Investigations into the Functionalisation of Polyisobutylene

by

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Abstract

The work described in this thesis is concerned with the functionalisation of polyisobutene (PIB), which is an important intermediate in the production of oil additives for the automotive industry. These include dispersants which derive their dispersency from the polar endgroups attached to an alkyl chain. A number of problems are encountered with the present synthetic procedures and this thesis details investigations into the nature of some of these problems and their possible solutions. The complex nature of PIB makes it a difficult substrate to employ for mechanistic studies. To circumvent this problem a number of model alkenes have been employed to mimic the behaviour of PIB.

Chapter 1 contains a general introduction to oil additives concentrating on the formation of dispersants from PIB, and also contains a summary of the halogenation of alkenes and of the Alder-ene reaction. In Chapter 2 the halogenation of the model alkenes has been studied using chlorine, bromine and interhalogen compounds such as ICl and IBr. The selectivity of the halogenation process, and the consequent incorporation of chlorine into the final product has been studied and ways of eliminating the problem of residual chlorine are reported.

Chapter 3 details experiments concerned with the formation of diamines from the epoxides derived from the model alkenes. This it was hoped might provide a new route to functionalised PIB. Although, ring-opening of the model alkene epoxides was usually not a problem, attempts to synthesis diamines from the resultant amino-alcohols proved unsuccessful.

Chapter 4 is concerned with an investigation into the preparation of polyisobutylene succinic anhydride (PIBSA), which is manufactured by the thermal ene reaction between maleic anhydride (MA) and PIB. The production of coloured by-products from this reaction have been studied using two alkenes as models. The experiments show that the intensity of the colour in the reaction mixture depends on the proportion of MA used. However, attempts to isolate and identify the coloured components were not completely successful. It is suggested that the decomposition of MA or related material results in the formation of involatile coloured resin. Chapter 5 contains details of the experiments studying the thermal decomposition of

MA. The synthesis of polymeric MA by radical and base initiated routes has been effected in the hope that this would aid the identification of the coloured polymer.

Finally, Chapter 6 contains the detailed experimental procedures used in Chapters 2 to 5.

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1. Introduction.

2. Electrophilic addition of halogens to alkenes.

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Abbreviations

ASA	Alkenyl succinic anhydride
atm	atmospheres
br	broad (NMR)
CI	Chemical Ionization
CTC	Charge-Transfer Complex
DIBSA	Diisobutylene Succinic Anhydride
d	doublet (NMR)
dd	doublet of doublets (NMR)
ddt	doublet of doublet of triplets (EPR)
DMF	N,N-Dimethyl formamide
EI	Electron Impact
EPR	Electron Paramagnetic Resonance
ESI	Electrospray Ionisation
FAB	Fast Atom Bombardment
FID	Flame Ionisation Detector
FM	Friction Modifier
GC	Gas Chromatography
GC/MS	Gas Chromatography/Mass Spectrometry
HOMO	Highest Occupied Molecular Orbital
HPLC	High Performance Liquid Chromatography
HR	High resolution
IR	Infra-red
λ_{MAX}	absorption maximum
LC/MS	Liquid Chromatography/Mass Spectrometry
LUMO	Lowest Unoccupied Molecular Orbital
m	multiplet (NMR)
m-	meta (as in *m*-CPBA, *meta*-Chloroperbenzoic acid)
MA	Maleic Anhydride
MI	Molecular Ion
mm Hg	millimetres of mercury

MsCl	Mesyl Chloride
NMP	2,2-Methylnitrosopropane
NMR	Nuclear Magnetic Resonance
p-	para
PIB	Polyisobutylene
PIBSA	Polyisobutylene Succinic Anhydride
PMA	Poly(Maleic Anhydride)
p.p.m.	parts per million
q	quartet (NMR)
s	singlet (NMR)
$\Delta S^{\neq}$	activation entropy
t	triplet (NMR)
t-Bu	tertiary butyl
$TBABr_3$	Tetrabutylammonium tribromide
TBNB	2,4,6-Tribromonitrosobenzene
TDDA	Tetradehydrodianthracene
THF	Tetrahydrofuran
TMP-1	2,4,4-Trimethyl-1-pentene
TMP-2	2,4,4-Trimethyl-2-pentene
TNPE	Tetraneopentylethene
UV-Vis	ultraviolet-Visible
$\Delta V^{\neq}$	activation volume
VI	Viscosity Index
ZDDP	Zinc Dithiophosphates

Chapter 1

Introduction

A lubricant is defined as a substance which can be used to reduce friction. Indeed for many thousands of years people have used oils on moving parts to prevent friction, which creates high temperature and wear. The advent of the industrial revolution increased the demand for animal and vegetable oils for decreasing friction and wear in machinery.[1] It was during this historical period (1750 - 1850) that mineral oils were first produced commercially, because of their availability, cost and diversity of uses.[2] Following their introduction, mineral oils rapidly overtook animal and vegetable oils as the essential lubricant. However, major developments in engine design in the 1950s following on from the advances made during the second world war put increasing demands on the oils used. To meet the high demands of these new engines significant effort was put into improving engine oil, which by this time included both mineral and synthetic oils. These developments have continued to the present time.

In the internal combustion engine lubricants were first employed to counteract the friction between moving parts, leading to high temperatures and wear. In modern automotive engines the function of a lubricant is also to maintain a clean efficient engine, thereby minimising harmful engine exhaust emissions, increasing the engines lifetime (by minimising friction, deposits and varnish, and preventing corrosion and wear) and controlling oil consumption (volatility and stability). The ability of the lubricant to respond to these demands is affected by the stability of the oil to the hostile environment in which it operates. Inside an internal combustion engine the oil stability depends on; temperature (which can reach 200 °C), oxidation potential and contamination by water. Chemical attack from fuel combustion products, such as partially burned fuel and other blow-by products and corrosive acids, also causes degradation of the lubricant oil. The increase in acidity that results leads to corrosive wear, rust formation and insoluble deposits (sludge and resin) which can among other things lead to excess oil thickening. This constant degradation of the lubricant and the engine can, in the long term, lead to irreversible damage and engine failure. Additives are therefore added to the lubricant to enhance the performance of the base oil and extend its useful lifetime. These demands cannot be met by a single lubricant: a complex combination of chemical additives is needed.

The aim of this section is to describe the use of lubricant packages in modern engines and to specify the design, structure and functions of the various additives contained within automotive lubricating oils.

1.1 Composition of engine oil.

Table 1.1: Composition of engine oils.

Function	Additive type	Composition / Percent
Base oil	Mineral (petroleum) or synthetic	71.5 - 96.0
Friction and wear	Viscosity index (VI) improvers	0 - 5
	Anti-wear additives	0.1 - 3.0
	Friction modifiers	0.1 - 3.0
	Anti-rust / Corrosion inhibitors	0.5 - 3.0
Contamination / Cleanliness	Antioxidant	0.1 - 2.0
	Detergents	2 - 10
	Dispersants	1 - 9
Maintaining fluid properties	Pour point depressants	0 - 0.5
	Foam inhibitors	0.0002 - 0.0015

A lubricant usually consists of a base oil, which is normally mineral oil, in combination with additive chemicals which protect and enhance the desirable properties of the base fluid. A very small percentage of lubricant which is sold is mineral oil without any additives. Within the transportation field the composition of the oil package depends greatly on the performance specifications. As the amount of each additive added to the base oil is specific to the usage the exact composition of the lubricant is highly variable. However, all contain performance additives ranging from 1% to 25% by weight, but ultimately it is the solubility of such molecules in the base fluid which is the limiting factor. A typical composition of an automotive engine oil is shown above (table 1.1) with the range of amounts that would generally be used shown as percentage by weight.[3]

1.2 The chemical properties of lubricants and the role of additives.

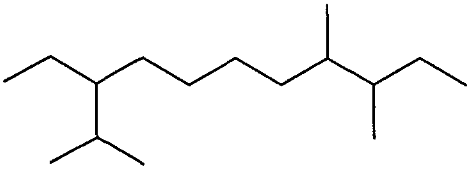
A brief overview of the properties and chemistries of the major components of the lubricant package follows.

1.2.1 Base oil.

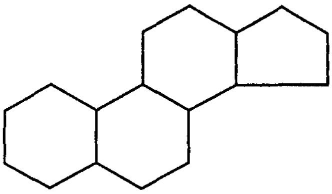
The bulk of the lubricant package, as shown in table 1.1, consists of the base fluid, the majority of which is produced by refining crude petroleum oil. Bromilow (1990) estimated that in 1989 the amount of petroleum base oil used in the world was approximately 39 million tonnes.[4] This corresponds to a massive amount of crude oil considering that the base stocks used for lubricants only contain a mixture of C_{20}-C_{45} hydrocarbons isomers. The base oil is produced from the distillation residue after the major lighter fractions are removed, therefore overall output of base oil (after vacuum distillation, extraction, dewaxing and hydrofinishing) can be as low as 10% of the initial crude oil.[5]

Crude oil contains many different types of organic molecules, mainly hydrocarbons although small quantities of non-hydrocarbon impurities (sulfur, nitrogen and oxygen compounds) are present. The petroleum oil consists mostly of saturated linear and branched chain alkanes, saturated five and six membered alicyclics, polyaromatics and complex hydrocarbons which combine these structural types.[5] Some examples are shown in figure 1.1. The relative amounts of these compounds, and their isomers, found in crude oil is greatly dependent on the origin of the oil.

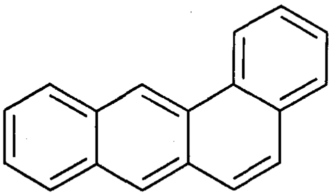
Figure 1.1: Examples of hydrocarbons present in crude oil.



Branched alkane



Alicyclics



Polycyclic aromatics

Alkanes, alicyclics and aromatics of the same molecular weight have very different physical and chemical properties. Lubricant oils which have high alkane content are referred to as paraffinic crude oils. Paraffinic base oils are typically used as the mineral oil base fluid for the automotive industry because of their good viscosity/temperature characteristics [viscosity index (VI) can be over 100].[5]

Despite their good viscosity/temperature properties mineral oils readily oxidize at temperatures above 100 °C and have poor flow characteristics at temperatures lower than about – 10 to – 20 °C, referred to as the pour point. Therefore synthetic base oils are occasionally used for applications where mineral oils are not capable of operating effectively *e.g.* aerospace applications. However, their limited supply and narrow applications means that they represent only a minor volume of base oil sold. In the automotive industry four main types of synthetic base oils are used: olefin polymers (PAO), dibasic acid esters, polyol esters and alkylated aromatics.[6] General advantages over comparable mineral oils include, the absence of wax (discussed later), lower pour point (below – 40 °C), improved thermal and oxidative stability, higher VI (> 100) and superior volatility characteristics.[6] Due to their preferential properties synthetic base stocks are often blended with mineral oils to enhance their temperature range.

Degradation of the lubricating oil by oxidation can lead to a dramatic loss of performance through a number of processes such as: corrosion from organic acids, sludge and resin formation, viscosity change due to contamination with degradation products and carbon deposits at high temperatures. Additives are therefore added to the lubricating oil to protect against degradation and to extend its lifetime (increase the change interval). The following sections summarise the chemical and physical properties which are used to enhance the performance of the lubricant.

1.2.2 Viscosity index (VI) improvers[7] / pour point depressants.[8]

Flow characteristics, such as viscosity, are largely dependent on the individual properties of the base oil. However the temperature range over which the lubricant is especially effective can be enhanced by viscosity index (VI) improvers and pour point depressants

Viscosity modifiers improve the viscosity/temperature characteristics of the lubricant by reducing the rate of viscosity change with temperature. These types of additives are generally high molecular weight (10, 000 to 1 million) oil-soluble polymers and co-polymers, typically made from olefins (methacrylates and polyisobutenes), alkylated styrenes and dienes.[7] In contrast to the base fluid, the viscosity index of these polymers decreases at higher temperatures as the polymer molecule is swollen by oil.

Although paraffinic oils are the preferred base stock for the automotive industry, because of their viscosity/temperature characteristics, they contain a lot of high melting linear alkenes which form waxes.[8] Many wax constituents are removed from the base oil during the refining process, however residual wax is still present. Pour point depressants prevent the wax crystals from crystallizing out of the mineral oil. Their function is to be absorbed onto the wax crystal in preference to oil. Lubricant flow properties at low temperatures thus alter very little as the crystal volume remains relatively constant. The most widely used pour point depressants are polymethacrylates, although alkylated naphthalenes and phenolic polymers are also used.[6]

1.2.3 Friction modifiers[8] / anti-wear additives.[9]

In an internal combustion engine the metal-metal contact between moving surfaces creates friction, heat and wear. Lubricant oils form a film on the metal surface which gives some protection against this. However, they are only weakly absorbed onto the surface and are easily removed by high sheer rates and heat. Friction modifiers and anti-wear additives work in a similar way but have been specifically designed to overcome this problem.

In the base oil the polar head of friction modifiers (FM) is attracted to metal surfaces and the long hydrocarbon tail is solubilised in the oil. All the FM molecules line the metal surface with their hydrocarbon tails perpendicular to the surface and parallel to each other. This orientating of the absorbed layer can also induce multilayers of FM molecules to stack the absorbed molecules. These clusters are hard to compress but, under normal stress conditions, are easy to break and shear. The effect of this is to reduce the coefficient of friction, thus decreasing the friction between the two surfaces. Carboxylic acids, amides and phosphorous and phosphoric esters make ideal FMs.[8]

The main factors contributing to wear are metal-metal contact, presence of abrasive particles and attack by corrosive acids. Metal-metal contact can be prevented by additives that form a protective film on the metal surface by physical absorption or chemical reaction. This is very similar to the way in which FM protect surfaces, so it is not surprising that anti-wear additives also consist of a non-polar tail which is absorbed onto the surface by interaction of the metal with a polar end-group. Long chain carboxylic acids such as palmitic or stearic acids and their ester derivatives are widely used.[9] However, the most effective anti-wear additives are actually chemisorbed through electron transfer from an absorbed molecule to the surface. This process is irreversible and the molecule can then only be removed when the component to which it is attached is removed by wear. The most successful anti-wear additives are zinc dithiophosphates, although di-lauryl phosphate, di-dodecanyl phosphite and zinc dialkyl dithiocarbonates have also been used.[6]

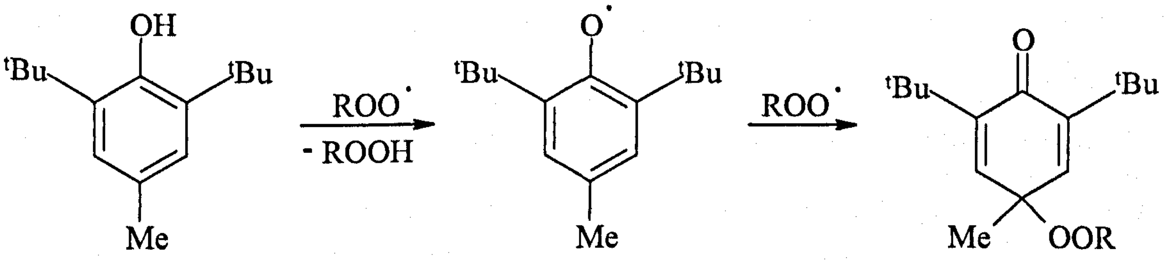
1.2.4 Corrosion inhibitors.[8]

Corrosion of metal surfaces in the engine is due largely to reaction of acids with the metal oxide surface. These acids originate either from incomplete fuel combustion and blow-by of the resultant gases or by oxidation of the lubricant oil. Corrosion inhibitors, typically zinc dithiophosphates (**1.1**) and dodecenylsuccinic esters or imides, are preferentially absorbed onto the metal surface to provide a protective film. They are also effective at disrupting electrochemical processes such as rust formation.

1.2.5 Anti-oxidants.

Oxidation inhibitors are added to the lubricant to prevent degradation of the oil occurring through oxidation by air. There are two types of inhibitor; phenols and zinc dithiophosphates. These differ in their modes of action. Phenols act as inhibitors by breaking the free radical chain process through reaction with radicals. As shown in scheme 1.1, each phenol molecule is able to quench two radicals, the first radical abstracts a hydrogen atom from the phenol forming a stable phenoxy radical then an additional peroxy radical is scavenged to form a cyclohexadienone peroxide.[10]

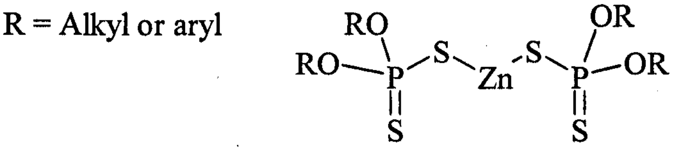
Scheme 1.1: Action of phenolic inhibitors.



2,6-di-*t*-butyl-4-methyl phenol

The efficiency of the radical scavenger has been shown to increase when the ortho and para positions possess alkyl substituents, especially when the ortho substituents are bulky *t*-butyl groups.

The second class of anti-oxidants, zinc dithiophosphates (ZDDP, general formula **1.1**), are able to destroy peroxides. As mentioned earlier, ZDDPs are also anti-wear additives and corrosion inhibitors, which makes them of great commercial importance. Alkyl derivatives make good anti-wear additives, whilst aryl derivatives have higher thermal stability.[6]

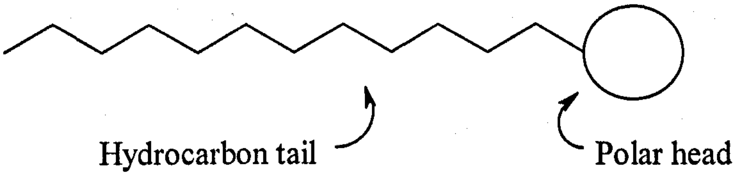


1.1

1.3 Detergents and dispersants.[11]

Detergents and dispersants are typical surfactants. Both contain a hydrophobic end (hydrocarbon chain) and a hydrophilic end (anionic, cationic or neutral). The hydrocarbon portion of the molecule is hydrophobic and soluble in the nonpolar oil, while the ionic end is hydrophilic and potentially water soluble.

Figure 1.2: Stylised detergent molecule.



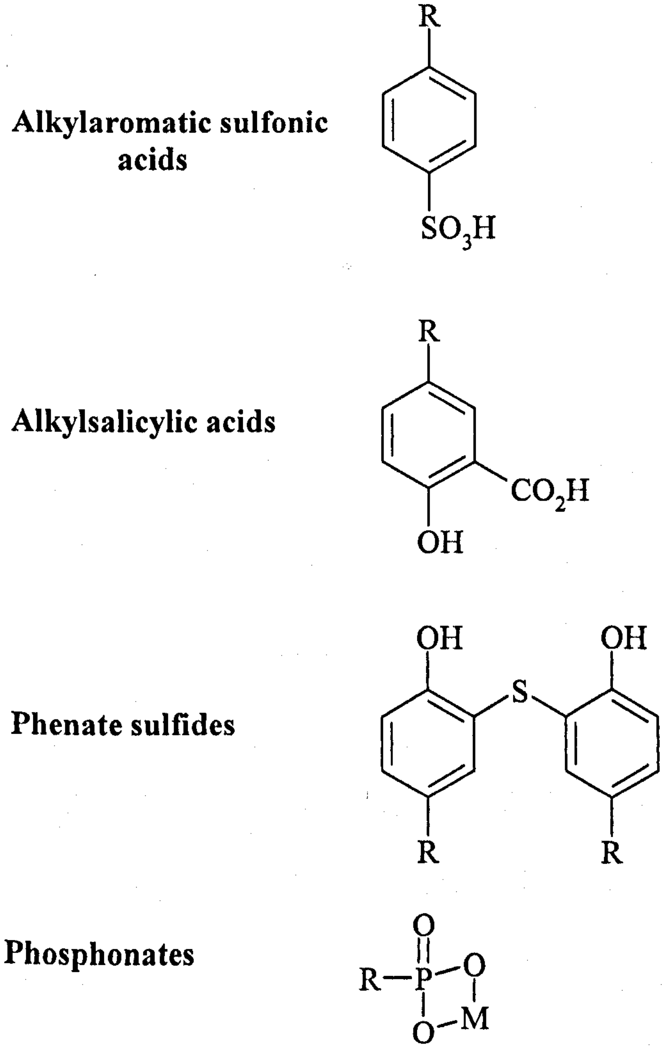
A detergent molecule (figure 1.2), such as sodium stearate, contains a long hydrocarbon chain and an ionic carboxylate group. The polar end of the soap molecule is not soluble in the base fluid. Instead detergents, in oil, form micelle clusters of 50-100 molecules with their hydrophilic heads grouped together and the hydrophobic hydrocarbon tails acting as a solubilizer.

Using detergents and dispersants in the lubricant package is essential to the prevention of harmful carbon and sludge deposits, which is why they make up the majority of additives in a lubricant package. Both additive types keep insoluble combustion debris and oil oxidation products dispersed in the oil. These deposits lead to poor oil flow and eventually could result in engine seizure. The polar end of the surfactant molecule dissolves in contaminants, such as sludge and water, whilst the long hydrocarbon tail keeps the micelle suspended in the oil and stops sludge coalescing.

1.3.1 Detergents.

Dispersants are metal salts but those of three metals, Ca, Mg and Na, are most commonly used. Detergents serve to protect the engine from acids (sulfur and nitrogen based) produced from fuel combustion products. The detergent thus neutralizes the corrosive acids leading to wear. There are four major types of detergents, those based on; sulfonic acids, phenates, salicylates and phosphonates (figure 1.3). Oil solubility is provided by an alkyl group (R), which is generally at least eight carbons long.[11]

Figure 1.3: The four classes of surfactants that are used as detergents.



Sulfonic acids are the most widely used and subsequently this discussion focuses on these. They can be produced from mineral (natural) or synthetic base stocks and the acid is formed by treating a benzene derivative with sulfur trioxide (SO_3) and sulfuric acid respectively.[11] Formation of neutral sulfonates is accomplished by reacting the sulfonic acid with either a divalent metal oxide or hydroxide (scheme 1.2a).

Sulfonate additives which contain metal in excess of the stoichiometric amount required to produce a neutral sulfonate are called overbased detergents *i.e.* basic sulfonates. Because they contain far more metal ions than neutral sulfonates, overbased soaps have a greater ability to neutralize acids. Overbased sulfonates can be produced from the reaction of a neutral sulfonate with a metallic base (scheme 1.2b). However, this is a complex reaction that takes place in the presence of carbon dioxide and a promoter. The overbased detergent, effectively, contains an excess of metal carbonate.

Scheme 1.2: Neutralization and overbasing of sulfonic acid.

a)

$$\underset{\textbf{Sulfonic acid}}{RSO_3H} + \underset{\textbf{Metal oxide or hydroxide}}{MO \text{ or } MOH} \longrightarrow \underset{\textbf{Neutral sulfonate}}{RSO_3M} + H_2O$$

b)

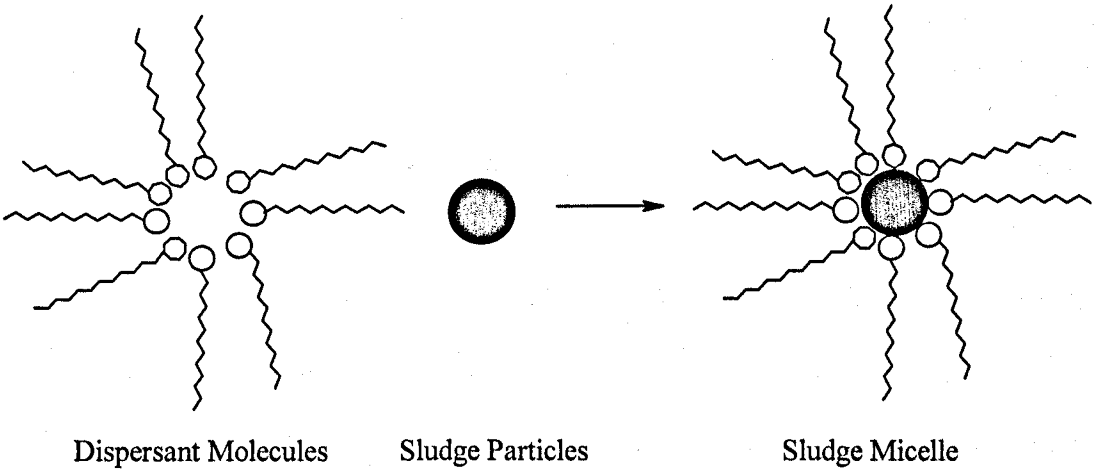
$$\underset{\textbf{Neutral sulfonate}}{RSO_3M} + \underset{\textbf{Metal hydroxide}}{MOH} \xrightarrow[CO_2]{\text{Promoter}} \underset{\textbf{Overbased sulfonate}}{RSO_3M\text{-}xMCO_3} + H_2O$$

1.3.2 Dispersants.

The detergents, described in the previous section (section 1.3.1), undergo chemical reaction with sludge and varnish precursors to neutralize them and keep them soluble. However, their detergency is only effective at high engine temperature. Modern passenger vehicles are more frequently designed, and used, for low-temperature, short-distance or stop-and-go driving which leads to severe oil oxidation and ultimately high levels of insoluble particles in the oil. Stop-and-go driving results in engine temperatures too low to vaporise water contamination from the oil.[11] The condensed water mixed in with the oil promotes increased sludge formation. Dispersants are much more effective than detergents in controlling sludge and 'varnish' deposits that result from low-temperature operation.

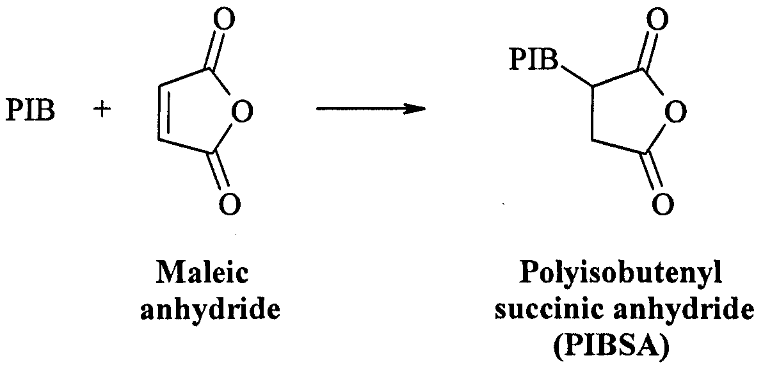
Dispersants are very similar in structure to detergents in that they contain a oil solubilizing hydrocarbon tail and a polar head (figure 1.2). The polarity of dispersants is derived from the inclusion of oxygen and/or nitrogen atoms in the molecule. As shown in figure 1.4 potentially harmful deposits are prevented from agglomerating and are kept suspended in solution by formation of a sludge miscelle. A brief overview, only, of the additives of interest to the work described in the thesis is given.

Figure 1.4: Suspension of harmful sludge debris in the oil.



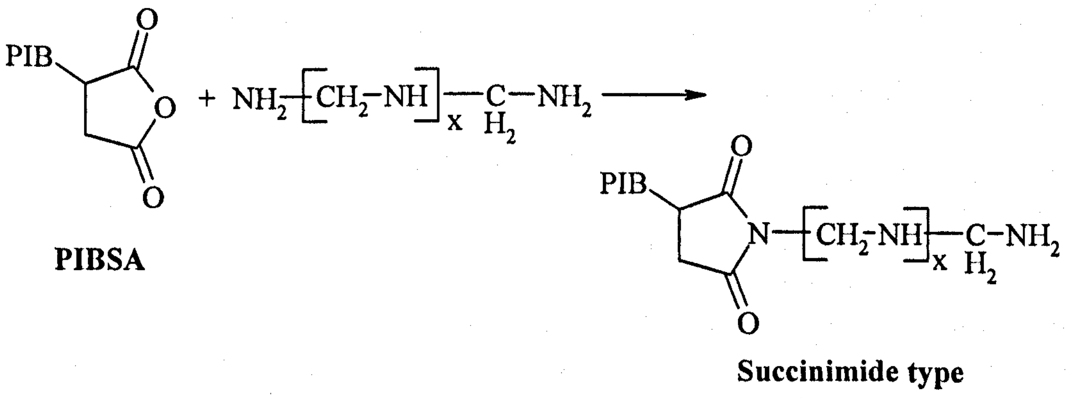
Commercially there are four distinct types of dispersants: alkylsuccinate esters, alkylsuccinimides, alkylamines and Mannich bases.[6] The solubilizing chain of these dispersants are of greater length than those in detergents (*e.g.* polyisobutylenes (PIB) of 1000 to 10, 000 molecular weight). Alkenyl succinimides are currently the most favoured.[11] Succinimides and succinic esters are both made from a common chemical intermediate, polyisobutenyl succinic anhydride (PIBSA). This alkenyl anhydride intermediate is produced by condensing polyisobutene with maleic anhydride in an 'ene' reaction (scheme 1.3), as will be described in more detail later in the thesis.

Scheme 1.3: Preparation of the PIBSA additive.



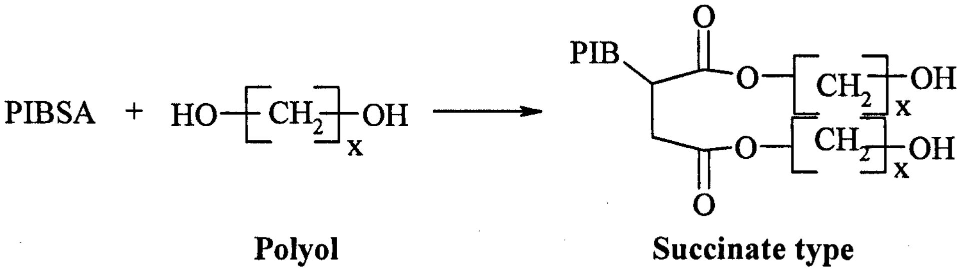
As shown in scheme 1.4 the succinimide additive is formed by reacting the PIBSA intermediate with polyamines to form *N*-amino alkylpolyamines. The most popular procedures include - dehydrative condensation of an anhydride and an amine at high temperature[12] and cyclization of amic acid intermediate in the presence of acidic reagents.[13] The basicity of the additive depends on the number of free nitrogens, thus polyamines are usually preferred as reagents. Pre-selection of the molar ratio of amine to succinic anhydride groups results in control over nitrogen content thus at 1 molar ratio the polyamine substitutes one succinic anhydride while at 0.5 molar ratios a disuccinimide is formed.

Scheme 1.4: Succinimide formation.



High molecular weight esters are produced by ring opening and esterification of the succinic acid group present in PIBSA (scheme 1.5).[6] Esterification is carried out with either mono or polyaliphatic alcohols, the hydrocarbon component contains at least 50 carbons.

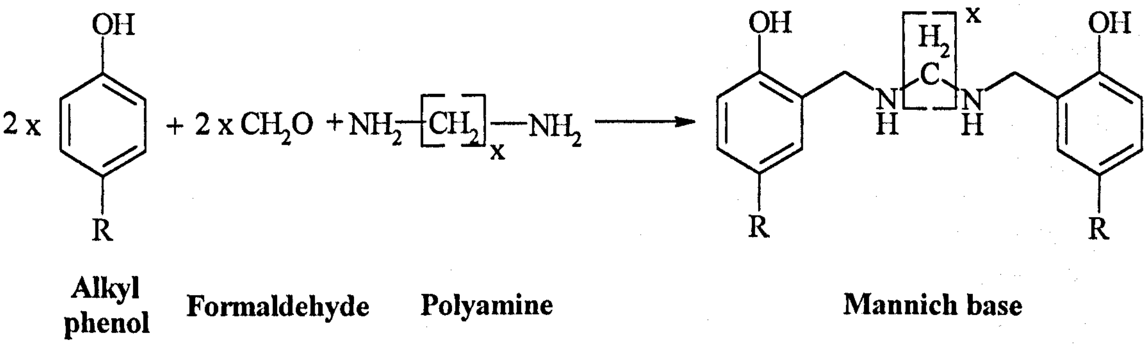
Scheme 1.5: Simple representation of the succinate type additive.



An alternative to the functionalisation of PIB by the thermal ene reaction is the addition of halogens. Production of surfactant amines is achieved chiefly by reacting PIB with chlorine, the polar group needed for additives being introduced by nucleophilic substitution with amines. This reaction is discussed in more detail in section 1.6 and Chapter 2.

The fourth type of additive used results from the Mannich reaction. The Mannich base is produced from the reaction of a high molecular weight monosubstituted phenol with a substituted aminomethyl group formed through the reaction of formaldehyde with a primary or secondary amine. Polyamines react further as shown in scheme 1.6.

Scheme 1.6: Formation of Mannich type dispersants.



Engine oil formulations may contain more than one dispersant to provide optimum performance, at both high and low temperatures.[14] The high molecular weight of many dispersants along with their surfactant ability means they also act as viscosity modifiers. They have high thermal stability and burn without leaving deposits.

1.4 Polyisobutene.

Polybutenes are usually produced from isobutylene monomers and therefore are often referred to as polyisobutenes (PIBs). As mentioned previously PIBs of various molecular weights (1000 up to 10, 000) are used due to their ability to break down without leaving deposits, those over mw 10, 000 are usually employed as VI improvers because of their high shear stability. Unfortunately, the application of PIB as a base oil is limited since it depolymerises and oxidizes on heating, but a favourable characteristic of PIB is that, being a hydrocarbon, it is compatible with mineral oils.

Generally, polybutenes are produced by polymerizing a mixed C_4 stream from a catalytic cracking process.[15] Typical feedstock is a butane-butene mixture containing both n-butene and isobutylene. The polymerisation process is cationic ($AlCl_3/HCl$ or $BF_3/MeOH$ are used as catalysts) and isobutene is selectively polymerised in the presence of the other C_4 compounds. Polymerisation produces PIBs of varying structures and reactivity, which are classed from the major end-group they contain. The reactivity of the double bond depends on its position in the polyisobutene chain. The highest reactivity is obtained for α-olefin where the double bond is situated at the end of the chain. Thus, Ultravis is a highly desirable oil which contains mostly type A and B structures, whilst Hyvis is less reactive containing type C end-groups although the other structures are present to a lesser degree (figure 1.5).

1.5. Model systems.

In the investigations to be described in this thesis, to overcome the problems caused by long chain olefins, which contain a mixture of alkenes, various model alkenes have been used which contain a much shorter hydrocarbon chain (figure 1.5). These model alkenes have end-group functionalities which mimic the reactivity of Ultravis and Hyvis. Another advantage to using pure model alkenes is that the reactivity at one type of alkene end-group can be examined separately.

Figure 1.5: Model alkenes.

Type A: Ultravis

Type B: Ultravis

Model: 2,4,4-trimethyl-1-pentene (TMP-1)

2,4,4-trimethyl-2-pentene (TMP-2)

Type C: Hyvis

Type D:

Cis and trans 3-methyl-2-pentene

No model used, only trace amounts in PIB.

These studies have been supplemented by the use of linear chain alkenes, 1-octene and 1-decene. The model alkenes are simpler to use and much more volatile than PIB, enabling the products of reactions to be identified by GC/MS. One drawback is that high temperature reactions on model alkenes have to be carried out in an autoclave because of their volatility.

1.6 Reaction of electrophiles with alkenes.

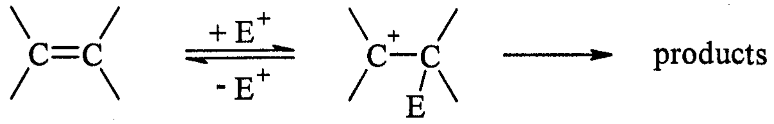
It has been mentioned that an alternative to the 'ene' reaction is the electrophilic addition of chlorine to an alkene followed by displacement of chloride by an amine. This section gives a brief overview of the literature covering the reaction of electrophiles, especially halogens, with alkenes.

Unsaturated compounds, such as alkenes, contain high electron density around their γ-bond. Typical reactions of alkenes, which involve addition of electrophilic reagents to their carbon-carbon double bond, have been widely studied.[16] One of the commonest and most extensively examined transformation of alkenes is halogenation - for reviews see Fahey (1968),[17] House (1972),[18] De la Mare (1976),[19] Schmid (1989),[20] particularly bromination - Ruasse (1993).[21]

1.6.1 Reaction sequence; intermediate formation.

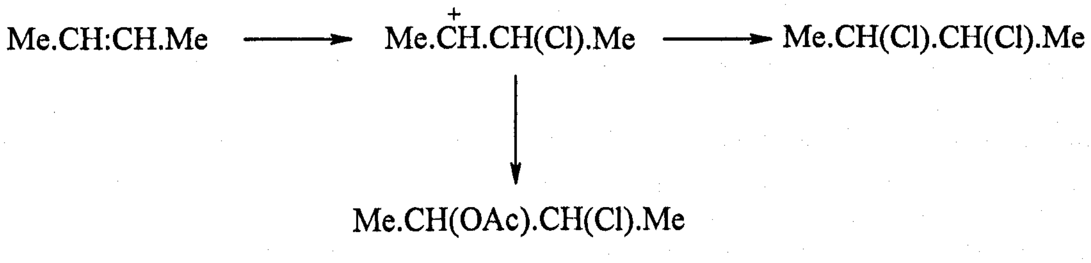
It has long been accepted that electrophilic addition of a halogen to unsaturated compounds takes place by attack of the polarized halogen molecule on the alkene double bond in a first step followed by attack of a nucleophile, the halide ion or another nucleophilic additive, on the intermediate (scheme 1.7).

Scheme 1.7: General scheme for addition to alkenes

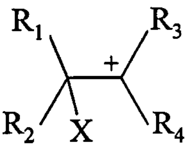


The development of positive charge in the intermediate has been inferred in part from the effect of solvent polarity, but especially from the incorporation of an added nucleophiles in the product.[19] Thus the reaction of chlorine with 2-butene in acetic acid gives not only the 1,2-dichloro adduct but also a co-product involving the intervention of the nucleophilic solvent (scheme 1.8).[22]

Scheme 1.8: Chlorination of 2-butene in acetic acid.



Similarly the addition of bromine to ethylene in aqueous NaCl solution yields, besides the dihalide adduct and bromohydrin, 1-bromo-2-chloroethane.[23] Some 60 years ago Bartlett and Tarbell suggested that the first step in the addition of halogens to alkenic compounds involves the formation of a carbocation ion and a negatively charged halide ion.[24] Whilst this may be the case in some systems, the formation of a freely rotating positively charged structure (**1.2**),[25] postulated for many years to be the reaction intermediate,[26] is inconsistent with the stereospecificity found in the product forming step unless addition to the carbocation ion is faster than a change in configuration of this intermediate.[27] This hypothesis is unlikely, therefore. Another explanation for the preference for *trans*-addition of halogens to unsaturated substrates is required.



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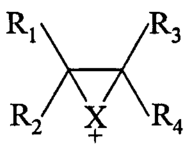

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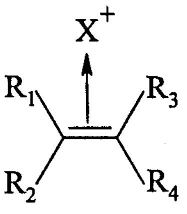
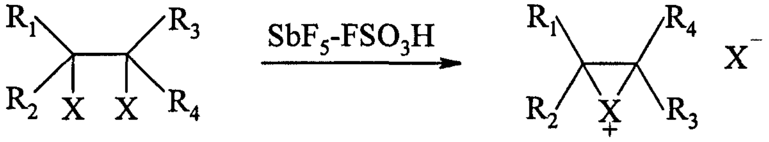


1.4

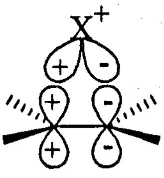
The formation of halonium ions as intermediates in the addition of halogens to alkenes was first proposed by Roberts and Kimball.[28] Halonium ions (**1.3**) are generally depicted as three-membered rings with the positive charge on the halogen atom; free rotation about the carbon-carbon bond in the intermediate structure is prevented by formation of a covalent σ-bond between the halogen atom and the carbon atom.[28] The positive halogen atom is isoelectronic with the group 16 elements, therefore halonium ions should show similarities to the analogous epoxides. Thus the second step, attack of the halide ion on the three-membered intermediate, is similar to the S_N2 ring-opening of epoxides in that the nucleophile approaches one of the carbon atoms from the side opposite to the "leaving group", here X^+. This always results in the product being formed by exclusive *trans*-addition onto the olefin.

Direct evidence for the existence of halonium ion intermediates has come from the isolation of stable chlorine,[29] bromine[30] and iodine[31] halonium ion salts with adamantylideneadamantane. The halonium ion is stable in the adamantylideneadamantane system because collapse of the σ-complex by nucleophilic attack of the counter ion from the backside is prevented due to steric hindrance in the substrate. In the cases of the bromonium and iodonium ion salts crystal structures are available.[31, 32] Further substantiation comes from extensive low-temperature NMR studies of halonium ions in highly acidic conditions by Olah and various co-workers.[33, 34] Stable halonium ions were prepared from the corresponding dihaloalkane precursors in magic acid (SbF_5-FSO_3H) at – 60 °C as illustrated in scheme 1.9. Simple alkyl substituted halonium ions have been prepared by this method and NMR studies show these to be symmetrical or slightly asymmetrical three-membered rings dependent on the bridging ion and substitution of the carbon atoms.[35] The bromine and iodine ethylene derivatives give symmetrical halonium ions, which are observed in the ^{1}H NMR spectrum as singlets at 5.53 and 5.77 p.p.m. respectively. However, it is arguable that because of the unusual conditions used in these experiments these observations have little meaning for halogenation carried out under more normal conditions.

Scheme 1.9: Formation of halonium ion from dihaloalkanes.



An alternative view, suggested by Dewar, is that the intermediate can be represented as a π-complex (**1.4**) which is essentially equivalent to the halonium ion structure (**1.3**).[36] In π-complexes a dative bond interaction is formed between the filled π-orbital of the alkene with the empty valence orbital of the acceptor X^+. The structure and function of π-complexes as potential reaction intermediates during the addition to unsaturated systems has been reviewed by Banthorpe.[37] The main difference between **1.3** and **1.4** lies in the hybridisation of the carbon atom, **1.4** retains the sp^2 hybridised carbon-carbon double bond and the substituents on the alkene remain co-planar. If the electrophile (X) has π-electrons, or unshared p- or d-electrons as is the case for Br^+ and I^+, feedback into the anti-bonding orbital of the carbon atoms will result in direct bonding to the carbons in the π-complex (**1.5**). Overall, this 'back-donation' from the d_{xy} orbital (or other $d_{Y\text{-}p}$ hybrid orbitals) will stabilize the intermediate as shown by **1.6**.



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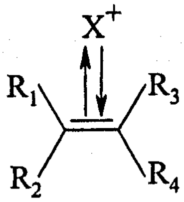


1.6

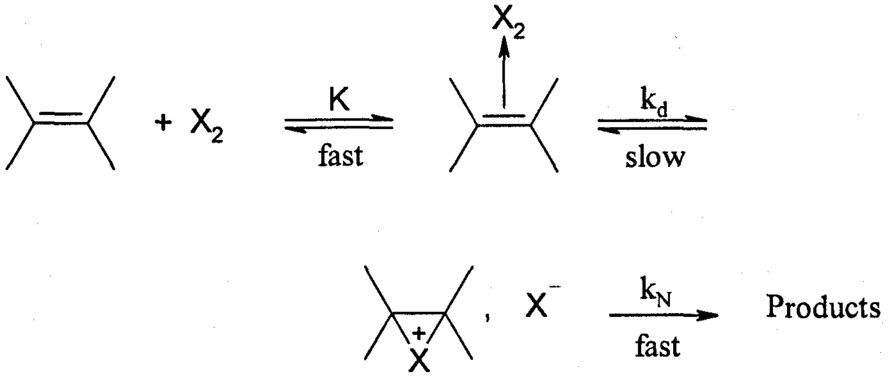
In agreement with Dewar's proposal the characteristic charge-transfer bands seen in the spectra of olefin:halogen mixtures are indicative of weakly bonded donor-acceptor complexes *e.g.* halogen adducts π-d overlap rather than π-p, which provide very little stabilisation.[37, 38] According to theoretical calculations by Cossi[39] and co-workers the π-complex of ethene and bromine is about 3 to 4 kcal mol^{-1} more stable than the starting materials, however the main contribution to the stabilisation is due to dispersion energy rather than charge-transfer (Van der Waals forces).[40]

White and Robertson showed that the addition of chlorine to olefinic compounds is bimolecular, while Br_2, I_2, ICl and IBr add termolecularly.[41] However, the homolytic pathways are possible and can be competitive, especially for chlorine in direct sunlight.[42] What is evident is that electrophilic halogenations are highly solvent-dependent reactions, involving large separation of charge in the activation step.[43] It is now generally excepted that the reversible formation of a 1:1 olefin-halogen charge-transfer complex (CTC) is involved during the halogenation of alkenes prior to the rate-determining step *i.e.* formation of the halonium ion intermediate.[44, 45] Furthermore, CTCs have been observed using UV-Vis detectors and stopped-flow apparatus on the reaction pathway during the electrophilic additions of chlorine,[46] bromine[47] and iodine monochloride[48] (ICl) to alkenes.

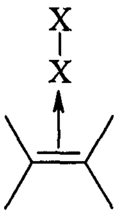
Electrophilic addition of the halogens, especially fluorine (explosive with alkenes), chlorine and bromine, to ethylenic compounds occur very rapidly. This means that reliable kinetic data for their addition to unsaturated compounds has only become available in the last 30 years, since the invention of spectrophotometric or electrochemical methods. Spectrokinetic methods, such as "stopped-flow" which follow the disappearance of the halogens absorption band with UV-Vis detectors, are highly sensitive at low reagents concentrations and have given great insight into the mechanism of the reaction of halogens with olefins, especially bromination.[45, 49] In halogenated solvents, using stopped-flow equipment, the highest bromination rate constants available are in the order of 10^5 M^{-1} s^{-1} whereas the limit for obtaining reliable bromination rate constants from titration techniques is 10^1 M^{-1} s^{-1}.[21]

Initial interaction between the polarised halogen molecule and the alkene π-system occurs via the back lobe of the anti-bonding orbital of bromine and leads to a three-centred bound π-complex (scheme 1.10).[50] Unimolecular, S_N1-like, dissociation of the CTC in the rate-determining step leads to the formation of a halonium-halide (polyhalide) ion-pair intermediate (σ-complex). This intermediate undergoes a fast nucleophilic ring-opening resulting in the products.

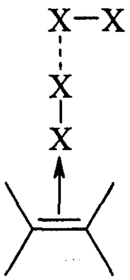
Scheme 1.10: General mechanism for the halogenation of olefins.



The second order dependence of the reaction kinetics on $[X_2]$ has led to a belief that molecular complexes involving 1:2 molar ratios of the alkene and the halogen occur along the reaction coordinate between the 1:1 complex and the ionic intermediate. In fact Schmid and Gordon have proposed that 1:1 and 2:1 ICl-alkene molecular complexes are involved in a pre-rate-determining step during the addition of ICl to 2,3-dimethyl-2-butene.[51] This has recently been reinforced by observation of a 2:1 bromine-olefin complex for a highly hindered olefin, tetraneopentylethene (TNPE), using UV-spectrophotometric techniques.[52] The 1:1 complex has a "T-type" structure (**1.7**),[53] the second bromine molecule in the 2:1 complex is thought to be perpendicular to the first bromine molecule, hinged centrally along the Br_2-olefin axis (**1.8**).[52] Formation of the bromonium-tribromide ion pair is favoured over formation of the bromonium-bromide ion pair because the second bromine molecule aids charge separation.



1.7



1.8

1.6.1.1 Addition of bromine to alkenes.

The ionic addition of bromine to alkenes has been extensively studied and shown to be a kinetically rather complicated reaction.[21] The rate equation contains terms for the contribution of bromide ions, bromine and tribromide ions (equation 1).

$$-d[Br_2]/dt = k_2[Br_2][\text{olefin}] + k_3[Br_2]^2[\text{Olefin}] + k_3'[Br_3^-][\text{Olefin}] \qquad \textbf{(1)}$$

Thus, in order to make kinetic studies feasible, low concentrations of bromine have to be used, e.g. in acetic acid 10^{-3} mol dm^{-3} is the highest that can be used to obtain a workable kinetic equation.[21] The rate-determining step for bromine addition appears to be the formation of a σ-complex. Competitive bromination rate studies carried out in polar[54] and less polar[50] solvents systems (table 1.2) show a large order of difference in magnitude for the former and a relatively small change in the latter.

Table 1.2: Relative rates of bromine addition to selected olefins compared to ethene.

Alkene	**Br_2 in $CF_2ClCFCl_2$** k_{rel}[a]	**Br_2 in MeOH** k_{rel}[b]
Ethene	1.0	1.0
1-Butene	20	96
cis-2-Pentene	881	4160
cis-3-Methyl-2-pentene	1030	118, 800
2,3-Dimethyl-2-butene	5680	924, 000

a : Data from reference 50.

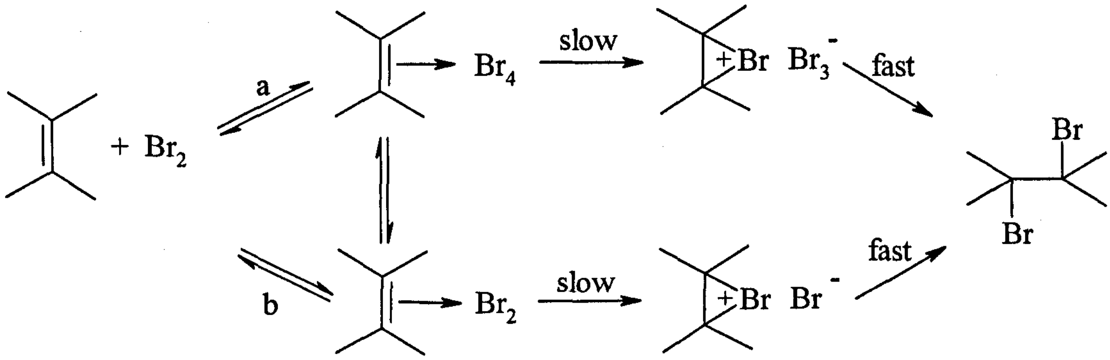
b : Data from reference 54.

The data in table 1.2 show that solvent effects are very important in the addition of bromine to unsaturated compounds. However, the main difference between halogenation in the two solvents concerns the kinetic rate law. The breaking of the bromine-bromine bond in the CTC complex resulting in the three-centred two-electron intermediate is assisted by the second bromine molecule. This can be seen in the change in the kinetic rate law on moving from a protic to non-protic solvent. In protic solvents the reaction is first order in bromine, while in the non-protic media such as halogenated solvents a second bromine is need to aid the dissociation of the CTC and the reaction is second order in the halogen.

Rearrangement of the CTC is accompanied by negligible charge development in the transition state, thus formation of the bromonium-tribromide ion pair is relatively insensitive to substituent and solvent effects.[55] It can be seen from the data in table 1.2 that in a low polarity halogenated solvent the increase in reaction rate is smaller than for polar solvents, suggesting that the degree of charge development in low-polarity solvents is smaller. Therefore, the transition state is early on the reaction coordinate, resembling the CTC (π-complex type) and there is a relatively small demand for electronic stabilisation from substituents. For polar solvents the transition state is late on the reaction coordinate (σ-complex type) and charge separation is stabilised by interaction with the solvent.

In non-polar solvents the reaction follows an Ad_EC1 mechanism, the dissociation of the olefin-bromine charge-transfer complex (CTC) is assisted by a second bromine (scheme 1.11a).[56] The main driving force for the ionization of the 1:2 olefin-bromine complex is the formation of the bromonium-bromocarbenium tribromide ion pair intermediate, which then collapses to dibromide and molecular bromine.[57] One explanation of this step involves attack of a bromide ion on the three-centred σ-complex intermediate, overall there is very little charge development on the unsaturated carbons. Various authors have suggested that the formation of halonium ions is energetically unfavourable in solvents of low polarity and that the reaction is catalysed by traces of polar materials, such as water or HBr.[26]

Scheme 1.11: Two possible mechanistic pathways for the electrophilic bromination of alkenes.



In stark contrast in polar solvents, such as water, methanol and acetic acid, the transition state is late and resembles a σ-complex (scheme 1.11b). In methanol the pronounced effect of the +I electronic alkyl substituents on the rate of addition is seen in table 1.2. Electrophilic bromination takes place by an analogous mechanism to that shown in figure 1.10, but dissociation of the CTC is aided by solvation of the leaving bromide ion (or the carbon atom that has the most positive charge located on it).[58] Solvation is the driving force for the reaction as it lowers the energy of the transition state and thus increases the reaction rate of electrophilic bromination in methanol compared to nonhydroxylic solvents.[53] Furthermore, Modro and co-workers have studied the effect of olefin structure on the rate of the bromine addition in hydroxylic and non-hydroxylic solvents.[59] In non-hydroxylic solvents the positive charge is relatively localised in the transition state, thus the reaction rate is more sensitive to electron-releasing substituents on the double bond. Whereas for hydroxylic solvents structural effects on the reaction rates are approximately constant. At higher bromine concentrations the reaction again becomes second order in bromine and the mechanism in scheme 1.11a is followed.[60]

1.6.1.2 Addition of chlorine to alkenes.

Both homolytic and heterolytic pathways are present during the liquid-phase chlorination of alkenes in non-polar solvents, however the ionic mechanism is predominant for alkenes in dilute solutions in the presence of oxygen.[42, 61, 62] A small negative activation energy for the chlorination of alkenes in non-polar solvents has been taken as evidence for the formation of the donor-acceptor complex on the reaction pathway.[20] Similar solvent effects have been found to those seen in the bromination reactions, the reaction rate is greater in polar solvents such as acetic acid than non-polar solvents like CCl_4. This is consistent with a mechanism in which charge development occurs in the rate-determining step and the transition state resembles a π-complex (**1.7**), rather than σ-complex (**1.3**). In non-polar solvents the solvent separation of the chloronium-chloride ion-pair is inhibited, therefore it is assumed that the product forming steps occur from a tight ion-pair, rather than a stabilised polyhalide ion as in the case of bromine[57] and interhalogens.[51]

Comparative studies on the rate of chlorination of alkyl substituted alkenes shows that the rate increases equally through additive kinetic substituent effects and correlates with the Taft equation.[62] This lends further support for a the bridged transition state, where positive charge is balanced between the two olefinic carbons.

1.6.1.3 Addition of iodine electrophiles to alkenes. The reaction of iodine with alkenes differs from that of other halogens in that it is readily reversible. Bythell and Robertson isolated the forward reaction by using excess olefin and found that the reaction is second order in iodine.[63] However, the non-reversible addition of electrophilic iodine to unsaturated substrates can be achieved using reagents such as IF,[64] ICl,[65, 66] IBr,[41] IN_3,[67, 68] or ICN,[69] ring-opening of the iodonium ion intermediate is regio- and stereospecific.

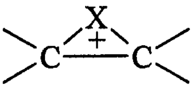
White and Robertson reported that the addition of ICl to allyl acetate in acetic acid follows an overall third-order rate law, first order in olefin and second order in ICl.[41] Similar rate law has been reported for the addition of ICl to some allyl and vinyl compounds in acetic acid.[70] This suggests that addition of ICl is an ionic process proceeding by a similar mechanistic pathway to bromination (scheme 1.11a), but the complex anion in this case would be ICl_2^-. Again the rate-determining step involves the disappearance of the charge transfer complex. From the complex rate law for the addition of ICl to various alkenes in CCl_4 the formation constant for the ICl-alkene complex was determined. Other interhalogens, BrCl and IBr additions are also found kinetically to be third order, but the dissociation of these compounds complicates measurement of rate constants.[60]

1.6.2 Reaction sequence: bridged bromonium ion or open β-carbocation.

In limiting cases the three-centred addition of the halogen can give way to a two-centre process. There is general agreement about the participation of ionic intermediates on the halogenation reaction pathway, but acceptance of the fully bridged ion is not general and the magnitude of charge born by the β-carbon is dependent on the substitution pattern of the double bond. Olah and co-workers have shown that the extent to which the halogen participates in the stabilisation of the positive charge at the β-carbon depends on the electronic needs of the carbon.[33-35] Stable halonium ions were prepared from the corresponding dihaloalkane precursor in magic acid (scheme 1.9). In their admittedly abnormal system, the dependence of the chemical shifts (from ^{1}H and ^{13}C NMR) of the three-membered ring carbon atoms on the number of methyl substitutents was discussed in terms of an open β-bromocarbocation or bridged halonium ion. Such experiments suggest the 2,2-dimethylethylenechloronium ion exists as the β-halocarbenium ion, whereas the corresponding bromine and iodine derivatives, which can accommodate the positive charge on the halogen atom more easily, form fully bridged ions.

Dubois and Chretien discussed the nucleophilic ring-opening of alkyl substituted ethylenebromonium ions in terms of charge distribution in the ionic intermediate.[71] The regio- and stereoselectivity in the product forming step was determined for various alkyl substituted bromonium ions in methanol. Their results showed that whilst ring-opening of dissymmetrical bromonium ions was regiospecific the corresponding symmetrical halonium ions gave non-regiospecific addition, but was stereospecific. Numerous examples of this type can be found in the literature *i.e.* ionic addition of BrCl to 1-hexene in CCl_4 results in a significant amount (40%) of the anti-Markovnikov (AM) addition product.[72] Such observations have been interpreted as development of carbocation character at the C_α carbon in dissymmetrically substituted systems and formation of bridged halonium ions in more symmetrical ones. Steric factors can also influence the regioselectivity of interhalogen addition to alkyl substituted alkenes.[73] In Chapter 2 the addition of molecular halogens such as chlorine, bromine and iodine to the model alkenes have been carried out in halogenated solvents, therefore regio- and chemoselectivity cannot be determined directly. However, addition of dissymmetric halogens, such as ICl and IBr, to the model alkenes gives products for which the regioselectivity can be determined. These results can be discussed in terms of the structure of the intermediate.

The well documented *trans*-stereospecific addition of halogens suggests that there is some neighbouring group interaction in the ionic intermediate to inhibit free rotation around the C-C bond.[28] This stereospecificity can be accounted for by a bridged halonium ion intermediate which is either symmetrical (**1.9**) or unsymmetrical (**1.10**). The dotted line indicates an electrostatic interaction that is strong enough to prevent rotation and ultimately formation of the *cis*-isomer.



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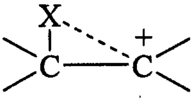
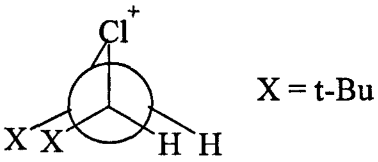


1.10

When X is chlorine the balance between the stabilisation energies of the carbenium ion and the halonium ion are close and the introduction of a single electron donating group can push the balance in favour of the open ion structure.[74] Studies of product stereochemistry indicate that phenyl groups lead to open benzyl-type cation intermediate,[75] whereas alkyl substitution results in bridged halonium ion intermediates.[22] In contrast Poutsma found that the chlorination of neat cyclohexene,[42] *cis*- or *trans*-butene[61] under an oxygen atmosphere is stereospecific implying the chloronium ion is an intermediate. Overall, formation of halonium ions depends on the capacity of the halogen atom to bear positive charge, chlorine is reluctant to expand its shell and it forms halide anions more easily than bromine or iodine.[26] However, there are exceptions as shown by the chlorination of *cis*-di-t-butylethylene in CCl_4. This reaction proceeds exclusively *trans*-selectively through the highly disfavoured symmetrical chloronium ion intermediate (**1.11**), rather than the open carbocation which is less sterically strained but would result in a rearranged product.[76]



1.11

As discussed above, the majority of work carried out into the understanding of the electrophilic halogenation of olefins is based around bromine. However, the stereospecificity of halogen addition to alkenes is also dependent on the electrophile.[77] Fahey and Schneider found that the stereoselectivity decreases with increasing solvent polarity, electron-donating substituents on the double bond and a decrease in the bridging power of the electrophile ($I^+ > Br^+ > Cl^+ > F^+$).[75] This they attributed to the formation of open-carbocation or non-symmetrical bridged halonium ion intermediates. Thus Herges and Neumann reported that the addition of iodine, which is the best halogen bridging atom, to tetradehydrodianthracene (TDDA) in all solvents is exclusively *trans*. The structure of the intermediate in the case of bromine or chlorine, with low to middle of the range bridging ability, are dependent on the solvent polarity and olefin structure.

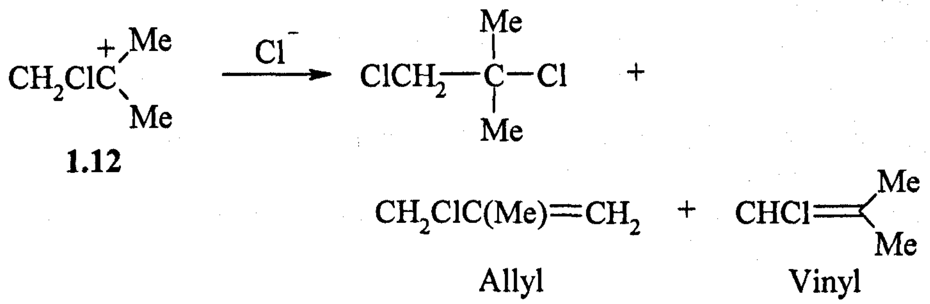
1.6.3 Product forming step: substitution versus addition.

Generally, chlorine and bromine react rapidly with unsaturated materials, *i.e.* exothermically, and side reactions including skeletal rearrangements[78, 79] are not infrequent, depending upon the electrophile and the structure of the olefin. Side-reactions are especially important in electrophilic addition to alkenes which contain α-methylenic end-groups. In chlorination reactions substitution at the ethylenic carbons can be more important than the addition reaction even under conditions which favour heterolytic reactions[80] and where the addition product is known to be stable *i.e.* an addition-elimination sequence is not responsible for substitution.[81]

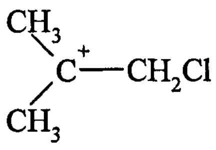
Molecular rearrangements occur during chlorine or bromine addition to alkyl substituted alkenes (2-ethyl-1-hexene),[81] aryl substituted alkenes (1-phenylpropenes)[22] and sterically hindered alkenes such as 1,2,3-tri-t-butyl butadiene,[82] t-butylethylene.[62] Rearrangements in halogenation reactions have been taken as evidence for carbocation character in the intermediate. Presumably, cation-stabilising substituents on the double bond lead to distorted or even non-bridged cations. In general, rearrangements during halogenations are enhanced by polar solvents, the presence of electron-donating substituents, such as phenyl or t-alkyl groups, and by the presence of certain neighbouring groups which favour rearrangement.

One of the first examples of this type was observed in the gaseous chlorination of isobutylene.[83] Isobutylene reacts with 'Cl^+' to form a carbenium ion (**1.12**) which can then decompose as shown in scheme 1.12. The expected dihalide adduct is formed as a minor product, constituting 6% of the reaction mixture, the majority of the reaction mixture is made-up of allyl chloride (87%), with trace amounts of vinyl chloride (3%).[83] The reaction mixture also contains other minor products including a hydrogen halide adduct (1%) and a variety of trichloride components (1%). The ratio of allyl to vinyl chloride products changes little with varying reaction conditions. Later, radioactive labeling experiments confirmed that the position of the substituted chlorine atom in allyl chloride is the original unsaturated carbon atom in the alkene and that it is the double bond that shifts to form the product.[84] As can be seen from the above allyl:vinyl chloride ratios the elimination of a proton from the β-chloro-substituted carbenium ion (**1.12**) occurs preferentially from a methyl group rather than the chloromethyl group.

Scheme 1.12: Substitution and addition products formed during the ionic chlorination of isobutylene.



Several theories have been put forward to explain the preference for substitution with rearrangement in highly substituted systems. Firstly, Taft[79] proposed that the ionic intermediate is a carbocation ion (**1.13**) where there is no neighbouring group interaction between the chlorine and the carbocation. Correlation was made between the number of α-hydrogens adjacent to the carbonium ion and the addition:substitution ratio obtained. The preference for the allylic chloride over vinylic chloride formation is attributed to the inductive effect of the chlorine and the 3:1 ratio of hydrogens in the respective groups.



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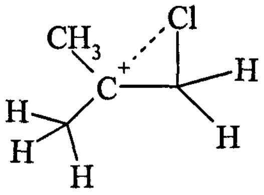
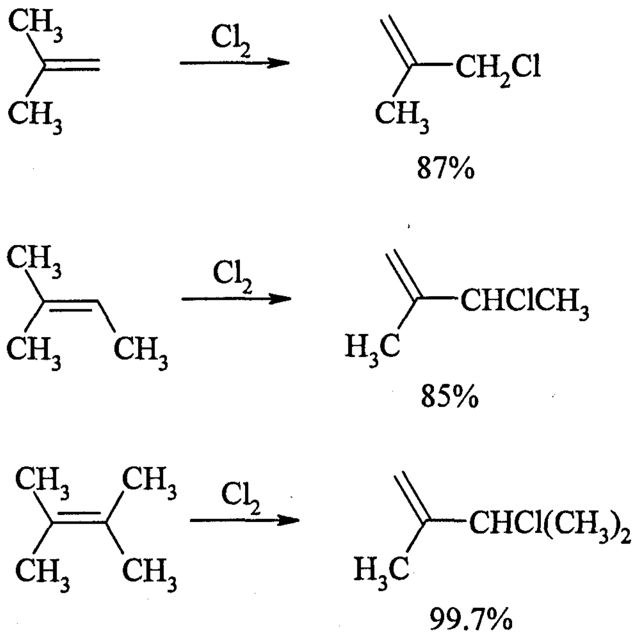


1.14

A more satisfactory explanation for the elimination product was given by De la Mare.[78, 85] He argued that on electronic grounds, neighbouring group interaction of the chlorine with the carbenium ion (**1.14**) results in a configuration from which proton elimination is unfavourable from the attacked carbon. In a bridged ion proton loss from the chloromethyl group is inhibited, relative to elimination from one of the methyl groups, since the movement of electrons is stereo-electronically restricted. The hydrogens of the methyl groups have no problem in adopting a geometry favourable to form allylic chlorides.

