The ring-opening polymerisation of some fluorinated cycloalkenes

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THE RING-OPENING POLYMERISATION OF SOME FLUORINATED CYCLOALKENES

by

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ABSTRACT

The work described in this thesis was concerned with an investigation of the ring-opening polymerisation of fluorinated cyclopentenes, bicyclo[2.2.1]hept-2-enes and bicyclo[2.2.1]hepta-2,5-dienes and indene. The questions the research set out to answer are discussed and placed in context in Chapter 1.

The syntheses and characterisation of the monomers required for this work are described in Chapter 4.

An investigation into the polymerisability of fluorinated cyclopentenes is recorded in Chapter 3. Chapters 5 and 6 describe the successful polymerisation and copolymerisation of a variety of partially fluorinated bicyclo[2.2.1]hept-2-enes and bicyclo[2.2.1]hepta-2,5-dienes, together with their characterisation.

The final chapter describes some apparently succesful preliminary results concerning attempts to ring-open polymerise indene.

ACKNOWLEDGEMENTS

The author is indebted to Dr. W.J. Feast for his continual help and encouragement during the supervision of this work and to Professor W.K.R. Musgrave for his advice and interest. Thanks are also due to Professor K.J. Ivin and co-workers (Queens' University Belfast) for recording ^{13}C n.m.r. spectra, to Dr. R.S. Matthews (this Department) for recording some of the ^{1}H n.m.r. and ^{19}F n.m.r. spectra and to Dr. J. McConville (Rubber and Plastics Research Association, Shawbury) for the G.P.C. molecular weight distribution analyses.

Assistance from various members of the technical staff is greatly appreciated, especially Mr. D. Hunter.

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MEMORANDUM

The work in this thesis was carried out in the Chemistry Laboratories of the University of Durham between October 1975 and September 1978. This work has not been submitted for any other degree and is the original work of the author except where acknowledged by references.

Part of this work has been the subject of a provisional patent taken out by the National Research and Development Corporation, 35211/78, 31st August (1978).

NOTE TO READER

The nomenclature of many of the compounds discussed in this work is cumbersome, an attempt has been made to simplify this by using large Roman numerals for the important monomers and polymers (I) to (XVI), whilst other compounds which are used or mentioned are designated by small arabic numerals (1) to (140). For the convenience of the reader there is a summary of the important monomers and polymers, and their respective names on the end papers at the back of this thesis.

For convenience the abbreviations of n.m.r. and i.r. spectroscopy have been used for nuclear magnetic resonance and infrared spectroscopy.

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EXPERIMENTAL

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EXPERIMENTAL

EXPERIMENTAL

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CHAPTER 1

ORIGINS AND OBJECTIVES OF THE WORK REPORTED IN THIS THESIS

1.1 The original question which initiated the research described in this thesis

The high performance elastomeric materials required by today's technology must show, thermal and oxidative stability at elevated temperatures, chemical inertness, good mechanical strength and retention of elastomeric behaviour at and below normal operating conditions.

Highly fluorinated polymers have been investigated and developed on account of their unusually high thermal and chemical stabilities,[1] which are attributed to the strength of the carbon-fluorine bond compared to that of the carbon-hydrogen bond and to the shielding of the carbon backbone by the fluorine atoms.[2]

The most successful materials currently used are the copolymers of fluorinated alkenes, especially the copolymers of vinylidene fluoride and hexafluoropropylene (Viton A) (1)[3,4] and the terpolymer of vinylidene fluoride, hexafluoropropylene and tetrafluoroethylene (Viton B) (2).[5,6] These materials, however, show poor low temperature behaviour not maintaining useful elastomeric properties much below 0°, and in common with other polymers containing both hydrogen and fluorine they evolve HF when they begin to degrade thermally.

In attempts to overcome these restrictions it has been found necessary to sacrifice one property in order to improve another. To increase the thermal stability of elastomers, perfluorinated materials containing no carbon-hydrogen bonds or other labile groups have been sought. The first examples were copolymers of perfluoroalkylene triazines and although they were extremely thermally stable (3),[7] their elastomeric behaviour and chemical stability were limited.

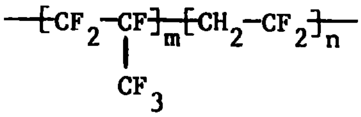
A very promising material was the copolymer of tetrafluoroethylene and perfluoro(methyl vinyl ether) (4), which is a soft, flexible elastomer at room temperature, retaining the high thermal and chemical stability characteristic of polytetrafluoroethylene, but its Tg of about -12° restricts its low temperature use as an elastomer.[8,9]

Research directed towards low temperature flexibility has involved investigations into copolymers of tetrafluoroethylene and perfluoroalkyl nitroso compounds (5),[10] which retain their elastomeric properties at low temperatures, are extremely solvent resistant and non-flammable, but unfortunately decompose at about 210° and are subject to attack by bases.

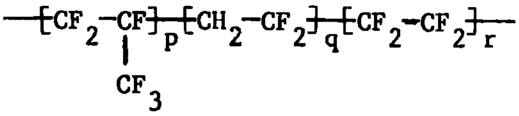
Several fluorine containing siloxanes, for example (6), have been studied and have proved to be solvent resistant elastomers retaining the low and high temperature flexibility of the siloxane backbone.[11,12] However, their usefulness is restricted, because of their limited hydrolytic stability.

Numerous other fluorinated polymers have been investigated for their elastomeric behaviour,[13] including, polyethers, polyketals, polyfluorals, polythiocarbonyls and polyesters, but for one reason or another none have so far found a useful commercial application.

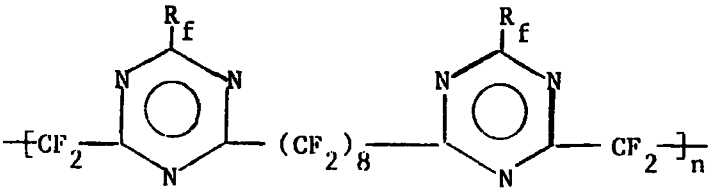
Work carried out in this department, proposed and financed by the Ministry of Defence through the Material's Department of the Royal Aircraft Establishment at Farnborough, involved in the synthesis of fluorinated polycarbonates[14] and polyethers,[15] and formed part of a programme aimed at the synthesis of new low-temperature, solvent resistant elastomers which would also be thermally stable. Although the synthetic work was arduous and sometimes experimentally difficult, several of the polymer structures proposed for investigation were realised. None of the new polymers prepared in this work showed a significant improvement in low temperature flexibility or high temperature stability when compared with available materials.



$$-\!\left[CF_2-\underset{\underset{\displaystyle CF_3}{|}}{CF}\right]_m\!\left[CH_2-CF_2\right]_n- \qquad (1)$$



$$-\!\left[CF_2-\underset{\underset{\displaystyle CF_3}{|}}{CF}\right]_p\!\left[CH_2-CF_2\right]_q\!\left[CF_2-CF_2\right]_r- \qquad (2)$$



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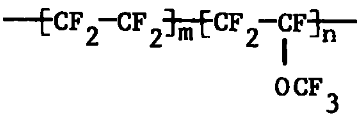
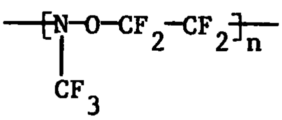
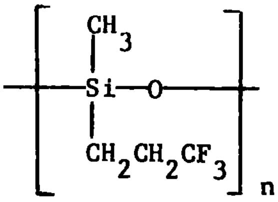


$$-\!\left[CF_2-CF_2\right]_m\!\left[CF_2-\underset{\underset{\displaystyle OCF_3}{|}}{CF}\right]_n- \qquad (4)$$

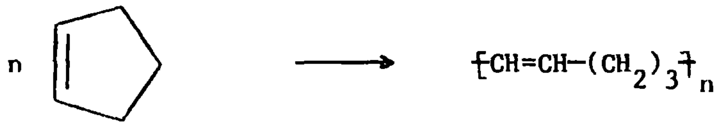


$$-\!\left[\underset{\underset{\displaystyle CF_3}{|}}{N}-O-CF_2-CF_2\right]_n- \qquad (5)$$



$$-\!\left[\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_2CH_2CF_3}{|}}{Si}}-O\right]_n- \qquad (6)$$

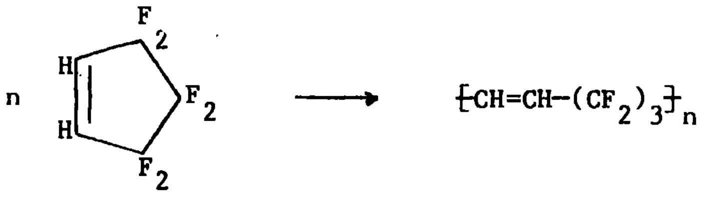
Of the materials described in this brief review none possesses an overall balance of properties required by today's technology, especially in the aerospace and related industries. Therefore, because of the lack of success and the inadequacies of the currently available elastomers it was considered to be worthwhile examining the possibility of making a fluorinated analogue of the well established,[16] scientifically[17,18] and commercially[19] important linear hydrocarbon elastomer poly(1-pentenylene) (8). This polymer is produced by the ring-opening polymerisation of cyclopentene (7), using olefin metathesis catalysts. The catalyst systems consist of a transition metal complex, in combination with an organometallic compound of Group III or IV, usually a trialkyl aluminium or alkyl aluminium chloride, and an oxygen containing activator.



(7) (8)

The backbone of poly(1-pentenylene) consists of methylene sequences and vinylene double bonds, giving it a high degree of flexibility and vulcanisability, and together with the high degree of stereo-regularity with which it can be prepared, it is an ideal substitute for natural rubber.[16]

The fluorinated analogue initially chosen for investigation was 1H,2H-hexafluorocyclopentene (9), because it was fairly readily available[20] and was considered to be the most highly fluorinated cyclopentene which was likely to undergo ring-opening polymerisation.



(9) (10)

It was hoped that the polymer that would be produced (10) would retain the elastomeric properties of the hydrocarbon polymer, to a substantial degree and that the partially fluorinated backbone would give it solvent resistance and thermal stability. An easy thermal decomposition route liberating hydrogen fluoride would be less likely than in other partially fluorinated polymers, because of the absence of such groups as $-CH_2-CF_2-$ and $-CHF-$.

1.2 Considerations and arguments supporting an investigation of the initial question

The ring-opening polymersiation of cycloalkenes is a special case of the more general olefin metathesis reaction,[21,22] which will be discussed in more detail in Chapter 2.

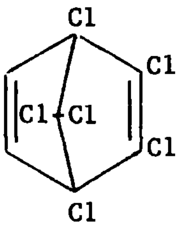
The catalysts used in the ring-opening polymerisation of cycloalkenes are closely related to the catalysts used in the classic Ziegler-Natta polymerisation of ethylene and propylene.[16] The use of the Ziegler-Natta type catalysts for the polymerisation of fluorinated acyclic alkenes was first reported by Sanesi and Caporiccio in 1962.[23] They claimed to have polymerised both tetrafluoroethylene and hexafluoropropylene using the binary catalyst system titanium tetraisopropylate and tri-isobutylaluminium in a chlorinated solvent, producing highly crystalline materials in low yields and of low molecular weight. It might be expected that such a potentially useful process would have been developed in industrial laboratories and the absence of evidence for such developments casts some doubt on the original observation.

In 1969 Overberger and Khattab[24] using the catalyst system vanadium pentachloride and tri-isobutylaluminium reported the homopolymerisation of partially fluorinated monomers, namely 4,4,4-trifluorobut-1-ene, 3-trifluoromethylbut-1-ene, 5,5,5-trifluoropent-1-ene and 4-trifluoromethylpent-1-ene. The trifluorobutenes were found to be reluctant to polymerise, giving low melting point polymers with a low fluorine content. While the polymers obtained from the trifluoropentenes were soluble in hexamethylenephosphoramide or perfluorokerosene, having moderately high intrinsic viscosities. The low reactivity of the trifluorobutenes was attributed to two possible causes:

(i) the inductive effect of the polar trifluoromethyl group decreases the electron density in the double bond of the fluoromonomers, therefore reducing the tendancy of these monomers to coordinate to the transition metal;

(ii) deactivation of the active catalytic sites by the fluorine substituents. The matter in which the fluorine substituents caused this deactivation was not dealt with in great detail.

The coordination of an alkene to a transition metal complex is considered to be a vital step in the mechanism of both the Ziegler-Natta polymerisation reaction[25] and the ring-opening polymerisation reaction.[26] At the beginning of this work, when the feasibility of the proposed research was under examination, it was known that cycloalkenes with a variety of substituents, but not fluorine, had been reported to undergo ring-opening polymerisation, producing linear polymers in high yields and of high molecular weight. The presence of a hydrocarbon substituent at the allylic position of the cycloalkene double bond e.g. 3-methylcyclopentene;[27] did not seem to affect the mode of polymerisation. Chlorine substituted cycloalkenes had also been found to undergo ring-opening polymersiation, Ofstead[28] had reported that highly chlorinated cycloalkenes (11) and (12)



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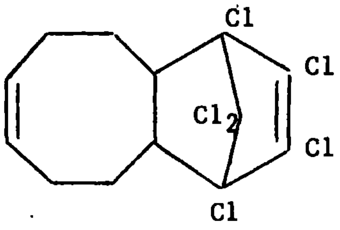
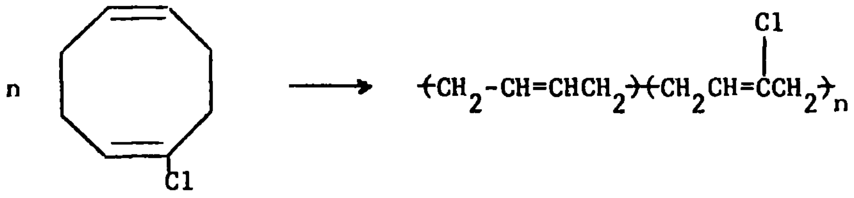


(12)

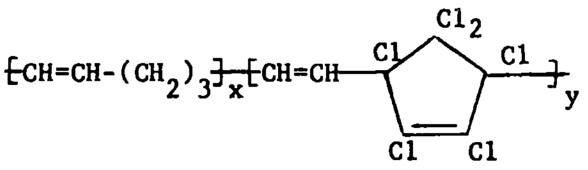
had been copolymerised with cyclopentene. The chlorine atoms do not act as catalyst deactivators unless the substitution is at the vinylic site; for example, 1-chlorocyclo-octa-1,5-diene (13) ring-opens only at the unsubstituted double-bond yielding a polymer which may be represented as a perfectly alternating copolymer of butadiene and chloropropene[29] (14),



$$\text{-(}CH_2\text{-}CH{=}CHCH_2\text{)(}CH_2CH{=}\overset{Cl}{C}CH_2\text{)}_n$$

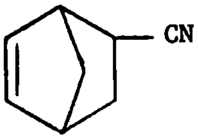
(13)   (14)

and the copolymer of (11) and (7) has the structure (15).



(15)

The ring-opening polymerisation of nitrile, ester, pyridyl and acid anhydride substituted derivatives of bicyclo[2.2.1]hept-2-enes (16) - (19), had been disclosed by Hepworth[30] and by Ueshima et al.[31,32]



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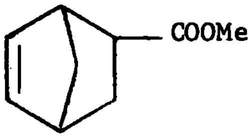

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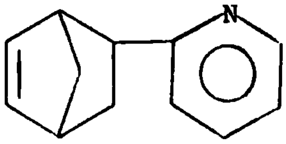

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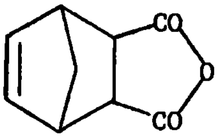


(19)

In expanding the scope of the substituents to fluorine, a limiting factor might be the possible poisoning effect of this substituent on the catalyst system. One possible objection to the proposed work was that abstraction of a fluoride ion from the fluorocycloalkene by an active site on the transition metal, would be thermodynamically favoured since it results in the formation of a stable metal-fluorine bond, such a process might well result in the poisoning of the catalyst system. However, transition metal fluoride complexes had previously been used as ring-open polymerisation catalysts; for example, using the system $WF_6/EtAlCl_2$, cyclopentene had been polymerised to poly(1-pentenylene)[33] with virtually 100% cis-double bonds and cis-cyclo-octene to poly(1-octenylene)[34] with 93% cis-double bonds. Therefore even if a transition metal fluoride complex was produced it need not necessarily result in catalyst poisoning and might be an active ring-opening polymerisation catalyst.

On the evidence available it was concluded that there was no reason why 1H,2H-hexafluorocyclopentene should not ring-open polymerise; although it was realised that there would be difficulties to overcome. There was no direct experience of the necessary techniques and methods needed in the area of olefin metathesis although advice was available within the department, since there was and is active research in the relevant fields of transition metal chemistry and organometallic chemistry.

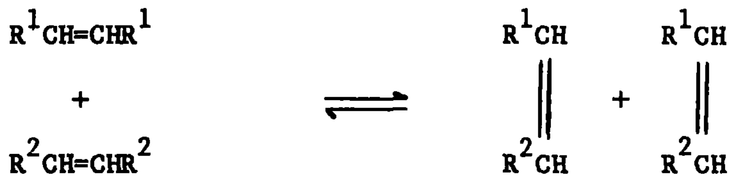
It was therefore decided to carry out the investigation for academic, practical and technological reasons and this thesis describes the attempted ring-opening polymerisation of 1H,2H-hexafluorocyclopentene and the work which subsequently developed from this initial attempt.

CHAPTER 2

OLEFIN METATHESIS

2.1 Historical background of olefin metathesis

Olefin metathesis is a bond reorganisation reaction in which the total number and type of chemical bonds remain unchanged during the transformation of the initial alkenes into equimolar amounts of two new alkenes as shown in Figure 2.1. These transformations are catalytically induced by the combination of the alkenes with a variety of catalysts, most commonly containing, tungsten, molybdenum or rhenium.



$$\begin{array}{c} R^1CH{=}CHR^1 \\ + \\ R^2CH{=}CHR^2 \end{array} \rightleftharpoons \begin{array}{c} R^1CH \\ \| \\ R^2CH \end{array} + \begin{array}{c} R^1CH \\ \| \\ R^2CH \end{array}$$

Figure 2.1

The first examples of the metathesis of linear alkenes were reported by Banks and Baily in 1964,[35] who named the reaction 'olefin disproportionation'. This opened the way for the development and study of a very important field of chemistry and over the years the range of substrate types has been increased to include; substituted alkenes, dienes, polyenes, alkynes and of great importance cycloalkenes. The latter ring-open polymerise, producing linear polymers known as polyalkenylenes. This type of polymerisation was not recognised as a special case of olefin metathesis until 1968,[21,22] however, the reaction itself had been known for several years. In fact the first citation of the metathesis reaction catalysed by a transition metal was the polymerisation of bicyclo[2.2.1]hept-2-ene by a mixture of titanium tetrachloride and either ethylmagnesium bromide or lithium tetrabutylaluminium recorded in 1955,[36] but it was not until 1960 that the polymer was shown to be a polyalkenylene.[37]

In 1959 Eleuterio[38] using a catalyst prepared from a supported molybdenum oxide on alumina, activated by hydrogen reduction and further reacted with lithium aluminium hydride was able to ring-open polymerise a variety of cycloalkenes including cyclopentene to form trans-poly(1-pentenylene) with a high degree of stereo-regular structure, but only in low yield.

The possibility of producing stereo-regular polymers from cycloalkenes was further demonstrated in 1963 by Natta et al;[39] by varying the catalyst and reaction conditions, cyclobutene was polymerised to predominantly or exclusively cis- or trans-poly(1-butenylene) as shown in Table 2.1. The following year Natta et al,[40] employing tungsten and molybdenum halides in combination with organoaluminium compounds as catalysts, ring-open polymerised cyclopentene under mild conditions and control of the double bond stereochemistry was again demonstrated.

Table 2.1

Cyclobutene polymers by transition metal catalysts[39]

Catalyst system	Polymer structure
$TiCl_4/Et_3Al$/n-heptane	Predominantly cis
$TiCl_4/R_3Al$/toluene	Predominantly trans
$MoCl_5/Et_3Al$/toluene	Predominantly cis
$RuCl_3/H_2O$	Mixed cis and trans
$RuCl_3$/EtOH	Trans

In 1967 Calderon et al,[21,41] using for the first time the term 'olefin metathesis' for the overall result of the reaction, showed that the metathesis of acyclic alkenes was possible in the presence of catalysts derived from tungsten hexachloride and an organoaluminium compound similar to those used by Natta for the ring-opening polymerisation of cycloalkenes. This was a significant contribution to the evolution of the metathesis concept, since it confirmed that olefin metathesis of acyclic alkenes and ring-opening polymerisation of cycloalkenes were special cases of an entirely new metal-catalysed reaction known generally as 'Olefin Metathesis'.

Within the last decade a great deal of intensive work in many branches of chemistry has been carried out on the metathesis reaction and significant advances in understanding the mechanism, developing the scope and the catalyst systems used in the reaction have been made and extensively reviewed.[16,17,18,26,41-50] However, many problems remain to be solved.

The scope and synthetic applications, the catalyst systems used and mechanistic aspects of the olefin metathesis reaction are dealt with in the following sections of this chapter.

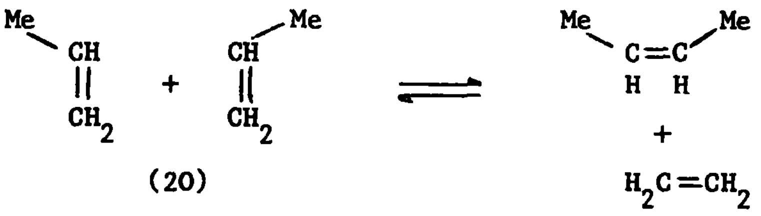
2.2 The scope and synthetic applications of the olefin metathesis reaction

The olefin metathesis reaction is a very versatile tool in synthetic organic chemistry. The various types of unsaturated hydrocarbons which undergo metathesis will be briefly reviewed, together with the more important applications of the reaction.

Applications include: improved utilisation of refinery streams; synthesis of high-octane fuel components; conversion of unwanted fractions of the molecular weight distribution of synthetic alkenes into usable materials; production of intermediates for flame retardants, stabilisers, perfumes, novel polymers and copolymers which may contain function groups; and degradation of polymers.[51]

2.2a Acyclic alkenes

The olefin metathesis of terminal and internal acyclic mono-alkenes has been reviewed in great detail.[42,44,45] The most widely studied example is the metathesis of propylene (20) to produce ethylene (21) and but-2-ene (22). This process was used industrially to produce polymerisation grade ethylene and high purity but-2-ene,[52] but for economic reasons this has been discontinued.



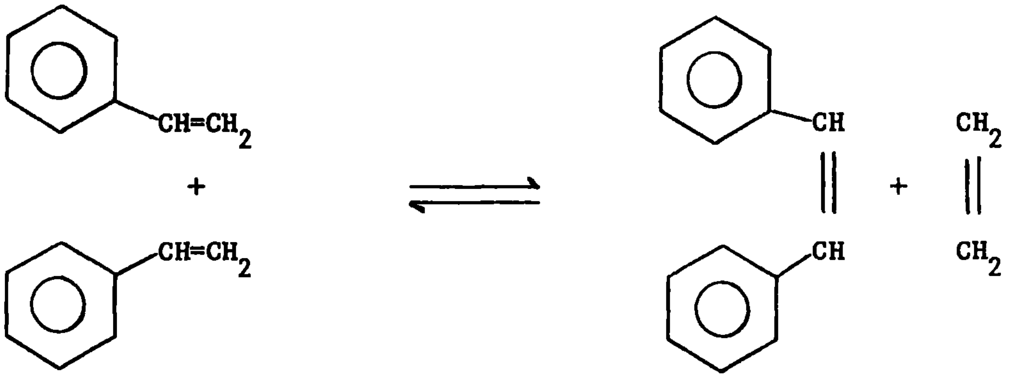
(20)

(22)

(21)

Acyclic alkenes can be used to degrade polymers which contain unsaturation by cross-metathesis, for example styrene-butadiene copolymer may be degraded using but-2-ene and from the degradation products information about the monomer sequence distribution in the copolymer may be obtained.[53]

Substitution of acyclic mono-alkenes with hydrocarbon groups such as cycloalkyl, cycloalkenyl or aryl groups does not seem to affect their ability to metathesis, for example styrene (23) is converted to ethylene and 1,2-diphenylethylene (24).[54] The rate of metathesis, however, is

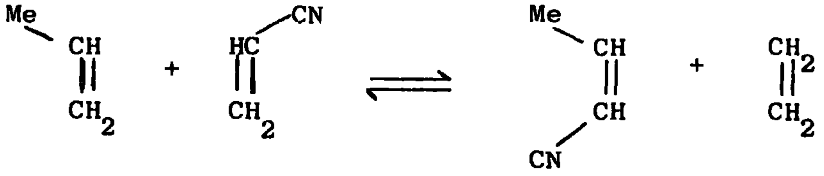


(23)

(24)

influenced by steric factors and Calderon[26] has shown that the effect of substitution on the ease of participation in the olefin metathesis reaction is $CH_2= \; > \; RCH_2CH= \; > \; R_2CHCH= \; > \; R_2C=$.

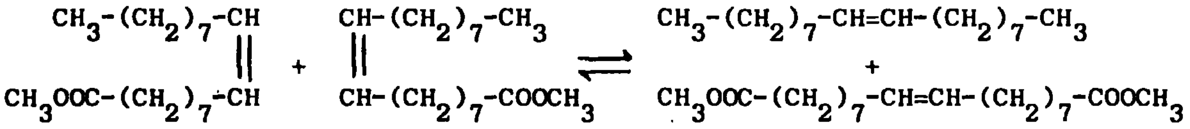
A few examples of acyclic mono-alkenes substituted with functional groups have been reported. Acrylonitrile (25) is claimed to react with propylene to produce crotonitrile (26) and ethylene.[55]



(25) (26)

Unsaturated esters have been found to undergo metathesis providing new synthetic routes in the field of fat chemistry, for example, the metathesis of methyl oleate (27) into octadec-9-ene (28) and octadec-9-enedioic dimethylester (29).[56]

(28)

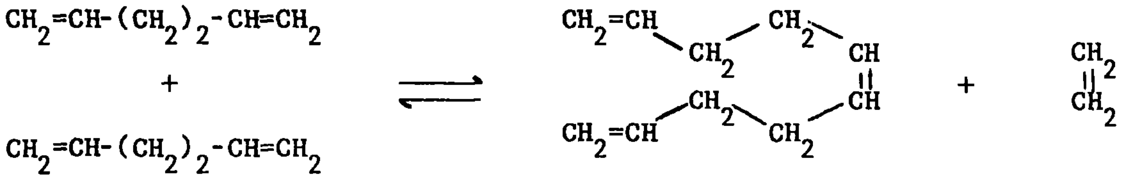


(27) (29)

Effective catalysts have been reported for the metathesis of alkenes having various functional groups such as -COOR, -OCOR, -OR, -CN, -COR and $-CONR_2$. It has been suggested that these reactions could be quite important in the synthesis of various perfumes, insect pheromones, base materials for cosmetics, natural higher carboxylic acids and alcohols.[57]

2.2b Acyclic polyalkenes

Acyclic α,ω-dienes and higher polyenes may undergo either inter- or intra-molecular reactions depending upon the relative stabilities of the ring and chain products, for example, hexa-1,5-diene (30) is converted into 1,5,9-decatriene (31) and ethylene via intermolecular metathesis,[58] whereas octa-1,7-diene (32) is converted via intra-molecular metathesis to cyclohexene (33) and ethylene.[58]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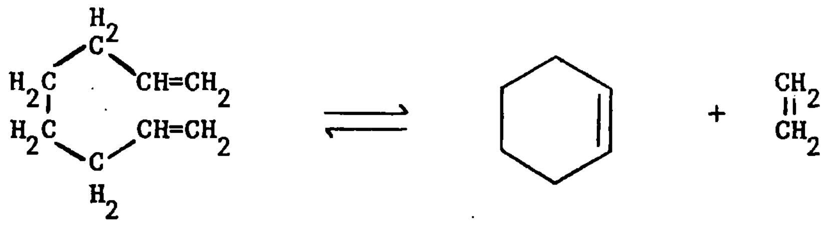

(32) (33)

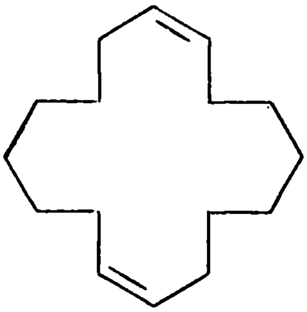
2.2c Cycloalkenes

The synthetic potential of the olefin metathesis reaction to polymer chemistry is enormous. The ring-opening polymerisation of cycloalkenes to linear polymers by metathesis provides an interesting class of polymers that differ from conventional polymers in that they maintain the unsaturation of the monomer, as described for cyclopentene in Chapter (1.1).[16]

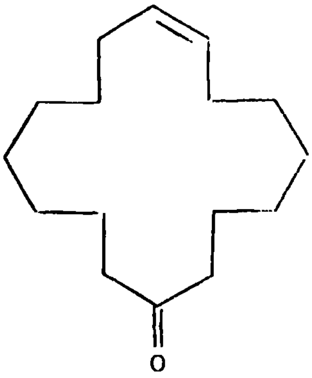
Mono-cyclic alkenes from C_4 to C_{12} with the exception of cyclohexene[16] undergo ring-opening polymerisation to produce polyalkenylenes and depending upon the structure of the repeat unit and the double bond configuration these polymers may possess properties ranging from amorphous elastomers to crystalline materials. By careful choice of the catalyst system employed and adjustment of the reaction conditions the double bonds of the polyalkenylenes can be exclusively or principally of the cis- or trans-geometry as illustrated in Table 2.1. Of particular industrial interest is poly(1-pentenylene), because of the availability of the monomer; cyclopentene; and the useful properties of the polymer.

Cis-poly(1-pentenylene)[23] and trans-poly(1-pentenylene)[16] are both elastomeric materials, the former having very good low temperature characteristics, which allows it to be competitive with the more expensive low temperature elastomers such as silicone rubber and the latter is a very good substitute for natural rubber, especially in the tyre industry, however, due to economic factors it is not being produced commercially at the present time.

The metathesis of cycloalkenes at high dilution produces macrocyclic compounds in high yields.[59] The possible mechanism of formation of these materials is discussed in greater detail later in this chapter. Two interesting materials have been prepared by this technique; namely, cyclohexadeca-1,9-diene (34), the cyclic dimer of cyclooct-1-ene, which when oxidised produced a ketone (35) with a musk-like odour,[60] and catenanes, the



(34)



(35)

interlinked ring systems which form part of the product from the metathesis of cyclododecene, Figure 2.2.[61,62]

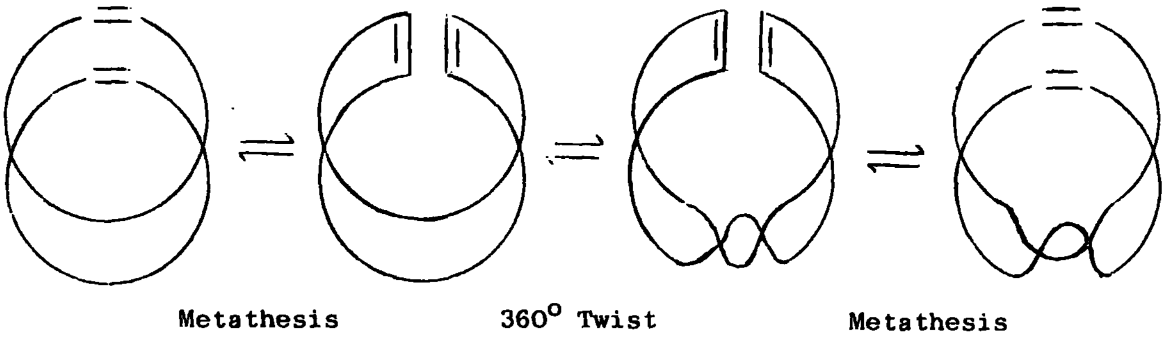
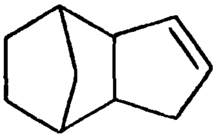


Figure 2.2

Polycyclic alkenes such as bicyclo[2.2.1]hept-2-ene and bicyclo[2.2.2]-oct-2-ene undergo metathesis, although there are exceptions, for example, the fused-ring cyclopentenes (36) and (37).[63] Of commercial importance are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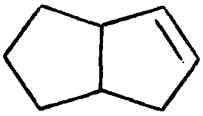
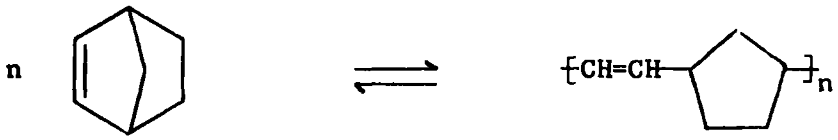
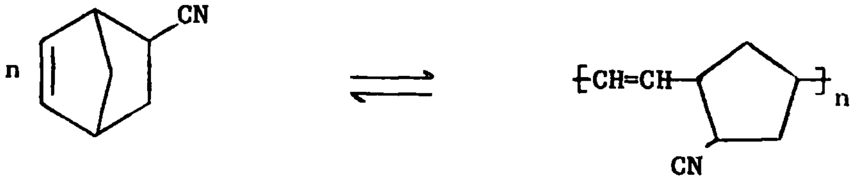

(37)

the speciality polymers produced from bicyclo[2.2.1]hept-2-ene and its substituted derivatives. The polymer produced from bicyclo[2.2.1]hept-2-ene (38), poly(1,3-cyclopentylenevinylene) (39), is the first polyalkenylene to



(38) (39)

be commercially exploited under the trade name Norsorex[64] and the polymer from 5-cyano-bicyclo[2.2.1]hept-2-ene (16), poly(4-cyano-1,3-cyclopentylene-vinylene) (40), is under market research as a thermoplastic resin.[65]



(16) (40)

Other substituted cycloalkenes which undergo ring-opening polymerisation were described in the previous Chapter (1.2).

The ring-opening polymerisation by metathesis does not only apply to unsaturated cyclichydrocarbons, but also to unsaturated heterocyclic compounds. Ast and co-workers[66] have ring-open polymerised several lactones, for example 7-hexadecen-16-olide (41) to produce an unsaturated polyester (42).

(41) (42)

2.2d Alkynes

The metathesis of linear alkynes such as 1-pentyne, 2-pentyne and 3-hexyne, with heterogeneous catalyst systems have been reported[67,68,69] and the reaction was found to be analogous to the metathesis of alkenes as shown below, Figure 2.3. Terminal alkynes cyclotrimerise to benzene derivatives, although small amounts of metathetic products are observed.[70]

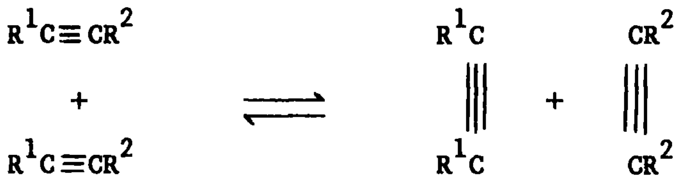


Figure 2.3

The conversion of cyclodecyne to a series of oligomers $(C_{10}H_{16})_n$, up to the hexamer (n=6) has been demonstrated[71] and phenylacetylenes have been readily polymerised by tungsten hexachloride and molybdenum pentachloride to produce polymers[72] which may have interesting electrical properties.[73]

2.3 Olefin metathesis catalyst systems

The olefin metathesis of acyclic alkenes and the ring-opening polymerisation of cycloalkenes, although governed by a common mechanism, differ in many chemical, kinetic and thermodynamic aspects. Consequently different efficiencies, operating conditions, and applicabilities are found for the various catalysts.

A wide range of catalyst systems have been claimed to be active towards metathesis, they may be divided into two categories:

(i) Heterogeneous catalysts which usually acquire metathesis activity only at high temperatures (100° to 400°) are useful in a continuous flow type of process and are employed for the metathesis of acyclic alkenes.

(ii) Homogeneous catalysts which bring about reactions under mild conditions and are applicable to both the metathesis of acyclic alkenes and cycloalkenes.

For both homogeneous and heterogeneous catalyst systems the greatest activity towards metathesis is found from catalysts derived from molybdenum, tungsten and rhenium.

2.3a Heterogeneous catalysts

Solid heterogeneous catalysts for the metathesis reaction normally comprise of a high surface area refractory support, such as alumina or silica on which is deposited a transition metal promotor which can be an oxide, carbonyl or sulphide as shown in Table 2.2. The catalysts derived from the oxides of Mo, W and Re show greatest activity,[35] while the rest are usually less active.

Table 2.2

Heterogeneous catalysts for olefin metathesis

Oxides	Sulphides	Carbonyls
Mo W Re V Sn Te Nb Ta La Ru Os Ir Rh Sr Ba	Mo W	Mo W Re

Heterogeneous catalysts can be prepared in a number of ways, for example, dry mixing of the individual components, coprecipitation, or impregnation of the support with substances which decompose at high temperatures to leave the active promoter.

Due to side reactions such as isomerisation, dimerisation, oligomerisation and polymerisation the selectivity of these metathesis processes is usually less than 100%. However, side reactions can be minimised by the addition of small amounts of either alkali and alkaline earth metal ions,[74,75] or copper and silver[76] prior to the activation of the catalyst. Enhancement of the catalyst activity may be achieved by numerous methods, including, treatment of the support prior to the impregnation of the promoter with strong acid[77] and treatment of the alkene feed with chelating agents[78] and hydrogen.[79] Recently heterogeneous catalysts based on rhenium oxide/alumina[80] have been gaining popularity because of their high activity at relatively low temperatures, high selectivity and resistance to catalyst poisons. More detailed examinations of the composition, preparation, activation and regeneration procedures, poisons and catalytic modifications have been given by Bailey[42] and Banks.[45]

2.3b Homogeneous catalysts

Homogeneous catalyst systems usually consist of two components. A transition metal compound of tungsten, molybdenum, rhenium or tantalum, preferably a halide, or oxyhalide, or an organo-alkene, or carbene complex. All these compounds being particularly effective towards the metathesis of both acyclic alkenes and cycloalkenes. Tungsten compounds themselves yielding the most efficient catalysts for the ring-opening polymerisation of cycloalkenes. The second component is an organometallic compound of a metal from Group I to IV (usually referred to as the cocatalysts). Of special importance are aluminium alkyls, alkyl aluminium halides, Grignard reagents, lithium alkyls, tin alkyls, lithium aluminium hydride and sodium borohydride.

With some two component catalyst systems there are drawbacks, especially in the ring-opening polymerisation of cycloalkenes, such as poor reproducibility of results, instability and insolubility of the catalyst system and low polymer conversion. To overcome these difficulties a third component known as an activator is often added. This activator generally contains an oxygen-oxygen or an oxygen-hydrogen bond, for example, alcohols, organic acids, peroxides, water and molecular oxygen. Activation by such compounds is generally most effective if the amount of activator and transition metal are stoichiometrically equivalent, and if reaction with the transition metal occurs prior to the addition of the alkene or organometallic cocatalyst. The main advantage of such systems over the two component catalysts are, good reproducibility of results, increased stability and solubility of the catalyst in the reaction medium, very low catalyst consumption and reduced side reactions of the Friedel-Crafts type.

Olefin metathesis by homogeneous catalysts are conducted in the liquid phase either neat or in the presence of a solvent. Frequently the catalyst components are soluble in the monomer-solvent medium or become soluble after reaction with the monomer, or with another catalyst component. However, not all catalyst systems maintain their solubility after formation and subsequent reaction. Therefore the term 'homogeneous' catalyst does not strictly apply to all the systems. The designation of some catalysts as homogeneous has recently been brought into question by Muetterties and Busch.[81] However, in this thesis in accord with common practice 'homogeneous catalysts' will mean those normally taken as homogeneous in the reviews by Dall'Asta[16] and Hughes.[45]

Since the number of homogeneous catalyst combinations are endless, the choice of the best catalyst system for the metathesis of a particular alkene is virtually impossible and requires careful scanning of the literature.

Detailed information about some of the systems for the metathesis of acyclic alkenes and cyclic alkenes is given by Hughes[45] and Dall'Asta[16] respectively.

The roles of the various catalyst components can only be tentatively assigned. This applies particularly to the oxygen containing activators which will be discussed later in this Chapter (2.4), in light of the presently accepted mechanism. The organometallic cocatalysts play a major role in providing vacant coordination sites on the transition metal for the incoming alkene ligands and a pathway for subsequent reactions to proceed. This may occur by the organometallic compound acting as a complexing agent with either the alkene or the transition metal complex. The insertion of alkenes into aluminium-halogen bonds to form aluminium haloalkyls and subsequent reaction with the transition metal,[48] or the formation of briding species between the cocatalyst and the transition metal, which are well established bonding modes in aluminium and lithium compounds[82] or an acid-base equilibria of the type shown below, Figure 2.4, are all possible modes of reaction by which the cocatalyst may be acting in order to promote the metathesis reaction.

$$\mathrm{WCl_x} + \mathrm{AlCl_3} \rightleftharpoons \left[\mathrm{WCl_{x-1}}\right]^+\left[\mathrm{AlCl_4}\right]^-$$

Figure 2.4

A number of other systems promote the metathesis of acyclic alkenes and cycloalkenes, but for various reasons are not at present commercially viable. Homogeneous catalysts from Group VIII transition metals are interesting in that they are effective in protic media such as water and alcohol and are used simply as the halide without a cocatalyst, however, the addition of trifluoroacetic acid has been found to be beneficial. The preferred metals are ruthenium, osmium and iridium, but due to the high cost of these metals interest in such catalyst systems is limited.

In recent years photochemically activated catalysts have been reported for the metathesis of acyclic alkenes and the ring-opening polymerisation of cycloalkenes, using $W(CO)_6$,[85] WCl_6[86] and $TiCl_4$.[87]

2.4 The mechanism of olefin metathesis

The complete mechanistic scheme involved in olefin metathesis is not fully understood at the present time and numerous schemes have been put forward in the past.

There are two possible reaction pathways which would lead to the observed reaction products:-

(i) a transalkylation scheme, Figure 2.5, which involves cleavage of a carbon-carbon single bond adjacent to the double bond,

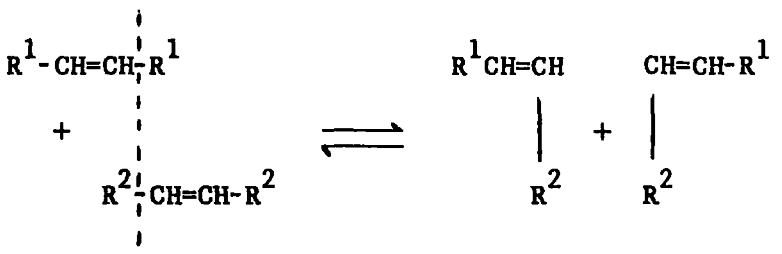


Figure 2.5

(ii) a transalkylidenation scheme, Figure 2.6, which involves the cleavage of the double bond itself as a means of alkylidene moiety exchange.

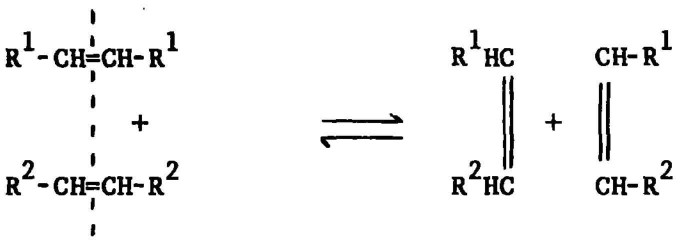
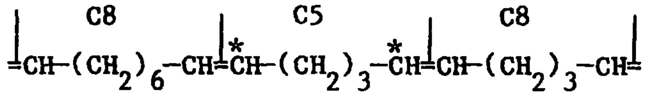


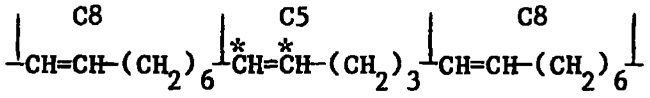
Figure 2.6

Results from ^{14}C isotopic labelling[88,89] and deuterium labelling experiments[21c,41] are completely consistent with a transalkylidenation scheme and excludes a transalkylation reaction. Dall'Asta and Motroni[90,91] have provided direct experimental evidence that in the ring-opening polymerisation of cycloalkenes the cleavage occurs at the double bond. By copolymerising cyclooctene and cyclopentene, in which the cyclopentene double-bond was labelled with ^{14}C, the resulting polymeric units may be (43) or (44) depending on whether cleavage takes place at the double bond or at the carbon-carbon single bond adjacent to the double bond.



$$\Big| \overset{C8}{=CH-(CH_2)_6-CH=} \Big| \overset{C5}{\overset{*}{C}H-(CH_2)_3-\overset{*}{C}H=} \Big| \overset{C8}{CH-(CH_2)_3-CH=} \Big|$$

(43)



$$\Big| \overset{C8}{-CH=CH-(CH_2)_6-} \Big| \overset{C5}{\overset{*}{C}H=\overset{*}{C}H-(CH_2)_3-} \Big| \overset{C8}{CH=CH-(CH_2)_6-} \Big|$$

(44)

[* denotes ^{14}C labelling]

Ozonolysis of the copolymer followed by reductive cleavage and radiochemical analysis of the resulting diols, showed that all the radioactivity was contained in the 1,5-diol, proving that ring-opening polymerisation had proceeded via cleavage of the double bonds.

2.4a Development of the mechanism

1 Quasi-cyclobutane intermediate

In 1967 Bradshaw et al[74] interpreted the olefin metathesis of acyclic alkenes as the coordination of two alkene double bonds to the transition metal complex, the simultaneous cleavage of the double bonds and the rearrangement via a 'quasi-cyclobutane' intermediate as depicted in Figure 2.7.

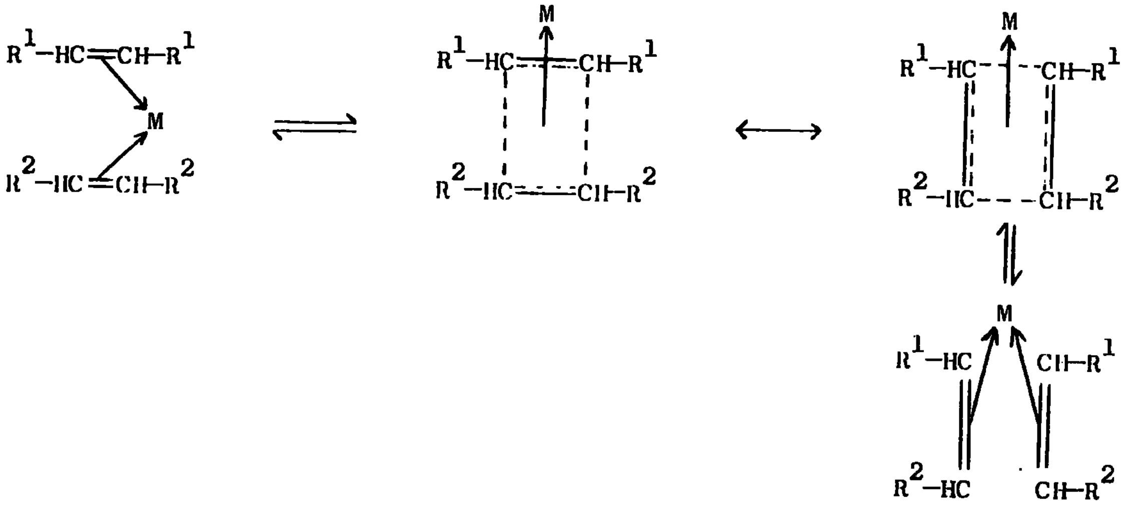


Figure 2.7

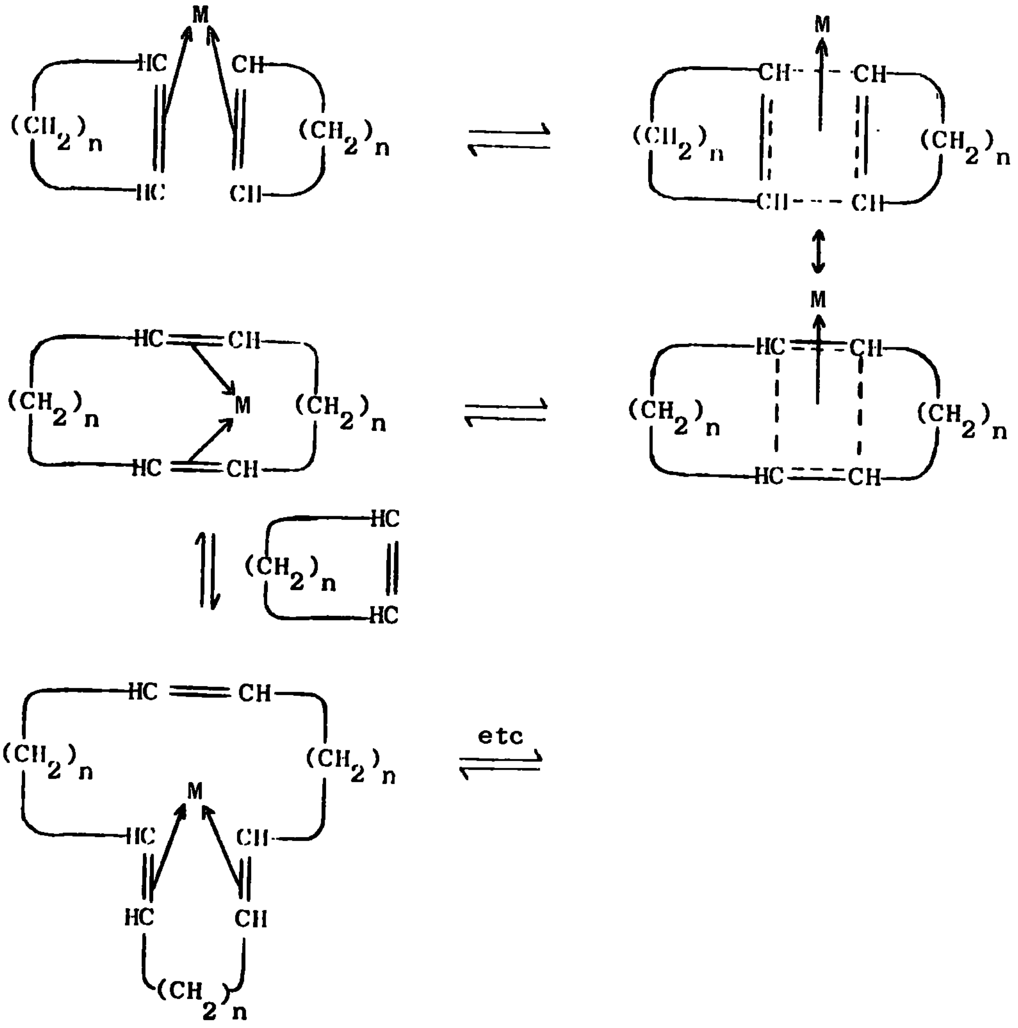


Figure 2.8

Calderon[21b] postulated an analogous reaction scheme for the ring-opening polymerisation of cycloalkenes involving a quasi-cyclobutane intermediate and the formation of macrocyclic species, Figure 2.8. The interaction of these growing macrocycles with an acyclic alkene, present as an impurity in the reaction causing cleavage of the macrocycle, was proposed as one of the modes by which linear polyalkenylenes were produced.[92] Alternatively chain termination of a coordinated growing polymer macrocycle would be due to migration of the coordinated double-bond, accompanied by decomplexation, thus giving rise to an acyclic macromolecule having two vinyl end groups, Figure 2.9.[93]

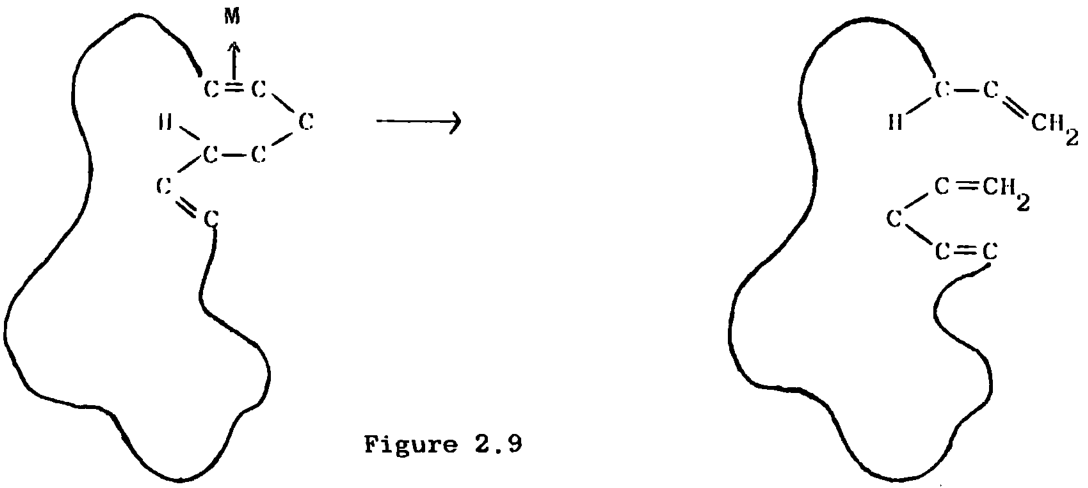
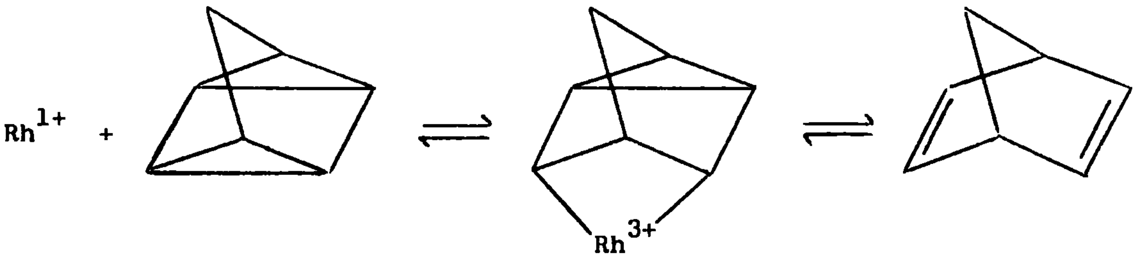


Figure 2.9

If the reaction scheme in Figure 2.7 is a concerted one, the formation of the quasi-cyclobutane transition state and its transformation into a bis-alkene-metal complex should be viewed as a cycloaddition reaction, hence the principles of orbital symmetry conservation of Woodward-Hoffmann must be considered.[94]

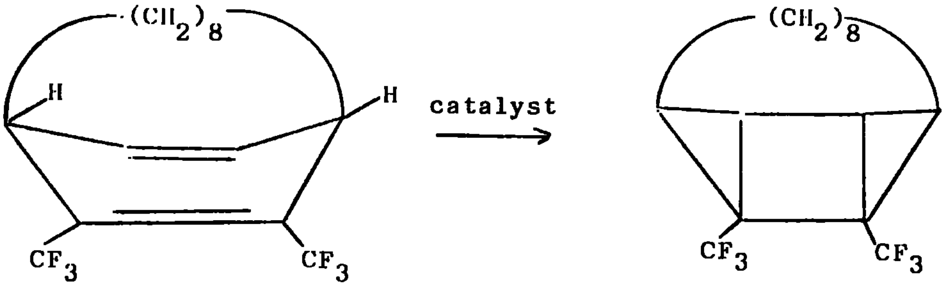
The concerted $[\pi2_s + \pi2_s]$ bond fusion of two alkenes is a symmetry forbidden process. However, Mango[95] stated that transition elements having atomic orbitals of the correct symmetry and an available electron pair can conceivably switch a symmetry forbidden cycloaddition into a symmetry allowed transformation and quoted the valence isomerisation of quadricyclene (45) to bicyclo[2.2.1]hepta-2,5-diene (46)[96] in the presence of the catalyst $Rh_2(CO)_4Cl_2$ as an example of a forbidden-to-allowed process. However, it



(45) (48) (46)

now appears that this reaction is a stepwise process involving the opening of only one σ-bond via an oxidative addition to Rh^{1+} forming the Rh^{3+} metallocycle intermediate (48), which rearranges to the corresponding dialkene (46).[97] A similar process has been demonstrated for the valence isomerisation of cubane to syn-tricyclooctadiene by Rh^{1+} catalyst systems[98] and other cycloaddition processes.[99]

If quasi-cyclobutane species were the intermediates in the mechanism of olefin metathesis then since one molecule of cyclobutane has almost the same free energy of formation as two molecules of ethylene, cyclobutanes should be present as side products and undergo reaction with metathesis catalysts. Although substrates with appropriately chosen non-conjugated diene (49) and cyclobutanes (50) and (51) are converted in the presence of a typical metathesis catalysts into the corresponding cyclobutane (52) and non-conjugated dienes (53) and (54),[100] cyclobutanes are not formed from simple alkenes. It will be demonstrated later, Chapter 5.5, that the non-conjugated diene (53) readily undergoes ring-opening polymerisation.



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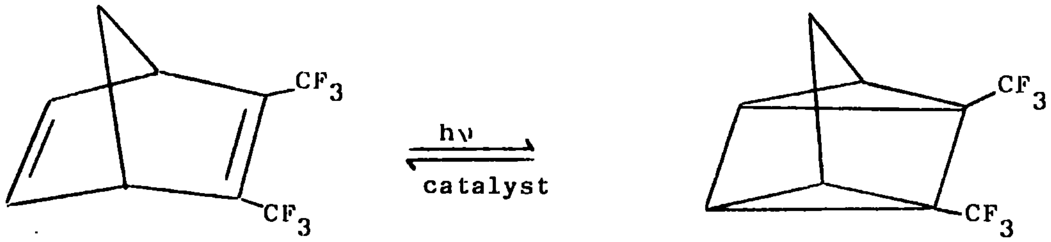
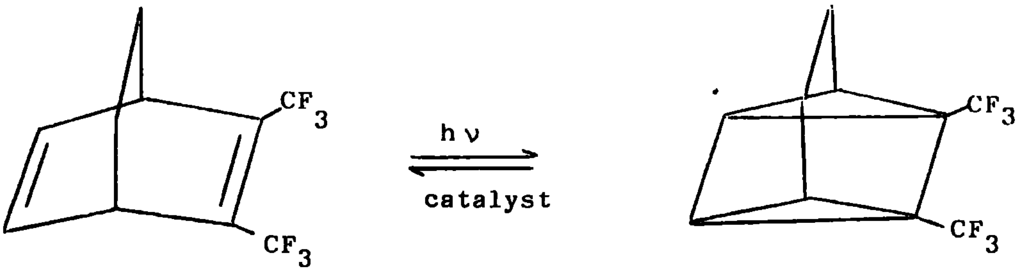


(53) (50)



(54) (51)

2 Tetramethylene transition state

To account for the absence of cyclobutanes in the metathesis reaction an alternative transition state to that of the quasi-cyclobutane complex was proposed by Lewandos and Pettit,[101] which involved the alkene molecules reacting with the metal to form a bis-alkene-π-complex which reorganises to a multi-centred organometallic system, Figure 2.10. The bonding in this transition state is most conveniently described as resulting from the interaction of a basic set of metal atomic orbitals and four methylenic units and involves the donation of four electrons from the filled ligand orbitals to empty metal orbitals, and back donation of four electrons from filled metal orbitals to empty ligand orbitals.

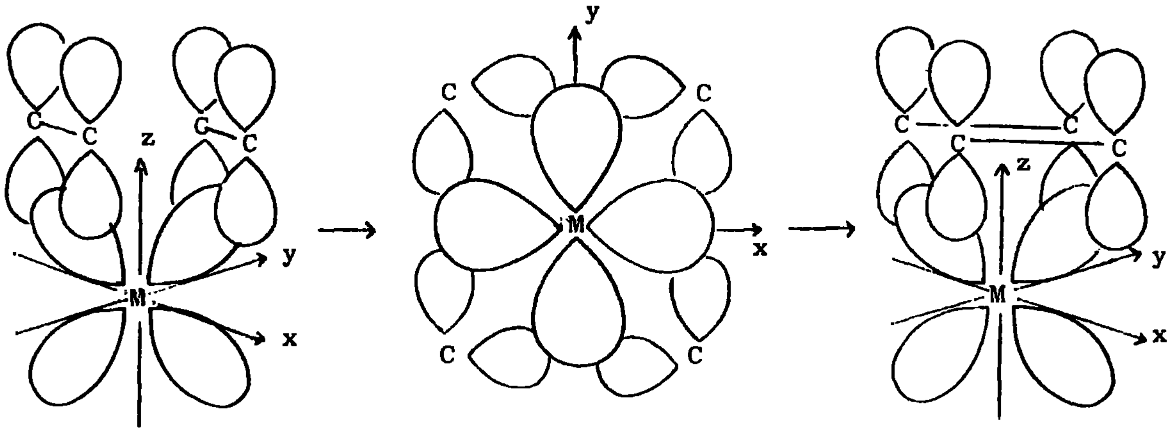


Figure 2.10

The difference between the quasi-cyclobutane intermediate and the tetramethylene complex does not seem to be fundamental, because the symmetry of the two intermediates is the same. However, in the former case the initial carbon-carbon sigma bonds of the molecules remained unaffected and the π-bonds are transformed into the new sigma bonds effecting cyclisation. In the case presented by Lewandos and Pettit, the carbon-carbon sigma bonds of the initial alkene are ruptured concurrently with the π-bonds, so that the cyclobutane molecule is never realised.

3 Metallocyclopentane transition state

The main assumption of the mechanisms considered so far is that the olefin metathesis is a concerted process. A number of schemes have been proposed in which the mechanism is not concerted.

As stated previously the rhodium catalysed rearrangement of strained carbocyclic ring systems involves a carbon-metal σ-bonded intermediate as shown in (48). Grubbs and Brunck[102] proposed that a carbon-metal σ-bonded species was a possible intermediate in the tungsten-catalysed olefin metathesis. They formulated a mechanism for the reaction based on the intermediates demonstrated by Katz and Eaton (48) as follows:

(i) a rearrangement of the complexed alkenes to a metallocyclopentane intermediate followed by -

(ii) a rearrangement of the metallocycle and -

(iii) the rearrangement of this new intermediate into the new complexed alkenes, Figure 2.11.

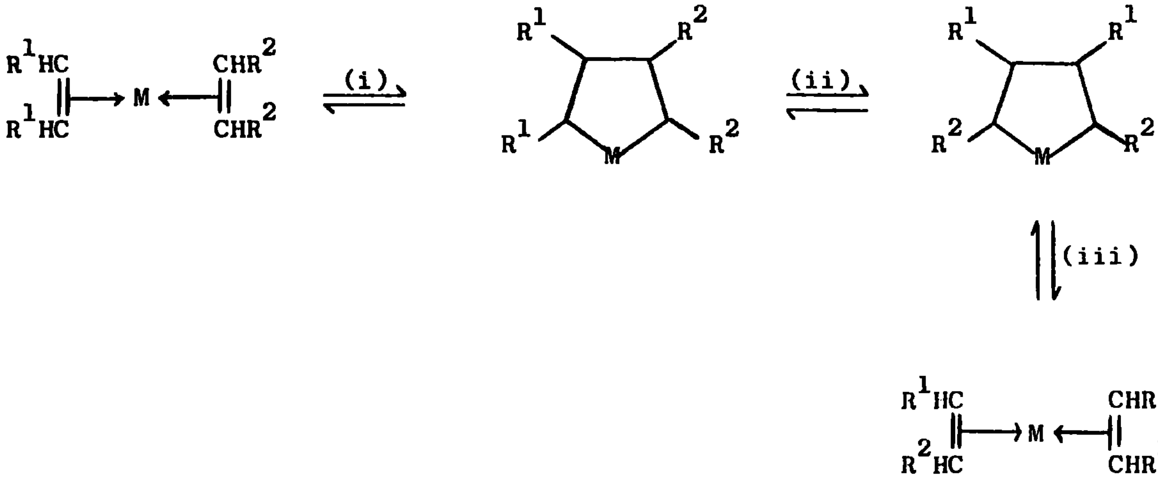


Figure 2.11

Grubbs and Brunck based their proposals mainly on the observation that when an ether solution of tungsten hexachloride reacted with 1,4-dilithiobutane a rapid evolution of ethylene was observed, the scheme they postulated is shown in Figure 2.12. Using deuterium labelling the

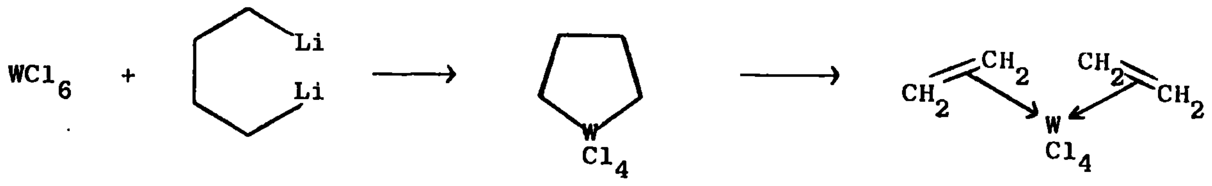


Figure 2.12

ethylene mixtures produced from 1,4-dilithio-1,3-dideuteriobutane and tungsten hexachloride contained CH_2=CHD, CHD=CHD and CH_2=CH_2, which suggests that a rearrangement had taken place. Grubbs et al[103] suggested the transformations represented in Figure 2.13 involving a carbene-metallocycle route and Figure 2.14 a concerted route.

