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SYNTHESIS AND POLYMERIZATION OF SOME
HALOGENATED POLYCYCLIC ALKENES

By

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Thesis submitted for the Degree of Doctor of Philosophy to
the University of Durham, England

Graduate Society

1982

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To

my wife Rohana bte Ariffin,

my daughter Nor Salleha,

my mother Djusnah,

my late father Alimuniar and

my late uncle Hj. Mohd Johari.

ABSTRACT

This thesis describes work on the ring opening polymerization of some lightly fluorinated and chlorinated polycyclic monomers. The thesis is divided into three chapters.

The first chapter reviews the utility of the metathesis reaction in organic chemistry in general and polymer chemistry in particular. Present understanding of the value and limitations of the reaction is discussed along with related mechanistic and theoretical background.

The second chapter is concerned with the synthesis, characterization and polymerization of some new fluorinated monomers. The way in which the choice of catalyst can influence the details of polymer chain microstructure is discussed for the particular case of polymers prepared from 2,3-bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene using tungsten and molybdenum based catalysts. Catalyst selectivity in the polymerization of endo/exo mixtures of isomeric monomers is also examined.

The third chapter describes work directed towards the synthesis of polyarylenevinylenes. The main part of this chapter is concerned with the synthesis, characterization and examination for polymerizability by metathesis ring opening, of a range of chlorinated bicyclo[3.2.1]octa-2,6-dienes. It is concluded that the presence of a 4-endo chlorine atom in such molecules acts as an inhibitor for polymerization without acting as a catalyst poison.

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I wish to express my appreciation to all my friends and relatives particularly my late uncle and his family. Finally, to my wife and my daughter, whose encouragement and understanding during our stay in Durham, made this period of study possible and enjoyable.

MEMORANDUM

The work reported in this thesis was carried out in the Chemistry Department of the University of Durham between October 1979 and August 1982. This work has not been submitted for any other degree and is the original work of the author except where acknowledged by references.

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using $WCl_6/(CH_3)_4Sn$ and $MoCl_5/(CH_3)_4Sn$ catalysts

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CHAPTER 1

RING-OPENING POLYMERIZATION

VIA

OLEFIN METATHESIS

1.1. Historical Background of Ring-opening Polymerization by Olefin Metathesis Catalysts

Ring-opening polymerization of cycloalkenes may be considered¹ as a bond reorganization process, whereby for every bond which undergoes scission in the cyclic monomer, a new and similar bond is formed in the polyalkenamer and/or macrocyclic product, as shown in Figure 1.1.

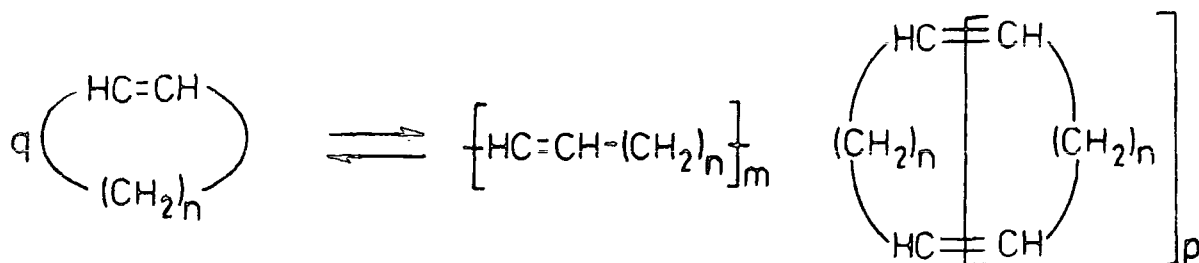


Figure 1.1.

That is, during ring-opening polymerization, the total number and type of chemical bonds in the system remains unchanged. This reaction is similar to a reaction of acyclic alkenes reported by Banks and Bailey² in 1964, see Figure 1.2, and initially described as olefin disproportionation.

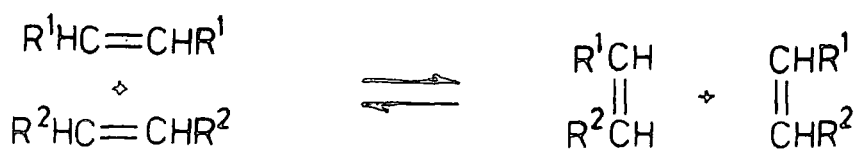


Figure 1.2.

In 1967, Calderon et al³ were the first to use the term 'olefin metathesis' for the overall result of these reactions and later in 1968, Calderon⁴ and Wassermann⁵ recognized ring-opening polymerization as a special case of olefin metathesis.

These transformations are induced by a transition metal system which is frequently similar in composition to the Ziegler-Natta catalysts,

and recently it has been suggested that the two processes are mechanistically related.⁶

Probably the first description of the ring-opening polymerization reaction catalyzed by a transition metal was reported by Anderson and Merckling⁷ in 1955, when they successfully polymerized bicyclo[2.2.1]-hept-2-ene to a high molecular-weight polymer using a mixture of titanium tetrachloride activated by reducing agents.

Later, Truett and coworkers^{8,9} showed that the catalyst system used by Anderson and Merckling worked by ring-opening if the molar ratio Ti:Al was 1:2. They obtained a flexible polymer in 30% yield and, on the basis of chemical and spectroscopic (i.r.) analysis, concluded that this bicyclo[2.2.1]hept-2-ene polymer had a structure consisting of 1,3-cis substituted cyclopentane rings which were interconnected by trans-vinylene groups, Figure 1.3.

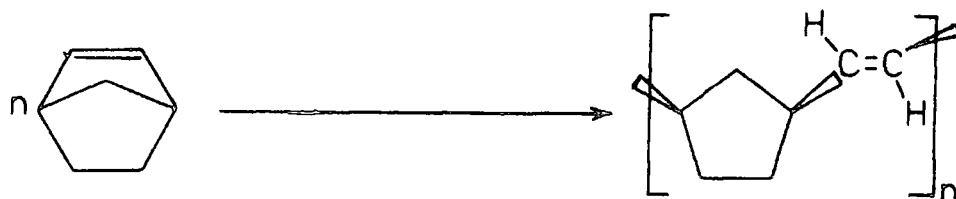


Figure 1.3.

Expanding Anderson and Merckling's work, Eleuterio¹⁰ disclosed an additional catalyst combination derived from molybdenum oxide on alumina, activated by hydrogen reduction and further reacted with aluminium hydride, which was capable of inducing the ring-opening polymerization of a variety of monocyclic, bicyclic and tricyclic olefins. In the case of cyclopentene, trans-poly(1-pentenylene) was formed with a high degree of stereoregular structure but only in low yield.

In 1962, Natta and coworkers¹¹ reported the successful ring-opening polymerization of cyclobutene employing Ziegler-type catalysts. Later, the same authors^{12,13} demonstrated the possibility of producing stereoregular polymers from cyclobutene using different catalyst systems and reaction conditions; some of their results are listed in Table 1.1.

Table 1.1. Ring-opened Cyclobutene Polymers Prepared Using Transition Metal Catalysts

Catalyst System	Polymer Structure	Reference
TiCl ₄ /Et ₃ Al/n-heptane	Predominantly cis	11
TiCl ₄ /R ₃ Al/toluene	Predominantly trans	12
MoCl ₅ /Et ₃ Al/toluene	Predominantly cis	12
RuCl ₃ /H ₂ O	50/50 cis and trans	13
RuCl ₃ /EtOH	Trans	13

In 1964, the same authors¹⁴ investigated tungsten and molybdenum halides in combination with organoaluminium compounds as catalysts for the polymerization of cyclopentene by ring-opening under mild conditions, and were able to prepare high cis- and trans-poly(1-pentenylene). This disclosure triggered an avalanche of research activity on ring-opening polymerization of cycloalkenes.

In 1967, Calderon and coworkers¹⁵⁻¹⁷ reported results on the metathesis of acyclic alkenes with tungsten-based homogeneous catalysts. A unique metathetic transformation occurred rapidly under mild conditions (Figure 1.2.) when acyclic alkenes were treated with a catalyst derived from tungsten hexachloride (or the product of the reaction of equimolar amounts of tungsten hexachloride and an alcohol) and an organoaluminium compound.

The contribution of this work to the evolution of the olefin metathesis concept was significant as it confirmed that the seemingly unrelated olefin

disproportionation and the cycloalkene polymerization reaction are special cases of an entirely new transition-metal-catalyzed reaction. These authors also point out that a macrocyclization process accompanies cycloalkene metathesis.

This observation was the beginning of a large increase in the number of papers concerned with ring-opening polymerization by olefin metathesis catalysts, and already many reviews of the expanding literature of the topic have been published,^{1,18-24} the more general aspects of the olefin metathesis reaction have also been extensively reviewed.²⁵⁻³⁸

1.2. Olefin Metathesis Catalyst Systems

Metathesis catalysts promote two main types of reaction namely ring-opening polymerization of cycloalkenes and disproportionation reactions of acyclic alkenes, although governed by a common mechanism, these reactions differ in many chemical, kinetic and thermodynamic aspects, and this results in different catalyst efficiencies, operating conditions and applicabilities. A wide variety of transition metal derivatives from Group IVA-VIIIA have been reported²²⁻³⁷ to exhibit metathesis activity, by far the most important and practical catalysts are based on tungsten, molybdenum and rhenium. Generally, olefin metathesis catalysts are classified in two main categories; heterogeneous catalysts and homogeneous catalysts.

1.2.a. Heterogeneous Catalysts

Generally, heterogeneous catalysts are comprised of two main components; a high surface area support, such as alumina or silica, on which is deposited a transition metal promoter such as oxides, sulphides or carbonyls of tungsten, molybdenum or rhenium. Usually, a third component is introduced to reduce the poisoning of the catalyst and to

increase the reactivity or to reduce side reactions such as double bond migration. Heterogeneous catalysts are used in the continuous flow type of process at elevated temperature and generally without diluent, hence they are not convenient for ring-opening polymerization of cycloalkenes.

Historically, Eleuterio¹⁰ was the first to report the polymerization of cycloalkenes by heterogeneous catalysts. Since then, several other systems which are capable of catalysing ring-opening polymerization have been described, such as ammonium perrhenate,^{39,40} mixtures of oxides of Re, W or Mo with oxides of K, Ru, S or Co^{41,42} and recently $\text{Re}_2\text{O}_7\text{-Bu}_4\text{Sn}$.⁴³

1.2.b. Homogeneous Catalysts

Calderon et al¹⁶ were the first to describe homogeneous catalysts for olefin metathesis using the $\text{WCl}_6/\text{EtOH}/\text{Et}_2\text{AlCl}$ catalyst system. Arguments about the exact structure and mode of action of particular catalysts are frequent, and indeed the designation "homogeneous" has been questioned for several systems.⁴⁴

Generally, homogeneous catalysts consist of a transition metal derivative (usually of W, Mo or Re) as main component. A second component is added as cocatalyst which increases the activity of the catalyst system, and a third component may be added as activator or modifier.

These catalyst systems are applicable to both acyclic and cycloalkenes, and may act on neat monomer or its solution in an inert solvent. Homogeneous catalysts are classified in three categories below.

1.2.b.i. One-component Metathesis Catalysts For Ring-opening Polymerization

Generally, ring-opening polymerization by this type of catalyst is initiated by halides, oxyhalides or stable carbene complexes of the transition metal. Hydrates of RuCl_3 , OsCl_3 and IrCl_3 in alcoholic solvent

such as ethanol were the first single component catalysts to be used for ring-opening polymerization.^{13,45-47} Later, several transition metal derivatives were shown to be capable of polymerizing cycloalkenes, including WCl_6 , WBr_6 , $ReCl_5$ and $PhWCl_3$.⁴⁸⁻⁵⁰

Stable $W(0)$ metal-carbene complexes have also been reported⁵¹⁻⁵⁴ to ring-open several cycloalkenes. Generally, there are two main types of metal-carbene complexes: (diphenylcarbene) complex (1) which was first synthesized by Casey⁵⁵ and (phenylmethoxycarbene) complex (2) which was synthesized by Fischer,⁵⁶ see Figure 1.4.

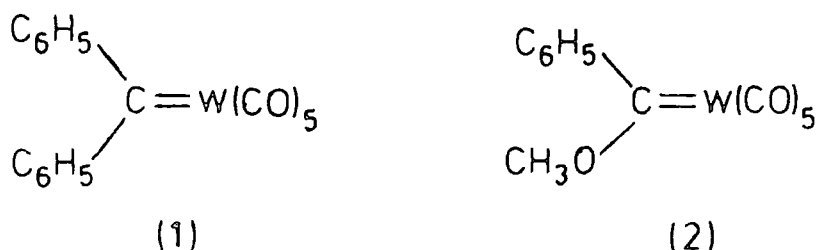


Figure 1.4.

Recently, other transition metal-carbene complexes,⁵⁷⁻⁵⁹ have been developed, see Figure 1.5.

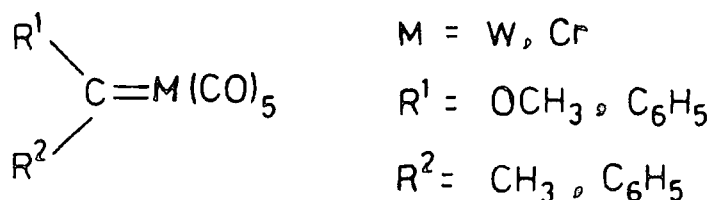


Figure 1.5.

Transition metal-carbene catalysts are reported³⁶ to give high cis-stereospecificity, as shown in Table 1.2. Their reactions are generally cleaner and without the side reactions which sometimes occur with more complex systems.⁵⁷

Table 1.2. Cis-stereospecificity In Polymerization Initiated By Stable Metal-carbene Complexes

Metal-carbene Complex	Monomer	% Cis (Polymer)	Reference
$(CO)_5W=C(OCH_3)C_6H_5$	Cyclobutene	92	51
$(CO)_5W=C(C_6H_5)_2$	Cyclobutene	92	54
$(CO)_5W=C(OCH_3)C_6H_5$	Bicyclo[2.2.1]hept-2-ene	95	51
$(CO)_5W=C(C_6H_5)_2$	Bicyclo[2.2.1]hept-2-ene	72	54

1.2.b.ii. Two-component Metathesis Catalysts For Ring-opening Polymerization

Generally, these catalysts consist of a transition metal derivative as first component with a second component as cocatalyst, preferably aluminium or tin compounds which increase the activities of the catalyst systems.

The catalyst consisting of $TiCl_4/LiAl(C_7H_{13})_4$ was the first homogeneous catalyst⁷⁻⁹ for ring-opening polymerization. Later, Natta and coworkers^{11,14,60,61} described several combinations which are similar to Ziegler-Natta type catalysts.

A cocatalyst derived from alkyl or aryl tin compounds was introduced by Hein⁶² and found to be capable of inducing ring-opening polymerization of several cycloalkenes. Many two-component catalysts derived from combinations of tungsten or molybdenum derivatives with several cocatalysts were introduced, but there was a problem of exact definition and reproducibility.^{62,63}

The stereoregularity of polyalkenamers obtained in the presence of two-component catalysts, depends on numerous factors, such as catalyst composition, polymerization temperature,^{14,20,49,64} type of cocatalysts,^{60,}⁶⁴ type of cycloalkene,^{57,61} variation of the ratio of transition metal to cocatalyst⁶⁴ and concentration of monomer.⁶²

Metal-carbenes such as the Fischer Carbene can be activated by TiCl_4 ^{65,66} or alkynes,^{67,68} but the role of this activator is not well understood. Compounds such as EtAlCl_2 , which are normally regarded as cocatalysts, have been reported^{69,70} to be capable of inducing ring-opening polymerization with some cross-linking. Recently, oxygen has been reported^{25,71-73} to act as activator for ring-opening polymerization without a requirement for other cocatalysts.

1.2.b.iii. Three-component Metathesis Catalysts For Ring-opening Polymerization

In some cases, activators or modifiers were added to the two component metathesis catalysts. An activator was first introduced by Dall'Asta and Corella,⁷⁴ who found that these system have advantages such as good reproducibility, increased stability and solubility of the catalyst in the reaction medium, high polymerization rate and polymer conversion, low catalyst conversion and reduced side reactions. Generally, the activator is an oxygen containing compound such as alcohol, oxygen or water. Recently, it was reported⁷⁵ that unsaturated organic halides such as 1,2-dichloroethene activated the catalyst system in the polymerization of cyclooctene and produced low trans-contents as compared to the untreated catalyst.

In some cases, the third component acts as a modifier, thus addition of a Lewis base may suppress side reactions such as isomerization or Friedel-Craft activity.⁷⁶⁻⁷⁸ Similarly, Ivin and coworkers⁷⁰ have shown that several metathesis catalysts for ring-opening polymerization do not give a pure metathesis polymerization product, they used bases such as sarcosine or pyridine to suppress cationic polymerization.

Recently, new three-component catalysts consisting of an oxide of W or Mo, with an halide of P, Al, B, Ti, Sn, U or Si and Et_2AlCl or LiAlH_4 have been described.⁷⁹⁻⁸¹

I.3. Mechanistic Aspects of Ring-opening Polymerization

Cycloalkene monomers can undergo polymerization by two distinct pathways,^{21,24} Figure 1.6.

(i) Path A, double-bond opening, is conventional addition polymerization. The polymer produced by this path is saturated and retains the cyclic unit.

(ii) Path B, ring-opening, results in a retention of unsaturation and loss of a ring system. The total number and type of carbon-carbon bonds being the same before and after the polymerization. Path B may produce linear and/or macrocyclic products.

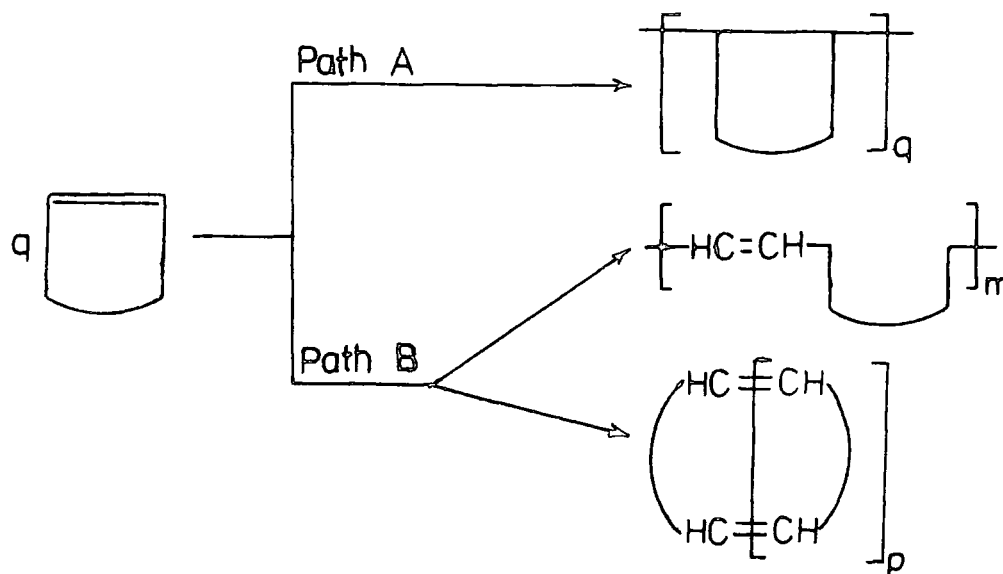


Figure 1.6.

Metathesis catalysts give predominantly the products derived from Path B, although in many cases products arising from both Path A and Path B can be detected.^{12,21,24,70,82,83} Generally, the activity of the cycloalkene and the type of polymerization observed depends closely⁸⁴ on:

the ring size of the cycloalkene; the degree of substitution; whether the ring is part of a mono or polycyclic system; the nature of the metathesis catalyst; and the polymerization conditions.

I.3.a. The Overall Result of Ring-opening Polymerization

The first problem to be solved was the identification of the bonds which are broken and made during the reaction. There are two possible reaction schemes:

(i) a transalkylation scheme, which involves cleavage of a carbon-carbon single-bond adjacent to the double-bond as shown in Figure 1.7,

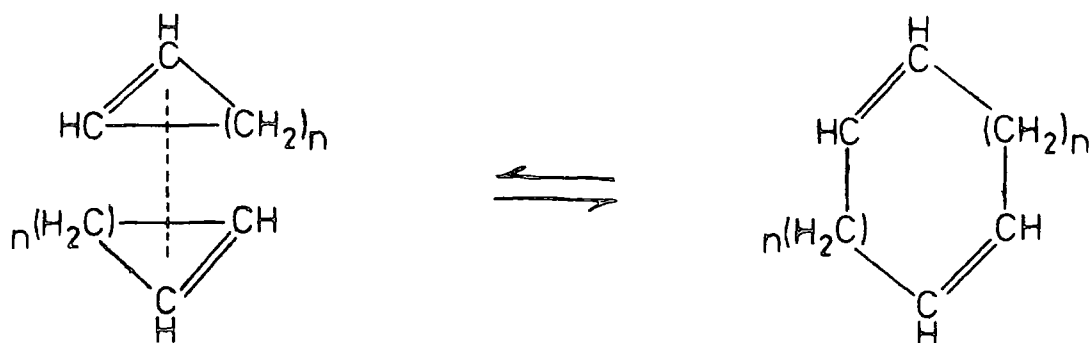


Figure 1.7.

and (ii) a transalkylidenation scheme, which involves the cleavage of the double-bond itself as shown in Figure 1.8.

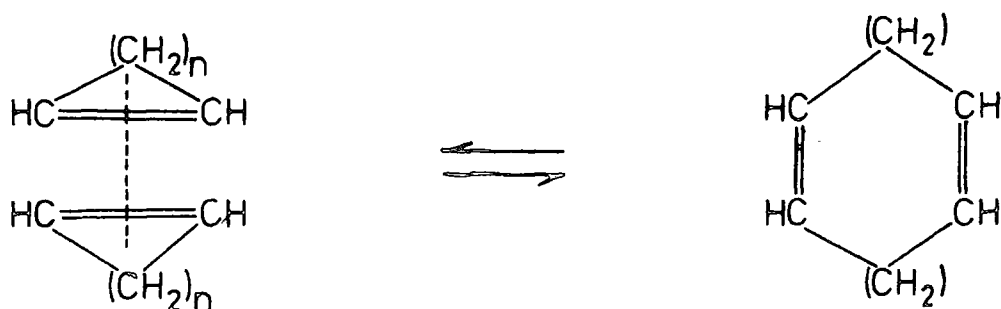


Figure 1.8.

Calderon proposed the transalkylidenation scheme for ring-opening polymerization of cycloalkenes and metathesis of acyclic alkenes, ruling out Natta's¹⁴ earlier proposal of transalkylation. Later, Dall'Asta and Motroni^{21,85} provided direct experimental evidence that in ring-opening

polymerization of cycloalkenes, the cleavage occurs at the double-bond. This was done by copolymerization of samples of cyclooctene and cyclopentene in which the cyclopentene vinyl carbons were labelled with ^{14}C . The resulting polymers may have the structures shown in Figure 1.9, depending on whether cleavage takes place at the double-bond or at the carbon-carbon single-bond adjacent to the double-bond. Ozonolysis of the copolymer, followed by reduction produced the glycols shown in Figure 1.10.

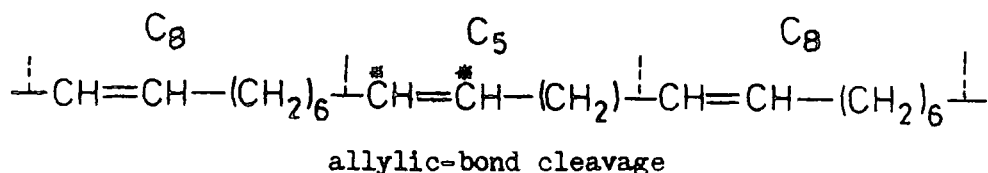
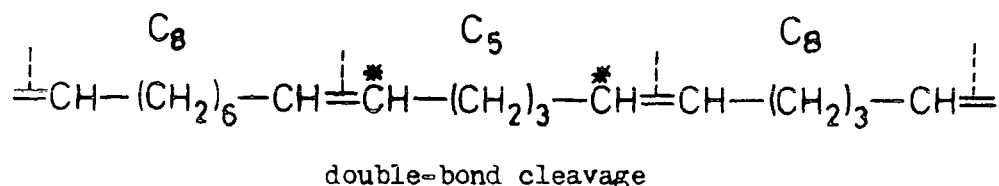


Figure 1.9. (* denotes ^{14}C labelling)

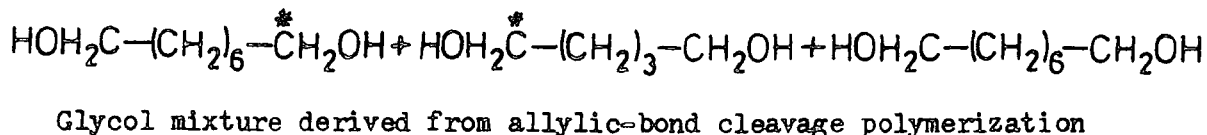
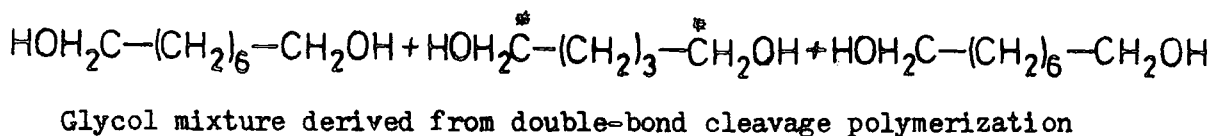


Figure 1.10.

They showed that essentially all starting radioactivity was retained by pentane diol.

Confirmation of this result was obtained from analogous studies of cyclobutene/3-methylcyclobutene copolymerization⁸⁶ using ¹⁴C labelling, and related studies using deuterium labelling of acyclic alkenes.^{16,43,87,88}

1.3.b. The Detailed Mechanistic Pathway of Metathesis Ring-opening Polymerization

The detailed mechanistic pathway is more complicated and difficult to establish, it has been the subject of many investigations, and several mechanistic proposals. Three schemes for the transalkylidene pathway have been proposed:-

(i) the intermediacy of a 'Quasi-Cyclobutane',^{17,26,89}

(ii) a metallocyclopentane intermediate,⁹⁰⁻⁹³

and (iii) a process involving metallocyclobutane/metal-carbene intermediates.^{94,95}

To date, the most widely accepted mechanism for both metathesis of acyclic alkenes and ring-opening polymerization is the third proposal which will be examined in more detail.

1.3.c Metallocyclobutane and Metal-carbene Intermediates in Ring-opening Polymerization

This non-concerted mechanism which involves an alkylidene interchange via a metallocyclobutane intermediate was proposed by Herrisson and Chauvin⁹⁴ and the essential idea is shown in Figure 1.11.

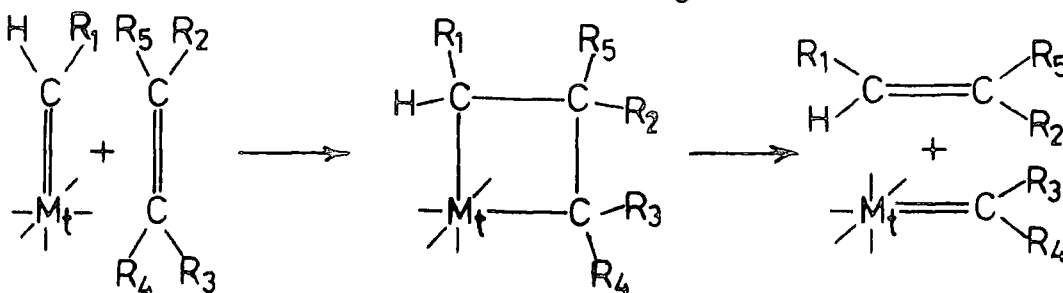


Figure 1.11.

Although various pairwise macrocyclization mechanistic rationalizations were popular for several years, there is much evidence for this mechanism and it is now generally accepted that ring-opening polymerization of cycloalkenes proceeds via chain reaction with the carbene as the chain carrier. Some of the main evidence supporting the Chauvin mechanism as opposed to a pairwise macrocyclization is listed below.

(i) High molecular-weight linear polymer is observed as the main fraction in the ring-opening polymerization of cyclooctene and cyclo-dodecene.⁹⁶

(ii) High molecular-weight polymer is obtained when the ring-opening polymerization is terminated at low conversion,^{37,97} which is characteristic of a chain process as opposed to step-growth process.

(iii) In early work,⁹⁷ the use of very small quantities of PhCHN_2 with WCl_6 or MoCl_5 lead to polymerization which was rationalized in terms of the formation metal-carbene complexes as shown in Figure 1.12.

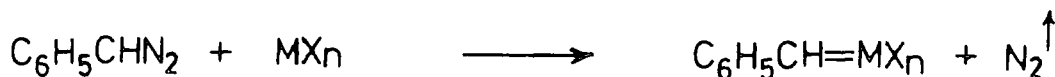


Figure 1.12.

The major breakthrough in support of the metallocyclobutane/metal-carbene pathway was the synthesis and demonstrated metathesis activity of the stable carbene complex, $(\text{CO})_5\text{W}=\text{C}(\text{C}_6\text{H}_5)_2$.⁵⁴ Later, it was used to initiated ring-opening polymerization of several cycloalkenes without the requirement of a cocatalyst.⁵¹⁻⁵⁴

The metallocyclobutane mechanism accounts for ring-opening polymerization which can be understood in terms of chain growth as shown in Figure 1.13.

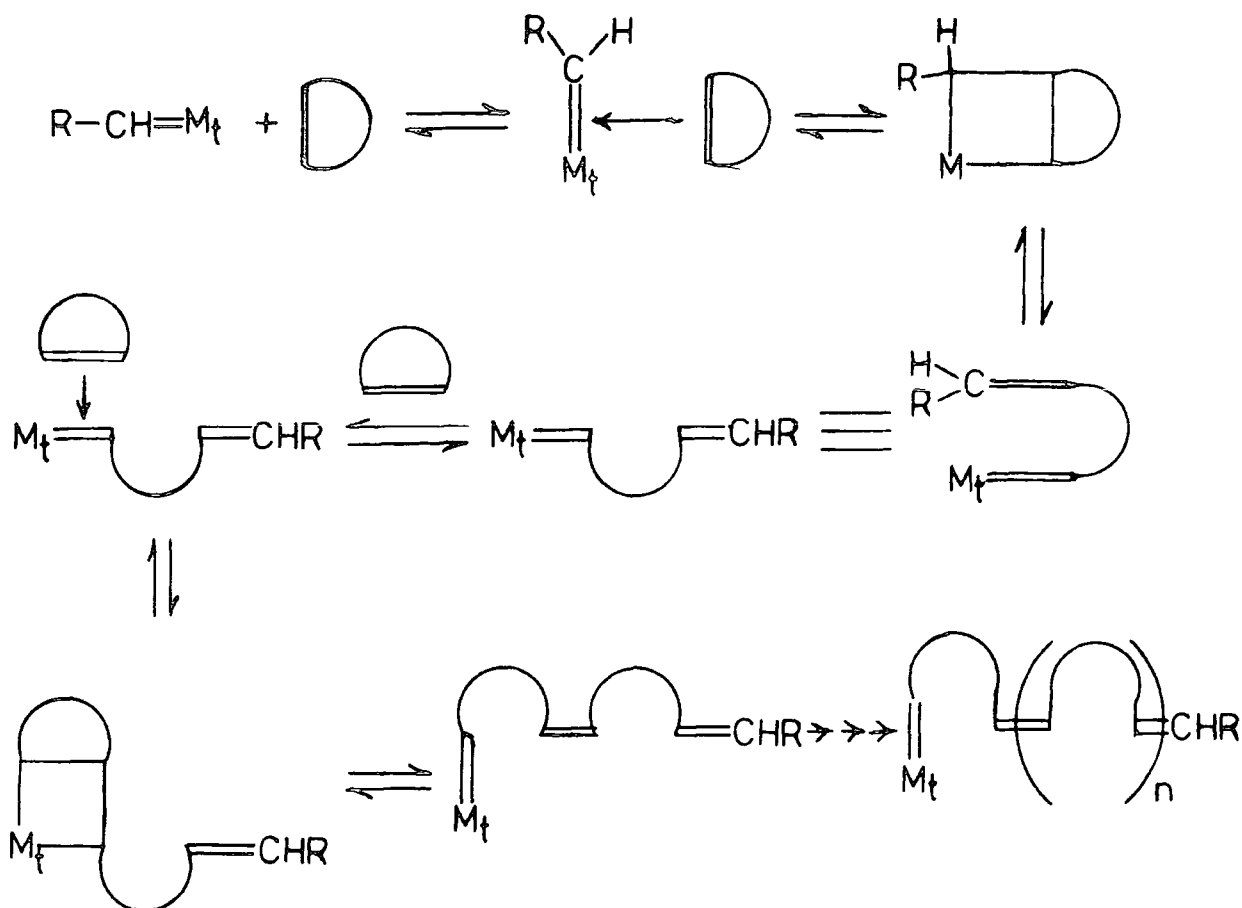


Figure 1.13.

The primary processes for all chain reactions are initiation, propagation and termination and these are discussed in the following three sections.

1.3.c.i. Metal-carbene Initiation

There is now much evidence to support the proposal^{25,98-102} that a metal-carbene is both an active center and a chain carrier in ring-opening polymerization. Particularly strong support for the metal-carbene involvement was provided by the exchange of alkylidene fragments between the stable metal-carbene, $(CO)_5W=C(C_6H_5)_2$ and acyclic alkenes,⁵⁵ and initiation of ring-opening polymerization by stable metal-carbenes.

Generally, metal-carbenes are classified into three categories.

The first group are stable metal-carbene compounds such as the Casey⁵⁵

and Fischer carbenes⁵¹⁻⁵³ (see Figure 1.4.)

The second group are metal-carbenes generated by a catalyst system, sometimes with the assistance of the substrate olefin.²⁵ Many modes of interaction have been reported to generate metal-carbene complexes, and this is presently an active area of investigation.¹⁰³⁻¹¹⁸ Metal-carbenes generated from σ -bonded alkyl-metal cocatalysts were proposed by Muettterties,¹¹⁹⁻¹²⁰ when he observed CH_4 generation by reacting $(\text{CH}_3)_2\text{Zn}$ with WCl_6 as shown in Figure 1.14.

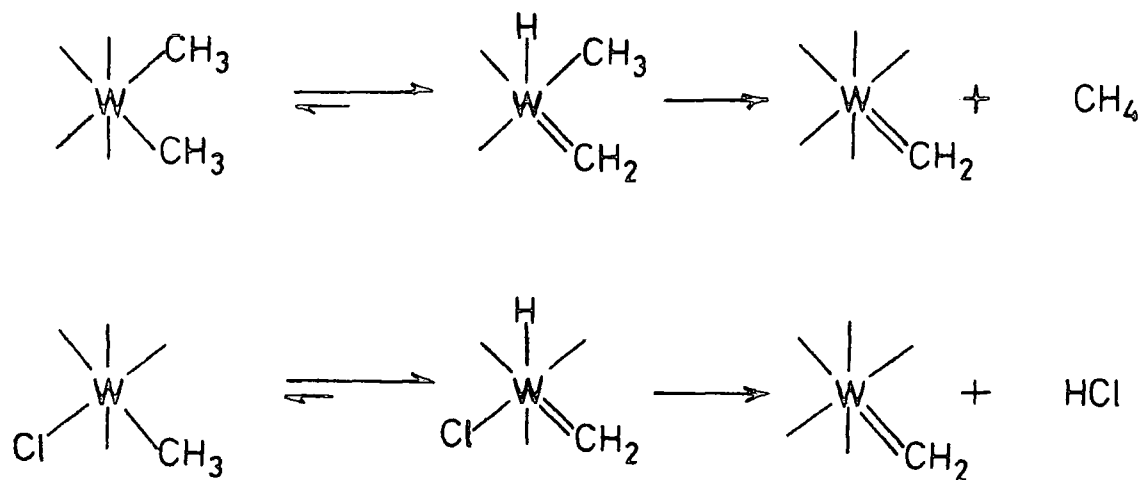


Figure 1.14.

Grubbs¹²¹ observed that $(\text{CH}_3)_4\text{Sn}$ and WCl_6 formed carbenoid species from which alkenes could be generated, this was demonstrated using $(\text{CD}_3)_4\text{Sn}$ as cocatalyst as shown in Figure 1.15. Formation of carbenoid species by α -hydrogen migration from an alkyl group to the metal, as shown in Figure 1.14, has been postulated earlier¹²² and received support from Rooney.²⁵



Figure 1.15.

These observation suggested that alkyl- or aryl-groups play an important role in generating metal-carbenes; however this leaves the

problem of how catalysts which do not contain any alkyl- or aryl-groups generate a metal-carbene. Recently, Amass^{71,72} reported that oxygen activated some catalyst systems and proposed the formation of a W=O site as shown in Figure 1.16.

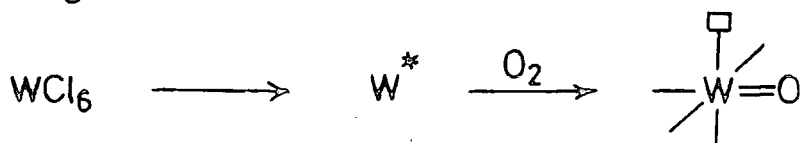


Figure 1.16.

Generally, stable metallocarbenes^{52,53} have a six-coordinate structure, but the metallocarbenes generated in a metathesis reaction are harder to define¹²³ with respect to the oxidation state of the transition metal, the nature and the number of permanent ligands and their spatial arrangement. It has been assumed that the geometry is pseudooctahedral with one position occupied by the carbene-ligand and at least one position left vacant for coordination of the substrate. This topic is one in which it is difficult to obtain definitive information.

1.3.c.ii. Propagation

It is widely accepted that the propagating species in ring-opening polymerization is a metal-carbene operating as a chain carrier and represented as $[\text{M}_t]=\text{CHP}_n$ where P_n is the polymer chain. There are a number of ligands around $[\text{M}_t]$ but vacant sites allow the monomer to coordinate and subsequently to generate an intermediate metallocyclobutane as shown in Figure 1.17.

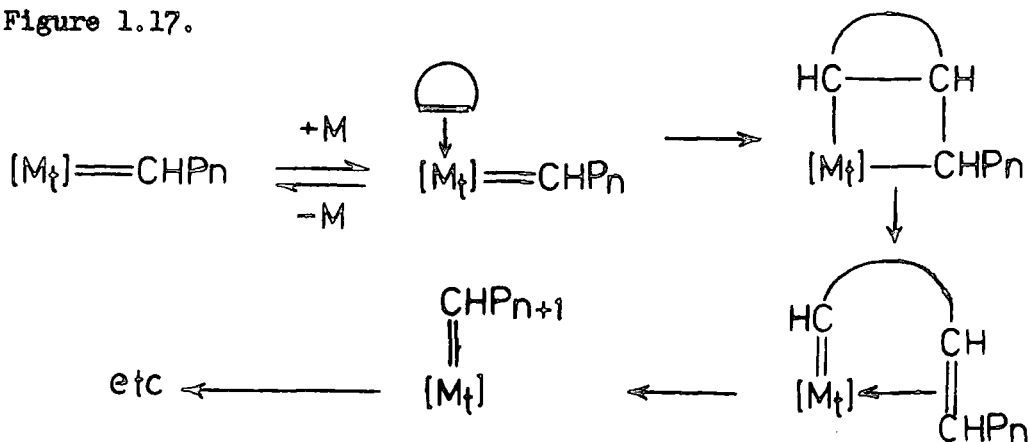


Figure 1.17.

The initial metallocyclobutane has not been definitively established^{65, 95, 124} because very high molecular-weight polyalkenamers are formed at very low conversion. Often, the ring-opening polymerization of cycloalkenes may result in the formation of cyclic oligomers and linear polyalkenamers,^{5, 94, 125-127} which can be rationalized in terms of intramolecular metathesis as shown in Figure 1.18.

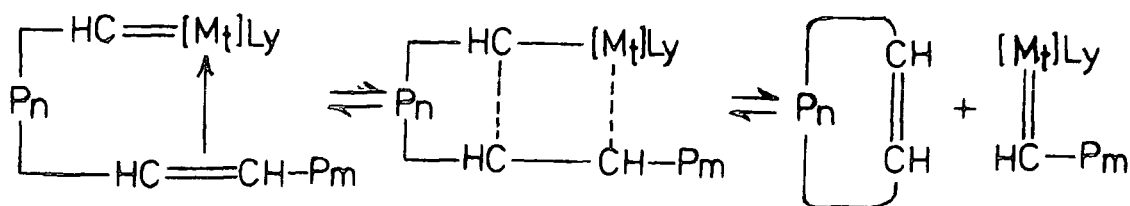


Figure 1.18.

There is evidence to support the formation of a metallocyclobutane as an intermediate.^{50, 51, 120, 128-137} Recently, Green et al¹³⁸ observed that the reaction of a stable metallocyclobutane by thermolysis or photolysis gave a metal-carbene plus an alkene which was rationalized as shown in Figure 1.19.

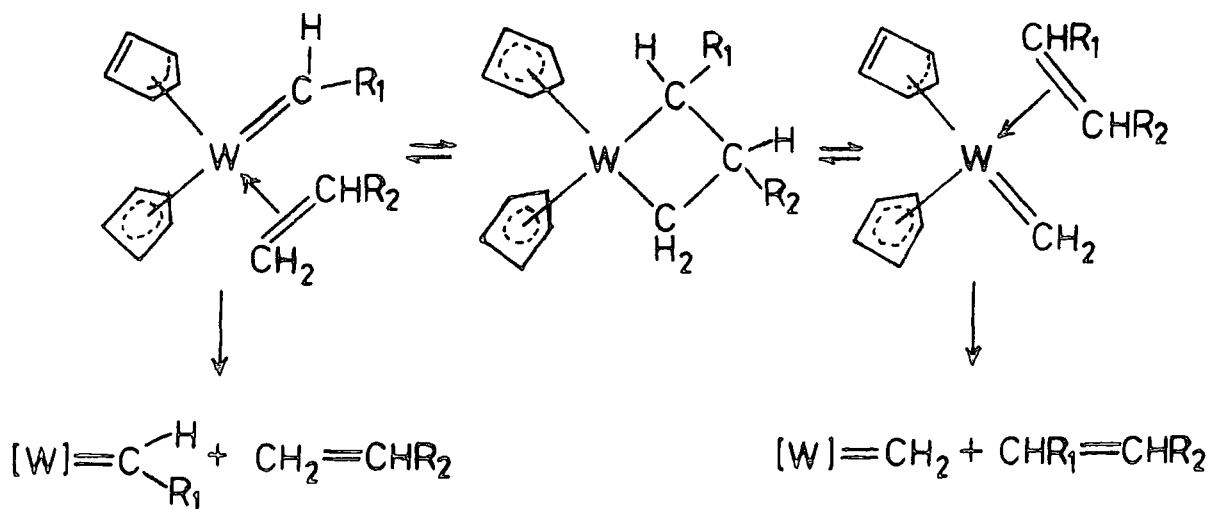


Figure 1.19.

The propagation step is important in controlling the stereoselectivity of the polymer and much work has been carried out by Ivin and coworkers. This will be discussed in Section 1.3.d.

1.3.c.iii. Termination

Generally, termination can be divided into two modes;

- (i) the active species being destroyed by impurities,^{105,139-143}
- or (ii) the active species being consumed via a side reaction.

For the first mode, it is well established that compounds such as alcohol, oxygen or water can destroy the active catalysts. The second mode is not very well established and several schemes have been proposed for different systems.

A common reaction of carbenes is the formation of a cyclopropane, as shown in Figure 1.20, and this is a plausible chain terminating step.

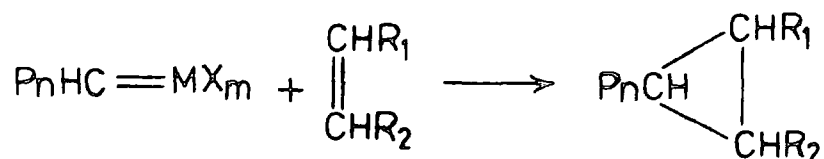


Figure 1.20.

Recently, it was suggested that ring-opening polymerization and Ziegler-Natta polymerization are mechanistically related⁶ as shown in Figure 1.21, termination could occur by β -hydrogen atom abstraction as shown in Figure 1.22.

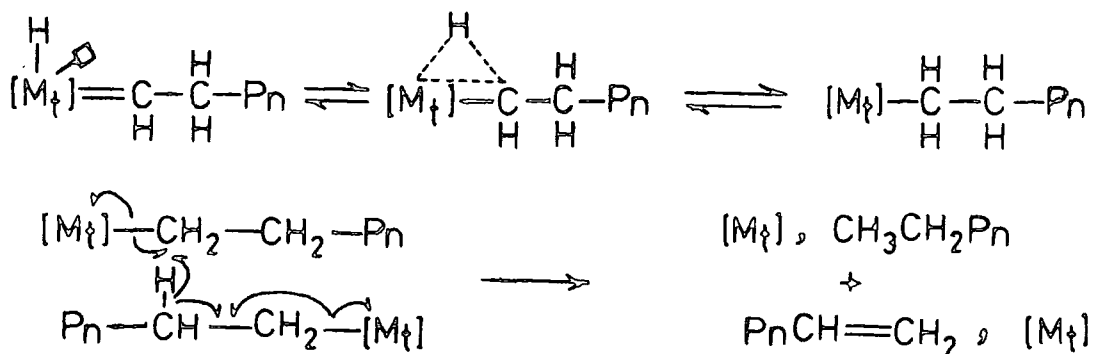
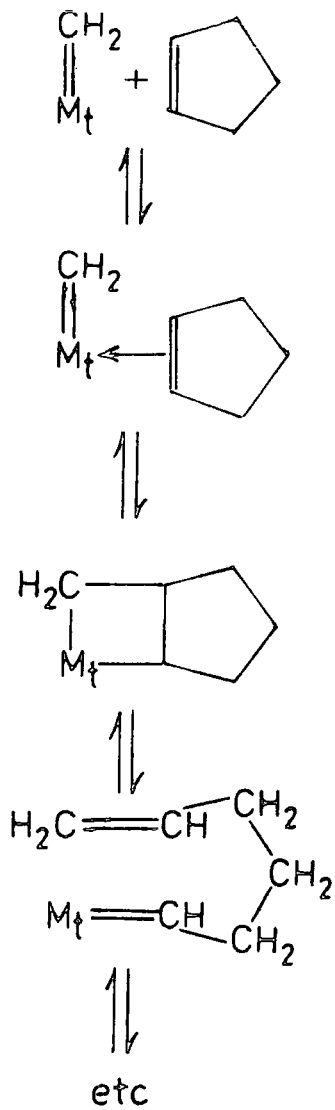
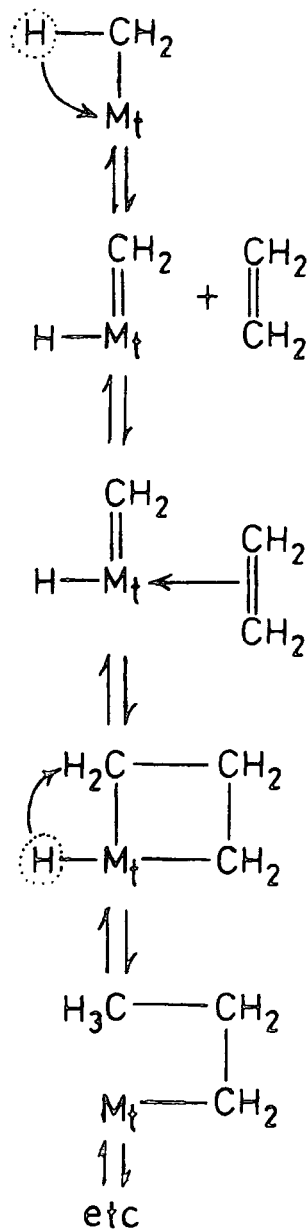


Figure 1.22.

Olefin Metathesis
 Mechanism For The Ring-
 opening Polymerization
 of cycloalkenes



Unconventional Ziegler-
 Natta Polymerization
 Mechanism



Conventional
 Ziegler-Natta
 Polymerization
 Mechanism

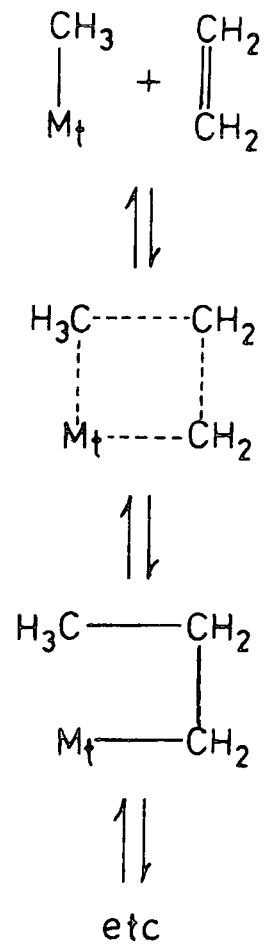


Figure 1.21.

1.3.d. Stereochemical Control

The most important attributes of metathesis catalysts are their ability to retain unsaturation and to control stereoregularity throughout the polymerization. Generally, monomers for ring-opening polymerization via metathesis can be classified in two main types; monocyclic, such as cyclobutene (3) and cyclopentene, and polycyclic, such as bicyclo[2.2.1]-hept-2-ene (4) and its derivatives. In the ring-opening polymerization of a monocyclic compound, the catalyst controls the distribution of cis and trans carbon-carbon double-bonds in the product. With polycyclic compounds, polymerization is more complicated and in addition to cis/trans isomerization, the tacticities of ring placements have to be considered, see Figure 1.23.

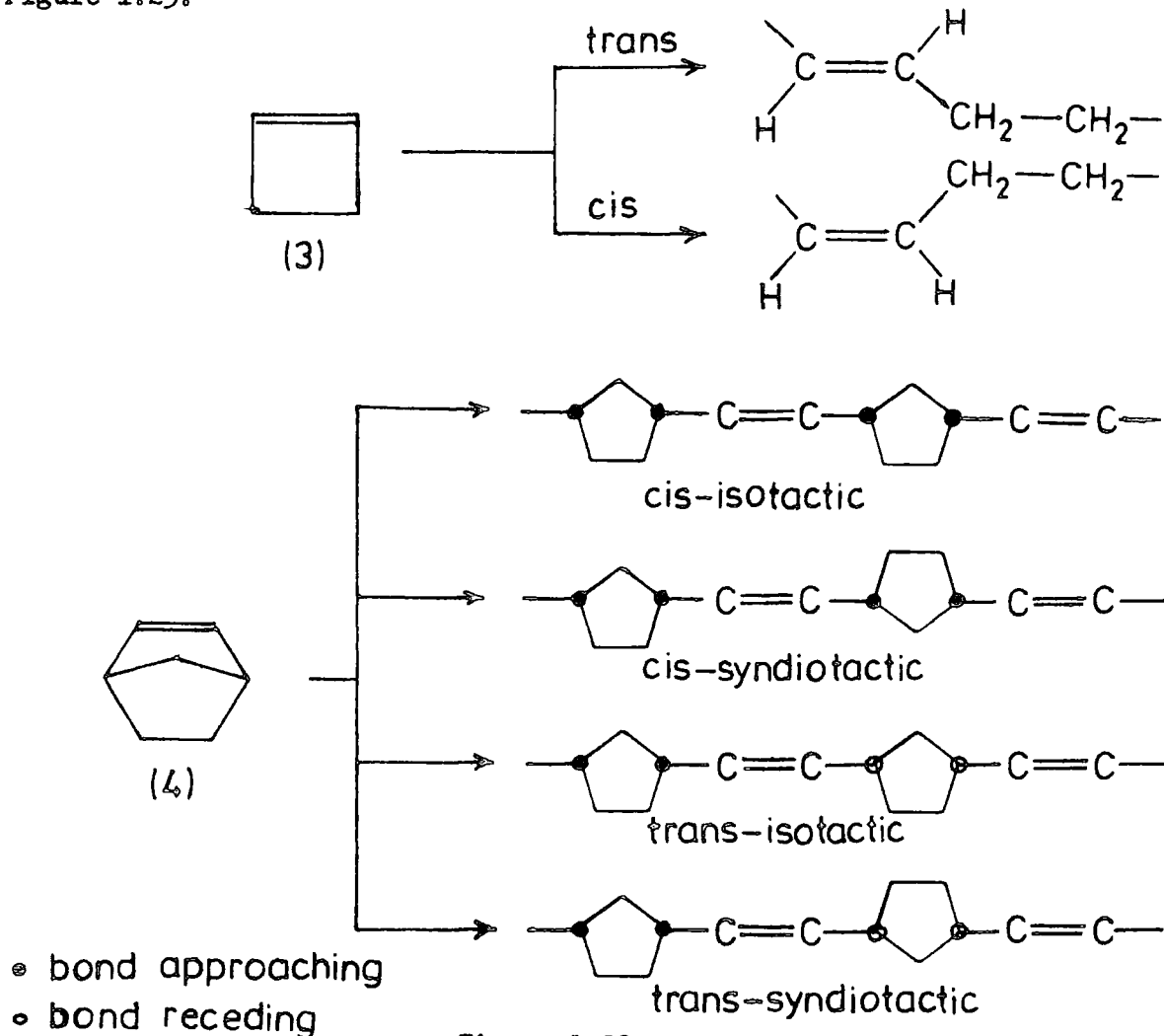


Figure 1.23.

