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RING-OPENING POLYMERIZATION OF SOME ARYL SUBSTITUTED POLYCYCLIC ALKENES

By

ISAM F.A.F. EL-SAAFIN (Graduate Society)
B.Sc. (Riyad University, Saudi Arabia)
M.Sc. (Durham University, England)

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the University of Durham, England

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To the memory of my father, with love to my mother, and with indebtedness to my brothers, Hisham and Ziyad.

ABSTRACT

The work described in this thesis is concerned with an investigation of the polymerizability of aryl substituted polycyclic alkenes by ring-opening using metathesis catalyst systems.

The synthesis, purification and characterization of the monomers required for this work are described in Chapter 2.

Successful ring-open polymerizations are described in Chapter 3 together with the unsuccessful attempts to ring open polymerize some heteroatom substituted compounds. The characterization of the new polymers is discussed in Chapter 4 together with some preliminary results concerning the susceptibility of these polymers to the photo-oxidative degradation.

ACKNOWLEDGEMENTS

I wish to express and record my deep gratitude and sincere appreciation to my supervisor, Dr. W.J. Feast, his guidance, inexhaustible assistance and invaluable discussions were of great help in the achievement of this work. I also acknowledge with deep appreciation Dr. J.H. Edwards for helpful discussions.

My grateful thanks are due to Professor K.J. Ivin and co-workers (Queen's University, Belfast) for recording the ^{13}C n.m.r. of some of the polymers; to Dr. R.S. Matthews for recording some ^{1}H and ^{13}C n.m.r. spectra; and to Dr. M. Jones for recording the mass spectra.

I am grateful for the assistance of members of the technical staff whose help made the progress of this work possible in particular to Mrs. E.M. Nevins for the photographic work, Mrs. M. Cocks for the elemental analyses, Mr. J.A. Parkinson for the G.P.C. molecular weight distribution curves, Mr. R. Hart and Mr. W.H. Fettis for their help in making the vacuum line, molecular distillation apparatus, and other specialist items. All my thanks go to the Storekeeper, Mr. T.M. Argument, who made apparatus and chemicals available without argument!!

I am greatly indebted to Mrs. E. Duddy for typing this thesis and eliminating some of my grammatical mistakes. I am also thankful to all my colleagues in Lab. 9 and 25 for their friendship, help and encouragement, in particular, Mr. A. Tate. The kindness and warmth of the people both in the Department and outside made me enjoy my stay here, and overcome the effects of the climate.

Finally, I am greatly indebted to my family for their unlimited help, encouragement and generous financial support. In particular, my brother Hisham who supported me throughout my studies for my B.Sc., M.Sc. and Ph.D. Thanks are also due to Mr. Z. Yassin for contribution and encouragement.

MEMORANDUM

The work reported in this thesis was carried out in the Chemistry Department of the University of Durham between October 1979 and September 1981. 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 will be published in J. Mol. Catalysis early in 1982, and has been presented at the 4th International Symposium on Olefin Metathesis, Belfast, September 1981.

Note to Reader

Many of the compounds discussed in this thesis have long and inconvenient systematic names. To avoid excessive repetition the author has adopted a compound numbering system, the compounds most frequently referred to are shown on the key below and a loose copy of this is provided as an aid to the reader.

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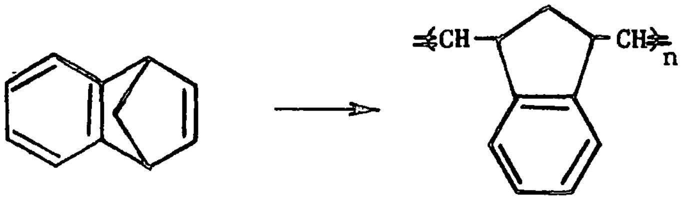

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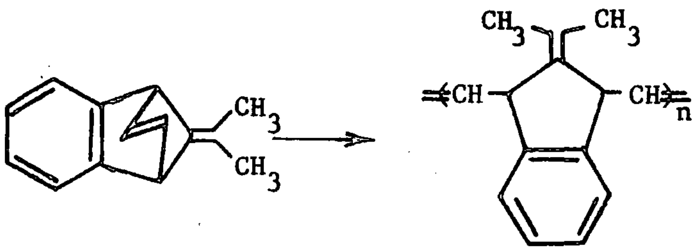

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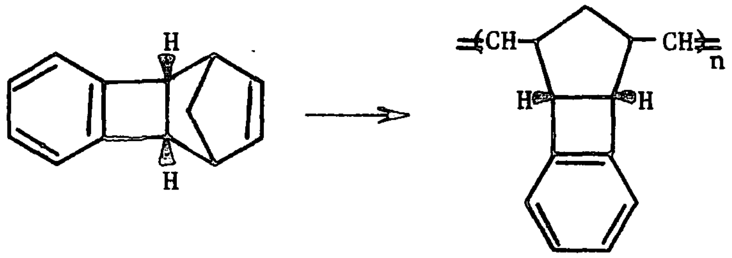

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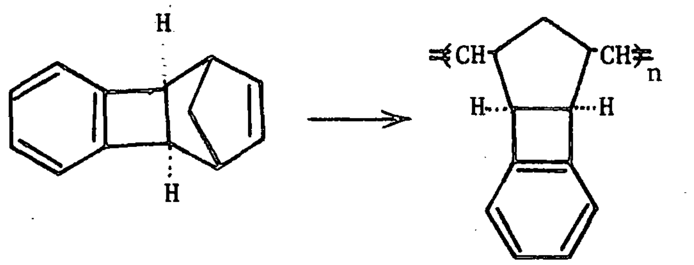

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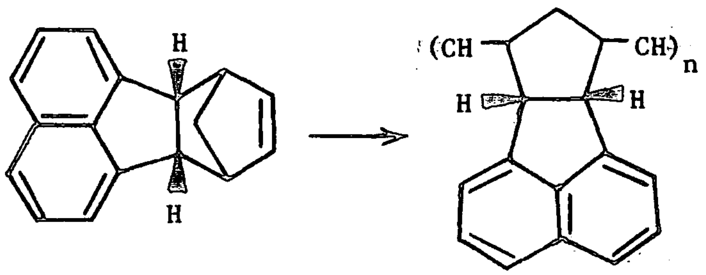

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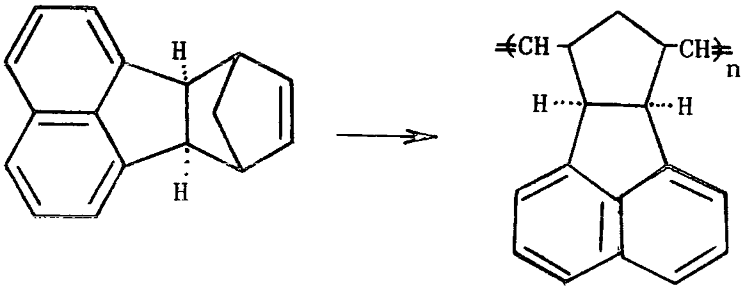

+ polyacenaphthylene

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* Contaminated with acenaphthalene.

CONTENTS

CHAPTER II. Synthesis and Characterization of Monomers

EXPERIMENTAL

CHAPTER III. Ring-opening Polymerization of Arylcycloalkenes

CHAPTER 1

General Introduction and Background

1.1. Origins and Background of Olefin Metathesis

Olefins in the presence of a variety of catalysts, most commonly containing tungsten, molybdenum or rhenium with either organotin or aluminium compounds undergo the metathesis reaction in accordance with Figure 1.1. The reaction may be considered as a bond-reorganization process and proceeds via the cleavage and reformation of the double bonds. This reaction is characterized by the fact that the total number and types of chemical bonds remains unchanged during the transformation of the reactants into products. The metathesis reaction of alkenes constitutes a major development in the field of hydrocarbon chemistry in the last two decades. The versatility of the metathesis reaction not only gives many new pathways for organic synthesis but also offers new openings for the chemical industry.

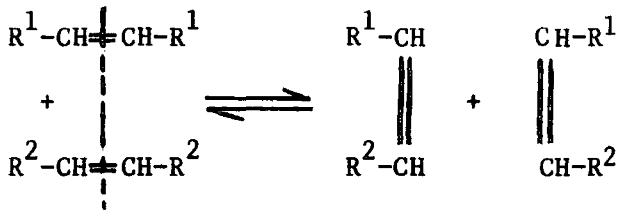

Figure 1.1.

In 1964, Banks and Bailey[1] reported the first example of the metathesis reaction of linear alkenes, they called the reaction 'olefin disproportionation'. The equilibrium shown in Figure 1.1. was demonstrated, the reaction allows the selective conversion of an unsymmetrical linear alkene into equimolar amounts of higher and lower molecular weight olefins. They used heterogeneous catalysts derived from molybdenum or tungsten hexacarbonyls deposited on alumina and they examined linear olefins with three to eight carbon atoms. This early work opened the way for the development and study of a very important new field of organic chemistry. The metathesis reaction has been investigated intensively and many kinds of reactant types have been studied, including alkenes, dienes, polyenes, alkyns and cycloalkenes. The last mentioned reactants giving rise to interesting polymeric and/or macrocyclic products as shown in Figure 1.2.

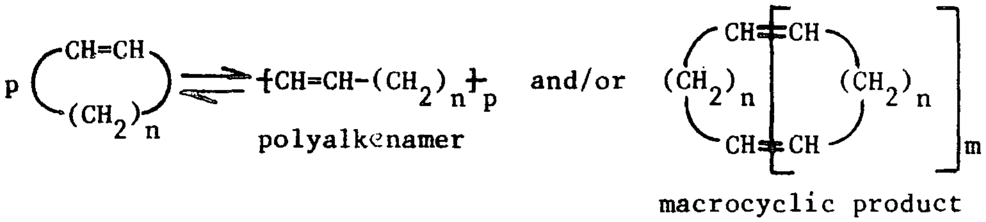

Figure 1.2.

In 1968 Calderon[2] and Wassermann,[3] recognized this ring-opening polymerization as a special case of olefin metathesis.*

In fact the first description of an olefin metathesis reaction catalyzed by a transition metal was reported by Anderson and Merckling,[7] in 1955, when they successfully polymerized bicyclo[2,2,1]hept-2-ene to a high molecular weight polymer using a mixture of ethyl magnesium bromide and titanium tetrachloride; later Truett et al.,[8] demonstated that the catalyst system used by Anderson and Merckling worked by ring-opening bicyclo[2,2,1]hept-2-ene. In 1963 Eleuterio,[9] demonstated the ring-opening polymerization of a variety of cycloolefins, using a catalyst

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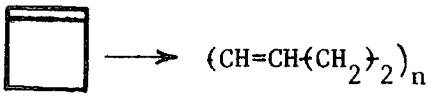
* *Different names for the reaction were used in the early publications, this can lead to some confusion. The term 'disproportionation' was often applied to this reaction for historical reasons, it was first used to describe heterogeneously catalyzed reactions of acyclic alkenes, while the name 'metathesis'[2,3] was applied to homogeneously catalyzed reactions and in particular to ring-opening polymerization. Bradshaw et al,[4] suggested the name 'dismutation' and they also used the term 'ethanolysis' for the reaction when ethylene was one of the reactants. Kenton et al.,[5] used the name 'olefin reaction', while Crain[6] suggested 'mutual cleavage' and 'ethylene cleavage'. The term 'disproportionation' was eventually thought to be inadequate, since it does not really indicate the nature and the scope of the reaction and was sometimes misleading. Thus the term 'disproportionation' already had a well established use in chemistry as in, for example, disproportionation of metal oxidation states and the two uses were not equivalent; the term 'dismutation' is subject to similar objections. The name 'metathesis', meaning literally exchange of parts, is not subject to these objections and it is an appropriate name for this reaction, since it conveys the nature and the scope of the reaction, and is therefore preferred.*

derived from molybdenum oxide on alumina, activated by hydrogen reduction and further reacted with aluminium hydride. He polymerized cycloalkenes such as, bicyclo[2,2,1]hept-2-ene, tricyclo[4,2,1,$0^{2,6}$]deca-3,8-diene (cyclopentadiene dimer), tricyclo[5,2,1,$0^{2,6}$]dec-8-ene and cyclopentene. In the case of cyclopentene, trans-poly(1-pentenylene) was formed with a high degree of stereo-regular structure but only in low yield. In 1963 Dall'Asta and Natta,[10] demonstrated the possibility of producing stereo-regular polymers from cycloalkenes using different catalyst systems and reaction conditions; some of their results are listed in Table 1.1.

Table 1.1. Cyclobutene Polymers Prepared Using Transition Metal Catalysts.[10]

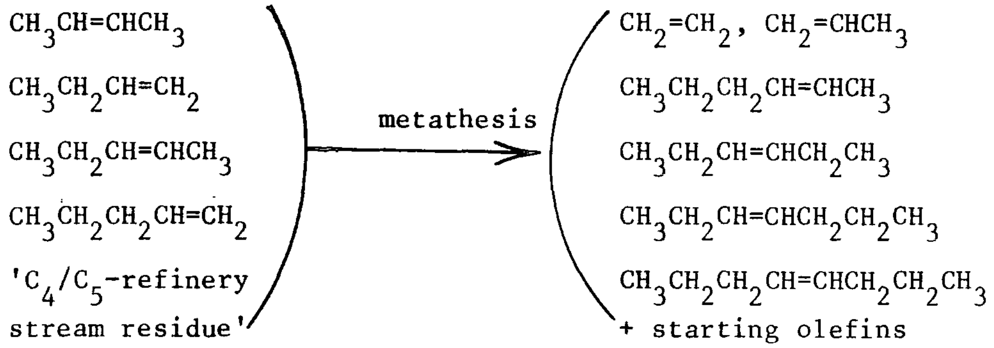


Catalyst System	Polymer Structure
$TiCl_4/Et_3Al$/n-heptane	Predominantly cis
$TiCl_4/R_3Al$/toluene	Predominantly trans
$MoCl_5/Et_3Al$/toluene	Predominantly cis
$RuCl_3/H_2O$	50/50 cis and trans
$RuCl_3$/EtOH	Trans

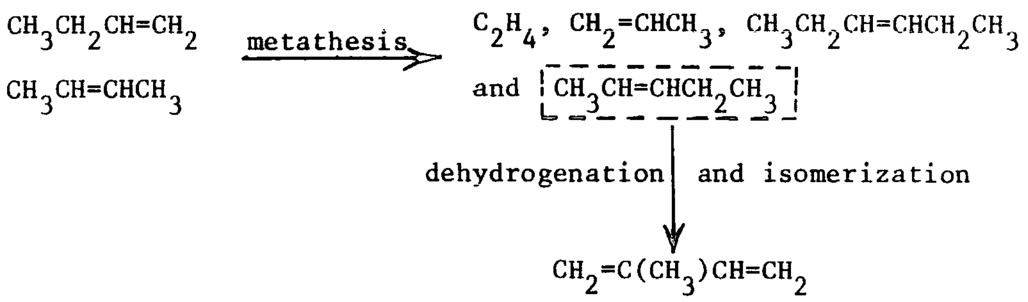
In 1964 the same authors,[11] investigated tungsten and molybdenum halides in combination with organoaluminium compounds as catalysts, cyclopentene was polymerized by ring-opening under mild conditions, again stereo-selectivity was demonstrated. In 1967 Calderon et al.[12,13] were the first to use the term 'olefin metathesis' for the overall result of the reaction in which they converted 2-pentene into a mixture containing at equilibrium a 25:50:25 molar ratio of 2-butene, 2-pentene and 3-hexene respectively; the catalyst system used was WCl_6-$EtAlCl_2$-EtOH. This result was very important in the evolution of the metathesis concept because it demonstrated that ring-opening reactions and the reactions of acyclic olefins belonged to the same class of reaction and were effected by similar catalysts. This observation was the beginning of a big increase in the number of papers concerned with metathesis reactions, and already many reviews of the expanding literature of the topic have been published.[14-33]

1.2. The Scope and Synthetic Applications of the Olefin Metathesis Reaction

The synthetic applications of olefin metathesis reactions are numerous. The high purity of the products obtained is one of the valuable characteristics of the reaction. The industrial application of this reaction was achieved comparatively rapidly, particularly in areas such as enhancing the market value of petrochemical streams; for example, by converting C_4 and C_5 alkenes into a mixture containing ethylene and propene together with higher molecular weight materials.[34,35]



Similarly metathesis of straight-chain butenes yields straight-chain pentenes which may be used as the starting material for the synthesis of isoprene.



These processes are examples of the use of metathesis to produce commodity chemicals and for some years the Phillips Petroleum Company operated their 'Triolefin process', although it was reported at the Fourth International Symposium on Olefin Metathesis in Belfast, September 1981, that the process is not currently operated because of the present economic situation.[36]

Some speciality polymers are made by the metathesis route for example poly(norbornene) is marketed under the trade name Norsorex and is used as the elastomer component of shock absorbers in some cars. Also, at the symposium referred to above, it was reported that Chemische Werke Hüls AG, are introducing a new speciality elastomer under the trade name Vestenamer 8012, this being a metathesis polymer of cyclooctene.[37]

Speciality chemicals are increasingly being made via processes involving metathesis. Two examples reported at the same conference illustrate this point.[36] Phillips Petroleum Company prepare neohexene from iso-butene by the route shown in Figure 1.3.:-

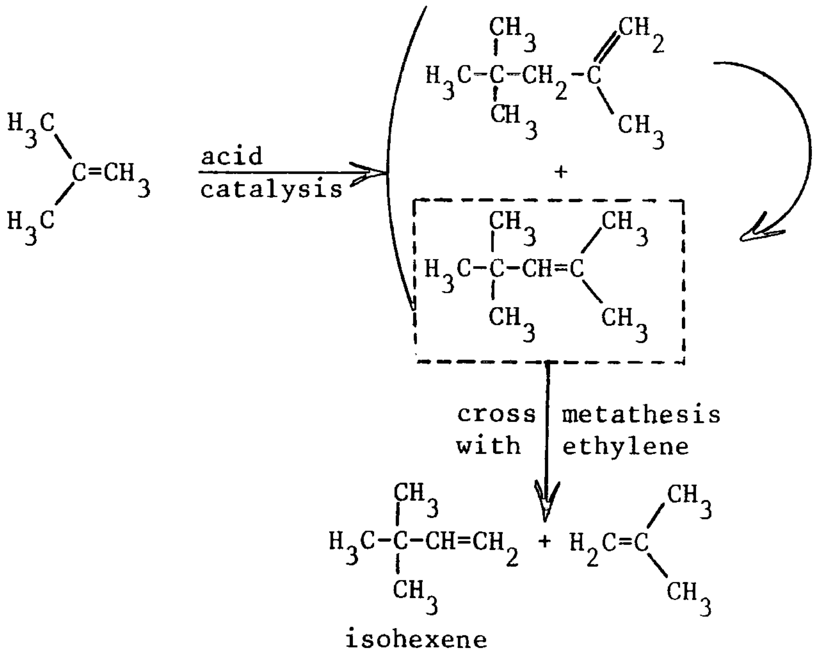


Figure 1.3.

Isohexene is reacted with cymene to make a commercially important cheap musk substitute as shown in Figure 1.4.:-

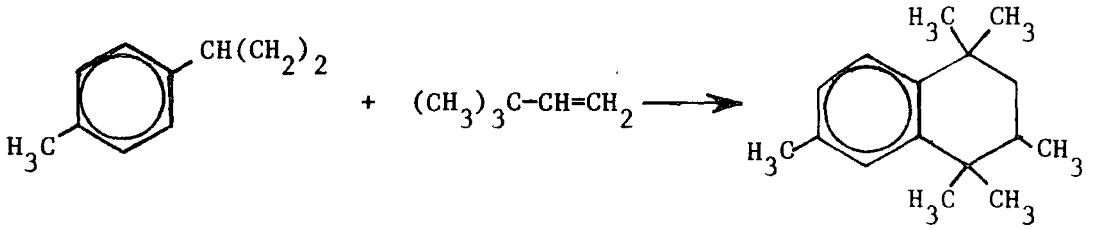
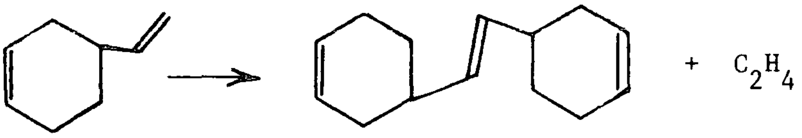


Figure 1.4.

4-Vinylcyclohexene undergoes metathesis to give a triene which after bromination gives a useful flame-retardant additive for plastics.



The syntheses shown above are examples of the great variety of processes which use metathesis to make useful products. In the field of polymer science metathesis is finding increasing application in the preparation of novel polymers and in the synthesis of telechelic compounds and bioactive substances.[38] Degradation via metathesis is also of interest since it gives a method for establishing the details of the structure of unsaturated polymers and particularly cross-linked networks of such polymers.[39-42]

1.3. Reactions of Acyclic Alkenes

The metathesis of many acyclic monoolefins and mixtures of olefins both linear and branched proceeds in accordance with the general reaction equation shown in Figure 1.5. where R represents hydrogen or hydrocarbon groups. The general relationship for acyclic linear olefins is given in Figure 1.6., where n is the carbon chain length and m is the position of the double bond in the chain. The subject has been reviewed in detail.[18,20-31]

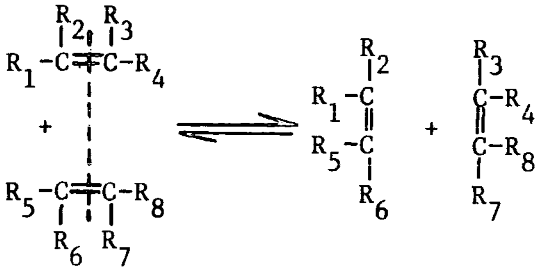


Figure 1.5.

$$2C_n^m \rightleftharpoons C_{2m}^m + C_{2(n-m)}^{n-m}$$

Figure 1.6.

Banks,[20] has classified the metathesis reactions of acyclic mono-olefins into three types:-

Type I. Those in which the reactant is a single olefin, 'self-metathesis', as shown in Figure 1.7. There are two possible cases;

$$2A \rightleftharpoons B + C$$

e.g. 2 1-Butene $\rightleftharpoons$ Ethylene + 3-Hexene Refs. 41,42

Figure 1.7.

firstly, an unsymmetrical olefin which will give a higher and a lower molecular weight product and secondly, a symmetrical olefin which on metathesis will regenerate itself (degenerate metathesis). The most widely studied example of this type is the metathesis of propylene,[1,43,44] which was converted to but-2-ene and ethylene by different catalysts under a variety of conditions.[45-47] This process was used industrially to produce polymerization grade ethylene and high purity but-2-ene, Figure 1.8.

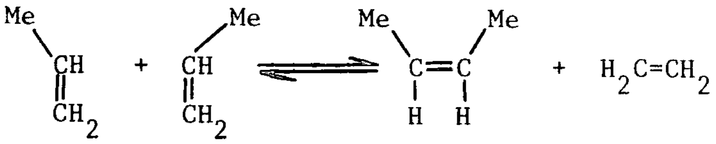


Figure 1.8.

Type II in Banks' classification covers cases where the reactants are double-bond isomers as shown in Figure 1.9. In this type the metathesis

$$A + A^1 \rightleftharpoons B + C$$

e.g. 1-Butene + 2-Butene $\rightleftharpoons$ Propylene + 2-Pentene

Figure 1.9.

reaction of a mixture of symmetrical and non-symmetrical double bond isomers will yield two olefins with longer and shorter chains as indicated above. It should be noted that in this case self metathesis (Type I) of the individual components may also occur and that if time for equilibration is allowed, a complex mixture will result.

Reactions of Type III are those where the reactants are different olefins as indicated in Figure 1.10. It will be recognized that the second

$$A + B \rightleftharpoons C + D \text{ (or to 2C)}$$

e.g. 1-Butene + 2-Pentene $\rightleftharpoons$ Propylene + 3-Hexene

Ethylene + 2-Butene $\rightleftharpoons$ 2(Propylene)

Figure 1.10.

example of Type III is simply the reverse of the Type I reaction shown in Figure 1.8., and thus Banks' classification is not concerned with fundamental chemical differences between the types but rather indicates the kind of process manipulation which is possible using metathesis and various olefin feedstocks.

1.3.a. Reactions of Functionalized Acyclooléfins

The metathesis of substituted olefins with functional groups is a relatively new area of the metathesis reaction, it has been reviewed in detail by Streck.[25] It has been claimed that substitution of acyclic mono-olefins with hydrocarbon groups does not destroy their ability to participate in metathesis; for example, styrene[48,49] was converted to ethylene and

1,2-diphenylethylene, Figure 1.11.

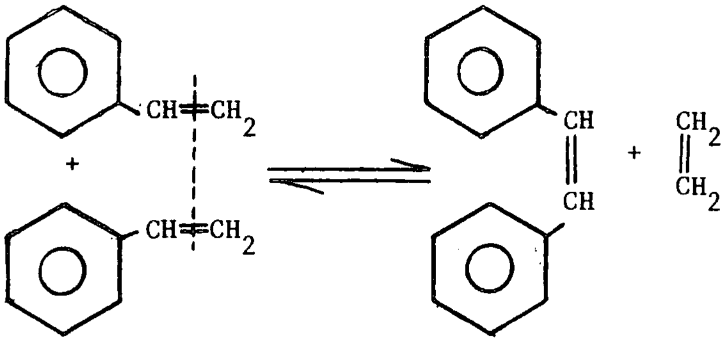


Figure 1.11.

Calderon,[17] reported that the effect of substitution on the ease of participation in olefin metathesis is given by the series shown in Figure 1.12., indicating steric control of reaction. Several examples of the metathesis

$$CH_2= \; > \; RCH_2CH= \; > \; R_2CHCH= \; > \; R_2C=$$

Figure 1.12.

of olefins having different functional groups have been reported.[50-54] In 1971, Foster,[55] reported the reaction of acrylonitrile with propene to give crotononitrile (cis and trans) and ethylene as shown in Figure 1.13.

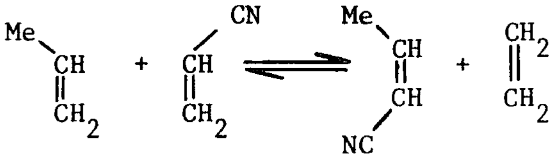


Figure 1.13.

One year later, it was demonstrated that halogen-substituted alkenes can participate in the metathesis reactions;[53] for example, 5-bromo-1-pentene[56] and 1-chloro-1,5-cyclooctadiene.[57] In 1972, Boelhouwer and co-workers,[50] reported that long-chain unsaturated fatty acid esters undergo metathesis; for example, methyl oleate gives octadec-9-ene and the dimethyl ester of 9-octadecene-1,18-dioic acid in the presence of the catalyst system $WCl_6/(CH_3)_4Sn$, as indicated in Figure 1.14.,[58] while the cross metathesis of

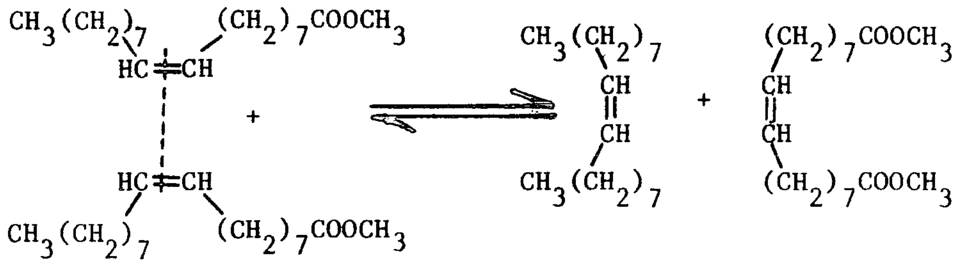


Figure 1.14.

methyl oleate with 3-hexene gives in addition to the products shown in Figure 1.14., 3-dodecene and the methyl ester of 9-dodecenoic acid. They also reported the metathesis of the terminally unsaturated ester shown in Figure 1.15. Boelhouwer and co-workers have extended this work to include

$$2CH_2{=}CH(CH_2)_8CO_2CH_3 \rightleftharpoons C_2H_4 + CH_3O_2C(CH_2)_8CH{=}CH{-}(CH_2)_8CO_2CH_3$$

Figure 1.15.

poly unsaturated fatty acid esters and the topic has proved of interest to many workers.[59-63] Nakamura and co-workers[64,65] have investigated the metathesis of acyclic olefins bearing various function groups such as esters, nitriles, ketones, amides and oxysilanes, and other workers have examined ethers,[50,66] and amines.[67] Ast and co-workers,[68] reported the olefin metathesis of unsaturated ethers using homogeneous catalyst systems. They metathesised 1-pentenylbutyl-ether as shown in Figure 1.16. They also examined the influence of the ether oxygen on the reactivity of the

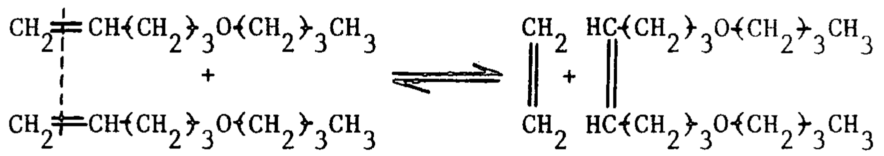


Figure 1.16.

double bond and they concluded that the minimum number of methylene groups between ether and double bond required for reaction is two. Recently Varagnat et al.,[53] also discussed the factors which govern the metathesis of functionalised olefins of the type shown below, where ψ represents the functional group and n the distance between the double bond and the

$$R\text{-}CH{=}CH\text{-}(CH_2)_n\text{-}\psi$$

functional group.

The possibility of carrying out metathesis reaction on functionalized olefins greatly increases the potential value of the reaction in organic synthesis. For example, the diester resulting from the metathesis of methyl oleate is a starting material for the synthesis of civetone which is a valuable perfume component, see Figure 1.17.

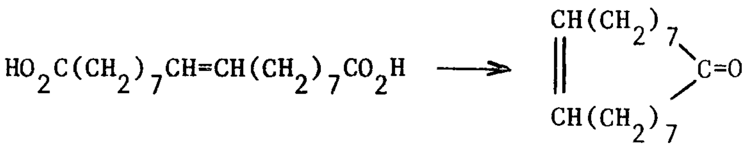


Figure 1.17.

Bioactive substances such as insect pheromones have also been synthesised by metathesis of appropriate compounds as shown below; Figure 1.18.[69] The cis-9-tricosene formed in this is the sex attractant of the common house fly.

1. $CH_2{=}CH(CH_2)_7CH_3 + CH_2{=}CH(CH_2)_{12}CH_3 \rightleftharpoons CH_3(CH_2)_7CH{=}CH(CH_2)_{12}CH_3 + C_2H_4$
2. $CH_3CH{=}CH(CH_2)_{12}CH_3 + CH_3(CH_2)_7CH{=}CH(CH_2)_7CH_3 \rightleftharpoons CH_3CH{=}CH(CH_2)_7CH_3 + CH_3(CH_2)_{12}CH{=}CH(CH_2)_7CH_3$

Figure 1.18.

It can be expected that this reaction will find increasing use in synthetic chemistry.

1.4. Reactions of Acyclic Polyenes

Metathesis of acyclic alkadienes can proceed via intra- or inter-molecular processes to yield cycloalkenes or acyclic polyenes respectively, Figure 1.19.[39,69] The inter-molecular process does not change the number of molecules in the resulting product but redistributes the molecular weights, while the intramolecular process increases the number of molecules with formation of a cyclic polyene. The predominating reaction being governed by

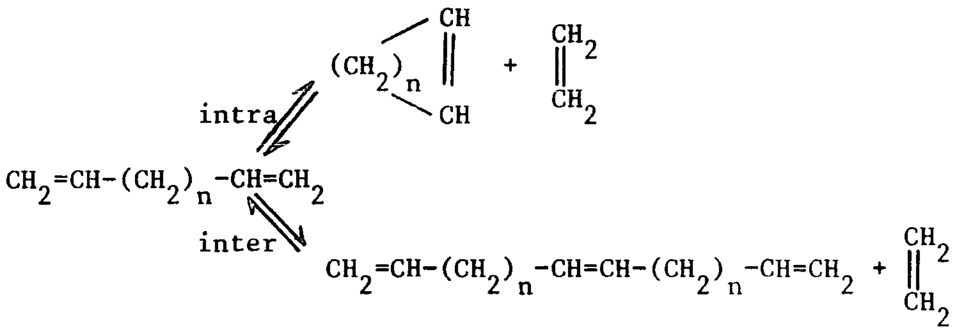


Figure 1.19.

the relative stabilities of the ring and chain products, an example of an intermolecular pathway is the conversion of 1,5-hexadiene into 1,5,9-decatriene and ethylene,[27] as shown in Figure 1.20. and an example of an intra-

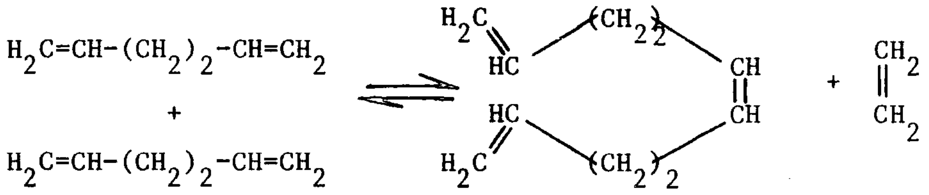


Figure 1.20.

molecular process,[69,70] when octa-1,7-diene is converted exclusively to cyclohexene and ethylene as shown in Figure 1.21. When removing ethylene by reduced pressure, cyclohexene was formed in 99% yield.[48]

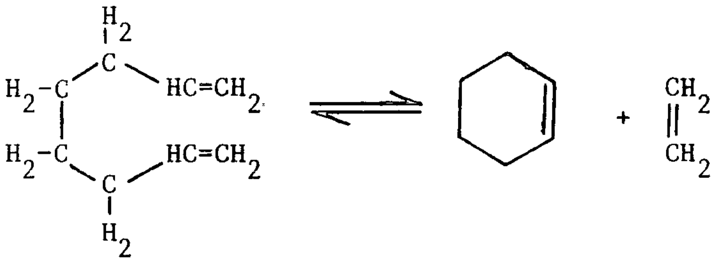


Figure 1.21.

1.5. Reactions of Cyclic and Acyclic Olefins

In 1966, Ray and Crain,[71] reported the reaction between a cyclo olefin and an acyclic olefin in the presence of supported MoO_3/CoO catalyst, this leads to ring cleavage and formation of a diene. Many compounds have been synthesised using this route.[72,73] α,ω-Dienes will be the only products when the reaction involves ethylene as the acyclic alkene, and some examples of this process are shown in Figure 1.22.[69,74] The reaction products will be

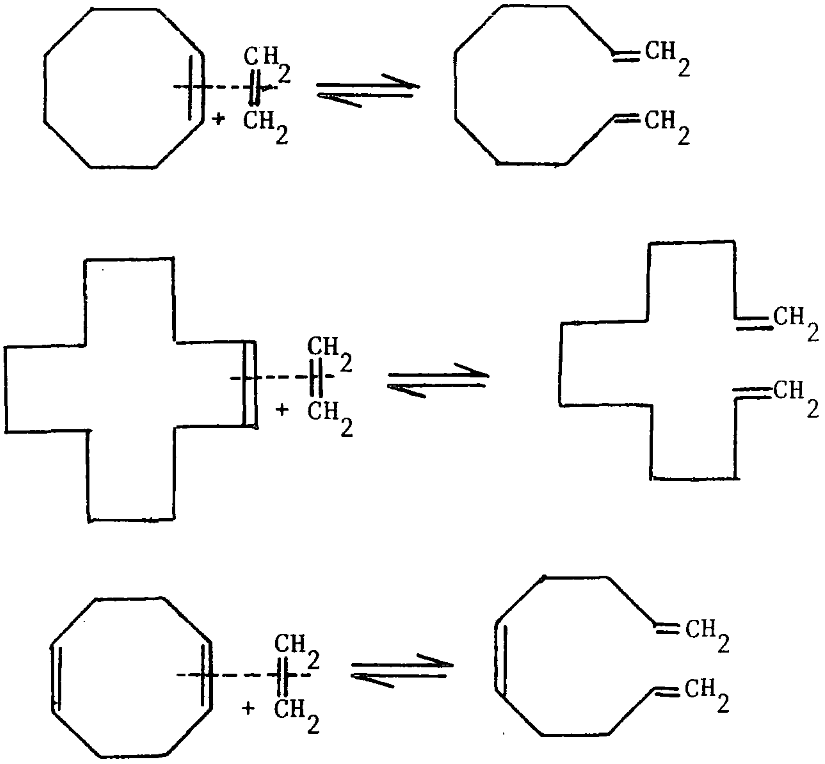


Figure 1.22.

complex when the acyclic olefin is an unsymmetrical internal olefin. Herisson and Chauvin,[75] reported the cross-metathesis reaction of cyclopentene with 2-pentene in the presence of the catalyst systems $WOCl_4/Sn(C_4H_9)_4$ or $WOCl_4/(C_2H_5)_2AlCl$, they observed three homologous series of polyenes symmetric, unsymmetric and symmetric in 1:2:1 distribution as shown in Figure 1.23.

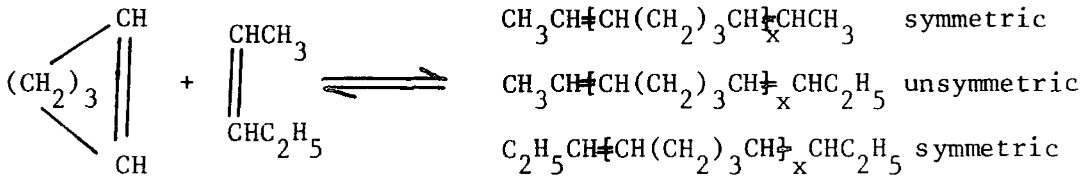


Figure 1.23.

The cross-metathesis of cyclopentene and 1-pentene was also reported to give three polyenes, two symmetric and one unsymmetric. It was found that in this case the symmetric polyenes constitute less than 5% of the total products as shown in Figure 1.24.

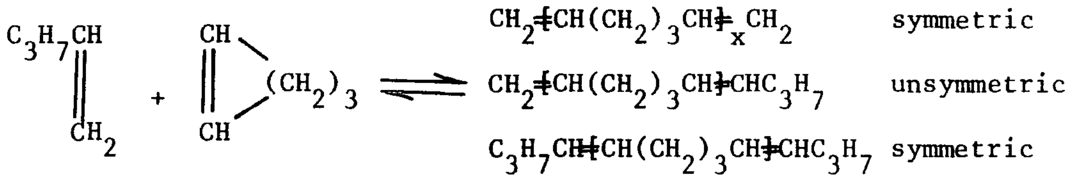


Figure 1.24.

The metathesis reaction of a mixture of cyclic dienes and acyclic alkenes is a very useful route for the preparation of the open-chain polyenes, furthermore, Pinazzi and Rey,[76,77] were able to control the position of the double bonds of the products by careful choice of reactants. They prepared diene in 70% yield by reacting 1,5-cyclooctadiene with 4-octene in the presence of metathesis catalyst as shown in Figure 1.25. The synthesis of triene can proceed via the cross-metathesis reaction of a cyclic diene with an acyclic diene,[67] as example, the preparation of 1,5,9-decatriene as shown in Figure 1.26.

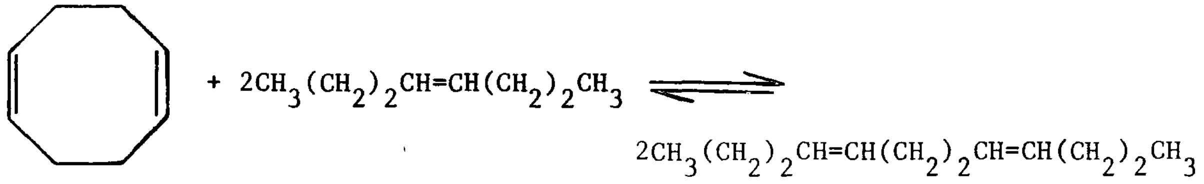


Figure 1.25.

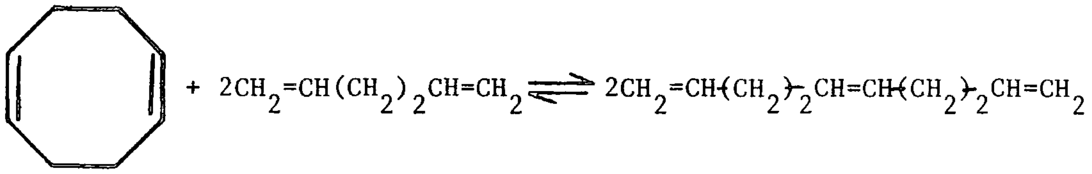


Figure 1.26.

In 1976, this reaction was used to prepare bisalkenylcycloalkenes, for example, norbornene reacts with 2-butene to yield 1,3-dipropenylcyclopentane,[74,78] as shown in Figure 1.27.

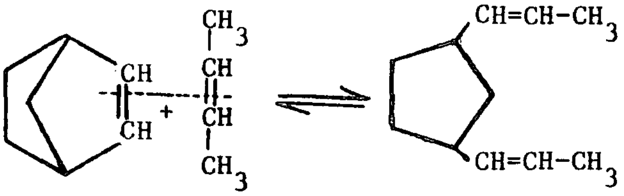


Figure 1.27.

1.6. Reactions of Alkynes

In 1968, Pennella et al.[79] reported the first example of the metathesis of a linear alkyne when they converted 2-pentyne into a mixture of 2-butyne and 3-hexyne using heterogeneous catalyst based on tungsten oxide on silica. A few years later the metathesis of many linear alkyns such as propyne, 1-pentyne, 2-pentyne, 2-hexyne and 3-hexyne was reported using heterogeneous catalyst systems.[79-81] Homogeneous catalysts for this process were reported for the first time by Höcker and Müsch who polymerized 1-hexyne to cyclic trimers (benzene derivatives) and linear polymer.[82] It was found that both terminal and internal alkynes undergo the metathesis reaction, but the reactions of terminal acetylenes were less useful than the internal because the cyclo trimerization to benzene derivatives can become the major reaction. Recently Hall and co-workers,[83] reported new catalyst systems derived from niobium and tantalum which polymerize both internal and terminal acetylenes, previously catalyst systems for the polymerization of internal alkyenes were uncommon.[84] Cycloalkynes[85] are reported to undergo ring-opening polymerization, for example, oligomerization of cyclodecyne using the catalyst system $WCl_6/EtAlCl_2$-EtOH leads to a series of cyclic compounds of the formula $(C_{10}H_{16})_n$ up to hexamer.

Substituted acetylenes have been reported to undergo polymerization in the presence of metathesis catalysts. Masuda,[86,87] reported that WCl_6 and $MoCl_5$ were catalysts for the polymerization of phenylacetylenes at ambient temperature, Figure 1.28. They also used the catalyst system

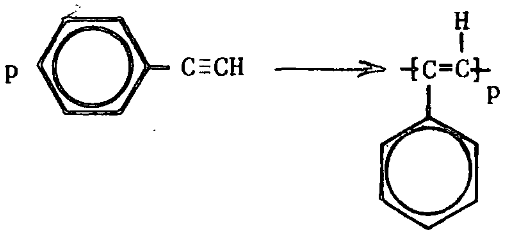


Figure 1.28.

WCl_6/Ph_4Sn to polymerize several terminal and internal acetylenes to linear polyconjugated compounds.[88,89] Farona, reported that polymerization of acetylenes catalyzed by arene group VIB carbonyls $[ArM(CO)_3]$ gave high molecular weight polymers.[90,91]

1.7. Reaction of Cycloolefins

Metathesis of cyclic olefins would be expected to give macrocyclic polyenes or unsaturated polymers as shown in Figure 1.29., both these processes can be carried out by appropriate choice of reactants, catalysts,

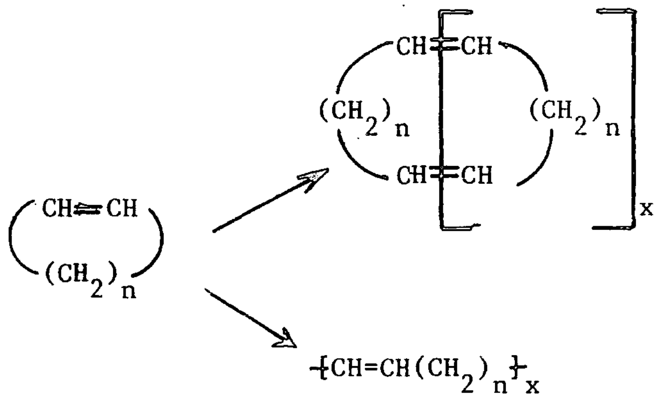


Figure 1.29.

and conditions. Ring opening polymerization of cycloalkenes is a very thoroughly studied topic, and as mentioned earlier some polymers are produced commercially by this route.

It is possible to prepare polymers in which the double bond is largely cis[92-94] or trans[95,96] by proper choice of catalyst (see Table 1.1.), reaction time and reaction temperature.[97] Cycloolefins from C_4 to C_{12}, with the exception of cyclohexene[17] undergo ring opening polymerization to yield polyalkenamers; these polymers have properties ranging from amorphous elastomers to crystalline thermoplastics. For example, cis-poly(pentylene) is a good low temperature elastomer, and trans-poly(pentylene) is a good substitute for natural rubber for the car tyre industry. It has been stated that if there was a requirement for increased capacity for synthetic rubber any new production unit would be designed to make polypentanamer,[98] since as a raw material cyclopentene is much cheaper than isoprene or butadiene.

The macrocyclization of small and medium sized cycloalkenes is favoured by conducting the reaction at high dilution.[99] This technique was used to prepare cyclohexadeca-1,9-diene from cyclooctene, the diene being oxidized to a monoketone with a musk-like odour, Figure 1.30.

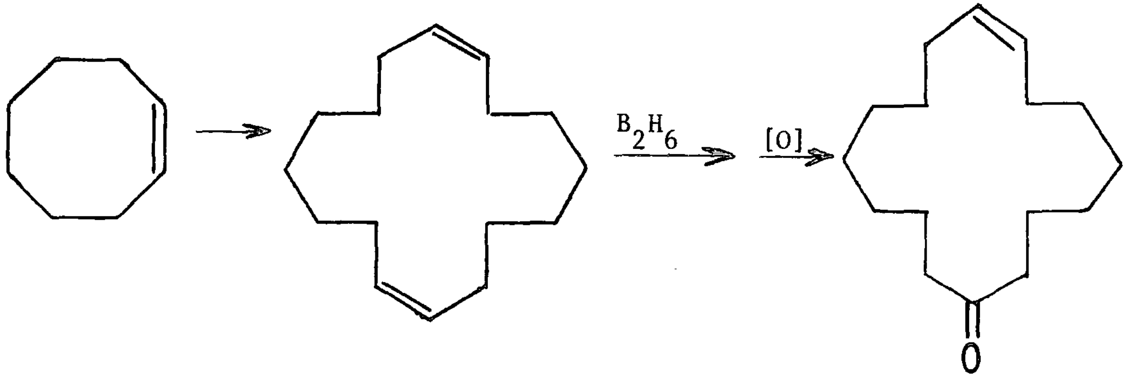


Figure 1.30.

