METAL CATALYSED ALKENE ADDITION REACTIONS IN ORGANIC SYNTHESIS

by

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DECLARATION

During the period of registration as a candidate for the degree of PhD, the author has not been registered for any other award of the CNAA or any other university.

The material contained in this thesis has not been used in any other submission for an academic award.

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ABSTRACT:

Metal catalysed alkene addition reactions in organic synthesis.

K. Lewandowska

The reaction between $[Co_2(CO)_8]$ and CCl_4 has previously been reported to lead to the formation of dichlorocarbene. In the presence of cyclohexene, the carbene was reported to add to the alkene giving 7,7-dichlorobicyclo[4.1.0]heptane. This reaction has been reinvestigated and it has been shown that the principal pathway involves formation of CCl_3 radicals, which react with cyclohexene to form almost equal proportions of two isomers of 1-chloro-2-(trichloromethyl)cyclohexene (adduct). Carbene formation has been shown to be only a minor pathway. A mechanism has been proposed which accounts for these findings.

The addition of CCl_4 to cyclohexene in the presence of a range of metal complexes has been studied. Use of other dinuclear metal carbonyls gave a higher yield of the adduct than observed with $[Co_2(CO_8)]$. The reactions were also more stereoselective. $[RuCl_2(PPh_3)_3]$, $[RuH_2(PPh_3)_4]$ and $[RuH_3(SiPhMe_2)(PPh_3)_3]$ all gave much higher yields and stereoselectivities. It has been suggested this is a consequence of a metal complex catalysed reaction mechanism in which radical pair formation plays an important role. The three ruthenium complexes appear to generate the same active catalytic species.

The effect of variation of the phosphine ligand has been studied using $[RuCl_2\{(4\text{-}X\text{-}C_6H_4)_3P\}_3]$ (where X=Cl, H, Me and MeO) and a clear relationship between catalytic efficiency and the electronic nature of the ligand has been demonstrated for the reaction between oct-1-ene and CCl_4. The relationship is more complex in the case of the analogous cyclohexene reactions which also displayed marked solvent effects. The reactions of both oct-1-ene, cyclohexene and CCl_4 in the presence of $[RuCl_2(PPh_3)_3]$ have been studied in a wide range of solvents. The importance of solvent viscosity in determining yields in these radical reactions has been demonstrated.

A preliminary study of the addition of CCl_4 to cyclo-1,3-dienes was also made with specific emphasis on the investigation of the stereochemistry of the addition products.

A study has also been made of the catalysed synthesis of lactones by addition of trichloroacetic acid to alkenes in the presence of $[RuCl_2(PPh_3)_3]$. The reaction has been extended to the synthesis of dibrominated lactones from tribromoacetic acid and alkenes. A method was developed for purification of the bromolactones, as they were found to be susceptable to thermal decomposition.

Abbreviations

1) Chemicals , ligands etc.

bipy	-	bipyridyl
Cp	-	cyclopentadienyl , C_5H_5
Cp*	-	pentamethylcyclopentadienyl , C_5Me_5
DIPHOS	-	bis(diphenylphosphino)-ethane
DIOP	-	(-)-2,3-o-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphine)-butane
diglyme	-	diethyleneglycol dimethyl ether , $CH_3(CH_2CH_2O)_2CH_3$
Me	-	methyl , CH_3
phen	-	1,10 - phenanthroline
Ph	-	phenyl , C_6H_5
R	-	alkyl , C_nH_{2n+1}

2) Other terms

cm^{-1}	-	wavenumber
δ	-	chemical shift (ppm)
GLC	-	gas liquid chromatography
GC/MS	-	gas chromatography-mass spectrometry
HOMO	-	highest occupied molecular orbital
NMR	-	nuclear magnetic reasonance
ppm	-	parts per million
tr	-	trace

TABLE OF CONTENTS - CHAPTER 1

TABLE OF CONTENTS - CHAPTER 2

TABLE OF CONTENTS - CHAPTER 3

CHAPTER 1 : INTRODUCTION

General Introduction

This thesis is concerned with reactions involving the addition of halogen-containing organic molecules across the double bonds of alkenes catalysed by transition metal complexes. Such processes are attracting increased interest since they provide routes to new molecules and alternative procedures for the synthesis of known molecules. Traditional organic synthetic methods have long been used for alkene addition reactions leading to the formation of new carbon-carbon bonds, but all of these have some shortcomings. Thus, nucleophilic additions involve drastic conditions (unless the alkene has strong electron withdrawing substituents), electrophilic additions require polar reagents and radical additions are not very controllable, being significantly effected by light, oxygen, peroxides and inhibitors. Metal catalysed reactions offer the potential of high selectivity and applicability to a wide range of reagents.

The thesis is divided into three chapters of which the first is a literature survey of radical and catalysed addition reactions. The second chapter deals with the addition of tetrachloromethane to cyclohexene and oct-1-ene in the presence of $[RuCl_2(PPh_3)_3]$ and other catalysts. The third chapter is concerned with the study of the addition reactions resulting in halogenated lactones.

1.1 HISTORICAL BACKGROUND

The earliest observations of the formation of carbon-carbon bonds using free radical methods was by two independent research groups at Du Pont and the U.S. Rubber Company[1]. These involved the addition of tetrachloromethane to alkenes forming low molecular weight polymeric products. However the first published example of a simple 1 : 1 addition reaction was in 1945 by Kharasch[2]. This involved the formation of 1,1,1,3-tetrachlorononane and 1,1,1-trichlorononane from the addition of tetrachloromethane and trichloromethane respectively, to oct-1-ene. This addition to alkenes was quantified and the results (Table 1.1) showed high yields for peroxide initiated reactions, but no reaction was observed when initiation by visible light was attempted[3]. Such reactions have become known as "Kharasch addition reactions".

Many other examples of these types of addition reaction have since been observed. These include addition of aldehydes, esters, amines primary and secondary alcohols to form ketones, α-alkylesters, α-alkylamines, secondary and tertiary alcohols respectively. This was extended to derivatives of chlorinated acetic acid which add to alkenes to give excellent yields of the products shown in equations 1.1 and 1.2[4].

$$RCH{=}CH_2 + CHCl_2COOCH_3 \longrightarrow RCH_2CH_2CCl_2COOCH_3 \qquad (1.1)$$

$$RCH{=}CH_2 + CCl_3COCl \longrightarrow RCHClCH_2CCl_2COCl \qquad (1.2)$$

Table 1.1 : Quantification of the addition products resulting from the reaction between oct-1-ene and haloalkanes under various conditions[a].

Haloakane	Initiator	Product	% Yield[a]
CCl_4	Ac_2O_2	1,1,1,3-tetrachlorononane	85
CCl_4	Bz_2O_2	1,1,1,3-tetrachlorononane	75
CCl_4	UV	No reaction	-
CCl_4	Visible light	No reaction	-
$CHCl_3$	Bz_2O_2	1,1,1-trichlorononane	22

[a]Yield based on alkene charged.

Kharasch addition reactions take place by a free radical mechanism, as shown in scheme 1.1. The overall reaction is exemplified in equation 1.3, where ROOR is a free radical initiator.

$$CCl_4 + CH_2{=}CHC_6H_{13} \xrightarrow{ROOR} CCl_3CH_2CHClC_6H_{13} \qquad (1.3)$$

In this mechanism, equations 1.4 and 1.5 represent initiation which involves the generation of a free radical by homolytic fission of the C-Cl bond. This can be carried out chemically (as shown), thermally (but this requires high temperatures), by use of ultraviolet light or by high energy radiation.

Scheme 1.1 : Mechanism of free radical additions[2]:-

Initiation :

$$ROOR \longrightarrow 2RO\bullet \quad (1.4)$$

$$RO\bullet + Cl\text{-}CCl_3 \longrightarrow ROCl + CCl_3\bullet \quad (1.5)$$

Propagation :

$$CCl_3\bullet + CH_2{=}CHC_6H_{13} \longrightarrow CCl_3CH_2\underset{\bullet}{C}HC_6H_{13} \quad (1.6)$$

$$CCl_3CH_2\underset{\bullet}{C}HC_6H_{13} + Cl\text{-}CCl_3 \longrightarrow CCl_3CH_2CHClC_6H_{13} + CCl_3\bullet \quad (1.7)$$

Termination :

$$2CCl_3\bullet \longrightarrow C_2Cl_6 \quad (1.8)$$

$$2CCl_3CH_2\underset{\bullet}{C}HC_6H_{13} \longrightarrow \begin{array}{l} CCl_3CH_2CHC_6H_{13} \\ \quad\quad\quad\;\; | \\ CCl_3CH_2CHC_6H_{13} \end{array} \quad (1.9)$$

$$CCl_3\bullet + CCl_3CH_2\underset{\bullet}{C}HC_6H_{13} \longrightarrow \begin{array}{l} CCl_3CH_2CHC_6H_{13} \\ \quad\quad\quad\;\; | \\ \quad\quad\quad\;\; CCl_3 \end{array} \quad (1.10)$$

The chemical initiator can be of three types : (i) diacyl peroxide, (ii) dialkyl peroxide, (iii) azobis(nitriles).

(i) Acyl peroxides

The two most commonly used are benzoyl peroxide and acetyl peroxide. These thermally decompose as shown in equations 1.11 and 1.12[6].

$$(RCO)_2O_2 \longrightarrow 2\ R\overset{\overset{O}{\|}}{C}O\bullet \quad (1.11)$$

$$R\underset{\underset{O}{\|}}{C}O \longrightarrow R\bullet + CO_2 \quad (1.12)$$

where $R{=}CH_3$ or C_6H_5.

The decomposition of acetyl peroxides proceeds nearly completely to methyl radicals and carbon dioxide whereas benzoyl peroxide produces some benzoyloxy radicals. Further elimination is dependant on the nature of the solvent and other reagents present.

(ii) Dialkyl peroxides

The most commmonly used peroxide is di-t-butyl peroxide (equations 1.13 and 1.14).

$$(CH_3)_3COOC(CH_3)_3 \longrightarrow 2(CH_3)_3CO\cdot \qquad (1.13)$$

$$(CH_3)_3CO\cdot \longrightarrow CH_3COCH_3 + CH_3\cdot \qquad (1.14)$$

In this case, as previously, the secondary elimination is dependant on the reactivity of the solvent towards the t-butoxy radical. However, the rate of decomposition is independent of the solvent.

(iii) Azobis(nitriles)

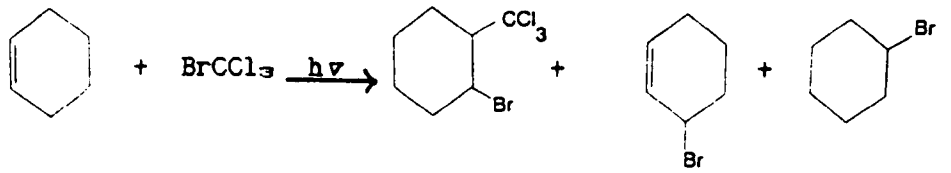
The most frequently used chemical initiator is azobis(isobutylnitrile) (equation 1.15).

$$(CH_3)_2\overset{\overset{\displaystyle CN}{|}}{C}-N=N-\overset{\overset{\displaystyle CN}{|}}{C}(CH_3)_2 \longrightarrow 2(CH_3)_2\overset{\overset{\displaystyle CN}{|}}{C}\cdot + N_2 \qquad (1.15)$$

This is the least reactive initiator, as the cyanoisopropyl radical is quite unreactive. It is usually used to initiate highly reactive species such as bromotrichloromethane.

Initiation of free radical addition reactions can also be carried out by ultraviolet light or high energy radiation. An example of a reaction which is readily photoinitiated is the addition of

bromotrichloromethane to cyclohexene (equation 1.16)[6].



(1.16)

60 % 28 % 12 %

45cis-55trans

Returning to the propagation steps (Scheme 1.1), the addition of the radical occurs by the Anti-Markovnikov mechanism (equation 1.6), thereby adding $CCl_3^{\bullet}$ to the least substituted alkenic carbon atom. This minimises steric hindrance and forms the most stable radical. Thus terminal alkenes undergo addition reactions with greater ease and produce fewer side products then internal alkenes. The termination steps (equations 1.8-1.10), although only forming a small number of products (due to the low concentration of radicals), have an effect on the overall yield of the reaction.

Radical displacements and additions are effected by the polar nature of the radicals. If these radicals have a strong electron withdrawing ability they show enhanced reactivity with substrates containing electron donating groups and vice versa. Addition reactions proceeding by free radical mechanisms are subject to many side reactions which often cause a reduction in the yield of the desired 1 : 1 product. These fall into three main categories :
(1) telomerisation, (2) allylic attack, (3) rearrangements.

(1) Telomerisation

Telomerisation is a series of reactions which compete with step (1.7) of scheme 1.1, producing longer chain products and hence diminishing the yield of the simple addition product. This can be illustrated by considering scheme 1.2.

Scheme 1.2 : Example of telomerisation

$$CCl_3CH_2\dot{C}HC_6H_{13} \xrightarrow{CCl_4} CCl_3CH_2CHClC_6H_{13} + CCl_3^{\bullet} \quad (1.7)$$

$$\downarrow CH_2{=}CHC_6H_{13}$$

$$CCl_3CH_2CHC_6H_{13}CH_2\dot{C}HC_6H_{13} \xrightarrow{CH_2{=}CHC_6H_{13}} \text{etc} \quad (1.17)$$

$$\downarrow CCl_4$$

$$CCl_3CH_2CHC_6H_{13}CH_2CHClC_6H_{13} + CCl_3^{\bullet} \quad (1.18)$$

These long molecules are telomers and in most cases are the undesired products (except in the case of ethene and tetrafluoroethene).

(2) Allylic attack

Another reaction that may compete with formation of the 1 : 1 adduct in scheme 1.1 is allylic substitution, which arises as a consequence of hydrogen atom abstraction from the allylic position by $CCl_3^{\bullet}$. This competes with step (1.6) of scheme 1.1. Allylic hydrogen atoms are susceptible to attack because of the high resonance stabilisation of the resulting allylic radical (scheme 1.3).

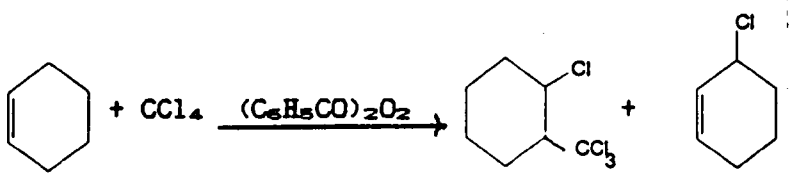
Scheme 1.3 : Example of allylic attack

$$CCl_3^{\bullet} + CH_2{=}CHCH_2C_6H_{11} \longrightarrow CH_2{=}CH\dot{C}HC_6H_{11} + HCCl_3 \qquad (1.19)$$

$$\downarrow$$

$$CCl_3CH_2\dot{C}HCH_2C_6H_{11} \qquad (1.6)$$

Allylic attack can be an unfortunate complication as it may lead to termination of chains resulting in a reduction of the overall product yield. Non-terminal alkenes and cycloalkenes are most susceptible to this type of attack as they have more reactive allylic hydrogens compared to the terminal alkenes. For example, investigation of the reaction between cyclohexene and tetrachloromethane in the presence of benzoyl peroxide showed that this competing reaction was occurring (equation 1.20)[7].



(1.20)

(3) Rearrangements

Radical rearrangements are common and be classified into

(i) hydrogen shifts and (ii) ring closing or opening.

(i) Hydrogen shifts

These are well documented, typically involving 1,3 or 1,5 shifts[8]. For example, the addition of tetrachloromethane to oct-1-ene can result in both these types of hydrogen migrations (schemes 1.4 and 1.5).

Scheme 1.4 : 1,3-hydrogen shift

$$CCl_3\cdot + C_6H_{13}CH{=}CH_2 \longrightarrow CH_3CH_2CH_2CH_2CH_2CH_2\dot{C}HCH_2CCl_3 \quad (1.6)$$

$$CH_3CH_2CH_2CH_2CH_2CH_2\dot{C}HCH_2CCl_3 \xrightarrow[\text{shift}]{1,3\text{-}H} CH_3CH_2CH_2CH_2\dot{C}HCH_2CH_2CH_2CCl_3 \quad (1.21)$$

$$CH_3CH_2CH_2CH_2\dot{C}HCH_2CH_2CH_2CCl_3 \xrightarrow{Cl} CH_3CH_2CH_2CH_2CHClCH_2CH_2CH_2CCl_3 \quad (1.22)$$

Scheme 1.5 : 1,5-hydrogen shift

$$CH_3CH_2CH_2CH_2CH_2CH_2\dot{C}HCH_2CCl_3 \xrightarrow[\text{shift}]{1,5\text{-}H} CH_3CH_2\dot{C}HCH_2CH_2CH_2CH_2CH_2CCl_3 \quad (1.23)$$

$$CH_3CH_2\dot{C}HCH_2CH_2CH_2CH_2CH_2CCl_3 \xrightarrow{Cl} CH_3CH_2CHClCH_2CH_2CH_2CH_2CH_2CCl_3 \quad (1.24)$$

Less commonly 1,2-shifts also occur which involve halogen migration as shown in scheme 1.6

Scheme 1.6 : Halogen migration in the addition of bromotrichloromethane to 3,3,3-trichloropropene[9,10].

$$CH_2{=}CHCCl_3 + CCl_3\cdot \longrightarrow CCl_3CH_2\dot{C}HCCl_3 \longrightarrow CCl_3CH_2CHCl\dot{C}Cl_2 \quad (1.25)$$

$$\left.\begin{array}{l} CCl_3CH_2\dot{C}HCCl_3 \\ \\ CCl_3CH_2CHCl\dot{C}Cl_2 \end{array}\right\} \longrightarrow CCl_3CH_2CH{=}CCl_2 + Cl\cdot \quad (1.26)$$

$$CCl_3CH_2CHCl\dot{C}Cl_2 + BrCCl_3 \longrightarrow CCl_3CH_2CHClCCl_2Br + CCl_3\cdot \quad (1.27)$$

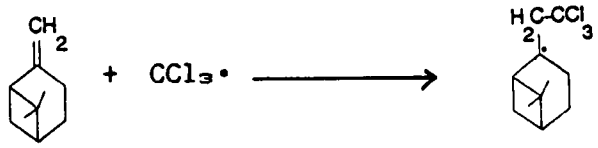
Ring opening and closing

These reactions usually take place when highly strained systems are involved. An example of this is the peroxide catalysed addition of tetrachloromethane to β-pinene[11]. The mechanism proposed for this is shown in scheme 1.7.

Scheme 1.7 : The mechanism of addition of tetrachloromethane to β-pinene[11].

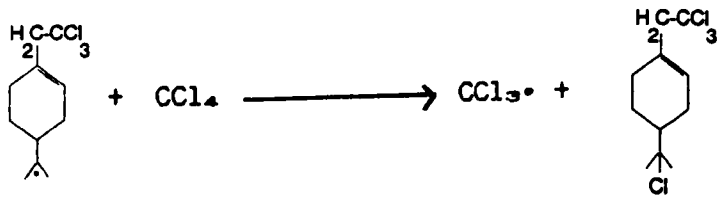
$$ROOR \longrightarrow R\bullet \qquad (1.28)$$

$$R\bullet + CCl_4 \longrightarrow RCl + CCl_3\bullet \qquad (1.29)$$



(1.30)

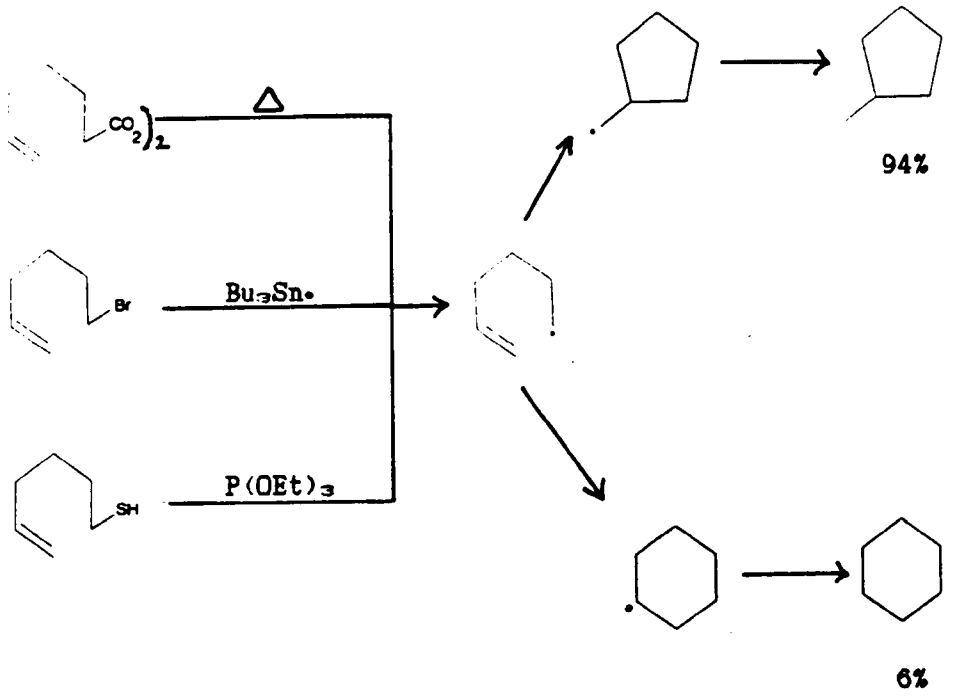
(1.31)



(1.32)

Radical ring closures occur by intramolecular additions. Scheme 1.8 shows how the hex-5-en-1-yl radical undergoes such a reaction to give cyclised products.

Scheme 1.8 : Cyclisation of hex-5-en-1-yl



(1.33)

(1.34)

1.2 Catalysed addition reactions

1.2.1 Metal salts

The earliest catalysed addition reactions which resulted in the formation of new carbon-carbon bonds were discovered by chance in 1956. Minisci et al intended to carry out a thermal polymerisation of acetonitrile in the presence of tetrachloromethane or trichloromethane by heating the mixture in a steel autoclave at 160°C[12]. However, instead of the expected polymerisation products, considerable quantities of the 1 : 1 addition products, $CCl_3CH_2CHClCN$ and $CHCl_2CH_2CHClCN$ resulted. It was suggested that this reaction was caused by the iron present in the autoclave acting as a catalyst as outlined in scheme 1.9.

Scheme 1.9 : Addition of tetrachloromethane to acrylonitrile catalysed by $FeCl_2$[13]

$$CCl_4 + Fe^{2+} \longrightarrow CCl_3\bullet + (FeCl)^{2+} \quad (1.35)$$

$$CH_2{=}CHCN + CCl_3\bullet \longrightarrow CCl_3CH_2\underset{\bullet}{C}HCN \quad (1.36)$$

$$CCl_3CH_2\underset{\bullet}{C}HCN + (FeCl)^{2+} \longrightarrow CCl_3CH_2CHClCN + Fe^{2+} \quad (1.37)$$

Iron is converted to $FeCl_2$ by reaction with tetrachloromethane and the iron (II) salt then undergoes a one electron oxidation and reduction sequence as shown in equations 1.35-1.37. These types of reaction are, thus, frequently referred to as redox transfer reactions. Copper has also been shown to catalyse this reaction[14]. Further work has shown that both Fe^{II} and Fe^{III} and both Cu^{I} and Cu^{II} salts can also be used to catalyse the addition of tetrachloromethane and trichloromethane to

alkenes[15,16]. The general mechanism is shown in scheme 1.10.

Scheme 1.10 : Metal catalysed addition of tetrachloromethane to alkenes.

$$M^{n+} + CCl_4 \rightleftharpoons M^{(n+1)+} + CCl_3\bullet + Cl^- \quad (1.38)$$

$$M^{(n+1)+} + Cl^- \longrightarrow (MCl)^{n+} \quad (1.39)$$

$$CCl_3\bullet + CH_2{=}CHR \longrightarrow CCl_3CH_2\dot{C}HR \quad (1.40)$$

$$CCl_3CH_2\dot{C}HR + (MCl)^{n+} \longrightarrow CCl_3CH_2CHClR + M^{n+} \quad (1.41)$$

where M^{n+}=Cu^+ or Fe^{2+}.

The metal ion is observed to act as a chlorine atom transfer agent. In step 1.41, copper(I) chloride is more reactive than iron(III) chloride[17] and thus consequently it supresses telomerisation. In the case of trichloromethane, redox transfer catalysis leads to the addition of $CHCl_2\bullet$ as opposed to $CCl_3\bullet$ (scheme 1.11) as the metal ion is involved in chlorine atom transfer. This contrasts with analogous reactions proceeding by a radical chain mechanism.

Scheme 1.11 : Metal catalysed addition of trichloromethane to alkenes.

$$M^{n+} + CHCl_3 \longrightarrow (MCl)^{n+} + CHCl_2\bullet \quad (1.42)$$

$$CHCl_2\bullet + CH_2{=}CHR \longrightarrow Cl_2CHCH_2\dot{C}HR \quad (1.43)$$

$$Cl_2CHCH_2\dot{C}HR + (MCl)^{n+} \longrightarrow Cl_2CHCH_2CHClR + M^{n+} \quad (1.44)$$

where M^{n+}=Cu^+ or Fe^{2+}.

When redox transfer catalysed reactions were carried out in the presence of an amine, less vigorous reaction conditions were required. This observation was further investigated by Burton et al who noted that using a copper chloride-ethanolamine redox system resulted in the initiation of the addition of a variety of polyhaloalkanes to oct-1-ene with improved yields of adduct (Table 1.2)[18].

Table 1.2 : Effect of the presence and absence of ethanolamine on the CuCl catalysed addition of polyhaloalkanes to oct-1-ene[18].

Haloalkane	CuCl/$HOCH_2CH_2NH_2$		CuCl only	
	%yield	%conversion	%yield	%conversion
$CF_2BrCFClBr$ (I)	95	96	88	73
CF_2BrCF_2Br (II)	77	57	10	4
$CF_2ClCFCl_2$ (III)	62	45	0	0

The table shows that when the more reactive polyalkane (I) was used the copper chloride was not required. However, (II) and (III) were found to undergo an addition reaction only in the presence of both the copper salt and ethanolamine. Interestingly, it was observed that when the addition reaction of (I) was attempted in the presence of CuCl only, there was no reaction. Other experiments showed that the yield of adduct was independent of the oxidation state of copper. (Both CuCl and $CuCl_2.2H_2O$ gave a 62 % yield of adduct with $CF_2ClCFCl_2$). The other variable investigated was the amine used. The study showed that

equally good results could be obtained in the presence of either butylamine or ethanolamine, but both aniline and triethylamine were considerably less effective. It was concluded that as the addition of the less reactive haloalkanes will not take place in the absence of either copper salt or the amine, a complex of amine with copper ion is being formed :

$$Cu(amine)_nCl + CCl_4 \longrightarrow Cu(amine)_nCl_2 + CCl_3 \qquad (1.45)$$

This is not the only addition reaction which takes place in the presence of a copper salt and an added ligand. Another example is the addition of α-chloroesters to alkenes or dienes in the presence of bipyridyl or 1,10-phenanthroline and copper chloride leading to γ-chloroesters or unsaturated esters (equation 1.46)[19].

$$ClCH_2CO_2Me + RCH{=}CH_2 \xrightarrow[CuCl]{bipy} RCHClCH_2CH_2CO_2Me + RCH{=}CHCH_2CO_2Me \qquad (1.46)$$

where R=Ph, n-C_8H_{17} R=Ph, n-C_8H_{17} R=Ph

In summary, it can be concluded that the redox system has several advantages over traditional peroxide initiation. These are :

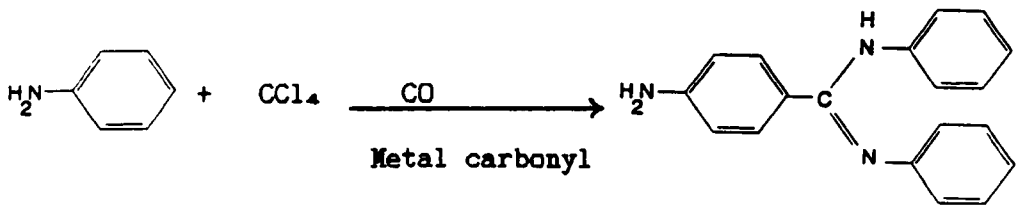
(i) Telomerisation is minimised, thereby increasing the yield of 1 : 1 adducts.

(ii) Reactions proceed with good yield without the necessity for a large excess of haloalkane.

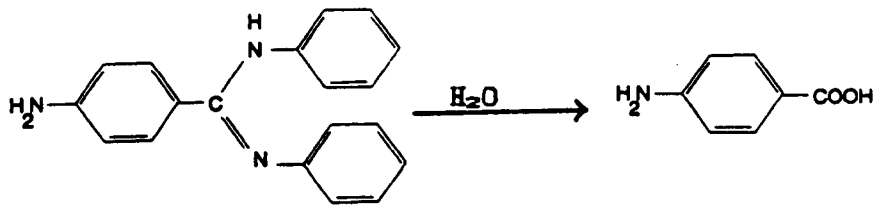
(iii) The reactions can be carried out under less vigorous conditions.

1.2.2 Metal carbonyls

Various metal carbonyls, such as $[Fe(CO)_5]$, $[Mo(CO)_6]$ and $[Cr(CO)_6]$ have been used in the addition of haloalkanes to alkenes. However, mononuclear carbonyls tend to produce mixtures of telomers whilst dinuclear carbonyls, such as $[Co_2(CO)_8]$, $[CpMo(CO)_3]_2$ and $[CpFe(CO)_2]_2$, were found to be more effective for producing 1 : 1 adducts[20]. Mononuclear metal carbonyls can, however, be used to advantage for some reactions, such as that between aniline and tetrachloromethane in the presence of carbon monoxide (equations 1.47 and 1.48)[21,22].



(1.47)



(1.48)

It was suggested that when a radical species is formed by the reaction of tetrachloromethane with the metal carbonyl, it causes the formation of a nitrogeneous radical. Migration of the radical centre to the ortho or para position of the aromatic ring was followed by reaction with $CCl_3M(CO)_n$ or CCl_4, and then with aniline to form the amidine. The subsequent hydrolysis of the amidine gives p-aminobenzoic acid in high yield.

Table 1.3 : Comparison of metal carbonyls as catalysts[21]

Catalyst	% Yield[a] of benzamidine hydrochloride
$[Mo(CO)_6]$	94.5
$[Cr(CO)_6]$	73.8
$[Co_2(CO)_8]$	86.8
$[CpMo(CO)_3]_2$	89.3

[a]yield was based on aniline charged.

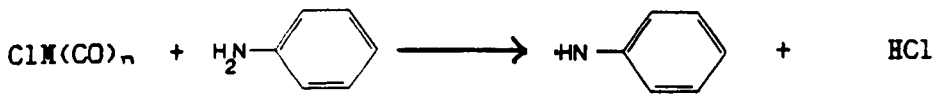
The results showed that $[Mo(CO)_6]$ was the most effective catalyst. It should be noted that this catalytic reaction is stereospecific so only the para-substituted amidine was detected. When the reaction was carried out under nitrogen the same products resulted. The mechanism suggested for this reaction (scheme 1.12) involves the formation of $CCl_3\bullet$ radicals. However, it is proposed that these remain attached to the metal by means of a covalent bond or a weaker interaction. The reason for this is that if the $CCl_3\bullet$ radicals were free, the reaction would not be selective and would give rise to a mixture of ortho, meta and para derivatives. The importance of the interaction of the radical species with the metal complex was further confirmed by carrying out the reaction using $[Fe(CO)_5]$, $[CpFe(CO)_2]_2$, CuO and benzoyl peroxide which are well known for generating $CCl_3\bullet$ radicals from tetrachloromethane. With these catalysts no amidine formation took place. It can be concluded that all these catalysts are effective at generating $CCl_3\bullet$ radicals and forming a radical-metal intermediate to a similar degree.

Scheme 1.12 : Mechanism of reaction for metal carbonyl catalysed addition of tetrachloromethane to aniline.

$$CCl_4 + [M(CO)_n]_2 \longrightarrow CCl_3M(CO)_n + ClM(CO)_n \quad (1.49)$$

or

$$CCl_4 + [M(CO)_n] \longrightarrow \begin{matrix} CCl_3 \\ M(CO)_n \\ Cl \end{matrix} \quad (1.50)$$



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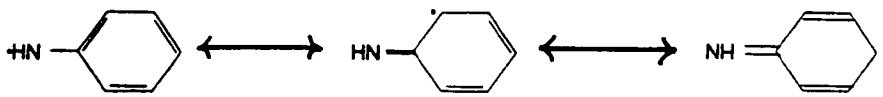

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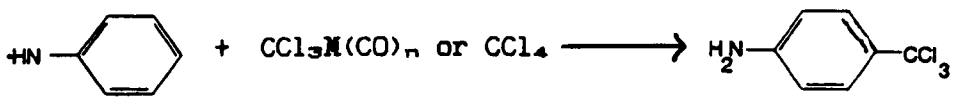

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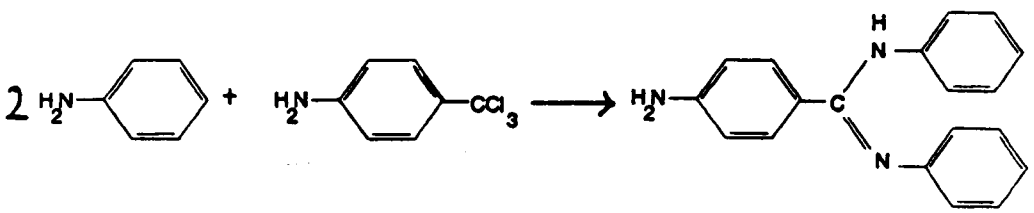


(1.54)

Dinuclear metal carbonyls are more effective catalysts for the addition reactions of haloalkanes to alkenes as they produce higher yields of the 1 : 1 adducts and thus, less telomerisation occurs. The effect of various dinuclear metal carbonyl species on the addition of tetrachloromethane to alkenes in the presence of carbon monoxide (equation 1.55)[23] is shown in Table 1.4[24].

$$RCH{=}CH_2 + CO + CCl_4 \longrightarrow \underset{\underset{COCl}{|}}{RCHCH_2CCl_3} + \underset{\underset{Cl}{|}}{RCHCH_2CCl_3} \qquad (1.55)$$

The three catalysts, $[Co_2(CO)_8]$ (IV), $[CpFe(CO)_2]_2$ (V), and $[CpMo(CO)_3]_2$ (VI), show similar activity. The mechanism proposed for this reaction is shown in scheme 1.13.

<u>Scheme 1.13 : Mechanism of addition reactions catalysed by dinuclear metal carbonyl complexes[24]</u>

$$[M(CO)_nCp]_2 + CCl_4 \longrightarrow ClM(CO)_nCp + CCl_3M(CO)_nCp \qquad (1.56)$$

$$CCl_3M(CO)_nCp + RCH{=}CH_2 \longrightarrow CCl_3CH_2\underset{\underset{R}{|}}{C}HM(CO)_nCp \qquad (1.57)$$

$$CCl_3CH_2\underset{\underset{R}{|}}{C}HM(CO)_nCp + CCl_4 \longrightarrow RCHClCH_2CCl_3 + CCl_3M(CO)_nCp \qquad (1.58)$$

$$CCl_3CH_2\underset{\underset{R}{|}}{C}HM(CO)_nCp + CO \longrightarrow CCl_3CH_2\underset{\underset{R}{|}}{C}H(CO)M(CO)_nCp \qquad (1.59)$$

$$CCl_3CH_2\underset{\underset{R}{|}}{C}H(CO)M(CO)_nCp + CCl_4 \rightarrow \underset{\underset{COCl}{|}}{RCHCH_2CCl_3} + CCl_3M(CO)_nCp \qquad (1.60)$$

In more recent work the addition of tetrachloromethane to alkenes has been studied in the presence of $[CpMo(CO)_3]_2$[25]. This study shows that much milder conditions can be employed for these reactions. The mechanism of the reaction was studied by kinetic and spectroscopic means and the alternative scheme shown in scheme 1.14 was advanced.

Table 1.4 : Reaction between alkenes, CCl_4 and CO catalysed by $[Co_2(CO)_8]$(IV), $[CpFe(CO)_2]_2$(V) and $[CpMo(CO)_3]_2$(VI)[24]

ALKENE	CATALYST	PRODUCTS $R\text{-}\underset{\underset{COCl}{\vert}}{C}HCH_2CCl_3$ + $R\text{-}\underset{\underset{Cl}{\vert}}{C}HCH_2CCl_3$		YIELD (%)		TEMPERATURE °C
		(1)	(2)	(1)	(2)	
PROP-1-ENE	IV	$Cl_3CCH_2CH(CH_3)COCl$	(1)	10	5	83
	V			18	14	118
	VI	$Cl_3CCH_2CHClCH_3$	(2)	15	15	95
BUT-1-ENE	IV	$Cl_3CCH_2CH(C_2H_5)COCl$	(1)	15	16	160
	V			19	10	90
	VI	$Cl_3CCH_2CH(C_2H_5)Cl$	(2)	13	8	93
OCT-1-ENE	IV	$Cl_3CCH_2CH(C_6H_{13})COCl$	(1)	35	36	130
	V	$Cl_3CCH_2CH(C_6H_{13})Cl$	(2)	41	21	118

Scheme 1.14 : Alternative mechanism of addition catalysed by $[CpMo(CO)_3]_2$[25]

$$[CpMo(CO)_3]_2 + CCl_4 \longrightarrow [CpMo(CO)_3Cl] + \{CpMo(CO)_3^{\bullet}\}\{CCl_3^{\bullet}\} \quad (1.61)$$

$$\{CCl_3^{\bullet}\} + RCH{=}CH_2 \longrightarrow \{R\dot{C}HCH_2CCl_3\} \quad (1.62)$$

$$[CpMo(CO)_3Cl] + \{R\dot{C}HCH_2CCl_3\} \rightarrow \{CpMo(CO)_3^{\bullet}\} + RCHClCH_2CCl_3 \quad (1.63)$$

$$2\{CpMo(CO)_3^{\bullet}\} \longrightarrow [CpMo(CO)_3]_2 \quad (1.64)$$

These workers also carried out a comparative study of the effect of various carbonyl complexes on the addition of tetrachloromethane to alkenes (Table 1.5).

Table 1.5 : Comparison of the effect of carbonyl complexes on the addition of tetrachloromethane to alkenes.

Metal carbonyl	% Yield at temperature T		
	T=80°C	T=100°C	T=120°C
$[CpMo(CO)_3]_2$	19.6	36.5	47.5
$[CpFe(CO)_2]_2$	8.2	12.3	50.3
$[Co_2(CO)_8]$	3.9	4.8	4.9
$[Cr(CO)_6]$	6.4	9.2	20.6
$[Mo(CO)_6]$	12.1	23.6	23.2
$[(C_{10}H_8)Cr(CO)_3]$	12.4	11.6	11.7

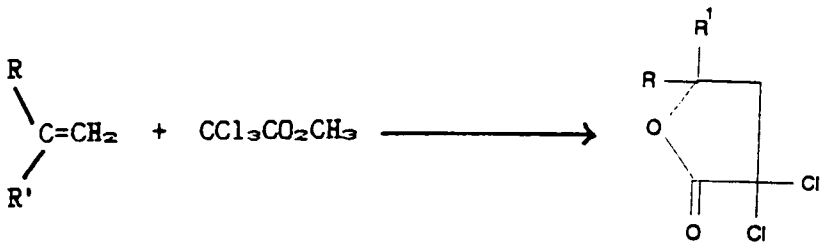
These results show that the dinuclear catalysts are more effective then mononuclear complexes, particularly at high temperatures.

Other addition reactions are known to be catalysed by dinuclear metal carbonyl complexes[26]. The addition of

methyl trichloroacetate to alkenes (equation 1.65) has been observed to be catalysed by complexes (IV), (V) and (VI).

$$CH_3(CH_2)_3CH{=}CH_2 \;+\; CCl_3CO_2CH_3 \longrightarrow CH_3(CH_2)_3\underset{\underset{Cl}{|}}{C}HCH_2CCl_2CO_2CH_3 \qquad (1.65)$$

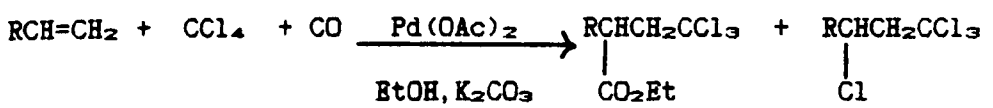
However, in the case of (V) and (VI), lactone formation is also observed (equation 1.66). Lactone formation will be fully explored in section 1.3.



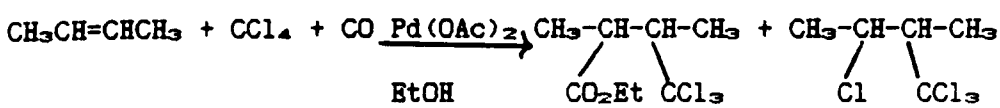
(1.66)

1.2.3 Other catalysts

Palladium catalysts have been reported to exhibit excellent catalytic ability for carbonylation reactions involving organic halides (equations 1.67 and 1.68)[27].



(1.67)

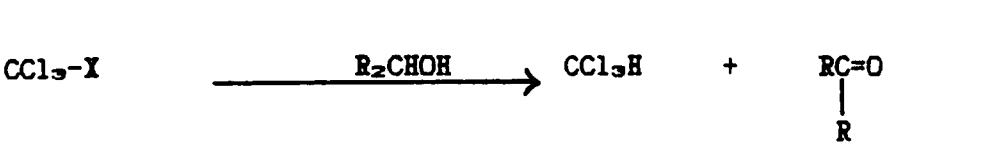


(1.68)

P_{CO}=40atm, 5 days

From cis-but-2-ene	36 %	23 %
trans-but-2-ene	33 %	28 %

The exact mechanism of these reactions is currently unknown. Palladium complexes have also been reported to catalyse other reactions of polyhaloalkanes (equations 1.69 and 1.70)[28].

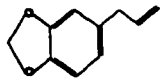


(1.69)

(1.70)

The addition of tetrachloromethane, bromotrichloromethane and methyl trichloroacetate to various alkenes was studied using a catalytic system consisting of palladium acetate, triphenylphosphine and potassium or sodium carbonate (equation 1.71)[29,30].

Table 1.6 : Addition reaction of polyhaloalkanes to alkenes and functionalised alkenes in the presence of $Pd(OAc)_2$.[28]

ALKENE	POLY-HALOALKANE	PRODUCT	YIELD (%)	CONDITIONS TEMP (°C)	TIME (hr)	ATMOSPHERE
$n\text{-}C_8H_{17}CH{=}CH_2$	CCl_4	$C_8H_{17}\underset{\underset{Cl}{\vert}}{C}HCH_2CCl_3$	77	100	5	Ar
			(54)	100	3	Ar
			(60)	80	3	CO
			(20)	40	5	CO
			90	20	120	CO
$n\text{-}C_8H_{17}CH{=}CH_2$	$BrCCl_3$	$C_8H_{17}\underset{\underset{Br}{\vert}}{C}HCH_2CCl_3$	(88)	40	5	Ar
			90	100	3.5	Ar
$CCl_3CO_2CH_3$	$CCl_3CO_2CH_3$	$C_8H_{17}\underset{\underset{Cl}{\vert}}{C}HCH_2CCl_2CO_2CH_3$	64	100	15	Ar
			62	80	7	CO
$CH_2{=}CHC_8H_{16}CO_2CH_3$	CCl_4	$CCl_3CH_2\underset{\underset{Cl}{\vert}}{C}HC_8H_{16}CO_2CH_3$	58	80	5	CO
	CCl_4		39	110	38	CO
	$BrCCl_3$		52	80	9	CO

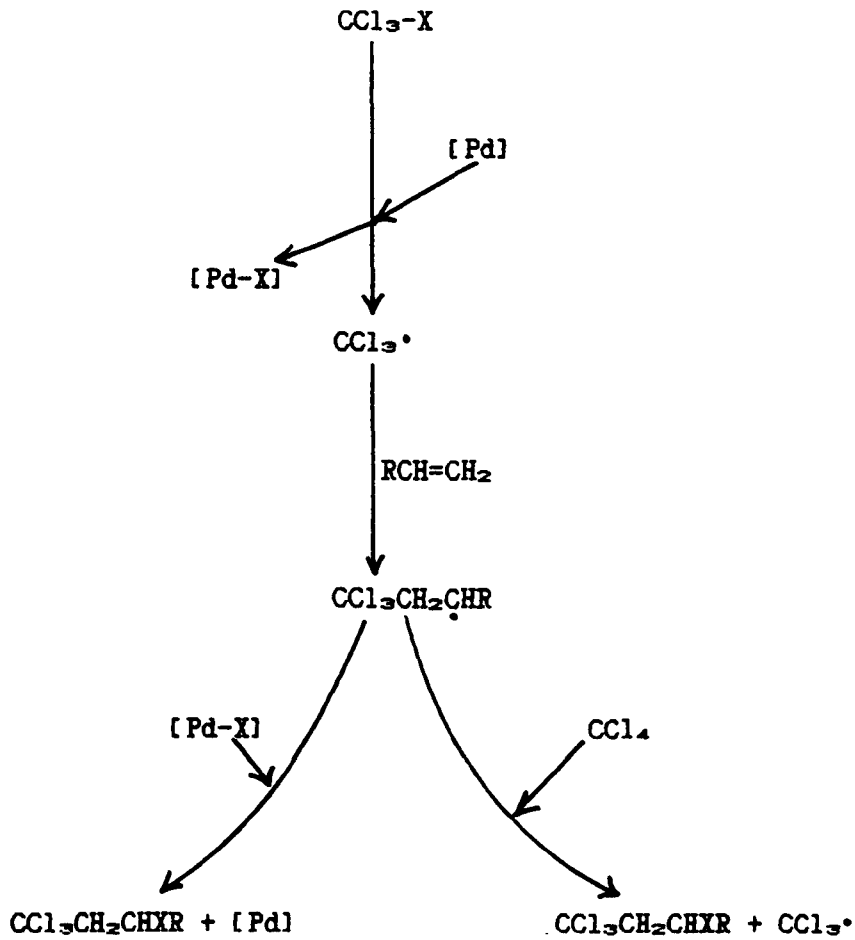
$$RCH{=}CH_2 \;+\; XCCl_2Y \xrightarrow{Pd(OAc)_2} RCH(X)CH_2CCl_2 \qquad (1.71)$$

Table 1.6 shows that high yields of addition products are obtained when tetrachloromethane and bromotrichloromethane are reacted with dec-1-ene. It was observed that the reactions were influenced by the presence of base. Higher yields of products were obtained when the concentration of base was increased. However, bases such as pyridine or triethylamine could not be used as salt formation resulted. An optimised concentration of triphenylphosphine was also determined, since the reaction was inhibited at high concentrations, whilst in its absence no product could be detected. The reactions were observed to proceed more readily under CO as this suppressed the formation of the by-products. In the addition of methyl trichloroacetate to dec-1-ene only the ester was formed with no lactone being observed. This contrasts with reactions involving dinuclear metal carbonyls discussed above. As well as the reactions shown in the table, the reactions between tetrachloromethane or bromotrichloromethane and cyclohexene were carried out. In both cases, these showed the same results as uncatalysed reactions, forming almost equimolar mixtures of the trans and cis-adducts. This contrasts with the behaviour of $[RuCl_2(PPh_3)_3]$ discussed later.

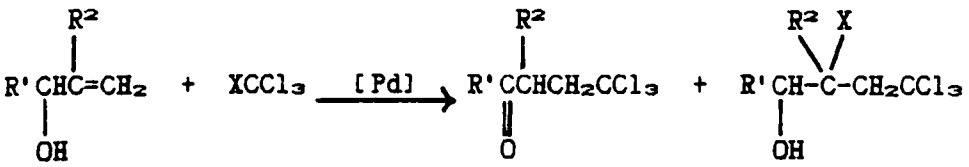
The mechanism proposed for the catalysis of these additions involves the formation of a Pd(0) species (scheme 1.15). Tayin and Akl reported that the complex $[Pd(PPh_3)_4]$ reacts with tetrachloromethane to produce $[PdCl_2(PPh_3)_3]$, confirming the oxidation of Pd(0) with this reagent[31]. This would explain the importance of the base and carbon monoxide as it is known that these reduce the Pd(II) species to the zero-valent state[32]. Scheme 1.15 shows one electron transfer from

Pd(0) to polyhaloalkanes producing a trichloromethyl radical which can then add to the alkene forming an alkyl radical. This reactive intermediate can then either abstract a chlorine atom from tetrachloromethane initiating the radical chain reaction or react with the Pd-Cl species causing the palladium catalyst to be regenerated.

Scheme 1.15 : Mechanism of reaction for the addition of tetrachloromethane to alkenes catalysed by $[Pd(PPh_3)_4]$.



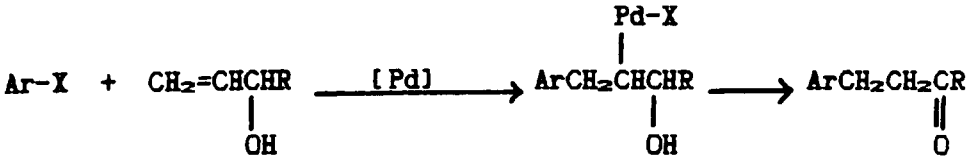
Earlier work by the same authors has shown that the palladium catalysed reaction of tetrachloromethane or bromotrichloromethane with allylalcohols produces γ-trichloroketones (equation 1.72)[33].



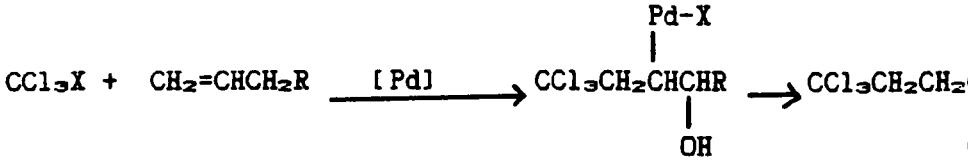
(1.72)

X=Cl, Br

These types of reaction were carried out in the presence of $Pd(OAc)_2$, tri-o-tolylphosphine and potassium carbonate at 110°C. The reaction of bromotrichloromethane with hepten-3-ol was investigated further using other catalysts, such as $[RuCl_2(PPh_3)_3]$ and CuCl, known to display good catalytic activity in related reactions. In the case of the former only the 1 : 1 addition product was formed, while in the second case, no products resulted. Therefore it appears that palladium is a specific catalyst for ketone formation. The mechanism of this reaction is believed to be analogous to the arylhalide system (equation 1.73), whereby an σ-alkylpalladium complex is formed as an intermediate which then undergoes β-hydride elimination (equation 1.74).



(1.73)



(1.74)

Another example of the many catalysts known to effect addition is $[NiCl_2(PPh_3)_2]$[34]. This is an interesting case as the nickel complex is able to catalyse the addition of dichloromethane to alkenes (equation 1.75) far more effectively than any of the other commonly used catalysts, such as metal carbonyls, palladium salts or ruthenium catalysts (Table 1.7).

$$CH_2Cl_2 + RCH{=}CH_2 \xrightarrow{[NiCl_2(PPh_3)_2]} RCH_2ClCH_2Cl \qquad (1.75)$$

Table 1.7 : Addition of dichloromethane to hex-1-ene catalysed by group VIII metal compounds[34].

Catalyst	% Yield of adduct
$[NiCl_2(PPh_3)_2]$	30
$[RuCl_2(PPh_3)_3]$	14
$[PdCl_2(PPh_3)_2]$	9
$[RhCl(PPh_3)_3]$	trace
$[CoCl_2(PPh_3)_2]$	trace

Additions of dichloromethane to other alkenes has also been observed (Table 1.8). The mechanism proposed for this reaction is the same as that proposed for $[RuCl_2(PPh_3)_3]$ catalysis of CCl_4-$RCH{=}CH_2$ reactions which will be discussed in the next section.

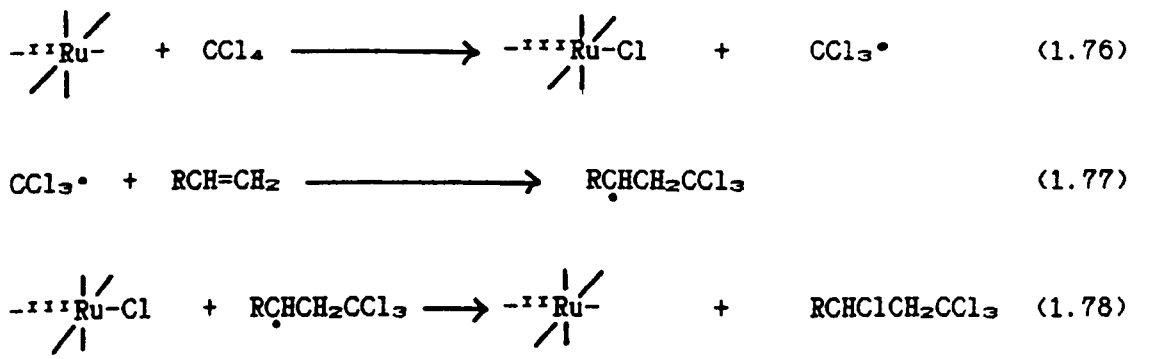
Table 1.8 : Addition of CH_2CH_2 to alkenes in the presence of $[NiCl_2(PPh_3)_2]$[34]

Alkene	Product	% Yield
Pent-1-ene	$ClCH_2CH_2CHClC_3H_7$	19
Hex-1-ene	$ClCH_2CH_2CHClC_4H_9$	18
Oct-1-ene	$ClCH_2CH_2CHCl(CH_2)_5CH_3$	13
4-Methylpent-1-ene	$ClCH_2CH_2CHClC_6H_{13}$	7

1.2.4 Catalysis by $[RuCl_2(PPh_3)_3]$

Early work showed that in the presence of this catalyst the addition of tetrachloromethane or trichloromethane to alkenes proceeded under mild conditions and gave 1 : 1 adducts in yields varying from 66-100 %[35]. These good yields indicatate that telomerisation is not taking place. The mechanism proposed is analogous to that for metal salts (scheme 1.16) :

Scheme 1.16 : Mechanism of catalysis by $[RuCl_2(PPh_3)_3]$ of the addition of tetrachloromethane to alkenes[35].



Evidence for such a homolytic mechanism was solely based on the fact that the reaction was completely inhibited by adding a small quantity of galvinoyl, a free radical inhibitor, to the reaction mixture. $[RuCl_2(PPh_3)_3]$ also effects a 1 : 1 addition between alkenes and polychloroacetic acid.

When methyl dichloroacetate was reacted with oct-1-ene in the presence of $[RuCl_2(PPh_3)_3]$ (equation 1.79) the only product was methyl-2,4-dichlorodecanoate in a 95 % yield. However, when the same reaction was carried out in the presence of a peroxide (equation 1.80) the main product was methyl-2,2-dichlorodecanoate. The suggested mechanism is entirely analogous to that outlined in scheme 1.16.

$$CHCl_2CO_2CH_3 + C_6H_{13}CH{=}CH_2 \xrightarrow{[RuCl_2(PPh_3)_3]} C_6H_{13}CHClCH_2CHClCO_2CH_3 \quad (1.79)$$

$$\xrightarrow{\text{peroxide}} C_6H_{13}CH_2CH_2CCl_2CO_2CH_3 \quad (1.80)$$

More detailed studies have shown that $[RuCl_2(PPh_3)_3]$ does not act merely as a redox catalyst. Bland, Davis, and Durrant have proposed the mechanism shown in scheme 1.17[36]. This involves dissociation of $[RuCl_2(PPh_3)_3]$ (equation 1.81), forming the four coordinate reactive intermediate $[RuCl_2(PPh_3)_2]$ which in turn reacts with CCl_4 giving rise to radical pair formation. Reaction with the alkene produces a new radical pair (equation 1.83), which collapses to the product and $[RuCl_2(PPh_3)_2]$ (equation 1.84).

<u>Scheme 1.17 : Mechanism of addition of tetrachloromethane to alkenes in the presence of $[RuCl_2(PPh_3)_3]$[36]</u>

$$[RuCl_2(PPh_3)_3] \rightleftharpoons [RuCl_2(PPh_3)_2] + PPh_3 \quad (1.81)$$

$$[RuCl_2(PPh_3)_2] + CCl_4 \rightleftharpoons \{RuCl_3(PPh_3)_2^{\bullet}\}\{CCl_3^{\bullet}\} \quad (1.82)$$

$$\{RuCl_3(PPh_3)_2^{\bullet}\}\{CCl_3^{\bullet}\} + RCH{=}CH_2 \rightarrow \{RuCl_3(PPh_3)_2^{\bullet}\}\{RCHCH_2CCl_3^{\bullet}\} \quad (1.83)$$

$$\{RuCl_3(PPh_3)_2^{\bullet}\}\{RCHCH_2CCl_3^{\bullet}\} \longrightarrow [RuCl_2(PPh_3)_2^{\bullet}] + RCHClCH_2CCl_3 \quad (1.84)$$

The mechanism is derived from kinetic studies and an examination of reaction intermediates. The fact that a radical pair is formed rather than an intermediate involving a Ru-CCl_3 covalent bond was confirmed by performing a "cross-over" experiment in which oct-1-ene was treated with an equimolar mixture of tetrabromomethane and tetrachloromethane in the presence of $[RuCl_2(PPh_3)_3]$. The "cross-over" products 1,1,1-tribromo-3-chlorononane (TBCN), 1,1,1-trichloro-3-bromononane (TCBN), as well as 1,1,1,3-tetrabromononane (TBN), and

1,1,1,3-tetrachlorononane (TCN) were observed. A non-radical addition involving oxidative addition of CX_4 to the metal centre, followed by alkene coordination, migratory insertion and reductive elimination of the product should not produce cross-over products. A comparison of the use of $[RuCl_2(PPh_3)_3]$ and $[RuCl_2(PPh_3)_4]$ is given in Table 1.9[35]. This table shows that $[RuCl_2(PPh_3)_3]$ is a better catalyst than $[RuCl_2(PPh_3)_4]$ which suggests that the coordination number of the complex is important. Presumably $[RuCl_2(PPh_3)_4]$ is a precursor of its activitive form.

The preparation of chloro-α,ω-dioic acids has been successfully achieved by the addition of tetrachloromethane to alk-1-ene-ω-carboxylic acid esters in the presence of $[RuCl_2(PPh_3)_3]$ followed by dehydrochlorination and hydrolysis of the addition product (equation 1.85 and 86)[37].

$$CH_2CR(CH_2)_nCO_2R' + CCl_4 \xrightarrow{[RuCl_2(PPh_3)_3]} CCl_3CH_2CClR(CH_2)_nCO_2R' \quad (1.85)$$

$$CCl_3CH_2CClR(CH_2)_nCO_2R' \xrightarrow[P_2O_5]{\text{Fuming } HNO_3} HO_2CCH_2CClR(CH_2)_nCO_2H \quad (1.86)$$

where (a) R=H, R'=Me, n=0

(b) R=R'=Me, n=0

(c) R=H, R'=Me, n=1

(d) R=R'=H, n=8

It has also been shown that $[RuCl_2(PPh_3)_3]$ will catalyse the addition of trichloroacetyl chloride to alkenes, which produces α,α,γ-trichloro-substituted acid chloride[38]. This is a useful compound as it can be readily hydrolysed to α,γ-polychloroalkenoic acids (equations 1.87 and 1.88) which are used as lubricating oil additives

Table 1.9 : The Addition of $CHCl_3$ and CCl_4 to terminal alkenes in the presence of $[RuCl_2(PPh_3)_3]$ (VII) and $[RuCl_2(PPh_3)_4]$ (VIII)[35]

CATYLYST	ALKENE	HALOALKENE	PRODUCT	% CONVERSION	% YIELD
VII	Hex-1-ene	CCl_4	$Cl_3CCH_2CHCl(CH_2)_3CH_3$	90	88
VIII	Hex-1-ene	CCl_4	$Cl_3CCH_2CHCl(CH_2)_3CH_3$	42	88
VII	Hept-1-ene	CCl_4	$Cl_3CCH_2CHCl(CH_2)_4CH_3$	68	99
VIII	Hept-1-ene	CCl_4	$Cl_3CCH_2CHCl(CH_2)_4CH_3$	45	81
VII	Oct-1-ene	CCl_4	$Cl_3CCH_2CHCl(CH_2)_5CH_3$	76	97
VIII	Oct-1-ene	CCl_4	$Cl_3CCH_2CHCl(CH_2)_5CH_3$	60	100
VII	Oct-1-ene	$CHCl_3$	$Cl_2CHCH_2CHCl(CH_2)_5CH_3$	75	67
VIII	Oct-1-ene	$CHCl_3$	$Cl_2CHCH_2CHCl(CH_2)_5CH_3$	71	66
VII	Non-1-ene	CCl_4	$Cl_3CCH_2CHCl(CH_2)_6CH_3$	80	95
VIII	Non-1-ene	CCl_4	$Cl_3CCH_2CHCl(CH_2)_6CH_3$	48	92

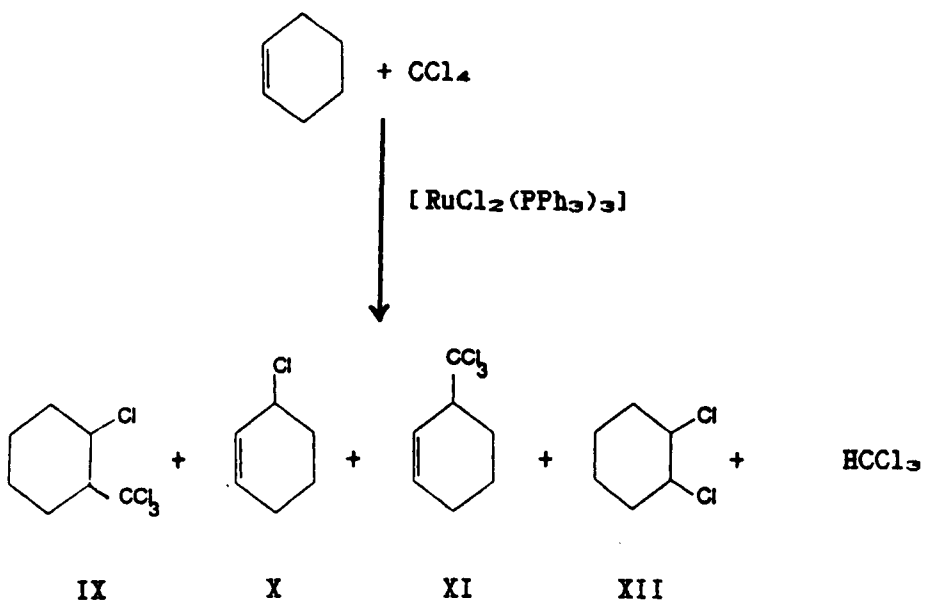
and as activators for bleaching textiles with chlorites[39,40]. Also, their structure is related to antibiotic amino-γ-polychloroalkenic acids and they have potential in this area[41].

$$RCH{=}CHR' + CCl_3COCl \xrightarrow{[RuCl_2(PPh_3)_3]} \underset{Cl}{RCH}-\underset{CCl_2COCl}{CHR'} \qquad (1.87)$$

$$\underset{Cl}{RCH}-\underset{CCl_2COCl}{CHR'} + H_2O \longrightarrow \underset{Cl}{RCH}-\underset{CCl_2COOH}{CHR'} \qquad (1.88)$$

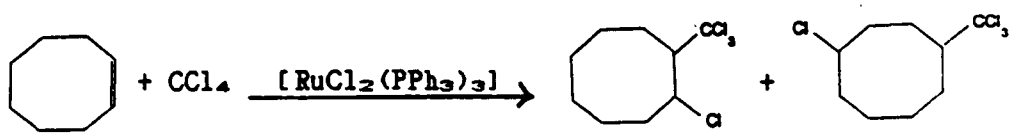
Although $[RuCl_2(PPh_3)_3]$ does not catalyse the addition of trichloroacetic acid esters to form 4-alkyl-2,2-dichloro-γ-butyrolactone, as does $[CpMo(CO)_3]_2$ and $[CpFe(CO)_2]_2$, it does catalyse the addition of dichloroacetic acids to form lactones[42]. This will be discussed more fully in section 1.3.

Dichlorotris(triphenylphosphine)ruthenium(II) is also active for the addition of haloalkanes to cycloalkenes (equation 1.89)[43].



(1.89)

The reaction is highly stereospecific, the major product being 1-trichloromethyl-2-chlorocyclohexane (IX) in a 77 % yield with a trans : cis ratio of 96 : 4. This contrasts with the 50 : 50 ratio obtained with peroxide initiators and palladium catalysts. However, the studies reported in this thesis have shown that this sterospecificity is very dependent on the reaction conditions (Chapter 2). In this reaction, the other products formed were 3-chloro-cyclohexene (X) (trace amount), 3-trichlorocyclohexene (XI) (trace amount), 1,2-dichlorocyclohexane (XII) (6 %) and trichloromethane (25 %). This result shows that this catalytic route is more effective than the peroxide initiated reaction as the yield of IX is 10 % higher. It has been shown that $[RuCl_2(PPh_3)_3]$ also effectively catalyses the addition of tetrachloromethane to cyclooctene (equation 1.90)[44].



