by microdistillation and characterized as the title compound (175) (Scheme 92).

\[
\begin{align*}
\text{O}_2\text{S} & \quad \text{N-CH}_2\text{Ph} \quad \Delta \\
(122) & \quad \rightarrow \\
\text{N-CH}_2\text{Ph} & \quad (175) \quad 58\%
\end{align*}
\]

Scheme 92

Elemental analysis of the oil obtained by microdistillation gave percentage composition for carbon, hydrogen and nitrogen consistent with an empirical formula \( C_{15}H_{19}N \). This was confirmed by observation in the mass spectrum of a parent ion peak at m/e 213.

The \(^1\)H n.m.r. spectrum of (175) was entirely consistent with the assigned structure and showed strong similarities to that just described for cis-3, 4-divinyltetrahydrofuran (170).

Also as with the oxygen and sulphur analogues there was no evidence to indicate any Cope rearrangement. However when the pyrolysis was carried out above 550°C total breakdown of the product occurred to give unidentified aromatic compounds as indicated by \(^1\)H n.m.r. spectroscopy.
E. Pyrolysis of 3-Thiabicyclo[3.2.0]hept-6-ene 3, 3-dioxide and its Adducts

E.1 Pyrolysis of 3-thiabicyclo[3.2.0]hept-6-ene 3, 3-dioxide

The preparation of the title compound (123) has already been described in Section C as well as its reactions with carbenes, nitrenes and 1, 3-dipoles in an effort to prepare a wider range of potential cis-divinyl precursors. The pyrolysis of the alkene (123) itself provided a convenient starting point for the investigation.

Thus when the alkene (123) was pyrolysed in a flow system at 500 °C the product obtained was identified by $^1$H n.m.r. spectroscopy as 1, 3-cyclohexadiene (176). The formation of the latter can be explained in terms of a cheletropic extrusion of sulphur dioxide to give cis-1, 3, 5-hexatriene which under the pyrolytic conditions undergoes an electrocyclic ring closure reaction as indicated in Scheme 93.

Support for this pathway was obtained by lowering the temperature of the pyrolysis to 400 °C whereupon cis-1, 3, 5-hexatriene, 1, 3-cyclohexadiene (176) together with unchanged alkene were detected in the pyrolysate in approximately equal amounts. At temperatures below 400 °C, the starting alkene sublimed through the furnace unchanged.
The formation of cis-1, 3, 5-hexatriene can be envisaged to occur by two different routes. Firstly compound (123) could extrude SO₂ in the normal linear disrotatory manner and give cis-1, 3, 5-hexatriene directly. Alternatively (123) could undergo an initial ring opening reaction, in a manner analogous to that reported for bicyclo[3, 2. 0]hept-6-ene, 176 to afford 2, 7-dihydrothiepin 1, 1-dioxide (22) which is known to lose SO₂ under the pyrolytic conditions 50, 51 to give cis-1, 3, 5-hexatriene (Scheme 94). No evidence is available to differentiate between these two pathways but the former is preferred on the grounds that it is an allowed process whereas the isomerization of (123) into (22) is disfavoured by orbital symmetry considerations.

Following the report by Gaoni 66 that sulphones such as (177) are smoothly converted to the corresponding diene (178) by reaction with lithium aluminium hydride as outlined in Scheme 95, the alkene (123) was treated in a similar manner and the resultant mixture
analysed by gas chromatography. This showed the presence of only two products which were identified as cis and trans-hexa-1, 3, 5-trienes by peak enhancement experiments using authentic samples prepared by the method of Hwa et al. The lack of stereospecificity indicates that loss of SO\textsubscript{2} presumably occurs via a radical or polar mechanism rather than a cheletropic elimination.

In order to rule out the possibility that the reaction conditions had caused isomerization of the resultant trienes a control experiment was carried out using an authentic mixture of cis and trans-hexa-1, 3, 5-trienes. However after boiling the mixture for 1 h, gas chromatographic analysis showed no change in the ratio of cis to trans isomers.

E. 2 Pyrolysis of 8-oxa-4-thiatricyclo[5.1.0.0\textsubscript{2,6}]octane 4,4-dioxide.

The title compound (143) was prepared by the method outlined in Section C. 2 as a potential precursor of cis-2, 3-divinylloxirane (83, X=O) which upon Cope rearrangement is known to give 4, 5-dihydrooxepine (84, X=O). When the epoxide (143) was pyrolysed under f. v. p. conditions at 580\textdegree C a clear liquid was obtained in 55% yield. This was identified as 4, 5-dihydrooxepin (84, X=O) by comparison of the \textsuperscript{1}H n.m.r. and \textsuperscript{13}C n.m.r. spectroscopy data with known literature values.