A large number of cycloolefins and cycloolefin derivatives have been polymerized; but there are some notable exceptions, in particular, cyclopropenes and cyclohexenes. The variety of polymers that can be prepared from cycloalkenes is illustrated by the case of cyclobutene, which can give polymers by ring-opening or by conventional addition polymerization as shown in Figure 1.31.; all four structures shown have been isolated and characterized.[16,100,101]

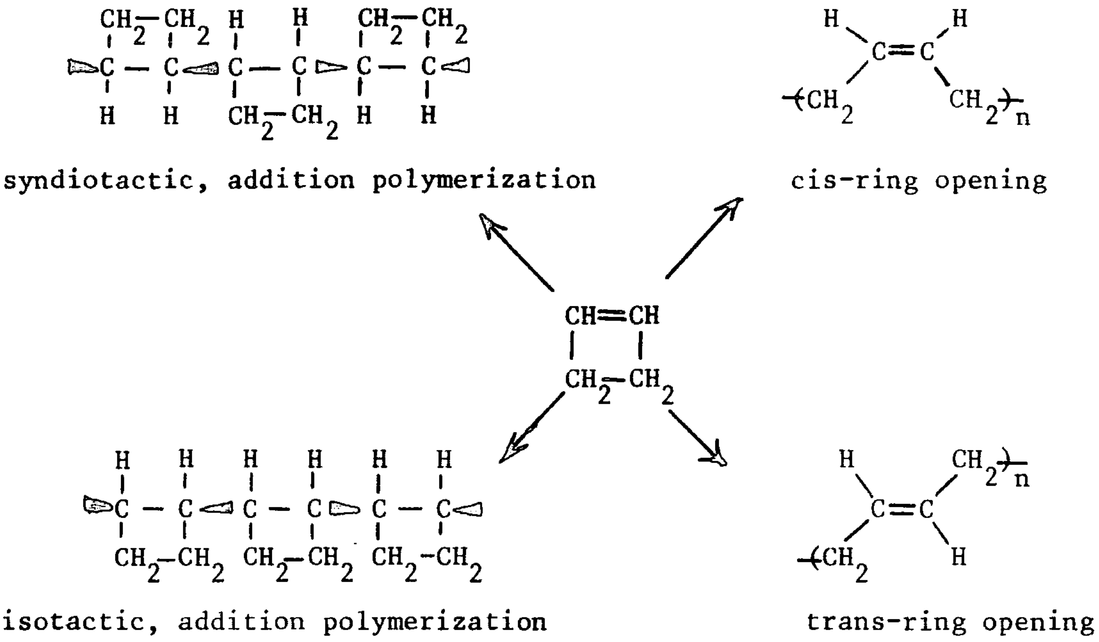


Figure 1.31.

Bicyclic olefins are also readily polymerized, for example norbornene, and it is interesting that bicyclo[2,2,2]oct-2-ene has been claimed to be polymerizable by metathesis catalysts.[102] If confirmed, this would be an example of ring-opening of a six membered ring and it has been suggested that the polymerizability results from the strain energy in the cyclohexene unit held in the boat conformation in the monomer. However, attempts in this Department to ring-open polymerize related bicyclo[2,2,2]oct-2-enes and -octa-2,5-dienes have all met with failure.[103]

1.7.a. Reaction of Functionalized Cycloolefins

Numerous functionalized polymers have been prepared by the ring-opening polymerization of substituted cycloolefins.[100, 101, 104-106] Monomers containing ester, ether, carboxyl, hydroxyl, halogen, and imide groups have been successfully polymerized. A particularly extensively investigated set of monomers being the substituted norbornenes, Figure 1.32., where the substituents are ester,[105,107] hydroxy,[105] chlorine,[104b] imide[107a] or

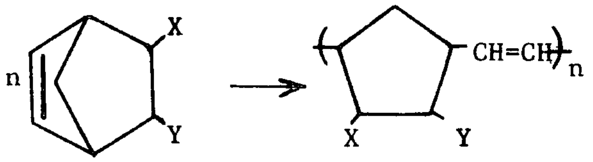


Figure 1.32.

alkoxy[107b] units. It was also shown that the presence of a hydrocarbon substituent at the allylic position of a cycloalkene did not effect the polymerizability, for example 3-methylcyclopentene is readily polymerized.[93] The metathesis of chlorinated monomers[61] and monomers containing other electron withdrawing substituents has also been reported.[63] The highly chlorinated cycloalkenes shown below, Figure 1.33. may be homopolymerized or copolymerized with cyclopentene.[108] Recently Feast and Wilson[109] reported the successful ring opening polymerization of the fluorinated bicyclo[2.2.1]-hept-2-enes and bicyclo[2.2.1]hepta-2,5-dienes shown in Figure 1.34.

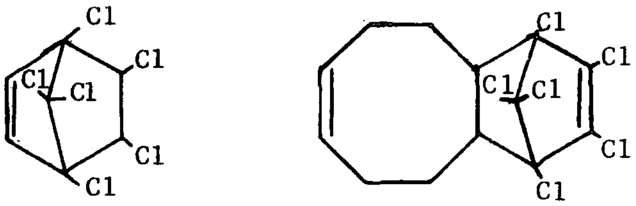


Figure 1.33.

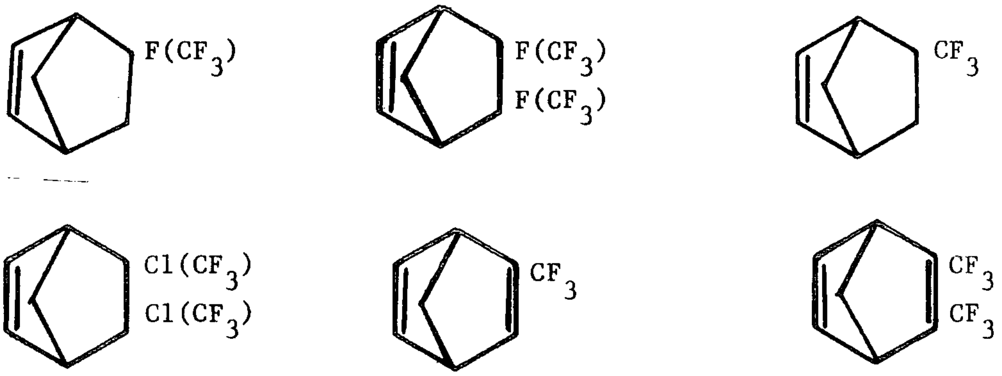


Figure 1.34.

High molecular weight unsaturated polyesters were prepared by the ring-opening polymerization of lactones, as shown in Figure 1.35.[110]

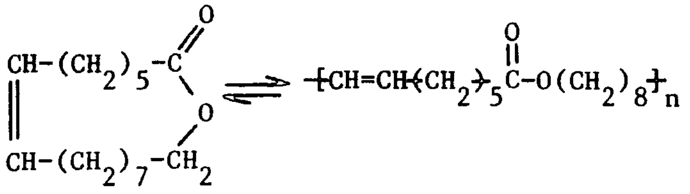


Figure 1.35.

Monomers containing cyclopropane groups[44b] were also found to undergo ring-opening polymerization and Figure 1.36. gives two examples.

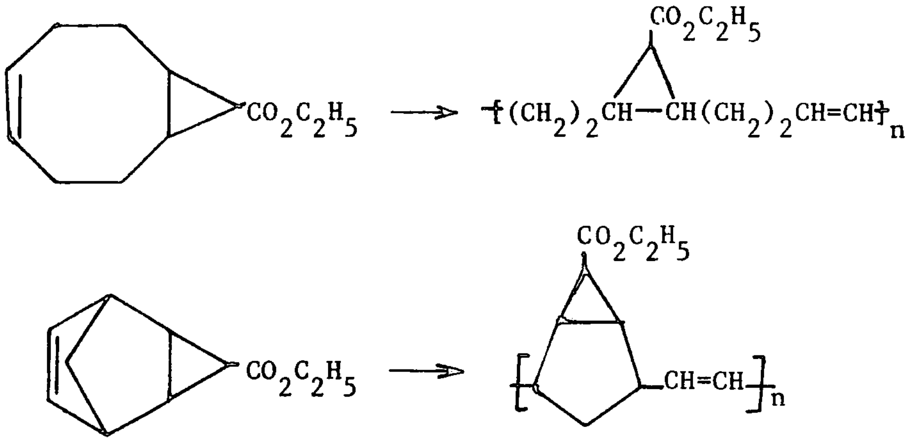


Figure 1.36.

Perfectly alternating copolymers were successfully synthesised by ring-opening polymerization of some substituted cyclic dienes,[12,111] the polymerization occurred exclusively through the unsubstituted double bond and two examples are shown in Figure 1.37. The range of substituted

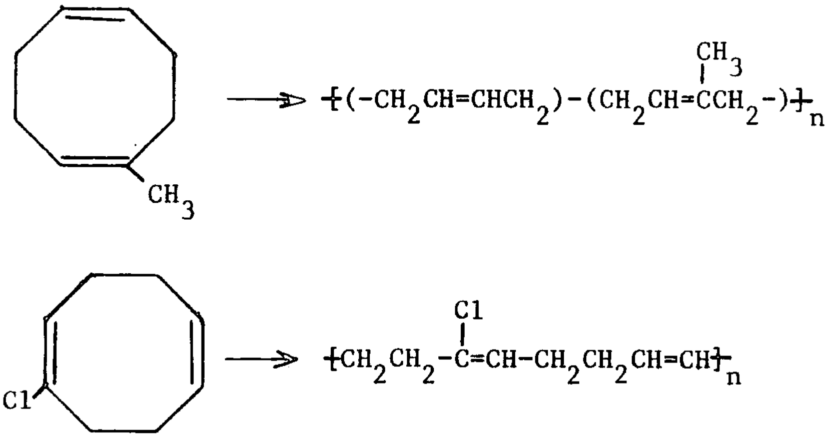


Figure 1.37.

systems which undergo ring opening polymerization is continually being expanded, for example, Streck[37] recently reported new silicon and tin containing polymers prepared from the monomers shown in Figure 1.38., the products derived having useful properties as adhesion promotors and biocides respectively.

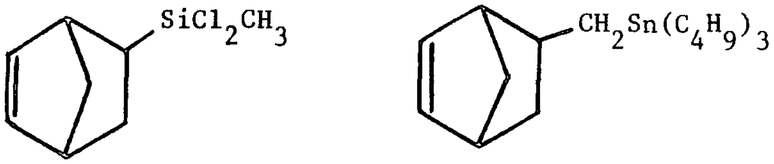


Figure 1.38.

1.8. Reaction of Aryl-Substituted Alkenes and Cycloalkenes

There are relatively few examples of the metathesis of aryl alkenes, some which were reported by Calderon[112] and Doyle[48] in 1970, are shown in Figure 1.39. It was believed that the aromatic system, which is capable of

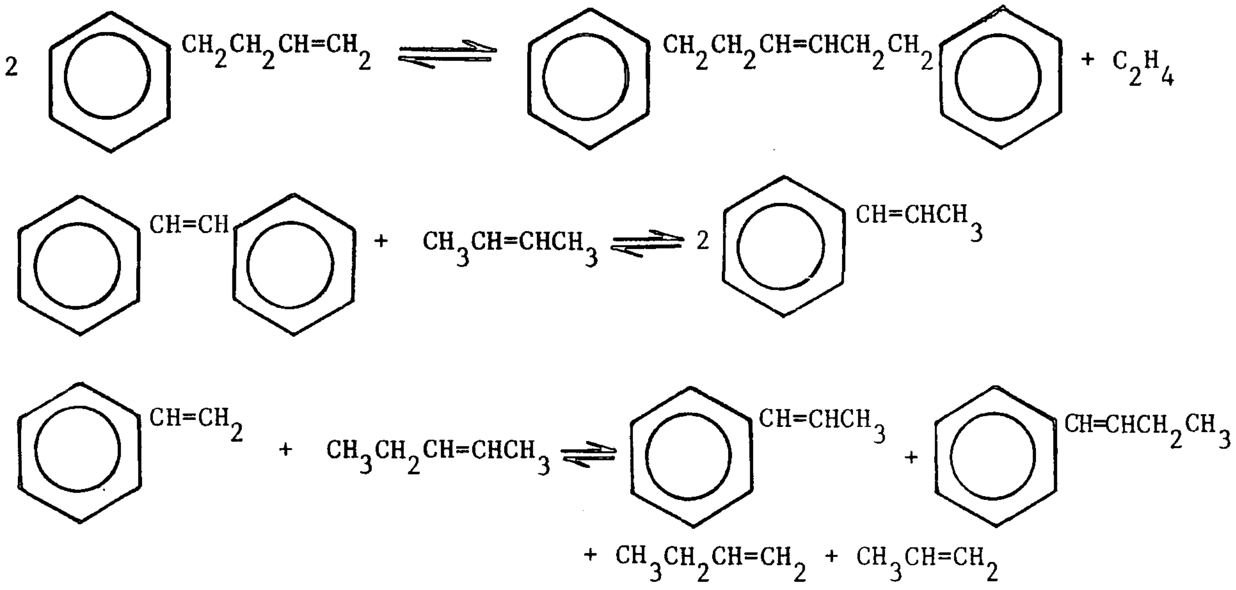


Figure 1.39.

co-ordinating to low-valent transition metals such as W and Mo, could retard the rate of reaction or deactivate particular catalyst systems.[21]

In 1976, Basset and co-workers,[113] investigated the kinetics of metathesis reactions of ω-aryl alkenes. They examined the effects of the structure of the alkenes on the reaction paying attention to two points; firstly, the distance between the aromatic unit and the double bond, and secondly the effect of substituents either on the double bond or on the aromatic ring. They metathesised system I to give products II and III, as shown in Figure 1.40. They reported that if the chain length varied between n = 1 and n = 6 the reaction occurred via metathesis to give ω,ω-diaryl alkenes and ethylene. Methyl substituents on the double bond could be tolerated but metathesis does not occur with tetra- or tri-substituted double bonds. Electron-donor or acceptor substituents on the aromatic ring were examined and it was found that the presence of para-methoxy group inhibits metathesis while halogens, methyl or t-butyl groups do not significantly effect the reaction as compared with the unsubstituted case. In addition to the examples listed here, metathesis of other aryl alkenes were already mentioned earlier, see Figures 1.11. and 1.28. Recently, some aryl substituted alkenes were subject to degradation by olefin metathesis reaction when Hummel and co-workers,[114] reported that 1,4-polybutadienes substituted with aryl groups were degraded with 4-octene using typical metathesis catalysts. The basic reactions and products are shown in Figure 1.41.

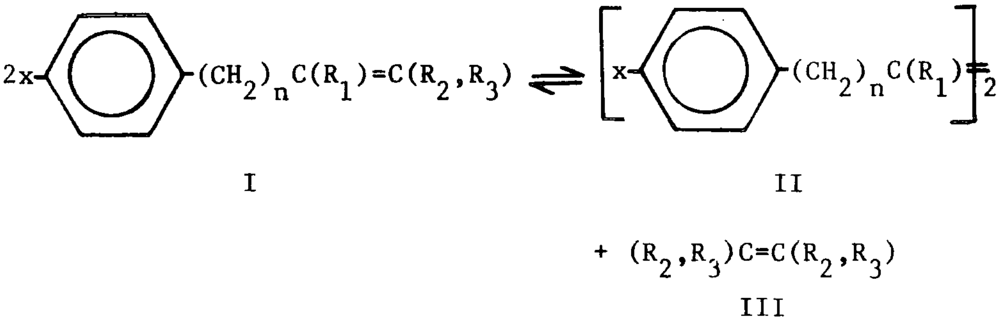
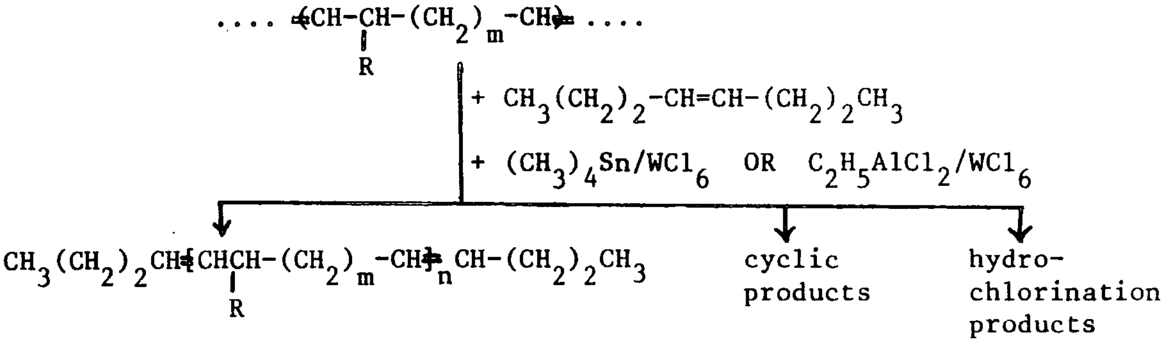


Figure 1.40.



(R = aryl group and m = 1 or 2 and n $\geqslant$ 1)

Figure 1.41.

To date, there is only one example in the literature of the metathesis of aryl substituted cycloalkenes. Calderon ring open polymerized 3-phenylcyclooctene,[12] as shown in Figure 1.42.

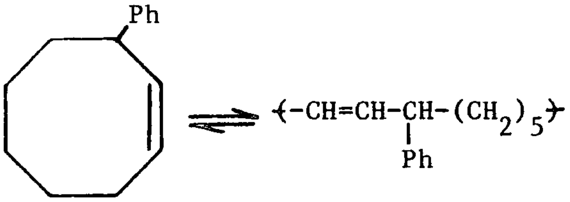
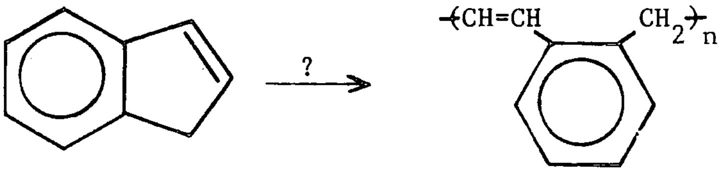


Figure 1.42.

We started studying the polymerizability of aryl cycloalkenes by examining the behaviour of indene as a potential monomer for ring-opening polymerization.[115] Indene maybe regarded as a 3,4-substituted cyclopentene



and although in general substituents at the α- or β-position with respect to the double bond inhibit metathesis polymerization, there are a number of exceptions to this generalization (see above). In the event, almost all attempts to ring open polymerize indene led only to the formation of conventional poly(indene), that is the product of olefin polymerization rather than ring opening. Some experiments using a catalyst derived from

WCl_6:Ph_4Sn (1:2) gave products which apparently had a considerable degree of vinylic unsaturation as indicated by bromine addition. The technique used for this analysis[116] was standardized using indane, indene and cyclohexene and checked against well characterized unsaturated polymers (Table 1.2.). The first four entries in the Table indicate a reasonable degree of reliability for the method adopted and it is clear that poly(indenes) 5 and 6 reacted with bromine to a greater extent than would be expected for conventional poly(indene). However, the infrared and ^{13}C n.m.r. spectra of these materials were not significantly different from those of conventional poly(indene). It may be that indene does ring open under the influence of metathesis catalysts to a limited extent but unfortunately the data we were able to obtain do not provide conclusive proof. A similar examination of the reaction of acenaphthylene with typical metathesis catalysts gave exclusively the product of vinyl polymerization as shown in Figure 1.43.

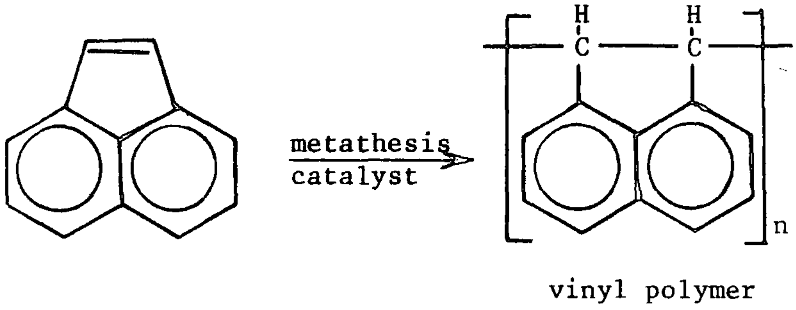
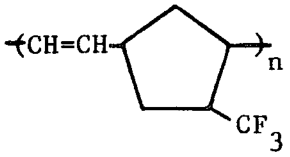


Figure 1.43.

In view of the, at best, ambiguous results described above it was decided to investigate other aryl cycloalkenes in which the aryl and olefinic units were not directly conjugated. Benzonorbornadiene was the first monomer examined, it was successfully polymerized via ring opening to give a polymer which is susceptible to oxidation,[115] Figure 1.44.

Table 1.2. Bromination of Unsaturated Polymers

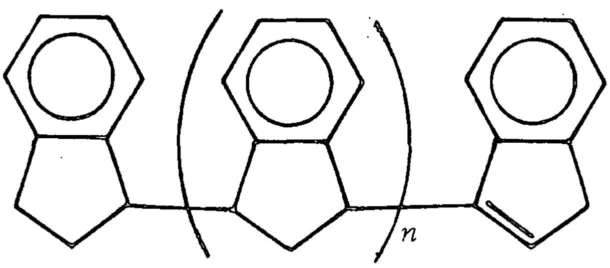
Polymer	% Reaction ($\gt C{=}C\lt + Br_2 \rightarrow Br-\overset{\vert}{\underset{\vert}{C}}-\overset{\vert}{\underset{\vert}{C}}-Br$)	
	Observed	Calculated[a]
1. Poly(butadiene)	92	100[b]
2. Styrene/butadiene copolymer (23 mole % styrene)	67	63.5
3. 	103	100
4. Poly(indene) [thermal, d.p. 5][c]	22	20[d]
5. Poly(indene) [WCl_6:Ph_4Sn, d.p. 73][c]	26	1.4[d]
6. Poly(indene) [" " , d.p. 12][c]	20	8[d]

[a] *Extent of reaction calculated on the assumption that one double bond is equivalent to one molecule of bromine.*

[b] *Sample claimed to be random cis/trans-1,4-poly(butadiene).*

[c] *D.p. values by g.p.c. using standard poly(styrene) as calibrant.*

[d] *Extent of reaction calculated assuming the structure*



i.e. one double bond per chain, giving a calculated % reaction = $^{100}/\mathrm{d.p.}$

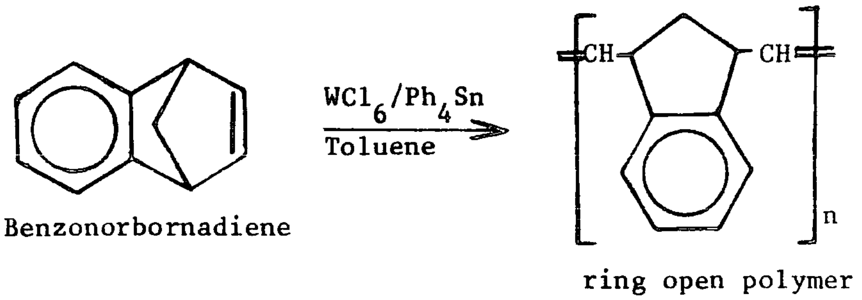


Figure 1.44.

In view of this successful result, it was decided to continue this project by examining the polymerizability of other aryl substituted norbornene derivatives this work is discussed in Chapters III and IV.

1.9. Olefin Metathesis Catalyst Systems

A wide variety of materials are claimed to be active metathesis catalysts. Metathesis catalysts promote two main types of reaction namely ring-opening polymerization of cyclo-olefins and disproportionation reactions of acyclic olefins, although governed by a common mechanism, these reactions differ in many chemical, kinetic and thermodynamic aspects and this causes different catalyst efficiencies, operating conditions and applicabilities. Almost all the systems contain a transition and a non-transition metal component. The majority of catalyst systems are derived from the group VIA metals, molybdenum and tungsten, the non-transition metal component is more varied but is often a group IIIb or IVb element, particularly aluminium and tin. The nature of the non-transition metal component has a significant effect on catalytic activity, for example, the relative effectiveness of the catalysts obtained from tungsten hexachloride and several alkyl-lithium reagents was found to be in the order n-butyl > s-butyl > t-butyl.[117] Catalysts maybe homogeneous or heterogeneous and the generalizations above apply to both groups, for example co-catalysts can promote the activity of both homogeneous and heterogeneous catalysts.[118]

The most efficient catalysts for ring-opening polymerizations of cycloolefins are composed of halides, oxyhalides or alkoxyhalides of tungsten and organometallic derivatives of aluminium and tin. A second group of metals comprising molybdenum, rhenium and tantalum also give quite efficient catalysts for ring-opening polymerizations. A third group of metals comprising titanium, zirconium, vanadium, niobium and some lanthanides have lower catalytic activity and promote metathesis only in some special cases. A very great number of catalysts have been described, particularly in the patent literature and reviewed.[17,23,31,50,51,64,119-125]

1.9.a. Heterogeneous catalysts

It is well known that the solid heterogeneous catalysts for olefin metathesis reaction comprise of two main components: high surface-area material which is a support such as alumina or silica on which is deposited a transition metal promoter such as oxides, sulphides or the carbonyls of the metals. Usually the third component is introduced to reduce the poisoning of the catalyst and increase the reactivity or to reduce side reactions such as double bond migration.[126] The catalysts derived from oxides and carbonyls of molybdenum, tungsten and rhenium have the greatest activity.[1,44a,127,128] Whilst the remainder of the promoters are less effective,[44b] sulphides of Mo and W provide poor catalysts,[129] but in special conditions MoS_2 alone is quite active.[130] The preparation of heterogeneous catalysts is carried out in many ways; for example, by dry mixing of the individual components by co-precipitation or impregnation of the supports with substances which decompose at high temperature to leave the active promoter. These catalysts can be activated by passing a stream of inert gas or dry air over the catalyst at elevated temperatures or by heating under vacuum. The catalysts are sensitive to poisoning by polar compounds.[131] Banks,[20] Bailey[18] and Calderon[31] in recent reviews have given details concerning analysis, preparation, activation and regeneration procedures.

1.9.b. Homogeneous Catalysts

Homogeneous catalyst systems generally consist of two components, a transition metal compound of tungsten, molybdenum, rhenium or tantalum and a co-catalyst which is usually an organometallic compound from Groups I to IV, in some cases addition of a third component which can be an oxygenated compound such as an alcohol, an ether, a peroxide, or water improves the effectiveness of the catalyst system.[2a]

In 1967 Calderon and Scott[13] were the first to describe homogeneous catalysts for olefin metathesis. Tungsten compounds give the most efficient catalysts for ring-opening polymerization of cycloolefins, and a large number of catalysts are derived from WCl_6 combined with suitable co-catalyst. Reactions are usually conducted in the liquid phase in neat monomer, or in a solvent. The area has been reviewed by Dall'Asta[14] and Hughes.[21] Recent developments include photochemically activated catalysts such as $W(CO)_6$,[132] WCl_6[133] and $TiCl_4$[124] and the observation that metallocarbenes such as $(CO)_5W{=}CPh_2$ are active catalysts for the ring-opening polymerization of cycloalkenes.[134-136]

1.10. The Olefin Metathesis Mechanism

The mechanism of the metathesis reaction has been the subject of many investigations and much discussion. Opinions have changed as new evidence was established, and consequently the literature is somewhat difficult to follow since different workers changed their opinions at different times. In discussing the mechanism there are two basic questions to answer:-

(i) What is the overall result of the reaction? That is, which bonds are broken and made during reaction?

(ii) What is the detailed mechanistic pathway by which the overall result is obtained?

1.10.a. The Overall Result of Reaction

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

(i) A transalkylation scheme, which involves cleavage of a carbon-carbon single bond adjacent to the double bond as shown in Figure 1.45.

(a) In the case of acyclic alkenes

(b) In the case of cycloalkene

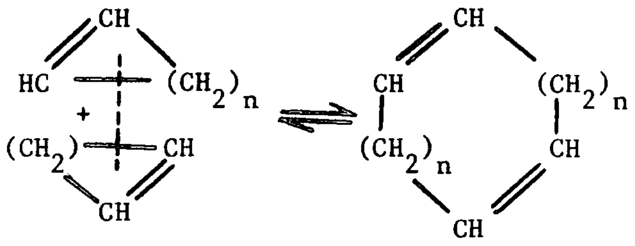
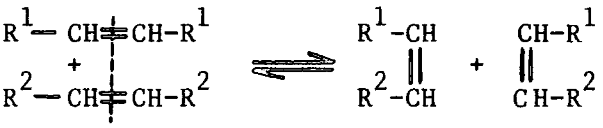


Figure 1.45.

(ii) A transalkylidenation scheme, which involves the cleavage of the double bond itself as shown in Figure 1.46.

(a) In the case of acyclic alkenes



(b) In the case of cycloalkenes

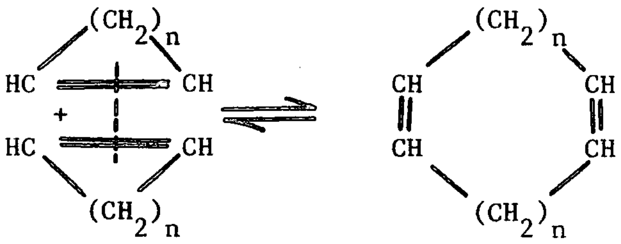
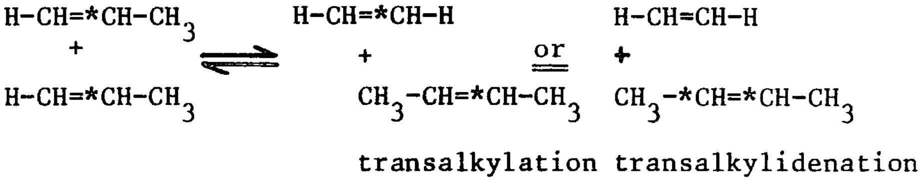


Figure 1.46.

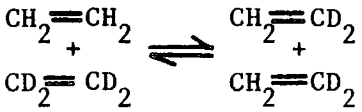
Isotopic labelling was employed to distinguish between these two schemes and the results have been reported by several workers.[137-139] They metathesised propene labelled with ^{14}C at C-2 and studied the label distribution in the products. If Scheme 1 is correct the label should be equally distributed between both products, but it was found that the radioactivity was located only in the butene and was twice as high as that of the starting propene. This result supported the transalkylidenation scheme, see Figure 1.47 below.



$$\begin{array}{c} \text{H-CH=*CH-CH}_3 \\ + \\ \text{H-CH=*CH-CH}_3 \end{array} \rightleftharpoons \begin{array}{c} \text{H-CH=*CH-H} \\ + \\ \text{CH}_3\text{-CH=*CH-CH}_3 \end{array} \;\underline{\underline{\text{or}}}\; \begin{array}{c} \text{H-CH=CH-H} \\ + \\ \text{CH}_3\text{-*CH=*CH-CH}_3 \end{array}$$

Figure 1.47.

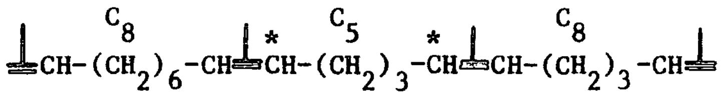
Further evidence supporting the transalkylidenation scheme was provided by the deuterium labelling experiments shown in Figure 1.48.[2a,2b,140]



$$\begin{array}{c} CH_2{=}CH_2 \\ + \\ CD_2{=}CD_2 \end{array} \rightleftharpoons \begin{array}{c} CH_2{=}CD_2 \\ + \\ CH_2{=}CD_2 \end{array}$$

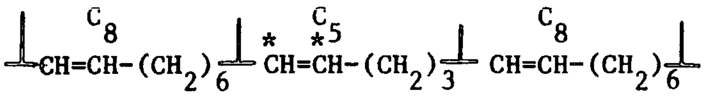
Figure 1.48.

Calderon[2a,b] first proposed the transalkylidenation scheme for the mechanism of ring-opening polymerization of cycloalkenes and ruled out Natta's[11] earlier proposal of transalkylation. Later, Dall'Asta and Motroni[97,141] provided direct experimental evidence that in the ring-opening polymerization of cycloalkenes the cleavage occurs at the double bond by copolymerization of cyclooctene and cyclopentene where the cyclopentene double bond was labelled with ^{14}C, the resulting polymeric units may be (3) or (4) depending on whether cleavage takes place at the double bond or at the carbon-carbon single bond adjacent to the double bond.



$$=\overset{C_8}{CH-(CH_2)_6-CH}=\overset{*\quad C_5\quad *}{CH-(CH_2)_3-CH}=\overset{C_8}{CH-(CH_2)_3-CH}=$$

(3) double bond cleavage



$$\overset{C_8}{CH=CH-(CH_2)_6}\;\overset{*\;\;*C_5}{CH=CH-(CH_2)_3}\;\overset{C_8}{CH=CH-(CH_2)_6}$$

(4) allylic bond cleavage

[* donotes ^{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 polymerization had proceeded via cleavage of the double bond.

1.10.b. The Detailed Mechanistic Pathway

The question of the detailed mechanistic pathway is much more complicated and difficult to establish definitely. Several mechanistic proposals have been put forward, and the area is still one of active discussion.

1.10.b.(i). The Intermediacy of a 'Quasi-Cyclobutane'

In 1967 Bradshaw[142] et al. proposed a mechanistic rationalization of olefin metathesis reaction based on the formation of a 'quasi-cyclobutane' intermediate, this results from two olefin molecules in the co-ordination sphere at the transition metal, the transition state being characterized by having all four carbons equally related to the metal, they applied their proposal to a linear alkene, shown in Figure 1.49. This proposal received quite widespread acceptance and was used by Calderon[2a,17] to rationalize ring-opening polymerization, the mechanism was assumed to proceed via formation of macrocyclic species as depicted in Figure 1.50. While this

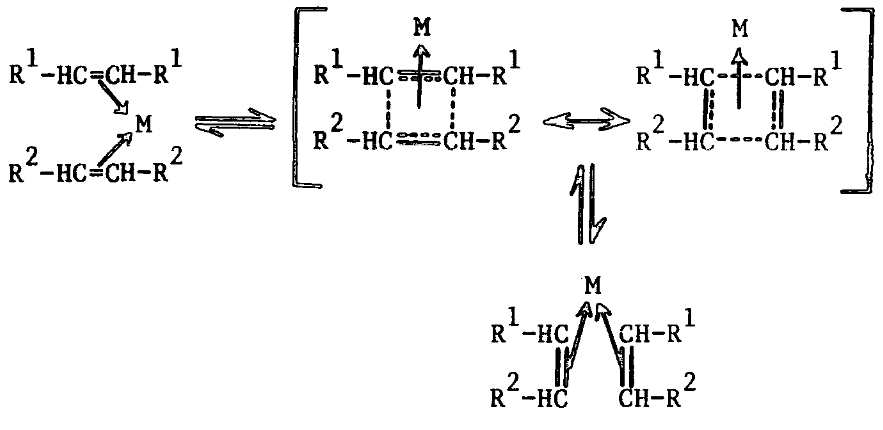


Figure 1.49.

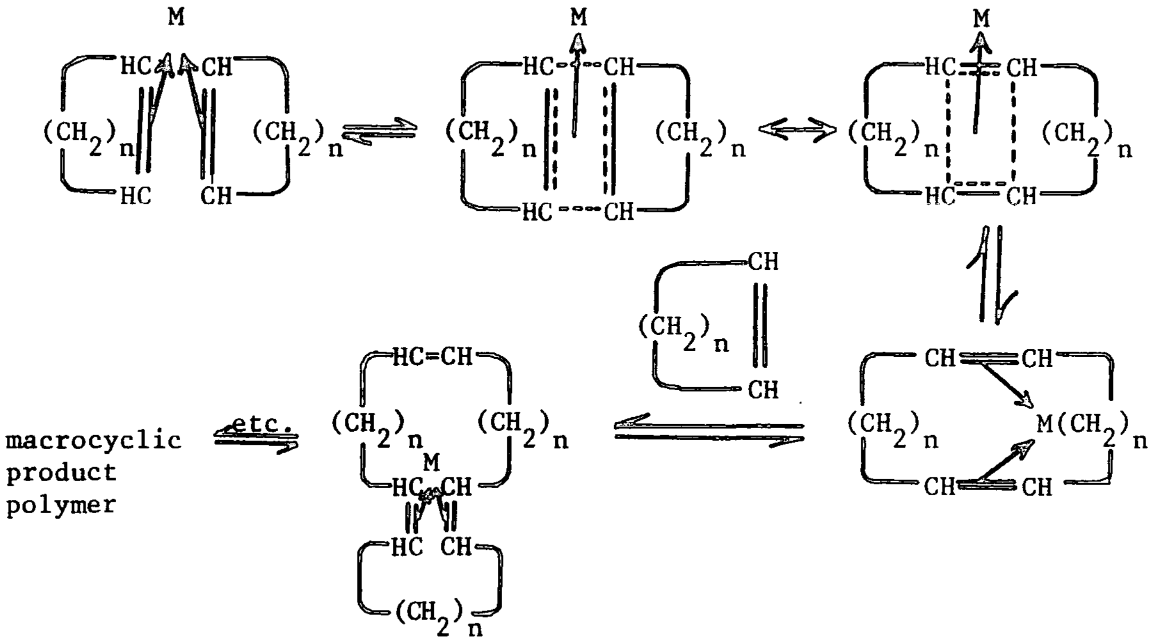


Figure 1.50.

mechanism accounts for a large amount of experimental observation, including isotopic labelling studies,[137-139] it has some weaknesses, for example, cyclobutanes might reasonably be expected to be found as by-products or at least to participate in metathesis reactions; and polyalkenamers might be expected to be cyclic molecules. In fact polyalkenamers frequently consist of a mixture of cyclic and linear molecules, this difficulty was relatively easily overcome by suggesting that the linear polymers arose via interaction of the growing macrocycles with an acyclic alkene, present as an impurity.[143] Alternatively chain termination of a co-ordinated growing polymer macrocycle could be achieved by the migration of the co-ordinated double bond, accompanied by decomplexation, giving rise to a linear macromolecule having two vinyl end groups, Figure 1.51.[21] On the other hand very little evidence for the involvement of cyclobutanes in metathesis has been published, the results of Gassman and Johnson,[144] being the most widely cited. They observed a diene to cyclobutane conversion when compound (7) was reacted with an accepted metathesis catalyst $PhWCl_3/AlCl_3$, and cyclobutane to diene conversions for compounds (9) and (11) reacting to give (10) and (12) respectively. These authors also reported that the bicyclic dienes were

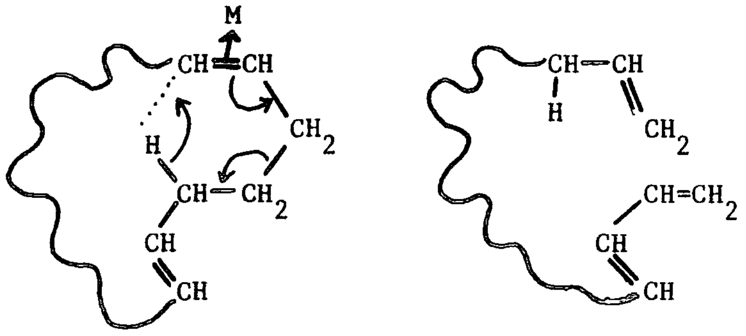
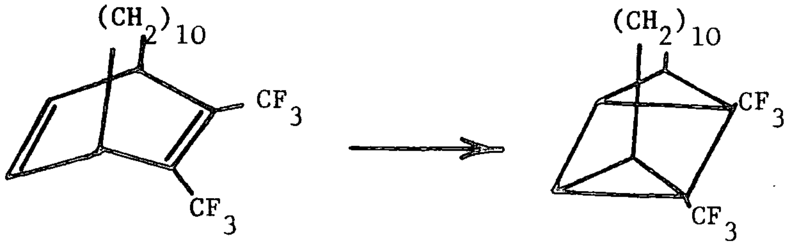
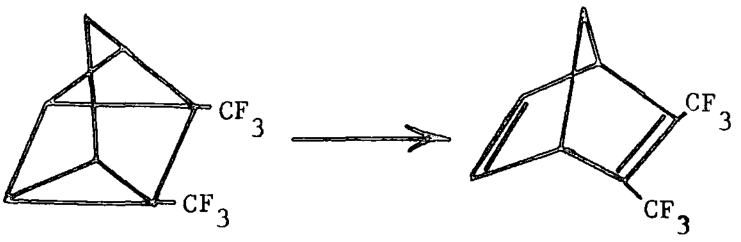


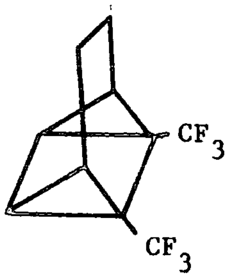
Figure 1.51.



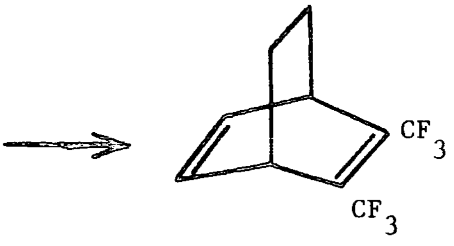
(7) (8)



(9) (10)



(11)



(12)

unaffected by their catalyst although it retained its activity for the cyclobutane-diene interconversion even after 'normal metathesis activity had been quenched by the addition of Michael acceptors'. Wilson,[145] observed that the bicyclic diene (10) is particularly susceptible to ring-opening polymerization by a range of metathesis catalysts and is even polymerized by pure tungsten hexachloride, this contrasts with its reported lack of reactivity with the $PhWCl_3/AlCl_3$ catalyst and suggests that interesting cyclobutane-diene interconversions observed with this catalyst have little relevance to the mechanism of the generality of metathesis polymerizations. It should be noted that ethylene and cyclobutane are not equilibrated in the presence of metathesis catalysts, neither are cyclobutanes formed from simple alkenes nor do they split in the manner required by this mechanism. For this reason another concerted pairwise exchange mechanism was proposed by Lewandos and Pettit[146] which involved the alkene molecules reacting with the metal to form a bis-alkene-π complex, this is called 'tetramethylene' transition state hypothesis and is represented in Figure 1.52. The

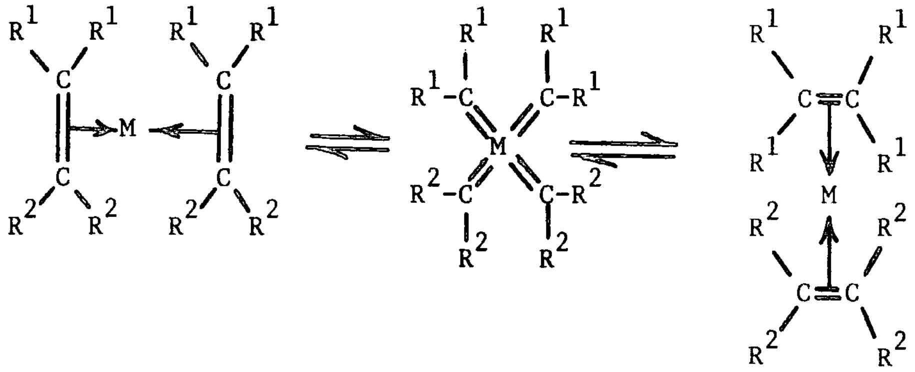


Figure 1.52.

theoretical implications of these concerted mechanisms have been reviewed by Haines and Leigh.[23]

1.10.b.ii. Metallocyclopentanes as Intermediates

Although the mechanisms described in the previous Section accounted for most of the evidence the weaknesses described made workers look for alternative rationalizations. The main assumption of the mechanisms considered so far is that olefin metathesis is a concerted process. A number of Schemes have been proposed in which the mechanism is not concerted.

It was suggested by Katz and Cerefice[147] that rhodium catalysed carbocyclic ring rearrangements proceed via metal-carbon σ-bonded intermediates. They demonstrated the intermediate which resulted from a rearrangement of complexed alkenes to metallocyclopentane followed by rearrangement of the metallocycle and finally rearrangement to new complexed alkenes as shown in Figure 1.53.

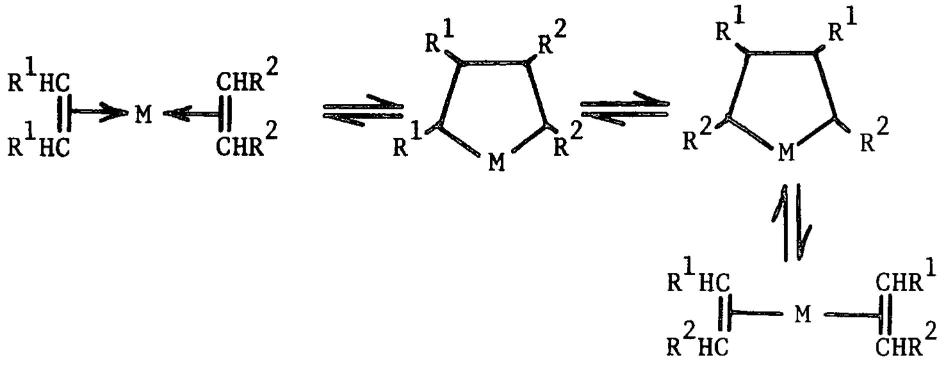


Figure 1.53.

Grubbs and Brunck[148] proposed that a carbon-metal-σ-bonded species was a possible intermediate in tungsten-catalysed olefin metathesis, they based their proposals on the observation that WCl_6 reacted with 1,4-dilithiobutane in benzene to give a quantitative yield of ethylene as shown in Figure 1.54.

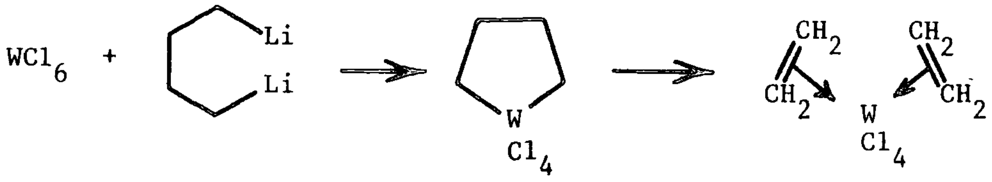


Figure 1.54.

