1969

Studies Of Some High-energy Reactions

Colin Leslie Mcintosh

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STUDIES OF SOME HIGH ENERGY REACTIONS

by

Colin Leslie McIntosh

Department of Chemistry

Submitted in partial fulfillment

of the requirements for the degree of

Doctor of Philosophy

Faculty of Graduate Studies

The University of Western Ontario

London, Canada.

November, 1968

ABSTRACT

The thesis consists of three parts. Part A describes the attempts to produce cyclooctatetraenes from 2-pyrones by photochemical dimerization and subsequent thermal decarboxylation. Irradiation of 2-pyrone gave dimers, however, pyrolysis gave only a low yield of cyclooctatetraene. Irradiation of 4-methoxy-6-methyl-2-pyrone in benzene gave no dimer, but instead a polymer consisting of cyclobutene carboxylic ester groups. Irradiation in water, however, led to the formation of β-methyl glutaconic acids and mono esters. A proposed mechanism and the intermediates involved are discussed.

Part B describes the photolysis of β-keto sulfones. The purpose of these irradiations was to produce sulfenes by a Norrish Type II cleavage. The formation of vinyl sulfonates on irradiation seemed to indicate such an intermediate. However, irradiation of t-butyl acetonyl sulfone was also found to produce vinyl sulfonates, thus ruling out the sulfene as an intermediate. This fact along with the lack of effect of radical scavengers on the vinyl sulfonate formation indicated an intramolecular or solvent cage rearrangement instead. The other products

formed could be rationalized by a homolytic cleavage of the carbon-sulfur bond β to the carbonyl group.

Part C describes the high temperature pyrolysis of several thietane 1,1-dioxides in the gas phase at very short contact times. Pyrolysis of thietane 1,1-dioxides gave olefinic products derived from the extrusion of sulfur dioxide. Similarly, the 3-thietanone 1,1-dioxides gave olefins resulting from extrusion of both sulfur dioxide and carbon monoxide. The thiete 1,1-dioxides, however, formed different products depending on the temperature. Pyrolysis at low temperatures gave cyclic sulfinates, while pyrolysis at higher temperatures produced carbonyl compounds plus sulfur monoxide. Both products can be rationalized by a vinyl sulfene intermediate.

Thietanol 1,1-dioxide gave a variety of products, two of which, acetone and propionaldehyde, resulted from extrusion of sulfur dioxide. The acrolein was formed by an initial dehydration to the thiete 1,1-dioxide which was further pyrolysed. It was proposed that the formation of acetaldehyde which was found in high yield was the result of an electrocyclic ring opening to give acetaldehyde and sulfene.

ACKNOWLEDGEMENTS

I should like to express my thanks to Professor P. de Mayo for his guidance, advice and encouragement during the course of this work.

My thanks also to the faculty members, staff and fellow graduate students for their individual efforts on my behalf. In particular, my thanks to Dr. J.B. Stothers and Dr. J. F. King for their suggestions and revelations concerning nuclear magnetic spectroscopy and sulfur chemistry respectively.

TABLE OF CONTENTS

LIST OF FIGURES

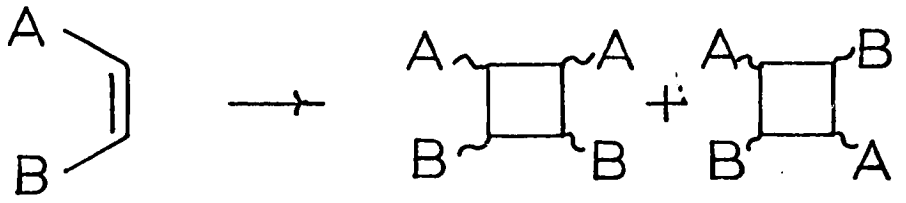
LIST OF TABLES

PART I. THE PHOTOLYSIS OF SOME 2-PYRONES

A. INTRODUCTION

The formation of photodimers is one of the oldest known reactions. As long ago as 1867, Fritzsche[1], and later Elbs[2] among others, noted that anthracene formed an insoluble dimer when exposed in benzene solution to sunlight. Since then, photocycloaddition reactions have been applied to the synthesis of such compounds as cubane[3], caryophyllene[4], and α-caryophyllene alcohol[5], and have been used in the synthesis of tropolones[6], oxetans[7,8], bicyclic and polycyclic systems[9,10], and cyclobutanes[11]. Since several extensive reviews[12-15] have recently appeared, only a short discussion of the pertinent material will be given here.

The formal methods of forming dimers can be divided into three groups: a) a 1,2 cycloaddition to give cyclobutanes, b) a Diels-Alder combination to form six membered rings, and c) a 1,4 cycloaddition of dienes. A single product is not obtained in most cases, however, since the stereochemical possibilities can be extremely large. For example, a 1,2 addition involving two cyclic olefins could give rise to a total of 12 possible isomers depending on whether the addition was head-to-head or head-to-



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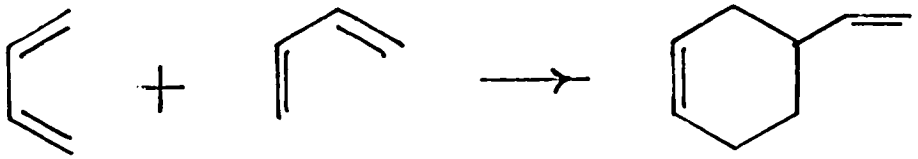

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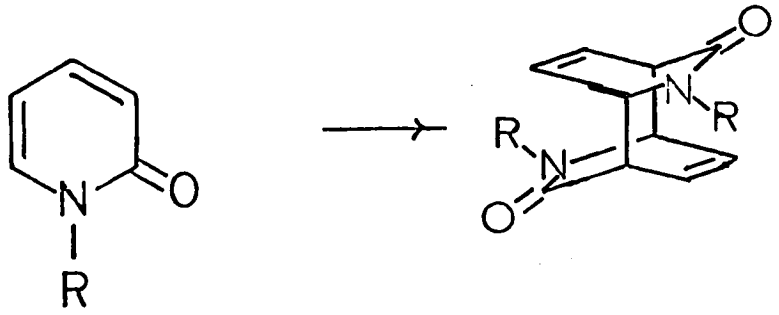

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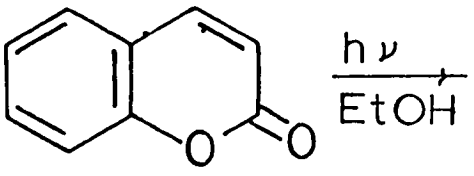

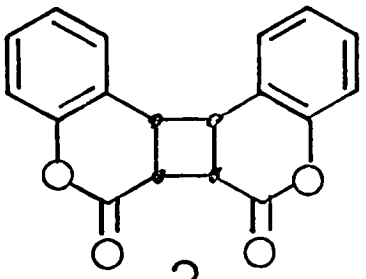

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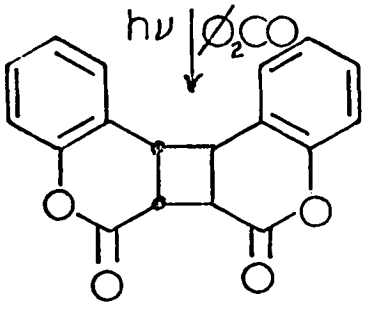
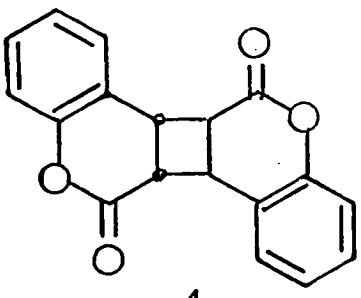




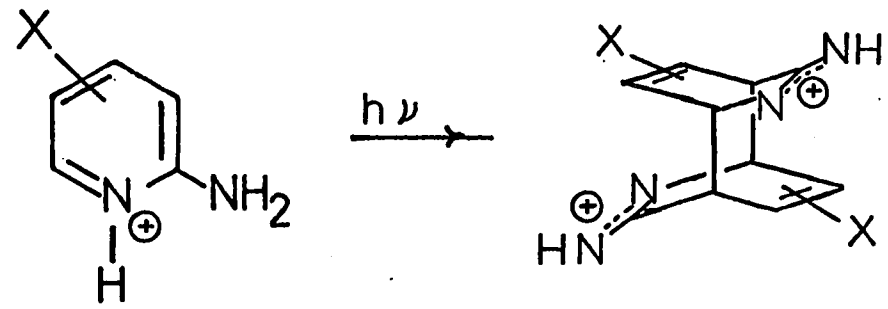
3 4

tail with either a syn or anti configuration and a cis or trans ring fusion. In most cases though, not all of the possible isomers are observed, and usually one or two isomers predominate.

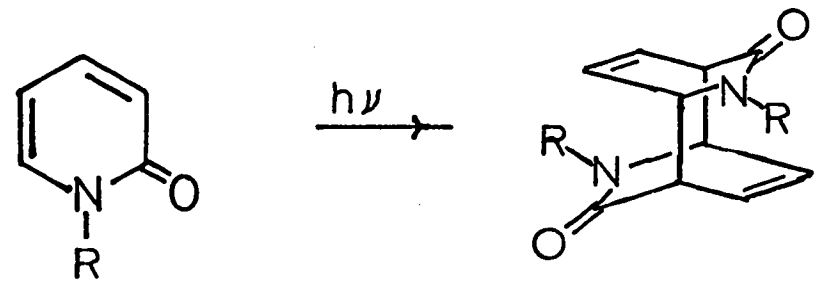
The reasons for this dominance of a small number of isomers are not entirely understood, although two of the most important factors involved are the electron multiplicity of the reactant states and the polarizability of the solvent.

The importance of electron multiplicity has been recognized for some time. For example, an excited state intermediate can react in a concerted manner with a ground state singlet, whereas an excited triplet must proceed via a two step mechanism with inversion of the electron spin intervening. An example of the effect of electron multiplicity has been reported by Hammond[16]. He has shown that direct irradiation of coumarin 1 gave only the symetrical head-to-head dimer 2, as a result of reaction through an excited singlet intermediate. Irradiation using a triplet sensitizer such as benzophenone, on the other hand, gave none of the dimer 2, but rather the head-to-head dimer 3 and a head-to-tail dimer 4.

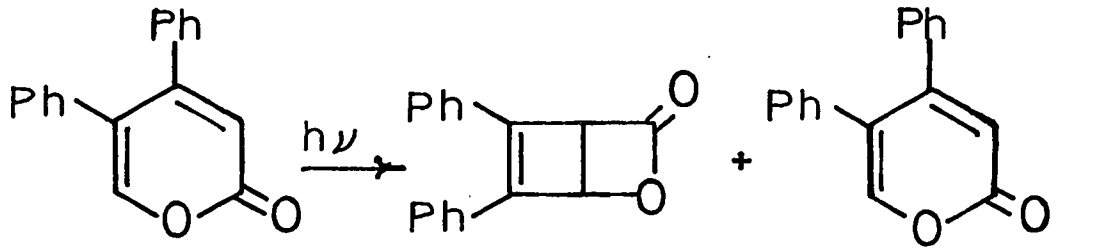
With respect to the second factor, some work has been carried out by Schenck[17], among others, who found a direct relationship between the molar polarizability of the solvent and the ratio of isomers obtained from the photodimerization of acenaphthylene.



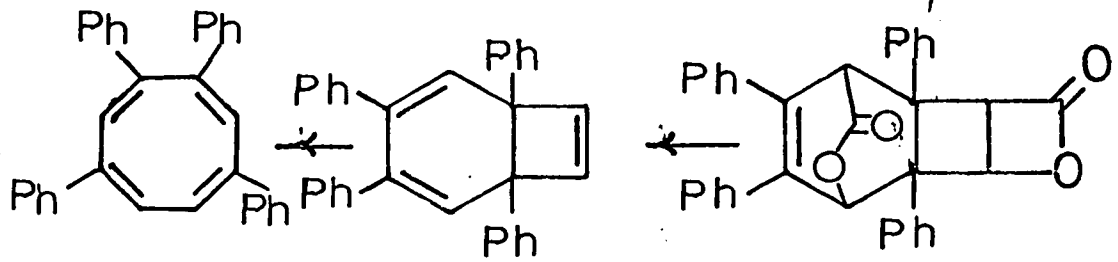
6 → 8



5 → 7



9 → 10 + (Ph)

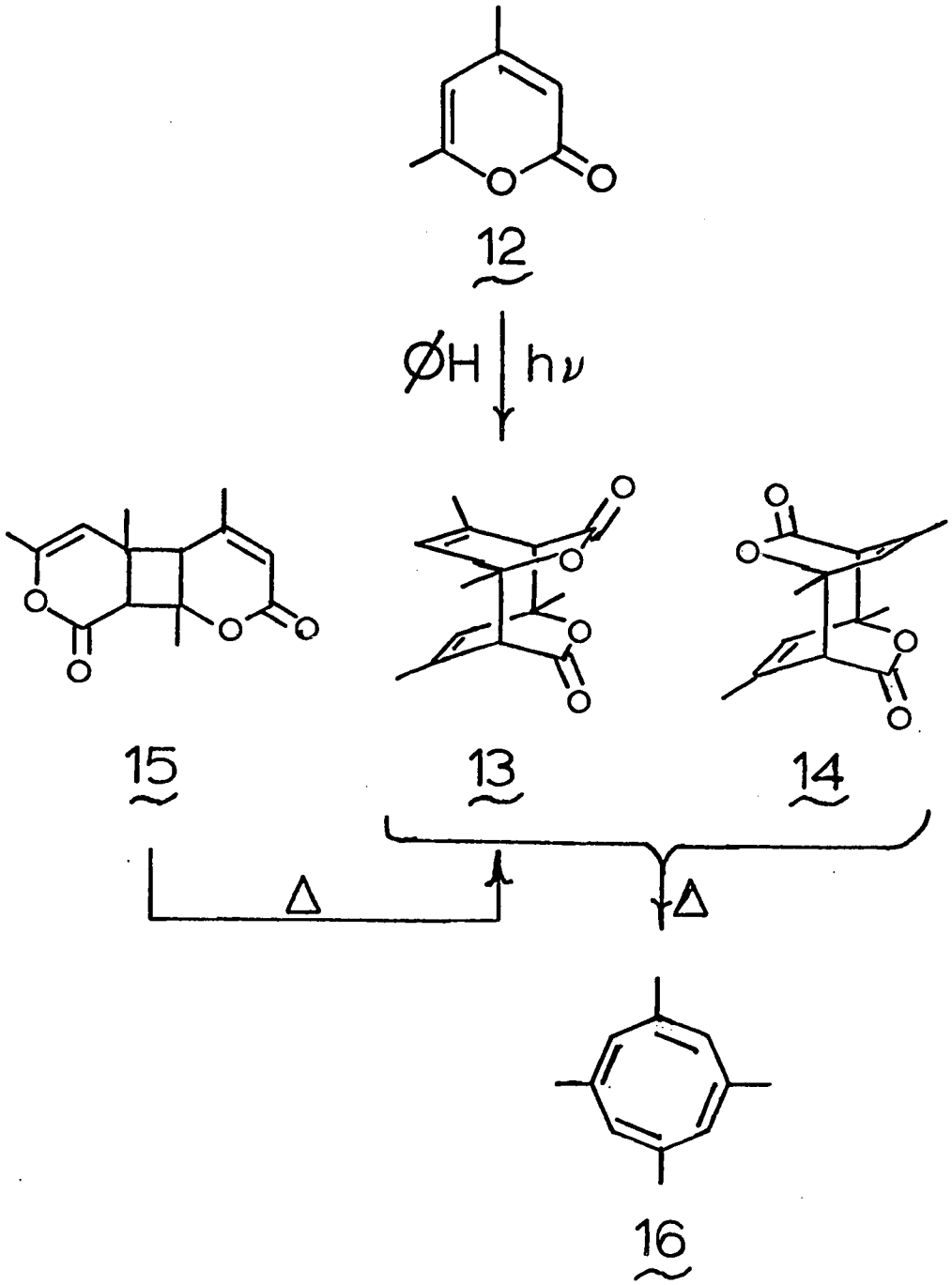


11

The photodimerization of unsaturated heterocyclic compounds has been studied by a number of groups. Taylor and coworkers[18-21] as well as others[22] have reported the dimerization of a number of 2-pyridones 5 and 2-aminopyridines 6, on irradiation. However, the products, in all cases, have been identified as the 1,4 dimers 7 and 8, both of which have the head-to-tail configuration.

Padwa and Hartman[23] have also reported a dimerization of a heterocycle, 4,5-diphenyl-2-pyrone. They found that irradiation of 4,5-diphenyl-2-pyrone 9 gave the 1,2,4,7-tetraphenyl-cyclooctatetraene 11. They proposed that an initially formed cyclobutene β-lactone reacted with a second molecule of starting material to give a dimer. Spontaneous loss of two molecules of carbon dioxide followed by valence isomerization then gave the observed product.

Prior to the start of the work to be described in the discussion, Mayo and Yip[24] working from their observation that 1,4 dimers were obtained from 2-pyridones on irradiation devised a procedure to synthesize a 1,3,5,7-cyclooctatetraene. Irradiation of 4,6-dimethyl-2-pyrone 12 gave rise to four dimeric products. Two of these were identified as the 1,4 dimers 13 and 14, and the third as an unsymmetrical 1,2 dimer 15 which rearranged thermally to the 1,4 dimer 13. As is shown in the diagram, the two 1,4 dimers are β,γ-unsaturated lactones and such compounds are known to decarboxylate readily


12
ØH | hν
15
13
14
Δ
Δ
16

on pyrolysis. In agreement with expectation, heating of the dimers at a temperature above their melting point for a short time converted them in twenty-five percent yield to 1,3,5,7-tetramethylcyclooctatetraene 16.

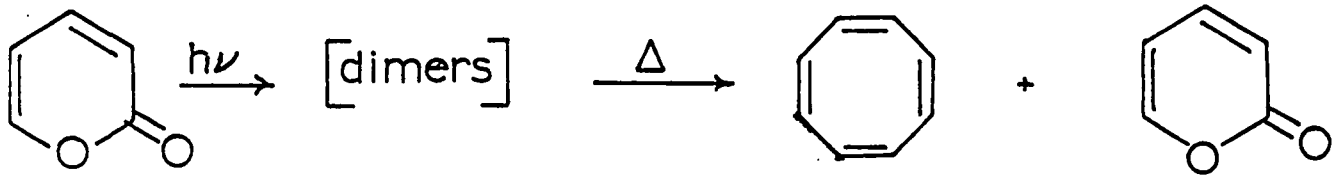
Since no other convenient synthesis of symmetrical cyclooctatetraenes is known, it was decided to explore the possibility of extending this reaction to other 2-pyrones with the same chromophore. In particular, 2-pyrone and 4-methoxy-6-methyl-2-pyrone were studied.

B. Discussion

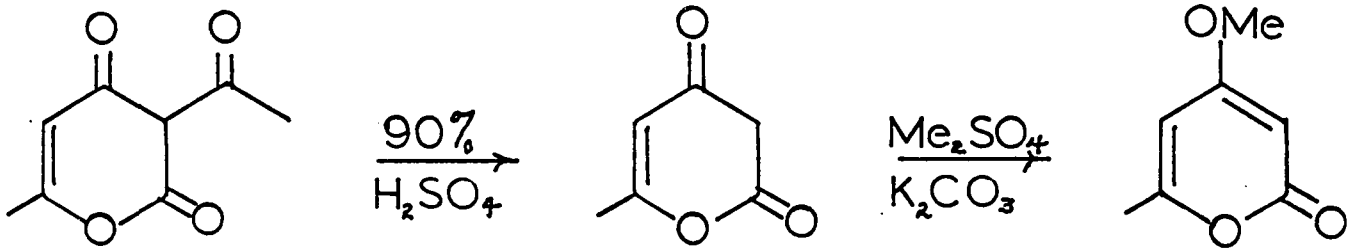
Photolysis of the two pyrones, 4-methoxy-6-methyl-2-pyrone and 2-pyrone however did not result in high yields of cyclooctatraene as desired. Rather they reacted in different manners to give a polymer and dimer respectively. The results and mechanistic implications are discussed below.

The copper catalysed decarboxylation of coumalic acid, described by Zimmerman[25], was used to prepare 2-pyrone 17. Irradiation through Pyrex of a concentrated solution of 17 (65% w/v) in dry benzene with a 450 watt medium pressure mercury arc for five days gave a 40% yield of crystalline products. Attempted separation of these products by fractional recrystallization was unsuccessful, and so the exact structures are unknown. The infrared absorption was consistent with their being dimers, since no strong absorption was observed at 1560 cm^{-1} which is characteristic of 2-pyrone.

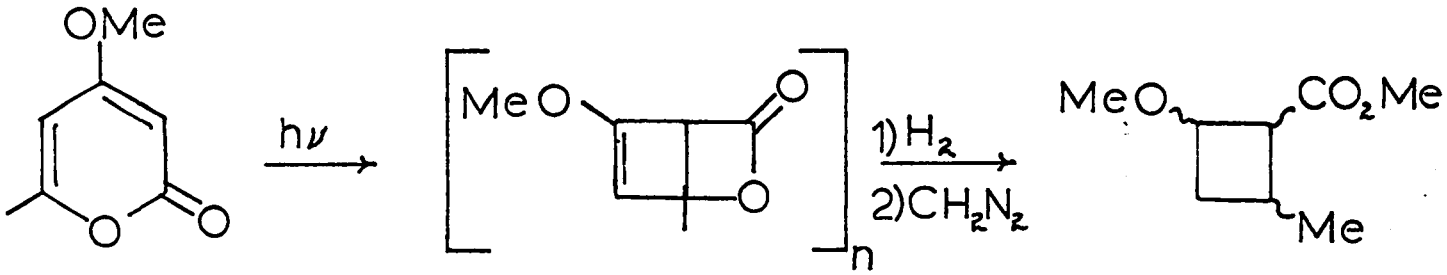
The total crystalline product was then pyrolysed in a twenty-five millilitre flask, connected to a standard distillation apparatus, by heating the material with a free flame. The products were distilled and separated by thin layer chromatography (tlc). Comparison of their infrared and nuclear magnetic resonance (NMR) absorptions showed the products to be 1,3,5,7-cyclooctatetraene 18 (2.4%) and 2-pyrone (33.6%) respectively, the remainder being undistilled pot residue. The yield of cyclooctatetraene was estimated by quantitative



17 18



19 20 21



21 29 22

vapor phase chromatography (vpc), whereas the 2-pyrone yield was calculated by integration of the double bond absorption in the infrared.

Although, as stated before, the exact structures of the dimers are not known, the low yield of cyclooctatetraene obtained may be some indication of their type. Mayo and Yip[24] have shown that the formation of 1,3,5,7-tetramethyl cyclooctatetraene from 4,6-dimethyl-2-pyrone was the result of decarboxylation of the 1,4 dimers and of the unsymmetrical 1,2 dimer thermally converted into one of the 1,4 dimers. The symmetrical 1,2 dimer characterised, regenerated starting material on pyrolysis, as would, indeed, have been expected, since a decarboxylation mechanism was not available.

If this is generally true, then the low yield of cyclooctatetraene and the correspondingly high yield of starting material obtained from the pyrolysis of the 2-pyrone dimers would indicate that a high percentage of thesymmetrical 1,2 dimers were formed in preference to the 1,4.

The other 2-pyrone studied, 4-methoxy-6-methyl-2-pyrone, was prepared by the method of Bu'Lock and Smith[26]. Treatment of dehydroacetic acid 19 with 90% sulfuric acid gave the triacetic acid lactone 20 which was methylated with methyl sulfate and anhydrous potassium carbonate in refluxing ethyl methyl ketone to give the desired 4-methoxy-6-methyl-2-pyrone 21.

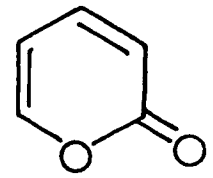
This pyrone was irradiated in a manner similar to

that described above, but in lower concentration because of its low solubility in benzene. The reaction was followed by the disappearance of the ultraviolet absorption of the 2-pyrone at 280 nm and continued to completion. Careful evaporation of the solvent under anhydrous conditions gave no dimeric material as hoped, but rather a polymeric substance whose average molecular weight was near 510 or approximately five times the monomer weight of the starting material.

The infrared spectrum of this product revealed an ester carbonyl absorption at 1740 cm^{-1} and a double-bond absorption at 1645 cm^{-1}, but no strong absorption in the region of 1560 cm^{-1} which could be attributed to a 2-pyrone. The NMR was characteristic of a polymer, having a series of broad peaks at 1.75 (3), 3.30 (3), 5.30 (1/5), 6.00 (1/5), 6.55 (8.5/10). The approximate relative numbers of protons are given in parenthesis.

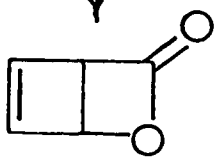
Hydrogenation of this polymeric material using prehydrogenated platinum oxide as catalyst in anhydrous ethyl acetate gave an acid whose infrared carbonyl absorption showed a maximum at 1705 cm^{-1}. Treatment of this acid with diazomethane gave an ester which was purified by tlc. On the basis of the infrared and NMR absorption of this ester it has been assigned the structure of a 2-methoxy-4-methyl-cyclobutane carboxylic acid methyl ester 22.

The infrared absorption spectrum showed an ester carbonyl absorption at 1740 cm^{-1}, while the NMR spectrum



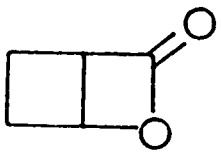
23

$h\nu$



25

H_2



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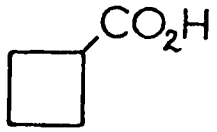

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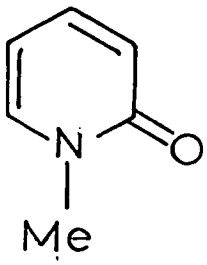
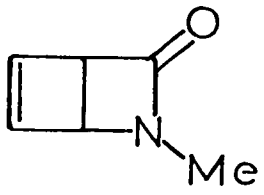


24

$h\nu$ →

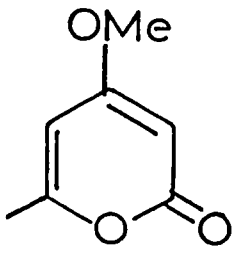


26

consisted of a broad three hydrogen doublet at 1.15 ppm attributed to the methyl protons, a three hydrogen multiplet at 2.19 ppm assigned to the two methylene protons and the methine proton on carbon-4, a three hydrogen singlet at 3.19 due to the methoxy group, a one hydrogen multiplet at 3.26 ppm assigned to the methine proton on carbon-1, a three hydrogen singlet at 3.65 ppm due to the carbomethoxy protons, and a one hydrogen multiplet at 3.70 ppm due to the methine proton on carbon-2. The elemental analysis was also consistent with an empirical formula of $C_8H_{14}O_3$.

Corey has also reported the isolation of a cyclobutane carboxylic acid as a result of hydrogenation of the photoproducts of a 2-pyrone irradiation. He found that irradiation of 2-pyrone 23 or N-methyl-2-pyridone 24 in ether at low temperatures gave a high yield of the isomeric cyclobutene β-lactone 25 and β-lactam 26 respectively. Hydrogenation of 25 gave as expected a mixture of the saturated cyclobutane β-lactone 27 and cyclobutane carboxylic acid 28.

It would seem reasonable to assume, therefore, that the 4-methoxy-6-methyl-2-pyrone undergoes a similar photoisomerization to give the corresponding β-lactone 29. Hydrogenation of this would then give the observed cyclobutane carboxylic acid 22 by hydrogenolysis and reduction of the double bond. In view of the molecular weight of the photoproduct and the fact that no saturated β-lactone absorption was observed in the infrared



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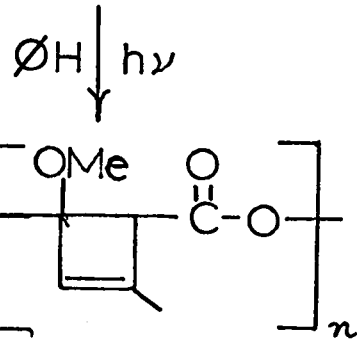

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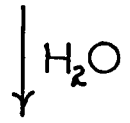

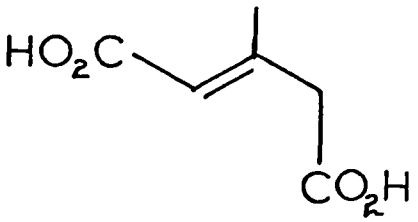

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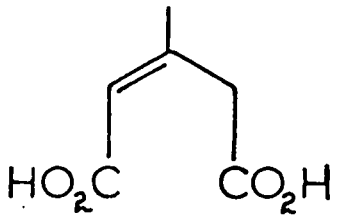

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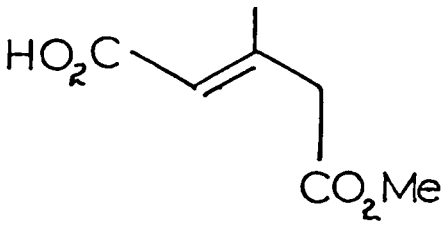

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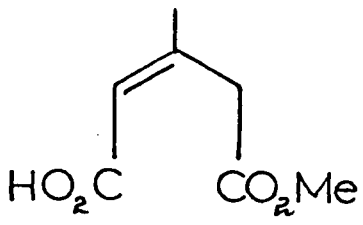

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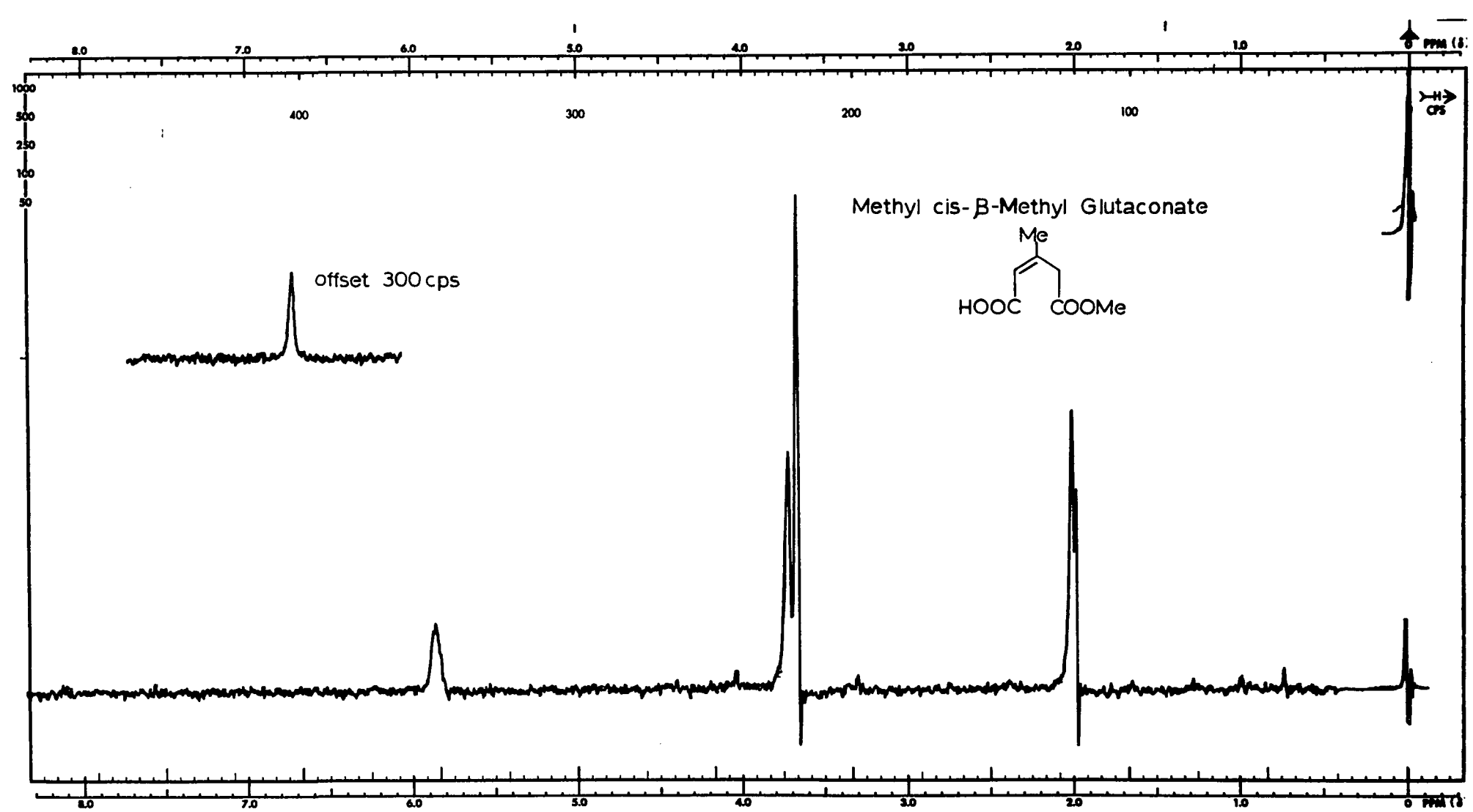
Methyl cis-β-Methyl Glutaconate
Me
HOOC
COOMe
offset 300 cps
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0 PPM (δ)
1000
500
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100
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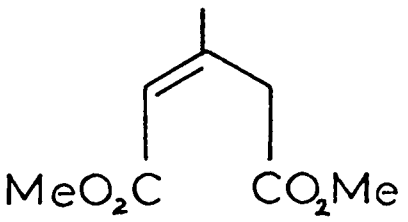
300
200
100
CPS

Figure 1

30, 31, 32, 33

CH_2N_2



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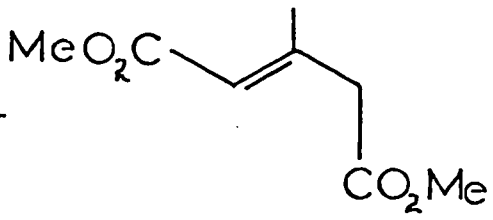


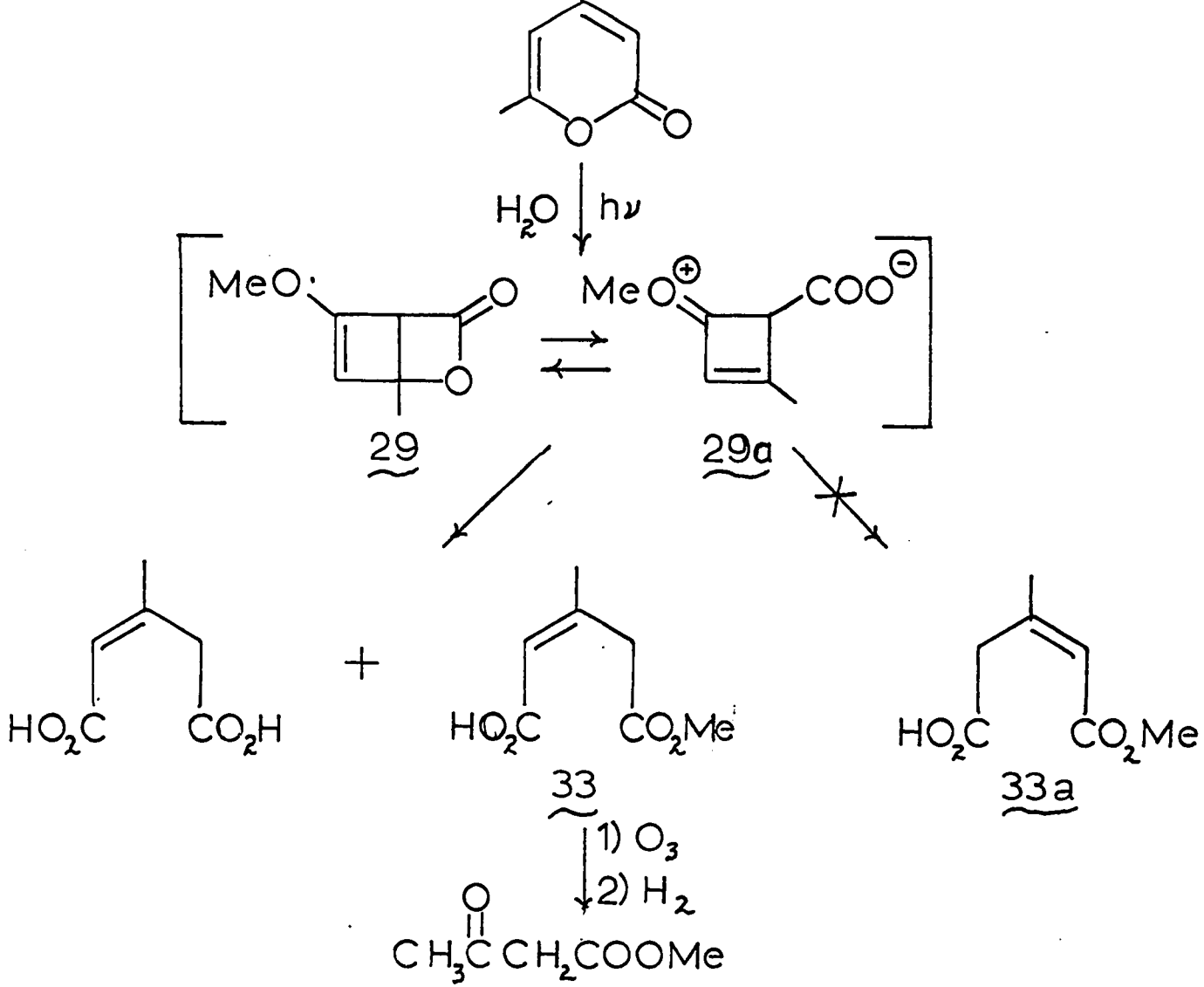
35

spectrum, the existence of a monomer is ruled out. However, the same product could be obtained from a polyester derived from the initially formed cyclobutene β-lactone.

Further insight into the structure of this polymer was afforded by the observation that treatment of the crude irradiation product with either aqueous dioxane or methanol gave a mixture of diacids and half esters. Separation of this mixture by tlc gave two products which were identified as a cis- and trans- mixture of β-methylglutaconic acids 30 and 31 and a mixture of cis- and trans-β-methylglutaconic acid monomethyl esters 32 and 33.

The mixture of diacids was identified by their infrared and NMR spectra which were identical with the values reported by Jackman[28]. The mixture of mono esters was also identified by their physical properties, the NMR approximating that of the diacids with the addition of a peak at approximately 3.6 ppm due to the carbomethoxy protons. Treatment of either of these mixtures with diazomethane gave a mixture of diesters which was separable by vpc into dimethyl cis-β-methylglutaconate 34 and dimethyl trans-β-methylglutaconate 35, each identical in infrared and NMR with the values given by Jackman[28].

The β-methylglutaconic acid and its half ester were also isolated when 4-methoxy-6-methyl-2-pyrone was irradiated in water. In this case, however, only the cis isomers were formed as determined by comparison of the physical data with Jackman's[28]. Irradiation in meth-


H2O
hν
MeO·
O
O
Me O⊕
COO⊖
29
29a
HO2C
CO2H
+
HO2C
CO2Me
33
HO2C
CO2Me
33a
1) O3
2) H2
O
CH3C CH2COOMe

anol on the other hand gave only a very low yield of the dimethyl β-methylglutaconate.

The position of the double-bond in the half esters, not ascertainable from the spectral data, was determined by ozonolysis of the cis-β-methylglutaconic acid monomethyl ester. Reduction of the ozonide by hydrogenation gave methyl acetoacetate which was isolated as its 2,4-dinitrophenyl hydrazone, indicating the correct structure of the half ester to be 33 rather than the alternative 33a.

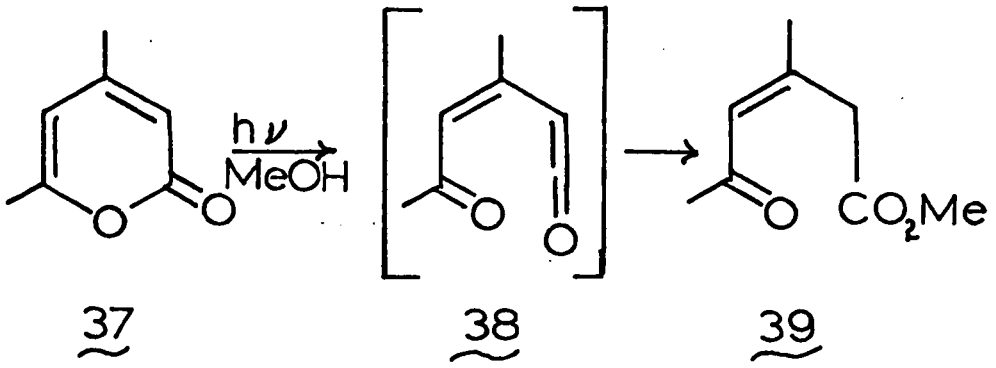
Although the position of the double-bond in the products obtained by irradiation in benzene followed by hydrolysis was not determined directly, this mixture of half esters was virtually identical in infrared absorption with the material obtained from irradiation in water, ie. absorption at 1747 cm^{-1} attributable to a saturated ester carbonyl and at 1698 cm^{-1} due to an α,β-unsaturated acid carbonyl. This similarity, although not conclusive, gives strong support to the assumption that the position of the double bonds is identical in the two products.