The formation of (84, X=O) is easily explained in terms of a cheletropic extrusion of sulphur dioxide from (143) in the normal manner.
leading to \textit{cis}-2, 3-divinylloxirane (83, X=O) which subsequently undergoes a Cope rearrangement to form 4, 5-dihydrooxepin (84, X=O) as shown in Scheme 96.

\[
\begin{array}{c}
\text{O}_2\text{S} \text{O} \\
(143) \\
\text{\large $\Delta$} \text{-SO}_2 \\
\end{array}
\xrightarrow{\text{[}}
\begin{array}{c}
\text{\textit{cis}-2, 3-divinylloxirane (83, X=O)} \\
(83, X=O) \\
\end{array}
\xrightarrow{\text{}}
\begin{array}{c}
\text{4, 5-dihydrooxepin (84, X=O)} \\
(84, X=O) \\
\end{array}
\]

\textbf{Scheme 96}


**E. 3 Pyrolysis of adducts obtained by nitrile oxide addition to 3-thiabicyclo[3.2.0]hept-6-ene 3, 3-dioxide.**

The adduct (162) from the addition of anisonitrile oxide to 3-thiabicyclo[3.2.0]hept-6-ene 3, 3-dioxide (123) was pyrolysed in the usual way at 500 °C in a flow system and the pyrolysate obtained sublimed to give a 33% yield of a colourless translucent solid, m. p. 58-60 °C. Analytical and spectral data established the structure of this solid to be 4, 5-dihydro-3-(p-methoxyphenyl)-\textit{cis}-4, 5-divinylisoxazole (179) (Scheme 97). Thus elemental analysis gave percentage

\[
\begin{array}{c}
\text{O}_2\text{S} \text{O} \\
(162) X=\text{OMe} \\
\text{\large $\Delta$} \text{-SO}_2 \\
(164) X=\text{H} \\
\end{array}
\xrightarrow{\text{[}}
\begin{array}{c}
\text{4, 5-dihydro-3-(p-methoxyphenyl)-\textit{cis}-4, 5-divinylisoxazole (179)} \\
(179) X=\text{OMe} 33\% \\
(180) X=\text{H} 19\% \\
\end{array}
\]

\textbf{Scheme 97}
composition for carbon, hydrogen and nitrogen consistent with an empirical formula $\text{C}_{14}\text{H}_{15}\text{O}_2\text{N}$. This was confirmed by observation in the mass spectrum of a parent ion peak at m/e 229.

The $^1\text{H n.m.r.}$ spectrum (179) was exceptionally complicated in the olefinic region due to overlapping signals of the non-equivalent vinyl groups. The $^{13}\text{C n.m.r.}$ spectrum contained twelve lines in keeping with the assigned structure.

Similar pyrolysis of compound (164) at $500^\circ\text{C}$ yielded a brown-coloured pyrolysate which after distillation at $100^\circ\text{C}/0.1\text{mmHg}$ provided a 19% yield of a colourless oil. This compound was identified as 4,5-dihydro-3-phenyl-cis-4,5-divinylisoxazole (180) on the basis of analytical and spectral data (Scheme 97). As expected the spectral data for compound (180) showed strong similarities to the data for compound (179).

E.4 Pyrolysis and photolysis of 4-thia-9,10-diazatricyclo[5.3.0.0$^{2,6}$]-dec-9-ene 4,4-dioxide.

The title compound (165) was of some interest as it provided the first example in the present study of a molecule which could extrude either sulphur dioxide or nitrogen or both under pyrolytic conditions. In particular the loss of nitrogen might be expected to lead to the formation of the potential cis-divinylcyclopropane precursor (181) (Scheme 98).

Slow sublimation of compound (165) through a furnace at $450^\circ\text{C}$ under f.v.p. conditions gave a pyrolysate which according to g.c.
analysis contained five components, none of which could be positively identified. The proton n.m.r. spectrum of the pyrolysate suggested the presence of cyclohepta-1,4-diene (81) but this was not confirmed. Apparently under these conditions loss of both nitrogen and sulphur dioxide occurred simultaneously giving rise to the plethora of products observed.

In certain circumstances nitrogen can be selectively removed in the presence of a sulphone moiety by photolysis in acetonitrile. For example Mock has shown that irradiation of the pyrazolines (182a-d), prepared by addition of diazomethane to the appropriate sulpholene, gave the cyclopropanes (183a-d) in 25-55% yield (Scheme 99).

