Syntheses and reactions of some polychloro-polycyclic alkenes

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SYNTHESES AND REACTIONS OF SOME POLYCHLORO-POLYCYCLIC ALKENES

A thesis submitted for the degree of Master of Science

by

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With my respect to my father and my mother.

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MEMORANDUM

The work reported in this thesis was carried out in the Chemistry Department of the University of Durham between January 1980 and November 1981. This work has not been submitted for any other degree and is the original work of the author except where acknowledged by references.

ABSTRACT

This thesis is divided into two sections. In the first section the syntheses and some reactions, in particular fluorination, of perchloroindene and perchloroindenone are described. The second section is concerned with the ring-opening polymerization of some chlorinated monomers using the catalyst system tungsten hexachloride/tetramethyl tin in toluene.

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SECTION I

SYNTHESIS AND SOME REACTIONS OF PERCHLOROINDENE AND PERCHLOROINDENONE

CHAPTER 1

INTRODUCTION AND BACKGROUND

1.1. Introduction

The work to be described in this section had as its initial objective the synthesis of perfluoroindene from perchloroindenone by halogen exchange. In practice this objective was not achieved. Before describing the work carried out the topic will be set in context by a brief discussion of the development of fluorine chemistry.

1.2. Historical background of organic fluorine chemistry

Fluorine is the most electronegative element and its reactions differ greatly from those of the other halogens not only in degree, but in type, making fluorine chemistry a special part of organic chemistry.[1] Although hydrogen fluoride was isolated by Scheel in 1771, organic fluorine chemistry grew rather slowly, partly because very few fluorinated compounds occur naturally, and partly because no simple methods for the synthesis of C-F bonds were found in the early years.[2] Its earliest beginnings can be traced to France, where Dumas and Peligot achieved what is claimed to have been this first recorded synthesis of an organic fluoride (methyl fluoride) in 1836, and where Moissan and Meslaus were active from 1880 onwards.[3] However, the Belgian chemist Swarts was perhaps the principal pioneer of the subject. In the period 1892 - 1938 he prepared a range of simple aliphatic fluoro-compounds, notably alkanes, alkenes and carboxylic acids, an activity which involved development of the halogen exchange reaction using mainly antimony

$$RX + \text{metal fluoride} \longrightarrow RF + \text{metal halide}$$

(where, X = Cl, Br or I)

and mercurous fluorides.[4] Swarts also defined the most important reactions and influences of fluorine as a substituent in an aliphatic environment. Swarts' studies allowed the introduction of dichloro-

difluoromethane in 1930 as an inert, non-toxic refrigerant, following work by Midgley and Henne of General Motors in the U.S.A.[5] This compound and related chlorofluorocarbons have been used widely as aerosol propellants. Interest in these chlorofluorocarbons was a major stimulus to organic fluorine chemistry but now, after many years of commercial application, they are suspected of causing damage to the Earth's ozone shield.

In 1927, Balz and Schiemann discovered the general route to aryl fluorides which now bears their names, this initiated interest in aromatic fluorine chemistry. Although the reaction is increasingly difficult to apply as the number of fluorines is increased, this method is still widely used for the synthesis of mono and difluorides.[1]

$$P\text{-}ClC_6H_4NH_2 \xrightarrow[(ii)\,NaBF_4]{(i)\,HNO_2/0^oC} P\text{-}ClC_6H_4N_2^+BF_4^- \xrightarrow{\Delta} P\text{-}ClC_6H_4F + N_2 + BF_3$$

In 1937 the saturated C_1-C_7 perfluorocarbons were isolated and characterised by Simons and Block.[6] These highly stable compounds became available at just the right time to be applied as working fluids in the atomic bomb (Manhattan) project, which required manipulation of the volatile uranium derivative UF_6, which is itself a powerful fluorinating agent. New synthetic methods were quickly developed to enable a whole range of fluorocarbon materials to be manufactured on a large scale, these included fluorination of hydrocarbons with elemental fluorine and with high valency metal fluorides such as CoF_3, these techniques required rather special apparatus. Another important pre-war (1938) discovery, made by Plunkett in Dupont's Laboratories, was that tetrafluoroethylene readily polymerized to high-molecular weight material (PTFE) which had outstanding chemical and physical properties. This discovery initiated the progressive development of fluoro-polymers. By the end of World War II,

during which Simons discovered his electrochemical fluorination technique, the stage was set for the rapid development of organofluorine chemistry which occurred in the immediate post-war period. Of particular note

$$C_3H_7CO_2H \xrightarrow[\text{anhydrous HF}]{\text{electrolysis in}} C_3F_7COF \xrightarrow{H_2O} C_3F_7CO_2H$$

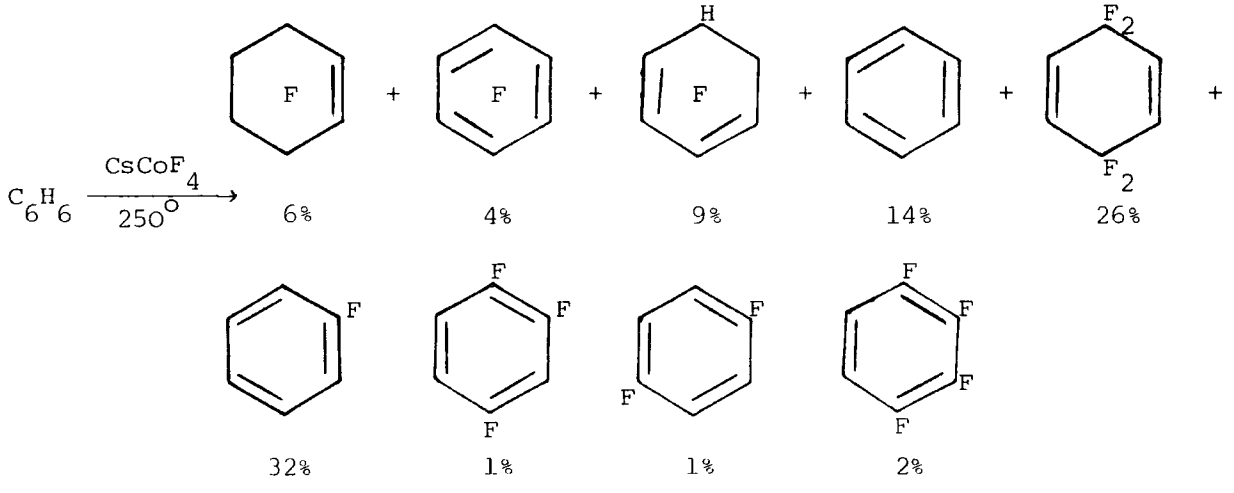
during this period are Henne's work on chlorofluoro compounds and halogen exchange techniques, and Miller's realization of the importance of fluoride ion in fluorocarbon chemistry. The subject has grown rapidly, and a great number of basic structures, involving a wide variety of different functional groups, have been synthesized and studied.[6-11] Very large numbers of compounds having a particular fluorinated grouping in an otherwise hydrocarbon based molecule have been made and have aroused interest as a consequence of the unusual physical properties and biological effects observed. Such compounds can often be made from commercially available fluorinated precursors, using syntheses which do not require specialized apparatus.

1.3. Fluorinated aromatic compounds

Aromatic compounds containing relatively few fluorine atoms, e.g. benzotrifluoride and fluorobenzene, have been known for over seventy years, none of them have achieved large-scale production. More recently methods have been developed for the synthesis of highly fluorinated aromatic compounds.[12] Hexa and pentafluorobenzene, decafluorobiphenyl, octafluoronaphthalene and numerous derived compounds are now commercially available. Some of these compounds show promise in various applications as pharmaceutical chemicals, bacteriocides and fungicides, and as intermediates for the preparation of fluids and polymers.

The limitations of the classical Balz-Schiemann route[13,14] to

fluorinated aromatic compounds were mentioned above, a large number of alternative syntheses have been developed in the last few years. Direct conversion of a readily available hydrocarbon aromatic compound to a fluorocarbon aromatic compound is, of course, a highly desirable objective, unfortunately it is not generally available yet. When organic compounds are fluorinated by the classical techniques using cobaltic fluoride,[15,16] elemental fluorine[17] or electrochemical fluorination[18] the usual result is saturation and elimination of functional groups. This statement generalizes a great amount of information and for example, the production of unfragmented perfluorocarbons from hydrocarbons by direct elemental fluorination involves complicated technologies which took many years to develop. In recent years direct electrophilic fluorination of aromatic compounds by CF_3OF,[19] CF_3COOF,[20] $CsSO_4F$,[21] and the element itself[22] have been extensively investigated. However, these investigations have provided routes to small quantities of lightly fluorinated aromatic compounds but not to perfluoro compounds. One promising development for the direct route is the work of the Birmingham group on complex metallic fluorides such as $CsCoF_4$,[23] an example of fluorination with this reagent is summarized below.



The first general route to highly fluorinated aromatic compounds involved fluorination over cobaltic fluoride, followed by dehydrofluorination with base and/or defluorination over active metal or metal oxide surfaces. For example, the fluorination of benzene over[24,25] cobaltic fluoride gives a complex mixture of hydrofluorocyclohexanes which can be used as starting materials for synthesis of fluorinated cyclohexenes, cyclohexadienes and aromatic compounds as shown schematically in Figure 1.1.

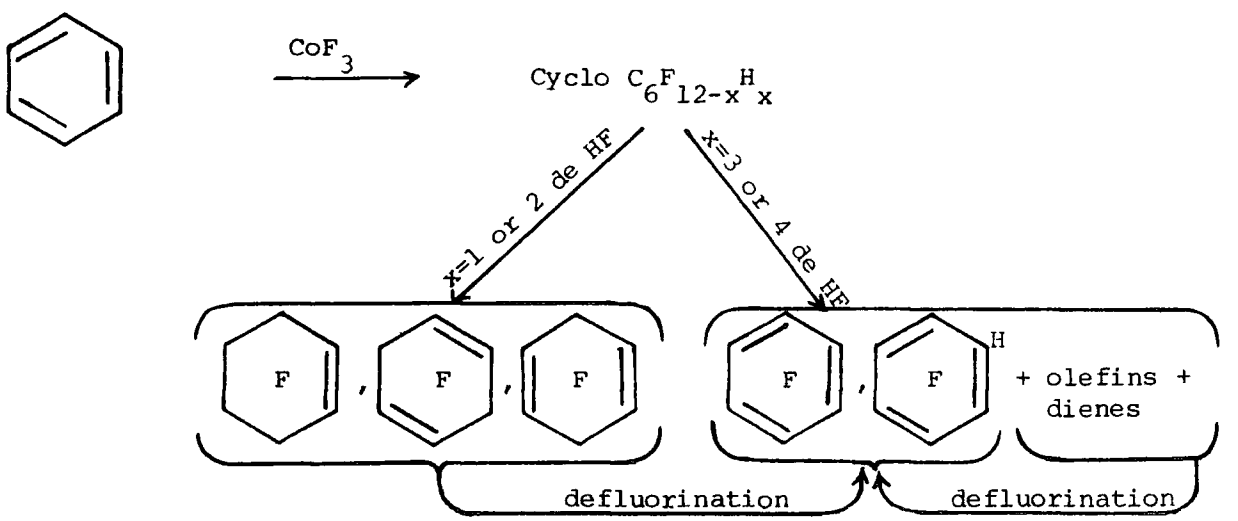


Figure 1.1. Schematic for fluorination-dehydrofluorination-defluorination route to polyfluorobenzenes.

This route has been generalized for the synthesis of perfluorinated alkyl benzenes, naphthalene, and other polycyclic aromatic compounds.[26]

An alternative approach to the synthesis of highly fluorinated aromatic compounds involves halogen exchange, which has been considerably developed during the last 20 to 25 years. The preparation of hexafluorobenzene was first described in 1947.[27] It was prepared in 1955 by the pyrolysis of tribromofluoromethane,[28] as shown below.

$$CBr_3F \xrightarrow[\text{Pt. tube}]{630 - 640/1 \text{ atm.}} C_6F_6 + 2Br$$

The yield obtained from this route was low, and the route starting with

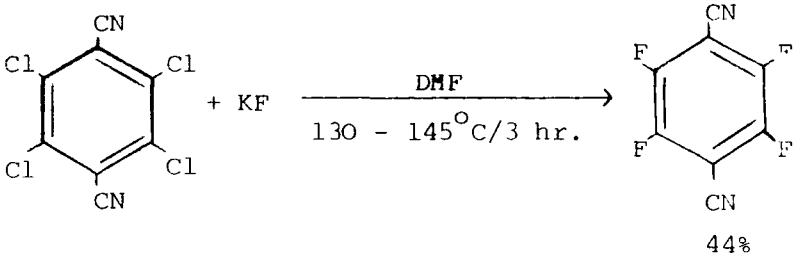
CoF_3 fluorination of benzene (Figure 1.1) is more economical. An alternative route uses halogen exchange from perchlorobenzene, initial fluorination with either chlorine trifluoride[29] or with fluorine gas,[30] gives a mixture of chlorofluorocyclohexanes which may be dehalogenated to give hexafluorobenzene and various chlorofluorobenzenes

$$C_6Cl_6 + 3F_2 \xrightarrow{CF_2ClCCl_2F} C_6Cl_xF_{12-x} \xrightarrow[330^oC]{Fe} C_6F_6 + C_6ClF_5 + C_6Cl_2F_4 + C_6Cl_3F_3$$

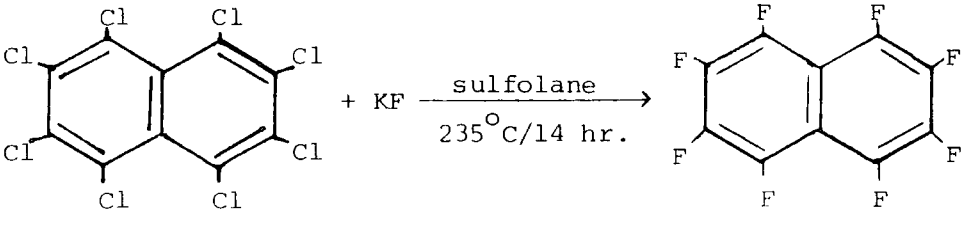
where x = 5, 6, 7.

More recently, a more direct route to aromatic fluorocarbons has been developed. This is based on the reaction of perchloro aromatic compounds with potassium fluoride in solvents,[31-33] as illustrated below

$$C_6Cl_6 + KF \xrightarrow[230 - 240^oC/18\ hr.]{sulfolane} \underset{25\%}{C_6ClF_5} + \underset{24\%}{C_6Cl_2F_4} + \underset{30\%}{C_6Cl_3F_3}$$



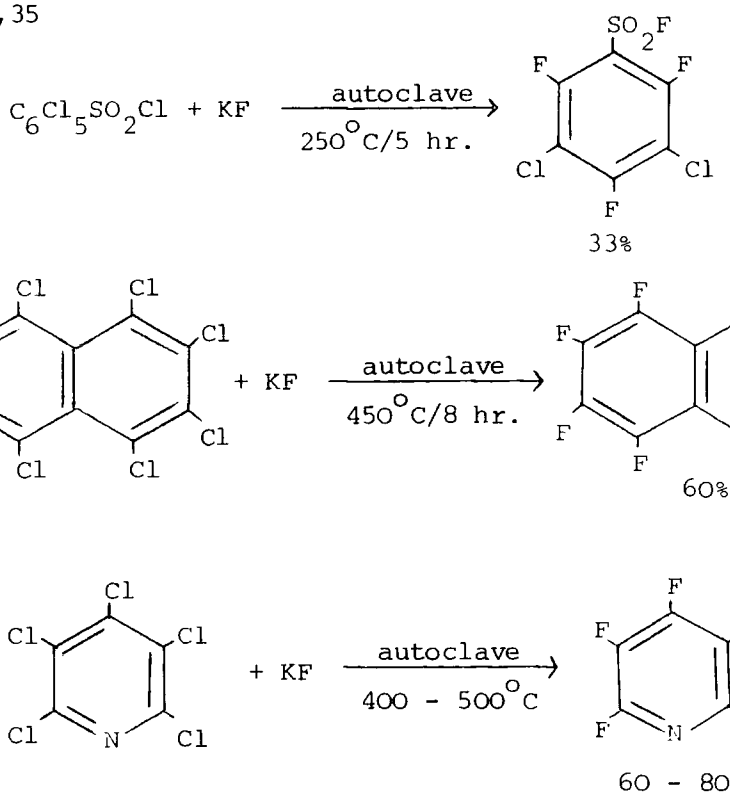
44%



50 - 60%

Fluorination by halogen exchange also takes place in the absence of solvent if the reactants are heated in a closed vessel under autogeneous pressure. Hexachlorobenzene reacts with potassium fluoride at 450 - 500°C to give a mixture of hexafluorobenzene and chlorofluoro-

benzene other perchloro aromatic compounds react similarly as shown below.[30,34,35]



During the last few years the pyrolytic elimination of bridging units from polycyclic compounds has found widespread use in synthesis, the elimination of the one carbon bridge from norbornadienes and related systems is a typical example of the process. For example, the elimination of ethylene from compounds (1) and (2) allows the isolation of the unstable compounds isobenzofuran (3) and tetrafluoro-isoindole (4)[36,37,38] Figure 1.2.

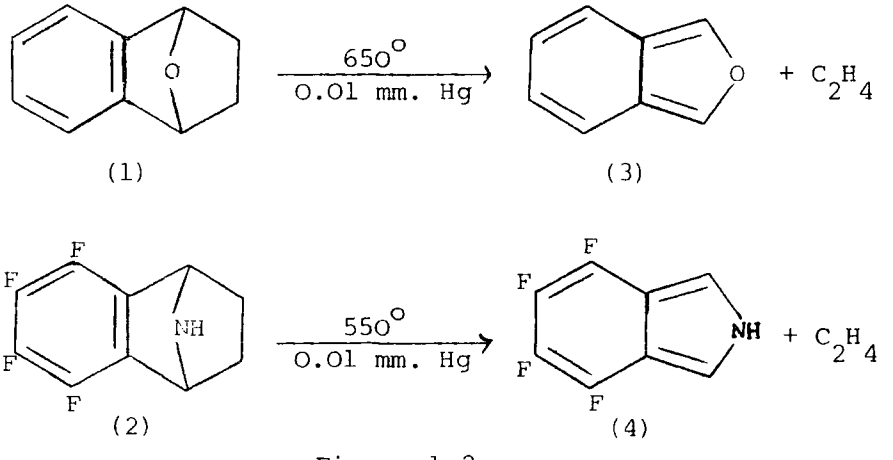
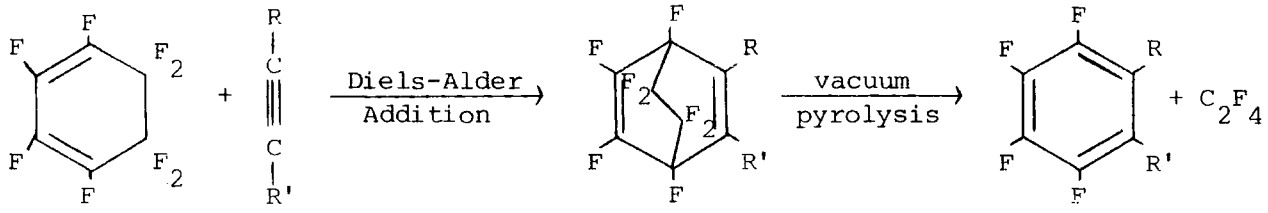
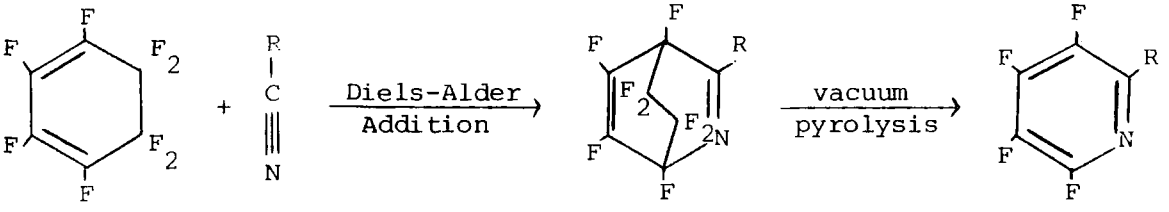


Figure 1.2

This pyrolysis route has also found application in the chemistry of fluorinated compounds; thus, a series of syntheses of fluorinated aromatic compounds has been reported which uses a route based on an initial Diels-Alder reaction of fluorinated dienes followed by pyrolysis of the primary adducts. Feast et.al. have described the syntheses summarized below:[39,40,41]





This route was subsequently extended to the syntheses of 2,3-disubstituted hexafluoro-naphthalenes and fluorinated isoquinolines.[42] These preparations are summarized in Figure 1.3.

