KINETIC STUDIES OF THE METATHESIS OF 1-HEXENE USING Re_2O_7/γ $-Al_2O_3$, AND THE SYNTHESIS AND METATHESIS OF OXAZOLINES

IDA MARCIA HOHN

A thesis submitted for the degree of

DOCTOR OF PHILOSOPHY

THE UNIVERSITY OF ASTON IN BIRMINGHAM

APRIL 1991

1

SUMMARY

The kinetics of the metathesis of 1-hexene using Re$_2$O$_7$/γ-Al$_2$O$_3$ as the catalyst was investigated under a variety of conditions. The experiments were carried out under high vacuum conditions. The product solutions were characterised by gas liquid chromatography and mass spectroscopy.

The initial kinetics of the metathesis of 1-hexene showed that the reaction was first order in the weight of the catalyst and second order in the concentration of 1-hexene. A kinetic scheme which correlated the experimental data with the metallocarbene chain mechanism postulated by Herisson and Chauvin and the kinetics of the reaction was explained using a model based on the Langmuir-Hinshelwood theory. The low conversion of 1-hexene to its products is due to termination reactions which most likely occur by the decomposition of the metallocyclobutane intermediate to produce a cyclopropane derivative and an inactive centre. The optimum temperature for the metathesis of 1-hexene over Re$_2$O$_7$/γ-Al$_2$O$_3$ is 45°C and above this temperature, the rate of metathesis decreases rapidly. Co-catalysts alter the active sites for metathesis so that the catalyst is more selective to the metathesis of 1-hexene. However, the regeneration of metathesis activity is much worse for promoted catalysts than for the unpromoted.

The synthesis and metathesis of 4,4-dimethyl-2-(9-decenyl)-1,3-oxazoline and 4,4-dimethyl-2-(3-pentenyl)-1,3-oxazoline was attempted and the products were analysed by thin layer chromatography, infra-red, ^{13}C and ^{1}H nmr and mass spectroscopy. Obtaining the oxazolines in a good yield with high purity was difficult and consequently metathesis of the impure products did not occur.

KEYWORDS: METATHESIS, 1-HEXENE, KINETICS, Re$_2$O$_7$/γ-Al$_2$O$_3$, OXAZOLINES.

To my parents

3

ACKNOWLEDGEMENT

First of all I would like to sincerely thank Dr Allan J. Amass for allowing me to do this research project under his supervision. His support, patience (which I reckon is threadbare by now!) and his constant urge for me to propagate (experimentally) has taught me that if you want to achieve anything, you must work towards it. I would also like to express my thanks to B.P. Chemicals in Hull for their monetary support. I am also grateful to the University of Aston for allowing me to use its facilities.

The completion of the experimental work in this project would not have been possible without the help of all the technical staff in and outside the Department of Chemistry. Particular thanks go to Alex Stuart for my 'Christmas Tree', Stan Stan, The Storeroom Man for my constant supply of yellow gloves, Steve Ludlow for always being by the phone, and Mike and Denise, . for letting me loose on the glc machine for three consecutive years. Thanks guys!

I would also like to extend my thanks and appreciation to my fellow colleagues (Hi guys!) but most particularly to Davinder 'Sikhman' Riat. For two years it was just him and I, alone in Lab 362, doing our thing and I will always remember those times.

I would also like to express my appreciation to my family, particularly my mother, and my brothers, Andy and Andrew. Where would I be without them? I would like to simply thank them for the decades they have spent putting up with me, for being towers of strength, for teaching me to believe in myself and to never give up. I would like to thank my late father for teaching me to always try to be the best that I can.

Lastly, I would like to thank my Heavenly Father for blessing me with the attributes which I needed to complete this mammoth task.

Thank you everybody!

LIST OF CONTENTS

CHAPTER 2: EXPERIMENTAL

CHAPTER 3: THE KINETICS OF THE METATHESIS OF 1-HEXENE USING RHENIUM OXIDE ON γ - ALUMINA AS THE CATALYST

CHAPTER 7   CONCLUSIONS AND FURTHER WORK

REFERENCES   194

LIST OF FIGURES

LIST OF SCHEMES

LIST OF TABLES

CHAPTER ONE: INTRODUCTION

1.1 General description of olefin metathesis

The field of olefin metathesis has been very active since it came to the notice of the scientific community as a new major chemical reaction in 1964[1]. Since then it has developed rapidly and its applications include ring opening polymerization of cyclic olefins to produce polyolefins, and the metathesis of acyclic olefins.

The metathesis reaction can be represented by the following general equation:

$$2R^1CH{=}CHR^2 \rightleftharpoons R^1CH{=}CHR^1 + R^2CH{=}CHR^2$$

In general, olefin metathesis involves the interchange of carbon atoms between a pair of double bonds and it can be divided into three categories[2]:

(i) olefin metathesis (exchange),

$$2CH_2{=}CHCH_3 \rightleftharpoons CH_2{=}CH_2 + CH_3CH{=}CHCH_3$$

The alkylidene units between the two substrate olefins are exchanged to produce two product olefins. Acyclic olefins undergo this reaction in the presence of a catalyst system.

(ii) ring opening metathesis polymerization,

$$n \; \text{(cyclopentene)} \rightleftharpoons [{=}CHCH_2CH_2CH_2CH{=}]_n$$
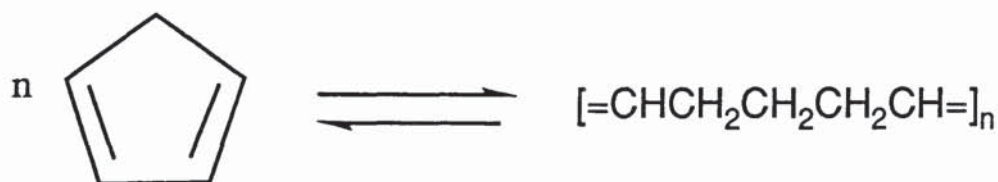
The internal double bonds of, for example cyclopentene, undergo cleavage to produce an acyclic polymer. Bicyclic compounds, for example norbornene, also undergo bond cleavage to a polymer with in-chain cyclopentane rings where the carbon carbon bonds are *cis* to one another in the ring,

17
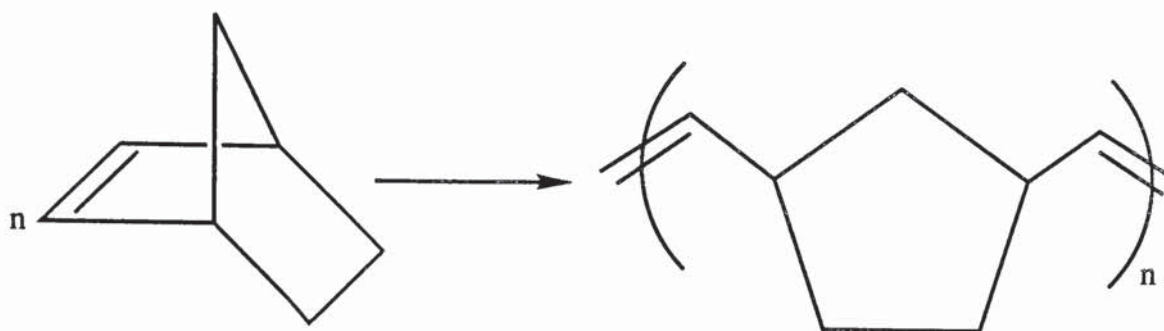
and (iii) degradation metathesis.
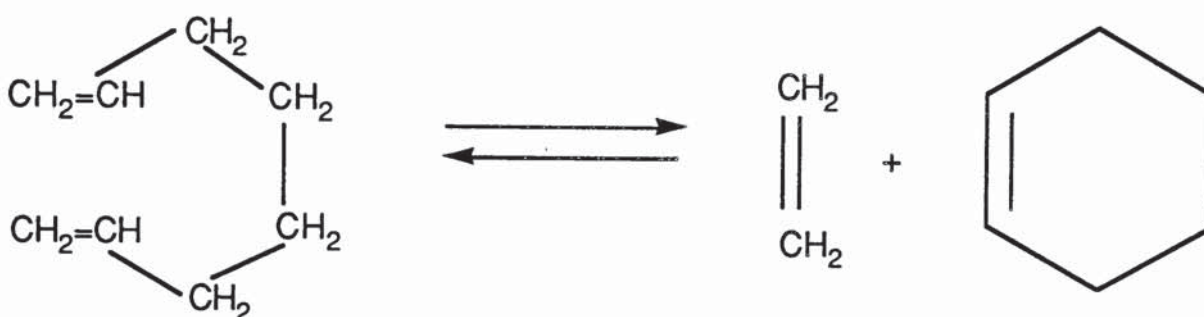
An intramolecular reaction occurs when a diene has two terminal double bonds. A type of backbiting reaction occurs and an acylic and a cyclic compound are formed. This is particularly effective when the ring formed is cyclohexene.

1.2. Historical overview

In 1931 Schneider and Frohlich[3] investigated the mechanisms of simple cracking and polymerization, to convert aliphatic hydrocarbons into aromatic hydrocarbons. They found that higher hydrocarbons could be made from the lower members by cracking (pyrolysis) as well as by simple polymerization; propene pyrolysed at 825°C to produce ethene and 2-butene in an uncatalysed reaction. It was later realised that this was the first example of a metathesis reaction but, because the reaction is symmetry forbidden[4] according to the Woodward-Hofmann rules, the reaction temperature needed to be high.

In 1964 Banks and Bailey reported a new, catalytic, disproportionation reaction in which unsymmetrical, linear olefins of three to eight carbon atoms produced a mixture of shorter and

18

longer chain olefins[1]. A heterogeneous catalytic system was used in which the active catalyst was $Mo(CO)_6$ supported on alumina.

As well as the foregoing information, Banks and Bailey also discovered that:

(i) terminal α-olefins disproportionated more rapidly than the corresponding β-olefins and

(ii) the catalyst had some activity towards double bond isomerization.

In 1967 Bradshaw et al., referred to the reaction as *dismutation* [5]. It was found that the dismutation of 1-butene produced isomerized as well as dismuted products on catalysts containing Co or Mo supported on Al_2O_3. The reaction was made more selective towards dismutation by controlling the conditions or by poisoning the catalyst with controlled amounts of sodium ions. They also showed that dismutation was a reversible reaction.

Prior to the realization of olefin metathesis, ring opening polymerization was already known. In 1957, Eleuterio polymerized cyclopentene using an alumina supported molybdenum trioxide catalyst[6]. Natta et al. polymerized cyclobutene using homogeneous catalysts derived from the transition metal compounds of groups III to VIII of the periodic table and an organometallic compound[7]. The catalysts were similar in composition to those used by Ziegler. They found that the highest activities were obtained with titanium, vanadium, chromium and tungsten compounds; molybdenum showed a lower activity. The product obtained was polybutadiene with a mixture of cis and trans double bonds. The same catalyst was later applied to other strained cycloolefins such as cycloheptene and *cis* -cyclooctene[8] which were found to polymerize with a good yield of the product polyolefin. Cyclohexene, a strain free cycloolefin, did not polymerize.

In 1967 Calderon referred to the reaction as *metathesis* [9]. This was the first time that a homogeneous catalyst had been used for acyclic olefin metathesis. 2-Pentene was reacted with a catalyst comprised of tungsten hexachloride, ethanol and ethylaluminium dichloride, a selective catalyst prepared from soluble precursors. Calderon was the first to realise that

acyclic olefin metathesis and ring opening polymerization of cycloolefins were, in fact, one and the same reaction.

The potential of the metathesis reaction had already begun to be realised. In the sixties, the Phillips petroleum company, commissioned a plant for the production of high purity ethene and 2-butene from propene[6]:

$$2CH_2=CHCH_3 \rightleftharpoons CH_2=CH_2 + CH_3CH=CHCH_3$$

The plant operated for six years but due to an increase in the demand for propene, it was closed in 1972.

Although the commercial potential for the products of the metathesis of functionalised olefins was known, it was proved difficult to perform the reaction catalytically. The activity of the catalyst was rapidly lost with olefins which had groups containing oxygen and other nucleophilic atoms. The first successful report of the metathesis of functional olefins was not until 1972 when van Dam et al. reported the use of a homogeneous catalyst system[10]. Methyl esters of unsaturated fatty acids were metathesised using a WCl_6-$Sn(CH_3)_4$ catalyst and the expected olefins and dicarboxylic acid dimethyl ethers were obtained under mild conditions (40°C). Tetramethyl tin proved to be the best organometallic compound, giving optimum activity and selectivity. In 1977 Verkuijlen et al. studied the heterogeneous metathesis of functionalized olefins[11]. They found that Re_2O_7 supported on γ- alumina, and small amounts of tin tetramethyl, metathesized fatty acid esters easily.

Since its discovery by Banks and Bailey[1], a great deal of work has been carried out in order to elucidate the mechanism of the reaction. One of the first proposals to account for the mechanism was put forward by Bradshaw et al., who suggested that two olefin molecules bonded to the transition metal atom rearranged to form a quasicyclobutane intermediate, which then dissociated to yield two product olefins[5]. This was an example of a pairwise mechanism and all of the initial mechanisms proposed belong to this class. Unfortunately, many features of the reacting system could not be explained by the pairwise mechanisms and alternative

mechanisms had to be considered. The disclosure of a non-pairwise chain mechanism by Herisson and Chauvin provided an attractive and probable alternative[12]. According to this mechanism, carbenes and metallocyclobutane intermediates were the propagating species for the metathesis reaction and this led to an increase in activity in the field of carbene and metallocyclobutane synthesis. Casey showed that carbenes could initiate the metathesis reaction when $(CO_5)W=CPh_2$, the Casey carbene, was reacted with isobutene[13]:

$$(CO_5)W=CPh_2 + Me_2C=CH_2 \longrightarrow W(CO_6) + Ph_2=CH_2 +$$
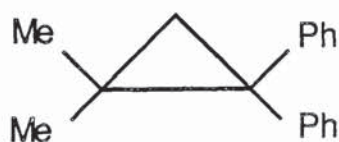
Metallocyclobutanes are very highly reactive species but Grubbs has managed to isolate titanocyclobutane using the "Tebbe" reagent and neohexene[14]:

21

"Tebbe" reagent

$R-CH=CH_2$ +

↓

titanocyclobutane + $(CH_3)_2AlCl$
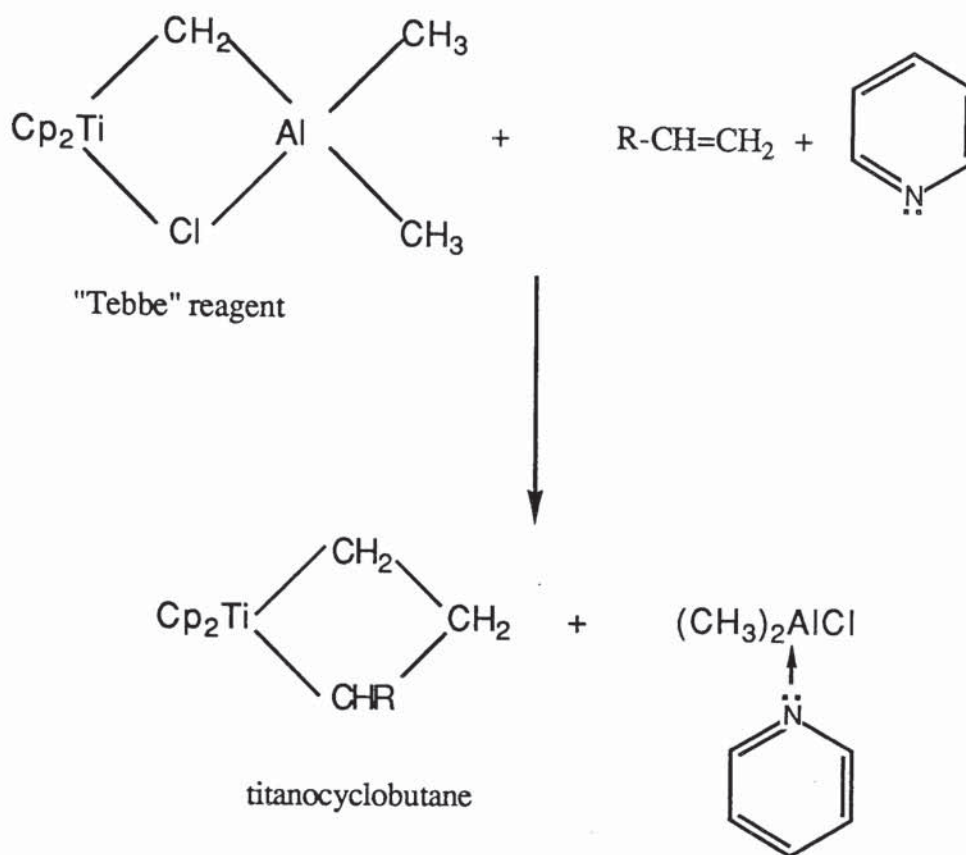
The compound has been shown to be an active metathesis catalyst and this will be discussed in section 1.5.3.3.

Recently, the metathesis of 1-oxonorbornene in the presence of air and water using $RuCl_3$(hydrate) as the catalyst has been reported[15]. This is a very significant development because metathesis catalysts are very quickly rendered inactive in the presence of air and moisture, which makes the execution of the reaction, at times, very difficult. Solvents, reactants and apparatus must be rigorously dried and evacuated before attempting the reaction. On an industrial scale, this makes the reaction a very expensive one to perform and if these two disadvantages could be overcome, the reaction would become very attractive.

1.3. Catalyst systems

Olefin metathesis is not a spontaneous reaction but requires the interaction between the substrate and a catalyst. Generally the catalyst comprises a transition metal compound and a co-catalyst. Sometimes a third component, known as the promoter, is present.

A large number of catalyst systems are now known to promote the metathesis reaction and they fall into two categories:

(i) homogeneous and

(ii) heterogeneous.

1.3.1. Homogeneous catalysts:

Homogeneous catalysts are those catalysts which are in the same physical phase as one or more of the reactants. The catalysts are usually soluble complexes of transition metals and are used extensively throughout industry in numerous processes[16]. The major attraction of homogeneous catalysis is selectivity, the ability to produce pure products in high yield, which is an essential requirement in the pharmaceutical and polymer industries. Subsequently the concept of a homogeneous catalyst can be ascribed one of the following expositions:

(i) it operates in a single phase and

(ii) only a few types of catalytic species are present in the reaction medium.

The latter attribute is essential to the selectivity of the catalyst because the presence of several types of catalytic species may lead to an increased probability of there being impurity-forming side reactions. Better selectivity is obtainable in the homogeneous phase than in the heterogeneous phase because temperature and mixing are more readily controlled. Also the catalyst and ligand concentrations are controlled more easily than those on the surface of a solid; thus the active species is regulated more effectively. In general, homogeneous metathesis catalysts can be divided into three groups: one (unary), two (binary) and three (ternary) component systems.

1.3.1.1. Two component catalysts

These usually consist of a transition metal salt from groups VI or VII of the periodic table, and a cocatalyst. Depending upon the nature of the cocatalyst, this class of catalysts can be subdivided into two groups: Ziegler-Natta type and Friedel-Crafts type two component catalysts[2,6]. In the former case the cocatalyst is an organometallic compound whilst in the latter case, it is a Lewis acid.

1.3.1.1.a. Two component catalysts of the Ziegler-Natta type

This class is by far the more widely used for the binary system. When investigating the mode
of cleavage in the cross metathesis between 2-butene and 2-butene-d$_8$, Calderon used the two
component catalytic system of WCl_6 and $C_2H_5AlCl_2$[17]. It was found that this was less active
than the three component analog, which contained ethanol. Wang and Menapace described the
metathesis of *cis* -2-pentene and *trans* -2-pentene using WCl_6 and n-C_4H_9Li[18], a very active
catalyst, and very good product selectivity was achieved. Greenlee and Farona found that the
transition metal pentacarbonyl halides from group VII were all very good metathesis catalysts
but $Re(CO_5)Cl/C_2H_5AlCl_2$ was the most effective for terminal and internal olefins[19]. The
information Muetterties obtained from his observations on the reaction of an olefin on
WCl_6/Me_2Zn, led to a proposal for the initiation mechanism for the metathesis reaction[20].
Soluble binary catalysts have also been used in the metathesis of functional olefins.
$WCl_6/SnMe_4$ metathesised methyl esters of certain unsaturated fatty acids to give the expected
products[10]. Ziegler-Natta binary systems have also been used in ring opening metathesis
polymerization. Natta et al.reported that various catalysts based on the first, second and third
row transtion metals along with an organometallic compound were effective in the ring opening
polymerization of cyclobutene[7]. They later investigated the ring opening polymerization of
higher cycloolefins using catalyst systems based on $WCl_6/Al(C_2H_5)_3$, $WCl_6/Al(C_2H_5)_2Cl$ and
$MoCl_5/Al(alkyl)_3$. All the cycloolefins were found to be polymerized to their respective
polyolefin[8]. Feast and Shahada ring opened 5,6-bis(chloromethyl)bicyclo[2.2.1]hepta-2-ene
using $MoCl_5/Me_4Sn$ and WCl_6/Me_4Sn to give poly{1,4-[2,3-bis(chloromethyl)-
cyclopentylene] vinylene}[21]. The former catalyst gave a predominantly atactic*trans* polymer
whereas the latter gave a predominantly atactic*cis* polymer:
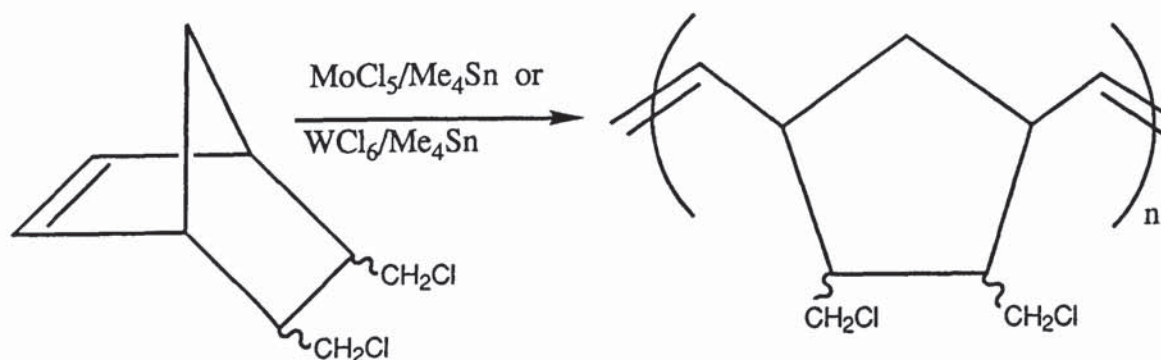
1.3.1.1.b. Two component catalysts of the Friedal Crafts-type

This catalyst type system has been very effective in the ring opening metathesis polymerization of cycloolefins. Dall'Asta and Carella were very successful in polymerizing cyclopentene using WCl_6, $WOCl_4$, or WBr_5, with $AlCl_3$ or $AlBr_3$ as Lewis acids[2].

1.3.1.2. Three component (ternary) catalysts

In many cases a third component is added to a binary catalyst to act as an activator or promotor for the catalyst. In particular, it was thought that oxygen containing species induced a higher activity, but this was not realised until long after Calderon's classical system of $WCl_6/C_2H_5AlCl_2/EtOH$ had been first used[22,23]. This system was also used in the metathesis of other acyclic olefins and was again found to very effective[24]; 2-pentene, 2-hexene, 2-heptene, and 2-octene all gave 2-butene and an internal olefin with equilibrium conversions being obtained. The optimum catalyst ratios were found to vary from between 1 : 1 : 2 and 1 : 1 : 4 for the catalytic components WCl_6 : EtOH : $C_2H_5AlCl_2$. Calderon also used his classical catalyst system, $WCl_6/C_2H_5AlCl_2/EtOH$, in the ring opening metathesis of cycloolefins and high product yields were obtained[25]. Cyclooctene polymerized to yield a mixture of linear high molecular weight polymer and lower molecular weight macrocyclic species. Besides ethanol, other oxygen containing third components could also be used eg. methanol and phenol which were found to be just as effective[22] ,thus indicating the importance of oxygen. The presence of a halide ligand was also thought to be an important requirement for catalytic activity[22]. Motz and Farona modified the very active catalyst of $Mo(CO)_5py/RAlCl_2$ (where $R = C_2H_5$ or CH_3) by adding $(C_4H_9)_4NCl$ as the cocatalyst[26] to produce an effective catalyst for the metathesis of terminal olefins. For optimum activity, the Al : Mo ratio varied between 4 : 1 and 8 : 1 with the activity increasing towards the latter. The maximum ratio of the cocatalyst added was 2 : 1.

1.3.1.3. One component (unary) catalysts

The largest group of one component catalysts for olefin metathesis, are those with structures that are believed to be analogous to the structures of the intermediates involved in the metathesis reaction. In 1970 Herisson and Chauvin put forward a chain mechanism to explain the reaction[12]. Involved in the mechanism were intermediates with carbene and metallocyclobutane

characteristics. Consequently, in order to provide evidence for this type of mechanism, compounds having the structures of the intermediates were synthesised and used as metathetic catalysts. The following discussion will be based on the work involving carbene and metallocyclobutane type compounds.