The isolation of both cis and trans isomers of the diacid from the benzene irradiation is in agreement with the supposition of a polyester cyclobutane intermediate 36 which does not hydrolyse stereospecifically. The fact that only the cis isomer is obtained from the water irradiation, however, would argue against the polymer being involved in this reaction. Rather the zwitterion 29a, which is formed from the initially formed β-lactone

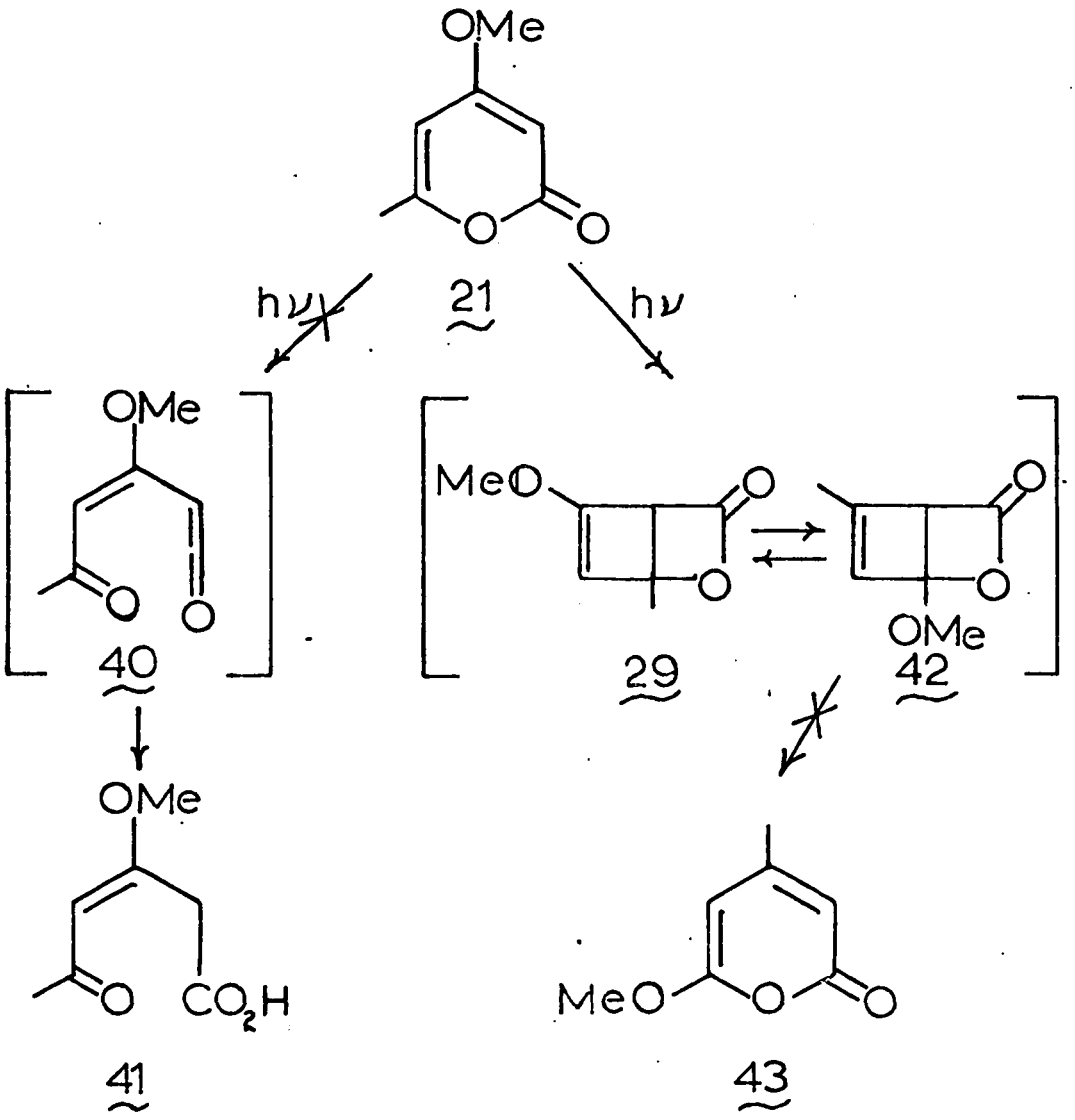
29 is immediately hydrolysed to the observed cis product. It is not clear, however, why the polymer formed in the benzene irradiation is hydrolysed with such ease in aqueous dioxane to the glutaconic acids, or why ring opening of the zwitterion 29a formed in the water irradiation is followed by protonation at carbon-3 rather than carbon-1, as might be expected, to give the half ester 33 rather than 33a.

The formation of a ketene intermediate 40 in the water irradiation analogous to that suggested by Mayo[29] for the methanol irradiation of dimethyl coumalin 37 would be hard to rationalize. Mayo proposed that irradiation of 37 resulted in the formation of the ketene 38 which added methanol to give the observed keto ester 39. By analogy, a ketene 40 formed on irradiation of 4-methoxy-6-methyl-2-pyrone would be expected to give the keto acid 41, none of which was observed.

Although hydrolysis of the cyclobutene β-lactone 29 would give the observed products, a third possibility also exists. The initially formed β-lactone could readily rearrange to the isomeric β-lactone 42. This compound is now the expected photointermediate of 6-methoxy-4-methyl-2-pyrone 43. Since 43 is merely the methyl ether of β-methylglutaconic anhydride, any isomerization of the β-lactone 43 to the pyrone would be immediately followed by hydrolysis to the observed cis-β-methyl glutaconic acid methyl ester 33. The 6-methoxy-4-methyl-2-pyrone 43 was therefore synthesised and irradiated in an



37 38 39

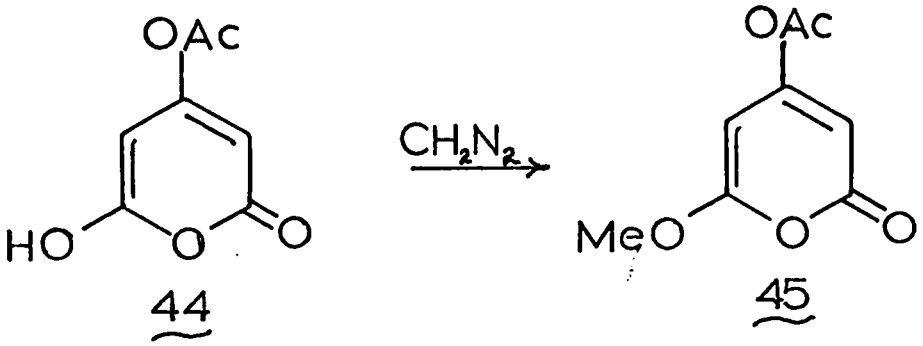


40 29 42 41 43

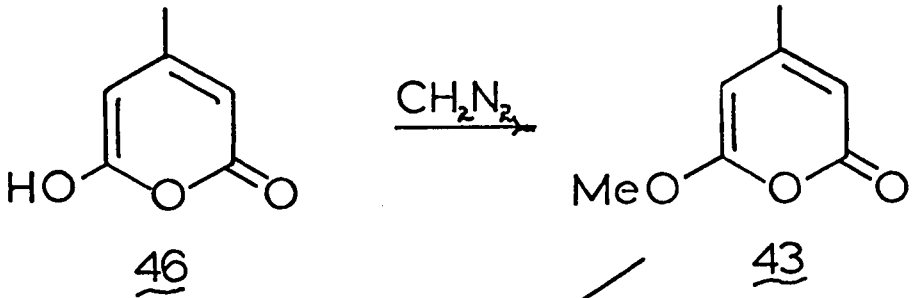
attempt to see if indeed the two pyrones were in equilibrium.

Several authors[26,30] have shown that enols will react rapidly with diazomethane to give the enol ether. For example, the 4-acetate of acetone dicarboxylic acid 44 readily forms the 4-acetoxy-6-methoxy-2-pyrone 45 in high yield on treatment with diazomethane[31]. Therefore, since the ultraviolet spectrum of β-methylglutaconic anhydride indicates that it exists in solution mainly as the enol 41[32], treatment with diazomethane seemed a reasonable route to synthesis of the desired 2-pyrone. The β-methylglutaconic anhydride itself was synthesised as described by Wiley[33] and, indeed, on treatment with diazomethane gave 6-methoxy-4-methyl-2-pyrone 43. This compound showed infrared carbonyl absorption at 1755 cm^{-1} and characteristic double bond absorption at 1640, 1595, and 1560 cm^{-1}: the NMR consisted of two three hydrogen singlets at 2.07 and 3.84 ppm due to the 4-methyl and 6-methoxy protons, and two one hydrogen multiplets at 5.14 and 5.44 attributed to the vinyl protons. The ultraviolet absorption showed a maxima at 281 nm(ε4,200).

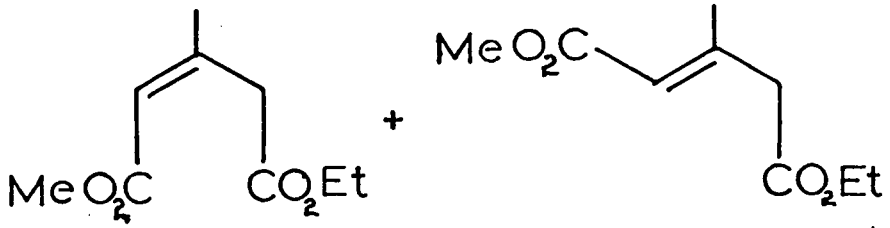
Irradiation of this compound in benzene, as described before, for 24 hours gave only starting material and some hydrolysis products, cis- and trans-β-methylglutaconic acid and monomethyl esters. No indication was found of any 4-methoxy-6-methyl-2-pyrone as would be expected if 43 and the β-lactone 29 were in equilibrium.



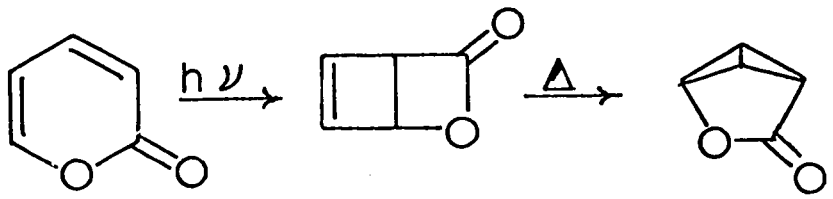
44 45



46 43



47 48



23 25 49

As expected, hydrolysis of 43 in ethanol gave a high yield of a mixture of cis- and trans-β-methylglutaconic acid ethyl methyl esters 47 and 48, which were identified by their infrared and NMR spectra. This was in contrast to the 4-methoxy-6-methyl-2-pyrone benzene irradiation product which gave none of the dimethyl ester on hydrolysis in methanol.

This failure to observe any reversal of the 6-methoxy-4-methyl-2-pyrone to the 4-methoxy-6-methyl isomer coupled with the low yield of dimethyl ester obtained on irradiation in methanol of the latter, would indicate that the 6-methoxy-4-methyl-2-pyrone plays no part in the irradiation of the 4-methoxy-6-methyl isomer.

The initial reaction of the 4-methoxy-6-methyl-2-pyrone on irradiation is therefore a photoisomerization analogous to that reported by Corey[27] for 2-pyrone. The presence of a nucleophile at this stage, such as water, traps the resultant cyclobutene β-lactone 29 resulting in the formation of β-methylglutaconates. However, in the absence of a trapping agent, the β-lactone polymerizes to the polyester 36. The polymerization of β-lactones is a well known reaction[34] proceeding either spontaneously or catalysed by acid, base or salt. In the case of the cyclobutane β-lactone above, the presence of a strong electron donating group, the methoxy, at carbon-2 facilitates ring opening and thus polymerization.

The failure to observe 1,4 dimers in the irradiation of 4-methoxy-6-methyl-2-pyrone may be attributed to a number of causes. Conceivably the explanation is no more complex than that, because of solubility problems, low concentrations were used. However, the presence of the methoxy substituent could modify the importance of the various reaction pathways (as compared to the 4,6-dimethyl-2-pyrone) in several ways.

First, the dimerization itself may be slow. Secondly, there are two cyclic pathways available from the singlet-cyclobutene and ketene formation. The rates of both of these may be affected (as may the normal reverse processes) and both may compete more effectively with dimerization. Thirdly, it has not been established that a singlet process is involved. If dimerization proceeds through the triplet, then the quantum yield of the triplet may be affected by the substituents.

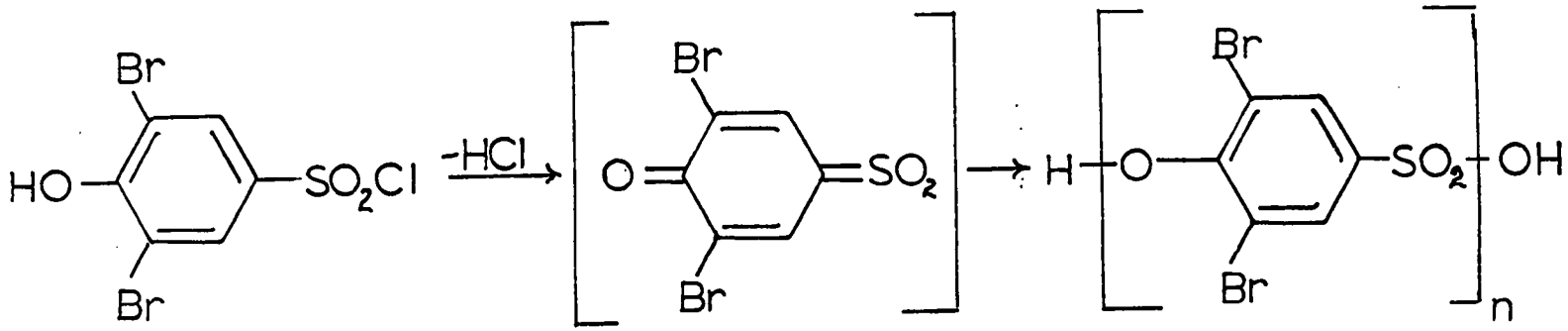
Finally, it may be noted that the cyclobutene β-lactone formation, though reversible to regenerate pyrone, may, in fact, drain away the pyrone by the formation of polymeric ester. This would be expected to be much slower for the 2-pyrone itself. In fact yet another transformation,[35] the formation of the tricyclic 49, appears to be preferred although it, itself, is slow.

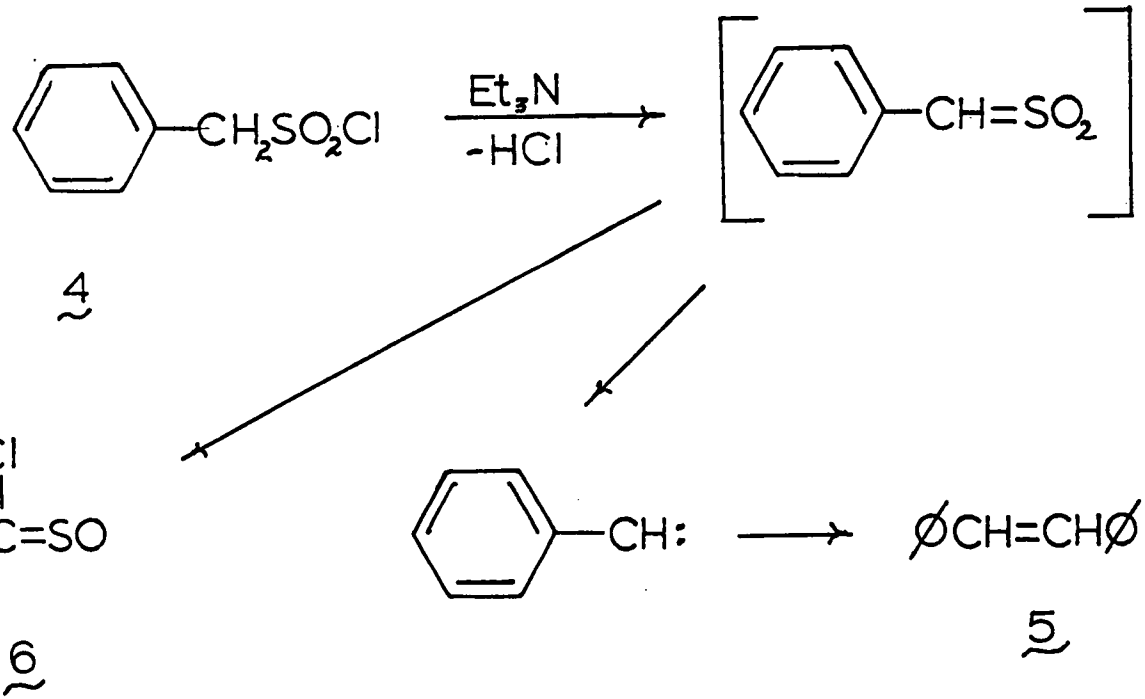
Part II: The Photolysis of β-Keto Sulfones.

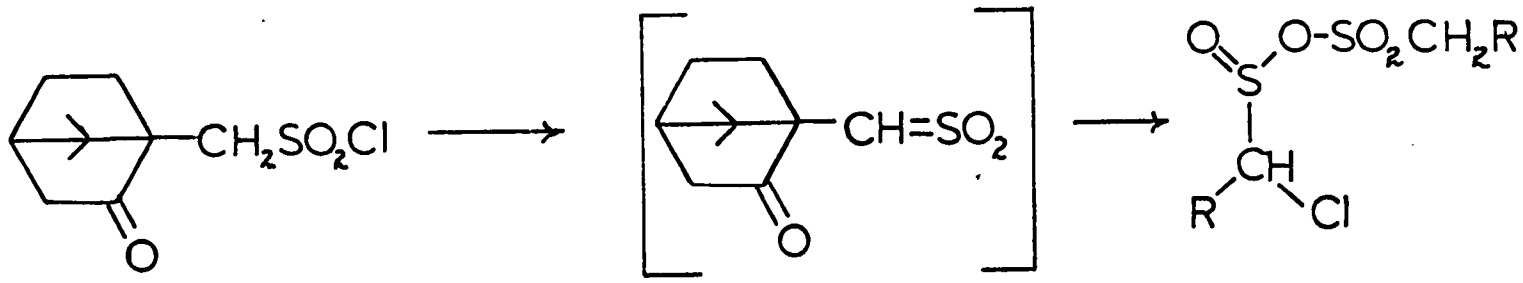
A. Introduction.

The first reference to sulfenes as intermediates can be found in the work of Zinche and Brune[37] who observed that 2,6-dibromophenol-4-sulfonyl chloride 1 lost hydrogen chloride when treated with aqueous sodium acetate. The resulting intense yellow colouration was attributed by them to the formation of semiquinone sulfene 2; and the polymeric colourless product, to a dimer or trimer of the sulfene. In 1966, Hall[38] reinvestigated this reaction and reported that the yellow colour was due to the phenoxide anion of the sulfonyl chloride rather than a sulfene, and that probably this was converted to the product, which according to Oae[39] has structure 3, without going through a sulfene intermediate.

The first real evidence for the formation of a sulfene came with the discovery of Wedekind and Schenk[40] in 1911 that triethylamine treatment of α-toluenesulfonyl chloride 4 gave triethylamine hydrochloride, sulfur dioxide, and stilbene.5. They suggested that the latter product was a result of the loss of sulfur dioxide from the initially formed sulfene to give phenyl carbene, which then dimerized. In a repetition of this work, King and


Br
HO
SO2Cl
Br
1
-HCl
Br
O
SO2
Br
2
H
O
Br
SO2
OH
Br
n
3

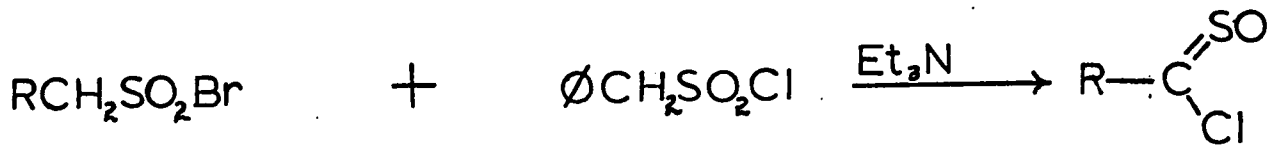

CH2SO2Cl
4
Et3N
-HCl
CH=SO2
Cl
ØC=SO
6
CH:
ØCH=CHØ
5


CH2SO2Cl
O
CH=SO2
O
O
S
O-SO2CH2R
CH
R
Cl

7 8


SO
R-C
Cl
+
RCH2SO3H

9 10

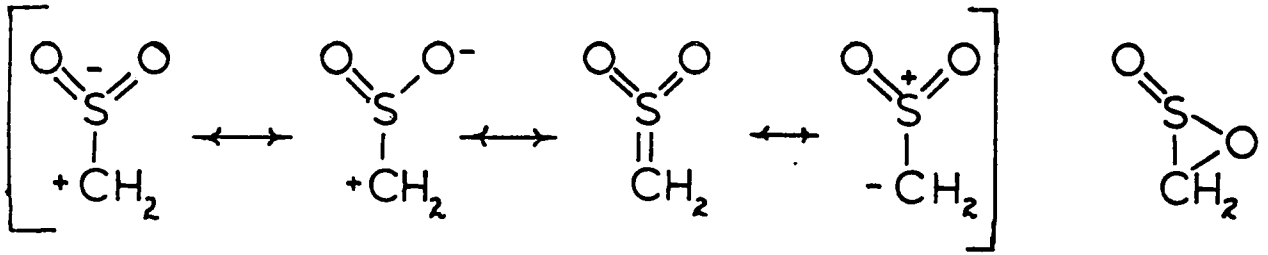

RCH2SO2Br
+
ØCH2SO2Cl
Et3N
SO
R—C
Cl

11 12

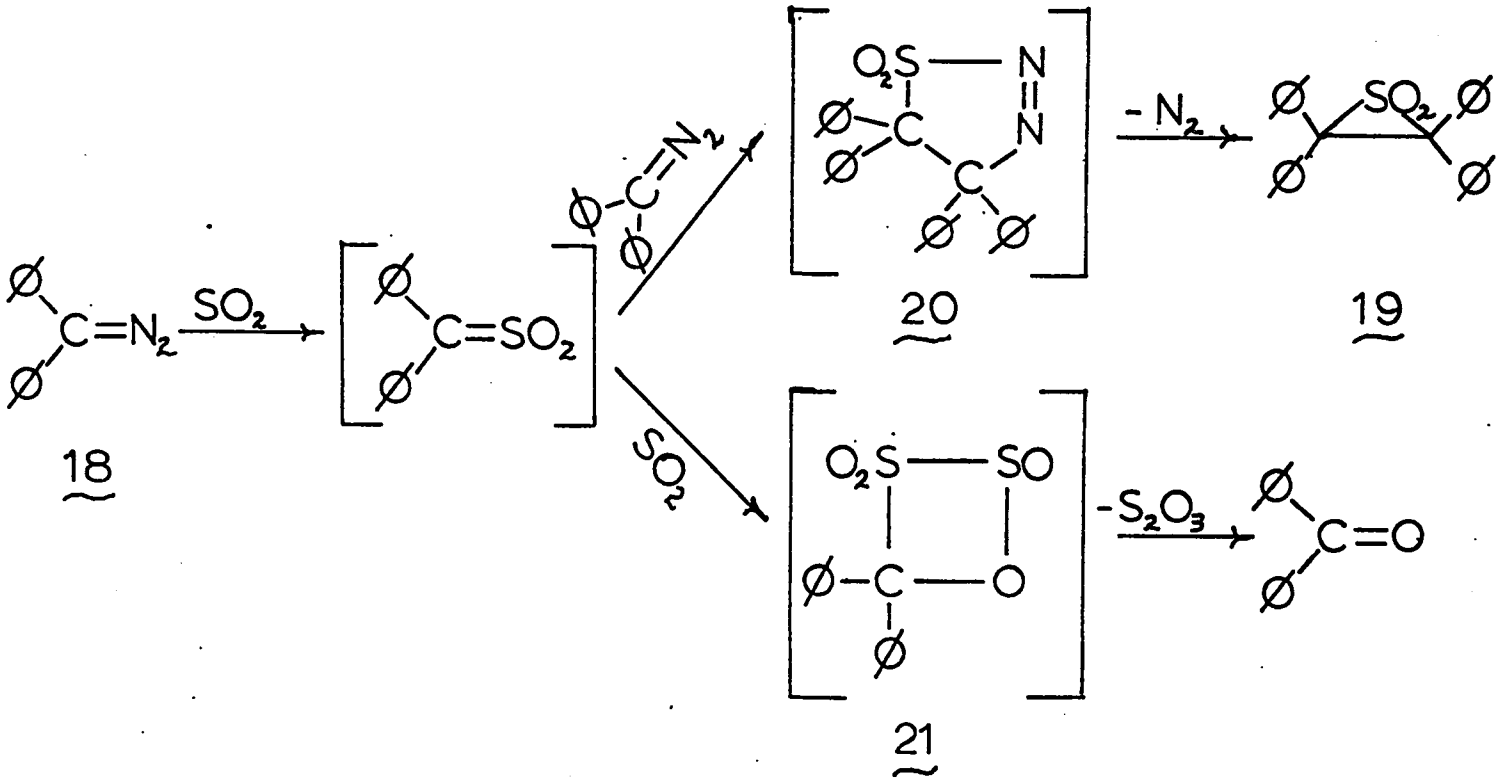
Durst[41] were able to isolate, in addition, triethylammonium phenylmethanesulfonate and thiobenzoyl chloride S-oxide 6 (both cis and trans forms).

The latter type of product had also been observed in the reaction of 10-camphorsulfonyl chloride 7 with triethylamine which gave exclusively the thiocarbonyl S-oxide 9 and no olefin. The mechanism[42] proposed for this reaction involved a 1,3 addition of the initially formed sulfene to a second molecule of sulfonyl chloride to give the intermediate 9. Subsequent loss of sulfonic acid 10 resulted in the observed thiocarbonyl S-oxide. This mechanism was supported by the observation[43] that reaction of 10-camphorsulfonyl bromide 11 in the presence of tosyl chloride resulted in the exclusive formation of thiocarbonyl chloride S-oxide 12. Although this necessitates the intermediacy of a halogen-free intermediate, a 1,3-addition reaction has not been proven, and in fact, it is the only presently known 1,3 reaction of sulfenes.

The exact structure of sulfenes is not entirely clear at this time, since several canonical and a cyclic form can be envisaged ranging from the 1,3 dipolar 13, 14, 15 and through the non-polar 16 to the cyclic 17. Clearly, in structure 13 the sulfur has assumed an oxidation state equivalent to a sulfonic acid, whereas in the cyclic structure 17, it is equivalent to that of sulfinic acid. On the other hand, in the neutral form 16, the ability to react in either of these two directions is concealed. Structures 14 and 15, however, are "carbonyl"



14 15 16 13 17



18 20 19 21

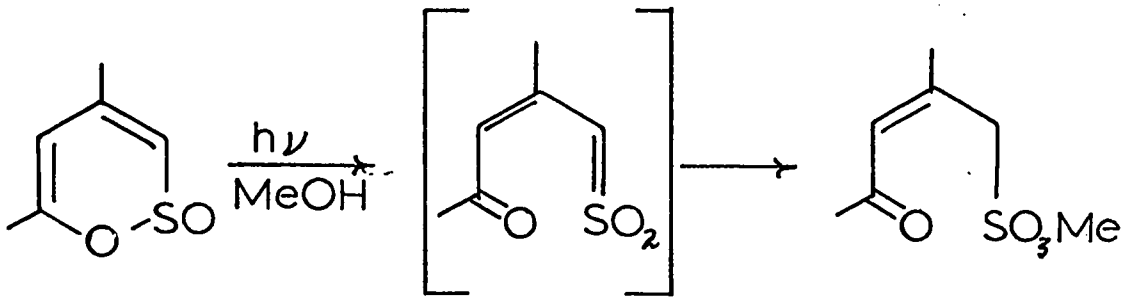
in nature being stabilized by the highly electronegative oxygen atoms. Since no conclusive proof is yet available to differentiate among them, it may be advisable to consider sulfenes as existing not just as one definitive form, but rather as a combination of all of the above-mentioned structures, with the ability to react accordingly.

The formation of sulfenes in solution under basic conditions has been investigated, however. King and Durst have systematically argued[44] that the formation of sulfenes in the reaction of base on sulfonyl chlorides occursvia a concerted elimination of hydrogen chloride. Their arguments were based on the observation that α-toluenesulfonyl chloride, when treated with base in deuteromethanol yielded only undeuterated or monodeuterated methyl sulfonates. Any mechanism other than that stated above would be expected to yield in addition a certain percentage of dideuterated material. Their theory was supported by that of Truce and coworkers[45,46] who studied a series of primary sulfonyl chlorides, mesyl chloride, mesyl bromide, 2-propene-, and 1-propen-1-sulfonyl chlorides. The production of monodeuterated material could be rationalized by a sulfene intermediate, whereas the undeuterated products could be explained by either a hydrogen abstraction by the sulfene from the trialkylamine hydrochloride in the solvent cage, or by an S_N2 reaction of alkoxide on a sulfonyl triethylammonium salt. This hypothesis would

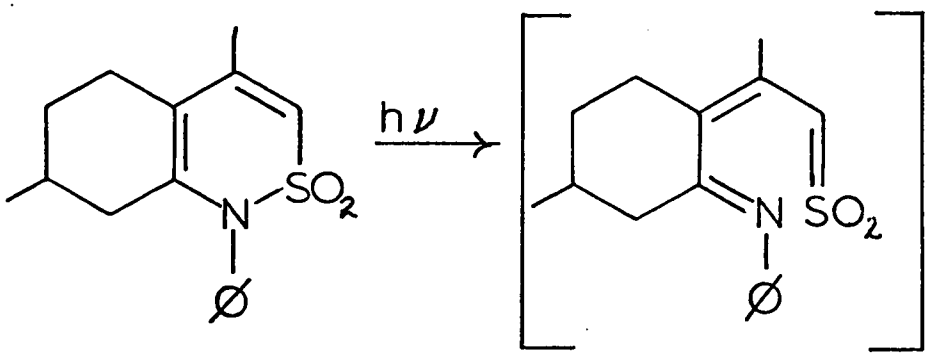
explain the product distribution from 1-propene-sulfonyl chloride which consisted of monodeuterated 2-propene sulfonic acid methyl ester and undeuterated 1-propene sulfonic acid methyl ester.

In 1916 Staudinger and Pfenninger[47] discovered a second method of producing sulfenes. They found that the addition of sulfur dioxide to diphenyldiazomethane 18 gave tetraphenylethylene sulfone 19. But if the reaction conditions were reversed, with the diazomethane being added to sulfur dioxide, the isolated product was benzophenone. The authors proposed an addition of the initially formed sulfene to a second molecule of starting material which was in excess, giving a cyclic intermediate. In the first case, addition of the sulfene to a molecule of diphenyldiazomethane would give the Δ^2-[1,2,3] thiadiazoline 20, which on loss of nitrogen would give the observed tetraphenylethylene sulfone. In the other case, addition to a second molecule of sulfur dioxide would result in formation of the cyclic intermediate 21, which could give benzophenone and S_2O_3.

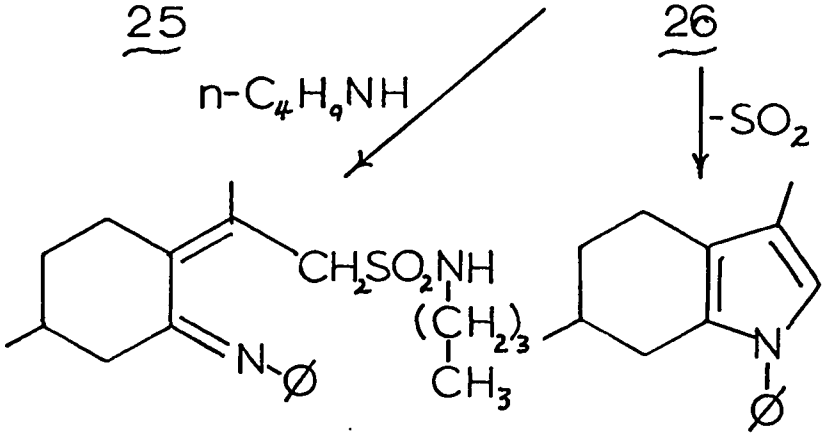
More recently, it has been proposed that the irradiation[48] of α,β-γ,δ-unsaturated sultones 22 in methanol proceeds through a sulfene intermediate 23, since the product isolated is the methyl sulfonate 24. King and Durst[49] have also found that irradiation or pyrolysis of the sultam 25 in the presence of n-butylamine gave the N-butylsulfonamide 27 and the pyrrole 28. They have rationalized their results by assuming the existence of



22 23 24



25 26



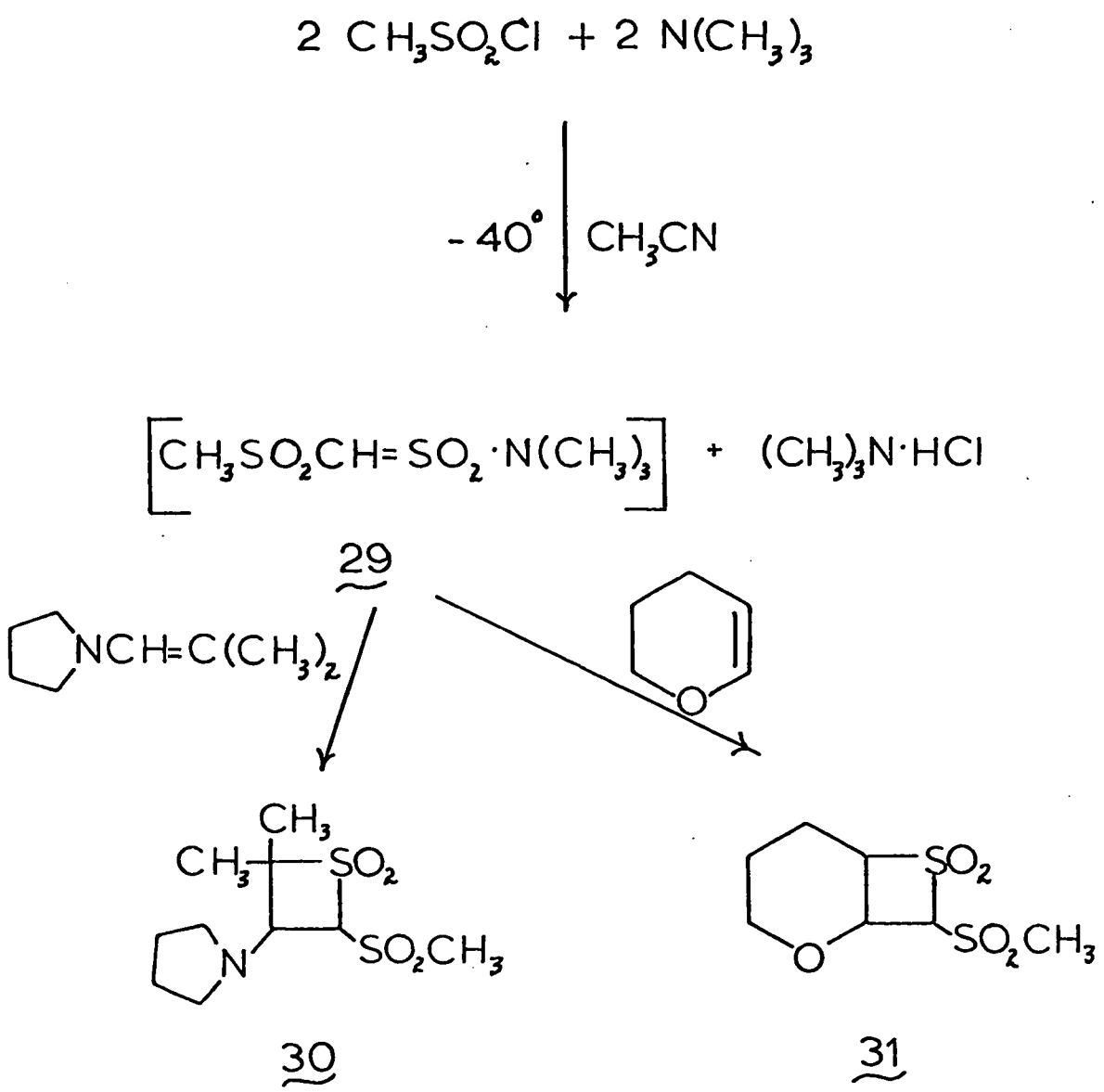
27 28

a sulfene intermediate 26, which gave the sulfonamide product 27 by a "normal" addition of n-butylamine to the sulfene, and the pyrrole 28 by a so-called "abnormal" attack of the imine nitrogen on the sulfene carbon, with a subsequent loss of sulfur dioxide. "Abnormal" attack has been defined as the nucleophilic attack on a sulfene at the carbon or oxygen atom[50] resulting in the formation of a sulfinic acid or derivative.

Charlton and Mayo[51] have restudied the photolysis of unsaturated sultones using the flash photolysis technique, and were unable to observe an intermediate with absorption greater than 320 nm and lifetime longer than 20μseconds in cyclohexane. They therefore concluded that participation of a sulfene in these reactions is improbable.

The only reported isolated of a stable sulfene complex is that of Opitz[52] who claimed that a trialkylamine adduct was formed by the addition of triethyl- or trimethylamine to methanesulfonyl chloride in acetonitrile at -40°. On the basis of its infrared and NMR spectrum, he has assigned the structure 29 to this sulfene adduct. In support of this structure, he reported that addition of enamines or vinyl ethers to this complex resulted in the formation of the corresponding thietane 1,1 dioxides, 30, 31 which is characteristic of sulfenes.[53]

After several decades, a resumption of interest in sulfenes was stimulated by the discovery[53] that N-(1-propenyl)-piperidine 32 was not C-alkylated by mesyl


2 CH3SO2Cl + 2 N(CH3)3
-40°
CH3CN
[CH3SO2CH=SO2·N(CH3)3]
+ (CH3)3N·HCl
29
NCH=C(CH3)2
O
CH3
CH3
SO2
N
SO2CH3
SO2
O
SO2CH3

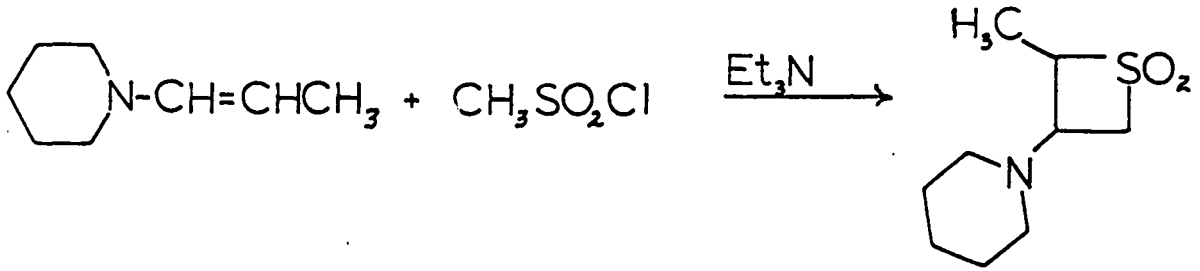
30

31

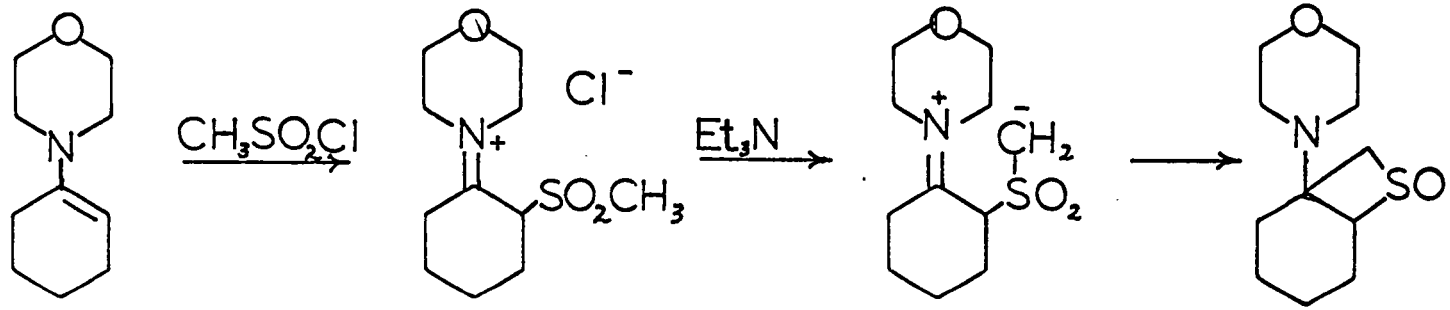
chloride/triethylamine as expected, but rather was converted to 2-methyl-3-piperidinothietane 1,1 dioxide 33. Since that time, this reaction has been extended to a large variety of primary sulfonyl chlorides and a wide variety of enamines of aldehydes and ketones. The reaction has also been extended to include ketene O,N , N,N, and O,O acetals as well as vinyl ethers(54). A full discussion of these latter reactions can be found in the introduction to Part III.