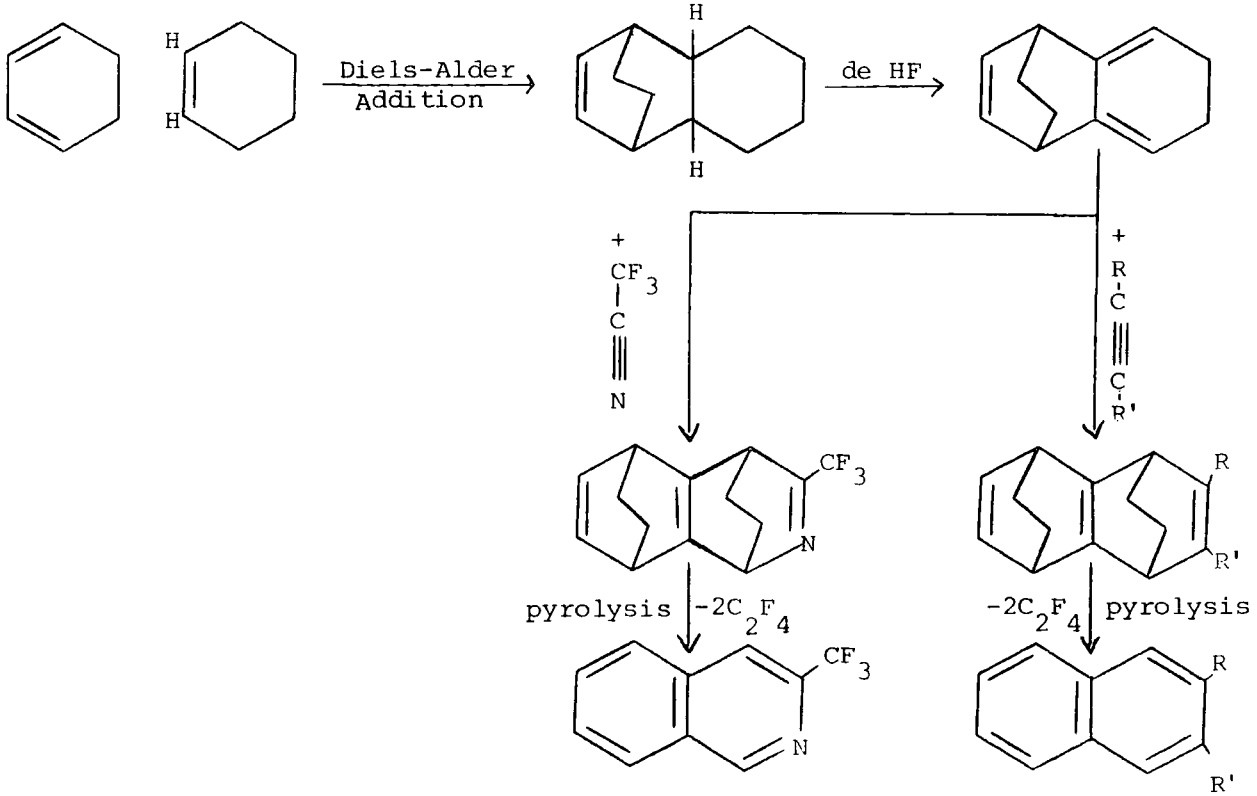
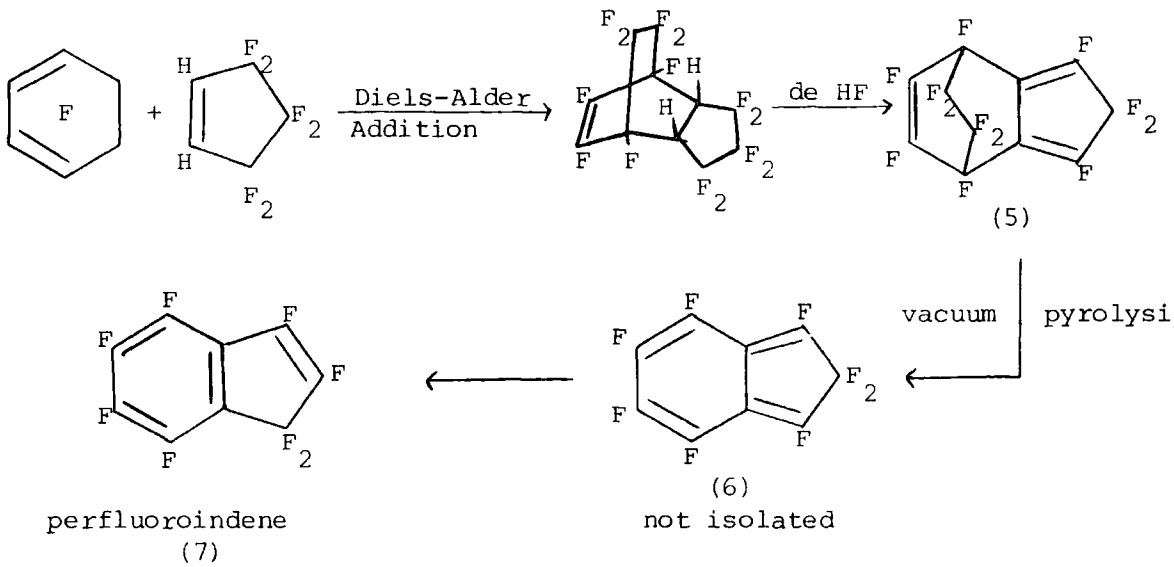


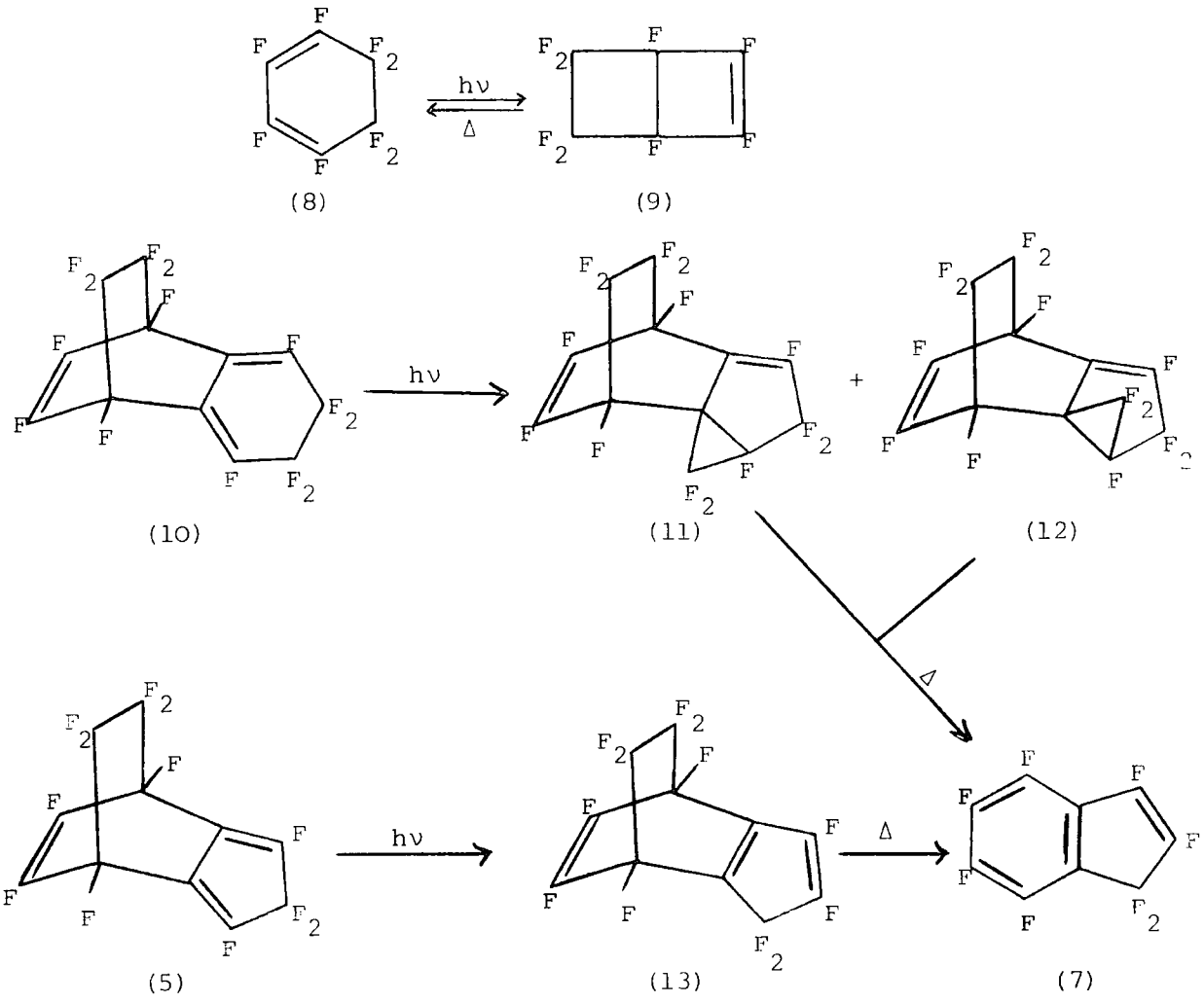
Figure 1.3. (Unmarked bonds to fluorine)

The expected primary product of extrusion of the bridging unit in most cases gives the expected aromatic product, (as was indicated earlier) but, in some cases, the expected product was not isolated. Thus, the flash vacuum pyrolysis of compound (5) yields perfluoroindene (7) and not the anticipated primary product perfluoroisoindene (6) as shown below[38,43]

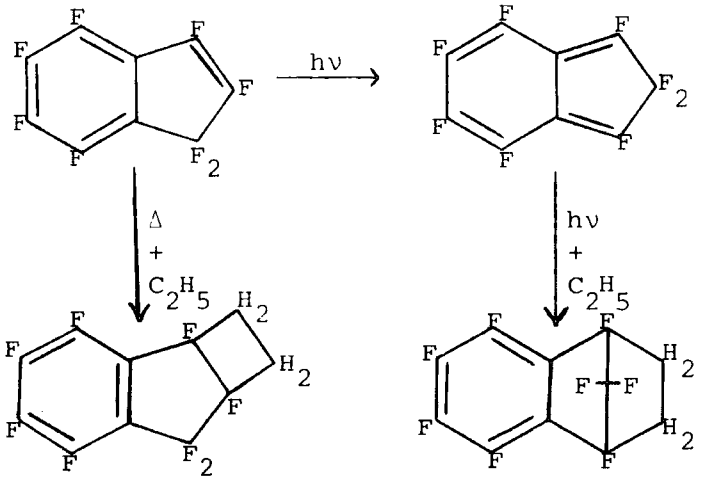


Feast et.al. reported recently the photochemical isomerization of perfluorocyclohexa-1,3 diene (8), when irradiated in the vapour phase this diene gives compound (9) quantitatively. They also synthesized two perfluoropolycyclic compounds which contain cyclic conjugated diene systems and studied their photochemical isomerization. Irradiation of compounds (10) and (5) in the vapour phase with UV light results in their isomerization to isomers (11 and 12) and 13 respectively. Compound 13 probably arises from 5 by way of a photochemical 1,5-sigmatropic migration of a fluorine atom. Vacuum pyrolysis of 13 and 5 gives perfluoroindene in a good yield. While isomers 11 and 12 were interconverted and under conditions similar to those where breakdown occured, CF_2 and C_2F_4 units were expelled giving

perfluoroindene. These isomerizations are summarized below.[43]

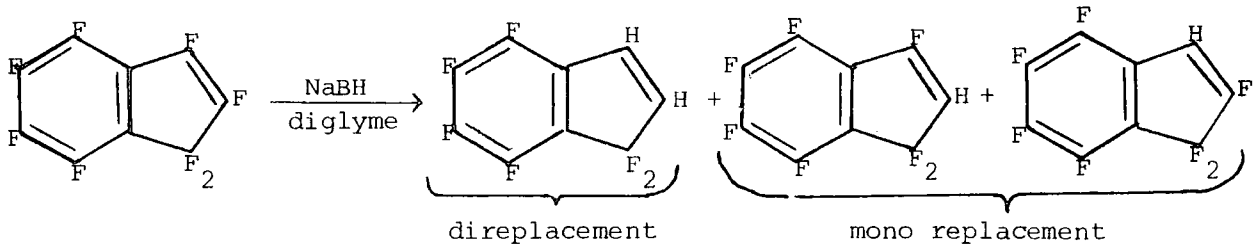


Perfluoroindene, when irradiated in the vapour phase, isomerizes via a sigmatropic fluorine shift to perfluoroisoindene which can be trapped as its Diels-Alder adduct with ethylene; the thermal reaction between perfluoroindene and ethylene gives the 1,2-adduct,[44] as shown in the scheme below.



Nucleophilic substitution in perfluoroindene

The reactions of polyfluoro polynuclear aromatic compounds with nucleophiles have occupied the practical and theoretical interests of a number of workers for some years.[45-47] The nucleophilic substitution reactions of perfluoroindene have also received some attention; thus it was shown to react cleanly with sodium borohydride in diglyme, the reaction could be regulated[48] to give either the mono (C_9HF_7) or di ($C_9H_2F_6$) replacement product following the equation:[49]



The foregoing brief discussion shows that perfluoroindene is an interesting compound. The available route to perfluoroindene was rather difficult and the starting materials relatively expensive, because of this we set out to see if we could make it more cheaply. The route investigated is described in Chapter 2.

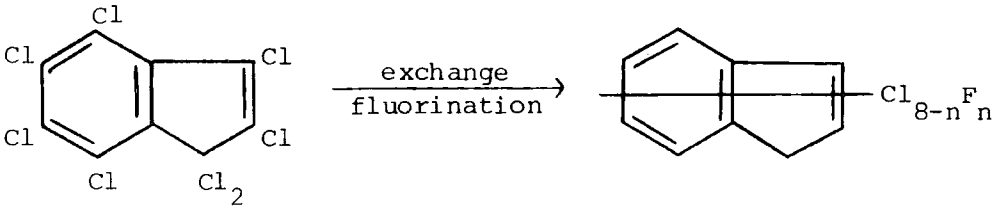
SECTION I

CHAPTER 2

ATTEMPTED EXCHANGE FLUORINATION OF PERCHLOROINDENE

2.1. Introduction

The objective of the work described in this Chapter was the synthesis of chlorofluoroindenes by exchange fluorination of perchloroindene;

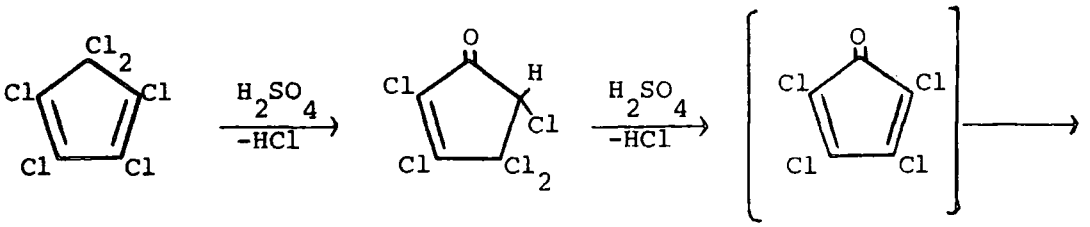


The first step in this process was the synthesis of perchloroindene, the route chosen was via the chlorination of perchloroindenone which in turn can be made from the commercially available perchlorocyclopentadiene. This Chapter describes both the work involved in the synthesis of the perchloro compounds and the characterization of compounds actually obtained from the fluorination attempts.

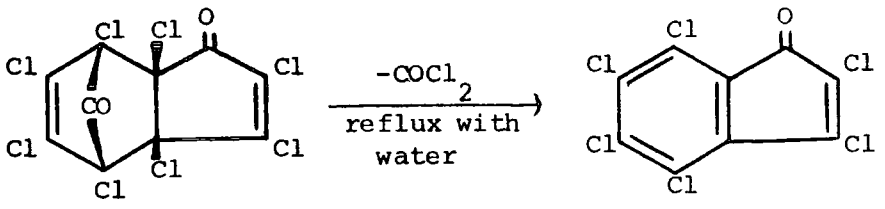
2.2. Synthesis of Hexachloroindenone

Several syntheses of hexachloroindenone have been described.[50-58,60] In this work it was decided to use one of the earliest methods reported.[51] The first step in this synthesis involved the reaction of hexachlorocyclopentadiene (14) with concentrated sulphuric acid, hydrogen-chloride is evolved and the initial product is the enone (15). Tetrachlorocyclopentadienone (16) is formed as a reactive intermediate by dehydrochlorination of (15) and dimerizes spontaneously to give the endo Diels-Alder dimer,[52] octachlorotricyclo [5,2,1,$O^{2,6}$]deca-4,8-dien-3,10-dione* (17). The reaction between this diketone and water gives hexachloroindenone, the syntheses is summarized below:

* *In the early literature, particularly patents, this compound is named as a derivative of indene, i.e. octachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene-1,8-dione.*

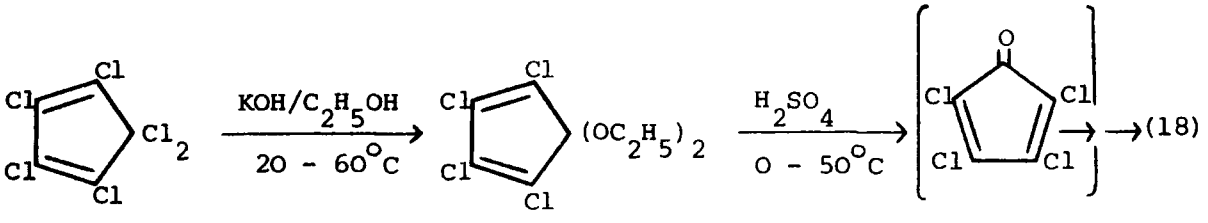


(14) (15) (16) not isolated

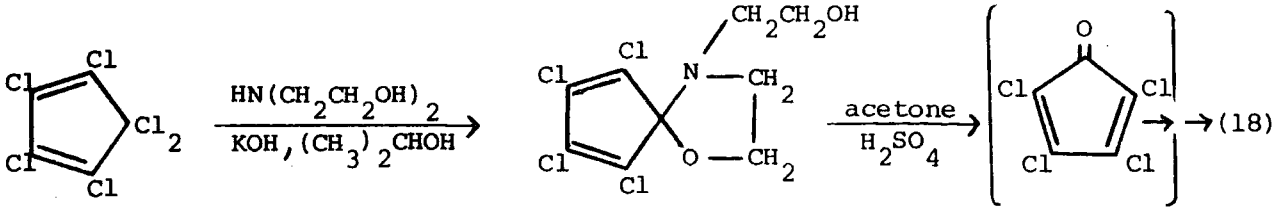


(17) (18)

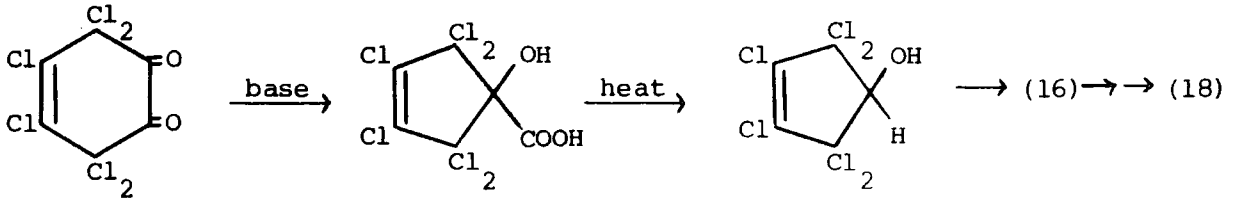
Several alternative syntheses of hexachloroindenone have been described, most of these involve the last two steps shown in the scheme above but use different routes from perchlorocyclopentadiene to tetrachlorocyclopentadienone. Thus, hexachlorocyclopentadiene reacts with alcohols in the presence of alkali metal hydroxides to give 5,5-dialkoxyltetrachlorocyclopentadienes, which can be decomposed in several different ways to give tetrachlorocyclopentadienone.[53,54,55] One example is given below.



A closely related route involves the reaction of diethanolamine with the same starting material as illustrated below.[56]

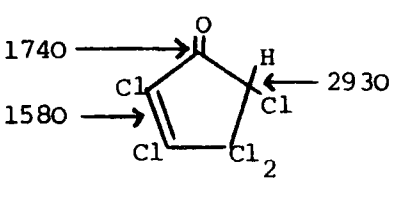


Vollmann has reported an alternative syntheses starting from hexachlorodiketocyclohexene.[57]

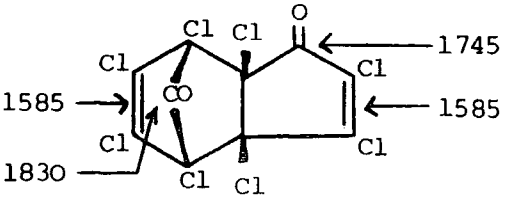


Several other authors have noted that hexachloroindenone is readily formed from octachloroindene; for example, by hydrolysis,[57] or reaction with sulphur trioxide.[58]

The original route reported by Newcomer and McBee in 1949 has the advantages of using simple experimental procedures and relatively cheap starting materials, and although the yield from this reaction is not very high it was chosen as a convenient way of making hexachloroindenone.[51] The preparation involved adding an excess of concentrated sulphuric acid to vigorously stirred hexachlorocyclopentadiene and heating the mixture at 80° - 90°C for 19 hours, during which time HCl was evolved. After cooling this mixture it was poured onto ice and the resulting brown solid was recovered by filtration, washed with water to remove residual acid, and dried. The infra red spectrum of this product showed no CH absorbtions but in the carbonyl region there were bands at ca. 1835, 1750 and 1730 cm.$^{-1}$, therefore it was deduced that this product was not a pure compound but a mixture. Authentic samples of (15) and (17) were available from earlier work (D. Hunter this department)[59] and the infra red spectra of these compounds showed the characteristic frequencies as indicated below:



(15)



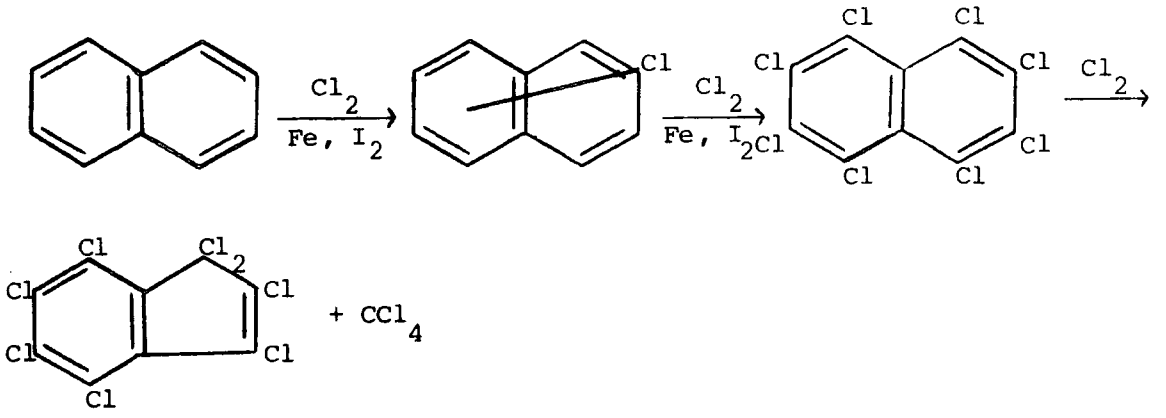
(17)

The absence of a CH stretching absorption in the spectrum of the crude product excluded (15) from the mixture. The bands at ca. 1835, 1750 and 1585 probably arose from (17) as the major component in the mixture, and the extra bands at ca. 1730 clearly belonged to another carbonyl compound possibly (18). The initial product was dissolved in petroleum ether and boiled with activated charcoal, then filtered through a hyflo plug; the resulting solution gave brown crystals on cooling, and evaporation of the solvent gave an orange semi-solid residue. The infra red spectrum of the brown crystals showed several bands in the carbonyl and C=C region, as did the infra red spectrum of the orange residue. It seemed likely that both the crystalized material and the residue were mixtures. At this stage it was realized that compound (18) could be prepared directly from (17) by simply boiling with water and since (18) was the desired product futher attempts to purify (17) were abandoned. The brown crystals obtained as described above were mixed with a large excess of water and the mixture refluxed for half an hour, on cooling a solid orange product separated which was recovered by filtration and recrystallized from acetone to give orange crystals of perchloroindenone, the infra red spectrum of this product showed no absorbtions in CH region and strong bands at 1730 (>C=O) and 1575 $cm.^{-1}$ (-CCl=CCl-), the compound had correct elemental analysis and its other physical characteristics were in good agreement with those described in the literature.[56,60,61] The semi solid orange residue was treated in the same manner to give perchloroindenone.