In Figure 1.23, monomers having a plane of symmetry bisecting the opened double-bond were considered, where the monomers lack this symmetry further complications arise through the possibility of Head-Head, Tail-Tail and Head-Tail placements.

The stereochemistry of olefin metathesis has been the subject of much investigation^{25,35,36,144-155} which has tried to rationalize the interaction of a metal-carbene with a substrate olefin. Many hypotheses have been advanced to account for the stereoselectivity observed, including:-

- (i) steric effects during the coordination of the olefin to the metal-carbene,
- (ii) stability of the various conformations of the metallocyclobutane intermediate,
- (iii) steric effects of the ligands at the active centers or steric effects at a surface,
- and (iv) the opening of the carbon-metal bond in the metallocyclobutane intermediate and formation of a substituted metallopropyl cation in which the remaining bonds rotate.¹⁴⁶

The stereoselectivity observed in the acyclic alkenes does not seem to be the same as that observed in cycloalkene polymerization,^{4,35,36,153-155} probably because the metal-carbene remains attached to the polymeric chain as a chain carrier, which does not occur in the acyclic alkene case.

It has been suggested^{4,155} that chelating phenomena favour the concept of precoordination prior to rearrangement to a metallocyclobutane intermediate, with cis-specific catalysts proceeding by a 'three ligand' sequence (5), whereas non-specific catalysts involve a 'two ligand' sequence (6) as shown in Figure 1.24. This hypothesis was based on data concerned with cis-selectivity and the regulation of molecular-weight by added acyclic alkene.

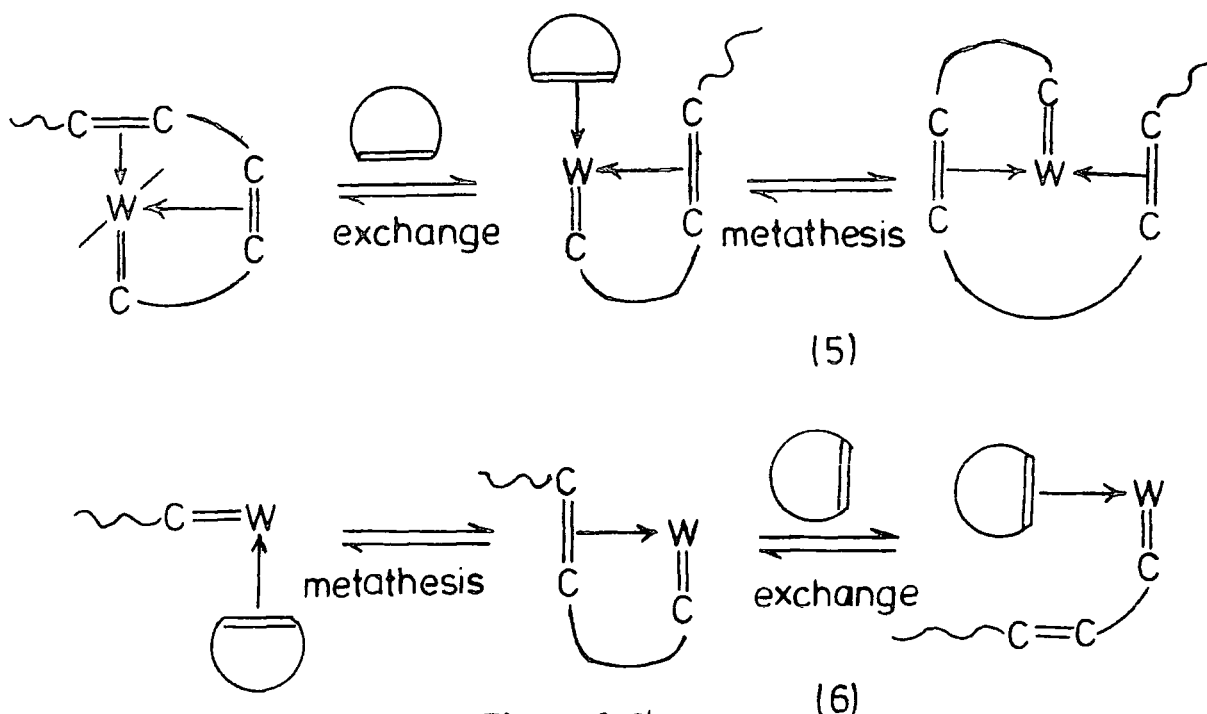


Figure 1.24.

Ivin and coworkers^{100,123,156-161} reported that the detailed analysis of ^{13}C n.m.r. spectra of polymers produced by metathesis gave information on stereochemistry and tacticity which could reveal the mechanism of formation of the polymers.

These authors proposed,^{123,158-161} after analysis of the ^{13}C n.m.r. spectra of high-cis and -trans poly(endo/exo-5-methylbicyclo[2.2.1]-hept-2-ene), that ring-opening polymerization of cycloalkenes involves at least two types of active metal-carbene species which may or may not interconvert during the polymerization. For example, one chain carrying carbene is postulated to be chiral, probably octahedral, and adds monomer to give predominantly cis double-bonds and providing the carbene retains its stereochemical integrity between monomer additions, the product polymer has syndiotactic ring placements.

This view can be understood with the aid of a diagram or model. The propagating metal-carbene is represented as $M_t = \text{CHP}_n$ where P_n is the polymer chain. M_t is pseudo-octahedral with one position occupied by

the carbene ligand and at least one position left vacant for coordination of the substrate olefin.¹²³ The carbene ligand may have one of four possible orientations¹⁵⁰ with respect to the vacancy \square as depicted in Figure 1.25.

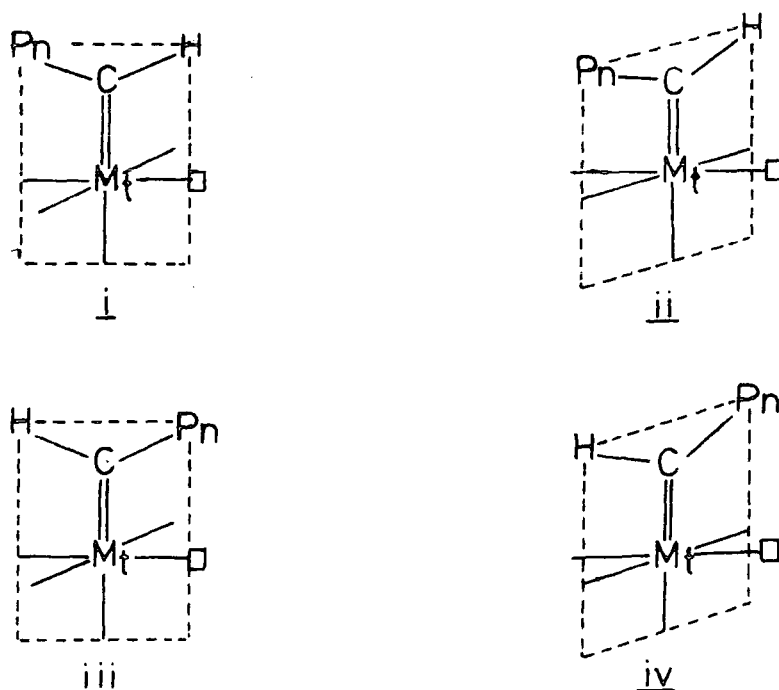


Figure 1.25.

Orientations i. and iii.¹²³ may be ruled out on steric grounds. The exo face of bicyclo[2.2.1]hept-2-ene derivatives is the least hindered¹⁶² and is favoured for coordination with the metal-carbene. There are two ways of coupling the monomer to the metal-carbene according to the relative positions of the bridging methylene (C_7) of the monomer and the polymer chain, P_n ; i.e. whether they are on the same side or the opposite sides. These authors considered the case where the metal-carbene was immobile, this generates four possibilities for coupling since there are four non-equivalent modes of approach of the olefin to the metal-carbene, one mode and its stereochemical consequence is shown in Figure 1.26.

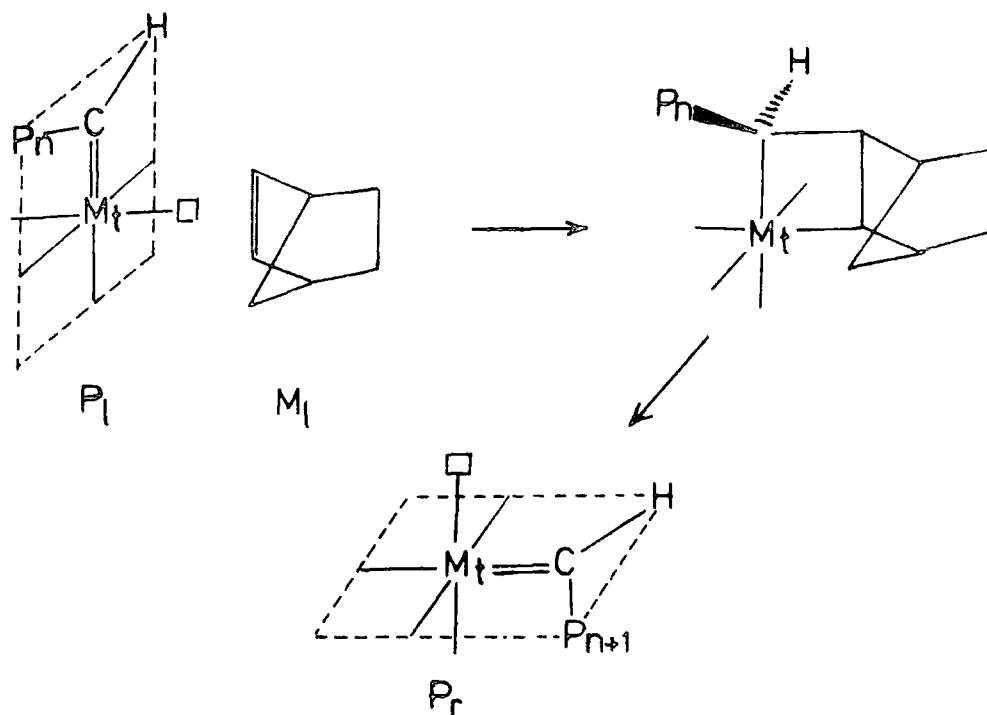


Figure 1.26.

The stereochemical consequences, deduced by Ivin and coworkers, for all possibilities are listed in Table 1.3.

Table 1.3. Stereochemical Consequences Of Different Assembly Modes¹²³

No.	Assembly Modes	Double-bond Form
i.	$P_l + M_l \longrightarrow P_r$	Cis
ii.	$P_r + M_r \longrightarrow P_l$	Cis
iii.	$P_l + M_r \longrightarrow P_l$	Trans
iv.	$P_r + M_l \longrightarrow P_r$	Trans

From Table 1.3, it can be shown that an all-cis polymer is produced when processes i. and ii. occur in strict alternation, or in otherwords that for every insertion of monomer into the metal-carbene, the monomer-C₇ and the polymer chain (P_n) are on the same side in the catalyst complex; and that all-trans polymer proceeds by continuous repetition of process iii. or iv, in otherwords that for every insertion of monomer, the monomer-C₇ and the polymer chain are on opposite sides.

Configuration of the ring or tacticity, depends on the modes of addition of the monomer which can be predicted from Table 1.3 if it is assumed the structure P_r and P_l are preserved between additions of monomer, i.e. that the carbene is conformationally immobile, the all-cis polymer will have a syndiotactic structure. Similar reasoning indicates that an isotactic structure is required for the all-trans polymer, in following this argument in the original literature it is important to recognize that the authors are using the Fischer stereochemical rotation and in the writer's experience the argument is best followed with the aid of molecular models. If each addition is accompanied by racemization, an atactic product will result regardless of the cis or trans double-bond content. In elaborating this theory, these authors proposed that in the formation of high trans polymer there may be total relaxation of the metal-carbene to a structure which is not necessarily octahedral, probably square pyramidal or trigonal bipyramidal with no formal vacant position, and which has an equal chance of adding monomer as M_l or M_r .

Table 1.4. Summary Of Some Observations By Ivin et al. On The Effect Of Different Metal Centers On Stereospecificity Of Cycloalkene Polymerization¹⁵⁷

Metal Center And Postulated Oxidation State	c	Cis and Trans Distribution	Tacticity (with respect to cis)
Re (V) d^2	1.00		Fully syndiotactic
W (IV) d^2	0.36 ↓ 0.79	Various from random to blocky depending on system	Partly atactic to syndiotactic
W (III) d^3			
W (II) d^4			
Mo (IV) d^2	0.35 ↓ 0.76		
Mo (III) d^3			
Mo (II) d^4			
Os (III) d^5	0.46	Random	
Ir (III) d^6	0.21 ↓ 0.44	Random	Atactic
Ru (III) d^5	0.11	Random	Atactic

1.4. Thermodynamic Aspect Of Ring-opening Polymerization

A remarkable feature of the ring-opening polymerization is that the total number and type of the chemical bonds before and after reaction are equal, which for acyclic alkenes means that the enthalpy different is virtually zero.³¹ The questions are: what is the driving force for the cycloalkenes to polymerize?, and why are some cycloalkenes unpolymerizable while others are very reactive with almost any metathesis catalysts? Therefore, an understanding of the thermodynamic aspects of the polymerization processes is of great importance.^{1,22,31,163-165}

1.4.a. The Effect Of Ring Size And Ring Strain

It has been recognized that the tendency of cycloalkenes to polymerize is largely dependant on the ring stability, this is a function of the ease of ring closure,¹⁶³ which depends on entropic and enthalpic factors. Dainton et al¹⁶⁴ described the thermodynamic data for the homologous series of ring compounds as shown in Table 1.5.

Table 1.5. Calculated Enthalpy, Entropy and Free Energy For The Hypothetical Polymerization Of Cycloalkanes at 298 K

Ring size	$\Delta H^{\circ}/\text{kcal. mol.}^{-1}$	$\Delta S^{\circ}/\text{cal. mol.}^{-1} \text{ deg.}^{-1}$	$\Delta G^{\circ}/\text{kcal. mol.}^{-1}$
3	-27.0	-16.5	-22.1
4	-25.1	-13.5	-21.5
5	- 5.2	-10.2	- 2.2
6	+ 0.7	- 2.5	+ 1.4
7	- 5.2	- 0.7	- 4.9
8	- 8.3	+ 8.9	-11.0

The entropy decreases with increase of ring size, but the enthalpy (which arises from the release of ring strain) becomes more favourable to

closure as the ring size increases from three- to six-membered ring, then less favourable up to nine-membered rings and then more favourable again for the larger rings.^{1,164} It can be shown that small ring polymerization is an anti-entropic and enthalpy favoured process, whereas for large rings, it is both enthalpy and entropy favoured. Cyclohexene is exceptional, being a strain free monomer and inert to ring-opening polymerization.^{61,166-168}

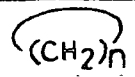
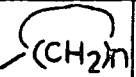
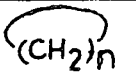
When ring strain is increased for example by some type of bridging, the monomer is able to undergo polymerization because there is a substantial reaction enthalpy and this compensates for the unfavourable reaction entropy. Bicyclo[2.2.1]hept-2-ene is a good example and is an active monomer compared to cyclopentene. Bicyclo[2.2.2]oct-2-ene has been reported to polymerize which has been explained in terms of the two cyclohexene rings being in a boat conformation which has higher strain energy than a chair conformation; however, these reports have not been substantiated by further publication and attempts to repeat this and related polymerizations of bicyclo[2.2.2]oct-2-ene ring system in these laboratories have not met with any success.

Recently,^{53,165} it was reported that some trisubstituted cycloalkenes such as 2-methylbicyclo[2.2.1]hept-2-ene, 1-methyl- and 1-trimethylsilyl-cyclobutene were susceptible to ring-opening polymerization. This was accounted for in terms of the high strain in such monomers.

1.4.b. The Effect Of Substitution

Dainton et al^{164,169} pointed out that substituents on cycloalkanes generally cause an increase in the free energy of polymerization, they compared thermodynamic values of unsubstituted and methyl-substituted cycloalkanes at 25°C as shown in Table 1.6.

Table 1.6. Calculated Enthalpy, Entropy and Free Energy For The Hypothetical Polymerization Of Cycloalkanes¹

Ring size	$\Delta H^{\circ}/\text{kcal.s.mol.}^{-1}$	$\Delta S^{\circ}/\text{cal.mol.}^{-1}\text{deg.}^{-1}$	$\Delta G^{\circ}/\text{kcal.s.mol.}^{-1}$
			
3	-27.0	-25.1	-16.5
4	-25.1	-23.1	-13.2
5	- 5.2	- 4.1	-10.2
6	+ 0.7	+ 2.2	- 2.5

Later, Ivin¹⁷⁰ presented evidence to show that successive alkyl substitution on the same carbon atom makes ΔG° more positive as shown in Figure 1.27 which is a plot of the free energy of polymerization of cycloalkanes versus the number of atoms in the ring for the unsubstituted, mono- and di-substituted cycloalkanes.

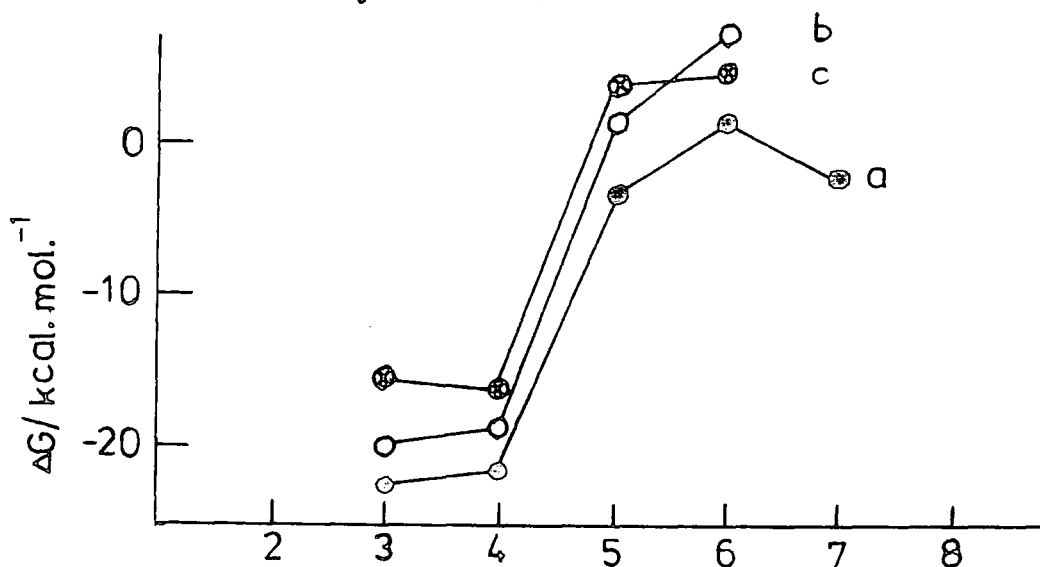


Figure 1.27.

Calculated free energy of polymerization of cycloalkanes as a function of the number of atoms in the rings (n),

(a) unsubstituted (b) methyl-substituted and (c) 1,1-dimethyl-substituted.

Substitution on the ring increases steric hindrance which will reduce the polymerizability of the monomer, for example 1-methylcyclopentene, 3-methylcyclopentene, 3-isopropylcyclopentene and 1H,2H-hexafluorocyclopentene are non-polymerizable, but cyclopentene and 4-methylcyclopentene are very easily polymerized.

Steric factors are also important in situations where alternate modes of reaction are available. Dall'Asta examined the ring-opening polymerization of 3-methyl-cis-cyclooctene and observed that 90% of the links in the poly(methyloctenamer) were of the Head-Tail type and the unfavoured Head-Head links constituted about 5%. Ofstead¹⁷¹ investigated the ring-opening of some cycloocta-1,5-dienes substituted at one of the two double-bonds with an ethyl group, chlorine atoms or two methyl group, the substituted double-bond did not participate in the reaction and the cleavage occurred at the unsubstituted double-bond. This clearly showed that reactivity of double-bonds is strongly reduced or even completely suppressed by steric hindrance, except for highly strained systems.

1.4.c. Temperature Dependence Of The Equilibrium Composition

Ring-opening polymerization by olefin metathesis has been reported^{19,34} 126,165,168 to be a reversible processes which can produce an equilibrium between monomer, oligomer and high molecular-weight polymer, the equilibrium being dependant on reaction conditions. Analysis of the oligomer fraction showed it to consist of cyclic molecules, this can be explained by the metallocarbene mechanism as shown in Figure 1.28, the processes is called⁹⁵ 'back-biting'.

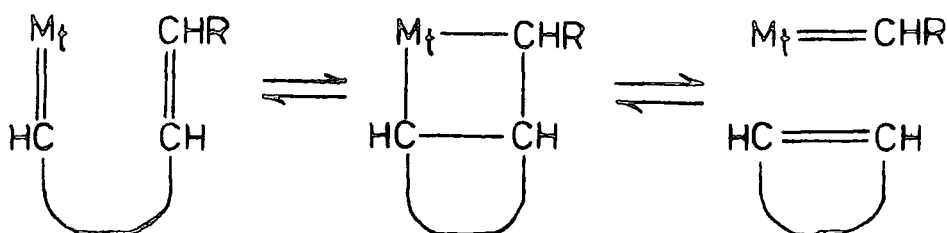


Figure 1.28.

A quantitative determination of the concentration of each cyclic or open chain component in an equilibrated cycloalkene metathesis system is experimentally unattainable; thus, a complete thermodynamic characterization of cycloalkene metathesis is not achievable. However, the monomer-polymer equilibrium for the cyclopentene/poly(1-pentenylene) system has been investigated by Calderon and Ofstead.¹⁶⁸ In this case, the free energy of polymerization (ΔG) is small and very sensitive to small changes in reaction conditions. In two parallel experiment carried out at 0° and 25°, the limiting conversions were approximately 80% and 50% respectively. The reversible interconversion of polymer to monomer was proved; clearly demonstrating that under certain conditions, the polymer is thermodynamically unstable with respect to the monomer.

Theory predicts the relationship

$$\ln[M]_e = \frac{\Delta H_p}{RT} - \frac{\Delta S_p^0}{R}$$

where

$[M]_e$ is the monomer concentration at equilibrium,
 ΔH_p is the enthalpy change during polymerization and
 ΔS_p^0 is the standard entropy change accompanying the polymerization when the monomer concentration is 1 mol.dm.⁻³

The temperature above which long chain polymers are not formed,¹⁵ known as the 'ceiling temperature'.¹⁷⁰ For cyclopentene undergoing ring-opening polymerization to predominantly trans-poly(1-pentenylene), a plot of $\ln[M]_e$ against $1/T$ and extrapolation to $\ln M$ ^{bulk monomer} for λ gives a ceiling temperature of approximately 150°. From the graph values of -4.4 kcal.mol.⁻¹ and -14.9 cal.mol.⁻¹ deg.⁻¹ were derived for ΔH_p and ΔS_p^0 respectively. The enthalpy value (ΔH_p) obtained is close to

the ring strain energy of $4.9 \text{ kcal. mol.}^{-1}$ reported by Cox.¹⁷² This is entirely consistent with the theory that in the ring-opening polymerization of cycloalkenes, the main contribution to ΔH_p is strain energy. For cyclopentene undergoing ring-opening polymerization to predominantly cis-poly(1-pentenylene) using the catalyst system $\text{WCl}_6/\text{tetraallylsilane}$, a 'ceiling temperature' for the formation of cis-poly(1-pentenylene) is 51° .¹⁷³

1.5. Side Reactions In Ring-opening Polymerization

It is often the case in the study of catalysts by kinetic measurements or in the synthesis of polymers by ring-opening polymerization, that reproducibility is poor and side reactions often occur although the experiment is carried out under dry and inert conditions.

1.5.a. Catalyst Deactivation

It is difficult to obtain a catalyst with a constant reproducible activity³⁴ because of catalyst decay which can lead to varying induction periods. Poor reproducibility can be caused by many factors, including sensitivity of the catalyst to traces of impurities in the reactants which are usually difficult to remove, dependence of the catalytic activity on storage conditions, activation method and general experimental procedure. Generally, olefin metathesis catalysts are deactivated by oxygen and moisture, but a trace amount of oxygen may improved the activity of the catalyst. The activator or modifier which is used as a third component is usually in stoichiometric amounts, because an excess of it would often destroy the catalyst activity.

1.5.b. Addition Polymerization

Ivin and coworkers⁷⁰ reported that most catalyst systems of the metathesis type do not give pure metathetical polymerization, but also cationic type reaction. Thus, polymerization of 5-methylenebicyclo[2.2.1]hept-2-ene with many metathesis catalysts leads to substantial amounts of the product of route (I), Figure 1.29.

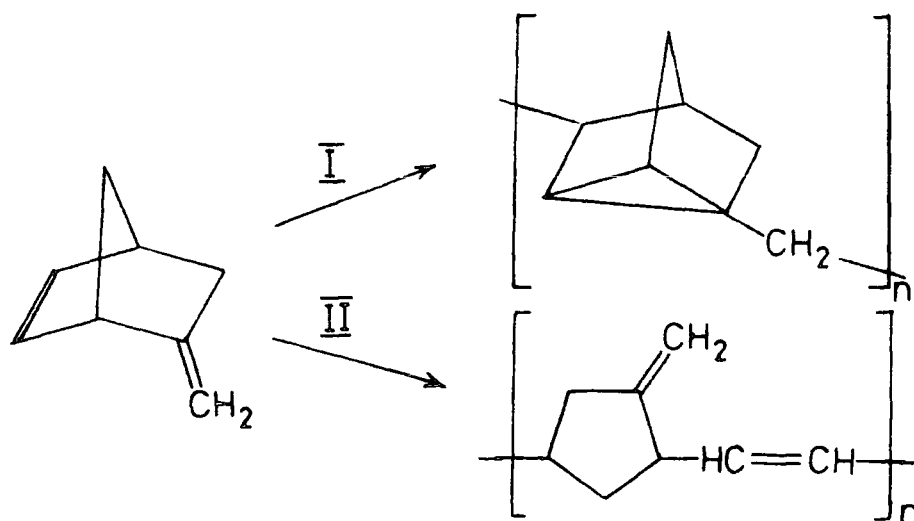


Figure 1.29.

However, three catalyst systems which gave only ring-opening polymerization were $\text{WCl}_6/\text{Et}_3\text{Al}$ (1:1 to 1:5) in chlorobenzene or dichloroethylene, $\text{MoCl}_5/\text{Et}_3\text{Al}$ (1:2) in dichloroethylene and $\text{WCl}_6/\text{Me}_4\text{Sn}/\text{spartein}$ (1:1.3:1) in chlorobenzene. It was reported that premixing of the catalyst and cocatalyst is important before adding the monomer and the proportion of spartein is also very critical. Other bases can be used, but complete suppression of reaction (I) is not always achieved.

The stoichiometric relationship of catalyst and cocatalyst also plays an important role,⁹ as in the polymerization of bicyclo[2.2.1]hept-2-ene using $\text{TiCl}_4/\text{Et}_2\text{AlCl}$ catalyst. A molar ratio 1:2 proceeds via ring-opening, whereas at 2:1 addition polymerization occurs exclusively.

1.5.c. Friedel-Crafts Activity

Along with metathesis activity, halides of transition metal compounds i.e. WCl_6 and $MoCl_5$ also exhibit strong Friedel-Crafts activity and may easily induce extensive side reactions i.e. alkylation of solvent,¹⁷⁴⁻¹⁷⁸ shift of the double-bonds along the chain,^{77,160,179} cis/trans isomerization¹⁶⁰ and cross-linking of polyalkenamers.

1.6. Some Recent Application Of Olefin Metathesis In Polymerization

The synthetic applications of olefin metathesis to polymer chemistry are numerous and some are described in this section, but the commercial-scale applications are limited due to economic factors.

1.6.a. Synthesis Of Unsaturated Polymers

Cycloalkenes possessing unsaturation sites as constituents of the cyclic ring or one of the rings and not being conjugated³ have the potential to undergo polymerization by ring-opening. This provides an interesting class of polymers which differ from conventional polymers in that they maintain the unsaturation of the monomer. Cycloalkenes with four or more carbons in the ring, with the exception of cyclohexene, have been polymerized to produce polyalkenylenes and, depending upon the structure of the repeat unit and the double-bond configuration, these polymers may possess properties ranging from amorphous elastomers to crystalline materials. Some of the polyalkenylenes which have commercial potential are trans-poly(1-pentenylene)^{22,180} and trans-1,5-polyalkenamer²⁴ for tyre manufacture, poly(4-cyano-1,3-cyclopentylenevinylene) as a thermoplastic resin,¹⁸¹ poly(1,3-cyclopentylenevinylene) and poly(1-octenamer) were commercialized under the trade names Norsorex¹⁸² and Vestenamer 8012^R.¹⁸³

1.6.b. New Routes To Alternating Copolymers

Ring-opening polymerization of substituted cycloalkenes provides a route to perfectly alternating copolymers which cannot be prepared by conventional polymerization.^{3,171,184} For example, 1-chloro-1,5-cyclooctadiene yields the alternating copolymer of butadiene and chloroprene (Figure 1.30, X=Cl); 1-methyl-1,5-cyclooctadiene yields alternating copolymer of butadiene and isoprene (Figure 1.30, X=CH₃).

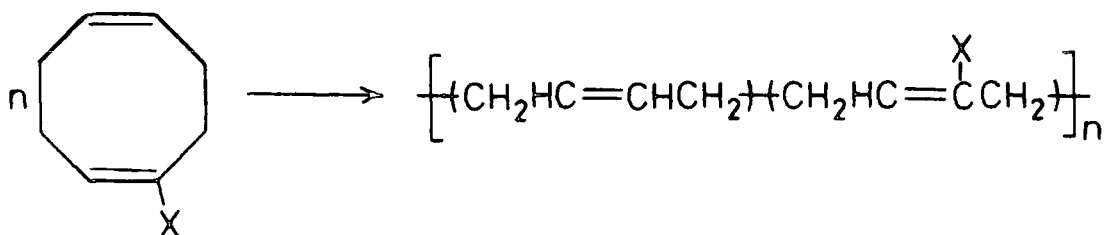


Figure 1.30.

Ring-opening polymerization of 5-methylcyclooctene gives the perfectly alternating terpolymer of butadiene, ethylene and propylene as shown in Figure 1.31.

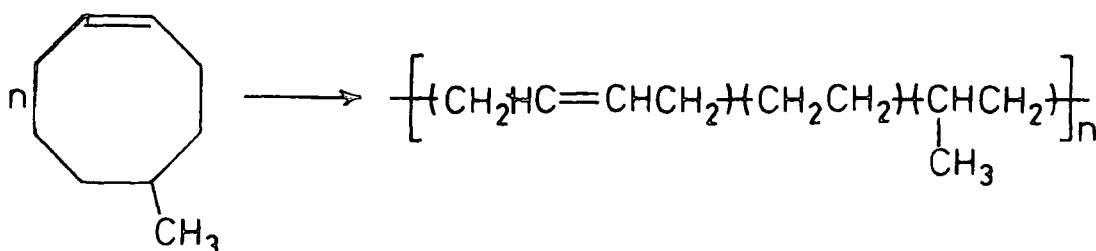
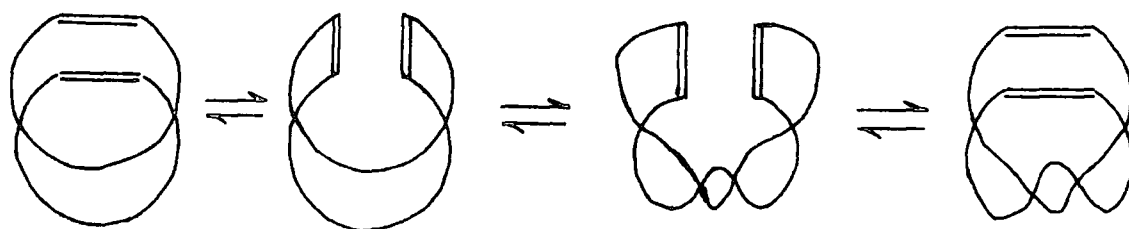
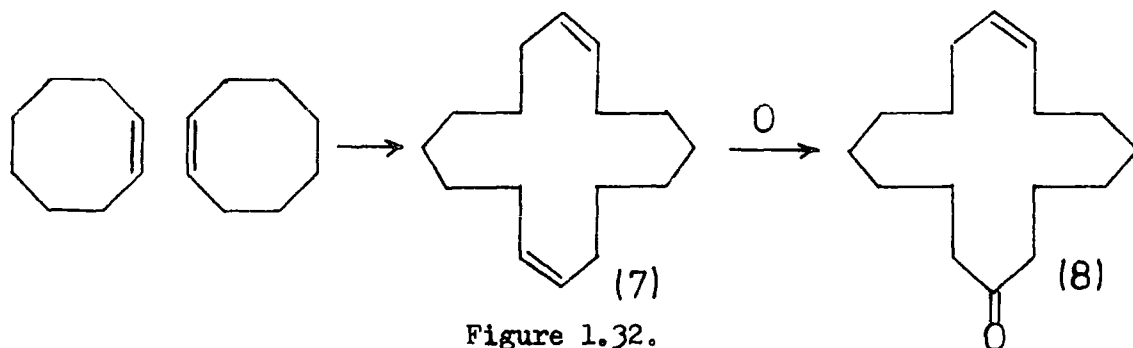


Figure 1.31.

1.6.c. Synthesis Of Macrocyclic Compounds

A significant feature of ring-opening polymerization by metathesis catalysts is formation of cyclic oligomers^{95,185} which can be isolated from linear high molecular-weight polymers. The position of the ring-chain equilibrium in the reaction can be changed by conducting the reaction at high dilution, this usually leads to the formation of high yields of macrocyclic compounds.¹⁸⁵ Two interesting materials have been prepared

by this technique; namely cyclohexadeca-1,9-diene (7), the cyclic dimer of cyclooctene which when oxidized produced a ketone (8) with a musk-like odour,¹⁸⁶ Figure 1.32 and catenanes, the interlinked ring systems, which form part of the product from the metathesis of cyclodecene,^{187,188} Figure 1.33.



1.6.d. Cross-metathesis with Acyclic Alkenes

The cross-metathesis reaction of acyclic alkenes with cycloalkenes can be directed towards the formation of dienes, trienes, higher polyenes¹⁸⁹⁻¹⁹¹ and gives rise to formation of liquid polymers of α,ω -difunctionalized polyenic molecules,¹⁹²⁻¹⁹⁵ depending on the prevailing ratio of acyclic to cyclic olefins employed.

Some examples of α,ω -dienes¹⁸⁹ are 1,9-decadiene ($n=6$), 1,13-tetradecadiene ($n=10$) obtained by cross-metathesis of cyclooctene and cyclododecene respectively with ethylene as shown in Figure 1.34.

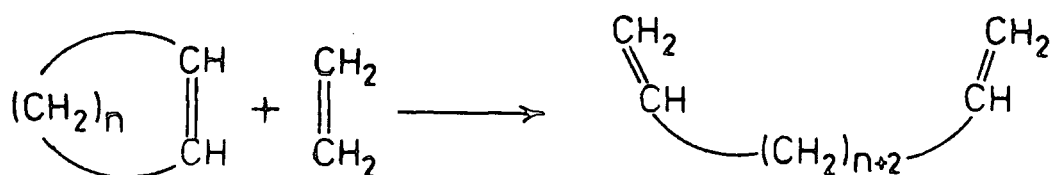


Figure 1.34.

The type of product can be controlled using different molar ratios of reactants, as shown in Figure 1.35 for the cross-metathesis of 1,5-cyclooctadiene with ethylene which produces either triene or diene.

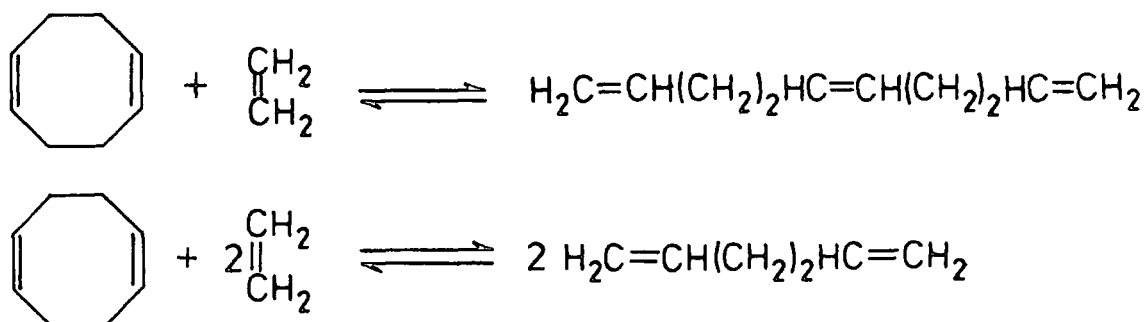


Figure 1.35.

The cross-metathesis also can be used to prepare trienes,¹⁹⁶ eg. 1,5,9-decatriene by cross-metathesis of 1,5-cyclooctadiene with 1,5-hexadiene as shown in Figure 1.36.

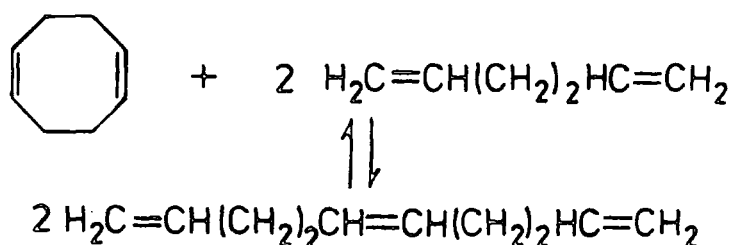


Figure 1.36.

Bis(alkenyl)cycloalkenes^{197,198} can be prepared by metathesis of bicyclic olefins with acyclic olefins as shown in Figure 1.37.

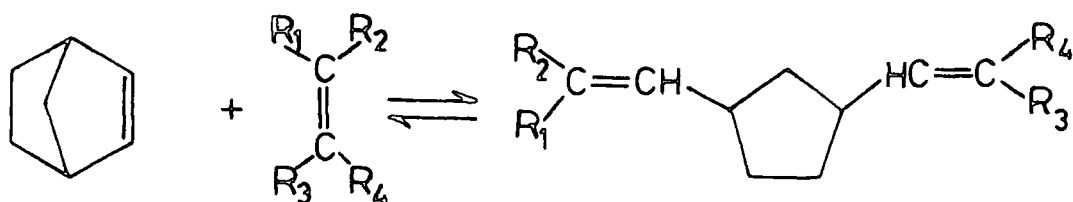


Figure 1.37.

Cross-metathesis between cycloalkenes and functionalized alkenes gives new routes to long-chain linear mono- or di-functionalized compounds which are industrially attractive. Some of the examples are cyclooctene with olefinic ethers,¹⁹⁹ cyclooctene with olefinic esters or diesters,²⁰⁰ 1,5-cyclooctadiene with unsaturated esters which leads to an α,ω -diester 1,4-polybutadiene like polyene²⁰¹⁻²⁰⁴ and cyclohexene with vinyl chloride.²⁰⁵

1.6.e. Polymer Degradation

High molecular-weight unsaturated polymers have been shown to undergo cleavage when cross-metathesized with a low molecular-weight olefin.²⁰⁶⁻²¹⁷ Generally, the reaction gives high yields of oligomers which may be separated and characterized yielding information on the microstructure of the parent polymer. Cyclodegradation of butadiene-propylene copolymer produces some 4-methylcyclohex-1-ene,²¹⁸ which arises from alternating diene/propene sequences in the parent polymer.

1.6.f. Miscellaneous Applications

Olefin metathesis catalysts have been reported to be used for control of molecular-weight and molecular-weight distribution of unsaturated polymers.²¹⁹ For example, polybutadiene with polydispersity lower than 1.5 can give a polydispersity 2 by treatment with $WCl_6/EtOH/EtAlCl_2$ (4:1:1).

Functionally terminated polyolefins can be prepared²²⁰ by olefin metathesis, e.g. polybutadiene when treated in dimethyl-3-hexenedioate with the WCl_6/Me_4Sn catalyst, yields ester terminated polymers which are useful prepolymers.

Recently, Edwards and Feast²²¹ described the preparation of a poly(acetylene) precursor polymer by olefin metathesis. This gives the product by thermally treating the precursor polymer as shown in Figure 1.38.

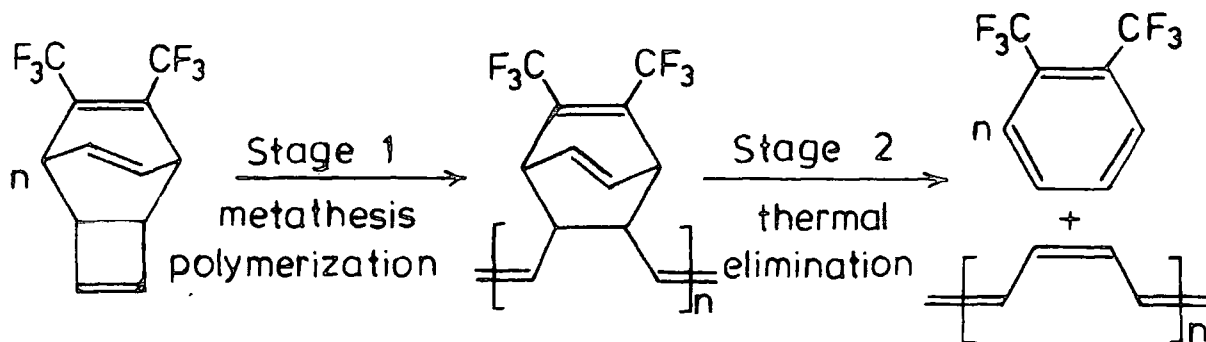


Figure 1.38.

1.7. Polymers By Ring-opening Polymerization Of Cycloalkenes

Monocyclic, bicyclic and tricyclic olefins with or without substituents of a polar or non-polar nature have been polymerized by olefin metathesis. The monomers include unsaturated cyclic hydrocarbons and unsaturated heterocyclic compounds, the latest comprehensive review was published by Dragutan et al.³⁸

1.7.a. Three-membered Ring Monomers

The reaction pathway that yields cleavage of the ring is difficult to achieve²²²⁻²²⁵ due to the extreme reactivity of this system. Cyclopropene polymerized by double-bond opening spontaneously above -80°C.²²³ 1,2-dimethylcyclopropene²²² was the only three-membered ring monomer polymerized by ring-opening with $(\pi\text{-allyl})_2\text{PdCl}_2$ in ether at 0°C, as shown in Figure 1.39.

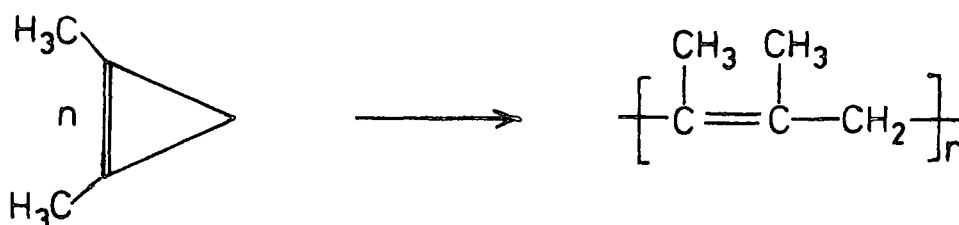
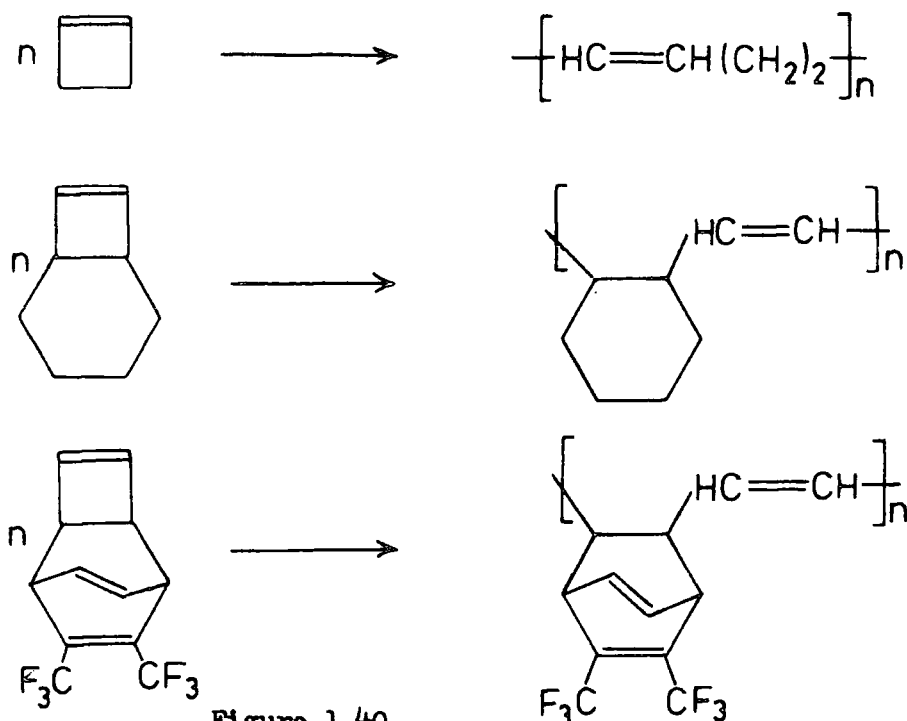


Figure 1.39.

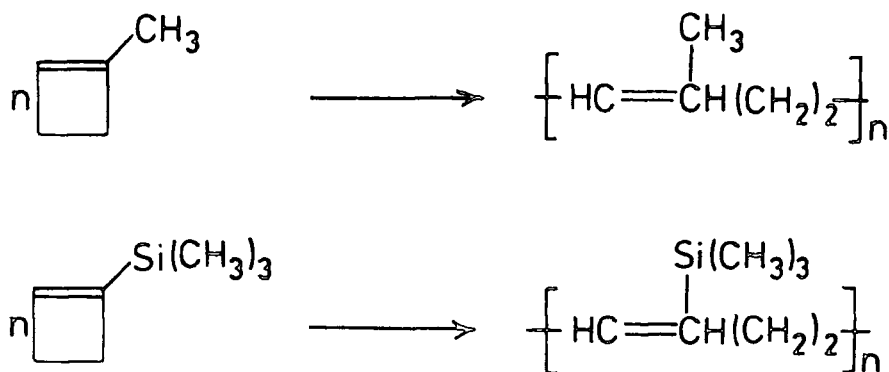
These authors did not discuss the mechanism of the polymerization, compounds of this type do behave as metathesis catalysts.^{22,226}

1.7.b. Four-membered Ring Monomers

Many four-membered rings from monocyclic to tricyclic have been polymerized by ring-opening, ^{11-13,46,53,58,59,82,221,227,228} some examples are shown in Figure 1.40.



1-Methylcyclobutene^{13,228} and 1-trimethylsilylcyclobutene⁵³ have been reported to undergo ring-opening polymerization as shown in Figure 1.41.



1.7.c. Five-membered Ring Monomers

Cyclopentene has been most extensively investigated because of the availability of the monomer and the useful properties of poly(1-pentenylene).²² Substitution on the cyclopentene ring has been reported to effect the polymerizability, this has been discussed in Section 1.4.b.

Heterocyclic cyclopentenoid compounds such as compound (9)^{43,229} and (10)²³⁰ (Figure 1.42) have been reported to polymerize by ring-opening to give linear polysilapentenamer and polygermapentenamer.

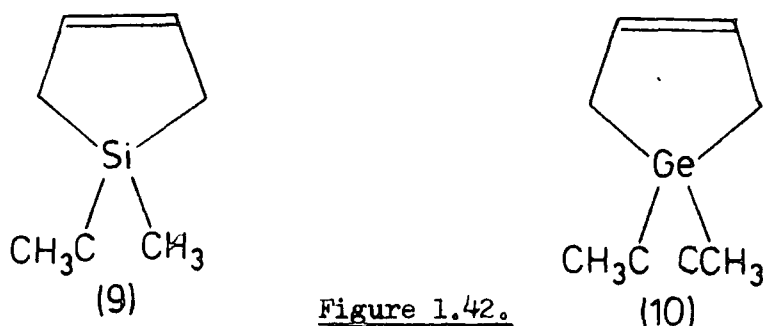


Figure 1.42.

The bicyclo[2.2.1]hept-2-ene ring system polymerizes easily by ring-opening due to its strained five-membered ring; thus numerous functionalized polymers have been prepared by the sequence depicted in Figure 1.43, where the substituents are ester,²³¹⁻²⁴⁰ hydroxy,²³² chlorine,^{45,241} fluorine,²⁴² alkoxy,^{243,244} amide,²⁴⁵ imide,^{233,246} anhydride,²⁴⁰ pyridyl,²⁴⁰ nitrile,^{238,241,247} aryl²⁴⁸ and cyanide.^{243,249} Recently, Streck^{183,250} reported new silicone and tin containing polymers prepared from monomers as shown in Figure 1.44.

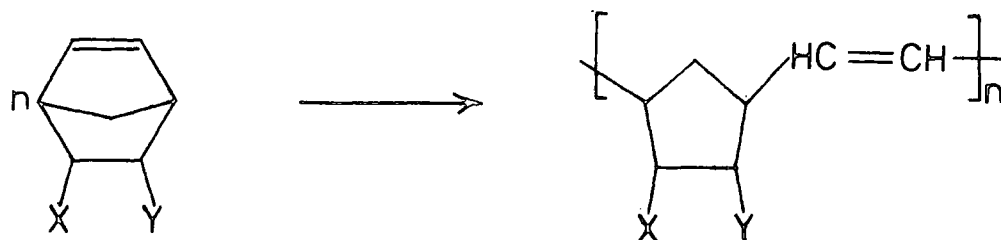


Figure 1.43.

Ofstead^{171,251} reported that ^{the} highly chlorinated bicyclo[2.2.1]hept-2-ene ring system as shown in Figure 1.44, may be homopolymerized or copolymerized with cyclopentene.

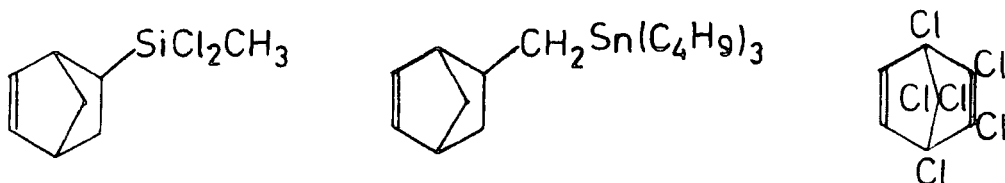


Figure 1.44.

Recently, Katz et al⁵³ reported that 2-methylbicyclo[2.2.1]hept-2-ene polymerized by ring-opening as shown in Figure 1.45.

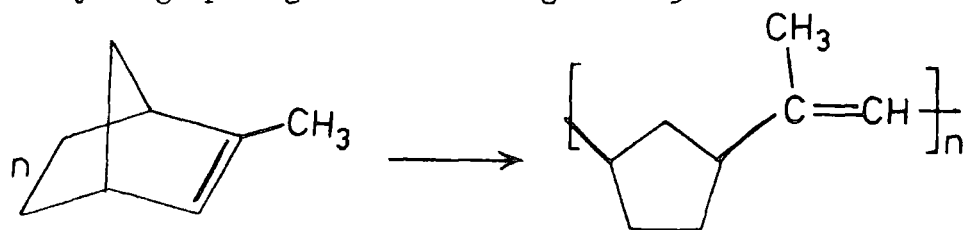


Figure 1.45.