The proposed mechanism for the formation of the thietanes is as follows: the elements of hydrogen chloride are removed from the sulfonyl chloride by the base resulting in the formation of a sulfene. The sulfene is then immediately attacked by the nucleophilic enamine to give the observed thietane 1,1-dioxide.

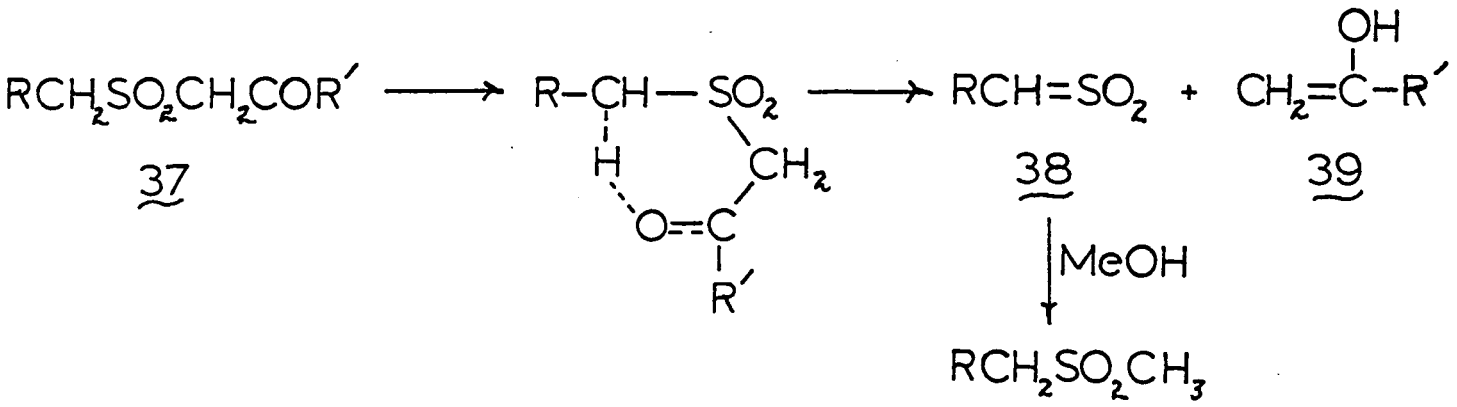
An alternative mechanism for these reactions could involve initial formation of an acyclic immonium salt 34 which, after proton abstraction, rearranges to an unstable cyclic immonium salt 35. Subsequent rearrangement would yield the cyclic sulfone 36. However, this possibility seems unlikely since, in the absence of triethylamine, reaction of an excess of enamine with methanesulfonyl chloride produced only a trace of the corresponding methyl sulfonyl ketone(55). It was found also that the enamine must be present when the sulfonyl chloride and triethylamine are initially mixed. In the absence of enamine, rapid reaction between the amine



32 33



34 35 36



37 38 39

hydrochloride and the sulfonyl chloride took place to give amine hydrochloride and polymeric sulfene. Subsequent addition of enamine gave only a low yield of cyclic sulfone.(55)

Therefore, although considerable work had been done and a large amount of evidence obtained to justify the existence of sulfenes, there still existed a need for a neutral aprotic synthesis of sulfene intermediates. It was thought that photolysis of β-keto sulfones 37 which contained a hydrogen γ-to the carbonyl and α- to the sulfonyl groups might result in such a route. Excitation of the carbonyl could well result in a Norrish Type II cleavage by abstraction of the aforementioned proton to give the enol 39 and a sulfene 38. Evidence for the formation of this intermediate could then be obtained by trapping it as the methyl ester by performing the photolysis in methanol solution.

B. Discussion

Benzyl acetonyl sulfone[56] was irradiated in methanol at 0° using a 450 watt mercury arc lamp through Corex. The volatile product, acetone, was distilled from the product mixture and analysed quantitatively by gas chromatography.

The rest of the products were separated by thin layer chromatography (TLC) and identified as dibenzyl, benzylacetone, benzylsulfinic acid, and benzylsulfonic acid isopropenyl ester. The yields are given in Table I.

Table I

Yield (%: Isolated)

RSO_2CH_2COR'	RSO_2H	R-R	RCH_2COR'	CH_3COR'	$RSO_3C(=CH_2)R'$
$R=C_6H_5CH_2$ R'=Me	44	22	13	59	6
$R=C_6H_5CH_2$ $R=C_6H_5$	22	24	-	78	-
$R=(CH_3)_3C$ R'=Me	28 16[a]	-	-	56	16

(a) t-butyl sulfonic acid

The identity of the first three above-mentioned products was determined by comparison of infrared and nuclear magnetic resonance (NMR) spectra with authentic samples, and by mixed melting point (the dinitrophenylhydrazone of acetone being used). The infrared and NMR spectra of benzylsulfinic acid were identical with a sam-

ple prepared as described by Durst[57] by the reaction of sodium bisulfite and α-toluenesulfonyl chloride.

The more interesting benzylsulfonic acid isopropenyl ester was identified on the basis of its infrared absorption at 1670 and 882 cm^{-1} which is indicative of an olefinic methylene, and at 1365, 1167 and 953 cm^{-1}, characteristic of a sulfonate ester. The NMR was in agreement, showing a three hydrogen singlet at 1.87 ppm of a methyl group on a carbon bearing oxygen, a two hydrogen singlet at 4.34 ppm attributed to a benzylic methylene group, a two hydrogen multiplet at 4.74 ppm due to a vinyl group, and a five hydrogen singlet at 7.40 ppm due to a phenyl group. The elemental analysis was correct for $C_{10}H_{12}O_3S$, indicating the compound to be isomeric with the starting material.

Contrary to expectation, however, no benzylsulfonic acid methyl ester was observed either in the NMR of the total product mixture, or in the isolated products. Failure to observe this product, had it been formed, cannot be attributed to secondary reactions, since the sulfonate was shown to be stable under the photolysis and separation conditions.

Irradiation of benzyl phenacyl sulfone in methanol under conditions similar to those described above, gave a similar set of products, which were identified as dibenzyl, acetophenone, and benzylsulfinic acid. In contrast with the previous case, however, no 1-phenyl-

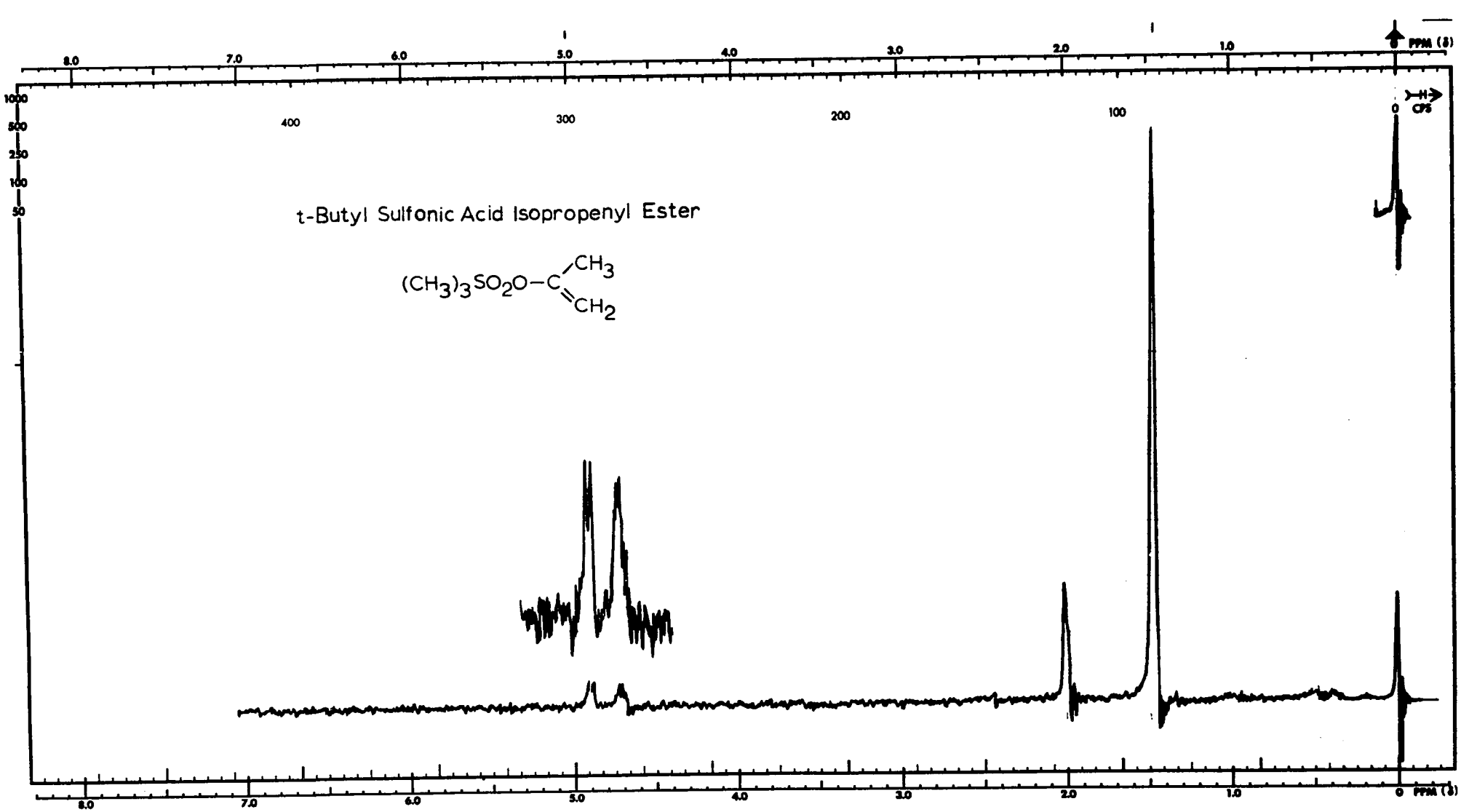

t-Butyl Sulfonic Acid Isopropenyl Ester
$(CH_3)_3SO_2O-C(=CH_2)-CH_3$
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
PPM (δ)
1000
500
250
100
50
400
300
200
100
0
CPS

Figure 2

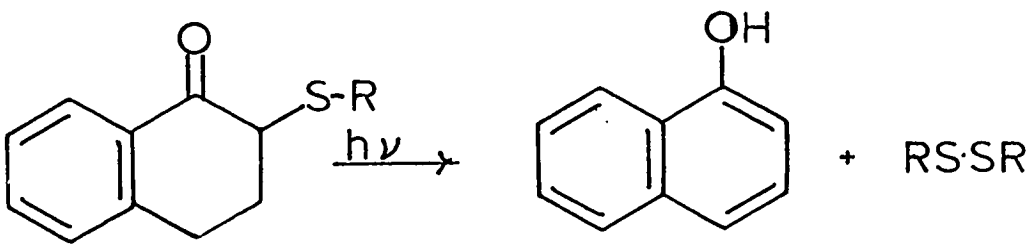
propiophenone nor vinyl sulfonate was obtained. This failure to observe any vinyl sulfinate was not unexpected, since the styryl moiety of the ester would be extremely susceptible to hydrolysis and polymerization by the numerous free radicals and acidic products produced during the reaction.

The absence of 1-phenylpropiophenone seemed peculiar, however; but may be the result of a faster rate of hydrogen abstraction by the phenacyl radical relative to the acetonyl radical of the preceding reaction. Although no literature values for abstraction by this type of radical could be found, the increase in the yield of acetophenone (78%) over the yield of acetone (59%) more than compensates for the yield of benzylacetone observed in the first reaction.

It would appear, therefore, that all of the products have arisen from an initial cleavage of the carbon-sulfur bond β to the carbonyl group. Subsequent loss of sulfur dioxide and/or radical recombination, as well as hydrogen abstraction, accounts for all the products observed (see figure I).

Such a cleavage is analogous to that recently reported by Hill[59] for β-keto sulfides. It was found that irradiation of 2-substituted tetralones 1 gave α-naphthol 2 and disulfides. These products are again a result of an exclusive cleavage of the carbon-sulfur bond β to the carbonyl group.

The formation of benzylsulfonic acid isopropenyl ester was of particular interest, both since syntheses



1 2 3

Figure I

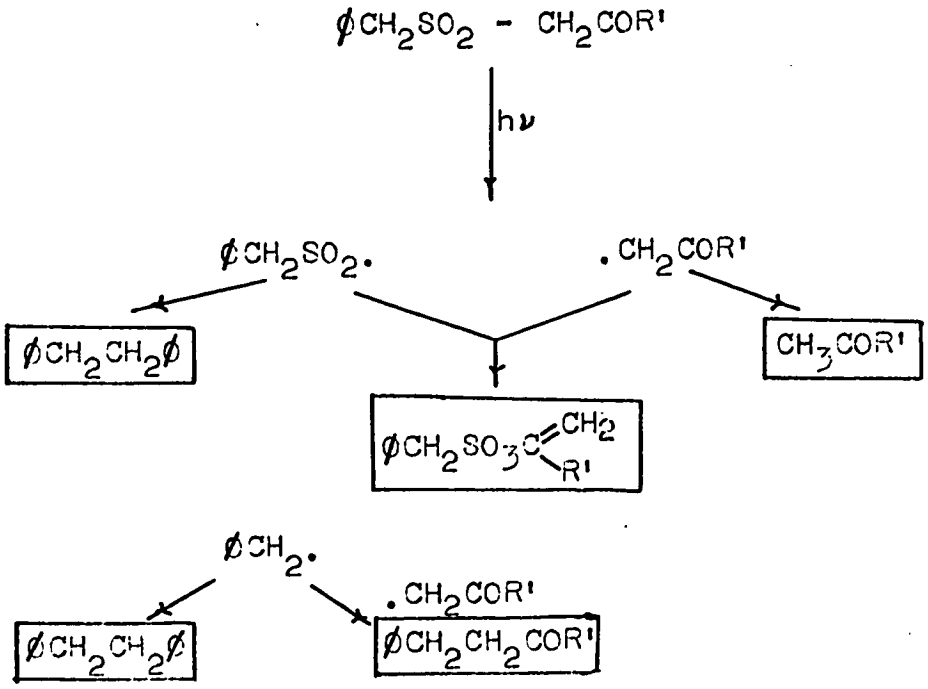
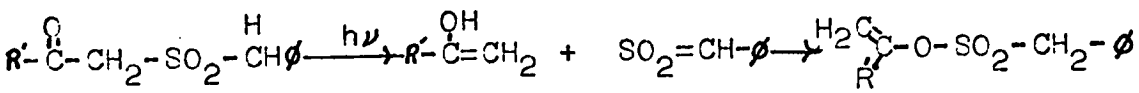
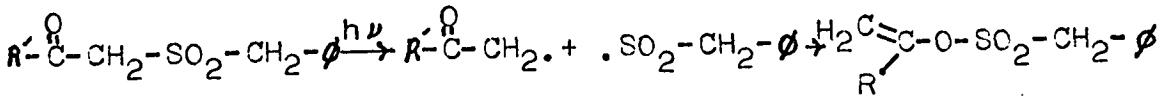


Figure II





of enolic esters of this type are rare[60-62], and also because the possibility existed that it may have arisen as the result of a Norrish Type II cleavage giving the sulfene and an enol, followed by cage recombination before solvent intervention (see figure II, reaction 1).

To distinguish between this possibility and the alternative homolytic cleavage followed by radical recombination (see figure II, equation 2), t-butyl acetonyl sulfone was synthesised. This sulfone was readily prepared from t-butyl acetonyl sulfide[63] by oxidation with 30% hydrogen peroxide in acetic acid. Since no hydrogen atom β to the carbonyl group is present in this molecule, any vinyl sulfonate found on irradiation must by necessity be formed as a result of homolytic cleavage rather than a Norrish Type II-sulfene mechanism.

Irradiation of t-butyl acetonyl sulfone in methanol as before gave the usual assortment of products, which were identified as acetone, t-butylsulfinic acid, t-butylsulfonic acid, and t-butylsulfonic acid isopropenyl ester.

The t-butylsulfinic acid and t-butylsulfonic acid were identical in infrared absorption and NMR with samples prepared as described by Barnard[64] from t-butyl Grignard and sulfur dioxide, and from t-butylmercaptan and 30% hydrogen peroxide as described by Zuffanti[65], respectively. The structure of t-butylsulfonic acid isopropenyl ester was assigned on the basis of its infrared absorption at 1668 and 870 cm^{-1} characteristic of a

terminal methylene, and at 1345, 1149 and 951 cm^{-1} attributable to a sulfonate ester. The NMR consisted of a nine-hydrogen singlet at 1.46 ppm due to the t-butyl group, a three-hydrogen singlet at 2.02 ppm due to methyl group on carbon-bearing oxygen, and a two-hydrogen doublet of doublets at 4.80 ppm, J_{AB}=2.0 cps, $\delta_A-\delta_B$=10.7 cps, due to the terminal vinyl protons. The elemental analysis indicated a molecular formula of $C_7H_{14}O_3S$, isomeric with the starting material.

Again no ketone corresponding to benzylacetone, i.e. 4,4 dimethyl-2-pentanone, observed among the products. However, in view of the high steric hindrance of the t-butyl radicals, it is not surprising that no radical coupling occurs between it and the acetonyl radicals.

The formation of a large amount of sulfonic acid in this reaction, a product not observed in previous reactions, was probably a result of air oxidation of the t-butylsulfinic acid during separation of the products. This is a well-known reaction of sulfinic acids and is used for the preparation of both aliphatic and aromatic sulfonic acids[66].

The mechanism of formation of the benzyl sulfonic acid isopropyl ester would, therefore, appear to be at least superficially related to the interconversion of β-diketones, enol esters and lactones[67-71], and enol amides with β-keto enamines[72].

The conversion of nonenolizable β-diketones to enol lactones has been studied by two groups. Both Cookson[70]

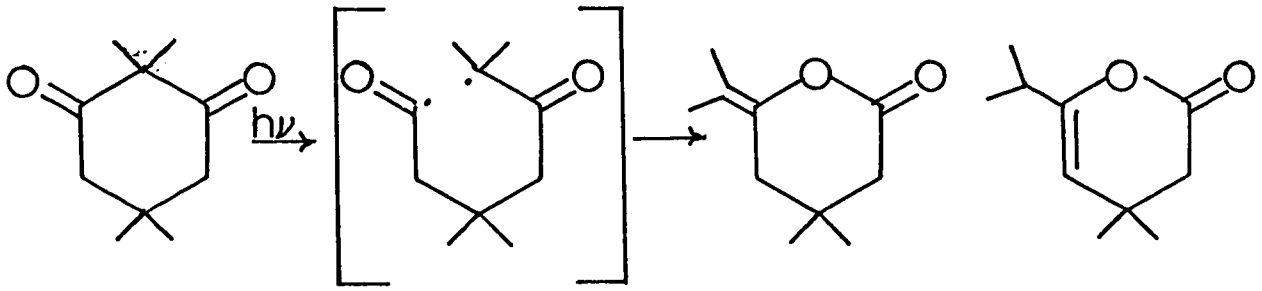
and Nozaki[71] have shown that irradiation of dimethyldimedone 4 results in the formation of the enol lactones 5 and 6. The reversibility of this reaction has also been demonstrated by the fact that irradiation of 5 will give dimethyldimedone. Nozaki has proposed a diradical intermediate 7 for this reaction, which readily explains the formation of the observed products, although no proof for this intermediate is given.

Mazur has also studied the reverse reaction and found that irradiation of exocyclic enol lactones[69] such as 7 do in fact give β-diketone products 8. If, however, the double bond is endocyclic, a different set of products is obtained as well, which involves elimination of carbon monoxide[70] i.e. 9, 10, and 11. Again the formation of a diradical by cleavage of the carbon-oxygen bond is proposed, although no proof is given.

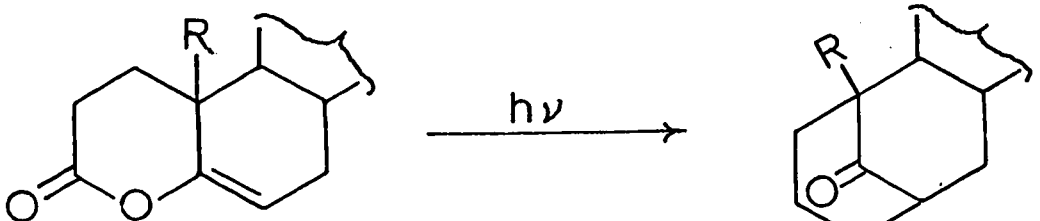
More recently, an analogous reaction involving the nitrogen analogue has been reported[72]. Yang has shown that irradiation of the enamide 12 gave the two β-keto enamines 13 and 14, the latter arising from a secondary photoisomerization reaction.

Mazur and co-workers have also carried out extensive studies on the rearrangement of enol[73] and dienol esters[74]. Irradiation of these compounds is reported to result in a photo Fries reaction to give β-diketonic products.

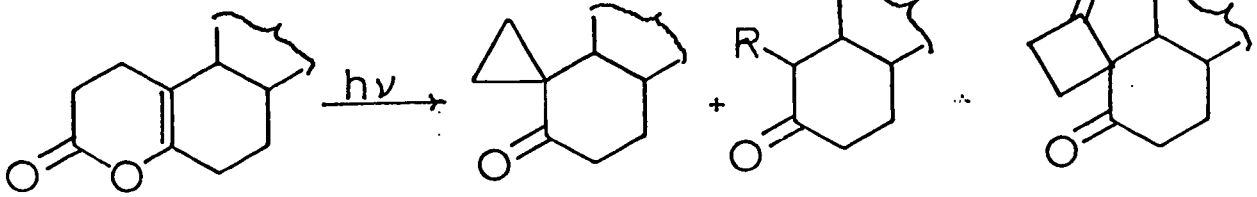
Cyclohexen-1-yl benzoate 15 on irradiation[73] in cyclohexane at 254 nm gave initially[75] 2-benzoyl-cyclo-



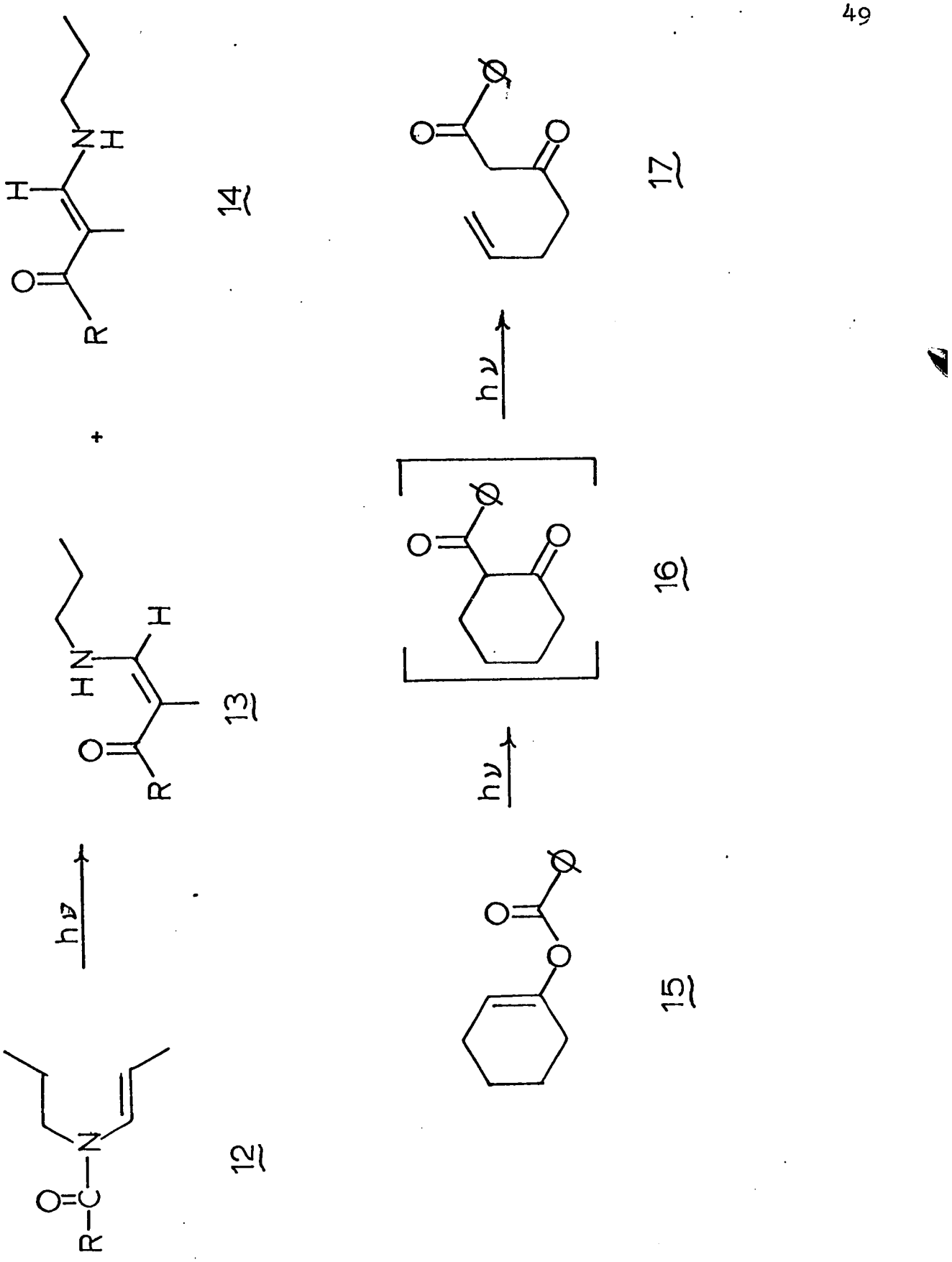
4 7 5 6



7 8



9 10 11



12 13 14 15 16 17

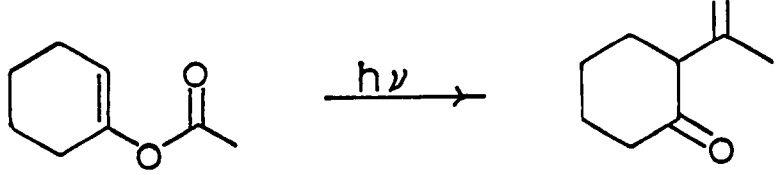
hexanone 16 , which, due to the fact that it is enolized only to the extent of 25%, is further photolysed to 1-benzoylcyclohex-5-en-2-one 17 by means of a Norrish Type II cleavage. Cyclohexen-1-yl acetate 18 , on the other hand, gives[68] only 2-acetylcyclohexanone 19 since this product is completely enolized and so cannot react further.

A radical process, involving recombination within a solvent cage, rather than a four-centred concerted process, has been suggested for these reactions[68]. Mazur based this proposal on the observations that substitution at the two position, as in 2-methyl-cyclohexen-1-yl acetate 20 gives 2-methyl-cyclohexanone 21 and a 2-methyl-cyclohexanone dimer as well as 2-acetyl-2-methyl-cyclohexanone 22 : products which can be rationalized best by a radical mechanism.

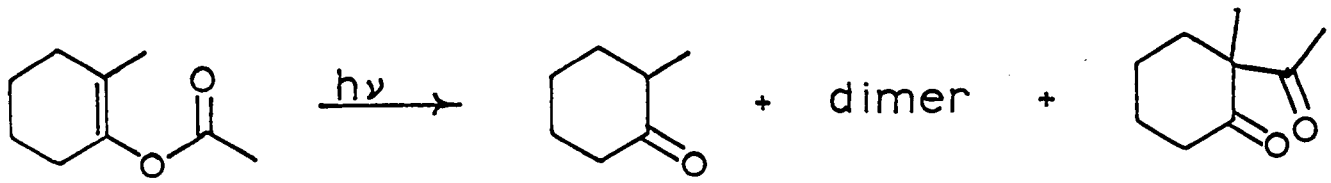
This is further substantiated by the photolysis of androsta-3,5-diene,3,17-β-diol 23 which on photolysis gives not only the expected acetyl migration to the C-3 position 24 but also to the C-6 position 25 which cannot be derived from a four-centered concerted reaction.

The formation of the enol sulfonates, therefore, by analogy could be considered as proceeding by either a four-centered mechanism, or a radical recombination within a solvent cage of an initially generated radical pair.

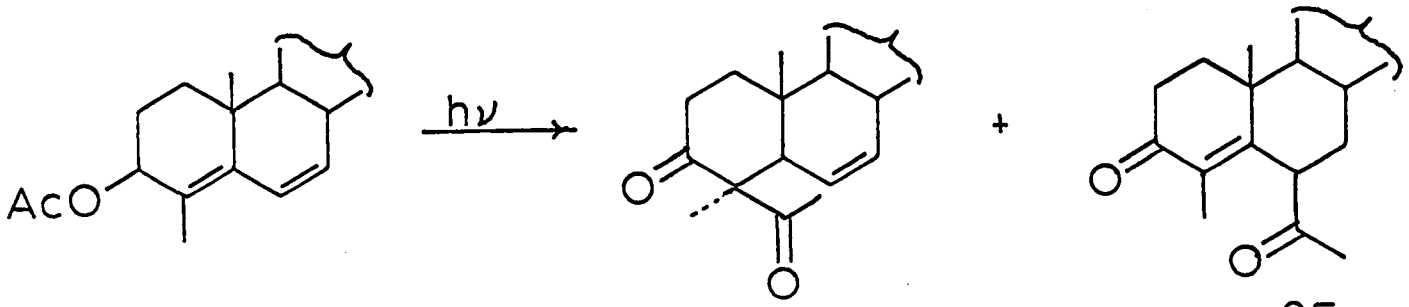
The involvement of solvent cages for bimolecular collisions in liquid media was first proposed by Franck and Rabinowitch[76] in 1934. It was not until 1955, how-



18 19



20 21 22



23 24 25

ever, that Noyes[77] developed a theory to explain these effects. He considered three different possibilities; the first, which he called "primary recombinations" were those in which the initially formed diradicals were at no time separated by more than one molecular diameter, which necessitates that the recombination be of the order of molecular vibrations, i.e. 10^{-13} sec. Thus interference by the cage molecules could occur only when the mole fraction of the scavenger approached unity.

The second case called "secondary recombination" covers recombination of geminal radicals which have diffused to distances greater than a molecular diameter but have not completely escaped the solvent cage. Since the diffusion rate is of the order of 10^{11} sec^{-1} in liquids of ordinary viscosity, recombination must occur within 10^{-9} sec. Therefore in order to get scavenging, the concentration of scavengers would have to be of the order of 0.01 moles per litre or greater.

If the radicals escape both primary and secondary recombination, they will have diffused far enough apart to become "free". Scavengers could then compete on an equal basis with other radicals in solution for these "free" radicals. Therefore, at low concentrations of scavengers, most of the radicals would be expected to combine with other radicals. As the concentration is increased, the number of radicals trapped would also increase up to a limiting value at which all radicals escaping primary and secondary recombinations would be

scavenged. This limiting value cannot be exceeded even with pure scavenger solvents unless the rate of radical trapping by the scavengers is greater than 10^7 litres per mole sec., i.e. a highly reactive material. If this were true, then competition with secondary recombinations could occur at scavenger concentrations greater than 0.01 moles per litre and the observed efficiency would be proportional to the square root of the scavenger concentration.

This theory is supported by Rembaum and Szwarc[78] who found that the addition of iodine had little or no effect on the ethane/carbon dioxide product ratio from the liquid phase thermal decomposition of peracetic acid anhydride, but decreased the methane/carbon dioxide ratio to zero. However, in the vapor phase, addition of iodine vapour reduced both ratios to zero. These results are in agreement with the theory of Noyes for a "secondary recombination" in the liquid phase which is not possible in the gas phase where all the radicals would be trapped by scavengers.

Hammond and co-workers have done extensive work on the decomposition of azoalkanes which he has proposed undergo primary and secondary recombination reactions[79] because of their inefficiency as oxidation and polmerization initiators. In support of this, Hammond has found that radical scavenging occurs on addition of such things as iodine and bromine to solutions of azoisobutylnitrile,[79] although some dinitrile formation is still observed. Only

in liquid bromine solution was the formation of the dinitrile completely eliminated[79].

Studies[80] on the effect of concentration of scavengers in solutions of azo-1-cyanocyclohexane do not, however, conform with the theory of Noyes. It was found that no scavenging occurred with either iodine or bromine until the concentration was in excess of 0.1 molar and no dependence on the square root of the concentration was observed. Hammond has interpreted these results as meaning that no distinction can be observed experimentally between primary and secondary recombination reactions, only between these and "free" radical reactions. In an attempt to penetrate or modify the solvent cage of the photochemical reaction which results in the formation of the vinyl sulfinate, several free radical traps and/or different solvents were employed in order to distinguish between the two types of radical recombination reactions. Benzyl acetonyl sulfone was used and the results noted in Table II.

As can be seen, the addition of isobutylene and oxygen, both well known radical traps, had pronounced effects on the yields of all products except that of the vinyl sulfonate. In the case of oxygen, the yields of both dibenzyl and benzyl acetone are reduced to zero, and the benzylsulfinic acid has been completely oxidized to the sulfonic acid. These results are completely in accord with the theory that the radical precursors of these three products have escaped the solvent cage to

Table II

Yield (%: isolated or by NMR)

Solvent	Additive	$(\phi CH_2)_2$	ϕCH_2SO_2H	$\phi CH_2SO_3C_3H_5$	$\phi CH_2CH_2COCH_3$
MeOH[a]	-	31	18[b]	11	12
MeOH[a]	C_4H_8(20%[w]/v)	9	-	11	5
MeOH[a]	O_2	-	8[c]	13	trace
MeOH[d]	-	22	44	6	13
C_6H_6[a]	-	40	-	10	32
Diisopropyl-ether[d]				6	
95% EtOH[d]					

(a) Yields estimated by NMR (b) Minimum value doe to insolubility of acid (c) Benzyl sulfonic acid (d) Isolated yields

become "free" radicals which are then scavenged.

Attempts to modify the solvent cage by changing the nature of the solvent, i.e. from polar to nonpolar, from hydrogen donating to non-hydrogen donating, also had little if any effect on the yield of vinyl sulfonate, although in benzene the formation of benzylsulfinic acid was eliminated due to the lack of available hydrogens for abstraction.

It is clear then that the formation of several of the products observed from this reaction are by a radical mechanism. The complete failure to observe quenching by either isobutylene or oxygen, however, argues against a

secondary radical recombination process at least, since the oxygen, if not the isobutylene, was of sufficiently high reactivity and concentration[79] to interfere with such a reaction. On the other hand, since Hammond found[81] that something as reactive as liquid bromine was required to completely arrest both the primary and secondary recombination processes, one cannot unequivocally rule out a radical process in favour of a four-centered one. A four-centered concerted process involving expansion of the sulfur shell, on the other hand, is a distinct possibility for this reaction.

PART III. FLASH THERMOLYSIS

A. Introduction

It has been suggested[84] that a number of photochemical reactions proceed from a higher vibrational level of the ground state. That is, absorption of a quantum of light by the molecule induces excitation to a higher electronic level. By isoenergetic conversion, the molecule may find itself in the ground state - necessarily at a higher vibrational level. It is from this higher vibrational level that the reaction is presumed to take place. For instance, Srinivasan[85] has suggested that the gas phase photolysis of cyclohexanone takes place in this manner, and not directly from the first excited singlet.

If these proposals be correct, then it should be possible to simulate the photochemical reaction by populating the higher vibrational levels by direct thermal excitation from the ground state.

Reactions which proceed at high vibrational levels are not necessarily the same as those which proceed at lower levels, differing merely in the relative rates. For example, the pyrolysis of propionaldehyde at low temperatures gave exclusively ethyl radicals[86], but at

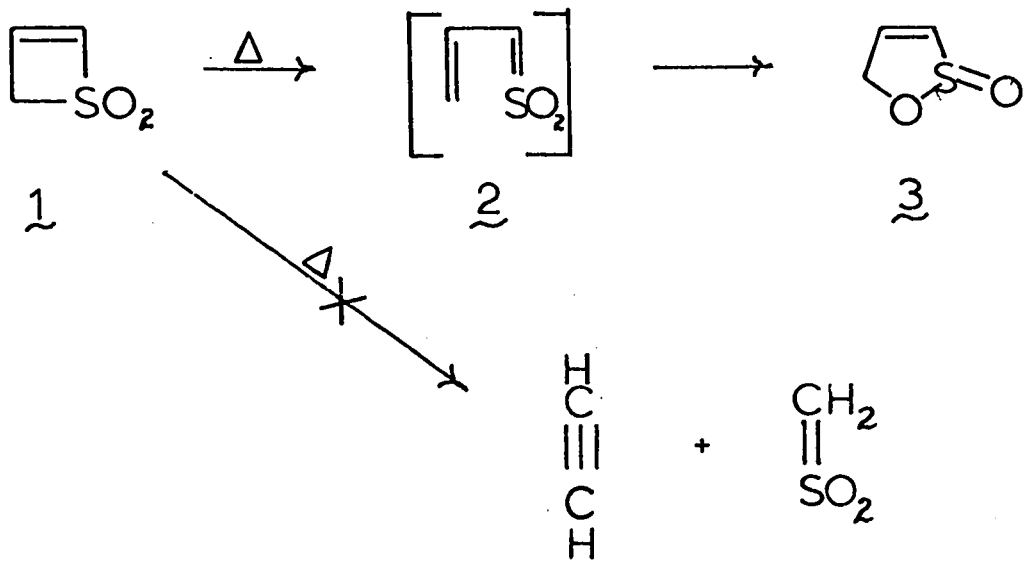
higher temperatures, both ethyl and methyl radicals were produced in equal amounts, the methyl radicals not being produced from the ethyl radicals but arising from a new reaction which became important at the higher temperature.

In general then, at higher temperatures the possibility exists that a second pathway might cross the normally observed one and subsequently new products would be found.

A study of these two problems could be made by high temperature flow pyrolysis, which we have called Flash Thermolysis. Such a study would, of necessity, have to be carried out on a simple system about which the background is well known, in order to interpret the results successfully.

As is discussed in the introduction to Part II, considerable evidence has been amassed which indicates the intermediacy of sulfenes in certain reactions. Part of this evidence is the formation of four-membered cyclic sulfones as the result of reaction of enamines, acetals, and aminals with sulfonyl chloride/triethylamine mixtures.

Since it has been proposed that the formation of these thietane 1,1-dioxides proceeds via a sulfene intermediate, it was felt that a sulfene might be regenerated from them under the appropriate conditions. In particular, the thiete 1,1-dioxide 1 seemed likely to undergo such a reaction. An electrocyclic opening of 1 would give the vinyl sulfene 2, or alternatively a reverse cycloaddition reaction would give sulfene plus acetylene. The former possibility was given support by King and



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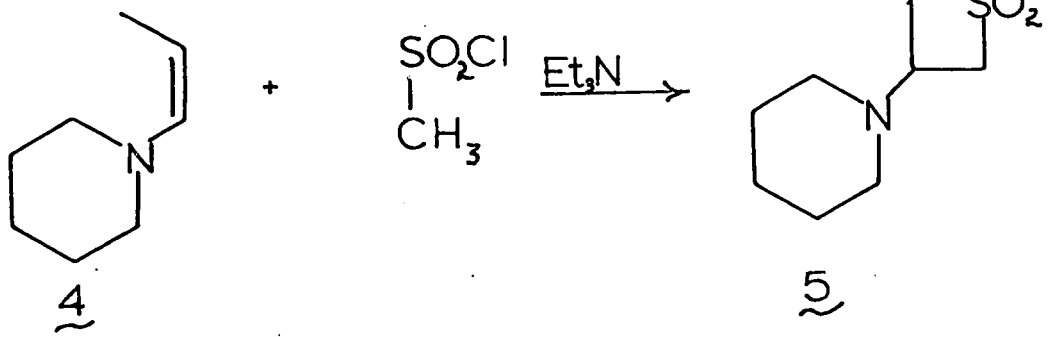

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coworkers[87] who found that pyrolysis of thiete 1,1-dioxide 1 at moderately high temperatures gave the ring expanded product 1,2$^{\Delta 3}$-oxathiole S-oxide 3. The formation of this compound could conceivably have arisen by an "abnormal" attack of the initially formed vinyl sulfene 2 upon itself. In order to further substantiate and extend this hypothesis, an attempt was made to prepare several thietane 1,1-dioxides and their derivatives.