2.3. Synthesis of octachloroindene

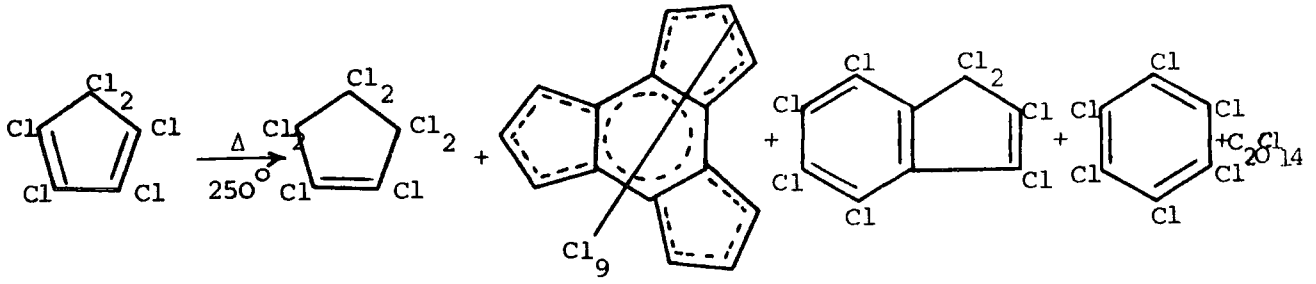
Octachloroindene has been synthesized in several ways.[62-68] Rössler has described the preparation of octachloroindene from

naphthalene by direct chlorination in the presence of a halogen carrier, this reaction can be regulated to give predominantly mono chloronaphthalene, octachloronaphthalene, or perchloroindene, the sequence is shown below:[62]



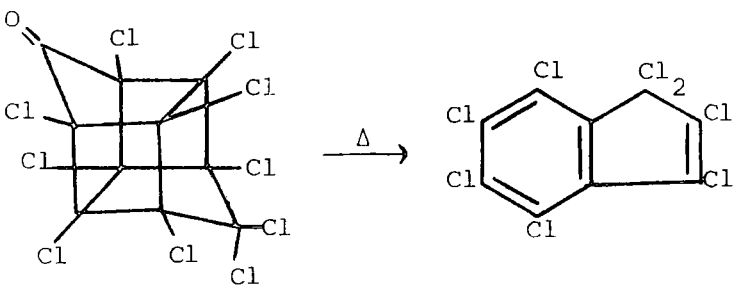
The ring system of perchloronaphthalene is degraded to perchloroindene with loss of one carbon atom, which is chlorinated to carbontetrachloride. Perchloroindene itself is subject to futher chlorination to give perchloroindane; this last reaction is reversible and when perchloroindane is heated above 250°C it eliminates chlorine to give perchloroindene.[62,63,64,58]

Ruetman has described the synthesis of octachloroindene by direct chlorination at 600°C in the absence of catalyst, of n-propylbenzene, carbontetrachloride was used as a diluent to control the exothermic reaction, he also reported that the chlorination of indene under similar conditions gave octachloroindene.[65] McBee et.al. have reported that the pyrolysis of hexachlorocyclopentadiene gave octachloroindene together with several other compounds as shown below.[66]



11 - 22% 30% 9% 1% 1%

Eaton and coworkers showed pyrolysis of decachloropentacyclo [5.3.0.$0^{2,6}$.$0^{4,10}$.$0^{5,9}$]decan-3-one gave octachloroindene, they also



reported that octachloroindene was formed by the reaction of phosphorus pentachloride with hexachloroindenone.[58] This latter preparation of octachloroindene had been reported previously by Zincke and Gunther,[67] and this procedure has been used in this work. The experimental method involves heating hexachloroindenone with an excess of phosphorus pentachloride in a Carius tube at 200 - 250°C for 2 hours. Octachloroindene is a white crystalline solid, the melting point of the material obtained in this work was 130°C; other workers have reported values in the range 84° - 138.5°C.[63,67,68] It is soluble in carbontetrachloride and diethyl ether and slightly soluble in xylene and the lower aliphatic alcohols e.g. ethanol, methanol and isopropanol and insoluble in water. The material produced in this work had correct elemental analysis, i.r. and mass spectrum, and was a single component on HPLC analysis. Octachloroindene is stable when stored in the dark under dry conditions, however, it is very readily hydrolysed to octachloroindenone and is light sensitive.

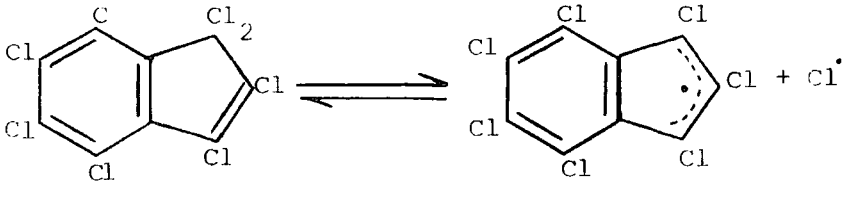
2.4. Light sensitivity of octachloroindene

Octachloroindene is very sensitive to the light, when the bright white crystals were exposed to day light they changed to a light pink within ten minutes. Some preliminary experiments were carried out to try to establish the cause of the observed colour

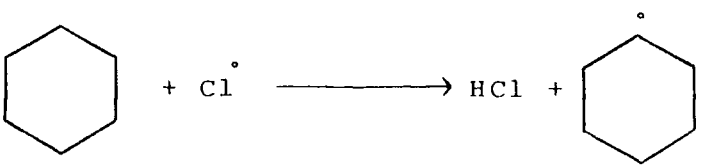
change. A solution of octachloroindene in cyclohexane (0.14M) was streamed with dry nitrogen to remove dissolved oxygen. Two cylindrical pyrex reaction vessels were filled in this way, one of these tubes was covered and stored in the dark while the other was put on the window sill. The initially colourless liquid in the tube on the window sill started to change to pink after about forty minutes, the colour of the solution became progressively darker turning from pink to violet, after one week, the glass-stopper was removed and an acid gas (Litmus) was evolved. The solvent was evaporated and the violet product was dried on the vacuum line, examination by i.r. spectroscopy showed a weak band in the CH aliphatic stretching frequency region (2860 - 2960 $cm.^{-1}$), as well as all the bands of octachloroindene. Thin Layer Chromatography showed that the product was a mixture of at least five components. An attempt was made to separate this mixture by "dry column" chromatography (see Experimental); the first fraction from the column was perchloroindene and the constituted 79% of the mixture, the remaining 21% consisting of a complex mixture of overlapping bands. The tube which was stored in the dark was still colourless after one month, its colour started to change when it was exposed to day light.

The procedure was repeated using carbontetrachloride as solvent, the tube on the window sill was still colourless after one week, and evaporation of the solvent gave perchloroindene.

The observations reported above are consistent with a hypothesis of a photochemical homolysis of a carbon chlorine bond to produce a heptachloroindenyl radical and a chlorine atom.

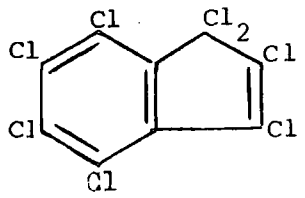


When the reaction is carried out in cyclohexane the chlorine atom can abstract a hydrogen atom from solvent to give cyclohexyl radical plus hydrogen chloride. The heptachloroindenyl and cyclohexyl radicals



formed initially may undergo a variety of further reactions such as dimerization, coupling, transfer and abstraction. The products of these reactions may undergo further reaction to give the complicated mixture actually observed. As intensely coloured species are formed they eventually absorb all the incident light and restrict further reaction of perchloroindene, it may also be that accumulated hydrogen chloride has an influence in the course of reaction. It was decided to investigate the light induced reaction between octachloroindene and toluene. This system was chosen in the hope of obtaining a simpler reaction product than was observed with cyclohexane. A solution of octachloroindene in toluene was irradiated in a Rayonet photochemical reactor using 3500Å lamps, the solution was continually streamed with dry nitrogen and the gas emerging from the reactor was bubbled through a standard solution of sodium hydroxide which was protected from atmospheric contamination by a Drechsel bottle containing heavy white oil. Estimation of the amount of hydrogen chloride evolved by titrating the sodium hydroxide solution from the Drechsel bottle and careful monitoring of the mass balance showed that for every mole of perchloroindene irradiated 2.8 moles of HCl were evolved during this reaction, and also that incorporation of residues derived from toluene into the crude product resulted in an increase in mass of 16%.

The overall reaction can be represented as follows:-



$+ nC_6H_5CH_3 \longrightarrow$ crude product + 2.8 HCl
mass increased by 16%

mol. wt. 392 92 36.46

If there was one toluene residue for each HCl evolved then the increase in mass of the crude product should correspond to

$$\frac{2.8 \times 92 - 2.8 \times 36.46}{392} \times 100,$$

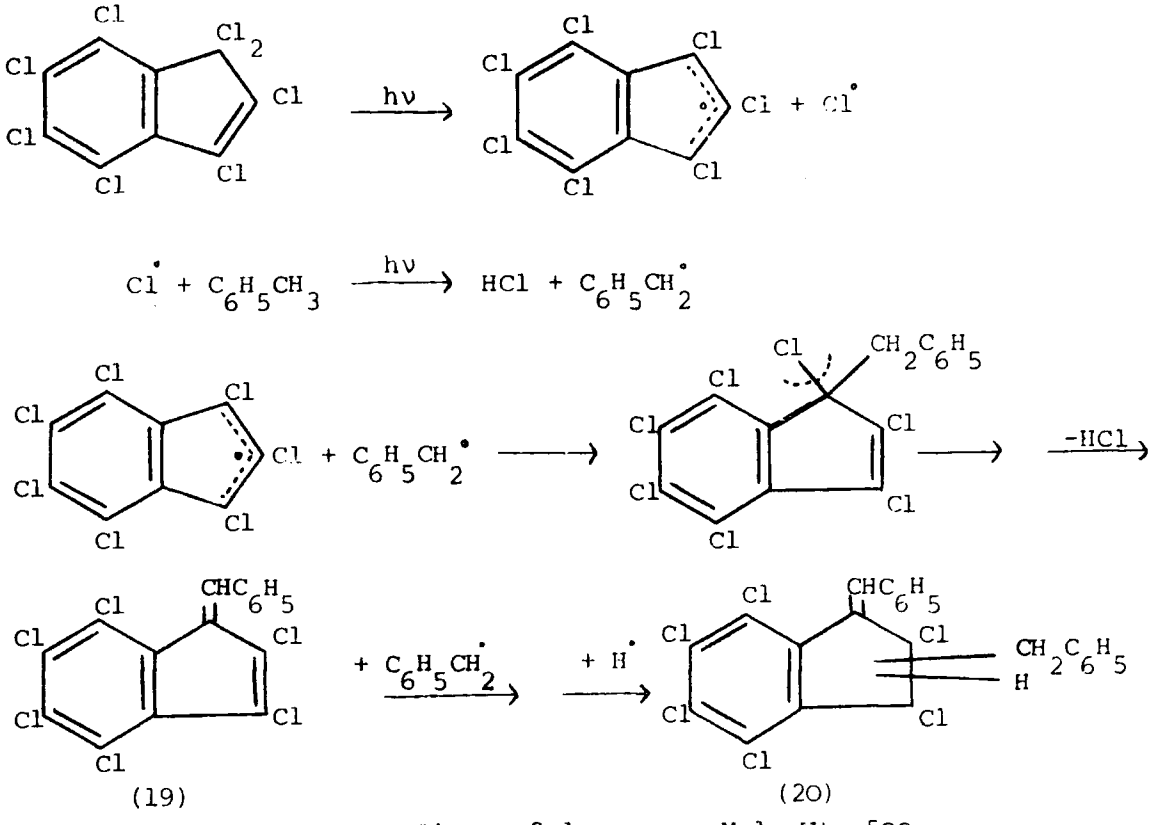
that is an approximate increase of 40%, this clearly is not in agreement with experimental observation. If, on the other hand, one toluene residue gives rise to 2HCl molecules the increase in mass of the crude produce is given by

$$\frac{1.4 \times 92 - 2.8 \times 36.46}{392} \times 100 = \underline{ca}.\ 7\%$$

The observed result was a 16% mass increase suggesting that the real situation lies somewhere between the two possibilities considered above, that is some of the toluene residues are incorporated with loss of 2HCl molecules per molecule of toluene and some are incorporated with the loss of only one HCl residue.

The crude product was separated by column chromatography into four fractions. Each fraction contained chlorine as evidenced by the isotope patterns in the mass spectra. The C-H stretching region in the infra red spectrum of each fraction indicated both aromatic and aliphatic CH structural features, and the spectra of the separated fractions were very similar. The mass spectrum of the first fraction had a highest mass peak m/e = 500 and an isotope pattern indicating the presence of six chlorine atoms; the base peak of the spectrum was

at m/e 91 ($C_7H_7^+$) confirming the presence of benzyl residues suggested by the i.r. data and the mass balance analysis; there were also peaks in the mass spectrum corresponding to the loss of 91 and 35 from the ion at highest mass. A possible reaction sequence leading to a product consistent with the above data can be postulated as shown in Figure 2.1. It is clear that the sequence shown could lead to a complex



(19) (20)

Figure 2.1 Mol. Wt. 500

mixture since the benzilidene derivative (19) can exist as cis- and trans- isomers and subsequent reaction with benzyl radicals could occur at a number of sites.

The second and third fractions had similar spectroscopic properties to fraction 1. The fourth fraction had a somewhat similar infra red spectrum but the mass spectrum was very complex showing peaks up to m/e values of at least 1150, these high mass peaks all contained many chlorine atoms and the material is clearly product of combination

of at least three polychloroindenyl units. The outcome of this reaction is consistent with the occurrence of a free radical chain process initiated by photolysis of a carbon-chlorine bond in the initial perchloroindenyl molecule. The product mixture was complex and a detailed assignment was not possible.

2.5. Attempted fluorination of octachloroindene using potassium fluoride

As discussed in Chapter 1, the synthesis of fluorinated compounds has been achieved by a variety of techniques. Exchange fluorination has found widespread use in the preparation of fluoro-aromatic compounds from their perchloro-analogues. Alkali metal fluorides are widely used in this process,[69] and an effective fluorinating agent of this type is potassium fluoride.

Potassium fluoride is deliquescent, and for all fluorinations it must be thoroughly dried. It may be used in glass or metal vessels, and the reactions are particularly sensitive to temperature.[70] Fluorination using potassium fluoride takes place either in a polar aprotic or in the absence of solvent,[30-35] as was described in Chapter 1. Potassium fluoride was used in this attempt to make chlorofluoroindenes having the molecular formulae $C_9Cl_{8-n}F_n$ (where n is an integer from 1 to 8) by exchange fluorination of octachloroindene in the absence of solvent. The reactions were carried out by heating mixtures of perchloroindene with excess of dry potassium fluoride in flame dry Carius tubes. Any trace of water will result in hydrolysis of octachloroindene to give hexachloroindenone and hydrogen chloride which will both decrease the possible product yield and create the risk of pressure build up in the Carius tube. Consequently great care was taken to make sure that water was excluded. The Carius tube was sealed

under vacuum and heated. In practice the optimum conditions for reaction were obtained after numerous trial experiments, a few of which are recorded in Table 2.1.

Table 2.1

Experiment no.	Starting materials g		T°C	Time (hrs.)	
	KF	C_9Cl_8			
1	15	2	380	17	Ca. 3% C_9Cl_8 recovered, plus fragmentation products and uncharacterized black resin
2	13.36	3	300	17	As above
3	15	3.1	260	23	Mixed chlorofluoro-indenes ca. 66% by weight
4	16.76	2.2	250	17	Trace reaction, ca. 70% C_9Cl_8 recovered
5	16.6	2	200	17	No reaction

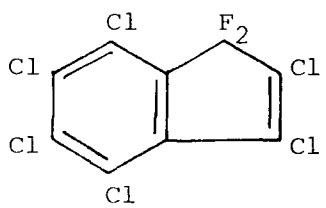
It is clear that at temperatures lower than 250°C the reaction will not occur, but below 300°C chlorofluoroindenes can be isolated from the reaction product and at temperatures greater than 300°C the materials begin to decompose and only fragmentation products and tars are obtained. A temperature of 260°C and reaction time of 23 hours were found to produce the best yield of chlorofluoroindene (run 3). The material was extracted from inorganic salts as described in the experimental section. The yellow brown product was analysed by i.r. spectroscopy which showed two strong absorptions in the double bond region, the peak at 1662 $cm.^{-1}$ confirmed the presence of -CF=CCl-, the other peak at 1585 $cm.^{-1}$ indicating a -CCl=CCl- unit. Perfluoroindene shows a -CF=CF-

absorption at 1740 $cm.^{-1}$ and perchloroindenone shows a carbonyl absorption at 1730 $cm.^{-1}$, the absence of either of these peaks showed that extensive fluorination was not achieved and also showed that the isolation technique did not result in hydrolysis of the gem dihalo group. The product was examined by t.l.c. using n-hexane as solvent, which established that the product was a mixture and that neither perchloroindene or indenone were present. An attempt to separate the mixture into its components was made using "dry column" chromatography (see experimental). The first fraction collected gave, on partial evaporation of the solvent, a yellow crystalline product. Examination of this product by t.l.c. indicated a single component. When the product was analysed by mass spectroscopy the data in Table 2.2 were obtained. The peak at highest mass (m/e 356) showed an isotope pattern indicating six chlorines and is consistent with the molecular formula $C_9F_2Cl_6$; expulsion of Cl from this parent leads to a fragment ion at m/e 321, and a peak at this mass with a five chlorine isotope pattern is observed, loss of a further Cl leads to m/e 286 ($C_9F_2Cl_4$). However, there is another peak showing a five chlorine isotope pattern at m/e

	M/e	
	356	$C_9F_2Cl_6$
	340	$C_9F_3Cl_5$
Compound (21)	321	$C_9F_2Cl_5$
	305	$C_9F_3Cl_4$
Compound (22)	286	$C_9F_2Cl_4$
	270	$C_9F_3Cl_3$
	251	$C_9F_2Cl_3$
	235	$C_9F_3Cl_2$

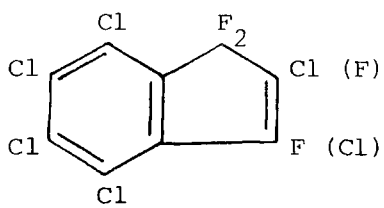
Table 2.2

340 which can not reasonably be derived from the highest mass ion (m/e 356) but does fit the molecular formula $C_9F_3Cl_5$; this gives rise to a set of fragment ions at 305, 270 and 235 by successive losses of chlorine atoms. Thus, the mass spectrum strongly suggests that this component is a mixture of two compounds $C_9F_2Cl_6$ and $C_9F_3Cl_5$, both giving expected parent and fragment ions, there being one fragment ion in common at m/e 251. High performance liquid chromatography showed that there were indeed two components in this first fraction. Further structural evidence for the two components of fraction 1 was provided by ^{19}F and i.r. spectroscopy. Two absorptions in the double bond region indicated the presence of a -CF=CCl- unit (1665 $cm.^{-1}$) and a -CCl=CCl- unit (1590 $cm.^{-1}$) in the mixture. The ^{19}F n.m.r. spectrum showed three resonances, a triplet 123.6 p.p.m. up field from $CFCl_3$ ($J = 7.5\ H_z$), a singlet at 124.6 p.p.m. and a doublet at 126.2 p.p.m. ($J = 7.5\ H_z$); taken together with the mass spectroscopic data the signals at 123.6 and 126.2 p.p.m. can be assigned to the pentachlorotrifluoroindene and indicate a difluoromethylene group coupling with a single fluorine, the singlet at 124.6 p.p.m. being assigned to the hexachlorodifluoroindene and this product must therefore be the 1,1-difluoro compound. Nucleophilic substitution is expected to be easiest in the five membered ring and it appears that this first fraction arises from fluorination in the five membered ring and that the two products detected can be assigned the structures:-



(21)

and



(22)

The position of the vinylic fluorine in the trifluoro product can not be assigned with certainty on the basis of shift and coupling constant, but the integrated intensities indicate that the trifluoride amounts to 46% of this mixture.