The conclusions of De la Mare and Salama[78] that the ionic intermediate in the chlorination of isobutylene is bridged are consistent with Poutsma's findings that the reaction of various alkyl substituted alkenes proceeds *trans*-stereospecifically.[61] In non-ionizing media the ionic pathway presumably takes place by a Ad_EC1 mechanism, the rate-limiting step involving a tight chloronium-chloride ion-pair.

Addition is the major process for straight chain olefins such as 1-butene or 2-butene, giving > 97% of the respective dichloroalkane. However, a small amount of the rearranged allylic chloride (2 to 3%) is also formed from the collapse of the bridged intermediate.[61] The substitutive ability of the carbons next to the double bond are greatly increased by the presence of alkyl groups as shown below.[62]



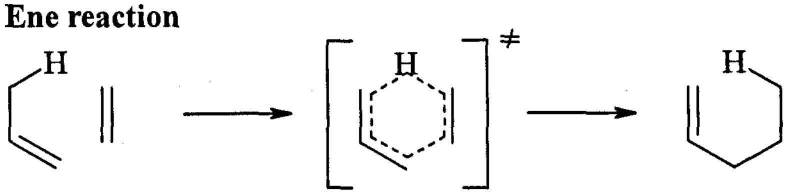
Chlorine and bromine are electron-withdrawing groups, attached to an unsaturated system they act to deactivate the substrate to further electrophilic reactions relative to unsubstituted olefinic groups. However, many of the adducts formed contain reactive double bonds and secondary products, where more than one mole of halogen reacts with the alkene, have been observed in many halogenation reactions notably chlorination.[62, 81]

1.7 Alder-ene reaction.

The Alder-Ene reaction is an example of a pericyclic process. In comparison to the well known Diels-Alder reaction, the ene reaction has been little studied, although some reviews on the inter-[86] and intramolecular[87] ene reaction do exist. Alder and co-workers were the first to investigate systematically the reaction of a variety of dienophiles with mono-olefins and defined the reaction as a 'indirect substituting addition'.[88] This involves an allylic shift of one of the double bonds, migration of an allylic hydrogen from the 'ene' component (**1.15** in scheme 1.13) to another alkene the so-called 'enophile' (**1.16** in scheme 1.13) and bonding between the two unsaturated termini through a cyclic transition state. Mechanistically the ene resembles the [1,5] sigmatropic rearrangement of a hydrogen atom (scheme 1.13), a process which is sometimes classed as an intramolecular ene reaction. Formally, the ene reaction is a thermally allowed six-electron reorganisation process *i.e.* [$2\pi s + 2\pi s + 2\sigma s$]. The two electrons of the C-H σ-bond replace the two π-electrons of the diene in the Diels-Alder reaction.

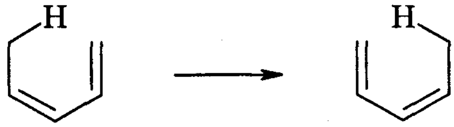
Scheme 1.13: Simple representations of two pericyclic reactions.

Ene reaction



1.15 **1.16**

[1,5] Sigmatropic shift

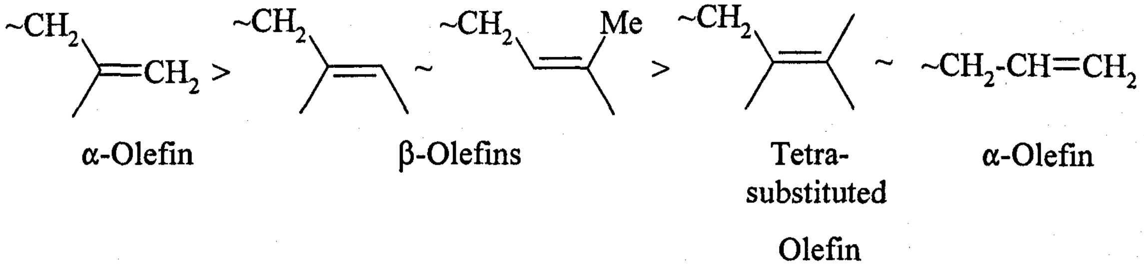


Typically, electron-withdrawing substituents on the enophile facilitate the reaction, although the reaction rate can be accelerated, or less reactive enophiles incorporated, by using Lewis acid catalysts.[89]

The reaction of mono-olefins with maleic anhydride to produce the corresponding alkenyl succinic anhydride has been the focus of significant patent activity.[90] In part this has been stimulated by interest in the production of PIBSA to convert into succinimides for use as additives in engine oil (section 1.3.2). For conciseness this section will concentrate on maleic anhydride (MA) as the enophile reacting with mono-olefins at elevated temperatures, although the ene reaction is not limited to alkenic π-systems. Alder and co-workers[88] investigated the reaction of dimethyl azodicarboxylate with various olefins and other researchers have found that many heterodienophiles are useful in ene synthesis (e.g. N=N, C=O, C=N)[86]; the ene component is limited to allylic systems (CH-C=C). The 'indirectness' of the substitutive addition has been demonstrated by the fact that ethene fails to give the 1:1 adduct with MA between 220-230 °C, while propene gives ally succinic anhydride.[88] Thus hydrogens next to the double bond are required for the ene reaction to proceed.

The generality of the ene reaction for a number of alkenes has been demonstrated and a wide variety of alkenyl succinic anhydride (ASA) adducts have been produced.[91] The reactivity of the alkene and therefore the yield of ASA is markedly improved if α-olefins are employed.[92] Additive manufacturers strive to produce polyisobutylene oligomers with a high α-olefin content to increase the reactivity of the feedstock, thereby giving high conversions upon reaction with MA. The reactivity of open-chain olefins and polyisobutylene oligomers are in the order shown below (figure 1.6).[91, 92] Their reactivity not only depends on the number of β-hydrogens but the steric hindrance of the alkyl groups around the double bond.

Figure 1.6: Relative reactivities of alkyl substituted olefins.



1.7.1 Reaction conditions.

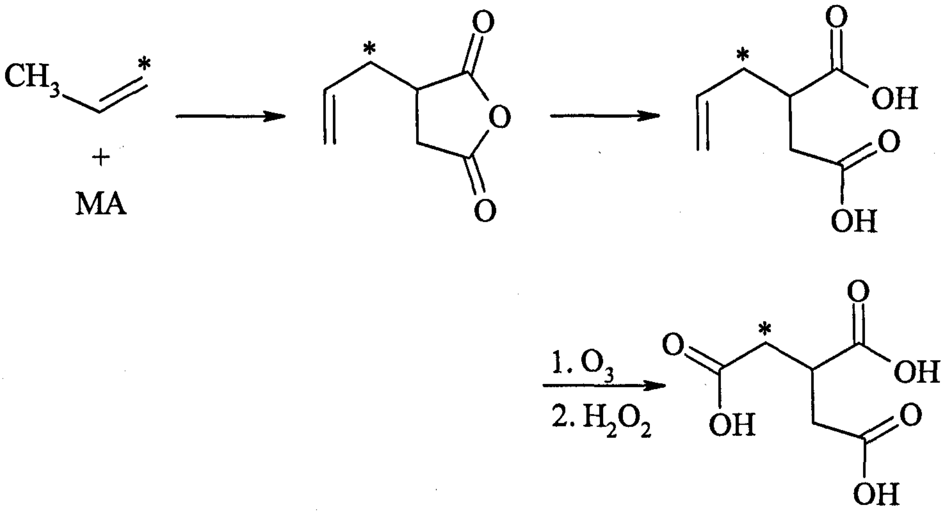
Typical conditions for the ene reaction of simple allylic compounds are prolonged heating (~ 20 h) in a suitable solvent (aromatic solvents are generally used due to their high boiling points and low reactivity) at 140 to 250 °C.[91] For more volatile alkenes, such as the model alkenes (section 1.5), sealed systems have to be used. However, in the thermal maleinisation of polyisobutylene at 200 to 220 °C, resulting in the formation PIBSA, the boiling points of the oligomers are sufficiently high that the reaction can be run without external pressure.

Side reactions resulting from radicals present in the system are common. In the absence of an inhibitor the polymer formed has been attributed to a maleic anhydride-alkene co-polymer stemming from radical induced polymerisation.[93] A systematic study of the effect of radical inhibitors on the conversion of MA, the yield of ASA and the reduction of polymer by-product has shown that the reaction efficiency can be increased and polymer formation inhibited by including a controlled amount (~ 1% / g of MA) of a phenol or an amino benzene derivative. Many of the examples included in this patent were claimed to increase the yield of the ASA, the best being phenothiazine which increased the efficiency to 100%, although conversion of MA was not complete.

1.7.2 Mechanism.

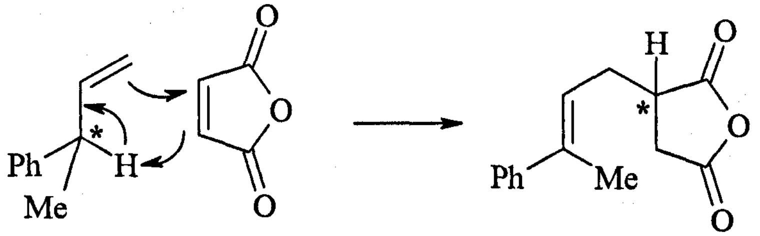
The concerted, six-centred, cyclic mechanism for the ene reaction was first suggested by Arnold and Dowdall to explain the products obtained from the reaction of methylenecyclohexane with various enophiles.[94] The same group later observed a concerted reaction between β-pinene, a terpene with an exocyclic double bond, and MA.[95] The product formed was free from Wagner-Meerwein rearrangements or ring-opening which would be expected of cationic or free-radical mechanisms. Gladysz and Yu[96] examined the effect of pressure on the yield of the ene adduct from β-pinene and MA and found that high pressure conditions (40 kbars) at ambient temperatures promote the reaction, giving a yield of 74% in 17 h in contrast to a yield of only 31% after 22 h at 160 °C at atmospheric pressure. It would be expected that the pressure would increase the yield for reactions with a negative activation volume (${}_{\tau}V^{(}$). Sublett and Bowman[97] condensed propene-1-^{14}C with MA and demonstrated that the derivative formed from hydrolysis and ozonolysis of the ASA retained the ^{14}C label as shown in the scheme 1.14.

Scheme 1.14: Reaction of MA with propene-1-^{14}C followed by ozonolysis of the reaction product.



Retention of the isotopic label in the product after ozonolysis comfirms that migration of the double bond takes place and no long-lived ionic or free-radical species derived from propene is formed, since a long-lived intermediate would lead to scrambling of the label between the 1- and 3-positions in propene. This result suggests that the ene reaction is an 'indirect' rather than a 'direct' addition reaction and proceeds via a concerted mechanism.

Scheme 1.15: Transfer of the asymmetric centre during the ene reaction of (R)(–) -3-phenyl-1-butene with MA.



The thermal reaction between MA and optically active alkenes, such as (R)(–) -3-phenyl-1-butene, leads to optically active products (scheme 1.15).[98] Transfer of the optical asymmetry from the substrate to a different site in the product has been taken as strong evidence for a concerted rather than a stepwise mechanism.

Rondestvedt and Wark examined the reaction of allylbenzene with various ratios of MA and found that a 1:1 adduct was not formed in the presence of a radical initiator, acetyl peroxide.[99] Instead a coloured polymer was formed, further suggesting that the tar-like polymer found by Irwin and Selwitz[100] in the absence of radical inhibitors is radical based. Rondestvedt and Wark[99] also found that the formation of the 1:1 adduct was second order overall, first order in each component. The same overall order has been observed from the thermal reaction of various linear alkenes with MA in the presence of a radical inhibitor.[93] The absence of inhibitor does not affect the rate of disappearance of reactants or appearance of product suggesting that a free radical chain reaction is not operating.

Table 1.3: Kinetics of the reaction of alkenes with MA.[a]

Alkene	Temperature / K	Rate Constant, 10^7 x k / kg^{-1} s^{-1}
1-Octene	398	3.72
	421	21.97
	448	93.49
1-Dodecene	398	4.15
	448	91.66
	477	353.33
	497	846.80
cis-5-Decene	411	6.49
	433	18.09
	455	55.74
trans-5-Decene	411	17.86
	433	51.67
	455	161.17

a : From reference 93.

Benn and co-workers[93] ruled out discrete ionic species as intermediates in the ene reaction based on rate studies in various solvents, which showed negligible solvent effects. However, these experimental observations do not rule out the possibility of a donor-acceptor complex transition state leading to a short lived zwitterion. The effects of alkene structure, chain length and temperature were also investigated. Some of these results are shown in table 1.3. As can be seen from these results the chain length has a negligible effect on the rate of the ene reaction at constant temperature, suggesting that the alkyl chain orientates itself away from the MA in the transition state. Using the kinetic data in table 1.3 Benn and co-workers[93] were able to calculate the activation energy and entropies from Arrhenius plots (table 1.4).

Table 1.4: Kinetic parameters for MA reaction with olefins.[a]

Alkenes	**Energy of Activation, E / kJ mol^{-1}**	**Entropy of Activation, $\Delta S^{\neq}$ / J mol^{-1} K^{-1}**
1-Alkenes	90.0 ± 3.0	– 152 ± 4.4
cis-5-Decene	75.5 ± 6.4	– 191 ± 14.8
trans-5-Decene	77.1 ± 6.4	– 178 ± 14.8

a : From reference 93.

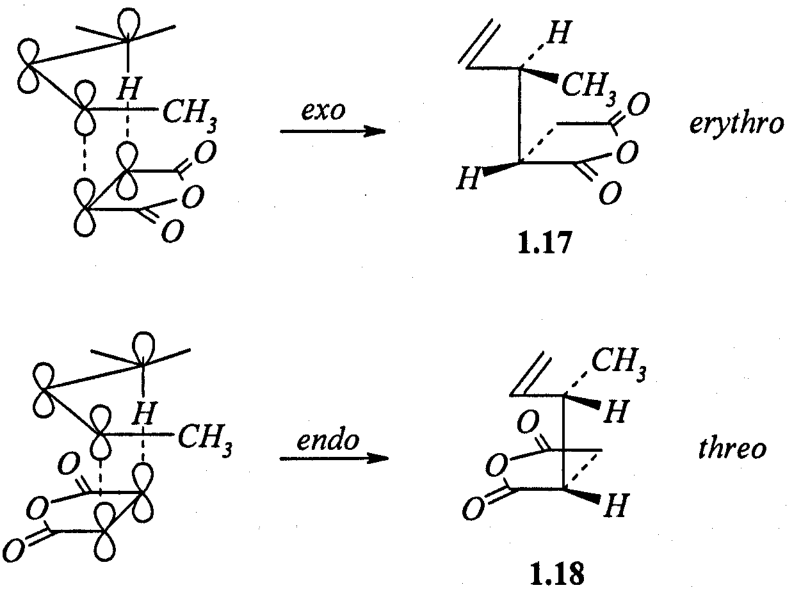
The calculated activation energies are higher than in the Diels-Alder reaction, so higher temperatures are needed. Presumably, this is because the ene reaction involves (C...H...C) hydrogen abstraction, which does not occur readily at lower temperatures since transfer of the hydrogen atom results in an unfavourable change in the hybridisation of the carbon atom.[101] The entropy of activation is highly negative suggesting a very ordered transition state, and is similar to the values seen in the Diels-Alder reactions (– 130 J mol^{-1} K^{-1}), providing supporting proof of a concerted mechanism for the ene reaction.

The activation volumes ($\Delta V^{\neq}$), determined from a study of the pressure dependence of rate constants show a high negative value for $\Delta V^{[}$, in the range of – 36 to – 48 cm^3 mol^{-1}, which has been taken as evidence of a concerted reaction pathway.[102] This conclusion is supported by the high activation entropies ($\Delta S^{\neq}$ = – 120 to – 170 J mol^{-1} K^{-1}) of a closely related system.[103] Furthermore, there was no significant solvent effect on the rate of reaction.

Further support for the proposed mechanism is provided by the Woodward-Hoffmann orbital symmetry rules, which show that a concerted ene reaction is symmetry allowed.[104] The ene reaction mechanism was regarded by Fukui and co-workers as a three orbital interaction involving partial electron transfer from the HOMO π-bond of the ene to the LUMO π-bond of the enophile and 'back donation' from the LUMO of the C-H bond in the ene component.[105]

In the ene reaction internal asymmetric induction takes place in the newly formed chiral centre which is determined by the geometry in the transition state. The *endo* versus *exo* preference in the transition state can be determined from the diasteroselectivity, *threo* or *erythro*, shown in product formtion. Berson and co-workers[106] showed that the thermal reaction between MA and *cis*-2-butene at 225 °C gives a 20 to 30% yield of the diastereomeric 3-(1-butenyl)succinic anhydrides after 8 h. The product distribution was 15 to 20% of the *erythro* isomer (**1.17**) and 80 to 85% of the *threo* isomer (**1.18**), as shown in figure 1.7. There is a preference for endoid addition on orbital overlap and steric grounds. *trans*-2-Butene gave a lower ratio of the diastereoisomers due to unfavourable steric interactions in the transition state (57% **1.17** to 43% **1.18**), although the stereochemical direction of the reaction was preserved.

Figure 1.7: Products from the thermal addition of MA to *cis*-2-butene.



Nahm and Cheng[107] also observed a preference for endoid (*i.e.* 'endo-like') addition in their study of the thermal reaction of all nine decenes with MA. Decenes with a *cis* double bond give a 85:15 ratio of the diastereoisomers in favour of the *endo* product and exclusive formation of the *trans* isomer. Whilst *trans* decenes exhibit only a 60:40 *endo* preference leading to a 81:19 mixture of *trans/cis* isomers. The endo effect appears to be preferred, but is subject to steric effects.

1.8 Addition of carboxylic acids to alkenes.

Alder and co-workers[88] noted that during the condensation between isobutylene and MA at 200 °C a lactone by-product was produced along with the ASA, isobutylene succinic anhydride. Later it was found that the lactone could be formed in 78% yield from the hydrolysis of isobutylene succinic anhydride in aqueous hydrochloric acid.[108]

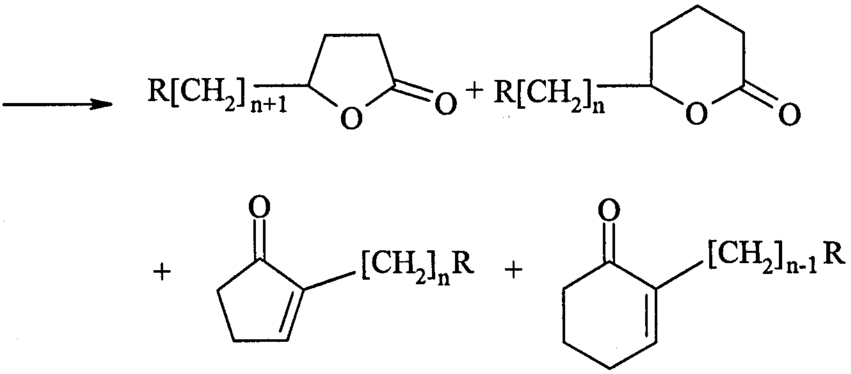
Under acid-catalysed conditions carboxylic acids can add to unsaturated compounds to produce carboxylic esters. If a compound contains both functional groups, as in the case of olefinic acids, treatment with strong acids results in internal addition. Since strong acids also catalyse double bond migration, isomerization can occur to allow the addition to proceed whatever the position of the original double bond in the substrate. The products of this internal addition process are cyclic lactones and enones (scheme 1.16).

Predominance of one pathway over the other depends mainly on which type of acid is used as the catalyst. Proton-donating acids e.g. H_2SO_4, HCOOH and HF lead to lactones, while Lewis acids e.g. $AlCl_3$, $ZnCl_2$ and polyphosphoric acid (P_2O_5) give enones.[109] The difference between these reagents can be explained in terms of their action, the first group protonates the ethylene linkage whereas the latter group preferentially attack the carbonyl group producing acylium ions. Lactonisation is an isomerization of the olefinic acid and the formation of cycloalkenones is an overall cyclodehydration reaction, which is favoured by vigorously dehydrating reagents such as $AlCl_3$, P_2O_5. Thus the hydrochloric acid catalysed hydrolysis of isobutylene succinic anhydride results in the formation of a γ-lactone, whilst $AlCl_3$ yields a 3,5-substituted cyclohexanone.[110]

Scheme 1.16: The cyclisation of olefinic acids to lactones and ketones.

$R[CH_2]_{n+1}CH{=}CH(CH_2)_2CO_2H$

$n + 1 \geq 0$



1.9 Aims.

The work set out in this thesis has two main aims both of which involve the functionalisation of polyisobutylene (PIB), which is an important intermediate in the production of additives used in lubricant packages (section 1.3.2). Currently, two processes are used industrially to produce these intermediates: 1) chlorination of PIB and; 2) the thermal ene reaction with maleic anhydride (MA) to produce polyisobutylene succinic anhydride (PIBSA). Both processes have major drawbacks which are to be investigated.

The chlorination of PIB is very efficient, however the product obtained by aminodechlorination contains residual chlorine which proves extremely difficult to remove. The aim of Chapter 2 is to investigate the origin of this residual chlorine in the final products. The difficulty in using PIB for laboratory reactions, discussed in section 1.5, has been overcome by using model alkenes that mimic the end-groups present in PIB and have much lower molecular weights. The results obtained from the chlorination studies will be used to extend the investigation to other halogen electrophiles in the hope that the selectivity of the process can be improved.

A recent publication on the formation of diamines from styrene oxide[111] and the ready availability of PIB oxide led to an investigation of potential new route to the functionalisation of PIB. In an attempt to apply this new synthetic approach to PIB additives the epoxides of the model alkenes have been employed (Chapter 3).

The current method for the preparation of PIBSA, the ene reaction between PIB and MA, results in a discoloured product mixture. There is no satisfactory explanation for the formation of coloured residues during this reaction. However, it has been postulated that the discolouration is a result of the thermal decomposition of MA.[112] Therefore an investigation into the formation of these coloured by-products was performed, again using model alkenes. The work detailing the study of the by-products is set out in Chapter 4, whilst the results concerning the thermal decomposition of maleic anhydride form Chapter 5.

Chapter 2

Electrophilic Addition of Halogens to Alkenes

As described in section 1.3.2, one of the additives used in oil packages is PIB-amine. The first step in the preparation of surfactant amines from polyisobutene (PIB) involves the reaction of the alkene with halogens, the halogen then being displaced from the substrate by an amino function in a substitution reaction. The current method for the functionalisation of PIB involves halogenation with molecular chlorine. However, after the amination step low levels of residual halogen (< 1 p.p.m.) are left in the additive package which are unacceptable under new European legislation. The aim of the work described in this chapter is to study the formation of the haloalkanes to find an explanation for the residual chlorine. As was noted previously (section 1.5) four model alkenes have been used to mimic the reactivity of the range of endgroups present in PIB.

2.1 Electrophilic addition of chlorine to the model alkenes.

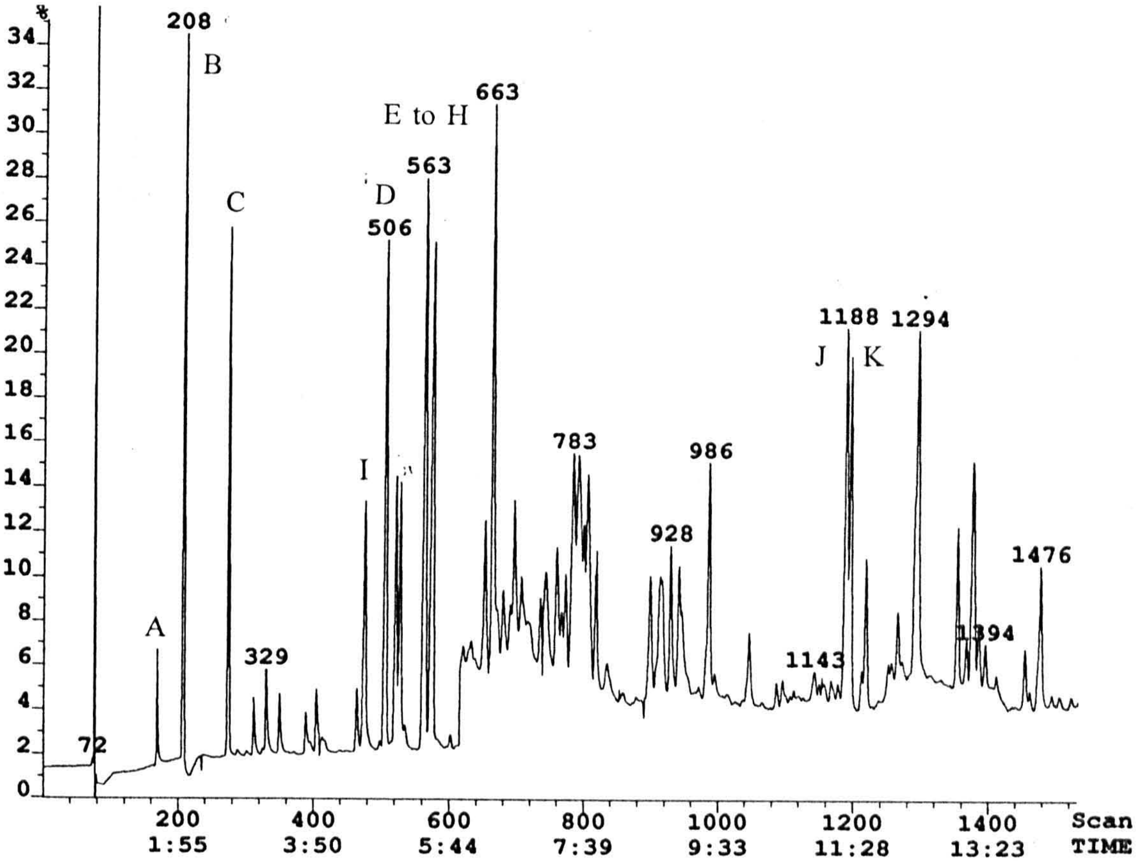
The model alkenes were chlorinated with an excess of chlorine at room temperature using a standard procedure adapted from the industrial chlorination of PIB. The procedure involved bubbling chlorine gas through a 1:1 solution of the model alkene in 1,4-dimethylbenzene (*p*-xylene) for approximately 0.25 h. The solvent, *p*-xylene, is a non-polar aromatic hydrocarbon which is used industrially as the solvent because it is a cheap and readily available material. However, many of the observed reactions products result from the electrophilic chlorination of the solvent, which is the subject of section 2.1.1. All the reaction mixtures developed a yellow colouration during chlorination due to the presence of excess chlorine in the solution. This was removed from the reaction mixture by washing with 10% aqueous sodium thiosulfate solution before work-up by extraction of the organic components from the water layer with diethyl ether.

At room temperature the chlorination of the model alkenes is rapid and exothermic. It is well known that molecular chlorine is easily able to sustain free-radical chain reactions, especially when its dissociation into atoms is activated photochemically or by the use of radical initiators. However, thermal activation of the free-radical addition process is possible at relatively low temperatures even in the absence of light.[19] During the chlorination of the model alkenes in a non-polar solvent, therefore, it is possible that two competing processes are occurring, one polar and one radical. The balance between these pathways is determined not only by olefin structure but also by the concentration of alkene.[42] The importance of the radical pathway decreases with decreasing alkene concentration, thus the ionic pathway becomes increasingly important at low concentrations of alkene. Therefore we would assume that under our standard reaction conditions, in the air (oxygen is a radical inhibitor) and in dilute solutions of alkene, the ionic pathway will predominate.

In each case analysis of the crude reaction mixtures by gas chromatography (GC) showed the presence of many compounds, produced from the reaction of model alkenes and the solvent with chlorine. These products contained two to six chlorine atoms, and of particular interest to our study, many of the compounds were found to be unsaturated. In fact contrary to our expectations the proportion of unsaturated compounds containing two chlorine atoms is always greater than the proportion of the saturated dichloride. Due to the complex nature of the reaction mixtures the components cannot be separated out fully. As a result the work detailed here is qualitative rather than quantitative. The components responsible for the individual GC peaks have been identified from their mass spectra and the proportions of each structural type has been determined from uncalibrated GC peak areas. Ideally products should be identified and quantified by comparison with authentic samples. However the large range of products and the non-availability commercially of these made this an impossible task, hence the general nature of the subsequent discussion.

The results from the chlorination of 1-octene are typical of the chlorination results from all four model alkenes with an excess of chlorine, although the proportions and structures of each reaction type vary somewhat. The crude reaction mixture showed a wide range of products, as can be seen from the GC trace in figure 2.1.

Figure 2.1: The GC trace (obtained from a GC/MS run) of the products from the chlorination of 1-octene in 1,4-dimethylbenzene (*p*-xylene).



A = 1-Chloro-2,5-dimethylbenzene (**2.1**), B = 4-methyl benzyl chloride (**2.2**), C = dichlorooctane, D = dichlorinated substituted xylene product, E to H = Dichlorooctenes, I = trichlorooctane, J to K = pentachlorinated substituted and addition xylene products.

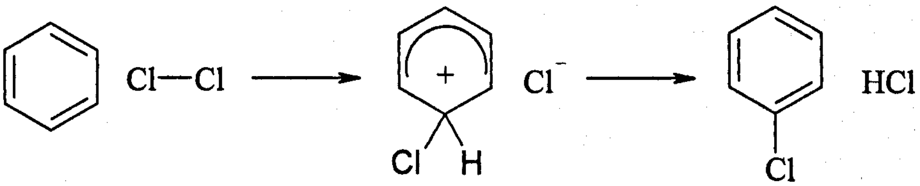
Many significant reaction products were detected and analysed by gas chromatography/mass spectrometry (GC/MS). The MS of these components, those constituting greater than 1% of the total peak area, were obtained. Their identification was based, primarily, on the fragmentation patterns, isotopic patterns and molecular ions (MI) where these were present. The structural formulae of the adducts cannot be determined from their mass spectra alone, although their molecular formulae and some idea of their general characteristics can be obtained.

As mentioned earlier the chlorination of the model alkenes in *p*-xylene gives a whole range of halogenated compounds including chlorinated solvent. The next section details our study of the chlorination of the solvent.

2.1.1 Solvent halogenation. Following the discovery of chlorinated xylenes in the chlorination reactions of the model alkenes in *p*-xylene the reaction of the solvent alone was studied. The chlorination of neat *p*-xylene results in a variety of halogenated products; mono-, di- and polyhalogenated derivatives of dimethylbenzene. The structures of these products have not been fully determined in all cases, although the structures of the monohalogenated compounds have been established. Substitution can occur at the benzylic and ring positions to give mono- and dichlorinated xylenes, such as 1-chloro-2,5-dimethylbenzene (**2.1**), 4-methylbenzyl chloride (**2.2**) and 1,4-dichloro-2,5-dimethylbenzene which have been identified by comparison with mass spectra reported in the literature.[115] Further reaction of these products with chlorine leads to the formation of polychloro(xylenes) and polychloro(cyclohexenes), although the precise structure of these products has not been established.

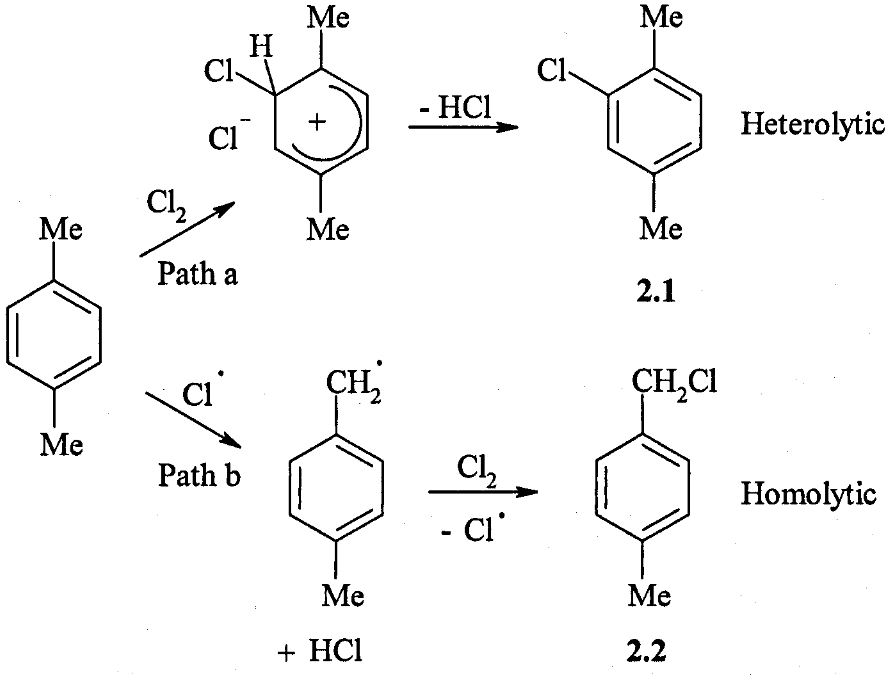
The polychloro(cyclohexenes) (tetra-, penta- and hexachlorinated compounds) are formed by addition of chlorine to the aromatic ring, as well as substitution. These compounds, therefore, are no longer aromatic and can be identified because their molecular ions in the MS appear at higher *m/z* values than would be expected for the simple chlorine substituted derivative(s). There is a preference for substitution over addition (ratio of substituted halogenated products to addition products for the chlorination of neat solvent at room temperature is 3:1), which reflects the greater stabilisation[116] of the substituted product (scheme 2.1).

Scheme 2.1: Resonance stabilized intermediate formed during the aromatic substitution of benzene with chlorine.



The molecular formulae for all the peaks (relative peak area > 1%) detected by GC have been determined by GC/MS. Many of the compounds formed from the chlorination of *p*-xylene have similar mass spectra and fragmentation patterns. This type of reaction product displays an intense molecular ion, and fragments by sequential loss of the chlorine atoms from the molecular ion. Due to the natural abundance of the isotopes of chlorine (3 to 1 for ^{35}Cl to ^{37}Cl) the number of chlorine atoms a compound contains can be determined from the isotopic patterns of the peaks in the molecular ion region of the mass spectrum.

Scheme 2.2: Halogenation of 1,4-dimethylbenzene by chlorine.

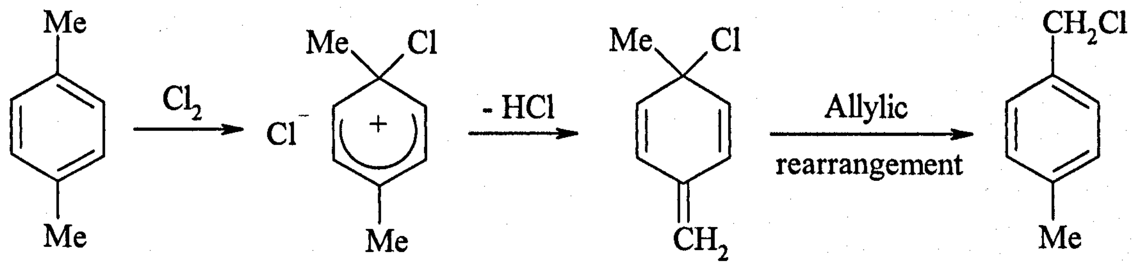


Initially our suspicion was that 1-chloro-2,5-dimethylbenzene (**2.1**) was the product of the electrophilic substitution of *p*-xylene, whilst 4-methylbenzyl chloride (**2.2**) is the product of radical chlorination. Hence, the chlorination of *p*-xylene is probably occurring by competitive homolytic/heterolytic processes (scheme 2.2).[117] Substitution of chlorine at the benzylic position in *p*-xylene is envisaged to involve initial abstraction of a methyl hydrogen by a chlorine radical. Propagation of the free-radical chain process results in the formation of another chlorine radical and 4-methylbenzyl chloride (**2.2**). The radical process is presumably the faster as it involves the more reactive radical species, while electrophilic substitution resulting in the formation of **2.1** involves loss of aromaticity in the initial step. This is reinforced by the experimental observations, as the major monochloroxylene product has been identified as 4-methylbenzyl chloride (**2.2**) (percentage peak area of **2.1** is 2% and **2.2** is 28%).

Electrophilic substitution in aromatic systems (as shown in scheme 2.1) is unusual without a Friedel-Crafts catalyst. However, the aromatic ring of 1,4-dimethylbenzene is activated to electrophiles compared to benzene due to the presence of the two electron donating methyl groups. The formation of **2.2**, therefore, is likely to proceed via the formation of a carbocation intermediate, the positive charge developed is stabilised by the formation of Wheland intermediates. The most stable Wheland intermediate has the positive charge on the *ipso*-positions next to a methyl-substituent (scheme 2.2a).

Whilst side-chain chlorination would normally be considered typical of a radical process it has been suggested that such products can arise through ionic mechanisms. Halogenation of the side-chain of hexamethylbenzene involves an allylic rearrangement of a carbocation intermediate formed by *ipso* attack.[118] Other examples exist in the literature which show that dimethylbenzene may also be capable of this type of rearrangement, a suggested mechanism for the formation of 4-methylbenzyl chloride (**2.2**) by allylic rearrangement is shown below (scheme 2.3).[119] This product is formed because unlike chlorine addition-elimination at any other ring position, where the substituted product is formed by the loss of a proton from the intermediate, chlorination substitution at the *ipso* position requires the breaking of a carbon-carbon bond. This type of substitution requires a high amount of energy, therefore, the lower energy route involving side-chain chlorination is favoured.[119b]

Scheme 2.3: Mechanism for the formation of 4-methylbenzyl chloride (**2.2**) by an ionic process.



2.2

The halogenation of *p*-xylene was studied in the presence and the absence of the four model alkenes and the results are given in table 2.1.

Table 2.1: Solvent chlorination products.

Model alkene	**Solvent chlorination products (Peak area / %)**[a]			
	1-Chloro-2,5-dimethylbenzene **(2.1)**	4-Methyl benzyl chloride **(2.2)**	Dichloro-xylene $C_8H_8Cl_2$	Polychloro-xylene
None	2	28	36	30[b]
1-Octene	3	27	9	10[c]
TMP-1	0	0	0	0
TMP-2	5	0	trace	0
3-Methyl-2-pentene	16	29	3	0

a : Compared to all other halogenated compounds peak areas in the GC trace.
b : Mixture of compounds; $C_8H_7Cl_3$ (Peak area 6%), $C_8H_{10}Cl_4$ (1), $C_8H_9Cl_5$ (19), $C_8H_8Cl_6$ (4).
c : All addition and substitution product $C_8H_9Cl_5$.

It can be seen from the results in table 2.1 that there is a substantial difference in the amounts of chlorinated solvent produced when the structure of the alkene is changed. As the number of alkyl substituents on the alkene is increased there is a decrease in the level of chlorinated xylenes, except for 3-methyl-2-pentene which will be discussed later. This coincides with the increase in the reactivity of the individual alkenes, which would be expected to increase with alkyl substitution.[16] For example when 2,4,4-trimethyl-1-pentene (TMP-1) and 2,4,4-trimethyl-2-pentene (TMP-2) are employed there is little chlorination of the solvent, only 1-chloro-2,5-dimethylbenzene **(2.1)** (relative peak area 5%) being formed during the chlorination of TMP-2. This suggests that the solvent and model alkene compete during the chlorination reaction, thus the ratio change seen in table 2.1 can be explained in terms of the relative reactivity of the alkene compared to *p*-xylene. The selectivity in the cases of TMP-1 and TMP-2, *i.e.* the near exclusive halogenation of the alkene, suggests that the chlorination of these two alkenes is too rapid for the solvent to compete. An anomaly is observed for the chlorination of 3-methyl-2-pentene, although this should be the most reactive alkene large amounts of halogenated solvent products are detected by GC/MS analysis. It is possible that steric hindrance of the alkenic π-system leads to slow chlorination of the alkene and allows chlorination of the xylene to compete.

As for the chlorination of neat *p*-xylene discussed earlier there are two explanations for the plethora of chlorinated products observed for all the experiments listed in table 2.1:

1) two simultaneous processes occurring as shown in scheme 2.2, the dominant pathway being free-radical chlorination with minor amounts of electrophilic substitution

2) ionic chlorination is occurring alone, the formation of benzylic chloride products being accounted for by allylic rearrangement of the carbocation intermediate.

The second explanation is favoured because the chlorination reactions in this work were carried out under conditions which ought to disfavour the radical process, such as dilute solutions of the model alkenes and an air atmosphere.[42, 61, 62] The radical pathway is also tentatively ruled out because it would not be expected to show a selectivity towards either the alkene or the solvent during a competitive chlorination process (table 2.1). To conclude this section it is noted that halogenation of the solvent during the chlorination of the model alkenes produces ring substituted adducts such as **2.1**. Our expectation is that chlorine atoms in these types of compound are not likely to undergo nucleophilic substitution reactions and therefore may be a source of residual chlorine.

2.1.2 Halogenation of the model alkenes.

The previous section concentrated on the identification of reactions products formed from chlorination of the solvent. This section addresses the identity of the adducts formed during the chlorination of the model alkenes: again assignment is based primarily on GC/MS analysis. Much of this data is difficult to interpret in mechanistic terms for two reasons:

1) MS data can not be interpreted fully in terms of structure, double bond location and site of chlorination

2) also the chlorination reactions have been carried out to such great conversions that secondary products, *i.e.* those products formed by the reaction of the alkene with more than one molecule of chlorine, seriously complicate the determination of the primary pathways.

The aim of this section is to determine the selectivity of the addition of chlorine to the model alkenes.

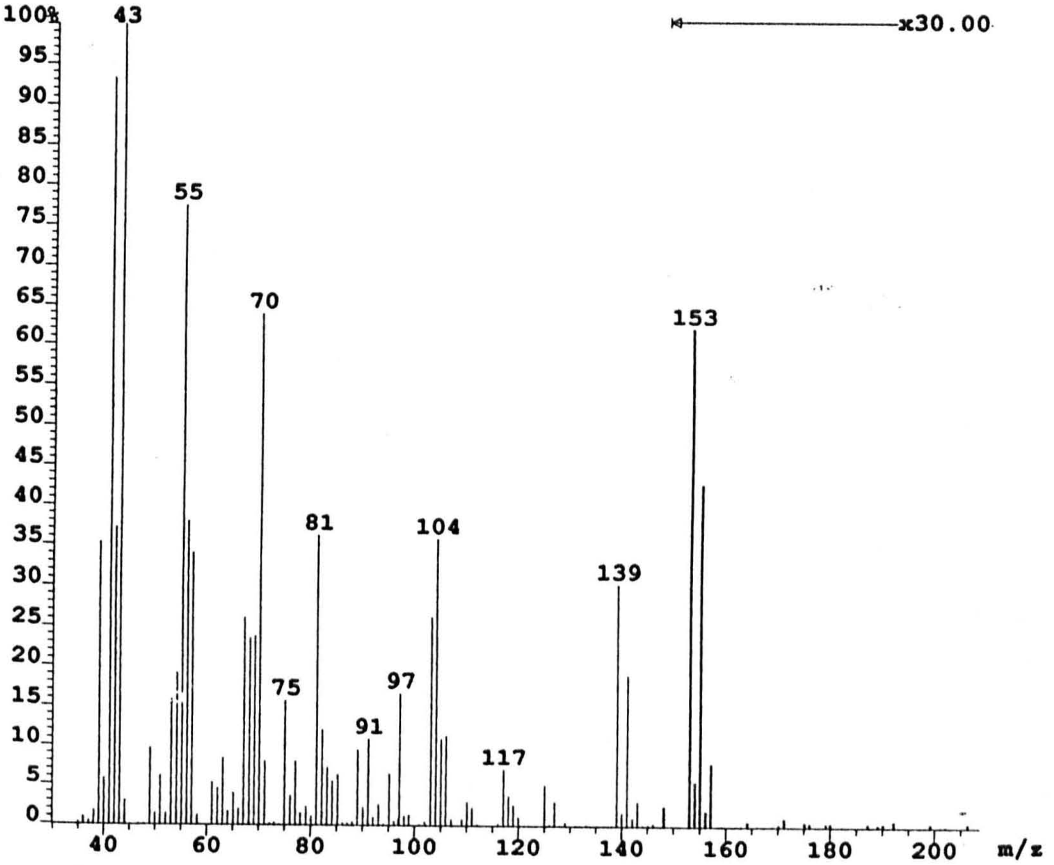
2.1.2.1 Chlorination of 1-octene.

Identification of the reaction products from the chlorination of 1-octene with molecular chlorine, using *p*-xylene as the solvent (1:1 ratio alkene:solvent), has been achieved by analysis of their MS. It is thought that peak C in figure 2.1 represents the alkene addition adduct, the mass spectrum of which is shown in figure 2.2. In general it was found that the saturated chlorine-containing components detected by GC/MS have molecular ions which are very weak or non-existent. Overall this means it is difficult to establish the molecular formulae of these chlorinated products with any certainty. For example the most intense fragment ions observed in figure 2.2 result from alkyl fragments which do not contain any halogen atoms, such as *m/z* 70 ($C_5H_{10}^+$, 64), 55 ($C_4H_7^+$, 77), 43 ($C_3H_7^+$, 100), 41 ($C_3H_5^+$, 93). Although these peaks tell us that this component is based on an alkyl chain, they do not help us assign the overall structural formula.

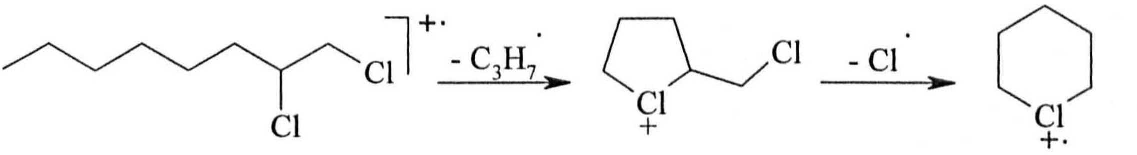
However, the molecular formula of the component in figure 2.2 can be inferred from the isotopic pattern of fragment ions which contain chlorine. The fragment ions observed in the MS with *m/z* 139/141/143 display a 9:6:1 ratio which is a characteristic isotopic pattern for an ion containing two chlorine atoms.[114] The formation of relatively stable 5-membered halonium ions is important in the MS of halogenated alkanes containing more than five carbon atoms in their alkyl chain.[113] It is suggested, therefore, that these three fragment ions correspond to the formation of a chloronium ion through the loss of a C_3H_7 fragment from the molecular ion (scheme 2.4). Further fragmentations involve the loss of a chlorine atom from this cation to form a radical cation with molecular weight 104 and 106, relative ratio 3:1 respectively. The relatively weak fragment ions of *m/z* 153/155/157 (ratio of peaks

9:6:1) are thought to correspond to the formation of the less stable 6-membered chloronium ion via the loss of a C_2H_5 fragment from the molecular ion.

Figure 2.2: The mass spectrum for a dichloroalkane adduct (peak C), obtained from the GC/MS run shown in figure 2.1.



Scheme 2.4: Main fragmentations of 1,2-dichlorooctane.



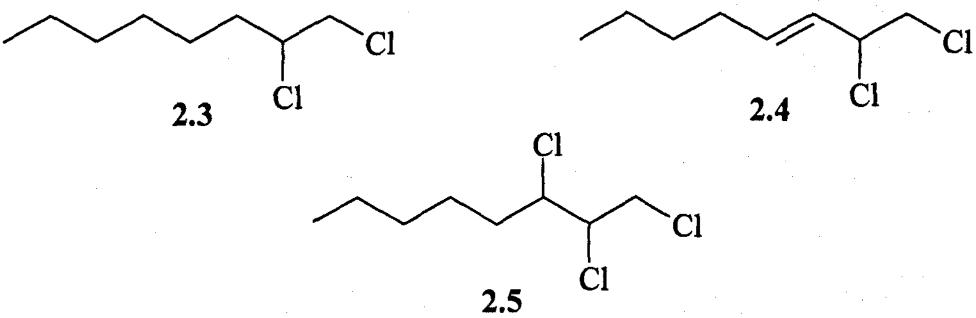
m/z 139, 141 and 143 (30, 20 and 3%)

m/z 104 and 106 (36 and 12%)

The unsaturated compounds display similar fragmentation patterns to those of the saturated derivative, shown in figure 2.2. However, the MS of the dichloroalkenes usually contain molecular ions along with more intense fragment ions for the sequential loss of the halogen atoms. For example dichlorooctene (peak F in figure 2.1) loses chlorine (M – Cl, 16%) and then hydrogen chloride (M – Cl – HCl, 54%), but it also forms cyclic halonium ions, *m/z* 138/140/142 (M – C_3H_6, 5/3/0.6%) and 104/106 (M – C_3H_5 – Cl, 54/17%).

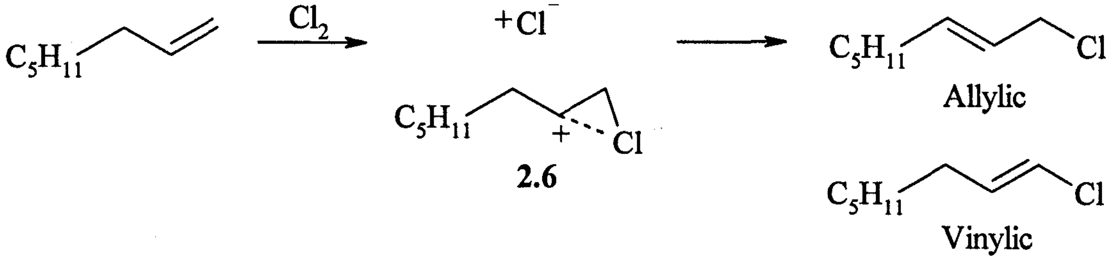
It is difficult to quantify each adduct detected by GC/MS due to the number produced, including chlorinated xylene derivatives (53% of the peak area), as can be seen by the GC trace in figure 2.1. However, if the GC peak areas of chlorinated products resulting from the alkene alone are standardised to 100% then the reaction mixture contains 30% dichloroalkane, 62% dichloroalkenes (four peaks) and 8% trichloroalkane. These three product types have been represented in figure 2.3, although the positions of the chlorines and/or double bonds shown for **2.3** to **2.5** do not represent necessarily the actual structures of the reaction products.

Figure 2.3: Representation of the primary and secondary products formed during the chlorination of 1-octene.



The major products resulting from the chlorination of 1-octene were four unsaturated compounds which contained two chlorine atoms. Our expectation is that the formation of these dichloroalkenes is consistent with the initial formation of a monochloroalkene via an addition-elimination mechanism (scheme 2.5). As discussed in section 1.6 there is general agreement in the literature about the participation of ionic intermediates during the halogenation process and relatively unsubstituted alkenes such as 1-octene would be expected to form halonium ion intermediates (**1.9**). However, chlorine is a poor bridging atom so it has been proposed that a weakly bridged intermediate (**2.6**) is more likely, and elimination of a hydrogen atom would be expected to occur more readily from this than a true chloronium ion.[75, 77] This explains the surprisingly minor amounts of the addition product formed during the process.

Scheme 2.5: Possible mechanism for the formation of a monochloroalkene during the chlorination of 1-octene.



As shown in scheme 2.5 there are two possible isomeric structures of this monochloroalkene, with the chlorine atom situated either in a vinylic or allylic position. However, no detectable quantities of any unsaturated compounds containing only one chlorine atom were seen in the GC/MS analysis of the 1-octene chlorination reaction mixture (figure 2.1). It is suspected, therefore, that the reaction sequence in scheme 2.5 has been repeated with the monochloroalkenes resulting in the formation of the secondary addition product, a trichloroalkane, and the elimination products, four dichloroalkenes.

Compounds containing a chloride atom in an allylic or a vinylic positions would be expected to display different fragmentation patterns in their MS, for the differences in these two reaction types see the discussion for monobromoalkenes (section 2.2.1). Unfortunately, the mass spectra of all four dichlorinated alkenes (peaks E to H, figure 2.1) are virtually identical, containing weak molecular ions of *m/z* 180/182/184 and have fragment ions of similar intensity. It is impossible to distinguish between the dichloroalkenes from the MS data any of which could contain vinylic and/or allylic chlorides.

Although 1-octene is a linear alkene, and therefore does not have a typical unsaturated end-group that is found in PIB, results from this initial experiment show that chlorination is a unselective method of functionalising even simple alkenes. The methods used to identify the reaction products formed during the chlorination of 1-octene have been used to elucidate the molecular formulae of the compounds formed with the other model alkenes. The majority of the reaction mixtures are comprised of unsaturated adducts containing two chlorine atoms. However, using MS we were unable to distinguish between components with allylic or vinylic chloride groups. A summary of the results obtained for TMP-1 and TMP-2 is given in table 2.2, it can be seen that each reaction mixture contains similar reaction types although the yield of each component does vary somewhat.

Table 2.2: Products from the chlorination of the model alkenes.

Molecular formula	**Model alkene (peak areas / %)**[a]		
	1-octene	**TMP-1**	**TMP-2**
$C_8H_{16}Cl_2$	30	4	0
$C_8H_{14}Cl_2$	62	84	73
$C_8H_{13}Cl_3$	0	3	8
$C_8H_{15}Cl_3$	8	9	6
$C_8H_{14}Cl_4$	0	trace	3
$C_8H_{12}Cl_4$	0	trace	3

a : Relative peak areas for the products discounting the chlorinated solvent peaks were standardised to 100%.

2.1.2.2 Chlorination of 2,4,4-trimethyl-1-pentene (TMP-1).

Unlike the chlorination of 1-octene in *p*-xylene the reaction of TMP-1 produces no detectable amounts of chlorinated solvent, as discussed in section 2.1.1. However, the reaction of TMP-1 with an excess of Cl_2 does produce a wide range of reaction types (table 2.2). Again the dichloroalkane adduct is only produced in minor amounts (relative peak area 4%), the rest of the reaction mixture consists of compounds containing two, three or even four chlorine atoms. The major product formed by the chlorination of 2,4,4-trimethyl-1-pentene (TMP-1) in dimethylbenzene is a dichloroalkene, relative GC peak area 59%. Three more isomers of this type are also produced in smaller amounts, peak areas 6, 11 and 8% respectively.

The formation of the dichloroalkenes is consistent with the initial formation of an unsaturated monochlorinated compound. However, this compound is not seen in the reaction mixture and therefore must have reacted with a further mole of chlorine, as described in the previous section (section 2.1.2.1). Furthermore, the formation of polyhalogenated adducts, such as tetrachloroalkanes and tetrachloroalkenes, is thought to result from the reaction of excess molecular chlorine with unsaturated chlorine-containing compounds, such as the dichloroalkenes. Assuming that all of the secondary products result from the initial formation of the monochloroalkenes then our results closely resemble those for similar alkenes published in the literature. For example at 25 °C chlorination of neat 2-methyl-1-butene gives only 5% of the expected addition product with the rest being an isomeric mixture of monochlorinated alkenes.[62] Due to the complexity of our reaction mixture no attempt has been made to separate out the various products for characterisation and therefore their structures have not been established.

The increase in the amount of secondary reaction products formed with TMP-1 and TMP-2, compared to 1-octene, is thought to signify the added stabilisation of having a tertiary carbocation intermediate for this process.

2.1.2.3. Chlorination of 2,4,4-trimethyl-2-pentene (TMP-2).

The products formed during the chlorination of TMP-2 are listed in table 2.2. Clearly the product distributions for both TMP-1 and TMP-2 are similar, as would be expected for these isomeric alkenes. 2,4,4-Trimethyl-2-pentene is an internal olefin which contains three alkyl substitutents around the double bond, one of which is a tertiary butyl group. Therefore, if the intermediate for the chlorination process resembles a carbocation with the positively charged carbon next to the *t*-butyl group our expectation is that methyl migration could occur. This rearrangement would result in an unsaturated monochloride compound with a different skeletal arrangement than the starting alkene. These compounds can presumably be distinguished by their MS which would no longer contain the distinctive intense fragment ion of *m/z* 57 which is indicative of this group.

However, no monochloroalkene is detected in the reaction mixture due to the formation of secondary products and all the dichloroalkenes still contain a tertiary butyl group, seen as the strongest fragment ion [*m/z* 57 (C_4H_7+, peak intensity 100%)] in their MS. Furthermore, the mass spectra of the dichloroalkenes produced from

TMP-2 contain virtually the same ions in their MS as the dichloroalkenes produced during the chlorination of TMP-1. This suggests that these two model alkenes share a common intermediate.

2.1.2.4 Chlorination of 3-methyl-2-pentene.

The results obtained from the chlorination of 3-methyl-2-pentene are discussed separately since the molecular formula of this alkene is different from the other model alkenes. This alkene has a structure very similar to TMP-2 and so our expectation was that a similar product distribution would be found. However, as with the reactions performed with 1-octene the major peaks in the GC trace result from the chlorinated solvent adducts. The ring and side-chain monosubstituted xylenes **2.1** and **2.2** are formed in 16 and 29% respectively. The competitive chlorination of the solvent suggests that the reactivity of the alkene is lowered by steric crowding of the double bond.

Apart from chlorinated solvent molecules the GC trace of the reaction mixture contains two dichloroalkanes (total peak areas 19%), three unsaturated dichlorides (total peak areas 37%) and three unsaturated trichlorides (total peak areas 44%). The relative peak areas for these products have been calculated by discounting the relative peak areas for the halogenated solvent products and then summing the other peak areas to 100%. Again no peak in the GC trace is seen as a result of the monochloroalkene. It is noted that the reaction mixture for this alkene contains very similar amounts of secondary chlorinated products as the reaction mixtures obtained from the chlorination of TMP-1 and TMP-2.

The results discussed in this section (section 2.1.2) show that the chlorination process used industrially is a highly unselective reaction. Analysis of the reaction mixtures produced by the model alkenes shows that in all cases substitution of chlorine exceeds simple addition. Further reaction results in the formation of a whole plethora of saturated and unsaturated products containing between two and four chlorine atoms. In some cases the reaction of chlorine with the alkene is so slow that competitive chlorination of the solvent occurs. Although, the formation of unsaturated compounds in the PIB system would not inhibit the production of additives, formation of vinylic chlorides, which are unreactive to nucleophilic substitution by amines and could lead to residual levels of chlorine. However, in the model systems our studies have shown that it is impossible to interpret the MS for unsaturated compounds containing more than one chlorine atom in terms of allylic or vinylic structures, although the molecular formulae of many unsaturated components have been determined. It is suggested that many of the problems associated with the chlorination of the model alkenes, which is a rapid and unselective process, could be eliminated with a less reactive electrophile. Many of the problems seen using this electrophile stem from the fact that the intermediate formed is likely to be an open carbocation rather than a bridged halonium ion. As discussed in the introduction (section 1.6) the bridging ability of the halogen increases down the group, therefore more selective halogenation of the model alkenes should occur with bromine and iodine containing electrophiles.

2.2 Addition of bromine to the model alkenes.

Bromination is a milder reaction than chlorination, more controllable, and therefore capable of giving a simpler distribution of products. As expected the reaction of molecular bromine with the model alkenes is not as rapid as the equivalent reaction with chlorine.[16]

In a standard procedure the halogenation of the model alkenes was carried out using one equivalent of molecular bromine at room temperature in a variety of solvent systems. Our investigations have been carried out in unreactive solvents which are usually associated with halogenation reactions of this type, such as chloroform and carbon tetrachloride. Initially the red-brown colour quickly disappeared when bromine was slowly added to the colourless alkene solution, showing that a reaction had occurred. After 2.5 hours stirring, the reaction was quenched by adding sodium thiosulfate (10% aqueous solution) and the organic products were diluted with diethyl ether as described for the chlorination reactions. Analysis of the crude reaction mixture by gas chromatography/mass spectrometry (GC/MS) showed that in all cases bromine had reacted with the alkene to form a number of products. In many cases the major product of the reaction was present in sufficient enough concentration to be characterised directly by NMR analysis.

2.2.1 Bromination of 1-octene.

As discussed in the introduction (section 1.6.1) the addition of halogens to alkenes involves a high degree of charge separation in the initial step.[43] In the case of bromine, which is second order in the halogen, this charge separation (especially in non-polar solvents) is aided by a second molecule of bromine.[56] The ability of bromine to act as a bridging atom in the halonium ion intermediate is also greater than chlorine, which is first order in the halogen and therefore presumably involves a relatively high degree of charge separation in the transition state.[77] Overall, this means that the model alkenes are less likely to form substitution products during bromine addition. Consistent with the product forming step occurring from a bromonium-tribromide ion-pair the 1,2-dibromooctane (**2.7**) is the major product formed in carbon tetrachloride (CCl_4) (table 2.3). The minor products were a monobrominated alkane adduct and three tribrominated alkanes. Although the exact structures of each component is not known a representation of each reaction product is shown in figure 2.4.

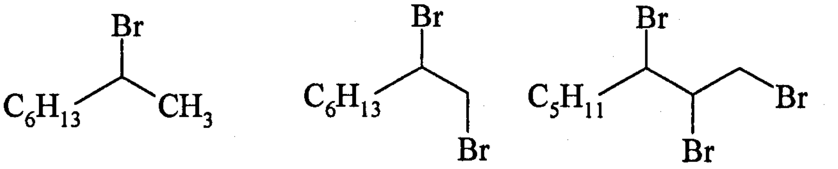
Table 2.3: Product distribution for the bromination of 1-octene.[a]

Conditions[b]	**% Monobromide**	**% Monobromo alkene**	**% Dibromide (2.10)**	**% Tribromo alkanes**
Br_2, CCl_4	1.0	-	95.4	3.6
Br_2, $CHCl_3$	1.5	-	94.9	3.6
Br_2, 60°C, $CHCl_3$	7.8	3.1	89.1	-
$TBABr_3$	2.0	-	98.0	-

a : Uncalibrated and normalised GC peak areas.

b : Experiments performed using chloroform as the solvent and a reaction temperature of 21 °C unless otherwise stated.

Figure 2.4: Representation of the product distribution for the bromination of 1-octene.



Monobromide Dibromide Tribromide

The dibromide, 1,2-dibromooctane (**2.7**), has been identified on the basis of the MS and NMR data. In the mass spectrum the highest fragmentation peak is seen at *m/z* 191/193 as a result of the loss of Br from the molecular ion. Indicating the presence of a saturated compound with a molecular formula of $C_8H_{12}Br_2$ the MS contains a fragment peak at *m/z* 111 (M+ – Br – HBr, 45%). More conclusively the ^1H and ^{13}C NMR spectra of the crude reaction mixture do not contain any peaks in the alkenic region. These NMR spectra contain resonances for the dibromide adduct which are indicative of the CHBr and CH_2Br groups as can be seen below:

	^1H	^{13}C
CHBr chemical shifts (p.p.m.);	4.20-4.00 (m)	53.2
CH_2Br chemical shifts (p.p.m.);	3.84 (1H, dd, *J* 4.4 and 10.5)	36.0
	3.62 (1H, t, *J* 9.5)	

These assignments have been made by comparison of the spectra for this compound with those of similar halogenated alkanes found in the literature.[120] The CHBr and CH_2Br assignments made above match those of 1,2-dibromobutane, which gives peaks in the ^{13}C NMR spectrum at 55 and 35 p.p.m. respectively. Attempted separation of 1,2-dibromooctane (**2.7**) by TLC analysis was unsuccessful due to decomposition of the components on silica, and purification by vacuum distillation gave no better purity of the dibromide, although this adduct is thermally stable.

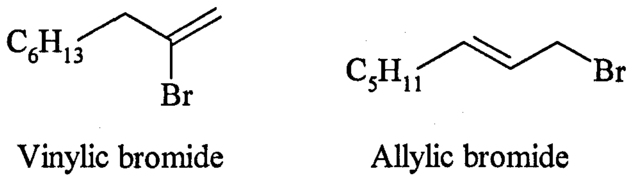
In all cases a small amount of the saturated monobromide was observed (table 2.3). The mass spectrum of this GC peak contains molecular ions with *m/z* 192/194 (relative intensities 4/4%). Presumably, this compound is produced by the addition of HBr to 1-octene. It is tentatively suggested that a white gas which was seen escaping from the reaction mixture on addition of the bromine solution was hydrogen bromide. Assuming that HBr is not eliminated by the decomposition of 1,2-dibromooctane to give the unsaturated bromide adduct, this acid must be formed from the reaction of Br_2 with adventitious water in the system.[26] The dibromide is stable to an increase in the initial temperature of the GC from 70 to 120 °C and was stable to distillation at high temperatures.