The first preparative reaction for thietane 1,1-dioxides was reported in 1960 by Opitz[53], who found that N-(1-propenyl)-piperidine 4 reacted with mesyl chloride/triethylamine in cold ether to give 2-methyl-3-piperidino thietane 1,1-dioxide 5. This reaction has since been extended to a large number of sulfonyl chlorides reacting with enamines of ketones and aldehydes using a wide variety of solvents and temperatures.

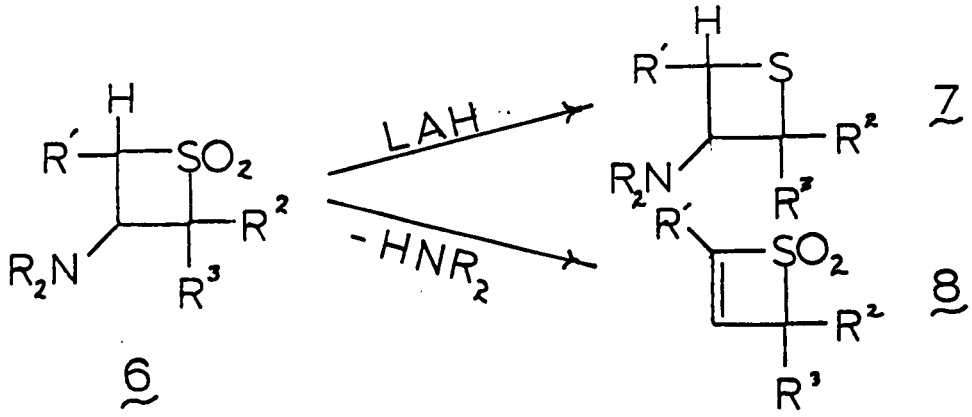
The use of secondary sulfonyl chlorides in the formation of cyclic sulfones, however, is limited. The reaction has been found to proceed only in acetonitrile at -40°[53]. Also, as the amount of substitution of both the sulfonyl chloride and the enamine is increased, acyclic products begin to appear[88], the yield of which increased in a direct relationship with the degree of substitution. In general, cycloaddition is favoured by high basicity of the enamine and by mild reaction conditions, while the open-chain sulfones are formed from the reaction of sulfene or primary sulfene with enamines of ketones, and secondary sulfenes with enamines of alde-

hydes or ketones.[89]

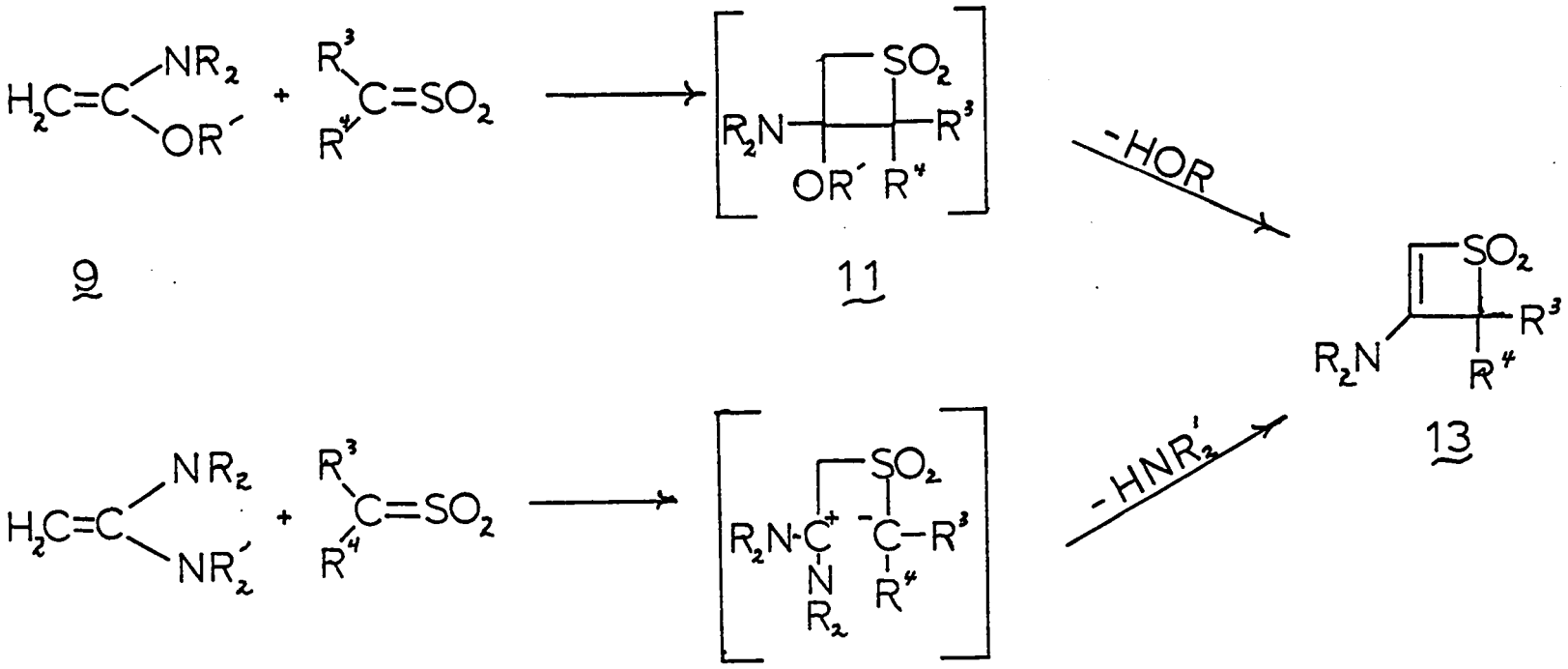
It is not known whether the cycloaddition step is a concerted multicentered reaction (reaction path a), or a two step addition (reaction path b). The latter hypothesis is preferred, however, since it provides a better explanation of why strongly electron rich olefins are required, and why large amounts of acyclic sulfones are produced from sterically hindered reactants. Although route b should be stereospecific, assuming a sufficiently short lifetime of the zwitterion intermediate, the fact that only one product was obtained[54] from the trans-N-(1-propenyl) morpholine with sulfene reaction, whereas two were found from the cis-isomer, should be viewed with caution since cis enamines are known[89] to be quite labile with respect to cis-trans isomerization.

The products obtained from the reaction of enamines with sulfenes are 3-amino thietane 1,1-dioxides 6. They are generally weakly basic and can be reduced[90] to the corresponding 3-amino thietane 7 by reaction with lithium aluminium hydride. On the other hand, the amino group may be eliminated via the quaternary salt[91], or through pyrolysis of the amine oxide[92] to give the corresponding thiete 1,1-dioxide 8.

The cycloaddition reaction of sulfonyl chloride/triethylamine has been extended[93] to include O,N and N,N acetals 9 and 10 (called aminals). In both cases, the initially formed cyclic sulfones 11 and 12 spontaneously lose a molecule of alcohol or amine respectively



6 7 8



9 10 11 12 13

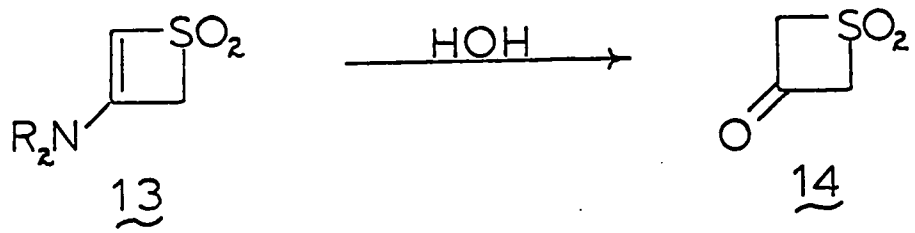
to give the corresponding 3-amino thiete 1,1-dioxide 13 as the isolated product.

The use of N,N aminals is quite often accompanied by the formation of acyclic sulfones(94). This is not surprising, however, in view of the degree of stabilization of the positive charge of the intermediate zwitterion by the highly electronegative nitrogen. This latter reaction, i.e. the formation of acyclic sulfones, is further facilitated by the use of R^4 groups such as phenyl, which can stabilize the negative charge of the zwitterion as well, thus enhancing its stability.

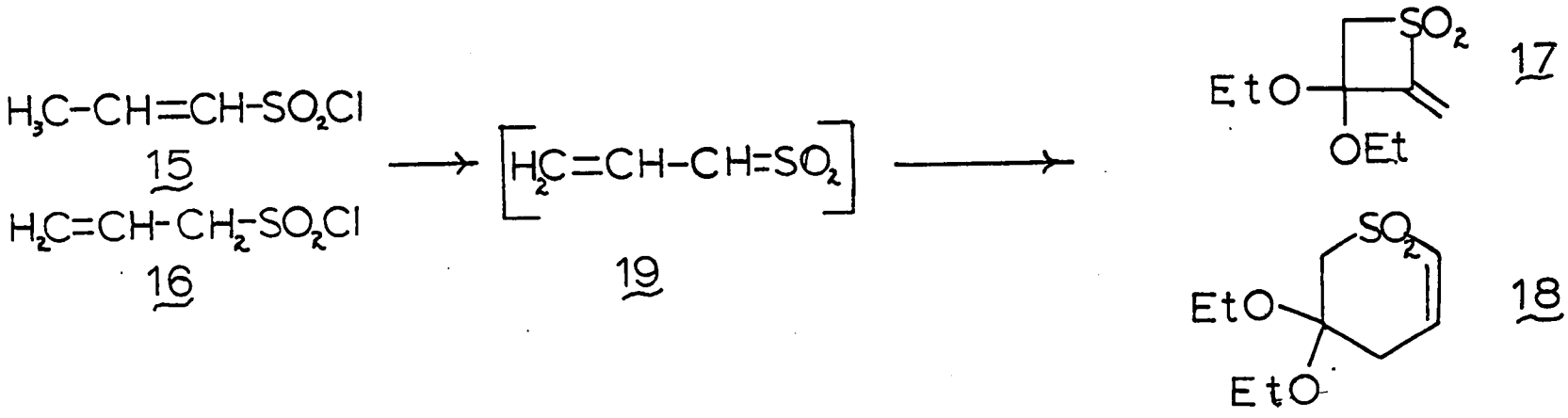
The enamine sulfones resulting from these cyclization reactions are readily hydrolysed to the corresponding 3-thietanone 1,1-dioxides 14. Care must be taken, however, since the resultant ketones are readily hydrolysed further with ring opening(93).

The more reactive ketene acetals have also been found to form cyclic sulfones by reaction with sulfenes. A large number of these 3,3-dialkyoxythietane 1,1-dioxides have been prepared and characterized by Truce and coworkers(95,96). Although the structure of the intermediate is not known with certainty, reaction of both 1-propenyl sulfonyl chloride 15 and 2-propenyl sulfonyl chloride 16 with diethoxy ketene acetal to give the same 1,2 and 1,4 cyclic sulfones 17 and 18, would indicate a vinyl sulfene intermediate 19.

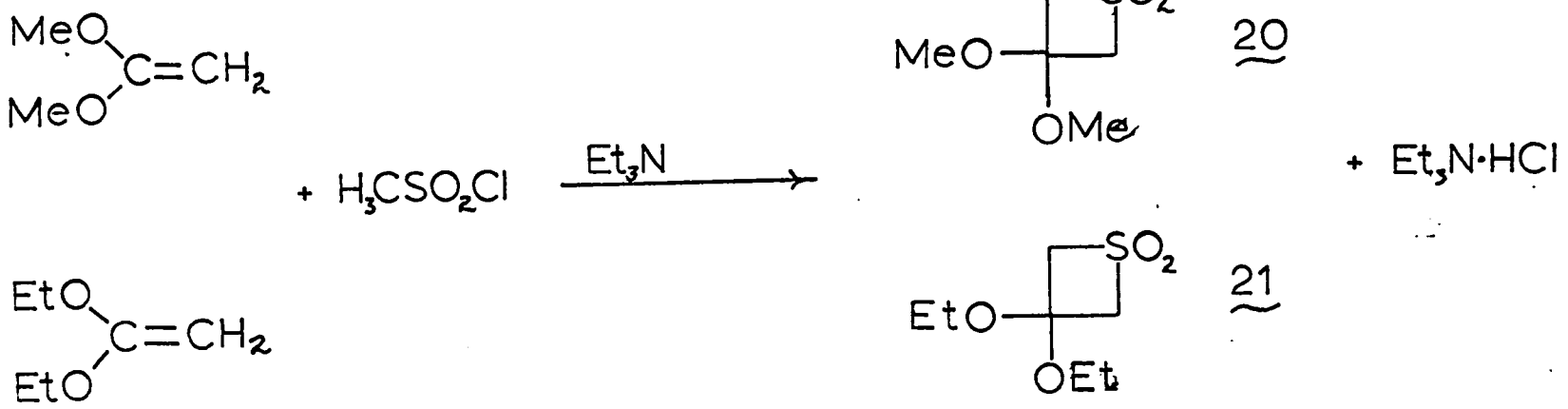
The 3,3-dialk oxythietane 1,1-dioxides are easily hydrolysed in most cases(96) to the corresponding 3-



13 14



15 16 19 17 18



20 21

thietanone 1,1-dioxides by reaction with concentrated hydrochloric acid. Further treatment with diborane followed by hydrolysis gives the 3-thietanol 1,1-dioxides[96].

A large variety of olefinic compounds have been unsuccessfully used in attempts to trap sulfenes as the cyclic sulfones. These include cyclohexene[97], 1,1-dichloroethylene, diphenylketene[98], vinyl ethyl ether,[98] and many others. In general, their inability to react is probably a consequence of their insufficient nucleophilicity.

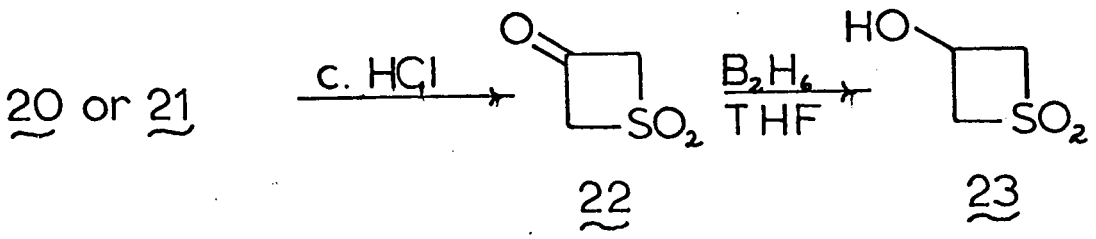
On the basis of these and related sulfene reactions, a number of thietane 1,1-dioxides were prepared for pyrolysis as described in the next section.

B. Preparation of the Thietane 1,1-Dioxides

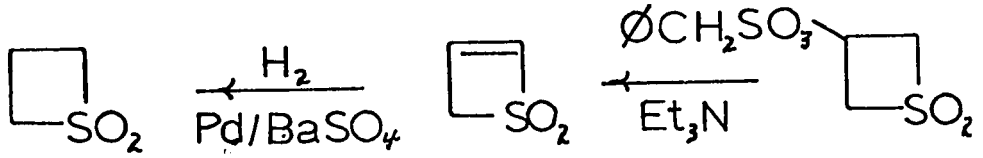
The preparation of thietane 1,1-dioxide, 3-thietanone 1,1-dioxide, 3-thietanol 1,1-dioxide, and thiete 1,1-dioxide are described below. To study the effects, if any, of substituents, the 2-phenyl and 2,2-dimethyl substituted derivatives of the above compounds were also synthesised. The preparation of the 2,2-diphenyl derivatives was unsuccessfully attempted, and the results discussed.

The preparation of 3-thietanone 1,1-dioxide and 3-thietanol 1,1-dioxide have been described by Truce[95]. Reaction of diethoxy or dimethoxy ketene acetal with methanesulfonyl chloride/triethylamine in ether gave 3,3-diethoxy and 3,3-dimethoxy thietane 1,1-dioxide 20 and 21 respectively. Hydrolysis[96] of either of these compounds in concentrated hydrochloric acid at room temperature gave 3-thietanone 1,1-dioxide 22. The ketone 22 was reduced with diborane in tetrahydrofuran to yield 3-thietanol 1,1-dioxide 23.

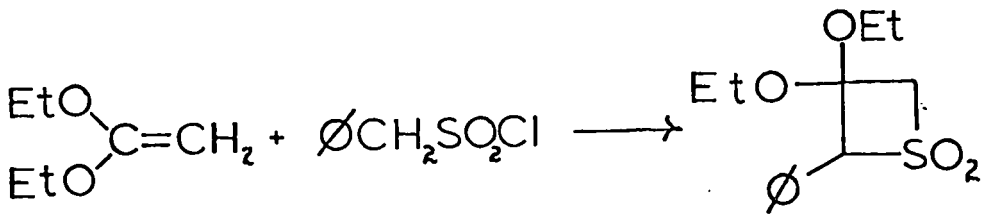
Thiete 1,1-dioxide could then be prepared from the alcohol using the method devised by Smith[99]. The 3-thietanol 1,1-dioxide was treated with an equimolar amount of phenyl sulfene, generated *in situ* from α-toluenesulfonyl chloride and triethylamine in ether at 0°. The resultant tosylate 24 on treatment with triethylamine at 80° in benzene detosylated to give the desired thiete 1,1-dioxide 25. This compound was identical with that reported by Dittmer[100], who synthesised it by a



22 23



26 25 24



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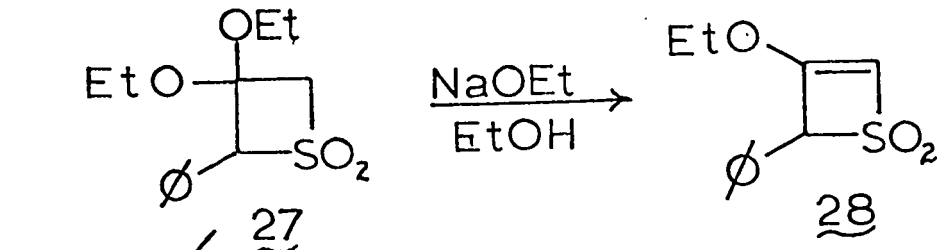
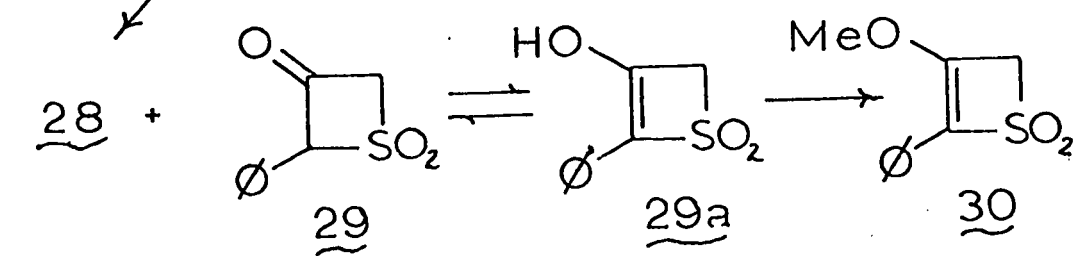


27 28

c.HCl



29 29a 30

more tedious route. Hydrogenation of the thiete 1,1-dioxide in 95% ethanol using 5% palladium on barium sulfate catalyst gave thietane 1,1-dioxide 26 as expected, identical with the known trimethylene sulfone[101].

Using the same general method as described above, the reaction of α-toluenesulfonyl chloride/triethylamine with diethoxyketene acetal in ether gave the 3,3-diethoxy thietane 1,1-dioxide 27 reported by Truce[95]. He has also reported[96] that on treatment with sodium ethoxide in ethanol, 27 loses a molecule of ethanol to give 3-ethoxy-2-phenyl thiete 1,1-dioxide 28. Acid hydrolysis with concentrated hydrochloric acid, however, is reported to give only a polymeric substance and recovered starting material. Contrary to this report, compound 27 was found to hydrolyse in concentrated hydrochloric acid at room temperature to give a mixture of 3-ethoxy-2-phenyl thiete 1,1-dioxide 28 and 2-phenyl 3-thietanone 1,1-dioxide 29. These two compounds were readily separable, since the ketone was only sparingly soluble in chloroform, whereas the enol ether was readily soluble.

The infrared absorption of the 2-phenyl 3-thietanone 1,1-dioxide showed strong absorption at 1680 cm^{-1} attributable to a double bond and at 1265 and 1105 cm^{-1} due to a cyclic sulfone; the NMR in hexadeuteroacetone consisted of a two hydrogen singlet at 4.55 ppm of a methylene next to sulfur, and a five hydrogen multiplet at 7.92 ppm due to a phenyl ring; and the ultraviolet absorption in ethanol had a maximum at 265 nm (ε 13,200). On the basis

of this data the structure of the 2-phenyl 3-thietanone 1,1-dioxide was reassigned 3-hydroxy-2-phenyl 2-thiete 1,1-dioxide 29a. This assignment was substantiated by the observation that 29a reacted immediately with diazomethane to give the enol ether 30, which exhibited infrared absorption at 1662 cm^{-1} due to the double bond and 1307 and 1117 cm^{-1} due to the cyclic sulfone. The NMR consisted of a three hydrogen singlet at 3.90 ppm due to the methoxy protons, a two hydrogen singlet due to the methylene next to sulfur, and a five hydrogen multiplet at 7.39 ppm due to the phenyl ring; and the ultraviolet absorption had a maximum at 264 nm (ϵ 14,500).

This complete existence of the ketone as an enol at room temperature is without precedent. Other four ring analogues such as 2-phenyl cyclobutanone[102] and 2,2-dimethyl-3-morpholine-4-phenyl cyclobutanone[103] show no noticable enolization, although 2,2-dimethyl 1,3-butadione[104] does exist as the enol.

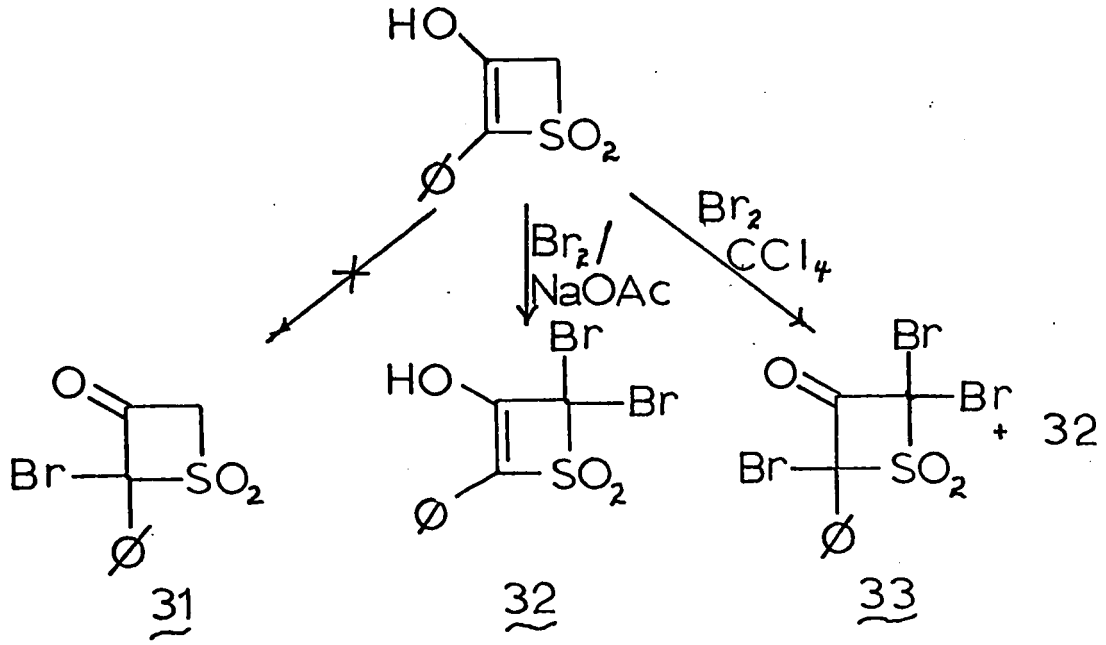
Attempted reduction of the 2-phenyl 3-thietanone 1,1-dioxide 29a with diborane as described above gave only a chloroform insoluble mixture which is presumably an alkyl borane complex[105]. The reduction of double bonds with diborane is a well documented phenomenon resulting in the formation of alkyl boranes.[105] These complexes in most cases can be decomposed to the corresponding saturated analogue by refluxing organic acids. Although the above mixture did decompose in refluxing acetic acid, none of the desired 2-phenyl 3-thietanol

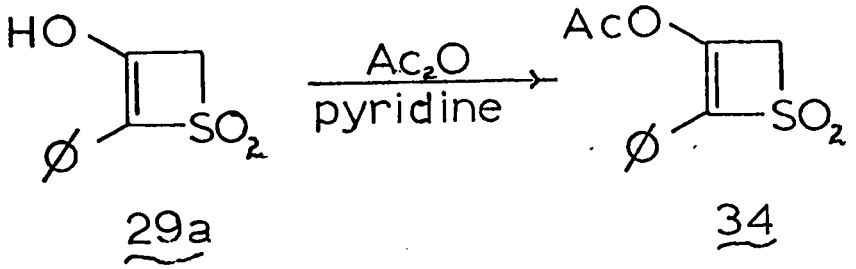
1,1-dioxide was observed. Milder treatment with organic acids, mineral acids, or base had no effect.

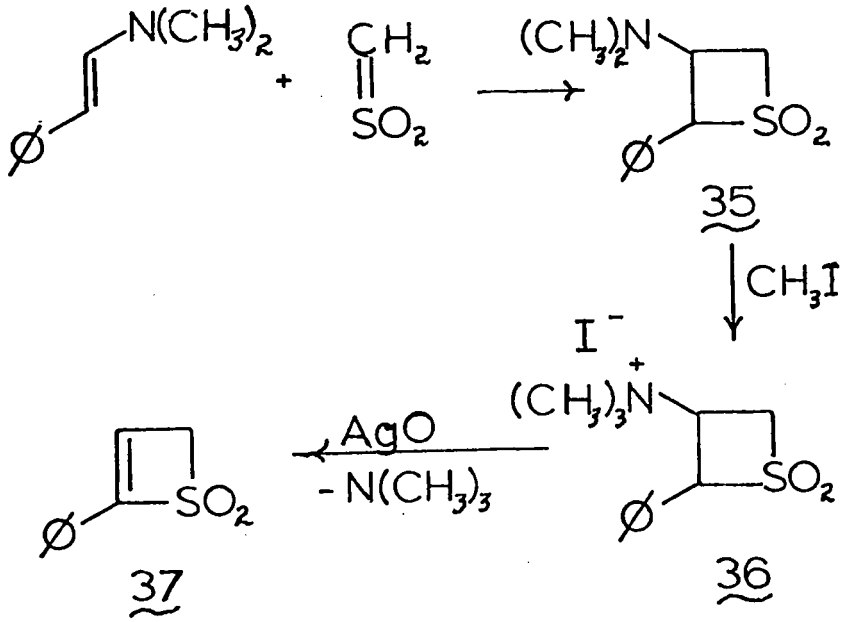
To prevent enolization and thus allow reduction of the ketone to the alcohol, 29a was treated with bromine in an attempt to prepare the monobromo derivative . Addition of 29a to bromine in carbon tetrachloride buffered with sodium acetate, however, gave none of the desired 2-bromo-2-phenyl 3-thietanone 1,1-dioxide 31, but rather a compound which analysed for $C_9H_6Br_2O_3S$, and showed infrared absorption at 3500 cm^{-1} due to a hydroxyl, and 1670 cm^{-1} due to a double bond. The NMR consisted of a five hydrogen multiplet at 7.50 ppm due to a phenyl group and a one proton peak at 8.50 ppm which disappeared on the addition of deuterium oxide. On the basis of this evidence, this compound was given the structure 4,4-dibromo-3-hydroxy-2-phenyl 2-thiete 1,1-dioxide 32.

Only when 29a was treated with bromine in carbon tetrachloride for a prolonged period was a four-membered ring ketone isolated. The structure of this compound has been assigned as a 2,4,4-tribromo-2-phenyl 3-thietanone 1,1-dioxide 33 on the basis of its infrared absorptions at 1800 and 1790 cm^{-1} attributable to a four-membered ring ketone, and its NMR which consisted of a singlet at 7.45 ppm due to the phenyl protons.

This anomalous behaviour of 29a would indicate that the enol is of lower energy (more stable), although the reason for this is not obvious. Thus the first two additions of bromine were immediately followed by transfer


HO
SO2
Ø
Br2/
NaOAc
Br2
CCl4
Br
O
Br
+ 32
31
32
33


HO
Ac2O
pyridine
AcO
SO2
Ø
29a
34


N(CH3)2
CH2
SO2
(CH3)2N
35
CH3I
I-
(CH3)3N+
AgO
- N(CH3)3
37
36

across the ring to carbon-4. Only after the addition of a third bromine, which occurred only after prolonged treatment, was the 2-position blocked, thus forcing the molecule to remain ketonized. No attempt to reduce 33 was made due to the difficulties which might be encountered in attempting to completely remove the three residual bromine atoms.

Several attempts were made to hydrogenate the enol 29a using a wide variety of solvents ranging from ethanol to acetic acid, with both palladium and platinum catalysts at both atmospheric and higher pressures. All attempts, as shown in Table IVof the experimental were unsuccessful, with nothing but starting material being recovered in all cases. No apparent explanation for this is obvious, other than steric hindrance by the phenyl group preventing approach by the catalyst.

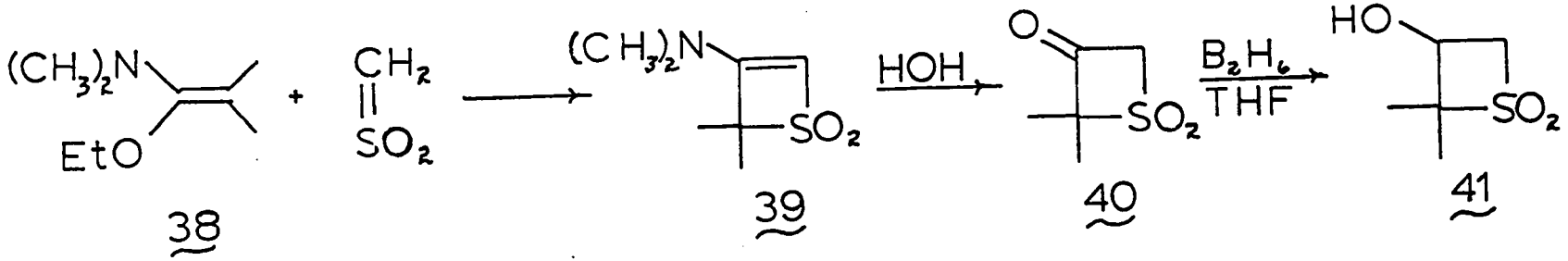
The enol acetate 34 of 2-phenyl 3-thietanone 1,1-dioxide was prepared by reaction with excess pyridine in acetic acid. The infrared absorption showed peaks at 1795 and 1665 cm^{-1} due to the enol acetate and at 1315 and 1112 cm^{-1} due to the cyclic sulfone; the NMR consisted of a three hydrogen singlet at 2.38 ppm attributable to the acetate protons, a two hydrogen singlet at 4.95 ppm due to the methylene next to sulfur, and a five hydrogen multiplet due to the phenyl group. Attempted hydrogenation of this material in either ethyl acetate or acetic acid over platinum oxide was also unsuccessful.

Using a modification of a procedure reported by Wells

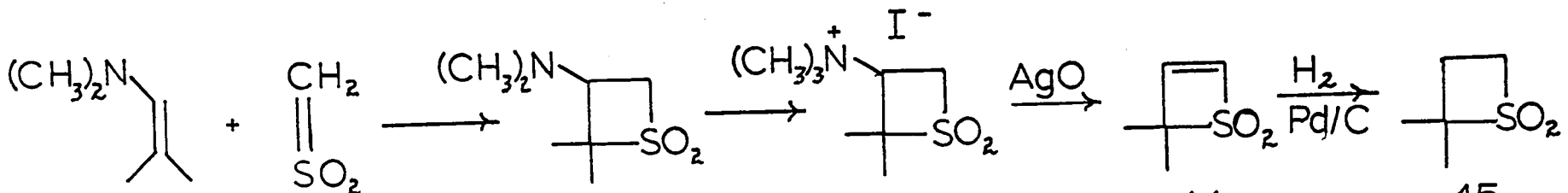
and Abbott[90], thiete 1,1-dioxide was prepared. The reaction of 2-phenyl-N,N-dimethylethyleneamine in ether with methanesulfonyl chloride/triethylamine gave 3-(N, N-dimethyl)amino-2-phenyl thietane 1,1-dioxide 35. Treatment of this amine with excess methyl iodide in methanol at room temperature gave the trimethylamine salt 36, which lost trimethylamine when reacted with silver oxide in water. The resulting 2-phenyl 2-thiete 1,1-dioxide 37 was identical in infrared and NMR absorption with that prepared by Wells and Abbott using the amine oxide pyrolysis method.

The required 2,2-dimethyl derivatives were prepared from 2,2-dimethyl 3-thietanone 1,1-dioxide which was synthesised as described by Martin.[105a] The reaction of 2,2-dimethyl-1-(N,N-dimethyl)amino-1-ethoxyethylene 38 with methanesulfonyl chloride/triethylamine gave 3-(N,N-dimethyl)amino-2,2-dimethyl thiete 1,1-dioxide 39.

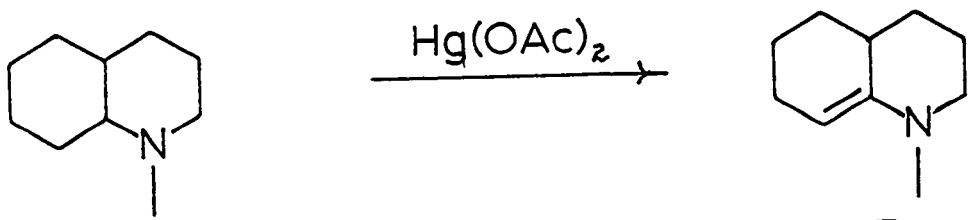
Hydrolysis proceeded smoothly in water using a cation exchange resin (Dowex 50-X2) as catalyst to give the desired 2,2-dimethyl 3-thietanone 1,1-dioxide 40. Reduction of this ketone with diborane, as described above, gave 2,2-dimethyl 3-thietanol 1,1-dioxide 41, m.p. 107-108°, whose infrared showed absorption at 3600 cm^{-1} due to the alcohol and at 1310 and 1195 cm^{-1} due to the cyclic sulfone. The NMR was also in agreement with the assigned structure having two three hydrogen singlets at 1.52 and 1.56 ppm attributable to the two methyl groups,



38 39 40 41



42 43 44 45



46 47

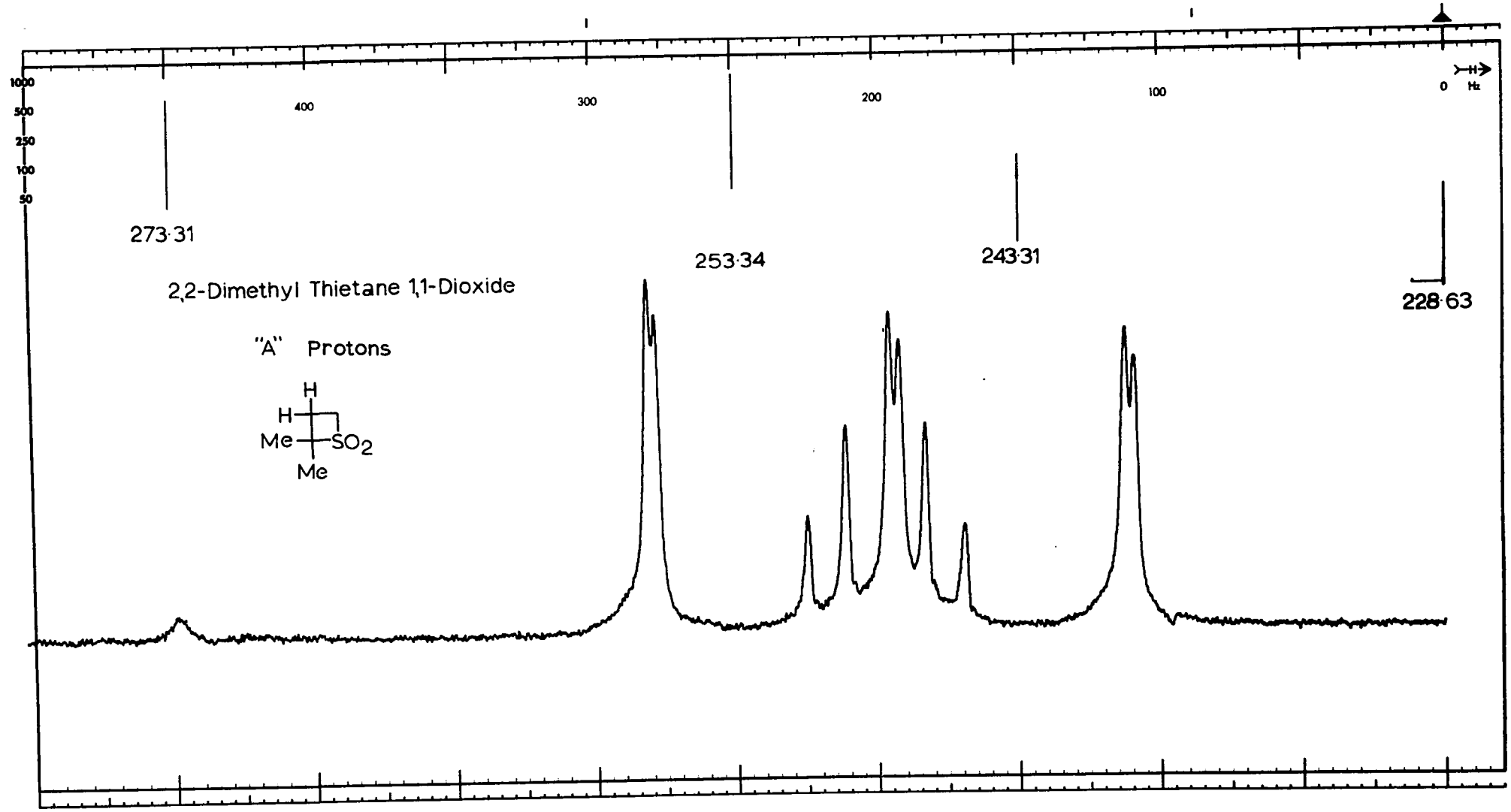

1000
500
250
100
50
400
300
200
100
0 Hz
273·31
253·34
243·31
228·63
2,2-Dimethyl Thietane 1,1-Dioxide
"A" Protons
H
H
Me
SO2
Me

Figure 3

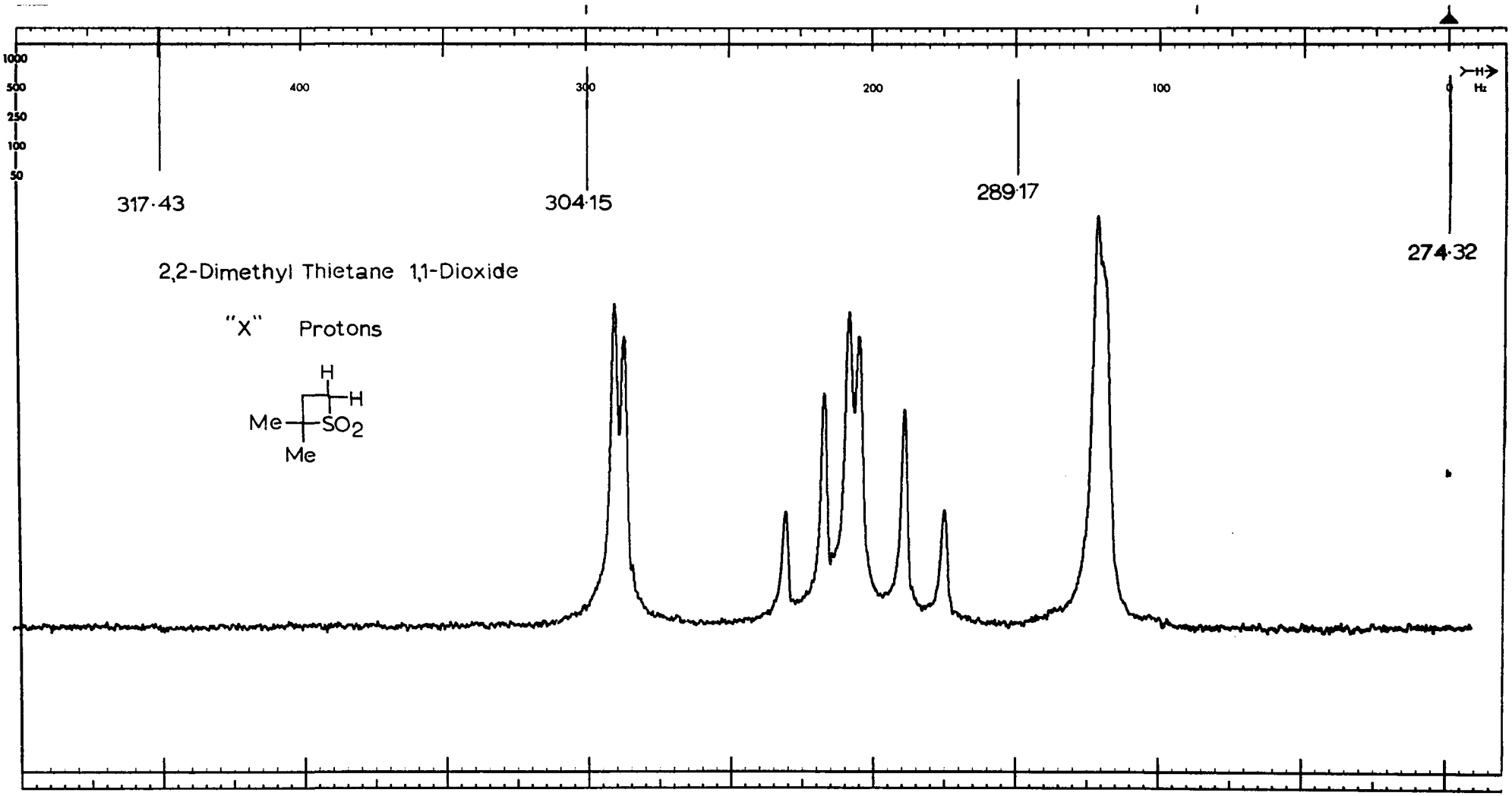

1000
500
250
100
50
400
300
200
100
0
Hz
317·43
304·15
289·17
274·32
2,2-Dimethyl Thietane 1,1-Dioxide
"X" Protons
H
H
Me
SO2
Me

Figure 4

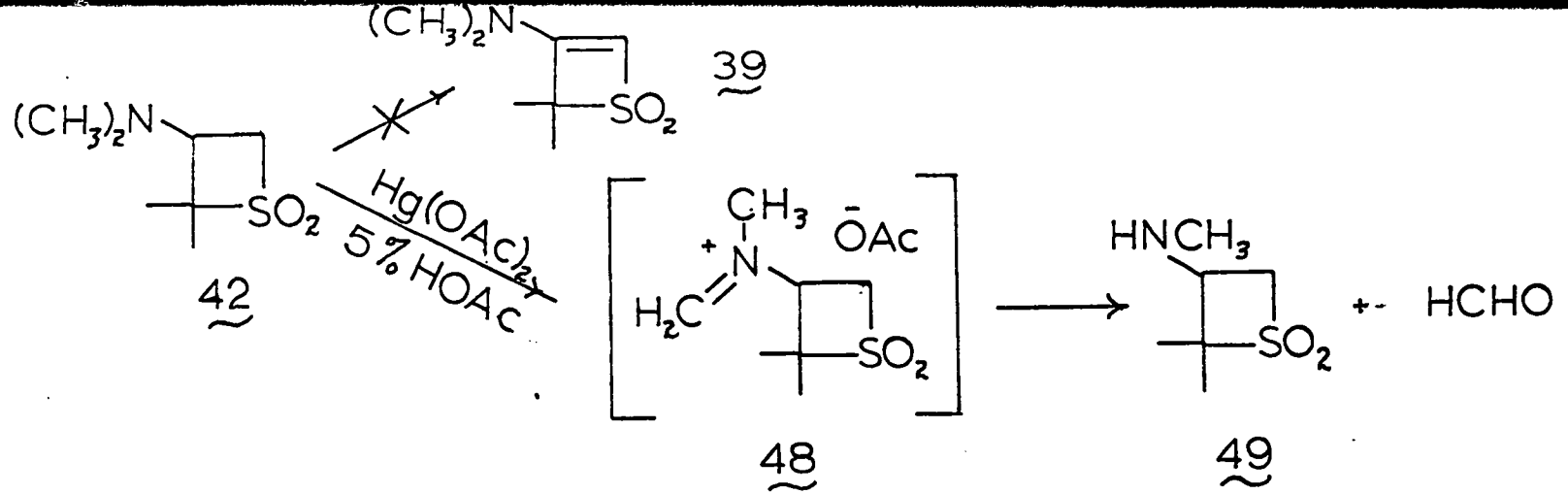
a one hydrogen peak at 2.96 ppm, which disappeared on addition of deuterium oxide attributable to the hydroxyl proton, and a broad multiplet at 3.7 to 4.6 ppm which integrated for three hydrogens, attributable to the methylene and methine protons.