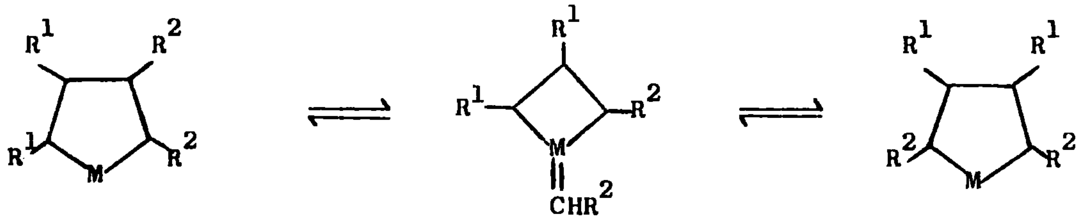


Figure 2.13

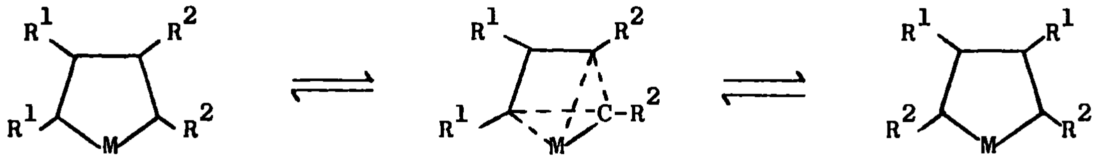
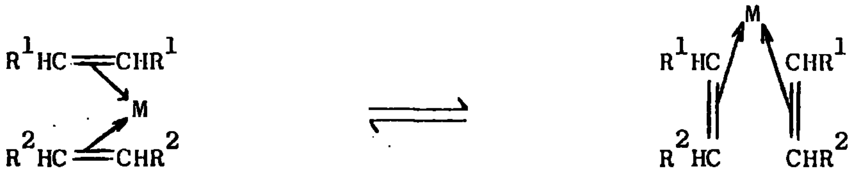


Figure 2.14

These speculations have not been substantiated by experimental evidence, although metallocyclic complexes of platinum and iridium have been prepared and characterised[104] they have not been reported to be active as olefin metathesis catalysts.

4 Metallocyclobutane and metal-carbene intermediates

The mechanisms so far described have all involved a pairwise scrambling that required an initial bis-alkene-metal entity (55) bearing two alkene ligands about a central metal atom, transforming into the corresponding product complex (56), via either a quasi-cyclobutane transition state, tetramethylene-



(55) (56)

metal complex or a metallocyclopentane intermediate.

There now seems a growing amount of experimental evidence which suggests a non-pairwise scrambling which may involve metal-carbene and metallocyclobutane intermediates as shown in Figure 2.15. Calderon, Judy and Ofstead[105] have comprehensively reviewed this evidence and discussed the

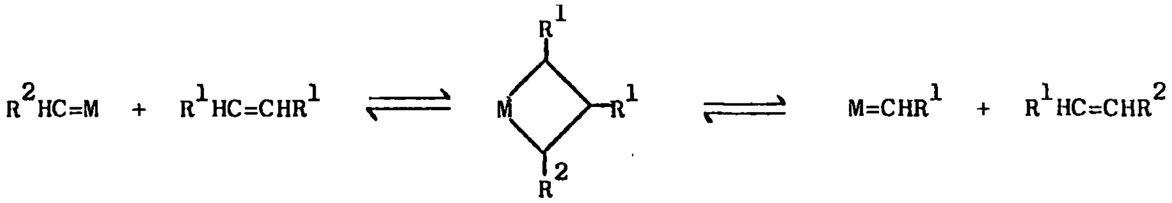


Figure 2.15

relative merits of the pairwise and non-pairwise mechanisms.

The non-pairwise mechanism involving metal-carbenes was initially proposed by Herisson and Chauvin in 1970,[106] but was overlooked until recently. This scheme more satisfactorily accounts for the facts than did the mechanisms proposed by earlier workers. Thus, the absence of cyclobutanes as side products of the reaction and the failure of cyclobutane to enter the reaction, both of which should be expected if quasi-cyclobutane intermediates were involved in the mechanism is readily accounted for.

Also, it explains more satisfactorily the metathesis of acetylenes, Figure 2.16, involving carbynes and metallocyclobutadienes.[107] The formation of linear high molecular weight polyalkenylenes in the metathesis of cycloalkenes is adequately understood in terms of chain end growth, Figure 2.17,[106]

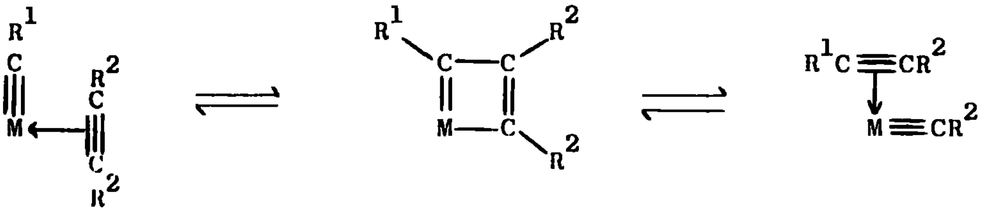


Figure 2.16

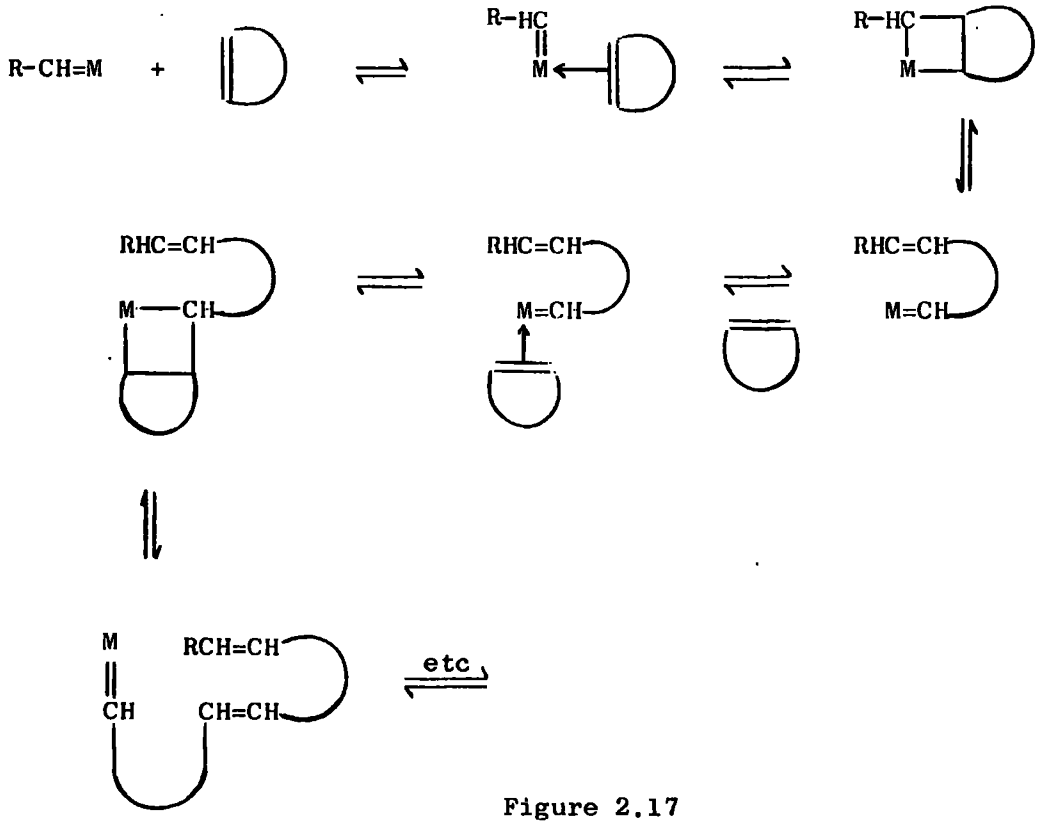


Figure 2.17

without the necessity of involving a macrocyclisation pathway and subsequent reaction with acyclic alkenes to produce linear polymers. The macrocyclic oligomers sometimes observed, being formed by intramolecular 'back-biting' of the growing polymer chain with any internal double bond on the same chain as exemplified in Figure 2.18.[105]

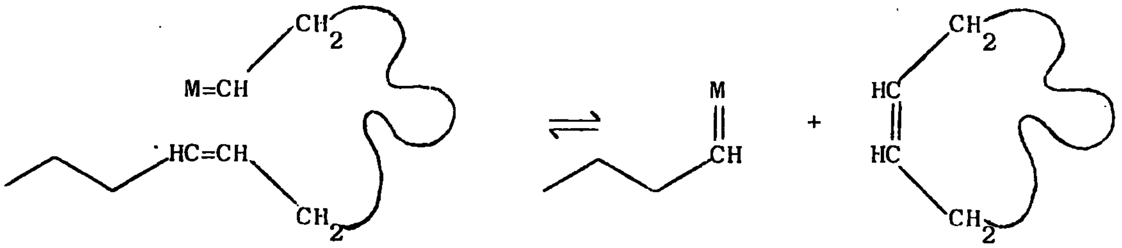
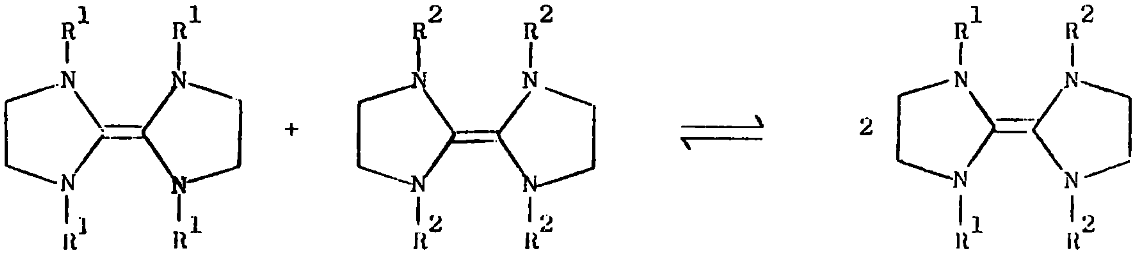


Figure 2.18

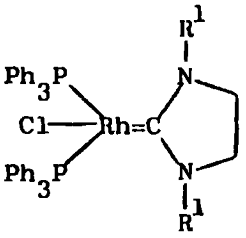
2.4b Evidence for metal-carbene and metallocyclobutane involvement

The involvement of a metal-carbene in the metathesis reaction receives some support from experimental evidence. Cardin et al[108] demonstrated that the metathesis of electron rich unsaturated amines with a rhodium phosphate catalyst involved carbene intermediates, Figure 2.19, as a side product, a rhodium(I) complex with one half of the electron-rich alkene was isolated, from which structure (57) was proposed. The analogous compound with R^2 instead of R^1 has also been found.



$R^1 = C_6H_5$; $R^2 = p\text{-}CH_3C_6H_4$

Figure 2.19



(57)

The decomposition of diazo-compounds with some transition metal complexes is known to be a common method of carbene generation. Dolgoplosk et al[109] have shown that the decomposition of phenyldiazomethane, under the influence of tungsten and molybdenum chlorides in the presence of cycloalkenes initiates ring-opening polymerisation producing polyalkenylenes of extremely high molecular weight. The mechanism they proposed for chain propogation resulting in the formation of linear macromolecules was an abbreviated version of Figure 2.17 and is depicted in Figure 2.20.

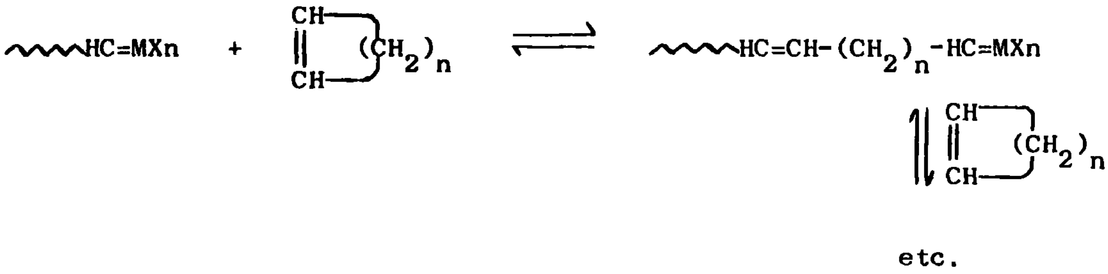


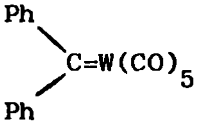
Figure 2.20

There are several kinetic studies of the metathesis of model compounds the results of which can only be explained by the metal-carbene chain mechanism.[17] Grubbs et al[110] carried out the metathesis of a mixture of [1,1,8,8-D_4]-octa-1,7-diene and octa-1,7-diene using three different catalyst systems, producing ethylene and cyclohexene. The pairwise mechanism was not able to account for the observed ratios of [D_4]-, [D_2]- and [D_0]-ethylene, which agreed well with the statistical distribution required by the metal-carbene chain mechanism.

A similar deuterium labelling metathesis experiment was reported by Katz and Rothchild[111] using equal amounts of $[D_4]$2,2'-divinylbiphenyl and 2,2'-divinylbiphenyl to produce phenanthrene and ethylene. Again the mixture of $[D_4]$-, $[D_2]$- and $[D_0]$-ethylene was only compatible with the metal-carbene mechanism.

A kinetic study for the metathesis of cyclooctene with a mixture of but-2-ene and oct-4-ene was reported by Katz and McGinnis.[107] For a pairwise mechanism involving the formation of a four-centred transition state which is the rate-determining step, the ratios of C_{14} : C_{12} and C_{14} : C_{16} dienes should initially be zero, whereas in the carbene chain mechanism the major initial product is predicted to be the C_{14} diene; this was the result obtained.

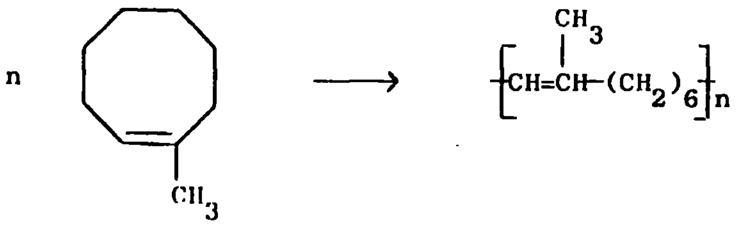
The synthesis and metathesis reactivity of diphenyl carbene pentacarbonyl tungsten (58)[112,113] was perhaps one of the major contributions of



$Ph_2C{=}W(CO)_5$

(58)

experimental evidence in support of the non-pairwise mechanism. Until its preparation[112] it was believed that metal-carbene complexes required an electron donor heteroatom directly attached to the $C_{carbene}$. This material has been widely used as an active metathesis catalyst, for example, the ring-opening polymerisation of 1-methyl-trans-cyclooctene (59)[114] to produce the regular polymer (60). The presence in the u.v. spectrum of the polymer of an absorption at the point where 1,1-diphenyl-1-propene exhibits its u.v. absorption maximum suggests 1,1-diphenylethylene end groups, there being approximately one diphenylethylene per seventy methylcyclooctene residues. This is further evidence that in the olefin metathesis reaction the chain carriers are metal-carbene entities.


(59) (60)

Although the evidence in support of the involvement of a metal-carbene entity in the mechanism of olefin metathesis is substantial there are still a number of areas of the mechanism which remain unresolved.

2.4c Unsolved problems in the mechanism of olefin metathesis

1 Formation of the metal-carbene species

Since many different catalyst systems, whether uni- or multi-component, heterogeneous or homogeneous, catalyse the olefin metathesis reaction, the exact mode of formation of the initial metal-carbene entity is very difficult to determine. For this purpose it is convenient to classify metathesis catalysts into three major categories.

(i) Complexes possessing stable carbenes e.g. $Ph_2C{=}W(CO)_5$.

(ii) Complexes activated by organometallic cocatalysts, e.g. $RAlCl_2/WCl_6$, R_4Sn/WCl_6.

(iii) Complexes void of organometallic cocatalysts e.g. classical heterogeneous catalysts MoO_3/Al_2O_3, $WCl_6/AlCl_3$ and photoactivated W^0 and W^{VI} catalysts.

In category (i) there is no problem as to how the initiating carbene species arises. Explanations have been put forward for the formation of the metal-carbene species described in category (ii) and a great deal of experimental evidence has been reported to support these explanations.

Muetterties[81,115] observed that in the reaction of WCl_6 with metal alkyls a significant evolution of alkanes occurred and especially instructive was the reaction of dimethylzinc and WCl_6 in benzene. Methane was produced, which contained no deuterium when the reaction was allowed to proceed in a deuterated solvent medium. Two plausible rationalisations were proposed to account for these observations, Figure 2.21 and Figure 2.22.

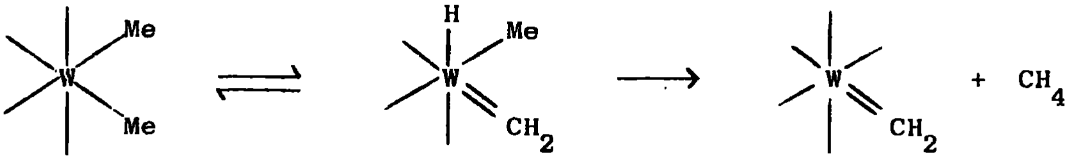


Figure 2.21

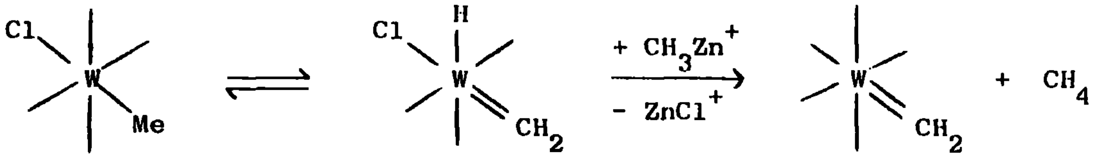


Figure 2.22

Similar schemes can be written for organo-aluminium compounds such as R_3Al, R_2AlCl and $RAlCl_2$. The formation of the metal-carbene entities are proposed to occur via α-hydrogen elimination from a tungsten-alkyl group. This is supported by work by Schrock[116] on the preparation and reactions of carbene-tantalum compounds, for example, $CH_2{=}Ta(C_5H_5)_2CH_3$. He has shown that an alkyl ligand's α-hydrogen atoms are in some instances quite acidic and can be removed by base.

Muetterties suggested that a simple WCl_xCH_3 complex forming the initial metal-carbene is probably unlikely and suggested that the alkylating agents interact with the tungsten complex intermediates through halogen, alkyl and carbene bridges. Three-centre two electron bonds between the tungsten, carbon and the second metal could be formed, these are well established bonding modes in lithium and aluminium compounds.[82]

The scheme put forward by Muetterties for the formation of a coordinated metal-carbene is not valid in the case of the catalyst system $Re(CO)_5Cl/C_2H_5AlCl_2$ reacting with octa-1,7-diene, according to Farona and Greenloe[117] who carried out experiments using this system and proposed an alternative route for the formation of the initial metal-carbene entity, Figure 2.23.

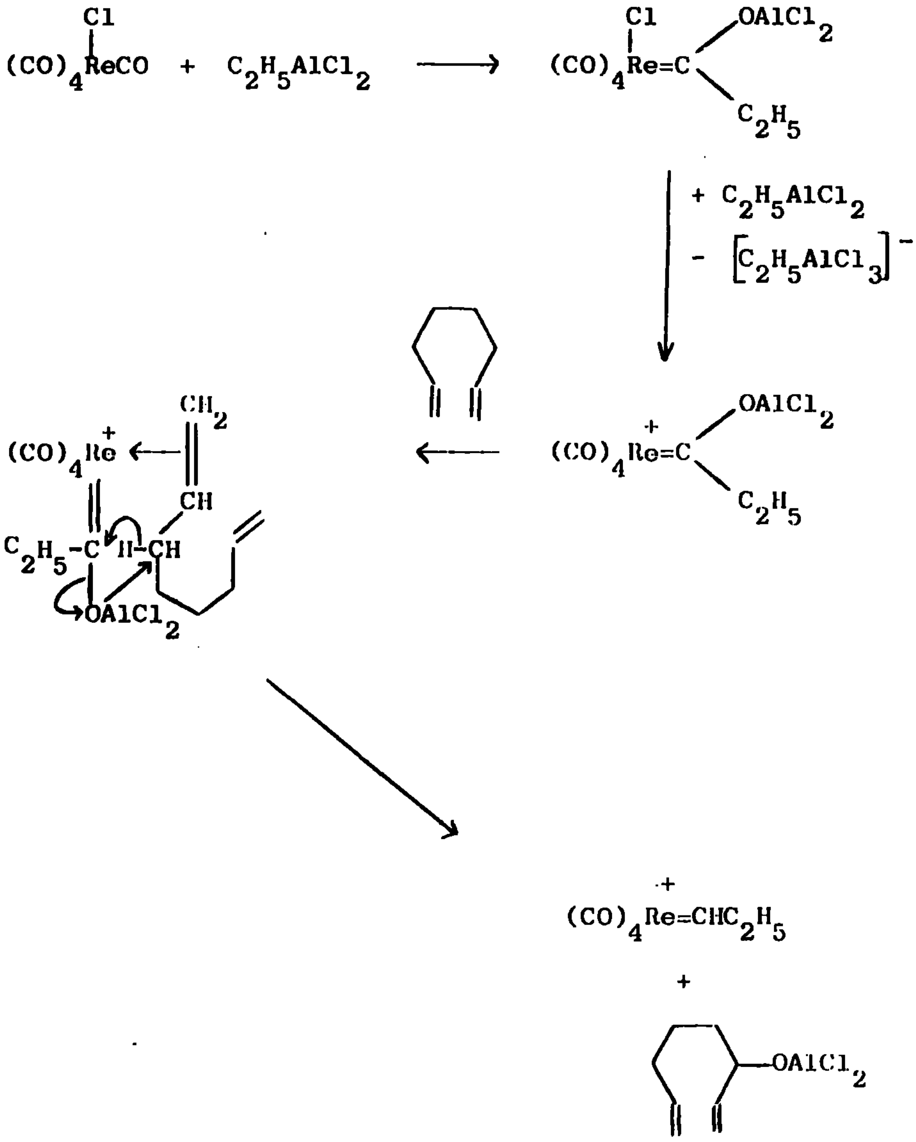


Figure 2.23

The proposed scheme involved the addition of ethylaluminium dichloride to a coordinated carbonyl ligand, followed by the exchange of an oxygen atom for a hydrogen atom to create a coordinated propylidene molecule; the second site of alkene coordination comes about by the transfer of a chlorine atom from rhenium to aluminium. The evidence supporting this scheme was the formation of octa-1,7-diene-3-one as a by-product.

For systems where organometallic cocatalysts are not present, that is, category (iii), three schemes have been proposed. Dolgoplosk et al[109] proposed a scheme involving the conversion of a coordinated alkene to a carbene via a 1,2-hydride shift as shown in Figure 2.24, an analogous scheme

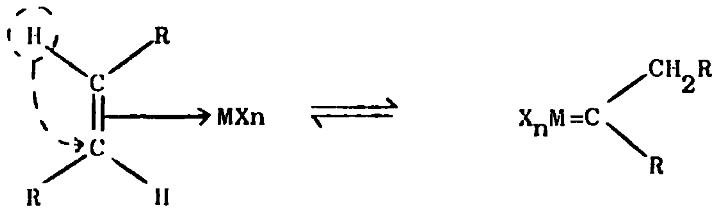


Figure 2.24

was adopted by Chisholm and Clark to explain the formation of some stable complexes of platinum.[118] This scheme would not be possible for sterically constrained cycloalkenes, such as bicyclo[2.2.1]hept-2-ene, since the transition state requires considerable distortion from planarity. However, this may be overcome by a 1,2-hydride transfer via a metal-hydride, Figure 2.25.[17]

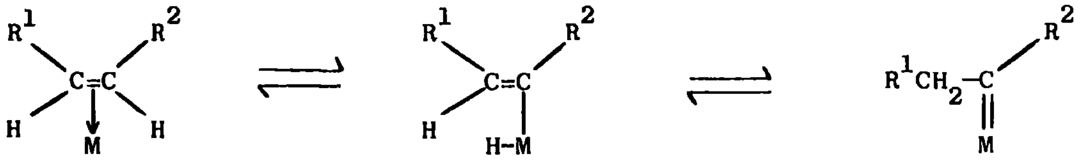


Figure 2.25

A second scheme, Figure 2.26, which only requires a metal and coordinated alkene to produce the metallocyclobutane intermediate and omits the need for a metal-carbene species was proposed by Green et al.,[119] who found that nucleophilic attack by H^- or Me^- on $[W(\eta^5-C_5H_5)_2(\eta^3-CH_2CHCH_2)]^+PF_6^-$ at the central carbon atom of the η^3-allyl gave the metallocyclobutane intermediate (61). However, a scheme such as that described in Figure 2.26 will not be possible for compounds such as bicyclo[2.2.1]hept-2-ene, since η^3-allyl formation is not possible.

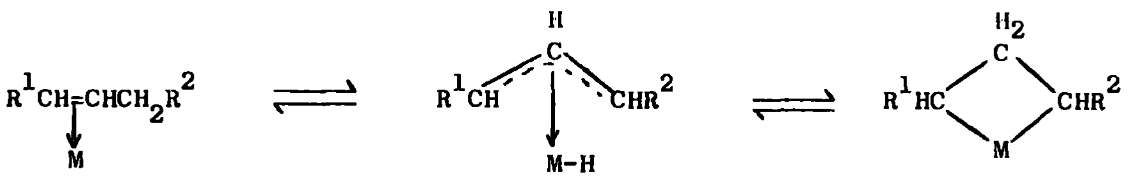
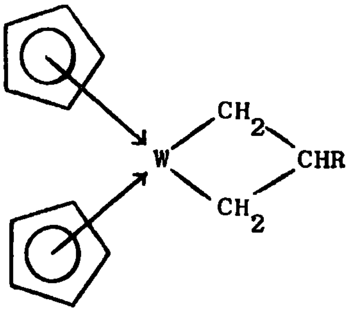


Figure 2.26



(R=H, or CH_3)

(61)

The third scheme which has been proposed involves a transition metal-hydride, either present in the catalyst or formed during its preparation, Figure 2.27.

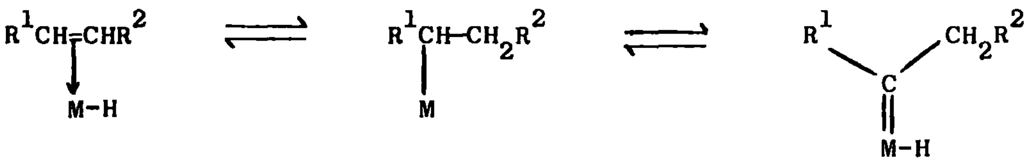


Figure 2.27

The transition metal-hydride may be formed by initial reaction between the transition metal and an oxygen containing activator such as an alcohol or even water or oxygen. Muetterties et al[120] have observed that WCl_6 in combination with different alkyl metal compounds was inactive at 25^o for the metathesis of acyclic internal alkenes when performed in scrupulously dried and oxygen free conditions. Similarly Sherman[121] reported that under anhydrous conditions WCl_6-$EtAlCl_2$ is an inefficient metathesis catalyst, but addition of 1 to 10 ppm of water renders the system extremely active.

The role of oxygen containing activators may be rationalised as arising from the double bond character of the metal oxide bond in two ways; the first, shown in Figure 2.28, involves a number of hydride shifts; the second implies a more direct involvement of M=O in the formation of the metal-carbene, Figure 2.29. However, the strength of the M=O bond, compared to that of the M=C bond, is probably too large for the forward reaction in Figure 2.29 to occur.

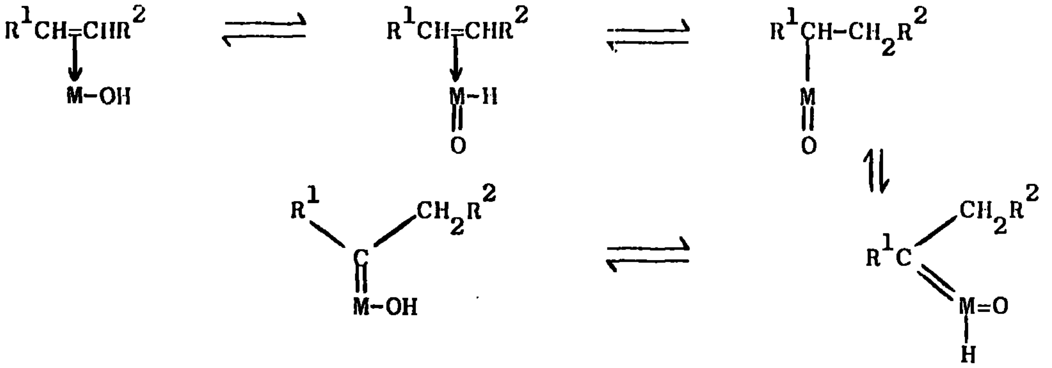


Figure 2.28

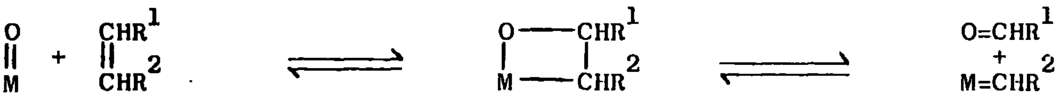
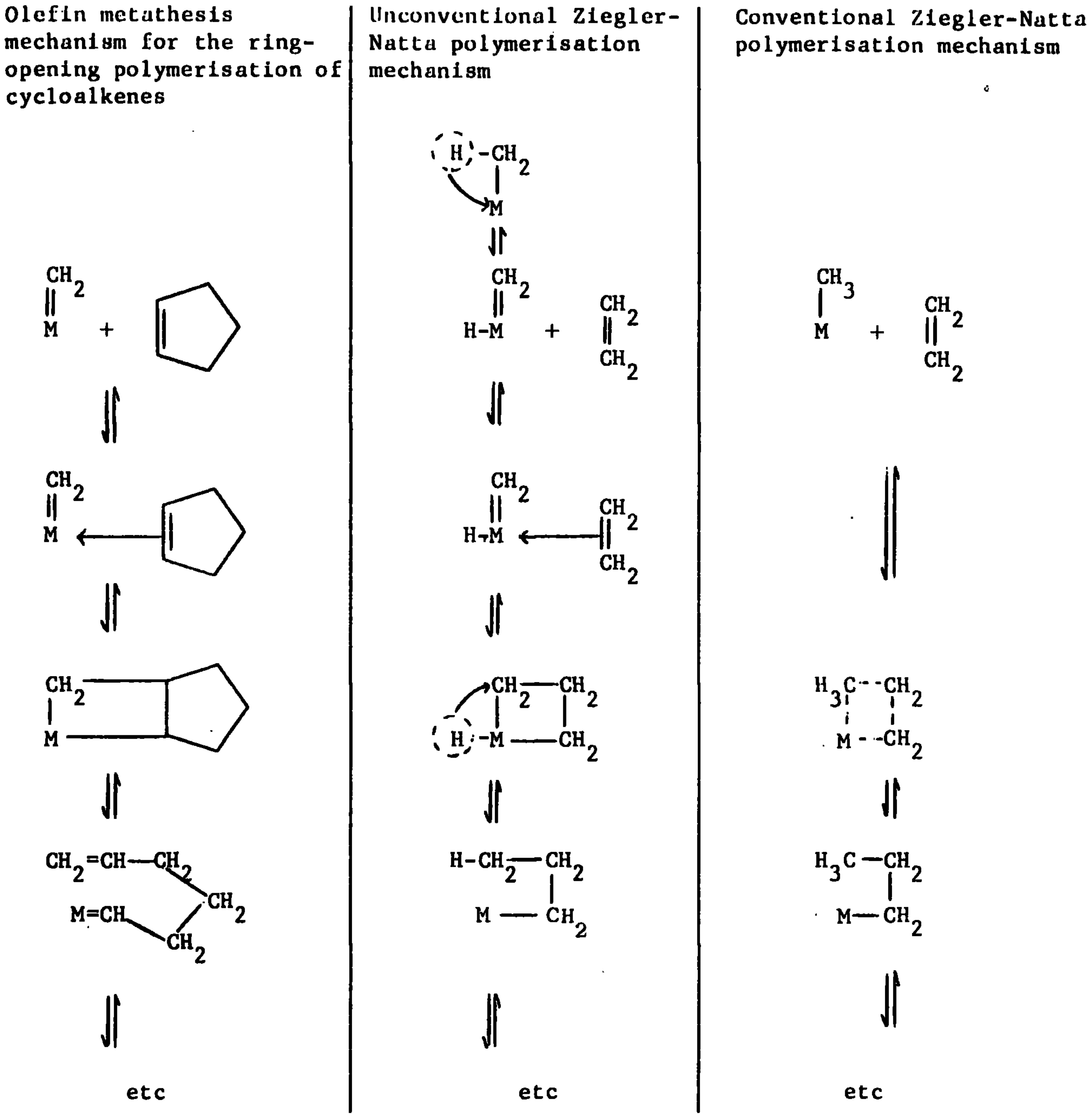


Figure 2.29

The involvement of a metal-hydride in the formation of the initial metal-carbene species enables the side reactions such as dimerisation, oligomerisation and isomerisation to be better understood and explains why the addition of polar protic additives, molecular hydrogen and other hydride sources to heterogeneous and homogeneous catalysts are usually beneficial, or in some cases essential, to the olefin metathesis reaction.

In the future a better understanding of the relationship between olefin metathesis and Ziegler-Natta polymerisation may be found. Ivin[122] has proposed a scheme for Ziegler-Natta polymerisation, Figure 2.30, which closely parallels that proposed for olefin metathesis in the ring-opening polymerisation of cyclopentene, involving metal-hydride shifts. The reactions of alkenes with transition metal complexes range from extension of the alkyl chain as in Ziegler-Natta polymerisation with metals on the extreme left of the transition metal series such as Ti and Zr, to the formation of strong alkene-metal-π-complexes with the metal ions of Group VIII on the extreme right of the series. This variation arises because the metals in the former case lack sufficient d-electrons to form strong d_{π}-p_{π} back-bonding with the alkene, whereas in the latter case with filled d-orbitals back-bonding is strong. For metals in the middle of the series, for example Group VI, the competitive reaction of metal-alkyl and metal-alkene formation is delicately balanced. The catalyst system WCl_6/Me_4Sn polymerises ethylene to polyethylene by the Ziegler-Natta mechanism and ring-opening polymerises cyclopentene to poly(1-pentenylene) by olefin metathesis.[123] Likewise the addition polymerisation of bicyclo[2.2.1]hept-2-ene is favoured at an Al : Ti ratio of 1 : 2 (Ziegler-Natta behaviour) with ring-opening polymerisation predominating at a 2 : 1 ratio using the catalyst system $TiCl_4$-$LiAl(C_7H_{13})_4$.[37]



Olefin metathesis mechanism for the ring-opening polymerisation of cycloalkenes

Unconventional Ziegler-Natta polymerisation mechanism

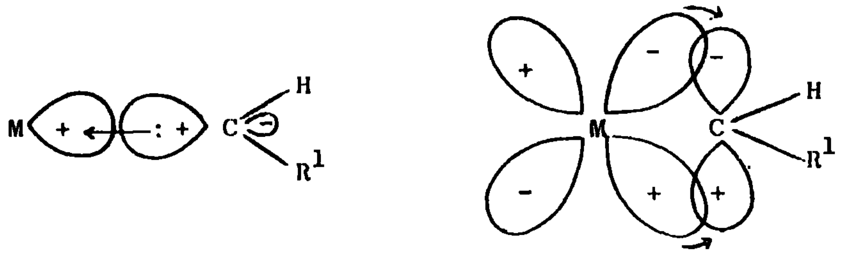
Conventional Ziegler-Natta polymerisation mechanism

Figure 2.30

2 The transformation of the metal-carbene to the metallocyclobutane intermediate

The transformation of the metal-carbene to the metallocyclobutane intermediate and subsequent rearrangement to the products depends upon the nature of the bonding in the metal-carbene species.

It has been proposed[124] that the carbene may be viewed as a singlet and the nature of the bonding in the metal-carbene complex somewhat analogous to carbon monoxide or an alkene bonded to a metal. Two bonding modes are involved; (i) a forward donation of an electron pair from the occupied sp^2 orbital of the $C_{carbene}$ to the metal, and (ii) a back donation element from the metal to the empty p_z orbital of the $C_{carbene}$, Figure 2.31



(i) (ii)

Figure 2.31

The mechanism for formation of a metallocyclobutane intermediate involves an incoming alkene undergoing π-coordination with an active metal site. The metal, $C_{carbene}$ and the two substituents (R^1 and H) all lie in the same plane, with the coordinated alkene molecule in a plane perpendicular to the metal-carbene plane, Figure 2.32. To form the four-membered ring the $C_{carbene}$ expands from sp^2 to sp^3 hybridisation, while the carbene-to-metal

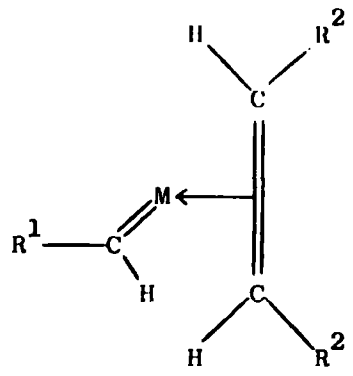


Figure 2.32

bond transforms into a conventional σ-carbon-metal bond and the carbon assumes a tetrahedral configuration. The π-bonded alkene undergoes a process analogous to Ziegler's cis-ligand insertion, sliding and rotating to align the alkene carbons with their respective bonding counterparts, thus forming the metallocyclobutane intermediate.

However, evidence has been presented by Casey[125] that the carbon atom of the carbene group bonded to the metal is best described as a cationic centre and hence electrophilic in character. Therefore the metal-carbene to metallocyclobutane transformation may occur as shown in Figure 2.33.

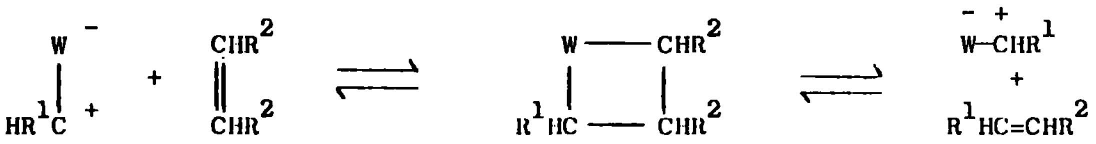


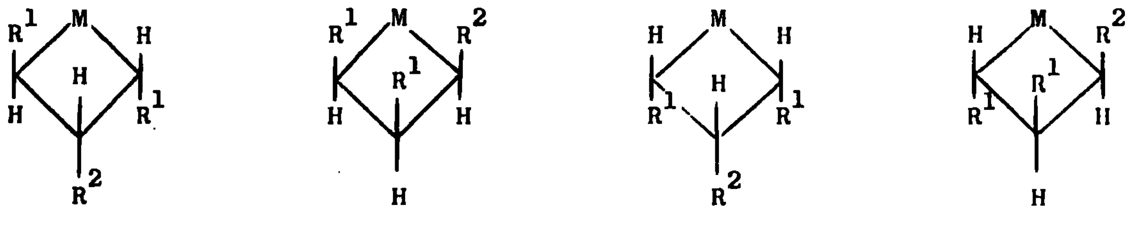
Figure 2.33

This problem is further complicated by the results reported by Gassman and Johnson[126] in which α,β-unsaturated esters, Michael acceptors, efficiently trap metal-complexed carbenes generated during metathesis of alk-2-enes, which were explained by assuming that such carbenes are nucleophilic in character. However, Gassman's and Johnson's assumptions may be questioned, since Michael acceptors have been reported to react with cationic carbenes in compounds R(MeO)CM$(CO)_5$ (where M = Cr, Mo or W; R = aryl or alkyl) to give the corresponding cyclopropanes.[127] Therefore, the details of the transformation of the metal-carbene to the metallocyclobutane intermediate remain to be clarified.

3 The origin of stereospecificity in metathesis reaction

The cis and trans isomers produced in olefin metathesis reactions are a consequence of the reactions themselves and not side reactions. For acyclic alkenes the metathesis reaction is generally non-selective, the cis-trans ratio for each product alkene being that determined thermodynamically. The only example of a stereoselective catalyst for the metathesis of acyclic alkenes is $Ph_2CW(CO)_5$ which converts cis-pent-2-ene to but-2-ene with 93% cis-double bonds. However, cycloalkenes can be converted into polymers with exclusively or predominantly cis- or trans-geometry using numerous catalyst systems, for example, with $WF_6/EtAlCl_2$ cyclopentene produces poly(1-pentenylene)[33] with virtually 100% cis-double bonds, with $WCl_6/EtOH/EtAlCl_2$ it produces poly(1-pentenylene) with 84% trans-double bonds.[27]

To accommodate the virtual non-selectivity for acyclic alkenes it was initially suggested that rotation of the carbene and coordinated alkene about the central metal atom must occur, Figure 2.32.[124] Such rotations would be very facile processes and the metallocyclobutane intermediates formed are shown in Figure 2.34.



trans cis cis trans

Figure 2.34

If the carbene and alkene rotate in the same direction either clockwise or anti-clockwise a trans-metallocyclobutane is formed, whereas if they rotate in opposite directions cis-metallocyclobutanes are formed and hence trans-acyclic alkenes and cis-acyclic alkenes are produced as products respectively. It has been suggested that the stereo-selectivity observed in the ring-opening polymerisation of cycloalkenes with certain catalyst systems may be due to the growing chain forming multiple coordination with the active catalyst site hence preventing rotation of the bound metal-carbene,[105] Figure 2.35, such coordination cannot occur with acyclic alkenes.

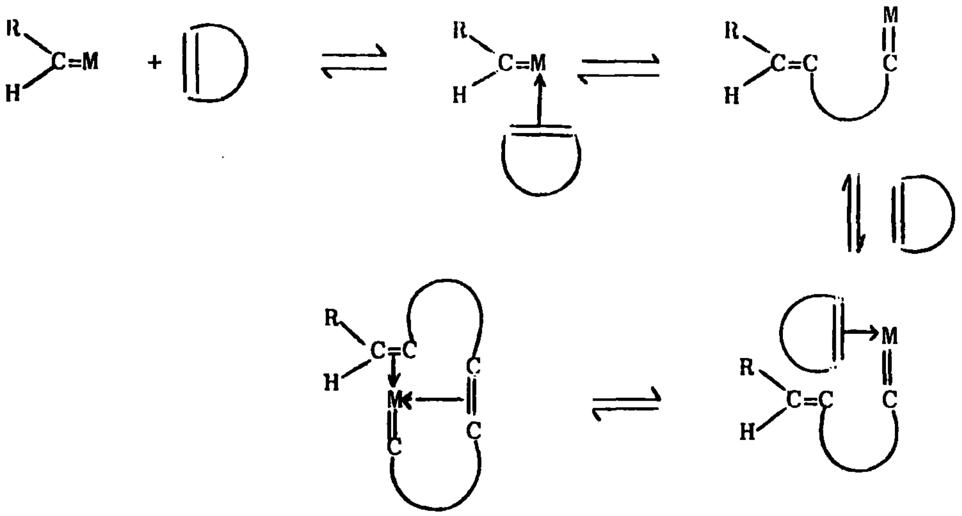


Figure 2.35

From a study of the cross-metathesis reaction of terminal with internal alkenes[124] a preference for certain metallocyclobutane transition states has been suggested. The relative distribution of the various cross-metathesis products of pent-1-ene with cis-pent-2-ene is shown in Table 2.3.

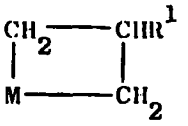
Table 2.3

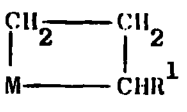
Cross metathesis of pent-1-ene and cis-pent-2-ene

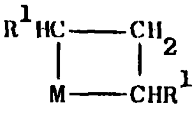
Relative Concentrations			
Symmetric		Unsymmetric	
$CH_2=CH_2$	1	$CH_3CH=CH_2$	4
$C_3H_7CH=CHC_3H_7$	1	$C_2H_5CH=CHC_3H_7$	4
$CH_3CH=CHCH_3$	2	$C_2H_5CH=CH_2$	12
$C_2H_5CH=CHC_2H_5$	2	$CH_3CH=CHC_3H_7$	12

The self-metathesis from either alkene leads to symmetric products, whereas the products from cross-metathesis are unsymmetrical. The significance of the results shown in Table 2.3 are that, although pent-1-ene undergoes a small amount of self-metathesis it readily reacts with cis-pent-2-ene to produce cross-metathesis unsymmetrical products. The terminal alkene, pent-1-ene, in fact inhibits the self-metathesis of cis-pent-2-ene to the extent that the tendency of cis-pent-2-ene to yield cross-products with pent-1-ene is eight times greater than its tendency to self-metathesise. A possible explanation for this is that terminal alkenes are more reactive than internal alkenes, undergoing regenerative metathesis and occupying all the catalytic sites, inhibiting the self-metathesis of the internal alkenes. However, occasionally an internal alkene enters the catalytic site, whereupon metathesis yields an unsymmetric product. The regenerative metathesis of terminal alkenes was confirmed by examining the cross-metathesis of pent-1-ene and $[D_{10}]$-pent-1-ene[105] which gave almost exclusively scrambling of the C_4D_4 and CD_2 units in the recovered pent-1-ene.

Since the terminal alkenes flood the catalytic sites the possible metallocyclobutane intermediates are (62) - (65). However, transition states (63) and (65) are incompatible with predominantly regenerative


(62)


(63)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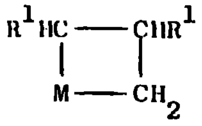

(65)

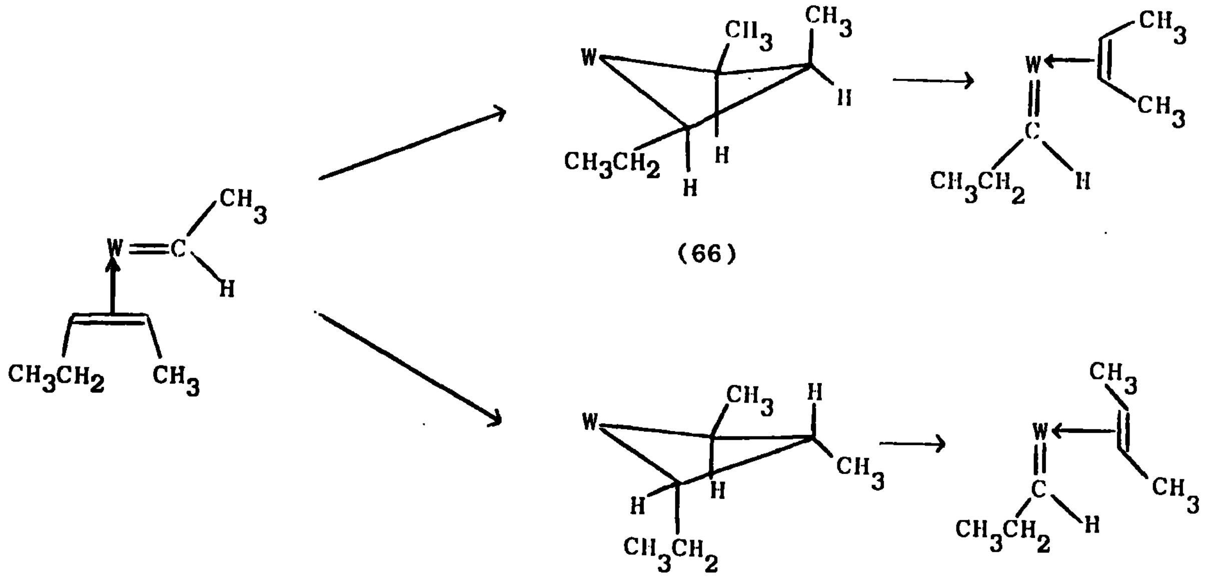
metathesis, thus favouring (62) and (64). Preference between these latter two transition states depends upon steric and electronic factors.

If as stated previously, Chapter 2.4c-2, the active metal-carbene species has electrophilic character (i.e. may be represented as $\overset{-}{M}$-$\overset{+}{C}$HR), it should preferentially attack the electron rich end of the double bond of the incoming alkene, which is the CH_2= entity in terminal alkenes, to transfer the least substituted alkylidene unit and to regenerate the M=CHR complex. This argument favours (64) over (62). However, the reaction may proceed by a $\overset{+}{M}$-$\overset{-}{C}H_2$ like carbene which would react selectively with a terminal alkene to transfer the most substituted alkylidene unit and to regenerate a M=CH_2 carbene, then (62) may be preferred to (64).

The steric factors which influence the structure of the metallocyclobutane intermediate and hence the stereochemistry of the metathesis products are not clearly understood at the present time. Casey[128] has suggested that the stereochemistry of metathesis can be explained on the basis of the stereochemistry of a puckered metallocyclobutane intermediate. Stable metallocyclobutane complexes have been shown by X-ray crystallography[129,130] to exist in a puckered conformation, for example $(C_3H_6)Pt(C_6H_5N)_2Cl_2$. As a consequence of puckering, the substituents on the ring occupy pseudoaxial and pseudoequitorial positions. The most important steric interaction in the intermediate would be expected to be a 1,3-diaxial interaction between the substituents attached to the carbons bonded to the metal.

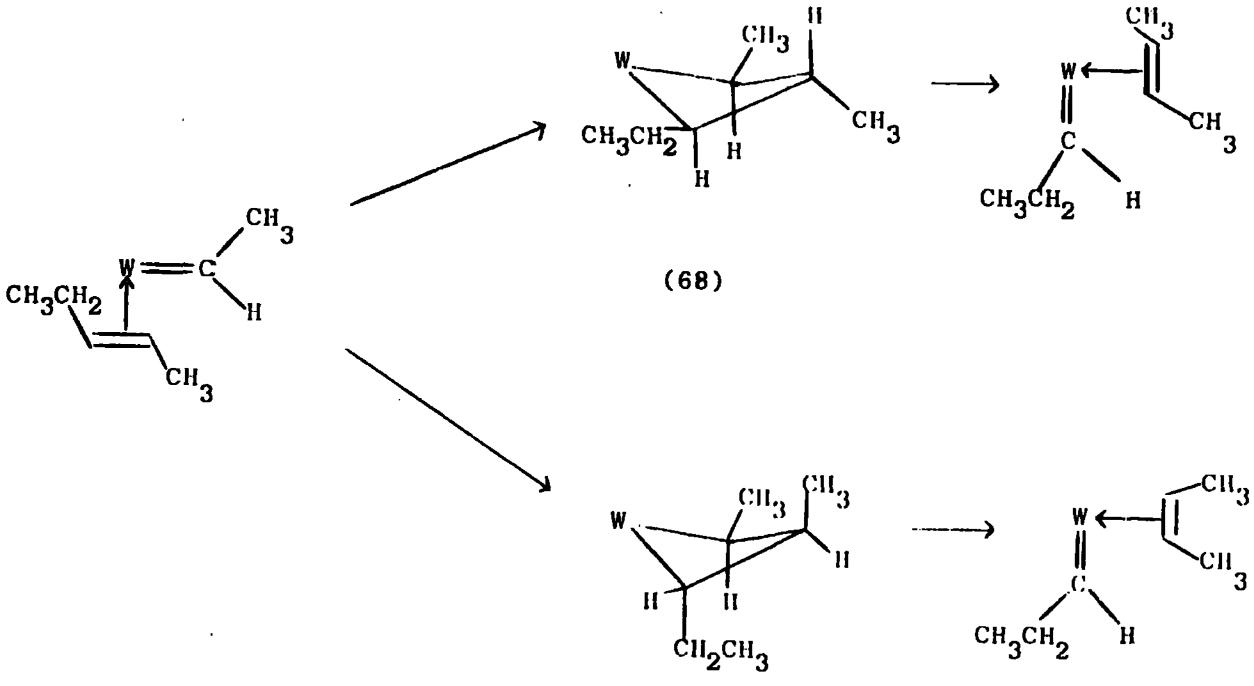
Casey based his suggestion on the metathesis products obtained from the reactions of cis-pent-2-ene and trans-pent-2-ene. The former initially giving predominately cis-products and the latter trans-products.

From a consideration of the possible stereochemically different metallocyclobutane intermediates for the reaction of cis-pent-2-ene with a metal complex bearing an ethylidene ligand (66) and (67), the former is more stable than the latter which has a destabilising 1,3-diaxial interaction between the ethyl group and the proton. Consequently, cyclisation to give (66) should be preferred and cis-but-2-ene which arises from the decomposition of (66) should be kinetically favoured. Similarly, the greater stability of (68) relative to (69) explains the preferred formation of trans-but-2-ene from trans-pent-2-ene. A similar argument has been proposed by Katz.[131]



(66)

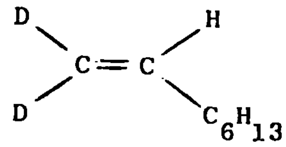
(67)



(68)

(69)

However, Calderon[132] has stated that from the metathesis of both cis-4-methyl-pent-2-ene and trans-4-methyl-pent-2-ene in which the products from both reactions had predominately trans-configuration the stereochemistry of metathesis can be explained by 1,2-interactions in the metallocyclobutane intermediate which is planar. If the stereochemistry of the products was controlled by 1,3-diaxial interactions of a puckered metallocyclobutane intermediate then the products from the cis-4-methyl-pent-2-ene should have had cis-configuration. The views of Calderon and Casey appear to be diametrically opposed and it seems likely that the resolution of this difficult, but important problem will occupy some time. At the time of writing the most recent communication from Casey's group[133] provides evidence consistent with the intervention of a puckered metallocyclobutane in which 1,3-interactions are important. Mixtures of 1,1-dideutero-oct-1-ene (70) and Z-1-deuterodec-1-ene (71) were metathesised and the 1-deutero-oct-1-ene (72) product was shown to retain Z-configuration.



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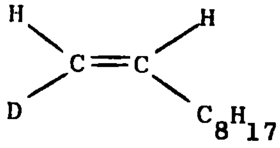

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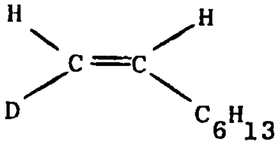
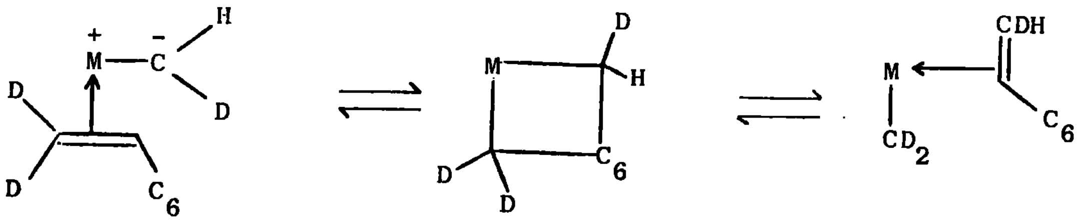


(72)

Two sequences can be used to account for the formation of 1-deutero-oct-1-ene (72) as shown below, Figure 2.36. Since the steric requirements of

Scheme 1 $\overset{+}{M}\text{-}\overset{-}{C}H_2$



Scheme 2 $\overset{-}{M}\text{-}\overset{+}{C}HR$

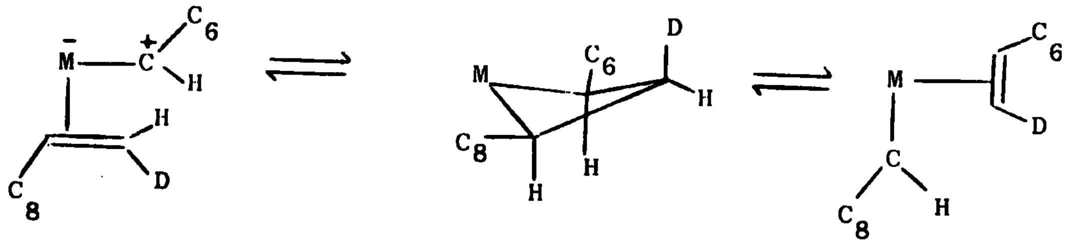


Figure 2.36

H and D are assumed to be effectively the same, Scheme 1 should give equimolar mixtures of Z and E isomers of (72); whereas in Scheme 2 steric integrity should be retained as was in fact observed.

4 The effect of Lewis acids and temperature on the stereospecificity of metathesis reaction

To account for the low stereospecificities in metathesis reactions catalysed by systems which contain Lewis acids such as organo-aluminium compounds compared with systems which do not, for example, using the catalyst system $(Ph)_2C{=}W(CO)_5$ cis-pent-2-ene gives but-2-ene that is 93% cis, whereas with the system $WCl_6/EtOH/EtAlCl_2$ cis-pent-2-ene gives but-2-ene that is only 63% cis, Katz has proposed the formation of a 3-metallopropyl cationic species, by the cleavage of a carbon-metal bond in the metallocyclobutane.[131] Such an intermediate would allow rotation prior to reforming the metallocyclobutane and hence account for the reduced stereospecificity. The formation of such a species would be facilitated by the presence of Lewis acids, for example, the stereospecificity of cyclopentene's metathesis when initiated at -30^o by mixtures of WF_6 and $Et_3Al_2Cl_3$ diminishes with an increase in the Al : W ratio.[27]

Increasing the temperature may also facilitate the formation of such species. The temperature dependence of the cis content of poly(1-pentenylene) using the catalyst system WCl_6/tetraallylsilane[134] is shown in Figure 2.37. The polymer obtained at -78^o to -20^o contains 99-94% cis-units; i.e. the stereospecificity is independent of temperature below -20^o. Above this temperature the amount of trans-units increases gradually attaining about 80% at 30^o. Similar temperature dependence of polymer microstructure has been observed for the polymerisation of cyclopentene using the catalyst system $WCl_6/(C_2H_5)_4Sn$[135] and $MoCl_5/Et_3Al$.[136]

Dependence on polymorisation temperature of cis content of poly(1-pentenylene) obtained with WCl_6/TAS catalyst

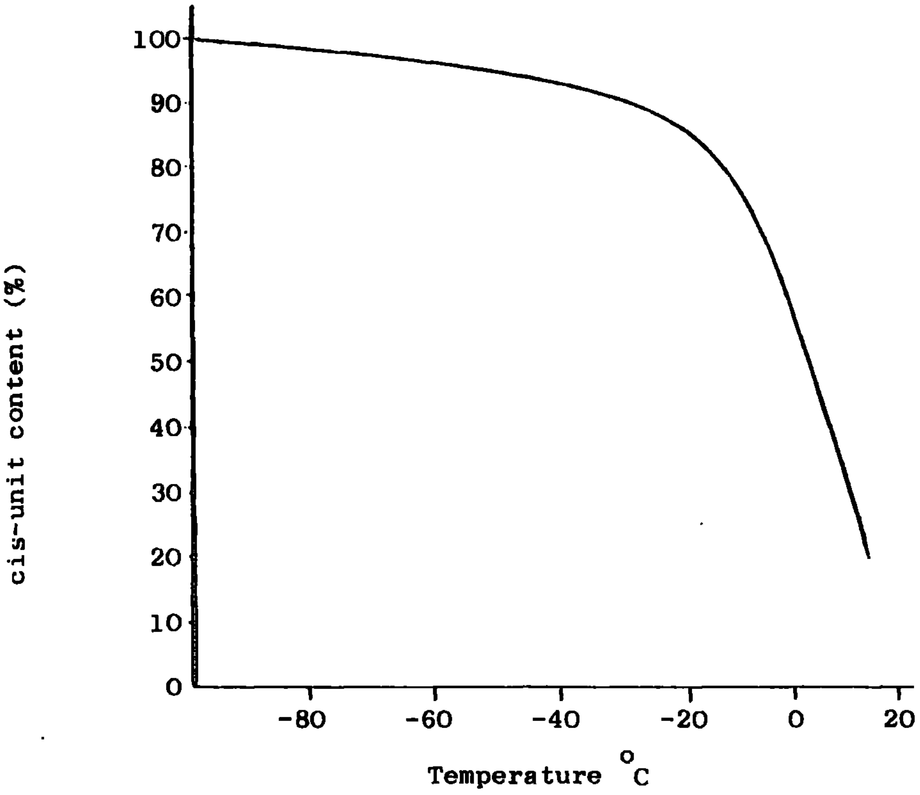


Figure 2.37

CHAPTER 3

1H,2H-HEXAFLUOROCYCLOPENTENE AS A POTENTIAL MONOMER FOR RING-OPENING POLYMERISATION

3.1 Work carried out in an attempt to ring-open polymerise 1H,2H-hexafluorocyclopentene

3.1a Introduction

It was initially decided to attempt the ring-opening polymerisation of cyclopentene to establish experimental competence and confidence in using the techniques required for olefin metathesis work. Generally three component homogeneous catalyst systems are used for the polymerisation of cycloalkenes;[16] tungsten hexchloride is the preferred transition metal component; as the cocatalyst, dialkyl aluminium chloride or tri-isobutyl-aluminium are preferred over other alkylaluminium compounds, because their weaker Friedel-Crafts activity avoids undesired side reactions especially cyclisation and hydrogenation; and the oxygen containing activator can be an alcohol, preferably 2-chloroethanol, or a peroxide.

A detailed description of the solution polymerisation of cyclopentene to trans-poly(1-pentenylene) has been given by Günther et al.[27] The polymerisations are generally performed under conditions which stringently exclude moisture and oxygen from the reaction system, in the temperature range $-10^o/+10^o$, under an inert atmosphere of dry nitrogen or argon with a 15-20% solution of the monomer in a dry solvent such as benzene, toluene or chlorobenzene.

A pre-mixed solution of the tungsten complex and the oxygen containing activator and the organo-aluminium compound are added to the monomer solution. With three component catalyst systems the order of addition of the individual components is critical.[137] When the tungsten complex/activator mixture is added to the monomer solution followed by the organo-aluminium compound the polymerisation takes place rapidly. However, no polymerisation takes place if the catalyst components are pre-mixed, because the tungsten complex and the organo-aluminium complex form a product which is inactive as an olefin metathesis catalyst.

The monomer : tungsten molar ratio may vary from 3000 : 1 to as high as 20,000 : 1. The optimum aluminium : tungsten molar ratio somewhat depends on the catalyst composition, for example, for $WCl_6/2CHOH(CH_2Cl)_2/Et_3Al$ [138] and $WCl_6/Na_2O_2/(i\text{-butyl})_3Al$ [139] systems, molar ratios of 2.5 : 1 and 1.5 : 1 respectively are recommended.