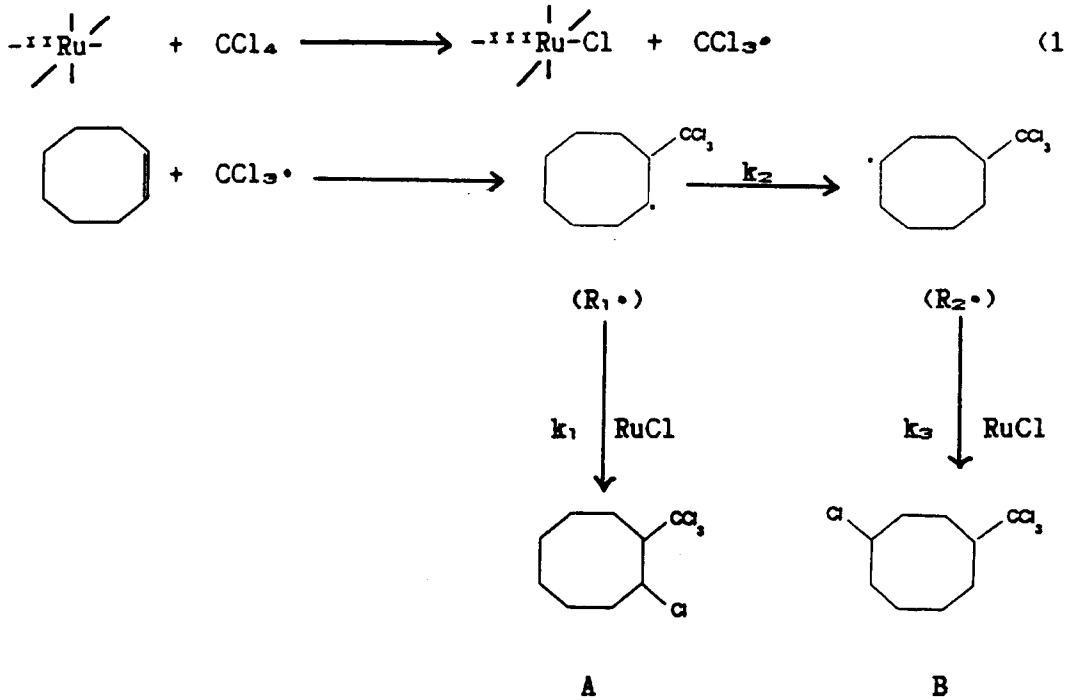
(1.90)

cis-cyclooctene 25 % 75 %

A B

When this reaction is initiated, either photochemically or thermally, 1-chloro-4-(trichloromethyl)cyclooctane (B) is observed with only trace amounts of 1-chloro-2-(trichloromethyl)cyclooctane (A). It was observed that the ratio of A : B depended on the concentration of $[RuCl_2(PPh_3)_3]$. This ratio increased with greater concentrations of $[RuCl_2(PPh_3)_3]$. The mechanism of this catalyst is explained by scheme 1.18.

Scheme 1.18 : Mechanism of the addition of tetrachloromethane to cyclooctene in the presence of $[RuCl_2(PPh_3)_3]$



The rate expressions for the formation of products A and B are :

$$d[A]/dt = k_1[R_1\bullet][Ru^{III}Cl] \quad (1.94)$$

$$d[B]/dt = k_3[R_2\bullet][Ru^{III}Cl] \quad (1.95)$$

The steady state approximation can be applied to the intermediate R_2

$$d[R_2]/dt = k_2[R_1\bullet] - k_3[R_2\bullet][Ru^{III}Cl] = 0 \quad (1.96)$$

therefore, $k_2[R_1\bullet] = k_3[R_2\bullet][Ru^{III}Cl]$ (1.97)

so then, $d[B]/dt = k_2[R_1\bullet]$ (1.98)

From equations 1.94 and 1.98 it can be seen that

$$[A]/[B] = (k_1/k_2)C[RuCl_2(PPh_3)_3] \quad (1.99)$$

where c is a proportionality constant. Equation 1.99 is in agreement with the findings that the ratio of product concentrations is related to the initial concentration of the catalyst.

$[RuCl_2(PPh_3)_3]$ also catalyses additions to dienes. The reactions studied involved the addition of tetrachloromethane to conjugated 1,3-dienes such as buta-1,3-diene, isoprene, cyclohexa-1,3-diene and cycloocta-1,3-diene[45]. This resulted in the formation of the corresponding 1,4-addition products in very good yields as indicated in Table 1.10. When the addition to isoprene was carried out, it was found that the reaction was very highly regioselective to produce 1,1,1,5-tetrachloro-3-methylpent-3-ene only (equations 1.100 and 1.101)

$$CH_2{=}C(CH_3)CH{=}CH_2 + CCl_4 \xrightarrow{[RuCl_2(PPh_3)_3]} CCl_3CH_2C(CH_3){=}CHCCH_2Cl \quad (1.100)$$

$$\not\longrightarrow ClCH_2C(CH_3){=}CHCH_2CCl_3 \quad (1.101)$$

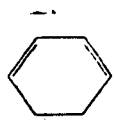
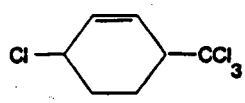
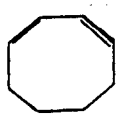
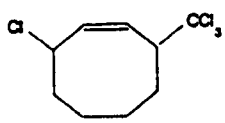
When these reactions were carried out in the presence of peroxide in place of $[RuCl_2(PPh_3)_3]$, they resulted in undistallable viscous materials and the yields of the expected 1 : 1 adducts never exceeded 5 %.

Recently work has been carried out on the addition of tetrachloromethane to a range of 1,ω-dienes in the presence of $[RuCl_2(PPh_3)_3]$ and the less frequently used catalyst $[ReCl_3(PPh_3)_2(CH_3CN)]$[46]. The rhenium complex is not quite as effective as $[RuCl_2(PPh_3)_3]$ for additions of tetrachloromethane to alkenes. This is shown in the case of tetrachloromethane to cyclohexene, the yield of adduct being 20 % and the trans : cis product ratio being identical to that obtained from dibenzoyl peroxide initiated reactions. Thus this complex is believed to behave as simple radical chain initiator, but with the additional factor of acetonitrile ligand dissociation influencing the reaction (equation 1.102)

$$[ReCl_3(PPh_3)_2(CH_3CN)] \rightleftharpoons [ReCl_3(PPh_3)_2] + CH_3CN \quad (1.102)$$

However, when $[RuCl_2(PPh_3)_3]$ and $[ReCl_3(PPh_3)_2(CH_3CN)]$ catalysed the addition of tetrachloromethane to a range of 1,ω-dienes, the latter was found to be an efficient catalyst (Table 1.11), requiring shorter reaction times then the former, but producing similar yields of adducts.

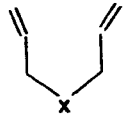
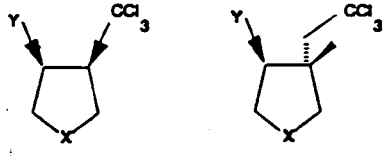
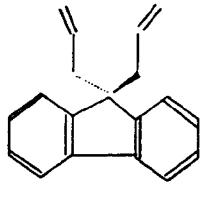
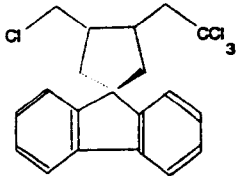
Table 1.10 : Addition reaction of tetrachloromethane to conjugated 1,3-dienes in the presence of $[RuCl_2(PPh_3)_3]$[a] [45]

Diene	Product	Yield[b] (%)	Time (hr)
$CH_2=CHCH=CH_2$	$ClCH_2CH=CHCH_2CCl_3$	86	4
$CH_3CH=CHCH=CH_2$	$CH_3CHClCH=CHCH_2CCl_3$	82	5
$CH_2=C(CH_3)CH=CH_2$	$CCl_3CH_2C(CH_3)=CHCH_2Cl$	85	5
		81[c]	8
		83	9

[a]The addition reactions were carried out at 80°C in a steel vessel using a 1 : 3 : 0.002 mixture of a diene, CCl_4 and the ruthenium (II) complex.

[b]Yields were isolated, except [c] which was determined by GC.

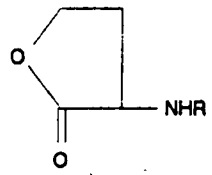
Table 1.11 : Addition of CCl_4 and $BrCCl_3$ to 1,6 - dienes catalysed by metal complexes $RuCl_2(PPh_3)_3$ (VII) and $[ReCl_3(PPh_3)_2(MeCN)]$ (VIIB)[46]

CATALYST	SUBSTRATE	PRODUCTS	YIELD(%)	PRODUCT cis : trans	TIME (hrs)
VII			86.5	-	16
VIIB	$X=C(CO_2Et)_2$	$Y=Cl$	74	5 : 1	2
VII	$X=C(COPh)_2$	$Y=Cl$	84	3.2 : 1	30
VIIB			73	4.2 : 1	2
VII	X=NCOMe	Y=Cl	77	6.1 : 1	8
			64	6.1 : 1	2
VIIB			79	4.2 : 1	10

1.3 Catalysed addition reactions resulting in lactone formation

1.3.1 Background

The usefulness of γ-butyrolactones and their derivatives is only beginning to emerge.



α-Alkylamino-γ-butyrolactones (R is a linear or branched alkyl radical containing 3 to 5 atoms) are used for treating alcohol dependance and show some important advantages over those drugs currently being used[47]. These are :

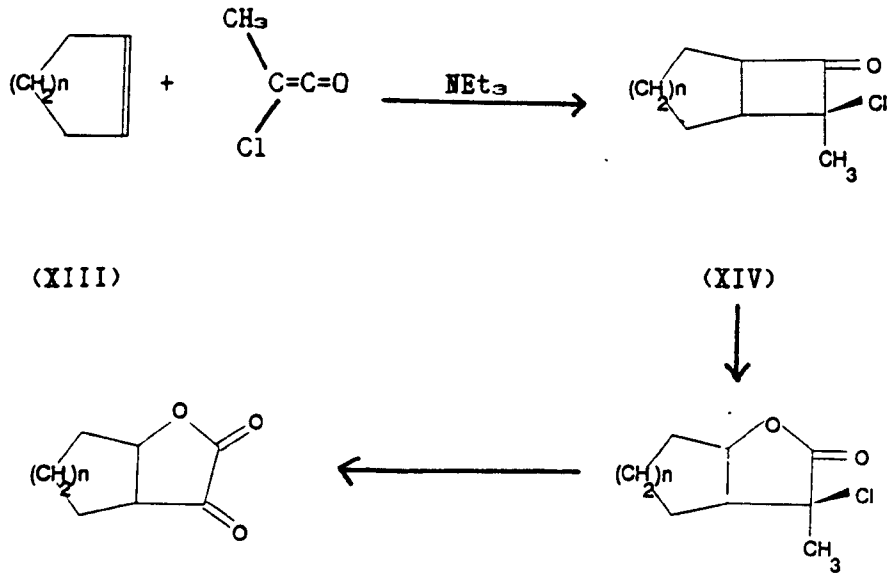
(i) They do not cause dangerous effects derived from association of the drug with the alcohol, as are shown by other preparations.

(ii) Their effectiveness lasts a long time.

(iii)They do not have convulsant effects.

The α-methylene-γ-lactones have also been found to be biologically active[48] and many act as antitumour agents[49,50]. Consequently, recent research has been directed towards the development of new synthetic routes for molecules of this type. There are many synthetic methods for the preparation of these compounds[51].

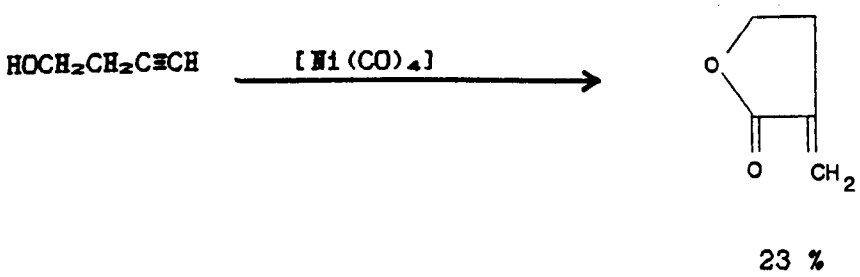
Scheme 1.19 : Preparation of α-methylene lactone



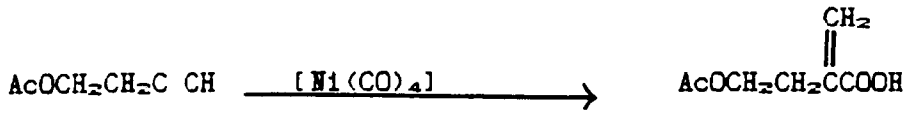
(1.103)

The ketene cycloaddition shown in scheme 1.19 is highly stereoselective as only one chloroketone is isolated. Subsequent Bayer-Villiger oxidation of the cyclobutanone (XIV) leads to the lactone formation (equation 1.104)[52]. The α-methylene lactone (XVI) was obtained after base catalysed dehydrochlorination.

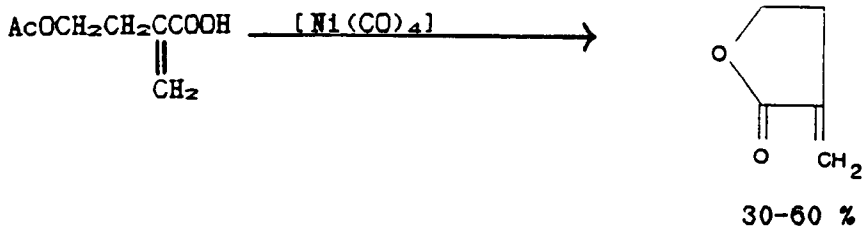
Other methods include reactions catalysed by $[Ni(CO)_4]$ (equations 1.106-1.109).



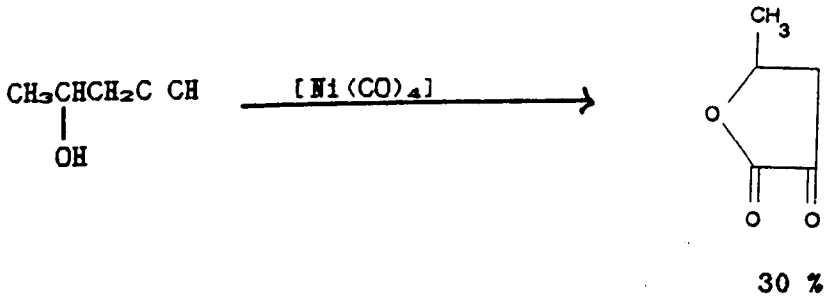
(1.106)



(1.107)



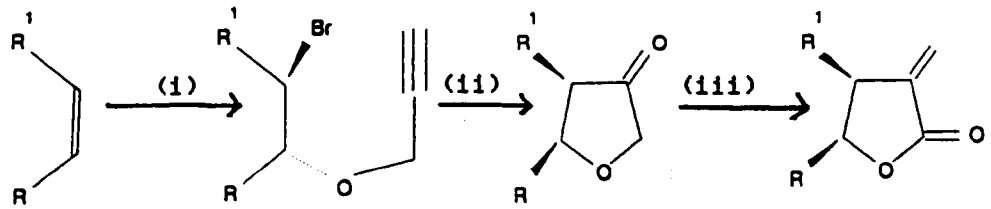
(1.108)



(1.109)

However, as can be seen these do not lead to particularly good yields. A more effective method involved a radical cyclisation route (scheme 1.20)[53]. Yields of these reactions are shown in Table 1.12.

Scheme 1.20 : α-methylene lactone preparation by radical cyclisation



(1.110)

XVII XVIII XIX XX

Reagents: (i) N-bromosuccinimide, HC CCH2OH

(ii) Bu_3^nSnCl, $NaCNBH_3$, Bu^tOH, Azobis(isobutylnitrile) (catalytic quantity) 5-7 hours.

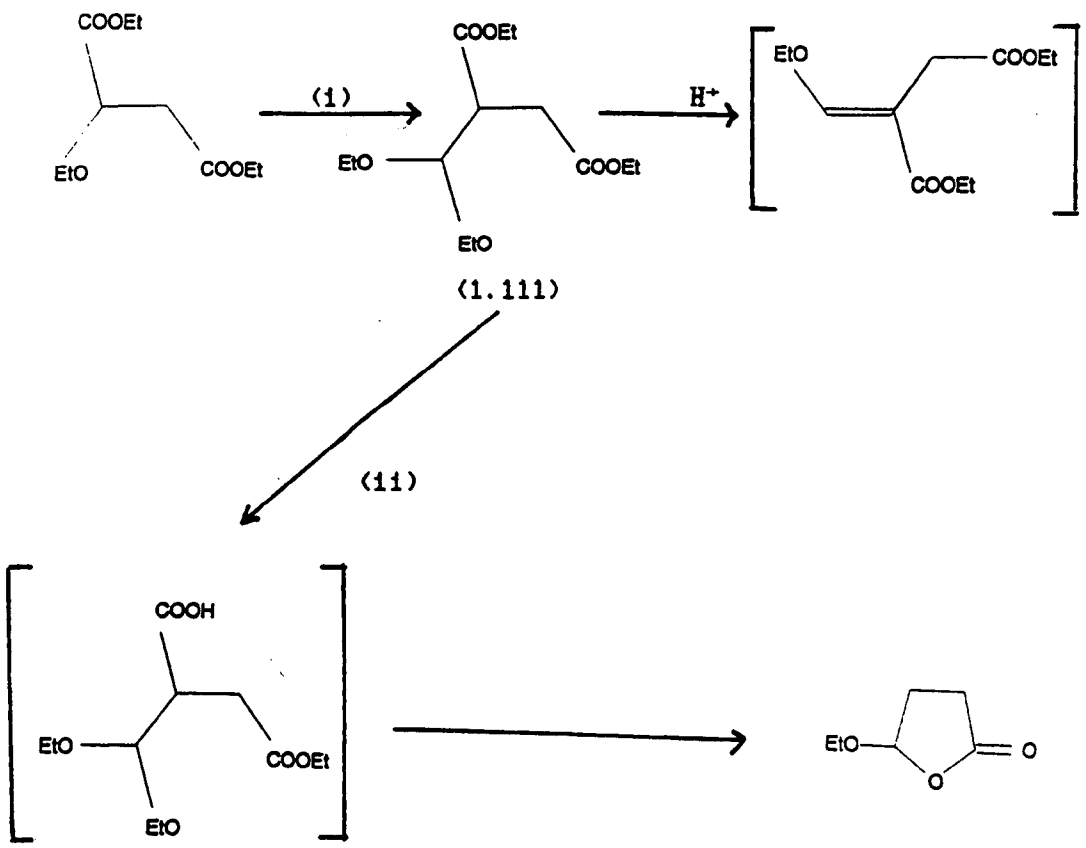
(iii) Pyridinium dichromate, dimethylformamide.

Table 1.12 : Quantification of yields of lactones XIX and XX

Substituent	% Yield XIX	% Yield XX
$R^1, R^2 = -(CH_2)_4-$	96	60
$R^1, R^2 = -(CH_2)_6-$	68	48
$R^1, R^2 = -(CH_2)_3O-$	97	-
$R^1 = H,\ R^2 = -(CH_2)_8CO_2CH_3-$	92	55

γ-Butyrolactones can also be prepared by the route shown in scheme 1.21[54].

Scheme 1.21 : Preparation of γ-butyrolactones

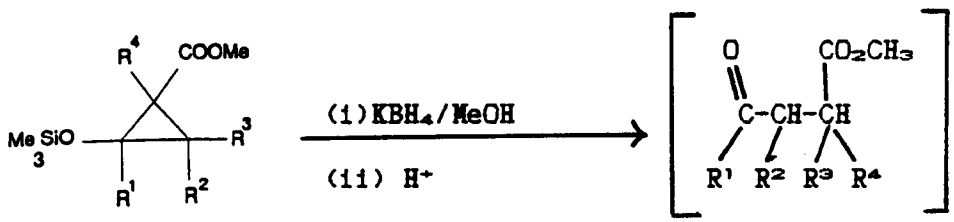


74 % (1.112)

Reagents : (i) Ethanol, p-toluenesulphonic acid, ethyl orthoformate.

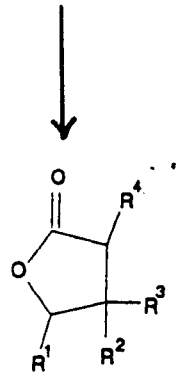
(ii) Potassium hydroxide, ethanol, reflux 2 hours.

Although the reaction involves two stages the overall yield is good. A "one pot" route to lactones involves using 2-siloxy substituted methylcyclopropanecarboxylate[55]. The reaction (equation 1.113) involves desilylation of XXI by potassium methylate (generated in situ from potassium borohydride and methanol) and ring opening to methyl-4-oxoalkanoate XXII, which is then lactonised to XXIII.



(1.113)

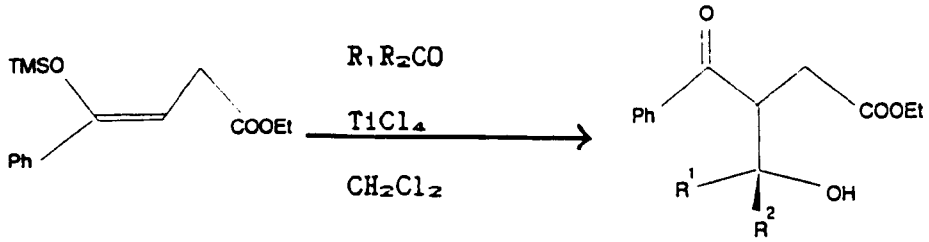
XXI XXII



XXIII (1.114).

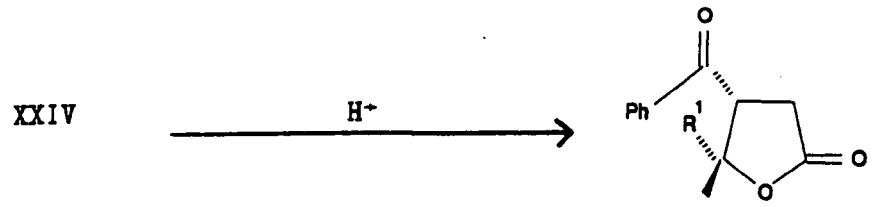
Table 1.13 shows that many substituted lactones can be formed in high yields by this method.

Other substituted lactones have been prepared in high yields using trimethylsilylenol esters[56]. An example of this reaction is shown in equation 1.115



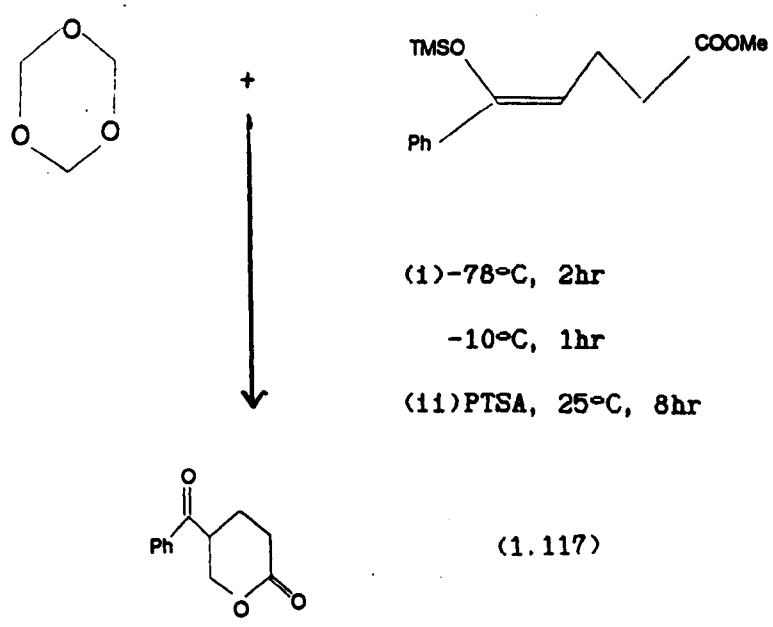
(1.115)

XXIV



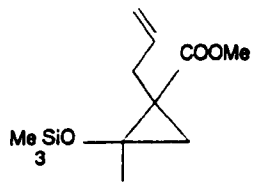
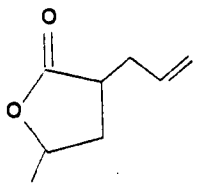
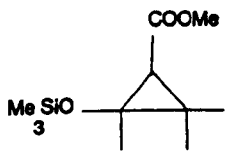
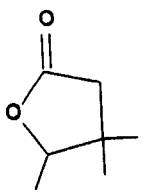
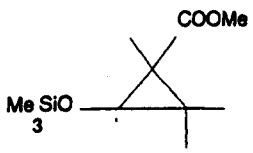
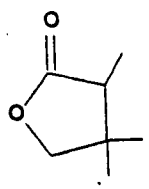
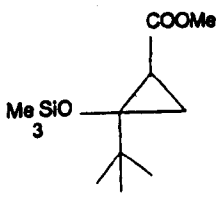
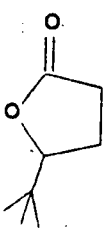
(1.116)

The cyclisation is rapid when protic acids such as p-toluenesulphonic acid are used (equation 1.116). The reaction is a general one and when aldehydes are used, aldols are initially produced but the γ-butyrolactones are formed on workup. It was observed that when ketones are used the aldol formed takes much longer to lactonise and often requires treatment with acid. It should noted that this procedure is not limited to γ-butyrolactones (equation 1.117).



(1.117)

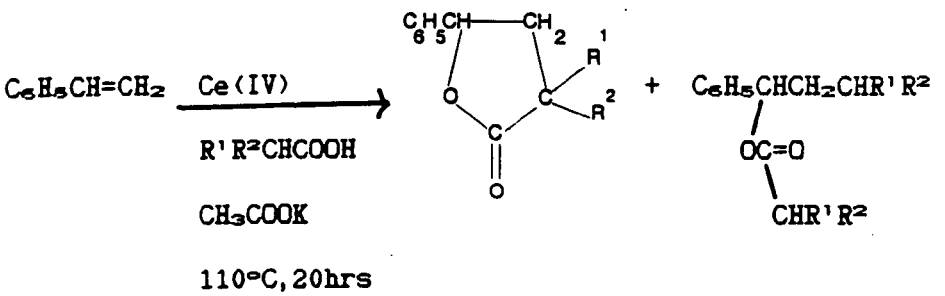
Table 1.13 : Conversion of methyl-2-siloxycyclopropanecarboxylates to γ-butyrolactones[55].

Methylsiloxycyclopropane-carboxylate	γ-butyrolactone	% Yield
		78
		95
		89
		91

1.3.2 Metal assisted lactone formation

1.3.2.1 Metal salts

The reactions of cerium(IV) carboxylates with alkenes and aromatic hydrocarbons have been shown to be useful in the formation of γ-butyrolactones and arylacetic acids (equation 1.119)[57].

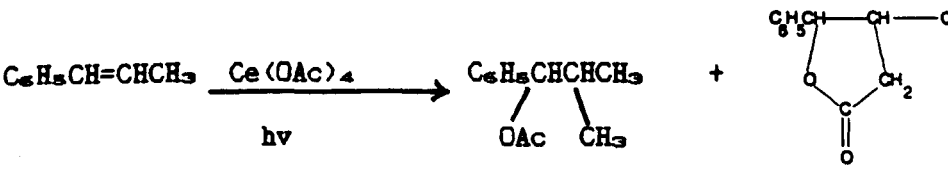


(1.118)

XXV	XXVI
70%	0.2%

XXVa $R^1 = R^2 = H$	XXVIa $R^1 = R^2 = H$
XXVb $R^1 = CH_3$; $R^2 = H$	XXVIb $R^1 = CH_3$; $R^2 = H$
XXVc $R^1 = R^2 = CH_3$	XXVIc $R^1 = R^2 = CH_3$

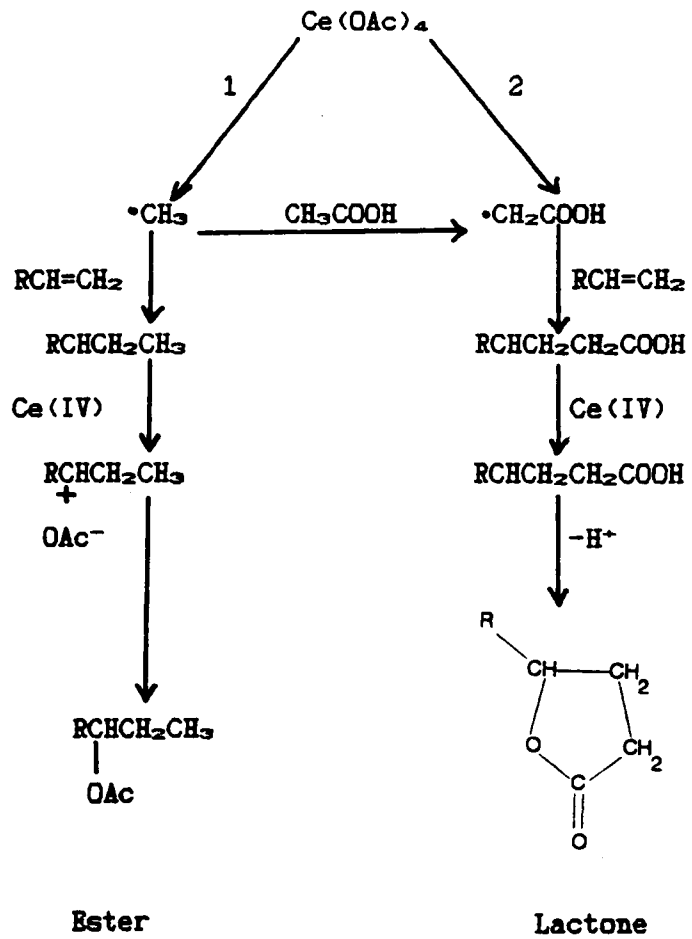
This reaction can be carried out thermally as in equation 1.118 or photochemically as in equation 1.119.



(1.119)

The mechanism suggested for the reaction between cerium(IV) carboxylate and alkenes follows two pathways (scheme 1.22) :

Scheme 1.22 : Mechanism for the reaction between cerium(IV) carboxylate and alkenes[57].



(1)A decarboxylative pathway in which a methyl radical is generated

$$Ce(OAc)_4 \longrightarrow CH_3\bullet + CO_2 + Ce(OAc)_3 \qquad (1.120)$$

$$CH_3\bullet + CH_3COOH \longrightarrow \bullet CH_2COOH + CH_4 \qquad (1.121)$$

(2)A non-decarboxylative pathway in which carboxyalkyl radicals are formed directly :

$$Ce(OAc)_4 \longrightarrow \bullet CH_2COOH + Ce(OAc)_3 \qquad (1.122)$$

The mechanism suggests that ester formation only results if the reaction proceeds as described in pathway 1. However, the lactones can be produced by either route as both result in direct or indirect formation of carboxyalkyl radicals.

This work showed that when the reaction was carried out under thermal conditions the mechanism was mainly non-decarboxylative (2). In contrast, photochemical decomposition of cerium(IV) acetate resulted in similar product distribution to the known decarboxylative pathway followed by lead tetraacetate[58,59]. Table 1.14 shows that in the presence of lead tetraacetate only small quantities of lactones are formed, the main product being the ester.

Manganese(III) carboxylates have also been used in a one step synthesis of γ-lactones (Table 1.15). It is suggested that carboxyalkyl radical formation occurs (when the reaction is carried out thermally) for Mn^{3+} and Ce^{4+} (equation 1.123) whereas Pb^{4+} follows a decarboxylative pathway (equations 1.124 and 1.125).

$$M(OOCCHR^1R^2) \longrightarrow R^1R^2\dot{C}COOH \qquad (1.123)$$

$$M(OOCCHR^1R^2) \longrightarrow CO_2 + \dot{C}HR^1R^2 \qquad (1.124)$$

$$\dot{C}HR^1R^2 + R^1R^2CHCOOH \longrightarrow R^1R^2\dot{C}\text{-}COOH + R^1R^2CH_2 \qquad (1.125)$$

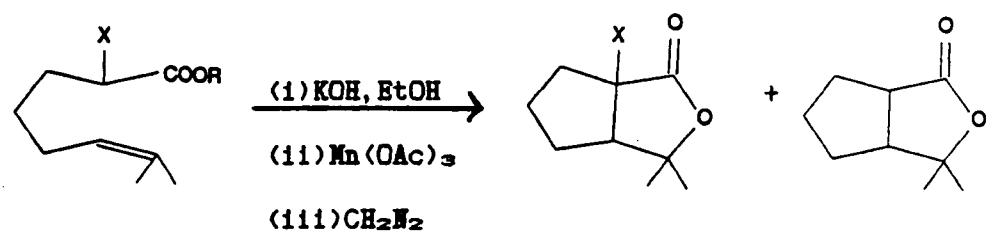
Table 1.14 : Comparison of the reaction between acid and alkene in the presence of cerium (IV) and lead (IV) carboxylates[5]

ACID	OXIDANT	YIELD (%) LACTONE	ESTER
Acetic	Ce (IV)	70	<0.2
Acetic	Pb (IV)	<0.4	37
Propionic	Ce (IV)	60	<0.2
Propionic	Pb (IV)	0.5	52
Isobutyric	Ce (IV)	3	1
Isobutyric	Pb (IV)	1	23

Table 1.15 : The effect of various metal oxidants on lactone yields, when using acetic acid[60].

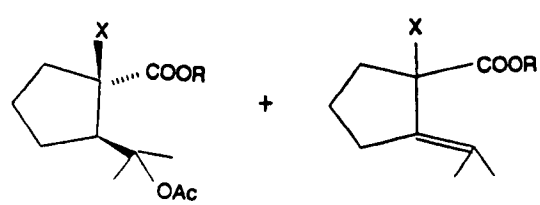
Metal oxidant	Alkene	Lactone yield (%)
$Mn(OAc)_3.2H_2O$	oct-1-ene	74
$Mn(OAc)_3$(anhydrous)	oct-1-ene	65
MnO_2(activated)	oct-1-ene	46-67
Mn_2O_3	oct-1-ene	61
$Mn(OAc)_3$(in situ)	dec-1-ene	67
$Ce(OAc)_4$	styrene	70

Manganese (III) acetate complexes are also known to catalyse carboxylic esters forming bicyclo[3.3.0] and [4.3.0] lactones (equation 1.126)[61,62].



(1.126)

XXVII XXVIII



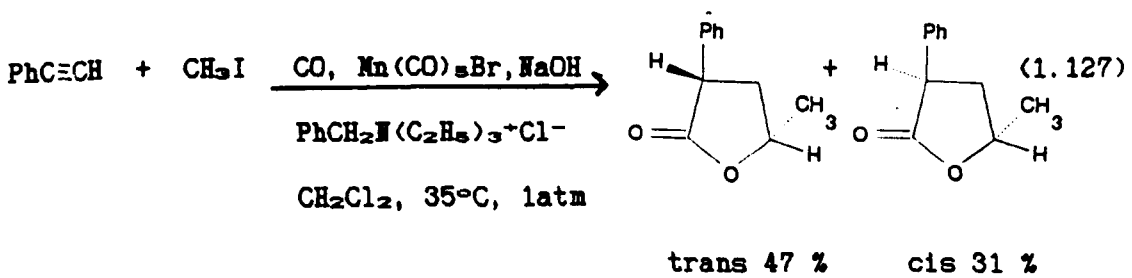
XXIX XXX

Table 1.16 : Yields of bicyclic lactones XXVII, XXVIII and derivatives XXIX and XXX (1.127)[62]

Substituents	Temperature °C	% Yields (isolated) XXVII	XXVIII	XXIX	XXX
X=CN, R=Et	70	17	0	17	9
X=CO_2Me, R=Me	70	20	6	2	-
X=CN, R=Et	25	14	-	7	-
X=CO_2Et, R=Me	25	41	3	-	-

1.3.3 Metal carbonyls

γ-Butyrolactones are formed under mild conditions (35°C, 1atm) when alkynes are treated with iodomethane in the presence of manganese carbonyls and carbon monoxide (equation 1.127)[62].



Many different lactones can be formed by this reaction as is illustrated in Table 1.17. The mechanism of this reaction is not known. Other metal carbonyls used to catalyse lactone formation are $[Co_2(CO)_8]$ (IV), $[CpFe(CO)_2]_2$ (V), and $[CpMo(CO)_3]_2$ (VI). However, as was discussed earlier, (IV) did not catalyse the lactone only the ester, whilst (V) and (VI) catalysed lactone formation (Table 1.18).

Table 1.17 : Catalysed lactone formation with manganese complexes from reactions of alkynes, CH_3I and CO, and a phase - transfer catalyst [63]

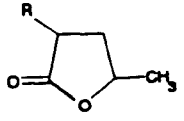
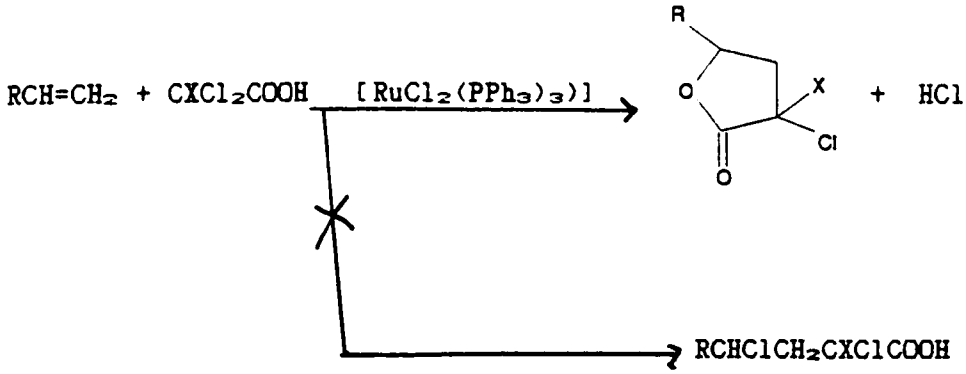
Phase transfer catalyst	Manganese complex	Substrate	Lactone 	(%) Yield isolated
$PhCH_2N(C_2H_5)_3^+ Cl^-$	$Mn(CO)_5Br$	$PhC{\equiv}CH$	4-methyl-2-phenyl-γ-butyrolactone	78
none	-"-	-"-	-"-	17
PEG-400	-"-	-"-	-"-	73
$PhCH_2N(C_2H_5)_3^+ Cl^-$	$Mn_2(CO)_{10}$	-"-	4-methyl-2-phenyl-γ-butyrolactone	65
PEG-400	-"-	-"-	-"-	64
$PhCH_2N(C_2H_5)_3^+ Cl^-$	$Mn(CO)_5Br$	$n\text{-}C_4H_9C{\equiv}CH$	4-methyl-2-n-butyl-γ-butyrolactone	35
PEG-400	-"-	-"-	-"-	42
$PhCH_2N(C_2H_5)_3^+ Cl^-$	$Mn(CO)_5Br$	$n\text{-}C_6H_{13}C{\equiv}CH$	4-methyl-2-n-hexyl-γ-butyrolactone	44
-"-	$Mn_2(CO)_{10}$	-"-	-"-	56
-"-	$Mn(CO)_5Br$	$4\text{-}CH_3C_6H_{11}C{\equiv}CH$	4-methyl-2-tolyl-γ-butyrolactone	75

Table 1.18 : Catalysed formation of lactones with $[CpMo(CO)_3]_2$ (VI) and $[CpFe(CO)_2]$ (V) formed by the reaction of methyl trichloroacetate with prop-1-ene[26]

CATALYST	PRODUCT YIELD (%) isolated		SOLVENT	REACTION CONDITIONS
	LACTONE	ESTER		REAGENTS
VI	81.5	1.3	-	$CCl_3CO_2CH_3$ (30g), prop-1-ene (30ml), catalyst (0.5g) at 150 C for 16 hr
V	46.1	13.1	-	
VI	88.8	3.9	methanol	$CCl_3CO_2CH_3$ (17g),
	98.7	tr	benzene	prop-1-ene (20ml),
	75.2	20.5	THF	solvent (20ml),
	79.4	1.5	dichloromethane	catalyst (0.5g)
	70.1	tr	n-hexane	at 150 C for 6hr

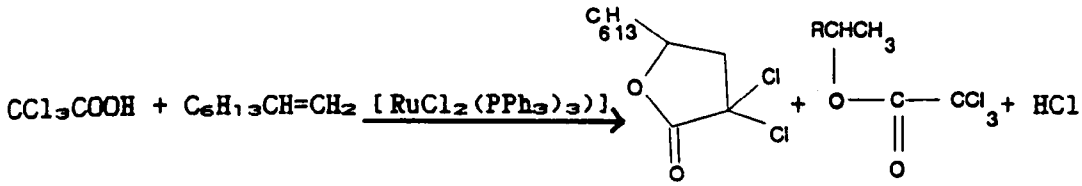
1.3.4 Catalysis by $[RuCl_2(PPh_3)_3)]$.

Trichloro and dichloro acids are known to undergo addition reactions with alkenes in the presence of $[RuCl_2(PPh_3)_3)]$ (Table 1.19)[42].



(1.128)

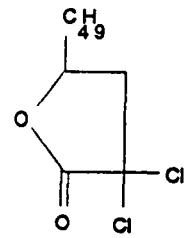
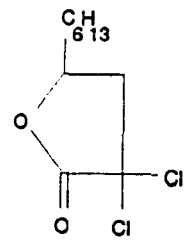
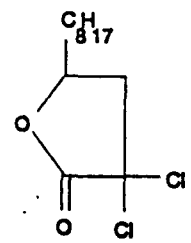
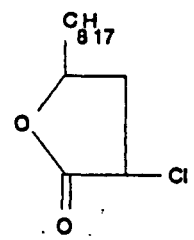
Other work has shown the formation of the Markovnikov addition product as well as the lactone (equation 1.129)[64]



(1.129)

A comparison has been made of the quantities of the Markovnikov adduct and the γ-lactone formed by different catalysts (Table 1.20). This table shows that $[RuCl_2(PPh_3)_3)]$ is the most effective catalyst for the formation of lactone.

Table 1.19 : Reaction of dichloro and trichloroacetic acids with alkenes in the presence of $[RuCl_2(PPh_3)_3]$[42]

Alk-1-ene	Acid	Lactone	% Yield*
hex-1-ene	CCl_3COOH		79(67)
oct-1-ene	CCl_3COOH		81(62)
dec-1-ene	CCl_3COOH		85(70)
dec-1-ene	CCl_2COOH		74(56)

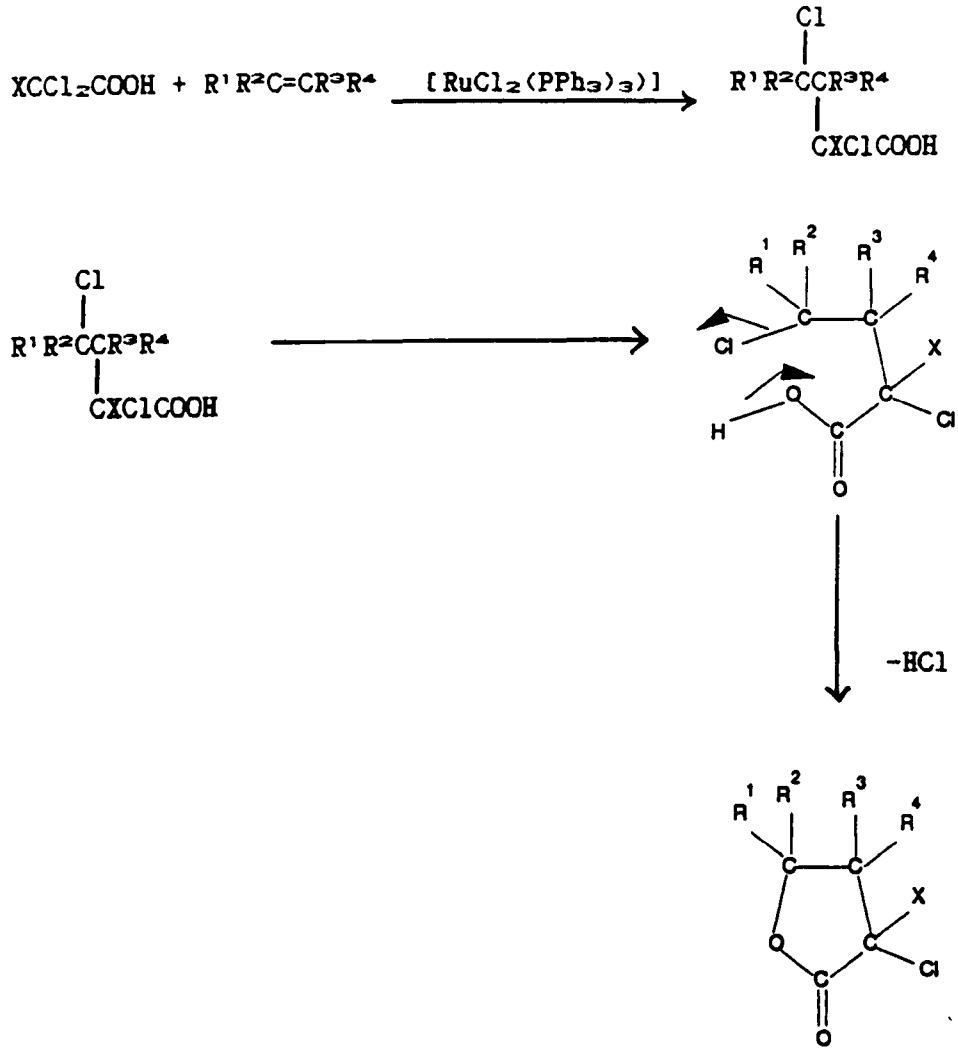
*Yields were based on alkene charged via GC, in parenthesis is the isolated yield.

Table 1.20 : Comparison of the effect of catalysts on the reaction between alkenes and trichloroacetic acid.[65]

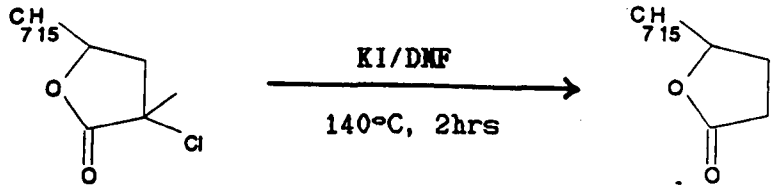
Catalyst	% Yield	
	γ-lactone	Markovnikov adduct
$[RuCl_2(PPh_3)_3)]$	83	11
$[RhCl(PPh_3)_3)]$	31	53
$[NiCl_2(PPh_3)_2)]$	0	85
$[PdCl_2(PPh_3)_2)]$	0	95
$[Pt(PPh_3)_4)]$	0	95
$CuCl_2$-Et_2NH_2Cl	0	8

The mechanism suggested by these authors is represented in scheme 1.23[65] and involves the addition of the acid followed by dehydrochlorination.

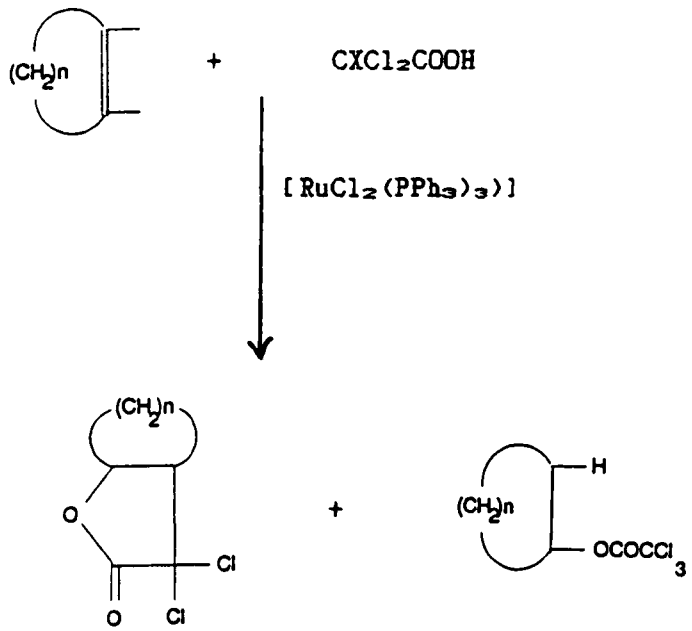
Scheme 1.23 : Mechanism of the addition of carboxylic acid to alkenes in the presence of $[RuCl_2(PPh_3)_3)]$[66]



In a more recent publication it has been observed that the lactones may be dechlorinated with alkali metal halides and N,N-dimethylformamide, (equation 1.133)[66].



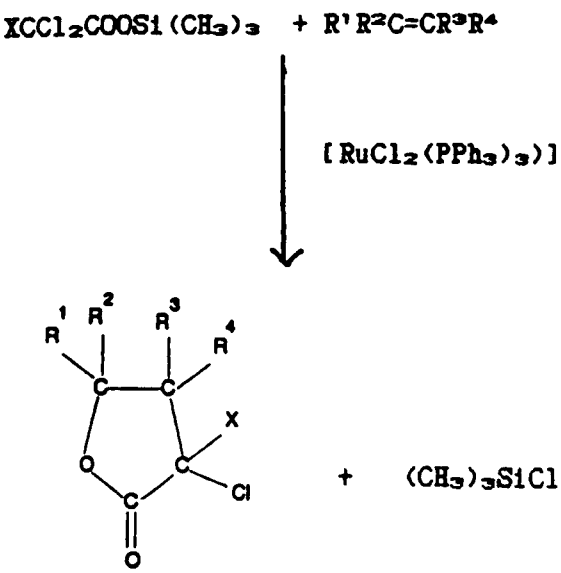
The addition reactions have been extended to give bicyclic systems by using a wide range of cyclic alkenes (equation 1.134)[67].



(1.134)

where n=3-5

The formation of lactones was also observed when trimethylsilyl-dichlorocarboxylates react with alkenes in the presence of [$RuCl_2(PPh_3)_3$)] (equation 1.135)[66,67]



(1.135)

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CHAPTER 2 : METAL CATALYSED ADDITION OF CCl_4 TO ALKENES AND DIENES

2.1 INTRODUCTION

This chapter is concerned with the investigation of the effect of various catalysts and radical chain initiators on the reaction between cyclohexene and tetrachloromethane. This reaction is of interest since two isomers of the addition product and a number of side products are formed, thus allowing the selectivity and stereospecificity of these catalysts to be studied. Catalysis by $[Co_2(CO)_8]$ was studied since it was felt that the results in the literature were open to question. These will be discussed in section 2.2.

The bulk of the work involved use of $[RuCl_2(PPh_3)_3]$ as the catalyst, since this was found to be the most effective of those studied. We report here an investigation of solvent effects, the effect of added resin capable of absorbing triphenylphosphine, and the effect of ligand variation in the catalyst upon the reaction yields. A parallel study was carried out using oct-1-ene and tetrachloromethane in the presence of $[RuCl_2(PPh_3)_3]$ to investigate whether the solvent effects are influenced by the substrate. Finally, the addition of tetrachloromethane to cyclohexa-1,3-diene in the presence of $[RuCl_2(PPh_3)_3]$ was studied.

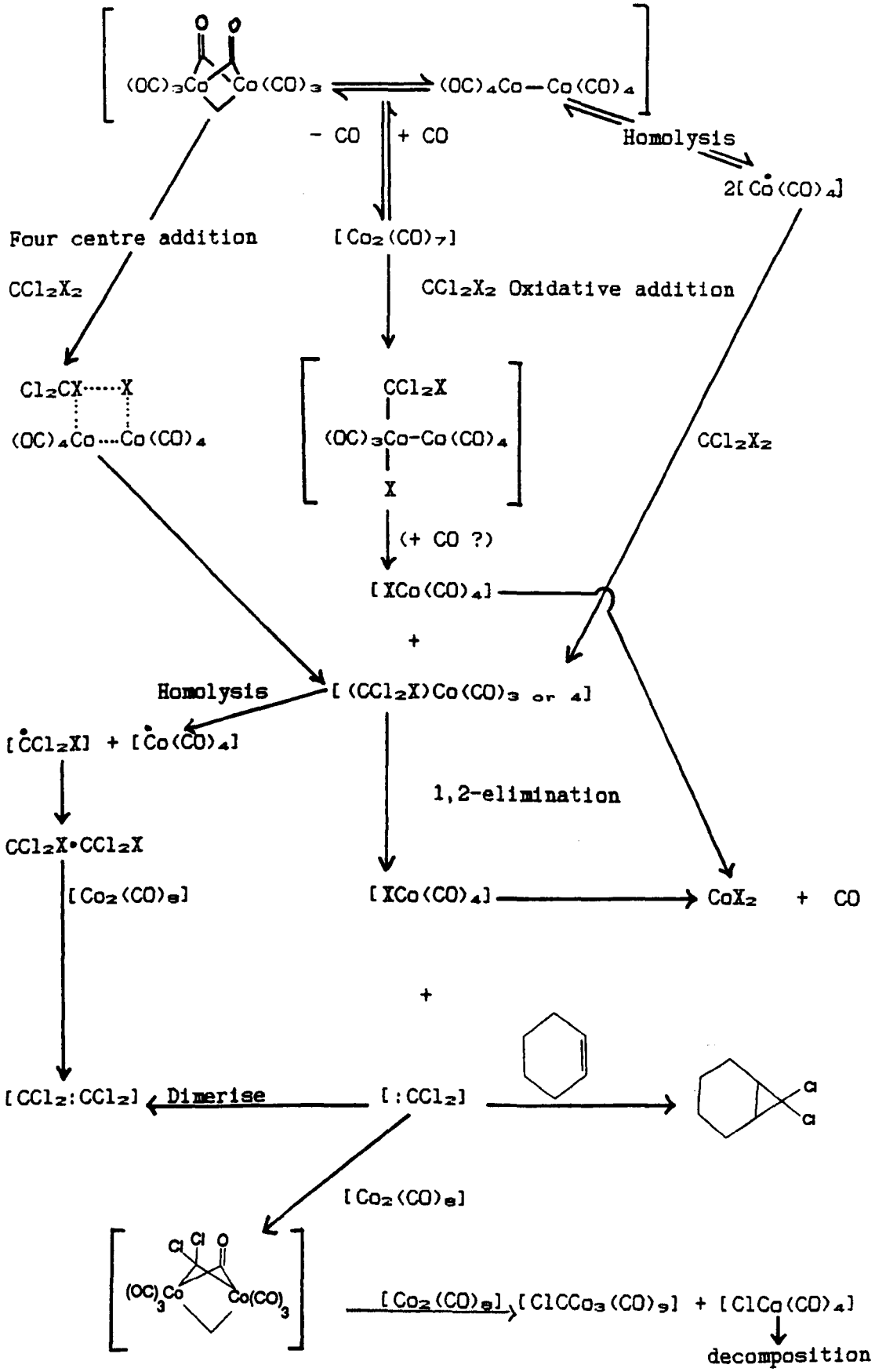
2.2 A study of the octacarbonyldicobalt [$Co_2(CO)_8$] catalysed addition of tetrachloromethane to cyclohexene.

2.2.1 Introduction

Booth, Casey, and Haszeldine have proposed that carbenes are formed during reactions between chlorinated hydrocarbons, X_2CCl_2 and [$Co_2(CO)_8$] in non-polar solvents.[1] The reaction of [$Co_2(CO)_8$] with CCl_4 (and also $CBrCl_3$ or CBr_2Cl_2) was found to produce tetrachloroethene in addition to the cluster [$ClCCo_3(CO)_9$] and cobalt(II) chloride. When the reaction was carried out in the presence of excess cyclohexene (employed as a dichlorocarbene trap), it was reported that the yield of cluster was reduced by approximately 10 % and an unspecified quantity of the dichlorocarbene adduct, 7,7-dichloronorcarane, was identified by gas chromatography. A reaction scheme (scheme 2.1) was proposed for the processes occurring. In this scheme it was suggested that X_2CCl_2 can attack [$Co_2(CO)_8$] in three ways to give the intermediate complex, [$(CCl_2X)Co(CO)_4$]. This, in turn, can either undergo homolysis, eventually reacting with more [$Co_2(CO)_8$] to form tetrachloroethene, or alternatively it may undergo 1,2-elimination giving rise to $:CCl_2$, which then reacts with more [$Co_2(CO)_8$] eventually producing the cluster,[$ClCCo_3(CO)_9$].

In view of the fact that [$Co_2(CO)_8$] has been reported to promote the Kharasch addition reaction of tetrachloromethane across double bonds[2], a finding that has been verified in these laboratories[3], it was surprising that the products of this addition reaction were not described by Booth et al. It also appeared to us that 7,7-dichloronorcarane (II in equation 2.1) may be produced by [$Co_2(CO)_8$] promoted dechlorination of 1-chloro-2-(trichloromethyl)-cyclohexane, the product of the Kharasch addition reaction.

Scheme 2.1 : Mechanism of cluster formation[1].

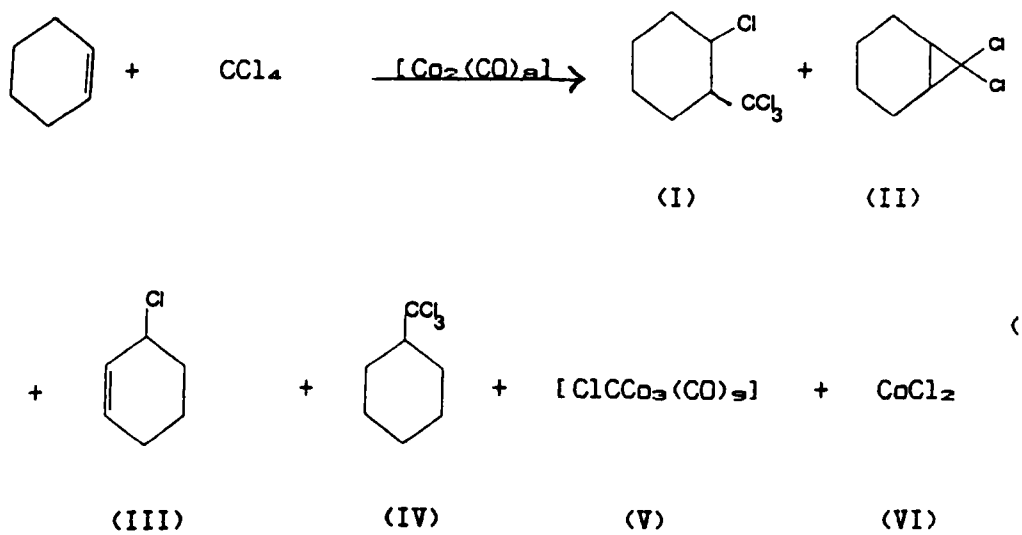


Furthermore, tetrachloroethene may be produced by a similar reaction of hexachloroethane, a known termination product of Kharasch addition. If this were so, then an alternative mechanism for the reaction of $[Co_2(CO)_8]$ and tetrachloromethane, not involving dichlorocarbene, would be required. In an attempt to resolve these points, the work of Booth et al has been repeated and these findings and others are reported here.

2.2.2 Results

2.2.2.1 Investigation of the reaction between $[Co_2(CO)_8]$ and CCl_4 in the presence of cyclohexene.

This reaction was carried out as described in the literature[1].



The products of the reaction shown in equation 2.1 included both the trans and cis isomers of the 1:1 adduct, 1-chloro-2-(trichloromethyl)-cyclohexane (I), (in a 14 % yield based on $[Co_2(CO)_8]$, 0.65 % based on CCl_4 charged) in the ratio of 1.3 : 1 respectively. A small quantity of 7,7-dichloronorcarane (II) (3 % yield based on $[Co_2(CO)_8]$, 0.15 % based on CCl_4 charged) was also obtained, as well as two additional products, 3-(trichloromethyl)cyclohex-1-ene (III) and

(trichloromethyl)cyclohexane (IV). These last two products were identified by GC/MS. As these products could not be isolated, the yields were calculated in an approximate fashion on the basis that, since they have similar structures to the adduct (I), they might be expected to have comparable response factors in the GLC analysis. The yields were estimated to be: (III), 97 % based on $[Co_2(CO)_8]$, 4.40 % based on CCl_4 charged and (IV), 34 % based on $[Co_2(CO)_8]$, 1.53 % based on CCl_4 charged. As can be seen from the chromatogram of the mixture (figure 2.1), all the major components have been identified. The other products formed were the cluster, $[ClCCo_3(CO)_9]$ (V) in 22 % yield (isolated) based on $[Co_2(CO)_8]$ and cobalt(II) chloride mixed with metallic cobalt (0.19g). These results are summarised in Table 2.1.

2.2.2.2 <u>Investigation of the reaction between $[Co_2(CO)_8]$ and CCl_4 in the absence of cyclohexene.</u>

The reaction was carried out as reported by Booth et al[1]. The results showed comparable yields of the cluster, $[ClCCo_3(CO)_9]$ (40 % based on $[Co_2(CO)_8]$, compared to 42 % reported) and cobalt(II) chloride (1.83g). A trace amount of $[Co_4(CO)_{12}]$ was also identified by mass spectrometry. However, no tetrachloroethene or hexachloroethane was detected. The gas chromatogram showed one peak which could not be identified but which had a different retention time to the expected compounds (which was confirmed by spiking the sample) (Appendix 1).

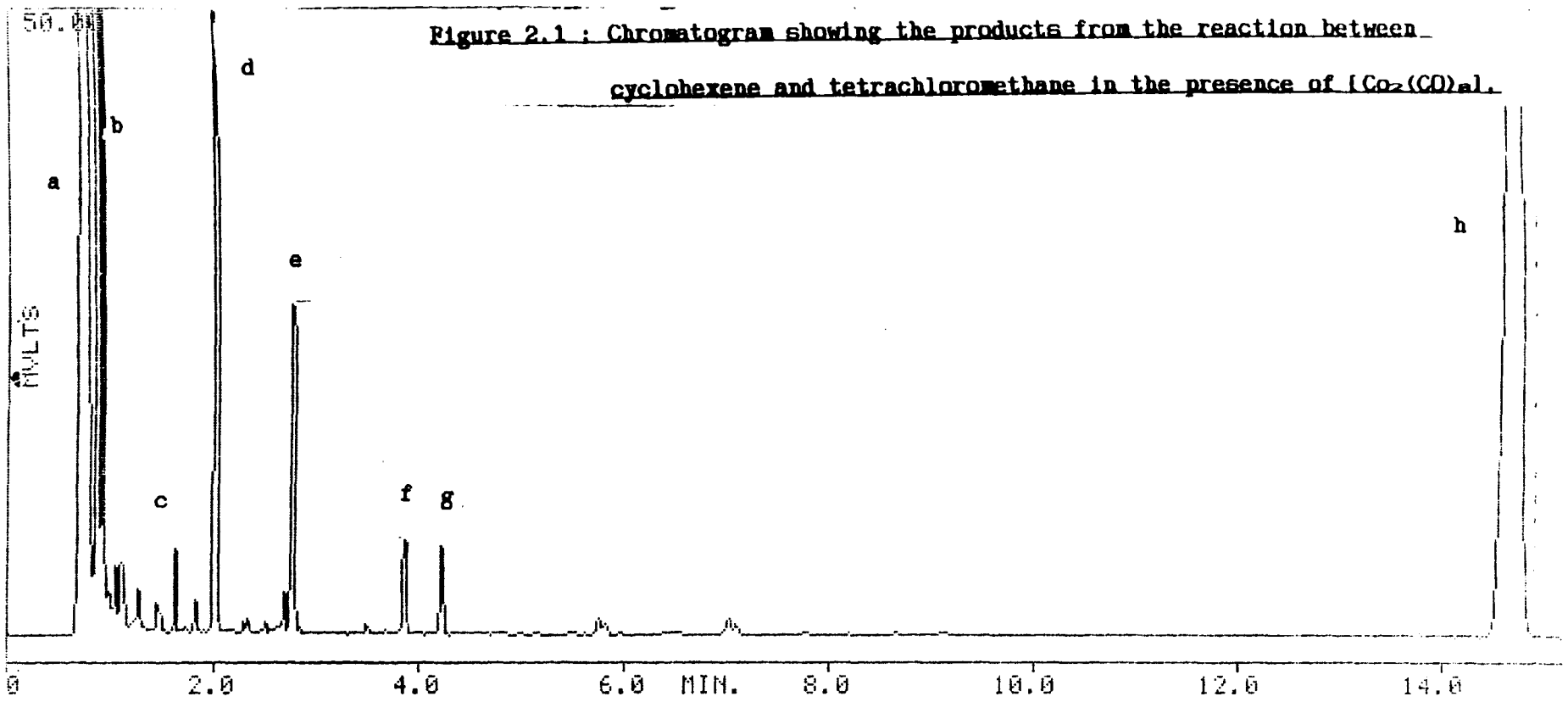


Figure 2.1 : Chromatogram showing the products from the reaction between cyclohexene and tetrachloromethane in the presence of $[Co_2(CO)_8]$.

a=hexane(solvent) , b=cyclohexene and CCl_4, c=7,7-dichloronocarane (II),

d=3-(trichloromethyl)cyclohex-1-ene (III), e=(trichloromethyl)cyclohexane (IV),

f=trans-1-chloro-2-(trichloromethyl)cyclohexane (trans-I),

g=cis-1-chloro-2-(trichloromethyl)cyclohexane (cis-I), h=methyl myristate (standard).

Table 2.1 : Summary of reagents and products in the reaction between $[Co_2(CO)_8]$ and CCl_4 in the presence and absence of cyclohexene.

