Some Reactions of Unsaturated Ring Systems Containing Sulphonyl Groups

by

Donald K. Cameron, B.Sc.

Thesis presented for the degree of
Doctor of Philosophy

University of Edinburgh

April 1987

For my family.

DECLARATION

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

The thesis describes the results of research carried out in the Department of Chemistry, University of Edinburgh under the supervision of Dr. I. Gosney since 1st October 1983, the date of my admission as a research student.

[redacted]

POSTGRADUATE LECTURE COURSES

The following is a statement of the courses attended during the period of research.

Organic Research Seminars (3 years attendance).

Current Topics in Organic Chemistry, various lectures (15 lectures).

Modern Synthetic Methods in Organic Chemistry, Prof. R. Ramage, (5 lectures).

Industrial Chemistry, Drs. R. Sinclair and I. Mustoe, Paisley College of Technology (5 lectures).

Organo-Silicon Chemistry, Dr. E. Colvin, University of Glasgow, (5 lectures).

Organic Photochemistry, Dr. D. Leaver, (5 lectures).

Departmental Technical German Lectures and Examination.

ACKNOWLEDGEMENTS

Firstly, I would like to thank Dr. I. Gosney for his excellent supervision and unceasing infectious enthusiasm over the three years, and also Prof. J.I.G. Cadogan for his continuing interest. Many thanks also, to my colleagues in the department, to the technical staff for their help and to Mrs. M. Gibb for the typing of this manuscript. I would like to thank British Petroleum p.l.c. for their financial assistance. Last but not least, I would like to express my gratitude to my family for all their support.

ABSTRACT

Investigations into potential new routes to the conducting polymer poly(acetylene) were carried out based on the 'prepolymer stratagem', whereby a monomer is polymerised to an intermediate polymer which is then subjected to thermolysis with simultaneous formation of poly(acetylene) and thermal extrusion of a small molecular fragment.

The aforementioned investigations brought to light a highly unusual stereoselective syn-addition of molecular bromine under ionic conditions to the bicyclic sulphone 3-thiabicyclo[3.2.0]hepta-6-ene- 3,3'-dioxide, brought about by an unprecedented long range Coulombic stabilisation of an open carbocation by the sulphonyl moiety. This effect was also shown to hold for the related oxirane. It was also shown that supression of this effect can be achieved through aqueous solvation of the hydrophilic sulphonyl group. Extension to unsaturated bicycloheptene systems containing sulphonyl groups showed that atypical cis-exo stereo and regiospecificity can be achieved with regard to electrophilic addition, due to a hitherto unreported neighbouring group participation by an endo-sulphonyl group, culminating in the successful capture of an intermediate bromonium ion.

Finally, a comparison is made between the behaviour

of α-aryloxy sulphoxides under different thermolytic conditions. Flash vacuum pyrolysis of these compounds results in homolytic cleavage of the C-S bond, yielding an aromatic aldehyde and a thiolsulphonate, whereas solution thermolysis results in rearrangement to a thermally stable sulphenate ester.

CONTENTS

INTRODUCTION

INTRODUCTION

Contents

A. INTRODUCTION TO POLY(ACETYLENE)

1. Introduction to organic conducting polymers

The current world-wide interest in electroactive polymers is focussed on electrically conducting and semiconducting polymers. These are an entirely new class of electrically active materials which offer new preparative routes, unconventional properties and thus quite possibly a wide range of novel applications.

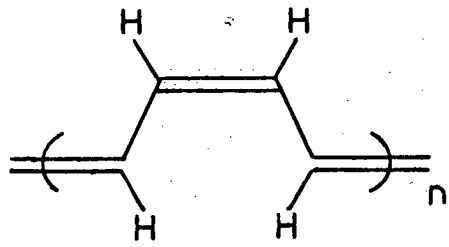
Present electronic devices and electrically active materials are composed of a variety of metals, semimetals, ceramics and other inorganic substances. These materials serve as electrodes, electrical conductors, semiconductors, and as transducers of electromagnetic radiation. Systems in which these materials are found include computers, communications equipment, solar cells, batteries etc. Depending on the application, the utility of available electrically active materials may be limited by factors such as weight, mechanical strength, fabrication problems, corrosion, scarcity and high cost.

For many applications, if electrical functionality were possible, the physical and chemical properties of polymers make them extremely attractive, e.g. high strength to weight ratio, durability, low cost, molecular tailoring of desired properties, and

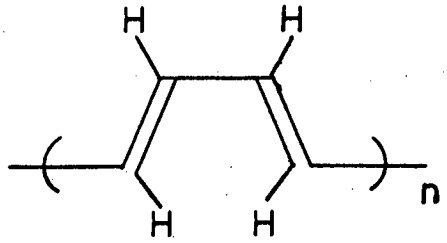
ease of processing into films, filaments and complex shapes. This in theory, opens up the prospect of a whole new generation of novel devices. Poly(acetylene) is the simplest organic polymer to display these conducting and semiconducting properties, and will be discussed further in the following sections.

2. Structure of Poly(acetylene)

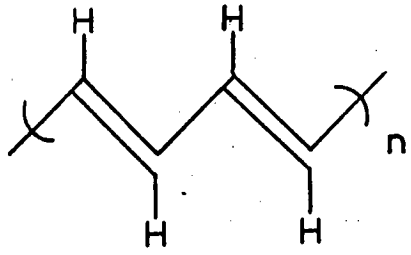
Poly(acetylene) is the polymer formed from acetylene. Polymerisation gives an extended carbon backbone joined by alternating double and single bonds. The presence of the double bond moiety confers isomerism on the structure, hence poly(acetylene) may exist in two forms of difference thermodynamic stability. At low temperatures the cis form is produced by all known direct polymerisation routes.



Strictly, this is the 'cis-transoid' structure. A rearrangement of the π-electrons gives rise to the 'trans-cisoid' structure.



However, at temperatures above 100°C, there occurs rotation of the cis-linkage to give the thermodynamically more stable 'trans-transoid' form.



3. History

The first major synthesis of poly(acetylene) was carried out by Natta[1] at Milan Polytechnic in 1958, by the direct polymerisation of acetylene gas using a mixture of triethylaluminium and titanium tetrabutoxide as catalyst. The product obtained was an insoluble and infusable black powder. It was shown at this time that poly(acetylene) was a semiconductor, whose conductivity varied according to the structural isomeric form, degree

of crystallinity and exposure to oxygen. However, more importantly it was shown that exposure to donor or acceptor gases markedly increased its electrical conductivity.

Further interest in poly(acetylene) waned and it was not until 1974 that another major breakthrough came by a group of workers headed by Shirakawa at the Tokyo Institute of Technology. They found that by passing acetylene gas over the surface of a vessel coated with concentrated catalyst solution, that a free standing flexible thin film of poly(acetylene) was produced.[2] It was shown by electron microscopy that these 'films' were in fact tangled fibrillar mats. The poly-(acetylene) formed by this method, although still insoluble and infusable, was now in a form which could be readily handled and used.

Shirakawa, the Principal worker in this group, spent 1977 on sabbatical leave at the University of Pennsylvania working with Professors MacDiarmid and Heeger. Here they showed that doping the poly-(acetylene) produced by the 'Shirakawa method' with electron acceptors such as iodine and arsenic pentafluoride and donors such as sodium could increase the conductivity of the undoped polymer by up to 10 orders of magnitiude, to give conductivities of up to 10 Scm^{-1}. From this work they published a series of papers on the analysis of the doped and undoped materials and their possible

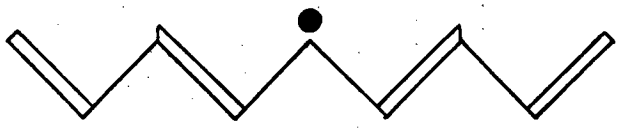
applications.[3-8]

It should be stated that the vast majority of published material in recent years comes not from organic or macromolecular chemistry but from solid state and semiconductor physics. This stems from the fact that the relationships between molecular structure and electrical properties are not yet fully understood. In particular, the crystalline structure, degree of delocalisation, conduction mechanism and the effect of the catalyst on the course of polymerisation are all sources of controversy.

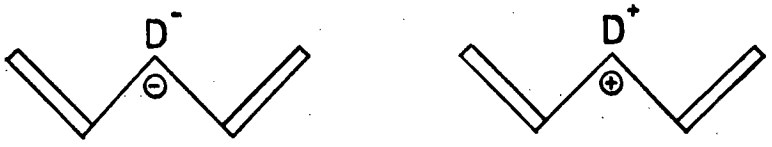
As a consequence of the monopoly of the subject by solid state physicists, who have consistently based their work on the 'unoptimised' Shirakawa polymer, there has been little work on the development of alternative routes to poly(acetylene). The Shirakawa polymer is 'unoptimised' in the sense that, although elaborate purification procedures have been developed, the polymer still remains contaminated by catalyst residues. This factor must in part be responsible for some of the conflicting results, as regards electrical properties and measured conductivities together with its susceptibility to oxidising and reducing atmospheres, especially once doped.

4. Conduction Mechanisms

There have been two main conduction mechanisms proposed, the 'soliton' and the 'percolation' mechanism. The soliton mechanism involves the rearrangement of the π-electrons on the main backbone, which also provides a mechanism for isomerisation as well as conduction. The soliton itself is an inversion of the π-electron wave function and can be imagined as the interchanging of the single and double bonds along the backbone. This inversion is thought to be spread over 12-16 double bonds, and can be detected by electron spin resonance spectroscopy as a free electron.

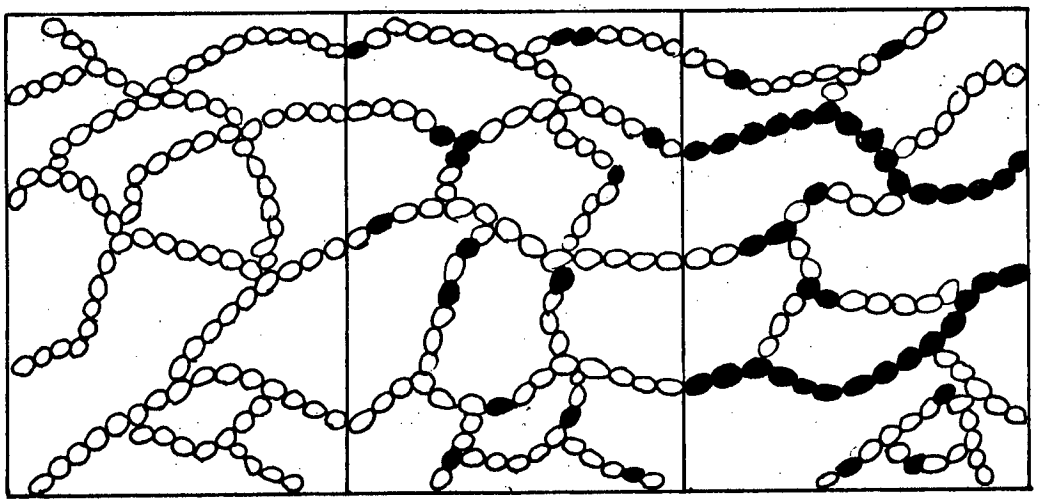


Doping the poly(acetylene) with an oxidising agent, involves either donating or abstracting an electron from this structure, and as a consequence the free spin is destroyed.



This in turn induces charge carriers which migrate along single chains within the fibril. Since first published in 1979 a series of papers have been published to explain experimental results based on this model.[9-14]

However, a group at IBM subsequently published a challenge to this theory,[15] proposing the 'percolation' model. They argued that instead, doping proceeds inhomogeneously and produces random metallic like droplets, whose number increases until at the semiconductor-metal transition they form continuous paths throughout the material.

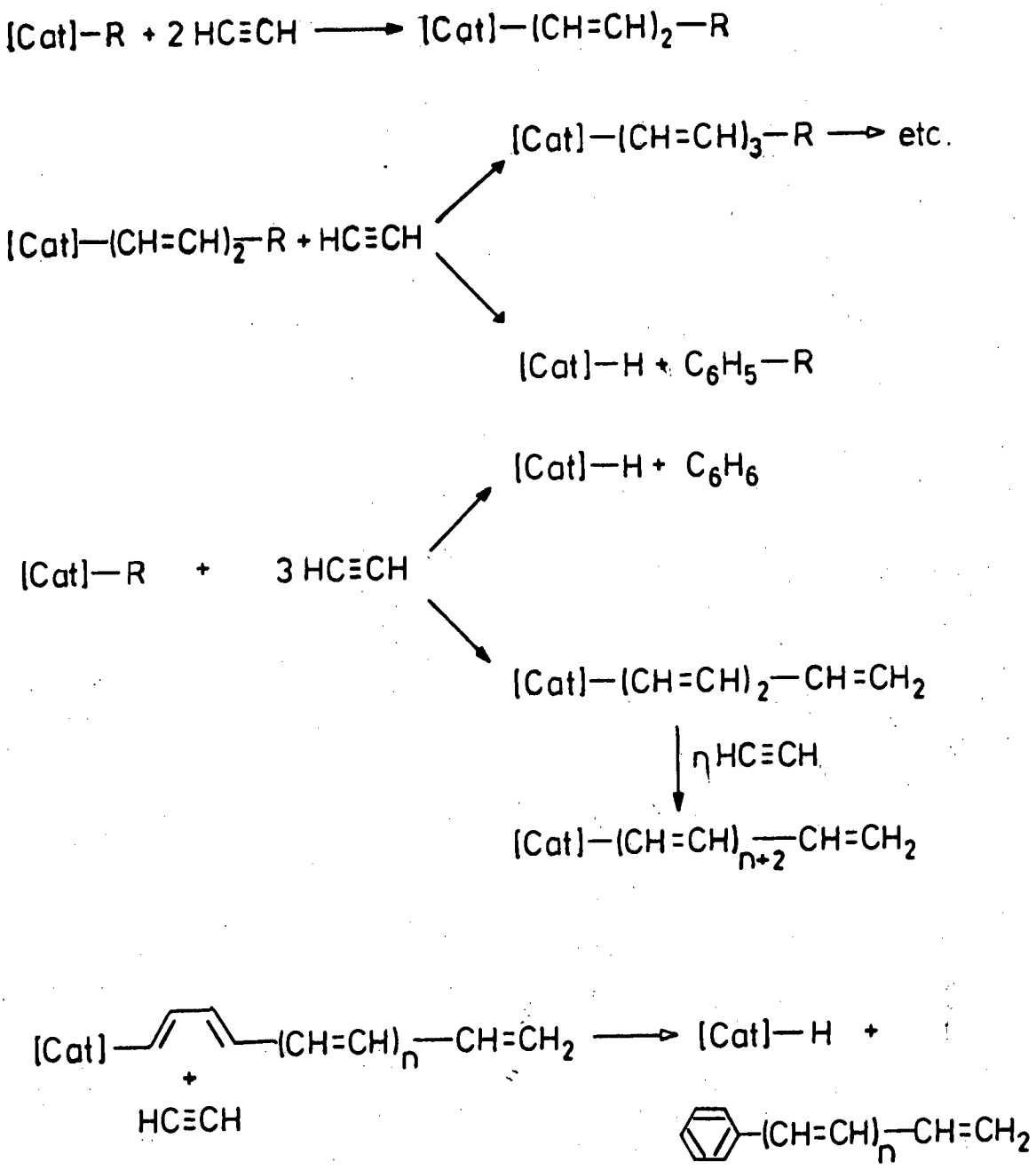


However, as yet the controversy surrounding the mechanism by which poly(acetylene) conducts remains unresolved.

5. Polymerisation and molecular weight

Little is known about the mechanism of the polymerisation of acetylene. The majority of Ziegler catalysts cyclomerise acetylene to benzene, cyclooctatetraene, styrene and other similar products.[16-20] Similar results are also found with other catalyst systems, in particular those based on nickel. The catalyst discovered by Natta which is the basis for the Shirakawa technique is the optimal for the maximum yield of poly(acetylene). Nevertheless, cyclomerisation also proceeds as side reaction.

Ikeda and Tamaki[20] have demonstrated that ethylbenzene is produced in small quantities when the typical Ziegler catalyst $TiCl_4/AlEt_3$ is used and that the ethyl groups originate from the catalyst. These possible reactions are shown in Scheme 1.

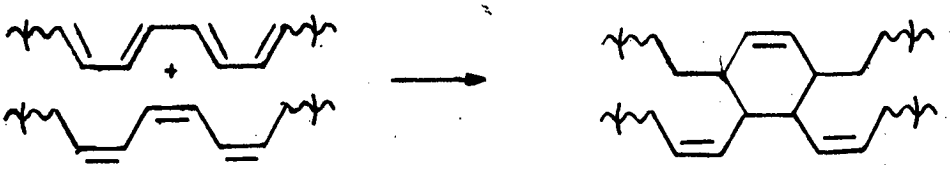


Scheme 1.

In the above scheme, the formation of benzene, styrene, cyclooctatetraene etc. result from transfer

reactions with the monomer. In addition, the chain length of the polymer is limited by transfer reactions with the monomer.

The insolubility of the polymer has prevented a direct determination of the end groups and molecular weights. However, soluble derivatives of poly-(acetylene) have been obtained and this has enabled molecular weights and their distributions to be determined. Soluble derivatives of poly(acetylene) can be prepared by chlorination and hydrogenation. If poly(acetylene) is chlorinated immediately after polymerisation at -30°C, an insoluble portion forms which increases with time. The increase in the insoluble fraction can be taken as a measure of the spontaneous cross-linking which takes place even at such a low temperature. A possible cross-linking reaction of the Diels-Alder cycloaddition type is shown in Scheme 2.



Scheme 2.

6. Applications

Several groups worldwide are working on the application of poly(acetylene) to photovoltaic cells. Although some work has been carried out on cells consisting of poly(acetylene) in combination with a conventional crystalline semiconductor,[7,21-26] it is the development of a poly(acetylene) homojunction or poly-(acetylene) Schottky barrier cell which could provide a route to cheap large area solar cells.

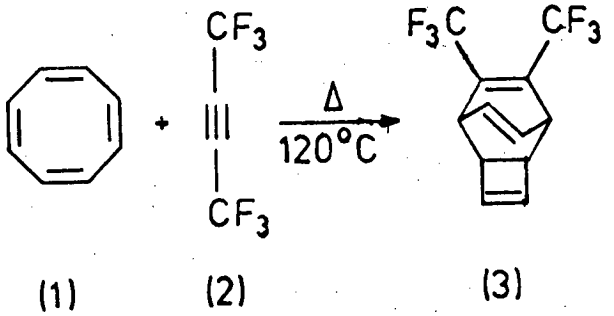
Batteries were developed by the University of Pennsylvania group as a spin-off from their investigation into electrochemical doping. Figures in the literature[27] suggest energy and power densities of 176 watt-hour/kg and 680 watt/kg (cf. lead-acid 20-50 watt-hour/kg and 80-250 watt/kg). These quoted parameters seem impressive when compared to conventional lead-acid cells.

B. POLY(ACETYLENE) *via* PRECURSOR POLYMERS

1. 'Durham' route to poly(acetylene)

In 1980 Drs. Feast and Edwards from the University of Durham published a novel synthesis of poly(acetylene).[28] This involved the synthesis of a soluble precursor polymer, which could then be converted to poly(acetylene) *via* a thermally-promoted elimination reaction. This in theory provides a route to high purity poly(acetylene), as the soluble precursor polymer can be rigorously purified prior to the thermal elimination step. This appears to be a distinct advantage over the direct polymerisation method, in which the poly(acetylene) is always contaminated by catalyst residues and once fomed it is non-processable.

The monomer of the precursor polymer was 7,8-*bis*(trifluoromethyl)tricylo[4.2.2.0.^{2,5}]deca-3,7,9-triene (3). This was readily prepared by the thermal Diels-Alder reaction between cyclooctatetraene (1) and hexafluorobut-2-yne (2) at 120°C in a sealed tube, (Scheme 3).

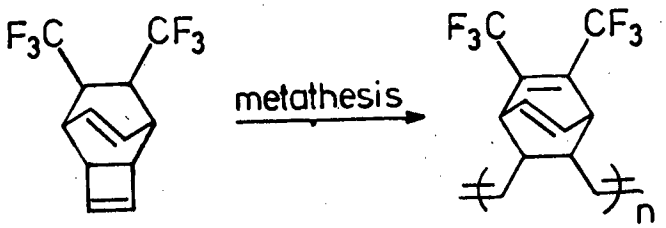


(1) (2) (3)

Scheme 3.

Now the proposed ring opening metathesis polymerisation of monomer (3) could occur at any of the three double bonds. However, it was found that the ring opening polymerisation took place only at the cyclobutene double bond. Presumably, the driving force for this reaction is the relief of ring strain in the four membered ring.

The metathesis catalysts employed were WCl_6:$(C_6H_5)_4Sn$ (1:2) and $TiCl_4$:$(C_2H_5)_3Al$ (1:2), with toluene being used as the solvent for both catalyst systems, (Scheme 4).



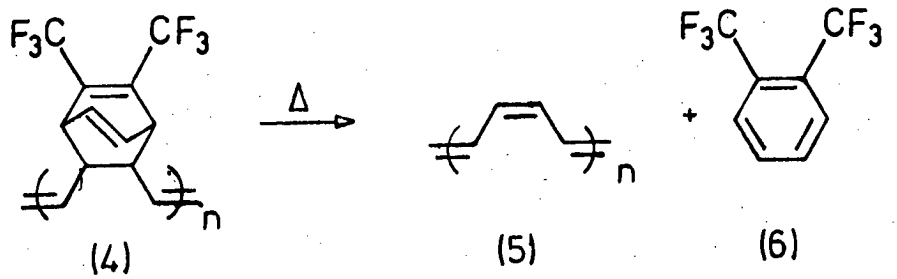
(3) (4)

Scheme 4.

In both cases polymerisation occurred readily. When the reaction mixtures became viscous, the polymerisation was terminated by the addition of methanol. This also caused the precipitation of polymer (4).

However, it was found that polymer (4) decomposed spontaneously on standing in the dark under an atmosphere of dry nitrogen and more rapidly in

solution. A sample of raw polymer (4) left in the dark for three days gave a black solid with a metallic lustre and a colourless oil identified as 1,2-bis-(trifluoromethyl)benzene (6), (Scheme 5).



(4) (5) (6)

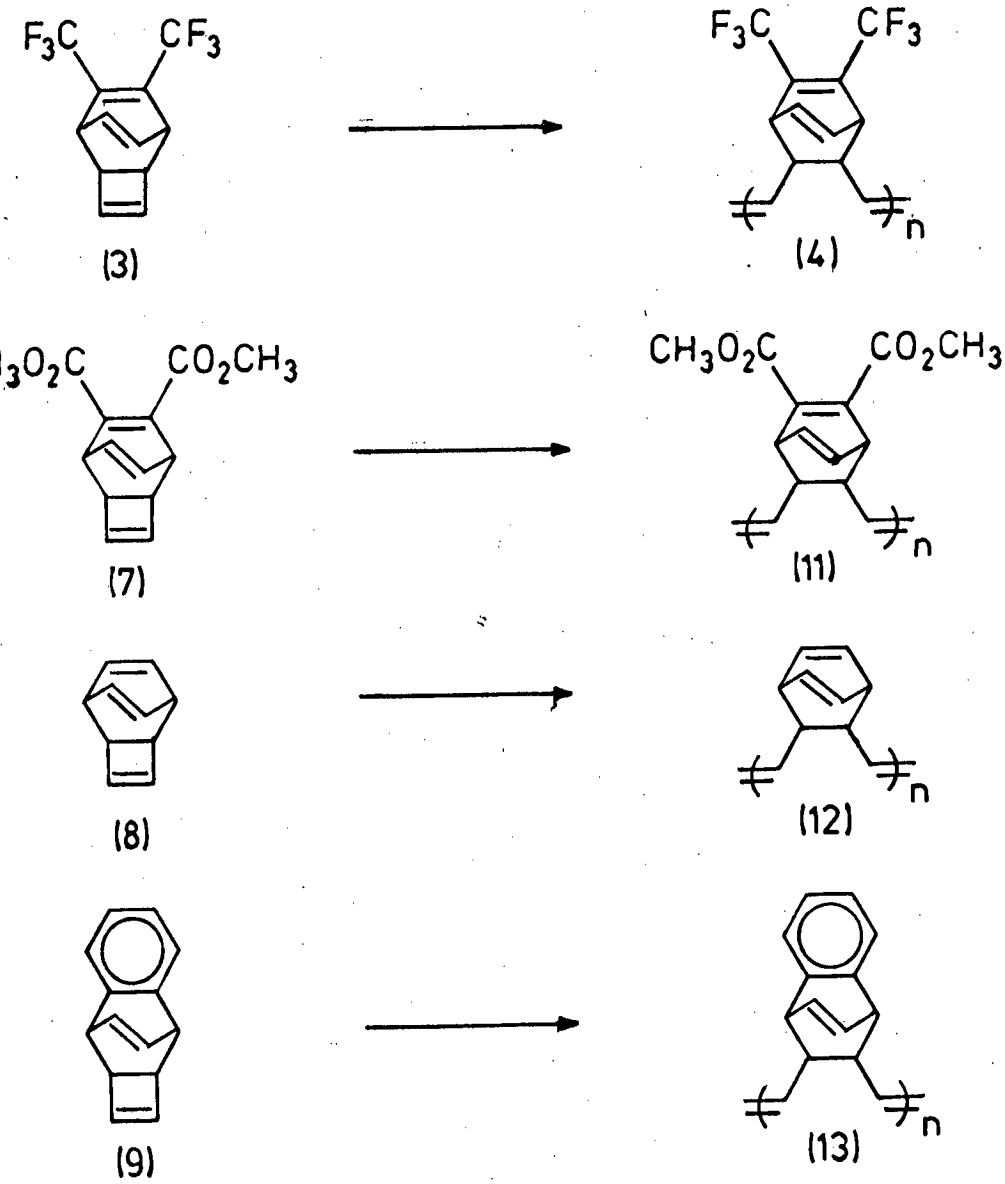
Scheme 5.

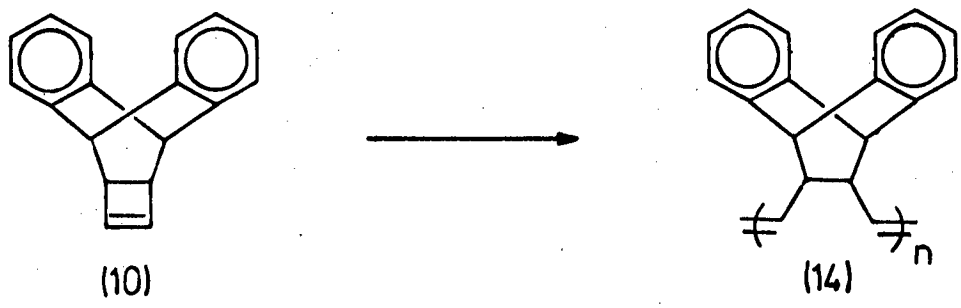
It would appear that the ease with which polymer (4) loses 1,2,-bis-(trifluoromethyl)benzene (6) means that this system is too labile for the convenient generation of poly(acetylene), (5).

Feast also reported that the product (5) showed reluctance to lose all its fluorine content even after prolonged heating. This he attributed to the eliminated aromatic molecules being trapped within the bulk matrix of the poly(acetylene). He also reported that atmospheric oxidation of the sample took place after a few days exposure, but this appeared to be a surface phenomenon only.

Their subsequent paper[29] investigated the viability of various other monomer systems, including the original (3). The monomers studied including (3)

were, dimethyltricyclo-[4.2.2.0.^{2,5}]deca-3,7,9-triene-7,8-dicarboxylate (7), tricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene (8), 7,8-benzotricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene (9) and 7,8,9,10-dibenzotricyclo-[4.2.2.0^{2,5}]deca-3,7,9-triene (10). Compound (10) has been prepared through a novel route by Wyse[30] within these laboratories. Compounds (7)-(10) were metathesised by a similar procedure to that described in the previous paper[28], (Scheme 6).





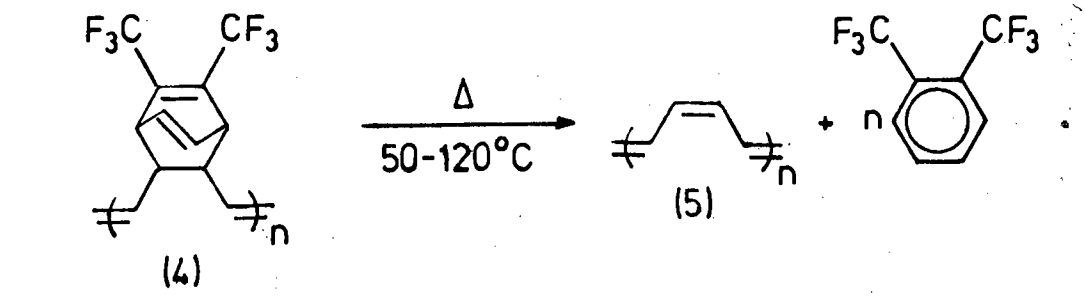
(10) (14)

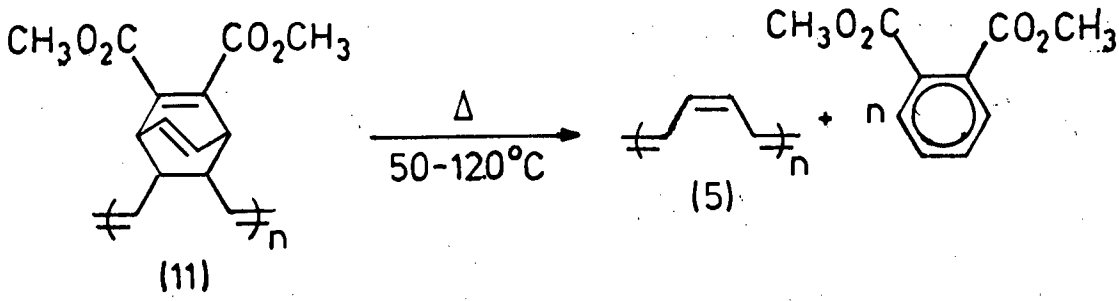
Scheme 6.

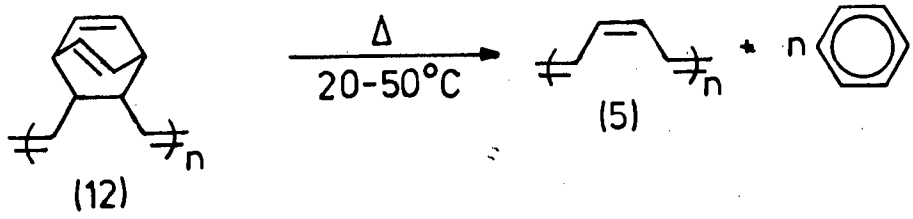
These metathesis reactions required that the reagents, solvents and apparatus were rigorously dried and that oxygen was excluded. It would appear that after many repetitions, these polymerisations were acknowledged to be sensitive to relatively small temperature changes and to the age of the catalyst solution. Also, variable induction periods and occasional failures were also observed. The resultant precursor polymers (4,11,12,13,14) were rigorously purified by repeated dissolution and reprecipitation from acetone by methanol, followed by vacuum drying at 0°C and storage under dry nitrogen at <-20°C.

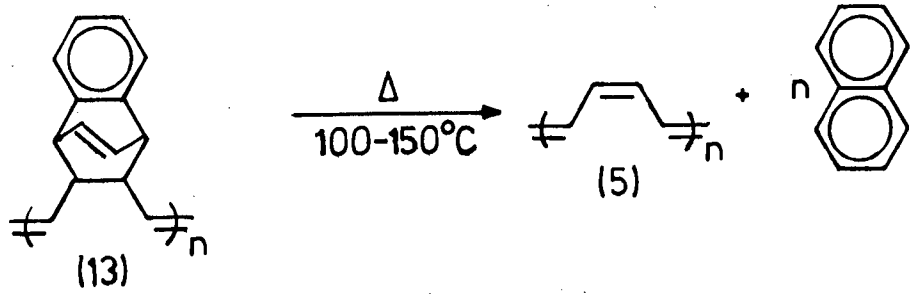
The precursor polymers (4),(11),(12),(13) and (14) all undergo a symmetry allowed thermal elimination reaction to yield poly(acetylene) and an extruded fragment, (Scheme 7). The temperatures given are those

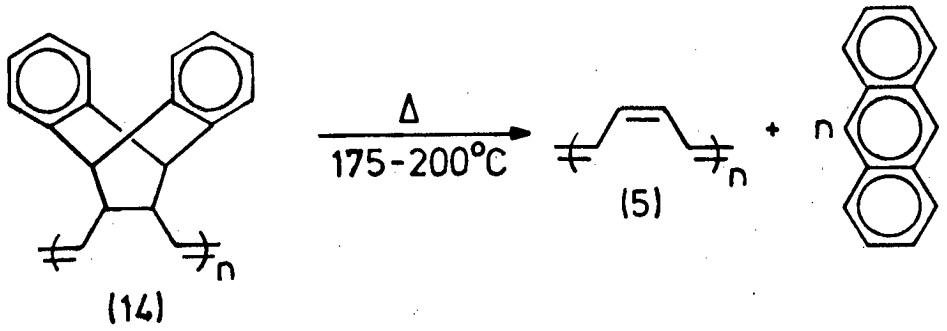
at which transformations can be achieved at an experimentally convenient rate. However, it was found that (4),(11) and (12) were unstable at room temperature and also the product (5) from (13) and (14) still contained some naphthalene and anthracene residues.











(14)

Scheme 7.

Feast also reported that the poly(acetylene) produced by this method has a completely different morphology to that produced by conventional direct polymerisation. The poly(acetylene) produced by this method is a thin solid amorphous film, in contrast to the disordered fibrillar mat produced by direct polymerisation. Although the thermal instability of products (4),(11) and (12) precluded accurate molecular weight determinations, analysis of (13) by low temperature gel permeation chromatography showed that it had a molecular weight of M>40,000. This poly-(acetylene) can also be doped to similar levels of conductivity when compared to the Shirakawa poly-(acetylene).

2. Advantages and disadvantages

The two stage nature of the aforementioned routes have several advantages over the conventional direct polymerisation method. Firstly, the ability to remove catalyst residues from the precursor polymer, via conventional techniques, prior to thermal extrusion allows the production of catalyst free poly(acetylene). This also allows recognition of the effect of residues on electrical properties. Secondly, the precursor polymers are processable, as they can be cast into thin films from solution. This provides the possibility of morphological control of the precursor polymer and hence of the final poly(acetylene). Although the poly(acetylene) produced by this route has a similar molecular structure to the material prepared by conventional routes, which was shown by essentially identical infrared, Raman and ^{13}C-n.m.r. spectra, the morphology of the free standing thin film is completely different. In particular, the ability to produce a thin, coherent film of poly(acetylene) is a significant development, since the material produced by direct polymerisation of acetylene gas is a disordered fibrillar mat.

Although, none of Feast's compounds so far show the correct extrusion characteristics i.e. stable at room temperature, while thermally eliminating a stable

molecule when heated to a moderate temperature, it seems reasonable to conclude that this problem will be overcome in time. However, a more serious problem is envisaged due to the fact that the extruded molecules are relatively large aromatic rings. While these appear to be completely extruded, a signficant proportion appear to be getting trapped within the matrix of the bulk poly(acetylene), thus precluding the formation of a high purity polymer. Also, the starting point for the monomer preparation is a thermal cyclisation between cyclooctatetraene and a functionalised adduct. Economically, cyclooctatetraene is a very expensive starting material for a commercially viable synthesis, coupled with the fact that BASF have a worldwide monopoly on the compound. Finally, there is a certain amount of 'double bond wastage', in that most of the molecule is lost in the extrusion step i.e. is not incorporated into the backbone of the π-system, which would increase the chain length.

3. Introduction to the metathesis reaction

At first sight the olefin metathesis reaction involves a simple molecular rearrangement, (Scheme 8).

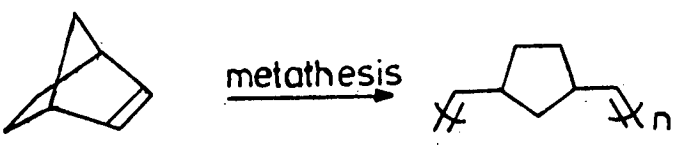
$$2\ R\text{-}CH{=}CH\text{-}R' \xrightleftharpoons{\text{catalyst}} R\text{-}CH{=}CH\text{-}R + R'\text{-}CH{=}CH\text{-}R'$$

Scheme 8.

However, despite the large amount of work carried out on mechanistic studies,[31-33] there remain many unanswered questions about the postulated mechanisms, structure of the catalysts and many of the subtle features associated with selectivity and rates of reaction.

The metathesis reaction has been found to be general for a large number of olefins and be catalysed by a variety of complexes. The majority of the metathesis inducing catalysts contain either tungsten or molybdenum as the transition metal e.g. WCl_6, $MoCO_5$ and usually a co-catalyst e.g. $SnMe_4$, Et_3Al is also present. The catalyst systems themselves may be either hetero[32,34] or homogeneous[35]. The catalyst systems are very sensitive to oxygen. Trace amounts of oxygen appear to activate the catalyst, whilst larger amounts destroy the catalytic activity.[36]

These catalysts can also be employed in the ring opening metathesis polymerisation of strained olefins.[37] An example is shown in Scheme 9 involving the polymerisation of norbornene.

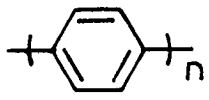
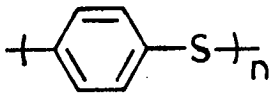
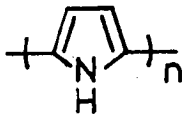
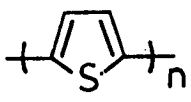


Scheme 9.

The mechanism of polymerisation is believed to proceed via metal-carbene complexes[38,39]. Indeed, Katz and Acton[40] have reported that stabilised carbene complexes had catalysed the ring opening metathesis of norbornene.

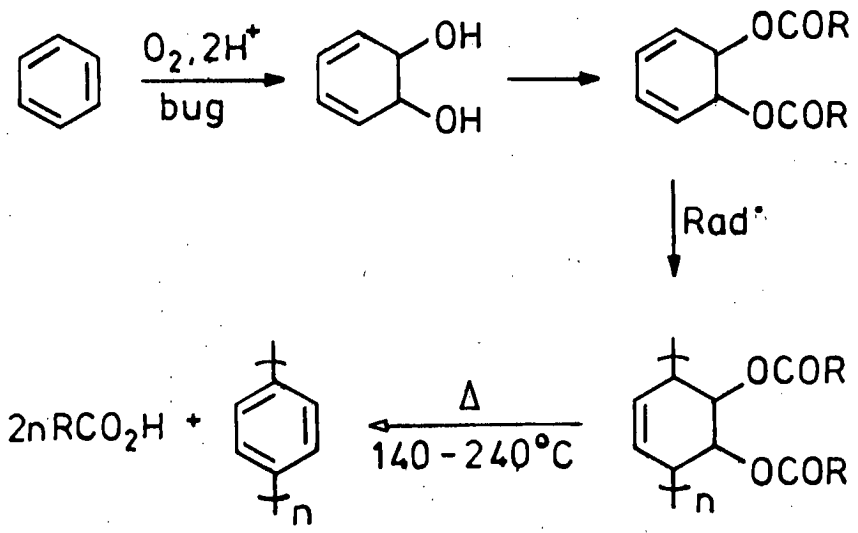
4. Other conducting polymers

Subsequent to the discovery of poly(acetylene) several other conducting polymers have been synthesised which show varying degrees of conductivity. These are shown below:-

Polymer	Undoped(Scm^{-1})	Doped(Scm^{-1})
Poly(para-phenylene) 	10^{-12}	5×10^{2}
Poly(para-phenylene sulphide) 	10^{-16}	1-10
Poly(pyrrole) 	10^{-11}	1-100
Poly(thiophene) 	10^{-20}	10^{-3}-10^{-4}

Poly(para-phenylene) is obtained when benzene is polymerised over $AlCl_3/CuCl_2$ as catalyst.[41] The reaction proceeds via radical cations, which also explains the formation of branches and cross-links as well as by-products.

I.C.I. have recently published a novel biotech route to polyphenylene.[42] Here, starting from benzene and oxygen the genetically modified bacteria pseudominium putidi is used as an oxidation catalyst, (Scheme 10).



Scheme 10.

Poly(para-phenylene sulphide) is obtained industrially by the reaction of dichlorobenzene with sodium sulphide in N-methyl-pyrrolidone,[43] and is commercially available as Phillips RYTON. In its undoped state it is moldable and soluble. However, the degree of polymerisation is not very large and the

conductivities shown so far are only moderate.

Poly(pyrrole) can be synthesised *via* an electrochemical route described by Kanazawa *et al*.[44-46] This polymerisation proceeds with simultaneous doping, when a solution of pyrrole in aqueous acetonitrile is electrolysed in the presence of $Et_4N^+BF_4^-$. The polymer precipitates as an insoluble film on the anode and contains BF_4^- ions in the molar ratio of *ca*. 1:4 with respect to the pyrrole rings.

Poly(thiophene) is structurally related to poly(pyrrole) but is handicapped by its very poor conductivity and lack of stability.

C. PROGRAMME OF RESEARCH

1. Poly(acetylene)

As has been previously stated in Section B, the 'Durham' route to poly(acetylene) *via* precursor polymers offers the best route towards achieving a high purity poly(acetylene) at present. However, there remain certain disadvantages with this process:-

(a) The extruded molecules are relatively large functionalised aromatic rings. These appear to be completely extruded, but a significant proportion are getting trapped within the bulk matrix of the polymer.

(b) Economically, cyclooctatetraene is a very expensive starting material for a commercially viable process.

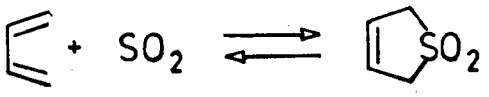
(c) There is a certain amount of 'double bond wastage', in that most of the molecule is lost in the extrusion step i.e. is not incorporated into the conjugated π-system.

It was anticipated that the aforementioned problems could be circumvented through the utilisation of SO_2 extrusion chemistry. Firstly, SO_2 is a small gaseous molecule, this would hopefully preclude the problems encountered in (a) by allowing complete

extrusion to the atmosphere. Secondly, by employing 3-sulpholene (15) or close derivatives as the starting material for such a process, since it is very cheap and commercially available, this would circumvent the necessity to use cyclooctatetraene.

2. History of SO_2 chemistry in Edinburgh

The reaction of 1,3-dienes with SO_2 was first reported by de Bruin in 1914,[47] when obtaining the crystalline adduct of SO_2 and isoprene. Many synthetic reactions now employ this reversible reaction with a variety of conjugated dienes. The best studied of these is the reaction of SO_2 with 1,3-butadiene to give 2,5-dihydrothiophene-1,1'-dioxide[48-51] (15) or 3-sulpholene, (Scheme 11).



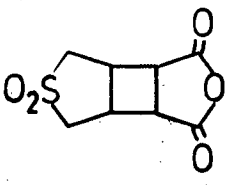
(15)

Scheme 11.

3-Sulpholene (15) decomposes at 125°C and can be used as a convenient source of 1,3-butadiene.[52] Thus

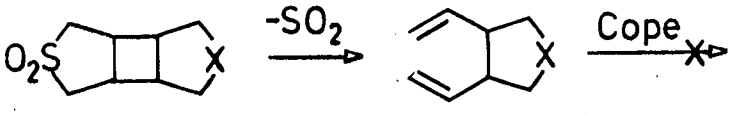
(15) and its derivatives have been widely utilised as versatile masked diene synthons in organic synthesis.[53-55]

Work in these laboratories has been concerned with the preparation and pyrolysis of the tricyclic anhydride (16) and its derivatives. Preparation of (16) was first reported in the literature by Shaihazieva et al. in 1972,[56] and was achieved by the photolysis of 3-sulpholene with maleic anhydride.



(16)

The extrusion of SO_2 from such compounds (17) leads to the formation of novel cis-1,2-divinyl compounds (18) which are stable and do not undergo Cope rearangement, (Scheme 12).

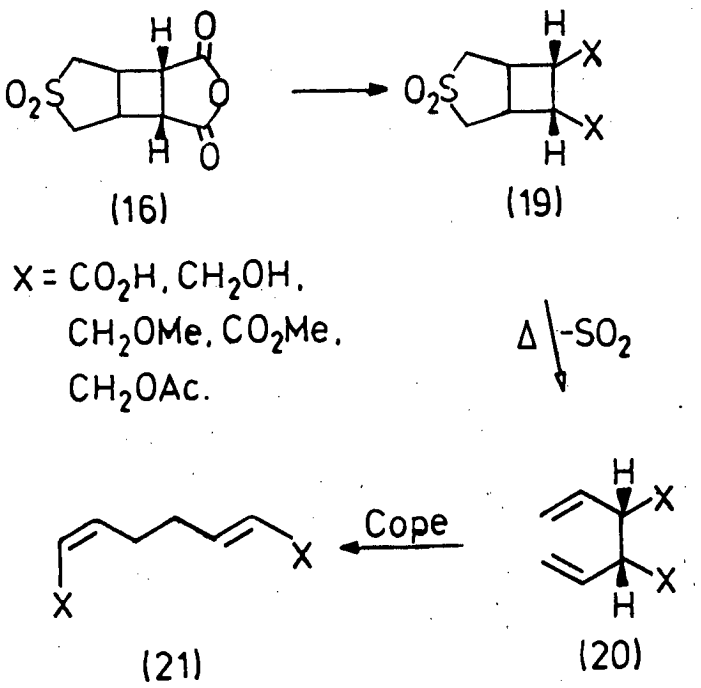


(17) (18)

Scheme 12.

Buchan et al.[57] showed that exo-3-thiabicyclo-[3.2.0]heptane-6,7-dicarboxylic anhydride (16) acts as a

general synthetic precursor for (E),(Z)-1,5-dienes (21) *via* functionalisation followed by the thermal extrusion of SO_2, (Scheme 13).