Unfortunately this first fraction was the only chlorofluoroindene fraction obtained. The chromatography column was used near a well illuminated window and although the initial product mixture was relatively light in colour the appearance of the column rapidly darkened and all further fractions contained C-H units as indicated by infra red spectroscopy (Appendix 1, No. 10, 11, 12, 13). The explanation of this is simple in the light of the photo-reactivity of perchloroindene discussed earlier, in fact this observation was made shortly before the photo-sensitivity of this type of compound had been realized. The materials eluted from the column were examined by elemental analysis, infra red, mass and ^{19}F n.m.r. spectroscopy. No unambiguously characterized single compounds were obtained but some clear generalizations can be made:-

(i) in no case was there extensive fluorination, exchange of three chlorines appears to be as far as the reaction goes under the condition investigated;

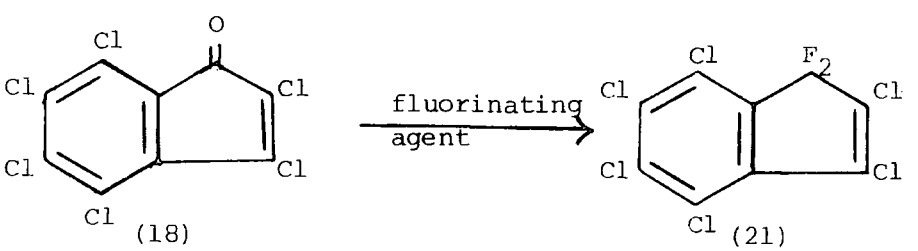
(ii) all fractions contained C-H bonds consistent with reaction of the initial product mixture with solvent during separation by a photochemically promoted radical process;

(iii) the longer retained products appeared, on the basis of mass spectroscopy, to be dimers of the original chlorofluoro-indenes, coupled with hydrocarbon residues derived from solvent.

2.6. Attempted fluorination of the carbonyl group in Hexachloroindenone

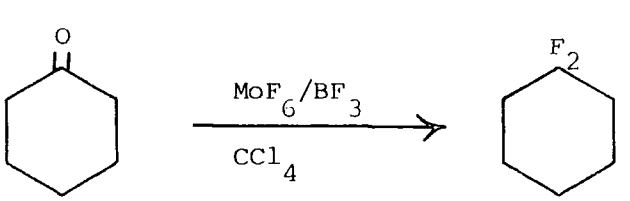
The selective replacement of oxygen atoms by fluorine in many types of organic compounds has been accomplished with sulphur tetra-

fluoride,[71] phenyl sulfur trifluoride,[72] carbonyl fluoride,[73] dialkyl amino sulfur trifluoride,[74] seleniumtetrafluoride,[75] and more recently with a mixture of molybdenumhexafluoride and borontrifluoride.[76] Of particular relevance to this work was the conversion of carbonyl to difluoromethylene by either of these reagents, since this provided a possible synthetic route to the 1,1-difluoride (21) from hexachloroindenone. It seemed possible that this compound might be a better starting material for exchange fluorination, since the photolability of perchloroindene is thought to be due to the ease with which the benzylic carbon chlorine bond can be cleaved, the benzylic carbon fluorine bonds in (21) would not be expected to be so easily cleaved and in consequence isolation of products might be easier.



(18) (21)

The high toxicity of sulphur tetrafluoride and the ease with which it hydrolyses to give hydrogen fluoride on contact with moisture make extreme care a prerequisite when working with this material and, since it is a gas, reactions at elevated temperatures require stainless steel autoclaves. On the other hand, although it reacts with moisture, reactions with molybdenumhexafluoride may be conveniently carried out in dry glassware; consequently the latter reagent catalysed by BF_3, was the preferred fluorinating agent. The fluorination of cyclohexanone using MoF_6/BF_3 in carbontetrachloride was attempted as a model reaction giving difluorocyclohexane following the procedure described in the experimental section. The product was characterised by mass



spectroscopy with a molecular ion M (m/e 120), and expulsion of HF from the molecular ion giving a fragment at m/e 100. The reaction between hexachloroindenone and MoF_6/BF_3 in carbontetrachloride at -15°C was unsuccessful the starting material being recovered unchanged. It is possible that the product expected, 1,1-difluorohexachloroindene, was formed as expected but destroyed by hydrolysis during work up of the product. To check this possibility the experiment was repeated using a modified method, anhydrous sodium fluoride powder and anhydrous aluminium fluoride powder were added at the termination stage instead of water. However, there was no detectable reaction and the starting material was recovered unchanged. Thus, it seems reasonable to conclude that MoF_6/BF_3 does not effect the fluorination of the carbonyl in perchloroindenone. Other workers in this group have had disappointing results with this reagent; thus, B. Wilson used the reagent in an attempt to prepare 1,1-difluorocyclopent-3-ene from cyclopent-3-ene-1-one, in the event the carbonyl group did not react although one of the allylic C-H bonds was replaced by a C-F bond. It can be concluded that MoF_6 is not such a universal reagent for carbonyl fluorination as it is generally thought to be.

2.7. Conclusions and suggestions for further work

The attempted fluorination of octachloroindene, using potassium fluoride as fluorinating agent was largely unsuccessful, although it is established that partial exchange fluorination can occur. One of the reasons for the very limited success of this work is the sensitivity to light of octachloroindene and related chlorofluoro-indenes. It seems very likely that this sensitivity is a consequence of the homolysis of a carbon chlorine bond in the dichloromethylene unit. These difficulties might be overcome if the starting material

was 1,1-difluorohexachloroindene rather than octachloroindene; the attempt to make the difluoro compound by fluorination of hexachloroindenone was unsuccessful with MoF_6 but in any continuation of this work alternative fluorinating agents such as SF_4 or $(C_2H_5)_2NSF_3$ would be worth investigating.

Another limitation on the exchange fluorination with KF which was demonstrated stems from the thermal instability of octachloroindene. Alternative fluorination procedures might be advantageous, such as the use of polar aprotic solvents, or CsF rather than KF, or inclusion of crown ethers.

SECTION I

CHAPTER 3

EXPERIMENTAL

3.1. Synthesis of hexachloroindenone via reaction of hexachlorocyclopentadiene with concentrated sulphuric acid

Hexachlorocyclopentadiene was obtained from stock supplied by Koch-Light Laboratories Ltd.

Hexachlorocyclopentadiene (320 ml, 544 g, 2 moles) was placed in a 3-necked round bottomed flask fitted with an efficient mechanical stirrer, a thermometer which dipped below the liquid level, and a water cooled reflux condenser. Sulphuric acid (concentrated, density 1.89, 320 mole) was added carefully in portions of ca. 50 ml with stirring. The mixture was stirred at room temperature for 10 minutes, there was no evidence of reaction. The mixture was then gently heated using an electrical heating mantle. At about 50° the mixture started to darken, and it became progressively darker turning from yellow to black during the course of reaction, an acid gas was evolved, the temperature of the mixture was kept at ca. 80 - 90° for 19 hours. The mixture was cooled to room temperature, carefully poured onto ice and left over night, the brown solid residue was recovered by filtration, washed with water until the washings were colourless and neutral and then dried in the air to give a solid product (239 g). This initial product was boiled with water for about half an hour, the solid product which separated on cooling was recovered by filtration. It was dissolved in acetone, boiled with activated charcoal and filtered through a Hyflo plug, the solid orange product which separated on cooling was recovered by filtration and recrystallized from acetone to give hexachloroindenone (81 g, 24.04 moles, 12%); m.p. 142°, found: C, 32.1; Cl, 63.4%, $M_{(\text{mass spec.})}$ 334, C_9Cl_6O requires, C, 32.1; Cl, 63.2%, M, 334 mass spectrum and infra red spectrum (Appendix 1 No. 1).

3.2. Synthesis of octachloroindene by reaction of hexachloroindenone with phosphorouspentachloride

Hexachloroindenone (10 g, 29.7 mmoles) and phosphorouspentachloride (20 g, 95.9 mmoles) were placed in a thick walled pyrex ampoule (Carius tube) which had previously been dried by heating under vacuum. The vessel was connected to the vacuum line, evacuated, and warmed to remove any trace of water which may have entered during the transfer processes; then it was sealed under vacuum. The tube was placed in a furnace and heated for about 2 hours at 200 - 250°C. After cooling to room temperature it was removed from the furnace and cooled in liquid air, the seal was broken by "hot spotting". The product was recovered by carefully adding water, followed by ether and acetone, the content of the tube was stirred using a long glass rod, a strongly exothermic reaction occurred and HCl was evolved. The mixture was diluted with distilled water and ether was added until all the precipitate dissolved. The organic layer was separated, washed again with water, separated, and dried over anhydrous sodium sulphate. After filtration and evaporation of the solvent crude perchloroindene was obtained (8.35 g, 21.3 mmoles, 72%) as white needles. An analytical sample was prepared by repeated recrystallization from methanol (Found: C, 27.78; Cl, 72.11%, $M_{(mass\ spec.)}$ 388, C_9Cl_8 requires C, 27.55; Cl, 72.45%, M, 388), m.p. 130° reported values ranged from (84° - 138.5)[63,67,68] with correct i.r. spectrum (Appendix 1, No. 2) and M(mass spectrum).

3.3. Photochemical reactions of octachloroindene

(a) Cyclohexane

Octachloroindene (2 g, 5.2 mmoles) was dissolved in 50 ml of cyclohexane, the solution was streamed with dry nitrogen for 40 minutes.

Two cylindrical tubes were filled with solution in this way. One of these tubes was covered and stored in the dark while the other was put on the window sill. The initially colourless liquid in the tube on the window sill started to change to pink after 40 minutes, the colour of the solution became progressively darker turning from pink to violet. After one week the tube on the window sill was opened, an acid gas was evolved (Litmus), the solvent was evaporated and the violet product (1.8 g) was dried under vacuum. It was examined by i.r. spectroscopy (Appendix 1, No. 3) and t.l.c. (silica, CCl_4) which indicated the presence of at least four components. An attempt was made to separate the components of this mixture by 'dry column' chromatography. A chromatography column (96 cm x 2.2 cm.dia.) was packed with dry silica (silica gel (Kiesel gel 60) from Fluka A.G.) taking care to eliminate voids and channels, the mixture (0.81 g) was dissolved in a small volume of carbontetrachloride and adsorbed as a tnin band on the top of the dry column. The column was then developed in the normal way using carbontetrachloride as eluent. The first fraction from the column was perchloroindene (0.64 g, 79%) identified by its infrared spectrum, no other components of the mixture were obtained in a pure state. The tube stored in the dark was still colourless after one month, its colour started to change as soon as it was exposed to day light.

(b) Carbontetrachloride

The same procedure as in (a) was used with carbontetrachloride replacing cyclohexane. The solution remained colourless on exposure to day light for one week, evaporation of the solvent gave perchloroindene identified by its i.r. spectrum.

(c) Toluene

Perchloroindene (1.6 g, 4.08 mmoles) was dissolved in toluene (50 ml) in a cylindrical pyrex vessel (50 cm. x 2.2 cm. dia.), the vessel was irradiated in a Rayonet photochemical reactor for 18.30 hours using 3500Å lamps, the solution was continually streamed with dry nitrogen and the gas evolved from the reaction was bubbled through a standard solution of sodium hydroxide (50 ml, 0.498N) which was protected from atmospheric contamination by a Drechsel bottle containing heavy white oil. The solvent was evaporated from the irradiated tube. The recovered product (1.85 g) was dried under vacuum, it was examined by i.r. (Appendix 1, No. 4), ^{1}H n.m.r. spectroscopy, and analytical t.l.c. (silica, CCl_4) which indicated the presence of more than three components. An attempt was made to separate the components of this mixture by 'dry column' chromatography by the procedure described above. The mixture (1.59 g) was separated into four fractions (0.055 g, 0.2 g, 0.138 g, 0.77 g) respectively, all these fractions were examined by i.r. spectroscopy (Appendix 1, No. 5, 6, 7, 8 respectively), and mass spectroscopy the details of which were discussed earlier (see section 2.4).

The sodium hydroxide solution from the Drechsel bottle was titrated against standard hydrochloric acid (0.1N) to determine the quantity of hydrogen chloride evolved during the reaction. This amounted to 2.8 moles of hydrogen chloride per mole of perchloroindene.

3.4. Attempt fluorination of octachloroindene using potassium fluoride

Potassium fluoride was dried by repeated heating over a bunsen and sieving, it was stored under reduced pressure at 100°C. Anhydrous ether was purchased from Macfarlan Smith Ltd., dichloromethane, hexane fraction and phosphorus pentachloride from Hopkin and Williams, carbon-

tetrachloride from B.D.H. Chemicals Ltd.

In a typical experiment perchloroindene (3.1 g, 7.9 mmoles) was charged in a dry pyrex Carius tube. It was evacuated and warmed (warmed and allowed to cool) using a hairdryer several times. Potassium fluoride (15 g, 25.86 mmoles) was added hot and dry. The Carius tube was evacuated again for about 10 - 15 minutes and warmed. It was then sealed under vacuum. The tube was placed in a furnace and heated for 23 hours at 260^{o}C, after cooling to room temperature the tube was removed from the furnace and cooled in liquid air, the seal was broken by 'hot spotting' and the product was treated with anhydrous ether. The inorganic salt was removed by filtration from the ether layer. The solvent was evaporated to give yellow-brown product (2.1 g) which was examined by i.r. spectroscopy (Appendix 1, No. 9), and t.l.c. (silica, C_6H_{14}) which showed at least four components. An attempt was made to separate these components by dry column chromatography. The column (133 cm. x 26 dia.) was packed with dry silica (Hopkin and Williams, silica gel M.F.L. 100 - 200). The product mixture was dissolved in a small amount of hexane, then it was applied by means of a small pipette to the top of the column without touching the surface of the adsorbent, after the sample solution was absorbed the column was developed with hexane in the normal way, a series of clearly differentiated coloured bands developed. Five fractions were collected:-

(a) the first fraction (0.3 g) gave yellow crystals on partial evaporation of the solution, examination by t.l.c. (silica, C_6H_{14}) indicated a single component, but HPLC indicated two components which were identified as a mixture of 1,1-difluoro-hexachloroindene and a trifluoropentachloroindene (see Discussion);

(b) the second fraction (0.35 g) was sublimed and examined by i.r., n.m.r. and mass spectroscopy, it was a product of reaction with the eluting solvent and was not completely characterized (see Discussion);

(c) the third fraction 0.19 g was also a product of reaction with solvent;

(d) the fourth fraction (0.048 g) was examined by i.r. spectroscopy, it also contained residues derived from reaction with solvent.

The column was washed with methanol to give (0.9 g) of black residue. The fluorination was carried out several times under different reaction conditions. The results were tabulated and discussed earlier.

3.5. Fluorination of hexachloroindenone using molybdenumhexafluoride and borontrifluoride

Dichloromethane (500 $cm.^3$) distilled from P_2O_5 was placed in a 2000 $cm.^3$, 3-necked round-bottomed flask, fitted with a mechanical stirrer, a gas inlet which extended under the solvent and a water cooled reflux condenser. Molybdenumhexafluoride (22 g, 104 moles) was added to the dichloromethane and stirred for 50 minutes. The mixture turned dark in colour. It was cooled to 0^oC using an external acetone/solid carbon dioxide bath and a fast stream of borontrifluoride was bubbled through the mixture for fifteen minutes with vigorous stirring. The solution became dark red. The gas inlet tube was replaced by a dropping funnel and hexachloroindenone (10.6 g, 31 mmoles) dissolved in dichloromethane (300 $cm.^3$) was added dropwise to the vigorously stirred reaction mixture at such a rate that the reaction temperature stayed between -15^oC and -20^oC. When addition was complete the solution was allowed to warm up slowly to room temperature while it was stirred. Anhydrous sodium fluoride powder (7.8 g, 186 mmoles) was added in small

portions to the reaction mixture. It was stirred for 30 minutes. Anhydrous aluminium fluoride powder (17.5 g, 209 mmoles) was added and stirred for 30 minutes and the precipitated materials were removed by filtration. The mixture was distilled under vacuum (water pump) to remove solvent and volatile residues. Analysis by i.r. spectroscopy and t.l.c. showed that the only material present was perchloroindenone.

3.6. Fluorination of cyclohexanone using molybdenumhexafluoride and borontrifluoride

Carbontetrachloride (500 $cm.^3$) distilled from P_2O_5 was placed in a 1000 $cm.^3$, 3-necked round-bottomed flask fitted with a mechanical stirrer, gas-inlet and water condenser. Molybdenumhexafluoride (15 g, 71 mmoles) was added to the solvent. It was cooled to 0^o using an external acetone/solid carbon dioxide bath and a fast stream of borontrifluoride was bubbled through the mixture for 10 minutes with vigorous stirring. The solution was cooled to -15^o. The gas-inlet tube was replaced by a dropping funnel and distilled cyclohexanone (15 g, 153 mmoles) dissolved in carbontetrachloride (100 $cm.^3$) was added dropwise, the solution became dark. When addition was complete the solution was allowed to warm up slowly to room temperature and stirred for 2 hours. Water (50 $cm.^3$) was added dropwise to the reaction mixture which was cooled in an external ice/water bath. The organic layer was separated analytical gas chromatography (130^oC column A) showed three peaks one for solvent, one for cyclohexanone and a third major peak which was identified as difluorocyclohexane by mass spectroscopy coupled to gas chromatography.

SECTION II

SOME ATTEMPTS TO POLYMERIZE CHLOROPOLYCYCLIC ALKENES BY METATHESIS RING-OPENING

SECTION II

CHAPTER 4

INTRODUCTION AND BACKGROUND

4.1. Historical Background of Olefin Metathesis

Olefin metathesis is a bond reorganization reaction in which the total number and type of chemical bonds remains unchanged during the transformation of the initial alkenes into equimolar amounts of two new products as shown in Figure 4.1.

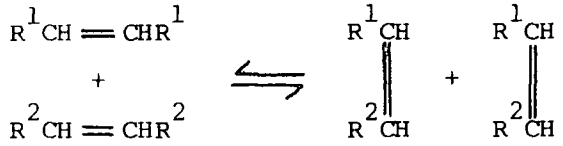


Figure 4.1

These transformations are induced by the combination of the alkenes with a variety of catalysts. The most common catalysts are based on tungsten, molybdenum or rhenium, together with activators which are usually organo aluminium or tin compounds. The reaction has been variously called 'metathesis', 'disproportionation' and sometimes 'dismutation'. The first examples of the metathesis of linear alkenes were reported by Banks and Baily in 1964.[77] This opened the way for the study and the development of a very important field of chemistry and over the years the range of substrate types has been increased to include substituted alkenes, dienes, polyenes, alkynes and cycloalkenes. The latter ring-open polymerize, producing linear polymers known as polyalkenylenes. This type of polymerization was not recognized as a special case of olefin metathesis until 1968,[78,79] see Figure 4.2.

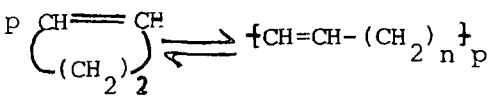


Figure 4.2

In fact the first mention of the metathesis reaction catalysed by a transition metal was the polymerization of bicyclo[2.2.1]hept-2-ene by

a mixture of titanium tetrachloride and either ethylmagnesiumbromide or lithium tetrabutylaluminium. This reaction was recorded in 1955,[80] but it was not until 1960 that the polymer was shown to be a polyalkenylene.[81] In 1959 Eleuterio,[82] using a catalyst prepared from molybdenum oxide on alumina and activated by reaction with hydrogen and further reaction with aluminium hydride, was able to ring-open polymerize a variety of cycloalkenes including cyclopentene to form trans-poly (1-pentenylene) with a high degree of stereo-regular structure, but only in low yield. In 1963 Dall'Asta and Natta,[83] demonstrated the possibility of producing stereo-regular polymers from cycloalkenes using different catalyst systems and reaction conditions, cyclobutene was polymerized to predominantly or exclusively cis or trans poly (1-butenylene) as shown in Table 4.1.

In 1964 the same authors employed tungsten and molybdenum halides in combination with organo aluminium compounds as catalysts, cyclopentene was polymerized by ring-opening under mild conditions, again stereo-selectivity was demonstrated. In 1967 Calderon et.al.,[84] using for the first time the term 'olefin metathesis' for the overall result of the reaction, converted 2-pentene into a mixture of 2-butene and 3-hexene using a WCl_6-$EtAlCl_2$-EtOH catalyst.

Table 4.1

Cyclobutene polymers via transition metal catalysts

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

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. Since then a great number of investigations of all aspects of the metathesis reaction have been carried out, and several detailed reviews have been published.[85-91]

4.2. The Scope and Applications of the Olefin Metathesis Reaction

The olefin metathesis reaction is a very versatile tool in synthetic organic chemistry. The applications include: improved utilisation of refinery streams, for example, by converting C_4 and C_5 alkenes into mixtures containing ethylene and propene together with higher molecular weight products; production of intermediates for flame retardants; stabilizers; perfumes; and novel polymers and copolymers.[92]

(a) Acyclic olefins

The conversion of many acyclic mono-olefins and mixtures of olefins, both linear and branched, has been effected according to the general equation in Figure 4.3, where R represents hydrogen or hydrocarbon groups.

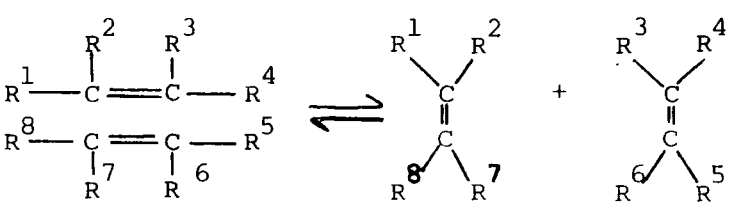


Figure 4.3

Terminal or internal acyclic olefins can be metathesized in the presence of the appropriate catalyst, the homo-metathesis reaction of an acyclic α-mono-olefin yields ethylene and a symmetrical internal olefin, the homo-metathesis reaction of an unsymmetrical internal mono-olefin usually gives two symmetrical internal olefins. The general

relationship for acyclic linear olefins is shown in Figure 4.4, where n is the carbon chain length and m is the position of the double bond in the chain.