Reagents	Quantity g (mmol)	Products	Quantity g (mmol)
$[Co_2(CO)_8]$	0.65 (2.0)	I	0.064 (0.27)
CCl_4	6.41 (40.0)	II	0.009 (0.06)
Cyclohexene	16.2 (197,0)	III	0.350 (1.76)
		IV	0.123 (0.61)
		V	0.200 (0.42)
		VI	0.190 -
$[Co_2(CO)_8]$	4.50 (13.2)	V	1.78 (3.78)
CCl_4	21.4 (139)	VI	1.83 -

2.2.2.3 The action of heat on (I) in the presence and absence of $[Co_2(CO)_8]$

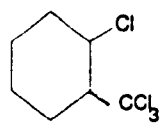
When (I) was heated in the absence of $[Co_2(CO)_8]$ for 15 hours in refluxing hexane, there was no observed decomposition. The isomeric ratio also remained unchanged after this time. However, when (I) was heated in the presence of $[Co_2(CO)_8]$, the formation of 3-(trichloromethyl)cyclohex-1-ene (III) and (trichloromethyl)cyclohexane (IV) were observed. The yield of (III) was estimated to be 30 %, the majority of the product being formed after 3 hours. The minor product (IV) was formed in 4.5 % yield after 15 hours. The adduct was observed to decompose to 30 % of its initial value, (figure 2.2). The isomeric ratio of I remained unaffected. No 7,7-dichloronorcarane was formed. At the same time, formation of the cluster and $CoCl_2$ was observed.

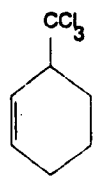
2.2.3 Discussion

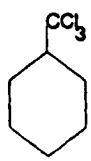
The results confirm reports that $[Co_2(CO)_8]$ is able to promote the Kharasch addition reaction of tetrachloromethane across alkenic double bonds. $[Co_2(CO)_8]$ could be acting as an initiator of a free radical chain reaction or acting as a catalyst. The formation of the trans and cis isomers of the adduct (I) in a 1.3 : 1 ratio suggests that the reaction does not involve extensive metal catalysis but proceeds principally by a free radical chain route.The results are in accordance with those of Booth et al for the formation of the cluster. The reaction of $[Co_2(CO)_8]$ (13.2mmol) with CCl_4 in hexane led to the isolation of 3.78 mmol of $[ClCCo_3(CO)_9]$ which represents 44 % of the available cobalt. The remainder of the cobalt appears as a dirty pink residue (1.83g) which was found to contain Co^{II} and Cl^- ions. This is probably a mixture of $CoCl_2$ (this product being hydrated during the

work up) and cobalt metal.

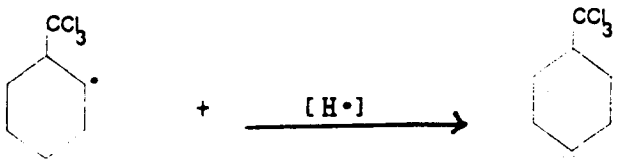
When this reaction was carried out in the presence of cyclohexene the amount of cluster was reduced. It was found that 1.9 mmoles of $[Co_2(CO)_8]$ produced 0.42 mmoles of cluster, (isolated), representing 33 % of the available cobalt so showing an 11 % decrease. This agrees well with the published work in which a 41 % cluster yield reduced to 29 % . It is suggested by Booth et al that this reduction in yield of cluster can be accounted for in terms of the formation of 7,7-dichloronorcarane. Clearly, not enough 7,7-dichloronorcarane is formed to account for this reduction, since this is produced in 3 % yield based on $[Co_2(CO)_8]$. However, other organic products are formed. These are

(I) 1-chloro-2-(trichloromethyl)cyclohexane, 

(III) 3-(trichloromethyl)cyclohex-1-ene, 

(IV) (trichloromethyl)cyclohexane, 

All these products originate from the attack of CCl_3 radicals or metal-CCl_3 intermediates, such as $CCl_3Co(CO)_4$, on cyclohexene. The adduct (I) is formed by a radical chain or metal catalysed addition, while (III) is formed by the dehydrochlorination of (I). (Trichloromethyl)cyclohexane (IV) results from a reaction of the (trichloromethyl)cyclohexyl radical with $[H\cdot]$ (2.2).



(2.2)

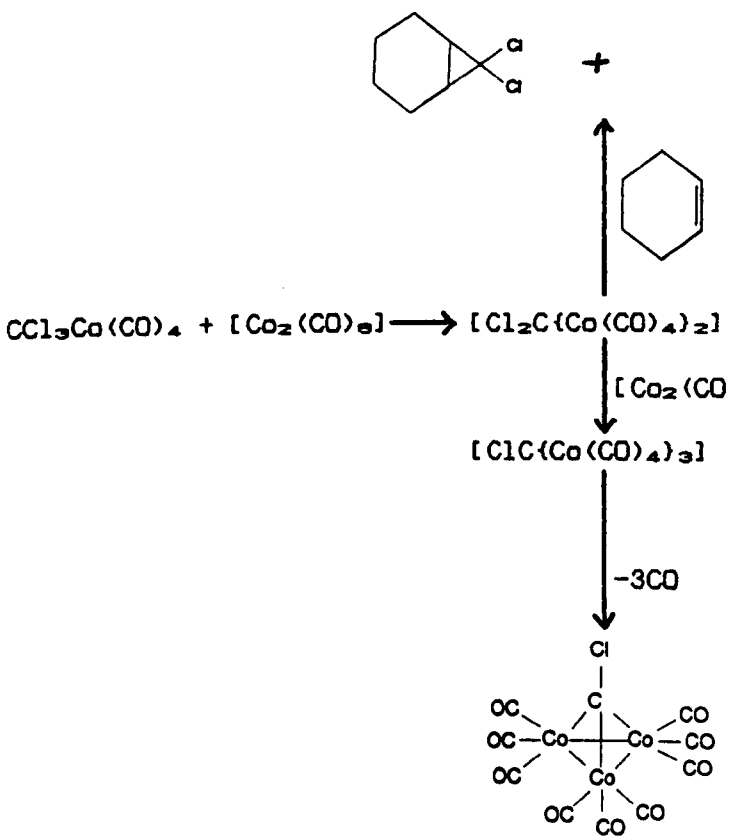
The likely source of such a radical is the solvent or cyclohexene.

It is likely that the yield of cluster becomes reduced because either CCl_3• radicals or $CCl_3Co(CO)_4$ are removed. The effect of removing the $CCl_3Co(CO)_4$ would cause a reduction in the yield of the cluster, if this complex is the first product of the reaction sequence between $[Co_2(CO)_8]$ and CCl_4 (equation 2.3).

$$[Co_2(CO)_8] + CCl_4 \longrightarrow [CCl_3Co(CO)_4] + [ClCo(CO)_4] \quad (2.3)$$

A mechanism (scheme 2.2) can be proposed for the cluster formation.

<u>Scheme 2.2 : Mechanism of cluster formation.</u>



This shows two additions of $[Co_2(CO)_8]$ to $[CCl_3Co(CO)_4]$ followed by decarbonylation forming the stable cluster. It is possible that some $:CCl_2$ will be formed from the decomposition of the intermediate $[Cl_2C(Co(CO)_4)_2]$ which in the presence of cyclohexene will form 7,7-dichloronorcarane. The other decomposition product $[Co(CO)_4^{\bullet}]$ will react with any $CCl_3^{\bullet}$ radicals forming more $[CCl_3Co(CO)_4]$. The reaction carried out between the adduct (I) and $[Co_2(CO)_8]$ does not result in any 7,7-dichloronorcarane formation and thus some production of $:CCl_2$ must occur as postulated in scheme 2.2. Alternative methods of cluster formation may be proposed (scheme 2.3).

This again involves addition of $[Co_2(CO)_8]$ to $CCl_3Co(CO)_4$, but the product then undergoes decarbonylation resulting in a bridged dinuclear species which could accept the addition of another molecule of $[Co_2(CO)_8]$. Subsequent loss of two moles of carbon monoxide from the product will form the cluster. It is likely that whichever mechanism leads to cluster formation, the initial reaction of CCl_4 with $Co_2(CO)_8$ involves initial electron transfer steps (equations 2.08 - 2.11).

$$CCl_4 + [Co_2(CO)_8] \longrightarrow [Co_2(CO)_8]^{+\bullet} + CCl_4^{-\bullet} \qquad (2.08)$$

$$CCl_4^{-\bullet} \longrightarrow CCl_3^{\bullet} + Cl^- \qquad (2.09)$$

$$[Co_2(CO)_8]^{+\bullet} + [Cl^-] \longrightarrow [ClCo(CO)_4] + Co(CO)_4^{\bullet} \qquad (2.10)$$

$$Co(CO)_4^{\bullet} + CCl_3^{\bullet} \longrightarrow [CCl_3Co(CO)_4] \qquad (2.11)$$

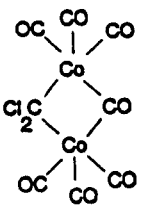
$[ClCo(CO)_4]$ is known to be unstable[1] and when formed under the reaction conditions employed will decompose (equation 2.12).

$$[ClCo(CO)_4] \longrightarrow \tfrac{1}{4}\, CoCl_2 + 4CO + \tfrac{1}{2}Co \qquad (2.12)$$

Scheme 2.3 : Alternative method of cluster formation.

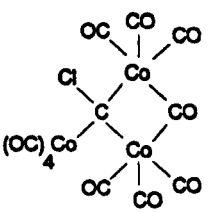
$$[CCl_3Co(CO)_4] + [Co_2(CO)_8] \longrightarrow [Cl_2C(Co(CO)_4)_2] + [ClCo(CO)_4] \quad (2.13)$$

$$\downarrow -CO$$



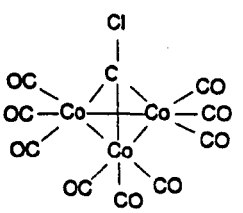
$$+ [ClCo(CO)_4] \quad (2.14)$$

$$\downarrow [Co_2(CO)_8]$$



(2.15)

$$\downarrow -2CO$$



(2.16)

The overall reaction between CCl_4 and $[Co_2(CO)_8]$ can therefore be represented by equation 2.19 :

$$3[Co_2(CO)_8] + CCl_4 \rightarrow [ClCCo_3(CO)_9] + 3[ClCo(CO)_4] + 3CO \quad (2.17)$$

$$3[ClCo(CO)_4] \longrightarrow 1\tfrac{1}{2}\ CoCl_2 + 1\tfrac{1}{2}\ Co + 12CO \quad (2.18)$$

$$3[Co_2(CO)_8] + CCl_4 \rightarrow [ClCCo_3(CO)_9] + 1\tfrac{1}{2}\ CoCl_2 + 1\tfrac{1}{2}\ Co + 15CO \quad (2.19)$$

From this equation it is apparent that 3 moles of $[Co_2(CO)_8]$ should produce only 1 mole of cluster. So in the experiment carried out between CCl_4 and $[Co_2(CO)_8]$, 13.2 mmoles of the latter should have produced 4.4 mmoles of the cluster. In practice 3.78 mmoles of the cluster were isolated. However, as the isolation was carried out by vacuum sublimation, recovery of the theoretical yield of the cluster would be very difficult.

The yield of cluster recovered is thus in accord with the stoichometry of equation 2.19. It is also possible to calculate the amount of $CoCl_2.6H_2O$ and cobalt metal formed for comparison with this overall reaction stoichiometry (equation 2.19).

In theory from equation 2.19, 4.40 mmoles of $[ClCCo_3(CO)_9]$ should be formed containing 0.78g of cobalt. In the experiment, the initial amount of dicobalt octacarbonyl used was 4.55g (13.2.mmoles) which contained 1.55g of cobalt. Thus the amount of cobalt unaccounted for (theoretically) is 1.55g - 0.78 = 0.77g. The total mass of pink residue recovered was 1.83g.

Assuming that the residue is an equimolar mixture of $CoCl_2.6H_2O$ and cobalt metal, it is possible to calculate the amount of cobalt this mixture contains, as follows

$$\underset{x}{CoCl_2}.\underset{y}{6H_2O} + \underset{z}{Co} = 1.83g.$$

Then x + y + z = 1.83g.

It is known from theory that the remaining cobalt, (x+z) is 0.77g so y = 1.83 - 0.77 is 1.06g which represents 5.95 mmoles. Therefore, the number of moles of cobalt in the complex will be 5.95 mmoles, which represents 0.35g of cobalt (ie. x = 0.35g).

Then, z = 0.77 - x = 0.77 - 0.35 = 0.42g. This represents 7.14 mmoles of cobalt. These results are summarised in Table 2.2. and compared with those predicted by equation 2.19. The results show good agreement between the overall reaction proposed and the actual yields obtained.

Table 2.2 : Summary of results.

Compound	Quantities (mmoles)	
	Theoretical	Isolated/Calculated
$[ClCCo_3(CO)_9]$	4.40	3.78
$CoCl_2.6H_2O$	6.60	5.95
Co	6.60	7.14

On the basis of the cluster obtained in the absence of cyclohexene, reaction in the presence of cyclohexene might be expected to lead to isolation of 0.572 mmoles (if the reaction was carried out on the same scale). The actual quantity recovered was 0.42 mmoles which is a discrepancy of 0.15 mmoles (based on the reaction in the absence of cyclohexene) or 0.247 mmoles (if based on the theoretical amount given

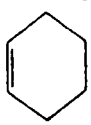
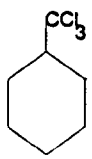
by equation 2.19 (0.667 mmoles)). Literature suggests that this difference can be accounted for in terms of the 7,7-dichloronorcarane formed. However, only 0.058 mmoles of this are produced, clearly not sufficient to cause such a reduction. The total amount of the other organic products (I), (III), and (IV) formed (Table 2.1) is 2.64 mmoles, which is much greater than the reduction in yield of cluster. This may be explained in terms of free radical chain reactions proceeding as shown in scheme 2.4.

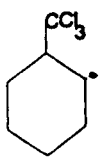
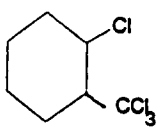
<u>Scheme 2.4 : Free radical chain reactions</u>

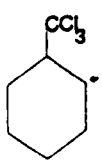
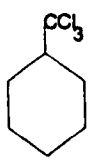
$$[Co_2(CO)_8] + CCl_4 \longrightarrow [CCl_3Co(CO)_4] + [ClCo(CO)_4] \quad (2.20)$$

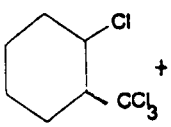
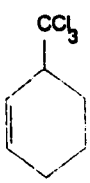
$$[CCl_3Co(CO)_4] \rightleftharpoons CCl_3\bullet + [Co(CO)_4\bullet] \quad (2.21)$$

$$2[Co(CO)_4\bullet] \longrightarrow [Co_2(CO)_8] \quad (2.22)$$

$CCl_3\bullet$ +  ⟶  (2.23)

 + CCl_4 ⟶  + $CCl_3\bullet$ (2.24)

 + $[H\bullet]$ ⟶  (2.25)

 + $[Co_2(CO)_8]$ ⟶  + $[HCo(CO)_4]$ + $[ClCo(CO)_4]$ (2.26)

$$2[HCo(CO)_4] \longrightarrow H_2 + [Co_2(CO)_8] \quad (2.27)$$

The reaction 2.26 was confirmed by heating the adduct (I) alone and in the presence of $[Co_2(CO)_8]$. As was expected, when the adduct was heated alone there was no observed decomposition. However, in the presence of $[Co_2(CO)_8]$, the products (III) and (IV) were observed (figure 2.2) formed by the mechanism already discussed (scheme 2.4). Clearly, figure 2.2 shows that the decomposition of adduct cannot be accounted for in terms of the formation of the these products alone, as 70 % of the adduct used initially is consumed after 15 hours. Formation of the products (III) and (IV) account for 37.5 % of this loss, leaving 32.5 % unaccounted. This can be explained in terms of the formation of cluster which is observed.

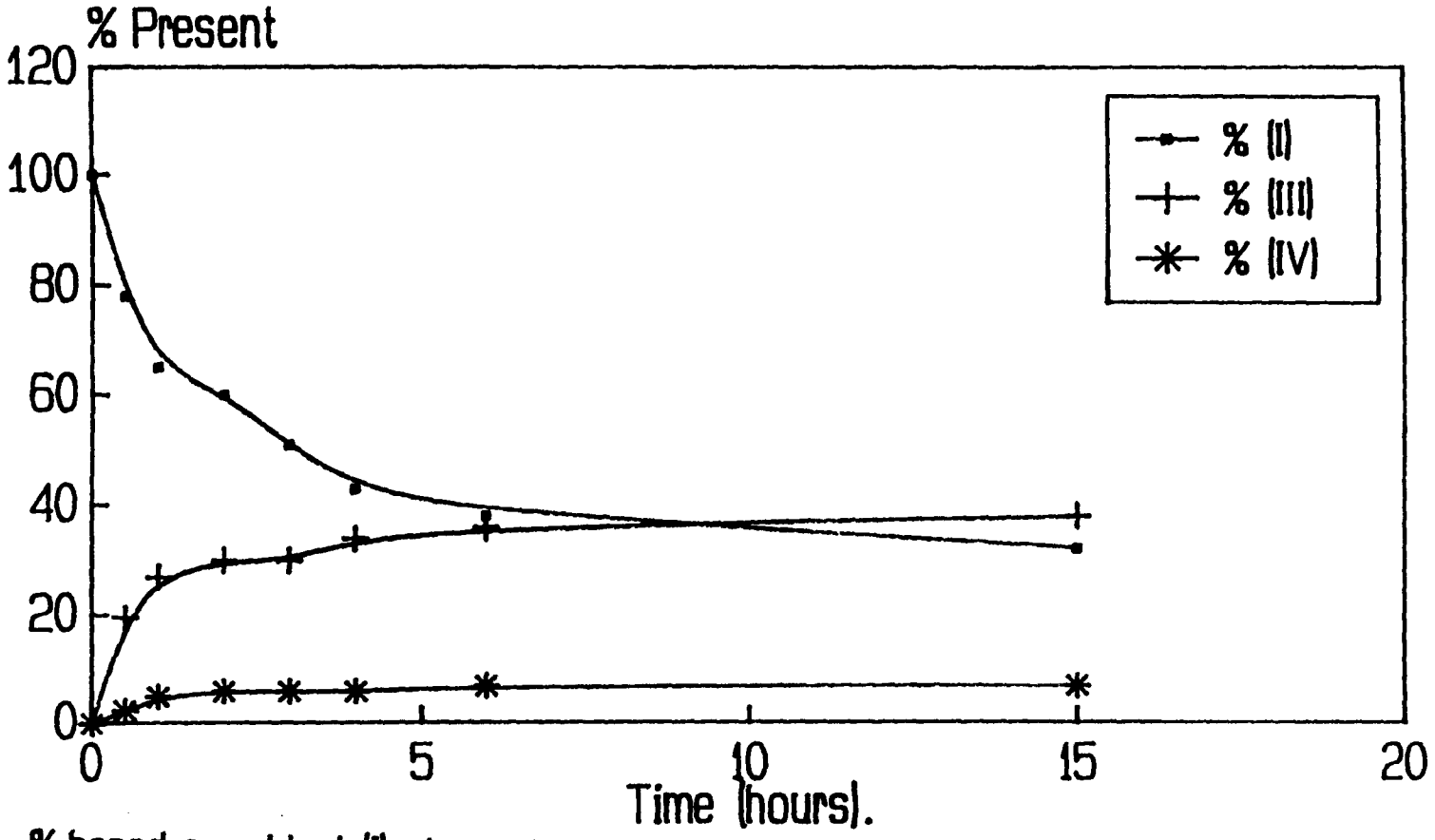
In summary, this study has shown that :

(1) $[Co_2(CO)_8]$ reacts with tetrachloromethane leading to cluster formation in good agreement with the yields reported in the literature[1]. However, the reduction in yield of cluster in the presence of cyclohexene is not due to the formation of 7,7-dichloronorcarane.

(2) $[Co_2(CO)_8]$ is able to catalyse the Kharasch addition of CCl_4 to cyclohexene and this process accounts for the reduced yield of cluster.

(3) Due to the free radical nature of the reaction, other free radical reactions were initiated which result in the formation of other side products.

Fig 2.2 : Heating (I) in the presence of $[Co_2(CO)_8]$



% based on adduct, (I) charged.

2.3 Survey of the effect of a variety of catalysts on the addition of tetrachloromethane to cyclohexene.

2.3.1. Introduction

Studies carried out on the addition of tetrachloromethane to cyclohexene in the presence of $[Co_2(CO)_8]$ in the previous section showed that the isomeric ratio of trans : cis isomers of the addition product approximated to 1 : 1. A similar ratio has been reported for reactions in the presence of radical initiators[4]. However, the isomeric ratio is reported to be 24 : 1 in the reactions employing $[RuCl_2(PPh_3)_3]$[4]. In view of the fact that $[RuCl_2(PPh_3)_3]$ is known to act as a catalyst towards addition reactions of this type, following a quite different reaction mechanism to the conventional radical chain process (section 1.2.4), it seemed that the isomeric ratio observed in this addition reaction might act as a guide to the reaction mechanism. During the course of this work, Grigg and co-workers published the same suggestion[5]. The effects of a variety of different types of catalyst on the stereospecificity and the yield of adduct were investigated. The catalysts used can be divided into three groups. These are :

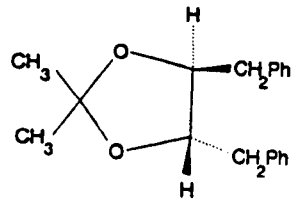
(i) Metal carbonyls where the metals include cobalt, iron, and molybdenum.

(ii) Ruthenium-based catalysts.

(iii) Ruthenium and rhodium catalysts with chiral phosphine ligands.

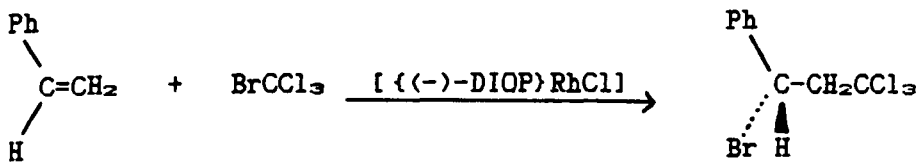
In addition to using these catalysts, the above reaction was carried out in the presence of a free radical initiator, benzoyl peroxide.

The effects of the catalysts in groups (i), (ii) and benzoyl peroxide were studied to give a direct comparison with $[Co_2(CO)_8]$. However, the rhodium and ruthenium catalysts containing the chiral ligand, DIOP ((-)-2,3-o-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphine)-butane) (VII) were also investigated as it has been suggested that these catalysts are active in stereospecific addition reactions.



(VII)

Thus, the reaction of bromotrichloromethane with styrene in the presence of the optically active rhodium complex [{(-)-DIOP}RhCl] gave the 1 : 1 adduct in a 26 % yield, with an enantiomeric excess greater than 32 % (equation 2.28)[6].



(2.28)

(S)-(-)

$[Ru_2Cl_4\{(-)DIOP\}_3]$ and $[Ru_2Cl_4\{(+)DIOP\}_3]$ are reported to effect the addition of arene sulphonyl chlorides to styrene to give optically active 1 : 1 adducts, 2-chloro-2-(phenylethyl)arylsulphones (equation 2.29)[7].

$$RSO_2Cl + R'C_6H_4CH{=}CH_2 \xrightarrow{[Ru_2Cl_4\{DIOP\}_3]} R'C_6H_4CHClCH_2SO_2R \qquad (2.29)$$

Tetrachloromethane also adds to styrene derivatives in the presence of this catalyst in good yields (Table 2.3, equation 2.30)[8].

Table 2.3 : Reaction of tetrachloromethane with styrene derivatives

Styrene derivative	DIOP	Product	Chemical yield %	Optical yield (%ee)
C_6H_5	(-)	$C_6H_5CH(Cl)CH_2CCl_3$	73	13
C_6H_5	(+)	$C_6H_5CH(Cl)CH_2CCl_3$	68	7
$4\text{-}CH_3C_6H_4$	(-)	$4\text{-}CH_3C_6H_4CH(Cl)CH_2CCl_3$	79	-
$4\text{-}CH_3C_6H_4$	(+)	$4\text{-}CH_3C_6H_4CH(Cl)CH_2CCl_3$	80	-
$4\text{-}ClC_6H_4$	(-)	$4\text{-}ClC_6H_4CH(Cl)CH_2CCl_3$	70	10
$4\text{-}ClC_6H_4$	(+)	$4\text{-}ClC_6H_4CH(Cl)CH_2CCl_3$	68	6

$$CCl_4 + ArCH{=}CH_2 \xrightarrow{[Ru_2Cl_4(DIOP)_3]} Ar^*CHClCH_2CCl_3 \qquad (2.30)$$

It seemed to us that these DIOP containing ligands may also exhibit high stereospecificity in the cyclohexene addition reaction, although no attempt has been made in the present study to obtain optical isomers.

2.3.2 Results and discussion.

All the reactions were carried out under identical conditions in sealed tubes at 80°C (except that employing $[Co_2(CO)_8]$ which was carried out under reflux), using the same concentration of catalyst, cylohexene and tetrachloromethane and the same solvents.

2.3.2.1 Metal carbonyl catalysts.

The $[Co_2(CO)_8]$ catalyst was the only one used to produce 7,7-dichloronorcarane (0.02 %), although many of the others produced the side products, 3-(trichloromethyl)cyclohex-1-ene and (trichloromethyl)cyclohexane. All the reactions were first carried out in hexane, but in most cases the yields were low (Table 2.4). Changing to benzene as solvent increased the yields allowing more meaningful comparisons. When the reaction was carried out in the presence of the free radical initiator, benzoyl peroxide, the trans : cis ratio was 1.1 : 1 demonstrating the expected lack of stereospecificity associated with free radical reactions. The stereospecificities of these metal carbonyl catalysts vary from 1.03 : 1 to 2.12 : 1 indicating a slightly higher selectivity than the free radical initiator in some cases, but suggesting that the reactions proceed by essentially free radical mechanisms under these conditions. When the reaction was carried out in benzene all the yields improved,

Table 2.4 : Investigation of the effect of a variety of catalysts on the addition of tetrachloromethane to cyclohexene

CATALYST	% YIELD OF (I) (±0.07)	ISOMERIC RATIO (±0.04)	% YIELD OF (III) (±0.03)	% YIELD OF (IV) (±0.02)	OTHER COMMENTS
$[Co_2(CO)_8]$	1.57	1.30	0.07	0.90	Refluxed in hexane, 0.02% (II) observed
$[CpMo(CO)_3]_2$	6.00	1.70	1.00	0.31	Sealed tube in hexane at 80 °C
	10.30	2.04	3.98	0.41	Sealed tube in benzene at 80 °C
$[Cp^*Mo(CO)_3]_2$	9.40	1.81	1.39	0.73	Sealed tube in hexane at 80 °C
$[\{CpMo(CO)_3\}_2CH_2]$	0.77	1.26	0.18	0.53	Sealed tube in hexane at 80 °C
$[(C_6H_5CO)_2]$	1.00	1.10	0.08	not detected	Refluxed in hexane (70 °C)
	1.20	1.05	0.07	not detected	Refluxed in benzene (80 °C)

Table 2.4 : continued :

CATALYST	% YIELD OF (I) (±0.07)	ISOMERIC RATIO (±0.04)	% YIELD OF (III) (±0.03)	% YIELD OF (IV) (±0.02)	OTHER COMMENTS
$[CpFe(CO)_2]_2$	3.60	1.22	0.80	1.39	Hexane as solvent
	4.55	1.03	1.78	1.90	Benzene as solvent
$[Cp^*Fe(CO)_2]_2$	4.72	1.50	1.02	1.24	Hexane as solvent
	10.90	1.59	3.16	0.59	Benzene as solvent
$[\{CpFe(CO)_2\}_2CH_2]$	1.68	1.31	0.22	0.13	Hexane as solvent
	13.30	2.12	2.42	1.84	Benzene as solvent

particularly that in the presence of $[\{CpFe(CO)_2\}_2CH_2]$ and also showed the highest selectivity (2.12 : 1). But the change of solvent did not affect the selectivity of $[CpFe(CO)_2]_2$, $[Cp^*Fe2(CO)_2]_2$ and effected only a slight increase in the case of $[CpMo(CO)_3]_2$. The reason for the higher yields in benzene is likely to be the greater solubility of these catalysts in this solvent compared with hexane. The results also show that in the case of both the molybdenum and iron catalysts with pentamethylcyclopentadienyl ligands, the reactions give higher yields of adduct and are more selective for the trans isomer than the cyclopentadienyl analogues. This suggests that electron donation from the ligand to the metal centre has some significance on this catalysis.

It is noteworthy that studies by Davies and Groves[9] and Davis and Khazal'[10] have shown that the dinuclear complexes $[CpMo(CO)_3]_2$, and $[CpFe(CO)_2]_2$ act as catalysts for halocarbon-alkene addition reactions at temperatures of 40-60°C (section 1.2.2.). At higher temperatures catalyst decomposition occurs, but the reactions continue by radical chain processes. Thus, the present results agree with these findings. Unfortunately, the yields of the cyclohexene-CCl_4 reactions in the presence of these complexes are too low to allow reliable measurement of the isomeric ratio at temperatures of 60°C and below.

2.3.2.2 Ruthenium-based catalysts.

When the addition is carried out in the presence of $[RuCl_2(PPh_3)_3]$ in hexane, 11.4 % of adduct is formed in a 4 : 1 trans : cis ratio, which is more specific than any of the metal carbonyl catalysts. However, if this same reaction is repeated in benzene instead of hexane the yield and stereoselectivity increase to 26.8 % and 7.9 : 1 respectively. In no reactions were the very high isomeric ratios previously reported

for $[RuCl_2(PPh_3)_3]$ observed. $[RuH_2(PPh_3)_4]$ and $[RuH_3(SiMe_2Ph)(PPh_3)_3]$ were also investigated, and in these cases solvent did not appear to markedly influence the yield (Table 2.5), but the stereoselectivity was affected. All three catalysts have very comparable yields of adduct and very similar selectivities in hexane and benzene. This suggests that the mechanisms by which the reactions proceed are similar. This is in agreement with the work of Davis and Furze[11] who carried out detailed mechanistic studies on CCl_4-oct-1-ene reactions in the presence of $[RuH_2(PPh_3)_4]$ and $[RuH_3(SiMe_2Ph)(PPh_3)_3]$. They have found that these reactions follow a mechanism which is very similar to that in the presence of $[RuCl_2(PPh_3)_3]$ and almost certainly involves the formation of a common catalytic species.

The question arises as to the origin of the stereoselectivity observed with these ruthenium complexes. These complexes follow a redox catalysed mechanism in alkene-halocarbon addition reactions (scheme 2.5). The two crucial intermediates are the radical pair species, $\{RuCl_2(PPh_3)_2^{\bullet}\}\{CCl_3^{\bullet}\}$ and $\{RuCl_2(PPh_3)_2^{\bullet}\}\{RCHCH_2CCl_3^{\bullet}\}$. Clearly, steric effects will dictate that the latter has a structure in which the metal-containing radical is remote from the bulky group (figure 2.3).

Figure 2.3 : Representation of steric effects

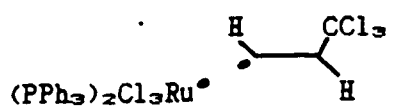
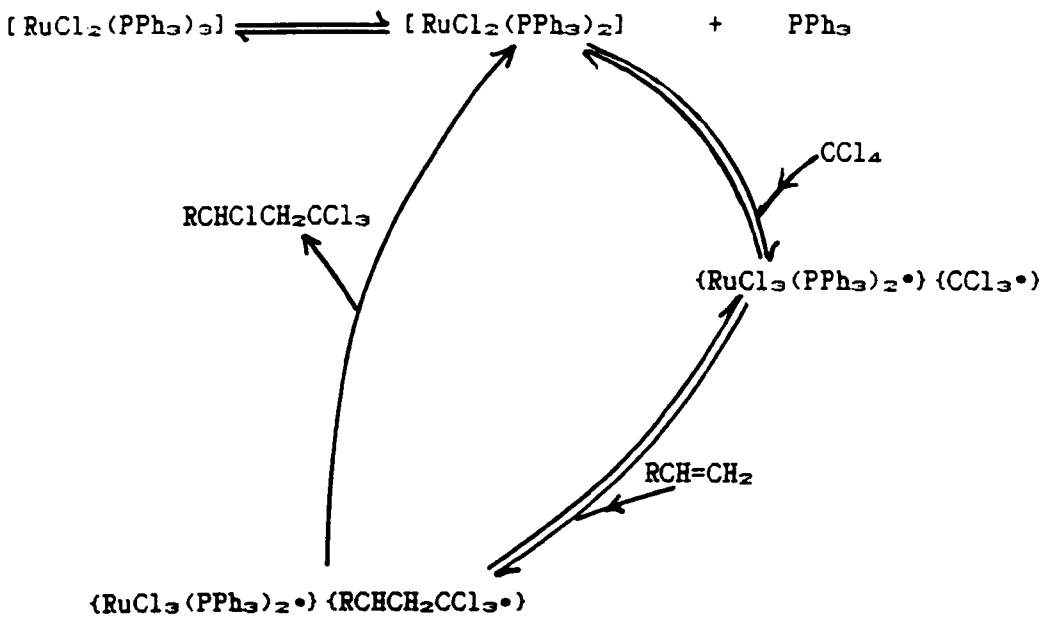


Table 2.5 : Investigation of the effect of Ruthenium based catalysts on the addition of tetrachloromethane to cyclohexene

CATALYST	% YIELD OF (I) (±0.5)	ISOMERIC RATIO (±0.04)	% YIELD OF (III) (±0.03)	% YIELD OF (IV) (±0.02)	OTHER COMMENTS
$[RuCl_2(PPh_3)_3]$	11.4	4.16	0.72	not detected	Hexane as solvent
	26.8	7.90	0.69	not detected	Benzene as solvent
$[RuH_2(PPh_3)_4]$	20.7	3.80	1.37	0.17	Hexane as solvent
	24.8	7.20	1.80	not detected	Benzene as solvent
$[RuH_3(SiMe_2Ph)(PPh_3)_3]$	24.0	3.64	2.57	0.22	Hexane as solvent
	22.4	5.80	1.09	0.74	Benzene as solvent

Scheme 2.5 : Redox catalysed mechanism for alkene-halocarbon addition reactions.



In the product forming step, the metal-containing group will prefer to deliver the chlorine atom to the cyclohexyl system on the opposite side of the ring to the $CCl_3^{\bullet}$ group.

2.3.2.3 Rhodium and ruthenium complexes containing DIOP and DIPHOS ligands.

The rhodium catalyst [RhCl(DIOP)] was generated in situ from [{Rh(COD)Cl}$_2$] and DIOP. The results showed that in the presence of this catalyst 4.5 % of adduct was formed with a 1.82 : 1 isomeric ratio. Although both the yield and the ratio are low, it is to be compared with a yield of 0.22 % in the presence of [{Rh(COD)Cl}$_2$]. When the reaction was carried out in the presence of [{Rh(COD)Cl}$_2$] and DIPHOS, a small quantity of adduct was observed (0.5 %). Blank reactions were also carried out in the presence of DIOP and DIPHOS alone, and no product was detected (Table 2.6).

Table 2.6 : Investigation of the effect of rhodium complexes and rhodium complexes containing DIOP and DIPHOS ligands on the addition of tetrachloromethane to cyclohexene

CATALYST	CONCENTRATION (mol dm^{-3}) catalyst x10^{-3}	cyclohexene	% YIELD OF (I) (±0.03)	ISOMERIC RATIO (±0.02)	% YIELD OF (III) (±0.03)	% YIELD OF (IV) (±0.01)	OTHER COMMENTS
$[RhCl(PPh_3)_3]$	4.58	0.61	1.32	1.58	3.56	0.34	Hexane as solvent
	4.57	0.61	3.61	2.14	0.71	0.06	Benzene as solvent
$[\{Rh(cod)Cl\}_2]$	2.10	0.29	0.22	2.26	0.05	not detected	Benzene as solvent
$[\{Rh(cod)Cl\}_2]$ /DIOP	2.08 (in Rh) (4.58 in DIOP)	0.28	4.50	1.82	0.42	not detected	Benzene as solvent
$[\{Rh(cod)Cl\}_2]$ /DIPHOS	2.12 (in Rh) (4.63 in DIPHOS)	0.29	0.54	1.23	not detected	not detected	Benzene as solvent

Reaction in the presence of $[Ru_2Cl_4(DIOP)_3]$ gave 5.25 % of adduct in a 3.51 : 1 isomeric ratio. Attempts were made at preparing this catalyst in situ, by the reaction of $[RuCl_2(PPh_3)_3]$ and DIOP. However, although these were probably successful (as a fluorescent green solution resulted) when used to catalyse the same reaction, only 0.85 % of adduct was formed. The reason for this low yield was probably the presence of triphenylphosphine which had an inhibiting effect on the reaction.

Clearly, these complexes do not display the stereoselectivity observed in additions to styrene and its derivatives. If one makes the assumption that these catalysts follow a redox catalysis pathway analogous to that shown by $[RuCl_2(PPh_3)_3]$ (Scheme 1.16), then for reasons that are not obvious they appear to be unable to form the tight radical pairs, $\{MCl_n(DIOP)\}\{c\text{-}C_6H_{10}CCl_3\}$, which presumably control the selectivity. Neither is it obvious why reactions involving styrene are stereoselective, however, they may involve additional arene-metal interaction in the radical pair (figure 2.4).

Figure 2.4 : Arene-metal interaction in the radical pair.

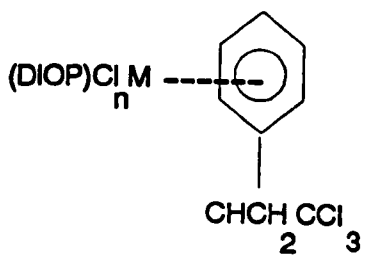


Table 2.7 : Investigation of the effect of ruthenium complexes containing DIOP and DIPHOS ligands on the addition of tetrachloromethane to cyclohexene

CATALYST	CONCENTRATION (mol dm^{-3}) catalyst×10^{-3}	cyclohexene	% YIELD OF (I) (±0.03)	ISOMERIC RATIO (±0.02)	% YIELD OF (III) (±0.03)	% YIELD OF (IV) (±0.01)	OTHER COMMENTS (Benzene used as solvent)
DIOP only	4.48	0.29	not detected	—	—	—	90.5% cyclohexene observed
DIPHOS only	4.58	0.29					93.0% cyclohexene observed
$[RuCl_2(PPh_3)_3]$ /DIOP[a]	2.09	0.29	0.85	1.78	0.15	not detected	95.0% cyclohexene observed green fluorescent solution
$[RuCl_2(PPh_3)_3]$ /DIPHOS[b]	2.25	0.29	0.07	1.16	0.38	not detected	91.0% cyclohexene observed
$[Ru_2Cl_4(DIOP)_3]$	4.88	0.61	5.25	3.51	0.92	0.57	

2.4 Studies of addition reactions catalysed by $[RuCl_2(PPh_3)_3]$

During the course of the survey into the effects of various catalysts on the addition of tetrachloromethane to cyclohexene, it was observed that the yields and the isomeric ratios were considerably increased by changing the solvent from hexane to benzene (section 2.4.2.2). Initially, this was thought to arise as a consequence of a solubility difference of the catalyst. However, at the reaction temperature and concentration used, $[RuCl_2(PPh_3)_3]$ is completely soluble in both solvents. In order to investigate whether there was a solvent effect occurring, a wide range of solvents was studied.

Studies have also been made on the effect of the following upon the efficiency of CCl_4-cyclohexene reactions in the presence of $[RuCl_2(PPh_3)_3]$:

(i) Addition of a resin reported as enhancing phosphine dissociation.

(ii) Variation in the nature of the phosphine ligand.

This section concludes with a preliminary study of the addition of CCl_4 to cyclodienes, particularly cyclohexa-1,3-diene in the presence of $[RuCl_2(PPh_3)_3]$.

2.4.1 An investigation of solvent effects on the addition reaction between tetrachloromethane and alkenes in the presence of $[RuCl_2(PPh_3)_3]$

2.4.1.1. Introduction

In approaching a study on the effect of different solvents in these reactions, it was believed that there were likely to be two important features to be considered. These are :

(i) the effect of a solvent on ligand dissociation of $[RuCl_2(PPh_3)_3]$,

(ii) the effect of a solvent on the free radicals and radical pairs in solution.

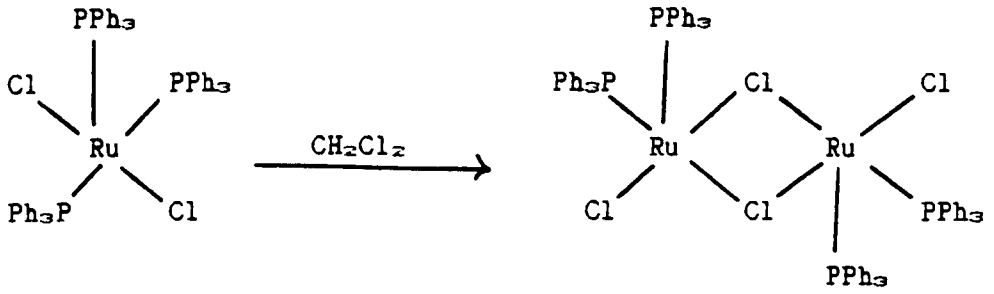
This section provides an introduction to these effects.

(i) Ligand dissociation of $[RuCl_2(PPh_3)_3]$.

It is well known that $[RuCl_2(PPh_3)_3]$ dissociates in various solvents (equation 2.31).

$$[RuCl_2(PPh_3)_3] \rightleftharpoons [RuCl_2(PPh_3)_2] + PPh_3 \qquad (2.31)$$

Consequently, since the active catalytic species has been shown to be $[RuCl_2(PPh_3)_2]$, the catalysis may be influenced by the solvent used and governed by the extent of dissociation in any particular solvent. Previous studies on ligand dissociation of $[RuCl_2(PPh_3)_3]$ are summarised in Table 2.8[12,13]. The dissociative behaviour of $[RuCl_2(PPh_3)_3]$ is affected by the solvent used as Table 2.8 shows. There is ^{31}P NMR evidence that the loss of triphenylphosphine gives rise to a dimeric species (equation 2.32)[13].



(2.32)

An exception to this dissociation is the behaviour of $[RuCl_2(PPh_3)_3]$ in N,N-dimethylacetamide, (DMA) in which it is known that ionisation takes place as shown in equation 2.33.

$$[RuCl_2(PPh_3)_3] + DMA \longrightarrow [RuCl(PPh_3)_3DMA]^+ + Cl^- \qquad (2.33)$$

Table 2.8 : Dissociation of $[RuCl_2(PPh_3)_3]$ in various solvents[12,13]

Solvent	Degree of dissociation (%)	Comments
Benzene	80	Results obtained by UV studies[12] 25°C
N,N-dimethyl-acetamide	100	
Toluene	59	Results obtained by ^{31}P-NMR[13] at -90°C
Trichloromethane	15	
Dichloromethane	15	

(ii) Effect of solvent on free radicals in solution.

Although free radical reactions are not so markedly solvent dependant as ionic reactions, they do display solvent effects. Free radicals are affected in two ways :

(a) internal volume

(b) solvation effects

(a) Internal volume.

The internal volume effect of a solvent restricts the motion of the solute as solvent molecules surround the free radicals (assuming that the solvent is 'regular' and does not undergo any specific solvation effects as well).

For any addition reaction to occur the reactants must diffuse together through the solvent. Consequently, the rate of combination will be dependant on the viscosity of the solvent. Additionally, when the two radicals have diffused through the solution they will be surrounded by solvent molecules effectively forming a cage around them, causing many collisions to occur before they diffuse apart. This effect was observed by Rabinowitch and Wood[14]. A typical example affected by the caging of the solvent is shown in equation 2.34

$$EtN_2Me + h\nu \longrightarrow Et\bullet + N_2 + Me\bullet \quad (2.34)$$

When the ethyl and methyl radicals are restrained by the solvent cage, the most likely product is propane. It is only if they manage to escape from this cage that they will form the symmetrical products ethane and n-butane. Clearly, the proportion of cage combination depends on the type of solvent used. An example of this was

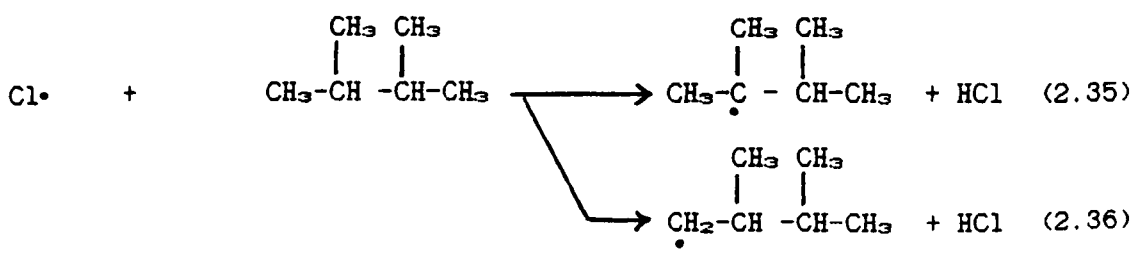
demonstrated by Kochi et al'[5]. A study was carried out on the decomposition of diacylperoxides in pentane and decalin. The results showed a greater yield of the symmetrical dimers formed in the more viscous solvent showing the strong cage effect. In pentane the cross-products were more abundant as the cage effect was less dominant and diffusion could take place more readily.

(b) Solvation effects.

Solvation effects are caused by the solvent not behaving in a 'regular way' and interacting with the reactants, intermediates or products of a free radical process. The effect of such an interaction is observed on the rate and selectivity of a reaction.

Solvation of a transition state lowers the activation energy leading to an increase in the rate, whereas solvation of the reactants leads to a retardation in the rate. Interaction of the solvent molecule with the product molecules has no direct effect on the rate of reaction. Generally, it is known that the more reactive a radical is, the less selective it is in its reactions. Consequently, solvation of the transition state, which increases reaction rate, leads to a decrease in the selectivity.

For these reasons the type of solvent used is of considerable importance. Work carried out by Russell showed that the selectivity of chlorination of alkenes (equtions 2.35 and 2.36) was solvent dependant'[6].



Aliphatic solvents have no effect on the relative selectivity. However, aromatic solvents contribute a significant effect to the solvation of the reactants. It was observed that solvents with electron donating substituents caused increased selectivity, whereas electron withdrawing substituents are least effective as they reduce the electron density of the aromatic ring. The explanation suggested for this is that the aromatic solvent forms as a 'π - complex' with the chlorine atom in an equilibrium process and it is this complex that reacts with the alkane. Since complex formation stabilizes the Cl atom, it reduces its reactivity and increases its selectivity.

$$Cl\bullet + C_6H_5X \longrightarrow [Cl\cdots\cdots C_6H_5X]^{\bullet} \qquad (2.37)$$

$$[Cl\cdots\cdots C_6H_5X]^{\bullet} + RH \longrightarrow R\bullet + C_6H_5X + HCl \qquad (2.38)$$

The more of the complex formed the more selective the reaction becomes.

2.4.2 Results and discussion.

The effect of the solvent on the reaction between CCl_4 and alkenes in the presence of $[RuCl_2(PPh_3)_3]$ is complicated as there are several steps in the reaction which may be subject to solvent effects. The mechanism for the addition of CCl_4 to alkenes in the presence of $[RuCl_2(PPh_3)_3]$ is given in steps (2.39)-(2.42).

$$[RuCl_2(PPh_3)_3] \rightleftharpoons [RuCl_2(PPh_3)_2] + PPh_3 \qquad (2.39)$$

$$[RuCl_2(PPh_3)_2] + CCl_4 \rightleftharpoons \{RuCl_3(PPh_3)_2\bullet\}\{CCl_3\bullet\} \qquad (2.40)$$

$$\{RuCl_3(PPh_3)_2\bullet\}\{CCl_3\bullet\} + RCH{=}CH_2 \rightarrow \{RuCl_3(PPh_3)_2\bullet\}\{R\dot{C}HCH_2CCl_3\} \qquad (2.41)$$

$$\{RuCl_3(PPh_3)_2\bullet\}\{R\dot{C}HCH_2CCl_3\} \rightarrow [RuCl_2(PPh_3)_2] + RCHClCH_2CCl_3 \qquad (2.42)$$

The solvent may affect both the dissociation of $[RuCl_2(PPh_3)_3]$ and have various effects on the free radicals and intermediates in the reaction. However, it is suggested that the solvent will predominate in the following processes :-

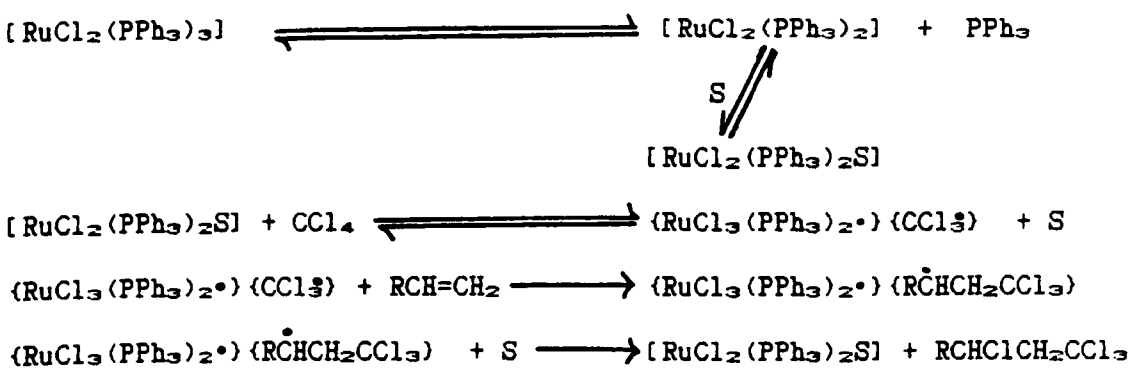
(1) The dissociative step (2.39). The dissociation of the catalyst involves the formation of the active species, (provided this does not dimerise immediately) so will presumably increase the yield of the products if it is present in a greater quantity. This area was investigated and will be discussed in section 2.4.2.1.

(2) The yield of products should be increased when the solvent is able to trap the radical pairs together, so enabling them to react. Therefore the physical properties of the solvent will become important, particularly viscosity.

(3) The reaction will be affected if the solvent is able to solvate $[RuCl_2(PPh_3)_2]$. This may be beneficial as it may prevent dimer formation.

(4) The solvent may also solvate the $[RuCl_3(PPh_3)_2]$ species which would be detrimental, as it would separate the radical pairs. If the mechanism is rewritten in the light of these suggestions (scheme 2.6), the importance of the solvent becomes apparent.

Scheme 2.6 : Effect of a solvent on the mechanism.



2.4.2.1 Investigation of the dissociation of $[RuCl_2(PPh_3)_3]$ by ^{31}P-NMR at low temperatures.

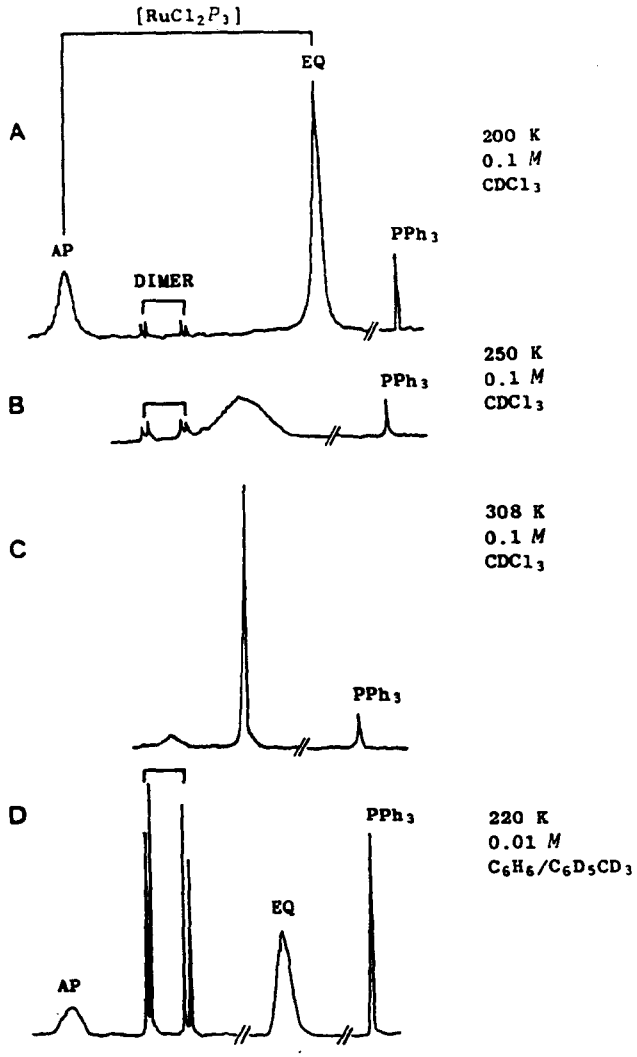
As the proposed mechanism involves the dissociation of the $[RuCl_2(PPh_3)_3]$ complex, the previously reported studies concerning the loss of triphenylphosphine are relevant[12,13]. An investigation of the above mentioned complex in dichloromethane suggests 15 % dissociation (Table 2.8). This was repeated in the present work and a value of 14 % dissociation was obtained (Table 2.8). The work was limited to solvents which did not freeze at -60°C. Therefore the dissociation was studied in toluene, dichloromethane, acetone, tetrahydrofuran and ethanol (Table 2.9).

Table 2.9 : Dissociation study of $[RuCl_2(PPh_3)_3]$ by ^{31}P-NMR.

Solvent Dissociation	Initial concentration (mol dm^{-3}) X 10^{-3}	Dissociation constant (mol dm^{-3}) X 10^{-4}	% Dissociation
Toluene	9.44	15.7	33
Dichloromethane	9.04	2.0	14
Acetone	2.19	1.3	21
	5.37	4.0	24
Tetrahydrofuran	7.20	30.2	47
Ethanol	9.03	-	100

The spectra obtained and a worked example of the dissociation constant and the percentage dissociation are shown in the appendices 2 and 3. A spectrum obtained from the literature is shown in Fig 2.7[17]. This illustrated that triphenylphosphine is obtained as well as indicating that dissociation is taking place, as two signals are recorded for the non-equivalent phosphines in this complex. As the sample is warmed, the phosphines interchange more rapidly so that only one signal is observed at 308 K. At low temperatures signals due to the dimer can also be observed. In the present work, this type of spectrum was observed in all the solvents mentioned above, except for ethanol. In this case, only one signal attributed to triphenylphosphine arose, indicating that the $[RuCl_2(PPh_3)_3]$ complex was fully dissociated. It should be noted that the value for the % dissociation of $[RuCl_2(PPh_3)_3]$ in toluene was significantly different from the

Figure 2.5 : Variable temperature ^{31}P NMR spectra of $[RuCl_2(PPh_3)_3]$.



literature value. The likely reason for this discrepancy is inaccuracy in the temperature control.

2.4.2.2 Investigating the reaction between oct-1-ene and CCl_4 in the presence of $[RuCl_2(PPh_3)_3]$ in various solvents.

As will be described in more detail in the experimental section, all the reactions were carried out in sealed tubes. The results are recorded in Table 2.10.

A comparison of the yield of 1,1,1,3-tetrachlorononane obtained with the degree of dissociation of $[RuCl_2(PPh_3)_3]$ is shown in figure 2.6. There is no clear relationship between the two, suggesting that the dissociation of $[RuCl_2(PPh_3)_3]$ is not of overriding importance.

A comparison of yields and solvent viscosity was also made (Table 2.10). It was found that the yield correlated reasonably well with viscosity for most of the solvents studied, (figure 2.7). The solvents which did not fit in well were ethanol, methanol, dichloromethane and, to a lesser extent, ethyl acetate. It is proposed that in the case of these solvents, with the exception of dichloromethane, the $[RuCl_3(PPh_3)_2^{\bullet}]$ species becomes strongly solvated so is unable to form tight radical pairs.

Therefore the donating abilities of these solvents were considered. The ability to donate can be expressed by an empirical parameter, defined as the negative enthalpy ΔH value in $Kcalmol^{-1}$ for the interaction of the electron pair with antimony(V) chloride in a highly diluted solution of dichloromethane, or the donor number, DN'[8]. The DN's for three of these solvents are very similar (Table 2.11).

Table 2.10 : Investigating solvent effects on the reaction between oct-1-ene and CCl_4 in the presence of $RuCl_2(PPh_3)_3$].

Solvent	Viscosity (at 25°C) X 10^{-3} (Pa.s)	% Yield of TCN* (±1.0)
Hexane	0.299	41.7
Cyclohexane	0.898	90.4
Toluene	0.552	59.0
Benzene	0.603	63.2
Tetrahydrofuran	0.460	51.0
Acetone	0.304	43.2
Ethyl acetate	0.426	42.6
Ethanol	1.078	44.0
Methanol	0.545	50.3
Dichloromethane	0.411	79.0

*TCN -1,1,1,3-Tetrachlorononane (GLC) yield based on oct-1-ene charged.

Fig 2.6 : Effect of $[RuCl_2(PPh_3)_3]$ dissociation on CCl_4 addition to oct-1-ene

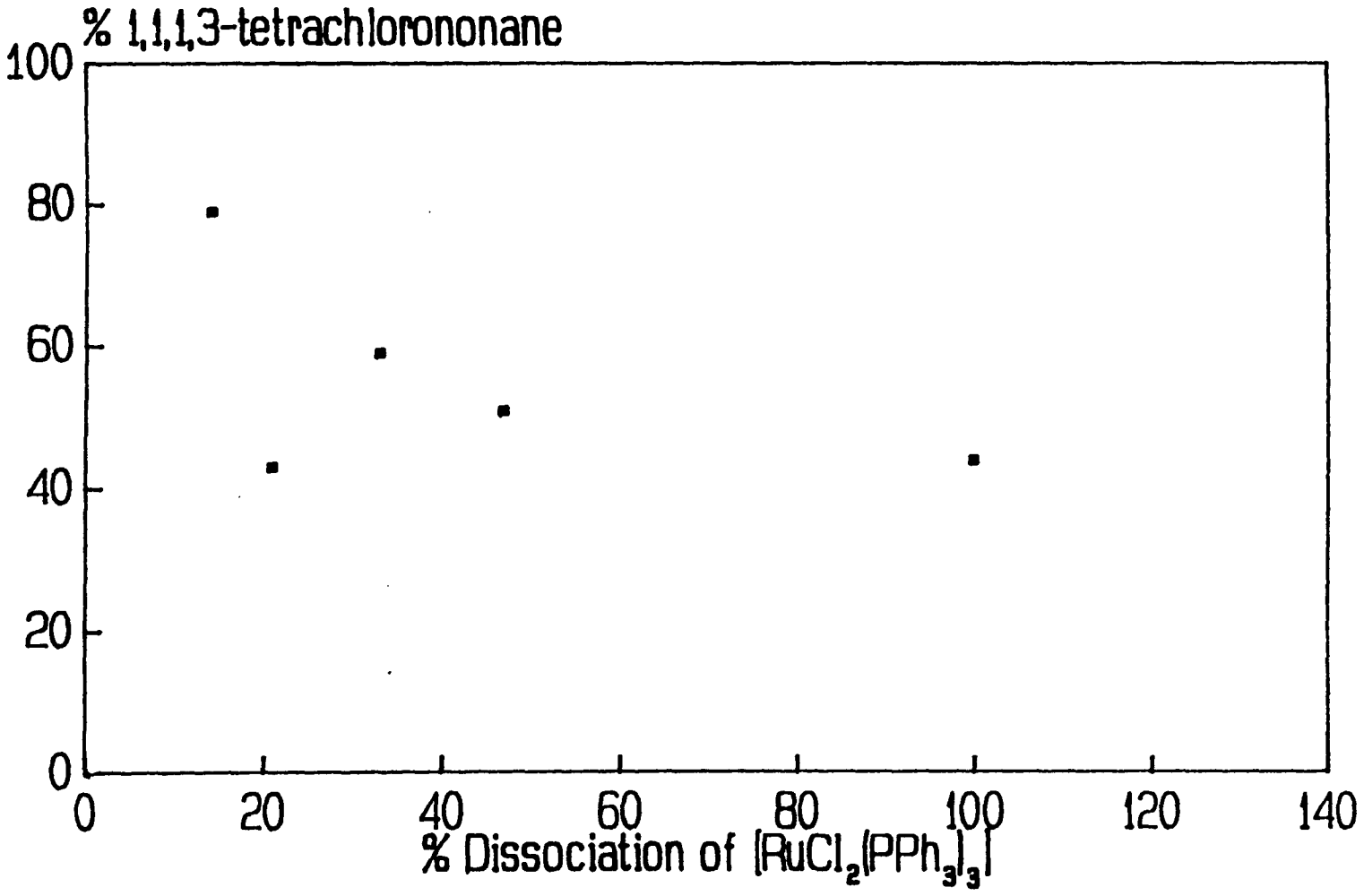


Fig 2.7 : Addition of CCl_4 to oct-1-ene in the presence of $[RuCl_2(PPh_3)_3]$

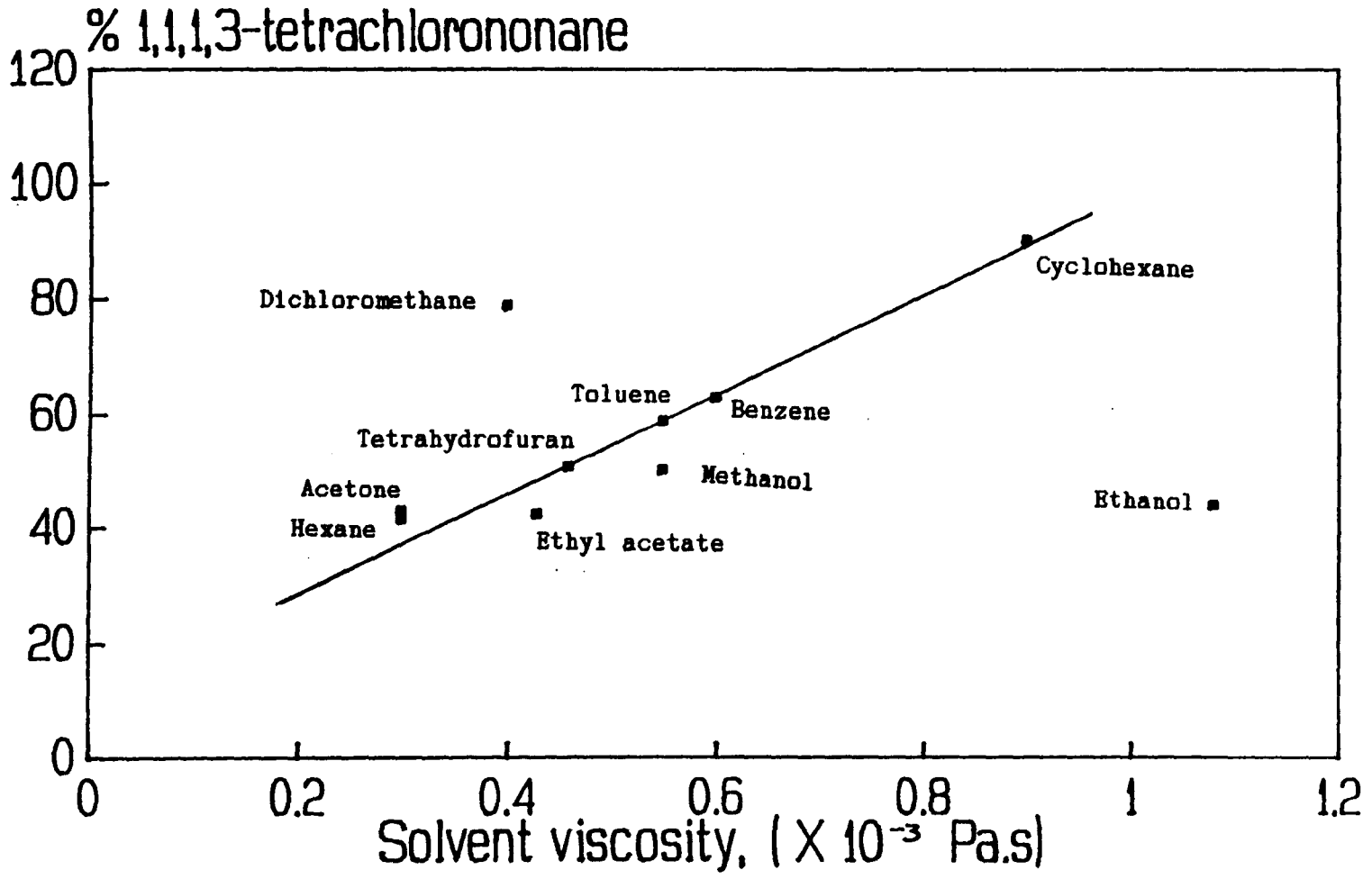


Table 2.11 : Correlation of donor numbers[19] and % yield of (I).

Solvent	Donor number	Acceptor number	% Yield of TCN
Methanol	19.0	41.3	50.3
Ethanol	18.0	37.1	44.0
Ethyl acetate	17.0	-	42.6
Dichloromethane	1.0	20.4	79.0
Hexane	0.0	0.0	41.7
Cyclohexane	0.0	0.0	90.4
Benzene	0.1	8.2	63.2
Toluene	0.1	-	59.0
Acetone	17.0	12.5	43.2
Tetrahydrofuran	20.0	8.0	51.0

In the same way, the acceptor properties of a given solvent relative to those of antimony(V) chloride are termed as an acceptor number, (AN). (These are dimentionless numbers)[19].