1.3.1.3.a. Carbenes

The first carbene to be used to initiate the metathesis of acyclic olefins was diphenylpentacarbonyltungsten carbene, $(C_6H_5)_2C=W(CO)_5$[13]. Katz et al first used it to cross-metathesise 1-octene with 1-hexene[27] and very high product selectivity was achieved. The same carbene was used for the ring opening metathesis polymerization of cyclobutene, cyclopentene, cycloheptene, cyclooctene, and norbornene and they were all converted to their respective polyolefins with more than 90% of the double bonds in the *cis* configuration[28]:

Parshall and Tebbe reported a slow but well defined catalyst, called the 'Tebbe' reagent, for the degenerate metathesis between isobutene and methylenecyclohexane, where the terminal methylene groups were selectively exchanged[29]:

$^{12}CH_2$

$^{13}CH_2$

Cp$_2$Ti — Al(CH$_3$)$_2$ / Cl

+

51°C

$^{13}CH_2$

$^{12}CH_2$

+

CH$_3$ CH$_3$
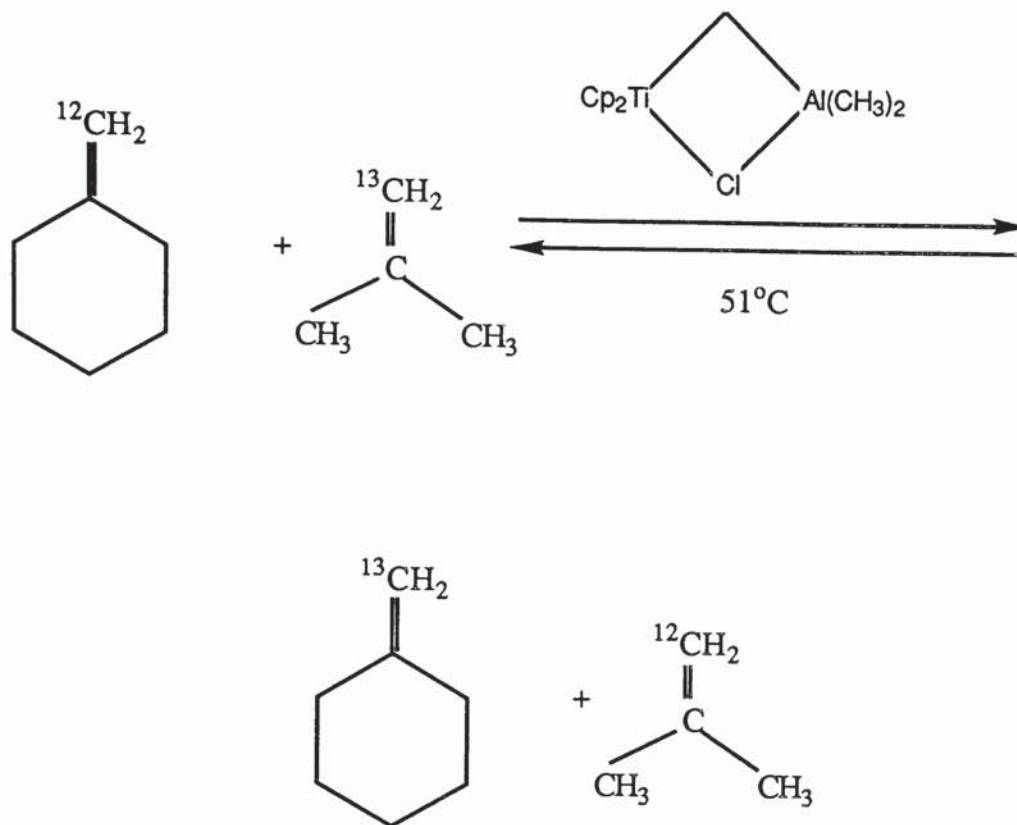
Grubbs et al disputed the fact that the 'Tebbe' reagent was the actual catalytic species. When the reagent was reacted with neohexene and one equivalent of pyridine a single metallocene product in near quantitative yield was obtained[14, 30]:

Cp$_2$Ti — Al(CH$_3$)$_2$ / Cl   +   D   D   ⟶

Cp$_2$Ti   +   Base.AlMe$_2$Cl

D   D

Titanocyclobutane

I
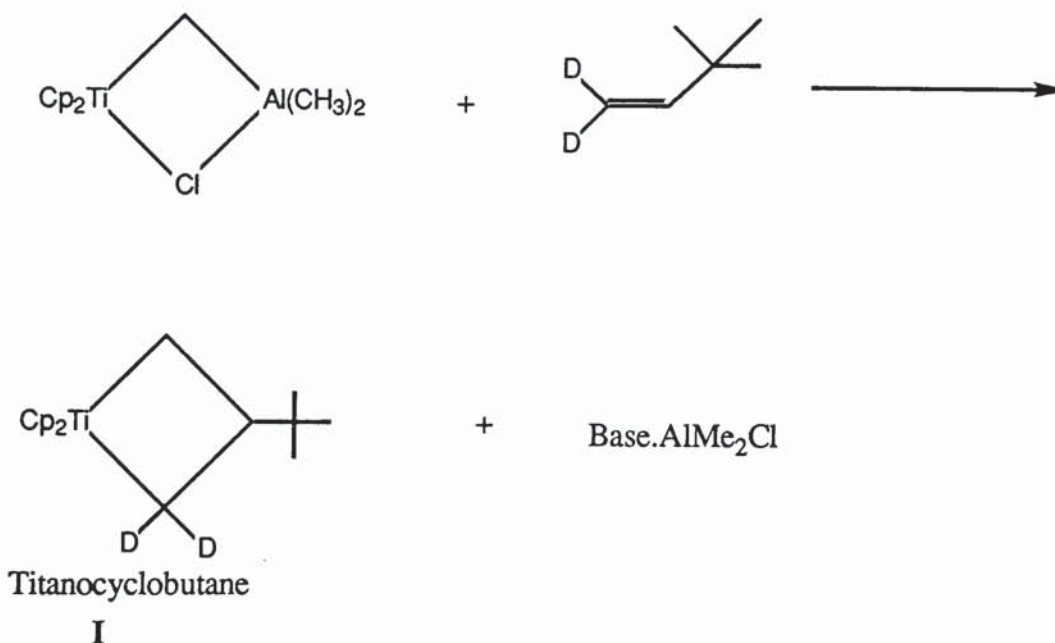
I was found to undergo a number of reactions, indicative of a metathesis catalyst:
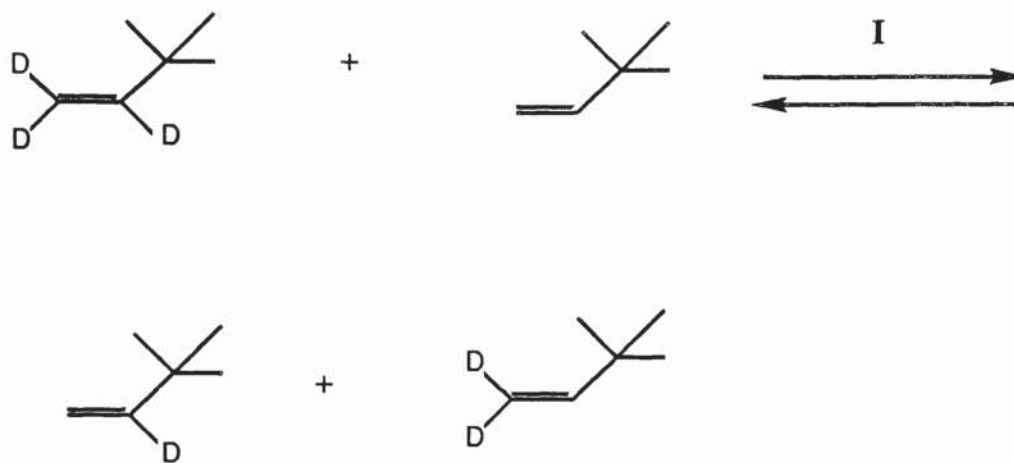
It was also demonstrated that titanocyclobutanes, **II**, derived from strained cyclic olefins are useful catalysts for metathesising norbornene[31]:
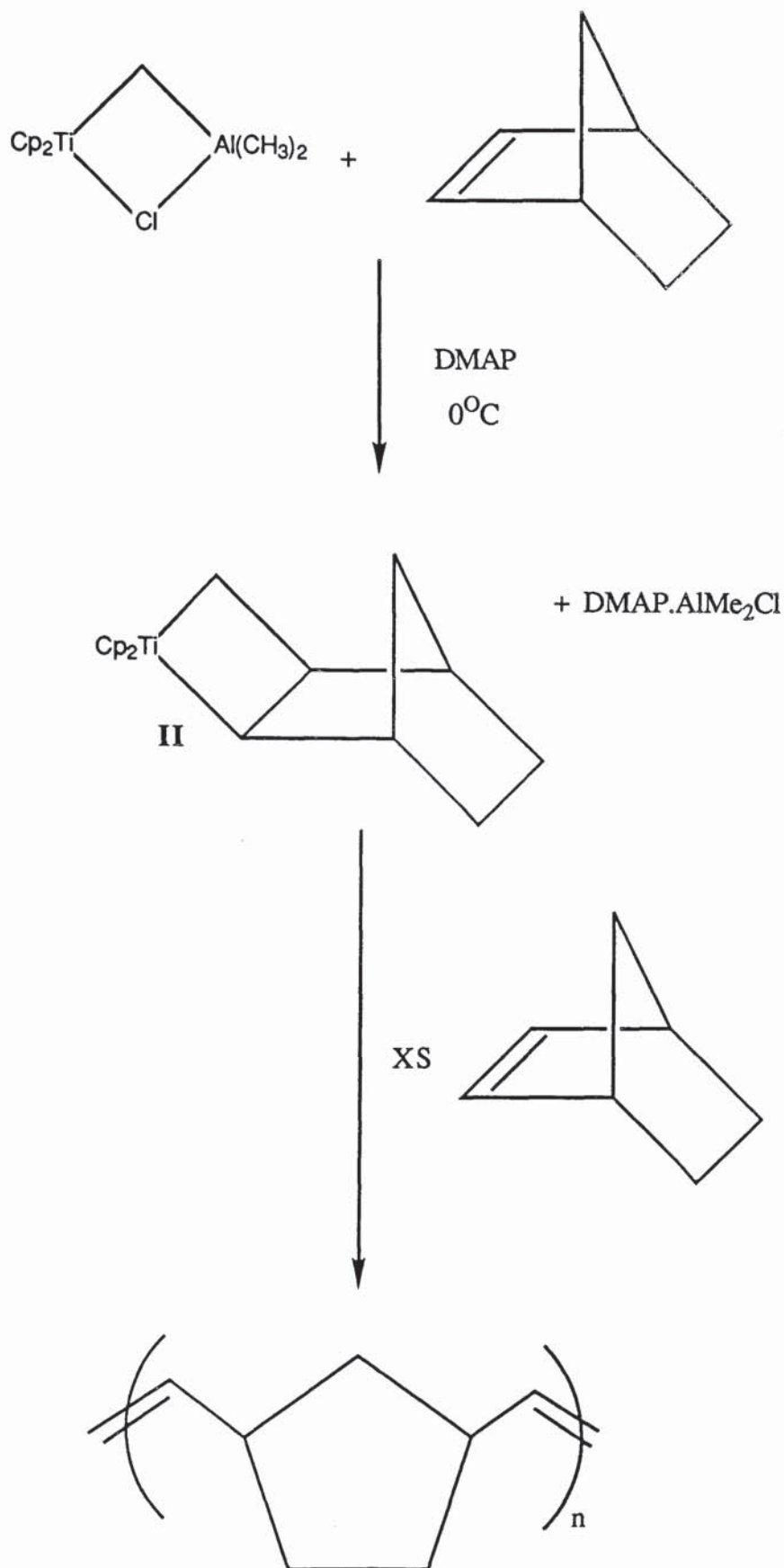
1.3.2. Heterogeneous catalysts

Heterogeneous catalysts are those catalysts which are in a different physical state from the reacting substrates. In the metathesis reaction, heterogeneous catalysts are nearly always solid and the substrate is either in the liquid or gas phase. In general, effective heterogeneous

catalysts comprise transition metal compounds, with the majority belonging to molybdenum, tungsten and rhenium in the form of an oxide, carbonyl or sulphide supported on either alumina or silica. The following is a brief classification of the more important catalyst systems.

1.3.2.1.a. Catalysts supported on metallic oxides

This is the most important group of catalysts for heterogeneous metathesis. These catalysts are usually prepared by impregnating the support with an aqueous solution of a transition metal salt, eg ammonium perrhenate or ammonium paramolybdate, which is then dried and calcined at very high temperatures (around $580^{\circ}C$)[6,32]. During the calcination, the salt decomposes and the supported metal oxide is obtained. This is known as the catalyst precursor, and it is believed that the metal is in its highest oxidation state at this stage. The catalyst is reduced by the reactant or the cocatalyst and this, in some way, generates the actual species responsible for the metathesis reaction.

Some of the more important catalysts in this category will now be reviewed briefly.

A) Rhenium oxide:

The oxide is most commonly supported on γ - alumina but much work has also been published using silica as the support. The catalyst is very effective in the metathesis of all types of olefin, particularly those with functional groups. Since this thesis is concerned with this catalyst, it will be discussed in greater detail in section 1.8.

B. Molybdenum oxide

MoO_3/Al_2O_3 (containing up to 13% MoO_3) was used by Banks and Bailey in the metathesis of propene into ethene and 2-butene in 11-12% yield[1]. Good activity was achieved at temperatures of around $50^{\circ}C$. MoO_3/Al_2O_3 is the precursor for the metathetically active species but the oxidation state and its structure has yet to be elucidated. Subsequent work has been done by depositing the oxide on different carriers and various degrees of conversion of propene have been reported[33].

30

C. Tungsten oxide

WO_3 has been supported on alumina and on silica (1-10% w/w WO_3) but the percentage conversions of olefins were not as high as with the molybdenum oxide catalyst[34]. This was thought to be due to the fact that tungsten oxide catalysts are more difficult to reduce than the ones based on molybdenum. Optimum activity is achieved at much higher temperatures, in the range 300 - 500°C.

1.3.2.1.b.   Catalysts based on metallic carbonyls

These catalyst are prepared differently from the supported oxide catalysts. After the support has been pretreated, (its hydroxylated surface is partially dehydroxylated by heating), it is brought into contact with the carbonyl complex, $M(CO)_6$. Heat treatment decomposes the complex and the necessary chemical interaction takes place[2]. The complex loses carbonyl ligands and interacts with the hydroxyl groups which causes a change in the oxidation state of the metal to form $M(CO)_3/Al_2O_3$, an air sensitive system. $Mo(CO)_6/Al_2O_3$ was the catalyst used by Banks and Bailey when the metathesis reaction was first reported as olefin disproportionation[1]. Propene, 1-butene, 1-pentene and 1-hexene were passed over the catalyst at 110°C with yields of ethene ranging from 10% for propene to 60% for 1-pentene. Isomerization was extensive using this catalyst and in the presence of ethene, cyclopropanation occurred as well as the cross metathesis reaction. $W(CO)_6/Al_2O_3$ behaves in a manner similar to its molybdenum counterpart[6].

Danilyuk has shown that $Re_2(CO)_{10}/Al_2O_3$ is inactive as a metathesis catalyst, but when the complex was decarbonylated and treated with oxygen, an active catalyst for propene metathesis was obtained[35]. Danilyuk believed that the oxidation state of the oxidized rhenium atom was either +6 or +5 in the active cetre.

1.3.2.1.c.   Catalysts based on metallic sulphides

Effective metathesis catalysts of molybdenum and tungsten sulphide supported on alumina and silica have been obtained using up to 10% loading of sulphide for olefins such as propene and 1-butene[33]. The working temperature of these catalysts is between 65 - 500°C, depending

upon the support used. High temperatures are not recommended, however, because of the promotion of dimerization and polymerization reactions.

1.3.2.2. Physical characteristics

The most important feature of heterogeneous catalysis is the surface of the catalyst[2]. The important physical surface characteristics are:

(i) **Surface area**: The greater the surface area of the catalyst, the greater the activity of the catalyst. Generally, catalysts are prepared with a specific area of over $100m^2g^{-1}$.

(ii) **Pore size**: Pore sizes with diameters between 5-20nm impart to the catalyst a high activity towards metathesis.

(iii) **Particle size**: This is best achieved using pellets prepared through extrusion. For an alumina support, particles of 20-40 mesh are usually chosen.

Heterogeneous catalysts are subject to physical and chemical factors which can alter their activity. Temperature plays a very important role in the activity of the catalysts. If it is too low, the catalyst is rendered inactive, If too high, the surface structure might be modified to the extent that the active surface species are deactivated. Alternatively, the active centres could be altered so that they produce secondary products from the side reactions. Heterogeneous catalysts are very susceptible to attack by moisture, oxygen, acids and other compounds containing polar groups. These may be chemisorbed onto the catalyst and block the active centres, thus changing the activity of the catalyst. This can be avoided by ensuring that all the starting materials and solvents are pure, particularly oxygen-free and dry.

1.4. Reactants for the metathesis reaction

Since the discovery of olefin metathesis in 1964 by Banks and Bailey, many acyclic olefins have been shown to undergo the metathesis reaction. The substrates for the reaction have also been extended to include acyclic dienes, unsaturated functional compounds, acetylenes, and cycloolefins.

1.4.1. Acyclic olefins

This is the largest single class of substrates that undergo the metathesis reaction. Banks and Bailey metathesised linear terminal olefins of 3 to 8 carbon atoms using $Mo(CO)_6/Al_2O_3$ as the catalyst to produce longer and shorter chain olefins[1]. The shorter chain olefin produced in all cases was ethene and the longer chain olefin an internal olefin eg,

$$2CH_2=CHCH_3 \rightleftharpoons CH_2=CH_2 + CH_3CH=CHCH_3$$

The reverse reaction is known as ethenolysis. Table 1.1 compares the activity of these olefins with respect to the metathesis reaction. The olefins were passed over the catalyst at 93°C and 500 psi.

α-olefins were found to metathesise more rapidly than β-olefins. The order of reactivity of acyclic olefins depends upon the degree of substitution around the double bond and this was investigated by Casey et al who found the following[36]:

degenerate exchange of methylene units between terminal olefins > cross metathesis between terminal and internal olefins > metathesis of internal olefins.

Table 1.1

The % conversion of various olefins over $Mo(CO)_6/Al_2O_3$

REACTANTS	% CONVERSION
propene	25
1-butene	10
1-pentene	60
1-hexene	54

1.4.2. Acyclic dienes

In 1969 Heckelsberg, Banks and Bailey reported that the metathesis reaction could also be extended to dienes[37]. A diene could react with another diene or with a mono-olefin, eg 1,3-butadiene plus propene produced ethene and 1,3-pentadiene:

$$CH_2=CH-CH=CH_2 \ + \ CH_2=CH-CH_3 \longrightarrow$$

$$CH_2=CH_2 \ + \ CH_2=CH-CH=CH-CH_3$$
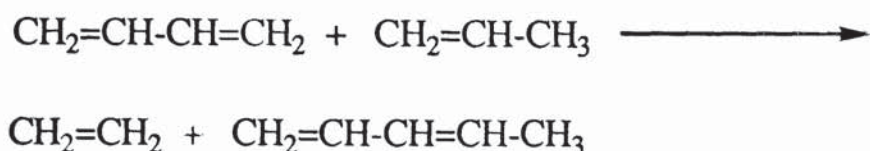
Depending upon the position of the double bond, dienes can undergo either inter- or intramolecular olefin metathesis. Short chain dienes, with conjugated or non-conjugated double bonds, usually undergo intermolecular metathesis reactions eg, 1,3-butadiene over tungsten-silica catalyst metathesises to give ethene and hexatriene. Hexatriene cyclises to give cyclohexadiene:

$$2CH_2=CH-CH=CH_2 \longrightarrow CH_2=CH_2 \ + \ CH_2=CH-CH=CH-CH=CH_2$$
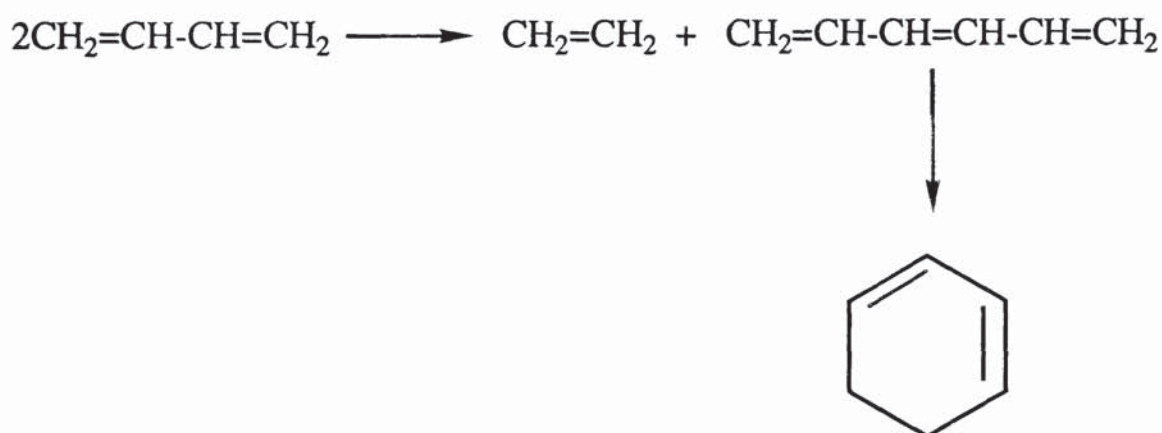
When Zuech carried out the metathesis of 1,7-octadiene using a molybdenum nitrosyl complex as the catalyst, cyclohexane was formed as the main product with traces of 1,7,13-tetradecatriene[38]:
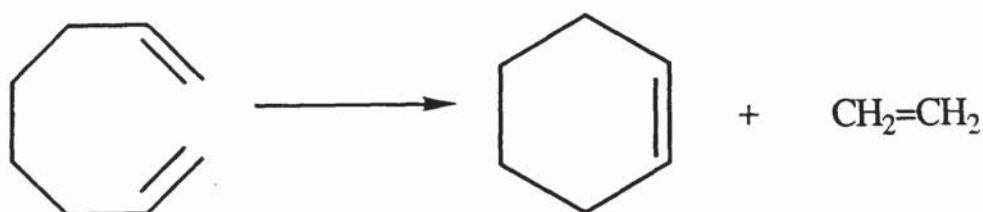
The formation of the stable six membered ring favours intramolecular metathesis.

1.4.3. Unsaturated functional compounds

The metathesis of functionalized olefins is hampered by the poisoning effect of the heteroatom, which usually tends to be oxygen, nitrogen or sulphur, on the catalyst. The heteroatom competes with the carbon-carbon double bond for complexation to the active site on the catalyst. Once the heteroatom is complexed to the active site, it stays there and blocks any incoming carbon-carbon double bonds:
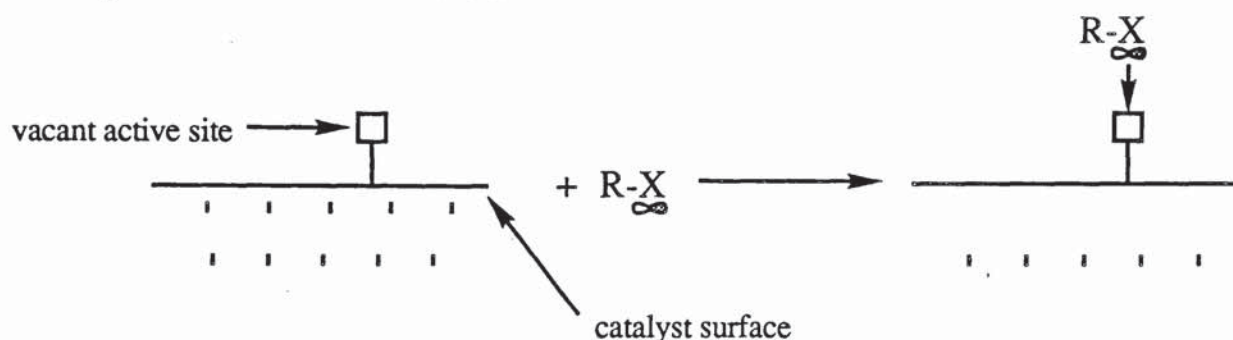
Both homogeneous ($WCl_6/Sn(Me_3)_4$) and heterogeneous (Re_2O_7/Al_2O_3) based catalysts have been used successfully in the metathesis of functional unsaturated compounds. The first report was by van Dam in the homogeneous metathesis of methyl esters of unsaturated fatty acids using a $WCl_6/Sn(CH_3)_4$ catalyst eg, methyl oleate[10]:

$$2CH_3(CH_2)_7CH=CH(CH_2)_7COOCH_3 \longrightarrow$$

$$H_3COOC(CH_2)_7CH=CH(CH_2)_7COOCH_3 + CH_3(CH_2)_7CH=CH(CH_2)_7CH_3$$
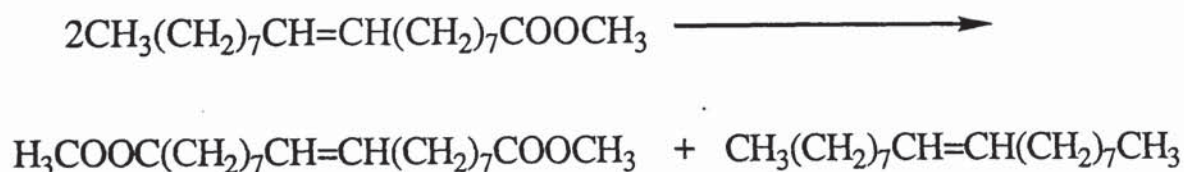
Verkuijlen reported a few years later the heterogeneous metathesis of methyl esters of unsaturated fatty acids using $Re_2O_7/Al_2O_3/Sn(CH_3)_4$ as the catalyst[11]. Since then functional olefins such as nitriles and ethers have been successfully metathesised[39,40]. The chloride group is not as deleterious towards metathesis catalysts as the oxygen group. Nakamura and Echigoya used oxide promoters eg, V_2O_5, MoO_3 and WO_3, to increase the activity of the

Re$_2$O$_7$/Al$_2$O$_3$ catalyst in the cross-metathesis of oleyl chloride (1-chloro-*cis* -9-octadecene) with olefins such as 1-hexene[41]:

$$CH_3(CH_2)_7CH=CH(CH_2)_8Cl \;\; + \;\; CH_2=CH(CH_2)_3CH_3 \longrightarrow$$

oleyl chloride   1-hexene

14-chloro-5-tetradecene + 5-tetradecene + 1-decene and 10-chloro-1-decene

The activity of the catalyst was high, even at low loadings of rhenium. Warwel cross-metathesised 10-undecenyl-trimethylsilylether with 4-octene to give a derivative of 10-tetradecenol and 1-pentene using Re$_2$O$_7$/Al$_2$O$_3$/Sn(CH$_3$)$_4$ as the catalyst[42]. Molar ratios of Re$_2$O$_7$: trimethylsilylether went as low as 1 : 500 and good activity was still achieved:

$$CH_2=CH-(CH_2)_9-O-Si(CH_3)_3 \;\; + \;\; CH_3-(CH_2)_2-CH=CH-(CH_2)_2-CH_3 \rightleftharpoons$$

$$CH_3-(CH_2)_2-CH=CH_2 \;\; + \;\; CH_3-(CH_2)_2-CH=CH-(CH_2)_9-O-Si(CH_3)_3$$

1.4.4.   Acetylenes

Productive olefin metathesis of acetylenes occurs only with the disubstituted compounds. In 1968 Pennella observed the metathesis of 2-pentyne on WO$_3$/SiO$_2$ at 350^{0}C[43]. Metathesis of unsymmetrical disubstituted acetylenes such as 3-heptyne leads to an equilibrium mixture as in the metathesis of olefins:

$$CH_3C\equiv CCH_2CH_3 \longrightarrow CH_3C\equiv CCH_3 \;\; + \;\; CH_3CH_2C\equiv CCH_2CH_3$$

Monosubstituted acetylenes cyclise or polymerise in the presence of metathesis catalysts, eg acetylene polymerises to polyacetylene and may also cyclise to benzene[44,45].