Using deuterium labelling, the ethylene mixtures produced from 1,4-dilithio-2,3-dideuteriobutane contained CH_2=CHD, CHD=CHD and CH_2=CH_2, which suggests that a rearrangement had taken place and that metallocyclopentanes might be involved as intermediates in a non-concerted pairwise exchange of alkylidenes in the mechanism for metathesis. These proposals have not been substantiated by experimental evidence, hence they found less support than the earlier mechanisms and were soon replaced by the currently accepted, non-concerted, non-pairwise mechanism.

1.10.b.iii. Metallocyclobutane and Metal-carbene Intermediates

To date the most widely accepted mechanism for olefin metathesis is one which involves as the active species, a metal-carbene complex. This complex reacts with an olefin via a metallocyclobutane to give a new olefin and another metal carbene complex as shown in Figure 1.55. This mechanism was proposed by Herrisson and Chauvin[75] and was independently put forward by Lappert and co-workers[149] when they reported that 'electron rich' olefins such as unsaturated amines undergo metathesis with a rhodium phosphate catalyst, Figure 1.56. The intermediate involved in this reaction was

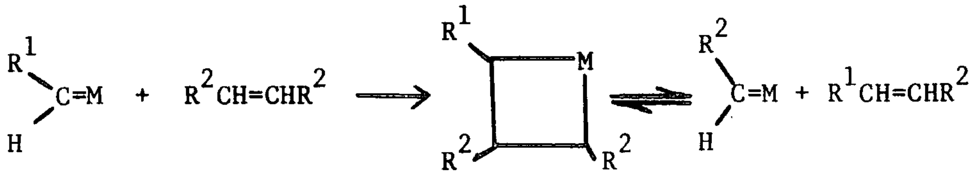
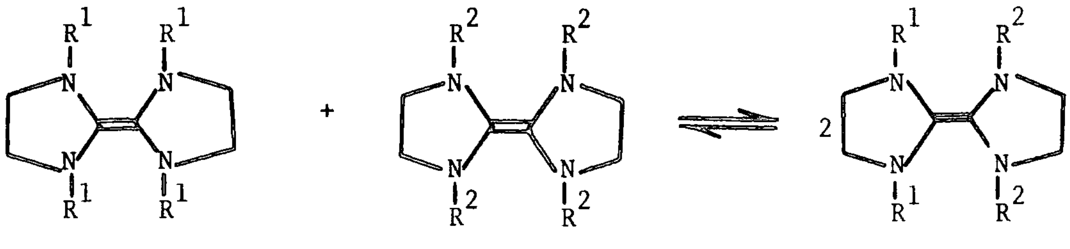


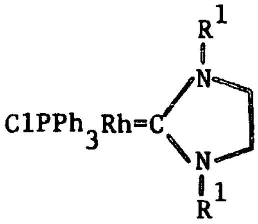
Figure 1.55.



where $R^1 = C_6H_5$; R_2 = P-$CH_3C_6H_4$

Figure 1.56.

isolated and identified as the complex metallocarbene (13).



(13)

It has been shown that metal carbenes can serve as initiators for ring opening polymerization.[84,149b] It was also found that metal carbenes catalysed metathesis of acetylenes.[84]

The metallocyclobutane mechanism accounts for ring-opening polymerization which can be understood in terms of chain end growth as shown in Figure 1.57.

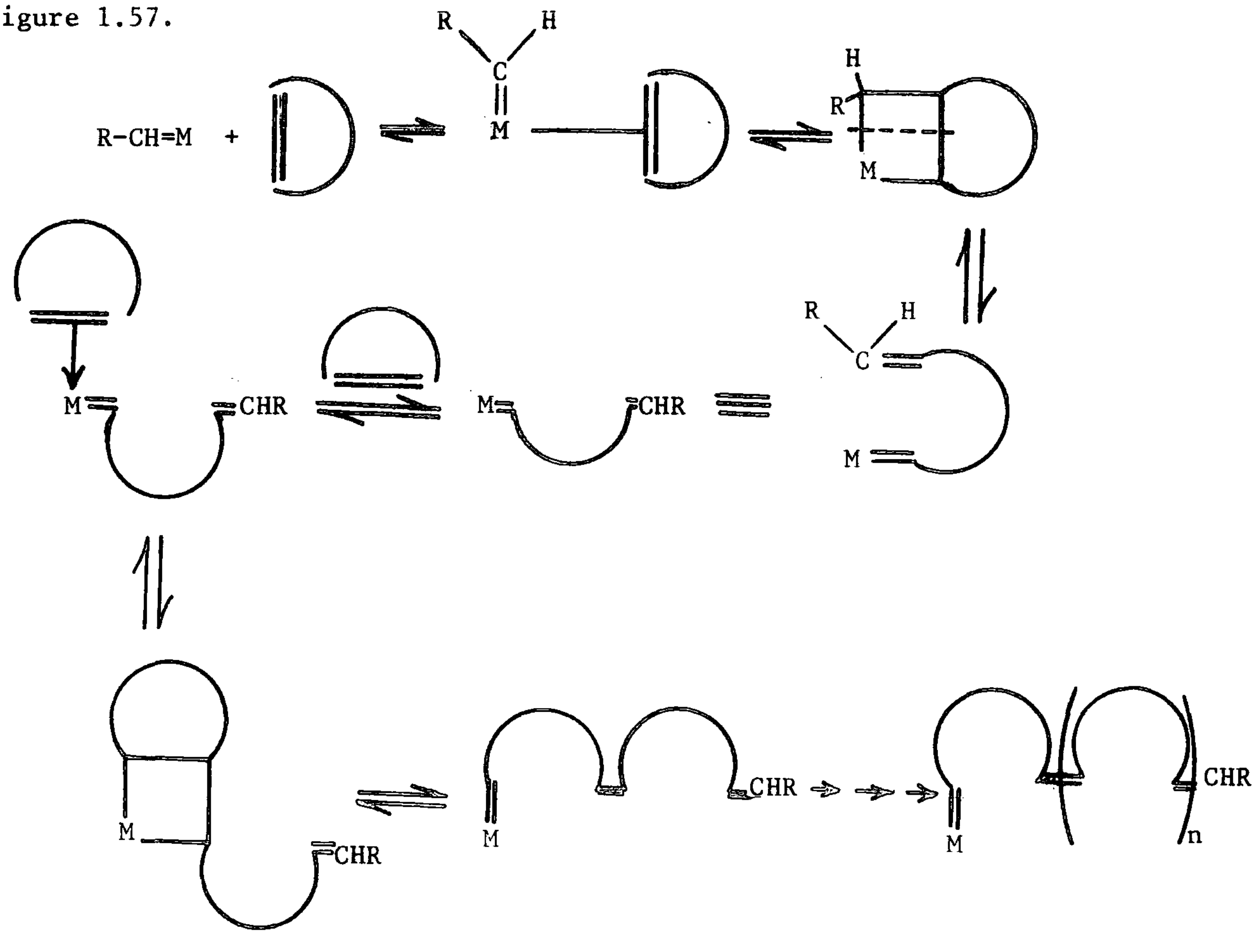


Figure 1.57.

Polymers are not formed by consecutive macrocyclization, as earlier pairwise mechanisms required, and the cyclic oligomers observed in some reactions are obtained when the carbene end reacts with a double bond within the growing polymer chain, Figure 1.58.

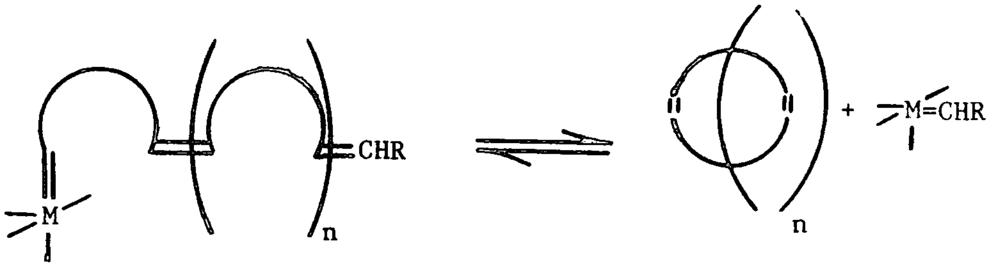
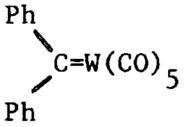


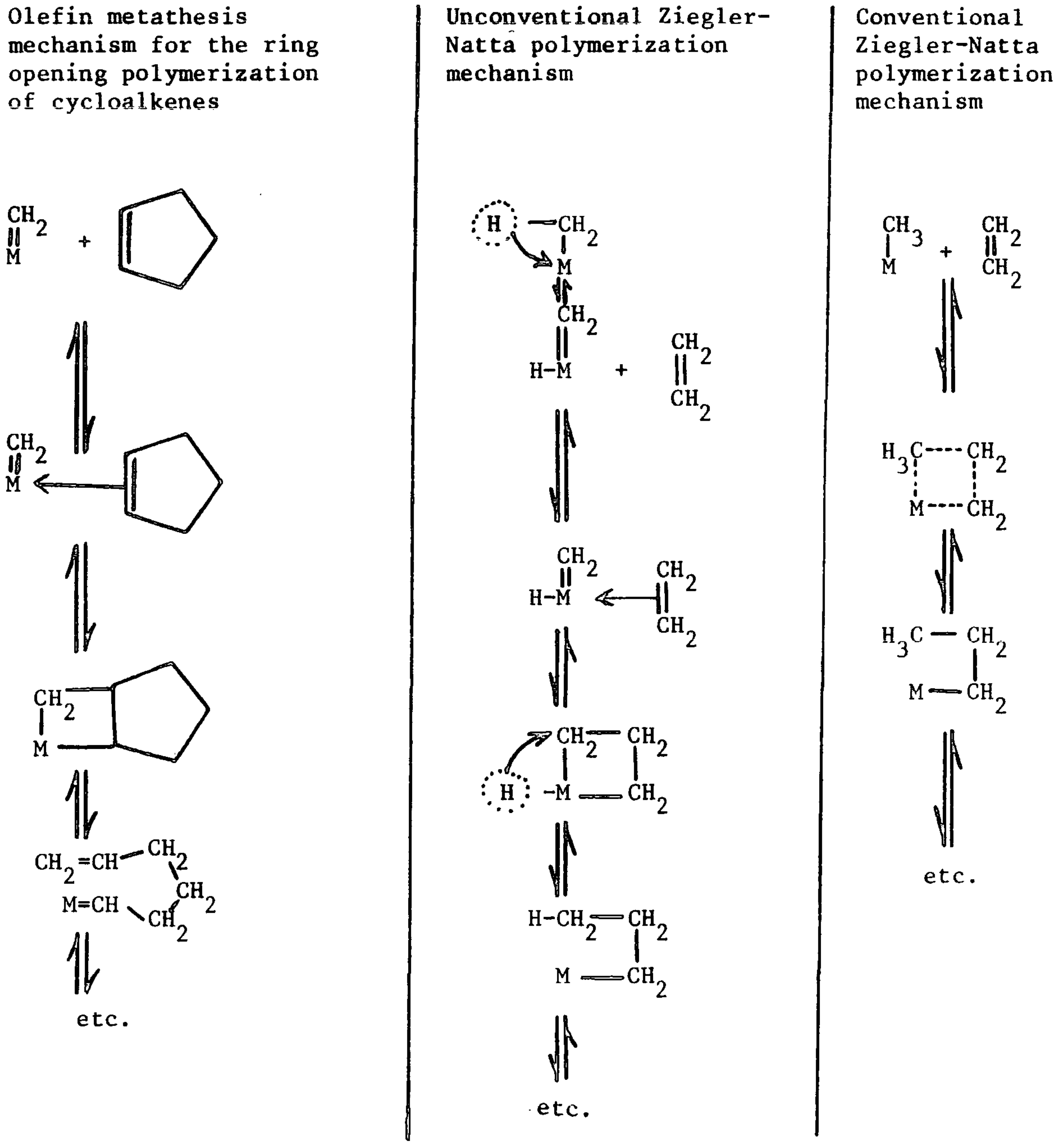
Figure 1.58.

A variety of labelling experiments and model studies support the metallocarbene/metallocyclobutane mechanism for the metathesis reaction.[15,29b,150,151,152] Some metal carbenes have been synthesised,[151,152,153] and shown to be active in metathesis. Katz and co-workers demonstrated that the carbene complex (14) may be employed as a metathesis catalyst, this was major experiment evidence in support of the non-pairwise mechanism.


$Ph_2C=W(CO)_5$

(14)

Ivin, Rooney and Green[154] have postulated that there is a close relationship between olefin metathesis and Ziegler-Natta polymerization, Figure 1.59. The catalyst system WCl_6/Me_4Sn polymerises ethylene to polyethylene by the Ziegler-Natta mechanism and ring-opening polymerizes cyclopentene to poly(1-pentenylene) by olefin metathesis,[155] thus some catalysts can effect both ring opening polymerization of cycloalkenes and Ziegler-Natta polymerization of alkenes.[11b,156] Further support for this



Olefin metathesis mechanism for the ring opening polymerization of cycloalkenes

Unconventional Ziegler-Natta polymerization mechanism

Conventional Ziegler-Natta polymerization mechanism

Figure 1.59.

idea comes from the observation that $EtAlCl_2$ can ring open polymerize norbornene and also cause ethylene polymerization;[28] also transition metal-alkyls are known to give rise to the reversible elimination of α-hydrogen which is simply a 1,2-hydrogen shift, Figure 1.60. However, this attempt

Figure 1.60.

to provide a unified mechanistic picture for Ziegler-Natta and metathesis polymerizations remains a subject of debate and argument.

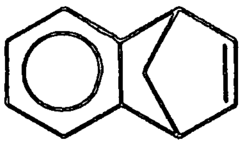
CHAPTER II

Synthesis and Characterization of Monomers

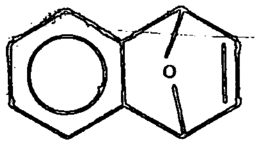
2.1. Introduction

Earlier attempts by the author[115] and Wilson[145] to effect the ring-opening polymerization of aryl substituted cyclic and bicyclic alkenes were briefly discussed at the end of the previous Chapter. The ambiguous results with indene, the unambiguous failure to ring-open polymerize acenaphthylene and the very ready polymerization of benzonorbornadiene led to the current inquiry into the effect of aryl substituents on this polymerization reaction. As a first step in the investigation it was necessary to extend the range of aryl substituted monomers investigated. This Chapter describes the synthesis, purification and characterization of the monomers investigated. The polymerization of these monomers is described in Chapter III.

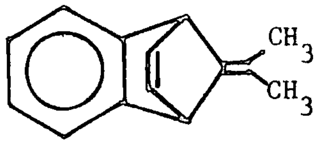
The six monomers shown below were obtained in a pure state:-



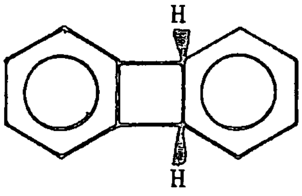
(15)



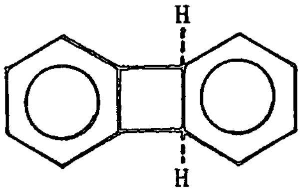
(16)



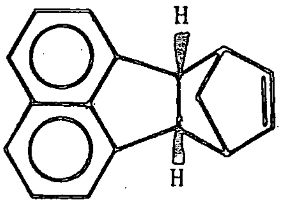
(17)



endo (18)

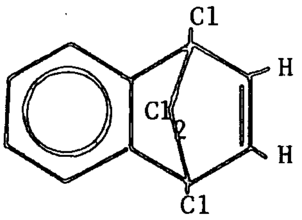


exo (19)

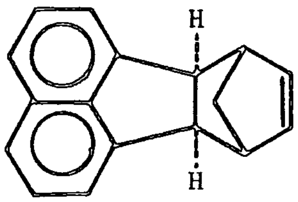


endo (20)

Attempts to obtain monomer (21) was unsuccessful; although (22) was obtained as a mixture with acenapthylene.



(21)



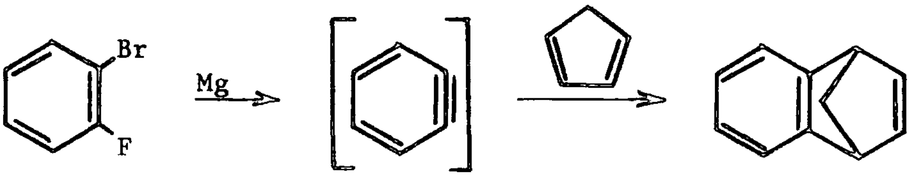
exo (22)

The synthesis, purification, characterization and relevant background chemistry for each monomer is described briefly below.

2.2. The Synthesis of Benzonorbornadiene (15)

2.2.a. Introduction

In 1958, Wittig and Krauss[158a] described the synthesis of benzonorbornadiene by a cycloaddition reaction between cyclopentadiene and benzyne generated from ortho-bromofluorobenzene and magnesium as shown in Figure 2.1.



(15)

Figure 2.1.

In general, benzynes have been generated under aprotic conditions by fragmentation of suitably ortho-disubstituted benzenes.[158a-g] In 1963, Friedman and Logullo,[159] reported the generation of benzyne from the diazotization of anthranilic acid with alkyl nitrites in aprotic media, and this is probably still the cheapest route to this reactive intermediate. Benzyne has been investigated by many researchers over the past four decades,[160] most work has concentrated on its preparative usefulness,[161-165] with relatively less work on the physical organic chemistry of this unstable intermediate.[166] The general chemistry of benzynes has been reviewed in great detail and comprehensive articles are available on the chemistry of the whole class of cycloalkynes.[167-172]

In 1968, Mich and co-workers[173] reported the synthesis of benzonorbornadiene via cyclopentadiene trapping of benzyne generated via the diazotization of anthranilic acid with amyl nitrite.[159] Their method suffered from the risk of a violent explosion caused by the formation of diazonium salts which accumulated in the reaction mixture under their reaction conditions. Such materials are well known to be unstable particularly if allowed to dry, Figure 2.2. The dehalogenation of orthobromofluorobenzene is an expensive route to benzyne and so it was decided to use Mich's route with appropriate modifications to avoid any risk of isolating the explosive diazonium salt. Monoglyme solutions of the reagents were added over three hours and at the same rate to the refluxing solvent, the diazonium salts decomposed immediately and the resulting benzyne was trapped with freshly distilled cyclopentadiene to give monomer (15) in 33.5% yield, Figure 2.3.

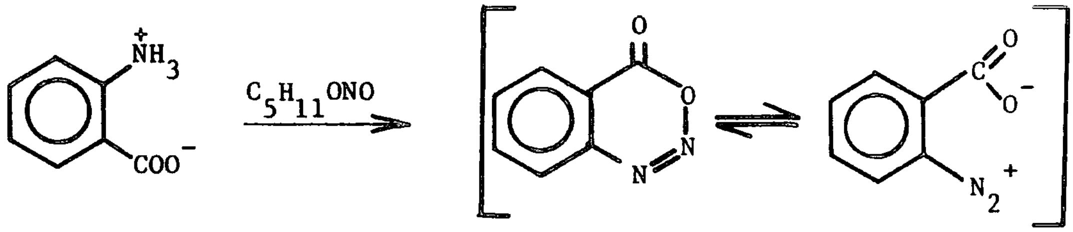
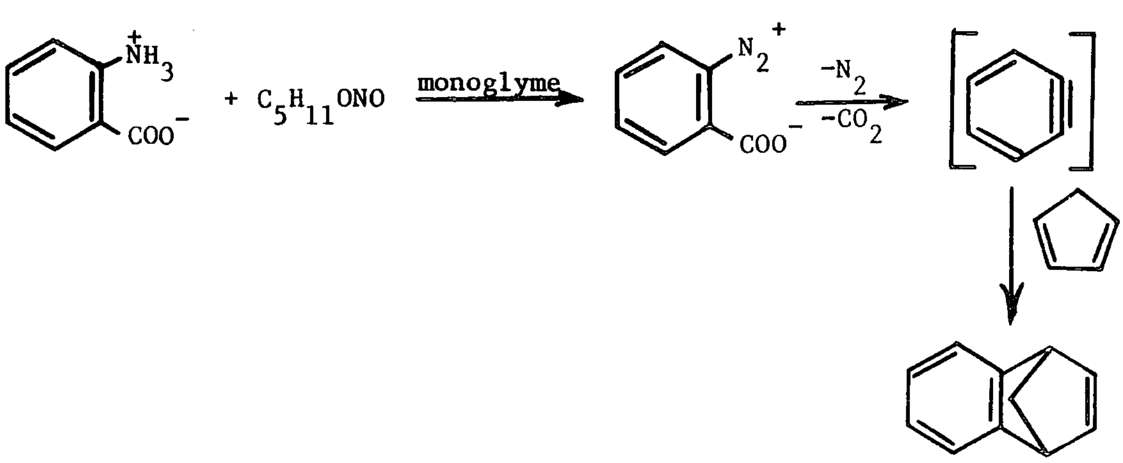


Figure 2.2.



(15)

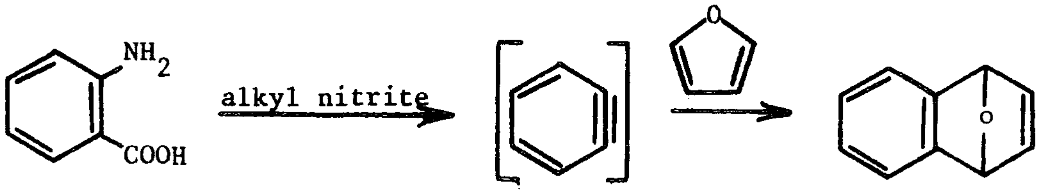
Figure 2.3.

The synthesis, purification, characterization and polymerization of this monomer has been described previously.[115]

2.3. The Synthesis of 1,4-Dihydronaphthalene-1,4-endo-oxide (16)

2.3.a. Introduction

Wittig[174] first prepared this compound in 1956 by shaking a solution of o-bromofluorobenzene in furan with lithium amalgam for four days. In 1960, Stiles[175] demonstrated the preparation in 55% yield by refluxing a suspension of benzene diazonium-2-carboxylate with furan for 64 hrs., the product was identified by conversion to 1-naphthol (81%) in methanolic hydrochlorid acid. Later, Fieser and Haddadin[176] modified the synthesis by generating benzyne from the reaction of anthranilic acid with amyl nitrite and trapping it in situ, Figure 2.4.



(16)

Figure 2.4.

Many organic chemists described the reactions between benzynes and furan and furan derivatives.[158a,159,177,178] The Fieser route[179] was used in this work to give monomer (16) in 51% yield. The monomer was easily purified by recrystallization from petroleum ether.

2.3.b. Characterization of 1,4-Dihydronaphthalene-1,4-endo-oxide

1,4-Dihydronaphthalene-1,4-endo-oxide is a known compound and its elemental analysis, m.p., mass spectrum (Appendix B, no. I), ^{1}H n.m.r. (Appendix C, no. I) and i.r. spectrum (Appendix D, no. I) were consistent with the assigned structure and in agreement with the literature data.[175,176,179]

2.4. The Synthesis of 7-Isopropylidene benzonorbornadiene (17)

This monomer has been synthesised by the cycloaddition reaction of benzyne and dimethylfulvene. Thiele in 1906 described the synthesis of fulvenes by condensation of cyclopentadiene with a ketone or an aromatic aldehyde in the presence of base,[180-182] Figure 2.5. Ever since fulvenes have been under investigation by many chemists and a variety of syntheses

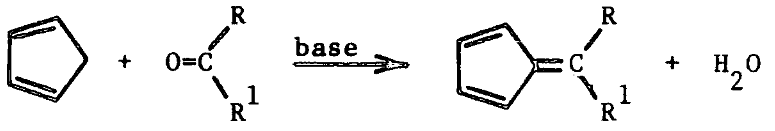


Figure 2.5.

have been reported.[183-186] Generally the reaction proceeds in low yield, very recently, Alper and Laycock[187] reported significant improvements in the yields of fulvenes by treating cyclopentadiene with KOH in the presence of a small amount of 18-crown-6-ether in tetrahydrofuran as shown in Figure 2.6. The chemistry of fulvenes has been reviewed in detail.[188,189]

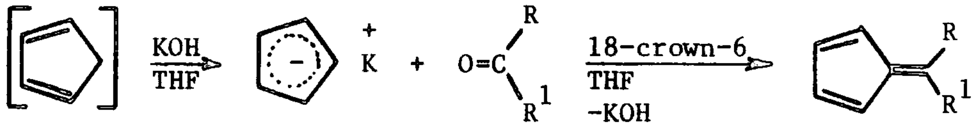
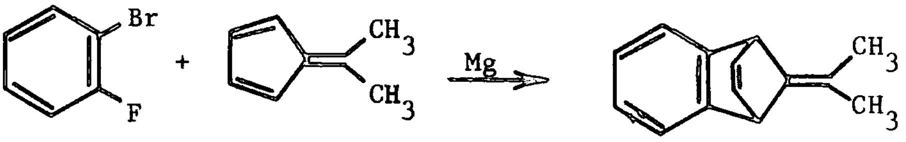


Figure 2.6.

7-Isopropylidene benzonorbornadiene (17) was first prepared in 1966 in 31% yield by Maneyki and Tanida,[161] they used Wittig's route to generate benzyne which was then trapped with dimethylfulvene as shown in Figure 2.7. A few years later Watson and Warrener,[190] modified the synthesis by generating



(17)

Figure 2.7.

benzyne from the reaction of anthranilic acid and amyl nitrite according to Friedman's method[159] and trapping it with dimethylfulvene to give (17) in 43% yield; the same route was used in this work. The synthetic and theoretical interest of this compound and its derivatives has received considerable attention.[191,192]

2.4.b. Characterization of 7-Isopropylidene Benzonorbornadiene

This monomer is a well known compound, its mass spectrum (Appendix B, no. II), ^{1}H n.m.r. (Appendix C, no. II) and i.r. (Appendix D, no. III); m.p. and elemental analysis were consistent with the assigned structure and in agreement with the literature data.[161,191]

2.5. The Synthesis of Endo-1,4,4a,8b-tetrahydro-1,4-methanocyclobutadibenzene (18)

2.5.a. The Generation of the Benzocyclobutadiene, bicyclo[4.2.0]-octa-1,3,5,7-tetraene

In 1910 Finkelsten[193] described a reaction which is now believed to proceed via a genuine benzocyclobutadiene intermediate, he reacted α,α,α',α'-tetrabromo-o-xylene with sodium iodide and obtained 1,2-dibromobenzocyclobutene. This dibromide was dehalogenated with activated zinc suspended in acetone, but he was unable to isolate the primary product, i.e. benzocyclobutadiene. This primary work was forgotten for some fifty years until Cava[194] in 1953 reinvestigated Finkelsten's reaction and isolated the dimer of benzocyclobutadiene in good yield as shown in Figure 2.8. Since this reaction was

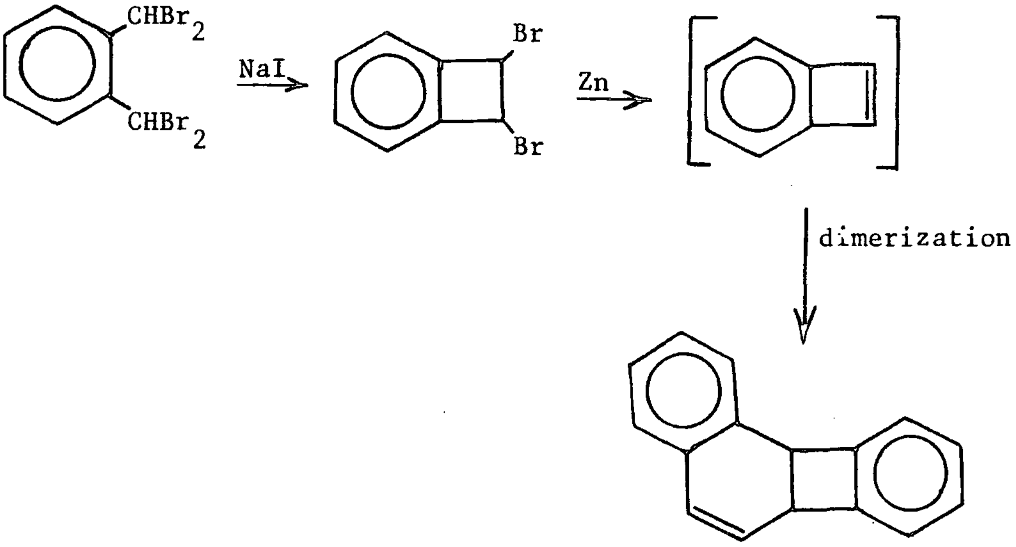


Figure 2.8.

first described, many chemists have studied the generation and reactions of benzocyclobutadiene. The syntheses developed include: (a) dehalogenation of 1,2-dihalobenzocyclobutenes with zinc,[195,196] lithium amalgam,[196,197] sodium amalgam,[196] sodium iodide[194a,198] and nickel tetracarbonyl.[196] It was reported that the generation of benzocyclobutadiene occurs more readily via dehalogenation of trans-1,2-diiodobenzocyclobutene, rather than the trans-1,2-dibromo derivative, with activated zinc dust,[194b,197a,b] Figure 2.9. An effective

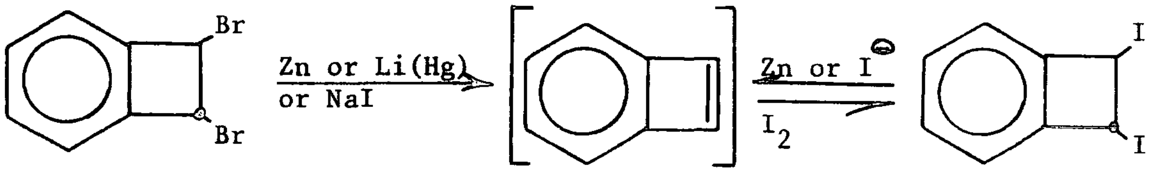


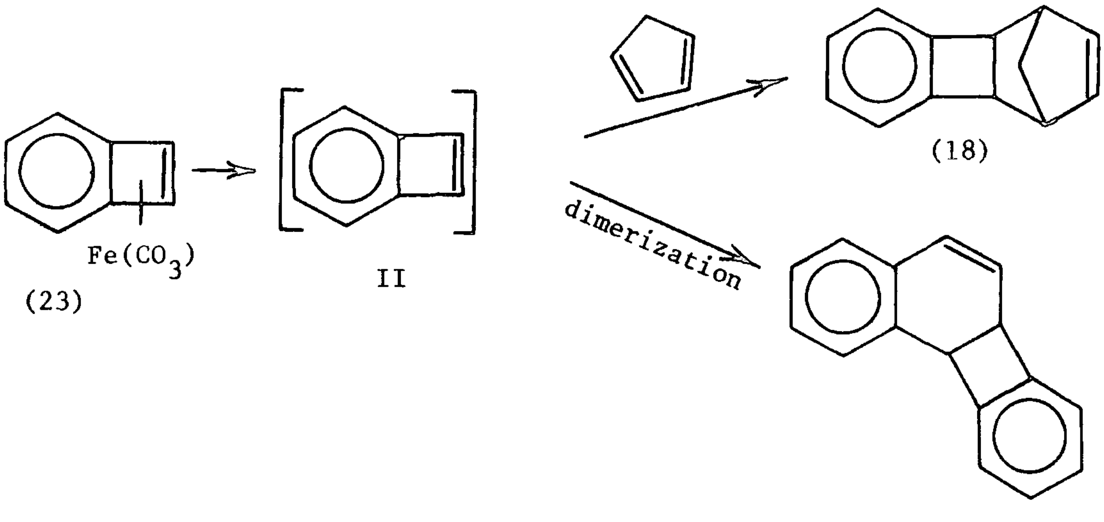
Figure 2.9.

preparation of cis- and trans-diiodobenzocyclobutene in 70-80% yield was reported by Jensen and Colemon,[198] and this route was chosen for the synthesis undertaken for this present study because no side reactions were reported.

(b) By dehydrohalogenation of 1-halobenzocyclobutenes with potassium tert-butoxide in tert-butyl alcohol this route gives good yields.[193,194b,c,196,199,200]

(c) By cycloaddition of benzyne to acetylenes but this method is limited.[158]

(d) The oxidative degradation of a complex (23) using lead tetraacetate in pyridine gave the dimer (24) in good yield and the hydrocarbon (18) when trapped with cyclopentadiene[194c,200b,201] as shown in Figure 2.10. (e) Recently Dieke and Hudell[202a] proposed the formation of benzocyclobutadiene by treatment



(23)

II

(18)

(24)

Figure 2.10.

of dihalide with solutions of solvated electrons. The spectroscopic observation and the photoelectron spectrum of benzocyclobutadiene have recently been reported.[203,204] Benzocyclobutadiene is a highly reactive intermediate and reacts as diene and dienophile to produce dimer in good yield in the absence of other dienes or dienophiles. The instability of this molecule is caused by the high reactivity of the double bond which undergoes addition reactions easily.[205] In the presence of dienes the course of reaction and the rate of product formation depends on the reactivity of the diene itself. Thus when benzocyclobutadiene is trapped with a very reactive diene such as cyclopentadiene the amount of dimer formation is low and product (18) predominates, while reaction with dienes, having moderate reactivity such as furan, the rate of dimerization (24) of benzocyclobutadiene becomes equal or greater than the rate of product formation (25) and with unreactive diene the dimer (24) predominates.[206] The reaction of benzocyclobutadiene with anthracene depends on the reaction temperature; at room temperature it gave dimer (24) while at higher temperatures both the dimer (24) and (26) were isolated, as shown in Figure 2.11. The reactions of benzocyclobutadiene as a highly reactive dieno-

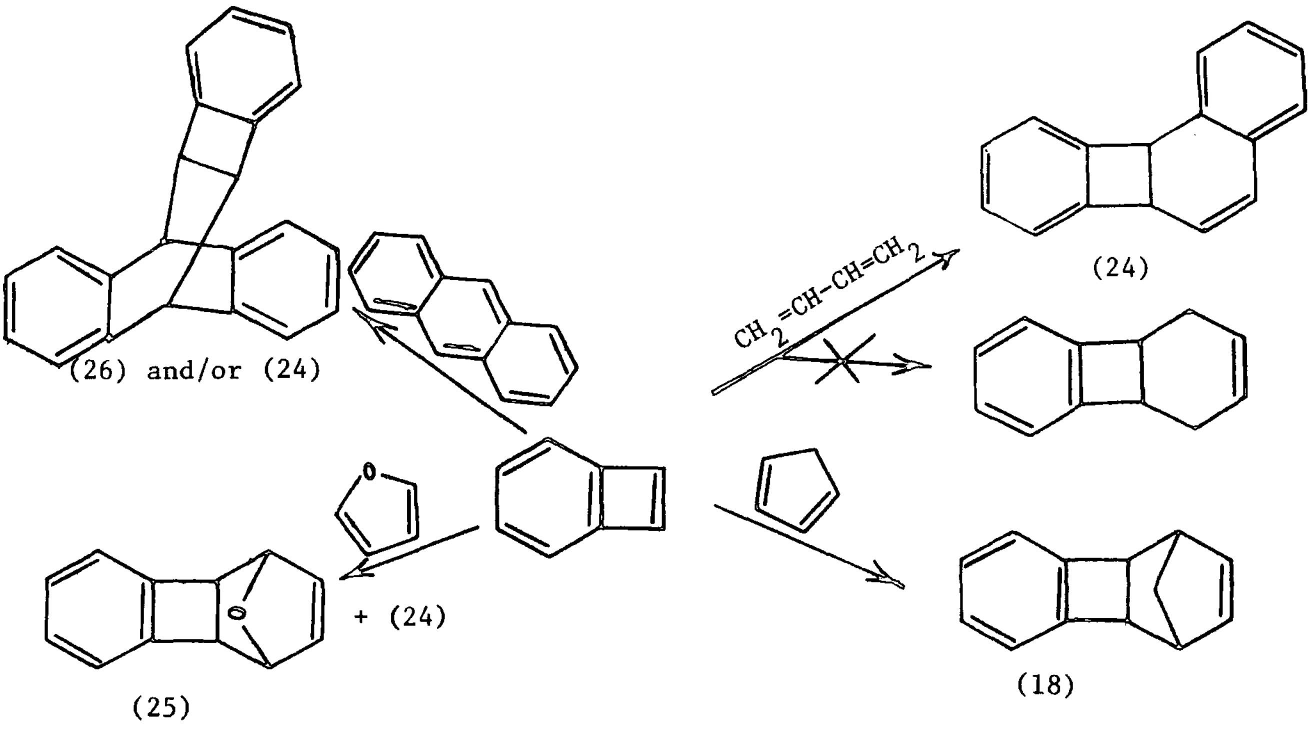
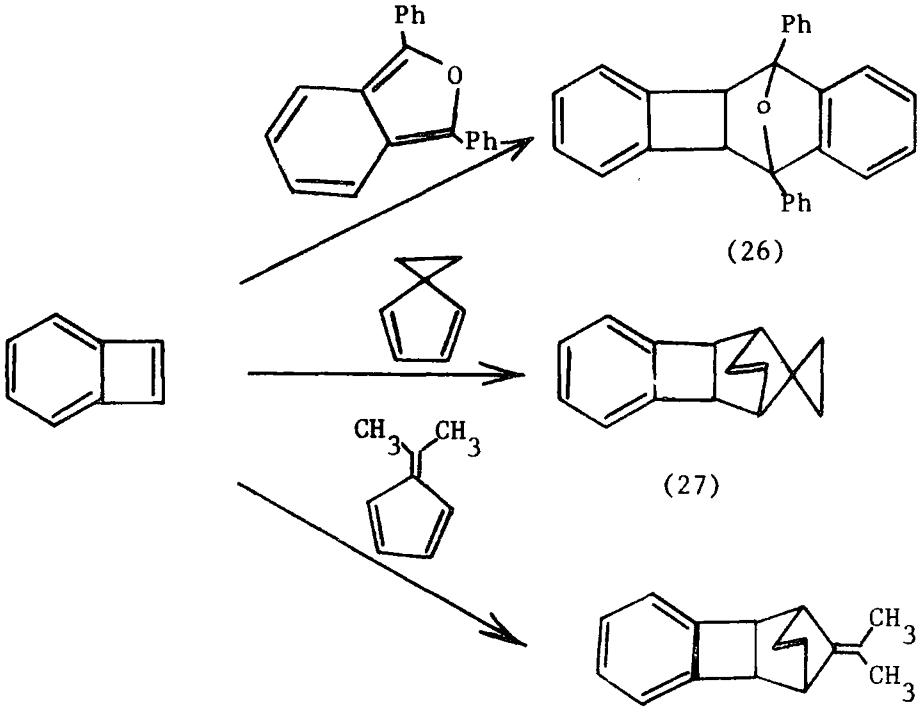


Figure 2.11.

phile are well established, it reacts readily with spiroheptadiene,[207] dimethylfulvene,[207] and 1,3-diphenylisobenzofuran[207,199] to give the adducts (26), (27) and (28) as indicated in Figure 2.12. Benzocyclobutadiene has limited



(26)

(27)

(28)

Figure 2.12.

reactivity as a diene, it gave no adducts with dimethylmaleate or dimethylacetylene dicarboxylate and gave only the dimer (24) even with the reactive dienophile N-phenyldimide.[206a]

In 1957, Nezitzescue[197a] and et al. described the reaction between benzocyclobutadiene and cyclopentadiene, later in 1959 Cava and Mitchell[206a] reported the preparation of this compound in 65% yield according to Figure 2.13. All the evidence, from the spectroscopic to the chemical, was in agreement with the assignment of the endo structure (18).[206a,208,209,210]

2.6. Characterization

2.6.a. The Characterization of Cis and Trans-1,2-diiodobenzocyclobutene

Jenson and Coleman[198] method was used in order to prepare these isomers. A mixture of sodium iodide, potassium iodide and ethanol was refluxed for

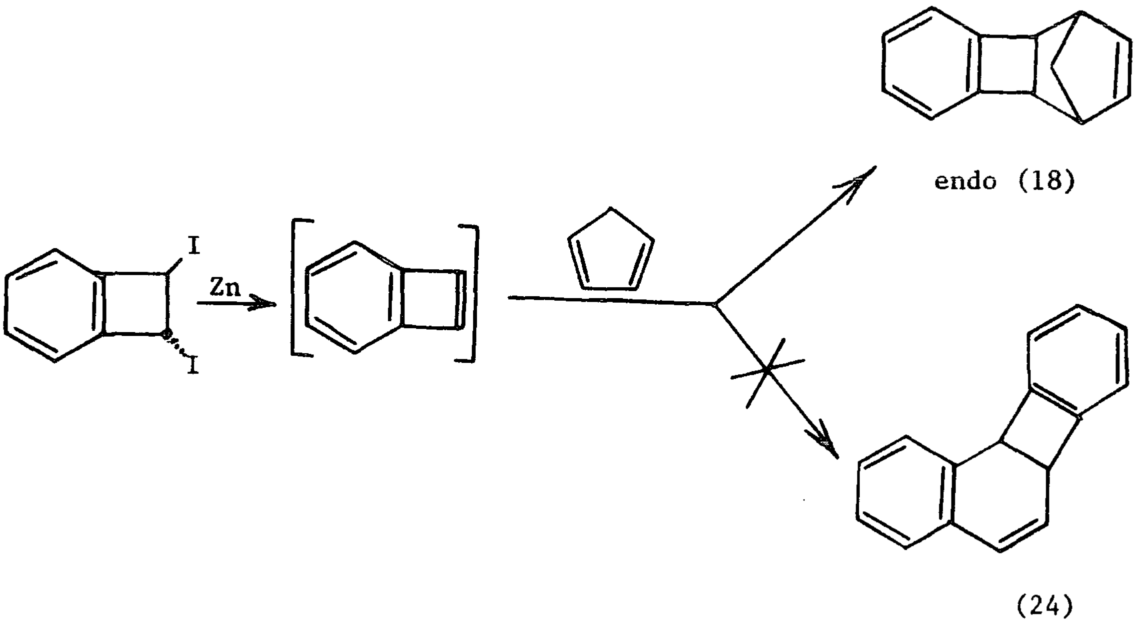


Figure 2.13.

30 min., 10% of the ethanol was removed and α,α,α,α-tetrabromo-o-xylene was added to the mixture which was refluxed for 10 days, with careful exclusion of moisture and light.*

The two isomers were separated by crystallization from petroleum ether 60-80°C to give the trans-isomer (91.2%) as prisms, m.p. 60-61°C and the cis-isomer (8.8%) as needles, m.p. 136°. Elemental analysis gave for the prisms C, 27.24; H, 1.73; I, 70.97 and for the needles C, 27.24; H, 1.68; I, 71.22 whereas the calculated figures for $C_8H_6I_2$ are C, 26.99; H, 1.70; I, 71.31; mass spectroscopy of trans and cis confirmed the molecular weight 356 (Appendix B, no. III and no. IV). The i.r. spectrum (Appendix D, no. IV) was in agreement with the assigned structure and the ^{1}H n.m.r. spectrum of the trans isomer (Appendix C, no. III) showed resonances at 2.44, 2.98 (aromatic) and 4.5 τ (benzylic) in relative intensity ratio 1:1:1.

* *Organic iodides are generally unstable to light and the product of this reaction is particularly sensitive, since the reaction takes 10 days it is important to exclude light in order to maximise the yield.*

The cis isomer (Appendix C, no. IV) showed resonances at 2.8, 3.0 (aromatic) and 4.1 τ (benzylic) in relative intensities 1:1:1. These spectra were recorded at 90 MHz using $CDCl_3$ as solvent, the chemical shifts are referred to external tetramethylsilane. The spectra were in agreement with the data reported.[198]

2.6.b. The Characterization of Endo-1,4,4a,8b-tetrahydro-1,4-methanocyclobutadibenzene

Cava and Mitchell route[206a] was used with small changes. A suspension of activated zinc dust in ethanol and freshly distilled cyclopentadiene was placed in the reaction flask, a slow stream of dry nitrogen was passing throughout the experiment, a solution of trans-1,2-diiodobenzocyclobutene in ethanol was added dropwise to the suspension during 5 hrs. The reaction mixture temperature was kept at 30°C throughout the experiment. The excess of the zinc was removed by filtration and the solution was concentrated and then treated with water; the resulting white suspension was extracted with petroleum ether which was dried and vacuum distilled to give coloured material which was molecular distilled twice to give the expected product in a pure state (59.2% yield).

The elemental analysis of the product was found to give C, 92.90; H, 7.20 comparing with the calculated figures for $C_{13}H_{12}$, C, 92.80; H, 7.20. The infrared spectrum of the pure sample (Appendix D, no. V) was in agreement with the spectrum which was recorded in the literature by Simmons.[210] The absorptions of C-H aliphatic and aromatic were found and all the bands in the region between 1700-2000 $cm.^{-1}$ were in agreement with those expected for an ortho-disubstituted benzene derivative. The spectrum was identical with that reported by Cava.

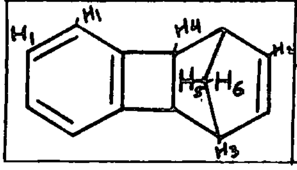
The ultraviolet spectra of (18) as prepared in this work was compared with that reported by Simmons (see Table 2.1.); the spectra were effectively the same apart from minor differences in extinction coefficients.

Table 2.1.

Band position (nm)		Extinction coefficient	
Simmons' sample	Sample (18)	Simmons' sample	Sample (18)
308 (sh)	-	13.4	-
275	275	2450	2165
269	268	2300	2152
262	262	1430	1365
-	256 (sh)	-	781
-	248 (sh)	-	328

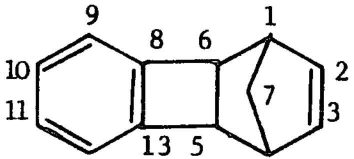
The proton n.m.r. spectrum of sample (18) (Appendix C, no. V) gave strong evidence for the assigned structure and was in agreement with the literature data, a comparison has been made in Table 2.2. below. The

Table 2.2.

Structure		H1	H_2	H_3	H_4	$H_{5,6}$
	sample (18)	3.15(4)	4.43(2)	7.14(2)	6.45(2)	8.27(2)
	Simmon's sample	3.32(4)	4.43(2)	7.20(2)	6.46(2)	8.28(2)

methylene bridge (H_5,H_6) have the spin-spin coupling of two non-equivalent protons. Four aromatic, two vinylic, two methine, two ethano bridges and two methylene signals would be expected and broad resonances at 3.15 (aromatic), 4.43 (vinylic), 6.45 (methine), 7.14 (bridgehead) and 8.27 τ (methylene) in relative ratio 2:1:1:1:1. The bridgehead protons (H_3) were in the expected range, cf. endo-dicyclopentadiene (7.20) and bicyclo[2.2.1]heptene (7.22).