Returning to the solvents under consideration, Table 2.11 shows that methanol, ethanol, and ethyl acetate all have similar values of DN's and AN's. Furthermore, there is a great similarity in the yield of 1,1,1,3-tetrachlorononane at 42-50 % . These yields are only 1-9 % greater than in hexane which suggests that these solvents solvate the $[RuCl_2(PPh_3)_2]$ radicals to a small extent or, alternatively, extensively solvate $[RuCl_3(PPh_3)_2]$ hence minimising the yield of 1,1,1,3-tetrachlorononane. The reason why the yield of product is so high in the case of dichloromethane in comparison to the

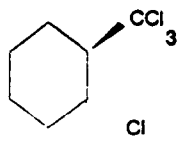
others is unclear, as this solvent does not dissociate the catalyst strongly, it does not solvate to an appreciable degree as expressed by the DN value and it is not particularly viscous.

A comparison of the DN's for the well behaved solvents, such as hexane, shows that the DN's do not have an overriding effect on the yield. This is exemplified in the case of acetone and hexane which have significantly different DN's, but similar yields of 1,1,1,3-tetrachlorononane, (Table 2.11).

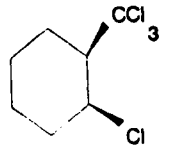
2.4.2.3 Investigation of the solvent effects on the reaction between cyclohexene and tetrachloromethane in the presence of $[RuCl_2(PPh_3)_3]$.

There was a significant difference observed in the yield and isomeric ratio of adduct when the above reaction was studied in hexane and benzene (section 2.3.2.2). Further studies have been carried out in a greater range of solvents so as to compare any trends with the addition reaction between oct-1-ene and CCl_4. This reaction is of particular value as it has the added feature of an isomeric ratio. The usefulness of such a property is that it provides an indication of the type of solvation occurring.

The isomeric ratio of the adduct is measured in terms of the ratio of areas (obtained by GLC). The two isomers produced are



Trans



Cis

It is clear from steric considerations that the trans isomer is favoured. Therefore the ratio of isomers can be described as a measure of the selectivity of the addition reaction.

The reaction was carried out in an identical manner as that of oct-1-ene and tetrachloromethane (described in sect 2.5) so that the results could be compared. However, blank reactions were carried out between both dichloromethane and trichloromethane and cyclohexene in the absence of tetrachloromethane (Table 2.12). There were no products observed in the case of dichloromethane. However, a small quantity of adduct (0.4 %) was formed in an unexpectedly high isomeric ratio for the trichloromethane case. This ratio is not considered to be too meaningful since the low yield means that measurement was made on very small areas, which means that any error could cause a large change in the trans : cis ratio. The reaction between cyclohexene and tetrachloromethane in the presence of $[RuCl_2(PPh_3)_3]$ was also carried out in excess tetrachloromethane, which gave a yield of 54.4 % in an isomeric ratio of 6.2 : 1. These are intermediate values for both yield and isomeric ratio as will be appreciated later.

Firstly, as in the addition reaction between oct-1-ene and tetrachloromethane, the relationship between dissociation of $[RuCl_2(PPh_3)_3]$, yield and isomeric ratio were studied and are represented in figure 2.8. However, although the trends were broadly similar to those shown in figure 2.6, no distinct correlation was observed. Therefore it was supposed that this feature was not of overwhelming importance on the outcome of the reaction. Furthermore, when the effect of the solvent viscosity of a wide range of solvents was investigated on this reaction (Table 2.13) there was no apparent correlation, figure 2.9. In general it seems that for this wide range of differing solvents there are many effects taking place so it may be

too complicated to disentangle completely. However, some of the effects taking place can be explained if the solvents are divided into the following groups :

(i) saturated hydrocarbon

(ii) aromatic

(iii)other

Fig 2.8 : Effect of $[RuCl_2(PPh_3)_3]$ dissociation on CCl_4 addition to cyclohexene

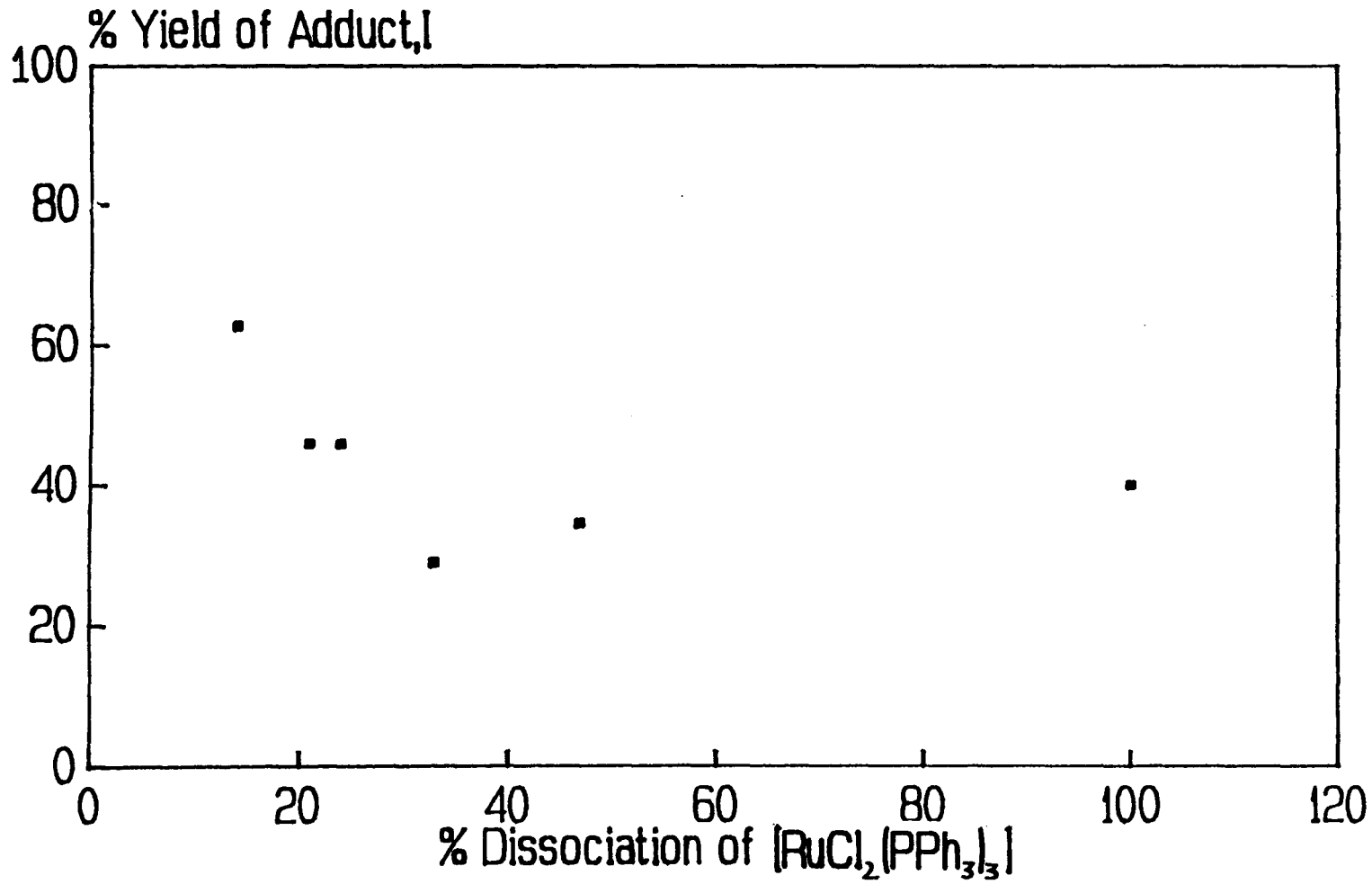


Table 2.12 : Investigating the reactions between cyclohexene and haloalkanes in the presence of $[RuCl_2(PPh_3)_3]$

Haloalkane	%Yield of (I)* (+0.05)	Isomeric ratio	%Yield of (III)* (+0.05)	%Yield of (IV)* (+0.06)
Dichloromethane	-	-	-	-
Trichloromethane	0.40	9.03	1.01	0.52
Tetrachloromethane	54.4	6.21	4.60	1.54

* GLC Yields based on cyclohexene charged.

(I) 1-chloro-2-(trichloromethyl)cyclohexane,

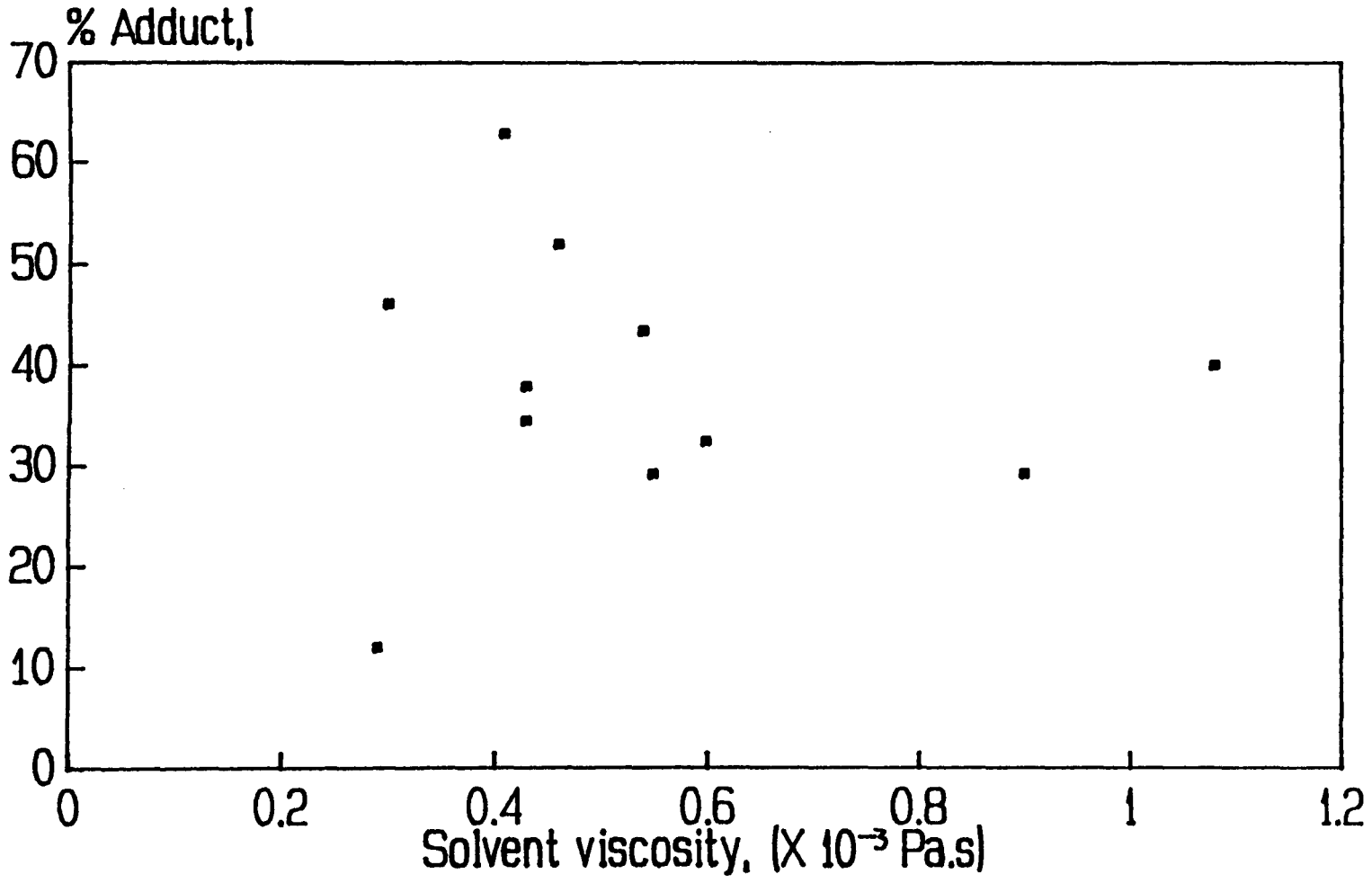
(III) 3-(trichloromethyl)cyclohex-1-ene,

(IV) (trichloromethyl)cyclohexane.

Table 2.13 : Investigation of solvent effects on the reaction between cyclohexene and CCl_4 in presence of $[RuCl_2(PPh_3)_3]$

SOLVENT	VISCOSITY ($\times 10^{-3}$) (pa.s) (at 25 °C)	% YIELD OF (I) (±1.1)	ISOMERIC RATIO OF (I) (±0.05)	% YIELD OF (III) (±0.03)	% YIELD OF (IV) (±0.01)
Hexane	0.299	12.0	4.99	2.60	0.08
Cyclohexane	0.898	29.2	7.42	2.44	0.04
Toluene	0.552	29.2	7.12	4.52	0.98
Benzene	0.603	32.5	7.08	4.06	0.04
Trichloromethane	0.460	52.5	7.27	2.55	not detected
Dichloromethane	0.411	62.8	7.43	4.98	0.04
Tetrahydrofuran	0.426	34.6	9.01	1.30	0.06
Acetone	0.304	46.1	8.41	1.30	0.13
Ethyl acetate	0.426	38.0	8.25	0.71	1.75
Ethanol	1.078	40.0	5.86	3.15	1.15
Methanol	0.545	43.4	5.28	1.59	0.04
Diglyme	-	48.4	5.80	1.80	2.06

Fig 2.9 : Addition of CCl_4 to cyclohexene in the presence of $[RuCl_2(PPh_3)_3]$



(i) Effect of saturated hydrocarbon solvents

Viscosity effects are clearly observed for this group of solvents. The yields, compared to other solvents, are much lower, probably because saturated hydrocarbon solvents are unable to coordinate to metal centres (Table 2.14). However, a good correlation is observed between % yield of adduct (and total % yield of products), isomeric ratio, and the viscosity (measured at 30 °C)[19]. The correlation shows that the yield increases when the viscosity is increased, suggesting that the radical pairs become trapped together, so giving them a greater opportunity to react (figures 2.10, 2.11). This was confirmed by the isomeric ratio as it also increases with viscosity. There is also good correlation between total yield of products and the solvent viscosity. The total yield was chosen as a parameter as both products, (II) and (III) are derived from (I).

(ii) Effect of aromatic solvents

In these solvents, (Table 2.15) there again is a good relationship between viscosity (measured at 25°C)[20] and yield of adduct. The same correlation occurs for total % yield of products with viscosity, figure 2.12. The greatest yield (71.7 %) is observed in the case of 1,2-dichlorobenzene. This cannot be purely a viscosity effect, as decalin has an eight times greater viscosity, but the yield is only 31.3 %. There is no obvious explanation for this difference. In a series of related solvents, such as the aromatics, yields can be linked to solvation abilities. The physical property of donor numbers[19] was considered where this data was available and a relationship between yield and donor number is shown in figure 2.13. This clearly illustrates that as the donor nature of the solvent is increased the yield (and to some extent isomeric ratio) is reduced.

Table 2.14 : Investigation of the effect of various saturated hydrocarbon solvents on the reaction between cyclohexene and CCl_4 in the presence of $[RuCl_2(PPh_3)_3]$

SOLVENT	VISCOSITY ($\times 10^{-3}$)(Pa.s) (at 30 °C)	% YIELD OF (I)[a] (±1.0)	ISOMERIC RATIO OF (I) (±0.05)	% YIELD OF (III)[a] (±0.05)	% YIELD OF (IV)[a] (±0.01)	% TOTAL YIELD OF PRODUCTS [a]
n-Pentane	0.215	9.0	3.51	2.77	0.76	12.53
n-Hexane	0.283	12.0	4.49	2.60	0.08	14.68
n-Octane	0.485	15.1	4.61	2.18	1.48	18.76
Cyclohexane	0.824	29.2	7.42	2.44	0.09	31.73
Methylcyclohexane	0.639	24.0	5.10	1.32	3.44	28.76
Cycloheptane	1.64	33.5	6.70	6.55	3.73	43.78
Decalin	8.00	31.3	6.40	11.6	7.40	50.30

[a] % Yield (GLC) based on cyclohexene charged

Reaction mixture used in ratio 400:125:1 of CCl_4 : cyclohexene : $[RuCl_2(PPh_3)_3]$

(I) 1-chloro-2-(trichloromethyl)cyclohexane

(III) 3-(trichloromethyl)cyclohex-1-ene

(IV) (trichloromethyl)cyclohexane

Fig 2.10 : Addition of CCl_4 to cyclohexene in saturated hydrocarbon solvents .

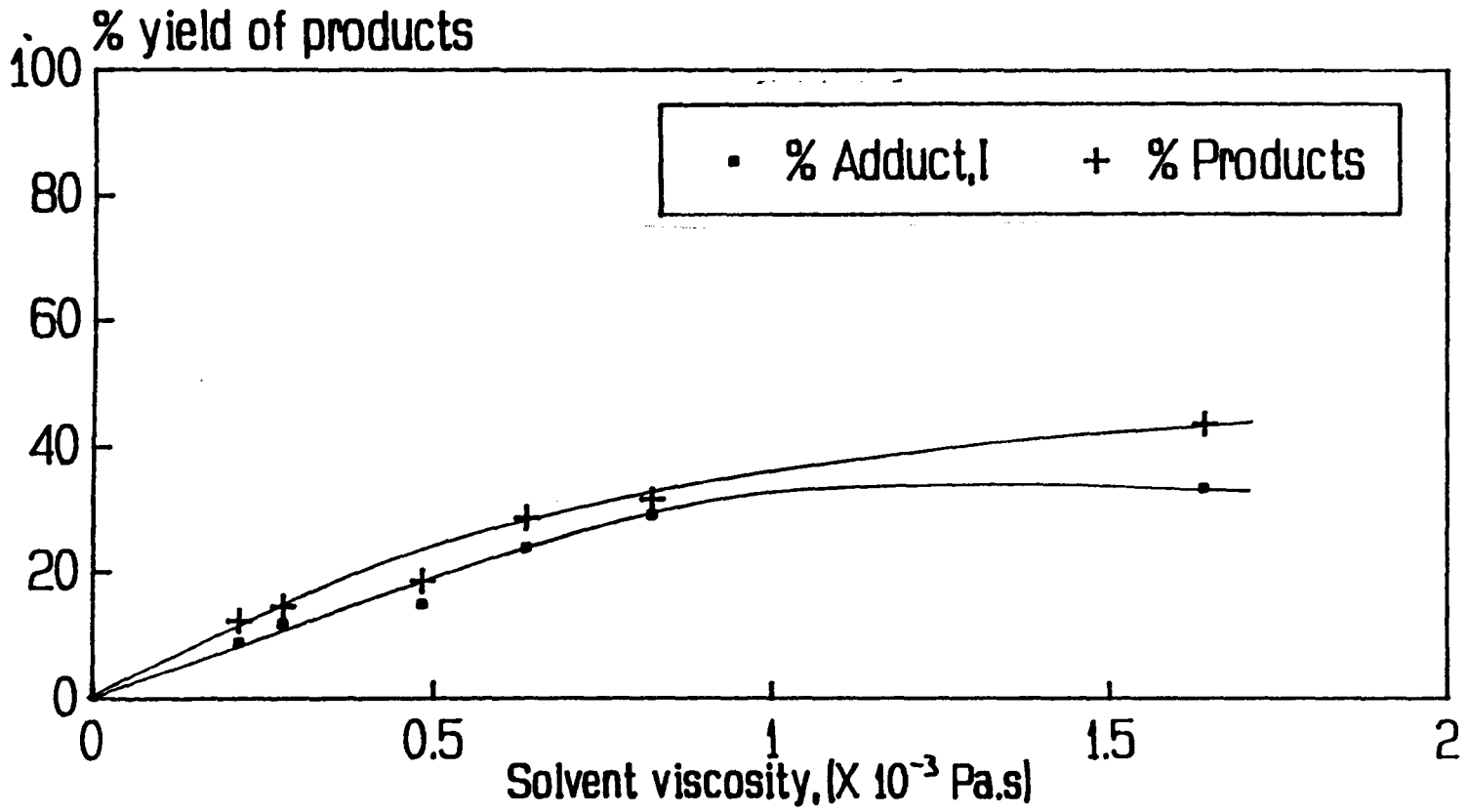


Fig 2.11 : Addition of CCl_4 to cyclohexene in hydrocarbon solvents.

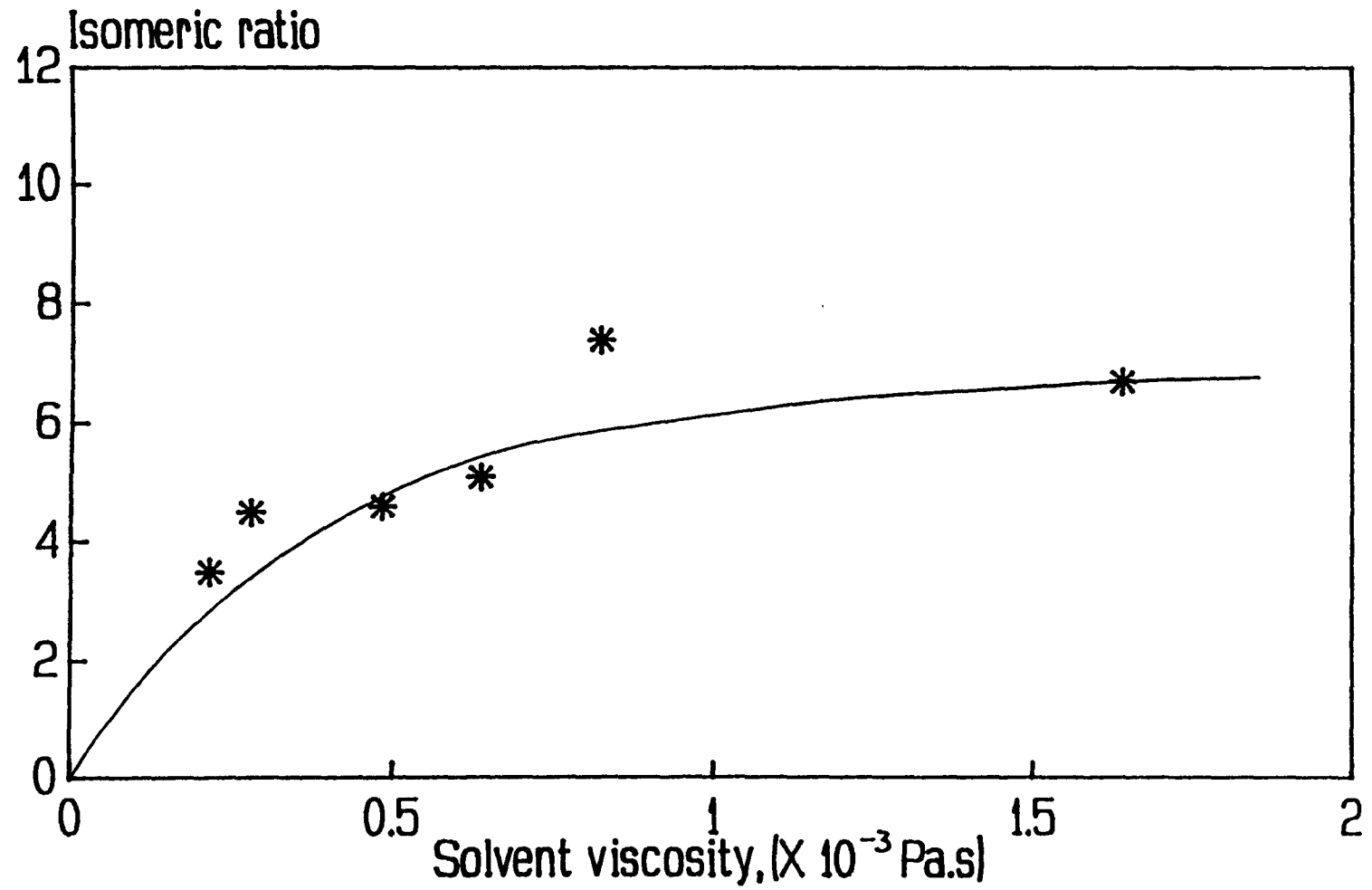


Table 2.15 : Investigation of the effect of aromatic solvents on the reaction between cyclohexene and CCl_4 in the presence of $[RuCl_2(PPh_3)_3]$

SOLVENT	VISCOSITY ($\times 10^{-3}$)(Pa.s) (at 25°C)	% YIELD OF (I)[a] (±1.0)	ISOMERIC RATIO OF (I) (±0.2)	% YIELD OF (III)[a] (±0.4)	% YIELD OF (IV)[a] (±0.02)
Benzene	0.603	32.5	7.08	4.06	0.04
Toluene	0.552	29.2	7.12	4.52	0.98
1,2-dichlorobenzene	1.324	71.7	6.65	3.00	7.35
1,2-dimethylbenzene	0.754	32.2	5.93	5.68	1.85
1,3-dimethylbenzene	0.579	28.8	7.62	3.50	1.00
Bromobenzene	1.012	55.8	6.51	2.58	3.67
Nitrobenzene	1.795	0.6	2.46	not detected	not detected
Methoxybenzene	0.895	15.5	5.78	2.60	1.00

[a] % Yield (GLC) based on cyclohexene charged

Reaction mixture used in ratio 400:125:1 of CCl_4 : cyclohexene : $[RuCl_2(PPh_3)_3]$

(I) 1-chloro-2-(trichloromethyl)cyclohexane

(III) 3-(trichloromethyl)cyclohex-1-ene

(IV) (trichloromethyl)cyclohexane

Fig 2.12 : Addition of CCl_4 to cyclohexene in aromatic solvents.

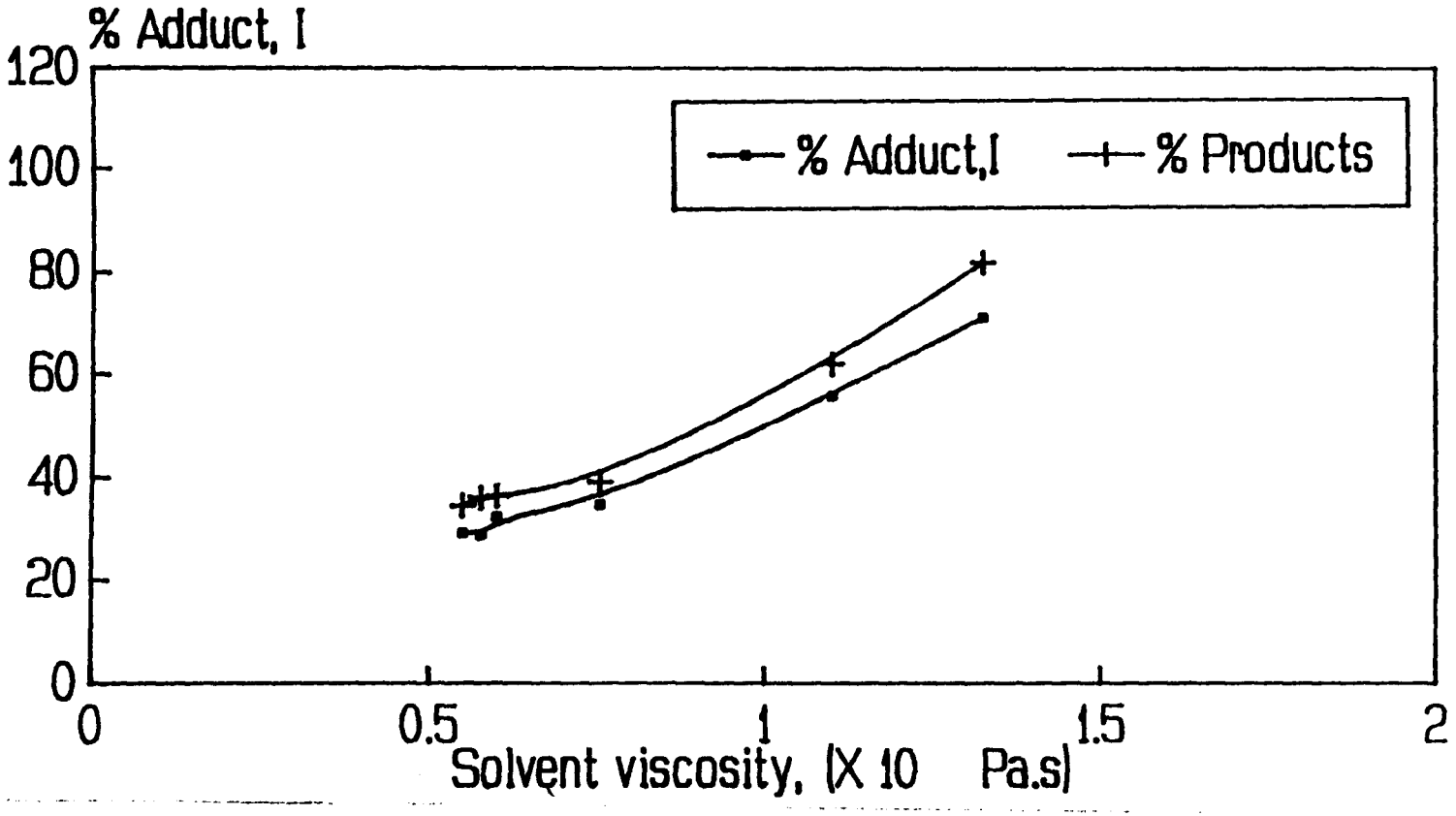
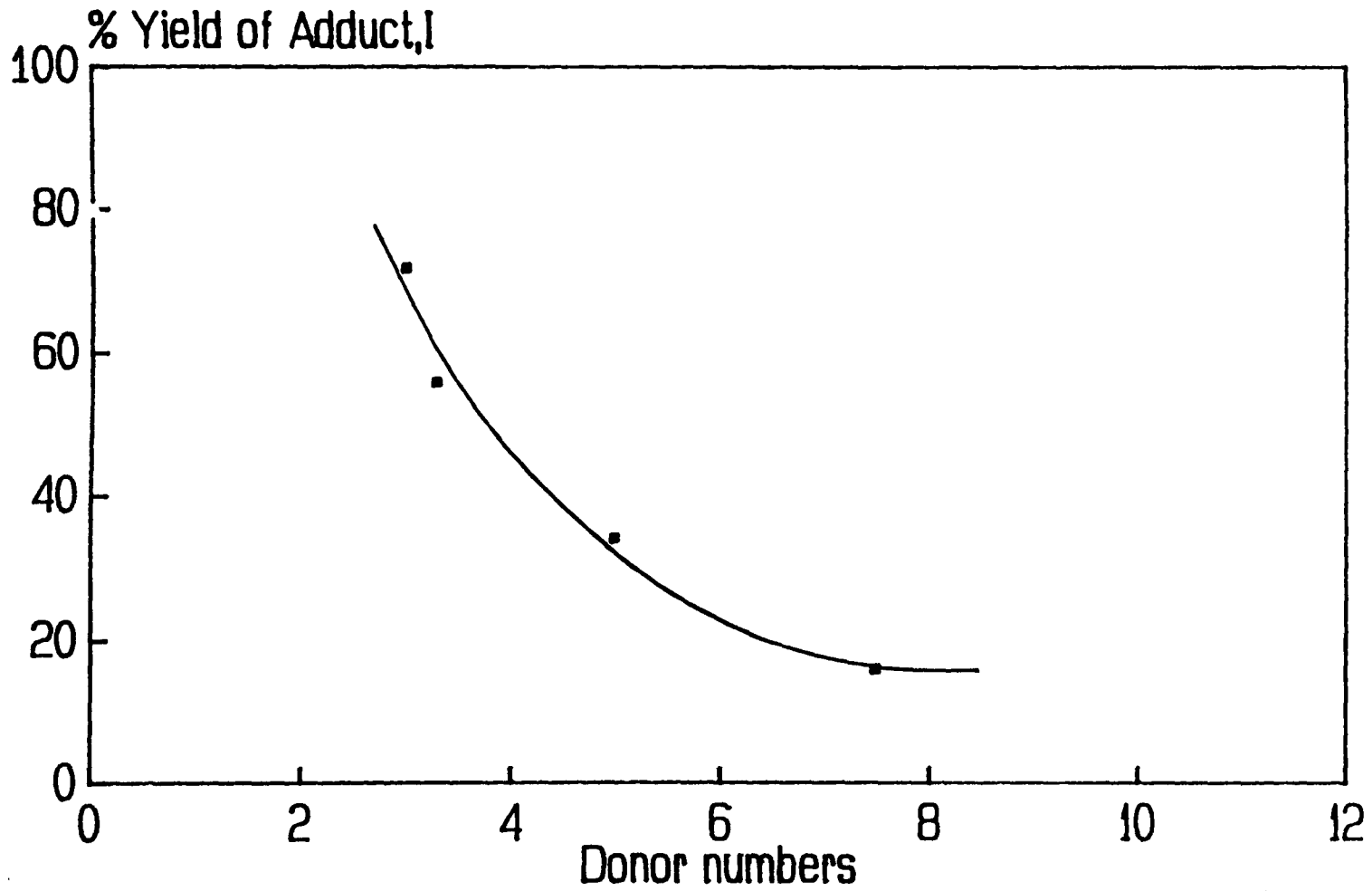


Fig 2.13 : Effect of solvent donicity on CCl_4 addition to cyclohexene



(The donor number of benzene is too small to be included). If the donor nature increases, it may be suggested that the solvent coordinates not only the $[RuCl_2(PPh_3)_2]$, which would be beneficial, and that the overriding factor must be the solvation of $[RuCl_3(PPh_3)_2]$ radicals resulting in reduced yields causing the separation of radical pairs. The isomeric ratio is not affected to any significant extent either by viscosity or donor number, only changing by + 1 unit.

Finally, the reaction was also carried out in nitrobenzene (NB) which caused the yield to decrease to 0.6 %. However, it is known that nitrobenzene solutions of $[RuCl_2(PPh_3)_3]$ are pale yellow and conduct electricity. It is known from other studies that ionisation takes place.

$$[RuCl_2(PPh_3)_3] + NB \rightleftharpoons [RuCl(PPh_3)_3NB]^+ + Cl^- \quad (2.43)$$

Additionally the formation of a dinuclear ion has been suggested

$$2[RuCl_2(PPh_3)_3] \rightleftharpoons [Ru_2Cl_3(PPh_3)_6]^+ + Cl^- \quad (2.44)$$

but this complex has not been isolated from a nitrobenzene solution . This reaction has to be compared with N,N-dimethylacetamide (DMA) in which it is known that the catalyst behaves similarly as suggested in (2.45)

$$[RuCl_2(PPh_3)_3] + DMA \rightleftharpoons [RuCl(PPh_3)_3DMA]^+ + Cl^- \quad (2.45)$$

Table 2.16 : Investigation of the effect of strongly dissociative solvents on the reaction between cyclohexene and CCl_4 in the presence of $[RuCl_2(PPh_3)_3]$

SOLVENT	VISCOSITY ($\times 10^{-3}$)(Pa.s) (at 25 °C)	% YIELD OF (I)[a] (±0.2)	ISOMERIC RATIO OF (I) (±0.02)	% YIELD OF (III)[a] (±0.01)	% YIELD OF (IV)[a] (±0.01)
Acetonitrile	0.341	1.2	2.10	not detected	
N,N-dimethylacetamide	0.880	18.7	5.29	0.61	2.18

% Yield (GLC) based on cyclohexene charged

Reaction mixture used in ratio 400:125:1 of CCl_4 : cyclohexene : $[RuCl_2(PPh_3)_3]$

(I) 1-chloro-2-(trichloromethyl)cyclohexane

(III) 3-(trichloromethyl)cyclohex-1-ene

(IV) (trichloromethyl)cyclohexane

However, in this solvent the yield is comparatively high at 18.7 % (Table 2.16). The viscosity of nitrobenzene is 1.7795×10^{-3} Pa.s (25°C) whilst that of N,N-dimethylacetamide is only 0.88×10^{-3} Pa.s (25°C), therefore this greater yield cannot be accounted for in terms of viscosity. It is possible that in nitrobenzene a greater proportion of the catalyst becomes ionised, reducing its catalytic abilities. The isomeric ratio in N,N-dimethylacetamide is comparable to the values obtained in hydrocarbon solvents suggesting that the most important factor involved in this case is viscosity.

(iii) Effect of other solvents.

The remaining solvents studied, acetone, methanol, ethanol, ethyl acetate and tetrahydrofuran (Table 2.13) do not show a clear relationship between yield of adduct and viscosity, whilst the isomeric ratio shows a very random pattern. Therefore viscosity is not a very important factor in the case of these solvents. In the same way the donor numbers do not correlate at all with yield or isomeric ratio. It is suggested that in these solvents, where the yields are relatively high compared to hydrocarbons and the isomeric ratio are low, adverse solvation of $[RuCl_3(PPh_3)_2]$ is overidden by the solvation of $[RuCl_2(PPh_3)_2]$. The same applies to diglyme (bis-γ-methoxyethyl ether). However in this solvent the yield is higher, as it has the the additional benefit of having an exceptionally high viscosity.

The only remaining solvents which were studied were trichloromethane and dichloromethane. In these the yields are exceptionally high for both reactions considered, suggesting that perhaps it is caused by an effect on $[RuCl_2(PPh_3)_3]$. It is feasible

that in these solvents the $[RuCl_2(PPh_3)_3]$ can react directly with tetrachloromethane, prior to triphenylphosphine dissociation.

$$[RuCl_2(PPh_3)_3] + CCl_4 \xrightarrow{CH_2Cl_2} \{RuCl_3(PPh_3)_3^{\bullet}\}\{CCl_3^{\bullet}\} + CH_2Cl_2 \quad (2.46)$$

$$\Updownarrow$$

$$\{RuCl_3(PPh_3)_2^{\bullet}\}\{CCl_3^{\bullet}\} + PPh_3 \quad (2.47)$$

Possibly the catalyst behaves in the same way when 1,2-dichlorobenzene and bromobenzene are used, as similar yields and isomeric ratios are obtained.

The study shows that the solvent employed plays a very important role in catalysed addition reactions. The physical properties that were shown to dominate were viscosity and solvation abilities of the solvents.

2.4.2 Effect of a polymeric co-factor on $[RuCl_2(PPh_3)_3]$ catalysis of the reaction between cyclohexene and tetrachloromethane.

2.4.2.1 Introduction

Studies carried out by Bergbreiter et al suggest that some polymeric reagents are capable of absorbing triphenylphosphine from solutions containing triphenylphosphine complexes of rhodium(I) and ruthenium(II)[21]. When complexes of this type are used as catalysts for the hydrogenation of alkenes, an increased rate of reaction was observed in the presence of the polymeric reagent. All the catalysts used involve a dissociative mechanism of the type shown below to generate the active species.

$$ML_n \rightleftharpoons ML_{n-1} + L \qquad (2.48)$$

Thus, removal of the uncoordinated ligand, L, increases the concentration of the active species, ML_{n-1}, thereby increasing the rate of hydrogenation. For some of the catalysts studied, the mechanism of generating the active species involves oxidative addition of hydrogen (equation 2.49), followed by reductive elimination of an alkyl halide (equation 2.50) :

$$MX + H_2 \rightleftharpoons MH_2X \qquad (2.49)$$

$$MH_2X \rightleftharpoons MH + HX \qquad (2.50)$$

The authors suggest that in cases where this mechanism is followed, the presence of a polymeric reagent is still beneficial as it may also absorb HX. The catalysts studied included $[RhH(CO)(PPh_3)_3]$,

$[RuH_2(PPh_3)_3]$ and $[RuH(OCOCH_3)(PPh_3)_3]$, which all showed modest increases in the rate of hydrogenation (Table 2.17).

Table 2.17: Effect of silver (I) polystyrene sulphonate as a co-factor on the alkene hydrogenations catalysed by various metal phosphine complexes.

Metal phosphine complex	Alkene	Relative rate.
$[RuH_2(PPh_3)_3]$	Hex-1-ene	1.4
$[RuH_2(PPh_3)_3]$	Styrene	1.1
$[RuH(OCOCH_3)(PPh_3)_3]$	Hex-1-ene	1.4
$[RuH(OCOCH_3)(PPh_3)_3]$	Styrene	1.6
$[RhH(CO)(PPh_3)_3]$	Styrene	1.4
$[RhH(CO)(PPh_3)_3]$	Hex-1-ene	1.0
$[IrCl(CO)(PPh_3)_2]$	Styrene	1.0

For $[RuCl_2(PPh_3)_3]$ and $[RuHCl(PPh_3)_3]$ much greater increases in the rate of hydrogenation were observed (the hydrogen uptake increasing eleven fold in the case of $[RuCl_2(PPh_3)_3]$). However, it was proposed that this extra catalyst activation was due to absorption of both triphenylphosphine[21] and hydrogen chloride, as in the presence of bases $[RuCl_2(PPh_3)_3]$ is known to form $[RuHCl(PPh_3)_3]$ (equation 2.51)[21] :

$$[RuCl_2(PPh_3)_3] + H_2 \xrightarrow[C_7H_8,\ 109^{\circ}C]{Et_3N} [RuHCl(PPh_3)_3] + [Et_3NH]Cl + PPh_3 \quad (2.51)$$

The polymeric reagent or resin used in all these experiments was prepared from Amberlyst 15 (a commercially available ion exchange resin) consisting of sulphonated cross-linked polystyrene, $PS-SO_3H$. The acidic proton can be exchanged with various metal ions such as copper(II), cobalt(II), nickel(II) and silver(I). However, the most effective co-factor proved to be the silver salt which was then used throughout the work. Since the addition of halocarbons to alkenes in the presence of $[RuCl_2(PPh_3)_3]$ is known to proceed by a mechanism which involves a phosphine dissociation step (section 2.4.1), an investigation was made of the use of this co-factor in a reaction of this type.

2.4.2.2 Results and dicussion

The polymeric co-factor was prepared as reported in the literature[21]. The reaction between cyclohexene and tetrachloromethane catalysed by $[RuCl_2(PPh_3)_3]$ was carried out in the presence and absence of the resin at various temperatures. When the reaction was carried out using 4.75×10^{-3} mol dm^{-3} of $[RuCl_2(PPh_3)_3]$ there was a small increase in the yield of adduct in the presence of the resin, (varying between between 0.5 and 1.9 %) at each temperature studied (Table 2.18). Other products, 3-(trichloromethyl)cyclohex-1-ene and (trichloromethyl)cyclohexane were observed both in the presence and absence of the resin. Under most conditions studied, the yield of both of these by-products was increased in the presence of resin. In addition to these side products, two other products were only observed in the presence of the resin, but these could not be identified. It is thought that they are similar to the adduct due to their comparable retention times (Appendix 4). The yield of addition product appears independent of the amount of resin used. This reaction was repeated

Table 2.18 : Effect of silver (I) polystyrene sulphonate as a co-factor on the reaction between cyclohexene and tetrachloromethane catalysed by $[RuCl_2(PPh_3)_3]$

TEMPERATURE °C	% YIELD OF (I) RESIN (±0.2)	% YIELD OF (I) NO RESIN (±0.1)	ISOMERIC RATIO RESIN (±0.05)	ISOMERIC RATIO NO RESIN (±0.05)	% YIELD OF (III) RESIN (±0.01)	% YIELD OF (III) NO RESIN (±0.01)	% YIELD OF (IV) RESIN (±0.02)	% YIELD OF (IV) NO RESIN (±0.01)
25	2.71	1.47	2.87	2.94	0.20	0.22	0.50	0.30
45	8.5	8.0	4.54	5.61	0.41	0.10	1.07	0.53
+45	7.9	-	4.55	-	0.18	-	0.60	-
80	31.9	30.0	5.79	6.43	0.93	0.55	1.91	0.58

+Reaction carried out with twice the concentration of resin

Concentration of [Ru] was 4.75×10^{-3} mol dm^{-3}

using a higher concentration of $[RuCl_2(PPh_3)_3]$ (0.019 mol dm^{-3}). This clearly showed that the resin enhances the activity of the catalyst (Table 2.19). The greatest increase in yield of the adduct (18.3 % of adduct in the presence of resin compared to 9.8 % in its absence) was observed at 45 °C. At higher temperatures (60°C and 80 °C) the yields of the adduct are not markedly affected by the presence of the resin. It is likely that the polymeric co-factor becomes destroyed or deactivated at these higher temperatures. The resin was also observed to have some effect on the isomeric ratio. In each case (and at every temperature) the ratio was slightly lower in the presence of resin. This is in line with the previous findings (see section 2.4.1) that higher reaction rates lead to lower selectivities.

It is clear from this study that the addition of a polymeric co-factor has a considerable effect on the rate of addition of tetrachloromethane to cyclohexene when the correct operating conditions of temperature and catalyst concentration are chosen. However, the synthetic utility of this method is limited by the fact that the co-factor degrades at temperatures of 60°C and above, which is the range in which the yields of reactions of this type become acceptable.

Table 2.19 : Effect of silver (I) polystyrene sulphonate as a co-factor on the reaction between cyclohexene and tetrachloromethane catalysed by $[RuCl_2(PPh_3)_3]$

TEMPERATURE °C	% YIELD OF (I) RESIN (±0.3)	% YIELD OF (I) NO RESIN (±0.3)	ISOMERIC RATIO RESIN (±0.2)	ISOMERIC RATIO NO RESIN (±0.2)	% YIELD OF (III) RESIN (±0.01)	% YIELD OF (III) NO RESIN (±0.01)	% YIELD OF (IV) RESIN (±0.03)	% YIELD OF (IV) NO RESIN (±0.03)
25	9.4	3.7	5.32	6.19	0.59	0.21	0.70	0.25
45	18.3	9.8	5.56	7.15	1.06	0.60	2.00	1.06
60	30.3	35.0	6.42	7.48	1.71	2.72	1.34	1.11
80	34.6	31.9	6.70	7.83	1.91	1.42	1.05	0.73

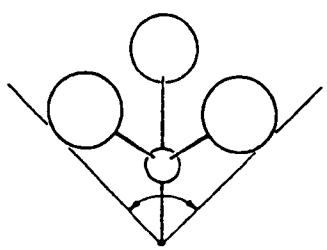
Concentration of [Ru] was 0.019 mol dm^{-3}

2.4.3 A study of the electronic effect of the phosphine ligands upon $[RuCl_2((4\text{-}X\text{-}C_6H_4)_3P)_3]$ catalysed addition of tetrachloromethane to cyclohexene and oct-1-ene

2.4.3.1 Introduction

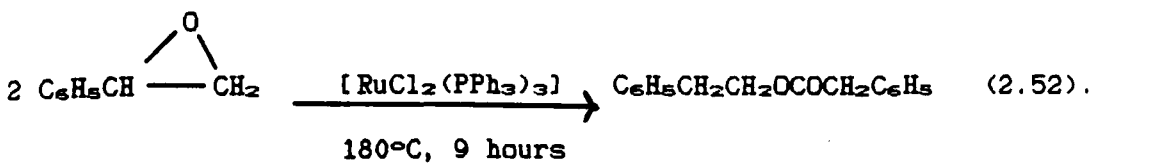
Electronic and steric effects of phosphorus ligands have been discussed in depth by Tolman[22]. Electronic effects were defined as changes in molecular properties which arise as a result of substitution of the R group in the ligand R_3P, leading to different transmission along a chemical bond. An example of this is changing from $(C_6H_5)_3P$ to $(4\text{-}Cl\text{-}C_6H_4)_3P$ in which the ligands are of comparable size, allowing electronic effects to be studied without the complication of steric changes. Steric effects can be classified in terms of ligand cone angles which historically come into use when the ability of the phosphorus to compete for coordination sites on a metal could not be explained in purely electronic terms. The ligand cone angle is defined schematically in figure 2.14.

Figure 2.14 : Schematic definition of the ligand cone angle.



It is not possible to synthesise a wide range of complexes of the type $[RuCl_2(PR_3)_3]$ in which the ligands differ in size and thus a study of steric effects is not possible. However, complexes of the type $[RuCl_2\{(4\text{-}X\text{-}C_6H_4)_3P\}_3]$ can be synthesised. Since a substituent in the 4-position has no effect on the ligand cone angle, any variation in properties arises solely as a consequence of the differing electronic effects of the X-groups.

Studies of the electronic effect of the phosphine ligand upon the catalytic properties of $[RuCl_2\{(4\text{-}X\text{-}C_6H_4)_3P\}_3]$ have been reported for various reactions[23,24,25]. In general it has been found that when the phosphine contains an electron withdrawing substituent X, there is a decrease in the electron density on the metal atom, causing a suppression of the rate of a catalysed reaction. Conversely, electron donating substituents enhance catalysis. These effects have been observed for a number of reactions. Thus, $[RuCl_2(PPh_3)_3]$ has been shown to catalyse the selective conversion of epoxides to carboxylic esters (equation 2.52).



(2.52).

A change in the initial rate of this reaction occurred when the substituent X on the catalyst was varied (Table 2.20). The reaction showed the highest initial rate when X is OCH_3 and lowest when X is Cl, in line with the above generalisation.

Table 2.20[22] : Effect of electronic changes in the catalyst $[RuCl_2\{(4\text{-}X\text{-}C_6H_4)_3\}_3]$ on the rate of reaction (2.52)

Substituent X	Initial rate of ester formation $L^{-1}min^{-1}$
OCH_3	61
CH_3	55
H	37
Cl	27

A second example of this effect is the catalysed isomerisation of 1,4-diarylbutenes[25]. When trans-1,4-diphenylbut-2-ene (VII) was heated in the presence of $[RuCl_2(PPh_3)_3]$ it was isomerised to trans-1,4-diphenylbut-1-ene (VIII) in 91 % yield (free from corresponding cis isomer)(equation 2.53).

$$\underset{\text{trans-(VII)}}{PhCH_2CH{=}CHCH_2Ph} \xrightarrow[185^{\circ}C]{[RuCl_2(PPh_3)_3]} \underset{\text{trans-(VIII)}}{PhCH{=}CHCH_2CH_2Ph} \quad (2.53)$$

91 %

In this reaction 1.5 % trans isomer (VII) remained, and 7.5 % of cis-1,4-diphenylbut-1-ene (IX) was formed.

The rate of isomerisation was found to vary depending on the substituent present (Table 2.21). The rate of isomerisation was the fastest when X is CH_3 and slowest when X is Cl. These results are consistent with those obtained in the previous example.

Table 2.21[25]: Effect of electronic changes in the catalyst $[RuCl_2((4\text{-}X\text{-}C_6H_4)_3)_3]$ on the isomerisation of trans-1,4-diphenylbut-2-ene.

Substituent X	Initial rate of isomerisation % min^{-1}
CH_3	6.0
OCH_3	2.3
H	1.1
Cl	0.6

However, in this case the greatest initial rate is observed when X is CH_3 rather than OCH_3.

In the present work the effect of changing the substituent was studied for the reactions between tetrachloromethane and both cyclohexene and oct-1-ene.

2.4.3.2 Results and discussion

The reaction between oct-1-ene and tetrachloromethane was carried out in the presence of $[RuCl_2\{(4\text{-}X\text{-}C_6H_4)_3\}_3P]$ where X=Cl, H, OCH_3, and CH_3 (Table 2.22). The results showed that the yield of 1,1,1,3-tetrachlorononane produced increased as the electron donating nature of the ligand is increased. This suggests that the ligand dissociation is not of overriding importance, as increasing the electron density on the phosphorus atom would be expected to increase the Ru-P bond strength, which should slow down the reaction rate. This is in agreement with the findings on ligand dissociation in the study of solvent effects (section 2.4.1). Increasing the electron density on the ruthenium should lower its oxidation potential and hence enable the halogen atom abstraction step, which probably proceeds by initial electron transfer, to take place more easily (equations 2.54 and 2.54).

$$Ru^{II} + CCl_4 \longrightarrow Ru^{III} + CCl_4^{\bullet-} \qquad (2.54)$$

$$Ru^{III} + CCl_4^{\bullet-} \longrightarrow \{Ru^{III}\text{-}Cl^{-}\}\{CCl_3\bullet\} \qquad (2.55)$$

The reason why increasing the electron density on the ruthenium reduces its oxidation potential can be explained in terms of molecular orbital diagrams, (figures 2.15 and 2.16)[26]. $[RuCl_2(PPh_3)_2]$ may adopt either a tetrahedral or a square planar structure. The HOMO of such a complex will be of either t_2 or a_{1g} symmetry respectively. Since both these levels are derived from ligand σ orbitals, any increase in the energy of the latter will increase the energy of the former, thereby reducing the oxidation potential. The increased electron density within the Ru^{III} species so formed would also cause a stronger interaction within the radical pair.

Table 2.22 : Investigation of the effect of substituting phosphine ligands of $[RuCl((4\text{-}X\text{-}C_6)H_4)_3P)_3]$ on the catalysed addition of tetrachloromethane to oct-1-ene

Substituent X	% Yield of 1,1,13-tetrachlorononane*
Cl	60.8
H	71.0
CH_3	75.8
OCH_3	86.8

*% Yield (GLC) was based on oct-1-ene charged.

Figure 2.15[26] : Molecular orbital diagram for most tetrahedral complexes in lower oxidation states.

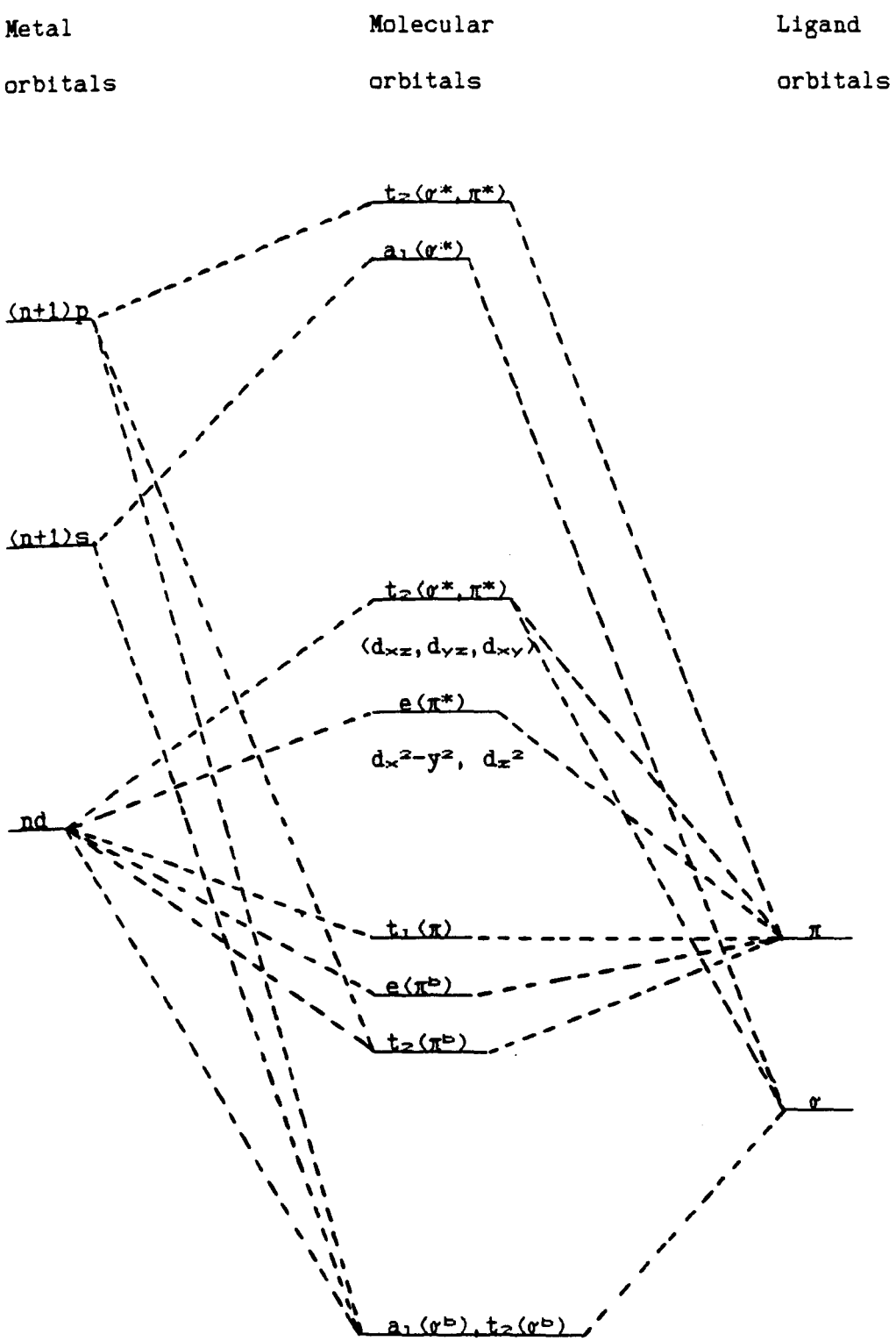
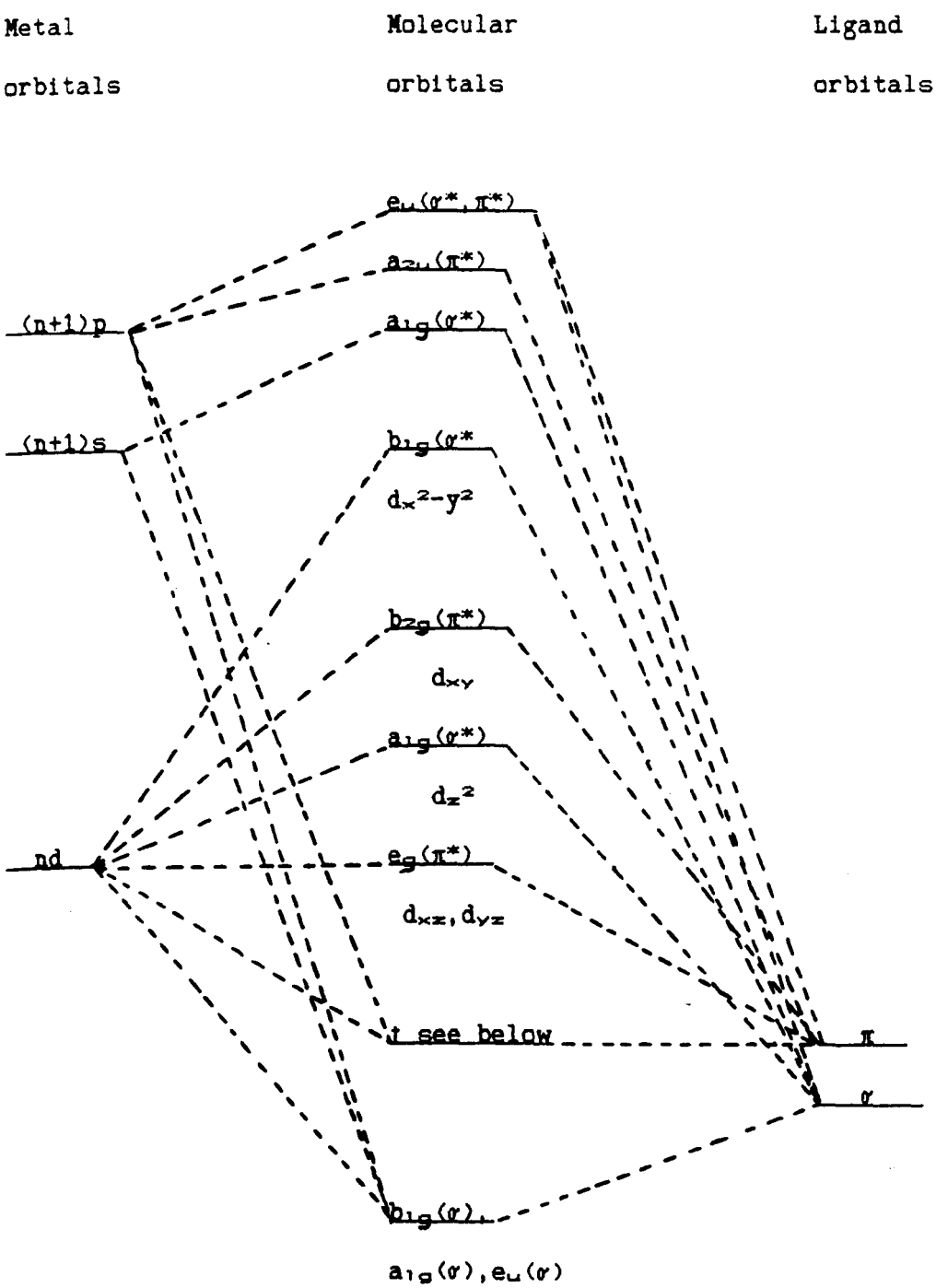


Figure 2.16[26] : Molecular orbital diagram for square planar complexes, ML_4



† bonding orbitals : $a_{2g}, b_{2u}, a_{2u}, b_{2g} e_g, e_u$.

The behaviour of these same catalysts was also studied in the reaction between cyclohexene and tetrachloromethane, so that the effect on the isomeric ratio could also be investigated. However, the results are not quite as clear cut as those of oct-1-ene and tetrachloromethane. These show (Table 2.23) that when the reaction was carried out in hex-1-ene the yield of adduct (I) was greater using the catalyst with the substituent X=CH_3 rather than with X=H. However, the yield of products for this reaction using the catalyst with X=OCH_3, was only 1.5 % suggesting that the catalyst had decomposed in hexane. (The reaction involving $[RuCl_2\{(4\text{-}Cl(C_6H_4)_3P\}_3]$ could not be carried out in hexane, as it is totally insoluble, even at 80°C).

The reaction was also performed in benzene which showed that the yield and isomeric ratio of adduct (I) were reduced when the catalyst had the substituent X=Cl compared to X=H. This result is in agreement with those for the reaction between oct-1-ene and tetrachloromethane. However, for both the catalysts where X=OCH_3, CH_3 the yield and isomeric yields were lower than for $[RuCl_2(PPh_3)_3]$. This effect could have arisen as a result of the solvation of the $\{RuCl_3((4\text{-}X\text{-}C_6H_4)_3P)_2^{\bullet}\}$ radical formed, which (as described in section 2.4.1) would cause the radicals to become separated. Presumably, this solvent effect is stronger than the electronic effect, causing a reduced yield of product.

The isomeric ratios are also affected by the substituents on the ligands. The effect is most marked in the case of X=Cl as it becomes reduced to 2.76 compared to 7.90 in the case when X=H. Presumably the electron withdrawing nature of this substituent reduces the electron density on the ruthenium sufficiently to lower its oxidation potential and hence its ability to catalyse the reaction. This effect is much less pronounced for the other catalysts where the values are the same

Table 2.23 : Investigation of the effect of changing phosphine ligands on $[RuCl_2\{(4\text{-}X\text{-}C_2H_4)_3P\}_3]$ catalysed addition of CCl_4 to cyclohexene

SUBSTITUENT , X	% YIELD OF (I)[a] (±0.2)	ISOMERIC RATIO OF (I) (±0.02)	% YIELD OF (III)[a] (±0.01)	% YIELD OF (IV)[a] (±0.01)
Cl	-	-	-	-
	10.1	2.76	0.91	0.51
H	11.4	4.49	0.72	not detected
	26.8	7.90	0.69	not detected
CH_3	22.1	8.43	0.25	1.77
	20.3	7.25	0.84	1.21
OCH_3	1.5	1.45	0.16	0.29
	18.7	6.95	2.40	0.70

Solvent used was benzene , in all other cases hexane was used

[a] % Yield (GLC) based on cyclohexene charged

Reaction mixture used in ratio 400:125:1 of CCl_4 : cyclohexene : $[RuCl_2(PPh_3)_3]$

(I) 1-chloro-2-(trichloromethyl)cyclohexane

(III) 3-(trichloromethyl)cyclohex-1-ene

(IV) (trichloromethyl)cyclohexane

within experimental errors, with one exception. In the case of X=CH_3 the value in hexane is doubled compared to X=H.

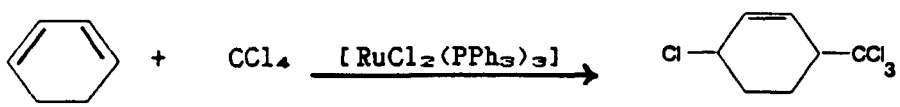
In conclusion, as is recognised in the literature, electronic effects can play a dramatic role on the yield (and stereoselectivity) of products, particularly when the substituents are electron withdrawing.

Clearly, the reaction involving cyclohexene is more complex than the oct-1-ene analogue, as has been demonstrated by the complex relationships between rate and both ligand electronic and solvent effects. The reason for this is not clear.

2.4.4 Investigating the effect of $[RuCl_2(PPh_3)_3]$ on the addition of tetrachloromethane to cyclohexa-1,3-diene.

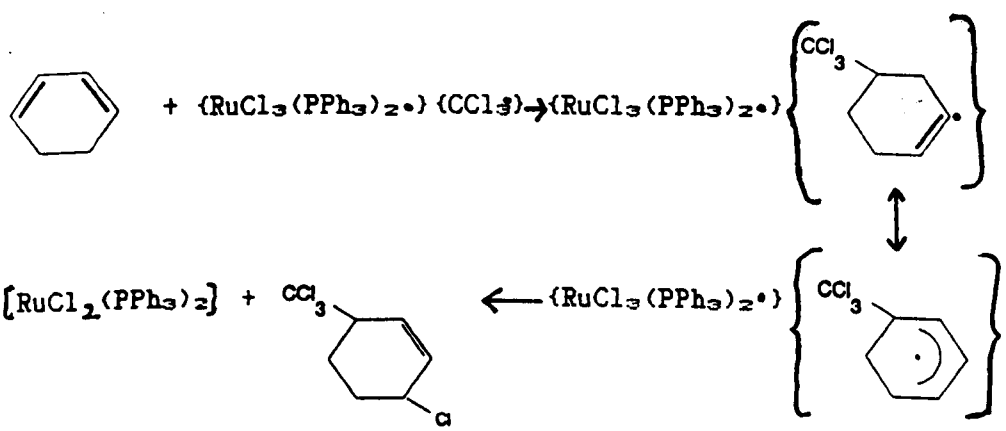
2.4.4.1 Introduction

Although the reaction between tetrachloromethane and cyclohexa-1,3-diene (equation 2.56) has been briefly reported in the literature (see chapter 1, section 1.24), few details are available. 1-chloro-4-(trichloromethyl)cyclohex-3-ene is reported to be formed in 81 % yield with none of the 1,2-isomer being formed. This might be expected since the 1,2-isomer would experience considerable steric crowding. Furthermore, the fact that the intermediate carbocyclic radical is allylic in nature allows ready formation of the 1,4-isomer (scheme 2.7). Similar reactions of cycloocta-1,3-diene were also described. However, there is no discussion of the stereochemistry of the 1 : 1 adducts of either cyclic diene.