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

Figure 4.4

Reactions, of terminal and internal acyclic mono-alkenes has been reported in great detail.[90,91]

Acyclic alkenes can be used to degrade polymers which contain unsaturation by cross-metathesis, which can be useful in structure investigations. Substitution of acyclic monoalkenes with hydrocarbon groups such as cycloalkyl, cycloalkenyl or aryl groups does not seem to affect their ability to undergo metathesis; for example, styrene is converted to ethylene and 1,2-diphenylethylene,[93] Figure 4.5.

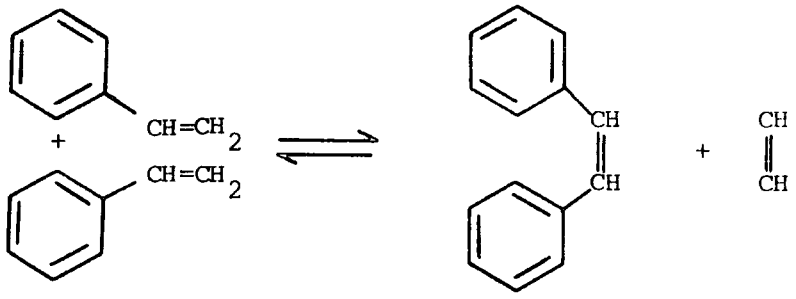


Figure 4.5

Calderon,[94] reported that the effect of substitution on the case of participation in the olefin metathesis is given by the series shown in Figure 4.6 indicating some steric control of reaction.

$$CH_2= > RCH_2CH= > R_2CHCH= > R_2C=$$

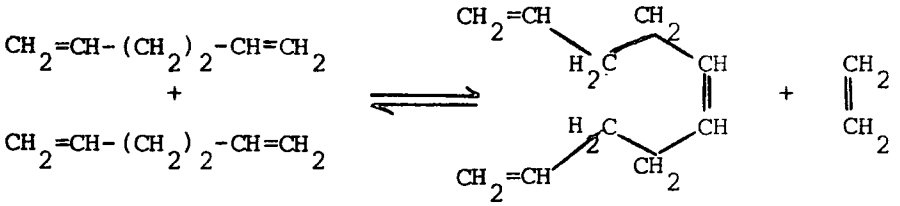
Figure 4.6

(b) Acyclic polyenes

Zuech and co-workers,[89] have reported that polyenes or cycloalkenes are formed from the reaction of α,ω-dienes with metathesis catalysts,

the substrates undergo either inter- or intra-molecular reactions depending upon the relative stabilities of the ring and chain product. For example, hexa-1,5-diene is converted into 1,5,9-decatriene and ethylene via inter-molecular metathesis, whereas octa-1,7-diene is converted via intra-molecular metathesis for cyclohexene and ethylene.

Figure 4.7



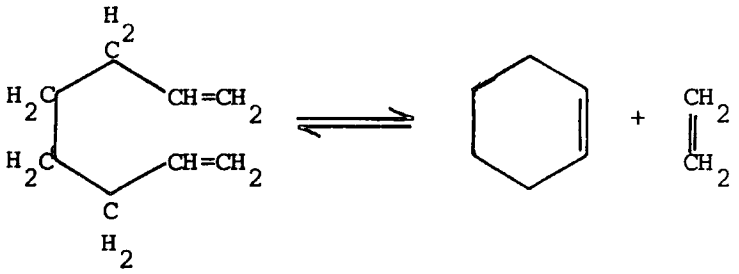


Figure 4.7

(c) Alkynes

The metathesis of linear alkynes, such as 1-pentyne, 2-pentyne and 3-hexyne, has been reported.[95,96] The overall reaction was shown to be analogous to the metathesis of acyclic olefins, Figure 4.8.

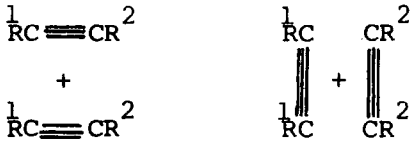


Figure 4.8

(d) Aryl-substituted olefins

A few examples have been reported[93,97] and some are shown in Figure 4.9

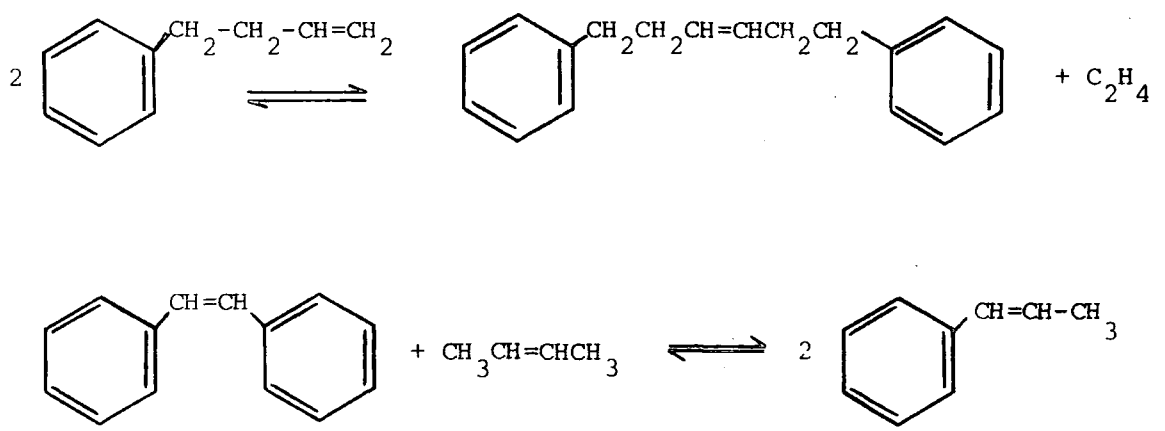


Figure 4.9

The aromatic system which is capable of coordinating to low-valent transition metals such as W and Mo, can retard the rate of reaction or deactivate particular catalyst systems.

(e) Cycloalkenes

The ring-opening polymerization of cycloalkenes to linear polymers by metathesis provides an interesting type of polymerization in that all the unsaturation of the monomer is retained in the polymer. The reaction may be generalized as shown in Figure 4.10.

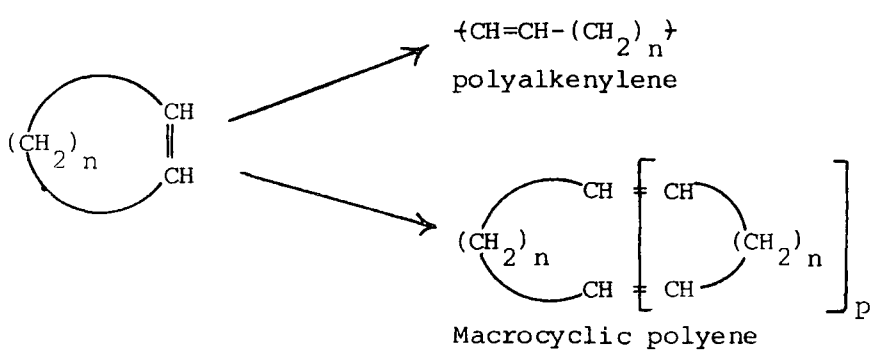
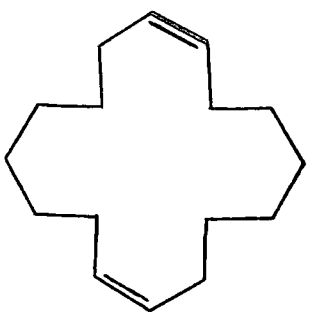


Figure 4.10

Mono-cyclic alkenes from C_4 to C_{12} with the exception of cyclohexene,[85] undergo ring-opening polymerization to yield products which vary from amorphous elastomers to crystalline materials. Ring-opening

can be controlled to yield polymers with either a high cis[98] or a high trans[85,99] content by varying the catalyst and by controlling the temperature of reaction. This point is very important in the regulation of this reaction especially in industry. Metathesis of poly(alkenamers) or their parent cycloalkenes at high dilution gives a mixture of macro-cyclic compound in high yield.[100] Two interesting materials prepared by this technique are cyclohexadeca-1,9-diene (23), the cyclic dimer of cyclooctene which when oxidized yielded a ketone with a musk-like odour (24),[101] and catenanes, the interlinked ring



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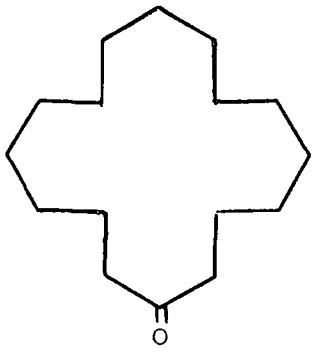


(24)

systems which form part of the product from the metathesis of cyclododecene, Figure 4.11.

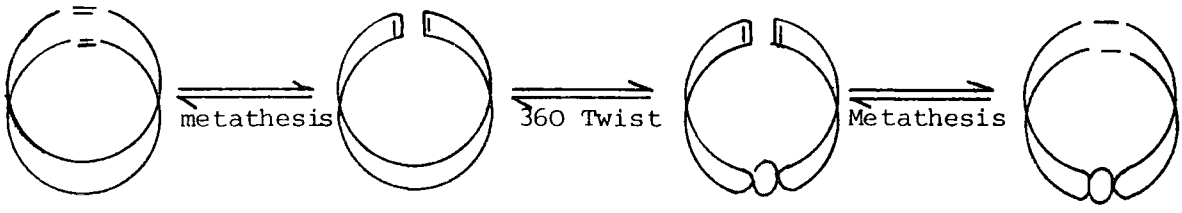
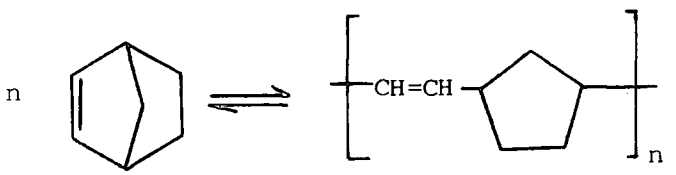


Figure 4.11

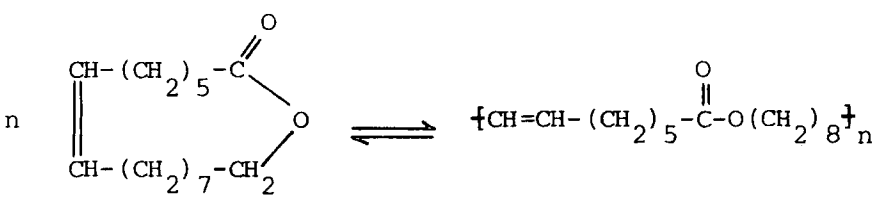
Cyclicdienes, polyenes, as well as mono- and poly-cyclic alkenes undergo ring-opening polymerization. The polymer produced from bicyclo[2.2.1]

hept-2-ene (25), poly(1,3-cyclopentylene vinylene) (26) is the first polyalkenylene to be commercially exploited under the trade name Norsorex,[103] it is used as part of a shock absorber system in some cars.



(25) (26)

In addition to the examples already mentioned, cycloheptene,[104] cyclodecene,[105] and heterocyclic olefins (such as unsaturated lactones),[106] have been shown to undergo ring-opening polymerization; for example, 7-hexadecen-16-olide gives an unsaturated polyester as shown below.



(f) Metathesis of functionalized olefins

In 1975 the number of papers dealing with the metathesis of functionalized olefins was very small.[107] The only successful reaction was published by Boelhowver et.al.,[108] who reported the metathesis of unsaturated esters using the homogeneous catalyst $WCl_6/Sn(Me)_4$; for example they prepared octadec-9-ene and octadec-9-enedoic dimethyl ester from methyl oleates as shown in Figure 4.12.[109]

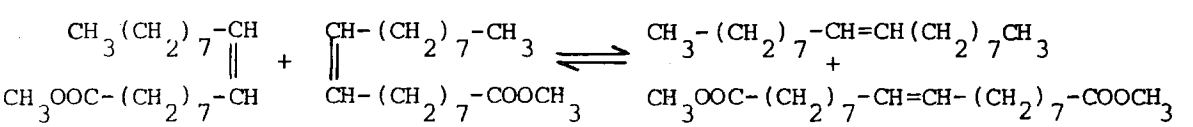
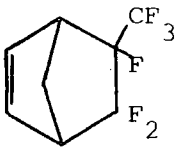


Figure 4.12

This provided new synthetic routes in the field of fat chemistry and was of some industrial interest. Although metathesis polymerization of other functionalized olefins have been reported, for example the

polymerization of fluorinated monomers such as 5,5,6-trifluoro-6-trifluoromethylbicyclo[2.2.1]hepta-2-ene (27),[110] chlorinated monomers as 1,10,11,12,13,13-hexachlorotricyclo[8,2,1,$O^{2,9}$]trideca-5,11-diene (28),[111] and other monomers containing electron withdrawing substituents such as 5-cyanobicyclo[2,2,1]hepta-2-ene (29).[112]



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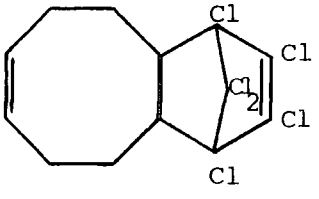

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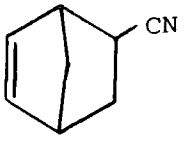


(29)

4.3. Olefin metathesis catalyst systems

Although olefin metathesis of acyclic alkenes and ring-opening polymerization of cycloalkenes are governed by a common mechanism the reactions differ in several respects, consequently good catalysts for the processes are only rarely interchangeable.

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

(a) Heterogeneous catalysts

These kinds of catalysts usually acquire metathesis activity only at high temperature (100^{o} to 400^{o}) and are useful in continuous processes they are employed for the metathesis of acyclic alkenes. They generally consist of transition metal oxides or carbonyls deposited on high surface area supports such as alumina or silica. The catalysts derived from oxides and carbonyls of Mo, W and Re have the greatest activity.[77,113,114] This kind of catalyst can be prepared by dry mixing of the individual components, coprecipitation, or impregnation of the supports with substances which decompose at high temperatures to leave the active catalyst. The catalysts are sensitive to poisoning by polar compounds,[115] more details have been given by Bailey,[90] and Banks,[116] about analysis of the composition, preparation, activation and regeneration procedure, poisons and catalytic modifications.

(b) Homogeneous catalysts

Homogeneous catalysts generally consist of two components; a transition metal compound of tungsten, molybdenum, rhenium or tantalum, usually the halide, oxyhalide or an organoalkene or carbene complex; the second component is an organometallic compound of a metal from group I to IV. Sometimes a third component known as an activator is added. This activator generally contains an oxygen-oxygen or oxygen-hydrogen bond (e.g. a peroxide, alcohol or water). Tungsten compounds give the most efficient catalysts for the ring-opening polymerization of cyclo-olefins and a large number of catalysts are derived from WCl_6 combined with suitable cocatalysts. Arguments about the exact structure and mode of action of particular catalysts are frequent and indeed the designation "homogeneous" has been questioned for several systems.[117] Detailed information about some of the systems for the metathesis of acyclic alkenes and cyclic alkenes is given by Hughes[91] and Dall'Asta[85] respectively. In recent years photochemically activated catalysts have been reported for the metathesis of acyclic alkenes and the ring-opening polymerization of cycloalkenes, using $W(CO)_6$,[118] WCl_6,[119] and $TiCl_4$.[120]

4.4. Olefin metathesis mechanism

The complete mechanistic scheme involved in olefin metathesis is not fully understood yet and numerous schemes have been put forward during recent years. 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?

(a) The overall result of reaction

There are two possible reaction schemes

(i) A transalkylation scheme, which involves cleavage of carbon-carbon single bond adjacent to the double bond as shown in Figure 4.13

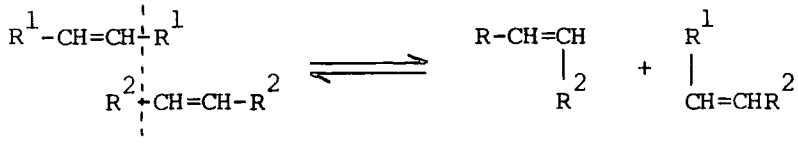


Figure 4.13

(ii) A transalkylidenation scheme, which involves the cleavage of the double bond itself as a means of alkylidene moiety exchange as shown in Figure 4.14

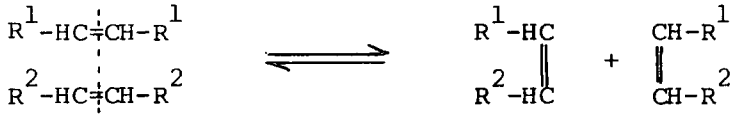
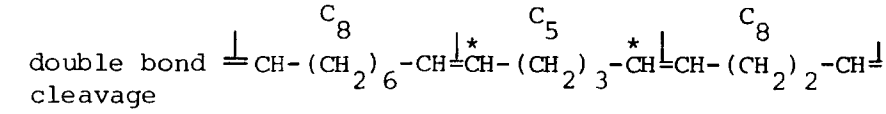


Figure 4.14

Results from C^{14} isotopic labelling[121] and deuterium labelling experiments[78c,84] are completely consistent with transalkylidenation scheme and exludes a transalkylation. Dall'Asta and Motroni[122] have given experimental evidence that in the ring-opening polymerization of cycloalkenes the cleavage occurs at the double bond. On copolymerizing cyclooctene and cyclopentene, in which the cyclopentene double bond was labelled with ^{14}C, the resulting polymeric units may be (30) or (31) depending on whether cleavage takes place at the double bond or at the carbon-carbon single bond adjacent to the double bond. Ozonolysis



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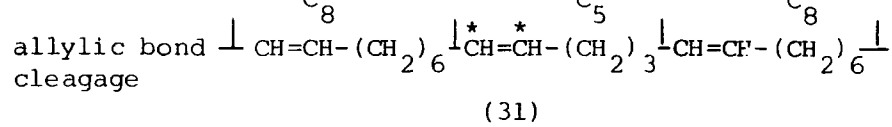


(31)

[* denotes ^{14}C labelling]

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 the ring-opening polymerization had proceeded via cleavage of the double bonds.

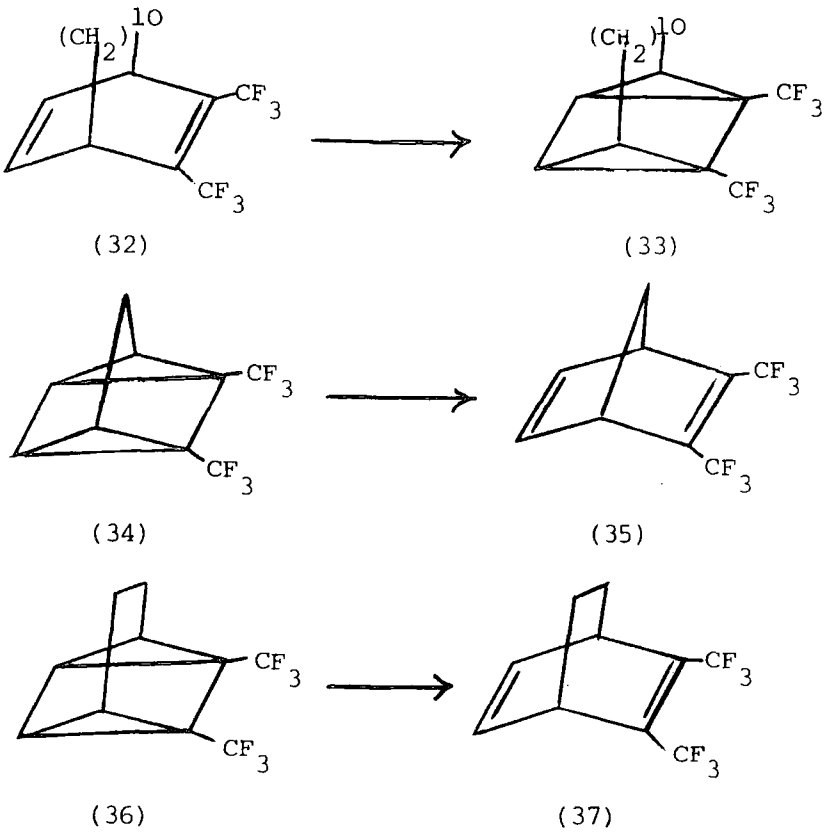
(b) The detailed mechanistic pathway

This question is much more complicated and difficult to answer definitely, it is still an area of active discussion.

(1) The intermediacy of a quasi-cyclobutane

Bradshaw[123] put forward the first mechanistic rationalization of olefin metathesis. He proposed that a four centre or "quasi-cyclobutane" intermediate could be used to explain the observed results, as shown in Figure 4.15. Calderon[78b] used this idea to rationalize ring-opening polymerization of cycloalkenes. The mechanism was assumed to proceed via formation of macrocyclic species as shown in Figure 4.16. While this mechanism accounts for a large amount of experimental observation, including isotopic labelling studies,[121,124] it has some weaknesses. For example, it predicts macrocyclic products whereas it is established that linear and macrocyclic products can be obtained. One rationalization for the formation of linear polymers is shown in Figure 4.17, alternatively the interaction of the growing macrocycles with an acyclic alkene, present as an impurity, could cause cleavage of the macrocycle.