In the ^{13}C n.m.r. spectrum (Appendix E, no. II) of compound (18), seven signals are seen, the high field signal at 148.5 is of low intensity and is assigned to carbons 8 and 13 which do not bear protons, the signal at 132.8 was assigned to the vinylic carbons 2 and 3, at 127 to C-9 and 12 and 123 to C-10 and 11 while the low field signals at 44.1 and 46.3 were assigned to C-1 and 4 and C-5 and 6 respectively, the methylene carbon (C-7) was found at 55.3 p.p.m.



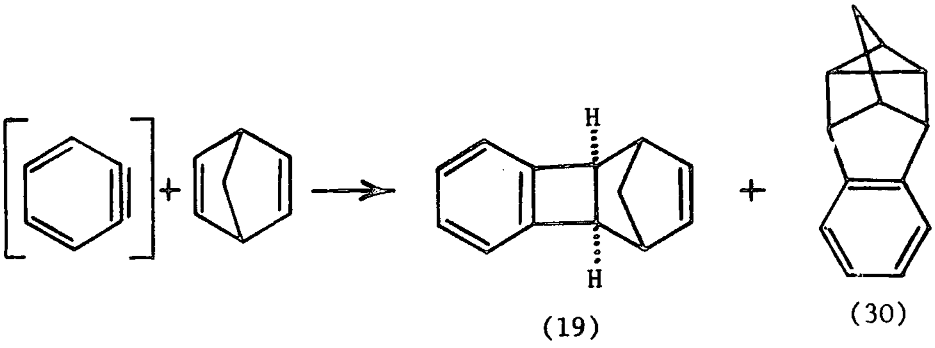
(18)

The mass spectrum of sample (18) (Appendix B, no. V) confirmed molecular weight at 168; and the compound gave one single peak by G.L.C.

2.7. The Synthesis of Exo-3,4-benzotricyclo[4.2.1.0^{2,5}]nona-3,7-diene (19)

2.7.a. Introduction

In 1961 Simmons[210] reported the cycloaddition reaction between benzyne and bicyclo[2.2.1]heptadiene which gave the exo-adduct (19) in 15-21% yield as well as another hydrocarbon compound (30) in the ratio 7:2, as shown in Figure 2.14.

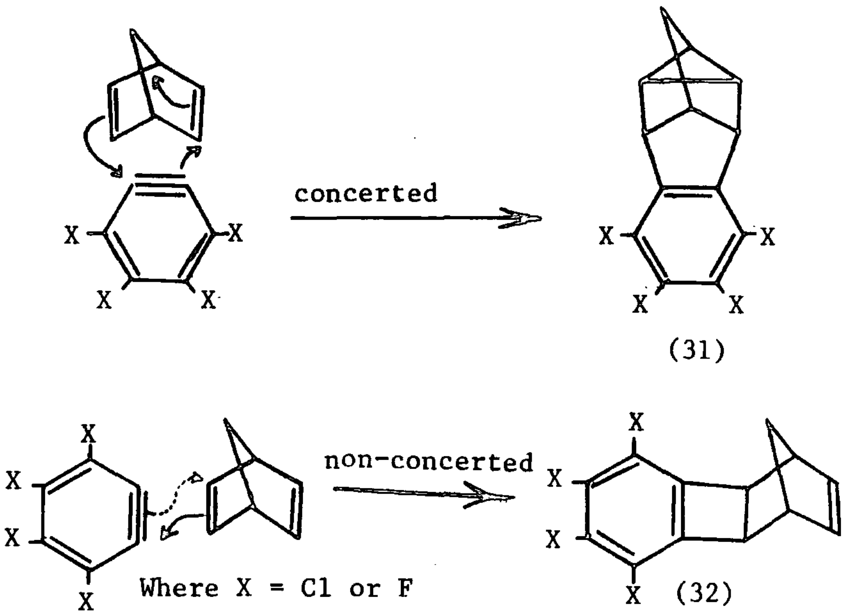


(19)

(30)

Figure 2.14.

In 1967 Heaney and Jablonski[211a] demonstrated the reaction of halogenated benzynes with norbornadiene which gave the corresponding adducts (31) and (32). They proposed that the adduct (31) was formed via a concerted addition of benzyne across the 2,6-positions of the diene, while the formation of the exo-adduct (32) occurs by a non-concerted mechanism,[211a,b] Figure 2.15.



(31)

Where X = Cl or F

(32)

Figure 2.15.

The endo (18) and exo (19) isomers have similar chemical behaviours[210] and some recent work has been published concerning the reduction of these compounds.[212,213] The author prepared this monomer by generating benzyne from the reaction of anthranilic acid with amyl nitrite and trapping it with norbornadiene, the resulting mixture was separated and purified by column chromatography on silica gel. Previous workers used silica gel treated with silver nitrate to improve the resolution of these compounds, however in this work 'dry column' development proved satisfactory and was, of course, much cheaper. Three products were isolated (19) and (30) and an unknown compound which remains unidentified. During the achievement of this work, Michael et al.[213] reported the synthesis of the exo-isomer (19) by the same route, they only mentioned two products.

2.7.b. Characterization

Dry monoglyme solutions of the reagents were added to refluxing norbornadiene in monoglyme at equal rates during two hours. The oily dark orange-red mixture was treated with sodium hydroxide 10% and extracted with petroleum ether, the extract was washed with water and dried. The solution was vacuum distilled to give a red liquid, which was separated by column chromatography, the two compounds (19) and (30) had similar R_f values but were clearly separated, the third component had a very low R_f value and was easily obtained pure. The last traces of solvent were difficult to remove and final purification was achieved by slow 'molecular' distillation to give compounds (19), (30) and the unknown in ratio 3.7:1:2 by weight.

2.7.b.i. Characterization of the Exo-adduct (19)

Elemental analysis of the pure sample of exo-adduct (19) gave: C, 92.54; H, 7.31%, whereas the calculated values for $C_{13}H_{12}$ are C, 92.81; H, 7.19%. The i.r. spectrum (Appendix D, no. VI) was in complete agreement with the spectrum reported by Simmons.[210] The ultraviolet spectra of Simmons' material and the sample prepared in this work were also compared and listed in Table 2.3., there was no detectable absorption above 285 nm. for the sample used in this work. The proton n.m.r. spectrum of compound (19) (Appendix C, no. VI) was identical with that reported by Simmons. The ^{13}C n.m.r. spectrum of 19 (Appendix E, no.III) was recorded and the peak assignments, made by analogy with well characterized compounds, are recorded below:

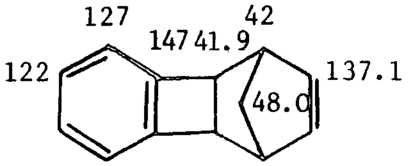


Table 2.3. U.V. Spectra of (19) in Cyclohexane

Bands positions		Extinction Coefficients	
Simmons' sample	Sample (19)	Simmons' sample	Sample (19)
301 (sh)	-	8.4	-
276	276	2970	2957
269	269	2770	2847
263	263	1730	1810
-	256 (sh)	-	886
-	247 (sh)	-	451

The mass spectroscopy of (19) (Appendix B, no. VI) confirmed the molecular weight with a strong parent ion at m/e 168. As can be seen all the spectroscopic analyses were in agreement with the structure (19) and with the data reported previously.[210]

2.7.b.ii. Characterization Compound (30)

Compound (30) is not very important for this work, elemental analysis gave C, 93.10; H, 7.3%, whereas the calculated figures for $C_{13}H_{12}$ are C, 92.81; H, 7.19. The i.r. spectrum (Appendix D, no. VII) showed no -OH, -OOH or carbonyl absorptions, weak aromatic C-H absorptions and strong aliphatic C-H absorptions were found. The region between 2000-1600 cm.$^{-1}$ showed weak bands assigned to o-disubstituted benzene derivatives. The proton n.m.r. spectrum (Appendix C, no. VII) and mass spectrum (Appendix B, no. VII) were in agreement with the assigned structure.

2.7.b.iii. The Long Retained Product

This material was a single component by t.l.c., its elemental analysis gave C, 73.8 and H, 8.1%, there was no nitrogen present. Peaks at the high mass end of the mass spectrum at m/e 168 (0.4), 167 (0.7), 165 (1.2), 164

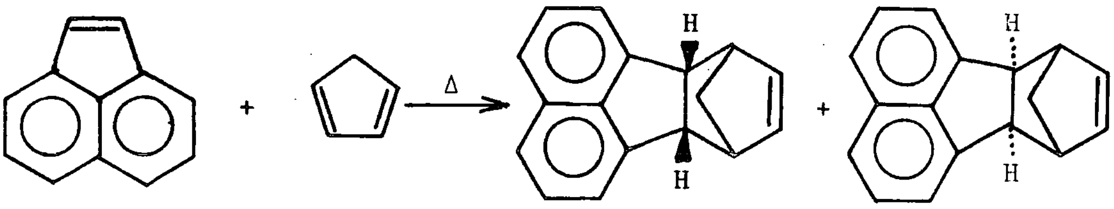
(6.9) and 152 (34.7%) suggest that the molecular ion is not detected since fragmentation to lose 12 amu (164 → 152) is most unusual. The very complex ^{1}H and ^{13}C n.m.r. spectra and the relatively long chromatographic retention volume suggest that this product may be a product of poly-addition. The i.r. (Appendix D, no. VIII) and mass spectrum (Appendix B, no. VIII) are recorded for reference but it has not proved possible to assign a structure for this product. Appendix C, no. VIII records the ^{1}H n.m.r. spectrum.

2.8. The Synthesis of Endo-7,10-methano-6b,7,10,10a-tetrahydrofluoranthene. The Reaction Between Acenaphthylene and Cyclopentadiene

2.8.a. Introduction

The Diels-Alder reaction generally results in the formation of endo-adducts.[214,215] Cyclic dienophiles[216] such as o- and p-benzoquinone, cyclopentadiene, cyclopentene, maleic anhydride, cyclobutadiene, cyclopropene[214] and benzocyclobutadiene[206] are all reported to give endo-addition in greater than 98.5% yield. Endo addition is the product of kinetic control and in certain cases the reaction can be manipulated to give the thermodynamically preferred exo-adduct, more often such attempts result in the production of an endo:exo mixture.[214]

The thermal reaction of acenapthylene with cyclopentadiene has been studied by several groups.[217,218,219] It has been shown that the endo-isomer (20) and exo-isomer (22) can be formed in a 3:1 ratio, Figure 2.16.



endo (20)

exo (22)

Figure 2.16.

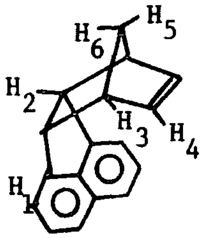
2.8.b. Characterization

The method of Baker and Mason[217] was used with minor modifications, the acenaphthylene, freshly distilled cyclopentadiene and quinol were heated in a sealed glass tube at 175-185°C for 6 hrs. The resulting viscous red oil was vacuum distilled rapidly to give a clear pale yellow liquid containing compounds (20) and (22), and residual acenaphthylene. Pure endo-adduct was obtained by using 'dry column' chromatography (silica gel). Separation of the pure exo-adduct was not achieved by this method. The exo-isomer (22) has been purified by chromatography on silver nitrate impregnated stationary phases, this technique was not plausible for the scale of operation used here. Attempts to separate the endo and the exo isomers by fractional vacuum distillation failed, the relatively long times required for equilibration of the fractionating column resulted in the retro-Diels-Alder reaction becoming predominant.

2.8.b.i. The Characterization of the Endo-Isomer (20)

Elemental analysis of the endo-adduct (20) gave C, 93.68; H, 6.07% whereas the calculated figures for $C_{17}H_{14}$ are C, 93.55; H, 6.45%. The infrared spectrum of the product (Appendix D, no. IX) showed the aromatic absorption of C-H over 3000 $cm.^{-1}$ as well as the aliphatic below 3000 $cm.^{-1}$, the spectrum was in complete agreement with the spectrum reported by Baker. The mass spectrum (Appendix B, no. IX) confirmed the molecular weight of 218, and showed the expected fragmentation pattern. The proton n.m.r. spectrum (Appendix C, no. IX), showed six aromatic, two vinylic, two methine, two bridgehead and two methylene protons as would be expected; comparison of the chemical shifts between this Sample (20) and the data reported by Baker is listed in Table 2.4. below and confirms the assignment.

Table 2.4.

Structure	Samples	H_1	H_2	H_3	H_4	$H_{5,6}$
	Sample (20)	2.65	5.96	6.75	4.62	8.35
	Baker's sample	2.65 (6H)	5.96 (2H)	6.79 (2H)	4.62 (2H)	8.36 (2H)

2.8.b.ii. The Characterization of the Exo-Adduct (22)

The exo-adduct (12) was obtained as a mixture with acenaphthylene and attempts to separate the pure isomer failed. The i.r. spectrum (Appendix D, no. X), ^{1}H n.m.r. (Appendix C, no. X) and mass spectra (Appendix B, no. X) of the product obtained were consistent with a mixture of (22) and acenaphthylene with no additional impurities and this product was used as a mixture for metathesis polymerization studies (see later).

EXPERIMENTAL

2.9. Reagents

Furan and anthranilic acid were purchased from Aldrich Chemical Co. Ltd., and were used without further purification. Isoamylnitrite was purchased from Aldrich Chemical Co. Ltd., and was distilled under dry nitrogen before use. Dry monoglyme was kindly supplied by Mr. B. Hall of this Department.

2.9.a. The Preparation of 1,4-Dihydronaphthalene-1,4-endo-oxide (16)

Dry monoglyme (300 ml.) and furan (300 ml., 310.8 g., 4.2 moles) were placed in a 3-necked round-bottomed flask (2 l.), the middle neck was fitted with a mechanical stirrer, the second neck was fitted with a dropping funnel containing a solution of anthranilic acid (82.2 g., 0.6 mole) in dry monoglyme (300 ml.), and the third neck was attached to a water-condenser which was fitted with a dropping funnel containing isoamylnitrite (120 ml., 104.4 g., 0.89 mole) in dry monoglyme (150 ml.).

The apparatus was purged with dry nitrogen. The mixture in the flask was heated from an oil bath until it refluxed gently, it was stirred continuously throughout the experiment. The reagent solutions in the two dropping funnels were added dropwise to the refluxing mixture in the reaction flask at the same rate. The addition took three hours and the reaction was left another one hour with stirring and refluxing. At this stage the evolution of gases had stopped, and the mixture which was oily and deep red in colour was left to cool to room temperature. The mixture was transferred to a separating funnel (5 l.), sodium hydroxide solution (15%) 400 ml. and petroleum ether 60-80^{o}C (700 ml.) were added. The mixture was shaken thoroughly, two layers separated, the upper one was recovered, washed several times with distilled water. The petroleum ether was then evaporated leaving a red-oily mixture which solidified on cooling, decolorization and recrystallization gave pure white 1,4-dihydronaphthalene-1,4-endo-oxide (42 g. - 51%).

2.10. Reagents

Dicyclopentadiene was purchased from Koch-Light Laboratories Ltd., analar acetone was purchased from Hopkin & Williams, potassium hydroxide was purchased from BDH Chemicals Ltd. Cyclopentadiene was prepared by thermal cracking of dicyclopentadiene and used directly.

2.10.a. Preparation of Dimethylfulvene

Freshly distilled cyclopentadiene (165 ml., 132 g., 2 moles) and an equivalent amount of analar acetone (147 ml., 116 g., 2 moles) were placed in a flask (1 l.) fitted with a reflux condenser which was cooled with ice. Potassium hydroxide in ethanol solution (50 ml., 20%) was carefully added through the reflux condenser. A vigorous exothermal reaction occurred, when this reaction subsided the reaction flask was stoppered tightly and kept cool overnight. The water layer was removed and the mixture was vacuum distilled to remove the low-boiling point materials, followed by dimethylfulvene which was distilled rapidly between 60-80°C. The yellow product was stored under dry nitrogen in the deep freeze, i.r. spectrum (Appendix D, no. II).

2.10.b. The Synthesis of 7-Isopropylidene benzonorbornadiene (17)

Dry monoglyme (200 ml.) and 6,6-dimethylfulvene (31.8 g., 0.3 mole) were placed in a 3-necked round-bottomed flask (1 l.), the middle neck was fitted with a mechanical stirrer, the second neck was fitted with a dropping funnel containing a solution of anthranilic acid (27.4 g., 0.2 mole) in dry monoglyme (100 ml.), and the third neck was attached to a water-condenser which was fitted with a dropping funnel containing isoamylnitrite (40 ml., 23 g., 0.3 mole) in dry monoglyme (40 ml.). The apparatus was purged with dry nitrogen throughout the experiment.

The mixture in the reaction flask was heated from an oil bath until it refluxed gently, it was stirred continuously throughout the experiment. The components in the two dropping funnels were added to the refluxing fulvene solution in the reaction flask at the same rate, the addition took 1½ hours and the flask was left with continual stirring and refluxing for one hour, the gas evolution stopped, and the mixture was allowed to cool to room temperature. The oily mixture which was deep orange to dark red in colour was transferred to a separating funnel (5 l.), sodium hydroxide solution (300 ml., 10%) was added to basify the solution, after thorough mixing petroleum ether 60-80°C (500 ml.) was added and the mixture was shaken vigorously, the upper layer was recovered, washed several times with distilled water, dried over sodium sulphate, the solvent was evaporated and the residual solution solidified on cooling. The crystals were washed and recrystallized twice from cold ethanol to yield 7-isopropylidene benzonorbornadiene as colourless crystal prisms (17 g., 31%, m.p. 91.5°C, lit. 91.5 - 92°C).

2.11. Reagents

α,α',α'-Tetrabromo-o-xylene was purchased from Aldrich Chemical Co. Ltd. and was used without further purification. Sodium iodide and potassium iodide were purchased from BDH Chemicals Ltd.

2.11.a. The Synthesis of Cis- and Trans-1,2-diiodobenzocyclobutene

A mixture of sodium iodide (510 g., 3.4 moles), potassium iodide (23 g., 0.14 mole) and absolute ethanol (1700 ml.) was placed in a 3-necked round-bottomed flask (3 l.), the middle neck was fitted with a water cooled condenser which was attached to a drying tube containing calcium chloride to protect the mixture from moisture. The reaction flask and the condenser were carefully covered with aluminium paper to exclude light and the experiment was carried out in subdued light to further reduce the amount of light reaching the reactants.

The mixture was refluxed gently from an electrical heater for 30 min., and then (240 ml.) of ethanol was removed by distillation. $\alpha,\alpha,\alpha',\alpha'$-Tetrabromo-o-xylene (202.2 g., 0.45 mole) was added to the mixture which was then refluxed continuously for 10 days.

The reaction mixture was allowed to cool slowly to room temperature. Methylene chloride (500 ml.) was added and the resultant slurry was added into cold water (3500 ml.), the water layer was treated with sodium thiosulphate solution to remove iodine, the mixture was shaken vigorously in order to bring the iodine from the methylene chloride layer into the water layer. After, the water layer had separated, it was extracted four times with methylene chloride the extracts were combined and the solvent was removed by evaporation. The residue was vacuum distilled to give a mixture of cis and trans (145 g. at 0.1 mm./60-64^{o}C). The product was allowed to cool slowly, two types of crystals, needles and prisms were noticed. The isomers were successfully separated by careful crystallization from petroleum ether 60-80^{o}C, it was noticed that if the solution of the mixture in petroleum ether was allowed to cool slowly needle crystals formed first and by filtering and transferring the remaining solution to another flask, the prism crystals would form with relatively few needle crystals. Several recrystallizations and separations were carried out in this way and the total weight of products recovered was (125 g., 73.2%). The cis-isomer, needle crystals, m.p. 130-140^{o}, lit. 150^{o} constituted 11.0 g., 8.8% of the product, and the trans-isomer, prism crystals, m.p. 61-62, lit. 62-63, 114 g., 91.2%. The trans-isomer was recrystallized several times and kept in a cool place and away from light.

2.12. Reagents

Trans-1,2-diiodobenzocyclobutene was prepared and purified in the previous experiment. Dicyclopentadiene was cracked by thermal distillation to give cyclopentadiene which was used immediately after preparation. The zinc dust was purchased from BDH Chemicals Ltd. and was activated before use by stirring in a 10% aqueous ammonium chloride solution and was subsequently washed six times each with water and ethanol.

2.12.a. The Synthesis of Endo-1,4,4a,8b-tetrahydro-1,4-methanocyclobutadibenzene (18)

A suspension of activated zinc dust (50 g.) in absolute ethanol (400 ml.), and freshly distilled cyclopentadiene (50 ml., 40 g., 0.61 mole) were placed in a four-necked round-bottomed flask. The middle neck was fitted with a mechanical stirrer, the second neck was fitted with a thermometer which contacted with electrical control at 30°C to keep the mixture temperature constant, the third neck was fitted with an inlet tube to pass a slow stream of dry nitrogen through the suspension and the fourth neck was fitted with a condenser which was attached to a dropping funnel containing a solution of trans-1,2-diiodobenzocyclobutene (17.0 g., 0.048 mole) in ethanol (300 ml.).

The reaction flask was heated gently from a water-bath and the ethanol suspension was maintained at 30°C throughout the experiment. When half of the diiodide solution was added (2½ hours) a further portion of freshly distilled cyclopentadiene (25 ml., 20 g., 0.3 mole) was poured into the reaction flask. When the addition of the diiodide solution was completed (5 hours), the flask was left for another one hour with continuous stirring. The reaction mixture was filtered to remove the excess zinc dust and the filtrate was concentrated to (∿ 100 ml.) by evaporation, the residual solution was poured into (150 ml.) of distilled water, the resulting white suspension was extracted three times with (150 ml.) portions of petroleum ether, the extracts were combined, washed twice with distilled water (70 ml.), and dried over dry sodium sulphate overnight. The dried solution was vacuum distilled to give 1,4,4a,8b-tetrahydro-1,4-methanocyclobutadibenzene (4.75 g. at 60°C/1 mm., 59.2% based on diiodide).

The experiment was repeated four times to give (19 g., 59.2%) which was carefully redistilled by molecular distillation to give (16 g.) of pure, colourless, liquid material. The material was kept in a cool place and under an atmosphere of dry nitrogen.

2.13. Reagents

Bicyclo[2.2.1]heptadiene was purchased from Aldrich Chemical Co. Ltd. and was distilled before use. Silica gel (Kieselgel 60) was purchased from Fluka AG, Chemische, Fabrick CH-9470 Buchs.

2.13.a. The Synthesis and Purification of Exo-3,4-benzotricyclo[4.2.1.0^{2,5}]-nona-3,7-diene. (The Reaction Between Benzyne with Bicyclo[2.2.1]-heptadiene) (19)

Dry monoglyme (300 ml.) and freshly distilled bicyclo[2.2.1]heptadiene (101 ml., 148.6 g., 1.6 moles) were placed in a 3-necked round-bottomed flask (2 l.), the middle neck was fitted with a mechanical stirrer, the second neck was attached to a water-condenser which was fitted with a dropping funnel containing a solution of amylnitrite (66 ml., 58.1 g., 0.5 mole) in dry monoglyme (150 ml.) and the third neck was fitted with a dropping funnel containing anthranilic acid (68.5 g., 0.5 mole) in dry monoglyme (200 ml.).

The apparatus was purged with dry nitrogen throughout the experiment. The solvent in the reaction flask was heated from an oil bath until it refluxed gently, it was stirred continuously throughout the experiment. The components in the two dropping funnels were added to the refluxing solvent at the same rate. There was considerable evolution of gases and the mixture was at reflux throughout the addition which took two hours. After complete addition of reagents the mixture was refluxed gently for another 1½ hours. At this stage the evolution of gases had stopped and the mixture was oily and dark-orange to dark red in colour, the mixture was allowed to cool down slowly to room temperature. Then the reaction mixture was poured into a separating funnel containing sodium hydroxide solution (200 ml.) which was shaken thoroughly.

The mixture was extracted with petroleum ether 60-80°C (600 ml.), the extracted layer was separated and washed with distilled water (2 l.) several times, the extracted layer was dried over magnesium sulphate overnight, filtered and the petroleum ether was removed by evaporation and the residual solution was kept in the fridge, 5°C.

The same experiment was repeated using dry tetrahydrofuran as solvent with the reagents amount as follows:- amylnitrite (66 ml.) in 180 ml. THF, anthranilic acid (68.5 g.) in (200 ml.) THF, and bicyclo[2.2.1]heptadiene (101 ml.) in 350 ml. THF. The extract from this experiment was combined with the extract from the previous one and both were vacuum distilled to give (24.5 g. at b.p. 88-100/2 mm.) of the pure product which was red in colour.

Two earlier attempts to prepare and purify this compound involved fractional vacuum distillation and were not successful. Consequently, it was decided to use a technique which did not involve heating. 'Dry column' chromatography was the technique selected.

The red liquid (5.5 g.) was dissolved in a small quantity of hexane and carefully introduced as a narrow band at the top of a dry silica gel column (190 x 2.5 cm.), the column was developed and eluted with hexane. The eluted fractions were monitored by t.l.c. which showed that the mixture contained three components. The main product was separated successfully after 10 hours and identified as the exo-adduct (19), 3.0 g.; the second component was also recovered using hexane as eluent and identified as compound (30), 0.8 g. and finally, the column was washed with ethylacetate to recover the third component (1.6 g.) which was not identified.

The experiment was repeated four times to separate the rest of the mixture to give: (i) exo-adduct (19), 14.3 g.; (ii) compound (30), 4.2 g.; and (iii) the unidentified product, 5.0 g. All three products were subjected to a final purification by molecular distillation to give: compound (19), 13.8 g., compound (30), 4.0 g., and the unidentified product, 3.0 g. The compounds were stored under an atmosphere of dry nitrogen in the dark at 5°C.

2.14. Reagents

Acenaphthylene was purchased from Aldrich Chemical Co. Ltd. and used without any further purification.

2.14.a. The Reaction Between Cyclopentadiene and Acenaphthylene

Five batches of acenaphthylene (20 g., 0.13 mole), freshly distilled cyclopentadiene (10 g., 0.15 mole) and quinol (100 mg.) were heated in a sealed glass tube at a temperature between 175-185°C for 6 hours. The resulting viscous red oil in each tube was combined and vacuum distilled to give: (i) unchanged starting materials; and (ii) a clear pale yellow viscous liquid collected in the boiling range 120-140°C/0.1 mm., 84 g.

A sample of endo-adduct was obtained by chromatography using a dry silica gel column (95 x 4.8 cm.). The mixture was eluted with petroleum ether 40-60°C (9 l.) to remove the residual acenaphthylene, the polarity of the solvent was then increased by using a 9:1 mixture of petroleum ether and toluene, pure endo-adduct (13.5 g.) was collected which solidified directly. No further products were eluted when the column was washed with ethylacetate. The exo-adduct was eluted with the acenaphthylene; several attempts were made to separate this mixture chromatographically but with no success. In further experiments, an attempt was made to remove unreacted acenaphthylene by sublimation and then fractionally vacuum distil the mixed adducts; this approach also failed because the prolonged heating required resulted in extensive retro-Diels-Alder reaction.

2.15. Reagents

Hexachlorocyclopentadiene was purchased from Koch-Light Laboratories Ltd. and was distilled under atmosphere of dry nitrogen prior to use.

2.15.a. Attempts to Synthesis Hexachlorobenzonorbornadiene (21)

Dry diglyme (400 ml.) was placed in a 3-necked round bottomed flask

(2 l.), the middle neck was fitted with a mechanical stirrer, the second was fitted with a dropping funnel containing a solution of amylnitrite (66.8 ml., 0.5 mole) in diglyme (200 ml.) and the third neck was attached to a water-condenser which was connected to a dropping funnel containing anthranilic acid (68.5, 0.5 mole), hexachlorocyclopentadiene (160.3 ml., 1 mole) and dry diglyme (600 ml.).

The solvent in the reaction flask was heated from a water-bath until it refluxed gently, the reagents in the two funnels were added slowly and at the same rate to the refluxing solvent. The experiment was carried out under atmosphere of dry nitrogen. The addition took two hours and the reaction was left another two hours with stirring and refluxing, at this stage gas evolution had stopped and the mixture which was oily dark red to black in colour was allowed to cool to room temperature. The solvent was removed and the mixture was vacuum distilled to give unchanged diene and an off-white solid material which by the end of the distillation blocked the condenser (102-110/9 mm.). The solid was recovered, recrystallized and identified as benzoic acid. There was a large quantity of intractable black tar left in the flask. A second attempt gave a similar result.

In a third attempt, the diene was mixed with the solvent in the reaction flask and the reagents were added into the refluxing diene in the reaction flask, the addition took one hour and the experiment was left another one hour with refluxing. The mixture, which was dark-brown in colour, was transferred to a separating funnel (5 l.), sodium hydroxide solution (200 ml., 20%) was added followed by the addition of petroleum ether (800 ml., 60-80°C), the mixture was shaken thoroughly, then distilled water (1500 ml.) was added, two layers separated, the organic layer was separated and evaporation of solvent gave a pale yellow liquid which was essentially perchlorocyclopentadiene. The experiment was abandoned at this stage.

CHAPTER III

Ring-Opening Polymerization of Aryl Cycloalkenes

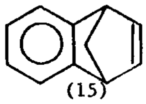
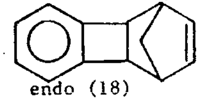
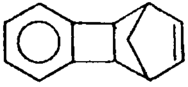
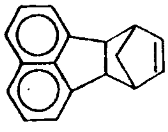
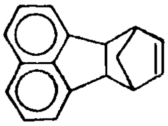
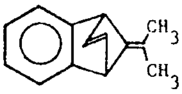
This Chapter describes the polymerization of the monomers whose synthesis was described in Chapter II.

3.1. Successful Polymerizations

The usual procedure for the ring-opening polymerization of a cycloalkene was followed. The catalyst was generated from tungsten hexachloride and a tetra alkyl or aryl tin used in a 1:2 ratio. Tungsten hexachloride was prepared from the reaction of the trioxide with hexachloropropene and purified by removal of oxychloride impurities by sublimation under vacuum. All vessels used were dried and purged with dry nitrogen for at least one hour. A blue-black solution of WCl_6 in dry chlorobenzene was transferred into the reaction flask against a counter current of dry nitrogen using an airtight syringe, the co-catalyst R_4Sn (R = Me or Ph) was then added in the same manner, the ageing time for the catalyst mixture was between (2 and 15 min.), during ageing the colour changed to dark brown in the case of Ph_4Sn and black in the case of Me_4Sn. The monomer solution was injected into the active catalyst mixture, there was an immediate change of colour to red-brown, and after a variable reaction period, the solution became viscous. Reactions were terminated by addition of a small quantity of degassed methanol. All the transformations and additions were carried out under an atmosphere of dry nitrogen. The product was purified by three to five reprecipitations from chlorobenzene into methanol. The products were dried under vacuum at $100^{o}C$ for at least 24 hrs. and kept in the dark at $5^{o}C$, they were usually white materials. The homopolymerization of monomers (15), (17), (18), (19), (20) and (22) were carried out using this procedure, and details are recorded in Table 3.1.

The results presented in Table 3.1. represent a selection from over a hundred polymerizations carried out by the author. The method is straightforward but suffers from irreproducibility, the detailed structure of the active catalyst is not properly understood despite a large volume of

Table 3.1. Reagents, Reaction Conditions, and Product Yields for Successful Ring-Opening Polymerizations[a]

Expt. No.	Monomer	Co-catalyst	W:Sn:monomer[b]	Ageing time (min.)	Volume of solvent[c] (ml.)	Time of obvious viscosity increase	Reaction duration	Yield %
1	 (15)	Ph_4Sn	1:2:67	15	25T	10 sec.	10 sec.	∿ 100[e]
2		Ph_4Sn	1:2:26	15	120T	30 min.	30 min.	79
3		Ph_4Sn	1:2:67	15	6	10 sec.	10 sec.	85
4		Me_4Sn	1:2:67	10	6	30 sec.	30 sec.	83
5		Me_4Sn	1:2:93	8	10	30 min.	30 min.	85
6	 endo (18)	Ph_4Sn	1:2:20	12	14	10 sec.	2 hrs.	71
7		Me_4Sn	1:2:20	10	9	25 min.	2 hrs.	53
8		Ph_4Sn	1:2:135	12	25	10 sec.	20 hrs.	71
9		Me_4Sn	1:2:135	13	25	-	20 hrs.	32
10	 exo (19)	Me_4Sn	1:2:23	15	13	2 min.	4 hrs.	71
11		Me_4Sn	1:2:250	10	20	d	20 hrs.	39
12		Ph_4Sn	1:2:250	10	20	d	20 hrs.	32
13		Ph_4Sn	1:2:250	10	15	d	30 hrs.	58
14		Ph_4Sn	1:2:238	10	12	1½ min.	3 hrs.	58
15	 endo (20)	Ph_4Sn	1:2:60	10	11	5 sec.	5 sec.	∿ 100[e]
16		Me_4Sn	1:2:60	15	11	1½ min.	5 min.	82
17		Ph_4Sn	1:2:139	10	36	8 min.	20 hrs.	100
18		Me_4Sn	1:2:139	10	36	15 min.	20 hrs.	100
19		Ph_4Sn	1:2:35	14	11	d	20 hrs.	100
20		Me_4Sn	1:2:35	14	11	d	-	100
21	 exo (22)	Me_4Sn	1:2:ca.140	10	25	increased in 1½ min., solidified in 10 min.	10 min.	ca.100[f]
22	 (17)	Ph_4Sn	1:2:13	15	122T	d	48 hrs.	49
23		Me_4Sn	1:2:11	2	11	d	20 hrs.	80

[a] *All reactions were carried out at laboratory temperature, i.e. in the range 12^o to 20^{o}C; some reactions appeared to be somewhat exothermic (particularly 15-21) but no attempt to thermostat the reaction vessels was undertaken.*

[b] *Molar ratios.*

[c] *Normally dry chlorobenzene; T indicates experiments where toluene was used.*

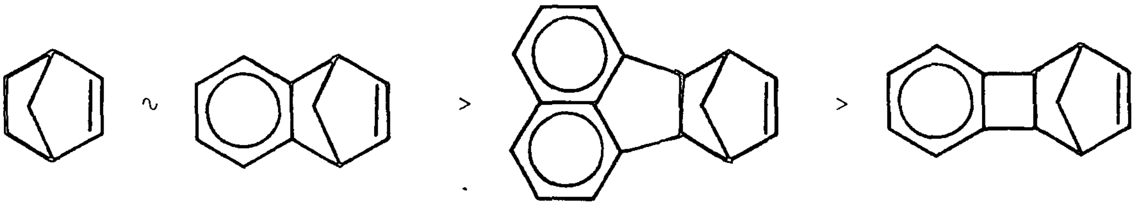
[d] *A slight increase in viscosity was observed during the reaction.*

[e] *The whole mass solidified and could not be redissolved.*

[f] *In this case the monomer was contaminated with acenaphthylene so reaction ratios and yields cannot be reliably quantified.*

published work (see Chapter I). Thus, for example it is not really definitely known whether the active catalyst is generated from $WOCl_4$ or WCl_6. It is established that some oxygen is beneficial with respect to catalytic activity but also that if more than a trace of oxygen gains access to the catalyst activity is destroyed. Similar comments apply to traces of water. These polymerizations were carried out following a standard routine yet on a few occasions reactions failed completely, sometimes variable induction periods were noted, and yields also showed some variability under these circumstances.

No quantitative comparison of the ease of polymerization of these monomers has been attempted, but accumulated experience suggests that the order of reactivity shown below is qualitatively correct.

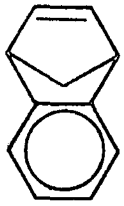
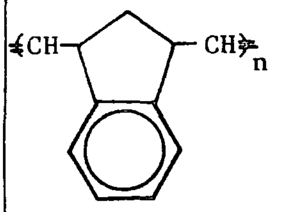
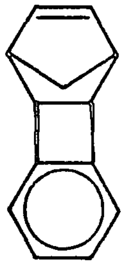
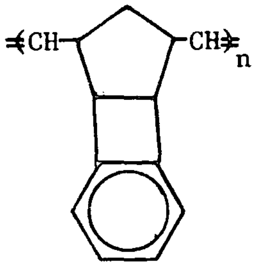
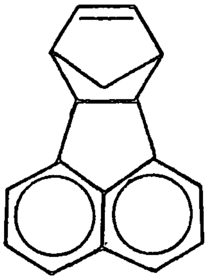
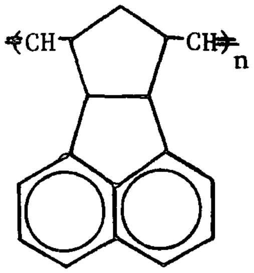
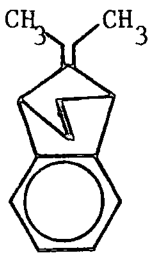
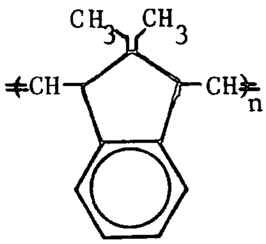


(15) (20), (22) (18), (19)

endo ∿ exo endo ∿ exo

The polymers derived from monomers (15), (17), (18), (19), (20) and (22) showed unsaturation when a solution of polymer immediately discharged the colour of a bromine solution. Also the polymers derived from monomers (15), (20) and (22) showed a marked susceptibility to oxidation which will be discussed in more detail in Chapter IV. One of the consequences of this ease of oxidation is seen in the results of elemental analysis for C and H; the %C values for these materials were marginally low, on the other hand polymers derived from monomers (18) and (19) were much less susceptible to atmospheric oxidation and consequently gave satisfactory analytical results, see Table 3.2.

Table 3.2. Elemental Analysis of Polymers

Monomers	Polymers structure	Polymer no.[a]	Found		Calculated	
			C%	H%	C%	H%
 (15)		poly(15)-2	89.9	7.4	92.9	7.1
		poly(15)-4	84.4	7.3		
		poly(15)-5	86.6	6.5		
 (18) endo (19) exo		poly(18)-9	91.7	7.9	92.8	7.2
		poly(18)-6	87.8	8.2		
		poly(18)-8	90.9	6.7		
		poly(19)-9	91.6	7.6		
		poly(19)-12	92.0	7.6		
		poly(19)-14	91.7	7.8		
 (20) endo (22) exo		poly(20)-16	85.0	7.3	93.6	6.5
		poly(20)-17	90.2	7.5		
		poly(20)-18	91.9	7.5		
		poly(22)-21	92.9	7.1		
 (17)		poly(17)-22	81.6	7.9	92.3	7.7
		poly(17)-23	87.9	7.8		

[a] *The numbering system indicates the monomer in parenthesis and the experiment number (see Table 3.1.) for the synthesis of the particular sample.*

3.1.a. Determination of the Molecular Weight by GPC

Gel permeation chromatography is a technique for separating molecules according to their hydrodynamic volume. Polymers in dilute solution exist as statistical coils, the size of the coil being determined predominantly by a combination of chain stiffness, polymer-polymer and polymer-solvent interactions. The average coil size for a polymer of a particular molecular weight in a specific solvent is its hydrodynamic volume. In practice a particular polymer solution will consist of a distribution of coils of different hydrodynamic volumes. The principle of GPC is that the polymer solution is passed through a chromatography column which sorts the constituents according to their hydrodynamic volumes. The experimental procedure consisted of preparing an approximately 1% solution of the polymer in THF, the solution is filtered through a Millipore filter to remove any particulate matter and injected into the solvent stream which is split into two, one stream is used as reference in the detector system and the other carries the sample through the GPC column and detector. The output from the instrument consists of a curve plotted on a potentiometric recorder, the highest molecular weight components emerging first. From these curves the value of $\bar{M}_n$ and $\bar{M}_w$ can be calculated using a calibration curve (derived from well characterized samples) of molecular weight vs. elution volume. For well characterized polymer systems where solution viscosity has been studied as a function of molecular weight it is possible to use Mark-Howink K and α values to convert the 'polystyrene equivalent' values of $\bar{M}_n$ and $\bar{M}_w$ to $\bar{M}_n$ and $\bar{M}_w$ values for the actual polymer. In the systems studied here this data is not available and the molecular weights recorded are those of polystyrene samples with the same hydrodynamic volume as these aryl substituted polyalkenylenes. A typical example of the calculations is presented in Table 3.3.

Table 3.3. Calculation of $\bar{M}_n$ and $\bar{M}_w$ of Polymer Sample from GPC Data Poly(19)-15

Elution volume (mls.)	Peak height (mm.)	M_i	$N_i = h_i/M_i$ ($\times 10^{-3}$)	$N_i.M_i$	$N_i.M_i^2$ ($\times 10^{-3}$)
12	0	735.095	0	0	
12.5	2	632.702	0.00316	2	1265.10^6
13	8	544.572	0.01469	8	4356.10^6
13.5	27	468.717	0.0576	27	12654.10^6
14	69	383.291	0.18002	69	26447.10^6
14.5	70	365.037	0.19176	70	25552.10^6
15	55	284.291	0.19346	55	15636.10^6
15.5	42	244.692	0.17164	42	10276.10^6
16	29	210.608	0.13770	29	6117.10^6
16.5	18	181.272	0.09930	18	3263.10^6
17	9	152.933	0.05885	9	1376.10^6
17.5	4	127.740	0.031314	4	511.10^6
18.5	2	94.632	0.02113	2	189.10^6
19	1	81.451	0.012277	1	81.10^6
20	0	60.340	0	0	0
			1.089666	336	107723.10^6

$$\bar{M}_n = \frac{\Sigma N_i.M_i}{\Sigma N_i} = \frac{336}{1.089666} = 308350 \rightarrow 308 \times 10^3$$

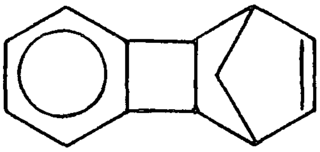
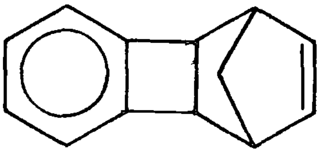
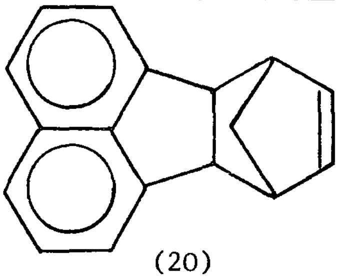
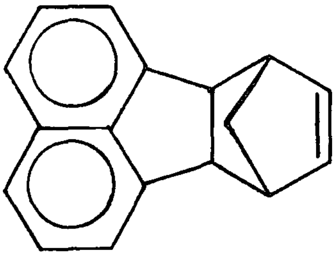
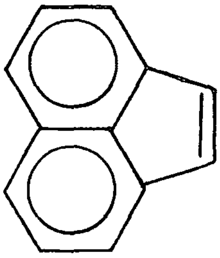
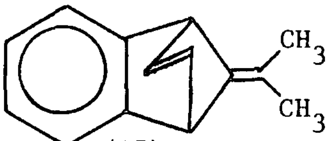
$$\bar{M}_w = \frac{\Sigma N_i.M_i^2}{\Sigma N_i.M_i} = \frac{107723}{336} = 320604 \rightarrow 321 \times 10^3$$

$$\text{poly dispersity} = \frac{\bar{M}_w}{\bar{M}_n} = \frac{321}{308} = 1.04$$

The height of the peak (h_i) is a measure of the number of molecules (N_i) with a given molecular weight (M_i); the molecular weight can be obtained from the pre-calibrated elution volume vs. molecular weight curve.

The GPC curves were measured for all the polymers which gave high viscosity in dilute solution. The observed solution viscosity and the GPC data demonstrates that they are genuine high polymers, in all cases a fairly symmetrical single GPC peak was observed. Table 3.4. summarizes the results of GPC analysis for all the samples analysed in this way.

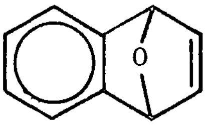
Table 3.4. The Molecular Weight Results of the Polymers

Monomer	Polymer no.	$\bar{M}_n$	$\bar{M}_w$	Poly dispersity
endo  (18)	poly(18)-9	26 x 10^3	187 x 10^3	7.1
exo  (19)	poly(19)-10	85 x 10^3	147 x 10^3	1.7
endo  (20)	poly(20)-18 poly(20)-15	73 x 10^3 308 x 10^3	320 x 10^3 321 x 10^3	4.37 1.04
exo  (22)	poly(22)-21	237 x 10^3	279 x 10^3	1.2
	cationic	9.3 x 10^3	20 x 10^3	2.2
 (17)	poly(17)-22	13 x 10^3	25 x 10^3	1.9

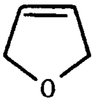
There is quite a wide variation in the molecular weight and polydispersity of the samples examined. However, these variations may depend on factors such as detailed reaction conditions (e.g. monomer:catalyst ratios, and concentrations) and on the structure of monomer and/or catalyst. There clearly are variations but there is insufficient data to detect any trends which might be explainable in terms of the factors mentioned above.

3.2. Unsuccessful Polymerizations and Copolymerization of Hetero-substituted Cycloalkenes

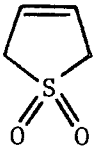
In an attempt to extend the range of monomers which can be polymerized by this technique, three heteroatom containing compounds (16), (33) and (34) were exposed to the catalyst system both alone and in mixtures with norbornene.



(16)

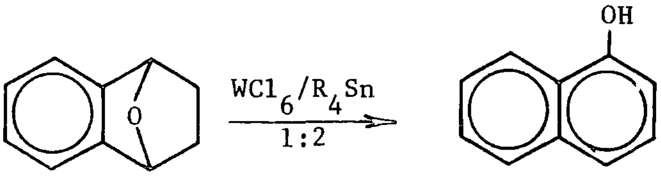


(33)



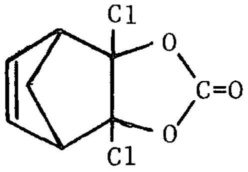
(34)

The usual procedure for the ring opening polymerization of cycloalkenes was applied here using the catalyst system WCl_6/R_4Sn. It was found that the reaction of (16) failed to give polymer and gave instead compound (35). The structure of (35) was confirmed by elemental analysis, i.r. and mass spectroscopy. The attempted polymerization of (33) and (34) also failed.

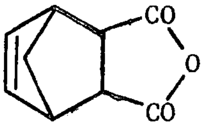


(16) (35)

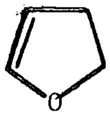
Attempted copolymerization of (33) and (34) also failed. Attempted copolymerization of (16) and (33) with norbornene failed to give either copolymer or polynorbornene. In all cases the reagents used were checked by generating a catalyst solution which successfully homopolymerized norbornene. The reaction results are listed in Table 3.5. As can be seen the catalyst system WCl_6/R_4Sn failed to ring open polymerize these monomers, indeed the monomers were found to inhibit the reaction and to prevent the polymerization of norbornene which is normally particularly susceptible. The heteroatom lone pairs are presumably so basic that they block any 'active sites' established on the transition metal, it is not unreasonable that they should be better donors than the π-electrons of alkenes. However, it is also worth noting that heteroatom containing monomers such as (35)[220a] and (36)[220b] can be polymerized by catalysts of the WCl_6/R_4Sn type, and that Höcker recently described[221] ring open polymerization of (37) using a catalyst based on chromium. Thus, the present failure with monomers (16), (33) and (34) should not be regarded as necessarily final. It may be that coordination of the double bond to the active site with these monomers brings the heteroatom into close proximity, whereas with monomers (35) and (36) the alkene and heteroatoms are well separated in space. Such a rationalization would not, of course, be applicable to monomer (37) and clearly much work remains to be done in this area of catalyst activity and monomer structure.