(2.56)

Scheme 2.7 : Reaction between tetrachloromethane and cyclohexa-1,3-diene in the presence of $[RuCl_2(PPh_3)_3]$

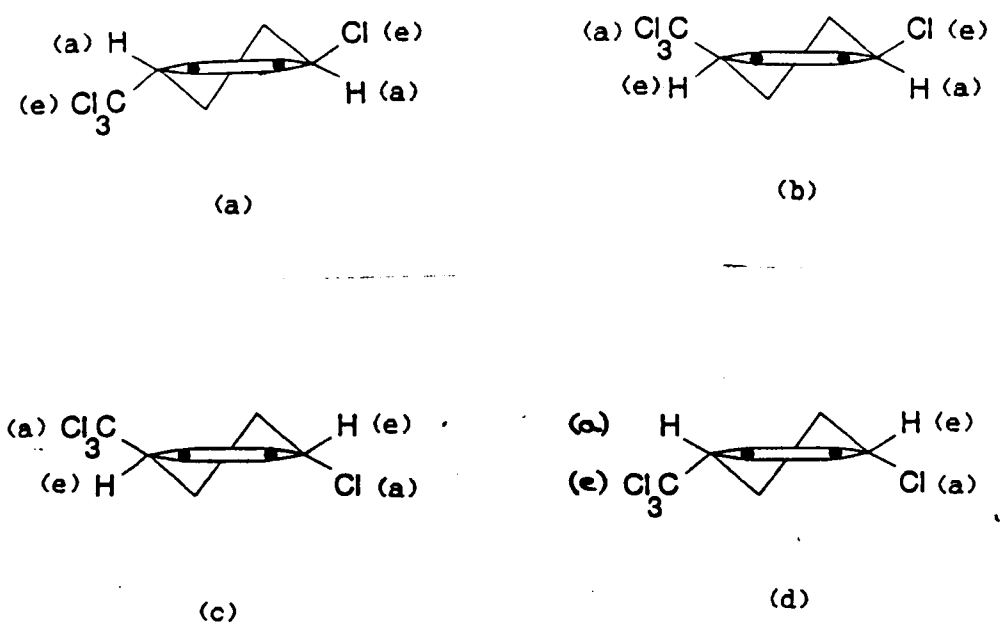


(2.57)

(2.58)

1,4-substituted cyclohexadienes usually adopt a half-chair structure and are thus, in principle, capable of existing in four isomeric forms (figure 2.17)(a-d)). In the case of the compound discussed above, these may be termed (a) trans-di-equatorial, (b) cis-axial-CCl_3-equatorial-Cl, (c) trans-di-axial and (d) cis-axial-Cl-equatorial-CCl_3.

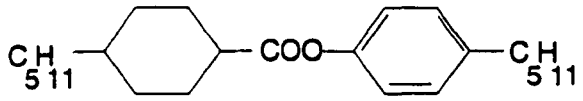
Figure 2.17 : Structures adopted by 1,4-substituted cyclohexadienes.



where (a)-axial, (e)-equatorial

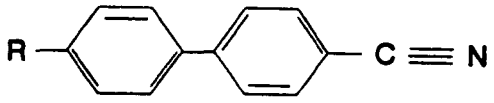
There is currently considerable interest in the synthesis of related 1,4-trans-di-equatorially substituted cyclohexanes (figure 2.18) since such molecules containing long chain substituents are capable of displaying liquid crystalline properties[27].

Figure 2.18 : Structure of a molecule with liquid crystalline properties.

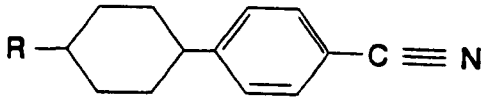


Cyclohexane analogues of known liquid crystals such as cyanobiphenyls were then developed (figure 2.19).

Figure 2.19 : Structures of a known liquid crystal and cyclohexane analogue



cyanobiphenyl



cyclohexane analogue

It is likely that suitably substituted 1,4-trans-di-equatorial-cyclohexenes will also exhibit mesomorphism and the reactivity of the CCl_3 and Cl substituents provide an entry into the synthesis of such molecules. Thus the CCl_3 group can be oxidised to a carboxylic acid and subsequently esterified with a long chain aliphatic or aromatic

alcohol. The Cl functionality can be converted into an ether unit, again carrying an appropriate substituent.

Molecular models suggest that the CCl_3 group of a 1,4-substituted cyclohexene cannot readily occupy the C-4 axial position since it would undergo severe steric crowding with the axial hydrogen atom on C-2. Thus, the formation of isomers 2.17(b) and 2.17(c) would appear to suffer steric crowding, while 2.17(d) may be subject to some interaction between the chlorine in an axial position on C-1 and the axial hydrogen on C-5. There may, therefore, be a preference for the di-equatorial isomer, 2.17(a).

The present study was, therefore, undertaken in order to investigate the stereochemistry of 1-chloro-4-(trichloromethyl)cyclohex-3-ene, produced by $[RuCl_2(PPh_3)_3]$ catalysed addition of tetrachloromethane to cyclohexa-1,3-diene.

2.4.4.2 Results

Addition of tetrachloromethane to cyclohexa-1,3-diene in the presence of $[RuCl_2(PPh_3)_3]$

The reaction between cyclohexa-1,3-diene and tetrachloromethane in the presence of $[RuCl_2(PPh_3)_3]$ led to the formation of the expected product. Capillary column GLC indicated that two isomers were formed. A range of reaction conditions was investigated. These and the yields are given in tables 2.24-2.27.

Table 2.24 : Effect of temperature

Temperature°C	Yield % *	Isomeric ratio
20	8.3	1.12
80	87.2	1.25
100	91.5	1.50

* Yield (GLC) of 1-chloro-4-(trichloromethyl)cyclohex-3-ene based on cyclohexa-1,3-diene charged.

Reactions were carried out in 816 : 250 : 1 of CCl_4 : cyclohexa-1,3-diene : $[RuCl_2(PPh_3)_3]$ for 5 hours.

No solvent was used.

Table 2.25 : Effect of catalyst concentration

Concentration of catalyst mol dm^{-3} X 10^{-3}	Yield % *	Isomeric ratio
0.73	53.0	1.12
3.13	81.7	1.26
13.5	87.2	1.26
56.0	90.5	0.93
220.0	70.2	0.84

* Yield (GLC) of 1-chloro-4-(trichloro)cyclohex-3-ene based on cyclohexa-1,3-diene charged. No solvent was used. The reactions were carried out at 80°C for 5 hours.

Table 2.26 : Effect of reaction time

Reaction time hrs	Yield % *	Isomeric ratio
1	25.2	1.08
2.5	39.2	1.07
3	46.5	1.12
4	64.3	1.12
5	87.2	1.12

* Yield (GLC) of 1-chloro-4-(trichloromethyl)cyclohex-3-ene based on cyclohexa-1,3-diene charged. The reactions were carried out in a mixture of 780 : 232 : 1 of CCl_4 : cyclohexa-1,3-diene : $[RuCl_2(PPh_3)_3]$ at 80 °C.

Table 2.27 : Effect of solvent

Solvent	Yield % *	Isomeric ratio
Tetrachloromethane	22.6	1.43
Tetrahydrofuran	23.9	1.38
Toluene	73.9	1.30
Ethanol	-	2.14

* Yield (GLC) of 1-chloro-4-(trichloromethyl)cyclohex-3-ene based on cyclohexa-1,3-diene charged. The reactions were carried out in a mixture of 825 : 250 : 1 of CCl_4 : cyclohexa-1,3-diene : $[RuCl_2(PPh_3)_3]$ for 5 hours at 80 °C.

2.4.4.3 Discussion

The addition of tetrachloromethane to cyclohexa-1,3-diene resulted in a mixture of products, the gas chromatogram of which is shown in figure 2.20 (obtained after fractional distillation of the reaction mixture). GC-MS analyses of this mixture gave spectra for the two major peaks in agreement with the formulation $C_7H_8Cl_4$ (figures 2.21 and 2.22). These showed ions at m/z 232/4/6, 197/9 ($M-Cl^+$), 161/3/5 ($M-Cl^+-HCl^+$). This is consistent with these two products being two isomers of the 1 : 1 addition product between tetrachloromethane and cyclohexa-1,3-diene. These products are formed in the ratio of about 1.27 : 1 depending on the reaction conditions. The yield of this adduct mixture also depended on the conditions used and Tables 2.24-2.27 show the result of variations in temperature, catalyst concentration, reaction time and solvent. The highest yields were obtained when the reaction was carried out at 80-100 °C for 5 hours. The results also show that the ratio of the isomers showed little variation with changes in reaction conditions.

The ^{1}H-NMR of the distilled product (mixture of isomers) is shown in figure 2.23. The assignments are given in Table 2.28.

Figure 2.24 : Assignment of 1-chloro-4-(trichloromethyl)-cyclohex-3-ene.

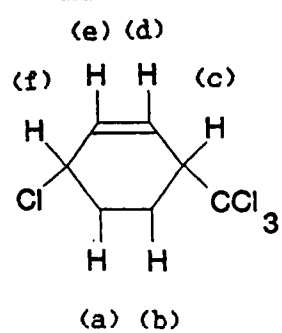
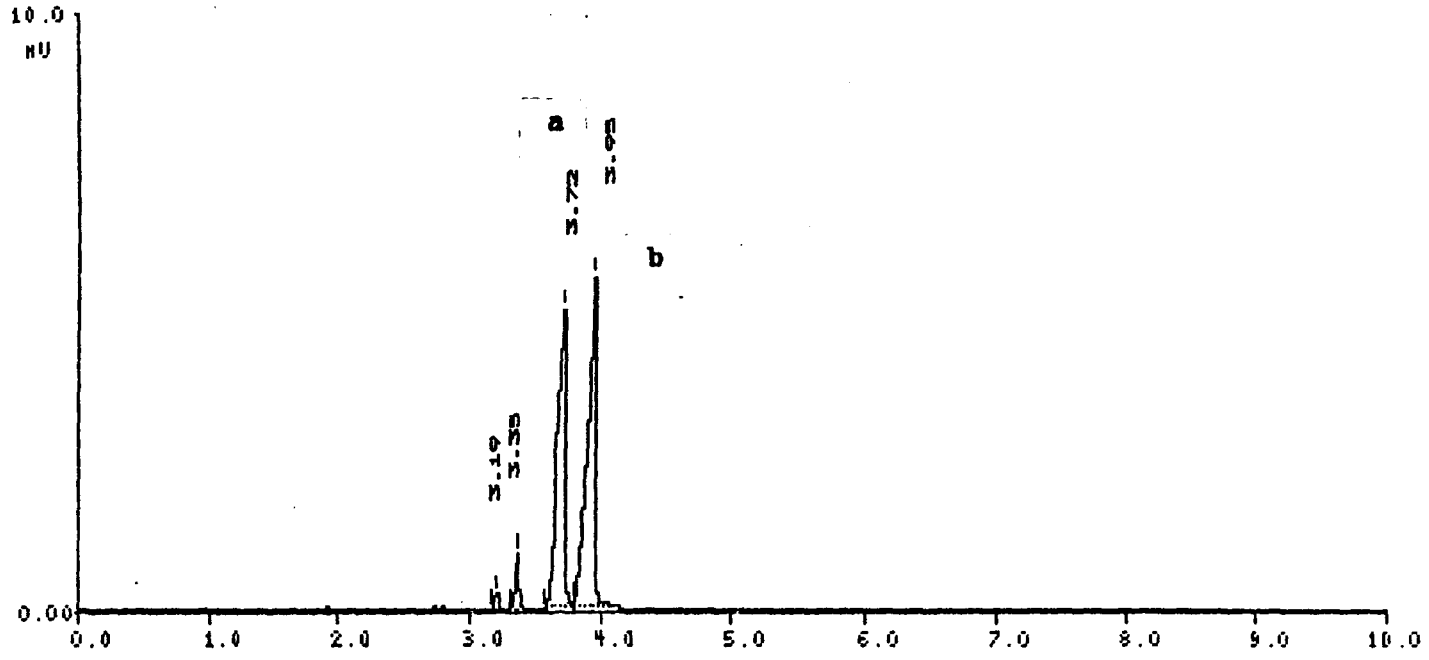


Figure 2.20 : Chromatogram of distilled reaction products resulting from the reaction between tetrachloromethane and cyclohexa-1,3-diene in the presence of $[RuCl_2(PPh_3)_3]$.



a,b- isomers of 1-chloro-4-(trichloromethyl)cyclohex-3-ene

Figure 2.21 : Mass spectrum of isomer (a)(fig.2.20) of 1-chloro-4-(trichloromethyl)-cyclohex-3-ene.

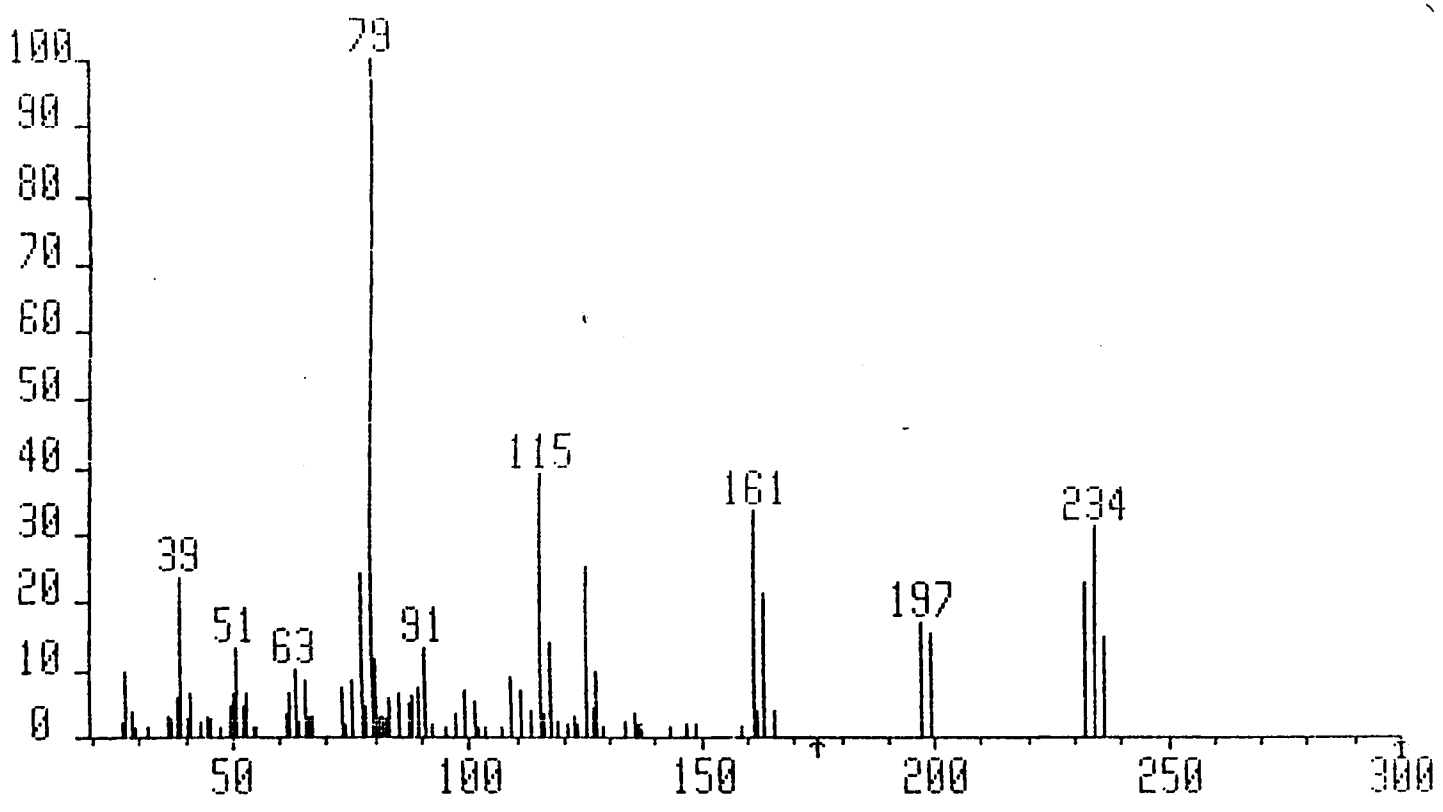


Figure 2.22 : Mass spectrum of isomer (b)(fig 2.20) of 1-chloro-4-(trichloromethyl)-cyclohex-3-ene.

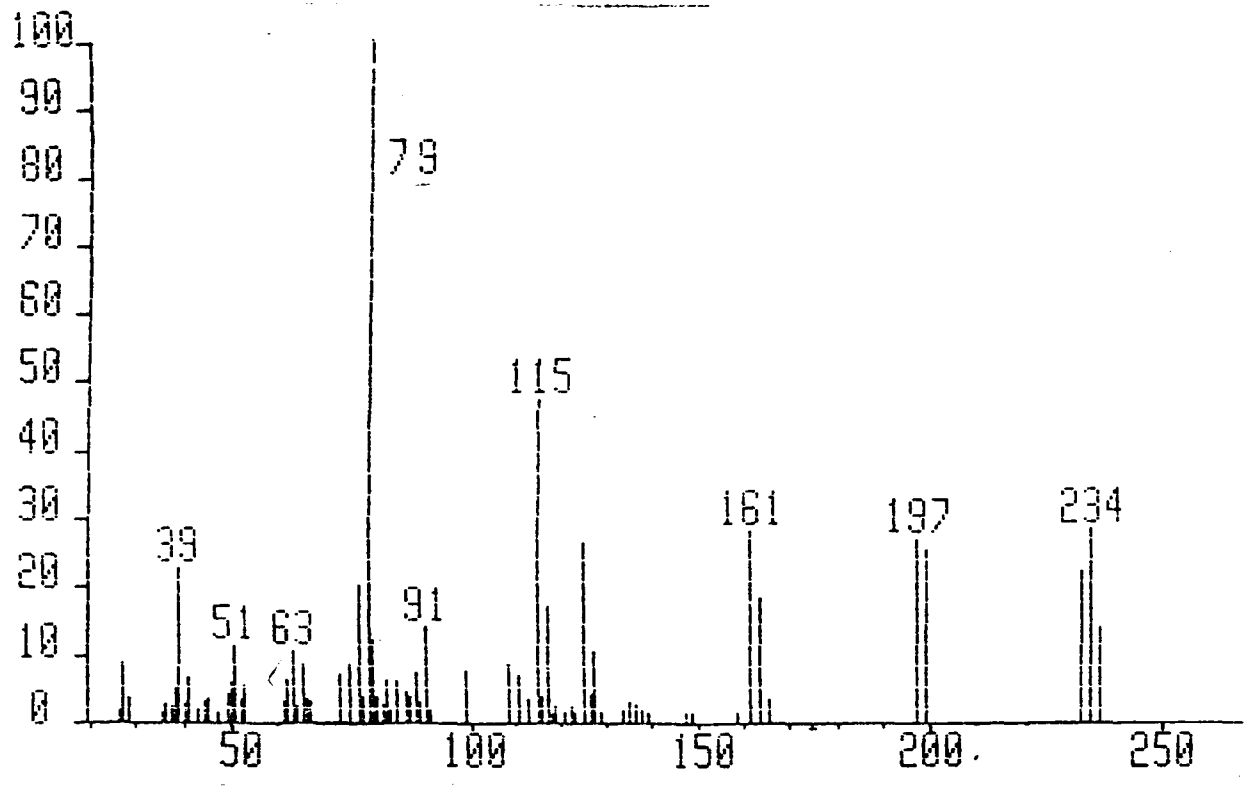


Figure 2.23 : ^{1}H NMR of an isomeric mixture of 1-chloro-4-(trichloromethyl)cyclohex-3-ene.

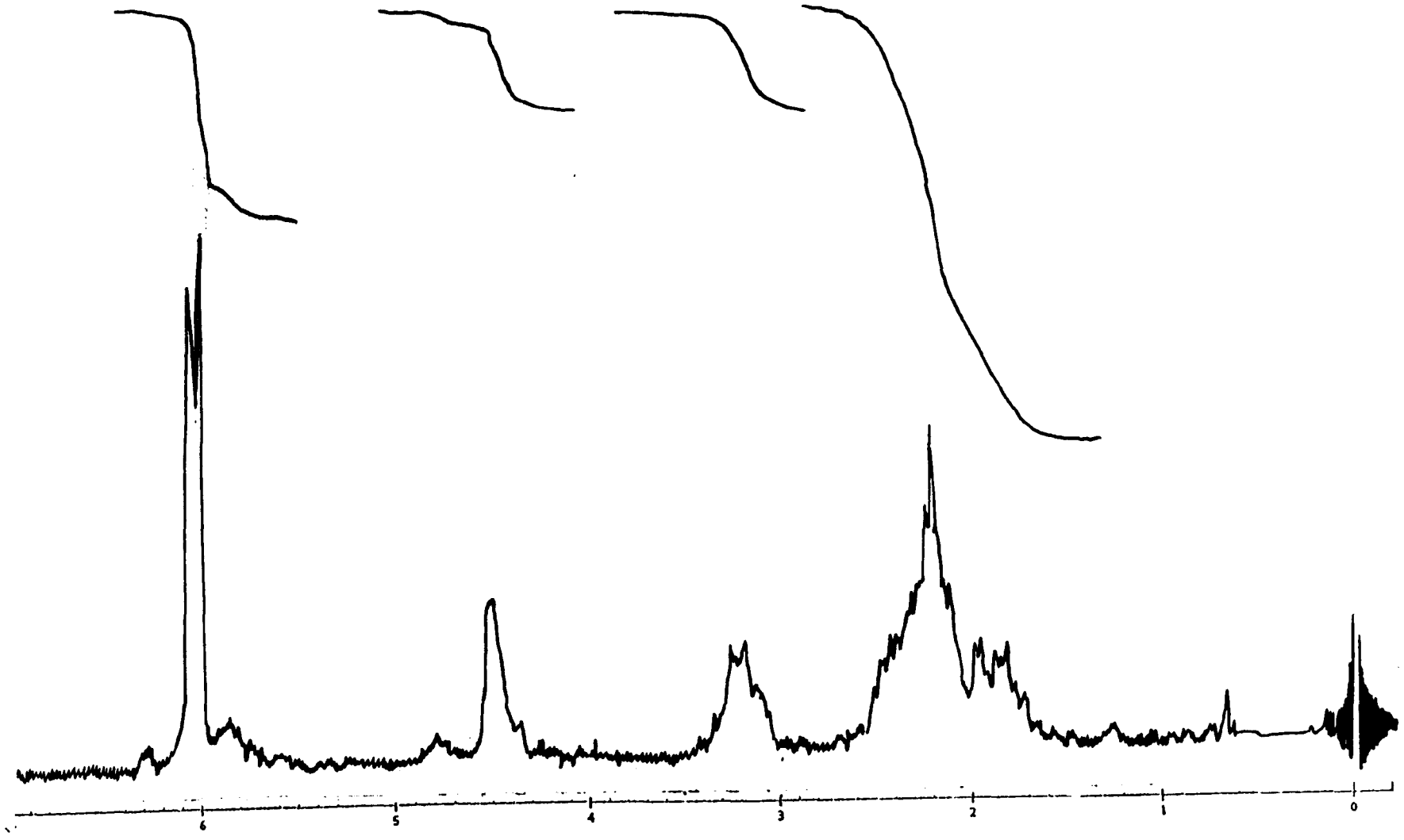


Table 2.28 : ^{1}H-NMR Assignments of 1-chloro-4-(trichloromethyl) cyclohex-3-ene.

Chemical shifts (ppm)	Number of protons (splitting)	Assigned proton
1.5-2.5	4 (m)	a+b
3.0-3.3	1 (m)	c
4.3-4.6	1 (m)	f
6.0-6.1	2 (d)	e+d

However, more information was needed to unequivocally confirm the presence of two isomers and then identify them. This was carried out by ^{13}C-NMR (figure 2.25). The ^{13}C-NMR shows 14 peaks, all in pairs, indicating the presence of two isomers of a 7 carbon containing molecule. The relative proportion of these isomers is not exactly 1 : 1, but this is in agreement with the ratios obtained by GLC. It is difficult to positively assign the carbon signals. In order to clarify the issue a DEPT experiment was carried out.

DEPT spectra.

This is a multipulse experiment, known as Distortionless Enhancement by Polarisation Transfer. This technique causes signals due to quaternary carbon atoms to disappear, whilst those due to methylene carbons are inverted, but signals arising from methine carbons are unaffected. The spectrum of 1-chloro-4-(trichloromethyl)cyclohex-3-ene can now be assigned (Table 2.26).

Figure 2.25 : ^{13}C NMR of an isomeric mixture of 1-chloro-4-(trichloromethyl)cyclohex-3-ene.

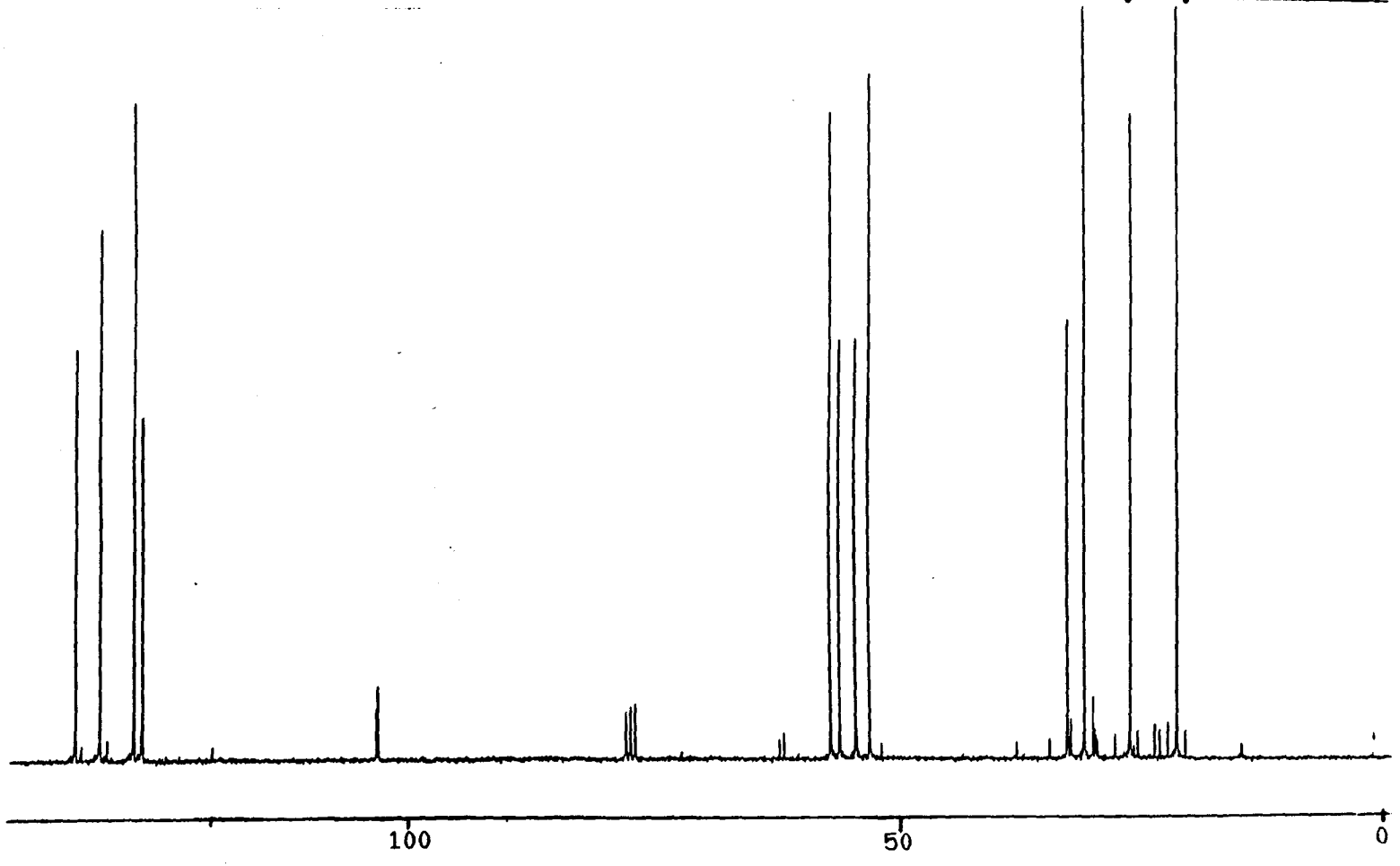


Figure 2.26 : DEPT spectrum of an isomeric mixture of 1-chloro-4-(trichloromethyl)-cyclohex-3-ene.

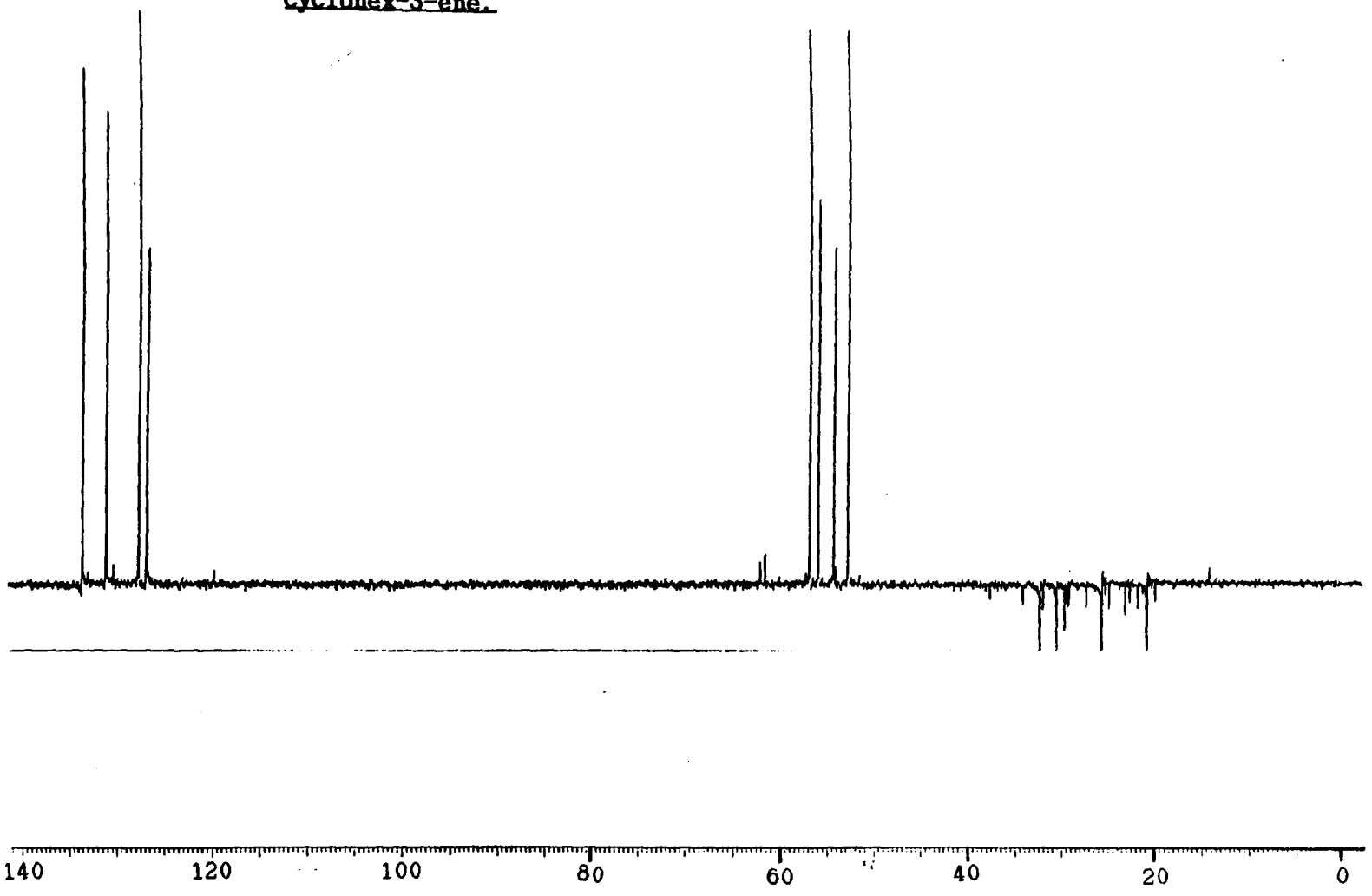


Figure 2.27 : Assignment of 1-chloro-4-(trichloromethyl)-cyclohex-3-ene.

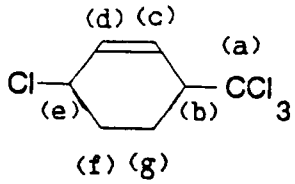


Table 2.28 : ^{13}C-NMR of 1-chloro-4-(trichloromethyl)cyclohex-3-ene.

Chemical shift (ppm)	Assignment of carbon atom	Comments
103	a	This signal disappears in the DEPT spectrum, therefore must be due to quaternary carbon.
20-30	f+g	4 peaks in this region have become inverted in the DEPT spectrum, due to the presence of methylene carbons.
50-60	c+d	Unchanged by DEPT, signal due to methine carbons.
130	e+b	Again unaffected by DEPT, but much further downfield, due to close presence of Cl and CCl_3 groups.

It has not proved possible to unequivocally identify which stereoisomers are formed. Even using high field (270 MHz) ^{1}H NMR, the coupling patterns are insufficiently resolved for complete analysis (figure 2.28). Attempted spin decoupling experiments did not further resolve the issue (figure 2.29). However, in view of the earlier comments, it is likely that the two isomers are 2.17(a) (di-equatorial) and 2.19(d) (cis-axial-Cl-equatorial-CCl_3), with the former predominating slightly in the mixture. It has not proved possible to separate these isomers on a preparative scale.

The reaction between tetrachloromethane and cycloocta-1,3-diene was also studied. The gas chromatogram (figure 2.30) of an undistilled reaction mixture shows the formation of two products, in a similar isomeric ratio to the 1-chloro-4-(trichloromethyl)cyclohex-3-ene (1.27 : 1 compared to 1.25 : 1, respectively). Attempts to isolate these products by vacuum distillation were unsuccessful. The GC-MS of the reaction mixture showed that both product peaks have essentially the same mass spectrum (figures 2.31 and 2.32). Ions corresponding to the formulation $C_9H_{12}Cl_4$ were observed, although the quality of the spectra were not as good as those observed for the products of the cyclohexadiene reaction.

This work shows that the 1-chloro-4-(trichloromethyl)-cyclohex-3-ene is formed in two isomers as was suggested earlier. In the same way it is likely that 1-chloro-4-(trichloromethyl)-cyclooct-3-ene is also formed with isomers on steric grounds analogous to the former case.

Figure 2.28 : High field ^1H NMR of spectrrum of an isomeric mixture of 1-chloro-4-(trichloromethyl)cyclohex-3-ene.

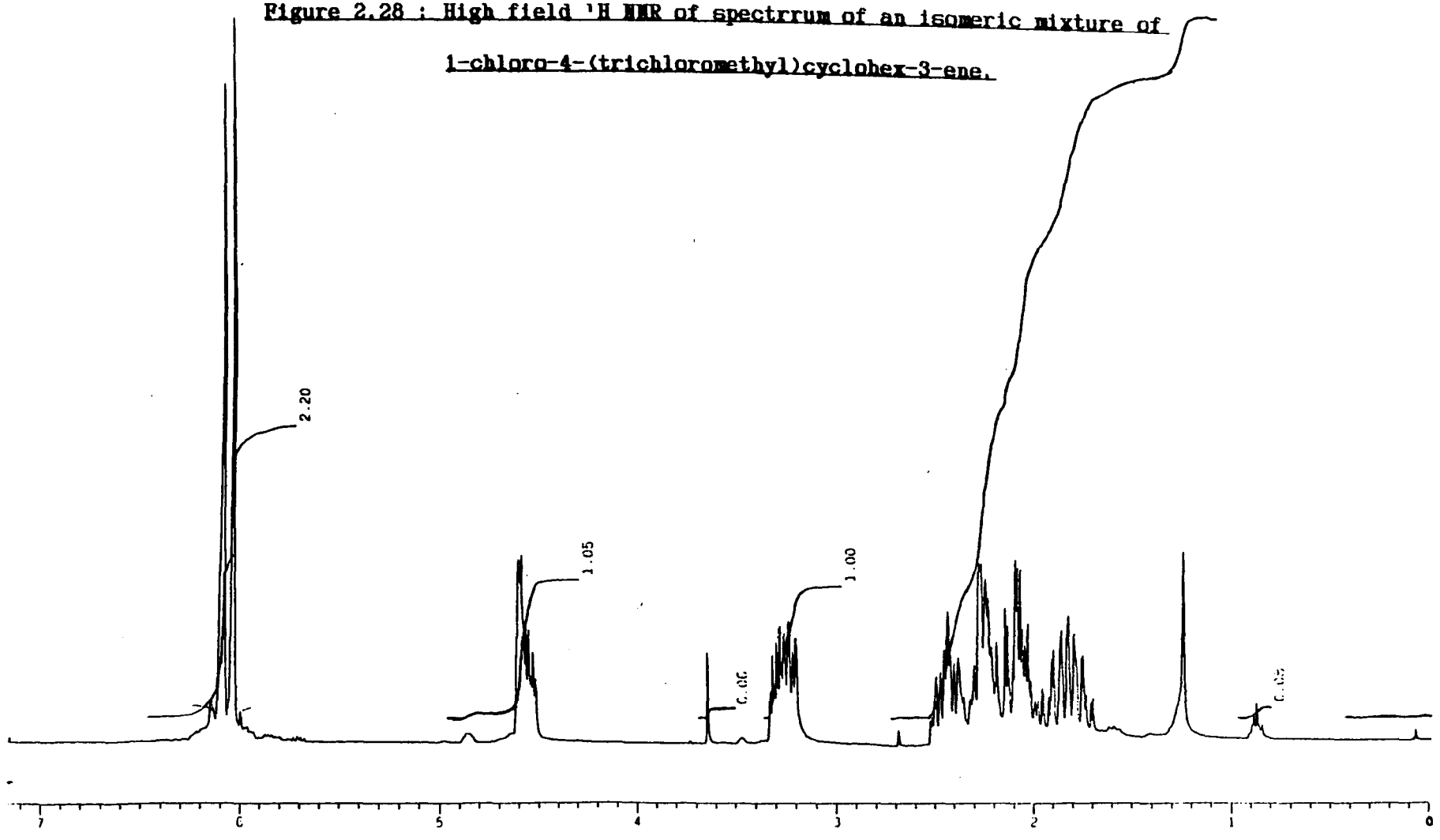


Figure 2.29 : Spin decoupled ^1H NMR spectra of an isomeric mixture of 1-chloro-4-(trichloromethyl)cyclohex-3-ene.

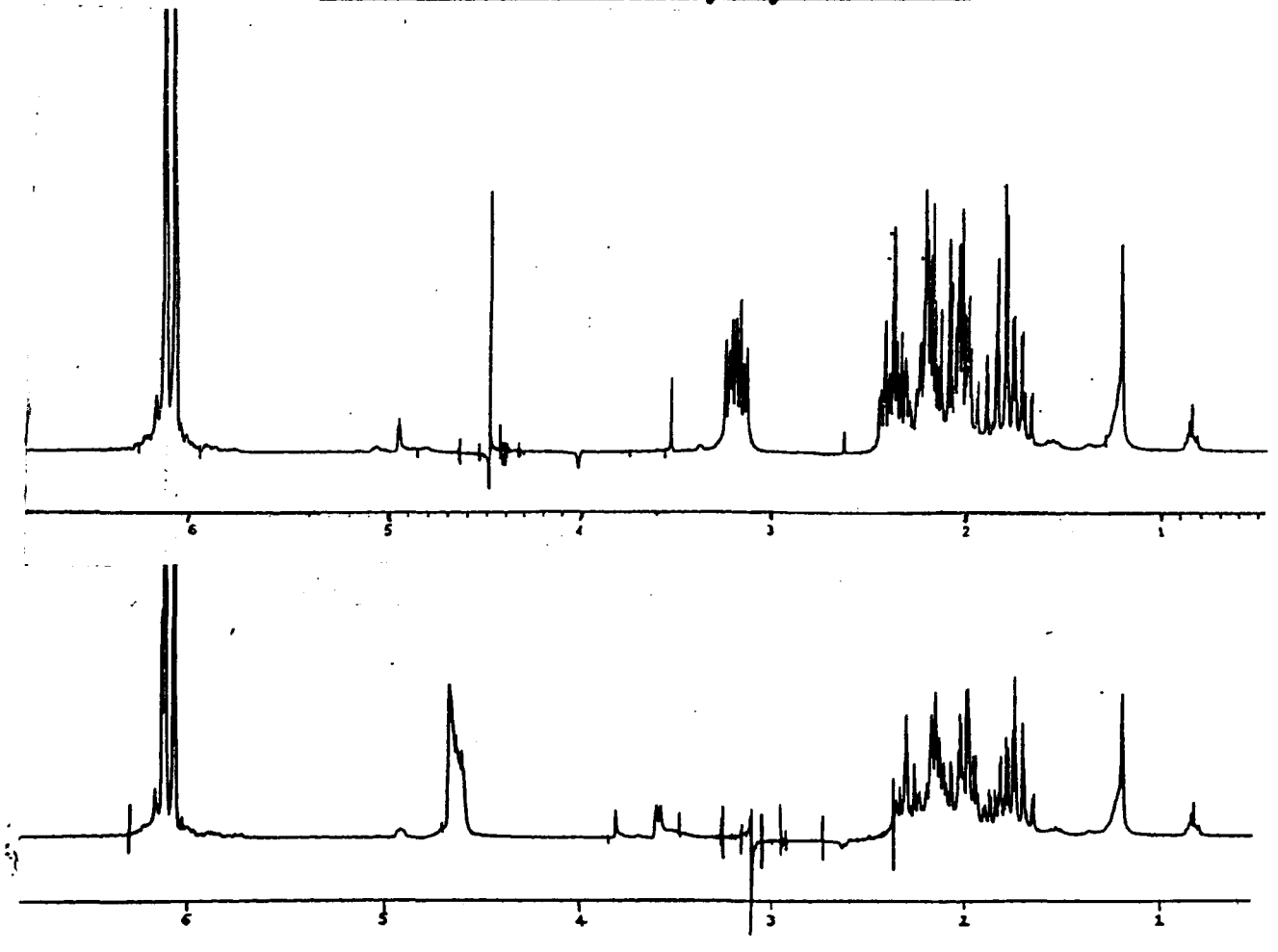
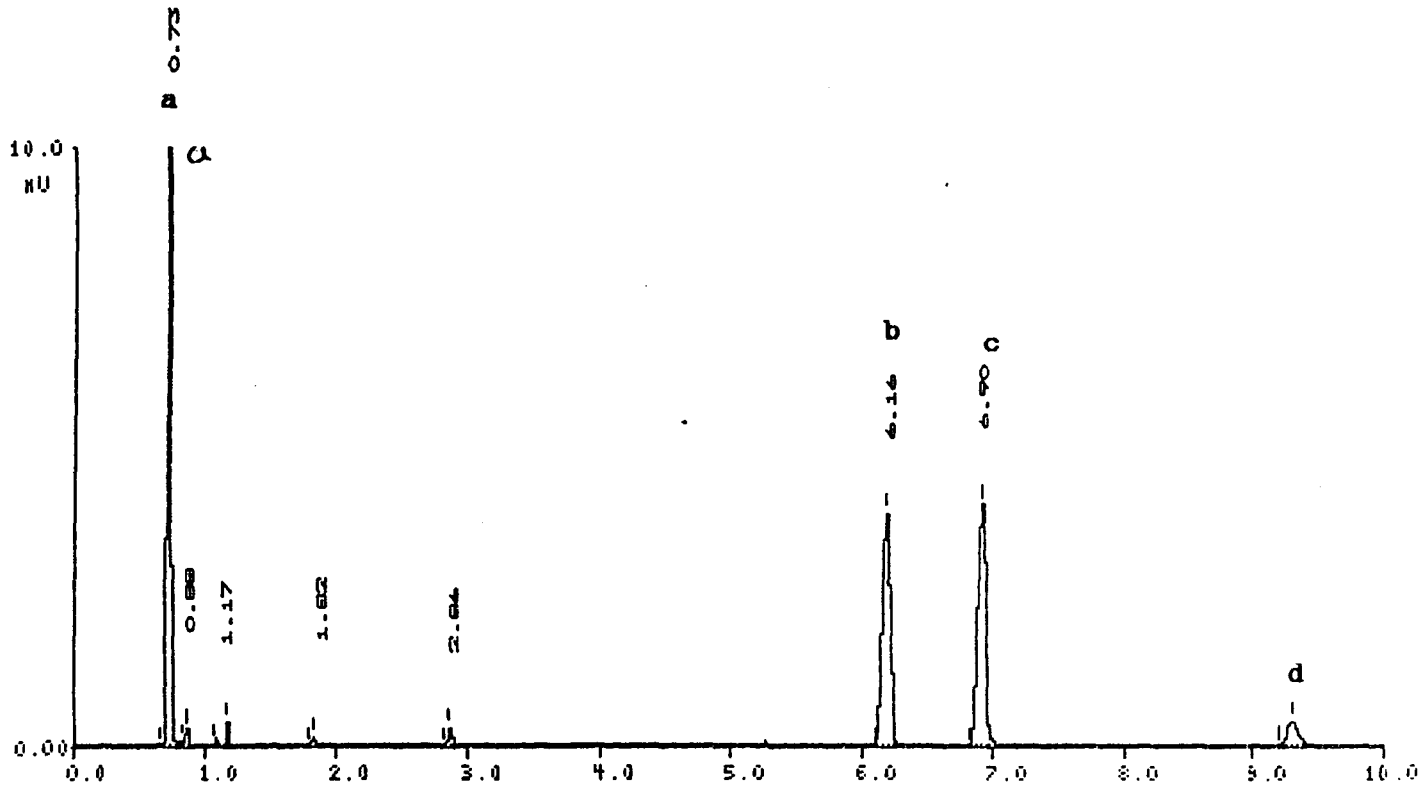


Figure 3.30 : Chromatogram of distilled reaction products resulting from the reaction between tetrachloromethane and cycloocta-1,3-diene in the presence $[RuCl_2(PPh_3)_3]$.



a - tetrachloromethane, b + c - isomers of 1-chloro-4-(trichloromethyl)cycloocta-3-ene

d - methyl myristate (internal standard)

Figure 2.31 : Mass spectrum of isomer (a)(fig 2.30) of 1-chloro-4-(trichloromethyl)-cyclooeta-3-ene.

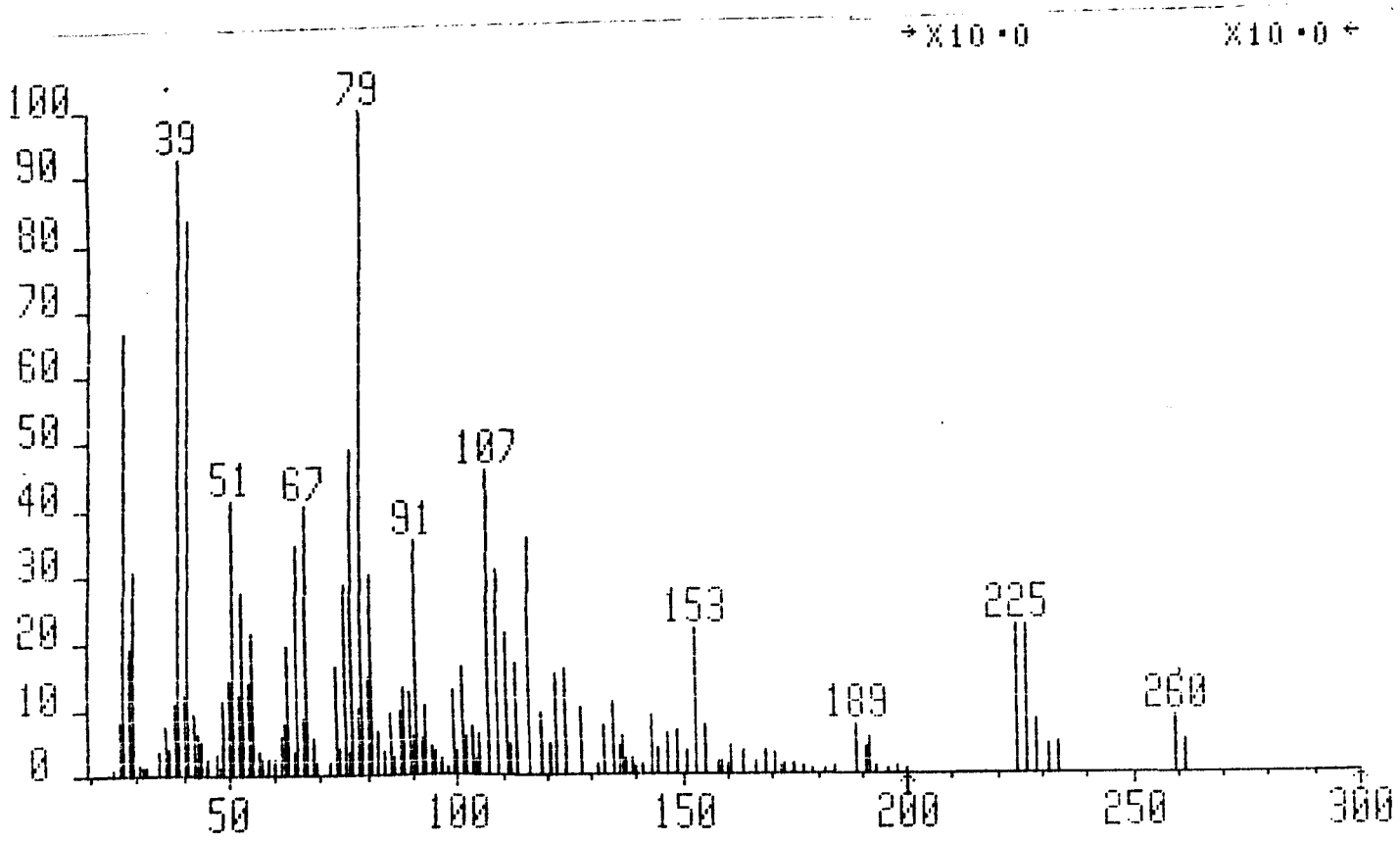
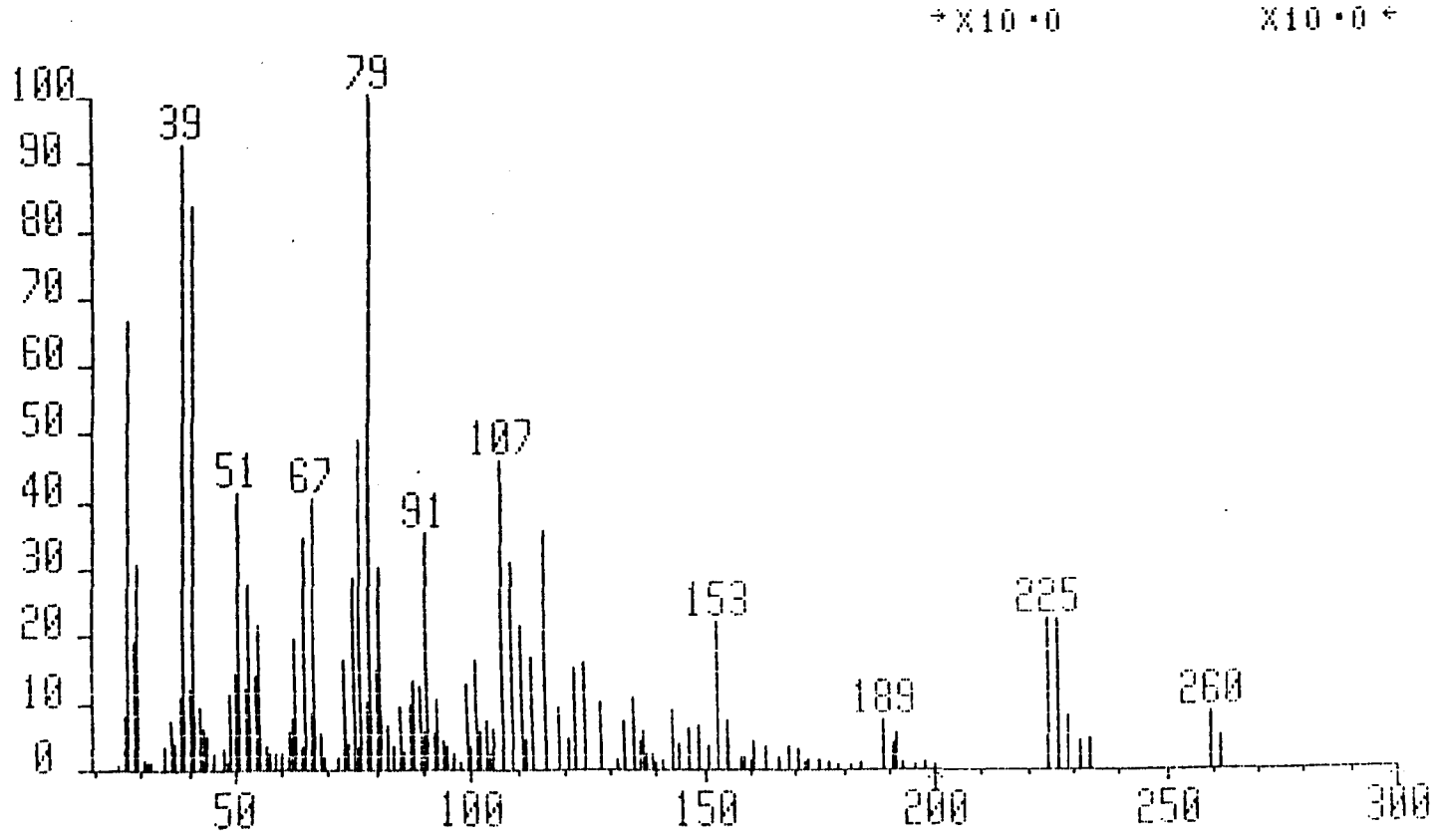


Figure 2.32 : Mass spectrum of isomer (b)(fig. 2.30) of 1-chloro-4-(trichloromethyl)-cycloocta-3-ene.



2.5 EXPERIMENTAL SECTION

All the reactions were carried out under an atmosphere of dry nitrogen, except where stated otherwise. All reagents were obtained from commercial sources when available and others were prepared as will be described later. The sources of catalysts used are summarised in Table 2.30 The solvents used were all purified and / or dried as summarised in Table 2.31. Tetrachloromethane was dried over phosphorus pentoxide, whilst the alkenes (and cycloalkenes) were dried over sodium and distilled prior to use. All GLC analyses were carried out on a Perkin-Elmer Sigma 2B chromatograph with an intelligent terminal. Infrared spectra were recorded on a Perkin-Elmer 457 spectrometer. ^{1}H-NMR were run on a Perkin-Elmer R32 spectrometer. Mass spectra were recorded on an AEI MS9 instrument using the direct insertion probe and GC-MS was carried out on a VG-Trio 2.

2.5.1.1 The study of $[Co_2(CO)_8]$ catalysed addition of tetrachloromethane to cyclohexene.

The volatile products of the reaction were identified by GC-MS. Pure samples were prepared so that they could be used as standards. These included 1-chloro-2-(trichloromethyl)cyclohexane, (as an isomeric mixture), 7,7-dichloronorcarane and 3-chlorocyclohex-1-ene.
The other products identified in the reaction were 3-(trichloromethyl)cyclohex-1-ene and (trichloromethyl)cyclohexane. It was not possible to isolate these as they proved too volatile. They were not prepared by other routes as these compounds were minor by-products of this reaction.

Table 2.30 : Source of catalyst.

Catalyst	Source
$[Co_2(CO)_8]$	Donated by B.P. Research centre.
$[Mo_2(CO)_6Cp_2]$	Prepared by literature method [28].
$[Mo_2(CO)_6Cp_2^*]$	Prepared by Dr. N.Khazal
$[\{Mo_2(CO)_6Cp_2\}CH_2]$	Donated by Dr.T.Bitterwolf
$[\{Fe_2(CO)_4Cp_2\}CH_2]$	Donated by Dr.T.Bitterwolf
$[RuCl_2(PPh_3)_3]$	Prepared by literature method[29].
$[RuH_2(PPh_3)_3]$	Prepared by Dr.J.Furze.[30]
$[RuHMe_2(SiPhH_2)(PPh_3)_3]$	Prepared by Dr.J.Furze[30]
$[RuCl_2\{(4\text{-}Cl\text{-}C_6H_4)_3P\}_3]$	Prepared by literature methods[31]
$[RuCl_2\{(4\text{-}CH_3\text{-}C_6H_4)_3P\}_3]$	Prepared by literature methods[31]
$[RuCl_2\{(4\text{-}OCH_3\text{-}C_6H_4)_3P\}_3]$	Prepared by literature methods[31]
$[Ru_2Cl_4\{DIOP\}_3]$	Prepared by literature methods[32].
$[RhCl(PPh_3)_3]$	Prepared by literature method[33].
$[\{Rh(COD)Cl\}_2]$	Prepared by T.Black.

Table 2.31 : Solvent purification

Solvent	Grade	Method
Hexane	GPR	Refluxed over sodium, then distilled.
Pentane	GPR	Refluxed over sodium, then distilled.
Octane	GPR	Refluxed over sodium, then distilled.
Cyclohexane	GPR	Refluxed over sodium, then distilled.
Cycloheptane	GPR	Refluxed over sodium, then distilled.
Methylcyclohexane	GPR	Refluxed over sodium, then distilled.
Decalin	GPR	Refluxed over sodium, then distilled.
Benzene	AR	Used as received.
Toluene	GPR	Refluxed over sodium, then distilled.
Bromobenzene	GPR	Passed through activated alumina, then distilled from sodium.
1,2-dichlorobenzene	GPR	Passed through activated alumina, then distilled from sodium.
Methoxybenzene	GPR	Passed through activated alumina, then distilled from sodium.
1,2-dimethylbenzene	GPR	Fractionally distilled from P_2O_5.
1,3-dimethylbenzene	GPR	Fractionally distilled from P_2O_5.
Nitrobenzene	GPR	Passed through activated alumina, distilled from P_2O_5.

Table 2.31 continued :

Solvent	Grade	Method
Dichloromethane	AR	Used as received.
Trichloromethane	AR	Used as received.
Tetrachloromethane	GPR	Distilled from P_2O_5
Methanol	AR	Used as received
Ethanol (Absolute)	AR	Used as received
Ethyl acetate	GPR	Distilled from P_2O_5 prior to use.
Tetrahydrofuran	GPR	Dried over sodium/potassium and distilled prior to use.
Diglyme	GPR	Dried over sodium, then distilled prior to use.

2.5.1.2 Preparation of 1-chloro-2-(trichloromethyl)cyclohexane (I).

Tetrachloromethane (50ml, 0.52 moles), cyclohexene (1.74g, 0.02 moles), and $[RuCl_2(PPh_3)_3]$ (0.5g, 5.2×10^{-4} moles) were refluxed under nitrogen for 48 hours. The solvent was removed under reduced pressure and the remaining reaction mixture then fractionally distilled. Two fractions were collected, of which the second (80°-84°C) was found to contain a mixture of trans and cis isomers of the required product (2.15g, 43 %). This was characterised by ^1H NMR and mass spectra. The ^1H NMR spectrum in tetrachloromethane shows resonances due to both trans and cis isomers, at the chemical shifts reported in the literature (Table 2.32)[4].

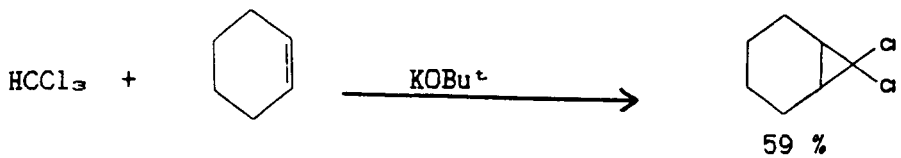
Table 2.32[4] : Chemical shifts of protons in the two isomers of (I).

Isomer	H-CCl (δ)	$H-CCl_3$ (δ)	$-(CH_2)_4-$ (δ)
cis	4.93 (m)	2.6 (m)	1.37-2.53 (m)
trans	4.51 (m)	2.8 (m)	1.37-2.53 (m)

The mass spectrum showed ions at m/z 234 (M^+ based on ^{35}Cl), 199 ($M-Cl^+$), 163 ($M-H-2Cl^+$), 127 ($M-2H-3Cl^+$). The purity was assessed by GLC and found to be 99 %.

2.5.1.3. Preparation of 7,7-dichlorobicyclo[4.1.0]heptane (7,7-dichloronorcarane)[34].

This was prepared according to the literature method which involved the reaction of a strong base with a haloalkane to generate the dichlorocarbene which in the presence of cyclohexene forms 7,7-dichloronorcarane (equation 2.59)[34].



(2.59)

Potassium metal (12g, 0.3 mole) and t-butanol (300 ml) (which had been dried over activated magnesium filings prior to the reaction) were refluxed with stirring until all the potassium had reacted. The stirred solution was evaporated down to dryness then dried in a vacuum oven at 150°C. Cyclohexene (200 ml) was slowly added to the resulting white powder. The flask was then placed in an ice bath and the contents allowed to cool. Trichloromethane (24 ml) was added in a dropwise fashion, the mixture reacting vigorously, forming a gelatinous mass, which was difficult to stir. Pentane (50 ml) was added, and with stirring the remainder of the trichloromethane could be added. The dark brown mixture was stirred for a further 30 minutes at room temperature, then poured into water (250 ml). The organic layer was separated, combined with a further pentane extract of the aqueous layer and dried over anhydrous magnesium sulphate. The solution was distilled, to remove the solvent and then fractionally distilled in vacuo to give 50.2g (21.2 %, yield based on trichloromethane used) of 7,7-dichloronorcarane. This was identified by IR, ^{1}H-NMR and mass spectra. The IR showed a characteristic C-H stretch at 3012 cm^{-1} and a ring deformation mode of the cyclopropyl

ring[35] at 1025 cm^{-1}.

The ^{1}H-NMR showed peaks consisting of multiplets at δ1.38 and δ1.70 ppm which are assigned to α-methylene and β-methylene protons respectively[36]. The mass spectrum showed ions at m/z M^+ 164 (based on ^{35}Cl), 93($C_7H_9^+$), 81($C_6H_9^+$), 55($C_4H_7^+$).

The purity of 7,7-dichloronorcarane was assessed by GLC to be 99.0 %.

2.5.1.4 Preparation of 3-chlorocyclohex-1-ene.

3-chlorocyclohex-1-ene was prepared by chlorinating cyclohexen-3-ol with thionyl chloride[37]. Thionyl chloride was purified by distilling twice over sulphur prior to use. A stirred solution of thionyl chloride (3.05g, 0.026 mmoles) in diether ether (25 ml) under nitrogen was cooled in an ice-bath maintained at -15°C by the addition of ammonium chloride. A solution of cyclohexen-3-ol (5g, 0.05 moles) in diethyl ether (25 ml) was added dropwise and an exothermic reaction ensued. Once the reaction was completed, the diethyl ether was removed under vacuum whilst maintaining the solution at -15°C. The residue was flash distilled, resulting in 0.65g (11 %) of 3-chlorocyclohex-1-ene. The mass spectrum showed M^+ 116 (based on ^{35}Cl). Other fragments included 81($C_6H_9^+$),and 55($C_4H_7^+$). The ^{1}H-NMR ($CDCl_3$), showed the peaks at δ1.50-2.50 (m, 6H, CH_2), δ4.55 (br s, 1H) and δ5.80-5.90 (br s, 2H). The ^{1}H-NMR also showed the presence of some diethyl ether. However, due to the low yield of the reaction and the high volatility of the material it was not further purified. The purity as assessed by GLC was found to be 76 %.

2.5.1.5 Reaction between cyclohexene and tetrachloromethane in the presence of $[Co_2(CO)_8]$

The reaction was carried out as described in the literature[1]. Tetrachloromethane (6.41g, 40 mmoles), cyclohexene (16.2g, 197 mmoles) and $[Co_2(CO)_8]$ (0.65g, 2 mmoles) were refluxed in hexane (25 ml) for 6 hours (after being degassed three times by the freeze-pump-thaw method). After the reaction was complete a small sample (3 ml) was syringed out for GLC analysis.

This analysis was carried out on a 25m BP10 column with an oven temperature of 150°C; an injector temperature of 225°C; a detector temperature of 250°C and a flow rate of 1 ml min^{-1}. Methyl myristate was employed as internal standard. The response factor was measured three times during the analysis. The yield was calculated as illustrated in Appendix 5. The chromatogram (figure 2.1) shows two peaks which were identified by GC-MS, as arising from 3-(trichloromethyl)cyclohex-1-ene and (trichloromethyl)cyclohexane. The mass spectra are represented in Appendix 6.

The remainder of the reaction mixture was filtered under nitrogen. A dirty pink solid (1.83g) was collected and found to contain Co^{II} and Cl^- ions, whilst the filtrate was reduced and the residue was vacuum sublimed at 45°C producing $[ClCCo_3(CO)_9]$ (0.2g, 22 %).