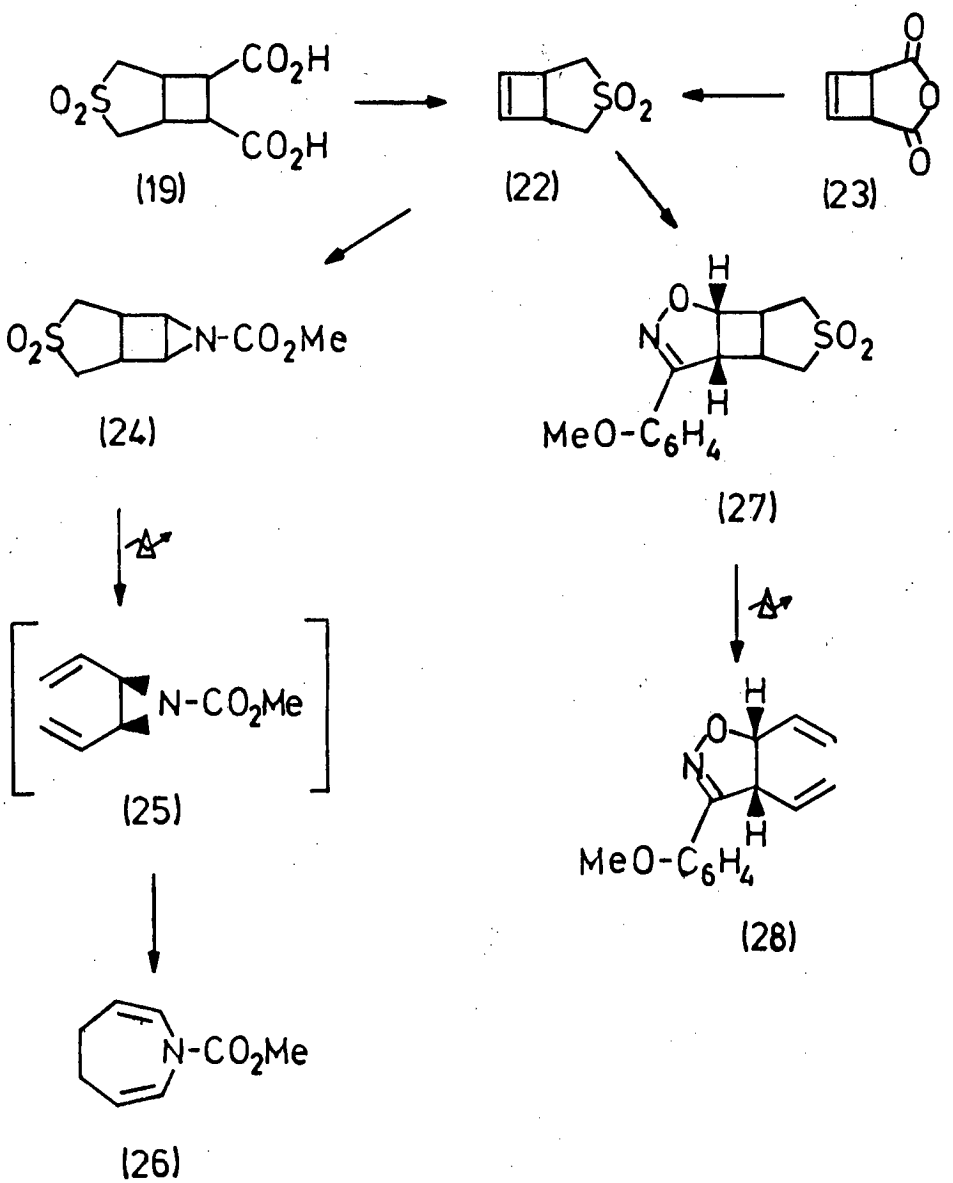


Scheme 13.

The stereochemical course of the procedure outlined in Scheme 13 relies on the usual chair like transition state of the Cope rearrangement of *meso*-1,2-divinyl compounds (20) generated by thermal extrusion of SO_2 from (19).

McLaughlin *et al.*[58] have also shown that functionalisation of the 6,7-double bond in the bicyclic sulphone (22), followed by the thermal extrusion of SO_2,

allowed a direct entry into seven membered ring systems *via* a Cope rearrangement of the *cis*-1,2-divinyl intermediates (25), (Scheme 14).



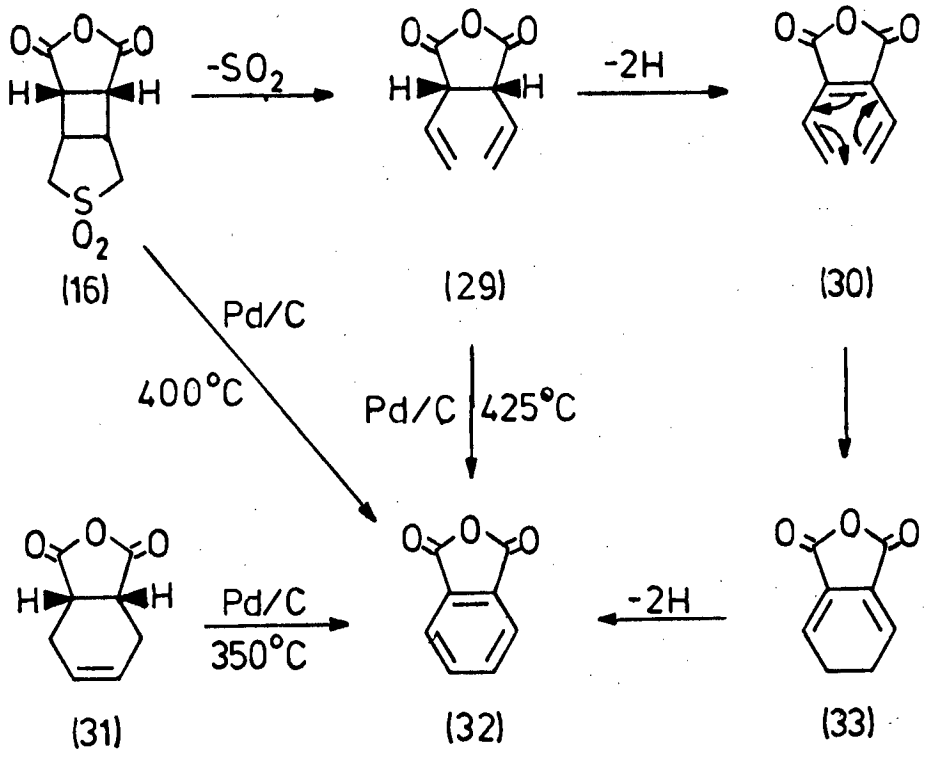
Scheme 14.

The key synthon (22) was obtained by either oxidative *bis*-decarboxylation of the diacid (19) or from

cyclobutene-3,4-dicarboxylic anhydride (23). When (22) was subjected to flash vacuum pyrolysis at 400°C and 10^{-3}mm Hg it was found that a 1:1 mixture of cis-hexa-1,3,5-triene and cyclohexa-1,3-diene resulted. The latter due to an electrocyclisation reaction. However, when (22) was converted to the aziridine (24) by the photolysis of (22) with ethyl azidoformate, pyrolysis of (24) at 500°C resulted in the formation of the dihydro-azepine (26) via the intermediacy of the cis-1,2-divinyl aziridine (25).

The above behaviour was contrasted with the pyrolysis of the cycloadduct (27) which was prepared by the reaction of (22) with anisonitrile oxide. The pyrolysis of which at 500°C and 10^{-3}mm Hg gave the cis-divinyl derivative (28). Thus it was concluded that the ease with which these cyclic cis-1,2-divinyl compounds undergo the Cope rearrangement depended on the size of the attached ring system.

Buchan et al.[59] have also reported on the utilisation of flash vacuum pyrolysis used simultaneously in the presence of a dehydrogenation catalyst (Scheme 15).

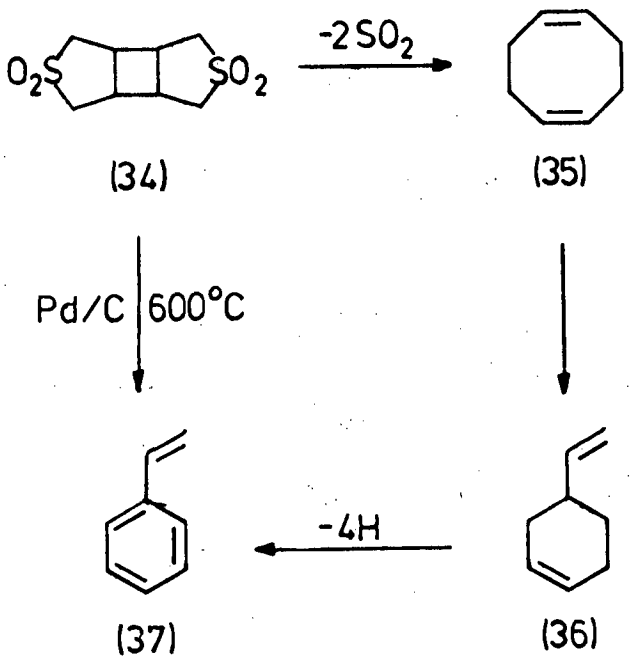


Scheme 15.

The tricyclic anhydride (16) was pyrolysed at 400°C and 10^{-3}mm Hg through a catalyst bed of 5% palladium on activated carbon to give phthalic anydride (32) in high yield, due to the removal of the ring junction hydrogens in (29) followed by an electrocyclisation of the intermediate (30) prior to the further reduction of the dihydrophthalic anhydride (33). Similarly, it was reported that the pyrolysis of cis-2,3-divinylsuccinic anhydride (29) at 425°C and cis-1,2,5,6-tetrahydrophthalic anhydride (31) at 350°C also gave phthalic

anhydride (32) in high yield.

In addition to the above results, mention was made on the pyrolysis of the bis-sulphone (34), (Scheme 16). This resulted in a 4:1 mixture of 4-vinyl-cyclohexene (36) and cycloocta-1,5-diene (35), identified by g.l.c. However, when (34) was subjected to pyrolysis at 600°C over 5% palladium on activated carbon, rearrangement and dehydrogenation occurred simultaneously to yield styrene (37) as the major product.



Scheme 16.

In conclusion, it was proposed that whilst looking at potential sulphone monomer systems for

DISCUSSION

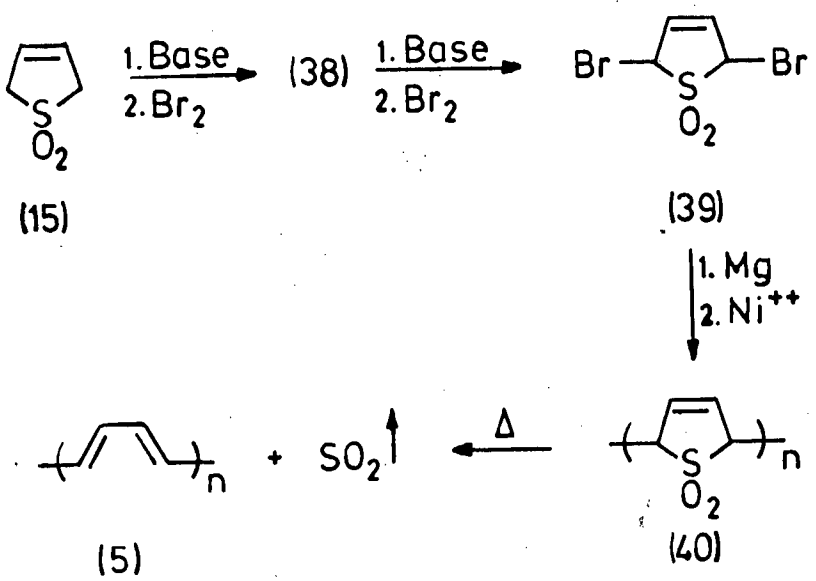
DISCUSSION

CONTENTS

A. ATTEMPTS TO PREPARE POLY(ACETYLENE) via A SOLUBLE PREPOLYMER ROUTE

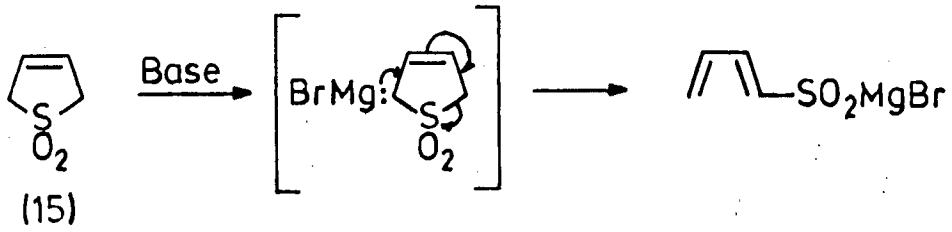
1. From 2,5-dihydrothiophene-1,1'-dioxide

Initial attempts to synthesise poly(acetylene) centred on the synthesis of the potential monomer 2,5-dibromo-2,5-dihydrothiophene-1,1'-dioxide (39). This could then be polymerised to the prepolymer (40), by 2,5-bis-Grignard formation followed by nickel catalysed polymerisation. Prepolymer (40), would then undergo thermal elimination of sulphur dioxide to give poly(acetylene), (5). This route in theory would incorporate all the desirable features concomitant with the prepolymer stratagem outlined in the introduction, (Scheme 17).



Scheme 17.

A wide variety of bases and reaction conditions were used in an attempt to prepare the mono-bromo compound (38). However, these were all unsuccessful except in the case of ethylmagnesium bromide as base in which a 4% yield of the desired product was isolated. The reason for this is that the introduction of electrophiles to the α-position under basic conditions is highly limited, because the 3-sulpholene α-carbanion is extremely labile and undergoes ring opening before it can react with an electrophile, (Scheme 18).



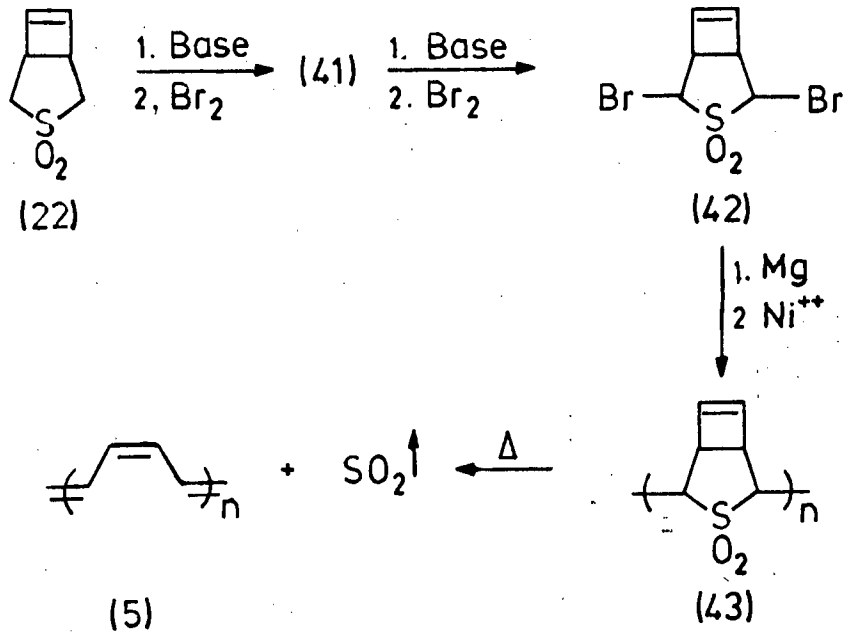
(15)

Scheme 18.

This problem has been overcome by Yamada et al.[54] with respect to α-alkylation. Here the 3-sulpholene α-carbanion, generated by the base lithium bis-trimethylsilylamide, was trapped by the electrophile (alkyl iodide) in situ at -78°C in the presence of HMPA as cation trapping agent. Similar results have also been achieved by Chou et al.[55] using sodium hydride as base also with respect to α-alkylation. However, all attempted modifications of these methods with respect to α-bromination proved unsuccessful.

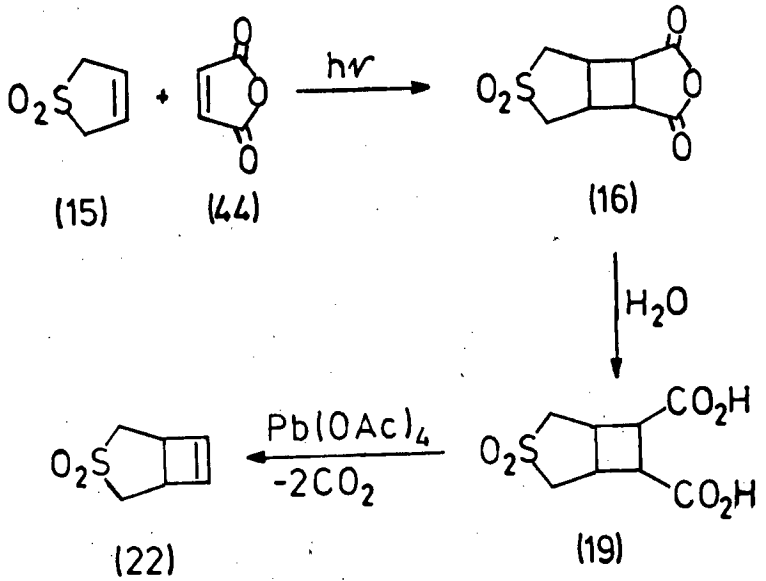
2. From 3-thiabicyclo[3.2.0]hepta-6-ene-3,3'-dioxide

To overcome this problem associated with α-bromination of 3-sulpholene (15), it was decided to move to the higher analogue 3-thiabicyclo[3.2.0]hepta-6-ene-3,3'-dioxide (22), (Scheme 19).



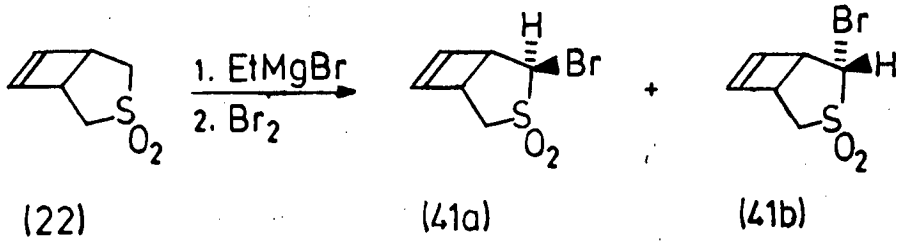
Scheme 19.

Alkene (22) was prepared by the photolysis of maleic anhydride (44) with 3-sulpholene (15), followed by hydrolysis of the photoadduct (16) and oxidative bis-decarboxylation of the diacid (19) using lead tetra-acetate,[60] (Scheme 20).



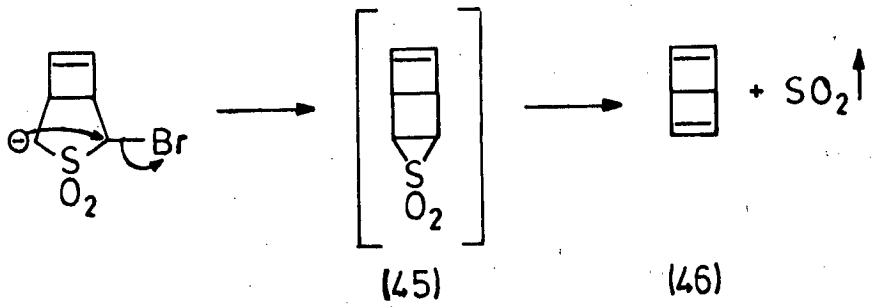
Scheme 20.

Using the method of Becker and Labhart[61], (22) was successfully α-brominated in 26% yield to give 2-bromo-3-thiabicyclo[3.2.0]hepta-6-ene-3,3'-dioxide as a mixture of isomers. These were readily separable by flash chromatography to give the exo (41a) and endo (41b) isomers in 4:1 ratio respectively, (Scheme 21). The assignment of each isomer was based on the proton-proton coupling constant between the α-proton C(2)H and the ring junction proton C(1)H.



Scheme 21.

The repeat reaction on the isomeric mixture to give the potential dibromide monomer (42) resulted in the return of a small amount of starting material with no other observable products present. This somewhat unusual situation may be attributed to an intramolecular Ramberg-Backlund reaction, whereby after initial deprotonation there is intramolecular elimination of Br^-, followed by collapse of the intermediate episulphone (45) to give Dewar benzene (46), (Scheme 22).



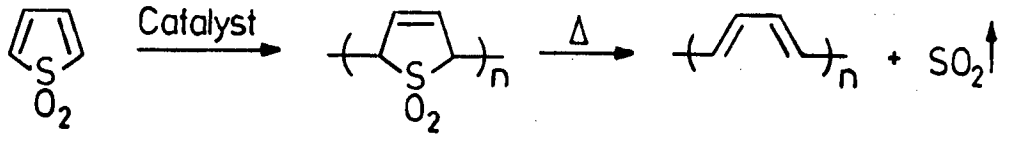
(45) (46)

Scheme 22.

When an n.m.r. sample of (41a, 41b) was treated with potassium tert-butoxide in d^6 DMSO the ^1H-n.m.r. spectrum did show a singlet at 7.25ppm corresponding to the formation of benzene, albeit in low yield.

3. From thiophene-1,1'-dioxide and 3,4-dichloro-thiophene-1,1'-dioxide

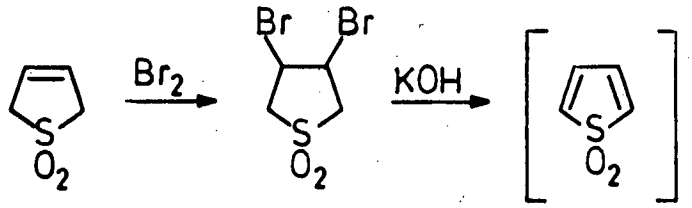
An alternative strategy employed was in the synthesis of thiophene-1,1'-dioxide (47). This in theory could be polymerised to the prepolymer (40), followed by the thermal extrusion of sulphur dioxide to give poly(acetylene), (5), (Scheme 23).



(47) (40) (5)

Scheme 23.

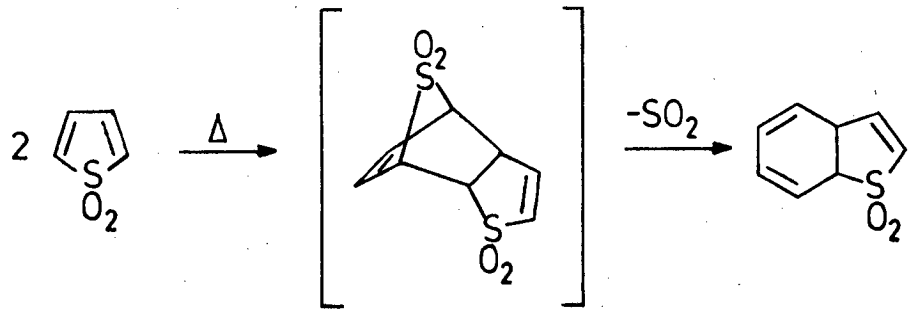
Thiophene-1,1'-dioxide (47) was prepared by the method of Bailey and Cummins,[62] involving the base induced bis-dehydrobromination of 3,4-dibromo-2,5-dihydrothiophene-1,1'-dioxide (48) (Scheme 24).



(15) (48) (47)

Scheme 24.

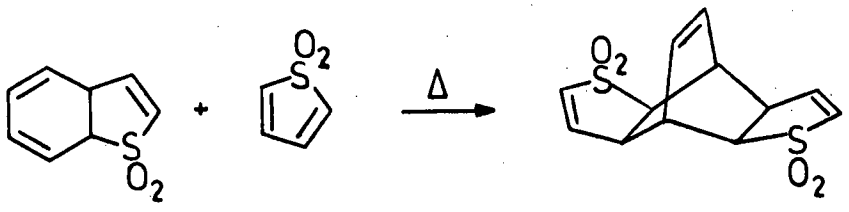
Thiophene-1,1'-dioxide (47) cannot be isolated as it undergoes a $4\pi+2\pi$ cycloaddition with itself to give the benzothiophene (49), (Scheme 25). Therefore, in order to prevent this it must be kept at 5°C and in dilute solution (0.1M).



(47) (49)

Scheme 25.

As well as (49), Bailey and Cummins also reported the formation of an unidentified 'highly insoluble polymer'. It was decided to examine this to ascertain whether it might be the desired prepolymer (40). However, it was subsequently revealed by ^{1}H and ^{13}C-n.m.r. spectra that the compound in question (47a) was the Diels-Alder adduct of the parent (47) and the dimer-SO_2 (49), (Scheme 26). Of the six possible isomers that could be formed in this reaction, the 6-line ^{13}C-n.m.r. spectrum clearly showed that it must be either of the two forms in which the SO_2 groups are diagonally situated with respect to each other, with the exo-exo form being preferred due to expected favourable secondary orbital interactions in the transition state.

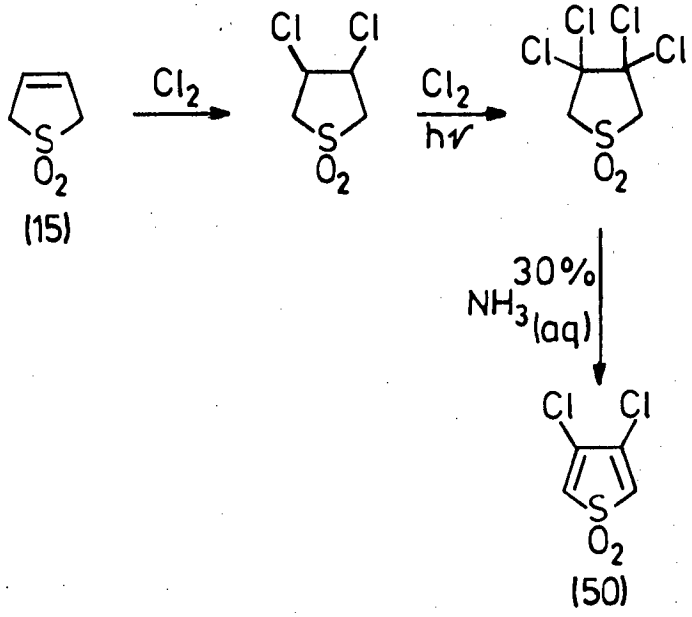


(49) (47) (47a)

Scheme 26.

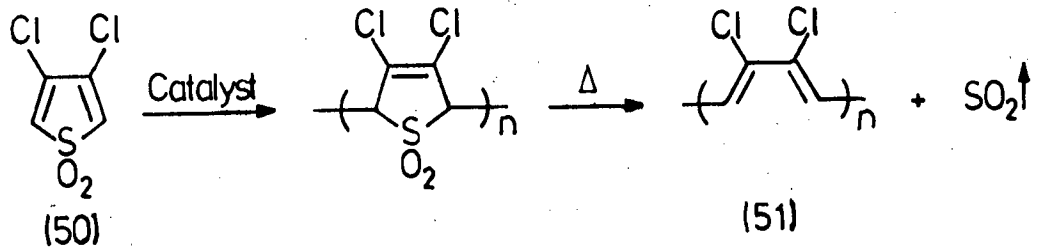
All attempts to polymerise solutions of thiophene-1,1'-dioxide (47) using conventional anionic initiators such as n-butyl lithium[63] and sodium naphthalide[64] proved unsuccessful. The reason for this probably stems from the fact that in the bis-dehydrobromination step (Scheme 24), water is formed as a by-product. Consequently, the initiator system is being destroyed before attack can take place. Attempts to overcome this problem by the use of desiccants and molecular sieves in conjunction with the injection of excess initiator were also unsuccessful.

In an attempt to circumvent the inherent problems associated with (47), the stable derivative 3,4-dichlorothiophene-1,1'-dioxide (50) was prepared by the method of Mandel et al.[65] (Scheme 27).



Scheme 27.

Polymerisation of (50) followed by thermal extrusion of sulphur dioxide would not of course lead to poly-(acetylene) itself, but the dichloro-derivative (51), (Scheme 28).



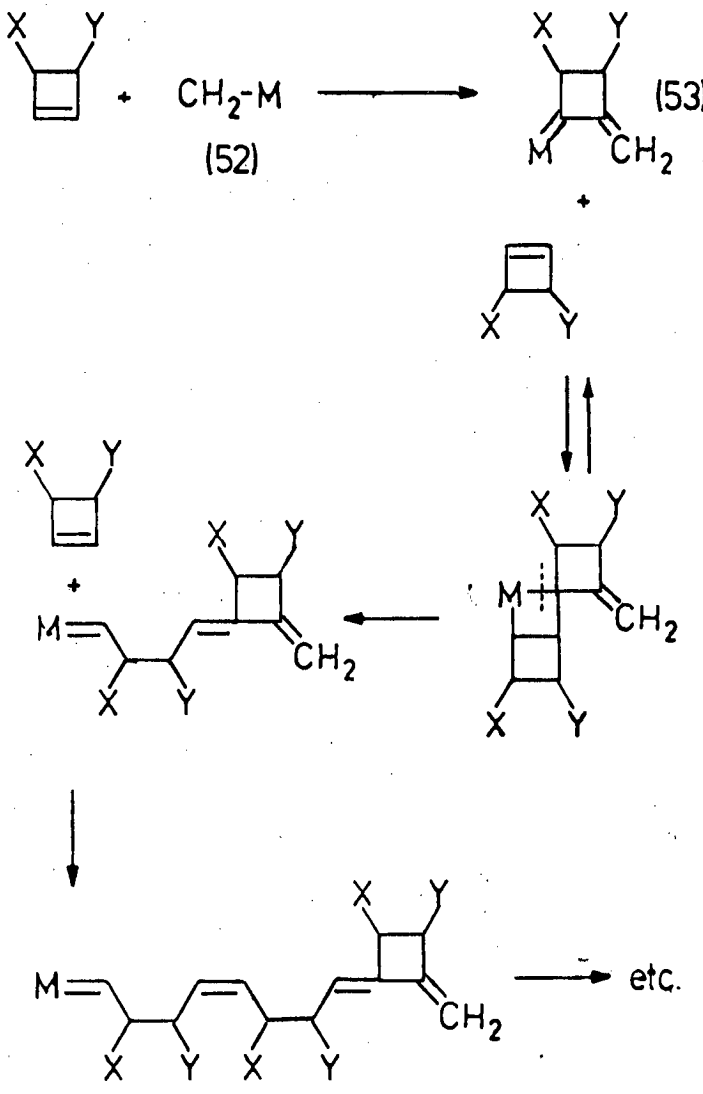
Scheme 28.

In the event, (50) could not be polymerised by either sodium naphthalide[64] or the Ziegler-Natta catalyst system of triethyl aluminium/titanium tetrachloride.[66] In

contrast, in control experiments, freshly distilled cyclopentadiene was successfully polymerised to poly(cyclopentadiene).

4. General background to the ring opening metathesis polymerisation

The olefin metathesis reaction has been and continues to be of wide interest with regard to the mechanistic pathways involved.[67] The specific case of ring opening polymerisation of strained cyclo-olefins seems to proceed *via* a chain reaction initiated by a metal-carbene complex (52) generated from the catalyst and co-catalyst. This reacts reversibly with the olefin *via* a metallocyclobutane intermediate (53), resulting in the formation of a long chain linear polymer. The mechanism for the reaction with a disubstituted cyclobutene is shown in Scheme 29.



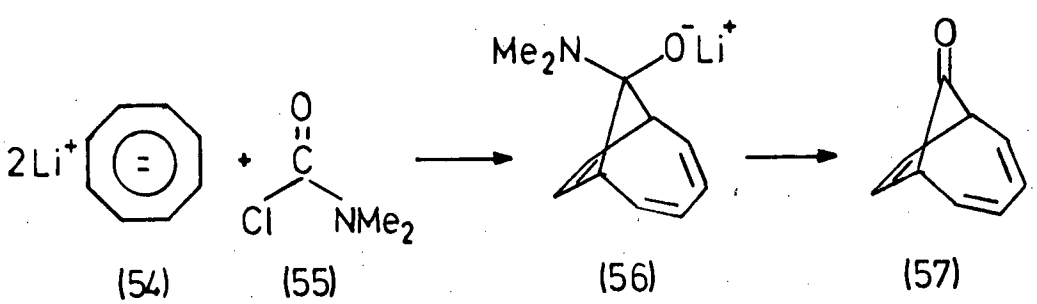
Scheme 29.

There are a wide variety of catalyst systems that have been employed for metathesis reactions[67]. These have proved to be very variable with regard to their reactivity and selectivity. The vast majority are based on tungsten although others incorporating molybdenum, rhenium, irridium etc. have been successful in particular

cases. The catalyst system that is by far the most widely used in homogeneous metathesis is the system based on tungsten hexachloride and tetramethyl tin as co-catalyst. This was first discovered by van Dam et al. in 1972,[68] who were able to metathesise long chain fatty acid esters using this system. This was the first report on the successful metathesis of an olefin bearing polar functional groups.

5. From 9-oxa and 9-thiabicyclo[4.2.1]nona-2,4,7-trienes and other strained cyclo-olefins.

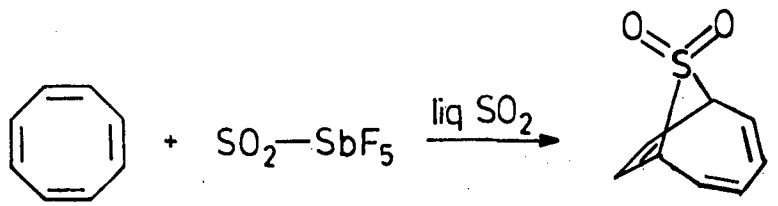
The 9-oxa and 9-thiabicyclo[4.2.1]nona-2,4,7-triene (57,60) systems were chosen as potential monomers. The 9-oxa compound (57) was prepared by the method of Antkowiak et al.[69] This involved the reaction of the cyclooctatetraene dianion (54), prepared from COT and lithium shavings, with dimethylcarbamoyl chloride (55) followed by hydrolysis of the intermediate salt (56), (Scheme 30)



(54) (55) (56) (57)

Scheme 30.

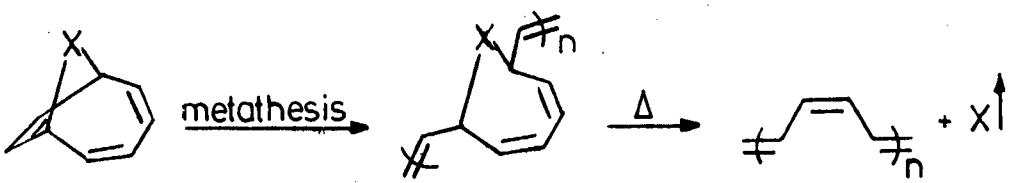
The 9-thia compound (60) was prepared by the method of Paquette et al.[70] In this case cyclooctatetraene (58) was treated with a sulphur dioxide-antimony pentafluoride complex (59), (Scheme 31).



(58) (59) (60)

Scheme 31.

These monomers could in theory undergo metathesis at any of three double bonds, (Scheme 32). However, it was anticipated that attack would take place at the relatively more strained and non-conjugated double bond at the 7-position. This selectivity has been shown to operate in the case of the 'Durham monomer' (Page 14), where the cyclobutene ring is opened in preference to the double bonds in the norbornadiene ring.

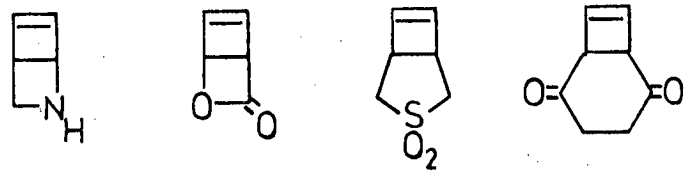


X=CO, SO_2

(57,60) (5)

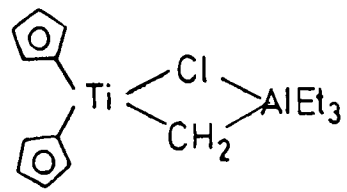
Scheme 32.

In the event, neither (57) nor (60) could be polymerised using the $WCl_6/SnMe_4$ catalyst system. Whereas in control experiments, both the 'Durham monomer' and norbornene were successfully polymerised. These control experiments were carried out at each new trial to test the activity of the catalyst, as it can be variable on occasions[28]. Other examples including (61), (62), (22) and (63) were tried, but again no polymerisation was achieved.



(61) (62) (22) (63)

An alternative catalyst system using μ-chloro-μ-methylene-bis(cyclopentadienyl)titanium triethylaluminium (64) and triethylamine as co-catalyst was also tried. Again no polymerisations took place except in the case of the two control monomers. These in turn polymerised considerably more slowly than the $WCl_6/SnMe_4$ system.



(64)

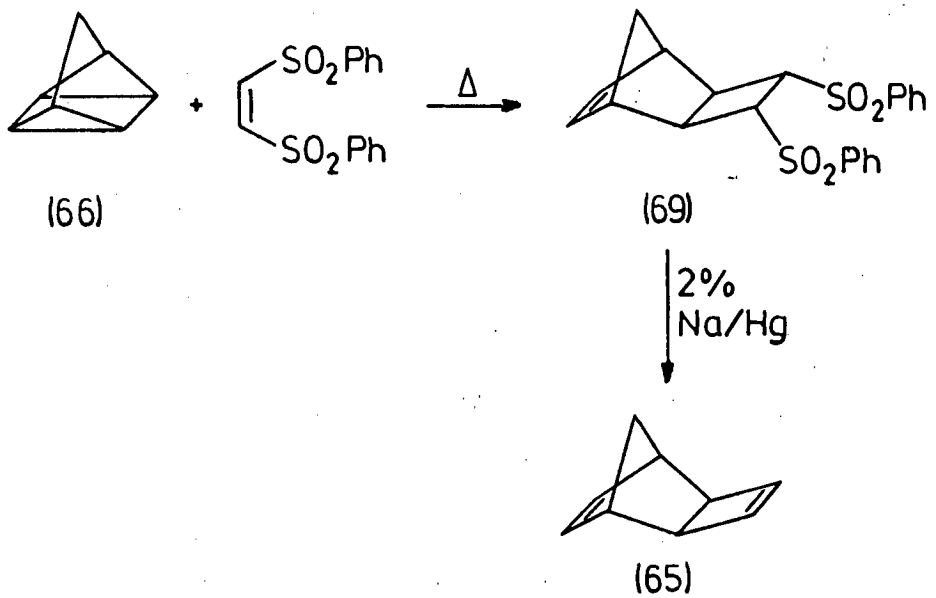
6. From tricyclo[4.2.1.$0^{2,5}$]nona-3,7-diene and related systems.

The aforementioned catalyst mixtures are extremely fragile and are prone to rapid decomposition unless rigorous handling procedures are maintained, which no doubt explains the variable induction periods observed on occasions. Notwithstanding the aforesaid, there seems to be one particular underlying reason for the failure of these compounds to polymerise. That is the presence of polar functional groups present in these molecules. In effect, the catalyst is being poisoned so rapidly that metathesis cannot occur at the olefinic centre. Preferential complexation with the p-orbitals of the heteroatoms taking place at the expense of metallocyclobutane formation with the π-orbitals of the alkene.

In order to circumvent this problem, it was decided to synthesise the tricyclic diene (65), which after metathesis to the prepolymer would undergo a retro Diels-Alder elimination of cyclopentadiene to give poly-(acetylene), (Scheme 33).

Tabushi reported that the cycloaddition reaction of quadricyclane (66) with maleic anydride (44) was both stereo and regiospecific. Only the exo-anti-adduct was formed with the anti-arrangement presumably being favoured due to adverse steric interactions encountered in a syn-arrangement.

An alternative higher yielding method was also adopted. This method employed was that of De Lucchi et al.[72], whereby quadricyclane (66) is coupled to (Z)-bis(phenylsulphonyl)ethylene, followed by reductive bis-elimination of phenylsulphenic acid from the adduct (69) with a 2% sodium amalgam, (Scheme 35).

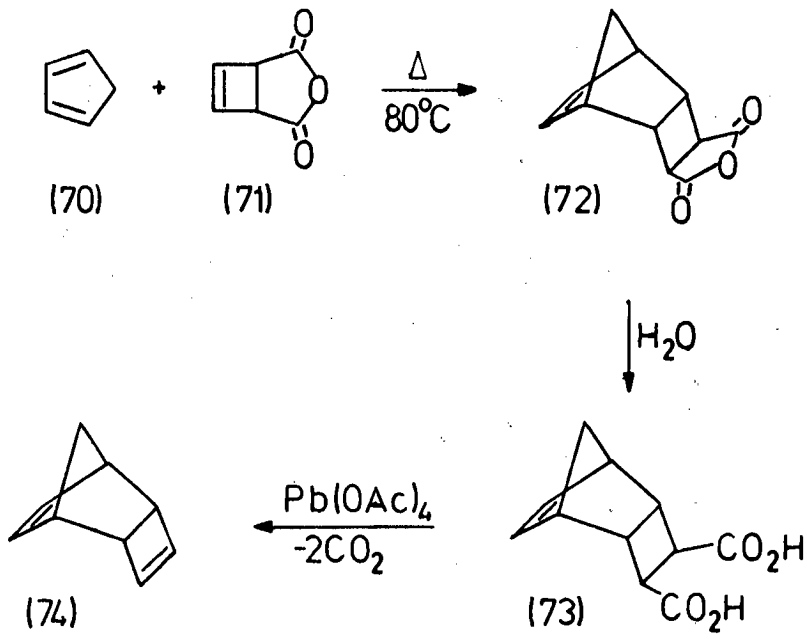


(66) (69) (65)

Scheme 35.

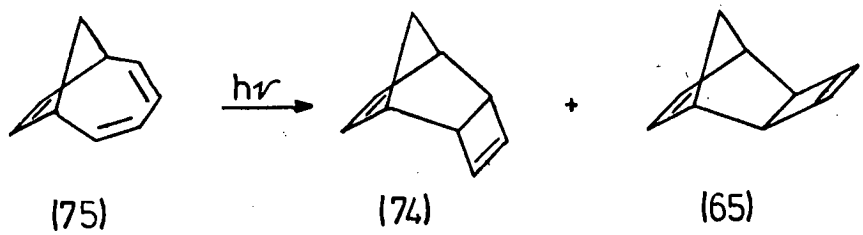
The endo-isomer (74) was also synthesised by a novel route. This involved the initial cycloaddition

reaction between cyclopentadiene (70) and bicyclo[3.2.0]-hepta-6-ene-2,4-dicarboxylic anhydride (71) in boiling benzene, to give the anhydride (72) in quantitative yield. Hydrolysis of (72) gave the tricyclic diacid (73). Oxidative bis-decarboxylation of (73) using lead tetra- acetate gave the desired diene (74) in 15% yield, (Scheme 36).



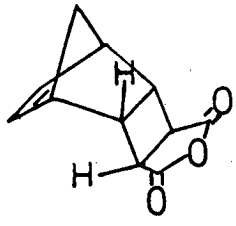
Scheme 36.

Previously, this compound could only be synthesised as an isomeric mixture with the exo-isomer (65) by a photochemical rearrangement of (75),[73] (Scheme 37).

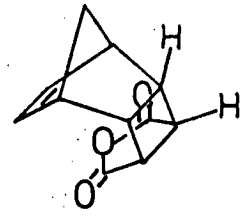


Scheme 37.

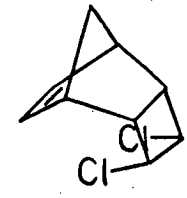
The anti-stereochemistry of (72) followed from its ^{1}H-n.m.r. spectrum which showed a cyclobutane ring trans-coupling constant, with $J_{2,3}$ of 1.6 Hz. This is in contrast to the minimum value of 5Hz expected for the cis-interaction of adjacent protons, in the possible syn-isomer (76).[74] Addition on to the anti-face of (71) contrasts with the behavior of cis-3,4-dichlorobutene[75] which undergoes a similar cycloaddition to form only the syn-endo isomer (77) by virtue of favourable secondary orbital interactions.[76] However, in the case of (72) an overwhelming unfavourable steric interaction by the anhydride moiety precludes syn-endo addition. Notwithstanding this, as steric demands for exo and endo addition are similar, the exclusive observation of the latter points to a well defined secondary interaction.



(72)



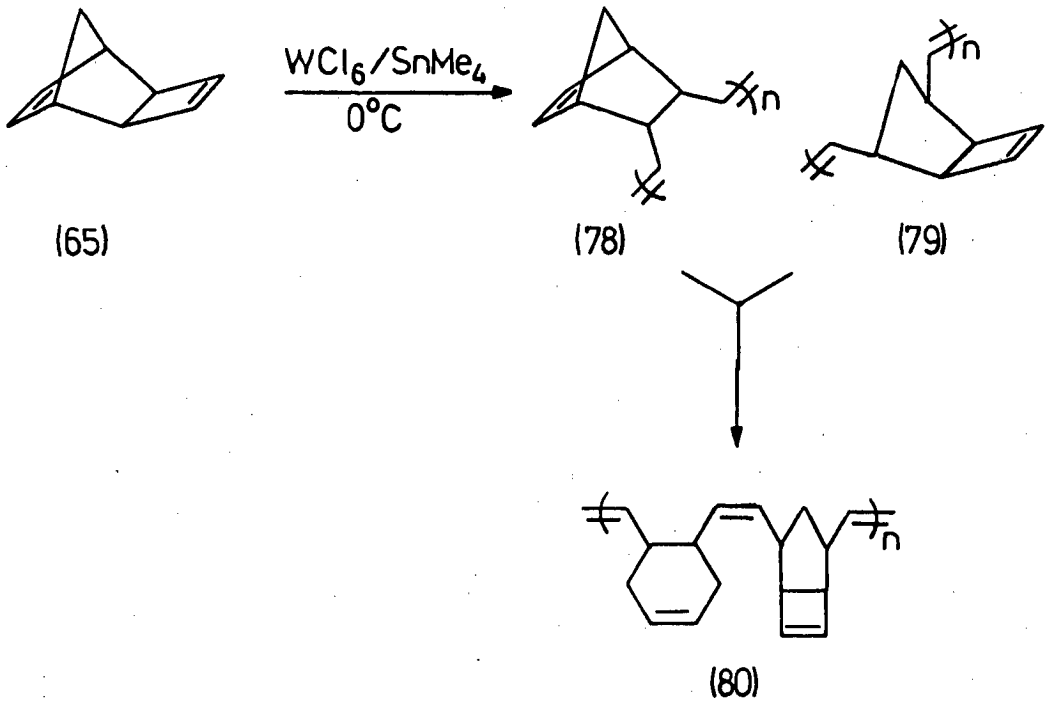
(76)



(77)

Returning to the polymerisation of the diene (65), (Scheme 33), reaction of this with $WCl_6/SnMe_4$ in chlorobenzene at 0°C resulted in the formation of a uniformly viscous reaction mixture after 40 minutes. The polymerisation was then terminated by the addition of

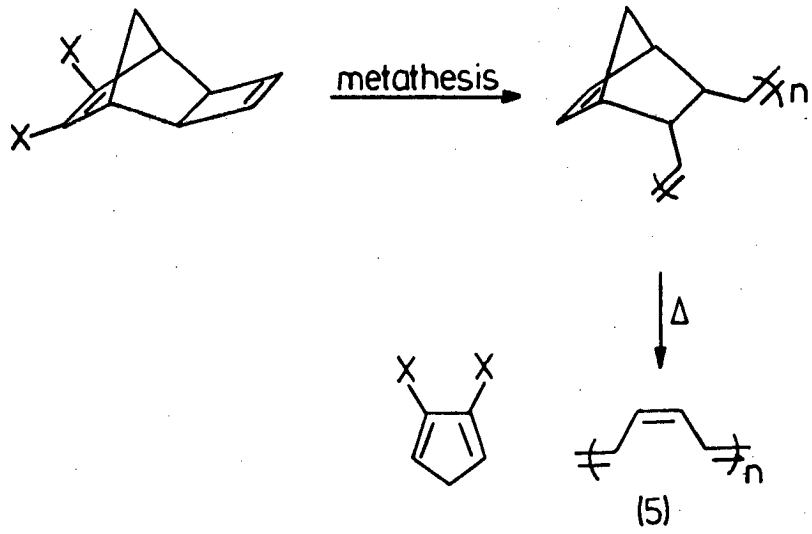
a few drops of methanol. The reaction mixture was then poured into a large excess of methanol which precipitated the polymer as a white solid, in 54% yield. The polymer was found to be completely insoluble in solvents of all polarities. This precluded rigorous purification by the standard method of dissolution and reprecipitation. Therefore the subsequent combustion analysis was erroneous due to occluded catalyst residues, although the C:H ratio was correct for a polymer of empirical formula (C_9H_{10}). A solid state ^{13}C-n.m.r. was carried out on the polymer, and this indicated that polymerisation had taken place not only at the cyclobutene double bond but also at the norbornene double bond. Also, heating the polymer to 300°C did not result in the extrusion of any cyclopentadiene. This lack of selectivity was somewhat unexpected in view of the regiospecificity shown in the 'Durham' monomer towards the cyclobutene double bond. Thus in actuality, some type of co-polymer (80) of the two systems (78,79) had been formed (Scheme 38). In addition to this a certain amount of cross-linking seems probable.