The bromination of 1-octene seems to be much more selective than the corresponding chlorination reaction. There is a distinct absence of unsaturated products; however the formation of three tribromide adducts at 3.6% of the GC trace for the bromination in carbon tetrachloride is consistent with the initial formation of an unsaturated monobromide. A very similar situation is observed when a polar solvent such as chloroform ($CHCl_3$) is used (table 2.3).

Increasing the reaction temperature from 21 to 60 °C, in $CHCl_3$, increases the elimination of HBr, seen as a white gas escaping from the reaction vessel, and decreases somewhat the yield of the dibromide (peak areas 95 to 89% respectively) (table 2.3). The larger amount of HBr produced accounts for the increase in the amount of monobromooctane seen at 60 °C compared to room temperature. The monobromoalkene component, present in the GC trace, obtained from the bromination of 1-octene at 60 °C in chloroform is formed in similar amounts to the saturated tribrominated, observed in chloroform or carbon tetrachloride at room temperature (table 2.3). Assuming that the tribromide is formed by the reaction of a unsaturated compound containing one bromine atom with another molecule of bromine, then the absence of secondary products for the reaction carried out at 60 °C is probably due to the increased volatility of bromine at this temperature.

Assuming that monobromooctene (peak area 3%) is a substitution product formed as a by-product during the ionic addition of Br_2 to 1-octene by an addition-elimination mechanism (as discussed in section 2.1.2.1 for the chlorination process), then there are only two possible isomers for the unsaturated products (figure 2.5).

Figure 2.5: Possible structures of the monobromoalkene formed during the bromination of 1-octene.



However, due to the overwhelming proportions of the dibromide adduct present in the reaction mixture NMR analysis was unable to help us elucidate the position of the double bond in the unsaturated product. The mass spectra of the unsaturated monobrominated adduct, obtained from GC/MS runs, suggests that it is in fact an allylic bromide since the molecular ion peak is very weak (*m/z* 190/192, relative intensities 0.6/0.6%) and the most intense primary fragmentation involves loss of a bromine radical [*m/z* 111 (M+ – Br), relative intensity 30%]. This is consistent with Weiss and Touchette's work which showed that vinyl bromides have large molecular ion peaks in their mass spectra and allylic bromides show no peaks containing bromine.[121]

The results for 1-octene are very promising in terms of selectivity, much less of the reaction mixture consists of unsaturated compounds and secondary reaction products than for chlorine. However, bromine is much more expensive than chlorine and therefore it is not suitable for industrial scale reactions with PIB. Tetrabutylammonium tribromide ($TBABr_3$) is a safe and inexpensive brominating agent that can be used in a variety of organic solvents.[122] Organic tribromide salts, such as TBABr$_3$, are soluble in most organic solvents, and are easier to handle than liquid bromine.[122] These reagents can be used for the bromination of olefins under mild conditions, although the mechanism for the addition of tribromide salts differs slightly from that of molecular bromine. Unlike bromine the overall order of the reaction is second, first order in the olefin and in tribromide salt, due to the extra stabilisation that the tribromide ion gives to the intermediate.[57, 123] TBABr$_3$ was used in an attempt to prepare a standard sample of 1,2-dibromooctane, but the reaction mixture again contained a small amount of monobromoalkane impurity (table 2.3). Overall this brominating reagent is more selective than bromine, producing 98% of the dibromide compared to 95% in chloroform and no unsaturated compounds.

2.2.2 Bromination of 2,4,4-trimethyl-1-pentene (TMP-1).

Unexpectedly, attack on the solvent to produce 1-bromo-2,5-dimethylbenzene (**2.8**) and 4-methylbenzyl bromide (**2.9**) (peak areas 1.5 and 15% respectively) has occurred on bromination of TMP-1 in *p*-xylene in contrast to the less selective chlorination (section 2.1.2.1). These components have been identified by comparison of their mass spectra with those reported in the literature.[115] Di-substitution of the solvent also takes place (peak area 1%), although the exact structure of this product has not be determined. The standardised values for the alkene halogenation product peak area discounting the solvent product peaks are shown in table 2.4.

These results show that halogenation of the solvent competes significantly with bromination of the olefin. However, these side-reactions complicate our study of the halogenation of the model alkenes, therefore investigations have been conducted in unreactive solvents which are usually associated with halogenation reactions of this type, such as chloroform and carbon tetrachloride. This enabled us to observe which system best mimics the reaction in *p*-xylene without the complication of solvent by-products.

Table 2.4: Product distribution for the bromination of TMP-1.[a]

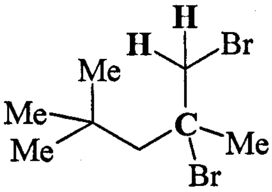
Conditions[b]	**% Mono bromide**	**% Monobromo alkenes**	**% Dibromide (2.10)**	**% Dibromo alkenes**	**% Tribromo alkanes**
p-xylene, Br_2	28	10	42	9	10
Br_2, CCl_4	16	3	39	-	41
Br_2	8	-	22	26	42
0.5 equiv. Br_2	26	31	20	13	7
Br_2, 60 °C	5	41	31	15	9
$TBABr_3$	-	26	74	-	-

a : Uncalibrated and normalised GC peak areas.

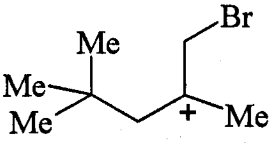
b : Experiments performed using chloroform as the solvent and a reaction temperature of 21 °C unless otherwise stated.

Overall, it can be seen from table 2.4 that the amount of dibromide produced by the bromination of TMP-1 is substantially lower than that given by comparable reactions of 1-octene. The substitution:addition ratio is much higher for TMP-1, reflecting the increased alkyl substitution of the substrate. The formation of compounds like the tribromide product (relative peak area 10%) from the reaction of bromine with TMP-1, in *p*-xylene, can be accounted for by secondary reactions involving addition of a bromine molecule to unsaturated monobromides. Again, an experimental observation that helps to explain the formation of the saturated monobrominated adduct is the evolution of a white gas which accompanies addition of bromine in many cases. It has been assumed from the presence of a saturated compound containing one bromine atom in the GC trace that this gas is HBr; reaction of the alkene takes place with the HBr present in the reaction mixture.

In order to understand the processes involved in the formation of residual halides the secondary products are not initially needed, they only serve to complicate this issue. The investigation into the structure of the primary products, such as the unsaturated monobromides and saturated dibromide adducts, gives us more insight into the mechanism taking place. For instance the major product formed during the reaction of bromine with TMP-1 using *p*-xylene as the solvent is the addition product. This has been identified as 1,2-dibromo-2,4,4-trimethylpentane (**2.10**) by comparison of its MS and GC retention time with that of the dibromide adduct produced using TBABr$_3$ as the brominating agent. For TBABr$_3$ the dibromide (**2.10**) was present in large enough quantities, and in excess of the other products, to give the major peaks in the NMR spectrum of the crude reaction mixture. In the ^{1}H NMR spectrum the two hydrogens highlighted below were shifted down-field by approximately 2 p.p.m. as a result of being on a carbon attached to a bromine atom, each gave a doublet at 3.89 and 3.87 p.p.m.. The quaternary carbon shown below was also at a high frequency of 66.8 p.p.m. in the ^{13}C NMR spectrum whereas a saturated quaternary carbon would be expected at nearer 30 p.p.m..[114]



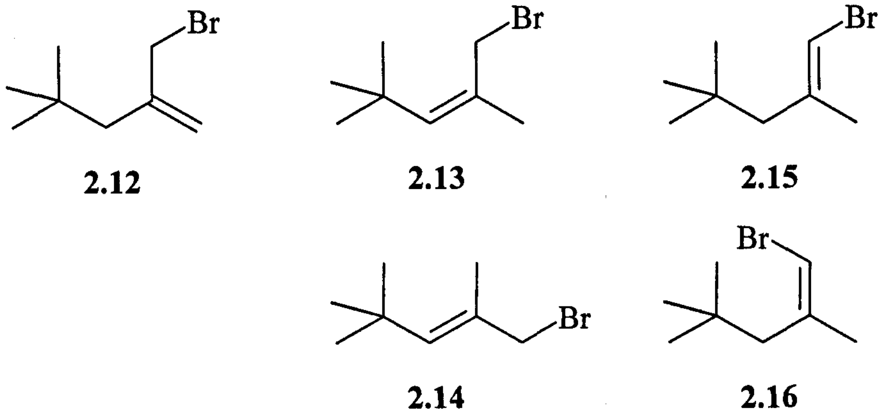
2.10



2.11

With both the bromination of TMP-1 in *p*-xylene using Br$_2$ and in CHCl$_3$ using TBABr$_3$ a number of unsaturated monobromides are formed along with the dibrominated adduct (table 2.4). These compounds were detected as five separate peaks in the GC trace of the TBABr$_3$ reaction mixture (in CHCl$_3$) and six peaks for Br$_2$ (in *p*-xylene). The large amounts of this type of by-product results either from the extra stability of the carbocation intermediate for highly branched alkene or steric crowding preventing halonium ion formation (as discussed for chlorination in section 2.1.2). The intermediate presumably has a structure resembling **2.11** and seven β-hydrogens which can be abstracted. There are five possible structures for the unsaturated monobrominated product resulting from elimination of a proton from **2.11**; three allylic bromides with either an internal or external double bond (**2.12**, **2.13** and **2.14**) and two vinylic bromide isomers (**2.15** and **2.15**) (figure 2.6).

Figure 2.6: Five possible structures for monobromopentene.



2.12 **2.13** **2.15**

2.14 **2.16**

As described in section 2.2.1, the two types of unsaturated monobromoalkenes (allylic and vinylic bromides) would be expected to show differences in their mass spectra. All five GC peaks in the region corresponding to the monobromoalkenes for the TMP-1/TBABr$_3$ reaction mixture have weak or non-existent molecular ions [*m/z* 190/192 (0.3/0.3%)] and only minor fragments containing bromine [*m/z* 111 (M+ – Br, 25%)]. From our experience with the monobromoalkenes resulting from 1-octene this MS data seems to indicate the presence of allylic bromine atoms alone. Our expectation is that **2.12** would have a very similar MS to the two isomers **2.13** and **2.14** as all three are allylic bromide isomers. This leaves two GC peaks for the TMP-1/TBABr$_3$ which display ions in their MS consistent with a allylic configuration of the bromide but do not contain the *t*-butyl fragment of *m/z* 57. It is possible that these components result from a rearranged product, such rearrangements would be expected to proceed by methyl migration from the *t*-butyl group.[76]

When *p*-xylene is used as the solvent analysis of the reaction mixture by GC/MS contains an extra monobromopentene component. This compound displays more intense molecular ions in its MS [*m/z* 190/192 (relative intensities 4.5/4.5%)] compared to relative intensities of the molecular ions for the allylic isomers. Vinylic bromides fragment by the loss of a bromine radical less readily than do allylic bromides.[121] This is reflected in the relative intensity of the *m/z* 111 (M+ – Br) ion which is strongest in the latter's MS, relative intensities 2% and 25% respectively. The mass spectrum of this extra peak also contains a fragment indicative of the presence of a *t*-butyl group, *m/z* 57 (100%). This evidence points to a compound with a structure like **2.15** or **2.16** containing a vinylic bromide group. In each case this compound, which is very important to our investigations, is only present in minor amounts. In the GC trace for the bromination of TMP-1 *p*-xylene for example the vinylic bromide represents only 1.5%, from the uncalibrated peak area, of the reaction mixture. The reactions performed with the various other solvents, temperatures and reagents contain the vinylic bromide peaks in their respective GC traces to the same or a lesser extent (in some cases the peak area is < 1%).

Unlike the reactions carried out with 1-octene the product distribution obtained from the reaction of bromine with TMP-1 seems to be more solvent dependent. For example changing the solvent from chloroform to carbon tetrachloride with TMP-1 at room temperature results in an increased yield of the dibromide from 22 to 39% respectively. This suggests that relatively polar solvents, such as chloroform, stabilize the developing positive charged in the reaction intermediate leading to an increased substitution over addition. As can be seen in table 2.4 relatively large amounts of secondary products are formed in many cases, which is unexpected because only one equivalent of bromine was added to the reaction mixtures. For example, bromine addition to TMP-1 in chloroform at room temperature the majority of the reaction mixture is composed of substitution secondary products. The yield of primary products can be increased by performing the bromination in presence of excess alkene or by increasing the reaction temperature to 60 °C. Presumably, due to the increased volatility of bromine at 60 °C there is an excess of the alkene in the reaction mixture, as described earlier (section 2.2.1). These two results suggest that the secondary products are formed by the reaction of the monobromoalkenes with a second molecule of bromine. However, we are unable to explain fully why so many secondary products have been formed (table 2.4) when only one equivalent of bromine was used, but it does suggest that the monobromoalkenes are of similar reactivity as TMP-1.

Many saturated and unsaturated adducts containing one, two or even three bromine atoms have been detected in the reaction mixture from the bromination of TMP-1. However, compared to the chlorination of TMP-1 (table 2.2) the relative amount of unsaturated compounds, produced from the equivalent reaction with bromine (table 2.4), is substantially reduced.

2.2.3 Bromination of 2,4,4-trimethyl-2-pentene (TMP-2).

A similar situation as described for the bromination of TMP-1 occurs for the internal isomer, TMP-2. As can be seen in table 2.5 a range of experiments have been performed with this alkene. The only significant difference for this substrate is the amount of dibromide detected by GC/MS analysis of the reaction mixtures, which is presumably lower due to the steric hindrance of the double bond in TMP-2. Even for bromine, which is a relatively good bridging atom, this highly substituted alkene seems to have an intermediate with a high degree of carbocation character because the formation of unsaturated compounds is increased relative to TMP-1. However, the reaction is more selective than the corresponding chlorination of this alkene (section 2.1.2.3) in a relatively non-polar solvent.

Table 2.5: Product distribution for the bromination of TMP-2.[a]

Conditions[b]	**% Mono bromides**	**% Monobromo alkene**	**% Dibromide**	**% Dibromo alkenes**	**% Tribromo alkane**	**% Tribromo alkene**
Br_2, CCl_4	37	-	19	3	28	13
Br_2	10	-	8	48	24	10
Br_2, 60 °C	16	17	16	35	11	4
$TBABr_3$	54	-	29	17	-	-

a : Uncalibrated GC peak areas.

b : Experiments performed using chloroform as the solvent and a reaction temperature of 21 °C unless otherwise stated.

Only the reaction of TMP-2 with bromine at 60 °C produces any detectable quantities of a monobromoalkene. However, the MS of this component suggests that the bromide is in an allylic rather than a vinylic position, having a weak molecular ion peaks [*m/z* 190/192 (2/2%)] and only minor peaks containing bromine. Consistent with the MS of allylic bromides described in section 2.2.2 the MS of this component contains a intense fragment ion of *m/z* 111 (M+ – Br, relative intensity 100%).

2.2.4 Bromination of 3-ethyl-2-pentene.

In contrast to the chlorination experiments, which used 3-methyl-2-pentene as the fourth model alkene, 3-ethyl-2-pentene has been employed here and later (section 2.3). This was done for two reasons 1) the extra expense of 3-methyl-2-pentene and 2) products formed from this alkene contain an asymmetric centre which complicates the reaction mixture.

Addition of bromine to 3-ethyl-2-pentene with $TBABr_3$ results exclusively in the formation of the 1,2-addition product, 2,3-dibromo-3-ethylpentane (**2.17**). The percentage yield of the dibromide using this reagent was 91.2%. Overall, the bromination of this alkene is much more selective than the other two end-groups present in PIB, TMP-1 and TMP-2. The bromination of 3-ethyl-2-pentene in $CHCl_3$ at room temperature with bromine resulted in relative peak area of 84% corresponding to the dibromide and 16% for a saturated tribromide.

2.3 Addition of iodine electrophiles to the model alkenes.

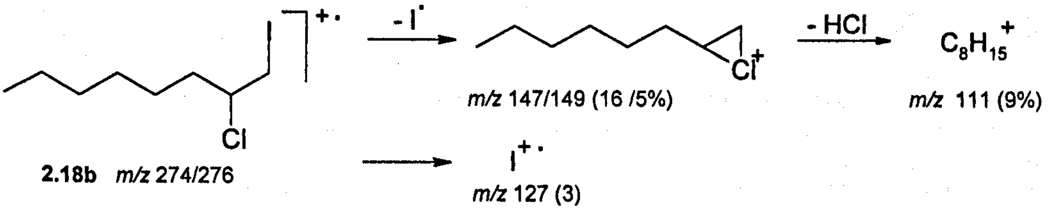
Following on from the last section, where bromine was found to be much more selective in its addition to the model alkenes, the obvious step is to investigate the addition of iodine. However, the addition of a iodine molecule to alkenes is reversible therefore iodine electrophiles have been investigated instead. The iodine electrophiles, iodine monochloride (ICl) and iodine monobromide (IBr), were added to the four model alkenes. The dihaloalkanes produced were found to be stable to analysis by capillary gas chromatography. However, attempts to isolate products by column chromatography or vacuum distillation failed due to decomposition. The iodine electrophiles were used as received (1M solutions in CH_2Cl_2). Unfortunately this means that there is no direct comparison to earlier halogenation experiments performed in non-polar solvents. However, as dichloromethane and chloroform are of a similar polarity some comparsion can be made between the addition of the iodine electrophiles and bromine to the model alkenes in these solvents.

In a standard procedure used for both ICl and IBr one equivalent of the interhalogen was added to a solution of the model alkene in dried dichloromethane. Due to the unstable nature of the electrophiles the reactions were performed in the dark and under a nitrogen atmosphere. After 3.5 hours stirring the reaction was quenched by adding sodium thiosulfate (10% aqueous solution) and the organic products were diluted with diethyl ether as described for previous halogenation procedures. Analysis of the crude reaction mixture by gas chromatography/mass spectrometry (GC/MS) showed that addition of these two reagents to the model alkenes is much more selective than the reaction described in sections 2.1 and 2.2. In many cases the major product was present in large enough concentration to be characterised readily by NMR analysis.

2.3.1 Reaction of ICl with the model alkenes.

Overall the reaction of iodine monochloride with the model alkenes results in a relatively simple reaction mixture. These reaction products were detected by GC, whilst their identification was achieved by mass spectral analysis, from assignment of isotopic patterns, molecular ion and fragment ion peaks. This allowed us to suggest structures for the products but unfortunately we were unable to define the regiochemistry of the addition products from their MS data. For example, addition of iodine monochloride in dichloromethane to 1-octene gives the Markovnikov and the anti-Markovnikov products, 1-iodo-2-chlorooctane (**2.18b**) and 1-chloro-2-iodooctane (**2.18a**) respectively, in a ratio of 60:40 (ratio obtained from the areas of the peaks in the GC trace). Apart from the alkyl fragments the most intense fragment ions in the MS of **2.18a** and **2.18b** correspond to the loss of iodine followed by hydrogen chloride from the molecular ion (figure 2.7). Compounds containing iodine also display an iodine cation radical of *m/z* 127 in the MS.

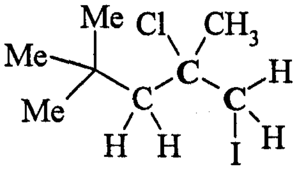
Figure 2.7: Mass spectra fragmentations for 1-iodo-2-chlorooctane



In the MS of iodochlorooctane the two molecular ion peaks display a chlorine isotopic pattern (*m/z* 274/276, relative intensities for **2.18b** 1.0 and 0.3% respectively). The strongest peaks in the MS belong to the alkyl fragments, such as $C_5H_9^+$ of *m/z* 69 (relative intensity 100%). The MS of these regioisomers are very similar and the orientation of halogens in the Markovnikov and anti-Markovnikov products has to be determined by NMR analysis. This method is explained below for the much simpler ICl/TMP-1 system which only contains one addition product.

For the reaction of iodine monochloride with TMP-1 the major product in the GC trace has been identified using MS as the ICl addition product (**2.19**, peak area 83%). The only other products which have sufficient peak areas to be analysed by GC/MS are unreacted alkene (peak area 8%) and a monoiodoalkene (peak area 2%). As shown in figure 2.8 the major product has been identified as the Markovnikov addition product, 1-iodo-2-chloro-2,4,4-trimethyl-pentane, by ^1H and ^{13}C NMR analysis.

Figure 2.8: Regioselectivity of the reaction of ICl with TMP-1.

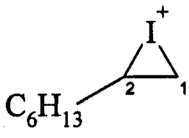


^{13}C NMR chemical shifts (p.p.m.): $CH_2I = 22.3$
qCCl = 70.0

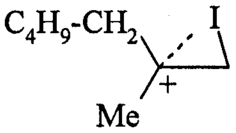
^1H NMR chemical shifts (p.p.m.): $CH_2I = 3.77$ (1H, d) and 3.72 (1H, d)

The regioiselectivity in all the addition products has been assigned on the basis of the ^{13}C and ^1H chemical shifts of the quaternary carbon and the methyl group bearing the chlorine and iodine atoms. Again these assignments have been made by comparison of these spectra to similar halogenated alkanes in the literature.[120] The carbon atom bearing the chlorine atom is deshielded relative to the one bearing an iodine atom.[73] In the ^1H NMR spectra the more electronegative the halogen attached to the alkyl group the greater the displacement to lower fields.[124]

In agreement with this the major product from the addition of ICl to 1-octene has a CHCl resonance in the ^{13}C NMR spectrum at 61.1 p.p.m., whilst the anti-Markovnikov addition product has a CHI peak at 33.5 p.p.m.. This result shows that for 1-octene anti- Markovnikov attack of the chloride ion on the iodonium ion is a significant pathway, a similar result was found by Heasley and co-workers[72] for the reaction between 1-hexene and BrCl and is taken to indicate a symmetrically bridged intermediate (**2.20**). The regioselectivity of the addition of ICl to TMP-1 suggests that the iodonium ion intermediate is unsymmetrical or weakly bridged (**2.21**).



2.20



2.21

The difference between the intermediates formed with 1-octene and TMP-1 is presumably due to the 1,1-dialkyl substitutents stabilising the developing cationic character on the more substituted carbon and/or steric crowding.[73] Possibly the development of carbocation character in the intermediate for TMP-1, as indicated by the increased regioselectivity is a combination of both these factors. The increased cationic character of the more substituted carbon for TMP-1 intermediate (**2.21**) is also reflected by the formation of iodine substituted alkenes, relative peak area 6%.

The results given from the addition of ICl to 3-methyl-2-pentene also suggest that the reaction proceeds through a symmetrical iodonium ion intermediate resembling **2.20**. The reaction mixture contains two peaks in the GC trace, identified as the Markovnikov and anti-Markovnikov addition products, in a ratio of 55:45. It is unlikely that these two components represent separable diastereoisomers because the ICl/3-ethyl-2-pentene addition product, which does not contain an assymetric centre, also gives two peaks in the GC trace. The MS of both contains molecular ion peaks at *m/z* 246/248 (relative intensity 1.0/0.3%). However, only the peaks for the major regioisomer were intense enough to be assigned unambiguously by NMR analysis. Once again the carbon atom bearing the chlorine is deshielded relative to the one bearing an iodine atom a tertiary carbon peak being observed at 80.2 p.p.m.

and the primary carbon coming at 36.6 p.p.m.. The difference in the Markovnikov:anti- Markovnikov ratio between 3-methyl-2-pentene and 1-octene is attributed to a small increased steric hindrance of the 1,1-dialkyl substituted carbon atom for the iodonium ion of 3-methyl-2-pentene compared to 1-octene. These results show that one alkyl substitutent can make a profound difference to the structure of the intermediate, although the electrophile and solvent polarity also have an effect.[77]

This electrophilic reagent appears to be much more selective in the addition to the model alkenes than bromine in chloroform at room temperature. However, for TMP-2 the addition of ICl is only a minor pathway, the relative peak area of monoiodomonochloropentane being only 2%. The other products which contain peaks with a 3:1 isotopic pattern indicative of one chlorine atom but not iodine [*m/z* 127 ($I^{+\cdot}$)] in their MS have been assigned as a saturated monochloride (relative peak area 49%) and several unsaturated monochlorides (combined relative peak area 47.5%). It is not clear how these compounds were formed but it appears that the reactivity of this alkene with the iodine electrophile is so low that the interhalogen compound has decomposed to form molecular iodine and chlorine. The equilibrium between interhalogens and their molecular components has been observed previously.[41]

2.3.2 Reaction of IBr with the model alkenes.

The results obtained using IBr were rather disappointing due to the decomposition of the interhalogen during the reaction. On the whole this interhalogen appears to be less stable than ICl, forming iodine and bromine in relative abundance. The increased reactivity from IBr to ICl is associated with the polarisation of the interhalogen bond with increased electronegativity difference between atoms.[60] Therefore, IBr is slower to react with the model alkenes thus the dissociation of the interhalogen has more time to occur.

Identification of the products formed during the reaction of this interhalogen with the model alkenes was achieved in a similar way to those described above. In the case of 1-octene the majority of the reaction mixture (relative peak area 74%)

consists of the Markovnikov and anti-Markovnikov addition products (ratio 40:60 respectively). However, 1,2-dibromooctane is also present and assuming that the intermediate involved in the formation of the two regioisomers above is a iodonium ion (**2.20**) then the formation of this product must involve the addition of molecular bromine to 1-octene.

For all the other olefins the reaction mixture comprises products formed from the reactions of the model alkene with bromine; there are no adducts that contain iodine. The reaction of bromine with the model alkenes appears to be more selective than the corresponding brominations detailed in section 2.2, however the reactions were performed in a more polar medium, which favours the polarisation of the Br-Br bond, thus addition dominates over substitution (Table 2.6). The compounds listed in the table have been identified by comparison of their MS, obtained from GC/MS runs, with the products formed during the bromination studies (see section 2.2).

Table 2.6: Product distribution for the reaction of IBr with the model alkenes.[a]

Model alkene	% Mono bromide	% Monobromo alkenes	% Dibromide	% Dibromo alkenes
TMP-1	-	27	72	-
TMP-2	34	46	16	2
3-Ethyl-2-pentene	44	-	56	-

a : Uncalibrated GC peak areas.

2.3.2 Reaction of ICl formed in-situ with TMP-1.

As shown above the use of the interhalogen compounds leads to a few problems. Firstly, the interhalogens are unstable (air and light sensitive) and dissociate in solution to form the molecular halogens, which then react with the model alkenes. Another drawback of the interhalogens is that they are expensive to produce. Unsaturated adducts are produced from the reaction of the interhalogens with the model alkenes, however these electrophiles are much more selective than chlorine and bromine. Overall, the most selective addition reactions resulted from using ICl.

Attempts to produce ICl *in-situ* by bubbling chlorine gas through a solution of *p*-xylene containing TMP-1 (1:1 ratio of solvent to alkene) and iodine have proven unsuccessful. Analysis of the reaction mixture by GC/MS shows that the reaction mixture contains a wide range of products, although none were found to contain iodine. As observed for the chlorination of the model alkenes (section 2.1.2.3) along with halogenation of the alkene the solvent has also participated in the reaction, 43% of the reaction mixture is 1-chloro-2,5-dimethylbenzene (**2.1**). The major products formed form the alkene are unsaturated adducts containing two chlorine atoms (relative peak area 34%).

2.4 Summary and conclusions.

The addition of chlorine to the four model alkenes was performed in *p*-xylene and has highlighted a number of problems. In each case a plethora of saturated and unsaturated compounds are produced which contain between two and four chlorine atoms, only minor amounts of the expected dichloroalkane addition product are formed (between 0% and 30%). As discussed in section 2.1.1 the reaction mixture is made more complex by competitive chlorination of the solvent. Halogenation of *p*-xylene occurs at both the benzylic and ring positions to give mono- and dichlorinated xylenes. However, for the more reactive alkenes, such as TMP-1 and TMP-2, these solvent products form only minor impurities.

The product distributions from the chlorination of each of the model alkenes are consistent with the reaction occurring via an addition-elimination mechanism.[79] Our expectation is that the intermediate for the addition of chlorine to the alkenes involves a carbocation intermediate rather than a chloronium ion.[74] The formation of such a large number of products is thought to be consistent with the formation of a monochloroalkene containing either an allylic or vinylic chlorine. The chlorine atoms in vinylic positions will not be susceptible to nucleophilic substitution reactions, and thus would form the residual chlorine in the PIB system. However, none of the monochloroalkenes are observed in the final reaction mixture due to the formation of secondary products and attempts to distinguish between the two types of chlorines in the dichloroalkene products from their mass spectra has proved impossible.

A simpler reaction sequence of the model alkenes occurs with less reactive halogens, such as bromine and iodine containing electrophiles. For example, the reaction of 1-octene with chlorine results in the formation of modest amounts of the dichlorinated adduct (30% of the total peak area for the chlorinated alkene products) with the majority of the reaction mixture consisting of a number of dichloroalkenes (peak area 62%). However, the bromination of 1-octene in carbon tetrachloride produces 95.4% of the dibromide, 1,2-dibromooctane (**2.7**), whilst ICl is the most selective electrophile resulting in only the Markovnikov and anti-Markovnikov addition products (peaks area 60% and 40% respectively). The increase in the selectivity of these halogens is a result of the ability of the halogen atom which act as an electrophile to expand its outer shell of electrons. In the case of bromine and iodine, therefore, the intermediate in the addition of the halogen to the 1-octene resembles a halonium ion. This is consistent with the following order for the bridging ability of halogens: I > Br >> Cl.[75] Thus the inability of chlorine to form a bridged intermediate means that a carbocation intermediate results even in non-polar solvents. This opens up the possibility of chlorination of 1-octene occurring by an addition-elimination mechanism and results in unselective chlorination.

Our experiments with the model alkenes, which contain a variety of alkyl substitution patterns, show that the structure of the alkene can also influence the nature of the intermediate and thus the product distribution. Even for the more selective halogens, such as bromine, the reaction with TMP-1 results in the formation of only 39% of the saturated dibromide compared to 95% for 1-octene under comparable conditions. This change in the selectivity reflects the increased stabilisation of a tertiary compared to a secondary carbocation centre or steric hindrance of the tertiary carbon (bromine is a rather large halogen atom). The steric crowding factor can also be seen during the same reaction with TMP-2 which gives only 3% of the expected saturated dibrominated compound. Use of ICl, the most selective halogenating reagent, gives a similar result.

In contrast to the chlorine system secondary reactions do not occur to such an extent during the bromination of TMP-1. This means that a number of unsaturated monobrominated compounds are present in the reaction mixture, which it is possible to tentatively assigned as allylic or vinylic bromide groups. The maximum amount of vinylic monobromide present in the reaction mixture was found to be no more than 1.5%. However, there are many vinylic type structures possible in the unsaturated compounds containing more than one halogen atom which cannot be identified. The results in this chapter suggest that the problems observed during the reaction of the halogens with the model alkenes come from the formation of unsaturated compounds. This problem can be overcome for the less substituted alkenes by using a more selective electrophile. However, in the case of the more substituted alkenes the formation of unsaturated products is mainly dependent upon their structure.

Chapter 3

Formation of Diamines from Epoxides

As described in the previous chapter halonium ions are important intermediates in the addition of halogens to alkenes, although simple carbocations may also play a role. Ring-opening of these cyclic intermediates can occur either by up take of a further halogen atom to give the addition product or elimination to give alkenic compounds containing a allylic or vinylic halogen atom. Selectivity in the addition to alkenes increases with decreasing electronegativity of the halogen molecule. Thus iodine is more selective than is bromine, which in turn is more selective than chlorine. Fluorine is too reactive to be used safely, *i.e.* a mixture of fluorine and a alkene is explosive. The instability of the halonium ion means that it is a short lived intermediate and therefore such species are not available as starting materials for organic synthesis. However, many three membered heterocyclic compounds are versatile intermediates in organic synthesis. Examples include epoxides, or oxiranes to use their systematic name, which are easily prepared from alkenes by a number of different routes and are, on the whole, relatively stable to ring-opening by water in the air at room temperature. The three-membered ring oxiranes are ethers but particularly reactive ones due to their large ring strain.[125] Compared to their analogous open-chain relatives, which are characterised by inertness, the polarity and strain of the three-membered ring structure makes them susceptible to reaction with a large number of nucleophilic reagents.[126]

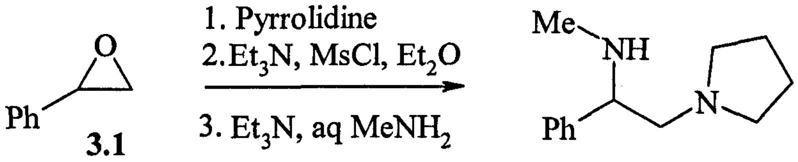
The aim of this work was to develop new or improved synthetic routes to compounds of interest as additives for engine oils; any method of functionalising the end group of polyisobutene (PIB) being of interest. A simple and effective route to convert styrene oxide (**3.1**) into a series of diamines in high yields has recently been reported, the overall reaction being set out in scheme 3.1.[111] This procedure might be of significance for the synthesis of diamine additives because:

1) PIB epoxide is readily available and the epoxidation of the four model alkenes is easily achieved by direct oxidation and

2) the types of primary and secondary amines that can be used for nucleophilic ring-opening of epoxides is fairly general.

This route will hopefully provide an effective way of making chlorine free additives.

Scheme 3.1: Typical procedure for the preparation of diamines from stryene oxide.

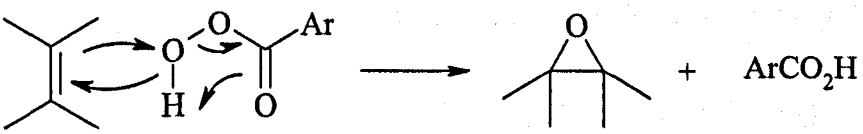


This methodology is more appealing to us than the direct aziridination of olefins followed by nucleophilic ring-opening with an amine which requires metal-catalysed, such as copper and rhenium complex, and PhI=NTs ([*N*-(p-toluene-sulfonyl) imino]phenyliodinane) as the nitrene source and results in relatively low yields after the aziridination step.[127]

3.1 Epoxidation of the model alkenes.

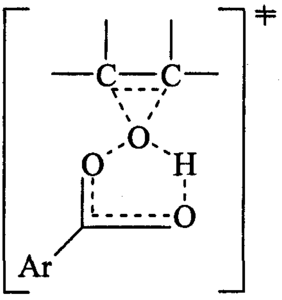
In this section, as in the previous chapter, model systems have been used to study the formation and nature of reaction products. The most frequently used method for the preparation of oxiranes in the laboratory is the Prilezhaev reaction, which involves peroxy acid oxidation of the alkenic compound. The mechanism for this reaction is thought to involve transfer of an oxygen directly from the peroxy acid to the alkene, as shown in scheme 3.2.[128]

Scheme 3.2: Epoxidation of alkenes with organic peracids.



The activated complex during the electrophilic addition of peracids to unsaturated compounds is claimed to be a symmetrical 3-membered cyclic transition state

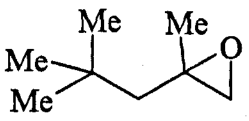
(**3.2**).[129] Consistent with the proposed mechanism the Hammett reaction constants (ρ) determined for a number of alkenes are negative and small suggesting that development of positive charge in the transition state is minimal.



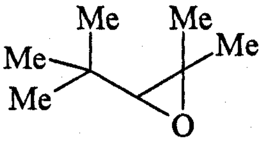
3.2

Electron-repelling groups on the alkene increase the rate of epoxidation and for simple alkyl-substituted olefins, the relative rate of reaction increases with the number of substitutents: $R_2C{=}CR_2$ > $R_2C{=}CHR$ > $R_2C{=}CH_2$, $RCH{=}CHR$ > $RCH{=}CH_2$ > $H_2C{=}CH_2$.[128, 130]

The most commonly employed peroxy acid for the direct oxidation of olefins is *m*-chloroperbenzoic acid (*m*-CPBA). Treatment of 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene with *m*-CPBA in an inert solvent (chloroform) yields the corresponding epoxides, 1,2-epoxy-2,4,4-trimethylpentane (**3.3**) and 2,3-epoxy-2,4,4-trimethylpentane (**3.4**) respectively. Although the peroxy acid oxidation of alkenes usually gives good yields of the epoxide the reaction of *m*-CPBA with the model alkenes gave poor yields. In previous chapter (Chapter 2) 1-octene was used as the monosubstituted alkene. Here 1,2-epoxydecane has been employed as the model because this compound is available commercially.



3.3



3.4

3.2 Ring-opening reactions of epoxides.

The initial step in the formation of diamines from styrene oxide (scheme 3.1) involves the nucleophilic ring-opening of the three-membered ring by an amine to form a 1,2-disubstituted product. Ring-opening of the strained three-membered ring can occur under acidic, basic or neutral conditions and results in a lower-energy, more stable product.[126] Epoxides can be opened by a whole range of nucleophiles including water, alcohols, amines and acids. In the course of the experiments described here only nitrogen containing nucleophiles have been used under neutral conditions.

Sharpless and co-workers found that 1,2-epoxydecane can be ring-opened by a range of secondary amines, *e.g.* dimethylamine (yield = 82%), pyrrolidine (85%) and dibenzylamine (65%), to form the amino-alcohol in good to excellent yields.[131] To check the process, the same epoxide was ring-opened by refluxing the epoxide in THF with 1.5 equivalent of the amine. Surprisingly, repetition of this experiment in our hands, using pyrrolidine as the amine, led to only the starting material being recovered. Even after refluxing in toluene at 111 °C for 16 h only 47% of the epoxide had been converted to the amino-alcohol. However, switching to a more polar solvent, ethanol, was more productive the hydroxyamine now being obtained. Regioselectively 1-(pyrrolidin-1-yl)-decan-2-ol (**3.5**) was produced in a yield of 86 %, as a yellow oil. The polarity of the solvent used seems to have an important effect on the ring-opening of epoxides under neutral conditions using amines. With water as the solvent simply mixing and standing the epoxide and pyrrolidine together at room temperature for 16 hours resulted in 86% yield of 1-(pyrrolidin-1-yl)-decan-2-ol, as the sole product by NMR (^{1}H and ^{13}C) and GC. It was noted that although in theory two isomers of the hydroxyamine could be formed only the α-amino-β-alcohol was recovered, the same regioselectivity was observed by Sharpless and co-workers using straight-chain epoxides.[131]

The experimental conditions developed above have been used to convert 1,2-epoxydecane into a number of hydroxyamines in good yields (scheme 3.3). The amino-alcohols formed by the various epoxide ring-opening reactions are shown in table 3.1.

Scheme 3.3: General reaction for nucleophilic ring-opening of 1,2-epoxydecane.

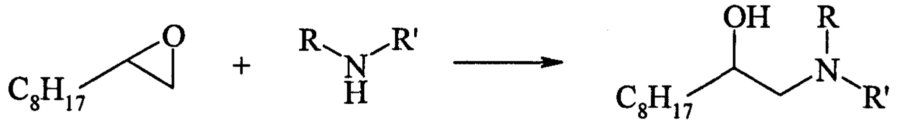


Table 3.1: Formation of amino-alcohols from 1,2-epoxydecane.

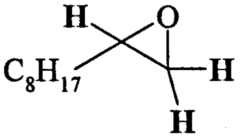
Amine	Solvent	R	R'	Yield (%)
Pyrrolidine	Ethanol or water	$-(CH_2)_4-$		86[a]
Octylamine	Ethanol	C_8H_{17}	H	81
Octylamine	Water	C_8H_{17}	H	80
Butylamine	Water	C_4H_9	H	84

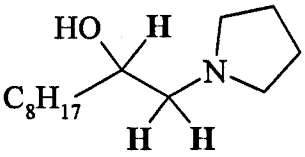
a : Both solvents (ethanol and water) gave approximately the same percentage yield.

Ring-opening of alkyl substituted epoxides results in the formation of an amino-alcohol. It is generally agreed that in neutral solutions nucleophilic attack on the epoxide takes place by an S_N2 mechanism.[126] The nucleophile attacks the backside of the epoxide carbon thus the stereochemistry of the final product should be *trans* although such stereochemical control would not be apparent in a monosubstituted epoxide. When the epoxide is unsymmetrical, as for 1,2-epoxydecane, nucleophilic substitution can occur in two positions, the regioselectivity is determined by the substituents on the epoxide and the reaction conditions employed. In all cases the sole product of our reactions (table 3.1) was a 1-amino-2-hydroxyl derivative, stemming from nucleophilic attack at the least substituted carbon atom. This would be expected for a S_N2 type reaction where electronic factors are generally of limited importance.[125] No secondary condensation products, due to the reaction of the amino-alcohol with a second epoxide molecule, were detected.

The amino-alcohols were identified by NMR and mass spectroscopy; for example with 1-(pyrrolidin-1-yl)-decan-2-ol (**3.5**) the multiplet CH proton resonance in 1,2-epoxydecane is shifted downfield in the product (figure 3.1). The regiochemistry is assigned on the basis that the CH_2 protons are at higher field than the CH signal, consistent with their being next to an atom of lower electronegativity, *i.e.* nitrogen rather than oxygen.

Figure 3.1: Selected ^1H NMR resonance's for 1,2-epoxydecane and 1-(pyrrolidin-1-yl)-decan-2-ol.





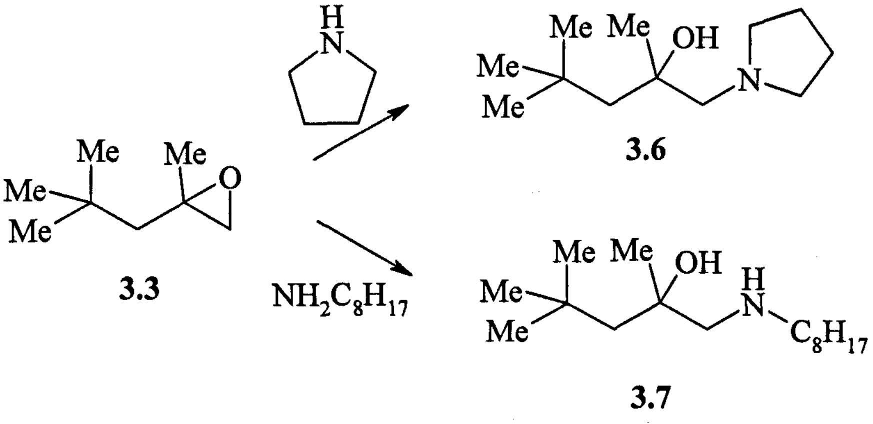
(3.5)

CH shift (p.p.m.);	δ_H	2.84-2.78 (1H, m)	3.60-3.55 (1H, m)
CH_2 shifts (p.p.m.);	δ_H	2.65 (1H, dd)	2.50 (1H, t)
		2.37 (1H, dd)	2.21 (1H, dd)

The GC trace of this product shows only one peak the mass spectrum of which is again consistent with its being 1-(pyrrolidin-1-yl)-decan-2-ol. The mass of the most intense fragment corresponds to the $[CH_2\text{-}C_4H_8N]^+$ ion (*m/z* 84, relative intensity 100%). This peak would not be expected if the amino-alcohol was the α-hydroxy amine.

The epoxides synthesized from 2,4,4-trimethyl-1-pentene (TMP-1) and 2,4,4-trimethyl-2-pentene (TMP-2) were treated with various amines. 1,2-Epoxy-2,4,4-trimethylpentane (**3.3**) has been ring-opened successfully in refluxing ethanol by pyrrolidine and octylamine, to yield the expected adducts (scheme 3.4). Nucleophilic substitution of the epoxide by pyrrolidine results in the formation of 1-(pyrrolidin-1-yl)-2,4,4-trimethylpentan-2-ol (**3.6**) and octylamine gives 1-(N-octylamino)-2,4,4-trimethylpentan-2-ol (**3.7**, percentage yield = 88%). Both crude products were purified by bulb-to-bulb vacuum distillation to give the amino-alcohol as a yellow oil. The yields of **3.6** and **3.7** were 85% and 88% respectively. As with the ring-opening of 1,2-epoxydecane, both of these reactions produce only the β-hydroxy isomer of the amino-alcohol as shown by a single peak in the GC trace and one set of peaks in the NMR spectrum of the product.

Scheme 3.4: Nucleophilic amination of 1,2-epoxy-2,4,4-trimethylpentane (**3.3**).

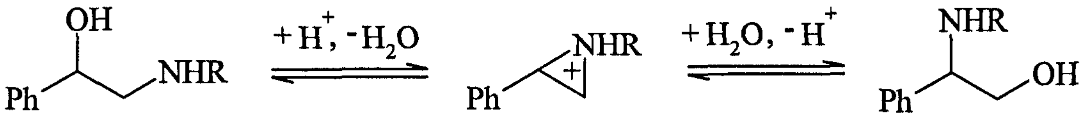


Graham and co-workers found that the sterically hindered epoxide 2,3-epoxy-2,4,4-trimethylpentane (**3.4**) could not be ring-opened by diethylamine in an ethanolic solution at 180 °C in a sealed tube.[132] Our studies confirm that the epoxide ring this compound is too hindered for ring-opening to occur under standard conditions (refluxing in ethanol with 1.5 equivalents of pyrrolidine). This result should not be a problem for this synthetic approach because the major end-group present in PIB resembles that found in TMP-1. Therefore we would expect ring-opening of PIB-epoxide to give similar results to those obtained for 1,2-epoxy-2,4,4-trimethylpentane. However, unpublished work performed at Adibis suggest that in fact PIB-epoxide cannot be ring-opened by amines. This unexpected result can only be due to the steric hindrance of the epoxide ring, as was the case for 2,3-epoxy-2,4,4-trimethylpentane, but with PIB this problem is amplified by the long alkyl chain.

3.3 Preparation of diamines.

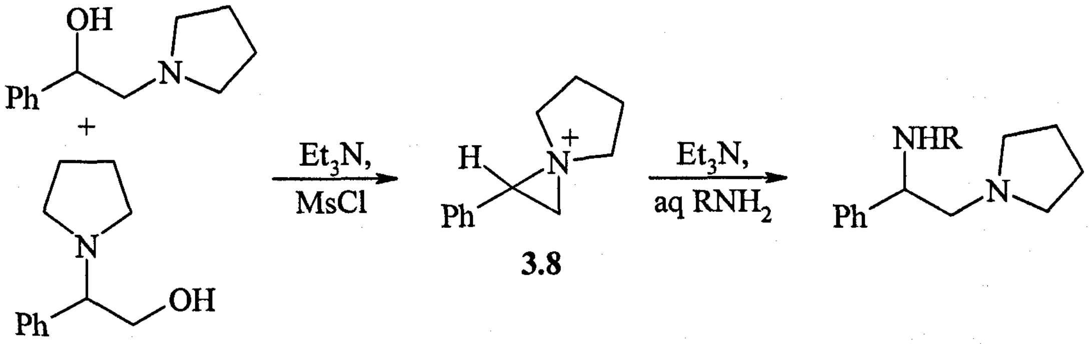
Surprisingly ring-opening of (R)-styrene oxide with pyrrolidine gives two alcohols which are regioisomers.[111] However, only the β-hydroxy isomer is formed from monoalkyl substituted epoxides. This suggests that an equilibrium exists between the regioisomers when the β-position of the amino-alcohol is benzylic, perhaps due to the stabilization of the carbocation by the phenyl ring or even to formation of an intermediate aziridinium ion (scheme 3.5). The ratio of the α- to β-hydoxy isomer is 30:70, representing preference for the benzylic ring-opening.

Scheme 3.5: Equilibrium between the α- and β-hydroxy derivatives from styrene oxide.



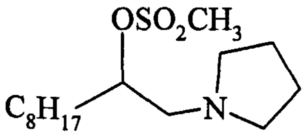
O'Brien and Poumellec have shown that treatment of these isomeric amino-alcohols with mesyl chloride, in the presence of triethylamine, results in a single aziridinium ion (**3.8**).[111] Formation of the diamine then proceeds by opening of the aziridinium ion with a second amine (added in aqueous solution) at the benzylic position (scheme 3.6).

Scheme 3.6: Formation of diamines from amino-alcohols.

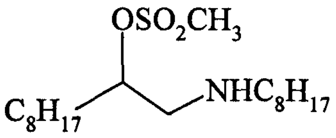


The process shown in this scheme appealed to us because the second nitrogen function can be derived from a wide range of amines including ammonia, methylamine, *t*-butylamine and aniline.

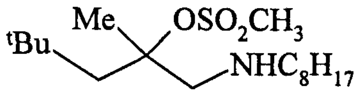
Addition of mesyl chloride to a solution of 1-(pyrrolidin-1-yl)-decan-2-ol (**3.5**) containing triethylamine (3 equivalents) results in the formation of insoluble triethylammonium chloride as a white solid. The formation of this precipitate suggests that the methanesulfonic acid ester derivative has in fact been produced. However, the second step was not as successful and after stirring with methylamine (40% aqueous solution) at room temperature for 16 h no diamine formation occurred. The material recovered, is not the original alcohol, but is believed to be the mesyl derivative of the alcohol, 1-(pyrrolidin-1-yl)-decan-2-yl methanesulfonate (**3.9**). The NMR spectra of the starting material and **3.9** are very similar except for the presence of an extra resonance in **3.9** assigned to the mesyl group [δ_H 2.39 (s, 3H, $-OS(O)_2C\underline{H}_3$)].[114] In the ^{13}C NMR spectrum the chemical shift for the CH carbon next to the O-Ms group has been displaced upfield relative to the same peak in the starting material [CH shift (p.p.m.); **3.5** $\delta_{CH} = 68.2$ and **3.9** $\delta_{CH} = 61.5$].



3.9



3.10



3.11

Conversion of the alcohol group to the methanesulfonic acid ester derivative was expected to result in an intermediate which could readily be converted to a diamine. As methanesulfonate esters are labile leaving groups, **3.9** might be expected to hydrolyse readily to the alcohol during the aqueous workup. One explanation for the lack of reactivity of the mesyl amine is that the two phase nature of the reaction mixture prevents interaction of the two compounds; the amine being more soluble in water and **3.9** in the organic phase. It was argued that the use of a homogenous reaction mixture might overcome this problem. However, no diamine was detected by GC analysis after 1-(pyrrolidin-1-yl)-decan-2-yl methanesulfonate (**3.9**) was refluxed for 16 h in ethanol (10 cm^3) with 2 equivalents of methylamine (1.1 cm^3 of 40% aqueous solution). This suggests that the aziridium ion, similar in structure to **3.8** (scheme 3.6), is not formed from 1-(pyrrolidin-1-yl)-decan-2-ol or its mesylated derivative. Unlike an alkyl group, the phenyl ring in the benzylic position of **3.8** appears to facilitate ring-closure by aiding the polarisation of the carbon-oxygen bond and thus making the carbon more susceptible to nucleophilic attack.

The alcohol group in 1-(pyrrolidin-1-yl)-2,4,4-trimethylpentan-2-ol (**3.6**) is considerably more hindered than that in 1-(pyrrolidin-1-yl)-decan-2-ol (**3.5**), due to the presence of an extra methyl and *t*-butyl group. It was thought that the presence of two electron-donating groups on the carbon next to the mesylated oxygen could well act to stabilize the positive charge developing on the β-carbon in the intermediate ion. However, in this case the steric factor of these extra groups must be too great since only the starting material (the amino-alcohol) was recovered after addition of methanesulfonyl chloride to **3.6**, under the same conditions used with **3.5**.

3.4 Preparation of aziridines.

Ring closure of the amino-alcohols produced by the ring-opening of the model epoxides with primary amines, such as octylamine, would result in neutral aziridines. This is in contrast to the aziridinium ions which are only short lived intermediates produced from the ring closure of amino-alcohols containing tertiary amines.[133] The synthesis and subsequent isolation of aziridines was attempted in order to study this reaction.

No aziridine formation was observed after treating 1-(N-octylamino)-decan-2-ol, in dry ether, with methanesulfonyl chloride in the presence of an excess of powdered potassium hydroxide. After refluxing the reaction mixture for 4 h this reaction product was isolated and identified as the O-mesyl derivative of 1-(N-octylamino)-decan-2-ol, 1-(N-octylamino)-decan-2-yl methanesulfonate (**3.10**): the chemical ionisation (CI) mass spectrum contains a molecular ion of *m/z* 364 (MH+, relative intensity 1%), which shows the lose of the mesyl group (*m/z* 284, M $-SO_2Me$, 5%), and an intense fragment ion of *m/z* 142 (relative intensity 100%) for $[CH_2\text{-}NH\text{-}C_8H_{17}]^+$. In addition the ^1H and ^{13}C NMR spectra contain new resonances for the extra methyl group [δ_H 2.83 (s, 3H, $-OSO_2C\underline{H}_3$) and δ_C 37.9 (CH_3, $-OSO_2\underline{CH_3}$)].

A similar result is obtained when 1-(N-octylamino)-2,4,4-trimethylpentan-2-ol (**3.7**) is subjected to the same reaction conditions, the new proton resonance in the ^1H NMR spectrum of the O-mesyl derivative (**3.11**) is observed as a singlet at 3.29 p.p.m. (3H) and the methyl carbon appears at 43.7 p.p.m. in the ^{13}C NMR spectrum.

Further treatment of 1-(N-octylamino)-2,4,4-trimethylpentan-2-yl methansulfonate (**3.11**), formed from the mesylation of 1-(N-octylamino)-decan-2-ol, with an excess of powdered potassium hydroxide (8 equivalents) in dry diethyl ether followed by refluxing for 16 h gave back only starting material. We considered the possibility that the powdered potassium hydroxide is not soluble enough in the ether to be able to extract a hydrogen atom from the amine group. However, even repetition of the reaction in water (15 cm^3) with potassium hydroxide (6 equivalents) resulted in no aziridine being formed. When the O-mesyl derivative was subjected to the procedure used for 1-(pyrrolidin-1-yl)-decan-2-ol (**3.5**) (methylamine and triethylamine) again no reaction occurred. This result suggests that either the aziridine is not stable enough to be isolated, although there is no evidence for its formation *i.e.* the ^{1}H NMR spectrum of the reaction mixture is the same as the starting material.

Sekera and Marvel reported that *n*-butyl *p*-toluenesulfonate readily alkylated *n*-butylamine, on refluxing the two compounds in dry toluene, to give a mixture of the secondary and tertiary amines.[134] Unfortunately, alkylation of *n*-butylamine (1.1 equivalents) with the methanesulfonate (**3.11**) by refluxing in dry toluene for 16 h was also unsuccessful.

3.5 Summary and conclusions.

A simple and effective route for converting styrene oxide into a series of diamines in high yields has been published.[111] This lead us to investigate a novel method for the functionalisation of PIB. Our aim was to see if this process could be developed to convert the epoxides of the model alkenes into diamines.

Epoxidation of the model alkenes was easily achieved, although often in relatively poor yields, by direct oxidation using *m*-CPBA. The epoxides of TMP-1, TMP-2 and decane were employed as models for PIB-epoxide in our attempt to produce diamines from alkyl substituted epoxides.

The initial step in the formation of diamines from the model epoxides is nucleophilic ring-opening with amines to form amino-alcohols. Ring-opening of 1,2-epoxydecane and 1,2-epoxy-2,4,4-trimethylpentane (**3.3**) was successful under relatively mild conditions with secondary and primary amines, pyrrolidine and octylamine. However, 2,3-epoxy-2,4,4-trimethylpentane is too sterically hindered to be ring-opened by amines. The nucleophilic attack of the amine on the epoxide was always regioselective and high yielding (percentage yield ranged from 80 to 88%).

For example 1-(pyrrolidin-1-yl)-decan-2-ol (**3.5**) was the sole product from the reaction of 1,2-epoxydecane with pyrrolidine in water at room temperature. The regioselectivity of this reaction is probably due to steric crowding of the alkyl substituted epoxide carbon.

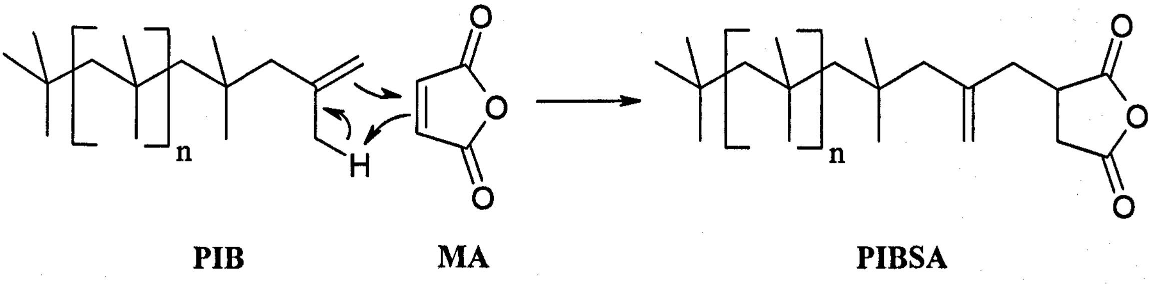
O'Brien and Poumellec have shown that treating the amino-alcohol, formed by ring-opening of styrene oxide with pyrrolidine, with mesyl chloride in the presence of a second amine, such as methylamine, leads to the formation of a diamine.[111] It has been suggested that the intermediate in this reaction is an aziridinium ion (**3.8**). However, our attempts to form diamines from **3.5**, and the other amino-alcohol derivatives of 1,2-epoxy-2,4,4-trimethylpentane (**3.3**) and 1,2-epoxydecane, under similar conditions as those used by O'Brien and Poumellec[111] have proven unsuccessful. The different results from the two systems has been attributed to the extra stabilisation of positive charge at the benzylic position during formation of the aziridinium ion (**3.8**). It is thought that in the case of the 1-amino-2-alcohol systems produced from the epoxides of the model alkenes the alkyl group does not provide enough stabilisation for the developing charge at the carbon attached to the mesylated oxygen. This hypothesis is reinforced by the fact that, unlike the case of styrene oxide analogue, mesyl ester derivatives of the amino-alcohols are stable enough to be isolated and characterised. Even with amino-alcohols, produced from the model alkenes, containing a secondary amine formation of the more stable aziridines on addition of mesyl chloride in the presence of a base does not occur. It appears, therefore, that the formation of diamines by the proposed route is not possible for alkyl, as opposed to benzyl, substituted epoxides. Overall, these results are consistent with the ring-closure of amino-alcohols having an early rather than a late transition state.

Chapter 4

Investigations into the PIBSA Reaction

Chapters 4 and 5 detail an investigation of the procedure for the preparation of polyisobutylene succinic anhydride (PIBSA). As was described in the introduction (section 1.3.2), PIBSA, a key intermediate in the production of oil additives, is produced by the thermal condensation of maleic anhydride (MA) and polyisobutylene (PIB) at temperatures between 200 and 250 °C. Scheme 4.1 depicts the reaction in which the ene component is PIB and the enophile MA.

Scheme 4.1: The ene reaction between PIB and MA.



This thermal process is very efficient, resulting in high conversions of PIB to PIBSA (~ 85%). However, problems arise because, amongst the reaction products, are unidentified coloured materials, which must be removed by an expensive and time consuming filtration process. It is believed that these coloured by-products are of a resinous nature. On the assumption that its origin is a free-radical process various free-radical inhibitors have been employed in attempts to reduce the amount of resin formed, but these have been found to have little or no effect on the formation of by-products.[136] The unidentified by-products do not interfere with the imidation of PIBSA to form the additive, or with the subsequent performance of the lubricant package. However they do contribute to the dark colour of the additive package which leads to significant market resistance. Up to the present the only investigations into the structure of the by-products have been internal industrial reports.[112, 136] These provide limited explanations for the nature of any resins based on the assumption that they are formed from MA. The aim of the work described here is to obtain more information on the nature and formation of these tars and resins.

As has been noted earlier PIB is a complex mixture of high molecular weight alkenes and as such is an unsuitable substrate for a detailed study of mechanistic features. To circumvent this problem various model alkenes have been used which contain a much shorter alkyl chain and have end-group functionalities which mimic the reactivity of Ultravis and Hyvis, the two principal industrial versions of PIB. Another advantage to using pure model alkenes is that the reactivity of a single type of substituted alkene can be examined at a time. The standard reaction conditions used for the ene reaction involve heating at 200 °C for between 4 and 6 h. Thus for more volatile alkenes a sealed system must be used.

To overcome the problems with low boiling point alkenes initial studies were carried out using 1-octadecene as the ene component (boiling point = 179 °C at 15 mm Hg). Due to the high boiling point of 1-octadecene it was possible to use similar conditions for the ene reaction to those employed by Adibis to produce PIBSA. This allows large scale reactions using 1-octadecene to be carried out in the laboratory with varying molar ratios of MA. To control the formation of poly(octadecenyl succinic anhydride) a radical inhibitor has been added to the reaction mixture before heating commences. The best results reported previously were when 2,6-di-t-butylphenol was employed at 1% by mass of alkene and therefore a similar arrangement was employed in this system.[136] An added advantage of this system is that the ene adduct, octadecenyl succinic anhydride, is available as a commercial material (Aldrich). However, the alkene contains a straight alkyl chain and it does not exactly mimic the branching of PIB. Therefore later investigation detailed in this chapter make use of diisobutylene. Unfortunately this is a relatively volatile alkene with no commercially available ene adduct.

4.1 Reaction of MA with 1-octadecene.

This procedure was adapted from that used for a standard PIBSA reaction.[137] The alkene is charged to the reaction vessel together with a 1.3 molar ratio of powdered MA. The stirred reaction mixture is then heated at 200 °C for 6 h. During reflux the reaction mixture develops a dark brown colouration due to the build-up of tar and resin. After refluxing for 6 h the temperature was raised to 205 °C and the unreacted MA stripped under reduced pressure (~ 5 mm Hg) for an hour. Finally, the stirring is stopped and the system discharged at 100 °C. The insoluble by-products were removed from the residue by filtration through a dry celite cake which was then washed with petroleum. The reaction mixture was collected as a liquid which solidified on cooling.

The ^1H NMR spectrum of the reaction mixture from the reaction of 1-octadecene with one molar ratio of MA shows that all unreacted starting materials (unreacted alkene and MA) have been removed (either by reacting or vacuum distillation). In the alkenic region of both the ^1H and ^{13}C NMR spectra there are only four sets of signals visible, which have been assigned to the sp^2 carbon atoms and their associated protons of the *cis* and *trans* isomers of the ene adduct.[107]

The crude reaction mixture was filtered through warmed celite in the same way as is used with PIBSA to remove the insoluble by-products. Unlike PIBSA, which is a viscous oil, octadecenylsuccinic anhydride is a yellow solid (melting point 60-64 °C), thus the reaction mixture needed to be handled when hot to avoid crystallisation of the product. Residual octadecenylsuccinic anhydride and the PIBSA soluble by-products were washed through the hot celite with hot SBP-5 (the petroleum cut boiling at 100-150 °C). The celite was then dried and weighed to calculate the amount of insoluble by-products.

With a one molar ratio of alkene to MA the amount of unreacted MA was 10%, suggesting that functionalisation of 1-octadecene is incomplete. In table 4.1 the results of a range of experiments are set out in which differing ratios of alkene to MA were subjected to the standard reaction conditions described above. As would be expected the amount of MA recovered is dependent on the molar ratios used. Assuming that only the 1:1 MA:alkene adduct is formed then the unreacted MA should all be recovered by distillation, however this is not the case. There is discrepancy between the theoretical amount of MA that we would expect to recover (theoretical amount of unreacted MA = molar equivalents of MA – 1) and the amount recovered by distillation, which is between 15 to 23% below the theoretical value. It was also noted that the colour of the reaction mixture increases with the molar ratio of MA used suggesting that the coloured by-products are either due to decomposition of MA, the 1:1 MA:alkene adduct or perhaps both.

Table 4.1: Reaction of 1-octadecene with various charge molar ratios of MA.

Entry	Alkene / Mol	MA / Mol	MR of MA:Alkene	Percentage MA recovered	Insoluble Material / g
1	0.28	0.0	0	0	0.1
2	0.28	0.14	0.5	a	0.4
3	0.28	0.28	1.0	10	5.6
4	0.28	0.42	1.5	a	a
5	0.43	0.86	2.0	34	2.5
6	0.28	0.69	2.5	44	0.5
7	0.43	1.30	3.0	48	a
8	0.28	0.97	3.5	42	a
9	0.24	0.97	4.0	47	0.2
10	0.28	1.25	4.5	52	0.2
11	0.43	2.16	5.0	57	0.8

a : Values not measured.

There are two explanations for the disappearance of MA:

1. Polyfunctionalisation of 1-octadecene by reaction of octadecenyl succinic anhydride with an additional molecule of MA.

2. Decomposition of MA or the alkenyl succinic anhydride (ASA) within the reaction system.

It is relatively simple to assess the stability of MA and octadecenyl succinic anhydride to the reaction conditions using appropriate samples of each (the stability of MA will be discussed later in this thesis, Chapter 5). After heating octadecenyl succinic anhydride, a yellow solid (6 g, Aldrich), for 6 h at 200 °C a slight colouration of the reaction mixture did develop. However, comparison of the ^1H NMR spectra of the reaction mixture with that of pure 1-octadecenyl succinic anhydride showed them to be identical with no evidence of decomposition products. It is assumed therefore that decomposition of the 1:1 MA:alkene adduct is not an important factor in the formation of by-products for this system. Another important observation is that the 1:1 adduct does not react further with MA as there is no evidence in the ^1H NMR spectrum of entry 3 (table 4.1) for the difunctionalised product, all the alkenic signals have already been assigned.[107] This is backed up by the report in the literature that the reaction of a second molecule of MA with PIBSA, even when it contains a reactive external double bond, is apparently insignificant due to steric hindrance (the neopentyl effect).[12b]

The amount of insoluble resin shows no relationship to the number of equivalents of MA employed or to the amount of alkene. For instance the change in the insoluble material recovered for entries 2-6 (table 4.1) is difficult to explain. It has been suggested that the inconsistency in insoluble by-product formation is due to small fluctuations in reaction conditions *e.g.* stirrer speed, reaction temperature or time. The effects of these variables has not been investigated in any detail.