Bicyclo[2.2.1]hept-2-ene containing a cyclopropane²⁵² or aryl group²⁴⁷ as shown in Figure 1.46 are examples of the tricyclic five-membered ring systems which undergo ring-opening polymerization.

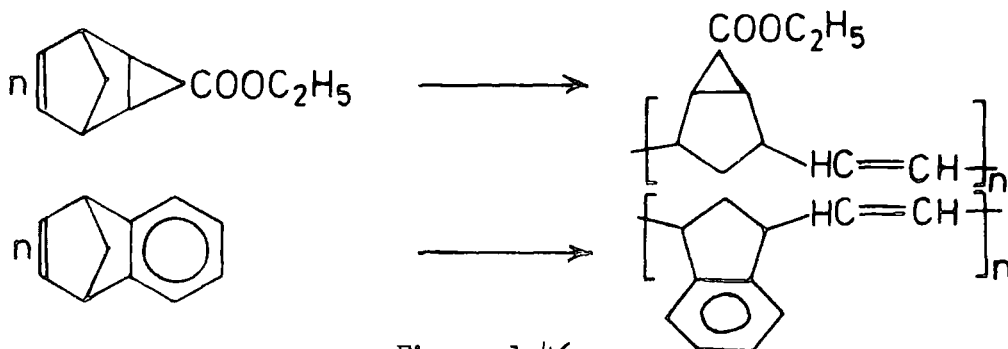


Figure 1.46.

One example of a pentacyclic five-membered ring monomer²⁴⁷ which can be polymerized by ring-opening as shown in Figure 1.47.

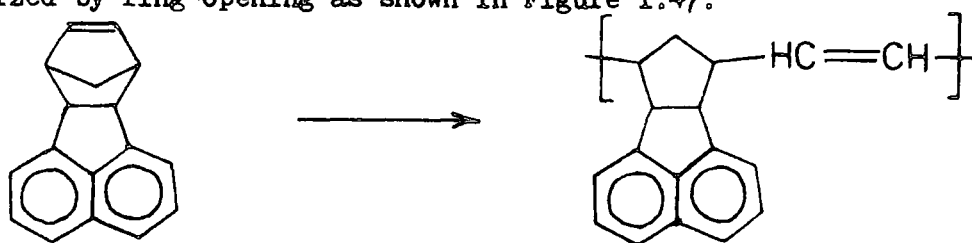


Figure 1.47.

1.7.d. Six-membered Ring Monomers

The inertness of cyclohexene towards ring-opening polymerization is known and confirmed by a number of authors.^{167,168,253,254} Ofstead²⁵⁵ showed that if the cyclohexene ring is part of a bicyclic system, then polymerization could occur because of the strain by ring-opening as shown in Figure 1.48; but work in this department failed to confirm this report.

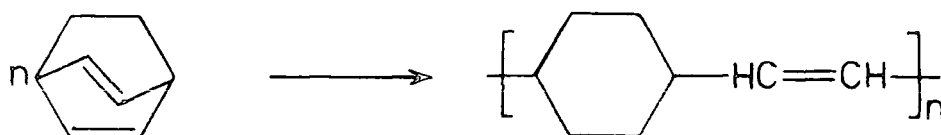


Figure 1.48.

1.7.e. Seven-membered Ring Monomers

Cycloheptene has received relatively little attention, but high cis⁵⁴ and high trans^{61,256,257} poly(1-heptenylene) have been prepared.

1.7.f. Eight-membered Ring Monomers

Polyalkenamers from eight-membered ring monomers have commercial potential¹⁸³ and many functionalized cyclooctene or cycloocta-1,5-dienes have been synthesized.^{3,61,64,171,203,256-259} Some of the examples are shown in Figure 1.49.

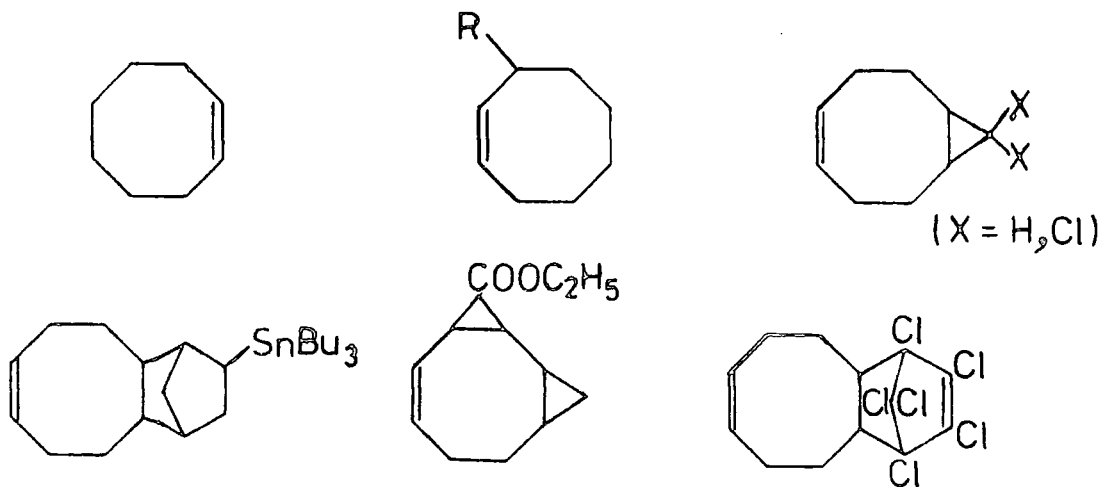


Figure 1.49.

1,5-Cyclooctadiene^{3,256} polymerized to give a polymer consisting of the same chemical structure as that of 1,4-polybutadiene [poly(2-butenylene)] as shown in Figure 1.50.

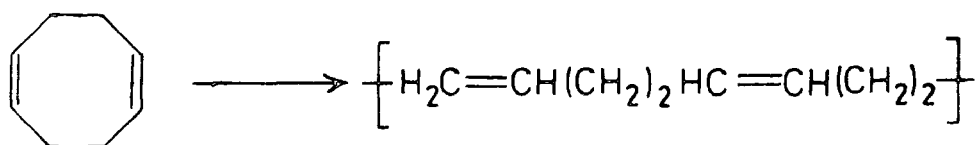


Figure 1.50.

Polymerization of substituted 1,5-cyclooctadiene providing a route to perfectly alternating copolymer as shown and discussed in Section 1.6.b. Recently, it was claimed that cycloocta-1,3-diene can be polymerized by ring-opening, this report contrasts with the general view of the polymerizability of conjugated double-bonds in the ring system, and the full experimental details are awaited with interest.²¹⁶

1.7.g. Higher-membered Ring Monomers

Some of the higher-membered rings which have been successfully polymerized are cyclononene,⁶¹ cyclonona-1,5-diene,²⁶⁰ cyclododecene²⁶¹ and cyclododecene^{3,60,183} as shown in Figure 1.51.

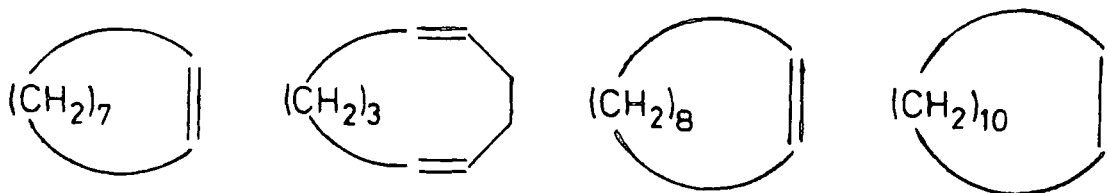


Figure 1.51.

1,5,9-cyclododecatriene polymerizes³ to yield poly(2-butenylene) as shown in Figure 1.52.

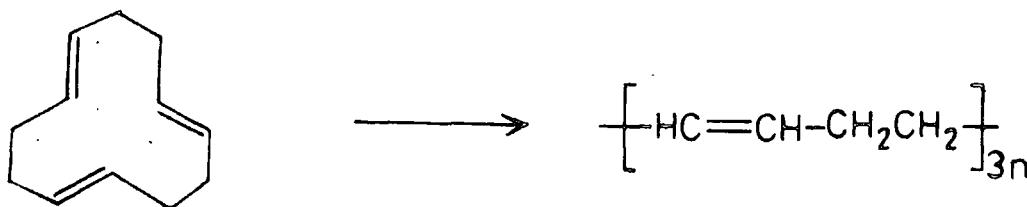


Figure 1.52.

1,9,17-Cyclotetraeicosatriene has been reported¹⁶⁸ to undergo ring-opening polymerization to yield poly(1-octenylene) as shown in Figure 1.53.

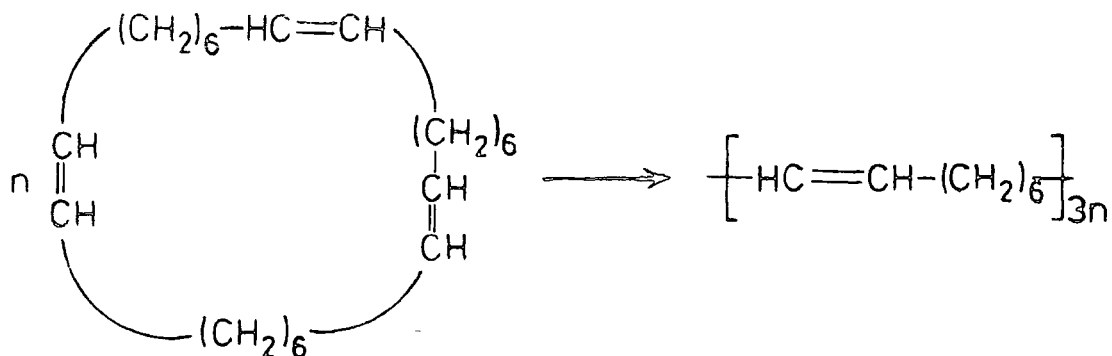


Figure 1.53.

A naturally occurring lactone, ambrettolite was polymerized to yield an unsaturated polyester²⁰³ as shown in Figure 1.54.

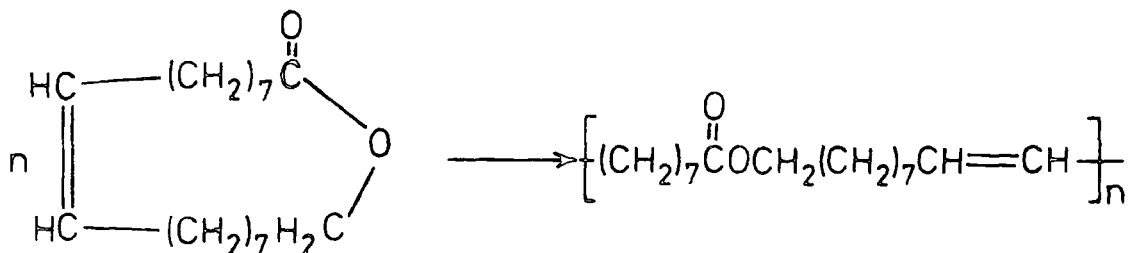


Figure 1.54.

1.7.h. Cycloalkynes As Monomers

Cyclodecyne²⁶² is the only example of this type of monomer which has been reported to undergo polymerization. With $\text{WCl}_6/\text{EtOH}/\text{EtAlCl}_2$, the monomer yielded cyclic oligomers of the formula $(\text{C}_{10}\text{H}_{16})_n$ where $n=1$ to 6.

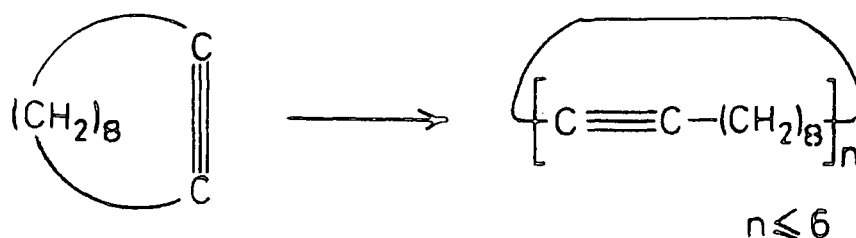


Figure 1.55.

1.8. Application Of Olefin Metathesis Of Acyclic Alkenes

The general form of this reaction is shown in Figure 1.2, as first reported in 1964 by Banks and Bailey.² The versatility of this reaction to organic syntheses is very great; it allows the conversion of simple, relatively inexpensive olefin into specialty, high purity olefin, and offer new openings for chemical industry.^{29,91,263,264} The reaction has been investigated intensively and there have been many reviews,²⁵⁻³⁸ the latest of there being provided by Banks.²⁶⁵

CHAPTER 2

THE METATHESIS POLYMERIZATION

OF

SOME FLUORINATED CYCLOALKENES

2.1. Introduction and Background

The metathesis ring-opening polymerization of partially fluorinated bicycloalkenes was described by Feast and Wilson²⁴² in 1978. They showed that typical metathesis catalysts, such as WCl_6/Ph_4Sn , $WCl_6/(C_2H_5)_2AlCl$ and WCl_6 alone, were effective in the ring-opening polymerization of the fluorinated monomers shown in Figure 2.1. The same authors also reported

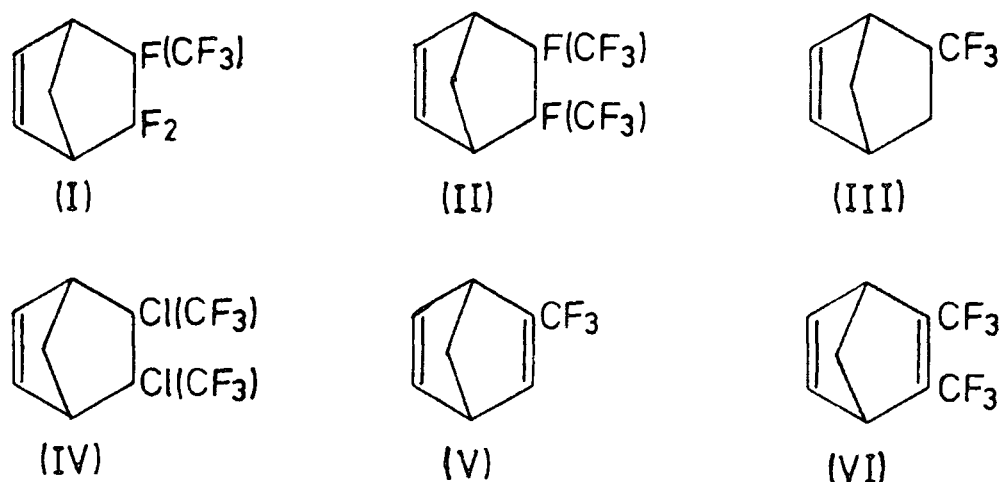
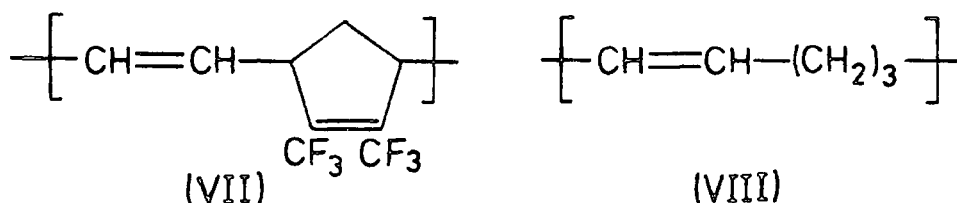


Figure 2.1.

that monomers (V) and (VI) readily copolymerized with cyclopentene; their preliminary results, using elemental analysis, showed that the copolymer had the repeat units (VII) and (VIII) in a ratio of approximately 2:1 when the monomers in the feed stock were in a 1:1 molar ratio.



There were three significant factors emerging from this earlier work.

(i) Fluorinated polymers have a wide technological importance but despite this, there are relatively few reports of investigations of the synthesis of stereoregular fluoro polymers with Ziegler-Natta catalysts.

Since stereoregular polymers extend the range of materials available from a particular monomer, this gap in the polymer literature is perhaps surprising. Metathesis catalysts and Ziegler-Natta catalysts have some similarities and this earlier work by Feast and Wilson²⁴² suggests that stereoregular fluoro polymers may be more readily accessible than is often believed. This point will be developed later.

(ii) One of the few pieces of evidence which supported the pairwise mechanism for metathesis which was popular in the early 1970ies was the observation that a "typical metathesis catalyst, PhWCl_3 " effected the transformation shown in Figure 2.2 which is the "cyclobutane to two olefins transformation" required in the most popular pairwise mechanism. The

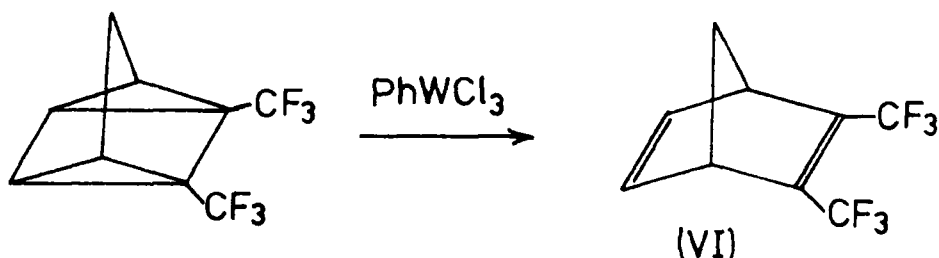


Figure 2.2.

catalyst PhWCl_3 is made from Ph_4Sn and WCl_6 and this early work showed that such catalysts in fact polymerize monomer (VI) very rapidly and by ring-opening, the observed quadricyclane to monomer (VI) conversion was therefore shown to be irrelevant to the mechanism of metathesis and one of the pieces of evidence for the pairwise process was ruled out.

(iii) The authors also pointed out the advantages of introducing fluorinated substituents into these polymers from the point of view of the effect on n.m.r. spectra. The fluorinated substituents are themselves visible through ^{19}F n.m.r. and have large effects on the ^{13}C and ^1H shifts. The spectra obtained by Feast and Wilson were complex and insufficiently well resolved for detailed interpretation, but this question has been

further explored in the work reported here.

In this work, the author has attempted to establish if a regular 1:2 copolymer between cyclopentene and monomer (VI) was formed independent of monomer feed stock ratio or merely coincidentally. Elemental analysis and ^{13}C n.m.r. were used in attempts to obtain more detailed information about the copolymer. In the study of the copolymer, it was necessary to assign all the ^{13}C resonances of the fluoromonomer units and this led to an examination of stereoregularity and tacticity distribution of the homopolymer of (VI) (see Section 1.3.d.). It was also hoped that analysis of the ^{13}C n.m.r. spectra of polymer (VII) would allow details of chain microstructure to be established as a function of catalyst used which in turn would lead to a better understanding of the polymerization mechanism (see Section 1.3.d.).

In this work, the author has extended the range of catalysts used by Wilson in the polymerization of monomer (VI). The monomer was polymerized with several catalyst systems in order to obtain high cis or trans forms of polymer (VII) which would help in the interpretation of spectra, monomer (VI) was used because it is symmetrical and would be expected to give relatively simple spectra.

The author also extended the range of partially fluorinated monomers by synthesizing the tricyclic ring systems shown in Figure 2.3. These new monomers were also polymerized by conventional metathesis catalysts.

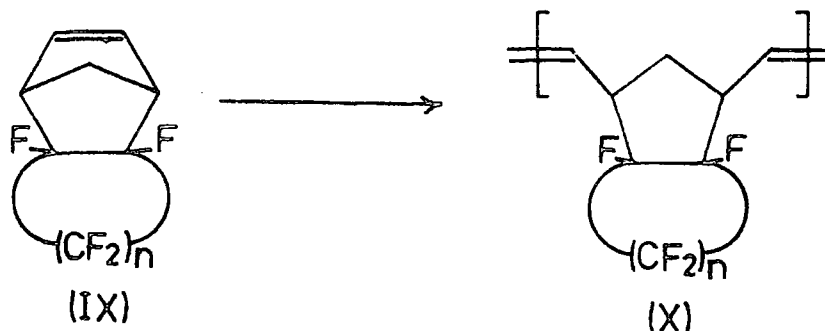


Figure 2.3.

The catalyst selectivity, for the WCl_6/Ph_4Sn system was also examined in the case of the polymerization of an endo/exo mixture of 2,3,3,4,4,5,5,6-octafluorotricyclo[5.2.1.0^{2,6}]dec-8-ene (**IX**), $n=3$). The author was unable to polymerize some other partially fluorinated monomers and these failures are briefly reported to indicated the problems and limitation encountered in this type of work.

2.2. Monomer syntheses and characterization

2.2.a. Introduction

This Section describes some background chemistry of the partially fluorinated monomers investigated. All monomers were synthesized by Diels-Alder addition, which involves the 1,4-addition of a conjugated diene and a dienophile as shown in Figure 2.4. Using this method, a wide range of

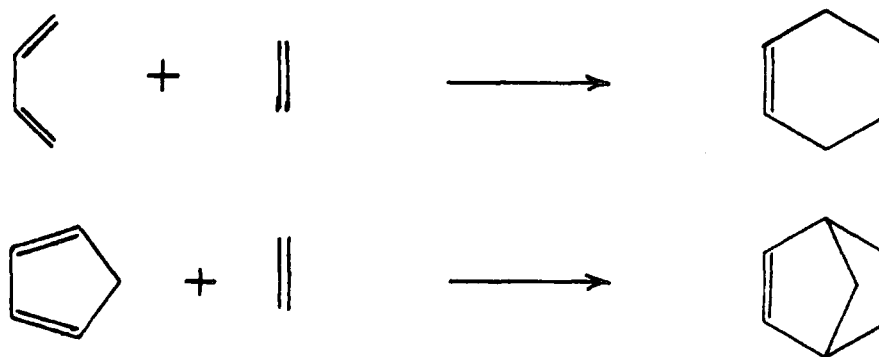


Figure 2.4.

possible partially fluorinated bicyclo[2.2.1]hept-2-enes and bicyclo[2.2.1]-hepta-2,5-dienes can be prepared, the area has been reviewed by Perry²⁶⁶ and Smart.²⁶⁷ Some of the monomers which were synthesized via Diels-Alder reactions between cyclopentadiene and appropriate fluorinated dienophiles are shown in Figure 2.1.

Stereoselectivity in the Diels-Alder reaction is a function of the structure of both the reactants and the reaction conditions, a mixture of endo and exo isomers is usually obtained in this reaction. Isomer assignment

was based on Stone's²⁶⁸ observation that signals due to trifluoromethyl groups and/or fluorine atoms in exo positions occur at lower field chemical shifts than those due to the same unit in the endo position. Thus, the assignment of some peaks in the ^{19}F n.m.r. spectrum was possible²⁴² for compound (I) - (IV).

The partially fluorinated tricyclic monomers investigated in this work were synthesized by Diels-Alder reaction between cyclopentadiene and appropriate perfluorocycloalkenes as dienophiles as shown in Figure 2.5.

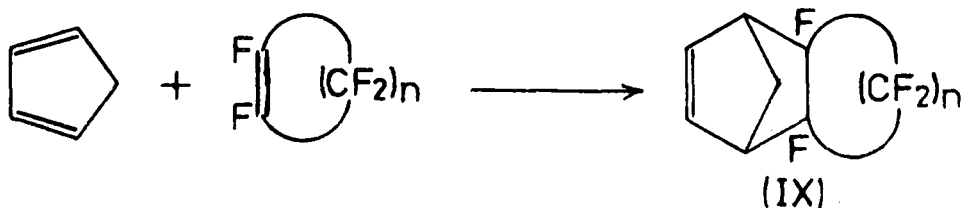


Figure 2.5.

The details of experimental conditions and yields are tabulated in the Experimental Section. Surprisingly, 1:1 Diels-Alder adducts were isolated from the reactions with perfluorocyclobutene and -pentene (ie $n=2$ and $n=3$ in Figure 2.5.) only in low yield compared to the reaction between cyclopentadiene and acyclic fluorinated olefins.²⁴²

Acyclic fluorinated olefins give 1:1 Diels-Alder adducts in high yield whereas in the author's experience, cyclic fluorinated olefins give poly-adducts as the main products, indeed for perfluorocyclohexene ($n=4$) mainly polyadducts were formed, with very low yields of 1:1 adduct. Apparently acyclic and cyclic fluorinated olefins have different dienophilic character and it also seems likely that the primary adducts also have very different characters. One question which is difficult to understand is why compound (XI) does not apparently compete with $\text{CF}_3\text{CF}=\text{CF}\text{CF}_3$ for diene, see Figure 2.6., whereas quite clearly tricyclic olefins (IX) compete very successfully for diene with perfluorocycloalkenes.

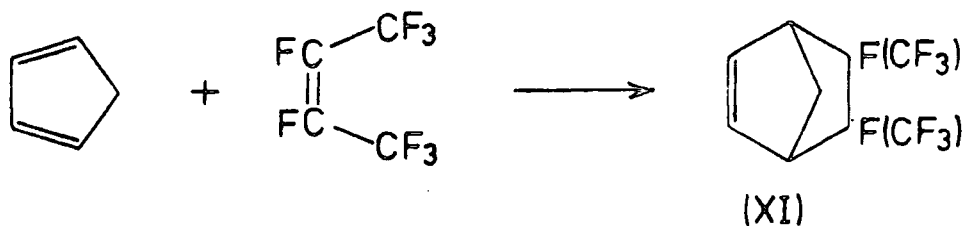


Figure 2.6.

Presumably, it is in some way a function of the ring structure, but no clear cut explanation is available, in fact one might have expected the 4 and 5 membered cyclic olefins to be rather better dienophiles than $\text{CF}_3\text{CF}=\text{CFCF}_3$ as a consequence of ring strain. Smart²⁶⁷ reported that polyadduct was formed in the reaction between cyclopentadiene and trifluoroethylene as shown in Figure 2.7.

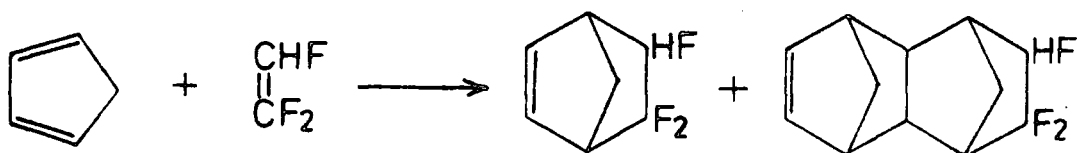
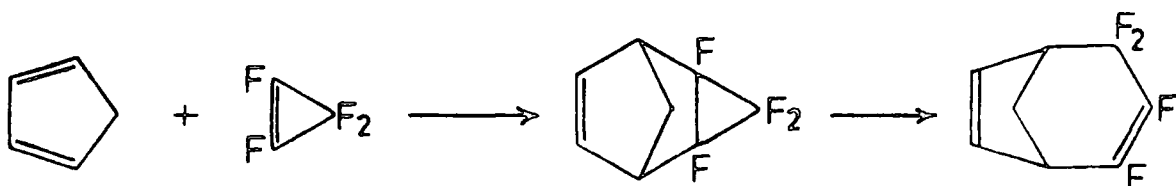


Figure 2.7.

Other workers have reported that polyfluorinated cyclopropene,²⁶⁹ cyclobutene^{270,271} and cyclopentene²⁷¹ undergo Diels-Alder reaction with cyclopentadiene and 1,3-butadiene as shown in Figure 2.8, yields were reasonably high with no mention of polyadducts.



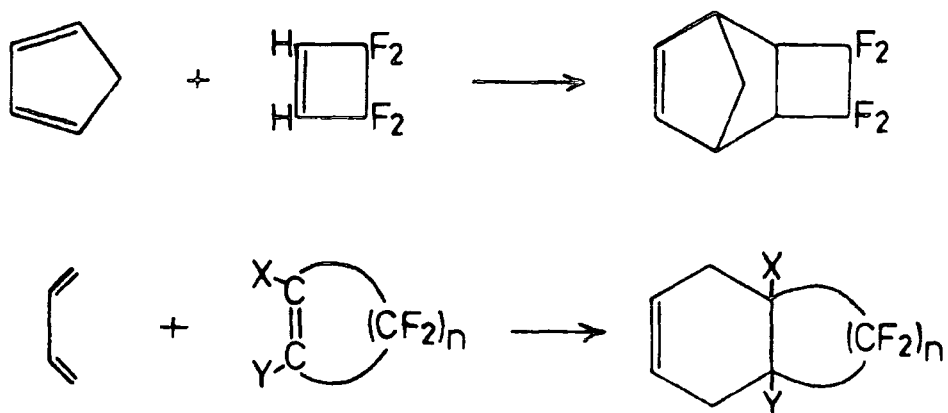


Figure 2.8.

Clearly there are some anomalies in this area of work but the author was primarily interested in obtaining monomers for polymerization studies and extensive investigation of these reactions has not been attempted. The author was unsuccessful in the attempted synthesis of the Diels-Alder adduct between cyclopentadiene and 1,2-dichloro-3,3,4,4,5,5-hexafluorocyclopentene, the proposed reaction is shown in Figure 2.9. This result

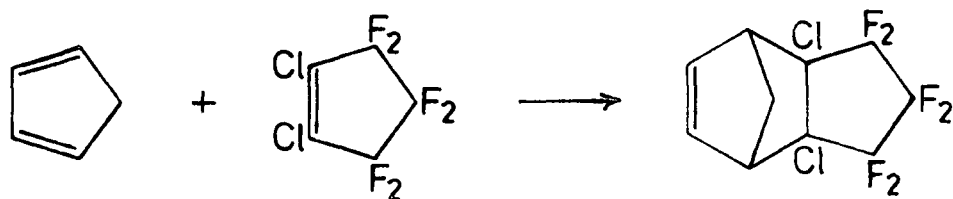


Figure 2.9.

was not too surprising in view of the earlier report²⁴² of a low yield in the synthesis of compound (IV). The low reactivity of this olefin is difficult to explain on the basis of steric effect because tetrachlorocyclopropene is a very reactive olefin in Diels-Alder reactions as will be discussed in Chapter 3.

The synthesis, purification and characterization of each monomer is described briefly below.

2.2.b. Synthesis of 2,3-bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene, 1,2-bis(trifluoromethyl)cyclohexa-1,4-diene, 5,5,6-trichloro-6-trifluoromethylbicyclo[2.2.1]hept-2-ene, 2,3,3,4,4,5-hexafluorotricyclo[4.2.1.0^{2,5}]non-7-ene and 2,3,3,4,4,5,5,6-octafluorotricyclo[5.2.1.0^{2,6}]dec-8-ene

2,3-Bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene^{242,272} and 1,2-bis-(trifluoromethyl)cyclohexa-1,4-diene²⁷³ were prepared by Diels-Alder reaction between hexafluorobut-2-yne and cyclopentadiene or 1,3-butadiene as shown in Figure 2.10. Both these syntheses follow established literature methods and the compounds were identified by their i.r. spectra (Appendix C, No I and II), mass spectra (Appendix B, No I and II) and ¹H and ¹⁹F n.m.r. spectra (see Table 2.1 for compound (XII))

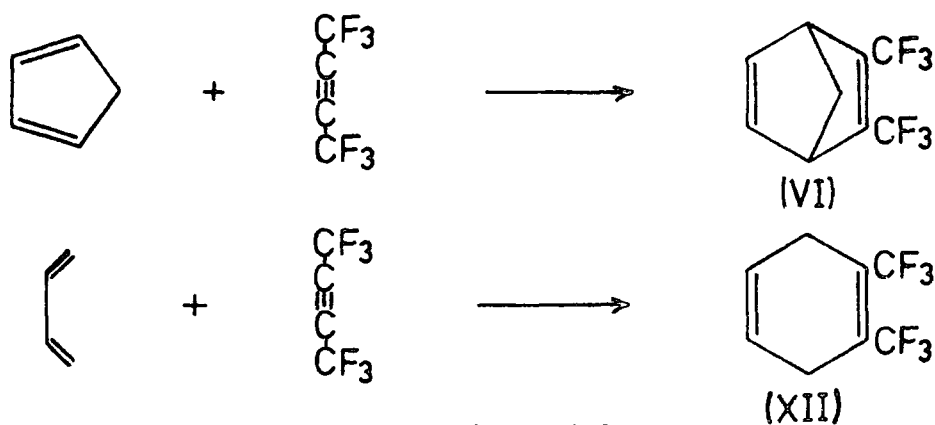


Figure 2.10.

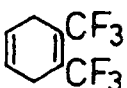
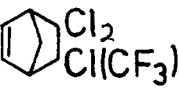
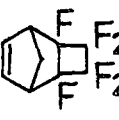
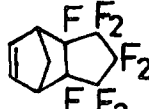
The reaction between 3,3,3-trifluoro-1,1,2-trichloropropene and cyclopentadiene produced 5,5,6-trichloro-6-trifluoromethylbicyclo[2.2.1]hept-2-ene in 27% yield, Figure 2.11. The i.r. spectrum (Appendix C, No III) and ¹⁹F and ¹H n.m.r. spectra (see Table 2.1.) were consistent with the proposed structure, but elemental analysis (see Experiment Section) and mass spectroscopy (Appendix B, No III) cast doubt upon this assignment; although several attempts have been made to improve the purification of this monomer, there are reservations as to it's purity. The ¹⁹F n.m.r. spectrum showed just

one peak at 61.8 ppm and probably the material is just one isomer, however it is possible that the starting dienophile was contaminated with a closely related material, undetected but responsible for the anomalous analytical results. It is probable that $\text{CF}_3\text{CCl}=\text{CCl}_2$ is prepared by halogen exchange from $\text{CCl}_3\text{CCl}=\text{CCl}_2$, if so it is quite possible that traces of $\text{CClF}_2\text{CCl}=\text{CCl}_2$, $\text{CCl}_2\text{FCCl}=\text{CCl}_2$ and $\text{CCl}_3\text{CCl}=\text{CCl}_2$ may remain in the product, such impurities could account for the problems described above.



Figure 2.11.

Table 2.1. N.m.r. spectral parameters for monomers described in this Chapter

Compound	^1H n.m.r.			^{19}F n.m.r.		
	$-\text{CH}_2-$	$-\text{CH}-$	$-\text{CH}=\text{}$	$-\text{CF}_3$	$-\text{CF}_2$	$-\text{CF}-$
	2.98		5.68	62.5		
	1.95					
	2.15	3.35				
	2.45	3.60	6.35	61.8		
	2.60					
	2.28					
	2.35	~ 3.3	~ 6.2			
	1.78	3.51	6.60		127.8	179.0
	1.86					
	2.27					
	2.41	3.40	6.24		119	173.92
	1.72	3.57	6.56		141	
	1.92				complex	173.57

The Diels-Alder reaction between cyclopentadiene and hexafluorocyclobutene, Figure 2.12 produced mixture of 1:1 and polyadducts, from which the 1:1 adduct was obtained by vacuum distillation. The structure of the 1:1 adduct from this reaction was confirmed by elemental analysis (see Experiment Section), mass (Appendix B, No IV) and i.r. (Appendix C, No IV) spectroscopy. Characterization by ^1H and ^{19}F n.m.r. (see Table 2.1) spectra showed the compound contained one major isomer, assignment of the isomer structure will be discussed later in Section 2.2.c.

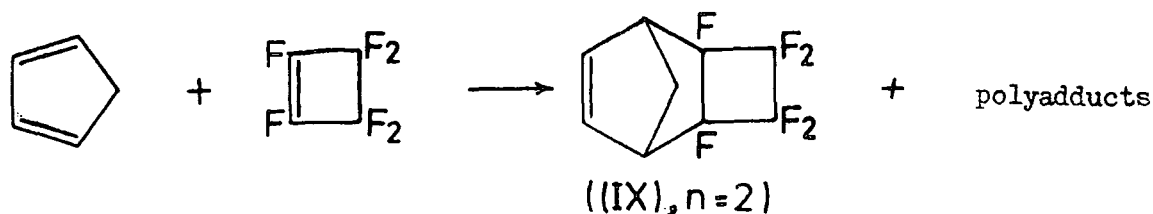


Figure 2.12.

2,3,3,4,4,5,5,6-Octafluorotricyclo[5.2.1.0^{2,6}]dec-8-ene was prepared by Diels-Alder reaction between cyclopentadiene and octafluorocyclopentene, Figure 2.13, from which the 1:1 adducts were obtained as a semisolid by vacuum distillation. This product was confirmed as a mixture of 1:1 adducts by elemental and spectroscopic analysis. Elemental analysis and mass spectroscopy (Appendix B, No V) established that the product had the molecular formula $\text{C}_{10}\text{H}_6\text{F}_8$ and the i.r. spectra (Appendix C, No V) was consistent with the structure ((IX), n=3). Although the product gave a broad single peak on analytical g.l.c., the ^1H , ^{13}C and ^{19}F n.m.r. spectra all confirm that it consisted of a roughly 50:50 mixture of two isomers. The assignment of structure for compounds of the general formula (IX) is discussed below.

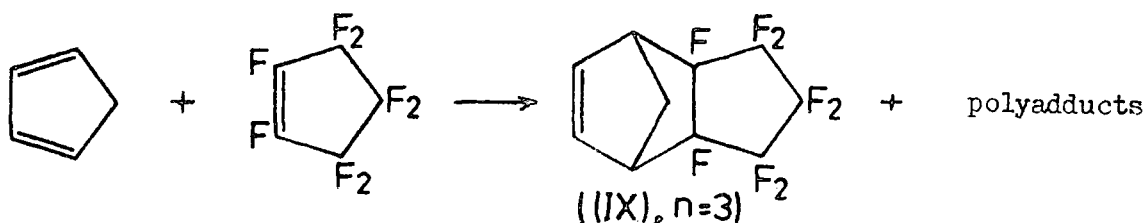
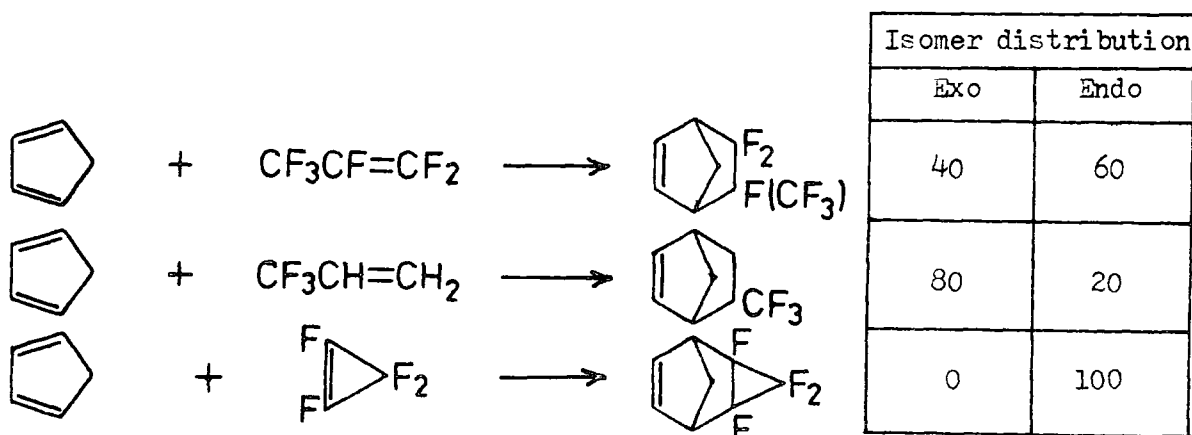


Figure 2.13.

2.2.c. Structural assignment of endo/exo isomers of fluorinated polycyclic systems

Structural assignment for the Diels-Alder adducts of fluoro-olefins with cyclopentadiene rests heavily on spectroscopic evidence. Most of the adducts which have been described in the literature are volatile liquids or low melting solids, so it is not surprising that there appear to have been no X-ray diffraction studies, and since the molecules are also relatively large and complex, no electron diffraction studies appear to have been carried out either. Although the spectroscopic arguments constructed seem convincing it is regrettable that there are no reliable crystal structures which could be used as fixed points in the arguments. As mentioned earlier, Stone²⁶⁸ and Smart²⁶⁷ have analysed the n.m.r. spectra of a number of adducts and have concluded that in bicyclo[2.2.1]hept-2-enes, exo F or CF₃ units occur at lower field than analogous endo units.

There are many examples of structures of this type produced via the Diels-Alder reaction and there appear to be some anomalies, for example consider the three reactions shown below:

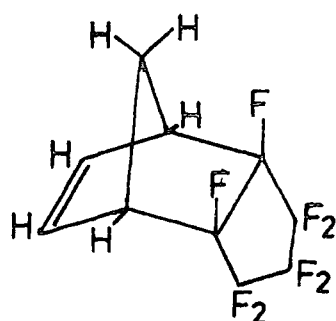


There is clearly a wide variation in endo/exo selectivity between apparently similar dienophiles; all these structural assignments are in agreement with Stone and Smart's generalization, but the anomalies exemplified here cause some reservations as to the certainty of these widely used

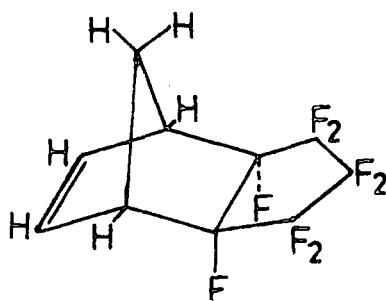
chemical shift generalizations. In this work we have tried to make a more secure assignment by detailed analysis of ^{19}F , ^{13}C and ^1H n.m.r. spectra and are indebted to Dr. I. Sadler (Edinburgh University) for recording some of the spectra discussed below.

We will first consider the ^{19}F n.m.r. spectra obtained for the 1:1 adduct mixture of cyclopentadiene and octafluorocyclopentene, see Figure 2.14. The complete spectrum is shown at the top of the page and consists of a complex set of overlapping AB quartets in the region 119-141 ppm upfield from CFCl_3 which are assigned to the difluoromethylene units, and two resonances near 174 ppm which are assigned to the tertiary fluorines. On expansion, the CF_2 resonances can be accounted for in terms of two sets of two AB quartets in an approximately 2:1 intensity ratio in each case; in the H-decoupled spectrum of the difluoromethylenes, there are no significant changes in the peak multiplicities and therefore H-F coupling can be regarded as negligibly small, the J_{AB} values observed are quite reasonable for difluoromethylenes in five-membered rings.

Expansion of the tertiary fluorine region showed a doublet, $J=7.6$ Hz at 173.3 ppm and a broad singlet at 173.6 ppm, in the intensity ratio 60:40; H-decoupling collapses the doublet to a sharp singlet but has only a marginal effect on the line width of the resonance at higher field. Following Stone and Smart's generalization, we should say that this adduct mixture consists of 60% of the endo-adduct and 40% of the exo-adduct.



(IX), endo



(IX), exo

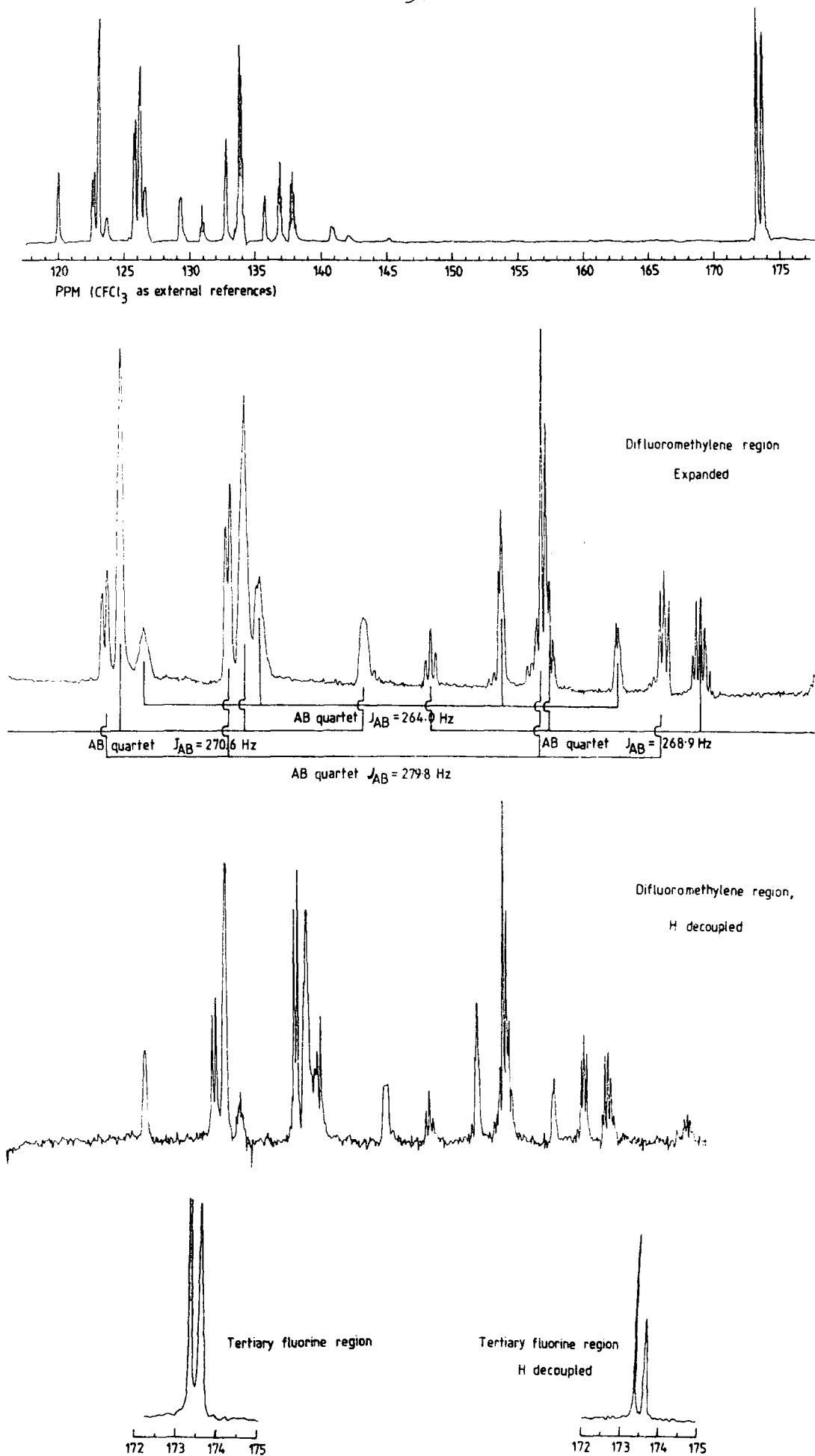


Figure 2.14.

If this assignment is correct, the doublet signal from the tertiary exo-fluorines of the endo-adduct ((IX), endo) must be split as a result of H-F coupling with one of the protons at C₁₀, i.e. the bridging methylene carbon. The complex overlapping nature of the difluoromethylene resonances does not allow confirmation of this assignment.

The ¹H n.m.r. spectra for this mixture was recorded with the 360 MHz instrument in Edinburgh and the spectrum is shown in Figure 2.15. It is readily assigned as arising from a mixture of endo and exo isomers and the excellent signal to noise and resolution obtained with this instrument, allows an unambiguous definition of the isomers ratio as 53:47, the same result being obtained from the relative intensities of the vinylic H, tertiary H and methylene AB quartet signals. The major isomer has the lower field vinylic and tertiary signals, and the higher field AB quartet, these assignments being confirmed by H-H decoupling experiments.

The lower limb of the AB quartet of the major isomer has a complex form which can be resolved with the aid of a complete H-H decoupling study. On irradiation of the vinyl H signal, the higher field limb of the AB system showed an altered splitting pattern but the lower field limb remained unchanged. When the tertiary H signal was irradiated, both limbs of the AB quartet showed altered splitting patterns and the lower limb simplified to a system consisting of the two lines of unequal intensity of the AB quartet ($J_{AB}=11.8$ Hz), with each of these lines split into a triplet ($J=8$ Hz) of triplets ($J=1.3$ Hz), since the vinyl H decoupling established that there was no coupling between it and the proton under consideration both these triplet splitting must result from H-F interactions. We therefore assign the major isomer as the endo-isomer with the significant coupling constants as shown below:

¹H N.m.r. spectra for 2,3,3,4,4,5,5,6-octafluorotricyclo[5.2.1.0^{2,6}]dec-8-ene

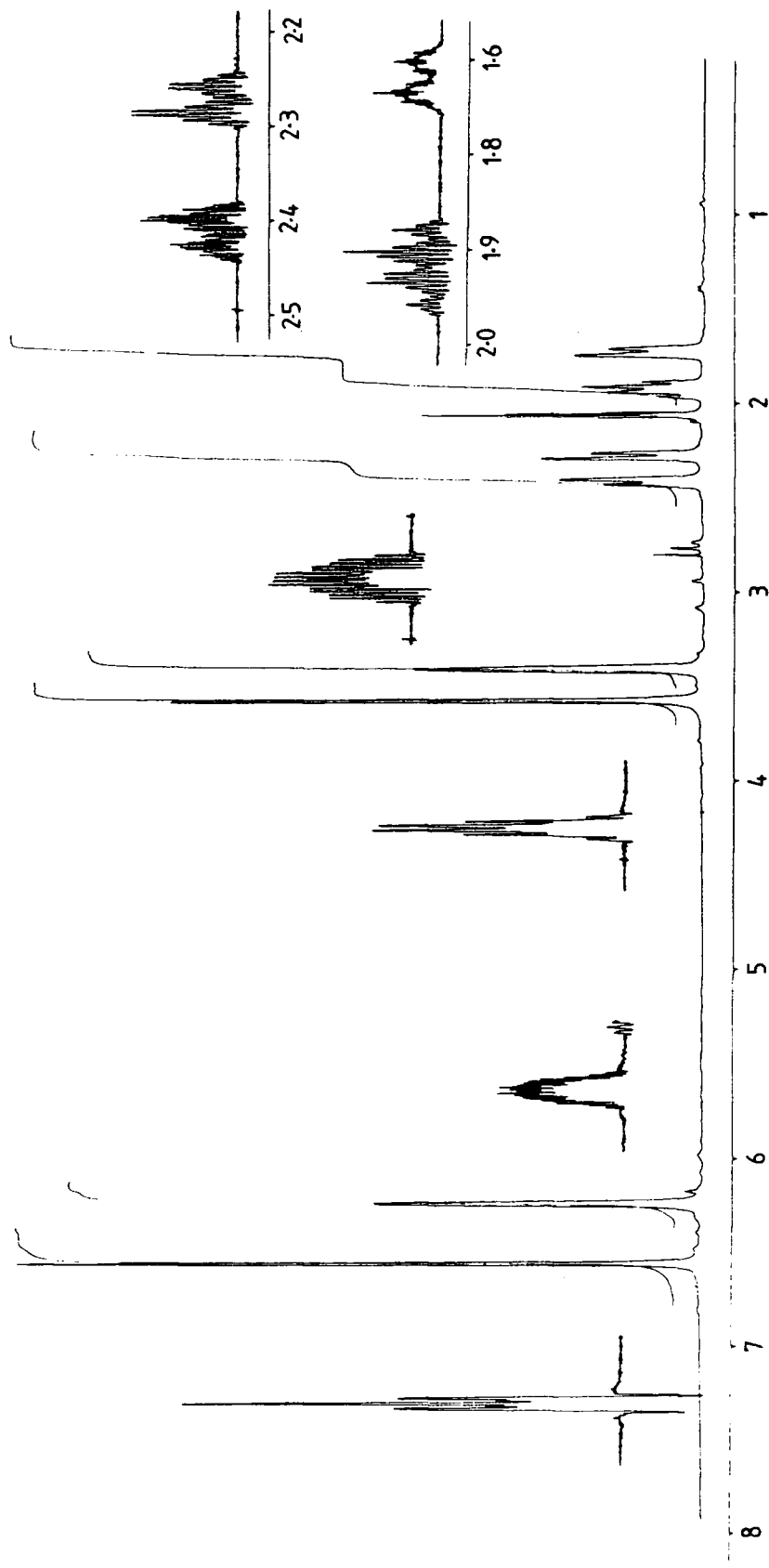
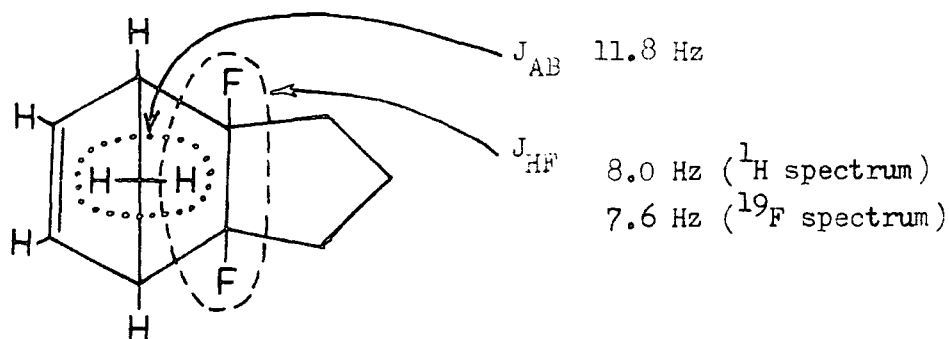


Figure 2.15



Only the main lines of the argument have been presented but the important observation of the doublet splitting of the tertiary fluorine resonance in the ^{19}F n.m.r. spectra and the triplet splitting of the bridging methylene hydrogen in the ^1H n.m.r. spectra was made only for one isomer. Thus, the assignment made on the basis of this analysis of the ^1H and ^{19}F n.m.r. spectra are in agreement; with the superior ^1H n.m.r. spectra giving a more reliable quantitative analysis of the isomers ratio.