The catalyst system which was eventually used was $WCl_6/Na_2O_2/(i\text{-butyl})_3Al$, with toluene as the solvent, because of the availability of the individual components and the high degree of success of this system in polymerising cyclopentene. It is claimed that with this system elastomeric poly(1-pentenylene) with 90% or more of the double bonds in the trans-configuration can be obtained in 85% conversion after one hour.[139]

3.1b The polymerisation of cyclopentene

In the first instance the polymerisation procedure was carried out, using toluene which had been dried over sodium wire and degassed, commercial unpurified cyclopentene was degassed prior to use, commercial sodium peroxide and tungsten hexachloride were used as suppled and tri-isobutylaluminium was freshly prepared. The pre-mixed WCl_6/Na_2O_2 solution in toluene was prepared under an inert atmosphere of dry nitrogen in a glove-box, and the catalyst components were injected using air-tight syringes into the reaction vessel; which was maintained under an atmosphere of dry nitrogen and contained the degassed monomer. The reaction was unsuccessful, no polymer was produced.

There were several factors which could have influenced the failure of the reaction. The nitrogen gas, toluene and cyclopentene may not have been sufficiently dry and the tungsten hexachloride may have been impure. Although catalytic amounts of water or oxygen are beneficial to the reaction, excess readily deactivates the catalyst.

The nitrogen was dried more thoroughly by passing it through a bubbler of concentrated sulphuric acid and then through a glass trap immersed in liquid air. The nitrogen system, in which all the connections were either glass or nylon tubing was connected directly to the vacuum line. The reaction vessel was evacuated and the toluene and cyclopentene after being degassed were vacuum transferred into it. The entire system was let down to an atmosphere of dry nitrogen so that no time after the commencement of the reaction was air allowed into the reaction vessel.

The dryness of the toluene was improved by refluxing it over sodium under a dry nitrogen atmosphere, until a permanent blue colour was obtained on addition of benzophenone,[140] followed by distillation under dry nitrogen.

The tungsten hexachloride which had been bought from a commercial supplier was a mixture of yellow, red and blue solid material, whereas pure anhydrous WCl_6 should be steel-blue in colour. This was prepared from hexachloropropene and tungsten trioxide under stringently dry and oxygen free conditions.[141] The crystals produced were steel-blue in colour.

The polymerisation of cyclopentene was attempted using the improved conditions and purified solvents and reagents. The colour changes, which are reported in the literature,[139] on addition of the WCl_6/Na_2O_2 solution to the monomer solution (blue black to deep-red) and on the addition of the $(i\text{-butyl})_3Al$ to the reaction mixture (deep-red to dark brown), were observed. A small amount of creamy-white material was produced, it had a soft, sticky texture and was slightly elastic when drawn. In a final modification, designed to increase the yield of product, the cyclopentene was refluxed over calcium hydride and then distilled under dry nitrogen onto 4A molecular sieve. This material readily polymerised, giving a creamy-white solid (74% yield). I.r. spectroscopy (Appendix C(I)) and ^1H n.m.r. spectroscopy showed it to be identical to poly(1-pentenylene) with predominantly trans-double bonds.[142]

The determination of the type and number of double bonds in polyalkenylenes was initially carried out by i.r. spectroscopic analysis.[143] Trans vinylene double bonds were generally determined by using the i.r. absorption band at 966 cm^{-1}, the cis vinylene double bonds either by using the band at 1404 cm^{-1} or that at 726 cm^{-1}. A determination of the amount of trans and cis double bonds requires an evaluation of the extinction coefficients of the individual bands. Originally quantitative analyses were generally based on the extinction coefficients used for cis- and trans-1,4-polybutadiene and to a first approximation this method was justified, however, it is inadequate for an exact structure determination and contradictory results were frequently reported in the literature.[144] There are three major reasons why this analysis fails:

(i) it is likely that some errors are inherent in the assumption that extinction coefficients for polyalkenylenes are identical with those found for other compounds;

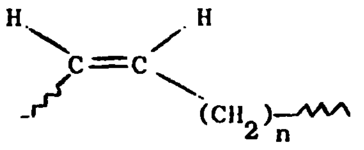
(ii) there may be units other than cis- and trans-pentenylenes in the polymer backbone, for example, saturated units and neglect of these can also lead to error;

(iii) absorption bands may have been used which overlap with other bands making reliable integration very difficult.

From work carried out by Calderon, Scott, Ofstead and coworkers[145,146] the ^{1}H n.m.r. of polyalkenylenes consists of three different absorption regions: (A) the signal due to the vinylic protons of the disubstituted double bond was always found at 5.3-5.5 ppm; (B) that of the allylic protons, α to the double bonds at 1.9-2.1 ppm; and (C) that of the β protons at 1.3

ppm (chemical shifts downfield from TMS). Combining the data available from i.r. and ^{1}H n.m.r. spectroscopy, Tosi, Ciampelli and Dall'Asta[142] proposed a more complete and accurate method for the quantitative determination of the units generally occurring in polyalkeneylenes derived from different cycloalkenes.

This method differs from others for two reasons. Firstly, it takes into account not only the primary alkenylene units, cis-unit (73) and trans-unit (74), but also saturated units originating from transformations of the primary units by the action of acidic catalysts (75) and u.v. irradiation (76), as well as those arising from hydrogenation.



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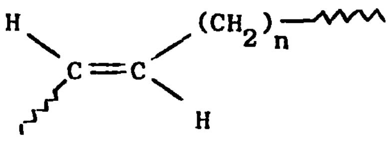

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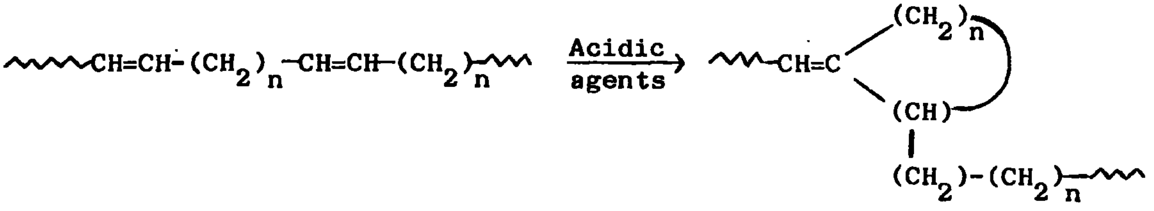

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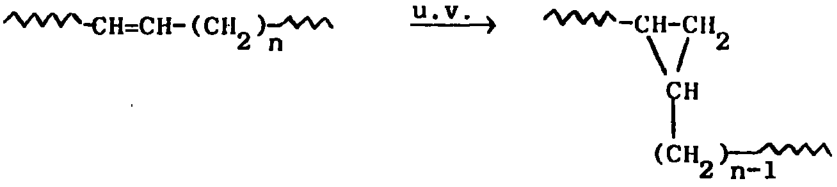


(76)

Such reactions are not appreciable in fresh samples, but may be observed in unstabilised samples after standing. These saturated units may be detected in the ^1H n.m.r. of the polymer. In a chemically regular poly(1-pentenylene) the ratio of absorptions A : B : C should be 1 : 2 : 1, therefore the integrated intensities for the different proton signals gives a quantitative representation of the different types of units present in the polymer. In the sample prepared, Figure 3.1, the ratio of A : B : C was 1 : 2 : 1.15 which suggests the presence of approximately 4% of saturated units.

Secondly the method assigns proper extinction coefficients to the i.r. bands of the trans- and cis-double bonds, these were experimentally determined[146] by using pairs of predominantly trans and cis polymers of each single polyalkenylene type and are listed in Table 3.1

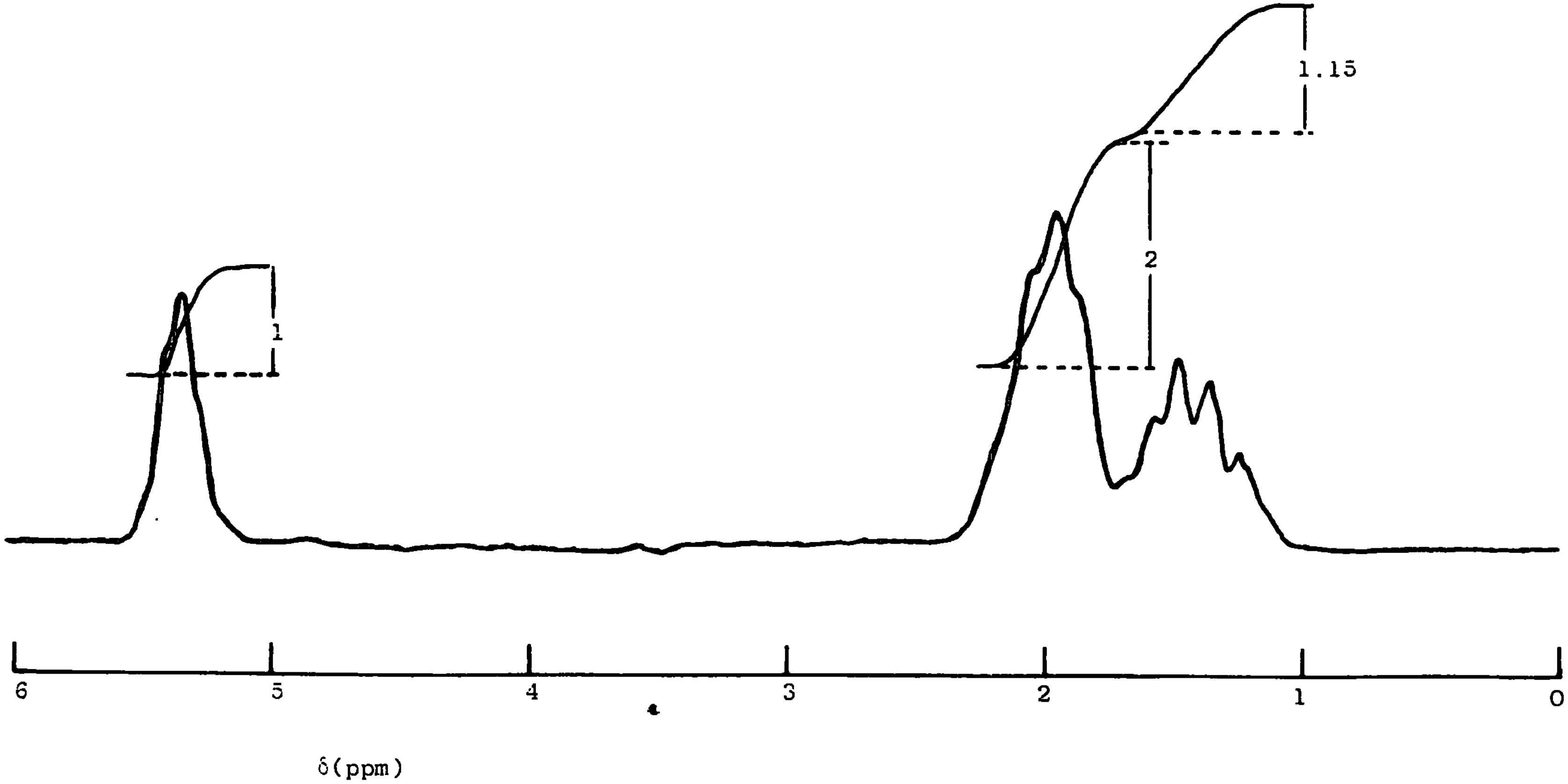
Table 3.1[146]

Extinction coefficients of i.r. bands

Polymer	ϵ_{trans} (966 cm^{-1}) l.$mole^{-1}cm^{-1}$	ϵ_{cis} (1404 cm^{-1}) l.$mole^{-1}cm^{-1}$
1,4-polybutadiene	132	5.0
poly(1-pentenylene)	152	9.4
poly(1-heptenylene)	137	not determined
poly(1-octenylene)	135	8.7
poly(1-decenylene)	134	not determined
poly(1-dodecenylene)	133	8.6

Figure 3.1 The ^{1}H n.m.r. spectrum of poly(1-1-pentenylene)

$-CH=CH-(CH_2)_3-$



The percentage cis-double bonds may be calculated using the expression Figure 3.2.

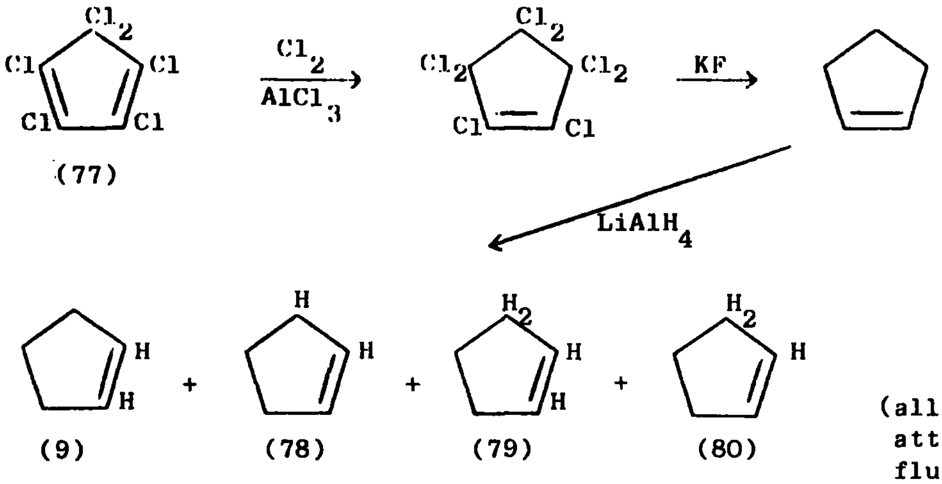
$$\% \text{ cis-double bonds} = 100 \left[\frac{xA_c}{xA_c + A_t} \right]$$

Figure 3.2

where A_c and A_t are the respective absorbances of the cis- and trans-double bonds and x is the ratio of the trans-extinction coefficient (ε_{trans}) to the cis-extinction coefficient (ε_{cis}), which in the case of poly(1-pentenylene) is 16.5 for the absorption bands representing cis- and trans-double bonds at 1404 cm^{-1} and 966 cm^{-1} respectively.

3.1c The synthesis of 1H,2H-hexafluorocyclopentene

1H,2H-Hexafluorocyclopentene (9) was prepared from relatively cheap starting material, perchlorocyclopentadiene (77) by the synthetic route shown.[20]



(all unmarked bonds attached to fluorine atoms)

Products (9) and (78) can easily be separated from (79) and (80) using preparative g.l.c. techniques. However, it is more difficult to separate (9) and (78), but the amount of (78) present is very small.

3.1d Attempts to ring-open polymerise 1H,2H-hexafluorocyclopentene

1 Using the catalyst system $WCl_6/Na_2O_2/(i\text{-butyl})_3Al$

In light of the successful polymerisation of cyclopentene using the catalyst system $WCl_6/Na_2O_2/(i\text{-butyl})_3Al$ in toluene the polymerisation of (9) was attempted using the same system, experimental procedure and conditions. The polymerisation proved unsuccessful, although the colour changes from blue-black to deep-red was observed on the addition of the pre-mixed WCl_6/Na_2O_2 solution to the monomer solution and deep-red to dark-brown on the addition of the $(i\text{-butyl})_3Al$. To check the experimental technique an identical polymerisation experiment was performed, but with the same result.

2 Using the catalyst system $WCl_6/Na_2O_2/Et_2AlCl$

From the colour changes which were observed during the attempted polymerisation of (9) using the catalyst $WCl_6/Na_2O_2/(i\text{-butyl})_3Al$, it was possible that the system was not active enough to polymerise the fluoromonomer. It has been reported that the catalytic activity increases with increasing the chlorine content of the cocatalyst in the series $EtAlCl_2 > Et_2AlCl > Et_3Al$.[145] Therefore the polymerisation of 1H,2H-hexafluorocyclopentene was attempted using a more reactive cocatalyst. Diethylaluminium chloride was chosen and prepared from tri-ethylaluminium and anhydrous aluminium chloride.[147] Its activity as a component of a ring-opening polymerisation catalyst system was tested by attempting the polymerisation of cyclopentene using the system $WCl_6/Na_2O_2/Et_2AlCl$. This was successful producing poly(1-pentenylene) (74% yield). However, the attempted polymerisation of (9) using this new catalyst system was unsuccessful.

3.2 Examination of the factors responsible for the failure to ring-open polymerise 1H,2H-hexafluorocyclopentene

3.2a Possible deactivation of the catalyst system by the fluorocycloalkene

In Chapter 1 it was stated that one possible objection to the proposed work was the abstraction of a fluoride ion from the fluorocycloalkene by an active site on the transition metal and hence deactivating the catalyst. Since WF_6 is an active catalyst for the ring-opening polymerisation of cycloalkenes,[27] it was believed that even if fluorine abstraction did occur the transition metal fluoride complex formed might still be an active catalyst. However, the organo-aluminium cocatalyst may have abstracted a fluorine atom producing an organo-aluminium fluoride which may not have been an active cocatalyst.

A further problem may have been the presence of 1H,5H-hexafluorocyclopentene (78) as an impurity in the (9). This possesses a -CHF- group, fluorine abstraction from which is a more facile process than from the $-CF_2-$ groups in (9).

Purification of (9) by the removal of (78) was attempted. Compounds such as RCHFCH=CFR are known to isomerise to $RCF_2CH=CHR$ on pyrolysis over sodium fluoride at temperatures about 300°.[148] The isomeric mixture of (9) and (78) was repeatedly pyrolysed over sodium fluoride at 300°, but no detectable reduction in the amount of (78) was observed.

The copolymerisation of an equimolar mixture of cyclopentene and (9) containing the small amount of impurity of (78) was attempted using the catalyst system $WCl_6/Na_2O_2/(i\text{-butyl})_3Al$ and the established procedure. A creamy-white material was produced, which from i.r. and ^1H n.m.r. spectroscopy was identified as poly(1-pentenylene) containing no detectable fluorine.

It may be concluded that (9) does not copolymerise with cyclopentene using the catalyst system described and conditions employed and that (9) and (78) do not deactivate the catalyst system with respect to the ring-opening polymerisation of cyclopentene.

3.2b Thermodynamic aspects of ring-opening polymerisation of cycloalkenes

1 The effect of ring size and substitution on the ring-opening polymerisation of cycloalkenes

An unpolymerisable monomer may sometimes be rendered polymerisable by changing the reaction conditions, for example, α-methylstyrene polymerises at 0° yet does not polymerise at 100°[149] and α-methoxystyrene copolymerises with styrene, yet does not homopolymerise at any temperature.[150] Therefore an understanding of the thermodynamic aspects of polymerisation processes are of great importance to the polymer chemist.

Dainton et al[151] stated that within a given homologous series of ring compounds the two most significant factors that affect the polymerisability of a member of that series are ring size and substitution.

For the olefin metathesis of acyclic alkenes the attainment of a statistical equilibrium composition is essentially entropy determined, because the enthalpy difference between the reactants and products is virtually zero, the total number and types of chemical bonds are equal before and after the reaction. However, for the ring-opening polymerisation of cycloalkenes, although possessing the features of an equilibrium reaction, comprising monomer-oligomer, oligomer-polymer and ring-chain equilibria, the thermodynamic considerations are quite different. The equilibria are shifted from a statistical composition due to the negative enthalpy term arising from the release of ring strain. Its value being high in four-membered rings, but small in higher membered rings, except cyclohexene, which is virtually strain free and for this reason is the only unsubstituted monocycloalkene that does not polymerise by ring-opening.

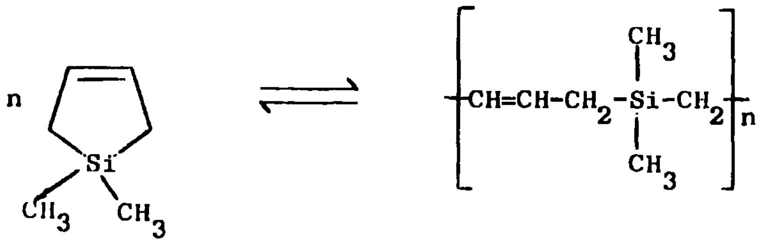
Based on a comparison of entropies estimated by Dainton et al [151] for the hypothetical ring-opening polymerisation of a homologous series of saturated hydrocarbons as shown in Table 3.2, which are expected to hold at least qualitatively for polymerisation of cycloalkenes, the entropy term involved in cycloalkene polymerisation appears to be negative for small rings up to cyclohexene, close to zero for cycloheptene and positive for higher membered rings. Therefore, the cyclopentene polymerisation is an anti-entropic and enthalpy favoured polymerisation, whereas that of cyclooctene is an enthalpy and entropy favoured polymerisation.

Table 3.2 [151]

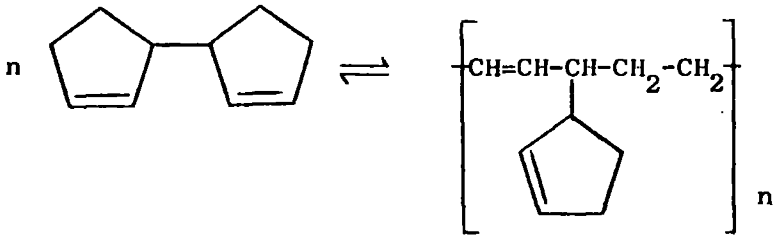
Calculated heats, entropies and free energies for the hypothetical polymerisation of cycloalkanes

Ring Size	ΔH^o k.cals.mol^{-1}	ΔS^o cal.mol^{-1}deg^{-1}	ΔG^o k.cals.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

For monomers where the free energy of polymerisation (ΔG) is small, for example cyclopentene, and very sensitive to small changes in physical condition and chemical structure, substitution in the ring may render the monomer effectively unpolymerisable. The free energy of polymerisation of cycloalkanes as a function of the number of atoms in the ring is shown in Figure 3.3.[152] It is evident that successive alkyl substitution on the same carbon atom make ΔG more positive. As stated in Chapter 1, mono-substituted cyclopentenes have been reported to undergo ring-opening polymerisations, other examples of polymerisable substituted cyclopentenes being 1,1-dimethyl-1-silacyclopent-3-ene (81)[153] and 3,3'-bicyclopentene (83)[63] giving polymers with structures (82) and (84) respectively. However, no



(81) (82)



(83) (84)

examples have been reported of the polymerisation of poly-substituted cyclopentenes. It may be that successive substitution of cyclopentene as in the case of (9) may have caused the free energy of polymerisation to become positive hence rendering the monomer thermodynamically unpolymerisable under the reaction conditions employed. It has been suggested that fluorine substitution stabilises cyclic compounds;[154] and, although data are not available, it may be that the fluorinated cyclopentene has a reduced strain energy when compared to the hydrocarbon analogue. If this is so the driving force for ring-opening polymerisation would be absent in the case of the fluorinated monomer.

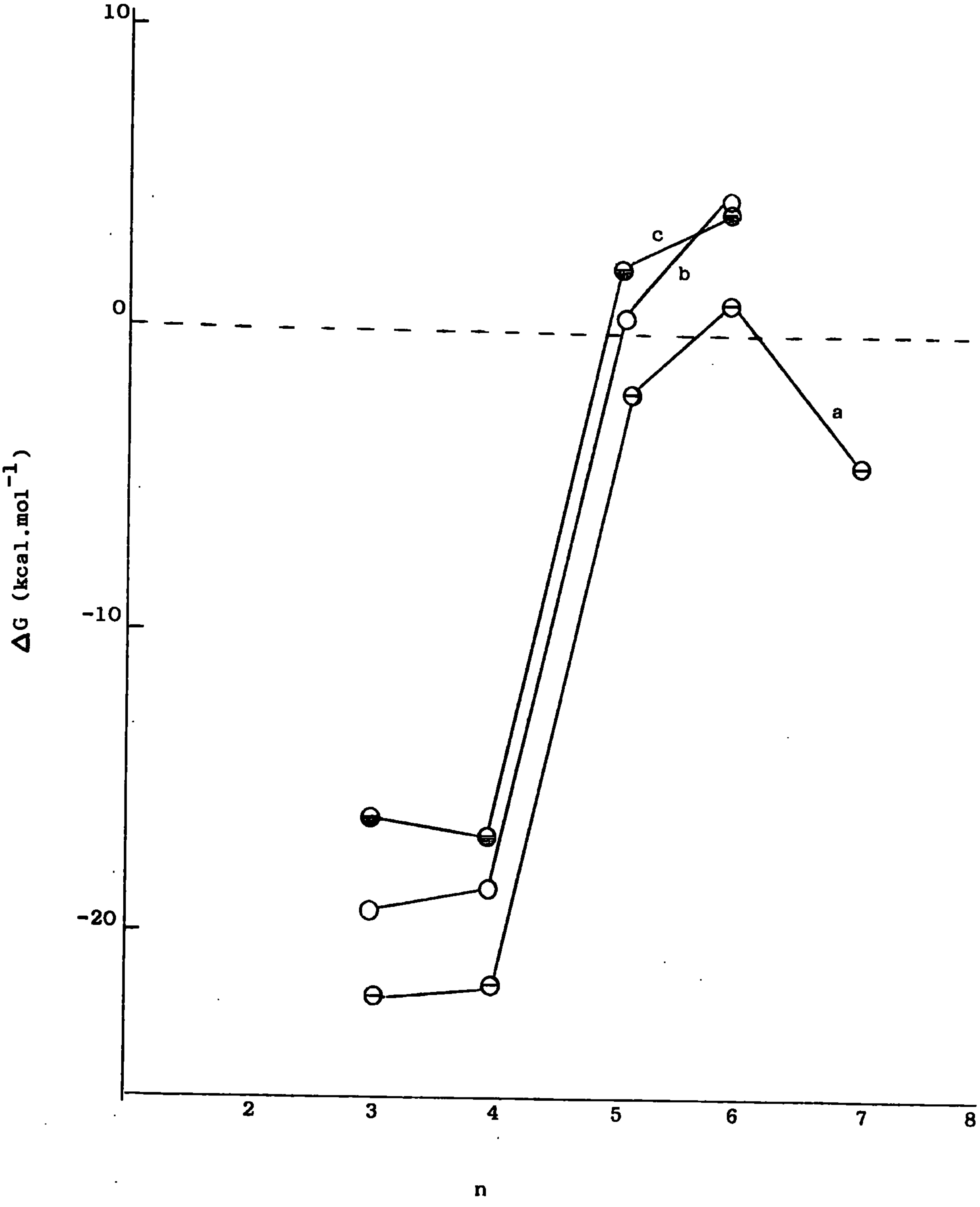


Figure 3.3[152]

Calculated free energy of polymerisation of cycloalkanes as a function of the number of atoms in the ring, n, (a) unsubstituted; (b) methyl substituted; (c) 1,1-dimethylsubstituted.

2 The temperature dependence of the equilibrium composition for the ring-opening polymerisation of cycloalkenes

Calderon and Ofstead[63] have demonstrated the temperature dependence of the monomer-polymer equilibrium for cyclopentene. In two parallel experiments 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

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

where $[M]_e$ is the equilibrium monomer concentration ΔH_p the enthalpy change during polymerisation and ΔS_p^o the standard entropy change accompanying the polymerisation when the monomer concentration is $1 mol.dm^{-3}$.

The temperature above which long chain polymers are not formed, known as the 'ceiling temperature'[152] occurs when $[M]_e = 1$. For cyclopentene undergoing ring-opening polymerisation to predominantly trans-poly(1-pentenylene) a plot of $\ln[M]_e$ against $^1/T$ on the basis of equilibrium monomer concentrations at various temperatures and extrapolation to $\ln[M]_e = 0$ a ceiling temperature of approximately 150° has been obtained.[63] 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^o respectively. The enthalpy value (ΔH_p) obtained, is close to the ring strain energy of 4.9 $kcal.mol^{-1}$ reported by Cox.[155] This is entirely consistent with the theory that in the ring-opening polymerisation of cycloalkenes the main contribution to ΔH_p is strain energy. For cyclopentene undergoing ring-opening polymerisation to predominantly cis-poly(1-pentenylene) using the catalyst system WCl_6/tetraallylsilane, a ceiling temperature for the formation of cis-poly(1-pentenylene) is 51°.[134]

In the light of the above considerations it may be that for (9) the ceiling temperature might be lower than -10°, the temperature at which all previous unsuccessful polymerisations had been carried out. Polymerisation reactions using (9) were therefore attempted with the catalyst system $WCl_6/Na_2O_2/Et_2AlCl$ at -20° and -60° for 4 hours and 7 hours respectively. No polymerisation occurred in either case.

3.2c The ability of the fluorocycloalkene to coordinate to the transition metal complex

As discussed in Chapter 2, the formation of the metallocyclobutane intermediate is not completely understood. It may involve the initial π-coordination of the alkene to the metal-carbene, followed by rearrangement into the metallocyclobutane intermediate or a direct reaction between the carbon atom of the carbene group bonded to the metal which may have electrophilic or nucleophilic character and the alkene forming the metallocyclobutane. Whichever mechanism is involved the ability of the alkene to react will depend upon the donating capacity of the π-electrons of the alkene's double bond. In (9) the presence of the fluorine atoms may have rendered the π-donor capacity of the cycloalkenes insufficient for formation of the metallocyclobutane intermediate.

A measure of the availability of a cycloalkene's π-electrons may be obtained from its π-ionisation potential determined by photo-electron spectroscopy. As shown in Table 3.3 cyclopentene has a π-ionisation potential almost 3 eV less than (9) and this would suggest that the fluorocycloalkene would be less effective than cyclopentene in reacting with the active metal-carbene entity. However, it is perhaps worth noting that fluorine substituted alkenes are particularly susceptible to nucleophilic reagents and the failure to react may be taken as evidence against an assignment of a nucleophilic character to the metal-carbene (see Chapter 2).

Table 3.3

π-Ionisation potentials of some fluorinated cycloalkenes

Cycloalkene	π-Ionisation Potential	Ref.
Cyclopentene	9.0	157
1H,2H-Hexafluorocyclopentene	12.01	156
1H,2H-Tetrafluorocyclobutene	11.94	156
1,4,5,5,6,6-Hexafluorobicyclo[2.2.2]oct-2-ene	10.50	156
4,4-Dichlorocyclopentene	9.8	158

From the colour changes which were observed on the addition of the WCl_6/Na_2O_2 solution to (9) (blue-black to dark-red) and $(i\text{-butyl})_3Al$ or Et_2AlCl to the resultant mixture (deep-red to dark brown) suggests that a reaction has occurred, but the fluorocycloalkene is not active enough to cause polymerisation.

3.3 Conclusions

From the results of the attempted copolymerisation of (9) with cyclopentene, the mere presence of fluorine does not appear to prevent the metathesis reaction. The substitution of the cyclopentene by fluorine may have either, from a thermodynamic aspect caused the free energy of polymerisation to become positive, hence rendering the monomer unpolymerisable under the conditions employed, or deactivated the π-system of the cycloalkene towards reaction with the active metal-carbene entity.

For these reasons it was decided to synthesise fluorinated monomers in which the fluorine substituents were further removed from the double bond of the cycloalkene in the hope of reducing the deactivation of the π-system and achieving polymerisation. The synthesis of these monomers is described in the next chapter and their polymerisation described in Chapter 5.

EXPERIMENTAL

3.4a Reagents

Tungsten hexachloride, tungsten trioxide and sodium peroxide were used as purchased from BDH Chemicals Ltd., cyclopentene (puriss) and hexachloropropene were used as purchased from Koch-Light Laboratories Ltd., without further purification. Anhydrous aluminium chloride was purchased from Hopkin and Williams and purified by reduced pressure sublimation. Tri-isobutylaluminium and tri-ethylaluminium were provided by Dr. K. Wade (this Department). The toluene was Analar Grade stored over sodium wire.

3.4b Attempted polymerisation of cyclopentene using the catalyst system $WCl_6/Na_2O_2/(i\text{-butyl})_3Al$

A dry 50cm^3, 2-necked, round-bottomed flask was placed in a glove-box containing a dry nitrogen atmosphere. Tungsten hexachloride (0.4g, 1.0 mmoles) and sodium peroxide (0.10g,1.1mmoles) were weighed out in the glove-box, placed in the flask and dissolved in dried, degassed toluene (16cm^3). The resultant blue-black solution was shaken periodically for twenty-four hours.

Dry toluene (30cm^3) and cyclopentene (7.74g, 110mmoles) were thoroughly degassed using the freeze-thaw procedure, then vacuum transferred into a 100cm^3, 3-necked, round-bottomed flask equipped with an air-tight thermometer well, a nitrogen inlet and a serum cap. The flask was let down to an atmosphere of nitrogen.

The pre-mixed WCl_6/Na_2O_2 solution (1.5cm^3), which was pale red in colour, was injected using an air-tight syringe through the serum cap into the reaction vessel. The solution changed colour to very pale red, it was cooled to -10^o, using an external acetone/solid carbon dioxide bath.

Tri-isobutylaluminium (0.028g, 0.17mmoles) was injected into the reaction mixture using a micro-syringe. The temperature of the reaction was allowed to rise to 0°, then cooled to -10°. The reaction was maintained at this temperature with continuous stirring under an atmosphere of dry nitrogen for 1 hour then terminated by the addition of methanol ($2cm^{3}$). A five-fold excess of methanol was added to precipitate any polymer produced; no material precipitated. Analytical g.l.c. (Column O, 150°) showed that only three components were present, the retention times corresponded to cyclopentene, methanol and toluene.

3.4c Preparation of anhydrous tungsten hexachloride

Hexachloropropene (30g, 140mmoles) and tungsten trioxide (3g, 13mmoles) were placed in a $100cm^{3}$, 1-necked, round-bottomed flask, fitted with an air-condenser and terminated in a drying tube containing anhydrous calcium chloride. The hexachloropropene was brought to the boil and refluxed for four hours. The resultant reddy-brown solution was allowed to cool slowly to room temperature. Tungsten hexachloride crystals were formed under the solution.

The flask was removed from the condenser, closed immediately with a glass stopper and placed in the glove-box containing an atmosphere of dry nitrogen. The reaction mixture was filtered through a sintered-glass crucible using suction in the glove-box. The tungsten hexachloride crystals were washed several times with dried, degassed carbon tetrachloride, sucked dry, transferred to a clean pre-weighed flask, removed from the glove-box and evacuated for two hours on the vacuum line to remove traces of chlorocarbons from the tungsten hexachloride crystals (3.8g, 9.6mmoles, 74%), which were steel-blue in colour.

3.4d Polymerisation of cyclopentene using the catalyst system $WCl_6/Na_2O_2/(i\text{-butyl})_3Al$

The procedure and apparatus were as described previously (3.4b), using the improvements made to the nitrogen system (see section 3.1b), the toluene was freshly distilled after refluxing over sodium under an atmosphere of dry nitrogen until a permanent blue colouration was obtained on the addition of a small crystal of benzophenone, the cyclopentene was freshly distilled from calcium hydride under dry nitrogen onto activated 4A molecular sieve, the tungsten hexachloride was prepared as described previously (3.4c), and the sodium peroxide and tri-isobutylaluminium were used as before without further purification.

The pre-mixed WCl_6/Na_2O_2 catalyst solution (1.5cm^3), as prepared previously (3.4b) was blue-black in colour and was injected using an air-tight syringe through a serum cap into the reaction vessel, containing a magnetic stirrer follower, dried, degassed toluene (30cm^3) and dried, degassed cyclopentene (7.74g, 110mmoles), under an atmosphere of dry nitrogen at room temperature. The solution immediately turned dark-red in colour, it was cooled to -10^o using an external acetone/solid carbon dioxide bath and tri-isobutylaluminium was injected using a micro-syringe.

The temperature of the reaction mixture was allowed to rise to 0^o, and then cooled to -10^o, being continually stirred and maintained under an atmosphere of dry nitrogen. After twenty minutes the reaction mixture was slightly viscous and after one hour its viscosity was such that the stirrer was unable to move. The reaction was terminated by the addition of methanol (2cm^3) with vigorous stirring. Precipitation of the polymer was accomplished by the addition of a five-fold excess of methanol. The poly(1-pentenylene) was dried under reduced pressure producing a creamy-white, elastic material (5.5g, 81mmoles, 74%), with correct i.r. and ^1H n.m.r. spectra (see section 3.1b). Details of the experiment are summarised in Table 3.4.

3.4e Attempted isomerisation of 1H,5H-hexafluorocyclopentene to 1H,2H-hexafluorocyclopentene by the pyrolysis with sodium fluoride

A mixture of 1H,2H-hexafluorocyclopentene and 1H,5H-hexafluorocyclopentene (3g, 17mmoles) was placed in a 25cm^3 test tube fitted with a Dreshel-head, the inlet of which was connected to a dry nitrogen supply and extended almost to the bottom of the tube and terminated in a narrow aperture. The outlet was connected to a silica pyrolysis tube (60cm x 14mm) packed with sodium fluoride pellets, the middle 40cm were heated in an electric furnace and the temperature at the outer surface of the silica tube was measured with a chrome-alumel thermocouple. The outlet of the furnace was connected to a trap immersed in liquid air, which was itself connected to a gas flow-meter.

The isomeric mixture of fluorocycloalkenes was slowly evaporated by bubbling a fine stream of dry nitrogen through the liquid at a rate of 20cm^{3}min^{-1}. The vapour was carried by the nitrogen stream through the pyrolysis zone heated to 300^o. The vapour which emerged from the tube was collected in the trap immersed in liquid air. Analytical g.l.c. (Column A, 150^o) of the product, showed that no observable isomerisation had taken place.

The same experiment was repeated with reduced flow rates of 15cm^{3}min^{-1} and 12cm^{3}min^{-1} and increased pyrolysis temperatures of 320^o and 340^o respectively. Analytical g.l.c. (Column A, 150^o) again showed that no observable isomerisation had taken place in either case.

3.4f Preparation of diethylaluminium chloride

Crude aluminium trichloride was purified by sublimation under reduced pressure (120°, 0.1mm Hg).

The purified anhydrous aluminium trichloride (3.65g, 27mmoles) was placed in a 50cm^3, 2-necked, round-bottomed flask containing a magnetic stirrer, fitted with a serum cap and stopper, in the glove-box under an atmosphere of dry nitrogen. The flask was removed from the glove-box, the stopper removed and the flask was quickly fitted to a distillation apparatus, which was purged with dry nitrogen. The flask was immersed in liquid nitrogen and tri-ethylaluminium (6.3g, 54mmoles) was slowly injected into the flask through the serum cap, using an air-tight syringe.

When addition was complete the flask was allowed to warm up slowly with stirring to room temperature, the mixture gradually darkened. It was heated at 60° for 30 minutes followed by fractional distillation under reduced pressure, to give a colourless liquid, diethylaluminium chloride (8.0g, 76%), b.p. 70-75° at 3mm Hg.

The experimental procedure and apparatus for:-

3.4g Attempted polymerisation of 1H,2H-hexafluorocyclopentene using the catalyst system $WCl_6/Na_2O_2/(i\text{-butyl})_3Al$

3.4h Attempted polymerisation of 1H,2H-hexafluorocyclopentene using the catalyst system $WCl_6/Na_2O_2/Et_2AlCl$

3.4i Polymerisation of cyclopentene using the catalyst system $WCl_6/Na_2O_2/Et_2AlCl$

3.4j Attempted polymerisation of 1H,2H-hexafluorocyclopentene using the catlyst system $WCl_6/Na_2O_2/Et_2AlCl$ at -20° and -60°

3.4k Attempted copolymerisation of 1H,2H-hexafluorocyclopentene and cyclopentene using the catalyst system $WCl_6/Na_2O_2/(i\text{-butyl})_3Al$

were identical to those used in the successful polymerisation of cyclopentene described previously (3.4d). A summary of the details of the individual experiments are given in Table 3.4.

All the polymerisation experiments were carried out under an atmosphere of dry nitrogen. The toluene, cyclopentene and tungsten hexachloride were purified as described (3.4d). The 1H,2H-hexafluorocyclopentene was purified using preparative g.l.c. (Column B, 70^o) and dried by vacuum transfer from P_2O_5. Before use all liquids were degassed using the freeze-thaw procedure. The order of addition of the various components to the polymerisation reactions were, solvent, cycloalkene, pre-mixed WCl_6/Na_2O_2 solution and finally the organo-aluminium compound. All the reactions were quenched by the addition of a small quantity of methanol and any polymer produced was precipitated by the addition of a five-fold excess of methanol.

Table 3.4

The ring-opening polymerisation of cyclopentene and the attempted ring-opening polymerisation of 1H,2H-hexafluorocyclopentene

Expt.[a,b]	Cycloalkene		WCl_6	Na_2O_2	Organo-aluminium component	Temperature during reaction	Reaction time	Yield
		mmole	mmole	mmole	mmole	°C	hours	%
3.4d	Cyclopentene	110	0.10	0.11	$(i\text{-butyl})_3Al$ 0.17	-10	1	74
3.4g	1H,2H-Hexafluorocyclopentene	67	0.05	0.077	$(i\text{-butyl})_3Al$ 0.10	-10	1	0
3.4i	Cyclopentene	114	0.10	0.12	Et_2AlCl 0.17	-10	1	75
3.4h	1H,2H-Hexafluorocyclopentene	66	0.07	0.08	Et_2AlCl 0.17	-10	2	0
3.4j	1H,2H-Hexafluorocyclopentene	66	0.07	0.08	Et_2AlCl 0.17	-20	4	0
	1H,2H-Hexafluorocyclopentene	66	0.07	0.08	Et_2AlCl 0.17	-60	7	0
3.4k	1H,2H-Hexafluorocyclopentene Cyclopentene	55 56	0.10	0.15	$(i\text{-butyl})_3Al$ 0.15	-10	2	77[c]

(a) In each experiment the pre-mixed WCl_6/Na_2O_2 solution was added to the monomer solution at 20°, and a colour change from blue-black to deep red was observed.

(b) In each experiment on addition of the organo-aluminium component to the reaction mixture a colour change from deep red to dark brown was observed.

(c) Yield was calculated for poly(1-pentenylene) based on the initial amount of cyclopentene.

CHAPTER 4

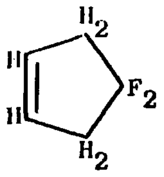
SYNTHESES AND ATTEMPTED SYNTHESES OF PARTIALLY FLUORINATED MONOCYCLOALKENES AND BICYCLOALKENES

4.1 Introduction

After the failure of the attempt to affect the ring-opening polymerisation of 1H,2H-hexafluorocyclopentene the course of the research work was directed towards the synthesis of fluorinated monomers in which the fluorine atoms were further removed from the carbon-carbon double bond than in 1H,2H-hexafluorocyclopentene. Mono- and bi-cyclic compounds were considered and this chapter describes both the work directed towards their synthesis and the characterisation of the compounds actually obtained.

4.2 Attempted synthesis of 4,4-difluorocyclopentene

4,4-Difluorocyclopentene (85) has the fluorine atoms as far away as possible, in a five-membered ring, from the carbon-carbon double bond and was therefore a primary objective. This section describes some possible synthetic routes to this substituted cyclopentene, unfortunately for one reason or another none of these routes were successful. However, they highlight some of the difficulties which can be encountered in synthetic organic chemistry even when the attempted synthesis involves only a small extrapolation from apparently well established chemistry.

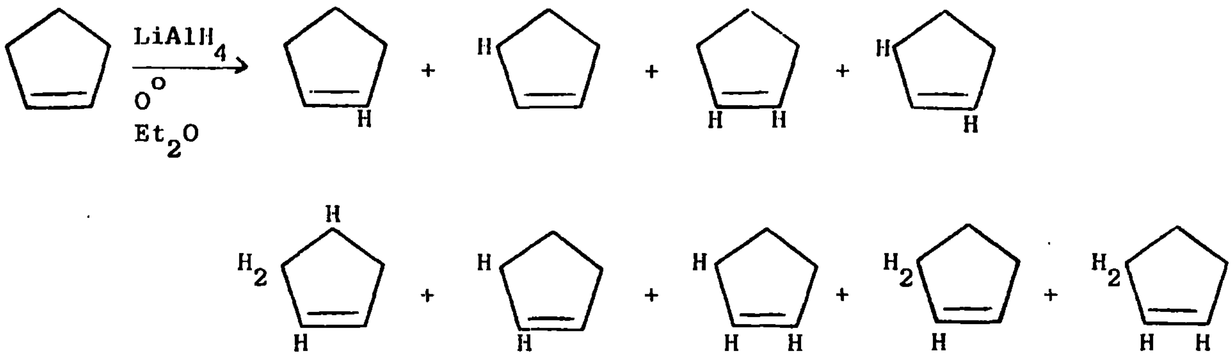


(85)

4.2a Reaction of perfluorocyclopentene with lithium aluminium hydride

The reactions of fluorocycloalkenes with lithium aluminium hydride have received considerable attention and have been extensively reviewed.[159]

Vinyl and allylic fluorines may be replaced by hydrogen whereas fluorine atoms on saturated non-allylic carbons are in general inert to attack. At first sight it may be thought that an extension of the reaction used to obtain 1H,2H-hexafluorocyclopentene, i.e. the lithium aluminium hydride reduction of the readily accessible perfluorocyclopentene, might yield the required product; however, in practice exhaustive reaction of perfluorocyclopentene with lithium aluminium hydride gives a complex mixture as shown in Figure 4.1, but no 4,4-difluorocyclopentene.[20] The outcome of the



(All unmarked bonds attached to fluorine atoms)

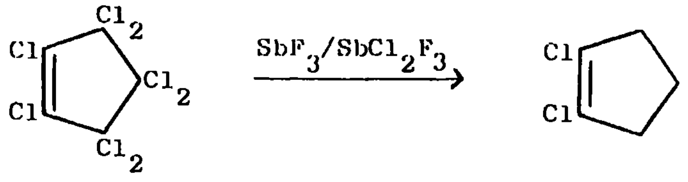
Figure 4.1

Products of lithium aluminium hydride reduction of perfluorocyclopentene

reaction can be rationalised in terms of addition-elimination process with hydride as the nucleophile, the reaction stopping when the number of allylic and vinylic fluorines is insufficient to activate the double bond to further attack.

4.2b Preparation of 4,4-dichlorocyclopentene

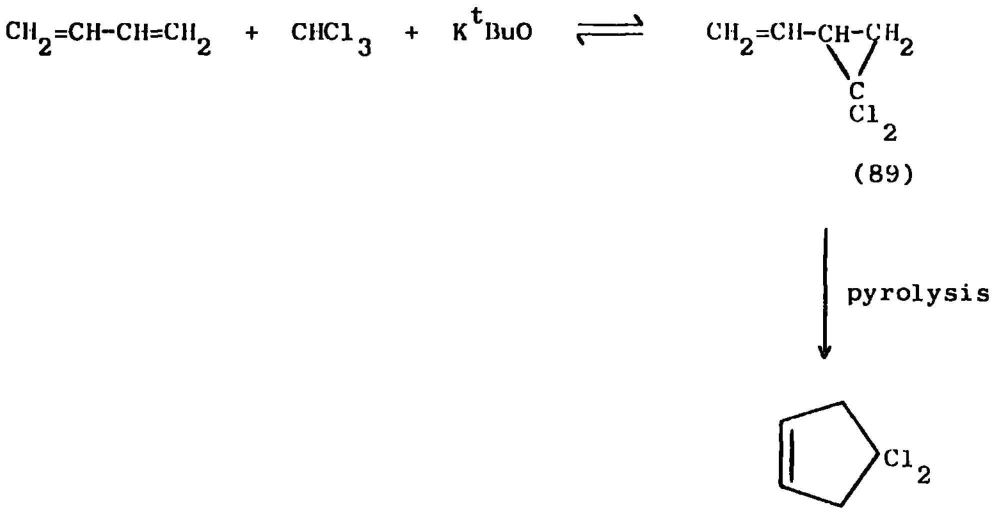
The synthesis of fluorinated compounds has been achieved by a variety of techniques, such as; reaction of an organic compound with hydrogen fluoride;[160] or elemental fluorine;[161] or metal fluorides,[162] the latter being the most important practical procedure. Antimony fluorides are also widely used in exchange fluorination of chlorinated organic compounds.[163] A very effective fluorinating agent of this type is a mixture of antimony trifluoride with a catalytic amount of either antimony pentafluoride or the mixed halide $SbCl_2F_3$; for example, perchlorocyclopentene (86) can be converted into 1,2-dichloro-hexafluorocyclopentene (87) in 72% yield using $SbF_3/SbCl_2F_3$.[164]



(86) (87)

(All unmarked bonds attached to fluorine atoms)

A possible route for the synthesis of 4,4-difluorocyclopentene is the exchange fluorination of 4,4-dichlorocyclopentene (88), which can be prepared as shown in Figure 4.2. This route was investigated and 1,1-dichloro-2-vinylcyclopropane (89) was prepared by the reaction of 1,3-



(88)

Figure 4.2

Synthesis of 4,4-dichlorocyclopentene

butadiene, chloroform and potassium t-butoxide.[165] The reaction of potassium t-butoxide on chloroform generates dichlorocarbene which reacts with 1,3-butadiene to form (89), the product was characterised by i.r. spectroscopy (Appendix C(II)), mass spectroscopy (Appendix B(I)) which establishes the molecular formula as $C_5H_6Cl_2$ with the parent ion M (m/e 136), the (M+4) and (M+2) peaks being 12% and 64% of the parent ion as required for a dichloro-compound. The thermal rearrangement of (89) produces 4,4-dichlorocyclopentene (88).

The pyrolysis was carried out in a dry nitrogen atmosphere to avoid side reactions. Accoring to the literature the temperature of the reaction is critical,[165] at temperatures lower than 250° isomerisation will not occur in significant amounts, at temperatures higher than 250° polymerisation of (89) becomes increasingly evident and at temperatures greater than 300° (88) begins to dehydrochlorinate. In practice the optimum conditions for pyrolysis were obtained after numerous trial runs. A pyrolysis temperature of 350° and a nitrogen flow rate of 70cm^3/min were found to produce the best results with the apparatus used in this work. Analytical g.l.c. indicated that the yield of (88) was 70%; the material recovery was in the region of 90%.

Earlier workers separated the isomers by small scale preparative g.l.c. using an Aerograph Model A350B which had a dual column with a packing comprised of 80% Chromosorb and 20% Carbowax 4000, terminated in terephthalic acid and a programmed temperature, ranging from 50° to 180° increasing at a rate of 6°/minute;[165] such equipment was not available to the author. However, the analytical g.l.c. trace (Column A, 150°) of the isomer mixture indicated that the separation of the individual components was quite good on available stationary phases, therefore separation of the isomers was attempted using a "home-made" large scale preparative gaschromatograph (Column B, 98°) which had an injection capacity of approximately 40g. Unfortunately, the material recovery from this attempt was only 20%, a fact attributed to decomposition of the isomer mixture on the hot nickel shot (150°) used in the pre-heater section of the column to ensure rapid vapourisation of the injected material. Although the pre-heater temperature was well below the polymerisation temperature of (89) and the dehydrochlorination temperature of (88), the hot metal surface may have acted as a catalyst for either or both reactions.

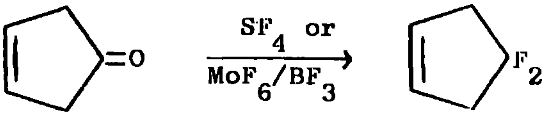
The boiling points of the two isomers are very similar, (89) 125° at 748mm Hg and (88) 123° at 760mm Hg. Separation using a Fischer Spaltrohr-system concentric tube fractionating column (HMS500, 75 theoretical plates) was attempted, but the isomers co-distilled. This was particularly surprising and disappointing in view of a recent report that separation could be accomplished by vacuum distillation.[158]

A small quantity of (88) was obtained pure by preparative g.l.c. (Column C, 150°) and was characterised by mass spectroscopy (Appendix B(II); parent peak M (m/e 136) and the expected (M+4) and (M+2) peak intensities for a dichloro-compound), i.r. (Appendix C(III)) and ^1H n.m.r. spectroscopy, Table 4.1.

The exchange fluorination of (88) using SbF_3/SbF_5 was not attempted, because of the difficulty in obtaining a large quantity of pure (88). Alternative routes to (85) were therefore examined.

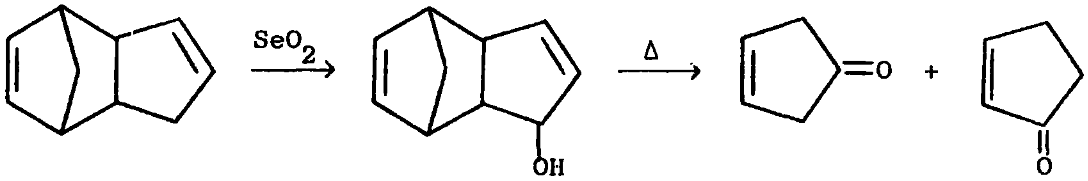
4.2c Synthesis and attempted fluorination of cyclopent-3-en-1-one

The selective replacement of oxygen atoms by fluorine in many types of organic compounds has been accomplished with sulphur tetrafluoride[166] and more recently with a mixture of molybdenum hexafluoride and boron trifluoride.[167] Of particular relevance to this work is the conversion of carbonyl to difluoromethylene, by either of these reagents, since this provided a possible synthetic route to (85) from cyclopent-3-en-1-one (90).



(90) (85)

Dashkevich reported the preparation of (90) by the pyrolysis of calcium adipate,[168] but Murdock et al were unable to repeat the work.[169] A more successful synthesis involves the selenium dioxide oxidation of dicyclopentadiene (91) to tricyclo[3.2.1.0^{2,6}]deca-3,8-dien-5-ol (92),[170] followed by the pyrolysis of the alcohol at 140° to give a mixture of cyclopent-2-en-1-one (93) and (90) which can be separated by fractional distillation.[171]



(91) (92) (90) (93)

Tsuchihashi et al have reported the synthesis of (90) using the synthetic route outlined in Figure 4.3.[172] The quoted yield of (90) was 53%, which is twice that quoted for the selenium dioxide oxidation/pyrolysis route; however, on the basis of starting material costs it is almost ten times cheaper to prepare (90) from dicyclopentadiene.

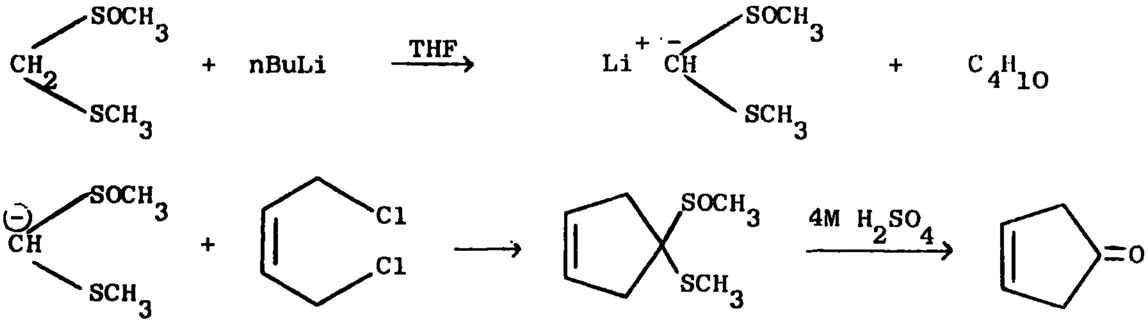
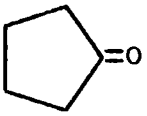


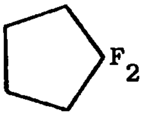
Figure 4.3

The high toxicity of sulphur tetrafluoride and the ease with which it hydrolyses to give hydrogen fluoride on contact with moisture make extreme care a prerequisite when working with this material, and since it is a gas, reactions at elevated temperatures require stainless steel autoclaves. On the other hand, although it reacts with moisture, reactions with molybdenum hexafluoride may be conveniently carried out in dry glassware; consequently the latter reagent catalysed by BF_3, was the preferred fluorinating agent.

The fluorination of cyclopentanone (94) using MoF_6/BF_3 in carbon tetrachloride was attempted as a model reaction, giving difluorocyclopentane (95) in 48% yield, after purification by preparative g.l.c., the product was fully characterised by mass spectroscopy (Appendix B(III)) with a parent peak M (m/e 106), i.r. (Appendix C(IV)), and ^1H n.m.r. and ^{19}F n.m.r. spectroscopy (see Table 4.1).



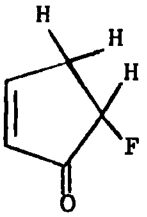
(94)



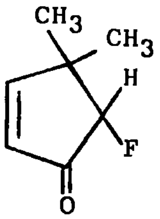
(95)

The synthesis and separation of (90) and (93) was accomplished without difficulty, both materials were characterised by i.r. (Appendix C(VI) and (VII)) and ^1H n.m.r. spectroscopy (Table 4.1), which were identical with reference spectra.

The product from the reaction of (90) with MoF_6/BF_3 was analysed by g.l.c. and found to contain two major components (estimated as an approximately 50 : 50 mixture), one of which was identified by g.l.c. enrichment experiments as (93) the isomer of the starting material, the other was assigned structure (96), 5-fluorocyclopent-2-en-1-one by comparison of the ^1H n.m.r., ^{19}F n.m.r. (Table 4.1) and i.r. (Appendix C(VIII)) spectra of the mixture with those available for pure cyclopent-2-en-1-one (93) and 5-fluoro-4,4-dimethylcyclopent-2-en-1-one (97).[173] Separation of the mixture was



(96)



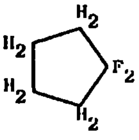
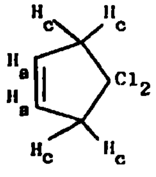
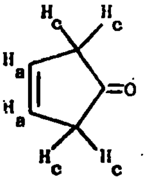
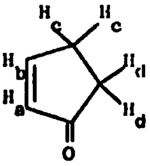
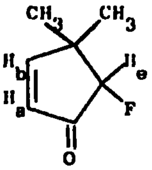
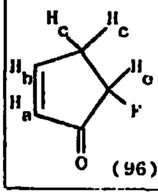
(97)

attempted by fractional distillation, but the material decomposed exothermically in the distillation apparatus liberating hydrogen fluoride.

The ^1H n.m.r. spectrum, Table (4.1), of the mixture was extremely complex, however, by subtracting those bands due to cyclopent-2-en-1-one the bands for (96) could be identified. The spectrum obtained showed two vinylic protons with chemical shifts and splitting patterns almost identical to those for the vinylic protons in (93) and (97); one tertiary proton, split into a double (J_{AB} = 51.5Hz), this coupling constant was identical to the coupling constant for the tertiary proton in (97) and the large coupling was observed in the ^{19}F n.m.r. spectrum for the tertiary fluorine (δ = 192.5ppm); and two methylene protons which had identical chemical shifts to the methylene protons in (93). The i.r. spectrum of the mixture showed a very broad band characteristic of $>$C=O stretch in the region 1710-1650cm^{-1} the broadness could not be accounted for by the $>$C=O stretch of (93) alone, however, the position of the absorptions definitely excludes a non-conjugated cyclopentenone as an acceptable structure for (96). This admittedly limited data allows the second component to be provisionally assigned as structure (96); the only plausible alternative, 4-fluorocyclopent-2-en-1-one, was disregarded, since an allylic fluorine substituent would be expected to have a more marked effect on the observed vinylic proton shifts.

Table 4.1

Spectroscopic data on substituted cyclopentane and cyclopentenes

Compound	^1H n.m.r. [a]					^{19}F n.m.r.	I.R. cm^{-1}		Reference
	H_a	H_b	H_c	H_d	H_e		$\nu_{C=O}$	$\nu_{C=C}$	
 (95)						94.0 [c]			
 (88)	5.50 (2)		3.03 (4)					1625	165,174
 (90)	6.12 (2)		2.80 (4)				1755	1608	171
 (93)	6.10 (1)	7.66 (1)	2.62 (2)	2.20 (2)			1702	1536	171,175
 (97)	6.00 (1)	7.50 (1)			4.54 (1)	205.9 [b] J_{FHe}=51.5Hz	1735		173
 (96)	6.27 (1)	7.61 (1)	2.62 (1)	2.20 (1)	5.73 (1)	192.5 [c] J_{FHe}=51.5Hz	1700	1580	

---

[a] Chemical shifts are given in ppm relative to Me_4Si as external reference. Integrated intensities are given in parentheses.

[b] This chemical shift was reported in ppm relative to C_6F_6 as external reference and for comparison purposes was converted to the $\delta_{(CFCl_3)}$ scale using the relation $\delta_{(CFCl_3)} \approx \delta_{(C_6F_6)} + 162.3$.

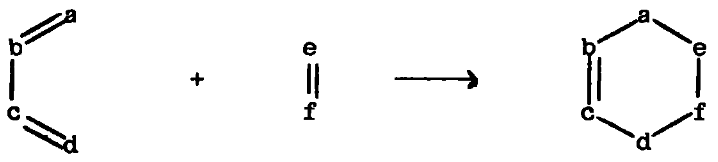
[c] Chemical shift is given in ppm relative to $CFCl_3$ as esternal reference.

[d] Data was obtained from i.r., ^1H n.m.r. and ^{19}F n.m.r. spectra of mixture.

4.3 Synthesis of partially fluorinated bicycloalkenes

4.3a The Diels-Alder reaction

The Diels-Alder reaction, which involves the 1,4-addition of a conjugated diene (98) and a dienophile (99), is a very useful synthetic method for the preparation of six-membered rings (100), because of the almost unlimited possibilities for variation of both diene and dienophile. One restriction is that the diene must be conjugated with the double bonds cis-orientated at the time of reaction, but the dienophile can be practically any unsaturated compound.



(98) (99) (100)

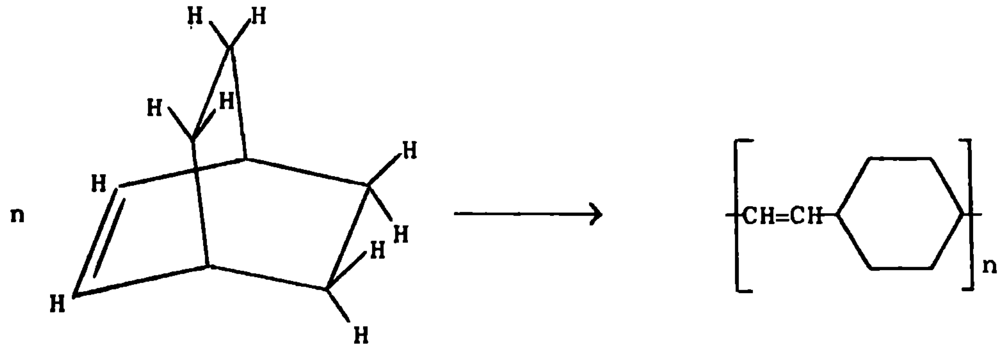
The Diels-Alder reaction may be divided into two extreme reaction types, firstly the normal Diels-Alder reaction in which dienes are activated by electron donating substituents, for example, $-NMe_2$, -OMe, $-CH_3$ and dienophiles are activated by electron withdrawing substituents, for example -CN, -COOMe, -CHO, $-NO_2$[176] and secondly the Diels-Alder reaction with Inverse Electron Demand, in which the diene is activated by electron-withdrawing substituents and the dienophile by electron-donating substituents.[177] If both components in the Diels-Alder reaction are either 'electron-rich' or 'electron-poor' the reaction is generally sluggish or does not occur; the greater the difference in character the faster the reaction proceeds.

The stereochemical outcome of the Diels-Alder reaction was initially formulated by Alder and Stein in their 'cis-principle',[178] which states that "the configurational relationships of the dienophile and diene are retained in the adduct". This fact is now recognised to be a consequence of the concerted nature of the cycloaddition. Hence the principles of orbital symmetry conservation elaborated by Woodward and Hoffmann may be applied, in which the Diels-Alder reaction is classified as a ($\pi2_s + \pi4_s$) cycloaddition reaction and is thermally allowed.[94]

Fluorinated dienes are in general less active in the Diels-Alder reaction than their hydrocarbon equivalent whereas fluorinated dienophiles are generally more reactive than their hydrocarbon equivalents. The Diels-Alder reactions of fluorinated compounds have been reviewed.[179]

4.3b Synthesis of 1,4,5,5,6,6-hexafluorobicyclo[2.2.2]oct-2-ene

Ofstead and Calderon have reported the ring-opening polymerisation of bicyclo[2.2.2]oct-2-ene (101),[63] to give poly(1,4-cyclohexylenevinylene) (102). This is the only example of a bicyclo[2.2.2]oct-2-ene ring system to undergo such a reaction. Polymerisation of this monomer is energetically favourable, since it removes the unfavourable eclipsing which occurs between four adjacent pairs of hydrogen atoms in the monomer and ring strain is released in going from the monomer to the polymer, because the monomer possesses two six-membered unsaturated rings constrained in the boat conformation, whereas in the linear polymer the cyclohexane ring is free to assume the less strained and more favourable chair conformation.