One observation of, perhaps, some relevance was that the reactants are immiscible at 200 °C, vigorous agitation of the reaction mixture (containing the ene and enophile) being needed to ensure good mixing of the two phases. The ene reaction can still presumably take place at the interface between the two layers but the process is hindered by poor mixing and the reaction rate will be related to interface surface area. From ^1H NMR measurements on the two phases it has been shown that the top layer contains mostly 1-octadecene [δ_H ($CDCl_3$) 5.91 (ddt, 1H, CH=), 5.05

(m, 2H, $CH_2=$)], whilst analysis of the larger bottom layer, which develops a dark brown colouration over the first 0.5 h of heating, suggests this to be the MA phase [δ_H ($CDCl_3$) 7.33 p.p.m. (s, 1H)]. A high stirring rate results in a more homogenous reaction mixture *i.e.* a fine dispersion of alkene in MA. However, the product mixture still develops a brown colouration due to the formation of soluble by-products irrespective of the rate of stirring.

Many of the experimental observations mentioned above, such as the increase in colour of the reaction mixture with the molar ratio of MA, point to the decomposition of MA as a possible cause for the coloured PIBSA soluble by-products. A more quantitative method for determining the concentration and structure of the coloured resin is required, given that none of the expected products absorb in the visible region of the spectrum. A possibility is that formation of resin could be monitored by UV-Vis spectroscopy. However, these by-products are present only as minor components in the reaction mixture, as shown by the NMR spectra of entry 3 in table 4.1 which only gives observable signals from 1-octedecenyl succinic anhydride. It would be preferable to separate and concentrate the coloured by-products before further analysis: this can be achieved using column chromatography or liquid chromatography (LC).

4.1.1 Separation of the coloured by-products.

Unreacted starting materials, octadecenylsuccinic anhydride and soluble by-products have been separated with some success by column chromatography of the crude reaction mixture (flash silica, initially 9:1 hexane:ethyl acetate as eluent). The sample used resulted from the reaction of 1-octadecene with two molar equivalents of MA (entry 5 in table 4.1). The column needs to be run quickly as slow decomposition of the anhydride-containing compounds can occur on the silica. Several later fractions were collected after increasing the ratio of ethyl acetate in the eluting solvent system. The first fraction of material recovered was identified by NMR as unreacted alkene, 1-octadecene (5.9% of the crude product). Recovery of unreacted alkene lends further evidence to the speculation that either difunctionalisation of 1-octadecene or decomposition of MA is taking place during the reaction. The major product, which accounted for 75% of the recovered material, has been identified from its ^{1}H and ^{13}C NMR spectra as a mixture of the *cis* and *trans* octadecenyl succinic anhydride through comparison of the NMR data of the ASA product formed from 1-decene.[107] However, a dark band of material remained on the column which could not be removed by washing even with a polar solvent such as methanol.

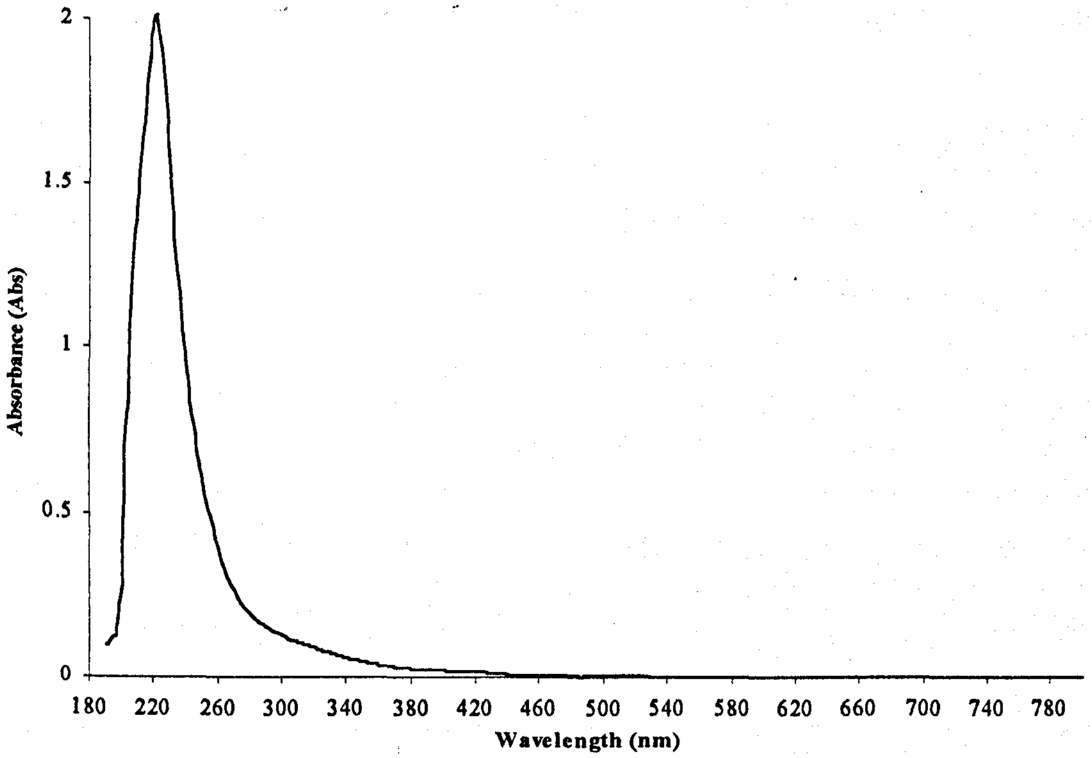
4.1.2 UV-VIS Spectrometry of the Crude Reaction Mixture.

The by-products that we are attempting to identify absorb in the visible region of the electromagnetic spectrum. It is suspected that the colour may come from a conjugated double bond system present in the resin. Problems arise due to the poor solubility of the reaction mixture in solvents that can be used to measure UV-Vis spectra and obtain LC/UV-Vis data. The reaction mixture is not soluble in low polarity solvents such as hexane (UV cutoff = 195 nm), which would be ideal for polarity gradient elution in LC experiments. The ideal solvent for solubility is acetone but this solvent has a UV-Vis cutoff of 360 nm. Thus a mixture of 10% ethyl acetate (UV cutoff = 256 nm) and hexane has been used to increase solubility and allow UV absorption of the components of the reaction mixture to be measured.

The $\pi \rightarrow \pi^*$ transition for octadecenyl succinic anhydride shows as a strong absorbance at a wavelength maximum (λ_{max}) of 222 nm, which is not terribly reliable because it coincides with the absorbance of ethyl acetate, whilst the $n \rightarrow \pi^*$ transition ($\lambda_{max} = \sim 330$ nm) is too weak to be detected at low concentrations. All the UV-Vis spectra recorded for entries 1 to 11 (table 4.1) contain a $\pi \rightarrow \pi^*$ transition at $\lambda_{max} = 256$ nm which is consistent with the formation of octadecenyl succinic anhydride. A typical UV-Vis spectrum of the crude reaction mixture, after removal of the excess MA, is shown in the spectrum in figure 4.1.

All the UV-Vis spectra run for the samples in table 4.1 showed the same general trend as that seen in figure 4.1, *i.e.* an increase in the intensity of the $\pi \rightarrow \pi^*$ transition with the molar ratio of MA, although the concentration of the ASA present in each reaction mixture should be constant. However, no absorption peak is observed in the visible region of the spectra although the samples are intensely coloured. As shown in figure 4.1 the peak at 222 nm tails into the visible part of the spectrum due to its broadness. This suggests that there may be unidentified compounds present in the reaction mixture which have a π→π* transition peak in the same region of the UV spectrum as octadecenyl succinic anhydride. Thus, our conclusion is that the increase in the π→π* transition intensity is produced by a by-product or by-products with higher absorbance coefficients than octadecenyl succinic anhydride. The concentration of these compounds presumably increases with the amount of MA present in the reaction mixture.

Figure 4.1: UV-Vis spectra of the crude reaction mixture obtained from the reaction of 1-octadecene with one molar equivalent of MA at 200 °C. This spectrum was recorded for 0.007 g of the reaction mixture in 10 cm^3 of solvent system (10% ethyl acetate: 90% hexane). All UV-Vis spectra were recorded against a solvent blank.

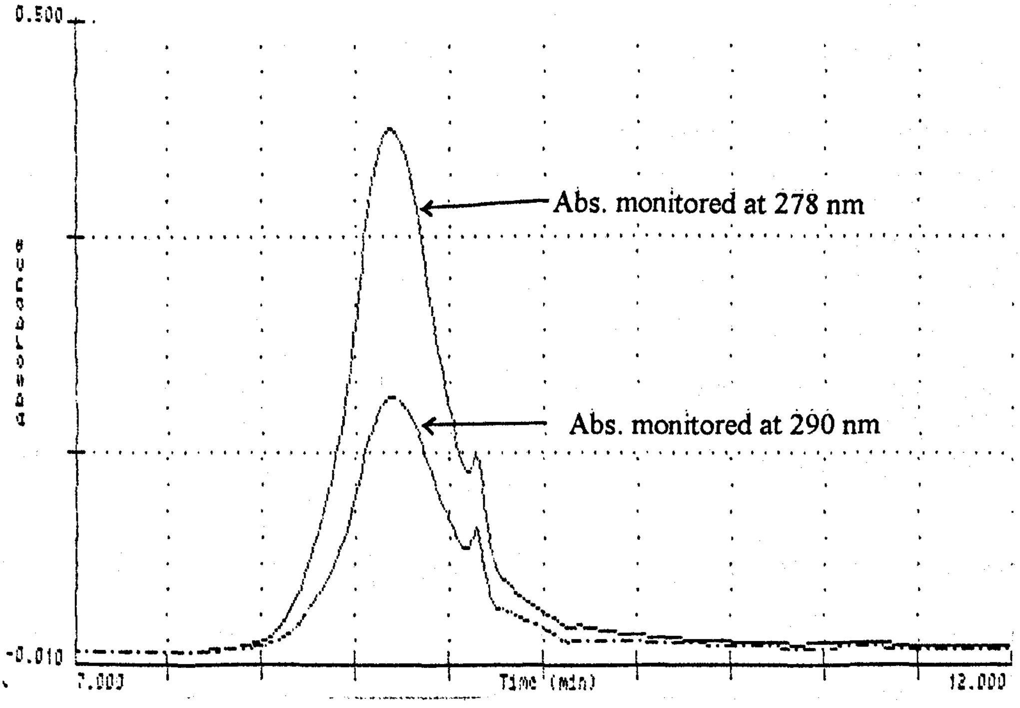


4.1.3 Liquid Chromatography (HPLC).

An explanation of the work described above (section 4.1.2) is that by-products formed during the ene reaction contain groups with strong π→π* transitions which tail into the visible region of the spectrum, resulting in the observed colour of the samples. It was hoped that separation of these by-products could be performed using liquid phase chromatography or high performance liquid chromatography (HPLC).

HPLC experiments were performed on a reverse phase column and elution of compounds was monitored using a UV-Vis detector (flow rate = 0.36 ml min^{-1}). The UV absorbance of the eluted liquid was monitored at various wavelengths (278, 290, 310 and 325 nm) which lie on the tail of the intense peak seen in the UV-Vis experiments (figure 4.1). Our aim was to elute the coloured by-products by gradually increasing the solvent polarity through the column.

Figure 4.2: LC trace of the crude reaction mixture obtained from the reaction of 1-octadecene with two molar equivalents of MA at 200 °C, result from a solution of 0.075 g filtered reaction mixture in 10 cm^3 of solvent system (10% ethyl acetate: 90% hexane). Method: 10% ethyl acetate: 90% hexane for 25 mins then increased polarity to 90% ethyl acetate:10% hexane over 26 mins.



A typical LC trace is shown in figure 4.2. Results obtained for all the reaction mixtures shown in table 4.1 are similar, the broad peak corresponds in retention time and absorbance to octadecenyl succinic anhydride. However, no peaks were observed at higher retention times, as a result of other reaction by-products. This remained the case when the percentage ethyl acetate in the elutent was increased to 95% or up to 100% methanol. Monitoring at higher wavelengths (above 400 nm) failed to detected any compounds, even for octadecenyl succinic anhydride, lending support to the hypothesis that the reaction mixture colour results from the tail of the broad UV absorption band at 256 nm (figure 4.1). However, separation of reaction products responsible for this peak was not possible using this method as they are probably all very similar in polarity and structure.

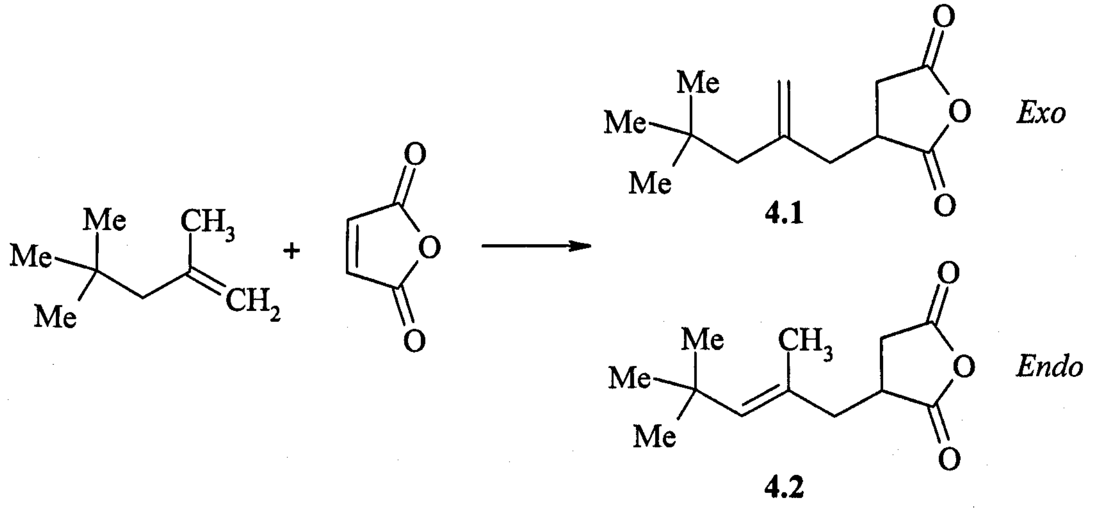
Using GC would enable better separation of the reaction mixture as it is more sensitive to differences in volatility, and the flame ionisation detector (FID) can detect tiny amounts of any organic impurities. Another advantage of GC analysis is that products can be identified after coupling to a mass spectrometer. However, the reaction products formed with 1-octadecene are not volatile. Therefore, it was decided to refocus our work on an ene reaction between MA and a more volatile alkene, such as 2,4,4-trimethyl-1-pentene (TMP-1). A further benefit of using this as a model system for the PIBSA reaction is that the alkene contains one of the end-groups found in PIB.

4.2 Preparation of diisobutylene succinic anhydride.

2,4,4-Trimethyl-1-pentene (TMP-1) was reacted with an excess of maleic anhydride (MA, 1.3 equivalents) at 200 °C in an autoclave for 4 h. After this reaction period the autoclave was left standing to cool for 0.5 h before opening. The reaction mixture was recovered as a dark brown/orange oil, similar in colour to PIBSA, although, unlike PIBSA, the reaction mixture did not contain any insoluble by-products. ^{1}H NMR analysis of this oil showed that the mixture contained unreacted MA (singlet at 7.33 p.p.m.), but no unreacted alkene was observed.

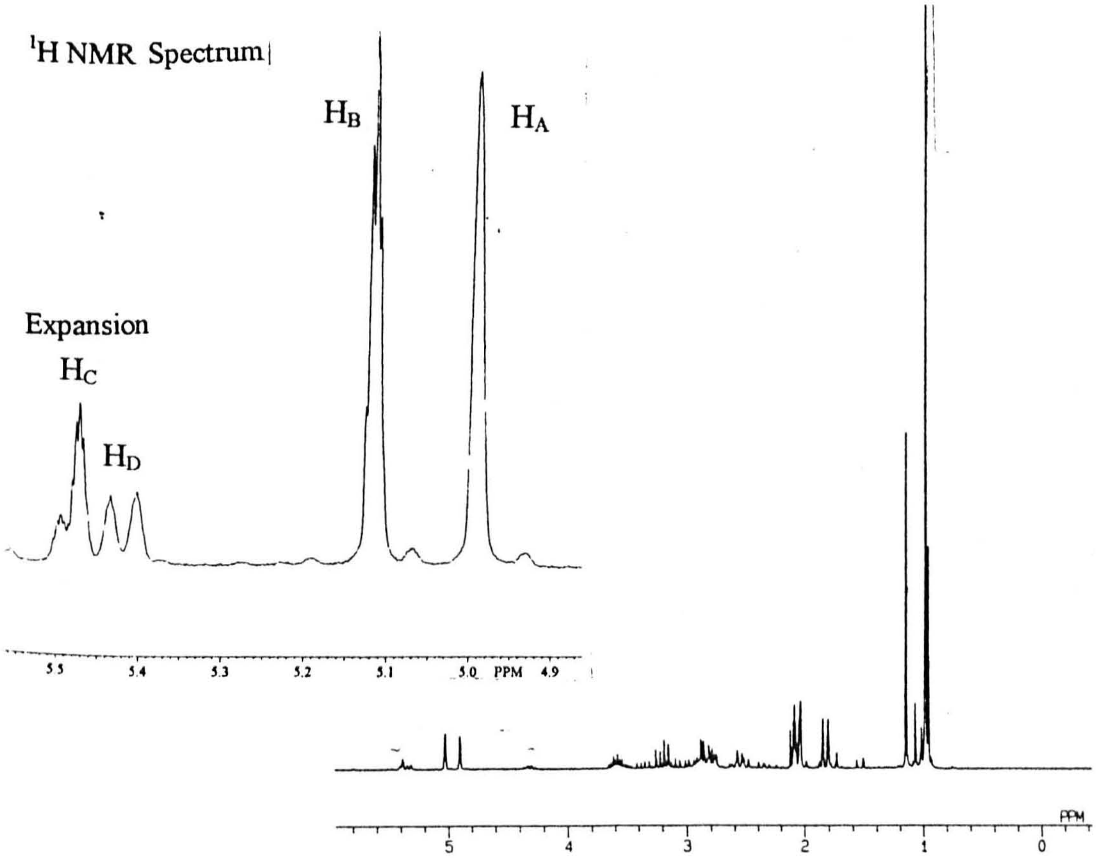
The excess MA was removed from the crude reaction mixture by bulb to bulb distillation (< 1 mm Hg) and collected as a white solid (recovery 58.7%). The second fraction distilled from the reaction mixture was a yellow oil containing a mixture of products (see analysis below). The residue left following the purification process was a brown sticky resin.

Scheme 4.2: Ene reaction between 2,4,4-trimethyl-1-pentene (TMP-1) and MA.

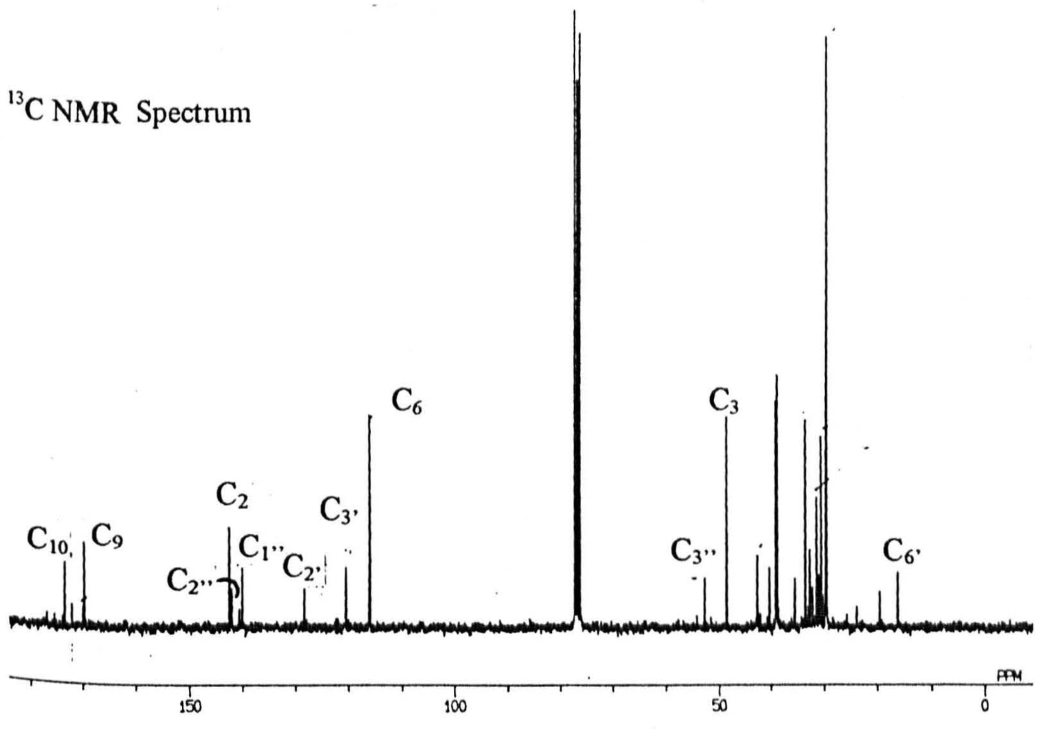


TMP-1 possesses two types of allylic hydrogen atoms which can lead to two adducts, conveniently named *exo* and *endo*, which are observed in the second fraction collected from bulb-to-bulb distillation (scheme 4.2). One has an external double bond ('*exo*') and the other an internal double bond ('*endo*'), 2-(2,2-dimethylpropyl)-propen-2-yl succinic anhydride (**4.1**) and (*cis*- and *trans*-) 2,4,4-trimethyl-2-pentenyl succinic anhydride (**4.2**) respectively.[138] The ^1H and ^{13}C NMR spectra of the second distillation fraction resulting from the reaction of MA with TMP-1 are shown in figures 4.3a and 4.3b respectively.

Figure 4.3: ^{1}H and ^{13}C NMR spectra of the purified reaction mixture resulting from the ene reaction between TMP-1 and MA ($CDCl_3$).



^{1}H NMR Spectrum



^{13}C NMR Spectrum

The signals in figure 4.3 which can be unambiguously assigned to each isomer (**4.1** and **4.2**) have been numbered on the spectra, these are in the alkenic region (and carbonyl signals in the ^{13}C spectrum). A more detailed list of these assignments is given in table 4.2 along with a quantitative analysis of the ratio of each compound in the mixture obtained from ^{1}H NMR integration of the alkenic protons.

Unlike the product formed in the reaction of 1-octadecene with MA the presence of a reactive double bond and allylic hydrogens in 2-(2,2-dimethylpropyl)-propen-2-yl succinic anhydride (**4.1**) allows the addition of a second molecule of MA to take place, resulting in a difunctionalised adduct (table 4.2). Again a mixture of two di-ene adducts (**4.3** and **4.4**) is possible due to the presence of two types of allylic hydrogens in **4.1** (scheme 4.3). The ratio of these components, compared to the integration areas of the olefinic protons for **4.1** and **4.2**, is shown in table 4.2, only **4.4** is present in large enough amounts to be charaterised. Production of these adducts in this ene reaction has been detailed by Tessier and Marechal.[138]

Scheme 4.3: Reaction of TMP-1 with two equivalents of MA.

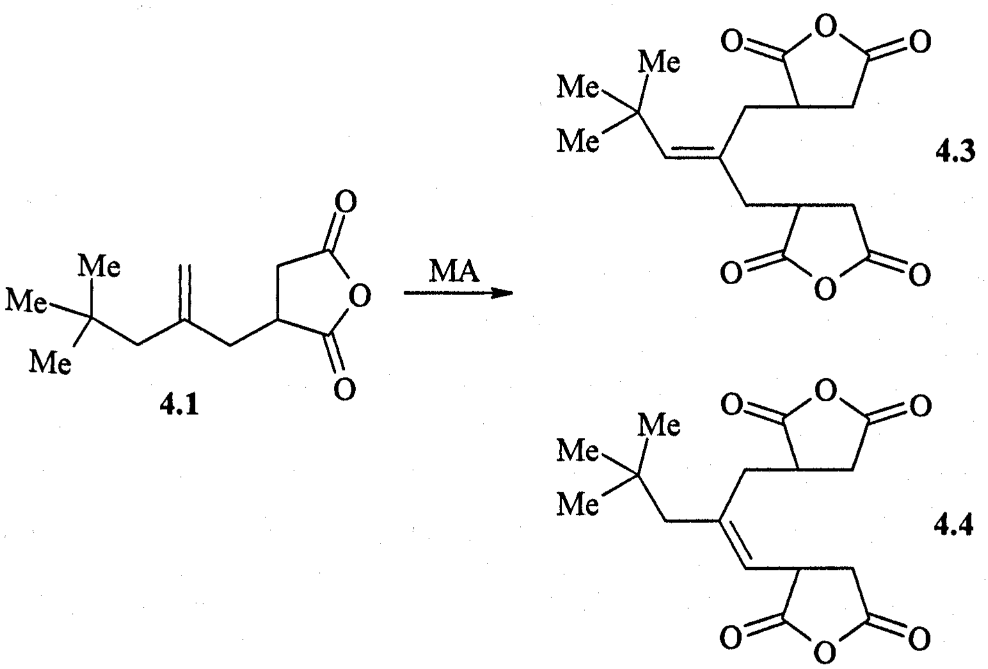
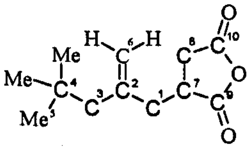
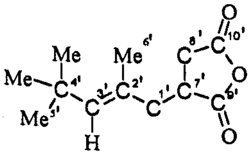
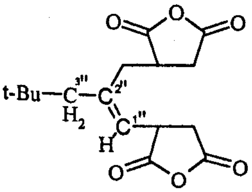


Table 4.2: Chemical shifts (p.p.m.) and assignments of ^{1}H (in d_6-Acetone) and ^{13}C (in $CDCl_3$) NMR spectra for second distillation fraction resulting from the reaction of MA with TMP-1.

Structure	**^{13}C NMR data**		**^{1}H NMR data**		**Ratio**[a]
	Assignment	**p.p.m.**	**Assignment**	**p.p.m.**	
	C_2 C_3 C_6 C_9 C_{10}	142.7 48.8 116.3 170.0 173.6	H_A H_B	4.99[b] 5.12[b]	3.3
	$C_{2'}$ $C_{3'}$ $C_{6'}$ $C_{9'}$ $C_{10'}$	128.6 *trans*[c] 120.7 *trans*[c] 16.4 170.0 173.6	H_C	5.48	1.3
	$C_{1''}$ $C_{2''}$ $C_{3''}$	140.3 *trans*[c] 142.3 *trans*[c] 53.0	H_D	5.45-5.39	1

a : Calculated by comparison of the percentage areas of the alkenic resonances of these three products obtained from ^{1}H NMR integrals.

b : Alkenic protons give only a singlet when the ^{1}H NMR spectrum is run in $CDCl_3$.

c : Only the peaks of the trans isomer were intense enough to be identified.

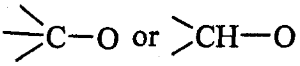
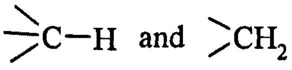
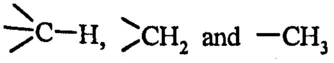
As expected the major product from the condensation of MA with TMP-1 is the *exo* product 2-(2,2-dimethylpropyl)-propen-2-yl succinic anhydride (**4.1**) (ratio 3.3 from integration of the alkenic proton signals at 4.99 and 5.12 p.p.m. compared to the alkenic signals of the other two compounds).[112, 138] The IR spectrum of the semi-purified reaction mixture shows two intense carbonyl signals (νC=O) at 1861 and 1783 cm^{-1} for the anhydride carbonyl stretching modes in diisobutylene succinic anhydride (DIBSA).[12b]

4.2.1 Analysis of the residual solid produced in the TMP-1/MA ene reaction.

The work described here is designed to investigate the formation of by-products during the thermal ene reaction between PIB and MA, particularly the formation of coloured by-products. During the thermal reaction of TMP-1 with an excess of MA at 200 °C, along with the ene adducts discussed previously, a significant amount of coloured by-products are formed in 4 h. Separation and characterisation of the ene reaction products is relatively simple. Our results show that the lower boiling point components of the reaction mixture are colourless, as is to be expected from their structure. However the residue left after this separation process is a dark brown sticky solid. This material is more tractable to study and therefore the tar was subjected to a much more detailed study.

Analysis of this brown solid by NMR (^{1}H and ^{13}C) gives an indication of the complex nature of the coloured material. The ^{13}C NMR spectrum of the residue, given in figure 4.4b, contains various peaks due to sp^2 hybridised carbons (100 to 160 p.p.m.) and, interestingly, signals for carbons attached to oxygen (quaternary carbon peaks between 80 to 90 p.p.m.) perhaps due to the formation of lactones in the autoclave system. Figure 4.4a shows the ^{1}H NMR of the coloured resin and assignments of groups from the chemical shift regions for each of the spectra in figure 4.4 are listed in table 4.3.[114]

Table 4.3: Chemical shifts regions (δ p.p.m.) of ^{1}H and ^{13}C NMR spectra for the coloured residue resulting from the reaction of MA with TMP-1 (in d$_6$-Acetone).

Group	**^{13}C δ range / p.p.m.**	**^{1}H δ range / p.p.m.**
Carbonyl, C=O	180-170	-
Olefinic	155-115	6.5-4.3
 $\succ\!\!-\mathrm{C{-}O}$ or $>\mathrm{CH{-}O}$	90-80	-
 $\succ\!\!-\mathrm{C{-}H}$ and $>\mathrm{CH_2}$	55-47	3.8-2.0
 $\succ\!\!-\mathrm{C{-}H}$, $>\mathrm{CH_2}$ and $-\mathrm{CH_3}$	44-29	1.2-0.8 (t-Bu only)

These spectra (figure 4.4) contain many more peaks than can be accounted for by the starting materials and reaction products alone. This data led to the supposition that the colour in resin originates from conjugated alkene systems formed by thermal decomposition of reactants, products or both. However, as shown by these spectra (figure 4.4) the resin contains such a complex mixture of compounds it is impossible to reliably identify each component.

4.3 Reactions of diisobutylene succinic anhydride (DIBSA).

To elucidate the pathway by which by-products are formed during the ene reaction between 2,4,4-trimethyl-1-pentene (TMP-1) and maleic anhydride (MA), standards have been synthesised from diisobutylene succinic anhydride (DIBSA) and characterised. It was hoped that these compounds would help to explain the number of components observed in the NMR spectra of the residual solid (section 4.2.1) and the presence of the colour. Prior to using these procedures on DIBSA, for which the preparation and separation is relatively easy but not trivial, these reactions have also been carried out using isobutylene succinic anhydride which is commercially available and has a similar alkenic end-group to DIBSA. However, isobutylene succinic anhydride has a much simpler structure than DIBSA and thus the NMR spectra of the reaction mixtures are less complex and easier to interpret.

4.3.1 Hydrolysis of diisobutylene succinic anhydride.

Hydrolysis of DIBSA was achieved in almost quantitative yield by standing the anhydride in distilled water for 48 h. Evaporation of the water afforded a white solid which is insoluble in deuterated chloroform. Some of the more important peaks present in the NMR spectra (^1H and ^{13}C) of the hydrolysed material are shown in table 4.4.

Figure 4.4: ^1H and ^{13}C NMR spectra of the dark brown residue obtained after separation of the lighter fractions from the crude reaction mixture resulting from the ene reaction between TMP-1 and MA (in d_6-Acetone).

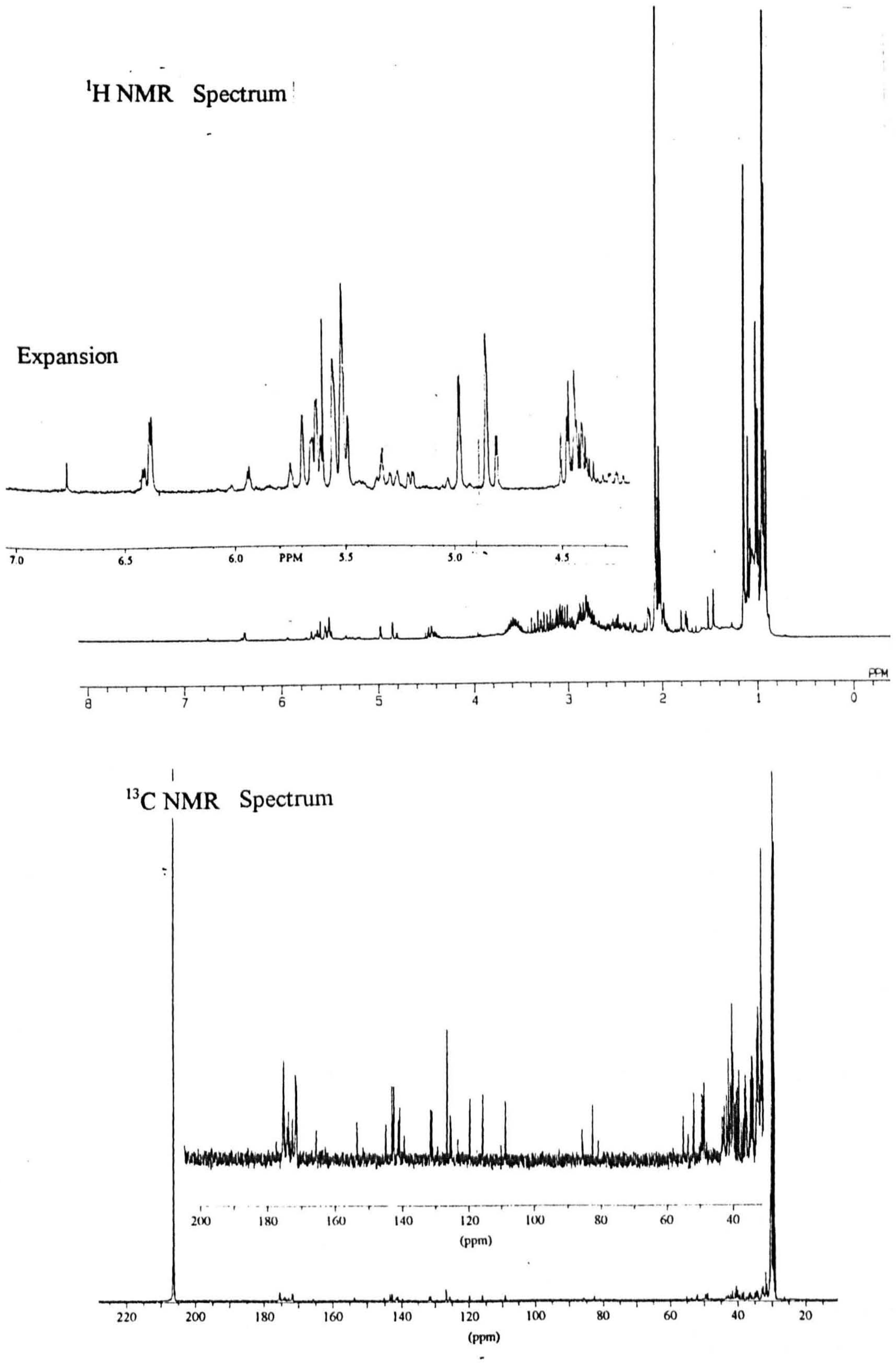
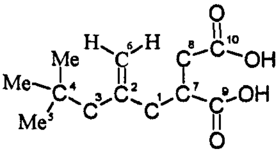
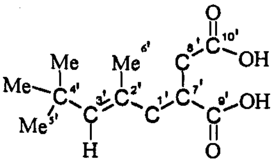


Table 4.4: Chemical shifts (p.p.m.) and assignments of ^1H and ^{13}C NMR spectra (in d_6-Acetone) for diisobutylene succinic acid.

Structure	^{13}C NMR data		^1H NMR data		Ratio[a]
	Assignment	p.p.m.	Assignment	p.p.m.	
	C_2 C_3 C_6 C_9 C_{10}	145.5 49.2 115.9 173.5 176.4	H_A H_B	4.95[b] 4.81[b]	5.3
	$C_{2'}$ $C_{3'}$ $C_{6'}$ $C_{9'}$ $C_{10'}$	128.6 *trans*[c] 132.0 *trans*[c] 16.8 173.5 176.4	H_C	5.25	1

a : Calculated from the peaks areas of the olefinic protons obtained from ^1H NMR integrals.

b : Alkenic protons give only a singlet when the ^1H NMR spectrum is run in $CDCl_3$.

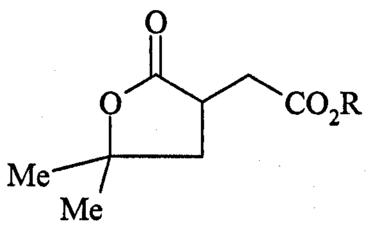
c : Only the peaks of the trans isomer were intense enough to be identified.

Compared to the data in table 4.2 for DIBSA, there appears to be little difference between the chemical shifts of the signals for the anhydride and the hydrolysed di-acid in their ^1H and ^{13}C NMR spectra. This was also found to be the case when isobutylene succinic anhydride and isobutylene succinic acid were compared. As expected the mixture of diisobutylene succinic acids (**4.5** and **4.6**) have a MS which contains a molecular ion of *m/z* 228 (relative intensity 0.5%). After methylation with diazomethane GC analysis confirms that the hydrolysed DIBSA contains two isomers ratio 1 to 3.6. Prior to hydrolysis the ratio of isomers in DIBSA was 1 to 6.6. The difference, therefore, is either a result of differing response factors of the acid and anhydride and/or acid-catalysed isomerisation from the external to internal double bond structure.[109] The latter is thought to be more likely, even though standardisation was not carried out, because generally compounds of the same molecular formula and similar structure have similar response factors. From the integration ratios of the alkenic protons, which are not subject to response factors, for the distilled starting material (DIBSA) and its acid derivative, the ratio of the internal and external isomers is 6.6 to 1 and 5.3 to 1 respectively. It seems likely, therefore, that isomerisation of DIBSA occurs under relatively mild conditions.

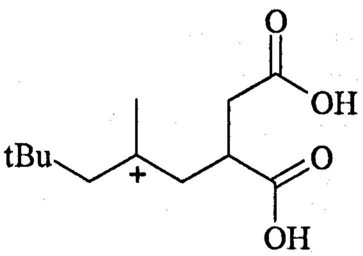
The ^{1}H NMR spectrum of the dimethyl ester derivative is virtually identical to that of diisobutylene succinic acid except for two extra singlets at 3.70 (3H, OMe) and 3.69 (3H, OMe) p.p.m.. As the NMR spectra of the hydrolysed di-acid is very similar to that of the anhydride starting materials (**4.1** and **4.2**) it is very difficult to say whether it is present in the residual solid.

4.3.2 Lactonisation of diisobutylene succinic anhydride.

As described in the introduction (section 1.8) acid-catalysed hydrolysis of isobutylene succinic anhydride results in the formation of a lactone.[108] Thus, as expected refluxing isobutylene succinic anhydride in 1:1 mixture of concentrated HCl and water produces a pure lactone as a white solid in excellent yield (88.8%). The NMR spectra of this solid do not contain any alkenic signals and the ^{13}C NMR spectrum shows a new resonance for the quaternary carbon in the lactone ring at δ 82.5 p.p.m. (qC, $(Me)_2C(O)$-). Solution infra-red experiments on the lactone shows a strong carbonyl band at 1762 cm^{-1} (s, C=O stretch) suggesting that **4.7** contains a 5-membered ring.[114] The methyl ester derivative, which was formed quantitatively by methylation of **4.7** with diazomethane, gives only one peak in its GC trace as expected for (2,2-dimethyl-2-oxo-tetrahydro-furan-3-yl)-acetic acid methyl ester (**4.8**).



4.7 R = H
4.8 R = Me



4.9

Unlike isobutylene succinic anhydride, DIBSA is a mixture of isomers (**4.1** and **4.2**), as explained in section 4.2. Subjecting DIBSA to the same conditions used to produce **4.7** from isobutylene succinic anhydride gives a white solid (yield = 98%). Both **4.1** and **4.2** are expected to form the same carbocation ion intermediate (**4.9**), thus cyclisation results in the formation of the same products whatever the original position of the double bond in DIBSA. Lactonisation takes place by nucleophilic attack of one of the carboxylic acid groups on the carbocation centre.[109]

It is thought that the initial step in this process is formation of diisobutylene succinic acid, further protonation of the mixture of isomers takes place on the ethylenic linkage.[109] Formation of diisobutylene succinic acid prior to cyclisation is reinforced by the experimental observations that hydrolysis of DIBSA without an acid-catalyst, refluxing in water for 17 h, gives a reaction mixture which contains both diisobutylene succinic acids and lactones, percentage of the total (uncalibrated) GC peak area for their methylated derivatives was 15.8% and 84.2% respectively.

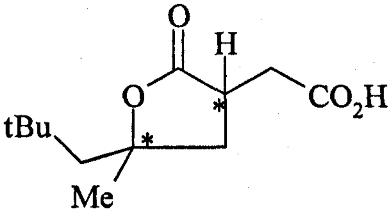
The ^1H and ^{13}C NMR spectra of DIBSA after refluxing in dilute HCl no longer contains the alkenic peaks seen in the starting material, however there are two resonances in the ^{13}C NMR spectrum at 85.9 p.p.m. (qC) and 85.7 p.p.m. (qC), which are indicative of lactones.[114] The methylated sample displays two peaks in the GC trace (ratio 39 to 61%) which are separated by only 0.2 minutes. It was initially thought that these two peaks were due to the five and six membered lactones, in contrast to isobutylene succinic anhydride under the same conditions which only produces the γ-lactone (**4.7**). A more likely explanation, therefore, is that the product is a mixture of diastereoisomers.

The difficulty in our situation is demonstrated by examination of two standard lactones which contain 5- or 6-membered rings, γ-decanolactone and δ-decanolactone respectively. It is very difficult to resolve 5- and 6-membered lactones from their ^1H and ^{13}C NMR signals. Table 4.5 shows selected ^1H and ^{13}C NMR data for these two lactones, the only significant difference between the decanolactones is seen in the carbonyl region of the ^{13}C NMR spectrum. The lactonisation mixture produced from DIBSA contains two peaks at 177.6 and 172.8 p.p.m. in this region, one for the lactone carbonyl and the other for the carboxylic acid group, which unfortunately coincide with these carbonyl signals and therefore cannot be assigned with any confidence.

Table 4.5: NMR data (^{1}H and ^{13}C) for γ-decanolactone and δ-decanolactone (Aldrich, purity 97%), spectra recorded in $CDCl_3$.

Structure	^{13}C NMR data / p.p.m.	^{1}H NMR data / p.p.m.
γ-decanolactone	CH 81.0 C=O 177.2	CH 4.45
δ-decanolactone	CH 80.5 C=O 171.9	CH 4.35

Again solution infra-red experiments on the lactone mixture served to clarify this situation. The IR spectrum of the lactone mixture shows a strong carbonyl band at 1757 cm^{-1} (s, C=O stretch) suggesting that the structure only contains a 5-membered ring, 6-membered derivative would be expected have a carbonyl band between 1735 and 1748 cm^{-1}.[114] Thus the two compounds observed by ^{13}C NMR and GC analysis can be accounted for by the two diastereomeric five membered ring lactones **4.10** (the chiral centres are indicated in the diagram below by asterisk).



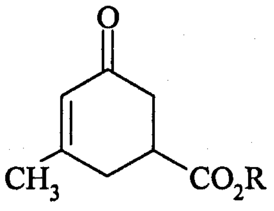
4.10

Comparison of the ^{13}C signals for these lactone diastereoisomers, especially those indicative of lactones at 85.9 p.p.m. (qC) and 85.7 p.p.m. (qC), with the signals in figure 4.5b, suggests that the coloured residue contains lactones. These compounds are presumably produced by the acid-catalysed lactonisation of DIBSA in the autoclave. However, both the cyclic lactone and the di-acid derivatives of DIBSA are white solids. Thus they can be ruled out of the residual solid as contributing to the colour of DIBSA. As will be shown, however, the GC retention times and MS data for the methyl ester derivatives of **4.10** have enabled us to identify peaks D and E (figure 4.5) as these in the GC/MS analysis of the coloured resin mixture.

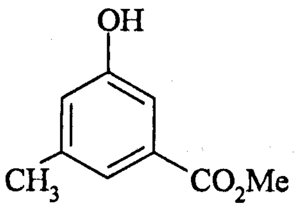
4.3.3 Intramolecular acylation of diisobutylene succinic anhydride.

During the lactonisation of many olefinic acids Ansell and Palmer noticed the production of varying amounts of the corresponding enone (section 1.8).[109] Thus it was thought that the same process is possible for DIBSA in the autoclave. The formation of enones would help to explain the number of sp^2 hybridised carbons and their associated protons in figure 4.4. Also enones contain a conjugated carbonyl and alkene system, therefore, the presence of this type of compound in the reaction mixture may help explain its colour.

Initially, the synthesis of 3-methyl-5-oxo-cyclohex-3-ene carboxylic acid (**4.11**) was carried out by Lewis acid-catalysed ($AlCl_3$[110] or $SnCl_4$[139]) cyclisation of isobutylene succinic anhydride following the procedures in the literature. However, in our hands the yields of the enone were lower than expected, apparently, due to acid-catalysed side reactions – by-products included the lactone and di-acid derivatives of the isobutylene succinic anhydride. Separation of the enone (**4.11**) from the by-products was accomplished by recrystallisation from a light petroleum-$CHCl_3$ mixture to give an off-white solid, yield ~ 10%.



4.11 R = H
4.12 R = Me



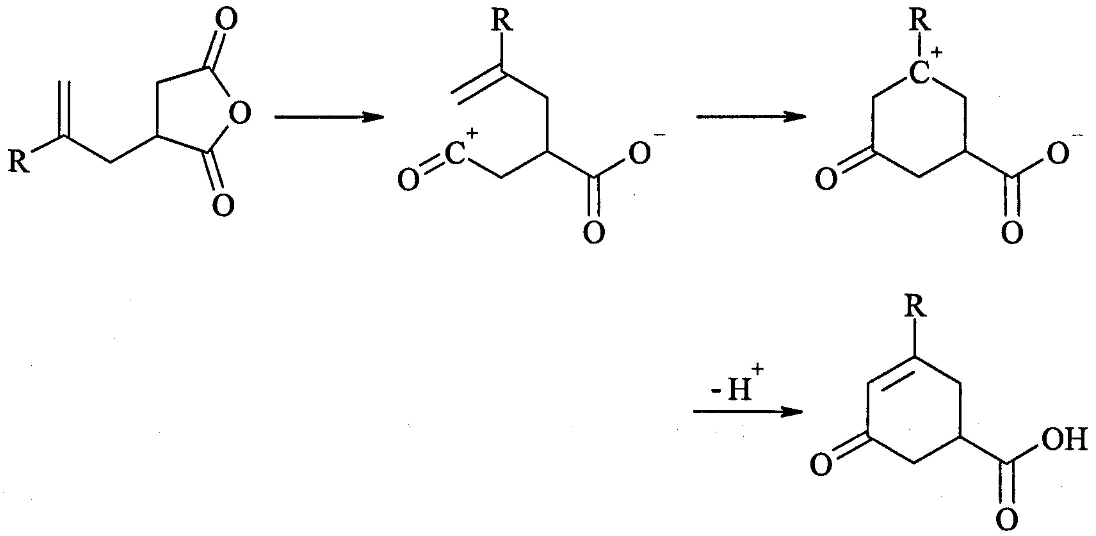
4.13

The structure of **4.11** was established in a variety of ways. UV-Vis and IR studies show absorbancies at 245 nm and 1667 cm^{-1}, respectively, in agreement with a six membered enone[139] and dehydrogenation of the methyl ester derivative gives methyl 3-hydroxy-5-methylbenzoate (**4.13**).[110] As expected the ^1H NMR spectrum of the enone (**4.11**) only contained one alkenic peak at 5.79 p.p.m. (sextet, 1H, *J* 1.5, CH=), and in the ^{13}C NMR spectrum a number of new peaks are observed for the cyclic enone at 196.7 p.p.m. for the enone carbonyl carbon resonance, and 161.0 p.p.m. (qC, -CH=<u>qC</u>-) and 126.7 p.p.m. (CH, -<u>CH</u>=qC-) for the enones alkenic carbon resonance, which is consistent with the predicted structure.

Using the methodology developed for the internal acylation of isobutylene succinic anhydride the corresponding reaction has been performed on DIBSA. The enone (**4.14**) was formed as a yellow solid, in poor yield (yield = 13%). As with the previous enone (**4.11**) the UV-Vis spectrum contains a maximum absorbance for a $\pi \rightarrow \pi^*$ transition at 245 nm (log $\epsilon = 3.24$) but the weaker $n \rightarrow \pi^*$ transition is not observed, and the IR spectrum shows a strong absorbance at 1666 cm^{-1}, which is consistent with a six member αβ-unsaturated ketone.[114] As expected the ^1H NMR spectrum of this compound shows only one alkenic resonance at 5.92 p.p.m., and the ^{13}C NMR spectrum contains two quaternary carbon signals at 197.5 p.p.m. and 177.8 p.p.m., the former is indicative of a ketone carbon and the latter a carboxylic acid group (qC, CO_2H). Although the NMR spectra of the residual solid produced in the TMP-1/MA ene reaction contains many unidentified peaks (figure 4.4, section 4.2.1), none of the resonances in either the ^1H or ^{13}C NMR spectra can be assigned as cyclic enones. It will be shown later, using GC/MS analysis, that **4.14** is present in very low concentrations in the residual solid (figure 4.5, section 4.4). However, as shown by the UV-Vis spectrum of this compound, **4.14** does not contain a strong absorption peak in the visible region of the spectrum and is a yellow solid. There must be another reason for the colour of the residual solid.

Formation of cyclohexenones, such as **4.11** and **4.14**, is thought to proceed through an acylium ion intermediate as shown below (scheme 4.4).[109] With Lewis acids the catalyst acts to complex and polarize the carbonyl group, thus facilitating C-O bond cleavage. In agreement with this mechanism only one peak is seen in the GC trace of **4.14**. This suggests that DIBSA forms a common carbocation ion intermediate from all three of its isomers. The MS of this methyl ester derivative contains a molecular ion of *m/z* 224 (relative intensity 3%) and displays a strong fragment ion of *m/z* 109 (relative intensity 100%) due to the loss of C_4H_8 and $C(O)OCH_3$.

Scheme 4.4: Mechanism for the formation of the enones **4.11** and **4.14**.



4.11 R = Me

4.14 R = CH_2-tBu

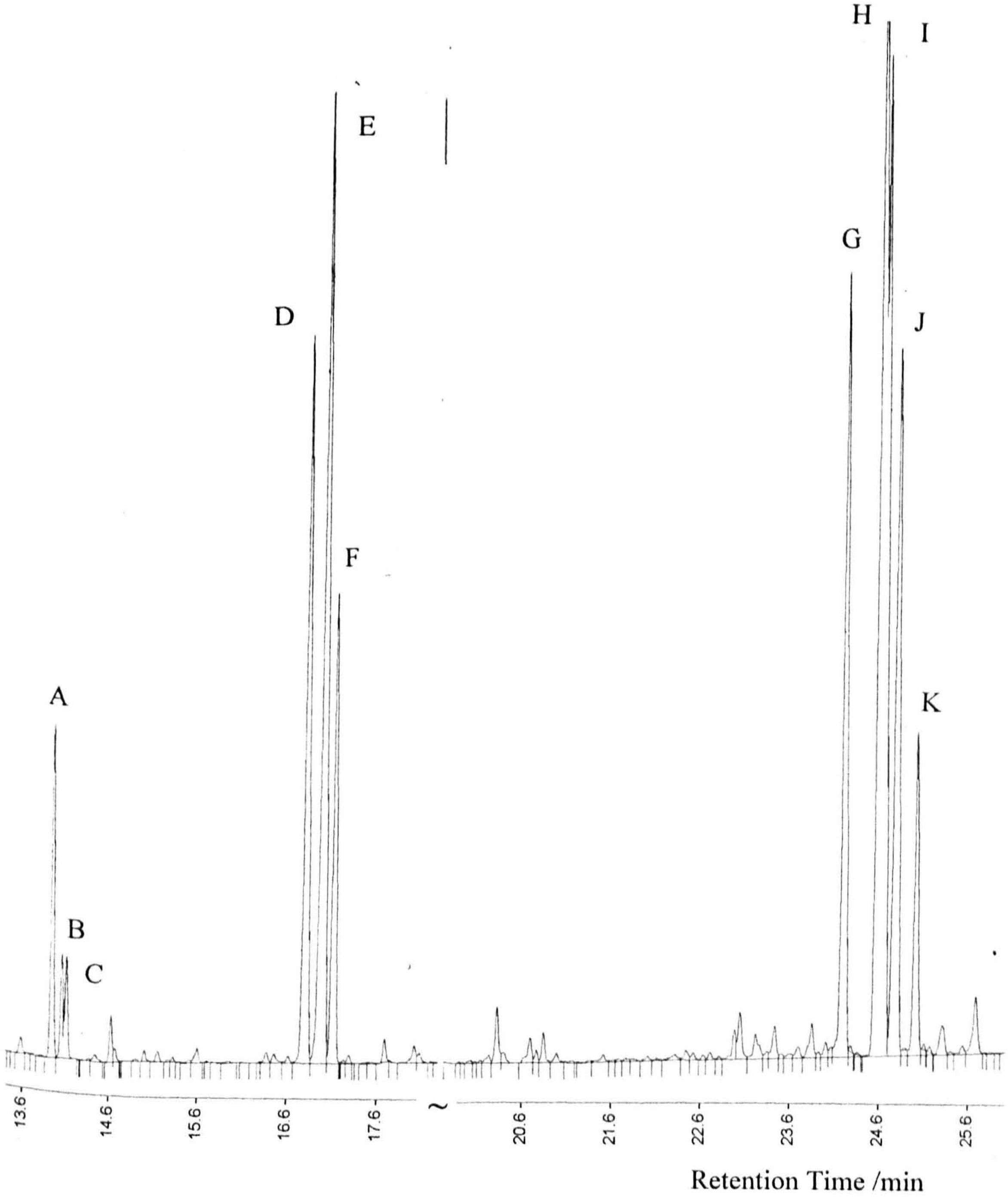
4.4 GC/MS analysis of the ene reaction residue.

This section reports the use of GC/MS in an attempt to identify the major components of the coloured resin, collected after distillation of the TMP-1/MA ene reaction mixture described in section 4.2. The value of this method was shown in the identification of the reaction products from the halogenation of the model alkenes in Chapter 2. Although it may not always be possible to identify the exact structure of the adducts from their MS, the molecular formula can usually be obtained in addition to some details of the molecular structure. Due to the presence of succinic anhydride groups in the reaction mixture, which are easily hydrolysed, the sample must be methylated prior to analysis to avoid the hydrolysed acidic components sticking to the column. This can be achieved quantitatively with diazomethane, resulting in the formation of the methyl ester derivative of the carboxylic acid. The GC trace given by a methylated sample of resin is shown in figure 4.5. A comparison between the GC trace for the crude reaction mixture and the isolated coloured solid shows that, as we would expect, only the longer retention time peaks remain after distillation of the more volatile components from the ene reaction mixture. However, a drawback to this technique is that, because standard compounds are not available for all the components present in the in the reaction mixture, the analysis is qualitative rather than quantitative. Another problem is that some compounds in the resin may not be volatile enough to be observed by GC analysis.

The peaks in the GC trace (figure 4.5) have been labelled from A to K for identification purposes. All the mass spectra contain a strong ion at *m/z* 57, which is indicative of compounds containing a tertiary butyl group. Further analysis of the longer retention time peaks by high resolution electron impact mass spectrometry (HR EI MS) suggests that these compounds are related to the more volatile components. Peaks A to F have been identified by comparison with standard compounds synthesised from purified DIBSA, which is a mixture of 2-(2,2-dimethylpropyl)-propen-2-yl succinic anhydride (**4.1**) and (*cis*- and *trans*-**4.2**) 2,4,4-trimethyl-2-pentenyl succinic anhydride. Synthesis and characterisation of these standards has been described earlier in this Chapter (section 4.3).

In agreement with the signals seen in the NMR spectra of the alkenyl succinic anhydrides **4.1** and **4.2**, which show the presence of all three isomers, peaks A to C in the GC trace (figure 4.5) have molecular ions of *m/z* 256 (HR EI MS shows that these peaks have a molecular formula of $C_{14}H_{24}O_4$) corresponding to the dimethyl ester derivatives of these anhydrides. The molecular ion peak and the fragmentation patterns seen in the MS of peaks A to C are very similar and only differ in the intensity of the peaks, this is typical of compounds which differ only in the position of double bonds in a carbon skeleton. The retention time and MS of peaks A to C correspond to those expected for the ring opened and methylated (dimethyl ester) derivatives of DIBSA.

Figure 4.5: GC trace for a sample of the coloured resin isolated from the thermal reaction between TMP-1 and MA at 200 °C for 4 h, after methylation with diazomethane.

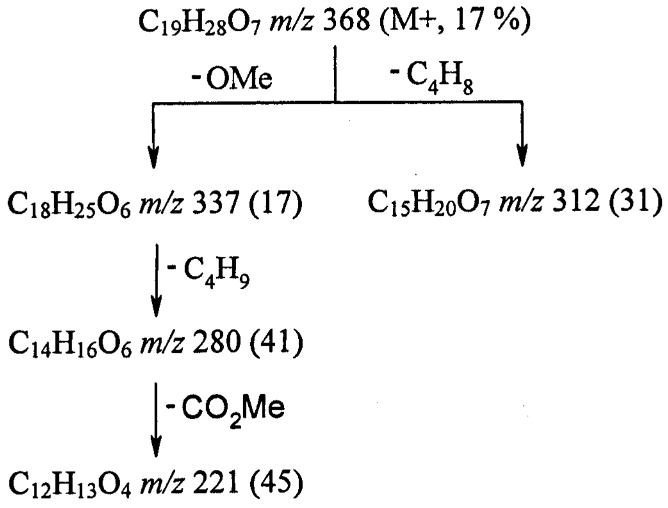


As discussed in the introduction (section 1.8), olefinic acids are known to produce lactones and cyclic enones by an internal addition process (scheme 1.16).[109] Correspondingly, the formation of lactones from DIBSA is consistent with the earlier observations that a lactone product is formed as a by-product from the thermal reaction between isobutylene and MA.[88] The diastereomeric five membered ring lactones (**4.10**), detected by GC/MS analysis as peaks D and E, have been identified by comparison of their MS with those of the synthesized mixed standards. The MS of both diastereoisomers contains a molecular ion of *m/z* 243 for the protonated molecular ion (MH+), whilst the strongest peak results from the relatively stable ring after loss of C_5H_{11} (relative intensity 100%) from the lactone. The standard lactones also display characteristic C-O signals in the ^{13}C NMR spectrum at ~ 85 p.p.m. which are indicative of this type of structure.[114]

Peak F (figure 4.5) has also been identified by comparison of its MS data with the standards described earlier. This peak is indicative of the unsaturated cyclic enone (**4.14**) with a molecular ion peak at *m/z* 224, which fragments readily through loss of C_4H_8 followed by CO_2Me to give a fragment ion in the MS of *m/z* 109. An authentic sample of this compound (section 4.3.3) displays a characteristic signal in the ^{13}C NMR spectrum at 196.7 p.p.m. (qC, C=O). However this signal being of a quaternary carbon is weak and it was not evident in the resin NMR spectrum (figure 4.4).

The majority of the components detected by GC/MS (53% by GC peak area) in the methylated resin correspond to peaks G to K, which all display very similar fragmentation patterns and a molecular ion of *m/z* 368. The structural assignment for these compounds is by no means certain because no standard material is available for comparison with the MS data, a tentative structural assignment of peak G is set out below from HR EI MS data:

Figure 4.6: Fragmentation tree from the LR and HR EI MS of peak G in figure 4.5.



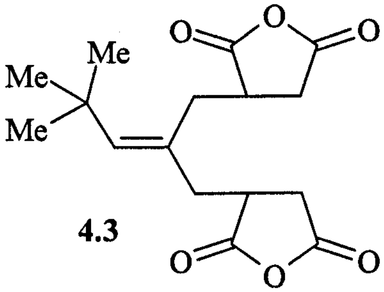
These fragmentations have been taken to indicate the following:

1. The compound contains at least one molecule of the alkene TMP-1, *m/z* 57 (C_4H_9+, 100) and that no carbon skeletal rearrangement has occurred in this component.
2. Also the presence of two fragmentations with the loss of methoxy groups point to a structure with at least one full MA molecule.

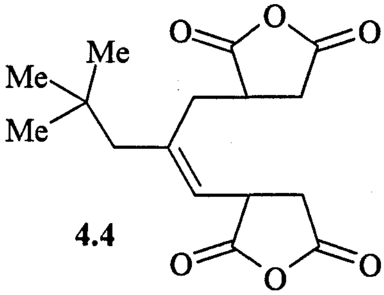
Considering these points there are two possible structures that correspond to the identified molecular weights of these compounds. Firstly, a structure containing a cyclohexanone (**4.15**) or pentanone (**4.16**) ring and three methyl ester groups. These compounds, which can in theory be formed by the intermolecular acylation of the di-ene adduct, each contain three chiral centres and therefore have numerous stereoisomers explaining the complex mixture of long retention time components with the same molecular weight and fragmentation patterns seen in ene reaction residues (peaks G to K in figure 4.5).

Alternatively, it can be suggested that peaks G to K in figure 4.5 represent the di-adducts (**4.3** and **4.4**) and that no molecular ion seen in their MS, the highest ion in the MS resulting from their cyclisation on electron impact. In order to clarify this the synthesis of standards of **4.3** and **4.4** by reaction of purified DIBSA with an excess of MA at 200 °C for 4 h was attempted but proved unsuccessful. The product mixture was a dark brown solid, although it is likely that none of the compounds

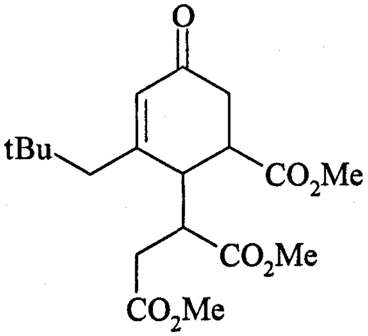
4.3, **4.4**, **4.15** and **4.16** are coloured. Methylation and analysis of this dark brown solid by GC/MS showed it to contain only by-products from the thermal decomposition of DIBSA, as will be discussed in section 4.5. Overall, it appears that GC/MS is not able to separate or detect the coloured components of the residual solid. This would suggest that they are either too involatile or too polar to be eluted from a GC column.



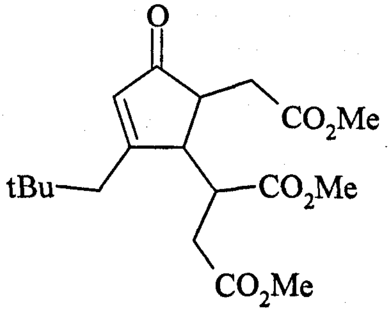
4.3



4.4



4.15



4.16

4.5 Thermal decomposition of diisobutylene succinic anhydride.

Heating DIBSA, which is a colourless oil, at 200 °C for 4 h produces a dark brown solid. The major components of this solid, by NMR, are the starting material and its acid derivatives. Analysis of the methylated solid by GC/MS gives further evidence for the presence of these compounds, but also shows that the reaction mixture contains small amounts of the diastereomeric lactones (**4.10**, percentage peak area = 6%) and enone (**4.14**, percentage peak area = 1%). Assignment of these peaks in the NMR spectra and GC/MS was performed by comparison of the experimental data with those of the pure materials described previously (section 4.3). The GC trace of the reaction mixture bears a striking resemblance to that obtained from the thermal reaction of TMP-1 with an excess of MA, shown in figure 4.5, apart from the lack of longer retention time peaks. It is also worth noting that thermolysis of DIBSA under these reaction conditions gives no detectable quanities of MA or alkene, thus it is assumed that the 'retro-ene' reaction,[86] which is known to occur in some systems at high temperatures,[140] is not important in our case.

Subjecting diisobutylene succinic acid to these conditions, *i.e.* heating at 200 °C for 4 h, also gives a dark brown solid. The reaction product was methylated with diazomethane and analysed by GC/MS. Along with the starting material (DIBSA, relative peak area 25.2%), formed by dehydration of the diacid, the coloured solid contained two peaks for the methyl ester derivatives of the lactones (**4.10**, relative peak area 74.9%). However, no other peaks were observed in this GC trace which could account for the change in colour of diisobutylene succinic acid as presumably the coloured components are not volatile enough to be observed by this method.