Scheme 38.

The two main problems that detract from this route are the lack of solubility of the prepolymer (80) and that polymerisation is occurring at both olefinic centres instead of at the cyclobutene double bond exclusively. It should be possible to kill two birds with one stone by introducing functionality at the norbornene double bond (7 and 8 positions). This would effectively block off metathesis at this position due to steric hindrance, while at the same time increasing the solubility of the prepolymer by the incorporation of good solvating groups, (Scheme 39). However, one must bear in mind the

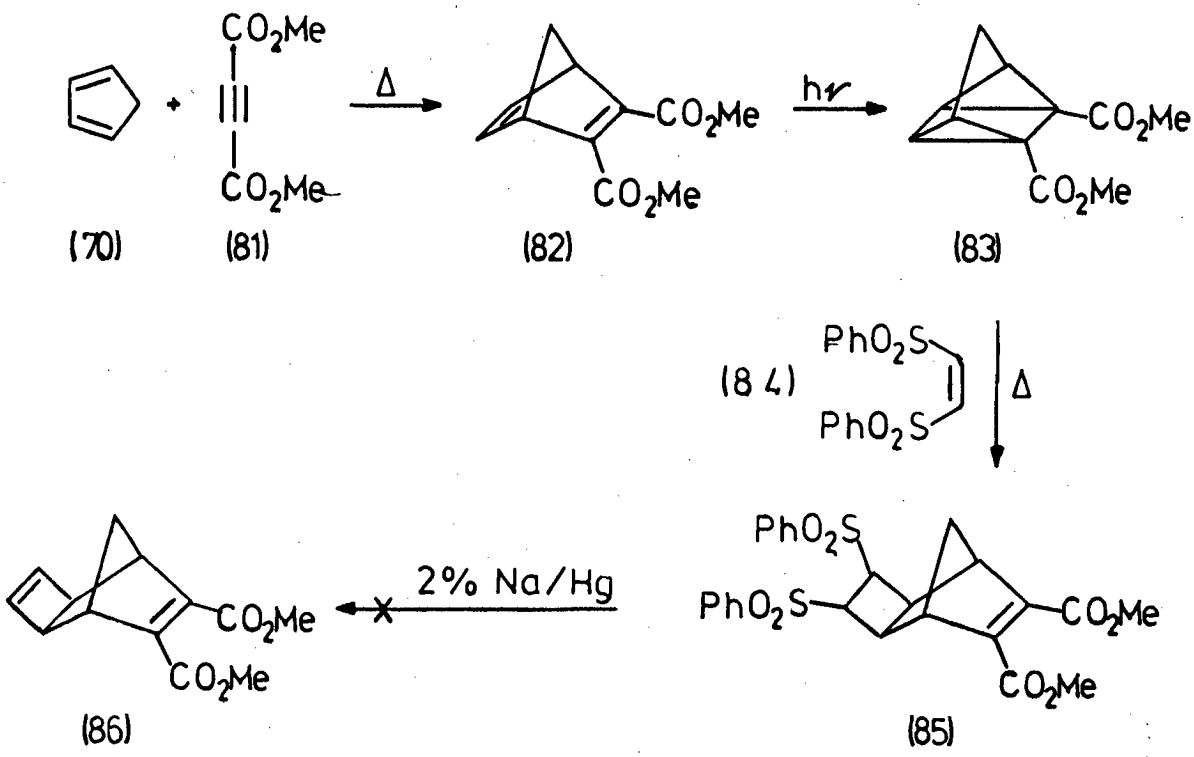
pitfalls associated with catalyst deactivation when applying these principles.



(5)

Scheme 39.

To these ends the 7,8-dimethyl ester (86) seemed a likely candidate, in view of the fact that it was known from van Dam[68] that the $WCl_6/SnMe_4$ system could withstand the presence of the ester groups providing that they were a minimum of two bonds distant from the metathesis centre. The reaction sequence towards the synthesis of (86) is shown in Scheme 40.

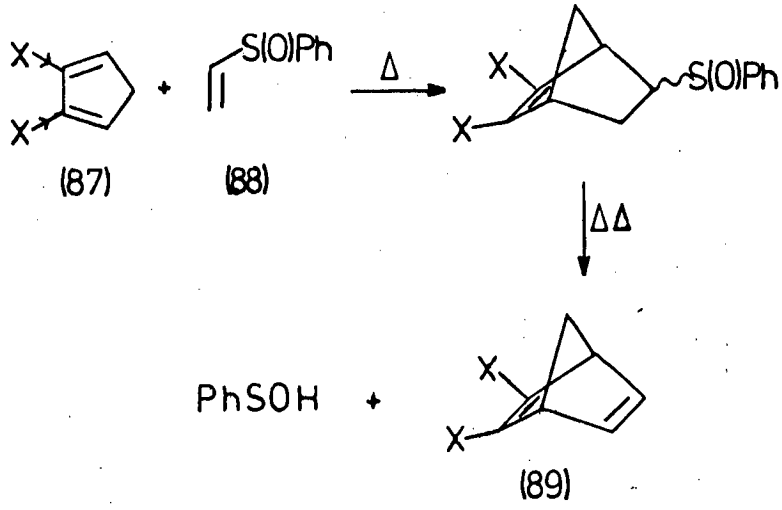


Scheme 40.

The initial Diels-Alder reaction between cyclopentadiene (70) and dimethylacetylene dicarboxylate (81), gave the norbornadiene-2,3-dimethylester (82) in quantitative yield, as did the unsensitised photoisomerisation to the quadricyclane-2,3-dimethylester (83). The cycloaddition between (83) and (Z)-1,2-bis(phenylsulphonyl)ethylene (84) in boiling chloroform over an extended period gave (85) in 32% yield. Unfortunately, in the final step the use of the 2% sodium amalgam not only bis-desulphonated but also reduced or partly reduced the ester functions, resulting in the formation of a very complex reaction mixture which precluded isolation of the desired compound

(86).

Paquette et al.[77] had reported that phenyl vinyl sulphoxide (88) underwent a Diels-Alder cycloaddition with an activated cyclopentadiene derivative (87) in boiling toluene with concomitant loss of phenylsulphenic acid on prolonged heating to give the substituted norbornadiene (89), (Scheme 41).

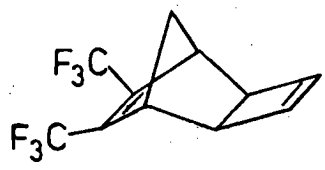


Scheme 41.

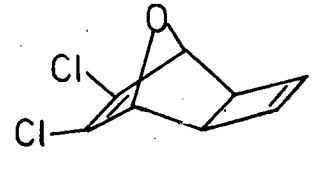
When this was attempted with the quadricyclane diester (83) in place of Paquette's activated cyclopentadiene (87), no reaction took place even after three days in boiling toluene. This can only be attributed to the low dienophilic activity of phenyl vinyl sulphoxide. Phenyl vinyl sulphone is a much more reactive dienophile; however, as an acetylene synthon its use is highly limited as there is no easy way of desulphonating the

adduct to effect olefin formation.

Although work in this area was terminated at this stage, it was anticipated that success might have been achieved through monomers (90) and (91). The dichloro compound (91) would have been particularly attractive, as the substituents at the 7 and 8 positions would have precluded polymerisation from occurring at the norbornene double bond, while at the same time furnishing a degree of solubility on the prepolymer to enable purification procedures to take place. Additionally, the oxo-bridge would provide a favourable thermodynamic route for the retro Diels-Alder reaction as the extruded fragment would be an aromatic molecule.



(90)



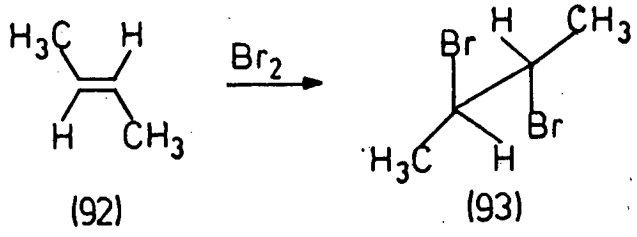
(91)

During the execution of the work associated with poly(acetylene), some interesting results arose with particular respect to the bicyclic sulphone 3-thiabicyclo[3.2.0]hepta-6-ene-3,3'-dioxide (22). These results, and other related observations are the subject of the following chapter.

B. ELECTROPHILIC ADDITION TO NON-CONJUGATED CYCLIC OLEFINS CONTAINING SULPHONYL GROUPS

1. Brief introduction to bromination reactions

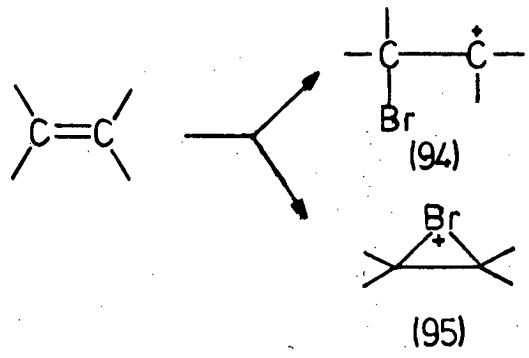
The addition of molecular bromine to a double bond is one of the oldest and best known reactions in organic chemistry. For example, the bromination of trans-2-butene (92) gives (E)-2,3-dibromobutane (93) exclusively, (Scheme 42).



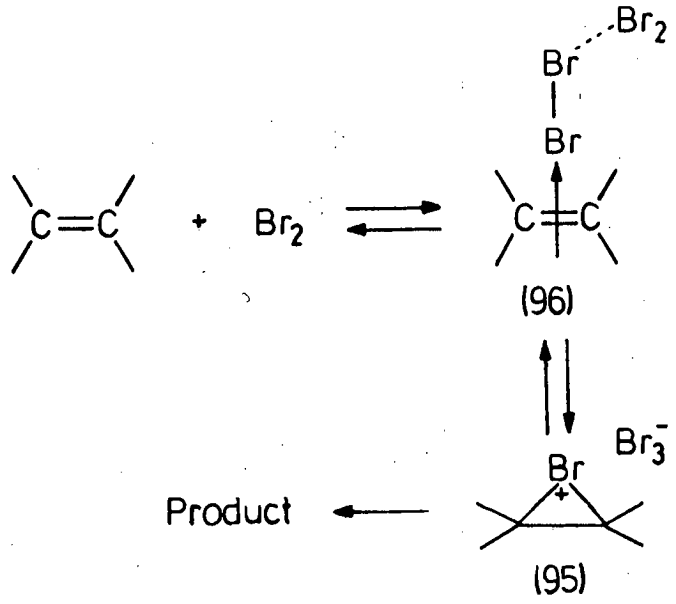
(92) (93)

Scheme 42.

In 1937 Roberts and Kimball[78] pointed out that the observed stereochemistry of this reaction was incompatible with the formation of an intermediate carbocation (94) and suggested that an intermediate bromonium ion (95) is formed in which the bromine uses one of its unshared pairs of electrons and bonds to both carbon atoms of the double bond. Thus rotation about the C-C bond in (95) is impossible and Br^- must attack from the backside to give anti-addition.

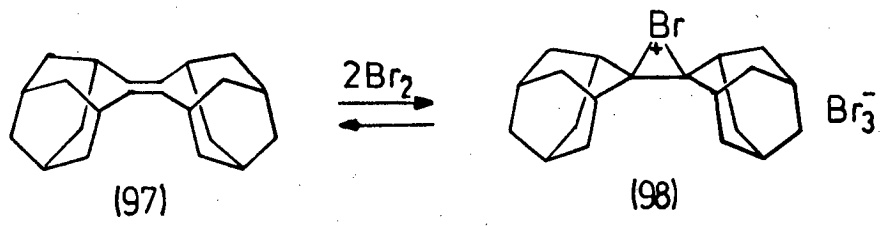


Bromonium ion theory is now well accepted. Olah et al. have given n.m.r. evidence for the existance of cyclic bromonium ions under stable ion conditions[79], Olah and Hockswender[80,81] have also proposed that the transition state in bromonium ion formation is a charge transfer π-complex (96) which then cleaves to form the bromonium ion (95), (Scheme 43).



Scheme 43.

There exists a single example of a stable 'trapped bromonium ion' in the literature. Wynberg et al.[82] reported that on treating adamantylideneadamantane (97) with two equivalents of bromine resulted in the formation of the tribromide salt (98), (Scheme 44).



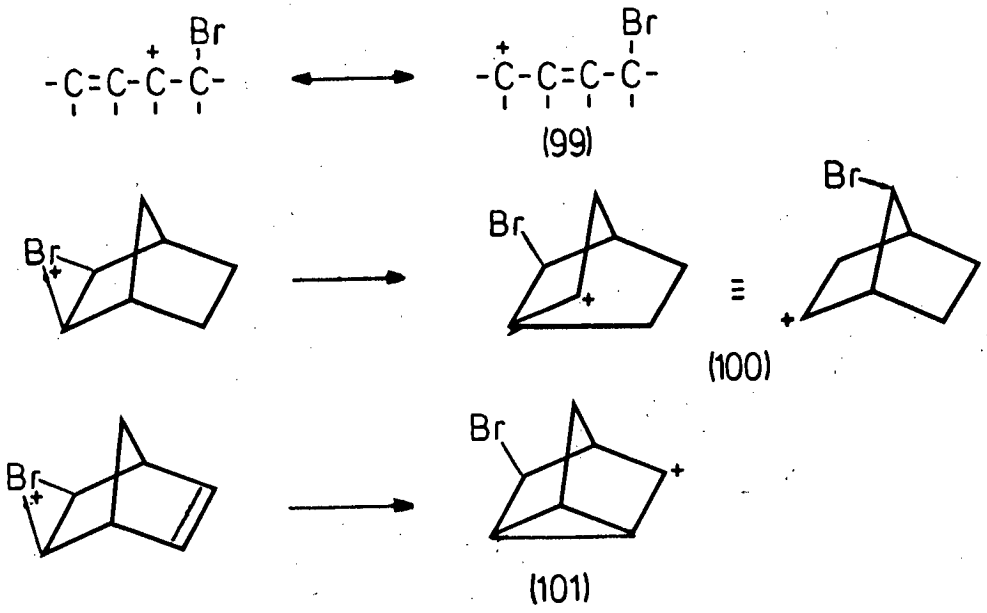
(97) (98)

Scheme 44.

Brown et al.[83] have recently vindicated this by carrying out an X-ray crystal structure analysis on the salt. The structure revealed that there was severe crowding on the side opposite to the bonded bromine atom, thus preventing nucleophilic attack from the rear, so furnishing the stable ion pair.

The bromonium ion concept rationalises the stereochemistry of bromine additions satisfactorally if it recognised that olefins that can form highly stabilised carbocations or where molecular rearrangements can occur, need not form such a structure. Exceptions to the bromonium ion rule include: conjugated dienes in which an intermediate carbocation can be resonance stabilised (99), norbornene systems which can undergo Wagner-Meerwein σ-bond shifts (100) and norbornadienes

which although are non-conjugated, can give rise to π-shifts to form nortricyclyl structures (101), (Scheme 45). A notable exception to the stereospecificity of ionic bromine addition in the absence of conjugation or skeletal rearrangements, was that observed by van Tamelin et al.[84] This concerned the bromination of Dewar benzene, and will be discussed in a subsequent section.



(99)

(100)

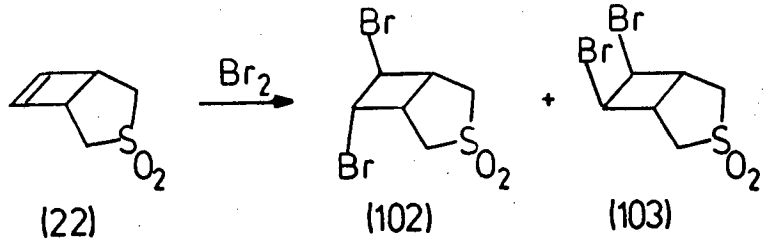
(101)

Scheme 45.

2. Electrophilic addition to 3-thiabicyclo[3.2.0]hepta-6-ene-3,3'dioxide

The bromination of 3-thiabicyclo[3.2.0]hepta-6-ene-3,3'dioxide (22) proceeded sluggishly to give a

quantitative 1:1 mixture (by n.m.r.) of isomeric dibromides,[85] which could be readily separated by flash chromatography (Scheme 46). That the mixture represented a kinetically controlled product distribution was established by the stability of the isomeric dibromides to the reaction conditions.



(22) (102) (103)

Scheme 46.

The stereochemical arrangement was most clearly seen from the 3-line ^{13}C-n.m.r. spectrum of the cis-dibromide (103), and the 6-line ^{13}C-n.m.r. spectrum corresponding to the trans-dibromide (102), indicating the symmetrical and unsymmetrical nature of the products. However, as ionic syn-addition of bromine to a non-conjugated cyclic olefin is almost unprecedented, an X-ray diffraction study was carried out to validate the cis-exo nature of the product (103), (Figure 1).

Radical involvement was precluded on the basis of the sluggish nature of the reaction (which is infinitely slow at -78°C), together with normal precautions of carrying out the reaction in the dark, using an oxygen purge and control experiments using radical scavengers.

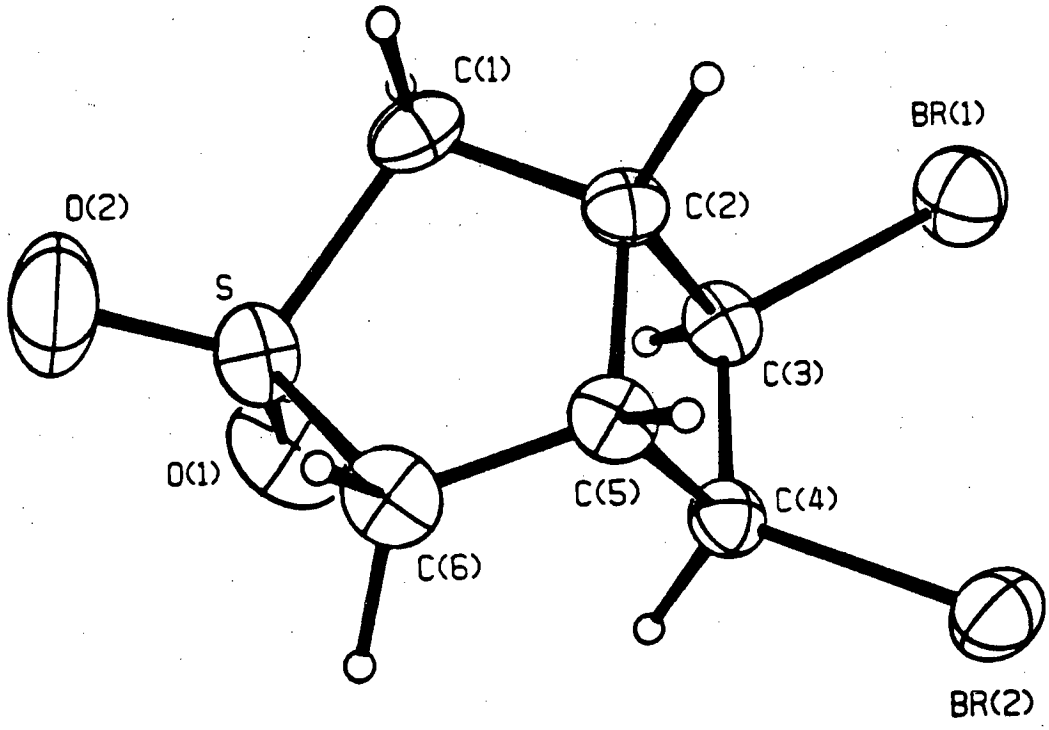
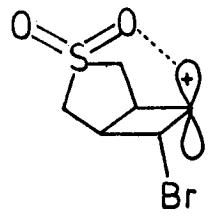
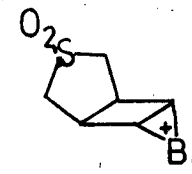


Figure 1. Molecular structure of (103). Selected bond lengths (Å) are: S-O(1) 1.436(5), S-O(2) 1.435(5), S-C(1) 1.791(8), S-C(6) 1.793(7), C(1)-C(2) 1.527(9), C(2)-C(3) 1.520(9), C(2)-C(5) 1.574(9), C(3)-C(4) 1.527(9), C(3)-Br(1) 1.947(6), C(4)-C(5) 1.544(9), C(4)-Br(2) 1.962(6), C(5)-C(6) 1.520(9).

Now, the formation of (103) at the expense of an equal amount of the expected trans-product (102), requires the intermediacy of the open carbocation (104), followed by the subsequent syn-attack by Br^- at a rate that is competative with normal anti-collapse of the bromonium ion (105). Though the formation of (102) itself, via the open carbocation (104) cannot be ruled out.



(104)



(105)

From an inspection of Dreiding models, there is no question that the SO_2 moiety can provide sufficient steric bias to divert the incoming Br^- away from the anti-face, hence causing the syn-attachment of two large bromine atoms. Also discounted was a formal neighbouring group participation by the sulphone group, in the sense of a fully fledged intramolecular bonding participation. This is supported by X-ray evidence which shows that the distance of the exo-oxygen of the sulphone group is at least 3.23Å distant from the double bond moiety, (Figure 2). Furthermore, even if bonding could occur, it should lead to overall syn-addition,

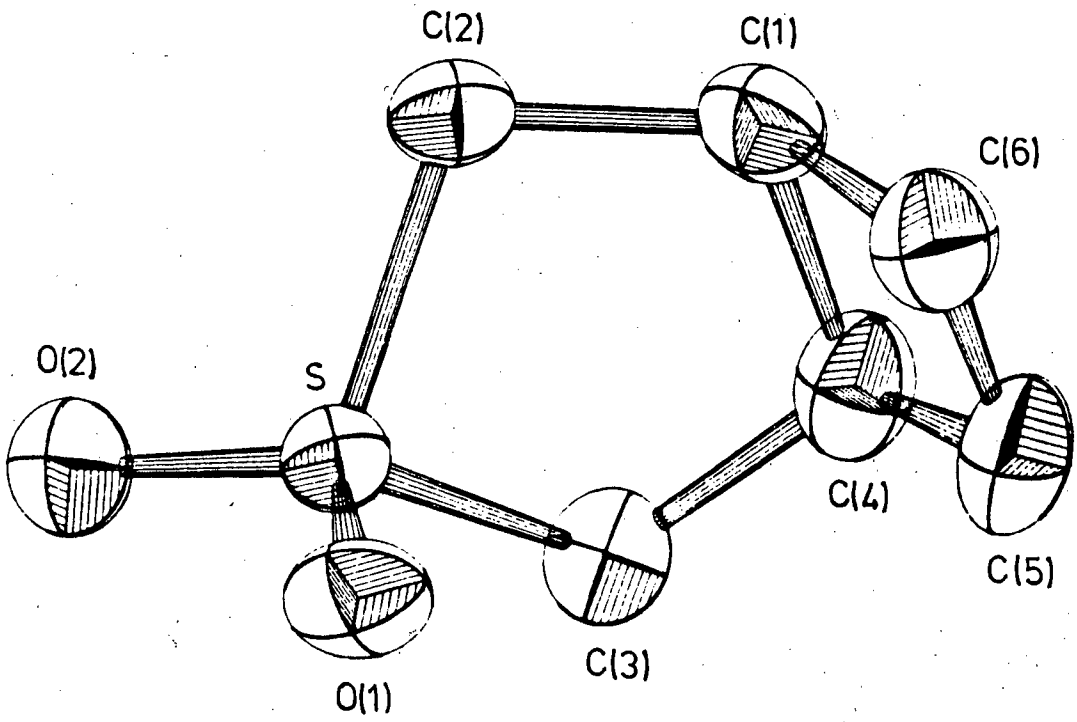
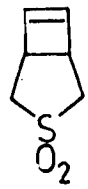


Figure 2. Molecular Structure of (22). Selected bond lengths (Å) are S-O(1) 1.401, S-O(2) 1.445, S-C(2) 1.790, S-C(3) 1.780, C(1)-C(2) 1.509, C(1)-C(4) 1.579, C(1)-C(6) 1.507, C(5)-C(6) 1.316, C(4)-C(5) 1.501, C(3)-C(4) 1.504.

whereas in practice there is an equal preference for anti-addition.

Thus the relaxation in the usual demand for bromonium ion formation followed by backside attack is brought about by an unprecedented favourable stabilising effect of a long range Coulombic (orbital) interaction between the polar SO_2 group and the carbocation centre as depicted in (104). Evidence for a long range interaction of this nature can be supported on both physical and chemical grounds. Examining the X-ray bond parameters of both (103) and (22), it can be seen that in the cis-dibromide the S-O bond lengths are almost identical at 1.436 and 1.435Å for S-O(1) and S-O(2) respectively, whereas in the parent alkene (22), S-O(1) is 1.401Å and S-O(2) is 1.445Å. This difference of 0.044A between S-O(1) and S-O(2) in (22) is by no means an insignificant discrepancy, but in fact a clear indication that there is an electronic interaction between the sulphone group and the π-electron cloud of the double bond. This can be borne out further when examining the photoelectron spectrum (p.e.s.) of (22)[86].

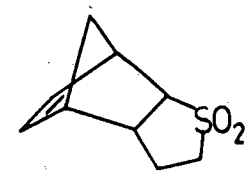


πIp= 10.25eV

(22)

9.43eV

(106)

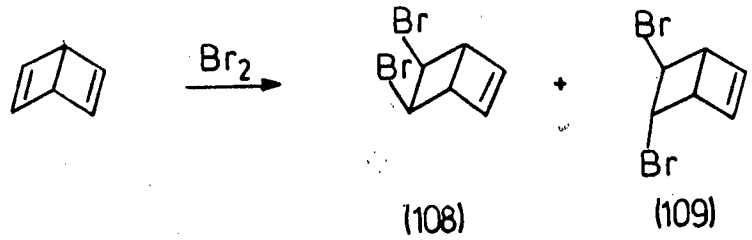


9.55eV

(107)

As can be seen, the π-ionisation potential (πIp) of (22) is significantly higher than that of the parent cyclobutene (106) or of the comparison sulphone (107), where the SO_2 group is remote from the double bond. This is a direct consequence of the sulphone group's effect on the double bond in (22). Thus the olefinic centre is relatively more deactivated with respect to analogous compounds. Chemically, this in turn would account for the sluggish nature in the progression of the bromination, and also why (22) fails to react with carboethoxynitrene under homogeneous conditions.

As mentioned in the introduction to bromination reactions, van Tamelin et al.[84] have reported that ionic addition of bromine to bicyclo[2.2.0]hexa-2,5-diene (Dewar benzene) gave a 30:70 mixture of cis (108) and trans (109) dibromides respectively, (Scheme 47).



(108) (109)

Scheme 47.

Only simple additions occurred, therefore no skeletal rearrangements were observed. However, only the trans- isomer (109) could be isolated.

Identification of the cis-compound (108) rested on chemical and n.m.r. evidence. The ^{1}H-n.m.r. spectrum is shown below in Figure 3.

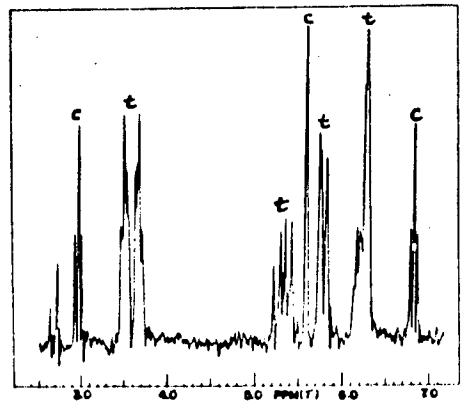
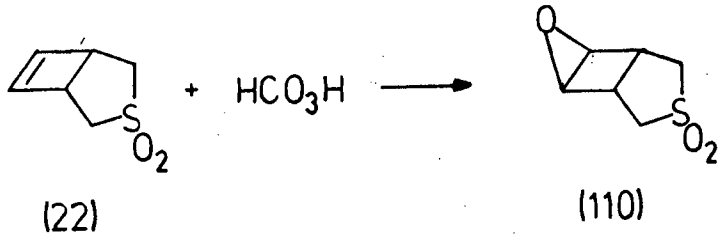


Figure 3.

It is possible that the cis-isomer (108) is formed due to a through space orbital interaction between the π-orbitals of the double bond with an open carbocation, with subsequent attack by the incoming nucleophile from the exo-direction. This would be analogous to the situation found in the bromination of 3-thiabicyclo-[3.2.0]hepta-6-ene-3,3'dioxide (22).

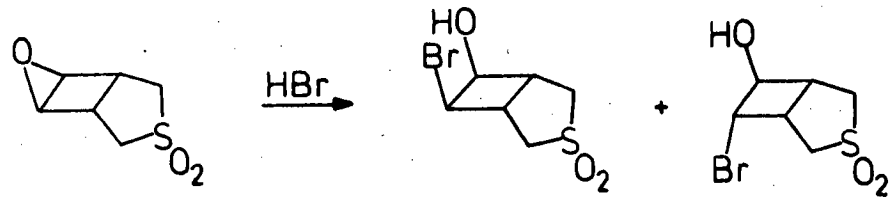
To investigate this phenomenon further, the epoxide of (22) was prepared in 45% yield by reaction with performic acid, (Scheme 48). The anti-stereochemical arrangement of the tricyclic ring system in (110) was confirmed by a Nuclear Overhauser Enhancement study.



(22) (110)

Scheme 48.

Treatment of the expoxide (110) with hydrogen bromide in glacial acetic acid resulted in the formation of a 37:63 mixture (by n.m.r.) of the cis (111) and trans (112) bromohydrins respectively, (Scheme 49).



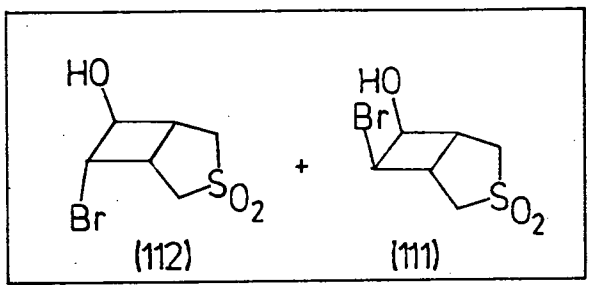
(110) (111) (112)

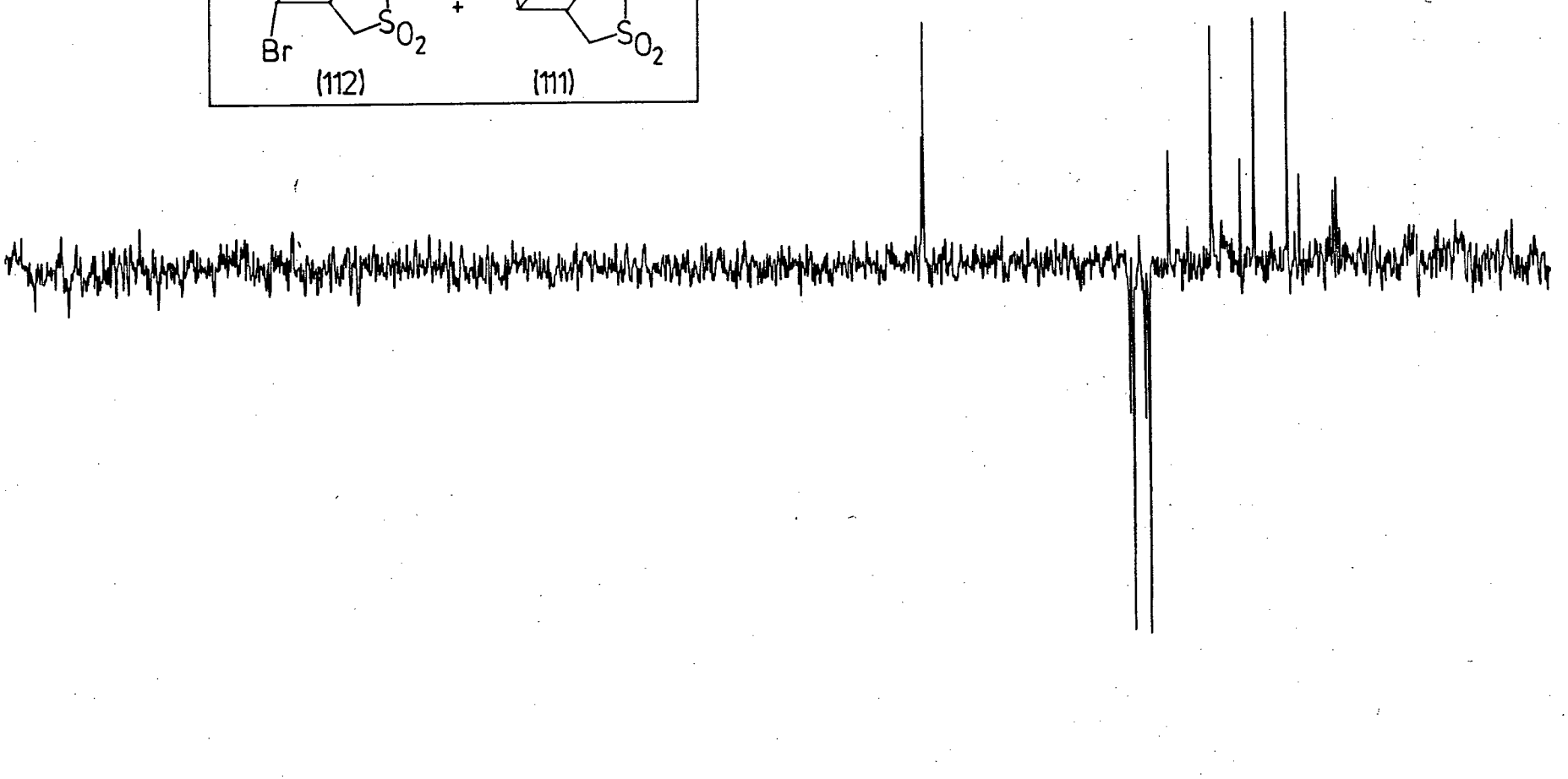
Scheme 49.

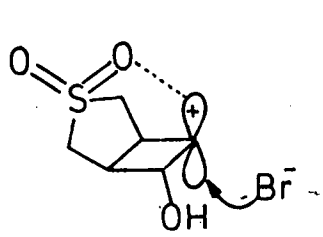
All attempts to isolate these isomers by thin layer chromatography resulted in decomposition of the products, thus precluding separation. The ^{13}C-n.m.r. spectrum of the isomeric mixture is shown in Figure 4. The assignment of the signals could be determined from the proton-proton coupling constants and a Nuclear Overhauser Enhancement study.

Acid catalysed cleavage of epoxides, in the absence of conjugation, normally proceeds with trans-stereochemistry, which is well documented by Akhrem[87]. Thus in order to explain the presence of the cis-stereochemistry we must again invoke the intermediacy of the open carbocation (113), whose formation is brought about by the stabilising effect of the SO_2 group on the carbocation centre, followed by syn-attack by the incoming nucleophile.

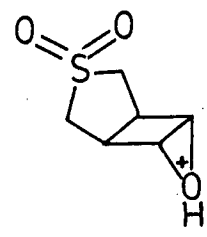
Figure 4.







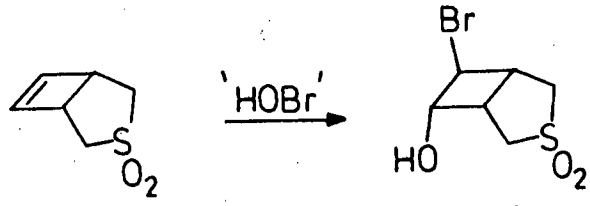
(113)



(114)

This result is entirely consistent with the previous findings as regards bromination and is comparable in that the protonated epoxide (114) is to all intensive purposes a bromonium ion analogue.

The reaction of the alkene (22) with N-bromoacetamide in aqueous acetone or N-bromosuccinimide in aqueous t-butyl alcohol, both of which are synthetic equivalents of hypobromous acid 'HOBr', resulted in the formation of the trans-bromohydrin (115) in 62% yield as the sole product, (Scheme 50).

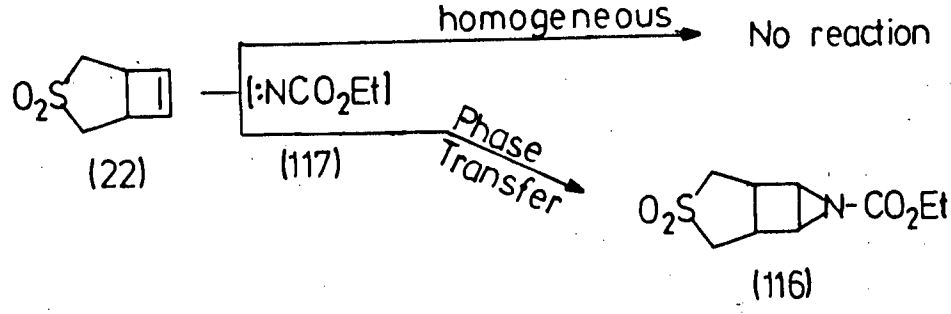


(22) (115)

Scheme 50.

It had been anticipated that the aforementioned reactions would have again furnished an isomeric mixture of cis and trans bromohydrins, by virture of previous

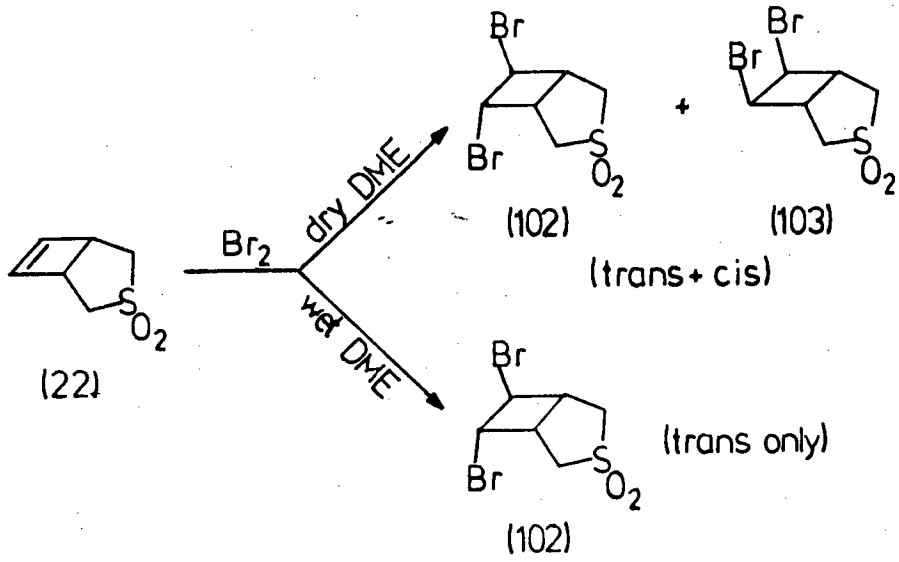
arguments. However, as is often the case, fact defied speculation. In order to explain this seemingly anomolous behaviour, recourse was made to previous work from these laboratories with respect to the reactivity of the alkene (22) to nitrene addition[86]. Under homogeneous conditions, carboethoxynitrene (117) generated *in situ* does not react with (22), whereas under phase transfer conditions (22) was satisfactorally converted into the corresponding N-ethoxycarbonylaziridine (116) in 43% yield (Scheme 51).



Scheme 51.

In this two phase system, the sulphone group, because of its hydrophilic nature will be solvated by penetration into the aqueous layer, thus quenching any electronic influence it may have on the olefinic centre. This would also account for the formation of the single isomer in the hydroxybromination reactions, as these are both conducted in semi-aqueous media.

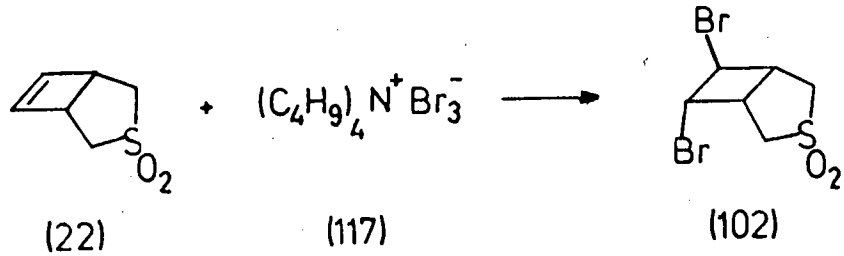
In order to test this hypothesis further, the bromination of alkene (22) was repeated in both wet and dry dimethoxyethane, (Scheme 52).



Scheme 52.

In dry DME, the reaction proceeded to give the cis/trans isomeric mixture as previously received. However, in aqueous DME, bromination of (22) gave the trans-isomer only. This would seem to confirm that the presence of water in the reaction medium does indeed supress the sulphone group's ability to influence the stereochemical course of the aforesaid reactions.

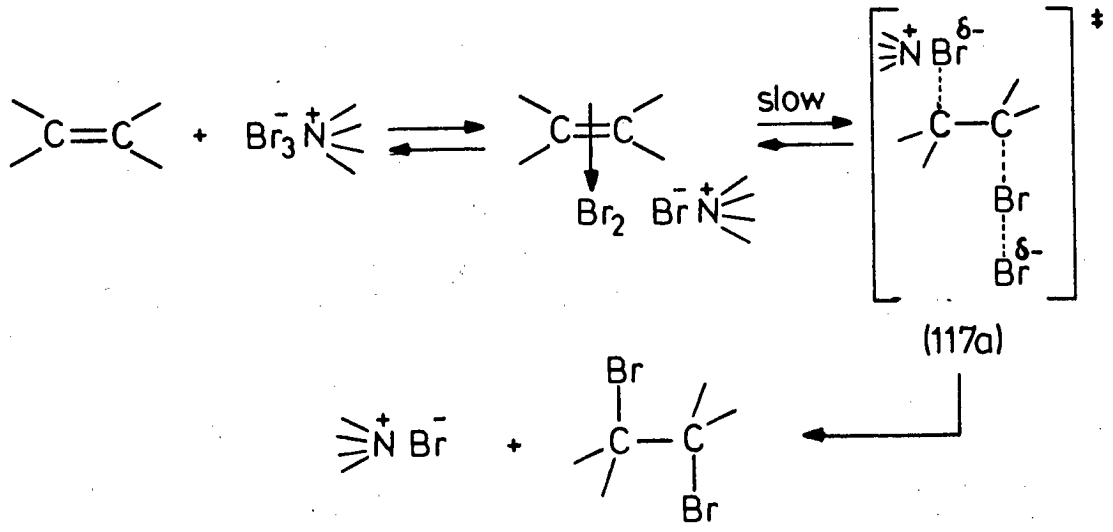
The reaction of (22) with the bromine synthon tetrabutylammonium tribromide (117) in chloroform gave (E)-6,7-dibromo-3-thiabicyclo[3.2.0]heptane-3,3'- dioxide (102) as the sole product, (Scheme 53).



Scheme 53.

Organic tribromide salts like pyridine hydrobromide perbromide (PHP) and tetra-butylammonium tribromide (TBAT) can be used as synthetic equivalents for molecular bromine in additions to carbon-carbon double bonds. However, these reagents frequently give different results. For instance, the bromination of both cis and trans-stilbene with free bromine always leads to mixtures of meso and d,l-dibromides[88], while PHP gives only the product of anti-addition of bromine.[89] Also, the addition of free bromine to 1,3-butadiene in chloroform gives mostly the 1,4-adduct, but PHP and TBAT yield almost exclusively the 1,2-dibromide.[90,91] These synthetically interesting differences on stereo and regioselectivity of free Br_2 and Br_3^- addition reactions clearly point to different mechanistic pathways. Bellucci et al.[92] have recently carried out a kinetic comparison study on the bromination of cyclohexene in low polarity aprotic solvents such as chloroform, in which the majority of preparative brominations are carried out. This has shown that while free bromine addition proceeds according to the mechanism outlined in Scheme 43, tribromide ion addition occurs via the mechanism shown in Scheme 53a, whereby the rate determining step involves the formation of a non-ionic transition state (117a), this being in contradistinction to the formation of the bromonium ion-tribromide ion pair in Scheme 43. This non-ionic transition state serves to explain the

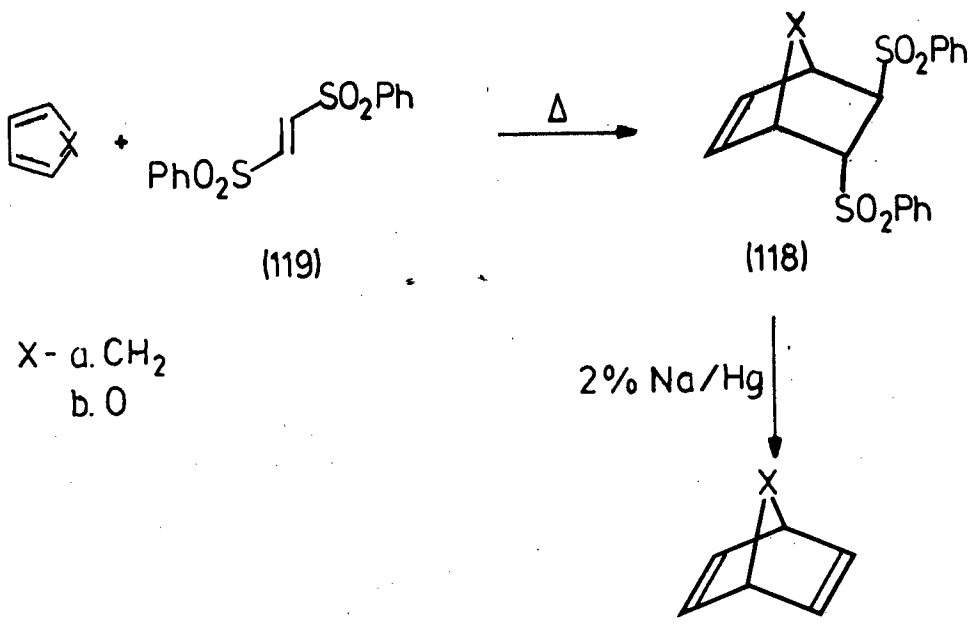
supression of syn-addition to conjugated olefins and of 1,4-addition to dienes. Also, this would account for the observation of the single isomer encountered in the bromination of (22).



Scheme 53a.