2.5.1.6 Reaction between tetrachloromethane and $[Co_2(CO)_8]$ in hexane

Tetrachloromethane (21.4g, 139 mmoles) was added to $[Co_2(CO)_8]$ (4.50g, 13.2 mmoles) in hexane (fraction) (100 ml) and the mixture stirred at 65°C for 7 hours (controlled via a thermostatically regulated water bath). The product was filtered under nitrogen producing a pink-grey precipitate containing Co^{II} and Cl^- ions. The volatiles were removed from the filtrate under reduced pressure and separated by fractional distillation. GLC analysis was carried out (using a 25m BP10 column at 60°C, other conditions as described previously (sect 2.5.1.5)), the highest boiling fraction showing that the major peak was not due to tetrachloroethene (Appendix 1). (The large number of peaks in the solvent front is due to using hexane fraction). The other fractions were also investigated by GLC for tetrachloroethene but again none were found. The involatile residue was taken up in hexane and analysed for hexachloroethane but none was detected (using a BP10 column at 150°C other conditions as previously described). After this solution was concentrated under reduced pressure, column chromatography of the residual liquor using pentane as eluant yielded $[ClCCo_3(CO)_9]$ (40 %) identified by its mass and infrared spectra. A trace amount of $[Co_4(CO)_{12}]$ was also detected by infrared and mass spectroscopy.

2.5.1.7 Reaction of 1-chloro-2-(trichloromethyl)cyclohexane in hexane in the (a) absence and (b) presence of $[Co_2(CO)_8]$

(a) Absence of $[Co_2(CO)_8]$

The adduct (0.331g, 1.40 mmoles) was heated in hexane (25 ml) (with methyl myristate present (0.21g); employed as a GLC standard) under nitrogen for 15 hours. Periodically, over the first 5 hours, the reaction was sampled (by syringe) and the samples analysed by GLC (conditions as 2.5.1.5). A final sample was taken after 15 hours. The gas chromatograms recorded during this experiment showed that 1-chloro-2-(trichloromethyl)cyclohexane did not decompose on heating. The isomeric ratio also remained unaffected.

(b) Presence of $[Co_2(CO)_8]$

The reaction was carried out in an identical manner to (a) but $[Co_2(CO)_8]$ (0.722g, 2.11 mmol) was present. In this case the adduct was observed to decompose to 30 % of its initial value, (figure 2.2). The products observed in this reaction were 3-(trichloromethyl)cyclohex-1-ene, (trichloromethyl)cyclohexane, the cluster, $[ClCCo_3(CO)_9)]$ and cobalt(II) chloride.

2.4.2 The effect of using a variety of catalysts on the addition of tetrachloromethane to cyclohexene.

2.4.2.1 Preparation of catalysts

The source of all the catalysts used is shown in Table 2.30.

(a) Preparation of cyclopentadienyltricarbonylmolybdenum dimer $[Mo_2(CO)_6Cp_2]$

$$2NaH + 2Cp \xrightarrow{THF} 2NaCp + H_2 \quad (2.60)$$

$$NaCp + [Mo(CO)_6] \xrightarrow{THF} [Na^+(Mo(CO)_3Cp)^-] \quad (2.61)$$

$$2[Na^+(Mo(CO)_3Cp)^-] + [Fe_2(SO_4)(aq)] \longrightarrow [Mo_2(CO)_6Cp_2] + 2Fe(SO_4)_2 + Na_2SO_4 \quad (2.62)$$

This complex was prepared according to the literature method[28]. Sodium cyclopentadienyl was prepared from sodium hydride (0.18g, 7.5 mmole) and freshly distilled cyclopentadiene (1.45ml, 7.5 mmole) in freshly distilled tetrahydrofuran (40ml). Molybdenum hexacarbonyl (1.33g, 5.04 mmole) was added against a nitrogen counterstream, then the solution was degassed by the freeze-pump-thaw technique. This solution was refluxed for 6 hours, after which an acidified solution of iron(III) sulphate (1.38g, 2.46 mmole in 20ml of distilled water, acidified with 2ml of glacial acetic acid) was added at -10°C, which resulted in the immediate formation of purple crystals of $[Mo_2(CO)_6Cp_2]$. Part of the solvent (20ml) was then removed under vacuum and the remainder of the solution was filtered (under nitrogen). The crystals were washed with distilled water and n-pentane and dried in vacuo.(Yield 82 %). The complex was identified by IR spectroscopy (in isooctane solution) and elemental analysis.

IR : ν_{CO} 1889, 1859 cm^{-1}.

Elemental analysis : Found : C, 39.28 %; H, 2.60 %.

Calculated : C, 39.37 %; H, 2.06.

(b) Preparation of dichlorotris(triphenylphosphine)ruthenium(II), $[RuCl_2(PPh_3)_3]$.

$$RuCl_3.3H_2O + 6\ PPh_3 \xrightarrow[65^{o}C,\ N_2,\ 3\ hours]{Methanol} [RuCl_2(PPh_3)_3] + \text{Other Products} \quad (2.63)$$

The reaction was carried out according to the literature method[29]. Ruthenium(III) chloride trihydrate (0.5g, 1.91 mmole) was dissolved in methanol (120ml) then degassed by heating under nitrogen for 2 hours. Triphenylphosphine (3g, 11.0 mmoles) was then added under a nitrogen counterstream and the mixture was refluxed for 3 hours. Black crystals of the product were formed and these were filtered, washed with ether under nitrogen and dried in vacuo. (Yield 83 %).

Elemental analysis Found : C, 67.80 %; H, 4.76 %; Cl, 7.34 %.

Calculated : C, 67.64 %; H, 4.73 %; Cl, 7.34 %.

(c) Preparation of μ-DIOPbis(dichloromono(DIOP)ruthenium(II), $[Ru_2Cl_4(DIOP)_3]$.

$$2[RuCl_2(PPh_3)_3] + 3DIOP \xrightarrow[Hexane]{N_2} [Ru_2Cl_4(DIOP)_3] + 6PPh_3 \quad (2.64)$$

The reaction was carried out according to a literature method[32]. Dichlorotris(triphenylphosphine)ruthenium(II) (0.17g, 0.17 mmole) and (-)-DIOP (0.14g, 0.209 mmole) were dissolved in hexane (20ml), degassed and then refluxed under nitrogen for 6 hours. A green precipitate of $[Ru_2Cl_4(DIOP)_3]$ resulted which was collected by filtration, washed with hexane and vacuum dried. (Yield 50 %). The

complex was identified by its IR spectrum which showed ν(Ru-Cl) at 310 cm^{-1}. Its electronic spectrum showed the expected maxima at 455nm and 700nm. The purity was assessed by TLC on silica plates which showed only one component.

(d) Preparation of chlorotris(triphenylphosphine)rhodium(I), $[RhCl(PPh_3)_3]$.

$$RhCl_3.3H_2O + 6\ PPh_3 \xrightarrow[N_2,\ 3\ hours]{Ethanol} [RhCl(PPh_3)_3] + \text{Other Products} \qquad (2.65)$$

The reaction was carried out according to the literature method[33]. Ethanol (95 %, 150ml) was degassed by refluxing for 2 hours under nitrogen. Rhodium(III) chloride trihydrate (0.5g, 0.19 mmoles) and recrystallised triphenylphosphine (3g, 11.0 mmoles) was added. The mixture was refluxed under nitrogen for 3 hours which resulted in a red crystalline solid of $[RhCl(PPh_3)_3]$. This was removed by filtration and dried in a vacuum oven. (Yield 92 %).

Elemental analysis Found : C, 70.08 %; H, 4.89 %; Cl, 3.83 %.

Calculated : C, 70.10 %; H, 4.89 %; Cl, 3.83 %.

2.5.2.2 A study of the reaction between tetrachloromethane and cyclohexene in the presence of various catalysts.

The reactions were carried out in an identical manner so that the results would be comparable. The series of reactions which were studied in sealed tubes were

(i) Metal carbonyl catalysts (except $[Co_2(CO)_8]$ and $[(C_6H_5CO)_2O_2]$ which were carried out as refluxes).

(ii) Ruthenium based catalysts.

The reactions with ruthenium and rhodium complexes containing DIOP and DIPHOS ligands were carried out under reflux.

Typically, The catalyst (4.0×10^{-5} moles) was weighed into the tube, the reagents (tetrachloromethane (1.5 ml, 0.0155 moles), cyclohexene (0.5 ml, 5.1×10^{-3} moles) in a solvent (6.3ml) were then syringed into the tube and immediately afterwards, the tube and its contents were degassed by the freeze-pump-thaw method (three times). The tube was sealed, allowed to warm up to room temperature and then heated in an oven at 80°C for 6 hours. The ratio of reagents used of CCl_4 : cyclohexene : [Catalyst] was 388 : 125 : 1.

When the reaction was carried out as a reflux the same ratio of tetrachloromethane to cyclohexene to catalyst was used on a larger scale. In the case of $[(C_6H_5CO)_2O_2]$, this compound was dried over anhydrous sodium sulphite in toluene under nitrogen overnight. Then the appropriate quantity was syringed into the rest of the degassed mixture and refluxed under nitrogen for 6 hours.

All reactions were performed in duplicate.

2.5.2.3 A study of the reaction between tetrachloromethane and cyclohexene in the presence of rhodium and ruthenium complexes containing DIOP and DIPHOS ligands.

The catalyst was generated in situ and the reaction was carried out as suggested in the literature[6].

Typically, the catalyst $[Rh(COD)_2Cl_2]$ (0.18g, 0.0375 mmoles) and (-)-DIOP (0.0406g, 0.0825 mmoles) were added to benzene (3.5ml) in a Schlenck tube and then degassed (by the freeze-pump-thaw method). This solution of catalyst was added to a reaction vessel (by means of a transfer needle) containing cyclohexene (0.42g, 5.1 mmoles), CCl_4 (2.32g, 0.015 moles), methyl myristate (0.1g) and benzene (12.5 ml). The mixture was refluxed under nitrogen at 80°C for 18 hours.

The reactions with $\{[Rh(COD)_2Cl_2]/(DIPHOS)\}$, $\{[RuCl_2(PPh_3)_3]/(DIOP)]$, $\{[RuCl_2(PPh_3)_3]/(DIPHOS)\}$ and the appropriate blank reactions (with phosphine only) were all carried out in this way.

2.5.4.1 The effect of the addition of tetrachloromethane to alkenes in the presence of $[RuCl_2(PPh_3)_3]$.

All the reactions were carried out in sealed tubes. The solvents used were purified by methods described in Table 2.31. Typically, $[RuCl_2(PPh_3)_3]$ (0.037g, 0.039 mmoles) was weighed into the tube. Cyclohexene (0.41g, 5.0 mmoles), tetrachloromethane (2.35g, 1.54 moles), methyl myristate (0.1g) (internal standard) and solvent were mixed and then syringed into the tube. The tube was immediately degassed, sealed and then allowed to equilibrate to room temperature. Finally the tube was placed in an oven at 80°C for 6 hours. The reaction mixture was analysed by GLC (conditions as in sect. 2.5.1.8).

It should be noted that methyl myristate was used as internal standard for all the reactions except those carried out in ethanol and ethyl acetate. It was found that in these solvents, in the presence of $[RuCl_2(PPh_3)_3]$, methyl myristate becomes trans-esterified to ethyl myristate. Therefore, in these solvents heptane was used as an internal standard.

2.4.3.2 The effect of a resin on the addition of tetrachloromethane to cyclohexene in the presence of $[RuCl_2(PPh_3)_3]$

(a) Preparation of resin

This was prepared according to the literature method of Berbreiter et al[21].

Amberlyst 15, a macroreticular sulphonated polystyrene, $PS-SO_3H$ (purchased from Aldrich) (50g) was slurried with distilled water (200ml) and poured in a column (40 X 2.5 cm) with a plug of glass wool at the bottom. A solution of sodium hydroxide (1 mol dm^{-3}, 550ml) was passed through the column over a period of 2 hours, in order to convert the resin to $PS-SO_3Na$. The column was washed with distilled water (2 dm^{-3}), until the effluent became neutral to pH paper. An aqueous solution of silver nitrate (47g, 0.28 moles in 2 dm^{-3} of distilled water) was passed through the column over 24 hours until a precipitate of silver chloride was formed in the effluent on addition of aqueous sodium chloride solution. The resin was then washed with distilled water until all the excess silver had been removed (checked by the above test). The resin was then transferred to a beaker washed with ethanol, drained, washed with diethyl ether, air dried and finally dried in a vacuum oven for 24 hours.

(b) The effect of the resin on the addition of tetrachloromethane to cyclohexene in the presence of $[RuCl_2(PPh_3)_3]$.

These reactions were carried out in exactly the same way as in section 2.5.3.1, but with the addition of resin (0.5g) to the tube. When each resin reaction was carried out, a blank was run simultaneously.

2.5.3.3 The effect of the catalysts $[RuCl_2\{(4\text{-}X\text{-}C_6H_4)_3P\}_3]$ on the addition of tetrachloromethane to cyclohexene and oct-1-ene.

All the catalysts were prepared according to the literature methods, with some amendments[31,39].

(a) Preparation of $[RuCl_2\{(4\text{-}Cl\text{-}C_6H_4)_3P\}_3]$[31].

$$RuCl_3 3H_2O + 3\{(4\text{-}Cl\text{-}C_6H_4)_3P\} \xrightarrow{\text{Methanol}} [RuCl_2\{(4\text{-}Cl\text{-}C_6H_4)_3P\}_3] \quad (2.66)$$

Methanol (40ml) was added to ruthenium(III) chloride trihydrate (0.14g, 0.53 mmoles) then the solution was degassed by heating under nitrogen for 2 hours. This solution was transferred via a transfer needle to a reaction vessel containing tris(4-chlorophenyl)phosphine (0.64g, 1.75 mmoles). This mixture was refluxed for 18 hours. After this time the solution became orange, with a green precipitate at the bottom of the vessel. The solution was filtered under nitrogen. The solid green material was collected. (M.p 171 °C). This melting point suggests that the compound is likely to be $[RuCl_2\{(4\text{-}Cl\text{-}C_6H_4)_3P\}_2MeOH]$. The filtrate was concentrated by vacuum to half its volume. This resulted in an orange product being precipitated. The solution was placed in the refrigerator for 12 hours. The solid was collected by filtration, washed with methanol and petroleum ether and dried under vacuum. (Yield 55 %). M.p 178-182°C

(lit. 182°C).

Elemental analysis Found : C, 50.23 %; H, 2.99 %; Cl,31.31 %.

Calculated : C, 51.12 %; H, 2.86 %; Cl,30.74 %.

(b) Preparation of $[RuCl_2\{(4\text{-}CH_3O\text{-}C_6H_4)_3P\}_3]$[39]

$$RuCl_3.3H_2O + 6\{(4\text{-}CH_3O\text{-}C_6H_4)_3P\} \longrightarrow [RuCl_2\{(4\text{-}CH_3O\text{-}C_6H_4)_3P\}_3] + \text{Other products} \quad (2.67)$$

Ethanol (80ml) was added to ruthenium(III) chloride trihydrate (0.425g, 1.6 mmoles) and tris(4-methoxyphenyl)phosphine (3.43g, 9.6 mmoles) and the solution was refluxed under nitrogen for 6 hours. Deep red crystals of the product were filtered off before the solution cooled (Yield 81 %).

Elemental analysis Found : C,60.78 %; H, 5.19 %.

Calculated : C,61.57 %; H, 5.17 %.

(c) Preparation of $[RuCl_2\{(4\text{-}CH_3\text{-}C_6H_4)_3P\}_3]$

The reaction was carried out in the same way as (b) using ruthenium(III) chloride trihydrate (0.2125g, 0.81 mmoles) and tris(4-methylphenyl)-phosphine (1.48g, 4.87 mmoles), resulting in deep red crystals. (Yield 50 %).

Elemental analysis : Found : C, 69.09 %; H, 6.34 %; Cl 7.11 %.

Calculated : C, 69.74 %; H, 5.85 %; Cl 6.53 %.

The effect of the catalysts $[RuCl_2\{(4\text{-}X\text{-}C_6H_4)_3P\}_3]$ on the reaction between tetrachloromethane and cyclohexene/oct-1-ene

This series of reactions was carried out by reflux under nitrogen for 6 hours. In each reaction, cyclohexene (0.41g, 5.0 mmoles), (or oct-1-ene), tetrachloromethane (2.35g, 0.0155 moles), the catalyst (4.0×10^{-5} moles) and the solvent (hexane and benzene) were degassed and heated. The solutions were then analysed by GLC (as in sect. 2.5.1.8).

2.5.3.4 The effect of $[RuCl_2(PPh_3)_3]$ on the addition of tetrachloromethane to cyclohexa-1,3-diene.

Cyclohexa-1,3-diene was purified before use by distilling from sodium borohydride. The adduct formed was isolated by vacuum distillation. Typically, cyclohexa-1,3-diene (0.26g, 3.25 mmole), tetrachloromethane (1.65g, 10.5 mmoles) and $[RuCl_2(PPh_3)_3]$ (0.013g, 0.0135 mmoles) were syringed into a tube, degassed, sealed, allowed to equilibrate to room temperature and then heated in an oven at 80°C for 5 hours.

Analysis

The reaction mixtures were analysed using a HRGC 5160 mega series chromatograph with a 25m WCOT column. The oven temperature was 150°C, the injector temperature was 225°C, the detector temperature was 250°C and the flow rate was 75 $ml\,min^{-1}$. Methyl myristate was included as internal standard throughout.

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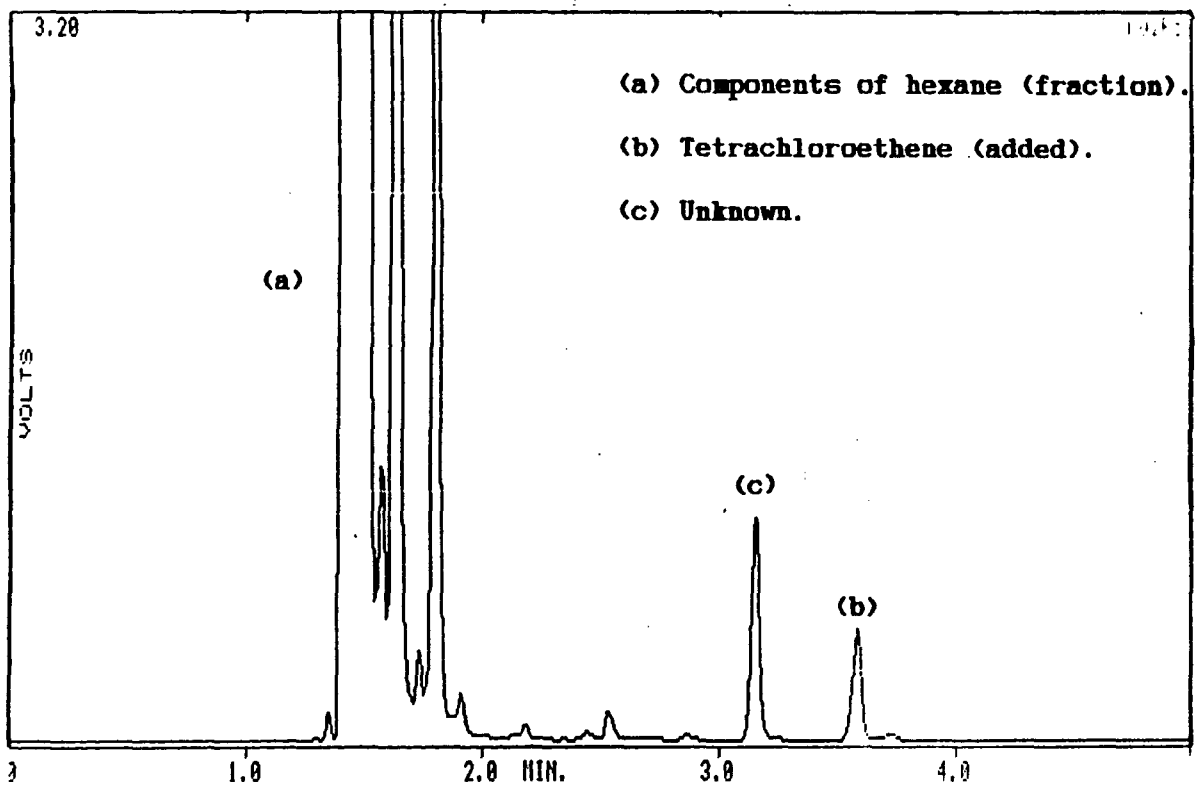
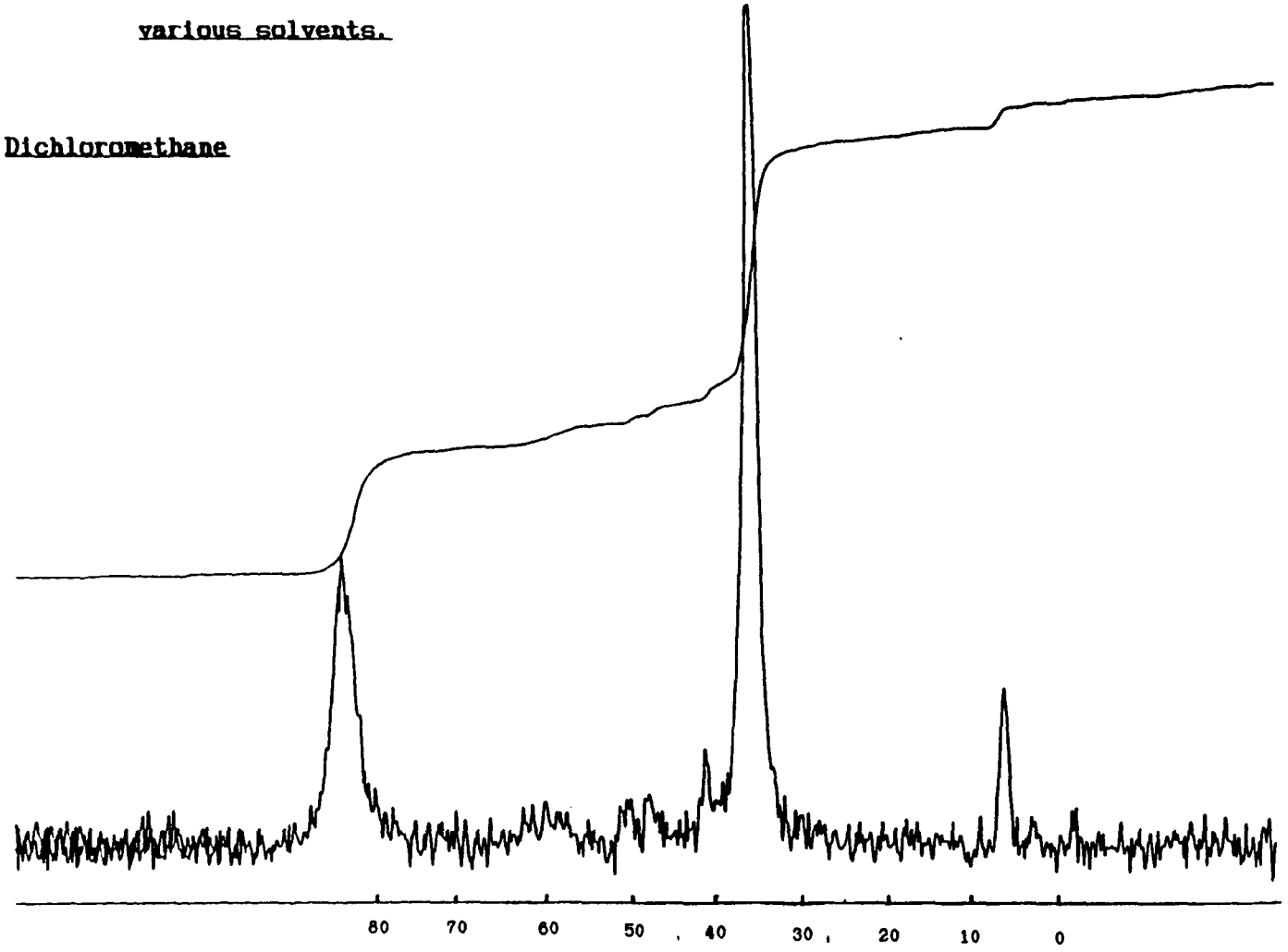
Appendix 1 : Chromatogram showing the volatile components from the filtrate of the reaction between $[Co_2(CO)_8]$ and CCl_4.



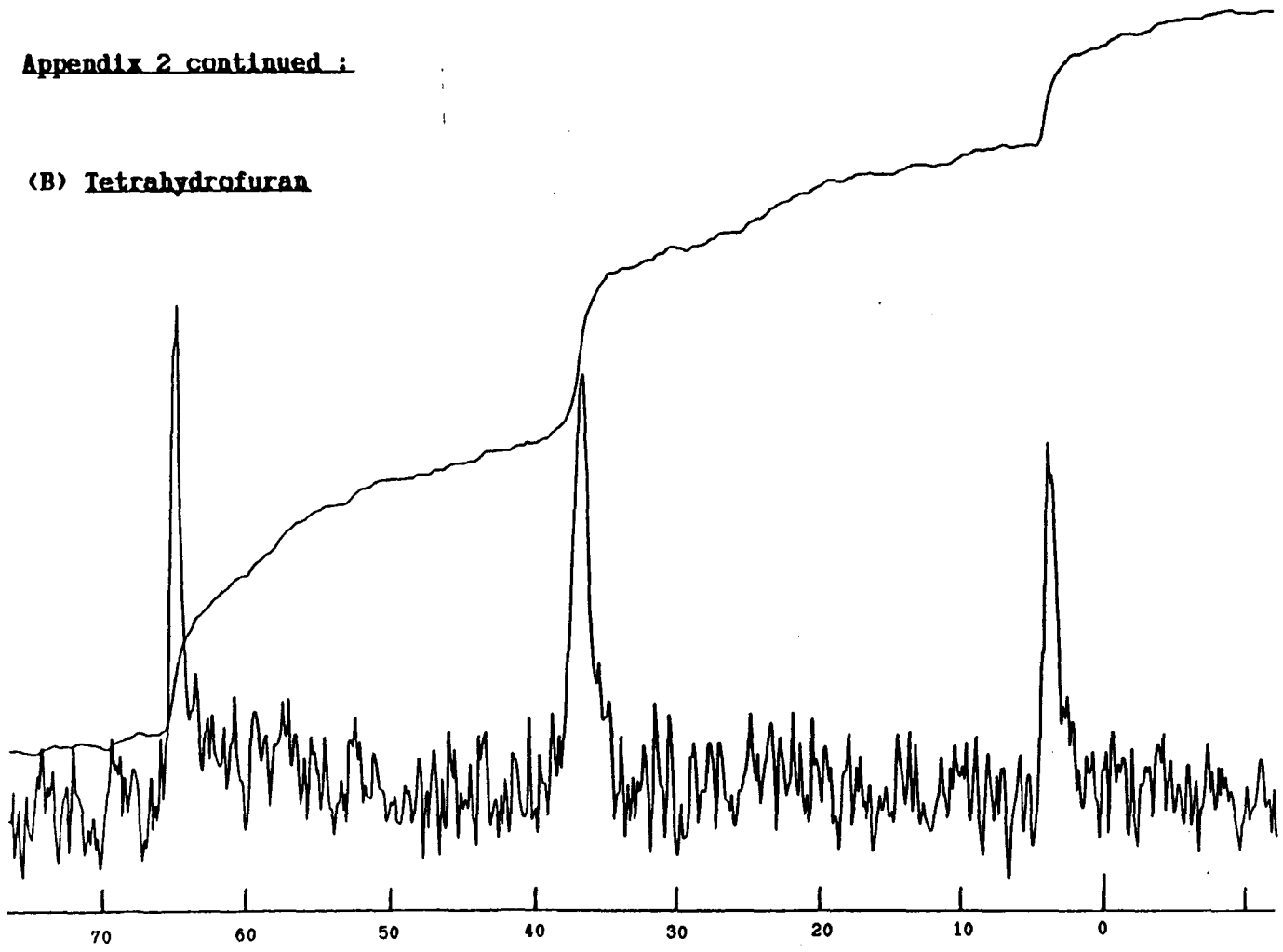
Appendix 2 : ^1H NMR spectra showing the dissociation of $[RuCl_2(PPh_3)_3]$ at -60°C in various solvents.

(A) Dichloromethane



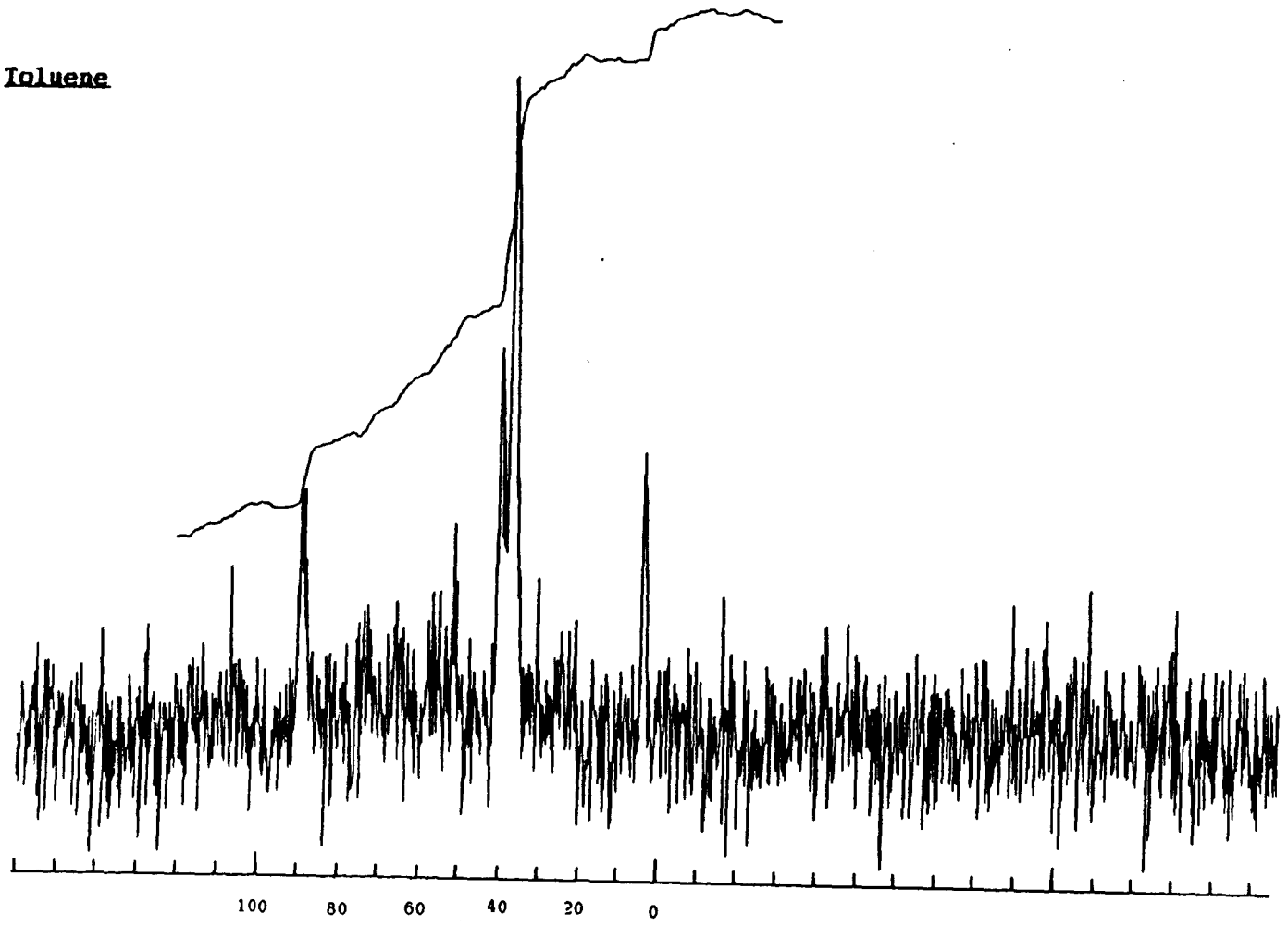
Appendix 2 continued :

(B) Tetrahydrofuran



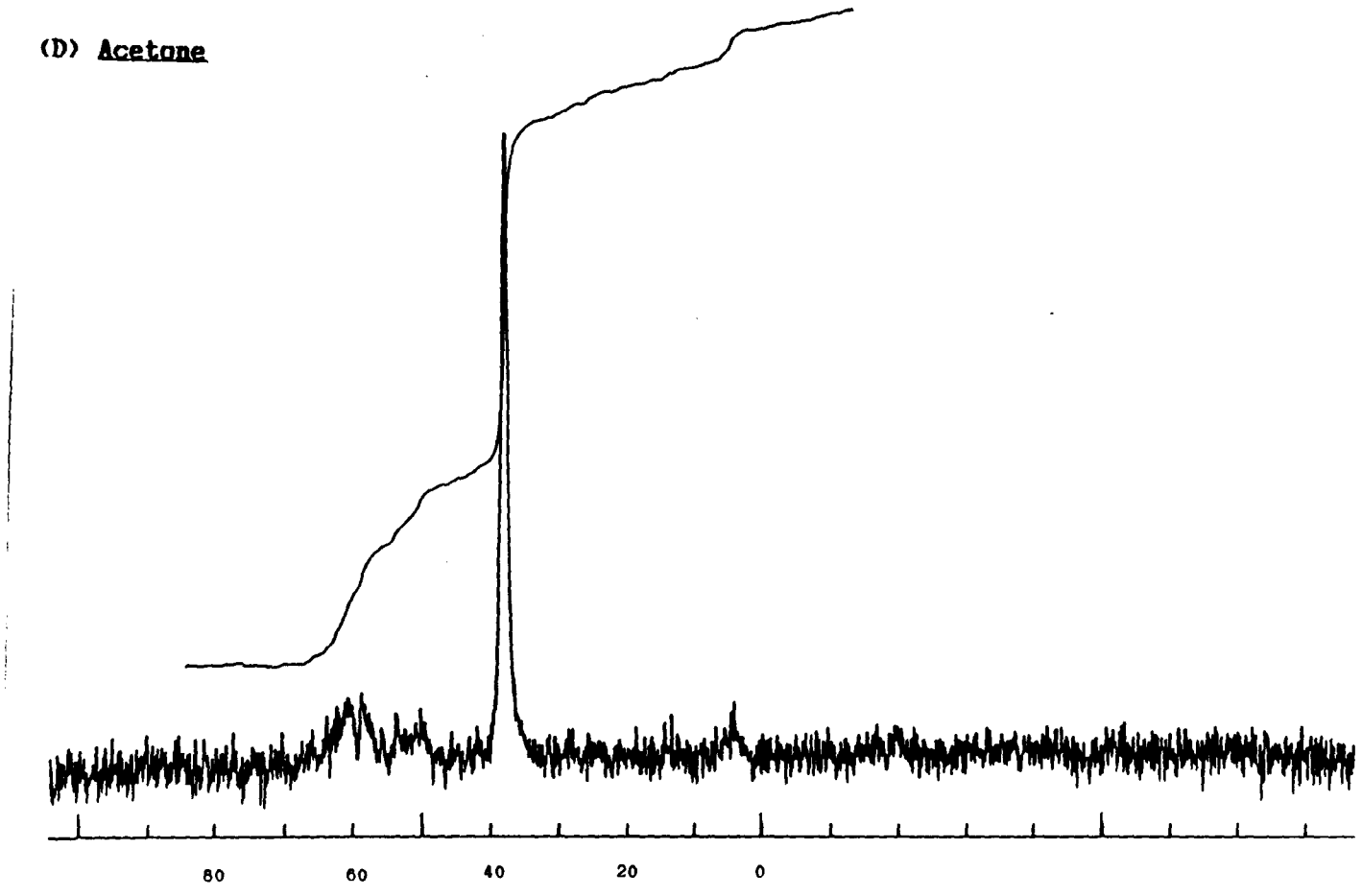
Appendix 2 continued :

(C) **Toluene**



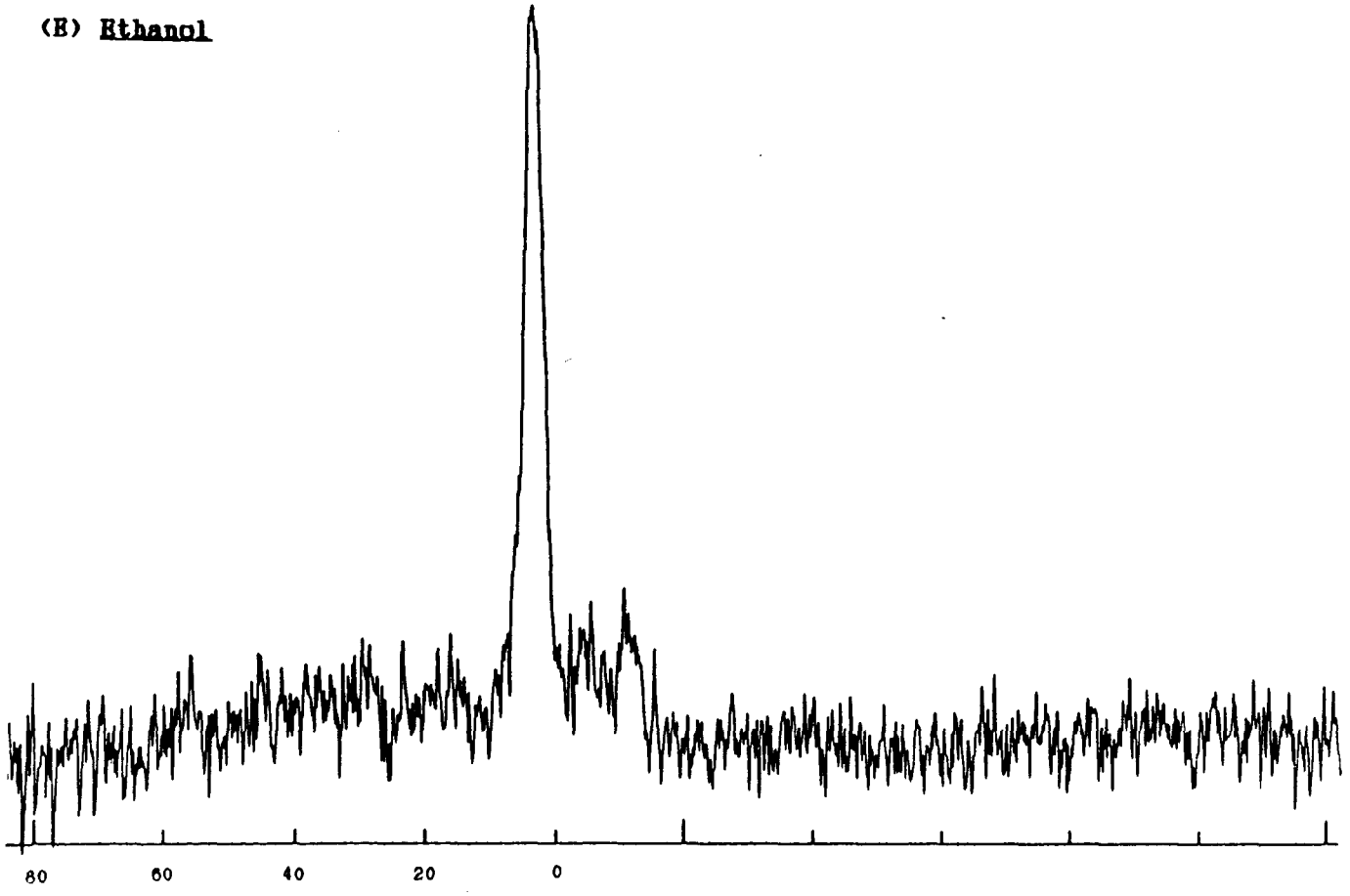
Appendix 2 continued :

(D) **Acetone**



Appendix 2 continued :

(E) **Ethanol**



Appendix 3 : Worked example of the calculation of the dissociation constant for $[RuCl_2(PPh_3)_3]$

$[RuCl_2(PPh_3)_3]$ is known to dissociate in solution according to the equilibrium :

$$\underset{x}{[RuCl_2(PPh_3)_3]} \rightleftharpoons \underset{y}{[RuCl_2(PPh_3)_2]} + \underset{z}{PPh_3}$$

The ^{31}P NMR spectrum at -60°C shows three resonances in most solvents:

Resonance, ppm	Assigned species
4-8	Free triphenylphosphine
40	$[RuCl_2(PPh_3)_3]$
70-90	$[RuCl_2(PPh_3)_3]$

Two resonances are observed for the non-equivalent phosphines in the complex. At lower temperatures (-90°C) resonances due the dimer can also be observed (figure 2.5).

The total concentration of complex, c is given by:

$$c = x + y.$$

Integration of the spectrum gives the ratio x/y.

Thus x and y can be defined and used to calculate the equilibrium constant K where

$$K = y^2 / x \quad \text{and}$$

$$\% \text{ Dissociation} = (y / c) \times 100$$

<u>For Dichloromethane</u>

$x / y = 6.25$ and $c = 9.04 \times 10^{-3}$ mol dm^{-3}

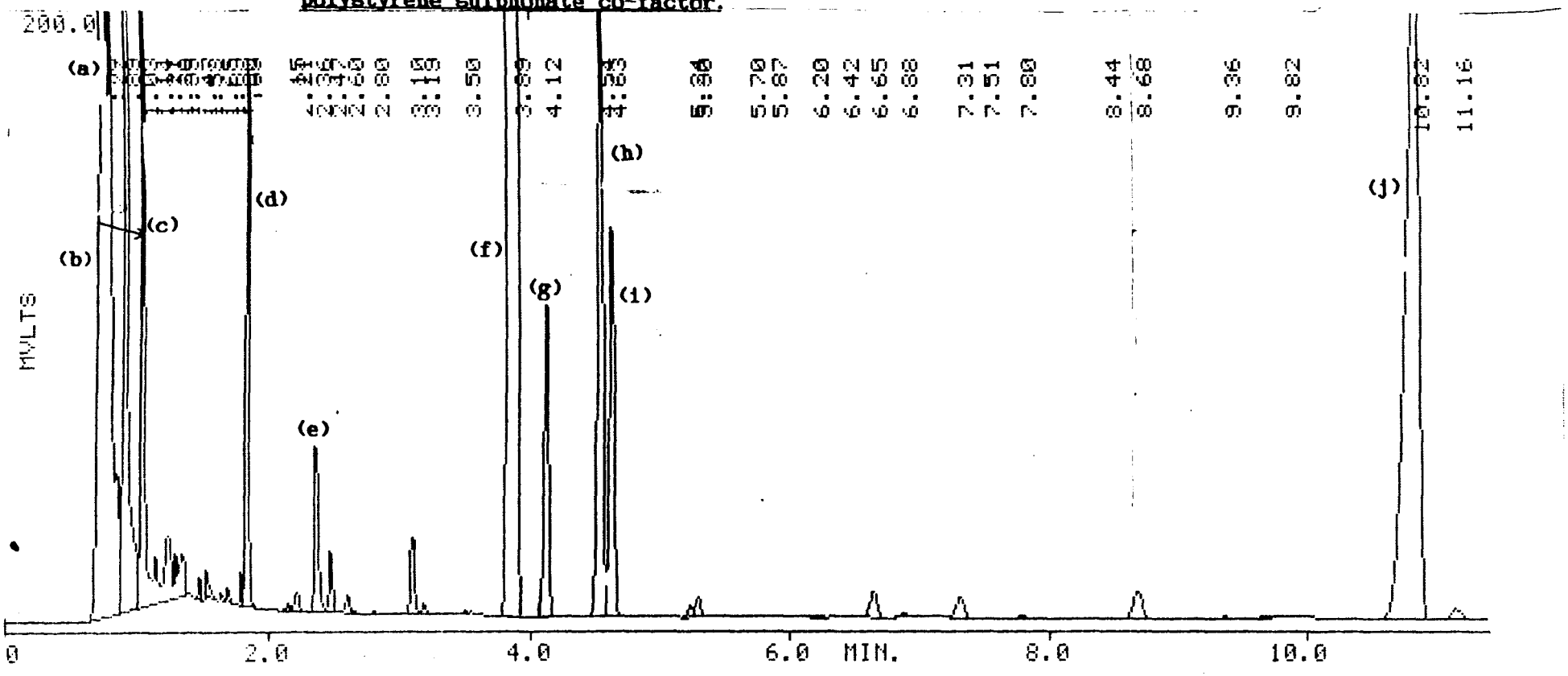
then $y = 9.04 \times 10^{-3} / 6.25 = 1.25 \times 10^{-3}$ mol dm^{-3}

$x = 6.25 \times 1.25 \times 10^{-3}$ mol dm^{-3}

Therefore, $K = (1.25 \times 10^{-3})^2 / 7.79 \times 10^{-3} = 2.0 \times 10^{-4}$

% Dissociation $= (1.25 \times 10^{-3} / 9.04 \times 10^{-3}) \times 100 = 14$ %.

Appendix 4 : Chromatogram showing the products of the reaction between cyclohexene and tetrachlomethane in the presence of $[RuCl_2(PPh_3)_3]$ and a silver(I) polystyrene sulphonate co-factor.



(a) Benzene, (b) cyclohexene, (c) tetrachloromethane, (h) cis-1-chloro-2-(trichloromethyl)cyclohexane, (d) 3-(trichloromethyl)cyclohex-1-ene, (e) (trichloromethyl)cyclohexane, (i) unknown, (f) trans-1-chloro-2-(trichloromethyl)cyclohexane, (g) unknown (j) methyl myristate.

Appendix 5 : Calculation of yield from GLC.

These can be carried out by measuring the integrated area of a peak which is directly proportional to the amount of solute eluted. Peak height may also be used but generally is less reliable. If all the components of a reaction mixture are similar in chemical composition so that detection sensitivity is the same for each peak then the percentage weight of a component i, is given by

$$\text{Percentage } i = \frac{\text{area of component, } i}{\text{total area}} \times 100$$

However, this assumption cannot be made for these experiments as the response does vary. This can be accounted for by a response factor, R_f.

$$R_f = \frac{\text{area of component, } i}{\text{area of standard}} \times \frac{\text{weight of standard}}{\text{weight of component , } i}$$

The standard used may be (1) external or (2) internal.

(1) External standard

A known quantity of a standard is added to the reaction mixture, after the reaction has been completed. Then the component and standard areas can be compared, and the quantity of component i can be calculated on the basis of the known quantity of standard.

(2) Internal standard

An internal standard is a material which is added to the reaction mixture before the reaction is started, so it is an inert substance which does not participate. This method was used for all the GLC work carried out, using methylmyristate (except where stated otherwise) as the internal standard. The yield was calculated as :

Weight of component i in injected sample, w_i

$$= \frac{\text{area of component, i}}{\text{area of standard}} \times \frac{\text{Response factor}}{\text{weight of standard}}$$

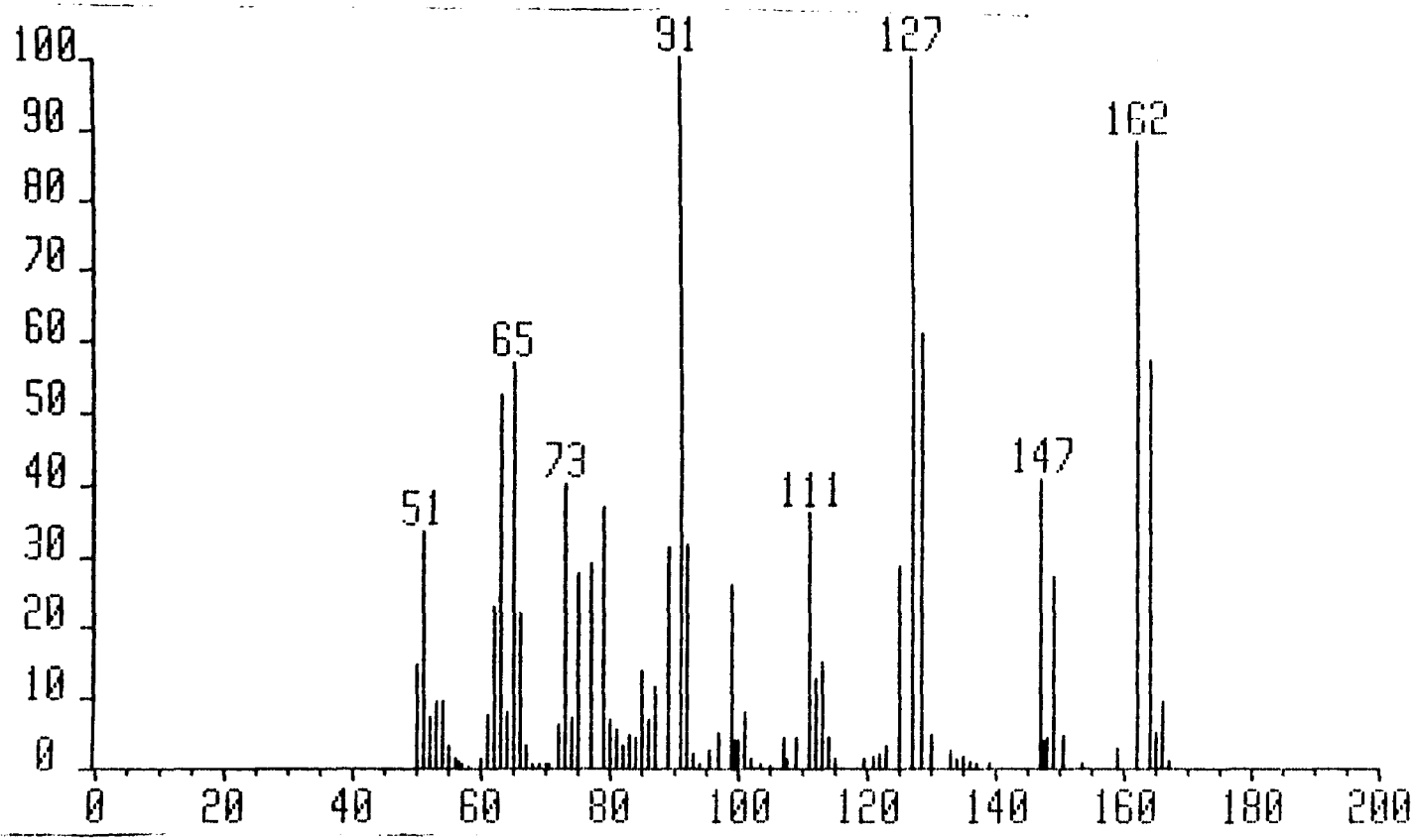
Total number of moles of component i produced, n_i

$$= \frac{w_i}{\text{Molecular weight of component, i}}$$

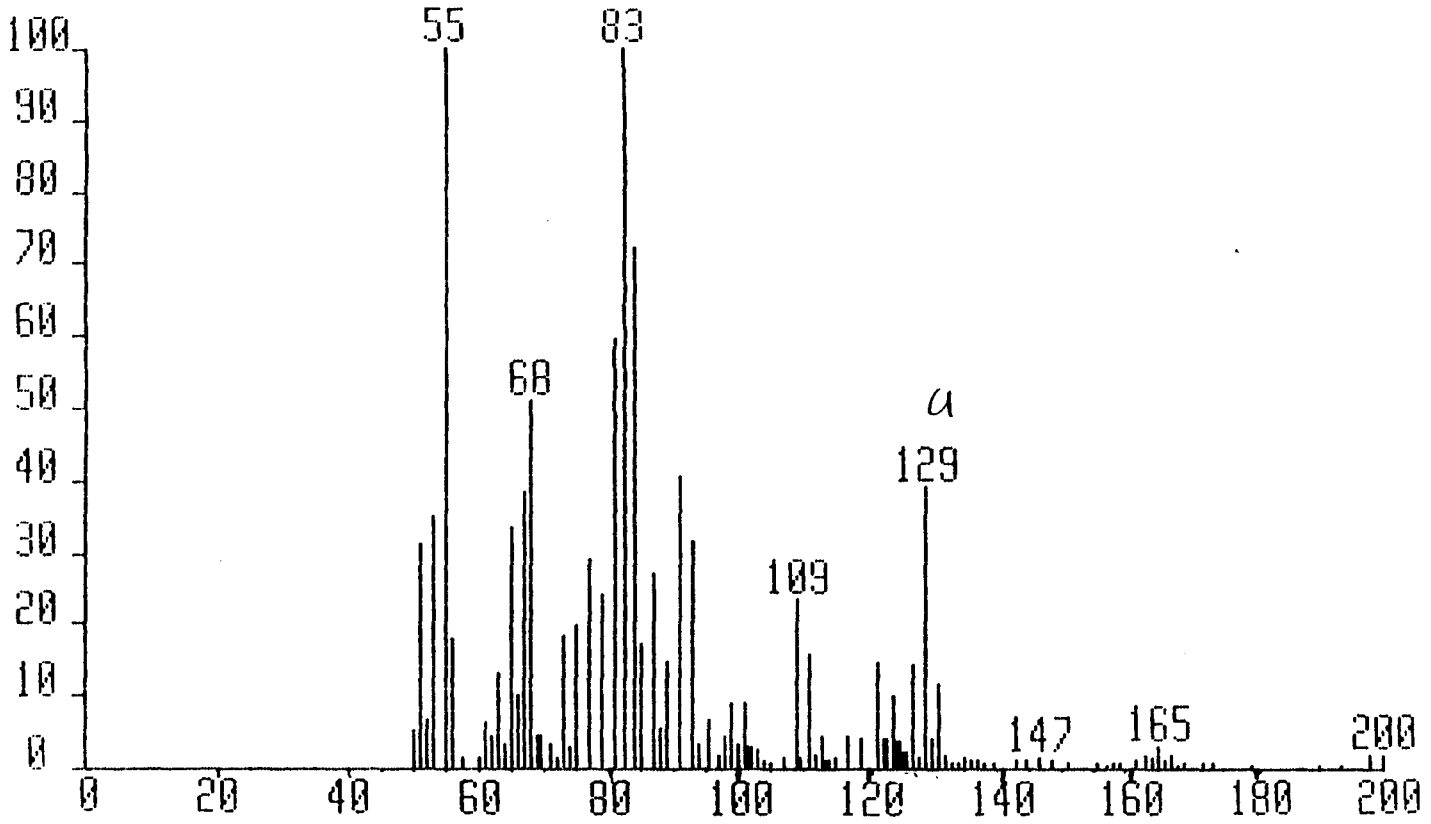
Therefore,

$$\text{percentage yield \%} = \frac{n_i}{\text{number of moles of starting material}} \times 100$$

Appendix 6 : Mass spectrum of 3-(trichloromethyl)cyclohex-1-ene (peak (d)



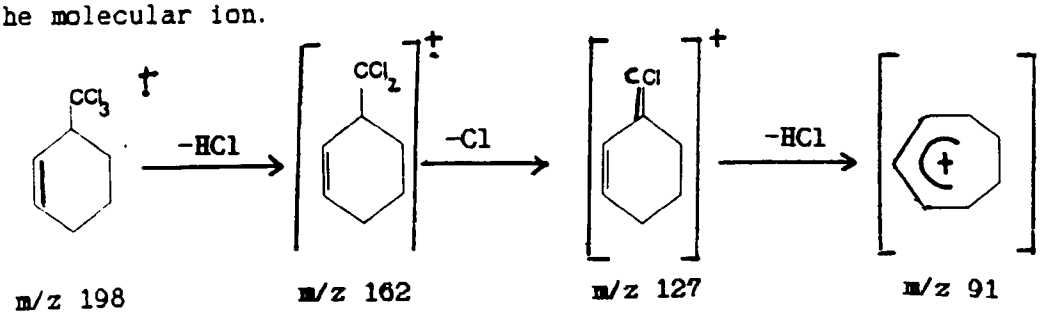
Appendix 6 : Mass spectrum of (trichloromethyl)cyclohexane (peak (e)



Appendix 6 : Explanation of mass spectra of peaks (d) and (e).

Peak (d) :

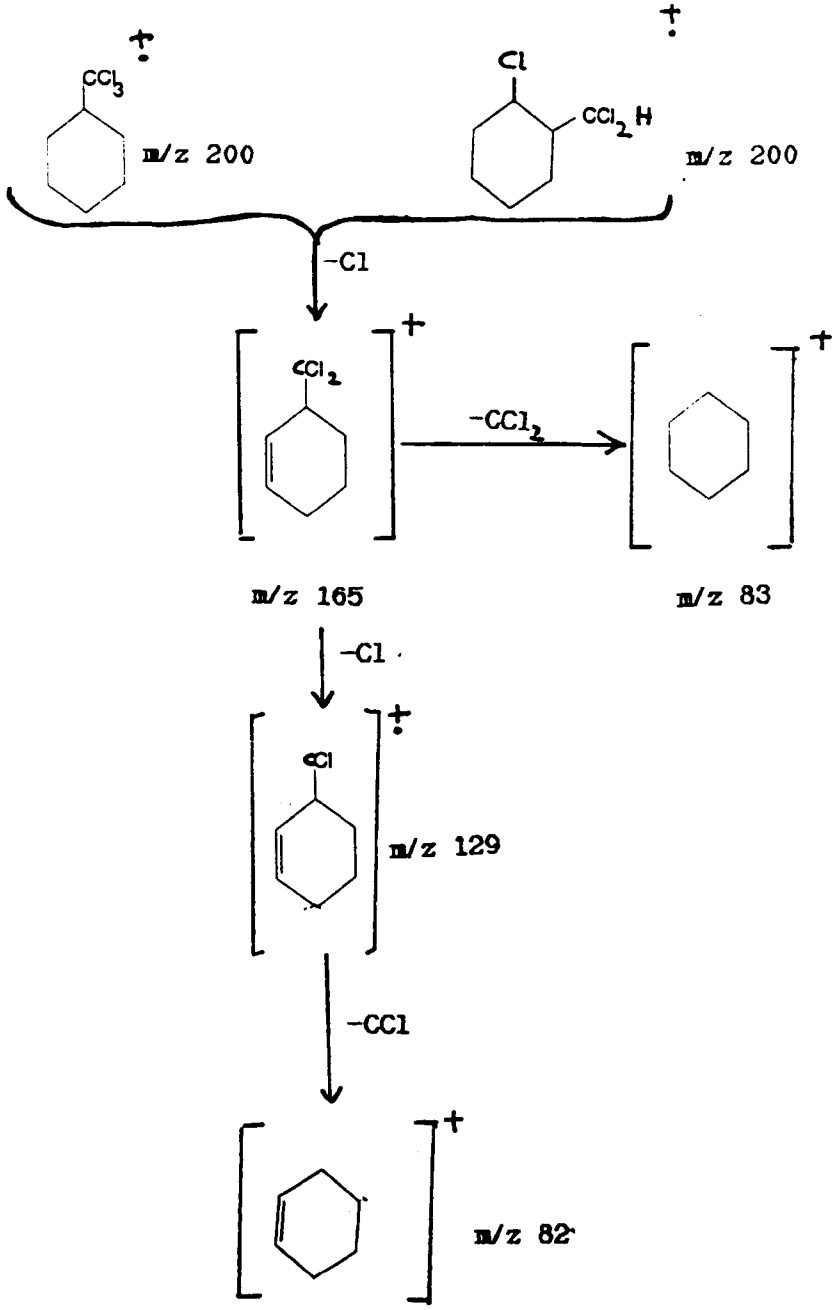
The mass spectrum of peak (d) does not show a molecular ion which would be expected at m/z 198. However the largest fragment at 162 shows a dichlorinated pattern corresponding to the loss of HCl from the molecular ion.



The further loss of chlorine leaves a monochlorinated fragment with a molecular weight of 127. This undergoes further loss of HClresulting in the formation of the tropylium ion (m/z 91). This suggests that peak A is 3-trichloromethylcyclohexene.

Peak B :

This mass spectrum shows a very small molecular ion peaks at m/z 200, however due to their small size the isotope pattern cannot be clearly distinguished. However, both trichlorocyclohexene and 1-chloro-2-(dichloromethyl)cyclohexane could also show this pattern. This can be explained by the losses :


CCl3
m/z 200
Cl
CCl2H
m/z 200
-Cl
CCl2
-CCl2
m/z 165
m/z 83
-Cl
Cl
m/z 129
-CCl
m/z 82

CHAPTER 3 : METAL CATALYSED FORMATION OF LACTONES

3.1 Introduction

It has been reported that dichloro and trichloroacetic acids react with alkenes in the presence of $[RuCl_2(PPh_3)_3]$ forming chloro-substituted lactones in high yields (see chapter 1, sect. 1.3.4). The present work has been concerned with reassessing the efficiency of these reactions and extending them to bromo-substituted lactones. Such compounds, containing the weaker C-Br bond should be more amenable to further reaction, allowing the formation of other substituted lactones. The reactions involving trichloroacetic acid in the presence of iron- and molybdenum-containing catalysts have also been studied.

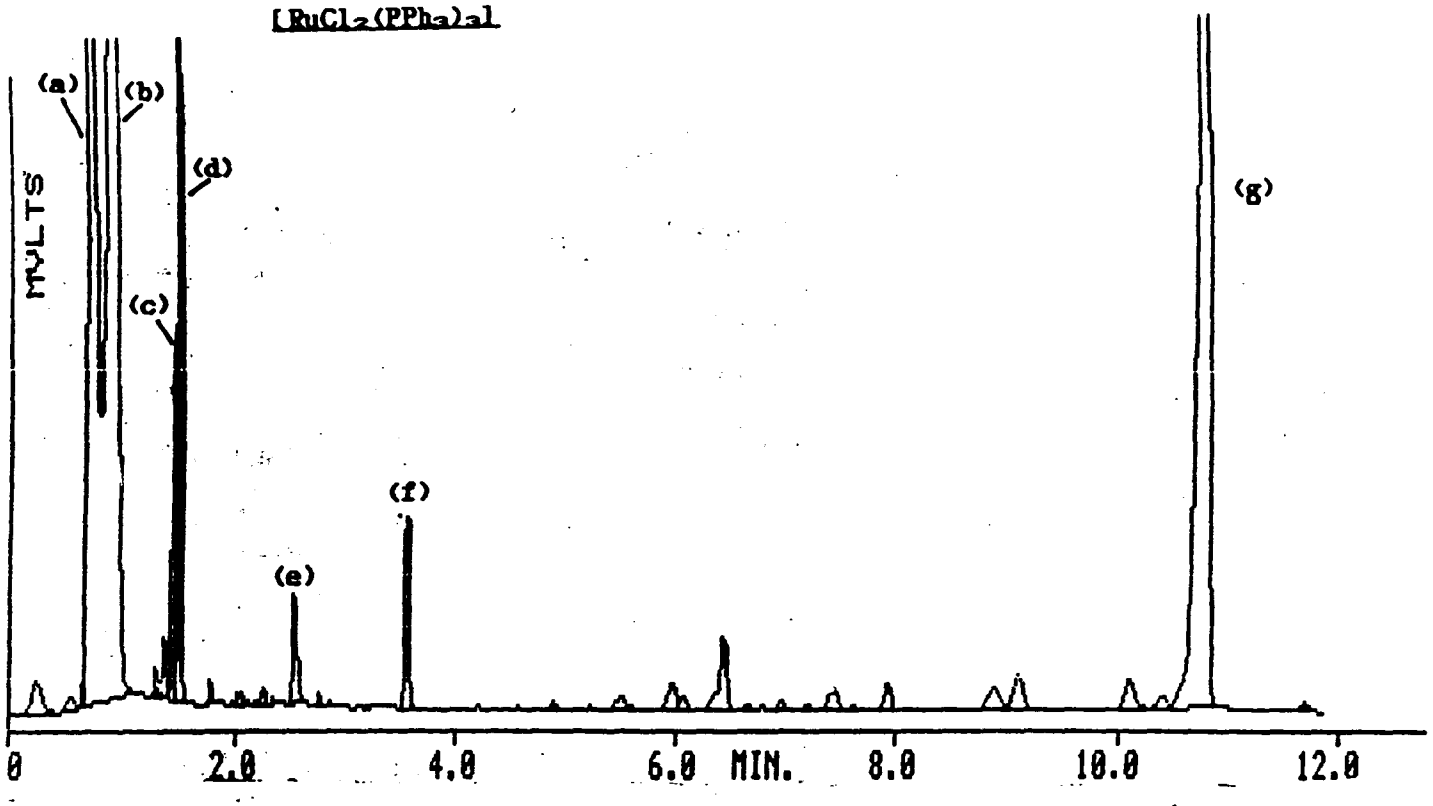
3.2 The reactions between trichloroacetic acid and alkenes.

3.2.1 Results and discussion.

3.2.1.1 The reaction between trichloroacetic acid and alkenes in the presence of $[RuCl_2(PPh_3)_3]$

The reactions studied (equation 3.1) were carried out according to literature methods[1]. A typical composition of the reaction mixture obtained from dodec-1-ene after 6 hours at 110°C is shown in Fig 3.1. In all cases, lower yields of lactone were obtained than those previously reported (Table 3.1). The overall mass balance of these reactions can be accounted for in terms of the presence of unreacted alkene and the formation of small quantities of esters ($RCH(OCOCCl_3)CH_3$) formed by a Markovnikov addition reaction (see later). (Activity tests were carried out on the catalysts prior to the experiments in order to check that the catalytic activity of the $[RuCl_2(PPh_3)_3]$ complex had not deteriorated. This was accomplished by

Figure 3.1 : Reaction between dodec-1-ene and trichloroacetic acid in the presence of $[RuCl_2(PPh_3)_3]$

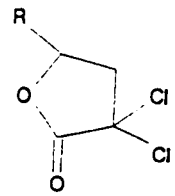


(a) = toluene, (b) = dodec-1-ene, (c) = 3-dodecyl trichloroacetate,

(d) = 2-dodecyl trichloroacetate, (e) = unknown,

(f) = methyl myristate, (g) = 4-decyl-2,2-dichloro-γ-butyrolactone.