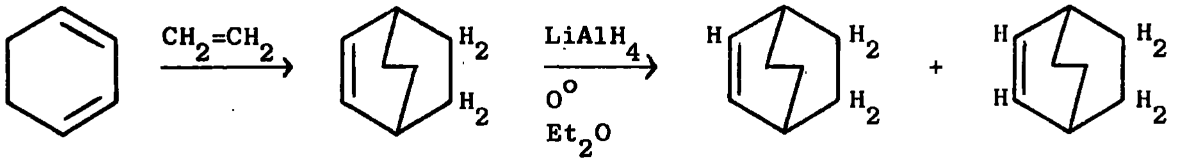
(101) (102)

As reported earlier (Table 3.3), the π-ionisation potential of 1,4,5,5,6,6-hexafluorobicyclo[2.2.2]oct-2-ene (103) is 10.50eV, this is midway between the values for cyclopentene (9.0eV) and 1H,2H-hexafluorocyclopentene (9) (12.05eV). Therefore (103) might be expected to coordinate more strongly to the transition metal complex than (9) and from the discussion above the bicyclo[2.2.2]oct-2-ene system is also susceptible to ring-opening polymerisation. For these reasons the synthesis of pure (103) was undertaken.

1 Synthesis of 1,4,5,5,6,6-hexafluorobicyclo[2.2.2]oct-2-ene from perfluorocyclohexa-1,3-diene

Perfluorocyclohexa-1,3-diene (104) was chosen as the starting material for the synthesis of (103), because it was relatively readily available, being prepared by a well established method.[180] It is stable with respect to dimerisation up to 250°, hence the yields of Diels-Alder adducts with moderately reactive dienophiles are not reduced by the formation of the diene-dimer. It is a typical electron-poor diene, giving high yields of adducts with electron-rich dienophiles, for example, $CH_2=CHOCH_3$, $CH_2=CHPh$ and $CH_2=CH_2$.

The synthetic route shown in Figure 4.4 was used;[181] (104) was reacted



(104) (105) (106) (103)

(All unmarked bonds attached to fluorine atoms)

Figure 4.4.

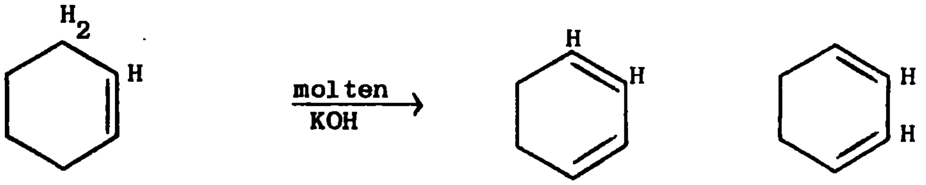
with ethylene at 200° in a sealed tube giving the Diels-Alder adduct 1,2,3,4,5,5,6,6-octafluorobicyclo[2.2.2]oct-2-ene (105) in good yield.

Proof that 1,4-addition of ethylene to the diene (104) had occurred and not 1,2-addition has been provided by Feast and Weston[182] who showed that the ^{19}F n.m.r. spectrum of (105) possessed only single resonances in the bridgehead and vinylic regions which is consistent only with the 1,4-addition product.

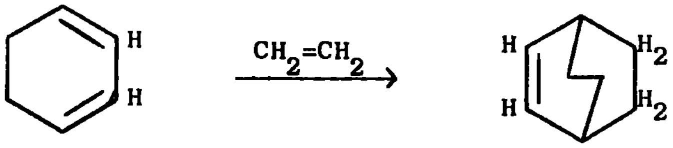
The nucleophilic replacement of vinylic fluorine atoms by hydride ions using an ethereal solution of excess lithium aluminium hydride at 0° gave a mixture of products (106) and (103). The large scale separation of these products was found to be very difficult and therefore an alternative route to (103) was examined.

2 Synthesis of 1,4,5,5,6,6-hexafluorobicyclo[2.2.2]oct-2-ene from 2H,3H-hexafluorocyclohexa-1,3-diene

One of the products from the lithium aluminium hydride reduction of perfluorocyclohexene is 1H,6H,6H-heptafluorocyclohexene (107); limited quantities of (107) were available and the two stage synthesis of (103) outlined below was undertaken.



(107) (108) (109)



(103)

(All unmarked bonds attached to fluorine atoms)

The dehydrofluorination of 1H,6H,6H-heptafluorocyclohexene (107) using molten potassium hydroxide produced a mixture of 2H,3H-hexafluorocyclohexa-1,3-diene (109) and 1H,2H-hexafluorocyclohexa-1,3-diene (108).[181] These were easily separated in large quantities (up to 40g/injection) using the 'home-made' preparative gaschromatograph. The i.r. spectra of pure (108) and (109) (Appendix C(X) and (XI) respectively) were identical with reference spectra.[181]

2H,3H-Hexafluorocyclohexa-1,3-diene (109) is a volatile liquid which is stable indefinitely when stored in the dark at room temperature. Its reactivity is similar to (104), acting as an electron-poor diene; with ethylene at 200° yields greater than 90% of the required Diels-Alder adduct (103) were attained. The absence of a strong absorption in the i.r. spectrum of (103) (Appendix C(XII)) due to -CH=CF- readily discounts the presence of any 1,2-addition product. Its i.r. spectrum was identical with a reference spectrum.[181]

Although this synthetic route did provide the required material (103) pure, the limited availability of the starting material (107) was a handicap for the preparation of the monomer (103) which would be required in reasonable quantities for extensive polymerisation studies.

Since none of the syntheses examined so far provided reasonable quantities of pure monomer without considerable labour, alternative partially fluorinated bicycloalkene systems were investigated; namely partially fluorinated bicyclo[2.2.1]hept-2-enes and bicyclo[2.2.1]hepta-2,5-dienes.

4.3c Synthesis of partially fluorinated bicyclo[2.2.1]hept-2-enes and bicyclo[2.2.1]hepta-2,5-dienes

As discussed in Chapter (1.2) and as will be discussed in more detail in Chapter (5.1) the ring-opening polymerisation of substituted bicyclo[2.2.1]-hept-2-enes and bicyclo[2.2.1]hepta-2,5-dienes has been extensively studied, where the substituents have been polar groups or atoms including, nitrile, ester, ether, imide, chlorine, bromine, acid anhydride and amine, but not fluorine. This section describes the synthesis and characterisation of a number of partially fluorinated bicyclo[2.2.1]hept-2-enes and bicyclo-[2.2.1]hepta-2,5-dienes.

These compounds are usually prepared in reasonable yields by the Diels-Alder reaction between cyclopentadiene and the appropriate fluorinated alkene or alkyne. This method provides a wide range of possible monomers and the work has been reviewed by Perry.[179] The choice of adducts to prepare was made on the grounds of:

(i) availability and cost of the fluorinated dienophile,

(ii) the recorded yield of the adduct.

The fluorinated dienophiles were purchased with the exception of 3,3,3-trifluoropropyne which was prepared by a well established synthetic method, namely the reaction of 3,3,3-trifluoro-1,1,2-trichloropropene with a mixture of zinc metal and zinc dichloride in N,N-dimethylacetamide, Figure 4.5.[183]

$$\mathrm{CF_3CCl{=}CCl_2} \xrightarrow[\text{N,N-dimethylacetamide}]{\mathrm{Zn,\ ZnCl_2}} \mathrm{CF_3C{\equiv}CH}$$

Figure 4.5

The 3,3,3-trifluoropropyne was characterised by mass spectroscopy (Appendix B(IV)) showing a parent peak M (m/e 94 (100%)) with the loss of a fluorine from the parent ion giving a strong peak M-F (m/e 73 (63%)). Its i.r. spectrum (Appendix C(XIII)) showed the characteristic $\equiv$C-H stretch, -C$\equiv$C- stretch and -C-F stretches at 3320cm^{-1}, 2150cm^{-1} and 1250-1150cm^{-1} respectively.

In general cyclopentadiene, freshly prepared by the thermal cracking of its dimer,[184] was sealed in vacuo in a Pyrex ampoule with the appropriate fluorinated dienophile and heated at the required temperature for the required time. The adducts (I) - (VI) which were synthesised, the reaction temperatures, duration of the experiments and yields of the adducts after purification are summarised in Table (4.2). All the adducts prepared, except (VI), have previously been reported in the literature.

Table 4.2

Preparation of partially fluorinated bicyclo[2.2.1]hept-2-enes and bicyclo[2.2.1]hepta-2,5-dienes

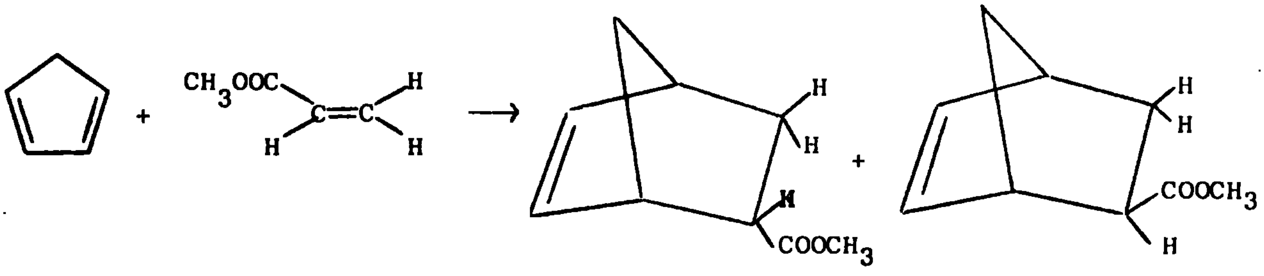
Adduct	Dienophile	Duration of Experiment Hours	Reaction Temperature °C	Yield [a] %	Reference
I	$CF_3CF{=}CF_2$	72	160	85	185
II	$CF_3CF{=}CFCF_3$	24	100	90	186
III	$CF_3CH{=}CH_2$	72	160	65	187
IV	$CF_3ClC{=}CClCF_3$	72	160	35	180
V	$CF_3C{\equiv}CCF_3$	24	100	90	186
VI	$CF_3C{\equiv}CH$	48	155	82	

[a] Based upon initial weight of cyclopentadiene

4.4 Characterisation and stereochemistry of partially fluorinated bicyclo[2.2.1]hept-2-enes

Each adduct was fully characterised by analysis and spectroscopy. Elemental analysis and mass spectroscopy (Appendix B(V)-(VIII)) confirmed the molecular formulae of the adducts (I) - (IV), they all exhibited a base peak at m/e 66 ($C_5H_6^+$), presumably arising from the retro-Diels-Alder reaction of the parent ion, this fragmentation mode is characteristic of bicyclo[2.2.1]hept-2-enes.[188] The i.r. spectra (Appendix C(XIV) - (XVII)) showed the characteristic, vinylic C-H stretch (3080cm^{-1}, weak), -CH=CH- stretch (1610-1631cm^{-1}, weak) and C-F stretches (1390-1000cm^{-1}, strong). The ^{19}F n.m.r. and ^{1}H n.m.r. spectra were generally more complex than would be expected for a single component, however, they can be explained by the fact that the individual adducts are produced as mixtures of geometric isomers.

The Diels-Alder addition of an unsymmetrically substituted or a symmetrically 1,2-disubstituted acyclic alkene to an unsubstituted or a symmetrically substituted cyclic diene leads to more than one geometric alternative, as is illustrated below for the reaction of ethyl acrylate and cyclopentadiene. In this case there are two products, the endo-(111) and exo-(112) isomers and they are formed in a ratio 76 : 24.[189] Clearly both

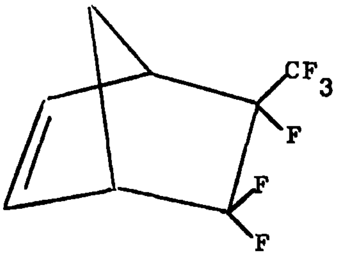


(110) (111) (112)

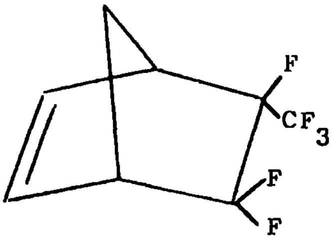
these isomers are dissymmetric and will be formed as a racemic mixture of enantiomers, however, since no attempt to separate enantiomers has been undertaken this aspect of adduct stereochemistry will be ignored in the following discussion. The adducts (I)-(IV) from the reaction of cyclopentadiene with the appropriate fluorinated alkene are formed as isomeric mixtures, the ratio of the individual isomers present can be obtained from an analysis of the ^{19}F n.m.r. spectra of the mixtures, Table (4.3), as will be explained below.

5,5,6-Trifluoro-6-trifluoromethylbicyclo[2.2.1]hept-2-ene (I)

The product obtained from the reaction of cyclopentadiene and hexafluoropropene gave two sets of signals in the ^{19}F n.m.r. spectrum in a ratio 60 : 40, corresponding to the two possible geometric isomers (Ia) and (Ib). The stereochemical assignment of these adducts were made by Stone et al and

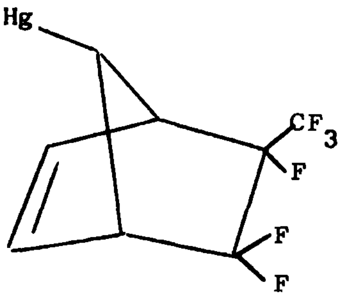


(Ia)

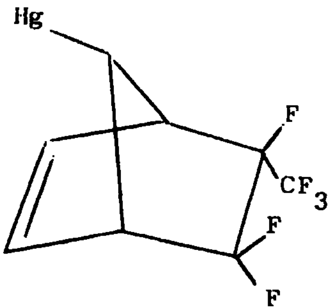


(Ib)

depends on assignments made for analogous bis(cyclopentadienyl)mercury compounds (113) and (114) prepared by them,[190] together with work reported

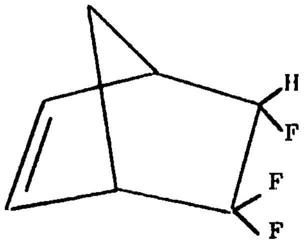


(113)

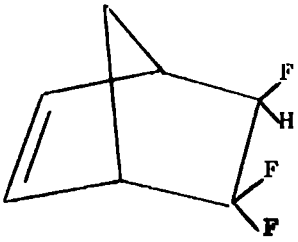


(114)

by Smart on the Diels-Alder adducts of trifluoroethylene with cyclopentadiene.[191] Smart assigned the major isomer the structure (115) on the basis of a detailed analysis of the ^{1}H and ^{19}F n.m.r. spectra of (115) and (116) assisted by selective decoupling experiments.



(115)

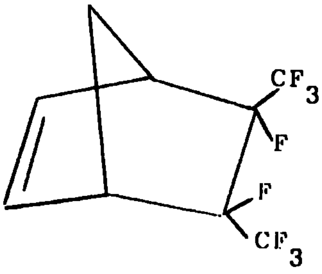


(116)

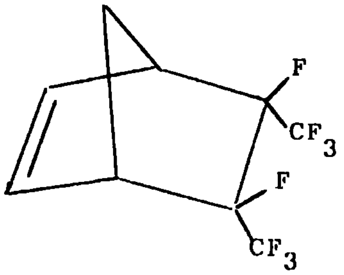
For adduct (115) there was no coupling between the endo-fluorine atoms whereas in adduct (116) the coupling between the exo-fluorine atoms was 12.5Hz. Stone used this observation to assign the $-CF_3$ group with the lower field chemical shift to the exo-structure (Ia), since none of the other fluorine signals associated with this isomer showed coupling of the order of 12.5Hz, whereas fluorine signals associated with the $-CF_3$ group with the higher field chemical shift showed coupling of 12.5Hz. This allowed them to make the generalisation 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 units in endo-positions, thus the assignment of all the peaks in the ^{19}F n.m.r. spectrum of adduct (I) was possible (Table 4.3); adduct (Ib) being the major component (60%). The signals in the ^{1}H n.m.r. spectrum of adduct (I) (Table 4.3) appear as broad unresolved bands.

5,6-Difluoro-5,6-bis(trifluoromethyl)bicyclo[2.2.1]hept-2-ene (II)

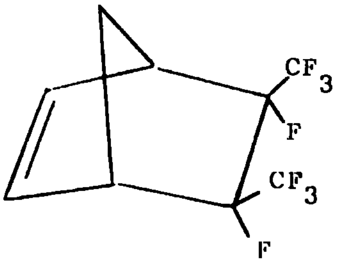
Analysis of the ^{19}F n.m.r. spectrum of the adduct obtained from perfluorobut-2-ene and cyclopentadiene revealed the presence of three isomers corresponding to (IIa), (IIb) and (IIc), this was an expected consequence of the fact that the perfluorobut-2-ene used was a mixture of cis and trans isomers.



(IIa)



(IIb)



(IIc)

Using the generalisation for the chemical shifts of exo- and endo-fluorine atoms the composition of the adduct mixture was determined. In the ^{19}F n.m.r. spectrum of the mixed product the major component (90%) has two signals in the $-CF_3$ region of equal intensity, and two signals in the tertiary fluorine region again of equal intensity. Therefore the major component must have structure (IIa), which has one exo-CF_3, one endo-CF_3, one exo-F and one endo-F. The remaining signals were attributed to the two possible cis-adducts (IIb) and (IIc), the integrated intensities were not sufficiently reliable to allow a calculation of their relative abundance. This assignment is in agreement with the results obtained by Stone et al.[186]

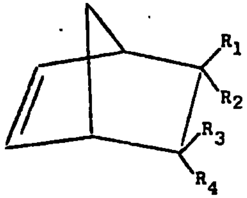
5-Trifluoromethylbicyclo[2.2.1]hept-2-ene (III)

In the case of the adducts from cyclopentadiene and 3,3,3-trifluoropropene the ^{19}F n.m.r. spectrum possessed two signals in the $-CF_3$ region revealing the presence of the two geometric isomers (IIIa) and (IIIb).

The peak with the lower field chemical shift was the major component (80%) and was assigned structure (IIIa) and the minor component (20%) with the higher field chemical shift peak was assigned structure (IIIb). The ^1H n.m.r. spectrum of the isomeric mixture was extremely complex and was not interpreted in detail.

Table 4.3.

^{1}H n.m.r. and ^{19}F n.m.r. data for partially fluorinated bicyclo[2.2.1]hept-2-enes



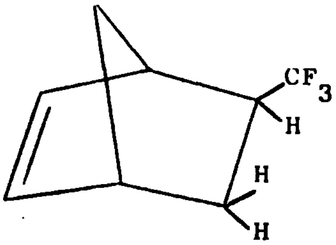
	Adduct					^{19}F n.m.r. [b]			^{1}H n.m.r. [c]			Reference
	%[a]	R_1	R_2	R_3	R_4	$-\overset{\mid}{\underset{\mid}{C}}-F$	$-CF_2-$	$-CF_3$	=CH-	$-CH_2-$	$-\overset{\mid}{\underset{\mid}{C}}-H$	
Ia	40	CF_3	F	F	F	167.97	105.68	72.65	6.41 (2)	2.30 (2)	3.35 (2)	28
Ib	60	F	CF_3	F	F	167.28	106.82	74.05	6.50 (2)	2.20 (2)	3.20 (2)	
IIa	90	CF_3	F	F	CF_3	168.2; 167.0 endo exo		72.2; 72.8 exo endo	6.56 (2)	2.36 (2)	3.50 (2)	29
IIb		CF_3	F	CF_3	F	162.6		71.0				
IIc		F	CF_3	F	CF_3	160.3		71.8				
IV	35	CF_3	Cl	Cl	CF_3[d]			62.57 (3) 65.11 (1)	6.41 (1) 6.31 (1)	δ_A 2.56 (1) δ_B 2.03 (1)	3.47 (1) 3.36 (3)	
IIIa	80	CF_3	H	H	H			63.94	5.96 (1) 6.19 (1)		2.00 (1)	30
IIIb	20	H	CF_3	H	H			68.62	6.19 (2)	1.50 (4)	2.92 (1) 2.98 (1)	

[a] Refers to the percentage of adduct in the isomer mixture.

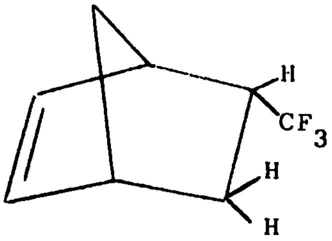
[b] Chemical shifts are given in ppm relative to $CFCl_3$ as external reference. Integrated intensities are given in parentheses.

[c] Chemical shifts are given in ppm relative to Me_4Si as external reference. Integrated intensities are given in parentheses.

[d] Unknown stereochemistry.



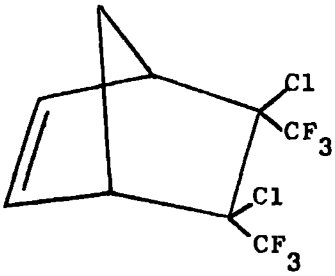
(IIIa)



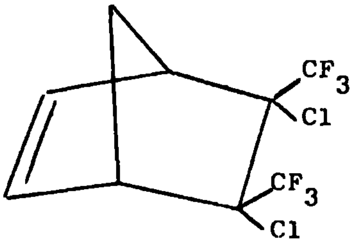
(IIIb)

5,6-Dichloro-5,6-bis(trifluoromethyl)bicyclo[2.2.1]hept-2-ene (IV)

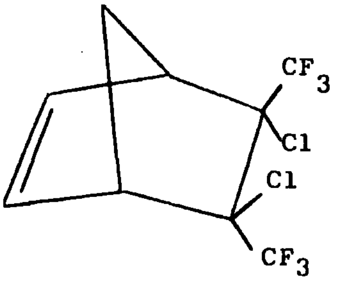
A complete stereochemical analysis of adduct (IV) prepared from the reaction of cyclopentadiene with 2,3-dichloro-2,3-bis(trifluoromethyl)but-2-ene was not possible. The geometric isomers which could be formed are (IVa), (IVb) and (IVc).



(IVa)



(IVb)



(IVc)

The ^{19}F n.m.r. spectrum of (IV) possessed at least two different -CF$_3$ signals with that at lower field chemical shift (62.57ppm) having an integrated intensity three times greater than that at higher field chemical shift (65.11ppm). The ^{1}H n.m.r. spectrum contain two distinct signals for the vinylic protons (6.41 and 6.31ppm) with equal integrated intensity (1 : 1), two signals for the tertiary protons (3.47 and 3.36ppm) with an integrated intensity ratio of 1 : 3, and an AB quartet (δ_A = 2.56, δ_B = 2.03 ppm; J_{AB} = 10Hz), with a total integrated intensity of 4. Analytical g.l.c.

(Column E, 150°) showed the presence of two components. However, it is not possible to reconcile the ^{19}F n.m.r. and ^{1}H n.m.r. spectra with a two or even three component mixture and it seems very likely that other products than isomers (IVa,b and c) are present in the mixture, possibly 2+2 adducts.

Separation of the individual geometric isomers of adducts (I), (II) and (III) has not been reported. Small scale preparative g.l.c. (Column F, 130°) allowed pure samples of isomers (Ib), (IIa), (IIIa) and (IIIb) to be obtained together with a 16 : 84 mixture of isomers (Ib) and (Ia), this latter was a low melting point waxy solid whereas pure (Ib) is a colourless liquid (b.p. 119°) which suggests that (Ia) would be a low melting point solid in the pure state.

4.5 Characterisation of the partially fluorinated bicyclo[2.2.1]hepta-2,5-dienes

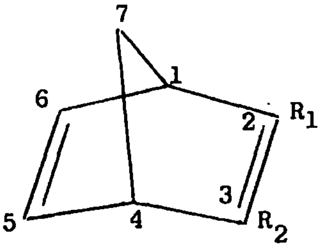
Both adducts (V) and (VI) were fully characterised by analysis and spectroscopy. Elemental analysis and mass spectroscopy (Appendix B(IX) and (X) respectively) confirmed their molecular formulae as $C_9H_6F_6$ (V) and $C_8H_7F_3$ (VI). Both adducts showed abundant parent ions, adduct (V) m/e 228 (26%) and adduct (VI) m/e 160 (22%) and their base peaks arose from the loss of CF_3.

The i.r. spectrum of adduct (V) (Appendix C(XVIII)) indicated the characteristic absorption at 1689cm^{-1} of the $-CF_3C{=}CCF_3-$ substituted double bond, while the i.r. spectrum of adduct (VI) (Appendix C(XIX)) indicated the characteristic absorption at 1645cm^{-1} of the $-CF_3C{=}CH-$ substituted double bond.

The ^{1}H n.m.r. and ^{19}F n.m.r. spectra of the two adducts, Table (4.4), were consistent with the proposed structures. The lack of symmetry in adduct (VI) produced bands in the ^1H n.m.r. spectrum with very complex splitting patterns.

Table 4.4

^1H n.m.r. and ^{19}F n.m.r. data for partially fluorinated bicyclo[2.2.1]hepta-2,5-dienes



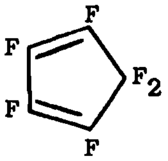
Adduct		^1H n.m.r. [a]				^{19}F n.m.r. [b]	IR	Reference
R_1	R_2	H_1,H_4	H_6,H_5	H_7	H_3		ν-CR_1=CR_2-	
CF_3	CF_3	3.97	7.02	2.23		63.3	1689	29
CF_3	H	3.70	6.90	2.20	7.20	67.4	1645	

[a] Chemical shifts are given in ppm relative to Me_4Si as external reference

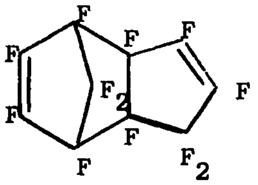
[b] Chemical shifts are given in ppm relative to $CFCl_3$ as external reference

4.6 The dehydrofluorination of 1H,5H,5H-pentafluorocyclopentene

Perfluorocyclopentadiene (117) dimerises readily at room temperature and slowly even at -22° to give the Diels-Alder dimer (118),[192] which has been

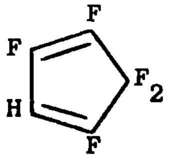


(117)

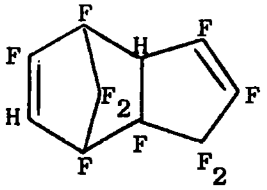


(118)

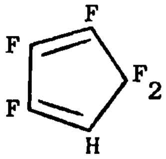
assigned endo-stereochemistry on the basis of detailed analysis of its ^{19}F n.m.r. spectrum.[193] 2H-Pentafluorocyclopentadiene (119) dimerises extremely rapidly to give as the major product (80-90%) the endo isomer of (120),[194] while 1H-pentafluorocyclopentadiene (121) is more stable towards dimerisation than (119) and appears to give two dimers in the ratio 5 : 2.[195]



(119)



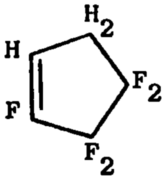
(120)



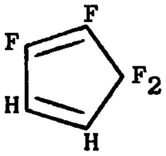
(121)

Diene (121) was prepared by the dehydrofluorination of 1H,5H-hexafluorocyclopentene using molten potassium hydroxide.

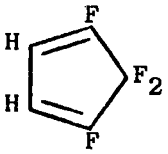
1H,5H,5H-Pentafluorocyclopentene (122) was available during the course of this work and it was believed that the dehydrofluorination of this material might give a mixture of dienes (123) and (124). It was hoped that these



(122)

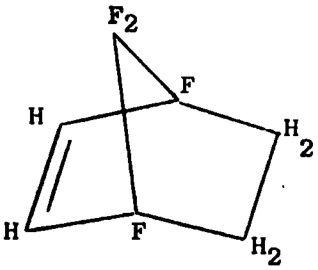


(123)



(124)

dienes would undergo dimerisation less readily than dienes (119) and (121) and therefore provide a synthetic route to the fluorinated bicyclo[2.2.1]hept-2-ene (125) by a Diels-Alder reaction of diene (124) with ethylene.



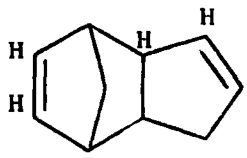
(125)

1,4,7,7-Tetrafluorobicyclo[2.2.1]hept-2-ene (125) shows some similarity to 1H,2H-hexafluorocyclopentene in the position of the fluorine atoms with respect to the carbon-carbon double bond. However, the increased ring strain of the bicyclo[2.2.1]hept-2-ene system may make the ring-opening polymerisation of (125) more favourable, consequently this monomer was of interest.

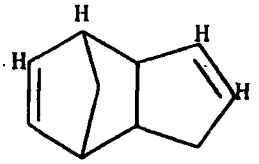
Dehydrofluorination of (122) was accomplished in a flow system using the action of molten potassium hydroxide upon the vapour of the fluoroalkene and condensing the products from the carrier gas (N_2) in a trap cooled in liquid air. Immediate g.l.c. analysis of the product showed the presence of four components. The shortest retained being identified by g.l.c. enrichment experiments as unreacted starting material. From g.c. mass spectroscopy all three longer retained compounds were found to have a parent ion m/e 276 (Appendix B(XI)), which establishes their molecular formulae as $C_{10}H_4F_8$, suggesting that they are dimers of dienes (123) and/or (124), with base peaks at m/e 138 ($C_5H_2F_4$) presumably arising from the retro-Diels-Alder reaction of the dimers.[188]

Separation of the dimers was attempted using the 'home-made' preparative g.l.c. apparatus, but unfortunately the recovery of the injected material (20g) was low (4g). Probably due to polymerisation or pyrolysis of the injected mixture on the pre-heater of the column. The retention time of the materials which were eventually eluted were extremely long and hence they were eluted with relatively large amounts of column packing. Separation of the pure adducts from this material was difficult and only one dimer was obtained in a pure state.

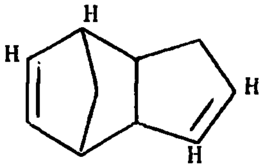
All the possible dimers which could be formed from the two dienes (123) and (124) are shown below (126) - (134), for each structure both exo- and endo-stereochemistries are possible.



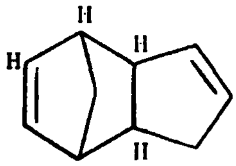
(126)



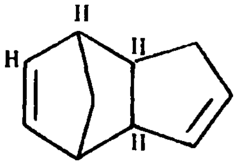
(127)



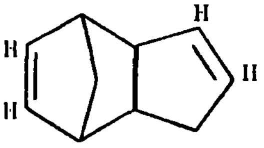
(128)



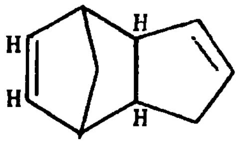
(129)



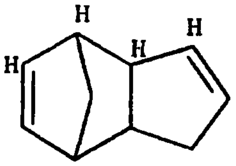
(130)



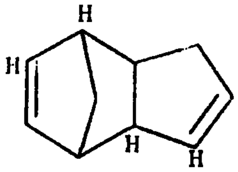
(131)



(132)



(133)



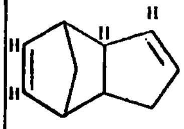
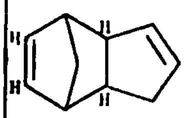
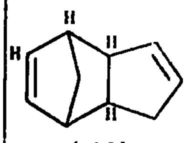
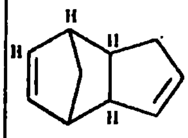
(134)

(All unmarked bonds attached to fluorine atoms)

The i.r. spectrum (Appendix C(XX)) of the pure dimer showed the characteristic absorptions at 1590cm^{-1} and 1690cm^{-1} of the -CH=CH- unsubstituted double bond and the -CF=CH- substituted double bond respectively. This suggests that the dimer has either structure (126) or (127) or (128). The ^{19}F n.m.r. spectrum, Table (4.5), confirms structure (126), showing: three tertiary fluorines, two at the bridgeheads and one at C-6; one vinylic fluorine assigned to C-4; and two AB quartets with that at lower field (δ_A = 103.9, δ_B = 113.8ppm; J_{AB} = 280Hz and integrating to two fluorine atoms) being assigned to the geminal fluorine atoms at C-5 and that at higher field (δ_A = 125.3, δ_B = 138.6ppm; J_{AB} = 180Hz and integrating to two fluorine atoms) to the geminal fluorine atoms at C-10, in accordance with

Table 4.5

Data on dimers from dienes (123) and (124)

Adduct	^{19}F n.m.r.^{a}					I.R. cm^{-1}			% ^{b}
	=CF-	$\geq$C-F	-CF$_2$-						
			δ_A	δ_B	J_{AB}	ν-FC=CF-	ν-HC=CF-	ν-CH=CH-	
 (126)	127.6 (1)	187.2 (1) 195.9 (1) 203.9 (1)	103.9 125.3	113.8 138.6	280 180		1690	1590	47
 (132)	129.9 (1) 155.6 (1)	191.4 (1) 194.7 (1)	82.4 130.9	101.7 142.5	250 180	1780		1600	38
 (129)	124.8 (1) 128.3 (1) 154.2 (1)	181.6 (2)	82.9 119.0	99.9 135.9	260 180	1780	1700		5
 (130	118.1 (1) 118.6 (1) 168.4 (1)		105.1 116.4	111.0 133.3	250 195				10

[a] Chemical shifts are given in ppm relative to CFCl$_3$ as external reference. Integrated intensities are given in parentheses.

[b] Percentage of dimer in original product mixture calculated from relative integrated intensities of tertiary fluorines.

previously published data on dimers (118) and (120).[196] A large coupling (doublet 35Hz) is observed in the lower field part of the AB quartet due to the fluorine atoms at C-10, which suggests that one of these fluorine atoms is strongly coupled to another fluorine atom. This splitting can be identified in the signal of the tertiary fluorine atom at C-6. Similar couplings have been observed between fluorine atoms at C-10 and C-6 in compounds (118) and (120) and this suggests that the dimer has an endo-configuration, since such coupling would not occur in the exo-structure. If a tertiary fluorine atom was present at C-2 as well as C-6, as in structure (118), the lower field part of the AB quartet at C-10 would be more complex; as was observed in the case of (118) where it occurred as a doublet of doublets, with couplings of 37Hz and 24Hz to the tertiary fluorines at C-6 and C-2 respectively.

The structure of the other two dimers can be assigned although for these materials complete separation from the column packing was not achieved. ^{19}F N.m.r. data were obtained, Table (4.5), since this was not affected by the impurities and i.r. data were obtained by comparison of the i.r. spectrum of the mixture of dimers plus impurities with that of the impurities. For one of the dimers absorptions at 1780cm^{-1} and 1600cm^{-1} are characteristic of the -CF=CF- substituted double bond and -CH=CH- unsubstituted double bond respectively, suggesting that the dimer has structure (132). The ^{19}F n.m.r. spectrum confirms this assignment showing: two signals in the tertiary fluorine region, of similar intensity and chemical shift and integrating to one fluorine atom each and assigned to the bridgehead fluorines; two vinylic fluorines; and two AB quartets, that at lower field (δ_A = 82.4, δ_B = 101.7ppm; J_{AB} = 250Hz and integrating to two fluorine atoms) assigned to the geminal fluorine atoms at C-5 and that at higher field (δ_A = 130.9,

δ_B = 142.5ppm; J_{AB} = 180Hz and integrating to two fluorine atoms) assigned to the geminal fluorine atoms at C-10, as before.

For the remaining dimer the i.r. spectrum showed absorption at 1700cm^{-1} and 1780cm^{-1} characteristic of the -CH=CF- and -CF=CF- substituted double bonds respectively, suggesting the structure (129) or (130). The ^{19}F n.m.r. spectrum was complex, but the integrated intensities of the different fluorine signals may be divided into two groups, consistent with a mixture of the two dimers, (129) and (130).

The integrated intensities of the signals due to the tertiary fluorines in the ^{19}F n.m.r. spectrum of the original product from the dehydrofluorination of (122) allows the amount of each dimer present to be calculated, Table (4.5). From which it may be concluded that dienes (124) and (123) were produced in a 2 : 1 ratio on dehydrofluorination of (122) and that 1,2- rather than 1,4-dehydrofluorination is the preferred mode of reaction. The dimers were more reactive than had been hoped and the original objective of this work, the synthesis of 1,4,7,7-tetrafluorobicyclo[2.2.1]hept-2-ene (125), was not attained.

EXPERIMENTAL

4.7 Attempted preparations of 4,4-difluorocyclopentene

4.7a Reagents

Analar chloroform, 1,4-dioxane, 1,3-butadiene and selenium dioxide were purchased from BDH Chemicals Ltd.; dicyclopentadiene was purchased from Koch-Light Laboratories Ltd; and molybdenum hexafluoride and boron trifluoride were purchased from Bristol Organics Ltd.; all these reagents were used without further purification. Analar n-pentane purchased from BDH Chemicals Ltd. and purified by fractional distillation.

4.7b Preparation of 1,1-dichloro-2-vinylcyclopropane (89)

Potassium t-butoxide (53g, 552mmoles), prepared by an established route,[197] and freshly distilled analar n-pentane (400cm^3) were placed in a 1dm^3, 3-necked, round-bottomed flask, fitted with a mechanical stirrer, thermometer, a gas-inlet and a condenser cooled by an acetone/solid carbon dioxide mixture. The flask was cooled to -24° using an external acetone/solid carbon dioxide bath and 1,3-butadiene (28g, 520mmoles) was bubbled into the mixture over a period of two hours. When addition of butadiene was complete the gas inlet tube was replaced by a dropping funnel and chloroform (57g, 535mmoles) was added dropwise to the vigorously stirred reaction mixture at such a rate that the reaction temperature did not rise above -10°. The mixture became yellow during the addition of chloroform. After addition of all the reagents the mixture was stirred vigorously for 90 minutes at -24° and then allowed to warm up slowly to room temperature, unreacted 1,3-butadiene was evolved as the temperature increased. Dilute hydrochloric acid (100cm^3) was carefully added, the organic layer separated, washed with distilled water, separated, dried over anhydrous magnesium sulphate, filtered and the filtrate fractionally distilled (vacuum-jacketed column, 60cm x 1.5cm, Fenske glass helices).

Analytical g.l.c. (Column A, 90°) of the major fraction from the distillation showed the presence of one major component, 1,1-dichloro-2-vinylcyclopropane (89) (59g, 430mmoles, 86%), b.p. 126°, with the correct i.r. spectrum.[165]

4.7c Preparation of 4,4-dichlorocyclopentene (88)

The apparatus consisted of a silica tube (60cm x 2cm internal diameter) lightly packed with glass wool. The tube was clamped in a vertical position, with the middle 40cm heated in an electric furnace and the temperature at the outer surface of the tube was measured with a chrome-alumel thermocouple. Samples were admitted under an atmosphere of dry nitrogen at the top of the silica tube using a pressure-equalised dropping funnel and the other end of the tube was connected to a trap cooled in liquid air, which in turn was connected to a gas flow meter.

1,1-Dichloro-2-vinylcyclopropane (10g, 73mmoles) was added dropwise over a period of one hour with a nitrogen flow rate of 70cm^3/minute and a furnace temperature (at the centre) of 350°. Analytical g.l.c. (Column A, 90°) of the product showed it to contain: (i) 4,4-dichlorocyclopentene (88) (about 70%); (ii) unreacted 1,1-dichloro-2-vinylcyclopropane (about 20%) and (iii) unidentified minor products (about 10%). Pure (88) was obtained using preparative g.l.c. (Column C, 150°), B.p. 122°, with the correct i.r. and ^{1}H n.m.r. spectra.[165,174]

4.7d Preparation of cyclopent-3-en-1-one (90) and cyclopent-2-en-1-one (93)

Dicyclopentadiene (182g, 1.38 moles) was mixed with 1,4-dioxane (500cm^3) and water (50cm^3) in a 3dm^3, 3-necked, round-bottomed flask, fitted with a nitrogen inlet, mechanical stirrer and reflux condenser. Selenium dioxide (62g, 0.56 moles) was added to the mixture and the solution was stirred under reflux for three hours. The resultant dark brown mixture was allowed to cool to room temperature, the metallic selenium was filtered off and the filtrate was poured slowly into a separating funnel containing water (2dm^3). The heavy dark brown oil which separated to the bottom of the funnel was drawn off and the aqueous layer was extracted with diethyl ether (200cm^3). The original oil and ether extract were combined, dried over anhydrous magnesium sulphate, filtered, the solvents removed under reduced pressure. The residual oil was fractionally distilled under reduced pressure using a Vigreux fractionating column (22cm x 2cm internal diameter) to give tricyclo[3.2.1.0^{2,6}]deca-3,8-dien-5-ol (92) (98g, 0.67moles, 48%) as a very viscous, pale yellow liquid, which solidified on standing, B.p. 84^o at 3mm Hg (Lit: 84^o at 3mm Hg),[170] ν_{max} 3320cm^{-1} (-OH).

The alcohol (92) (41.7g, 0.28moles) was placed in a 500cm^3, 1-necked, round-bottomed flask, fitted with a claisen head with a 15cm-long side-arm and a gas inlet which extended almost to the bottom of the flask through which a slow stream of dry nitrogen flowed. The material was heated using a free flame, the temperature at the distillation head was maintained between 140-150^o. The products were collected in a flask cooled in liquid air and immediately fractionated using a Fischer Spaltrohr-system concentric tube fractionating column (HMS500, 75 theoretical plates) to give: (i) cyclopent-3-en-1-one (90) (9.61g, 135mmoles, 24%), B.p. 50^o at 66mm Hg (Lit:[171] 41^o at 44mm Hg), ν_{max} 1755cm^{-1} ($\rangle$C=O); (ii) cyclopent-2-en-1-one (93) (8.5g, 118mmoles, 21%), B.p. 58-60^o at 27mm Hg (Lit:[172] 151^o at 763mm Hg), ν_{max} 1702cm^{-1} ($\rangle$C=O); (iii) cyclopentadiene (17.2g, 260mmoles, 46%); (iv) unidentified polymeric pot residue (4g).

4.7e Fluorination of cyclopentanone using molybdenum hexafluoride and boron trifluoride

Carbon tetrachloride (100cm^3) distilled from P_2O_5 and stored over 4A molecular sieve was placed in a 500cm^3, 3-necked, round-bottomed flask, fitted with a mechanical stirrer, a gas-inlet, a dropping funnel and water condenser. Molybdenum hexafluoride (8g, 42mmoles) was added dropwise, the mixture immediately turned dark brown in colour. It was cooled to 0^{o} using an external acetone/solid carbon dioxide bath and a fast stream of boron trifluoride was bubbled through the mixture for eight minutes with vigorous stirring. The solution was cooled to -15^{o} and freshly distilled cyclopentanone (7.5g, 89mmoles) diluted in carbon tetrachloride ($45cm^{3}$) was added dropwise, the solution became dark red. When addition was complete the solution was allowed to warm up slowly to room temperature and stirred for four hours. Water ($50cm^{3}$) was added dropwise to the reaction mixture which was cooled in an external ice/water bath. The organic layer was separated, dried over anhydrous sodium sulphate and filtered. Analytical g.l.c. (Column A, 70^{o}) showed the presence of three components which were separated by preparative g.l.c. (Column D, 100^{o}) to give: (i) difluorocyclopentane (95) (4.5g, 42mmoles, 48%), ^{19}F n.m.r. a quintet at 94.0 ppm (J = 14Hz), ν_{max} 1350-1100cm^{-1} (-C-F absorptions); (ii) carbon tetrachloride; (iii) unreacted cyclopentanone (2.7g, 36mmoles).

4.7f Attempted fluorination of cyclopent-3-en-1-one using molybdenum hexafluoride and boron trifluoride

Using the procedure described above (4.6e), cyclopent-3-en-1-one (14.3g, 174mmoles), molybdenum hexafluoride ($14cm^{3}$, 73mmoles) and boron trifluoride were reacted together using dichloromethane as solvent. Analytical g.l.c. (Column E, 125^{o}) of the product showed the presence of two components one of which was identified as cyclopent-2-en-1-one and the other was assigned 5-fluorocyclopent-2-en-1-one (96) (4.2c). Attempted separation of this mixture by fractional distillation using a Fischer Spaltrohr-system concentric tube fractionating column (FB-MMS200, 30 theoretical plates) resulted in the material polymerising in the distillation flask, no tractable products were isolated.

4.8 Preparation of 1,4,5,5,6,6-hexafluorobicyclo[2.2.2]oct-2-ene

4.8a Reagents

Ethylene was used as purchased from BDH Chemicals Ltd., and lithium aluminium hydride was used as purchased from Hopkin and Williams without further purification. Perfluorocyclohexa-1,3-diene and 1H,6H,6H-heptafluorocyclohexene were available having been prepared by well established routes by earlier workers.[181]

4.8b Preparation of 1,2,3,4,5,5,6,6-octafluorobicyclo[2.2.2]oct-2-ene (105)

A mixture of perfluorocyclohexa-1,3-diene (104) (6.88g, 30.6mmoles) and ethylene (1.26g, 45mmoles) was sealed in vacuo in a 150cm^3 Pyrex ampoule which was heated for 15 hours at 180°. After the tube had cooled to room temperature the volatile materials were removed by vacuum transfer and the major product, a white waxy solid, was dissolved in dry ether. Evaporation of the solvent and bulb to bulb vacuum transfer gave 1,2,3,4,5,5,6,6-octafluorobicyclo[2.2.2]oct-2-ene (105) (7.3g, 29mmoles, 90%) M.p. 98-99.5° (Lit:[181] 98-99°), with correct (Appendix C(IX)) i.r. spectrum, ν_{max} 1751cm^{-1} (-CF=CF-).

4.8c Reaction of 1,2,3,4,5,5,6,6-octafluorobicyclo[2.2.2]oct-2-ene with lithium aluminium hydride

A solution of 1,2,3,4,5,5,6,6-octafluorobicyclo[2.2.2]oct-2-ene (105) (28g, 111mmoles) in dry ether (50cm^3) was added dropwise at room temperature under an atmosphere of dry nitrogen to a vigorously stirred suspension of lithium aluminium hydride (10g, 259mmoles) in dry ether (500cm^3), the mixture was then refluxed for four hours. Excess lithium aluminium hydride was destroyed by the cautious dropwise addition of water to the vigorously stirred mixture, maintained at room temperature by a large water bath. Sufficient dilute sulphuric acid was added to dissolve all the inorganic salts and the ether layer was separated, dried over anhydrous magnesium sulphate, filtered and the bulk of the ether removed by fractional distillation (vacuum-jacketted column; 50cm x 1cm i.d., Fenske glass helices). Careful bulb to bulb vacuum transfer gave a white waxy solid (20.5g). Analytical g.l.c. (Column A, 150°) of an ethereal solution of the product showed the presence of two components. Separation was carried out using a 'home-made' preparative gaschromatograph (Column B, 102°), to give: (i) 1,2,4,5,5,6,6-heptafluorobicyclo[2.2.2]oct-2-ene (106) (3.5g, 15mmoles, 14%), M.p. 119-120°, (Lit:[181] 120-121°), M (Mass spectroscopy), 234, with correct i.r. spectrum, ν_{max} 1681cm^{-1} (-CH=CF-); (ii) 1,4,5,5,6,6-hexafluorobicyclo[2.2.2]oct-2-ene (103) (1.2g, 5.6mmoles, 5%), M.p. 142-144°, (Lit:[181] 145-146°), M (Mass spectroscopy), 216, with correct i.r. spectrum, ν_{max} 1623cm^{-1} (-CH=CH-); (iii) a 50 : 50 mixture of (106) and (103) (3.0g).

4.8d Preparation of 1H,2H- and 2H,3H-hexafluorocyclohexa-1,3-dienes

1H,6H,6H-Heptafluorocyclohexene (107) (10.2g, 49mmoles) was bubbled through molten potassium hydroxide at 190° in a fast stream of nitrogen. The product vapours were trapped in a glass trap cooled in liquid air. Analytical g.l.c. (Column A, 150°) of the product (6.8g) showed the presence of three components, a trace amount of starting material and a mixture of 1H,2H- and 2H,3H-hexafluorocyclohexa-1,3-dienes, the latter being present in a larger amount than the former. The mixture was separated using a 'home-made' preparative gaschromatograph (Column B, 100°). The materials obtained in a typical separation from the injection of the mixture (18.7g) were: (i) 1H,2H-hexafluorocyclohexa-1,3-diene (108) (6.7g), with correct[181] i.r. spectrum, ν_{max} 1750cm^{-1} (-CF=CF-); (ii) 2H,3H-hexafluorocyclohexa-1,3-

diene (109) (7.0g), with correct[181] i.r. spectrum, ν_{max} 1590cm^{-1} (-CH=CF-); and (iii) an intermediate fraction 3g of (108) and (109); overall material recovery 89%.

4.8e Preparation of 1,4,5,5,6,6-hexafluorobicyclo[2.2.2]oct-2-ene from 2H,3H-hexafluorocyclohexa-1,3-diene

A mixture of 2H,3H-hexafluorocyclohexa-1,3-diene (2.3g, 12.2mmoles) and ethylene (1.26g, 45mmoles) were sealed in vacuo in a 150cm^3 Pyrex ampoule which was heated for 14 hours at 200°. After the tube had cooled to room temperature the products were removed by conventional vacuum transfer techniques to give: (i) a trace amount of unreacted 2H,3H-hexafluorocyclohexa-1,3-diene; (ii) 1,4,5,5,6,6-hexafluorobicyclo[2.2.2]oct-2-ene (103) (2.24g, 10.4mmoles, 85%), M.p. 143-144°, (Lit:[181] 145-146°), with correct i.r. spectrum, ν_{max} 1623cm^{-1} (-CH=CH-), M (mass spectroscopy), 216.

4.9 Preparation of partially fluorinated bicyclo[2.2.1]hept-2-enes and bicyclo[2.2.1]hepta-2,5-dienes

4.9a Reagents

Cyclopentadiene was freshly prepared by thermal cracking[184] from dicyclopentadiene purchased from Koch-Light. The fluoroalkenes and fluoroalkyne were purchased from Bristol Organics Ltd., and used without further purification, except for 3,3,3-trifluoropropyne which was prepared as described below. N,N-Dimethylacetamide was purchased from BDH Chemicals Ltd., and fractionally distilled. All liquid reagents were degassed using the freeze-thaw procedure before being sealed in vacuo in a Pyrex ampoule (approximately 150cm^3 capacity).

4.9b Preparation of 3,3,3-trifluoropropyne[183]

Zinc (36g, 554mmoles), zinc chloride (3.4g, 25mmoles) and freshly distilled N,N-dimethylacetamide (300cm^3) were stirred and heated to 100^o in a 1dm^3, 3-necked, round-bottomed flask, fitted with a mechanical stirrer, water cooled condenser, thermometer, and pressure equalised dropping funnel. The temperature was maintained between 85-100^o by careful addition of 3,3,3-trifluoro-1,1,2-trichloropropene (50g, 250mmoles). The reaction mixture was allowed to cool to 50-60^o under a positive pressure of nitrogen. Water (100cm^3) was carefully added dropwise to the vigorously stirred mixture, the temperature being maintained between 50-60^o. The gas evolved slowly, was collected in a trap immersed in liquid air, when addition of the water was complete the reaction mixture was heated at 80^o for 2 hours. The gaseous product was allowed to distil under reduced pressure into a pre-weighed metal can to give 3,3,3-trifluoropropyne (22.6g, 240mmoles, 96%), M (mass spectroscopy), 94, with correct i.r. spectrum, ν_{max} 3320cm^{-1}, 2150cm^{-1} and 1250-1150cm^{-1} ($\equiv$C-H stretch, -C$\equiv$C- stretch and -CF stretches respectively).

4.9c Reaction of cyclopentadiene with fluoroalkene or fluoroalkyne

General procedure

The required amount of cyclopentadiene was injected into the Pyrex carius tube together with a small quantity of hydroquinone and degassed by the freeze-thaw procedure. A known volume of the fluoroalkene or fluoroalkyne was condensed into the tube (except for the case of 2,3-dichlorohexafluorobut-2-ene which was injected into the tube), which was then sealed under vacuum. The tube was placed in a furnace and heated for the required time and at the required temperature. After cooling to room temperature, the tube was removed from the furnace and cooled in liquid air, the seal was broken by 'hot spotting' and the products recovered by careful bulb to bulb vacuum transfer.

1. Hexafluoropropene (10g, 67mmoles), cyclopentadiene (4.43g, 67mmoles) and hydroquinone (0.45g) were sealed in vacuo and heated at 160° for 72 hours to give: (i) 5,5,6-trifluoro-6-trifluoromethylbicyclo[2.2.1]hept-2-ene (I) (12.27g, 57mmoles, 85%) [Found: C,44.7; H, 3.0; F, 52.3%; $C_8H_6F_6$ requires C, 44.5; H, 2.8; F, 52.7%], M (mass spectroscopy), 216, B.p. 140-141° (Lit:[185] 140-140.5°), with correct i.r. spectrum; (ii) dicyclopentadiene and cyclopentadiene.

2. Perfluorobut-2-ene (13.4g, 67mmoles), cyclopentadiene (4.46g, 67mmoles) and hydroquinone (0.45g) were sealed in vacuo and heated at 100° for 24 hours to give: (i) 5,6-difluoro-5,6-bis(trifluoromethyl)bicyclo[2.2.1]hept-2-ene (II) (16.07g, 60mmoles, 90%) [Found: C, 40.9; H, 2.6; F, 56.8%; $C_9H_6F_8$ requires C, 40.6; H, 2.3; F, 57.1%], M (mass spectroscopy), 266; B.p. 116-117° (Lit;[186] 117°), with correct i.r. spectrum; (ii) dicyclopentadiene and unreacted cyclopentadiene.

3. 2,3-Dichlorohexafluorobut-2-ene (15.4g, 67mmoles), cyclopentadiene (4.46g, 67mmoles) and hydroquinone (0.45g) were sealed in vacuo and heated at 160° for 72 hours to give 5,6-dichloro-5,6-bis(trifluoromethyl)bicyclo-[2.2.1]hept-2-ene (IV) (6.95g, 23mmoles, 35%), M (mass spectroscopy), 299; (ii) dicyclopentadiene and unreacted cyclopentadiene and 2,3-dichlorohexafluorobut-2-ene.

4. 3,3,3-Trifluoropropene (6.43g, 67mmoles), cyclopentadiene (4.46g, 67mmoles) and hydroquinone (0.45g) were sealed in vacuo and heated at 160° for 72 hours to give: (i) 5-trifluoromethylbicyclo[2.2.1]hept-2-ene (III) (6g, 37mmoles, 55%) [Found: C, 59.0; H, 5.9; F, 34.8%; $C_8H_9F_3$ requires C, 59.3; H, 5.6; F, 35.2%], M (mass spectroscopy), 162; B.p. 117-119°, (Lit:[187] 119°), with correct i.r. spectrum; (ii) dicyclopentadiene and unreacted cyclopentadiene.

5. Hexafluorobut-2-yne (10.85g, 67mmoles), cyclopentadiene (4.46g, 67mmoles) and hydroquinone (0.45g) were sealed in vacuo and heated at 100° for 24 hours to give: (i) 2,3-bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene (V) (15.15g, 66mmoles, 99%) [Found: C, 48.1; H, 2.82%; $C_9H_6F_6$ requires C, 47.4; H, 2.7%]; M (mass spectroscopy), 228; B.p. 110-112°, (Lit:[186] 109-111°); with correct i.r. spectrum, ν_{max} 1688cm^{-1} ($-CF_3C{=}CCF_3-$); (ii) and a trace amount of dicyclopentadiene and unreacted cyclopentadiene.

6. 3,3,3-Trifluoropropyne (7g, 74mmoles), cyclopentadiene (4.48g, 74mmoles) and hydroquinone (0.45g) were sealed in vacuo and heated at 155° for 48 hours to give: (i) 2-<u>trifluoromethylbicyclo</u>[2.2.1]<u>hepta</u>-2,5-<u>diene</u> (VI) (9.7g, 60.6mmoles, 82%) [Found: C, 59.7; H, 4.5; F, 36.0%; $C_8H_7F_6$ requires C, 60.0; H, 4.4; F, 35.6%]; M (mass spectroscopy), 160; ν_{max} 1645cm^{-1} ($-CF_3C{=}CH-$); (ii) dicyclopentadiene and unreacted cyclopentadiene.

4.10 Dehydrofluorination of 1H,5H,5H-pentafluorocyclopentene using molten potassium hydroxide

1H,5H,5H-Pentafluorocyclopentene (7.0g, 44mmoles) vapour in a stream of nitrogen was bubbled through molten potassium hydroxide at 190°. The product vapours were trapped in a glass trap cooled in liquid air. Analytical g.l.c. (Column A, 150°) of the just melted product (4.5g) showed the presence of four components, unreacted 1H,5H,5H-pentafluorocyclopentene and dimers of the dienes (123) and (124). Separation was attempted using a 'home-made' preparative g.l.c. apparatus (Column B, 93°) giving: (i) unreacted 1H,5H,5H-pentafluorocyclopentene (trace); (ii) <u>1,3,4,5,5,7,10,10-octafluorotricyclo[5.2.1.0^{2,6}]deca-3,8-diene</u> (132); ν_{max} 1590cm^{-1} (-CH=CH-) and 1765cm^{-1} (-FC=CF-); M (g.c. mass spectroscopy), 276; (iii) <u>3,4,5,5,7,8,-10,10-octafluorotricyclo[5.2.1.0^{2,6}]deca-3,8-diene</u> (129) and <u>3,3,4,5,7,8,-</u>

10,10-octafluorotricyclo[5.2.1.0^{2,6}]deca-3,8-diene (130), ν_{max} 1760cm^{-1} (-FC=CF-) and 1690cm^{-1} (-HC=CF-); M (g.c. mass spectroscopy), 276;

(iv) 1,4,5,5,6,7,10,10-octafluorotricyclo[5.2.1.0^{2,6}]deca-3,8-diene (126); ν_{max} 1590cm^{-1} (-HC=CH-) and 1690cm^{-1} (-FC=CH-); M, (g.c. mass spectroscopy), 276.

CHAPTER 5

THE RING-OPENING POLYMERISATION OF PARTIALLY FLUORINATED BICYCLO[2.2.1]HEPT-2-ENES AND BICYCLO[2.2.1]HEPTA-2,5-DIENES

5.1 Introduction

As was mentioned in Chapter 2, the first citation of an olefin metathesis reaction catalysed by a transition metal was published in 1955 and described the ring-opening polymerisation of bicyclo[2.2.1]hept-2-ene to give poly(1,3-cyclopentylenevinylene).[36] Since then the ring-opening polymerisation of bicyclo[2.2.1]hept-2-ene and its nitrile, amide, imide, ester, pyridyl, acid anhydride, chlorine and bromine substituted derivatives have been well established and numerous patents have been published concerning such reactions.[49,198,199]

Poly(1,3-cyclopentylenevinylene) is at present exploited commercially under the trade name Norsorex as a speciality elastomer, being a low softening point plastic, which gives elastomeric compositions of considerable strength when mixed with substantial quantities of carbon black and oil, the commercial product having up to four times as much oil and filler as polymer.[64] A substituted derivative poly(4-cyano-1,3-cyclopentylenevinylene) (16), is presently available in market research quantities from a Japanese Company, it is described as a thermoplastic resin.[65]

The current interest in finding outlets for the polymers produced by the ring-opening polymerisation of bicyclo[2.2.1]hept-2-ene and its substituted derivatives is partly due to economic considerations. The monomers are all prepared by the Diels-Alder addition between cyclopentadiene and the appropriately substituted alkene. The source of cyclopentadiene is the C_5 stream from the steam cracking of heavy hydrocarbons, naphtha and gas oil. Steam cracking has attained great importance in Europe and Japan as the main source of ethylene and propylene, and due to the shortage of natural gas the U.S.A. is also reluctantly moving towards naphtha cracking.[19]

The C_5 cut from a steam cracker amounts to about 20% of the ethylene stream. The average composition (weight per cent) of a typical C_5 cut is shown in Table 5.1.[16] Until recently the major useful component from this cut was isoprene, the remainder was used as a fuel. Therefore the ring-opening polymerisation of bicyclo[2.2.1]hept-2-ene and its substituted derivatives potentially provides a worthwhile use for a material which would otherwise be burnt.

Table 5.1

Composition of C_5 cut from steam cracking of naphtha and gas oil.[16]

Fraction	%
Cyclopentene	2.5
Dicyclopentadiene and cyclopentadiene	16.5
Isoprene	17.0
Piperylenes	11.5
C_5 acyclic alkenes	17.0
C_5 alkanes	31.0
C_4 + C_6 impurities	4.5

At the present time no fluorine substituted bicyclo[2.2.1]hept-2-enes or bicyclo[2.2.1]hepta-2,5-dienes have been specifically reported to undergo ring-opening polymerisation, however, in numerous Japanese patents the polymerisation of halogen substituted bicyclo[2.2.1]hept-2-enes and bicyclo[2.2.1]hepta-2,5-dienes have been reported in which the halogen substituent is either unspecified or chlorine or bromine.[200,201] The only reaction of a fluorinated derivative with a metathesis catalyst which has been described is due to Gassman and Johnson;[100] they did not mention whether any polymerisation occurred and used the conversion of (49) to (52) as an argument supportingthe quasicyclobutane mechanistic hypothesis (see Chapter 2).

This chapter describes the attempts to polymerise the fluorinated bicyclic monomers (I) - (VI), described in Chapter 4, using the established catalyst systems of $WCl_6/Na_2O_2/(i\text{-butyl})_3Al$ and $WCl_6/Na_2O_2/Et_2AlCl$ and the gradual development of a more active catalyst system for the polymerisation of these monomers.

5.2 The attempted ring-opening polymerisation of 5,5,6-trifluoro-6-trifluoromethylbicyclo[2.2.1]hept-2-ene using the catalyst systems $WCl_6/Na_2O_2/(i\text{-butyl})_3Al$ or $WCl_6/Na_2O_2/Et_2AlCl$ or WCl_6/Et_2AlCl or $WCl_6/EtOH/Et_2AlCl$

At the time of these initial attempts to ring-open polymerise 5,5,6-trifluoro-6-trifluoromethylbicyclo[2.2.1]hept-2-ene (I), the separation of the material into its geometric isomers had not been accomplished, consequently the material used was a 60 : 40 mixture of adducts (Ib) and (Ia).

Experimental details of successful ring-opening polymerisations of bicyclo[2.2.1]hept-2-ene and derivatives which contain a carbonyl group, a nitrile group, or a halogen atom substituent in the 5-position have been reported in the literature ;[30] the Al : W varied from 2 : 1 to 10 : 1, the W : monomer molar ratio was at least 1 : 60, the reaction was carried out at ambient temperature and the reaction time was 1 hour. Therefore, in order to become familiar with the reaction procedure the catalyst system $WCl_6/Na_2O_2/(i\text{-butyl})_3Al$ with a monomer : W molar ratio of 100 : 1, a Al : W molar ratio of 4 : 1 and a reaction temperature of 20^o was used to polymerise bicyclo[2.2.1]hept-2-ene. A creamy white polymeric material was produced in 65% yield its i.r. spectrum (Appendix C(XXI)) was identical with a reference spectrum of poly(1,3-cyclopentylenevinylene), containing predominantly trans-double bonds. Using this procedure the ring-opening polymerisation of (I) was attempted.

On addition of the pre-mixed WCl_6/Na_2O_2 toluene solution to (I) a colour change from blue-black to dark-brown and the appearance of a very fine solid was observed, but no further colour change occurred on the addition of $(i\text{-butyl})_3Al$. The reaction was terminated by addition of methanol, producing a small quantity of white fibrous material (0.79g, 3.7mmoles, 9%), with an i.r. spectrum (Appendix C(XXII)) very similar to the starting material. It was insoluble in acetone, methyl ethyl ketone, chloroform, dimethyl sulphoxide and toluene. The methanol solution was evaporated to dryness under reduced pressure leaving a very small quantity of brown material which was not analysed.