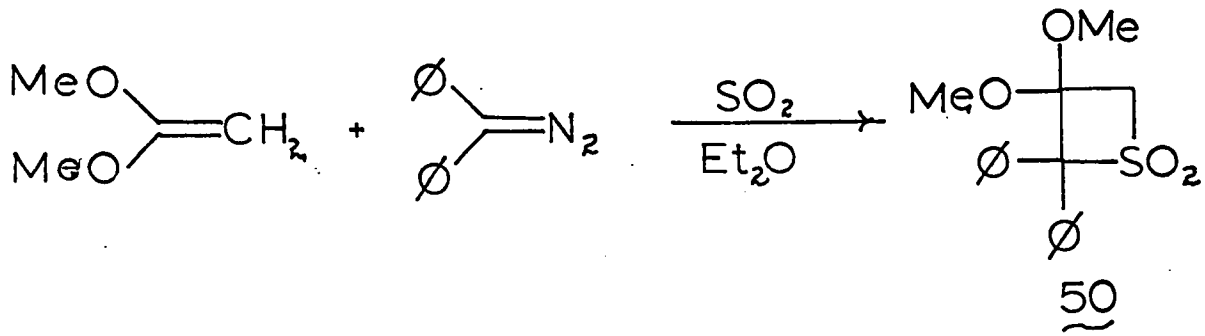
Using the method of Truce[91], 2,2-dimethyl 3-thiete 1,1-dioxide was prepared from 1-(N,N-dimethyl)amino-2-methyl-propene and methanesulfonyl chloride/triethylamine. The 3-(N,N-dimethyl)amino-2,2-dimethyl thietane 1,1-dioxide 42 thus obtained, was treated with excess methyl iodide and the iodide salt 43 which formed, deaminated with silver oxide to give the 2,2-dimethyl 3-thiete 1,1-dioxide 44. Hydrogenation of 44 in 95% ethanol using 5% palladium on carbon as catalyst gave 2,2-dimethyl thietane 1,1-dioxide 45, m.p. 61-62°. The infrared was consistent with this structure having absorption at 1323 and 1128 cm^{-1} due to the cyclic sulfone. The NMR consisted of a six hydrogen singlet at 1.57 ppm due to methyl protons, and an A_2X_2 pattern due to the methylenes at $\delta_A = 4.14$ and $\delta_X = 6.57$ with coupling constants of $J_{AA'} = -18.59$ cps, $J_{XX'} = -17.70$ cps, $J_{AX} = 6.48$ cps, $J_{AX'} = 10.43$ cps, $J_{A'X} = 10.43$ cps, and $J_{A'X'} = 6.48$ cps. The spectrum was obtained using an HA 100 spectrometer and calculated with a LAOCOON III computer program.[106]

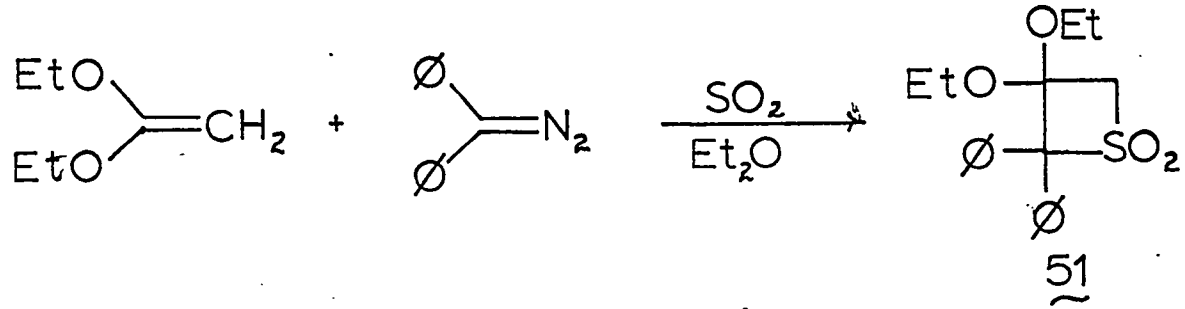
Since the preparation of the O,N acetal 38 used in the preparation of the 2,2-dimethyl 3-thietanone 1,1-dioxide 40 was long and gave only low yields, the possibility of preparing 3-(N,N-dimethyl)amino 3-thiete

1,1-dioxide 39 by means of mercuric acetate oxidation of the saturated analogue 42 was investigated. Leonard[107] has employed mercuric acetate extensively in the preparation of enamines from cyclic tertiary amines, i.e. 46 to 47. Reaction of 42 with mercuric acetate in 5% acetic acid, however, gave none of the desired enamine 39, but rather a secondary amine 49. The structure was based on the infrared absorption at 3340 cm^{-1} (NH), 1310 and 1105 cm^{-1} attributable to a cyclic sulfone and its NMR which showed two three hydrogen singlets at 1.48 and 1.58 ppm due to the geminal methyls, a three hydrogen singlet at 2.40 ppm due to the amine methyl protons and an ABX pattern at δ_A = 3.89 ppm, δ_B = 3.25 ppm, δ_X = 3.25 ppm, J_{AB} = -13.0 cps, J_{AX} = 6.0 cps and J_{BX} = 8.0 cps due to the methylene and methine protons. It would appear, therefore, that one of the amine methyl groups has been preferentially oxidized rather than the ring methylene as desired. The initially formed imine 48 was then hydrolysed to give the observed secondary amine 49.

One of the earliest discoveries of a preparation of sulfenes was by Staudinger[108], who found that sulfur dioxide treatment of diphenyldiazomethane gave tetraphenylethylene. He suggested that this reaction involved a sulfene intermediate which reacted with a second molecule of starting material to give the observed product on loss of nitrogen. It was considered possible, therefore, that the sulfene so formed might also react


(CH3)2N
SO2
39
(CH3)2N
SO2
42
Hg(OAc)2
5% HOAc
CH3
N
H2C
OAc
SO2
48
HNCH3
SO2
+- HCHO
49


MeO
MeO
CH2
+
N2
SO2
Et2O
OMe
MeO
SO2
50


EtO
EtO
CH2
+
N2
SO2
Et2O
OEt
EtO
SO2
51

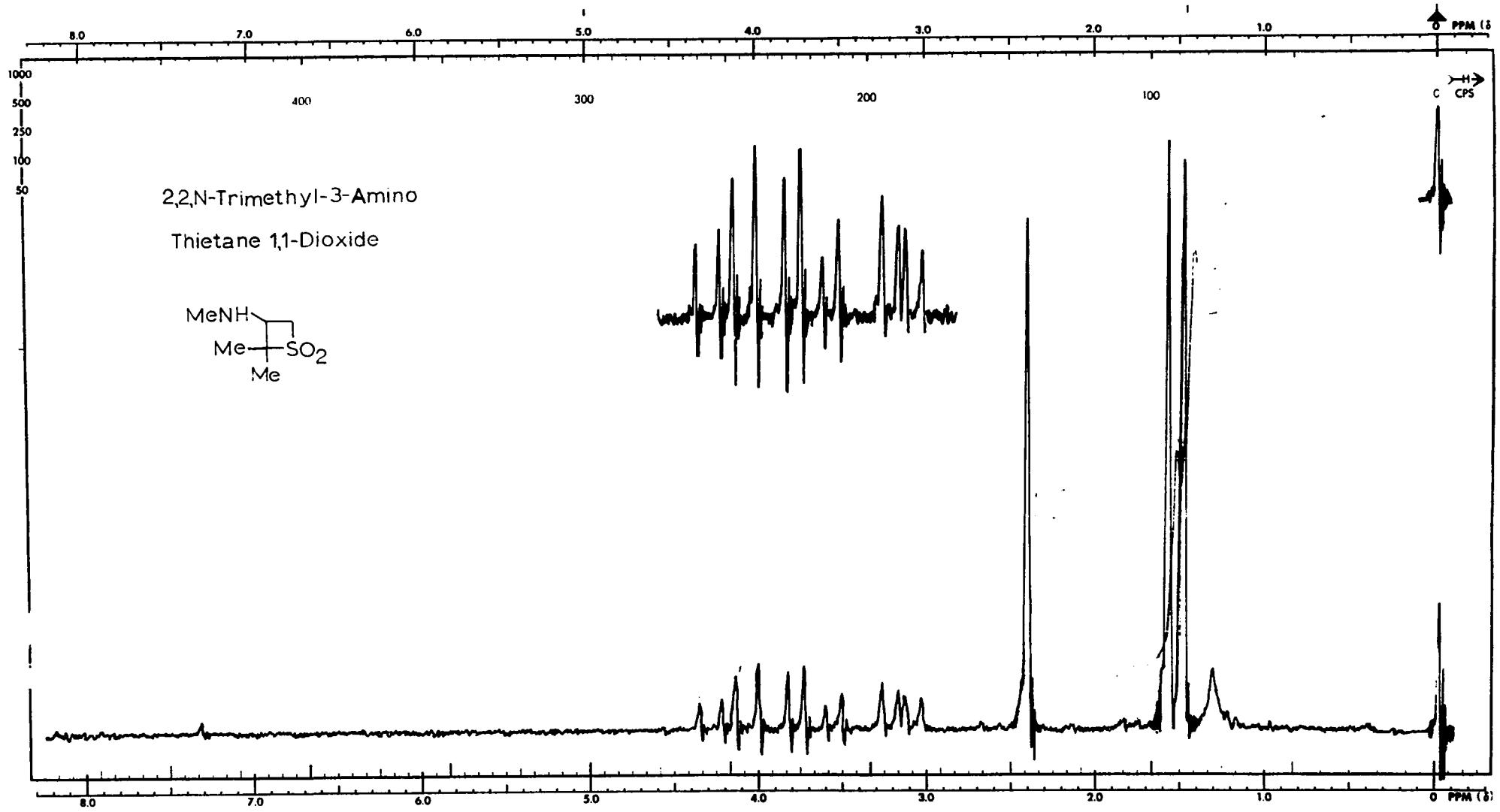

2,2,N-Trimethyl-3-Amino
Thietane 1,1-Dioxide
MeNH
Me
SO2
Me
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0 PPM (δ)
1000
500
250
100
50
400
300
200
100
0
CPS

Figure 5

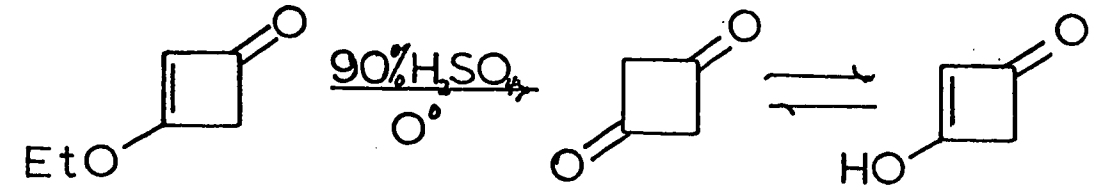
with a nucleophilic olefin, such as a ketene acetal, to give a 2,2-diphenyl-3,3-dialkoxy thietane 1,1-dioxide. Addition of sulfur dioxide to an ethereal solution of diphenyldiazomethane[149] and dimethoxyketene gave a crystalline precipitate of 2,2-diphenyl-3,3-dimethoxy thietane 1,1-dioxide 50, m.p. 155.5-156.0°. The structure was confirmed by its infrared absorption at 1330 and 1110 cm^{-1} due to a cyclic sulfone and by its NMR which showed a six hydrogen singlet at 3.17 ppm attributable to the methoxy protons, a two hydrogen singlet at 4.41 ppm due to the methylene next to sulfur, and a ten hydrogen singlet at 7.35 ppm due to the two phenyl groups.

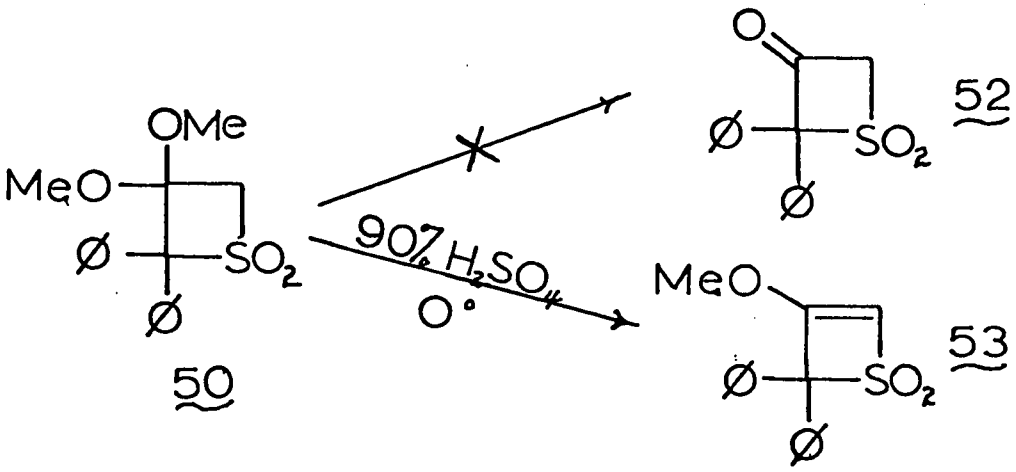
When diethoxyketene was used, the isolated product was 3,3-diethoxy-2,2-diphenyl thietane 1,1 dioxide 51. Its infrared showed absorption due to the cyclic sulfone at 1335 and 1095 cm^{-1}, and the NMR was composed of a six hydrogen triplet at 0.95 ppm (J = 7.0 cps), a four hydrogen multiplet at 3.35 ppm attributed to the two ethoxy groups, a two hydrogen singlet at 4.29 ppm due to the methylene group, and a ten hydrogen singlet at 7.30 ppm due to the two phenyl groups. The multiplicity of the absorption due to the two methylene protons of the ethoxy groups, which was more complicated than two overlapping quartets, is probably an indication of restricted rotation due to steric interference with each other and the phenyl groups, resulting in non-equal environments for the methylene protons. A similar type

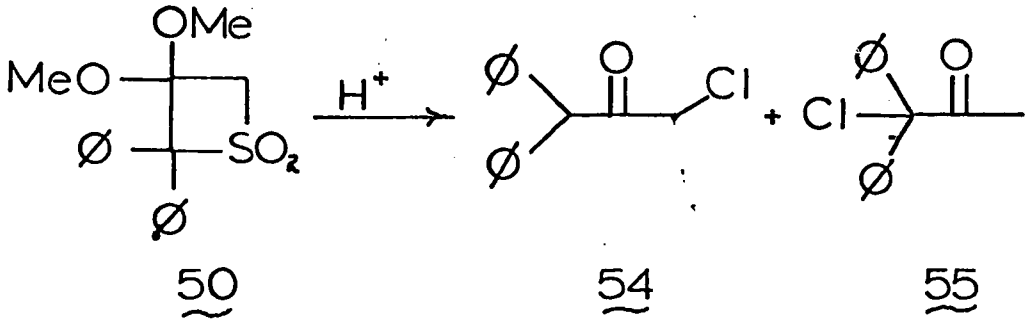
of spectrum is reported by Truce[94].

Wasserman and Dehmlov[109] found that hydrolysis of the monoenol ether of cyclobutadione could only be accomplished successfully in cold 90% sulfuric acid. Any other reagent which was tried resulted in the isolated of ring-opened products only. When the dimethoxy ketene acetal 50 was treated with cold 90% sulfuric acid, however, none of the expected 2,2-diphenyl 3-thietanone 1,1-dioxide 52 was isolated. Instead, 2,2-diphenyl-3-methoxy 3-thiete 1,1-dioxide 53 was formed. The structure of 53 was based on its olefinic infrared absorption at 1615 cm^{-1}, its NMR which had a three hydrogen singlet at 3.81 ppm due to the methoxy protons, a one hydrogen singlet at 5.81 ppm attributed to the olefinic proton, and a ten hydrogen multiplet at 7.41 ppm due to the two phenyl groups, and its ultraviolet spectrum which showed end absorption with an extinction of 10,000 at 205 nm.

Attempted hydrolysis of the dimethyl ketal 50 in a manner analogous to that used for the other ketals, that is in 50% hydrochloric acid in dioxane at 70° for 15 hours, again gave none of the desired ketone 52. Rather a mixture of 1- and 3-chloro-1,1-diphenyl-2-propanones 54 and 55 was isolated. The ketones were separated by tlc and identified by comparison of literature values for their m.p., infrared, and NMR spectra[110,111]. The use of concentrated hydrochloric acid at room temperature gave similar results, although the hydrolysis was not complete, with the NMR of the total product mixture show-


EtO
90% H2SO4
0°
HO


OMe
MeO
Ø
SO2
Ø
50
90% H2SO4
0°
O
Ø
SO2
Ø
52
MeO
Ø
SO2
Ø
53


OMe
MeO
Ø
SO2
Ø
50
H+
Ø
O
Cl
Ø
54
+
Cl
Ø
O
Ø
55

ing some starting material as well as the two chloroketones. This was also the case when less severe conditions were employed, i.e. 50% hydrochloric acid in dioxane at 60° for four hours. In this case, as well as starting material and the chloroketones, the NMR showed a quantity of 2,2-diphenyl-3-methoxy 3-thiete 1,1-dioxide 53.

The appearance of 53 was not unexpected since it could well be an intermediate in the hydrolysis of 50 to 52.[112] It would appear, however, that the ketone 52 is extremely labile, and once formed is immediately attacked by chloride ion with ring opening and subsequent loss of sulfur dioxide to give the observed chloroketones. Both the intermediate anions of this reaction would be stabilized, the one by the two phenyl groups, and the other by the carbonyl. The latter, 54, would be in the majority, however, due to the ease of attack of chloride at carbon-4 over the sterically hindered carbon-2.

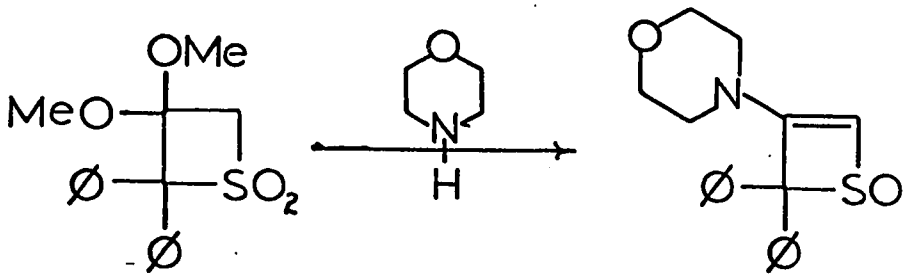
Brannock[113] has shown that under very mild conditions such as stirring with an ion exchange resin in water labile ketones, such as 2,2-dimethyl 3-thietanone 1,1 dioxide, can be formed from the corresponding enamine. Therefore, the morpholine enamine of 2,2-diphenyl 3-thietanone 1,1-dioxide 52 was synthesised[114] from the dimethoxyketal 50 by heating it in morpholine at 95° for 6 hours to give the desired 2,2-diphenyl-3-morpholino 3-thiete 1,1-dioxide 56. The NMR consisted of two four

hydrogen quartets at 3.05 ppm and 3.49 ppm J = 2.5 cps due the morpholine groups, a one hydrogen singlet at 5.34 ppm due the olefinic proton and a ten hydrogen multiplet at 7.50 ppm attributed to the two phenyl products.

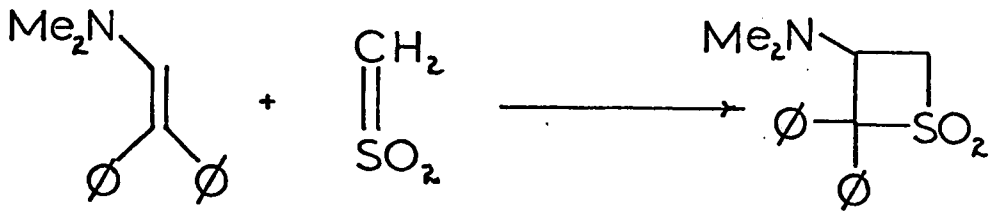
Attempted hydrolysis of this compound in water with a cationic ion exchange resin as catalyst had no effect. Treatment with concentrated hydrochloric acid for 24 hours, however, resulted in complete destruction of the enamine with only morpholine hydrochloride and a material which showed no carbonyl nor sulfone absorption in its infrared, being recovered.

The attempted preparation of 2,2-diphenyl thiete 1,1-dioxide 57, in a manner analogous to that used for the 2-phenyl derivative 37, using 1-(N,N-dimethyl)amino-2,2-diphenylethylene[115] and methanesulfonyl chloride/triethylamine in ether at 0°, was also unsuccessful. The only material recovered from the reaction mixture was unchanged enamine.

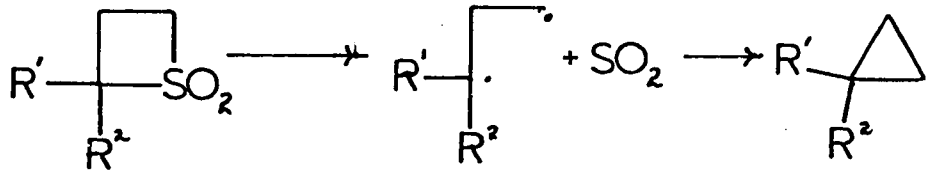
Those compounds successfully prepared therefore were 3-thietanone 1,1-dioxide, 2-thiete 1,1-dioxide, thietane 1,1-dioxide, 3-thietanol 1,1-dioxide, the 2,2-dimethyl derivatives of these, 2-phenyl 3-thietanone 1,1-dioxide, and 2-phenyl 2-thiete 1,1-dioxide.



50 56



57



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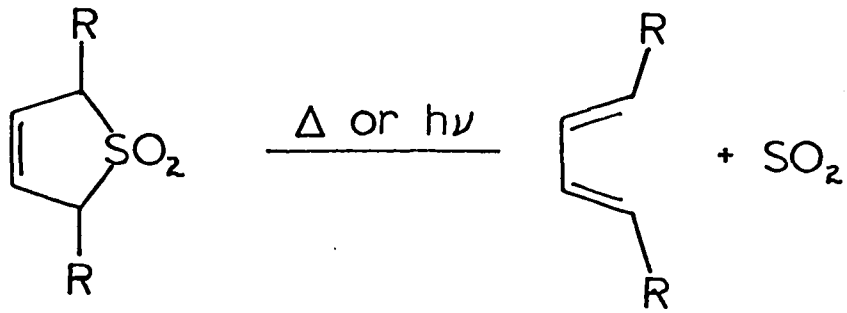


59

C. Pyrolysis

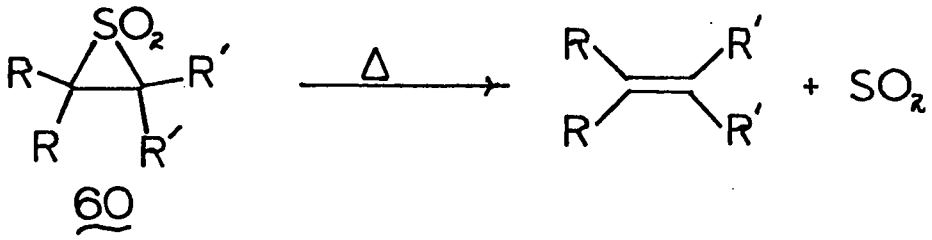
The compounds prepared as described in the previous section were pyrolysed in the flash apparatus at 950° and at approximately 1 micron pressure. These conditions corresponded to a contact time in the hot zone of the reactor of 1 millisecond. All condensable products were trapped immediately after formation by a liquid nitrogen cooled cold finger placed 2.5 centimeters from the end of the hot tube. In certain cases this cold finger was initially covered with methanol to trap any reactive products such as ketene or sulfene. The products were identified and then analysed quantitatively by gas chromatography (vpc). The results and a discussion of the proposed mechanisms follow.

The pyrolysis of thietane 1,1-dioxide 26 gave three product which were identified by infrared, NMR, and vpc retention times as cyclopropane, propylene and sulfur dioxide. Similarly, 2,2-dimethyl thietane 1,1-dioxide 45 was found to give 3-methyl-1-butene, 2-methyl-2-butene, 2-methyl-1-butene, and sulfur dioxide. The initial process would appear, therefore, to be the initial loss of sulfur dioxide to give the diradical 58. Subsequent ring closure to the cyclopropane or hydrogen migration would give the observed products. The formation of cyclopropane and propene from a 1,3 diradical is proposed by Flowers and Frey for the gas phase photolysis of cyclobutanone.[116]

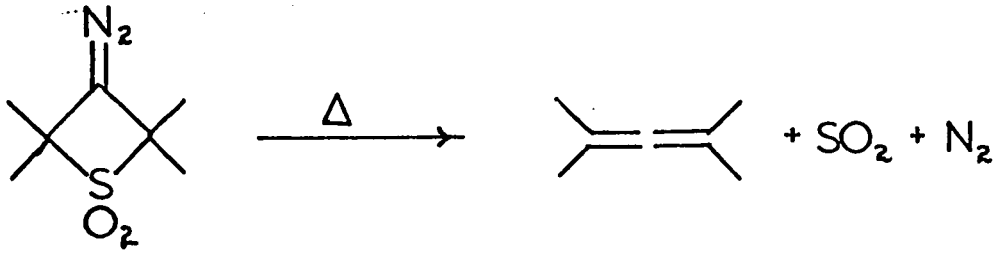
A large number of examples of the thermal and photochemical extrusion of sulfur dioxide are known. Several workers[117] have studied the thermal and photochemical extrusion of sulfur dioxide from sulfolenes 59 which results in the formation of dienes. Although this reaction has been known for some time, only recently has the stereochemical aspect been examined. McGregor and Lemal[118] and also Mock[119] in 1967 examined the thermal reaction of substituted sulfolanes, while Saltiel and Metts[120] studied the photochemical one. In both cases, the results indicated a concerted elimination of the sulfur dioxide with the reaction obeying the symmetry rules of Woodward and Hoffmann.[121]

Thiirane 1,1-dioxides 60 have also been reported to lose sulfur dioxide on heating to give the corresponding olefins, although a two step process may be occurring in these cases.[122,123] The only reported cases of extrusion of sulfur dioxide from four membered rings are those of Karish and Pirkle[124] and Dittmer.[125] Karish and Pirkle found that sulfur dioxide was extruded, along with nitrogen, from the diazothietane 1,1-dioxide 61 to give the olefin, while Dittmer has reported that the pyrazoline 62, prepared from thiete 1,1-dioxide and phenyldiazomethane, loses sulfur dioxide thermally to give the 5-methyl-3-phenylpyrazole 63.

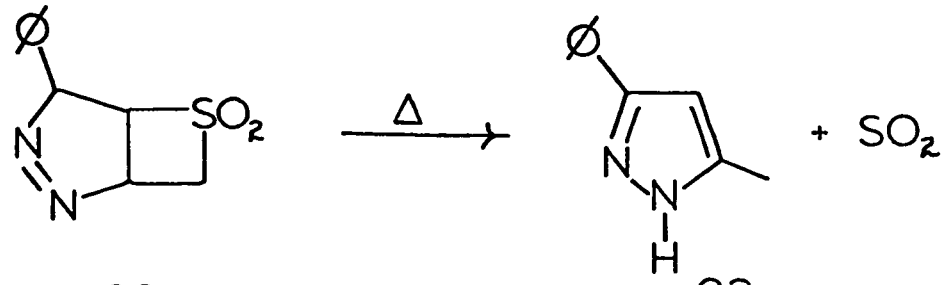
The ratio of methyl butenes formed in the pyrolysis of the 2,2-dimethyl thietane 1,1-dioxide parallels the findings of Flowers and Frey[126], who found that on



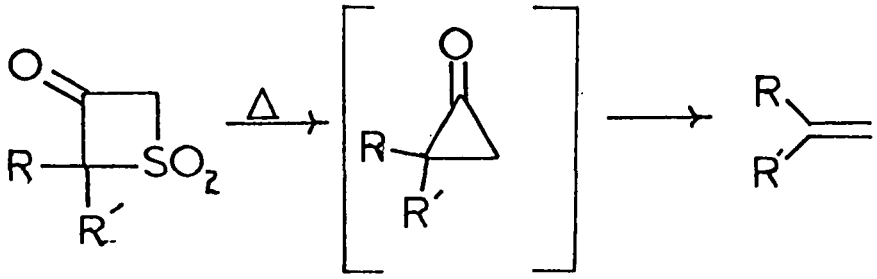
60



61



62 63



pyrolysis of dimethylcyclopropane at 441° to 511°, 3-methyl-1-butene and 2-methyl-2-butene plus 2-methyl-1-butene were formed in the ratios of 1.0/0.96. This compares to a value of 1.0/0.77 obtained from the thietane pyrolysis. Although the formation of polymer was not reported by Flowers and Frey, its formation in the thietane pyrolysis is no doubt a result of acid polymerization by the sulfurous acid, the latter being formed on the cold finger from sulfur dioxide and water.

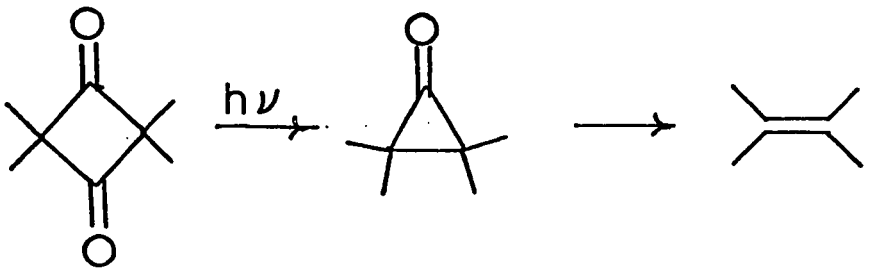
The isolation of cyclopropane and sulfur dioxide, as well as the agreement of the methylbutene ratios with those of Flowers and Frey, all support the hypothesis involving the initial extrusion of sulfur dioxide followed by cyclopropane formation or hydrogen migration.

The 3-thietanone 1,1-dioxides were found to follow a somewhat parallel reaction path. Pyrolysis of 3-thietanone 1,1-dioxide 22 gave only ethylene and sulfur dioxide as isolable products. The 2,2-dimethyl 3-thietanone 1,1-dioxide 40 gave isobutylene and sulfur dioxide, and 2-phenyl 3-thietanone 2,2-dioxide 29 gave styrene and sulfur dioxide in virtually quantitative yields. Extrusion of sulfur dioxide would again seem to be the initial reaction to give the corresponding cyclopropanone after ring closure. Subsequent loss of carbon monoxide results in formation of the observed olefins.

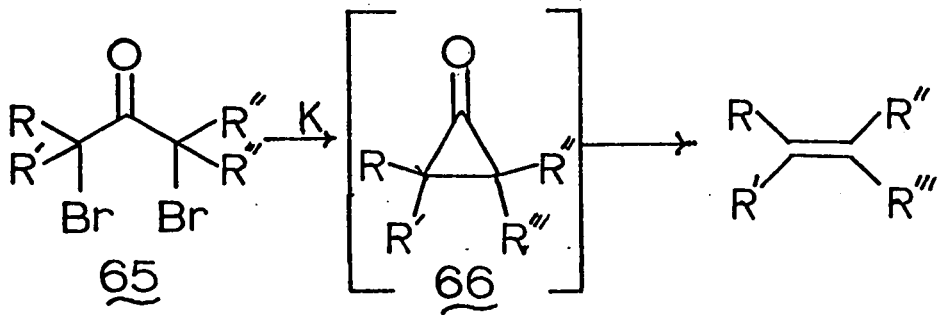
The intermediacy of a cyclopropanone in these reactions is only speculative since no one has reported the

pyrolysis of cyclopropanone in order to examine the products. Several authors have invoked their intermediacy, however, to explain the formation of the observed olefinic products. Kistiakowsky and Sauer[127], while studying the photolysis of ketene, found, among other products, ethylene and carbon monoxide. They proposed that the attack of carbene from the ketene photolysis reacted with a second molecule of ketene to give cyclopropanone. This then decomposed to give the observed ethylene and carbon monoxide. Similarly, Leermakers and coworkers[128] invoked a tetramethylcyclopropanone to explain the formation of tetramethylethylene from the photolysis of 1,3-tetramethylcyclobutadione 64. Doerr and Skell[129] on the other hand were able to provide more direct proof. They reported that debromination of 1,3-dibromoacetone 65 gave ethylene, which they proposed arose by the spontaneous decomposition of an intermediate cyclopropanone 66. This was supported by their observation that if the dimethyl ketal 67 was used instead of the ketone, some cyclopropanone dimethyl ketal 68 was recovered from the product mixture.

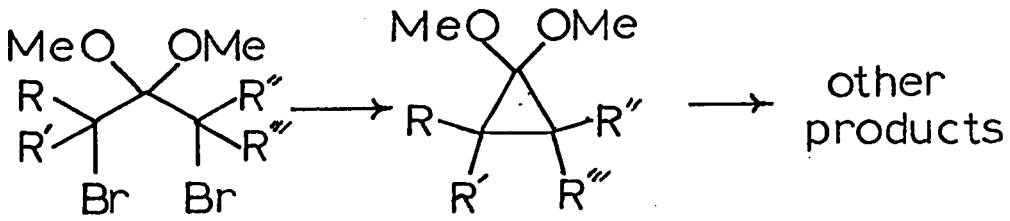
Whether sulfur dioxide or carbon monoxide is eliminated first is not known. The isolated products would be expected to be the same in either case, however, since the loss of sulfur dioxide from ethylene sulfones is an equally well known reaction, as was mentioned above. On the basis of bond strengths alone, one would expect that the sulfur dioxide would be extruded first, since the



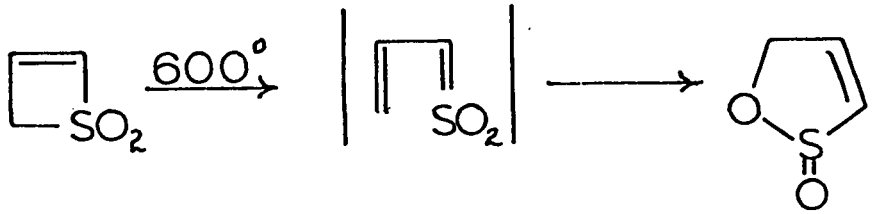
64



65 66



67 68



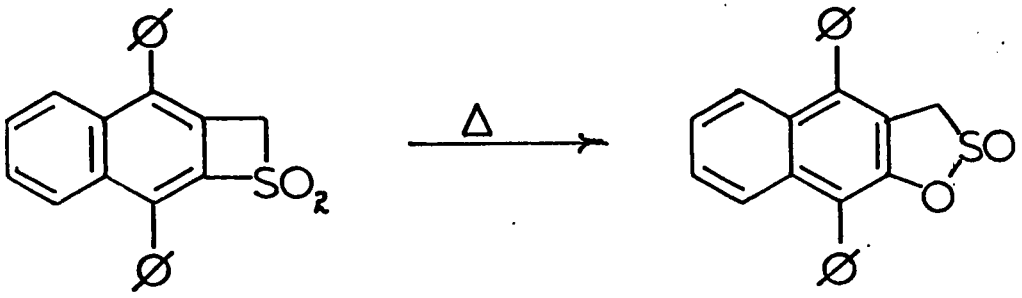
25 74 69

bond energy of the C-S bond is only 65 kilocalories versus 82.6 kilocalories for the C-C bond.