Table 3.1 : The reaction between trichloroacetic acid and alkenes in the presence of $[RuCl_2(PPh_3)_3]$

$$RCH{=}CH_2 + Cl_3CCO_2H \xrightarrow{[RuCl_2(PPh_3)_3]}$$  (3.1)

Alkene	% Yield[a]			% Unreacted alkene
	Lactone		Ester	
Hex-1-ene	72.5	(79)	5.6	16.3
Oct-1-ene	58.3	(81)	2.4	39.3
Dec-1-ene[b]	55.0	(85)	3.9	3.0
Dodec-1-ene	62.4	(74)	24.1	11.2

[a] % Yields (GLC) based on alkene charged. The yields are the average of four runs in each case.

(%) represent literature values[1].

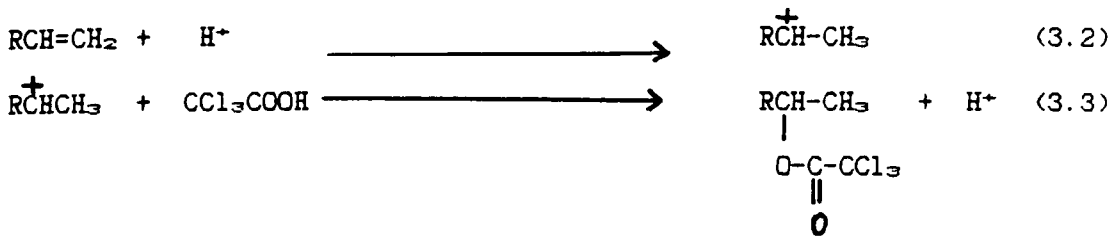
[b]One peak present in GLC which is unidentified (26 % by area).

testing the catalysts on a known reaction, the addition of tetrachloromethane to oct-1-ene). The reason for the differences observed, compared with the published results, was not apparent.

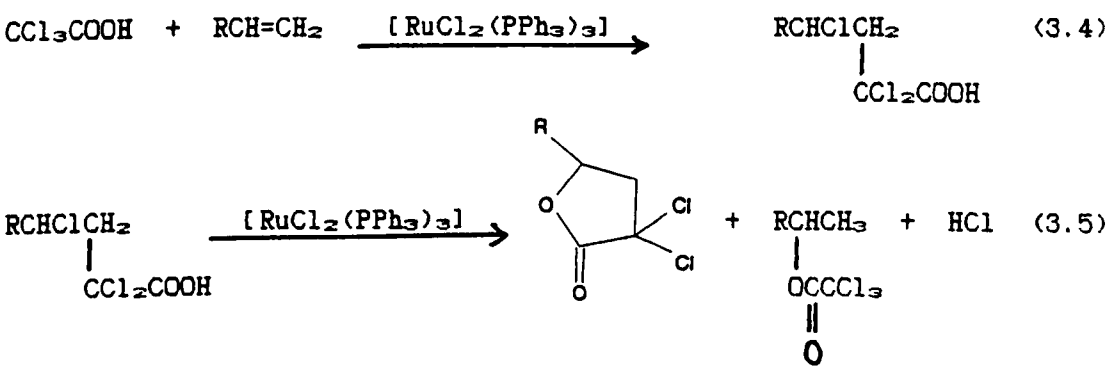
In order to eliminate any possibility of solvent loss during reflux reactions, the reaction was carried out several times in sealed tubes. The results were similar to those obtained when the reaction was carried out by reflux (e.g.55 % yield of 4-hexyl-2,2-dichloro-γ-butyrolactone based on oct-1-ene).

This study shows that the major product of the reaction is a lactone, as suggested by the literature[1]. However, a small quantity of an ester formed by a Markovnikov addition is also present in each case. In reactions employing hex-1-ene, oct-1-ene, and dec-1-ene the yield of ester was very small (2-6 %), whereas in the case of dodec-1-ene the yield of ester was 24 %. There is no obvious reason for this change in behaviour.

It is likely that the formation of the ester is an acid catalysed process initiated by hydrogen chloride released on lactone formation which promotes ester formation (equations 3.2 and 3.3).



It has been suggested in literature that the mechanism by which the lactone is formed involves the catalytic dehydrochlorination of an intermediate acid (equations 3.4 and 3.5).



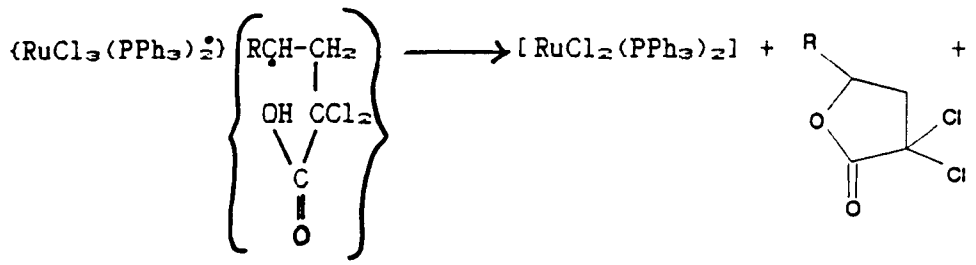
However, an alternative mechanism (scheme 3.1) which is consistent with previous mechanistic studies on $RCH=CH_2$-CCl_4 reactions in the presence of $[RuCl_2(PPh_3)_3]$ can be advanced.

Scheme 3.1 : Alternative mechanism for the addition of trichloroacetic acid to alkenes in the presence of $[RuCl_2(PPh_3)_3]$

$$[RuCl_2(PPh_3)_3] \rightleftharpoons [RuCl_2(PPh_3)_2] + PPh_3 \quad (3.6)$$

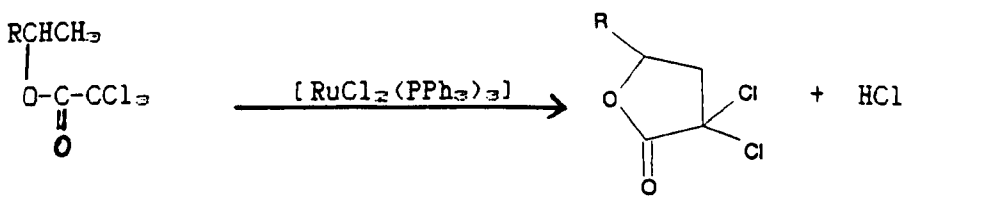
$$[RuCl_2(PPh_3)_2] + CCl_3CO_2H \longrightarrow \{RuCl_3(PPh_3)_2^{\bullet}\}\{\dot{C}Cl_2CO_2H\} \quad (3.7)$$

$$\{RuCl_3(PPh_3)_2^{\bullet}\}\{\dot{C}Cl_2CO_2H\} + RCH{=}CH_2 \rightarrow \{RuCl_3(PPh_3)_2^{\bullet}\}\{R\dot{C}HCH_2CCl_2CO_2H\} \quad (3.8)$$



Thus reaction of $[RuCl_2(PPh_3)_3]$ with CCl_3CO_2H will give the radical pair shown in equation 3.7. Subsequent reaction with $RCH{=}CH_2$ will generate the new radical pair $\{RuCl_3(PPh_3)_2^{\bullet}\}\{R\dot{C}HCH_2CCl_2CO_2H\}$. Collapse of this radical pair, in the normal way, by chlorine atom abstraction from ruthenium(III) will give the acid. However, an alternative mechanism involving the elimination of HCl from the radical pair will yield the lactone directly (scheme 3.1). These two mechanistic possibilities could presumably be tested by synthesising the acid and investigating its reaction with $[RuCl_2(PPh_3)_3]^2$. Unfortunately, time did not permit this to be done in the present work.

It is also possible that the lactone could be formed from the ester by dehydrochlorination in the presence of $[RuCl_2(PPh_3)_3]$ (equation 3.10).



However, when this experiment was carried out, no lactone was formed. This is not perhaps unexpected as the required C-H bond cleavage is energetically unfavourable. When the reaction between trichloroacetic acid and alkene was carried out in the presence of a variety of iron and molybdenum-containing catalysts, the yields of lactone were 8-12 % whilst those of the esters were 50-58 % (Table 3.2). $[\{CpMo(CO)_3\}_2CH_2]$ showed somewhat exceptional behaviour in this series in producing the lactone in a 30 % yield.

Table 3.2 : The reaction between trichloroacetic acid and oct-1-ene in the presence of various catalysts.

Catalyst	% Yield of lactone*	% Yield of ester*
$[CpFe(CO)_2]_2$	9.9	57.0
$[Cp^*Fe(CO)_2]_2$	12.1	49.5
$[CpMeFe(CO)_2]_2$	11.1	58.0
$[\{CpFe(CO)_2\}_2CH_2]$	8.9	50.4
$[\{CpMo(CO)_3\}_2CH_2]$	30.8	48.4

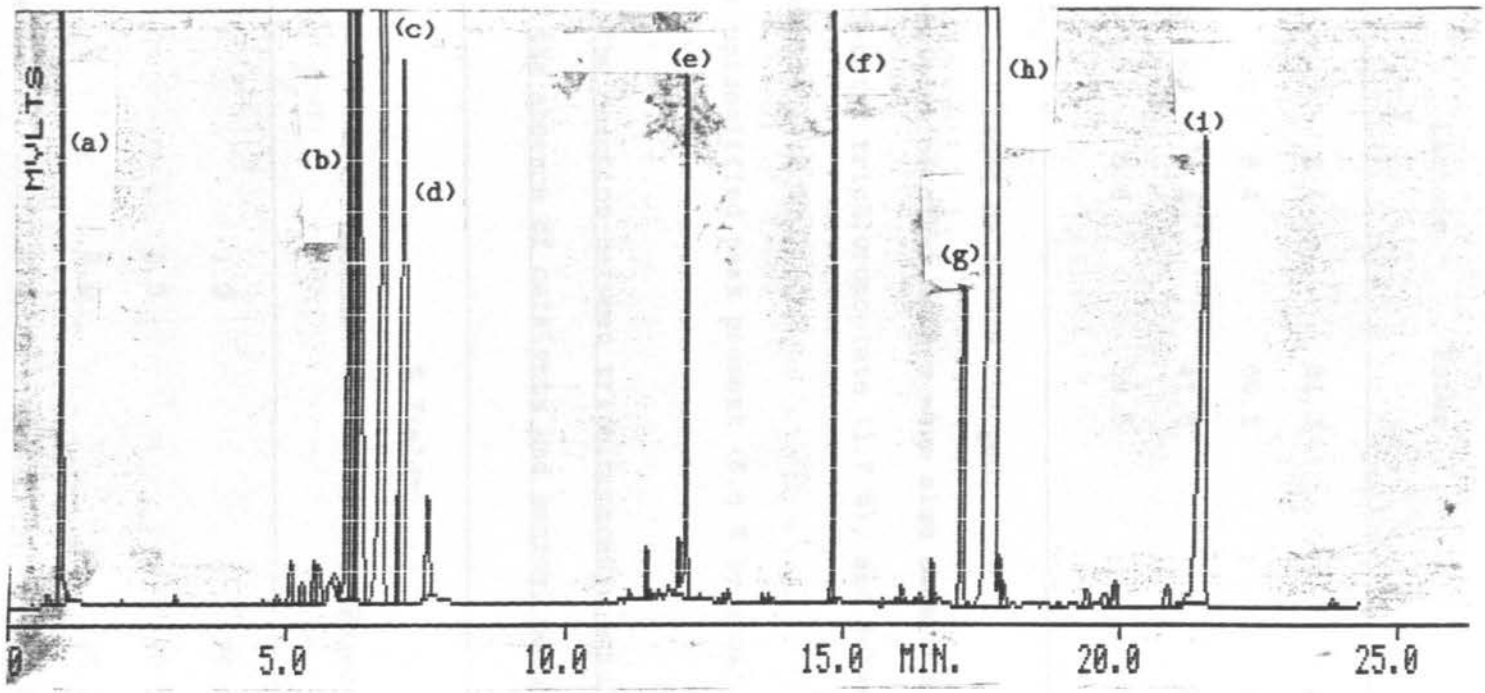
* % Yields (GLC) based on alkene charged.

3.2.1.2 The reaction between trichloroacetic acid and alkenes in the presence of benzoyl peroxide.

When this reaction was carried out in the presence of benzoyl peroxide the major product was found to be the Markovnikov ester as shown in Figure 3.2. The results (Table 3.3) showed that with increased chain length, the yield of ester decreased, (figure 3.3) in an approximately linear fashion until dodec-1-ene. The yield of lactone formed was small, varying between 2-8 %. The reaction between trichloroacetic acid and the alkene was also studied in the absence of free radical initiators and catalysts in the dark. The results showed that some ester (20 %) and lactone (1 %) were formed (Table 3.4).

It is noteworthy that, in addition to the major products, there is a minor product in each reaction, identified as $R'CH(OCOCCl_3)CH_2CH_3$. This is always present but its yield depends on the catalyst or initiator used. It was observed that the percentage area of this product expressed as a percentage of the area of the Markovnikov ester (analysed by GLC) increased in the presence of the ruthenium catalyst and decreased in the presence of free radical initiators and in the blank reaction (Table 3.5). This same product was also observed for the reactions catalysed by iron and molybdenum catalysts (Table 3.6).

Figure 3.2 : Reaction between dodec-1-ene and trichloroacetic acid in the presence of benzoyl peroxide



(a) = toluene, (b) = dodec-1-ene, (c) = unknown

(d) = unknown, (e) = unknown, (f) = methyl myristate,

(g) = 3-dodecyl trichloroacetate, (h) = 2-dodecyl trichloroacetate,

(i) = 4-decyl-2,2-dichloro-γ-butyrolactone.

Table 3.3 : The reaction between trichloroacetic acid and alkenes in the presence of benzoyl peroxide

Alkene	% Yield[a]		% Unreacted alkene
	Lactone	Ester	
Hex-1-ene	2.4	81.3	13.3
Oct-1-ene	8.4	60.1	20.8
Dec-1-ene[b]	5.4	41.6	21.4
Dodec-1-ene[c]	5.8	39.5	38.1

[a] % Yields (GLC) based on alkene charged.

[b] Small quantities of other esters were also observed in this case. These were 2-octyl trichloroacetate (1.7 %), and 2-hexyl trichloroacetate (4.2 %)

[c] One other unidentified peak present (8.6 % by area).

Table 3.4 : The reaction between trichloroacetic acid and alkenes in the absence of catalysts and benzoyl peroxide.

Alkene	% Yield[a]	
	Lactone	Ester
Hex-1-ene	1.9	20.2
Oct-1-ene	2.5	25.1
Dec-1-ene	3.0	28.0
Dodec-1-ene	9.0	28.8

[a] % Yields (GLC) based on alkene charged.

Figure 3.3 : Relationship between yield of ester and alkene chain length.

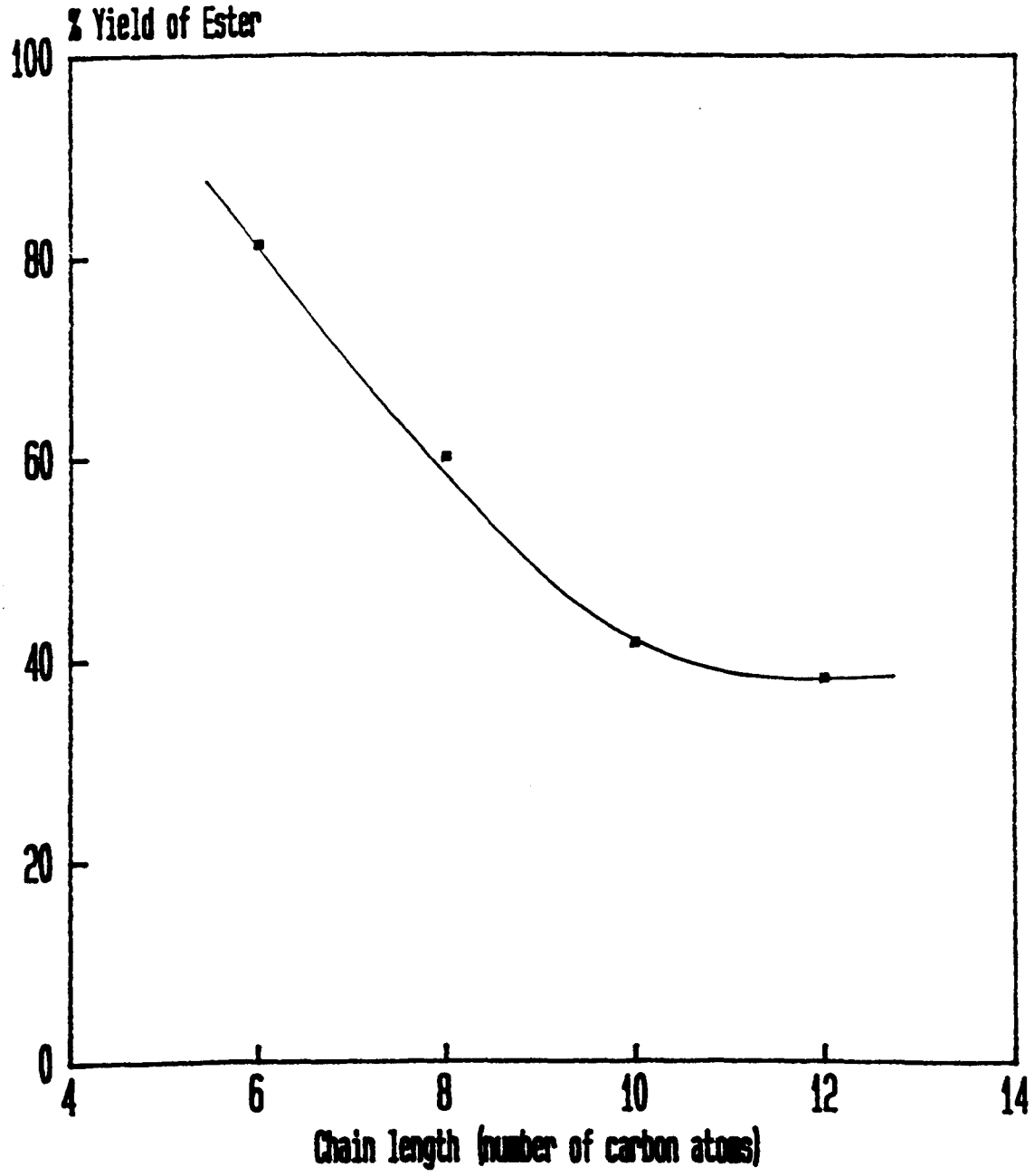


Table 3.5 : Investigation of 3-alkyl trichloroacetate formation

Alkene	Ratio (by % area*) of 2- : 3-alkyl trichloroacetate in the presence of		
	$[RuCl_2(PPh_3)_3]$	Benzoyl peroxide	No catalyst
Hex-1-ene	7 : 1	16 : 1	10 : 1
Oct-1-ene	6 : 1	18 : 1	12 : 1
Dec-1-ene	5 : 1	18 : 1	11 : 1
Dodec-1-ene	8 : 1	15 : 1	16 : 1

* Area measured by GLC.

Table 3.6 : Investigation of 3-alkyl trichloroacetate formation in the presence of various iron- and molybdenum- catalysts

Catalyst	Ratio (by % area) of 2-octyl trichloroacetate : 3-octyl trichloroacete
$[CpFe(CO)_2]_2$	15 : 1
$[Cp^*Fe(CO)_2]_2$	16 : 1
$[CpMeFe(CO)_2]_2$	15 : 1
$[\{CpFe(CO)_2\}_2CH_2]$	16 : 1
$[\{CpMo(CO)_3\}_2CH_2]$	18 : 1

This product was identified by GC/MS where the characteristic fragment ion $[CH_3CH_2CH\text{-}OCOCCl_3]^+$ was observed. However, quantitative work was not carried out since it required a pure sample of the 3-alkyl trichloroacetate in order to establish GLC response factors. This would be difficult to achieve as the product would be difficult to separate from the isomer i.e. 2-alkyl trichloroacetate when present as a relatively small proportion. It is suggested that the product is formed by the isomerisation of the alk-1-ene to alk-2-ene in the presence of $[RuCl_2(PPh_3)_3]$, followed by an acid catalysed addition of trichloroacetic acid (equations 3.11-3.12).

$$CH_2{=}CHCH_2CH_2CH_2CH_3 \xrightarrow{[RuCl_2(PPh_3)_3]} CH_3CH{=}CH\text{-}CH_2CH_2CH_3 \qquad (3.11)$$

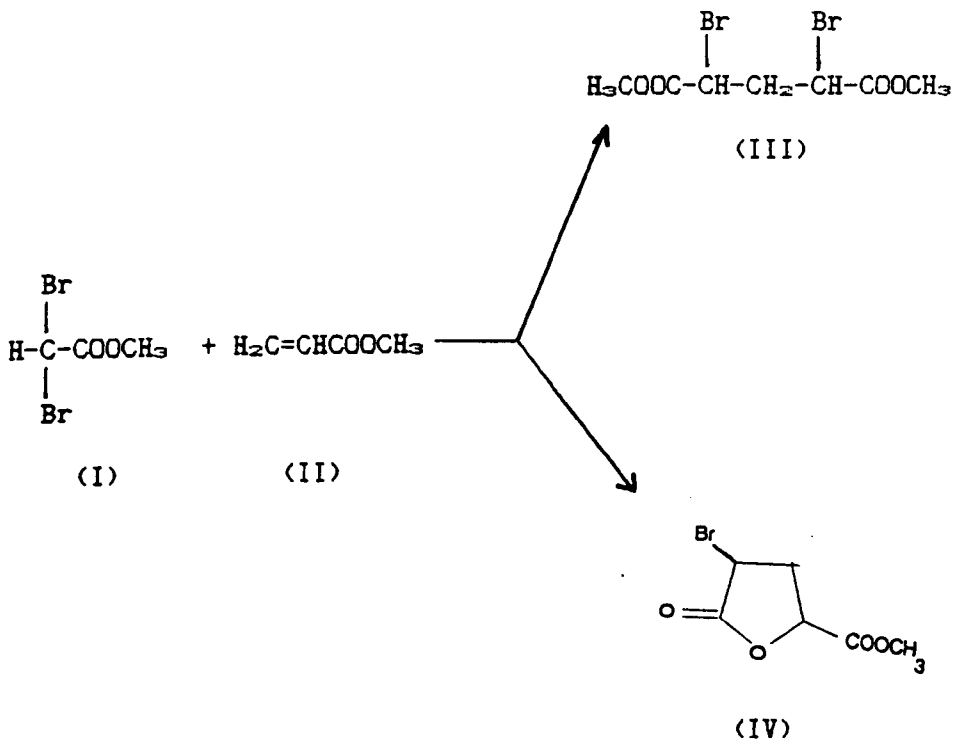
$$CH_3CH{=}CH\text{-}CH_2CH_2CH_3 + CCl_3COOH \xrightarrow{H^+} CH_3CH_2\underset{\underset{\displaystyle O\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}CCl_3}{|}}{CH}CH_2CH_2CH_3 \qquad (3.12)$$

In the presence of the iron catalysts, very little lactone was formed (9-12 % yield) and the major product was the Markovnikov ester in 50-58 % yield as well as the 3-alkyl trichloroacetate. It thus appears that for these reactions the iron catalysts act as free radical initiators with a reduced catalytic activity for lactone formation. The molybdenum catalyst used was a more effective catalyst for the production of the lactone and, like the ruthenium catalyst, also effected the isomerisation of alkenes resulting in the formation of 3-alkyl trichloroacetates.

3.3 The reaction between tribromoacetic acid and alkenes

3.3.1 Introduction

Reactions which involve the homolytic addition of electrophiles containing bromine to double bonds have been reported to result in various products, including lactones[3]. In this paper radical additions were studied since these were considered to be simpler routes to the desired products than traditional organic routes. It was found that methyl dibromoacetate undergoes addition to methyl propenoate in the presence of iron pentacarbonyl or iron (III) chloride (equation 3.13).

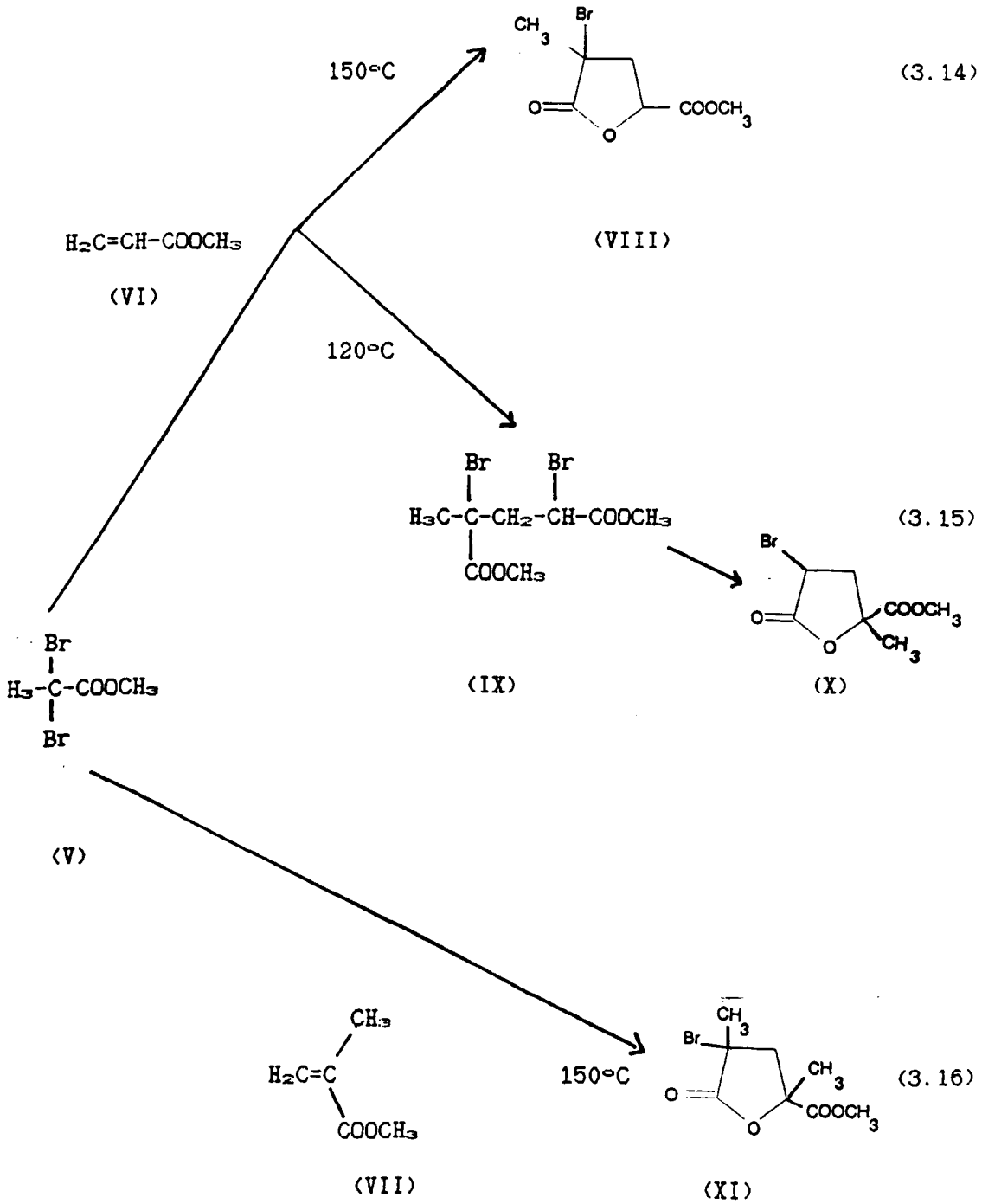


(3.13)

This reaction is dependent on the reaction conditions used (and usually) produces the addition product (III). However, in the presence of N,N-dimethylaniline as a co-catalyst at temperatures below 100°C

the bromolactone (IV) is formed in small yields (1-3 %)[4]. When the reaction conditions are suitably altered the lactone can become the major product. This can be demonstrated by the reactions shown in scheme 3.2.

Scheme 3.2: The effect of changing reaction conditions on lactone formation.



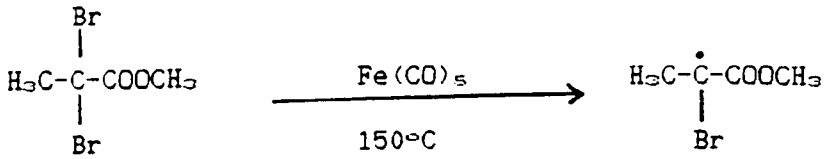
The scheme shows that the main products of the reaction between methyl 2,2-dibromopropanoate and the acrylic compounds (VI) and (VII) are the lactones. Their yields and reaction conditions are shown in Table 3.7.

Table 3.7 : The effect of reaction conditions on lactone formation.

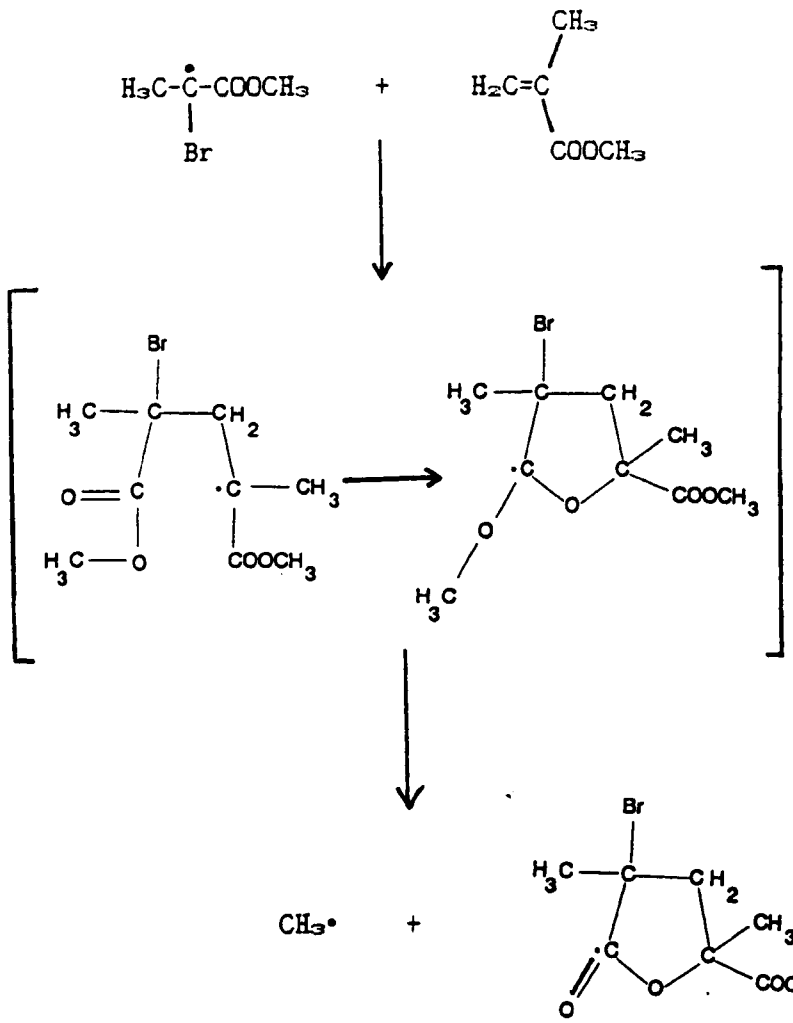
Addend	Monomer	Initiating system	Temp °C	Product (% yield)
$Br_2CHCOOCH_3$	$H_2C=CHCOOCH_3$	$Fe(CO)_5$ + C_6H_5CN	150	(VIII)+(X) 62-69
$Br_2CHCOOCH_3$	$H_2C=C(CH_3)COOCH_3$	$Fe(CO)_5$ + C_6H_5CN	150	(XI) 42-48
$Br_2CHCOOCH_3$	$H_2C=C(CH_3)COOCH_3$	$FeCl_3$ + C_6H_5CN	150	(XI) 48

The mechanism proposed for these reactions is shown in scheme 3.3. It is suggested that [$Fe(CO)_5$] is acting as an initiator by cleaving the C-Br bond and so generating a radical (equation 3.17). Formation of the lactone occurs via attack of this radical on the CH_2 group of the alkene, followed by intramolecular cyclisation (equation 3.18) and loss of an alkyl radical (equation 3.19).

Scheme 3.3 : Mechanism for the formation of bromolactones.



(3.17)

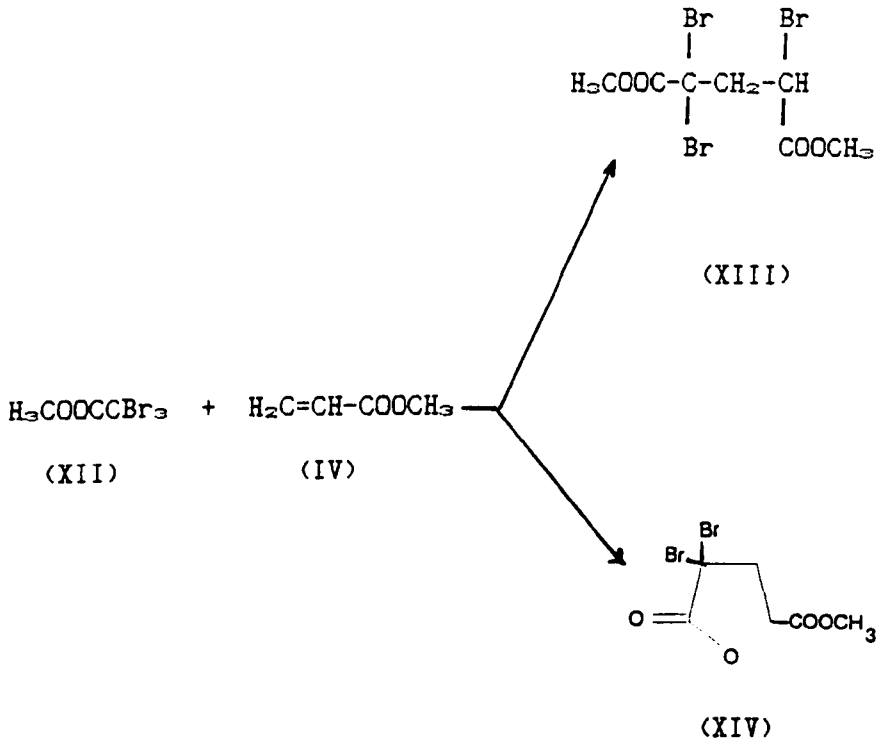


(3.18)

(3.19)

Methyl tribromoacetate (XII) has also been added to methyl propenoate (IV) forming a dibromolactone (XIV). When the reaction is carried out in the presence of benzoyl peroxide this lactone (XIV) is formed in a 6-11 % yield, the main product being (XIII) (equation 3.21). If a

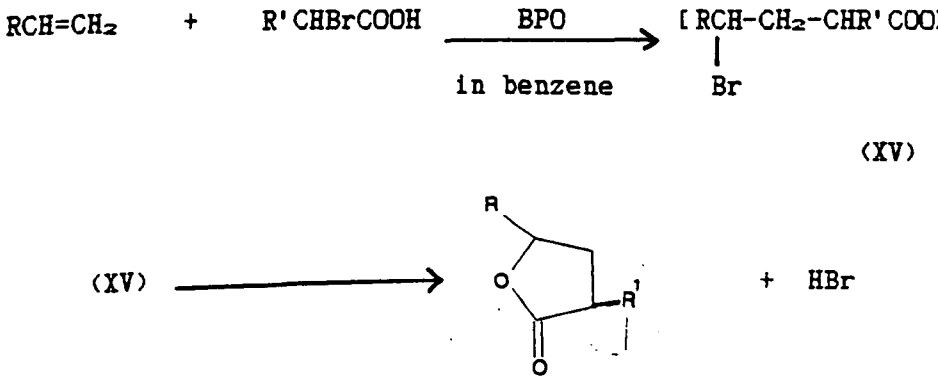
coordination initiator is present the yield of (XIII) increases to 60-70 % at 70°C and to 70-82 % at 100°C (determined by GLC) but with no lactone formation (equation 3.20).



(3.20)

(3.21)

It has also been shown that in the presence of benzoyl peroxide lactones can be formed (equations 3.22 and 2.23)[5].



(3.22)

(3.23)

This reaction has been investigated using various alkenes as shown in Table 3.8[5].

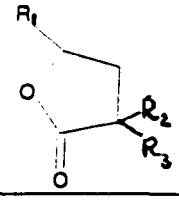
In summary previous work has shown that lactones can be formed by free radical initiated reactions. The work described below considers whether dibromolactones can be formed by the reaction of tribromoacetic acid and alkenes in the presence of benzoyl peroxide and $[RuCl_2(PPh_3)_3]$.

3.3.2 Results

3.3.2.1 The reaction between tribromoacetic acid and oct-1-ene in the presence of $[RuCl_2(PPh_3)_3]$

The preparation of 4-alkyl-2,2-dibromo-γ-butyrolactones was more difficult than at first anticipated. The reaction between tribromoacetic acid and oct-1-ene was carried out in the presence of $[RuCl_2(PPh_3)_3]$ in a molar ratio of 400 : 350 : 1 respectively, in refluxing toluene, for 6 hours . After this time the reaction mixture was analysed by GLC. This showed some volatile components, but no significant quantities of less volatile products. (It was expected that the lactone should appear between retention times of 10-30 minutes based on the experience of the dichlorolactones). The mixture was then vacuum distilled which resulted in several fractions. At the same time some HBr was evolved, with the formation of a large quantity of a black product thought to be due to the decomposition of the lactone or other products. A ^1H NMR spectrum of the undistilled reaction mixture was recorded and is shown in Appendix 1 and the assignments are described in Table 3.9.

Table 3.8 : Reactions of alk-1-enes with α-bromocarboxylic acids.

Alkene	α-βromocarboxlic acid	Lactone	% Yield[a]
			
Hex-1-ene	$CH_2BrCOOH$	$R_1=C_4H_9$, $R_2=R_3=H$	65 (58)
Oct-1-ene	$CH_2BrCOOH$	$R_1=C_6H_{13}$, $R_2=R_3=H$	72 (68)
Non-1-ene	$CH_2BrCOOH$	$R_1=C_7H_{15}$, $R_2=R_3=H$	73 (58)
Dec-1-ene	$CH_2BrCOOH$	$R_1=C_8H_{17}$, $R_2=R_3=H$	77 (54)
Oct-1-ene	$CH_3CHBrCOOH$	$R_1=C_6H_{13}$, $R_2=CH_3$, $R_3=H$.	79 (45)
Oct-1-ene	$CH_3CH_2CHBrCOOH$	$R_1=C_6H_{13}$, $R_2=CH_2CH_3$, $R_3=H$.	42 (31)

[a] % Yields were determined by GLC. Yields in parenthesis were isolated.

Table 3.9 : Assignments of ^1H NMR spectrum (Appendix 1) of the undistilled reaction mixture.

Chemical shift		Assignment	Source
0.89	(t)	$-CH_3$	Methyl group at the end of alkyl chain from lactone, ester or oct-1-ene.
1.10-1.80	(m)	$-CH_2$	Alkyl chain from lactone, ester or oct-1-ene.
2.20-2.25	(s)	$-CH_3$	Methyl group adjacent to aromatic ring ring due to toluene.
2.75-3.00	(d of d)	$-CH_2$	Two doublets of doublets due to non-equivalent methylene adjacent methine protons as in lactones or possibly esters. Also other peaks superimposed.
4.04-4.30	(m)	-CH	Methine proton next to methylene protons as in lactone or possibly ester
5.00-5.20	(m)	$=CH_2$	Methylene and methine protons in oct-1-ene.
5.70-6.00	(m)	=CH	
7.00-7.60	(m)	-Ph	Phenyl group in toluene.
9.00	(s)	-OH	Due to tribromoacetic acid.

The ^1H NMR spectum indicates that lactone may be formed. However, only a very small amount is present as shown by the GLC. There does not appear to be decomposition of products at GLC oven temperatures of less than 150°C. So the reaction was scaled up and repeated in the same way but the co-solvent ethanol was added as there were solubility problems with tribromoacetic acid in toluene. This reaction mixture was not distilled, but the solvent was removed under vacuum and the resulting mixture was subjected to column chromatography, under various conditions, described in the experimental section (3.4.6.1). This resulted in small amounts of lactone and other products. These products were identified as 4-hexyl-2,2-dibromo-γ-butyrolactone (0.03g, 0.29 %), 2,2,4-tribromodecanoic acid (0.10g, 1.1 %), and ethyl tribromoacetate (1.05g, 11.6%). (The yields of products are based on tribromoacetic acid as oct-1-ene was in excess).

3.3.2.2 Characterisation of the reaction products by spectroscopic methods

3.3.2.2.1 4-Hexyl-2,2-dibromo-γ-butyrolactone

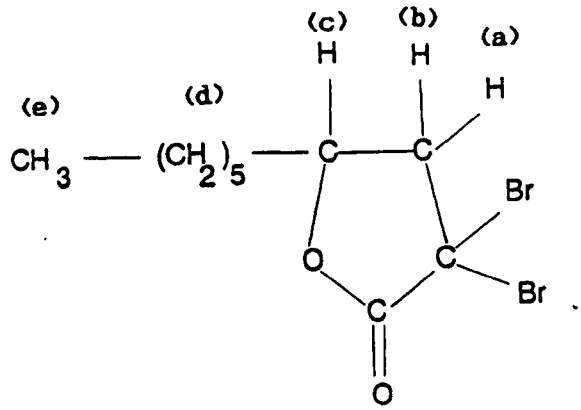
3.3.2.2.1.a Infrared spectrum

The IR spectrum is represented in Appendix 2. This shows the C=O overtone at 3440-3480 cm^{-1} whilst the C=O and the C-O stretches are at 1790 and 1175 cm^{-1} respectively. These occur at similar wavenumbers to those of the chlorinated lactones. However, from the IR spectrum it is obvious that there is a contaminant with a C=O stretch present at 1750cm^{-1}. This cannot be tribromoacetic acid although its C=O stretch is very similar at 1745 cm^{-1}, as there is no broad band at 3000-3500 cm^{-1} due to a OH group.

3.3.2.2.1.b ^{1}H NMR spectrum

The ^{1}H NMR is shown in appendices 3 and 4. The spectrum is very similar to that of the chlorine substituted lactones although the chemical shifts of the protons adjacent to the C-Br bond have slightly different values. Again there is a triplet at δ0.89-1.00 assigned to methyl protons at the end of an alkyl chain (e). A large peak at δ1.00-1.90 arises due to the CH_2 chain (d).

Fig 3.4 : Assignment of 4-hexyl-2,2-dibromo-γ-butyrolactone



The multiplet due to the proton at (c) has now been shifted to δ4.00-4.35 as compared to δ4.30-4.70 for this proton in the analogous dichloro- lactone. The proton at position (b) has a chemical shift at δ2.60-2.95 and that of (a) at δ2.15-2.50 compared to δ3.00-3.25 and δ2.40-2.70 for (b) and (a), respectively in the equivalent chlorine-containing case. The splitting patterns are analysed in Appendix 4, and the coupling constants were measured. These compare very well with those obtained for the dichloro-lactones and are shown in Table 3.10.

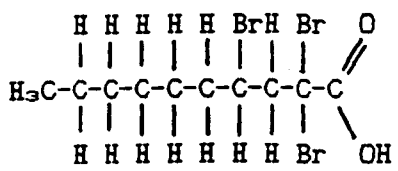
Table 3.10 : Comparison of splitting constants, J for dichloro and dibromo lactones.

Constant, J	Dibromo lactone (Hz)	Dichloro lactone (Hz)
J_{ab}	14.4	14.1
J_{ac}	4.9	5.1
J_{bc}	9.5	9.5

3.3.2.2.1.c Mass spectrum

The mass spectrum, represented in Appendix 5 ,showed the molecular ion of this lactone (only when the mass spectrometer was run at low temperatures). The fragmentation pattern, shown in scheme 3.4, involves the sequential breakup of the alkyl chain, which is followed by the loss of two bromines.

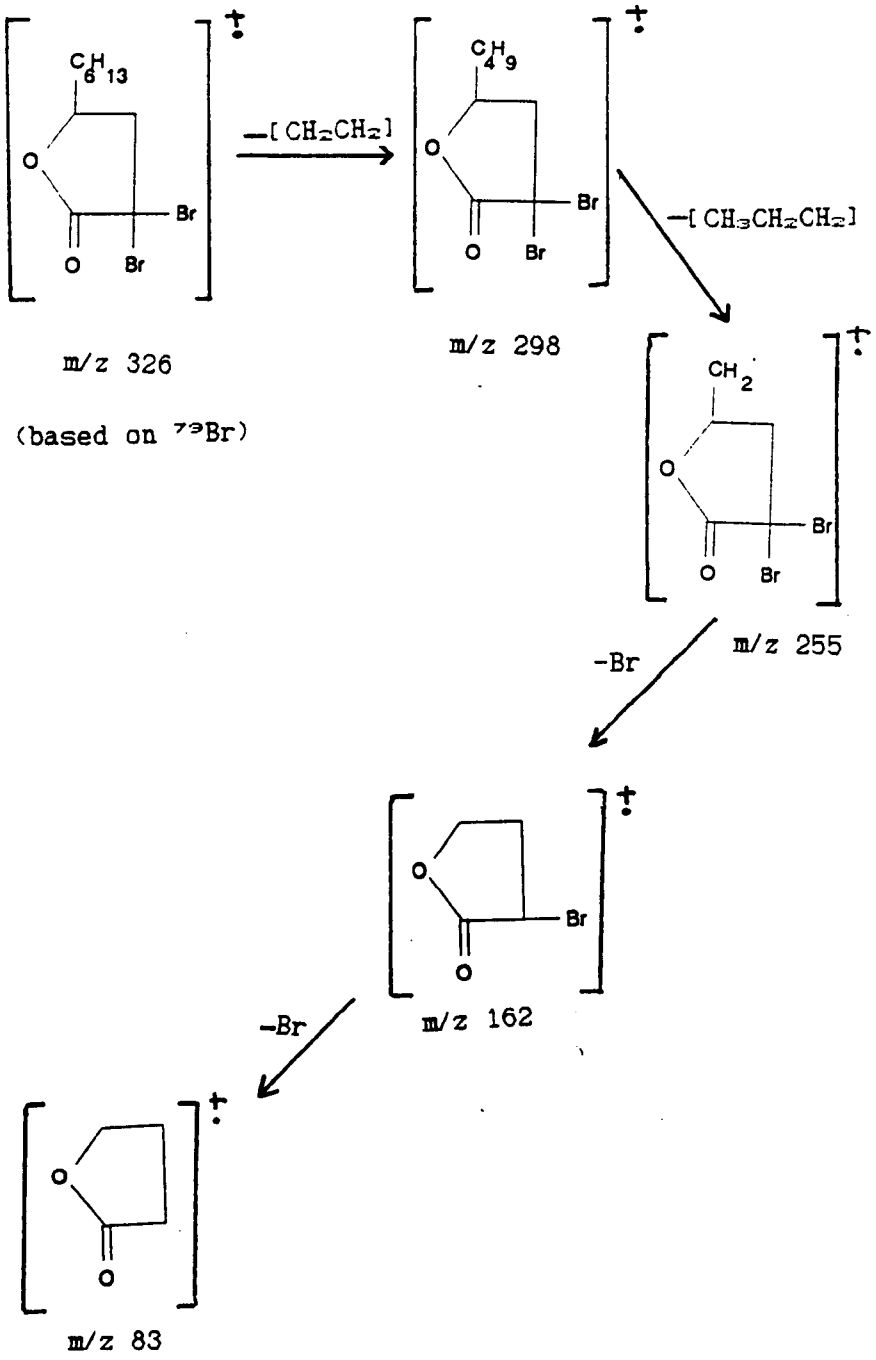
3.3.3.2 2,2,4-tribromodecanoic acid



3.3.3.2.a Infrared spectrum

This is shown in Appendix 6, indicating the presence of an acid by the characteristic broad OH absorption at 2500-3500 cm^{-1}, an overtone due to C=O at 3480 cm^{-1}, C=O and C-O stretches at 1725 and 1260 cm^{-1}.

Scheme 3.4 : Mass spectral fragmentation of 4-Hexyl-2,2-dibromo-γ-butyrolactone



Unfortunately, despite the column chromatography the fraction was not pure as there was some lactone present as indicated by the C=O stretch at 1790 cm^{-1} and also some contamination due to a compound giving rise to a C=O stretch at 1750 cm^{-1}.

3.3.2.2.2.b <u>^1H NMR spectrum</u>

The ^1H NMR spectum of this ester has strong similarities to the lactone and is shown in Appendix 7. This shows a triplet at δ0.89 which can be assigned to a $-CH_3$ at the end of the alkyl chain. A large multiplet is observed at δ1.10-2.00 due to the ($-CH_2-$) groups in the alkyl chain. The CH_2 protons are once again non-equivalent (due to restricted rotation of the C2 bond) and consequently there are two double doublets at δ2.00-3.20 and at δ3.20-3.40. The C-4 proton gives rise to a quintet (as its resonance is split by the four adjacent CH_2 protons) at δ4.05-4.35. The coupling constants are different to those of the lactone and were calculated to be :

$$J_{ab} = 16.0 \text{ Hz}$$

$$J_{ac} = 6.0 \text{ Hz}$$

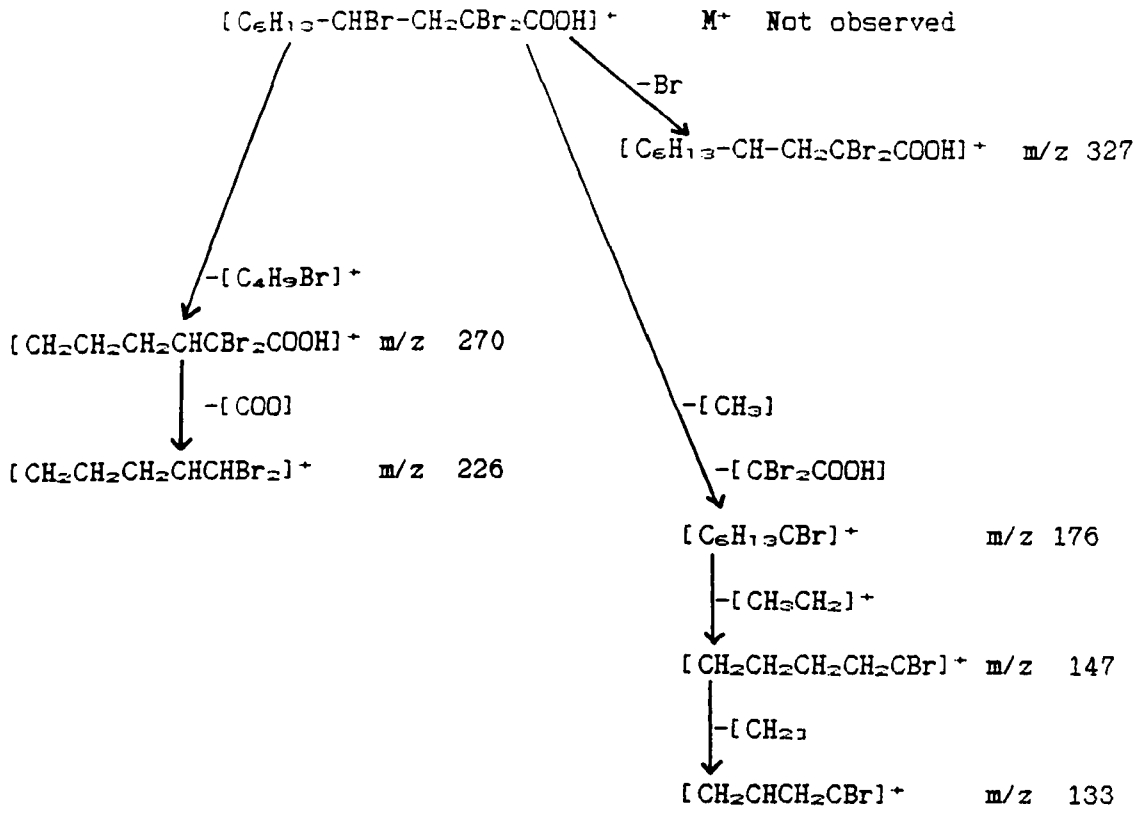
$$J_{bc} = 6.0 \text{ Hz}$$

There was also a singlet at δ12.0 due to the OH proton.

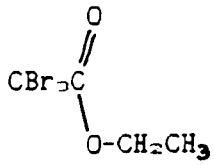
3.3.2.2.2.c <u>Mass spectrum</u>

The mass spectrum is shown in Appendix 8. No molecular ion is observed, the ion of highest mass arising from loss of Br from M^+. This is followed by the loss of HBr and further fragmentation of the molecule described in scheme 3.5. The molecular ion was not observed.

Scheme 3.5 : Fragmentation of 2,2,4-tribromdecanoic acid



3.3.2.2.3 Ethyltribromoacetate



3.3.2.2.3.a Infrared spectrum

The infrared spectrum shows an overtone due to C=O at 3480 cm^{-1}, as well as the C=O and C-O stretches at 1750 and 1240 cm^{-1}. Another interesting feature of this spectrum is the lower intensity of the CH_2 band at 2920 cm^{-1} compared with the C=O stretch. In all cases involving compounds containing a hexyl chain the CH_2 and the C=O bands have been of approximately equal intensity.

3.3.2.2.3.b ^1H NMR spectrum

The ^1H NMR spectrum shows a triplet at δ1.30-1.50 and a quartet at δ4.25-4.50. The integration is in the ratio of 3:2 suggesting the presence of an ethyl group. No other functional groups were observed.

3.3.2.2.3.c Mass spectrum

The mass spectrum does not show the molecular ion. The most abundant fragment was $[CH_3CH_2]^+$ and $[CBr_3]^+$ was also observed.

When the evidence of these three techniques was put together it suggests that ethyl tribromoacetate is formed as a by-product of a reaction between tribromoacetic acid in ethanol. This was confirmed by investigating the effect of refluxing tribromoacetic acid and ethanol in the presence of $[RuCl_2(PPh_3)_3]$. Ethyl tribromoacetate was the only product found.

3.3.2.3 The reaction between tribromoacetic acid and oct-1-ene in the presence of benzoyl peroxide.

When this reaction was carried out, ethanol was not used so as to avoid the formation of any ethyl tribromacetate. As in the reaction in the presence of $[RuCl_2(PPh_3)_3]$ (in toluene) there were two products 4-hexyl-2,2-dibromo-γ-butyrolactone and 2,2,4-tribromodecanoic acid. However in this reaction, only a small amount of the lactone was isolated (0.05g, 0.3 %), whereas there was more acid recovered (0.4g, 1.6 %). The reaction was also repeated in the absence of benzoyl peroxide or $[RuCl_2(PPh_3)_3]$. However, only trace amounts of products were detected, the yields of which were too low for isolation.

3.3.3 Discussion

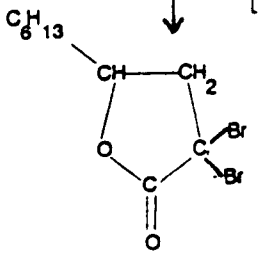
The results show that 4-hexyl-2,2-dibromo-γ-butyrolactone could be isolated from the reaction between tribromoacetic acid and oct-1-ene in the presence of $[RuCl_2(PPh_3)_3]$ and benzoyl peroxide, but in very low yields. The study also showed that this compound is temperature sensitive so cannot be purified by distillation and GLC analysis at temperatures greater than 100°C is difficult. A summary of the reactions studied is shown in scheme 3.6.

Scheme 3.6 : Summary of reactions studied.

$$CBr_3COOH + C_6H_{13}CH{=}CH_2 \xrightarrow[{[RuCl_2(PPh_3)_3]}]{EtOH/Toluene} CBr_3COOC_2H_5 + \text{Others} \quad (3.24)$$

$$\downarrow$$

$[RuCl_2(PPh_3)_3]$/Benzoyl peroxide



$$+ \quad C_6H_{13}CHBrCH_2CBr_2COOH \quad (3.25)$$

The scheme shows that in the presence of ethanol, tribromoacetic acid reacts with this solvent forming ethyl tribromoacetate. It also shows that the lactone is formed in the presence of $[RuCl_2(PPh_3)_3]$ and benzoyl peroxide. But it appears that less lactone is formed as less was isolated (by the same methods as in the $[RuCl_2(PPh_3)_3]$ catalysed reaction) in the presence of benzoyl peroxide. The proposed mechanism for lactone formation in the presence of benzoyl peroxide case is shown in scheme 3.7.

Scheme 3.7 : Mechanism for the benzoyl peroxide initiated reaction.

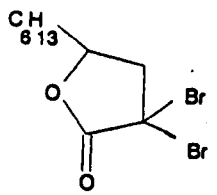
$$[(C_6H_5CO)_2O_2] \longrightarrow 2C_6H_5COO\bullet \quad (3.26)$$

$$CBr_3COOH + C_6H_5COO\bullet \longrightarrow \dot{C}Br_2COOH + C_6H_5COOBr \quad (3.27)$$

$$\dot{C}Br_2COOH + C_6H_{13}CH{=}CH_2 \longrightarrow C_6H_{13}\dot{C}HCH_2CBr_2COOH \quad (3.28)$$

$$C_6H_{13}\dot{C}HCH_2CBr_2COOH + CBr_3COOH \longrightarrow C_6H_{13}\underset{\underset{Br}{|}}{C}HCH_2CBr_2COOH + \dot{C}Br_2COOH \quad (3.29)$$

$$C_6H_{13}\underset{\underset{Br}{|}}{C}HCH_2CBr_2COOH \longrightarrow$$



$$+ HBr \quad (3.30)$$

The first steps involve generation of a free radical via benzoyl peroxide initiation (equations 3.26 and 3.27), which then undergoes propagation (equations 3.28 and 3.29) eventually resulting in the acid. The acid then undergoes dehydrobromination resulting in the lactone. In the case of the reaction initiated by $[RuCl_2(PPh_3)_3]$, the process is more controlled. An analogous mechanism (shown in scheme 3.8) can be proposed to that for the addition of trichloroacetic acid to oct-1-ene (see section 3.2.1.1).

Scheme 3.8 : Mechanism for the $[RuCl_2(PPh_3)_3]$ catalysed reaction.

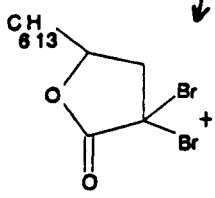
$$[RuCl_2(PPh_3)_3] \rightleftharpoons [RuCl_2(PPh_3)_2] + PPh_3 \quad (3.31)$$

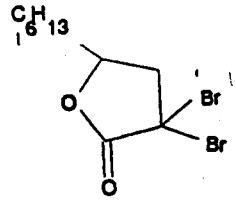
$$[RuCl_2(PPh_3)_2] + CBr_3COOH \longrightarrow \{RuCl_2Br(PPh_3)_2^{\bullet}\}\{\dot{C}Br_2COOH\} \quad (3.32)$$

$$\{RuCl_2Br(PPh_3)_2^{\bullet}\}\{\dot{C}Br_2COOH\} + C_6H_{13}CH{=}CH_2 \longrightarrow \{RuCl_2Br(PPh_3)_2^{\bullet}\}\{C_6H_{13}\dot{C}H{-}CH_2CBr_2COOH\} \quad (3.33)$$

$$\{RuCl_2Br(PPh_3)_2^{\bullet}\}\{C_6H_{13}\dot{C}H{-}CH_2CBr_2COOH\} \longrightarrow C_6H_{13}CH(Br)CH_2CBr_2COOH + [RuCl_2(PPh_3)_2] \quad (3.34)$$

$$C_6H_{13}CH(Br)CH_2CBr_2COOH \longrightarrow \text{[lactone]} + [RuCl_2(PPh_3)_3] + HBr \quad (3.35)$$



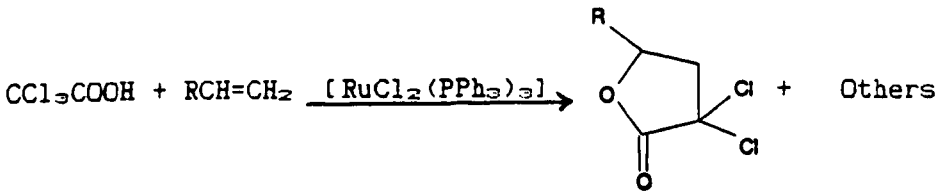


3.4 Experimental section

In order that the reactions between alkenes and trichloroacetic acid could be studied quantitatively, the dichlorolactones had to be isolated and purified, so that their GLC response factors compared to an added standard could be determined.

3.4.1 Preparation of lactones

The lactones were all prepared by the same method.



(3.36)

Typically, trichloroacetic acid (36.2g, 220 mmoles), the alkene (210 mmol), $[RuCl(PPh_3)_3]$ (0.74g, 0.77 mmoles) and toluene (20ml) were placed in a flask, degassed three times by the freeze- pump-thaw-technique and then refluxed for 6 hours. The mixture was then vacuum distilled. In all cases several fractions resulted. The higher boiling fractions contained mainly lactone, whereas the lower boiling fractions consisted of various mixtures of the lactone, the ester ($CH_3(CH_2)_5CH(OOCCCl_3)CH_3$), and trichloroacetic acid. The former were then recombined and redistilled. The resulting lactones were analysed by GLC for purity and to be found to be greater than 99%. The yields, physical and spectroscopic properties of the lactones are sumarised in Table 3.11.

Table 3.11: Physical and spectroscopic properties of 4-alkyl -2,2-dichloro-γ-butyrolactone

Alkyl Group	% Yield (isolated)	Boiling pt. °C/5 mm Hg	Infrared spectrum cm^{-1}	H -N.M.R. spectrum δ	H -N.M.R. spectrum Areas	Mass spectra m/z
Butyl	31.4	123 - 125	All showed similar features - C=O overtone 3440 - C=O stretch 1790	All showed similar features 0.89 -1.1 (m, 9- 21 H)	9 : 2 : 1	211 $(M+1)^+$, 175 $(M-Cl)^+$ 140 $(M-2Cl)^+$, 153 $(M-C_4H_9)^+$
Hexyl	37.6	132 - 136	- CH_3 asym. 2960 - CH_3 sym 2870 - CH_2 asym. 2930		13 : 2 : 1	239 $(M+1)^+$, 203 $(M-Cl)^+$ 168 $(M-2Cl)^+$
Octyl	35.6	143 - 145	- C-O stretch 1185 - CH_3 asym. 1465 - CH_3 sym. 1380	2.4 -3.25 (4 doublets, 2 H)	17 : 2 : 1	no observed M^+, 232 $(M-Cl)^+$, 196 $(M-2Cl)^+$
Decyl	45.0	154 - 161	- C-Cl stretch 960 (CH_2) rock 730	4.30 - 4.70 (m, 1H)	21 : 2 : 1	no observed M^+, 260 $(M+1-Cl)^+$ 224 $(M+1-2Cl)^+$

3.4.2 Spectroscopic data for the lactones.

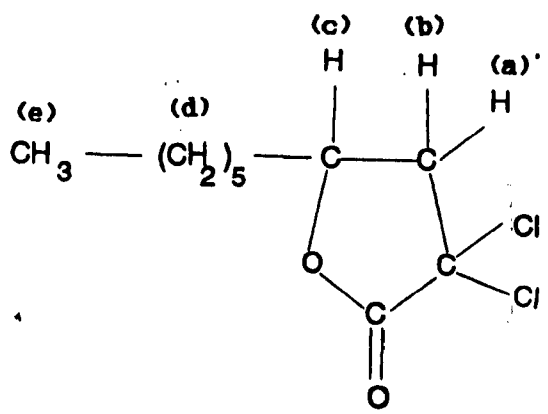
3.4.2.1 Infrared spectra

All the lactones had the same characteristic infrared spectra which showed a prominent C=O overtone at 3440cm^{-1}, the C=O and C-O stretch at 1790 and 1180cm^{-1}, respectively. The most prominent peaks are assigned in Table 3.11. The only difference in the spectra was the intensity of the CH_2 asymmetric and symmetric stretches. A typical infrared spectrum of (4-Hexyl-2,2-dichloro-γ-butyrolactone) is represented in Appendix 9.

3.4.2.2 ^{1}H NMR spectra

After preparation of the pure fractions each was analysed by ^{1}H NMR. The spectra for all the different lactones showed the same characteristics, only varying due to the differences in the length of the alkyl chain. A typical spectrum is represented in Appendix 10. and 11).

Fig 3.5 : Nomenclature of 4-alkyl-2,2-dichloro-γ-butyrolactone



A triplet/multiplet was observed at δ0.89 which was assigned to the methyl protons (e) (Figure 3.5) at the end of the alkyl chain. A large multiplet arises at δ1.0-1.9 due to the $-(CH_2)_n-$ chain(d). The resonance due to the proton at position (c) occurs at δ4.3-4.7 and is a multiplet as suggested by the literature.[1]. However, according to this literature the resonance due to the protons at positions (a) and (b) should result in a multiplet at δ2.88. This was found not to be the case. The protons are in non-equivalent environments consequently the resonance due to (b) consists of two doublets at δ2.60-3.10 and that of (a) also comprises of two doublets but at at δ3.20-3.60. These protons have resonances which are double doublets as proton (a) is split by protons (c) and (b) whilst proton (b) is split by protons (a) and (c). If the splitting pattern is analysed (Appendix 11) the coupling constants can be measured. It was found that :

J_{ab}=14.1Hz

J_{bc}= 9.5Hz

J_{ac}= 5.1Hz.