Similar photolysis of compound (165) on an n.m.r. scale using a 100w medium pressure lamp resulted in a gradual evolution of gas which ceased after 3 days. Examination of the resulting solution by $^1$H n.m.r. spectroscopy revealed a spectrum profile which suggested that the sulphone moiety had been retained intact. However removal
of the solvent gave a small amount of a brown solid which on the basis of spectoscopic evidence, appeared to be polymeric in nature. No evidence could be obtained to indicate the formation of the desired cyclopropane derivative (181).
F. Miscellaneous Preparations and Pyrolyses.

F.1 Attempted preparation of 5, 6-divinyl-3, 8-dioxadeca-1, 9-diene.

As discussed in the introduction Ziegler \(^{105}\) has recently reported the first example of a tandem Cope-Claisen rearrangement (see Scheme 46, p.43) and this prompted an effort to seek further examples using the f.v.p. technique. The conversion of the diol (116) to the vinyl ether (184) followed by \(\text{SO}_2\) extrusion offered the possibility of another example of a tandem Cope-Claisen rearrangement leading to the aldehyde (187) as outlined in Scheme 100.

The usual method for preparing vinyl ethers from an alcohol is to boil the latter in ethyl vinyl ether in the presence of mercuric acetate and one drop of sulphuric acid \(^{138}\). However in the case of the diol (116) this procedure failed due to its extreme insolubility in ethyl vinyl ether. Attempts to overcome this problem by using Soxhlet extraction also failed.

In order to circumvent this problem it was decided to try to prepare compound (185) by vinylation of meso-3, 4-dihydroxymethyl-1, 5-hexadiene (172), prepared as described previously (see Scheme 89, p.174), as shown in Scheme 101. On heating the diol (172) in boiling ethyl vinyl ether with mercuric acetate and one drop of sulphuric acid followed by careful removal of solvent at low temperature, a colourless oil was obtained which was purified by bulb-to-bulb distillation.
Scheme 100

(116) \[ \rightarrow \text{Hg}^{2+} \rightarrow (184) \]

\[ \Delta \rightarrow -\text{SO}_2 \rightarrow (185) \]

(186)

(187)
The $^1$H n.m.r. spectrum of this oil was consistent with the assigned structure (185). Likewise the $^{13}$C n.m.r. spectrum contained six lines and so supported the assigned structure. However correct analytical data could not be obtained due to the extreme volatility of the oil.

A sample of the oil was pyrolysed in a flow system at 500°C and the pyrolysate was analysed by $^1$H n.m.r. spectroscopy. The most characteristic feature of the spectrum obtained was a peak at 9.66 indicative of an aldehyde function. The presence of an aldehyde can be rationalized in terms of a tandem Cope-Claisen rearrangement of compound (185) as indicated in Scheme 100. Thus this provides further evidence that the oil was indeed compound (185).

An attempt to achieve the rearrangement by heating the same oil in [$^{2}$H$_8$]toluene in a sealed n.m.r. tube at 150°C resulting in no change even after five days.

F.2 Pyrolysis of Dimethyl-3-thiabicyclo[3.2.0]heptane-6,7-dicarboxylate 3,3-dioxide.

On pyrolysis at 625°C under f.v.p. conditions dimethyl-3-thiabicyclo[3.2.0]heptane-6,7-dicarboxylate 3,3-dioxide (115) gave a
76% yield of cis, trans-octa-2, 6-diene-1, 8-dicarboxylic acid dimethyl ester (188) the structure of which was assigned on the basis of $^1$H n.m.r. and $^{13}$C n.m.r. spectroscopic evidence comparison with known literature values. The proton n.m.r. spectrum of (188) was recorded at a frequency of 360MHz and this spectrum is reproduced in figure 29. The signal at 6.96 is a doublet of triplets due to the proton (3-H) cis to the carbomethoxy group ($J_{2, 3} = 16$Hz, $J_{3, 4} = 7$Hz). Similarly the proton (6-H) which is trans to a carbomethoxy group gives rise to the doublet of triplets at 6.25 ($J_{6, 7} = 12$Hz, $J_{5, 6} = 8$Hz).

The multiplet at 5.85 can be interpreted as an overlapping pair of doublets due to the remaining olefinic protons (2-H, 7-H) ($J_{2, 3} = 16$Hz, $J_{6, 7} = 12$Hz). The signals due to the carbomethoxy groups occur as singlets at 3.73 and 3.72. The allylic CH$_2$ cis to the carbomethoxy group give rise to the multiplet at 2.86, while the multiplet due to the remaining CH$_2$ group occurs at 2.45. All these assignments agree well with data for compounds similar to (188).

The $^{13}$C n.m.r. spectrum of (188), shown in figure 30, exhibits five pairs of resonances. The pair of signals at 166$\delta$ are due to the carbonyl carbons. The signals due to C$_2$ and C$_7$ occur at 148$\delta$ and those due to C$_3$ and C$_6$ at ca. 121$\delta$. The signal due to the methylene groups occur at ca. 51$\delta$.