1.4.5. Cycloolefins

Much of the early work on ring opening metathesis polymerisation was performed by Natta et al[7,8]. Strained monocyclic cycloolefins, eg cyclobutene and cyclopentene, were found to undergo ring opening quite readily in the presence of homogeneous catalysts whilst strain free monomers, such as cyclohexene, do not undergo the reaction. 1,5-cyclooctadiene undergoes intermolecular metathesis leading to the formation of dimers and trimers[46]:
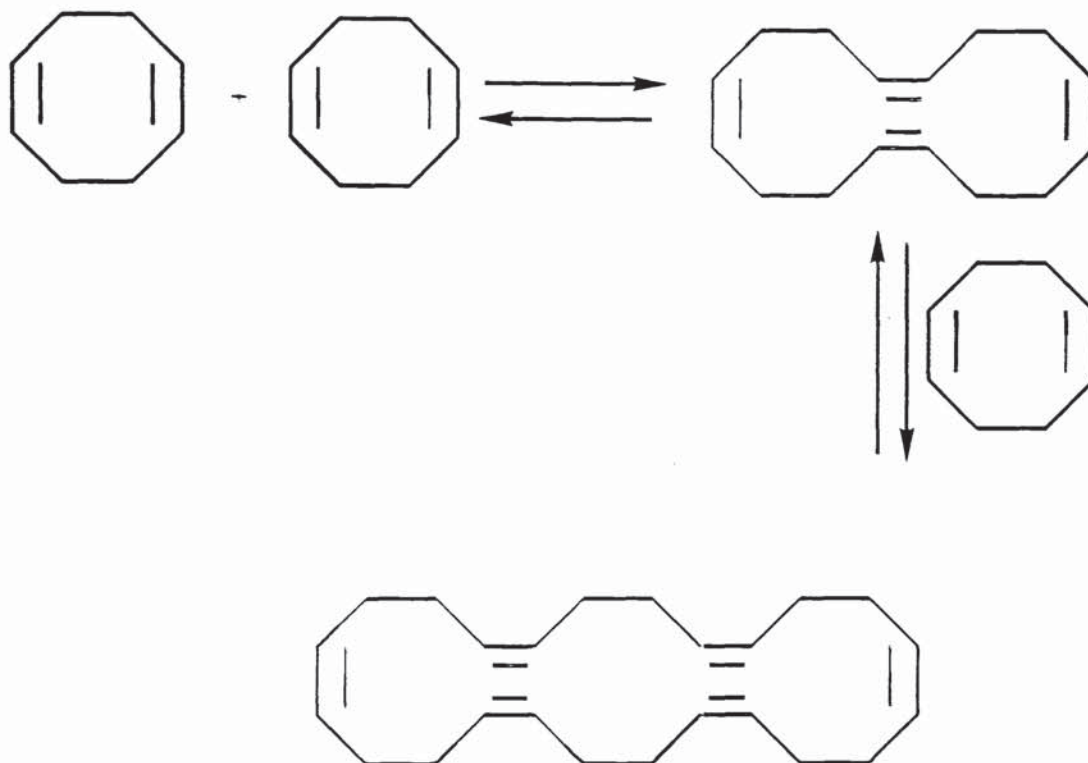
Potentially it can also undergo intramolecular metathesis to form cyclobutene but due to the high strain of the product, the reaction hardly proceeds:
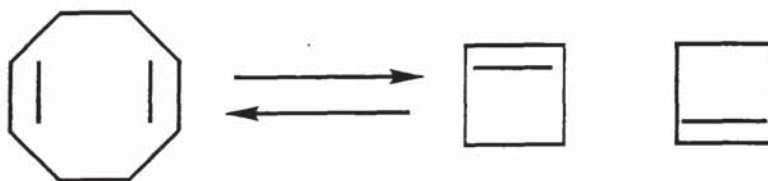
The equilibrium conversion of cyclopentene and cycloheptene is temperature dependent since the ring strain of these monomers is moderate. Substituted cycloolefins may also undergo ring opening polymerization with the majority of conventional metathesis catalysts, provided the substituents do not contain nucleophilic groups such as nitrogen and oxygen. Monomers with the alkyl substituents bonded to the carbon-carbon double bond, eg 1-methylcyclopentene[47],

will not polymerize but monomers such as 3-methylcyclopentene polymerize readily[48]. The stereochemistry and the molecular weight distribution of the polymer may be affected by secondary reactions, which can occur as a result of the carbon-carbon double bonds in the polymer chain being susceptible to attack by the catalyst.

Bicyclic monomers, such as norbornene, are also polymerized by metathesis catalysts[49]. The monomer usually possesses a double bond that is part of a highly strained ring system and so polymerizes to almost 100% conversion. Much of the investigation into the kinetics of ring opening metathesis polymerization is done using norbornene because the polymer does not readily undergo secondary reactions.

Feast has investigated the effects of halogen substituents on the reactivity of monocyclic and bicyclic monomers towards ring opening polymerization[21]. If a halogen atom is bonded to the carbon-carbon double bond or if a fluorine atom is bonded to the ring containing the unsaturated carbon atoms, the monomer will not polymerize. If the substituent is part of the ring which does not contain the unsaturation, then the monomer will polymerize with ease. Fig 1.1 shows some of the fluorinated polymers synthesised from bicyclic monomers.

<div align="center">

Fig 1.1

Flourinated polymers synthesised by ring opening metathesis polymerization

</div>
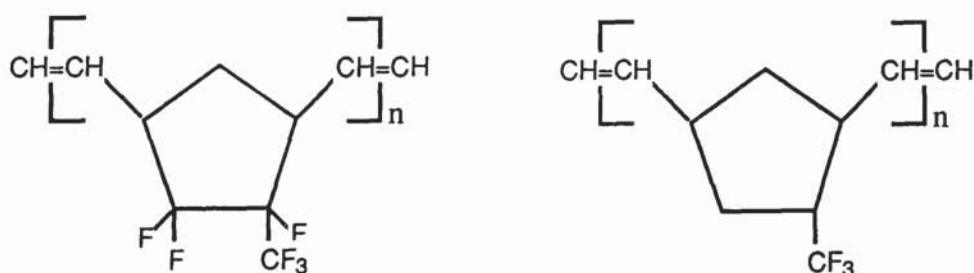
1.5. The mechanistic pathways

Since the discovery of the metathesis reaction, a considerable amount of work related to the elucidation of the mechanistic aspects of metathesis has been carried out. Two questions

immediately arise concerning the reaction mechanism, the site of cleavage of the olefin and the nature and structures of intermediate species formed during the reaction. The following discussion will provide a definitive answer to the first question but, with regard to the second, different postulates have been put forward.

1.5.1. The site of cleavage

The site of cleavage of the olefin in a metathesis reaction has been considered from two points of view, transalkylation and transalkylidenation[17,50,51].

Transalkylation involves the interchange of alkyl groups bonded to the carbon-carbon double bonds of the reacting olefin molecules, scheme 1.1.

Scheme 1.1

The transalkylation mechanism

$$R^1-CH=CH-R^2 \quad\longrightarrow\quad R^1-CH=CH \quad + \quad R^2$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad |_{R^1} \qquad\quad |_{CH=CH-R}$$
$$R^1-CH=CH-R^2$$
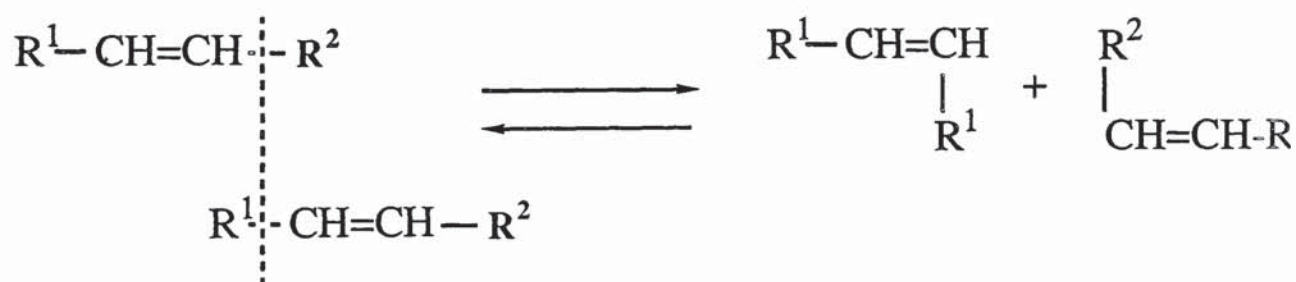
In contrast, transalkylidenation involves the interchange of an alkylidene fragment (R-CH=) of one olefin, with that of another, scheme 2.

Scheme 1.2

The transalkylidention mechanism

$$R^1\text{-CH} \doteq \text{CH-}R^2 \quad\quad R^1\text{-CH} \quad\quad \text{CH-}R^2$$

$$\xrightleftharpoons{\quad\quad} \quad \| \quad + \quad \|$$

$$R^1\text{-CH} \doteq \text{CH-}R^2 \quad\quad R^1\text{-CH} \quad\quad \text{CH-}R^2$$
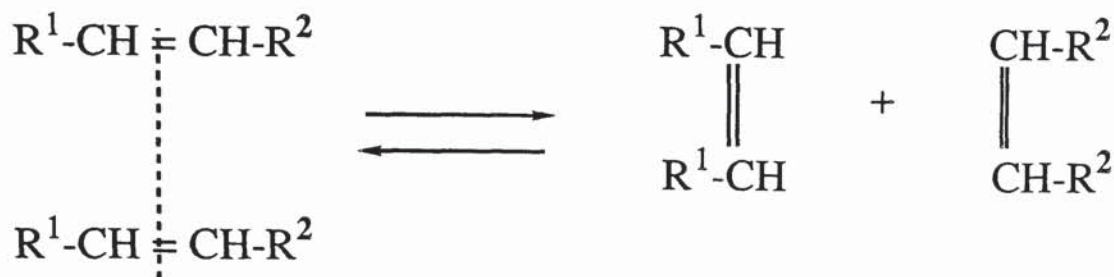
Calderon et al. studied the cross metathesis of perdeutero-2-butene and 2-butene using the homogeneous catalyst $WCl_6/C_2H_5AlCl_2/EtOH$. The product observed, 2-butene-d_4, was consistent only with a transalkylidenation route[17]:

$$CH_3CH\doteq CHCH_3$$

$$\xrightleftharpoons{\quad\quad} \quad 2\ CH_3CH=CDCD_3$$

$$CD_3CD\doteq CDCD_3$$
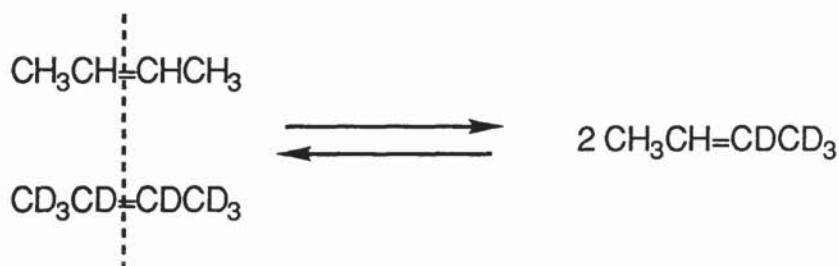
2-butene-d_3 and d_5, which would have arisen if transalkylation had taken place, were absent from the final product mixture.

Confirmatory results were obtained by Mol et al. who studied the metathesis of propene labelled with ^{14}C[52]. It was found that the metathesis of labelled 2-^{14}C-propene produced radioactive 2-butene and non-radioactive ethene and the specific radioactivity of the 2-butene produced was twice that of the propene used:

$$CH_2\doteq {}^{14}CHCH_3 \quad\quad\quad CH_2 \quad\quad {}^{14}CHCH_3$$

$$\xrightleftharpoons{\quad\quad} \quad\quad \| \quad\quad\quad \|$$

$$CH_2\doteq {}^{14}CHCH_3 \quad\quad\quad CH_2 \quad\quad {}^{14}CHCH_3$$
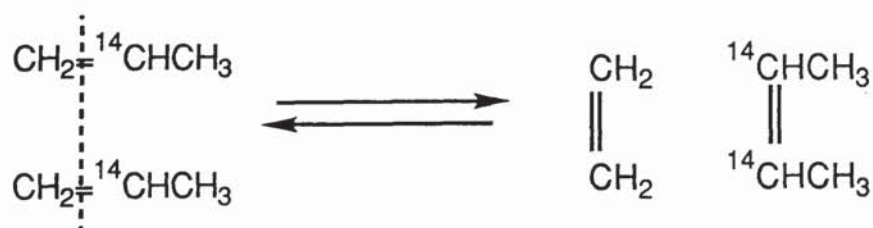
Radioactively labelled 1-^{14}C propene and 3-^{14}C-propene were also studied and these gave radioactive ethene and 2-butene respectively.

It having been established unambiguously that the site of cleavage of the olefin in metathesis reactions was the carbon-carbon double bond, many mechanisms were then proposed to account for reactions in this way. Those that were proposed initially were within a class known as pairwise reactions which involved the simultaneous exchange of alkylidene groups between two olefin molecules, catalysed by a transition metal complex. Later a non-pairwise mechanism was proposed by Chauvin[12], which has gained universal acceptance. However, for completeness, a discussion of pairwise mechanisms will now be undertaken.

1.5.2. Pairwise mechanisms

After establishing that the alkylidene groups of the olefins interchanged, Calderon proposed a three step mechanism involving the formation of a bis olefin-metal complex[9,17].

i) Bis olefin-metal complex formation:

It was proposed that the transition metal was the site at which the reaction took place and that the catalyst and the cocatalyst reacted in some way to form the active centre. The transition metal was thought to possess two vacant co-ordination sites or labile ligands at which two reacting olefin molecules could co-ordinate:

$$2RCH{=}CHR^1 \xrightarrow{\quad W^* \quad}$$

$$\overset{W^*}{\diagup \quad \diagdown}$$

$$RCH{=}CHR^1 \qquad RCH{=}CHR^1$$
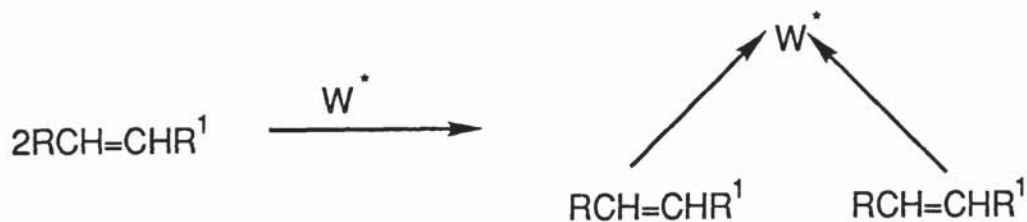
ii) Transalkylidenation

The bis-olefin complex would then rearrange to form a quasi-cyclobutane intermediate. The reaction then proceeded by a subsequent electronic rearrangement which involved the d orbitals of the metal:

41

W*

RCH=CHR¹   RCH=CHR¹   ⇌   [diagram] ← — → [diagram]

W*   W*

CHR¹   CHR¹

CHR   CHR¹   CHR   CHR¹

CHR   CHR

W*

CHR   CHR¹
‖   ‖
CHR   CHR¹
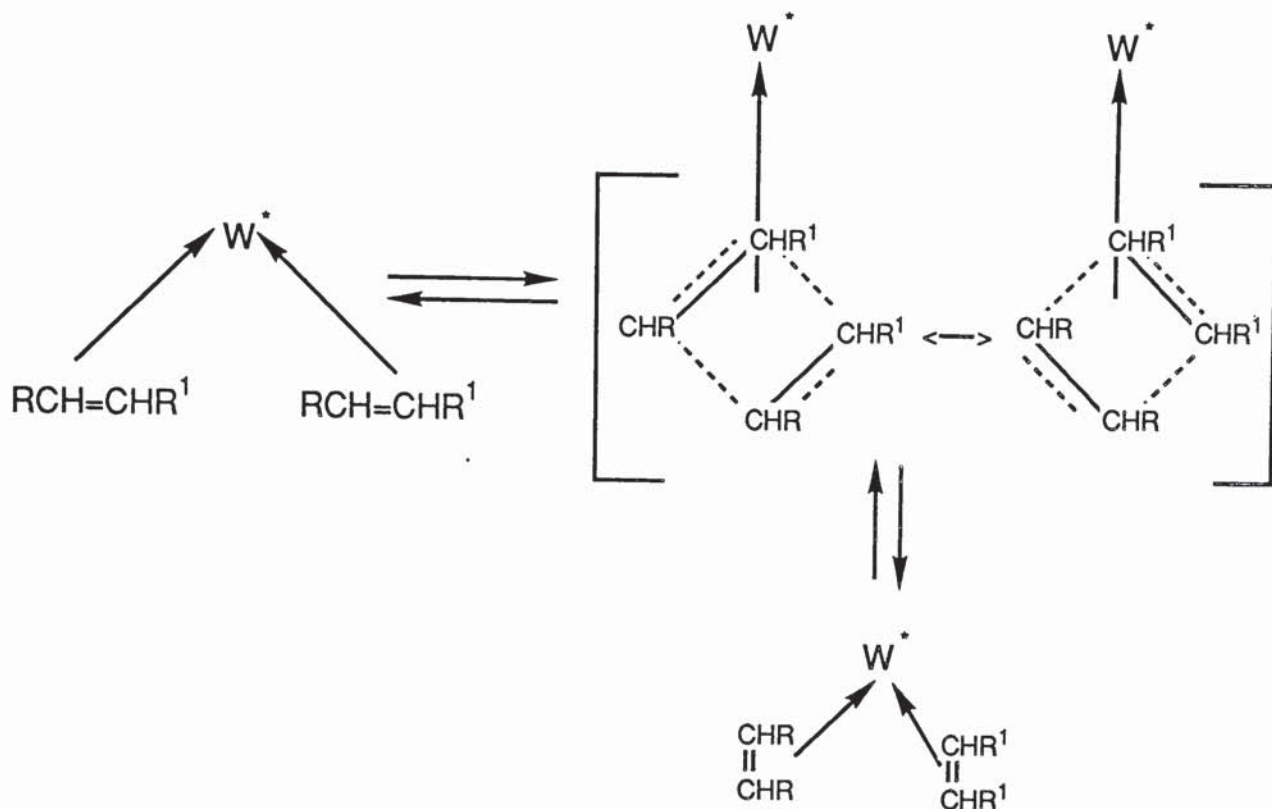
iii) Olefin exchange

The final step in the reaction involved substitution of one or both product olefins by reactant olefins at the transition metal:

W*

CHR   CHR¹
‖   ‖   + RCH=CHR¹   ⇌
CHR   CHR¹

W*

RCH=CHR   RCH=CHR¹

+

R¹CH=CHR¹
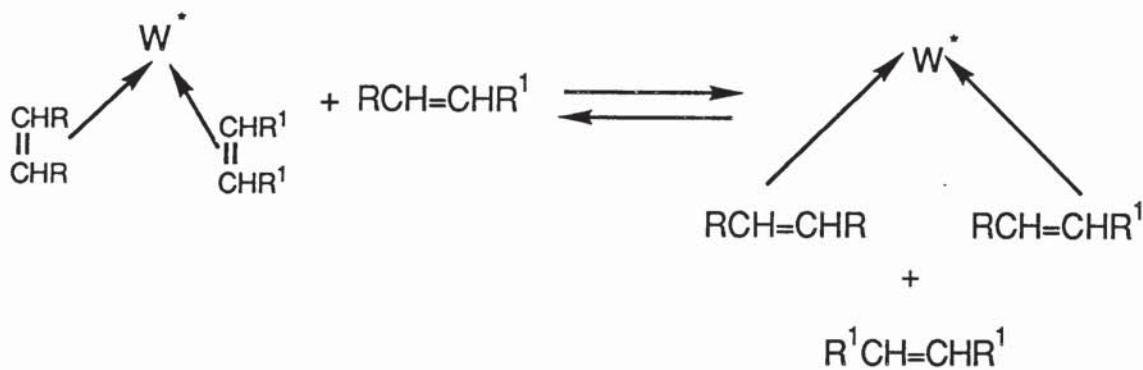
W* = metal centre with ligands

To account for the high catalytic activity, alternating transalkylidenation and olefin exchange were supposed to occur rapidly. Complexes which undergo rapid olefin exchange were well known at the time eg , Zeise's complex[53].