In the case of the cyclopentadiene adduct with hexafluorocyclobutene, the major isomer ($\sim 95\%$) can be straight forwardly assigned as the endo-adduct; this assignment following from the close similarity of shifts and splitting patterns observed between this product and the endo-adduct of cyclopentadiene and octafluorocyclopentene (see Table 2.1).

2.3. Polymerization of some partially fluorinated polycyclic alkenes

2.3.a. Investigation of stereoregulation in poly(4,5-bis(trifluoromethyl)-1,3-cyclopentenylenevinylene) by ^{13}C n.m.r. spectroscopy

The detailed interpretation of ^{13}C n.m.r. spectra of the ring-opened polymers was pioneered by Ivin et al. It was established that ^{13}C n.m.r. spectroscopy offers a powerful tool for looking at the microstructure of the polymer chain including cis/trans isomerization, tacticity, and Head-Head vs Head-Tail monomer placement; together with the distribution of these variables. These authors studied high cis and high trans forms of the polymer derived from endo- and exo-5-methylbicyclo[2.2.1]hept-2-ene, there

are four possibilities for assembly of these polymers excluding cis/trans isomerization at the vinylene units, these possibilities are shown below, Figure 2.16.

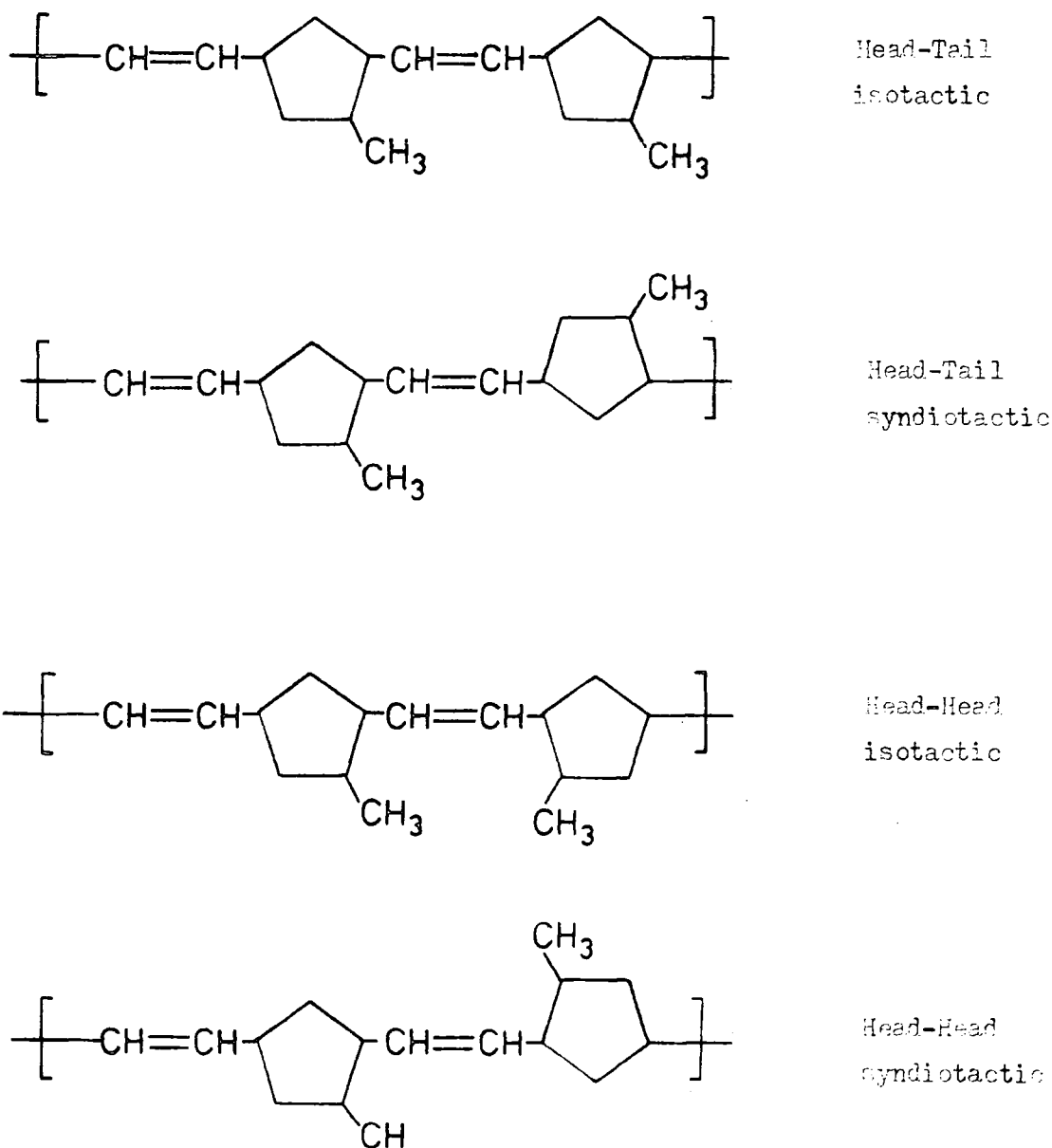


Figure 2.16.

They have prepared the fully trans- and fully cis-polymers and established that a polymer having all cis geometry has a fully syndiotactic ring-sequence with the methyl-group alternating Tail-Tail and Head-Head.^{158,160,}

161 Polymers having more than 80% trans vinylene content have an atactic ring sequence, while the polymers having a 74:26 cis/trans ratio have mainly syndiotactic cis-junctions and isotactic trans-junctions. They also showed the relation of these results to the mechanism of ring-opening polymerization of bicyclo[2.2.1]hept-2-ene,¹²³ which was discussed earlier in Section 1.3.d. Most of the interpretation of cis/trans and tacticity distributions was based on detailed analysis of the olefinic area of ¹³C n.m.r. spectra which is generally extremely complex.

In order to reduce this complexity, Ivin and co-workers have resorted to the resolution of the enantiomers of endo and exo-5-methylbicyclo[2.2.1]hept-2-ene, and preparation of high cis and high trans polymers from these chiral monomers. The deductions made from this work require the development of a complicated argument which is too long to be reproduced here, however Ivin's conclusion can be summarized in terms of a flow diagram which records the stereochemical consequences of the deduced mechanism.

In Figure 2.17, one case of Ivin's mechanistic rationalization is drawn out at length for the situation where the chain carrying carbene is immobile and the polymer chain and the bridging methylene carbon have a syn stereochemical relationship in the initial metallocarbene/monomer complex. This example would lead to an all cis syndiotactic chain microstructure, similarly, exo approach with the polymer chain and the bridging methylene adopting an anti stereochemistry would lead to an all trans isotactic chain microstructure.

In the work described here, the author has investigated the possibility of monitoring the stereoregularity of the polymer formed from 2,3-bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene (VI) by different catalysts. This monomer is symmetrical and consequently the number of monomer assembly possibilities is halved since no Head-Head and Head-Tail isomers are possible.

Diagram summarizing the conclusions reached by K.J. Ivin for the case of polymerization of a substituted bicyclo[2.2.1]hepta-2,5-diene with a conformationally immobile carbene as the chain carrying species

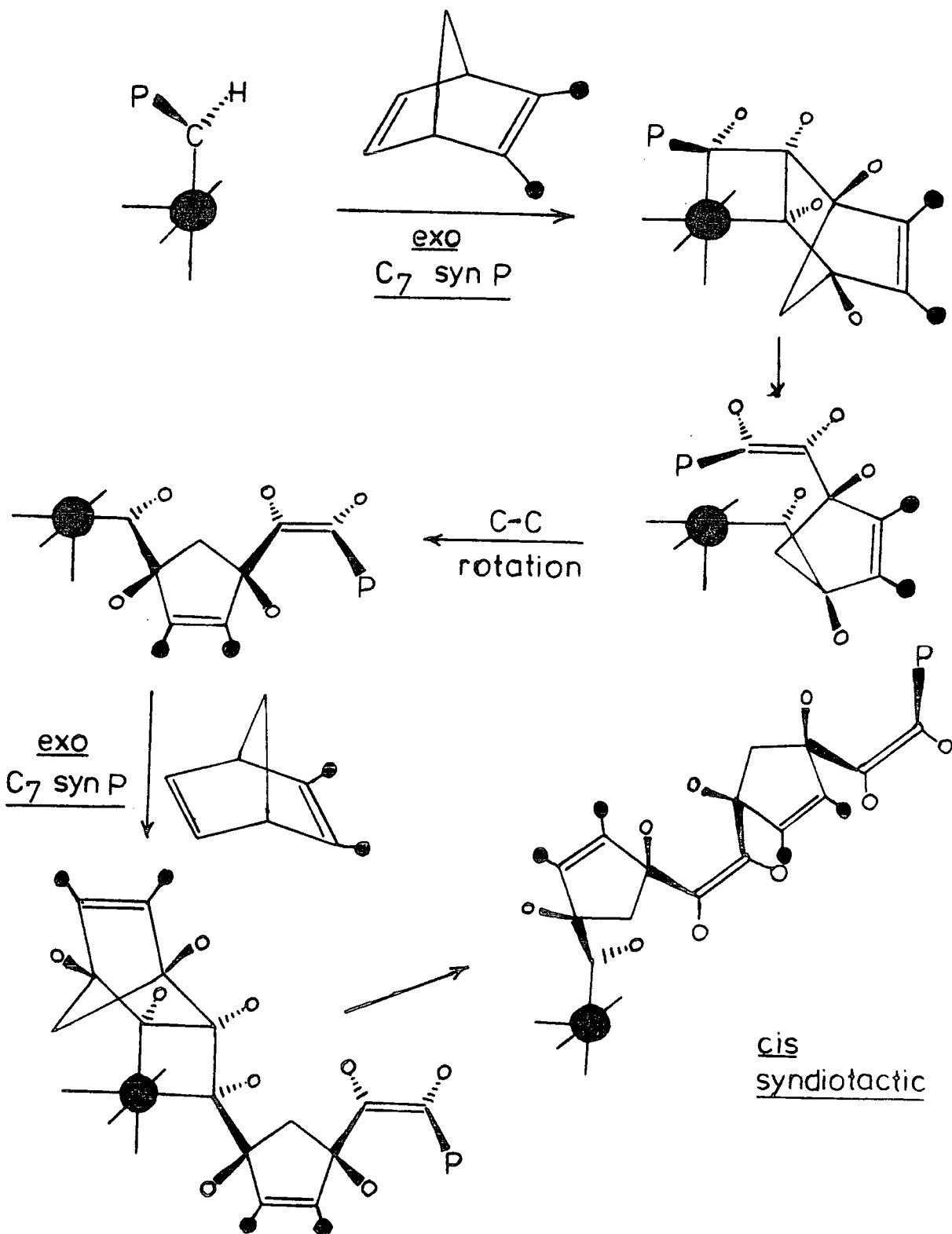


Figure 2.17.

The four possible structural sub-units are shown below, Figure 2.18.

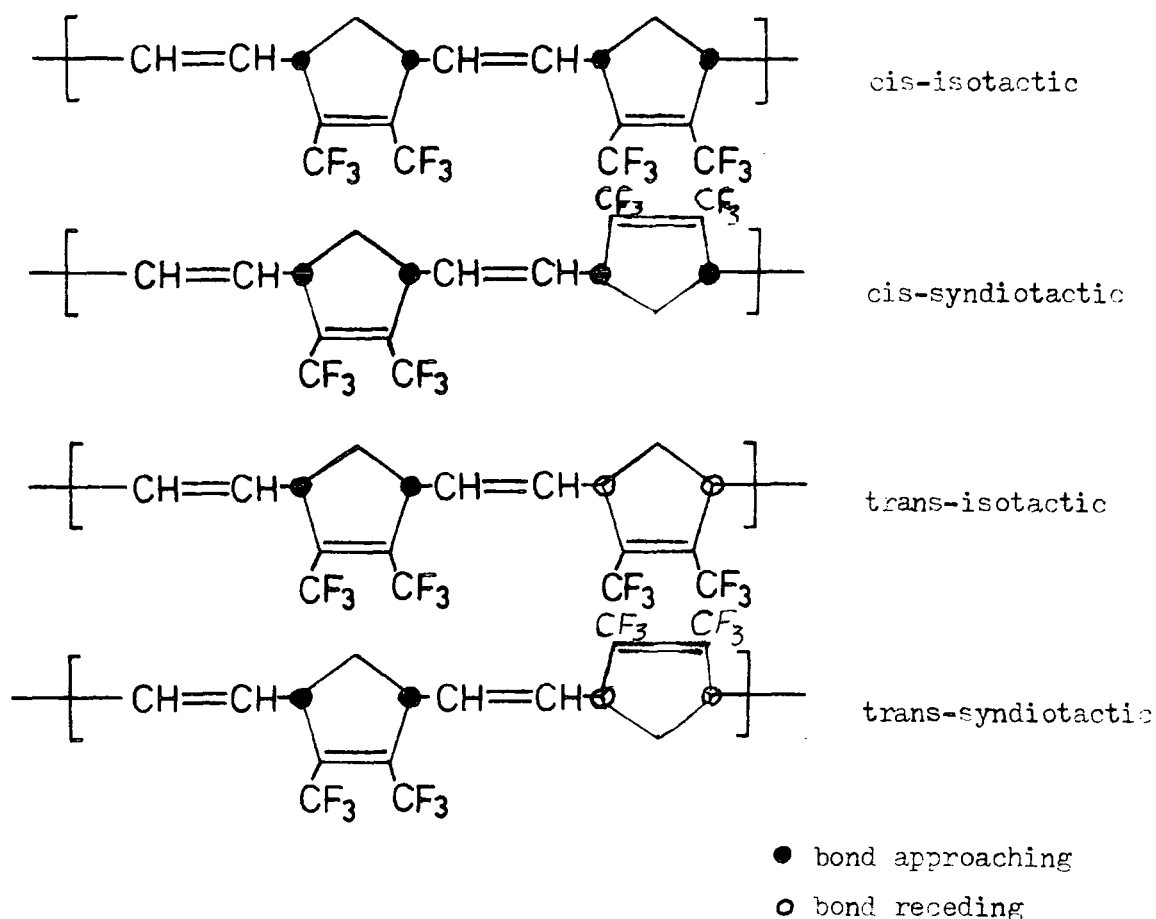


Figure 2.18.

It was hoped that the large chemical shifts induced by CF_3 -substituents would result in good resolution of the vinylic carbons in the product polymers, and that in the light of Ivin's mechanistic rationalization, it would be possible to monitor the stereoregulating capability of various catalysts.

2,3-Bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene was treated with various tungsten, molybdenum, rhenium and ruthenium based catalysts (see Experiment Section), with the hope of obtaining a range of stereoregular polymers. Unfortunately, the monomer was not polymerized by ReCl_5 and RuCl_3 based catalysts although an earlier report¹⁵⁶ established that these

catalysts gave respectively all cis and high trans polymers from bicyclo-[2.2.1]hept-2-ene; surprisingly, Fischer carbene did not effect the polymerization, except when $TiCl_4$ was added as an activator.^{65,66}

2,3-Bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene was readily polymerized with WCl_6/Ph_4Sn , WCl_6/Bu_4Sn , WCl_6/Me_4Sn and $(CO)_5W=C(OCH_3)C_6H_5/-TiCl_4$ (RT or $50^\circ C$) to produce 50:50 cis/trans polymers, and with $MoCl_5/Ph_4Sn$, $MoCl_5/Me_4Sn$ and $MoCl_5/Me_2AlCl$ to produce high cis polymers. The polymers produced were purified by successive precipitation from acetone solution into n-pentane; they all gave viscous solutions in acetone at ca 5% concentration and could be cast to give tough clear films, these observations may be taken as evidence that we were dealing with genuine polymeric materials.

The main conclusions to be drawn from an analysis of the ^{13}C n.m.r. spectra of these polymers can be illustrated by reference to two products, these are the polymers prepared using a very active non-discriminating initiator system ($WCl_6:2(CH_3)_4Sn$) and that produced with a less active catalyst which generally gives polymers with a high cis content ($MoCl_5:2(CH_3)_4Sn$), both polymerizations were carried out at room temperature in chlorobenzene. The ^{13}C n.m.r. spectrum of the polymer (VII) has been described previously²⁴² and the spectroscopic parameters for samples produced in this work are tabulated in Table 2.2 (see page 73).

If we first examine Figure 2.19, that is the low field region of the spectrum of the polymer produced using $WCl_6/2(CH_3)_4Sn$, we see that under low resolution the quartet due to the CF_3 groups occurs at ca 120 ppm with the two groups of vinylic carbon signals at ca 130 and 140 ppm; the lower field and lower intensity signals are clearly those of the vinyl carbons carrying CF_3 substituents since their low intensity results from the lack of any Nuclear Overhauser Enhancement, whereas the hydrogen carrying vinylene

carbons give the strong signals @ ca 130 ppm. The lower field signal of this intense pair is assigned, by reference to accumulated tables of data, to the cis vinylene unit and the signal at higher field to the trans vinylene unit. Inspection of the expanded spectrum shows that both vinylene carbon signals consist of two overlapping resonances and so we have, with this catalyst, four vinylene signals corresponding to the four possible stereochemical assembly modes illustrated in Figure 2.18.

If we now look at the spectrum of the sample prepared using the $\text{MoCl}_5/2(\text{CH}_3)_4\text{Sn}$ catalyst, Figure 2.20, we see that the region assigned to the vinylene carbon resonances is greatly altered. The low field resonance corresponding to the cis-vinylene unit becomes relatively more intense than the trans-vinylene resonance, and it is clear that the cis-vinylene resonance consists mainly of one signal rather than the overlapping pair seen in Figure 2.19. This observation is consistent with Ivin's¹⁵⁶ conclusion that high cis polymers exhibit mainly cis syndiotactic microstructure and we can conclude that the sharp resonance at 131.3 probably belongs to a cis syndiotactic sequence and the other signal in this pair belongs to the isotactic sequence. The other pair of signals at 130 ppm have not been assigned as yet as a consequence of our failure to find a catalyst which gives a high trans polymer with this monomer.

In Figure 2.21, the complete ^{13}C n.m.r. spectra for another pair of polymers are reproduced, in this case the samples were obtained by initiation with the activated 'Fischer Carbene' ($(\text{CO})_5\text{W}=\text{C}(\text{OCH}_3)\text{C}_6\text{H}_5/\text{TiCl}_4$) and $\text{MoCl}_5/(\text{CH}_3)_2\text{AlCl}$ respectively. As is clear from an examination of the vinylene region, the former catalyst gives ca 50:50 cis/trans polymer whereas the latter gives a largely cis syndiotactic product. The methine and methylene signals at higher field provide an internal check on the cis/trans content of the polymers, the methine signals are both allylic and nearer to the

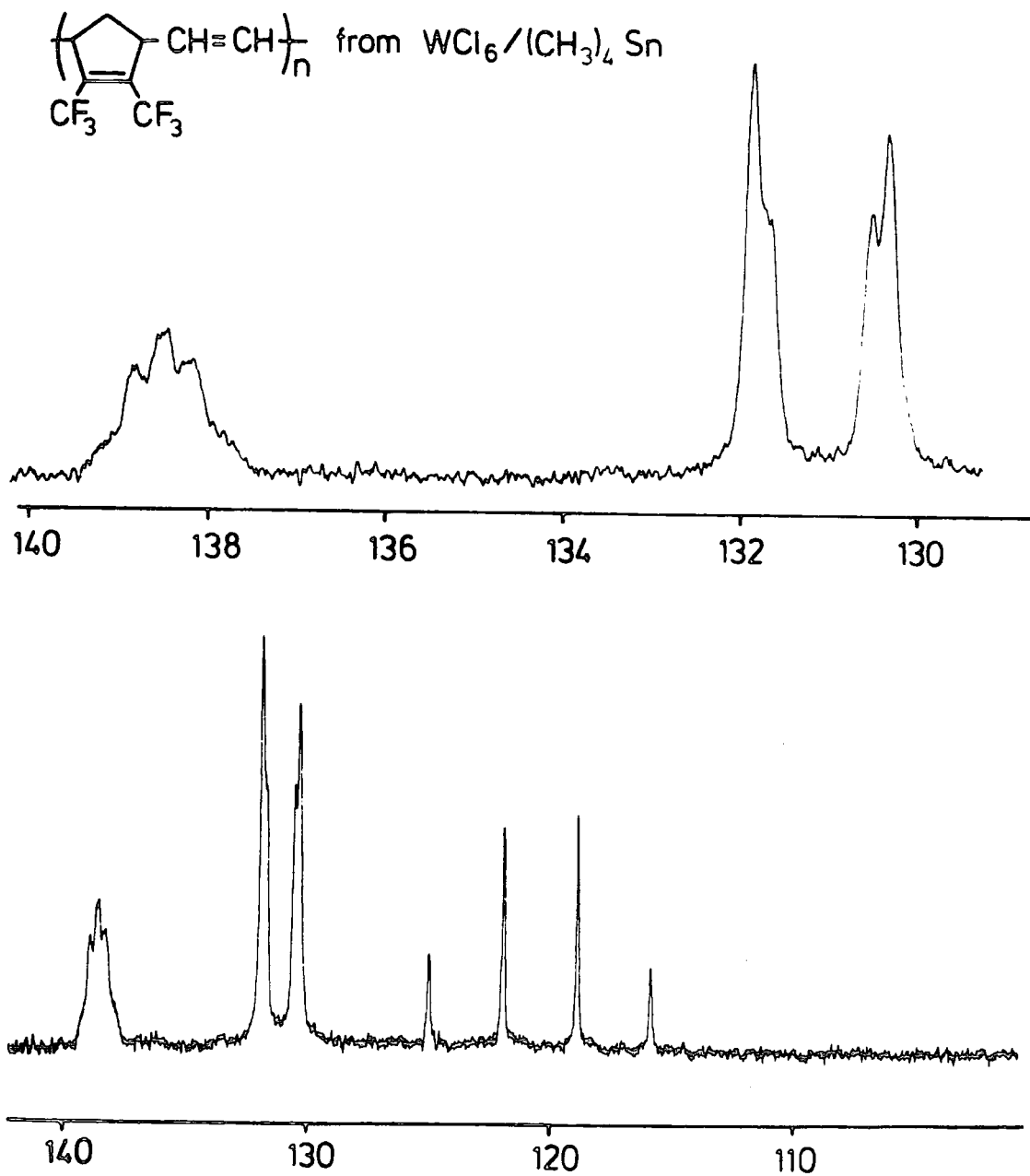


Figure 2.19

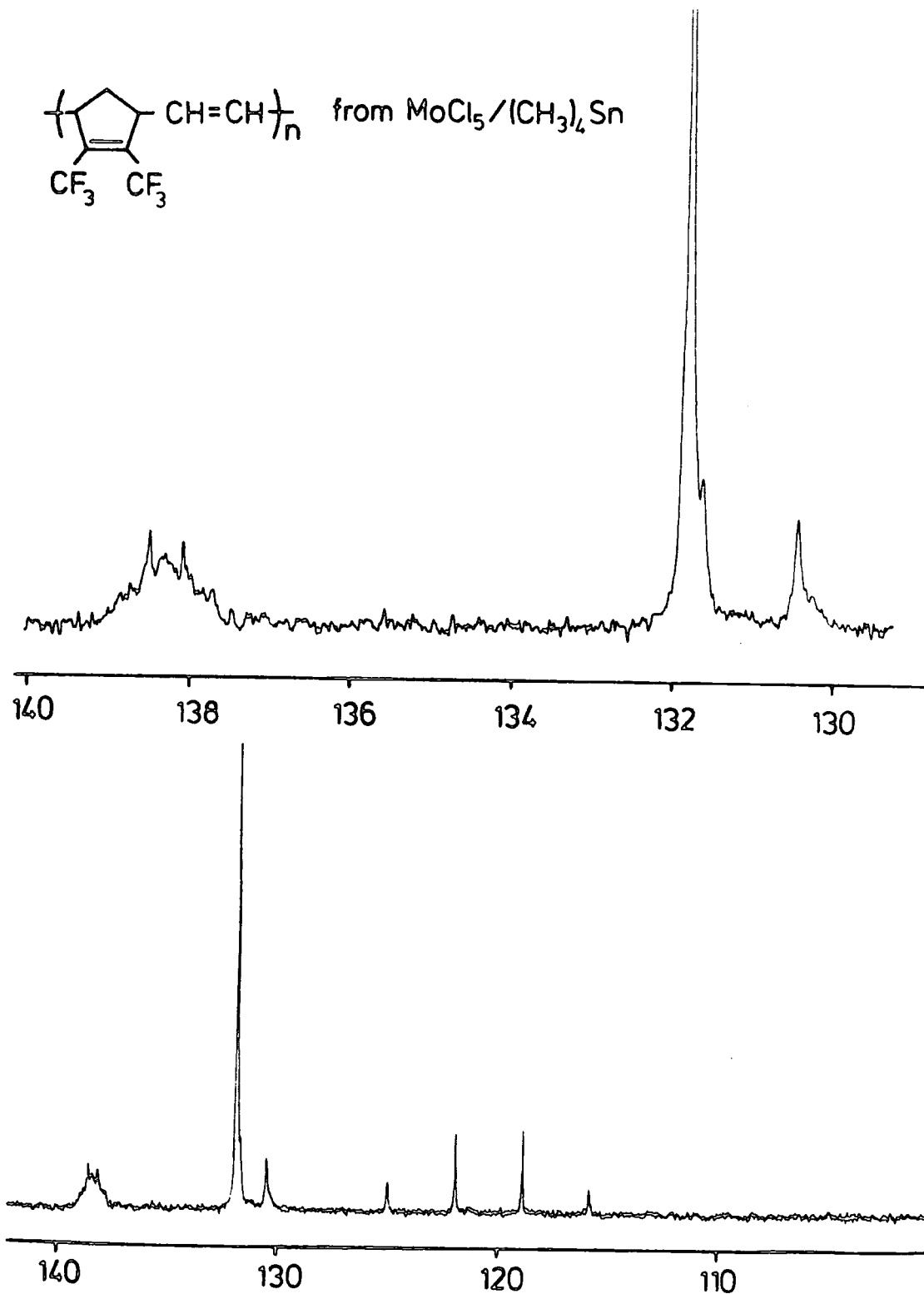
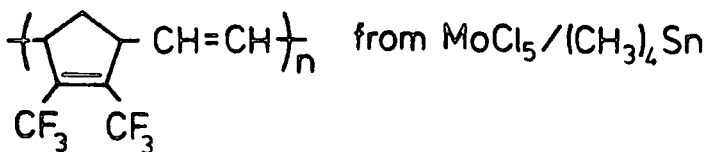


Figure 2.20

electronegative trifluoromethyl substituent and consequently occur at lower field than the methylene carbon signals. Comparison of the two spectra in Figure 2.21 allows a confident assignment of the signal @ 48.1 ppm to the methine carbon adjacent to a cis double bond with that adjacent to a trans double bond occurring at 43.1 ppm; this reverses the assignment given by Feast and Wilson²⁴² and based on relative intensities in an approximately 50:50 cis/trans polymer, and illustrates the sensitivity of signal intensity in ^{13}C n.m.r. spectroscopy to small variations in structure and environment.

The high cis polymer, Figure 2.21 (D), has only two signals in the methylene region both of which are fairly sharp, the more intense signal presumably arises from the cis syndiotactic sequences, the smaller signal may arise from one of several possible assembly modes. In the methylene region of the spectra for sample (C), we can observe at least five resonances. So it is clear that the methylene carbons are a much more sensitive probe of environment than the methine carbons which appear to give only one unresolved signal depending on whether they are adjacent to a cis or trans vinylene; these observations are somewhat different from those made by Ivin and coworkers on fairly closely related norbornene polymers.

In Ivin's work, the methine carbons were invariably resolved into four signals corresponding, according to Ivin, to the situations labelled cc, ct, tc and tt where the first letter indicates the geometry of the vinylene adjacent to the methine carbon (c-cis, t-trans) and the second letter indicates the geometry at the next nearest vinylene; similarly Ivin and coworkers invariably see only three signals for the methylene carbons in this type of polymer (cc, ct etc, tt). The observation in these high resolution spectra of only two methine resonances and five methylene

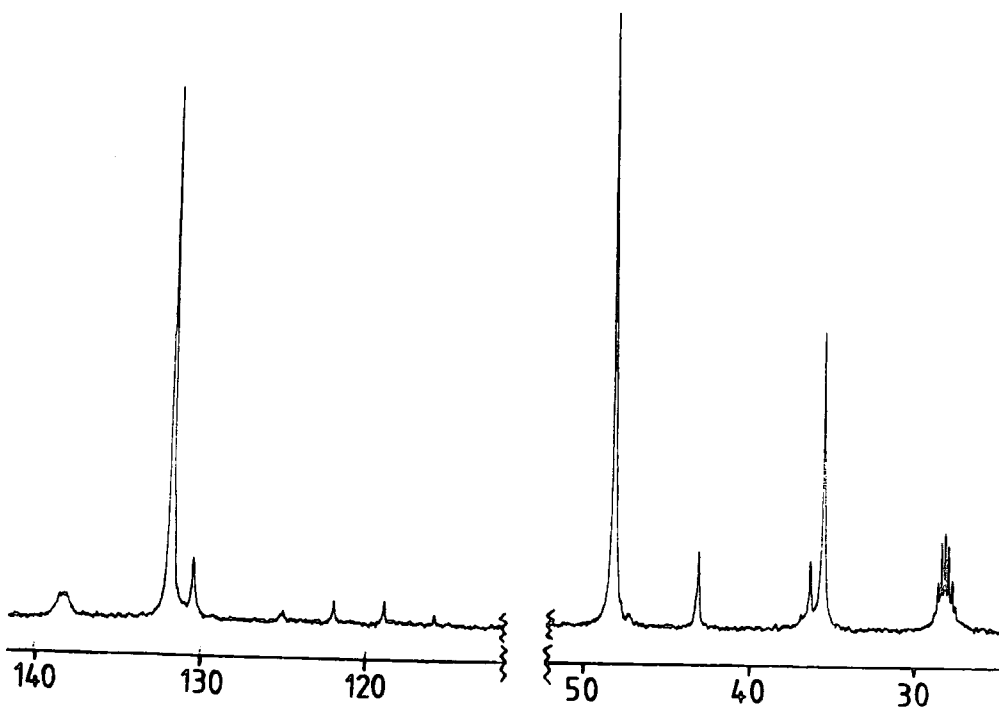
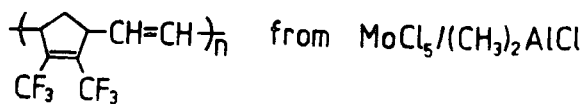
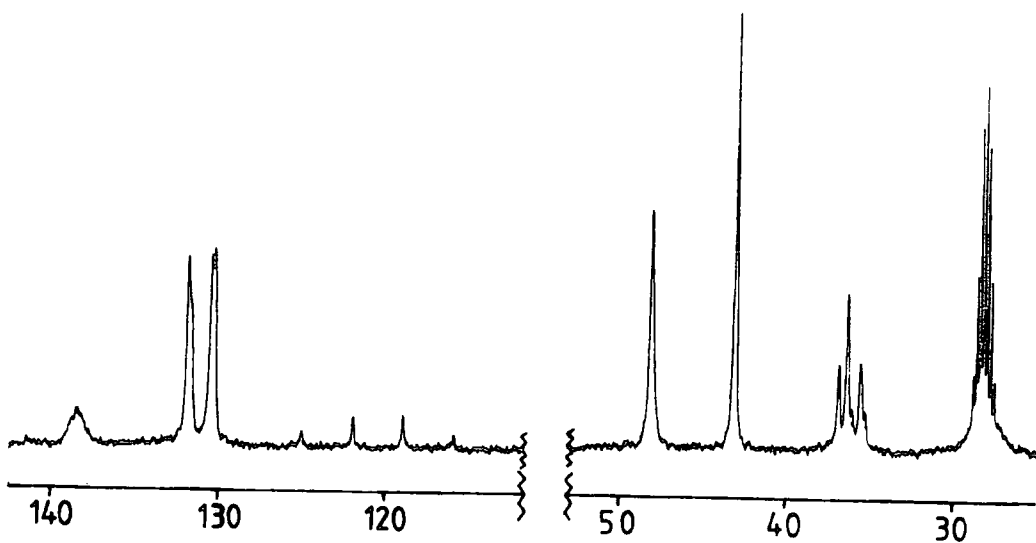
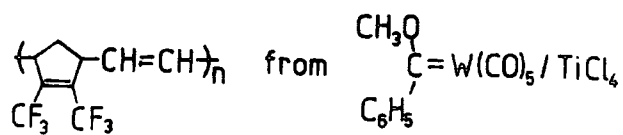


Figure 2.21

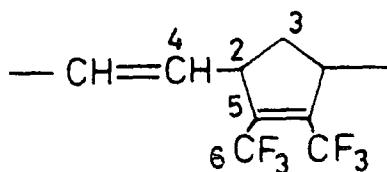
resonances is very interesting as far as its implications for chain microstructure are concerned, unfortunately it has so far proved impossible to obtain a wider range of polymer stereochemistries than the two types discussed above and this makes it difficult to draw any detailed conclusions about the assignment of specific resonances.

Clearly in these polymers most information about details of microstructure is to be obtained from the vinylene carbon signals (discussed earlier) and the methylene carbons. The methylene carbons in polymer (VII) can be in either syndiotactic or isotactic sequences and the adjacent vinylene may be both cis, both trans or one cis and one trans. This gives rise to six possibilities and in the best spectra recorded so far, we observe five resonances. By reference to the spectra in Figure 2.19, 2.20 and 2.21 and the assignments established in the above discussion, it is possible to assign the methylene carbon signals in Table 2.2 as follows.

- (i) The signal at an average shift 35.53 ppm is associated with methylene carbons in cis-syndiotactic sequence.
- (ii) The signal at 34.90 ppm (only one case observed) is associated with cis-isotactic placements.
- (iii) The signal at an average shift of 36.34 ppm is associated with a methylene with adjacent cis and trans vinylene, as is the signal at 36.08 ppm (only one example), but the tacticity of the ring placements is not certain in this case.
- (iv) The signal at an average shift of 36.83 ppm (2 examples) is associated with a methylene between two trans vinylene units.

These assignments lead to the conclusions that in the high cis polymers the residual trans vinylene units are randomly distributed and not found as trans blocks. This analysis, although reasonable, would be more firmly based if there were more types of microstructure available for study.

Table 2.2. Chemical shifts in the ^{13}C n.m.r. spectra of poly(4,5-bis(trifluoromethyl)-1,3-cyclopentadienevinylene) initiated by $\text{WCl}_6/(\text{CH}_3)_4\text{Sn}$ (A), $\text{MoCl}_5/(\text{CH}_3)_4\text{Sn}$ (B), $(\text{CO})_5\text{W}(\text{OCH}_3)\text{C}_6\text{H}_5/$ TiCl_4 (C) and $\text{MoCl}_5/(\text{CH}_3)_2\text{AlCl}$ (D). See Figure 2.19, 2.20 and 2.21.



Chemical shift				Assignment	Relative Area			
(A)	(B)	(C)	(D)		(A)	(B)	(C)	(D)
34.90				3cc	0.98			
35.54	35.55	35.48	35.53		17.40	20.42	9.87	30.03
36.08				3ct 3tc	4.80			
36.38	36.35	36.31	36.33		12.76	5.25	17.12	7.07
36.85		36.81			13.33		3.47	
43.09	43.04	43.03	43.02	2t	45.72	7.51	36.33	6.47
48.15	48.11	48.11	48.11	2c	51.75	43.74	34.41	55.70
115.87	115.83	115.84	115.85	6				
118.39	118.85	118.82	118.85					
121.92	121.88	121.90	121.92					
124.92	124.90	124.90	124.94					
130.32		130.24		4t	24.75		16.76	
130.48	130.42	130.43	130.42		17.82	7.65	21.13	7.29
131.10	131.63			4c	1.86	7.90		
131.85	131.82	131.82	131.81		45.30	35.84	32.09	51.72
137.50	137.50	137.50	137.50	5				
139.00	139.00	139.00	139.00					

Fraction of cis (σ_c)

calculated from:

	(A)	(B)	(C)	(D)
Vinylene region	52.82	35.04	45.36	87.65
Methine region	53.09	35.40	48.64	39.59
Methylene region	54.65	89.78	51.97	90.53

The detailed spectroscopic parameters for polymers A, B, C and D are recorded in Table 2.2 with the proportion of cis double bonds (σ_c) calculated following Ivin's method.¹⁵⁶

2.3.b. Copolymerization of 2,3-bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene with cyclopentene, some preliminary observations

The objectives of this work have been discussed earlier in this Chapter, it was hoped that the structure of copolymer could be established if possible. Wilson's earlier report was based only on elemental analysis results and involved relatively high conversions. In this work, the copolymerizations were terminated at an early stage in order to get a more accurate indication of monomer reactivity. In the first attempts, three widely different feed stock ratios were tried (see Experiment Section).

The products from the copolymerization were characterized by elemental analysis (see Experiment Section), i.r. (Appendix C, No IX and X) and ¹³C n.m.r. spectroscopy (Figure 2.22); the reaction using a 1:5 ratio of diene to cyclopentene gave too low a yield to examine properly. The two copolymers obtained in reasonable quantity were soluble in toluene, acetone and methylethylketone.

Both copolymers were analyzed by i.r. spectroscopy (Appendix C, No IX and X) showing that they were essentially the same and contained a combination of peaks from poly(1-pentenylene) and poly(4,5-bis(trifluoromethyl)-1,3-cyclopentenylenevinylene). The spectra were complex and it was not possible to determine the monomer composition in a satisfactorily quantitative way.

¹³C N.m.r. spectroscopy (Figure 2.22) of the polymers obtained from the 1:1 feed stock and from the 5:1 feed stock showed that both of them contained combinations of peaks assigned to poly(1-pentenylene) and

poly(4,5-bis(trifluoromethyl)-1,3-cyclopentenylenevinylene) units. The spectra obtained were very complicated because the catalyst system used (WCl_6/Ph_4Sn) produces a mixture of double bond isomers as in the homopolymerizations of both monomers. Reliable compositions could not be determined since sufficiently well resolved spectra were not obtained, and it has to be acknowledged that even if better resolved spectra were available the assignment of all the observed peaks would present great difficulties. Never-the-less, a preliminary assignment would suggest that in the vinylene region, the relative intensities of carbons from each monomer are approximately equal in intensity indicating that in the early stages a 1:1 incorporation is observed. It is certainly clear from the expanded vinylene region (Figure 2.22) that these copolymers have very similar microstructures.

Elemental analysis of both products indicated that the copolymers contained repeat units (VII) and (VIII) in a ratio between 1:1 to 2:1. In theory, the three sets of analytical data can be used to calculate the monomers incorporation ratio and should provide three internally consistent determinations. In practice, the calculated monomer incorporation from the analytical results showed considerable differences and thus this technique cannot be regarded as a reliable method (Table 2.3)

The reason why this method failed is not completely clear, but it has to be acknowledged that very small amounts of solvent contamination can have a significant effect on the elemental analysis figures and although the copolymer were dried under vacuum for several hours before analysis, they may well have been slight contamination by solvent. In view of the problems encountered in this work, it was decided to abandon further work on copolymerization of 2,3-bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene. It is clear that this fluoromonomer is readily incorporated with

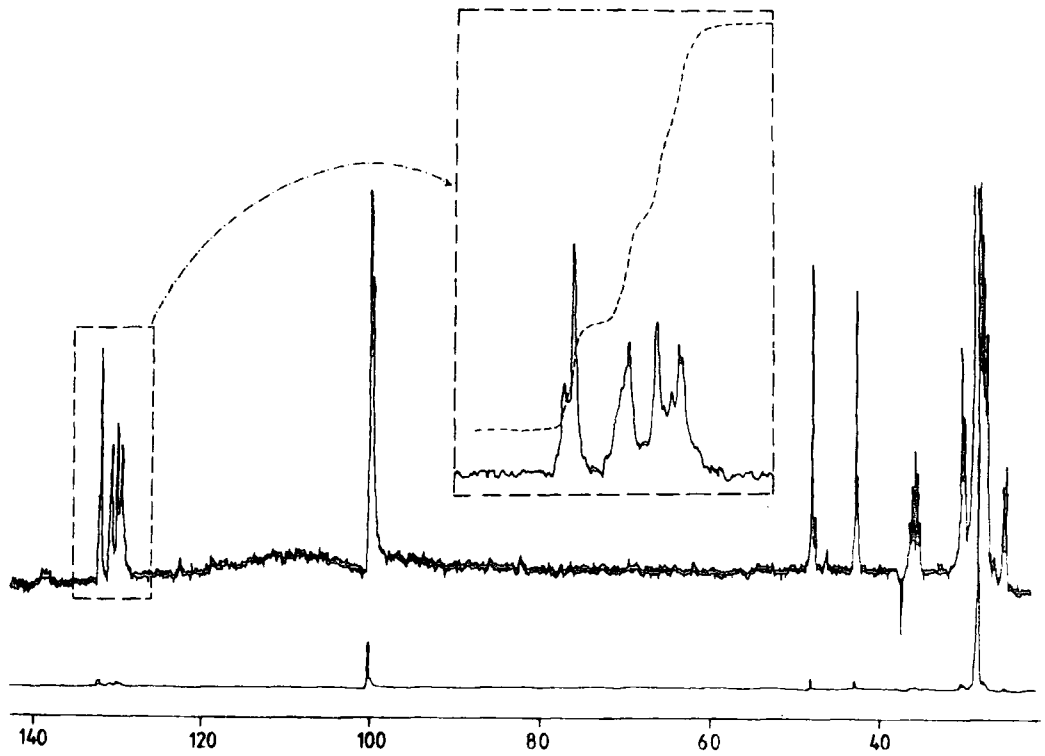
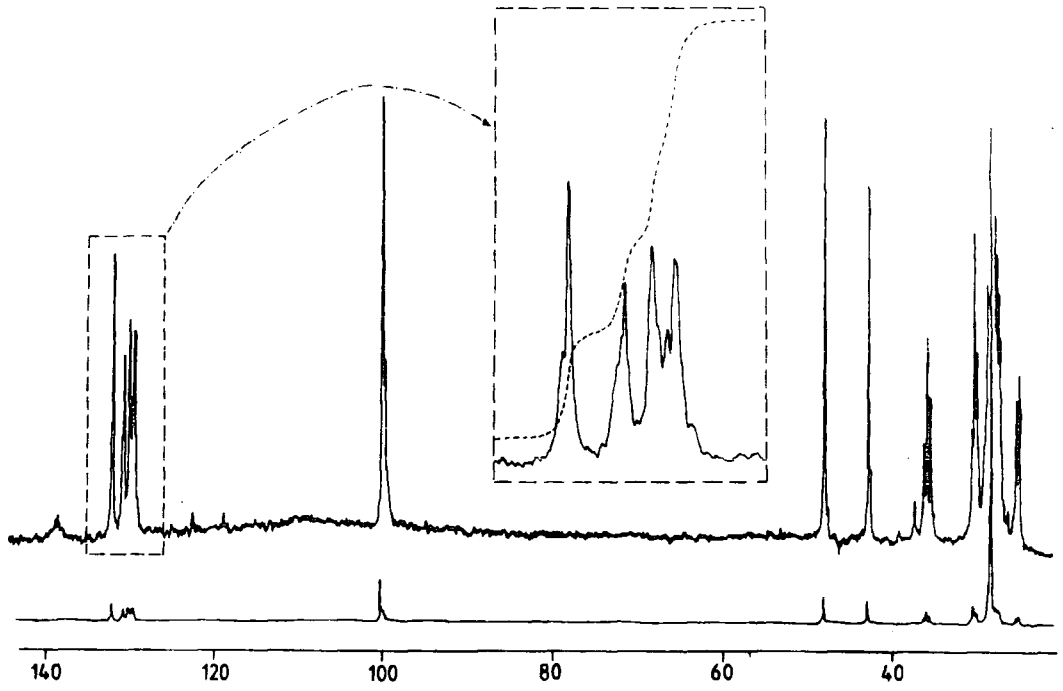


Figure 2.22.

cyclopentene in the copolymer with the catalyst system examined here. This observation showed that this diene probably has a reactivity somewhere between that of cyclopentene and bicyclo[2.2.1]hept-2-ene, which is reasonable since the reactivity of the -CH=CH- double-bond in 2,3-bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene should be increased by strain as compared to cyclopentene, but the π -donor capacity might reasonably be expected to be reduced by the electronegative CF_3 substituents.

On the other hand, it may be that copolymerization with cyclopentene is not a good test of reactivity since it is known that the cyclopentene to poly(1-pentenylene) reaction is reversible, whereas the 2,3-bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene (like bicyclo[2.2.1]hept-2-ene) is not reversible, therefore analysis of copolymers with cyclopentene may underestimate the reactivity of cyclopentene and over estimate that of 2,3-bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene.

Table 2.3. Copolymer compositions calculated from elemental analysis results(% of cyclopentene incorporated)

Calculated from	Copolymer from 1:1 feed stock	Copolymer from 5:1 feed stock
% C	43.7	42.3
% H	48.3	38.3
% F	40.0	51.3

2.3.c. New fluorinated polymers

2.3.c.i. Introduction

In this section, the synthesis of some new fluorinated polymers are described, this work expands that initiated by Wilson.²⁴² Part of the reason for this study was to examine the possibility of synthesizing conjugated polymers via a dehydrohalogenation route shown below, Figure 2.23, and in relation to this project, the thermal degradation of these new material has been examined. The relative ease of polymerization of

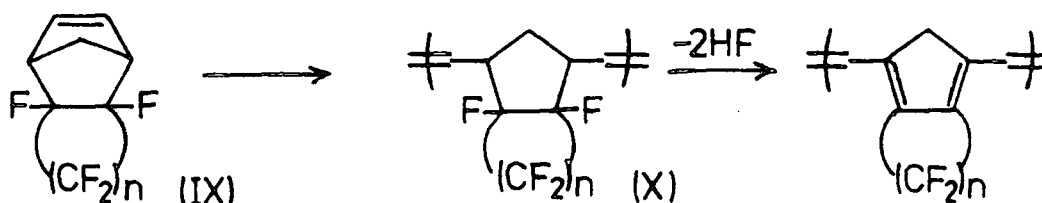


Figure 2.23.

endo and exo isomers has also been examined, and some unsuccessful attempts to prepare new fluoropolymers are also recorded.

The syntheses and characterization of all the monomers used in studies described in this section have been described in Section 2.2.

2.3.c.ii. Metathesis polymerization of perfluorotricycloalkenes

2,3,3,4,4,5-Hexafluorotricyclo[4.2.1.0^{2,5}]non-7-ene, consisting of about 95% of the endo isomer, was readily polymerized by the catalyst systems WCl_6/Ph_4Sn , $MoCl_5/Me_4Sn$ and $(CO)_5W=C(OCH_3)C_8H_5/TiCl_4$, the overall result is shown in Figure 2.24. The polymer ((X), $n=2$) after reprecipitation was obtained as a white, acetone soluble, powder. Its elemental analysis (Found C, 46.62; H, 2.18; F, 50.65; $C_8H_6F_6$ requires C, 47.73; H, 2.81; F, 49.79%), i.r. (Appendix C, No XII) and 1H n.m.r. spectrum (methylene H, 2.05; tertiary H, 2.75; vinylene H, 5.75), were consistent with the assigned structure. Its polymeric nature was evidenced by the formation of viscous

dilute solutions from which tough films could be cast.

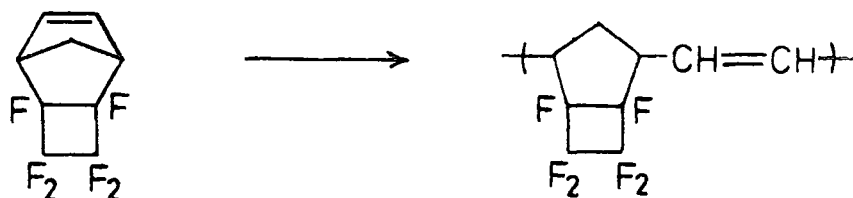


Figure 2.24.

2,3,3,4,4,5,5,6-Octafluorotricyclo[5.2.1.0^{2,6}]dec-8-ene also readily polymerized with $\text{WCl}_6/\text{Ph}_4\text{Sn}$ catalyst to give a similar white polymer, Figure 2.25. Again the observed elemental analysis (Found C, 43.33; H, 2.07; F, 54.08; $\text{C}_{10}\text{H}_6\text{F}_8$ requires C, 43.17; H, 2.16; F, 54.68%), i.r. (Appendix C, No XIV) and ^1H n.m.r. spectrum (methylene H, 1.66; tertiary H, 2.75; vinylene H, 5.85) were consistent with the assigned structure and the dilute solution-viscosity and formation of tough films were taken as evidence of the polymeric nature of the material.

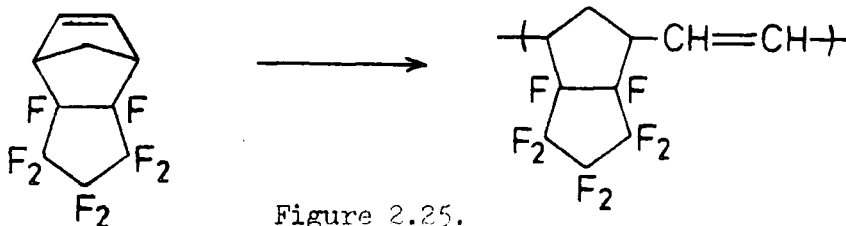


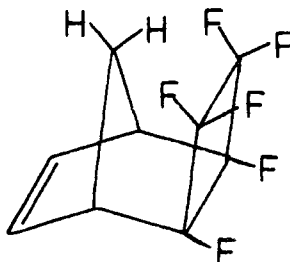
Figure 2.25.

^{13}C N.m.r. spectroscopy has proved to be a powerful tool in assigning structure in polymer of this kind (see earlier). In the two cases considered here, the ^{13}C n.m.r. spectra of monomer and resultant polymer are reproduced in Figure 2.26 and 2.27 and the spectroscopic parameters are collected in Table 2.4.

Considering first the polymer derived from the perfluorocyclobutene/cyclopentadiene adduct, it can be seen (top spectrum Figure 2.26) that the vinylic, methine and methylene carbons of the major component (endo-adduct see Section 2.2) give strong signals at 137.67, 45.93 and 39.91 ppm

respectively, and that the fluorine substituted carbons give weak broad signals centered at 115.8 ppm for the difluoromethylene carbon and 101.4 ppm for the fluoromethine carbon, the signals having the appropriate multiplicities with $J_{CF} = 290$ Hz. The exo-adduct signals are all weak with the fluorine bearing carbons in this case either being masked by the signal due to the major isomer or lost in the background noise.

One interesting feature is the very low field position (52.05 ppm) of the bridging methylene carbon, this is believed to be a consequence of the field effect of the adjacent fluorocarbon unit in the exo-adduct as shown below; the methylene protons in the 1H n.m.r. spectrum of the exo



adduct also occur at a much lower field than might have been expected (see Table 2.1). Completely analogous effects are seen in the spectra of the perfluorocyclopentene adducts.