(35)

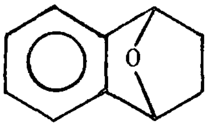
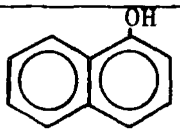
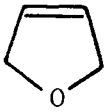
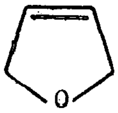
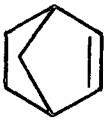
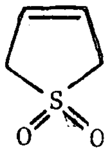


(36)



(37)

Table 3.5. Unsuccessful Attempts to Polymerize and Co-polymerize Monomers (16), (33) and (34)

No.	Monomers	Monomers' ratio	Catalyst, ratio 1:2	Recovered material
1			WCl_6/Ph_4Sn	 80% of the starting
2	"		WCl_6/Me_4Sn	" ∿ 80% of the starting
3	" + 	1:1	WCl_6/Ph_4Sn	Ph_4Sn
4	" "	1:1	WCl_6/Me_4Sn	-
5			WCl_6/Ph_4Sn	Ph_4Sn
6	"		WCl_6/Me_4Sn	-
7	 + 	1:1	WCl_6/Me_4Sn	-
8	" + "	1:1	WCl_6/Ph_4Sn	Ph_4Sn
9			WCl_6/Ph_4Sn	Ph_4Sn
10			WCl_6/Ph_4Sn	Polynorbornene

EXPERIMENTAL

3.3. Reagents and Technical Methods

Analar chlorobenzene was purchased from B.D.H. Chemical Co. distilled under dry N_2 from P_2O_5 and used directly as solvent for catalyst and monomers; WCl_6 was prepared[115] and purified by sublimation to remove oxychlorides and impurities. WCl_6 was dissolved in chlorobenzene and measured out by volume of solution, this procedure was more convenient and reproducible than weighing out WCl_6 in a glove box (as previously), WCl_6 solutions were stable for upto six weeks. Tetraphenyl tin and tetramethyl tin were purchased from Aldrich Chemical Company Inc. and they were used without any further purification. Precautions were taken to dry solvents, equipment and nitrogen. The nitrogen gas was dried by passing it through a bubbler of concentrated sulphuric acid and then through a column of P_2O_5 and a glass trap immersed in liquid air, the nitrogen system connections were glass or nylon tubes, teflon sleeves were used around stoppers instead of using silicon grease, while three way taps were used to bring the nitrogen into the reaction flask, one way was connected to the nitrogen system and the other to bubbler to avoid any chance of introducing air. All the transformations of the solvents, catalyst mixtures and monomers were carried out under an atmosphere of dry nitrogen using air-tight syringes. All the reaction flasks were dried overnight in the oven and purged with dry nitrogen for at least one hour before the polymerization.

3.4. Typical Example of the Polymerization Procedure

One typical example of the reaction will be described here.

A two necked round-bottomed flask (100 ml.) containing a magnetic follower was used for all polymerizations, the first neck was closed with a stopper and the second neck was fitted with a three way tap which was connected to the nitrogen system and a bubbler containing heavy white oil. The reaction flask was purged with dry nitrogen for at least one hour.

1 to 2 ml. of prepared WCl_6 in solvent was placed in the reaction flask along with solvent (2 to 5 ml.) Tetraphenyltin or tetramethyltin was then added, the mixture was stirred for (2 to 15 min.). The colour usually changed from blue-black to dark brown and to dark black in the case of Me_4Sn. The monomer was dissolved in 5 ml. of solvent and was added to the active catalyst solution using a dry air-tight syringe. All additions were carried out against a counter current of nitrogen. An immediate colour change to dark blue or to dark red/brown in the case of Me_4Sn was clearly observed. An increase in viscosity was noticed for all the reactions, the time and magnitude of this viscosity increase was dependent on the details of the particular experiment. The experiment was usually left for some time with stirring then the polymerization was terminated by addition of a small quantity of degassed methanol and the polymer was precipitated using a five-fold excess of methanol. Usually white material was recovered which was purified by 3 to 5 reprecipitations from C_6H_5Cl into CH_3OH; the products were dried carefully under vacuum at 100^oC for at least 24 hrs. and kept in the dark at ca. 5^o.

CHAPTER IV

Characterization and Properties of the Polymers Prepared in this Study

4.1. Structural Characterization of the Polymers

The polymers produced from monomers 15, 17, 18, 19, 20 and 22 were formed via ring-opening polymerization, this was confirmed by the combination of several analytical techniques. Elemental analysis and G.P.C. determination of molecular weight (previous Chapter) confirmed that the products were all simple addition polymers. In this Chapter the elucidation of molecular structure will be described, three spectroscopic methods form the basis of the analysis, i.r., ^1H n.m.r. and ^{13}C n.m.r. The Chapter concludes with some observations on the oxidative stability of these materials.

4.1.a. Infrared Spectroscopy

The infrared spectra of the freshly prepared polymers were recorded either as solvent cast films or as KBr discs. All the spectra showed the expected C-H aromatic absorptions above 3000 cm.$^{-1}$ as well as aliphatic C-H absorptions in the 2840-2950 cm.$^{-1}$ region; similarly absorptions at 1600 cm.$^{-1}$ in all the spectra are assigned to aromatic breathing modes. A strong band at _ca._ 970 cm.$^{-1}$ was found in the spectra of all the polymers and was not present in the monomer spectra. In unsaturated hydrocarbon polymers the out-of-plane C-H deformation mode has been used extensively to identify cis- and trans-CH=CH-units; the trans unit giving rise to an absorption at _ca._ 970 cm.$^{-1}$ and the cis to an absorption _ca._ 740 cm.$^{-1}$ Thus the presence of a new band at 970 cm.$^{-1}$ in all these polymers indicates trans main chain vinylene units. There were also bands at _ca._ 740 cm.$^{-1}$ in all the monomer and polymer spectra, therefore it can be concluded that the unsaturated units are present with both cis- and trans-geometry in all the polymers. This is in agreement with expectation for ring opening polymerization with catalysts of the type used in this work.

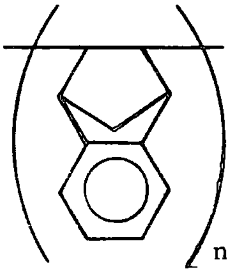
It should be noted that polymer 22 was produced from impure monomer, and that detailed comparison of the i.r. spectrum of poly(22-21) (Appendix D, no. XXVII) with that of pure poly(acenaphthylene) (Appendix D, no. XXVIII) confirms that the product is the expected mixture of ring-opened poly(22) and the vinyl polymer from the acenaphthylene impurity, earlier work had established that acenaphthylene does not undergo ring opening polymerization with the catalyst systems used in this work.[115] Table 4.1. lists the locations for the i.r. spectra of selected polymers, identification of the polymers is according to systems described in Table 3.1.

Table 4.1. I.r. Spectra of the Polymers

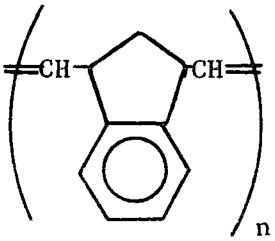
Polymer no.	Method of preparing the sample	Spectrum no. in Appendix D	Polymer no.	Method of preparing the sample	Spectrum no. in Appendix D
poly(15-3)	Film	XII	poly(19-10)	Film	XIX
poly(15-4)	"	XIII	poly(19-12)	KBr	XX
			poly(19-13)	KBr	XXI
poly(17-22)	KBr disc	XIV	poly(19-14)	KBr	XXII
poly(17-23)	" "	XV			
			poly(20-15)	Film	XXIII
poly(18-7)	KBr disc	XVI	poly(20-17)	KBr	XXIV
poly(18-8)	Film	XVII	poly(20-18)	Film	XXV
poly(18-9)	Film	XVIII	poly(20-19)	KBr	XXVI
			poly(22-21)	Film	XXVII

4.1.b. ^{1}H n.m.r. Spectroscopy

The ^{1}H n.m.r. spectra of the polymers were in agreement with the structures proposed. As a typical example consider poly(15). Polymerization of benzonorbornadiene (15) by WCl_6/Ph_4Sn could give rise to a vinyl polymer (15-A) as well as expected ring opening polymer (15-B). It was found that the polymer



(15-A)



(15-B)

actually produced was rapidly photo-oxidized, 15-A would not be expected to be so easily oxidized as 15-B, this observation will be discussed in more detail later in this Chapter. In the ^{1}H n.m.r. spectrum of the polybenzonorbornadiene with Structure (15-B) four aromatic, two vinylic, two methine and two methylene signals would be expected; whereas structure (15-A) would be expected to give rise to four aromatic, four methine and two methylene signals. In the event the ^{1}H n.m.r. spectrum of the freshly prepared polymer showed signals which were only consistent with the structure (15-B), with broad resonances at 7.2 (aromatic), 5.6 (vinylic), 3.9 (methine) and 1.5 p.p.m. (methylene) in the relative intensity ratio 2:1:1:1; thus providing good proof that the structure of the polymer repeat unit was (15-B) and not (15-A).

The ^{1}H n.m.r spectra for all samples were recorded at 90 MHz using FT accumulation, none of the spectra showed well resolved bands and the data in Table 4.2. refers to centres of broad bands.

Table 4.2. ^{1}H n.m.r. Spectral Parameters

Polymer no.	Chemical shifts[a] and assignments				
	aromatic	vinylic	benzylic	allylic	methylene
poly(15)	7.2 4H	5.6 2H	3.9 2H	-	1.5 2H
poly(18-9)	7.1 + 6.9 4H	5.5 2H	3.8 2H	3.0 + 2.6 2H	1.6 + 1.2 2H
poly(19-16)	7.1 4H	5.6 + 5.5 2H	3.8 2H	3.1 + 2.7 2H	2.1 + 1.7 2H
poly(20-18)	7.6 + 7.2 6H	5.5 2H	4.2 2H	3.1 + 2.7 2H	1.6 2H

[a] *Chemical shifts in p.p.m. downfield from external TMS.*

Despite the poor resolution of these spectra there were some indications of structure to be deduced. Thus the band assigned to the vinylic hydrogens generally had the appearance of two overlapping peaks of approximately equal intensity and in the case of poly(19-10) was actually resolved into two distinct bands, this observation is consistent with approximately equal amounts of cis- and trans-double bond units in the main chain. As indicated in Table 4.2. the benzylic hydrogens were observed as single peaks, whereas the allylic and methylene hydrogens were generally resolved into two broad bands of approximately equal intensity. It is difficult to attach a clear interpretation to these later observations although the methylene hydrogens will be in different environments and may be expected to give rise to an AB quartet which is broadened into the two bands observed. The two allylic absorptions may result from different environments arising from the various chain tacticities which are possible; however, the data are not good enough to justify extensive speculation.

4.1.c. ^{13}C Nmr Spectroscopy

^{13}C Nmr spectroscopy provides a powerful tool for looking not only at the cis/trans content of unsaturated polymers but also, in favourable cases, at the detailed tacticity of the repeat units. Ivin and co-workers have investigated the ^{13}C nmr spectra of many polymers prepared by ring-opening of cyclic and bicyclic olefins, including poly(1-pentenylene),[222] poly(1,3-cyclopentylene vinylene)[223] and related norbornene derivatives.[224-228]

The first problem they looked at was that of defining the relative proportions of cis- and trans-linkages. As was mentioned earlier, this question can also be answered by analysis of the intensities of the out-of plane bending modes of vinylic C-H bonds, however work by Ivin's group established that ^{13}C nmr spectroscopy provides a more reliable quantitative analysis than infrared spectroscopy. They also showed that ^{13}C nmr spectroscopy allows several different independent measurements of the cis/trans ratio to be made and the internal consistency of these measurements may be taken as good evidence of their accuracy. They recorded the ^{13}C nmr spectra of poly(1,3-cyclopentylene vinylene) with varying amounts of cis- and trans-unsaturation. Three samples of poly(1,3-cyclopentylene vinylene) (Figure 4.1.) were prepared and examined, on the basis of i.r. analysis they were known to be all cis (spectrum a), 50:50 cis/trans, > 80% trans (spectrum c). The spectra are reproduced in Figure 4.2. In the spectrum of the 50:50 cis/trans polymer the number of signals observed

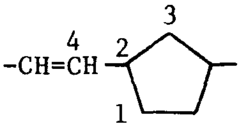


Figure 4.1.

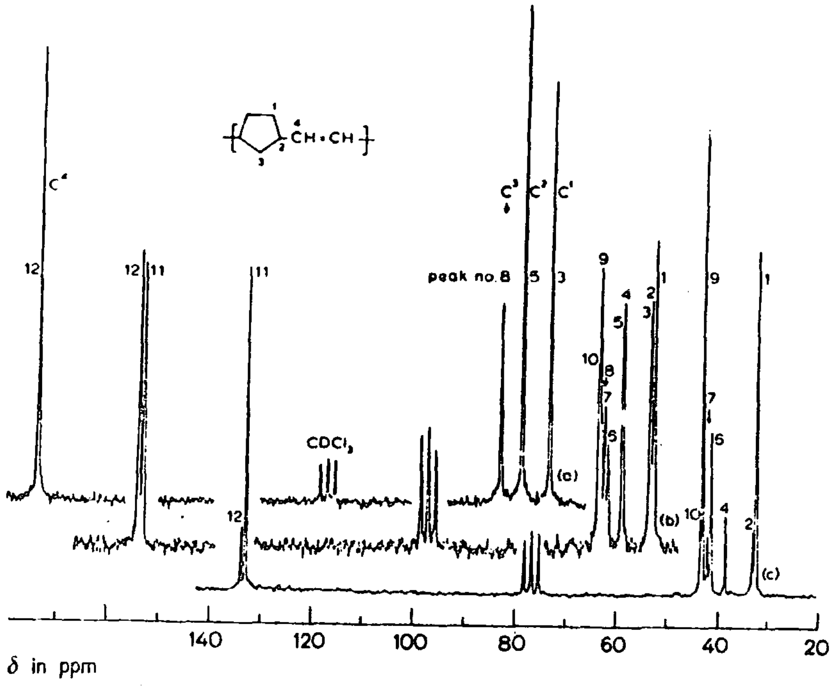


Fig. 4.2. ^{13}C nmr spectra of three samples (a), (b), (c) of poly(1,3-cyclopentylene vinylene) in $CDCl_3$. Polymers prepared using (a) $ReCl_5$, (b) $WCl_6/C_2H_5AlCl_2$, (c) ruthenium complex, as initiators. The scale refers to spectrum (c). Spectra (b) and (a) are offset by 20 p.p.m. and 40 p.p.m. respectively.

cannot be explained simply by the fact that the chemical shifts of the C^1, C^2 and C^3 carbon atoms (Figure 4.1.), are sensitive to the geometrical isomerism about the nearest double bond, but requires that they are also sensitive to the geometrical isomerism about the next nearest double bond. Therefore, four peaks should be observed for the poly(1,3-cyclopentylene vinylene) containing both cis- and trans-unsaturation for both C^2 and C^1, i.e. 2tt, 2tc, 2tc and 2ct* and 1tt, 1tc, 1ct and 1cc respectively. For C^3, which is symmetrically situated between two double bonds, three signals should be expected corresponding to 3tt, 3tc ≡ 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 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 intensities of the signals due to cis-C^4 and trans-C^4, i.e. the vinylic carbons, where:-

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

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

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

$$\sigma_c = \frac{3cc + 0.5\ (3ct + 3tc)}{(3tc + 3ct) + 3cc + 3tt}$$

Using this argument, and the fact that in simple alkenes the α-cis carbon atoms always appear about 5 p.p.m. upfield from α-trans carbon atoms,[229] together with a comparison of the ^{13}C n.m.r. spectra of 100% cis-poly-(1,3-cyclopentylene vinylene) and > 80% trans-poly(1,3-cyclopentylene vinylene) [i.e. Figures 4.2a. and 4.2c. respectively], all the signals in the spectrum of the 50% cis-poly(1,3-cyclopentylene vinylene) could be assigned

---

* *The nomenclature used was proposed by Ivin et al.,*[222] *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.*

as shown in Table 4.3. Further, the relative proportion of cis-vinylene

Table 4.3.[222] Chemical Shifts in the ^{13}C N.m.r. Spectra of three samples (a), (b) and (c) of poly(1,3-cyclopentylene vinylene)

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 p.p.m. downfield from TMS.*

units (σ_c) in each polymer as determined from the C^1, C^2, C^3 and C^4 signals were internally consistent within 1%.

The question of determining tacticity of ring placements in ring-opened poly(norbornene) and related polymers is rather complicated. Ivin and co-workers have prepared fully trans- and fully cis-polymers in order to study this problem and have established that a polymer of one enantiomer of exo-5-methylbicyclo[2.2.1]hept-2-ene having all cis geometry has a fully syndiotactic ring sequence with the methyl group alternating tail-tail

(TT) and head-head (HH).[226] Polymers having more than 80% trans have an atactic ring sequence while the polymer having a 74:26 cis/trans ratio has mainly syndiotactic cis-junctions and isotactic trans-junctions (Figure 4.3.). They also showed how these results may be related to the mechanism of ring opening polymerization of norbornene.[227] They postulated four stereochemical possibilities for the way in which successive monomers can be attached to the reactive metallo-carbene chain end;[222] it was assumed that the most likely direction of approach of the monomer to the transition metal would involve the exo-face.[224] The metallocyclobutane intermediate so formed would open to give a specific chain geometry and tacticity. One of the four possibilities is shown in Figure 4.4.

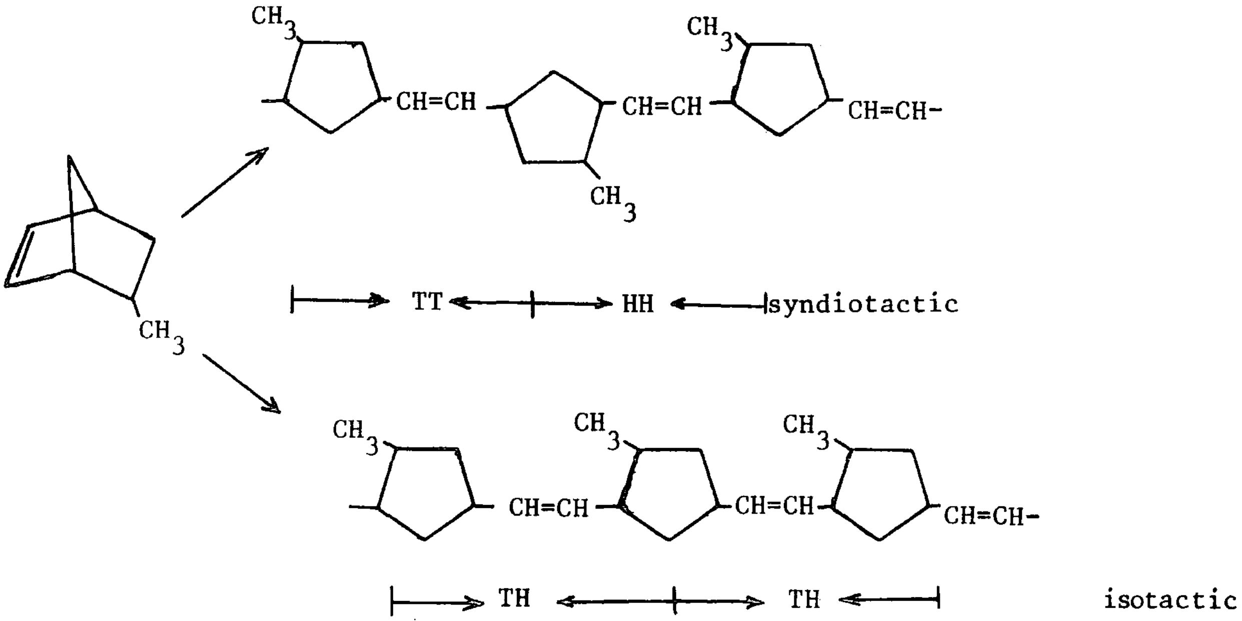


Figure 4.3.

In this example the polymer chain and the methylene bridge of the incoming monomer have a syn relationship, and this leads to a cis unit in the polymer chain and to successive syndiotactic ring placements. The other three modes of monomer incorporation involve firstly monomer approach via the exo-face with the growing polymer chain and the monomer methylene

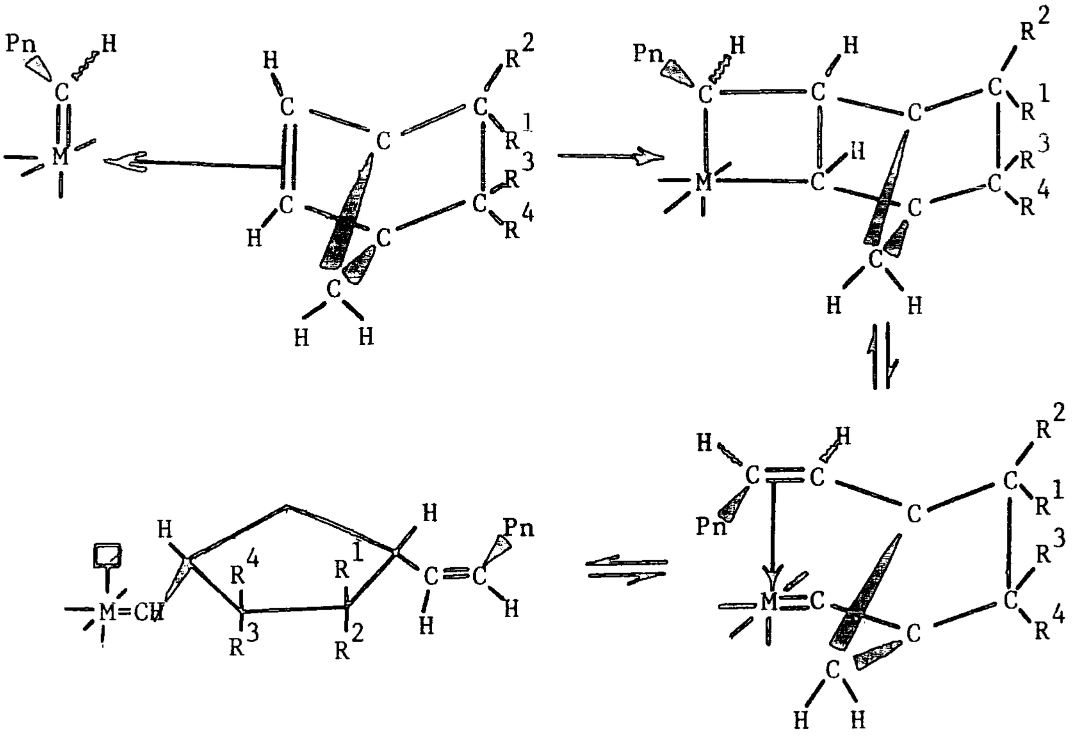


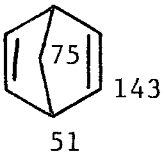
Figure 4.4.

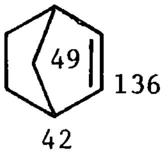
(Pn is the polymer chain containing n monomeric units)

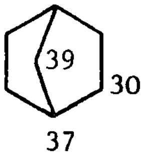
bridge in an anti-relationship (giving trans double bonds and isotactic ring placements), and then two other modes in which the growing polymer chain points along the direction of monomer approach or away from the direction of monomer approach (giving random cis/trans units and atactic chains). The formation of polymers with a high cis vinylene content and syndiotactic ring placement generally occurs with catalysts active at low temperatures and assumed to have relatively low conformational mobility of the metallo-carbene unit, as the temperature is raised the conformational mobility increases and the tendency to stereoregularity decreases. The results of these complicated arguments, reviewed only briefly above, apply to a small group of catalysts and monomers, and although they appear convincing several more systems will have to be analysed before the conclusions can be generalized.

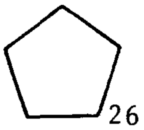
The above discussion provides a background for the analysis of the ^{13}C nmr spectra of the polymers produced in this work. As with the analysis of the ^{1}H nmr spectral data the spectrum of the relatively simple poly(benzonorbornadiene) [poly(15)] will be discussed in some detail prior to summarizing the results for the other materials.

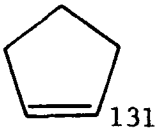
The ^{13}C nmr spectra of the benzonorbornadiene (Appendix E, no. I) and the freshly prepared polymer (Appendix E, no. V) were recorded as solutions in $CDCl_3$ at 22.635 MHz using tetramethylsilane as internal reference. The prediction of shift in ^{13}C nmr spectroscopy is complicated and small changes in structure can result in very large changes in shift. Before discussing the spectra of benzonorbornadiene and its polymer it is necessary to consider the observed shifts for the related systems shown below:



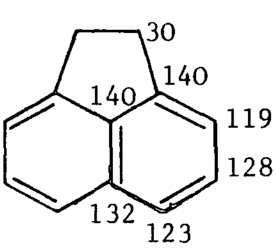


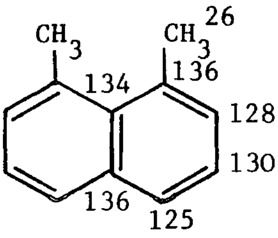




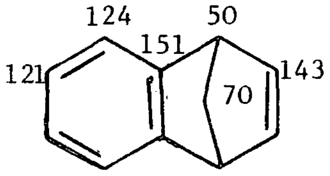


The quoted chemical shifts are in p.p.m. downfield from tetramethylsilane; it can be seen that for all types of carbon decreasing ring strain results in an upfield shift. A similar effect is seen in the two structures shown below, thus all the signals for the carbons in the five membered ring are shifted to higher field in the unstrained analogue, 1,8-dimethylnaphthalene.

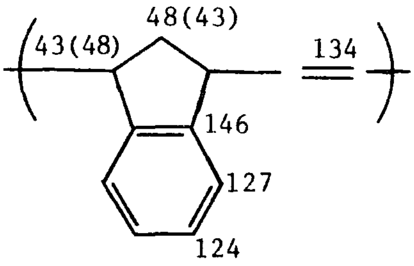




In this last example it is also interesting to note that the aromatic carbons not initially part of the five membered ring experience a downfield shift in the less strained system. In the spectrum of benzonorbornadiene (15) six signals are seen; the highfield signals at 50 and 70 p.p.m. are



(15)



poly(15-B)

assigned to the methine and methylene carbons by analogy with the data given above; the bridging aromatic carbons give a low intensity signal as expected and are assigned to the signal at 151; the two other aromatic signals at 121 and 124 are assigned by analogy with other ortho-substituted aromatics, leaving the vinylic signal at 143. The spectrum of the freshly prepared polymer also showed six signals at 43, 48, 124, 127, 134 and 146 p.p.m. The first point to note is that this spectrum is only consistent with structure (15-B) because there are two aliphatic and four aromatic and vinylic signals, structure (15-A) would require three aliphatic and three aromatic signals. By analogy with the data given above an assignment of the observed signals can be made as shown above, all the observed shift changes are consistent with the trends discussed above, although the assignment is not totally unambiguous particularly for the aliphatic carbons. The vinylic carbon signal appeared to be partially resolved into a doublet, most ring-opening polymerizations with WCl_6/Ph_4Sn give an approximately equal amount of cis- and trans-double bonds along the polymer chains, the partial resolution of the vinylic carbon signal suggest that this also occurs in the ring-opening polymerization of benzonorbornadiene. In this case the spectrum of the polymer was not sufficiently well resolved to justify more detailed analysis.

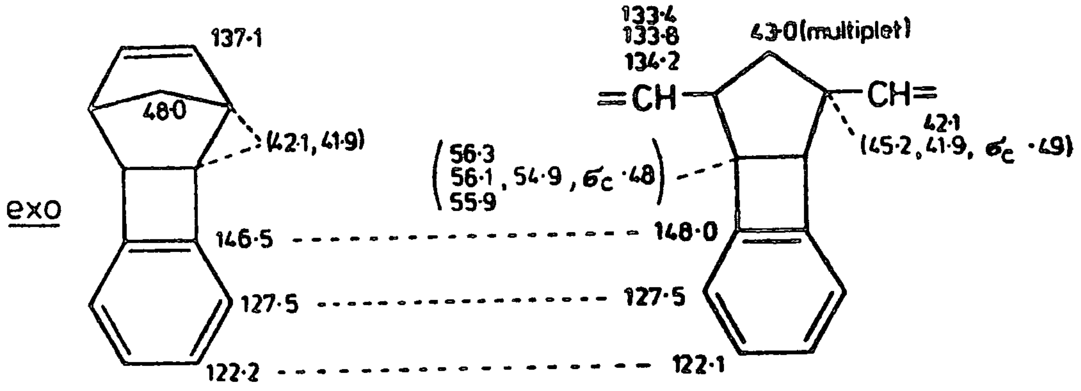
The ^{13}C nmr spectral assignments for monomers 15, 18, 19 and 20 (Appendix E, nos. I, II, III and IV respectively) and the polymers derived from them poly(15-2), poly(18-9), poly(19-10), poly(20-15), poly(22-21) and the cationic polymer of acenaphthylene (Appendix E, nos. V, VI, VII, VIII, IX and X respectively) follow fairly straightforwardly from the background data presented in the discussion of benzonorbornadiene's polymerization (see above) and the analysis of the spectra of norbornene polymers presented by Ivin and co-workers;[227,230] these assignments are recorded diagrammatically in Figure 4.5.

Unfortunately in these spectra there is some overlap between the various signals assigned to methylene and methine carbons in the polymers, this makes totally unambiguous calculation of the proportion of cis/trans isomerism in the vinylene units difficult. However, where the spectra are sufficiently well resolved to be assigned the cis:trans ratio is close to 1:1 as would be expected for catalyst systems based on WCl_6 activated by organo-tin compounds. Thus, in poly(19-10) the proportion of cis vinylene units (σ_c) calculated from the benzylic carbon signals is 0.48 and from the allylic carbon signal 0.49; for poly(18-9) the allylic carbon signal gives $\sigma_c = 0.45$ and analysis of the aromatic carbon signals gives $\sigma = 0.44$; for poly(20-15) values of σ_c of 0.50 and 0.49 are obtained from allylic and aromatic signals respectively. Although the signal to noise ratio and resolution obtained to-date do not allow a detailed analysis of polymer chain structures for these materials there are some interesting differences between the spectra obtained from polymers(19-10) and (18-9). In particular, the splitting of the signals due to four of the aromatic carbons in poly(18-9) when compared with the sharp singlets observed for the analogous carbons in poly(19-10) (see Figure 4.5.) imply an interaction between these nuclei and the adjacent cis- and trans-vinylene carbons, this would not

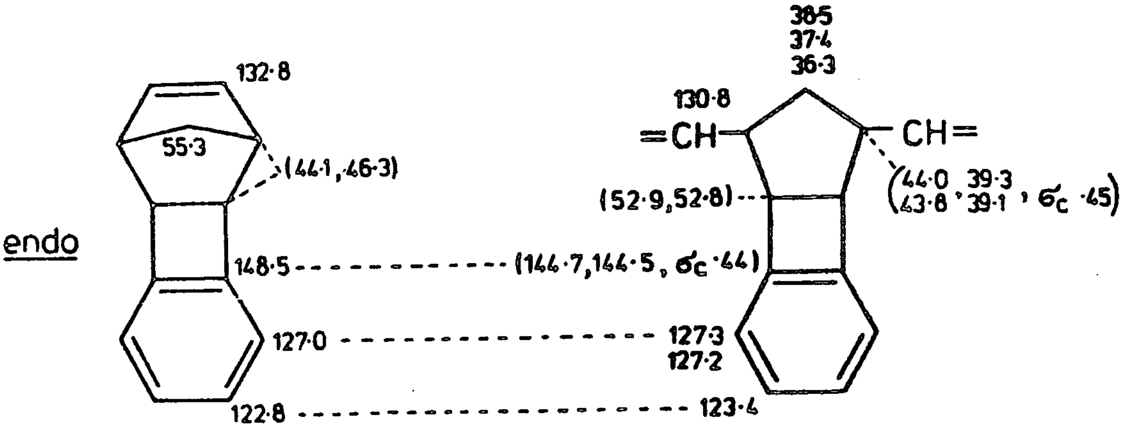
Figure 4·5

^{13}C N.m.r. chemical shift assignments^{a}

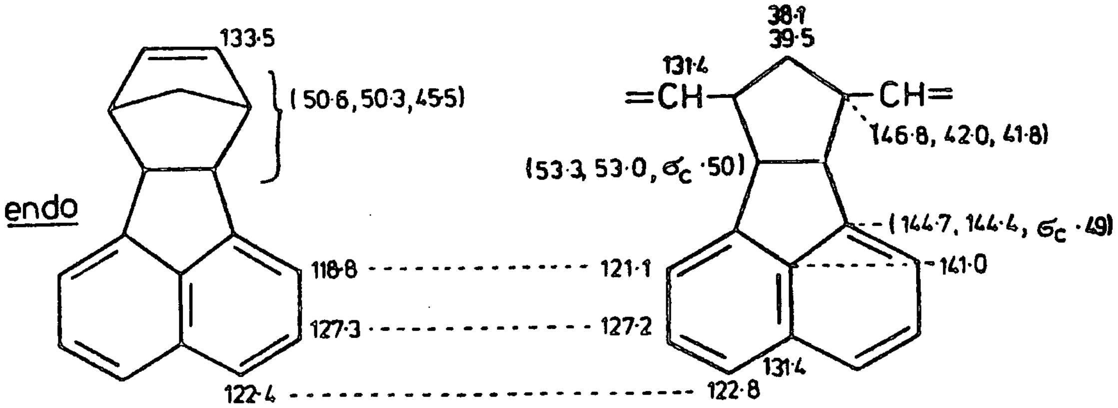
Monomer Polymer



(19) poly (19-10)



(18) poly (18-9)



(20) poly (20-15)

a) Spectra recorded as $CDCl_3$ solutions, shifts in ppm downfield from TMS, σ_c represents the fractional content of cis double bonds derived from the relative intensities of the signals quoted following the analysis of Ivin (Ref. 230) be unreasonable since in poly(18-9) the aromatic and vinylene units are constrained to be fairly close to each other. Further examination of this matter was not possible since unfortunately the vinylene carbons appear as an unresolved broad signal. Similarly, the benzylic carbons in poly(19-10) appear as a combination of a triplet (56.3, 56.1, 55.9) and a singlet 54.9 whereas the analogous signal in (18-9) is a doublet (52.9, 52.8). These observations indicate that detailed structural information is encoded in the ^{13}C spectra but a reliable interpretation requires spectra with a better signal to noise and resolution, and preferably simpler spectra from polymers where the vinylene units are exclusively cis or trans rather than a 1:1 mixture of these geometries.

4.2. Susceptibility of Polymers to Oxidation

The first polymer prepared in this work was poly(benzonorbornadiene). It was expected that this material would be relatively easily oxidized and that it might make an interesting structure for the study of polymer-oxidation and photo-oxidation. The tertiary hydrogens in poly(benzonorbornadiene) are both allylic and benzylic and would be expected to be particularly susceptible sites at which oxidative degradation could be initiated. Both singlet and triplet oxygen might be involved in the process as shown schematically in Figure 4.6.

In fact poly(benzonorbornadiene) proved to be so susceptible to oxidation that even after several attempts, and despite taking precautions to avoid exposure to air at any stage, the author has been unable to prepare a completely unoxidized sample of this material. This question was discussed in the author's M.Sc. Thesis and further work since that date has not succeeded in obtaining the pure hydrocarbon polymer, although much better film samples have been prepared than was originally possible. It has to be concluded that the facilities presently available in these

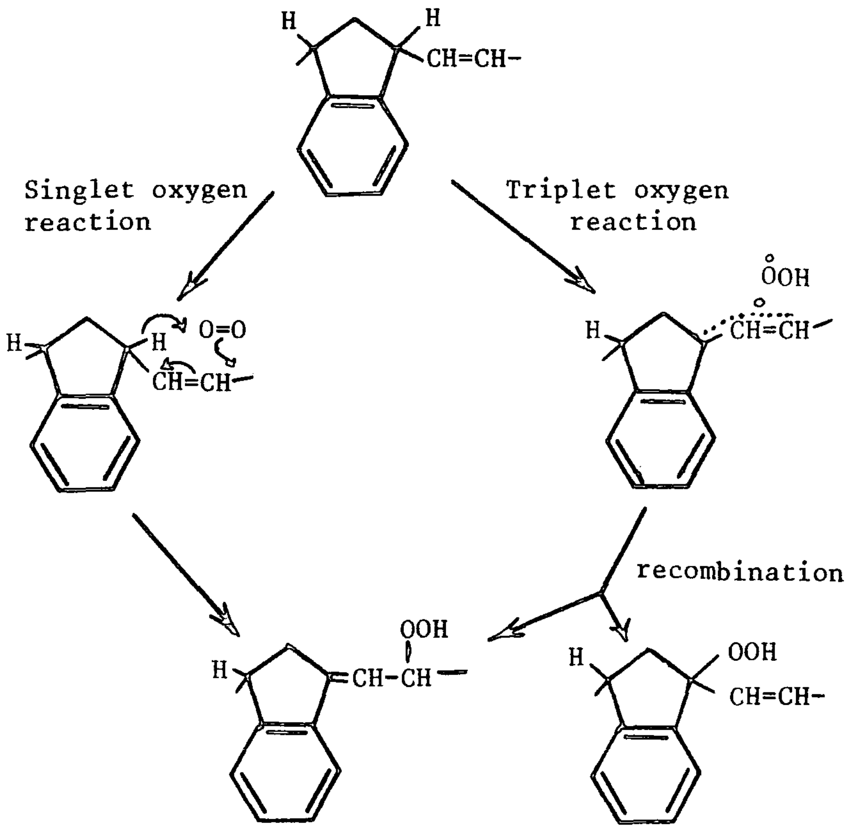


Figure 4.6. Possible primary steps in the oxidative degradation of poly(benzonorbornadiene)

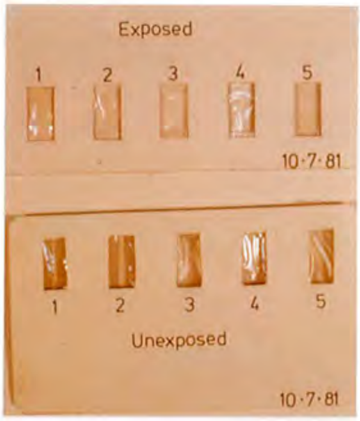
laboratories for carrying out studies under an inert atmosphere are not adequate for manipulation of this extremely readily oxidized material. If such facilities were to be available in the future it seems likely that the initial stages of oxidation should be readily detected and the two types of primary peroxy product should be readily distinguished by a variety of spectroscopic techniques.

The new poly(arylene cycloalkenylene vinylenes) produced in this work (i.e. poly(18), poly(19), poly(20) and poly(22)) might be expected to be less susceptible to oxidation than poly(benzonorbornadiene). Consideration of the repeat unit structures shows that in poly(benzonorbornadiene) the tertiary hydrogens are both allylic and benzylic, whereas in the polymers from monomers (18), (19), (20) and (22) there are two types of tertiary hydrogen which are either allylic or benzylic, consequently it might be expected that these polymers would be less susceptible to oxidation than poly(benzonorbornadiene). Initial observations, particularly elemental analysis results, suggested that poly(20-18) and poly(22-21) were as readily oxidized as poly(benzonorbornadiene) (15-2) whereas poly(18-7) and poly(19-12) appeared to be significantly more stable.

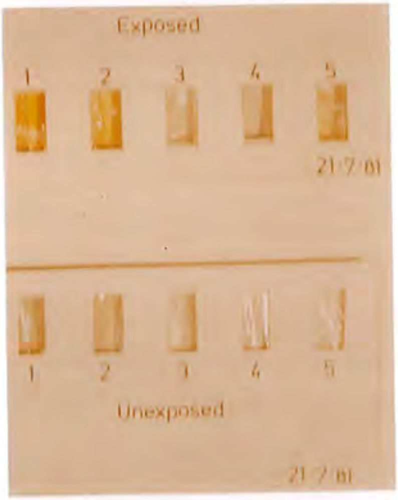
A qualitative indication of the susceptibility of these polymers to degradation is provided by the results of exposing dilute solutions of the polymers in chloroform to direct sunlight. Solutions of poly(15-2), poly-(20-18) and poly(22-21), which were colourless as made up in the subdued lighting of the laboratory, darkened rapidly on exposure to direct sunlight (Pyrex test tubes). After 10 to 15 minutes a distinct yellow colour was visible, this was dark enough to be opaque after 30 mins. and the solution was black after about 1½ to 2 hours. This evident degradation was accompanied by a marked increase in solution viscosity. Solutions of polymers (18-7) and (19-12) also degraded but in a much less dramatic manner, the visible degradation only resulted in a yellowing of the solution after several hours and further darkening and the observation of viscosity increase required several days' exposure.

In an attempt to place these observations on a firmer basis films of the five polymer samples were spun-cast from chloroform solution under identical conditions (i.e. the same weight of each polymer in the same volume of solvent spun in the same teflon spinner) so as to produce directly comparable thin transparent films of each polymer. These films were mounted in card frames in an identical manner, one set of samples was exposed to light and air in a thick walled glass vessel while an identical set were stored in the dark at the same temperature. The infrared spectra of the films were recorded periodically. It is clear both from the infrared spectra and from simple visual inspection that samples (15-2), (20-18) and (22-21) oxidize much faster than samples (18-7) and (19-12). In Figure 4.7.

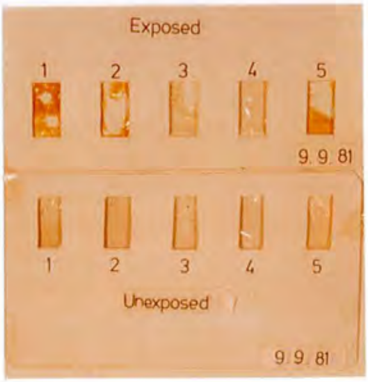
Figure 4.7. Visual deterioration of polymers on exposure to air and light.



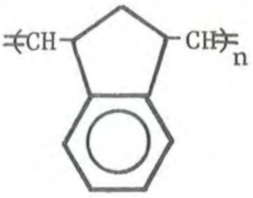
Photograph no. 1. Freshly prepared samples.
Date: 10.7.81



Photograph no. 2. After 11 days' exposure.
Date: 21.7.81



Photograph no. 3.. After 60 days' exposure
Date: 9.9.81



poly(15-2).5

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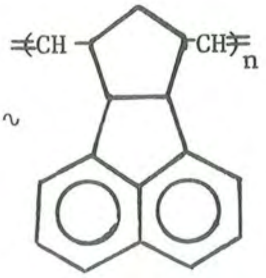

poly(20-18).1,endo
poly(22-21).2,exo

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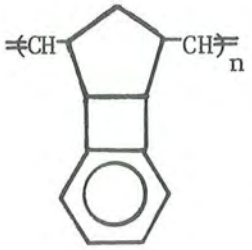
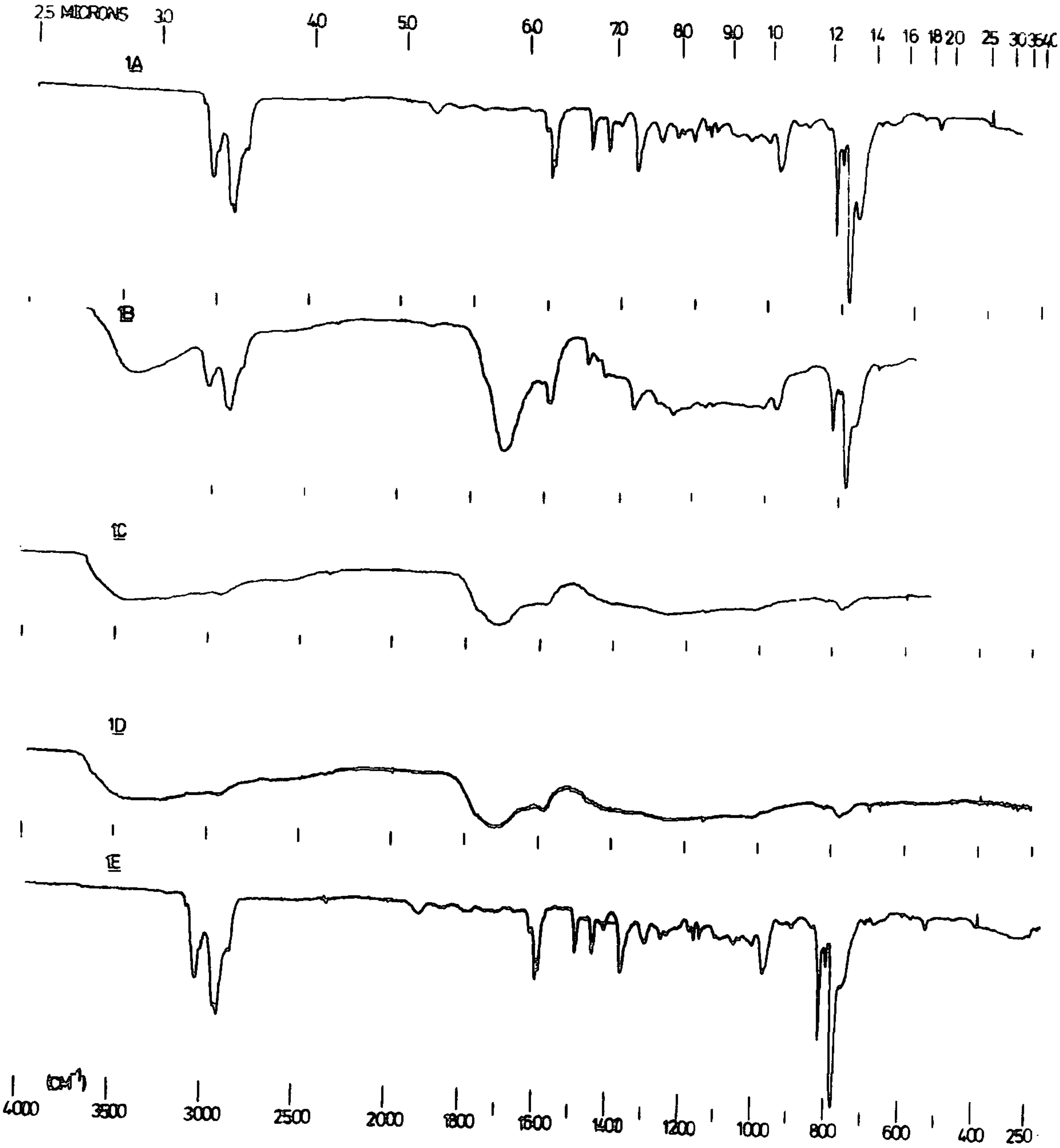


poly(18-7).3,endo
poly(19-12).4.exo

it can be readily seen that these differences are very marked. There seemed to be no significant difference between exo- and endo-structures with respect to oxidative stability. All the films were colourless and completely transparent at the start of the experiment and there were no significant carbonyl or hydroxyl group absorptions in the spectra (see photograph no. 1, Figure 4.7. dated 10.7.81, and spectra nos. 1A, 2A, 3A, 4A and 5A, Figures 4.8 → 4.12). After eleven days' exposure to diffuse daylight (north facing window, Durham, July) the films of polymers (20-18, 22-21 and 15-2) which are numbered 1, 2 and 5 respectively in the photographs had yellowed and showed signs of brittleness whereas polymers (18-7) and (19-12) which are numbered 3 and 4 were unchanged (see photograph 2, dated 21.7.81, Figure 4.7.). The i.r. spectra of the exposed films (1, 2 and 5) reveal strong absorptions between 1720-1785 $cm.^{-1}$ assigned to the presence of carbonyl groups and broad absorptions between 3450-3550 $cm.^{-1}$ which arise from -OH and/or -OOH units, while films 3 and 4 showed negligible changes in both regions (see spectra nos. 1B, 2B, 3B, 4B and 5B in Figure 4.8. → 4.12.). The films were photographed again after sixty days (photograph no. 3, Figure 4.7.); the films numbered 1, 2 and 5 were a darker yellow/brown colour and cracks and extensive mechanical degradation was apparent, whereas films 3 and 4 were only slightly discoloured and did not have any cracks (the hole in photograph 3, sample 3, is the result of an accident not photodegradation). The i.r. spectra after sixty days were recorded for both the exposed and the unexposed film, exposed films (1, 2 and 5) had undergone more extensive oxidation as evidenced by the increased intensities of the carbonyl and hydroxyl groups, while exposed films 3 and 4 were beginning to show the presence of the carbonyl and hydroxyl peak (see spectra nos. 1C, 2C, 3C, 4C and 5C, Figures 4.8. → 4.12.). The unexposed films were recorded at the same time and showed no detectable changes for all five samples.