The experiment was repeated using the catalyst system $WCl_6/Na_2O_2/Et_2AlCl$, the same colour change was observed on addition of the pre-mixed WCl_6/Na_2O_2 toluene solution and again a small quantity of creamy white material was produced on the addition of excess methanol, its i.r. spectrum was identical to that obtained previously.

The experiment was repeated again using the catalyst system WCl_6/Et_2AlCl, without an oxygen containing activator. On addition of the blue-black toluene solution of WCl_6 to the monomer at 20^o the mixture turned dark brown, and deepened in colour on the addition of Et_2AlCl. Samples were removed at regular intervals from the reaction mixture during the reaction and quenched by addition to excess methanol. White powdery material was precipitated in each sample and the liquid was analysed by g.l.c. There was a slight decrease in the concentration of monomer during the first four hour period, however, no subsequent decrease was observed. The reaction was terminated after 22 hours by the addition of methanol. A small quantity of material was precipitated and after being dried under reduced pressure its i.r. spectrum was recorded and found to be identical to the previous two.

In literature reports[30] the oxygen containing activator used in the ring-opening polymerisation of substituted bicyclo[2.2.1]hept-2-enes was ethanol in a 1 : 1 molar ratio with WCl_6 and the organoaluminium compound was aluminium sesquichloride. This catalyst system $WCl_6/EtOH/Et_2AlCl$, has been reported to be very active in metathesis reactions and therefore the polymerisation of (I) was attempted using it, but again only a small quantity of solid material was produced on the addition of excess methanol, in this case even less than in the previous experiments.

A summary of the details for these four experiments is given in Table 5.2. It appeared that some polymerisation was occurring, the insolubility of the products hindered a detailed investigation. The catalyst systems $WCl_6/Na_2O_2/(i\text{-butyl})_3Al$, $WCl_6/Na_2O_2/Et_2AlCl$ and WCl_6/Et_2AlCl appeared to be of roughly equal reactivity, whereas $WCl_6/EtOH/Et_2AlCl$ was less reactive. It has been reported that the lifetime of the active catalyst in the $WCl_6/EtOH/EtAlCl_2$ system is about 30 minutes at 25°,[202] so if the polymerisation of (I) is slow then the active species in the catalyst system may have been consumed before extensive polymerisation had taken place.

To obtain an insight into the activity of the fluorocycloalkene (I) towards a metathesis catalyst system a set of three experiments were performed using the catalyst system $WCl_6/Na_2O_2/Et_2AlCl$ with the monomers: (i) pure cyclopentene; (ii) an equimolar mixture of cyclopentene and adduct (I); (iii) pure adduct (I). All three experiments were carried out at the same time using the same catalyst mixture and terminated after 2 hours by the addition of methanol. The reaction products were poured into a five-fold excess of methanol to precipitate any polymer; details of these experiments are given in Table 5.2. The material from experiment (i) was soft and elastomeric, its i.r. spectrum was identical to poly(1-pentenylene) with predominantly trans-double bonds (2.53g, 37mmoles; 75%); the product from

Table 5.2

The attempted ring-opening polymerisation of 5,5,6-trifluoro-6-trifluoromethylbicyclo[2.2.1]hept-2-ene

Expt.	Monomer	mmoles	WCl_6 mmoles	Activator mmoles	Organo-aluminium cocatalyst mmoles	Temperature °C	Reaction Time hrs.	Yield %
	Bicyclo[2.2.1]-hept-2-ene	59	0.6	0.6 A	2.4 C	-10	1	65
	I	41.7	0.5	0.48 A	2.0 C	20	18	9
	I	14.6	0.32	0.32 B	1.3 D	20	60	9
	I	41.7	0.75	0.75 A	3.0 D	20	23	
	I	46	0.46		2.0 D	20	22	9
(i)	Cyclopentene	48.2	0.2	0.2 A	0.8 D	-10	2	75
(ii)	Cyclopentene + I	24.1 25.4	0.2	0.2 A	0.8 D	-10	2	
(iii)	I	23.3	0.1	0.1A	0.4D	-10	2	6

A - Na_2O_2 ; B - EtOH ; C - $(i\text{-butyl})_3Al$; D - Et_2AlCl

experiment (ii) was a brittle material, its i.r. spectrum showed it to be predominantly poly(1-pentenylene) (Appendix C(XXIII)), but absorptions in the region 1390-1000cm^{-1} (region of C-F absorptions) suggested the possible presence of some fluorinated material, however, there were no detectable signals in the ^{19}F n.m.r. spectrum of the sample; the product from experiment (iii) was a brittle material with an i.r. spectrum (Appendix C(XXIV)) identical to the material produced from previous attempted polymerisations of adduct (I). Thus, from this series of experiments it appeared that adduct (I) was much less reactive towards metathesis catalysts than cyclopentene and if reasonable quantities of product were to be obtained a much more active catalyst was required.

5.3 The use of organo-tin-compounds as cocatalysts in olefin metathesis

It has been suggested that phenyltungsten trichloride is the most active catalyst for the ring-opening polymerisation of cycloalkenes,[203] and this material alone or together with aluminium chloride has been used by numerous workers in this field. Ulbricht[204] has reported the use of phenyltungsten trichloride as a catalyst for the ring-opening polymerisation of cyclopentene, producing 80% poly(1-pentenylene) with predominantly trans-double bonds, after 2 hours reaction at 0°. It was reported that the addition of aluminium trichloride enhanced the activity of the catalyst and a mixture of $PhWCl_3/AlCl_3$ was used by Gassman and Johnson in their studies of the isomerisation of fluorinated bicyclic alkenes and quadricyclane derivatives.[100]

In the literature the preparation of phenyltungsten trichloride is reported simply as the reaction of tungsten hexachloride and tetraphenyltin in a 1 : 2 molar ratio in refluxing n-pentane.[205] The phenyltungsten trichloride is described as a fine dark brown solid which is recovered by filtration under an atmosphere of dry nitrogen; no indication is given of the reflux time or the amount of n-pentane required. The synthesis was attempted using a reflux time of 4½ hours, a fine dark brown solid was produced; however, the yield of the material (150%) was not consistent with the product being assigned as phenyltungsten trichloride. Nevertheless this material was used as a catalyst for the polymerisation of cyclopentene, following the conditions reported by Ulbricht. The reaction was allowed to proceed for 2 hours then terminated by the addition of excess methanol. A very small quantity of solid material was precipitated and its i.r. spectrum was identical to poly(1-pentenylene), but the yield was less than 15%. The preparation of phenyltungsten trichloride was attempted twice more, but a satisfactory product from the point of view of material balance and catalytic activity, was not attained. One possible explanation was that refluxing the mixture for 4½ hours may have been too much and besides monophenylation of the tungsten hexachloride taking place, di- and polyphenylation may have resulted. The use of this material as a catalyst was not investigated further.

The catalyst system WCl_6/R_xSnCl_y (where R = alkyl, or aryl; x = 3 or 4 and y = 4-x) has been extensively used for the olefin metathesis of acyclic alkenes and cycloalkenes, especially substituted materials. The development of the homogeneous catalyst system $WCl_6/Sn(CH_3)_4$ for the metathesis of acyclic unsaturated esters has been of great importance in the chemistry of fats.[56] This catalyst system shows very good thermal stability and allows applications at temperatures up to at least 125°. It is a suitable metathesis catalyst for the ring-opening polymerisation of ester-group substituted cycloalkenes leading to polyalkenylenes of high molecular weight with pendant ester groups;[206] also unsaturated lactones may be polymerised to linear unsaturated polyesters.[66]

Hein has reported the use of a number of organo-tin compounds as cocatalysts for the polymerisation of cyclopentene and bicyclo[2.2.1]hept-

2-ene.[207] Using the catalyst system $WCl_6/(butyl)_4Sn$ with cyclopentene, the polymer conversion ranged from 3 to 65%, the majority of polymers possessed both cis- and trans-unsaturation and were clear, tacky materials of low number average molecular weights (3000-6000). The catalyst systems WCl_6/Ph_3SnCl and WCl_6/Ph_4Sn were much more reactive with cyclopentene, most reactions were exothermic and in some cases where no solvent was used there were explosions on the addition of the monomer. The reproducibility of the experiments was rather poor and Table 5.3 summarises some of the experiments.

The effect of varying the molar ratio of W : Sn is summarised in Table 5.4 for the polymerisation of cyclopentene using the system WCl_6/Ph_4Sn and comparing that with the conversion using $PhWCl_3$ and the system WCl_6/Ph_3SnCl. It appears that $PhWCl_3$ is the most reactive catalyst of the group considered.

Some interesting results have been reported by Masuda et al on the polymerisation of phenylacetylenes using the catalyst system WCl_6/Ph_4Sn,[208] the mechanism of which is assumed to be analogous to olefin metathesis.[107] A small amount of tetraphenyltin was found to greatly increase the initial polymerisation rate of phenylacetylene by tungsten hexachloride in benzene. When the molar ratio of Ph_4Sn to WCl_6 was in the range 1 : 1 to 2 : 1, the polymerisation rate reached a maximum and with a ratio greater than 2 : 1 both the reaction rate and polymer yield decreased, Figure 5.1.

When the tungsten hexachloride and tetraphenyltin were mixed together in benzene, the colour of the solution gradually changed from blue-black to brown and the catalyst activity varied with the change in colour. Figure 5.2 shows the effect of the aging time (i.e. the period from preparation of the catalyst mixture to the addition of the monomer) on the course of the reaction. When the tetraphenyltin was added to the monomer solution before the tungsten hexachloride, the polymerisation rate was almost the same as

Table 5.3[207]

Polymerisation of cyclopentene using tungsten hexachloride and organo-tin compounds as the catalyst system

WCl_6 mmole	Organo-tin mmole	Toluene mmole	Cyclopentene mmole	Reaction Time hours	Yield %	Type unsaturation	Appearance of polymer
1.0	A 2.0		50	1.17	65	cis + trans	clear, tacky
1.0	A 2.0		50	1.17	59	cis + trans	clear, tacky
1.0	A 2.0	18.9	50	4.0	49	cis + trans	clear, tacky
1.0	A 2.0	37.8	50	4.0	53	cis + trans	clear, tacky
0.1	B 0.2		50	exploded on addition of monomer			
0.1	B 0.2	37.8	50	1.0	40	Pred. trans	elastomeric
1.0	B 2.0	37.8	50	3.0	36	Pred. trans	elastomeric
1.0	C 2.0		50	exploded on addition of monomer			
1.0	C 2.0	18.9	50	3.0	47	Pred. trans	elastomeric
1.0	C 2.0	37.8	50	3.0	38	Pred. trans	elastomeric

A - tetrabutyltin
B - triphenyltin chloride
C - tetraphenyltin

Order of addition of components was:-

WCl_6 - organotin compound - toluene - monomer

Table 5.4

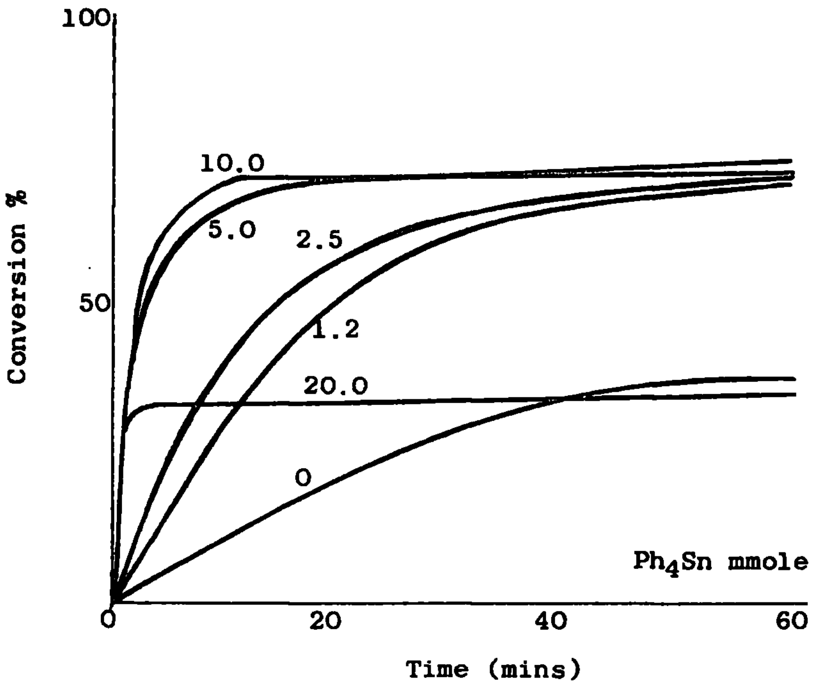
A comparison of the activity of various organotin compounds as olefin metathesis catalysts for the ring-opening polymerisation of cyclopentene

Tungsten Compound	Cocatalyst	W : Sn	W : monomer	Polymerisation Temperature °C	Reaction Time hours	Yield %	Ref.
$C_6H_5WCl_3$			1 : 900	0	2	78	204
WCl_6	Ph_4Sn	1 : 1	1 : 800	0	2	40	207
WCl_6	Ph_4Sn	1 : 2	1 : 800	0	2	26	207
WCl_6	Ph_4Sn	1 : 2	1 : 50	R.T.	3	38	207
WCl_6	Ph_4Sn	1 : 2	1 : 50	R.T.	3	47	207
WCl_6	Ph_3SnCl	1 : 2	1 : 50	R.T.	3.5	40	207

R.T. - room temperature

Figure 5.1[208]

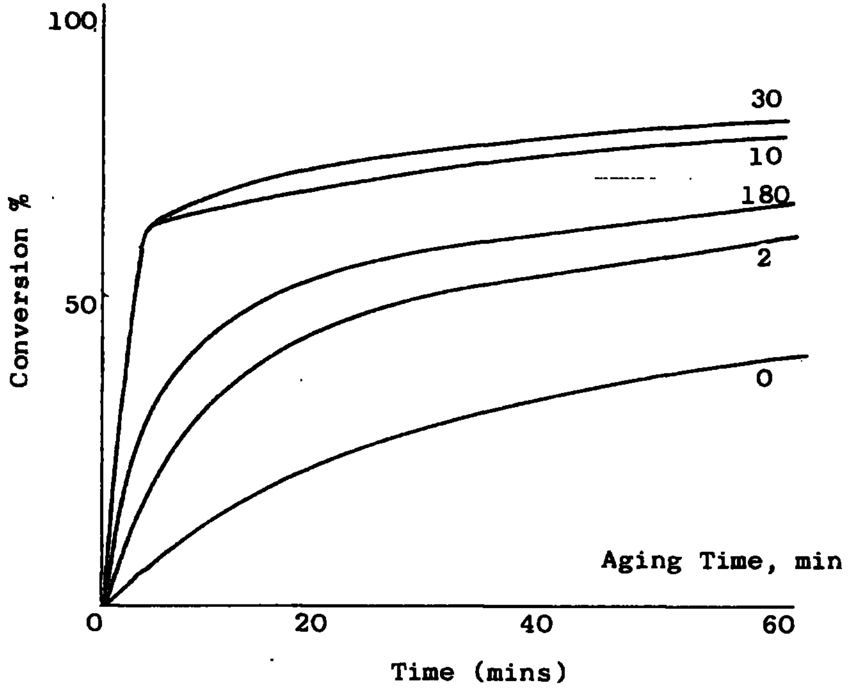
Effect of tetraphenyltin concentration on the polymerisation of phenylacetylene by tungsten hexachloride



Polymerisations carried out in benzene at 30°; aging time 10 minutes, ratio monomer : W was 200 : 1; [WCl = 5.0mmole]

Figure 5.2[208]

Effect of aging time of WCl_6/Ph_4Sn on polymerisation of phenylacetylene



Polymerisations carried out in benzene at 30°; ratio monomer : W : Ph was 200 : 1 : 1

that of the polymerisation in the absence of tetraphenyltin. The polymerisation rate increased with an increase in aging time and a maximum was reached when the aging time was 10-30 minutes. With a longer aging time the mixture tended to be a fine suspension and the polymerisation rate decreased. The best conditions quoted for the polymerisation of phenylacetylene using the catalyst system WCl_6/Ph_4Sn were: an equimolar mixture of the catalyst components, which were reacted together 10 minutes before the addition of the monomer. This system was also very effective for the polymerisation of phenylpropyne.[209]

In the work reported by Hein[207] for the polymerisation of cyclopentene using the catalyst system WCl_6/Ph_4Sn the monomer was added to the catalyst mixture after an interval of about 2 minutes, a longer aging time might have given a higher polymer conversion.

The ring-opening polymerisations of cyclopentene and bicyclo[2.2.1]hept-2-ene were therefore examined using the catalyst system WCl_6/Ph_4Sn. Details of the individual experiments are given in Table 5.5. In all the experiments the mixture became viscous immediately on addition of the monomer to the WCl_6/Ph_4Sn system in toluene. The reactions were terminated by the addition of a small quantity of methanol, and then added dropwise to a vigorously stirred five-fold excess of methanol. The precipitated material was recovered by filtration and dried under reduced pressure. The three samples of poly(1-pentenylene) prepared experiments (i) - (iii) were soluble in chloroform, carbon tetrachloride and toluene and were identified by their i.r. spectra. Poly(1-pentenylene) prepared experiment (ii) was characterised by elemental analysis and i.r. (Appendix C(XXV)) and ^1H n.m.r. spectroscopy. Both samples of poly(1,3-cyclopentylene-vinylene) which were prepared in experiments (iv) and (v) were initially soluble in toluene and chloroform, but on standing for a few weeks they

Table 5.5

The ring-opening polymerisation of cyclopentene and bicyclo[2.2.1]hept-2-ene using the catalyst system tungsten hexachloride and tetraphenyltin

Expt.	Monomer		WCl_6	Ph_4Sn	Toluene	Aging Time	Reaction Temp.	Reaction Time	Yield
		mmole	mmole	mmole	mmole	mins.	^oC	hours	%
(i)	Cyclopentene	50	0.086	0.086	94	12	0	2	41
(ii)	Cyclopentene	67	0.17	0.34	83	12	0	1	65
(iii)	Cyclopentene	80	0.17	0.34	94	12	0	2	69
(iv)	Bicyclo[2.2.1]hept-2-ene	76	0.19	0.38	94	12	20	1	62
(v)	Bicyclo[2.2.1]hept-2-ene	63	0.155	0.31	94	12	0	2	61

were found to be more difficult to dissolve and had also become brittle.

For the polymerisation of cyclopentene with an equimolar mixture of WCl_6/Ph_4Sn, experiment (i), the polymer conversion was identical to that obtained by Hein, except the monomer : W molar ratio was 600 : 1 whereas Hein used 50 : 1. However, with a WCl_6 : Ph_4Sn molar ratio of 1 : 2 the polymer conversion was very much greater. Allowing the catalyst components to react together before the addition of the monomer appears to be beneficial with respect to polymer conversion. Although the polymer conversion for bicyclo[2.2.1]hept-2-ene in experiments (iv) and (v) was relatively high a comprehensive analysis was not possible, because of the insolubility of the polymers.

5.4 The ring-opening polymerisation of partially fluorinated bicyclo[2.2.1]-hept-2-enes using tungsten hexachloride and tetraphenyltin as the catalyst system

Using the catalyst system WCl_6/Ph_4Sn in a W : Sn molar ratio of 1 : 2 and an aging time for the catalyst mixture of 12-15 minutes, the ring-opening polymerisation of adduct (I) was attempted at 0^o and 20^o. The conditions and results are summarised in Table 5.6.

In all three experiments the monomer was degassed and vacuum transferred from P_2O_5 then injected, using an air-tight syringe, into the pre-mixed WCl_6/Ph_4Sn toluene solution, which was dark brown in colour. No immediate reaction was observed, but gradually small pieces of solid material collected on the sides of the reaction vessel and the amount slowly increased as the reaction proceeded. The appearance of solid material took longer in experiment (i) than in experiments (ii) and (iii). The colour of the reaction mixture became lighter as the reaction proceeded, they were terminated by the addition of a small quantity of methanol. On

Table 5.6

The ring-opening polymerisation of 5,5,6-trifluoro-6-trifluoromethylbicyclo[2.2.1]hept-2-ene using tungsten hexachloride and tetraphenyltin as the catalyst system

Expt.	Monomer mmole	WCl_6 mmole	Ph_4Sn mmole	Aging Time mins	Toluene mmole	Reaction Temp. ^{o}C	Reaction Time hours	Yield %	$[\eta]$[a] dl/g
(i)	15.7	0.047	0.098	12	94	0	3	21.5	
(ii)	15.7	0.047	0.093	12	94	20	3	63	1.06
(iii)	24.6	0.059	0.118	12	94	20	3	68	1.54

[a] Solvent was methyl ethyl ketone at 25.00 ± 0.01^{o}. Details about determination are given in Chapter 6.

initial addition of methanol some of the solid material appeared to dissolve and as more methanol was added more of the solid material dissolved, eventually producing a homogeneous solution. In the experiments to ring-open polymerise adduct (I) using the catalyst systems $WCl_6/Na_2O_2/$ organo-aluminium compound (Table 5.2) no methanol soluble material was produced, after the insoluble products had been recovered, the methanol solutions were evaporated to dryness under reduced pressure and in no case was a substantial amount of solid residue produced.

The methanol solutions from experiments (i) - (iii) were filtered, the excess methanol removed under reduced pressure and the viscous solutions were added dropwise into a five-fold excess of toluene. However, the toluene proved difficult to remove from the products even under reduced pressure, they were therefore dissolved in analar acetone and reprecipitated in n-pentane, which was easily removed under reduced pressure. The solid material from experiment (ii) was characterised by elemental analysis, i.r. (Appendix C(XXVI)), ^{1}H n.m.r. and ^{19}F n.m.r. spectroscopy and identified as poly(4,4,5-trifluoro-5-trifluoromethyl-1,3-cyclopentylenevinylene) (VII) the polyalkenylene of adduct (I); the analysis of this material will be discussed in greater detail in Chapter 6. The i.r. spectra of the solids from experiments (i) and (iii) were identical to the i.r. spectrum of the material from experiment (ii). All three materials were soluble in methanol, acetone, methyl ethyl ketone and tetrahydrofuran.

In this series of experiments the polymer conversion was higher when the reaction temperature was 20^{o} than when it was 0^{o}, consequently the majority of subsequent experiments were performed at 20^{o}.

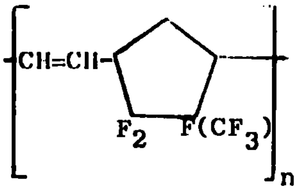
Using this polymerisation technique the ring-opening polymerisations of the partially fluorinated bicyclo[2.2.1]hept-2-enes, adducts (II) - (IV) were attempted, the details are shown in Table 5.7. The polymeric materials produced (VIII) - (IX) were fully characterised by elemental analysis, i.r.

Table 5.7

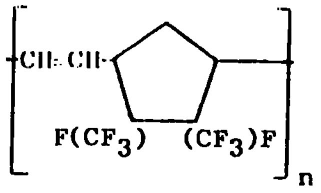
The ring-opening polymerisation of partially fluorinated bicyclo[2.2.1]hept-2-enes using tungsten hexachloride and tetraphenyltin as the catalyst system.

Monomer	mmole	WCl_6 mmole	Ph_4Sn mmole	Aging Time mins	Toluene mmole	Reaction Temp. ^oC	Reaction Time hours	Yield %	$[\eta]$[a] dl/g
Ib	8.75	0.023	0.0475	12	80	22	4	64	5.8
Ib : Ia 14 : 86	3.0	0.007	0.015	12	19	20	3.5	20	
IIa + IIb + IIc 90 : 10	12.6	0.032	0.065	12	94	21	27	65	1.54
IIa	13.1	0.0375	0.076	12	94	20	27	63	2.46
IV	7.55	0.0368	0.077	12	47	22	65	37	
IIIa	12.05	0.032	0.065	12	112	22	2	93	0.96

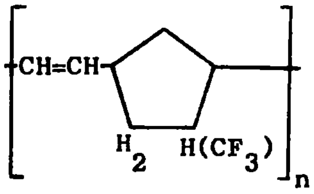
[a] Solvent methyl ethyl ketone at 25.00 ± 0.01^o. Details about determination are given in Chapter 6.



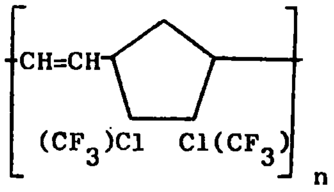
(VII)



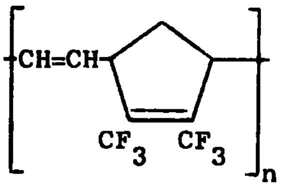
(VIII)



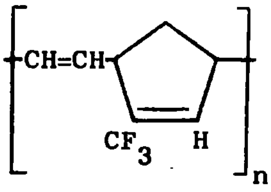
(IX)



(X)



(XI)



(XII)

(Appendix C(XXVll) - (XXIX) respectively), ^{1}H n.m.r. and ^{19}F n.m.r. spectroscopy and identified as the ring-opened polymers of the corresponding monomers (II) - (IV) respectively. The complete analyses of the polymers will be discussed in Chapter 6.

5.5 The ring-opening polymerisation of partially fluorinated bicyclo[2.2.1]-hepta-2,5-dienes using tungsten hexachloride and tetraphenyltin as the catalyst system

Using identical conditions to those successfully applied to the polymerisation of partially fluorinated bicyclo[2.2.1]hept-2-enes with the catalyst system WCl_6/Ph_4Sn, the polymerisations of 2,3-bis(trifluoromethyl)-bicyclo[2.2.1]hepta-2,5-diene, adduct (V), and 2-trifluoromethylbicyclo-[2.2.1]hepta-2,5-diene, adduct (VI), were attempted, Table 5.8.

Both reactions were exothermic and became extremely viscous almost immediately after the addition of the monomer. The product from adduct (V) was insoluble in toluene and precipitated out during the reaction, while that from adduct (VI) was soluble. The reactions were terminated by the addition of methanol, dissolved in analar acetone, filtered, the excess acetone was removed under reduced pressure, producing a viscous solution which was added dropwise to a vigorously stirred excess of n-pentane and the precipitated materials were recovered by filtration and dried under reduced pressure.

The polymer (XI) produced from adduct (V), was a pale yellow, brittle material, i.r. spectroscopy (Appendix C(XXX)) showed the characteristic absorption at $1689cm.^{-1}$ for the $-CF_3C{=}CCF_3-$ substituted double bond. This precipitated material would only swell in hot and cold analar acetone, however, in refluxing methyl ethyl ketone it dissolved quite readily.

The polymer (XII) from adduct (VI) was a pale yellow powdery material, i.r. spectroscopy (Appendix C(XXXI)) showed the characteristic absorption at $1640cm.^{-1}$ for the $-CF_3C{=}CH-$ substituted double bond and similar to polymer (XI), this precipitated material would only swell in cold and hot acetone, but dissolved readily in refluxing methyl ethyl ketone. Complete analyses of both polymers will be discussed in more detail in Chapter 6.

Table 5.8

The ring-opening polymerisation of partially fluorinated bicyclo[2.2.1]hepta-2,5-dienes using tungsten hexachloride and tetraphenyltin as the catalyst system

Monomer	mmole	WCl_6 mmole	Ph_4Sn mmole	Aging Time mins.	Toluene mmole	Reaction Temp.[a] °C	Reaction Time hours	Yield %	[η][b] dl/g
V	9.5	0.025	0.05	15	94	20	3	70	0.65
VI	18	0.044	0.086	15	94	20	0.5	70	0.50

[a] Initial temperature 20°, both experiments were exothermic

[b] Solvent methyl ethyl ketone at 25.00 ± 0.01°. Details about determination are given in Chapter 6

5.6 The ring-opening polymerisation of partially fluorinated bicyclo[2.2.1]hept-2-enes and bicyclo[2.2.1]hepta-2,5-dienes using different combinations of WCl_6, Na_2O_2 and $(i\text{-butyl})_3Al$ as the catalyst systems

After the successful ring-opening polymerisation of partially fluorinated bicyclo[2.2.1]hept-2-enes and bicyclo[2.2.1]hepta-2,5-dienes using the catalyst system WCl_6/Ph_4Sn, the earlier attempts to polymerise adduct (I) using $WCl_6/Na_2O_2/(i\text{-butyl})_3Al$ as the catalyst system was repeated. The details are given in Table 5.9. The procedure adopted was identical to that used in the original attempt to polymerise this adduct. When the pre-mixed toluene solution of WCl_6/Na_2O_2 was added to the monomer a colour change from blue-black to deep reddy-brown was observed, and on the addition of the $(i\text{-butyl})_3Al$ the reaction mixture became cloudy and turned dark brown in colour. After 2 hours a small quantity of solid material had appeared on the sides of the reaction vessel. The reaction was terminated after 38 hours by the addition of methanol. The solid product was dissolved in a minimum amount of analar acetone and precipitated by addition to a five-fold

Table 5.9

The ring-opening polymerisation of partially fluorinated bicyclo[2.2.1]hept-2-enes using $WCl_6/Na_2O_2/(i\text{-butyl})_3Al$ as the catalyst system

Monomer	mmole	WCl_6 mmole	Na_2O_2 mmole	$(i\text{-butyl})_3Al$ mmole	Toluene mmole	Reaction Temp. ^oC	Reaction Time hours	Yield %
I	29	0.075	0.073	0.3	70	20	38	10
II	31	0.075	0.073	0.3	70	20	38	2

excess of n-pentane. The precipitated material was dried under reduced pressure, producing a hard white solid (0.65g, 10%), whose i.r. spectrum (Appendix C(XXXII)) was identical to that of poly(4,4,5-trifluoro-5-trifluoromethyl-1,3-cyclopentylenevinylene) (VII) produced by the ring-opening polymerisation of adduct (I) using WCl_6/Ph_4Sn as the catalyst system.

The procedure was repeated using adduct (II), Table 5.9. The colour changes on the addition of the catalyst components to the reaction mixture was identical to those in the previous experiment and the reaction was terminated after 38 hours. A very small amount of solid material was produced, after purification (0.16g, 2%) and its i.r. spectrum (Appendix C(XXXIII)) was identical to that of poly(4,5-difluoro-4,5-bis(trifluoromethyl)-1,3-cyclopentylenevinylene) (VIII) produced by the ring-opening polymerisation of adduct (II) using WCl_6/Ph_4Sn as the catalyst system.

Although the catalyst system $WCl_6/Na_2O_2/(i\text{-butyl})_3Al$ does ring-open polymerise adducts (I) and (II) to give the corresponding partially fluorinated poly(1,3-cyclopentylenevinylene) it does not appear, from the reactions performed, to be as active as the catalyst system WCl_6/Ph_4Sn. These results confirm those obtained previously and show that the failure to recover reasonable yields of polymer using this catalyst system was not a consequence of the isolation technique.

The ring-opening polymerisation of adduct (VI) using the catalyst system $WCl_6/Na_2O_2/(i\text{-butyl})_3Al$ was also examined, following the standard procedure and the details are given in Table 5.10.

The blue-black, pre-mixed toluene solution of WCl_6/Na_2O_2 was injected into the reaction vessel containing the neat monomer, and the reaction mixture immediately turned deep reddy-brown in colour and became viscous. No $(i\text{-butyl})_3Al$ cocatalyst was added. The reaction was terminated after

Table 5.10

The ring-opening polymerisation of partially fluorinated bicyclo[2.2.1]hept-2-enes and bicyclo[2.2.1]hepta-2,5-dienes using WCl_6/Na_2O_2 and WCl_6 as the catalyst systems

Monomer	mmole	WCl_6 mmole	Na_2O_2 mmole	$(i\text{-butyl})_3Al$ mmole	Toluene mmole	Reaction Temp. °C	Reaction Time hours	Yield %
V	18	0.051	0.051	0.153	94	20	3	77
VI	20	0.051	0.051		94	20	1	10
VI	11	0.03			38	20	3	11
IIIa	14	0.03			94	20	24	17

3 hours by the addition of methanol, and the product was dissolved in the minimum volume of analar toluene and re-precipitated by addition to a five-fold excess of methanol. The precipitated material was recovered by filtration and dried under reduced pressure, giving a light brown material. Its i.r. spectrum was identical to poly(4-trifluoromethyl-1,3-cyclopentenylene-vinylene) (XII) produced by the ring-opening polymerisation of adduct (VI) using WCl_6/Ph_4Sn as the catalyst system.

The sensitivity of the polymerisation process to small structural variations is indicated by the difference in behaviour between adducts (VI) and (V). When a pre-mixed toluene solution of WCl_6/Na_2O_2 was added to adduct (V), the usual colour change was observed, but there was no immediate change in the viscosity. After 15 minutes $(i\text{-butyl})_3Al$ was added and after a further 15 minutes the mixture became cloudy and viscous. The reaction was terminated after 3 hours and after purification a hard, white solid was produced. Its i.r. spectrum was identical with that of poly(4,5-bis(trifluoromethyl)-1,3-cyclopentenylenevinylene) (XI), produced by the ring-opening polymerisation of adduct (V) using WCl_6/Ph_4Sn as the catalyst system.

In a further modification of the experimental procedure a toluene solution of WCl_6 was added to adducts (VI) and (IIIa), in the former case there was an immediate exotherm and the reaction became viscous while in the latter case the exotherm occurred after 15 minutes and then the mixture became viscous. Details of both experiments are given in Table 5.10. They were terminated after 3 and 24 hours respectively by the addition of methanol, both were purified by reprecipitation from toluene solutions using methanol as the non-solvent. The polymer from adduct (VI) was a light brown material with an i.r. spectrum identical to polymer (XII) and the polymer from adduct (IIIa) was a white material with an i.r. spectrum identical to poly(4-trifluoromethyl-1,3-cyclopentylenevinylene) produced by the ring-opening polymerisation of adduct (IIIa) using WCl_6/Ph_4Sn as the catalyst system.

5.7 The relative rates at which partially fluorinated bicyclo[2.2.1]hept-2-enes and bicyclo[2.2.1]hepta-2,5-dienes undergo ring-opening polymerisation

From this brief study of the ring-opening polymerisation of partially fluorinated bicyclo[2.2.1]hept-2-enes and bicyclo[2.2.1]hepta-2,5-dienes one or two general points may be made concerning their relative rates of polymerisation and the activity of the catalyst systems used. However, in view of the problems of reproducibility commonly encountered in this field,[207] the conclusions drawn must be regarded as only provisional and a great deal of experimental work is required before they can be made more definite.

The nature and the yields of the polymers produced from the 60 : 40 mixture of adducts (Ib) and (Ia), pure adduct (Ib) and 14 : 86 mixture of adducts (Ib) and (Ia) are quite different. The polymer from the pure adduct (Ib) is a very hard white solid, that from the 60 : 40 mixture of adducts (Ib) and (Ia) is a white fibrous material and that from the 14 : 86 mixture of adducts (Ib) and (Ia) is a fine white powder. The yield of the polymers from pure adduct (Ib) and the 60 : 40 mixture of adducts (Ib) and (Ia) are quite similar, about 65%, but their intrinsic viscosities are different, 5.8dl/g and 1.54dl/g respectively, while the yield from the 14 : 86 mixture of adducts (Ib) and (Ia) is much lower, 20%.

This series of results suggests that 5,5,6-trifluoro-exo-6-trifluoromethylbicyclo[2.2.1]hept-2-ene, adduct (Ia), is less reactive towards ring-opening polymerisation than 5,5,6-trifluoro-endo-6-trifluoromethylbicyclo-[2.2.1]hept-2-ene, adduct (Ib). From the ^{19}F n.m.r. spectrum of the polymer from the 60 : 40 mixture of adducts (Ib) and (Ia), which will be discussed in more detail in Chapter 6, it appears that more endo-isomer was polymerised than the exo-isomer. For some reason the exo-CF_3 appears to hinder the polymerisation process. Further evidence to support this observation comes from the polymerisation of adduct (II); this material requires 27 hours to attain a polymer conversion of 63% (c.f. (Ib) gives 64% yield in 4 hours), its stereochemical structure may be considered as a combination of adducts (Ia) and (Ib), since it possesses one endo-CF_3 and one exo-CF_3. No definite conclusion may be made about the effect of stereochemistry on the yield of polymer (X) from adduct (IV), although it was low (37%), because a complete stereochemical analysis of adduct (IV) was not possible on the data available.

In contrast to the above observations it was found that exo-4-trifluoromethylbicyclo[2.2.1]hept-2-ene, adduct (IIIa) polymerised extremely rapidly and the conversion was high (93%). This result does not necessarily contradict the observations made for the polymerisation of adducts (I) and (II), since the polymer from adduct (IIIa) was soluble in the polymerisation medium and the system remained homogeneous throughout the reaction; whereas, for adducts (I) and (II), the polymers were insoluble in the reaction medium and precipitated during reaction. The active catalyst may be considered as heterogeneous in the latter case and homogeneous in the former, therefore the rates of reaction are not comparable.

The homogeneity and heterogeneity of a polymerisation reaction may be the cause of the difference in the activity of adducts (V) and (VI) to metathesis catalysts. It was shown that adduct (VI) will rapidly undergo ring-opening polymerisation using only WCl_6 as the catalyst system i.e. in the absence of a cocatalyst and an activator, however, adduct (V) required the presence of a cocatalyst in order to initiate rapid polymerisation. The polymer from adduct (VI) was soluble in toluene, while the polymer from adduct (V) was insoluble in toluene.

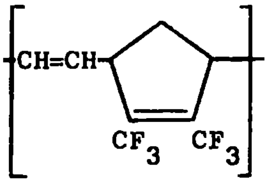
Although no firm conclusions can be drawn from this limited set of data the large variations in behaviour associated with relatively small changes in monomer structure and/or catalyst composition suggest that useful information concerning the detailed mechanism of metathesis polymerisation may be acquired from a more extensive investigation of this area.

5.8 The copolymerisation of partially fluorinated bicyclo[2.2.1]hepta-2,5-dienes with cyclopentene

The partially fluorinated bicyclo[2.2.1]hepta-2,5-dienes were by far the most active of the fluorinated bicycloalkenes towards olefin metathesis. Therefore the copolymerisation of adducts (V) and (VI) with cyclopentene was examined using WCl_6/Ph_4Sn as the catalyst system.

Equimolar mixtures of adduct (V) and cyclopentene, and adduct (VI) and cyclopentene were reacted together with the catalyst system WCl_6/Ph_4Sn using the standard procedure; details are recorded in Table 5.11. In both reactions a colour change from dark brown to light brown and an exotherm was observed on the addition of the monomer mixtures to the catalyst. The reactions became extremely viscous, but no material was precipitated. Both reactions were terminated after 2½ hours by the addition of methanol and the products were purified by precipitation from toluene solutions, with methanol as the non-solvent.

The organic solvents were removed from the precipitated materials under reduced pressure, producing creamy white solids. The product (XIII) from the copolymerisation of adduct (V) and cyclopentene, was analysed by i.r. spectrscopy (Appendix C(XXXIV)) showing the characteristic absorption at 1680cm^{-1} for the $-CF_3C=CCF_3-$ substituted double bond, and elemental analysis which indicated a copolymer with repeat units (XI) and (8) in a ratio of 2 : 1 respectively. The material was found to be soluble in acetone, toluene and methyl ethyl ketone.



(XI)

$\left[CH=CH-(CH_2)_3 \right]$

(8)

The copolymer of adduct (VI) and cyclopentene, (XIV), was analysed by i.r. spectroscopy (Appendix C(XXXV)) showing the characteristic absorption at 1650cm^{-1} for the $-CF_3C=CH-$ substituted double bond, and elemental analysis which indicated a copolymer with repeat units (XII) and (8) in a ratio of 2 : 1 respectively. Initially the copolymer was soluble in toluene and acetone, but gradually over a period of approximately

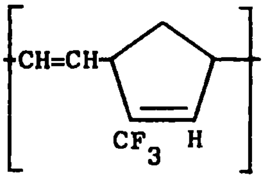
Table 5.11

The copolymerisation of partially fluorinated bicyclo[2.2.1]hepta-2,5-dienes with cyclopentene using tungsten hexachloride and tetraphenyltin as the catalyst system

Fluorinated Monomer		Cyclopentene	WCl_6	Ph_4Sn	Toluene	Aging Time	Reaction Temp.[a]	Reaction Time	Yield[b]
	mmole	mmole	mmole	mmole	mmole	mins	°C	hours	%
V	16.6	16.5	0.084	0.168	94	12	20	2.5	61
VI	16.4	16.5	0.084	0.167	94	12	20	2.5	76

[a] Both reactions were initially exothermic

[b] Based on total weight of monomers



(XII)

$$\left[CH{=}CH{-}(CH_2)_3 \right]$$

(8)

one month it darkened in colour to deep yellow and became insoluble, consequently ^{1}H n.m.r. and ^{19}F n.m.r. analysis and intrinsic viscosity measurements were not possible. This change in solubility and colour did not occur with the other copolymer and both materials were stored under identical conditions, that is, in the dark and under an atmosphere of dry nitrogen. It may be possible that cross-linking in copolymer (XIV) may have occurred due to the presence of residual active catalyst in the material.

Time restrictions prevented a more extensive investigation of these copolymerisations, however, these preliminary results suggest that useful information concerning the mechanism of polymerisation may be forthcoming from a more detailed study. The obvious first step would be to establish whether or not the 2 : 1 incorporation ratio observed from both systems was independent of the monomer feed stock ratio or merely coincidental.

EXPERIMENTAL

5.9a Reagents

Tungsten hexachloride, cyclopentene and toluene were purified as described in Chapter 3. Sodium peroxide and bicyclo[2.2.1]hept-2-ene were used as purchased from BDH Chemicals Ltd., and Koch-Light Laboratories Ltd., respectively. Tri-isobutylaluminium was provided by Dr. K. Wade (this Department). Tetraphenyltin was purchased from BDH Chemicals Ltd., and purified by repeated extraction of the tetraphenyltin with hot toluene, using Soxhlet Extraction Apparatus. Partially fluorinatad bicyclo[2.2.1]-hept-2-enes and bicyclo[2.2.1]hepta-2,5-dienes were prepared as described in Chapter 4. All liquid monomers were degassed and dried over P_2O_5, vacuum transferred into a clean, dry flask, let down to an atmosphere of dry nitrogen and transferred into the reaction vessel using an air-tight syringe.

5.9b Apparatus

All polymerisation reactions were performed in 30cm^3 capacity 2-necked flasks containing a magnetic follower, one neck was fitted with a serum cap and the other was connected directly to the vacuum system. During all reactions the flasks were continuously purged with dry nitrogen.

5.9c The ring-opening polymerisation of bicyclo[2.2.1]hept-2-ene using $WCl_6/Na_2O_2/(i\text{-butyl})_3Al$ as the catalyst system

Bicyclo[2.2.1]hept-2-ene (5.5g, 59mmoles) was dissolved in dried, degassed toluene (10cm^3) in the reaction vessel, the solution was degassed again and then let down to an atmosphere of dry nitrogen. The toluene solution of WCl_6/Na_2O_2 was prepared by dissolving WCl_6 (2.38g, 6.0mmoles) and Na_2O_2 (0.45g, 6.0mmoles) in dried, degassed toluene (10cm^3) under an atmosphere of dry nitrogen in the glove-box. The pre-mixed WCl_6/Na_2O_2 solution (2cm^3) was injected using an air-tight syringe into the monomer solution. The mixture changed colour from blue-black to deep-red, it was cooled to -10° and (i-butyl)$_3$Al (0.4g, 1.7mmoles) was injected into the reaction mixture using a micro-syringe. The mixture became viscous, it was first allowed to warm up to 0° then cooled to -10°. The reaction was terminated after 1 hour by the addition of methanol (2cm^3). The reaction mixture was added dropwise to a five-fold excess of methanol. The precipitated material was dried under reduced pressure, producing a creamy-white solid (3.6g, 38mmoles, 65%) which was soluble in toluene, carbon tetrachloride and chloroform. Its i.r. spectrum (Appendix C(XXI)) was identical with a reference spectrum of poly(1,3-cyclopentylenevinylene), ν_{max} 964cm^{-1} (trans-HC=CH-) and 737cm^{-1} (cis-HC=CH-).

5.9d General procedure for the attempted and successful ring-opening polymerisation of partially fluorinated bicyclo[2.2.1]hept-2-enes using WCl_6/Na_2O_2/(i-butyl)$_3$Al or WCl_6/Na_2O_2/Et_2AlCl or WCl_6/EtOH/Et_2AlCl or WCl_6/Et_2AlCl as the catalyst system

The reaction vessel was charged with the required amount of dried, degassed partially fluorinated bicyclo[2.2.1]hept-2-ene and purged continuously with dry nitrogen.

When sodium peroxide was used as the activator, the WCl_6 and Na_2O_2 were pre-mixed in dried, degassed toluene under an atomosphere of dry nitrogen in the glove-box. The mixture was injected into the reaction vessel at room temperature using an air-tight syringe. Using ethanol as the activator, the WCl_6 was dissolved in dried, degassed toluene in the glove-box and injected into the reaction vessel. The ethanol was dissolved in dried toluene, degassed, then injected into the reaction vessel after the WCl_6 solution. The reaction vessel was purged continuously with dry nitrogen and the mixture was stirred.

After the addition of the WCl_6/activator the reaction was cooled to -10^{o}, and the required amount of organo-aluminium compound was added using a micro-syringe. The reaction was maintained at the required temperature for the duration of the experiment then terminated by the addition of a few cm^3 of methanol.

The above procedure was followed for the experiments recorded in Tables 5.2 and 5.9. In the former case on the addition of methanol to the reaction mixture an insoluble product was produced, this was recovered and pumped dry under reduced pressure. The residual methanol solution was evaporated under reduced pressure and produced in every case only a small quantity of solid material, which was not analysed. In the latter case the reaction products were found to be soluble in methanol. A homogeneous solution was prepared by dissolving the product in analar acetone, the solution was filtered and added dropwise to a five-fold excess of n-pentane. The precipitated materials were recovered by filtration and dried under reduced pressure (45^{o}, 10^{-3}mm Hg).

5.9e The ring opening polymerisation of: (i) Cyclopentene; (ii) Equimolar mixture of cyclopentene and 5,5,6-trifluoro-6-trifluoromethylbicyclo-[2.2.1]hept-2-ene and (iii) 5,5,6-Trifluoro-6-trifluoromethylbicyclo-[2.2.1]hept-2-ene using $WCl_6/Na_2O_2/Et_2AlCl$ as the catalyst system

Three reaction vessels were separately charged with dried and degassed (i) cyclopentene, (ii) an equimolar mixture of cyclopentene and 5,5,6-trifluoro-6-trifluoromethylbicyclo[2.2.1]hept-2-ene and (iii) 5,5,6-trifluoro-6-trifluoromethylbicyclo[2.2.1]hept-2-ene and purged continuously with dry nitrogen. To each flask dried, degassed toluene (10cm^3) was added.

WCl_6 (0.3g, 0.76mmoles) and Na_2O_2 (0.06g, 0.8mmoles) were dissolved in dried, degassed toluene (20cm^3) under an atmosphere of dry nitrogen in the glove-box. A 5cm^3 aliquot of this solution was injected into reactions (i) and (ii) and a 2.5cm^3 aliquot into reaction (iii) at 20^o. All three solutions changed colour from blue-black to dark red, the solutions were cooled to -10^o, Et_2AlCl was injected into each solution using a micro-syringe [(i) and (ii) (0.085g, 0.77mmoles) and (iii) (0.049g, 0.39mmoles)]; a colour change from dark red to dark brown was observed in all three cases. The temperature was maintained at -10^o and an increase was observed in the solution viscosity for reaction (i) a similar but smaller increase was observed in (ii) and in the case of reaction (iii) the solution became cloudy. The reactions were terminated after 2 hours by the addition of a small quantity of methanol, producing after purification: from (i), poly(1-pentenylene) (2.9g, 43mmoles, 75%) a creamy-white material with an i.r. spectrum identical to an authentic sample of poly(1-pentenylene); from (ii), a white brittle material (0.65g), the i.r. spectrum of which (Appendix C(XXIII)) was very similar to poly(1-pentenylene), but displaying additional absorptions in the region 1390-1000cm^{-1} (characteristic region for C-F absorptions); and from (iii) a hard material (0.3g, 1.4mmoles, 6%) which was insoluble in methanol, acetone and chloroform, its i.r. spectrum (Appendix C(XXIV)) was identical to the spectra of the insoluble materials produced in the initial attempts to ring-open polymerise adduct (I).

5.9f General procedure for the ring-opening polymerisation of cycloalkenes using tungsten hexachloride and tetraphenyltin as the catalyst system

The reaction vessel was charged with required quantity of tetraphenyltin and purged for at least 1 hour with dry nitrogen. The required amount of a toluene solution of tungsten hexachloride was injected into the vessel using an air-tight syringe. The mixture was stirred vigorously for 12-15 minutes, and during that period of time a colour change from blue-black to dark brown was observed. The dried, degassed monomer was injected into the active catalyst system using an air-tight syringe.

The reaction was allowed to proceed for the appropriate amount of time and terminated by the addition of a few cm^3 of methanol. The product was dissolved in a solvent and filtered; some of the solvent was then removed under reduced pressure to give a viscous solution, which was added dropwise to a large excess of non-solvent. The precipitate was recovered and the residual solvent and non-solvent were removed from the precipitated material under reduced pressure (45^o, 10^{-3}mm Hg).

Using this procedure cyclopentene, bicyclo[2.2.1]hept-2-ene, partially fluorinated bicyclo[2.2.1]hept-2-enes, adducts (I) - (IV) and partially fluorinated bicyclo[2.2.1]hepta-2,5-dienes, adducts (V) and (VI) were ring-open polymerised using WCl_6/Ph_4Sn as the catalyst system. Experimental details are recorded in Tables 5.5, 5.6, 5.7 and 5.8.

For the copolymerisations of adducts (V) and (VI) with cyclopentene the procedure above was followed. In each copolymerisation the monomers were mixed in equimolar proportions before injection into the reaction mixture. The work up procedure was as described above. Details of the individual experiments are given in Table 5.11.

5.9g The ring-opening polymerisation of 2,3-bis(trifluoromethyl)bicyclo-[2.2.1]hepta-2,5-diene using $WCl_6/Na_2O_2/(i\text{-butyl})_3Al$ as the catalyst system

Dried, degassed 2,3-bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene (4.1g, 18mmoles) was vacuum transferred into the reaction vessel and let down to an atmosphere of dry nitrogen. WCl_6 (0.02g, 0.051mmoles) and Na_2O_2 (0.04g, 0.051mmoles) were dissolved in dry, degassed toluene ($10cm^3$) under an atmosphere of dry nitrogen in the glove-box and injected into the reaction vessel at room temperature, there was a colour change from blue-black to deep red. After 15 minutes $(i\text{-butyl})_3Al$ (0.034g, 0.153mmoles) was injected into the reaction mixture using a micro-syringe and after a further 15 minutes the reaction became cloudy and viscous, small pieces of solid material appeared on the sides of the reaction vessel. The reaction was terminated after 3 hours by the addition of methanol ($2cm^3$). After purification by reprecipitation and drying of the recovered product under reduced pressure (45^o, 10^{-3}mm Hg) a hard white solid was produced (3.16g, 13.8mmoles, 77%) ν_{max} 1689cm^{-1} ($-CF_3C{=}CCF_3-$).

The above procedure was repeated using 2-trifluoromethyl bicyclo[2.2.1]-hepta-2,5-diene (3.2g, 20mmoles) as the monomer. On the addition of the pre-mixed WCl_6/Na_2O_2 solution the reaction mixture immediately turned deep-reddy brown in colour and became viscous, no (i-butyl)$_3$Al was added. The reaction was terminated after 1 hour by the addition of methanol, after purification by reprecipitation a light brown material was produced (0.32g, 2mmoles, 10%) ν_{max} 1640cm^{-1} ($-CF_3C{=}CH-$).

5.9h The ring-opening polymerisation of 2-trifluoromethylbicyclo[2.2.1]-hepta-2,5-diene and exo-5-trifluoromethylbicyclo[2.2.1]hept-2-ene using tungsten hexachloride as the catalyst system

Dried, degassed exo-5-trifluoromethylbicyclo[2.2.1]hept-2-ene (IIIa) (2.05g, 14mmoles) was vacuum transferred into the reaction vessel, which was then let down to an atmosphere of dry nitrogen. WCl_6 (0.0125g, 0.0314 mmoles) dissolved in dry, degassed toluene ($10cm^3$) was injected into the reaction vessel at room temperature. The initial blue-black colouration of the mixture changed to deep red then dark brown. After 15 minutes the reaction had become slightly viscous. The reaction was allowed to proceed for 24 hours with stirring and was terminated by the addition of methanol. The reaction mixture was poured dropwise into a five-fold excess of methanol. The precipitated material was recovered by filtration and pumped dry under reduced pressure (45^{o}, 10^{-3}mm Hg) producing a white material (0.35g, 2.15 mmoles, 17%).

The procedure above was repeated using 2-trifluoromethylbicyclo[2.2.1]-hepta-2,5-diene (V) (1.76g, 11mmoles) as the monomer. The reaction was terminated after 3 hours and the product was reprecipitated from a toluene solution using methanol as the non-solvent (0.19g, 1.2mmoles, 11%) ν_{max} 1640cm^{-1} ($-CF_3C=CH-$).

CHAPTER 6

CHARACTERISATION AND SOME PHYSICAL PROPERTIES OF SOME PARTIALLY FLUORINATED POLY(1,3-CYCLOPENTYLENEVINYLENES) AND POLY(1,3-CYCLOPENTENYLENEVINYLENES)

6.1 Structural characterisation

The partially fluorinated poly(1,3-cyclopentylenevinylenes) and poly(1,3-cyclopentenylenevinylenes) prepared as described in Chapter 5 were characterised by elemental analysis, i.r., ^{1}H n.m.r., ^{19}F n.m.r., and ^{13}C n.m.r. spectroscopy. These methods of analysis confirmed that the polymers were produced by ring-opening polymerisation, the information derived from each technique is discussed in this Chapter.

6.1a Elemental analysis

The results of elemental analyses of all the polymers were in good agreement with the calculated values and are summarised in Table 6.1.

6.1b Infrared spectroscopy

Infrared spectra of the polymers were recorded for thin films cast from dilute solutions of the polymers in volatile solvents, on potassium bromide plates.

As discussed in Chapter 3, absorptions in the i.r. spectra of hydrocarbon polyalkenylenes at 980 and 1404 cm^{-1} have been used to estimate the relative amounts of trans- and cis-double bonds present in the polymers. In the case of the partially fluorinated poly(1,3-cyclopentylenevinylenes) and poly(1,3-cyclopentenylenevinylenes) discussed here, the presence of many strong absorptions in the region 1400-900cm^{-1}, assigned at least in part to C-F absorptions, make the unambiguous identification of bands due to trans- and cis-double bonds difficult, and no definite conclusions about the relative amounts of trans- and cis-double bonds in the fluorinated polymers can be made from an analysis of their i.r. spectra. In general, as might reasonably be expected, there was a very close similarity between spectra of the monomers and those of the resultant polymers, with the absorptions of the latter being much broader.

Table 6.1

Elemental analyses of partially fluorinated poly(1,3-cyclopentylenevinylenes) and poly(1,3-cyclopentenylenevinylenes)

Polymer	Calculated				Found			
	C	H	Cl	F	C	H	Cl	F
VII [a]	44.5	2.8		52.7	44.4	3.1		52.8
VIII	40.6	2.3		57.1	41.7	2.3		
IX	59.3	5.6		35.2	59.0	6.0		34.8
X	36.2	2.02	23.7	38.1	36.0	2.3	24.5	37.4
XI	47.4	2.7		50.0	47.1	2.7		49.5
XII	60.0	4.4		35.6	59.9	4.0		36.0
XIII [b]	52.7	3.9		43.5	52.8	4.1		43.1
XIV [b]	65.0	5.7		29.4	64.3	4.8		30.1
cyclopentene	88.1	11.8			87.9	11.9		

[a] Analysis on the polymer prepared from the 60 : 40 mixture of adducts (Ib) and (Ia).

[b] Calculated values are for a copolymer with the partially fluorinated poly(1,3-cyclopentenylenevinylene) and poly(1-pentenylene) repeat units in a 2 : 1 ratio.

As stated in Chapter 5, the i.r. spectra of polymers (XI) and (XII), that is the polymers derived from the partially fluorinated bicyclo[2.2.1]-hepta-2,5-diene monomers, showed absorptions at 1680cm^{-1} and 1640cm^{-1} characteristic of the substituted double bonds $-CF_3C{=}CCF_3-$ and $-CF_3C{=}CH-$ respectively. The absence of an absorption for the $-CF_3C{=}CH-$ double bond in polymer (XI) and for the $-CF_3C{=}CCF_3-$ double bond in polymer (XII) requires that ring-opening in both cases was either exclusively at the unsubstituted double bonds or exclusively at the substituted double bonds; in the case of polymer (XII) the further condition of exclusively head-to-tail assembly would have to be included. Analysis of the ^{13}C n.m.r. spectrum of polymer (XI) (see below) establishes that ring-opening occurred only at the unsubstituted double bonds.

6.1c N.m.r. spectroscopic analysis

When an unsymmetrically substituted bicyclo[2.2.1]hept-2-ene undergoes ring-opening polymerisation there are a variety of ways in which the monomer unit can be incorporated in the polymer chain. If it could be obtained, a detailed knowledge of the stereochemistries of such polymers might well provide useful insights into the mechanism of polymerisation. It was hoped that the combination of three structural probes, namely ^{1}H n.m.r., ^{19}F n.m.r. and ^{13}C n.m.r. spectroscopy would allow the elucidation of the required stereochemistries. In practice only a partial solution to the problem was obtained, however, the work reported here establishes the potential and value of this approach.

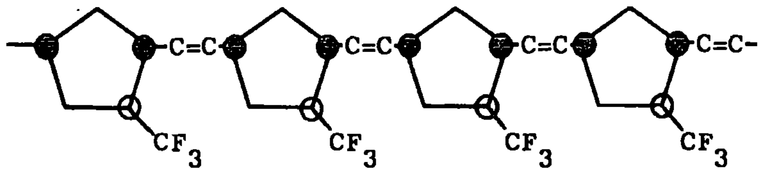
The variety of possible stereochemistries can best be appreciated by considering a specific case, for example, the polymer produced from exo-5-trifluoromethylbicyclo[2.2.1]hept-2-ene. In this case stereoisomerism can result from three structural features of the repeat unit, the main chain double bond may display cis- or trans-geometry, the unsymmetrical repeat unit may be incorporated in a head-to-tail or head-to-head fashion, and finally the chirality of the repeat unit allows isotactic, syndiotactic or atactic sequences of monomer incorporation. Figure 6.1 illustrates some of these possibilities for the cases where each structural feature remains constant for the whole polymer chain, it must also be realised that other structurally regular possibilities exist, such as head-to-head sequences and alternating cis- and trans-double bonds, along with a range of random and block copolymeric structures.

At the time of writing this thesis the only detailed analysis of the stereochemistry of polyalkenylenes which has been reported is that carried out using ^{13}C n.m.r. spectroscopy, and of particular interest with respect to the work reported here are the papers by Ivin et al on poly(1-pentenylene) and poly(1,3-cyclopentylenevinylene) and derivatives.[210,211,212] It was initially hoped that analysis of the n.m.r. spectra of the series of partially fluorinated poly(1,3-cyclopentylenevinylenes) and poly(1,3-cyclopentenylenevinylenes) produced in this work would enable their stereochemistries to be completely established. It was anticipated that fluorine substituents in different stereochemical environments would produce relatively large effects on the chemical shifts not only in the ^{19}F n.m.r. spectra, but also in the ^{1}H n.m.r. and ^{13}C n.m.r. spectra.

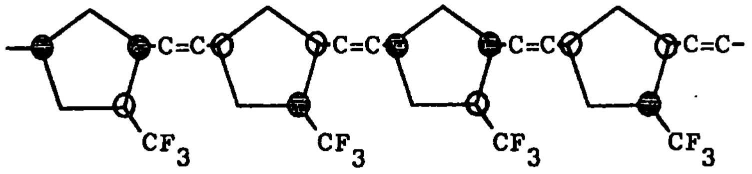
For substituted bicyclo[2.2.1]hept-2-ene monomers the detailed stereochemical structure of the polymer will depend on the orientation of the coordinating monomer, i.e. exo or endo on approach to the active catalyst system. In other reactions of bicyclo[2.2.1]hept-2-ene with transition metals, approach from the exo-direction is favoured.[213] Assuming that the mechanism for ring-opening polymerisation of cycloalkenes involves metal-carbene and metallocyclobutane intermediates a substituted bicyclo[2.2.1]hept-

Figure 6.1

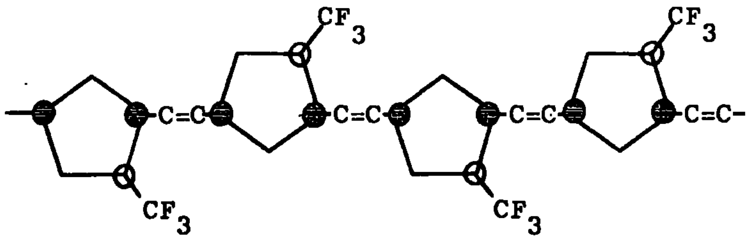
Regular head-to-head poly(4-trifluoromethyl-1,3-cyclopentylenevinylene)



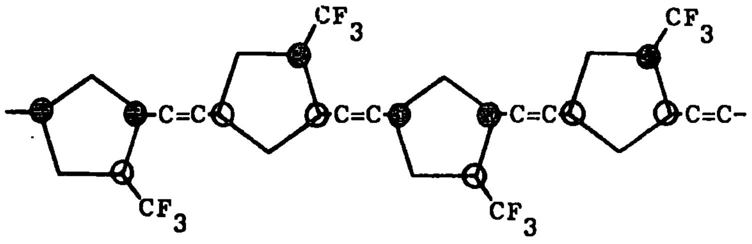
isotactic poly(4-trifluoromethyl-1,3-cyclopentylene-cis-vinylene)



isotactic poly(4-trifluoromethyl-1,3-cyclopentylene-trans-vinylene)



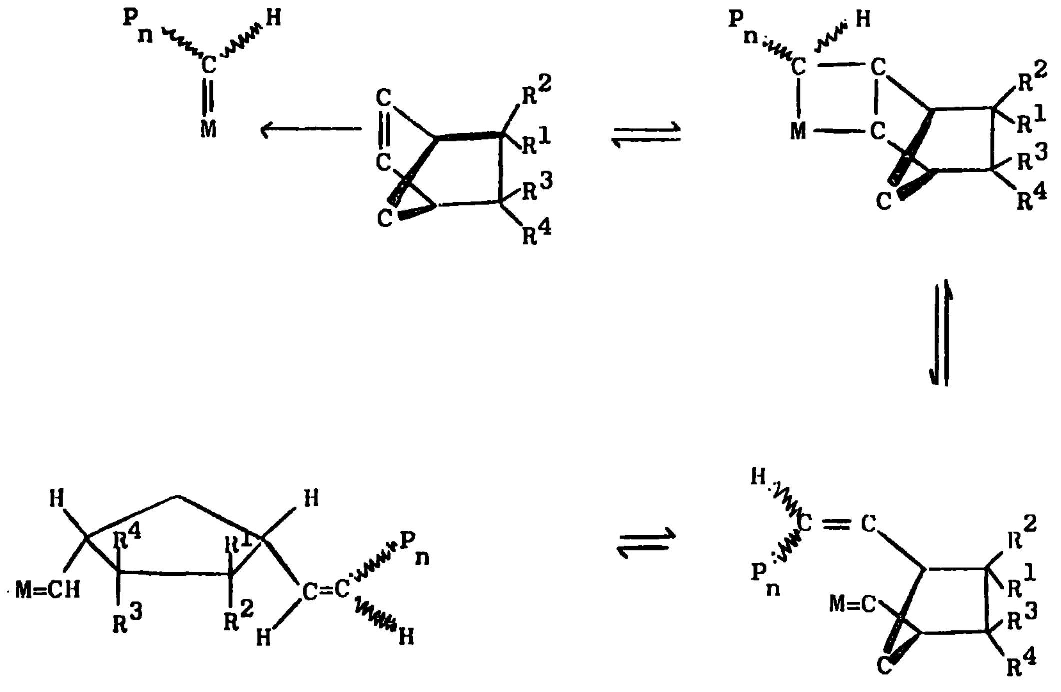
syndiotactic poly(4-trifluoromethyl-1,3-cyclopentylene-cis-vinylene)



syndiotactic poly(4-trifluoromethyl-1,3-cyclopentylene-trans-vinylene)

(● - bond approaching, O - bond receding)

2-ene monomer will approach the metal carbene species, form the metallocyclobutane intermediate and hence the extended polymer chain as depicted in Figure 6.2. If approach is exclusively from the exo-direction and if the



Key: P_n is the polymer chain containing n monomeric units;

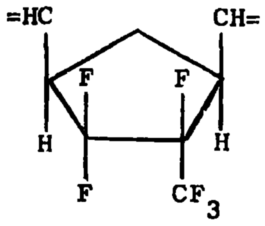
∿∿∿ indicates undefined stereochemistry.