In the polymer, no signals which might have been derived from the exo-adduct can be detected, however since it was present in such low concentration, this is not surprising and probably not significant. The signals which are seen are readily assigned, going from low to high field, as due to vinylene, CF_2 , tertiary CF , methine and methylene carbons respectively. Each carbon resonance is found at slightly higher field than it was in the monomer which is consistent with the reduction in strain throughout the system following ring-opening. The methine and methylene signals are multiplets, but unresolved and therefore of little use in defining microstructure, the vinylene signal is split into that resulting from cis units (lower field) and that due to trans units, and the integrated intensities

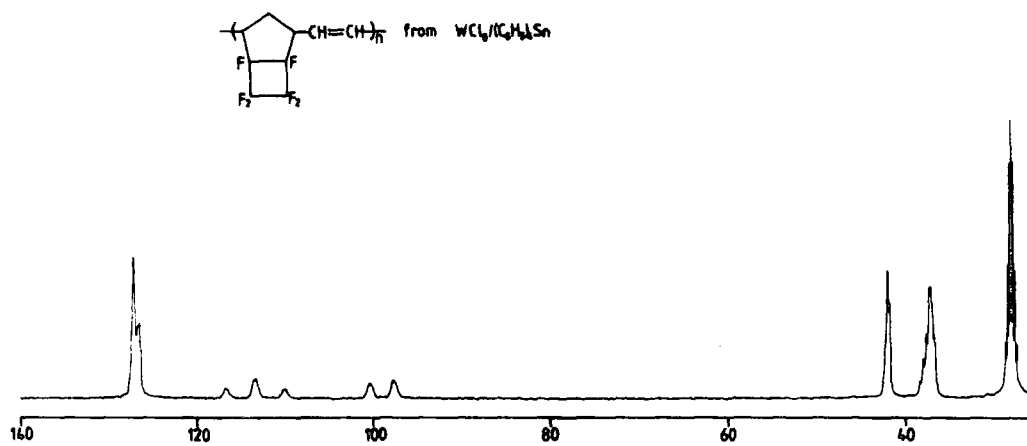
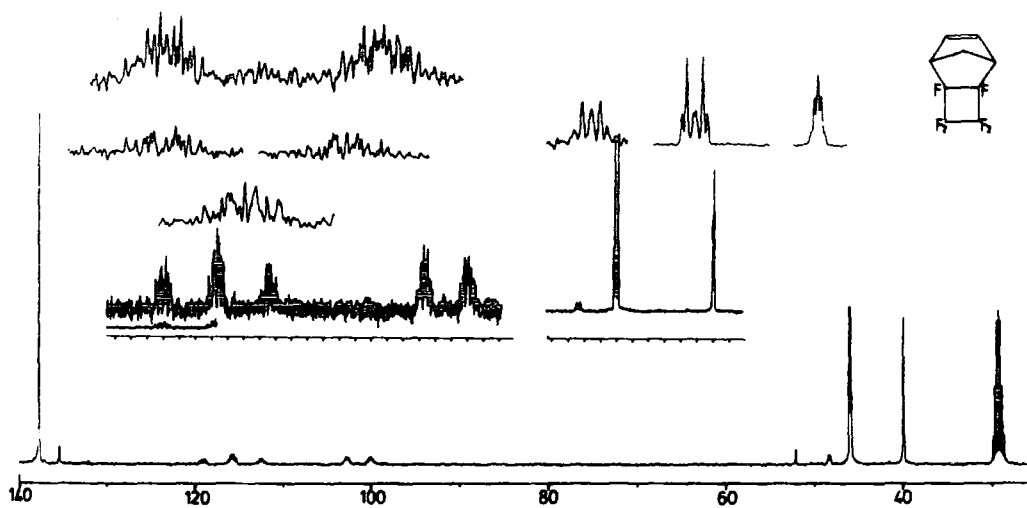
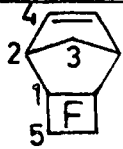
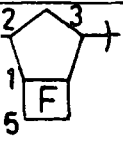
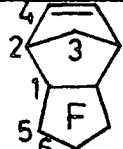
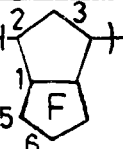


Figure 2.26. ^{13}C N.m.r. spectra for 2,3,3,4,4,5-hexafluorotricyclo
[4.2.1.0^{2,5}]non-7-ene and derived polymer

indicate 64.4% of cis double-bonds which is a marginally higher cis content than is normally obtained from these catalysts.

When the ^{13}C n.m.r. spectrum for the mixture of 1:1 adducts of cyclopentadiene and perfluorocyclopentene is examined (Figure 2.27), the assignments shown in Table 2.4 follow fairly straight forwardly given the assignment of the isomer mixture discussed at length in Section 2.2. The ^{13}C spectrum of the polymer derived from this mixture of monomers, while being consistent with the expected polymer structure, has a rather poor signal/noise ratio and indifferent resolution. This was a considerable disappointment as we had hoped to investigate the relative reactivity of endo and exo isomers towards metathesis ring-opening using this analytical probe; this matter is discussed in the next Section.

Table 2.4. ^{13}C N.m.r. data for polymers (X, n=2) and (X, n=3)

				
	Endo	Exo	Endo	Exo
C_4	137.67	135.38	127.24, 126.7	
C_2	45.93	48.29	41.81 (m)	
C_1	101.4 (d, J 290 Hz)		99.02 (d, J 290 Hz)	
C_5	115.8 (t, J 290 Hz)		113.50 (t, J 290 Hz)	
C_3	39.91	52.05	37.37 (m)	
				
C_4	136.10	134.63	125.80, 127.15, 128.29 (complex multiplet, not well resolved)	
C_2	44.18	47.56	34.62 (complex series of	
C_3	40.31	43.06	47.40 resonances, unassigned)	
C_1	98.00 (d, J 290 Hz)		98.60 (d, J 290 Hz)	
$\text{C}_{5,6}$	113.2 (t, J 290 Hz)		112.0 (m, not well resolved)	

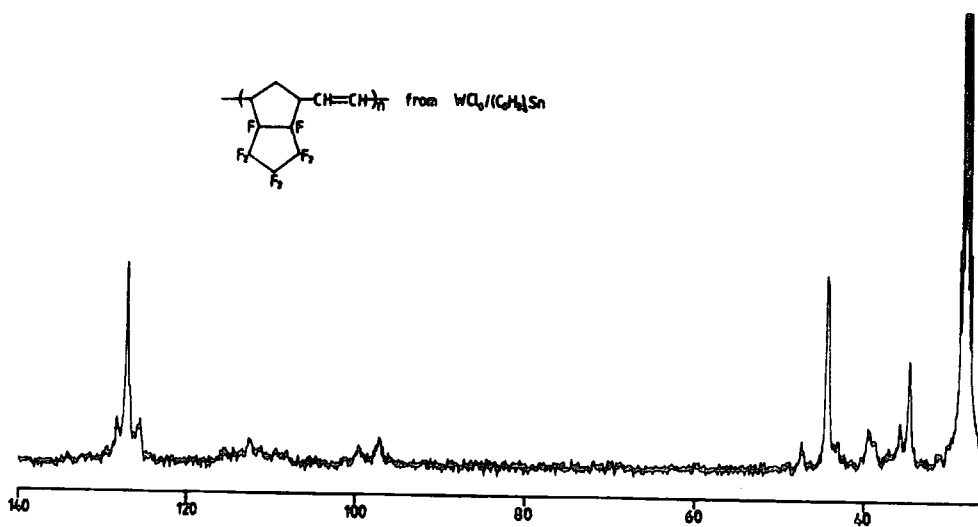
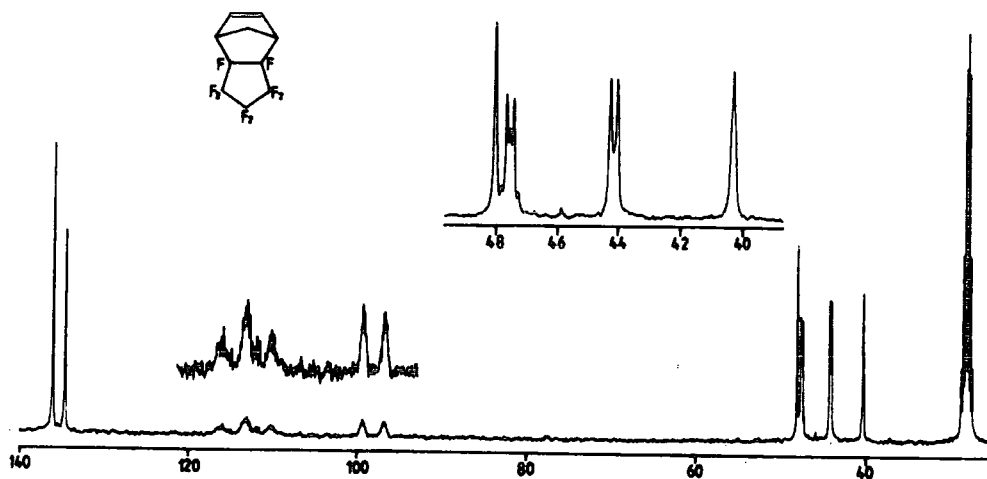
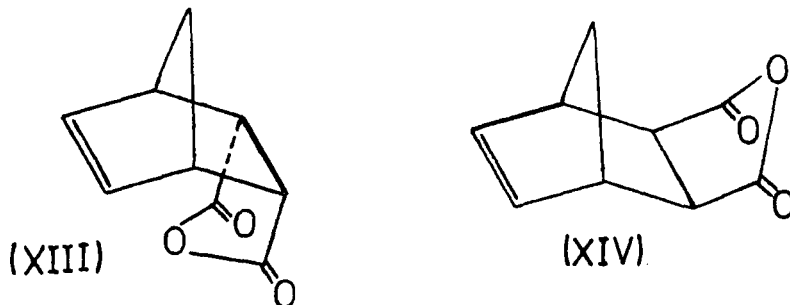


Figure 2.27. ^{13}C N.m.r. spectra for 2,3,3,4,4,5,5,6-octafluorotriclo[5.2.1.0^{2,6}]dec-8-ene and deriver polymer

2.3.c.iii. Selectivity studies in metathesis polymerization of endo/exo
2,3,3,4,4,5,5,6-octafluorotricyclo[5.2.1.0^{2,6}]dec-8-ene

Calderon and Castner²⁷⁴ observed that pure endo-5-norbornene-2,3-dicarboxylic anhydride (XIII) is inert to metathesis polymerization, whereas the exo-isomer (XIV) undergoes smooth homopolymerization and copolymerization. The same authors also found that when an exo/endo mixture was polymerized, the conversion was dependant on the amount of exo-isomer in the monomer mixture. Analysis of the recovered monomer from the polymerization of 45:55 endo/exo mixture, clearly indicated that the exo-isomer polymerized preferentially. Nevertheless, some endo-isomer does become incorporated into the polymer.



By contrast, an earlier unpublished observation by Wilson²⁴² suggested that the isomer of compound (I), (Figure 2.1) in which the CF_3 group is in the endo position polymerized preferentially when an exo/endo mixture of compound (I) is treated with a WCl_6 based catalyst. This observation was based on the ^{19}F n.m.r. spectra of polymers prepared from the pure endo-trifluoromethyl isomer of (I) and a 60:40 endo/exo mixture of isomers of (I).

As mentioned in the previous Section, the author has polymerized a 53:47, endo:exo mixture of 2,3,3,4,4,5,5,6-octafluorotricyclo[5.2.1.0^{2,6}]dec-8-ene, and here we examine the isomer selectivity.

The monomer mixture was polymerized with $\text{WCl}_6/\text{Ph}_4\text{Sn}$ catalyst in toluene for 2 hours, the reaction was terminated by addition of THF. The solvent and the unpolymerized monomers collected by filtration from polymeric

product, and the ^{19}F n.m.r. spectra of both the starting monomer mixture and recovered monomer mixture were recorded and compared, Figure 2.28. The lengthy discussion in Section 2.2 of the ^{19}F n.m.r. spectrum of the monomer mixture established that the lower field signal in the tertiary CF region was derived from the endo-adduct, it is this signal which is markedly decreased in intensity in the recovered monomer spectrum. Therefore this observation of preferential polymerization of the endo isomer is in agreement with Wilson's earlier observation and contrasts with the observations of Calderon and Castner on the analogous anhydride systems.

The differences between the fluorocarbon substituted norbornene and the anhydride substituted norbornene are unambiguously established. The causes for these differences in behaviour are rather hard to understand. Calderon attributed the exo-isomer preference in the anhydride systems to a possible unfavourable interaction between the reacting double bond and the anhydride oxygens in the endo isomer, as shown in structure (XIII). This seems reasonable if catalyst attack comes from the exo face then as the double bond distorts it may be forced to interact with the anhydride ring in an unfavourable way.

When we consider the fluorinated system (IX, $n=3$) such distortion of the reacting double bond will lead to an interaction with either a trio of difluoromethylenes (endo adduct polymerizing) or a pair of fluorine atoms (exo adduct polymerizing) in this case it is more difficult to predict the likely outcome. Indeed it is not really clear why an endo anhydride should really hinder the reaction since the double bond will be donating its π -electron density to the catalyst, which is approaching the exo-face, and an electronegative group behind the double bond might be expected to assist this process.

Clearly there is no simple rationalization for the combined observations

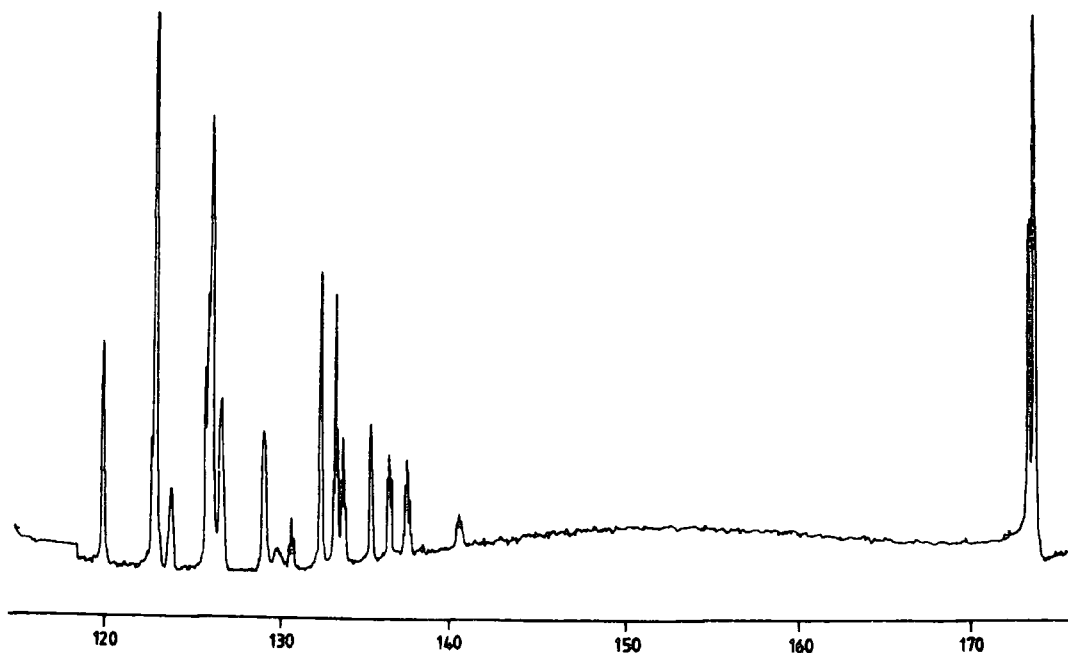
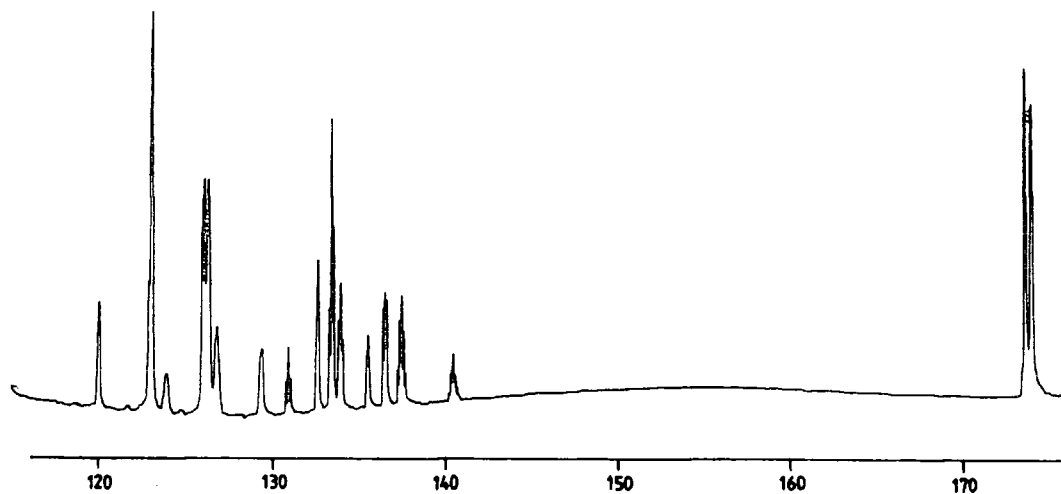


Figure 2.28. ^{19}F N.m.r. spectra of starting and recovered monomers
from polymerization of endo/exo-2,3,3,4,4,5,5,6-octa-
fluorotricyclo 5.2.1.0^{2,6} dec-8-ene

of Calderon, Wilson and the results given here, and the true explanation probably lies in a subtle balance of stereochemical and electronic factors.

2.3.c.iv. Thermal degradation of fluorinated polymers (X, n=2 and n=3)

As will be discussed at greater length in Chapter 3, the synthesis of polyconjugated materials is of considerable current interest. In this group thermal elimination reactions have been successfully used to generate polyacetylene (see page 38, Figure 1.38), and one of the earliest routes to conjugated sequences was established by Marvel.²⁷⁵ Marvel's dehydrochlorination of PVC is not able to give pure polyacetylene because in a random dehydrochlorination process isolated chloromethylenes and methylenes will limit the conjugated path length (Figure 2.29). In the process postulated in Figure 2.23, it was expected that the non-random loss of tertiary allylic H and tertiary F would occur, reasonably readily to yield the novel conjugated structure shown.

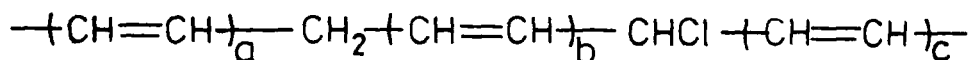


Figure 2.29.

Thermal decomposition studies were carried out using a Stanton Redcroft TG 750 Thermobalance operating in a percentage weight loss mode and temperature programme mode from ambient to about 700^oC at 1^o/minute under a nitrogen atmosphere. Three polymers were examined, the material derived from monomer (II) (Figure 2.1) and polymers (X,n=2) and (X,n=3). Their thermograms are shown in Figures 2.30, 2.31 and 2.32 respectively.

The results were disappointing in that only one polymer appeared to show a step-like loss of weight, that was polymer (X,n=3), Figure 2.32. However even in this case, the weight loss 38% did not correspond to a loss of 2HF per repeat unit which requires a loss of 14.4%; further the residue

Figure 2.30.

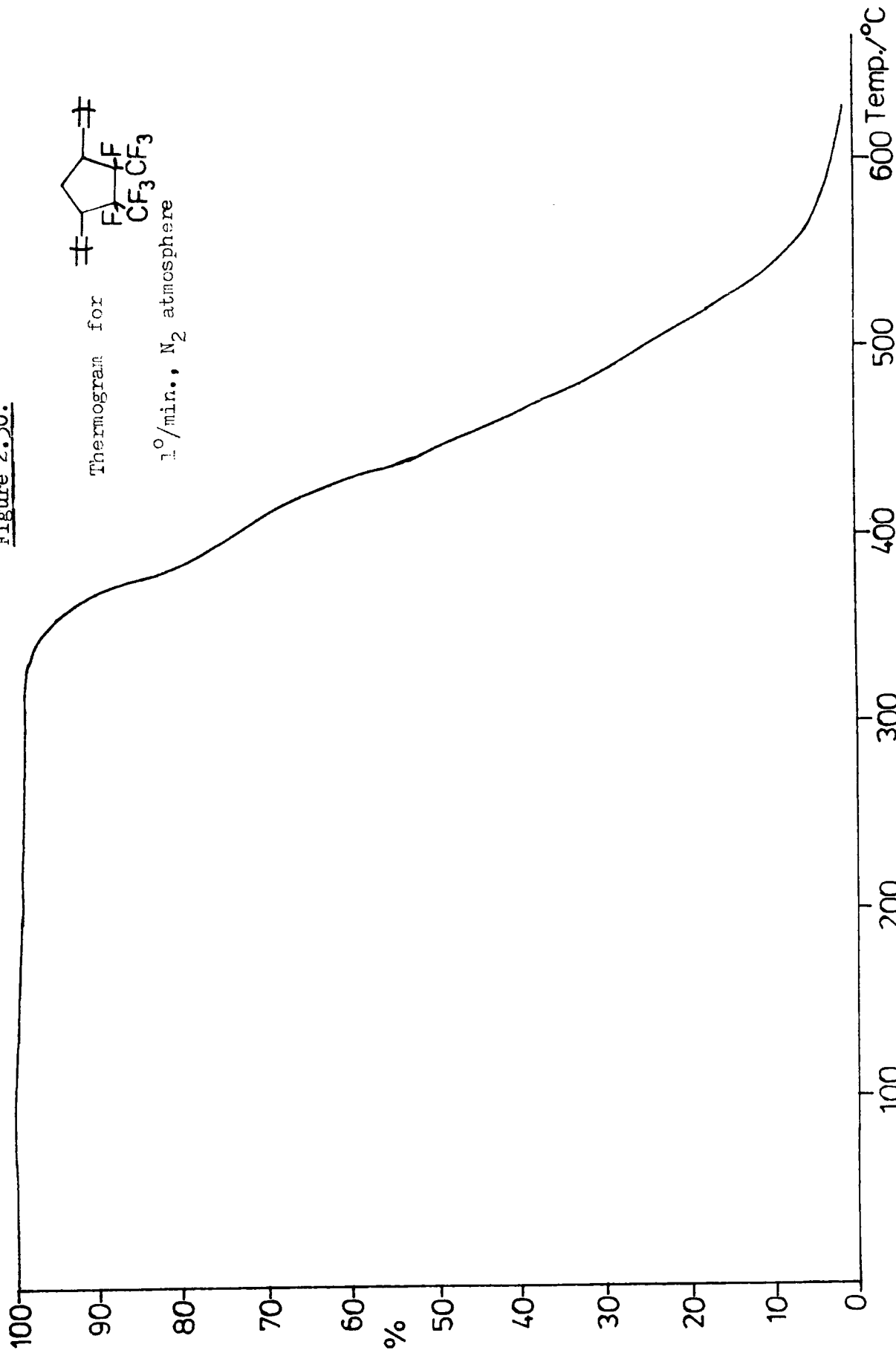


Figure 2.21.

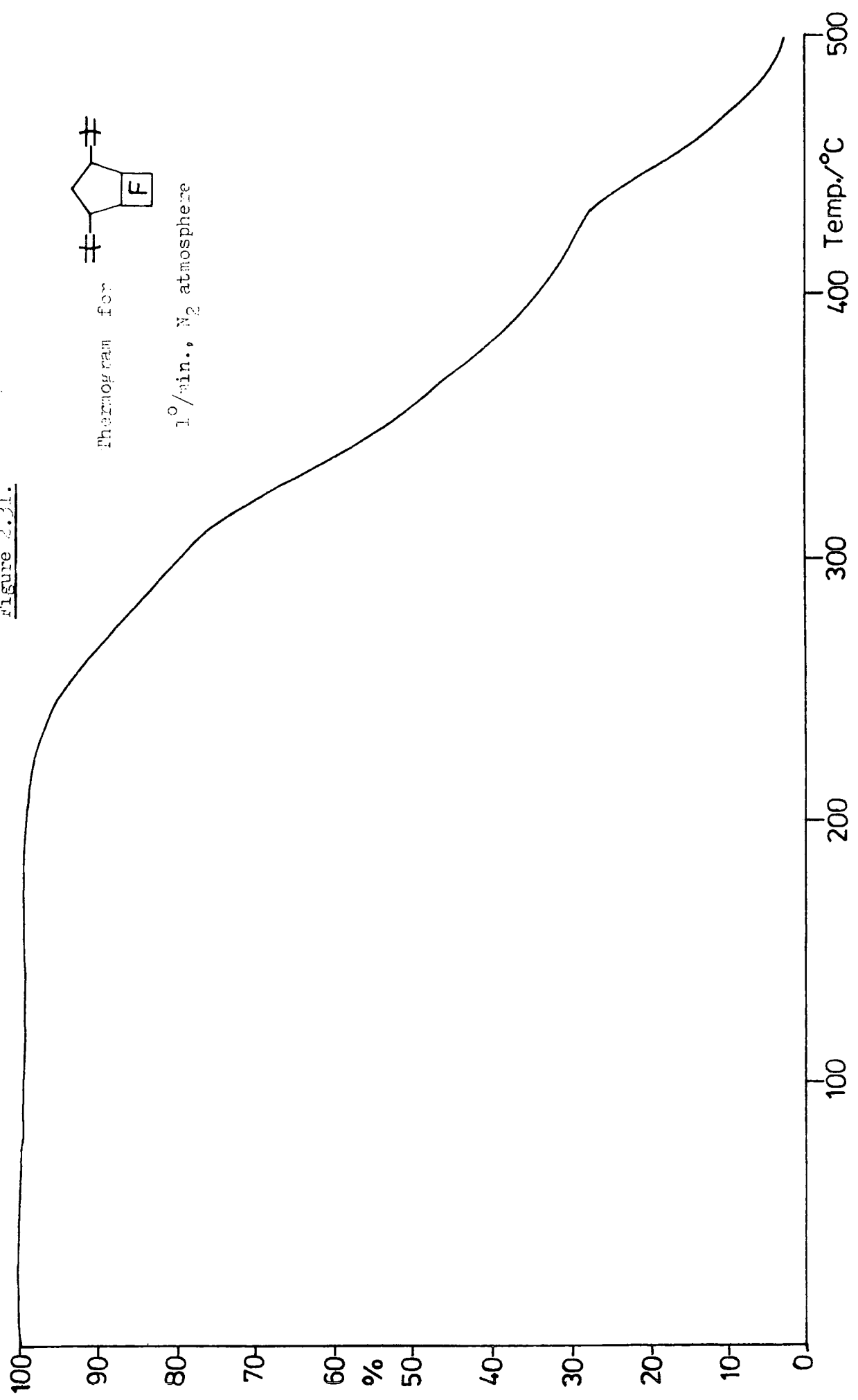
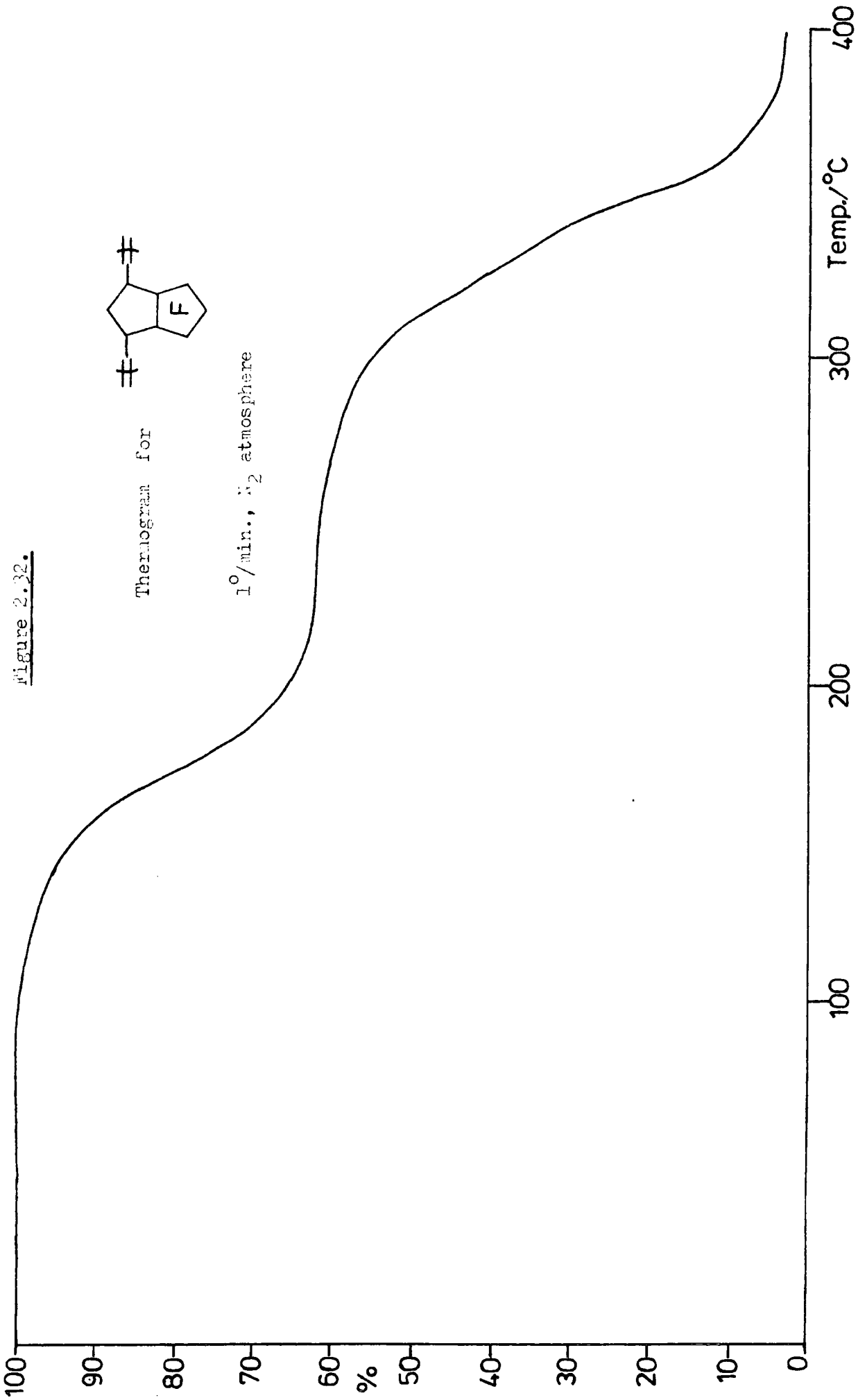


Figure 2.32.



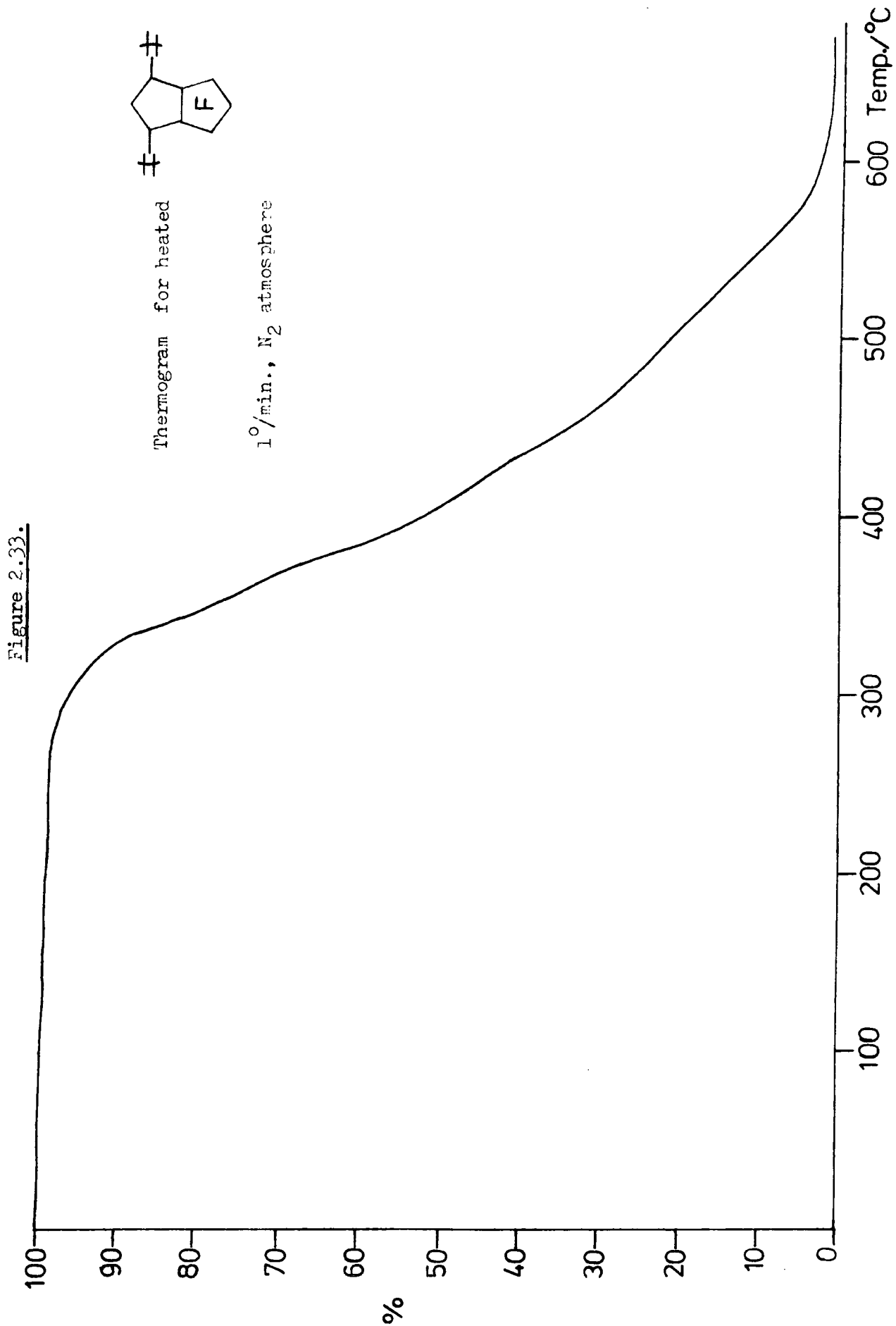
in the thermobalance pan was white which would not be expected had a conjugated material been formed. It was decided to investigate this material a little further and so a larger sample of polymer ($X, n=3$) was heated at 240°C and under vacuum (1 mm Hg) for 10 hours, at this stage a white solid had sublimed from the flask and the weight loss was 11%. The author has been unable to identify the white solid sublimate, the mass spectrum showed peaks extending to m/e values in excess of 400 (the monomer parent ion occur at m/e 228) and the infrared spectrum showed the presence of C-H, CF and probably $-\text{CH}=\text{CH}-$ units but did not strongly resemble either monomer or polymer; it may be that the material is a low molecular weight telomer or polymer fragment. There was no evidence for the evolution of HF under these conditions. When the thermogravimetric analysis of this heated sample was recorded, Figure 2.33, it resemble the thermograms of the other polymers and was typical of a material undergoing a random thermal degradation process.

Clearly thermal degradation of polymers of the type discussed here is not a plausible route to polyconjugated systems. The resistance of these materials to thermal elimination of HF was unexpected in view of the ready loss of HF from most fluorohydro polymers.

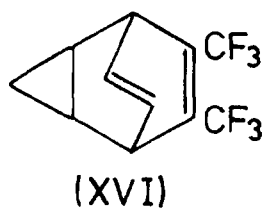
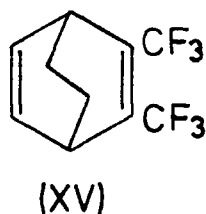
2.3.c.v. Some unsuccessful attempts to polymerize cyclic fluorinated monomers

1,2-Bis(trifluoromethyl)cyclohexa-1,4-diene and 5,5,6-trichloro-6-trifluoromethylbicyclo[2.2.1]hept-2-ene were not polymerized despite many attempts and long exposure to active catalysts. These catalysts polymerized cyclopentene or bicyclo[2.2.1]hept-2-ene as comonomer added at the end of polymerization attempts.

The inertness of the cyclohexene ring to metathesis catalysts is well established, and has been discussed in Chapter 1. The author attempted to



find out if increased ring strain might make a cyclohexene derivative polymerizable. 1,2-Bis(trifluoromethyl)cyclohexa-1,4-diene is marginally more strained than cyclohexene, as is compound (XV) prepared by Dr. J.H. Edwards,²⁷⁶ neither could be polymerized; increasing the ring strain by including a cyclopropane unit (XVI) also fails to make the six-membered ring susceptible to ring-opening polymerization.²⁷⁶



The nonpolymerizability of 5,5,6-trichloro-6-trifluoromethylbicyc[2.2.1]hept-2-ene was more surprising since the related compound, 5,6-dichloro-5,6-bis(trifluoromethyl)bicyclo[2.2.1]hept-2-ene (IV, Figure 2.1) readily polymerized.²⁴² Several other chlorinated monomers will be discussed in Chapter 3 and this matter will be returned to then.

EXPERIMENTAL

2.4. Preparation of Partially Fluorinated Cycloalkenes

2.4.a. Reagents

Cyclopentadiene was freshly prepared by thermal cracking²⁷⁷ from dicyclopentadiene which was purchased from Koch-Light Laboratories Ltd. Hexafluorobut-2-yne, decafluorocyclohexene and 1,3-butadiene were purchased from Bristol Organics Ltd; 1,2-dichlorohexafluorocyclopentene-1 and 3,3,3-trifluoro-1,1,2-trichloropropene were purchased from Peninsular Chemical Research Inc; hexafluorocyclobutene and octafluorocyclopentene were prepared by Mr. D. Hunter of this Department. All these reagents were used without further purification, liquid reagents were degassed using the freeze-thaw procedure before use.

2.4.b. Reactions of Fluorinated Olefins with Dienes

General Procedure

Pyrex Carius tubes were charged with hydroquinone (<0.05g.), attached to the vacuum line, and evacuated. Gaseous dienophiles were vacuum transferred into the tube, while liquid reagents were injected with a syringe after purging the tube with nitrogen. The amount transferred was weighed and then fresh cyclopentadiene was injected to make up a 1:1, 2:1 or 1:2 mixture. The tube was sealed under vacuum, then heated in a furnace for the required time at the required temperature. The tube was opened by 'hot spotting' and the products separated and purified using conventional vacuum-line techniques.

The adducts were analysed and characterized by analytical gas-liquid-chromatography, elemental analysis, mass and ^1H , ^{19}F and ^{13}C n.m.r. spectroscopy.

2.4.b.i. Preparation of 2,3-Bis(trifluoromethyl)bicyclo[2.2.1]-hepta-2,5-diene

Hexafluorobut-2-yne (33.9 g., 209 mmole), cyclopentadiene (13.8 g., 209 mmole) and hydroquinone (0.05 g.) were sealed in vacuum and left at room temperature for 24 hours to give (i) 2,3-bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene (38.5 g., 169 mmole, 80% yield); b.p. 124-125° (Lit:²⁷² 109-111°, Lit:²⁴² 110-112°); M (m.s.), 228 (calculated M, 228) with correct i.r. spectrum,²⁴² and (ii) a brown liquid, probably cyclopentadiene dimer.

2.4.b.ii. Preparation of 1,2-Bis(trifluoromethyl)cyclohexa-1,4-diene

Hexafluorobut-2-yne (22.0 g., 136 mmole) and 1,3-butadiene (8.5 g., 157 mmole) were condensed in an autoclave and left at room temperature for 48 hours to give (i) 1,2-bis(trifluoromethyl)cyclohexa-1,4-diene (10.5 g., 46 mmole, 34% yield); b.p. 130-132° (Lit:²⁷³ 135°); i.r. spectrum, ν_{\max} 1665 and 1698 cm^{-1} (Lit:²⁷³ 1670 and 1710 cm^{-1}); M (m.s.), 216 (calculated M, 216); the ^1H and ^{19}F n.m.r. spectra were consistent with the proposed structure (see Table 2.1) (ii) low boiling point liquid (25%), probably starting material; and (iii) a black solid residue (10%).

2.4.b.iii. Preparation of 5,5,6-Trichloro-6-trifluoromethylbicyclo[2.2.1]-hept-2-ene

3,3,3-Trifluoro-1,1,2-trichloropropene (31.9 g., 120 mmole), cyclopentadiene (8.6 g., 130 mmole) and hydroquinone (0.05 g.) were sealed in vacuum and heated at 150° for 72 hours to give (i) 5,5,6-trichloro-6-trifluoromethylbicyclo[2.2.1]hept-2-ene (8.5 g., 32 mmole, 27% yield), as a waxy white solid, m.p. 135°; [Found C, 37.72; H, 2.24%; $\text{C}_8\text{H}_6\text{Cl}_3\text{F}_3$ requires C, 36.16; H, 2.26%]; M (m.s.), 230 (M-Cl); the structure was confirmed by ^1H and ^{19}F n.m.r. spectra (see Table 2.1) (ii) white crystals (15%) with molecular-weight (450) and containing several chlorine atoms; and (iii) a

brown solid residue (10%), probably dicyclopentadiene.

2.4.b.iv. Preparation of 2,3,3,4,4,5-Hexafluorotricyclo[4.2.1.0^{2,5}]-non-7-ene

Hexafluorocyclobutene, cyclopentadiene and hydroquinone (0.05 g.), in the amounts shown in Table 2.5, were sealed under vacuum and heated to give (i) 2,3,3,4,4,5-hexafluorotricyclo[4.2.1.0^{2,5}]non-7-ene as a colourless liquid, b.p. 27° at 5 mm. Hg; Found C, 47.63; H, 2.81; F, 49.79%; C₉H₆F₆ requires C, 47.37; H, 2.63; F, 50.00% ; M (m.s.), 228 (calculated M, 228); the structure was confirmed by ¹H, ¹⁹F and ¹³C n.m.r. spectra, (ii) white crystals (20%), probably a mixture of polyadducts, mass specrometry showed the parent ion for 3:1 adduct of diene/olefin.

Table 2.5. Reaction Between Cyclopentadiene and Hexafluorocyclobutene

No.	Ratio olefin/diene	Amount of hexafluorocyclobutene (mmole)	Amount of cyclopentadiene (mmole)	Reaction temperature (°C)	Time (hours)	Yield of 1:1 adduct (%)
1.	1:1	88	91	170	24	5
2.	1:1	56	46	150	48	38
3.	2:1	177	91	150	24	23

2.4.b.v. Preparation of 2,3,3,4,4,5,5,6-Octafluorotricyclo[5.2.1.0^{2,6}]-dec-8-ene

Octafluorocyclopentene, cyclopentadiene and hydroquinone (0.05 g.) in the amounts shown in Table 2.6, were sealed under vacuum and heated to give (i) 2,3,3,4,4,5,5,6-octafluorotricyclo[5.2.1.0^{2,6}]dec-8-ene as a waxy white solid material; [Found C, 43.66; H, 2.02; F, 53.95%; C₁₀H₆F₈ requires C, 43.17; H, 2.16; F, 54.67%]; M (m.s.), 278 (calculated M, 278). The ¹H, ¹⁹F and ¹³C spectra, showed that the product was a mixture of endo/exo isomer in 53:47 ratio (see Table 2.1 and discussion); (ii) white crystals (20%) which were shown by gas-chromatography-mass-specrometry to be a mixture

of 2:1 and 3:1 adducts; and (iii) brown liquid, probably dicyclopentadiene.

Table 2.6. Reaction Between Cyclopentadiene and Octafluorocyclopentene

No.	Ratio olefin/diene	Amount of octafluorocyclopentene (mmole)	Amount of cyclopentadiene (mmole)	Reaction condition (°C)	Time (hours)	Yield of 1:1 adduct (%)
1.	2:1	142	72	150	24	15
2.	1:1	71	67	170	24	20
3.	1:2	53	109	170	24	-

2.4.b.vi. attempts to Prepare 2,3,3,4,4,5,5,6,6,7-Decafluorotricyclo-[6.2.1.0^{2,7}]undec-9-ene

Decafluorocyclohexene, cyclopentadiene and hydroquinone (0.05 g.) in the amounts shown in Table 2.7 were sealed under vacuum and heated. Several attempts were made to prepare the 1:1 adduct. The product was invariably a high molecular-weight, white solid and mass spectrometric analysis showed that it was an adduct of several molecules of diene to one of dienophile; the highest observed mass corresponded to a 3:1 adduct, whereas the elemental analysis indicated a 7:1 or 8:1 adduct, presumably the polyadducts undergo Retro Diels-Alder reactions under the conditions used to record the mass spectrum (high vacuum and moderate temperature).

Table 2.7. Reaction Between Cyclopentadiene and Decafluorocyclohexene

No.	Ratio olefin/diene	Amount of decafluorocyclohexene (mmole)	Amount of cyclopentadiene (mmole)	Reaction condition (°C)	Time (hours)	Yield of 1:1 adduct (%)
1.	2:1	122	61	120	48	no reaction
2.	2:1	123	61	170	24	—
3.	2:1	120	61	200	24	—
4.	1:1	60	61	200	24	—

2.4.b.vii. attempts to Prepare 2,6-Dichloro-3,3,4,4,5,5-hexafluorotricyclo-
[5.2.1.0^{2,6}]dec-8-ene

1,2-Dichloro-3,3,4,4,5,5-hexafluorocyclopentene, cyclopentadiene and hydroquinone (0.05 g.) in the amounts shown in Table 2.8, were sealed under vacuum and heated. Several attempts were made but the 1:1 adduct was not obtained in a pure state.

Table 2.8. Reaction Between Cyclopentadiene and 1,2-Dichloro-3,3,4,4,5,5-
hexafluorocyclopentene

No.	Ratio olefin/diene	Amount of olefin (mmole)	Amount of cyclopentadiene (mmole)	Reaction condition (°C)	Time (hours)	Yield of 1:1 adduct (%)
1.	1:2	69	37	170	48	3
2.	1:1	74	74	170	48	impure
3.	1:1	55	56	120	72	no reaction
4.	1:1	16	15	RT	7d	no reaction
5.	1:1	69	69	200	72	impure

2.5. Polymerization

2.5.a. Reagents and Methods

Analar toluene (Hopkin and William) was dried by refluxing over molten sodium in a nitrogen atmosphere until a permanent deep blue colour was obtained on adding benzophenone, the solvent was then distilled directly into carefully dried reaction vessels. Analar chlorobenzene was refluxed over P₂O₅ and distilled (N₂ atmosphere) immediately prior to use. WCl₆ was prepared and purified by sublimation to remove oxychlorides. MoCl₅, ReCl₅ and RuCl₃ were used directly without any purification. A RuCl₃/2COD complex was prepared by the literature route¹⁵⁶ although this was active for metathesis of bicyclo[2.2.1]hept-2-ene, it seems unlikely that it was the material claimed in the literatures (see discussion).

$(CO)_5W=C(OCH_3)C_6H_5$ and $TiCl_4$ were provided by Dr. J.H. Edwards of this Department. Tetraphenyl-, tetrabutyl- and tetramethyltin were purchased from Aldrich Chemical Company Inc. and were used without further purification. Me_2AlCl was provided by Mr. B. Hall of this Department. The nitrogen gas was dried by passing it through a bubbler of concentrated sulphuric acid and then through a column of P_2O_5 . Precaution were taken to dry the equipment and monomers, and usually the monomer was degassed by the freeze-thaw procedure. All the manipulations of solvents, catalyst solutions and cocatalysts (if liquid) were carried out under an atmosphere of dry nitrogen using an air-tight syringe.

2.5.b. Polymerization Procedure

One typical example of the reaction will be described here, the details of other syntheses being tabulated.

A two necked round-bottomed flask (50 or 100 ml) containing a magnetic follower was used as reaction flask, both necks were fitted with three way teflon taps, one lead was connected to the nitrogen system and the other lead to a pump. The required amount of monomer was placed in the reaction flask and degassed using the freeze-thaw procedure. The flask was purged with nitrogen and then connected to the nitrogen system in the fume cupboard, with the outlet connected to a pump to ensure effective purging with dry nitrogen. The required amount of cocatalyst and solvent were added making sure that the system was effectively purging with nitrogen at all times. 1 to 2 ml of prepared solution of catalyst was injected into the reaction flask and an immediate colour change to a dark red-brown for tungsten-based catalysts and dark red for molybdenum-based catalysts was observed. An increase in the viscosity of the solution was generally noticed for successful reactions, the time of occurrence and magnitude of this viscosity increase was dependent on the details of the particular

experiment. The experiment was allowed to proceed for a period and then the polymerization was terminated by addition of a small quantity of methanol or tetrahydrofuran. Any precipitate was collected, dried, dissolved in solvent and reprecipitated by drop-wise addition of a viscous solution of polymer to a vigorously stirred excess of non-solvent. The precipitates were recovered by filtration and dried under reduced pressure, for at least 5 hours.

2.5.c. Polymerization of 2,3-Bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene with Different Catalyst Systems

Using the procedure described above, 2,3-bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene was polymerized with variety of catalysts as tabulated below.

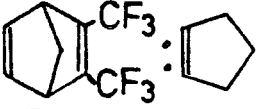
Catalyst System	Molar Ratio Cat:Cocat:Mon	Solvent (5-10 ml)	Reaction time	Yield (%)
WCl ₆ /Ph ₄ Sn	1 : 2 : 150	toluene	1.0	80
WCl ₆ /Bu ₄ Sn	1 : 2 : 60	toluene	1.0	75
WCl ₆ /Me ₄ Sn	1 : 2 : 60	toluene	1.5	20
MoCl ₅ /Ph ₄ Sn	1 : 2 : 60	toluene	18.0	75
MoCl ₅ /Me ₄ Sn	1 : 2 : 70	PhCl	3.0	70
MoCl ₅ /Me ₂ AlCl	1 : 2 : 60	toluene	18.0	74
(CO) ₅ W=C(OCH ₃)C ₆ H ₅	1 : 2 : 60	toluene	48.0	no reaction
(CO) ₅ W=C(OCH ₃)C ₆ H ₅ / TiCl ₄	1 : 2 : 60	toluene	18.0	30
(CO) ₅ W=C(OCH ₃)C ₆ H ₅ / TiCl ₄	1 : 2 : 60	toluene	2.0 ^{50°C}	25

attempts to polymerize 2,3-bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene with ReCl₅, ReCl₅/Me₄Sn, ReCl₅ in benzene and with the RuCl₃/2COD complex were unsuccessful. These catalysts were shown to effectively

polymerize bicyclo[2.2.1]hept-2-ene under the same reaction conditions.

2.5.d. Copolymerization of 2,3-Bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene with Cyclopentene

Mixture of 2,3-bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene and cyclopentene were polymerized with WCl_6/Ph_4Sn as described above. The reaction was terminated early in order to obtain sample of polymer at low conversion. Reaction condition are recorded below.

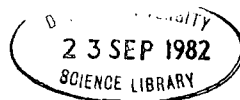
	WCl_6 mmole	Ph_4Sn mmole	Toluene mmole	Reaction Time(hrs)	Yield (%)
60 : 301 (1:5)	1	2	7300	2	<0.05
180 : 179 (1:1)	1	2	7300	2	6.0
299 : 60 (5:1)	1	2	7300	2	3.0

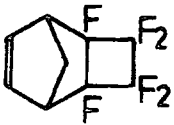
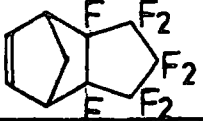

Reliable quantitative characterization of copolymer samples was difficult. I.r. spectroscopic analysis showed both expected units were present, but the technique was not suitable for quantitative analysis. Elemental analysis results were also not good enough for reliable compositional analysis, and the ^{13}C n.m.r. spectra were also unsuitable for this purpose (see discussion).

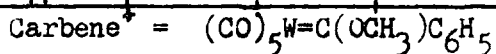
Copolymer	C/%	H/%	F/%	Total/%
1:1 feed stock, found	55.04	4.61	41.80	101.45
5:1 feed stock, found	54.60	4.06	38.30	96.96
Calc. 1:1 repeat unit	56.76	4.73	38.53	100.00
Calc. 2:1 repeat unit	52.67	3.83	43.51	100.00

2.5.e. Polymerization of Partially Fluorinated Cycloalkenes

Reagents, reaction conditions and product yields for successful ring-opening polymerizations are recorded below.