4.6 Thermal decomposition of the lactones (4.10) produced from DIBSA.

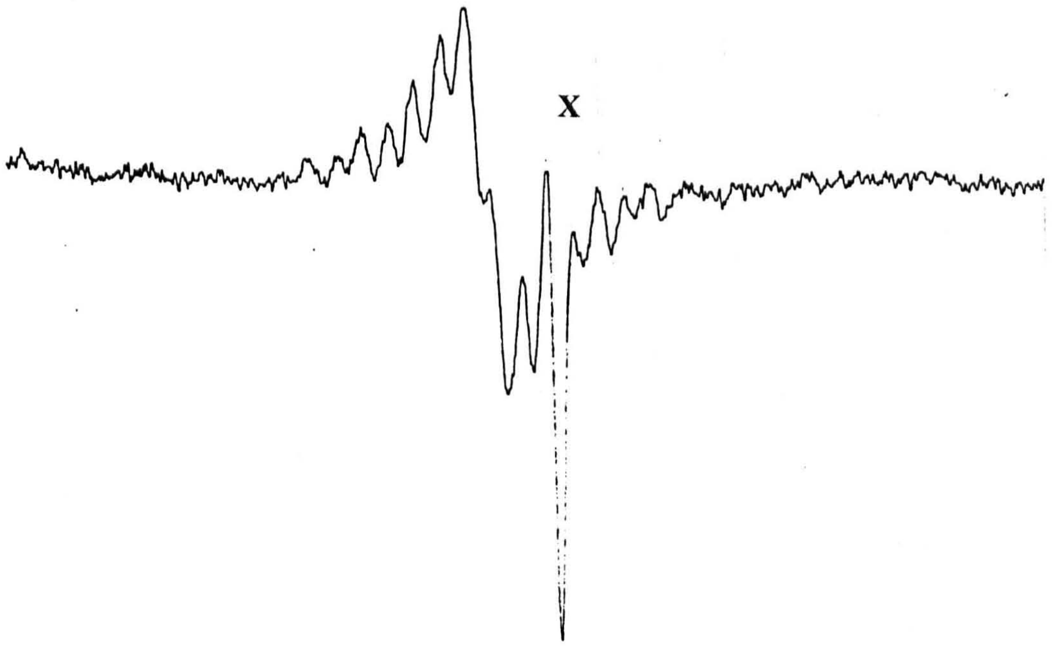
The stability of lactones produced from olefinic acids is dependent on their structure.[141] Experiments were, therefore, carried out to see if the five-membered lactones (**4.10**) were stable to heating in the autoclave for 4 h at 200 °C. In contrast to diisobutylene succinic anhydride and its diacid derivative the only peaks seen in the GC trace of the methylated reaction mixture was the starting material. Removal of the lactone by bulb-to-bulb vacuum distillation (> 1 mm Hg) gave a black powder solid, 2.4% by weight of the initial mass. However, the coloured components of this reaction mixture have not been identified, the GC/MS and NMR results only show peaks for the starting material alone.

Hydrolysis under normal conditions used to hydrolyse DIBSA, *i.e.* concentrated HCl, do not ring-open the lactone. Only in refluxing concentrated H_2SO_4 does ring-opening occur and then the major product is the six-membered enone, which was identified by comparison of the spectroscopic data with that for **4.14**. These results suggests that the lactone is relatively stable because only starting material is recovered if weaker acids (such as HCl) are used in place of H_2SO_4. It is not thought that this type of decomposition of the lactones will occur in the autoclave, although this means that the identity of the colour compounds formed during thermolysis of the lactone is not known.

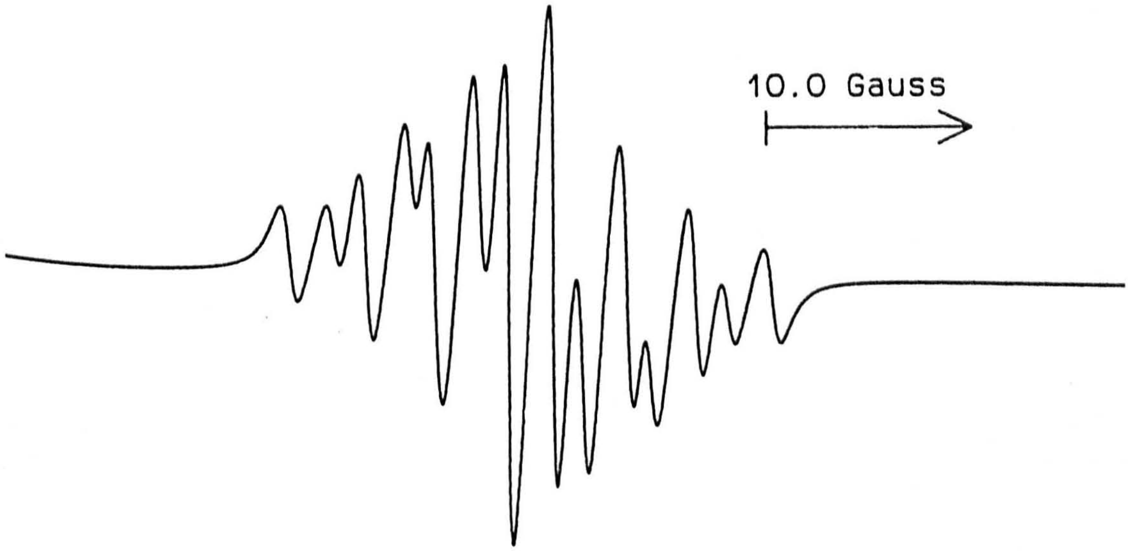
4.7 EPR studies.

Even though radical inhibitors have no significant effect on the colour of the PIBSA reaction mixture, many researchers still believe that the formation of the coloured by-products is based on radicals. One explanation is that these small concentrations of radical species (species containing one or more unpaired electrons), formed under the harsh reaction conditions, lead to polymerisation processes resulting in involatile coloured compounds. Electron paramagnetic resonance (EPR) experiments have been carried out using the model systems to establish the presence and the identity of any such radical species. Using this method we were capable of detecting concentrations of radical species in the order of 10^{-8} mol dm^{-3}.[141] The standard method for obtaining a EPR spectrum was as follows; a sample of the crude reaction mixture, produced by reacting TMP-1 with 1.3 molar equivalents of MA at 200 °C for 4 hours, was taken from the autoclave after allowing it to cool for 0.5 h. Analysis of the sample at 100 °C showed it to contain a radical species (figure 4.7a), assigned as a doublet of triplets of triplets ($a_H = 0.213$ mT, $a_{2H} = 0.373$ mT and $a_{2H} = 0.707$ mT), and a g-value of 2.0033, indicative of a carbon-centred radical next to electron-withdrawing groups.[141] The signal broadening, apparent in the spectrum, is probably due to the slow tumbling of the radical. Figure 4.7b illustrates a simulation of the radicals splitting pattern with the line width increased to account for broadening. This signal closely resembles figure 4.7a lending credence to the splitting pattern above.

Figure 4.7: a) EPR spectra recorded for the ene reaction mixture obtained from reacting TMP-1 with 1.3 molar equivalents of MA at 200 °C for 4 h. Spectrum obtained for the melt of the sample at 100 °C [X = signal for the glass peak of the EPR cell].



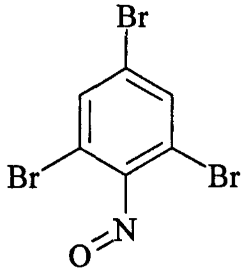
b) Simulation of the EPR spectrum shown in figure 4.7a with the line width equal to 1.25 accounting for broadening.



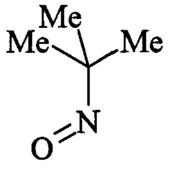
An EPR study of this system over time shows that the intense signal decays to a broad peak, line width 0.31 mT. However, this event occurs over minutes rather than milliseconds, indicating that this radical species is relatively stable. These observations and the measured splitting values led to the suggestion that a carbon-centred radical species (figure 4.7a) is formed from a highly stabilized intermediate, and may even be an aromatic radical such as benzyl, phenoxyl or an cation radical.[141] It is envisaged that these type of compounds could be created by the high temperatures used to achieve satisfactory yields in the ene reaction.[112]

A single radical species with the same g-value (2.0033) has been observed in the product mixtures obtained by heating a range of compounds at 200 °C for 4 h. Diisobutylene succinic anhydride, maleic anhydride and 2-octenyl succinic anhydride all give rise to the same signal pattern. When 2,4,4-trimethylpent-1-ene (TMP-1) is heated alone at 200 °C for 4 h no radical species is detected, the same result has been previously obtained for PIB.[112] It would appear therefore that the formation of colour and a carbon-centred radical in autoclave reactions is linked to the presence of dicarboxylic functions. The formation of anhydride based radicals will be discussed in the following chapter (Chapter 5).

'Spin traps' provide a convenient method for obtaining information on short lived reactive radicals.[143] The most common, nitrone and nitroso-compounds, add to the radical species to produce an aminoxyl radical detectable by EPR.[144] In an attempt to identify the carbon-centred radical formed in the high temperature autoclave reaction (figure 4.7a) two nitroso spin traps have been employed, 2,4,6-tribromonitrosobenzene (TBNB, **4.17**) and 2,2-methylnitrosopropane (NMP, **4.18**). In contrast to the previous EPR experiments the spin trap experiments were performed at room temperature due to the thermal instability of **4.17** and **4.18**. The spin traps were used at ~ 50 mM concentration in acetone or acetonitrile.



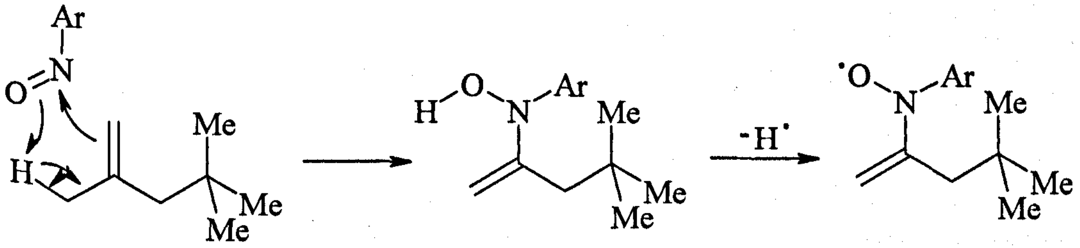
4.17



4.18

Addition of the solution of TBNB to a sample taken from the autoclave reaction results in the intense EPR spectrum shown in figure 4.8. The same spectrum is obtained when TMP-1 and TBNB are mixed alone. This hyperfine split aminoxyl radical (**4.19**) which is observed in both solvents is produced by the ene reaction between TMP-1 and TBNB followed by oxidation of the hydroxylamine product by the nitroso compound (scheme 4.5). The thermal reaction of the spin trap with this olefin severely limits its use in identifying the carbon-centred radical species (figure 4.7a). Hydroxylamines and the resulting aminoxyl radicals are readily produced by thermal ene reactions[86] which occur when aryl nitroso compounds are mixed with a wide variety of olefins containing allylic hydrogens.[145]

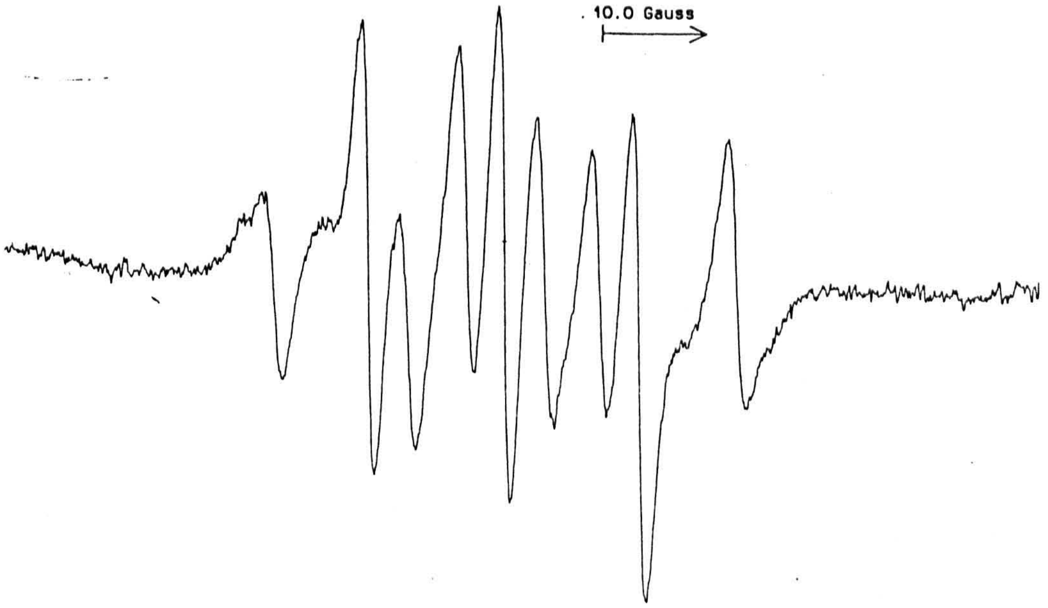
Scheme 4.5: Ene reaction at room temperature between TMP-1 and TBNB (**4.17**).



4.19

However, the less reactive nitroso compound (**4.18**) under the same conditions gave no signal resulting from the formation of an ene-adduct similar to **4.19**. However, it also was unable to trap the radical species observed previously (figure 4.7a). In conclusion the spin traps employed here have failed to react with the radical seen previously in the high temperature EPR experiments. Overall this suggests the radical species is relatively stable, which is consistent with the predictions made previously.

Figure 4.8: EPR spectrum of a conjugated nitroxide radical resulting from the ene reaction between TMP-1 and 2,4,6-tribromonitrosobenzene (**4.17**).



4.8 Summary.

In efforts to identify the coloured by-products formed during the thermal ene reaction between PIB and MA, two model systems have been employed. The first involved a high boiling alkene (1-octadecene) which is convenient for studying the large scale laboratory reaction, whilst the second uses TMP-1 as the ene component, an alkene which is more volatile but mimics the end-groups present in PIB more closely. The reaction of both model alkenes with MA was performed at 200 °C, over variable periods of time.

The reaction of 1-octadecene with various molar equivalents of MA produced a dark brown reaction mixture similar in colouration to that found for reactions of PIBSA. The colour of the mixture was found to increase with the amount of MA in the system which suggests that the coloured by-products result from the decomposition of MA. However, ^{1}H and ^{13}C NMR analysis of the mixture only shows the resonances associated with 1-octadecenyl succinic anhydride and no other compounds. Samples of the reaction mixtures produced with various molar equivalents were also analysed by UV-Vis spectroscopy but no absorbance was seen in the visible region of the spectrum. The only explanation for the colour of the samples is that the intense $\pi \rightarrow \pi^*$ transition at 222 nm tails into the visible region of the spectrum. Attempts to isolate the coloured components using LC and column chromatography were unsuccessful.

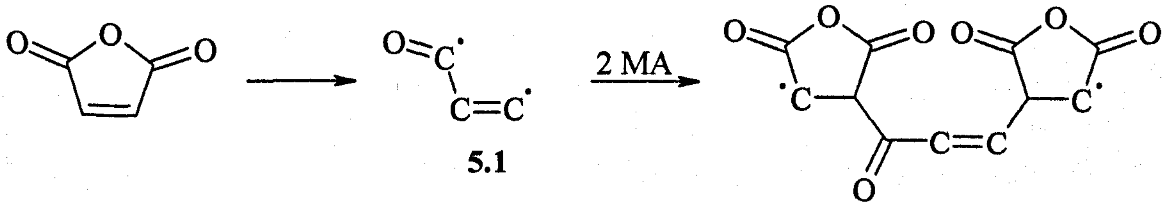
The ene reaction between TMP-1 and 1.3 molar equivalents of MA was carried out in a sealed autoclave. The product of this reaction was volatile enough to be analysed by GC. The reaction produces a dark brown oil which is a complex mixture of compounds many of which have been formed from the ene adduct (DIBSA) as a result of side-reactions of the anhydride group with its own reactive double bond. Concentration of the residue given by this ene reaction results in a dark brown resin which when methylated and analysed by GC/MS contains a number of isomeric long retention time components, which contain fragment ions in their MS consistent with di-ene adducts or derivatives thereof (section 4.4). However, it is thought that the coloured components of this residual solid are either too involatile or too polar to be eluted from a GC column. EPR studies of the TMP-1/MA reaction system show the presence of a carbon-centred radical species. Radical species with similar g-values are also detected in the DIBSA and MA thermolysis products, suggesting that the presence of a radical species is linked to the dicarboxylic function. However, the observation of radical species does not prove that the formation of coloured products is directly linked with a radical process, more work is needed in this area. The formation of polymeric MA and the formation of coloured reaction components during the thermolysis of MA is discussed in more detail in Chapter 5.

Chapter 5

Thermal Decomposition of Maleic Anhydride

The general conclusion arrived at in Chapter 4 was that the colour, tar and resin formed during the PIBSA reaction are derived from maleic anhydride (MA) or at least anhydride containing compounds. Moreover no structure or mechanism for the formation of MA decomposition products has been proposed. However, it has been suggested that such by-products are formed due to the thermal decomposition of MA alone. There is a precedent in the literature for the thermal decomposition of MA in the gas phase at temperatures between 372 and 487 °C and at pressures between 0.7 and 20 Torr to give equimolar quantities of carbon dioxide, carbon monoxide and ethene for which a concerted mechanism has been proposed.[146] However, the temperatures used in the PIBSA and model systems are nowhere near this high but above 210 °C MA is prone to decompose leading to homopolymerisation with the loss of CO_2.[112] This suggests that instead of total decomposition of MA to small fragments, partial decomposition of MA takes place resulting in highly reactive fragments which can form polymeric material, apparent as tar and resin.

Scheme 5.1: Proposed mechanism for the formation of a MA based polymer.



It has been suggested that the formation of an biradical species (**5.1**) is the initial step in this polymerisation process (scheme 5.1),[136] the decomposition of many cyclic compounds being thought to proceed by a biradical mechanism.[146] Thus it can be envisaged that this intermediate will react with MA to propagate the radical species.

However, the energy needed to form a biradical species by simple ring-opening of MA is estimated to be 314 kJ mol^{-1}, which is well above the observed activation energy (255 kJ mol^{-1}) for the vapour phase decomposition of MA.[146] The formation of a biradical species from the thermal decomposition of MA is, therefore, considered unlikely at 200 °C.

Using model alkenes to investigate the formation of resin during the PIBSA reaction has, so far, proven unsuccessful. The conclusions of the previous chapter have led us to test further our observation that heating MA alone results in the formation of the coloured material.

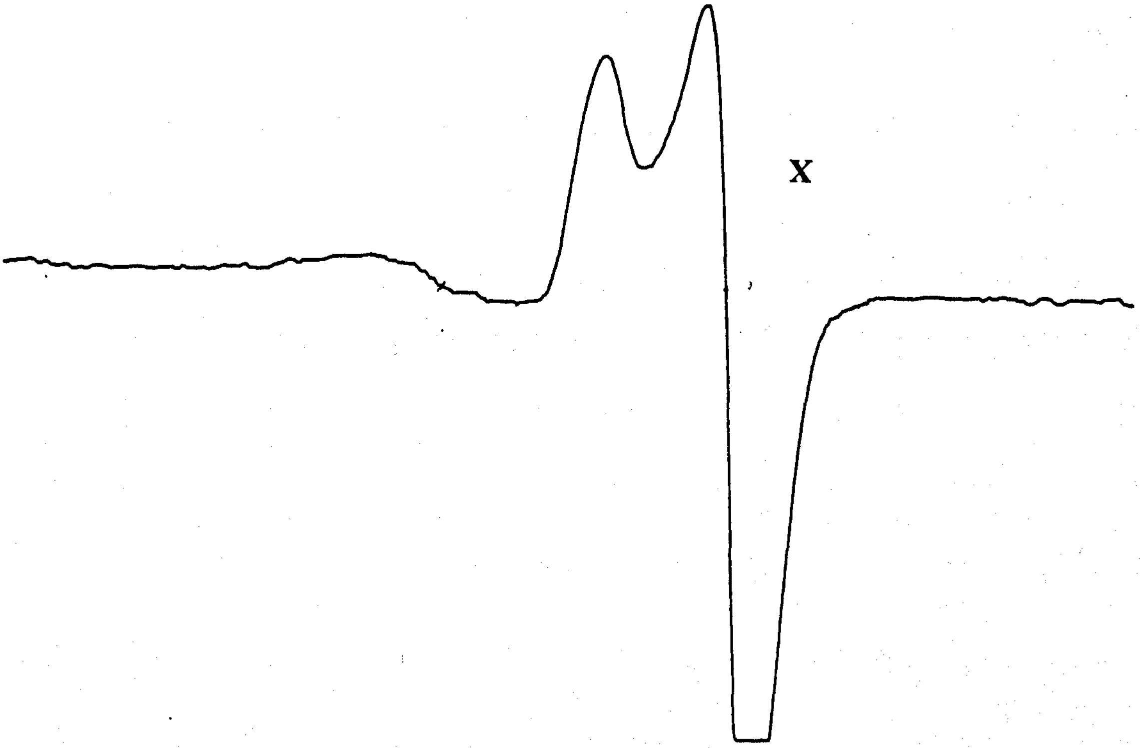
5.1 Autoclave experiments

In order to test the hypothesis outlined above initial experiments were carried out involving thermolysis under standard autoclave conditions in the absence of the ene component. It was thought that this would enable us to study the MA decomposition products in greater detail.

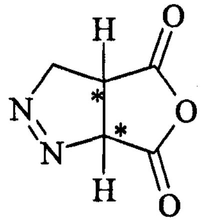
5.1.1 Thermolysis of neat maleic anhydride.

Freshly crushed maleic anhydride (MA, a white solid) was placed in the autoclave and the sealed system heated to 200 °C in a bomb equipped with a thermostat. Heating was continued for 4 h during which time the pressure inside the autoclave increased as a result of the formation of volatile products, possibly CO_2. After heating the reaction product had developed a brown colouration and contained a paramagnetic species, observed as a broad single line spectrum ($g \sim 2.0033$, line width = 0.21 mT) in an EPR experiment (figure 5.1). This spectrum does not contain the hyperfine splitting seen in figure 4.7a (pg 119) for the radical species produced in the TMP-1/MA reaction system. As was the case for the previous EPR experiments the presence of this radical species does not mean that the decomposition of MA, and the formation of coloured compounds, takes place via a radical mechanism. The spectrum in figure 5.1 gives us no further structural information other than the obvious assumption that the carbon-based radical results from MA, which is after all the only compound present in the autoclave. The mechanism of the formation of this radical species in the autoclave is unknown, but the presence of radical species would seem to indicate a radical homopolymerisation of MA at high temperatures. Nakayama and co-workers obtained EPR spectra for realtively stable radicals during the radical initiated polymerisation of MA.[142] The presence of radicals in their system was put down to conjugated molecular systems containing dehydrogenated MA units.

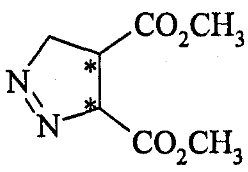
Figure 5.1: EPR spectrum measured for the crude autoclave mixture resulting from the thermolysis of MA at 200 °C for 4 h . Spectrum obtained for the melt of the sample at 100 °C [X = signal for the glass peak of the EPR cell].



It was hoped that further insight into the nature of the coloured product might be gained by separating the components by GC. The decomposition products were analysed by GC/MS, after the anhydride groups in the reaction mixture had been converted into their dimethyl ester derivative in two steps, namely hydrolysis in water followed by methylation of the resultant diacids with diazomethane. Only two volatile components were present in the GC trace. These peaks are separated by only 0.02 minutes and contain the same molecular ions and fragments in their MS which suggests that they are isomers. Both adducts show a molecular ion of *m/z* 186 (relative intensity 1.5%) and fragment via the loss of 59 and 31 daltons, corresponding to CO_2Me and OMe respectively, suggesting that these compounds are based on MA. Diazomethane is a reactive 1,3-dipolar reagent which is known to undergo cycloaddition reactions with MA in cooled (5 °C) ether solutions.[147] This product has been assigned the structure **5.2**. The MS data of both adducts seen in the MA pyrolysis reaction mixture after hydrolysis and methylation is consistent with the dimethyl ester derivative of this compound (**5.3**). The observation of two peaks is due to separation of the distereomeric mixture of diazomethane/MA cycloaddition product (**5.3**) (the chiral centres are indicated in the diagram below by asterisk). The same GC trace is observed when maleic acid has been methylated with diazomethane in a cooled ether solution.



5.2



5.3

The lack of any other peaks in the GC trace not only serves to confirm our suspicion that the coloured by-products, as discussed earlier (section 4.4), are involatile materials, but it also means that an alternative method for methylating MA derivatives must be used. Thus can be achieved can be achieved by a longer route (~ 4 h) which involves refluxing the sample in methanol with a few drops of H_2SO_4.[148] However, using this method on the MA thermolysis reaction product still only gives a peak for the presence of dimethyl maleate alone. The next section is dedicated to the experimental data collected from our studies of the MA thermolysis product using NMR analysis.

5.1.2. ^{1}H NMR analysis of the MA pyrolysis reaction mixture.

The crude reaction mixtures obtained at various MA thermolysis times were analysed by ^{1}H NMR spectroscopy. The colouration of the reaction product was found to vary, from beige to dark brown, depending upon the period of heating. The reaction mixtures were found to contain a number of compounds not present in the starting material. The spectrum shown in figure 5.2 in which d_6-acetone was employed as the solvent has an intense resonance at 7.33 p.p.m. (singlet) due to the presence of MA as well as singlets at 6.40 p.p.m. and 6.77 p.p.m., indicative of fumaric acid and maleic acid respectively. Presumably fumaric acid is formed by the isomerisation of maleic acid, the latter presumably being the result of the presence of formed adventitious water in the system. In table 5.1 we can see how the composition of the thermolysis mixture changes with the period of time MA is heated. Hydrolysis of MA to maleic acid occurs slowly in air, but isomerisation and discolouration do not take place without heating due to the energy barrier of double bond rotation[91] (table 5.1).

Table 5.1: Composition of the crude reaction product from MA thermolysis.

Entry	Heating Period[a] / h	Ratio[b]		
		MA	Maleic Acid	Fumaric Acid
1	0	99.6	0.4	trace
2	0 [c]	98.4	1.6	trace
3	4	99.4	0.0	0.6
4	48	97.4	0.4	1.3
5	71	96.4	0.3	1.6

a : Heating carried out in the autoclave under standard reaction conditions and at 200 °C.

b : Percentage areas by integrating all peaks in the ^{1}H NMR spectra.

c : Crushed MA left to stand in air for 2 days.

The fall in the amount of maleic acid in the thermolysis mixture after 4 h heating at 200 °C (entry 4, table 5.1) is presumably due to the isomerisation of the double bond to fumaric acid. The total area of the maleic and fumaric acid peaks varies little for entries 4 and 5 (table 5.1) and as will be discussed later (in sections 5.1.4) maleic acid and fumaric acid are both white solids which appear to be stable under the standard reaction conditions. Interestingly, the decrease in the amount of MA corresponds to increasing reaction time and colour of the crude reaction mixture. This suggests that the decomposition or loss of MA may be linked to the formation of coloured material. However, the main components of the reaction mixture are MA, maleic acid and fumaric acid which are all white solids, therefore the amount of coloured material must be very small. As well as fumaric and maleic acid the crude ^1H NMR spectra of entries 4 and 5 contain small peaks, just visible above the baseline between 3.5 p.p.m. and 0.9 p.p.m. seen in figure 5.2. An expansion of these minor peaks is shown in figure 5.3. Several signals are observed, the strongest of these peaks being located at 1.18 p.p.m. (singlet peak in the saturated methyl proton region), but their areas do not change with reaction time. The region between 3.2 p.p.m. and 2.5 p.p.m. includes a broad peak, which is not removed by the addition of D_2O. The two singlets at 3.05 p.p.m. and 2.59 p.p.m. have very similar chemical shifts to succinic anhydride (3.04 p.p.m., s) and succinic acid (2.57 p.p.m., s) and are assigned as such. Only the area of the peaks between 3.2 p.p.m. and 2.5 p.p.m., including succinic anhydride and succinic acid peaks, varies significantly with reaction time and therefore it is thought that the resonances in this region could represent the coloured components.

Table 5.2: Vacuum distillation of the crude MA autoclave mixture.

Entry	Reaction Time / h	Distillate / %	Residual brown solid / %
1	4	99.5	0.5
2	48	94.1	5.9
3	71	74.3	25.7 [a]

a : Still contains small amounts of MA and fumaric acid by ^1H NMR.

All the crude reaction mixtures contain major amounts of unreacted MA. The excess MA can be removed by vacuum distillation. MA is distilled as a white solid, leaving the coloured by-products as a residual brown solid. Table 5.2 shows how the amount of the volatile materials recovered by distillation changes with thermolysis time. However, maleic acid and fumaric acid are not removed by distillation and are still present in the residual solid. It should be noted that there is a substantial increase in the amount of residual solid after 71 h which cannot all be accounted for by the inclusion of MA and fumaric acid.

Analysis of the brown solid (entry 3, Table 5.2) by ^1H NMR (solvent d_6-acetone) shows that in all cases the residue contains MA, although the major components are fumaric and maleic anhydride (Figure 5.4). The minor peaks seen previously in the crude reaction mixture become more intense after distillation, there is still a large peak at 3.05 p.p.m. which is attributed to succinic anhydride. The succinic acid seen in the crude reaction mixture presumably dehydrates to form the anhydride during the vacuum distillation process. This spectrum contains a broad peak between 4.2 and 2.8 p.p.m., which is not removed after addition of D_2O, with other signals superimposed ontop in three regions: between 4.2-4.0 p.p.m., 3.4-3.1 p.p.m. and 3.0-2.8 p.p.m.. The resonances in these regions are thought to represent saturated CH and/or CH_2 protons attached to electron withdrawing groups and a ^1H-^1H correlation spectroscopy experiment (COSY) showed that these signals are coupling to each other, but not interacting with any other ^1H nuclei present in the spectrum.

The ^{13}C NMR spectrum of the coloured solid (entry 3, table 5.2) contains a number of regions with broad resonances: 174-168 p.p.m. (br, qC), 51-40 p.p.m. (br, CH) and 34-28 p.p.m. (br, CH_2) p.p.m. (The mutiplicity of the signals has been assigned on the basis of DEPT experiments). Once the strongest peaks in the spectrum are assigned to maleic anhydride and fumaric acid we are left with low intensity resonances in these three regions. The signals at high field are attributed to carbonyl groups, either carboxylic or anhydridic. The signals at lower frequency have been assigned as CH and CH_2 groups resulting from compounds perhaps containing substituted succinic acids or anhydride groups. The shifts for model compounds used to aid our interpretation of the spectra are shown in table 5.3.

Table 5.3: Selected chemical shifts of model compounds.[120]

Model Compound	Chemical shift for backbone, p.p.m.	Chemical shift qC group, p.p.m.	Solvent
2,3-Dimethylsuccinic acid	42.0 (CH)	175.8	$CDCl_3$
2,2-Dimethylsuccinic anhydride	42.8 (CH_2)	169.5, 177.3	$CDCl_3$

The low intensity and broadness of the signals in the ^{13}C NMR spectrum described above is thought to result from the mutiplicity of compounds with very similar structures present in the sample. Another suggestion is that MA polymerises through the double bond to form poly(maleic anhydride) (PMA) which contains succinic anhydride or acid units. This could explain the observation of radical species in the crude MA thermolysis reaction mixture (section 5.1.1).

It has been suggested that the colour of the MA thermolysis reaction mixture results from the formation of a polymer containing conjugated keto-olefinic units. However neither the ^1H and ^{13}C NMR spectra contain any olefinic resonances, in addition the UV-Vis spectrum for a solution of the residual solid (entry 3, table 5.2) in acetonitrile (0.002% by weight) shows only an intense signal (absorbance = 0.57) at λ_{MAX} = 208 nm resulting from the $\pi \rightarrow \pi^*$ transition of the carbonyl groups.[114] The intensity of this absorbance band means that the broad peak tails into the visible region of the spectrum, although there is no evidence for the presence of any conjugated double bonds in the coloured solid. Another suggestion is that MA totally decomposes at 200 °C and under the pressure of the autoclave system to form small particles of carbon black which are undetectable but highly coloured.

In order to determine whether the sample contains polymeric maleic anhydride and to measure the molecular weight of any such polymer mass spectral analysis of the residual solid, from entry 1 in table 5.2, has been attempted. However, due to their high molecular weight the MS of such polymers is measured using Fast Atom Bombardment (FAB) ionisation method in the positive mode. Figure 5.5 shows the

MS obtained from this experiment, no significant ions are observed higher than *m/z* 307.1 and none of the ions below this value are divisible by 98 mass units, the molecular weight of MA. However, the FAB MS of poly(maleic anhydride) in the literature contains significant ions separated by 98 mass units up to *m/z* 1180, therefore the presence of oligo(maleic anhydride) is not confirmed by this method.[149]

As can be seen in figure 5.4 the residual solids which have been analysed so far still contain the starting material and fumaric acid. It would be beneficial to our future studies if these compounds could be removed. The boiling point of MA is 200 °C, which means that it can easily be removed by vacuum distillation. However, maleic acid and fumaric acid have very high boiling points and therefore cannot be removed by this method, but their more volatile methylated derivatives can. The residual solid, obtained from entry 2 (table 5.2), was methylated by reflux in methanol with a few drops of acid. GC analysis of the methylated product shows only two peaks assigned to dimethyl fumarate and dimethyl maleate. After removal of these dimethyl esters from the methylated product by vacuum distillation a much simpler ^{1}H NMR spectrum is obtained (figure 5.6). This spectrum contains a set of overlapping methyl ester signals at 3.7 p.p.m. and a broad resonance centred at 3.2 p.p.m. for the saturated CH/CH_2 groups. The ^{13}C NMR spectrum of the methylated derivative of entry 2 in table 5.2 contains a broad signal at 54-51 p.p.m. representing the methyl groups of the ester groups. The results from this experiment suggest that the residual solid represented in figure 5.4 contains carboxylic or anhydridic groups. IR spectroscopy confirms this with a number of peaks in the carbonyl region at 1781.9, 1754.0 and 1742.6 cm^{-1}.

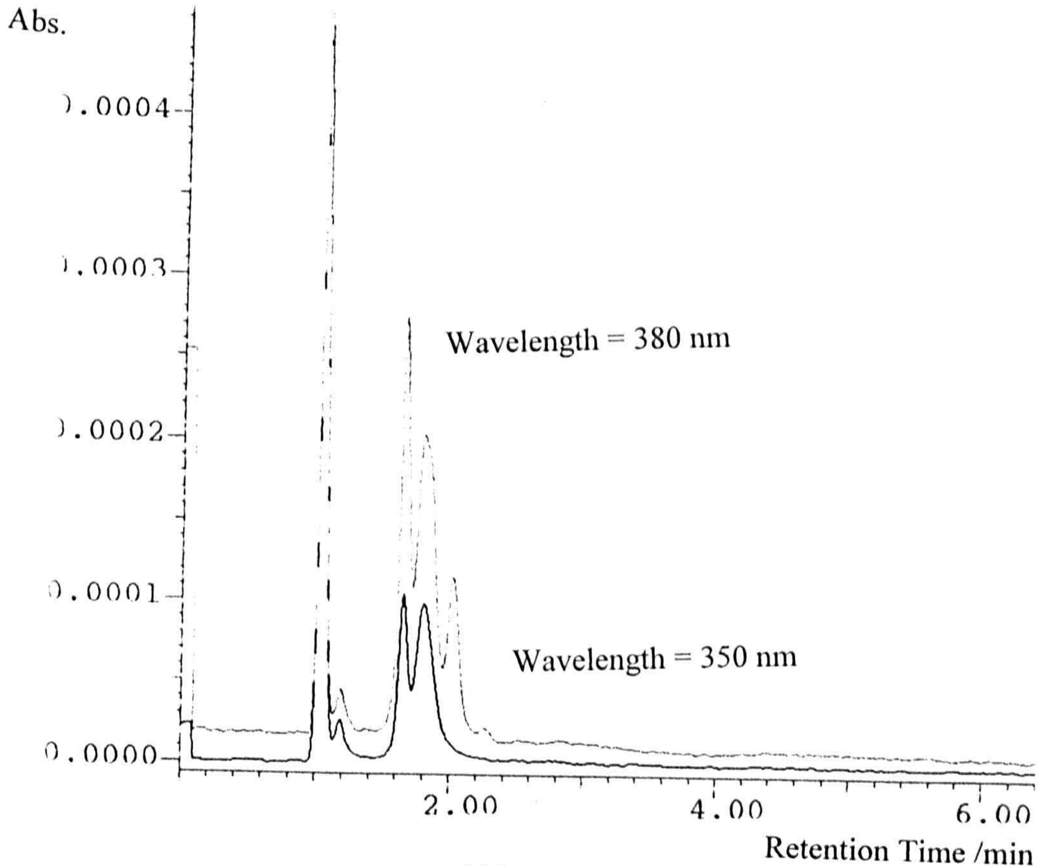
5.1.3 Analysis of the MA thermolysis reaction mixture using LC/MS.

We have seen earlier that the coloured constituents of the MA thermolysis reaction mixture are not volatile (polymeric) or too polar to be separated by GC. The alternative method for the separation of polymers or highly polar materials is liquid chromatography (LC). In order to determine whether the MA thermolysis product contained separable components the hydrolysed and methylated residual solid (entry

1, table 5.2) was analysed by high-pressure liquid chromatography (HPLC). Figure 5.7 shows the HPLC trace of the methylated solid measured at UV wavelengths of 350 and 380 nm. There appear to be several short retention time peaks in the LC trace so LC/MS, using an electrospray interface, was employed.

However, electrospray ionisation (ESI) in the positive mode failed to give any ions stronger than the background noise. Figure 5.8 shows a MS obtained with this method. As can be seen in this spectrum there is a envelope of low intensity ions between *m/z* 300 and 1500 which is thought to be background noise. The only major ion that rises above the background noise has a *m/z* of 1150. However, comparison of this spectrum (figure 5.8) with those run without the sample also show this ion, therefore this is also thought to be a background ion. ESI experiments on the unmethylated residual solid (entry 1, table 5.2) also did not contain any significant ions above the background noise. The homopolymer of MA would be expected to show ions which differ by *m/z* 98 corresponding to the (succinic anhydride)$_x$ units.

Figure 5.7: LC trace of the methylated residual solid (Entry 1 in Table 5.2). Components eluted with in 100% acetonitrile on a C18 reverse phase column.



5.1.4 Thermolysis of maleic acid and fumaric acid.

Presumably, hydrolysis of MA in the autoclave reactions to give maleic acid occurs due to the presence of adventitious water and isomerisation to fumaric acid occurs on heating maleic acid. However, it is necessary to determine the stability of these reaction products to the harsh conditions used in the autoclave. Initially the autoclave was charged with maleic acid (a white solid) and then heated under the standard conditions (200 °C for 4 h). Thermolysis of maleic acid results in a beige coloured product, which contains 84% fumaric acid, 12% maleic acid and 0.8% maleic anhydride by ^1H NMR. Neither MA or fumaric acid could be identified in the ^1H NMR spectrum of the commercial sample of maleic acid. The crude product was refluxed in methanol overnight, and the dimethyl fumarate and maleate produced were subsequently removed by distillation. The resulting brown residue contained a small amount of dimethyl fumarate, resonances at 6.78 p.p.m. (s, 2H, CH=) and 3.77 p.p.m. (s, 6H, OMe). As with the MA thermolysis (section 1.1) this spectrum contains a broad methyl ester peak at 3.6 p.p.m., suggesting that this sample contains a number of compounds which contain methyl ester groups in chemical environments that only differ very slightly. This spectrum also contains peaks in the aliphatic proton region, 1.3-0.8 p.p.m., which are similar to those previously seen in the MA experiments. A broad singlet peak at 2.9 p.p.m. in the ^1H NMR spectrum is probably due to CH hydrogens in the PMA derivative.

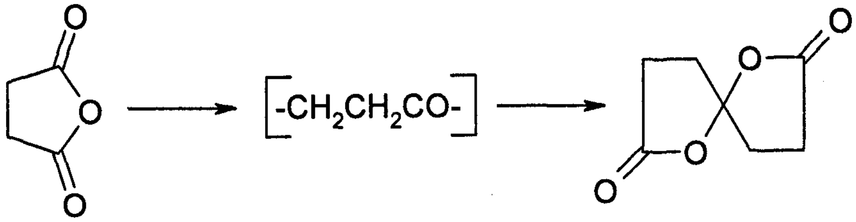
Thermolysis of fumaric acid (a white solid) was carried out in a similar manner to MA by heating in the autoclave at 200 °C for 4 h. After heating the autoclave was allowed to cool for 30 minutes before opening. However, unlike maleic acid, there was no visible change to the colour of the material recovered from the autoclave with fumaric acid suggesting that no decomposition had occurred. This was confirmed by ^1H NMR (solvent d_6-acetone) which contained only one peak, a singlet at 6.70 p.p.m., indicative of fumaric acid. It appears that fumaric acid is stable to our thermolysis conditions. The colouration of the reaction product resulting from the thermolysis of maleic acid, therefore, is probably due to the decomposition of MA, which is formed by dehydration of maleic acid at 200 °C.

5.1.5 Thermolysis of succinic acid and succinic anhydride.

Thermolysis of MA produces small quantities of succinic anhydride and succinic acid. To determine whether these compounds are intermediates in the formation of the coloured components they have been subjected to the standard autoclave conditions (200 °C for 4 h). The standard sample of succinic acid, a white solid, was found to contain minor amounts of fumaric acid, 0.3% by integration of the respective peaks in the ^{1}H NMR spectrum. The intensity of the signal for fumaric acid is very similar even after thermolysis, this is not surprising as fumaric acid has been found to be stable at 200 °C (section 5.1.4). The thermolysis mixture was extracted from the autoclave with acetone and evaporated to give a beige solid. Analysis of the crude reaction mixture by ^{1}H NMR showed only two peaks, apart from fumaric acid, both were singlets corresponding to 99.7% of the starting material (2.57 p.p.m.) and 0.3% succinic anhydride (3.04 p.p.m.).

The ^{1}H NMR spectrum of the commercial succinic anhydride contained a minor peak apart from the expected signal at 3.04 p.p.m.. This peak integrated to 2.0% of the sample and was assigned to the hydrolysed derivative, succinic acid. After thermolysis of this mixture in an autoclave at 200 °C for 4 h the colour of the resultant solid was much more pronounced than that seen after the thermolysis of succinic acid, a black solid being obtained. In contrast to the analysis of succinic acid, as well as peaks for succinic anhydride (93.7 %) and succinic acid (4.7 %), minor peaks were also seen in the aliphatic hydrogen region at 1.27 (br s), 1.10 (t, *J* 7.0) and 0.86 (qd, *J* 1.7 and *J* 6.3). The compound(s) responsible for these peaks have not been identified, although it is not thought that they are responsible for the samples colour. The thermolysis of succinic anhydride between 250 and 300 °C has been studied by Brown and Richie. On heating, the anhydride eliminated CO_2 followed by addition of the resulting diradical fragment to a carbonyl group of a further anhydride molecule to yield a spiro-lactone (**5.4**) (scheme 5.2).[150] The exact nature of the intermediate is unclear: a bi-radical seems unlikely and there is no obvious reason why such a species should add to a carbonyl function. However, no evidence was found in the ^{1}H NMR spectrum of our succinic anhydride thermolysis product for this type of product.

Scheme 5.2: Proposed mechanism for the decomposition of succinic anhydride



5.4

The formation of the coloured product from the thermolysis of succinic anhydride remains a mystery and, unlike the MA system (section 5.1.2), the excess starting material cannot be removed by distillation. However, due to the intense colour of the reaction mixture succinic anhydride remains a suspect for decomposition to give coloured materials, although the lack of any other compounds in the ^{1}H NMR spectrum is strange. One explanation for the absence of any spectroscopic data which points to coloured by-products in the MA and succinic anhydride thermolysis mixtures is that they totally decompose to carbon black. This is undetectable by any spectroscopic techniques but is intensely coloured.

5.3 Formation of poly(maleic anhydride)(PMA).

Overall, the data set out in section 5.1 and 5.2 leads to the suggestion that the residual solid contains polymeric material based on succinic anhydride units. PMA, polymerised through the double bond of MA rather than the carbonyl groups, would be expected to contain a range of hydrogen environments resulting in multiple signals in the NMR spectra with similar chemical shifts to the CH_2 hydrogens in succinic anhydride. Many of the published reports in this area are concerned with the polymerisation of MA via routes other than thermolysis. Therefore, a study of the various forms and methods for producing polymeric MA was undertaken in the hope that further insight might be provided into our thermolysis experiments and a standard sample of PMA could be obtained.

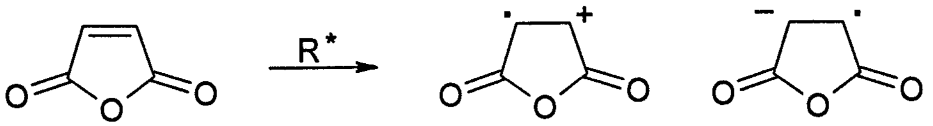
However, recent papers on the melt functionalisation of polypropylene with MA have shown that poly(maleic anhydride) chains are formed.[149, 151] In a study by de

Roover and co-workers[149] low molecular PMA chains were observed by low molecular weight size exclusion chromatography (SEC). A detailed review of the various techniques used for the homopolymerization of MA has been presented by Trivedi and Culbertson.[152] Initiation of the homopolymerisation process can be achieved using many methods, including UV and γ-radiation, free radical catalyst and organic bases. However, there is still uncertainty about the mechanism for the formation and the exact structure of PMA. An EPR signal similar to that observed in the MA thermolysis reaction mixture (figure 5.1) has also been seen in the anionic[153] and radical[142] initiated polymerisation processes. The presence of an EPR signal has been taken to indicate a paramagnetic character in the polymer due to cross-conjugation, which it has been suggested is characteristic of keto-olefinic structures.[142] However, no other spectroscopic data has been put foward to backup these conclusions.

5.3.1 Initiation by free radicals.

Free-radical polymerisation of MA would be expected to form a polymer through the vinyl function rather than the through the anhydride function. Many of the papers on the homopolymerisation of MA using free-radical initiators have been published by Gaylord and co-workers.[154-156] Normally, free-radical catalysts promote polymerisation of vinyl monomers, however complete polymerisation of MA needs high concentrations of initiator. An exception is when conventional amounts of monomer are heated at temperatures where the half life of the catalyst is < 1 h, preferably < 30 mins.[155] Polymerisation of MA is normally initiated by slow addition of peroxides, such as dibenzoyl or di-*t*-butyl peroxide, to molten MA at temperatures between 80 to 180 °C.[154] Under these conditions the initiator decomposes rapidly to produce an excited species which transfers its excitation energy to MA. This process produces polymerisable MA in the form of an excited monomer complex or excimer (scheme 5.3).[155, 156]

Scheme 5.3: Proposed mechanism for the transfer of excitation energy from the excited initiator to MA.



Radical inhibitors have no effect on the homopolymerisation of MA suggesting that the active species is ionic rather than free radical. Gaylord proposed that the polymerisation proceeds by coupling of the excimer with the catalyst radical or hydrogen abstraction from MA or PMA.[154] The propagating species is the MA excimer which creates a terminal radical, therefore, the sequence is repeated to generate an excited complex at the end of the propagating chain.[154]

5.3.2 Synthesis of PMA.

In order to compare the spectroscopic properties of PMA and the coloured solid obtained from the pyrolysis of MA it was deemed necessary to synthesise a standard sample of this polymer using literature methods. The polymerisation process was initiated using a peroxide, which was cleaved at high temperatures to produce the excited radical species which transfers the required energy to the monomer. In a standard procedure the peroxide (2 mol %, di-*t*-butyl or dibenzoyl peroxide) was added over a 10 minute period to molten MA. Formation of PMA was found to increase with the temperature at which the polymerisation was carried out (table 5.4). It can be seen from entry 1 in table 5.4 that the peroxide acts to catalyse the polymerisation process. After MA was heated at 120 °C for 18 h without the initiator only small amounts of MA were precipitated in toluene, no PMA was formed. Many papers describe similar procedures to polymerise MA, the solvents used to precipitate the product varies. Our experiments show that a higher accountability of MA is given by dibenzoyl peroxide compared to di-*t*-butyl peroxide, entries 2 and 3 in table 5.4 [Accountability = (Mass of polymer precipitated / Initial mass of MA) × 100]. Varying the experimental conditions of the polymerisation process using dibenzoyl peroxide as the initiator (entries 3 to 7, table 5.4) shows an increased accountability with an increase in the reaction time and temperature. The colour of the resulting polymer is highly variable ranging from off-white to dark brown. The accountability also varies for entries 4 to 6, which were carried out under the same experimental conditions, depending on the solvent used to precipitate the polymer.

Table 5.4: Conditions and results obtained from the radical-catalysed polymerisation of MA.

Entry	**Peroxide, 2 mol %, $(RO)_2$ R =**	**Temperature / °C**	**Time / h**	**Colour**	**Accountability / %**
1	None	120	18	white	3.1[a] (MA)
2	t-Bu-	80	1	Pink	9.4[a]
3	PhC(O)-	80	1	Off-White	10.5[a]
4	PhC(O)-	120	3	Brown	27.9[a]
5	PhC(O)-	120	3	Brown	16.0[b]
6	PhC(O)-	120	3	Beige	7.6[c]
7	PhC(O)-	120	18	Brown	30.6[a]

a : Precipitated with toluene. Reference 157

b : Precipitated with chloroform. Reference 154

c : Reaction performed under N_2 atmosphere and ppt with chloroform from acetone solution. Reference 156

However, accountability of the polymerisation process can be a misleading way to analysis these polymers. As shown by ^{1}H NMR analysis of entries 4 to 6 in table 5.4 these reaction products, along with PMA, also contain MA and various other by-products, mostly maleic acid and fumaric acid (table 5.5). It was thought that maleic acid and fumaric acid may also be polymerising. However, attempts to form poly(maleic acid) from maleic acid using dibenzoyl peroxide at 140 °C were unsuccessful. Higher temperatures were not used in fear of degrading the peroxide initiator, thus a similar reaction with fumaric acid was not possible because of the temperature which would be required to melt this acid. These results seem to further confirm our suspicion that maleic acid and fumaric acid are not involved in the formation of polymer in the MA thermolysis reactions reported in section 5.1.1.

Table 5.5: ^{1}H NMR analysis (in d_6-acetone) of polymerized MA in table 5.4.

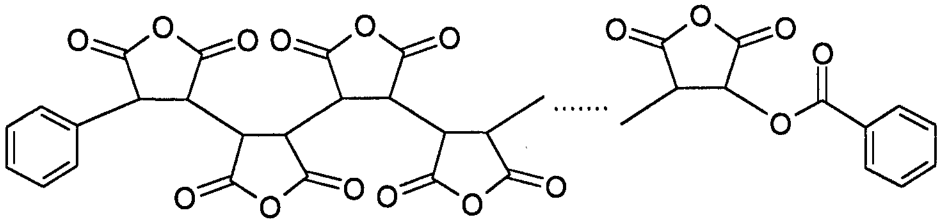
Entry	Accountability / %	Ratio[a]		
		MA	Maleic Acid	PMA
4	27.9	54.2	1.7	43.9
5	16.0	23.4	8.9	67.7
6	7.6	10.7	6.2	83.0
8	3.9	0.5	1.7	97.8

a : Ratio of peaks obtained from integration areas in the ^{1}H NMR spectra.

The purity of the polymer can be improved by reprecipitation, for example the polymer shown as entry 6 in tables 5.4 and 5.5 was reprecipitated a second time from an acetone solution with $CHCl_3$. The polymer was obtained as a dark yellow solid which was dried under vacuum for several hours. Analysis of this solid by ^{1}H NMR showed that the sample is virtually pure PMA. Further characterisation and reactions were, therefore, performed using this sample.

In agreement with the published spectroscopic data the ^{1}H NMR spectrum (figure 5.9) contains a broad peak in the region of 5.10-3.81 p.p.m. which has been assigned as the CH resonance of the succinic anhydride backbone of the polymer.[157, 158] This broad signal is not removed after addition of D_2O and is indicative of a polymer formed by polymerisation of the monomer through the double bond functionality. PMA prepared by the free-radical initiated route is a low molecular weight polymer[152] as indicated by the relatively intense signals resulting from the phenyl and benzoyl end-groups in the ^{1}H NMR spectrum (between 8.1 to 7.3 p.p.m.). Typically, PMA contains between 10 and 25 succinic anhydride groups per phenyl or benzoyl group arranged in the following sequence (figure 5.10).[158]

Figure 5.10: Structure of poly(maleic anhydride) produced by benzoyl peroxide radical initiated homopolymerization of MA.



Like MA, PMA is hydrolysed relatively easily if left to stand in the air. The CH backbone resonance of the hydrolysed product is seen as a broad peak between 4.8 p.p.m. and 3.6 p.p.m. in the ^{1}H NMR spectrum, the dimethyl ester derivative of this compound can be formed by methylation with diazomethane. This displays a new broad signal at 3.71 p.p.m. due to the CH_3 resonance of the methyl ester groups, which confirms that PMA formed contains an anhydride function. The ^{13}C NMR spectrum of this polymer (in d_6-acetn) contains three broad resonances at 174-171 p.p.m. (qC, C=O), 53.6 p.p.m. (CH_3, OMe) and 47.5-43.5 p.p.m. (CH, CH backbone of the polymer).

The UV-Vis spectrum of PMA was measured for comparison with the spectrum recorded for the MA thermolysis product (entry 3, table 5.2). However, the molecular weight of the polymer is not known, therefore the concentration of the solution used to record these spectra cannot be calculated. An arbitrary concentration based on weight % is used instead. The uv-vis spectrum of PMA was recorded using 0.002% by weight of the polymer, the $\pi \rightarrow \pi^*$ transition of carbonyl groups observed at 191 nm is very intense resulting in an absorbance maximum of 0.57. On the other hand the $n \rightarrow \pi^*$ transition ($\lambda_{MAX} = \sim 330$ nm) is too weak to be detected at low concentrations. Even though PMA is coloured there is no evidence in these spectra for conjugated products, such as the ketoolefinic structures suggested by some authors.[159] The IR spectrum of PMA contains characteristic bands for the carbonyl groups of cyclic anhydride at 1781.7 and 1738.4 cm^{-1}.in similar positions to those reported earlier (section 5.1.2) for the MA thermolysis residual solid.

5.3.3 Excited species and radical-catalysed PMA.

In agreement with the proposed mechanism[154], addition of a sensitizier [N,N-dimethyl formamide (DMF) or caprolactam] having a triplet energy < 68 kcal mol^{-1} to the MA melt prior to initiation of homopolymerisation process was found to completely inhibit the formation of PMA. Inhibition presumably involves electron donation from the additive to the MA radical cation, which is an important intermediate in the homopolymerisation of MA.[156] Reactions were performed as described in section 5.3.2 apart from the inclusion of an additive.

Both additives, having a triplet energy < 68 kcal mol^{-1}, completely inhibited the formation of PMA (table 5.6). However, the reaction mixture develops a dark colouration (deep purple), which persists when the initiator is excluded. The colour of these reaction mixtures can, perhaps, be explained by the formation of a charge transfer complex (CTC) between MA and the amide. The formation of CTCs between MA and amines have been studied.[160-162] This colour is similar to that observed in the product recovered from the autoclave after thermolysis of MA. The formation of CTC and the anionic polymerisation of MA have been investigated further in the following section.

Table 5.6: Effect of additives on the radical polymerization of MA.

Entry	Additive, 1 mmol	Peroxide, 1 mmol, $(RO)_2$ R =	Temperature / °C	Time / h	Accountability / %
5[a]	None	PhC(O)-	120	3	16.0
9	DMF	PhC(O)-	120	3	0.0
10	Caprolactam	PhC(O)-	120	3	0.0
11	DMF	None	120	3	0.0
12	Caprolactam	None	120	3	0.0

a : Entry 5 from table 5.4.

5.3.4 Initiation by organic bases.

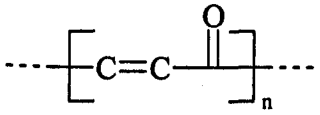
Several previous studies have described the polymerisation of MA in the presence of organic bases, such as pyridine and triethyl amine.[157,159,163] A spontaneous exothermic reaction, accompanied by evolution of a gas, occurs on addition of a catalytic amount of pyridine to the anhydride. This reaction results in a dark-coloured polymeric material soluble in polar solvents. Pyridine is incorporated in the polymer chain as an end group.

Using pyridine in this manner resulted in the formation of only small amounts of the black solid. In the presence of organic bases higher temperatures are known to increase the yield of the polymerisation.[163] Therefore autoclave reactions were carried out using 1 mmol of DMF or caprolactam as the base catalysed at 200 °C. In both cases the product extracted from the autoclave after 4 h with acetone was a black foam. The polymer was precipitated from the acetone solution with chloroform to give a dark brown solid (Accountability = 54% with DMF and 56% with caprolactam). It seems, therefore, that these additives act to catalyse the decomposition of MA at higher temperatures. The dark brown solids obtained with DMF and caprolactam gave very similar ^{1}H NMR spectra, but for simplicity only the analysis of DMF material is described below.

The ^{1}H NMR spectrum (in d_6-acetone) of the material obtained using DMF as the catalyst is shown in figure 5.11. The peaks between 7.3 and 6.4 represent the starting material and its hydrolysed derivatives, maleic acid and fumaric acid, as was the case for the thermolysis of MA alone. The formation of a DMF:MA complex, which leads to ring-opening of MA by DMF, is shown by the peak at 8.0 p.p.m., which is removed by hydrolysis of the sample in H_2O at 60 °C. Figure 5.11 contains a broad resonance between 3.7 p.p.m. and 2.2 p.p.m., which is not removed after addition of D_2O, with other signals superimposed ontop [H_2O resonance seen at 4.1-3.8 p.p.m. (br s)]. Unlike PMA obtained with radical initiators the peaks in the ^{1}H NMR spectrum (figure 5.11) closely resemble those seen in figure 5.4 in the region between 3.7 p.p.m. and 2.2 p.p.m.. The resonances in this region are thought to represent saturated CH and/or CH_2 protons attached to electron withdrawing groups.

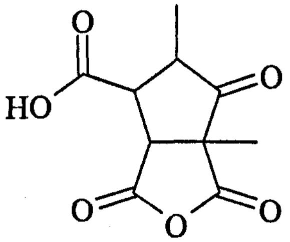
As seen previously in figure 5.4 for the residual solid obtained from the thermolysis of MA alone, the main components in the region can be assigned as succinic anhydride (3.05 p.p.m.) and succinic acid (2.57 p.p.m.). The formation of succinic anhydride and succinic acid during the base catalysed polymerisation of MA is not fully understood but these two compounds have also been observed by Wurn and co-workers using pyridine as the base.[161] Published results involving pyridine-d_5 as the initiator showed that succinic anhydride is formed by hydride shift from MA alone.[161] However, the exact structure and the mechanism for the formation of the resulting polymer is not known.

It has been proposed that initiation of this polymerisation process involves the formation of a 1:1 charge-transfer complex between MA and the base.[160] Wurn and co-workers, however, regarded the polymerisation reaction intermediate to be a 2:1 MA:pyridine compound.[161] It has also been suggested that the colour of the polymer results from a structure containing conjugated poly(vinylene-keto anhydride) units (**5.5**), with some cyclopentanone (**5.6**) and anhydride (**5.7**) units. Although, no conclusive evidence has been given in the literature for any one structure and their validity has been questioned by Bacskai[157].

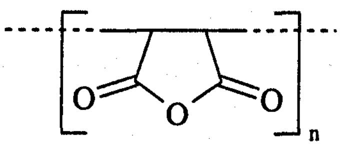


$$\cdots\!\left[\mathrm{C{=}C{-}}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\right]_n\!\cdots$$

5.5



5.6



5.7

However, the proposed structure appears to be unacceptable because the absorption characteristics of our product are inconsistent with the presence of **5.5**. The spectrum of the polymer formed by the thermolysis of MA in the presence of DMF does not contain any alkenic resonances (figure 5.11). It is unlikely, therefore, that the polymer contains a conjugated keto-olefinic structure. However, it is possible that the polymer could contain repeating units of the other **5.6** and/or **5.7**, but a material containing these components would not be expected to absorb in the visible region of the electromagnetic spectrum. We are unable to give a confident prediction for the origin of the colour in this polymer. The ^{1}H NMR data suggests that the structure of the majority of the reaction mixture, as seen previously for the MA thermolysis residue (figure 5.4), is a structure containing substituted succinic acid and/or anhydride units.

5.4 Summary and conclusions.

Thermolysis of MA at 200 °C in the autoclave system gives a number of decomposition products. The reaction mixture is also coloured and the intensity has been shown to increase with the reaction period. The major by-products are maleic acid and fumaric acid formed as a result of adventitious water in the system. Fumaric acid has been shown to be stable to the standard reaction conditions and maleic acid only dehydrates to MA or isomerises to fumaric acid. Also produced during the autoclave reactions of MA are succinic anhydride and succinic acid. Decomposition of succinic anhydride, although resulting in a coloured material, does not give any detectable reaction products by NMR. This suggests that a further decomposition of succinic ahydride, formed during the thermolysis of MA, might be responsible for the colour of the reaction mixture even though these components cannot be detected.

The ^{1}H NMR spectrum of the MA thermolysis reaction mixture also shows a broad resonance between 4.2 p.p.m. and 2.8 p.p.m. which is thought to originate from a polymeric compound containing CH and/or CH_2 groups attatched to an electron withdrawing functionality. This is supported by peaks in the ^{13}C NMR spectrum. The chemical shifts of these peaks are, however, not consistent with a conjugated sp^2 hybridised carbon environment which might be expected to be coloured. An EPR spectrum has been observed for the MA decomposition mixture which may be consistent with radical polymerisation of MA. A model polymer has been synthesised by radical initiated polymerisation through the double bond of MA. However, the ^{1}H NMR chemical shift of this poly(maleic anhydride) is inconsistent with the broad peak observed in the spectrum of the MA decomposition products although both give similar ^{13}C NMR, UV-Vis and IR spectra suggesting a similar but non-identical structure. Base-catalysed homopolymerisation of MA, however, gives a ^{1}H NMR spectra which is consistent with the spectrum obtained from the MA decomposition products. Previous authors have obtained a coloured polymeric material during the bulk homopolymerisation of MA using pyridine and have attributed this colour to the formation of conjugated keto-olefinic units (**5.5**).[157] An alternative explanation for the lack of spectroscopic evidence for the origin of the colour is that there is total decomposition of some organic molecules to carbon black. This is undetectable by any spectroscopic techniques but would be intensely coloured.

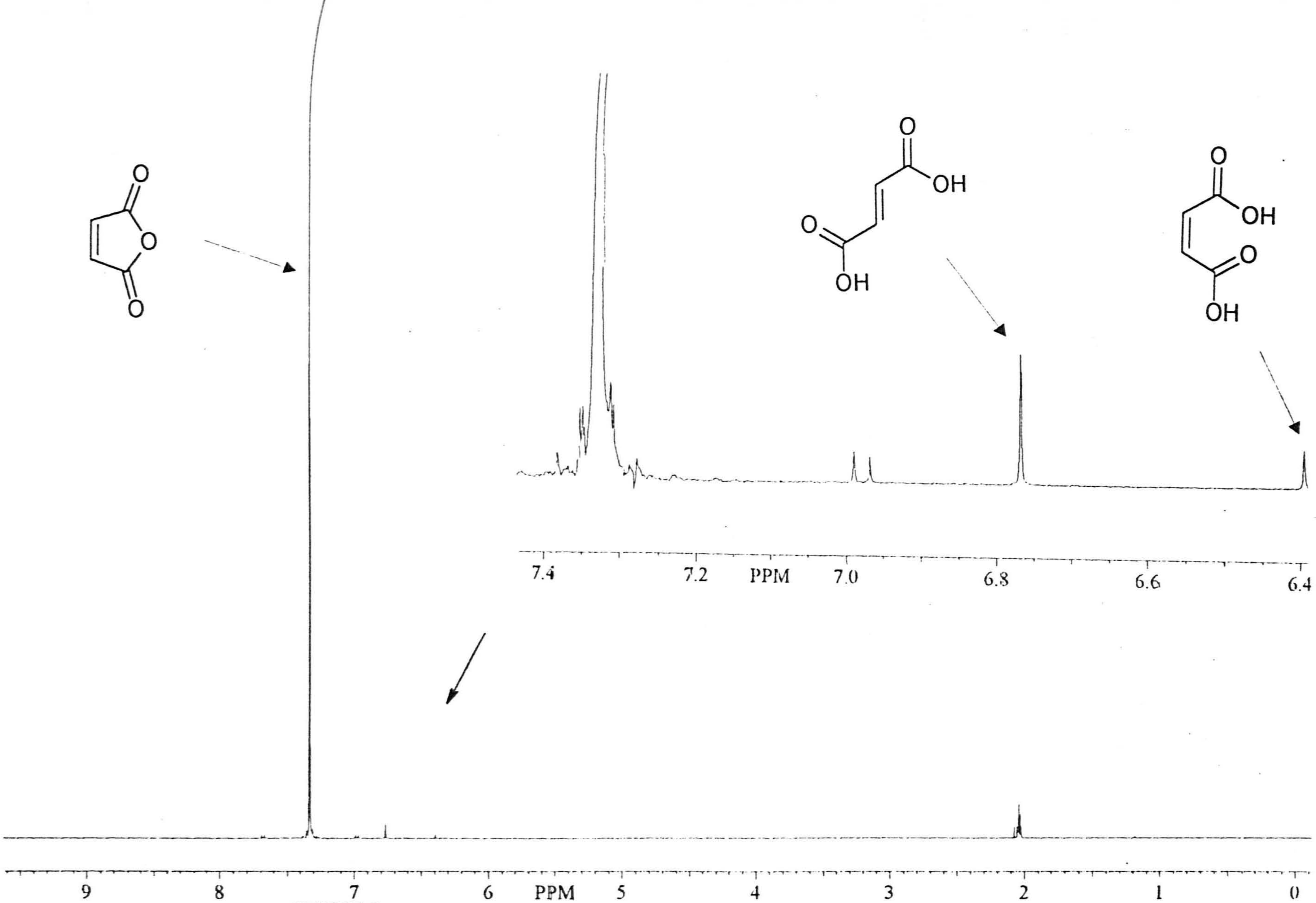


Figure 5.2: ^{1}H NMR spectrum (d$_6$-Acetone) of the crude reaction mixture from the Thermolysis of MA for 48 hours.