Figure 4.8. I.R. spectra of poly(20-18), film no. 1 exposed to light and air



A) - Fresh sample.
B) - After 11 days.
C) - After 60 days.
D) - After 87 days.
E) - Unexposed sample after 87 days in air.

Figure 4.9. I.R. spectra of poly(22-21), film no. 2 exposed to light and air

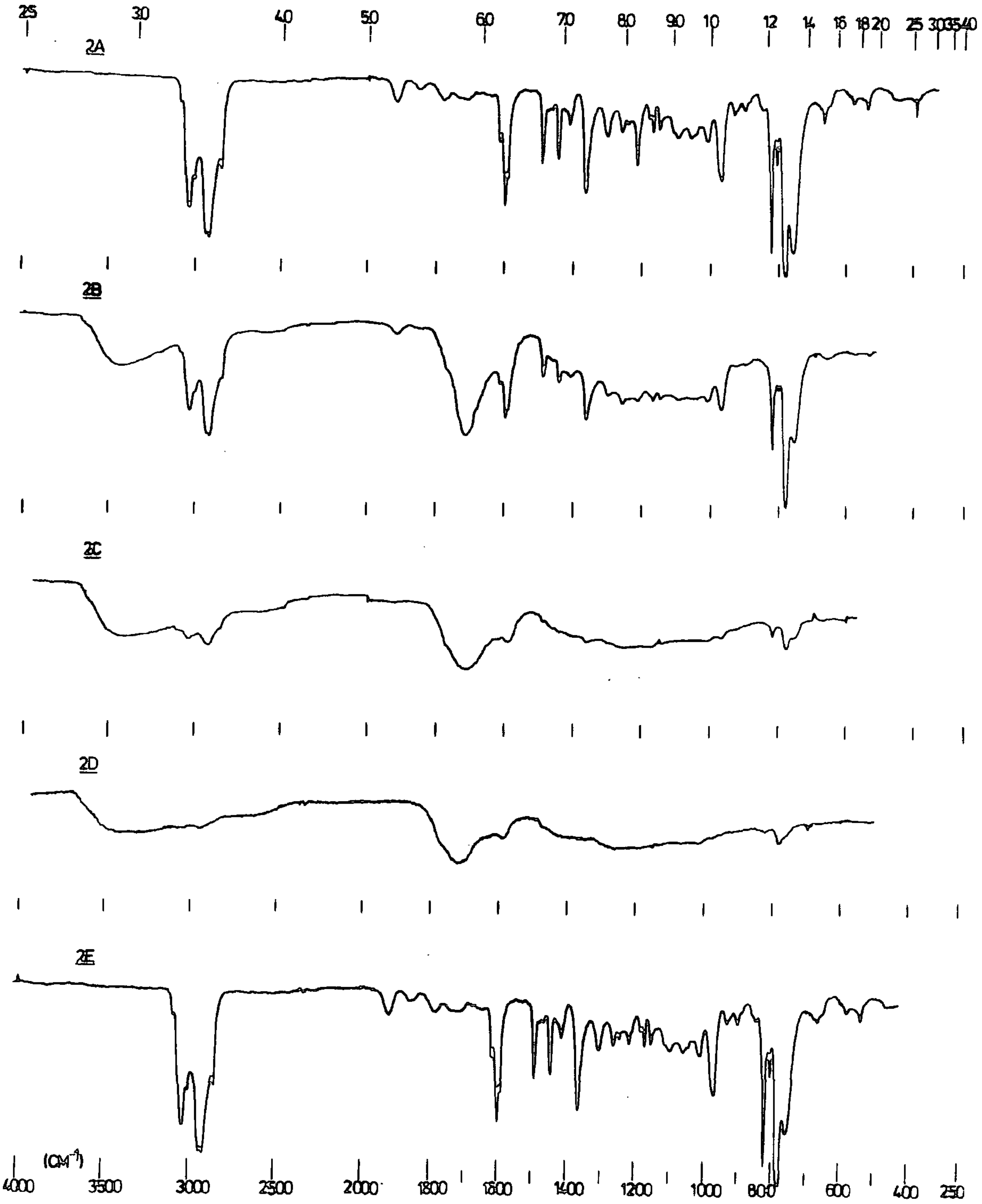


Figure 4.10. I.R. spectra of poly(15-2), film no. 5 exposed to light and air

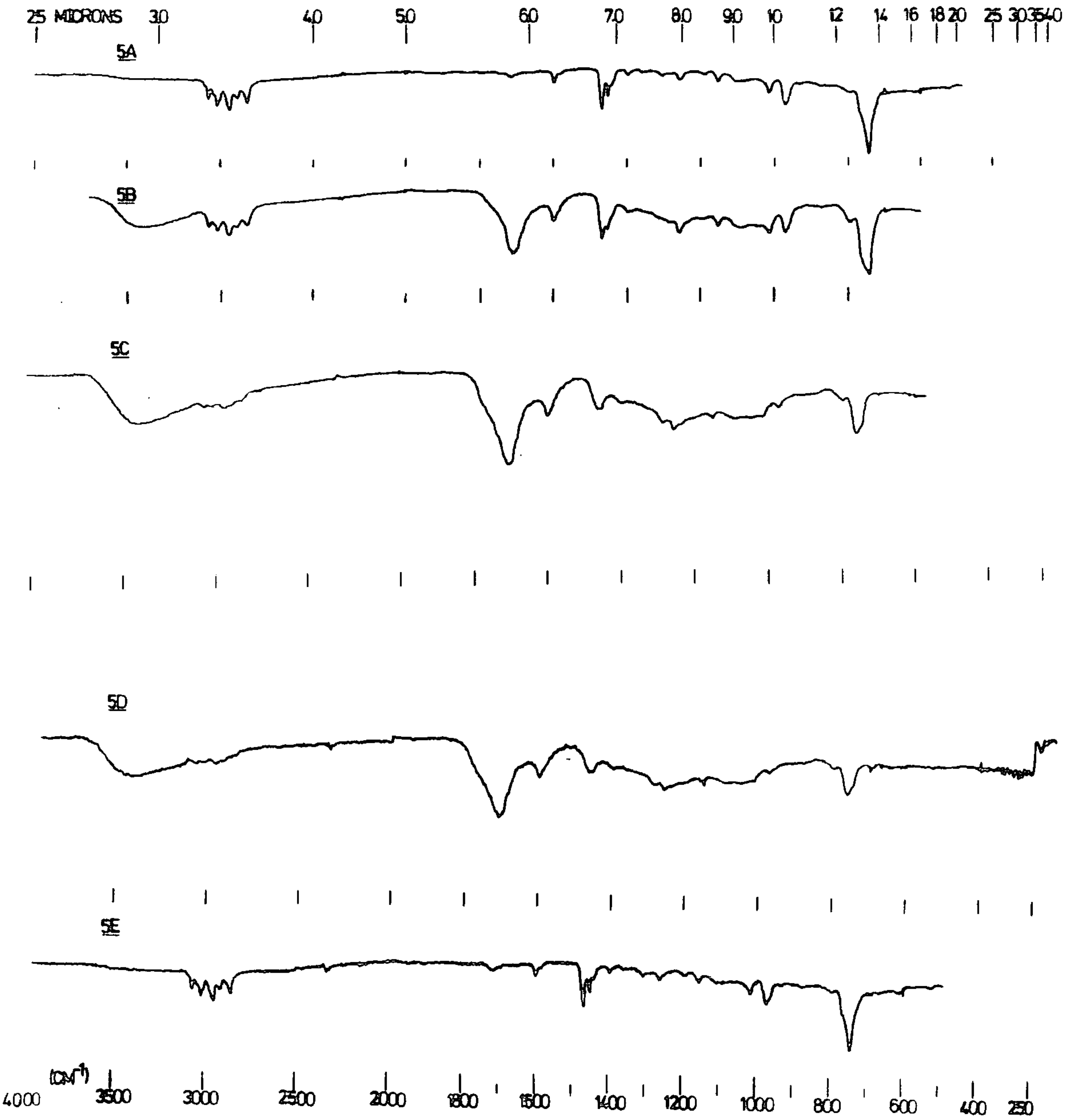


Figure 4.11. I.R. spectra of poly(18-7), film no. 3 exposed to light and air

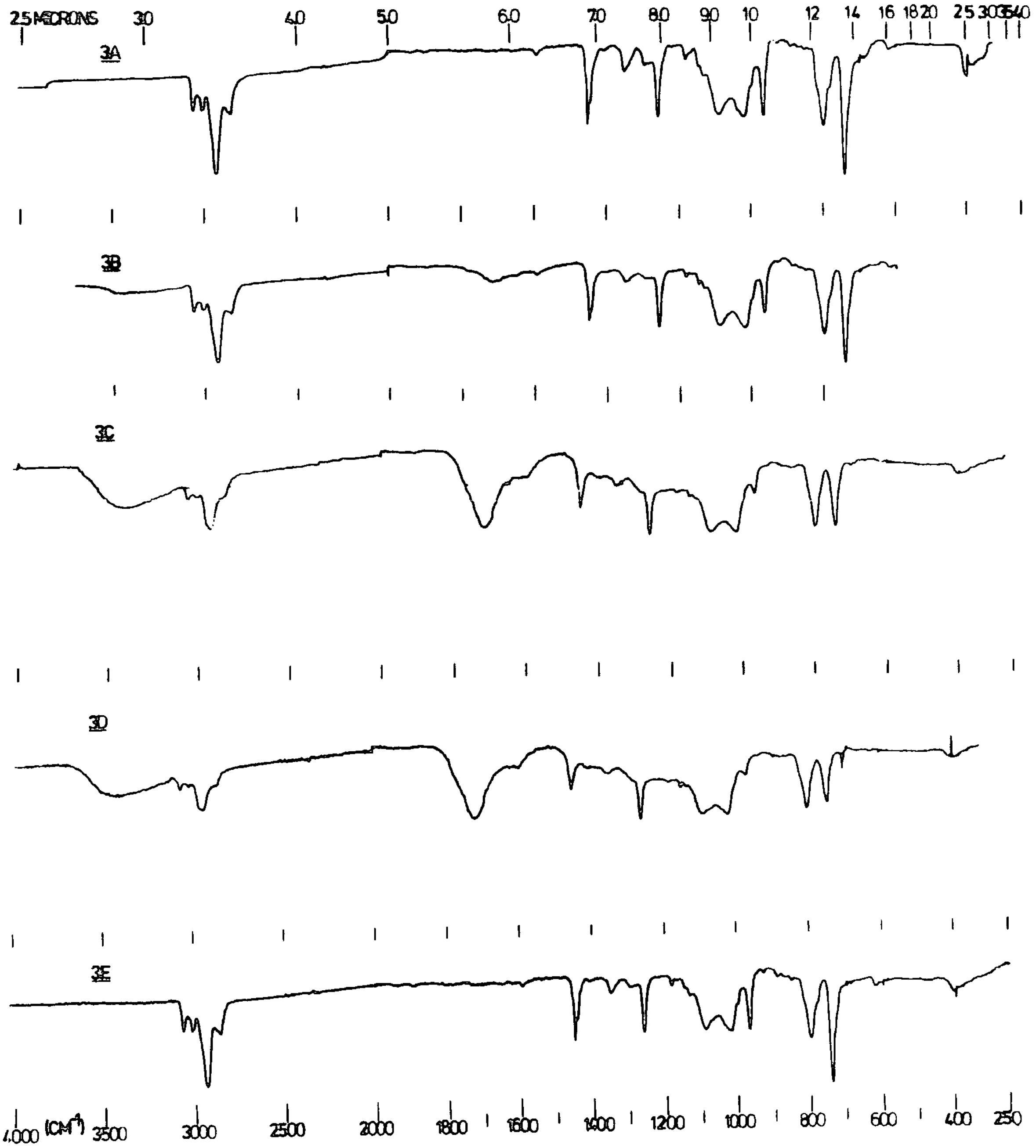
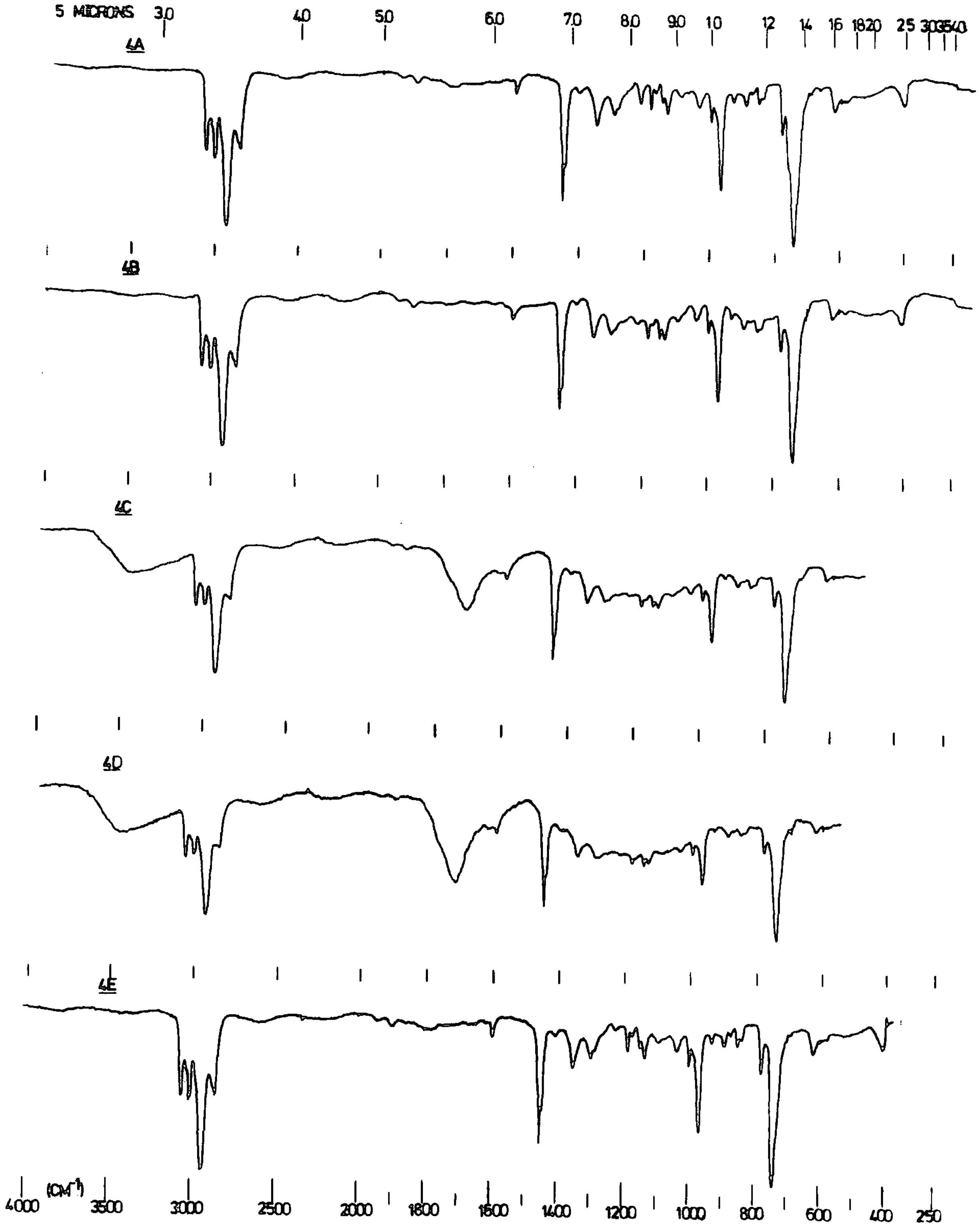
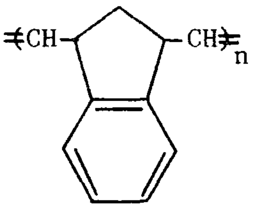


Figure 4.12. I.R. spectra of poly(19-12), film no. 4 exposed to light and air



The last records were made after 87 days and by this stage films (1, 2 and 5) were so fragile that it was difficult to obtain spectra, while films 3 and 4 had developed strong carbonyl and hydroxyl absorptions, although the peaks associated with the original polymer were still clearly in evidence (see spectra nos. 1D, 2D, 3D, 4D and 4D of Figures 4.8 → 4.12). The unexposed polymers were virtually unchanged after 87 days and their spectra are recorded (1E, 2E, 3E, 4E and 5E in Figures 4.8 → 4.12).

The results reported above establish that the processes observed involve both light and air, in the absence of light the films appear to be relatively stable and the thin films stored in the dark in air at room temperature were still transparent, colourless and mechanically intact after four months. Elemental analysis of the degraded films shows that the carbon content decreases with time, and infrared spectroscopy and preliminary ESCA measurements indicate the accumulation of oxygen containing functionalities during degradation. The degradation observed is clearly a photo-oxidative process, or at least is a photo-oxidatively initiated process. It is at first sight surprising that the approximate order of ease of degradation is as shown below; since it was anticipated that polymers (18), (19), (20) and (22) would all be less easily oxidized than poly(15).



poly(15)

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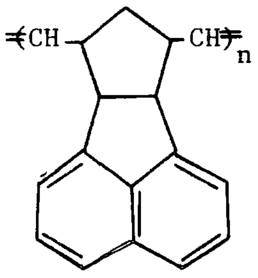

poly(20) and (22)

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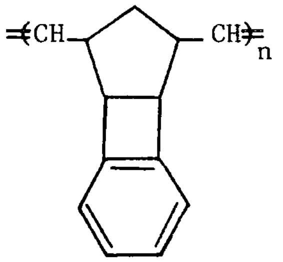


poly(18) and (19)

A number of explanations are possible. Some depend on purely physical effects, for example, the morphology and glass transition temperature are important determinants of the rate of diffusion of gases in polymers; thus, highly ordered polymers are much less permeable than amorphous samples of the same basic structure and gases diffuse more rapidly in samples which are maintained at temperatures above their glass transiton temperatures. Unfortunately at the time this work was carried out the thermal analysis equipment used to measure glass transition temperatures was broken down so investigation of this aspect of the properties of these materials will have to await its repair or replacement. On the other hand there are chemical differences between the polymers with the 1,8-naphthylene residues [poly(20) + (22)] and those with the 1,2-phenylene units [poly(18) + (19)]; thus, abstraction of the tertiary hydrogen adjacent to the naphthylene ring leads to a more extensively delocalized and consequently more stabilized radical than is the case for the tertiary hydrogens adjacent to the phenylene residue; furthermore the tertiary hydrogens adjacent to the phenylene rings in poly(18) and poly(19) are attached to a cyclobutyl system and in such systems the carbon-carbon σ-bonds are forced to have relatively greater p-character than those in less strained systems, consequently the carbon-hydrogen bonds have relatively greater s-character and will be less readily subject to abstraction reactions. The effect of both the factors mentioned above is to make oxidation of poly(18) and poly(19) harder than oxidation of poly(20) and poly(22) for reaction pathways which involve initial reaction at the tertiary carbon-hydrogen bond adjacent to the aromatic ring; oxidation at the allylic carbon-hydrogen bond would be expected to have the same characteristics for all four structures. Although plausible this explanation lacks rigorous proof and it may be that the observed differences in susceptibility to oxidation result from more fundamental mechanistic differences or even from a simple difference in the physical state of the samples.

4.3. Conclusions and Suggestions for Further Work

The work reported in this thesis establishes that some aryl substituted polycyclic alkenes are readily polymerized by ring-opening at the double bond. The reactivity of the monomers is qualitatively independent of monomer isomerism; thus, endo- and exo-isomers react in the same manner and at the same rate, also the derived polymers display similar susceptibilities to oxidation. This implies that the aryl groups have no effect on the action of the polymerization catalyst which appears to contradict the reports of earlier workers on related (although not identical) systems (see Chapter I). Also it should be noted that Calderon[98] has recently reported that the exo-Diels-Alder adduct of maleic anhydride and cyclopentadiene is readily ring-open polymerized whereas the endo-adduct is very resistant to polymerization by this technique, the capacity of the lone pairs on the anhydride oxygen to co-ordinate to 'active catalyst sites' is expected to be much greater than that of aromatic π-electrons, however the very marked stereochemical preference observed is slightly surprising in view of our observed lack of stereochemical differentiation.

The monomers used in this work are sterically crowded and it would be interesting to see what effect this has on the stereoregularity of polymerization. For this it would be necessary to use catalysts which are known to give highly stereoregular polymers (e.g. $ReCl_5$, which gives all cis-syndiotactic) and to obtain better ^{13}C nmr spectra than have been available to the author.

The preliminary oxidation studies have established some interesting questions and are worth following up. One approach would be to synthesise monomers which would give polymers analogous to those already available but with either or both tertiary carbon-hydrogen sites blocked by non-oxidizable groups (e.g. -F or -CN) and compare stabilities.

Finally, it has to be admitted that, unless some specialist application is found, these new materials appear to be too expensive and difficult to prepare to merit widespread interest. It is, of course, possible that a property such as a controlled rate of decomposition on exposure to daylight might find application in light sensitive devices. Also this work establishes in principle a new method for stereochemically controlled synthesis of polymers with pendant aromatic units, in this method the rigid geometry of the monomer ring system can be carried over into the polymer and the stereochemical disposition of the plane of the aromatic rings with respect to the polymer chain is controlled as well as the spatial disposition with respect to nearest neighbour units. This may open interesting possibilities for interactions between aromatic rings particularly for monomers with larger pendant groups such as anthracene or pyrene.

APPENDIX A

APPARATUS AND INSTRUMENTS

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

Mass spectra were recorded with either an A.E.I. MS9 or a V.G. Micromass 12B spectrometer.

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

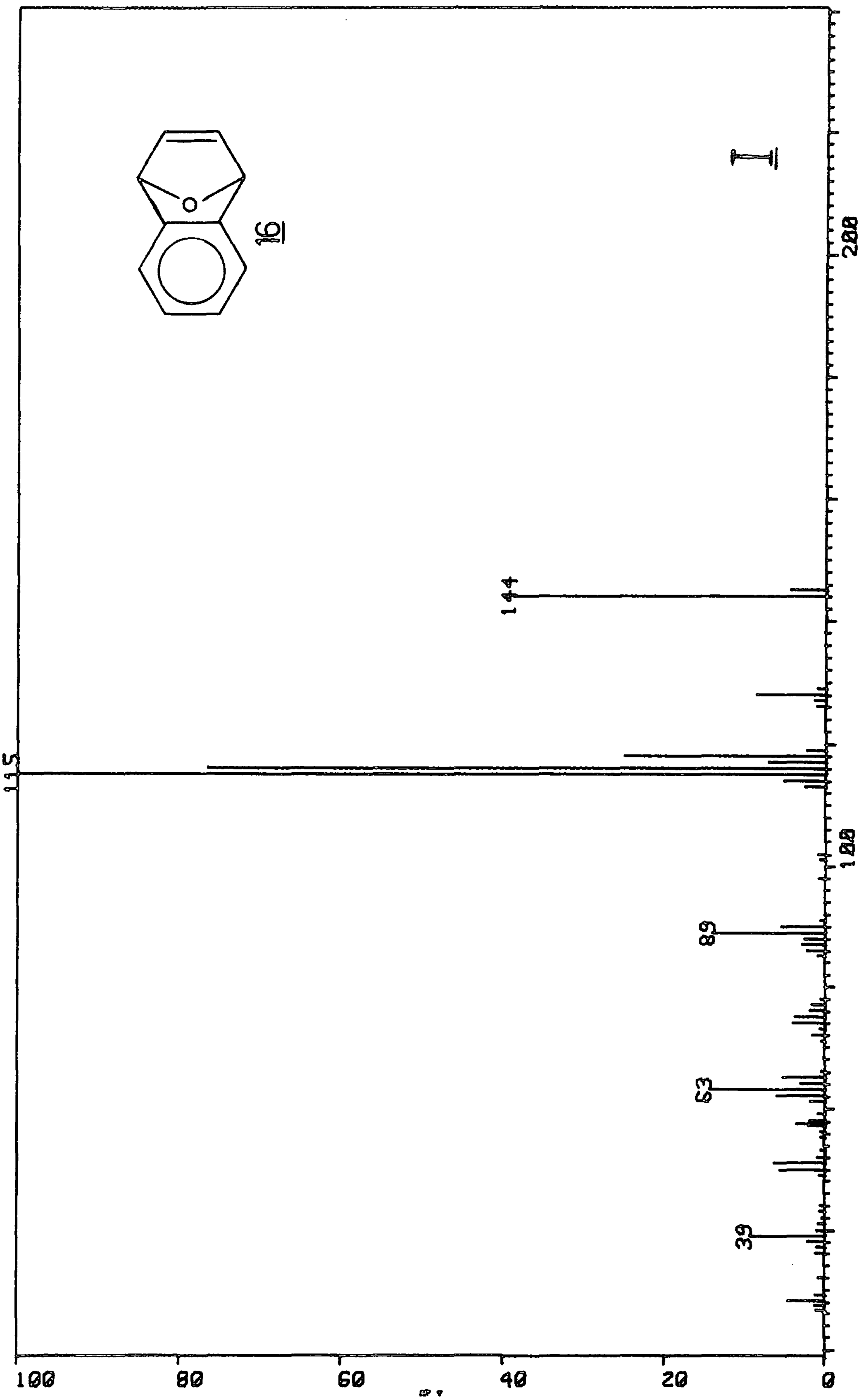
N.m.r. spectra were recorded with either a Bruker spectrospin HX90E high resolution n.m.r. spectrometer, operating at 90.00 MHz for ^1H n.m.r. and 22.63 MHz for ^{13}C, or a Varian EM360L NMR spectrometer operating at 60 MHz. ^1H Chemical shifts are measured on the δ scale relative to external tetramethylsilane and ^{13}C chemical shifts are in p.p.m. from internal tetramethylsilane.

I.R. spectra were recorded using Perkin-Elmer 577 Grating Infrared Spectrophotometer.

Gel permeation chromatography (G.P.C.) measurements were recorded using a Perkin-Elmer 601 Liquid Chromatography Apparatus, with a U.V. detector and 3 PL gel columns (10μ, 500Å, 10^3Å and 10^5Å) supplied by Polymer Laboratories Ltd.

APPENDIX B

MASS SPECTRA


16
I
115
144
89
63
39
100
200
100
80
60
40
20
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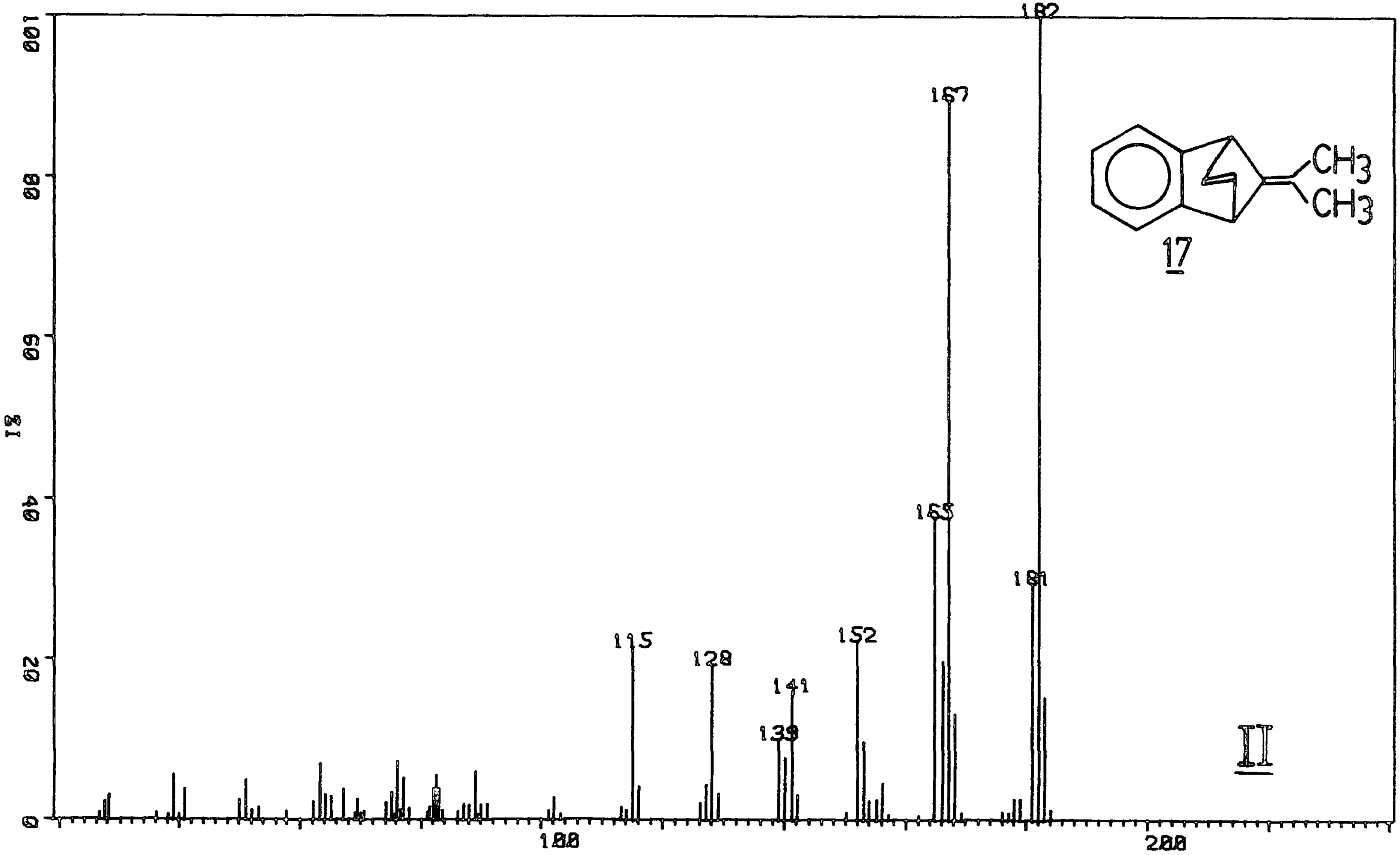
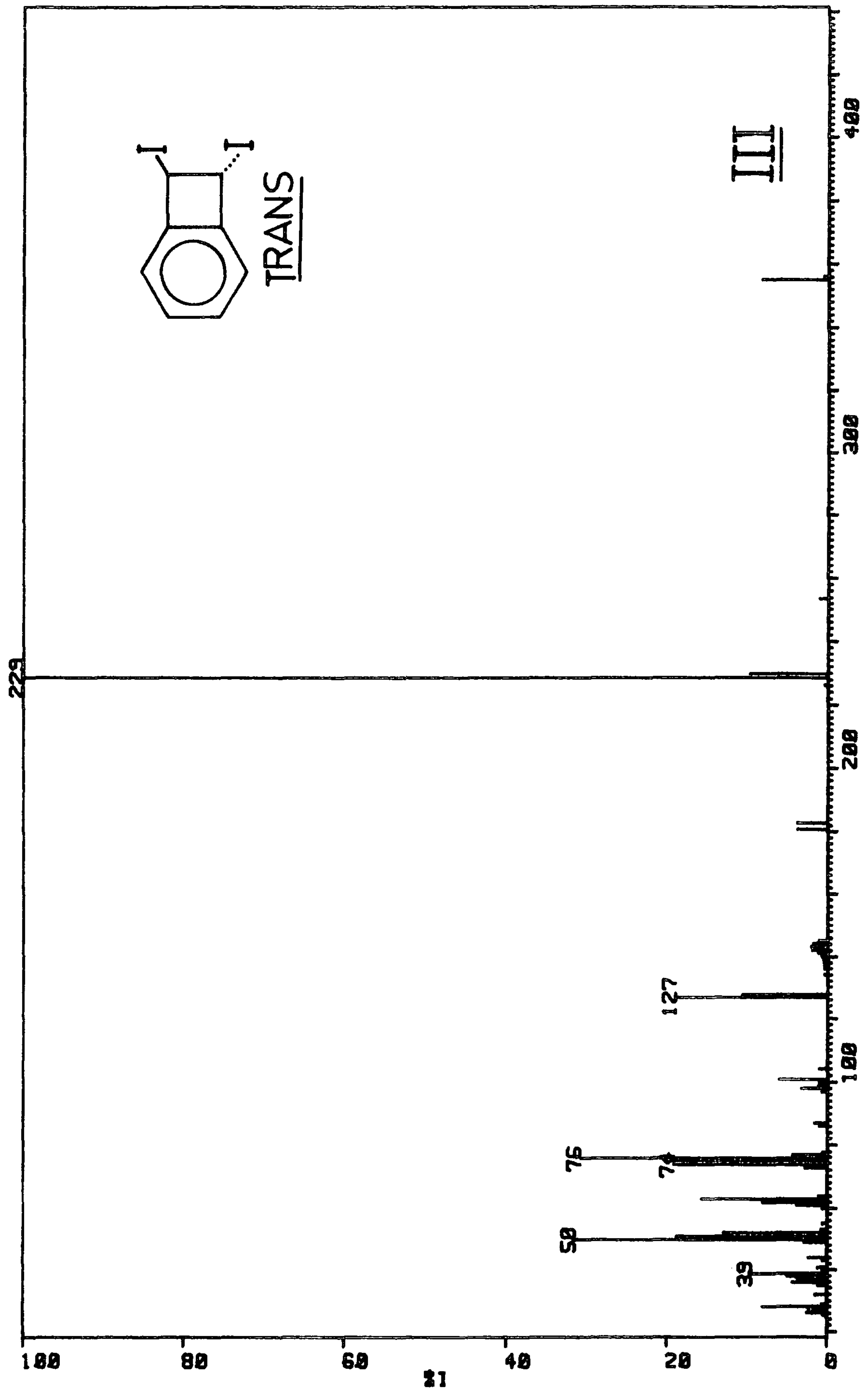
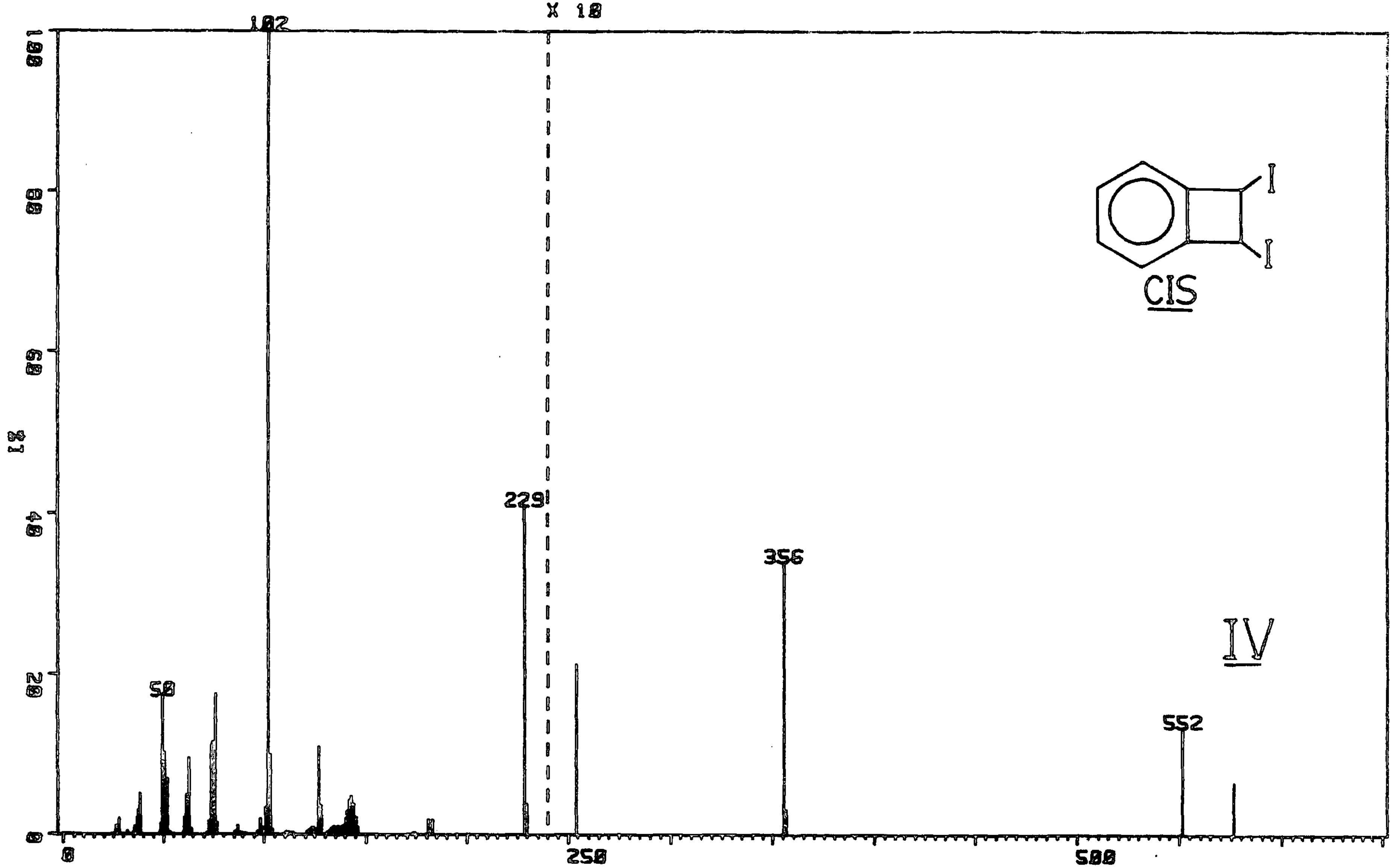
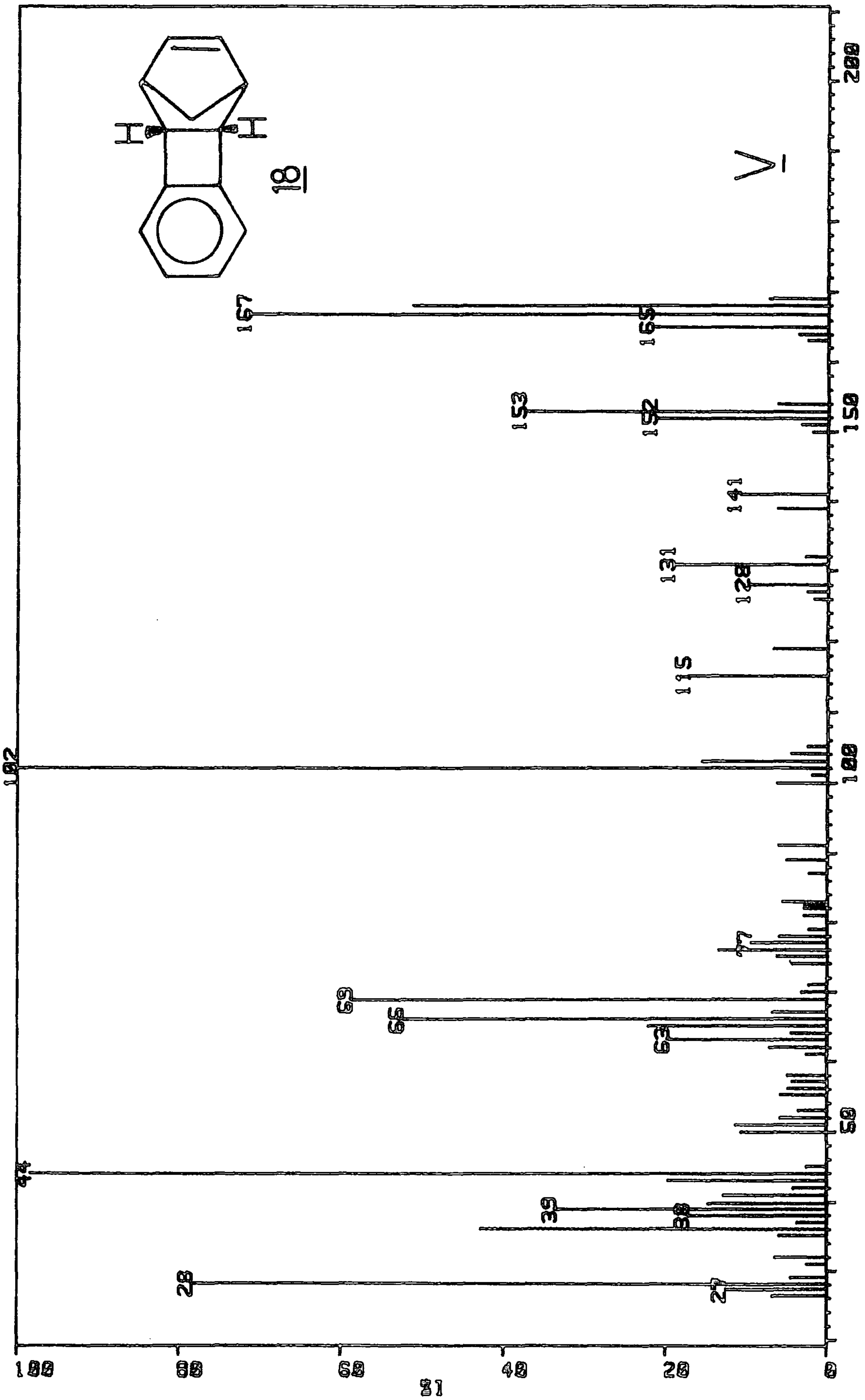
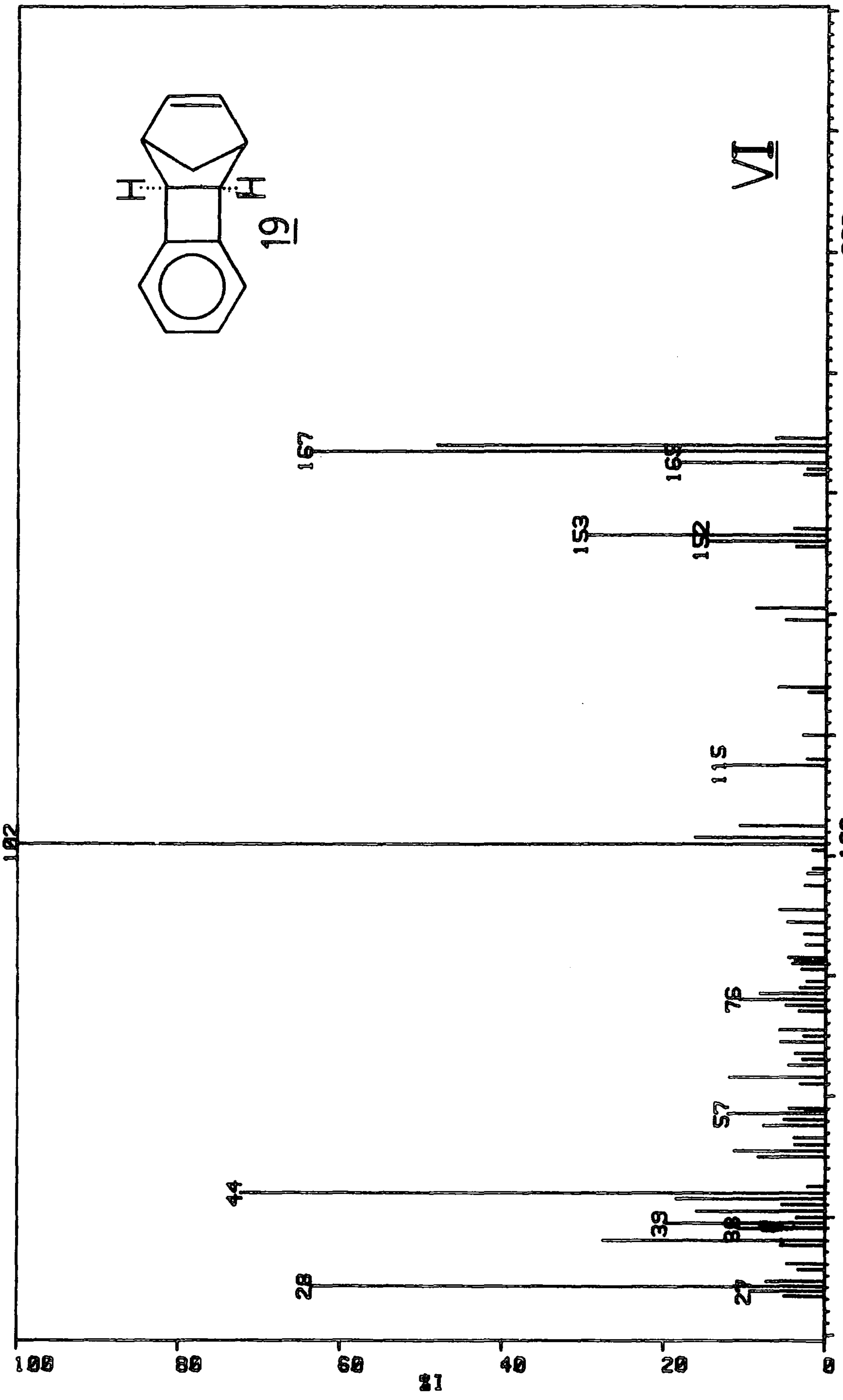