3. Preparation and reactions of bicyclo[2.2.1]hepta-2-ene systems containing mono and bis sulphonyl groups.

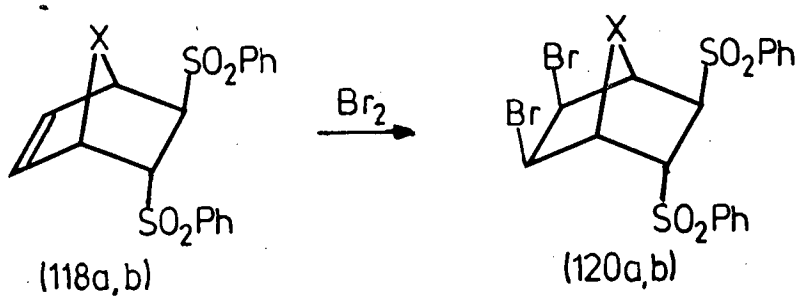
In order to investigate further, the stereochemical directing properties of the sulphonyl group, it was decided to look at a number of norbornene type systems in which phenylsulphonyl groups were present (118), (Scheme 54).



Scheme 54.

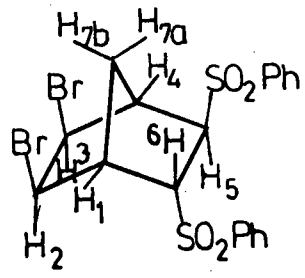
Diels-Alder cycloadditions, using (E)-1,2-bis-(phenylsulphonyl)ethylene (119) as the dieneophile have been used to great effect by De Lucchi et al.[72] Their dieneophile (119) is perhaps the best acetylene synthon discovered to date with regard to both its dienophilic reactivity and the ease with which the D/A adduct undergoes bis-elimination of phenylsulfenic acid in the presence of a 2% sodium amalgam.

Thus both the methylene (118a) and oxygen (118b) bridged compounds were prepared and subjected to ionic bromination, (Scheme 55).



Scheme 55.

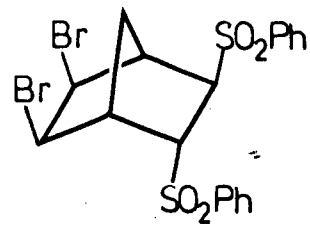
This resulted in the formation in 89-96% yield of the cis- exo dibromides (120a,120b) as the sole products. The stereochemical assignment of these compounds rest most convincingly on the proton-proton couplings and coupling constants in the ^1H-n.m.r. spectra, (Figure 5).



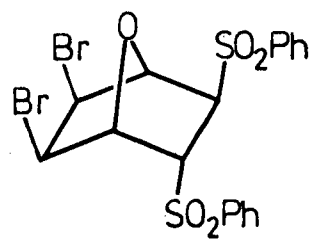
(120a)

In the case of the methylene bridged compound (120a), H_2 is the most deshielded (downfield) at 5.30-5.35ppm by virtue of being directly attached to a carbon bearing a bromine atom and also adjacent to the endo-phenylsulphonyl group. This appears as a doublet of doublets with J=6.8 and 2.0Hz. The former is typical of a cis-coupling constant in these systems,[93] (a trans-coupling would be ~3.2Hz). The latter is due to the long range W-coupling with H_{7a} again well precedented[94,95] and indicative that H_2 is endo, particularly as exo-protons do not couple with bridging protons. This long range coupling was of course not present in the oxo-bridged analogue. However, the absence of coupling between the endo-protons H_2,H_3 with

Figure 5.



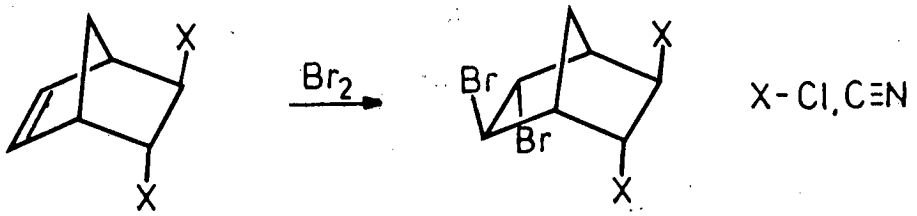
(120a)



(120b)

the bridgehead protons H_1 and H_4 respectively is further proof that the cis-protons are endo. This phenomenon is well documented[96,97] and can be understood on the basis of the Karplus rule.

This result is striking in that complete cis-exo-bromination was achieved, particularly in view of the fact that the trans-dichloro and dicyano-alkene analogues both undergo stereospecific anti-addition of bromine under ionic conditions,[93,96] (Scheme 56). In all these cases the reactions are stereospecific, no nortricyclyl halide or Wagner-Meerwein rearrangement products are observed as is the case for norbornene and norbornadiene.[98,99] The electron withdrawing substituents on C_5 and C_6 appreciably deactivate σ-bond participation and hydride shifts where positive charge is developed adjacent to these groups, hence rearrangement becomes unfavourable.

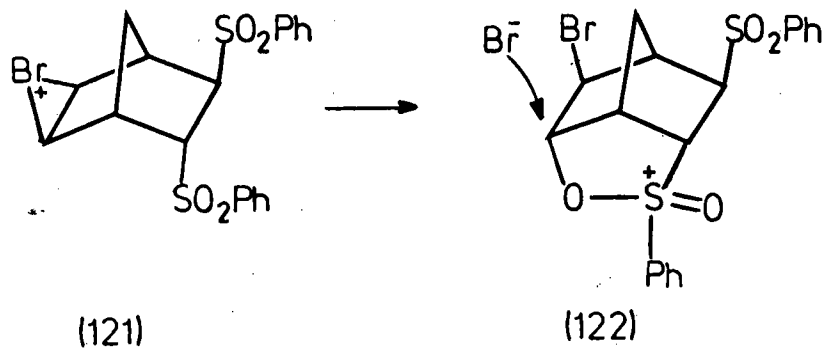


Scheme 56.

In order to account for this stereospecific syn-addition of bromine to alkenes (118a,b), we must invoke a formal intramolecular nucleophilic neighbouring group

participation by the sulphonyl group. An inspection of Dreiding models for these systems reveals that the sulphonyl oxygen atom is only 1.92Å away from the olefinic centre, so rendering a bonding situation entirely feasible. In effect, an initially formed bromonium ion (121) is captured by the SO_2 moiety of the endo-phenylsulphonyl group to give the intermediate (122). This then suffers attack by the incoming Br^- from the normally hindered exo-direction, (Scheme 57).

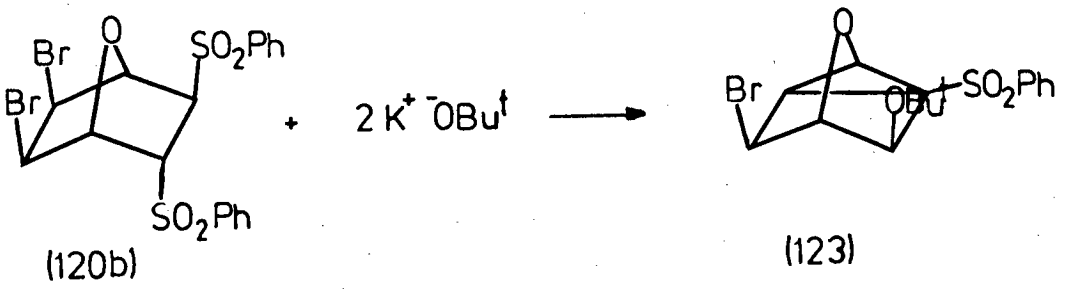
Such intramolecular behavior in norbornyl systems is not without precedent as regards other functional groups; e.g. the iodolactonisation of endo-carboxyl bicycloheptenes and sulphinyl oxygen transfer from sulphoxides to form iodohydrins[100]. However, the aforementioned reactions represent the first positive evidence that the sulphonyl group, normally regarded as a poor nucleophile, displays a similar behavior, resulting in the unprecedented stereospecific ionic syn- addition of bromine.



(121) (122)

Scheme 57.

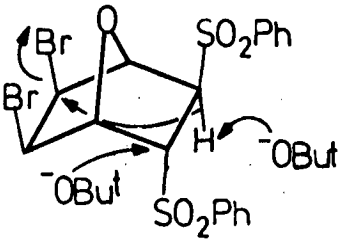
Chemical evidence which further substantiates the cis-exo-dibromo stereochemistry of (120a,b) was realised, when the oxo-bridged dibromide (120b) was treated with two equivalents of potassium t-butoxide in THF. This gave the nortricyclyl compound (123) in 67% yield, (Scheme 58).



(120b) (123)

Scheme 58

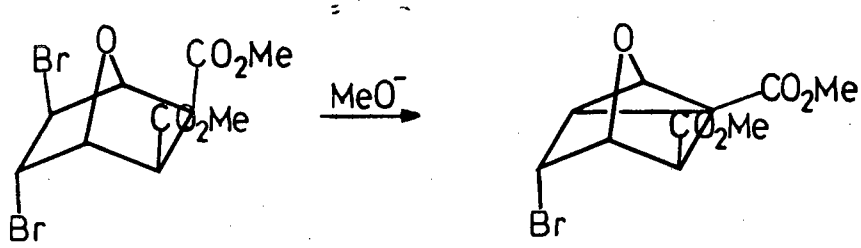
In this reaction, there is a stepwise or simultaneous elimination of HBr and displacement of $PhSO_2^-$ by the t-butoxide.



(120b)

Previous evidence for such a γ-elimination has been reported by Payo et al, [101], when treating (124) with sodium methoxide, to give the nortricyclyl diester (125) (Scheme 59). For this elimination to be successful it

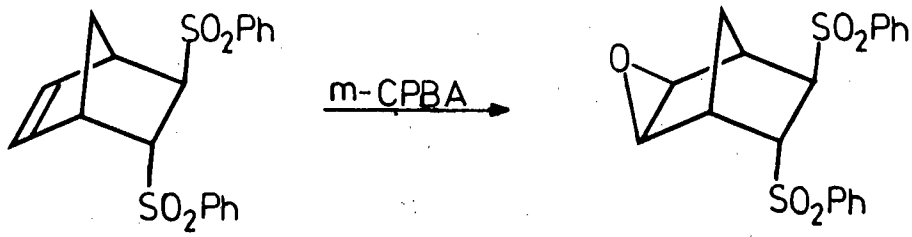
seems clear that the stereochemistry must be of a desired orientation, namely that there be an α-endo proton and a γ-exo leaving group.



(124) (125)

Scheme 59.

Returning to the (E)-6,7-bis(phenylsulphonyl) alkene (118a). This was oxidised by m-chloroperoxybenzoic acid to the exo-expoxide (126) in almost quantitative yield, (Scheme 60).



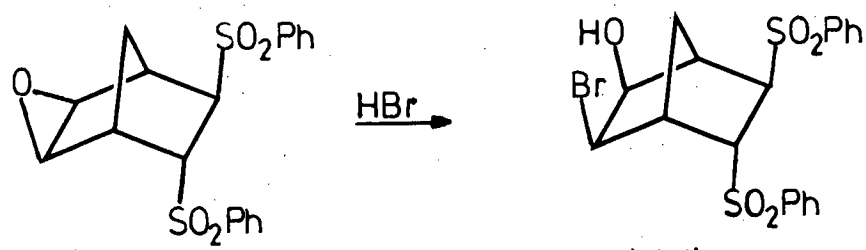
(118a) (126)

Scheme 60.

The exo nature of the oxirane ring was established by the same methods as employed for the cis-exo-dibromide (120b). Namely, the cis-coupling constant between H_2 and H_3, the long range coupling between H_2, H_3, and the

bridging proton H_{7a} and the absence of any coupling between H_2 and H_3 with the bridgehead protons H_1 and H_4 respectively. All other couplings were consistent with the proposed structure.

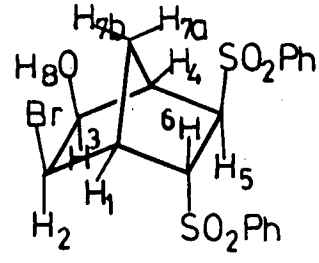
The reaction of this epoxide with hydrogen bromide in glacial acetic acid resulted in the formation of the cis-bromohydrin (127) in 70% yield as the sole product, (Scheme 61).



(126) (127)

Scheme 61.

The stereochemistry in (127) was determined via proton-proton coupling constants, double resonance and Nuclear Overhauser Enhancement studies.



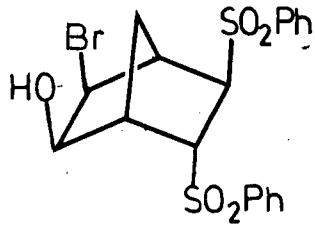
(127)

H_1 appears as a doublet of doublets at 2.97-3.00ppm with J=1.8Hz due to the long range coupling with H_4 and

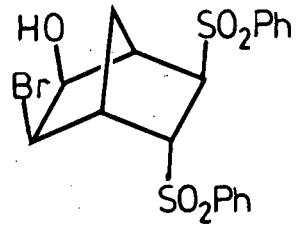
J=4.0Hz due to the coupling with exo H_6. H_2 appears as a doublet of doublets at 5.27-5.32ppm with J=2.0Hz from a long range coupling with H_{7a} and J=6.0Hz due to the cis-coupling with H_3. H_3 appears as a multiplet 3.78-3.84 with identical couplings to H_2 with the exception of an additional coupling of J=4.8Hz to the hydroxyl proton H_8. H_4 appears as a discrete doublet at 2.62-2.63ppm with J=1.8Hz from the long range coupling to H_1. H_5 appears as a doublet of doublets at 3.52-3.55ppm with J=1.7Hz from the long range coupling to H_{7b} and J=5.7Hz due to the trans coupling with H_6. H_6 appears as a doublet of doublets at 4.06-4.11ppm with J=4.0Hz as the coupling to H_1 and J=5.7Hz as the coupling to H_5. H_{7a} appears as a doublet of doublets at 1.95-2.06ppm with J=2.0Hz from the coupling to endo H_2 and H_3 and J=12.0Hz due to the geminal coupling to H_{7b}. Similarly H_{7b} occurs as a doublet of doublets at 2.12-2.20ppm. with J=1.7Hz from the coupling to H_5 and J=12.0Hz from the geminal coupling to H_{7a}. Finally, H_8 the hydroxyl proton appears at 2.25-2.27ppm as a doublet with J=4.8Hz from the coupling to endo H_3.

However, even after the detailed assignment of signals on the basis of proton-proton couplings, it could not be ruled out that the structure could in fact be the isomeric cis-bromohydrin (128) and not the proposed structure (127). Evidence for (127) would thus lie on the shoulders of chemical shift values for distinction.

Such a situation is undesirable and can sometimes lead to misinterpretations.



(128)

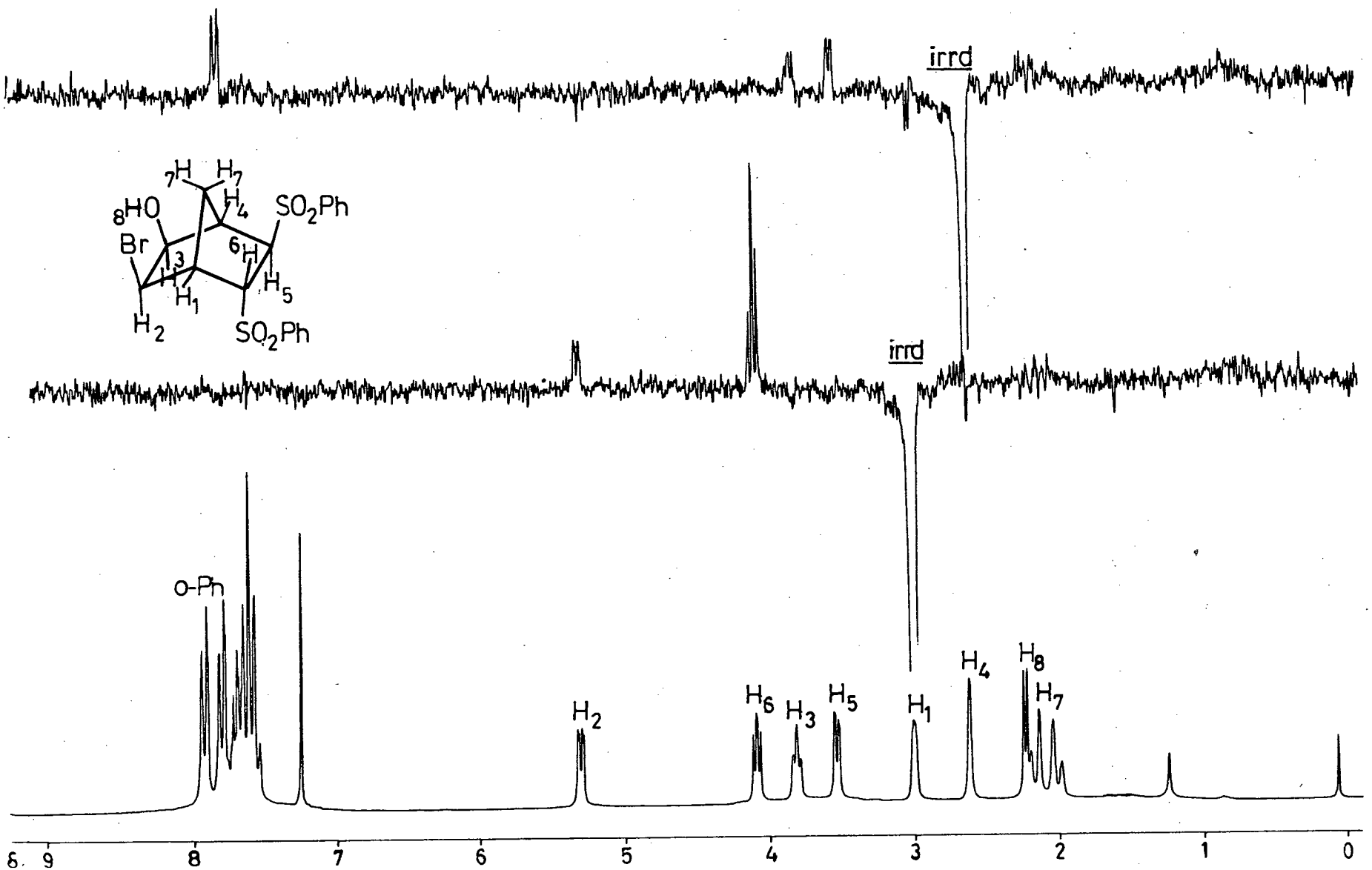


(127)

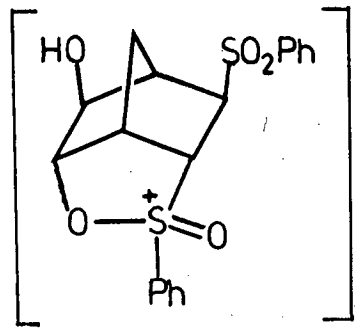
Clarification of this point was obtained from an N.O.E. study, (Figure 6). From coupling constants it was known that H_1 is on the same side of the ring as the endo phenylsulphonyl group, due to its coupling to H_6. Similarly, H_4 must be on the same side of the ring as the exo-phenylsulphonyl group from the absence of coupling with H_5. Thus irradiation at H_1 and H_4 should lead to enhancements of H_2, H_6 and H_3, H_5 respectively. As can be seen from the spectra this indeed was the case. In addition, with respect to irradiation at H_4, an N.O.E. was also seen from the ortho protons of the phenylsulphonyl group geminal to H_5 indicating its exo nature.

Notwithstanding the fact that not only is the normally favoured trans-product absent, but that the actual product is a single isomer which was both stereo and regiospecifically controlled, militates most strongly for the intramolecular nucleophilic participation of the

Figure 6.


irrd
irrd
$_7$H H$_7$
$_8$HO
H$_4$
SO$_2$Ph
Br
$_6$H
$_3$
$_1$
H$_1$
H$_5$
H$_2$
SO$_2$Ph
o-Ph
H$_2$
H$_6$
H$_3$
H$_5$
H$_1$
H$_4$
H$_8$
H$_7$
δ 9
8
7
6
5
4
3
2
1
0

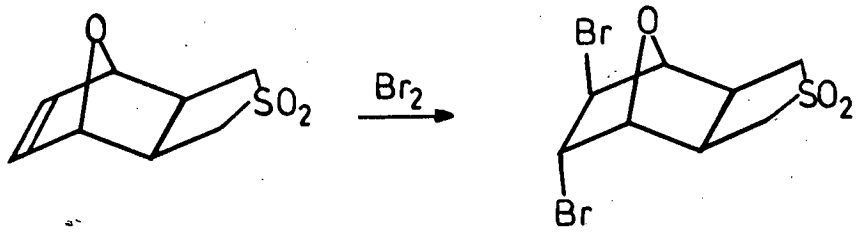
sulphonyl group via intermediate (129). An inspection of Dreiding models showed that the sulphonyl oxygen would be some 1.95Å from a developing carbocation centre at carbon C(2).



(129)

All attempts to hydroxybrominate alkene (118a) using the 'HOBr' synthons NBA in aqueous acetone and NBS in aqueous t-butyl alcohol proved unsuccessful.

In contradistinction to previous observations, the ionic addition of molecular bromine to the oxo-bridged sulphone (130) resulted in anti-electrophilic addition, (Scheme 62).

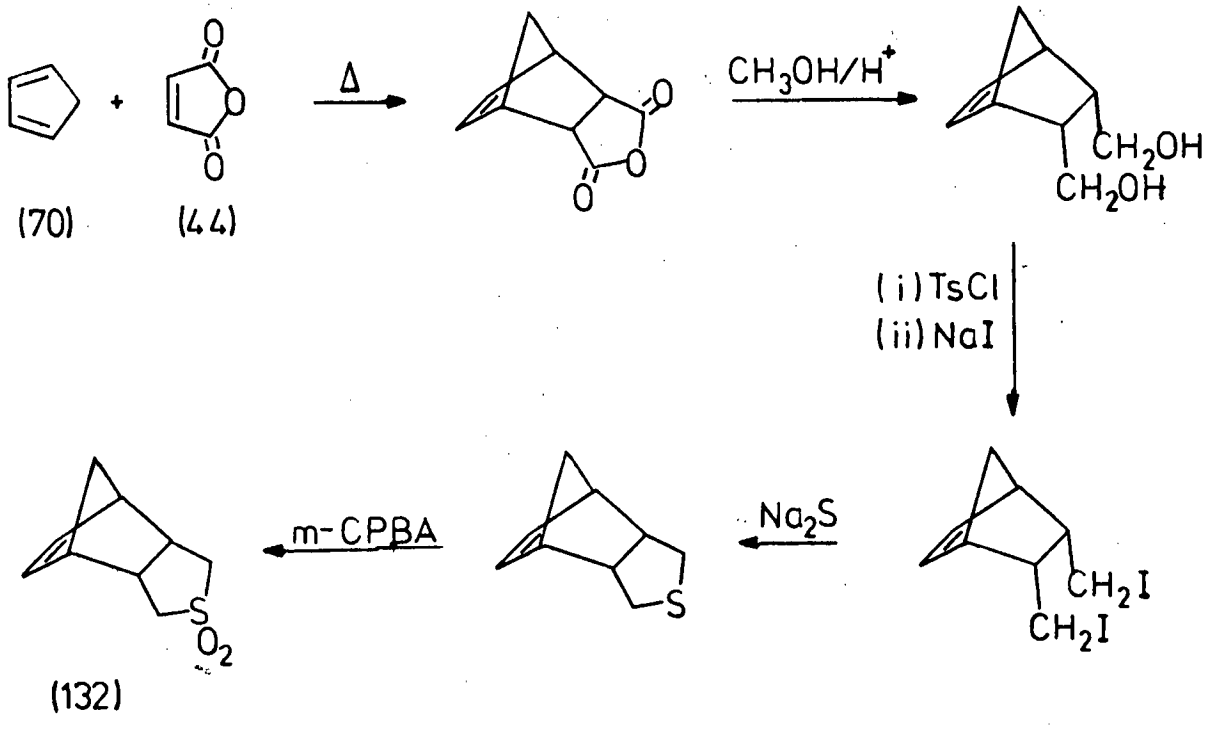


(130) (131)

Scheme 62.

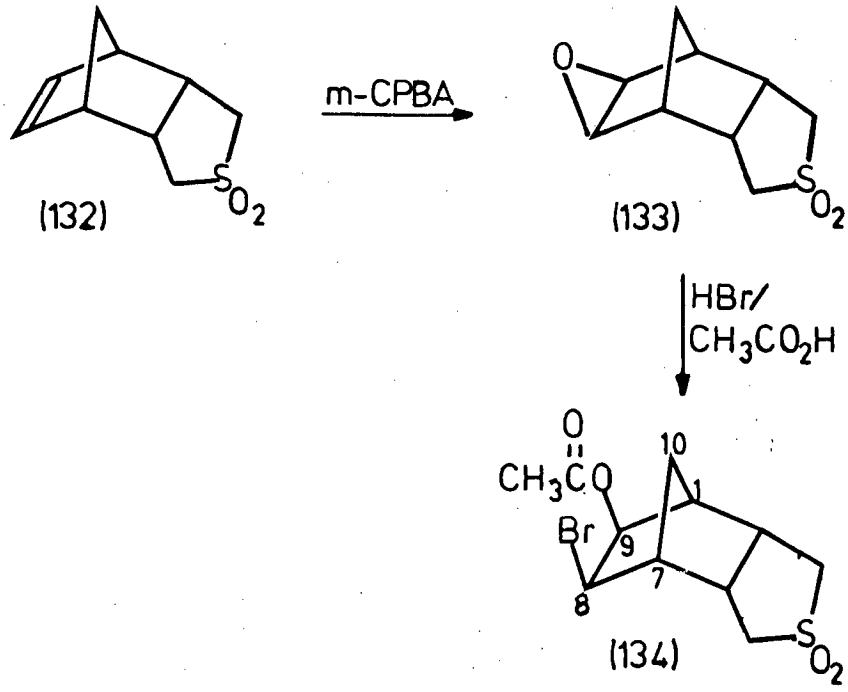
The unsymmetrical nature and hence trans-stereochemistry of the product (131) was confirmed by the 8-line ^{13}C-n.m.r. spectrum. The olefin had exo-stereochemistry at the ring junction. As a result, the sulphonyl group is now some considerable distance from the double bond (5.8Å). Therefore, in the absence of any stereoelectronic influence by the SO_2 group, the bromination proceeds predictably to give anti-addition.

The tricyclic sulphone (132) can be prepared in five steps by the method of Wilder and Otero[102] from cyclopentadiene (70) and maleic anhydride (44), (Scheme 63).



Scheme 63.

Oxidation of (132), in which the SO_2 group is endo to the ring junction, with m-chloroperoxybenzoic acid, resulted in the formation of the cis-exo-epoxide (133) in 72% yield. Treatment of this with HBr in glacial acetic acid gave the (Z)-8-exo-bromo-9-exo-acetoxy compound (134) in 86% yield, (Scheme 64).

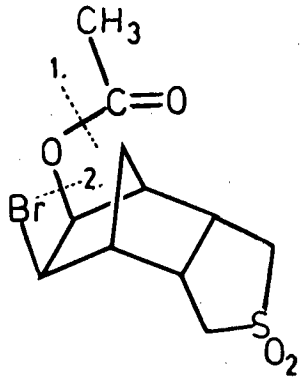


Scheme 64.

Normally the latter reaction would yield the bromohydrin. However, in this case, after the initial reaction had taken place, the reaction mixture was subjected to prolonged heating at 90°C during the removal of the solvent thus effecting conversion into the α-bromoester (134). This heating had not taken place in previous examples. The cis-exo nature of (134) was

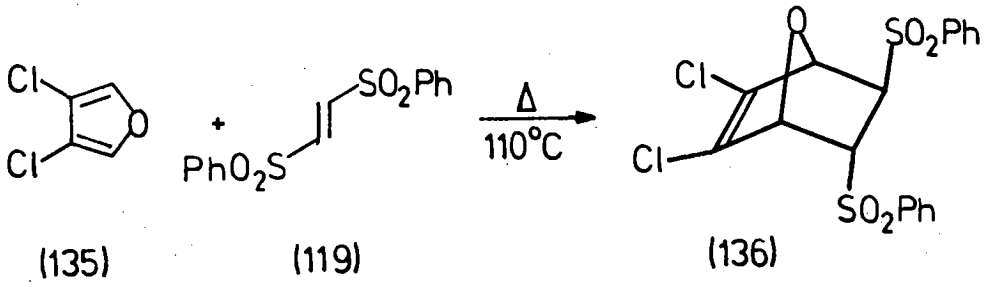
confirmed by the cis-coupling constant of J=6.0Hz between H_8 and H_9, the long range coupling to the bridging proton H_{10} and by the absence of coupling to the bridgehead protons H_1 and H_7. A large N.O.E. was also observed between H_8 and H_9.

There is of course the possibility that after initial bromohydrin formation that O-acyl (1) or O-alkyl (2) cleavage could take place. In the case of O-acyl cleavage (1), the stereochemistry of an initially formed bromohydrin must be retained showing that stereocontrol has been maintained. If on the other hand O-alkyl cleavage (2) had taken place, then again we are observing stereocontrol, as attack on an open carbocation has resulted in the preferential cis-exo attack by a bulky nucleophile next to a large bromine atom. This reaction could perhaps be elucidated further by the use of ^{18}O labelled acetic acid. In any case a neighouring group participation or through space orbital interaction by the sulphonyl group seems likely in order to account for the stereospecificity shown in this reaction.



(134)

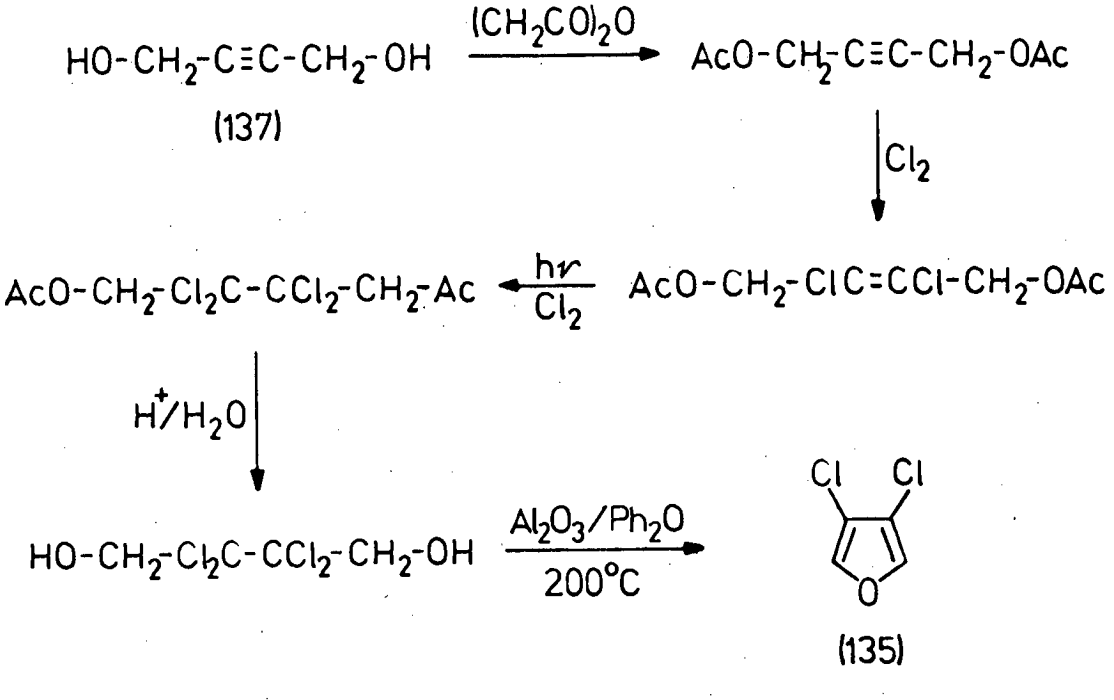
In an attempt to trap the intermediate involved in the previous reactions of electrophilic addition of bromine to norbornene systems containing an endo-phenylsulphonyl group, the compound (136) was synthesised in 81% yield, (Scheme 65). This was achieved by the Diels-Alder cycloaddition of 3,4-dichlorofuran (135) with (E)-bis(phenylsulphonyl)ethylene, (119).



(135) (119) (136)

Scheme 65.

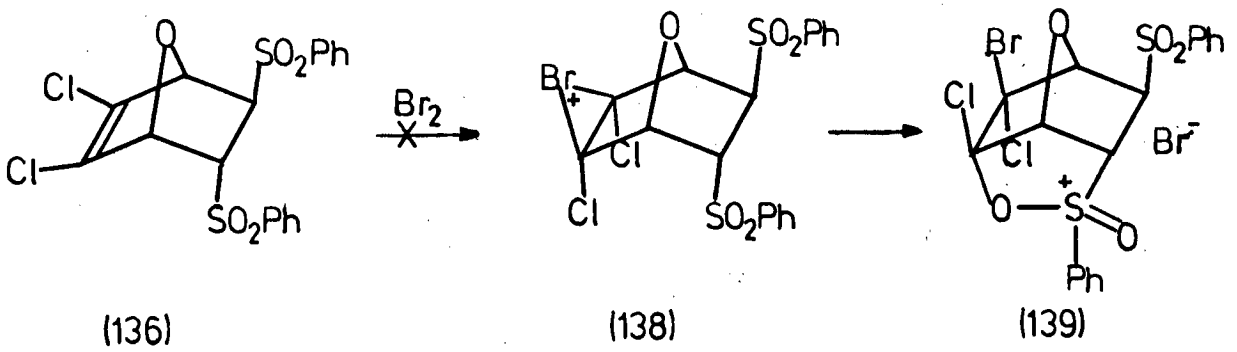
The diene (135) was prepared by the method of Mkryan et al.[103] in five steps from butyne-1,4-diol (137), (Scheme 66).



(135)

Scheme 66.

It had been hoped that when the cycloadduct (136) was treated with bromine, that an initially formed bromonium ion (138) would collapse to a stable salt (139) by virtue of the nucleophilic neighbouring group participation of the SO_2 group. This in turn would not now be susceptible to exo-attack by an incipient Br^-, due to a steric blocking effect of the exo-chlorine atom, so furnishing the 'captured bromonium ion salt' (139), (Scheme 67).



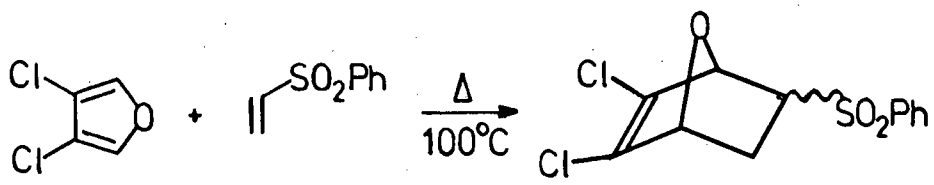
(136) (138) (139)

Scheme 67.

Unfortunately, on addition of bromine to a chloroform solution of (136), no reaction took place, even after a protracted period at ambient temperature and a further period under reflux. This can only be attributed to the severe deactivation of the double bond by the electron withdrawing chlorine and phenylsulphonyl substituents in combination with the steric hindrance provided by the two chlorine atoms. The attempted epoxidation of (136) with m-CPBA was also unsuccessful,

as was the treatment with HBr in acetic acid.

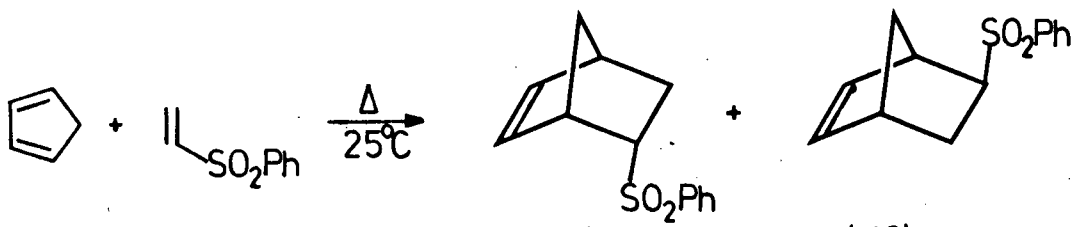
The mono-phenylsulphonyl analogues were also obtained as a mixture of the endo and exo (141a,b) isomers by the reaction of (136) with phenylvinylsulphone (140) at 100°C in toluene, (Scheme 68). Once again, no reaction took place with either bromine or m-chloroperoxybenzoic acid.



(135) (140) (141a,b)

Scheme 68.

Cyclopentadiene was also reacted with phenylvinylsulphone[104] (140) to give a mixture of endo (142) and exo (143) 2-phenylsulphonylbicyclo[2.2.1]-hepta-5-ene, (Scheme 69), in 40% and 16% yields respectively.

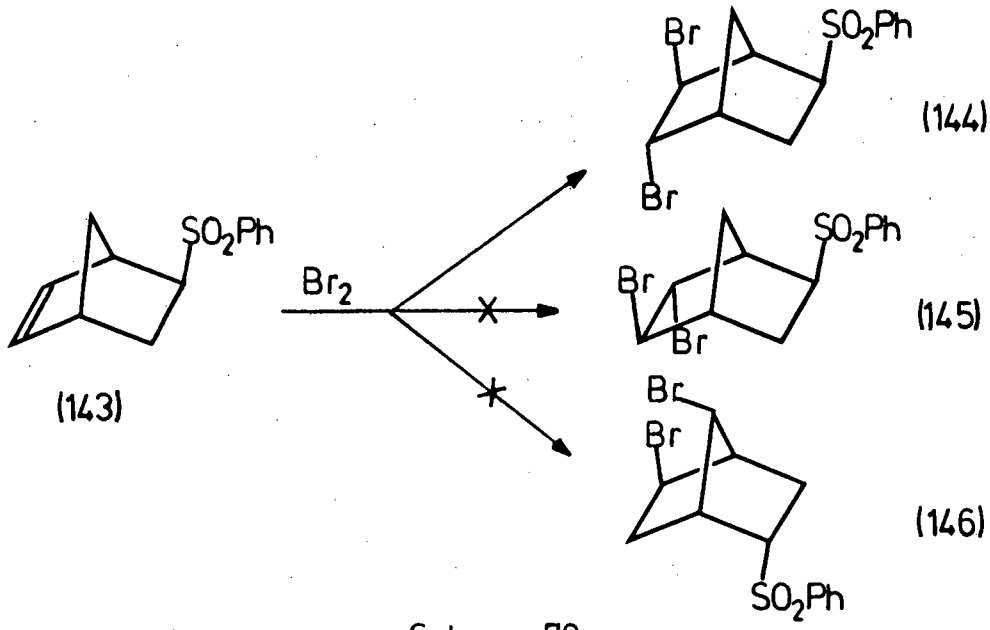


(70) (140) (142) (143)

Scheme 69.

When a chloroform solution of the exo-isomer (143) was treated with bromine at room temperature, instantaneous decolourisation took place. This is in contradistinction to the general observation of sluggish reaction progression where there is nucleophilic participation by the sulphonyl group. Indeed, this instantaneous decolourisation was expected because the phenylsulphonyl group is exo to the norbornene ring, hence there is now no possibilty of nucleophilic neighbouring group participation by the sulphonyl group as in previous examples.

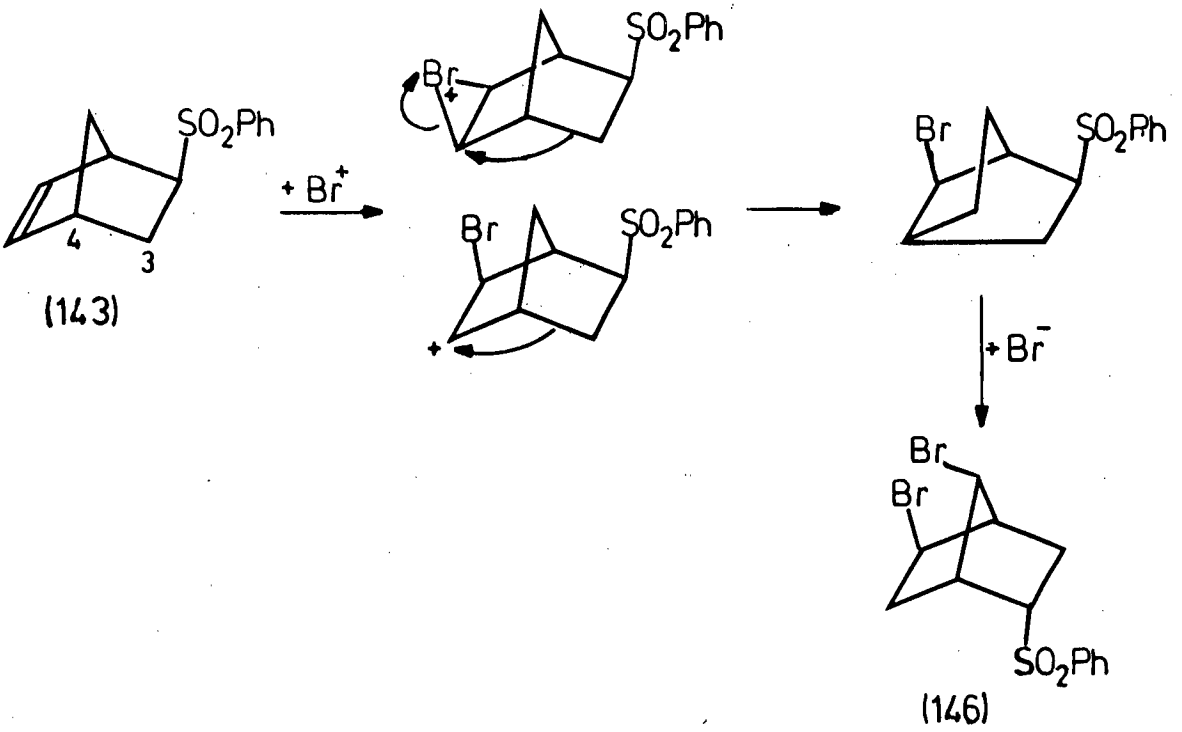
Given the structural characteristics of the starting material (143) and the experimental observations, one would predict three possible products from this reaction. These being, two distinct trans-isomers (144,145) arising from simple addition and the rearrangment product (146), (Scheme 70).



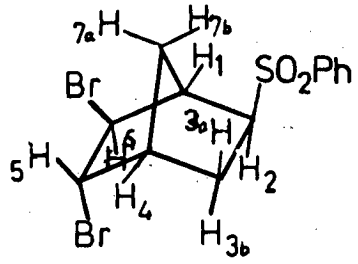
Scheme 70.

In practice, the reaction proceeds to give a single product isolated in 87% yield. That a single isomer resulted from this reaction was evidenced from a single spot on t.l.c. and the seven aliphatic signals in the ^{13}C-n.m.r. of the crude reaction mixture. This product was positively identified from ^{1}H-n.m.r. proton decoupling and Nuclear Overhauser Enhancement experiments, the results of which are summarised in Figure 7. This result is somewhat surprising in that all three isomers seemed to be distinct posibilities.

The rearrangement product (146) would have been formed by a σ-migration of the C_3-C_4 carbon-carbon bond, (Scheme 71).



Scheme 71.



N.O.E. irrd. /	H_1	H_2	H_3	H_4	H_5	H_6	H_7	Ph
$H_{1,2}$			X_l			X_l		X_l
H_4			X_l		X_l			
H_5				X_l		X_s		
H_6	X_s	X_l			X_s			
Ph	X_l	X_l						
J_{Hz} irrd. /								
H_1				0.8				
H_2			a				a	
H_4	0.8		3.7		4.5			
H_5			1.7	4.5		2.5		
H_6					2.5		2.0	

s-small , l-large

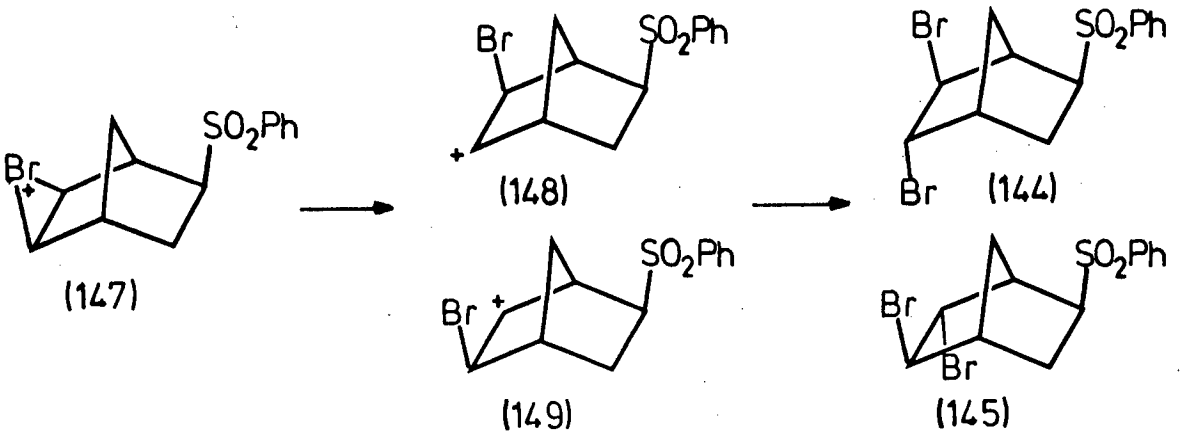
a- $J = J_{3a} + J_{3b} + J_{7a} = 12.$ Hz

Figure 7.

From previously illustrated examples and literature citations[93,96], it was known that rearrangements are not observed when both positions on the opposite side of the ring from the double bond are occupied by electron withdrawing substituents. However, in this case only one such position is occupied, so in theory this should leave the other position (C_3-C_4) open to ϵ-migration. Therefore in practice as no such rearrangement is observed, the driving force for the formation of (144) must be so favoured that it renders this possibility inauspicious.

On steric grounds, with respect to simple trans-addition, a cyclic bromonium ion (147) should be equally susceptible to posterior attack at either of the two possible endo positions (Scheme 72). This would in turn lead to a mixture of (144) and (145) being formed. As this is clearly not the case, there must in all likelihood be an actuation towards unequal charge distribution leading to carbonium ion formation (148,149) in the ultimate.

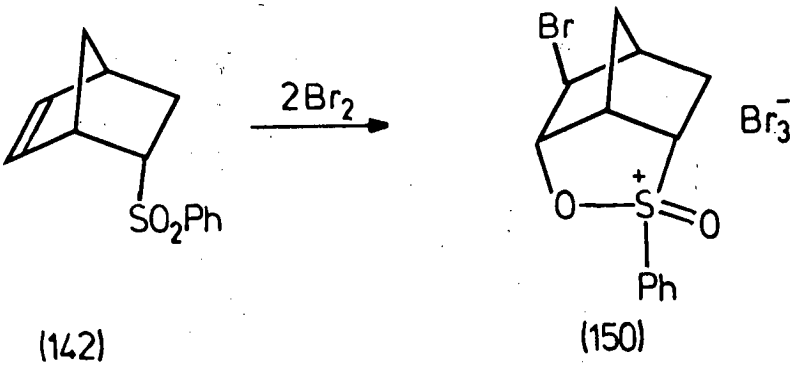
The development of positive charge at the 6-position relative to the 5-position would be less favourable than the converse as the electron withdrawing phenysulphonyl group would tend to concentrate this and consequently destabilise it. Therefore, although this is a somewhat long range inductive effect, it is sufficiently powerful enough to effect the observed regio and stereo-specificity.