Figure 6.2

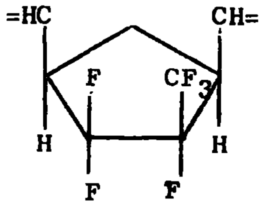
<u>A possible mechanism for the ring-opening polymerisation of substituted bicyclo[2.2.1]hept-2-ene</u>

monomer exist as a racemic mixture, as is the case for 5-trifluoromethylbicyclo[2.2.1]hept-2-ene, the only totally stereoregular products possible would be the ones in which the enantiomers of the monomer were incorporated in a regular alternating fashion; that is, head-to-head poly(4-trifluoromethyl-1,3-cyclopentylene-cis-vinylene) or its all trans isomer.

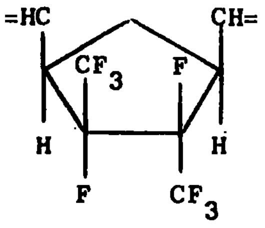
It has been proved by ozonolysis experiments that in poly(1,3-cyclopentylenevinylene) the cyclopentane ring has a cis-1,3-structure. From the mechanistic scheme shown in Figure 6.2 the endo-substituents R_2 and R_3 will be on the same side of the ring as the carbon-carbon double bond in the polymer chain. Hence, the stereochemistry of the individual repeat units arising from adducts (Ia), (Ib), (IIa),(IIIa), (V) and (VI) will be, (VIIa), (VIIb), (VIII), (IX), (XI) and (XII) respectively, as shown in Figure 6.3.



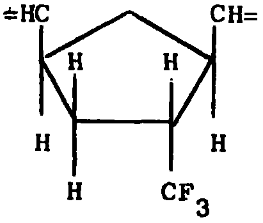
(VIIa)



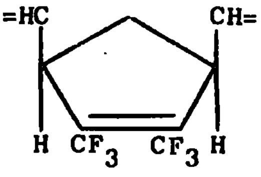
(VIIb)



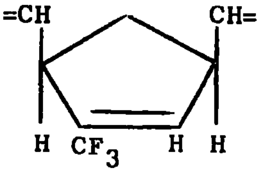
(VIII)



(IX)



(XI)



(XII)

Figure 6.3

A complete structural and stereochemical analysis requires high quality n.m.r. spectra, however, due to both practical and instrumental limitations, well resolved ^{1}H and ^{19}F n.m.r. spectra were not always obtained, despite extensive work and the considerable efforts of Dr. R.S. Matthews (this Department) with a 'home-made' FT adaption of a Bruker Spectrospin HX 90E high resolution n.m.r. spectrometer. The same limitations applied to the recording of ^{13}C n.m.r. spectra in this department, however, good spectra were obtained for some samples through the generosity of Professor K.J. Ivin and coworkers at Queen's University Belfast.

From the ^{1}H, ^{19}F and ^{13}C n.m.r. spectra which were obtained it is clear that fluorine substitution does produce some differences in chemical shifts which are possibly caused by structural variation. Only a partial interpretation of the spectra has been obtained and if a complete unambiguous understanding of these systems is to be obtained less complex structures are required, e.g. polymers which have exclusively or predominantly cis- or trans-geometry. The analyses accomplished are discussed in detail below.

1. ^{1}H and ^{19}F n.m.r. spectroscopic analysis

The data from the ^{1}H and ^{19}F n.m.r. spectra of the polymers are summarised in Table 6.2. The ^{1}H n.m.r. spectra consist of complex, broad signals, but each showed the expected signal for the vinylic protons. The spectra of polymers (IX) and (XI) showed some interesting features, the former showed at least two distinct signals for the vinylic protons, and the latter showed at least three signals in the vinylic region together with two broad bands for the tertiary protons and two broad bands for the methylene protons. The possible causes for these different signals will be discussed later.

The ^{19}F n.m.r. spectrum of the polymer which was prepared from the 60 : 40 mixture of adducts (Ib) and (Ia) is very complex, Figure 6.4a.

Table 6.2

^1H n.m.r. and ^{19}F n.m.r. data for partially fluorinated poly(1,3-cyclopentylenevinylenes) and poly(1,3-cyclopentenylenevinylenes)

Polymer repeat unit	^{19}F n.m.r. [a]			^1H n.m.r. [b]		
	$-CF_3$	$-CF_2-$	$-\overset{\vert}{\underset{\vert}{C}}-F$	$-CH_2-$	$-\overset{\vert}{\underset{\vert}{C}}-H$	=CH-
VIIb	74.05	δ_A δ_B 102.8 115.9 J_{AB}=235Hz	190.26	2.02	3.35	5.80
VIIa	70.99	δ_A δ_B 113.7 123.5 J_{AB}=210Hz	158.46			
VIII	70.67 73.44		163.26 165.01 185.97 187.03	2.02	3.59	5.78
IX	63.04			1.03 to 2.25	2.37 to 3.35	5.41 5.52
X [c]	67.85 64.00 62.25 60.42			1.84, 2.56	3.89	5.84
XI	57.34 57.80			1.56, 2.77 (1) (1)	4.23, 3.79 (1) (1)	5.66) 5.57) (2) 5.40)
XII	62.40 62.82					

[a] Chemical shifts were recorded in ppm relative to C_6F_6 as internal reference and for comparison purposes were converted to the $\delta_{(CFCl_3)}$ scale using the relation $\delta_{(CFCl_3)} \approx \delta_{(C_6F_6)} + 162.3$

[b] Chemical shifts are given in ppm relative to Me_4Si as external reference. Integrated intensities are given in parentheses.

[c] Unknown stereochemistry.

Figure 6.4

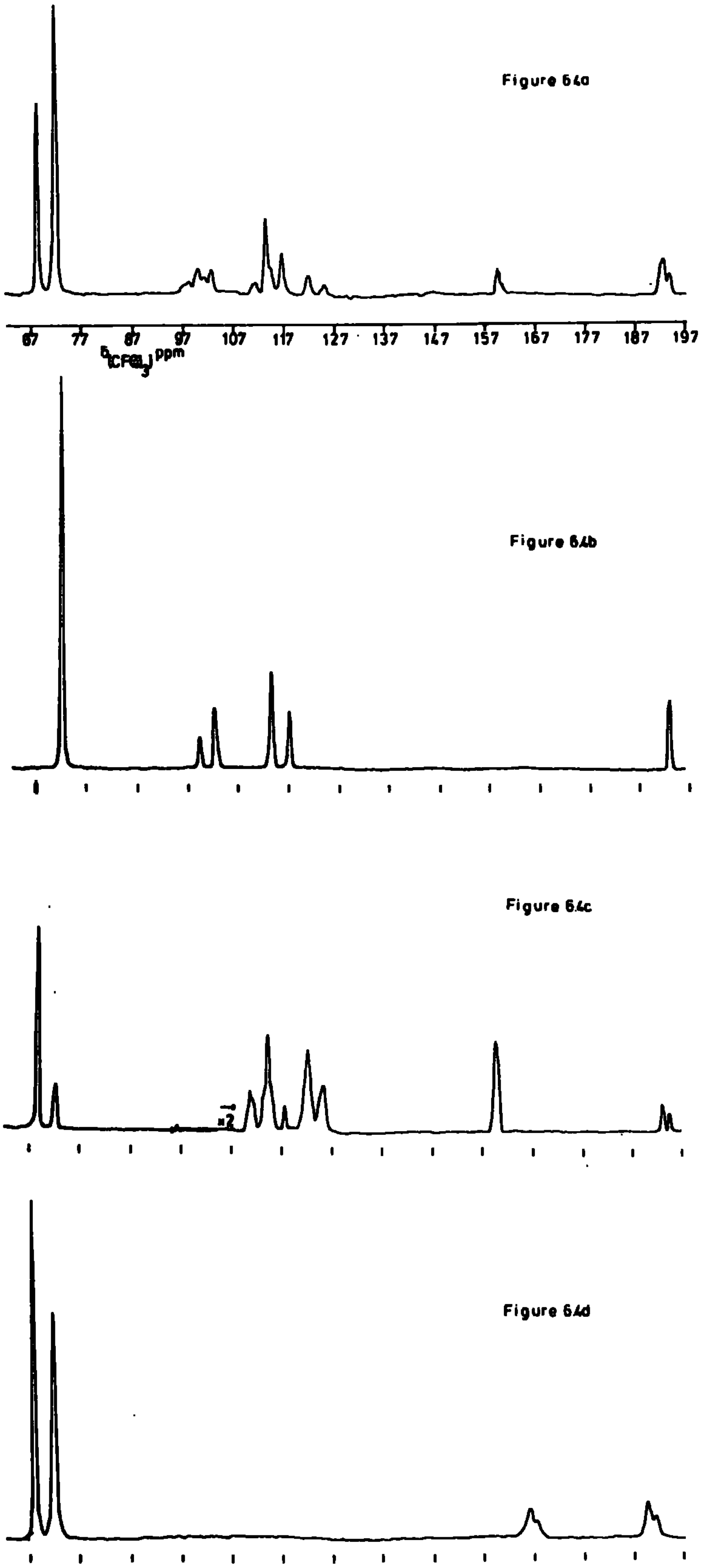


Figure 6.4a
67
77
87
97
107
117
127
137
147
157
167
177
187
197
δ(CFCl$_3$) ppm
Figure 6.4b
Figure 6.4c
×2
Figure 6.4d

It was initially assumed, on the basis of monomer composition and polymer yield, that the most intense signals belonged to the repeat units formed from adduct (Ib), i.e. (VIIb), and the least intense signals belonged to the repeat units from adduct (Ia), i.e. (VIIa). From the relative intensities of the trifluoromethyl and tertiary fluorine signals in this spectrum the ratio of (VIIb) : (VIIa) units was 70 : 30; thus, it appeared that adduct (Ib) had polymerised to a greater extent than adduct (Ia). This initial assignment of the signals was confirmed by the ^{19}F n.m.r. spectrum of the polymer prepared from pure adduct (Ib), Figure 6.4b, having exclusively repeat unit (VIIb) and that of the polymer prepared from the 16 : 84 mixture of adducts (Ib) and (Ia), Figure 6.4c, having predominantly repeat unit (VIIa). Each of the latter two spectra consisted of a sharp signal for the trifluoromethyl group, an AB quartet for the $>CF_2$ group and a sharp signal for the tertiary fluorine atom, in the case of the polymer with (VIIb) as repeat unit the tertiary fluorine occurs as a doublet. In the spectrum of the polymer derived from the 60 : 40 mixture of (Ib) and (Ia) the lower field limb of the AB quartet at lowest field consisted of what appeared to be four broad signals, two of low intensity; also the tertiary fluorine at highest field consisted of two signals, again one of low intensity. These low intensity signals are not present in the polymer obtained from pure adduct (Ib) and must have arisen due to the presence of the other repeat unit. This hypothesis receives support from the observation that the tertiary signal from the minor component in the polymer derived from the 16 : 84 mixture of adducts (Ib) and (Ia) also appears as two peaks (see the high field part of spectrum, Figure 6.4c). However, the observation that the spectrum of the copolymer produced from the 60 : 40 mixture of adducts (Ib) and (Ia) appears to be essentially the sum of the spectra of the homopolymers of (Ib) and (Ia) may be interpreted as evidence that the copolymer is formed predominantly from blocks of (VIIb) and (VIIa) units; the low intensity signals exclusive to the copolymer (which appear to be associated with a difluoromethylene fluorine and a tertiary fluorine in (VIIb) type units) could then be assigned to either junctions between blocks or alternating sequences. This is necessarily a tentative hypothesis since it seems unlikely that the polymers derived from pure monomers are structurally homogeneous.

In view of the sensitivity of the chemical shift of tertiary fluorines to their environments, observed for the copolymers of (Ia) and (Ib), it was anticipated that the polymer derived from adduct (II) would show a multiplicity of signals in the tertiary fluorine region as a consequence of different stereochemical chain sequences. In practice the ^{19}F n.m.r. spectrum of this polymer, Figure 6.4d, shows the expected multiplicity of signals in the tertiary fluorine region as well as line broadening of the higher field signal arising from a trifluoromethyl group. There is clearly structural information to be obtained from this approach, but the spectrum resolution obtained in this case does not justify further speculation, better resolved spectra are required.

The ^{19}F n.m.r. spectrum of polymer (IX) is simple, consisting of only one signal, due to the single trifluoromethyl group. By contrast, the spectrum of polymer (X) showed at least four well resolved signals, some with fine structure, at chemical shifts typical of trifluoromethyl groups; unfortunately in this case the polymer was derived from a mixture of at least three monomer isomers whose structure and distribution was not fully characterised.

For polymers (XI) and (XII) produced from the two partially fluorinated bicyclo[2.2.1]hepta-2,5-dienes, adducts (V) and (VI) respectively, at least two and maybe three broad signals in the CF_3 region are observed. This phenomenon may be explained by taking into account the different trifluoromethyl group environments caused by ring tacticity and cis- and trans-geometry of the repeat units. The cyclopentene ring may be incorporated into the growing polymer chain in two ways, either isotactic or syndiotactic as shown in Figure 6.5.

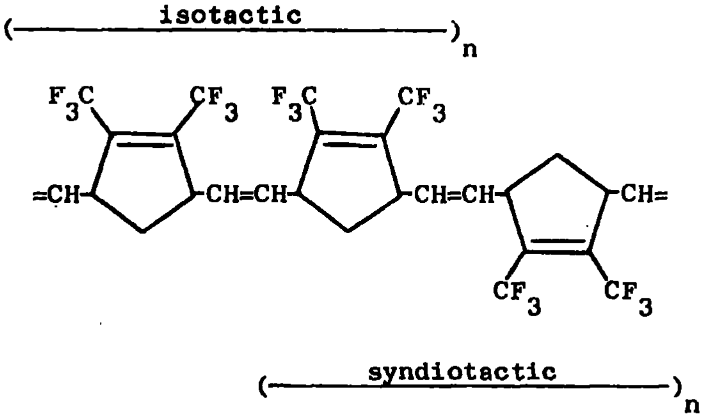


Figure 6.5

For polymer (XI), with successive rings in the chain with the same orientation (isotactic) and the repeat units in the cis-geometry, CF_3 groups on neighbouring rings will be in different environments to those associated with syndiotactic sequences, Figure 6.6. The former may be expected to experience steric compression, whereas very little, if any, steric compression

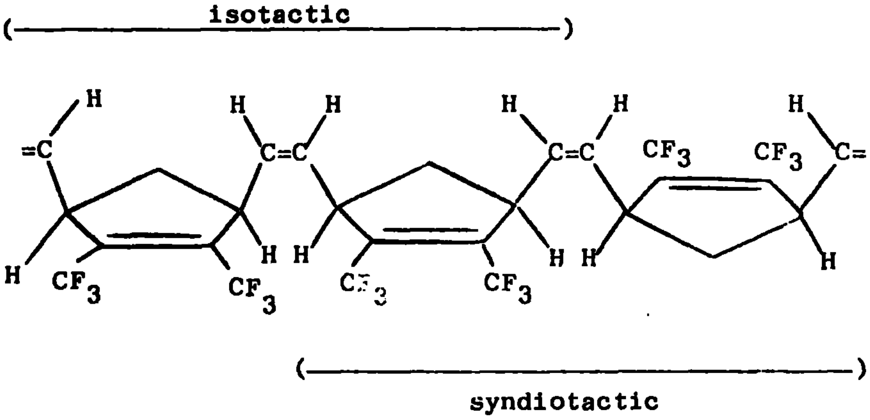


Figure 6.6

will be experienced by the latter. In the trans-geometry even with successive rings in the same orientation steric compression will not occur, however, the trifluoromethyl groups will be in different environments in isotactic and syndiotactic sequences. This analysis could account for the different signals observed in the ^{19}F n.m.r. spectrum. The suggestion that the CF_3 group causes steric compression is also used in the interpretation of the ^{13}C n.m.r. spectrum, which will be discussed later. The analysis presented above accounts for the presence of at least two vinylic protons, two different methylene protons and two different methine protons in the ^{1}H n.m.r. spectrum of the polymer.

For polymer (XII), the only time that the $-CF_3$ group will cause steric compression is when the successive rings are in the same orientation, the repeat units are in cis-geometry and in a head-to-head arrangement, Figure 6.7.

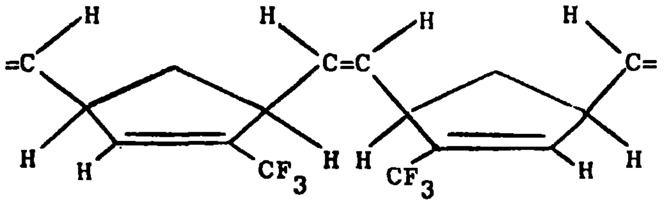


Figure 6.7

An analysis similar to that given above for (XI) would account for the multiplicity of signals observed in the ^{19}F n.m.r. spectrum of this polymer. This may provide a method for determining regularity in the polymer and opens up another area for future investigation; the initial requirement would be for polymers with all cis- or trans-sequences as a first step in assigning signals to structural features.

2. ^{13}C N.m.r. spectroscopic analysis

^{13}C N.m.r. spectroscopy for the study of non-fluorine substituted poly(1,3-cyclopentylenevinylenes) has been developed in recent years. It provides a powerful tool for investigating the cis/trans content of the unsaturated polymers much more accurately than i.r. spectroscopy and without the need for calibration. Ivin et al have investigated the ^{13}C n.m.r. spectra of poly(1,3-cyclopentylenevinylene) with varying amounts of cis- and trans-unsaturation.[210] In the spectrum of an almost 50% cis-poly(1,3-cyclopentylenevinylene), Figure 6.8b, the number of signals observed cannot be explained simply by the fact that the chemical shifts of the C^1, C^2 and C^3 carbon atoms, Figure 6.9, are sensitive to the isomerism about the nearest double bond, but that they are also sensitive to the isomerism about the next nearest double bond. Therefore, in a poly(1,3-cyclopentylenevinylene) containing both cis- and trans-unsaturation, four signals should be observed for both C^2 and C^1 i.e. 2tt, 2tc, 2cc and 2ct (using the nomenclature proposed by Ivin et al,[210] in which the number denotes the carbon atom; the first letter, the cis(c) or trans(t) structure at the nearest double bond; the second letter that at the next nearest double bond) and 1tt, 1tc, 1ct and 1cc respectively; for C^3 which is symmetrically situated between two double bonds three signals should be observed corresponding to 3tt, 3tc $\equiv$ 3ct and 3cc. The relative intensities of these signals may be used to calculate the amount of cis- and trans-unsaturation in the polymer using the formulae for

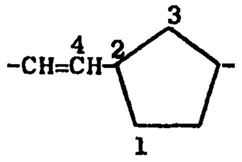
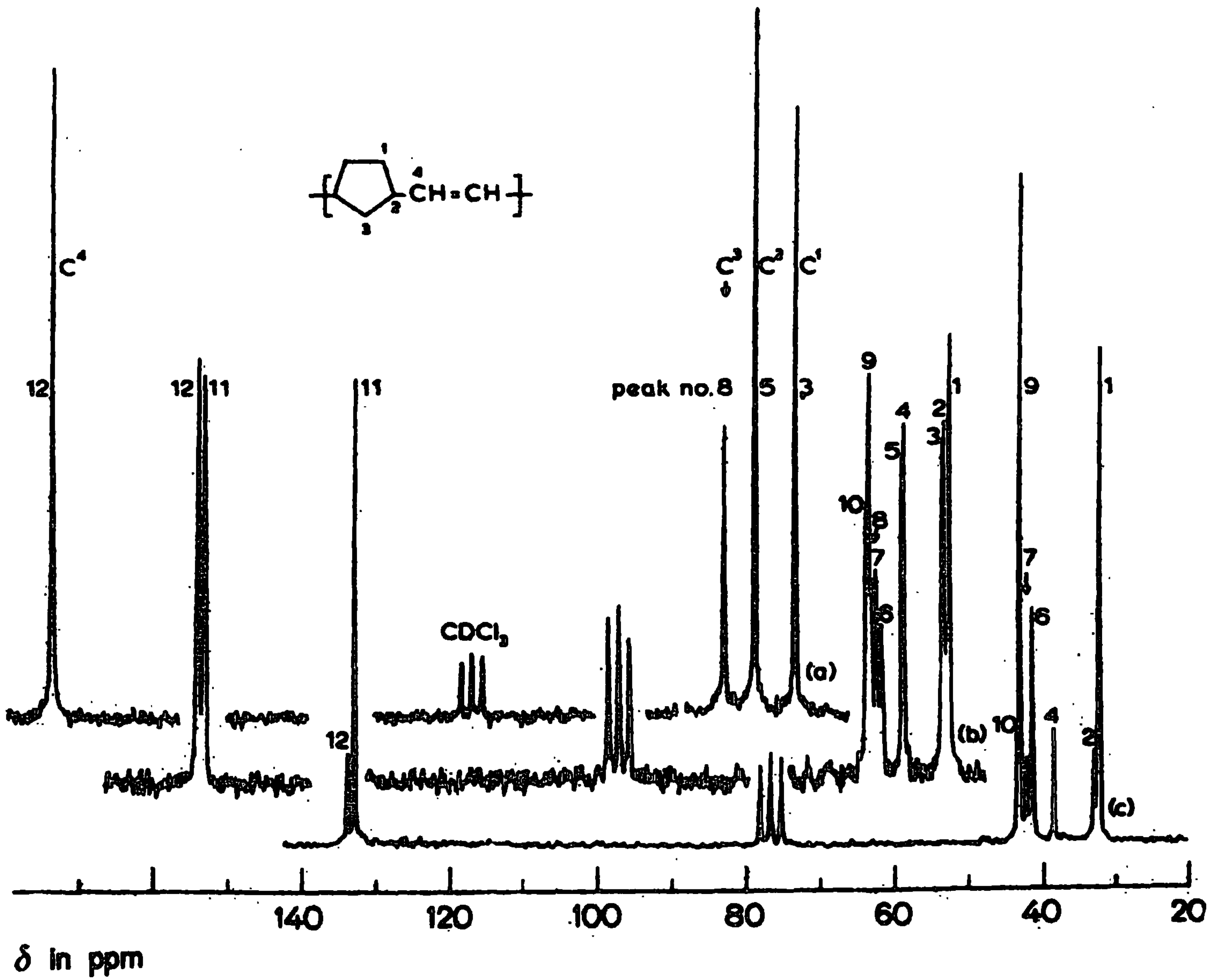


Figure 6.9

Figure 6.8 ^{13}C N.m.r. spectrum of poly(1,3-cyclopentylenevinylene)



the determination of the fraction of cis-unsaturation, σ_c, for each set of signals shown below and compared with the value obtained from the intensitites

$$\sigma_c = \frac{1ct + 1cc}{1tt + 1tc + 1ct + 1cc} ,$$

$$\sigma_c = \frac{2ct + 2cc}{2tt + 2tc + 2ct + 2cc} ,$$

$$\sigma_c = \frac{3cc + 0.5\ (3ct + 3tc)}{(3tc + 3ct) + 3cc + 3tt}$$ where 3ct and 3tc are equivalent,

of the signals due to cis-C^4 and trans-C^4, i.e. vinylic carbons where

$$\sigma_c = \frac{4c}{4c + 4t}$$

Using this argument and the fact that in simple alkenes the α-cis carbon atoms always appear about 5ppm upfield from α-trans carbon atoms[214] together with a comparison of the ^{13}C n.m.r. spectra of 100% cis-poly(1,3-cyclopentylenevinylene) and 84% trans-poly(1,3-cyclopentylenevinylene), Figures 6.8a and 6.8c respectively, all the signals in the spectrum of the 50% cis-poly(1,3-cyclopentylenevinylene) are able to be assigned as shown in Table 6.3.

The ^{13}C n.m.r. spectra of the partially fluorinated poly(1,3-cyclopentylenevinylenes) (VII), (VIII) and (IX) and the partially fluorinated poly(1,3-cyclo pentenylenevinylene) (XI) are shown in Figure 6.10a-d respectively. The spectrum of polymer (XI) was the easiest to interpret and a complete analysis has been made, Table 6.4.

Assignment made for signals in that spectrum helped solve the assignment of signals in more complex spectra of other polymers. Signals (2) and (3) were assigned to cis-C^2 and trans-C^2 respectively, the cis-C^2 signal being shifted exactly 5ppm upfield from the trans-C^2. Signals (7)

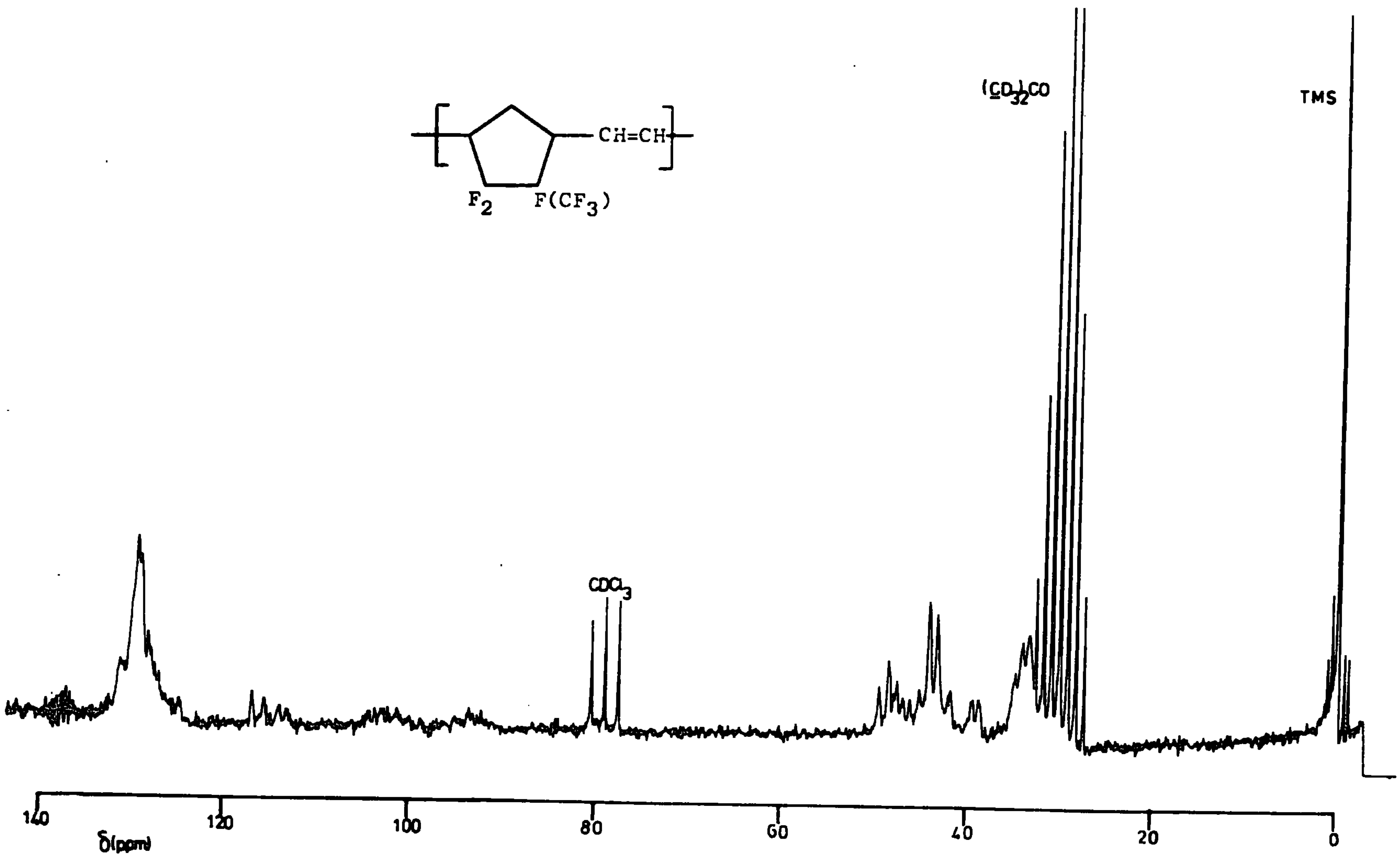
Table 6.3[210]

Chemical shifts in the ^{13}C n.m.r. spectra of three samples (a), (b) and (c) of poly(1,3-cyclopentylenevinylene)

Peak No.	Chemical Shift [a]			Assignment
	(a)	(b)	(c)	
1		32.30	32.30	1tt 1tc
2		33.01	32.94	1ct
3	33.21	33.14		1cc
4		38.47	38.47	2ct
5	38.60	38.67		2cc
6		41.40	41.40	3tt
7		42.11	42.11	3tc ≡ 3ct
8	42.70	42.83		3cc
9		43.15	43.15	2tt
10		43.41	43.41	2tc
11		133.10	133.10	4t
12	133.88	133.88	133.94	4c

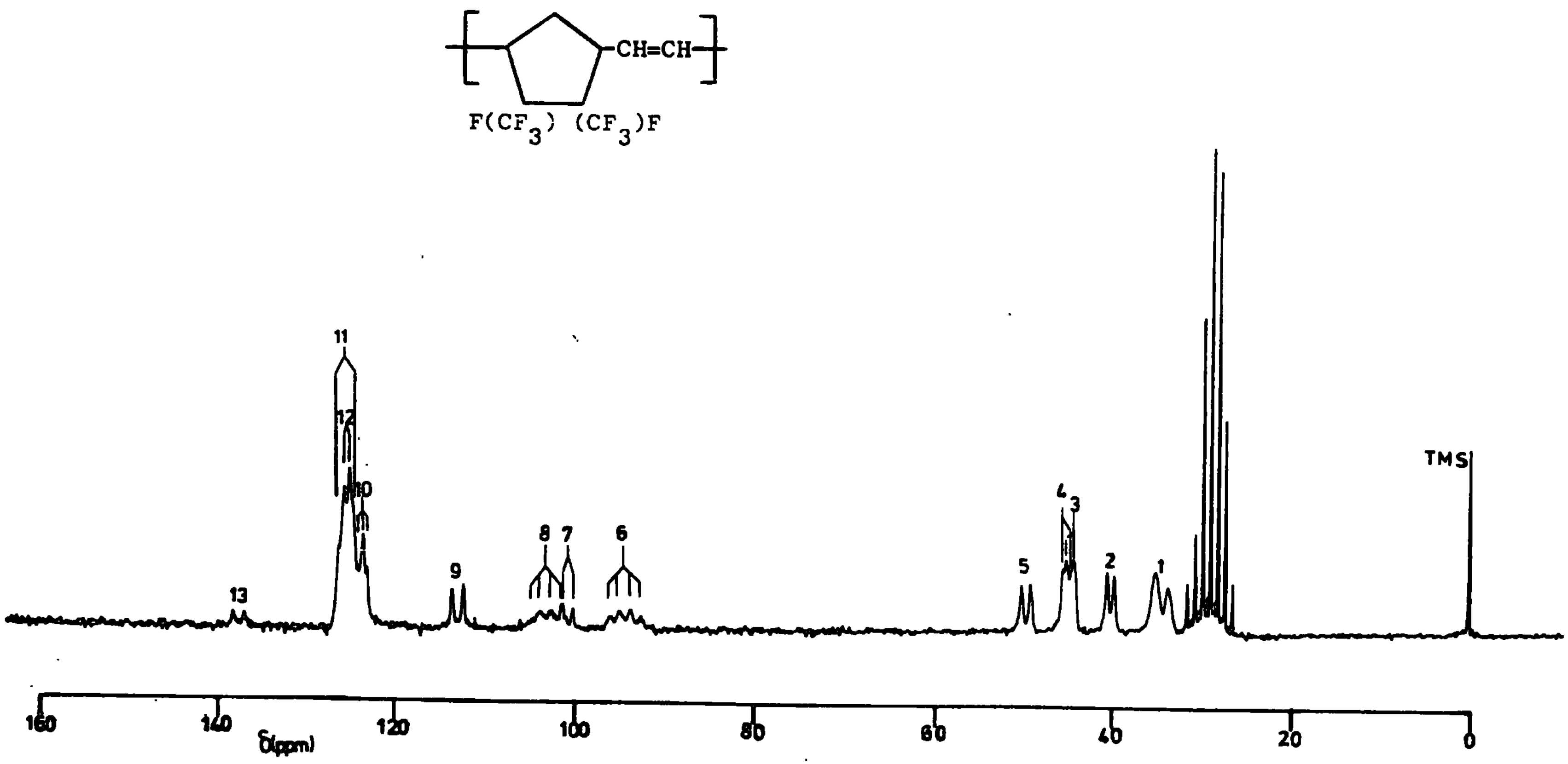
[a] in ppm downfield from TMS

Figure 6.10a ^{13}C N.m.r. spectrum of poly(4,4,5-trifluoro-5-trifluoromethyl-1,3-cyclopentylenevinylene) [e]



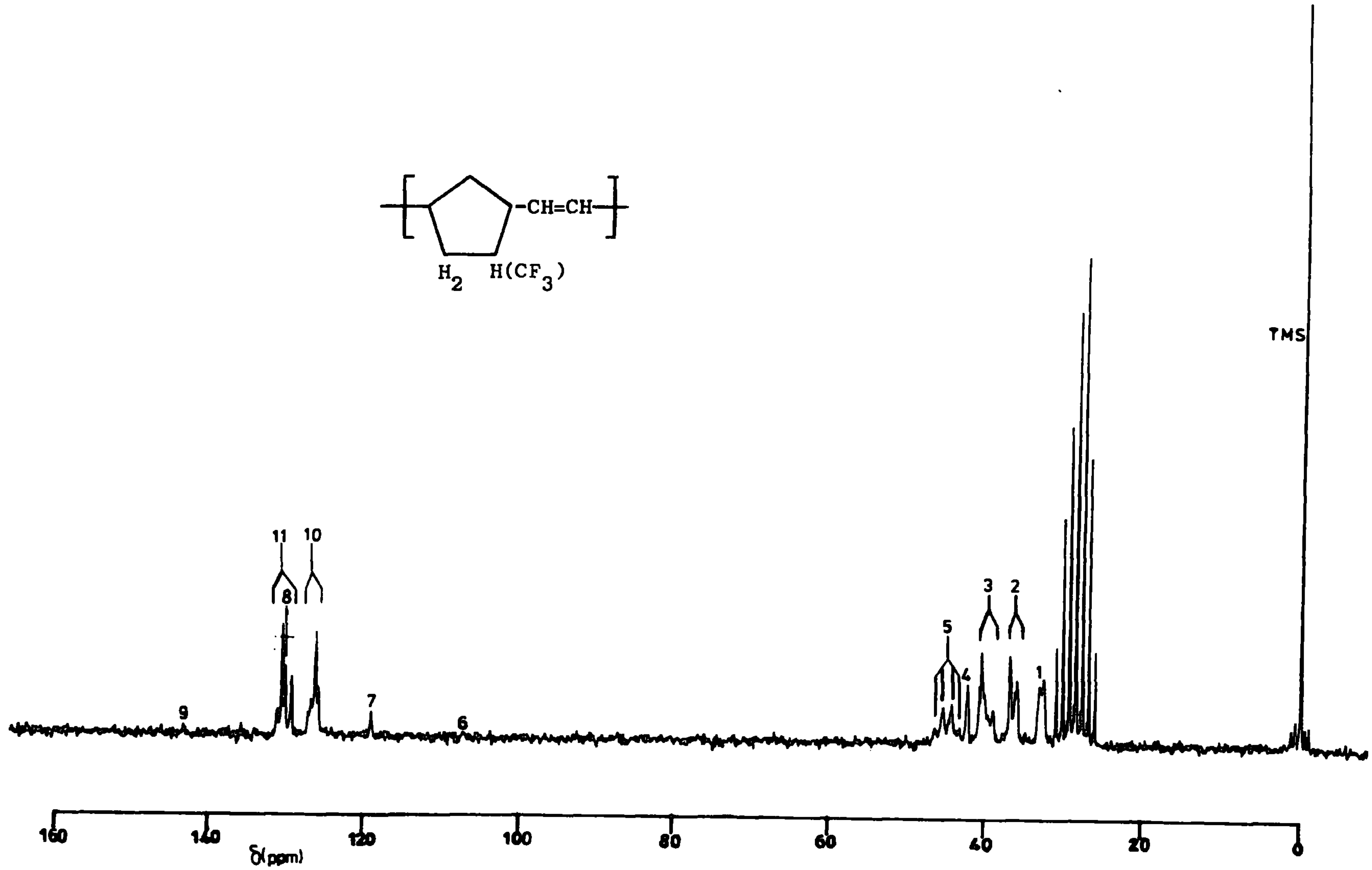
[e] Prepared from 60 : 40 mixture of adducts (Ib) and (Ia)

Figure 6.10b ^{13}C N.m.r. spectrum of poly(4,5-trifluoro-4,5-trifluoromethyl-1,3-cyclopentylenevinylene) [e]



[e] Prepared from pure adduct (IIa)

Figure 6.10c ^{13}C N.m.r. spectrum of poly(4-trifluoromethyl-1,3-cyclopentylenevinylene) (IX) [e]



[e] Prepared from pure adduct (IIIa)

Figure 6.10d ^{13}C N.m.r. spectrum of poly(4,5-bis(trifluoromethyl)-1,3-cyclopentenylenevinylene) (XI)

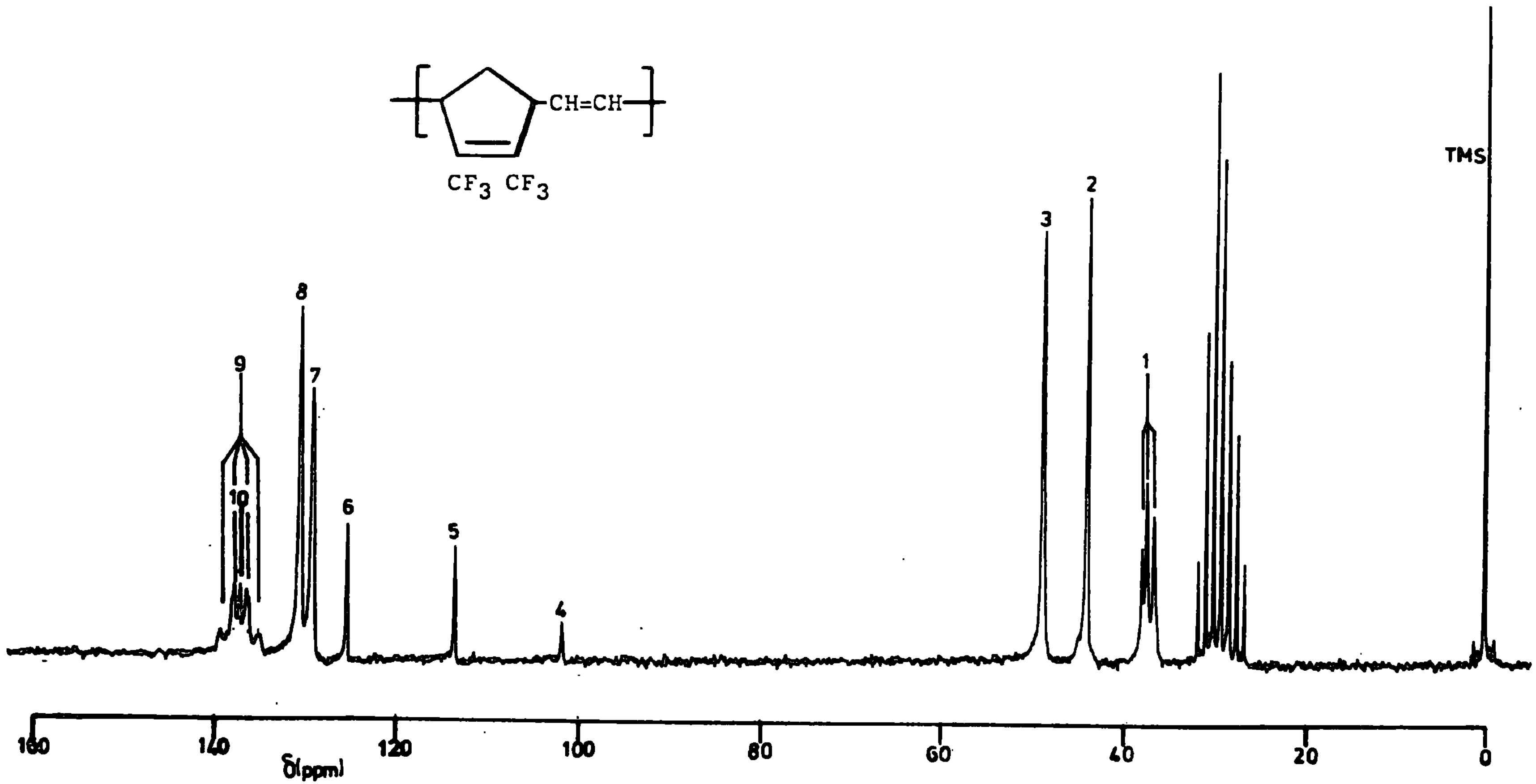
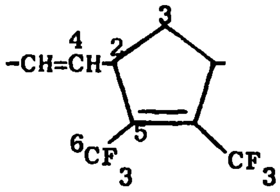


Table 6.4

Chemical shifts in the ^{13}C n.m.r. spectrum of

poly(4,5-bis(trifluoromethyl)-1,3-cyclopentenylenevinylene) (XI)



Peak No.	Chemical Shift[a]	Assignment	Relative Area
1	37.2 38.1 38.5	3cc 3ct ≡ 3tc 3tt	234 284 187
2	44.8	2c	708
3	49.8	2t	657
4,5,6,10	122(q) J_{CF}=273Hz	6	
7	132.1	4t	412
8	133.5	4c	531
9	140.1(q) J_{CCF}=31.8Hz	5	

q = quartet

[a] in ppm downfield from TMS

and (8) were assigned to the vinylic carbon, trans-C^4 and cis-C^4 respectively. This line order was based on the relative intensities of the two signals compared with the signals for cis-C^2 and trans-C^2 and the line order proposed for the vinylic carbons in poly(1,3-cyclopentylenevinylene),[210] poly(1-butenylene),[215] and simple 2-alkenes.[214]

The CH_2 carbon, i.e. C^3 shows a clear triplet, signal (1), and the individual signals were assigned as shown in Table 6.4. This line order does not parallel that made by Ivin et al for C^3 in poly(1,3-cyclopentylenevinylene)[210] and poly(1,3-cyclopentenylenevinylene),[211] but the observed line order can be rationalised using the same principles of steric compression proposed by Ivin et al to account for their observed spectra. For polymer (XI) the steric compression at C^3 in the trans structure (for all ring tacticities) is probably no greater than in poly(1,3-cyclopentylenevinylene); whereas for the structure having cis-geometry the steric compression at C^3 is probably significantly greater in (XI) than in poly(1,3-cyclopentylenevinylene) as a consequence of the requirements of the CF_3 groups, therefore, overall the signal for C^3 in all cis-sequences of polymer (XI) will be shifted upfield with respect to the signal associated with all trans-sequences giving the observed line order.

Using the formulae described previously the proportion of cis-double bonds calculated from the C^4 signals was $\sigma_c = 0.56$; the C^2 signal was $\sigma_c = 0.52$ and the C^3 signal was 0.53. The agreement between σ_c from C^3 and C^2 is very good, the discrepancy between these values and that derived from C^4 may well be due to the fact that the spectrum phase appears to be out marginally in the C^4 region.

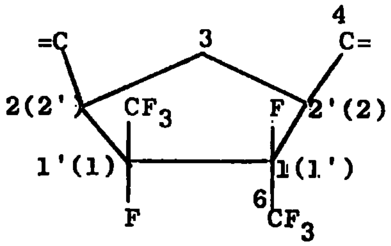
In fluorinated materials, due to CF coupling, complex ^{13}C n.m.r. spectra are usually observed; however, in the case of polymer (XI), the signals are simple and can be interpreted. C^6, the carbon atom of the trifluoromethyl group was assigned to the quartet (4), (5), (6) and (10) (δ = 122.0ppm; J_{CF} = 273Hz) and C^5, the ring vinylic carbon atom is also coupled to the three equivalent fluorine atoms on C^6 and appears as a quartet (9) (δ = 140.1ppm; J_{CCF} = 31.8Hz). As can be seen the relative intensities of the carbon atoms attached to hydrogen atoms are much greater than those attached to fluorine atoms, because in the former the Nuclear Overhauser Effect is operating and enhancing the intensity of the signals while in the latter no such effect occurs.

For polymer (VIII) the assignment of the various signals is given in Table 6.5. The most noticeable feature about the spectrum was the number of doublets, which can be accounted for by CF and CCF couplings. The carbon atom of the trifluoromethyl group, C^6 is split into a quartet of doublets, signals (7), (9), (11) and (13), the quartet splitting is due to the coupling with the three equivalent fluorine atoms and the doublet splitting is caused by coupling with the fluorine atom attached to C^1 (or $C^{1'}$). The doublet signal (11) of the quartet is in fact coincident with the signal due to the cis-vinylic carbon, C^4, signal (12), with the trans-C^4 assigned to signal (10). The signals due to C^1 and $C^{1'}$ appear as a double of quartets (6) and (8); the doublet splitting caused by coupling with the attached fluorine atom and the quartet splitting caused by coupling with the fluorine atoms attached to C^6.

The vinylic carbon atom, C^4, was assigned as usual, with the cis-C^4 downfield from the trans-C^4 (signals (12) and (10) respectively). The assignment of the signals for C^2 is more difficult and the structure of the repeat unit has to be taken into account, since it is apparent that there are two different environments for C^2, designated 2 and 2', two sets of signals will be present. It is not possible to say which set belongs to which atom, but signals (2) and (4) belong to one set and signals (3) and (5) belong to

Table 6.5

Chemical shifts in the ^{13}C n.m.r. spectrum of poly(4,5-difluoro-4,5-bis(trifluoromethyl)-1,3-cyclopentylenevinylene) (VIII)



Peak numbers	Chemical shifts[a]	Assignment	Relative Areas
1	34.4 36.0	3tt 3cc	63 90
2	41.1(d) J_{CCF}=18Hz	2'c(2c)	176
3	45.8(d) J_{CCF}=20Hz	2c(2'c)	205
4	46.1(d) J_{CCF}=20Hz	2't(2t)	193
5	50.5(d) J_{CCF}=21Hz	2t(2't)	142
6,8	97.9(d) J_{CF}=205Hz J_{CCF}=29Hz	1(1')	
10	126.5 127.0 127.6	4t	87 135 89
12	128.6 129.1	4c	230 203
7,9,11,13	123.1(q) J_{CF}=273Hz J_{CCF}=35Hz	6	

d = doublet

q = quartet

[a] in ppm upfield from TMS

another. Where (2) and (3) are the cis-C^2 (or $C^{2'}$) signals and (4) and (5) are the trans-C^2 (or $C^{2'}$) signals, with (2) 5ppm upfield from (4), and (3) 4.7ppm upfield from (5). The doublet splitting of each signal was due to coupling between C^2 (or $C^{2'}$) and the tertiary fluorine on C^1 (or $C^{1'}$). Finally signal (1) was assigned to C^3.

The proportion of the cis-double bonds calculated from the C^4 signals was $\sigma_c = 0.58$, from the $C^2(C^{2'})$ signals was $\sigma_c = 0.55$ (using signals (2) and (5)) and from the C^3 signals was $\sigma_c = 0.59$.

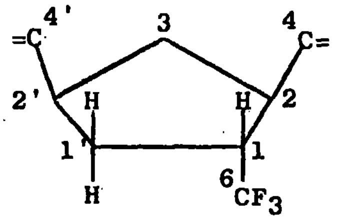
The above assignments are self consistent, but even better resolved spectra are required for a complete structural assignment; for example, there is the question of the C^3 signal being apparently due to 3cc and 3tt with no 3ct component.

The spectrum of polymer (1X) is very complex and a tentative assignment of the signals is given in Table 6.6. C^6, appears as a quartet and was assigned signals (6), (7), (8) and (9) ($\delta = 128.5$ppm; $J_{CF} = 256$Hz) and C^1 was assigned to signal (5), again a quartet ($\delta = 46.7$ppm; $J_{CCF} = 25$Hz). The vinylic carbons were assigned to signals (10), trans-C^4 and (11) cis-C^4. The fine structure of both signals is extremely complex and it may be that the chemical shift of C^4 is sensitive to the head-to-tail isomerism of the repeat units, this may account for the two signals in the vinylic region of the ^1H n.m.r. The assignments of the other bands were only tentative, because of the very complex set of signals and limited amount of information available. However, the assignment must be along the correct lines, since the proportion of cis-double bonds calculated by using the various sets of signals are in quite good agreement i.e. from the C^4 signals $\sigma_c = 0.53$; from the C^3 signals $\sigma_c = 0.53$ and from the C^2 signals $\sigma_c = 0.54$.

For polymer (VII) the assignment of the bands was impossible, because of the complex nature of the spectrum, caused by CF coupling and the fact that

Table 6.6

Chemical shifts in the ^{13}C n.m.r. spectrum of poly(4-trifluoromethyl-1,3-cyclopentylenevinylene) (IX)



Peak number	Chemical shift[a]	Assignment	Relative Area
1	34.0 34.6	3c 3t	72 63
2	37.6 37.9 38.1 38.5	2c	70 57 36 96
3	41.9 42.2 42.6	2t	55 100 62
4	44.1	1'	65
5	46.7(q) J_{CCF}=25Hz	1	
6,7,8,9	128.5(q) J_{CF}=256Hz	6	
10	129.7 130.1 130.7 131.1	4t	52 112 39 25
11	133.3 134.1 134.5 135.1	4c	64 48 120 28

q = quartet

[a] in ppm downfield from TMS

the polymer consisted of two different types of repeat units i.e. (VIIa) and (VIIb). Since the amount of polymer produced from pure adduct (Ib) was small and adduct (Ia) could not be obtained pure, ^{13}C n.m.r. spectra of the pure homopolymers were not obtained during the course of this work. These would have simplified the spectra considerably.

The polymers whose ^{13}C n.m.r. spectra have been discussed above were all prepared from their respective monomers using WCl_6/Ph_4Sn as the catalyst system. However, the ^{13}C n.m.r. spectrum of polymer (XI), prepared from adduct (V) using $WCl_6/Na_2O_2/(i\text{-butyl})_3Al$ as the catalyst system was also recorded and it was found that the proportion of cis-unsaturation was virtually the same as for the other sample of the polymer.

From this brief study of the ^{13}C n.m.r. spectra of partially fluorinated poly(1,3-cyclopentylenevinylenes) and poly(1,3-cyclopentenylenevinylenes) it is clear that a great deal of information is potentially available from this approach. However, catalyst systems which give exclusively cis- or trans-unsaturated polymers are required so that simpler spectra can be obtained and the assignment of signals can be made with greater confidence.

6.2 Determination of the molecular weight of partially fluorinated poly(1,3-cyclopentylenevinylenes) and poly(1,3-cyclopentenylenevinylenes)

6.2a Introduction

The molecular weight and molecular weight distribution of a polymer are important characterising parameters. The development of methods for establishing parameters has advanced alongside developments in synthesis and industrial application of polymers, and has involved a series of steps of advancement, each followed by a period of refinement, consolidation and application. A brief review of some of the methods used is given below.

The actual molecular weight determined is an average and the value obtained depends on the method used. For certain linear polymers it is possible to estimate the number of end-groups by both chemical and physical methods and so derive the number-average molecular weight $\bar{M}_n$; successful application of the end-group method requires that the nature of the end-groups should be reliably known. Condensation polymers have reactive functional end-groups and it is mainly to this type of polymer that end-group methods of molecular weight determination have been applied, for example, the titration of amino and carboxyl end-groups in polyamides. Physical methods, such as, i.r., u.v., and n.m.r. spectroscopy may also be used in end-group analysis. However, whatever method is used care must be taken when interpreting the results, since chain branching reactions and cyclomer formation can cause inaccuracies in the final result.

Several methods based on the colligative properties of dilute solutions have been established, these methods all give number average molecular weights. A widely used method of this type is vapour-pressure osmometry which can be used for samples whose molecular weight $<50,000$. Although the appropriate instrumentation was available in the department the molecular weight limit ruled out this technique for this work. Instrumentation for membrane osmometry, which allows the determination of higher molecular weights, was not available.

A widely used method for the determination of weight-average molecular weight $\bar{M}_w$, is light-scattering, the technique involves measuring the difference in scattered-light intensity between a polymer solution and its solvent. The light-scattering method is applicable to any polymer which can be dissolved in a solvent with refractive index different from that of the polymer. In most cases, the intensity of light-scattering from solutions of polymers with $\bar{M}_w <10,000$ differs so little from that of the pure solvent that the determination is not precise. This technique was not available for this work.

The viscosity of a solution of a material of high molecular weight is considerably greater than that of the pure solvent, even when the concentration of the material is quite small. Staudinger suggested in 1930 that the relative magnitude of this increase in viscosity could be quantitatively correlated with the molecular weight of the polymer in solution. The essential basis of Staudinger's suggestion has since been confirmed in the form of the Mark-Houwink equation,

$$[\eta] = kM^{\alpha}$$

where $[\eta]$ is the intrinsic viscosity and k and α are empirical constants which can only be obtained from viscosity measurements on samples of known molecular weight, though these values may be transferred to other polymers of closely related structure. Therefore viscosity studies on novel polymers are in general useful only to establish the order of magnitude of molecular weight. Nevertheless, this method is perhaps one of the most widely used, because it is cheap, quick and experimentally simple.

The intrinsic viscosity, $[\eta]$, is determined by the extrapolation of the inherent viscosity, η_{inh}, (logarithmic viscosity number) and reduced viscosity, η_{red}, (viscosity number) to infinite dilution where η_{inh} and η_{red} are given by:-

$$\eta_{inh} = (\ln \frac{t}{to})/c$$

$$\eta_{red} = (\frac{t-to}{to})/c$$

where t is the efflux time for a known volume of polymer solution to flow through a capillary, t_o is the efflux time for the pure solvent and c is the concentration of the polymer solution.

In all the techniques so far described only an average molecular weight is obtained. In recent years the development of gel permeation chromatography in combination with a technique such as light-scattering has provided a very efficient and reliable method for the determination of molecular weight distributions. The separation is based on molecular size; when a solution of the polymer in a relatively non-polar solvent is injected as a sample, the polymer molecules tend to diffuse from the mobile phase into the stationary phase. The larger the solute molecules the less of the stationary phase is accessible to it, and the less time it remains in the stationary phase as it traverses the column. Thus the largest polymer molecules have the smallest retention volumes.

A calibration curve of retention volume versus molecular weight is usually obtained by measuring the retention volumes of a series of polymers of known narrow molecular weight distribution, the standards have to be characterised by absolute methods ~~chemical techniques~~. This technique is particularly useful for the routine characterisation of samples of known structure; application to novel systems is, by definition, handicapped by the lack of suitable calibration materials.

6.2b Discussion

In this work dilute-solution viscosity was used as the major technique, to give some idea as to whether the polymers which had been produced were of high molecular weight or not. Viscometry determinations were made using an Ubbelohde viscometer immersed in a thermostatted water bath at 25.00 ± 0.01°. The elution time of a known volume of polymer solution of accurately known concentration (ca. 1% solution) through the viscometer was determined until four consecutive results were obtained (±0.1 seconds, stopwatch accuracy). Successive dilutions of the polymer solution were carried out in the viscometer, to allow elution time at various concentrations to be determined, enabling the intrinsic viscosity at infinite dilution to be obtained by extrapolation. For a few polymers a molecular weight distribution analysis was obtained by GPC using a refractive index detector and polystyrene as calibrant. These measurements were carried out through the SRC service at the Rubber and Plastics Research Association (Shawbury).

The intrinsic viscosities for the polymers are shown in Table 6.7 together with the values of $\bar{M}_w$ and $\bar{M}_n$ obtained from GPC.

Table 6.7

Intrinsic viscosities, weight average molecular weight and number average molecular weight for some partially fluorinated poly(1,3-cyclopentylenevinylenes) and poly(1,3-cyclopentenylenevinylenes)

Polymer	[η] [a] dl/g	GPC analysis		
		$\bar{M}_w$	$\bar{M}_n$	d.p
VII [b]	5.8			
VII [c,d]	1.5			
VIII [d]	2.5			
IX	1.0	256,600	121,100	748
XI	0.7	44,700	12,690	56
XII	0.5			
XIII	0.8			

[a] In methyl ethyl ketone at 25.00 ± 0.01°

[b] Polymer prepared from pure adduct (Ib)

[c] Polymer prepared from 60 : 40 mixture of adducts (Ib) and (Ia)

[d] GPC analysis performed, but unable to detect any material which was eluted.

For polymers (IX) and (XI) reasonable GPC distribution curves were obtained, from which values for $\bar{M}_n$ and $\bar{M}_w$ were calculated, showing that both polymers are of high molecular weight, polymer (IX) having a high degree of polymerisation (d.p). However, care must be taken when evalutating these results since the calibrating material was polystyrene and only direct interpretation of GPC results in terms of molecular weight distribution is applicable when the calibrating materials and test samples are of the same chemical type and this does not apply to the systems under investigation. In general terms, however, it appears on the basis of both viscosity and GPC measurements that the materials prepared by the ring-opening polymerisation method are of reasonably high molecular weight. The whole field of the solution properties of these materials requires investigation, this quite closely related group of polymers vary in solubility from those which are completely toluene soluble and methanol insoluble to those with exactly the opposite behaviour.

6.3 Thermal behaviour of some partially fluorinated poly(1,3-cyclopentylenevinylenes) and poly(1,3-cyclopentenylenevinylenes)

6.3a Introduction

A knowledge of the thermal behaviour of a polymer is required in order to determine the limits of its working range and hence its end-uses. In this work the thermal properties investigated were glass transition temperature and thermal degradation.

6.3b Glass transition temperature

In simple terms the glass transition temperature, Tg, is the temperature marking the transition of a polymer from glass-like to rubber-like behaviour and in molecular terms it is the onset of main chain segmental motion.[216]

It applies strictly only to amorphous polymers and in the presence of substantial crystallinity, the change of properties may occur over a wide temperature range and the glass transition may be obscured.

A number of physical properties change abruptly in the region of Tg, including heat capacity and the volume expansion coefficient, these are second derivatives of free energy and hence Tg is often referred to as a second order transition. A first order transition such as crystalline melting point, is characterised by changes in the heat content and specific volume, both of which are first derivatives of free energy.

These physical changes which occur in the region of Tg of a polymer are used to determine Tg. The signal output from a Differential Scanning Calorimeter is proportional to specific heat and hence this form of calorimetry has found ready application in the determination of Tg. The instrument used in this work was a Perkin-Elmer, Model DSC-2 Differential Scanning Calorimeter, with a sub-ambient facility enabling scans to be made from 150^{o}K to 500^{o}K and consisted of a pair of matched sample pans, each fitted with a temperature sensing element and electric heater. One pan contains the sample under investigation in an aluminium capsule, while the other contains an empty reference capsule. The power supplied to the two pan heaters continuously changes in response to thermal effects in the sample, so as to maintain the sample and reference at the same temperature. The difference in power required to maintain the two pans at the same temperature is recorded as output on a recorder. In operation the temperature of the sample and reference pans is raised at a constant rate, and while there is no change in the physical or chemical state of the sample the output recorded will be constant. However, at Tg the specific heat changes rapidly and so a deflection of the baseline will be observed, Figure 6.10.

There are at least two methods to determine Tg from the given output; either the point of intersection of the extrapolated baseline and the extrapolated straight line portion of the curve as shown in Figure 6.10a or the temperature at which the change in heat capacity is half its maximum value as shown in Figure 6.10b. In this work the latter method was used.

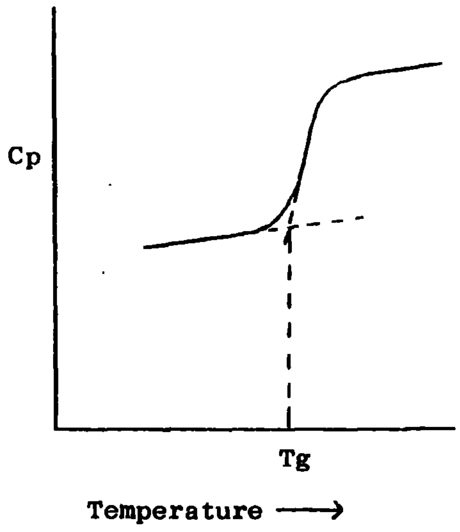


Figure 6.10a

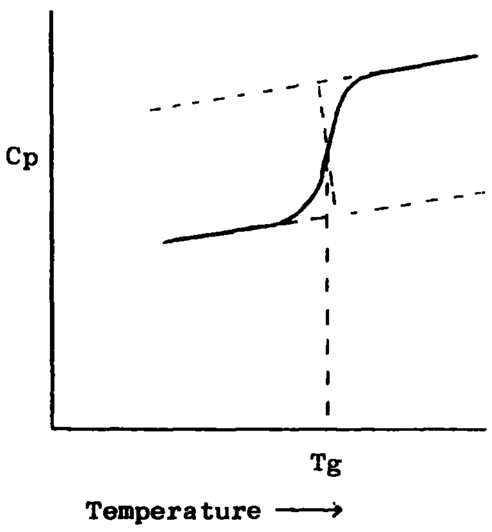


Figure 6.10b

Since the observed glass transition temperature is dependent on the heating rate employed, a standardised procedure was followed, in order that a comparison of the Tg's for various polymers could be made. The instrument was calibrated before and after a series of runs using materials of known melting point, i.e. cyclohexane (Tm = $186^{\circ}K$; Tcry = $279^{\circ}K$) and indium (Tm = $430^{\circ}K$). The melting point of each material was taken as the point of intersection of the extrapolated baseline and the extrapolated straight line portion of the leading edge of the transition peak, as shown in Figure 6.11.

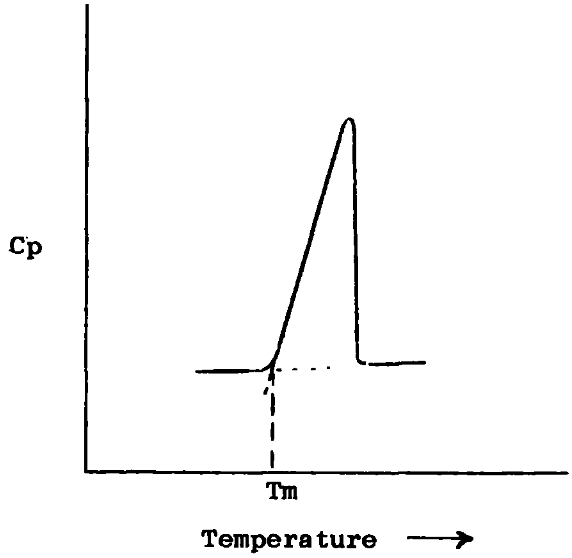


Figure 6.11

A sample was placed in an aluminium pan, which was sealed in a press and placed in the sample holder. An initial rapid scan was carried out in order to establish an approximate region of the Tg. The sample was annealed at approximately 30-40° above the observed transition temperature for 10-15 minutes, removing crystallinity and strain from the sample and allowing it to flow into an even layer on the base of the pan, ensuring good thermal contact. The sample was then cooled rapidly at the maximum cooling rate of the instrument (320°/min) to approximately 60° below the observed transition temperature, thereby maintaining as much of the sample as possible in the amorphous state. A scan was commenced at a programmed heating rate of 40°/minute through the transition region, this procedure was repeated until three values of Tg for a given sample were within the range ±1°.