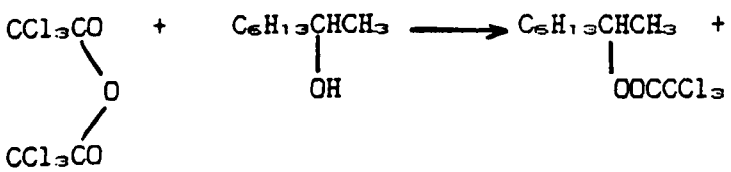
The analysis for proton (c) is complicated by the fact that it is being further split by the protons in the alkyl chain (d) consequently the expected quartet is observed as a somewhat more complex multiplet. These values of the coupling constants are approximately the same for all the lactones prepared. Finally, it may be observed that there is a small peak at δ5.4 in the ^{1}H NMR spectrum shown in Appendix 10. This is due to a small amount of water absorption while the sample was stored in the freezer. The identity of this peak was confirmed by carrying out a D_2O exchange on the sample.

3.4.2.3 Mass spectra

All the lactones prepared showed a similar fragmentation patterns (Table 3.11). The 4-hexyl and octyl-2,2-dichloro-γ-butyro-lactones show M+1 ions, but the two higher molecular weight compounds show no molecular or pseudo-molecular ions since they appear to be subject to more facile fragmentation. However, they all show the consecutive losses of two Cl atoms, followed by the fragmentation of the alkyl chain. A typical example of a mass spectrum (of 4-decyl-2,2-dichloro-γ-butyrolactone) is shown in Appendix 12. The fragmentation shown in this spectrum is as described by Scheme 3.9.

3.4.3. Preparation of 2-Alkyl trichloroacetates.

3.4.3.1. 2-Octyl trichloroacetate

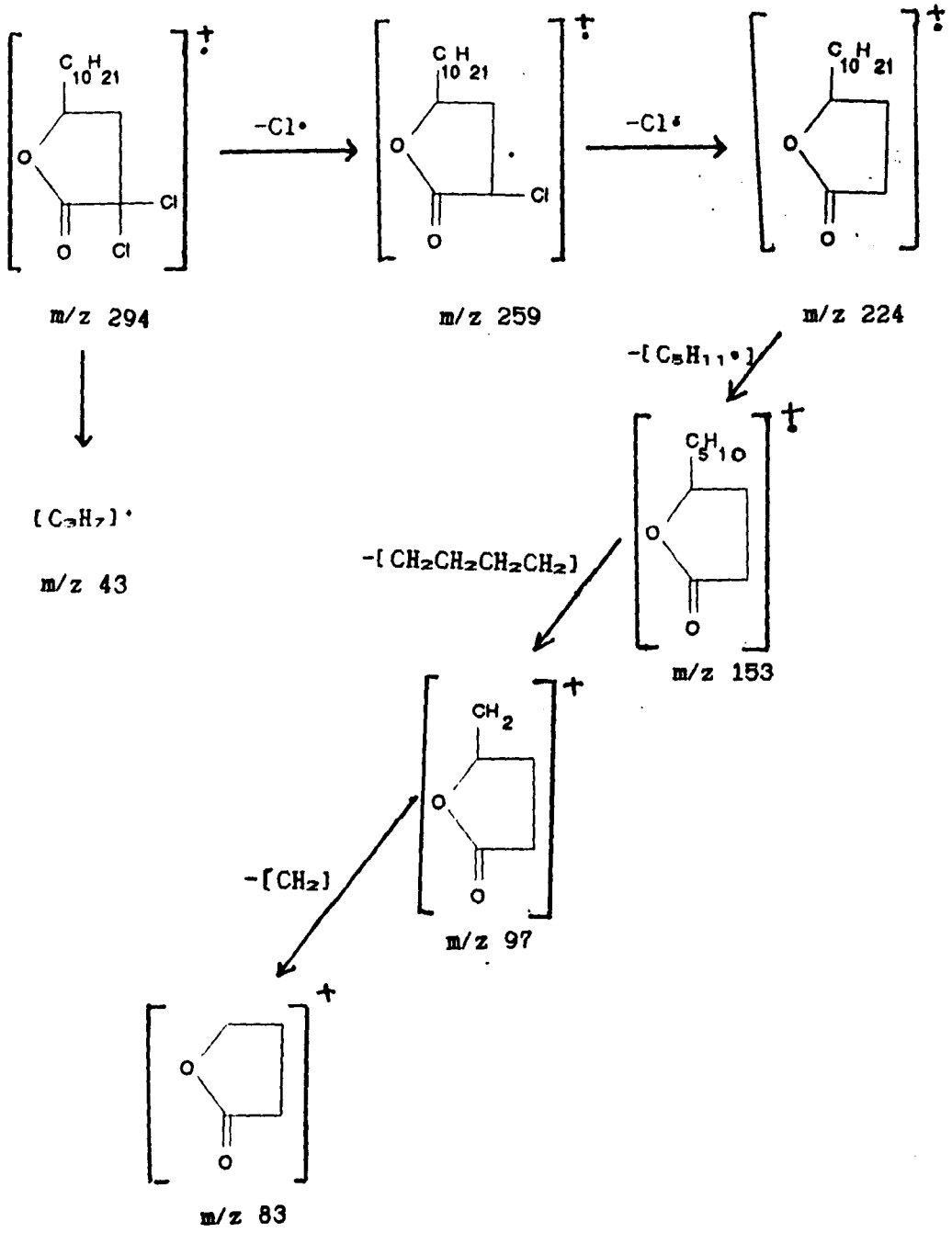


(3.32)

This ester was prepared according to the method suggested in the literature (equation 3.32)[6].

Trichloroacetic anhydride (5.9318g, 0.019mol) was slowly added to octan-2-ol (2.62g, 0.0247mol) in cold pyridine (5.96g, 20ml). The resulting reaction was vigorous, and after 15 seconds this mixture was poured into ice-water (100ml) which contained diethyl ether (20ml). Further diethyl ether (50ml) was added so that two layers were formed. These were separated, the water was further extracted with two portions of diethyl ether (2 x 20ml). The extracts were then combined and washed with two portions of dilute hydrochloric acid (2 x 30ml). The extract was washed further with water (100ml), followed by two

Scheme 3.9 : Mass spectral fragmentation of 4-decyl-2,2-dichloro-γ-butyrolactone



portions of sodium carbonate solution (2 x 30ml of 5% solution) and finally dried over anhydrous sodium sulphate. The dried extract was then filtered, and vacuum distilled . This resulted in 2-octyl trichloroacetate (2.60g, 35.6%).

3.4.3.2 Other Esters

The other esters : 2-butyl, 2-hexyl, and 2-decyl trichloroacetates were not prepared by the above method. It was found easier to isolate these esters from the reaction mixture after the reaction between trichloroacetic acid and the alkene in the presence of benzoyl peroxide had been completed.

Typically, trichloroacetic acid (18g, 0.11mol), alkene (0.10mol) and toluene (20ml), were placed in a two-necked flask and dried benzoyl peroxide in toluene (10ml of 0.044moldm^{-3} solution in toluene) was syringed in. (Benzoyl peroxide was dried over anhydrous sodium sulphite under nitrogen for several days prior to use.) The solution was degassed by the freeze-pump-thaw method, then refluxed for 6 hours. The mixture was vacuum distilled which resulted in two fractions. The second (higher boiling) fraction contained the ester concerned but generally there was some trichloroacetic acid carried over. The esters were further purified by a second distillation. The resulting esters were analysed by GLC and the purity was found to be 98% or greater. The yields, physical and spectroscopic properties of the esters are summarised in Table 3.12.

Table 3.12: Physical and spectroscopic properties of 2- Alkyl trichloroacetates

Alkyl Group	% Yield (isolated)	Infrared spectrum cm^{-1}	H -N.M.R spectrum δ	H -N.M.R spectrum Areas	Mass spectra
Butyl	67	All showed similar features - C=O overtone 3510 - C=O stretch 1768	All showed similar features 0.89 -1.0 (m, 6 H)	9 : 3 : 1	All showed similar spectra with m/z 189 / 191 / 193 $(M-C_nH_{2n+1})^+$ as the prominant ions
Hexyl	37	- CH_3 asym. 2960 - CH_3 sym 2870 - CH_2 asym. 2930	1.20 - 1.50 (m, 6 -18 H)	13 : 3 : 1	
Octyl	40	- C-O stretch 1250 - CH_3 asym. 1465 - CH_3 sym. 1380		17 : 3 : 1	
Decyl	45	- C-Cl stretch 980	4.80 - 5.20 (m, 1 H)	21 : 3 : 1	

3.4.4 Spectral data for 2-alkyl trichloroacetates

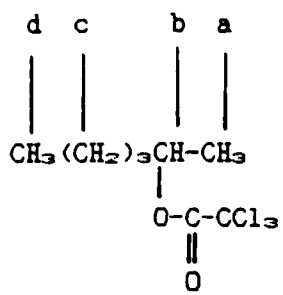
3.4.4.1 Infrared spectra

As would be expected, this series of esters have similar characteristic spectra. A typical spectrum is represented in Appendix 13 (2-octyl trichloroacetate). These spectra have a C=O overtone at 3620cm^{-1}, C=O and C-O stretches at 1760 and 1245cm^{-1} respectively.

3.4.4.2 ^{1}H NMR spectra

The ^{1}H NMR spectra are characteristic for this class of compounds. A typical example is represented in Appendix 14 of (2-hexyltrichloroacetate).

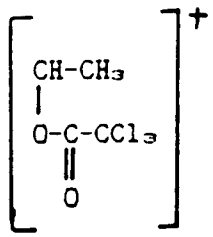
Fig 3.6 : Nomenclature of 2-hexyl trichloroacetate



This shows a multiplet at δ0.89-1.0 due to the methyl protons at the end of the alkyl chain (d) and the methyl group (a). The alkyl chain protons (c) are identified as a large singlet at δ1.1-1.7, whilst the proton at (b) is a multiplet at δ4.65-4.85 as its resonance is split by the methyl group (a) and by the α-methylene protons at (c). Other peaks are observed in the spectrum. That at δ5.0 is due to some water absorption by the sample and that at δ7.25 due to the solvent (C_6D_6).

3.4.4.3 Mass spectra

The mass spectra of none of these compounds showed molecular ion or M+1 ion. As this is the case the mass spectra can only be used to confirm the evidence from the other spectroscopic techniques. A typical spectrum is represented in Appendix 15. The largest fragment that appears for these compounds is



m/z 189

The other peaks represent the degradation of the alkyl chain (Scheme 3.10). In most of the spectra the m/z 117 peak is also present arising from the $[CCl_3]^+$ ion.

Scheme 3.10 : Mass spectral fragmentation pattern of 2-decyl trichloroacetate

$[C_{10}H_{21}CH{=}CH_2]^+$ m/z 168

$\downarrow -CH_2CH_2$

$[C_8H_{17}CH{=}CH_2]^+$ m/z 140

$\downarrow -CH_2$

$[C_7H_{15}CH{=}CH_2]^+$ m/z 126

$\downarrow -CH_2$

$[C_6H_{12}CH{=}CH_2]^+$ m/z 111

$\downarrow -CH_2$

$[C_5H_{10}CH{=}CH_2]^+$ m/z 97

$\downarrow -CH_2$

$[C_4H_8CH{=}CH_2]^+$ m/z 83

$\downarrow -CH_2$

$[C_3H_6CH{=}CH_2]^+$ m/z 69

3.4.5 Reaction between trichloroacetic acid and alkenes in the presence of $[RuCl_2(PPh_3)_3]$ and other catalysts.

3.4.5.1 Reactions carried out by reflux

Typically, trichloroacetic acid (9.05g, 56mmol), the alkene (50mmol), the catalyst (0.15mmol, 0.014moldm^{-3}) and methyl myristate (0.1g), (employed as internal standard) in toluene (6ml) were degassed three times by the freeze-pump-thaw method. The mixture was allowed to equilibrate to room temperature for ½ hour, then refluxed for 6 hours.

The mixtures were then analysed by GLC (using the same instrument as in section 2.4). The GLC conditions employed were : an oven temperature of 150°C; an injector temperature of 225°C; a detector temperature of 250°C and a flow rate of 1 ml min^{-1}.

3.4.5.2 Reaction between trichloroacetic acid and oct-1-ene in the presence of $[RuCl_2(PPh_3)_3]$ carried out in sealed tubes.

This reaction was carried in the same way as the reflux reaction but on a smaller scale. When the reaction was carried out in a sealed tube, trichloroacetic acid (4.55g, 28mmol) and $[RuCl_2(PPh_3)_3]$ (0.071g, 0.075mmol) were weighed directly into the tube. Oct-1-ene (2.8g, 25mmol), methyl myristate (0.1g) and toluene (6ml) were then added via a syringe. The tube was degassed three times by the freeze-pump-thaw technique, sealed and allowed to equilibrate to room temperature for ½ hour. It was then placed in the oven for 6 hours at 110°C. After the reaction had been completed the reaction mixture was analysed by GLC. (The same conditions were used as in section 3.4.5.1).

3.4.5.3 <u>The action of heat upon 2-octyl trichloroacetate in the presence of $[RuCl_2(PPh_3)_3]$.</u>

This reaction was investigated in order to determine whether the ester underwent dehydrochlorination in the presence of $[RuCl_2(PPh_3)_3]$. 2-octyl trichloroacetate (0.5g, 1.80mmol), methyl myristate (0.1g) and $[RuCl_2(PPh_3)_3]$ (0.15mmol) were placed in toluene (20ml) then degassed three times by the freeze-pump-thaw technique, allowed to equilibrate to room temperature for ½ hour and then refluxed for 6 hours. After this time the reaction mixture was analysed by GLC (as previously in 3.4.5.1). The lactone was not detected.

3.4.5.4 <u>Reaction between trichloroacetic acid and alkenes in the presence of benzoyl peroxide.</u>

The reactions were carried out in a similar manner to that in the presence of $[RuCl_2(PPh_3)_3]$, so that the results would be comparable. Typically, to a mixture of trichloroacetic acid (9.00g, 56mmol), the alkene (50mmol), methyl myristate (0.1g) and toluene (6ml) was added to dried benzoyl peroxide in toluene (5ml of 0.044moldm^{-3} solution in toluene) by syringe. The mixture was degassed by the freeze-pump-thaw method, allowed to equilibrate to room temperature for ½ hour, then refluxed for 6 hours. The mixture was then analysed by GLC (as in section 3.4.5.1).

3.4.5.5 Reaction between trichloroacetic acid and alkenes in the absence of catalysts or benzoyl peroxide.

Again, the reactions were carried out in precisely the same manner as those described earlier.

Typically, trichloroacetic acid (9.00g, 56mmol), the alkene (50mmol), methylmyristate (0.1g) and toluene (6ml) were degassed as described previously, then refluxed for 6 hours. The mixture was then analysed by GLC (as in section 3.4.5.1).

3.4.6.1 Reaction between tribromoacetic acid and oct-1-ene in the presence of $[RuCl_2(PPh_3)_3]$.

3.4.6.1.a In toluene.

The reaction was carried out in the same way as those involving trichloroacetic acid. Howevever a different ratio of reagents was used. Tribromoacetic acid (2.00g, 6.73 mmol), oct-1-ene (1.91g, 17mmol) and $[RuCl_2(PPh_3)_3]$ (0.0375g, 0.0375mmol), in toluene were degassed three times by the freeze-pump-thaw technique and refluxed under nitrogen for 6 hours. A H'NMR spectrum was recorded, and then the reaction mixture was distilled. The fractions were then analysed by IR,'H NMR and mass spectra as has been described in section 3.3.2.2.

3.4.6.1.b In toluene/ethanol

The reaction was scaled up in a mixed solvent system of toluene/ethanol (1:1), as $[RuCl_2(PPh_3)_3]$ is very soluble in toluene while tribromoacetic is very soluble in ethanol and only barely soluble in hot toluene. In this reaction, oct-1-ene (7.73g, 68mmol), tribromoacetic acid (8.01g, 6.73 mmol) and $RuCl_2(PPh_3)_3]$ (0.15g, 0.15mmol) in toluene/ethanol (20ml) were degassed in the usual way, and then refluxed under nitrogen for 6 hours. Several attempts were made at this preparation . In the earlier preparations, after refluxing, the reaction mixture was purified by vacuum distillation. The first fraction was observed to contain oct-1-ene and solvent, the second and third fractions contained varying amounts of ethyl tribromoacetate, whilst the remainder could not be distilled over without fumes of HBr being evolved. So in further work the solvent and volatiles were removed by applying a vacuum for several days. The

resulting mixture was then purifed by column chromatography.
A 25cm X 2.5cm column was used with silica as the support. The solvent used was hexane/diethyl ether in a 3:1 ratio. The mixture to be columned was a dark brown colour and bands were not observed on the column although separation took place. So $10cm^3$ fractions were collected and examined by IR spectroscopy. The acid came off first, followed by the lactone, requiring 180ml of eluting solvent for the separation (1g of reaction mixture being applied at one time) to take place. The amounts of the lactone and acid recovered in total were 0.03g, (0.29 %) and 0.1g, (1.1 %) respectively. In the earlier reaction where ethyl tribromacetate was distilled off 1.05g, (11.6%) was obtained. All yields are based on tribromoacetic acid.

3.4.6.2 Reaction between tribromoacetic acid and oct-1-ene in the presence of benzoyl peroxide.

In this reaction tribromoacetic acid (8g, 6.73mmol), oct-1-ene (7.63g, 68mmol) in benzene (20ml) were placed in a three necked flask with an equilibrating funnel stoppered with a superseal. The dried benzoyl peroxide (1.2g in 15ml) was carefully syringed into the dropping funnel. The mixture was degassed by the freeze-pump-thaw method. Explosion screens were in place throughout the entire reaction as a precaution. The reaction was then refluxed for 6 hours under nitrogen. The solution was then allowed to cool and water was syringed in very gradually. The reaction mixture was thoroughly washed three times with water, then separated and dried over anhydrous magnesium sulphate.The solution was filtered, and the benzene was removed by a rotary evaporation. The ^1H NMR spectum and gas chromatogram of the mixture were recorded and then the components were separated by column chromatography as described in section 3.4.6.1.b.

3.5 References

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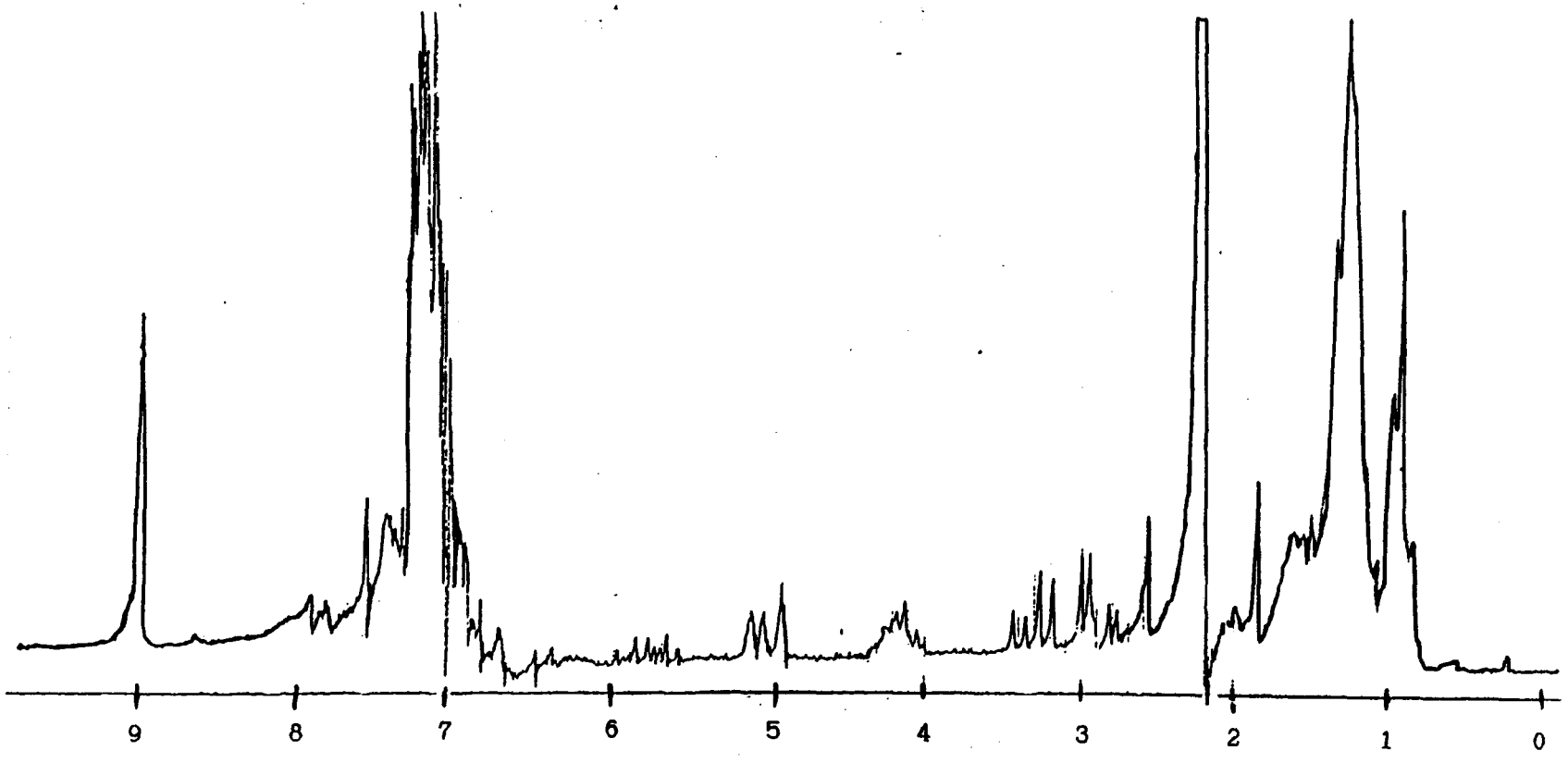
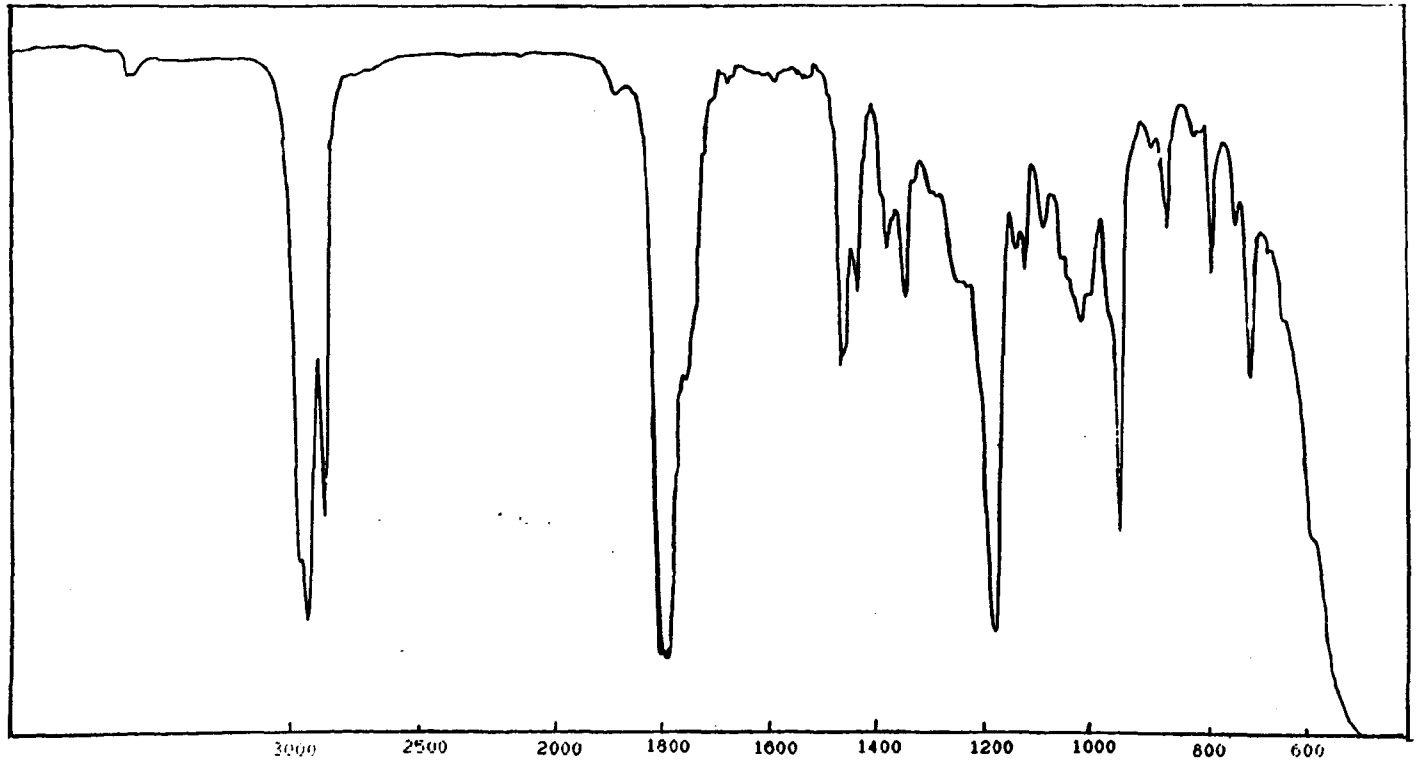
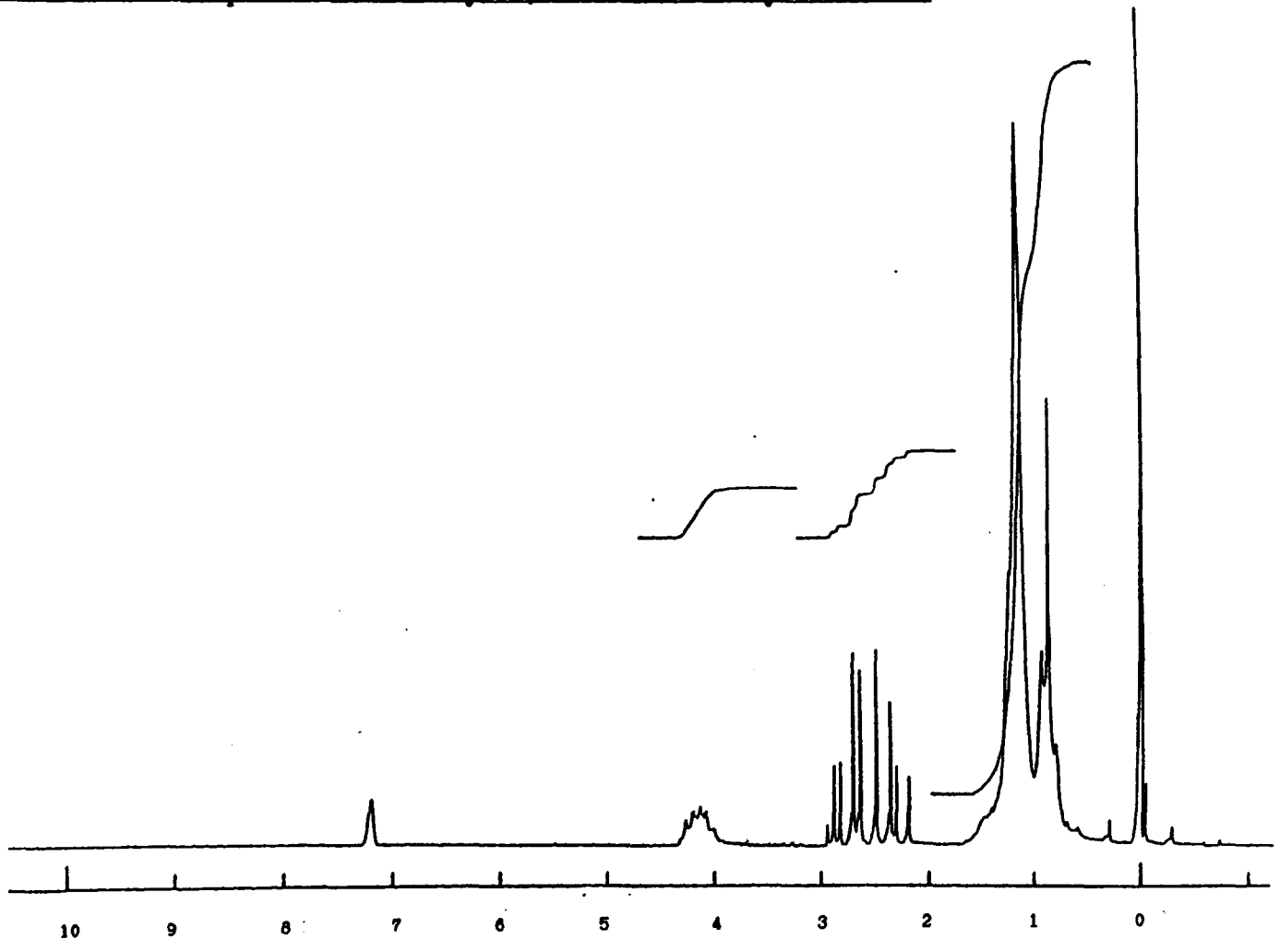
Appendix 1 : ^1H NMR spectrum of an undistilled mixture of the reaction between tribromoacetic acid and oct-1-ene in the presence of $[RuCl_2(PPh_3)_3]$.



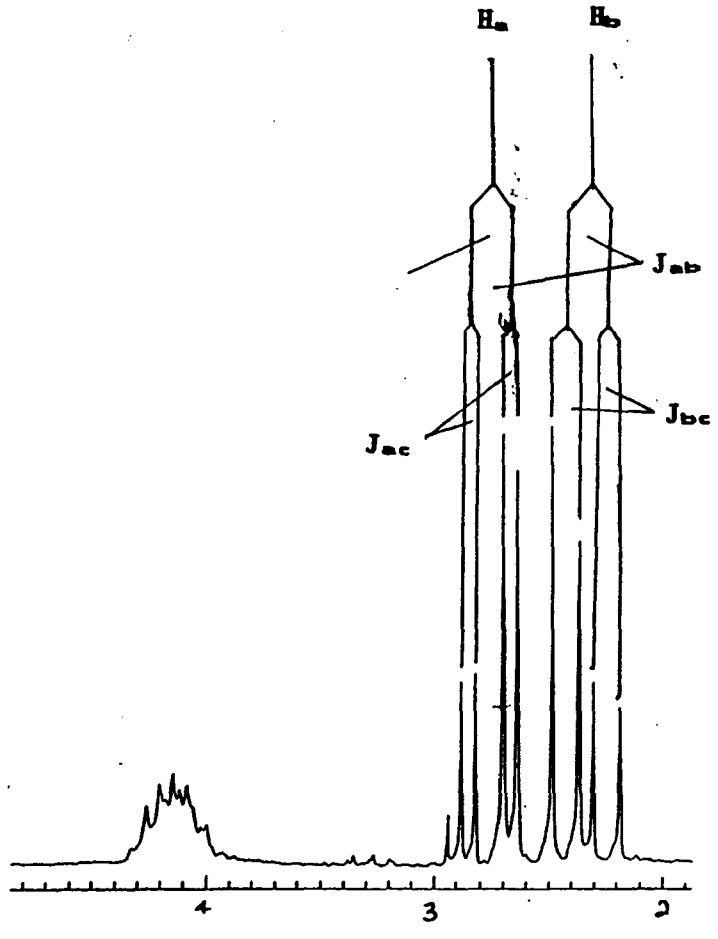
Appendix 2 : Infrared spectrum of 4-Hexyl-2,2-dibromo-γ-butyrolactone.



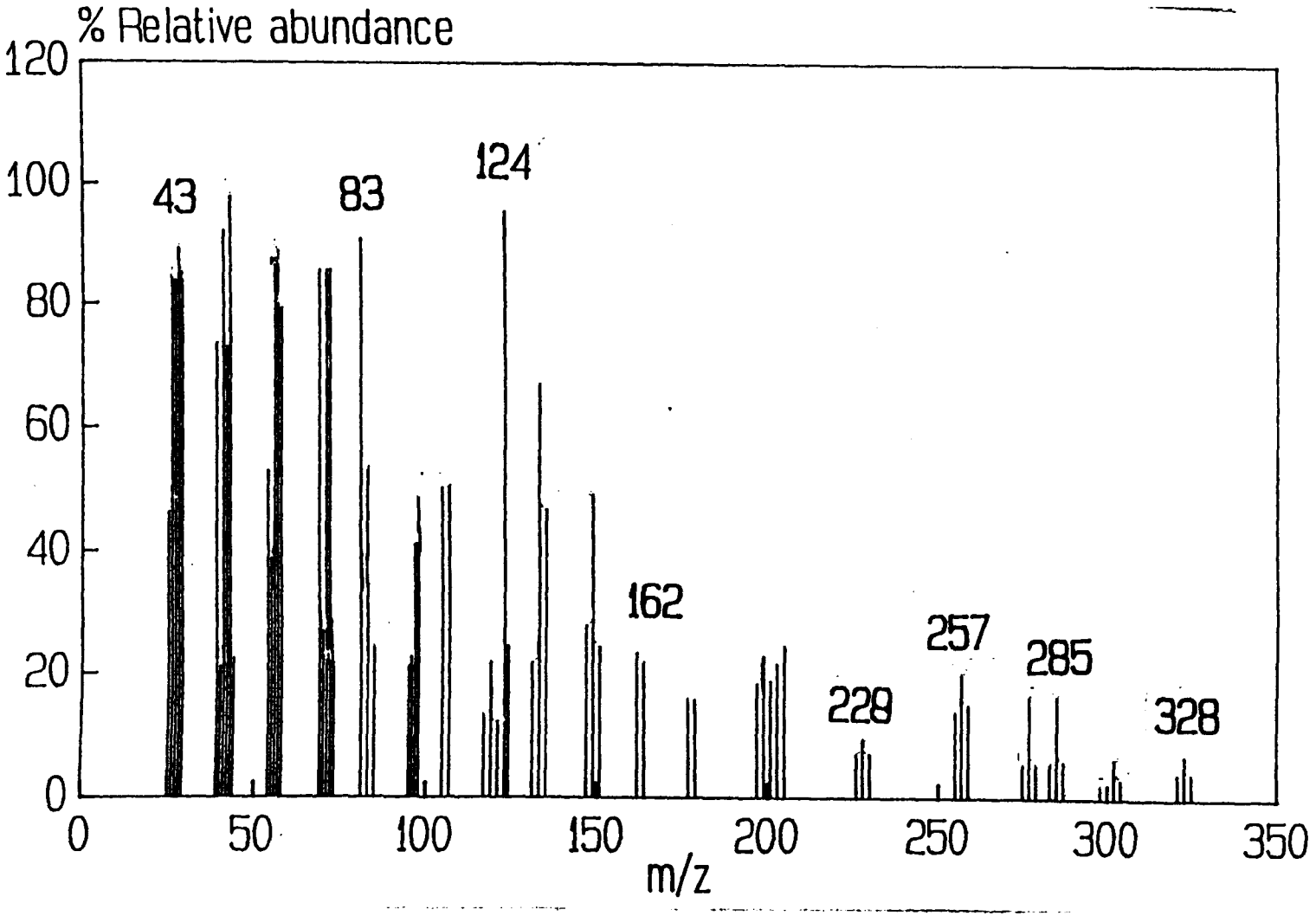
Appendix 3 : ^{1}H NMR spectrum of 4-Hexyl-2,2-dibromo-γ-butyrolactone.



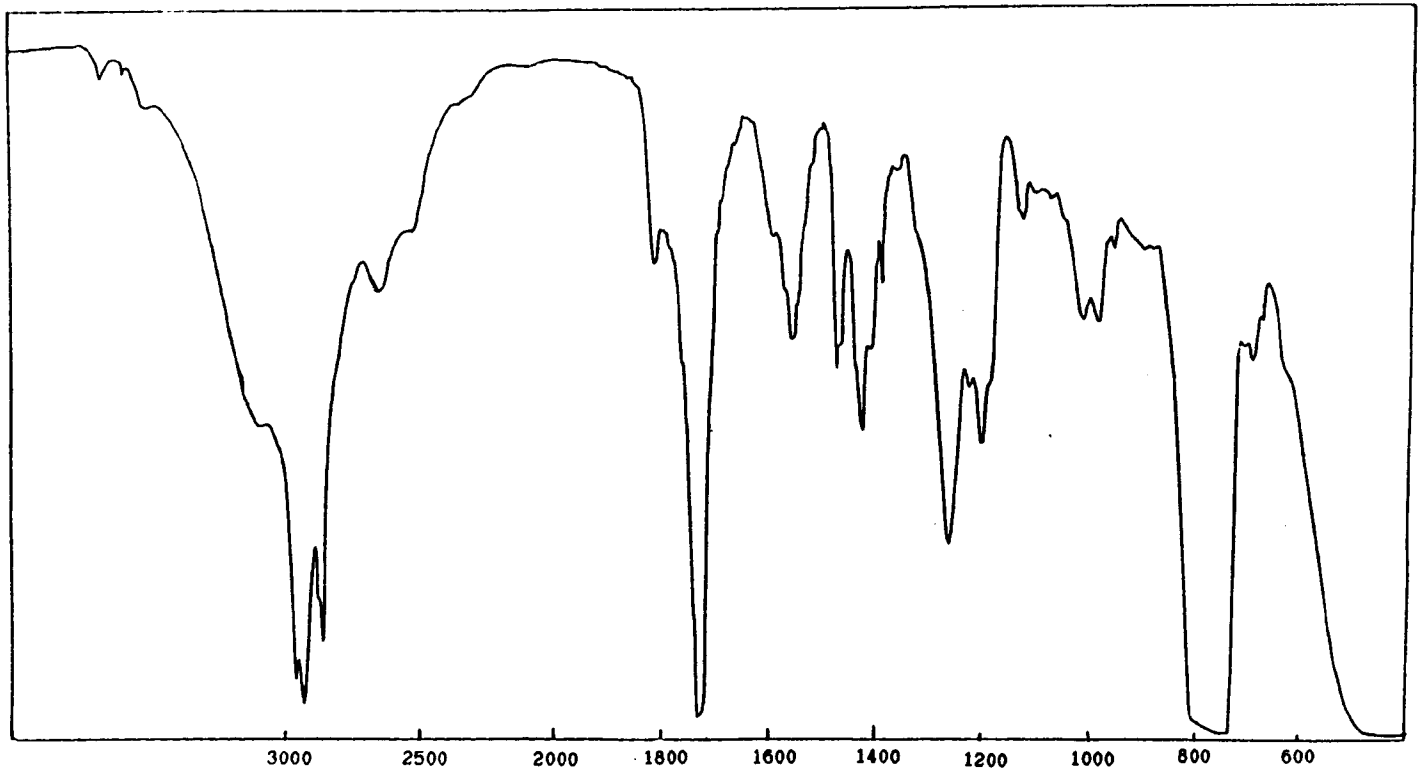
Appendix 4 : ^{1}H NMR spectrum showing coupling pattern for 4-hexyl-2,2-dibromoro-γ-butyrolactone.



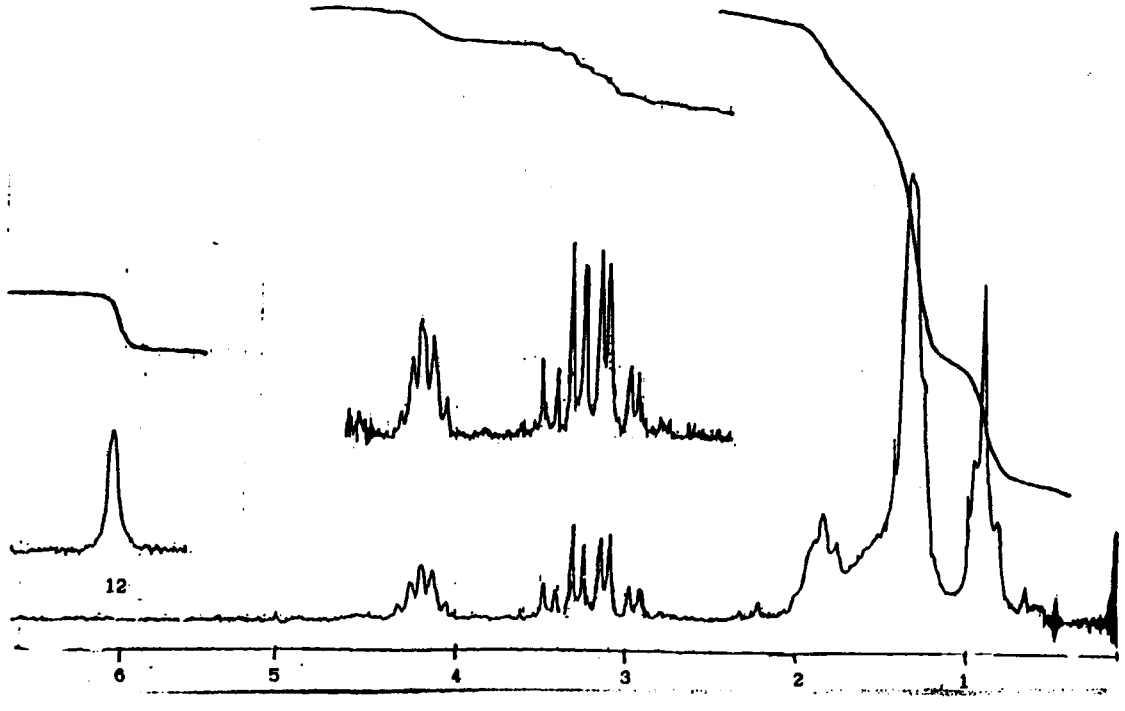
Appendix 5 : Mass spectrum of 4-hexyl-2,2-dibromo-γ-butyrolactone.



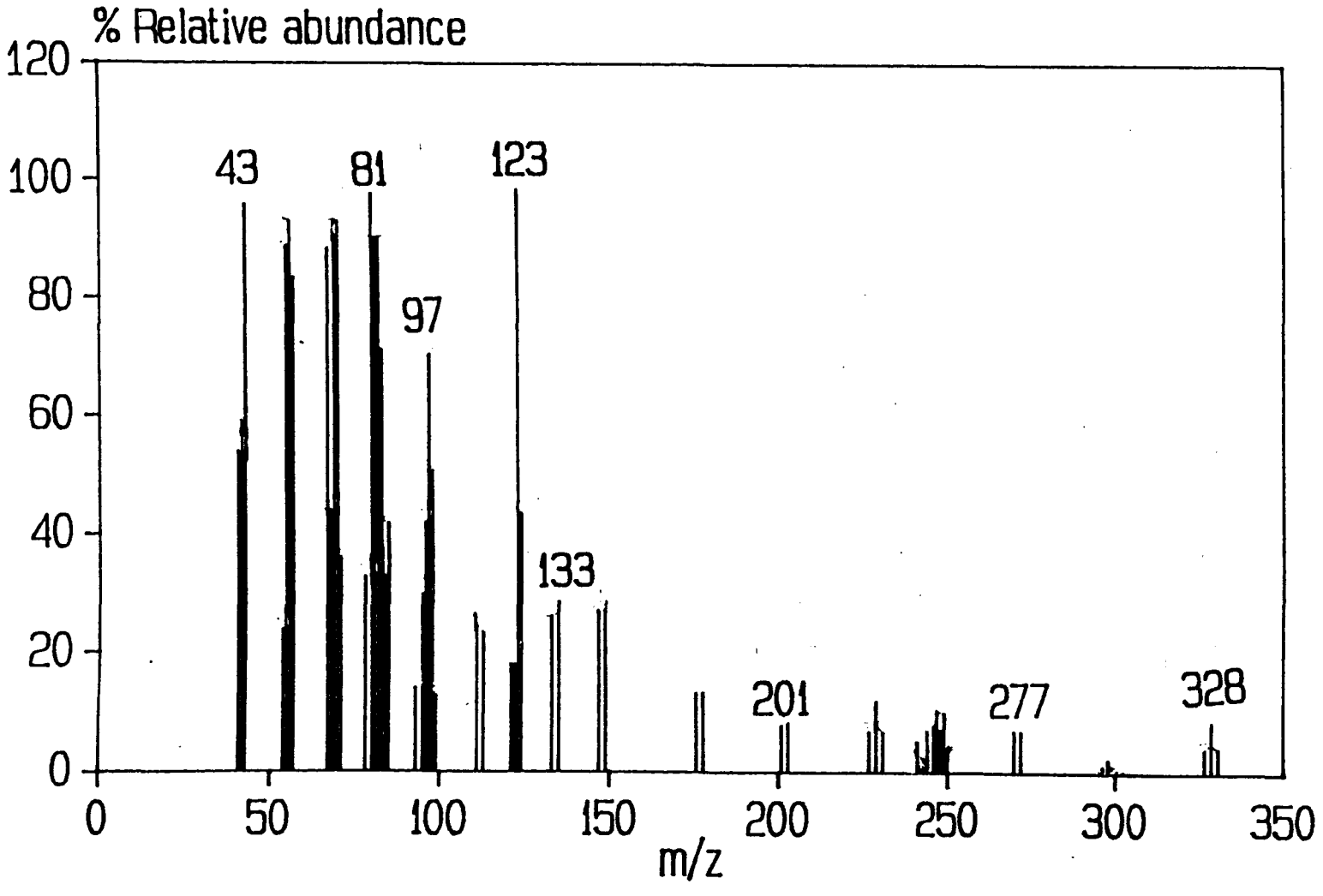
Appendix 6 : Infrared spectrum of 2,2,4-tribromodecanoic acid



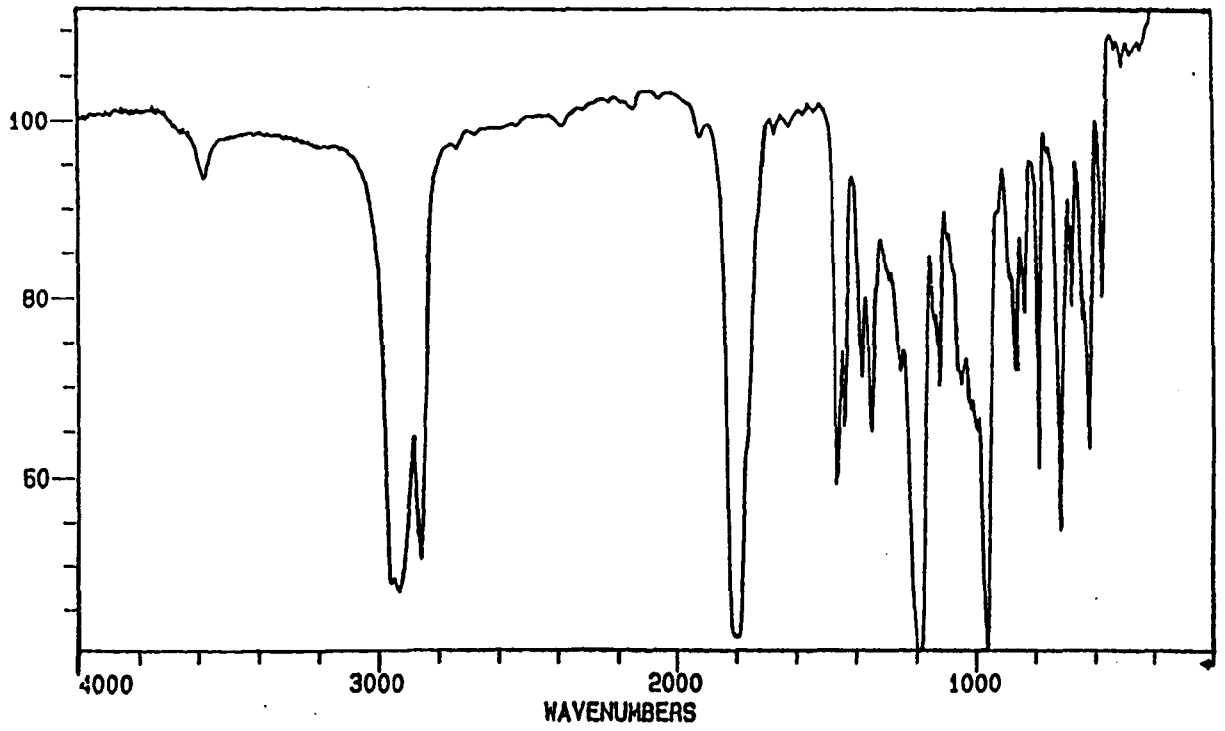
Appendix 7 : ^1H NMR spectrum of 2,2,4-tribromodecanoic acid.



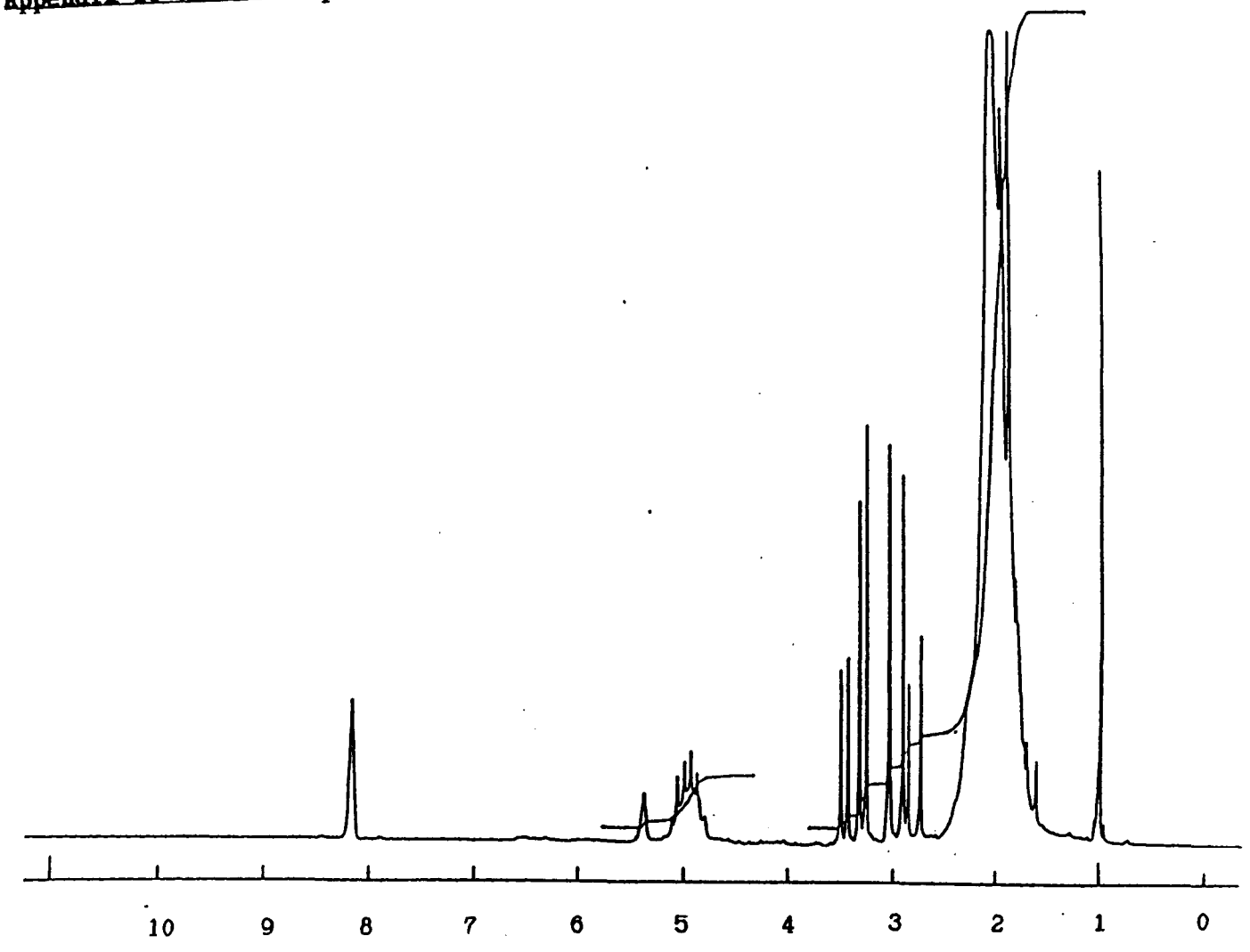
Appendix 8 : Mass spectrum of 2,2,4-tribromodecanoic acid.



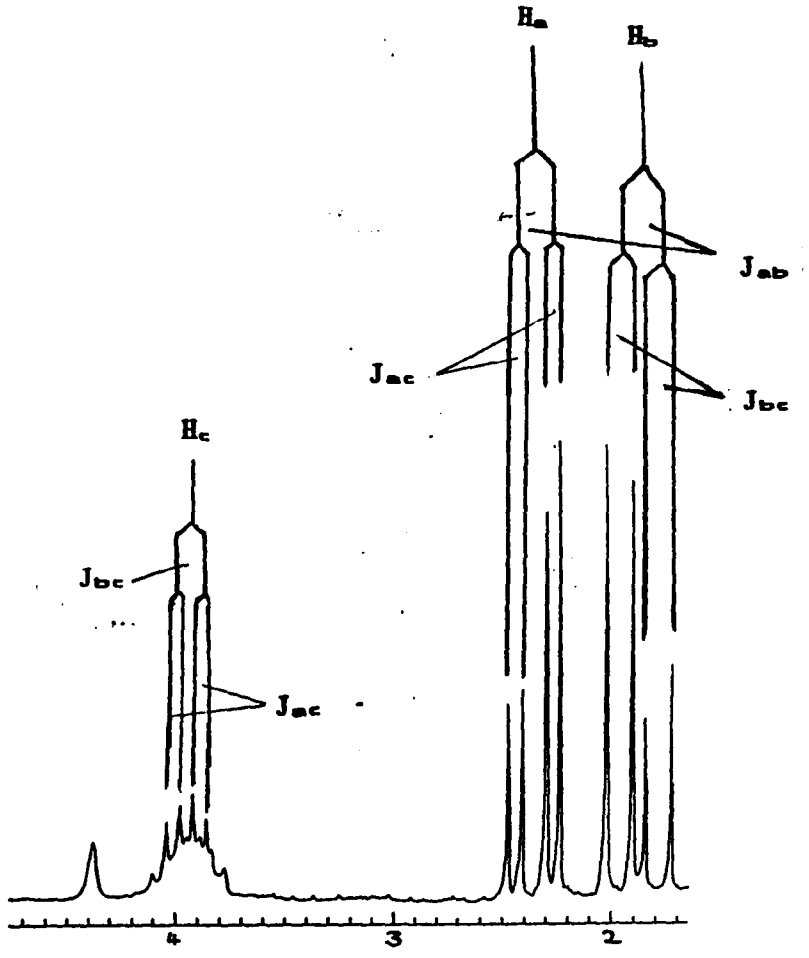
Appendix 9 : Infrared spectrum of 4-hexyl-2,2-dichloro-γ-butyrolactone.



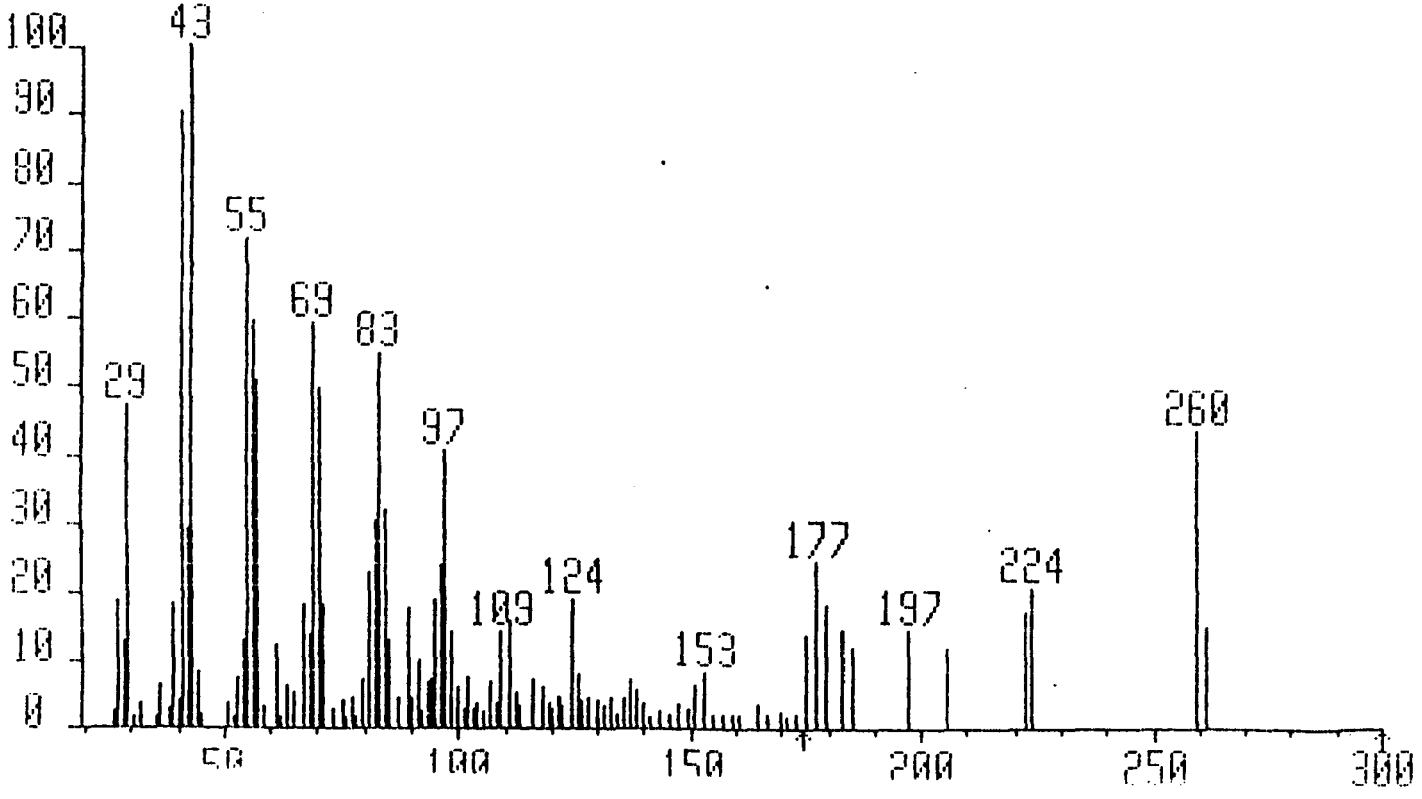
Appendix 10 : ^{1}H NMR spectrum of 4-hexyl-2,2-dichloro-γ-butyrolactone.



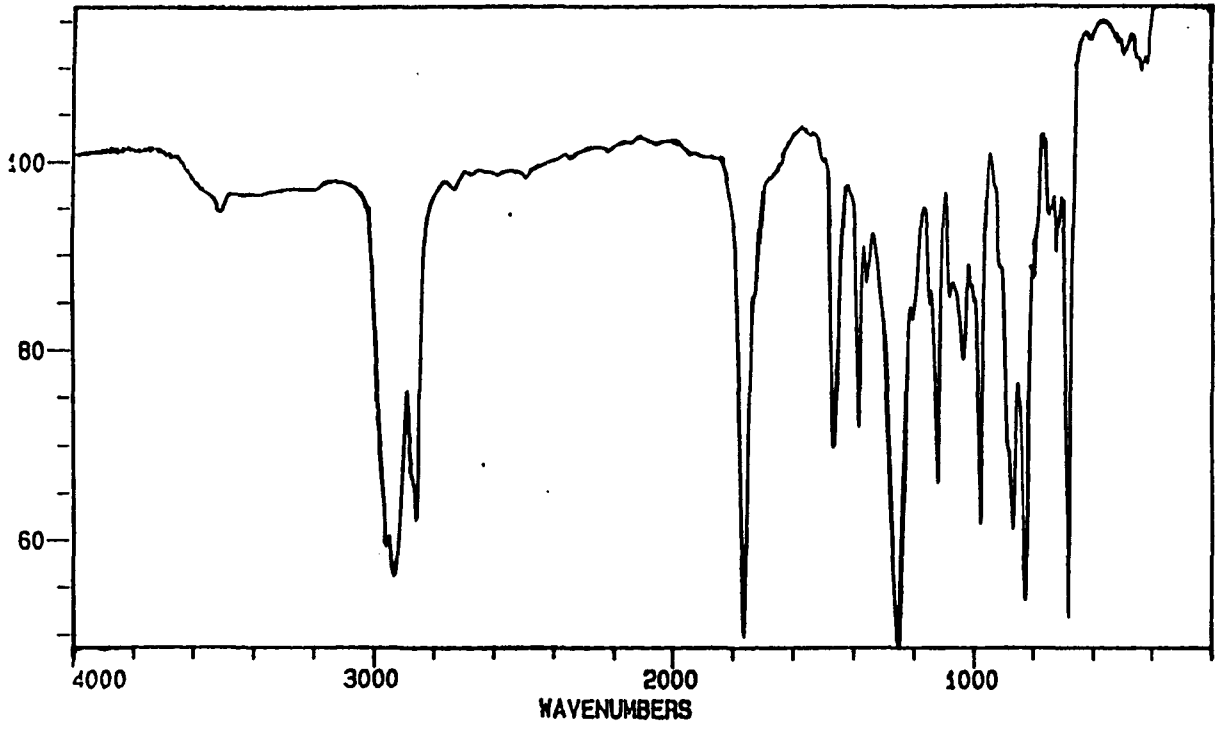
Appendix 11 : ^{1}H NMR spectrum showing the coupling pattern of 4-hexyl-2,2-dichloro-γ-butyrolactone.



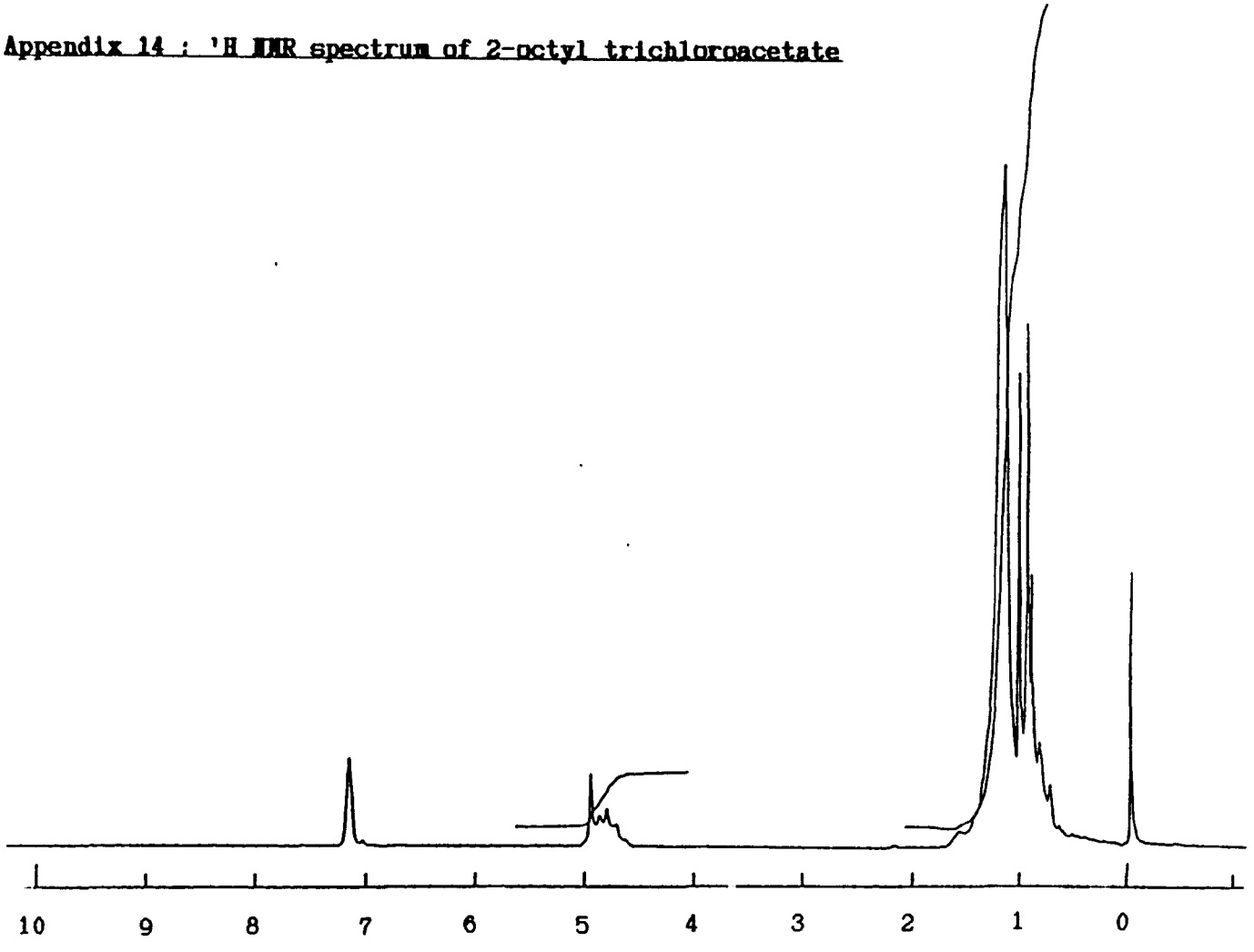
Appendix 12 : Mass spectrum of 4-Decyl-2,2-dichloro-γ-butyrolactone.



Appendix 13 : Infrared spectrum of 2-octyl trichloroacetate



Appendix 14 : ^{1}H NMR spectrum of 2-octyl trichloroacetate



Appendix 15 : Mass spectrum of 2-decyl trichloroacetate