Scheme 72.

When a chloroform solution of the endo-isomer (142) was treated dropwise with 1.1 equivalents of bromine, this resulted in the almost immediate precipitation of an orange solid. Examination of the mother liquor by t.l.c. showed that an appreciable amount of the starting material still remained. It was not until two equivalents of bromine had been added that that t.l.c. showed that all starting material had been consumed. When left open to the atmosphere at room temperature for 60 hours this material had largely decomposed to a white crystalline solid. If enclosed in a sample tube, this material was seen to release fumes of bromine after 24 hours. Decomposition was also encountered when left in suspension with the mother liquor, and was even more rapid when more than two equivalents of bromine had been added. Combustion analysis of the orange solid showed

it to have the empirical formula $C_{13}H_{14}Br_4O_2S$. Also, the melting point was uncharacteristically low at only 77°C. Taken as a whole, these features of consumption of two equivalents of bromine, insolubility in organic media and formula consistant with a tetrabromide, linked with the aforementioned examples of nucleophilic neighbouring group participation by the sulphonyl group would lead to the conclusion that we are finally observing an example of the 'captured bromonium ion' salt (150), (Scheme 73).

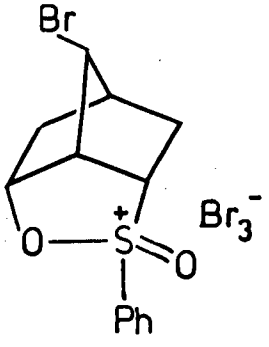


(142) (150)

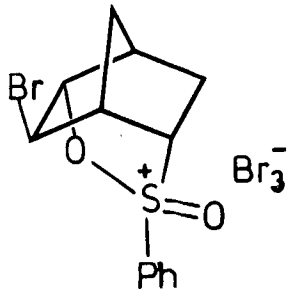
Scheme 73.

The ^{13}C-n.m.r. spectrum of this material could at best be achieved as an 80:20 mixture with the subsequent decomposition product. Excluding aromatic carbons, a total of fourteen signals were observed. The resonances of the salt could be assigned on the basis of the intensity differences between the two materials; these were subsequently verified due to the positive identification of the decomposition product. The

^{1}H-n.m.r. spectrum shown in Figure 8 was obtained at 360MHz in d^{3}acetonitrile within 15 minutes of its preparation. No decomposition had taken place during this time, with the nine aliphatic and five aromatic protons being clearly evident. Tentative assignments can be made on the basis of the chemical shift values and the accessable proton-proton coupling constants. However, an N.O.E. experiment carried out on this saline material casts some doubt on the proposed structure (150), the results of which are summarised in Figure 9. Alternatives to (150) could be the Wagner-Meerwein rearranged product (150a) or the distorted bicycloheptane (150b). However similarly, neither of these are consistent with the N.O.E. results.



(150a)



(150b)

The mass spectrum yielded no useful information, presumably due to the heat applied to effect volatilisation causing decomposition of the salt. The infrared spectra of these systems invariably show two strong S=O stretching frequencies at 1320-1300 and

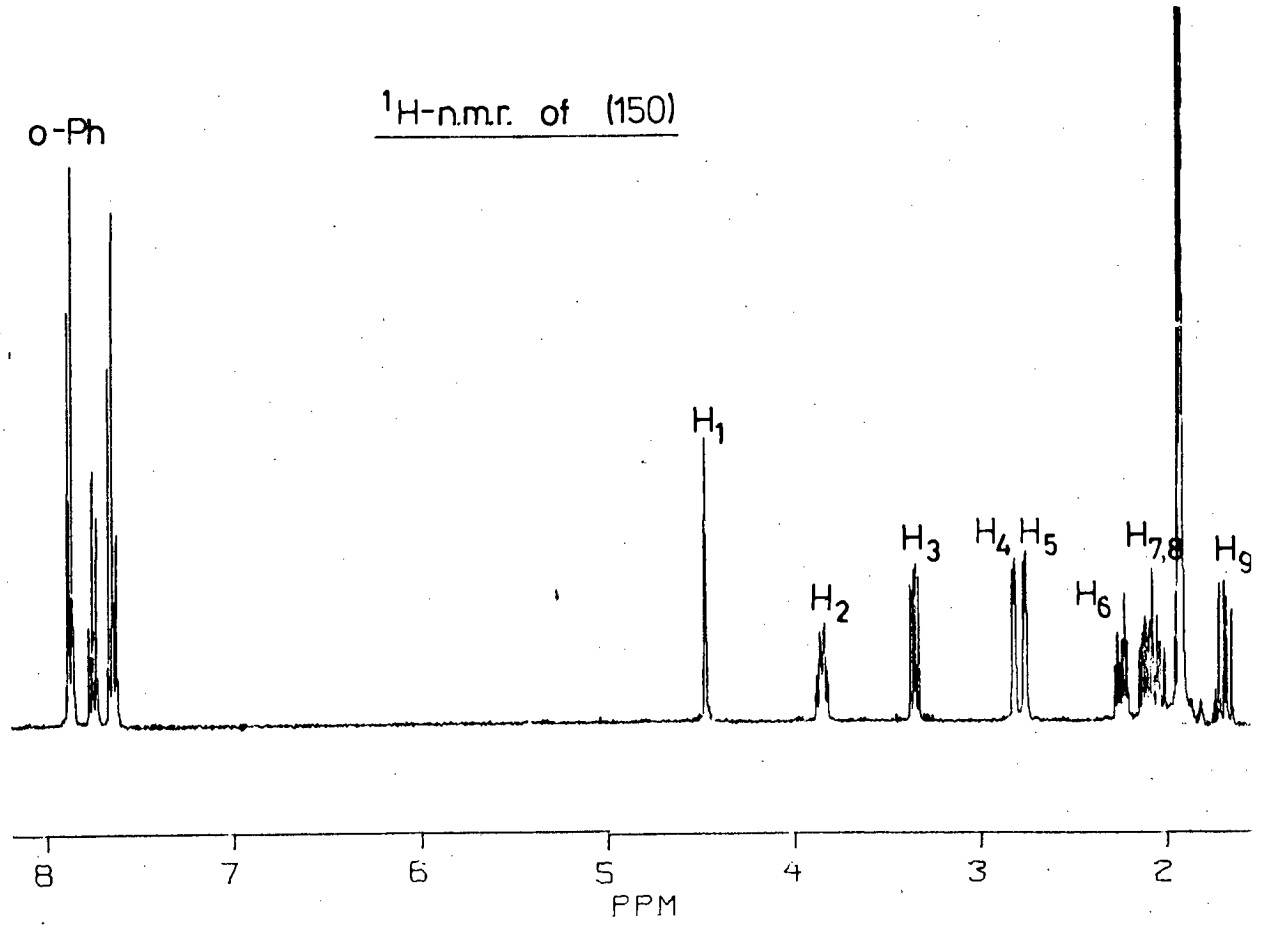


Figure 8.

% NOE / irr	H_1	H_2	H_3	H_4	H_5	H_6	H_7	H_8	H_9	Ph
H_1				3.5	3.5					
H_2			1.0		1.5				4.1	
H_3				2.0					3.0	1.8
H_4	3.3		1.8			4.3				1.5
H_5	4.6	1.2					2.2			
H_6			-1.5	5.1				6.8		
H_9		4.3	3.0				7.1			

Figure 9.

1150cm^{-1} for the symmetric and asymmetric stretching modes respectively. However in this case, whilst there is a strong signal at 1300cm^{-1} the other signal appears at 1082cm^{-1}. This would correspond to a weakening in the S-O bond strength and would be consistent with the reduced bond order observed for the oxygen atom participating in the intramolecular bonding. Person *et al.*[135] have reported that the tribromide ion in tetrabutylammonium tribromide (TBAT) absorbs in the infrared at 190cm^{-1}. Very few other absorptions are found in this region. Although such a low frequency infrared facility was unavailable to verify the existance of Br_3^- in this material, a Raman experiment was carried out instead. Irradiation at 457.9nm by an argon laser evidenced the appearance of a strong absorption at 149cm^{-1}, as shown in Figure 10. A similar experiment on TBAT showed that it likewise gave a strong absorption at 145cm^{-1}. This in conjunction with the other collaborating evidence would seem to confirm the existance of the tribromide counterion.

As mentioned previously, this tribromide salt gradually decomposes on standing to a white crystalline solid with liberation of molecular bromine. This solid has been positively identified as the *cis*-*exo*-dibromide (151). The formation of (151) would be consistant with the *exo*-attack by the tribromide counterion to give (151) and liberation of bromine, (Scheme 74).

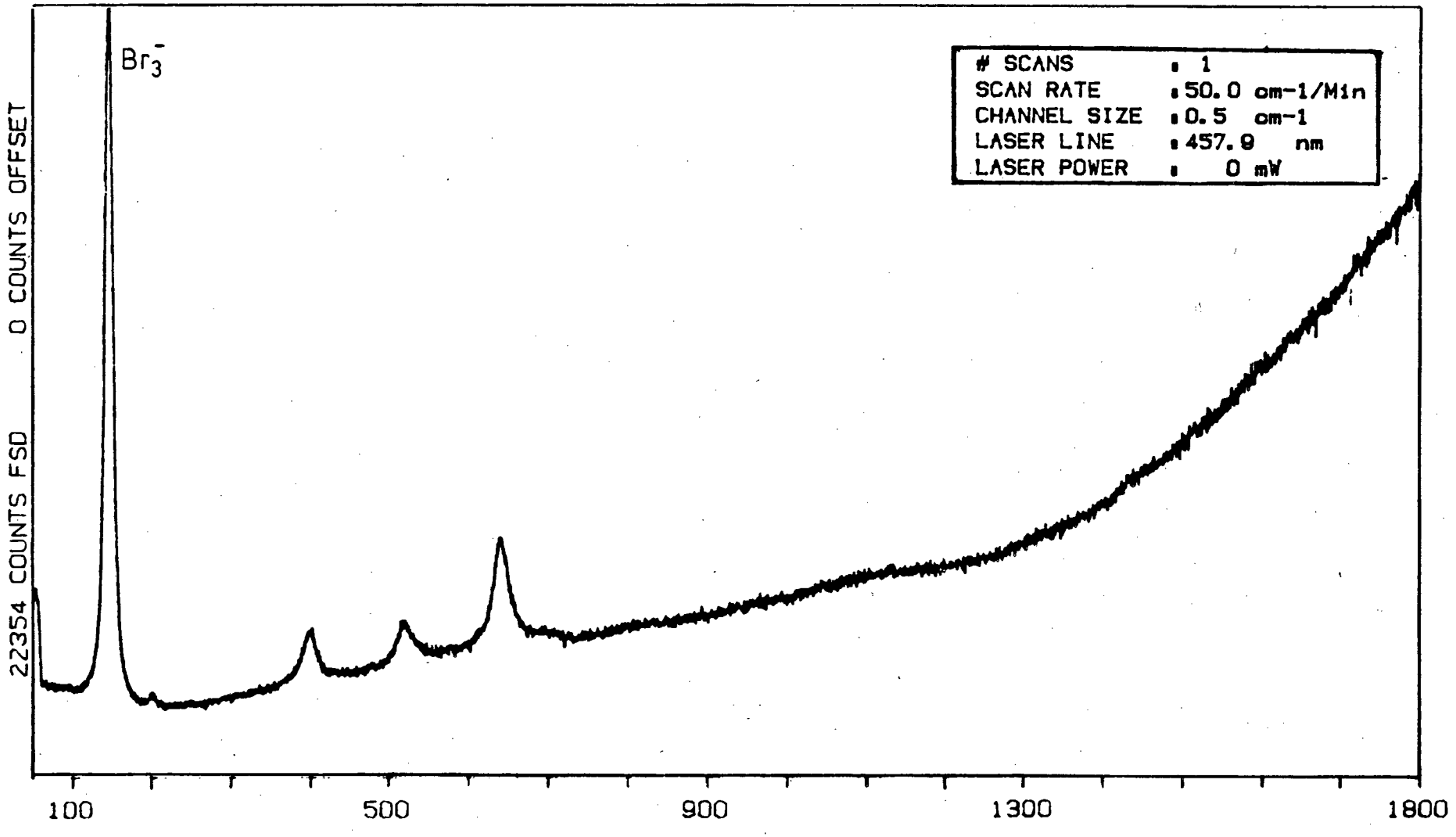
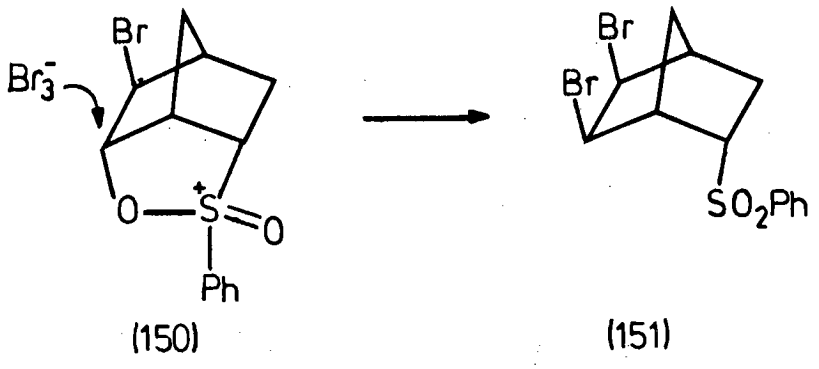

Br_3^-
SCANS : 1
SCAN RATE : 50.0 cm-1/Min
CHANNEL SIZE : 0.5 cm-1
LASER LINE : 457.9 nm
LASER POWER : 0 mW
22354 COUNTS FSD
0 COUNTS OFFSET
100
500
900
1300
1800

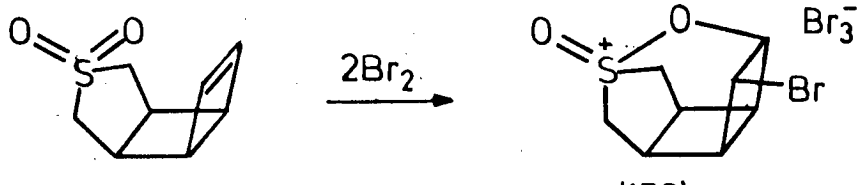
Figure 10.



(150) (151)

Scheme 74.

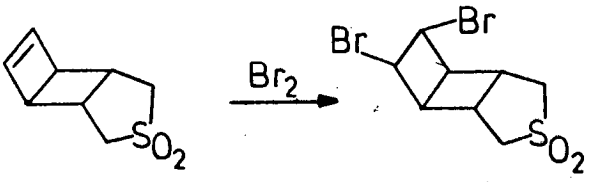
In concurrent studies within these laboratories it has been shown that the syn-tricyclic sulphone (152) undergoes a similar reaction to (142) when subjected to ionic bromination, to give the bromo-thiadecanylium tribromide (153)[105], (Scheme 75). Almost identical reaction observations were made as occurred for the bromination of (142). Namely, the dropwise addition of bromine resulted in the almost immediate precipitation of an orange solid, with the consumption of starting material only being complete on the addition of two equivalents of bromine. In both cases, decomposition in the solid state of these tribromide salts results in the formation of the cis-exo-dibromides, although (153) seems to be the more stable as it requires some heating. The greater stability of (153) may arise from a stronger C-O bond due to the greater molecular rigidity of (153).



(152) (153)

Scheme 75.

In contrast to the bromination of the syn-tricyclic sulphone (152), the anti-isomer (154) on bromination undergoes instantaneous decolourisation to yield the trans-dibromide (155) as the sole product, (Scheme 77).



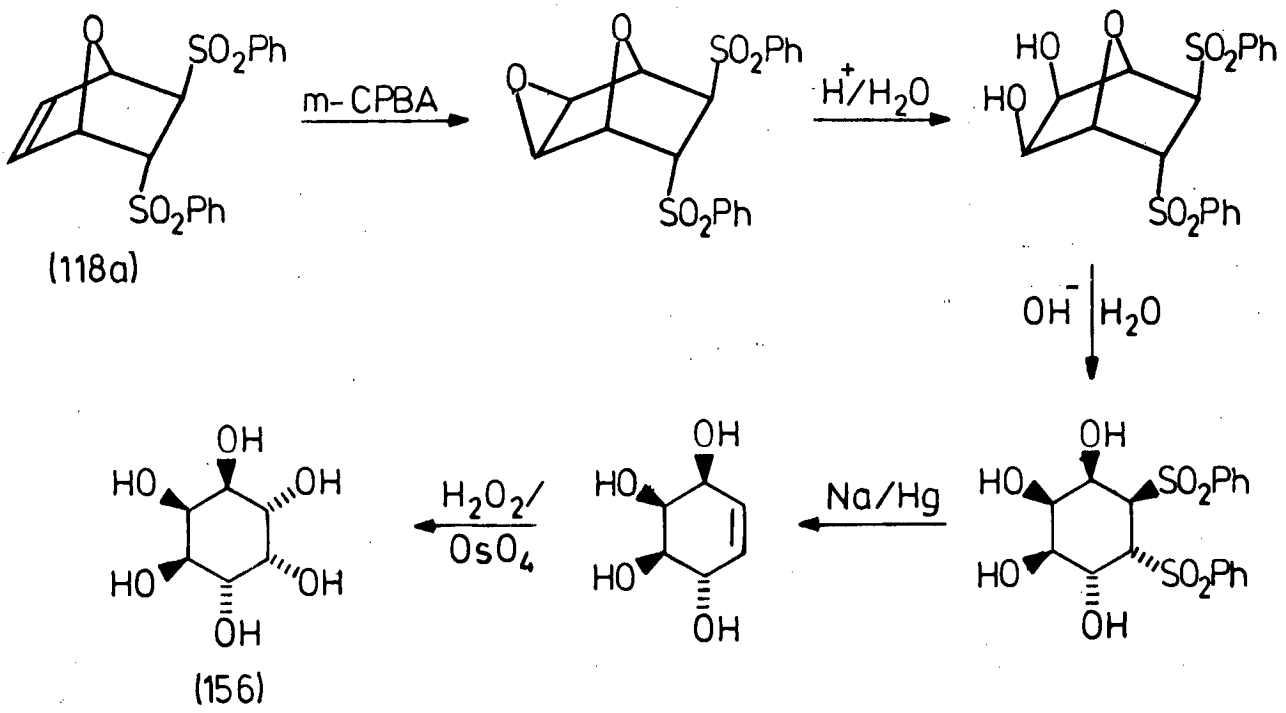
(154) (155)

Scheme 77

In this example, the sulphonyl group is spacially situated in an unfavourable position to effect nucleophilic participation. Therefore, the normal anti-addition is observed.

The results given in this section represent the first fully authenticated examples of syn-addition of bromine to non-conjugated cyclic-olefins, brought about by the hitherto unreported nucleophilic intramolecular participation properties of the sulphonyl group. Further work is merited in this area with respect to the investigation of different nucleophilic additions to the double bond in these systems. Additionally, the striking stereo and regiospecific control evidenced in e.g. Scheme 61, brought about by the sulphonyl group, could be a particularly fruitful area. A particular example could be in natural product synthesis, with

respect to a group of compounds known as the cyclitols. These are currently the subject of vigorous investigation,[106] due to their biological interest. Scheme 78 shows a possible synthetic route to one of these, myo-inositol[197] (156). However, it would be anticipated that by manipulation of the various parameters that a sequence of different cyclitols could be synthesised.

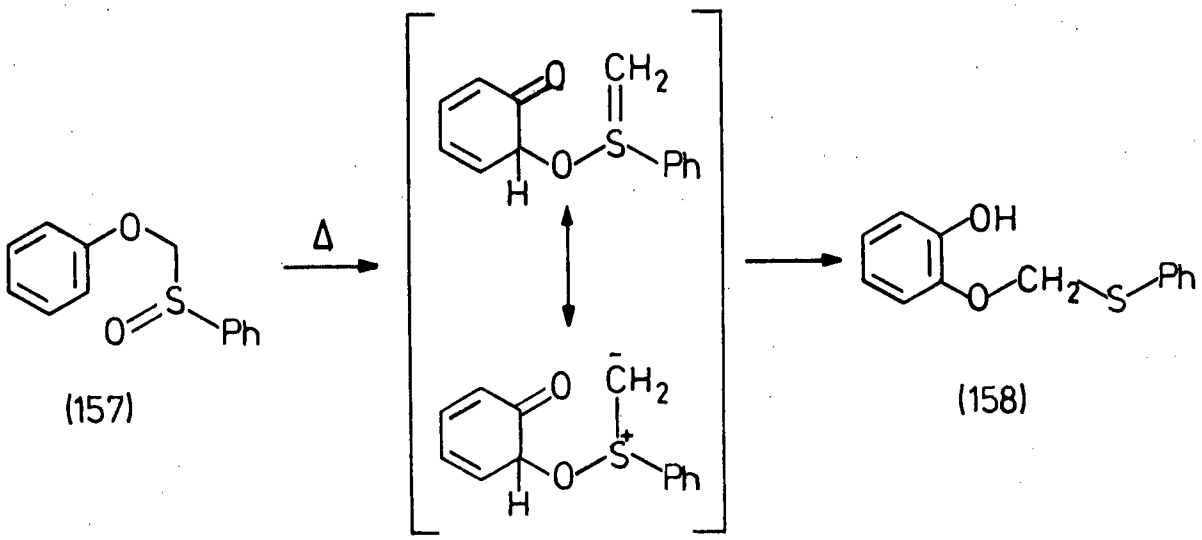


Scheme 78.

C. PREPARATION AND REACTIONS OF α-ARYLOXY SULPHOXIDES (MONOTHIOACETAL S-OXIDES)

1. Introduction and preparation

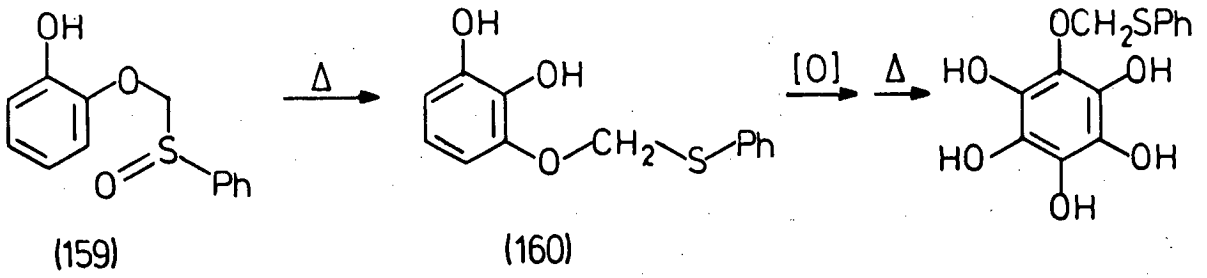
This section deals with the synthesis and thermally induced reactions of α-aryloxy sulphoxides or monothioacetal S-oxides. In contrast to the previous chapter regarding the nucleophilic properties of the sulphonyl group, such behavior by the sulphinyl group has been reported,[100] and indeed is to be expected in view of the polar nature of the S→O bond. However, no mention has been made in the literature of the possible Claisen type rearrangement of the aforementioned compounds, involving subsequent rearrangement of the Pummerer intermediate, (Scheme 79).



(157) (158)

Scheme 79.

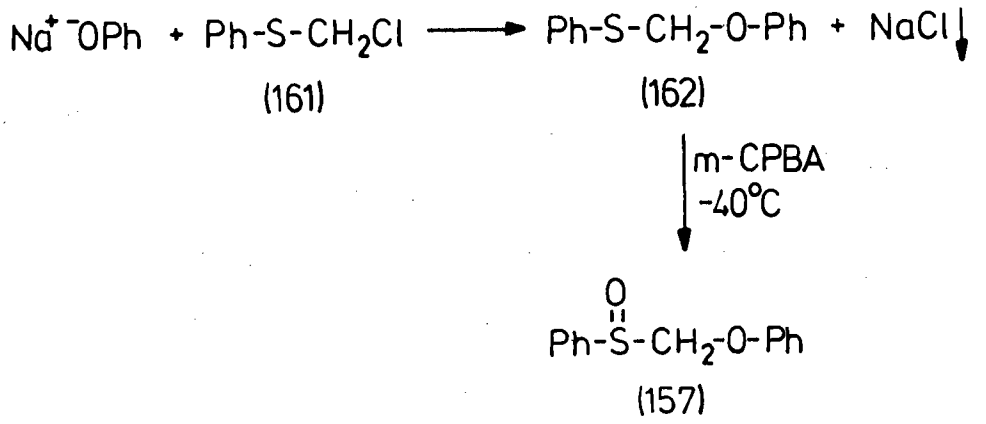
Should such a transformation be possible, it might be envisaged that re-oxidation of the product (158) to the sulphoxide (159), followed again by the tandem 'Claisen-Pummerer' rearrangement, would lead to the diol (160). Subsequent similar manipulations would lead to the sequential hydroxylation of the aryloxy-ring system, (Scheme 80).



(159) (160)

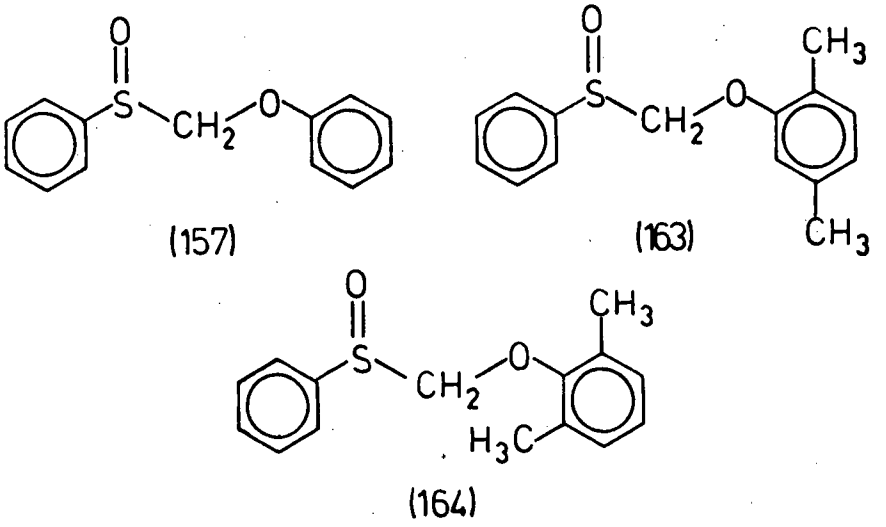
Scheme 80.

Returning to the synthesis of the ∝-aryloxy sulphoxide (157), this was achieved by a coupling reaction between sodium phenoxide and ∝-chlorothioanisole (161) in dimethylformamide at room temperature to give the monothioacetetal (162) in 75% yield. This was then oxidised with one equivalent of m-CPBA in methylene chloride at -40°C to give the desired phenoxymethylphenyl sulphoxide (157) in 57% yield, (Scheme 81).



Scheme 81.

As well as the parent (157), the derivatised analogues containing 2,5-dimethyl (163) and 2,6-dimethyl (164) substituents in the phenoxy ring system were also prepared using a similar strategy.



2. Flash vacuum pyrolysis of α-aryloxy sulphoxides

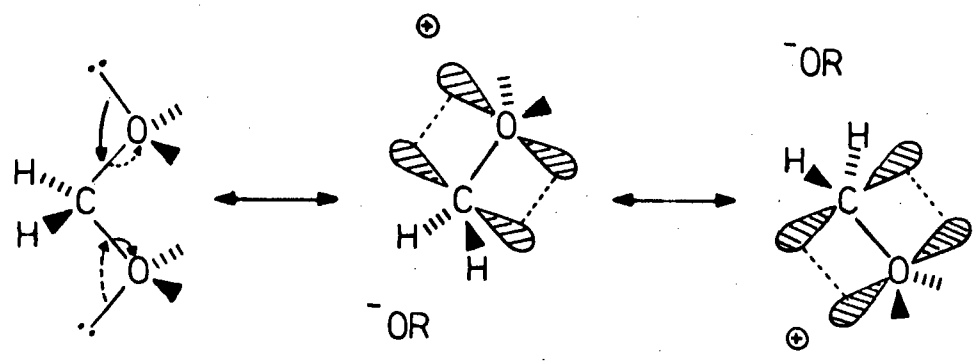
Pyrolyses were carried out on an apparatus based on the design of W.D. Crow of the Australian National University. A similar set-up is illustrated in a recent monograph by Brown.[108]

Briefly, the sample (25-100mg) is volatilised into and through a 30x25cm silica tube which can be heated to temperatures in the range of 350-900°C. The products were collected in a U-shaped trap which is immersed in liquid nitrogen. The whole system is maintained at pressures of 10^{-2}-10^{-3}mmHg by a high vacuum oil pump. Typically, under these conditions, the contact time in the hot zone is estimated at 1-10 milliseconds. On completion of the pyrolysis, the system is isolated from the oil pump and flooded with gaseous nitrogen.

The pyrolysis of phenoxymethylphenylsulphoxide (157) was satisfactorally carried out at an inlet sublimation temperature of 150°C, a furnace temperature of 600°C with the system being maintained at 5 x 10^{-3}mmHg. Fortuitously, the pyrolysate from this reaction was found to collect as two distinct 'fractions'. The first of these was collected from the side arm of the trap, just prior to its entry into the liquid nitrogen, whereas the second fraction was collected in the main body of the trap which is completely immersed in the liquid nitrogen. The 'side arm fraction' was found to consist almost entirely of phenyl benzenethiolsulphonate (171),

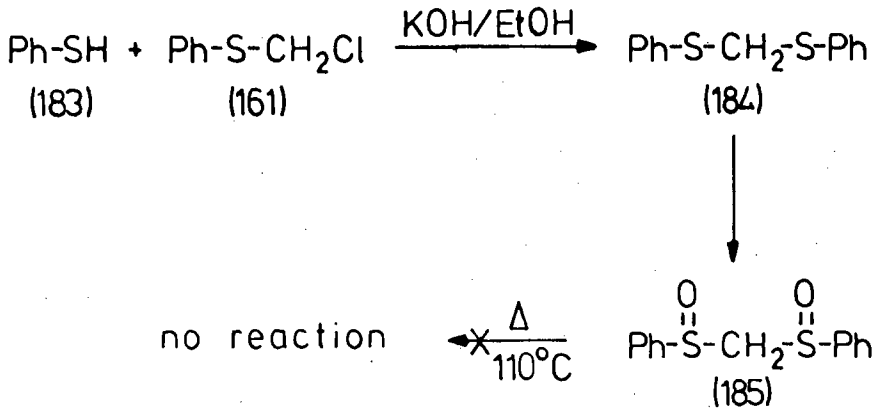
disproportionation of (179) to phenyl benzenethiolsulphinate and di-methoxymethyl ether after 4-5 days. This can be contrasted with the behaviour of (157) and (180), with the former being stable indefinitely at room temperature and decomposition of (180) only being complete after about two months. A German patent filed by Tsuchihashi[121], reported the deployment of analogous compounds as acaricides for both human and agricultural use. These included methoxymethylmethylsulphoxide as well as the di-ethyl and di-iso-propyl analogues. Curiously, no mention is made of any observations of rearrangement products, which is somewhat surprising in view of the fact that the method of preparation described involved prolonged heating at 60°C, during formation of the products.

As mentioned previously this S⟶O, 1,2-shift from a sulphoxide to a sulphenate ester is atypical with respect to analogous rearrangements. Why this rearrangement occurs is a question of thermodynamics and hence is indepdendent of the mechanistic pathway. The driving force may involve significant stereoelectronic factors (anomeric effects). It seems probable that (180) would take up a conformation whereby it could take advantage of the possible 'double anomeric effect', brought about by the acetal function, such that the lone pairs on the oxygen atoms take up an antiperiplanar arrangement relative to the other O-R group (181), to give the so called 'double bond- no bond resonance'[122,123], (182).



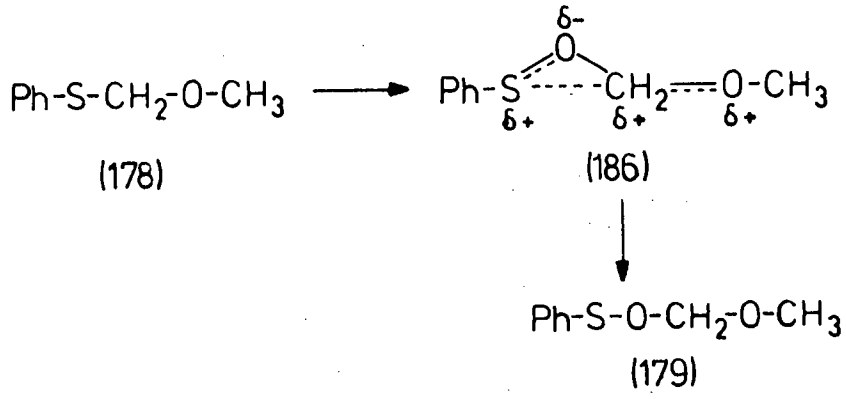
(181) (182)

The modern interpretation of this electronic delocalisation has been expressed in terms of overlap of an electron pair orbital of the oxygen atom with the antibonding orbital of the C-OR σ-bond.[124-125] Such stereoelectronic stabilisation is unavailable to (157). Furthermore, a possible destabilising anomeric effect might operate in (157), whereby there is 'lone pair-lone pair' repulsion between the sulphoxide and oxygen non-bonded electron pairs. It should be noted at this point that the bis-sulphoxide (185) does not undergo any thermally induced rearrangement in solution even after heating in toluene at 110°C over an extended period. Compound (185) was prepared by the reaction of thiophenol (183) with α-chlorothioanisole (161) to give the intermediate dithioacetal (184) in 84% yield, followed by oxidation with one equivalent of m-CPBA per sulphur atom to give the desired bis-sulphoxide (185) in 57% yield, (Scheme 90).



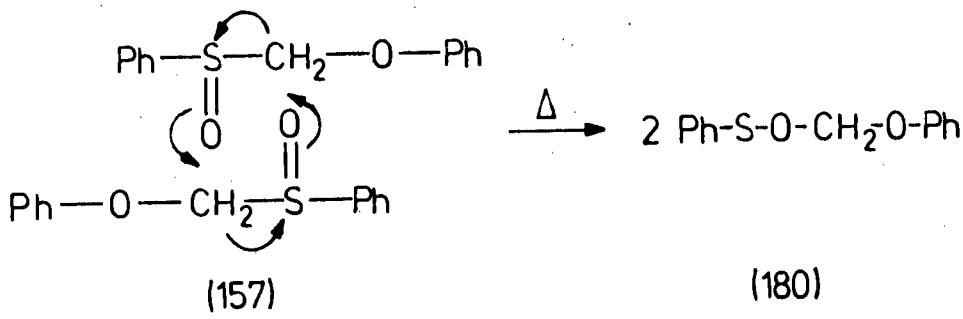
Scheme 90.

As regards the mechanistic pathway for these rearrangements, notwithstanding the fact that the Meisenheimer rearrangement has been shown to proceed via a radical pathway,[126] Maracich and Harrington[114] have proposed that methyoxymethylphenylsulphoxide (178) rearranges through an intramolecular mechanism involving a polarised activated complex (186), (Scheme 91).



Scheme 91.

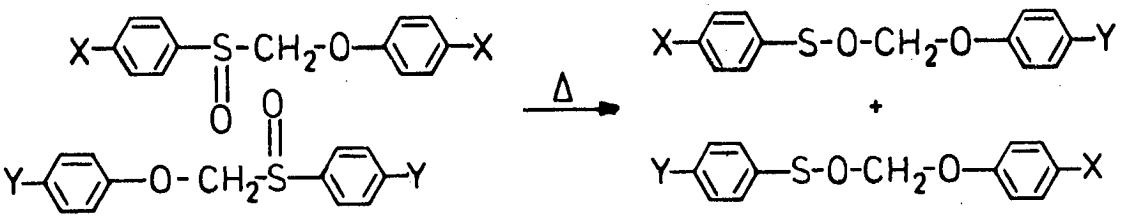
The fact that phenoxymethylphenylsulphoxide (157) proceeds to give a quantitative yield of (180) in toluene at 110°C would seem to confirm the preclusion of a radical pathway, as toluene is a notoriously bad reaction medium for such reactions due to the interference of side reactions even if a solvent cage mechanism were in operation. Although the intramolecular concerted mechanism is a distinct possibility, Schulman et al,[127] have reported that electron pair shifts through such small rings is sterically unfavourable. Another possibility might be a bimolecular oxygen transfer mechanism, whereby the sulphoxide oxygen is exchanged with that of another molecule, (Scheme 92).



(157) (180)

Scheme 92.

This possibility might be proven chemically if cross-products were obtained when thermolysing two differently substituted starting materials, (Scheme 93).



Scheme 93.

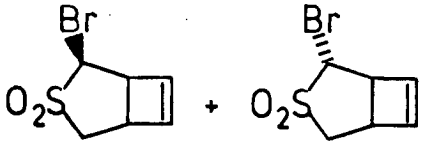
Kinetic investigations are now underway, and it is hoped that the order of the reaction and the magnitude of the reaction parameters will shed further light on the mechanistic pathway of this unusual rearrangement.

EXPERIMENTAL

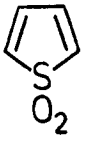
EXPERIMENTAL

CONTENTS

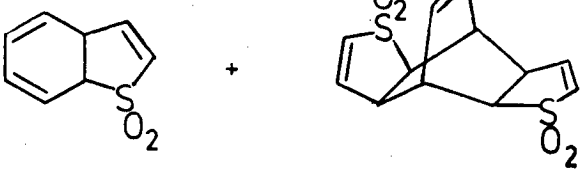
6. Preparation of:-



7. Preparation of:-



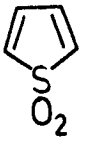
8. Preparation of:-



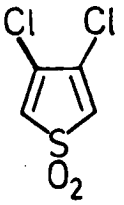
9. Attempted polymerisation of:-

(a) using n-butyl lithium

(b) Using sodium naphthalide



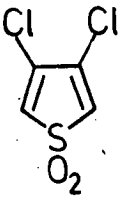
10. Preparation of:-



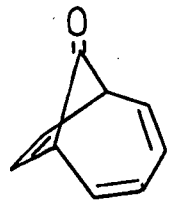
11. Attempted polymerisation of:

(a) using sodium naphthalide

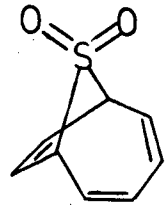
(b) using triethylaluminium/ titaniumtetrachloride



12. Preparation of:-



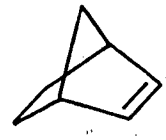
13. Preparation of:-



14. Metathesis of:-

(a) Using $WCl_6/SnMe_4$

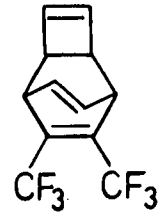
(b) using Tebbe's reagent/Et_3N



15. Metathesis of:-

(a) using $WCl_6/SnMe_4$

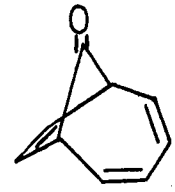
(b) using Tebbe's reagent/Et_3N



16. Metathesis of:-

(a) using $WCl_6/SnMe_4$

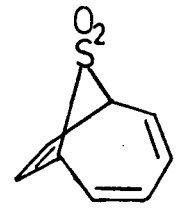
(b) using Tebbe's reagent/Et_3N



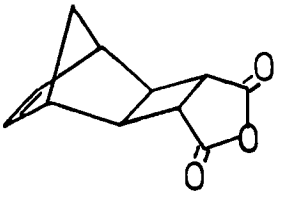
17. Attempted metathesis of:-

(a) using $WCl_6/SnMe_4$

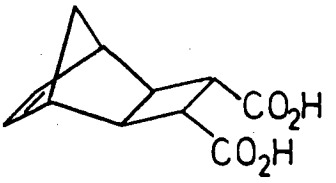
(b) using Tebbe's reagent/Et_3N



18. Preparation of:-



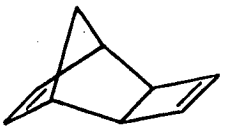
19. Preparation of:-



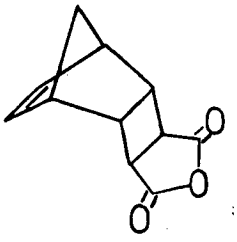
20. Preparation of:-

(a) by oxidative bis-decarboxylation

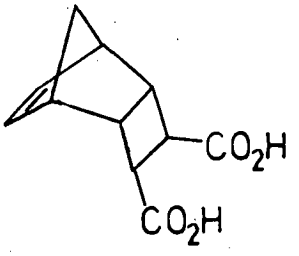
(b) by reductive desulphonylation



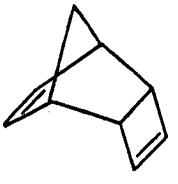
21. Preparation of:-



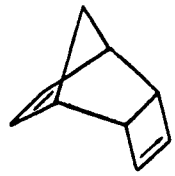
22. Preparation of:-



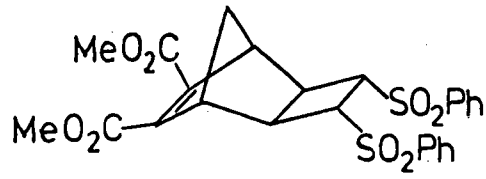
23. Preparation of:-



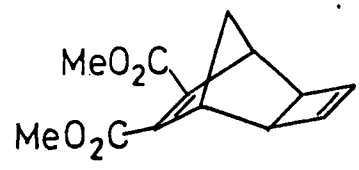
24. Metathesis of:-



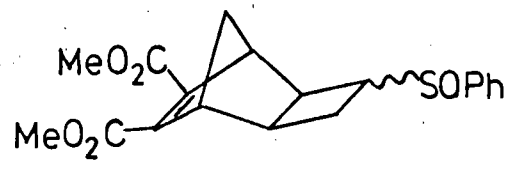
25. Preparation of:-



26. Attempted preparation of:-

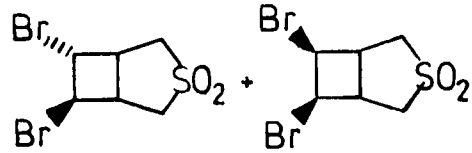


27. Attempted Preparation of:-



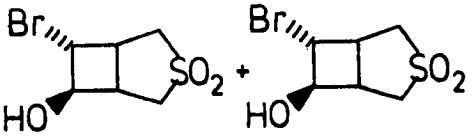
D. Preparation and reactions of cyclo-olefins containing sulphonyl groups 166

1. Preparation of:-



2. Preparation of:-

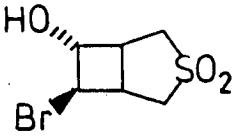
3. Preparation of:-



4. Preparation of:-

(a) using NBS

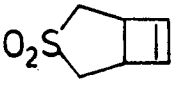
(b) using NBA



5. Bromination of:-

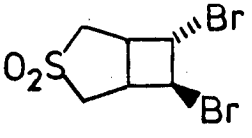
(a) in dry DME

(b) in wet DME

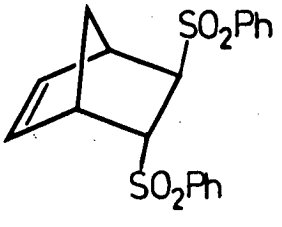


6. Preparation of:-

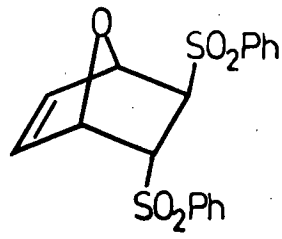
using TBAT



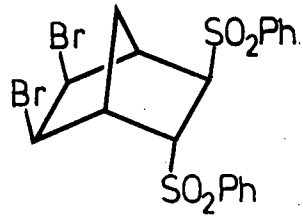
7. Preparation of:-



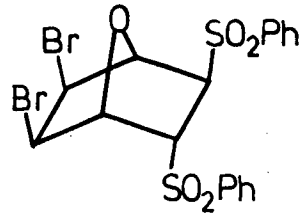
8. Preparation of:-



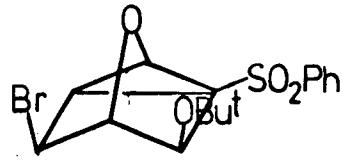
9. Preparation of:-



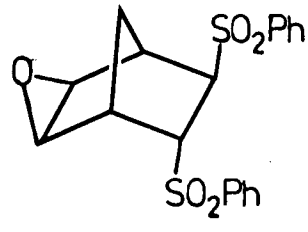
10. Preparation of:-



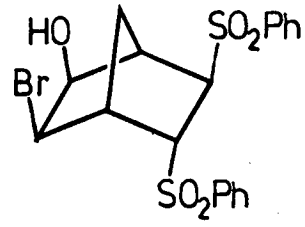
11. Preparation of:-



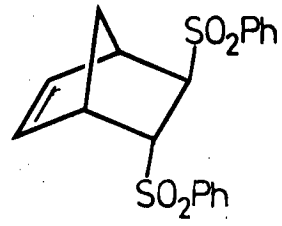
12. Preparation of:-



13. Preparation of:-



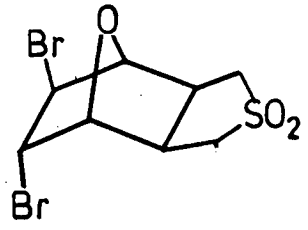
14. Attempted hydroxy-bromination of:-



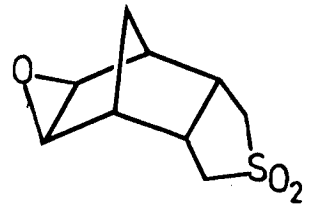
15. Attempted bromination of:- "

using TBAT

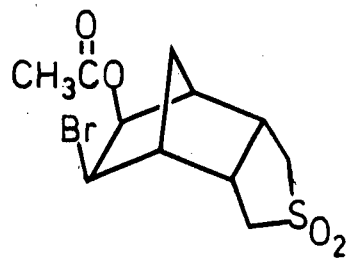
16. Preparation of:-



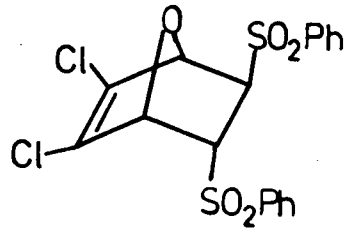
17. Preparation of:-



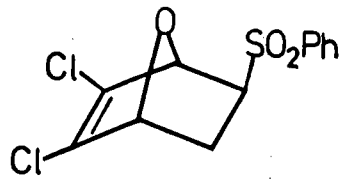
18. Preparation of:-



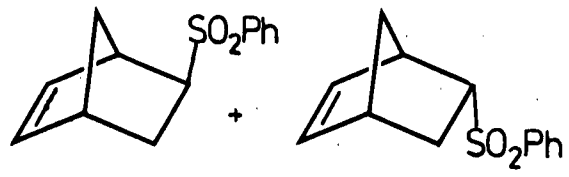
19. Preparation of:-



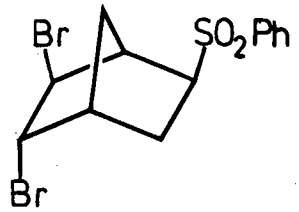
20. Preparation of:-

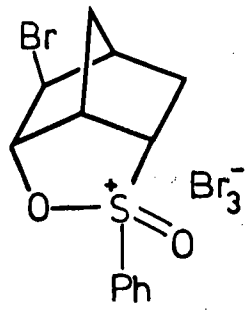


21. Preparation of:-



22. Preparation of:-

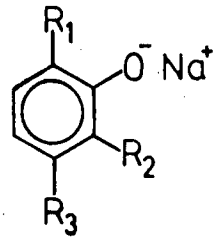


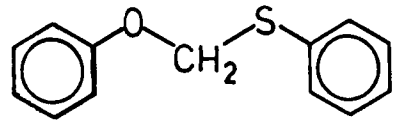
23. Preparation of:- 

24. Decomposition of:- "

E. Preparation of thermolysis of α-aryloxy sulphoxides and related compounds 191

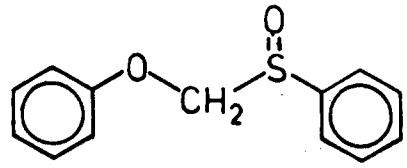
1. Preparation of:- Ph-S-CH_2Cl

2. Preparation of:- 

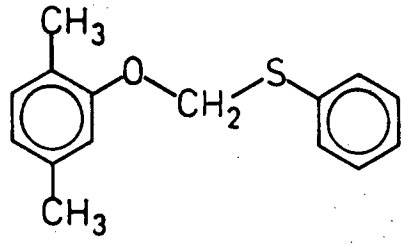
3. Preparation of:- 

4. Attempted oxidation of:- "

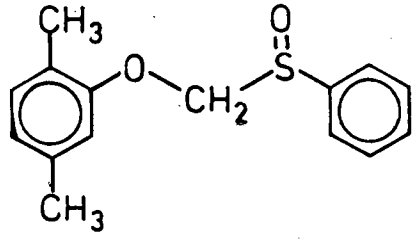
5. Preparation of:-



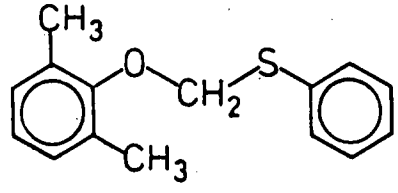
6. Preparation of:-



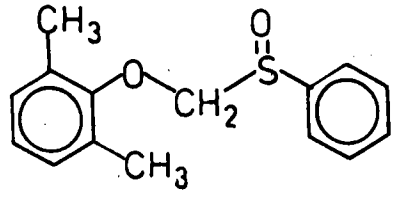
7. Preparation of:-



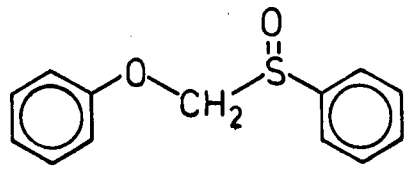
8. Preparation of:-



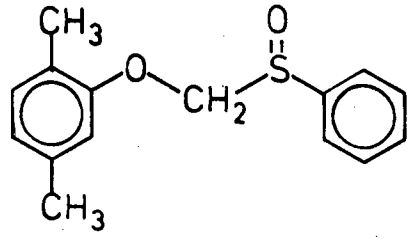
9. Preparation of:-



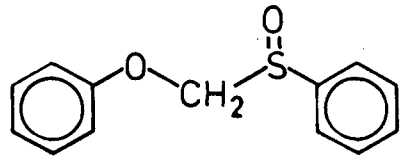
10. F.V.P. of:-



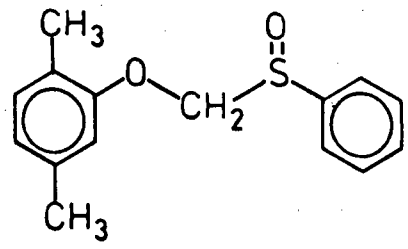
11. F.V.P. of:-



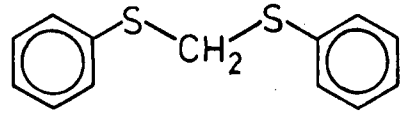
12. Solution thermolysis of:-

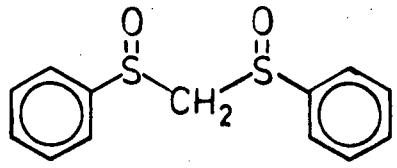


13. Solution thermolysis of:-



14. Preparation of:-



15. Preparation of:- 

16. Solution thermolysis of:- "

A. Symbols and Abbreviations

mol	moles
mmol	millimoles
m.p.	melting point
b.p.	boiling point
h,mins.	hours, minutes
A.R.	analytical reagent
n.m.r.	nuclear magnetic resonance
δ	chemical shift
s,d,t,	singlet, doublet, triplet,
m,cm,b	multiplet, complex multiplet, broad
J	spin-spin coupling constant
quat.C	quaternary carbon
N.O.E.	Nuclear Overhauser Enhancement
ν	wavenumber
m.s.	mass spectrometry
M^+	mass of molecular ion
B	Base peak
m/z	mass to charge ratio
F.V.P.	flash vacuum pyrolysis
a,b,c	unit cell dimensions
α,β,γ	interaxular angles
U	volume of unit cell
D_C	density of compound

B. INSTRUMENTATION AND GENERAL TECHNIQUES

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

a. ^{1}H-n.m.r.