The results obtained for the partially fluorinated poly(1,3-cyclopentylenevinylenes) and poly(1,3-cyclopentenylenevinylenes) are presented in Table 6.8 and may be compared with the Tg's of some non-fluorine substituted poly(1,3-cyclopentylenevinylenes) presented in Table 6.9.[217] None of the fluorinated homopolymers show a Tg low enough for them to be useful as elastomeric materials.

Table 6.8

Glass transition temperature of some partially fluorinated poly(1,3-cyclopentylenevinylenes) and poly(1,3-cyclopentenylenevinylenes)

Polymer	Catalyst system	Tg	
		^{o}K	^{o}C
poly(1-pentenylene)	WCl_6/Ph_4Sn	178	-95
(39) [d]	WCl_6/Ph_4Sn	310	37
VII [a]	WCl_6/Ph_4Sn	437	164
VII [a]	$WCl_6/Na_2O_2/(i\text{-}butyl)_3Al$	438	165
VII [b]	WCl_6/Ph_4Sn	422	149
VII [c]	WCl_6/Ph_4Sn	448	175
VIII	WCl_6/Ph_4Sn	433	160
IX	WCl_6/Ph_4Sn	369	96
XI	WCl_6/Ph_4Sn	388	115
XI	$WCl_6/Na_2O_2/(i\text{-}butyl)_3Al$	398	125
XII	WCl_6/Ph_4Sn	345	72
XII	WCl_6	340	67
copolymer XIII	WCl_6/Ph_4Sn	317	44
copolymer XIV	WCl_6/Ph_4Sn	267	-6

[a] Polymer prepared from 60 : 40 mixture of adducts (Ib) and (Ia)

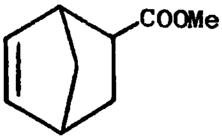
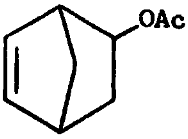
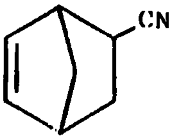
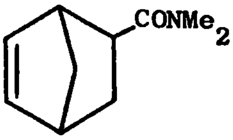
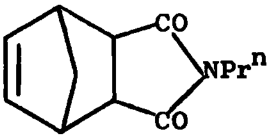
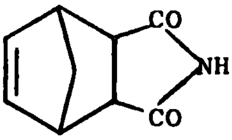
[b] Polymer prepared from pure adduct (Ib)

[c] Polymer prepared from 16 : 84 mixture of adducts (Ib) and (Ia)

[d] Poly(1,3-cyclopentylenevinylene)

Table 6.9 [217]

Glass transition temperatures of some polymers derived from non-fluorine substituted bicyclo[2.2.1]hept-2-enes

Monomer	[η] dl/g	Tg °C [c]
	3.16 [a]	62
	0.65 [a]	77
	0.65 [b]	140
	-	114
		> 200
		> 250

[a] Measured in toluene at 30°

[b] Measured in chloroform at 30°

[c] Measured by differential scanning calorimetry

However, in copolymers (XIII) and (XIV) the Tg's are very much lower than the fluorinated homo-polymers and these and related copolymers probably merit further investigation into their physical properties. The only polymer not showing a distinct transition was (X), all others showed reasonable deflections of the base-line.

The Tg's of the two hydrocarbon polyalkenylenes, poly(1-pentenylene) and poly(1,3-cyclopentylenevinylene), are in good agreement with the values quoted in the literature. For poly(1-pentenylene) with 99% cis-double bonds Tg = -114°[16] and 75% trans-double bonds Tg = -97°,[16] while for poly(1,3-cyclopentylenevinylene) Tg is quoted as being between 30-35°.[19]

6.3c Thermal degradation analysis

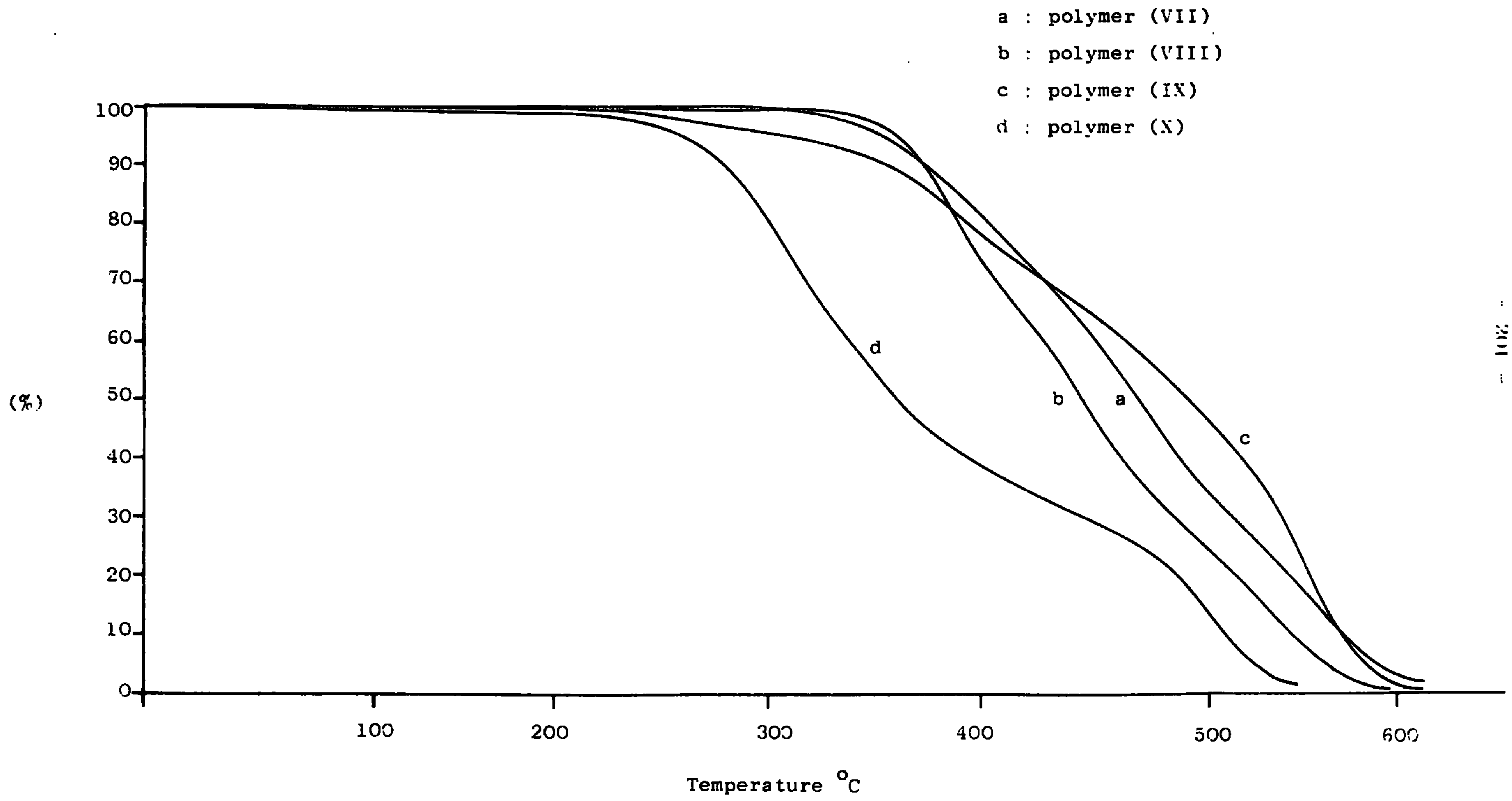
A great deal of effort has been devoted to the investigation of which factors in a polymeric structure lead to thermal stability, which in the case of a practical polymer must be considered in the presence of oxygen, moisture and other reagents depending on its eventual end-use.

Different workers, because of their different interests and equipment have used widely varying environments in which to carry out their stability tests on polymers. Commonly air is used for an oxidative study, while either nitrogen, helium or argon have been used as inert atmospheres. In some cases vacuum degradation has been used, but this had the disadvantage in that it minimises thermal contact between the sample, the furnace and the temperature measuring device. The criteria of stability used by different workers also varies substantially. A sample may be held at a constant temperature and the weight loss, after a convenient period of time, measured, however, if samples of varying stability are being tested the differences in the weight loss may vary greatly. An alternative method involves the temperature of the sample being increased at a constant rate through its decomposition range, most polymers follow an 'S' shaped decomposition curve. The temperature chosen for the actual point of decomposition varies, it is sometimes the temperature of initial weight loss, or the temperature at which the sample loses 10%, or 20%, or 50% of its original weight. No standard procedure has yet been adopted. Therefore a comparison of the results from various workers is very difficult and care must be taken in drawing conclusions from such decomposition temperatures.

By varying the conditions, in a series of runs, under which a polymer is decomposed, kinetic parameters, such as, activation energy of decomposition may be derived in some cases. MacCallum and Tanner have critically compared several methods available for processing such data and have concluded that none have any advantages over the traditional method of using isothermal conditions for each run.[218] This method will be discussed in more detail later in this section.

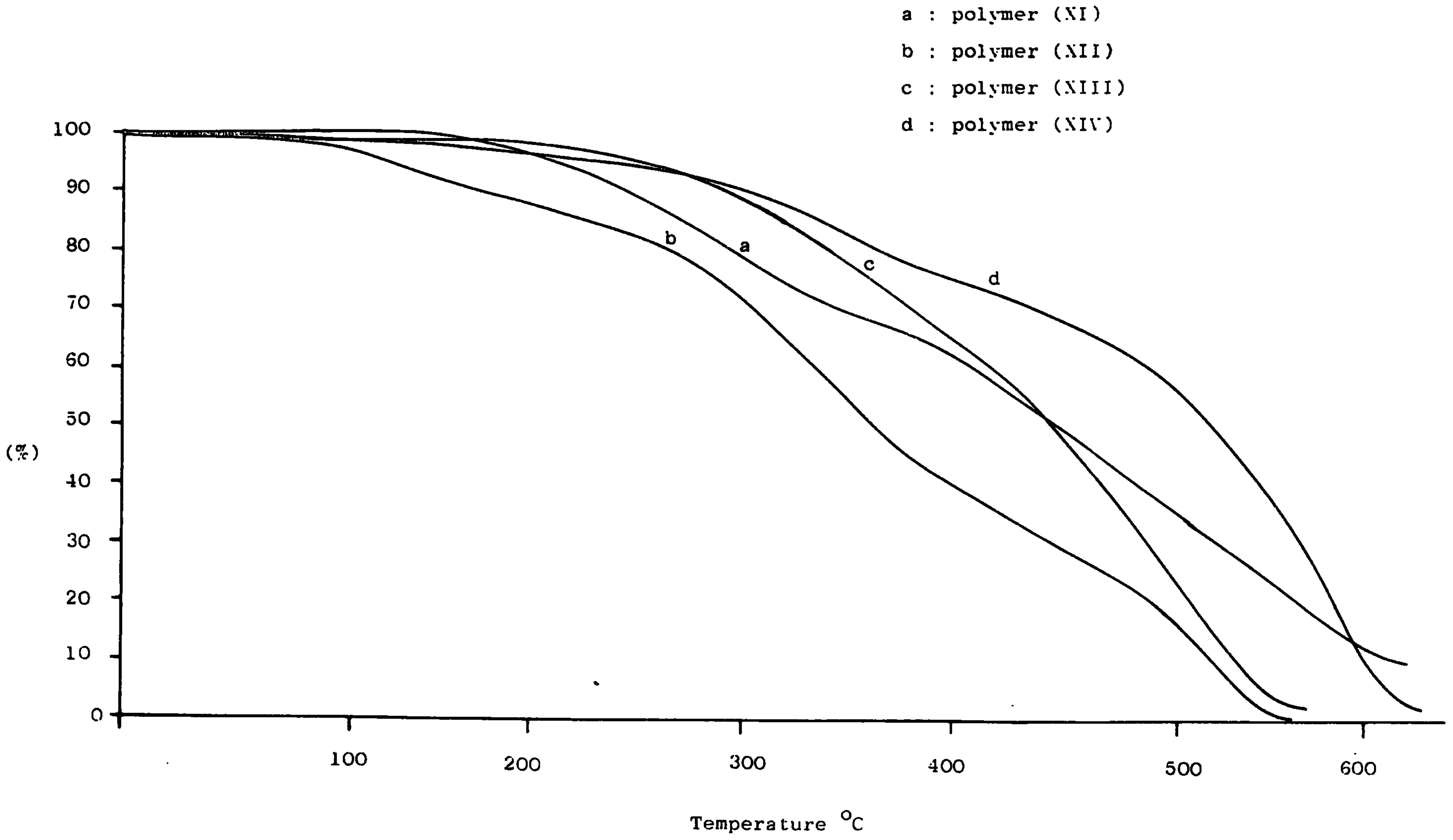
In this work the thermal decomposition studies were carried out using a Stanton Redcroft TG750 Thermobalance operating in a percentage weight loss mode. For the initial studies the temperature programme mode was operated. The sample was placed on the thermobalance, the furnace temperature adjusted to ambient and then programmed to increase at a rate of 1°/minute up to approximately 700°. At this temperature all the polymers had virtually completely decomposed. Samples were decomposed in atmospheres of oxygen-free nitrogen and air, the resulting decomposition curves are shown in Figures 6.12-6.15. For several polymers an initial small weight loss (1-5%) was observed before rapid decomposition occurred, therefore the estimation of the temperature of initial weight loss was extremely difficult. The decomposition temperatures of all the polymers are therefore reported as the temperature at which the polymers lost 10% of their original weight. The decomposition temperatures are summarised in Table 6.10 and quoted to the nearest 5°.

Figure 6.12 Thermograms of polymers (VII) - (X) [e]



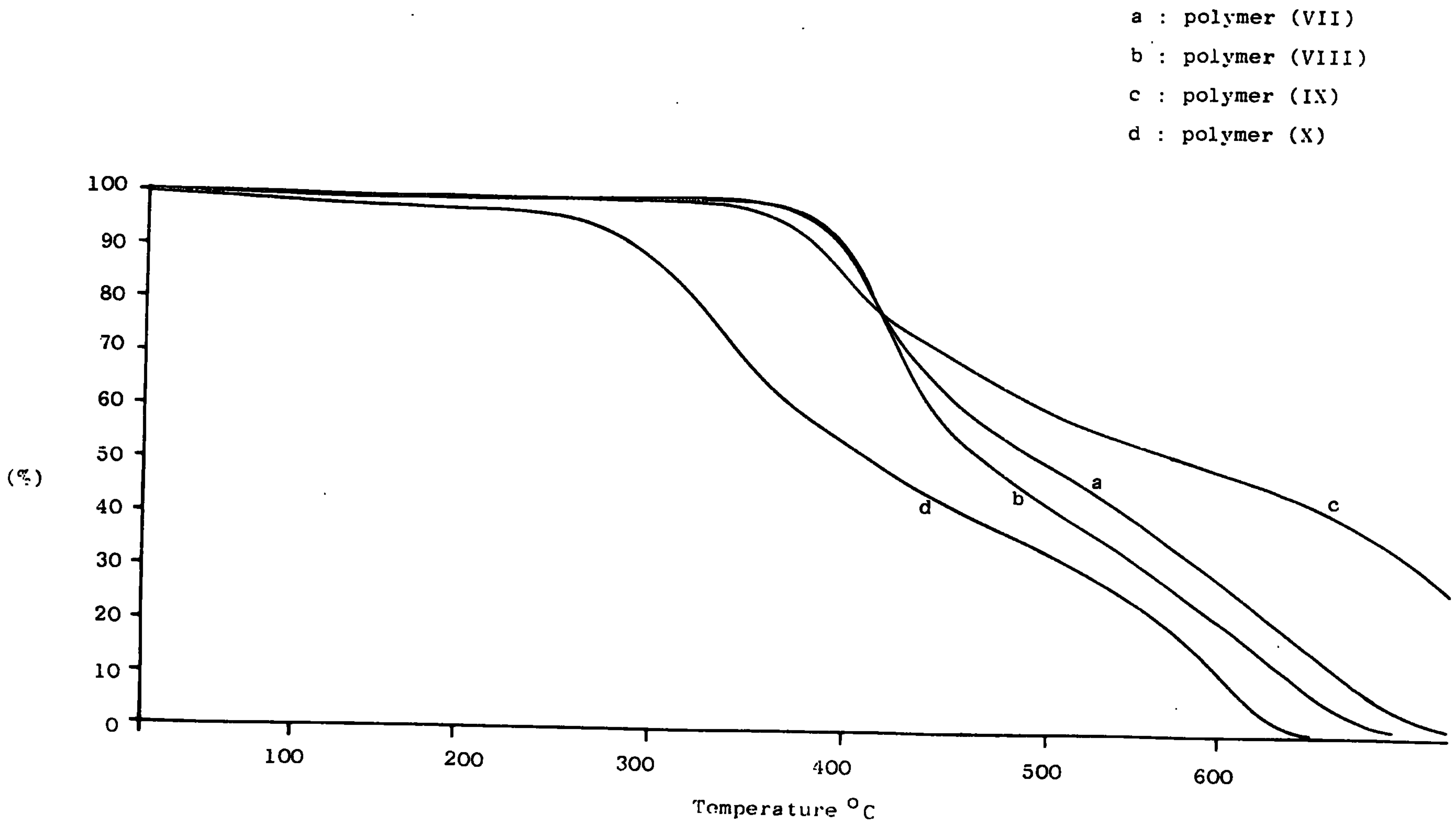
[e] Degradations performed in an atmosphere of air

Figure 6.13 Thermograms of polymers (XI) - (XIV) [e]



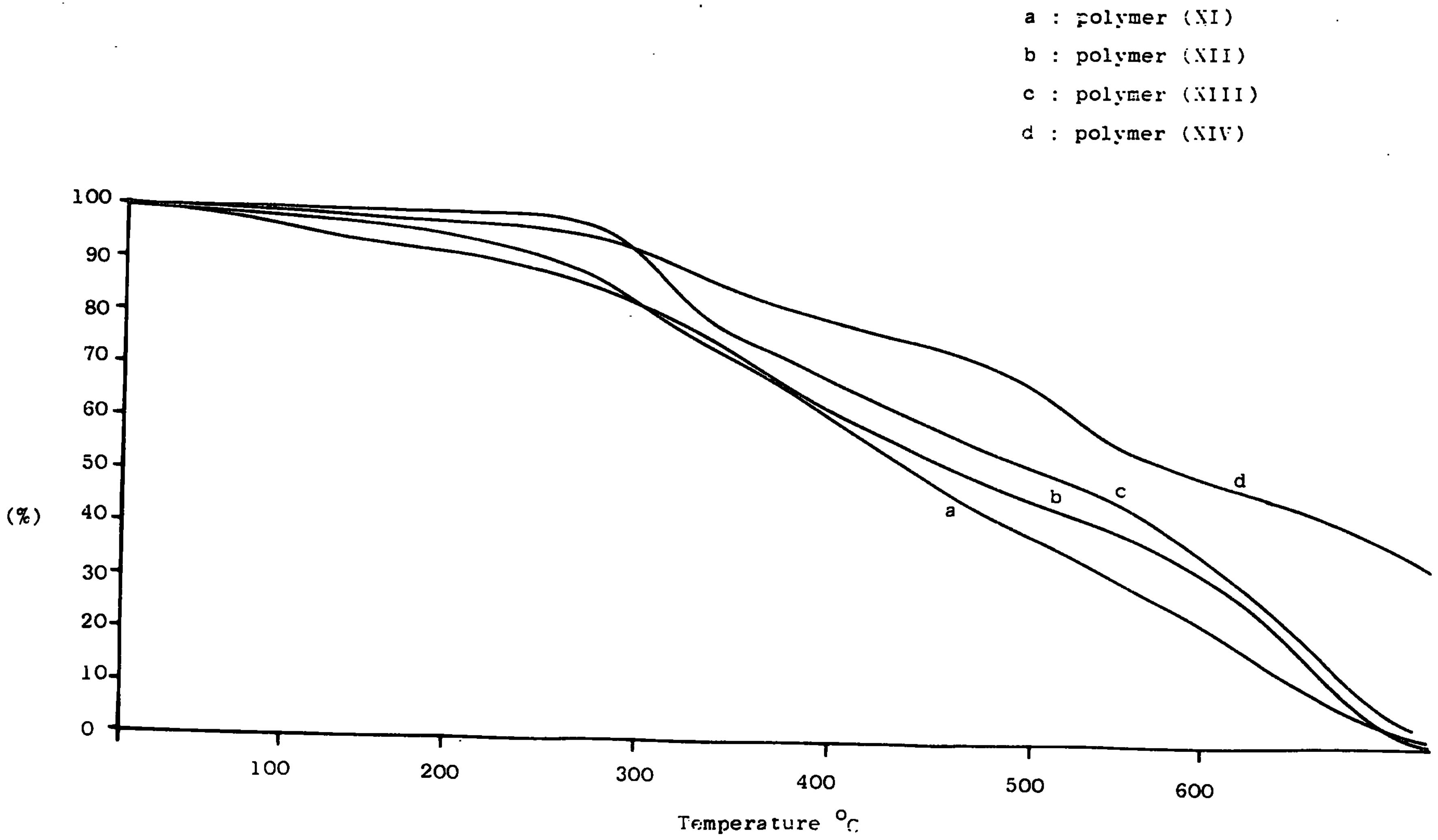
[e] Degradation performed in an atmosphere of air

Figure 6.14 Thermograms of polymers (VII) - (X) [e]



[e] Degradations performed in an atmosphere of nitrogen

Figure 6.15 Thermograms of polymers (XI) - (XIV) [e]



[e] Degradations performed in an atmosphere of nitrogen

Table 6.10

Decomposition temperatures of partially fluorinated poly(1,3-cyclopentylene vinylenes) and poly(1,3-cyclopentenylenevinylenes)

Polymer	Catalyst System	Decomposition Temerature °C	
		N_2	Air
(39) [d]	A	350	340
VII [a]	A	390	365
VII [b]	A	390	370
VII [c]	A	385	-
VII [a]	B	385	-
VIII	A	400	370
IX	A	380	355
X	A	295	280
XI	A	270	250
XI	B	280	-
XII	A	230	185
XII	C	238	-
XIII	A	320	290
XIV	A	320	300

A. WCl_6/Ph_4Sn B. $WCl_6/Na_2O_2/(i\text{-butyl})_3Al$ C. WCl_6

[a] Polymer prepared from 60 : 40 mixture of adducts (Ib) and (Ia)

[b] Polymer prepared from pure adduct (Ib)

[c] Polymer prepared from 16 : 84 mixture of adducts (Ib) and (Ia)

[d] poly(1,3-cyclopentylenevinylene)

The series of partially fluorinated poly(1,3-cyclopentylenevinylenes), (VII), (VIII) and (IX) all have virtually the same decomposition temperature and it is in the same region as that quoted for the decomposition of the fluorinated cyclic polymers listed in Table 6.11.[219] However, the partially fluorinated poly(1,3-cyclopentenylenevinylenes), (XI) and (XII), and the poly(1,3-cyclopentylenevinylene), (X) are not as thermally stable, decomposing some 100° or more lower than the other polymers, but all of them show a slight accelerated decomposition in air compared to nitrogen.

It was hoped that a better understanding of the decomposition of these fluorinated polymers would be obtained from a kinetic study of their degradation. The polymers chosen for a more detailed investigation were (VII), (VIII), (IX) and (XI).

Assuming a simple general rate equation for the decomposition in which the polymer weight loss is assumed to correspond to the degree of conversion C, then

$$\frac{dC}{dt} = \overset{k}{\cancel{K}}(1-C)^n e^{-E/RT}$$

where dC/dt is the rate of fractional weight loss, or rate of conversion, n is the order of the reaction, E is the experimental activation energy for the degradation, R is the gas constant and T is the absolute temperature. The pre-exponential constant $\overset{k}{\cancel{K}}$ is a chracteristic of the degradation. Taking natural logarithms,

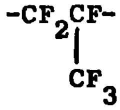
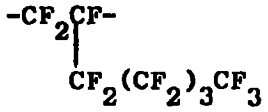
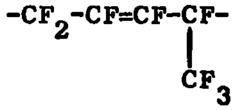
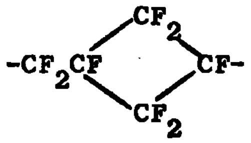
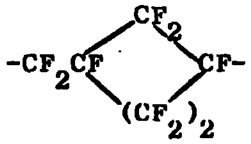
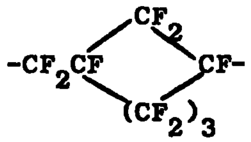
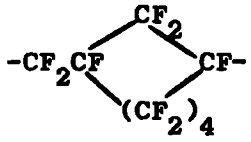
$$\ln\left(\frac{dC}{dt}\right) = \ln k + n\ln(1-C) - \frac{E}{RT}$$

when C = 0, then ln(1-C) = 0, and

$$\ln\left(\frac{dC}{dt}\right) = \ln k - \frac{E}{RT}$$

Table 6.11 [219]

Decomposition temperature of some perfluoro-polymers

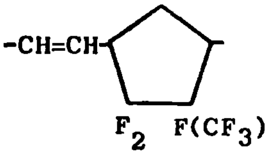
Polymer	Decomposition Temperature °C
 $-CF_2\underset{\overset{\vert}{CF_3}}{CF}-$	300
 $-CF_2\underset{\overset{\vert}{CF_2(CF_2)_3CF_3}}{CF}-$	250
 $-CF_2-CF{=}CF-\underset{\overset{\vert}{CF_3}}{CF}-$	300
	400
	400
	420
	354

If the polymer decompositions are performed under isothermal conditions and dC/dt determined at different values of C, a plot of ln(dC/dt) against ln(1-C) should theoretically give a straight line of slope n. However, in practice deviations from a straight line are observed at both high and low values of C, because the sample has not reached thermal equilibrium with the furnace and dC/dt is lower than expected in the former case, and solid residue remains at the end of the degradation in the latter case hence giving a low value of dC/dt.

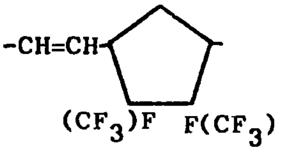
Extrapolation of ln(dC/dt) to C = 0 may be carried out, from which a plot of ln(dC/dt) (for C = 0) against $^1/T$ should give a straight line of slope -E/R and intercept lnk, from which the activation energy of decomposition may be calculated.

Using isothermal conditions, the degradation of polymers (VII), (VIII), (IX) and (XI) was investigated and plots of ln(dC/dt) against ln(1-C) are shown in Figures 6.16, 6.17, 6.18 and 6.19 respectively. It was hoped that this series of polymers would show some trend in their activation energies of degradation as there are only slight changes in structure in going from one polymer to another, in event a rather complicated situation emerged.

For polymers (VII) and (VIII) the expected straight line graphs were obtained, with slight variations at high and low values of C. From these

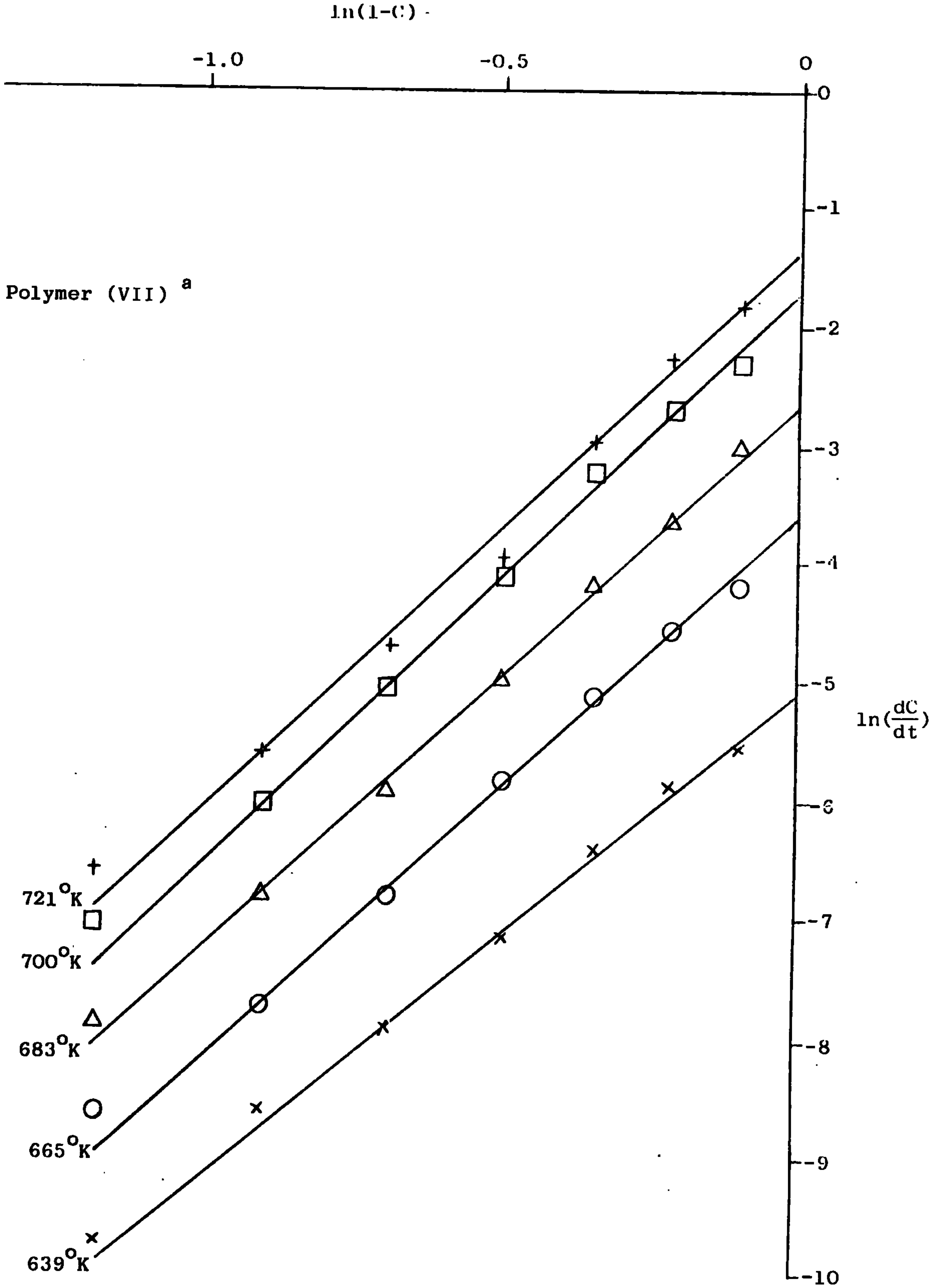


(VII)



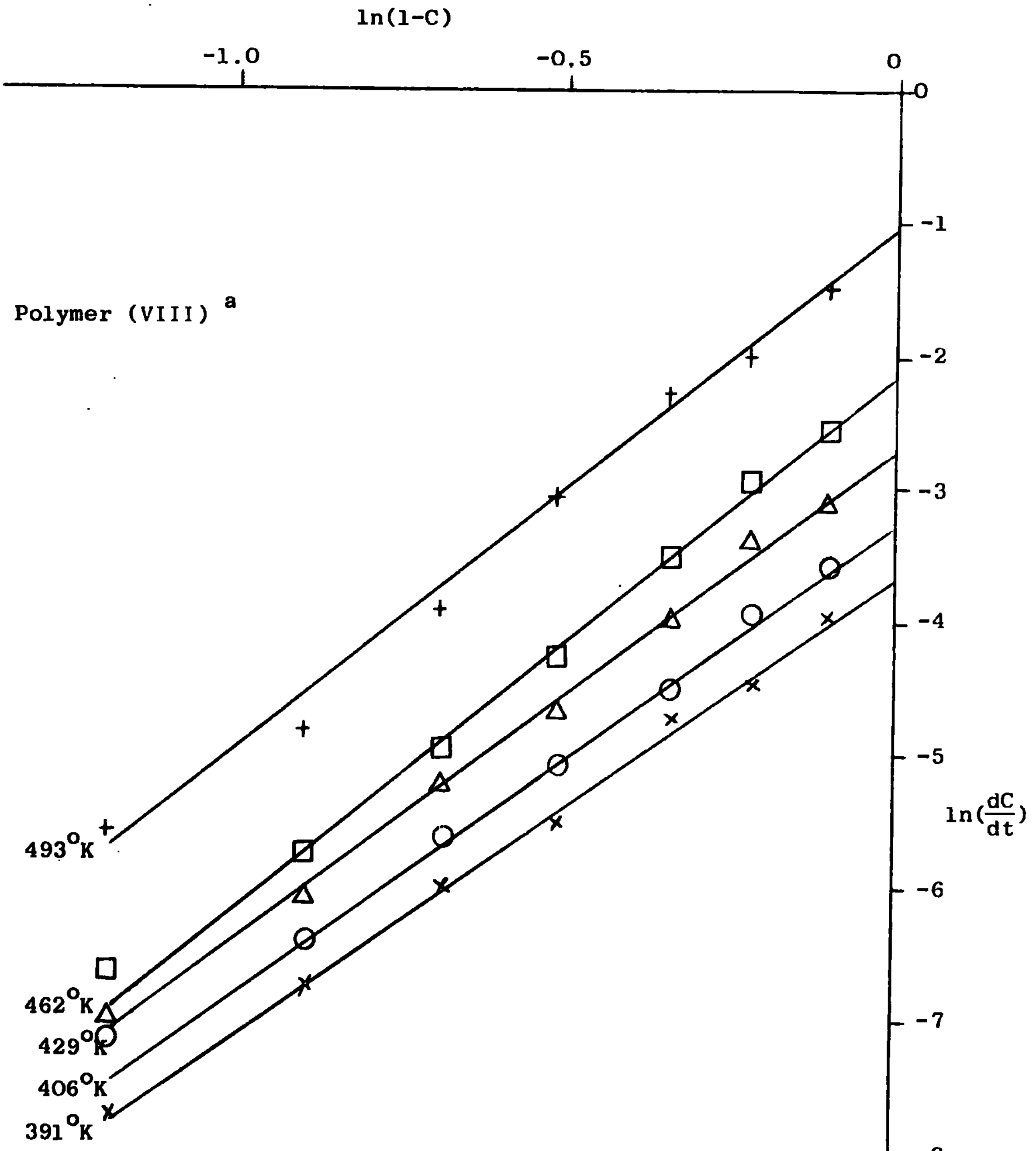
(VIII)

graphs, values of ln(dC/dt) at C = 0 were obtained for both polymers and graphs of ln(dC/dt) against $^1/T$ were plotted, Figure 6.20. Evaluation of



[a] Prepared from 60 : 40 mixture of adducts (Ib) and (Ia)

Figure 6.16



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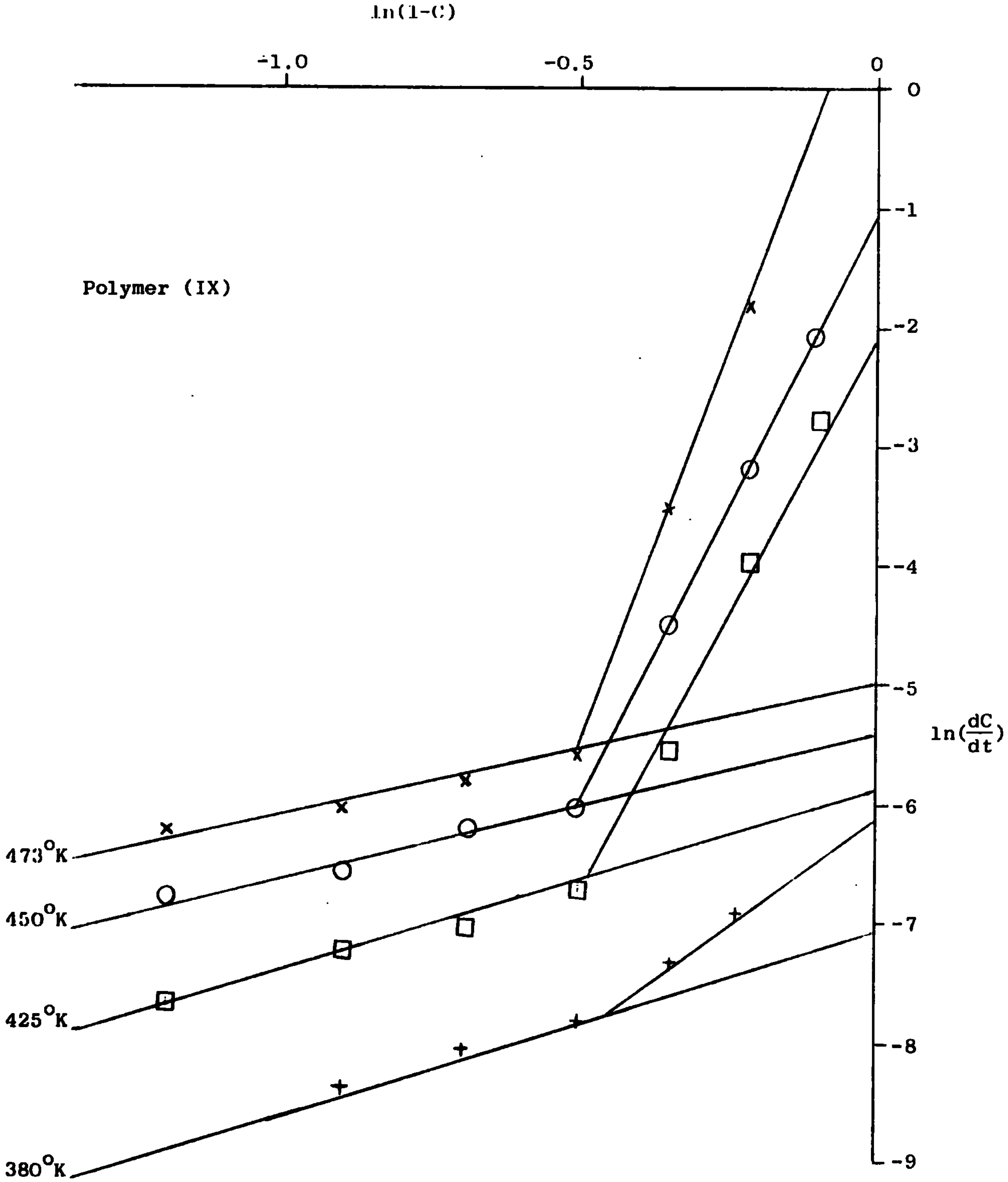
[a] Prepared from pure adduct (IIa)

Figure 6.17



[a] Prepared from pure adduct (IIIa)

Figure 6.18

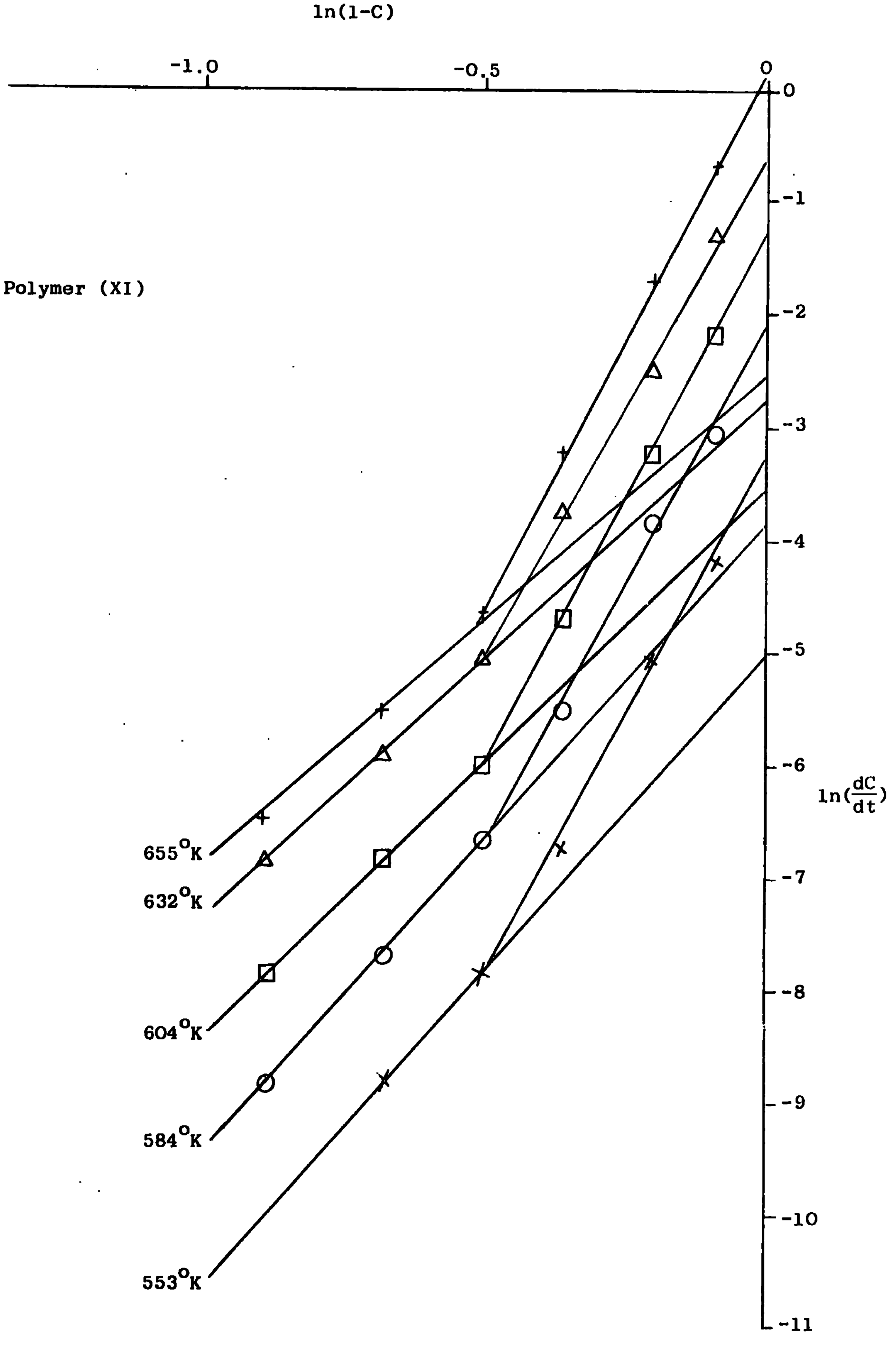
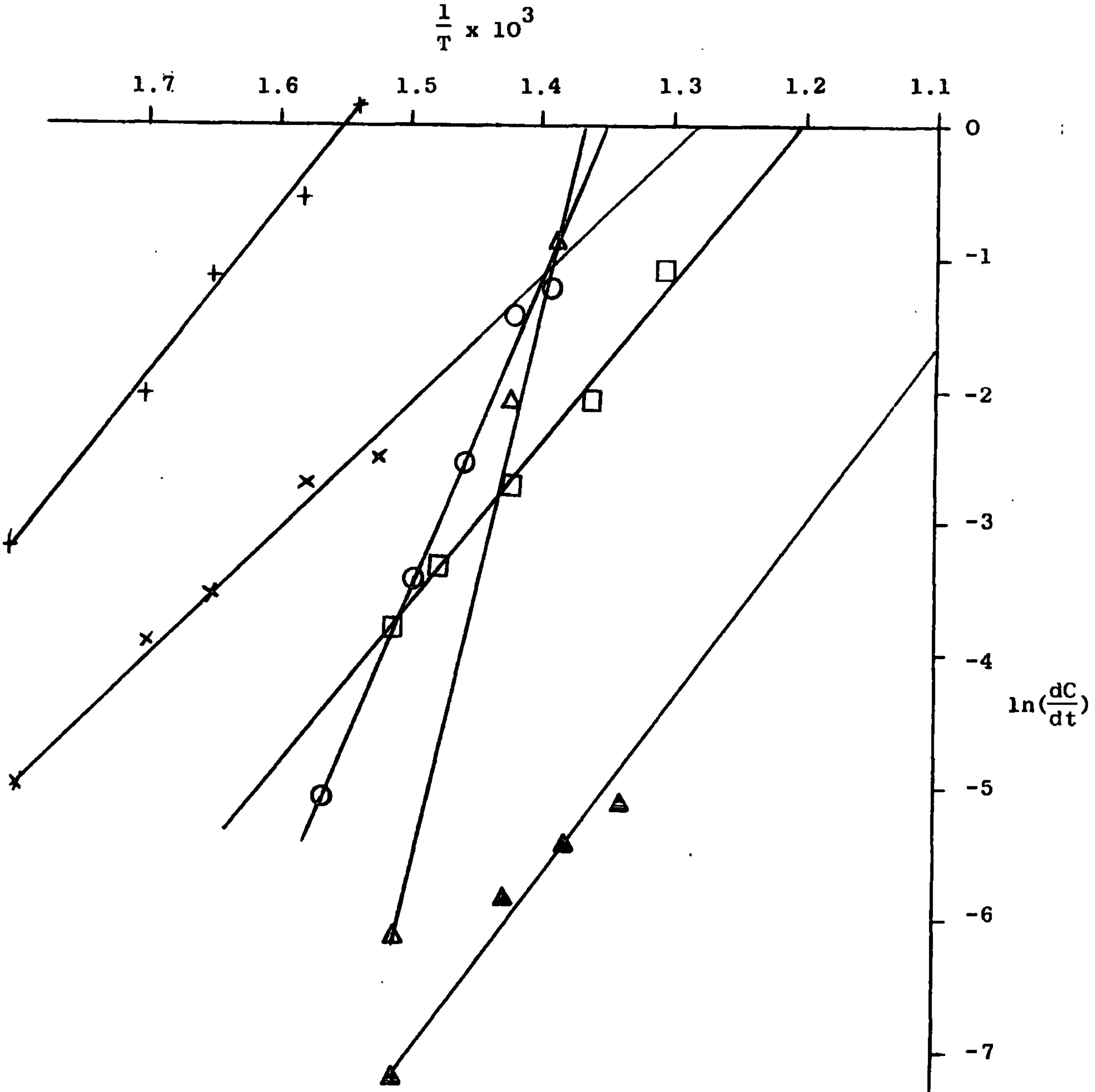

ln(1-C)
-1.0
-0.5
0
Polymer (XI)
0
-1
-2
-3
-4
-5
-6
-7
-8
-9
-10
-11
ln($\frac{dC}{dt}$)
655°K
632°K
604°K
584°K
553°K

Figure 6.19



○ Polymer (VIIc) decomposition 0-80%

□ Polymer (VIII) decomposition 0-80%

△ Polymer (IX) decomposition 10-40%

▲ Polymer (IX) decomposition 40-70%

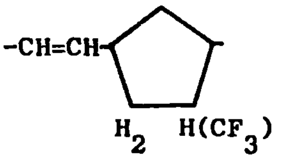
\+ Polymer (XI) decomposition 10-70%

x Polymer (XI) decomposition 40-70%

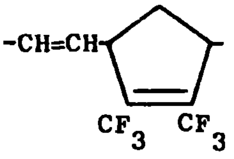
Figure 6.20

the slopes gave activation energies of degradation for polymers (VII) and (VIII) of 43.6 and 24.4kcals.mole^{-1} respectively, Table 6.12. It would therefore appear that the replacement of a fluorine atom by a trifluoromethyl group has reduced the activation energy quite considerably.

For the other two polymers (IX) and (XI), plots of ln(dC/dt) against ln(1-C) were quite different from the previous two. Both graphs appear to consist of two different sets of lines, extrapolation of both sets to C = 0 and plotting the values of ln(dC/dt) against $^1/T$ gave two different activation energies for degradation for both polymers. It is perhaps worth noting that these results were reproducible.



(IX)



(XI)

A possible explanation is that the two polymers (IX) and (XI) thermally degrade with activation energies 80 and 24kcals.mole^{-1} respectively, producing materials which then thermally degrade with activation energies 23 and 18kcals.mole^{-1} respectively. It has been suggested that in the thermal degradation reaction the initial degradation products may inhibit or accelerate the next stage of the degradation process, hence producing a two stage reaction. However, the author is unable to advance a simple mechanistic interpretation to account for the results reported here. Unlike the thermal degradation of polyvinylchloride, in which twodistinct reactions occur and can be distinguished as two different weight loss behaviours separated by a plateau of thermally stable behaviour during its degradation at a constant heating rate, these degradations do not show clear two step curves (Figures 6.12-6.15).

Table 6.12

Activation energies of some partially fluorinated polymers

Polymer	Activation Energy kcal.mole^{-1}	Decomposition range %
VII	44	0-80
VIII	24	0-80
IX	78	10-40
IX	23	40-70
XI	24	10-40
XI	18	40-70

The situation resulting from this work is clearly complex and apparently contradictory. An attempt to throw some light on what was happening was made by recording the i.r. spectra of samples submitted to respectively 30 and 70% weight loss, however, no useful information was obtained from this exercise; analysis of the volatile products of degradation might prove informative in any continuation of this work.

6.4 Conclusions

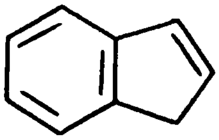
The work described in this Chapter establishes that the materials obtained are genuine high polymers resulting from the ring-opening polymerisation of the respective partially fluorinated bicyclo[2.2.1]hept-2-enes and bicyclo-[2.2.1]hepta-2,5-dienes. Their solution properties and thermal behaviours show a considerable variation for apparently small structural variations. These novel material would appear to be worth a more detailed investigation both from the point of view of possibly interesting physical properties and because they offer an opportunity of establishing details of chain stereochemistry and hence possibly illuminating the polymerisation mechanism.

CHAPTER 7

THE REACTION OF AN OLEFIN METATHESIS CATALYST SYSTEM WITH INDENE

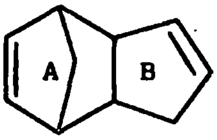
7.1 Introduction

During this work on the ring-opening polymerisation of cycloalkenes, it became apparent that a very interesting and readily available compound which has not been specifically reported to undergo ring-opening polymerisation is indene (XV). This compound may be thought of as a derivative of either cyclopentadiene or cyclopentene.

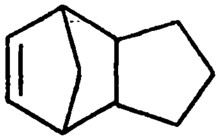


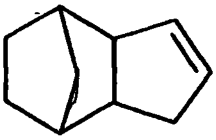
(XV)

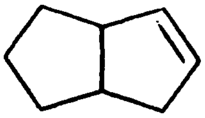
It has been reported that conjugated cyclic dienes, such as, cyclopentadiene do not undergo ring-opening polymerisation.[145] As described previously (see Chapter 2) it is very difficult to polymerise certain fused five-membered ring structures. Dicyclopentadiene (135), has two types of unsaturated five-membered rings, the highly strained bridged ring A and a fused five-membered ring B. Oshika and Tabuchi[220] have reported that, using a variety of catalyst systems, dicyclopentadiene polymerises exclusively by opening of the bridged ring A. Although (136) has been found to ring-open polymerise, (36) and the related compound (37) do not polymerise. Hence it would appear that fused five-membered rings of type-B do not ring-open



(135)


(136)


(36)


(37)

polymerise under the conditions used. However, Dall'Asta and Motroni have reported that using metathesis catalysts, prepared from W or Mo halides and organo-aluminium compounds, they have effected selective ring-opening polymerisation of tetrahydroindene (137),[221] however, with catalysts with predominantly cationic character (137) undergoes addition polymerisation.

For (137) two possible modes of ring-opening polymerisation exists, as shown in Figure 7.1. Both of which would appear unfavourable on the evidence

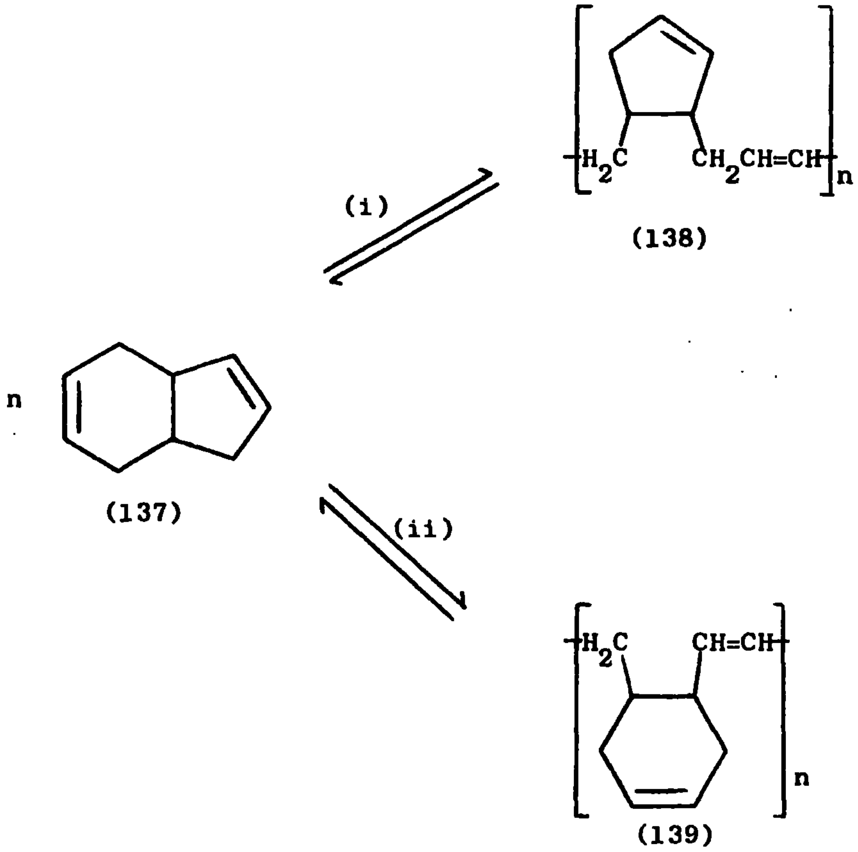
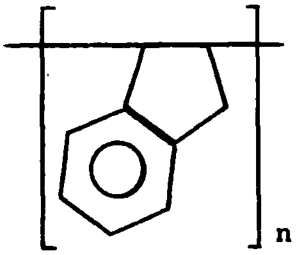


Figure 7.1

available; (i) involves the ring-opening of a cyclohexene ring giving a polymer with repeat unit (138), which is considered to be unpolymerisable and (ii) involves the ring-opening of a fused five-membered ring giving a polymer with repeat unit (139). Dall'Asta and Motroni proposed that the resulting polymer was formed from exclusive ring-opening of the five-membered ring, which allows the cyclohexene ring in the polymer chain to transform from the boat to the more stable half-chair conformation and the cyclopentene ring to release ring strain. Both processes are energetically favourable and sufficient to render the monomer polymerisable.

Indene was first shown to be a polymerisable alkene in 1890.[222] Polymerisations were achieved using various catalysts such as sulphuric acid, heat, antimony pentachloride and stannic chloride,[223] producing saturated polymers with repeat units of the type (140) of low molecular weight. More recently the susceptibility of indene to attack, particularly from cationic reagents has interested many workers and polymerisation of indene and its derivatives has been studied in some detail.[224] The list of Lewis acids used as initiators has been extended to include boron trifluoride and titanium tetrachloride. Low temperature experiments using these two catalysts,[225,226] have produced polymers with molecular weights of approximately 2 x 10^6. This section describes the effect of the catalyst system WCl_6/Ph_4Sn on the polymerisation of indene and the subsequent analysis of the polymer.

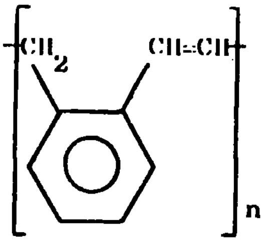


(140)

7.2 Discussion

The usual procedure for a polymerisation of a cycloalkene using the catalyst system WCl_6/Ph_4Sn was followed. On addition of the monomer to the dark brown active catalyst solution mixture an immediate colour change to deep blue was observed and after 20 minutes there was a noticeable increase in viscosity. The reaction was terminated after 3 hours by the addition of a small quantity of methanol and then poured into a five-fold excess of methanol. The white solid powdery material which was precipitated was removed by filtration, dissolved in analar toluene, filtered and reprecipitated by addition to excess methanol. The solid material was recovered by filtration and dried under reduced pressure. It was soluble in toluene, chloroform, carbon tetrachloride, methyl ethyl ketone and tetrahydrofuran.

The material was investigated by elemental analysis, i.r. spectroscopy, reaction with bromine, intrinsic viscosity, G.P.C. molecular weight distribution and thermogravimetric analysis. Elemental analysis confirmed the molecular formula as C_9H_8. A comparison was made between the i.r. spectrum of the polymer prepared by the above procedure (XVI) (Appendix C(XXXVI)) and that prepared by a standard cationic polymerisation method (this material was kindly provided by Dr. Bartlett, this department) (140) (Appendix C(XXXVII)). The difference between the two spectra was the presence of a strong absorption at $790cm^{-1}$ in spectrum (Appendix C(XXXVI)) and the absence of such a band in spectrum of cationic polyindene (Appendix C(XXXVII)). If the polymer prepared using the catalyst system WCl_6/Ph_4Sn was formed by the ring-opening polymerisation of the fused five-membered ring, then it would have the structure (XVIa) and the extra absorption at $790cm^{-1}$ could be due to a vibrational mode available to this structure which is not available to structure (140); suitable models for comparison were not available.



(XVIa)

A very simple reaction was performed which strongly suggests that unsaturation is present in polymer (XVI). It involved the addition of a dilute solution of bromine in carbon tetrachloride to a solution of the polymer in chloroform, immediate discharge of the bromine colour was observed. Using polymer (140) under the same conditions, the bromine colour persisted, even after vigorous stirring. This suggests that unsaturation is present in polymer (XVI) and not in polymer (140).

The intrinsic viscosity of polymer (XVI) was dtermined using the procedure described in Chapter 6, the result is given in Table 7.1 together with the $\bar{M}_n$ and $\bar{M}_w$ determined by G.P.C. analysis. These last two values are compared with those for polymer (140). As can be seen the molecular weight of the two polymers are quite different. Polymer (XVI) having a molecular weight at least five times greater than polymer (140).

Table 7.1

A comparison of $\bar{M}_n$ and $\bar{M}_w$ for polymers (XVI) and (140)

Polymer	$[\eta]$ [a] dl/g	$\bar{M}_w$	$\bar{M}_n$	d.p
(XVI)	0.21	22920	8420	73
(140)		3541	1671	14

[a] Solvent methyl ethyl ketone. Determined at 25.00 ± 0.01°

The thermogravimetric analysis of polymers (XVI) and (140) was performed on the Stanton Redcroft TG750 in an atmosphere of air, at a constant heating rate of 1°/minute from ambient to about 600°. Both polymers showed very distinctive two-stage decomposition curves, Figure 7.2 (similar in appearance to that of PVC), with similar decomposition temperatures for the initial 10% weight loss, of 336° and 346° for polymers (XVI) and (140) respectively. However, they showed a different percentage weight loss in the first stage of their decomposition; for polymer (XVI) it was 42%, corresponding to the possible loss of a C_4 unit and for polymer (140) it was 62%, corresponding to the possible loss of a C_6 unit. This is further evidence supporting the fact that polymers (XVI) and (140) have different structures.

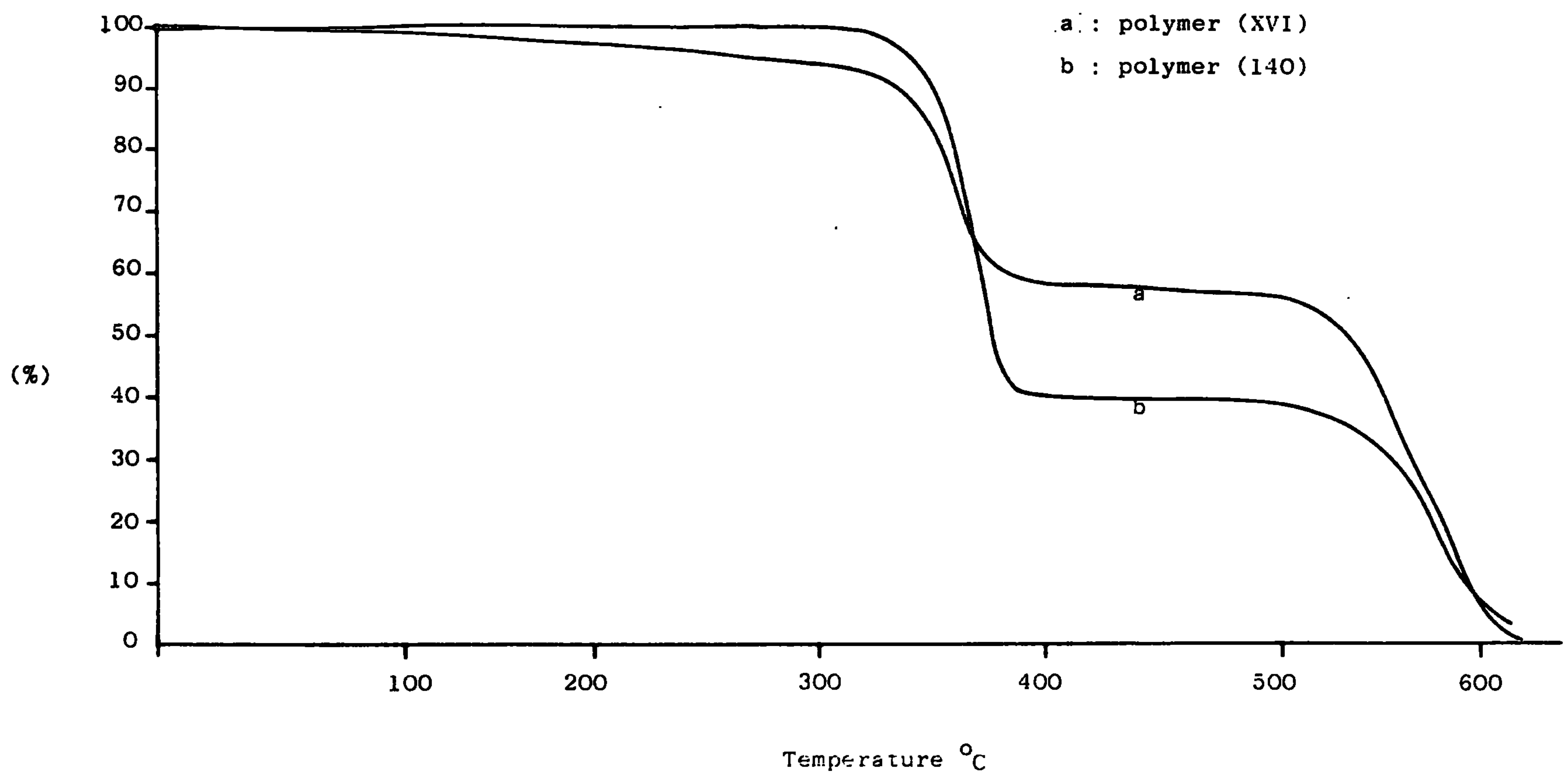
7.3 Conclusions

Although the amount of data available on polymer (XVI) is limited, it very strongly suggests that the material, which was produced by the reaction of the active olefin metathesis catalyst system WCl_6/Ph_4Sn on indene, is at least in part the ring-opened polymer with structure (XVIa).

This brief study indicates another area of interesting work for future investigations; which would initially be directed towards establishing conclusively that the polymer does arise by the ring-opening of the fused five-membered ring, using such techniques as ^{13}C n.m.r. spectroscopy and ozonolysis, followed by optimisation of the reaction conditions, variation of the catalyst system and the reaction of substituted indene derivatives.

Figure 7.2

Thermograms of polyindenes



EXPERIMENTAL

7.4a Reagents

Indene was purchased from Hopkin and Williams and purified by fractional distillation from calcium hydride.

7.4b The polymerisation of indene using tungsten hexachloride and tetraphenyltin as the catalyst system

The reaction vessel containing a magnetic follower was charged with tetraphenyltin (0.063g, 0.148mmoles) and purged for one hour with dry nitrogen. Tungsten hexachloride (0.029g, 0.072mmoles) dissolved in dried, degassed toluene (7.5cm^3) was injected into the reaction vessel using an air-tight syringe. The mixture was stirred for 12 minutes and the usual colour change from blue-black to dark brown was observed.