Monomer	Cat.	Cocat.	Molar Ratio Cat:Cocat:Mon	Amount solvent (ml)	Reaction time (hours)	Yield (%)
	WCl ₆	Ph ₄ Sn	1 : 2 : 15	6.0 ^t	3	82
	MoCl ₅	Me ₄ Sn	1 : 2 : 26	8.0 ^c	6	20
	Carbene ⁺	TiCl ₄	1 : 2 : 22	11.0 ^t	24	15
	WCl ₆	Ph ₄ Sn	1 : 2 : 36	6.0 ^t	3	56
	WCl ₆	Ph ₄ Sn	1 : 2 : 65	6.0 ^t	15	72
	WCl ₆	Ph ₄ Sn	1 : 2 : 20	50.0 ^t	0.5	70



t = toluene

c = chlorobenzene

2.5.f. Unsuccessful Attempts to Polymerize Partially Fluorinated Monomers

Attempts to polymerize 1,2-bis(trifluoromethyl)cyclohexa-1,4-diene using the catalyst systems and the conditions described earlier were unsuccessful. Even when the neat monomer was stirred with active catalyst for 3 days, no polymerization occurred although the catalyst remain active as was demonstrated by the polymerization of cyclopentene. Similarly, 5,5,6-trichloro-6-trifluoromethylbicyclo[2.2.1]hept-2-ene was not polymerized during long exposure to the active catalyst.

CHAPTER 3

SYNTHESES AND POLYMERIZATION

OF SOME

PARTIALLY CHLORINATED CYCLOALKENES

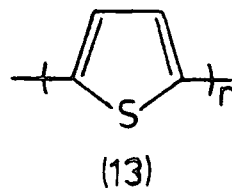
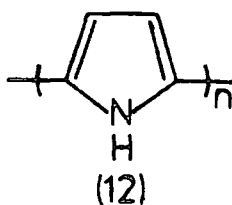
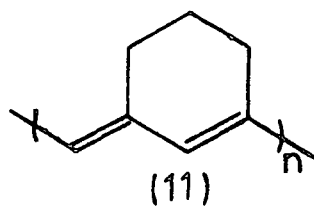
3.1 Introduction

The discovery of polymers such as polyacetylene and related poly-conjugated systems which can be transformed into semiconducting and metallic conductors via the addition of either electron donor or electron acceptor dopants has excited a great deal of attention recently. Although a large amount of research activity in the field of 'organic metals' has been described in several reviews,²⁷⁸⁻²⁸⁰ the problem of making such materials on a large scale and difficulties of processability remain serious drawbacks to progress. A wide variety of polymers which have potential have been developed and can be classified into three families depending upon the backbone type;²⁸⁰

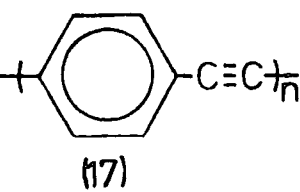
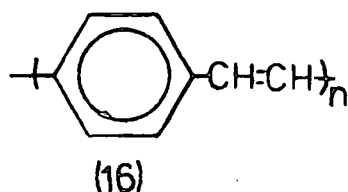
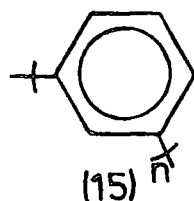
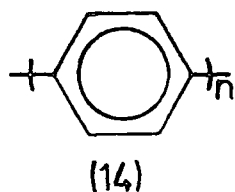
Type 1 has a polyene backbone, this class can be sub-divided into two categories:

(a) non-bridged polyenes such as polyacetylene, poly(phenylacetylene) and poly(dimethylacetylene), these materials can be regarded as the archetypal conjugated polymers.

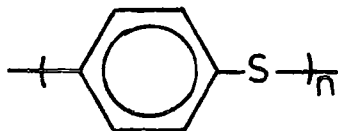
(b) chain-bridge polyenes such as poly(1,6-heptadiyne) (11), polypyrrole (12) and polythiophene (13); in this group, electrochemically deposited films of polypyrrole have attracted most attention.



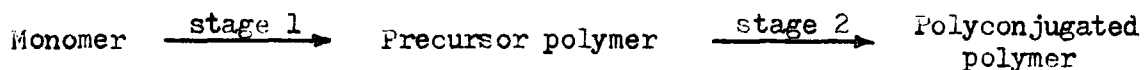
Type 2 materials have arylene units as part of the conjugated systems, examples are polyphenylenes such as poly(p-phenylene) (14), poly(m-phenylene) (15), poly(p-phenylenevinylene) (16) and poly(p-phenylenexylylidene) (17).



Type 3 includes all the materials where the formal conjugated system is interrupted by a heteroatom, the main group is the poly(phenylene chalcogenides); and of these poly(phenylene sulfide) is the most extensively investigated material.²⁸¹



Recently, Edwards and Feast^{221,282} reported a convenient synthesis of polyacetylene by the route indicated in Figure 1.38, page 38. The idea behind their approach to this problem is summarized below. Ideally, the



first stage should yield a polymer which can be purified and then conveniently fabricated into a desired form (fibre, film, surface coating etc), the second stage should be achieved quantitatively and without disruption of the physical integrity of the material. If successful, this approach would overcome the handling and fabrication problems often experienced with materials like polyacetylene.

The author has attempted to expand this approach to the syntheses of polyconjugated systems and in this case, the target was the polyarylene-vinylene type of polymer. The first scheme examined was an attempt to polymerize divinylbenzene by cross metathesis with WCl_6 and $MoCl_5$ based catalysts. The intended scheme is shown in Figure 3.1 and is simply a condensation polymerization of divinylbenzene with elimination of ethylene.

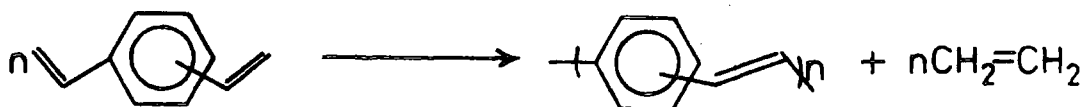
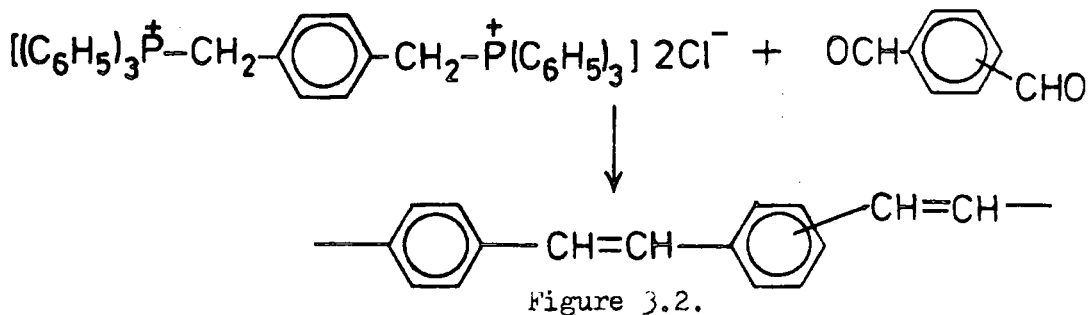


Figure 3.1.

This attempt was unsuccessful because the product was invariably a cross-linked polymer as was demonstrated by its properties such as insolubility. The model reaction, that is the conversion of styrene to stilbene, has been achieved²⁸³ by metathesis over a heterogeneous catalysts in a flow system; although generally olefins with aryl substituents do not readily metathesize under the milder homogeneous conditions.

Several attempts to cross metathesise divinylbenzene all lead to cross-linked material. Since the cross-linking was probably a consequence of cationic vinylic polymerization; the attempted metathesis was also carried out in the presence of pyridine. In this case, the divinylbenzene monomer was recovered unchanged. This approach was abandoned, although if a new highly active catalyst is described in the future, it may be worth re-examination.

The preparation of poly(ortho-, meta- and para-arylenevinylenes) has been described,²⁸⁴ the route involved a Wittig reaction between phthalaldehyde, isophthalaldehyde or terephthalaldehyde with 2,5-bis(triphenylphosphoniomethyl)thiophendichloride as shown in Figure 3.2. The poly(para-phenylenevinylene) is said to be a yellow photoconducting material.



The next project undertaken by the author was an attempt to synthesise the arylenevinylene type of polymer via a route involving metathesis polymerization, thermal and/or photochemical rearrangement and dehydrochlorination by the route shown in Figure 3.3. In the event attempts to

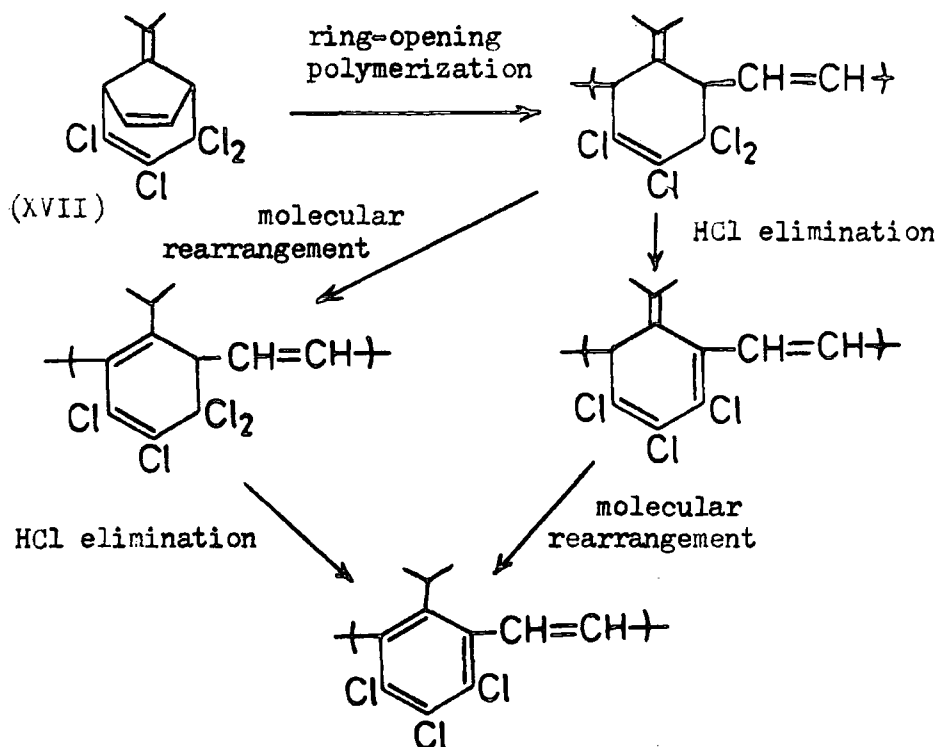
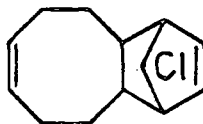


Figure 3.3.

polymerize compound (XVII) using metathesis catalysts were unsuccessful, although the catalyst systems were not deactivated. This result lead to an examination of similar types of monomer in order to try to establish the effect of chlorine as a substituent on reactions of this type.

It is known that the highly chlorinated^{251,285} cycloalkenes shown below and other chlorine substituted derivatives of bicyclo[2.2.1]hept-2-ene^{45,171,245} undergo metathesis polymerization and copolymerization with cyclopentene.



The result found with Compound (XVII) was therefore a surprise and a disappointment, but the causes for this failure seemed worth looking into since they must relate to the range of applicability of metathesis polymerization. This study, along with synthesis and characterization of the

monomers used, forms the major part of this Chapter.

3.2. Syntheses and characterization of monomers

3.2.a. Introduction

The disappointing results of the attempted dehydrofluorination of fluorinated polymers, cross metathesis of divinylbenzene and polymerization of 2,3,4,4-tetrachloro-8-isopropylidenebicyclo[3.2.1]octa-2,6-diene (XVII) frustrated our aim which was to make polyconjugated systems. This lead us to: (a) expand the variety of syntheses of polyconjugated systems investigated and (b) extend the range of chlorine substituted bicyclo[3.2.1]-octa-2,6-diene systems, so as to try to understand the failure of compound (XVII).

The range of partially chlorinated cycloalkenes which have been made and examined for polymerizability is shown in Figure 3.4.

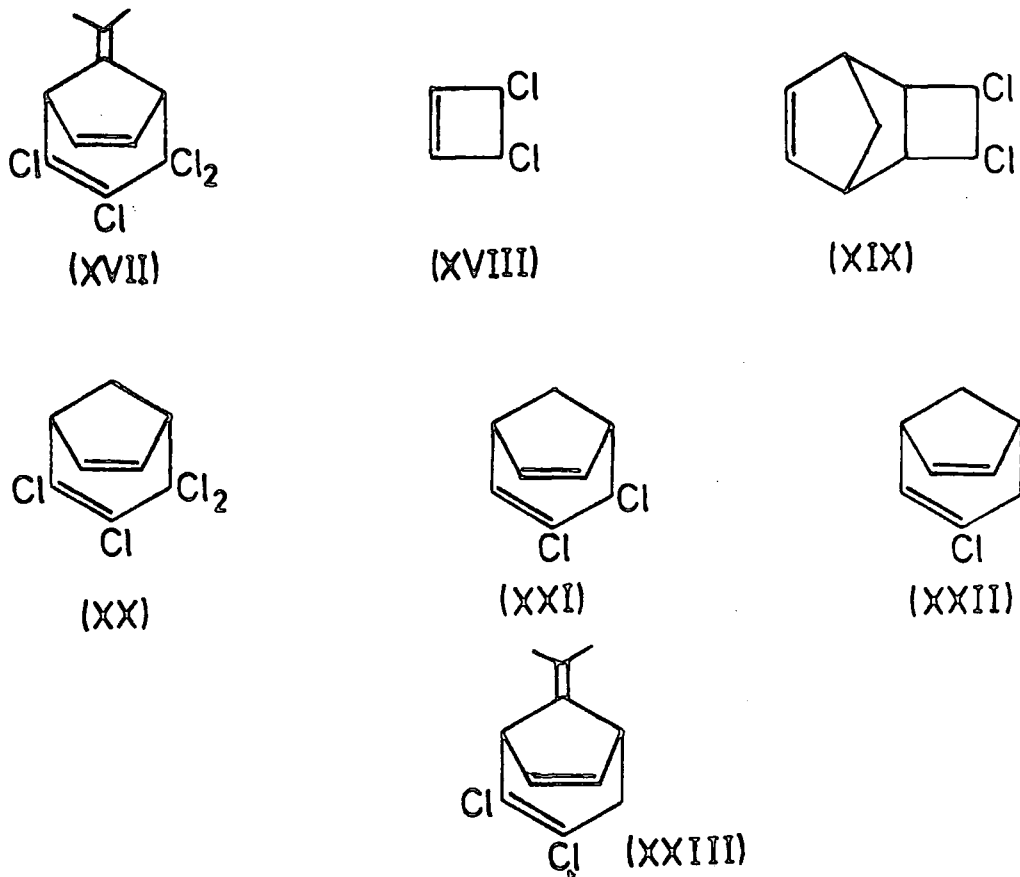


Figure 3.4.

1,6,7,8-Tetraphenyl-9-ketotricyclo[4.2.1.0^{2,5}]nona-3,7-diene was prepared as starting material for the scheme shown in Figure 3.5.

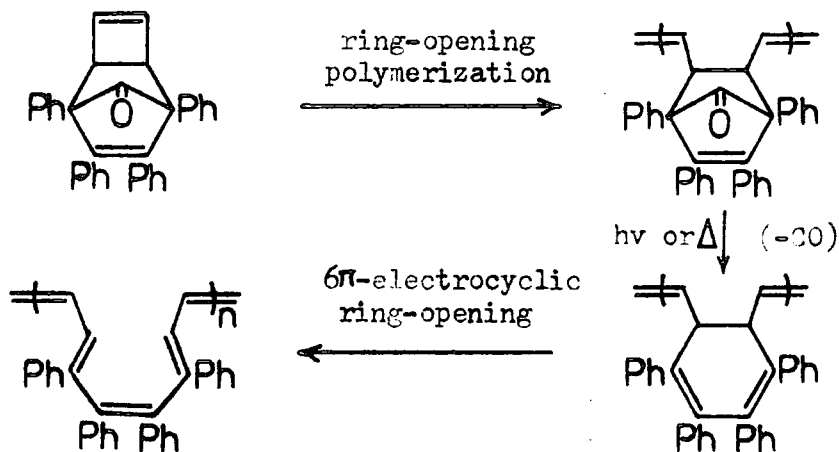


Figure 3.5.

Unfortunately, this monomer was not successfully polymerized, although preliminary results show that it did not deactivate the catalyst system and that it can be copolymerized with bicyclo[2.2.1]hept-2-ene.

In this Section, the synthesis, purification and characterization of the monomers is described. The investigation of the polymerization of these monomers is described in Section 3.3.

3.2.b. Syntheses of cis-3,4-dichlorocyclobutene, 3,4-dichlorotricyclo[4.2.1.0^{2,5}]non-7-ene, 2,3,4,4-tetrachloro-3-isopropylidenebicyclo[3.2.1]octa-2,6-diene, 3,4-dichlorobicyclo[3.2.1]octa-2,6-diene, 3-chlorobicyclo[3.2.1]octa-2,6-diene, 2,3,4,4-tetrachlorobicyclo[3.2.1]octa-2,6-diene and 2,3-dichloro-3-isopropylidenebicyclo[3.2.1]octa-2,6-diene

Cis-3,4-dichlorocyclobutene was synthesized^{286,287} by the route shown in Figure 3.6. The i.r. spectrum (Appendix C, No XV) was identical with that of an authentic sample²⁸⁶ but analysis by g.l.c. showed it was 98% pure. The trace of second component was most probably 1,4-dichlorobutadiene which may be formed by a thermal ring-opening of cis-3,4-dichlorocyclobutene.

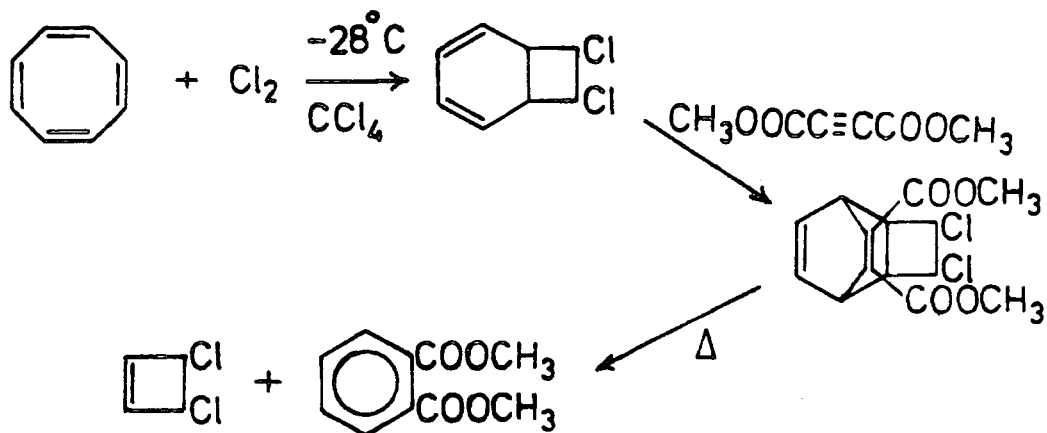


Figure 3.6.

3,4-Dichlorotricyclo[4.2.1.0^{2,5}]non-7-ene was prepared^{288,289} by Diels-Alder reaction between cyclopentadiene and *cis*-3,4-dichlorocyclobutene at 150°C for 2 hours, as shown in Figure 3.7. Nenitzescu²⁸⁸ reported that

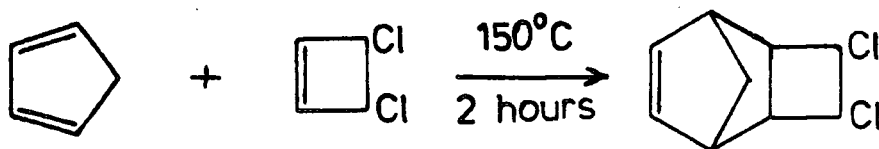


Figure 3.7.

single isomer (*endo-syn*-isomer) was formed in high yield, but Warrenner²⁸⁹ showed that the reaction yields primarily the *endo-anti*-isomer, with minor amounts of the *exo-syn*-isomer, an even smaller amount of the *endo-syn*-isomer and no *exo-anti*-isomer (see Figure 3.8). Characterization of the

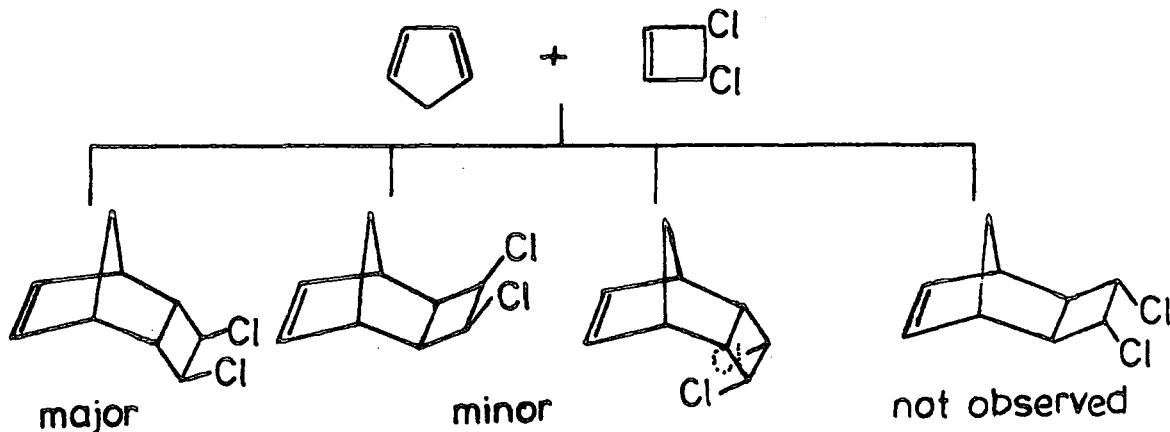


Figure 3.8.

product by tlc showed it was a mixture of one major isomer with 2 minor isomers; ^1H n.m.r. (Table 3.1), i.r. spectrum (Appendix J, No XVI) and elemental analyses (see Experiment Section) were consistent with the proposed structure, and in agreement with Warrenner's data.

The reaction between dichlorocarbene and bicyclo[2.2.1]hepta-2,5-diene has been reported by several authors,²⁹⁰⁻²⁹³ as shown in Figure 3.9.

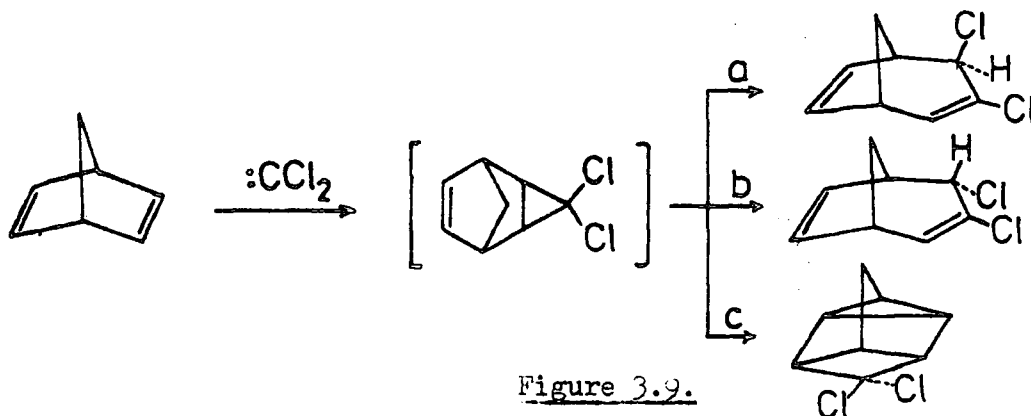


Figure 3.9.

In this study, dichlorocarbene was generated by the action of aqueous alkali on chloroform in the presence of a phase transfer catalyst.²⁹⁴ In the author's experience, only one isomer (XXI, a) can be readily obtained in a pure state. The ^1H n.m.r. (Table 3.1), i.r. spectrum (Appendix C, No XXI), mass spectrum (Appendix B, No VII) and elemental analysis (see Experiment Section) of this product showed it was exo-3,4-dichlorobicyclo[3.2.1]octa-2,6-diene in agreement with the literature.²⁹¹

3-Chlorobicyclo[3.2.1]octa-2,6-diene was prepared by reaction of exo-3,4-dichlorobicyclo[3.2.1]octa-2,6-diene with lithium aluminium hydride in dry diethylether, as shown in Figure 3.10. The ^1H n.m.r. (Table 3.1) and

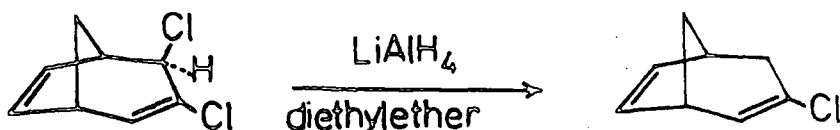


Figure 3.10.

mass spectrum (Appendix B, No IX) were consistent with those reported for an authentic sample.²⁹¹ The i.r. spectrum (Appendix C, No XXII) was

consistent with the assigned structure although the elemental analysis results were invariably poor. It turns out that this material is impure and this is demonstrated by ^{13}C n.m.r. spectroscopy which will be discussed in Section 3.3 along with the polymerization of this material.

Tetrachlorocyclopropene was synthesized²⁹⁵ from pentachlorocyclopropane, which was prepared by reaction of sodium trichloroacetate with trichloroethylene, by dehydrochlorination as shown in Figure 3.11. Penta-

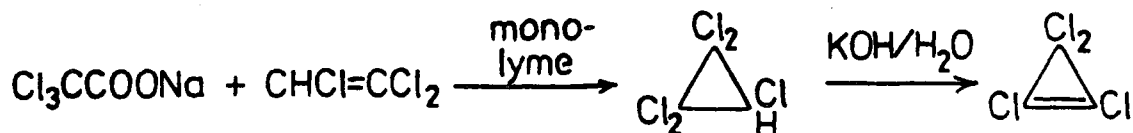


Figure 3.11.

chlorocyclopropane was characterized by i.r. (Appendix C, No XVII) and ^1H n.m.r. spectroscopy (3.9 ppm, singlet), the observed spectra being identical with the literature data.²⁹⁵ Tetrachlorocyclopropene is a colourless lachrymatory liquid with boiling point $85-88^\circ\text{C}$ at 165 mm Hg, the product had an i.r. spectrum (Appendix C, No XVIII) identical with that reported previously.²⁹⁵

All tetrahalocyclopropenes have been reported^{295,296} to undergo facile 1,4-addition with cyclopentadiene in spite of the large size of the halogen substituents; for example it has been observed that the relative reactivity toward furan follows the order cyclopropene > tetrabromocyclopropene > tetrachlorocyclopropene. In addition to effecting the rates of Diels-Alder adduct formation, the halogen substituents permit certain of the highly strained tricyclic cyclopropyl adducts to undergo skeletal rearrangement involving stereospecific ionization of the labile halide. These reactions are believed to involve concerted ionization and ring-opening as shown in Figure 3.12.

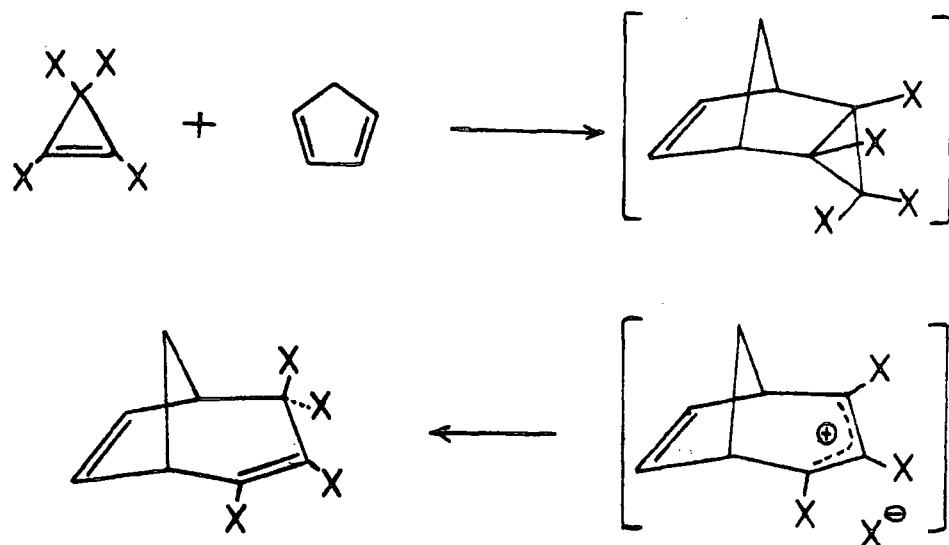


Figure 3.12.

Tetrafluorocyclopropene and 1,2-bis(trifluoromethyl)-3,3-difluorocyclopropene also have been observed to undergo Diels-Alder reaction followed by cyclopropyl-allyl rearrangement. Earlier, 3,3-dichloro- and 3,3-dibromotricyclo[3.2.1.0^{2,4}]octane and -oct-6-ene had been reported^{290, 291, 297, 298} to undergo such rearrangements, Figure 3.13.

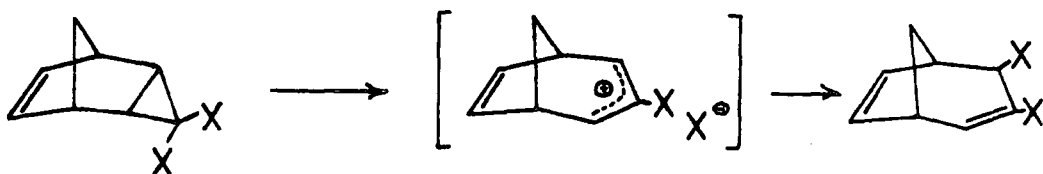


Figure 3.13.

The tricyclic adduct was claimed to be the endo adduct because this would be the least sterically strained adduct. In the ¹H n.m.r., the chemical shift of the bridge hydrogen syn to the double-bond is relatively constant at 1.8-2.0 ppm, whereas the chemical shift of the bridge hydrogen anti to the double-bond is dependent on the substituent at carbon 2 and 4. When the cyclopropane ring is exo, the anti bridge proton is sterically compressed by halogen at carbon 3 and the chemical shift occurs at lower field than the chemical shift of the syn hydrogen.²⁹⁶ In the author's hands bicyclo[3.2.1]octa-2,6-diene derivatives were the only products isolated, although it has been reported^{291, 299} that the tricyclic adduct can be

recovered.

Tetrachlorocyclopropene reacted readily with excess cyclopentadiene in carbon tetrachloride at room temperature to give 2,3,4,4-tetrachlorobicyclo[3.2.1]octa-2,6-diene as shown in Figure 3.12 (X=Cl). The ^1H n.m.r. (Table 3.1), i.r. (Appendix C, No XIX) and mass spectrum (Appendix B, No VI) were consistent with the proposed structure, and in agreement with literature data.²⁹⁶ Tetrachlorocyclopropene did not react with 6,6-dimethylfulvene under the same conditions. However, when the reaction mixture was refluxed for 24 hours, 2,3,4,4-tetrachloro-8-isopropylidenebicyclo[3.2.1]octa-2,6-diene was formed in good yield, Figure 3.14. This new compound was charac-

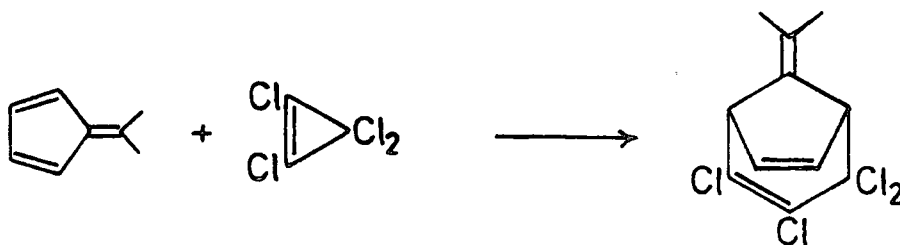


Figure 3.14.

terized by i.r. spectrum (Appendix C, No XXIV), ^1H n.m.r. spectrum (Table 3.1), mass spectrum (Appendix B, No VII) and elemental analysis (see Experiment Section).

Selective removal of one chlorine atom at the allylic position of a 2,3,4,4-tetrachloro-8-isopropylidenebicyclo[3.2.1]octa-2,6-diene using zinc in ethanolic potassium hydroxide was not successful. This was due to the difficulty of separating the product from the starting material and 2,3-dichloro-8-isopropylidenebicyclo[3.2.1]octa-2,6-diene (ie the product of replacement of both chlorines). In one case, 2,3,4-trichloro-8-isopropylidenebicyclo[3.2.1]octa-2,6-diene was successfully isolated, but in very low yield. 2,3-Dichloro-8-isopropylidenebicyclo[3.2.1]octa-2,6-diene can be prepared by dechlorination with zinc in ethanolic potassium hydroxide at 50°C as shown in Figure 3.15. This product could be purified and was

characterized by its i.r. spectrum (Appendix 3, No XXII), mass spectrum (Appendix B, No X) and ^1H n.m.r. spectrum (see Table 3.1).

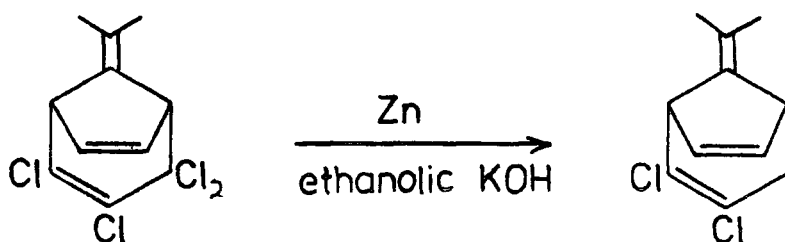


Figure 3.15.

The structure of the small sample of 2,3,4-trichloro-8-isopropylidenebicyclo[3.2.1]octa-2,6-diene was assigned chiefly on the basis of its C=C stretching absorption in the i.r. spectrum. For 2,3,4,4-tetrachloro-8-isopropylidenebicyclo[3.2.1]octa-2,6-diene, the C=C occurs at 1585 cm^{-1} , 2,3-dichloro-8-isopropylidenebicyclo[3.2.1]octa-2,6-diene @ 1625 cm^{-1} and for the trichloro analogue, the band is seen at 1605 cm^{-1} (Appendix 3, No XXIV).

The ^{13}C n.m.r. spectra for these partially chlorinated bicyclo[3.2.1]octa-2,6-dienes will be discussed in Section 3.3 along with the polymerization studies.

3.2.c. Preparation of 1,6,7,8-tetraphenyl-9-ketotricyclo[4.2.1.0^{2,5}]nona-3,7-diene

The above compound was prepared³⁰⁰ by dechlorination of 3,4-dichloro-1,6,7,8-tetraphenyl-9-ketotricyclo[4.2.1.0^{2,5}]non-7-ene which was prepared by refluxing cis-3,4-dichlorocyclobutene with tetraphenylcyclopentadienone in xylene, see Figure 3.16. By contrast with the reaction with cyclopentadiene, the first stage of the below scheme was reported to yield two isomers; namely, the endo-anti- and exo-anti-isomers and was established by Warrenner,³⁰¹ although earlier workers claimed²⁸³ that the endo-anti-isomer was the only product.

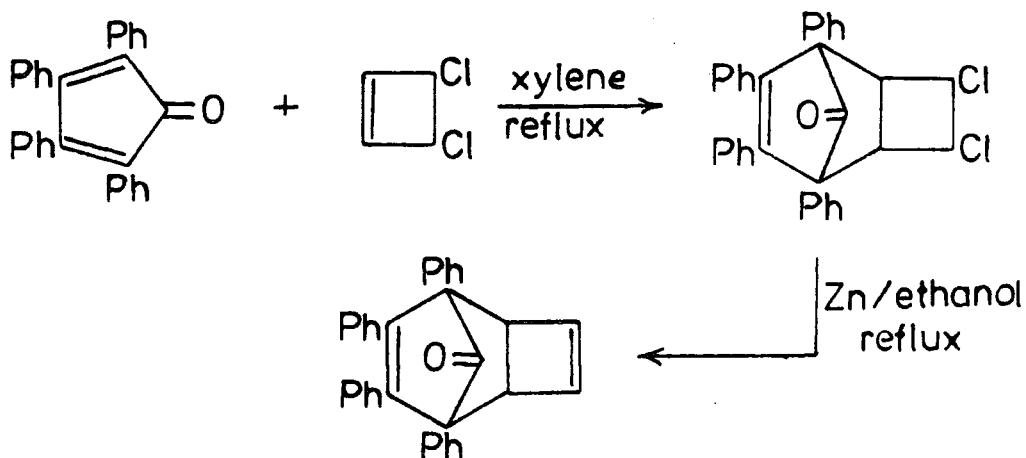


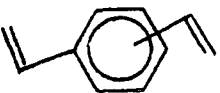
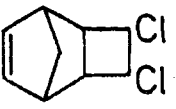
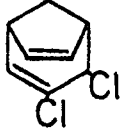

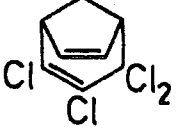
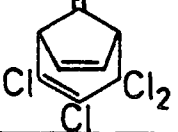
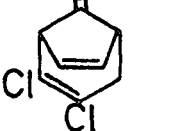
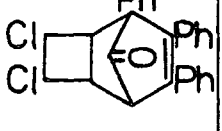
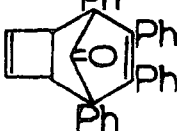
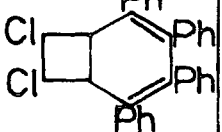
Figure 3.16.

Characterization of the product by ^1H n.m.r. spectroscopy (Table 3.1) showed only one isomer was isolated in this study and that it had endo-anti stereochemistry. The elemental analysis, mass spectrum and i.r. spectrum (Appendix C, No XXIX) were consistent with the proposed structure. The absence of the exo-anti-isomer may result from marginally different reaction conditions and isolation procedures between this work and Warrenner's.

The above compound was dechlorinated using zinc in refluxing ethanol for 48 hours to form 1,6,7,8-tetraphenyl-9-ketotricyclo[4.2.1.0^{2,5}]nona-3,7-diene. The proposed structure was confirmed by mass spectrum (Appendix B, No XI), i.r. spectrum (Appendix C, No XXXII) and ^1H n.m.r. spectrum³⁰¹ (Table 3.1), although the elemental analysis results were poor, possibly because of partial elimination of CO prior to combustion.

From the Diels-Alder reaction product, another two compounds were isolated. The first was shown to be 7,8-dichloro-2,3,4,5-tetraphenylbicyclo[4.2.0]octa-2,4-diene by elemental analysis, mass spectroscopy, i.r. spectrum (Appendix C, No XXIX) and ^1H n.m.r. spectrum (Table 3.1); a similar byproduct arises from the reaction between cis-3,4-dichlorocyclobutene and 2,5-dimethyl-3,4-diphenylcyclopentadienone.³⁰⁰ The second component was not identified, the spectroscopic data have been recorded i.r. spectrum (Appendix C, No XXXI), ^1H n.m.r. spectrum (Table 3.1) and the molecular weight by mass spectrometry was 520.

Table 3.1. ^1H N.m.r. parameters of monomers prepared in this chapter

Compound	$-\text{CH}_3$	$-\text{CH}_2-$	$-\text{CH}-$	$-\text{OH}=\text{OH}-$	Ph-	
				5.4	7.3	
		1.4	$\delta_{1,6/2,5}$ 3.3	$\delta_{3,4}$ 3.8	6.4	
		2.1	$\delta_{1,5}$ 2.9	δ_2 3.1	δ_4 4.2	5.9 6.5
		δ_8 1.8 δ_4 2.1	$\delta_{1,5}$ 2.5	δ_2 2.7	5.8 6.2	
		2.2	$\delta_{1,5}$ 3.0, 3.6		6.2 6.5	
	1.3		$\delta_{1,5}$ 3.8, 4.4		6.4 6.9	
	1.3 1.6	1.9 2.3	$\delta_{1,5}$ 3.4		6.1 7.2	
			$\delta_{2,5}$ 3.7	$\delta_{3,4}$ 4.3	6.7 7.3	
			3.9		6.8 7.3	
			$\delta_{2,5}$ 4.0	$\delta_{3,4}$ 5.0	6.7 7.0	
unidentified compound, see page 115			3.5		6.8 7.1	

3.3.a. Polymerization and attempted polymerization of partially chlorinated cycloalkenes

The non-polymerizability of 2,3,4,4-tetrachloro-8-isopropylidenebicyclo[3.2.1]octa-2,6-diene was curious and difficult to rationalize. At first we thought that it was possible that the crowded allylic carbon-chlorine bond in the monomer might be readily cleaved in the presence of catalyst since the vacant site has Lewis Acid character, this idea is summarized in Figure 3.17. However this idea cannot provide an explanation for the failure of compound (XVII) to polymerize since compound (XVII) did not

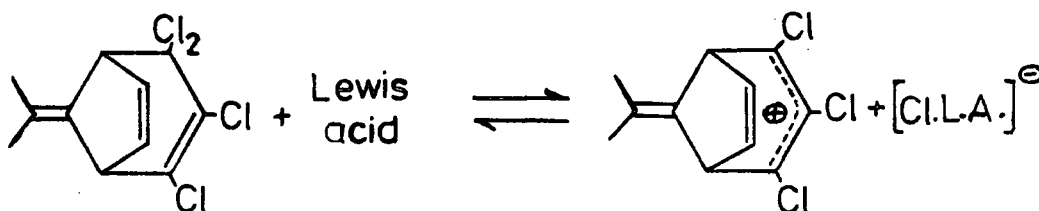


Figure 3.17.

deactivate either the $WCl_6/(CH_3)_4Sn$ or the $MoCl_5/(CH_3)_4Sn$ catalysts, and after prolonged stirring with compound (XVII), these catalysts were still effective in the polymerization of added bicyclo[2.2.1]hept-2-ene.

At this point, it was decided to examine a range of chlorinated monomers of varying structure to try to obtain an idea of the type of structure which would polymerize and those which would not. It was already known that some partially chlorinated bicyclo[2.2.1]hept-2-enes and cyclooctene derivatives would polymerize.

3,4-Dichlorotricyclo[4.2.1.0^{2,5}]non-7-ene was found to polymerize easily in chlorobenzene with $WCl_6/(CH_3)_4Sn$ catalyst. The product was characterized by i.r. spectroscopy (Appendix C, No XXV), ¹H n.m.r. spectrum (Table 3.2) and gave a viscous solution at a concentration of 5% in acetone. The monomer is believed to have polymerized as indicated in Figure 3.18, although a detailed characterization has not been carried out.

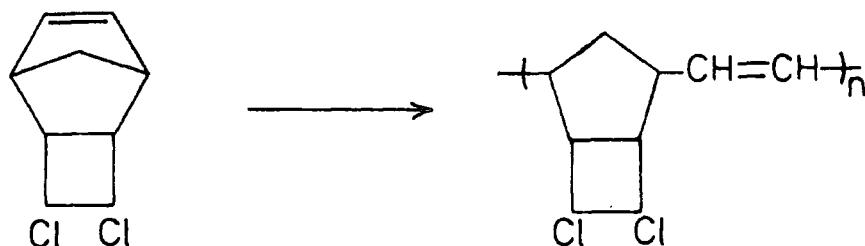


Figure 3.13.

By contrast, the monomers 2,3,4,4-tetrachlorobicyclo[3.2.1]octa-2,6-diene (XX), cis-3,4-dichlorocyclobutene (XVIII) and mixture of 2,3-dichloro-, 2,3,4-trichloro- and 2,3,4,4-tetrachloro-8-isopropylidenebicyclo[3.2.1]octa-2,6-dienes all failed to polymerize with metathesis catalysts although, like compound (XVII), they did not deactivate the catalyst system towards polymerization of bicyclo[2.2.1]hept-2-ene.

Surprisingly, 2,3-dichloro-8-isopropylidenebicyclo[3.2.1]octa-2,6-diene (XXIII) was easily polymerized with $\text{MoCl}_5/(\text{CH}_3)_4\text{Sn}$ catalyst giving a very viscous solution within half an hour @ room temperature. Ring-opening polymerization of the compound was confirmed by spectroscopic and elemental analysis; i.r. spectrum (Appendix C, No XXVIII), ^1H n.m.r. spectrum (Table 3.2) and ^{13}C n.m.r. spectrum (see Figure 3.19). The ^{13}C n.m.r. spectral parameters are collected together in Table 3.3 for a series of chlorinated monomers and the ^{13}C n.m.r. evidence will be discussed as a separate item later.

3,4-Dichlorobicyclo[3.2.1]octa-2,6-diene (XXI) was also polymerized with the $\text{WCl}_6/(\text{CH}_3)_4\text{Sn}$ and the $\text{MoCl}_5/(\text{CH}_3)_4\text{Sn}$ catalysts and this showed that an allylic chlorine does not necessarily inhibit the reaction, at least if it occupies an exo-position. Characterization of the polymer through its i.r. spectrum (Appendix C, No XXVI), ^1H n.m.r. spectrum (Table 3.2) and ^{13}C n.m.r. spectrum (Figure 3.20) was in agreement with the proposed structure. These two successful polymerizations are summarized in Figure 3.21.

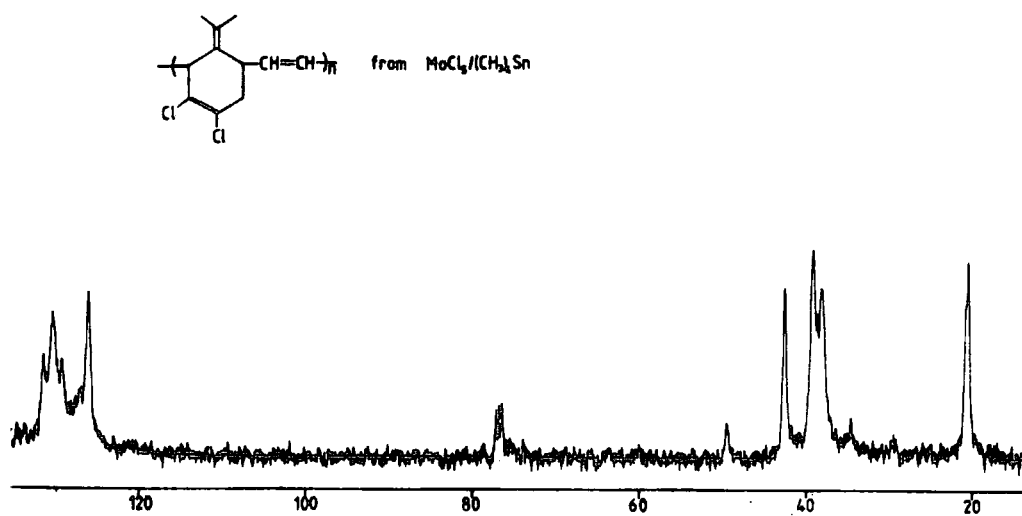
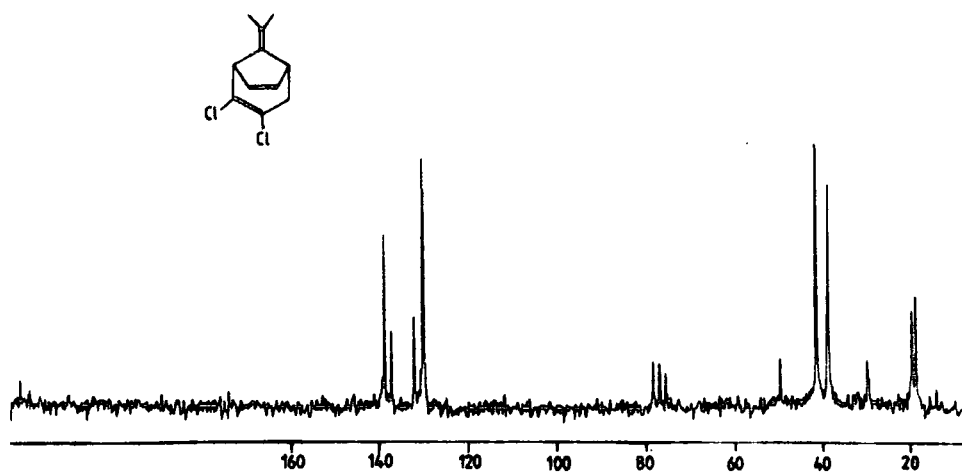


Figure 3.19. ^{13}C N.m.r. spectra for Compound (XXIII) and derived polymer

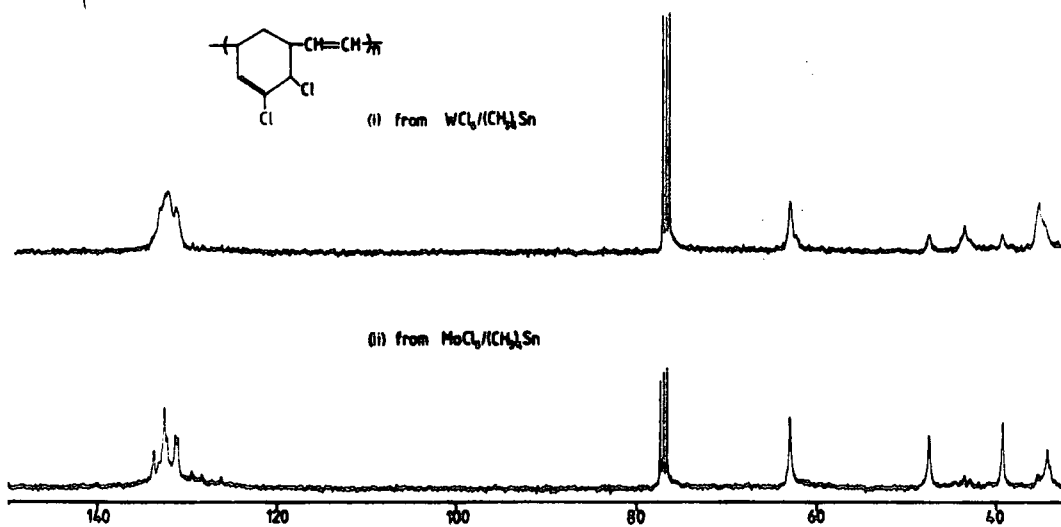
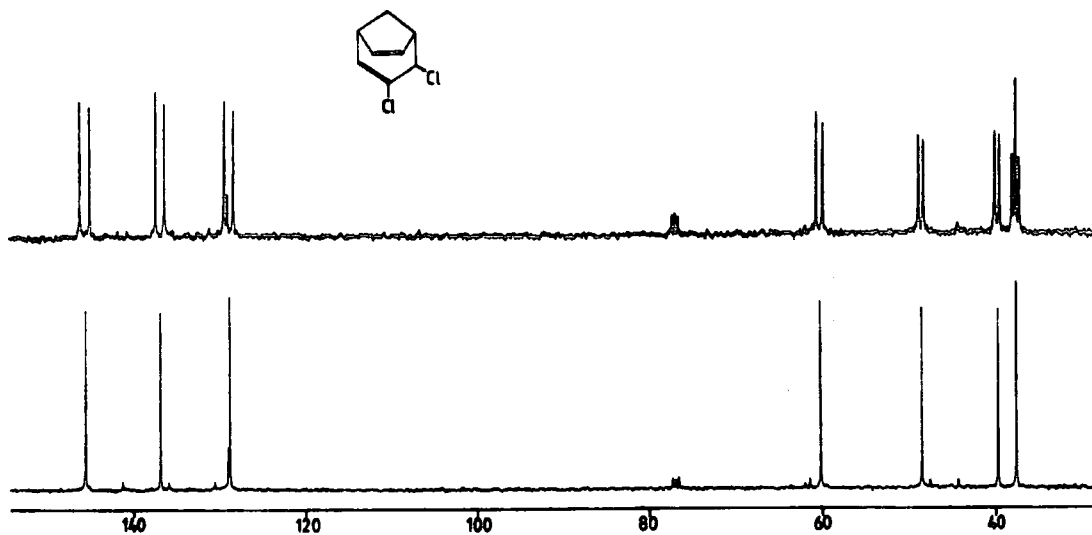


Figure 3.20. ¹³C N.m.r. spectra for Compound (XXI) and derived polymers

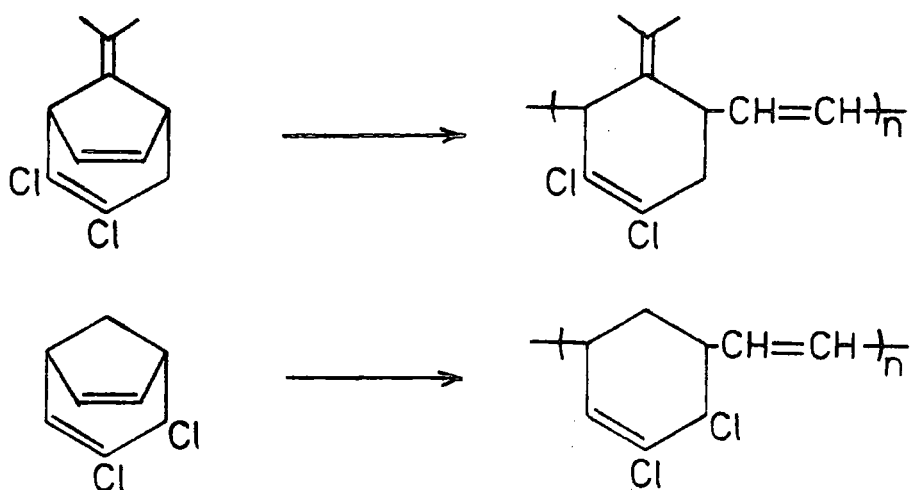
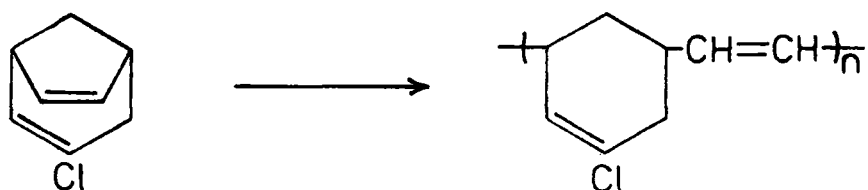


Figure 3.21.