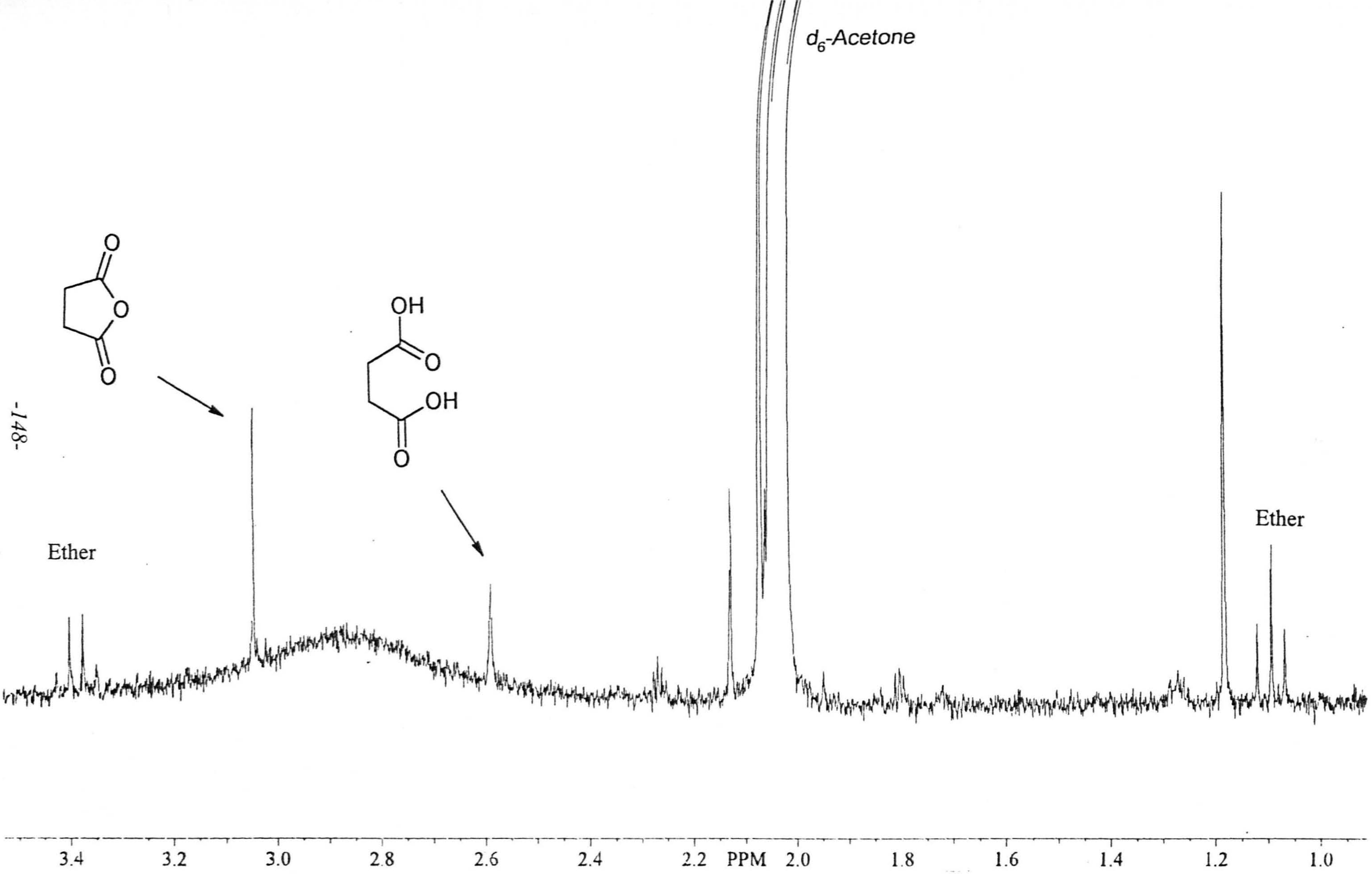


Figure 5.3: ^{1}H NMR spectrum (d_6-Acetone) of the crude reaction mixture from the thermolysis of MA for 48 hours, expansion between 3.5 p.p.m. and 0.9 p.p.m.

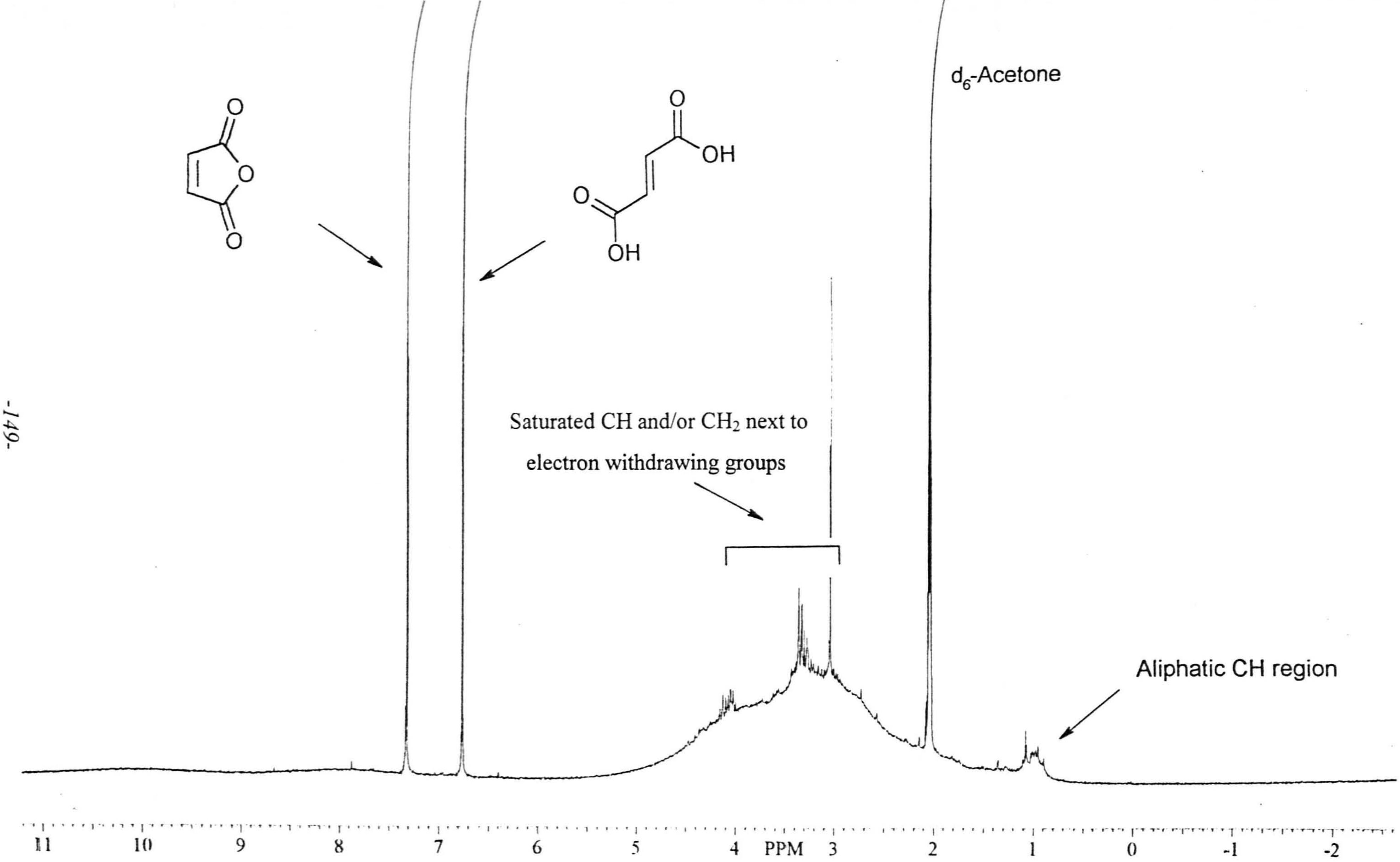


Figure 5.4: ^{1}H NMR spectrum (d_6-Acetone) of the distillation residue from the thermolysis of MA for 71 hours.

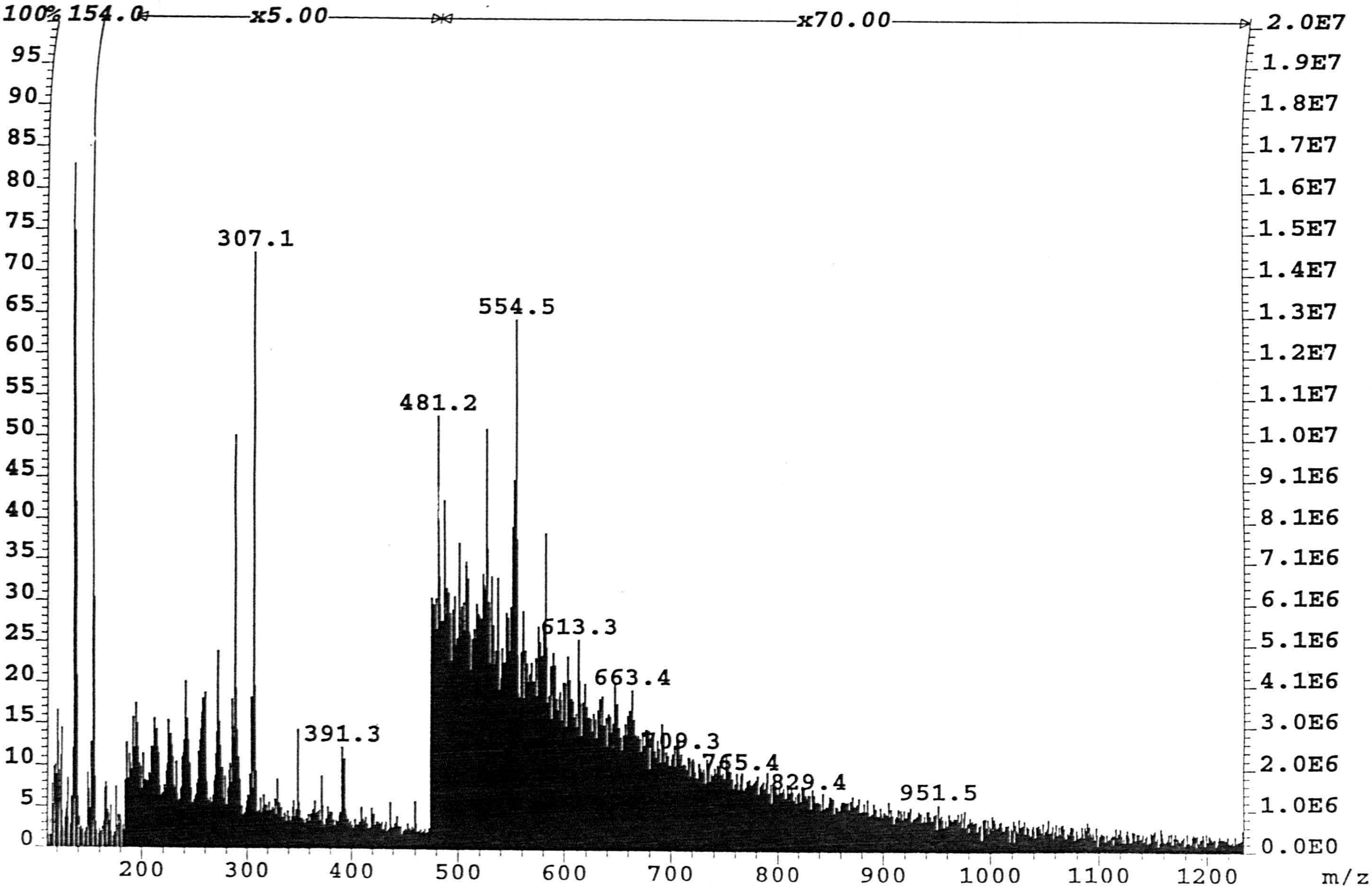


Figure 5.5: FAB MS of the distillation residue from the thermolysis of MA for 4 hours.

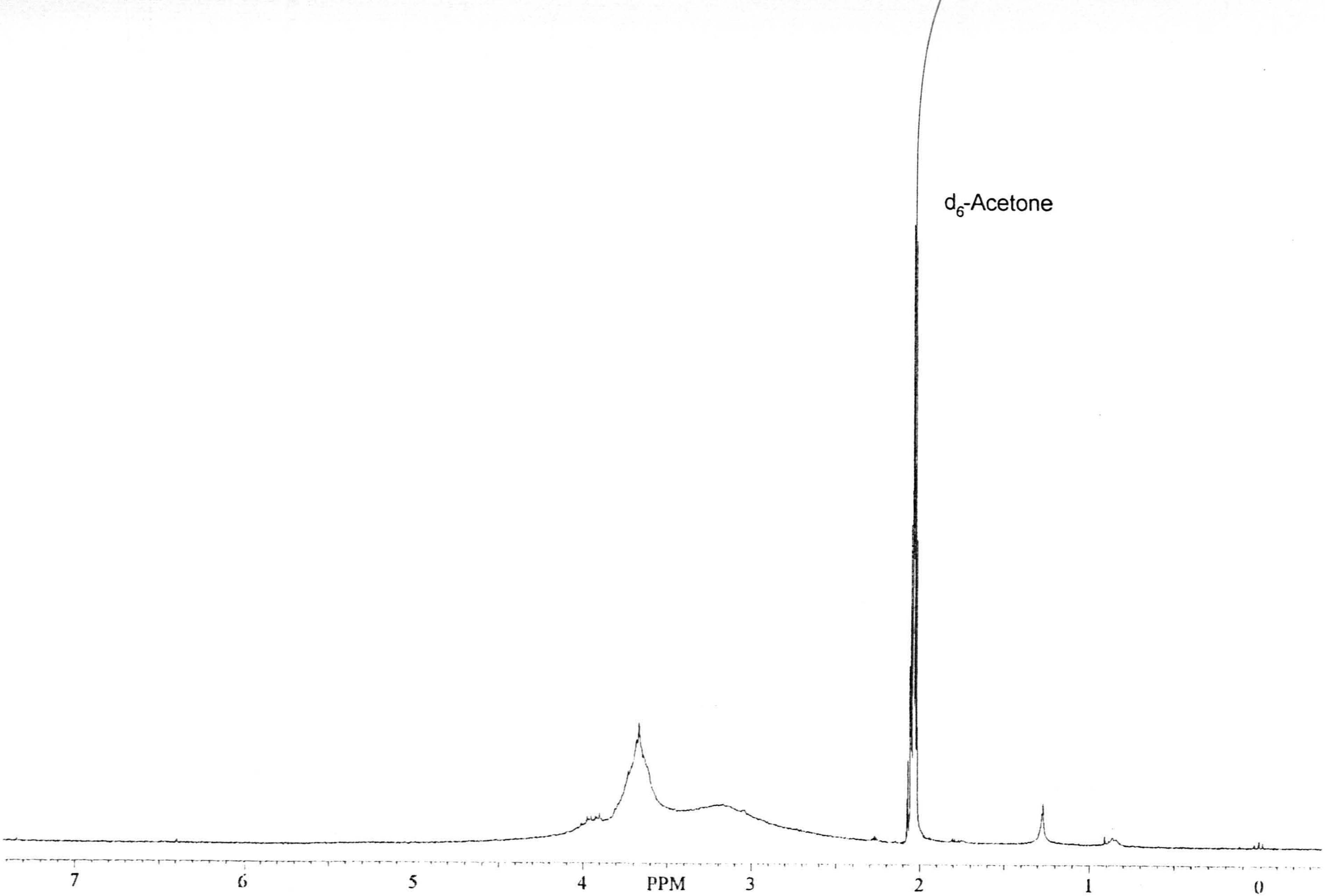


Figure 5.6: ^{1}H NMR spectrum (d$_6$-Acetone) of the distillation residue from the methylated resin, MA thermolysis time 48 hours.

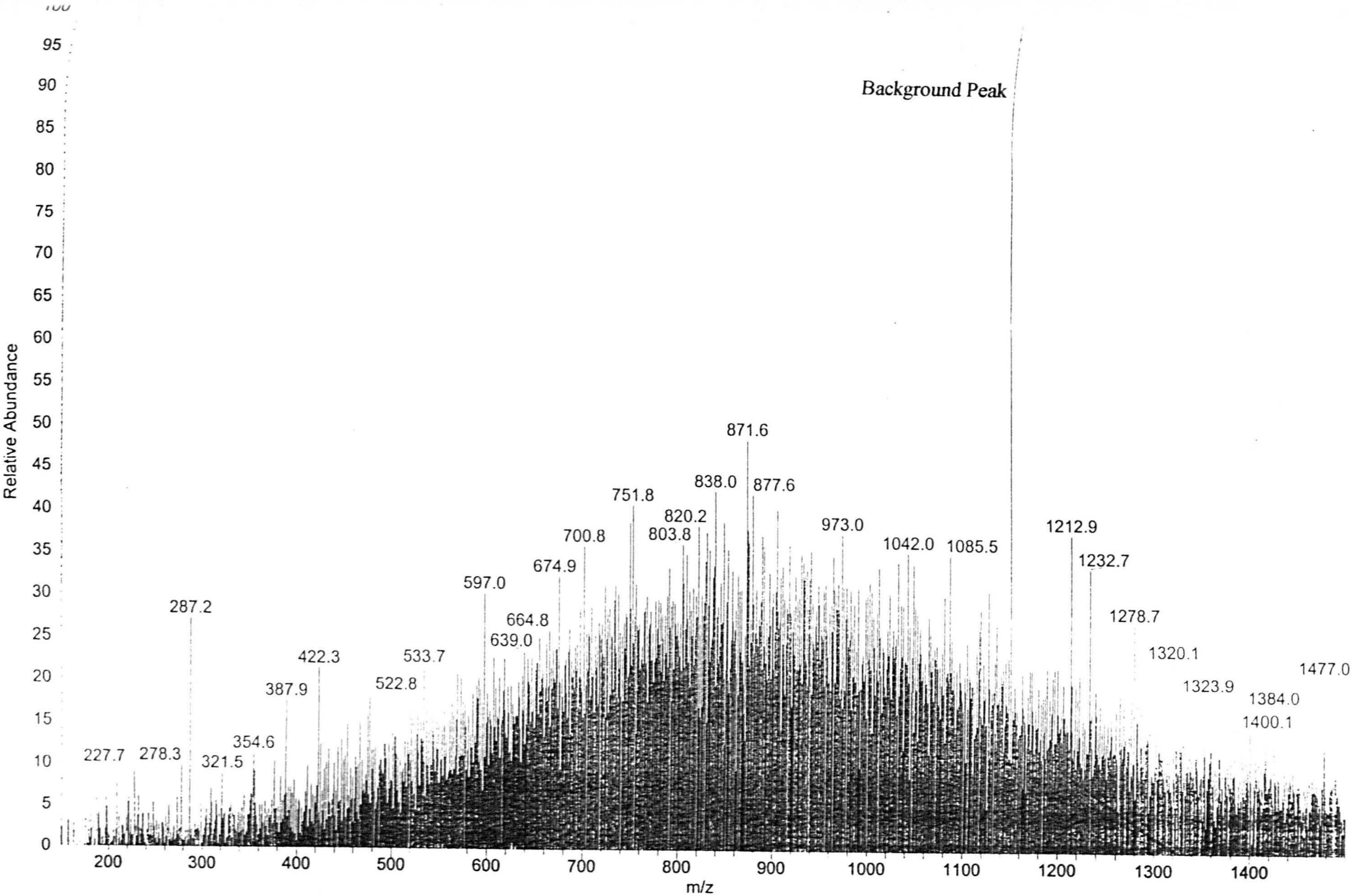


Figure 5.8: Electrospray ionization in the positive mode of the residual solid

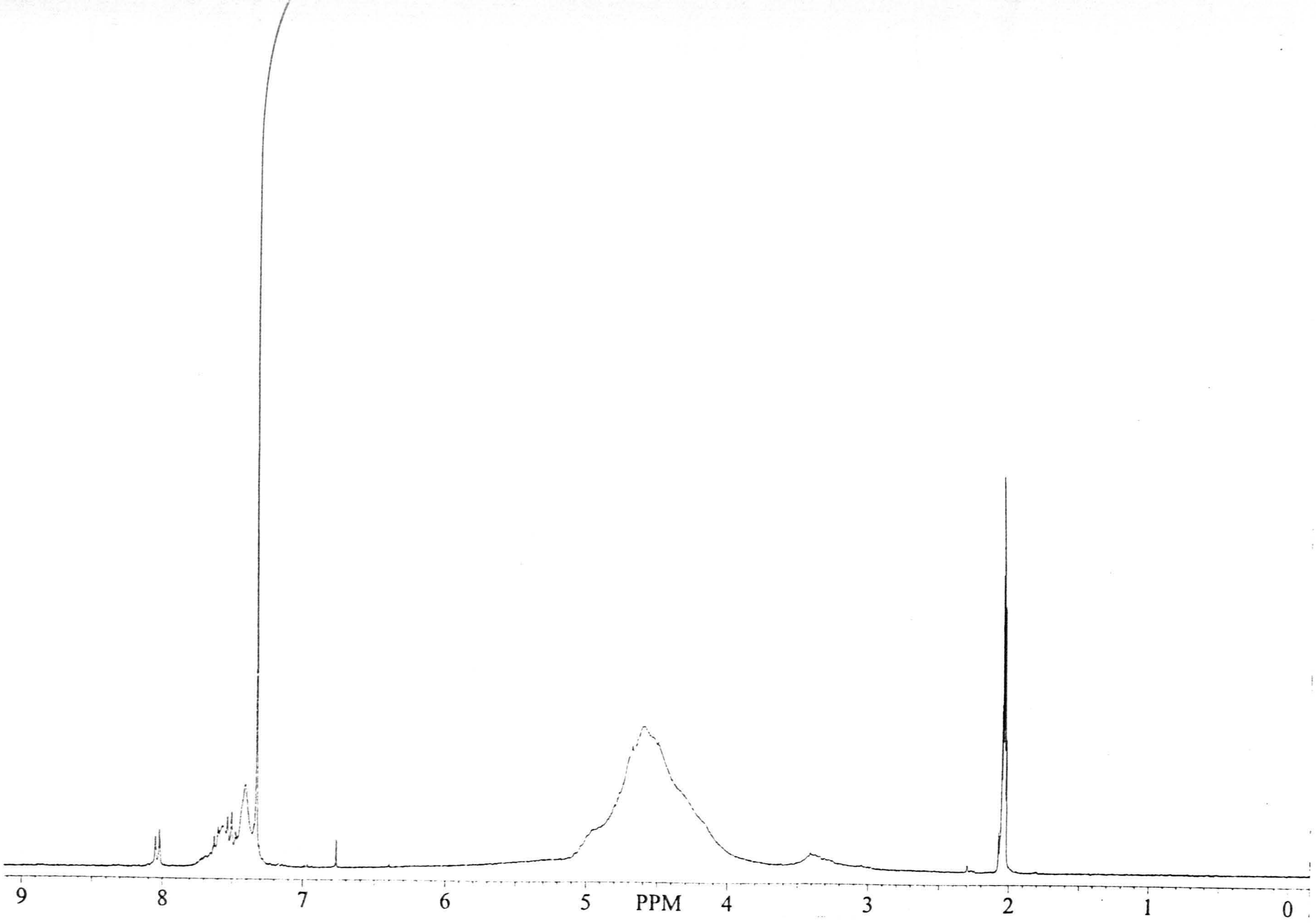


Figure 5.9: ^{1}H NMR spectrum (d$_6$-Acetone) of poly(maleic anhydride).

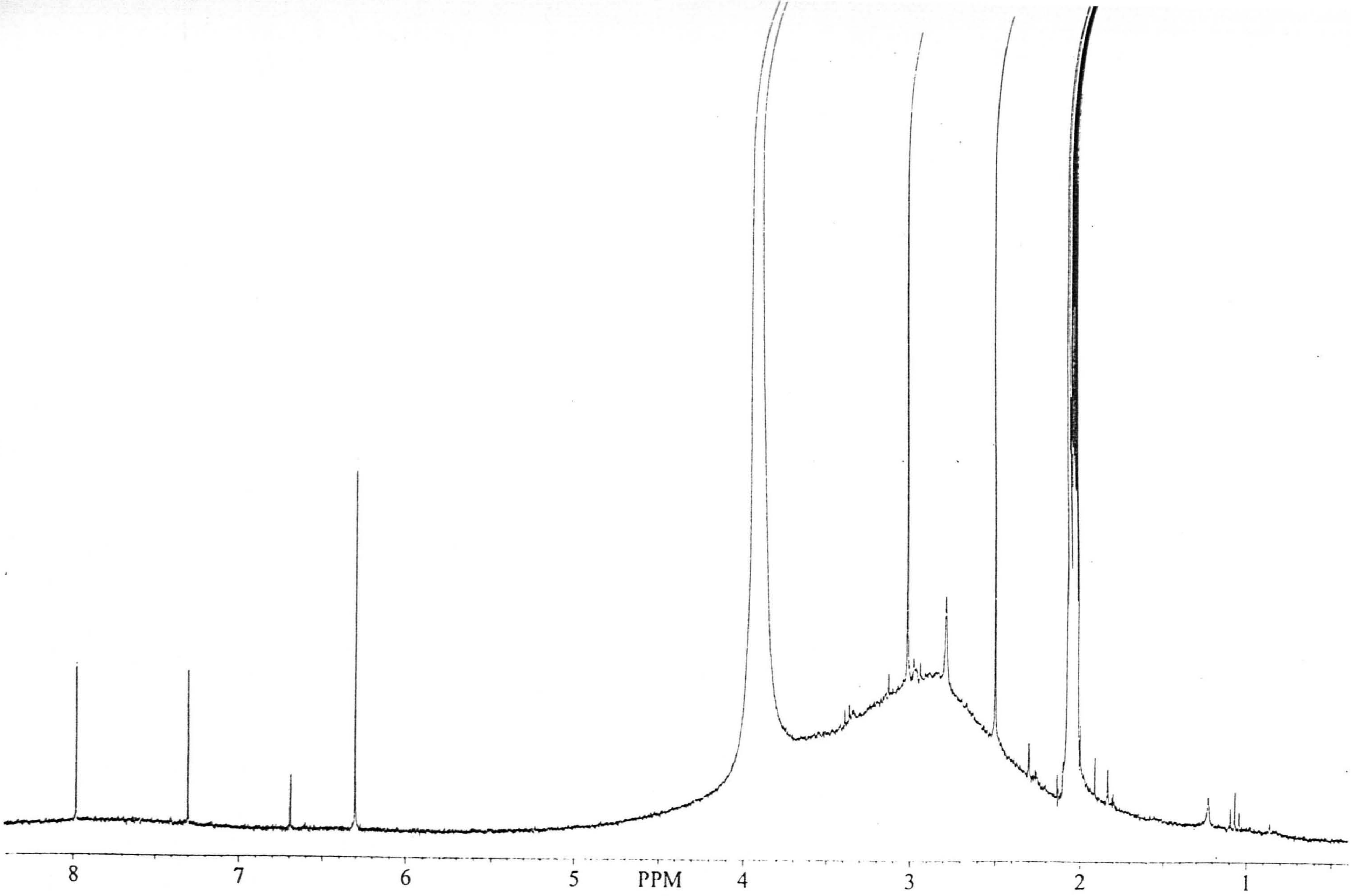


Figure 5.11: ^{1}H NMR spectrum (d_6-Acetone) of the DMF catalysed decomposition of MA.

Chapter 6

Experimental Procedures

In this chapter the experimental procedures leading to the results discussed in chapters 2 to 5 are detailed. The first section (6.1) is a general outline regarding instrumentation, chemicals and standard procedures. The later sections, section 6.2 through to 6.5, contain detailed experimental procedures relevent to research chapters 2 to 6 respectively.

6.1 General

6.1.1 Chemicals.

All the chemicals used in this thesis are available from Aldrich and Lancaster or used as available in the laboratory. Unless otherwise stated the chemicals were used as obtained.

Maleic anhydride (MA) was purchased from Aldrich and was > 99%, maleic anhydride: white solid; m.p. 54-56 °C (lit[164] 54-56 °C); NMR δ_H(d_6-acetn) 7.33 (s, 2H, CH=); δ_C(d_6-acetn) 166.0 (qC, CO_2-), 137.7 (CH, CH=).

2,4,4-Trimethyl-1-pentene (TMP-1) was purchased from Aldrich as a clear colourless liquid; NMR δ_H($CDCl_3$) 4.84 (m, 1H, CH=), 4.64 (m, 1H, CH=), 1.94 (s, 2H, CH_2), 1.78 (s, 3H, CH_3), 0.93 (s, 9H, $(CH_3)_3$); δ_C($CDCl_3$) 144.1 (qC, C=), 113.7 (CH_2, CH_2=), 51.7 (CH_2), 31.3 (qC, q$\underline{C}(CH_3)_3$), 30.0 (CH_3, qC($\underline{CH_3})_3$), 25.3 (CH_3).

1,2-Epoxydecane was purchased from Aldrich as a clear colourless liquid, 1,2-epoxydecane: NMR δ_H($CDCl_3$) 2.84-2.78 (m, 1H, CH), 2.65 (dd, 1H, *J* 1.0 and *J* 4.5, $C\underline{H_2}$(O)CH), 2.37 (dd, 1H, *J* 2.5 and *J* 5.0, $C\underline{H_2}$(O)CH), 1.42-1.18 (br s, 14H, CH_2-chain), 0.80 (t, 9H, *J* 6.5, CH_3); δ_C($CDCl_3$) 52.3 (CH, -$\underline{CH}$(O)CH_2), 47.0 (CH_2,

-CH(O)$\underline{CH_2}$), 32.5 (CH_2), 31.8, 29.5, 29.4, 29.2, 25.9, 22.6 (CH_2, CH_2-chain), 14.0 (CH_3).

1-Octadecene was purchased from Aldrich as a yellow solid: melting point 60-64 °C (Lit[164] m.p. 60-64 °C); NMR δ_H ($CDCl_3$) 5.91 (ddt, 1H, CH=), 5.05 (m, 2H, CH_2=), 2.00 (m, 2H, CH_2), 1.35-1.23 (br s, 28H, CH_2-chain), 0.86 (t, 3H, *J* 6.5, CH_3); δ_C ($CDCl_3$) 139.3 (CH, CH=), 114.0 (CH_2, CH_2=), 39.6, 32.0, 29.7, 29.5, 29.4, 29.2, 29.0, 22.7 (CH_2, CH_2-chain), 14.1 (CH_3).

Isobutylene succinic anhydride was purchased from Aldrich as a yellow solid, melting point 63-65 °C (Lit[164] m.p. 63-65 °C), isobutylene succinic anhydride: NMR δ_H(d_6-acetone) 4.86 (s, 1H, CH_2=), 4.81 (s, 1H, CH_2=), 3.59-3.47 (m, 1H, CH), 3.15 (dd, 1H, *J* 9.5 and *J* 18.5, CH_2-C$\underline{H}$-CH_2), 2.78 (dd, 1H, *J* 6.5 and *J* 18.5, CH_2-C$\underline{H}$-CH_2), 2.65 (dd, 1H, *J* 4.0 and *J* 14.5, -C$\underline{H_2}$CH-), 2.45 (dd, 1H, *J* 11.0 and *J* 14.5, -C$\underline{H_2}$CH-), 1.76 (br s, 3H, CH_3); δ_C (d_6-acetone) 175.4 (qC, CO_2-), 171.7 (qC, CO_2-), 142.8 (qC, qC=), 113.4 (CH_2, CH_2=), 39.8 (CH), 38.9 (CH_2), 34.4 (CH_2), 21.9 (CH_3).

Diazomethane was synthesised using a specialised diazomethane kit with smooth glass joints. To a mixture of ethanol (9 cm^3) and high purity water (1 cm^3) in a round bottom flask was added 0.4 g potassium hydroxide pellets. This was heated to 40 °C with the aid of a water bath. Diazald (2.14 g) was added to diethyl ether (30 cm^3) and this solution placed in a dropping funnel. The diazald mixture was then added over a period of about 30 min to the potassium hydroxide solution. The diazomethane was condensed in a round bottom flask cooled in an ice bath. A concentrated HCl trap was used to destroy any excess diazomethane.

6.1.2 Instrumentation.

Gas chromatography (GC) analysis was carried out on two different instruments: a Philips Pye Unicam PU4500 and a Varian 3350 connected to an integrator or a PC (using Varian *4.5 integrating package) respectively. Both GCs were fitted with flame ionisation detectors (FID) and a split injection system, with a split ratio of approximately 80:1 for the Pye Unicam and 50:1 for the Varian. In all cases the carrier gas used was helium, with the column head pressure ranging from 7 to 12 psi depending on the machine and column used. Injector and detector temperatures were 250 °C and 300 °C respectively for both GC machines. Two capillary columns were employed, each with a different stationary phase polarity, in an attempt to improve separation of the various components of the reaction mixtures. These columns were:

SE54 [30 m × 0.25 mm internal diameter, film thickness 0.25 μm]
ZB50 [30 m × 0.25 mm internal diameter, film thickness 0.25 μm]

The mass spectrometry or gas chromatography/mass spectrometry (GC/MS) results were obtained in the electron impact (EI) mode at 70 eV, unless otherwise stated, using a VG Autospectrometer. For GC/MS the mass spectrometer was coupled to a Hewlett Packard 5890 Series II gas chromatograph.

All NMR spectra were recorded on the Joel EX270 spectrometer at the following frequencies: ^{1}H NMR spectra were measured at 270 MHz and ^{13}C NMR spectra were measured at 67.5 MHz. Samples were prepared by the dissolution of 20-60 mg of material in 2 cm^3 of deuterated solvent. The deuterated solvent, either $CDCl_3$ or d_6-acetone, was used to calibrate the spectra and chemical shifts were measured in parts per million (p.p.m.) on the δ scale. Coupling constants (*J*) are quoted to the nearest 0.5 Hz. The ^{1}H-^{1}H COSY experiments were performed on a Joel EX500 NMR spectrometer.

EPR spectra were recorded on a Bruker ESP-300 X-band spectrometer equipped with 100 KHz modulation and a 4 mmo.d. quartz tube (All EPR experiments were carried out by Dr Adrian Whitwood, University of York). For EPR spectra recorded at 100 °C the temperature control was maintained using a Bruker VT 4111 attachment. Experiments were also performed at room temperature without this attachment.

IR spectra were recorded on a ATI Matison Genesis series FTIR using NaCl cells. UV-Vis spectra were measured on a Hewlett Packard 8453 UV-Vis spectrometer using a 1 cm pathlength quartz cell.

High Performance Liquid Chromatography (HPLC) experiments were performed on a Gilson 231 Liquid Chromatograph fitted with an Applied Biosystems 1000s Diode Array Detector. Separation was attempted with a reverse phase C18 column.

6.2 Addition of halogens to alkenes

In this section is detailed the experimental procedures and results which have been discussed in detail in chapter 2. Most of the experimental concerns GC/MS analysis of the crude reaction mixtures (GC conditions: Column = SE54, initial temperature was 70 or 120 °C for 2 minutes followed by ramping at 8 °C min^{-1} to 290 °C). GC peaks have been listed in order of their retention time, where appropriate and next to compounds with similar MS in other cases. Only peaks with percentage peak area greater than 1% of the total peak area have been listed and percentage areas given are based on uncalibrated GC areas. Only the intensities of the molecular ions and the fragment ions containing the lightest halogen isotopes are given for simplicity, *i.e.* for chlorine the peaks containing ^{35}Cl isotopes and for bromine those containing ^{79}Br isotopes.

6.2.1 Chlorination Reactions.

Chlorination of the model alkenes with an excess of chlorine.

In a typical procedure, chlorine gas was bubbled through a solution of alkene (8.91 mmol) in 1,4-dimethylbenzene (9.43 mmol) for 0.25 h at room temperature. The solution developed a yellow colouration due to the presence of excess chlorine. The reaction mixture was washed with 10 cm^3 of a 10% aqueous solution of sodium thiosulfate followed by distilled water. The organic layer was extracted with diethyl ether (3 x 30 cm^3) the extracts combined, dried over magnesium sulfate and evaporated under reduced pressure to afford a pale yellow liquid. The reaction mixture was not purified further and GC/MS analysis was carried out on each reaction product.

In each case the pale yellow liquid contained a substantial number of products which proved impossible to separate out fully. The yield of each compound therefore cannot be determined quantitatively; rather the uncalibrated peak areas have been used to quantify the products by structural types. The reaction mixtures contain unsaturated and saturated mono- and dichlorinated products and polychlorinated adducts, such as tri- and tetrachlorinated compounds. In many cases halogenation of the solvent has also taken place.

1-Octene.

The following reaction types were identified by GC/MS, although the precise structures could not be assigned by this technique. The composition of the product mixture by GC was:

1-Chloro-2,5-dimethylbenzene (2.1): Peak area 3%; C_8H_9Cl *m/z* 140 (M+, 43%), 125 (M – CH_3, 14), 106 (M + H – Cl, 9), 105 (M – Cl, 100), 103 (M – H – Cl, 13), 77 (C_6H_5+, 12), 51 (C_4H_3+, 17)

4-Methylbenzyl chloride (2.2): Peak area 27%; C_8H_9Cl *m/z* 140 (M+, 18%), 106 (M + H – Cl, 9), 105 (M – Cl, 100), 103 (M – H – Cl, 8), 79 (C_6H_7+, 8), 77 (C_6H_5+, 13), 51 (C_4H_3+, 12)

Dichloroalkane: Peak area 15%; $C_8H_{16}Cl_2$ *m/z* 153 (M – C_2H_5, 2%), 139 (M – C_3H_7, 30), 104 (M – C_3H_7 - Cl, 36), 70 (C_5H_{10}+, 64), 55 (C_4H_7+, 77), 43 (C_3H_7+, 100), 41 (C_3H_5+, 93)

Dichlorinated substituted xylene product: Peak area 9%; $C_8H_8Cl_2$ *m/z* 174 (M+, 20%), 139 (M – Cl, 100), 125 (M – CH_2Cl, 7), 104 (M – Cl – Cl, 33), 103 (M – Cl – HCl, 25), 77 (C_6H_5+, 13), 51 (C_4H_3+, 18)

Dichloroalkenes, four peaks with virtually identical mass spectra: Peak areas 4, 3, 11 and 13% respectively; $C_8H_{14}Cl_2$ *m/z* 180 (M+, 1%), 145 (M – Cl, 16), 138 (M – C_3H_6, 5), 109 (M – Cl – HCl, 54), 104 (C_5H_9Cl +, 54), 55 (C_4H_7+, 100), 41 (C_3H_5+, 80)

Trichloroalkane: Peak area 4%; $C_8H_{15}Cl_3$ *m/z* 187 (M – C_2H_5, 1%), 151 (M – C_2H_5 – HCl, 2.5), 138 (M – C_3H_7 – Cl, 24), 109 (M – Cl – HCl – HCl, 46), 83 (C_6H_{11}+, 57), 55 (C_4H_7+, 66), 41 (C_3H_5+, 100)

Pentachlorinated substituted and addition xylene products, three peaks with virtually identical mass spectra: Peak areas 4, 3 and 3% respectively; $C_8H_9Cl_5$ *m/z* 247/245 (M – Cl, 100/80), 209 (M – Cl – HCl, 68), 123 (M – Cl – HCl – C_4H_3Cl, 40), 87 (M – Cl – HCl – C_4H_3Cl – HCl, 20), 77 (C_6H_5+, 19), 51 (C_4H_3+, 31).

2,4,4-Trimethyl-1-pentene.

The following reaction types were identified by GC/MS, although the precise structures could not be assigned by this technique. The composition of the product mixture by GC, besides residual solvent, was:

Dichloroalkane: Peak area 4%; $C_8H_{16}Cl_2$ *m/z* 167 (M – CH_3, 1%), 131 (M – CH_3 – HCl, 13), 95 (M – CH_3 – HCl – HCl, 5), 57 (C_4H_9+, 100), 41 (C_3H_5+, 21)

Dichloroalkenes, 3 peaks giving virtually identical mass spectra: Peak areas 6, 59 and 11% respectively; $C_8H_{14}Cl_2$ *m/z* 180 (M+, 0.5%), 165 (M – CH_3, 1%), 129 (M – CH_3 – HCl, 4), 109 (M – Cl – HCl, 2), 93 (M – CH_3 – HCl – HCl, 6), 57 (C_4H_9+, 100), 41 (C_3H_5+, 22)

and: Peak area 8%; $C_8H_{14}Cl_2$ *m/z* 144 (M – HCl, 1%), 129 (M – CH_3 – HCl, 2), 93 (M – CH_3 – HCl – HCl, 4), 57 (C_4H_9+, 100), 41 (C_3H_5+, 26)

Trichloroalkene: Peak area 3%; $C_8H_{13}Cl_3$ *m/z* 163 (M – CH_3 – HCl, 2%), 127 (M – CH_3 – HCl – HCl, 2), 77 (C_3H_6Cl +, 3), 57 (C_4H_9+, 100), 41 (C_3H_5+, 21)

Trichloroalkane: Peak area 9%; $C_8H_{15}Cl_3$ *m/z* 201 (M – CH_3, 2%), 165 (M – CH_3 – HCl, 6), 129 (M – CH_3 – HCl – HCl, 5), 57 (C_4H_9+, 100), 41 (C_3H_5+, 24)

Tetrachloroalkane: Peak area <1%; $C_8H_{14}Cl_4$ *m/z* 163 (M – CH_3 – HCl – HCl, 1%), 145 (M – $C_5H_{10}Cl$, 2), 127 (M – CH_3 – HCl – HCl – HCl, 2), 93 ($C_4H_{10}Cl$+, 5), 57 (C_4H_9+, 100)

Tetrachloroalkene: Peak area <1%; $C_8H_{12}Cl_4$ *m/z* 248 (M+, 0.5%), 199 (M – CH_2Cl, 1), 177 (M – Cl – HCl, 2), 163 (M – CH_2Cl – HCl, 3),138 (M – $C_3H_4Cl_2$, 27), 103 (M – $C_3H_4Cl_3$, 34), 67 (C_5H_7+, 100), 41 (C_3H_5+, 22).

2,4,4-Trimethyl-2-pentene.

The following reaction types were identified by GC/MS, although the precise structures could not be assigned by this technique. The composition of the product mixture by GC, besides residual solvent, was:

1-Chloro-2,5-dimethylbenzene (2.1): Peak area 5%; C_8H_9Cl *m/z* 140 (M+, 45%) 125 (M – CH_3, 14), 106 (M + H – Cl, 9), 105 (M – Cl, 100), 103 (M – H – Cl, 13), 77 (C_6H_5+, 19), 51 (C_4H_3+, 18)

Dichloroalkenes, three peaks with virtually identical mass spectra: Peak areas 3, 7 and 63% respectively; $C_8H_{14}Cl_2$ *m/z* 180 (M+, 1%), 165 (M – CH_3, 2), 129 (M – CH_3 – HCl, 1), 109 (M – Cl – HCl, 1), 93 ($C_4H_{10}Cl$ +, 3), 57 (C_4H_9+, 100)

Trichloroalkane: Peak area 6%; $C_8H_{15}Cl_3$ *m/z* 165 (M – HCl – CH_3, 1%), 111 (M – Cl – Cl – Cl, 4), 105 (13), 69 (C_5H_9+, 13), 57 (C_4H_9+, 100), 41 (C_3H_5+, 28)

Trichloroalkene: Peak area 6%; $C_8H_{13}Cl_3$ *m/z* 163 (M – HCl – CH_3, 1%), 127 (M – HCl – HCl – CH_3, 2), 107 (M – Cl – HCl – HCl, 1), 91 (C_7H_7+, 4), 57 (C_4H_9+, 100), 41 (C_3H_5+, 22)

and: Peak area 2%; $C_8H_{13}Cl_3$ *m/z* 214 (M+, 11%), 179 (M – Cl, 17), 165 (M – Cl – CH_3, 26), 143 (M – Cl – HCl, 56), 107 (M – Cl – HCl – HCl, 72), 91 (C_7H_7+, 68), 77 (C_6H_5+, 100), 57 (C_4H_9+, 41), 41 (C_3H_5+, 61)

Tetrachloroalkane: Peak area 3%; $C_8H_{14}Cl_4$ *m/z* 199 (M – CH_3 – HCl, 0.5%), 163 (M – CH_3 – HCl – HCl, 1), 127 (M – CH_3 – HCl – HCl – HCl, 1), 57 (C_4H_9+, 100), 41 (C_3H_5+, 34)

and: Peak area 3%; $C_8H_{12}Cl_4$ *m/z* 248 (M+, 4%), 177 (M – Cl – HCl, 2), 172 (M – C_3H_5Cl, 10), 137 (M – $C_3H_5Cl_2$, 100), 101 (M – $C_3H_6Cl_3$, 80), 65 (C_5H_5+, 81), 39 (C_3H_3+, 49).

3-Methyl-2-pentene.

The following reaction types were identified by GC/MS, although the precise structures could not be assigned by this technique. The composition of the product mixture by GC was, besides residual solvent:

Dichloroalkanes, two peaks with virtually identical mass spectra: Peak areas 6 and 4% respectively; $C_6H_{12}Cl_2$ *m/z* 125 (M – C_2H_5, 2.5%), 119 (M – Cl, 1), 103 (M –

CH_3 – HCl, 2), 91 (M – C_2H_4Cl, 91), 83 (C_6H_{11}+, 28), 55 (C_4H_7+, 100), 41 (C_3H_5+, 23)

1-Chloro-2,5-dimethylbenzene (2.1): Peak area 16%; C_8H_9Cl *m/z* 140 (M+, 40%), 125 (M – CH_3, 13), 106 (M + H – Cl, 9), 105 (M – Cl, 100), 103 (M – H – Cl, 14), 77 (C_6H_5+, 21), 51 (C_4H_3+, 21)

4-Methylbenzyl chloride (2.2): Peak area 29%; C_8H_9Cl *m/z* 140 (M+, 20%), 125 (M – CH_3, 3), 106 (M + H – Cl, 10), 105 (M – Cl, 100), 103 (M – H – Cl, 10), 79 (C_6H_7+, 9), 77 (C_6H_5+, 14), 51 (C_4H_3+, 14)

Dichloroalkenes, two peaks with virtually identical mass spectra: Peak areas 6 and 11% respectively; $C_6H_{10}Cl_2$ *m/z* 152 (M+, 2%), 137 (M – CH_3, 5), 125 (M – C_2H_3, 52), 117 (M – Cl, 53), 90 (M – C_2H_3Cl, 100), 63 (46), 55 (C_4H_7+, 61)

and: Peak area 3%: $C_6H_{10}Cl_2$ *m/z* 125 (M – C_2H_3, 59%), 117 (M – Cl, 27), 90 (M – C_2H_3Cl, 100), 55 (C_4H_7+, 57)

1,4-Dichloro-3,6-dimethylbenzene: Peak area 3%; $C_8H_8Cl_2$ *m/z* 174 (M+, 50%), 159 (M – CH_3, 11), 139 (M – Cl, 100), 103 (M – Cl – HCl, 28), 102 (M – HCl - HCl, 11), 77 (C_6H_5+, 21), 51 (C_4H_3+, 24)

Trichloroalkenes, three peaks with virtually identical mass spectra: Peak areas 3, 9 and 12% respectively; $C_6H_9Cl_3$ *m/z* 186 (M+, 0.5%), 151 (M – Cl, 10), 124 (M – C_2H_3Cl, 100), 89 (M – C_2H_4Cl, 45), 53 (C_4H_5+, 22).

Chlorination of 1,4-dimethylbenzene with an excess of chlorine.

Chlorine gas was bubbled through 1,4-dimethylbenzene (1 g, 9.43 mmol) for a period of 0.25 h at room temperature. The solution developed a yellow colouration due to the presence of excess chlorine. The reaction mixture was washed with 10 cm^3 of a 10% aqueous solution of sodium thiosulfate and then distilled water. The organic layer was extracted with diethyl ether (3 x 30 cm^3) the extracts combined, dried over magnesium sulfate and evaporated under reduced pressure to afford pale yellow liquid. The reaction mixture was not purified further but the composition of the reaction product was determined by GC/MS analysis.

The composition of the reaction mixture by GC was as follows, where the name of a compound is not given the structure has not been fully determined:

1-Chloro-2,5-dimethylbenzene (2.1): Peak area 2%; C_8H_9Cl *m/z* 140 (M+, 40%), 125 (M – CH_3, 13), 106 (M + H – Cl, 9), 105 (M – Cl, 100), 103 (M – H – HCl, 15), 77 (C_6H_5+, 20), 51 (C_4H_3+, 15)

4-Methylbenzyl chloride (2.2): Peak area 28%; C_8H_9Cl *m/z* 140 (M+, 45%), 106 (M + H – Cl, 19), 105 (M – Cl, 100), 103 (M – H – HCl, 19), 79 (C_6H_7+, 27), 77 (C_6H_5+, 27), 51 (C_4H_3+, 23)

Dichlorinated substitution products, three peaks with virtually identical mass spectra: Peak areas 4, 2 and 4% respectively; $C_8H_8Cl_2$ *m/z* 174 (M+, 9%), 140 (M + H – Cl, 9), 139 (M – Cl, 100), 104 (M – Cl – Cl, 11), 103 (M – HCl – Cl, 20), 77 (C_6H_5+, 18), 51 (C_4H_3+, 14)

1,4-Dichloro-3,6-dimethylbenzene: Peak area 1%; $C_8H_8Cl_2$ *m/z* 174 (M+, 46%), 159 (M – CH_3, 12), 139 (M – Cl, 100), 103 (M – HCl – Cl, 30), 77 (C_6H_5+, 25), 51 (C_4H_3+, 21)

Dichlorinated substitution product: Peak area 25%; $C_8H_8Cl_2$ *m/z* 174 (M+, 21%), 139 (M – Cl, 100), 104 (M – Cl – Cl, 41), 103 (M – HCl – Cl, 33), 77 (C_6H_5+, 18), 51 (C_4H_3+, 22)

Trichlorinated substitution product: Peak area 1%; $C_8H_7Cl_3$ *m/z* 208 (M+, 67%), 173 (M – Cl, 100), 137 (M – HCl – Cl, 18), 102 (M – Cl – HCl – Cl, 28), 75 (C_6H_3+, 18), 51 (C_4H_3+, 21)

(1,1,1′-trichloro)-*p*-xylene: Peak area 5%; $C_8H_7Cl_3$ *m/z* 208 (M+, 8%), 174 (M + H – Cl, 12), 173 (M – Cl, 100), 138 (M – Cl – Cl, 48), 103 (M – Cl – Cl – Cl, 15), 77 (C_6H_5+, 17), 51 (C_4H_3+, 22)

Tetrachlorinated substitution and addition product: Peak area 1%; $C_8H_{10}Cl_4$ *m/z* 246 (M+, 1%), 211 (M – Cl, 12), 175 (M – HCl – Cl, 100), 140 (M – Cl – HCl – Cl, 18), 105 (M – Cl – Cl – HCl – Cl, 23), 77 (C_6H_5+, 22), 51 (C_4H_3+, 20)

Pentachlorinated substitution and addition products: Peak area 1%; $C_8H_9Cl_5$ *m/z* 280 (M+, 6%), 245 (M – Cl, 50), 209 (M – HCl – Cl, 100), 174 (M – Cl – HCl – Cl, 54), 139 (M – Cl – Cl – HCl – Cl, 35), 77 (C_6H_5+, 50), 51 (C_4H_3+, 61)

and: Peak area 4%; $C_8H_9Cl_5$ *m/z* 245 (M – Cl , 6), 209 (M – Cl – HCl, 39), 173 (M – Cl – HCl – HCl, 100), 139 (M – Cl – HCl – Cl – Cl, 27), 103 (M – Cl – HCl – Cl – Cl - HCl, 16), 77 (C_6H_5+, 25), 51 (C_4H_3+, 30)

and, three peaks with virtually identical mass spectra: Peak areas 4, 2 and 4% respectively; $C_8H_9Cl_5$ *m/z* 247/245 (M – Cl , 100/77), 209 (M – Cl – HCl, 81), 123 (M – Cl – HCl – C_4H_3Cl, 46), 87 (M – Cl – HCl – C_4H_3Cl – HCl, 28), 77 (C_6H_5+, 28), 51 (C_4H_3+, 42)

and: Peak area 4%; $C_8H_9Cl_5$ *m/z* 245 (M – Cl , 72), 209 (M – Cl – HCl, 100), 123 (M – Cl – HCl – C_4H_3Cl, 45), 77 (C_6H_5+, 47), 51 (C_4H_3+, 56)

Hexachlorinated substitution and addition products, three peaks with virtually identical mass spectra: Peak areas 1, 2 and 1% respectively; $C_8H_8Cl_6$ *m/z* 314 (M+, 0.4%), 281/279 (M – Cl , 100/64), 243 (M – HCl – Cl, 19), 207 (M – HCl – HCl – Cl, 38), 173 (M – Cl – Cl – HCl – Cl, 18), 63 (C_5H_3+, 23), 51 (C_4H_3+, 35).

6.2.2 Bromination Reactions.

Bromination of model alkenes with tetra-N-butylammonium tribromide ($TBABr_3$).

A solution of $TBABr_3$ (1 g, 2.1 mmol, 1 equivalent) in 15 cm^3 of chloroform was slowly added to a solution of the alkene (2.1 mmol) in 20 cm^3 of chloroform at room temperature. This solution was stirred at room temperature for a further 3 h. The reaction mixture was then diluted with 10% aqueous sodium thiosulphate, washed with water and the organic layer extracted with chloroform. The organic phase was dried over magnesium sulfate and evaporated under reduced pressure to afford a clear colourless oil.

The organic product mixture was analysed by EI GC/MS. Again the proportion of each type of compound has been evaluated by their GC areas. The reaction product contains mostly mono and dibrominated products. In most cases the major components of the reaction mixture has also been characterized by NMR analysis.

1-Octene.

The following reaction types were identified by GC/MS, although the precise structures could not be assigned by this technique. The composition of the product mixture by GC was:

Monobromide: Peak area 2%; $C_8H_{17}Br$ *m/z* 149 (M – C_3H_7, 3%), 135 (M – C_4H_9, 5), 121 (M – C_5H_{11}, 3), 111 (M – H – HBr, 40), 69 (C_5H_9+, 100), 55 (C_4H_7+, 80), 41 (C_3H_5+, 63)

1,2-Dibromooctane (2.7): Peak area 98%; $C_8H_{16}Br_2$ *m/z* 191 (M – Br, 3%), 149 (M – C_3H_5 – HBr, 9), 135 (M – C_4H_8Br, 9), 121 (M – C_5H_{10}Br, 5), 111 (M – Br – HBr, 35), 69 (C_5H_9+, 100), 55 (C_4H_7+, 72), 41 (C_3H_5+, 85).

NMR analysis of the crude reaction mixture (only the signals for **2.7** were identified); δ_H ($CDCl_3$) 4.20-4.00 (1H, m, CHBr), 3.84 (1H, dd, *J* 4.5 and *J* 10.5, CH_2Br), 3.62 (1H, apparent t, *J* 9.5, CH_2Br), 2.20-1.99 (1H, m, CH_2), 1.88-1.24 (9H, m, CH_2), 0.90 (3H, t, *J* 6.5, CH_3); δ_C ($CDCl_3$) 53.2 (CH, CHBr), 36.4 (CH_2), 36.0 (CH_2, CH_2Br), 31.5, 28.5, 26.7, 22.5 (CH_2, CH_2-chain), 14.0 (CH_3).

2,4,4-Trimethyl-1-pentene.

The following reaction types were identified by GC/MS, although the precise structures could not be assigned by this technique. The composition of the product mixture by GC was:

Allylic bromides, three peaks with virtually identical mass spectra: Peak areas 4.5, 1.5 and 14.5% respectively, $C_8H_{15}Br$ *m/z* 175 (M – CH_3, 1%), 134 (M – C_4H_8, 5), 111 (M – Br, 19), 69 (C_6H_9+, 23), 57 (C_4H_9+, 100), 41 (C_3H_5+, 43)

Vinylic bromide: Peak area > 1%, $C_8H_{15}Br$ *m/z* 190 (M+, 1.5%), 175 (M – CH_3, 1.5), 133 (M – C_4H_9, 1.0), 111 (M – Br, 4.5), 95 (M – CH_3 – HBr, 4.5), 57 (C_4H_9+, 100), 41 (C_3H_5+, 32)

Rearranged monobromoalkenes, two peaks with virtually identical mass spectra: Peak areas 2.5 and 3%, $C_8H_{15}Br$ *m/z* 190 (M+, 0.5%), 175 (M – CH_3, 3), 133 (M – C_4H_9, 3), 111 (M – Br, 100), 69 (C_6H_9+, 91), 55 (C_4H_{11}+, 63), 41 (C_3H_5+, 61)

1,2-Dibromo-2,4,4-trimethylpentane (2.10): Peak area 74%; $C_8H_{16}Br_2$ *m/z* 255 (M – CH_3, 0.2%), 191 (M – Br, 2), 175 (M – CH_3 – HBr, 4), 133 (M – C_4H_{10}Br, 2), 121 (M – C_5H_{10}Br, 5), 95 (M – Br – HBr – CH_3, 7), 57 (C_4H_9+, 100), 41 (C_3H_5+, 38).

NMR analysis of the crude reaction mixture (only the signals for **2.10** were identified); δ_H ($CDCl_3$) 3.89 (1H, d, *J* 10.0, CH_2Br), 3.87 (1H, d, *J* 10.0, CH_2Br), 2.13 (1H, d, *J* 15.5, CH_2), 2.00 (1H, d, *J* 15.5, CH_2), 1.91 (3H, s, qCBr-C$\underline{H}_3$), 1.08 (9H, s, C(C$\underline{H}_3$)$_3$); δ_C ($CDCl_3$) 66.8 (qC, qCBr), 53.1 (CH_2), 46.0 (CH_2, CH_2Br), 32.3 (qC), 31.9 (CH_3, qCBr-$\underline{C}H_3$), 31.2 (CH_3, C(C$\underline{H}_3$)$_3$).

2,4,4-Trimethyl-2-pentene.

The following reaction types were identified by GC/MS, although the precise structures could not be assigned by this technique. The composition of the product mixture by GC was:

Monobromide: Peak area 54%; $C_8H_{17}Br$ *m/z* 177 (M – CH_3, 0.5%), 135 (M – C_4H_9, 0.4), 121 (M – C_5H_{11}, 4), 113 (M – Br, 28), 97 (M – CH_3 – Br, 13), 57 (C_4H_9+, 100), 41 (C_3H_5+, 36)

Dibromoalkane: Peak area 29%; $C_8H_{16}Br_2$ *m/z* 191 (M – Br, 2),175 (M – CH_3 – HBr, 2), 133 (M – $C_4H_{10}Br$, 1), 121 (M – $C_5H_{10}Br$, 2), 57 (C_4H_9+, 100), 41 (C_3H_5+, 18)

Dibromoalkene: Peak area 17%; $C_8H_{14}Br_2$ *m/z* 268 (M+, 0.4%), 253 (M – CH_3, 0.5), 189 (M – Br, 6), 174 (M – CH_3 – Br, 1), 147 (M – C_3H_6Br, 1), 110 (M – Br – Br, 5), 95 (M – HBr – CH_2Br, 5), 67 (C_5H_7+, 6), 57 (C_4H_9+, 100), 41 (C_3H_5+, 21).

3-Ethyl-2-pentene.

The crude reaction product, a clear colourless oil (0.52g), was identified as **2,3-dibromo-3-ethylpentane (2.17)**, percentage yield 91.2%: MS $C_7H_{14}Br_2$ *m/z* 177 (M – Br, 14%), 135 (M – Br – C_3H_6, 3), 121 (M – Br – C_4H_8, 2), 107 (M – Br – C_5H_{10}, 5), 97 (M – Br – Br, 94), 69 (C_5H_9+, 45), 55 (C_4H_7+, 100), 41 (C_3H_5+, 62); NMR δ_H($CDCl_3$) 4.52 (1H, q, *J* 6.5, Me$\underline{CH}$Br), 2.19-1.96 (4H, m, 2 x ($\underline{CH_2}$Me)), 1.90 (3H, d, *J* 7.0, $\underline{CH_3}$CHBr), 1.07 (6H, t, *J* 7.5, 2 x ($\underline{CH_3}$$CH_2$)); δ_C ($CDCl_3$) 81.1 (qC, qCBr), 55.7 (CH, CHBr), 33.2 (CH_2), 30.8 (CH_2), 22.7 (CH_3, CHBr-$\underline{C}H_3$), 9.6 (CH_3, CH_2C$\underline{H}_3$), 9.3 (CH_3, CH_2C$\underline{H}_3$).

Bromination of 2,4,4-trimethyl-1-pentene in 1,4-dimethylbenzene with bromine.

Bromine (0.46 cm^3, 9 mmol, 1 equivalent) was slowly added to a solution of the alkene (8.91 mmol) in 5 cm^3 of 1,4-dimethylbenzene at room temperature. The solution was stirred at this temperature for 2.5 h. The reaction mixture was then washed with 10% aqueous sodium thiosulfate, and with water and the organic layer extracted with diethyl ether. The organic phase was dried over magnesium sulfate and evaporated under reduced pressure to afford a pale yellow liquid. The organic product mixture was analysed by EI GC/MS. For each alkene this mixture was found to contain a number of components which could not be fully separated, as a result the yield of each compound cannot be calculated. The proportion of each type of compound has been evaluated by GC areas.