Very little evidence for the involvement of cyclobutanes in metathesis has been published, Gassman and Johnson[125] observed a diene to cyclobutane conversion when compound (32) was reacted with the 'typical metathesis catalyst' $C_6H_5WCl_3/AlCl_3$, and cyclobutane to diene conversions for compound 34 and 36 reacting to give 35 and 37 respectively. These authors also reported that the bicyclic



dienes were not affected 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,[126] observed that the bicyclic diene (35) is particularly susceptible to ring-opening polymerization by a range of metathesis catalysts and is even polymerized by pure tungsten hexachloride, this

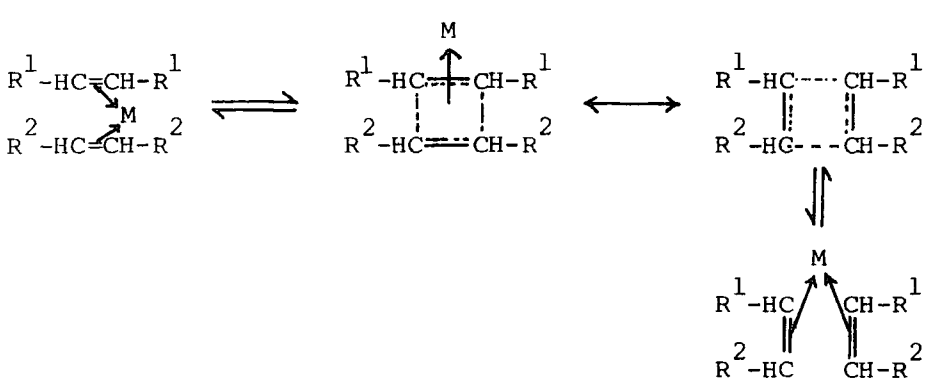


Figure 4.15

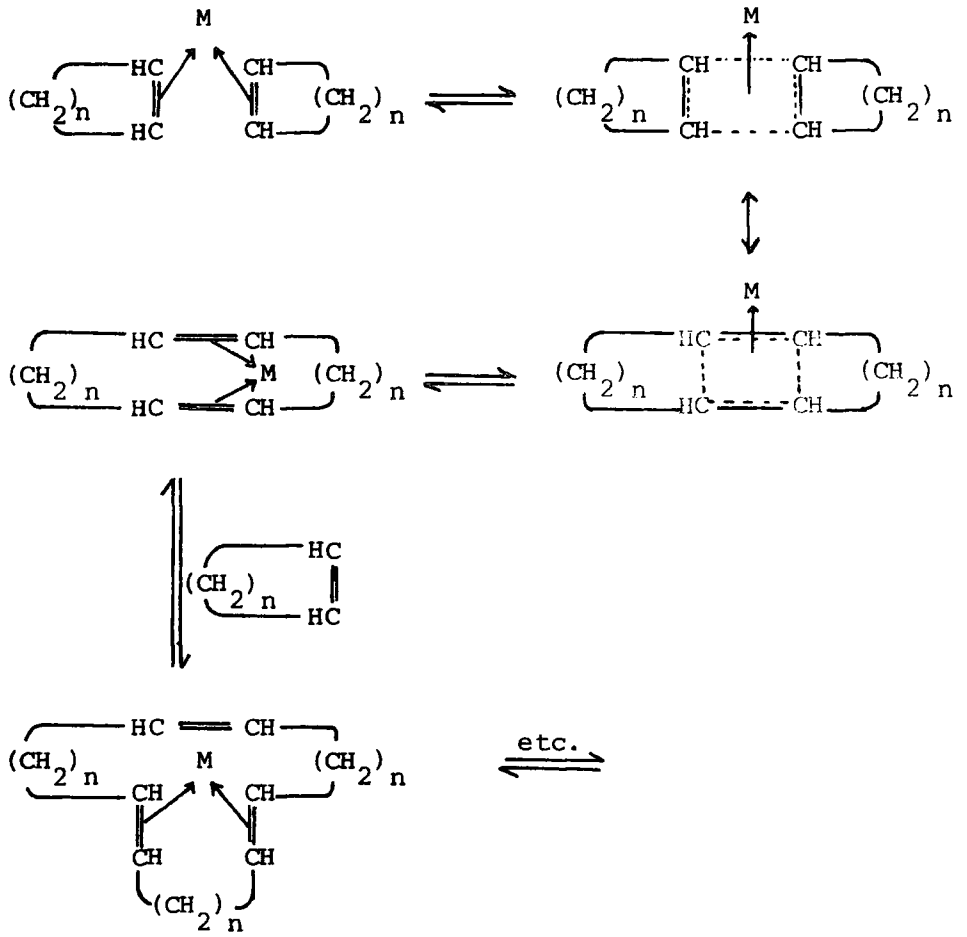


Figure 4.16

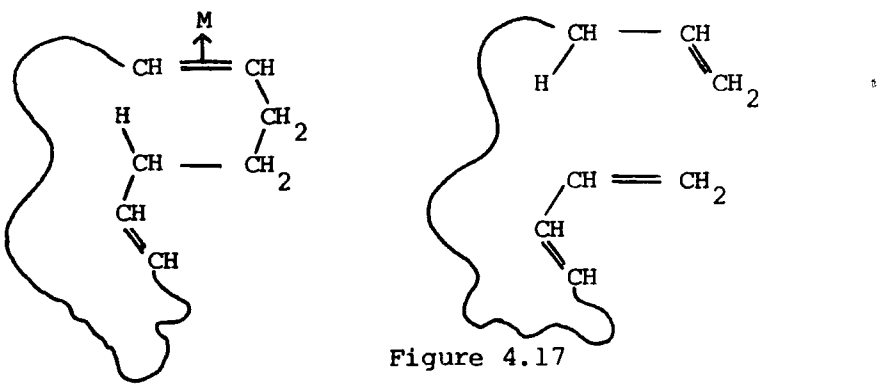


Figure 4.17

contrasts with its reported lack of reactivity with the $PhWCl_3/AlCl_3$ catalyst and suggests that the 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.

Another concerted pairwise exchange mechanism was proposed,[127] this is sometimes called the "tetramethylene transition state hypothesis" and is represented in Figure 4.18.

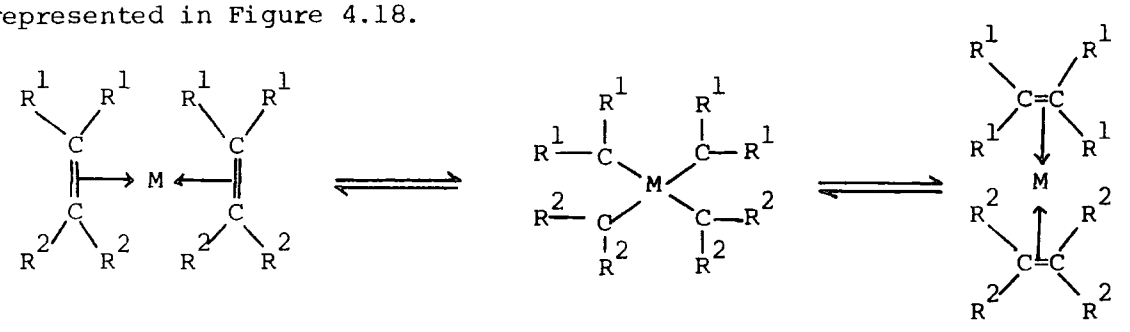


Figure 4.18

The theoretical implications of these concerted mechanisms have been reviewed by Haines and Leigh.[128]

(2) Metallocyclopentanes as intermediates

Because of the weaknesses of the mechanisms described above several workers have looked for alternative rationalizations. The observation that WCl_6 reacted with 1,4-dilithiobutane in benzene to give ethylene,[129] led to the suggestion that metallocyclopentanes might be involved as intermediates in a non-concerted pairwise exchange of alkylidenes in the mechanism for metathesis as shown in Figure 4.19, this proposal was soon replaced by the currently accepted hypothesis, non-concerted, non-pairwise mechanism.

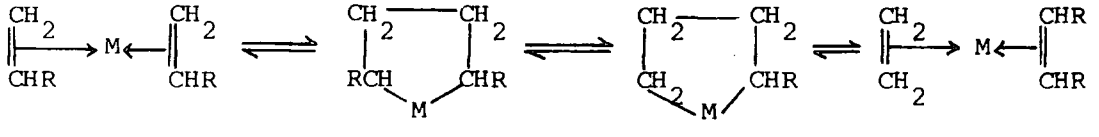


Figure 4.19

(3) Metallocyclobutane and metal-carbene intermediates

Herisson and Chauvin[130] proposed what is now the generally accepted mechanism for metathesis. This involves a reversible reaction between

an alkene and metallocarbene to give a metallocyclobutane, as indicated in Figure 4.20. This mechanism was independently put forward by Lappert and co-workers,[131] who had shown that 'electron rich' olefins such as compound (38) undergo metathesis with Rh catalysts at high temperatures, they also isolated an intermediate metallocarbene (39) which acted as a catalyst for the reaction.

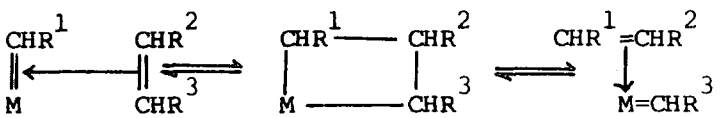
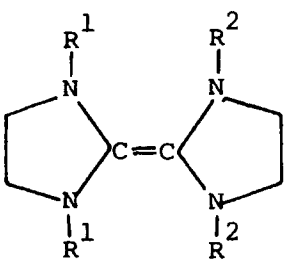
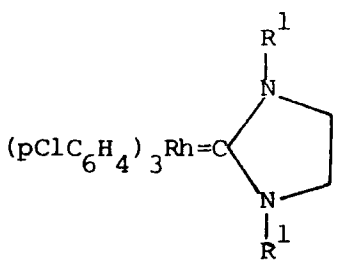


Figure 4.20



(38)



(39)

The metallocyclobutane mechanism accounts for ring-opening polymerization as shown in Figure 4.21, cyclic oligomers are obtained when the carbene end reacts with a double bond within the growing polymer chain, Figure 4.22. Roony and Stewart,[86] have reviewed in detail the evidence supporting the metallo-carbene/metacyclobutane mechanism; their recent work with Ivin and Green[132] has led to the suggestion that there is a close mechanistic relationship between Ziegler-Natta polymerization and ring-opening metathesis, as shown in Figure 4.23; this requires a 1,2-hydrogen shift to generate the active metallo-carbene postulated as an intermediate in the unconventional Ziegler-Natta mechanism.

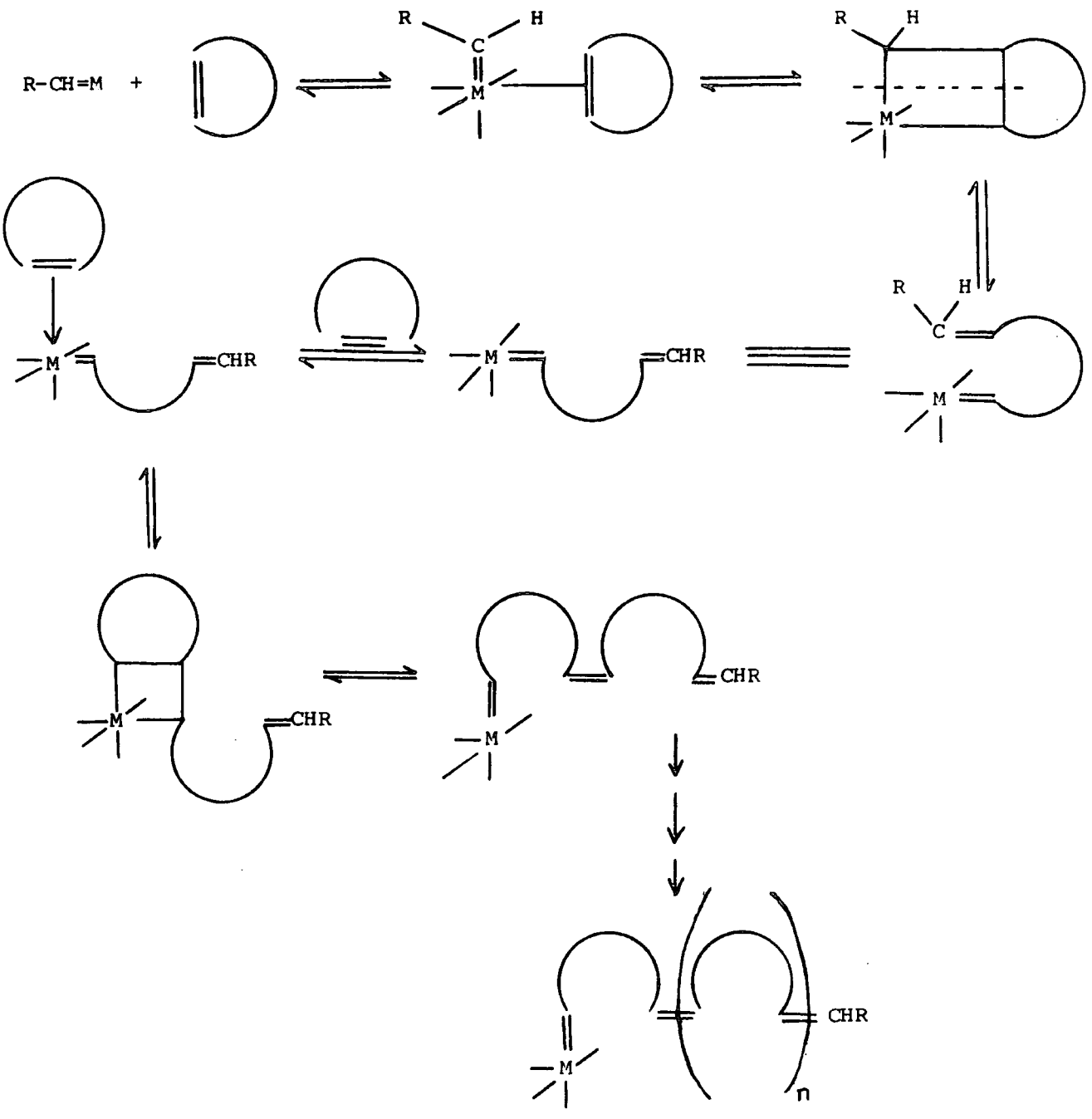


Figure 4.21

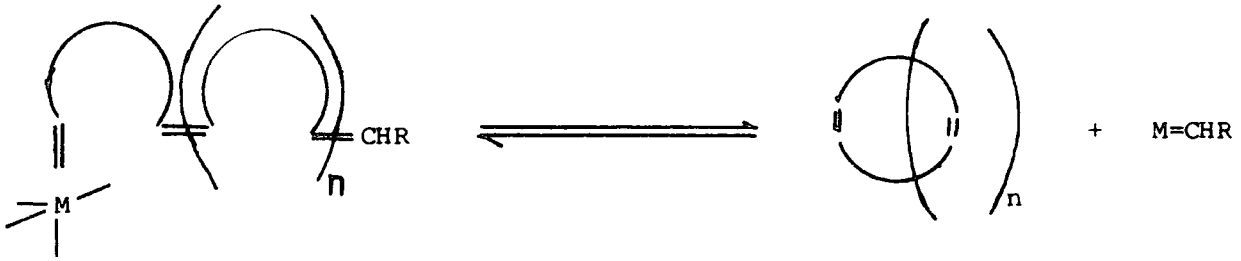
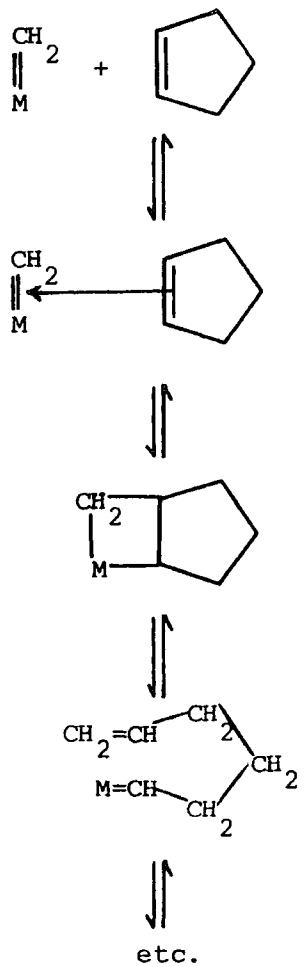
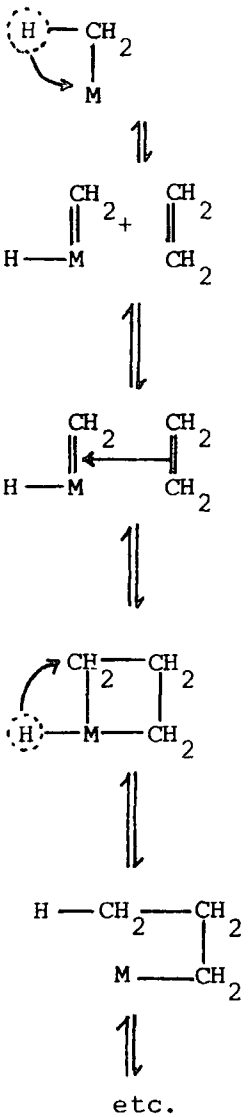


Figure 4.22

olefin metathesis mechanism for the ring opening polymerization of cycloalkenes



unconventional Ziegler-Natta polymerization mechanism



conventional Ziegler-Natta polymerization mechanism

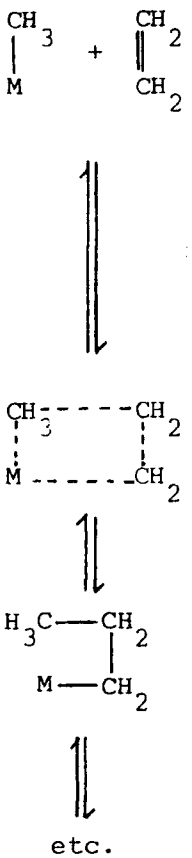


Figure 4.23

Although the metathesis mechanism is widely accepted, the new proposal for Ziegler-Natta polymerization has not been established and is a matter of dispute.[133]

SECTION II

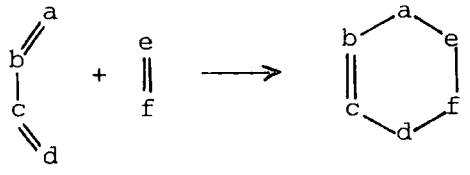
CHAPTER 5

MONOMER SYNTHESES AND ATTEMPTED POLYMERIZATIONS

5.1. Monomer Syntheses

(a) The Diels-Alder reaction

The Diels-Alder reaction, which involves the 1,4-addition of a conjugated diene (40) and a dienophile (41), is a very useful synthetic method for the preparation of six membered rings (42), because of the almost unlimited possibilities for variation of both diene and dienophile. One restriction is that the diene must be conjugated with the double bonds cis-oriented at the time of reaction, but the dienophile can be practically any unsaturated compound.



(40) (41) (42)

The Diels-Alder reaction may be divided into two extreme reaction types: firstly the normal Diels-Alder reaction in which dienes are activated by electron donating substituents, for example, $-NMe_2$, -OMe, $-CH_3$, and dienophiles are activated by electron withdrawing substituents, for example -CN, -COOMe, -CHO, $-NO_2$;[134] secondly, the Diels-Alder reaction with Inverse Electron Demand, in which the diene is activated by electron-withdrawing substituents and the dienophile by electron-donating substituents.[135] If both components in the Diels-Alder reaction are either 'electron-rich' or'electron poor' the reaction is generally sluggish or does not occur; the greater the difference in character the faster the reaction proceeds. The stereochemical outcome of the Diels-Alder reaction was initially formulated by Alder and Stein in their 'cis-principle'[136] which states that "the configurational relationships of the dienophile and diene are retained in the adduct". This fact is now

recognised to be a consequence of the concerted nature of the cyclo-addition. Hence the principles of orbital symmetry conservation elaborated by Woodward and Hoffman may be applied, in which the Diels-Alder reaction is classified as a ($\pi_s^2 + \pi_s^4$) cycloaddition reaction and is thermally allowed.[137]

(b) Diels-Alder adducts of cyclopentadiene with dichloromaleic anhydride and hexachloroindenone

Cyclopentadiene was chosen as a diene starting material for the synthesis of compound (43) and (44), because it was relatively readily available, since it can be freshly prepared by the thermal cracking of its dimer.[138] A solution of the diene and dienophile in carbon-tetrachloride was refluxed for the required time, experimental details are shown in Table 5.1. Two dienophiles were used, dichloromaleic anhydride reacts, as previously reported,[139] to give the endo-adduct in good yield; the second adduct was prepared using perchloroindenone as dienophile and is provisionally assigned endo-stereochemistry, this reaction has not been described previously. These reactions are summarized in Figure 5.1.

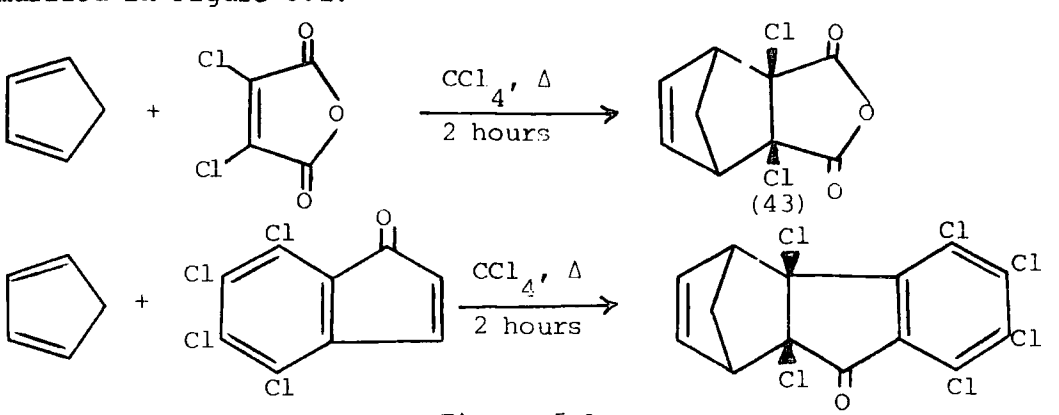


Figure 5.1

(44)

Full details of the preparation and purification of these two components is given in the Experimental section. Both adducts (43) and (44) were fully characterized by analysis and spectroscopy. Elemental analysis and

mass spectroscopy gave satisfactory data compared with the calculated figures. They confirmed the molecular formulae as $C_9H_6Cl_2O_3$ (43) and $C_{14}H_6Cl_6O$ (44). Both adducts showed abundant parent ions adduct (43) m/e 232 and adduct (44) m/e 400, in both cases the base peak was exhibited at m/e 66 $(C_5H_6)^+$, presumably arising from the retro-Diels-Alder reaction of the parent ion. The i.r. spectrum of adduct (43) showed characteristic vinylic CH stretching absorptions at 3040 $cm.^{-1}$, aliphatic C-H at 2840 $cm.^{-1}$, and a very broad band in the region 1700 - 1880 $cm.^{-1}$ assigned to the two carbonyl groups in the anhydride ring. The i.r. spectrum of adduct (44) showed similar CH stretching absorptions (3000 and 2840 $cm.^{-1}$) and a $\diagdown$C=O stretch (1730 $cm.^{-1}$). The ^1H n.m.r. spectrum of compound (43) was consistent with the presence of three kinds of hydrogens, the vinylic hydrogens occur at 6.4 p.p.m., the allylic bridgehead hydrogens (α to the double bond) occur at 3.5 p.p.m., and the methylene group appears as a AB quartet at 2.2 and 2.5 p.p.m. with J_{AB} = 10Hz. Adduct (44) was not sufficiently soluble in dichloromethane, chloroform, toluene, methanol, ether, hexane, acetone, chlorobenzene, acetonitrite or ethylacetate to obtain a ^1H n.m.r. spectrum.