$[(CH_2=CH_2)\,PtCl_3]^- + olefin \rightleftharpoons [(olefin)\,PtCl_3]^- + CH_2=CH_2$

Zeises complex

Bradshaw et al suggested that the quasi-cyclobutane intermediate was bonded in some way to the transtion metal atom as shown in scheme 1.3[5]:

Scheme 1.3

The pairwise mechanism involving a quasi-cyclobutane intermediate

R–CH=CH–R'

+ $\xrightarrow{W^*}$

R–CH=CH–R'

R–CH=CH–R'
↓
W*
↑
R–CH=CH–R'

R–CH=CH–R (ring intermediate with W* below)

R   R'
| |
CH   CH
‖ →W*← ‖
CH   CH
| |
R   R'

R–CH=CH–R   +   R'–CH=CH–R'
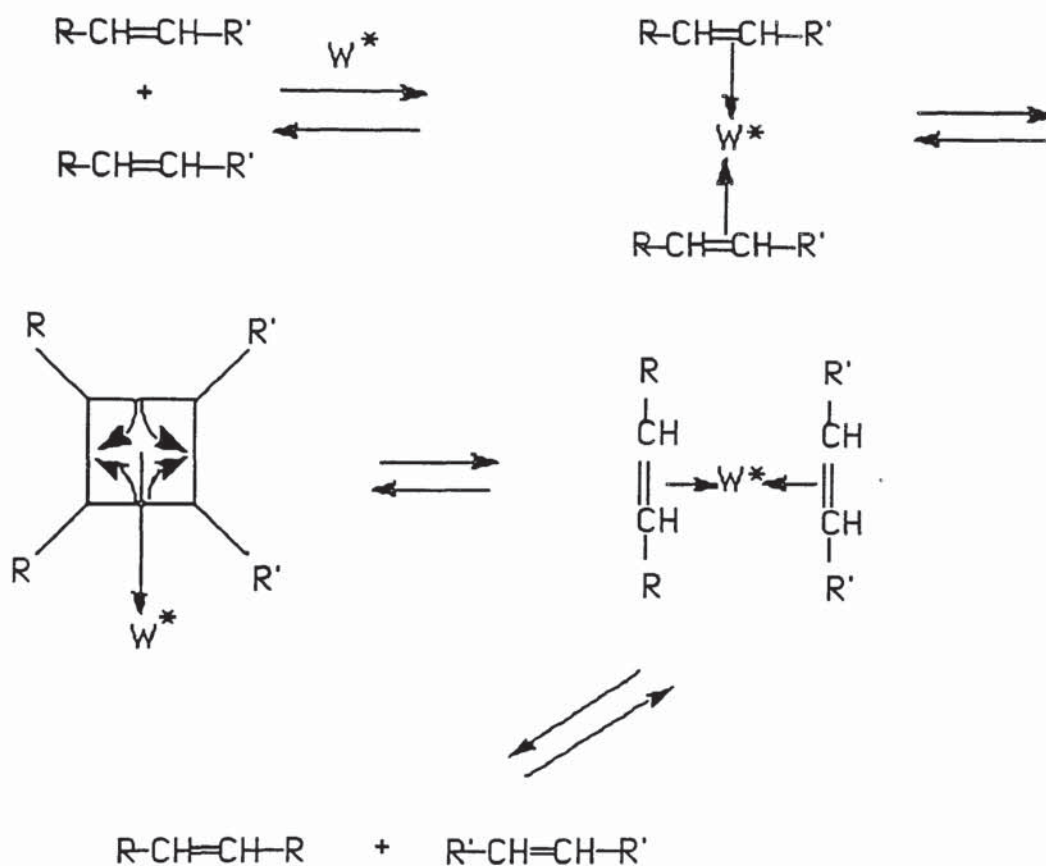
W* = metal centre with ligands

If the intermediate had considerable cyclobutane character, it would be reasonable to expect that cyclobutane would be produced in the reaction system in small yields; no cyclobutane has ever been detected. Pettit has demonstrated that cyclobutanes are unreactive under the usual metathesis conditions and the concerted conversion of two olefins into a cyclobutane is a high energy, symmetry forbidden process[54]. The validity of the quasi-cyclobutane mechanism was

therefore called into question and as a result other mechanisms were proposed to account for metathesis which did not involve the formation of a cyclobutane ring. Lewandos and Pettit suggested that the bis-olefin complex was followed by the formation of a tetramethylene carbene metal complex[55]:

Scheme 1.4

The pairwise mechanism involving the formation of a tetramethylene carbene metal complex
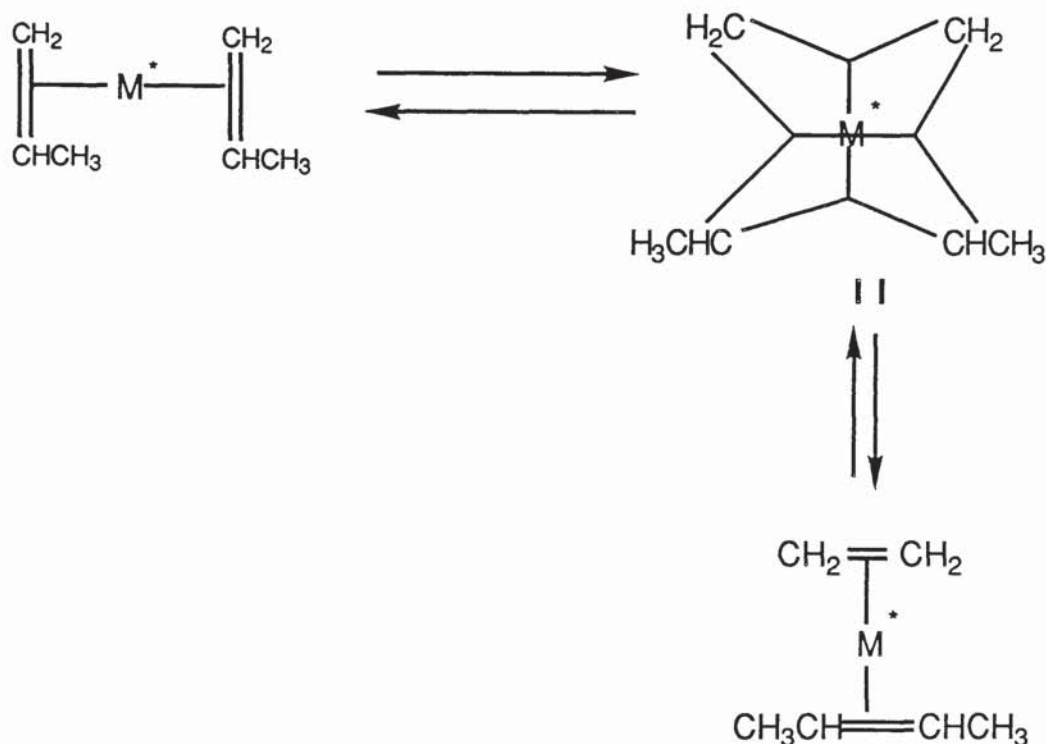
The mechanism suggested that a four centred diolefin complex was formed when the olefins interacted with the metal centre. Intermediate **II** was formed and this could rearrange either to form the products or the initial reactants. Lewandos and Pettit predicted, on the basis of molecular orbital theory, that the formation of **II** from the bis olefin complex was possible.

Grubbs et al. suggested a mechanism in which the bis-olefin complex and a metallocyclopentane intermediate were interconverted[56]. Two reactant olefins complex to the metal centre of the catalyst and form a metallocyclopentane intermediate **III**, which undergoes

44

rearrangement to form another metallocyclopentane intermediate **IV** that dissociates to yield product olefins and the metal centre, Scheme 1.5:

Scheme 1.5

The metallocyclopentane mechanism
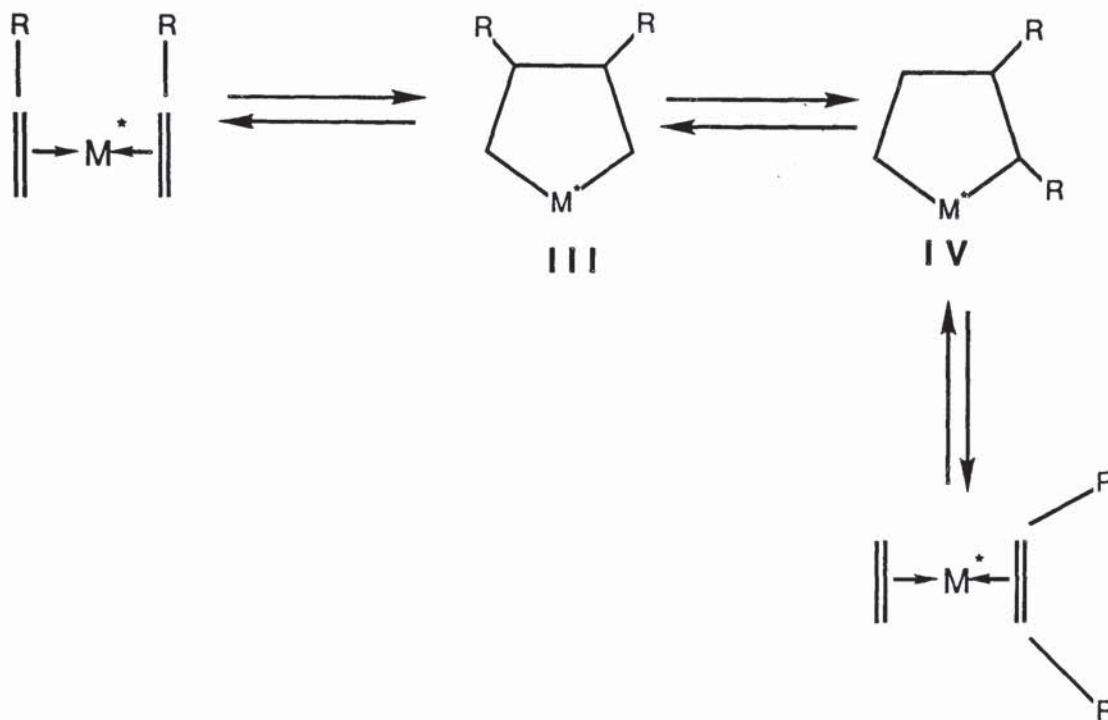
Support for this mechanism came from the formation of ethene from 1,4-dilithiobutane in the presence of a catalyst containing WCl_6 scheme 1.6. However it is probable that although such structures may be formed in the reaction between WCl_6 and $C_4H_8Li_2$, they do not play a significant role in the metathesis reaction itself.

Scheme 1.6

The decomposition of 1,4-dilithiobutane to produce ethene
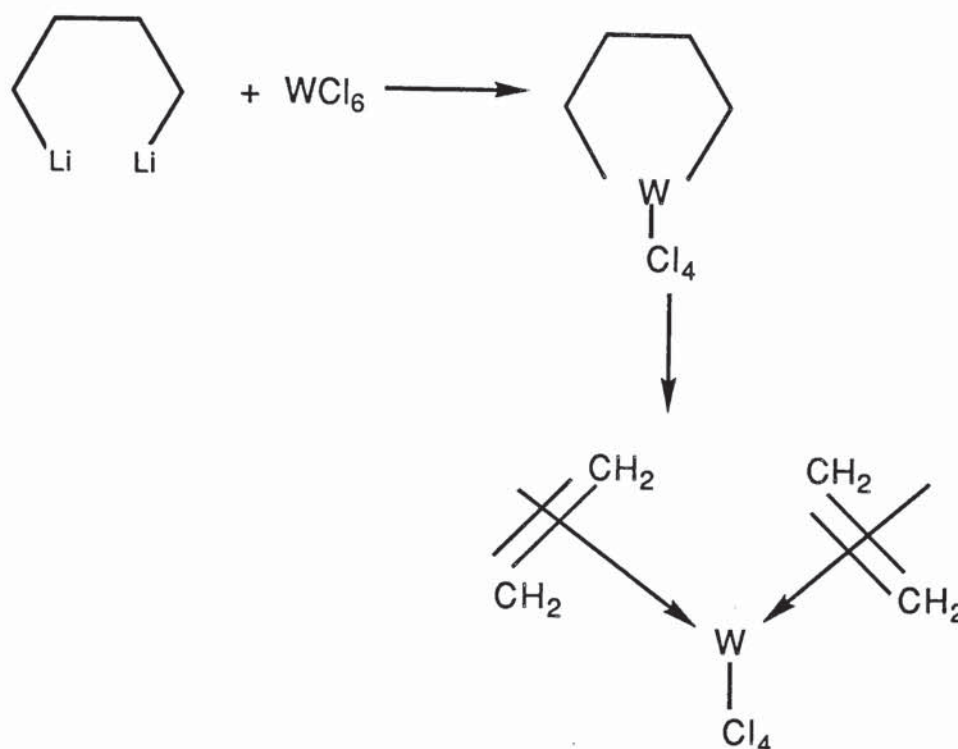
1.5.3. The carbene mechanism

Although the pairwise mechanisms could explain metathesis in terms of the direct exchange of alkylidene units between pairs of olefins, many features of reacting systems, whether olefin metathesis or ring opening polymerization, were unexplained. In ring opening metathesis polymerization, it was observed that the polymers obtained from the cyclo-olefins were of high molecular weight and predominantly linear in the initial stages of the reaction[57,58]. In the later stages, the concentration of cyclic oligomers increased significantly. Pairwise mechanisms indicate that cyclic polymer with a low molecular weight should be generated as the principal initial product and that the molecular weight would be expected to increase with conversion. Banks and Bailey found that the metathesis of ethene led to the formation of cyclopropane and methylcyclopropane[1]. The formation of these minor products could not be explained by a pairwise mechanism and precipitated the need for a mechanism that could explain these features of reacting systems. A mechanism which involved the breaking of carbon-carbon double bonds one at a time and transfered the alkylidene units, was first proposed by Herisson and Chauvin[12]. This non-pairwise mechanism later became known as the metallocarbene

46

mechanism and helped to explain the formation of high molecular weight, linear polymers as the initial products in ring opening metathesis polymerization.

It was known that cycloolefins and linear olefns could react in cross-metathesis reactions so that if $RCH=CHR^1$ were reacted with **VI** three classes of product were formed, which were

(i) $RCH=CH(CH_2)_xCH=CHR^1$ (A_1)

(ii) $RCH=CH(CH_2)_xCH=CHR$ (A_2) and

(iii) $R^1CH=CH(CH_2)_xCH=CHR^1$ (A_3)

VI

The distribution of products after significant reaction times was described by a thermodynamic equilibrium. Product A_1 could readily be explained on the basis of a pairwise mechanism as the interaction of $RCH=CHR^1$ with the cycloolefin whereas the formation of A_2 and and A_3 would result from secondary metathesis reactions. Either $RCH=CHR^1$ would have to undergo pairwise metathesis first to form $RCH=CHR$ and $R^1CH=CHR^1$ which would metathesise with cycloolefins or A_1 would undergo a metathesis of the terminal carbon-carbon double bond. Whichever of these explanations was appropriate the initial products of metathesis would not be expected to include A_2 and A_3.

Herisson and Chauvin explained the distribution of products on the basis of the mechanism shown in scheme 1.7:

Scheme 1.7

The metallocarbene mechanism for the metathesis of linear olefins

$$\overset{|}{\underset{|}{W}} = \text{vacant active site on catalyst}$$
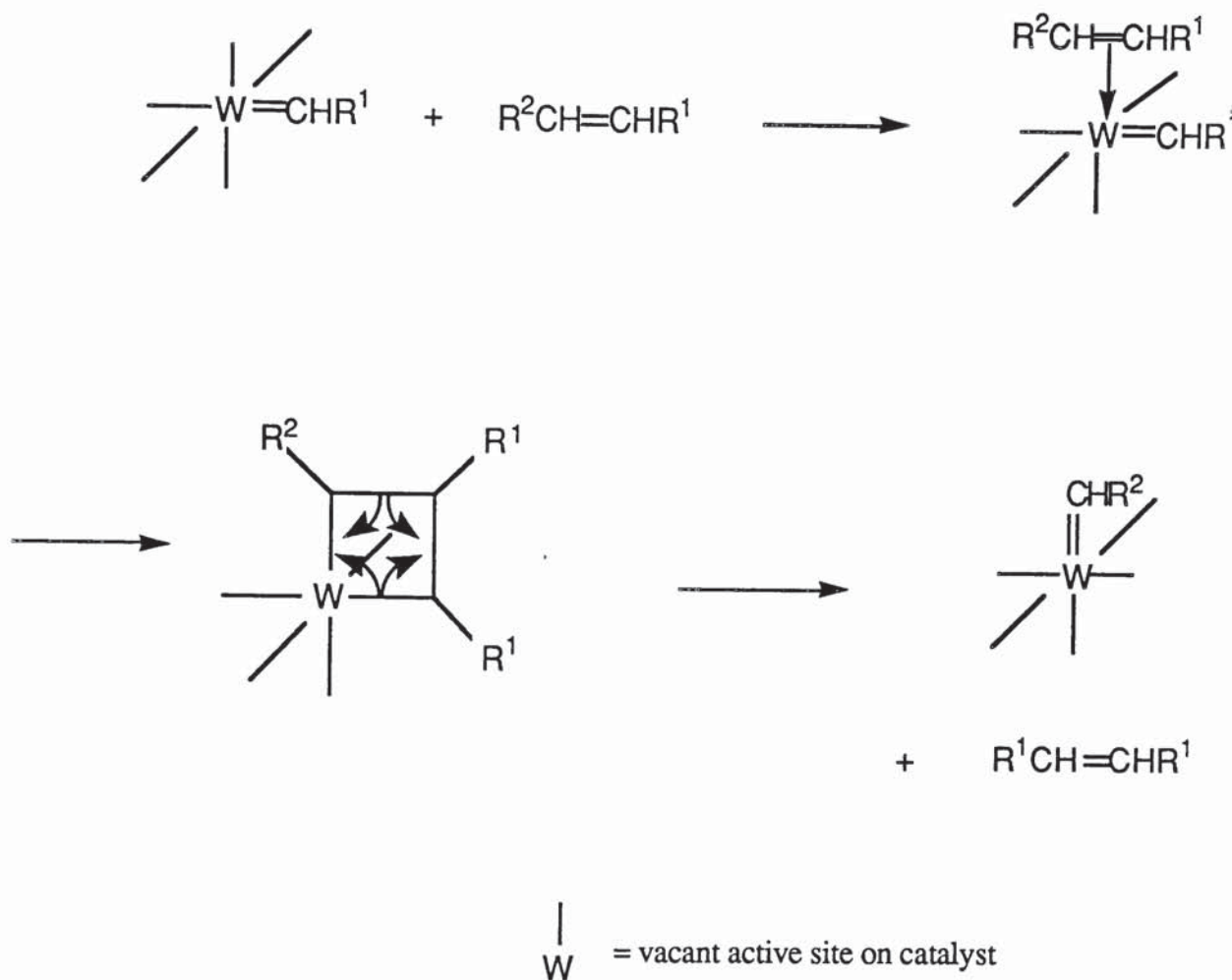
It was suggested that the active centre in the reaction was a transition metal carbene which possessed a vacant coordination site or a labile ligand. The carbon-carbon double bond of the reacting olefin then displaced the labile ligand and co-ordinated at the metal centre. The reaction proceeded by formation of an intermediate metallocyclobutane which could either revert to the original olefin or cleave along the alternative line to produce another metal carbene and a product olefin. The mechanism could also be applied to the polymerization of cycloolefins as shown in scheme 1.8 and the range of products obtained in the cross-metathesis were explained by application of scheme 1.9:

Scheme 1.8

The metallocarbene mechanism for the ring opening metathesis polymerization of cycloolefins
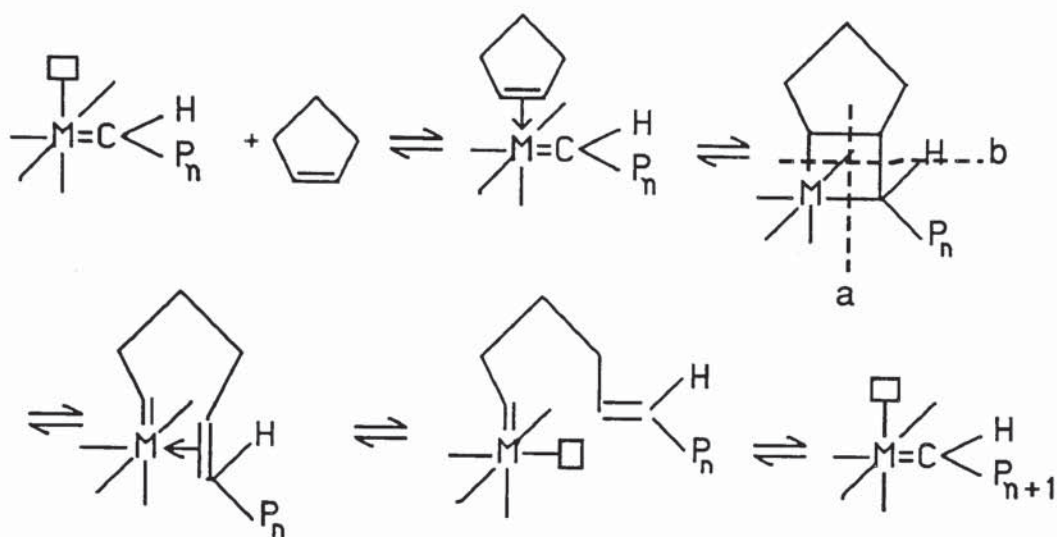
Confirmatory work by Katz and McGinnis helped to discount the pairwise mechanism and provided substantial evidence for the carbene mechanism[59]. A series of double cross experiments were performed to differentiate between the carbene and pairwise mechanisms, scheme 1.10 (a) and 1.10 (b). Cyclooctene was metathesised with a mixture of 2-butene and 4-octene. If the pairwise mechanism was in operation C_{12} and C_{16} would be the primary metathesis products obtained from pairwise metathesis of cyclooctene and C_4 and C_8 respectively; C_{14} would be a secondary product after first having formed C_6 by metathesis of C_4 and C_8. However, the metallo-carbene mechanism provides two routes to the formation C_{14} which do not rely on the prior metathesis of C_4 and C_8 to C_6. Furthermore, there are two routes to the formation of C_{14} to one each for the formation of C_{12} and C_{16}. Accordingly C_{14}/C_{12} and C_{14}/C_{16} would be expected to be greater than unity.

1.5.3.1. Studies concerned with the initially formed products

One of the major questions arising from the carbene mechanism is how are the metal centres of the catalyst systems converted into carbenes? Muetterites proposed that in homogeneous systems, alkylating reagents were important in the initial reaction to produce carbenes, eg tungsten hexachloride and dimethyl zinc[20]. It was suggested that the metal alkyl interacted with

the tungsten hexachloride followed by elimination of the α- H group through either paths 1 or 2 to produce the metallocarbene, scheme 1.11. Evidence for this comes from the use of tetramethyltin as a cocatalyst for the metathesis catalysts. Analysis in the initial stages of the reaction show the presence of methane.

The work by Greenlee and Farona provided direct evidence that the reaction was both initiated and propagated by coordinated carbenes[19]. When 1,7-octadiene was metathesised using $Re(CO)_5Cl/C_2H_5AlCl_2$, the first formed olefins were identified as 1-butene and 1,7-decadiene. This indicated the formation of a propylidene initiating carbene, scheme 1.12. Motz and Farona investigated the importance of the solvent in the formation of the initial carbene using the homogeneous catalyst $Mo(CO)_5py$ with $C_2H_5AlCl_2$ or CH_3AlCl_2 as the cocatalysts[26]. In chlorobenzene, the initial carbenes formed were ethylidene and methylene from the respective $C_2H_5AlCl_2$ and CH_3AlCl_2 cocatalysts, but in heptane they were propylidene and ethylidene respectively.

Scheme 1.9

The cross metathesis between 2-pentene and cyclopentene

$C_2H_5CH=CH(CH_2)_3CH=CHCH_3$

$CH_3CH=CHC_2H_5$

$M=CHCH_3$

$M=CH(CH_2)_3CH=CHCH_3$

$C_2H_5CH=CH(CH_2)_3CH=CHC_2H_5$

$CH_3CH=CHC_2H_5$

$CH_3CH=CH(CH_2)_3CH=CHCH_3$

$CH_3CH=CHC_2H_5$

$M=CH(CH_2)_3CH=CHC_2H_5$

$M=CHC_2H_5$

$CH_3CH=CHC_2H_5$

$C_2H_5CH=CH(CH_2)_3CH=CHCH_3$
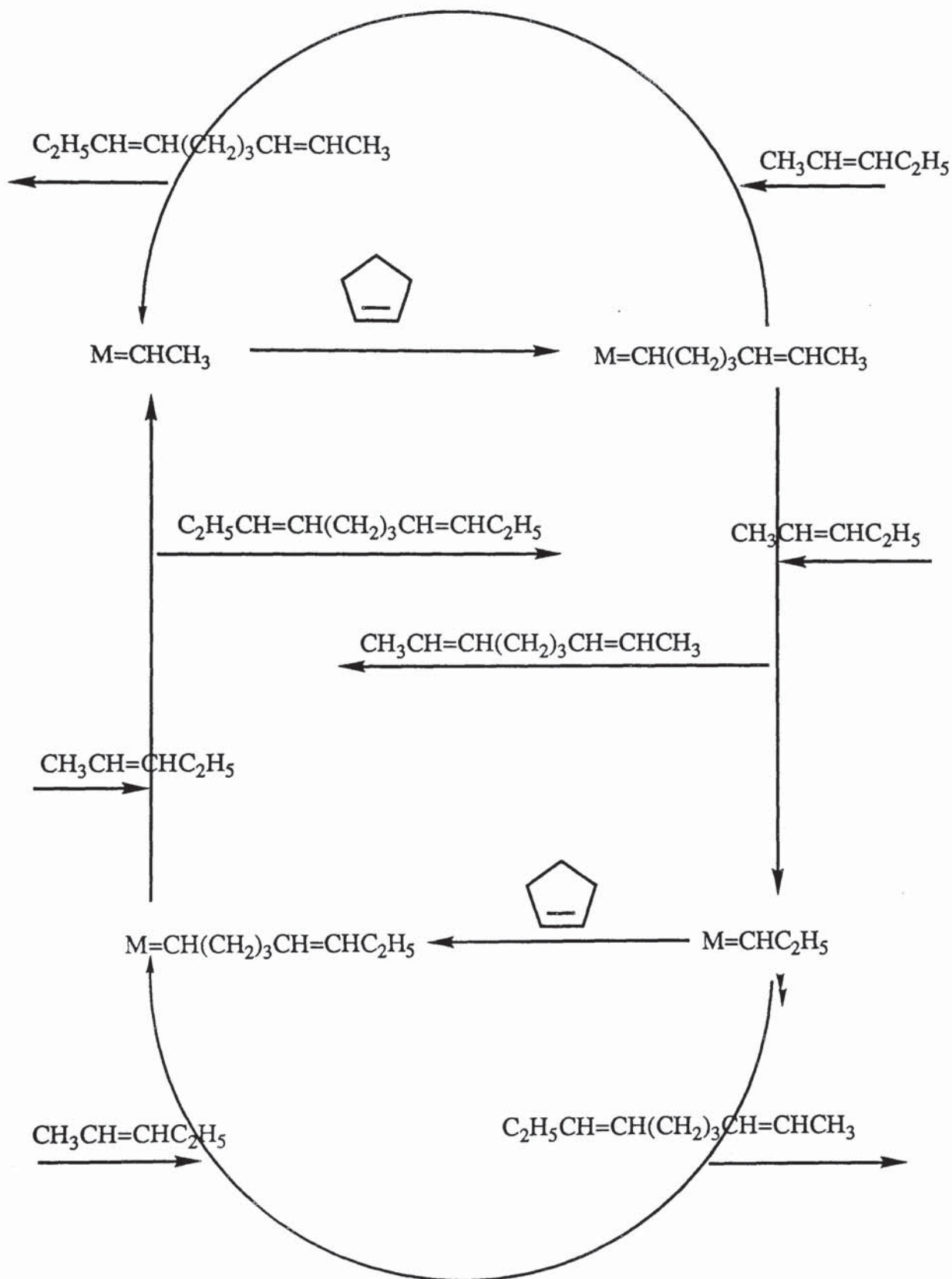
Scheme 1.10 (a)