The following reaction types were identified by GC/MS, although the precise structures could not be assigned by this technique. The composition of the product mixture by GC, besides residual solvent, was:

Monobromides, two peaks with virtually identical mass spectra: Peak areas 10.5 and 11% respectively; $C_8H_{17}Br$ *m/z* 177 (M – CH_3, 0.4%), 135 (M – C_4H_9, 0.3), 121 (M – C_5H_{11}, 2.5), 113 (M – Br, 21), 97 (M – CH_3 – HBr, 10), 57 (C_4H_9+, 100), 41 (C_3H_5+, 28)

Allylic bromides, three peaks with virtually identical mass spectra: Peak areas 1, < 1 and 4.5% respectively; $C_8H_{15}Br$ *m/z* 190 (M+, 0.3%), 175 (M – CH_3, 1.5), 134 (M – C_4H_8, 6), 111 (M – Br, 25), 69 (C_5H_9+, 22), 57 (C_4H_9+, 100), 41 (C_3H_5+, 35)

Vinylic bromide: Peak area 1.5%; $C_8H_{15}Br$ *m/z* 190 (M+, 4.5%), 175 (M – CH_3, 2.5), 134 (M – C_4H_8, 2), 111 (M – Br, 2), 95 (M – CH_3 – Br, 5.5), 57 (C_4H_9+, 100), 41 (C_3H_5+, 23)

Rearranged monobromoalkenes, two peaks with virtually identical mass spectra: Peak areas < 1 and 1% respectively; $C_8H_{15}Br$ *m/z* 190 (M+, 1.5%), 175 (M – CH_3, 3), 133 (M – C_4H_7, 2.5), 111 (M – Br, 100), 69 (C_5H_9+, 83), 55 (C_4H_7+, 52), 41 (C_3H_5+, 46)

1-Bromo-2,5-dimethylbenzene (2.8): Peak area 1.5%; C_8H_9Br *m/z* 184 (M+, 48%), 105 (M – Br, 100), 103 (M – H – HBr, 19), 79 (C_6H_7+, 15), 77 (C_6H_5+, 18), 51 (C_4H_3+, 19)

4-Methylbenzyl bromide (2.9): Peak area 15%; C_8H_9Br *m/z* 184 (M+, 5%), 105 (M – Br, 100), 103 (M – H - HBr, 8), 79 (C_6H_7+, 8), 77 (C_6H_5+, 12), 51 (C_4H_3+, 8)

1,2-Dibromo-2,4,4-trimethylpentane (2.10): Peak area 32%; $C_8H_{16}Br_2$ *m/z* 255 (M – CH_3, 0.2%), 191 (M – Br, 3), 175 (M – CH_3 – HBr, 2.5), 133 (M – $C_4H_{10}Br$, 1), 121 (M – $C_5H_{10}Br$, 3), 95 (M – CH_3 – HBr – HBr, 5), 69 (C_5H_9+, 3.5), 57 (C_4H_9+, 100), 41 (C_3H_5+, 22)

Dibromoalkenes, two peaks with virtually identical mass spectra: Peak area 1 and 4% respectively; $C_8H_{14}Br_2$ *m/z* 268 (M+, 1%), 253 (M – CH_3, 0.5), 189 (M – Br, 8), 147 (M – C_3H_6Br, 1), 133 (M – C_4H_8Br, 2.5), 109 (M – HBr – Br, 10), 67 (C_5H_7+, 6), 57 (C_4H_9+, 100), 41 (C_3H_5+, 23)

and: Peak area 2%; $C_8H_{14}Br_2$ *m/z* 253 (M – CH_3, 0.5%), 189 (M – Br, 19), 109 (M – HBr – Br, 100), 91 (C_7H_7+, 60), 67 (C_5H_7+, 41), 55 (C_4H_7+, 25), 41 (C_3H_5+, 21)

Dibrominated substituted xylene product: Peak area 1%; $C_8H_8Br_2$ *m/z* 262 (M+, 50%), 183 (M – Br, 65), 104 (M – Br – Br, 38), 103 (M – Br – HBr, 39), 77 (C_6H_5+, 34), 51 (C_4H_3+, 37)

Tribromoalkane: Peak area 13%; $C_8H_{15}Br_3$ *m/z* 269 (M – Br, 0.5%), 253 (M – CH_3 – HBr, 0.5), 173 (M – CH_3 – HBr – HBr, 1), 133 (M – Br – Br – C_4H_9, 2), 121 (M – Br – Br – C_4H_6, 3), 93 (C_7H_9+, 4), 67 (C_5H_7+, 3), 57 (C_4H_9+, 100), 41 (C_3H_5+, 20).

Bromination of model alkenes with bromine.

A solution of 0.46 cm^3 of bromine (9 mmol, 1 equivalent) in 5 cm^3 of chloroform was slowly added to a solution of the alkene (8.91 mmol) in 3 cm^3 of $CHCl_3$ at a range of temperatures (21 or 60 °C). The solution was stirred at the appropriate temperature for 2.5 h The reaction mixture was then washed with 10% aqueous sodium thiosulfate, and with water and the organic layer extracted with diethyl ether. The organic phase was dried over magnesium sulfate and evaporated under reduced pressure to afford a pale yellow liquid. The organic product mixture was analysed by EI GC/MS. The proportion of each type of compound has been evaluated by GC areas.

1-Octene at room temperature.

The composition of the product mixture by GC was:

Monobromide: Peak area 1.5%; $C_8H_{17}Br$ *m/z* 192 (M+, 4%), 149 (M – C_3H_7, 8), 135 (M – C_4H_9, 90), 121 (M – C_5H_{11}, 2), 71 (M – C_5H_{11}, 71), 57 (M – C_4H_9+, 92), 43 (C_3H_6+, 100)

1,2-Dibromooctane (2.7): Peak area 94.9%; $C_8H_{16}Br_2$ *m/z* 191 (M – Br, 14), 149 (M – Br – C_3H_6, 9), 135 (M – Br – C_4H_8, 8), 111 (M – Br – HBr, 45), 69 (C_5H_9+, 100), 55 (C_4H_7+, 66), 41 (C_3H_5+, 70)

Tribromooctanes, three peaks with virtually identical mass spectra: Peak areas 1, 1.4 and 1.3% respectively; $C_8H_{15}Br_3$ *m/z* 269 (M – Br, 8), 189 (M – Br – HBr, 33), 147 (M – Br – HBr – C_3H_6, 12), 133 (M – Br – HBr – C_4H_8, 6), 109 (M – Br – HBr – HBr, 100), 67 (C_5H_7+, 16), 55 (C_4H_7+, 24), 41 (C_3H_5+, 55).

NMR data for the crude reaction mixture is the same as that for 1-octene with $TBABr_3$. The major peaks in the ^{13}C NMR spectrum for this reaction were as follows; δ_C ($CDCl_3$) 53.2 (CH, CHBr), 36.4 (CH_2), 36.0 (CH_2, CH_2Br), 31.6, 28.5, 26.7, 22.5 (CH_2, CH_2 chain), 14.0 (CH_3).

Further experiments using 1-octene.

The experimental conditions and results are summarized in the table below:

Reaction solvent	Temperature / °C	Products (Uncalibrated GC areas / %) [1]
$CHCl_3$	60	Monobromoalkane (7.8), monobromoalkene (3.1), dibromoalkane (89.1)
CCl_4	21	Monobromoalkane (1.0), 1,2-dibromooctane (95.4)[2], tribromoalkanes (three peaks; 0.9, 1.4 and 1.3)

1 : Products identified from GC/MS analysis, MS data compared to the products formed from the bromination of 1-octene in $CHCl_3$ at room temperature (21 °C).

2 : NMR data for this reaction mixture is consistent with the major product being 1,2 dibromooctane (**2.7**).

2,4,4-Trimethyl-1-pentene at room temperature.

The following reaction types were identified by GC/MS, although the precise structures could not be assigned by this technique. The composition of the product mixture by GC was:

Monobromide: Peak area 8%; $C_8H_{17}Br$ *m/z* 177 (M – CH_3, 1%), 135 (M – C_4H_9, 1), 121 (M – C_5H_{11}, 3), 113 (M – Br, 21), 97 (M – CH_3 – HBr, 10), 57 (C_4H_9+, 100), 41 (C_3H_5+, 28)

1,2-Dibromo-2,4,4-trimethylpentane (2.10): Peak area 22%; $C_8H_{16}Br_2$ *m/z* 255 (M – CH_3, 0.3%), 191 (M – Br, 4), 175 (M – CH_3 – HBr, 8), 133 (M – $C_4H_{10}Br$, 4), 121 (M – $C_5H_{10}Br$, 11), 95 (M – CH_3 – HBr – HBr, 18), 69 (C_5H_9+, 14), 57 (C_4H_9+, 100), 41 (C_3H_5+, 79)

Dibromoalkene: Peak area 7%; $C_8H_{14}Br_2$ *m/z* 268 (M+, 1%), 253 (M – CH_3, 1), 189 (M – Br, 20), 147 (M – C_3H_6Br, 5), 133 (M – C_4H_8Br, 9), 109 (M – HBr – Br, 35), 67 (C_5H_7+, 20), 57 (C_4H_9+, 100), 41 (C_3H_5+, 79)

and: Peak area 3%; $C_8H_{14}Br_2$ *m/z* 253 (M – CH_3, 0.3%), 212 (M – C_4H_8, 1), 189 (M – Br, 5), 109 (M – HBr – Br, 56), 67 (C_5H_7+, 38), 57 (C_4H_9+, 100), 41 (C_3H_5+, 79)

and: Peak area 16%; $C_8H_{14}Br_2$ *m/z* 253 (M – CH_3, 2%), 211 (M – C_4H_9, 0.4), 189 (M – Br, 63), 147 (M – C_3H_6Br, 11), 133 (M – C_4H_8Br, 13), 109 (M – HBr – Br, 100), 95 (M – CH_3 – Br – Br, 62), 67 (C_5H_7+, 96), 55 (C_4H_7+, 93), 41 (C_3H_5+, 92)

1,2-Dibromo-2-bromomethyl-4,4-dimethylpentane: Peak areas 40%; $C_8H_{15}Br_3$ *m/z* 333 (M – CH_3, 0.2%), 269 (M – Br, 1), 253 (M – CH_3 – HBr, 2), 173 (M – CH_3 – HBr – HBr, 5), 147 (M – Br – Br – C_3H_7, 3), 133 (M – Br – Br – C_4H_9, 6), 109 (M – HBr – HBr – Br, 4), 93 (M – C_7H_9, 12), 67 (C_5H_7+, 14), 57 (C_4H_9+, 100), 41 (C_3H_5+, 77)

and: Peak area 2%; $C_8H_{15}Br_3$ *m/z* 269 (M – Br, 3), 253 (M – CH_3 – HBr, 1), 189 (M – Br – HBr, 14), 147 (M – Br – Br – C_3H_7, 9), 135 (M – Br – Br – C_4H_7, 38), 109 (M – HBr – HBr – Br, 12), 69 (C_5H_9+, 65), 57 (C_4H_9+, 57), 41 (C_3H_5+, 100).

NMR analysis of the crude reaction mixture (only the signals for 1,2-dibromo-2-bromomethyl-4,4-dimethylpentane were identified); δ_H ($CDCl_3$) 4.03 (2H, d, *J* 11.0, 2 x CH_2Br), 3.90 (2H, d, *J* 11.0, 2 x CH_2Br), 2.18 (2H, s, CH_2), 1.13 (9H, s, $C(C\underline{H}_3)_3$); δ_C ($CDCl_3$) 66.0 (qC, qCBr), 50.3 (CH_2), 42.0 (2 x CH_2, CH_2Br), 32.6 (qC), 31.5 (CH_3, $C(C\underline{H}_3)_3$).

2,4,4-Trimethyl-1-pentene at 60 °C.

The following reaction types were identified by GC/MS, although the precise structures could not be assigned by this technique. The composition of the product mixture by GC was:

Monobromide: Peak area 5%; $C_8H_{17}Br$ *m/z* 177 (M – CH_3, 0.2%), 135 (M – C_4H_9, 0.4), 121 (M – C_5H_{11}, 3), 113 (M – Br, 13), 97 (M – CH_3 – HBr, 10), 57 (C_4H_8+, 100), 41 (C_3H_5+, 31)

Allylic bromides, two peaks with virtually identical mass spectra: Peak areas < 1%; $C_8H_{15}Br$ *m/z* 175 (M – CH_3, 1%), 134 (M – C_4H_8, 5.5), 111 (M – Br, 19.5), 69 (C_5H_9+, 20.5), 57 (C_4H_9+, 100), 41 (C_3H_5+, 36)

2-Bromomethyl-4,4-dimethylpent-1-ene (2.12): Peak area 41%; $C_8H_{15}Br$ *m/z* 175 (M – CH_3, 0.5%), 111 (M – Br, 7), 95 (M – CH_3 – HBr, 11.5), 69 (C_5H_9+, 5), 57 (C_4H_9+, 100), 41 (C_3H_5+, 27)

Vinylic bromide: Peak area < 1%; $C_8H_{15}Br$ *m/z* 190 (M+, 5.5%), 175 (M – CH_3, 4), 133 (M – C_4H_9, 2.5), 95 (M – CH_3 – HBr, 4), 57 (C_4H_9+, 100), 41 (C_3H_5+, 17)

Rearranged monobromoalkenes, two peaks with virtually identical mass spectra: Peak areas < 1%; $C_8H_{15}Br$ *m/z* 190 (M+, 1%), 175 (M – CH_3, 3.5), 133 (M – C_4H_9, 2.5), 111 (M – Br, 100), 69 (C_6H_9+, 87), 55 (C_4H_{11}+, 61), 41 (C_3H_5+, 60)

1,2-Dibromo-2,4,4-trimethylpentane (2.10): Peak area 31%; $C_8H_{16}Br_2$ *m/z* 255 (M – CH_3, 0.2%), 191 (M – Br, 2), 175 (M – CH_3 – Br, 3), 133 (M – $C_4H_{10}Br$, 2), 111 (M – HBr – Br, 2), 95 (M – CH_3 – HBr – HBr, 6), 57 (C_4H_9+, 100), 41 (C_3H_5+, 37)

Dibromoalkene: Peak area 4%; $C_8H_{14}Br_2$ *m/z* 268 (M+, 0.4%), 253 (M – CH_3, 0.4), 189 (M – Br, 9), 147 (M – C_3H_6Br, 2), 133 (M – C_4H_8Br, 3), 109 (M – HBr – Br, 2), 67 (C_5H_7+, 7), 57 (C_4H_9+, 100), 41 (C_3H_5+, 26)

and: Peak area 6%; $C_8H_{14}Br_2$ *m/z* 253 (M – CH_3, 0.2%), 189 (M – Br, 3), 109 (M – HBr – Br, 14), 67 (C_5H_7+, 7), 57 (C_4H_9+, 100), 41 (C_3H_5+, 23)

and: Peak area 5%; $C_8H_{14}Br_2$ *m/z* 253 (M – CH_3, 0.5%), 189 (M – Br, 15), 147 (M – C_3H_6Br, 2), 133 (M – C_4H_8Br, 3), 109 (M – HBr – Br, 100), 95 (M – CH_3 – Br – Br, 14), 67 (C_5H_7+, 45), 55 (C_4H_7+, 32), 41 (C_3H_5+, 31)

Tribromoalkane: Peak area 5%; $C_8H_{15}Br_3$ *m/z* 269 (M – Br, 0.2%), 253 (M – CH_3 – HBr, 0.6), 173 (M – CH_3 – HBr – HBr, 1), 147 (M – Br – Br – C_3H_7, 1), 133 (M

– Br – Br – C_4H_9, 1), 109 (M – HBr – HBr – Br, 1), 93 (M – HBr – HBr – HBr – CH_3, 3), 57 (C_4H_9+, 100), 41 (C_3H_5+, 22).

and: Peak area 4%; $C_8H_{15}Br_3$ *m/z* 269 (M – Br, 1), 189 (M – Br – HBr, 5), 147 (M – Br – Br – C_3H_7, 4), 135 (M – Br – Br – C_4H_7, 13), 109 (M – HBr – HBr – Br, 4), 69 (C_5H_9+, 21), 57 (C_4H_9+, 100), 41 (C_3H_5+, 37).

NMR analysis of the crude reaction mixture (only the signals for **2.12** were identified); δ_H ($CDCl_3$) 5.32 (1H, d, *J* 0.5, CH_2=), 4.95 (1H, d, *J* 0.5, CH_2=), 4.02 (2H, s, CH_2Br), 1.93 (2H, s, CH_2), 0.94 (9H, s, $C(C\underline{H}_3)_3$); δ_C ($CDCl_3$) 137.0 (qC, qC=), 119.1 (CH_2, CH_2=), 53.1 (CH_2), 46.5 (CH_2, CH_2Br), 32.5 (qC), 29.7 (CH_3, $C(C\underline{H}_3)_3$).

2,4,4-Trimethyl-1-pentene in carbon tetrachloride at room temperature.

The following reaction types were identified by GC/MS, although the precise structures could not be assigned by this technique. The composition of the product mixture by GC was:

Monobromides, two peaks: Peak areas 13 and 3% respectively; $C_8H_{17}Br$ *m/z* 177 (M – CH_3, 0.2%), 149 (M – C_3H_7, 2), 133 (M – C_4H_{11}, 1), 121 (M – C_5H_{11}, 2), 113 (M – Br, 16), 97 (M – CH_3 – HBr, 9), 57 (C_4H_9+, 100), 41 (C_3H_5+, 36)

Allylic bromide: Peak area 3%; $C_8H_{15}Br$ *m/z* 175 (M – CH_3, 0.3%), 137 (M – C_4H_5, 33), 57 (C_4H_9+, 100), 41 (C_3H_5+, 21)

1,2-Dibromo-2,4,4-trimethylpentane (2.10): Peak area 39%; $C_8H_{16}Br_2$ *m/z* 255 (M – CH_3, 0.2%), 191 (M – Br, 3), 175 (M – CH_3 – Br, 3), 133 (M – $C_4H_{10}Br$, 2), 111 (M – HBr – Br, 1), 95 (M – CH_3 – HBr – HBr, 6), 57 (C_4H_9+, 100), 41 (C_3H_5+, 33)

1,2-Dibromo-2-bromomethyl-4,4-dimethylpentane: Peak area 35%; $C_8H_{15}Br_3$ *m/z* 269 (M – Br, 0.3%), 253 (M – CH_3 – HBr, 2), 147 (M – Br – Br – C_3H_7, 1), 133 (M – Br – Br – C_4H_9, 2), 109 (M – HBr – HBr – Br, 1), 93 (M – HBr – HBr – HBr – CH_3, 2), 57 (C_4H_9+, 100), 41 (C_3H_5+, 22)

Tribromoalkane: Peak area 6%; $C_8H_{15}Br_3$ *m/z* 269 (M – Br, 2), 199 (M – Br – C_4H_{10}, 2), 189 (M – Br – HBr, 7), 147 (M – Br – Br – C_3H_7, 5), 135 (M – Br – Br – C_4H_7, 18), 121 (M – Br – Br – C_5H_9, 11), 69 (C_5H_9+, 25), 57 (C_4H_9+, 100), 41 (C_3H_5+, 37)

Tribromoalkene: Peak area 2%; $C_8H_{13}Br_3$ *m/z* 267 (M – Br, 2), 199 (M – Br – C_5H_8, 1), 187 (M – Br – HBr, 1), 135 (M – Br – Br – C_4H_5, 9), 121 (M – Br – Br – C_5H_7, 6), 69 (C_5H_9+, 13), 57 (C_4H_9+, 100), 41 (C_3H_5+, 32).

NMR analysis of the crude reaction mixture (only the signals for **2.10** and 1,2-dibromo-2-bromomethyl-4,4-dimethylpentane were identified). The NMR data collated for these two compounds was the same as that given previously, therefore only the ^{13}C NMR data is shown here ($ indicates distinguishable signals for **2.10**); δ_C ($CDCl_3$) 66.8$^\$$ (qC, qCBr), 66.0 (qC, qCBr), 53.1$^\$$ (CH_2), 50.2 (CH_2), 46.0$^\$$ (CH_2, CH_2Br), 41.9 (2 x CH_2, CH_2Br), 32.6 (qC), 32.3$^\$$ (qC), 31.9$^\$$ (CH_3), 31.4 (CH_3, $C(C\underline{H}_3)_3$).

2,4,4-Trimethyl-1-pentene at room temperature 0.5 equivalents of bromine.

The following reaction types were identified by GC/MS, although the precise structures could not be assigned by this technique. The composition of the product mixture by GC was:

Monobromide: Peak area 26%; $C_8H_{17}Br$ *m/z* 177 (M – CH_3, 0.5%), 121 (M – C_5H_{11}, 2), 113 (M – Br, 15), 97 (M – CH_3 – HBr, 9), 69 (C_5H_9+, 2), 57 (C_4H_9+, 100), 41 (C_3H_5+, 25)

Allylic bromides: Peak areas 4 and 24% respectively; $C_8H_{15}Br$ *m/z* 190 (M+, 2%), 175 (M – CH_3, 2), 134 (M – C_4H_8, 4), 111 (M – Br, 13), 95 (M – CH_3 – HBr, 5), 57 (C_4H_9+, 100), 41 (C_3H_5+, 26)

and: Peak area 3%; $C_8H_{15}Br$ *m/z* 190 (M+, 2%), 175 (M – CH_3, 4), 133 (M – C_4H_9, 2), 111 (M – Br, 100), 95 (M – CH_3 – HBr, 15), 55 (C_4H_7+, 51), 41 (C_3H_5+, 45)

1,2-Dibromo-2,4,4-trimethylpentane (2.10): Peak area 20%; $C_8H_{16}Br_2$ *m/z* 255 (M – CH_3, 1%), 199 (M – C_5H_{11}, 1), 191 (M – Br, 14), 175 (M – CH_3 – HBr, 12), 133 (M – $C_4H_{10}Br$, 6), 111 (M – Br – HBr, 4), 95 (M – Br – HBr – CH_3, 14), 57 (C_4H_9+, 14), 41 (C_3H_5+, 14)

Dibromoalkene: Peak area 4%; $C_8H_{14}Br_2$ *m/z* 268 (M+, 2%), 253 (M – CH_3, 1), 189 (M – Br, 22), 174 (M – CH_3 – Br, 2), 147 (M – C_3H_6Br, 3), 133 (M – C_4H_8Br, 6), 110 (M – Br – Br, 16), 95 (M – HBr – CH_2Br, 10), 67 (C_5H_7+, 14), 57 (C_4H_9+, 100), 41 (C_3H_5+, 54)

and: Peak area 1%; $C_8H_{14}Br_2$ *m/z* 268 (M+, 1%), 253 (M – CH_3, 1), 189 (M – Br, 8), 173 (M – CH_3 – HBr, 1), 147 (M – C_3H_6Br, 2), 133 (M – C_4H_8Br, 4), 109 (M – HBr – Br, 15), 93 (M – CH_3 – HBr – HBr, 6), 57 (C_4H_9+, 100), 41 (C_3H_5+, 30)

and: Peak area 8%; $C_8H_{14}Br_2$ *m/z* 253 (M – CH_3, 1%), 189 (M – Br, 27), 173 (M – CH_3 – HBr, 2), 147 (M – C_3H_6Br, 3), 133 (M – C_4H_8Br, 6), 109 (M – HBr – Br, 94), 95 (M – CH_3 – Br – Br, 20), 67 (C_5H_7+, 68), 57 (C_4H_9+, 100), 41 (C_3H_5+, 68)

Tribromoalkane: Peak area 7%; $C_8H_{15}Br_3$ *m/z* 333 (M – CH_3, 0.4%), 269 (M – Br, 2), 253 (M – HBr – CH_3, 3), 199 (M – HBr – C_5H_9, 3), 173 (M – HBr – HBr – CH_3, 6), 147 (M – Br – Br – C_3H_7, 3), 133 (M – Br – Br – C_4H_9, 8), 109 (M – HBr – HBr – Br, 5), 93 (M – HBr – HBr – HBr – CH_3, 21), 67 (C_5H_7+, 17), 57 (C_4H_9+, 100), 41 (C_3H_5+, 90).

2,4,4-Trimethyl-2-pentene at room temperature.

The following reaction types were identified by GC/MS, although the precise structures could not be assigned by this technique. The composition of the product mixture by GC was:

Monobromide: Peak area 10%; $C_8H_{17}Br$ *m/z* 177 (M – CH_3, 0.5%), 135 (M – C_4H_9, 0.4), 121 (M – C_5H_{11}, 4), 113 (M – Br, 28), 97 (M – CH_3 – HBr, 13), 57 (C_4H_9+, 100), 41 (C_3H_5+, 36)

Dibromoalkane: Peak area 8%; $C_8H_{16}Br_2$ *m/z* 191 (M – Br, 2), 175 (M – CH_3 – HBr, 2), 133 (M – $C_4H_{10}Br$, 1), 121 (M – $C_5H_{10}Br$, 2), 57 (C_4H_9+, 100), 41 (C_3H_5+, 18)

Dibromoalkenes, three peaks with virtually identical mass spectra: Peak areas 5, 9 and 10% respectively; $C_8H_{14}Br_2$ *m/z* 268 (M+, 0.4%), 253 (M – CH_3, 0.5), 189 (M – Br, 6), 174 (M – CH_3 – Br, 1), 147 (M – C_3H_6Br, 1), 110 (M – Br – Br, 5), 95 (M – HBr – CH_2Br, 5), 67 (C_5H_7+, 6), 57 (C_4H_9+, 100), 41 (C_3H_5+, 21)

and: Peak area 24%; $C_8H_{14}Br_2$ *m/z* 268 (M+, 0.4%), 253 (M – CH_3, 1), 189 (M – Br, 49), 147 (M – C_3H_6Br, 5), 109 (M – HBr – Br, 100), 95 (M – HBr – CH_2Br, 29), 67 (C_5H_7+, 97), 55 (C_4H_7+, 68), 41 (C_3H_5+, 47)

Tribromoalkane: Peak area 24%; $C_8H_{15}Br_3$ *m/z* 333 (M – CH_3, 0.2%), 269 (M – Br, 1), 253 (M – HBr – CH_3, 2), 173 (M – HBr – HBr – CH_3, 3), 133 (M – Br – Br – C_4H_9, 3), 109 (M – HBr – HBr – Br, 2), 93 (M – HBr – HBr – HBr – CH_3, 6), 67 (C_5H_7+, 8), 57 (C_4H_9+, 100), 41 (C_3H_5+, 47)

Tribromoalkene: Peak area 10%; $C_8H_{13}Br_3$ 346 (M+, 0.3%), 331 (M – CH_3, 0.2), 267 (M – Br, 7), 187 (M – Br – HBr, 7), 147 (M – Br – HBr – C_3H_4, 8), 108 (M – Br – HBr – Br, 15), 69 (C_5H_9+, 39), 57 (C_4H_9+, 53), 41 (C_3H_5+, 100).

Further experiments using 2,4,4-trimethyl-2-pentene.

The experimental conditions and results are summarized in the table below

Reaction solvent	Temperature / °C	Products (Uncalibrated GC areas / %) [1]
$CHCl_3$	60	Monobromoalkane (16), monobromoalkene (17), dibromoalkane (16), dibromoalkenes (four peaks; 4, 7, 7 and 17), tribromoalkanes (two peaks; 8 and 3), tribromoalkene (4)
CCl_4	21	Monobromoalkane (three peaks; 6, 5 and 24), dibromoalkanes (three peaks; 4, 13 and 1), dibromoalkene (3), tribromoalkane (two peaks; 2 and 25), tribromoalkene (12)

1 : Products identified from GC/MS analysis, MS data compared to the products formed from the bromination of 2,4,4-trimethyl-2-pentene in $CHCl_3$ at room temperature (21 °C).

3-Ethyl-2-pentene at room temperature.

The following reaction types were identified by GC/MS, although the precise structures could not be assigned by this technique. The composition of the product mixture by GC was:

2,3-Dibromo-3-ethylpentane (2.17): Peak area 84%; $C_7H_{14}Br_2$ *m/z* 177 (M – Br, 14%), 135 (M – Br – C_3H_6, 3), 121 (M – Br – C_4H_8, 2), 107 (M – Br – C_5H_{10}, 5), 97 (M – Br – Br, 94), 69 (C_5H_9+, 45), 55 (C_4H_7+, 100), 41 (C_3H_5+, 62)

Tribromoalkane: Peak area 16%; $C_7H_{11}Br_3$ *m/z* 255 (M – Br, 14%), 175 (M – Br – HBr, 85), 133 (M – Br – HBr – C_3H_6, 15), 119 (M – Br – HBr – C_4H_7, 4), 107 (M – Br – HBr – C_5H_7, 21), 96 (M + H – Br – Br – Br, 92), 55 (C_4H_7+, 90), 41 (C_3H_5+, 100).

NMR analysis of the crude reaction mixture (only the signals for **2.17** were identified). The NMR data collated for this compound was the same as that given previously, therefore only the ^{13}C NMR data is shown here: δ_C ($CDCl_3$) 81.1 (qC, qCBr), 55.7 (CH, CHBr), 33.2 (CH_2), 30.8 (CH_2), 22.6 (CH_3, CHBr-$\underline{C}H_3$), 9.6 (CH_3, $CH_2C\underline{H}_3$), 9.3 (CH_3, $CH_2C\underline{H}_3$).

6.2.3 Interhalogen Reactions.

Halogenation of model alkenes with iodine monochloride.

In a typical procedure, a solution of iodine monochloride (1M in $CHCl_2$) (8.91 cm^3, 1 equivalent) was added to a solution of the alkene (8.91 mmol) in 5 cm^3 of dried dichloromethane under a nitrogen atmosphere. This solution was stirred in the dark for 3.5 h. After stirring for this period the solvent was removed under reduced pressure and the residue diluted with diethyl ether, washed with 10% aqueous sodium thiosulfate, saturated sodium chloride solution and water. The organic phase was dried over magnesium sulphate and the solvent removed once again.

The reaction mixture was analysed by GC/MS and NMR. Although attempts to isolate the major products were unsuccessful, in many cases their structures were determined by NMR analysis.

1-Octene.

The following reaction types were identified by GC/MS, although the precise structures could not be assigned by this technique. The composition of the product mixture by GC was:

1-Chloro-2-iodooctane (2.18a): Peak area 40%; $C_8H_{16}ICl$ *m/z* 274 (M+, 0.5%), 147 (M – I, 16), 127 (I+˙, 2), 111 (M – I – HCl, 9), 105 (M – I – C_3H_7, 9), 69 (C_5H_9+, 100), 57 (C_4H_9+, 62), 41 (C_3H_5+, 75)

1-Iodo-2-chlorooctane (2.18b): Peak area 60%; $C_8H_{16}ICl$ *m/z* 274 (M+, 1%), 147 (M – I, 13), 127 (I+˙, 3), 111 (M – I – HCl, 9), 105 (M – I – C_3H_7, 10), 91 (M – C_4H_8I, 6), 69 (C_5H_9+, 100), 57 (C_4H_9+, 62), 41 (C_3H_5+, 75).

NMR analysis of the crude reaction mixture ($ indicates distinguishable signals for **2.18b**); δ_H ($CDCl_3$) 4.21 (1H, m, CHI), 4.04 (1H, dd, *J* 4.5 and *J* 11.0, CH_2Cl), 3.96$^\$$ (1H, apparent tdd, *J* 3.5, *J* 5.0 and *J* 8.5, CHCl), 3.81 (1H, dd, *J* 10.0 and *J* 11.0, CH_2Cl), 3.57$^\$$ (1H, dd, *J* 5.0 and *J* 10.0, CH_2I), 3.42$^\$$ (1H, dd, *J* 8.5 and *J* 10.0, CH_2I), 2.10-1.20 (20H, m, CH_2), 0.90 (6H, t, *J* 6.5, CH_3); δ_C ($CDCl_3$) 61.1$^\$$ (CH, CH-Cl), 50.0 (CH_2, CH_2Cl), 37.2 (CH_2), 36.4 (CH_2), 33.5 (CH, CHI), 31.6, 28.8, 28.6, 28.3, 25.9, 22.5 (CH_2, CH_2 chain), 14.1 (CH_3), 11.0$^\$$ (CH_2, CH_2I).

2,4,4-Trimethyl-1-pentene.

The following reaction types were identified by GC/MS, although the precise structures could not be assigned by this technique. The composition of the product mixture by GC was:

Monochloroalkane: Peak area 1%; $C_8H_{17}Cl$ *m/z* 133 (M – CH_3, 1.5%), 112 (M – HCl, 2), 97 (M – CH_3 – HCl, 24), 57 (C_4H_9+, 100), 41 (C_3H_5+, 29)

Monoiodoalkene: Peak area 6%; $C_8H_{15}I$ *m/z* 238 (M+, 6%), 223 (M – CH_3, 1), 182 (M – C_4H_8, 7), 127 (I+·, 2), 111 (M – I, 30), 95 (M – CH_4I, 15), 56 (C_4H_8+, 100)

1-Iodo-2-chloro-2-methylpentane (2.19): Peak area 91%; $C_8H_{16}ICl$ *m/z* 274 (M+, 0.5%), 259 (M – CH_3, 1), 239 (M – Cl, 1), 223 (M – CH_3 – HCl, 2), 203 (M – C_5H_{11}, 4), 183 (M – C_4H_8Cl, 2), 169 (M – $C_5H_{10}Cl$, 5), 147 (M – I, 8), 127 (I+·, 3), 112 (M – ICl, 7),57 (C_4H_9+, 100).

NMR analysis of the crude reaction mixture (major peaks only); δ_H ($CDCl_3$) 3.61 (1H, d, *J* 10.0, CH_2I), 3.56 (1H, d, *J* 9.5, CH_2I), 1.97 (1H, d, *J* 15.5, CH_2), 1.87 (1H, d, *J* 15.0, CH_2), 1.70 (s, 3H, CH_3), 0.99 (s, 9H, $C(CH_3)_3$); δ_C ($CDCl_3$) 70.0 (qC, $\underline{C}$-Cl), 52.9 (CH_2, qC-$\underline{C}H_2$-qC), 31.7 (qC, $\underline{C}(CH_3)_3$), 31.6 (CH_3, $\underline{C}H_3$-qC-Cl), 30.7 (CH_3 , $C(\underline{C}H_3)_3$), 22.3 (CH_2, $\underline{C}H_2I$).

2,4,4-Trimethyl-2-pentene.

The following reaction types were identified by GC/MS, although the precise structures could not be assigned by this technique. The composition of the product mixture by GC was:

Monochloroalkane: Peak area 49%; $C_8H_{17}Cl$ *m/z* 133 (M – CH_3, 1%), 113 (M – Cl, 1), 97 (M – CH_3 – Cl, 17), 57 (C_4H_8+, 100), 41 (C_3H_5+, 38)

Monochloroalkene: Peak area 40%; $C_8H_{15}Cl$ *m/z* 131 (M – CH_3, 2%), 111 (M – Cl, 1), 95 (M – CH_3 – HCl, 5), 57 (C_4H_9+, 100), 41 (C_3H_5+, 32)

and: Peak area 6%; $C_8H_{15}Cl$ *m/z* 146 (M+, 15%), 131 (M – CH_3, 28), 111 (M – Cl, 18), 103 (M – C_3H_7, 9), 97 (M – CH_2Cl, 87), 69 (C_5H_9+, 70), 55 (C_4H_7+, 100), 41 (C_3H_5+, 79)

and: Peak area 2%; $C_8H_{15}Cl$ *m/z* 131 (M – CH_3, 1), 111 (M – Cl, 1), 105 (M – C_3H_5, 9), 97 (M – CH_2Cl, 5), 69 (C_5H_9+, 26), 57 (C_4H_9+, 100), 41 (C_3H_5+, 63)

Iodochloroalkane: Peak area 2%; $C_8H_{16}ICl$ *m/z* 223 (M – CH_3 – HCl, 1%), 203 (M – C_5H_{12}, 2), 183 (M – C_4H_9Cl, 1), 147 (M – I, 1), 167 (M – $C_5H_{11}Cl$, 3), 127 ($I^{+\cdot}$, 2), 112 (M – I – Cl, 4), 95 (M – CH_3 – HI – HCl, 3), 57 (C_4H_9+, 100), 42 (C_3H_6+, 34)

3-Methyl-2-pentene.

The composition of the product mixture by GC was:

2-Chloro-3-iodo-3-methylpentane: Peak area 45%; $C_6H_{12}ICl$ *m/z* 246 (M+, 1%), 217 (M – C_2H_5, 1), 211 (M – Cl, 11), 127 ($I^{+\cdot}$, 8), 119 (M – I, 64), 83 (M – HI – Cl, 97), 55 (C_4H_9+, 100), 43 (C_3H_7+, 75)

2-Iodo-3-chloro-3-methylpentane: Peak area 55%; $C_6H_{12}ICl$ *m/z* 246 (M+, 3%), 217 (M – C_2H_5, 1), 211 (M – Cl, 5), 127 ($I^{+\cdot}$, 8), 119 (M – I, 52), 83 (M – HI – Cl, 98), 55 (C_4H_7+, 100), 43 (C_3H_7+, 85).

GC/MS analysis for the reaction mixture from iodine monochloride and 3-ethyl-pent-2-ene is very similar to that given by 3-methyl-pent-1-ene [16% monochloropentane and 84% monoiodochloropentane (two peaks for two regioisomers)].

NMR analysis of the crude reaction mixture for 3-ethyl-pent-2-ene$^{\#}$ ($ indicates distinguishable signals for 2-iodo-3-chloro-3-methylpentane); δ_H ($CDCl_3$) 4.53$^{\$}$ (1H, q, *J* 7.0, qC-C$\underline{H}$I-Me), 4.29 (1H, q, *J* 7.0, qC-C$\underline{H}$Cl-Me), 2.04$^{\$}$ (3H, d, *J* 7.0, CHI-C$\underline{H}_3$), 2.03 (3H, d, *J* 7.0, CHCl-C$\underline{H}_3$), 2.00-1.55 (8H, m, CH_2), 1.10-0.90 (6H, m, CH_3); δ_C ($CDCl_3$) Only the signals for 2-iodo-3-chloro-3-methylpentane were intense enough to be assigned from the ^{13}C-Dept experiment 80.2$^{\$}$ (qC, qC-Cl), 36.6$^{\$}$ (CH, CHI), 32.5$^{\$}$ (CH_2), 31.6$^{\$}$ (CH_2), 24.5$^{\$}$ (CH_3, CHI-$\underline{C}H_3$), 8.3$^{\$}$ (CH_3, CH_2-$\underline{C}H_3$), 8.2$^{\$}$ (CH_3, CH_2-$\underline{C}H_3$).

Halogenation with Iodine Monochloride formed in-situ

In a typical procedure, a large crystal of iodine was dissolved in a solution of the alkene (8.91 mmol) in *p*-xylene (9.43 mmol). Chlorine gas was bubbled through this solution for a period of approximately 0.25 h at room temperature. After this period the reaction mixture was washed with 10 cm^3 of a 10% aqueous sodium thiosulfate solution and then distilled water. The aqueous layer was extracted with diethyl ether (3 x 30 cm^3) and combined, dried over magnesium sulfate and evaporated under reduced pressure to afford the crude reaction mixture. The reaction mixture was not purified further but the composition of each reaction product was determined by GC/MS analysis.

2,4,4-Trimethyl-1-pentene.

The following reaction types were identified by GC/MS, although the precise structures could not be assigned by this technique. The composition of the product mixture by GC, apart from residual solvent, was:

1-Chloro-2,5-dimethylbenzene (2.1): Peak area 43%; C_8H_9Cl *m/z* 140 (M+, 46%), 125 (M – CH_3, 15), 105 (M – Cl, 100), 77 (22), 63 (8), 51 (21), 39 (10)

Dichloroalkane: Peak area 6%; $C_8H_{16}Cl_2$ *m/z* 167 (M – CH_3, 1%), 131 (M – CH_3 – HCl, 15), 95 (M – CH_3 – HCl – HCl, 7), 57 (C_4H_9+, 100), 41 (C_3H_5+, 31)

Dichloroalkene: Peak area 27%; $C_8H_{14}Cl_2$ *m/z* 180 (M+, 1%), 165 (M – CH_3, 2), 129 (M – CH_3 – HCl, 5), 109 (M – HCl – Cl, 1), 57 (C_4H_9+, 100), 41 (C_3H_5+, 37)

and: Peak area 7%; $C_8H_{14}Cl_2$ *m/z* 180 (M+, 1%), 165 (M – CH_3, 3), 129 (M – CH_3 – HCl, 6), 57 (C_4H_9+, 100), 41 (C_3H_5+, 29)

Trichloroalkane: Peak area 6%; $C_8H_{15}Cl_3$ *m/z* 201 (M – CH_3, 2%), 165 (M – CH_3 – HCl, 6), 129 (M – CH_3 – HCl – HCl, 5), 57 (C_4H_9+, 100), 41 (C_3H_5+, 27)

Tetrachloroalkane: Peak area 2%; $C_8H_{14}Cl_4$ *m/z* 235 (M – CH_3, 2%), 199 (M – CH_3 – HCl, 2), 163 (M – CH_3 – HCl – HCl, 4), 127 (M – CH_3 – HCl – HCl – HCl, 6), 109 (2), 77 (19), 57 (C_4H_9+, 100), 41 (C_3H_5+, 31)

Trichloroxylene: Peak area 2%; $C_8H_{10}Cl_3$ *m/z* 211 (M+, 19%), 175 (M – HCl , 100), 139 (M – HCl – HCl, 28), 105 (M – HCl – Cl – Cl, 23), 91 (22), 77 (26), 63 (15), 51 (26), 39 (19)

Tetrachloroalkane: Peak area 2%; $C_8H_{14}Cl_4$ *m/z* 199 (M – CH_3 – HCl, 0.5%), 163 (M – CH_3 – HCl – HCl, 1.5), 127 (M – CH_3 – HCl – HCl – HCl, 2), 57 (C_4H_9+, 100), 41 (C_3H_5+, 37)

Halogenation of model alkenes with iodine monobromide.

In a typical procedure, a solution of iodine monobromide (1M in $CHCl_2$) (8.9 cm^3, 1 equivalents) was added to a solution of the alkene (8.91 mmol) in 5 cm^3 of dried dichloromethane under a nitrogen atmosphere. This solution was stirred in the dark for 3.5 h. After stirring for this period the solvent was removed under reduced pressure and the residue extracted with diethyl ether, washed with 10% aqueous sodium thiosulfate, saturated sodium chloride solution and water. The organic phase was dried over magnesium sulfate and the solvent removed once again, analysis of the crude reaction mixture was carried out by GC/MS and NMR.

1-Octene.

The following reaction types were identified by GC/MS, although the precise structures could not be assigned by this technique. The composition of the product mixture by GC was:

1,2-Dibromooctane (2.7): Peak area 26%; $C_8H_{16}Br_2$ *m/z* 191 (M – Br, 4), 149 (M – C_3H_7Br, 9), 135 (M – C_4H_9Br, 6), 111 (M – Br – HBr, 33), 69 (C_5H_9+, 100), 55 (C_4H_7+, 70), 41 (C_3H_5+, 75)

1-Bromo-2-iodooctane: Peak area 30%; C_8H_{16}IBr *m/z* 239 (M – Br, 1%), 197 (M – C_3H_6Br, 1), 191 (M – I, 6), 183 (M – C_4H_8Br, 1), 169 (M – C_5H_{10}Br, 1), 149 (M – C_3H_6I, 6), 135 (M – C_4H_8I, 6), 111 (M – I – Br, 20), 69 (C_5H_9+, 100), 55 (C_4H_7+, 73), 41 (C_3H_5+, 84)

1-Iodo-2-bromooctane: Peak area 44%; C_8H_{16}IBr *m/z* 239 (M – Br, 1%), 197 (M – C_3H_6Br, 1), 191 (M – I, 6), 183 (M – C_4H_8Br, 1), 169 (M – C_5H_{10}Br, 1), 149 (M –

C_3H_6I, 6), 135 (M – C_4H_8I, 6), 111 (M – I – Br, 20), 69 (C_5H_9+, 100), 55 (C_4H_7+, 73), 41 (C_3H_5+, 84).

NMR analysis of the crude reaction mixture (only the major peaks for 1-bromo-2-iodooctane and 1-iodo-2-bromooctane have been assigned) ($ indicates distinguishable signals for 1-iodo-2-bromooctane); δ_H ($CDCl_3$) 4.35-4.23$^\$$ (1H, m, CHI), 4.21-4.10 (1H, m, CHBr), 4.04$^\$$ (1H, dd, *J* 4.0 and *J* 10.0, CH_2Br), 3.79$^\$$ (1H, dd, *J* 4.0 and *J* 10.0, CH_2Br), 3.75 (1H, apparent t, *J* 10.0, CH_2I), 3.53 (1H, apparent t, *J* 10.0, CH_2I), 2.20-1.20 (20H, m, CH_2), 0.89 (6H, t, *J* 7.0, CH_3); δ_C ($CDCl_3$) 53.4 (CH, CH-Br), 38.2 (CH_2), 37.5 (CH_2), 37.2$^\$$ (CH_2, CH_2Br), 33.2$^\$$ (CH, CHI), 31.6, 28.7, 28.4, 28.3, 26.8, 22.5 (CH_2, CH_2 chain), 14.0 (CH_3), 11.2 (CH_2, CH_2I).

2,4,4-Trimethyl-1-pentene.

The composition of the product mixture by GC was:

Allylic bromides: Peak area 7%; $C_8H_{15}Br$ *m/z* 190 (M+, 1%), 175 (M – CH_3, 2), 134 (M – C_4H_8, 6), 111 (M – Br, 22), 95 (M – CH_3 – HBr, 6), 69 (C_5H_9+, 18), 57 (C_4H_9+, 100), 41 (C_3H_5+, 28)

and: Peak area 6%; $C_8H_{15}Br$ *m/z* 175 (M – CH_3, 0.5%), 133 (M – C_4H_9, 0.3), 111 (M – Br, 7), 95 (M – CH_3 – HBr, 10), 57 (C_4H_9+, 100), 41 (C_3H_5+, 21)

Rearranged monobromoalkene: Peak area 8%; $C_8H_{15}Br$ *m/z* 190 (M+, 1%), 175 (M – CH_3, 3), 133 (M – C_4H_9, 3), 111 (M – Br, 100), 95 (M – CH_3 – HBr, 16), 69 (C_5H_9+, 81), 55 (C_4H_7+, 56), 41 (C_3H_5+, 49)

and: Peak area 6%; $C_8H_{15}Br$ *m/z* 190 (M+, 1.5%), 175 (M – CH_3, 4), 133 (M – C_4H_9, 2), 111 (M – Br, 100), 95 (M – CH_3 – HBr, 15), 69 (C_5H_9+, 78), 55 (C_4H_7+, 52), 41 (C_3H_5+, 44)

1,2-Dibromo-2,4,4-trimethylpentane: Peak area 72%; $C_8H_{16}Br_2$ *m/z* 199 (M – C_5H_{11}, 0.2%), 191 (M – Br, 2), 175 (M – CH_3 – HBr, 2), 135 (M – C_4H_8Br, 2), 121 (M – $C_5H_{10}Br$, 3), 111 (M – HBr – Br, 1), 95 (M – CH_3 – HBr – HBr, 4), 69 (C_5H_9+, 4), 57 (C_4H_9+, 100), 41 (C_3H_5+, 23).

NMR analysis of the crude reaction mixture (major peaks only); δ_H ($CDCl_3$) 3.92 (1H, d, *J* 10.0, CH_2Br), 3.86 (1H, d, *J* 10.0, CH_2Br), 2.15 (1H, d, *J* 15.5, CH_2), 2.02 (1H, d, *J* 15.5, CH_2), 1.92 (s, 3H, CH_3), 1.10 (s, 9H, $C(CH_3)_3$); δ_C ($CDCl_3$) 66.7 (qC,

$\underline{C}$-Br), 53.1 (CH_2, qC-$\underline{C}H_2$-qC), 46.0 (CH_2, $\underline{C}H_2Br$), 32.4 (qC, $\underline{C}(CH_3)_3$), 31.9 (CH_3, $\underline{C}H_3$-qC-Cl), 31.3 (CH_3 , C($\underline{C}H_3)_3$).

2,4,4-Trimethyl-2-pentene.

The composition of the product mixture by GC was:

Monobromide: Peak area 34%; $C_8H_{17}Br$ *m/z* 177 (M – CH_3, 1%), 135 (M – C_4H_9, 1), 113 (M – Br, 55), 97 (M – CH_3 – HBr, 38), 69 (C_5H_9+, 9), 57 (C_4H_9+, 100), 41 (C_3H_5+, 88)

Allylic bromides: Peak area 29%; $C_8H_{15}Br$ *m/z* 190 (M+, 1%), 175 (M – CH_3, 7), 134 (M – C_4H_8, 22), 111 (M – Br, 73), 96 (M – CH_3 – Br, 14), 69 (C_5H_9+, 70), 57 (C_4H_9+, 100), 41 (C_3H_5+, 96)

and: Peak area 6%; $C_8H_{15}Br$ *m/z* 175 (M – CH_3, 1%), 133 (M – C_4H_9, 1),111 (M – Br, 13), 95 (M – CH_3 – HBr, 19), 69 (C_5H_9+, 9), 57 (C_4H_9+, 100), 41 (C_3H_5+, 43)

Rearranged monobromoalkene: Peak area 11%; $C_8H_{15}Br$ *m/z* 190 (M+, 2%), 175 (M – CH_3, 6), 133 (M – C_4H_9, 4), 111 (M – Br, 100), 95 (M – CH_3 – HBr, 27), 69 (C_5H_9+, 95), 55 (C_4H_7+, 90), 41 (C_3H_5+, 87)

Dibromoalkane: Peak area 16%; $C_8H_{16}Br_2$ *m/z* 255 (M – CH_3, 0.5%), 199 (M – C_5H_{11}, 1), 191 (M – Br, 7), 175 (M – CH_3 – HBr, 9), 133 (M – $C_4H_{10}Br$, 5), 121 (M – $C_5H_{10}Br$, 13), 111 (M – Br – HBr, 3), 95 (M – CH_3 – HBr – HBr , 20), 69 (C_5H_9+, 14), 57 (C_4H_9+, 100), 41 (C_3H_5+, 84)

Dibromoalkene: Peak area 1%; $C_8H_{14}Br_2$ *m/z* 189 (M – Br, 17), 175 (M – CH_2Br, 2), 147 (M – C_3H_6Br, 5), 133 (M – $C_4H_{10}Br$, 4), 121 (M – $C_5H_{10}Br$, 3), 109 (M – Br – Br, 52), 81 (C_6H_9+, 7), 69 (C_5H_9+, 100), 55 (C_4H_7+, 26), 41 (C_3H_5+, 79)

and: Peak area 1%; $C_8H_{14}Br_2$ *m/z* 189 (M – Br, 2), 147 (M – C_3H_6Br, 0.5), 133 (M – $C_4H_{10}Br$, 1), 109 (M – Br – Br, 12), 69 (C_5H_9+, 7), 57 (C_4H_9+, 100), 41 (C_3H_5+, 18)

3-Ethyl-2-pentene.

The composition of the product mixture by GC was:

2-Bromo-3-ethylpentane: Peak area 44%; $C_7H_{15}Br$ *m/z* 149 (M – C_2H_5, 0.3%), 99 (M – Br, 35), 69 (C_5H_9+, 14), 57 (C_4H_9+, 100), 41 (C_3H_5+, 43)

2,3-Dibromo-3-ethylpentane: Peak area 50%; $C_7H_{14}Br_2$ *m/z* 177 (M – Br, 19%), 149 (M – Br – C_2H_4, 2), 135 (M – Br – C_3H_6, 3),121 (M – Br – C_4H_8, 3), 107 (M – Br – C_5H_{10}, 4), 97 (M – Br – HBr, 97), 69 (C_5H_9+, 44), 55 (C_4H_7+, 100), 41 (C_3H_5+, 60)

Dibromoalkane: Peak area 6%; $C_7H_{14}Br_2$ *m/z* 177 (M – Br, 26%), 135 (M – Br – C_3H_6, 6), 121 (M – Br – C_4H_8, 4), 107 (M – Br – C_5H_{10}, 3), 97 (M – Br – HBr, 59), 69 (C_5H_9+, 20), 55 (C_4H_9+, 100), 41 (C_3H_5+, 51).

NMR analysis of the crude reaction mixture ($ indicates distinguishable signals for 2,3-dibromo-3-ethylpentane); δ_H ($CDCl_3$) 4.51$^\$$ (1H, q, *J* 6.5, qCBr-C$\underline{H}$Br-Me), 3.55-3.44 (1H, m, CH-C$\underline{H}$Br-Me), 2.43-1.93 (9H, m, CH_2), 1.89$^\$$ (3H, d, *J* 6.5, CHBr-C$\underline{H_3}$), 1.85 (3H, d, *J* 7.0, CHBr-C$\underline{H_3}$), 1.06 (3H, t, *J* 7.0, CH_3), 0.98$^\$$ (3H, t, *J* 7.5, CH_3); δ_C ($CDCl_3$) Only the signals for 2,3-dibromo-3-ethylpentane are intense enough to be assigned from the ^{13}C-Dept experiment 83.0$^\$$ (qC, qC-Br), 55.7$^\$$ (CH, CHBr), 33.3$^\$$ (CH_2), 22.7$^\$$ (CH_3, CHBr-$\underline{C}H_3$), 9.7$^\$$ (CH_3, CH_2-$\underline{C}H_3$).

6.3 Formation of diamines from epoxides

This section details the experiments procedures relevant to the work outlined in chapter 3. Analysis of the products and reaction mixtures were performed, where relevant, by ^{1}H and ^{13}C NMR, MS (EI and CI) and IR as detailed in section 6.1.2. GC/MS experiments were performed using an SE54 column (temperature program; initial temperature of 100 °C for 2 minutes followed by ramping at 8 °C/min to 290 °C).

6.3.1 Epoxidation reactions.

Epoxidation of the model alkenes with *m*-chloroperbenzoic acid (*m*-CPBA).
The model alkenes, 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene, were converted into the corresponding epoxides using *m*-CPBA.[165] In a typical procedure, the alkene (2.6 g, 23.2 mmol) in chloroform (5 cm^3) was cooled to 0 °C and a solution of *m*-CPBA (4 g, 1eq) in chloroform (10 cm^3) added slowly with stirring. The temperature of the solution was maintained at 0 °C for 24 h. 4-Chlorobenzoic acid was removed by shaking the chloroform solution with excess dilute aqueous sodium hydroxide solution (10%), followed by washing with water and drying the organic layer ($MgSO_4$). The solvent was removed under reduced pressure to give the crude product, which was purified by distillation. Characterization of the oxiranes for the following alkenes was achieved by NMR and mass spectroscopy.

Preparation of 1,2-epoxy-2,4,4-trimethylpentane (3.3)
The distilled reaction product, a clear colourless oil (1.06 g, 34.7%), was identified as 1,2-epoxy-2,4,4-trimethylpentane (**3.3**): MS (EI) $C_8H_{16}O$ *m/z* 128 (M+, 1%), 113 (M – CH_3, 6), 95 (M – CH_3 – H_2O, 14), 85 (M – C_3H_7, 9), 72 (M – C_4H_8, 23), 57 (C_4H_9+, 100), 43 (C_3H_7+, 50), 41 (C_3H_5+, 45); NMR δ_H($CDCl_3$) 2.56 (1H, apparent dd, *J* 0.5 and *J* 5.0, CH_2O), 2.52 (1H, apparent dd, *J* 1.5 and *J* 5.0, CH_2O), 1.67 (1H, apparent dd, *J* 1.5 and *J* 14.0, CH_2), 1.32 (3H, s, CH_3), 1.21 (1H, d, *J* 14.0, CH_2), 0.93 (s, 9H, CH_3); δ_C($CDCl_3$) 55.8 (qC, epoxide-qC), 54.6 (CH_2, epoxide-CH_2),

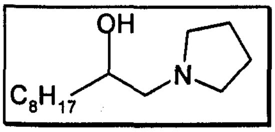
51.0 (CH_2, $(Me)_3C$-<u>CH_2</u>), 30.8 (qC, <u>C</u>$(Me)_3$), 30.6 (CH_3, -qC(<u>Me</u>)(O)-), 23.3 (CH_3, -C(<u>Me</u>)$_3$).

2,3-Epoxy-2,4,4-trimethylpentane (3.4).

The distilled reaction product, a clear colourless oil (0.55g, 19.0%), was identified as 2,3-epoxy-2,4,4-trimethylpentane (**3.4**): MS (EI) $C_8H_{16}O$ *m/z* 128 (M+, 1%), 113 (M – CH_3, 15), 85 (M –C_3H_7, 13), 72 (M –C_4H_8, 36), 57 (C_4H_9+, 98), 55 (C_4H_7+, 100), 43 (C_3H_7+, 63), 41 (C_3H_5+, 75); NMR δ_H($CDCl_3$) 2.42 (1H, s, -CH(O)-), 1.34 (3H, s, -C(O)(Me)CH_3), 1.22 (3H, s, -C(O)(CH_3)Me), 0.95 (s, 9H, $C(CH_3)_3$); δ_C($CDCl_3$) 72.5 (CH, epoxide-CH), 59.2 (qC, epoxide-qC), 31.5 (qC, -<u>C</u>$(Me)_3$), 27.7 (CH_3, -qC(<u>Me</u>)$_2$), 27.1 (CH_3, -qC(<u>Me</u>)$_2$), 19.5 (CH_3, -qC(<u>Me</u>)$_3$).

6.3.2 Epoxide Ring Opening Reactions.

Preparation of 1-(pyrrolidin-1-yl)-decan-2-ol (3.5).



To a solution of 1,2-epoxydecane (1 g, 6.41 mmol) in solvent (25 cm^3) (THF, toluene, ethanol or water) was added 1.5 equivalents of pyrrolidine (0.67 g, 0.80 cm^3, 9.62 mmol). After refluxing the solution for 16 h the solvent and excess pyrrolidine were removed under reduced pressure. The crude product was dried on a high vacuum line and analysed by NMR and/or GC/MS.

Reaction in tetrahydrofuran (THF).

Using THF as the solvent the crude product obtained was a clear yellow liquid. NMR analysis of the reaction mixture showed that the major component was starting material (1,2-epoxydecane) and only *ca.* 5% of the yellow liquid was the desired product, 1-(pyrrolidin-1-yl)-decan-2-ol.

Reaction in toluene.

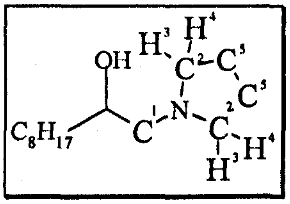
The solution obtained by a similar reaction in toluene was found to contain, by GC/MS, similar amounts of 1,2-epoxydecane and 1-(pyrrolidin-1-yl)-decan-2-ol. The composition of the product mixture by GC was:

1,2-epoxydecane: Peak area 53%; $C_{10}H_{20}O$ *m/z* 127 (M – C_2H_5, 1%), 113 (M – C_3H_7, 5), 95 (M – C_3H_9O, 19), 71 (C_5H_{11}+, 100), 55 (C_4H_7+, 77), 41 (C_3H_5+, 95)

1-(pyrrolidin-1-yl)-decan-2-ol (3.5): Peak area 47%; $C_{14}H_{29}NO$ *m/z* 227 (M, 1%), 114 (M – C_8H_{17}, 9), 84 (M – C_8H_{17} – CH(OH), 100), 55 (C_4H_7+, 9), 42 (C_3H_6+, 11).

Reaction in ethanol.

The crude reaction product from a reaction carried out using ethanol as the solvent was purified by bulb-bulb vacuum distillation to give a yellow oil, which was identified as 1-(pyrrolidin-1-yl)-2-decanol (**3.5**, 1.25 g, 86%): MS (EI) $C_{14}H_{29}NO$ *m/z* 227 (M, 0.4%), 114 (M – C_8H_{17}, 7), 84 ($C_5H_{10}N$+, 100), 55 (C_4H_7+, 6), 42 (C_3H_6+, 8); NMR $\delta_H(CDCl_3)$ 3.60-3.55 (m, 1H, $C\underline{H}(OH)$), 3.55-3.43 (br s, 1H, OH), 2.63-2.60 (m, 2H, H-3), 2.50 (apparent t, 1H, *J* 11.0, $-C\underline{H_2}CH(OH)$), 2.41-2.39 (m, 2H, H-4), 2.21 (dd, 1H, *J* 3.0 and *J* 11.0, $-C\underline{H_2}CH(OH)$), 1.71-1.69 (br s, 4H, 2 x $N(CH_2C\underline{H_2})_2$) 1.39-1.22 (br s, 14H, CH_2), 0.82 (t, 3H, *J* 6.5, CH_3); $\delta_C(CDCl_3)$ 68.2 (CH, $\underline{CH}(OH)$), 62.1 (CH_2, C-1), 53.9 (CH_2, 2 x C-2), 35.1 (CH_2, 2 x C-5), 31.8, 29.7, 29.5, 29.2, 25.6, 23.5, 22.6 (CH_2-chain), 14.0 (CH_3); IR (film) ɢ (cm^{-1}) 3447 (br), 2925, 2855, 2799, 1462, 1353, 1290, 1143, 1082, 886.[131]

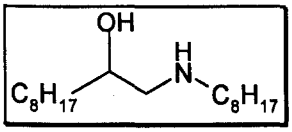


3.5

Reaction in water.

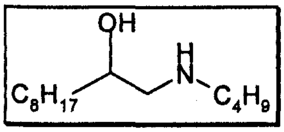
The reaction in water differed in some respects from the standard procedure: To a ice cooled mixture of 1,2-epoxydecane (0.5 g, 3.2 mmol, Aldrich) and water (0.22 cm^3) was added 1.5 equivalents of pyrrolidine (7.2 mmol). The reaction mixture was shaken and then left to stand for 16 hours at room temperature. Evaporation of the water and excess amine gave 1-(pyrrolidin-1-yl)-decan-2-ol (0.63 g, 85.9%) after vacuum distillation. The MS and NMR data were similar to those shown for **3.5** above.

Preparation of 1-(N-octylamino)-decan-2-ol.



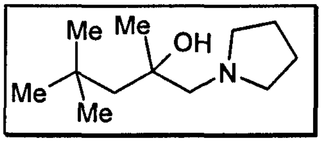
To a solution of 1,2-epoxydecane (0.87 g, 5.60 mmol, Aldrich) in ethanol (25 cm^3) was added 1.5 equivalents of octylamine (1.1 g, 8.50 mmol). After refluxing the solution for 16 h the solvent and excess amine was removed under reduced pressure. The crude product was a white solid (melting point 71-73 °C), which was identified as 1-(N-octylamino)-decan-2-ol (81.2%) by NMR and mass spectroscopy. A similar yield was found for the reaction in water. As in the case of 1-(pyrrolidin-1-yl)-decan-2-ol (**3.5**) both solvents resulted in exclusive formation of the amino-alcohol, 1-(N-octylamino)-decan-2-ol: MS (CI, NH_3) $C_{18}H_{39}NO$ *m/z* 286 (MH+, 100%), 142 (MH - $C_8H_{18}CH(OH)$, 12); NMR $\delta_H(CDCl_3)$ 3.55-3.49 (m, 1H, CH(OH)), 2.65 (dd, 1H, *J* 3.0 and *J* 12.0, -(OH)CH$C\underline{H_2}$NHR), 2.54 (apparent ddt, 2H, *J* 7.0, *J* 11.5 and *J* 21.5, $CH_3(CH_2)_7C\underline{H_2}NH$), 2.36 (dd, 1H, *J* 9.5 and *J* 12.0, -(OH)CH$C\underline{H_2}$NHR), 2.3-2.1 (br s, 1H, OH), 1.43-1.21 (br s, 26H, CH_2), 0.82 (t, 6H, *J* 6.5, 2 x CH_3); δ_C ($CDCl_3$) 69.4 (CH, CH(OH)), 55.3 (CH_2, -CH(OH)-$\underline{CH_2}$-NH-), 49.7 (CH_2, -CH_2-$\underline{CH_2}$-NH-), 35.1, 31.9, 31.8, 30.2, 29.8, 29.6, 29.5, 29.3, 27.3, 25.7 (CH_2-chain), 14.1 (CH_3, 2 x CH_3).

Preparation of 1-(N-butylamino)-decan-2-ol.



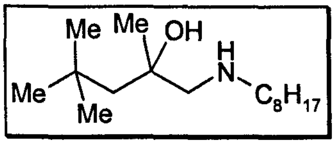
To a ice cooled solution of 1,2 epoxyoctane (0.50 g, 3.2 mmol, Aldrich) in water (0.22 cm^3) was added 1.5 equivalents of butylamine (0.35 g, 4.8mmol). This mixture was allowed to stand at room temperature for 16 h then the solvent and excess butylamine were removed under reduced pressure to give 1-(N-butylamino)-octan-2-ol (0.73 g, 84.0%) as a white crystalline solid (melting point 60-64 °C). The crude product was identified by MS and NMR: MS (EI) $C_{14}H_{31}NO$ *m/z* 229 (M+, 2%), 186 (M – C_3H_7, 12), 116 (M – C_8H_{17}, 12), 87 ($C_5H_{13}N$+, 100), 86 ($C_5H_{12}N$+, 58); NMR δ_H($CDCl_3$) 3.57-3.48 (m, 1H, -CH(OH)), 2.65 (dd, 1H, *J* 3.0 and *J* 12.0, -(HO)CHC$\underline{H}_2$NHR-), 2.55 (apparent ddt, 1H, *J* 7.0, *J* 12.0 and *J* 22.0, $CH_3(CH_2)_3C\underline{H}_2NH$), 2.36 (dd, 1H, *J* 9.5 and *J* 12.0, (HO)CHC$\underline{H}_2$-NHR-), 1.46-1.21 (m, 20H, CH_2), 0.85 (t, 3H, *J* 7.0, CH_3), 0.81 (t, 3H, *J* 6.5, CH_3); δ_C ($CDCl_3$) 69.3 (CH, CH(OH)), 55.3 (CH_2, CH-$\underline{CH_2}$-NH), 49.3 (CH_2, -CH_2-$\underline{CH_2}$-NH-), 35.1 , 32.2, 31.8, 29.7, 29.5, 29.2, 25.7, 22.6, 20.3 (CH_2, CH_2-chain), 14.1 (CH_3), 13.9 (CH_3).

Preparation of 1-(pyrrolidin-1-yl)-2,4,4-trimethylpentan-2-ol (3.6).