182
167
165
181
152
115
128
141
139
CH3
CH3
17
II
100
80
60
40
20
0
%I
100
200

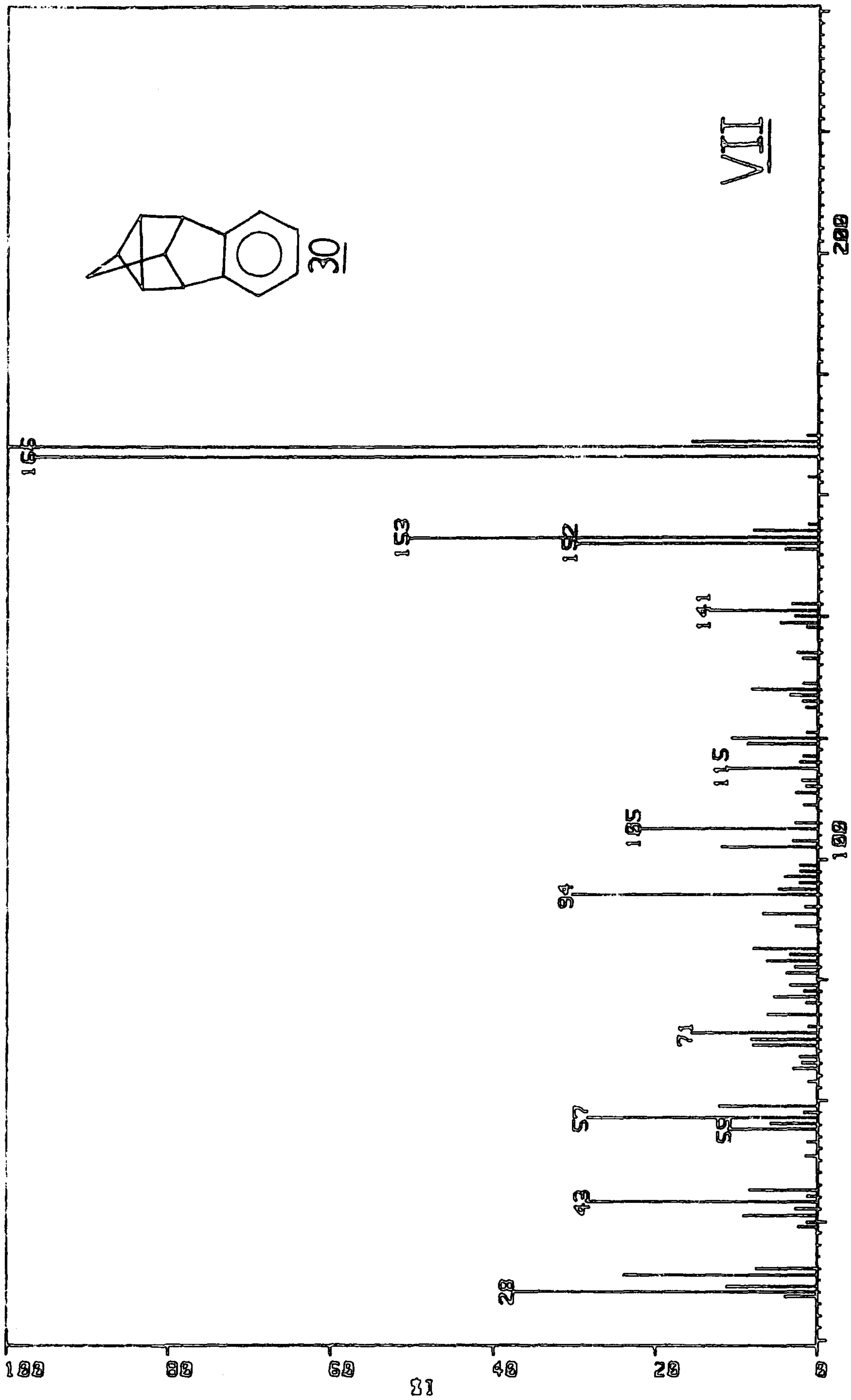

I
I
TRANS
III
229
127
76
74
50
39
100
80
60
40
20
0
%I
100
200
300
400

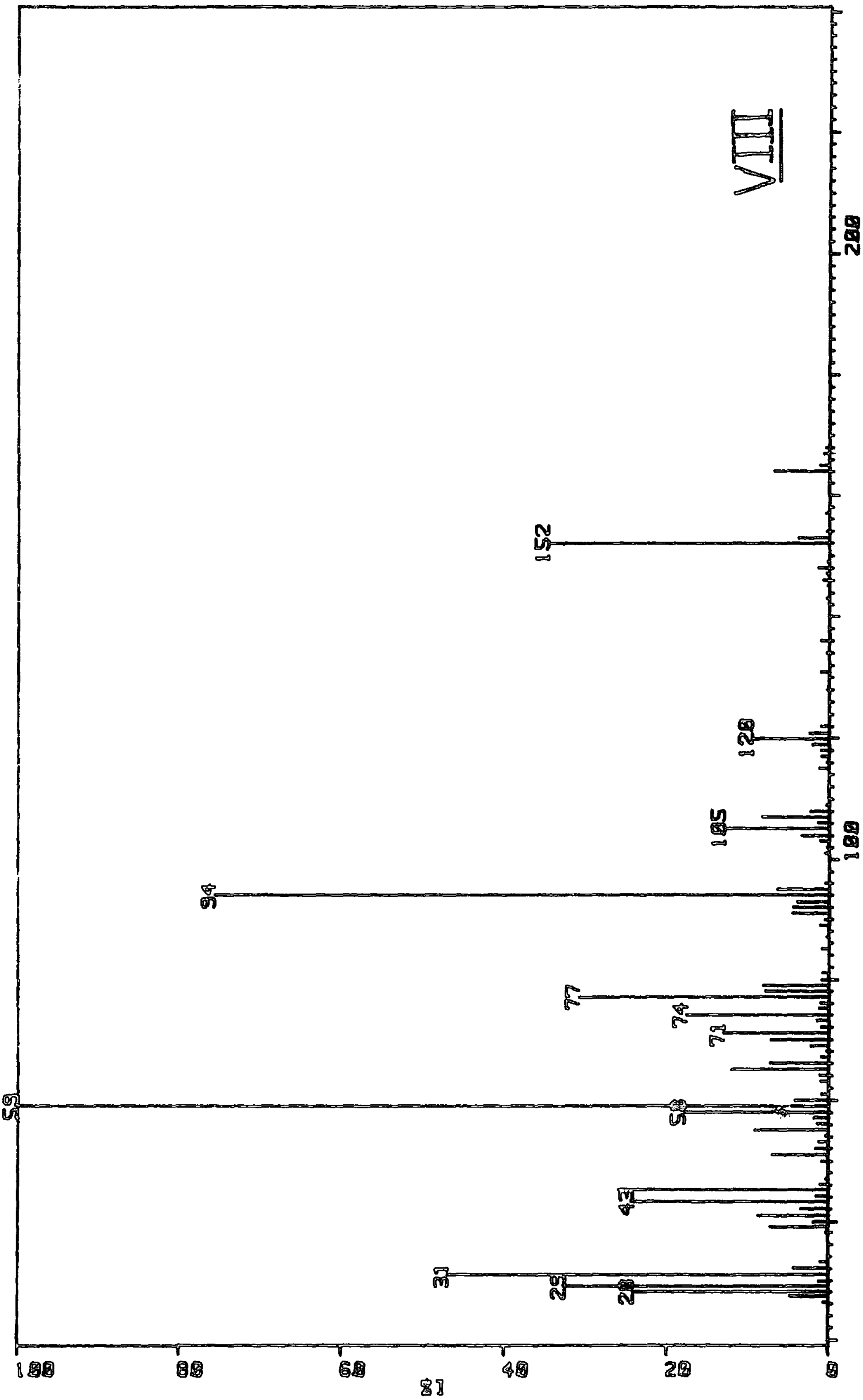


IV

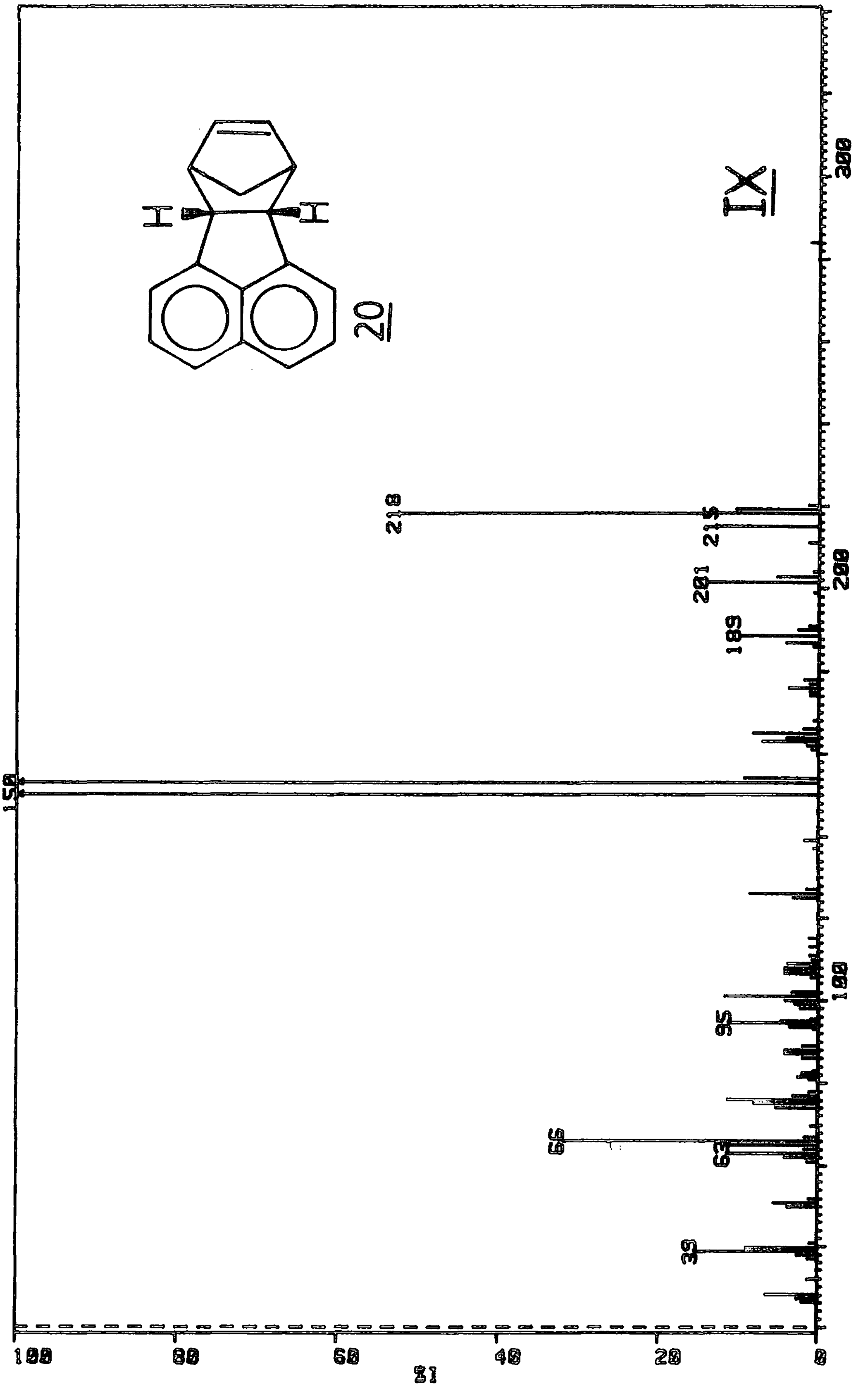

18
V
167
165
153
152
141
131
128
115
102
69
65
63
77
44
39
38
28
27
50
100
150
200
100
80
60
40
20
0
%I

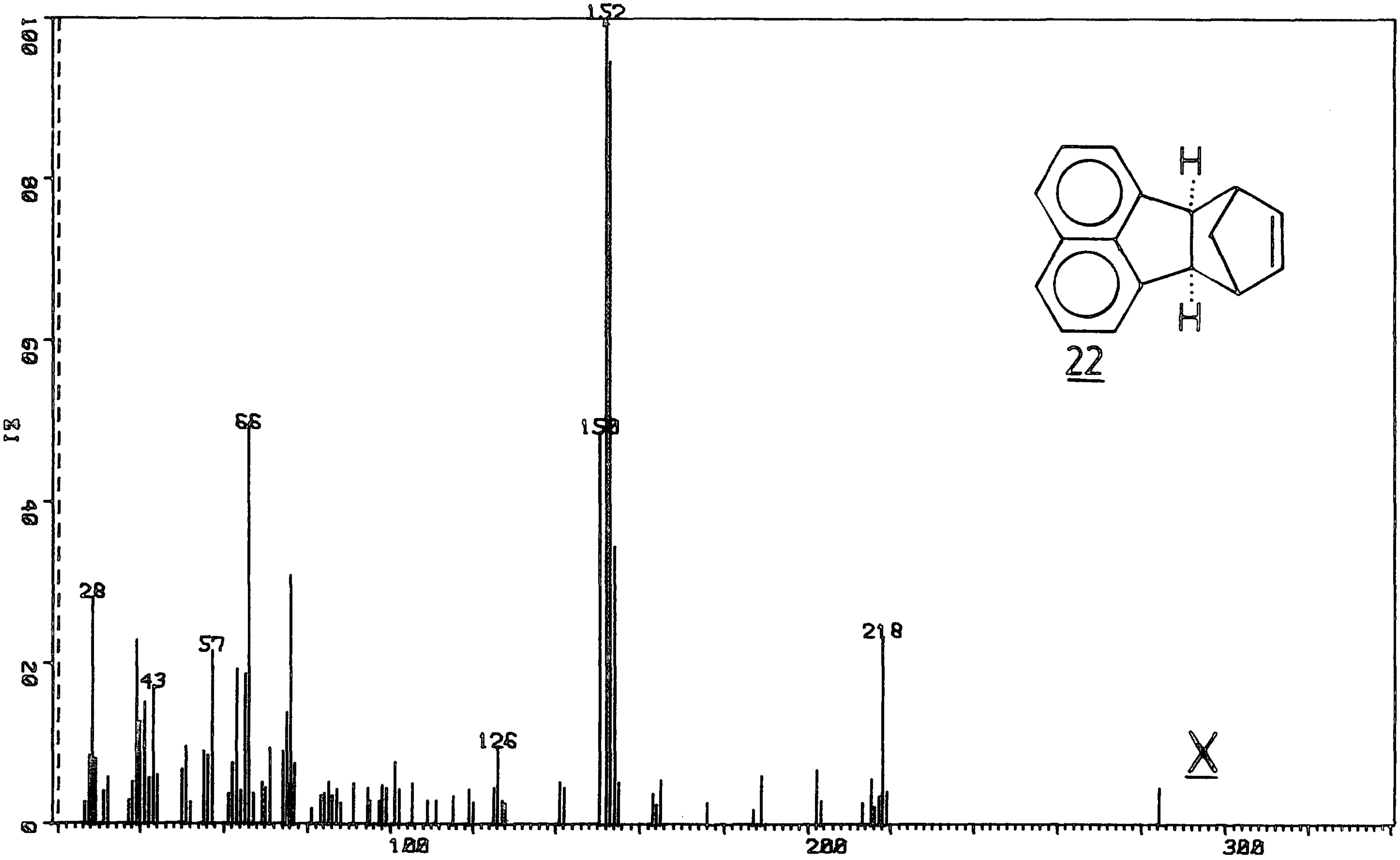

VI
19
H
H
167
165
153
152
115
102
76
57
44
39
38
28
27
200
100
0
20
40
60
80
100
%I


VII
30
165
153
152
141
115
105
94
71
57
55
43
28
200
100
100
80
60
40
20
0
%I



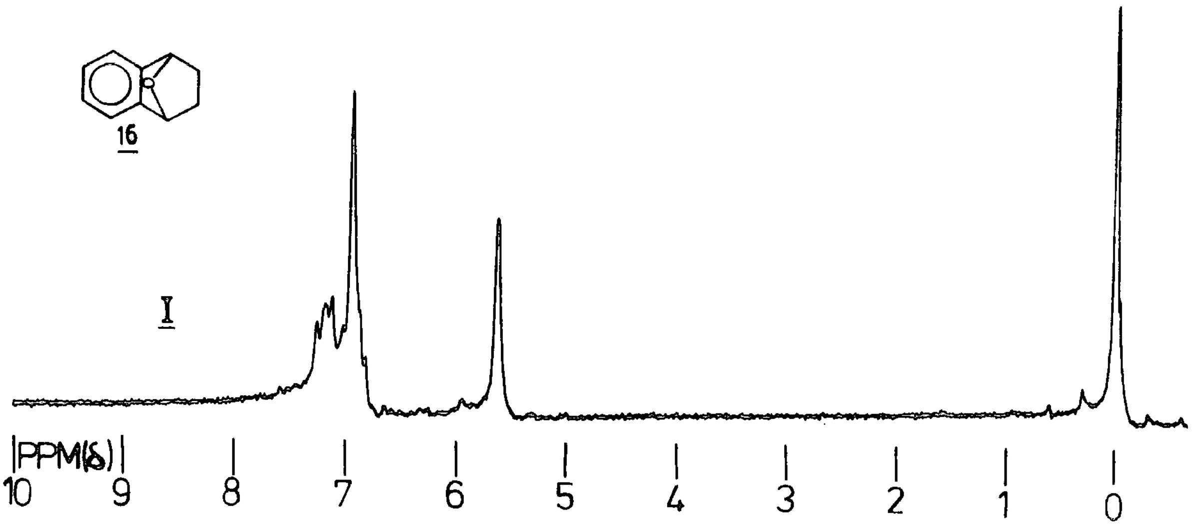
VIII

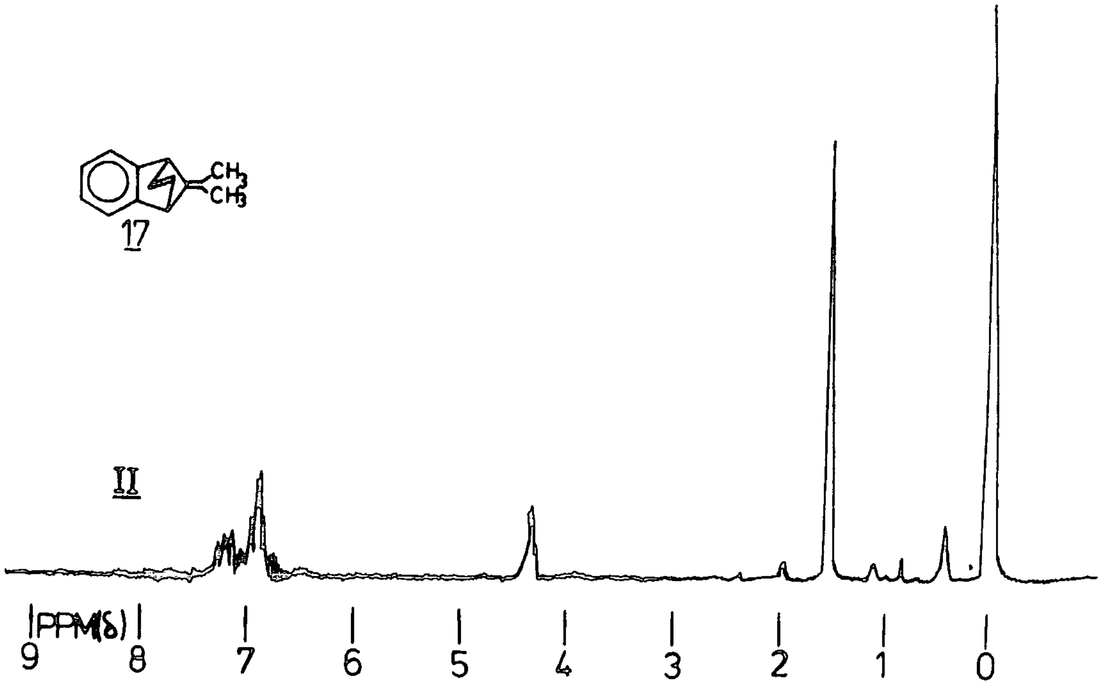

20
IX
218
215
201
189
150
95
66
63
39
100
200
300
100
80
60
40
20
0
%I

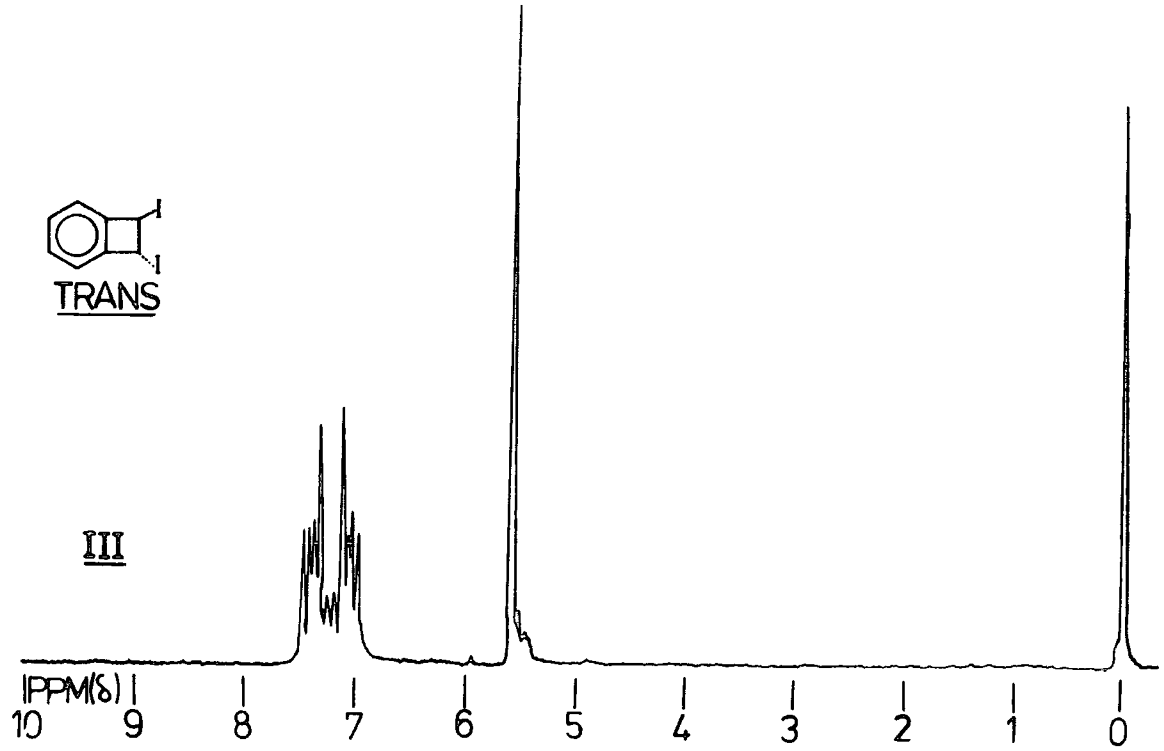

152
150
66
28
57
43
126
218
22
X
100
80
60
40
20
0
I%
100
200
300

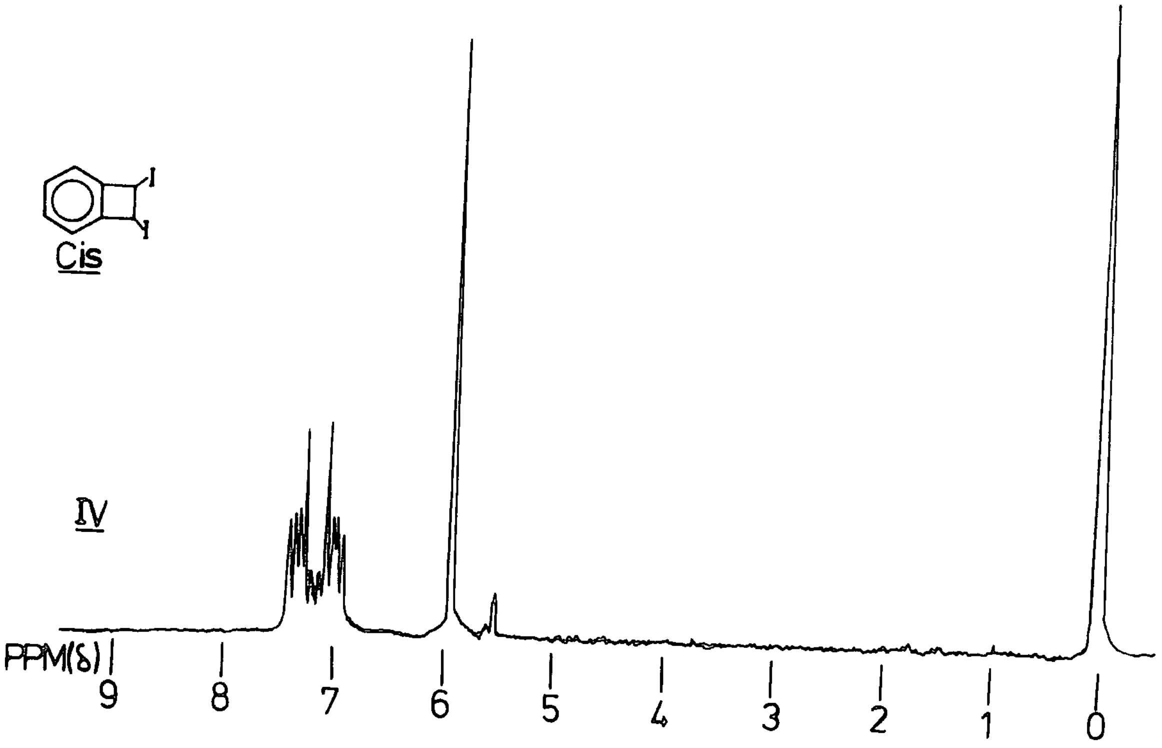
APPENDIX C

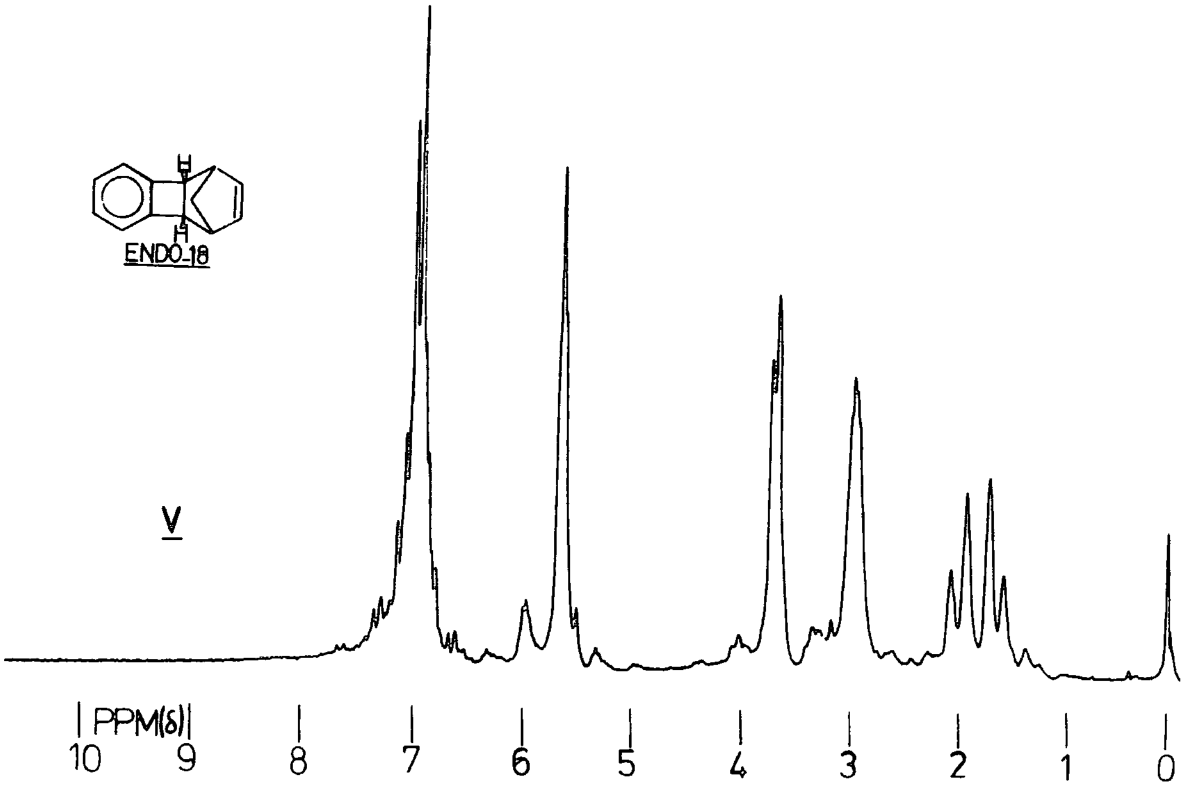
^{1}H N.M.R. SPECTRA


16
I
PPM(δ)
10
9
8
7
6
5
4
3
2
1
0


CH3
CH3
17
II
PPM(δ)
9
8
7
6
5
4
3
2
1
0

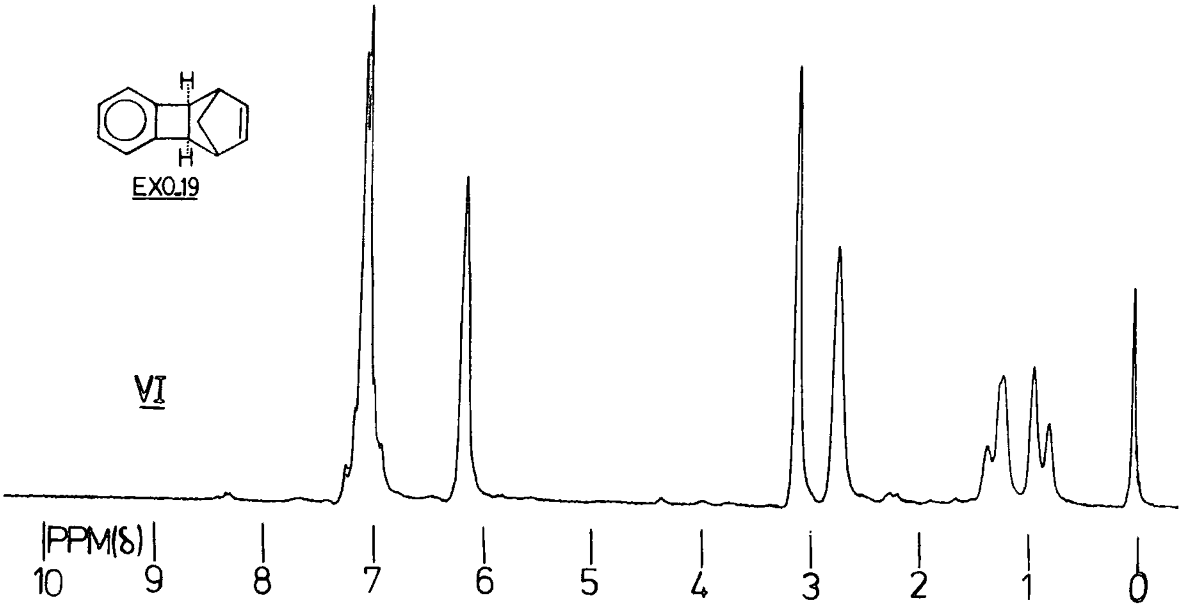

I
I
TRANS
III
PPM(δ)
10
9
8
7
6
5
4
3
2
1
0


I
I
Cis
IV
PPM(δ)
9
8
7
6
5
4
3
2
1
0



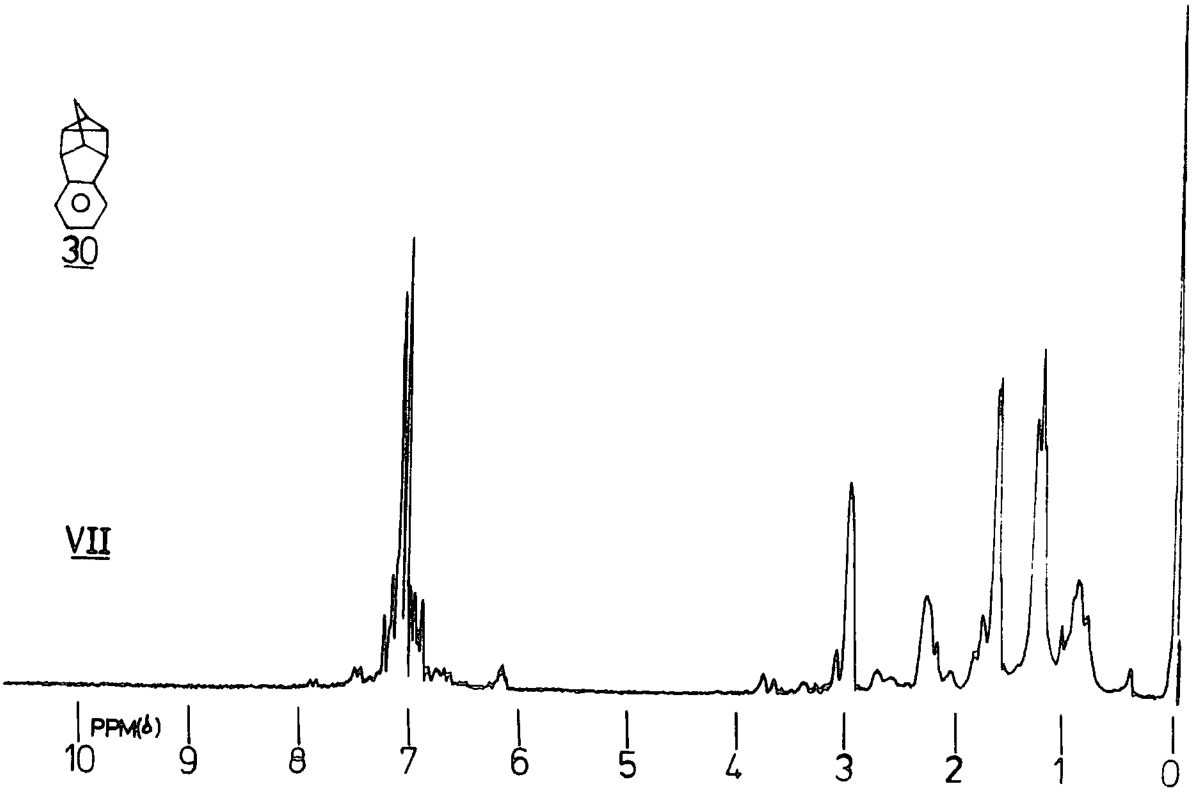
ENDO-18

V



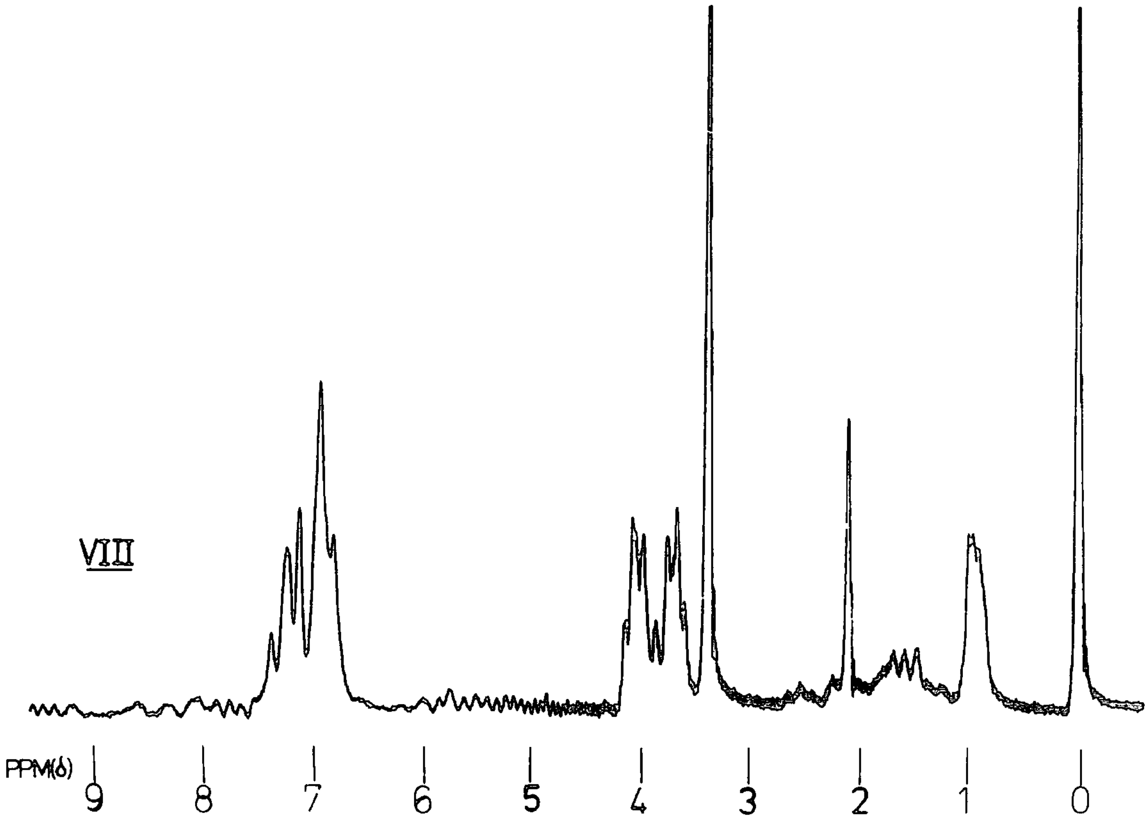
EXO-19

VI

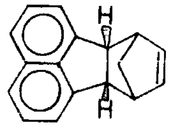


30

VII

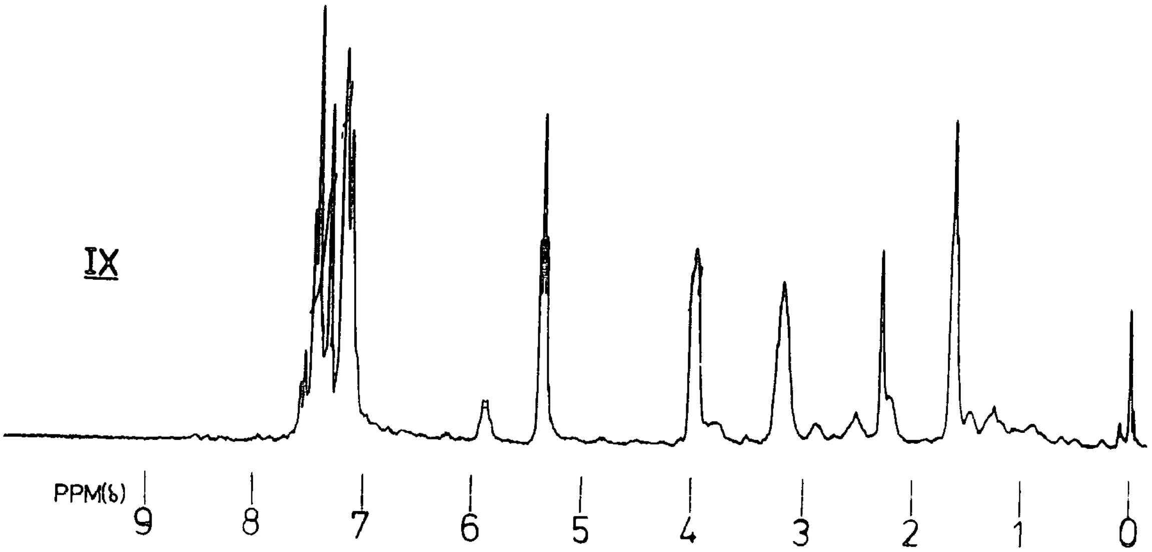


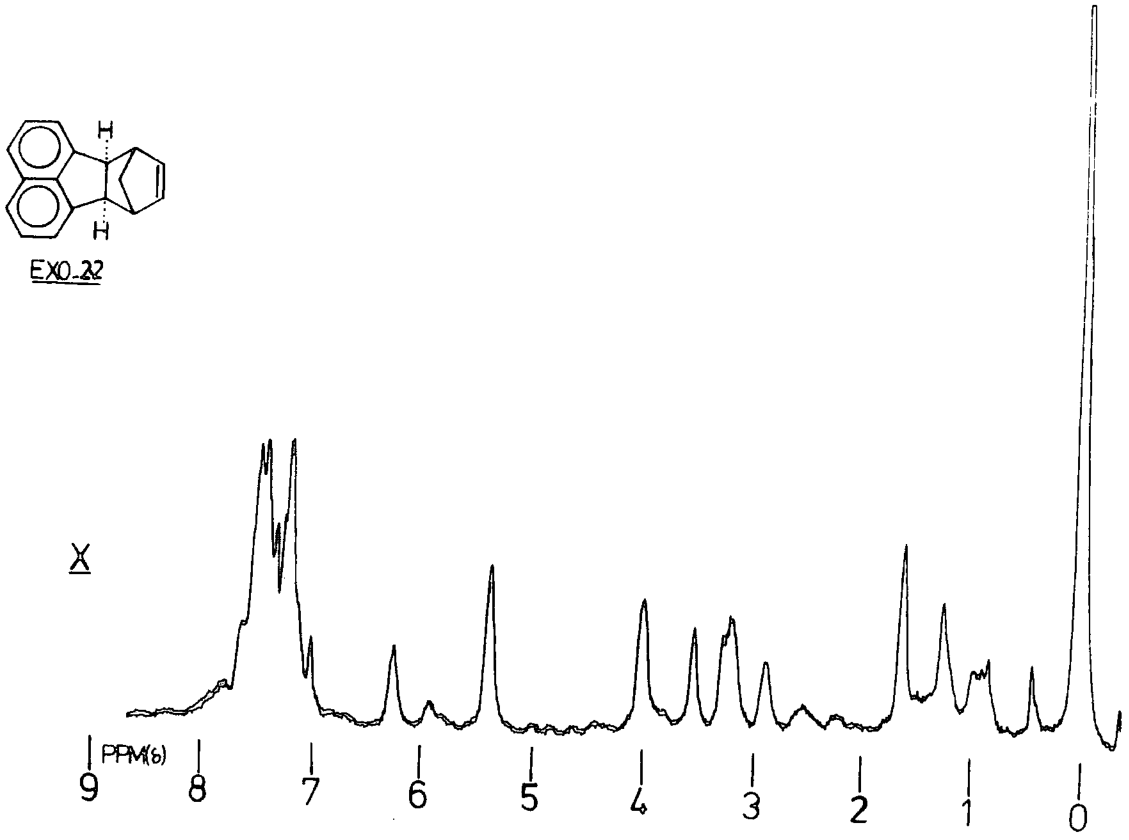
VIII



ENDO-20

IX





EXO-22

X

APPENDIX D

I.R. SPECTRA

All spectra were recorded using KBr cells, plates, pressed discs, or thin films and were run under conditions designated by:-

A - KBr disc

B - Thin liquid film

C - Thin polymer film (free standing)

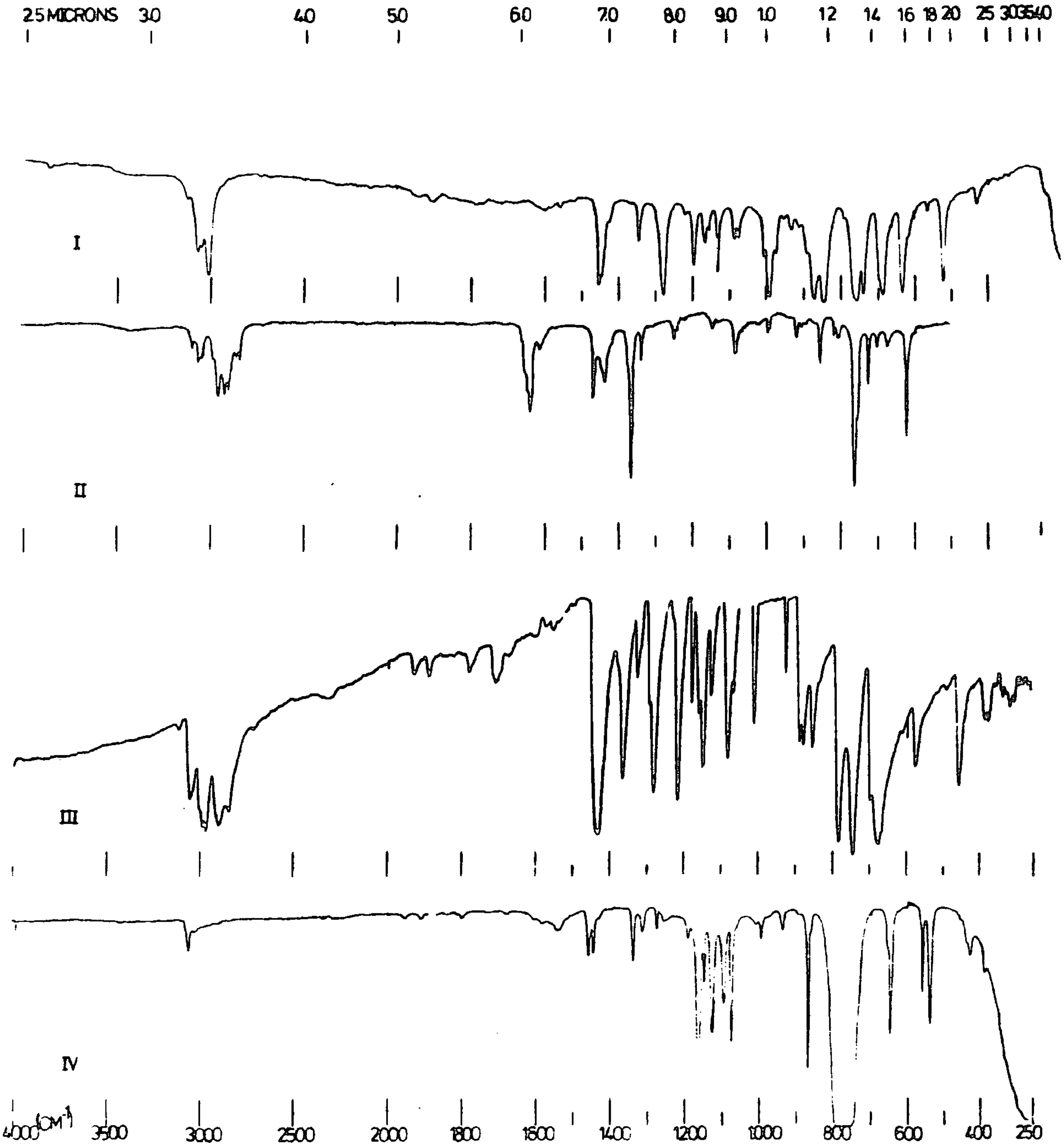
D - Thin polymer film (cast on KBr plate)

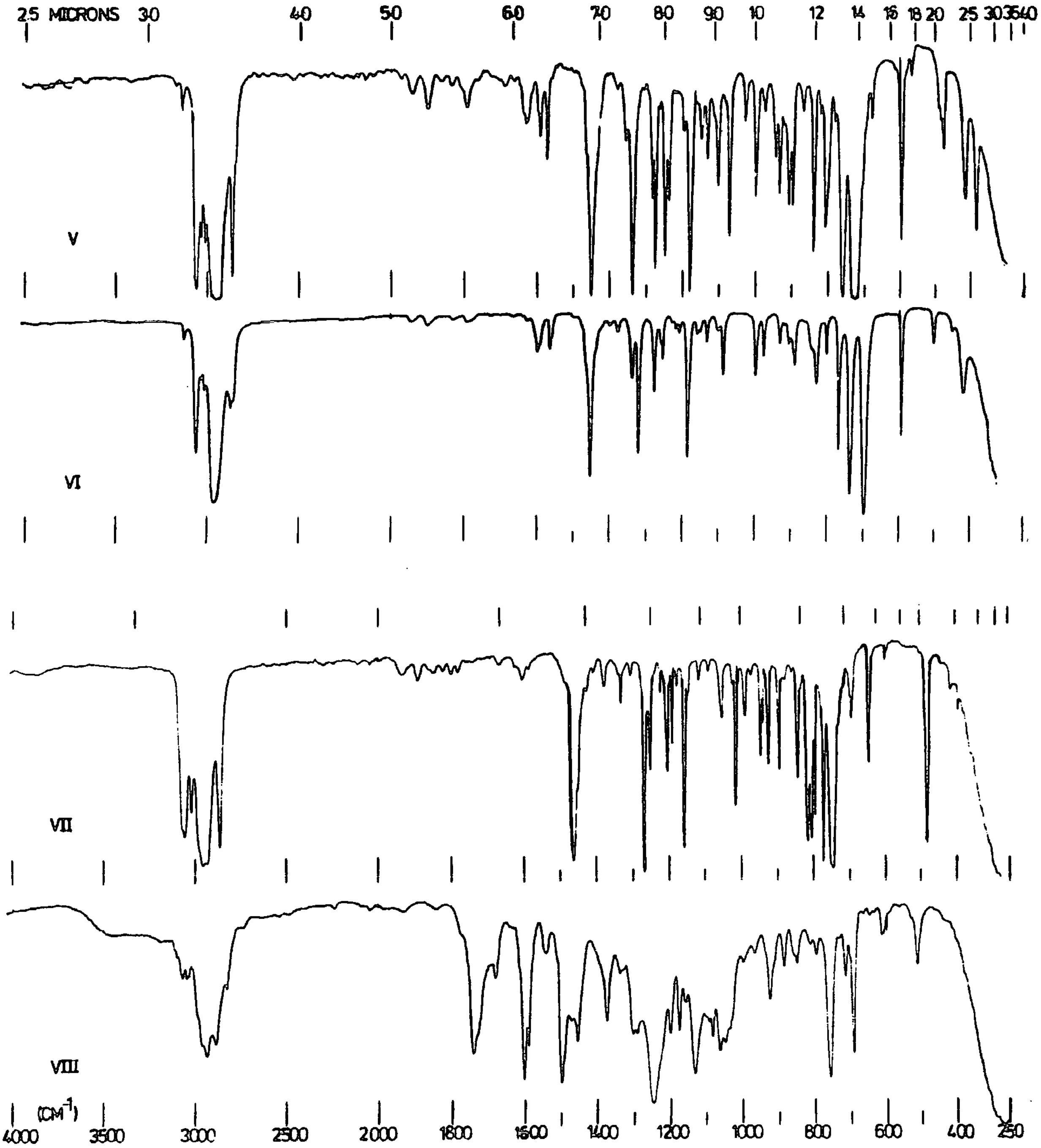
Spectrum IV is of a solution in CCl_4.