The polymerization of this type of ring system was also confirmed by polymerization of 3-chlorobicyclo[3.2.1]octa-2,6-diene (XXII) indicated below. The proposed structure for the polymer being consistent with



its i.r. spectrum (Appendix C, No XXVII), ^1H n.m.r. spectrum (Table 3.2), ^{13}C n.m.r. spectrum (Figure 3.22 and Table 3.3) and elemental analysis (Found C, 63.67; H, 6.27; $\text{C}_8\text{H}_7\text{Cl}$ requires C, 63.33; H, 6.41%).

In summary, it is certain from the above information that the present work establishes that the chlorinated monomers shown in Figure 3.23 do polymerize with metathesis catalysts; whereas the monomers shown in

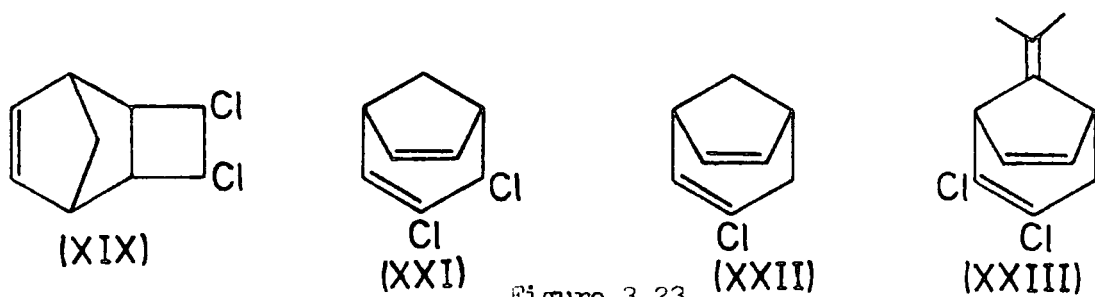


Figure 3.23.

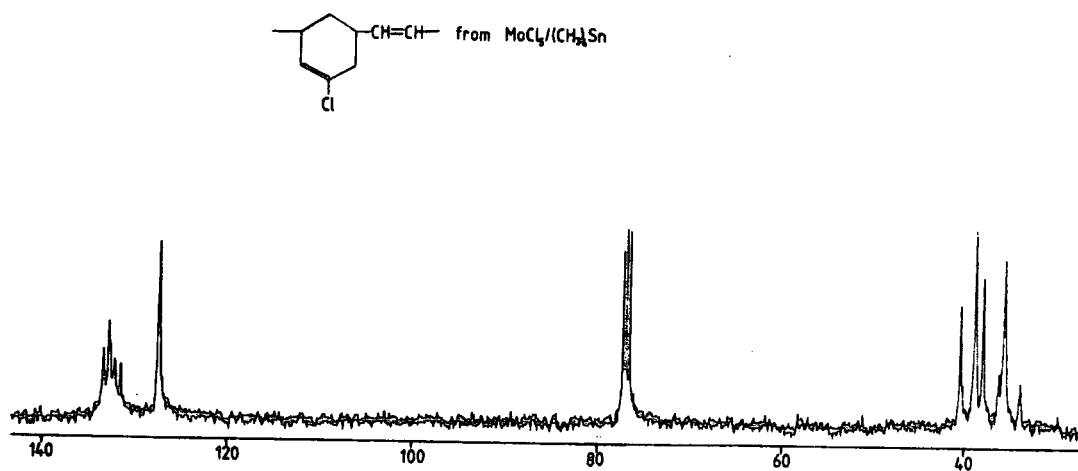
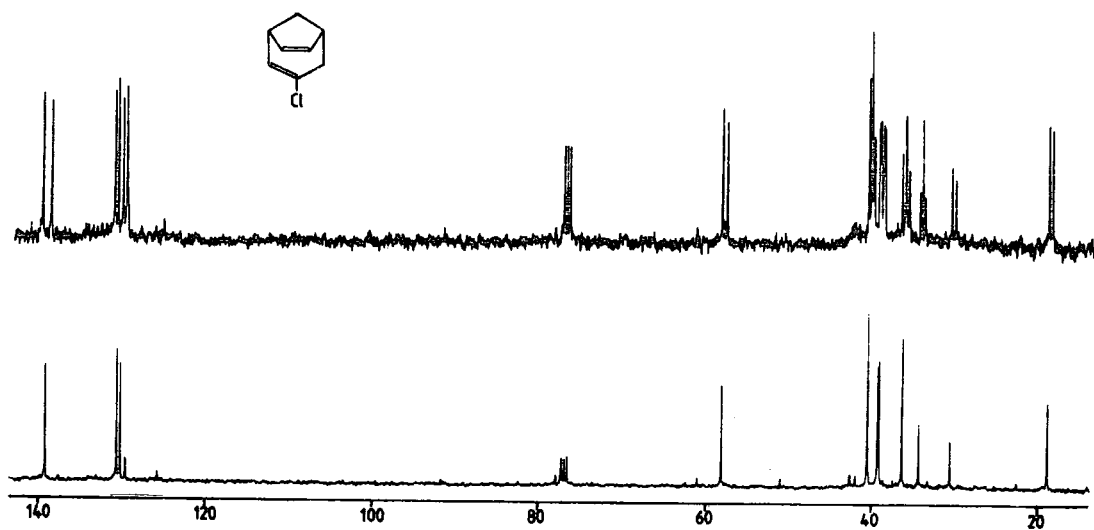


Figure 3.22. ^{13}C N.m.r. spectra for Compound (XXII) and derived polymer

Figure 3.24 do not polymerize with metathesis catalysts. A fourth non-

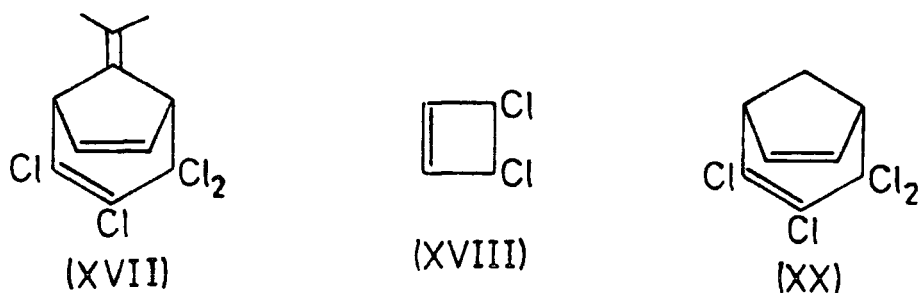
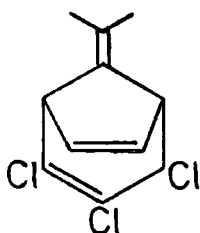


Figure 3.24.

polymerizable monomer is shown below, although in this case the monomer was not obtained in a pure state and the stereochemistry of the allylic chlorine is unknown. In order to make certain of the validity of this negative evidence, some bicyclo[2.2.1]hept-2-ene was added to those mixtures of monomers and catalyst where polymerisation failed to occur, the rapid polymerization of this added bicyclo[2.2.1]hept-2-ene was take as evidence of an active catalyst.



The question which requires an answer is whether or not we can see significant differences between those chlorinated monomers which do polymerize and those which do not. If we omit monomer (XVII) from consideration, which is not unreasonable since it has a markedly different structure to the others, it seems that the monomers (XVIII) and (XX) are only distinguished from the polymerizable monomers by the possession of an endo-+-chlorine. The other non-polymerizable monomer also has a chlorine atom at C₄ (stereochemistry unknown but presumably endo), whereas the one polymerizable monomer with a chlorine at C₄ has an established²⁹¹ exo-stereochemistry.

If we build space filling models of these monomers, it becomes clear that a 4-endo chlorine substituent is obliged to take up a position very close to the double-bond which has to coordinate to the catalyst. However, it is difficult to understand with any certainty why this should make such monomers unpolymerizable, certainly it would be difficult to make an a priory prediction of the outcome. The factors being much the same as those discussed earlier in relation to the polymerization of exo- and endo-adducts of maleic anhydride with cyclopentadiene (see Chapter 2, page 84). The failure of 5,5,6-trichloro-6-trifluoromethylbicyclo[2.2.1]hept-2-ene (Chapter 2, page 93) to polymerize falls into this pattern of inhibition by an endo chlorine substituent.

Thus, it appears that we have identified a common inhibiting factor, although we are not able to provide an unambiguous rationalization of this observation. Never the less, these preliminary results show that this type of ring system is polymerizable and the poly(arylenevinylene) type of polymer may still be accessible by a suitable modification of the scheme shown in Figure 3.3, if the isomerization and dehydrochlorination steps can be made to work.

Table 3.2. ¹H n.m.r. parameters of polymers

	-CH ₃ -	-CH ₂ -	-CH-	-CHCl-	-CH=CH-
		2.0	3.2	4.6	5.8
		1.3 2.3	2.9		5.5
		1.9	3.2	4.3	5.6
	1.8	2.5	3.4		5.5

3.3.b. ^{13}C N.m.r. spectroscopy of partially chlorinated bicyclo[3.2.1]octa-2,6-diene monomers and their polymers

^{13}C N.m.r. spectroscopy provides part of the evidence for the structure of these monomers and their polymers, but since the spectrum of an individual monomer or polymer can be fairly complex and its interpretation normally requires comparison with a set of similar materials, the discussion of this data has been collected together in this Section. The data in the spectra of the monomers presented in Figure 3.19, 3.20, 3.22 and the spectra of the unpolymerized monomers (XVII) and (XX), Figure 3.25, are summarized in Table 3.3.

Some of the peak assignments are made on the basis of the assumption that closely related structure will display similar shift patterns, some of the assignments are made on the basis of peak intensity as it relates to Nuclear Overhauser Enhancement, and some assignments are made on the basis of the peak multiplicities observed in "off-resonance" spectra, that is spectra in which the ^{13}C - ^1H couplings have not been eliminated by irradiating the protons.

For example, consider the spectrum of monomer (XXI) shown in Figure 3.20; the three strong low field resonances are all clearly vinylic carbons carrying an hydrogen atom, they display the expected NOE and appear as doublets in the off-resonance spectrum (the upper spectrum in Figure 3.20); the low intensity signal in this region is clearly the vinylic carbon carrying a chlorine, it is not split in the off-resonance experiment. At higher field, the carbons bearing one or two hydrogens appear as doublet and triplets respectively in the off-resonance experiment and the $-\text{CHCl}-$ carbon is readily assigned as the one at lowest field. In a similar way and by ensuring that assignments cross-check one with another a fairly complete assignment of all the peaks in all the monomer spectra can be

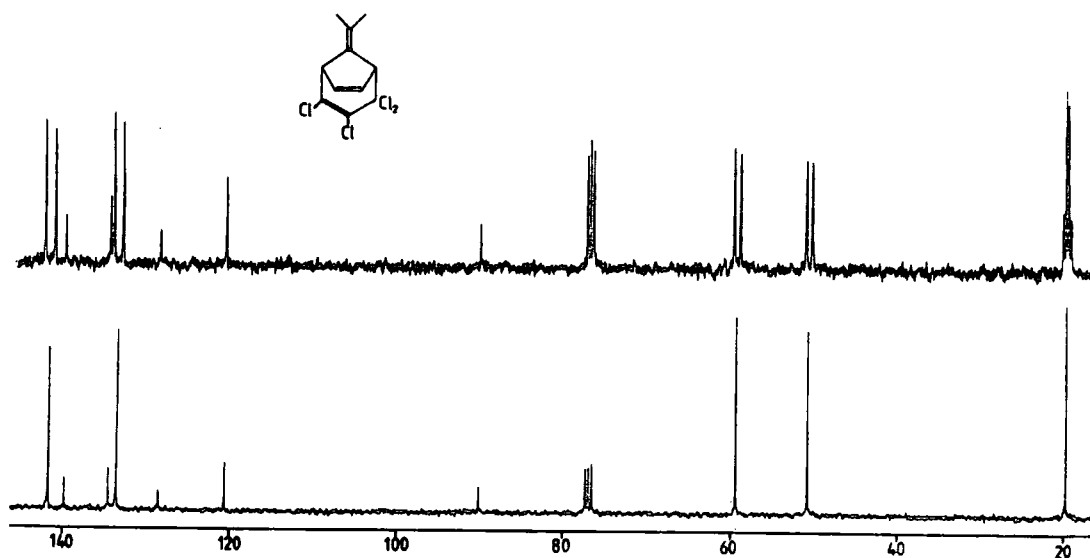
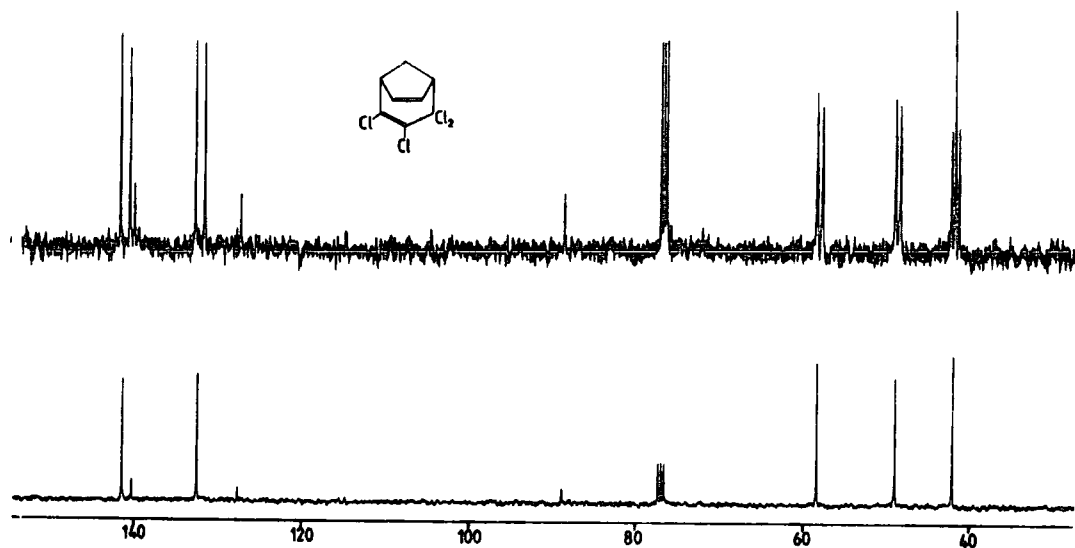


Figure 3.25. ^{13}C N.m.r. of Compound (XVII) and (XX)

built up. The result of this process is summarized in Table 3.3; as a result of this tabulation, it was possible to show that compound (XXII) was not a pure material although it displays the i.r. and ^1H n.m.r. spectral features and physical properties quoted in the literature.

The spectra of the polymers derived from monomers (XXI), (XXII) and (XXIII) are shown in the lower halves of Figures 3.19, 3.20 and 3.22 and while they support the structural assignments made here. It is clear that they are fairly complex and much stereochemical information is encoded in the spectra. The relative low quality of the resolution and the complexity of the spectra do not justify a detailed interpretation; however, in Figure 3.20 it is clear that the WCl_6 based catalyst gives rise to a much more complex spectra than the MoCl_5 based catalyst and this observation is in line with earlier discussion of the stereoregulating ability of these different catalysts (see Chapter 2).

3.3.c. Preliminary study of the dehydrochlorination of the polymer prepared from 3,4-dichlorobicyclo 3.2.1 octa-2,6-diene

The aim of this work was to see if the thermal dehydrochlorination of the polymer shown in Figure 3.26 proceeds as indicated in the figure.

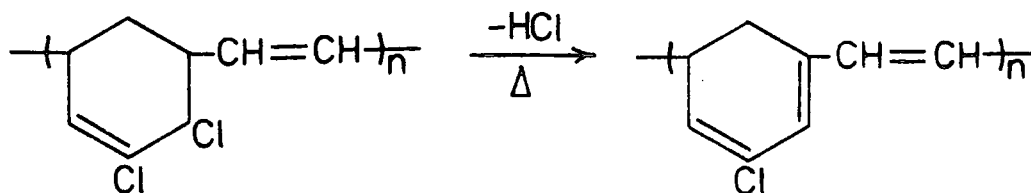


Figure 3.26.

The polymer was heated in a thermobalance at $1^\circ\text{C}/\text{minute}$ under a nitrogen atmosphere. The thermogram did not show any stepwise loss of weight, Figure 3.27. The polymer was then treated with an excess of triethylamine in

Table 3.3. ^{13}C N.m.r. parameters of partially chlorinated bicyclo[3.2.1]octa-2,6-dienes

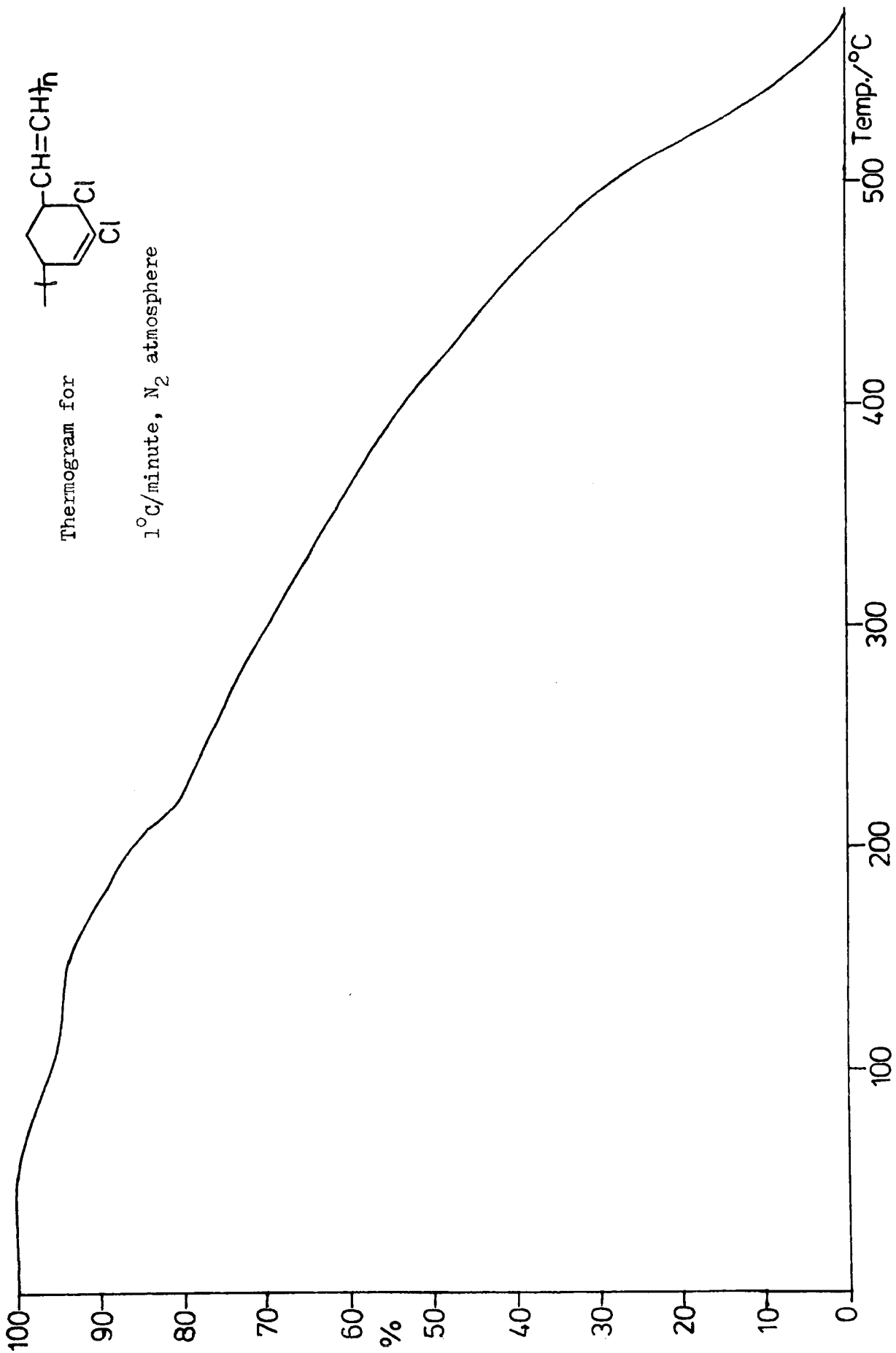
Compound	C ₁	C ₂	C ₃	C ₄	C ₅	C ₆	C ₇	C ₈	C ₉	C _{10,11}
	35.2	32.8	19.1	32.8	35.2	28.9	26.9	39.7		
	38.3 or 38.7	134.1	123.8	28.7	38.7 or 38.3	130.2	133.7	40.7		
	40.1	134.3	120.1	38.5	40.6	130.8	133.2	40.3		
	39.1	130.6	125.6	36.3	39.2	130.2	133.2	40.4		
	48.3	136.8	128.8	60.1	39.7	129.0	145.7	37.5		
	48.9	140.3	127.6	90.1	58.3	132.5	141.5	42.3		
	50.4	139.8	133.5	88.8	59.8	134.5	141.7	120.6	128.4	19.8
	40.9	138.1	130.8	38.1	49.2	132.4 or 139.7	139.7 or 132.4	-	-	18.6

a Established by J.S. Stothers, J.A. Swensen and C.T. Tan, Can. J. Chem., 53,581 (1975) and used as reference data.

b Impure (impurity shifts at 58.1, 36.3, 34.2, 30.5 and 18.8)

chlorobenzene at 50°C for one hour, the recovered material was a white powder with the same infrared spectrum as the starting material and gave a virtually identical thermogram.

Thus it appears that the anticipated loss of HCl from this polymer is not easily accomplished despite the fact that both the hydrogen and the chlorine atoms to be removed are allylic. The lack of a stepwise weight loss was surprising, however this is a preliminary observation and it may be that under appropriate conditions of isothermal treatment, a stepwise loss of HCl can be achieved.



EXPERIMENTAL

3.4.a. Preparation of Cis-3,4-dichlorocyclobutene

3.4.a.i. Reagents

Cyclooctatetraene and dimethylacetylenedicarboxylate were purchased from Aldrich Chemical Company Inc. and were used without further purification. Dry carbon tetrachloride was prepared by distillation of the commercial product, the first 10% of the distillate was rejected, the solvent was stored over molecular sieve (4A).

3.4.a.ii. Syntheses

Cyclooctatetraene (50.0 g., 0.48 mole) and dry carbon tetrachloride (159.0 g., 1.0 mole) were placed in 3-necked round-bottomed flask (500 ml) which was equipped with a gas inlet tube, a low temperature thermometer and a calcium chloride drying tube. The flask was cooled by using PhCl/liquid air slush bath (-28 to -33°C) and stirred using a mechanical stirrer. Chlorine (40.0 g., 1.13 mole) was admitted into the solution as a gas stream during 3 hours. The mixture was allowed to warm-up to 0°C by changing to an ice-bath, sodium carbonate powder (25.0 g., 0.24 mole) was added and the contents of the flask were shaken gently for several minutes to remove any HCl formed in the reaction. The mixture was then filtered directly into 1-necked round-bottomed flask (500 ml) which contained dimethylacetylenedicarboxylate (67.0 g., 0.47 mole). An efficient condenser was fitted to the flask which was heated gently to initiate the exothermic reaction, heating was stopped until the exothermic reaction had subsided and then the contents were refluxed for 3 hours. The solvent (CCl₄) was removed by evaporation at 45°C under reduced pressure (1 mm Hg), the residue was a viscous green material.

The crude adduct was transferred to a pressure-equalizing dropping funnel (500 ml) which was attached to a 3-necked round-bottomed flask (500 ml) immersed in an oil bath maintained at 200°C, another neck was fitted

with a distillation head, condenser and receiving flask. The pressure in the flask was slowly reduced to 20 mm Hg and the crude adduct was admitted to the heated flask dropwise, the pyrolysate was collected as a yellow liquid which was redistilled (3 times) to give cis-3,4-dichlorocyclobutene as a colourless liquid (24.0 g., 42% yield), b.p. 56-73°C at 14-18 mm Hg, with correct i.r. spectrum,²⁸⁶ 98% pure (glc). The impurities were most probably derived from 1,4-dichlorobutadiene.

3.4.b. Preparation of 3,4-Dichlorotricyclo[4.2.1.0^{2,5}]non-7-ene

3.4.b.i. Reagents

Cis-3,4-dichlorocyclobutene was prepared as described above, cyclopentadiene was freshly distilled from dicyclopentadiene which was purchased from Koch-Light Laboratories Ltd.

3.4.b.ii. Syntheses and Characterization

A mixture of cis-3,4-dichlorocyclobutene (8.2 g., 67 mmole) and cyclopentadiene (6.6 g., 100 mmole) were placed in 1-necked round-bottomed flask (200 ml) and stirred with magnetic follower. The reaction flask was heated at 150°C for 2 days with an oil bath. The reaction product was purified by column chromatography on silica (Kieselgel 60) using petroleum ether/chloroform as eluent to give 3,4-dichlorotricyclo[4.2.1.0^{2,5}]non-7-ene as a yellow liquid (9.5 g., 50 mmole, 75% yield), [Found C, 57.40; H, 5.60; C₉H₁₀Cl₂ requires C, 57.14; H, 5.29%]. The ¹H spectrum was the same as that of an authentic sample²⁸⁹ and showed that the product was a mixture of three isomers with the endo-anti-isomer as major component.

3.4.c. Preparation of Tetrachlorocyclopropene

3.4.c.i. Reagents

Trichloroethylene was purified by distillation from P₂O₅. Sodium trichloroacetate was prepared by neutralization of trichloroacetic acid

(130.0 g., 0.80 mole in 100 ml water) with aqueous NaOH (32.0 g., 0.80 mole in 150 ml water) to the phenolphthalein end point. The product was dried under reduced pressure for 9 hours to give a white solid material. Dry monoglyme was supplied by Mr. B. Hall of this Department.

3.4.c.ii. Syntheses and Characterization

Preparation of Pentachlorocyclopropane

Sodium trichloroacetate (127.0 g., 0.69 mole) and dried trichloroethylene (686 g., 5.2 mole) were placed in l-necked round-bottomed flask (1 liter) fitted with a Dean-Stark apparatus. The mixture was stirred and refluxed for 3 hours to insure that water was completely removed from the system. Dry monoglyme (70 ml) was added slowly using a syringe and the mixture was refluxed for 5 days. The reaction mixture was washed with water (500 ml), aqueous HCl (300 ml, 2N) and with water (500 ml), dried over CaCl_2 and distilled to give: (i) a liquid b.p. $< 91^\circ\text{C}$, probably solvent; (ii) pentachlorocyclopropane as a colourless liquid (50.0 g., 0.23 mole, 33% yield), b.p. $70-80^\circ\text{C}$ at 28/30 mm Hg (Ref:²⁹⁵ 25% yield, b.p. $55.5-56.0^\circ\text{C}$ at 7 mm Hg). The ^1H n.m.r. spectrum showed a singlet at 3.9 ppm (Ref:²⁹⁵ 3.84 ppm), and the i.r. spectrum²⁹⁵ showed no band in the $\text{C}=\text{C}$ region, but showed bands at 3040 cm^{-1} (cyclopropane $\text{C}-\text{H}$), a strong complex band between $950-880\text{ cm}^{-1}$ (highly chlorinated cyclopropane) and a strong band at 775 cm^{-1} ($>\text{CCl}_2$).

Preparation of Tetrachlorocyclopropene

Pentachlorocyclopropane (48.0 g., 0.22 mole) and a solution of KOH (35.5 g., 0.63 mole) in distilled water (40 ml) were placed in l-necked round bottomed flask (250 ml) with a magnetic follower. The two phase mixture was stirred and heated at $85-88^\circ\text{C}$ for 30 minutes, the reaction mixture was cooled to 50°C when ice-water (50 ml) and cold concentrated HCl (25 ml) were added. The mixture was placed in separating funnel and

extracted with dichloromethane (150 ml), the extract was washed with water (2 x 150 ml), dried over CaCl_2 , and the solvent evaporated. The residue was distilled under reduced pressure to give tetrachlorocyclopropene (27.5 g., 70% yield) as a colourless liquid, b.p. $85-88^\circ\text{C}$ at 165 mm Hg (Ref: ²⁹⁵ b.p. $129.5-130.0^\circ\text{C}$ at 745 mm Hg, 85% yield) with correct i.r. spectrum ²⁹⁵ which showed four strong bands at 615 cm^{-1} (C-Cl), 750 cm^{-1} (CCl_2), 1050 cm^{-1} and 1150 cm^{-1} (C-Cl).

3.4.d. Preparation of 2,3,4,4-Tetrachlorobicyclo[3.2.1]octa-2,6-diene

3.4.d.i. Reagents

Tetrachlorocyclopropene was prepared as described above, cyclopentadiene was freshly distilled from dicyclopentadiene (Koch-Light Lab. Ltd) and CCl_4 was purified as described in Section 3.4.a.i.

3.4.d.ii. Syntheses and Characterization

Tetrachlorocyclopropene (3.0 g., 17 mmole), dry carbon tetrachloride (4.0 ml) and cyclopentadiene (2.4 g., 36 mmole) were placed in 1-necked round-bottomed flask (50 ml) and stirrer at room temperature for 2 days. Solvent and unreacted material were removed by reduced pressure distillation and the residue was recrystallized (petroleum ether 30/40) to give 2,3,4,4-tetrachlorobicyclo 3.2.1 octa-2,6-diene (3.0 g., 72% yield) as white crystals m.p. $86-87^\circ\text{C}$; [Found C, 36.11; H, 2.66; Cl, 57.6; $\text{C}_8\text{H}_6\text{Cl}_4$ requires C, 39.34; H, 2.46; Cl, 58.22%]; M (m.s.), 244 (Calculated M, 244); with correct i.r. spectrum, ²⁹⁶ ν_{max} 1590 cm^{-1} (-ClC=CCl-) and 1440 cm^{-1} (=C=C-); and ^1H and ^{13}C n.m.r. spectra consistent with the proposed structure.

3.4.e. Preparation of Dimethylfulvene

Cyclopentadiene (32.0 g., 0.49 mole) and an equivalent amount of analar acetone (28.8 g., 0.50 mole) were placed in a flask (250 ml) fitted with a reflux condenser which was cooled with ice. Potassium hydroxide (5.0 g.,

0.09 mole) in ethanol (20 g., 0.44 mole) was carefully added through the reflux condenser. A vigorous exothermic reaction occurred, when this reaction subsided, the reaction flask was stoppered tightly and kept cool overnight. The aqueous layer was removed and the mixture was vacuum distilled to remove the low-boiling point materials, followed by dimethylfulvene which was distilled rapidly between 45-47°C at pressure 13-14 mm Hg. The yellow liquid was stored in the deep freeze and showed the correct i.r. spectrum.²⁴⁷

3.4.f. Preparation of 2,3,4,4-Tetrachloro-8-isopropylidenebicyclo[3.2.1]-octa-2,6-diene

Tetrachlorocyclopropene (3.02 g., 17 mmole), dimethylfulvene (4.0 g., 38 mmole) and dry carbon tetrachloride (4.0 ml) were placed in a flask (50 ml) fitted with a reflux condenser. The mixture was refluxed for 24 hours. The low-boiling point material was removed by reduced pressure distillation. Petroleum ether (20 ml) was added and the mixture refluxed, the hot solution was filtered, the solvent evaporated and the product purified using column chromatography on silica (Kieselgel 60) with petroleum ether 40/60 as eluent to give 2,3,4,4-tetrachloro-8-isopropylidenebicyclo-3.2.1 octa-2,6-diene (4.5 g., 65% yield) as white crystals with m.p. 82°C; [Found C, 46.38; H, 4.09; Cl, 51.2; C₁₁H₁₀Cl₄ requires C, 46.48; H, 3.52; Cl, 50.00%]; M (m.s.), 284 (Calculated M, 284); i.r. spectrum ν_{\max} 1585 cm⁻¹ (=ClC=CCL-), 1435 cm⁻¹ (-C=C-) and 1368 cm⁻¹ (>C=C<); with ¹H and ¹³C n.m.r. spectra consistent with the proposed structure.

3.4.g. Preparation of 3,4-Dichlorobicyclo[3.2.1]octa-2,6-diene

3.4.g.i. Reagents

Bicyclo[2.2.1]hepta-2,5-diene and myristyltrimethylammoniumbromide (a phase transfer catalyst) were purchased from Aldrich Chemical Com. Ltd., chloroform and sodium hydroxide were purchased from BDH Chemicals Ltd, and all the reagents were used without further purification.

3.4.g.ii. Syntheses and Characterization

Bicyclo[2.2.1]hepta-2,5-diene (40.0 g., 0.44 mole), myristyltrimethylammoniumbromide (14.0 g., 40 mole) and chloroform (135 ml, 1.7 mole) were placed in a flask (1 liter) which was warmed to 50°C, a solution of sodium hydroxide (130 g., 3.25 mole) in distilled water (270 ml) was carefully added through the reflux condenser and the reaction was left stirring for 3 hours. Ice-water (500 ml) was added slowly followed by sulphuric acid (10%) until the mixture was acidic. The reaction mixture was extracted with diethylether (2 x 250 ml), the extract was dried (MgSO₄) and the solvent evaporated. The residue was distilled under reduced pressure (85-94°C/ 6-8 mm Hg), and the product further purified by column chromatography on silica (Kieselgel 60) with petroleum ether as eluent to give 3,4-dichlorobicyclo[3.2.1]octa-2,6-diene (23.0 g., 30% yield) as a yellow liquid. [Found C, 55.0; H, 4.97; C₈H₈Cl₂ requires C, 54.85; H, 4.57%]; M (m.s.), 175 (Calculated M, 175); i.r. ν_{\max} 1618 cm⁻¹ (-C=CCl-) and 1438 cm⁻¹ (-C=C-), with correct ¹H n.m.r. spectrum.²⁹¹

3.4.h. Dechlorination of 3,4-Dichlorobicyclo[3.2.1]octa-2,6-diene

Lithium aluminium hydride (1.0 g., 26 mmole) and sodium-dry diethylether (70 ml) were placed in 2-necked round-bottomed flask (250 ml) equipped with two condensers and the apparatus was continually swept by dry nitrogen via the condensers. The mixture in the reaction flask was heated until it refluxed, 3,4-dichlorobicyclo[3.2.1]octa-2,6-diene (2.94 g., 17 mmole) in dry diethylether (15 ml) was added slowly through one condenser and the mixture refluxed for a further 5 hours. The reaction mixture was cooled to room temperature and treated carefully with aqueous KOH (12.5 ml, 5%), washed with water (50 ml). The solvent was removed by evaporation and the residue purified using column chromatography on silica (Kieselgel 60) with petroleum ether as eluent to give 3-chlorobicyclo[3.2.1]octa-2,6-diene

(1.2 g., 53% yield) as colourless liquid. The carbon and hydrogen elemental analyses results were poor in all of several attempts; thin layer and gas chromatography indicated that the product was a single component with a molecular-weight (m.s.) of 140 (Calculated for $C_8H_{10}Cl$, 139.5).

3.4.j. Dechlorination of 2,3,4,4-Tetrachloro-8-isopropylidenebicyclo[3.2.1]octa-2,6-diene

3.4.j.i. Preparation of 2,3-dichloro-8-isopropylidenebicyclo[3.2.1]octa-2,6-diene

Potassium hydroxide (2.0 g., 36 mmole), ethanol (18.0 g., 391 mmole) and the compound (2.0 g., 7 mmole) were placed in a flask (100 ml) and stirred with magnetic follower. The mixture in the reaction flask was heated to 50-60°C and zinc powder (6.0 g., 92 mmole) was added carefully. Gradually the solution turned yellow, the reaction was continued for 24 hours. Diethylether (100 ml) was added carefully via a dropping funnel and the mixture was filtered. The solvent from the filtrate was removed by evaporation and the residue purified by column chromatography on silica (Kieselgel 60) with petroleum ether/chloroform as eluent. The product was a yellow liquid (1.0 g., 66% yield). The elemental analyses was not good although several attempts have been made and the product approved to be a single component by chromatographic analyses (t.l.c. and g.l.c.); and had the expected molecular ion, M (m.s.), 215 (Calculated for $C_{11}H_{12}Cl_2$, 215).

3.4.j.ii. Attempts to Prepare 2,3,4-trichloro-8-isopropylidenebicyclo[3.2.1]octa-2,6-diene

The previous experiment was repeated in all respects except that the experiment was done at room temperature for 2 days. Two major components were collected on column chromatography; the second fraction was a single component (0.2 g.) and the first fraction had three components which proved inseparable under a wide variety of chromatographic proceeding. Characteri-

zation by i.r. spectroscopy (see discussion section) showed that the first fraction was mixture of 2,3,4,4-tetrachloro-8-isopropylidenebicyclo[3.2.1]octa-2,6-diene, 2,3-dichloro-8-isopropylidenebicyclo[3.2.1]octa-2,6-diene and 2,3,4-trichloro-8-isopropylidenebicyclo[3.2.1]octa-2,6-diene and the second fraction was most probably 2,3,4-trichloro-8-isopropylidenebicyclo[3.2.1]octa-2,6-diene.

Repetition of these last two experiments did not improved the results, the difficulty was primarily associated with insufficient resolution in the preparative chromatography stages. Although spectroscopic analyses suggested that the basis chemistry works satisfactorily.

3.4.k. Purification of divinylbenzene

3.4.k.i. Reagents

Divinylbenzene was purchased from BDH Ltd. Cuprous chloride was purified ³⁰² by dissolving commercial cuprous chloride (Hopkin and Williams) in hot concentrated hydrochloric acid and refluxing under dry nitrogen for 3 hours. Copper filings were added carefully and refluxing continued until a very deep-yellow solution formed. The hot solution was poured into cold distilled water which had previously been refluxed under dry nitrogen. The solvent was evaporated under reduced pressure and dried (100°C at 1 mm Hg) to leave cuprous chloride as a white powder.


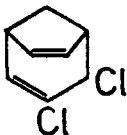

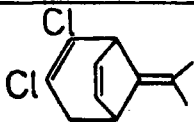
3.4.k.ii. Purification

Commercial divinylbenzene (60 ml, 54.6 g.) was degassed and heated (21-23°C) under dry nitrogen in 2-necked round-bottomed flask (200 ml). Cuprous chloride (83.0 g.) was added carefully under nitrogen and the mixture was washed with toluene (3 x 50 ml). The solvent was evaporated leaving a grey-brown powder (103.0 g.). Distilled carbon tetrachloride (70 ml) was added and heated to 76-78°C for 1½ hours. The slurry was filtered and the filtrate distilled under reduced pressure (26-30°C at 1 mm Hg) to give divinylbenzene (15 g., 23%) as a colourless liquid with traces of monovinyl compounds. ³⁰³

3.5.a. Polymerization of Partially Chlorinated Cycloalkenes


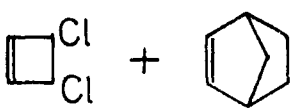
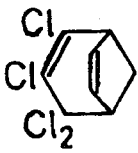
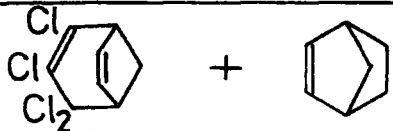
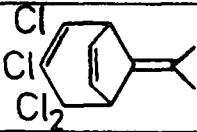
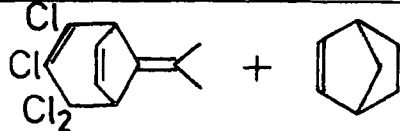
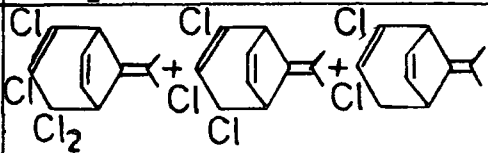

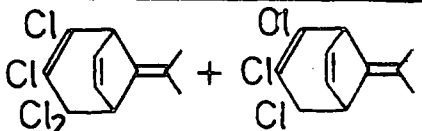
General procedure of the polymerization was same as described in the experiment section of Chapter 2.

3.5.b. Polymerization of Partially Chlorinated Cycloalkenes Using MoCl_5 or $\text{WCl}_6/\text{Me}_4\text{Sn}$ in Chlorobenzene

	Monomer	Catalyst	Ratio($\text{M}=\text{WCl}_6/\text{MoCl}_5$) M: Me_4Sn :Monomer	Volume of Solvent (ml)	Reaction Time (hours)	Yield (%)
1		WCl_6	1:2:26	4.0	1.0	80
2		WCl_6	1:2:34	11.0	3.0	50
		MoCl_5	1:2:28	11.0	3.0	60
3		MoCl_5	1:2:29	11.0	0.5	75
4		MoCl_5	1:2:19	11.0	0.5	85

3.5.c. Unsuccessful Attempts to Polymerize and Copolymerize Partially Chlorinated Cycloalkenes

In all cases the polymerizations were done in sets under the same conditions and one reference polymerization was included to ensure that an active catalyst was generated in each case. Thus each unsuccessful polymerization was carried out at the same time and under the same conditions as polymerization of bicyclo[2.2.1]hept-2-ene (i.e. same catalyst, cocatalyst, solvent batches, same dry nitrogen line, same type of flask dried and purged in the same way).

	Monomer or Comonomer	Catalyst (Ratio 1:2)	Ratio Cat.:Mon.	Reaction Time (hours)	Note
1		WCl_6/Me_4Sn	1:122	20	-
2		WCl_6/Me_4Sn	1:110:130	1.0	Poly-norbornene
3		WCl_6/Me_4Sn	1:20	24	-
		WCl_6/Me_4Sn	1:20	16 ^{60°C}	-
		$MoCl_5/Me_4Sn$	1:20	24	-
4		WCl_6/Me_4Sn	1:10:20	1.0	Poly-norbornene
5		$MoCl_5/Me_4Sn$	1:15	4	-
6		$MoCl_5/Me_4Sn$	1:10:20	1.0	Poly-norbornene
7		$MoCl_5/Me_4Sn$	(0.45 g.)	20	-
8	As above (7) plus 	$MoCl_5/Me_4Sn$	(0.3 g.)	1.0	Poly-norbornene
9		$MoCl_5/Me_4Sn$	(1.0 g.)	48	-

3.6.a. Preparation of 1,6,7,8-Tetraphenyl-9-ketotricyclo[4.2.1.0^{2,5}]-nona-3,7-diene

3.6.b. Reagents

Cis-3,4-dichlorocyclobutene was prepared as described previously in Section 3.4.a; tetraphenylcyclopentadienone was kindly supplied by Dr. J.H. Edwards of this Department and xylene was purchased from BDH Ltd.

3.6.c. Preparation of 3,4-Dichloro-1,6,7,8-tetraphenyl-9-ketotricyclo[4.2.1.0^{2,5}]non-7-ene

Tetraphenylcyclopentadienone (10.0 g., 26 mmole), cis-3,4-dichlorocyclobutene (6.25 g., 51 mmole) and xylene (20 ml) were placed in a flask (100 ml) and refluxed for 5 hours. The solvent was removed by reduced pressure and followed by purification using column chromatography on silica (Kieselgel 60) with petroleum ether/chloroform as eluent. Three fractions were collected, recrystallized from ethanol and dried under reduced pressure to give (i) 7,8-dichloro-2,3,4,5-tetraphenylbicyclo[4.2.0]octa-2,4-diene (1.5 g.); [Found C, 80.53; H, 4.84; C₃₂H₂₄Cl₂ requires C, 80.16; H, 5.01%]; M (m.s.), 479 (Calculated M, 479); (ii) 3,4-dichloro-1,6,7,8-tetraphenyl-9-ketotricyclo[4.2.1.0^{2,5}]non-7-ene (2.5 g., 20% yield); [Found C, 79.41; H, 4.34; C₃₃H₂₄Cl₂O requires C, 78.11; H, 4.73%]; M (m.s.) 507 (Calculated M, 507); The ¹H n.m.r. spectrum was the same as that published³⁰¹ and the molecule has the endo isomer; and (iii) an unidentified compound (1.5 g.); [Found C, 81.14; H, 4.52%]; M (m.s.), 520.

3.6.d. Dechlorination of endo-3,4-dichloro-1,6,7,8-tetraphenyl-9-ketotricyclo[4.2.1.0^{2,5}]non-7-ene

Endo-3,4-dichloro-1,6,7,8-tetraphenyl-9-ketotricyclo[4.2.1.0^{2,5}]non-7-ene (2.5g., 5 mmole) and activated zinc powder (50 g.) were refluxed in ethanol (65 ml) with stirring for 48 hours. The reaction mixture was diluted with diethylether (180 ml) and filtered. The filtrate was washed

with water (2 x 300 ml), and after evaporation of the solvents, the residue was recrystallized from ethanol to give 1,6,7,8-tetraphenyl-9-ketotricyclo[4.2.1.0^{2,5}]nona-3,7-diene (1.8 g., 80% yield) as white crystals; m.p. 186°C; [Found C, 85.02; H, 5.70; C₃₃H₂₄O requires C, 90.83; H, 5.51%]; M (m.s.), 436 (Calculated M, 436). The product had a ¹H n.m.r. spectrum which was identical with that published.

3.6.e. Attempts to Polymerize and Copolymerize 1,6,7,8-Tetraphenyl-9-ketotricyclo[4.2.1.0^{2,5}]nona-3,7-diene

All attempts to polymerize this monomer with WCl₆/Me₄Sn in chlorobenzene at room temperature and 65°C were unsuccessful, the monomer was recovered unchanged and identified by i.r. spectroscopy.

1,6,7,8-tetraphenyl-9-ketotricyclo[4.2.1.0^{2,5}]nona-3,7-diene (0.25 g., 0.6 mmole) was copolymerized with bicyclo[2.2.1]hept-2-ene (0.35 g., 3.7 mmole) with WCl₆/(CH₃)₄Sn (1:2 molar ratio) in chlorobenzene for 2 hours. White polymer (0.45 g., 75%) was collected and purified by dissolve in toluene and reprecipitating into methanol. (Found C, 90.32; H, 9.126); ¹H, ¹³C and i.r. spectroscopy showed that the polymer consisted of units derived from both starting materials (see Discussion).

3.7 Attempts to polymerize divinylbenzene by cross metathesis using WCl₆/(CH₃)₄Sn and MoCl₅/(CH₃)₄Sn catalysts

Divinylbenzene (see 3.4.k.) was treated with a solution of WCl₆/(CH₃)₄Sn or MoCl₅/(CH₃)₄Sn in chlorobenzene at room temperature. In all cases, insoluble polymer (cross-link polymer) was formed which could not be satisfactorily characterized. Attempts to modify the reaction by addition of a third component were also unsuccessful, in this case, 2,6-di-t-butylpyridine was the base used. This three-component metathesis catalyst did not initiate polymerization of divinylbenzene by either a cross-metathesis or a cationic mechanism although the same catalyst system initiated the ring-opening polymerization of bicyclo[2.2.1]hept-2-ene.

APPENDIX A

APPARATUS AND INSTRUMENTS

Vacuum system. A conventional vacuum system incorporating a mercury diffusion pump, and a rotary oil pump was used for degassing materials, vacuum distillations, removing volatile residues from polymer samples etc.

Mass spectra were recorded with either an A.E.I. MS 9 or a V.G. Micromass 12B spectrometer.

I.R. spectra were recorded using Perkin-Elmer 457 or 577 Grating Infrared Spectrophotometers.

N.m.r. spectra were recorded with either a Bruker Spectrospin HX 90E or a Varian EM 360L NMR spectrometer in this Department or recorded through the SERC NMR service @ Manchester or Edinburgh University.

Carbon and hydrogen analyses were carried out with a Perkin-Elmer 240 CHN Analyser.

Fluorine and chlorine analyses were carried out by the potassium fusion method.

Analytical gas liquid chromatography (g.l.c.). Pye Unicam GCD and Pye 104 gas chromatographs with nitrogen as the carrier gas and flame ionization detectors were used for analytical work. [Generally Column O₃₀ (1.52 m x 6 mm diameter) with a stationary phase of silicone grease/celite was used].

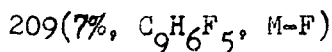
Thermogravimetric analyses were performed using a Stanton Redcroft TG 750 Thermobalance in the constant heating mode at a heating rate of 1°C/minute.

APPENDIX B

MASS SPECTRA

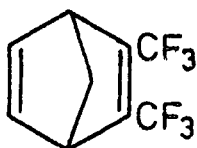
The mass spectra of compounds obtained in the course of this work are tabulated below. Compounds marked with an asterisk have not been reported previously. Ions are tabulated in the form:

e.g. (I)



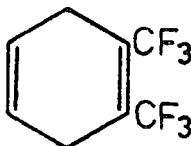
In this example, the ion has a mass number 209, its intensity is 7% of the intensity of the base peak of the spectrum, it has provisionally assigned the formula $\text{C}_9\text{H}_6\text{F}_5$ (the + being understood), and its supposed origin is loss of an F from the parent ion (M).

(I) 2,3-bis(trifluoromethyl)bicyclo 2.2.1 hepta-2,5-diene



228(26%, $\text{C}_9\text{H}_6\text{F}_6$, M), 209(7%, $\text{C}_9\text{H}_6\text{F}_5$, M-F), 208(7%, $\text{C}_9\text{H}_5\text{F}_5$, M-HF), 202(24%, $\text{C}_7\text{H}_4\text{F}_6$, M-C₂H₂), 189(10%, $\text{C}_9\text{H}_5\text{F}_4$, M-HF.F), 159(100%, $\text{C}_8\text{H}_6\text{F}_3$, M-CF₃), 133(11%, $\text{C}_6\text{H}_4\text{F}_3$, M-C₂H₂.CF₃), 119(8%, $\text{C}_5\text{H}_2\text{F}_3$, M-C₃H₄.CF₃), 109(22%, $\text{C}_7\text{H}_6\text{F}$, M-2CF₃), 69(12%, CF₃), 66(18%, C_5H_6), 51(10%, CHF₂).

(II) 1,2-bis(trifluoromethyl)cyclohexa-1,4-diene



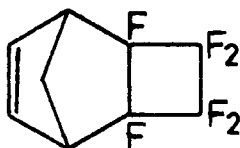
216(17%, $\text{C}_8\text{H}_6\text{F}_6$, M), 214(100%, $\text{C}_8\text{H}_4\text{F}_6$, M-2H), 195(39%, $\text{C}_8\text{H}_5\text{F}_5$, M-H₂F), 164(26%, $\text{C}_4\text{H}_2\text{F}_6$, M-C₄H₄), 163(9%, C_4HF_6 , M-C₄H₅), 147(21%, $\text{C}_7\text{H}_6\text{F}_3$, M-CF₃), 144(65%, $\text{C}_7\text{H}_3\text{F}_3$, M-3H.CF₃), 127(39%, $\text{C}_7\text{H}_5\text{F}_2$, M-HF.CF₃), 75(18%, C_3HF_2 , M-CH₂CF), 69(16%, CF₃), 51(10%, CHF₂).