The reaction was cooled to 0^o using an external acetone/solid carbon dioxide bath and the dried, degassed monomer (3.4g, 28.8mmoles) was injected into the active catalyst mixture using an air-tight syringe. There was an immediate colour change to dark blue. The reaction was maintained at 0^o under an atmosphere of dry nitrogen and continuous stirring. After 20 minutes the viscosity of the reaction mixture had increased slightly. The reaction was allowed to proceed for 3 hours then terminated by the addition of a small quantity of methanol, followed by the addition to a five-fold excess of methanol. The precipitated material was removed by filtration, dissolved in analar toluene and reprecipitated in excess methanol. The material which was recovered by filtration and dried under reduced pressure (45^o, 10^{-3}mm Hg), was a white powdery material (XVI) (2.0g, 60%) (Found: C, 92.8; H, 7.2%; C_9H_8 requires C, 93.0; H, 7.0%).

7.4c The reaction of polymers (XVI) and (140) with bromine

Separate solutions of polymers (XVI) and (140) were prepared by dissolving the individual polymers (0.1g) in chloroform (1cm^3). To each solution an equal volume of a dilute solution of bromine in carbon tetrachloride was added. The solution containing polymer (140) did not discharge the bromine colour; even after shaking. However, the solution containing polymer (XVI) immediately discharged the bromine colour. A further volume of the bromine solution was added and again immediate decolourisation occurred. On the addition of the third volume of the bromine solution decolourisation only occurred after shaking.

APPENDIX A

APPARATUS AND INSTRUMENTS

Vacuum System. A conventional vacuum system incorporating a mercury diffusion pump, a rotary oil pump and a standard volume bulb (510 ± $10cm^3$) was used for degassing materials, vacuum distillations, removing volatile residues from polymer samples and for measuring amounts of condensable gases.

Mass spectra were recorded with an A.E.I. MS9 spectrometer at an ionising beam energy of 70 eV.

Combined g.l.c./mass spectra were recorded on a V.G. Micromass 12B coupled to a Pye 104 Gas Chromatograph.

N.m.r. spectra were recorded with either a Bruker Spectrospin HX 90E high resolution n.m.r. spectrometer fitted with a 'home-made' FT unit (operating at 84.67MHz for ^{19}F and 90.00MHz for ^{1}H n.m.r. spectra), or a Varian A56/60 spectrometer (operating at 56.40MHz for ^{19}F and 60.00MHz for ^{1}H n.m.r. spectra, at an operating temperature of 40^{o}), or a Bruker WH90 pulsed FT n.m.r. spectrometer (operating at 22.63MHz for ^{13}C n.m.r.). ^{19}F Chemical shifts are in ppm from external fluorotrichloromethane (positive upfield), unless otherwise stated, ^{1}H chemical shifts are measured on the δ scale relative to external tetramethylsilane and ^{13}C chemical shifts are in ppm from internal tetramethylsilane.

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

Analytical gas liquid chromatography (g.l.c.)

Pye Unicam GCD and Pye 104 gas chromatographs with nitrogen as the carrier gas and flame ionisation detectors were used for analytical work.

Column designations were:

Column A : 1.52m x 6mm diam., with a stationary phase of di-n-decylphthalate/Celite (1 : 2).

Column E : 1.52m x 6mm diam., with a stationary phase of dinonylphthalate/Celite (1 : 2).

Column O : 1.52m x 6mm diam., with a stationary phase of silicone grease/Celite

Preparative gas liquid chromatography

Column designations were:

Column B : 'Home-made' preparative gas chromatograph. 4.9m x 75mm diam., with a stationary phase of dinonylphthalate/Celite (1 : 2); N_2 carrier gas (ca. 60dm^3/hour).

Column C : Perkin-Elmer F21 Preparative Gaschromograph. 4.5m x 0.95cm diam., 20% Carbowax 20MTPA on Chromosorb P 80-100; N_2 carrier gas (ca. 1.0 - 2.0 atmos.).

Column D : Perkin-Elmer F21 Preparative Gaschromatograph. 4.5m x 0.95cm diam., di-n-decylphthalate/Chromosorb P (1 : 4); N_2 carrier gas (ca. 1.0 - 2.0 atmos.).

Column F : Varian 920 Aerograph Preparative Gaschromatograph. 6.0m x 1.0cm diam., dinonylphthalate.

Differential scanning calorimetry was performed using a Perkin-Elmer DSC-2 Differential Scanning Calorimeter fitted with the liquid nitrogen cooled sub-ambient temperature accessory. Scans could be run from 150^{o}K to 500^{o}K, the heating rate used was 40^{o}/minute, and samples were sealed in aluminium sample pans.

Thermogravimetric analysis was performed using a Stanton Redcroft TG750 Thermobalance, either in the constant heating mode at a heating rate of 1^{o}/minute, or in the isothermal mode.

Viscometry determinations were made using an Ubbelohde viscometer which was immersed in a Thomson and Mercer thermostatted water bath maintained at 25.00 ± 0.01^{o}. The elution time of a standard volume of polymer solution of accurately known concentration (ca. 1% solution) through the viscometer was determined until four consecutive measurements were identical (±0.1 sec., stopwatch accuracy). Successive dilutions of the polymer solution were carried out in the viscometer.

Gel Permeation Chromatography (G.P.C.) measurements were carried out by workers at the Rubber and Plastics Research Association (Shawbury).

APPENDIX B

MASS SPECTRA

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

75(63%, C_3HF_2, M-F)

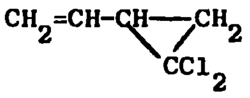
In this example the ion has a mass number 75, its intensity is 63% of the intensity of the base peak of the spectrum, it has provisionally assigned the formula C_3HF_2 (the + being understood), and its supposed origin is loss of an F from the parent ion (M). The base peak is designated B.

Metastable ion peaks, where observed, are tabulated underneath the main spectrum in the form $M^*(M_1 \xrightarrow{-F_r} M_2)$, where the metastable ion is understood to have been observed at

$$M^* = \frac{M_2^2}{M_1}$$

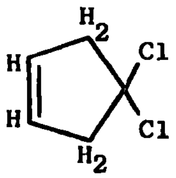
for the loss of neutral fragment F_r, from ion M_1^+ to give M_2^+.

I. 1,1-dichloro-2-vinylcyclopropane



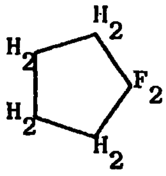
140(1%, M+4), 138(5%, M+2), 136(8%, $C_5H_6Cl_2$, M), 101(64%, C_5H_6Cl, M-Cl), 100(38%, C_5H_5Cl, M-HCl), 66(10%, C_5H_6, M-Cl_2), 65(100%, C_5H_5, B).

II. 4,4-dichlorocyclopentene



140(1%, M+4), 138(5%, M+2), 136(8%, $C_5H_6Cl_2$, M), 101(66%, C_5H_6Cl, M-Cl), 100(38%, C_5H_5Cl, M-HCl), 66(11%, C_5H_6, M-Cl_2), 65(100%, C_5H_5, B).

III*. difluorocyclopentane



106(10%, $C_5H_8F_2$, M), 86(21%, C_5H_7F, M-HF), 85(38%, C_5H_6F, M-H_2F), 78(21%, $C_3H_4F_2$, M-C_2H_4), 77(42%, $C_3H_3F_2$, M-C_2H_5), 65(8%, C_5H_5, M-H_3F_2), 55(35%, C_4H_7), 42(100%, C_3H_6, B), 40(10%, C_3H_4, M-$C_2H_4F_2$).

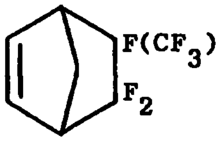
IV. 3,3,3-trifluoropropyne

$CF_3C{\equiv}CH$

95(8%, M+1), 94(100%, C_3HF_3, M and B), 93(5%, C_3F_3, M-H), 75(63%, C_3HF_2, M-F), 74(9%, C_3F_2, M-HF), 69(14%, CF_3), 56(5%, C_3HF, M-F_2), 55(5%, C_3F, M-HF_2).

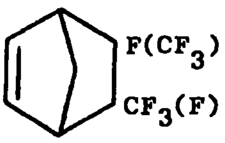
Metastable ion : 94 $\longrightarrow$ 25 (-CF_3)

V. 5,5,6-trifluoro-6-trifluoromethylbicyclo[2.2.1]hept-2-ene



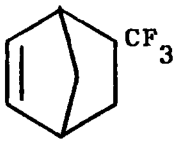
216(31%, $C_8H_6F_6$, M), 197(3%, $C_8H_6F_5$, M-F), 177(5%, $C_8H_5F_4$, M-HF_2), 165(9%, $C_7H_5F_4$, M-CHF_2), 147(6%, $C_7H_6F_3$, M-CF_3), 145(5%, $C_7H_4F_3$, M-CH_2F_3), 127(11%, $C_7H_5F_2$, M-CF_3.HF), 69(4%, CF_3), 66(100%, C_5H_6, B, M-C_3F_6), 65(8%, C_5H_5, B-H), 51(6%, CF_2H).

VI. 5,6-difluoro-5,6-bis(trifluoromethyl)bicyclo [2.2.1]hept-2-ene



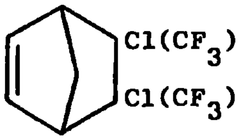
266(9%, $C_9H_6F_8$, M), 247(7%, $C_9H_6F_7$, M-F), 197(4%, $C_8H_6F_5$, M-CF_3), 127(10%, $C_7H_5F_2$, M-C_3HF_6), 69(10%, CF_3), 67(8%, C_5H_7, M-C_4HF_8), 66(100%, C_5H_6, B), 65(6%, C_5H_5, B-H), 51(6%, CF_2H).

VII. 5-trifluoromethylbicyclo[2.2.1]hept-2-ene



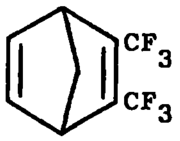
162(16%, $C_8H_9F_3$, M), 93(7%, C_7H_9, M-CF_3), 91(5%, C_7H_7, M-CH_2F_3), 77(10%, C_6H_5), 69(3%, CF_3), 67(8%, C_5H_7), 66(100%, C_5H_6, B), 65(7%, C_5H_5), 51(6%, CF_2H).

VIII. 5,6-dichloro-5,6-bis(trifluoromethyl)bicyclo[2.2.1]hept-2-ene



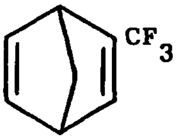
302(4%, M+4), 300(20%, M+2), 298(30%, $C_9H_6Cl_2F_6$, M), 209(30%, $C_9H_6F_5$, M-Cl_2.F), 207(30%, $C_9H_4F_2$, M-Cl_2.F.2H), 175(20%, $C_8H_3F_4$,M-2HCl.CF_2H), 67(8%, C_5H_7), 66(100%, C_5H_6, B), 65(8%, C_5H_5, B-H).

IX. 2,3-bis(trifluoromethyl)bicyclo[2.2.1]hept-2-ene



228(26%, $C_9H_6F_6$, M), 209(7%, $C_9H_6F_5$, M-F), 208(7%, $C_9H_5F_5$, M-HF), 202(24%, $C_7H_4F_6$, M-C_2H_2), 189(10%, $C_9H_5F_4$, M-HF.F), 159(100%, $C_8H_6F_3$, B, M-CF_3), 133(11%, $C_6H_4F_3$, B-C_2H_2), 119(8%, $C_5H_2F_3$), 109(22%, C_7H_6F), 69(12%, CF_3), 66(18%, C_5H_6), 51(10%, CHF_2).

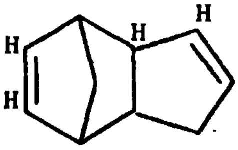
X*. 2-trifluoromethylbicyclo[2.2.1]hept-2-ene

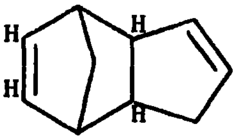


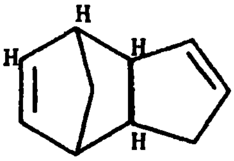
160(21%, $C_8H_7F_3$, M), 159(12%, $C_8H_6F_3$, M-H), 134(26%, $C_6H_5F_3$, M-C_2H_2), 114(8%, $C_6H_4F_2$, M-C_2H_2.HF), 109(11%, C_7H_6F, M-CF_2H), 91(100%, C_7H_7, B, M-CF_3), 84(6%, C_5H_5F), 69(11%, CF_3), 66(25%, C_5H_6), 65(21%, C_5H_5), 51(11%, CF_2H).

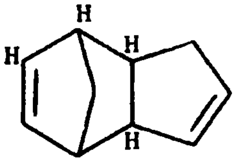
Metastable ions: 160 ⟶ 91 (-CF_3); 91 ⟶ 65 (-CH≡CH).

XI*. Dimers of dienes (123) and (124)









276($C_{10}H_4F_8$, M), 257($C_{10}H_4F_7$, M-F), 226($C_9H_4F_6$, M-CF_2), 207($C_9H_4F_5$, M-CF_3), 187($C_9H_3F_4$, M-CF_3.H), 138(100%, $C_5H_2F_4$, B), 119($C_5H_2F_3$,B-F), 88($C_4H_2F_2$, B-CF_2).

APPENDIX C

INFRARED SPECTRA

Infrared spectra are given below. All spectra were recorded using KBr cells, plates or discs, and were run under conditions designated by

(A) - KBr disc

(B) - thin liquid film

(C) - thin polymer film

(D) - gas phase

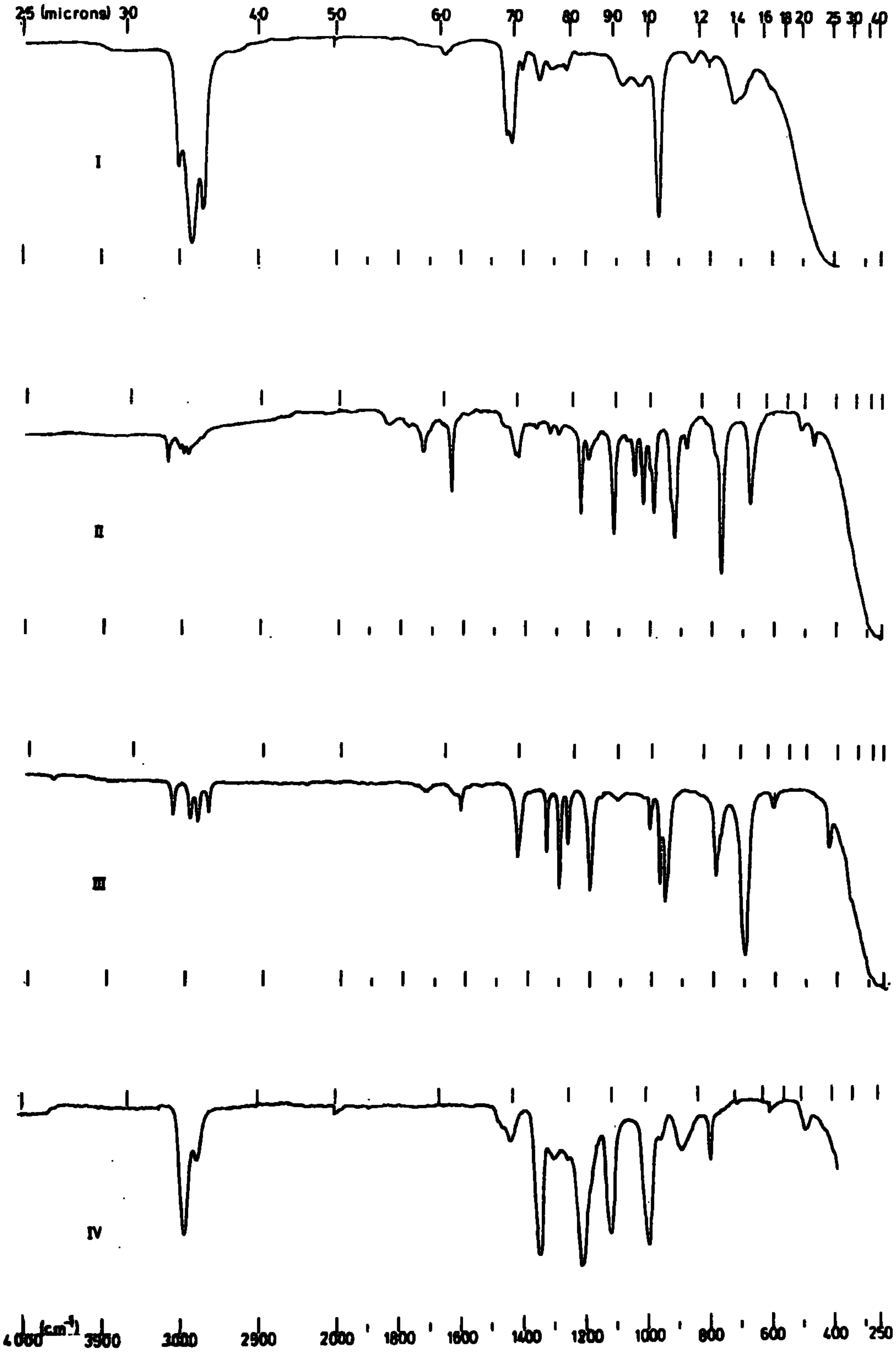
(E) - nujol mull; nujol bands are marked 'n' on the spectra.

Compounds which have been reported previously are marked with an asterisk, e.g. (I)*.

Spectrum No.	Name of Compound
(I)*	poly(1-pentenylene) (C)
(II)*	1,1-dichloro-2-vinylcyclopropane (B)
(III)*	4,4-dichlorocyclopentene (B)
(IV)	difluorocyclopentane (B)
(V)*	tricyclo[3.2.1.0^{2,6}]deca-3,8-dien-5-ol (B)
(VI)*	cyclopent-3-en-1-one (B)
(VII)*	cyclopent-2-en-1-one (B)
(VIII)	mixture of cyclopent-2-en-1-one and 5-fluorocyclopent-2-en-1-one (B)
(IX)*	1,2,3,4,5,5,6,6-octafluorobicyclo[2.2.2]oct-2-ene (A)
(X)*	1H,2H-hexafluorocyclohexa-1,3-diene (D)
(XI)*	2H,3H-hexafluorocyclohexa-1,3-diene (D)
(XII)*	1,4,5,5,6,6-hexafluorobicyclo[2.2.2]oct-2-ene (A)
(XIII)*	3,3,3-trifluoropropyne (D)
(XIV)*	5,5,6-trifluoro-6-trifluoromethylbicyclo[2.2.1]hept-2-ene (B)
(XV)*	5,6-difluoro-5,6-bis(trifluoromethyl)bicyclo[2.2.1]hept-2-ene (B)

Spectrum No.	Name of Compound
(XVI)*	5-trifluoromethylbicyclo[2.2.1]hept-2-ene (B)
(XVII)*	5,6-dichloro-5,6-bis(trifluoromethyl)bicyclo[2.2.1]hept-2-ene (B)
(XVIII)*	2,3-bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene (B)
(XIX)	2-trifluoromethylbicyclo[2.2.1]hepta-2,5-diene (B)
(XX)	1,4,5,5,6,7,10,10-octafluorotricyclo[5.2.1.0^{2,6}]deca-3,8-diene (A)
(XXI)*	poly(1,3-cyclopentylenevinylene) (C)
(XXII)	poly(4,4,5-trifluoro-5-trifluoromethyl-1,3-cyclopentylenevinylene) (C)
(XXIII)	polymer from the copolymerisation of cyclopentene and 5,5,6-trifluoro-6-trifluoromethylbicyclo[2.2.1]hept-2-ene (C)
(XXIV)	poly(4,4,5-trifluoro-5-trifluoromethyl-1,3-cyclopentylenevinylene) (C)
(XXV)*	poly(1-pentenylene) (C)
(XXVI)	poly(4,4,5-trifluoro-5-trifluoromethyl-1,3-cyclopentylenevinylene) (C)
(XXVII)	poly(4,5-difluoro-4,5-bis(trifluoromethyl)-1,3-cyclopentylenevinylene) (C)
(XXVIII)	poly(4-trifluoromethyl-1,3-cyclopentylenevinylene) (C)
(XXIX)	poly(4,5-dichloro-4,5-bis(trifluoromethyl)-1,3-cyclopentylenevinylene) (C)
(XXX)	poly(4,5-bis(trifluoromethyl)-1,3-cyclopentenylenevinylene) (C)
(XXXI)	poly(4-trifluoromethyl-1,3-cyclopentenylenevinylene) (C)
(XXXII)	poly(4,4,5-trifluoro-5-trifluoromethyl-1,3-cyclopentylenevinylene) (C)
(XXXIII)	poly(4,5-difluoro-4,5-bis(trifluoromethyl)-1,3-cyclopentylenevinylene) (C)
(XXXIV)	copolymer from 2,3-bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene and cyclopentene (C)

Spectrum No.	Name of Compound
(XXXV)	copolymer from 2-trifluoromethylbicyclo[2.2.1]hepta-2,5-diene and cyclopentene (C)
(XXXVI)	polyindene from the reaction of indene with WCl_6/Ph_4Sn (C)
(XXXVII)	cationic polyindene (C)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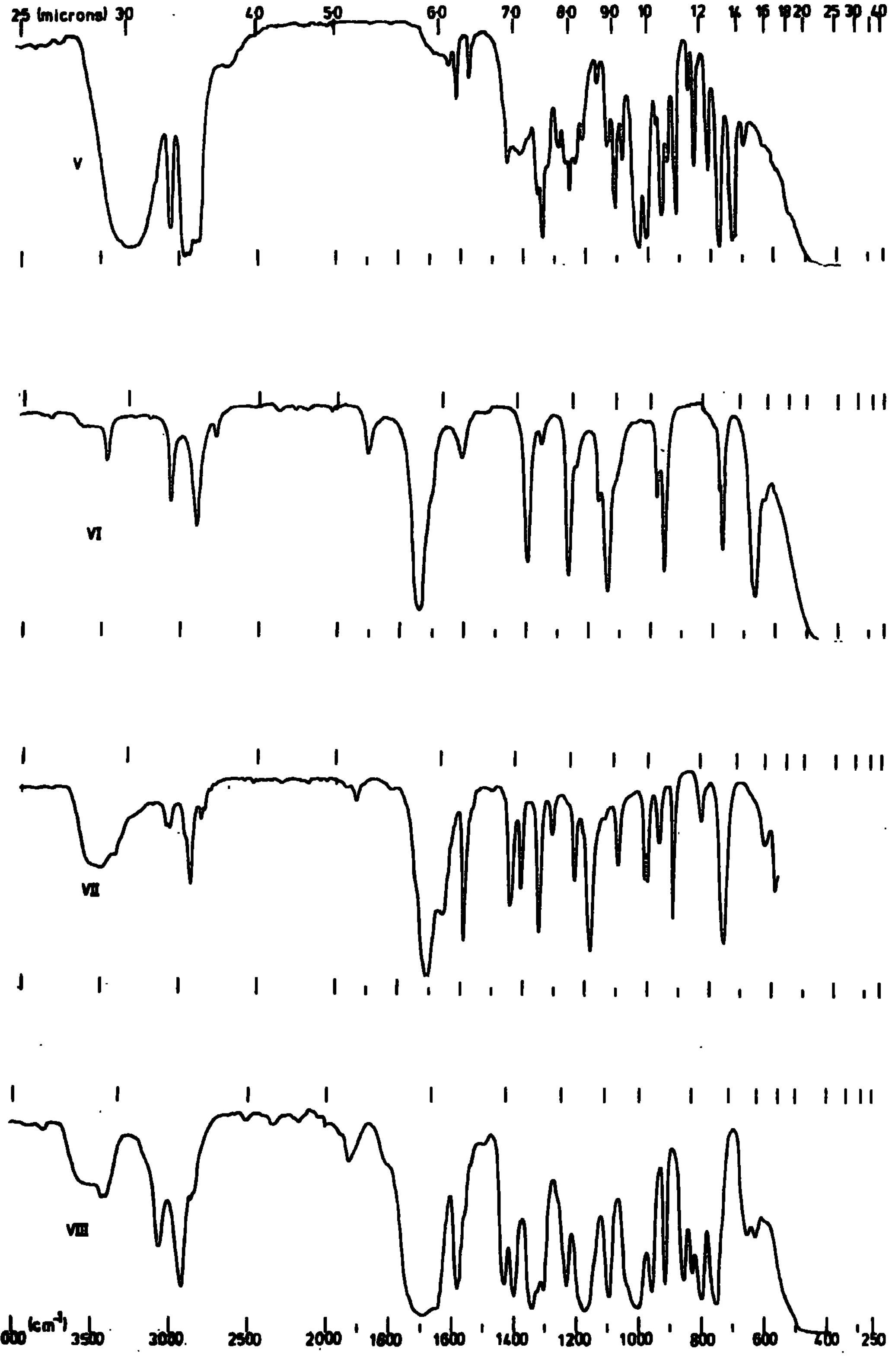
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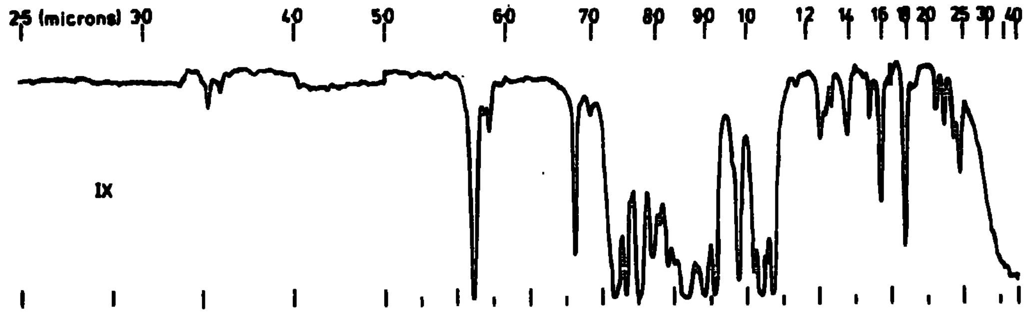

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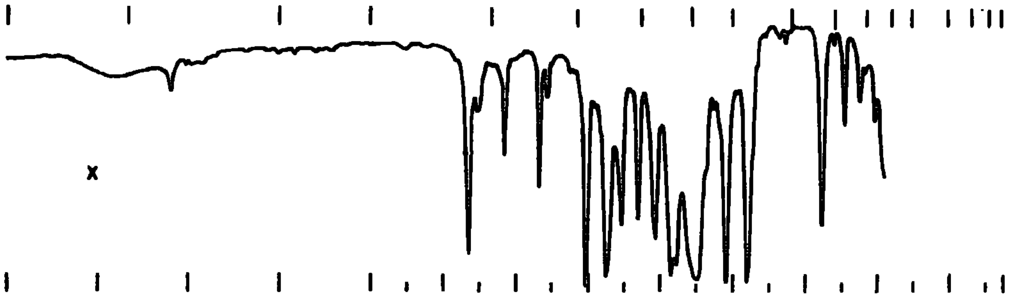

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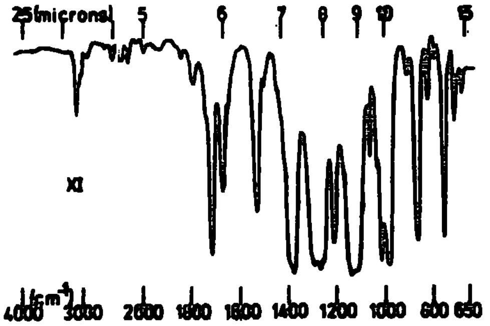

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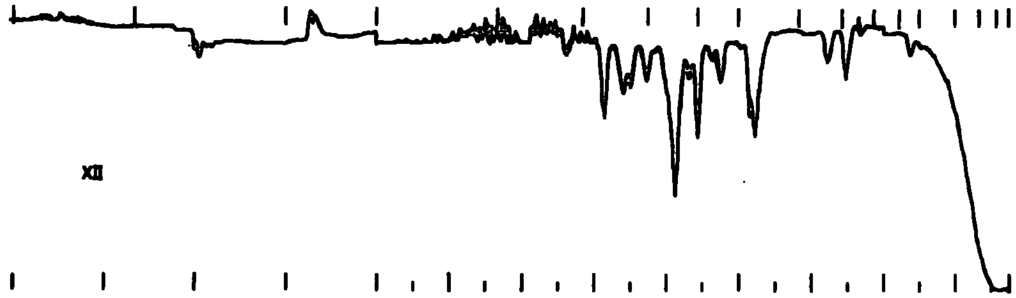

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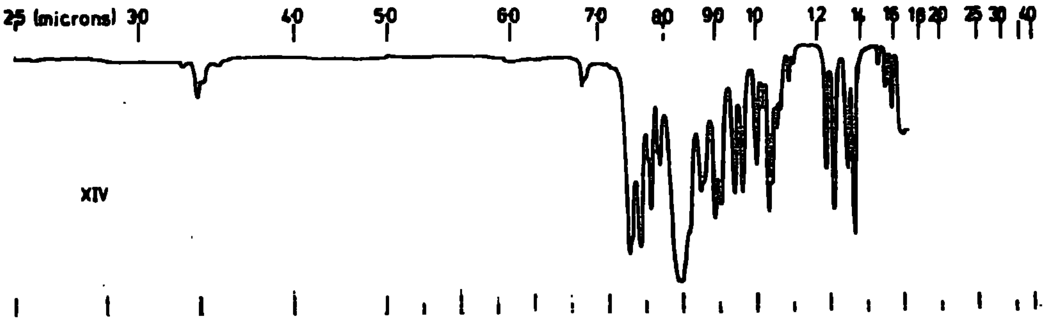

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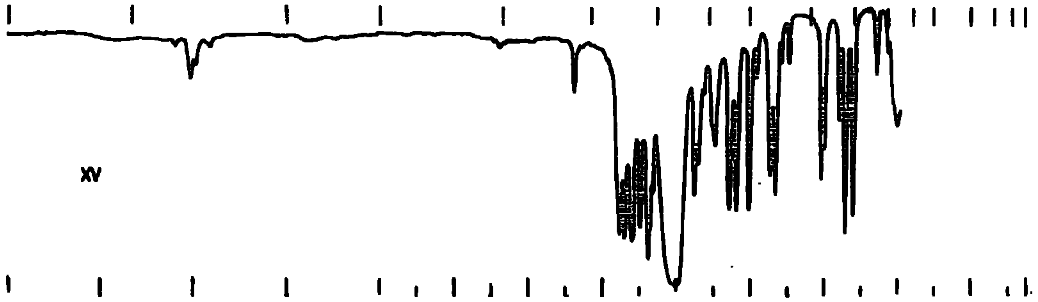

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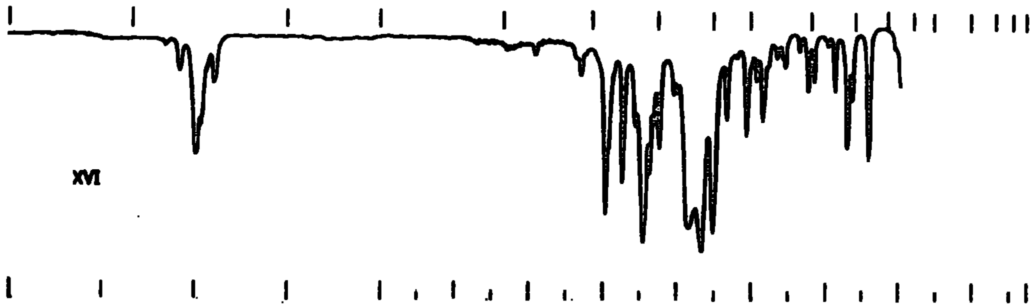

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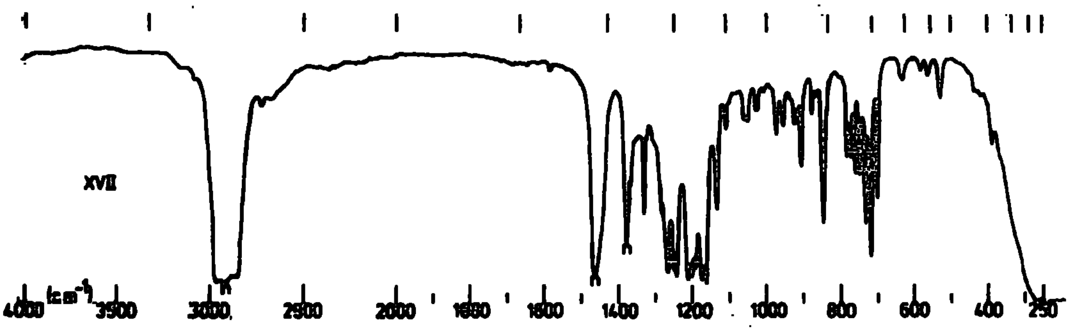

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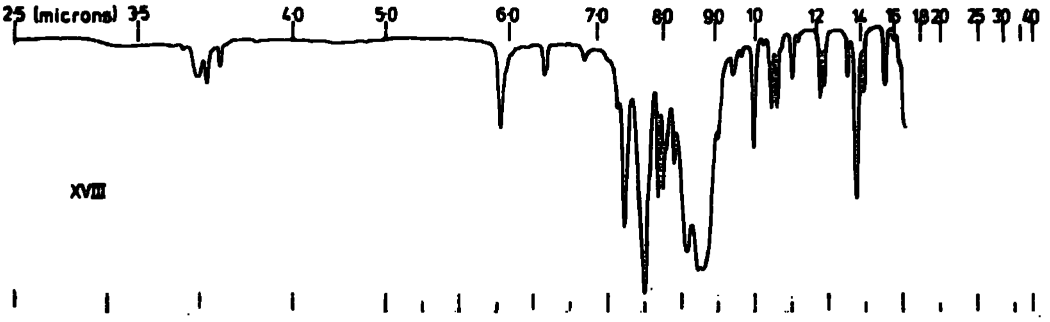
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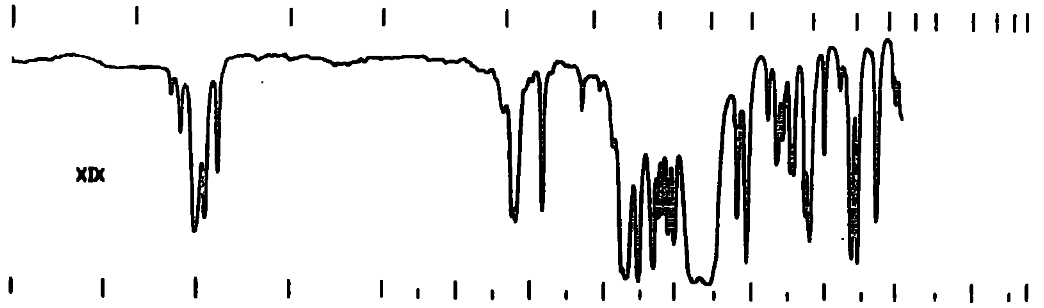
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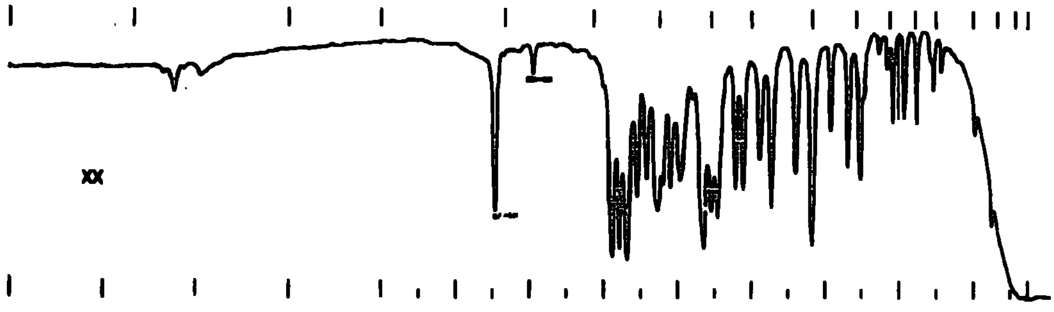
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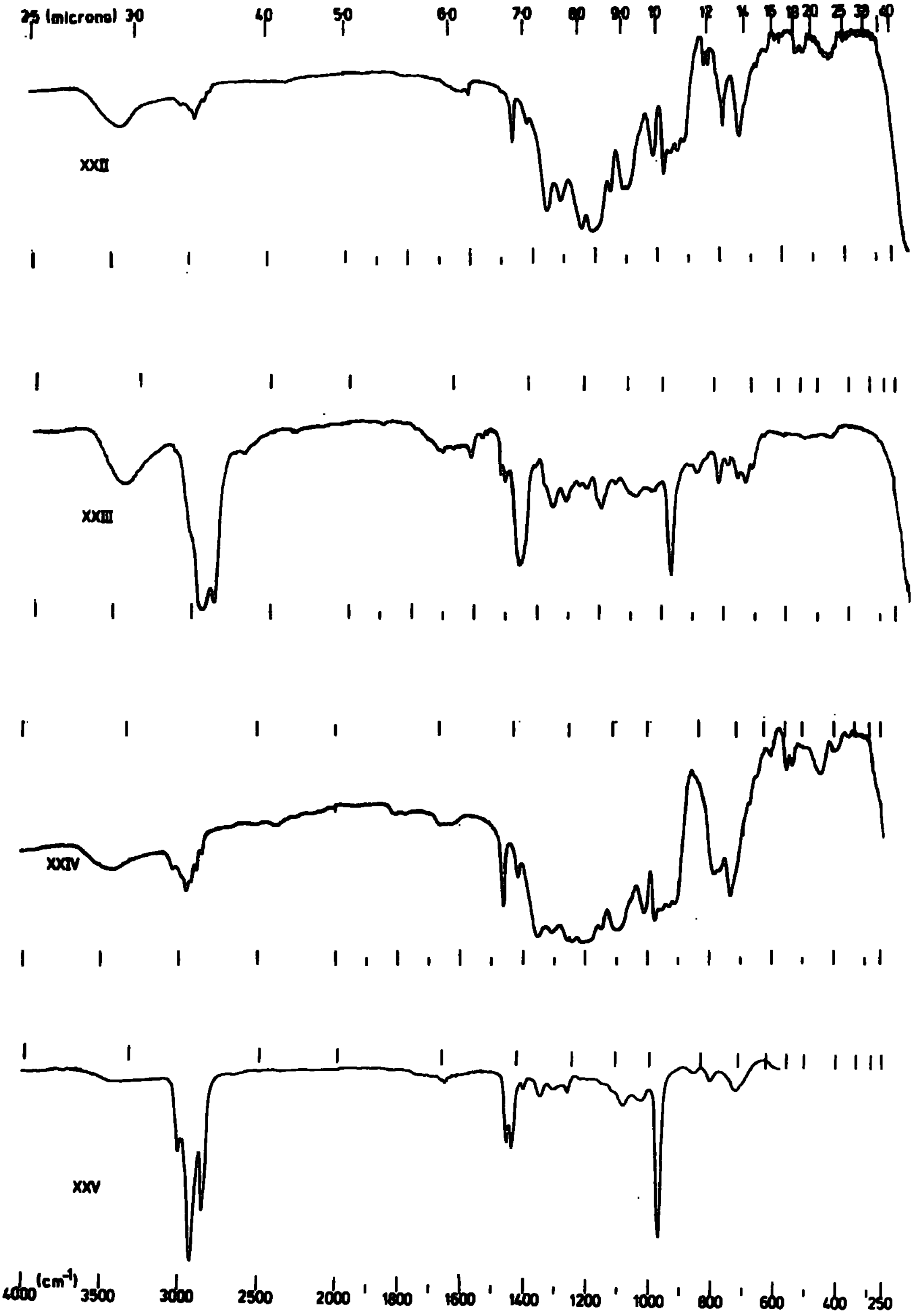
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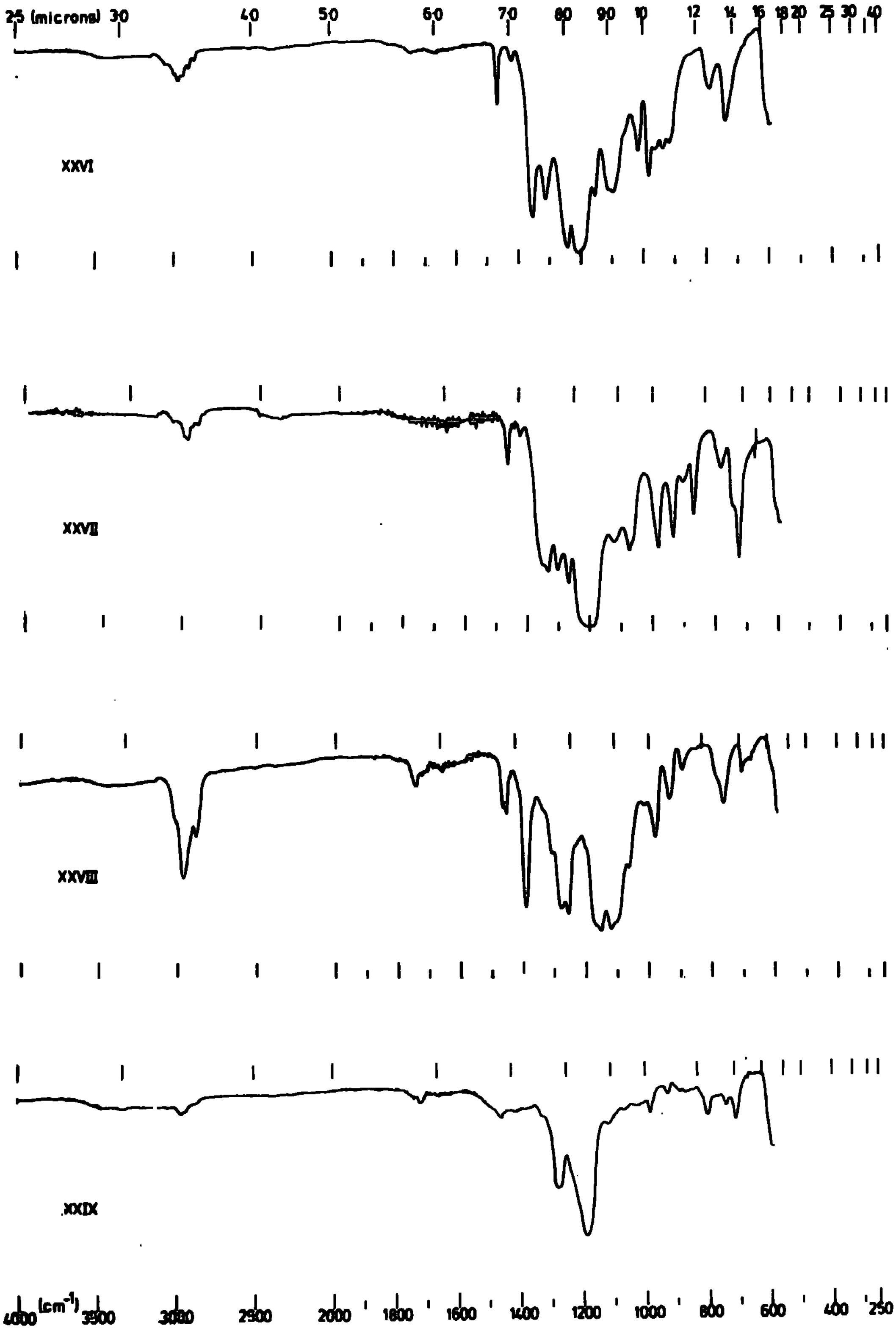
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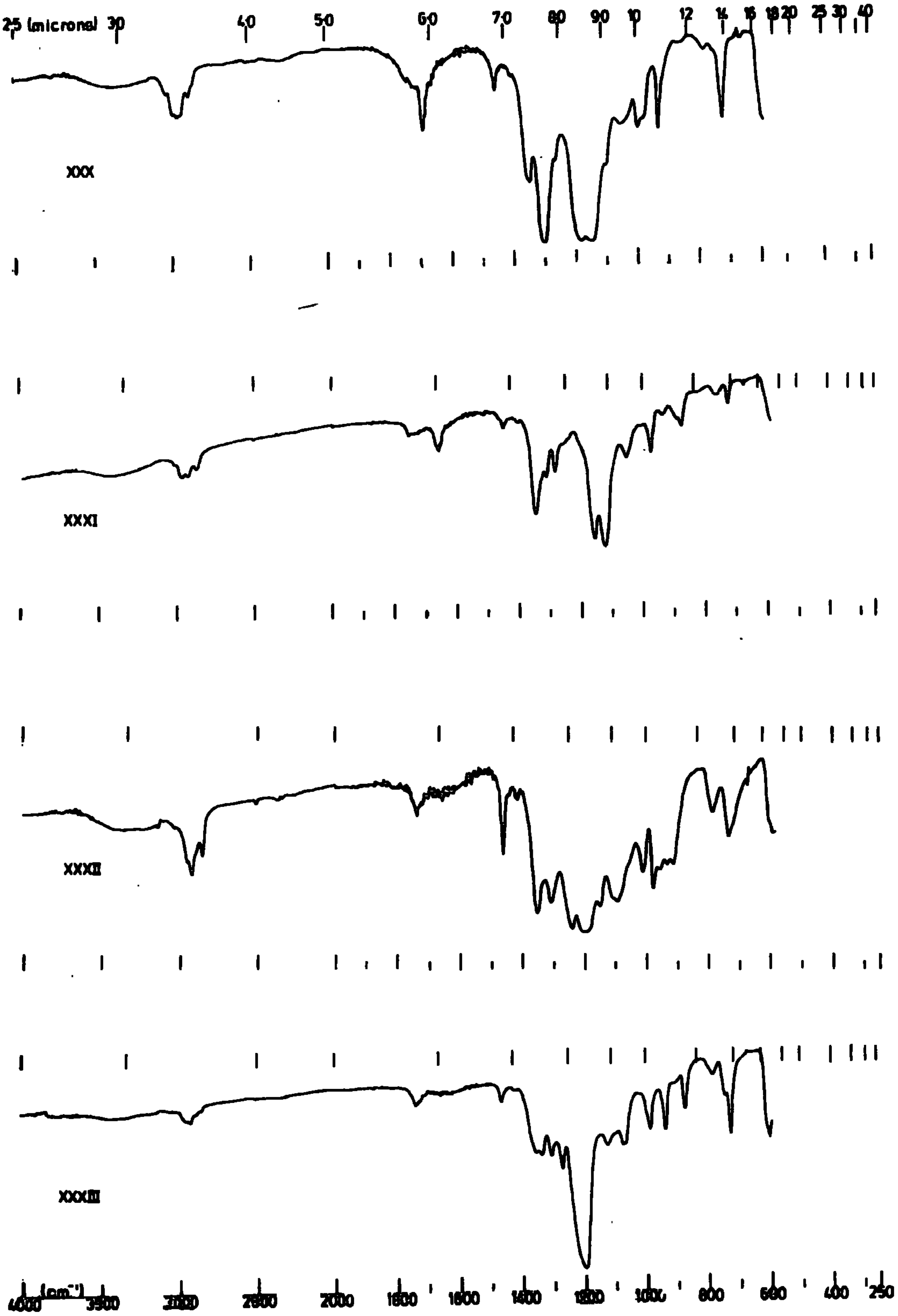
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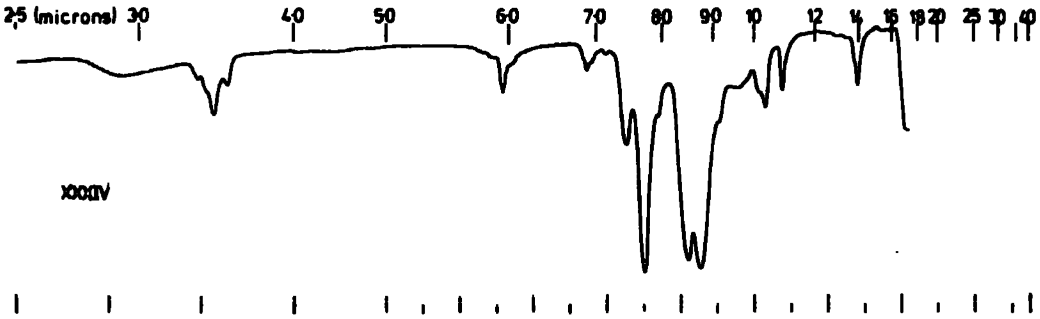

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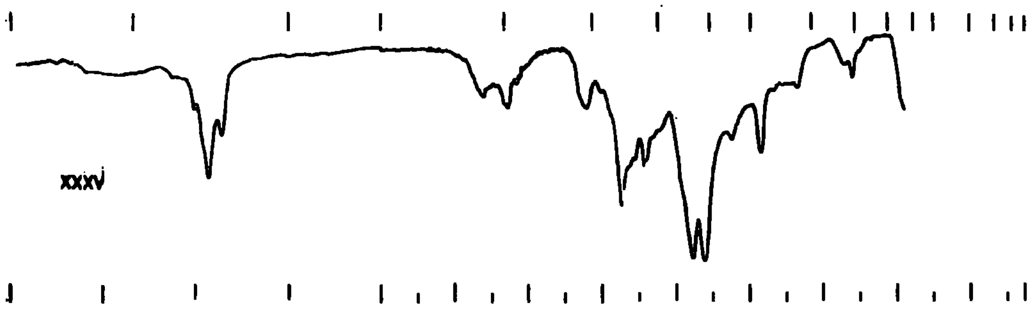

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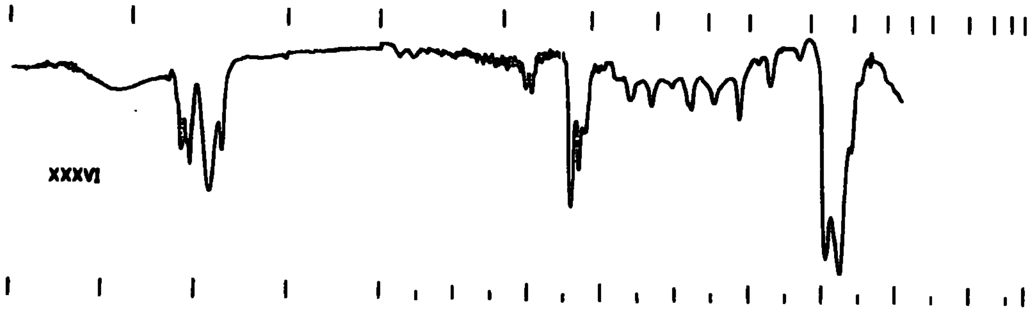

XXXVI

XXXVII

APPENDIX D

The Board of Studies in Chemistry requires that each postgraduate research thesis contain an appendix listing

(a) all research colloquia, research seminars and lectures (by external speaks) arranged by the Department of Chemistry since 1 October 1976;

and (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

1.1 1976-77

(a) University of Durham Chemistry Colloquia

Wednesday, 20th October

Professor J.B. Hyne (University of Calgary), "New Research on an Old Element - Sulphur".

Wednesday, 10th November

Dr. J.S. Ogden (Southampton University), "The Characterization of High Temperature Species by Matrix Isolation".

Wednesday, 17th November

Dr. B.E.F. Fender (University of Oxford), "Familiar but Remarkable Inorganic Solids".

Wednesday, 24th November

Dr. M.I. Page (Huddersfield Polytechnic), "Large and Small Rate Enhancements of Intramolecular Catalysed Reactions".

Wednesday, 8th December

Professor A.J. Leadbetter (University of Exeter), "Liquid Crystals".

Wednesday, 26th January

Dr. A. Davis (ERDR), "The Weathering of Polymeric Materials".

Wednesday, 2nd February

Dr. M. Falk, (NRC Canada), "Structural Deductions from the Vibrational Spectrum of Water in Condensed Phases".

Wednesday, 9th February

Professor R.O.C. Norman (University of York), "Radical Cations; Intermediates in Organic Reactions".

Wednesday, 23rd February

Dr. G. Harris (University of St. Andrews), "Halogen Adducts of Phosphines and Arsines".

Friday, 25th February

Professor H.T. Dieck (Frankfurt University), "Diazadienes - New Powerful Low-Valent Metal Ligands".

Wednesday, 2nd March

Dr. F. Hibbert (Birkbeck College, London), "Fast Reaction Studies of Slow Proton Transfers Involving Nitrogen and Oxygen Acids".

Friday, 4th March

Dr. G. Brink (Rhodes University, R.S.A.), "Dielectric Studies of Hydrogen Bonding in Alcohols".

Wednesday, 9th March

Dr. I.O. Sutherland (Sheffield University), "The Stevans' Rearrangement Orbital Symmetry and Radical Pairs".

Friday, 18th March

Professor Hans Bock (Frankfurt University), "Photoelectron Spectra and Molecular Properties: A Vademecum for the Chemist"

Wednesday, 30th March

Dr. J.R. MacCallum (University of St. Andrews), "Photooxidation of Polymers".

Wednesday, 20th April

Dr. D.M.J. Lilley (G.D. Searle, Research Div.), "Tails of Chromatin Structure - Progress towards a Working Model".

Wednesday, 27th April

Dr. N.P. Stevens (University of Hartford), "Photocycloaddition Polymerisation".

Wednesday, 4th May

Dr. G.C. Tabisz (University of Manitoba), "Collision Induced Light Scattering by Compressed Molecular Gases".

Wednesday, 11th May

Dr. R.E. Banks (UMIST), "The Reaction of Hexafluoropropene with Heterocyclic N-Oxides".

Wednesday, 18th May

Dr. J. Atwood (University of Alabama), "Novel Solution Behaviour of Anionic Organoaluminium Compounds: the Formation of Liquid Clathrates".

Wednesday, 25th May

Professor M.M. Kreevoy (University of Minnesota), "The Dynamics of Proton Transfer in Solution".

Wednesday, 1st June

Dr. J. McCleverty (University of Sheffield), "Consequences of Deprivation and Overcrowding on the Chemistry of Molybdenum and Tungsten".

Wednesday, 6th July

Professor J. Passmore (University of Brunswick), "Adducts Between Group V Pentahalides and a Postscript on S_7I^+".

(b) Durham University Chemical Society

Tuesday, 19th October

Dr. J.A. Salthouse (University of Manchester), "Chemistry and Energy".

Tuesday, 26th October

Dr. R.E. Richards (University of Oxford), "NMR Measurements on Intact Biological Tissue".

Tuesday, 2nd November

Dr. B. Sutcliffe (University of York), "The Chemical Bond as a Figment of the Imagination".

Tuesday, 16th November

Mr. R. Ficken (Rohm and Haas), "The Graduate in Industry".

Tuesday, 30th November

Dr. R.J. Donovan (University of Edinburgh), "The Chemistry of the Atmosphere".

Tuesday, 18th January

Professor I. Fells (University of Newcastle), "Energy Storage: the Chemists' Contribution to the Problem".

Tuesday, 8th February

Dr. M.J. Cleare (Johnson Matthey Research Centre), "Platinum Group Metal Compounds as Anti-Cancer Agents".

Tuesday, 1st March

Professor J.A.S. Smith (Q.E. College, London), "Double Resonance".

Tuesday, 8th March

Professor C. Eaborn (University of Sussex), "Structure and Reactivity".

1.2 1977-78

(a) University of Durham Chemistry Colloquia

Tuesday, 27th September

Dr. T.J. Broxton (La Trobe University, Australia), "Interaction of Aryldiazonium Salts and Arylazoalkyl Ethers in Basic Alcoholic Solvents".

Wednesday, 19th October

Dr. B. Heyn (University of Jena, D.D.R.), "σ-Organo-Molybdenum Complexes as Alkene Polymerisation Catalysts".

Thursday, 27th October

Professor R.A. Filler (Illinois Inst. of Technology, U.S.A.), "Reactions of Organic Compounds with Xenon Fluorides".

Wednesday, 2nd November

Dr. N. Boden (University of Leeds), "NMR Spin-Echo Experiments for Studying Structure and Dynamical Properties of Materials Containing Interacting Spin-½ Pairs".

Wednesday, 9th November

Dr. A.R. Butler (University of St. Andrews), "Why I lost Faith in Linear Free Energy Relationships".

Wednesday, 7th December

Dr. P.A. Madden (University of Cambridge), "Raman Studies of Molecular Motions in Liquids".

Wednesday, 14th December

Dr. R.O. Gould (University of Edinburgh), "Crystallography to the Rescue in Ruthenium Chemistry".

Wednesday, 25th January

Dr. G. Richards (University of Oxford), "Quantum Pharmacology".

Wednesday, 1st February

Professor K.J. Ivin (Queens University, Belfast), "The Olefin Metathesis Reaction: Mechanism of Ring-Opening Polymerisation of Cycloalkenes".

Friday, 3rd February

Dr. A. Hartog (Free University, Amsterdam, Holland), "Surprising Recent Studies in Organo-Magnesium Chemistry".

Wednesday, 22nd February

Professor J.D. Birchall (Mond Division, I.C.I. Ltd.), "Silicon in the Biosphere".

Wednesday, 1st March

Dr. A. Williams (University of Kent), "Acyl Group Transfer Reactions".

Friday, 3rd March

Dr. G. van Koten (University of Amsterdam, Holland), "Structure and Reactivity of Arylcopper Cluster Compounds".

Wednesday, 22nd March

Professor H. Vahrenkamp (University of Freiburg, Germany), "Metal-Metal Bonds in Organometallic Complexes".

Wednesday, 19th April

Dr. M. Barber (UMIST), "Secondary Ion Mass Spectra of Surfaces and Absorbed Species".

Tuesday, 16th May

Dr. P. Ferguson (C.N.R.S., Grenoble), "Surface Plasma Waves and Absorbed Species on Metals".

Thursday, 18th May

Professor M. Gordon (University of Essex), "Three Critical Points in Polymer Science".

Monday, 22nd May

Professor D. Tuck (University of Windsor, Ontario), "Electrochemical Synthesis of Inorganic and Organometallic Compounds".

Wednesday - Thursday, 24th-25th May

Professor P. von R. Schleyer (University of Erlangen, Nürnberg),

I. "Planar Tetra-coordinate Methanes, Perpendicular Ethylenes, and Planar Allenes",

II. "Aromaticity in Three Dimensions".

III. "Non-classical Carbocations".

Wednesday, 21st June

Dr. S.K. Tyrlik (Academy of Science, Warsaw), "Dimethylglyoxime-cobalt Complexes - Catalytic Black Boxes".

Friday, 23rd June

Professor W.B. Pearson (University of Florida), "Diode Laser Spectroscopy at 16 μm".

Friday, 30th June

Professor G. Mateescu (Case Western Reserve University), "A Concerted Spectroscopy Approach to the Characterization of Ions and Ion Pairs: Facts, Plans, and Dreams".

(b) Durham University Chemical Society

Thursday, 13th October

Dr. J.C. Young, Mr. A.J.S. Williams (University of Aberystwyth), "Experiments and Considerations Touching Colour".

Thursday 20th October

Dr. R.L. Williams (Metropolitan Police Forensic Science Dept.), "Science and Crime".

Thursday, 3rd November

Dr. G.W. Gray (University of Hull), "Liquid Crystals - Their Origins and Applications".

Thursday, 24th November

Mr. G. Russell (Alcan), "Designing for Social Acceptability".

Thursday, 1st December

Dr. B.F.G. Johnson (University of Cambridge), "Chemistry of Binary Metal Carbonyls".

Thursday, 2nd February

Professor R.A. Raphael (University of Cambridge), "Bizarre Reactions of Acetylenic Compounds".

Thursday, 16th February

Professor G.W.A. Fowles (University of Reading), "Home Winemaking".

Thursday, 2nd March

Professor M.W. Roberts (University of Bradford), "The Discovery of Molecular Events at Solid Surfaces".

Thursday, 9th March

Professor H. Suschitzky (University of Salford), "Fruitful Fissions of Benzofuroxans".

Thursday, 4th May

Professor J. Chatt (University of Sussex), "Reactions of Coordinated Dinitrogen".

Tuesday, 9th May

Professor G.A. Olah (Case Western Reserve University, Cleveland, Ohio), "Electrophilic Reactions of Hydrocarbons".

2. Research Conferences

(a) Polymer Surfaces Symposium, Macromolecular Group of the Chemical Society (Durham University, March 1977).

(b) Annual Chemical Congress, Chemical Society (Liverpool University, April 1978).

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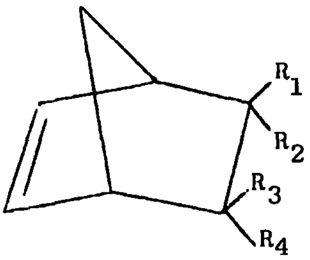
END PAPER I

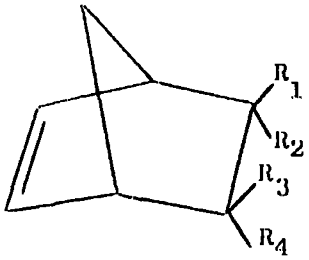
I



	R_1	R_2	R_3	R_4
Ia	CF_3	F	F	F
Ib	F	CF_3	F	F

5,5,6-trifluoro-6-trifluoromethylbicyclo[2.2.1]hept-2-ene

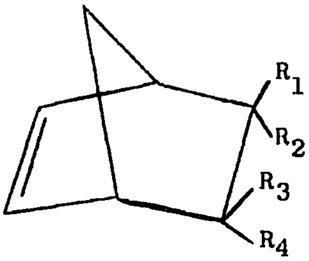
II



	R_1	R_2	R_3	R_4
IIa	CF_3	F	F	CF_3
IIb	CF_3	F	CF_3	F
IIc	F	CF_3	F	CF_3

5,6-difluoro-5,6-bis(trifluoromethyl)bicyclo[2.2.1]hept-2-ene

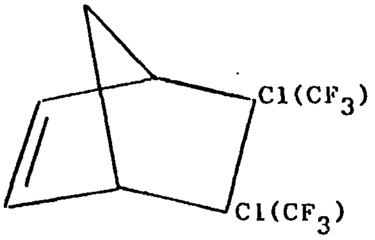
III



	R_1	R_2	R_3	R_4
IIIa	CF_3	H	H	H
IIIb	H	CF_3	H	H

5-trifluoromethylbicyclo[2.2.1]hept-2-ene

IV



unknown stereochemistry

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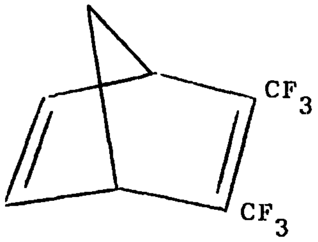
V



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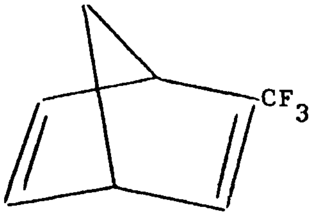

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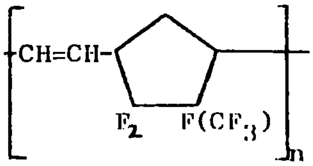
END PAPER II

VII



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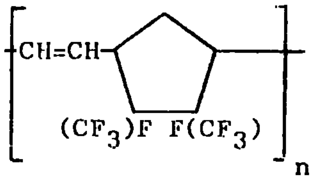
VIII



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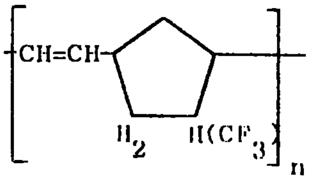
IX



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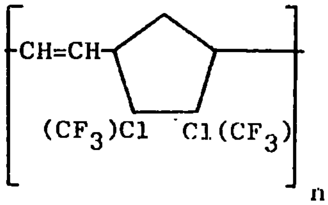
X



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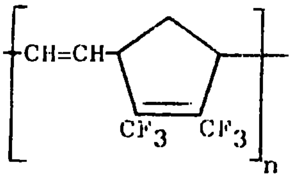
XI



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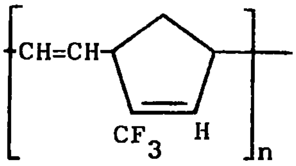
XII



poly(4-trifluoromethyl-1,3-cyclopentenylenevinylene)