An attempt to prepare the Diels-Alder adduct of hexachloroindenone with tetraphenylcyclopentadienone was unsuccessful. The reaction was attempted using refluxing carbontetrachloride and xylene, in both cases starting materials were recovered unchanged. Presumably this failure is a consequence of steric hindrance. It is well established that polychlorinated compounds are often distorted by steric strain, for example electron diffraction measurements have shown that even the perchlorobenzene molecule is distorted, with the chlorine atoms being displaced alternately above and below the mean plane of the benzene ring.[140] It is probably the steric interaction between the bridgehead phenyl group

and the tetrachlorophenylene unit which prevents the formation of the adduct in this case. This becomes abundantly clear if an attempt to construct a space filling model of such a molecule is undertaken.

Table 5.1

Experiment no.	Diene	Dienophile	Adduct no.	Duration of experiment hours	Yield %
1	cyclopentadiene	dichloro maleic-anhydride	43	2	92
2	cyclopentadiene	hexachloro-indenone	44	6	83
3	tetraphenylcyclo-pentadienone	hexachloro-indenone	-	23.5	-

5.2. Polymerization

(a) The ring-opening polymerization of endo-2,6-dichloro-3,5-diketo-4-oxa-tricyclo[5,2,1,$O^{2,6}$]dec-8-ene (43) using tungsten hexachloride and tetramethyl tin as the catalyst system

In the first instance the polymerization was carried out using toluene which had been dried over sodium, tungsten hexachloride activated by tetramethyl tin was used as the catalyst. The monomer was dissolved in dry toluene and injected, using an air-tight syringe, into the activated catalyst solution in a dry reaction vessel at room temperature. The reaction system was maintained under an atmosphere of dry nitrogen. After one hour and no apparent increase in viscosity the reaction was terminated by the addition of methanol, the solvent was evaporated and the product was dried under vacuum. It was examined by infra red spectroscopy which showed a very broad band extending through the region (2580 - 3200 $cm.^{-1}$) and indicating of a carboxylate group which was confirmed by a broad carbonyl stretching absorption (1710 - 1850 $cm.^{-1}$). It appeared that the

monomer was not polymerized but had reacted with methanol and given the half ester. There were several factors which could have influenced the failure of the reaction. The nitrogen gas, toluene and the monomer may not have been sufficiently dry and the tungsten hexachloride may have been impure. Although catalytic amounts of water or oxygen are beneficial to the reaction, an excess readily deactivates the catalyst. For subsequent attempts the nitrogen was dried more thoroughly by passing it through Drechsel bottles of concentrated sulphuric acid followed by heavy white oil, then through all the reaction system and to the other Drechsel bottle of heavy white oil, thus the entire system was maintained under an atmosphere of dry nitrogen so that at no time after the commencement of the reaction was air allowed into the reaction vessel. Toluene dryness was improved by refluxing it over sodium under a dry nitrogen atmosphere, until a permanent blue colour was obtained on addition of benzophenone, the solvent being distilled immediately before use. The monomer was dried and resublimed, and tetrahydrofuran was used instead of methanol for terminating the reaction without destroying the anhydride ring. The catalyst system WCl_6/Me_4Sn was used with an ageing time for the catalyst mixture of five minutes. The dark brown activated catalyst solution was injected, using an air-tight syringe, into the monomer solution. The solution was heated at $70^{o}C$, there was no immediate reaction and the experiment was left to run overnight during which time small pieces of solid material collected on the sides of the reaction vessel, the amount of solid slowly increased as the reaction proceeded. The appearance of this solid material took about 12 hours. The conditions and results are summarised in Table 5.2. The polymerization was terminated by addition of 50 ml tetrahydrofuran and all the solvents were evaporated. The dark brown material was dissolved in tetrahydrofuran

Table 5.2

The ring-opening polymerization of endo-2,6-dichloro-3,5-diketo-4-oxa-tricyclo[5,2,1,$O^{2,6}$] dec-8-ene using tungsten hexachloride and tetramethyl tin

Expt.	Monomer mmole	WCl_6 mmole	$(CH_3)_4Sn$ mmole	Toluene ml.	Ageing Time mins.	Reaction Temp. ^oC	Reaction Time	Yield
1	4.72	0.048	0.073	50	10	Room Temp.	1 hour	-
2	9.8	0.20	0.31	100	5	70	4.5 days	15%
3	20.6	0.40	0.62	125	5	60-70	3 days	29%

and the resulting solution added dropwise to a five-fold excess of toluene. A solid creamy-white material was produced which was recovered by filtration and dried under vacuum. It was characterised by elemental analysis which gave C, 43.44; H, 2.10; Cl, 29.48, the calculated values for the homopolymer being C, 46.39; H, 2.57; Cl, 30.43%. The infra red spectrum (Appendix 1, No. 16) was recorded for a thin film cast from tetrahydrofuran solution and indicated C-H stretching (2870 - 2970 $cm.^{-1}$) and intense carbonyl stretching absorptions (1730 - 1860 $cm.^{-1}$) assigned to the anhydride ring. In favourable cases absorption bands in the 970 - 960 $cm.^{-1}$ and 730 - 675 $cm.^{-1}$ region have been assigned to CH out-of-plane deformation of trans and cis double bonds, however in this case there is a fairly strong set of absorption peaks in the monomer spectrum at 980 - 950 $cm.^{-1}$ which appear as a broad band in the polymer spectrum, since there is no possibility of a trans CH=CH system in the monomer this observed band in the polymer can not be assigned with any certainty to a CH=CH trans system. On the other hand the absorption at 680 $cm.^{-1}$ in the monomer can be reasonably assigned to the out-of-plane CH deformation of the cis CH=CH system and this relatively strong monomer band is not seen in the polymer spectrum although there is a weak band at ca. 700 $cm.^{-1}$, this suggests that the double bonds in the polymer have predominantly trans geometry. There was a fairly close similarity between the spectrum of the monomer and the resultant polymer, with absorptions of the latter being much broader.

The ^{1}H n.m.r. spectrum for the polymer showed three very broad peaks in roughly the same regions as those observed for the monomer. The vinylic protons at 6.4 p.p.m. in the monomer experience an upfield shift to 6.8 p.p.m. in the polymer, and the bridgehead protons at 3.5 p.p.m. in the monomer are moved slightly downfieldto 3.7 p.p.m.,

with the methylene signal shifted marginally upfield. The ^{1}H spectrum of the polymer shows no fine structure and is not very informative; however the ^{13}C n.m.r. spectrum provides a much more detailed picture of the polymer structure and is discussed in a separate subsection.

(b) ^{13}C n.m.r. spectroscopic analysis

^{13}C n.m.r. spectroscopy for the study of poly[1,3-cyclopentylene-vinylenes] has been developed in recent years. It provides a powerful tool for investigating the cis/trans content of the unsaturated polymers much more accurately than i.r. spectroscopy and without the need for calibration. Ivin et.al. have investigated the ^{13}C n.m.r. spectra of poly(1,3-cyclopentylenevinylene), Figure 5.2,with varying amounts of cis and trans-unsaturation.[141] Ivin has shown that the chemical shifts

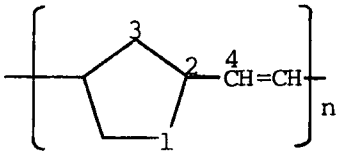
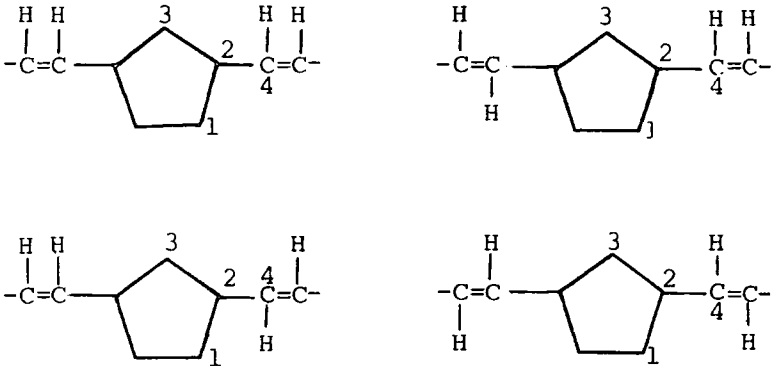


Figure 5.2

of the $\overset{1}{C}$, $\overset{2}{C}$ and $\overset{3}{C}$ carbon atoms are sensitive to isomerism about the nearest double bond that they are also sensitive to the isomerism about the next nearest double bond. Therefore, in a poly(1,3-cyclopentylenevinylene) containing both cis and trans-unsaturation, four signals should be observed for both $\overset{2}{C}$ and $\overset{1}{C}$ i.e. 2tt, 2tc, 2cc and 2ct (using the nomenclature proposed by Ivin et.al.,[141] in which the number denotes the carbon atom; the first letter, the cis (c) or trans (t) structure at the nearest double bond; the second letter that at the next nearest double bond) and 1tt, 1tc, 1ct and 1cc respectively; for $\overset{3}{C}$ which is symmetrically situated between two double bonds three signals should be observed corresponding to 3tt, 3tc≡3ct and 3cc as illustrated below



The relative intensities of these signals may be used to calculate the amount of cis and trans-unsaturation in the polymer using the formula for the determination of the fraction of cis-unsaturation,[142] σ_c, for each set of signals shown below and compared with the value obtained from the intensities

$$\sigma_c 1 = \frac{1ct + 1cc}{1tt + 1tc + 1ct + 1cc}, \quad \sigma_c 2 = \frac{2ct + 2cc}{2tt + 2tc + 2ct + 2cc}$$

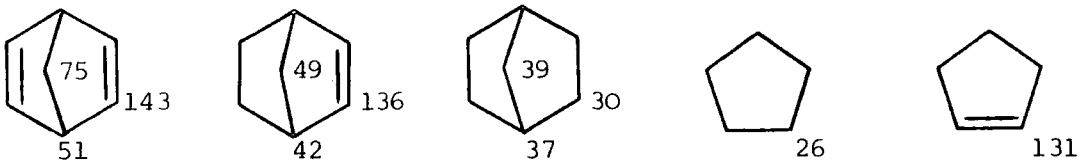
$$\sigma_c 3 = \frac{3cc + 0.5\ (3ct + 3tc)}{(3tc + 3ct) + 3cc + 3tt}$$ where 3ct and 3tc are equivalent

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

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

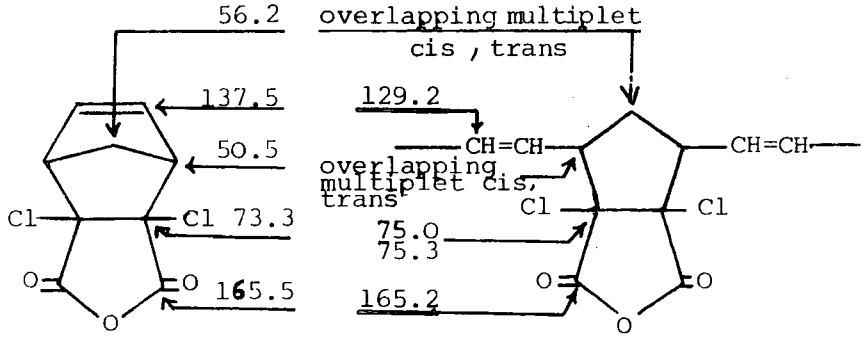
^{13}C n.m.r. spectra of the monomer (endo-2,6-dichloro-3,5-diketo-4-oxa-tricyclo[5,2,1,$O^{2,6}$]dec-8-ene) and the freshly prepared polymer were recorded as solutions in $CDCl_3$ at 75.4990NHz. The spectrum of the polymer is complicated and the prediction of shift in ^{13}C n.m.r. spectroscopy is also complicated since small changes in structure can result in very large changes in shift. A complete analysis for the polymer has been made in Table 5.3, but before discussing the spectra of the monomer and the polymer it is necessary to consider the observed shifts for related systems.[143]

^{13}C n.m.r. chemical shifts in five membered ring systems



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. This means that all the signals for the carbons in the five membered ring are shifted to higher field in the less strained systems.

In the spectrum of the monomer, five signals are seen, the spectroscopic data is summarized in Figure 5.3. The high field signals at 50.47 and 56.22 p.p.m. are assigned to the methine and methylene carbons by analogy with the data given above. The difference in the chemical shift between these two values and the chemical shift values for the methine and methylene carbons of norbornene, may result from the effect of the anhydride ring and the chlorine atom substituents.



The monomer The polymer

Figure 5.3

The signal at 137.5 p.p.m. was assigned to the vinylic carbons, its chemical shift is near to the chemical shift of the vinylic carbons in

norbornene (136 p.p.m.). The other two signals at 73.3 and 165.5 p.p.m. are assigned to CCl and C=O respectively.

The spectrum of the freshly prepared polymer showed twelve signals as shown in the Table 5.3 this increased number of signals as compared to the monomer spectrum is due to overlapping multiplets resulting from the presence of cis and trans main chain double bonds and the effect of this on the C^2, C^3 and C^4 carbon atoms. In general ring-opening polymerization using $WCl_6/(CH_3)_4Sn$ at high temperature gives a relatively greater amount of trans double bonds along the polymer chain. For C^2 carbon atom, which is α to the double bond, four signals would be expected by analogy with the polynorbornene spectrum and the signals (4,5,6,7) as shown in Table 1 are assigned respectively to 2ct, 2cc, 2tt and 2tc, using the measured relative intensities in the expression given above for the proportion of cis double bonds gives a value σ_c = 0.18. For the CH_2 carbon, i.e. C^3, the central position of this carbon atom with respect to adjacent double bonds (as described before for C^3 in poly(1,3-cyclopentylenevinylene) leads to an expectation of three signals corresponding to 3tt, 3tc≡3ct and 3cc and in practice peaks (1,2,3) in Table 5.3 have been so assigned, the measured intensities lead to a value of σ_c = 0.18. The vinylic carbon resonance is only partially resolved the main peak is assigned to the trans-CH=CH- unit and the shoulder to the downfield side is assumed to arise for the cis unit, σ_c from these intensities is 0.21. The two signals at 75.0 and 75.3 p.p.m. are due to $\underline{C}$-Cl carbons and are assigned as due to trans (8) and cis (9) environments. As with the vinyl carbons, the resolution is not very good and the value of σ_c obtained from the relative intensities is 0.22. The remaining signal at 165.2 has no fine structure and is assigned to the carbonyl carbon.

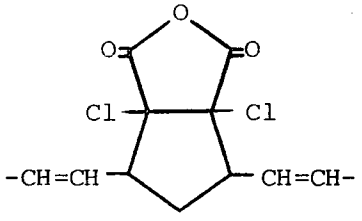
Thus, the analysis of the ^{13}C spectrum of the polymer leads to the conclusion that the double bonds in the chain have predominantly trans stereochemistry with a trans:cis ratio of ca. 4:1. In the majority of ring-opening polymerizations of cycloalkenes catalysed by WCl_6/R_4Sn at room temperature the trans:cis ratio is 1:1, and this increase in the proportion of trans double bonds is associated with the higher reaction temperature.

(c) Attempts to polymerize 2,5,6,7,8,10-hexachloro-3-keto tricyclo [9,2,1,$O^{2,10}$,$O^{4,9}$]tetradeca-4,6,8,12-tetraene (44)

Several attempts to polymerize monomer (44) were unsuccessful. In part these attempts were handicapped by the very low solubility of the monomer in toluene and chlorobenzene.

Table 5.3

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



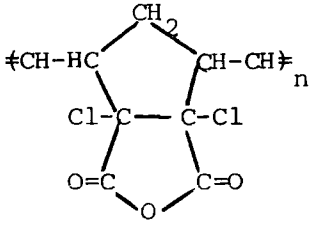
Peak no.	Chemical shift	Assignment	Relative intensity
1	32.7	3tt	70
2	34.6	3ct≡3tc	28
3	36.5	3cc	5
4	49.8	2ct	33
5	50.3	2cc	10
6	54.5	2tt	165
7	55.1	2tc	33
8	75.0	1t	35
9	75.3	1c	1
10	129.2	4t	141
11	ca. 129.5 (sholder)	4c	29
12	165.2	co	-

(d) Copolymerization attempts

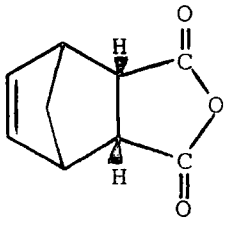
A mixture of monomer (43) and norbornene was polymerized using WCl_6/Me_4Sn as catalyst. The product was pure polynorbornene with no incorporation of monomer (43). This result is in complete accord with the very low reactivity of (43) already described.

5.3. Conclusions and suggestions for further work

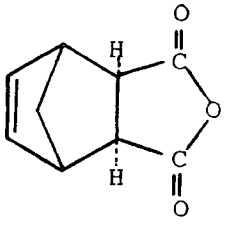
Although no molecular weight data is recorded in this thesis it is clear, from the viscosity of dilute solutions and the physical and spectroscopic properties of the product, that the material obtained from the reaction of (43) with WCl_6/Me_4Sn is the ring-opened polymer with the structure shown below:



At the time this work was reported Calderon described[144] related work on non-chlorinated systems:



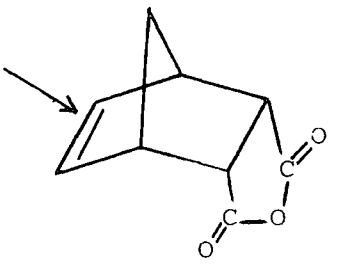
and



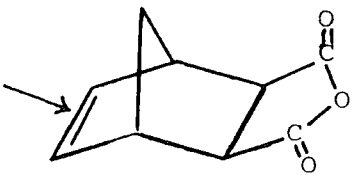
(45) (46)

The 'normal' Diels-Alder adduct is the endo-isomer (45), the exo-isomer (46) was obtained from the reaction of cyclopentadiene and maleic anhydride carried out at temperatures above 200°C. Calderon reported that the exo-adduct polymerized readily, but that the endo-adduct

polymerized only with some difficulty and in low yield. These results are in complete accord with the observations reported in this thesis since the monomer (43) was assumed to have endo-stereochemistry. The reason for the sluggish reaction of the endo isomers is not completely clear; it is generally assumed that catalyst attack on the norbornene type of monomer occurs for the exo-face, Calderon has postulated an interaction between the endo anhydride ring and the double bond. The



endo



exo

nature of this interaction is not clear and merits further examination.

The material produced in this work has some features which might make it technologically interesting, since it could form a cross-linked matrix via the double bond or anhydride functionalities. Its high chlorine content probably makes it non-flammable, and if its preparation was more efficiently carried out it might be worth further technological examination.

It would also be interesting to attempt to make the exo-isomer, by a process analogous to that reported by Calderon, and to examine its polymerization.

SECTION II

CHAPTER 6

EXPERIMENTAL

6.1. Reagents

Dicyclopentadiene was purchased from Koh-Licht Laboratories Ltd., 2,3-dichloro maleic anhyride from Fluka Ltd, tetraphenylcyclopentadienone was obtained from departmental stock, analar carbontetrachloride was purchased from BDH Chemicals Ltd., and n-hexane was purchased from Hopkin and Williams Ltd.

6.2. Cyclopentadiene

Cyclopentadiene was prepared by thermal cracking of dicyclopentadiene. A one-necked round-bottomed flask (1 l.) was quarter-filled with dicyclopentadiene, and an unlagged vigreux column (50 cm.) was connected via a distillation-head carrying a thermometer, and water-condenser to a receiver flask. The distillation flask was heated strongly using an electric heater the dicyclopentadiene boiled vigorously and liquid gradually ascended the column; the product (cyclopentadiene) distilled slowly in the range 40 - 45^{o}C and was used without further purification. When necessary it was stored in the deep freeze (-20^{o}) and under these conditions it could be kept for several days.

6.3. Diels-Alder reactions

(a) The reaction of hexachloroindenone with cyclopentadiene

Hexachloroindenone (10 g, 29.7 mmoles) was dissolved in analar carbontetrachloride (560 ml) in a 1 l., 3-necked round-bottomed flask, fitted with a mechanical stirrer, reflux condenser and dropping funnel. Cyclopentadiene (2.96 g, 3.70 ml, 44.8 mmoles) was diluted with 20 ml carbontetrachloride and added dropwise over a period of 30 minutes to the refluxing solvent. After addition of all the reagent the mixture was stirred vigorously for 6 hours. The solvent was

evaporated. The product was dried under vacuum to remove any trace of excess cyclopentadiene, then recrystallized from carbontetrachloride and n-hexane to give 2,5,6,7,8,10-hexachloro-3-keto-tricyclo[9,2,1,$o^{2,10}$, $o^{4,9}$]tetra-deca-4,6,8,12-tetraene (9.93 g, 94.6 mmoles, 83%) as pale yellow crystals m.p. 202 - 203°C which were examined by t.l.c. and infra red spectroscopy (Appendix 1, No. 14), $M_{(\text{mass spectroscopy})}$ 400 and elemental analysis [Found: C, 41.55; H, 1.39; Cl, 53.01% requires C, 41.68; H, 1.4; Cl, 52.85%].