The formation of (188) can be rationalized in terms of an initial extrusion of SO$_2$ to give meso-dimethyl-1, 5-hexadiene-3, 4-dicarboxylate (171) which under the conditions of the pyrolysis undergoes a Cope rearrangement as outlined in Scheme 102. The observed cis, trans
Fig. 29. 360MHz $^1$H n.m.r. spectrum of cis, trans-octa-2,6-diene-1,8-dicarboxylic acid dimethyl ester (188).

Fig. 30. 25.2MHz $^{13}$C n.m.r. spectrum of cis, trans-octa-2,6-diene-1,8-dicarboxylic acid dimethyl ester (188).
The stereochemistry of (188) is interesting in that it is the same stereochemistry as that in compound (189) which is a component of gossyplure, the sex attractant of the female pink volvorm moth *Pectinphora gossypiella*. For maximum potency synthetic sex pheromones require stereochemically pure alkenes. \(^{178}\) However (189) can only be prepared in ca. 84% purity and since (188) is obtained in virtually 100% purity it could possibly be used as a key intermediate in the preparation of (189). This approach is currently under investigation but appears to suffer from the drawback that one requires to
selectively protect one terminus of the molecule with retention of stereochemical purity. However as yet this problem has not been overcome.
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Flash Vacuum Pyrolysis of the 3-Thiabicyclo[3.2.0]heptane 3,3-Dioxide Ring System: a New Stereospecific Synthesis of cis-1,2-Divinyl Derivatives

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Summary A short and stereospecific route to cis-1,2-divinyl compounds from derivatives of the readily available 3,3-dioxide (1) of 3-thiabicyclo[3.2.0]heptane-6,7-dicarboxylic anhydride by cheletropic elimination of SO₂ is reported.

The considerable interest in cis-1,2-divinyl systems now current is tempered by difficulties in synthetic access through existing methods which usually give mixtures of cis- and trans-isomers. We now report a simple, stereospecific, and general route to novel cis-1,2-divinyl systems by thermal extrusion of SO₂ from derivatives of the 3,3-dioxide (1) of 3-thiabicyclo[3.2.0]heptane-6,7-dicarboxylic anhydride, easily prepared by photolysis of 2,5-dihydrothiophen-1,1-dioxide and maleic anhydride for 24 h in anhydrous acetone.

Thus, esterification of (1) followed by reduction with LiAlH₄ and subsequent cyclisation of the resulting diol (2) afforded 4-oxa-9-thiatricyclo[5.3.0.0²⁷]decane 9,9-dioxide (3, X=O; m.p. 129—130 °C)† which on pyrolysis under

† All new compounds were fully characterised by H and C n.m.r., i.r. and mass spectral and microanalytical data.
flash vacuum conditions (625 °C at 10−3 mmHg) gave exclusively cis-3,4-divinyltetrahydrofuran (4, X=O; b.p. 40 °C at 41 mmHg; 62%). Similar pyrolysis of the lactone (5); m.p. 157—168 °C, prepared by reduction of (1) with NaBH₄ in dimethylformamide, afforded the corresponding cis-1,2-divinyl derivative (6; b.p. 75 °C at 0·1 mmHg) in 31% overall yield from (1). Further transformations of (1), which serve to illustrate the potential of our procedure, have been effected leading to (4, X=S; b.p. 140 °C at 16 mmHg; 26%) and (4, X=NCH₂Ph; b.p. 100 °C at 0·01 mmHg; 87%) by pyrolysis of (3, X=S; m.p. 195—196 °C) [conversion of (2) into its dimethanesulphonate and treatment with Na₂S-OEt₂-EtOH; 89%] and (3, X=NCH₂Ph; m.p. 182—186 °C) [reaction of the ditosylate of (2) with benzylamine; 56%] respectively. We have also shown that flash vacuum pyrolysis of (1) gave cis-hexa-1,5-diene-3,4-dicarboxylic anhydride (7; b.p. 65 °C at 0·1 mmHg; 80%) from which cis-1,2-divinyl systems of type (4) could be obtained by conventional synthetic methods.

Stereospecificity in all cases exceeded 99.9% and the cis-stereochemistry, which is a consequence of the symmetrical structure of the starting anhydride (1), was validated by the essentially quantitative chemical transformation of (7) into meso-2,3-diethylsuccinic acid, m.p. 190—191 °C (decomp.) (lit. 192 °C; cf. racemic acid, m.p. 129 °C) by hydrolysis with boiling water and subsequent hydrogenation over 10% palladium-charcoal at room temperature.

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