To a solution of 1,2-epoxy-2,4,4-trimethylpentane (**3.3**, 0.25 g, 2.0 mmol) in ethanol (15 cm^3) was added 1.5 equivalents of pyrrolidine (0.2 g, 0.25 cm^3, 2.8 mmol). After refluxing this solution for 16 h the solvent and excess pyrrolidine were removed under reduced pressure. The crude product was purified by bulb-to-bulb vacuum distillation to give 1-(pyrrolidin-1-yl)-2,4,4-trimethylpentan-2-ol (**3.6**, 0.24 g, 85%) as a pale yellow oil: MS (EI) $C_{12}H_{25}NO$ *m/z* 199 (M+, 0.2%), 184 (M+ – CH_3, 2), 166 (M+ – CH_5O, 1), 128 (M+ – C_4H_9N, 12), 84 (M+ – $C_7H_{15}O$, 100), 57 (C_4H_9+, 7), 42 (C_3H_6+, 10); NMR δ_H($CDCl_3$) 3.39 (s, 1H, OH), 2.65-2.56 (m, 4H, $N(C\underline{H}_2CH_2)_2$), 2.50 (d, 1H, *J* 1.5, qC-C$\underline{H}_2$-N), 2.40 (d, 1H, *J* 1.5, qC-C$\underline{H}_2$-N), 1.68-1.63 (m, 4H, $N(CH_2C\underline{H}_2)_2$), 1.50 (d, 1H, *J* 14.5, tBu-C$\underline{H}_2$), 1.36 (d, 1H, *J* 14.5, tBu-C$\underline{H}_2$), 1.24 (s, 3H, C$\underline{H}_3$-qC(OH)-), 1.02 (s, 9H, qC(C$\underline{H}_3$)$_3$); δ_C ($CDCl_3$) 72.3 (CH_2, qC-$\underline{CH_2}$-N), 68.3 (qC, q$\underline{C}$-CH_2-N), 56.8 (CH_2, 2 x CH_2N), 53.0 (CH_2, 2 x CH_2N), 31.6 (CH_3, qC($\underline{CH_3}$)$_3$), 31.5 (qC, q$\underline{C}$(CH_3)$_3$), 27.3 (CH_3, qC-$\underline{CH_3}$), 24.1 (CH_2, qC-$\underline{CH_2}$-qC).

Preparation of 1-(N-octylamino)-2,4,4-trimethylpentan-2-ol (3.7).



To a solution of 1,2-epoxy-2,4,4-trimethylpentane (**3.3**, 1.0 g, 7.8 mmol) in ethanol (15 cm^3) was added 1.5 equivalents of octylamine (1.2 g, 1.6 cm^3, 11.7 mmol). After refluxing this solution for 16 h the solvent and excess amine were removed under reduced pressure. The crude product was purified by bulb-bulb vacuum distillation to give of 1-(N-octylamino)-2,4,4-trimethylpentan-2-ol (**3.7**, 1.75 g, 88%) as a clear yellow oil: MS (EI) $C_{16}H_{35}NO$ *m/z* 258 (MH+, 36%), 186 (M+ – $(CH_3)_3CCH_2$, 19), 142 (M+ – $C_8H_{17}NHCH_2$, 100), 57 (C_4H_9+, 33), 44 (C_3H_8+, 78); NMR δ_H($CDCl_3$) 2.70-2.60 (m, 4H), 2.54 (d, 1H, *J* 12.0, qC-C$\underline{H}_2$-N), 2.47 (d, 1H, *J* 12.0, qC-C$\underline{H}_2$-N), 1.49-1.22 (m, 14H), 1.21 (s, 3H, C$\underline{H}_3$-qC(OH)-), 1.03 (s, 9H, qC(C$\underline{H}_3$)$_3$), 0.88 (t, 3H, *J* 6.5, CH_3); δ_C ($CDCl_3$) 72.0 (qC, q$\underline{C}$-CH_2-NH), 60.8 (CH_2, qC-$\underline{CH_2}$-NH), 52.4 (CH_2, NH$\underline{CH_2}CH_2$-chain), 50.7 (CH_2, NH$CH_2\underline{CH_2}$-chain), 42.3, 33.9, 31.8 (CH_2-chain), 31.6 (CH_3, qC($\underline{CH_3}$)$_3$), 31.2 (qC, q$\underline{C}$(CH_3)$_3$), 29.4, 29.3 (CH_2-chain), 26.6 (CH_3, qC($\underline{CH_3}$)(OH)), 22.6 (CH_2, qC-$\underline{CH_2}$-qC), 14.1 (CH_3, $\underline{CH_3}$(CH_2-chain)).

3.3 Attempted preparation of diamines.

Reaction of 1-(pyrrolidin-1-yl)-decan-2-ol (3.5).

In a typical procedure, under nitrogen 1-(pyrrolidin-1-yl)-decan-2-ol (**3.5**)(0.7 g, 3.1 mmol) was dissolved in ether (20 cm^3), 3 equivalents of triethylamine (1.30 cm^3) was added and the solution was cooled to 0 °C. Then, 1.2 equivalents of methanesulfonyl chloride (0.29 cm^3) was added dropwise. A white precipitate formed which made stirring difficult and after 30 minutes a further 2 equivalents of triethylamine (0.86 cm^3) was added. After being allowed to warm to room temperature, the 40% aqueous methylamine solution (17 equivalents, 4.6 cm^3) was added and the resulting two phase reaction mixture was vigorously stirred for 16 h. The layers were separated and the light brown organic layer was extracted with ether. The combined organics were washed with 5% sodium bicarbonate solution (20 cm^3) and water (20 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure to give the crude product as a yellow oil (0.52 g, 55.8%). The sole product of the reaction was identified as 1-(pyrrolidin-1-yl)-2-decan-2-yl methanesulfonate (**3.9**): NMR $\delta_H(CDCl_3)$ 2.63-2.43 (m, 5H), 2.39 (s, 3H, CH_3-(SO_2)O-), 1.79-1.60 (brs, 4H, 2 x N($CH_2\underline{H_2}$)$_2$), 1.36-1.10 (brs, 14H), 0.83 (t, 3H, *J* 6.6, CH_3); δ_C ($CDCl_3$) 61.5 (CH, CH(OMs)), 53.3 (CH_2), 49.6 (CH_2), 36.7 (CH_3), 31.8, 30.0, 29.6, 29.3, 28.5, 26.6, 23.4, 22.6 (CH_2-chain), 14.0 (CH_3).

Reaction of 1-(pyrrolidin-1-yl)-2,4,4-trimethylpentan-2-ol (3.6).

1-(Pyrrolidin-1-yl)-2,4,4-trimethylpentan-2-ol (**3.6**)(0.08 g, 0.4 mmol) dissolved in 10 cm^3 dry ether under nitrogen atmosphere at 0 °C. To this stirred solution was added 1.2 equivalents of methanesulfonyl chloride (0.04 cm^3) dropwise and 3 equivalents of triethylamine (0.45 cm^3). This solution was allowed to warm to room temperature and 3 equivalents of methylamine (40% aqueous solution, 0.1 cm^3) were added. The resulting two phase mixture was vigorously stirred for 16 h. The layers were separated and the light brown organic layer diluted with ether. The combined organics were washed with 5% sodium bicarbonate solution (20 cm^3) and water (20 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure to give the starting material: NMR $\delta_H(CDCl_3)$ 3.39 (s, 1H, OH), 2.65-2.56 (m, 4H, N($C\underline{H_2}CH_2$)$_2$), 2.50 (d, 1H, *J* 1.5, qC-$C\underline{H_2}$-N), 2.40 (d, 1H, *J* 1.5, qC-$C\underline{H_2}$-N), 1.68-1.63 (m, 4H, N($CH_2C\underline{H_2}$)$_2$), 1.50 (d, 1H, *J* 14.5, tBu-CH_2), 1.36 (d, 1H, *J* 14.5, tBu-CH_2), 1.24 (s, 3H, $C\underline{H_3}$-qC(OH)-), 1.02 (s, 9H, qC($C\underline{H_3}$)$_3$).

3.4 Attempted preparation of aziridines.

Reaction of 1-(N-octylamino)-decan-2-ol.

Under nitrogen, 1-(N-octylamino)-decan-2-ol (0.13 g, 0.35 mmol) and 4 equivalents of freshly crushed KOH were dissolved in 10 cm^3 of ether. After adding 1.2 equivalents of methanesulfonyl chloride (0.04 cm^3) dropwise a white precipitate forms and the stirred solution was refluxed for 4 h. The reaction mixture was poured into a separating funnel filled with crushed ice. The organic phase was separated and washed with brine (20 cm^3), then water (20 cm^3), dried with $MgSO_4$ and the solvent was removed under reduced pressure to give a yellow oil. The crude product was purified by vacuum distillation to yield 1-(N-octylamino)-decan-2-yl methanesulfonate (**3.10**) (0.11 g, 67.5%) as a clear colourless oil: MS (EI) $C_{19}H_{41}NO_3S$ *m/z* 364 (MH+, 1%), 284 (M+ – SO_2CH_3, 5), 142 (M+ – SO_2CH_3 - $C_9H_{20}N$, 100); NMR δ_H($CDCl_3$) 3.80-3.69 (m, 1H, -C$\underline{H}$(OSO_2Me)), 3.26-3.10 (m, 2H), 3.04 (dd, 1H, *J* 3.0 and *J* 15.0), 2.83 (s, 3H, -CH($OSO_2\underline{Me}$)), 1.64-1.20 (brs, 28H), 0.81 (t, 6H, *J* 6.7, 2 × CH_3); δ_C ($CDCl_3$) 69.9 (CH, CH(OMs)), 54.2 (CH_2), 49.3 (CH_2), 37.9 (CH_3), 34.8, 31.8, 29.5, 29.1, 28.5, 26.6, 25.4, 22.6 (CH_2, CH_2-chain), 14.0 (CH_3, 2 × CH_3).

Reaction of 1-(N-octylamino)-2,4,4-trimethylpentan-2-ol (3.7).

Under nitrogen, 1-(N-octylamino)-2,4,4-trimethylpentan-2-ol (**3.7**) (0.5 g, 1.95 mmol) and 4 equivalents of freshly crushed KOH (0.44 g) were dissolved in 10 cm^3 of ether. After adding 1.2 equivalents of methanesulfonyl chloride (0.18 cm^3) dropwise a white precipitate forms and the stirred solution was refluxed for 4 h. The reaction mixture was poured into a separating funnel filled with crushed ice. The organic phase was separated and washed with brine (20 cm^3), then water (20 cm^3), dried with $MgSO_4$ and the solvent was removed under reduced pressure to give a yellow oil. The crude product was purified by vacuum distillation to yield 0.29g of 1-(N-octylamino)-methyl-nonyl methanesulfonate (**3.11**, percentage yield = 42.7%) as a clear colourless oil: NMR δ_H($CDCl_3$) 3.74-3.68 (m, 1H), 3.29 (s, 3H, CH_3-(SO_2)O-), 2.95 (d, 2H, *J* 8.0, qC-C$\underline{H}_2$-N), 1.67-1.27 (m, 20H), 1.06 (s, 9H, qC(C$\underline{H}_3$)$_3$), 0.88 (t, 3H, *J* 6.5, CH_3); δ_C ($CDCl_3$) 74.9 (qC, q$\underline{C}$-CH_2-NH), 59.0 (CH_2, qC-$\underline{CH_2}$-NH), 52.1 (CH_2), 51.2 (CH_2), 49.0 (CH_2), 43.2 (CH_2), 43.7 (CH_3), 31.6 (CH_3, qC($\underline{CH_3}$)$_3$), 31.2 (qC, q$\underline{C}$(CH_3)$_3$), 29.1 (CH_2), 28.9 (CH_2), 26.0 (CH_3, qC($\underline{CH_3}$)(OH)), 22.5 (CH_2, qC-$\underline{CH_2}$-qC), 14.0 (CH_3, CH_3).

6.4. Ene-reactions Between Maleic Anhydride and the Model Alkenes

This section details the experiments procedures relevent to the work outlined in chapter 4. Analysis of the products and reaction mixtures were performed, where relevent, by ^{1}H and ^{13}C NMR, MS (EI and CI) and IR as detailed in section 6.1.2. GC/MS experiments were performed using an ZB50 column (temperature program; initial temperature of 100 °C for 2 minutes followed by ramping at 8 °C/min to 290 °C). All high temperature experiments employing volatile components were performed in a steel autoclave, which was washed with acetone and dried thoroughly prior to use.

Preparation of *cis*- and *trans*-octadecenyl succinic anhydride.

In a standard procedure a flange flask, equipped with a condenser and an overhead stirrer, was charged with the required quantities of 1-octadecene (200 g, 1.2 mol) and MA (from 0 to 5 cmr, 0 to 212 g). The reaction mixture was heated to 200 °C with stirring. After refluxing for 6h the temperature is raised to 205 °C and the unreacted MA stripped under reduced pressure (~ 5 mm Hg) for an hour. The reaction mixture was then allowed to cool to 180 °C under vacuum. A note was made of the weight of unreacted MA distilled from the reaction system. The crude reaction mixture was then filtered through a celite pad under vacuum to separate the insoluble by-products. An external heat source, in the form of a I.R. lamp, was used to maintain the temperature of the crude product in the funnel. Insoluble by-products are then washed with SBP-5 (light petroleum solvent) and dry in an oven at 100 °C until at constant weight. A note of the amount of insouble by-products collected is made.

The major product of the reaction between 1-octadecene and 1 molar ratio of MA has been identified from the NMR analysis of the crude reaction mixture as *cis* and *trans* octadecenyl succinic anhydride: NMR δ_H(d_6-acetone) major peaks 5.90-5.71 (m, 1H), 5.02-4.86 (m, 1H), 3.41-3.36 (m, 1H, CH), 3.15 (dd, 1H, *J* 10.0 and *J* 18.5), 2.81 (dd, 1H, *J* 6.0 and *J* 18.5), 2.61-2.45 (m, 2H, CH_2), 1.41-1.28 (brs, 28H,

CH_3-($C\underline{H}_2$)$_{14}$), 0.87 (t, 3H, *J* 6.7, $C\underline{H}_3$-(CH_2)$_{14}$) separable minor peaks (ratio major:minor from alkenic resonances is 1.1:1) δ 5.51-5.32 (m, 1H), 5.70-5.52 (m, 1H); δ_C(d_6-acetone) 173.3 (qC, CO_2H), 170.1 (qC, CO_2H), 137.0 (qC, *trans*-C=), 135.7 (CH, *cis*-C=), 122.8 (CH_2, *trans*-C=), 122.1 (qC, *cis*-C=), 40.5 (CH), 33.8-22.6 (17 × CH_2), 14.1 (CH_3).

Preparation of diisobutylene succinic anhydride (4.1 and 4.2).

2,4,4-Trimethyl-1-pentene (2.0 g, 19.7 mmol) and maleic anhydride (2.3 g, 1.3 mmol) were reacted in an autoclave at 200 °C for 4 h, final pressure 2 atm. The contents of the autoclave were extracted with acetone (AR grade) and evaporated to yield a thick orange-brown oil, 3.7 g. Analysis of the reaction products have been carried out using NMR (^{1}H and ^{13}C) and GC/MS (LR and HR EI MS) techniques. Bulb to bulb distillation at reduced pressure (< 1 mm Hg) has been employed in an attempt to separate the reaction products.

GC/MS analysis of the methylated resin obtained after separation of the more volatile products from the reaction mixture by distillation gives the following results:

Peaks A to C, three peaks with virtually identical mass spectra: Combined relative peak areas 6%; $C_{14}H_{24}O_4$ *m/z* 256 (M+, 0.2 %), 224 (M – HOMe, 10), 200 (M – C_4H_8, 5.6), 168 (M – C_4H_8 – MeOH, 65), 109 (M – C_4H_9 – OMe – C(O)OMe, 43), 57 (C_4H_9+, 100), 41 (C_3H_5+, 34). EI (HR) Found 256.1681 $C_{14}H_{24}O_4$ calculated mass 256.1675, HR of fragments also calculated.

Peaks D to E, two peaks with virtually identical mass spectra: Combined relative peak areas 26%; $C_{13}H_{22}O_4$ *m/z* 243 (MH+, 0.4 %), 211 (M – OMe, 2), 171 (M – C_5H_{11}, 100), 111 (M – C_5H_{11} – HOMe – CO, 33), 57 (C_4H_9+, 53), 41 (C_3H_5+, 57). EI (HR) of major fragment Found 171.0689 $C_{13}H_{22}O_4$ calculated mass 171.0657.

Peak F: Relative peak area 6%; $C_{13}H_{20}O_3$ *m/z* 224 (M+, 2 %), 209 (M – CH_3, 6.7), 193 (M – OMe, 4), 168 (M – C_4H_8, 40), 109 (M – C_4H_8 – C(O)OMe, 100), 57 (C_4H_9+, 79), 41 (C_3H_5+, 23). EI (HR) Found 224.1396 $C_{13}H_{20}O_3$ calculated mass 224.1412, HR of fragments also calculated.

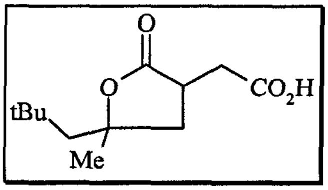
Peaks G to K, five peaks with virtually identical mass spectra: Combined relative peak areas 62%; $C_{19}H_{28}O_7$ *m/z* 368 (M+, 17 %), 337 (M – OMe, 17), 312 (M – C_4H_8, 31), 280 (M – C_4H_8 – HOMe, 41), 252 (M – C_4H_8 – HOMe – CO, 28), 220 (M – C_4H_8 – HOMe – CO – HOMe, 65), 188 (22), 160 (25), 105 (22), 57 (C_4H_9+, 100), 41 (C_3H_5+, 35). EI (HR) Found 368.1890 $C_{19}H_{28}O_7$ calculated mass 368.1835 (– 14.9 p.p.m.), HR of fragments also calculated.

6.4.1 Preparation of compounds from DIBSA.

Preparation of diisobutylene succinic acid (4.5 and 4.6).

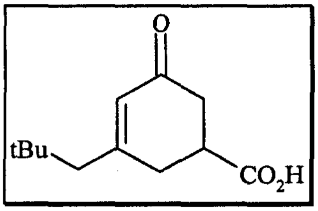
Hydrolysis of diisobutylenyl succinic anhydride was carried out by standing the anhydride in distilled water for 2 days. The water was removed to give a white solid in near to quantitative yield. This solid was identified as diisobutylene succinic acid with melting point 100-102 °C, a mixture of isomers relative percentages of each were 83.5% and 16.5% respectively: MS (EI) $C_{12}H_{20}O_4$ *m/z* 228 (M+, 0.5%), 210 (M – H_2O, 1), 195 (7), 154 (9), 128 (9), 109 (12), 97 (65), 57 (C_4H_9+, 100), 41 (C_3H_6+, 35); dimethyl ester derivative $C_{14}H_{24}O_4$ *m/z* 256 (M+, 1%), 224 (M – HOMe, 9), 200 (M – C_4H_8, 6), 168 (M – C_4H_8 – MeOH, 50), 109 (M – C_4H_9 – OMe – C(O)OMe, 32), 57 (C_4H_9+, 100), 41 (C_3H_5+, 52); NMR δ_H(d_6-acetone) major peaks 4.95 (m, 1H), 4.81 (m, 1H), 3.00 (m, 1H, CH), 2.62 (dd, 1H, *J* 9.0 and *J* 14.5), 2.47 (dd, 1H, *J* 5.0 and *J* 17.0), 2.26 (dd, 1H, *J* 8.5 and *J* 14.5), 1.99 (s, 2H, tBu-CH_2), 1.74 (dd, 1H, *J* 1.0 and *J* 15.5), 0.94 (s, 9H, tBu) separatable minor peaks δ 5.25 (m, 1H), 1.09 (s, 9H, tBu); δ_C(d_6-acetone) major peaks 176.4 (qC, CO_2H), 173.5 (qC, CO_2H), 145.5 (qC, C=), 115.9 (CH_2, C=), 49.2 (CH_2), 40.7 (CH_2), 40.4 (CH), 35.5 (CH_2), 31.9 (qC), 30.1 (CH_3) separable minor peaks 138.9 (CH, C=), 132.0 (qC, C=).

Preparation of 5-methyl-5-(2,2-dimethylpropyl-2-oxo-tetrahydro-furan-3-yl)-acetic acid (4.10).



Diisobutylene succinic anhydride (0.5 g, 2.3 mmol) was dissolved in 20 cm^3 of a 1:1 mixture of concentrated hydrochloric acid and distilled water and heated to reflux. The solution was maintained at reflux overnight. After cooling the water was removed under reduced pressure and the residue taken up in acteone. Filtration and concentration afforded a white solid (98%), melting point 97.0-99.0 °C. This has been identified as 5-methyl-5-(2,2-dimethylpropyl-2-oxo-tetrahydro-furan-3-yl)-acetic acid (**4.10**): MS (EI) methyl ester $C_{13}H_{22}O_4$ *m/z* 242 (M+, 6%), 227 (M – CH_3, 4), 211 (M – OMe, 3), 171 (M – C_5H_{11}, 100), 143 (M – $C_6H_{11}O$, 47), 111 (27), 84 (43), 57 (C_4H_9+, 73), 43 (C_3H_7+, 65); NMR δ_H(d_6-acetone) 3.25 (m, 1H, CH_2-$\underline{CH}$-CH_2), 2.68 (ddd, 1H, *J* 6.0, *J* 8.5 and *J* 17.0, qC-$\underline{CH_2}$-CH), 2.56 (ddd, 1H, *J* 9.5, *J* 12.5 and *J* 17.5, qC-$\underline{CH_2}$-CH), 2.91 (dd, 1H, *J* 1.0 and *J* 17.0, $\underline{CH_2}$-CO_2-), 2.89 (dd, 1H, *J* 1.0 and *J* 17.0, $\underline{CH_2}$-CO_2-), 2.14-1.80 (2H, t-Bu-$\underline{CH_2}$), 1.63 (d, 3H, *J* 15.0, CH_3-qC), 1.15 (s, 9H, t-Bu); δ_C(d_6-acetone) 177.6 (qC, qC$(O)_2$), 172.8 (qC, qC$(O)_2$), 85.9 (qC, qC-Me), 85.7 (qC, qC-Me), 55.3 (CH_2, t-Bu-$\underline{CH_2}$), 52.5 (CH_2, t-Bu-$\underline{CH_2}$), 43.7 (CH_2), 42.9 (CH_2), 37.8 (CH), 37.3 (CH), 35.0 (CH_2), 34.9 (CH_2), 32.0 (qC, q$\underline{C}(CH_3)_3$), 31.8 (CH_3, qC$(\underline{CH_3})_3$), 28.8 (CH_3). IR ($CHCl_3$) ν (cm^{-1}) 2959 (s), 1757 (vs, C=O stretch for 5-membered cyclic lactone), 1714 (vs, C=O stretch for carboxylic acid), 1283 (m), 1246 (m), 1181 (m), 741 (w).

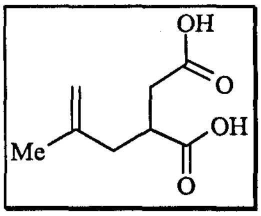
Preparation of 3-(2,2-dimethylpropyl)-5-oxo-cyclohex-3-ene carboxylic acid (4.14).



Diisobutylene succinic anhydride (1.2 g, 5 mmol) was dissolved in (10 cm^3) ethylene dichloride under nitrogen and the solution cooled to 0 °C. To this solution, at 0 °C, was added $AlCl_3$ (1 equivalent, 0.7 g, mw 133.4) over 1.5 h. The resulting creamy white complex was allowed to warm to room temperature and then stirred under nitrogen for a further 16 h. The crude reaction mixture was washed with water and potassium carbonate solution (10% aqueous solution). This was then acidified with HCl, the organic products were extracted with ether and concentrated under reduced pressure to give the crude product, a dark yellow oil (1.2 g). Fractional distillation gave the enone as a yellow solid, 0.15 g of 3-(2,2-dimethylpropyl)-5-oxo-cyclohex-3-ene carboxylic acid (**4.14**, Percentage yield = 13%), melting point 94.0-96.0 °C: MS (EI) for dimethyl ester derivative $C_{13}H_{20}O_3$ *m/z* 224 (M+, 3%), 209 (M – CH_3, 12), 193 (M – OCH_3, 7), 168 (M – C_4H_8, 13), 109 (M – C_4H_8 – $C(O)OCH_3$, 100), 57 (C_4H_9+, 97), 41 (C_3H_5+, 30); NMR δ_H(d_6-acetone) 8.8-8.6 (brs, COOH), 5.92 (s, 1H, CH=), 3.20-2.35 (m, 5H), 2.19 (s, 2H, tBu-C$\underline{H}_2$), 0.98 (s, 3H, (C$\underline{H}_3$)$_3$); δ_C(d_6-acetone) 197.5 (qC, C=O), 177.8 (qC, CO_2H), 162.8 (qC, -CH=$\underline{\text{qC}}$-), 128.7 (CH, -$\underline{\text{CH}}$=qC-), 51.8 (CH_2), 39.8 (CH), 38.4 (CH_2), 34.1 (CH_2), 32.4 (qC), 29.9 ((CH_3)$_3$); IR (film) ν (cm^{-1}) 2961 (s), 1711 (vs, C=O stretch for carboxylic acid), 1666 (s, six membered αβ-unsaturated ketone), 1433 (w), 1367 (w), 1279 (m), 1252 (m), 726 (w); UV-Vis (acetonitrile) λ_{MAX} 245 nm (log ϵ = 3.24).

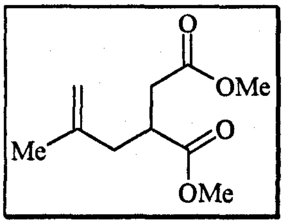
6.4.2 Preparation of compounds from isobutylene succinic anhydride.

Preparation of isobutylene succinic acid.



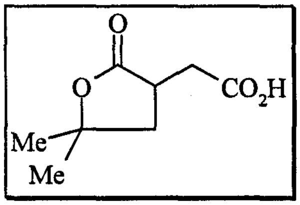
2.0 g of isobutylene succinic anhydride (13.0 mmol) stirred in 5 cm^3 of distilled water. The water was allowed to evaporate slowly to give isobutylene succinic acid as a white crystalline solid (2.2 g, percentage yield 98.2%) with melting point 122.4-124.0 °C (Lit[88] m.p. 127-128 °C solvent acetonitrile), isobutylene succinic acid: MS (EI) $C_8H_{12}O_4$ *m/z* 154 (M – H_2O, 17%), 136 (10), 126 (51), 109 (60), 81 (86), 67 (C_5H_7+, 68), 55 (C_4H_7+, 68), 39 (C_3H_3+, 100); NMR δ_H(d_6-acetone) 4.79 (brs, 1H, CH_2=), 4.75 (brs, 1H, CH_2=), 2.98 (dddd, 1H, *J* 5.0, *J* 6.0, *J* 8.5 and *J* 9.0, CH_2-C<u>H</u>-CH_2), 2.61 (dd, 1H, *J* 9.0 and *J* 17.0, -C<u>H</u>$_2$CH-), 2.47-2.39 (m, 2H), 2.23 (apparent ddd, 1H, *J* 1.0, *J* 8.5 and *J* 14.0, -C<u>H</u>$_2$CH-), 1.71 (brs, 3H, CH_3); δ_C (d_6-acetone) 176.0 (qC, CO_2H), 173.4 (qC, CO_2H), 143.4 (qC, qC=), 113.4 (CH_2, CH_2=), 40.7 (CH_2), 39.8 (CH), 35.3 (CH_2), 21.9 (CH_3).

Preparation of isobutylene succinic acid dimethyl ester.



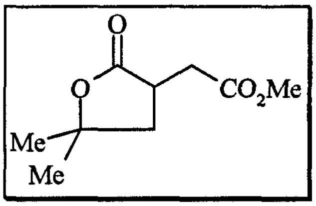
The acid above, isobutylene succinic acid, was quantitatively methylated with diazomethane as a dilute ether solution. Removal of the solvent under reduced pressure gave the dimethyl ester as a pale yellow oil, isobutylene succinic acid dimethyl ester: MS (EI) $C_{10}H_{16}O_4$ *m/z* 201 (MH+, 0.2%), 201 (M+, 0.1%), 168 (62), 140 (58), 109 (90), 95 (45), 81 (100), 55 (C_4H_7+, 42), 41 (C_3H_5+, 45); NMR δ_H(d_6-acetone) 4.78 (brs, 1H, CH_2=), 4.70 (brs, 1H, CH_2=), 3.61 (s, 3H, OMe), 3.60 (s, 3H, OMe), 2.99 (dddd, 1H, *J* 5.0, *J* 7.0, *J* 8.0 and *J* 9.0, CH_2-C<u>H</u>-CH_2), 2.60 (dd, 1H, *J* 9.0 and *J* 17.0, -C<u>H</u>$_2$CH-), 2.45 (dd, 1H, *J* 5.0 and *J* 17.0, -C<u>H</u>$_2$CH-), 2.38-2.33 (m, 1H), 2.20 (apparent ddd, 1H, *J* 0.5, *J* 8.5 and *J* 13.5, -CHC<u>H</u>$_2$-), 1.71 (brs, 3H, CH$_3$); δ_C(d$_6$-acetone) 175.2 (qC, CO$_2$Me), 172.6 (qC, CO$_2$Me), 143.3 (qC, qC=), 113.4 (CH$_2$, CH$_2$=), 51.8 (CH$_3$, OMe), 40.7 (CH$_2$), 40.1 (CH), 35.6 (CH$_2$), 21.9 (CH$_3$).

<u>Preparation of (2, 2-dimethyl-2-oxo-tetrahydro-furan-3-yl)-acetic acid (4.7).</u>



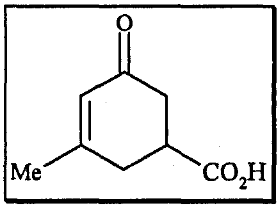
Isobutylene succinic anhydride (2 g, 13.0 mmol) was refluxed in a 1:1 solution of distilled water and concentrated HCl for 16 h. The solvent was removed under reduced pressure and the product distilled under vacuum. Solidification of the product occurred on cooling to give 1.98 g (88.8%) of (2,2-dimethyl-2-oxo-tetrahydro-furan-3-yl)-acetic acid as a white crystalline solid with melting point 135.5-138.5 °C (Lit.[108] m.p. 141-142 °C): MS (EI) $C_8H_{12}O_4$ *m/z* 173 (MH+, 0.4%), 157 (M – CH$_3$, 12), 139 (15), 129 (12), 111 (10), 97 (15), 69 (C_5H_9+, 48), 43 (C_3H_7+, 100); NMR δ_H(d$_6$-acetone) 3.17 (dddd, 1H, *J* 4.0, *J* 8.0, *J* 9.0 and *J* 12.0, CH$_2$-C<u>H</u>-CH$_2$), 2.78 (dd, 1H, *J* 4.5 and *J* 17.0, -C<u>H</u>$_2$CH-), 2.56 (dd, 1H, *J* 8.5 and *J* 17.0, -C<u>H</u>$_2$CH-), 2.38 (dd, 1H, *J* 9.0 and *J* 12.5, -C<u>H</u>$_2$CH-), 1.90 (apparent t, 1H, *J* 12.0), 1.42 (s, 3H, CH$_3$), 1.38 (s, 3H, CH$_3$); δ_C(d$_6$-acetone) 177.5 (qC, -OC(O)-), 172.8 (qC, -OC(O)-), 82.5 (qC, (Me)$_2$C(O)-), 41.2 (CH$_2$), 37.9 (CH), 34.6 (CH$_2$), 29.5 (CH$_3$), 27.0 (CH$_3$); IR (CHCl$_3$) ν (cm^{-1}) = 3070, 1762 (s, C=O stretch for 5-membered cyclic lactone), 1715 (s, C=O stretch carboxylic acid), 1288, 1136, 720.

Preparation of (2,2-dimethyl-2-oxo-tetrahydro-furan-3-yl)-acetic acid methyl ester (4.8).



The carboxylic acid group of (2,2-dimethyl-2-oxo-tetrahydro-furan-3-yl)-acetic acid (**4.7**) was methylated quantitatively with diazomethane: MS (EI) $C_9H_{14}O_4$ *m/z* 171 (M – CH_3, 34%), 151 (M – OCH_3, 34), 82 (100), 74 (31), 69 (C_5H_9+, 37), 43 (C_3H_7+, 77); NMR δ_H(d_6-acetone) 3.64 (s, 3H, OMe), 3.19 (dddd, 1H, *J* 4.5, *J* 8.0, *J* 9.0 and *J* 12.0, $CH_2\text{-}C\underline{H}\text{-}CH_2$), 2.76 (dd, 1H, *J* 4.5 and *J* 17.0, -$C\underline{H}_2CH$-), 2.56 (dd, 1H, *J* 8.5 and *J* 17.0, -$C\underline{H}_2CH$-), 2.38 (dd, 1H, *J* 9.0 and *J* 12.5, -$C\underline{H}_2CH$-), 1.91 (apparent t, 1H, *J* 12.0), 1.42 (s, 3H, CH_3), 1.38 (s, 3H, CH_3); δ_C(d_6-acetone) 177.3 (qC, -OC(O)-), 172.3 (qC, -OC(O)-), 82.6 (qC, $(Me)_2C(O)$-), 51.8 (CH_3, OMe), 41.1 (CH_2), 37.9 (CH), 34.8 (CH_2), 28.9 (CH_3), 27.0 (CH_3).

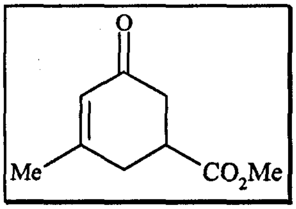
Preparation of 3-methyl-5-oxo-cyclohex-3-ene carboxylic acid (4.11).



To isobutylene succinic anhydride (6 g, 39 mmol) under nitrogen was added 39.0 cm^3 of 1 M $SnCl_4$ solution in DCM at 0 °C. Initially an off-white precipitate forms in the solution and after stirring for an hour at 0 °C the reaction mixture was warmed to room temperature, then stirred under nitrogen for a further 20 h. After this time the solution was a deep dark red colour. The reaction mixture was washed with water and dilute HCl (aqueous), the organic products were extracted with DCM and concentrated under reduced pressure to give the crude product, a dark brown solid. This solid was redissolved in aqueous HCl and extracted again with DCM, concentration. This last step was repeated followed by recrystalised of the crude product ($CHCl_3$-petroleum ether) to give 0.62 g of 3-methyl-5-oxo-cyclohex-

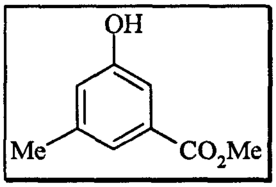
3-ene carboxylic acid as an off-white solid (**4.11**, Percentage yield = 10.3%), melting point 90.0-92.5 °C ($CHCl_3$-petroleum ether) (Lit.[110] value 91-92 °C): NMR δ_H(d_6-acetone) 5.79 (sextet, 1H, *J* 1.5, CH=), 3.10 (apparent ddt, 1H, *J* 6.0, *J* 7.5 and *J* 9.0, CH_2-C$\underline{H}$-CH_2), 2.61-2.47 (m, 4H), 1.98 (brs, 3H, CH_3); δ_C(d_6-acetone) δ 196.7 (qC, C=O), 174.7 (qC, CO_2H), 161.0 (qC, -CH=$\underline{qC}$-), 126.7 (CH, -$\underline{CH}$=qC-), 40.0 (CH), 39.3 (CH_2), 33.5 (CH_2), 24.2 (CH_3); IR (film) ɢ (cm^{-1}) = 3039 (s), 2999 (s), 1713 (vs, C=O stretch for carboxylic acid), 1667 (vs, six membered αβ-unsaturated ketone), 1435 (m), 1382 (m), 1255 (m), 734 (m); UV-Vis λ_{MAX} 245 nm.

Preparation of 3-methyl-5-oxo-cyclohex-3-ene carboxylic acid methyl ester (4.12).



3-Methyl-5-oxo-cyclohex-3-ene carboxylic acid (**4.11**) was methylated as a dilute ether solution using diazomethane. Removal of the solvent under reduced pressure gave the methyl ester derivative quantitatively as a yellow oil. This oil was identified as 3-methyl-5-oxo-cyclohex-3-ene carboxylic acid methyl ester (**4.12**): MS (EI) $C_9H_{12}O_3$ *m/z* 168 (M+, 8%), 137 (M – OCH_3, 9), 109 (M – C(O)OCH_3, 100), 82 (C_6H_{10}+, 96), 54 (C_4H_6+, 19), 39 (C_3H_3+, 38); NMR δ_H(d_6-acetone) 5.78 (sextet, 1H, *J* 1.5, CH=), 3.65 (s, 3H, OMe), 3.11 (m, 1H, CH_2-C$\underline{H}$-CH_2), 2.61-2.54 (m, 2H), 2.50-2.44 (m, 2H), 1.97 (s, 3H, CH_3); δ_C(d_6-acetone) 196.3 (qC, C=O), 174.1 (qC, CO_2Me), 160.8 (qC, -CH=$\underline{qC}$-), 126.7 (CH, -$\underline{CH}$=qC-), 52.1 (CH_3, OMe), 40.2 (CH), 39.3 (CH_2), 33.4 (CH_2), 24.1 (CH_3) IR (film) ν (cm^{-1}) = 2954 (w), 1736 (vs, C=O stretch for a methyl ester), 1669 (vs, six membered αβ-unsaturated ketone), 1633 (m), 1438 (m), 1381 (m), 1345 (w), 1274 (m), 1249 (s), 1197 (s), 1178 (m), 1048 (w).

Preparation of 3-hydroxy-5-methyl-benzoic acid methyl ester (4.13).



3-Methyl-5-oxo-cyclohex-3-ene carboxylic acid methyl ester (**4.12**, 0.2 g, 1.31 mmol) was mixed intimately with 10% palladium on activated carbon (0.05 g). The mixture was heated at 250 °C for 1.5 h, after being allowed to cool, the melt was taken up in ether, filtered (celite) and evaporated under reduced pressure. Oil titurated with hexane and the amorphous yellow solid sublimed to give 0.02 g of a white solid, 3-hydroxy-5-methyl-benzoic acid methyl ester (**4.13**, percentage yield = 9.2%), melting point 84-86 °C (diethyl ether-hexane) (Lit.[110] 90.5-91.5 °C): MS (EI) $C_9H_{10}O_3$ *m/z* 166 (M+, 53%), 135 (M – OCH_3, 100), 107 (M – C(O)OCH_3, 36), 77 (C_6H_5+, 19), 39 (C_3H_3+, 12); NMR δ_H(d_6-acetone) 8.6 (br s, 1H, phenol-OH), 7.31-7.27 (m, 2H, CH=), 6.91 (br s, 1H, CH=), 3.85-3.64 (br s, 3H, OMe), 2.30 (s, 3H, CH_3); δ_C(d_6-acetone) δ 167.2 (qC, CO_2Me), 158.2 (qC, qC=), 140.5 (qC, qC=), 132.2 (qC, qC=), 122.0 (CH, CH=), 121.4 (CH, CH=), 114.0 (CH, CH=), 52.1 (CH_3, OMe), 21.2 (CH_3); IR ($CHCl_3$) ν (cm^{-1}) = 3013 (s), 1718 (m), 1599 (w), 1438 (w), 1331 (m), 1240 (m), 729.4 (m); UV λ_{MAX} 242 nm (log ϵ = 3.54) and 301 nm (log ϵ = 3.16) (Lit.[166] 242 nm [log ϵ = 3.84] and 301 nm [log ϵ = 3.42]).

6.4.3 EPR experiments.

EPR experiments have been performed using the model systems to estabilish the presence and identity of any radical species (all the EPR data discussed in this thesis was collected by Dr Adrian Whitwood). A standard procedure was used to obtain the EPR results discussed in Chapter 4. EPR analysis was carried out on a variety of compounds after they were subjected to the standard autoclave reaction conditions (4 h at 200 °C). After allowing the autoclave to cool for 0.5 h a small amount of the crude reaction mixture was taken from the autoclave and placed in a glass cell. Analysis of the samples was performed at 100 °C to ensure that the samples remained in the liquid phase throughout the experiments. A single radical species with the same g-value (g ~ 2.0033) was observed in the product mixtures obtained from TMP-1/MA, diisobutylene succinic anhydride, maleic anhydride and 2-octenyl succinic anhydride. However, no signal was detected in the case of 2,4,4-trimethyl-1-pentene (TMP-1).

6.4.4 'Spin trap' experiments.

In the 'spin trap' experiments discussed in more detail in Chapter 4 two nitroso spin traps have been employed, 2,4,6-tribromonitrosobenzene (TBNB) and 2,2-methylnitrosopropane (NMP). These 'spin traps' were used in an attempt to identify the radical species produced from the autoclave reaction of TMP-1 with 1.3 equivalents of MA. In contrast to the previous EPR experiments (section 6.4.3) the spin trap experiments were performed at room temperature due to the thermal instability of TBNB and NMP. The spin traps were used at ~ 50 mM concentration in acetone or acetonitrile. The EPR spectra were recorded straight after the addition of the spin trap solution to the crude reaction mixture using the Bruker spectrometer.

6.5. Thermal decomposition of maleic anhydride

This section details the experiments procedures relevent to the work outlined in chapter 5. Analysis of the products and reaction mixtures were performed, where relevent, by ^1H and ^{13}C NMR, MS (EI and CI) and IR as detailed in section 6.1.2. GC/MS experiments were performed using an ZB50 column (temperature program; initial temperature of 100 °C for 2 minutes followed by ramping at 8 °C/min to 290 °C).

6.5.1 Procedure for the thermolysis of maleic anhydride and derivatives.

Thermolysis experiments were carried out in a steel autoclave system as described previously in section 6.4. In all cases, unless otherwise stated, the material to be pyrolysed was sealed in the autoclave system which was then heated to 200 °C for a period of 4 h. The reaction mixture was mixed thoroughly with the aid of a magnetic stirrer. The autoclave was left to cool to room temperature prior to opening after which the reaction mixture was extracted from the vessel with AR grade acetone. The product was recovered by removal of the solvent under reduced pressure.

The EPR experiments performed using MA were carried out by the same procedure detailed previously in section 6.4.3. MA was heated at 200 °C in the autoclave for 4 h. Samples of this reaction mixture analysed using the Bruker spectrometer with the EPR chamber thermostated at 100 °C.

GC/MS analysis of MA thermolysis at 200 °C for 4 h, reaction mixture was hydrolysed by standing in water for 24 h and methylated with diazomethane in ether solution. GC trace contains two peaks which have very similar mass spectra, differing only in the intensity of peaks: MS (EI) $C_7H_{10}O_4N_2$ *m/z* 186 (M+, 1.5%), 155 (M – OCH_3, 2.5), 127 (M – $C(O)OCH_3$, 31), 95 (M – $C(O)OCH_3$ – $HOCH_3$, 100), 59 (23), 42 (14).

6.5.2 Preparation of poly(maleic anhydride) (PMA).

The polymerisation of MA was performed at either 80 or 120 °C. The reaction time for the polymerisation was also varied between 1 to 18 h. In a standard procedure: The peroxide (2 mol %, di-t-butyl or dibenzoyl peroxide) was added over a 10 minute period to molten maleic anhydride (5 g, 51.0 mmol) at 120 °C. Almost instantaneously the clear colourless molten MA turned a black colour. After heating at 120 °C for 18 h recovery of the polymer was achieved by precipitation in toluene. The polymer was collected by filtration and dried under reduced pressure for several hours.

6.5.3 Inhibition of poly(maleic anhydride) formation.

This procedure is very similar to that described above (section 6.5.2). Reactions were performed using dibenzoyl peroxide (0.2 g, 1 mmol) as the initiator, which was added over a 10 min period to molten MA (5 g, 51.0 mmol) at 120 °C containing the additive (1 mmol). Two additives were used for these experiments; dimethyl formamide (DMF) and ϵ-caprolactam. On addition of the initiator it was noted that the darkening of the reaction mixture, seen without the additive, occurred much more slowly. Attempted precipitation of PMA after 3 h in toluene failed to give any product.

6.5.4 Thermolysis of MA in the presence of additives.

This reaction was carried out using the standard autoclave procedure (section 6.5.1), apart from the addition of the additive (DMF or caprolactam). The autoclave was charged with MA (5 g, 51.0 mmol) and the additive (1 mmol), then the sealed system was heated at 200 °C for 4 h. After allowing the autoclave to cool for 30 mins the contents, which was a black solid, was dissolved in acetone. The polymer was precipitated from the acetone solution by addition of chloroform. Filtration of this solution gave the product as a dark brown solid, which was dried under reduced pressure.

References

1. D. Dowson, in '*The Chemistry and Technology of Lubricants*', Ed., R. M. Mortier, S. T. Orszulik, Blackie Academic and Professional, 1997, p1.
2. D. Dowson, in '*Lubricants and Lubrication in the Nineteenth Century*', 1979.
3. P. Salino and P. Volpi, *Annali di Chimica*, 1987, **77**, 145.
4. I. G. Bromilow, in '*Supply and Demand of the Lube Oil: An Update of the Global Perspective*', 1990, AM-90-27 presented at the 1990 NPRA annual meeting.
5. R. J. Prince, in '*The Chemistry and Technology of Lubricants*', Reference 1, p2-33.
6. see Lubrication Theory and Practice, and Base Stocks, at Lubrizol's website *http://www.Lubrizol.com./referencelibrary.html*
7. R. L. Stanbaugh, in '*The Chemistry and Technology of Lubricants*', Reference 1, 1997, p144-176.
8. J. Crawford, A. Psaila and S. T. Orszulik, Reference 1, p181-202.
9. C. H. Bovington, Reference 1, p320-340.
10. M. Rasberger, Reference 1, p98-140.
11. C. C. Colyer and W. C. Gergel, Reference 1, p75-95.
12. a. A. I. Meyers, B. A. Lefker, T. J. Sowin and L. J. Westrum, *J. Org. Chem.*, 1989, **54**, 4243; b. E. Walch and R. J. Gaymans, *Polymer*, 1994, **35**, 1774.
13. T. F. Braish and D. E. Fox, *Synlett*, 1992, 979.
14. A. J. Mills, C. M. Lindsay and D. J. Atkinson, Reference 1, p203-227.
15. M. Brown, J. D. Fotheringham, T. J. Hoyes, R. M. Mortier, S. T. Orszulik, S. J. Randles and P. M. Stoud, Reference 1, p34-72.
16. F. Freeman, *Chem. Rev.*, 1975, **75**, 439.
17. R. C. Fahey, *Top. Stereochem.*, 1968, **3**, 237.
18. H. O. House, in '*Modern Synthetic Reactions*', W. A. Benjamin, 1972, p479.
19. P. B. D. de la Mare, in '*Electrophilic Halogenation*', Cambridge University Press, 1976.

20. G. H. Schmid, in *Supplement A 'The Chemistry of Double-bonded Functional Groups'*, S. Patai, Wiley, New York, **2**, part 1, 1989, Ch11, p695.
21. M.-F. Ruasse, in '*Advances in Physical Organic Chemistry*', 1993, **28**, 207.
22. R. C. Fahey and C. Schubert, *J. Am. Chem. Soc.*, 1965, **87**, 5172.
23. A. W. Francis, *J. Am. Chem. Soc.*, 1925, **47**, 2340.
24. a. P. D.Bartlett and D. S. Tarbell, *J. Am. Chem. Soc.*, 1936, **58**, 466; b. D. S. Tarbell and P. D. Bartlett *J. Am. Chem. Soc.*, 1937, **59**, 407.
25. C. K. Ingold and H. G. Smith, *Chem. Rev.*, 1934, **15**, 225.
26. G. Williams, *J. Chem. Soc., Trans. Faraday*, 1941, **37**, 749.
27. A. Ogg Jr., *J. Am. Chem. Soc.*, 1935, **57**, 2727.
28. I. Roberts and G. E. Kimball, *J. Am. Chem. Soc.*, 1937, **59**, 947.
29. J. Strating, J. H. Wieringa and H. Wynberg, *J. Chem. Soc., Chem. Comm.*, 1969, 907.
30. J. H. Wieringa, J. Strating and H. Wynberg, *Tetrahedron Lett.*, 1970, **52**, 4579.
31. R. S. Brown, R. W. Nagorski, A. J. Bennet, R. E. D. McClung, G. H. Aarts, M. Klobukowski, R. McDonald and B. D. Santasiero, *J. Am. Chem. Soc.*, 1994, **116**, 2448.
32. H. Siebocka-Tilk, R. G. Ball and R. S. Brown, *J. Am. Chem. Soc.*, 1985, **107**, 4504.
33. G. A. Olah and A. M. White, *J. Am. Chem. Soc.*, 1969, **91**, 5801.
34. a. G. A. Olah and J. M. Bollinger, *J. Am. Chem. Soc.*, 1967, **89**, 4744; b. G. A. Olah and J. M. Bollinger, *J. Am. Chem. Soc.*, 1968, **90**, 947; c. G. A. Olah, C. L. Jeuell and A. M. White, *J. Am. Chem. Soc.*, 1969, **91**, 3961.
35. G. A. Olah, in '*Halonium Ions*', Wiley, 1975.
36. M. J. S. Dewar, *Bull. Soc. Chim. France*, 1951, **18**, 71.
37. D. V. Banthorpe, *Chem. Rev.*, 1970, **70**, 295.
38. G. Bellucci, C. Chiappe, R. Bianchini, D. Lenoir and R. Herges, *J. Am. Chem. Soc.*, 1995, **117**, 12001.
39. M. Cossi, M. Persico and J. Tomasi, *J. Am. Chem. Soc.*, 1994, **116**, 5373.
40. E. Kochanski, *Quantum Theory Chem. React.* 1980-1982, 1981, **2**, 177.
41. E. P. White and P. W. Robertson, *J. Chem. Soc.*, 1939, 1509.

42. M. L. Poutsma, *J. Am. Chem. Soc.*, 1965, **87**, 2161.

43. C. Reichardt, in '*Solvents and Solvent Effects in Organic Chemistry*', V.7.134.

44. J. E. Dubois and F. Garnier, *Spectrochim. Acta*, 1967, **23A**, 2279.

45. G. Bellucci, R. Bianchini and R. Ambrosetti, *J. Am. Chem. Soc.*, 1985, **107**, 2464.

46. M. L. Poutsma, *J. Org. Chem.*, 1966, **31**, 4167.

47. S. Fukuzumi and J. K. Kochi, *J. Am. Chem. Soc.*, 1981, **103**, 2783.

48. N. Amirtha and S. Viswanathan, *Bull. Chem. Soc. Jpn.*, 1983, **56**, 314.

49. G. Bellucci, R. Bianchini, C. Chiappe, D. Lenoir and A. Attar, *J. Am. Chem. Soc.*, 1995, **117**, 6243.

50. G. A. Olah and T. R. Hockswender Jr., *J. Am. Chem. Soc.*, 1974, **96**, 3574.

51. G. H. Schmid and J. W. Gordon, *Can. J. Chem.*, 1984, **62**, 2526.

52. R. Bianchini, C. Chiappe, D. Lenoir, P. Lemmen, R. Herges and J. Grunenburg, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1284.

53. R. Herges, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 51.

54. J. E. Dubois and G. Mouvier, *Tetrahedron Lett.*, 1963, **18**, 1325.

55. J. E. Dubois and F. Garnier, *J. Chem. Soc., Chem. Comm.*, 1968, 241.

56. G. Bellucci, C. Chiappe and F. Marioni, *J. Am. Chem. Soc.*, 1987, **109**, 515.

57. G. Bellucci, R. Bianchini and R. Ambrosetti, *J. Org. Chem.*, 1985, **50**, 3313.

58. M.-F. Ruasse, *Acc. Chem. Res.*, 1990, **23**, 87.

59. A. Modro, G. H. Schmid and K. Yates, *J. Org. Chem.*, 1977, **42**, 3673.

60. P. B. D. de la Mare, *Chem. Soc. Quart. Rev.*, 1949, **3**, 126.

61. M. L. Poutsma, *J. Am. Chem. Soc.*, 1965, **87**, 2172.

62. M. L. Poutsma, *J. Am. Chem. Soc.*, 1965, **87**, 4285.

63. N. J. Bythell and P. W. Robertson, *J. Chem. Soc.*, 1938, 179.

64. A. Bowers, E. Denot and R. Becerra, *J. Am. Chem. Soc.*, 1960, **82**, 4007.

65. C. K. Ingold and H. G. Smith, *J. Chem. Soc.*, 1931, 2742.

66. R. C. Cambie, W. I. Noall, G. J. Potter, P. S. Rutledge and P. D. Woodgate, *J. Chem. Soc., Perkin Trans. 1*, 1977, 226.

67. A. Hassner, F. W. Fowler and L. A. Levy, *J. Am. Chem. Soc.*, 1967, **89**, 2077.

68. A. Hassner, F. P. Boerwinkle and A. L. Levy, *J. Am. Chem. Soc.*, 1970, **92**, 4879.

69. A. Hassner and C. H. Heathcock, *Tetrahedron Lett.*, 1964, **19**, 1125.

70. G. H. Schmid and J. W. Gordon, *Can. J. Chem.*, 1986, **64**, 2171.

71. J.-E. Dubois and J. R. Chretien, *J. Am. Chem. Soc.*, 1978, **100**, 3506.

72. V. L. Heasley, D. F. Shellhamer, J. A. Iskikian and D. L. Street, *J. Org. Chem.*, 1978, **43**, 3139.

73. T. Negoro and Y. Ikeda, *Bull. Chem. Soc. Jpn.*, 1986, **59**, 2547.

74. J. S. Dewer and R. C. Fahey, *Angew. Chem.*, *Int. Ed. Engl.*, 1964, **3**, 245.

75. R. C. Fahey and H.-J. Schneider, *J. Amer. Chem. Soc.*, 1968, **90**, 4429.

76. R. C. Fahey, *J. Amer. Chem. Soc.*, 1966, **88**, 4681.

77. R. Herges and H. Neumann, *Liebigs. Ann.*, 1995, 1283.

78. P. B. D. de la Mare and A. Salama, *J. Chem. Soc.*, 1956, 3337.

79. R. W. Taft Jr., *J. Am. Chem. Soc.*, 1948, **70**, 3364.

80. E. H. Farmer, *J. Chem. Soc., Faraday Trans.*, 1942, **38**, 340.

81. J. Wolinsky, R. W. Novak and K. L. Enckson, *J. Org. Chem.*, 1969, **34**, 490.

82. H. Hopf, R. Hänel, P. G. Jones and P. Bubenitschek, *Angew. Chem.*, *Int. Ed. Engl.*, 1994, **33**, 1369.

83. J. Burgin, W. Engs, H. P. A. Groll and G. Hearne, *Ind. Eng. Chem.*, 1939, **31**, 1413.

84. W. Reeve and D. H. Chambers, *J. Am. Chem. Soc.*, 1951, **73**, 4499;
W. Reeve, D. H. Chambers and C. S. Prickett, *J. Am. Chem. Soc.*, 1952, **74**, 5369.

85. P. B. D. de la Mare, in '*Molecular Rearrangements*', Ed. P. de Mayo, Part 1, Interscience, New York, 1963, p101.

86. G. V. Boyd, in *Supplement A* '*The Chemistry of Double-bonded Functional Groups*', S. Patai, Wiley: New York, **2**, part 1, 1989, Ch. 8, p477; E. C. Keung and H. Alper, *J. Chem.Ed.*, 1972, **49**, 97; H. M. R. Hoffmann, *Angew. Chem.*, *Int. Ed. Engl.*, 1969, **8**, 556.

87. D. F. Taber, in '*Intramolecular Diels-Alder and Alder Ene Reactions*', Springer, New York, 1984, Ch. 3, p61; W. Oppolzer and V. Snieckus, *Angew. Chem.*, *Int. Ed. Engl.*, 1978, **17**, 476.

88. K. Alder, F. Pasher and A. Schmitz, *Ber*, 1943, **76**, 27; K. Alder, and S. Sohl, *Liebigs Ann.*, 1949, **67**, 565.

89. B. B. Snider, *Acc. Chem. Res.*, 1980, **13**, 426.

90. M. A. Kise and R. F. Engle, U.S. Pat. 2, 411, 215, 1946; P. J. Cahill, and A. S. Kurasiewicz, U.S. Pat. 3, 819, 660, 1974.

91. B. C. Trivedi and B. M. Culbertson, in '*Maleic Anhydride*', Plenum, New York, 1982, Ch5, p147.

92. H. Mach, *Oil Gas - European Magazine*, 1996, **2**, 38.

93. F. R. Benn, J. Dwyer and I. Chappell, *J. Chem. Soc., Perkin Trans. 2*, 1977, 533.

94. R. T. Arnold and J. F. Dowdall, *J. Am. Chem. Soc.*, 1948, **70**, 2590.

95. R. T. Arnold and J. S. Showell, *J. Am. Chem. Soc.*, 1957, **79**, 419.

96. J. A. Gladysz and Y. S. Yu, *J. Chem. Soc., Chem. Comm.*, 1978, 599.

97. B. J. Sublett and N. S. Bowman, *J. Org. Chem*, 1961, **26**, 2594.

98. R. K. Hill and M. Rabinovitz, *J. Am. Chem. Soc.*, 1964, **86**, 965.

99. C. S. Rondestvedt and B. H. Wark, *J. Org. Chem*, 1955, **20**, 368.

100. P. G. Irwin and C. M. Selwitz, U.S. Pat. 3, 412, 111, 1968.

101. M. J. S. Dewar and R. C. Dougherty, in '*The PMO Theory of organic chemistry*', Plenum press, New York, 1975, section 5.11.

102. G. Jenner and M. Popadopoulos, *J. Org. Chem.*, 1982, **47**, 4201.

103. O. Achmatowicz Jr. and J. Szymoniak, *J.Org. Chem.*, 1980, **45**, 1228.

104. R. B. Woodward and R. Hoffmann, in '*The Conseravtion of Orbital Symmetry*', Verlag Chemie, GmBH: Weinheim, 1971.

105. S. Inagaki, H. Fujimoto and K. Fukui, *J. Am. Chem. Soc.*, 1976, **98**, 4693.

106. J. A. Berson, R. G. Wall and H. D. Perlmutter, *J. Am. Chem. Soc.*, 1966, **88**, 187.

107. S. H. Nahm and H. N. Cheng, *J.Org. Chem.*, 1986, **51**, 5093.

108. D. D. Phillips and A. W. Johnson, *J. Am. Chem. Soc.*, 1955, **77**, 5977.

109. M. F. Ansell and M. H. Palmer, *Chem. Soc. Quart. Rev.*, 1964, **18**, 211.

110. D. D. Phillips and A. W. Johnson, *J.Org. Chem.*, 1956, **21**, 587.

111. P. O'Brien and P. Poumellec, *Tetrahedron Lett.*, 1996, **37**, 5619.

112. J. R. Blackborrow, in '*An Investigation into the Formation of Resin in the Thermal Maleinisation Reaction*', Grangemouth report, BP Chemicals, 1996.

113. F. W. McLafferty and F. Turecek, in '*Interpretation of Mass Spectra*', 4th Edition, University Science Books, Sausalito, California, 1993.

114. D. H. Williams and I. Fleming, in '*Spectroscopic Methods in Organic Chemistry*', 5th edition, McGraw-Hill book company, London, 1995.

115. '*Eight peak index of mass spectrum*' 2 nd edition, 1974, **1**.

116. P. B. D. de la Mare and J. H. Ridd, in '*Aromatic Substitution*', Butterworths, London, 1959.

117. Reference 116, p113.

118. Reference 19, p73.

119. a. J. Bermejo, C. G. Blanco, A. Martinez and S. R. Moinelo, *J. Chem. Soc., Perkin Trans. II*, 1984, 1993; b. E. Baciocchi and G. Illuminati, *Tetrahedron Lett.*, 1962, **15**, 637.

120. C. J. Pouchett and J. Behnke, in '*The Aldrich library of ^{13}C and ^{1}H FT NMR spectra*', Edition 1.

121. H. M. Weiss and K. M. Touchette, *J. Chem. Soc., Perkin Trans. II*, 1998, 1523.

122. J. Berthelot and M. Fournier, *J. Chem. Ed.*, 1986, **63**, 1011.

123. G. Bellucci, C. Chiappe and G. Moro, *J. Org. Chem.*, 1997, **62**, 3176.

124. in '*The Chemistry of the Carbon-halogen Bond*', S. Patai, Wiley: London, part 1, 1989, p186.

125. A. Rosowsky, in '*Heterocyclic Compounds With 3- and 4-Membered Rings*', Ed. Weissberger, Part 1, John Wiley and Sons, New York, 1964, p316.

126. J. Gorzynski-Smith, *Synthesis*, 1984, 629.

127. D. A. Evans, M. M. Faul and M. T. Bilodeau, *J. Amer. Chem Soc.*, 1994, **116**, 2742; For a review on the formation and ring-opening of aziridines see R. S. Atkinson, *Tetrahedron*, 1999, **55**, 1519.

128. R. J. Fesseden and J. S. Fesseden, in '*Organic Chemistry*', Brookes/Cole publishing, 1990, p307.

129. P. D. Bartlett, *Rec. Chem. Prog.*, 1950, **11**, 51.

130. M. Bartók, and K. L. Láng, in '*The Chemistry of Ethers, Crown Ethers, Hydroxyl Groups and Their Sulfur Analogues*', Ed., E. S. Patai, Part II, John Wiley and Son, New York, 1980, p610.

131. S. Miyano, L. D-L. Lu, S. M. Viti and K. B. Sharpless, *J. Org. Chem.*, 1985, **50**, 4350.

132. A. R. Graham, A. F. Millidge and D. P. Young, *J. Chem. Soc.*, 1954, 2180.

133. Reference 125, p528-535; N. Yahiro, *Chemistry Letters*, 1982, 1479.

134. V. C. Sekera and C. S. Marvel, *J. Am. Chem. Soc.*, 1933, **55**, 345.

135. S. Winstein and R. B. Henderson, Ed. R. C. Elderfield., *Heterocyclic Compounds*, vol 1, Wiley, New York, 1950, p1.

136. R. Tye, in '*Reduction of Colour in PIB Succinimide Dispersants*', an internal Adibis report, Apr. 1997.

137. Experimental TM 021: General procedure for the preparation of polyisobutylene succinic anhydride (PIBSA).

138. M. Tessier and E. Marechal, *Eur. Polym. J.*, 1984, **20**, 269.

139. M. E. Kuehne and W. H. Parsons, *J. Org. Chem.*, 1977, **42**, 3408.

140. A. F. Thomas and M. Lander-Schouwey, *Helv. Chim. Acta*, 1984, **67**, 191.

141. J. Fossey, D. LeFort and J. Sorba, in '*Free Radicals in Organic Chemistry*', Wiley, New York, 1995.

142. Y. Nakayama, K. Hayashi and S. Okamura, *J. Applied Polym. Sci.*, 1974, **18**, 3633.

143. E. G. Janzen, *Free Radical Res. Comms.*, 1990, No 3 to 6, 163.

144. For a review on spin trapping see M. J. Perkins, *Adv. Phys. Org. Chem.*, 1980, **7**, 1.

145. C. Chatgilialoglu and K. U. Ingold, *J. Amer. Chem Soc.*, 1981, **103**, 14833; B. C. Gilbert, J. R. Lindsay-Smith, P. MacFaul and P. Taylor, *J. Chem. Soc., Perkin Trans II*, 1996, 511.

146. R. A. Back and J. M. Parsons, *Can. J. Chem.*, 1981, **59**, 1342.

147. W. Hempel, *Z. Chem.*, 1970, **10**, 225.

148. J.-E. Souchard, F. L. Wimmer, T. T. B. Ha and N. P. Johnson, *J. Chem. Soc., Dalton Trans.*, 1990, 307.

149. B. de Roover, J. Devaux and R. Legras, *J. Polym. Sci. Part A: Polym. Chem.*, 1996, **34**, 1195.

150. A. L. Brown and P. D. Richie, *J. Chem. Soc., Chem. Comm.*, 1968, 2007.

151. B. de Roover, M. Sclavons, V. Carlier, J. Devaux, R. Legras and A. Momtaz, *J. Polym. Sci. Part A: Polym. Chem.*, 1995, **33**, 829.

152. Reference 91, Ch 7, p215-238.

153. B. Hacioglu and U. Akbulut, *J. Polym. Sci. Part A: Polym. Chem.*, 1991, **29**, 219.

154. N. G. Gaylord and R. Mehta, *J. Polym. Sci. Part A: Polym. Chem.*, 1988, **26**, 1903.

155. N. G. Gaylord and S. Maiti, *J. Polym. Sci. Part C: Polym. Lett.*, 1973, **11**, 253.

156. N. G. Gaylord and J. Koo, *J. Polym. Sci. Part C: Polym. Lett.*, 1981, **19**, 107.

157. R. Bacskai, *J. Polym. Sci. Part A: Polym. Chem.*, 1976, **14**, 1797.

158. H. P. Fritz and R. Bertelmann, *Z. Naturforsch.*, 1992, **47B**, 614.

159. D. Braun and J. Pomdkis, *Makromol. Chem.*, 1974, **175**, 1411.

160. J. A. Chamizo, G. Mendoza-Diaz and J. L. Gazquez, *Polymer*, 1981, **22**, 129.

161. H. Wurn, W. Regel and M. L. Hallensleben, *Makromol. Chem.*, 1979, **180**, 1581; H. Wurn, M. L. Hallensleben and W. Regel, *Makromol. Chem.*, 1979, **180**, 1589.

162. M. F. Mayahi and M. F. El-Bermani, *Can. J. Chem.*, 1973, **51**, 3539.

163. U. S. Sahu, *Poly. Comm.*, 1983, **24**, 61.

164. Aldrich chemical catalogue, 1999 edition.

165. A. I. Vogel, in '*Textbook of Practical Organic Chemistry*' fourth edition, Longmann, London, 1978, p921.

166. K. Clinch, C. J. Marquez, M. J. Parrott and R. Ramage, *Tetrahedron*, 1989, **45**, 239.