The double cross experiments/Pairwise scheme

$$CH_3CH=CHCH_3 + C_3H_7CH=CHC_3H_7 \longrightarrow 2CH_3CH=CHC_3H_7$$
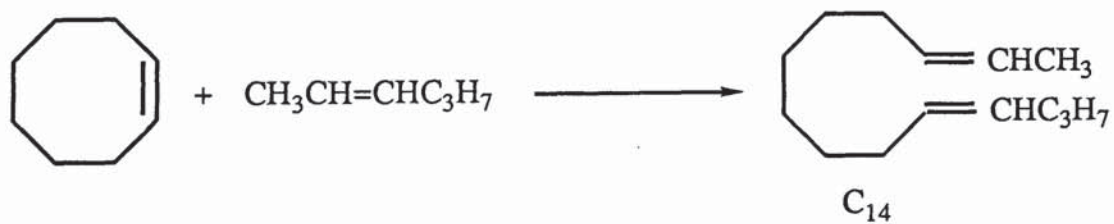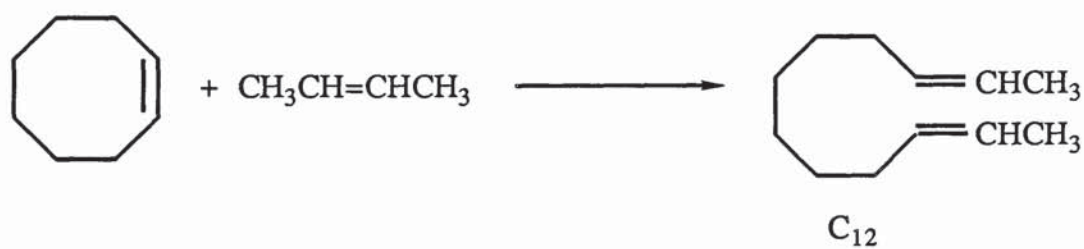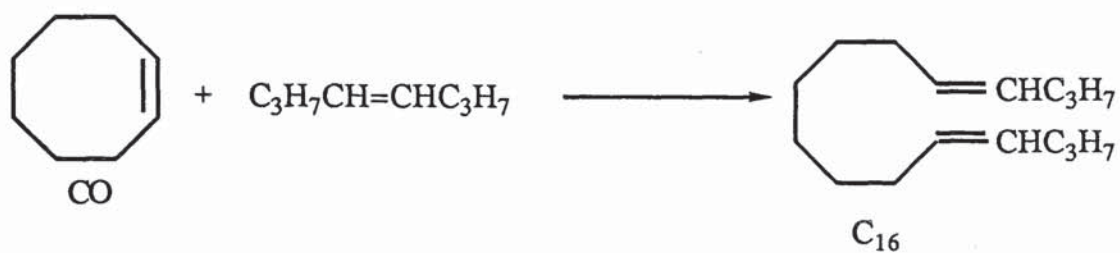
Scheme 1.10 (b)

The double cross experiments/Non-pairwise scheme

$$M=CHCH_3 \xrightarrow{CO} M=CH(CH_2)_6CH=CHCH_3$$

$$CH_3CH=CHCH_3 \rightarrow M=CHCH_3 + C_{12}$$

$$C_3H_7CH=CHC_3H_7 \rightarrow M=CHC_3H_7 + C_{14}$$

$$M=CHC_3H_7 \xrightarrow{CO} M=CH(CH_2)_6CH=CHC_3H_7$$

$$CH_3CH=CHCH_3 \rightarrow M=CHCH_3 + C_{14}$$

$$C_3H_7CH=CHC_3H_7 \rightarrow M=CHC_3H_7 + C_{16}$$
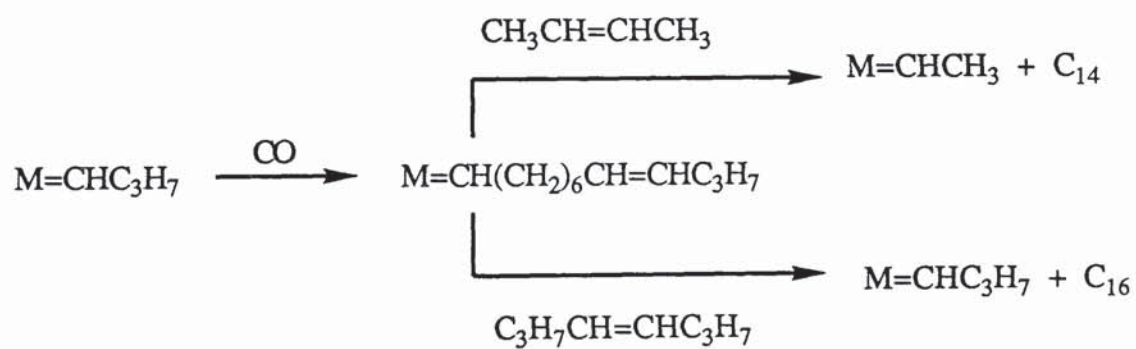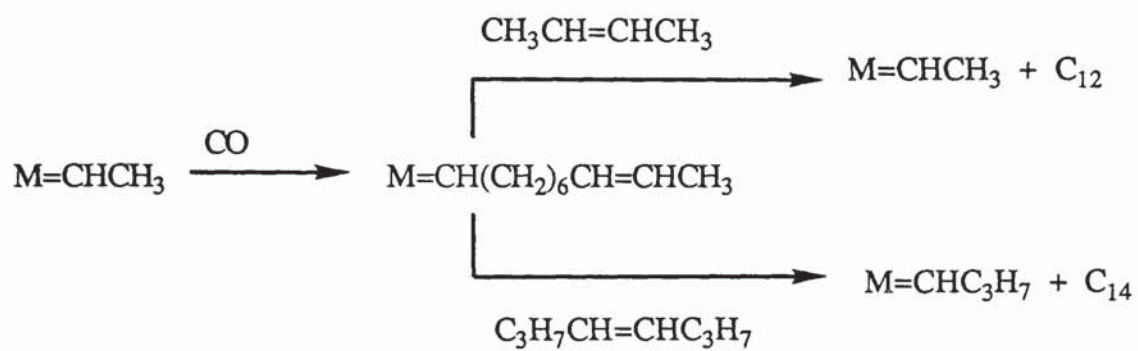
Scheme 1.11
Alkylation of the metal centre to produce the metallocarbene

1

2
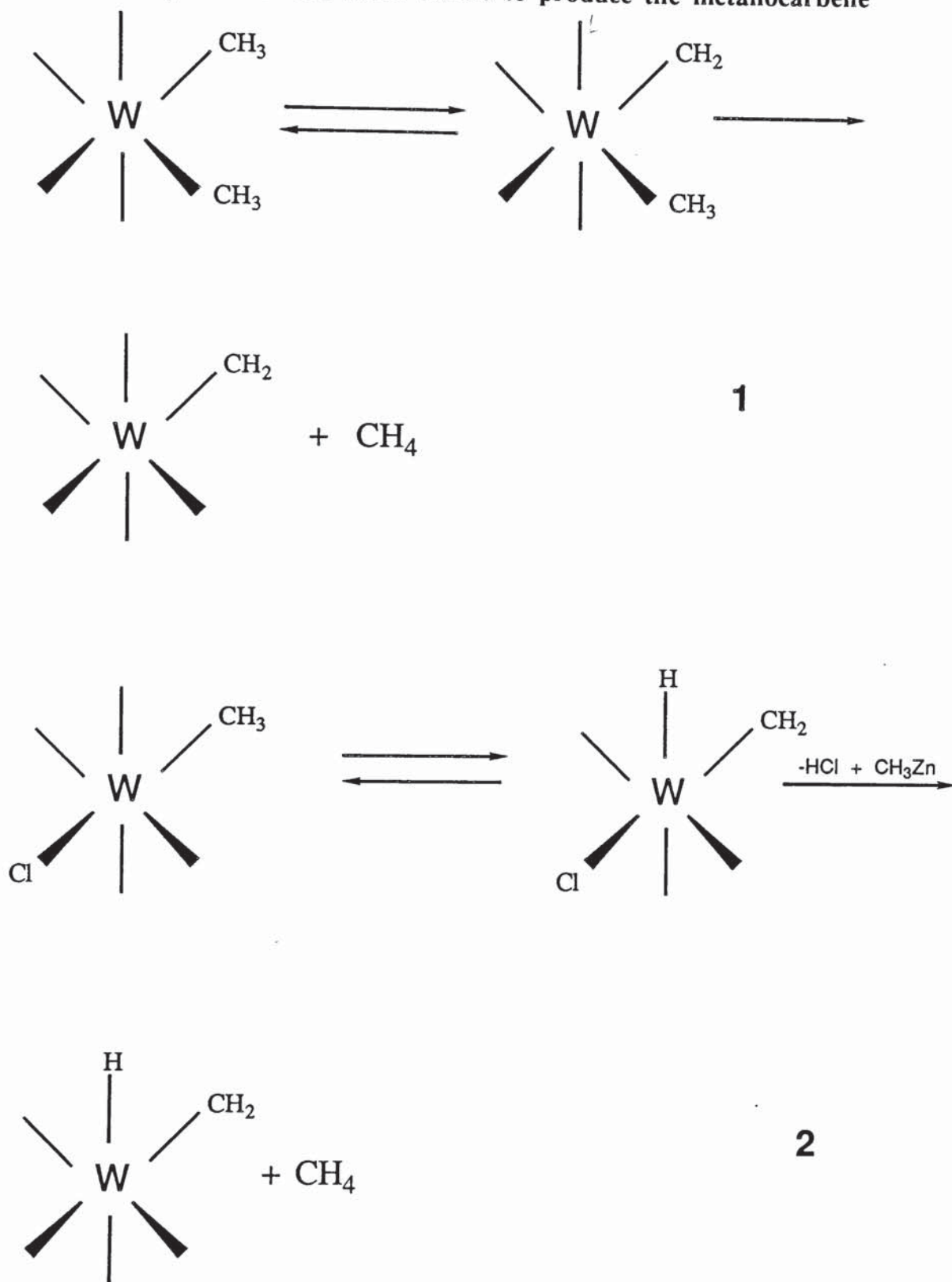
Scheme 1.12
Formation of the coordinated metallocarbene
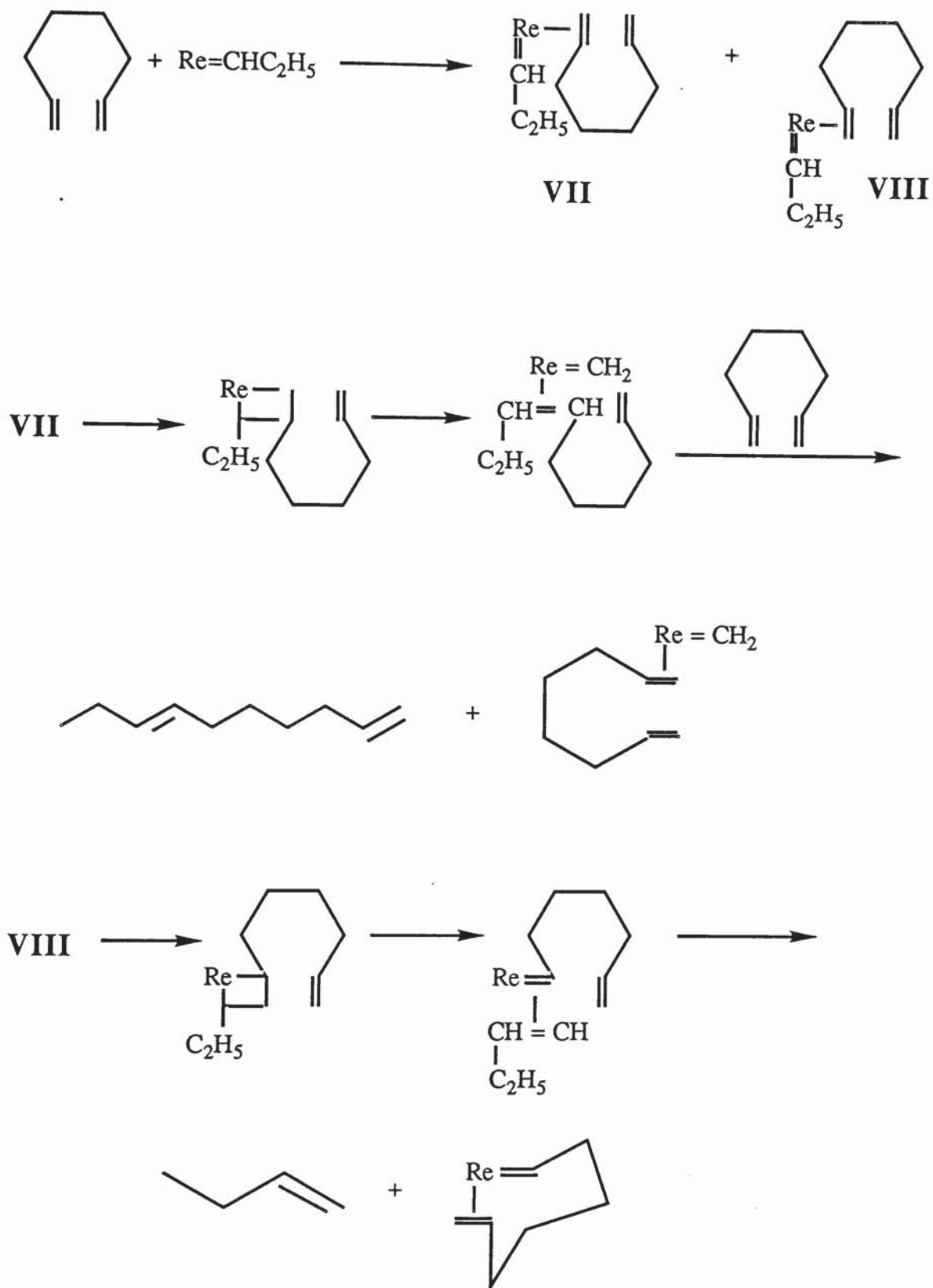
1.5.3.2. Carbene intermediates in the metathesis reaction

The mechanism proposed by Herisson and Chauvin postulated the participation of transition metal carbenes as intermediates in the reaction[12]. In general, transition metal carbenes are unstable species, but in 1964, Fischer disclosed the synthesis of a heteroatom stabilized transition metal carbene complex **IX** based on tungsten, which was air stable[60]. Transition metal carbenes require at least one heteroatom, usually oxygen or nitrogen, directly bonded to the carbene carbon atom if the compound is to be stable. The heteroatom stabilises the carbene by donating electrons to the electron deficient carbene carbon atom to form a conjugated system.

IX
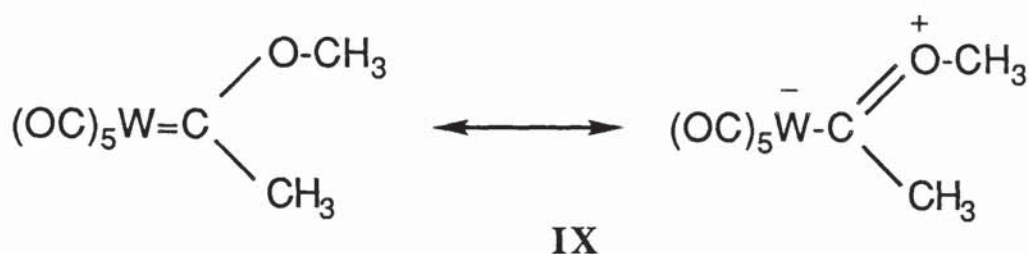
Carbenes containing only carbon and hydrogen were rarely isolated because they contained no stabilising heteroatoms and are therefore very reactive. However, Casey and Burkhardt managed to synthesise one of the first stable, heteroatom-free transition metal carbene complexes **X**, using the substitution reaction shown in the following equation[13]:

X
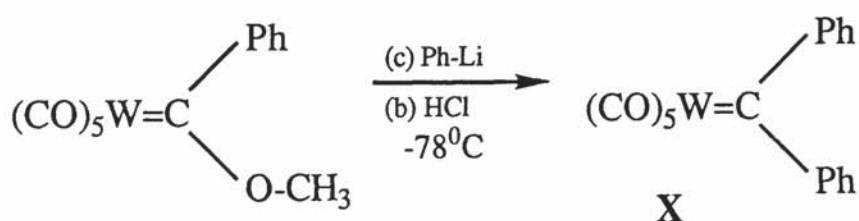
In this case the stability of the transition metal carbene was associated with conjugation of the phenyl rings with the tungsten-carbon double bond.

Schrock later reported the synthesis of heteroatom-free metal alkylidene complexes **XI** by reacting a metal alkyl such as neopentyl lithium with a metal halide, $TaCl_5$[61], eg

$$(X^-)_3 \, TaCl_2 \; + \; Li\text{-}CH_2C(CH_3)_3 \; \rightleftharpoons \; (X^-)_3 \, Ta{=}C\begin{smallmatrix} \nearrow\, C(CH_3)_3 \\[4pt] \searrow\, H \end{smallmatrix}$$

<div align="center">XI</div>
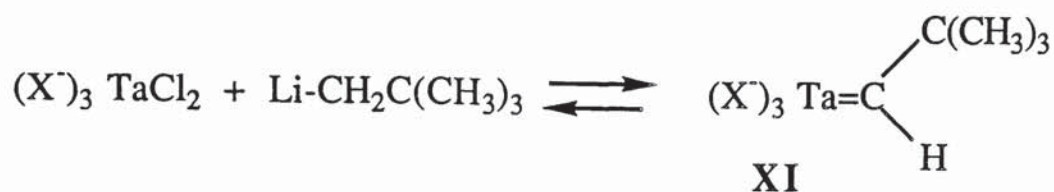
where X = halide groups

The electron donating alkyl and electron withdrawing effects of the halide groups stabilise the electron deficient metal centre to produce a stable complex, which was characterised by nmr and mass spectroscopy.

When the procedures for the synthesis of stable transition metal carbenes and alkylidenes had been established, complexes were prepared systematically to investigate their catalytic efficiency towards the metathesis reaction. Support for the participation of a metal carbene in the mechanism came when Casey and Burkhardt showed that their original carbene X, (diphenylcarbene)pentacarbonyltungsten, could react with electron rich olefins such as 1-phenoxy-1-phenylethene to produce a new olefin and a carbene complex, as summarised below[62]:

$$(CO)_5W{=}C\begin{smallmatrix} \nearrow\, Ph \\[4pt] \searrow\, Ph \end{smallmatrix} \;\;\; + \;\;\; CH_2{=}C\begin{smallmatrix} \nearrow\, O\text{-}Ph \\[4pt] \searrow\, Ph \end{smallmatrix} \;\;\; \longrightarrow$$

<div align="center">X</div>

$$(CO)_5W{=}C\begin{smallmatrix} \nearrow\, O\text{-}Ph \\[4pt] \searrow\, Ph \end{smallmatrix} \;\;\; + \;\;\; CH_2{=}C\begin{smallmatrix} \nearrow\, Ph \\[4pt] \searrow\, Ph \end{smallmatrix}$$
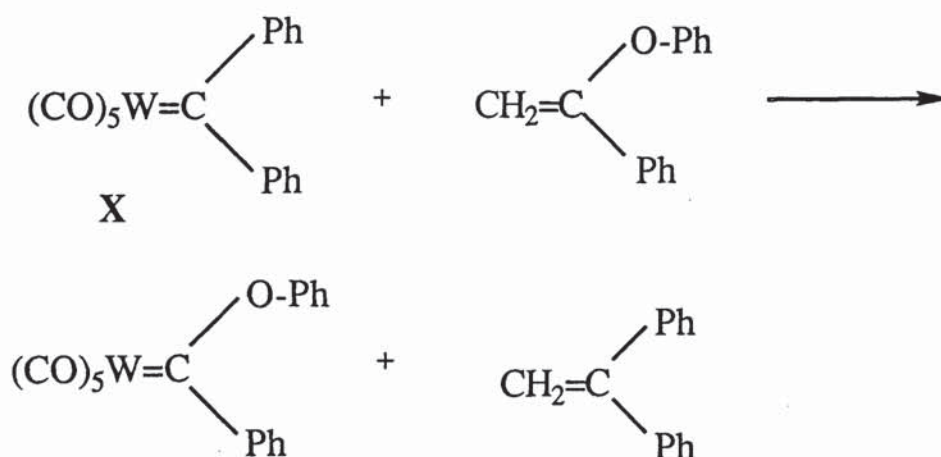
It was proposed that a metal complex intermediate, comprising a metallocarbene and an olefin, rearranged to form metallocyclobutane which could cleave to produce a new metal complex containing a new metallocarbene complexed to an olefin. The interconversion between the metal carbene and the metallocyclobutane provided supportive evidence for a chain mechanism

as suggested by Herisson and Chauvin. The initial studies of the participation of transition metal carbene complexes as intermediates produced circumstantial evidence that these complexes acted as reactive intermediates. After reacting $(CO)_5WC(Ph)_2$ with isobutene, the products of the initial metathesis steps, namely diphenylethene and a cyclopropane derivative, which was believed to arise from the reductive elimination of the the metallocyclobutane, were separated:
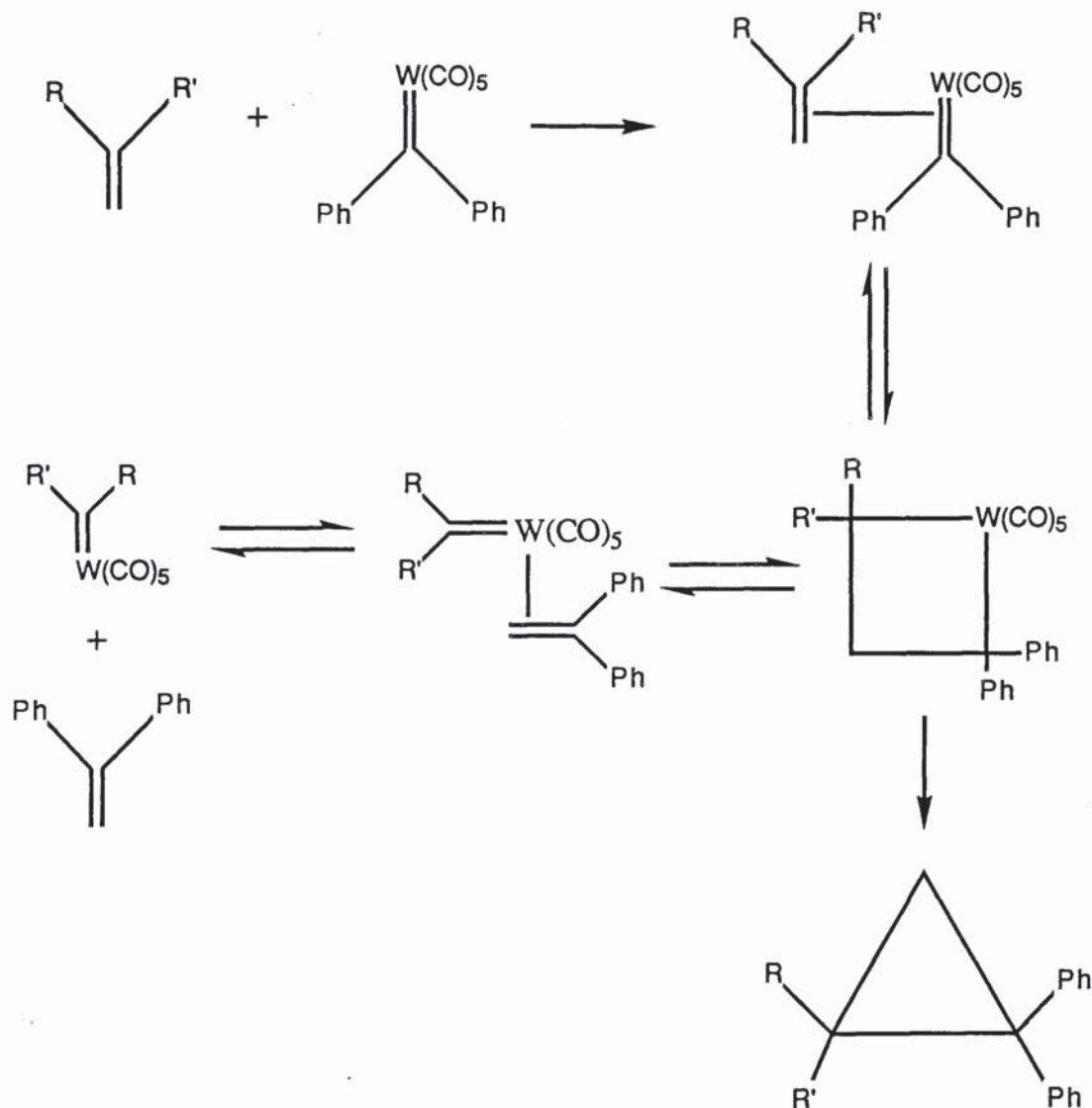
Until quite recently truly catalytic transition metal carbenes were not available. However, in 1980 Schrock synthesised a series of stable metal carbenes of the general formula W(CH-t-Bu)(O)(L$_2$Cl$_2$), where L = a trialkylphosphine, that were very active as initiators for the metathesis of terminal and internal olefins in the presence of AlCl$_3$[63]. Osborn has synthesised

similar stable complexes of the type $W(CHR)(OCH_2Bu^t)_2X_2$ which were able to initiate the metathesis of *cis* 2-pentene in the presence of Lewis acids such as $AlBr_3$ and $GaBr_3$[64].