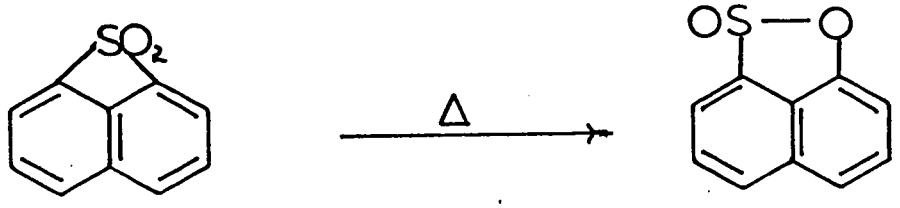
In both the thietane 1,1-dioxide and 3-thietanone 1,1-dioxides no evidence for the existence of a sulfene was found. It was expected, however, that thiete 1,1-dioxide would be more likely to give a sulfene on decomposition. This was based on the observation of King and co-workers[130] that the pyrolysis of thiete 1,1-dioxide 25 at moderately high temperatures in the gas phase or at lower temperatures in solution gave a good yield of $1,2^{\Delta 3}$ oxathiole S-oxide (an α,β unsaturated sultine 69). At about the same time, two similar reactions were reported by Dittmer[131] and Hoffman[132] respectively. The former involved the ring expansion of a substituted thiete 1,1-dioxide 70 to the corresponding sultine 71, while the latter was the ring opening of the diaryl thiete 1,1-dioxide 72 to 73.

King and coworkers have proposed an electrocyclic ring opening of the thiete 1,1-dioxide to the vinyl sulfene 74 which then closes by an "abnormal addition" mechanism[110] involving attack of the sulfonyl oxygen on the end of the vinyl group, to give the α,β unsaturated sultine 69. This theory is supported by their observation that trapping with phenol gave a low yield of 2-propenylsulfonic acid phenyl ester.

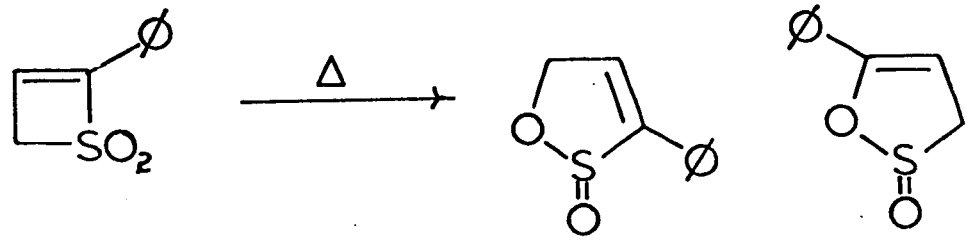
The pyrolysis of thiete 1,1-dioxide 25 was repeated in the flash apparatus at a temperature of 600°. The sultine 69 was isolated and shown to be identical with



70 71



72 73



37 75 76

the material obtained by King. Similarly, pyrolysis of 2-phenyl 2-thiete 1,1-dioxide 37 gave 2-phenyl-2-ene-sultine 75. This compound was identified by its infrared absorption at 1140 and 1025 cm^{-1} characteristic of sulfinates[133] and by its NMR which showed an ABX pattern at 5.32, 5.72 and 6.81 ppm with coupling constants of $J_{AB} = -15.96$ cps, $J_{AX} = 2.21$ cps, and $J_{AX} = 1.95$ cps and a five hydrogen multiplet at 7.47 ppm. The excellent agreement of this data with that of the parent sultine 69 proved the structure to be 75 rather than the alternative possibility 76.

A possible alternative method of preparing the α,β-unsaturated sultines might be the reaction of 1-propenyl- or 2-propenylsulfonyl chlorides with triethyl amine. Truce and coworkers[46] have shown by their deuteration experiments that such a system generates vinyl sulfene or its equivalent, which is also the proposed intermediate in the formation of sultines.

King and coworkers[134] have attempted to prepare a sultine by such a route with negative results. The importance of this result is not certain, however, since the stability of sultines in the presence of bases is unknown. Also, in view of Opitz's report of the isolation of triethylamine hydrochloride-sulfene adducts, it is not clear if in fact the same intermediate is involved in solution as in the vapor phase reaction where the sulfene is necessarily "free".

An alternative mechanism involving either a zwitter-

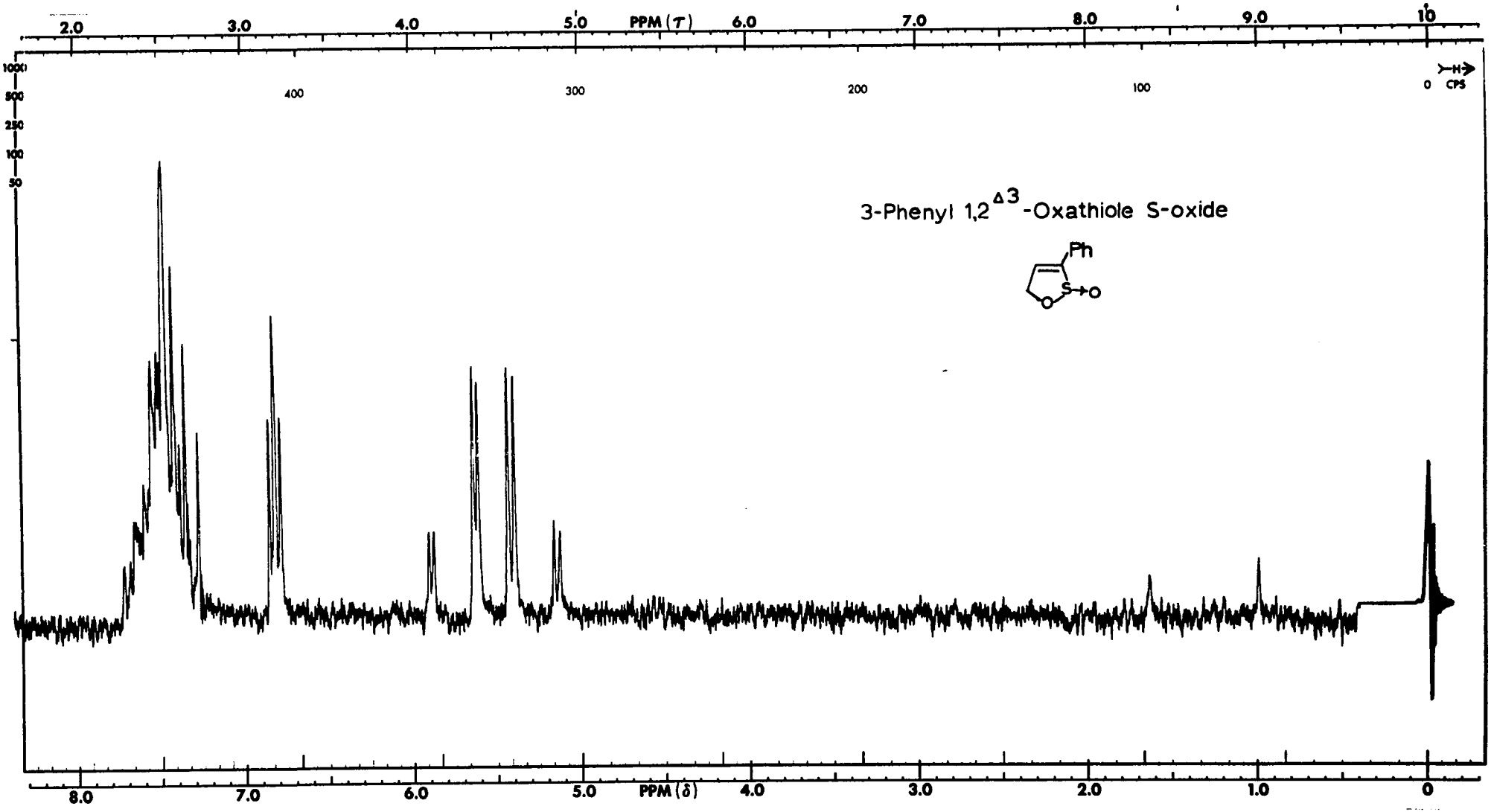
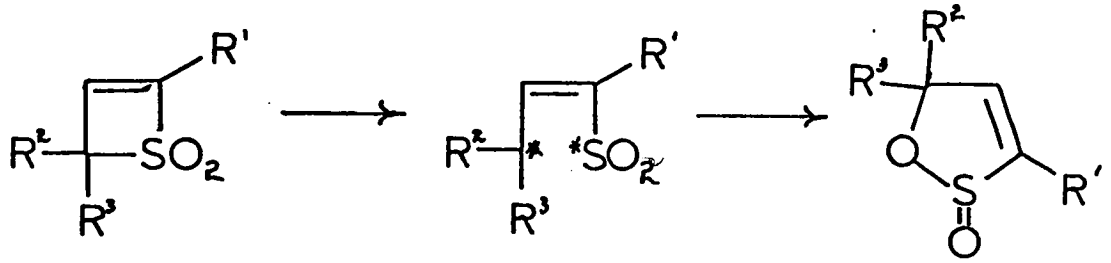

2.0
3.0
4.0
5.0
PPM (τ)
6.0
7.0
8.0
9.0
10
400
300
200
100
0 CPS
3-Phenyl 1,2 Δ3 -Oxathiole S-oxide
Ph
S→O
O
8.0
7.0
6.0
5.0
PPM (δ)
4.0
3.0
2.0
1.0
0

Figure 6

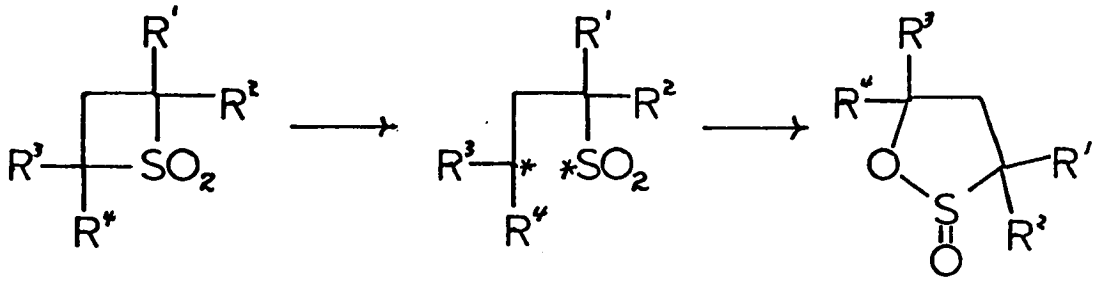
ion or diradical intermediate 77 for the formation of the α,β-unsaturated sultines was deemed unlikely on the basis of the low temperature pyrolysis of the thietane 1,1-dioxides. If either a zwitterion or diradical was involved, then the thietane 1,1-dioxides should undergo a similar reaction via the corresponding intermediate 78 to give saturated sultines 79. However, pyrolysis of thietane 1,1-dioxide 26 at 465°, 595°, and 765° gave starting material as the only nongaseous product in 92.5%, 78.6%, and 36.5% yields respectively. Similar results were obtained with 2,2-dimethyl thietane 1,1-dioxide at 465° and 610°.

No corresponding α,β unsaturated sultine could be isolated from pyrolysis of 2,2-dimethyl 3-thiete 1,1-dioxide 44 at 450° to 710°. This is probably a result of steric hind rance by the two methyl groups on the double bond preventing attack by the sulfonyl oxygen.

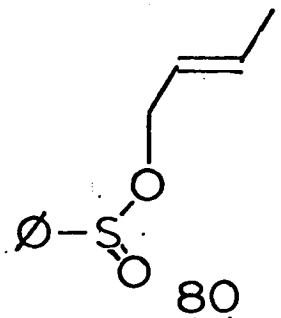
This formation of cyclic sulfinates is analogous to the rearrangement of the allyl sulfinate 80 to the allyl sulfone 81 observed by Cope[135]. Such an intramolecular rearrangement also appears to be occurring in the electron bombardment of cyclic sulfones. Fields and Meyerson[136] have reported the formation of a cyclic ether 84 on pyrolysis of the sulfone 82 which they suggested occurs via the sulfinate intermediate 83. This is supported by the mass spectrum of 82 which shows in addition to peaks corresponding to the loss of atomic oxygen, molecular oxygen, and sulfur dioxide, a series



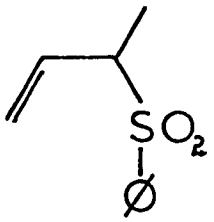
77



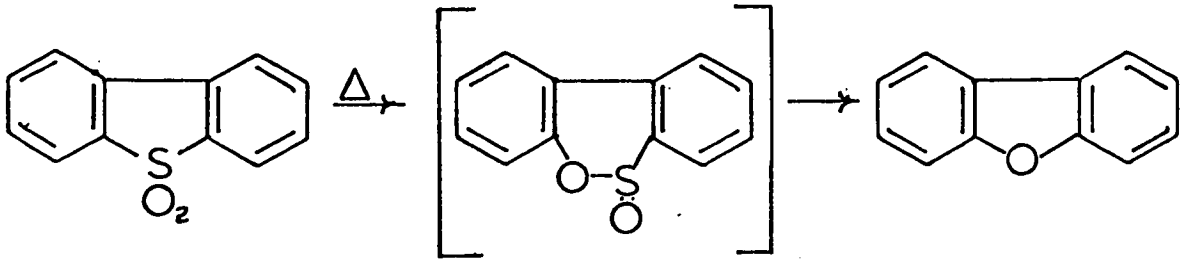
78 79



80



81



82 83 84

of peaks corresponding to the loss of sulfur monoxide, carbon monoxide or both, as expected from a rearrangement to the sulfinate 83.

These results are paralleled in the spectrum of 2-phenyl 2-thiete 1,1-dioxide. As well as the parent peak at m/e 180, peaks were observed at m/e 106 and 105 corresponding to the loss of SO_2 and SO_2H respectively, at m/e 132 due to the loss of sulfur monoxide and at m/e 135 from the loss of CO_2H (with a metastable peak at m/e 156 for the loss of CO). This breakdown pattern and the possible structures of the charged species are shown below.

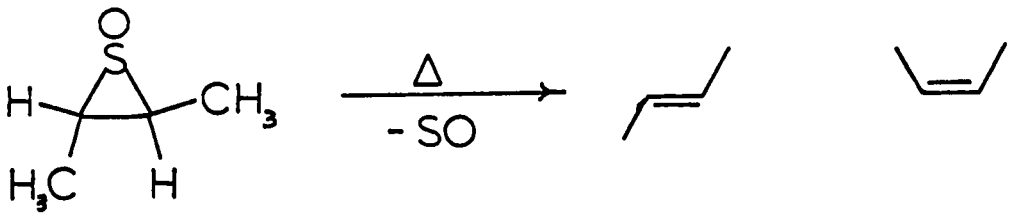
Pyrolysis of thiete 1,1-dioxide 25 at 950°, however, gave none of the previously observed sultine but rather a 84% yield of acrolein. No sulfur dioxide was found among the products either, but rather a yellow polymeric material which was presumed to have come from sulfur monoxide. This was supported by the observation that a bright red-coloured material formed on the cold finger during the pyrolysis and that this material changed to the yellow polymer on warming. Such a colour and colour change are indicative of disulfur monoxide[137] which is known to form spontaneously by the gas phase disproportionation of sulfur monoxide. Disulfur monoxide is unstable in the condensed phase, readily forming polysulfur oxides.

Similarly, 2,2-dimethyl 3-thiete 1,1-dioxide 44 gave 3-methyl-2-butenal and some sulfur dioxide, while 2-

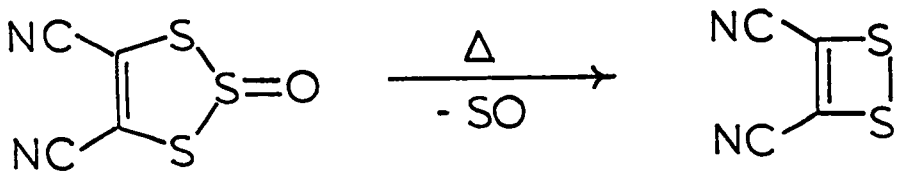
phenyl 2-thiete 1,1-dioxide 37 gave phenyl vinylketone, acrolein, and methyl phenylacetylene. All the products were identified by comparison with authentic samples.

The formation of the side product methyl phenylacetylene is probably a result of a sulfur dioxide extrusion reaction similar to that observed previously, since cyclopropenes are known to rearrange to acetylenes on heating. The acrolein, on the other hand, must have arisen by thermal cleavage of the phenyl-carbon bond with subsequent hydrogen abstraction, possibly from the solvent.

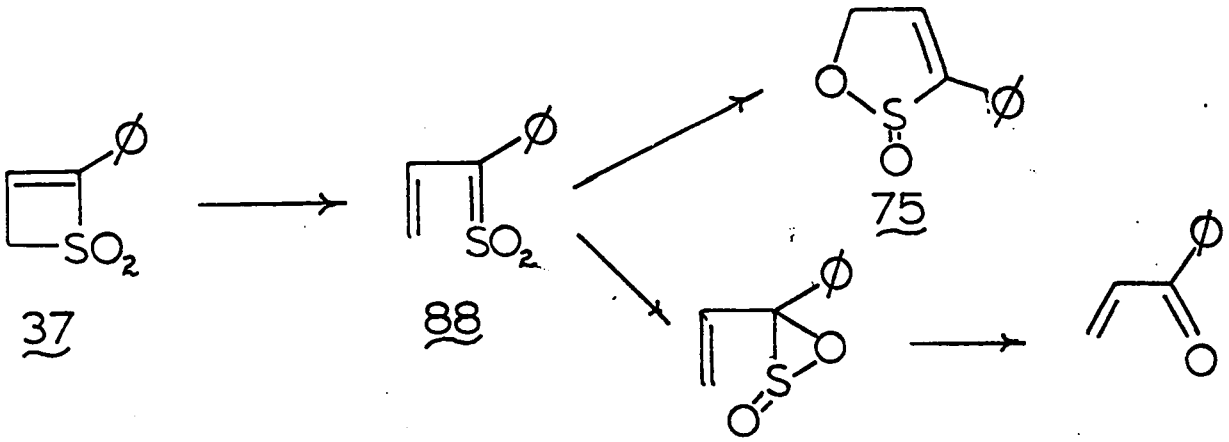
The extrusion of sulfur monoxide, as proposed above, is a well-known reaction. Hartzwell and Paige[138] have found that episulfoxides 85 lose sulfur monoxide at 100°-150° in a nonconcerted manner to give a cis-trans mixture of the corresponding olefins. The loss of sulfur monoxide has also been postulated by Fields and Meyerson[139] and Chambers and Cunningham[140] for the formation of cyclic ethers from diarylsulfones as previously described. Simmons and coworkers[141] have found as well that the dithiosulfite 66 loses sulfur monoxide spontaneously to give the four-membered ring disulfide 87. The possibility that these products might have arisen from the previously observed sultine was considered. In fact, pyrolysis of 2-phenyl-2-one sultine 75 under similar conditions gave the same products in the same ratios as observed from the pyrolysis of the 2-phenyl 2-thiete 1,1 dioxide 37.


O
S
H
CH3
H3C
H
Δ
- SO

85


NC
S
S=O
NC
S
Δ
- SO
NC
S
NC
S

86 87

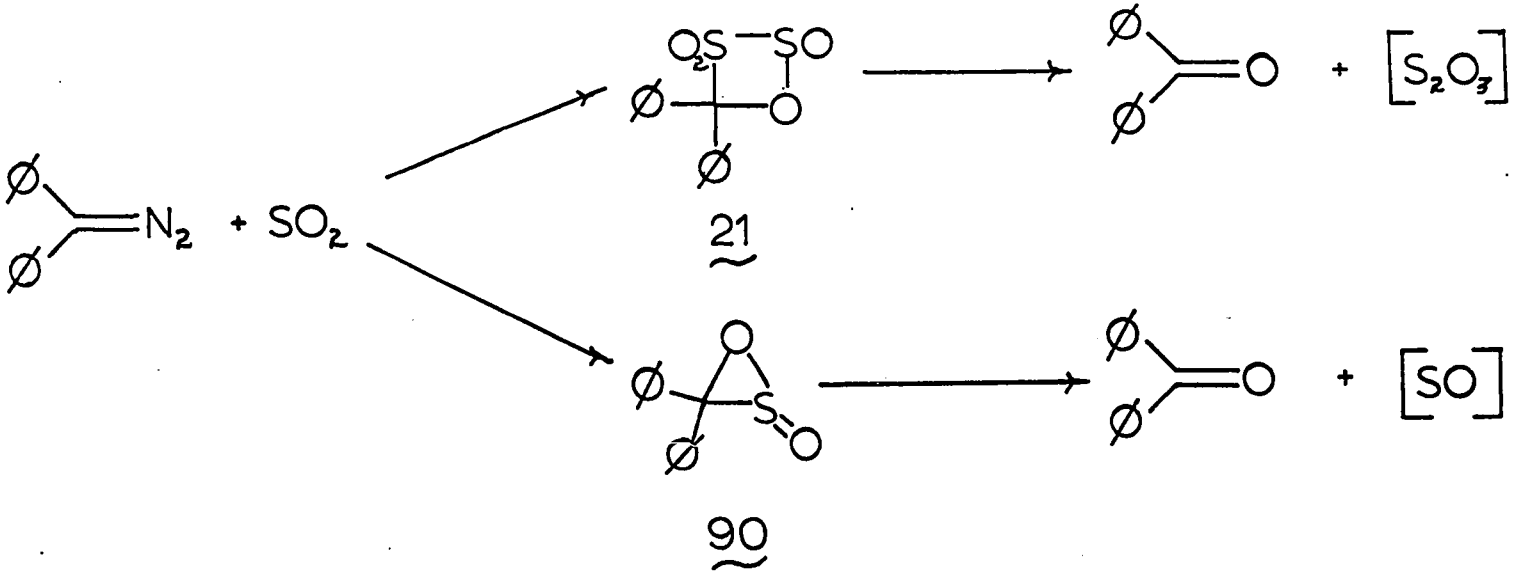

Ø
SO2
Ø
SO2
O
S
O
Ø
75
Ø
O
S
O
89
Ø
O

37 88

Phenyl vinyl ketone, however, is not the product expected from the loss of sulfur monoxide from 2-phenyl-2-ene sultine 75, but rather 3-phenylacrolein should be observed since the oxygen is attached to the carbon three away from the phenyl group, rather than the one bearing phenyl. It is proposed that rather than 75 being an intermediate in the high temperature pyrolysis, it is only the lower temperature product formed from the vinyl sulfene 88, which is readily reversed at higher temperatures. At the higher temperature a second reaction pattern becomes accessible to the sulfene which because of the loss of sulfur monoxide, is now irreversible. "Abnormal" attack of the sulfene upon itself to give the cyclic structure 89 followed by loss of sulfur monoxide thus accounts for the observed aldehydes and ketones.

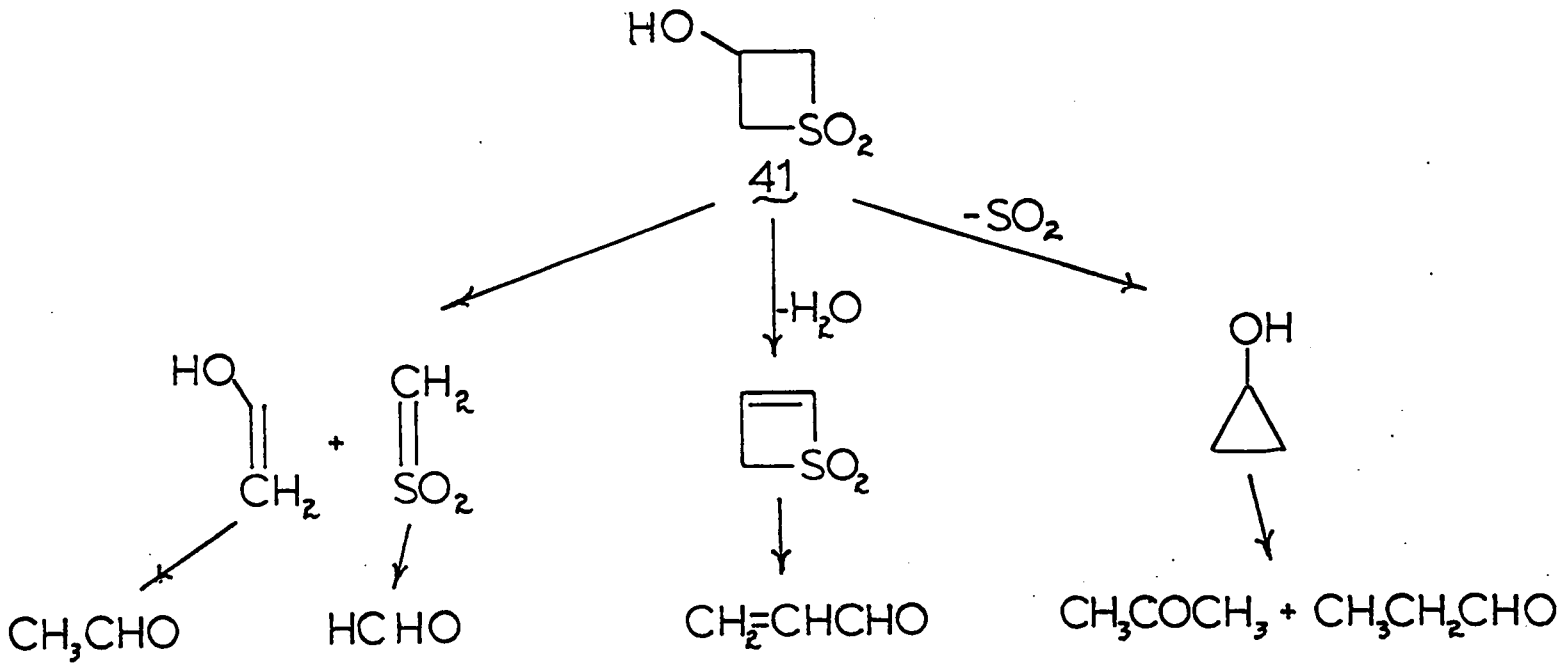
A three centered representation of sulfenes was considered previously by King and Durst[142]. It was rejected at that time, however, since the more familiar representation 88 explained the deuteration results more satisfactorily. Such an intermediate as 89 could conceivably be involved in the reaction of sulfur dioxide with diphenyldiazomethane as reported by Staudinger[47]. He found that if diphenyldiazomethane was added to sulfur dioxide, the isolated product was benzophenone which he proposed was formed by the loss of S_2O_3 from the cyclic intermediate 21. An intermediate 90, however, could explain the results equally well.

The formation of carbonyl compounds on pyrolysis of



21

90



thiete 1,1-dioxide, in conjunction with the formation of sultines at lower temperatures, provides further evidence for the existence of sulfenes as chemical intermediates. The exact structure of sulfenes is still debatable, however, and may best be represented by a series of canonical forms rather than a single structure.

The pyrolysis of 3-thietanol 1,1-dioxide 41 appears to be more complex than observed for the other compounds. When pyrolysed with no trapping agent on the cold finger, only a small percentage of chloroform soluble material was recovered and a large amount of polymer was formed. When methanol was placed on the cold finger prior to pyrolysis this problem was overcome, with the reactive products being trapped by the methanol. The products isolated consisted of ethane, ethylene, acetaldehyde, dimethoxymethane, propionaldehyde, acetone, 1,1-dimethoxy ethane, acrolein, and sulfur dioxide as shown in Table III.

Some of the products are readily explained on the basis of previously observed mechanisms. Extrusion of sulfur dioxide from the 3-thietanol 1,1-dioxide would be expected to give acetone and propionaldehyde either directly by hydrogen migration or via rearrangement of cyclopropanol.

It is also conceivable that under these reaction conditions, dehydration of the 3-thietanol 1,1-dioxide might occur to give the thiete 1,1-dioxide. As shown above, this compound could then be pyrolysed to acrolein and sul-

fur monoxide.

The formation of acetaldehyde and its dimethyl acetal, on the other hand, would indicate a third mechanism is operative, which is in fact the one originally desired; i.e. cleavage of the thiete 1,1-dioxide to give acetaldehyde and sulfene. The fate of the sulfene moiety is not certain although the observed ethylene and formaldehyde acetal could be some indication.

The formation of stilbene from phenyl sulfene is a well known reaction[40] and would explain the formation of the observed ethylene. Disproportionation of the sulfene would give methylene which could then dimerize to give ethylene. The sulfene could also undergo a reaction analogous to that observed for the vinyl sulfene to give formaldehyde and sulfur monoxide by an "abnormal" attack upon itself.

If these suppositions be true, then the yield of sulfur dioxide should approximate that of the acetone and propionaldehyde (47%), which it does. Although the yield of formaldehyde and ethylene are not as high as the acetaldehyde, as they should be, this is accountable for by polymerization of both the sulfene and the products as well as inefficient acetal formation.

The two purposes of this study would appear therefore to have been fulfilled. Evidence was obtained to indicate the presence of a sulfene intermediate in the thermal reaction of thietane 1,1-dioxides and secondly, a general reaction of sulfenes in the gas phase was dis-

covered, the formation of carbonyl compounds, a reaction previously unobserved at lower temperatures.

Table III

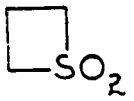
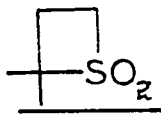
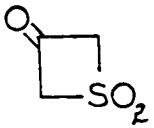
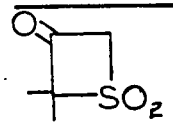
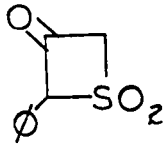
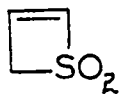
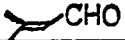
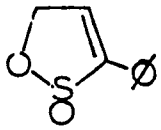
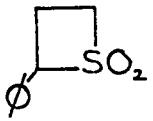
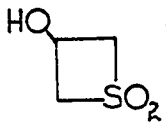
Cpd.	Temp. (°C)	Pressure (μ) pump	Pressure (μ) furnace	Time (min.)	Trap	Products (%)			
						C=C	C-C=C	Δ	SO_2
	960°	7	90	15	cold finger +gas U tube	trace	43.5	51.2	69.1
	950°	5	110	15	"	trace	46.2	52.5	50.6
								SO_2	polymer
	950°	5	150	15	U tube	21.2	15.6	79.5	64.8
	950°	4	100	15	U tube	20.8	15.9	50.2	63.0
						$H_2C=CH_2$			SO_2
	930°	1	200	30	U tube	96.1			46.1
	940°	5	100	30	cold finger + ss bomb	99.7			98.5(a) 96.0(b)
									SO_2
	940°	1	100	30	U tube	96.5			97.3
	945°	1	100	30	U tube	94.5			95.3
									SO_2
	930°	1	100	30	U tube	97.6			97.2
	950	1	50	15	U tube	91.5			90.5(a) 92.5(b)
							C≡C		SO_2
	950°	10	150	15	U tube	83.4	-		none
	940°	5	150	15	U tube	84.5	-		none
	935°	5	100	15	cold finger + ss bomb	-	5.0		none

Table III (cont.)

Cpd.	Temp. (°C)	Pressure (μ) pump	Pressure (μ) furnace	Time (min.)	Trap	Products (%)			
									SO_2
	950°	6	150	15	U tube	72.7			14.7
	935°	6	150	15	U tube	70.8			16.2
						$CH_2=CHCHO$	$CH_3C\equiv C\phi$	$CH_2=CHCO\phi$	SO_2
	915°	7	100	15	U tube	5.7	6.2	83.8	none
	930°	8	60	15	U tube	7.9	4.9	80.5	none
	940°	1	70	30	U tube	4.0	5.0	84.0	none
	930°	1	80	30	U tube	5.7	4.4	85.5	none
						CH_3CHO / $CH_2(OCH_3)_2$	CH_3CH_2CHO / CH_3COCH_3	$CH_3CH_2(OCH_3)_2$	$CH{=}CHCHO$
	960°	7	120	30	U tube	2.8 / 6.4	23.1 / 26.8	24.0	2.3
	930°	6	120	30	U tube	4.5 / 6.9	21.1 / 23.2	23.3	4.5
						C-C	C=C		SO_2
	940°	7	95	30	cold finger +gas U tube	1.4	10.0		31.2(a) 42.3(b)
	930°	5	150	30	cold finger +gas U tube	1.4	6.9		16.2

EXPERIMENTAL

A. The Photolysis of Some 2-Pyrones

Preparation of 2-Pyrone:

Coumalic acid was decarboxylated over a copper catalyst at 650° as described by Zimmerman[25] to give 2-pyrone, b.p. 94°/15 mm, λ_{max}^{EtOH} = 217 nm (ε2,720), 289 nm (ε7,500).

Irradiation and Pyrolysis of 2-Pyrone:

3.2 g of the pyrone were dissolved in 5 ml of dry benzene in a 9 mm pyrex tube, the solution was degassed for ½ hour with oxygen-free nitrogen, the tube sealed, then strapped to the outside of a water-cooled immersion well containing a Pyrex filter and a 450 watt Hanovia medium pressure mercury arc lamp. The whole apparatus was immersed in a four litre beaker and wrapped with aluminum foil, which acted as a reflector. The solution was irradiated for 120 hours, then the crystalline precipitate filtered, 1.28 g (40%). The infrared absorption of the solid showed little if any absorption at 1560 cm^{-1} due to 2-pyrone. Attempted separation of the crystalline products by fractional recrystallization was unsuccessful.

The crystals, 300 mg, were pyrolysed in a Pyrex distillation apparatus with a free flame by heating to above their melting point for 10 minutes. The resultant material was distilled under water pump vacuum into a dry ice-acetone cooled receiver. The products were a mixture of cyclooctatetraene, identified by infrared and vpc retention time, and 2-pyrone, identified by infrared and NMR.

The cyclooctatetraene was determined by adding a known weight of cyclohexanol to the distillate in chloroform. The mixture was then analysed by vpc (20% Carbowax 20M on Chromsorb P, 6'x$\frac{1}{4}$", 120°, 40 cc/min of helium) and the ratio of the peaks determined by integration. The yield calculated was 2.4%.

The amount of 2-pyrone produced by reverse cleavage of the dimers was calculated by making the distillate to a specific volume with chloroform and measuring the areas of the infrared absorption at 1546 and 1626 cm^{-1} on a Beckman IR7 using 0.1 mm cells. The amount of 2-pyrone was obtained by comparison with a graph of area versus concentration prepared by using pure 2-pyrone. The yield calculated was 36.6%.

83.3 mg of cyclooctatetraene were pyrolysed under similar conditions and distilled to give back 83.0 mg (99.5%) of the starting material.

Preparation of 4-Methoxy-6-Methyl-2-Pyrone:

The 2-pyrone was prepared as described by Lock and Smith[26] by the reaction of dehydroacetic acid in 90%

sulfuric acid to give triacetic acid lactone (48%), which was then methylated with dimethyl sulfate and anhydrous potassium carbonate in refluxing ethyl methyl ketone. Recrystallization from benzene gave the desired 4-methoxy-6-methyl-2-pyrone, m.p. 87-89° (lit.[26] m.p. 89-90°), $\nu_{max}^{CCl_4}$ = 1710 (C = O), 1650, 1570 (C = C) cm^{-1}, $\delta(CCl_4)$ = 2.17 (3H,s), 3.78 (3H,s), 5.28 (1H,m), λ_{max}^{EtOH} = 280 nm (ϵ 6,380). It was found necessary to sublime the material before use to ensure dryness, as the compound is hygroscopic.

Irradiation of 4-Methoxy-6-Methyl-2-Pyrone:

In general, a solution of the 2-pyrone (100-300 mg) was dissolved in 5 ml of dry benzene (distilled from calcium hydride and stored over sodium wire) in a 9 mm pyrex tube which had been flamed out. The solution was degassed and irradiated as before. The reaction was followed by taking aliquotes with a hypodermic needle through the septum and observing the disappearance of the ultraviolet absorption at 280 nm, (approximately 24 hrs).

The irradiated solution was transferred to a 100 ml flask, and either a) an equal volume of water with enough dioxane to make a homogeneous solution, or b) methanol was added. After standing at 50° for 12 hrs, the solvent was removed under reduced pressure and the products separated by thin layer chromatography (tlc) using 50/50 ether/benzene to give a mixture, R_f=0.6, of cis- and trans-β-methylglutaconic acid monomethyl esters, m.p.

71-73°, 38%, $\nu_{max}^{CCl_4}$ = 1747 (C = O), 1697 (C = C) cm^{-1}.
Analysis: Calc. for $C_7H_{10}O_4$, C 53.16%, H 6.37%, OMe 19.62%;
Found, C 53.29%, H 6.59%, OMe 20.02%.

Also a mixture, Rf= 0.3, of cis- and trans-β-methylglutaconic acids, m.p. 153.5-54.5°, was isolated, identical with that reported by Jackman[28].

Treatment of either of these mixtures with ethereal diazomethane gave a mixture of cis- and trans-β-methylglutaconic acids dimethyl esters, which were separated by vpc (10% Carbowax 20M on Chromosorb P, 20'x¼", 150°, 60 cc/min) to give dimethyl cis-β-methylglutaconate, $\delta(CCl_4)$= 1.97 (3H,s), 3.70 (6H,s), 3.75 (2H,s), 5.83 (1H, s).and dimethyl trans-β-methylglutaconate, $\delta(CCl_4)$= 2.22 (3H,s), 3.12 (2H,s), 3.70 (6H,s), 5.80 (1H,s). Both these compounds gave infrared and NMR spectra identical with those reported by Jackman[28].

Hydrogenation of Irradiation Products:

387 mg of 4-methoxy-6-methyl-2-pyrone were dissolved in anhydrous benzene, which had been passed through active neutral alumina, and the solution placed in a 10 mm Pyrex tube. After degassing by the freeze-thaw method on a high vacuum pump, the tube was strapped to an immersion well and irradiated as described above. The solvent was then removed at room temperature with a trolley pump to yield a polymeric material whose average molecular weight was 510 (vapor pressure osmometer in benzene), $\nu_{max}^{CCl_4}$ = 1740 (C = O), 1645 (C = C) cm^{-1}, $\delta(CCl_4)$ = 1.75 (3H,m), 3.30 (1H,m), 3.65 (3H,m), 5.30 (1/5H,m), 6.00

(1/5H,m), 6.55 (8.5/10H,m).

The product was hydrogenated in anhydrous ethyl acetate with 150 mg of prehydrogenated Pt_2O for 24 hours, the catalyst filtered off, and the solvent evaporated to give 290 mg of a material which distilled at a bath temperature of 130°/30 mm. This material was treated with ethereal diazomethane and separated by tlc using 20% ethyl acetate/petrol (60-80°) to give a mixture of isomeric esters, $\nu_{max}^{CCl_4} = 1740\ cm^{-1}$, $\delta(CCl_4) = 1.15$ (3H, d, J=6 cps), 2.19 (3H,m), 3.19 (3H,s), 3.26 (1H,m), 3.65 (3H,s), 3.66 (1H,m).

Analysis: Calc. for $C_8H_{14}O_3$, C 60.74%, H 8.92%;
Found, C 60.36%, H 8.95%.

Irradiation of 4-Methoxy-6-Methyl-2-Pyrone in Methanol:

100 mg of the 2-pyrone were irradiated as before in 5 ml of spectral grade methanol for 3 hours. The solvent was evaporated and the products distilled under vacuum (130°/750 mm) to give a low yield of a mixture of cis- and trans-dimethyl β-methylglutaconate, as identified by comparison of the vpc and tlc retention times with authentic samples.

Irradiation of 4-Methoxy-6-Methyl-2-Pyrone:

A solution of 100 mg of the 2-pyrone was dissolved in 200 ml of water and irradiated in an immersion apparatus with a 450 watt medium pressure mercury arc through Pyrex after degassing with oxygen-free nitrogen. The reaction was followed by the disappearance of the ultraviolet absorption at 280 nm (3.5 hrs). Solvent was

removed under vacuum and the products separated by tlc using 50/50 ether/benzene to give cis-β-methyl glutaconic acid monomethyl ester, R_f=0.6, 50%, m.p. 77-78°, $\nu_{max}^{CCl_4}$ = 1747, 1698 (C = O), 1651 (C = C) cm^{-1}, $\delta(CCl_4)$= 2.00 (3H,d,J=1.5 cps), 3.67 (2H,s), 3.71 (3H,s), 5.87 (1H, m), 11.71 (1H,s), λ_{max}^{EtOH} = 217 nm (ε8,000).