(III)* 5,5,6-trichloro-6-trifluoromethylbicyclo 2.2.1 hept-2-ene



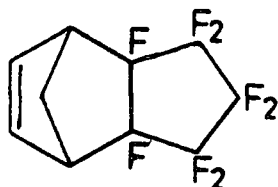
264.5(0%, $C_8H_6F_3Cl_3$, M), 229(17%, $C_8H_6F_3Cl_2$, M-Cl), 193(64%, $C_8H_5F_3Cl$, M-HCl₂), 181(19%, $C_7H_5F_3Cl$, M-CHCl₂), 159(33%, $C_4H_3F_2Cl_2$, M-C₄H₃FCl), 143(19%, $C_4H_3F_3Cl$, M-C₄H₃Cl₂), 125(33%, $C_4H_3F_3Cl$, M-C₄H₃Cl₂), 108(28%, $C_4H_3F_3$, M-C₄H₃Cl₃), 83(45%, $C_2H_2F_3$, M-C₆H₄Cl₃), 66(100%, C_5H_6).

(IV)* 2,3,3,4,4,5-hexafluorotricyclo 4.2.1.0^{2,5} non-7-ene



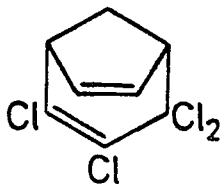
228(8%, $C_9H_6F_6$, M), 145(5%, $C_7H_4F_3$, M-C₂H₂F₃), 128(12%, $C_7H_6F_2$, M-2CF₂), 127(30%, $C_7H_5F_2$, M-H.2CF₂), 109(7%, C_7H_6F , M-HF.2CF₂), 102(6%, $C_7H_4F_2$, M-2HCF₂), 101(7%, $C_7H_3F_2$, M-3H.2CF₂), 95(5%, $C_3H_2F_3$, M-C₆H₄F₃), 77(7%, HF₄, M-C₉H₅), 67(10%, $C_2H_5F_2$, M-C₇HF₄), 66(100%, C_5H_6), 57(7%, C_3H_2F , M-C₆H₄F₅), 51(6%, CHF₂).

(V)* 2,3,3,4,4,5,5,6-octafluorotricyclo 5.2.1.0^{2,6} dec-8-ene



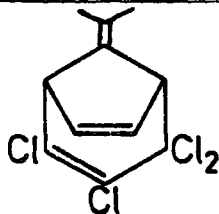
278(1%, $C_{10}H_6F_8$, M), 207(3%, $C_9H_4F_5$, M-CH₂F₃), 127(5%, $C_7H_5F_2$, M-C₃HF₆), 85(8%, C_5H_6F , M-C₅F₇), 83(14%, C_5H_3F , M-C₅H₃F₇), 73(3%, C_4H_6F , M-C₆F₇), 67(6%, $C_2H_5F_2$, M-C₈HF₆), 66(100%, C_5H_6), 65(3%, C_5H_5).

(VI) 2,3,4,4-tetrachlorobicyclo 3.2.1 octa-2,6-diene



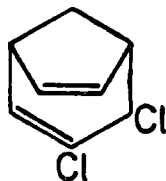
244(10%, $C_8H_6Cl_4$, M), 209(100%, $C_8H_6Cl_3$, M-Cl), 173(39%, $C_8H_5Cl_2$, M-Cl₂),
137(17%, C_8H_6Cl , M-Cl₃), 136(32%, C_8H_5Cl , M-HCl₃), 125(20%, C_7H_5Cl , M-CCl₃),
102(2%, C_8H_6 , M-Cl₄), 75(12%, C_3H_4Cl , M-C₅H₂Cl₃), 74(2%, C_3H_3Cl , M-C₅H₃Cl₃).

(VII)* 2,3,4,4-tetrachloro-8-isopropylidenebicyclo 3.2.1 octa-2,6-diene



284(10%, $C_{11}H_{10}Cl_4$, M), 249(100%, $C_{11}H_{10}Cl_3$, M-Cl), 213(48%, $C_{11}H_{10}Cl_2$,
M-Cl₂), 197(11%, $C_{10}H_7Cl_2$, M-CH₃Cl₂), 177(58%, $C_{11}H_{10}Cl$, M-Cl₃), 141(7%,
 $C_{11}H_9$, M-Cl₄).

(VIII) 3,4-dichlorobicyclo 3.2.1 octa-2,6-diene



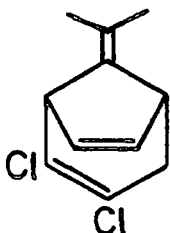
175(4%, $C_8H_8Cl_2$, M), 139(35%, C_8H_8Cl , M-Cl), 112(11%, C_6H_5Cl , M-C₂H₃Cl),
107(10%, C_3Cl_2 , M-C₅H₈), 102(100%, C_5H_7Cl , M-C₃HCl), 90(6%, C_7H_6 , M-CHCl₂),
86(7%, C_4H_3Cl , M-C₄H₅Cl), 79(30%, $C_2H_4Cl_2$, M-C₆H₅), 76(45%, C_3H_5Cl , M-C₅H₃Cl).

(IX) 3-chlorobicyclo 3.2.1 octa-2,6-diene



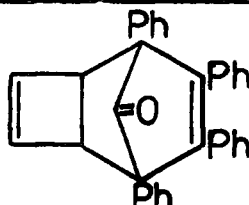
141(14%, C_8H_9Cl , M), 139(33%, C_8H_8Cl , M-H), 112(12%, C_6H_5Cl , M-C₂H₄),
105(100%, C_8H_9 , M-Cl), 104(15%, C_8H_8 , M-HCl), 103(48%, C_8H_7 , M-H₂Cl),
79(31%, C_6H_7 , M-C₂H₂Cl).

(X)* 2,3-dichloro-8-isopropylidenebicyclo 3.2.1 octa-2,6-diene



215(7%, $C_{11}H_{12}Cl_2$, M), 199(14%, $C_{10}H_8Cl_2$, M- CH_4), 180(30%, $C_{11}H_{12}Cl$, M-Cl), 167(32%, $C_{10}H_{12}Cl$, M-CCl), 165(100%, $C_{10}H_{10}Cl$, M- CH_2Cl), 144(48%, $C_{11}H_{12}$, M- Cl_2), 130(12%, $C_{10}H_{10}$, M- CH_2Cl_2), 117(16%, C_9H_9 , M- $C_2H_3Cl_2$), 105(20%, C_8H_9 , M- $C_4H_3Cl_2$), 90(36%, C_7H_6), 83(17%, C_6H_9).

(XI) 1,2,3,4-tetraphenyl-9-ketotricyclo 4.2.1.0^{5,8} nona-2,6-diene



436(5%, $C_{33}H_{24}O$, M), 412(15%, $C_{31}H_{20}$, M- C_2H_4), 408(100%, $C_{32}H_{24}$, M-CO), 333(62%, $C_{26}H_{19}$, M-CO. C_6H_5), 319(36%, $C_{25}H_{17}$, M-CO. C_6H_5 . CH_2), 256(30%, $C_{20}H_{14}$, M-CO. $2C_6H_5$), 231(75%, $C_{15}H_9O$, M- $3C_6H_5$).

APPENDIX C

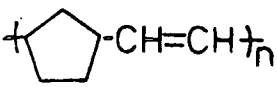
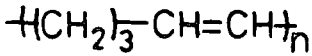
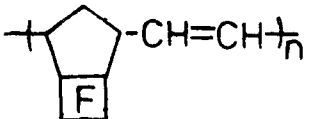
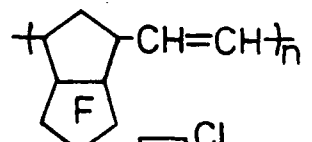

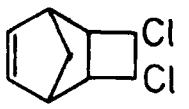
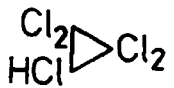

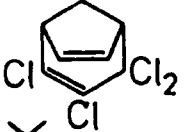
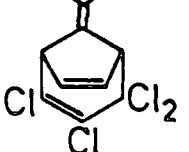
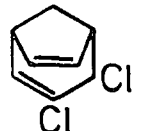

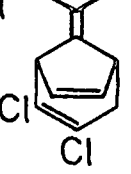
I.R. SPECTRA

All spectra were recorded using KBr plates, pressed discs or thin films and were run under condition designation by:-

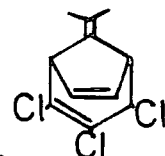
- (A) - KBr disc
- (B) - Thin liquid film
- (C) - Thin polymer film (free standing)
- (D) - Thin polymer film (cast on KBr plate)

Infrared spectra are tabulated below.

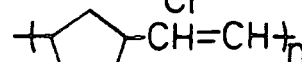
Spectrum No	Nature of sample	Structure
(I)	2,3-bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene (B)	
(II)	1,2-bis(trifluoromethyl)cyclohexa-1,4-diene (B)	
(III)	5,5,6-trichloro-6-trifluoromethylbicyclo[2.2.1]hept-2-ene (A)	
(IV)	2,3,3,4,4,5-hexafluorotricyclo[4.2.1.0 ^{2,5}]non-7-ene (B)	
(V)	2,3,3,4,4,5,5,6-octafluorotricyclo[5.2.1.0 ^{2,6}]dec-8-ene (B)	
(VI)	polyadducts of reaction between cyclopentadiene and perfluorocyclohexene (A)	
(VII)	poly(4,5-bis(trifluoromethyl)-1,3-cyclopentene)nylenevinylene from WCl_6/Me_4Sn (C)	
(VIII)	poly(4,5-bis(trifluoromethyl)-1,3-cyclopentene)nylenevinylene from $MoCl_5/Me_4Sn$ (C)	
(IX)	copolymer from 2,3-bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene and cyclopentene with 1:1 feed stock ratio, from WCl_6/Ph_4Sn (D)	

- (X) copolymer from 2,3-bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene and cyclopentene with 5:1 feed stock ratio, from WCl_6/Ph_4Sn (D)
- (XI) poly(1,3-cyclopentenylenevinylene) from WCl_6/Ph_4Sn (c) 
- (XII) poly(1-pentenylene) (c) 
- (XIII) polymer (X), n=2 (c) 
- (XIV) polymer (X), n=3 (c) 
- (XV) cis-3,4-dichlorocyclobutene (B) 
- (XVI) 3,4-dichlorotricyclo[4.2.1.0^{2,5}]non-7-ene (B) 
- (XVII) pentachlorocyclopropane (B) 
- (XVIII) tetrachlorocyclopropene (B) 
- (XIX) 2,3,4,4-tetrachlorobicyclo[3.2.1]octa-2,6-diene (A) 
- (XX) 2,3,4,4-tetrachloro-8-isopropylidenebicyclo[3.2.1]octa-2,6-diene (A) 
- (XXI) 3,4-dichlorobicyclo[3.2.1]octa-2,6-diene (B) 
- (XXII) 3-chlorobicyclo[3.2.1]octa-2,6-diene (B) 
- (XXIII) 2,3-dichloro-8-isopropylidenebicyclo[3.2.1]octa-2,6-diene 

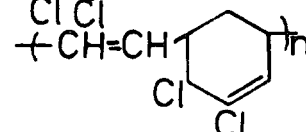
(XXIV) 2,3,4-trichloro-8-isopropylidenebicyclo[3.2.1]octa-2,6-diene (B)



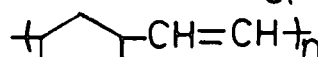
(XXV) polymer derived from monomer (XIX) using WCl_6/Me_4Sn (C)



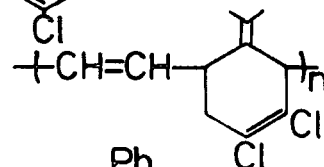
(XXVI) polymer derived from monomer (XXI) using WCl_6/Me_4Sn (D)



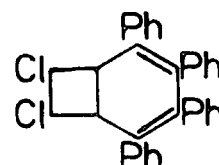
(XXVII) polymer derived from monomer (XXII) using $MoCl_5/Me_4Sn$ (D)



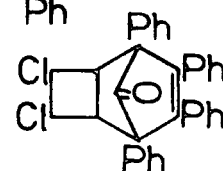
(XXVIII) polymer derived from monomer (XXIII) using $MoCl_5/Me_4Sn$ (D)



(XXIX) 3,4-dichloro-1,6,7,8-tetraphenylbicyclo[4.2.0]octa-1,6-diene (A)

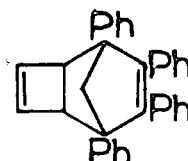


(XXX) 3,4-dichloro-1,6,7,8-tetraphenyl-9-ketotricyclo[4.2.1.0^{2,5}]non-7-ene (A)



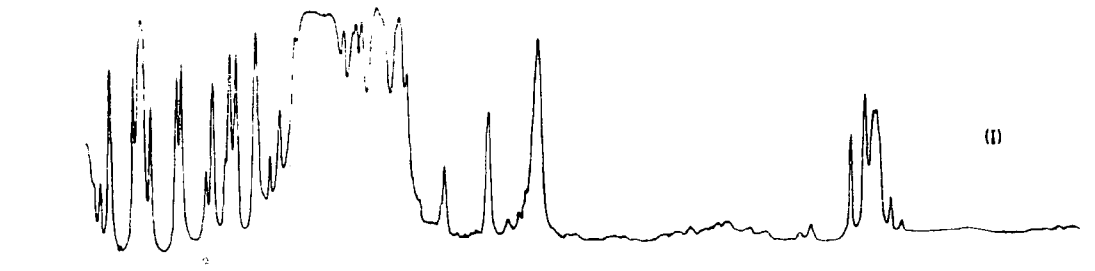
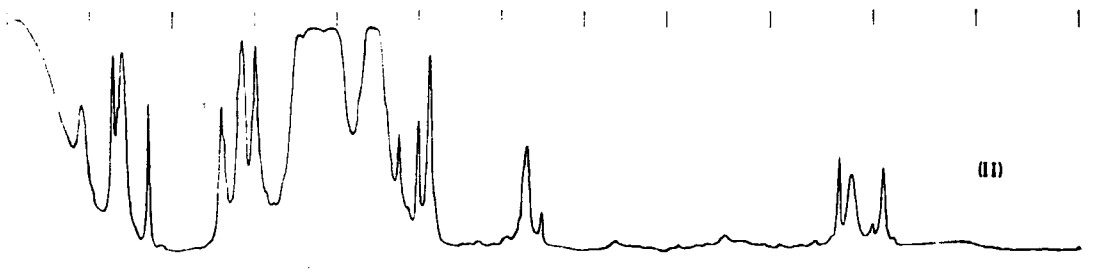
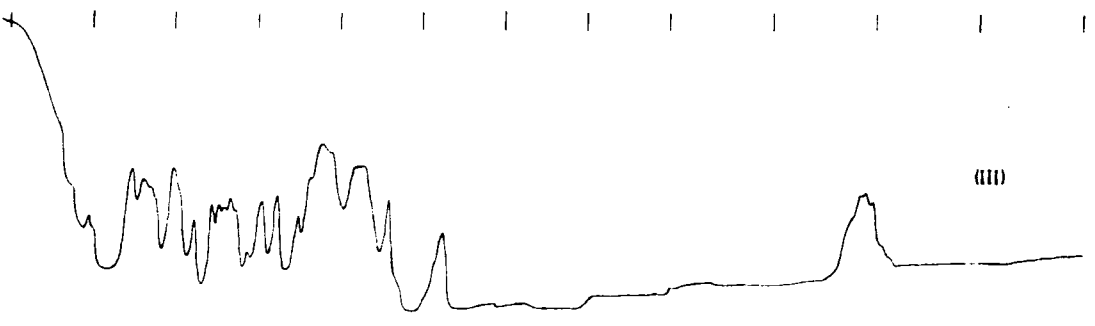
(XXXI) unidentified compound (see page 115) (A)

(XXXII) 1,6,7,8-tetraphenyl-9-ketotricyclo[4.2.1.0^{2,5}]nona-3,7-diene (A)



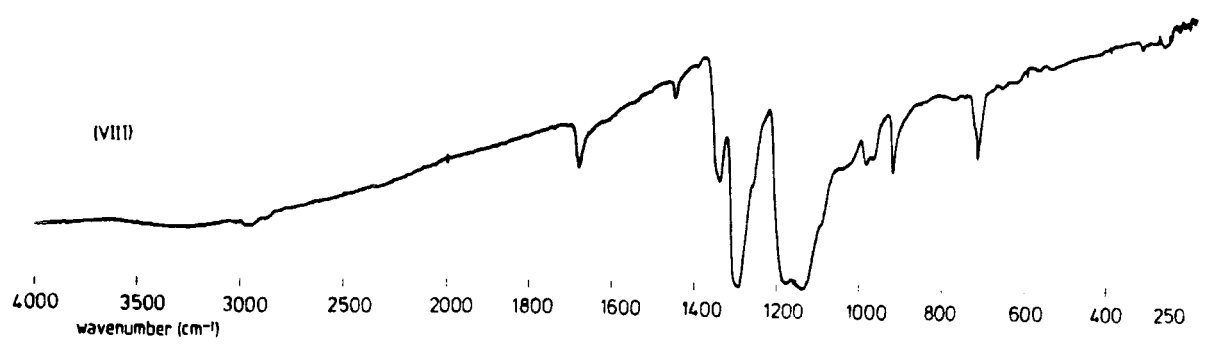
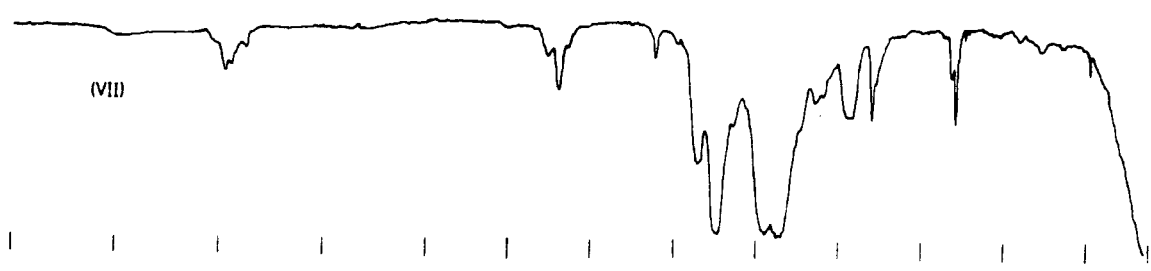
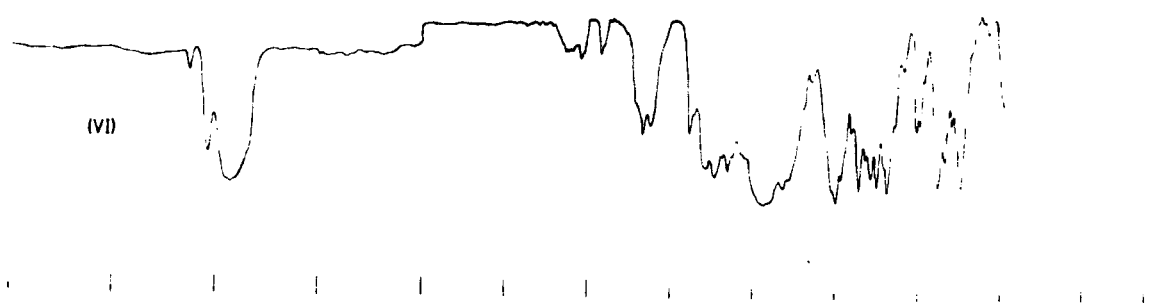
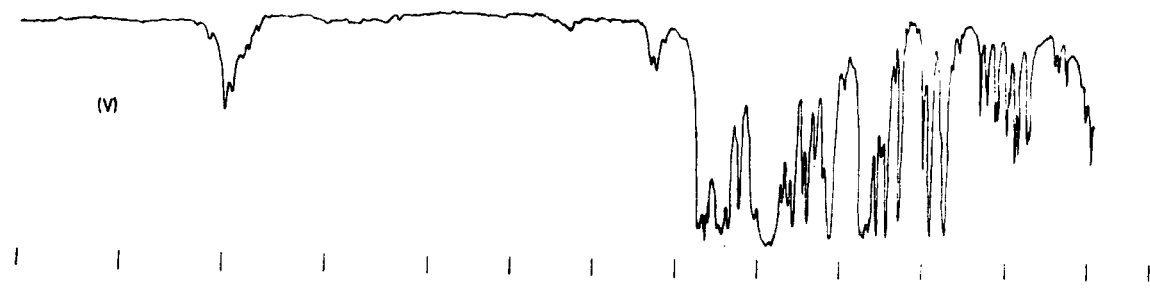
(XXXIII) copolymer from copolymerization of bicyclo 2.2.1 hept-2-ene and 1,6,7,8-tetraphenyl-9-ketotricyclo[4.2.1.0^{2,5}]nona-3,7-diene

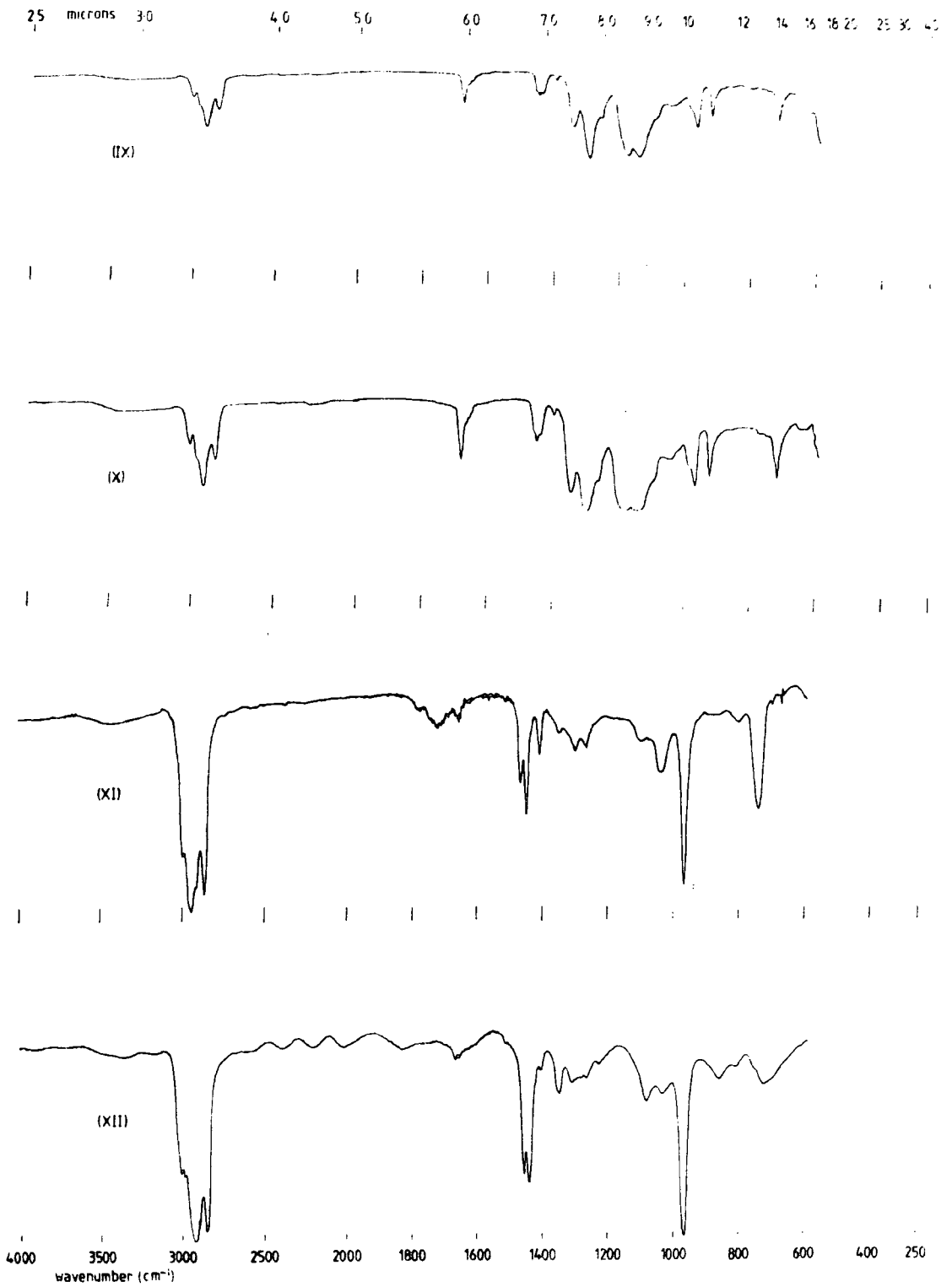
Wavenumber (cm⁻¹)



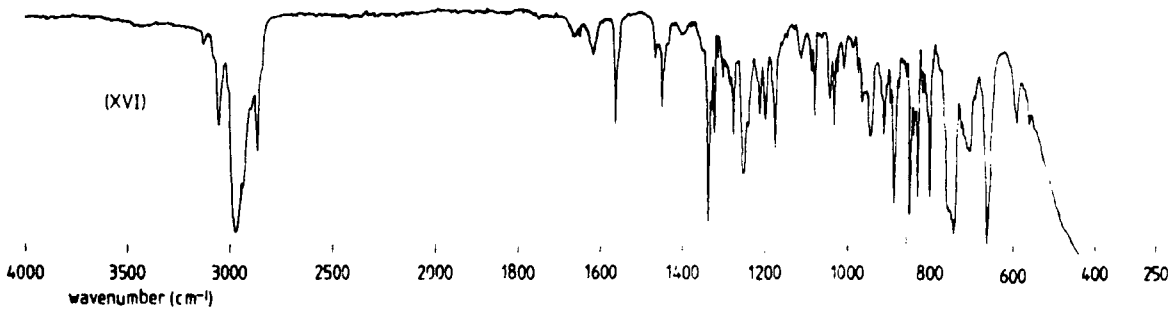
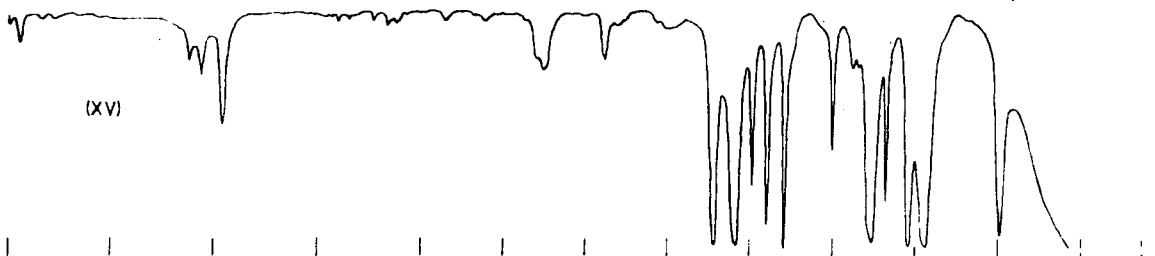
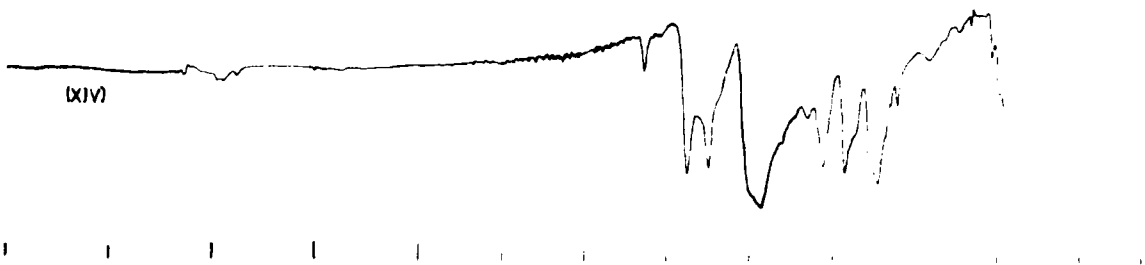
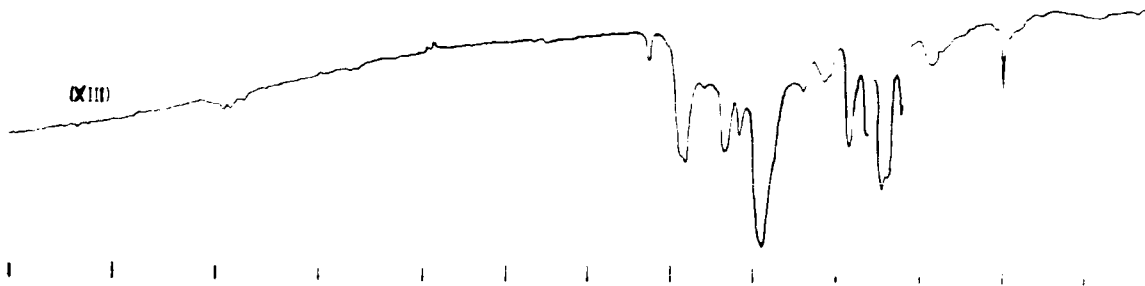
microns

2,5 microns 30 40 50 60 70 80 90 10 12 14 16 18 20 25 30 40

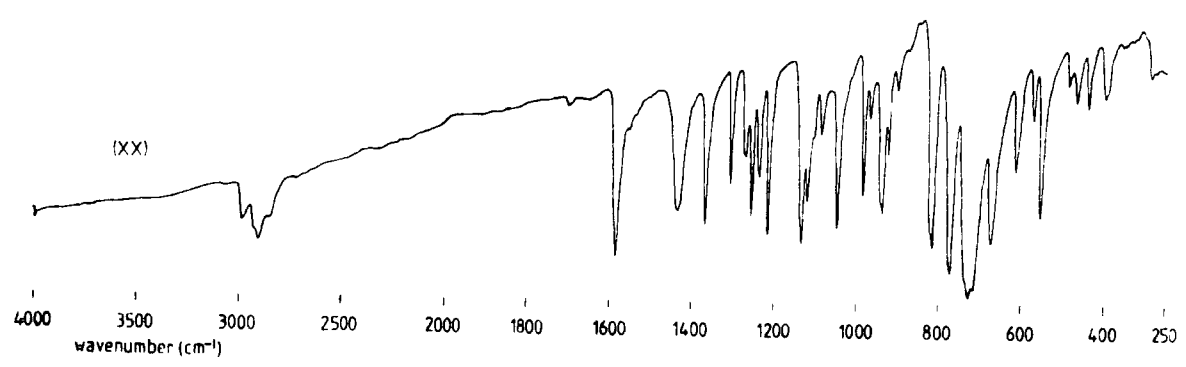
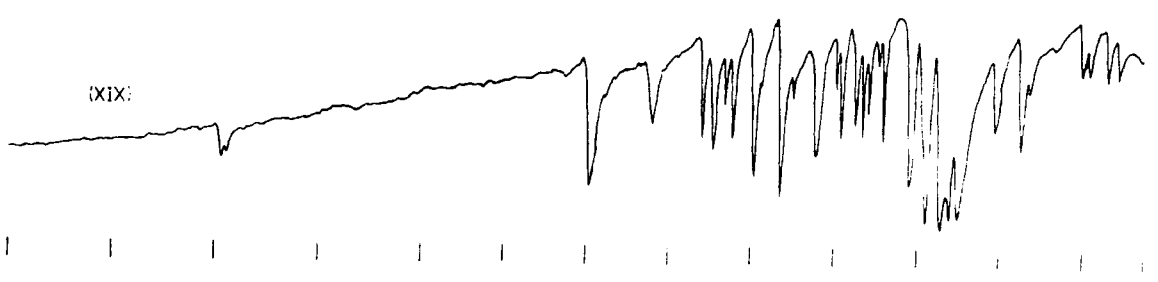
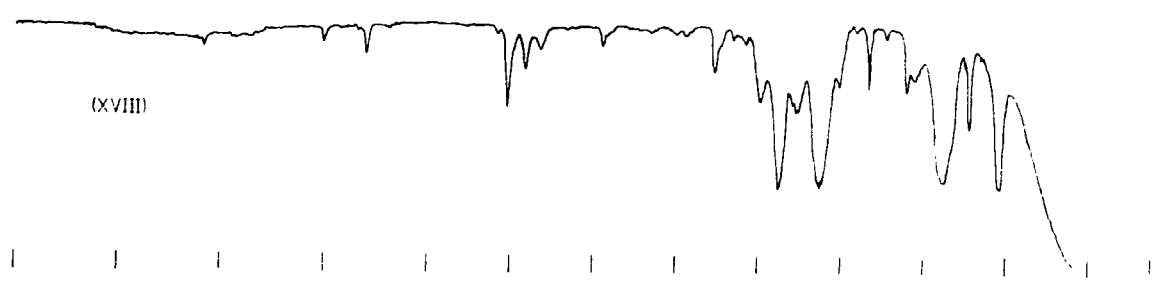
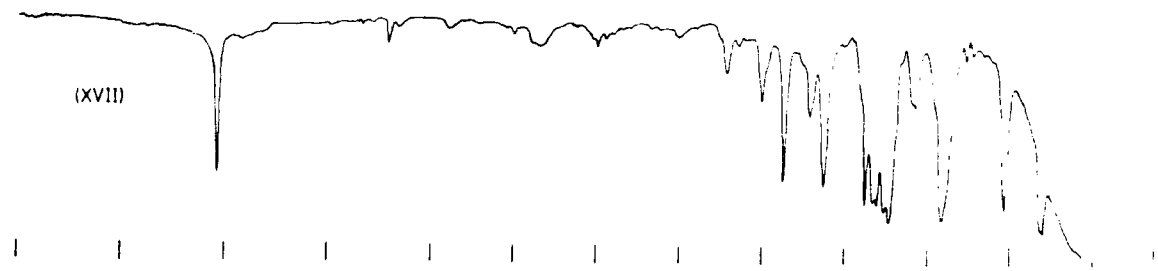




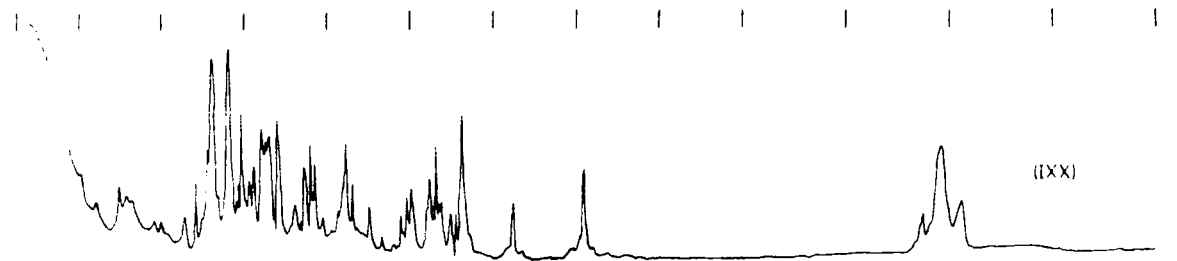
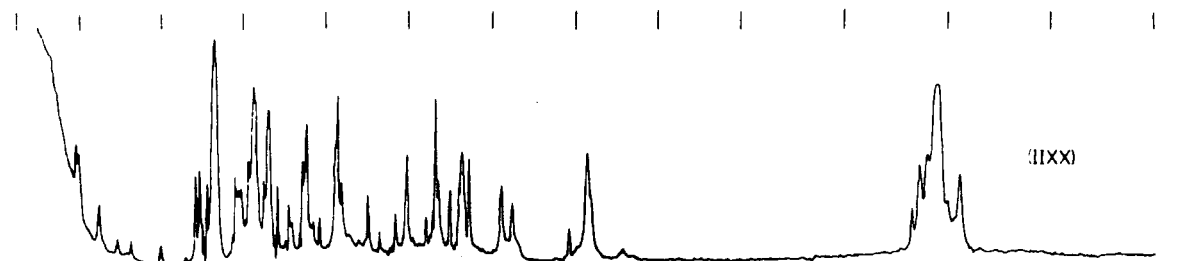
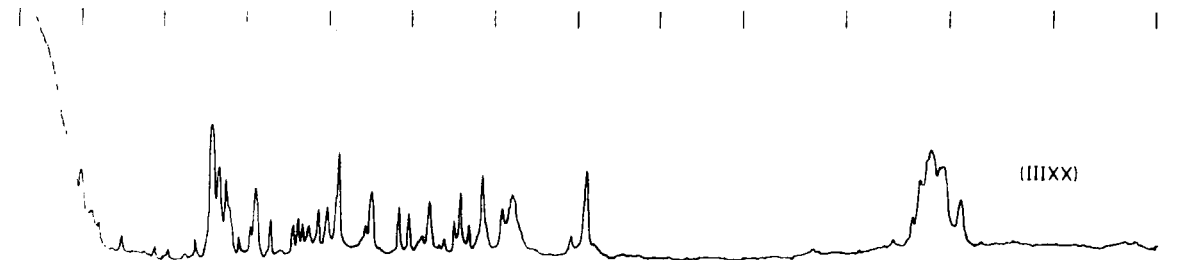
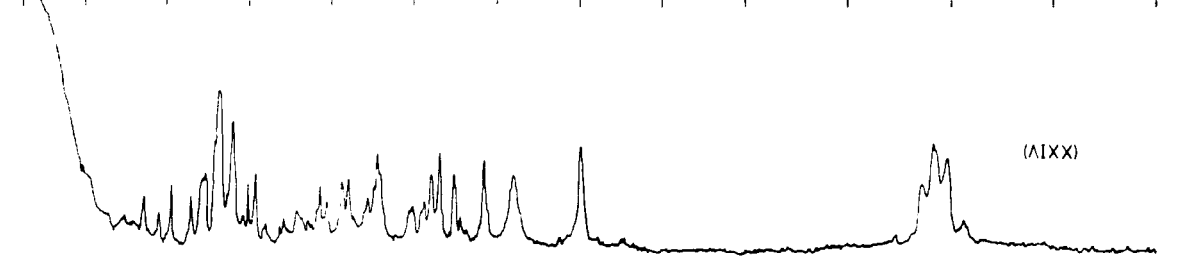
25 microns 30 40 50 60 70 80 90 10 12 14 16 18 20 25 30 40



25 microns 30 40 50 60 70 80 90 10 12 14 16 18 20 25 30 40

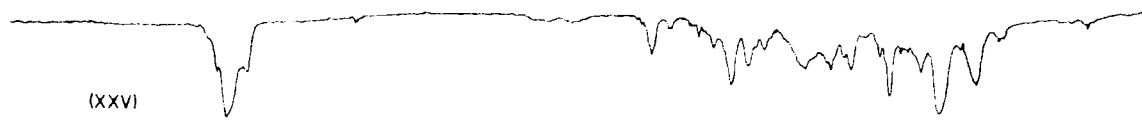


Wavenumber (cm⁻¹)



microns

25 microns 30 40 50 60 70 80 90 10 12 14 16 18 20 25 30 40



(XXV)

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(XXVI)

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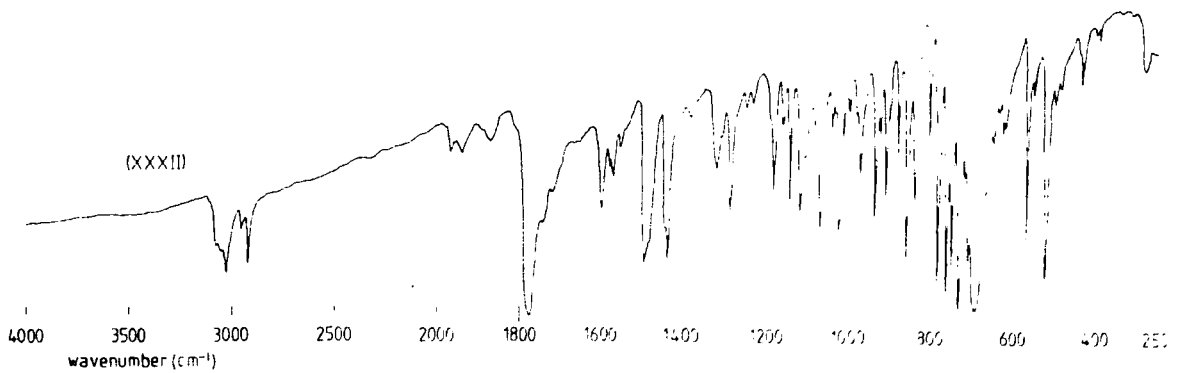
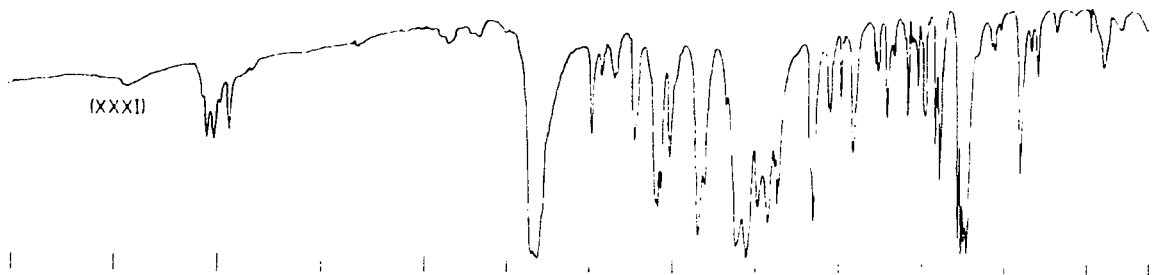
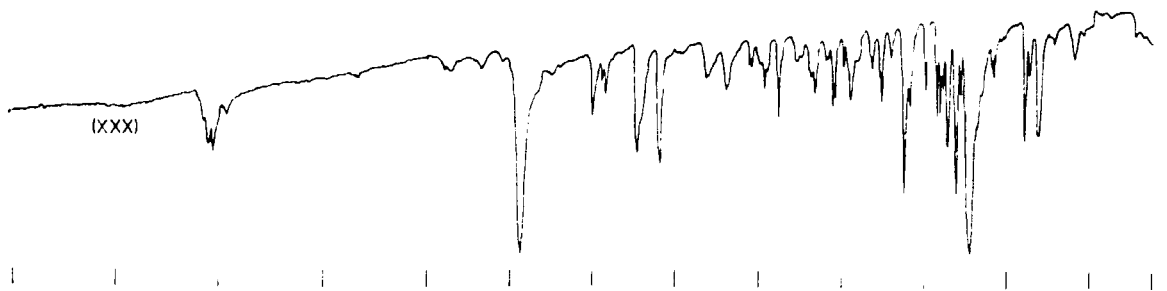
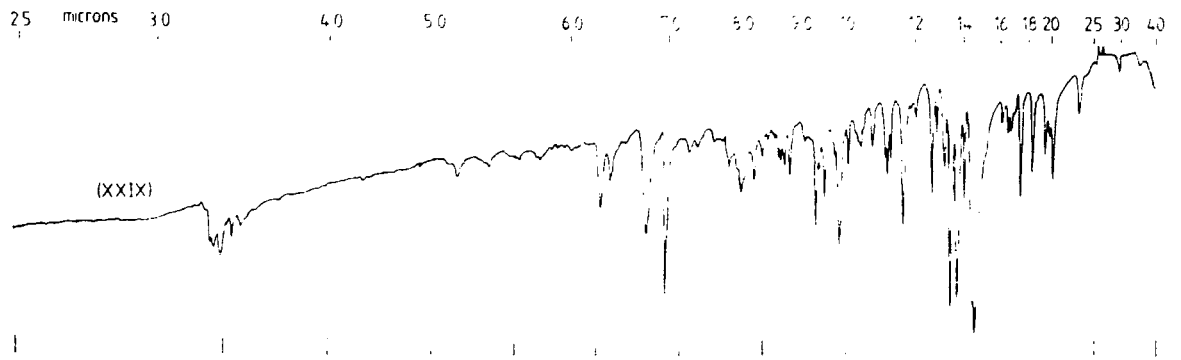
(XXVII)

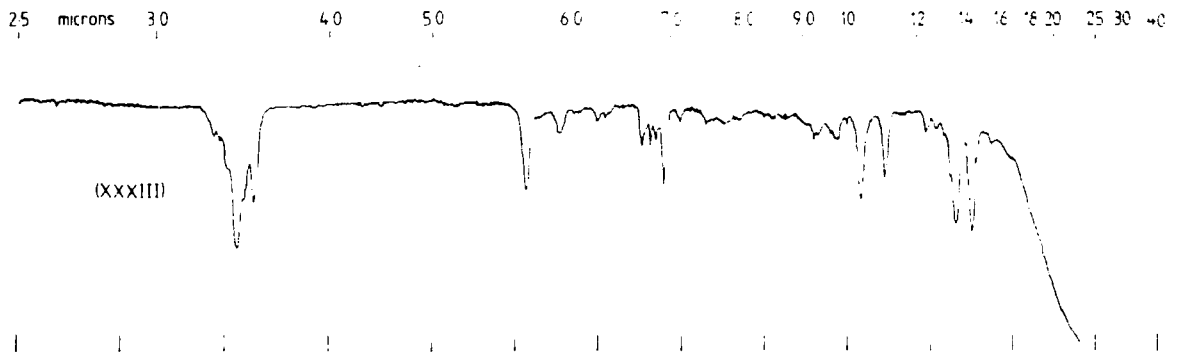
| | | | | | | | | | | | | | | | | | | | | |



(XXVIII)

4000 3500 3000 2500 2000 1800 1600 1400 1200 1000 800 600 400 250
wavenumber (cm⁻¹)





APPENDIX D

RESEARCH COLLOQUIA, SEMINARS AND LECTURES

The Board of Studies in Chemistry requires that each postgraduate research thesis contains an Appendix listing:

- (a) All research colloquia, research seminars and lectures (by external speakers) arranged by the Department of Chemistry since 1 October, 1979.
- (b) All research conferences attended by the writer of the thesis, during the period when the research for the thesis was carried out.

1. Research colloquia, seminars and lectures

21 November 1979

Dr. J. Muller (University of Bergen), 'Photochemical Reactions of Ammonia'.

28 November 1979

Dr. B. Cox (University of Stirling), 'Macrobicyclic Cryptate Complexes, Dynamics and Selectivity'.

5 December 1979

Dr. G.C. Eastmond (University of Liverpool), 'Synthesis and Properties of Some Multicomponent Polymers'.

12 December 1979

Dr. C.I. Ratcliffe (University of London), 'Rotor Motions in Solids'.

19 December 1979

Dr. K.E. Newman (University of Lausanne), 'High Pressure Multinuclear NMR in the Elucidation of the Mechanisms of Fast, Simple Inorganic Reactions'.

30 January 1980

Dr. M.J. Barrow (University of Edinburgh), 'The Structures of some Simple Inorganic Compounds of Silicon and Germanium - Pointers to Structural Trends in Group IV'.

6 February 1980

Dr. J.M.E. Quirke (University of Durham), 'Degradation of Chlorophyll-a in Sediments'.

23 February 1980

B. Grievson, B.Sc. (University of Durham), 'Halogen Radiopharmaceuticals'.

14 May 1980

Dr. R. Hutton (Waters Associates, U.S.A.), 'Recent Developments in Multi-milligram and Multi-gram Scale Preparative High Performance Liquid Chromatography'.

21 May 1980

Dr. T.W. Bentley (University of Swansea), 'Medium and Structural Effects in Solvolytic Reactions'.

7 October 1980

Professor T. Fehlner, 'Metalloboranes Cages or Coordination Compounds?'.

16 October 1980

Dr. D. Mass (Salford University), 'Reactions a Go-Go'.

23 October 1980

Professor T.M. Sugden (Cambridge University), 'Chemistry in Flames'.

30 October 1980

Professor N. Grassie (Glasgow University), 'Inflammability Hazards in Commercial Polymers'.

6 November 1980

Professor A.G. Sykes (Newcastle University), 'Metallo-proteins: An Inorganic Chemists Approach'.

12 November 1980

Dr. M. Gerloch (University of Cambridge), 'Magnetochemistry is about Chemistry'.

13 November 1980

Professor N.N. Greenwood (Leeds University), 'Metalloborane Chemistry'.

19 November 1980

Dr. T. Gilchrist (University of Liverpool), 'Nitroso-olefins as Synthetic Intermediates'.

4 December 1980

Reverend R. Lancaster, 'Fireworks'.

18 December 1980

Dr. R. Evans (University of Brisbane, Australia), 'Some Recent Communications to the Editor of the Australian Journal of Failed Chemistry'.

22 January 1981

Professor E.A. Dawes (Hull University), 'Magic and Mystery through the Ages'.

29 January 1981

Mr. H.J.F. MacLean (I.C.I. Ltd.), 'Managing in the Chemical Industry in the 1980's'.

5 February 1981

Professor F.G.A. Stone (Bristol University), 'Chemistry of Carbon to Metal Triple Bonds'.

12 February 1981

Dr. I. Fleming (Cambridge University), 'Some Uses of Silicon Compounds in Organic Synthesis'.

18 February 1981

Professor S. Kettle (University of East Anglia), 'Variations in the Molecular Dance at the Crystal Ball'.

25 February 1981

Dr. K. Bowden (University of Essex), 'The Transmission of Polar Effects of Substituents'.

11 March 1981

Dr. J.F. Stoddart (I.C.I. Ltd.), 'Stereochemical Principles in the Design and Function of Synthetic Molecular Receptors'.

17 March 1981

Professor W.P. Jencks (Brandell University, Massachusetts), 'When in a Intermediate not an Intermediate?'

18 March 1981

Dr. P.J. Smith (International Tin Research Institute), 'Organotin compounds - A Versatile Class of Organometalli Compounds'.

9 April 1981

Dr. W.H. Meyer (RCA Zurich), 'Properties of Aligned Polyacetylene'.

7 May 1981

Professor M. Gordon (Essex University), 'Do Scientists have to Count'.

10 June 1981

Dr. J. Rose (I.C.I. Plastic Division), 'New Engineering Plastics'.

17 June 1981

Dr. P. Moreau (University of Montpellier), 'Recent Results in Perfluor-organometallic Chemistry'.

21 September 1981

Dr. P. Plimmer (Du Pont), 'From Conception to Commercialization of a Polymers'.

14 October 1981

Professor E. Kluk (University of Kotowice), 'Some Aspects of the Study of Molecular Dynamics - Simple Molecular Liquid'.

22 October 1981

Dr. P.J. Gorrish (Dunlop Ltd.), 'What would Life be like without Rubber'.

6 November 1981

Dr. W. Moddeman (Monsanto Ltd., U.S.A), 'High Energy Materials'.

12 November 1981

Professor A.I. Scott (University of Edinburgh), 'An Organic Chemist's of Life in the NMR Tube'.

26 November 1981

Dr. W.O Ord (Northumbrian Water Authority), 'The Role of the Scientist in a Regional Water Authority'.

2 December 1981

Dr. G. Beamson (University of Durham), 'Photoelectron Spectroscopy in a Strong Magnetic Field'.

20 January 1982

Dr. M. Bryce (University of Durham), 'Organic Metal'.

28 January 1982

Professor I. Fells (University of Newcastle upon Tyne), 'Balancing the Energy Equations'.

3 February 1982

Dr. D. Parker (University of Durham), 'Modern Methods for the Determination of Enantiomeric Purity'.

10 February 1982

Dr. D. Pethrich (University of Strathclyde), 'Conformational Dynamics of Small and Large Molecules'.

17 February 1982

Professor D.T. Clark (University of Durham), 'Structure, Bonding, Reactivity and Syntheses of Surface as Revealed by ESCA'.

3 March 1982

Dr. P. Banfield (I.C.I., Organic Division), 'Computer Aided Syntheses Design: A view from Industry'.

19 May 1982

Professor R.D. Chambers (University of Durham), 'Fluorocarbanions - some Alice in the looking Glass Chemistry'.

28 Jun 1982

Professor D.J. Burton (University of Iowa), 'Some Aspects of the Chemistry of Fluorinated Phosphonium Salts and Phosphonates'.

2. Research conferences

(a) Royal Institute of Chemistry/Chemical Society Annual Congress, Durham, April 1980.

- (b) Advances in Polymer Characterization. An International Symposium, Durham, July 1981.
- (c) The Fourth International Symposium on Olefin Metathesis, Belfast, Northern Ireland, September 1981.

REFERENCES

REFERENCES

1. N. Calderon, J. Makromol. Sci. Revs. Macromol. Chem., C7, (1), 105 (1972).
2. R.L. Banks and G.C. Bailey, Ind. Eng. Chem. Prod. Res. Develop., 3, 170 (1964).
3. N. Calderon, E.A. Ofstead and W.A. Judy, J. Polymer Sci., A5, 2209 (1967).
4. N. Calderon, K.W. Scott, E.A. Ofstead and W.A. Judy, A.C.S. Meeting Abs., 155, L54 (1968).
5. E. Wasserman, D.A. Ben-Efran and R.J. Wolovsky, J. Amer. Chem. Soc., 90, 3286 (1968).
6. K.J. Ivin, J.J. Rooney, C.D. Stewart, M.L.H. Green and R. Mahtab, J. Chem. Soc. Chem. Commun., 604 (1978).
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