Routine spectra were obtained at 60 MHz on a Varian EM-360 spectrometer and a Bruker WP-80 operated by Mr. L.H. Bell. Spectra of all new compounds, decoupling studies and N.O.E. experiments were obtained at 200MHz on a Bruker WP-200 spectrometer, operated by Mr. J.R.A. Millar. High resolution and N.O.E. experiments were obtained at 360 MHz on a Bruker WH-360 spectrometer operated by Dr. D. Reed.

b. ^{13}C-n.m.r.

Spectra were obtained at 50 MHz on a Bruker WP-200 spectrometer operated by Mr. J.R.A. Millar. All chemical shifts expressed in parts per million to high frequency of tetramethylsilane.

2. Infrared Spectroscopy

Spectra were obtained on a Perkin-Elmer 781 infrared spectrophotometer. Solids were run as nujol mulls and liquids as thin films, both on sodium chloride discs. Spectra were calibrated with the polystyrene peak at 1603

cm^{-1}.

3. Mass Spectrometry

Mass spectra and accurate mass measurements were obtained on an Associated Electrical Industries ms-902 instrument operated by Miss E. Stevenson and on a Kratos MS50TC instrument operated by Mr. A. Taylor.

4. Elemental Analysis

Microanalysis for carbon, hydrogen and nitrogen were carried out on a Perkin-Elmer 240 Elemental Analyser operated by Mr. J. Grunbaum and on a Carlo-Erba 1106 Elemental Analyser operated by Mrs. E. McDougal.

5. Melting Points

Routine melting points were carried out on a Gallenkamp melting point apparatus. Melting points of new compounds were determined on a Reichert hot-stage microscope. All melting points are uncorrected for the emergent stem correction.

6. Analytical Thin Layer Chromatography

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

7. Preparative Thin Layer Chromatography

This was carried out using 1.00mm layers of the above supports. After locating the components with iodine vapour or ultra-violet light, the bands were scraped off and the product removed from their supports by stirring in a solution of methanol/chloroform.

8. Flash Chromatography

This was carried out according to the method of Still *et al*,[128] using silica (Merck, Kieselgel 60) and the desired solvent system at 10p.s.i. controlled by a rotaflow tap.

9. Dry Flash Chromatography

This was carried out according to the method described by Harwood,[129] using silica (Fluka, Kieselgel G_{240}) and recommended sinters. The principal solvent system used was ether/40-60°C Petroleum ether gradients.

10. Drying and Evaporation of Solvents

Organic solutions were dried over anhydrous magnesium sulphate prior to evaporation under reduced pressure either at the water aspirator or oil pump, on a rotary evaporator.

11. Drying of Nitrogen

Oxygen free nitrogen was dried by passing the gas through concentrated sulphuric acid followed by 'Drierite' before entering the reaction vessel.

12. Drying and Purification of Solvents

Commercially available solvents were used without further purification unless otherwise stated. Dry

diethyl ether, benzene and toluene were obtained by the addition of sodium wire to the A.R. grade solvents. Chloroform was dried by passing the A.R. grade solvent through a column of basic alumina (Grade 1) immediately prior to use. Tetrahydrofuran was dried by heating under reflux with powdered calcium hydride under an atmosphere of dry nitrogen followed by distillation onto molecular sieve. Pyridine was dried by heating under reflux with potassium hydroxide pellets followed by distillation onto potassium hydroxide pellets. Acetonitrile was dried by the addition of calcium hydride until hydrogen evolution had ceased followed by decantation and distillation onto Type 4A molecular sieve. Chlorobenzene and methylene chloride were dried by heating under reflux with phosphorus pentoxide followed by distillation and storage over Type 4A molecular sieve.

13. Drying and Purification of Reagents

Commercially available reagents were used without further purification unless otherwise stated. Dry chlorine was obtained by the passage of the gas through concentrated sulphuric acid. Dry bromine was obtained by shaking with an equal amount of concentrated sulphuric acid, followed by separation prior to use. Lead tetra-

acetate was filtered under dry nitrogen from the supernatant glacial acetic acid prior to drying in a vacuum desiccator over potassium hydroxide pellets.

14. Drying of Products

Products were dried either in a vacuum oven, vacuum desiccator or a vacuum drying pistol using a suitable desiccant.

15. Photochemical Reactions

The lamps used were 125 watt and 400 watt medium pressure water cooled, mercury vapour lamps, supplied by Applied Photophysics Ltd., London. Reactions were carried out using either quartz or pyrex immersion wells.

16. Sealed Tube Reactions

The Carius tubes used were constructed according to the specifications recommended by Forrester,[130] using PTFE rotaflow taps supplied by J. Young, Acton.

17. Flash Vacuum Pyrolyses

The apparatus used was based on the design of W.D. Crow, Australian National University, Canberra. A similar set-up is used in a recent monograph by Brown.[108]

18. Metathesis Reactions

Tungsten hexachloride (Aldrich, Gold Label) and tetramethyl tin (Aldrich) were used as the catalyst system. Dry chlorobenzene was used as the solvent. The molar ratios used were WCl_6:$SnMe_4$:monomer:solvent, 1:2:100:2000. In alternative reactions where (Tebbe's Reagent), μ-chloro-μ-methylene-bis(cyclopentadienyl) titanium triethylaluminium (Ventron, U.S.A.) and triethylamine were used as the catalyst system, the molar ratios used were; Tebbe's:Et_3N:monomer:solvent, 1:1:100:1000. All manipulations for these reactions were carried out in a glove box under dry nitrogen, and all glassware was rigorously flame vacuum dried, prior to use.

19. Raman Spectroscopy

Raman spectra were obtained on an Annaspec 33 Laser Raman Spectrometer using 457.9nm excitation from a Spectra Physics Model 171. argon ion laser, both operated by Dr. J.R. Walton and Miss H.J. Bowley, B.P. Research Centre, Sunbury.

C. PREPARATION AND POLYMERISATION OF POLY(ACETYLENE) PRECURSOR MONOMERS

1. Attempted Preparation of 2-Bromo-2,5-dihydrothiophene-1,1'-dioxide

To a stirred solution of n-butyl lithium (5.32cm^3 of 1.6M) in 20ml of dry tetrahydrofuran at -78°C under an atmosphere of dry nitrogen was added a solution of 3-sulpholene (1.0g, 8.47mmol) in 10ml of dry THF. Stirring was maintained for a further 0.5h, followed by the addition in one portion of dry bromine (1.5g,9.4mmol) in 10ml of dry THF The reaction mixture was then stirred for a further 2h at -78°C. After work-up, the reaction mixture was found to contain an intractable mixture of products with no desired product formed. A similar result was obtained when HMPA was used as a cation trapping agent.

Alternative bases such as potassium t-butoxide, lithium di-iso-propylamide, lithium bis-trimethylsilylamide were also tried as was N-bromosuccinimide, however all these proved unsuccessful.

2. Preparation of 2-Bromo-2,5-dihydrothiophene-1,1'-dioxide

The title compound was prepared using a modification of the method employed by Becker and Labhart.[61]

To a solution of ethylmagnesium bromide (0.06mol) in 40ml of dry THF at 0°C under an atmosphere of dry nitrogen, was added dropwise with stirring, a solution of 3-sulpholene (5.09,42.4mmol) in 150ml of dry THF. After the addition was complete, a solution of dry bromine (6.78g,42.4mmol) in 90ml of dry THF was added in one portion. The reaction mixture was then allowed to heat up to room temperature, and stirred for a further 1h. The reaction was then quenched by the addition of 200ml of ice water, followed by filtration and rotoevaporation of the THF. The aqueous phase was extracted with (4x50ml) of methylene chloride. The combined organic extracts were then washed successively with (2x100ml) of 5% aqueous sodium hydroxide and (2x100ml) of brine, followed by drying and rotoevaporation of the solvent. The resulting dark brown oil was subjected to flash chromatography over silica using 40-60°C P.E./ether as eluant to give 2-bromo-2,5-dihydrothiophene-1,1'-dioxide (0.32g,4%) as a sweet smelling pale brown liquid. $\delta^{1}H$(80MHz,$CDCl_3$) 3.58-3.77(2H,t,J=10 and 4.7Hz,C(5)H), 4.50-4.77(1H,m,J=4.7Hz,C(2)H), 6.28-6.39(1H,d,J=8.7Hz,-C(3)H), 6.47(1H,s,C(4)H); $\delta^{13}C$ (50MHz,$CDCl_3$) 33.94,

48.05, 111.85, 135.12; m/z 134(19%), 132(20), 81(19), 79(20), 53(B,100).

3. Preparation of 3-Thiabicyclo[3.2.0]heptane-3,3'-dioxide-6,7-dicarboxylic anhydride

By a modification of the method used by Shaikhrazieva et al.,[56] a solution of 3-sulpholene (60g, 0.51mol) and maleic anhydride (70g, 0.71mol) in 500ml of acetone were photolysed at room temperature for 16h by a 400W mercury vapour medium pressure lamp, using a quartz immersion well. The resultant white crystalline precipitate was filtered off, washed with cold acetone and vacuum dried to give 3-thiabicyclo[3.2.0]heptane-3,3'-dioxide-6,7-dicarboxylic anhydride (69.8g, 64%) as colourless crystals. m.p. 290-295°C, (lit 292-293°C).

4. Preparation of 3-Thiabicyclo[3.2.0]heptane-3,3'-dioxide-6,7-dicarboxylic acid

A suspension of 3-thiabicyclo[3.2.0]heptane-3,3'-dioxide-6,7-dicarboxylic anhydride (45.8g, 0.214mol) in 150ml of water was heated to reflux for 1h, after which time all starting material had been hydrolysed. The water was rotoevaporated to given an off-white solid.

Recrystallisation from ethanol gave 3-thiabicyclo[3.2.0]-heptane-3,3'-dioxide-6,7-dicarboxylic acid (45.0g, 90%) as colourless crystals. m.p. 194-195°C, (lit 194-195°C).

5. Preparation of 3-Thiabicyclo[3.2.0]hepta-6-ene-3,3'-dioxide

This was prepared by a modification of the method employed by McLaughlin et al.[60] To a solution of 3-thiabicyclo[3.2.0]heptane-3,3'-dioxide-6,7-dicarboxylic acid (20g, 0.085mol) in 200ml of dry pyridine was added lead tetra-acetate (57g 0.128mol). The resultant mixture was then immersed in a water bath at 70°C, with occasional stirring. After all the carbon dioxide had been liberated, indicated by the cessation of effervescence, the dark brown mixture was poured into a mixture of 250ml of 70% nitric acid in 1250ml of water. This was then extracted with (6x250ml) of methylene chloride. The combined organic extracts were washed successively with aqueous sodium hydrogen carbonate and brine, followed by drying and rotoevaporation of the solvent to give a dark brown oil. Vacuum sublimation of the residue at 100-120°C and 0.05mmHg gave 3-thiabicyclo-[3.2.0]hepta-6-ene-3,3'-dioxide (3.32g, 22%) as colourless crystals. m.p. 72-74°C, (lit 71-75°C).

6. Preparation of exo and endo-2-Bromo-3-thiabicyclo-[3.2.0]hepta-6-ene-3,3'-dioxide

This was prepared by the method employed by Becker and Labhart.[61]

Preparation of Grignard- Magnesium turnings (1.1g,-20mmol) were degreased by washing with dry ether followed by oven drying at 60°C. Approximately half of a solution of bromoethane (2.18g, 20mmol) in 20ml of dry ether was added to the magnesium turnings, containing a crystal of iodine. The mixture was heated under an atmosphere of nitrogen until refluxing began. The remainder of the bromoethane solution was then added in small portions over 30mins, followed by refluxing for 15-20mins after addition.

A solution of 3-thiabicyclo[3.2.0]hept-6-ene-3,3'-dioxide (2.0g, 13.9mmol) in 80ml of 1:1 benzene/ether was added dropwise with stirring under nitrogen to the solution of ethylmagnesium bromide at 0°C. After addition, the mixture was headed to reflux for 5mins followed by cooling to 0°C. A solution of dry bromine (1.12g, 13.9mmol) in 30ml of dry benzene was then added in one portion. The resulting pale yellow mixture was stirred at room temperature for 2h. The off-white reaction mixture was then quenched by the addition of 60ml of ice water. This was then filtered and separated, the aqueous layer was extracted with 50ml of

1:1 benzene/ether and combined with the organic extract. The organic phase was washed successively with 100ml of 5% aqueous HCl, 100ml of 10% aqueous sodium bisulphite and 100ml of brine, followed by drying and evaporation of the solvent to give 1.405g of a dirty brown liquid whose t.l.c. showed three spots, one of which was concurrent with starting material. Short column chromatography over silica gel using ether as eluant gave a satisfactory separation.

The first fraction eluted after recrystallisation from di-isopropyl ether gave exo-2-bromo-3-thiabicyclo-[3.2.0]hept-6-ene-3,3'-dioxide (0.643g, 20.7%) as colourless crystals. m.p. 103-105°C. (Found: C,32.12, H,3.12; $C_6H_7BrO_2S$ requires C,32.30, H,3.16%); νmax 1320 ($>SO_2$) and 1120 ($>SO_2$) cm^{-1}; δ^1H(200MHz,$CDCl_3$) 3.10-3.19(1H,d of d,J=2.3 and 13.9Hz,C(4)H), 3.34-3.45 (1H,d of d,J=8.2 and 13.9Hz,C(4)H), 3.69-3.76(1H,m,C(5)H), 3.87-3.90(1H,d of d,J=1.9 and 3.9Hz, C(1)H), 4.70-4.71(1H,d,J=1.9Hz,C(2)H), 6.21-6.25(2H,d of d,J=2,9 and 5.6Hz, C(6)H and C(7)H); $\delta^{13}C$(50MHz, DEPT 3π/4,$CDCl_3$) 40.47, 49.12, 51.69, 58.34, 138.65, 139.36.; m/z 224(M^+,B,100%), 222(91), 160(19), 158(29), 149(44), 143(49), 107(57).

The second fraction eluted after vacuum sublimation at 116°C and 0.15mmHg gave endo-2-bromo-3-thiabicyclo-[3.2.0]hept-6-ene-3,3'-dioxide (0.158g 5.1%) as colourless crystals. m.p.127.5-128°C; (Found: C,32.14, H,3.09; $C_6H_7BrO_2S$ requires C,32.30, H,3.16%); νmax 1310-($>SO_2$) and 1129 ($>SO_2$) cm^{-1}; δ^1H(200MHz,$CDCl_3$) 3.19-3.28

(2H,cm,C(4)H), 3.65-3.73(1H,m,C(5)H), 3.82-3.88(1H,d of d,J=4 and 8Hz,C(1)H), 4.83-4.87(1H,d,J=8Hz,C(2)H), 6.11-6.25(2H,d of d, J=2.8Hz,C(6)H and C(7)H); δ^{13}C(50MHz,DEPT 3π/4,$CDCl_3$) 39.52, 45.61, 49.13, 59.63, 137.51, 139.86.; m/z 224(M,68%), 222(64), 160(95), 158(B,100), 145(23), 143(27), 132(18), 121(23), 119(54) 117(45).

7. Preparation of Thiophene-1,1'-dioxide

The title compound was prepared by the method of Bailey and Cummins.[62]

To a stirred solution of 3,4-dibromo-2,5-dihydro-thiophene-1,1'-dioxide (2.085g,7.55mmol) in 250ml of dry tetrahydrofuran at 0°C, was added finely powdered sodium hydroxide (5.0g, 0.208mol) whilst under a constant dry nitrogen purge. The resulting heterogeneous mixture was subsequently stirred at 0°C until a maximum U.V. absorption was seen at 289nm. After which time the solid residues were filtered off and the resulting solution was stored at 1°C over 4A molecular sieve to prevent dimerisation. U.V. spectra show 98% conversion to the product.

8. Preparation of 3,7-Dihydrobenzothiophene-1,1'dioxide and $\Delta^{2,5}$-Hexahydro-4,8-endovinylene-benzodithiophene-1,7-tetroxide

The former title compound was identified by Bailey and Cummins[62]. A solution of thiophene-1,1'-dioxide (300ml, 0.5M) was prepared at 0°C as previously described. The solvent was then removed on a rotary evaporator whilst the pot temperature was maintained at 0°C. The residual pale yellow oil was allowed to heat up to room temperature, during which time SO_2 was evolved as indicated by moist litmus paper. After 0.75h, 1.135g of a pale yellow solid remained. Trituration of this solid with methylene chloride dissolved all but 0.311g of a sparingly soluble solid. This was recrystallised from acetone to give $\Delta^{2,5}$-hexahydro-4,8-endovinylene-benzodithiophene-1,7-tetroxide as a white powder. m.p. 350°C (dec) (Found: C,50.26, H,4.33; $C_{14}H_{12}O_4S_2$ requires C,50.68, H,4.25%); νmax 1604(C=C), 1286(>SO_2) and 1120 cm^{-1}; δ^1H (80MHz,d^6DMSO) 3.58(4H,bs), 5.80-5.89(2H,bt,-J=3.5Hz), 6.66-7.03(4H,d of d,J=6.8Hz); δ^{13}C(50MHz, DEPT 3π/4,- d^6DMSO) 34.19, 44.97, 59.52, 128.69, 133.55, 140.82; m/z 284(M,8%), 220(31), 185(33), 156(B,100), 128(56), 115(49), 103(90).

Evaporation of the residual methylene chloride extracts yielded a pale yellow solid. Low temperature recrystallisation from methylene chloride/ether gave 0.5g

of 3,7-dihydrobenzothiophene-1,1'-dioxide as colourless crystals. m.p. 91-92°C (lit 90-91.5°C).

9. Attempted polymerisation of Thiophene-1,1'-dioxide

(a) Using n-butyl lithium

The reaction was carried out according to the method employed by Hsieh.[63]

A previously prepared 0.5M solution of thiophene-1,1'-dioxide in dry tetrahydrofuran was stirred at 0°C under dry nitrogen. Into this solution was injected through a rubber serum cap n-butyl lithium (0.1ml of 1.6M). The solution was stirred for a further 1.5h after which time, no change was observed. The solvent was then rotoevaporated to give a pale yellow solid which was identified as a mixture of the dimer and trimer of thiophene-1,1'dioxide. The above reaction was repeated under identical conditions with the exception of the addition of benzo-15-crown-5 (54mg). As before, this resulted in the Diels/Alder formation of the dimer and trimer.

(b) Using sodium naphthalide

The reaction was carried out according to the method prescribed by Swarc et al.[64]

A previously prepared solution of thiophene-1,1'-dioxide (0.8g, 7.2mmol) in 100ml of dry THF was stirred at -70°C under an atmosphere of dry nitrogen. Into this solution was injected through a rubber serum cap 1.3ml of a previously prepared sodium naphthalide initiator solution. The reaction mixture turned orange immediately. This was then stirred at -70°C for a further 1h, followed by quenching with a few millilitres of methanol. The solvent was then rotoevaporated. The resultant residue was identified by i.r. as the above mixture as well as some residual naphthalene.

10. Preparation of 3,4-Dichlorothiophene-1,1'-dioxide

The title compound was prepared by the method of Mandel *et al*.[65] 3-Sulpholene was chlorinated to give 3,4-dichloro-2,5-dihydrothiophene-1,1'-dioxide. This was then subjected to photochemical chlorination to give 3,3,4,4-tetrachloro-2,5-dihydrothiophene-1,1'-dioxide. Subsequently this was *bis*-dehydrochlorinated using 30% aqueous ammonia to give 3,4-dichlorothiophene-1,1'-dioxide. m.p. 110-113°C (lit 112-113°C).

11. Attempted polymerisation of 3,4-Dichlorothiophene-1,1'-dioxide

(a) Using sodium naphthalide initiator

The reaction was carried out according to the method employed by Swarc et al.[64]

A solution of 3,4-dichlorothiophene-1,1'-dioxide (1.16g, 8mmol) in 100ml of dry THF was stirred at -70°C under an atmosphere of dry nitrogen. Into this solution was injected through a rubber serum cap 1.0ml of a previously prepared solution of sodium naphthalide initiator. The reaction mixture was stirred at -70°C for a further 1.5h. After this time no viscosity was observed and only starting material was recovered from the reaction mixture. A control experiment carried out on styrene resulted in the formation of poly(styrene) in high yield.

(b) Using triethyl aluminium/titanium tetrachloride

The reaction was carried out according to the method employed by Blatz.[66]

To 100ml of sodium dried toluene, under an atmosphere of dry nitrogen was added the catalyst mixture of triethyl aluminium (0.5ml, 0.0551g) and titanium tetrachloride (0.55ml). The catalyst mixture was allowed to age for 0.5 hours followed by cooling to

-70°C. The monomer 3,4-dichlorothiophene-1,1'-dioxide (5.0g, 27mmol) was then injected as a solution in 40ml of dry toluene. The reaction mixture was then stirred at -70°C under nitrogen for 14h, no viscosity was observed. No precipitate was found on pouring into excess methanol and work-up resulted in quantitative recovery of starting material. A control experiment carried out on cyclopentadiene gave poly(cyclopentadiene) in high yield as a white polymer.

12. Preparation of 9-Oxa-bicyclo[4.2.1]nona-2,4,7-triene

The title compound was prepared by the method of Antkowiak et al.[69] Preparation of cylooctatetraene dianion:- A suspension of lithium shavings (1.6g, 0.23mol) in 200ml of dry ether was cooled to -70°C, followed by the addition of cyclooctatetraene (10.4g, 0.10mol) in one portion. The mixture was mechanically stirred at -70°C for a further 4h under a constant dry nitrogen purge. The cooling bath was then removed and the reaction mixture was stirred overnight at room temperature.

About 100ml of dry ether was added to dissolve the residual COT dianion. Dimethyl carbamoyl chloride (11.9g, 0.11mol) in 70ml of dry ether was then added dropwise to the mixture, followed by stirring for a

further 2h. Dilute H_2SO_4(100ml,3N) was added to the reaction mixture, followed by separation. The aqueous phase was extracted with (3x50ml) of ether and combined with the organic phase. The combined organic extracts were washed successively with saturated $NaHCO_3$ and water, followed by drying and evaporation of the solvent. Vacuum distillation of the liquid residue at 36°C and 0.05mmHg gave 9-oxa-bicyclo[4.2.1]nona-2,4,7-triene (6.0g, 45%) as a colourless oil which solidifies on storing in the freezer. This turns yellow after a few weeks but redistillation effects purification. δ'H(200MHz,$CDCl_3$) 2.98-3.11(2H,m,C(1)H and C(6)H), 5.59-5.89-(6H,m,C(2)H,C(3)H,C(4)H,C(5)H,C(7)H,C(8)H), δ^{13}C(50MHz,-DEPT 3π/4,$CDCl_3$) 52.03, 124.61, 124.67, 128.48. νmax 1758(C=O) cm^{-1}.

13. Preparation of 9-Thiabicyclo[4.2.1]nona-2,4,7-triene-9,9'-dioxide

The title compound was prepared by the method of Paquette et al.[70] Into a 1l 3-necked flask fitted with a mechanical stirrer, dry ice condenser, dropping funnel and N_2 inlet was condensed at -78°C about 100ml of liquid SO_2, followed by the addition of cyclooctatetraene (11.5g, 0.11mol). To this was then added dropwise with stirring under dry nitrogen, a previously prepared

solution of antimony pentafluoride-liquid SO_2, SbF_5(24g, 0.11mol) in 100ml of liquid SO_2. After addition, the reaction mixture was stirred at -78°C for a further 2.5h. The SO_2 was then removed by a vacuum pump at -40°C and 2mmHg to leave a dark brown solid. To this was added 500ml of methylene chloride at -30°C, followed by pouring this into 600ml of ice chilled saturated aqueous sodium hydrogen carbonate. After separation of the layers, the aqueous phase was washed with (2x100ml) of methylene chloride. The combined organic extracts were then washed successively with (2x200ml) of water and (2x200ml) of brine, followed by drying and rotoevaporation of the solvent. The solid residue was recrystallised twice from chloroform to give 9-thiabicyclo[4.2.1]-nona-2,4,7- triene-9,9'-dioxide (6.36g, 34%) as colourless crystals. m.p. 192-193°C (lit 193-193.5°C).

14(a) Metathesis of Norbornene using $WCl_6/SnMe_4$ as catalyst

To a solution of norbornene (1.0g, 10.6mmol) in 25ml (23.83g) of dry chlorobenzene, under an atmosphere of dry nitrogen at 0°C, was added the catalyst solution of tungsten hexachloride (58mg, 0.14mmol) and tetramethyl tin (37.9mg, 29.22μl, 0.14mmol) in 1ml of dry chlorobenzene. The reaction mixture was stirred rapidly

for 15min, after which time it had turned jelly-like. After a further 0.5h, the polymerisation was terminated by the addition of a few drops of methanol. The reaction mixture was then poured into 250ml of methanol, which resulted in the precipitation of poly(norbornene) (0.86g, 86%) as a white rubbery solid.

14(b) Metathesis of Norbornene using 'Tebbe's Reagent as catalyst

To a solution of norbornene (0.94g, 10mmol) in 20ml of dry chlorobenzene was added the catalyst solution of Tebbe's reagent (30mg, 0.01mmol) and triethylamine (10mg, 0.01mmol) in 1ml of solvent. The resultant mixture was stirred for 24h at room temperature, after which time it had become viscous. This was subsequently quenched by the addition of a few mls of methanol. The polymer was precipitated by addition to 200ml of methanol, followed by filtration to give poly(norbornene) as a white rubbery solid.

15(a) Metathesis of 7,8-bis(Trifluoromethyl)tricyclo-[4.2.2.$0^{2,5}$]deca-3,7,9-triene using $WCl_6/SnMe_4$ as catalyst

To a solution of 7,8-bis(trifluoromethyl)tricyclo-[4.2.2.$0^{2,5}$]deca-3,7,9-triene (0.762g, 3.2mmol) in 4ml of dry chlorobenzene, under an atmosphere of dry nitrogen at 0°C, was added the catalyst solution of tungsten hexachloride (11.3mg, 0.028mmol) and tetramethyl tin (9.4mg, 7.86μl, 0.28mmol) in 1ml of solvent. The catalyst solution was shaken for 1min prior to use. The resultant mixture was then stirred rapidly for 40min, after which time the mixture had become uniformly viscous. The polymerisation was terminated by the addition of a few drops of methanol, followed by pouring into 75ml of methanol. The resultant precipitate was filtered to give poly(7,8-bis(trifluoromethyl)tricyclo-[4.2.2.$0^{2,5}$]deca-3,7,9-triene) (0.630g, 84%) as a white powder.

15(b) Metathesis of 7,8-bis(Trifluoromethyl)tricyclo-[4.2.2.$0^{2,5}$]deca-3,7,9-triene using 'Tebbe's Reagent' as catalyst

To a solution of 7,8-bis(trifluoromethyl)tricyclo-[4.2.2.$0^{2,5}$]deca-3,7,9-triene (1.0g, 4.1mmol) in 10ml of

dry chlorobenzene was added the catalyst solution of Tebbe's reagent (13mg, 0.03mmol) and triethylamine (5.2μl) in 1ml of the solvent. The reaction mixture was then stirred at room temperature for 4h, then for 1h at 40°C. The viscous solution was quenched by the addition of a few drops of methanol, then poured into 200ml of methanol to give an orange precipitate of poly(7,8-bis-(trifluoromethyl)tricyclo[4.2.2.$0^{2,5}$]deca-3,7,9-triene) (0.24g, 24%). A solution of this was heated which turned from orange-red-purple-black(metallic lustre) indicating the formation of poly(acetylene).

16(a) Attempted Metathesis of 9-Oxabicyclo[4.2.1]-nona-2,4,7-triene using $WCl_6/SnMe_4$ as catalyst

The reaction was carried out under similar conditions as for the polymerisation of norbornene. The ratios used were monomer (1.0g, 8.0mmol):WCl (40mg) : $SnMe_4$(20.86 μl). On addition of the catalyst solution the reaction mixture turned pale yellow. After stirring for 2h no viscosity was observed. The mixture was stirred overnight at room temperature but still no viscosity was observed, and no precipitate was received on pouring into methanol. Repeat experiments at room temperature and 70°C were also unsuccessful, whereas control experiments to check catalyst activity were all satisfactory.

16(b) Attempted Metathesis of 9-Oxabicyclo[4.2.1]-nona-2,4,7-triene using 'Tebbe's Reagent' as catalyst

The reaction was carried out under similar conditions to that for the polymerisation of norbornene. The ratios used were monomer (1.8g) : solvent (30ml) : Tebbe's (39mg) : Et_3N (19μl). After stirring for 48h, the reaction mixture was poured into 200 ml of methanol, whereupon only partially decomposed starting material was recovered.

17(a) Attempted Metathesis of 9-Thiabicyclo[4.2.1]-nona-2,4,7-triene-9,9'-dioxide using $WCl_6/SnMe_4$ as catalyst

The preparation was carried out under the standard conditions as for norbornene. Following addition of the catalyst solution, the reaction mixture was stirred for 5h, after which time no viscosity was observed. A sample was injected into methanol but no precipitate resulted. After 24h, only starting material was recovered from the reaction mixture. A control experiment on the 'Durham' monomer was successful.

17(b) Attempted Metathesis of 9-Thiabicyclo[4.2.1]-nona-2,4,7-triene-9,9'-dioxide using 'Tebbe's Reagent' as catalyst

The reaction was carried out under similar conditions as for the polymerisation of norbornene. The ratios used were, monomer (1.0g) : solvent (10ml) : Tebbe's (17mg) : Et_3N (8.2μl). In this experiment dry methylene chloride was used due to the insolubility of the monomer in chlorobenzene. After stirring for 65h, no viscosity was observed and only starting material was recovered from the reaction mixture.

18. Preparation of exo-Tricyclo[4.2.1.$0^{2,5}$]nona-7-ene-3,4-dicarboxylic anhydride

This title compound was prepared by the method of Tabushi et al.[71] Maleic anhydride (2.60g, 26.5mmol) was added to neat quadricyclane (3.255g, 35.4mmol). After swirling for 2-3min the homogeneous reaction mixture was heated in an oil bath at 90°C for 24h. The crude pale yellow solid was purified by vacuum sublimation at 110°C and 0.01mmHg to give exo-tricyclo[4.2.1.$0^{2,5}$]nona-7-ene-3,4-dicarboxylic anhydride (3.97g 79%) as colourless crystals. ^1H-n.m.r. and i.r. spectra were identical to the published spectra.

19. Preparation of exo-Tricyclo[4.2.1.$0^{2,5}$]nona-7-ene-3,4-dicarboxylic acid

exo-Tricyclo[4.2.1.$0^{2,5}$]nona-7-ene-3,4-dicarboxylic anhydride (16.0g, 84mmol) was suspended in 100ml of water. This was then heated to reflux for 1.5h. The water was then rotoevaporated to give a solid residue which was recrystallised from ethanol to give exo-tricyclo[4.2.1.$0^{2,5}$]nona-7-ene-3,4-dicarboxylic acid (15.5g, 89%) as colourless crystals. m.p. 193-195°C, νmax 2500(b,O-H), 1690(C=O), 1600(C=C), δ^{1}H(80MHz, d^{6}DMSO) 1.02-1.14(1H,d,J=9.6Hz,C(9)H), 1.82-1.94(1H,d,J=9.6Hz,-C(9)H), 2.05-2.16(2H,m,C(2)H and C(5)H), 3.06(2H,bs,C(3)H and C(4)H), 3.41-3.56(2H,m,C(1)H and C(6)H), 6.00(2H,bs,C(7)H and C(8)H), 11.89(2H,bs,O-H), δ^{13}C-(50MHz,d^{6}DMSO) 36.81, 37.36, 41.47, 42.50, 136.30, 172.47(quat.C), m/z : 208(M^{+}), 190, 162, 143, 125, 117, 97, 92, 91(B).

20(a) Preparation of exo-Tricyclo[4.2.1.$0^{2,5}$]nona-3,7-diene by oxidative, bis-decarboxylation

exo-Tricyclo[4.2.1.$0^{2,5}$]nona-3,7-dicarboxylic acid (5.33g, 25.6mmol) was dissolved in 100ml of dry pyridine. To this was added lead tetra-acetate (22.71g, 51.2mmol) in one portion. The reaction mixture was then immersed

in a preheated water bath at 68°C and was stirred occasionally. After CO_2 had been liberated indicated by the cessation of effervescence. The reaction mixture was poured into a mixture of 125ml of 70% HNO_3 in 500ml of water. This was then extracted with (3x250ml) of methylene chloride. The combined organic extracts were washed successively with 250ml portions of water, saturated $NaHCO_3$ and brine, followed by drying, and rotoevaporation of the solvent. The residue was then bulb to bulb distilled at 40°C and 18mmHg to give exo-tricyclo[4.2.1.$0^{2,5}$]nona- 3,7-diene (0.310g, 10.3%) as a colourless liquid. ^{1}H-n.m.r. and ^{13}C data is identical to literature values[71].

20(b) Preparation of exo-Tricyclo[4.2.1.$0^{2,5}$]nona-3,7-diene by reductive desulphonylation

The title compound was prepared by the method of De Lucchi et al.[72]

To a slurry of 3,4-bis(phenylsulphonyl)tricyclo-[4.2.1.$0^{2,5}$]nona-7-ene (4.0g, 10mmol) and sodium dihydrogen orthophosphate (24g) in 200ml of A.R. methanol was added a 2% sodium amalgam (1.84g Na,80mmol) in small portions. The reaction mixture was stirred at room temperature under an atmosphere of dry nitrogen for 24h followed by filtration. The filtrate was poured into

200ml of brine and extracted with (3x80ml) of pentane. The combined organic extracts were washed with brine, dried and carefully rotoevaporated to give a colourless liquid which was vacuum microdistilled at 55°C and 0.05mmHg to give exo-tricyclo[4.2.1.$0^{2,5}$]nona-3,7-triene. ^{1}H and ^{13}C-n.m.r. were identical to literature values.

21. Preparation of endo-Tricyclo[4.2.1.$0^{2,5}$]nona-7-ene-3,4-dicarboxyclic anhydride

Cyclopentadiene was prepared by the thermal cracking of dicyclopentadiene, by distillation through a 30cm Vigreaux column with the fraction between 40-42°C being collected and used immediately.

Cyclobutene-3,4-dicarboxylic anhydride (0.37g, 2.98mmol) was suspended in 30ml of dry benzene. To this was added cyclopentadiene (0.246g, 3.7mmol, 25% w/w excess). The resulting mixture was refluxed for 12h, after which time 53mg of an insoluble white solid was filtered off. This was later identified as 1,3-butadiene-1,4-dicarboxylic acid. The filtrate was rotoevaporated and the solid residue was vacuum sublimed at 140°C and 0.05mm Hg to give endo-tricyclo[4.2.1.$0^{2,5}$]-nona-7-ene-3,4-dicarboxyclic anhydride (0.528g, 93%) as colourless crystals. m.p. 98-99°C; (Found:C, 69.30, H,5.44 $C_{11}H_{10}O_3$ requires C,69.46, H,5.30%); νmax 1848

(C=O) 1780 (C=O) 1065 (C-O) cm^{-1}; $\delta^{1}H$(80MHz,$CDCl_3$) 1.09-1.20(1H,d,J=9Hz,C(9)H), 1.64-1.75 (1H,d,J=9Hz,C(9)H), 2.67-2.70(2H,m,C(2)H and C(5)H), 2.88-2.98(2H, m,C(3)H and C(4)H), 3.11-3.22(2H,m,C(1)H and C(6)H), 6.37-6.42 (2H,t,J=2Hz, C(7)H and C(8)H); ^{13}C(50- MHz, $CDCl_3$) 41.75, 42.11, 45.02, 50.50, 136.10, 173.26, (quat.C); m/z 190(M^+,Bl00%), 162(33), 145(28), 131(21).

22. Preparation of endo-Tricyclo[4.2.1.$0^{2,5}$]nona-7-ene-3,4-dicarboxylic acid

endo-Tricyclo[4.2.1.$0^{2,5}$]nona-7-ene-3,4-dicarboxylic anhydride (0.119g, 0.63mmol) was suspended in 5ml of water. This was then heated until all the starting anhydride had dissolved followed by evaporation of the water. The solid residue was recrystallised from ethanol to give endo-tricyclo[4.2.1.$0^{2,5}$]nona-7-ene-3,4-dicarboxylic acid (0.117g, 90%) as colourless needles. m.p. 189-190°C; (Found: C,63.29, H,5.73, $C_{11}H_{12}O_4$ requires C,63.45, H,5.81%); νmax 3400-2500 (b,O-H), 1695(C=O) cm^{-1}; $\delta^{1}H$(80MHz,d^6DMSO) 1.05-1.15 (1H,d,J=9Hz,C(9)H), 1.44-1.55 (1H,d,J=9Hz,C(9)H), 2.31-2.34(2H,d,C(2)H and C(5)H), 2.85(4H,s,C(1)H,C(3)H,C-(4)H), and C(6)H), 6.38(2H,s,C(7)H and C(8)H), 11.98(2H,bs,(O-H)); $\delta^{13}C$(50MHz,d^6DMSO) 38.67, 40.53,

44.33, 51.11, 135.71, 173.95,(quat.C); m/z 208(M^+,31%), 192(23), 162(79), 145(34), 144(31), 143(B,100), 125(84).

23. Preparation of endo-Tricyclo[4.2.1.$0^{2,5}$]nona-3,7-diene

endo-Tricyclo[4.2.1.$0^{2,5}$]nona-7-ene-3,4-dicarboxylic acid (6.19g, 29.8mmol) was dissolved in 100ml of dry pyridine. To this was added lead tetra-acetate (19.9g, 59.9mmol) in one portion. The reaction mixture was then immersed in a preheated water bath at 65°C with occasional stirring. After all CO_2 had been liberated indicated by the cessation of effervescence, the reaction mixture was poured into a solution of 125ml of 70% HNO_3 in 650ml of water. This was then extracted with (5x100ml) of methylene chloride. The combined organic extracts were washed successively with aqueous $NaHCO_3$ (2x250ml) and brine (1x250ml), followed by drying and careful rotoevaporation of the solvent. Bulb to bulb distillation of the residue at 2mm Hg and 50°C gave endo-tricyclo[4.2.1.$0^{2,5}$]nona-3,7-diene (0.51g, 14.5%) as a colourless liquid. ^{13}C and ^{1}H-n.m.r. are identical to literature values.[73,134]

24. Metathesis of exo-Tricyclo[4.2.1.$0^{2,5}$]nona-3,7-diene using $WCl_6/SnMe_4$ as catalyst

The preparation was carried out under similar conditions to the polymerisation of norbornene. Following the addition of the catalyst solution to the monomer (0.338g,2.9mmol) the reaction mixture turned dark green. After stirring for a further 1h the reaction mixture had become uniformly viscous. The polymerisation was terminated by the addition of a few drops of methanol, followed by pouring into 75ml of methanol. The resultant precipitate was filtered and dried to give poly(exo-tricyclo[4.2.1.$0^{2,5}$]nona-3,7-diene) (0.182g, 54%) as a white powder. The polymer proved to be highly insoluble so precluding purification by the reprecipitation technique. m.p. >350°C, (Found: C,86.4, H,7.8, $(C_9,H_{10})_x$ requires C,91.47, H,8.53%), $\delta^{13}C$(solid state) 40(broad), 125, 130 160(quat.C).

25. Preparation of (E)-3,4-bis(phenylsulphonyl)-exo-tricyclo[4.2.1.$0^{2,5}$]nona-7-ene-7,8-dimethylester

To a solution of quadricyclane dimethylester (3.78g, 18mmol) in 20ml of chloroform was added (E)-bis(phenylsulphonyl)ethylene (4.62g,15mmol). The resulting solution was stirred at 60°C for five days.

(2.70g,5.2mmol) and sodium dihydrogen orthophosphate (12.5g) in 100ml of A.R. methanol, was added, 2% sodium amalgam (49.12g, 0.98g Na) in small portions over 45min. The reaction mixture was then stirred at room temperature under an atmosphere of dry nitrogen for 24h followed by filtration of the salts. The filtrate was poured into 300ml of brine and extracted with (3x50ml) of ether. The combined organic extracts were washed with brine, dried and carefully rotoevaporated to give a colourless oil. This was bulb to bulb distilled at 150°C and 0.01mmHg to give a complex mixture of products as evidenced by t.l.c. and ^{13}C-n.m.r.

27. Attempted preparation of 3-Phenylsulphinyl-exo-tricyclo[4.2.1.$0^{2,5}$]nona-7-ene-7,8-dimethylester

The reaction was carried out by the method employed by Paquette.[77] A solution of quadricyclane-2,3-dimethylester (50mg,0.24mmol) and phenylvinylsulphoxide (45mg, 3.6mmol) in 0.5ml of d^8 toluene, was heated in an oil bath at 105°C for 72h. After periodic monitoring over this time, ^{1}H-n.m.r. showed that no product had formed.