Analysis: Calc. for $C_7H_{10}O_4$, C 53.16%, H 6.37%, OMe 19.62%;
Found, C 53.08%, H, 6.36%, OMe 19.12%.

Also, cis-β-methylglutaconic acid was isolated, R_f = 0.3, 50%, m.p. 152-53°, ν_{max}^{nujol} = 1715, 1688 (C = O), 1642 (C = C) cm^{-1}, $\delta(CF_3COOH)$= 2.13 (3H,d,J=2 cps), 3.90 (2H, s), 6.11 (1H,m), λ_{max}^{EtOH} = 2.17 nm (ε13,100), identical with that reported by Jackman[28].

A solution of the 2-pyrone was dissolved in water for 24 hours at room temperature. The water was then removed under vacuum to give back the 2-pyrone unchanged, as shown by infrared absorption.

Ozonolysis of cis-β-Methylglutaconic Acid Monomethyl Ester:

20 mg of cis-β-methylglutaconic acid monomethyl ester from the water irradiation were ozonized at -70° in chloroform for one-half hour. The excess ozone was removed with a stream of nitrogen and the reaction mixture hydrogenated at -70° for 5 minutes over 5% Pd/C catalyst. The catalyst was filtered off and the products treated with an excess of 2,4-dinitrophenylhydrazine-hydrochloride, then separated by tlc using 5% ethyl acetate in benzene to give 10 mg of methyl aceto-

acetate 2,4-dinitrophenylhydrazone, m.p. 120-21° (mixed m.p. 119.0-19.5° with an authentic sample[26] m.p. 119-20°).

Hydrogenation of 4-Methoxy-6-Methyl-2-Pyrone:

A solution of 284 mg of the 2-pyrone over 73 mg of 5% Palladium on Carbon in 5 ml of dry dioxane was hydrogenated for 7 hours at atmospheric pressure. The catalyst was filtered and the solvent removed under reduced pressure to give a 45/55 mixture (by NMR integration) of 5-hydroxy-3-methoxy-2-hexenoic acid δ-lactone and 5-hydroxy-3-methoxy-hexanoic acid δ-lactone which were separated by tlc (% ether/benzene). The former showed the following physical properties: $\nu_{max}^{CCl_4}$ = 1722 (C = O), 1635 (C = C) cm^{-1}, $\delta(CCl_4)$ = 1.40 (3H,d,J=6.5 cps), 2.28 (1H,s), 2.81(1H,s), 3.75 (3H,s), 4.47 (1H,m), 5.08 (1H, s), Analysis: Calc. for $C_7H_{10}O_3$, C 59.14%, H 7.09%; Found, C 58.96%, H 7.06%; and the latter: $\nu_{max}^{CCl_4}$ = 1747 (C = O) cm^{-1}, $\delta(CCl_4)$ = 1.35 (3H,d,J= 7 cps), 2.41 (4H, m), 3.25 (3H,s).

Analysis: Calc. for $C_7H_{12}O_3$, C 58.31%, H 8.39%;
Found, C 58.69%, H 7.97%.

Hydrogenation of β-Methylglutaconic Acid:

40 mg of cis-β-methylglutaconic acid were hydrogenated with 33 mg of 5% Pd/C in 5 ml of absolute ethanol at atmospheric pressure for 24 hours. The catalyst was filtered off and the product treated with ethereal diazomethane to give β-methylglutaric acid dimethyl ester[28], $\nu_{max}^{CCl_4}$ = 1740 (C = O) cm^{-1}, $\delta(CCl_4)$ = 1.01 (3H,m), 2.28

(5H,m), 3.62 (6H,s).

Preparation of 6-Methoxy-4-Methyl-2-Pyrone:

β-methylglutaconic acid was prepared as described by Wiley and Jarboe[31] via the base catalysed hydrolysis of ethyl isodehydroacetate. The anhydride was then formed by heating with acetic anhydride to give β-methylglutaconic anhydride. The anhydride was treated with ethereal diazomethane and the products recrystallized from ether-petrol (35-60°) to give 6-methoxy-4-methyl-2-pyrone, m.p. 53.0-53.5°, $\nu_{max}^{CCl_4}$ = 1755 (C = O), 1640, 1595, 1560 (C = C) cm^{-1}, $\delta(CCl_4)$= 2.07 (3H,s), 3.84 (3H, s), 5.14 (1H,m), 5.44 (1H,m), λ_{max}^{EtOH} = 281 nm (ε4,200), 315 nm (ε4,150).

Analysis: Calc. for $C_7H_8O_3$, C 59.99%, H 5.75%;

Found, C 59.45%, H 5.29%.

Irradiation of 6-Methoxy-4-Methyl-2-Pyrone:

140 mg of this 2-pyrone were irradiated in dry benzene for 24 hours under conditions identical to those used for 4-methoxy-6-methyl-2-pyrone. The solvent was evaporated to give material of average molecular weight 152 (vapor pressure osmometer in benzene). NMR examination of this material showed only peaks attributable to starting material, cis- and trans-β-methylglutaconic acid and its monomethyl esters.

Hydrolysis of 6-Methoxy-4-Methyl-2-Pyrone:

150 mg of the pyrone were dissolved in 40 ml of 95% ethanol and left at room temperature for 24 hours. The solvent was then removed under reduced pressure and the

products separated by tlc with 50/50 ether/benzene to give a mixture of cis- and trans-β-methylglutaconic acids ethyl methyl esters, $\nu_{max}^{CCl_4}$ = 1740, 1720 (C = O), 1660 (C = C) cm^{-1}, $\delta(CCl_4)$ = 1.24 (3H,t,J=7 cps), 1.92 (3/2H, d,J=1.5 cps), 2.20 (3/2H,d,J=1.5 cps), 3.07 (2/2H,s), 3.62 (3H,s), 3.78 (2/2H,s), 4.09 (2H,q,J=7 cps), 5.75 (1H,m).

Analysis: Calc. for $C_9H_{14}O_4$, C 58.05%, H, 7.58%;
Found, C 58.15%, H, 7.22%.

B. Photolysis of β-Keto Sulfones

Preparation of Benzyl Acetonylsulfone:

Benzyl mercaptan was condensed with chloroacetone using sodium ethoxide as described by Wahl[58], to give benzyl acetonyl sulfide. This sulfide was then oxidized with potassium permanganate to give the benzyl acetonyl-sulfone, m.p. 88-89° (lit. m.p. 89°[58]).

Irradiation of Benzyl Acetonylsulfone:

360 mg of the sulfone were dissolved in 40 ml of spectral grade methanol in a 2.5 x 20 cm quartz tube. The solution was degassed with oxygen-free nitrogen for one hour, then sealed with a rubber bulb and strapped to the side of a water-cooled immersion well containing a Corex filter and a 450 watt Hanovia medium pressure mercury arc lamp. The apparatus was immersed in a cold bath at 0° and irradiated for 3 hours.

The solvent was removed under water-pump vacuum at room temperature and the products separated by tlc using 50/50 ether/benzene to give:

a) R_f= 0.8, dibenzyl, m.p. 51.5-52.0°, (mixed m.p. 51.5-52.0° with an authentic sample m.p. 51-52°), 22%, infrared and NMR identical with an authentic sample.

b) R_f= 0.7, benzylsulfonic acid isopropenyl ester, 5.8%, $\nu_{max}^{CCl_4}$ = 1670 (C = C), 1365, 1167, 953 (SO_3R) cm^{-1}, $\delta(CCl_4)$ = 1.87 (3H,s), 4.34 (2H,s), 4.74 (2H,m), 7.40 (5H,s), ϵ_{220nm}^{EtOH} = 1,840.

Analysis: Calc for $C_{10}H_{12}O_3S$: C 56.60%, H 5.70%;
Found: C 56.52%, H 5.58%.

c) R_f = 0.65, benzyl acetone, 13%, 2,4-dinitrophenylhydrazone m.p. 127-29° (mixed m.p. 127-29° with authentic sample m.p. 127-29°), infrared and NMR identical with an authentic sample.

d) R_f = 0.2, benzylsulfinic acid, m.p. 108-12°, 32.1%, infrared and NMR identical with those of a sample prepared as described below.

e) acetone, 59%, 2,4-dinitrophenylhydrazone m.p. 125-27° (mixed m.p. 126-7° with authentic sample m.p. 126-27°). The yield of acetone was determined by distilling the volatile products and solvent into a carbon dioxide-isopropyl ether cooled receiver. The distillate was then made up with methanol in a 50 ml volumetric flask and aliquotes analysed by vpc (2.5% Carbowax 20M on 60-80 mesh firebrick, 25' x 3/16", 60°, 40 cc/min of helium) on a Varian HiFi vpc with flame ionization detectors. The apparatus had been previously calibrated with acetone in methanol solutions.

f) No benzylsulfonic acid methyl ester was observed by examination of the product mixture by NMR or tlc.

Preparation of Benzylsulfinic Acid:

25 g of sodium bisulfite were added to 18 g of α-toluenesulfonyl chloride in 100 ml of water, in a manner analogous to the method described by Durst[57] for the preparation of sulfinic acids. The mixture was acidified

with HCl, and the resultant white precipitate filtered. The acid was crystallized from chloroform/petrol (60-80°) to give pure benzylsulfinic acid, m.p. 110-12°, ν_{max}^{nujol}= 3400 (OH), 1070 (SO_2H) cm^{-1}, $\delta(CDCl_3)$= 4.02 (2H,s), 7.34 (5H,s), 10.41 (1H,s).

Part of the acid was treated with diazomethane to give methyl benzylsulfinate, $\nu_{max}^{CHCl_3}$ = 1110, 995 (SO_2R) cm^{-1}, $\delta(CCl_4)$ = 3.60 (3H,s), 3.89 (2H,s), 7.29 (5H,s).

Preparation and Irradiation of Methyl Benzylsulfonate:

One gram of α-toluene sulfonyl chloride was reacted with 5 ml of anhydrous triethylamine in 40 ml of methanol for one minute as described by Durst[57]. 50 ml of methylene chloride were then added and the solution washed with 50 ml of 5% HCl, and 50 ml of water. The hydrocarbon layer was dried over $MgSO_4$, filtered, and the solvent evaporated. The product was recrystallized from CH_2Cl_2/petrol (35-60°) to give methyl benzylsulfonate, m.p. 61-62° (lit. m.p. 61-62°), $\nu_{max}^{CCl_4}$= 1335, 1150, 990 (SO_3R) cm^{-1}, $\delta(CCl_4)$= 3.65 (3H,s), 4.24 (2H,s), 7.38 (5H,s).

122.2 mg of the ester were irradiated in 40 ml of methanol, as described above, for 4 hours. NMR and tlc examination of the products showed only methyl benzylsulfonate.

Attempts to Increase the Yield of Vinyl Sulfonate:

Various changes were made in the solvent, temperature, filter, and/or irradiation time in an attempt to

increase the yield of the isopropenyl benzylsulfonate. The results are given in Table II of the discussion.

Preparation of Benzyl Phenacyl Sulfone:

Benzyl mercaptan was reacted with chloroacetophenone as described by Wahl[56]. The resultant benzyl phenacyl sulfide was then oxidized with $KMnO_4$ to give the desired benzyl phenacyl sulfone, m.p. 111-12° (lit. m.p. 113°[56]), $\nu_{max}^{CHCl_3}$ 1730 (C = O), 1335, 1125 (SO_2) cm^{-1}, $\delta(CDCl_3)$= 4.38 (2H,s), 4.52 (2H,s), 7.2-8.0 (10H, m).

Irradiation of Benzyl Phenacyl Sulfone:

360 mg of the β-keto sulfone was irradiated in 40 ml of spectral grade methanol, as described above, for 7 hours. The solvent was removed under reduced pressure, the products treated with excess diazomethane, then separated by tlc, using 50/50 ether/benzene, to give:

a) R_f = 0.8, dibenzyl, m.p. 51-52°, 24%, infrared and NMR identical with an authentic sample.

b) R_f = 0.7, acetophenone, 77.5%, 2,4-dinitrophenylhydrazone m.p. 246-47° (mixed m.p. 245-46° with an authentic sample m.p. 245-47°), infrared and NMR identical with an authentic sample.

c) R_f = 0.5, methyl benzylsulfinate, identical with the material synthesised previously.

d) R_f = 0.4, an unidentified ketone, 32%, which by comparison of infrared and NMR spectra is not 2-phenylpropiophenone.

e) No vinyl sulfonate was isolated or observed in the product mixture.

Preparation of t-Butyl Acetonyl Sulfone:

t-Butylmercaptan was condensed[83] with chloroacetone as described above, using sodium ethoxide to give t-butyl acetonyl sulfide, b.p. 95-96°/30 mm (lit. b.p. 103.5-104.5°[83]), $\nu_{max}^{CCl_4}$ = 1717 (C = O) cm^{-1}, $\delta(CCl_4)$ = 1.33 (9H,s), 2.22 (3H,s), 3.38 (2H,s).

7.8 g of the sulfide were dissolved in 25 ml of acetic acid and 22.5 ml of water. To this was added slowly 12.5 ml of 30% H_2O_2 and the solution stirred for 18 hours. The mixture was extracted twice with 100 ml portions of ether and the combined ether layers then washed with sodium bisulfite solution until neutral as indicated by pH paper. The ether solution was then dried over $MgSO_4$, filtered, and distilled to give t-butyl acetonyl sulfone, b.p. 106-108°/1.2 mm, $\nu_{max}^{CCl_4}$ = 1720 (C = O), 1313, 1112 (SO_2), $\delta(CCl_4)$ = 1.36 (9H,s), 2.38 (3H,s), 3.96 (2H,s), ϵ_{200mm}^{EtOH} = 2,000.

Analysis: Calc. for $C_7H_{14}O_3S$: C 47.18%, H 7.92%;
Found: C 46.90%, H 7.81%.

2,4-dinitrophenylhydrazone, m.p. 171-72°, λ_{max}^{EtOH} = 355 (ε16,000), 253 (ε4,100), 227 (ε11,700) nm.

Analysis: Calc. for $C_{13}H_{18}N_4O_6S$: C 43.57%, H 5.06%, S 8.93%;
Found: C 43.88%, H 5.85%, S 8.67%.

Irradiation of t-Butyl Acetonyl Sulfone:

360 mg of t-butyl acetonyl sulfone were irradiated in 40 ml of methanol for 4 hours as described above. The solvent was removed under reduced pressure at room temperature, the products treated with diazomethane, and separated by tlc using 50/50 ether/benzene to give:

a) R_f= 0.8, t-butylsulfonic acid isopropenyl ester, 15.5%, $\nu_{max}^{CCl_4}$ = 1668 (C = C), 1345, 1149, 951 (SO_3R) cm^{-1}, $\delta(CCl_4)$= 1.46 (9H,s), 2.02 (3H,s), 4.80 (2H, doublet of doublets, J_{AB}= 2.0 cps, $\delta_B - \delta_A$ = 10.7 cps).

Analysis: Calc. for $C_7H_{14}O_3S$: C 47.18%, H 7.92%;

Found: C 46.46%, H 8.13%.

b) R_f= 0.7, t-butylsulfonic acid, methyl ester, 11.5%, infrared and NMR identical with the material prepared as described below.

c) R_f= 0.5, t-butylsulfinic acid, methyl ester, 28.4%, infrared and NMR identical with material prepared as described below.

d) R_f= 0.2, unidentified ketone which is not t-butyl-2-propanone.

e) acetone, 55.8%, estimated by vpc as described previously.

Preparation of t-Butylsulfonic Acid Methyl Ester:

9 g of t-butylmercaptan in 10 ml of glacial acetic acid were oxidized with 60 ml of 30% H_2O_2 for 10 hours as described by Zuffante[65]. The resultant white precipitate was filtered off and treated with diazomethane to give t-butylsulfonic acid, methyl ester, $\nu_{max}^{CCl_4}$ = 1335,

1140, 990 (SO_3R) cm^{-1}, $\delta(CCl_4)$ = 1.37 (9H,s), 3.97 (3H, s).

Preparation of t-Butylsulfinic Acid, Methyl Ester:

1.0 g of magnesium metal turnings were added to 5 g of t-butyl bromide in 50 ml of anhydrous ether. After the reaction had ceased, anhydrous SO_2 was bubbled into the solution for 2 minutes as described by Barnard(64). The ether was removed under reduced pressure and 20 ml of 95% ethanol, followed by 50 ml of water, were added. The aqueous layer was extracted with 50 ml of chloroform, the chloroform layer washed with 20 ml of water, dried over $MgSO_4$, filtered, and the solvent evaporated. The residue was treated with diazomethane to give t-butylsulfinic acid methyl ester, $\nu_{max}^{CCl_4}$ = 1130, 998 (SO_2R) cm^{-1}, $\delta(CCl_3)$= 1.18 (9H,s), 3.76 (3H,s).

Attempted Trapping of any Radical Intermediates:

Various free radical inhibitors were added to the irradiation mixture of benzyl acetonyl sulfone before irradiation. The solutions were then irradiated as usual, the solvent removed under reduced pressure, and the products treated with diazomethane. A known quantity of dimethyl maleate was added to the product mixture and yields obtained by integration of the NMR spectra of this mixture.

a) 251 mg of benzyl acetonyl sulfone were irradiated in 40 ml of spectral methanol at 0° for 3 hrs through Corex. The solvent was removed and the residue treated as above

except that no diazomethane was added.

b) 263 mg of benzyl acetonyl sulfone in 40 ml of spectral methanol and 9.25 g of isobutylene (20% w/v, 1/35 sulfone/olefin were irradiated at 0° through Corex for 3 hrs. The solvent was removed and the products treated as described above.

c) 323 mg of benzyl acetonyl sulfone were dissolved in 40 ml of spectral methanol. The solution was heated to boiling, then slowly cooled to 0° with oxygen bubbling through it. The solution was then irradiated at 0° through Corex for 4 hrs, with a continuous stream of oxygen bubbling through it. The solvent was removed and the products treated as described above.

d) 299 mg of benzyl acetonyl sulfone were dissolved in 40 ml of thiol free benzene and irradiated at 10° through Corex for 10 hrs. The solvent was removed and the products treated as described above.

e) 347 mg of benzyl acetonyl sulfone was irradiated in 40 ml of spectral methanol at 0° for 6 hrs. The solvent was removed under reduced pressure and the products separated by tlc (50/50 ether/benzene) to give 16.6 mg (9.2%) of the vinyl sulfonate.

f) 297 mg of benzyl acetonyl sulfone were dissolved in 100 ml of distilled isopropyl ether and irradiated in two lots at 15° through Pyrex for 2 hrs. The solvent was removed under reduced pressure and the products separated by tlc (chloroform) to give 17.9 mg (6.0%) of the vinyl

sulfonate.

The products are tabulated in Table II of the discussion.

C. Flash Thermolysis:

All melting points were obtained on a Kofler hot stage and are uncorrected. The gas IR spectra were obtained using a 100 mm NaCl cell and the liquid spectrum in a pair of 0.1 mm NaCl cells on a Beckman IR 5 or 10. The NMR spectra were done on a Varian A60 in CCl_4 or $CDCl_3$, using TMS as internal standard. The UV spectra were run on a Cary Model 14 spectrophotometer in 95% ethanol in 1.0 cm quartz cells. The vpc traces were obtained from a Varian Model 1520-1B gas chromatograph using helium as the carrier phase, with thermal conductivity detectors, and columns as indicated. The apparatus was calibrated with the various compounds over a range of concentrations of approximately the concentration of the samples to be analysed. The samples were injected into the machine either in solution with a 10 μl syringe or through a gas inlet port with helium pressurization. The vpc traces were integrated with a planimeter to obtain the peak areas.

The pyrolyses were carried out in the apparatus as described below by placing a known weight of material in the first section of the furnace. The material was then slowly sublimed through the hot zone with a small stream of nitrogen to minimize back sublimation. Any starting material which did sublime backwards was washed out, weighed, and the weight of pyrolysed material corrected for. All collection traps were cooled with liquid nitrogen. All materials pyrolysed were found to be sub-

limable unchanged under reduced pressure.

An alternative method of sulfur dioxide analysis was carried out by adding a known volume of N/10 iodine solution to the pyrolysis products in methanol, then titrating with N/10 sodium thiosulfate solution to a starch end point. The sodium thiosulfate was standardized by titrating 25 ml aliquotes of a potassium iodate solution, made from 1.0017g of anhydrous KIO_3 dissolved in 250 ml of water, plus 1g of potassium iodide.

Normality of the KIO_3 = 0.1123

Normality of the $Na_2S_2O_3 = \frac{0.1123 \times 10}{10.56} = 0.106$

The iodine solution was then standardized by titrating 5.00 ml of iodine solution with the standardized sodium thiosulfate solution to a starch end point.

Normality of the $I_2 = \frac{0.106 \times 4.710}{5.00} = 1.00$

The contact time was calculated using the following formula:

$$T = \frac{(V_r)(P_t)(t)}{(m)(0.082)(T_r)(760)}$$

where P_t = vapor pressure of the material (mmHg)

V_r = volume of the reactor (1)

T_r = reaction temperature (^oK)

t = time of reaction (sec.)

m = moles of material passed

T = contact time (sec)

A sample calculation is shown below:

$$T = \frac{(5.53 \times 10^{-3})(10^{-1})(7.2 \times 10^{2})}{(10^{-3})(0.082)(1.22 \times 10^{3})(760)}$$

$$= 5.2 \times 10^{-3} \text{ seconds}$$

It should be noted that this is an upper limit of the contact time since the pressure used is that of the inlet, and may not be the true pressure within the reactor itself. A more accurate estimation of the contact time is probably about one millisecond.

Pyrolysis Apparatus:

The pyrolysis apparatus consisted of two basic units; the furnace, and the collector(s).

A. The furnace unit was made up of a brass cylinder 11 inches long by $2\frac{1}{2}$ inches in diameter and 1/8 inches thick, which was wrapped with about nine coils of $\frac{1}{4}$ inch copper tubing through which cold water was circulated. To the ends of this cylinder were attached two 3/8 inch brass flanges five inches in diameter. An end plate which had a $\frac{1}{2}$ inch O ring connector, a Hastings gauge, and two pairs of metal to porcelain through connectors attached, was bolted to one end of the cylinder. A second plate with a one inch O ring butt connector was bolted to the other end. Both end plates were sealed vacuum tight to the flanges by means of 1/8 inch Viton O rings.

A reactor tube was inserted through the $\frac{1}{2}$ inch O ring connector into the cylinder. This tube consisted of an inner 1/8 inch ID porcelain thermocouple well and an outer $\frac{1}{2}$ inch OD porcelain tube. The two tubes are fused to Pyrex glass of the same diameter which are joined together at the inlet end outside the end plate,

whereas the opposite end of the inner tube is closed and the outer tube open. A 1/8 inch stainless steel shielded, MgO insulated chromel-alumel thermocouple was placed inside the thermocouple well and attached to a Barber-Coleman Model 471 temperature controller.

The first four inches of the outer tube were wound with six feet of 22 gauge Nichrome wire spaced between turns of 1/8 inch asbestos rope and covered with a layer of asbestos sheeting. The last four inches within the cylinder were loosely wound with an additional four feet of the same wire. The end of both windings were attached to separate pairs of through connectors which were in turn attached on the outside to separate Variacs that regulated the temperatures.

At the end of the reactor tube, which was outside the cylinder, was attached a Teflon needle valve through which could be introduced a stream of nitrogen and/or calibrating compounds, solvents, and trapping compounds.

The pyrolysis tube was inserted into the outer cylinder through the O ring connector at one end, which was vacuum tight, and extended through the O ring butt connector at the opposite end by about $\frac{1}{2}$ inch.

B. Several types of traps were employed depending on the nature of the material being collected.

For liquids, either a Pyrex cold finger attached to the O ring butt connector, with the cold face 2.5 cm from the end of the pyrolysis tube, or a U tube cooled in a Dewar of liquid nitrogen, was employed.

For gases, a combination of the cold finger and either a 75 ml stainless steel bomb, filled with 3/16 inch stainless steel balls, or a stoppered Pyrex U tube was employed.

C. The whole apparatus was evacuated using a Welch Model 1403 mechanical pump and a Consolidated Vacuum Corporation Model VMF-20 water cooled oil diffusion pump. The vacuum was monitored at both the furnace and the pump, using a Hastings gauge with several stations.

A typical pyrolysis was carried out as follows. The solid sample was weighed out and placed in an aluminium foil package into the pyrolysis tube under the first heater and the apparatus assembled. When the operating vacuum had been attained, the traps were filled with liquid nitrogen and the furnace heated to the desired temperature. The compound was then sublimed through the hot section by controlled heating of the first section with a slow stream of nitrogen passing through. During this time the pressure at both the pump and furnace were monitored.

In the case of liquid products, a calibrating compound of known wieght was added to the products and the mixture washed out for vpc analysis. For gases, a calibrating compound was added through the inlet valve and the gases then distilled from the cold finger into the second trap. This trap was then removed and the gases distilled from it into an evacuated 250 ml stainless steel bomb by cooling the latter in liquid nitrogen.

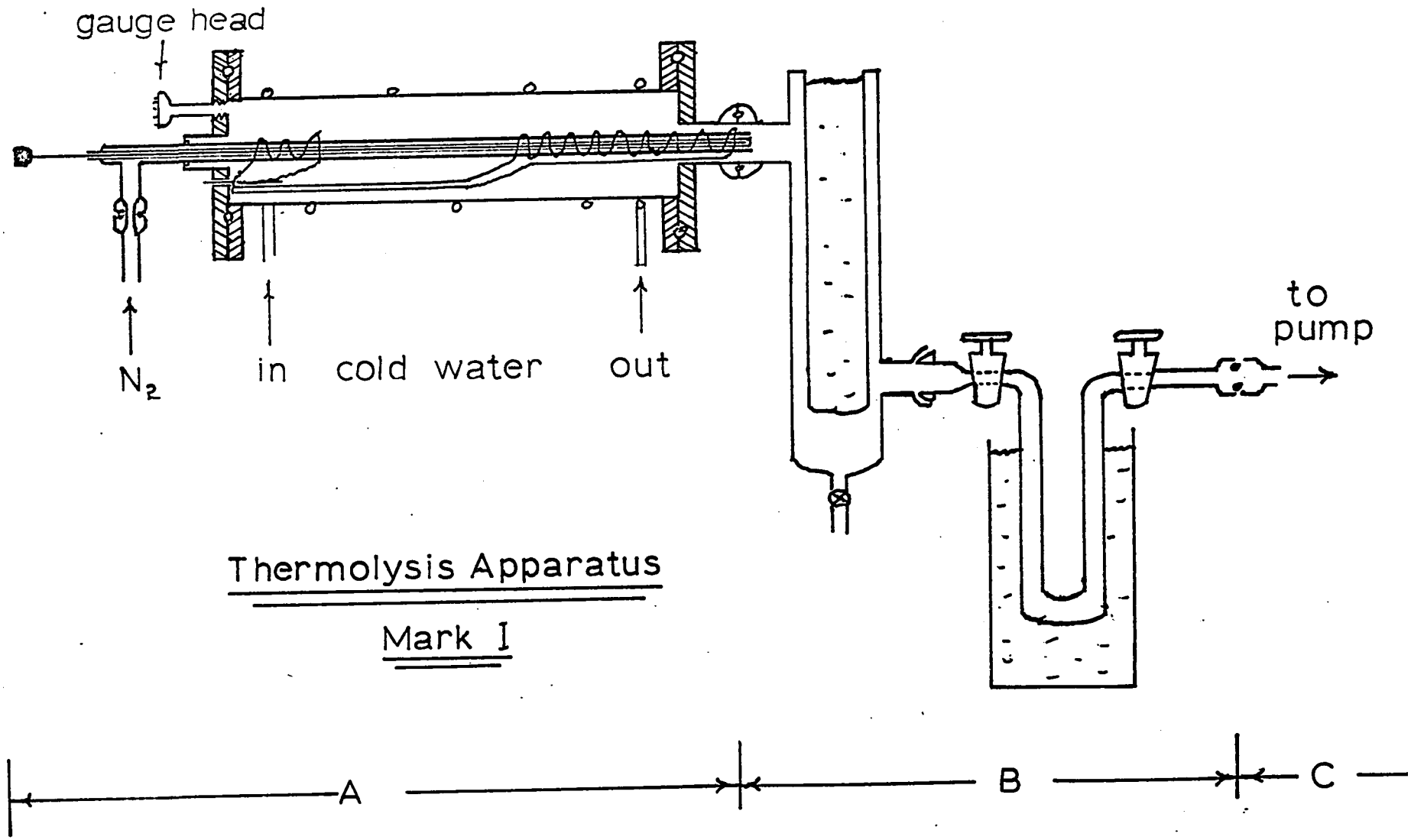

gauge head
N_2
in
cold water
out
to pump
Thermolysis Apparatus
Mark I
A
B
C

Figure 7

Temperature Profile

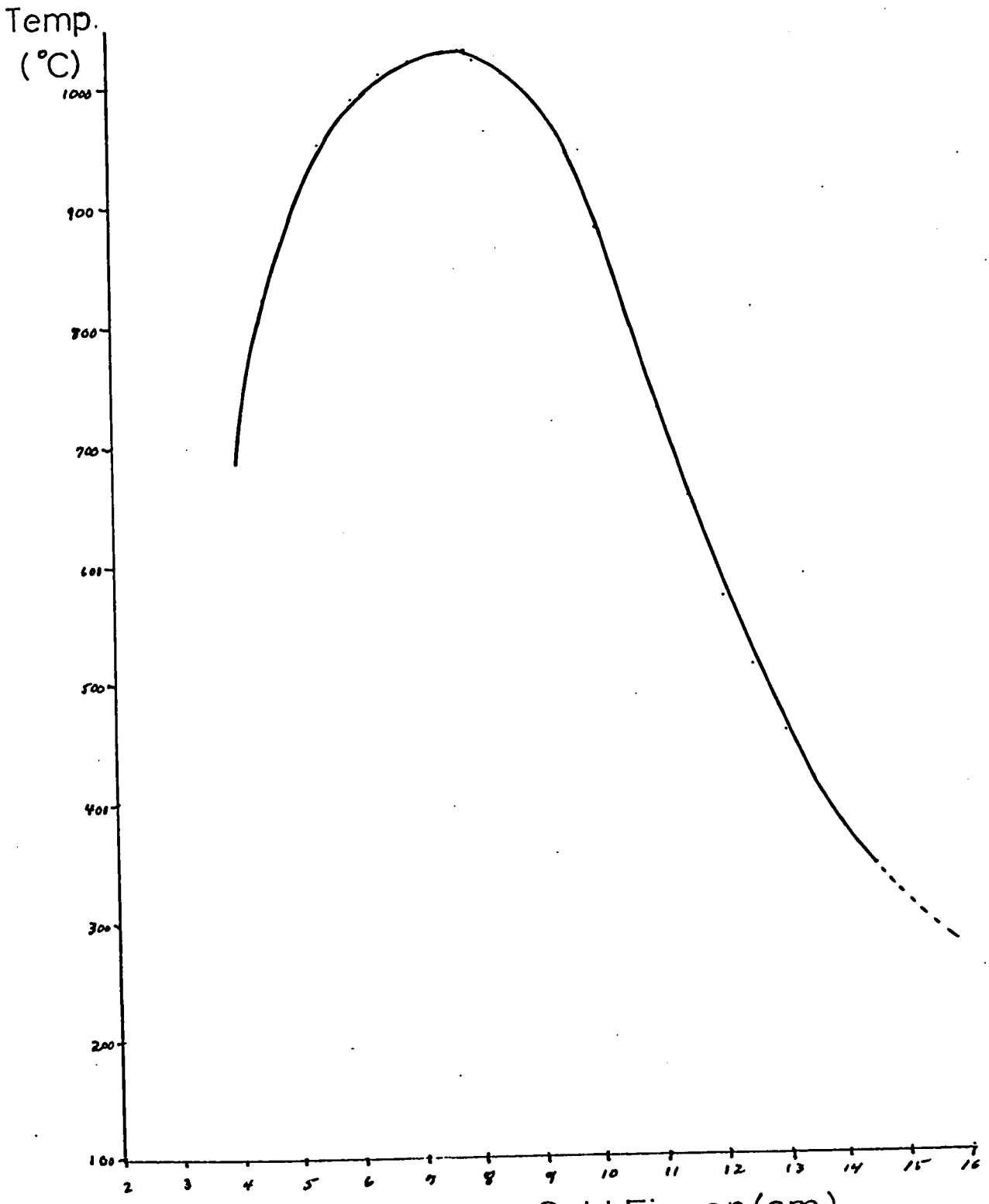


Figure 8

When the transfer was complete, the bomb was warmed and pressurized to about 30 psi with helium.

Preparation of 3-Thietanone 1,1-Dioxide:

A. To 10g of ketene dimethoxy acetal[143] in 150 ml of anhydrous ether containing 19.5g of triethylamine at 0° were added 13g of methanesulfonyl chloride in 50 ml of anhydrous ether dropwise. The solution was stirred an additional 3 hrs, then the solvent removed under reduced pressure. The product was dissolved in 200 ml of CH_2Cl_2 and washed with 100 ml of 10% HCl, twice with 100 ml portions of water, then dried over $MgSO_4$, filtered, and the solvent removed to give 14g of crude product. Two recrystallizations from CH_2Cl_2 gave 8.5g (45%) of 3,3-dimethoxy thietane 1,1-dioxide, m.p. 159-60°, $\nu_{max}^{CHCl_3}$ = 1335, 1092 (SO_2) cm^{-1}, $\delta(CDCl_3)$ = 3.25 (6H,s), 4.15 (4H, s).

Analysis: Calc. for $C_5H_{10}O_4S$, C 36.15%, H 6.07%:
Found, C 36.24%, H 6.01%.

B. The reaction of ketene diethoxy acetal[144] in an analogous manner[143] with triethylamine and methanesulfonyl chloride gave 3,3-diethoxy thietane 1,1-dioxide, m.p. 49-50° (lit. m.p. 49-50°[95]).

Hydrolysis of either of these ketals was carried out[95] by dissolving 8g of the ketal in 40 ml of concentrated HCl with stirring at room temperature for 12 hrs. The resulting precipitate was filtered and recrystallized from dioxane to give 6g (85%) of 3-thietanone 1,1-dioxide, m.p. 217-19° (lit. m.p. 219-21°[95]), $\delta(CD_3COCD_3)$ = 5.08 (s).

Preparation of 3-Thietanol 1,1-Dioxide:

4.7g of 3-thietanone 1,1-dioxide were reduced with an excess of biborane in anhydrous tetrahydrofuran as described by Truce[96]. The solvent was evaporated to dryness after 10 ml of water had been added, and the product recrystallized from ethanol/pentane to give 3.5g (74%) of 3-thietanol 1,1-dioxide, m.p. 98-99° (lit. m.p. 99.5-102°[96]).

Preparation of Thiete 1,1-Dioxide:

Using the method of Smith,[99] 4.5g of 3-thietanol 1,1-dioxide plus 8.0g of ∝-toluenesulfonyl chloride were dissolved in 100 ml of anhydrous tetrahydrofuran at 0° and 8g of triethylamine in 25 ml of tetrahydrofuran added dropwise. The mixture was stirred overnight, then 100 ml of 10% HCl added and the solution extracted twice with 100 ml portions of CH_2Cl_2. The combined CH_2Cl_2 layers were dried over $MgSO_4$, filtered, and the solvent evaporated to give 3.0g (27%) of 3-thietanol 1,1-dioxide benzylsulfonyl ester after recrystallization from $CHCl_3$/petro (60-80°), m.p. 183-84°, $\nu_{max}^{CHCl_3}$ = 1318, 1115, 977 (SO_2 and SO_3R) cm^{-1}.

Analysis: Calc. for $C_{10}H_{12}O_5S_2$, C 43.48%, H 4.38%, S 23.17%;
Found, C 43.47%, H 4.13%, S 23.15%.

2.7g of this ester were dissolved in 100 ml of dry benzene at 60°, then 8g of triethylamine were added in 30 ml of benzene dropwise over 30 min. The solution was cooled in the refrigerator overnight and the crystalline sulfonamide filtered off. The solvent was then evaporated

from the filtrate and the product recrystallized from ether to give 0.90g (95%) of 2-thiete 1,1-dioxide, m.p. 47-49° (lit. m.p. 48-50°[100]), $\delta(CDCl_3)$ = 4.74 (2H,d,J = 1.5 cps), 7.02 (1H,d,J = 4 cps), 7.45 (1H,d of d,J_{AX} = 1.5 cps, J_{XY} = 4 cps).

Preparation of Thietane 1,1-Dioxide:

0.493g of 5% palladium on barium carbonate were prehydrogenated in 20 ml of 95% ethanol for one-half hour. To this was then added 0.800g of thiete 1,1-dioxide and the material hydrogenated until 170 ml (1 equivalent) of hydrogen taken up. The catalyst was filtered off and the solvent removed under reduced pressure to give 0.790g of crude thietane 1,1-dioxide. Recrystallization from ethyl acetate gave 0.400g of pure material, m.p. 73-74°, (lit. m.p. 75.5-76.0°[101]). The mother liquors were evaporated and the residue sublimed at 70°/0.02 mm to give a further 0.100g of material, m.p. 72.5-73.5°, $\nu_{max}^{CHCl_3}$ = 1235, 1135 (SO_2) cm^{-1}, $\delta(CDCl_3)$ = 1.24 (2H,m), 4.30 (4H,m).

Preparation of 3,3-Diethoxy-2-Phenyl Thietane 1,1-Dioxide:

18g of ketene diethoxy acetal and 17g of triethylamine were dissolved in 100 ml of anhydrous ether at 0° and 25g of α-toluenesulfonyl chloride in 500 ml of ether added dropwise with stirring as described by Truce[95]. The solution was stirred overnight and the precipitate filtered off. The solvent was removed under vacuum and the products recrystallized from hexane to give 20g (52%) of 3,3-diethoxy-2-phenyl thietane 1,1-dioxide, m.p. 90-

91° (lit. m.p. 89-90°[95]).

Preparation of 2-Phenyl 3-Thietanone 1,1-Dioxide:

10g of this ketal were dissolved in 100 ml of concentrated HCl at room temperature and stirred for 18 hours. The crystalline precipitate (8.2g) which contained two compounds, was filtered off and titrated with 50 ml of chloroform, then crystallized from benzene/dioxane to give 5.6g (71%) of 2-phenyl 3-thietanone 1,1-dioxide, m.p. 172-74°, ν_{max}^{nujol} = 1680 (C = C), 1265, 1105 (SO_2) cm^{-1}, $\delta(CD_3COCD_3)$ = 7.92 (5H,m), 4.55 (2H,s), λ_{max}^{EtOH} = 265 nm (ϵ 13,200).

Analysis: Calc. for $C_9H_8O_3S$, C 55.10%, H 4.11%, S 16.31%;
Found, C 55.11%, H 4.13%, S 16.23%.

The chloroform soluble portion was separated on 20g of silica gel with $CHCl_3$ as eluent to give 0.5g (6%) of 3-ethoxy-2-phenyl 2-thiete 1,1-dioxide, m.p. 132.0-32.5°, (lit. m.p. 132°[96]), $\delta(CDCl_3)$ = 1.40 (3H,t,J = 7 cps), 4.15 (4H,q,J = 7 cps), 4.57 (2H,s), 7.40 (5H,m).

Some of the 2-phenyl 3-thietanone 1,1-dioxide was treated with diazomethane giving an instantaneous reaction which yielded on recrystallization from CCl_4/petrol (60-80°), 3-methoxy-2-phenyl 2-thiete 1,1-dioxide, m.p. 132.0-32.5°, $\nu_{max}^{CHCl_3}$ = 1662 (C = C), 1307, 1117 (SO_2) cm^{-1}, $\delta(CDCl_3)$ = 3.90 (3H,s), 4.59 (2H,s), 7.39 (5H,m), λ_{max}^{EtOH} = 264 nm (ϵ 14,500).

Analysis: Calc. for $C_{10}H_{10}O_3S$, C 57.14%, H 4.80%, S 15.22%;
Found, C 57.69%, H 5.02%, S 15.11%.

Attempted Reduction of 2-Phenyl 3-Thietanone 1,1-Dioxide:

2.0g of 2-phenyl 3-thietanone 1,1-dioxide were dissolved in 20 ml of anhydrous tetrahydrofuran and an excess of diborane added. After 3 hrs, the reaction was quenched with 10 ml of water and the solution extracted with CH_2Cl_2. The hydrocarbon layer was dried over $MgSO_4$, filtered, and the solvent evaporated to give 2.2g of white $CHCl_3$ insoluble material, m.p. 110-20°, ν_{max}^{nujol} = 3400 (OH), 1340 (C-B) cm^{-1}. Attempted decomposition of this material with cold HCl, $NaCO_3$, and dilute acetic acid were unsuccessful, however, when refluxed in concentrated acetic acid for 3 hours; it partially decomposed. None of the desired alcohol was found, however, as determined by the infrared absorption.