Shrock et al later prepared active, neutral, 4 coordinate complexes of the type $W(CH-t-Bu)(NAr)(OR)_2$ where OR, the ligand, varied from a relatively donating alkoxide, (O-t-Bu), to a highly electron withdrawing alkoxide, $OC(CF_3)(CF_2CF_2CF_3)$[65]. The activity of the various complexes as metathesis catalysts was investigated using *cis* 2-pentene and their metathetical activity was found to be dependent upon the electronegativity and the size of the alkoxide ligand. It was found that the greater the electronegativity of the alkoxide group the more rapidly the olefin underwent metathesis but if the ligand was large and bulky, steric hindrance became the limiting factor. It therefore appeared that electrophilicity of the metal in the carbene was a crucial factor in the activity of the catalyst. In line with this theory it was also discovered that the stability of the metallocyclobutane complex increased as the alkoxide group became more electronegative and hence as the metal became more electrophilic.

1.5.3.3. Metallocyclobutane intermediates in the metathesis reaction

The metathesis reaction has been studied extensively and it is now widely agreed that the reaction proceeds via a mechanism involving metal alkylidenes and metallocyclobutane intermediates. Many metal alkylidenes have been synthesised and isolated and their ability to behave as metathesis catalysts has helped to confirm the participation of such intermediates in metathesis. In contrast, the involvement of metallocyclobutane intermediates has not been well documented and much of the work in this area has been carried out by Grubbs.

Grubbs et al reported the isolation of a titanocyclobutane from the reaction of the 'Tebbe' reagent with neohexene, in the presence of pyridine[14,66]. Tebbe's reagent is a well-defined complex obtained from the reaction of titanocene dichloride and alum trimethyl[29]:

"Tebbe" reagent

titanocyclobutane
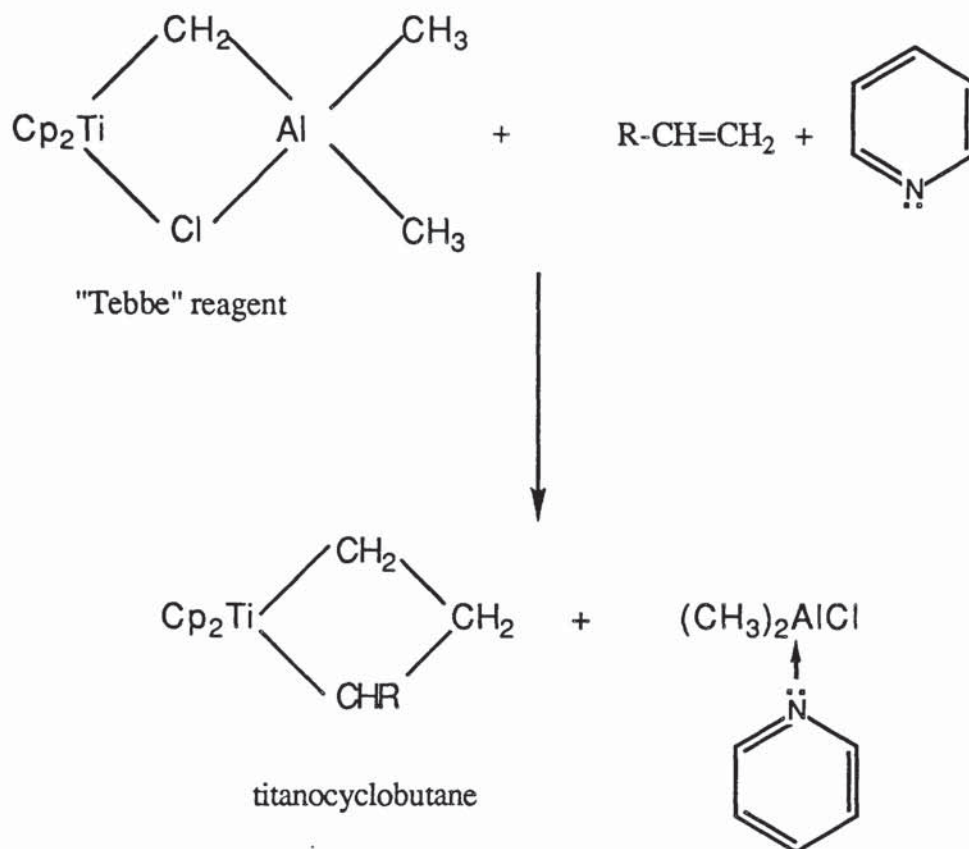
The titanocyclobutane intermediate has been shown to be an active metathesis catalyst towards the metathesis of terminal olefins[30], eg
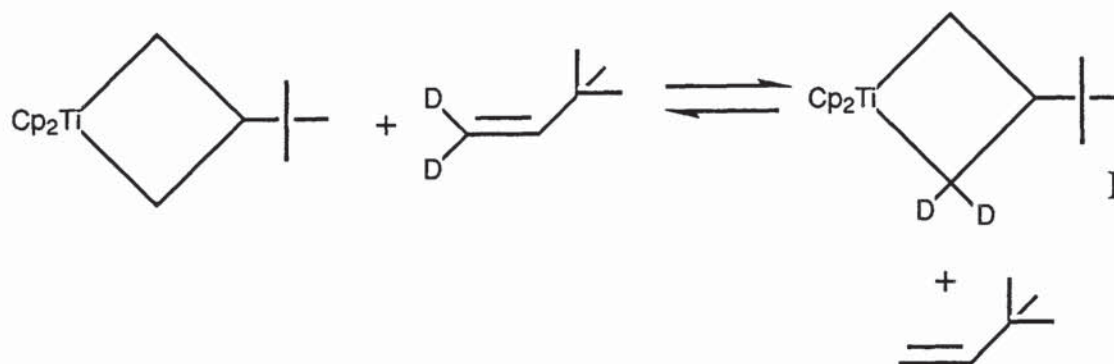
and has also been used to produce living polymers from norbornene[31], eg

$$+ \text{ DMAP.AlMe}_2\text{Cl}$$
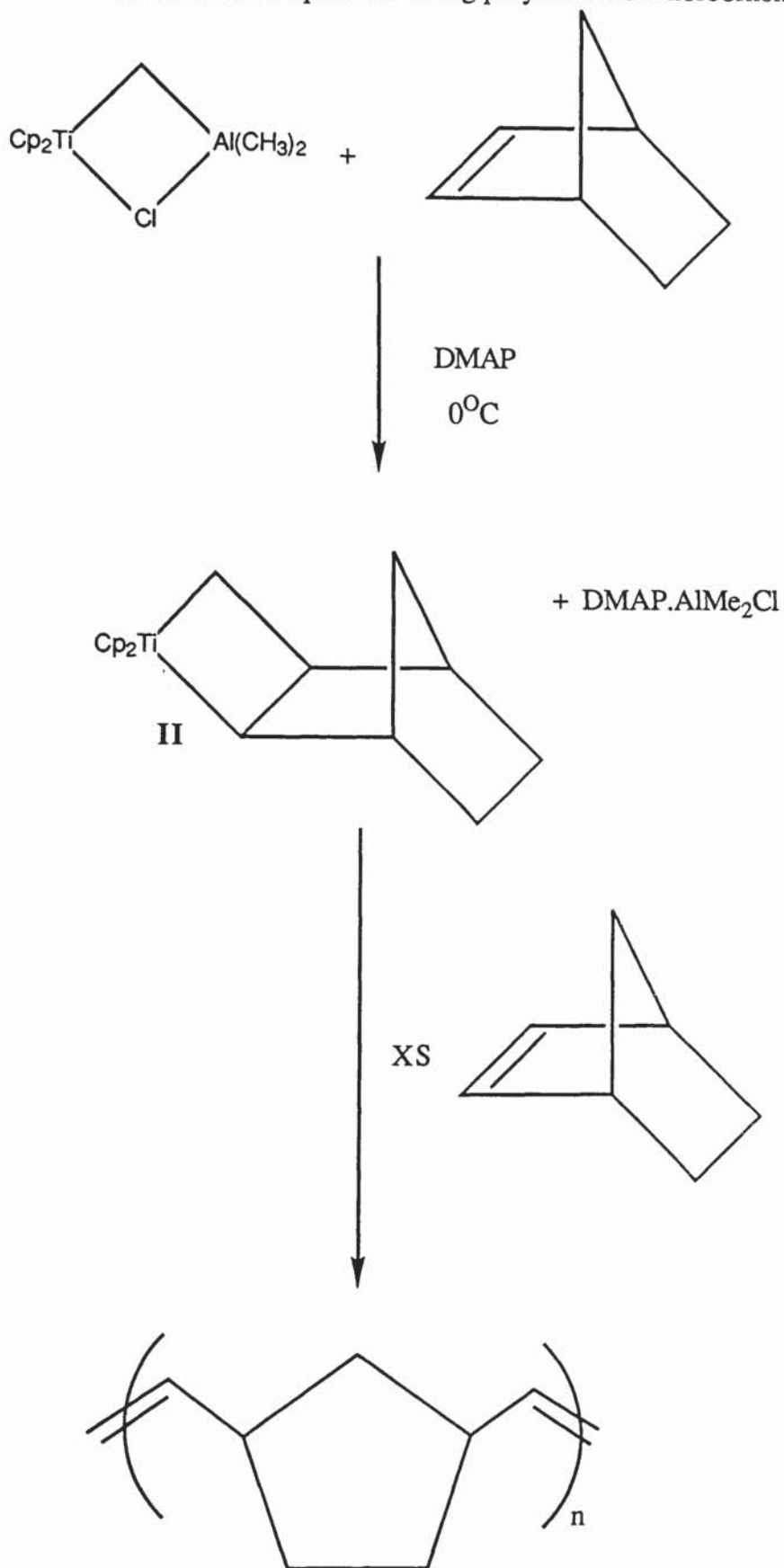
To determine the nature of the reactive intermediates in the above reaction, Grubbs et al examine the kinetic behaviour of **I** with diphenylacetylene to produce titanocyclobutene[30].

The reaction was found to be first order in **I** and independent of the concentration of diphenylacetylene over a wide range of concentrations.

The results suggested that the exchange of acetylenes with **I** occurred via the ring opening of the titanocyclobutane to the titanium-methylene-olefin complex **XII**, which reversibly loses olefin to produce the titanium-methylene complex **VX**. This is trapped rapidly by the incoming acetylene to produce titanocyclobutene. In the absence of a suitable substrate, **XIII** dimerizes to yield **XV** which represents the chain termination step of this metathesis system.

These results led Grubbs to suggest that the stable chain propagating species in the metathesis reaction is a metallocyclobutane and not the titanocene methylidene, the metal-alkylidene species, as suggested by workers such as Schrock.

1.6. The stereochemistry of olefin metathesis

The early workers on the olefin metathesis reaction observed geometric isomerization of internal acyclic olefins and the results led them to believe that such isomerization was affected by the mechanism for the metathesis reaction[1,5,50]. The stereochemistry of ring opening metathesis polymerization can be regulated by the reaction conditions and by the type of catalysts used. Consequently, this enables polymers with known properties to be synthesised specifically. Considerable interest has been shown on the control of stereochemistry of olefin metathesis which appears to be dependent on the ligand and metals used.

1.6.1. The stereochemistry of acyclic olefin metathesis

Calderon et al. investigated the homogeneous metathesis of pure *cis* and *trans* 2-pentene using the classical catalyst system of $WCl_6/EtOH/EtAlCl_2$[17]. The results showed that both the *cis* and *trans* isomers of 2-butene and 3-hexene were formed in the initial stages of the reaction but that the *cis* content of both products was somewhat higher than the thermodynamic equilibrium values for these olefins, regardless of the steric structure of the initial 2-pentene. It was also observed that throughout the reaction, the *cis* :*trans* ratio of 2-butene was lower than that corresponding to *cis* : *trans* 3-hexene.

Wang and Menapace demonstrated the dependence of the stereoselectivity of the metathesis reaction on the type of catalyst used[18]. Using $WCl_6/BuLi$ as the catalyst, it was found that the percentage conversion of *trans* 2-pentene was significantly lower than that of the *cis* isomer. This difference in behaviour was attributed to the steric hindrance that occurred when the *trans* isomer coordinated to the tungsten atom. The 2-butene product in all cases was predominantly *trans* . Similar results were recorded by Basset et al who noted that according to the carbene mechanism, the coordinated carbene had a high barrier to rotation and therefore, the stereochemistry of the product would depend mostly on the geometry of approach of the incoming olefin[67]. It was observed that in the metathesis of 2-pentene, *cis* olefins were better at initiating the formation of the metallocarbenes than were the *trans* isomers which was accounted for by steric effects. Consequently, steric effects during the coordination of the olefin to the metallocarbene, steric effects of the ligands on the transition metal, the stability of

63

the various conformations of the metallocyclobutane transition state, and cleavage and rotation about the metal-carbon in the metallocyclobutane intermediate were thought to be responsible for the stereoselectivities observed in homogeneous olefin metathesis of acyclic olefins.

1.6.2. The stereochemistry of olefins in ring opening metathesis polymerization

Polymers produced by ring opening metathesis polymerization of cyclic olefins potentially exhibit three different forms of isomerism depending upon whether they are monocyclic or bicyclic compounds[2,6,68]. In each case polymerization leads to an in-chain carbon-carbon double bond and the configuration around the carbon-carbon double bond in the polymer chain can be either E or Z. If the polymerization of a monocyclic olefin is catalysed by metathesis, then there is considerable evidence to suggest that the in-chain carbon-carbon double bond undergoes secondary metathesis reactions since the microstructure of the polymer changes during the course of the polymerization reaction. In contrast the polymerization of bicyclic monomers such as norbornene do not undergo such secondary metathesis reactions. Thus any stereochemistry introduced into the polymer chain during propagation remains unchanged since the carbon-carbon double bonds are so sterically hindered as to be unable to react. In addition to the stereochemistry associated with the carbon-carbon double bonds, polymers of norbornene and its derivatives show stereochemistry associated with the tacticity of the cyclopentyl ring.

Tacticity in a polymer is a form of isomerism which arises when the monomer unit contains a chiral methine carbon atom[68]. Various arrangements of these chiral centres along the polymer chain are possible but it is convenient to consider the chiral centres in parts. If within the polymer chain two consecutive chiral centres have the same configuration, this is referred to as a meso (m) dyad and if they have opposite configurations, a racemic (r) dyad, ie

CH=CH—[cyclopentane]—CH=CH—[cyclopentane]—CH=CH—[cyclopentane]   isotactic

S   m dyad   S   m dyad   S

CH=CH—[cyclopentane]—CH=CH—[cyclopentane]—CH=CH—[cyclopentane]   syndiotactic

r dyad   r dyad

S   R   S
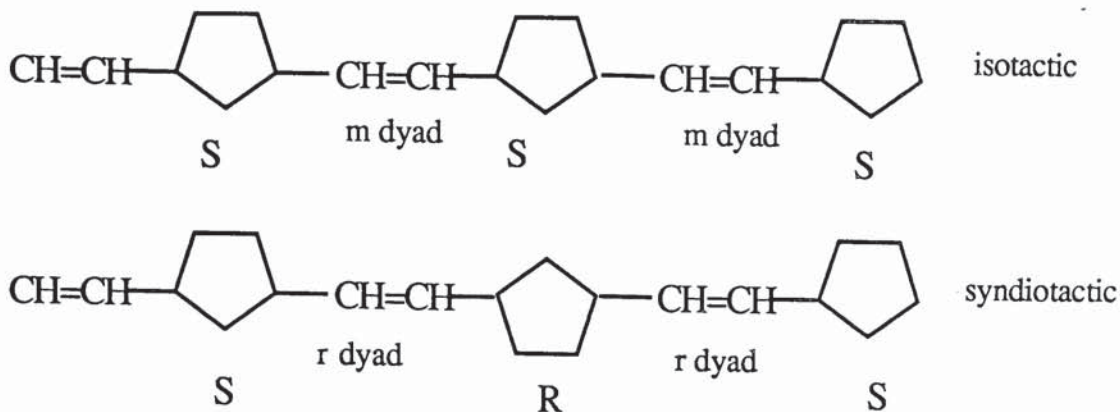
Two types of completely stereoregular polymers can exist: an isotactic polymer is one which is comprised exclusively of meso dyads and a syndiotactic polymer comprised exclusively of racemic dyads. Polymers which do not conform to either of these extremes are known as atactic. A further complication may arise when the monomer polymerised is a substituted norbornene such as 4-methylnorbornene:

Me   Me
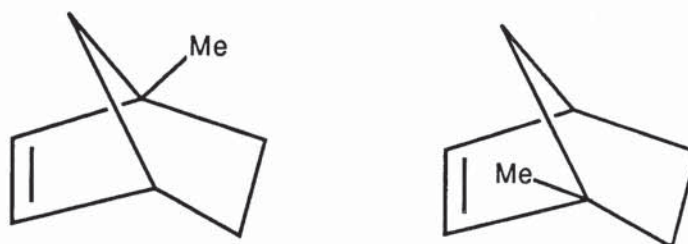
Polymerization by ring opening metathesis catalysts may now give rise to another form of stereoisomerism associated with the direction of cleavage of the ring containing the carbon-carbon double bond. Thus head-to-tail, head-to-head and tail-to-tail placements may be found, eg

=CH—[cyclopentane]—CH=CH—[cyclopentane]—CH=CH—[cyclopentane]—CH=

Me   Me   Me

tail to head (TH)   tail to tail (TT)
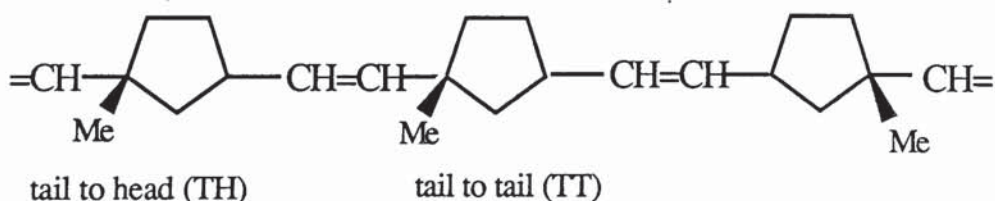
1.6.3.   The stereochemistry of norbornene and its derivatives

Ivin et al. have investigated the polymerization of norbornene and its derivatives using different catalysts and co-catalysts, analysing the polymers by ^{1}H and ^{13}C nmr, and found that the fraction of double bonds with a *cis* (Z) configuration, ρ_c, varied between 0.2 and 0.8[69]. It

was found that when ρ_c was less than 0.35, the distribution of *cis* and *trans* (E) double bonds was random, thus giving a random polymer. When ρ_c was between 0.5 and 0.85, polymers with long blocks of *cis* double bonds were produced. The transition metal of the catalyst and co-catalyst is not solely responsible for controlling the stereochemistry of the polymer because the same transition metal can produce different polymer structures. Ivin postulated the existence of at least two kinetically distinct propagation species which were in equilibrium with each other, but their rate of exchange was affected by the value of ρ_c for the particular catalyst. These species had structures that were postulated to be:
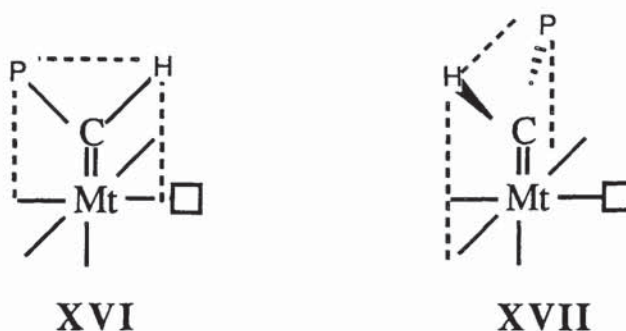
When the value of ρ_c is low, these species can exchange with each other rapidly so that the resulting polymer will consist of a random distribution of *cis* and *trans* double bonds. At higher values of ρ_c the rate of exchange between and **XVII** is reduced and blocky polymers are produced because if the active centre has a *cis* configuration, it will continue to produce *cis* polymer until it is disturbed from that mode.

In order to distinguish between isotactic, syndiotactic and atactic polymers and any association between ring tacticity and carbon-carbon double bond isomerism, it is necessary to use a monomer, eg 1-methylbicyclo[2.2.1]2-heptene (MNBE), which enables the two types of dyads (m and r) to be distinguished[69]. Experimental analysis has shown all combinations of arrangements are possible but not *cis* -head to head. There are two possible classes of propagating metallocarbenes for the polymerization of MNBE; one has the methyl group adjacent to the carbene, P_H, and the other has it removed from the carbene, P_T[70]. The metal centre can also be considered to be chiral and therefore each of the propagating species can exist in one of two enantiomeric forms (+ or -):

P_T^+

P_T^-

P_H^+

P_H^-
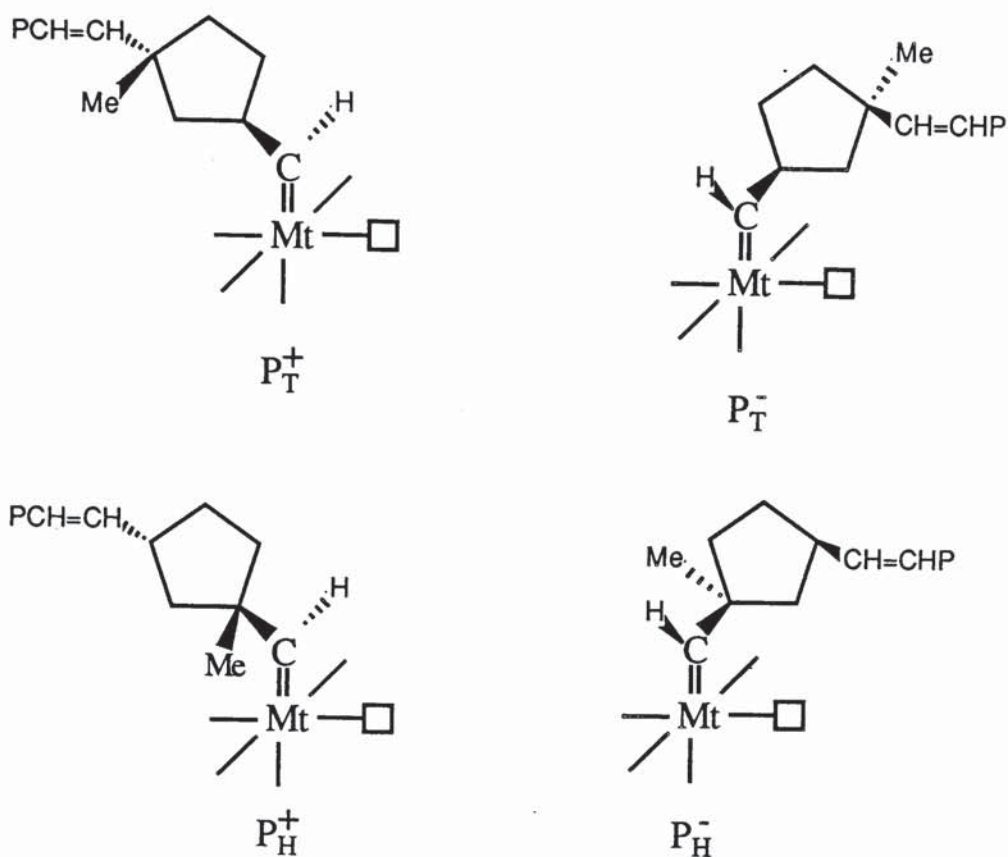
MNBE can exists in either of its enantiomeric forms, ie
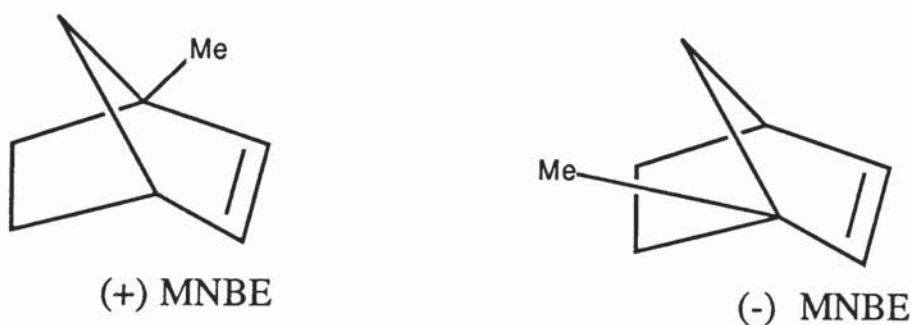
(+) MNBE

(-) MNBE

Detailed analysis of the structure of MNBE polymers showed that:

i) if the polymer had a high *cis* (Z) content, then the arrangements of the monomer were biased towards head-to-tail and the rings exhibited syndiotactic isomerism.

ii) if the polymer had a high trans (E) content, then head-to head followed by tail-to-tail arrangements were common and the rings were atactic.