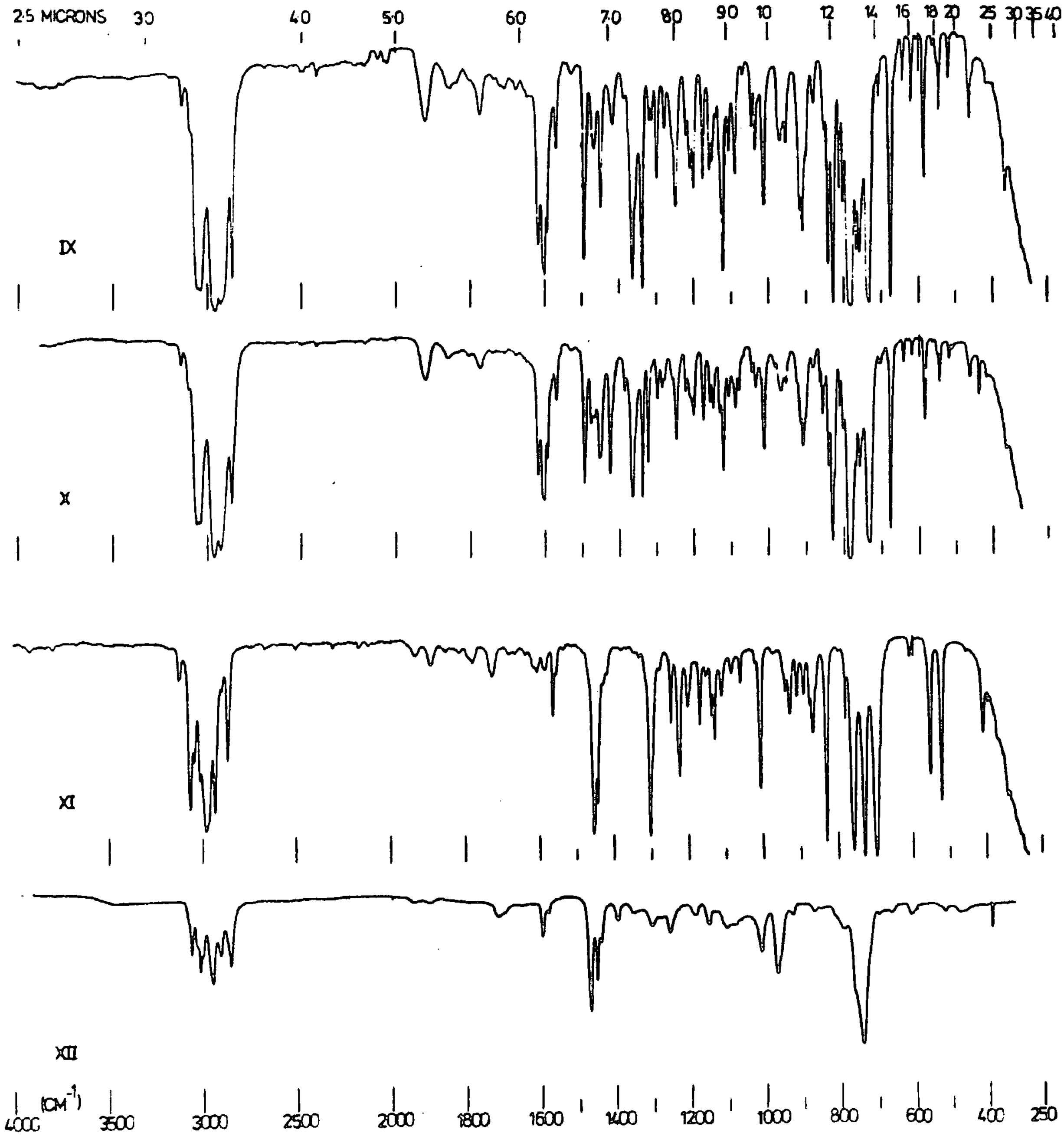
Infrared spectra are tabulated below. Compounds which have not been reported previously are marked with an asterisk.

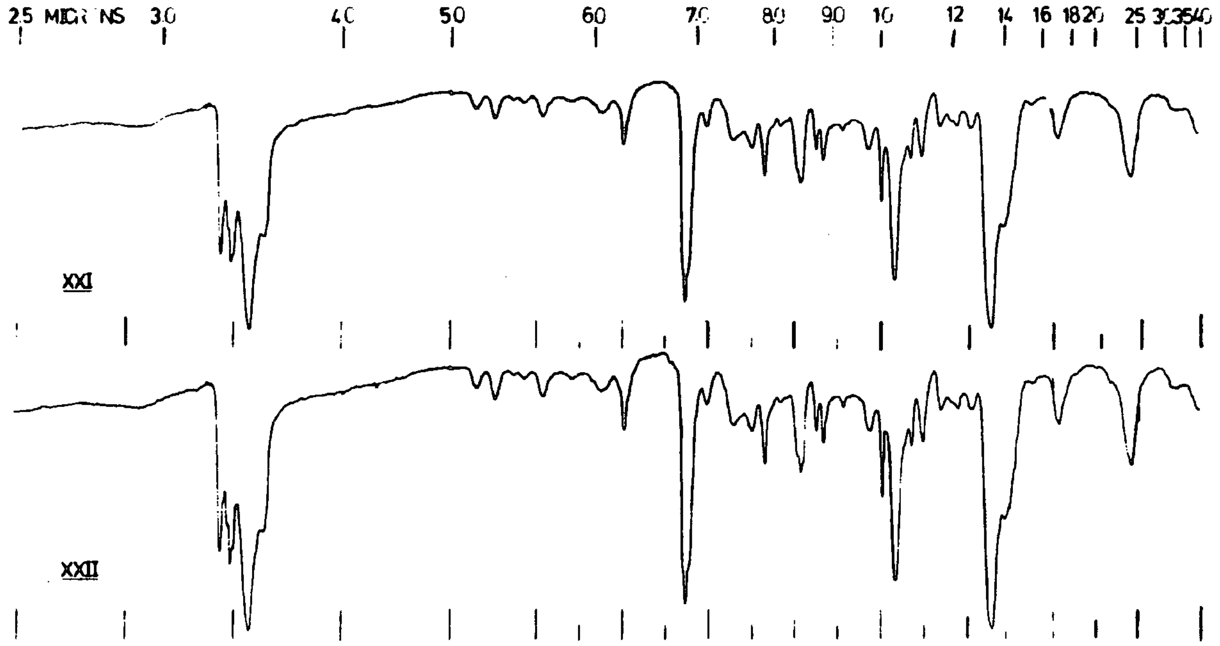
Spectrum No.	Nature of sample	Sample no.
I	1,4-Dihydronaphthalene-1,4-endo-oxide	16
II	Dimethylfulvene	
III	7-Isopropylidenebenzonorbornadiene	17
IV	Trans-1,2-diiodobenzocyclobutene	
V	Endo-1,4,4a,8b-tetrahydro-1,4-methanocyclobutadibenzene	18
VI	Exo-3,4-benzotricyclo[4.2.1.$0^{2,5}$]-nona-3,7-diene	19
VII	Pentacyclo[6.3.1.$1^{10,12}0^{2,7}0^{9,11}$]-trideca-2,4,6-triene	30
VIII*	Unidentified compound	
IX	Endo adduct	20
X	Exo adduct + acenaphthylene	22
XI	Benzonorbornadiene	15
XII	Poly(benzonorbornadiene) (WCl_6/Ph_4Sn)	poly(15-3)
XIII*	" (WCl_6/Me_4Sn)	poly(15-4)
XIV*	Poly(7-isopropylidene benzonorbornadiene) (WCl_6/Ph_4Sn)	poly(17-22)
XV*	Poly(7-isopropylidene benzonorbornadiene) (WCl_6/Me_4Sn)	poly(17-23)

Spectrum No.	Nature of sample	Sample no.
XVI*	Polymer from monomer 18 (WCl_6/Me_4Sn)	poly(18-7)
XVII*	" " " " (WCl_6/Ph_4Sn)	poly(18-8)
XVIII*	" " " " (WCl_6/Me_4Sn)	poly(18-9)
XIX*	Polymer from monomer 19 (WCl_6/Me_4Sn)	poly(19-10)
XX*	" " " " (WCl_6/Ph_4Sn)	poly(19-12)
XXI*	" " " " (WCl_6/Ph_4Sn)	poly(19-13)
XXII*	" " " " (WCl_6/Ph_4Sn)	poly(19-14)
XXIII*	Polymer from monomer 20 (WCl_6/Ph_4Sn)	poly(20-15)
XXIV*	" " " " (WCl_6/Ph_4Sn)	poly(20-17)
XXV*	" " " " (WCl_6/Me_4Sn)	poly(20-18)
XXVI*	" " " " (WCl_6/Ph_4Sn)	poly(20-19)
XXVII*	Polymer from monomer 22 (WCl_6/Me_4Sn)	poly(22-21)
XXVIII	Poly(acenaphthylene) (WCl_6/Ph_4Sn)	


2.5 MICRONS
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10
12
14
16
18
20
25
30
35
40
I
II
III
IV
4000 CM⁻¹
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
250


2.5 MICRONS
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10
12
14
16
18
20
25
30
35
40
V
VI
VII
VIII
(CM^{-1})
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
250


2·5 MICRONS
3·0
4·0
5·0
6·0
7·0
8·0
9·0
10
12
14
16
18
20
25
30
35
40
IX
X
XI
XII
(CM^{-1})
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
250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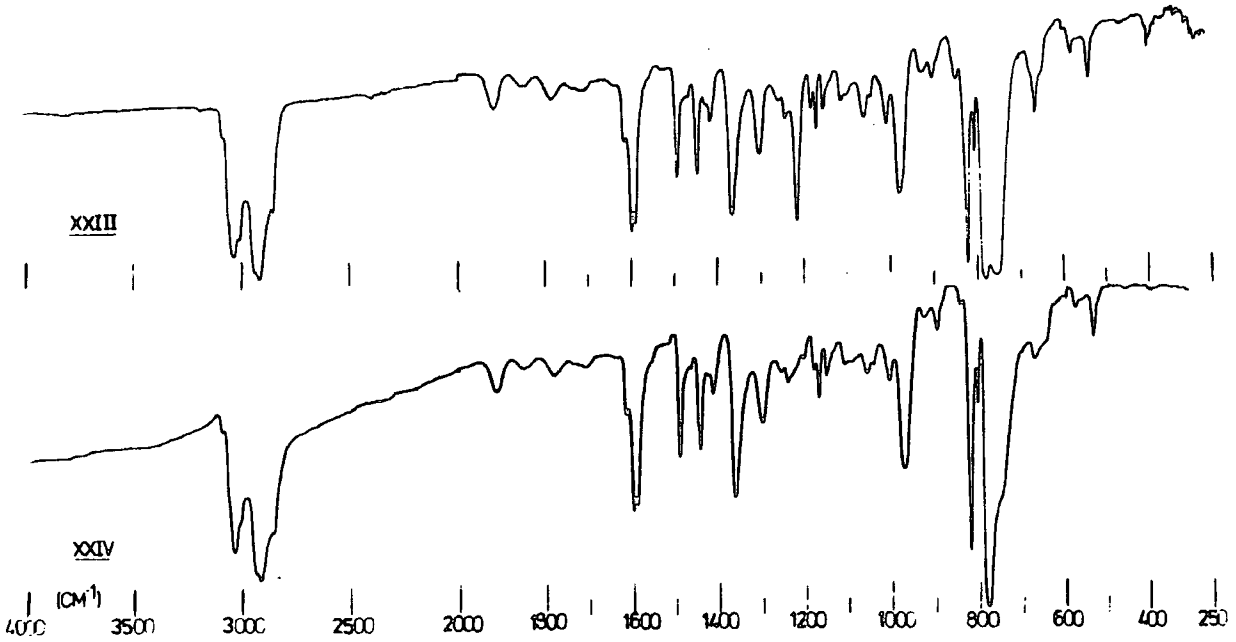
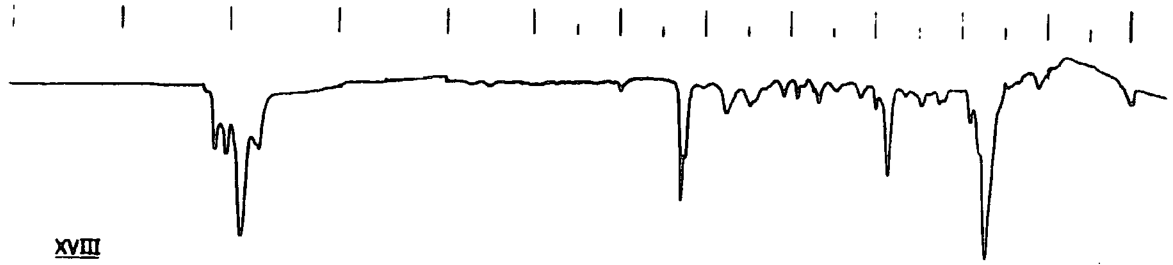
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10
12
14
16
18
20
25
30
35
40
XXI
XXII


XXIII
XXIV
(CM^{-1})
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
250

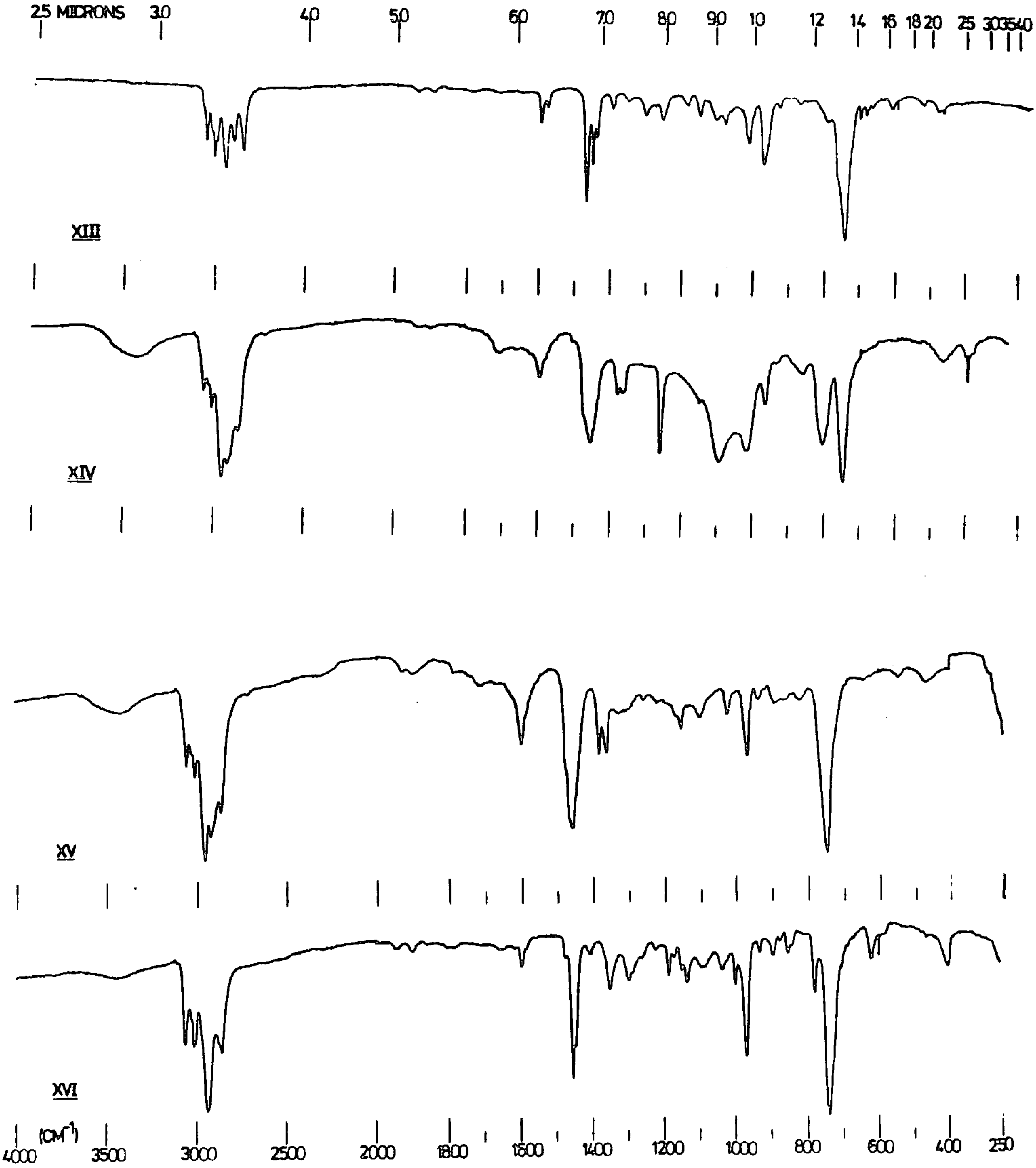
XVII

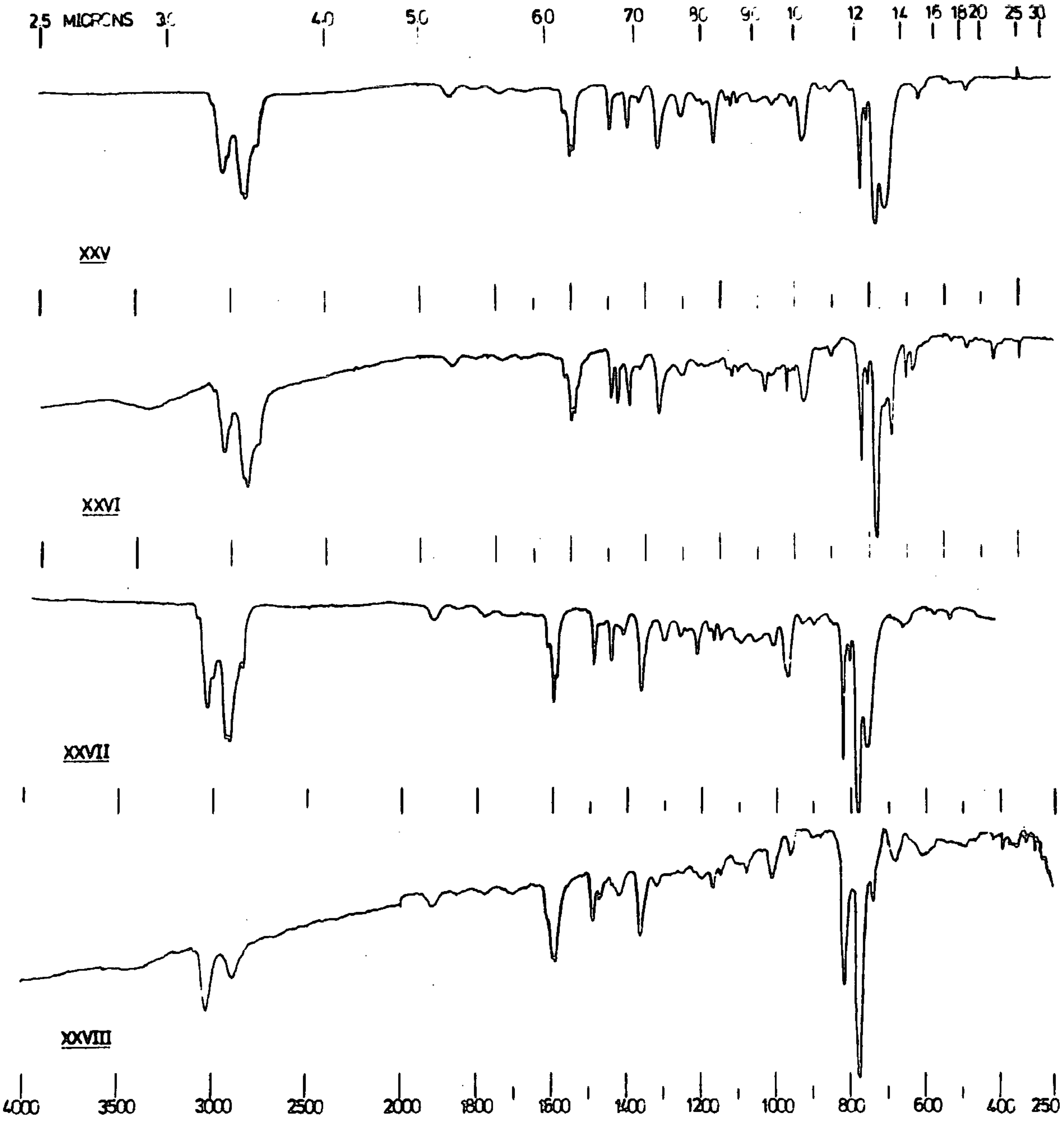


XVIII

XIX

XX


2.5 MICRONS
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10
12
14
16
18
20
25
30
35
40
XIII
XIV
XV
XVI
(CM⁻¹)
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
250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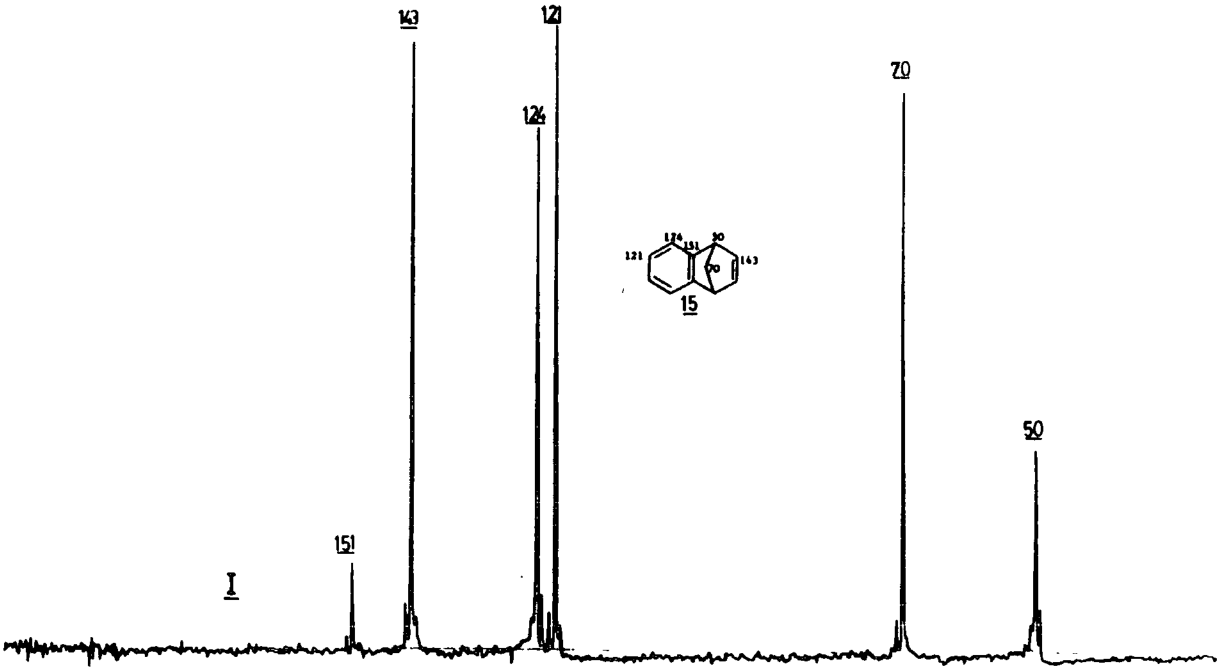
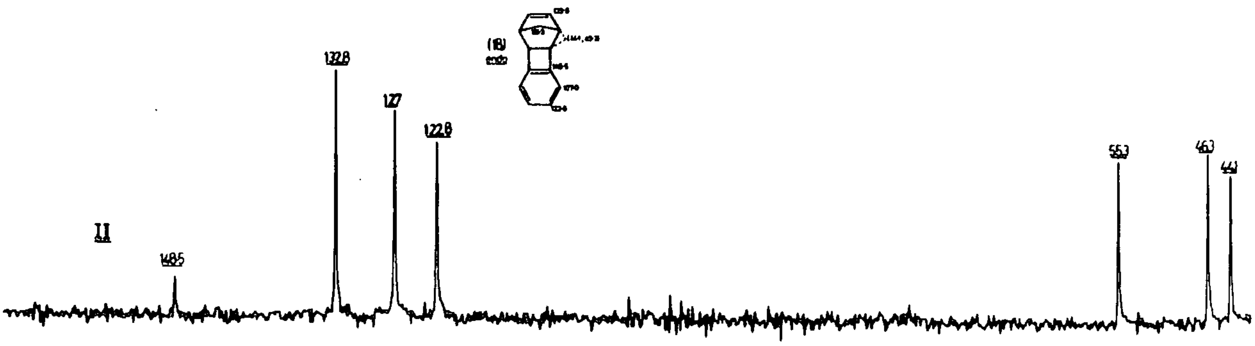
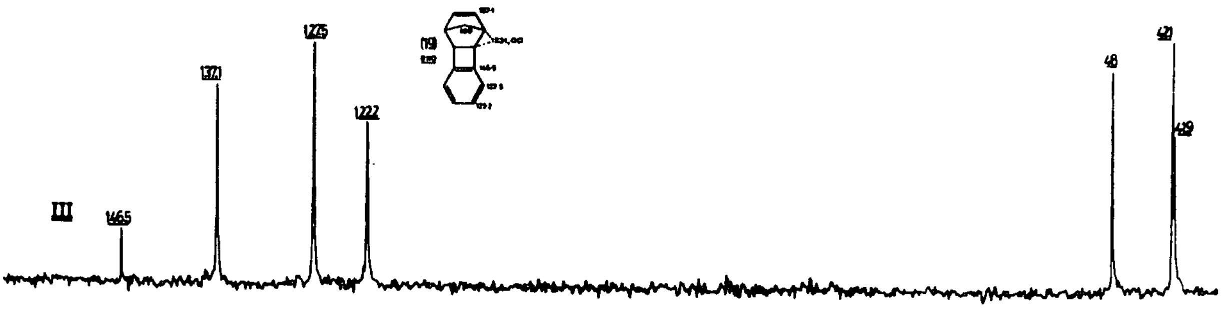
4.0
5.0
6.0
7.0
8.0
9.0
10
12
14
16
18
20
25
30
XXV
XXVI
XXVII
XXVIII
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
250

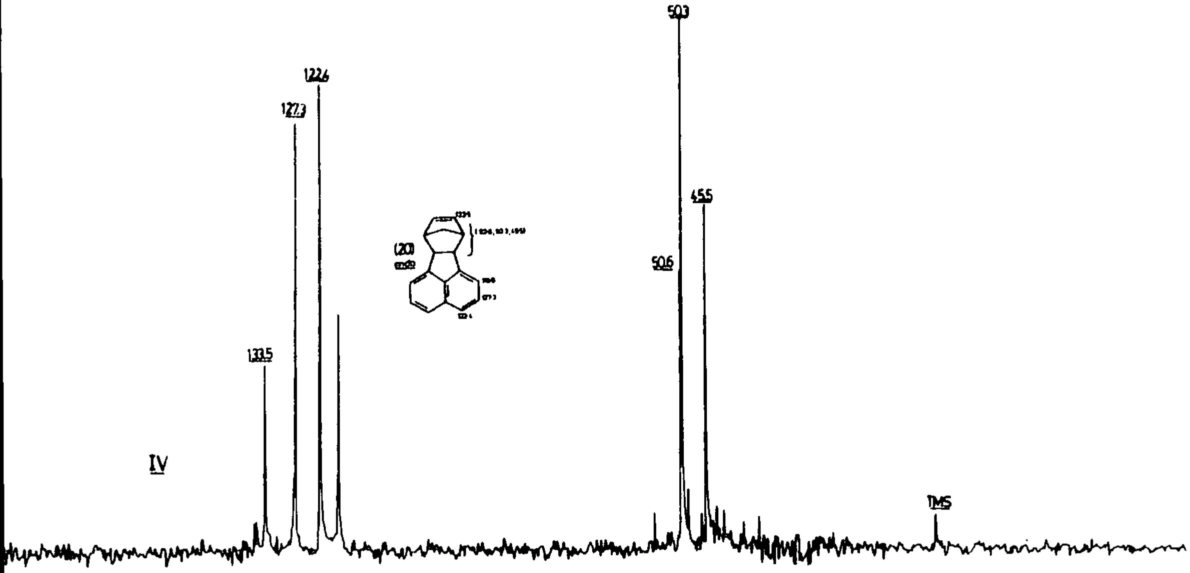
APPENDIX E

^{13}C N.M.R. SPECTRA

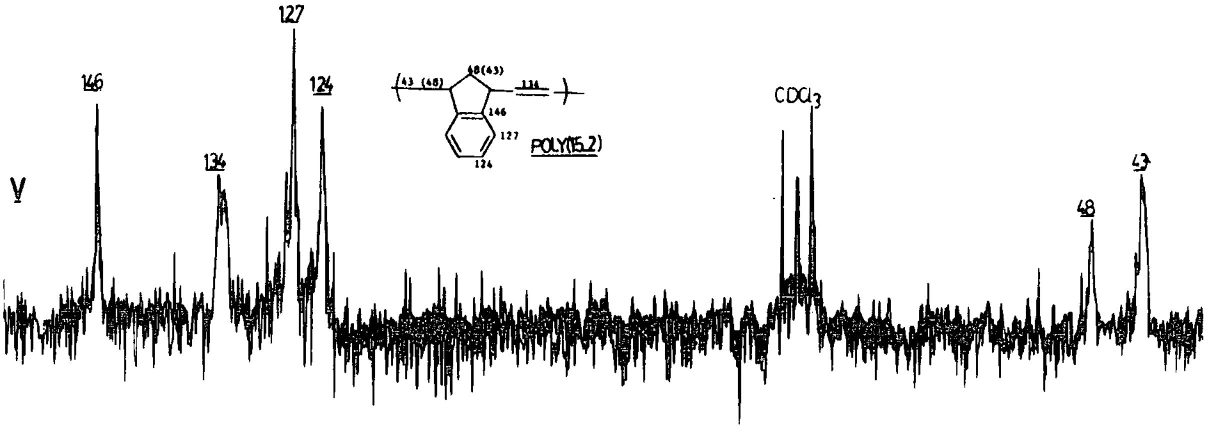

143
121
70
124
174
30
121
151
143
70
15
50
151
I


(18)
endo
132.8
127
122.8
55.3
46.3
44.1
II
148.5

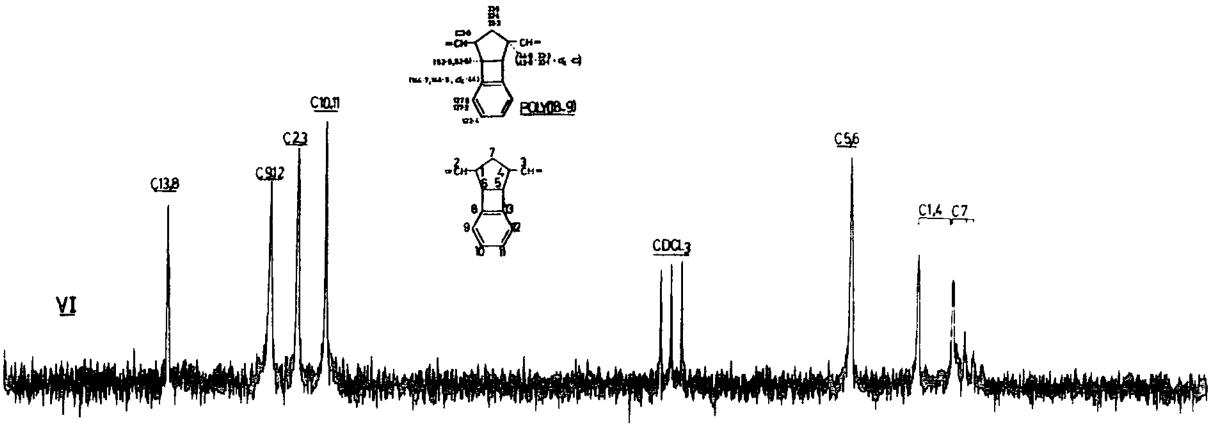

III
146.5
137.1
127.5
122.2
(19)
48
42.1
42.9

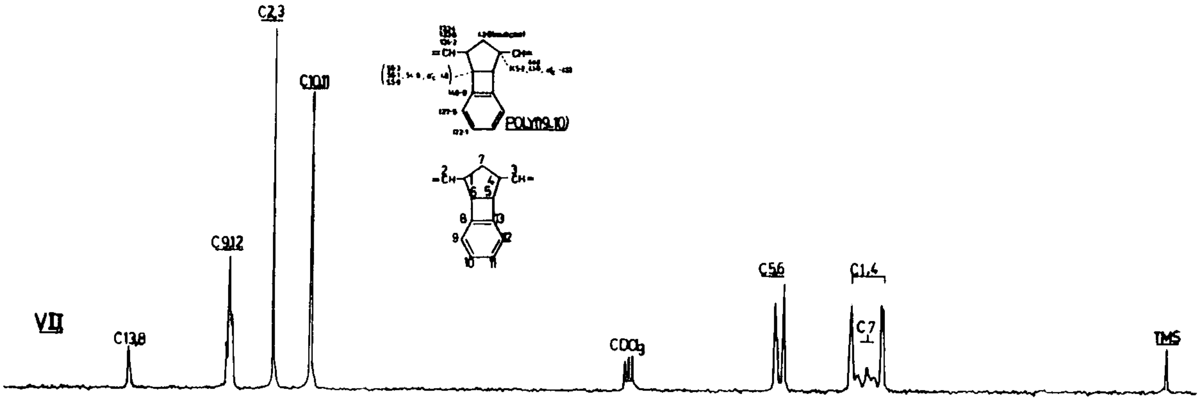

IV
133.5
127.3
122.6
(20)
50.3
50.6
45.5
TMS

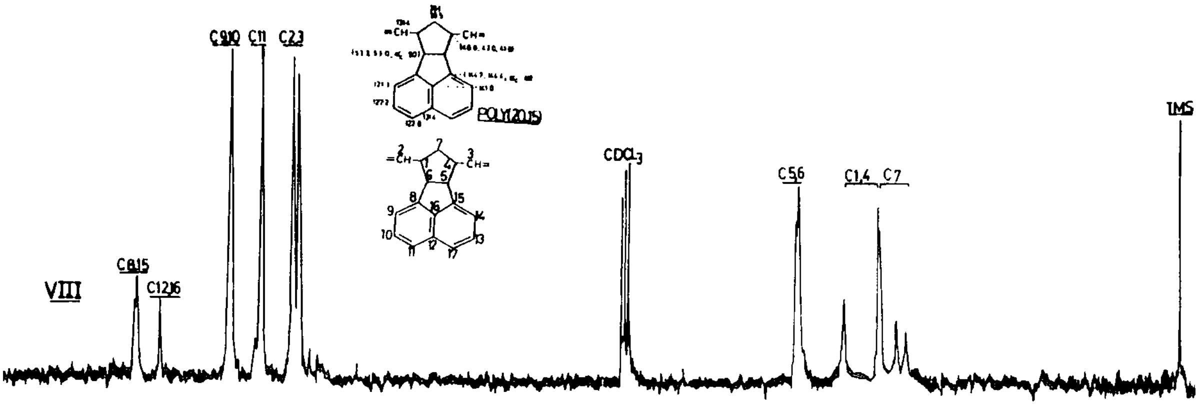
V


146
134
127
124
43 (48)
48(43)
134
146
127
124
POLY(15.2)
CDCl3
48
43

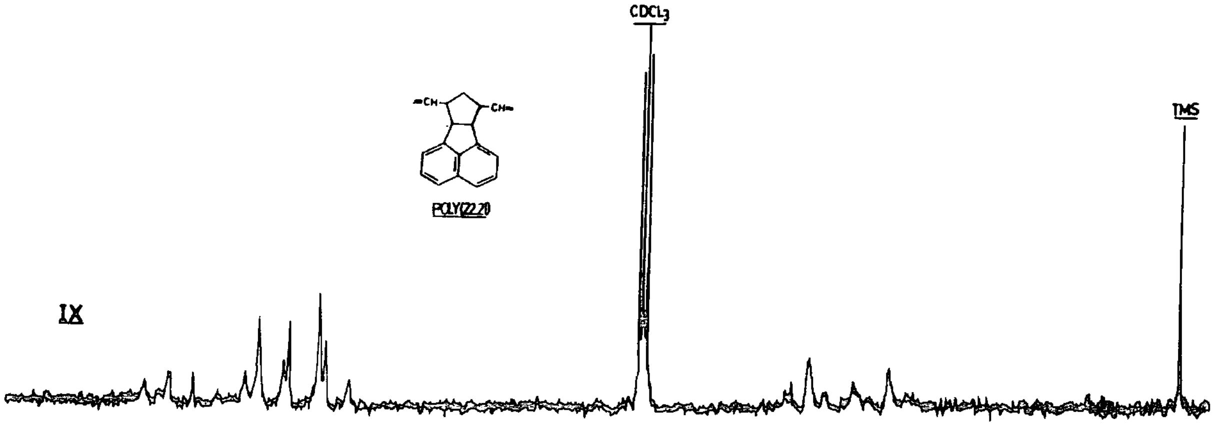
VI


C13,8
C9,12
C2,3
C10,11
CH–
POLY(18-9)
7
2
3
=CH
CH=
1
4
6
5
8
13
9
12
10
11
CDCl3
C5,6
C1,4
C7

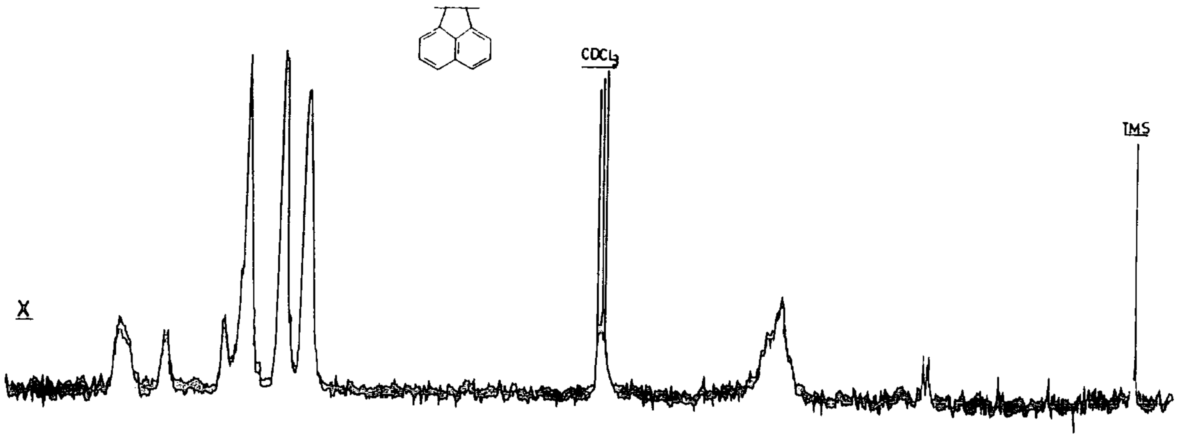

VII
C13,8
C9,12
C2,3
C10,11
POLY(9,10)
CDCl3
C5,6
C1,4
C7
TMS


VIII
C8,15
C12,16
C9,10
C11
C2,3
POLY(20,15)
CDCl3
C5,6
C1,4
C7
TMS

IX



X



APPENDIX F

RESEARCH COLLOQUIA, SEMINARS AND LECTURES

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

(a) All research colloquia, research seminars and lectures (by external speakers) arranged by the Department of Chemistry since 1 October, 1979.

(b) All research conferences attended by the writer of the thesis, during the period when the research for the thesis was carried out.

1. Research Colloquia, Seminars and Lectures

21 November 1979

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

28 November 1979

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

5 December 1979

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

12 December 1979

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

19 December 1979

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

30 January 1980

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

6 February 1980

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

23 April 1980

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

14 May 1980

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

21 May 1980

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

7 October 1980

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

16 October 1980

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

23 October 1980

Professor T.M. Sugden (Cambridge University).

30 October 1980

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

6 November 1980

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

12 November 1980

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

13 November 1980

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

19 November 1980

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

4 December 1980

Reverend R. Lancaster 'Fireworks'.

18 December 1980

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

22 January 1981

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

29 January 1981

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

5 February 1981

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

12 February 1981

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

18 February 1981

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

25 February 1981

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

11 March 1981

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

17 March 1981

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

7 May 1981

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

10 June 1981

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

2. Research Conferences

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

(b) Advances in Polymer Characterization. An International Symposium Durham, July 1981.

(c) The Fourth International Symposium on Olefin Metathesis, Belfast, Northern Ireland, September 1981.

REFERENCES

1. R.L. Banks and G.C. Bailey, Ind. Eng. Chem. Prod. Res. Develop., 3, 170 (1964).

2. N. Calderon, K.W. Scott, E.A. Ofstead, W.A. Judy, J. Amer. Chem. Soc., 90, 4133 (1968); Adv. Chem. Ser., 91, 399 (1968); A.C.S. Meeting Abs., 155, L54 (1968).

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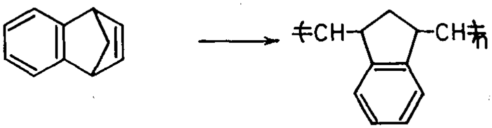
KEY MONOMER AND POLYMER STRUCTURES

15.



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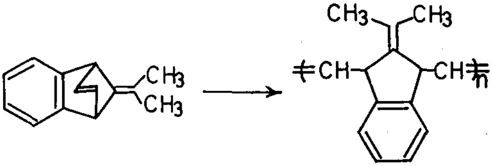

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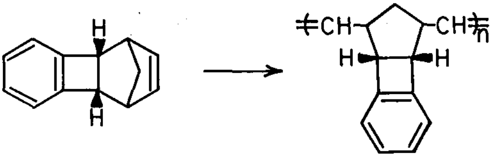

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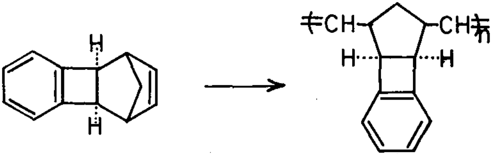

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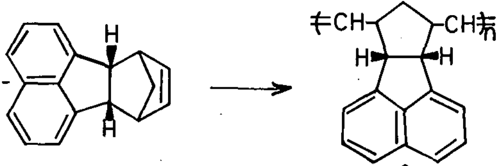

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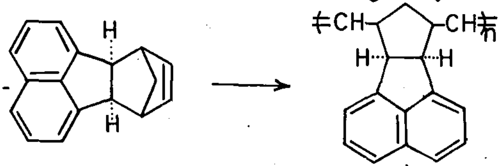

+ polyacenaphthylene