Bromination of 2-Phenyl 3-Thietanone 1,1-Dioxide:

a) 242 mg of 2-phenyl 3-thietanone 1,1-dioxide plus 306 mg of sodium acetate were treated with a slight excess of bromine. The solution was immediately filtered and evaporated to dryness. The product was recrystallized from CCl_4 to give 250 mg (58%) of 4,4-dibromo-2-phenyl 3-thietanone 1,1-dioxide, m.p. 117-18°, melts and recrystallizes, melting at 142-43°, $\nu_{max}^{CHCl_3}$ = 3500 (OH), 1670 (C = C) cm^{-1}, $\delta(CDCl_3)$ = 7.50 (5H,m), 8.50 (1H,m, which disappeared on the addition of D_2O).

Analysis: Calc. for $C_9H_6Br_2O_3S$, C 29.70%, H 1.65%, S 9.06%;
Found, C 30.49%, H 1.81%, S 8.92%.

b) 140 mg of 2-phenyl 3-thietanone 1,1-dioxide were

treated in 50 ml of $CHCl_3$ with an excess of bromine for 12 hrs. The solvent was removed under vacuum to give 321 mg of 2-phenyl-2,4,4-tribromo 3-thietanone 1,1-dioxide, $\nu_{max}^{CHCl_3}$ = 1790, 1800 (C = O), 1370, 1165 (SO_2) cm^{-1}, $\delta(CDCl_3)$ = 7.45 (m).

c) 72.7 mg of 2-phenyl 3-thietanone 1,1-dioxide in 50 ml of $CHCl_3$ were treated with an excess of bromine for 5 minutes. The solvent and excess bromine were removed under vacuum to give a mixture of 4,4-dibromo and 2,4,4-tribromo-2-phenyl 3-thietanone 1,1-dioxide as identified by infrared, NMR, and tlc.

Attempted Hydrogenation of 2-Phenyl 3-Thietanone 1,1-Dioxide:

Several attempts were made at hydrogenating this compound at atmospheric and higher pressures with a variety of catalysts and solvents. The conditions and results are listed in Table IV below.

Table IV

Catalyst	Solvent	Pressure	Time	Products
5% Pd/C	EtOH	50 psi	20 hrs	$PhCH_2SO_2CH_2CO_2Et$
5% Pd/C	HOAc	50 psi	24 hrs	starting material
5% Pd/C + $BaCO_3$	EtOAc	50 psi	22 hrs	starting material
Pt_2O	EtOH	1 atm	2 hrs	$PhCH_2SO_2CH_2CO_2Et$
Pt_2O	HOAc	1 atm	48 hrs	starting material
Pt_2O	HOAc	50 psi	3 hrs	starting material

Preparation of 3-Acetyl-2-Phenyl 2-Thiete 1,1-Dioxide:

179 mg of 2-phenyl 3-thietanone 1,1-dioxide were reacted with 2 ml of acetic anhydride and 2 ml of pyridine at room temperature for 18 hours. The pyridine and excess acetic anhydride were removed under vacuum, then 20 ml of water was added. The solution was extracted twice with 40 ml portions of CH_2Cl_2, the combined methylene chloride layers dried over $MgSO_4$, filtered, and the solvent removed under reduced pressure. The products were separated by tlc using ethyl acetate to give 49.2 mg (23%) of 3-acetyl-2-phenyl 2-thiete 1,1-dioxide, m.p. 145-46° after recrystallization twice from CH_2Cl_2/petrol (60-80°), $\nu_{max}^{CHCl_3}$ = 1795 (C = O), 1665 (C = C), 1315, 1112 (SO_2) cm^{-1}, $\delta(CDCl_3)$ = 2.38 (3H,s), 4.95 (2H,s), 7.47 (5H,s).

Attempted Hydrogenation of the Enol Acetate:

Attempted hydrogenation of the 3-acetyl-2-phenyl 2-thiete 1,1-dioxide in either ethyl acetate or acetic acid at atmospheric pressure over Pt_2O gave no reaction.

Preparation of 2-Phenyl 2-Thiete 1,1-Dioxide:

10g of 2-phenyl-N,N-dimethyl ethyleneamine[145] in 100 ml of anhydrous ether containing 12.2g of triethylamine were cooled to 0° and 7.3g of methanesulfonyl chloride in 20 ml of ether added dropwise. The solution was stirred overnight, the triethylamine hydrochloride was filtered off, and the solvent evaporated to give 14.4g of 3-(N,N-dimethyl)amino-2-phenyl thietane 1,1-dioxide, after recrystallization from CH_2Cl_2/petrol (60-80°), m.p.

124-24° (lit. m.p. 116-17°(90)).

1g of this amine was dissolved in 50 ml of methanol/chloroform mixture and 0.85 ml (3 fold excess) of methyl iodide added. After 24 hours, the white crystals which formed were filtered to give 1.05g (64%) of 3-(trimethyl)-amino-2-phenyl thietane iodide, m.p. 212°.

3g of the salt were dissolved in 120 ml of water and 3g of Ag_2O added. The resultant trimethylamine was removed under reduced pressure with warming as needed, then the aqueous solution filtered and extracted twice with 50 ml portions of CH_2Cl_2. The combined CH_2Cl_2 layers were dried over $MgSO_4$, filtered, and the solvent removed. The product was recrystallized from CH_2Cl_2/petrol (60-80°) to give 1.1g (74%) of 2-phenyl 2-thiete 1,1-dioxide, m.p. 94.5-95.0° (lit. m.p. 96°(90)), $\nu_{max}^{CHCl_3}$ = 1310, 1140 (SO_2) cm^{-1}, $\delta(CDCl_3)$ = 4.50 (2H,d,J = 2 cps), 7.02 (1H, t,J = 2 cps), 7.46 (5H,s).

Analysis: Calc. for $C_9H_8O_2S$, C 60.00%,H 4.48%, S 17.77%;
Found, C 60.07%,H 4.41%, S 17.98%.

This material was identical in physical data with that reported by Wells and Abbott(90), who prepared it by a different method.

Preparation of 2,2-Dimethyl 3-Thietanone 1,1-Dioxide:

12g of 2,2-dimethyl-1-(N,N-dimethyl)amino-1-ethoxy ethylene(146) and 9g of triethylamine were dissolved in 100 ml of ether at 0° and 10g of methanesulfonyl chloride in 30 ml of ether added dropwise as described by

Martin[147]. The mixture was stirred overnight, then filtered, and the solvent removed under vacuum. The residue was dissolved in 50 ml of water and 10g of 50-X2 (H^+) added. After being stirred overnight, the mixture was filtered and the water evaporated under vacuum. The product was recrystallized from benzene to give 1g (7%) of 2,2-dimethyl 3-thietanone 1,1-dioxide, m.p. 110.0-10.5° (lit. m.p. 108-10°[147]), $\delta(CDCl_3)$ = 1.67 (6H,s), 4.90 (4H,s).

Preparation of 2,2-Dimethyl 3-Thietanol 1,1-Dioxide:

180 mg of 2,2-dimethyl 3-thietanol 1,1-dioxide were treated with an excess of diborane in anhydrous tetrahydrofuran in a manner analogous to that used by Truce.[96] The excess was quenched with 20 ml of water and the solution extracted twice with 30 ml portions of CH_2Cl_2. The combined CH_2Cl_2 layers were dried over $MgSO_4$, filtered, and the solvent evaporated to give 112 mg (62%), after recrystallization from CH_2Cl_2/petrol (60-80°), of 2,2-dimethyl 3-thietanol 1,1-dioxide, m.p. 107-08°, $\nu_{max}^{CHCl_3}$ = 3600 (OH), 1310, 1195 (SO_2) cm^{-1}, $\delta(CDCl_3)$ = 1.52 (3H, s), 1.56 (3H,s), 2.96 (1H, broad singlet which disappeared on addition of D_2O), 3.7 to 4.6 (3H, series of multiplets).

Analysis: Calc. for $C_5H_{10}O_3S$, C 40.00%, H 6.71%, S 21.34%;
Found, C 40.02%, H 6.24%, S 21.30%.

Preparation of 2,2-Dimethyl 3-Thiete 1,1-Dioxide:

10g of 1-N,N-dimethyl)amino-2-methyl-propene[148] and 12g of triethylamine were dissolved in 100 ml of anhydrous ether at 0° and 6g of methanesulfonyl chloride in 50 ml of ether added dropwise as described by Truce[95]. The mixture was stirred overnight, then the precipitate filtered off and the solvent removed from the filtrate under vacuum to give 16.7g of crude 3-(N,N-dimethyl)-amino-2,2-dimethyl thietane 1,1-dioxide.

11.2g of the crude amine was dissolved in 120 ml of methanol and 20 ml of methyl iodide added. After 24 hours, the resulting white crystals were filtered, yielding 10.3g (30%) of 1-(N,N,N-trimethyl)amino-2,2-dimethyl thietane 1,1-dioxide iodide, m.p. 215° (lit. m.p. 210-11°[91]).

8.4g of the salt were dissolved in 60 ml of water and 10g of Ag_2O added. The resulting trimethylamine was removed under reduced pressure with warming as necessary. The solution was filtered, extracted 3X with 50 ml portions of CH_2Cl_2. The combined CH_2Cl_2 layers were dried over $MgSO_4$, filtered, and the solvent evaporated. The product was recrystallized from ether/petrol (60-80°) to give 2.0g (53%) of 2,2-dimethyl 3-thiete 1,1-dioxide, m.p. 39-40° (lit. m.p. 41-42°[91]), $\delta(CCl_4)$ = 1.61 (6H, s), 6.78 (1H,d,J = 4 cps), 7.09 (1H,d,J = 4 cps).

Preparation of 2,2-Dimethyl Thiete 1,1-Dioxide:

640 mg of 2,2-dimethyl thiete 1,1-dioxide were dissolved in 50 ml of 95% ethanol and 100 mg of Pd/C added. This mixture was hydrogenated at atmospheric pressure until 125 ml of hydrogen had been absorbed (1 equivalent). The catalyst was filtered off and the solvent removed under reduced pressure to give 625 mg of crude product, m.p. 61-62°. This material was sublimed at 60°/0.2 mm to yield 580 mg (90%) of 2,2-dimethyl thietane 1,1-dioxide, m.p. 70-71°, $\nu_{max}^{CCl_4}$ = 1323, 1128 (SO_2) cm^{-1}, $\delta(CCl_4)$ - 1.57 (6H,s), A_2X_2 pattern at $\delta_A = 4.14$, $\delta_X = 6.57$, $J_{AA'}$= -18.59 cps, $J_{XX'}$ =-17.70 cps, $J_{AX} = 6.48$ cps, $J_{AX'}$ = 10.43 cps, $J_{A'X} = 10.43$ cps, and $J_{A'X'} = 6.48$ cps.

Analysis: Calc. for $C_5H_{10}O_2S$, C 44.77%, H 7.52%, S 23.85%;
Found, C 44.81%, H 7.36%, S 23.76%.

The NMR spectrum was calculated using a LAOCOON III computer program with iteration.(106)

Attempted Oxidation of 3-(N,N-dimethyl)Amino-2,2-Dimethyl Thietane 1,1-Dioxide:

853 mg of 3-(N,N-dimethyl)amino-2,2-dimethyl thietane 1,1-dioxide were dissolved in 30 ml of 5% aqueous acetic acid and 6.99g of mercuric acetate added. The solution was heated to 70° in an oil bath for 14 hours, then cooled and the crystalline mercurous acetate filtered off. The filtrate was neutralized with $NaHCO_3$, then extracted 3X with 50 ml portions of CH_2Cl_2. The combined CH_2Cl_2 layers were dried over $MgSO_4$, filtered, and the solvent

removed to give 607 mg of a material whose infrared showed it to be a salt. This material was dissolved in 30 ml of water and stirred at room temperature for 15 hours with 10g of Dowex 1-2X (OH^-). The resin was filtered off and the solvent evaporated under vacuum. The residue was recrystallized twice from ether/petrol (60-80°) tc give 326 mg (45%) of 2,2-dimethyl-3-(N-methyl)amino thietane 1,1-dioxide, m.p. 49-50°, $\nu_{max}^{CHCl_3}$ = 3340 (NH), 1310, 1105 (SO_2) cm^{-1}, $\delta(CDCl_3)$ = 1.48 (3H, s), 1.58 (3H,s), 2.40 (3H,s), and an ABX pattern at δ_A= 3.70, δ_B= 4.15, δ_X= 3.16, J_{AB}= 12.91 cps, J_{AX}= 5.66 cps, J_{BX}=8.42 cps.

Analysis: Calc. for $C_6H_{13}NO_2S$, C 44.16%, H 8.03%, S 8.58%;
Found, C 44.31%, H 8.05%, S 8.52%.

Preparation of 2,2-Diphenyl-3,3-Dimethoxy Thietane 1,1-Dioxide:

2.0g of diphenyldiazomethane[149] and 2.0g of dimethoxy ketene acetal were dissolved in 50 ml of anhydrous ether at 0°. The system was flushed with nitrogen, then anhydrous sulfur dioxide bubbled into the solution until the red colour of the diazomethane had completely disappeared. The crystalline white precipitate which formed was filtered to give 1.8g (49%) of pure 2,2-diphenyl-3,3-dimethoxy thietane 1,1-dioxide, m.p. 155-56.0°. The solvent was evaporated and the residue recrystallized from CCl_4 to give an additional 350 mg of product (total yield 68%), $\nu_{max}^{CHCl_3}$ = 1330, 1110 (SO_2) cm^{-1}, $\delta(CDCl_3)$=

3.17 (6H,s), 4.41 (2H,s), 7.35 (10H,s).

Analysis: Calc. for $C_{17}H_{18}O_4S$, C 64.14%, H 5.70%, S 10.05%;
Found, C 64.21%, H 5.44%, S 10.00%.

Preparation of 3,3-Diethoxy-2,2-Diphenyl Thietane 1,1-Dioxide:

4g of diphenyldiazomethane and 4g of diethoxyketene acetal were dissolved in 100 ml of anhydrous ether and sulfur dioxide bubbled through as before until the red colour was completely gone. The mixture of crystals and liquid was evaporated to dryness under reduced pressure and the product recrystallized from CH_2Cl_2/petrol (60-80°) to give 2.6g (32%) of 3,3-diethoxy-2,2-diphenyl thietane 1,1-dioxide, m.p. 128-29°, $\nu_{max}^{CCl_4}$ = 1335, 1095 (SO_2) cm^{-1}, $\delta(CCl_4)$ = 0.95 (10H,t,J = 7 cps), 3.35 (4H, m), 4.29 (2H,s), 7.30 (10H,s).

Analysis: Calc. for $C_{19}H_{22}O_4S$, C 65.88%, H 6.40%, S 9.24%;
Found, C 66.09%, H 6.35%, S 9.26%.

Hydrolysis of 3,3-Diethoxy-2,2-Diphenyl Thietane 1,1-Dioxide:

746 mg of the diethoxy ketal were dissolved in a 50/50 mixture of HCl/dioxane at 70° and heated for 15 hours. The solvent was removed under vacuum to give 726 mg of material whose infrared had absorption at 1710 to 1730 cm^{-1} and no SO_2 absorption. The products were separated on 20g of silicic acid using benzene as eluent to give 372 mg (70%) of 3-chloro-1,1-diphenyl-2-propanone, m.p. 70.5-71.0° after recrystallization from ethanol (lit.

m.p. 71°(150), $\nu_{max}^{CCl_4}$ = 1745, 1735 (C = O) cm^{-1}, $\delta(CCl_4)$= 4.04 (2H,s), 5.43 (1H,s), 7.23 (10H,s); and 70 mg (13%) of 1-chloro-1,1-diphenyl-2-propanone, m.p. 65-66° (lit. m.p. 65-66°(151), $\nu_{max}^{CCl_4}$ = 1720 (C = O) cm^{-1}, $\delta(CCl_4)$ = 2.18 (3H,s), 7.30 (10H,s).

Hydrolysis of 3,3-Dimethoxy-2,2-Diphenyl Thietane 1,1-Dioxide:

270 mg of the dimethoxy ketal were dissolved in 10 ml of cold 90% sulfuric acid. The solution was kept cool for 2 hours, then poured onto 40 ml of ice water and extracted 3X with 25 ml portions of CH_2Cl_2. The combined CH_2Cl_2 layers were dried over $MgSO_4$, filtered, and the solvent evaporated to give 207 mg of product which was separated by tlc using 50/50 ether/benzene. The product, R_f= 0.3, was recrystallized from CH_2Cl_2/petrol (60-80°) to yield 85 mg (37%) of 2,2-diphenyl-3-methoxy 3-thiete 1,1-dioxide, m.p. 164-66°, $\nu_{max}^{CHCl_3}$ = 1615 (C = C) cm^{-1}, $\delta(CDCl_3)$ = 3.81 (3H,s), 5.81 (1H,s), 7.41 (10H,m), ϵ_{205}^{EtOH} = 10,100.

Analysis: Calc. for $C_{16}H_{14}O_3S$, C 67.12%, H 4.93%, S 11.18%;
Found, C 67.11%, H 4.91%, S 11.07%.

Attempted Hydrolysis in Hydrochloric acid:

1g of the dimethoxy ketal was suspended in 40 ml of concentrated HCl and stirred at room temperature for 72 hours. The solvent was removed under aspirator vacuum to give a mixture of starting material, 3-chloro-1,1-diphenyl-2-propanone, and 1-chloro-1,1-diphenyl-2-propanone, as identified from the NMR of the product mixture,

in the ratio of 0.4/1.7/1.0.

Similarly 240 mg were heated in 50 ml of 50/50 mixture of HCl/dioxane at 60° for 4 hours. The solution was cooled, then extracted twice with 40 ml portions of CH_2Cl_2, the combined CH_2Cl_2 layers were dried over $MgSO_4$, filtered, and the solvent evaporated to give a mixture of starting material, 2,2-diphenyl-3-methoxy 3-thiete 1,1-dioxide, 3-chloro-1,1-diphenyl-2-propanone, and 1-chloro-1,1-diphenyl-2-propanone, as determined by NMR, in the ratios of 0.5/1.1/1.6/1.0.

Preparation of 2,2-Diphenyl-3-Morpholino 3-Thiete 1,1-Dioxide:

1.5g of 3,3-dimethoxy-2,2-diphenyl thietane 1,1-dioxide were dissolved in 20 ml of freshly distilled morpholine and heated to 95° for 6 hours. The solvent was removed under vacuum and the product recrystallized twice from CCl_4 to give 1.23g (76%) of 2,2-diphenyl-3-morpholino 3-thiete 1,1-dioxide, m.p. 166-67°, $\nu_{max}^{CHCl_3}$ = 1345, 1180 (SO_2) cm^{-1}, $\delta(CDCl_3)$ = 3.05 (4H,q,J = 2.5 cps), 3.49 (4H,q,J = 2.5 cps), 5.34 (1H,s), 7.50 (10H,m).

Analysis: Calc. for $C_{19}H_{19}O_3S.H_2O$, C 63.75%, H 5.89%, S 3.90%;

Found, C 63.75%, H 5.87%, S 4.33%.

Attempted Hydrolysis of 2,2-Diphenyl-3-Morpholine 3-Thiete 1,1-Dioxide:

a) 217 mg of the thiete 1,1-dioxide were dissolved

in 40 ml of a 50/50 mixture of dioxane/water and 4.5g of Dowex 50-2X (H^+) added. The mixture was stirred for 20 hours at room temperature, then the resin filtered off and the solvent removed under vacuum to give 127 mg (58%) of starting material as the only recovered product. This material was identified by infrared and tlc comparison.

b) 236 mg of the thiete 1,1-dioxide were dissolved in 20 ml of concentrated HCl for 24 hours at room temperature. The solvent was removed under vacuum, and the residue dissolved in 20 ml of CH_2Cl_2 and washed with 20 ml of water. The CH_2Cl_2 layer was dried over $MgSO_4$, filtered, and the solvent evaporated to give 44 mg of material whose infrared showed no C=O or SO_2, only aromatic absorption.

Evaporation of the water layer under vacuum gave 107 mg of morpholine hydrochloride, identical (infrared) with a sample prepared from morpholine and dilute HCl.

Attempted Preparation of 2,2-Diphenyl Thiete 1,1-Dioxide:

25g of 2,2-diphenylacetaldehyde were dissolved in 200 ml of anhydrous ether at 0° and 10g of dimethylamine added slowly. 100g of anhydrous $CaCl_2$ were then added and the mixture left at room temperature for 24 hours. The solid material was filtered off and the solvent evaporated to give 15g (56%), after recrystallization from ether, of 1-(N,N-dimethyl)amino-2,2-diphenyl ethylene, m.p. 75-78°, $\nu_{max}^{CCl_4}$ = 1615, 1590, 900 cm^{-1}, $\delta(CCl_4)$ = 2.58 (1H,s), 7.05 (5H,s), 7.21 (5H,s).

5.0g of the enamine plus 4.7g ofttriethylamine were dissolved in 100 ml of anhydrous ether at 0°, and 20g of methanesulfonyl chloride in 25 ml of ether added dropwise. The mixture was stirred for 8 hours at room temperature, then filtered off and the solvent removed to give 4.6g of enamine as the only product, m.p. 74-77°.

Pyrolysis of Thietane 1,1-Dioxide:

a) Approximately 80 mg of thietane 1,1-dioxide were pyrolysed at 465, 595, and 765° at about 100 μ pressure with a U tube trap. The products were washed out with 1 ml of chloroform and the infrared absorption examined. The only non gaseous material observed was starting material in 92.5%, 78.6%, and 36.5% yields respectively.

b) Approximately 90 mg of thietane 1,1-dioxide were pyrolysed at 950° at 100 μ pressure with a cold finger and gas U tube traps. On completion of the pyrolysis, the reactor was allowed to cool, the 5.0 ml of propane added with a gas syringe to the products. The mixture was analysed by vpc (5'x3/16", 10% Ethofat on Chromsorb P at 100° and 50cc/min.) The products were identified by infrared and vpc retention times as ethylene, propylene, and sulfur dioxide by comparison with authentic samples. The yields are given in Table I of the discussion.

Pyrolysis of 2,2-Dimethyl Thietane 1,1-Dioxide:

a) Approximately 100 mg of this material were pyrolysed at 950° and 120 μ pressure using a U tube trap. On completion of the pyrolysis, a known weight of methyl

formate (approximately 40 mg) was added and the products washed out with 1 ml of ethyl acetate. The products were analysed by vpc (5'x3/16", Porapak S at 150° and 50 cc/min.) The products were identified by infrared, NMR, and vpc retention times as 2-methyl-2-butene, 3-methyl-1-butene, 2-methyl-1-butene, and sulfur dioxide by comparison with authentic samples. Considerable amounts of white polymer were also found in the U tube.

b) Approximately 90 mg of 2,2-dimethyl thietane 1,1-dioxide were pyrolysed at 465° and 610° at 180 μ pressure with a U tube trap. The products were washed out with chloroform and the infrared absorption taken. The only recovered material was starting material in 71% and 40% yields respectively.

Pyrolysis of 3-Thietanone 1,1-Dioxide:

Approximately 180 mg of 3-thietanone 1,1-dioxide were pyrolysed at 925° and 200 μ pressure using a U tube and stainless steel gas traps. After the pyrolysis was complete, the apparatus was allowed to cool and 5.0 ml of propane added. The products were analysed by vps (5'x3/16", Porapak S at 83° and 50 cc/min.) Examination of the infrared, NMR, and vpc retention times showed the products to be ethylene and sulfur dioxide. The sulfur dioxide analysis was checked by trapping the products in a U tube, adding 25 ml of N/10 iodine solution and titrating to a starch end point with N/10 $Na_2S_2O_3$ solution.

Pyrolysis of 2,2-Dimethyl 3-Thietanone 1,1-Dioxide:

Approximately 180 mg of 2,2-dimethyl 3-thietanone 1,1-dioxide were pyrolysed at 940° at 100 μ pressure using a U tube trap. A known weight (approximately 75 mg) of n-pentanol was then added to the trap, the products washed out with 1 ml of methanol, and analysed by vpc (20'x¼" 10% FFAP on Chrombsorb P at 110° at 40 cc/min.). The products were identified by infrared and vpc retention times as isobutylene and sulfur dioxide by comparison with authentic samples.

Pyrolysis of 2-Phenyl 3-Thietanone 1,1-Dioxide:

Approximately 210 mg of this compound were pyrolysed at 930° and 100 μ pressure using a U tube trap. A known weight of n-propanol was then added to the trap, the products washed out with 1 ml of methanol, and analysed by vpc (20'x¼", 10% FFAP on Chrombsorb P at 110° and 60 cc/min.). The products were identified as styrene and sulfur dioxide by infrared, NMR, and vpc retention time comparison with authentic samples. The sulfur dioxide analysis was checked by the iodine/$Na_2S_2O_3$ method.

Preparation of 1,2 ^{3}-Oxathiole S-Oxide:

146.6 mg of thiete 1,1-dioxide was pyrolysed at 615° and 10 μ pressure using a U tube trap. 55 mg of unpyrolysed material was recovered from the pyrolysis tube and 64.4 mg (70%) of 1,2$^{\Delta 3}$-oxathiole S-oxide from the trap, $\nu_{max}^{CCl_4}$ = 1135, 985 (SO_2R) cm^{-1}, $\delta(CCl_4)$ = 5.11 (2H,d,J = 4 cps), 7.10 (2H,m).

Pyrolysis of Thiete 1,1-Dioxide:

Approximately 120 mg of thiete 1,1-dioxide were pyrolysed at 950° and 150 μ pressure using a U tube trap. The chloroform soluble products were washed out with 1 ml of $CHCl_3$ after a known weight (approximately 40 mg) of acetophenone had been added. The products were analysed by vpc (6'x¼", 10% Ethofat on Chrombsorb P at 100° and 60 cc/min.). The only non-gaseous product was acrolein as identified by infrared, NMR, and DNP, m.p. 164-65° (lit. m.p. 165°(152)). During the pyrolysis a red coloured material formed in the U tube which changed to an insoluble yellow polymer on warming. When a cold finger and gas U tube traps were used, the gaseous products were analysed, after the addition of 5.0 ml of propane, by vpc (5'x3/16", Porapak S at 83° and 50 cc/min.).) The product was identified by infrared and vpc retention time as acetylene.

Pyrolysis of 2,2-Dimethyl 3-Thiete 1,1-Dioxide:

Approximately 100 mg of 2,2-dimethyl 3-thiete 1,1-dioxide were pyrolysed at 950° and 150 μ pressure with a U tube trap. A known weight of acetophenone (approximately 35 mg) was added on completion of the run, the products washed out with 1 ml of ethyl acetate, and analysed by vpc (6'x¼", 10% Ethofat on Chrombsorb P at 100° and 60 cc/min.). The only isolated products were 3-methyl-2-butenal, identical in infrared, NMR, and vpc retention time with an authentic sample prepared as described below, DNP m.p. 183-84° (lit. m.p. 182-83°(153)), and sulfur

dioxide as identified by infrared and vpc retention time.

As before, a red coloured material formed in the tube which changed to a yellow insoluble polymer on warming.

Preparation of 3-Phenyl $1,2^{\Delta 3}$-Oxathiole S-Oxide:

200 mg of 2-phenyl 2-thiete 1,1-dioxide were pyrolysed at 455° at 50 μ pressure in the usual manner with a liquid nitrogen cooled U trap. The product consisted of two compounds: a liquid whose infrared was identical with phenyl vinyl ketone as prepared below, and a solid which was separated by tlc using $CHCl_3$ as eluent to give 55 mg (27%) of 3-phenyl $1,2^{\Delta 3}$-oxathiole S-oxide, m.p. 74.5-75.5°, $\nu_{max}^{CCl_4}$ = 1135, 1028 (SO_2R) cm^{-1}, and an ABX pattern at $\delta_A = 5.32$, $\delta_B = 5.72$, $\delta_X = 6.81$, $J_{AB} = -15.96$ cps, $J_{AX} = 2.21$ cps, $J_{BX} = 1.95$ cps and a five proton singlet at $\delta = 7.47$.

Analysis: Calc. for $C_9H_8O_2S$, C 60.00%, H 4.48%, S 17.77%;
Found, C 60.18%, H 4.57%, S 17.87%.

Pyrolysis of 2-Phenyl 2-Thiete 1,1-Dioxide:

Approximately 150 mg of 2-phenyl 2-thiete 1,1-dioxide were pyrolysed at 940° and 80 μ pressure with a U tube trap. After the pyrolysis was complete, a known weight (approximately 50 mg) of acetophenone was added, the products washed out with 1 ml of chloroform, and analysed by vpc (6' x $\frac{1}{4}$", 10% Ethofat on Chrombsorb P at 100° and 60 cc/min.). The products were separated by vpc and shown to be: acrolein, DNP m.p. 163-64° (mixed m.p. 164-165° with an authentic sample m.p. 164-65°); methyl phenyl

acetylene, infrared, NMR, and vpc retention time identical with an authentic sample; phenyl vinyl ketone, infrared, NMR, and vpc retention time identical with a sample prepared as described below, DNP m.p. 153-54° (lit. m.p. 152-53°(154).

As before, a red coloured material formed in the tube during pyrolysis which turned to a yellow polymer on warming.

Pyrolysis of 3-Phenyl-1,2$^{\Delta 3}$-Oxathiole S-Oxide:

Approximately 20 mg of this compound was pyrolysed at 925° and 100 μ pressure with a U tube trap. On completion of the pyrolysis, a known weight of acetophone was added, the products washed out with 1 ml of chloroform, and analysed by vpc (6'x$\frac{1}{4}$", 10% Ethofat on Chrombsorb P at 100° and 60 cc/min.). The product mixture was the same as that found for the 2-phenyl 2-thiete 1,1-dioxide.

Attempted Trapping of 2-Propenyl Sulfene:

a) 87.5 mg of 2-thiete 1,1-dioxide were pyrolysed at 600° and 10 μ pressure with a liquid nitrogen cooled cold finger trap which had been previously covered with liquid ammonia. On warming, the cold finger was washed with $CHCl_3$, and the solvent evaporated. The product was an infrared opaque solid which reacted with frothing on addition of concentrated HCl.

b) 144.4 mg of 2-thiete 1,1-dioxide was pyrolysed at 600° and 20 μ using a liquid nitrogen cooled finger onto which had been placed 1.5 ml of methanol. The cold

finger was allowed to warm up after the pyrolysis was complete and the products washed off with more methanol. The solvent was evaporated to give 47.0 mg of 3-phenyl-1,$2^{\Delta 3}$-oxathiole S-oxide, identified as the only product by infrared and tlc examination of the products.

Pyrolysis of 3-Thietanol 1,1-Dioxide:

a) Initially 0.5 ml of methanol was placed on the U tube trap, then approximately 200 mg of 3-thietanol 1,1-dioxide were pyrolysed at 935° and 110 μ with a U tube trap. On completion of the pyrolysis, a known weight of methyl formate (approximately 20 mg) was added, the products were washed out with 0.5 ml of methanol, and analysed by vpc (20'x$\frac{1}{4}$", 10 FFAP on Chrombsorb P at 50° and 60 cc/min.). The products were separated by vpc and identified as: acetaldehyde, identical in NMR and vpc retention time with an authentic sample; dimethoxy methane, identical in infrared, NMR, and vpc retention time with an authentic sample; propionaldehyde, DNP m.p. 153-54° (mixed m.p. 152-53° with an authentic sample m.p. 152-53°); acetone, infrared, NMR, and vpc retention time identical with an authentic sample, DNP m.p. 125-27° (lit. m.p. 126°); methyl acetate, infrared, NMR, and vpc retention time identical with an authentic sample; acrolein, DNP m.p. 163-65° (lit. m.p. 165°), infrared identical with an authentic sample.

b) Approximately 180 mg of 3-thietanol 1,1-dioxide were pyrolysed at 940° and 100 μ pressure using a cold finger and gas U tube traps. On completion of the pyrol-

ysis, 5.0 ml of propane were added and the products analysed by vpc (5'x3/16", Porapak S at 83° and 50 cc/min.). The products were identified by vpc retention time and infrared absorption as ethane, ethylene, and sulfur dioxide.

The sulfur dioxide analysis was checked by the iodine method.

Preparation of 3-Methyl-2-Butenal:

This compound was prepared from 1-bromo-3-methyl-2-butene by the treatment with hexamethylenetetraamine as described by(155), $\nu_{max}^{CCl_4}$= 1675 (C = O), 1635, 1615 (C = C), $\delta(CCl_4)$ = 1.99 (3H,d,J = 1 cps), 2.19 (3H,d,J = 1 cps), 5.80 (1H,d.of q, J_{AX} = 1 cps, J_{BX}= 8 cps), 9.83 (1H,d,J = 8 cps), DNP m.p. 184-85° (lit. m.p. 182-83°(155)).

Preparation of Phenyl Vinyl Ketone:

This compound was prepared from diazoethane and benzoyl chloride followed by treatment with Ag_2O(156), b.p. 115-17°/18 mm, $\nu_{max}^{CCl_4}$ = 1675, 1660 (C = O), 1610, 1597, 1580 (C = C), DNP m.p. 153-54° (lit. m.p. 152-53°(156)).

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APPENDIX I

PREPARATION OF 1,3,5,7-TETRAMETHYL CYCLOOCTATETRAENE

A. Discussion

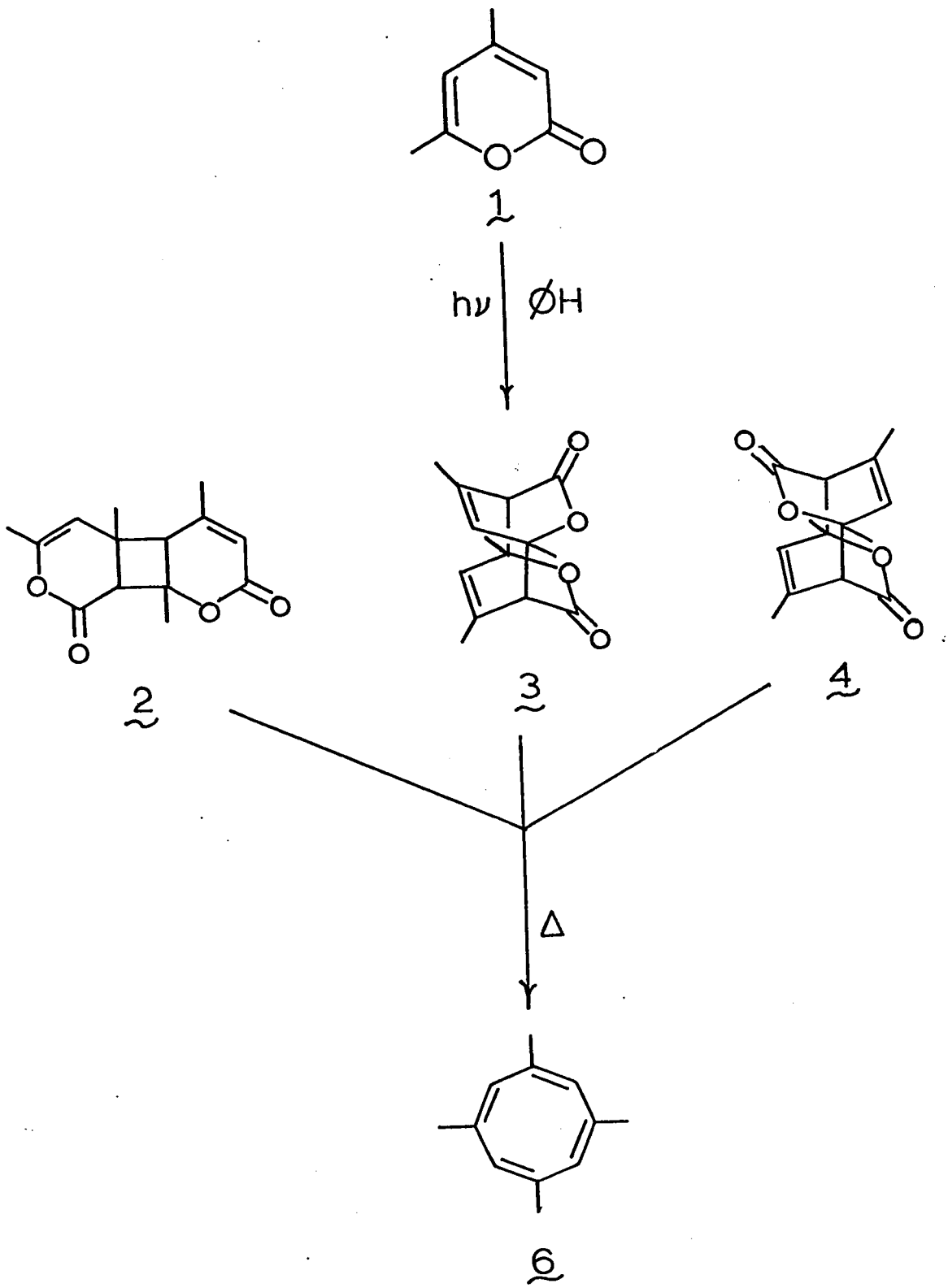
It has been shown by de Mayo and Yip[24] that irradiation of 4,6-dimethyl-2-pyrone 1 results in the formation of four photodimers 2-5. Pyrolysis of three of these dimers caused decarboxylation, resulting in rearrangement to 1,3,5,7-tetramethylcyclooctatetraene 6, a previously unknown compound.

Since no other synthesis has been reported for this compound, the reaction was repeated in order to obtain a method applicable to preparative synthesis of this cyclooctatetrene. No attempt was made to isolate the photodimers, but rather the starting material was irradiated until less than 10% remained. The total product was then pyrolysed to give a yield of 0.135 moles (17%, or 25% based on 2-pyrone consumed) of 1,3,5,7-tetramethylcyclooctatetraene.

B. Experimental

Preparation of 4,6 Dimethyl-2-Pyrone:

The 4,6-dimethyl-2- pyrone was prepared by the copper chromite (2g) catalysed decarboxylation of 4,6-dimethyl coumalic acid (30g) at 230-35° as described by Wiley[33].


1
hν
ØH
2
3
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Δ
6

The desired pyrone was distilled out of the reaction mixture at 144-6°/35 mm and recrystallized from ethyl acetate to give 13.5g (61%) m.p. 49-50° (lit. m.p. 50-51°), λ_{max}^{EtOH} = 295 nm (ϵ 6,200).

Preparation of 1,3,5,7-Tetramethylcyclooctatetraene:

20.0g of 4,6-dimethyl-2-pyrone was dissolved in 15 ml of dry benzene, placed in three 9 mm Pyrex tubes, and degassed with oxygen free nitrogen for ½ hour. The tubes were sealed with rubber stoppers, taped to the side of a water cooled immersion well containing a Pyrex filter and a 450 watt Hanovia medium pressure mercury arc lamp, then irradiated for 72 hours.

The reaction was followed by monitoring the infrared absorption at 1565 cm^{-1}. After 72 hours, a precipitate had filled the tube and the reaction had ceased. The contents of the tubes were filtered to give 4.5g of crystalline material, and the mothers returned to clean tubes. Further irradiation for 24 hours reduced the infrared absorption to less than 10% of its original value.

The total products were placed in a 50 ml flask with a side arm and vacuum distillation assembly. The benzene was removed and the residue pyrolysed with a free flame for 15 minutes taking care that none of the material distilled over. The vacuum was applied and the cyclooctatetrene distilled at 85-90°/15 mm. On completion of the distillation, the vacuum was released and the pot material pyrolysed for an additional 10 minutes. The distillation was then continued to give a total of 2.66g, m.p. 55-63-

67°.

Further distillation at 95-100°/3 mm gave 7.05g of 4,6-dimethyl-2-pyrone, which when recrystallized had m.p. 47-49°, 6.18g.

The cyclooctatetraene was purified by passage down a column of 25g of silicic acid using 35-60° petrol as eluent, to yield 2.17g (17.3%) of pure 1,3,5,7-tetramethylcyclooctatetraene m.p. 65-69-70° (lit. m.p. 69-70); $\nu_{max}^{CCl_4}$ = 1650 cm^{-1}; $\delta(CCl_4)$ = 1.68 (12H,s), 5.35 (4H,s); λ_{max}^{EtOH} = 285 nm (ϵ 470).