(b) Diels-Alder reaction of hexachloroindenone and tetraphenyl-cyclopentadienon

The same procedure described above was used in this reaction. Tetraphenylcyclopentadienone (5.75 g, 14.97 mmoles) was added to hexachloroindenon (5 g, 14.8 mmoles) using carbontetrachloride as a solvent. It was refluxed for 32.50 hours. There was no evidence of reaction by t.l.c. The procedure was repeated using xylene as a solvent but it gave the same result.

(c) The synthesis of endo-2,6-dichloro-3,5-diketo-4-oxa-tricyclo [5,2,1,$o^{2,6}$]dec-8-ene

Dichloro maleic anhydride (10.1 g, 60.4 mmoles) was dissolved in carbontetrachloride (300 ml) in a one-necked round-bottomed flask (1 l.) fitted with water condenser. The solvent was heated using an oil bath until it refluxed gently, it was stirred continuously using magnetic stirrer throughout the experiment. Cyclopentadiene (5.9 g, 89.4 mmoles, 7.37 ml) was added dropwise through the condenser using a dropper over a period of 30 minutes. After complete addition of reagent the mixture was left to reflux gently for 2 hours. The solvent was evaporated and the product was sublimed under reduced pressure (110°C, 10^{-3} mm.Hg.). A white powdery material was collected from the surface of the cold finger

(12.9 g, 55.36 mmoles, 92%). It was identified by i.r. spectroscopy (Appendix 1, No. 15) $M_{(\text{mass spectroscopy})}$ 232 and elemental analysis [Found: C, 46.43; H, 2.53; Cl, 30.04% $C_9H_6ClO_3$ requires C, 46.39; H, 2.57; Cl, 30.43%].

6.4. Polymerization

(a) Reagents

Toluene was purchased from B.D.H. Chemicals Ltd., purified and dried over sodium and distilled directly into the reaction flasks. Tungsten hexachloride was prepared by reaction of WO_3 with $CCl_3CCl{=}CCl_3$ and provided by Mr. A.B. Alimuniar (this department), tetrahydrofuran was provided by Mr. B. Hall (this department), tetramethyl tin and norbornene were purchased from Aldrich Chemical Co. Ltd.

(b) The ring-opening polymerization of endo-2,6-dichloro-3,5-diketo-4-oxa-tricyclo[5,2,1,$O^{2,6}$]dec-8-ene using tungsten hexachloride and tetramethyl tin as the catalyst system

All the reaction polymerization flasks contained a magnetic follower and were continuously purged with dry nitrogen.

To one neck of a 2-necked RB flask (250 ml) was fitted a serum cap and to the other an air condenser. The flask was charged with dried purified monomer (4.8 g) which was dissolved in dried toluene (75 ml) distilled directly into the reaction vessel. A separate flask (50 ml) was charged with a toluene solution of tungsten hexachloride (4 ml, 0.1 M) and tetramethyl tin (3 ml, 0.2 M). The catalyst mixture was stirred for five minutes until the colour changed from blue-black to dark brown. The active catalyst was injected into the monomer solution using an air-tight syringe (a dry nitrogen atmosphere was maintained throughout the experiment). The liquid was heated at

70°C using an oil bath. The experiment was left under these conditions for 3 days (another portion of active catalyst was added after one day). A dark brown viscous material separated around the surface of the flask mainly at the solvent gas interface. After this the reaction was terminated by the addition of 50 ml of tetrahydrofuran. All the solvents were evaporated, the product was dark in colour. It was dissolved in tetrahydrofuran to give viscous solution which was added dropwise to a five-flood excess of toluene. The precipitated material was recovered by filtration, dissolved in tetrahydrofuran and reprecipitated in excess toluene four times. The material was dried for 3 hours under vacuum to give creamy-white material (1.4 g, 29%). It was identified by i.r. spectroscopy (Appendix 1, No. 16), elemental analysis [Found: C, 43.44; H, 2.10; C, 29.48 requires C, 46.39; H, 2.57, Cl, 30.43%], ^{1}H n.m.r. and ^{13}C n.m.r.

(c) The ring-opening polymerization of 2,5,6,7,8,10-hexachloro-3-keto-tricyclo[9,2,1,$O^{2,10}$,$O^{4,9}$]tetradeca-4,6,8,12-tetraene (44)

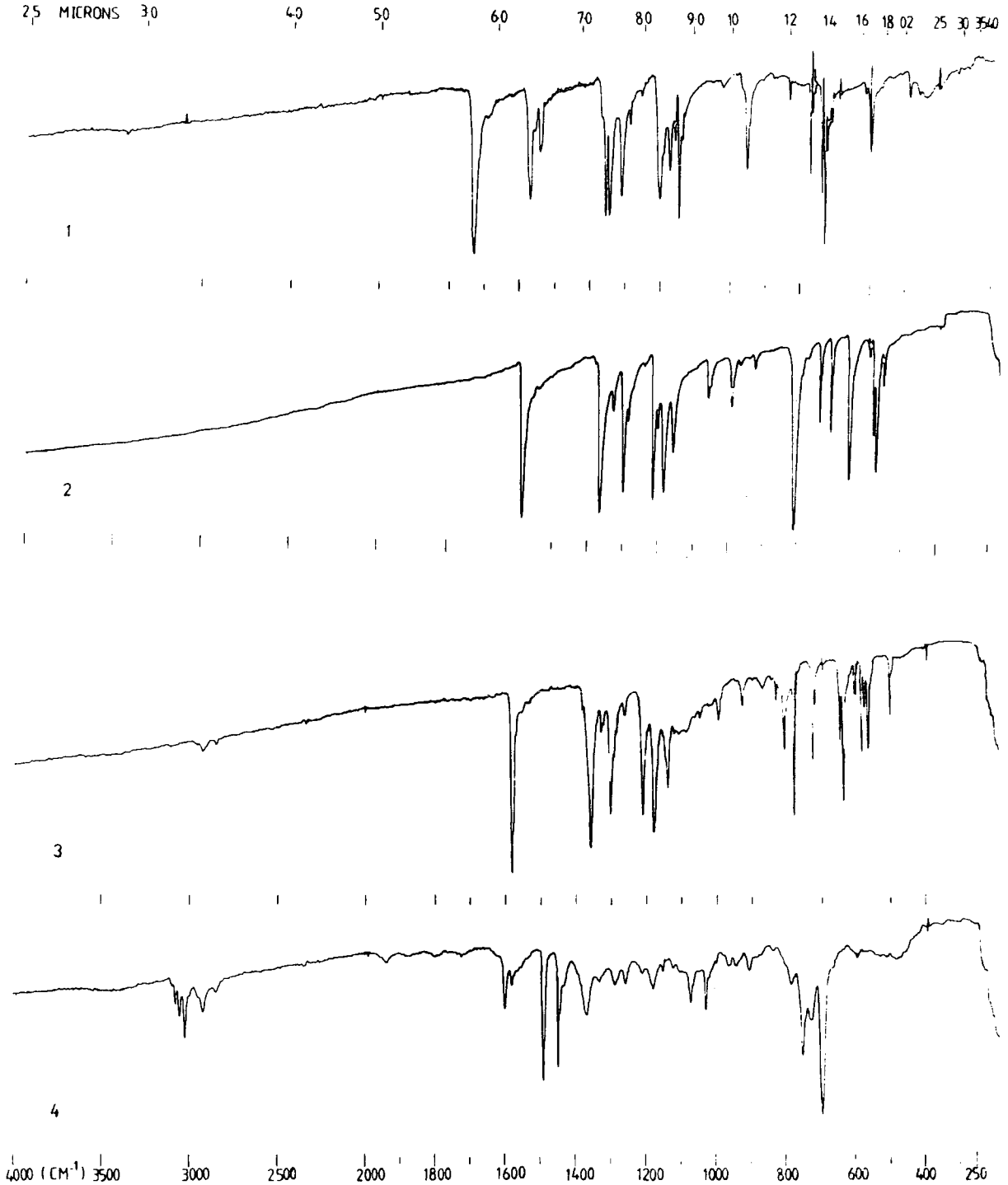
Following the procedure described above, the purified monomer (44) (8.0 g) was dissolved in dry chlorobenzene (75 ml). The active catalyst prepared by reacting tungsten hexachloride (4 ml, 0.1 M WCl_6 in C_6H_5Cl) with tetramethyl tin (3 ml, 0.2 M Me_4Sn in C_6H_5Cl) was injected into the monomer solution. The mixture was heated at 70°C for 3 days but there is no evidence of reaction and after destruction of the catalyst with THF the monomer was collected unchanged (8 g), identified by infra red spectroscopy.

APPENDIX 1

All spectra were recorded using KBr disc or casting thin films for the polymer.

Infra red spectra are given below:-

Spectrum No.	Sample
1	Perchloroindenone, see page 30;
2	Perchloroindene, see page 31;
3	Recovered material from the reaction of perchloro-indene with cyclohexane, see page 32;
4	Recovered material from the reaction of perchloro-indene with Toluene, see page 33;
5	The first fraction from the separation of 4 (above);
6	The second fraction from the separation of 4 (above);
7	The third fraction from the separation of 4 (above);
8	The fourth fraction from the separation of 4 (above);
9	Recovered material from the reaction of perchloro-indene with potassium fluoride, see page 34;
10	The first fraction from the separation of 9 (above);
11	The second fraction from the separation of 9 (above);
12	The third fraction from the separation of 9 (above);
13	The fourth fraction from the separation of 9 (above);
14	Recovered material from the reaction of cyclopentadiene with hexachloroindenone, see page 70;
15	Recovered material from the reaction of cyclopentadiene with dichloromaleic anhydride, page 71;
16	Recovered material from the reaction of endo-2,6-dichloro-3,5-diketo-4-oxa-tricyclo[5,2,1,$O^{2,6}$]dec-8-ene with WCl_6/Me_4Sn, page 72.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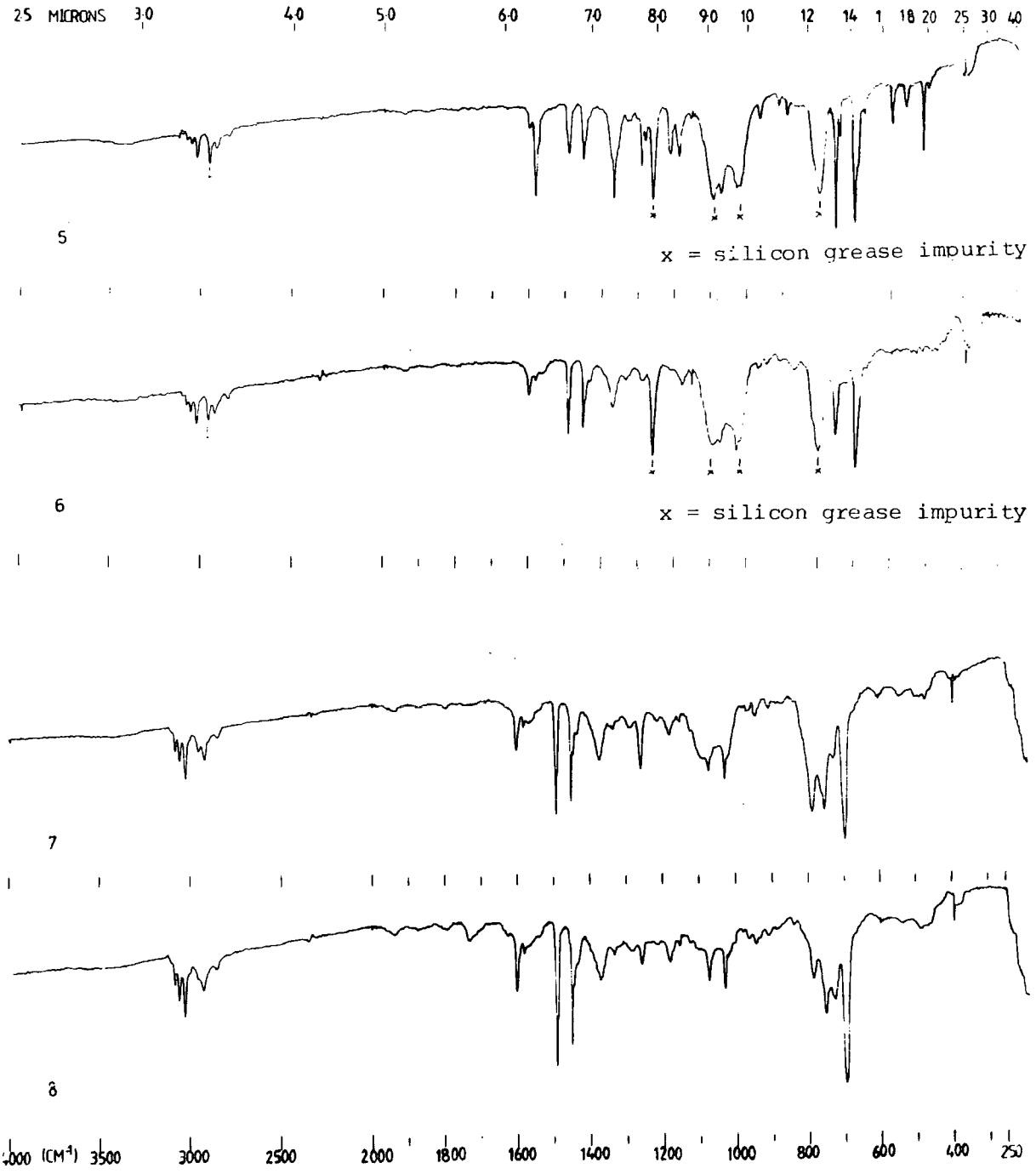
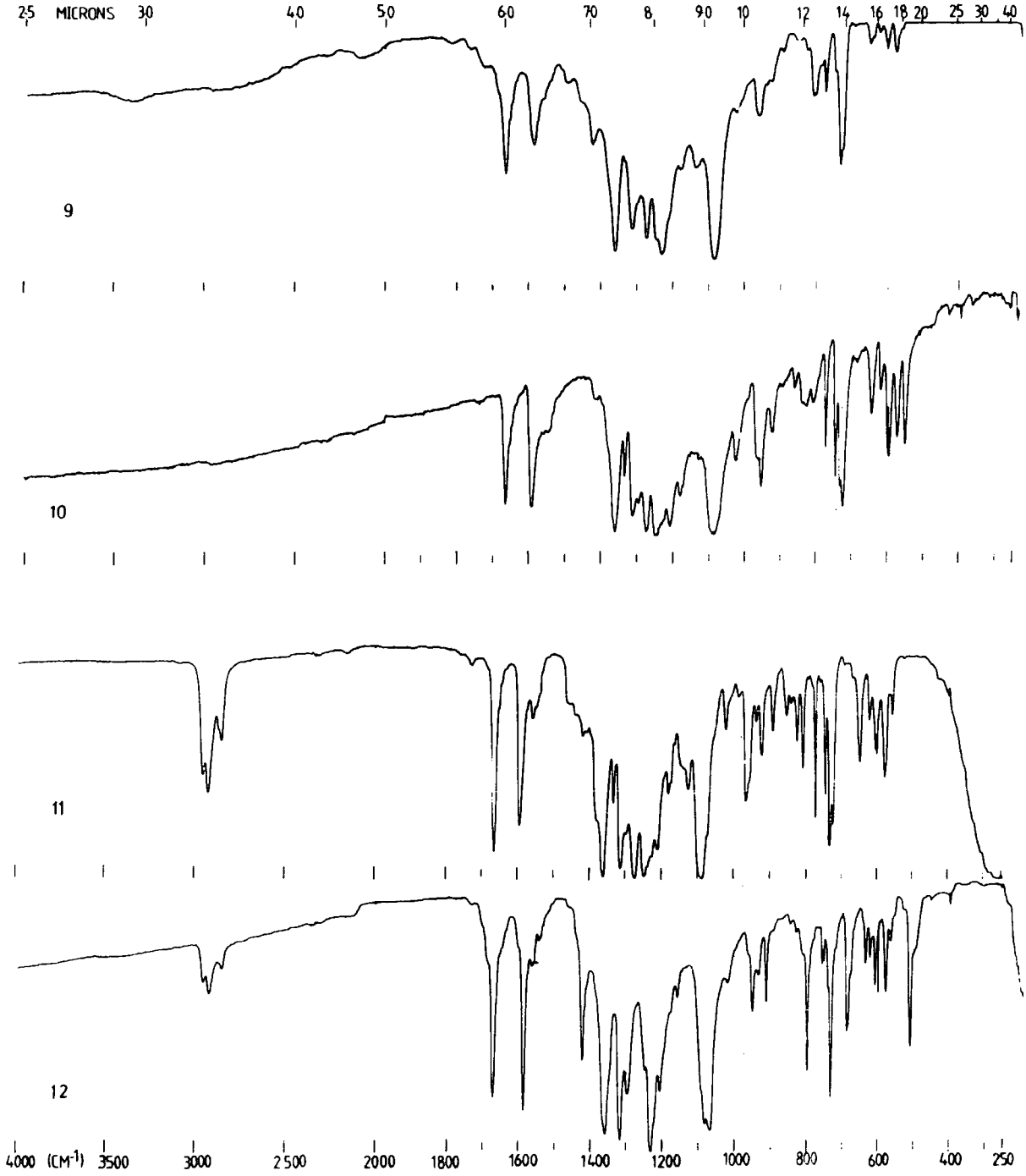
1
2
3
4
4000 (CM-1) 3500 3000 2500 2000 1800 1600 1400 1200 1000 800 600 400 250


2·5 MICRONS 3·0 4·0 5·0 6·0 7·0 8·0 9·0 10 12 14 1 18 20 25 30 40
5
x = silicon grease impurity
6
x = silicon grease impurity
7
8
4000 (CM⁻¹) 3500 3000 2500 2000 1800 1600 1400 1200 1000 800 600 400 250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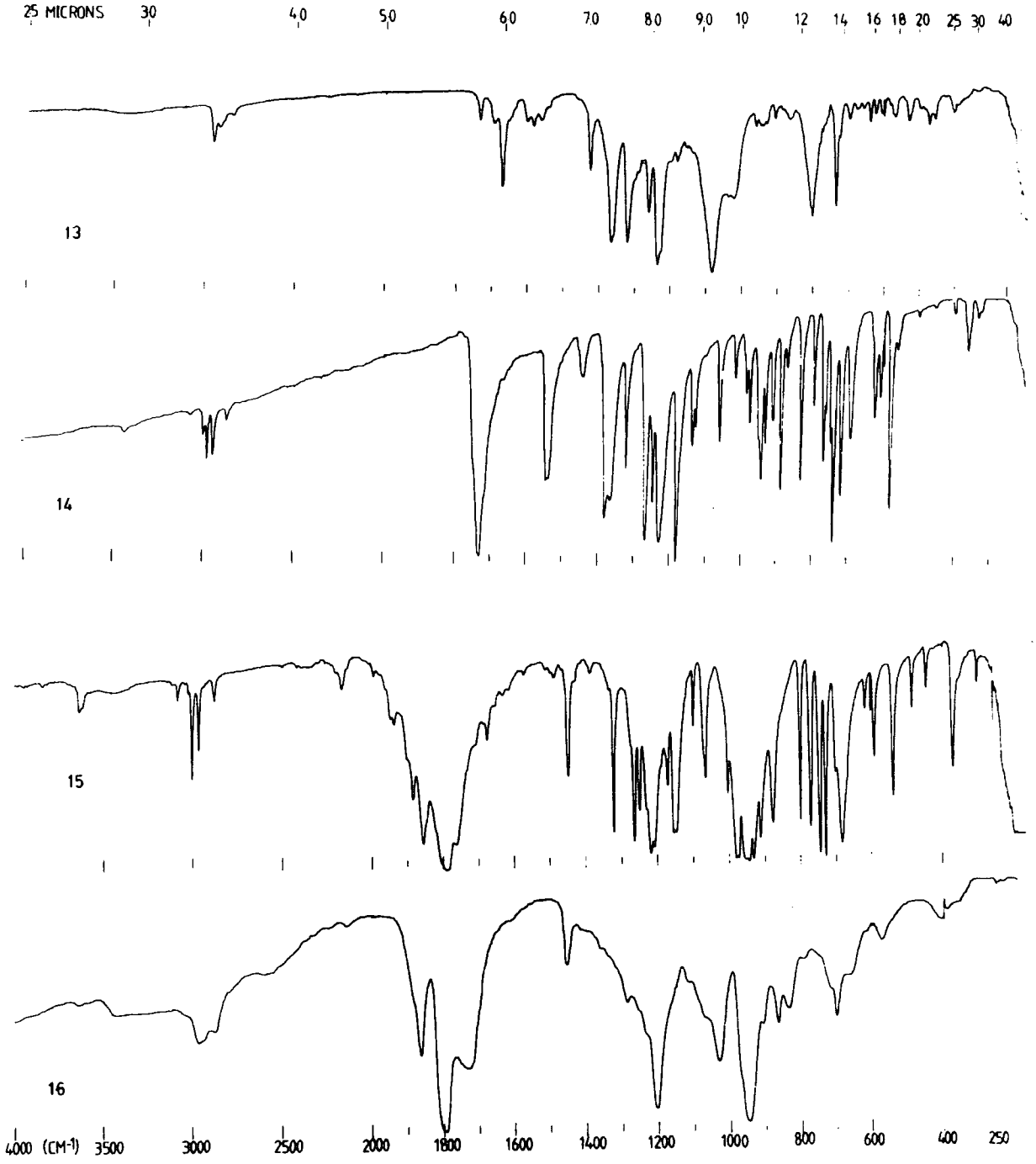
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13
14
15
16
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