D. PREPARATION AND REACTIONS OF CYCLO-OLEFINS CONTAINING SULPHONYL GROUPS

1. Preparation of (E) and (Z)-6,7-Dibromo-3-thiabicyclo[3.2.0]heptane-3,3'-dioxide

To a solution of 3-thiabicyclo[3.2.0]hepta-6-ene-3,3'-dioxide (2.837g, 19.7mmol) in 20ml of dry chloroform, was added dropwise with stirring in the dark, a solution of dry bromine (3.36g, 21.0mmol) in 5ml of dry chloroform. The reaction mixture was maintained at 34°C while the bromine was added over 2h, after which time the reaction mixture had turned pale orange with a white precipitate. The reaction mixture was stirred for a further 1h, followed by chilling in an ice bath and subsequent filtration of the precipitate (4.6g, 77%). This was subjected to flash chromatography over silica gel using 40-60°P.E./ether as eluant to give as the first fraction after recrystallisation from ethanol exo-(Z)-6,7-dibromo-3-thiabicyclo[3.2.0]heptane-3,3'-dioxide as colourless microneedles. m.p. 168°C; (Found: C,23.50, H,2.36, $C_6H_8Br_2O_2S$ requires C,23.70, H,2.65%); νmax 1300-(>SO_2), 1145(>SO_2)cm^{-1}, δ^1H(200MHz, $CDCl_3$) 3.19-3.22(4H,m,C- (2)H and C(4)H), 3.67-3.72(2H,m,C(1)H and C(5)H), 4.86-4.90(2H,d of d, J=1.4 and 4.1 Hz,C(6)H and C(7)H); (N.O.E.) irrd C(6)H,C(7)H-0% enhancement, irrd C(1)H, C(5)H-0% enhancement; δ^{13}C(50MHz,DEPT

$3\pi/4$,$CDCl_3$) 43.30, 48.54, 53.39; $\delta^{13}C$(50MHz,DEPT 3π /4,d^6acetone) 42.94, 49.19, 51.87; m/z 305(M^+,1%), 306(0.5), 304(0.5), 225(84), 223(81), 188(8), 184(15), 161(59), 159(77), 121(86), 119(B,100); Crystal Data: M=304.01, monoclinic, space group $P2_1/c$ (No.14), a=10.430, b=6.650, c=12.723, Å,β =91.2°, U=882 $Å^3$, Z=4, D_C=2.29gcm^{-3}, F(0,0,0)=584, μ(Mo-Kα)=92.8cm^{-1}, R=0.042 R=0.047 for 1366 reflections.

The second fraction after recrystallisation from ethanol gave (E)-6,7-dibromo-3-thiabicyclo[3.2.0]heptane-3,3'-dioxide as colourless rhombs. m.p. 160-163°C; (Found: C,23.44, H,2.56 $C_6H_8Br_2O_2S$ requires C,23.70, H,2.65%); νmax 1305(>SO_2), 1140(>SO_2), δ^1H(200MHz,$CDCl_3$) 3.19-3.75-(6H,cm,C(1)H,C(2)H,C(4)H and C(5)H), 4.56-4.63(1H,t, J=8 and 8Hz,C(7)H), 4.76-4.84(1H,t,J=8 and 8Hz, C(6)H); ^{13}C(50MHz,DEPT $3\pi/4$,$CDCl_3$) 39.45, 42.28, 48.32, 49.32, 52.03, 54.17; m/z 225(B,100%), 223(96), 188(12), 184(20), 161(68), 159(76), 121(76), 119(80).

2. Preparation of anti-3-Oxo-7-thiatricyclo-[3.3.0.$0^{2,4}$]octane-7,7'-dioxide

3-Thiabicyclo[3.2.0]hept-6-ene (2.5g, 17.3mmol) was added portionwise over 0.5h to a mixture of 12 ml of 30% hydrogen peroxide in 50ml of 90% formic acid at room temperature. The reaction mixture was stirred at 50°C

for 48h, followed by a further 48h at room temperature. The solvent was then rotoevaporated and the residual oil taken up in a small amount of ethanol. This was left in the ice box overnight after which time the product had crystallised. Recrystallisation from di-isopropyl ether gave anti-3-oxo-7-thiatricyclo[3.3.0.0.^{2,4}]octane-7,7'-dioxide (1.24g, 44.7%) as colourless crystals. m.p. 118-119°C; (Found: C,44.78, H,5.00, $C_6H_8O_3S$ requires C,44.99, H,5.03%), δ^1H(80MHz, $CDCl_3$) 2.85-2.90 (2H,m,C(1)H and C(5)H), 3.09-3.21(4H,cm,C(6)H and C(8)H), 3.88-3.91(2H,d,J=2Hz,C(2)H and C(4)H); (N.O.E.) irrd C(2)H,C(4)H- 2% enhancement on C(6)H and C(8)H endo protons, irrd C(1)H,C(5)H- 6% enhancement on C(6)H and C(8)H exo protons, irrd C(6)H,C(8)H endo protons- 12% enhancement on C(6)H and C(8)H exo protons and 3% on C(2)H and C(4)H, irrd C(6)H, C(8)H exo protons - 11% enhancement on C(6)H and C(8)H endo protons and 5% on C(1)H and C(5)H; δ^{13}C(50MHz, DEPT 3π/4, $CDCl_3$) 40.77, 49.57, 64.43.; m/z 159(M,13), 135(6), 131(6), 119(17), 104(30), 103(23), 95(97), 94(B,100).

3. Preparation of (E),(Z)-6-Bromo-7-hydroxy-3-thiabicyclo[3.2.0]heptane-3,3'-dioxide

To a solution of anti-3-oxo-7-thiatricyclo[3.3.0.0.^{2,4}]octane-7,7'-dioxide (0.10g, 0.62mmol) in 1ml of

glacial acetic acid at -10°C, was added, dropwise with stirring, a solution of 45% hydrogen bromide in glacial acetic acid (0.053g, 0.65mmol) over 15min. The reaction mixture was allowed to stir at 5°C for a further 3h, followed by rotoevaporation of the solvent at the oil pump. Subsequent preparative t.l.c. of the reaction mixture over silica resulted in the decomposition of the products. However, ^{13}C, ^{1}H n.m.r. and ^{1}H(N.O.E.) clearly indicate the presence to the two isomers. (Z)-6-bromo-7-hydroxy-3-thiabicyclo[3.2.0]heptane-3,3'-dioxide $\delta^{1}H$(360MHz,d^6acetone) 3.10-3.45(6H,cm,C(1)H,-C(2)H, C(4)H and C(5)H) 4.49-4.53(1H,t,J=7 and 7.5Hz,C(7)H), 4.58-4.62 (1H,t,J=7.5 and 7.5Hz,C(6)H); (N.O.E.) irrd C(6)H and C(7)H- signals are too close to irradiate without perturbation of the other signal. ^{13}C(50MHz,DEPT $3\pi/4$,d^6acetone) 33.04, 40.14, 48.87, 51.72, 53.57, 78.56; and (E)-6-Bromo-7-hydroxy-3-thiabicyclo[3.2.0]- heptane-3,3'- dioxide ^{1}H(360MHz,d^6acetone) 3.20-3.65- (6H,cm,C(1)H,C(2)H,C(4)H and C(5)H), 4.87-4.92(1H,d of d, J=7.5 and 8.8Hz,C(7)H), 5.27-5.32 (1H,t of d,J=7.5, 7.5 and 1.1Hz,C(6)H); (N.O.E.) irrd C(6)H- 0% enhancement on (C7)H, irrd C(7)H- 0% enhancement on C(6)H.; $\delta^{13}C$(50MHz,DEPT $3\pi/4$,d^6acetone) 34.45, 38.48, 43.72, 51.23, 53.16, 78.36.

4(a) Preparation of exo-6-Bromo-endo-7-hydroxy-3-thia-bicyclo[3.2.0]heptane-3,3'-dioxide

To a mixture of 3-thiabicyclo[3.2.0]hepta-6-ene-3,3'-dioxide (0.288g, 2.0mmol) and N-bromosuccinimide (0.427g, 2.4mmol) was added 3ml of t-butyl alcohol and 4ml of 1N H_2SO_4. The resulting solution was stirred at room temperature for 24h followed by the addition of 15ml of water. This was then extracted with (3x15ml) of methylene chloride. The combined organic extracts were washed with aqueous sodium thiosulphate and brine, followed by drying and evaporation of the solvent. The solid residue was recrystallised twice from chloroform/ethanol to give exo-6-bromo-endo-7-hydroxy-3-thia-bicyclo[3.2.0]heptane-3,3'-dioxide (0.3g, 62%) as colourless crystals. m.p. 141-142°C; νmax 3440(O-H), 1290(>SO_2), 1140(>SO_2)cm^{-1}; δ^1H(200MHz, d^6acetone) 3.05-3.62(6H,cm,C(1)H,C(2)H,C(4)H and C(5)H), 4.45-4.52(1H,t,J=7Hz,C(6)H), 4.55-4.59(1H,d of d, J=0.6 and 7Hz, C(7)H); δ^{13}C(50MHz, DEPT 3π/4, d^6acetone) 36.22, 39.39, 47.18, 51.01, 52.20, 71,78.; m/z 224(M,25), 222(25), 160(90), 158(B,100), 146(30), 144(45), 133(35), 131(35), 119(60), 117(55). (Exact m/z: Found 241.9436, $C_6H_8BrO_3S$ requires 241.9437).

4(b) Preparation of exo-6-Bromo-endo-7-hydroxy-3-thia-bicyclo[3.2.0]heptane-3,3'-dioxide

To a solution of 3-thiabicyclo[3.2.0]hepta-6-ene-3,3'-dioxide (0.20g, 1.39mmol) in 5ml of 4:1 acetone/water, was added, dropwise over 15mins, a solution of N-bromoacetamide (0.211g,1.8mmol). The reaction mixture was stirred at room temperature for 20h. The solution was evaporated and the residue taken up in 20ml of water, followed by extraction with (3x20ml) of methylene chloride. The combined organic extracts were washed successively with saturated aqueous $NaHCO_3$, water and brine, followed by drying and evaporation of the solvent. The residue was triturated with chloroform. The resulting white solid was recrystallised from ethanol/chloroform to give exo-6-bromo-endo-7-hydroxy-3-thiabicyclo[3.2.0]heptane-3,3'-dioxide as colourless crystals. m.p. 140-143°C; (Found: C,29.10, H,3.63, $C_6H_8BrO_3S$ requires C,28.89, H,3.76%); Spectral data is identical to the previous preparation.

5(a) Bromination of 3-thiabicyclo[3.2.0]hepta-6-ene-3,3'-dioxide in dry dimethoxyethane

To a solution of 3-thiabicyclo[3.2.0]hepta-6-ene-3,3'-dioxide (75mg, 0.52mmol) in 5ml of dry

dimethoxyethane was heated to 40°C. To this was added, dropwise with stirring, a solution of dry bromine (92mg, 0.57mmol) in 2.5ml of dry dimethoxyethane. The reaction mixture was stirred for a further 1h in the dark. The solvent was rotoevaporated to give an orange solid. This was submitted for ^{13}C n.m.r. which showed nine signals corresponding to a cis/trans mixture of 6,7-dibromo-3-thiabicyclo[3.2.0]heptane-3,3'-dioxide $\delta^{13}C$(50MHz, DEPT $3\pi/4$, $CDCl_3$) 39.56(trans), 42.28(trans), 43.28(cis), 48.57(trans), 48.87(cis), 49.35(trans), 52.01 (trans), 53.31(cis), 54.15(trans).

5(b) Bromination of 3-thiabicyclo[3.2.0]hepta-6-ene-3,3'-dioxide in wet dimethoxyethane

A solution of 3-thiabicyclo[3.2.0]hepta-6-ene-3,3'-dioxide (75mg, 0.52mmol) in 5ml of 4:1 dimethoxyethane/water was heated to 40°C. To this was added, dropwise with stirring, a solution of bromine (92mg, 0.57mmol) in 2.5ml of 4:1 dimethoxyethane/water. The reaction mixture was stirred for a further 1h in the dark. The solvent rotoevaporated and the crude residue submitted for ^{13}C-n.m.r. which showed six signals corresponding to the formation of (E)-6,7-dibromo-3-thiabicyclo[3.2.0]heptane-3,3'-dioxide only. $\delta^{13}C$-(50MHz, DEPT $3\pi/4$, $CDCl_3$) 39.45, 42.25, 48.33, 49.31, 52.10, 54.12.

6. Preparation of (E)-6,7-dibromo-3-thiabicyclo-[3.2.0]heptane-3,3'-dioxide

To a solution of tetra-butylammonium tribromide (0.625g, 0.54mmol) in 5ml of chloroform was added 3-thiabicyclo[3,2,0]hepta-6-ene-3,3'-dioxide (72mg, 0.5mmol) in one portion. The reaction mixture was stirred at room temperature for 2h, after which time t.l.c. showed that all the starting material had reacted. The reaction mixture was washed successively with aqueous sodium thiosulphate, water and brine. After separation the organic phase was dried and evaporated to give a pale yellow solid. This was recrystallised from ethanol to give (E)-6,7-dibromo-3-thiabicyclo[3.2.0]heptane-3,3'-dioxide (80mg, 71%) as colourless crystals. m.p. 159-163°C. νmax 1315($>SO_2$), 1140($>SO_2$). Fingerprint region identical to that of the trans-dibromide received from direct bromination.

7. Preparation of (E)-2,3-Bis(phenylsulphonyl)bicyclo-[2.2.1]hept-5-ene

The title compound was prepared by the method of De Lucchi et al.[72] A mixture of (E)-2,3-bis(phenylsulphonyl)ethylene (0.50g, 1.6mmol) and freshly distilled cyclopentadiene (0.15,2.2mmol) in 5ml of methylene

chloride were shaken occasionally for 1h until fully dissolved. The solvent was then partially rotoevaporated, followed by the addition of 20ml of ether. The resultant precipitate was filtered and recrystallised from chloroform to give (E)-2,3-bis-(phenylsulphonyl)bicyclo[2.2.1]hept-5-ene (0.531g, 89%) as colourless crystals. m.p. 151-152°C (lit 153°C).

8. Preparation of (E)-2,3-Bis(phenylsulphonyl)-7-oxabicyclo[2.2.1]hept-5-ene

The title compound was prepared by the method of De Lucchi et al.[72] To a suspension of (E)-2,3-bis-(phenylsulphonyl)ethylene (3.10g, 9.6mmol) in 30ml of methylene chloride was added freshly distilled furan (1.8g, 26.4mmol). The reaction mixture was stirred at room temperature for 7h, after which time all solid had dissolved. The solution was allowed to stand overnight, followed by the addition 50ml of ether. The precipitated solid was then filtered and recrystallised from chloroform to give (E)-2,3-bis-(phenylsulphonyl)--7-oxabicyclo[2.2.1]hept-5-ene (3.32lg, 91%) as colourless crystals. m.p. 220-223°C (lit 216-226°C).

9. Preparation of (Z)-exo-2,3-Dibromo-(E)-exo-5-endo-6-bis(phenylsulphonyl)bicyclo[2.2.1]heptane

To a solution of (E)-2,3-bis(phenylsulphonyl)-bicyclo[2.2.1]hept-5-ene (0.374g, 1.0mmol) in 15ml of dry chloroform at 0°C was added, a solution of dry bromine (0.176g, 1.1mmol) in 5ml of dry chloroform, dropwise over 0.5h, in the dark. The reaction mixture was stirred overnight at 5°C, followed by washing with 5% aqueous sodium thiosulphate and brine. The organic phase was then dried and rotoevaporated to give a solid residue which was recrystallised from ethanol to give (Z)-exo-2,3-dibromo-(E)-exo-5-endo-6-bis(phenylsulphonyl)bicyclo-[2.2.1]heptane (0.51g, 96%) as colourless crystals. m.p. 215-216.5°C; (Found: C,42.50, H,3.31; $C_{19}H_{18}Br_2O_4S_2$ requires C,42.71, H,3.39%); νmax 1315($>SO_2$), 1150($>SO_2$) cm^{-1}.; δ^1H(200MHz,CD_2Cl_2) 2.08-2.16(1H,d of t,J=2.0 and 11.5Hz,C(7)H), 2.38-2.46(1H,d of q,J=2.0 and 11.5Hz,-C(7)H), 3.01-3.04(2H,q,J=1.5 and 4.8Hz,C(1)H) and C(4)H), 3.61-3.68(1H,d of d,J=2.0 and 5.5Hz,C(5)H) 4.10-4.15(1H,m,J=4.8 and 5.5Hz,C(6)H), 4.34-4.38(1H,d of d,J=2.0 and 6.8Hz,C(3)H), 5.30.5.35(1H,d of d,J=2.0 and 6.8Hz,C(2)H), 7.55-7.96(10H,cm,Ar H's); $\delta^{13}C$(50MHz,DEPT 3π/4,CD_2Cl_2) 33.95, 51.34, 52.95, 53.21, 65.49, 66.07, 128.64, 128.79, 129.86, 129.94, 134.88; m/z 537(10%), 535(M^+,22), 533(10), 455(B,100), 453(95), 440(15), 393(52), 385(15), 348(20), 339(45), 311(37), 277(15), 261(25), 251(30).

10. Preparation of (Z)-exo-2,3-Dibromo-(E)-exo-5-endo-6-bis(phenylsulphonyl)-7-oxabicyclo[2.2.1]heptane

To a solution of (E)-2,3-bis(phenylsulphonyl)-7-oxabicyclo[2.2.1]hex-5-ene (0.188g, 0.50mmol) in 10 ml of dry chloroform at -5°C, was added a solution of dry bromine (0.90g, 0.56mmol) in 10ml of dry chloroform over 45mins, in the dark. The reaction mixture was stirred for a further 1h at -5°C. The reaction mixture was then washed successively with (1x25ml) of 5% aqueous sodium thiosulphate and brine, followed by drying and rotoevaporation of the solvent. The solid residue was recrystallised from ethanol to give (Z)-exo-2,3-dibromo-(E)-exo-5-endo-6-bis(phenylsulphonyl)-7-oxabicyclo-[2.2.1]heptane (0.237g, 89%) as colourless crystals. m.p. 265-266.5°C; (Found: C,40.48, H,2.98; $C_{18}H_{16}Br_2O_2S_2$ requires C,40.31, H.3.01%); νmax 1318($>SO_2$), 1147($>SO_2$) $cm.^{-1}$; δ^1H(200MHz,CD_2Cl_2) 3.80-3.82(1H,d,J=5.0Hz,C(5)H), 4.12-4.17(1H,t,J=5.0 and 6.0Hz,C(6)H), 4.51-4.54-(1H,d,J=7.0Hz,C(3)H), 4.93-4.96(1H,d of d, J=2.0 and 6.0Hz,C(1)H), 5.12-5.13(1H,d,J=2.0Hz,C(4)H), 5.34-5.37-(1H,d,J=7.0Hz,C(2)H), 7.53-7.93(10H,cm,Ar H's); δ^{13}C-(50MHz,DEPT $\pi/2$,d^6DMSO) 50.75, 52.09, 65.18, 65.92, 85,50, 88.07, 128.05, 128.45, 129.48, 129.63, 134.54, 134.84; m/z 536(m^+,10%), 456(10), 454(9), 438(42), 436(40), 315(B,100), 313(96), 251(8), 235(13), 208(38).

11. Preparation of exo-2-Tert-butoxy-3-phenylsulphonyl-exo-6-bromo-7-oxatricyclo[2.2.1.$0^{3,5}$]heptane

To a solution of potassium t-butoxide (50mg, 0.45mmol) in 10ml of dry THF under an atmosphere of dry nitrogen was added (Z)-exo-5,6-dibromo-(E)-2,3-bis-(phenylsulphonyl)-7-oxabicyclo[2.2.1]heptane (117mg, 0.22mmol). The solution turned brown almost immediately. This was stirred at room temperature under nitrogen overnight. The solvent was then rotoevaporated and the residue taken up in 20ml of methylene chloride. The organic phase was washed with (2x15ml) of water and (1x15ml) of brine prior to drying and rotoevaporation of the solvent. Dry flash chromatography was used to separate the product from some polar material. Recrystallisation of the solid from chloroform gave exo-2-tert-butoxy-3-phenylsulphonyl-exo-6-bromo-7-oxatricyclo[2.2.1.$0^{3,5}$]heptane as colourless rhombs. m.p. 166-167°C; (Found: C,49.62, H,4.84; $C_{16}H_{19}BrO_4S$ requires C,49.62, H,4.94%); νmax 1308($>SO_2$), 1150($>SO_2$), cm^{-1}.; ^1H(200MHz, $CDCl_3$) 1.02(9H,s, $(CH_3)_3$), 2.96-2.99(1H,d of t,J=1.3 and 4.0Hz,C(5)H), 4.08(1H,s,C(2)H), 4.12-4.13-(1H,d,J=1.3Hz,- C(4)H), 4.18(1H,s,C(2)H), 4.78-4.80(1H,d,J=4.0Hz,C(6)H), 7.47-7.93(5H,cm,Ar H's); ^{13}C(50MHz,$CDCl_3$) 27.77, 29.30, 43.40, 48.30(quat.C), 59.11, 71.94, 75.30(quat.C), 81.42, 128.11, 128.71, 133.37, 140.59(quat.C); m/z 389(M^+,4.8%), 387(4.2),

332(B,100), 330(100), 308(9), 286(24), 284(24), 253(76), 216(70), 181(42).

12. Preparation of exo-3-oxa-(E)-6,7-bis(phenylsulphonyl)tricyclo[3.2.1.$0^{2,4}$]octane

To a solution of (E)-2,3-bis(phenylsulphonyl)-bicyclo[2.2.1]hepta-5-ene (0.50g, 1.33mmol) in 10ml of dry methylene chloride was added a solution of m-chloroperoxybenzoic acid (0.288g, 80%) in 10ml of dry methylene chloride. The reaction mixture was stirred for four days at room temperature, then filtered and washed successively with (2x25ml) of 6% aqueous sodium hydroxide and (2x25ml) of brine, followed by drying and rotoevaporation of the solvent. The crude product was recrystallised from ethanol/chloroform to give exo-3-oxa-(E)-6,7-bis(phenylsulphonyl)tricyclo-[3.2.1.$0^{2,4}$]- octane (0.530g,97%) as colourless crystals. m.p. 203-205°C; νmax 1305(>SO_2), 1150(>SO_2), 1220(C-O) cm^{-1}.;

δ^1H(200MHz,$CDCl_3$) 1.44-1.45(1H,d,J=11Hz,C(7)H), 1.55-1.61(1H,d of d,J=1.8 and 11 Hz,C(7)H), 2.95-2.96-(1H,d,J=1.5Hz,C(4)H), 3.02-3.05(1H, d of d,J=1.5 and 3.5Hz, C(1)H), 3.22-3.25(1H,d of d, J=1.5 and 3.5Hz,-C(3)H), 3.59-3.63 (1H,d of d,J=1.8 and 5.5Hz,C(5)H), 3.87-3.88(1H,d,J=3.5Hz,C(2)H), 4.11-4.16(1H,d of d,J=3.5

and 5.5Hz, C(6)H), 7.24-7.92(10H,cm,Ar H's); $\delta^{13}C$-(50MHz,DEPT 3π/4,$CDCl_3$) 24.38, 41.48, 41.76, 48.64, 49.31, 63.98, 68.21. 128.19, 128.34, 129.20, 129.37, 134.08, 134.18; m/z 391(M^+, 0.8%), 331(1.2), 309(1.5), 266(2.4), 265(13), 250(11), 248(13), 247(26), 157(11), 127(7), 126(16), 125(B,100), 107(46). (Exact m/z: Found 390.0566, $C_{19}H_{18}O_5S_2$ requires 390.059).

13. Preparation of exo-2-Bromo-exo-3-hydroxy-exo-5-endo-6-bis(phenylsulphonyl)bicyclo[2.2.1]heptane

To a partial suspension of exo-3-oxa-(E)-bis-(phenylsulphonyl)tricyclo[3.2.1.$0^{2,4}$]octane (0.20g, 0.51mmol) in 15ml of glacial acetic acid was added, dropwise with stirring, a solution of 45% hydrogen bromide in glacial acetic acid (0.104g, 1.3mmol) in 5ml of glacial acetic acid. After 0.5h no undissolved solid remained. The reaction mixture was then allowed to stir at room temperature for 10h. The solvent was then rotoevaporated at the oil pump. The solid residue was recrystallised from ethanol to give exo-2-bromo-exo-3-hydroxy-exo-5-endo-6-bis(phenylsulphonyl)bicyclo[2.2.1]-heptane (0.167g,70%) as colourless crystals. m.p. 199-200°C νmax 3260(O-H), 1308(>SO_2), 1152(>SO_2)cm^{-1}, δ^1H(200- MHz,$CDCl_3$) 1.95-2.06 (1H,d of d, J=2 and 12Hz,C(7)H), 2.12-2.20(1H,d of d, J=1.7 and 12Hz, C(7)H),

2.25-2.27(1H,d,J=4.8Hz,(O-H)), 2.62-2.63(1H,d,J=1.8Hz,-C(4)H), 2.97-3.00(1H,d of d,J=1.8 and 4Hz,C(1)H), 3.52-3.55(1H,d of d, J=1.7 and 5.7Hz,C(5)H), 3.78-3.84(1H,m,J=2,4.8 and 6Hz,C(3)H), 4.06-4.11(1H,d of d, J=4 and 5.7Hz,C(6)H), 5.27-5.32(1H,d of d, J=2 and 6Hz,C(2)H); (N.O.E.) irrd C(1)H:-enhancement on C(6)H and C(2)H, irrd C(4)H:- enchancement on C(3)H, C(5)H and ortho aromatic protons of exo-phenylsulphonyl group.; $\delta^{13}C$(50MHz,$CDCl_3$) 32.71, 49.32, 55.74, 64.19, 65.27, 71.87, 128.42, 129.31, 129.46, 134.30, 137.87(quat.C), 138.70(quat.C); m/z 472(M^+, 5%), 470(3), 419(12), 391(3), 332(42), 330(33), 311(51), 249(70), 233(32), 189(15), 143(B,100), 125(29), 107(38); (Exact m/z:- Found 471.9825, $C_{19}H_{19}BrO_5S_2$ requires 471.9838).

14. Attempted Hydroxybromination of (E)-2,3-bis-(phenylsulphonyl)bicyclo[2.2.1]hept-5-ene

To a mixture of (E)-2,3-bis-(phenylsulphonyl)-bicyclo[2.2.1]hept-5-ene (0.93g, 2.5mmol) and N-bromo-succinimide (0.52g, 3.0mmol) was added 4ml of t-butyl alcohol and 6ml of 1N H_2SO_4. The resulting solution was then stirred at room temperature for 36h. Following a similar work-up to previous examples, it was found that only starting material was recovered unreacted.

15. Attempted Bromination of (E)-2,3-bis-(phenylsulphonyl)bicyclo[2.2.1]hept-5-ene

To a solution of tetra-butylammonium tribromide (0.530g,1.70mmol) dissolved in 5ml of dry chloroform was added (E)-2,3-bis(phenylsulphonyl)bicyclo[2.2.1]hept-5-ene (0.374g, 1.0mmol) in portions over 0.5h. The reaction mixture was then stirred at room temperature for 24h. After work-up of the reaction mixture it was found that the starting material was recovered unreacted.

16. Preparation of (E)-8,9-Dibromo-10-oxa-exo-4-thiatricyclo[5.2.1.$0^{2,6}$]decane-4,4'-dioxide

To a solution of 10-oxa-exo-4-thiatricyclo-[5.2.1.$0^{2,6}$]deca-8-ene-4,4'-dioxide (0.50g, 2.69mmol) dissolved in 35ml of dry chloroform at 38°C, was added a solution of dry bromine (0.473g,2.9mmol) in 15ml of dry chloroform, dropwise with stirring over 2h. The reaction mixture was stirred overnight at 38°C, followed by washing with aqueous sodium thiosulphate and brine. The organic phase was then dried and rotoevaporated to give a white solid. This was then recrystallised from ethanol to give (E)-8,9-dibromo-10-oxa-exo-4-thiatricyclo[5.2.1.$0^{2,6}$]decane-4,4'-dioxide (0.529g,57%) as colourless crystals. m.p. 232-233°C(dec.); (Found:

1.60(1H,d,J=11Hz,C(11)H), 2.7-3.1(8H,cm,C(1)H,C(2)H,-C(3)H,C(5)H,C(6)H and C(7)H), 3.26(2H,s,C(8)H and C(10)H), δ^{13}C(200MHz,$CDCl_3$) 27.68, 38.06, 38.62, 48.59, 48.81; m/z: 200(M^+,0.1%), 183(0.4), 172(0.4), 155(1), 135(5), 106(14), 91(20), 82(B,100), 81(64).

18. Preparation of exo-8-Bromo-exo-9-acetoxy-endo-4-thiatricyclo[5.2.1.$0^{2,6}$]decane-4,4'-dioxide

To a solution of endo-4-thiatricyclo[5.2.1.$0^{2,6}$]-deca-8-ene-4,4'-dioxide (0.50g, 2.7mmol) in 30ml of glacial acetic acid, was added a solution of 45% hydrogen bromide (0.22g,2.7mmol) in glacial acetic acid, dropwise with stirring over 20mins. The reaction mixture was then stirred at 35°C for 24h, followed by rotoevaporation of the solvent. The residue was taken up in 25ml of water and extracted with (2x25ml) of methylene chloride. The combined organic extracts were then washed with aqueous $NaHCO_3$ and brine prior to drying and rotoevaporation of the solvent. Recrystallisation from ethanol/chloroform gave exo-8-Bromo-exo-9-acetoxy-endo-4-thiatricyclo[5.2.1.$0^{2,6}$]decane-4,4'-dioxide as colourless crystals. m.p. 214-215°C; (Found: C,40.40, H,4.64; $C_9H_{13}BrO_3S$ requires C,40.84, H,4.68%); δ^1H(200MHz,$CDCl_3$) 1.55-1.61(1H,d,J=11Hz,C(10)H), 2.10(3H,s,CH_3), 2.31-2.37(1H,d of d, J=1.5 and 11Hz,C(10)H),

2.47-3.09(8H,cm,C(1)H,C(2)H,C(3)H,C(5)H,C(6)H and C(7)H), 4.39-4.44(1H,d of d, J=2.5 and 6Hz,C(9)H), 4.91-4.95(1H,d of d, J=1.5 and 6Hz,C(8)H); δ^{13}C(50MHz,$CDCl_3$) 20.70, 36.17, 37.78, 45.02, 48.71, 49.01, 49.43, 49.51, 50,48, 70.18, 169.80(quat.C); m/z 323(M^+,1%) 280(4), 265(3), 264(5), 254(4), 201(82), 146(26), 144(28), 121(7), 119(13), 91(B,100).

19 Preparation of 2,3-Dichloro-(E)-5,6-bis(phenylsulphonyl)-7-oxabicyclo[2.2.1]hept-2-ene

3,4-Dichlorofuran (0.30g,2.19mmol) and (E)-1,2-bis(phenylsulphonyl)ethylene (0.308g, 1.0mmol) together with 3ml of toluene were combined in a sealed tube. This was then heated in an oil bath at 95°C for 14h. After which time t.l.c. showed that none of the dienophile remained. The solvent was rotoevaporated to give a white solid which was recrystallised from 40-60°C P.E./chloroform to give 2,3-dichloro-(E)-5,6-bis(phenylsulphonyl)-7-oxabicyclo[2.2.1]hept-2-ene (0.362g, 81%) as colourless crystals. m.p. 213-215°C; (Found: C,48.2, H,3.09; $C_{18}H_{14}Cl_2O_5S_2$ requires C,48.5, H,3.17%); νmax 1615(C=C), 1315(>SO_2), 1150(>SO_2) cm^{-1}.; δ^1H(80MHz,$CDCl_3$) 3.74-3.80(1H,d,J=4.5Hz,C(5)H), 4.31-4.42(1H,t,J=4 and 4.5Hz,C(6)H), 5.05-5.12(1H,d of d, J=1.5 and 4.0Hz,-C(1)H), 5.23-5.25(1H,d,J=1.5Hz,C(4)H), 7.35-7.94 (10H,cm,Ar H's); δ^{13}C(50MHz,$CDCl_3$) 66.44, 83.58, 85.68 128.43, 128.54, 129.47. 132.88(quat.C), 134.11(quat.C),

134.52, 137.44(quat.C), 138.46(quat.C); m/z 445(M^+, 1%), 443(1), 308(16), 305(25), 303(31), 167(19), 141(69), 138(40), 136(62), 125(B,100).

20. Preparation of 2,3-Dichloro-6-phenylsulphonyl-7-oxabicyclo[2.2.1]hept-2-ene

3,4-Dichlorofuran (1.627g, 11.9mmol) and phenylvinylsulphone (1.0g, 5.95mmol) together with 2ml of toluene were combined in a sealed tube. This was then heated in an oil bath at 100°C for 20h. After this period t.l.c. showed that none of the starting dienophile remained. The solvent was rotoevaporated to give a white solid which was subjected to dry flash chromatography over silica using a 40-60°C P.E./ether gradient. The desired fraction was recrystalled from 40-60°C P.E./chloroform to give 2,3-dichloro-6-phenylsulphonyl-7-oxabicyclo[2.2.1]- hept-2-ene (0.425g, 25%) as colourless crystals. m.p. 146.5-148°C; νmax 1617(C=C) 1300(>SO_2), 1155(>SO_2) $cm.^{-1}$; δ^1H(200MHz,$CDCl_3$) 1.89-2.00(1H,d of d, J=8.5 and 12.5Hz,C(5)H), 2.32-2.42(1H,d of t,J=4.5,4.5 and 12.5Hz, C(5)H), 3.33-3.39(1H,d of d,J=4.5 and 8.3Hz,C(6)H), 4.91-4.93(1H, d of d,J=4.5 and 1.0Hz,C(4)H), 5.22(1H,d,J=1.0-Hz,C(1)H), 7.54-7.95 (5H,cm,Ar H's); δ^{13}C(50MHz,$CDCl_3$) 29.49, 64.10, 82.58, 83.17, 128.43, 129.35, 130.89(quat.C), 134.02, 135.17(quat.C), 138.20(quat.C);

m/z 306(28%), 304(M^+,40), 165(52), 140(55), 125(38), 107(9), 99(88), 77(B,100); (Exact m/z: Found 303.9750, $C_{12}H_{10}Cl_2O_3S$ requires 303.9728).

21. Preparation of exo and endo-2-Phenylsulphonyl-bicyclo[2.2.1]hept-5-ene

The title compounds were prepared by the method of Paquette and Carr.[104]

To a solution of freshly distilled cyclopentadiene (0.863g, 13.3mmol) in 2ml of benzene was added phenylvinylsulphone (2.0g, 11.9mmol). The resulting mixture was stirred at room temperature for 110h after which time t.l.c. showed that no starting material remained. The isomeric mixture was separated by flash chromatography over silica gel using 40-60°C P.E. as eluant. This gave as the first fraction exo-2-phenylsulphonyl-bicyclo[2.2.1]hept-5-ene (0.438g, 16%) as colourless crystals. δ^1H(200MHz,$CDCl_3$) 1.31-1.40 (1H,m,C(3)H), 1.31-1.41(2H,m,C(3)H and C(7)H), 1.89-1.93(1H,bd,J=8.6Hz,C(7)H), 2.03-2.13(1H,m,J=12.3, 4.7 and 3.5Hz, C(3)H, 2.83-2.90(1H,m,J=7.5,4.7 and 1.6Hz, C(2)H), 3.18(1H,bs,C(4)H), 3.19(1H,bs,C(1)H), 6.01-6.05(1H,d of d, J=5.6 and 3.1Hz, C(5)H), 6.17-6.21(1H,d of d, J=5.6 and 2.9Hz, C(6)H), 7.25-7.97(5H,cm,ArH's); δ^{13}C(50MHz,DEPT $3\pi/4$,$CDCl_3$)

28.33, 41.42, 44.28, 45.59, 64.14, 128.04, 129.04, 133.25, 135.24, 139.80. νmax 1310($>SO_2$), 1045($>SO_2$) cm^{-1}. and as the second fraction endo-2-phenylsulphonyl-bicyclo[2.2.1]hepta-5-ene (1.08g,39%) as colourless crystals. δ^1H(200MHz,$CDCl_3$) 1.20-1.24(1H,bd,J=8.6-Hz,C(7)H) 1.42-1.51(1H,cm,J=8.6Hz,C(7)H), 1.52-1.61-(1H,m,- J=12.2,5.1 and 2.5Hz, C(3)H-exo), 1.92-2.05-(1H,m,- J=12.2,9.2 and 3.7Hz,C(3)H-endo), 2.98(1H,bs,-C(4)H),3.08 (1H,bs,C(1)H), 3.55-3.64(1H,m,J=9.2, 5.1 and 3.2Hz, C(2)H), 6.09-6.13(1H,d of d, J=5.7 and 2.8Hz,C(5)H), 6.24-6.28(1H, d of d, J=5.7 and 3.1Hz,C(6)H), 7.25-7.86- (5H,cm,ArH's); δ^{13}C(50MHz,DEPT 3π/4,$CDCl_3$) 28.73, 42.61, 44.93, 64.70, 127.83, 128.99, 131.16, 133.15, 137.23,
νmax 1315($>SO_2$) and 1048($>SO_2$) cm^{-1}.

22. Preparation of exo-2-Phenylsulphonyl-(E)-endo-5-bromo-exo-6-bromobicyclo[2.2.1]heptane

To a solution of exo-2-phenylsulphonylbicyclo-[2.2.1]hept-5-ene (95mg, 0.406mmol) in 3ml of dry chloroform, was added dropwise with stirring in the dark at 0°C, a solution of dry bromine (71mg, 0.44mmol) in 2ml of dry chloroform. This resulted in instantaneous decolourisation. After addition, the reaction was complete as indicated by t.l.c. The reaction mixture

was then washed with 5ml portions of aqueous sodium thiosulphate and brine, prior to drying and rotoevaporation of the solvent. Recrystallisation from chloroform/ethanol gave exo-2-phenylsulphonyl-(E)-endo-5-bromo-exo-6-bromobicyclo[2.2.1]heptane (0.139g,87%) as colourless crystals. m.p. 156.5.157.5°C, (Found: C,39.50, H,3.54, $C_{13}H_{14}Br_2O_2S$ requires C,39.62, H,3.58%), νmax 1300(>SO_2), 1147(>SO_2) cm^{-1}, δ^1H(200MHz,$CDCl_3$) 1.99-2.27-(4H,cm,C(3)H and C(7)H, 2.63-2.67(1H,m,C(4)H), 2.88(1H,bs,C(1)H), 3.01-3.09(1H,ct,C(2)H), 3.77-3.78-(1H,t,C(6)H), 4.38-4.43(1H,m,C(5)H), 7.54-7.92(5H,cm,-Ar-H's), ^{1}H N.O.E. irrdn ortho Ph-H's:- large C(1)H and C(2)H, small C(3)H, irrdn C(5)H:- large C(4)H, small C(6)H and C(7)H, irrdn C(6)H:- large C(1)H and C(2)H, small C(5)H, irrdn C(1)H:- large C(6)H and ortho Ph-H's, irrdn C(4)H:- large C(5)H and C(3)H., δ^{13}C(50MHz,DEPT 3π/4,$CDCl_3$) 27.10, 33.35, 44.21, 48.36, 57.17, 59.12, 63.55, 128.33, 129.41, 133.98., m/z: 397(5.1%), 395(M^+ 9.8), 393(5.1), 317(5.4), 316(13), 315(B,100), 314(14), 313(92), 255(5), 253(9), 251(6).

23. Preparation of 2-bromo-4-oxa-5-oxo-5-phenyl-5-thiatricyclo[4.2.1.$0^{3,7}$]nonan-5-ylium tribromide

To a solution of endo-2-phenylsulphonylbicyclo-[2.2.1]hepta-5-ene (40mg,0.17mmol) in 0.5ml of chloroform

was added a solution of bromine (55mg,- 0.34mmol) in 0.5ml of chloroform. After a 3-4 drops of bromine had been added an orange precipitate was formed, this continued to accumulate during the addition of the remainder of the bromine solution. The preciptate was filtered and washed with 1ml of chloroform to give 2-bromo-4-oxa-5-oxo-5-phenyl-5-thiatricyclo[4.2.1.$0^{3,7}$]-nonan -5-ylium tribromide (85mg,81%) as an orange solid. m.p. 77°C, (Found: C,27.71, H,2.45, $C_{13}H_{14}Br_4O_2S$ requires C,28.19, H,2.55%), νmax 1570(C=C), 1300(S-O), 1082(S-O)cm^{-1}. δ^1H(360MHz,CD_3CN) 1.65-1.72(1H,d of d, J=9.8 and 13.8Hz), 2.01-2.08(1H,bd of d,J=14.2 and 8.7Hz), 2.09-2.14(1H,m,J=13.7,6.4 and 4.7Hz), 2.21-2.28(1H,d of t, J=14.2 and 4.5Hz), 2.76(1H,bd), 2.81(1H,bd), 3.33-3.37(1H,d of d, J=9.8 and 6.2Hz), 3.81-3.87(1H,bm), 4.47(1H,bs), 7.62-7.88(5H,ArH's); δ^{13}C(50MHz,DEPT $3\pi/4$,$CDCl_3$) 30.81, 40.86, 44.95, 46.16, 49.41(2), 62.60, 128.25, 129.44, 134.04.

24. Decomposition of 2-bromo-4-oxa-5-oxo-5-phenyl-5-thiatricyclo[4.2.1.$0^{3,7}$]nonan-5-ylium tribromide

A sample of the tribromide salt was left open to the atmosphere for five days. After this time the orange salt had decomposed to an off-white crystalline solid. This was subsequently identified as endo-2-phenylsul-

phonyl-(Z)-exo-5,6-dibromobicyclo[2.2.1]heptane. νmax 1299($>SO_2$), 1148($>SO_2$)cm^{-1}; δ^1H(200MHz,$CDCl_3$) 1.37-1.44(1H,d of d, J=11.1 and 1.6Hz,C(7)H), 1.89-1.96(2H,m,C(3)H), 2.36-2.44(1H,bd,J=11.1Hz,C(7)H), 2.73-2.76(1H,m,J=3.5 and 1.8Hz, C(4)H), 2.80-2.82(1H,d of d, J=3.8 and 1.8Hz,C(1)H), 3.34-3.44(1H,m,J=8.5 and 3.8Hz, C(2)H), 4.43-4.47(1H,d of d,J=6.8 and 2.1Hz,C(5)H), 5.37-5.41(1H, d of d, J=6.8 and 2.1Hz,C(6)-H), 7.53-7.90(5H,cm,ArH's); $\delta^{13}C$(50MHz,DEPT, 3π/4,$CDCl_3$) 29.41, 35.66, 49.03, 50.56, 51.17, 55.40, 63.90, 127.71, 129.43, 133.93; (Exact m/z: Found 393.9058, $C_{13}H_{14}Br_2O_2S$ requires 393.9063.

filtration. The filtrate was then poured into a large excess of 40-60°C P/E, and the resultant precipitate was filtered off under nitrogen. The sodium salt was then dried overnight in a vacuum desiccator, prior to use.

3. Preparation of Phenoxymethylphenylsulphide

A modification of the method employed by Kornblum[133] was used. To a partial suspension of sodium phenoxide (2.21g,19mmol) in 25ml of dry dimethylformamide was added a solution of α-chlorothioanisole (3.0g,25mmol) in 15ml of dry DMF. The reaction mixture was then stirred at room temperature for a further 17h, followed by pouring into 200ml of water. This was acidified with 10% aqueous HCl and extracted with (6x50ml) of pentane. The combined organic extracts were then washed with (4x50ml) of water, dried and rotoevaporated. The resultant yellow oil was bulb to bulb distilled at 130°C and 0.005mmHg to give phenoxymethylphenylsulphide (3.03g,75%) as colourless oil. νmax 3100(C-H), 2920(CH_2), 1598(C=C), 1586(C=C), 1480(C=C), 1438(CH), 1200(C-O), 740(C-H), 690(C-H)cm^{-1}. ^1H(60MHz,$CDCl_3$) 5.33(2H,s,CH_2), 6.69-7.60(10H,cm,-Ar-H's). $\delta^{13}C$(50MHz,$CDCl_3$) 72.83, 115.90, 121.76, 126.90, 128.78, 129.29, 130.31, 135.01(quat.C), 156.56(quat.C). m/z 216(M^+,50%), 156(24), 122(B,100), 108(10), 94(9), 77(52). (Exact m/z:- Found 216.0610, $C_{13}H_{12}OS$ requires 216.0609).

4. Attempted oxidation of phenoxymethylphenylsulphide

To a solution of sodium metaperiodate (1.65g,8mmol) in 30ml of water was added to a solution of phenoxymethylphenylsulphide (1.50g,7mmol) in 25ml of methanol, dropwise with stirring. The reaction mixture was stirred at room temperature for a further 48h, after which time t.l.c. showed that no appreciable oxidation had taken place.

5. Preparation of Phenoxymethylphenylsulphoxide

To a solution of phenoxymethylphenylsulphide (1.0g,4.63mmol) in 20ml of dry methylene chloride at -40°C, was added, dropwise with stirring over 15min, a solution of m-CPBA (0.779g,4.60mmol) in 20ml of dry methylene chloride. The resulting mixture was stirred at -40°C for a further 1h. Gaseous ammonia was then blown over the surface of the reaction mixture for about 1.5min, followed by filtration of the precipitated salts. The filtrate was washed with saturated $NaHCO_3$ and brine, filtered and rotoevaporated. The t.l.c. of the reaction mixture showed two spots, one of which was coicident with the starting material. This was then subject to dry flash chromatography over silica gel using a 40-60°C P.E./ether gradient to give phenoxymethyl-

phenylsulphoxide (0.57g,57%) as colourless platelets. m.p. 61.5-63°C, (Found: C,66.23, H,5.09, $C_{13}H_{12}O_2S$ requires C,66.22, H,5.21%), νmax 3060(C-H), 2918(CH_2), 1598(C=C), 1590(C=C), 1490(C=C), 1440(CH_2), 1200(C-O), 1042(S=O), 750(C-H), 690(C-H) cm^{-1}., δ^1H(200MHz,CD_2Br_2) 4.83-4.99(2H,d of d, J=10Hz,CH_2), 6.97-7.67(10H,cm,-Ar-H's), $\delta^{13}C$(50MHz,CD_2Br_2) 88.15, 115.66, 122.63, 124.37, 129.10, 129.52, 131.27, 140.87(quat.C), 157.14(quat.C), m/z 232(M^+,5%), 125(6), 123(10), 107(93), 93(12), 77(B,100), 51(25).

6. Preparation of 2,5-dimethylphenoxymethylphenyl-sulphide

To a suspension of sodium 2,5-dimethylphenoxide (3.0g,21mmol) in 20ml of dry DMF was added α-chloro-thioanisole (3.0g, 19mmol) in one portion. The reaction mixture was then made up to 50ml with dry DMF and stirred at room temperature for 24h. After which time the reaction mixture was poured into 250ml of water and acidified with 10% HCl. This was extracted with (4x75ml) of pentane. The combined organic extracts were washed with (4x50ml) of water prior to drying and rotoevaportion of the solvent. The resultant brown oil was bulb to bulb distilled at 150°C and 0.002mmHg to give 2,5-dimethylphenoxymethylphenylsulphide (3.92g,87%) as a

pale yellow oil. νmax 3028(C-H), 2976(C-H), 2960(C-H), 1585(C=C), 1478(C-H), 1438(C-H), 1237(C-O), 805(C-H), 740(C-H), 690(C-H) cm^{-1}., $\delta^{1}H$(60MHz,$CDCl_3$) 2.16(3H,s,CH_3), 2.39(3H,s,C_3), 5.56(2H,s,CH_2), 6.76-7.86(8H,cm,Ar-H's), $\delta^{13}C$(50MHz,DEPT $3\pi/4$,$CDCl_3$) 15.90, 21.31, 73.03, 122.28, 126.98, 130.48, 130.72, m/z 244(M^+,8%), 156(38), 135(50), 121(B,100), 105(30), 77(45), (Exact m/z: Found 244.0922, $C_{15}H_{16}OS$ requires 244.0922).