Analysis has shown that catalysts that produce high *cis* polymers also have head-to-tail, syndiotactic arrangements. This can be explained by assuming that the P_H^+ and the P_H^- forms

67

of the propagating centre are alternately involved. Each propagating centre will only react with one of the enantiomeric forms of the monomer and on completion of the reaction, the opposite form of the catalyst is generated. Thus

$$P_H^+ + (+) \text{ MNBE} \longrightarrow P_H^-$$

$$P_H^- + (-) \text{ MNBE} \longrightarrow P_H^+$$

In order for *cis* double bonds to be produced in the chain, the propagation reactions must proceed as follows:
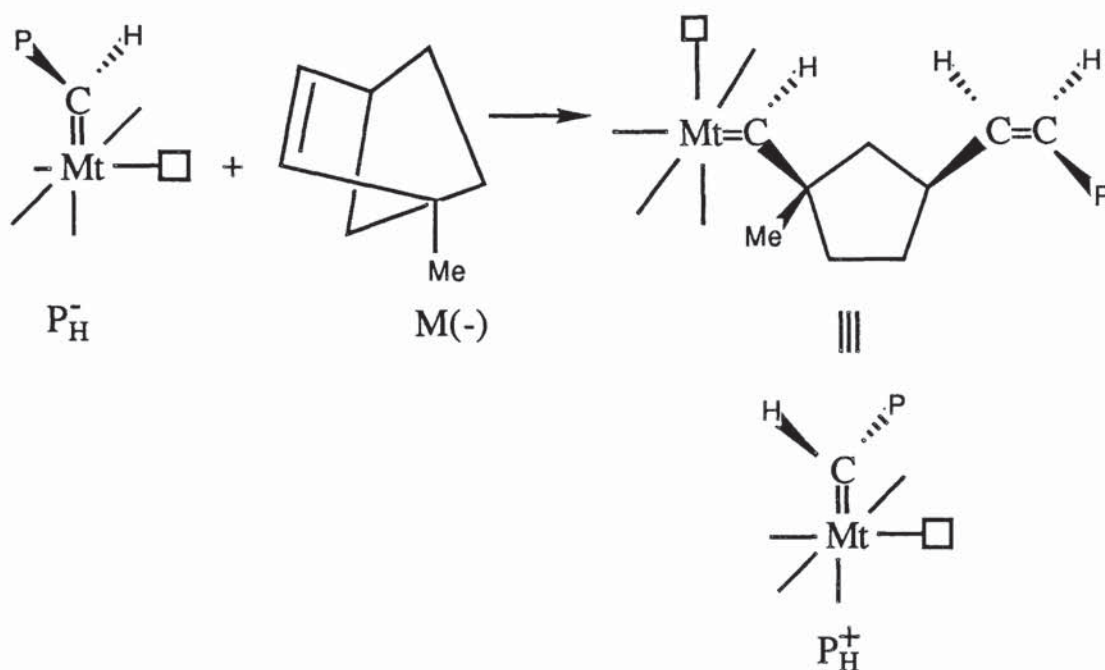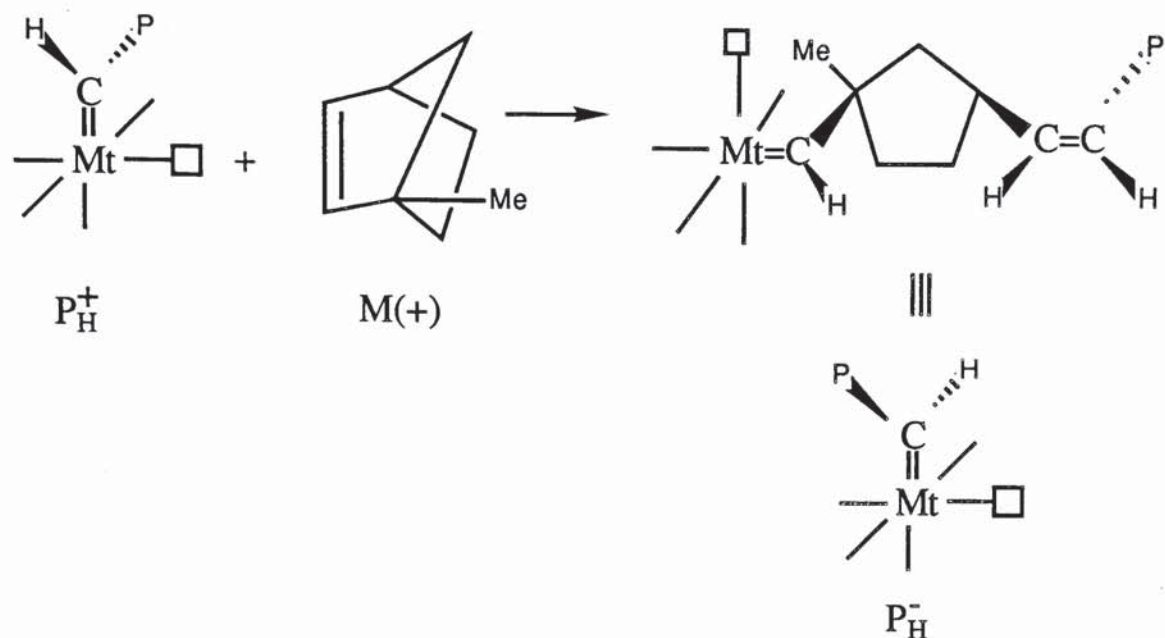
Assignment of the configurations to the chiral centres after propagation also indicates that the polymer is syndiotactic.

Rooney has observed that catalyst that polymerize racemic mixtures of MNBE to produce a high *cis* syndiotactic polymer will not polymerize a pure enantiomer because the (+) enantiomer of the monomer will only be polymerised by the (+) enantiomer of the catalyst site and similarly for the (-) enantiomers[71]. During the polymerization the (+) and (-) forms of the catalyst are exchanging, so if one of the monomer enantiomers is used up, the propagation reaction will cease to occur until that enantiomer has been replaced.

The head-to-tail reaction of MNBE gives rise to *trans* double bonds in the polymer and this will only occur by reaction of the propagating centres with monomers of opposite configuration. Therefore, P$^+$H will form a *trans* double bond by reacting with the (-) form of MNBE which will lead to a retention of configuration of the active site:

69
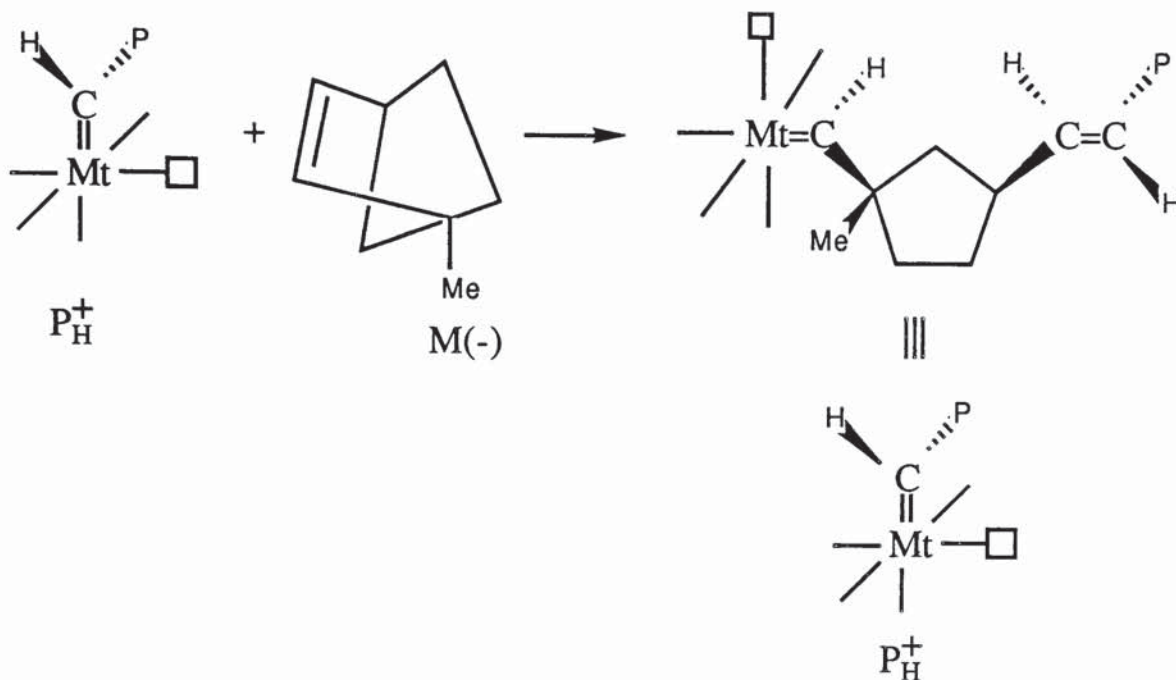
1.6.4. The stereochemistry of olefins using rhenium oxide/γ-alumina as the catalyst

Andreev et al have reported that double bond isomerization occurs in 1-butene over supported rhenium catalysts simultaneously with the metathesis reaction[72]. It was noticed that metathesis activity passed through a maximum whilst isomerization activity increased with temperature. These observations led to the assumption that both reactions took place on different active sites. To verify this assumption, the activities of Re_2O_7/Al_2O_3, Re_2O_7/MgO and Re_2O_7/SiO_2 were tested in the reaction of 1-butene isomerizing to *cis* and *trans* 2-butene under conditions where the catalysts were not active in olefin metathesis. This was achieved by pre-reducing the samples at appropriate temperatures. This technique also ensured that the support itself did not induce double bond migration. The results obtained led to the conclusion that olefin metathesis and isomerization took place on active sites with different oxidation states of rhenium. Metathesis activity occurred when Re(VI) coexisted with Re(VII) on the surface of the catalyst. Isomerization occurred in the presence of Re(IV). When the catalysts were reduced further, isomerization activity disappeared.

1.7. Kinetics of the metathesis reaction

A lot of research has been carried out to investigate the kinetics of the metathesis reaction but very little correlation between the various results exists which is due largely to the complexity of the mechanism of the reaction and the range of catalyst systems used.

1.7.1. Metathesis in the homogeneous phase

Detailed studies on the kinetics of olefin metathesis in the homogeneous phase have been carried out by Hughes in the reaction of 2-pentene with the catalytic system comprising molybdenum nitrosyl complexes and alkylaluminium halides[73]. The results indicated that metathesis followed first order kinetics with respect to the concentration of the catalyst and between 0.7 and 1.7 for 2-pentene concentration. Interpretation of these results led to the suggestion that the reaction was bimolecular and that the break down of the diolefin complex was the rate controlling step.

Amass and Tuck investigated the polymerization of cyclopentene in toluene catalysed by WCl_6 and $(i-C_4H_9)_3Al$ and observed complex kinetic behaviour[74]. The rate of polymerization was first order in the concentration of the catalyst but was more complex with respect to the olefin. The initial rate of polymerization was first order in cyclopentene concentration but as the reaction proceeded the order changed to one which was more complex and the rate decreased rapidly as the reaction proceeded. The results suggested that two active species had been formed during the course of the reaction. The first (**XVIII**) was thought to be formed when $WCl_6/(i-C_4H_9)_3Al$ reacted with cyclopentene. (**XVIII**) reacted further with cyclopentene to produce a less active species (**XIX**):

$$WCl_6 + CP \xrightarrow{k_1} W_1 \xrightarrow{2AliBu_3} W^*/Al_2 \quad \text{polymerizes}$$

XVIII

$$W_1 + CP \xrightarrow{k_2} W_2 \xrightarrow{AliBu_3} W^{**}/Al_x \quad \text{unknown activity}$$

XIX

71
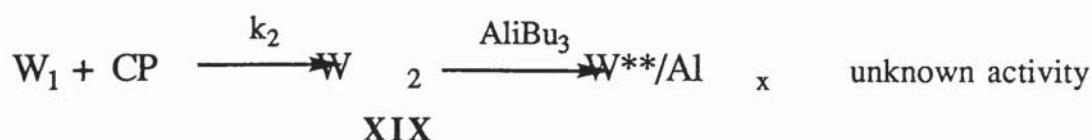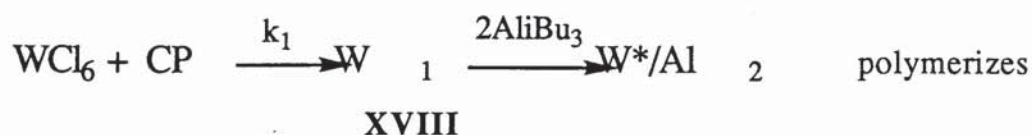
The rate of polymerization was found to be dependent upon the mixing time between the addition of $WCl_6/(i-C_4H_9)_3Al$ to cyclopentene. It was found that the optimum mixing time, t_{max} was inversely proportional to the the concentration of the monomer and was given by the following equation:

$$t_{max} = \frac{1}{(k_1-k_2)[M]_o} \ln \frac{k_1}{k_2}$$

where $[M]_o$ is the initial cyclopentene concentration.

Further investigations by Amass and Zurimendi on the kinetics of the polymerization of cyclopentene by dilatometry found that the decrease in the rate of propagation was not proportional to the decrease in monomer concentration[75]. It was postulated that the decrease in the rate of polymerization was second order in the concentration of the active species. It was also found that the termination reaction, which occurred during the polymerization, was second order with respect to the active species:

$$W_1 + W_1 \longrightarrow \text{Polymer}$$

1.7.2. Metathesis in the heterogeneous phase

Several kinetic models have been suggested to explain the mechanism of the metathesis reaction but two have featured predominantly in the literature. The Langmuir-Hinshelwood model is based upon the hypothesis that two adsorbed molecules on the surface of the catalyst interact which suggests that the reaction follows second order kinetics[2]. The Rideal model is based upon the hypothesis that the molecule adsorbed onto the surface of the catalyst interacts with a species in the gas phase and the reaction would therefore follow first order kinetics[2].

The factors involved in the metathesis of olefins in the heterogeneous phase are

(i) diffusion of the reactants over the surface of the catalyst,

(ii) adsorption of a molecule of the reactant by the active centres,

(iii) reaction of the adsorbed molecule on the surface of the catalyst,

(iv) desorption of the product molecule from the surface of the catalyst and

(v) diffusion of the product from the surface of the catalyst.

Anyone of the above steps could be the rate controlling step and this probably leads to the difficulty of distinguishing between unimolecular and bimolecular reaction kinetics.

Begley and Wilson carried out the metathesis of propene using WO_3/SiO_2 as the catalyst and the results indicated that the reaction followed first order kinetics which could be explained by the Rideal-type model[76]. Mol et al have also obtained results for the metathesis of propene which are consistent with a unimolecular mechanism[77]. In contrast, Lewis and Wills found that the initial rates of propene metathesis using a $WO_3/MoO_3/Al_2O_3$ catalyst, correlated with bimolecular kinetics which correlated with the Langmuir-Hinshelwood model[78]. Other investigators have also confirmed bimolecular kinetics for the metathesis of propene over a heterogeneous catalyst but, as mentioned before, all this information has yet to be reconciled to explain unequivocally the kinetics of metathesis. It would appear that a significant deficiency of the kinetic treatment of many workers is that allowance is not made in the model for the formation and destruction of active sites. The models generated assume that the active centre once generated is present in an unchanging state and concentration. This is a highly unlikely situation and will be addressed in this project. Lewis and Wills have made such assumptions in their work and have explained second order dependence in olefin concentration in terms of the need for two molecules on the surface to undergo collision. The mechanism of metathesis proposed by Chauvin and Herisson does not make such requirements.

1.8. The rhenium/alumina catalyst system

Rhenium(VII) oxide on γ-alumina (Re_2O_7/Al_2O_3) is a well known catalyst system for the heterogeneous metathesis of olefins. It was first reported by Davenport et al[79] and has been subsequently investigated by others. The catalyst is one of the more effective for the metathesis of functional olefins in the presence of tin alkyl compounds, eg tetramethyltin. Its activity can also be increased by using a modified support or a third oxide component. Since this project is concerned primarily with the rhenium oxide/alumina catalyst, the following will detail some of the recent work that has been carried out using this catalyst.

1.8.1. The stucture of the rhenium oxide/alumina catalyst

One of the most important factors in reactions catalysed by heterogeneous catalysts, is the structure of the surface of the catalyst. The surface of a catalyst has different characteristics from those of the bulk about which more may be known from crystallographic data. Because reactions such as metathesis occur on the surface of the catalyst, it is necessary to establish as much information as possible on the structure of the surface.

Maksimov et al studied the structural features of the rhenium oxide/alumina catalyst using differential thermal analysis (DTA) and x-ray diffraction[80]. DTA showed that a strong interaction between the rhenium and alumina occurs after impregnation and drying at 380K. The rhenium was also found to be present as a tightly bound surface compound that was thermally stable in air up to 1120K. X-ray diffraction revealed no reflections characteristic of rhenium (VII) oxide or ammonium perrhenate (NH_4ReO_4) in the calcined catalyst which indicated that rhenium was present on the surface of the alumina in the form of tightly bound surface compounds and not in the form of rhenium (VII) oxide particles, which was expected in the view of the work by Johnson and Leroy[81]. Similar results were obtained by Ellison et al who reported clusters of rhenium oxide on the surface of the support[82]. The X-ray data did not exclude the possibility of partial Al^{3+} replacement by Re^{7+} because the ionic radii of the two cations are very similar (0.57 and 0.52A for Al^{3+} and Re^{7+} respectively).

Conflicting results on the oxidation state of the rhenium were obtained by Nakamura and Echigoya who suggested that the Re^{7+} ions were in fact precursors of the active species which were lower valent rhenium ions[83]. Oxygen was adsorbed onto pre-reduced rhenium oxide/alumina catalyst and its activity to the metathesis of propene was found to be greatly enhanced. A paramagnetic species, denoted O_2^-, was detected on the surface of the catalyst and was found to be bound to Al^{3+} in the vicinity of the active site, $Re^{(n+1)+}$. It was therefore concluded that to form the active site, a catalytically inactive Re^{n+} ion, possibly Re^{4+}, transferred an electron to the adsorbing oxygen molecule to form O_2^-. Supportive work concerning the oxidation state of the rhenium came from electron spectroscopy for chemical analysis (ESCA) studies which have revealed that in calcined rhenium oxide/alumina catalysts,

74

the rhenium is in the +7 oxidation state whilst the active catalyst has been partially reduced to rhenium +6 and +4[84]. Similar results were obtained for the rhenium/silica catalyst.

Using infra red studies Nakamura et al. found that the rhenium oxide/alumina catalyst had two different surface rhenium species $(ReO_4)^-_{ads}$ and $(Re_2O_7)_{ads}$[85]. It was proposed that the $(Re_2O_7)_{ads}$ species was present only in the higher loading catalysts and was responsible for the high catalytic activity for the metathesis of olefins. It was not, however, the actual species responsible for the metathesis reaction but the precursor. Electron spectroscopy showed that the active catalyst contained Re^{6+} or Re^{4+}.

Mol and Moulijn have described rhenium as being present in the form of tetrahedrally coordinated ReO^-_4 ions which are stabilised by the support via Al-O-Re bonds[86]. Species of the form Re-O-Re were also detected and their concentration was found to increase with rhenium loading. Kerkhof et al. studied the catalyst using laser Raman infra red and found that the catalyst contained ReO^-_4 which was tetrahedrally distorted by the carrier surface hydroxyl groups[87].

1.8.2. Intermediates based on rhenium as active metathesis catalysts

Hermann et al. have shown that methylrhenium oxides (**XX** and **XXI**), synthesised from rhenium heptoxide and tetramethyl tin, are effective heterogeneous catalysts for the olefin metathesis reaction[88]:
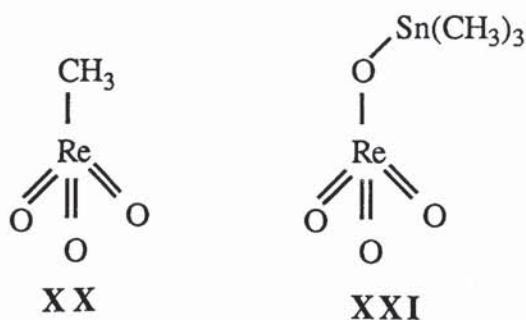
The activity of **XX** towards acyclic olefin metathesis is enhanced by the addition of aluminium chloride as a cocatalyst. If tetramethyl tin is used in addition to aluminium chloride, **XX** is also effective for the ring opening metathesis polymerisation of cycloolefins. From these results Hermann has suggested that **XX** and **XXI** are the actual catalytic precursors for

Hermann has suggested that **XX** and **XXI** are the actual catalytic precursors for the rhenium heptoxide/tetramethyl tin catalyst system.

Rybak and Ziolkowski investigated the use of oxo-rhenium compounds as olefin metathesis catalysts[89]. The results showed that the compounds containing no oxo ligands were ineffective as catalysts whilst those with oxo ligands were active catalysts. The results obtained are shown in table 1.8.1:

Table 1.8.1

The catalytic activity of rhenium complexes in the metathesis of 2-pentene

Rhenium complex	Initial rate (turnover min^{-1})	Comments
$ReCl_3py_3$	0	no reaction
$ReCl_3(PMePh_2)_3$	0	no reaction
$ReCl_3[P(OEt)_3]_3$	0	no reaction
$ReCl_3P_3^I + O_2$	indeterminate	previous O_2 treatment
$ReCl_3[P(OEt)_3]_2$	3.6	catalyst inactive at 16% conv.
$ReOCl_3(PPh_3)_2$	0.21	32% conv./110h
$ReOCl_3py_2$	0.032	-

^{I}P = $PMePh_2$ or $P(OEt)_3$

Schrock and Toreki recently reported what is thought to be the first rhenium alkylidene complex to initiate the olefin metathesis[90]:

$$Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu) [OCMe(CF_3)_2]_2 \quad (XXII)$$

XXII was found to be an effective catalyst for the metathesis of internal and functionalized olefins. Its activity was found to increase when smaller alkylidene ligands were formed, eg **XXII** metathesised 100 equivalent *cis* 2-pentene to an equilibrium mixture in 2.5h at 25°C. When another 100 equivalent of *cis* 2-pentene was added, equilibrium was reached in less than 30 min.

1.8.3. The surface acidity of the rhenium based metathesis catalyst

There is general agreement that surface acidity plays a major role in the activity of rhenium oxide supported on alumina. Xiaoding postulated that there may be two types of Lewis acid sites on the catalyst surface[91]. Infra red analysis indicated that the rhenium oxide may deposit preferentially onto the weak Lewis acid sites, thus rendering the Lewis sites stronger. However the increase in the metathesis activity correlated better with the Bronsted acidity. Hydrochloric acid impregnation of the alumina support increases Bronsted acidity and at low catalyst loading, the metathesis activities of these catalysts were found to be higher than those catalysts prepared without hydrochloric acid impregnation[92]. Rhenium (VII) oxide catalysts supported on silica-alumina show a higher activity towards metathesis than those supported on alumina. Silica-alumina exhibits high Bronsted acidity and this is thought to be responsible for the higher activity[93,94].

Poisoning of the Bronsted acid sites with hexamethyldisilazane (HMDS) decreases the activity of the catalyst and when an excess of the poison is added metathesis activity is terminated[93]. The reaction that is thought to occur is

$$
\text{surface}\left\{\begin{array}{l}\text{---OH}\\[2mm]\text{---OH}\end{array}\right. + HN\{Si(CH_3)_3\}_2 \longrightarrow \left\{\begin{array}{l}\text{---OSi(CH}_3)_3\\[2mm]\text{---OSi(CH}_3)_3\end{array}\right.
$$

$$
+
$$

$$
NH_3
$$

Poisoning by HMDS leaves the Lewis sites unaffected. However the decrease in activity is not directly proportional to the amount of HMDS added. This was explained as follows:

(i) The hydroxy groups were of different acidities and the participation of each one in the reaction would vary.

(ii) Only those groups in the vicinity of a rhenium oxide species will participate in the reaction.

(iii) A distinct amount of HMDS was physically adsorbed onto the surface which did not react with the surface hydroxyl groups.