7. Preparation of 2,5-dimethylphenoxymethylphenyl-sulphoxide

To a solution of 2,5-dimethylphenoxymethylphenyl-sulphide (0.50g,2.05mmol) in 10ml of dry methylene chloride at -60°C, was added, dropwise with stirring over 30mins, a solution of m-CPBA (0.44g, 2.05mmol) in 10ml of dry methylene chloride. The resulting mixture was stirred at -60°C for a further 0.75h. Gaseous ammonia was then blown over the surface of the reaction mixture for 1.5min, followed by filtration of the precipitated salts. The filtrate was washed with saturated $NaHCO_3$ and brine prior to drying and rotoevaporation of the solvent. The residue was subjected to dry flash chromatography over silica gel using a 40-60 P.E./ether gradient to separate the product from unreacted starting material. This gave 2,5-dimethylphenoxymethylphenyl-

sulphoxide (0.339g,64%) as colourless crystals. m.p. 57-59°C, νmax 3065(C-H), 1619(C=C), 1585(C=C), 1510(C=C), 1035(S=O), 859(C-H), 749(C-H) cm^{-1}., ^{1}H(200MHz,-d^{8}toluene) 2.02(3H,s,CH_3), 2.04(3H,s,CH_3), 4.33-4.58(2H,d of d, J=9.8Hz,CH_3), 6.83-7.40(8H,cm,Ar-H's), ^{13}C(50MHz,-DEPT 3π/4,d^{8}toluene) 14.83, 20.14, 87.65, 113.46, 122.33, 123.68, 128.02, 129.96, 130.01., m/z: 260(M^{+}), 230, 218, 159, 140, 135, 125, 122, 107., (Exact m/z: Found 260.0877, $C_{15}H_{16}O_2S$ requires 260.0871).

8. Preparation of 2,6-dimethylphenoxymethylphenyl-sulphide

The title compound was prepared according to the method employed for the related compound 2,5-dimethyl-phenoxymethylphenylsulphide, to give 2,6-dimethylphenoxy-methylphenylsulphide (79%) as a colourless oil. νmax 3060 (C-H), 2958(C-H), 2920(CH_2), 2858(CH_2), 1584(C=C), 1480(C=C), 1438(C-H), 1180(C-O), 770(C-H), 692(C-H) cm^{-1}., $\delta^{1}H$(80MHz,$CDCl_3$) 2.33(6H,s,CH_3), 5.38(2H,s,CH_2), 7.05-7.70(8H,cm, Ar H's), $\delta^{13}C$(50MHz,$CDCl_3$) 16.79, 76.90, 124.26, 126.70, 128.78, 130.88, 135.84, 154.82., m/z: 157, 135, 121, 109, 105., (Exact m/z: Found 244.0924, $C_{15}H_{16}OS$ requires 244.0922).

9. Preparation of 2,6-dimethylphenoxymethylphenyl-sulphoxide

The title compound was prepared by the method employed for the related 2,5-dimethylphenoxymethyl-phenylsulphoxide, to give 2,6-dimethylphenoxymethyl-phenylsulphoxide (54%) as a colourless oil. νmax 3062(C-H), 2980(C-H), 2924(C-H), 1585(C=C), 1448(CH_2), 1180(C-O), 1050(S=O), 730(C-H) cm^{-1}., δ^1H(200MHz,-d^8toluene) 2.02(6H,s,CH_3), 4.30(2H,s,CH_2), 6.77-7.36 (8H,cm,Ar-H's), δ^{13}C(50MHz,DEPT 3π/4,d^8toluene) 15.64, 92.09, 124.05, 128.38, 130.13, m/z: 260, 244, 176, 135, 123, 105, 77. (Exact m/z: Found 260.0867, $C_{15}H_{16}O_2S$ requires 260.0871).

10. F.V.P. of phenoxymethylphenylsulphoxide

Phenoxymethylphenylsulphoxide (50mg) was pyrolysed at 600°C and 0.003mmHg. The pyrolysate was collected in quantitative yield in two portions, one from the side arm of the trap and the other in the main body of the trap. The condensate on the main body, was shown by ^{1}H-n.m.r. and i.r. to consist almost completely of benzaldehyde, whereas the fraction collected from the side arm of the trap was found by ^{1}H-n.m.r. to consist almost entirely of phenyl benzenethiolsulphonate.

11. F.V.P. of 2,5-dimethylphenoxymethylphenylsulphoxide

2,5-dimethylphenoxymethylphenylsulphoxide (80mg) was pyrolysed at 600°C and 0.002mmHg, with an inlet sublimation temperature of 150°C. The pyrolysate was collected in two portions, one from the side arm of the trap and the other from the main body of the trap. The condensate on the side arm was found to consist mainly of phenyl benzenethiolsulphonate. The condensate in the main body of the trap was found by ^{1}H-n.m.r. and ^{13}C-n.m.r to consist almost entirely of 2,5-dimethylbenzaldehyde. $\delta^{1}H$(200MHz,$CDCl_3$) 2.38(3H,s,CH_3), 2.62(3H,s,-CH_3), 7.06-7.60(3H,m,Ar-H's), 10.23(1H,s,CHO), $\delta^{13}C$(50MHz,DEPT $3\pi/4$,$CDCl_3$) 18.82, 20.55, 131.56, 132.13, 134.34, 192.78.

12. Solution thermolysis of phenoxymethylphenylsulphoxide

A solution of phenoxymethylphenylsulphoxide (50mg) in 0.5ml of d^{8}toluene was heated in an oil bath at 110°C. The progression of the reaction was monitored by ^{1}H-n.m.r., after 75 mins the reaction had gone to completion to give phenoxymethylphenylsulphenate in quantitative yield. νmax 3060(C-H), 2922(C-H), 1600(C=C), 1590(C=C), 1494(C=C), 1220(C-O), 950(b,S-O),

756(C-H), 740(C-H), 690(C-H) cm^{-1}., $\delta^{1}H$(200MHz,CD_2Br_2) 5.40(2H,s,CH_2), 6.93-7.39(10H,m,Ar-H's), $\delta^{13}C$(50MHz,CD_2Br_2)98.47, 116.32, 122.40, 126.25, 127.55, 129.28, 139.09(quat.C), 156.44 (quat.C), m/z: 232(M^+,8%), 125(6), 123(2), 109(48), 107(B,100), 77(60), (Exact m/z: Found 232.0561, $C_{13}H_{12}O_2S$ requires 232.0558. This reaction also takes place in d^3nitromethane at 98°C and d^2dibromomethane at 100°C.

13. Solution thermolysis of 2,5-dimethylphenoxymethylphenylsulphoxide

A solution of 2,5-dimethylphenoxymethylphenylsulphoxide (50mg) in 0.5ml of d^8toluene was heated in an oil bath at 105°C for 6h. After this time the reaction had gone to completion to give 2,5-dimethylphenoxymethylphenylsulphenate. $\delta^{1}H$(200MHz,d^8toluene) 2.04(3H,s,CH_3), 2.06(3H,s,CH_3), 5.03(2H,s,CH_2), 6.51-7.38(8H,cm,Ar-H's).

14. Preparation of Phenylthiomethylphenylsulphide

To a solution of potassium hydroxide (2.24g, 40mmol) in 70ml of ethanol, was added thiophenol (2.20g,20mmol). α-Chlorothioanisole (3.17g, 20mmol) was then added dropwise with stirring. After addition the reaction

16. Attempted thermolysis of phenylsulphinylmethyl-phenylsulphoxide

A solution of phenylsulphinylmethylphenylsulphoxide (35mg) in 0.75ml of d^8toluene/d^3chloroform was heated in an oil bath for 24h. During this period the sample was intermittantly examined by ^{1}H-n.m.r. No reaction took place over this time as only unreacted starting material was observed from the spectra.

REFERENCES

REFERENCES

1. G. Natta, G. Mazzanti and P. Corradini, Att. Accad. Mazl. Lincel, Rend. Classe Sci. fis mat. et nat., 1958, 8, 3.
2. T. Ito, H. Shirakawa and S. Ikeda, J. Polym. Sci., 1974, 12, 11.
3. H. Shirakawa, E.J. Louis, A.G. MacDiarmid, C.K. Chiang and A.J. Heeger, J. Chem. Soc. Chem. Commun., 1977, 578.
4. C.K. Chiang, Y.W. Park, A.J. Heeger, H. Shirakawa, E.J. Louis and A.G. MacDiarmid, J. Chem. Phys., 1978 69(11), 5098.
5. C.K. Chiang, A.J. Heeger and A.G. MacDiarmid, Ber. Bunsenges, Phys. Chem., 1979, 83, 407.
6. C.K. Chiang, S.C. Gau, C.R. Fincher, Y.W. Park, A.G. MacDiarmid and A.J. Heeger, Appl. Phys. Letts., 1978, 33(1), 18.
7. M. Ozaki, D.L. Peebles, B.R. Weinberger, C.K. Chiang, S.C. Gau, A.J. Heeger and A.G. MacDiarmid, Appl. Phys. Letts., 1979, 35(1), 83.
8. S.C. Gau, A.J. Heeger, Z. Kiss, A.G. MacDiarmid, S.N. Chen, and D.L. Peebles Appl. Phys. Letts., 1980, 36(1), 96.
9. W. Su, J.R. Schrieffer and A.J. Heeger, Phys. Rev. Letts., 1979, 42, 1698.

10. B.R. Weinberger, E. Ehrenfreund, A. Pron, A.J. Heeger and A.G. MacDiarmid, J. Chem. Phys., 1980, 72(9), 4749.

11. W.P. Su and J.R. Shrieffer, Proc. Natl. Acad. Sci. U.S.A., 1980, 77(10), 5626.

12. N. Suzuki, M. Ozaki, S. Etemád, A.J. Heeger and A.G. MacDiarmid, Phys. Rev. Letts., 1980, 45(14), 1209.

13. S. Kivelson, Phys. Rev. Letts., 1980, 46(20), 1344.

14. J.C.W. Chien, J. Polym, Sci. Letts., 1981, 19, 249.

15. Y. Tomiewicz, T.D. Schultz, H.B. Broom, T.C. Clarke and G.B. Street, Phys. Rev. Letts., 1979, 43(20), 1532.

16. W.H. Watson, W.C. McMordic and L.G. Lands, J. Polym, Sci., 1961, 55, 137.

17. S. Kambara, M. Hatano and T. Hosoe, Kogyo Kagaku Zasshi, 1962, 65, 720.

18. A.F. Donda and G. Moretti, J. Org. Chem., 1966, 31, 985.

19. T.F. Rutledge, Acetylenes and Allenes, Reinhold Book, New York, 1969, 327.

20. S. Ikeda and A. Tamaki, J. Polym. Sci. Letts. Ed., 1966, 4, 605.

21. A.G. MacDiarmid, A.J. Heeger et al., J. Appl. Phys., 1980, 51(8), 4252.

22. S.C.Gau et al., Appl. Phys. Letts., 1981, 38(7), 555.

23. T. Torey et al., Jap. J. Appl. Phys., 1981, 20(2), 127.

24. S. Denko et al., Jap. Kokai Tokkyo Koho, 1979, 80, 138, 879.

25. H. Shirakawa et al., Polym. Preprints, (Japan), 1979, 28(3), 467.

26. H. Shirakawa et al., Kagaku Kogyo, 1980, 12, 1259.

27. P.J. Nigrey, D. MacInnes, D.P. Nairns, A.G. MacDiarmid and A.J.Heeger, J. Electrochem. Soc., 1980, 128(8), 1651.

28. J.H. Edwards and W.J. Feast, Polymer, 1980, 21, 595.

29. J.H. Edwards and W.J. Feast, Polymer, (in press).

30. S. Wyse, PhD thesis, University of Edinburgh, 1984.

31. J.L. Hrisson and Y. Chauvin, Makromol. Chem., 1970, 141, 161.

32. M.T. Mocella, R. Rouner and E.L. Muetterties, J. Am. Chem. Soc., 1970, 98, 4689.

33. R.G. Pearson, J. Am. Chem. Soc., 1972, 94, 8287.

34. R.L. Burwell and A. Brenner, J. Mol. Catal. 1975, 1, 77.

35. M.F. Farona and W.S. Greenlee, J. Chem. Soc. Chem. Commun., 1975, 759.

36. M.T. Mocella, M.A. Busch and E.L. Muetterties, J. Am. Chem. Soc., 1976, 98, 1283.

37. R. Rossi, P. Diversi, A. Lucherini and L. Porri, Tet. Letts., 1974, 11, 879.

38. J.P. Soufflet, D. Commereuc and V. Chauvin, C.R. Ser. C., 1973, 276, 169.

39. R.R. Schrock, J. Am. Chem. Soc., 1974, 96, 6796.

40. T.J. Katz and N. Acton., Tet. Letts., 1970, 47, 4251.

41. J.G. Speight, P. Kovacic and F.W. Koch, J. Macromol. Sci., 1971, 295.

42. D.G.H. Ballard, A. Courtis, I.M. Shirley and S.C. Taylor, J. Chem. Soc. Chem. Commun., 1983, 954.

43. J.N. Short and H.W. Hill, Chem. Technol., 1972, 2, 481.

44. K.K. Kanazawa, A.F. Diaz, R.H. Geiss, W.D. Gill, J.F. Kwak, J.A. Logan, J.F. Rabolt and G.B. Street, J. Chem. Soc. Chem. Commun., 1979, 854.

45. A.F. Diaz and J.I. Castillo, J. Chem. Soc. Chem. Commun., 1980, 397.

46. A.F. Diaz, K.K. Kanazawa and G.P. Gardini, J. Chem. Soc. Chem. Commun., 1979, 635.

47. (a) G. de Bruin, J. Chem. Soc. Abs., 1914, 106, 1197.

(b) G. De Bruin, Chem. Abs., 1915, 9, 623.

48. W.L. Mock, J. Am. Chem. Soc., 1975, 97, 3666.

49. W.L. Mock, J. Am. Chem. Soc., 1966, 88, 2857.

50. S.D. McGregor and D.M. Lemal, J. Am. Chem. Soc., 1966, 88, 2858.

51. P.D. Bartlett, G.E.H. Wallinbillich and L.K. Montgomery, J. Org. Chem., 1967, 32, 1290.

52. T.E. Sample and L.F. Hatch, J. Chem. Ed., 1968, 45, 55.

53. (a) R. Bloch and J. Abecassis, Tet. Letts., 1982, 23, 3277.
(b) R. Bloch and J. Abecassis, Tet. Letts., 1982, 24, 1247.

54. S. Yamada, T. Suzuki and H. Takayama, Chem. Letts., 1983, 1003.

55. T. Chou, H. Tso, L. Chang and L. Lin, J. Chem. Soc. Perkin Trans. I., 1985, 515.

56. V.Sh. Shaikhrazieva, R.S. Enikeev and G.A. Tolstikov, Zh. Org. Khim., 1972, 8, 377.

57. J.I.G. Cadogan, C.M. Buchan, I. Gosney, B.J. Hamill and L.M. McLaughlin, J. Chem. Soc. Chem. Commun., 1982, 325.

58. R.A. Aitken, J.I.G. Cadogan, I. Gosney, B.J. Hamill, and L.M. McLaughlin, J. Chem. Soc. Chem. Commun. 1982, 1164.

59. C.M. Buchan, J.I.G. Cadogan, I. Gosney, B.J. Hamill, S.F. Newlands and D.A. Whan, J. Chem. Soc. Chem. Commun., 1983, 725.

60. L. McLaughlin, PhD thesis, Univerisity of Edinburgh, 1980.

61. K.B. Becker and M.P. Labhart, Helv. Chim. Acta., 1983, 66, 1090.

62. W.J. Bailey and E.W. Cummins, J. Am. Chem. Soc., 1954, 76, 1932.

63. H.L. Hsieh, J. Polym. Sci., 1965, 3, 153.

64. R.L. Milkovic, M. Levy and M. Swarc, J. Am. Chem. Soc., 1956, 78, 2656.

65. H. Bluestone, R. Bimber, R. Berkey and Z. Mandel, J. Org. Chem., 1961, 26, 346.

66. P.E. Blatz, J. Polym. Sci., 1966, 4, 1335.

67. K.J. Ivin, Olefin Metathesis, Academic Press, London, 1983.

68. P.B. van Dam, M.C. Mittelmeijer and C. Boelhouwer, J. Chem. Soc. Chem. Commun., 1972, 1221.

69. T.A. Antkowiak, D.C. Saunders, G.B. Trimitsis, J.B. Press and H. Schechter, J. Am. Chem. Soc., 1972, 94, 5366.

70. L.A. Paquette, U. Jacobsson and S.V.Ley, J. Am. Chem. Soc., 1976, 98, 152.

71. I. Tabushi, K. Yamamura and Z. Yoshida, J. Am. Chem. Soc., 1972, 94, 787.

72. O. De Lucchi, V. Luccini, L. Pasquato and G. Modena, J. Org. Chem., 1984, 49, 596.

73. L.G. Cannel, Tet. Letts., 1966, 48, 5967.

74. G. Bianchini, C. De Micheli, A. Gamba, R. Gandolfi and B. Rezzani, J. Chem. Soc. Perkin Trans.I., 1977, 2222.

75. C.M. Anderson, I.W. McCoy and R.N. Warrender, Tet. Letts., 1970, 2735.

76. I. Fleming, Frontier Orbitals and Organic Chemical Reactivity, Wiley, New York, 1976.

77. L.A. Paquette, R.E. Moerck, B. Harirchian and P.D. Magnus, J. Am. Chem. Soc., 1978, 100, 1597.

78. I. Roberts and G.E. Kimball, J. Am. Chem. Soc., 1937, 59, 947.

79. G.A. Olah, J.M. Bollinger and J. Brinch, J. Am. Chem. Soc., 1968, 90, 2587.

80. G.A. Olah and J.M. Bollinger, J. Am. Chem. Soc., 1968, 90, 947.

81. G.A. Olah and T.R. Hockswender, J. Am. Chem. Soc., 1974, 96, 3574.

82. J. Strating, J.H. Wieringa and H. Wynberg, J. Chem. Soc. Chem. Commun., 1969, 907.

83. H. Slebocka-Tilk, R.G. Ball and R.S. Brown, J. Am. Soc. Chem. Commun., 1985, 107, 4504.

84. E.E. van Tamelin and D. Carty, J. Am. Chem. Soc., 1971, 93, 6102.

85. J.I.G. Cadogan, D.K. Cameron, I. Gosney, R.M. Highcock and S.F. Newlands, J. Chem. Soc. Chem. Commun., 1985, 1751.

86. R.A. Aitken, I. Gosney, H. Farries, M.H. Palmer and I. Simpson, Tetrahedron, 1984, 40, 2487.

87. A.A. Akhrem, A.M. Moiseenkov and V.N. Dobrynin, Russ. Chem. Revs., 1968, 37, 448.

88. G. Heublin, J. Prakt. Chem., 1966, 31, 84.

89. L.F. Fieser, J. Chem. Ed., 1954, 31, 291.

90. G.E. Heasley, J. McCall-Bundy, V.L. Heasley, S. Arnold, A. Gipe, D. McKee, R. Orr, S.L. Rodgers and D.F. Shellhamer, J. Org. Chem., 1978, 43, 2793.

91. G. Bellucci, G. Berti, R. Bianchini, G. Ingrosso and K.J. Yates, J. Org. Chem., 1981, 46, 2315.

92. G. Bellucci, R. Bianchini, R. Ambrosetti and G. Ingrosso, J. Org. Chem., 1985, 50, 3313.

93. B.E. Smart, J. Org. Chem., 1973, 38, 2366.

94. J.I. Musher, Mol. Phys., 1963, 6, 93.

95. J. Meinwald and Y.C. Meinwald, J. Am. Chem. Soc., 1963, 85, 2514.

96. B.E. Smart, J. Org. Chem., 1973, 38, 2027.

97. P.M. Subramanian, M.T. Emerson and N.A. LaBel, J. Org. Chem., 1965, 30, 2624.

98. D.R. Marshal and J.R. Robinson, Cad. J. Chem., 1971, 49, 885.

99. H. Kwart and L.A. Kaplan, J. Am. Chem. Soc., 1954, 76, 4072.

100. H. Hogenven, G. Maccagani and F. Montanari, J. Chem. Soc. (C), 1966, 1585.

101. E. Payo, J. Mantecon and L. Corte's, Acta. Cient. Venez., 1967, 3, 345.

102. P. Wilder and L.A. Feliu-Otero, J. Org. Chem., 1965, 30, 2560.

103. G.M. Mkryan, S.E. Zurabyan, A.V. Arutyunyan and R.A. Kazaryan, Arm. Khim. Zh., 1966, 19, 898.

104. R.V. Carr and L.A Paquette, J. Am. Chem. Soc., 1980, 102, 853.

105. J.I.G. Cadogan, D.K. Cameron, I. Gosney, R.M. Highcock and S.F. Newlands, J. Chem. Soc. Chem. Commun., 1986, 766.

106. S.V. Ley, F. Sternfeld and S. Taylor, Tet. Letts., 1987, 28, 225.

107. S. Ozaki, Y. Wunatabe, T. Ogasawara, Y. Koudo, N. Shotani, H. Nishi and T. Matsuki, Tet. Letts., 1986, 27, 3157.

108. R.F.C. Brown, 'Pyrolytic Methods in Organic Chemistry', Academic Press, New York, p.28, 1980.

109. F.A. Davis, T.W. Panunto, S.B. Awad and R.L. Billmers, J. Org. Chem., 1984, 49, 1228.

110. M.F.R. Mulcahy, B.G. Tucker, D.J. Williams and J.R. Wilmhurst, Aus. J. Chem., 1967, 20, 1155.

111. R.A. Marty and P. De Mayo, J. Chem. Soc. Chem. Commun., 1971, 127.

112. D. Barnard, J. Chem. Soc., 1957, 4673.

113. R.M. Topping and N. Kharasch, J. Org. Chem., 1962, 27, 4353.

114. T.J. Maricich and C.K. Harrington, J. Am. Chem. Soc., 1972, 94, 5115.

115. J. Meisenheimer, Chem. Ber., 1919, 52, 1667.

116. J. Meisenheimer, H. Greeske and A. Wilmersdorf, Chem. Ber., 1922, 55, 513.

117. Q.E. Thomson, J. Org. Chem., 1965, 30, 2703.

118. C.L. Arcus, M.P. Bulfe, and J. Kenyon, J. Chem. Soc., 1938, 485.

119. E.G. Miller, D.R. Rayner, H.T. Thomas and K. Mislow, J. Am. Chem. Soc., 1968, 90, 4861.

120. A.E. Arbuzov and K.V. Nikonorov., Zh. Obschch. Khim., 1948, 18, 2008.

121. G. Tsuchihashi and K. Ogura, Ger. Pat. Appl. 2130923, 22nd June, 1971.

122. L.O. Brokway, J. Phys. Chem., 1937, 41, 185.

123. L. Pauling, 'The Nature of the Chemical Bond', 3rd Ed., Cornell University Press, New York, 1960, pp.314-5.

124. C. Altona, PhD Thesis, University of Leiden, 1964.

125. E.L. Elliel and N.L. Allinger, Wiley-Interscience, New York, 1969, p.39.

126. H. Schollkopf, M. Patsch and H. Schafer, Tet. Letts., 1964, 36, 2515.

127. G.P. Schulman, P. Ellgen and M. Connor, Cad. J. Chem., 1965, 43, 3459.

128. W.C. Still, M. Kahn and A. Mitra, J. Org. Chem., 1978, 43, 2923.

129. L.M. Harwood, Aldrichimica Acta., 1985, 18, 25.

130. A.R. Forrester and G. Soutar, Chemistry in Industry, 1984, 21, 772.

131. F.G. Bordwell and B.M. Pitt, J. Am. Chem. Soc., 1955, 77, 572.

132. D.Y. Curtin, R.J. Crawford and M. Wilhelm, J. Am. Chem. Soc., 1958, 80, 1389.

133. N. Kornblum and A.P. Lurie, J. Am. Chem. Soc., 1959, 81, 2705.

134. L. Watts, J.D. Fitzpatrick and R. Pettit, J. Am. Chem. Soc., 1966, 88, 623.

135. W.B. Person, G.R. Anderson and J.N. Fordemwalt, J. Chem. Phys., 1961, 35, 908.

cis-Bromination of a Non-conjugated Cyclic Alkene. Unprecedented Electrophilic Stereoselection by Means of a Remote SO_2 Group

J. I. G. Cadogan,[a] Donald K. Cameron,[b] Ian Gosney,[b] Rona M. Highcock,[a] and Stephen F. Newlands[b]

[a] *B.P. Research Centre, Chertsey Road, Sunbury-on-Thames, Middlesex TW16 7LN, U.K.*
[b] *Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, Scotland, U.K.*

Contrary to expectation, addition of molecular bromine to 3-thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide (**1**) yields substantial amounts of the *cis*-1,2-dibromide (confirmed by *X*-ray diffraction), suggesting that the remote SO_2 group exerts an extraordinary directive influence by means of a long-range Coulomb interaction that stabilises an open carbocation intermediate at the expense of the usually favoured bridged bromonium ion.

Reprinted from the Journal of The Chemical Society

Chemical Communications 1985

cis-Bromination of a Non-conjugated Cyclic Alkene. Unprecedented Electrophilic Stereoselection by Means of a Remote SO_2 Group

J. I. G. Cadogan,[a] Donald K. Cameron,[b] Ian Gosney,[b] Rona M. Highcock,[a] and Stephen F. Newlands[b]

[a] *B.P. Research Centre, Chertsey Road, Sunbury-on-Thames, Middlesex TW16 7LN, U.K.*
[b] *Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, Scotland, U.K.*

Contrary to expectation, addition of molecular bromine to 3-thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide (**1**) yields substantial amounts of the *cis*-1,2-dibromide (confirmed by *X*-ray diffraction), suggesting that the remote SO_2 group exerts an extraordinary directive influence by means of a long-range Coulomb interaction that stabilises an open carbocation intermediate at the expense of the usually favoured bridged bromonium ion.

Formation of *cis*-1,2-dibromides by bromination of alkenes under ionic conditions is rare.[1] In the few cases reported, *syn*-addition is made kinetically attractive by the presence of conjugating groups on the double bond that stabilise open carbocations *vis-à-vis* a cyclic bromonium ion, equation (1). When such features are absent, the overwhelming preference is for *trans*-bromination. One notable exception is the reported[2] formation of a *cis*-1,2-dibromide (albeit as a 30:70 mixture with its *trans*-isomer) from Dewar benzene, but the compound was too unstable to be isolated and characterisation rested on chemical evidence. We now report another example, this time fully authenticated by a crystal structure determination, in which *syn*-addition to an isolated double bond is unexpectedly brought about by a favourable long-range Coulomb interaction between a remote SO_2 group and the open carbocation.

The compound in question is the bicyclic sulphone (**1**) formed by oxidative decarboxylation of the photoadduct of 2,5-dihydrothiophene 1,1-dioxide with maleic anhydride.[3] In contradistinction to the general behaviour of other non-conjugated alkenes, electrophilic addition of bromine to (**1**) in methylene chloride proceeded sluggishly and gave a 1:1 mixture (by n.m.r.) of isomeric dibromides which could be separated readily by 'flash' chromatography. That the mixture represented a kinetically controlled product distribution was established by the stability of the isomeric dibromides to the conditions of reaction. The structural assignment of one of the isomers, isolated as colourless rhombs (m.p. 160—163 °C), to the *trans*-dibromide (**2**)† followed convincingly from its ^{13}C n.m.r. spectrum which exhibited six signals at δ 54.17, 52.03, 49.32, 48.28, 42.28, and 39.45. The ^{13}C n.m.r. spectrum of the second isomer, also obtained in a pure state as stable colourless needles (m.p. 168–168.5 °C), was entirely compatible with the symmetry of the *cis*-dibromide structure (**3**) in that only three signals appeared, at δ($CDCl_3$) 53.39, 48.54, and 43.30. Because bromine addition to non-conjugated alkenes normally takes place with *trans*-stereochemistry, the structure of (**3**), shown in Figure 1 with relevant bond parameters, was validated by an *X*-ray diffraction study.‡

Formation of the *cis*-dibromide (**3**) at the expense of an equal amount of the expected *trans*-product (**2**) requires the intermediacy of the open carbocation (**5**) and subsequent *syn*-attack by Br^- at a rate that is competitive with *anti*-collapse of the bromonium ion (**4**). From an inspection of Dreiding models, there is no question that the SO_2 group can provide sufficient steric bias to divert the incoming Br^- away from the *anti*-face and hence cause the *syn*-attachment of two

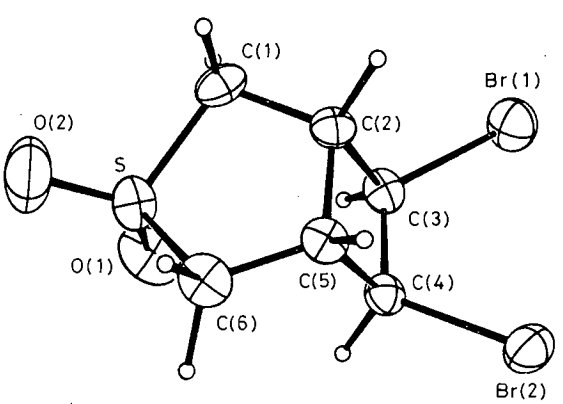
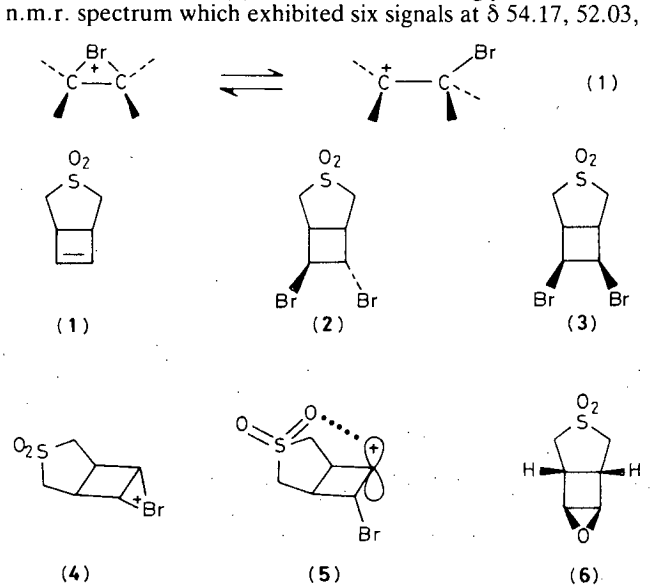


Figure 1. Molecular structure of (**3**). Selected bond lengths (Å) are: S–O(1) 1.436(5), S–O(2) 1.435(5), S–C(1) 1.791(8), S–C(6) 1.793(7), C(1)–C(2) 1.527(9), C(2)–C(3) 1.520(9), C(2)–C(5) 1.574(9), C(3)–C(4) 1.527(9), C(3)–Br(1) 1.947(6), C(4)–C(5) 1.544(9), C(4)–Br(2) 1.962(6), C(5)–C(6) 1.520(9).



† All new compounds were characterised by combustion analysis as well as by ^1H and ^{13}C n.m.r., i.r., and mass spectrometry

‡ *Crystal data:* (**3**), $C_6H_8Br_2O_2S$, M = 304.01, monoclinic, space group $P2_1/c$ (No. 14), a = 10.430(3), b = 6.650(2), c = 12.723(8) Å, β = 91.20(4)°, U = 882(1) Å^3, Z = 4, D_c = 2.29 g cm^{-3}, $F(000)$ = 584, μ(Mo-K_α) = 92.8 cm^{-1}, R = 0.042, R_w = 0.047 for 1366 reflections [293 K, 1.0 ≤ 2θ ≤56°, $I \geq 3.0\sigma(I)$, Enraf-Nonius CAD-4 diffractometer, Mo-K_α *X*-radiation (graphite monochromator), λ = 0.710 73 Å]. A weighting scheme of the form $w^{-1} = \sigma^2(F) + (0.22 \times F)^2 + 1.8$ {where $\sigma(F) = [F^2 + 2F \times \sigma(F)]^{-\frac{1}{2}} - F$} gave a satisfactory analysis of variance and a goodness-of-fit of 1.05.

The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

large bromine atoms.§ We have also discounted intramolecular participation by the SO_2 group as the source of the *cis*-stereoselection. The *X*-ray structure of the alkene (**1**) shows a least distance of 3.23 Å between the *exo*-oxygen atom of the SO_2 group and the double bond,¶ making any bonding to the reaction centre in (**4**) unlikely, particularly as the SO_2 group is a very poor nucleophile. Furthermore, even if bonding could occur, it should lead to overall *syn*-addition, whereas there is an equal preference for *anti*-addition. In our view, the relaxation in the usual demand for bridging by bromine in (**4**) is brought about by the unprecedented stabilising effect of a long-range Coulomb interaction between the highly polar SO_2 group and the carbocation centre as depicted in (**5**).

As a corollary to these findings we have observed the same type of proximity effect in the ring-opening of the *anti*-epoxide (**6**) with aqueous HBr (60%) in glacial acetic acid. This is borne out by the loss of the *trans*-stereospecificity usually associated with epoxides in which the effect of conjugation is absent.[5] Thus, on the basis of nuclear Overhauser enhancement studies, we found that the bromohydrins from (**6**) contained 37% of the *cis*-isomer, the formation of which demands the intermediacy of an open carbocation. In this connection it is of some significance that the reaction of the alkene (**1**) with *N*-bromoacetamide in aqueous acetone gives only a single bromohydrin which is derived by exclusive *anti*-attack on the bridged intermediate (**4**). This apparently paradoxical behaviour may be explained by hydration of the polar SO_2 group, resulting in a loss of its directive influence. This interpretation is supported by the observation that bromination of (**1**) in aqueous 1,2-dimethoxyethane proceeds normally to give, as the only product, the *trans*-1,2-dibromide (**2**).

Received, 4th April 1985; Com. 459

§ Even in the comparatively hindered system, 7,7-dimethylbicyclo-[3.2.0]hept-2-en-6-one, bromination occurs exclusively with *trans*-stereochemistry.[4]

¶ Full crystallographic data for (**1**) will be published elsewhere.

References

1 For a comprehensive account of the stereochemistry of electrophilic addition by bromine to double bonds, see P. B. D. De La Mare and R. Bolton, 'Electrophilic Additions to Unsaturated Systems,' Elsevier, 1982.
2 E. E. van Tamelen and D. Carty, *J. Am. Chem. Soc.*, 1971, **93**, 6102; see also, R. Caple, F. M. Hsu, and C. S. Islenda, *J. Org. Chem.*, 1968, **33**, 4111, for a report of the occurrence of formal *cis*-addition to *anti*-7-bromobenzonorbornadiene (*anti*-9-bromo-1,4-dihydro-1,4-methanonaphthalene), but the result is complicated by the possibility of skeletal rearrangements.
3 R. A. Aitken, J. I. G. Cadogan, I. Gosney, B. J. Hamill, and L. M. McLaughlin, *J. Chem. Soc., Chem. Commun.*, 1982, 1164.
4 S. M. Roberts and Z. Grudzinski, *J. Chem. Soc., Perkin Trans. 1*, 1975, 1767.
5 For a specialised review devoted to the stereospecificity in opening of an epoxide ring, see A. A. Akhrem, A. M. Moiseenkov, and V. N. Dobrynin, *Russ. Chem. Rev.*, 1968, **37**, 448.

The Sulphone Group as a Nucleophile: Intramolecular Formation of a Novel Thiadecanylium Tribromide *via* Addition of Bromine to a Double Bond in an Overcrowded Environment

J. I. G. Cadogan,[a] Donald K. Cameron,[b] Ian Gosney,[b] Rona M. Highcock,[a] and Stephen F. Newlands[b]

[a] *B.P. Research Centre, Chertsey Road, Sunbury-on-Thames, Middlesex TW16 7LN, England, U.K.*
[b] *Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, Scotland, U.K.*

Instead of furnishing a normal bromide addition product, bromination of 4-thiatricyclo[5.2.0.$0^{2,6}$]non-8-ene 4,4-dioxide (**1**) gives 5-bromo-1-oxo-10-oxa-1λ^6-thiatetracyclo[4.3.1.$0^{3,8}$.$0^{4,7}$]decan-1-ylium tribromide (**3**) through intramolecular reaction of the bromonium intermediate with the adjacent weakly nucleophilic sulphone group.

Reprinted from the Journal of The Chemical Society
Chemical Communications 1986

The Sulphone Group as a Nucleophile: Intramolecular Formation of a Novel Thiadecanylium Tribromide *via* Addition of Bromine to a Double Bond in an Overcrowded Environment

J. I. G. Cadogan,[a] Donald K. Cameron,[b] Ian Gosney,[b] Rona M. Highcock,[a] and Stephen F. Newlands[b]

[a] *B.P. Research Centre, Chertsey Road, Sunbury-on-Thames, Middlesex TW16 7LN, England, U.K.*

[b] *Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, Scotland, U.K.*

Instead of furnishing a normal bromide addition product, bromination of 4-thiatricyclo[5.2.0.$0^{2,6}$]non-8-ene 4,4-dioxide (**1**) gives 5-bromo-1-oxo-10-oxa-1λ^6-thiatetracyclo[4.3.1.$0^{3,8}$.$0^{4,7}$]decan-1-ylium tribromide (**3**) through intramolecular reaction of the bromonium intermediate with the adjacent weakly nucleophilic sulphone group.

Abnormal behaviour is rarely encountered in the electrophilic addition of bromine to an olefinic double bond despite this being one of the longest recognised and most widely studied reactions of alkenes.[1] We now report a unique reaction of an overcrowded alkene to which the addition of bromine is prematurely terminated by a remarkable transannular interaction between the bromonium intermediate and a sulphone group, hitherto not credited with being able to participate as a nucleophile.

Thus, reaction of novel 4-thiatricyclo[5.2.0.$0^{2,6}$]non-8-ene 4,4-dioxide (**1**) with bromine leads not to the normal dibromide, but to 5-bromo-1-oxo-10-oxa-1λ^6-thiatetracyclo[4.3.1.$0^{3,8}$.$0^{4,7}$]decan-1-ylium tribromide (**3**).

The synthesis of the tricyclic sulphone (**1**)† was achieved in five steps from the Diels–Alder adduct of cyclobutadiene with maleic anhydride. Its *syn*-cyclobutane structure was assigned on the basis of n.m.r. spectra‡ [including ^{1}H decoupling and nuclear Overhauser effect (n.O.e.) experiments] and by comparison with the *anti*-isomer (**4**) which can be obtained by conventional synthetic methods from the photo-adduct of 3-thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide[2] and maleic anhydride; the *anti*-orientation of the three rings in (**4**) was confirmed by *X*-ray analysis.§

When the olefin (**4**) was treated with an equimolar amount of bromine in methylene chloride at −78 °C reaction occurred in the normal way to give the *trans*-1,2-dibromide (**5**) (m.p. 135—136 °C, 89%) as evidenced by spectral data, especially its eight line ^{13}C n.m.r. spectrum [($CDCl_3$) δ 54.24, 53.76, 52.24, 51.80, 47.70, 44.48, 39.89, and 34.90]. In sharp contrast to this behaviour, the *syn*-isomer (**1**) consumed two equiv. of bromine at room temperature and gave an orange crystalline precipitate with the composition $C_8H_{10}Br_4O_2S$. Although reasonably stable, this compound decomposed on heating to 82—84 °C with loss of bromine. It was insoluble in diethyl ether, but dissolved in [$^2H_6$]acetone to give an orange solution which turned colourless almost immediately. Examination of this solution by ^{1}H n.m.r. spectroscopy revealed the presence of the starting olefin (**1**) and other products identified by g.l.c. analysis as being formed by irreversible bromination of the solvent. Structural evidence about the compound was obtained from n.m.r. spectroscopy in CD_3CN wherein reversal to free bromine and the olefin (**1**) resulted in an equilibrium mixture in which the compound predominated (60:40). The same equilibrium mixture was shown to be formed when the olefin (**1**) was treated with two equiv. of bromine in CD_3CN, while addition of excess bromine resulted in complete conversion into the olefin (**1**)–bromine complex. In keeping with the proposed structure (**3**) and its lack of symmetry, the ^{13}C n.m.r. spectrum of the complex displayed eight lines at δ (CD_3CN) 32.62, 34.77, 36.12, 42.88, 44.58, 45.12, 48.43, and 97.43.

The occurrence of a downfield resonance (δ 97.43) is consistent with the sulphonyl oxygen forming a bond to carbon. This is supported by the absence of i.r. bands characteristic of the SO_2 group and the observation of a corresponding resonance at δ 5.91 (1H, dd, *J* 6.0 and 4.3 Hz) in the 360 MHz ^{1}H n.m.r. spectrum of the compound which is in excellent agreement with the proposed structure (**3**).¶ A notable feature of the spectrum is the downfield position of *all resonances* relative to those of (**1**) as expected for such a positively charged species. The structure (**3**) is further supported by positive ion fast atom bombardment (f.a.b.) mass spectrometry which shows a strong peak (in thioglycerol) at *m/z* 249, 251 (1:1 doublet) for $[M-Br_3]^+$. Negative ion f.a.b. showed a strong Br^- signal, a small signal due to a Br_2^- cluster but no evidence for Br_3^-. Under electron impact conditions, (**3**) loses Br_2, yielding peaks no higher than *m/z* 170 which corresponds to the molecular ion of (**1**).

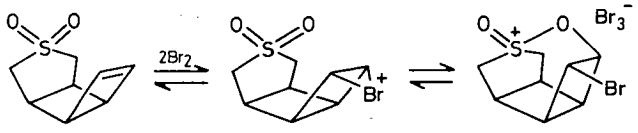
Nucleophilic behaviour by the sulphone group as reported above is without precedent.[3] It undoubtedly arises in this instance because the *syn*-sulphonyl oxygen, despite its extremely low nucleophilicity, is sited intramolecularly such that capture of the bromonium ion (**2**) from the *endo*-direction is stereoelectronically favourable. This is apparent from an inspection of Drieding models which shows a non-bonded distance of *ca.* 2.0 Å between the *syn*-oxygen atom of the sulphone group and the double bond in (**1**). In point of fact, it is this feature coupled with a molecular rigidity that inhibits the completion of the usual bromination pathway and leads to the stability of (**3**).

† All new compounds were characterised by combustion analysis as well as by ^{1}H and ^{13}C n.m.r., i.r., and mass spectrometry.

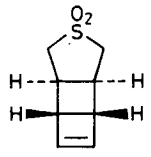
‡ (**1**): ^{1}H n.m.r. (360 MHz) ($CDCl_3$) δ 2.81—2.90 (sym. m, 2H), 3.07—3.15 (sym. m, 2H), 3.25—3.32 (sym. m, 2H), 3.47—3.50 (sym. m, 2H), 6.39 (dist. dd, *J* 1.7 and 1.4 Hz, 2H); ^{13}C n.m.r. ($CDCl_3$) δ 32.25, 44.14, 52.61, and 140.63. (**4**): ^{1}H n.m.r. (360 MHz) ($CDCl_3$) δ 2.83—2.87 (sym. m, 2H), 2.97—3.03 (sym. m, 2H), 3.22—3.23 (sym. m, 2H), 3.24—3.30 (sym. m, 2H), and 6.34 (dist. dd, *J* 1.4 and 1.2 Hz, 2H); ^{13}C n.m.r. ($CDCl_3$) δ 34.44, 47.85, 53.96, and 141.19.

§ *Crystal data* for (**4**): $C_8H_{10}O_2S$, *M* = 170.23, monoclinic, space group $P2_1/c$ (No. 14), *a* = 9.286(2), *b* = 10.034(2), *c* = 9.187(2) Å, β = 107.16(2)°, *U* = 818(1) Å^3, *Z* = 4, D_c = 1.38 g cm^{-3}, *F*(000) = 360, μ(Mo-K_α) = 3.3 cm^{-1}. *R* = 0.037, R_w = 0.035 for 1 636 reflections [293 K, 2.0 ≤ 2θ ≤ 56°, *I* ≥ 3.0 σ (*I*), Enraf–Nonius CAD-4 diffractometer, Mo-K_α *X*-radiation (graphite monochromator), λ = 0.71073 Å]. Unit weights gave a satisfactory analysis of variance and a goodness-of-fit of 0.49. The atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1, 1986. Full crystallographic details will be published elsewhere.

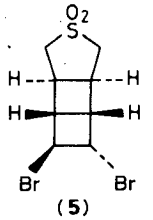
¶ (**3**): ^{1}H n.m.r. (CD_3CN) (360 MHz) δ 3.31 (d of t, *J* 7.6 and 4.3 Hz, 1H), 3.61 (d of d, *J* 6.0 and 3.0 Hz, 1H), 3.67 (d of d, *J* 15.5 and 8.74 Hz, 1H), 3.78—3.90 (m, 4H), 4.17 (d of d of d of d, *J* 16.2, 8.7 and 1.1 Hz, 1H), 4.43 (d of d, *J* 16.2 and 1.9 Hz, 1H), 5.91 (d of d, *J* 6.0 and 4.3 Hz, 1H).



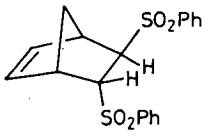
(1) (2) (3)



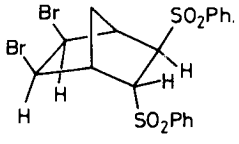
(4)



(5)



(6)



(7)

The capacity of the sulphone group to participate as an intramolecular nucleophile is further highlighted by the bromination of the norbornenyl derivative (**6**) to give *specifically exo,cis*-dibromide (**7**). This mode of addition is striking when compared with the exclusive *trans*-bromination of the corresponding dichloro-analogue under the same conditions.[4] It must similarly be attributed to the capture of the intermediate bromonium ion by the sulphone group, although in this particular case, there are no molecular constraints to restrict subsequent nucleophilic attack of Br^-, albeit from the normally hindered *exo*-direction.

We gratefully acknowledge mass spectrometry help from K. J. Bare, B. W. Chandler, and G. Goff at the B.P. Research Centre.

Received, 14th January 1986; Com. 066

References

1 For recent reviews on electrophilic bromine addition reactions, see P. B. D. De La Mare and R. Bolton, 'Electrophilic Additions to Unsaturated Systems,' 2nd edn., Elsevier, 1982; K. A. V'yunov and A. I. Ginak, *Russ. Chem. Rev. (Engl. Transl.)*, 1981, **50**, 151.
2 R. A. Aitken, J. I. G. Cadogan, I. Gosney, B. J. Hamill, and L. M. McLaughlin, *J. Chem. Soc., Chem. Commun.*, 1982, 1164.
3 See S. Braverman and D. Reisman, *J. Am. Chem. Soc.*, 1977, **99**, 605; *Tetrahedron Lett.*, 1977, 1753, for an isolated example of formal intramolecular trapping of a carbocation by a sulphone group for which it is not possible to exclude prior rearrangement to a sulphinate.
4 B. E. Smart, *J. Org. Chem.*, 1973, **38**, 2366.