Rhenium oxide/alumina/boria catalysts have also been investigated (boria = B_2O_3)[95]. Boria is an acidic oxide and it was found that the acidity of the catalyst was mainly Bronsted. The impregnation of rhenium oxide onto this support resulted in a highly active metathesis catalyst. Poisoning of the Bronsted acid sites by HMDS again decreased the activity of the catalyst thus confirming the participation of the Bronsted acid sites in the reaction:

$$2\text{-BH} + \text{Hn(SiMe}_3)_2 \longrightarrow NH_3 + 2\text{-B-Si(Me)}_3$$

1.8.4. The metathesis of functional olefins using rhenium oxide/alumina as the catalyst

From a synthetic and technological point of view, one of the most important applications of olefin metathesis is that involving unsaturated functional compounds. The metathesis of functional olefins yields difunctional unsaturated products whose functional groups can be modified to produce compounds which are produced only with difficulty via other routes, eg diesters. However, most active metathesis catalysts are poisoned by the polar atoms of the functional groups, probably because stronger complexes are formed which renders them inactive. Rhenium oxide/alumina has been found to be a very effective and highly selective catalyst for the metathesis of functional olefins. Verkuijlen was the first to report the heterogeneously catalysed metathesis of unsaturated esters using rhenium oxide/alumina, promoted with a small amount of tetramethyltin as the catalyst and methyl-4-pentenoate as the substrate[11]:

$$2CH_2=CHCH_2CH_2\text{-}\overset{\displaystyle O}{\overset{\displaystyle \|}{C}}\text{-O-CH}_3 \xrightarrow{Re_2O_7/Al_2O_3/Sn(Me)_4} CH_2=CH_2 +$$

$$CH_3\text{-O-}\overset{\displaystyle O}{\overset{\displaystyle \|}{C}}\text{-CH}_2CH_2CH=CHCH_2CH_2\text{-}\overset{\displaystyle O}{\overset{\displaystyle \|}{C}}\text{-O-CH}_3$$
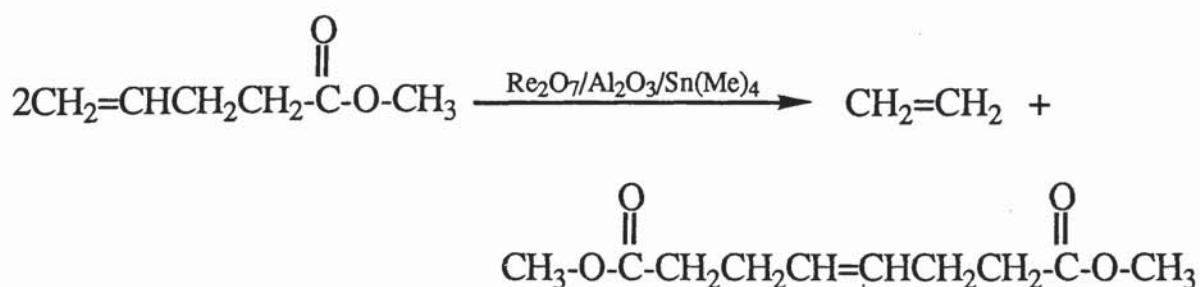
Unsaturated ethers, ketones, alcohols, halogeno-olefins and nitriles have also undergone successful metathesis with this catalyst[2,6,40].

Much of the investigative work on the metathesis of functional compounds has been carried out using unsaturated esters[10,96]. Studies have shown that the carbon-carbon double bond and the carbonyl group of the ester must be separated by at least one methylene group in order for the ester to be active towards metathesis. This is thought to be because the carbon-carbon double bond and the carbonyl group conjugate and the electrophilic carbonyl carbon atom withdraws electrons from the electron rich double bond and enriches the carbonyl oxygen atom. This disturbance of the electron density hinders the correct approach of the catalytic species involved in the metathesis reaction, reducing the effectiveness of the catalyst. The following table gives the activity of some esters towards metathesis:

Table 1.8.2

The effect of methylene groups on the metathesis of esters

SUBSTRATE	CONVERSION (mol %)	SELECTIVITY (%)
C=C-COO-C	0	-
C=C-C-COO-C	70	95
C=C-C-C-COO-C	70	95
C=C-CH$_3$-COO-C	0	-
C=C-O-COC	0	-

Methylmethacrylate (MMA) undergoes degenerate rather than productive metathesis due to steric effects which means that the molecules tend to align head to tail rather than tail to tail when forming the intermediate metallocyclobutane. Consequently, molecules identical to the starting material are formed[96]:

$$Re=CMeCOOMe$$
$$+$$
$$MeOOCCMe=CH_2$$

$\longrightarrow$

$$\overset{\displaystyle Re-CMeCOOMe}{\underset{\displaystyle MeOOCCMe-CH_2}{|\qquad|}}$$

$\downarrow$

$$CH_2=CMeCOOMe$$
$$+$$
$$MeOOCCMe=Re$$
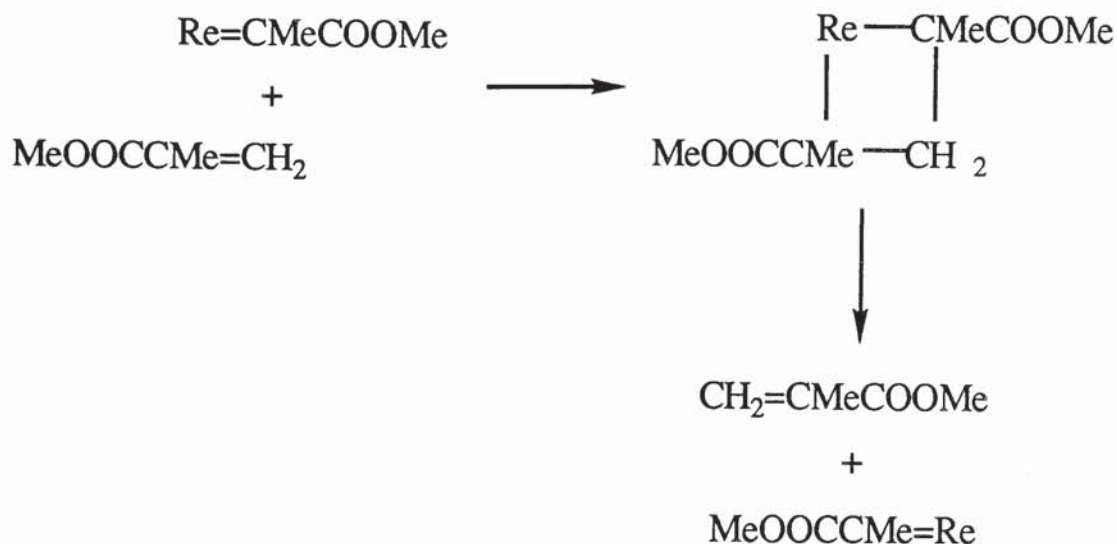
MMA has been shown to undergo co-metathesis with simple olefins to produce longer chain α-methyl unsaturated esters, eg

$$\underset{H_2C=C\text{-}COOCH_3}{\overset{CH_3}{|}} + CH_3CH=CHCH_3 \;\rightleftharpoons\; \underset{H_3C\text{-}CH=C\text{-}COOCH_3}{\overset{CH_3}{|}}$$
$$+$$
$$CH_2=CHCH_3$$
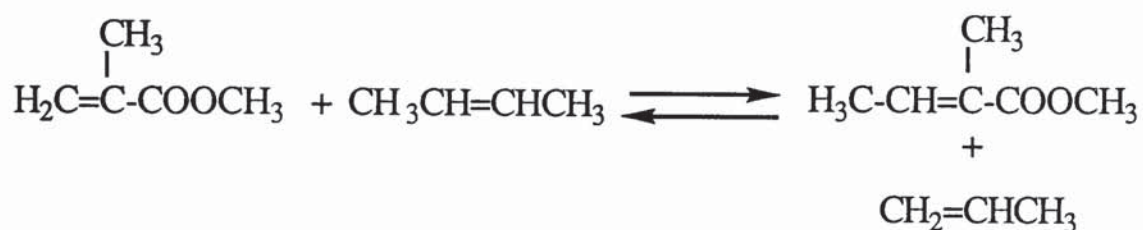
Ellison et al. showed, using crystallographic techniques, that ester molecules are strongly adsorbed onto the catalyst through the carbonyl group while being only weakly attached to the active site of the catalyst via the carbon carbon double bond[82]. Recovered catalysts always had a layer of the diester strongly adsorbed onto their surface, which was implied to show that one of the limiting factors in the rate of metathesis was the rate of desorption of the diester from the active sites on the catalyst. It follows that if the rate of desorption is low then the incoming esters will be greatly hindered from complexing to the active site thus reducing the product turnover rate. This is generally in agreement with the proposition that esters form strong complexes with the active site.

Other factors affect the activity of the catalyst in the metathesis of unsaturated esters and will now be reviewed briefly.

1.8.4.1. The effect of the rhenium content on the activity of the catalyst

The amount of rhenium deposited onto the surface of the support affects the efficiency of rhenium oxide metathesis catalysts. Mol et al showed that low loading (5%) rhenium oxide/alumina catalysts are hardly active whilst a 0.25wt% rhenium (VII) oxide/alumina/silica catalyst shows substantial activity[93,94]. Low loading rhenium oxide catalysts with an alumina/boria support also have a higher activity than those with an alumina base and this is thought to be due to the surface acidity of the support which was discussed earlier in section 1.7.3[95].

1.8.4.2. The effect of co-catalysts on the activity of the catalyst

Mol et al investigated the effect of three cocatalysts in the metathesis of methyl oleate and found that the order of activity was

$$Sn(C_2H_5)_4 > Sn(CH_3)_4 > Sn(n-C_4H_9)_4$$

However due to its lack of interference with the signals in gas liquid chromatography analysis, tetramethyltin was used[97].

The role of the cocatalyst has yet to be fully elucidated but what is certain is that it is essential for the metathesis of functional olefins. Mol et al observed that when tetramethyltin was added to the rhenium oxide/alumina catalyst, methane was formed. This suggested that the cocatalysts alkylate the rhenium followed by the formation of the active catalytic carbene species:

$$Re \xrightarrow{2Sn(CH_3)_4} Re\begin{smallmatrix} CH_3 \\ \\ CH_3 \end{smallmatrix} \longrightarrow Re=CH_2 + CH_4$$

Whether there is a need for $Re(CH_3)_2$ to form is uncertain. Ethane has also been detected but this is thought to be a product of a termination reaction.

1.9. Applications of the olefin metathesis reaction

In spite of its sensitivity towards air and moisture, the olefin metathesis reaction has found many industrial uses. However, due to the limitations mentioned above and the low activity of

the catalysts of metathesis, applications have been limited. The following will discuss some of the predominant industrial uses of the reaction.

1.9.1. The Phillips Triolefin Process

This was the first major industrial use of the olefin metathesis reaction and involves the conversion of propene to ethene and 2-butene[98]:

$$2CH_2=CHCH_3 \rightleftharpoons CH_2=CH_2 + CH_3CH=CHCH_3$$

The process was developed by the Phillips Petroleum Company, USA and the plant was operated in Montreal, Canada, from 1966. 30 000 tons of ethene was produced per year but due to a change in the economic climate and the increase in demand for propene, the plant had to be closed in 1972. Recently, however, there have been moves to reopen the plant with the view of doing the reverse process, ie produce propene from ethene and 2-butene. This illustrates the versatility of the metathesis reaction and the ability to change feedstock to produce different products.

1.9.2. The Shell Higher Olefin Process (SHOP)

This is one of the largest industrial applications of the olefin metathesis reaction in operation today[99]. n-Olefins in the range C_{10} - C_{20} are produced from mixtures of linear α-olefins (C_4 to C_{20}) obtained from the catalytic oligomerization of ethene (scheme 1.13). The olefins are separated by fractionation with the higher α-olefins (C > 20) being isomerized to internal olefins that can be subsequently metathesised to produce n-olefins of the desired molecular weight. The n-olefins are important in the detergent industry as base materials. Plants operate in Geismar, LA (270 000 tons per year) and Stanlow, GB (170 000 tons per year).

1.9.3. The Neohexene Process

Neohexene (3,3-dimethyl-1-butene) is an important base material for the manufacture of musk perfume, pesticides and herbicides[100]. It is produced from di-isobutene and ethene in the

presence of a $WO_3/SiO_2/MgO$ catalyst. In the production of bicyclic musks, it is reacted with *p*-cymene followed by acetylation to give 7-acetyl-1,1,3,4,4,6-hexamethyltetralin, scheme 1.14.

The plant is operated by the Phillips Petroleum Company in Houston, Texas with a capacity of 1400 tons per year.

1.9.4. The production of polynorbornene

Norbornene undergoes ring opening metathesis polymerization to produce polynorbornene:
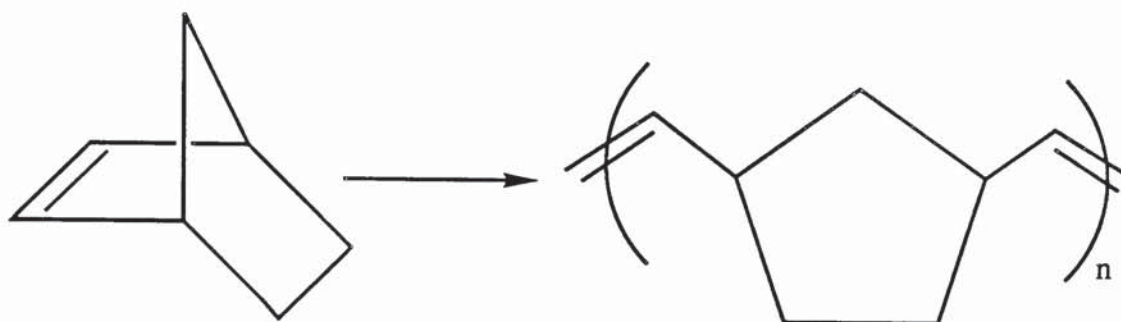
In 1976 CdF Chimie begun manufacturing 90% *trans* polynorbornene in north eastern France with a capacity of 5000 tons per year[101]. It is sold under the trade name Norsorex as a moulding powder. When plasticised, the glass transition temperature is depressed from 35°C to -60°C so producing a more pliable elastomer at room temperature for use in arm rests and printing rollers. The vulcanised material is important in anti-vibration mounts and shock-proof bumpers.

1.9.5. *Trans* - poly(1-octenylene)

Vestenamer 8012 is the trade name for the elastomer *trans* poly(1-octenylene) produced by the ring opening polymerization of cyclooctene[102]. 8012 signifies that the polymer contains 80% *trans* double bonds and has a viscosity number of $120 cm^3 g^{-1}$ when measured in 0.1% solution in toluene at 25°C. Because of it unsual properties, Vestenamer is used as a blending material to help to improve the properties of the more common elastomers. Its unusual properties include being hard at 20°C with a high viscosity and having the flow like consistency of honey abve 60°C. Consequently, it is suitable for use in blends with other elastomers which become more rigid at room temperature and flow more easily at 60°C.

Scheme 1.13

The Shell Higher Olefin Process

ETHENE AND CATALYST

↓

OLIGOMERIZATION

↓

FRACTIONATION ⟶ α-OLEFINS

$(C_{10}, C_{12}, C_{14}, C_{16}, C_{18}, C_{20})$

OLEFINS > C_{20} OLEFINS < C_{20}

PURIFICATION

↓

ISOMERIZATION

↓

METATHESIS ←

↓

> C_{14} i-OLEFINS ⟵ FRACTIONATION ⟶ < C_{11} i-OLEFINS

$C_{11/12}$ i-OLEFINS $C_{13/14}$ i-OLEFINS

84
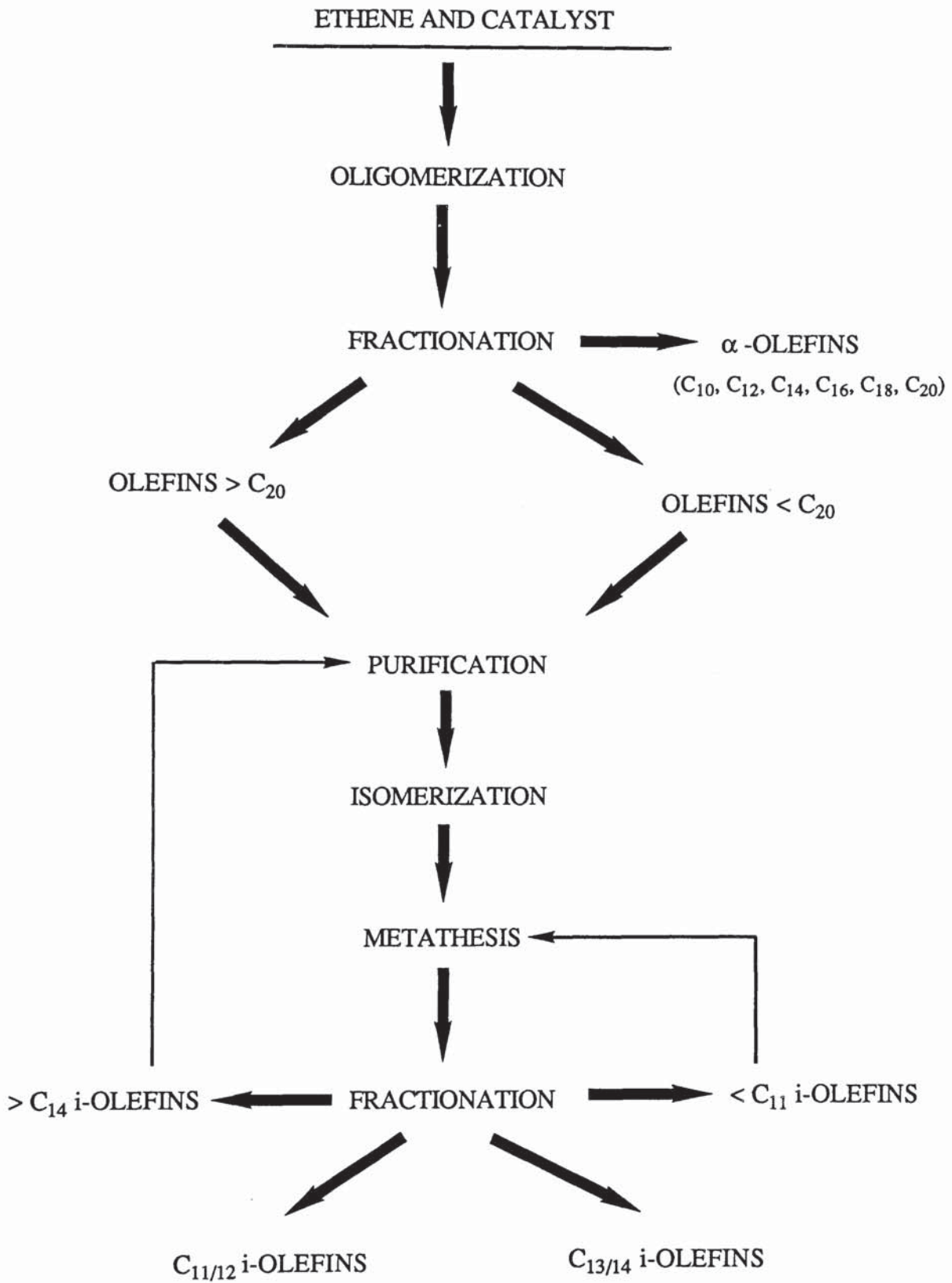
Scheme 1.14

The Neohexene Process

neohexene

p -cymene

1,1,3,4,4,6-hexamethyl tetralin

$$CH_3-C-Cl$$
(acetyl chloride)

7-acetyl-1,1,3,4,4,6-hexamethyl tetralin
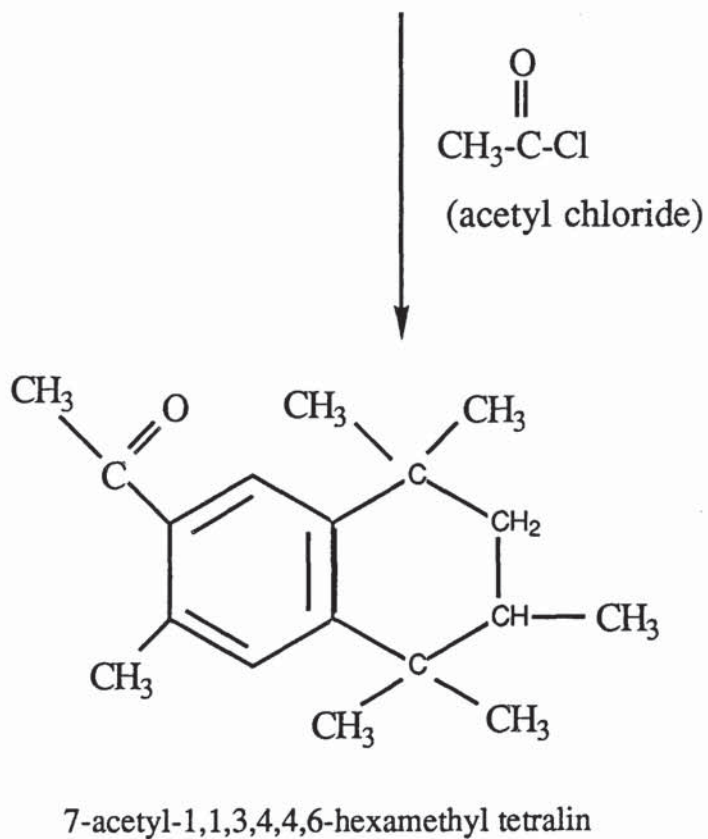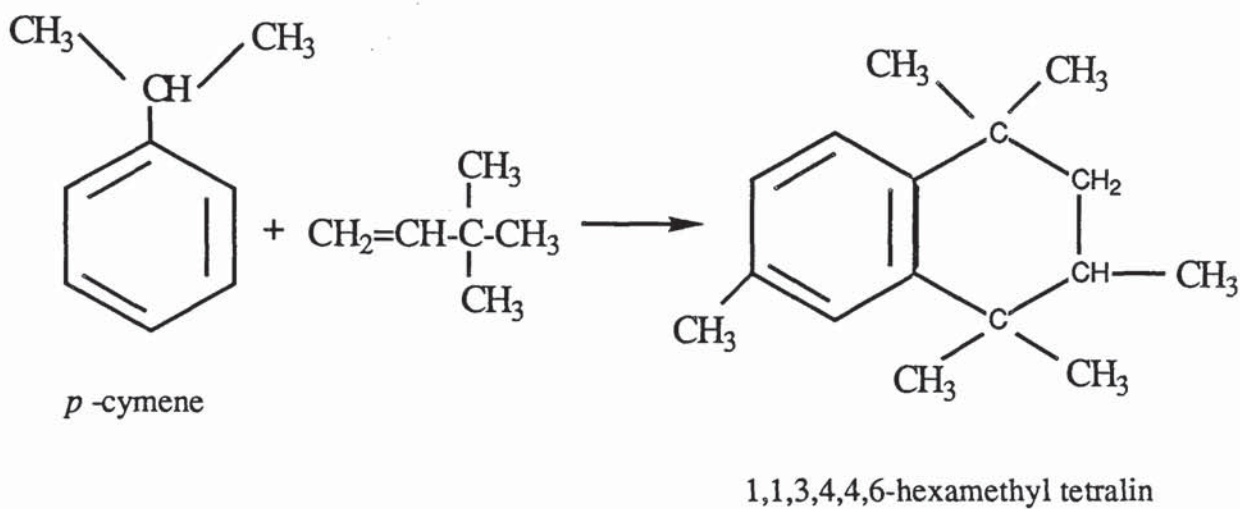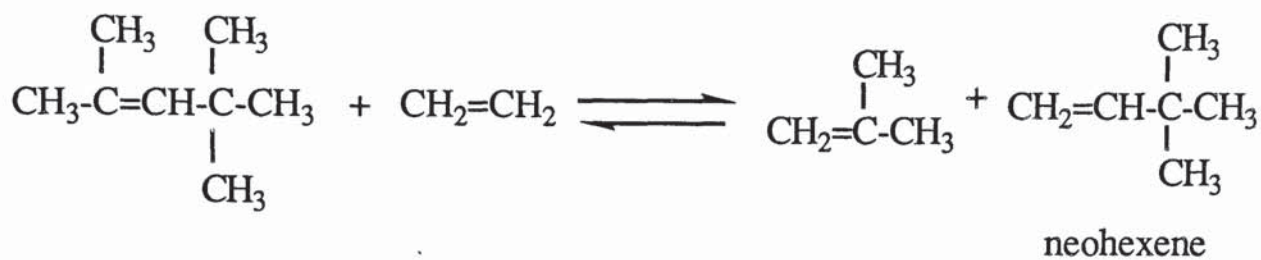
1.10. Aims of this project

The primary aims of this research program were

1) To investigate the initial kinetics of the metathesis of 1-hexene over Re_2O_7/γ-Al_2O_3.

2) To devise a mechanism using the kinetic data to offer an explanation for the initiation, propagation and termination steps.

3) To investigate the regeneration properties of Re_2O_7/γ-Al_2O_3.

4) To analyse the effect of co-catalysts on the activity of Re_2O_7/γ-Al_2O_3.

5) To investigate methods of improving the metathesis of functional compounds by way of use of protecting groups.

CHAPTER 2: EXPERIMENTAL

2.1. Vacuum techniques

The catalysts used for the olefin metathesis reaction are very sensitive to air and moisture. Consequently it is essential that these two components are excluded from the reactions. One method of achieving these conditions is to work under high vacuum conditions as far as possible.

2.1.1. The high vacuum line

The vacuum line was constructed from glass as shown in fig. 2.1.1. It consisted of a manifold (A), connected to which were four joints (B) where the solvent flasks and other vessels could be attached. The manifold was connected to two pumps via a greased tap (C). The tap was used to isolate the manifold from the pumps, one of which was an Edwards rotary pump (D) and the other a mercury diffusion pump (E). Pressures approaching 10^{-3} and 10^{-4} torr could be reached; a vacustat (F) was used to estimate the pressure in the system. A two litre bulb (G) allowed the volume of the vacuum line to be increased. High vacuum polytetrafluoroethylene greaseless taps connected the bulb and the joints to the manifold. The two traps (H) collected any vapours removed during evacuation. These vapours were frozen in the trap by immersing the traps in liquid nitrogen.

Fig 2.1.1

The High Vacuum Line
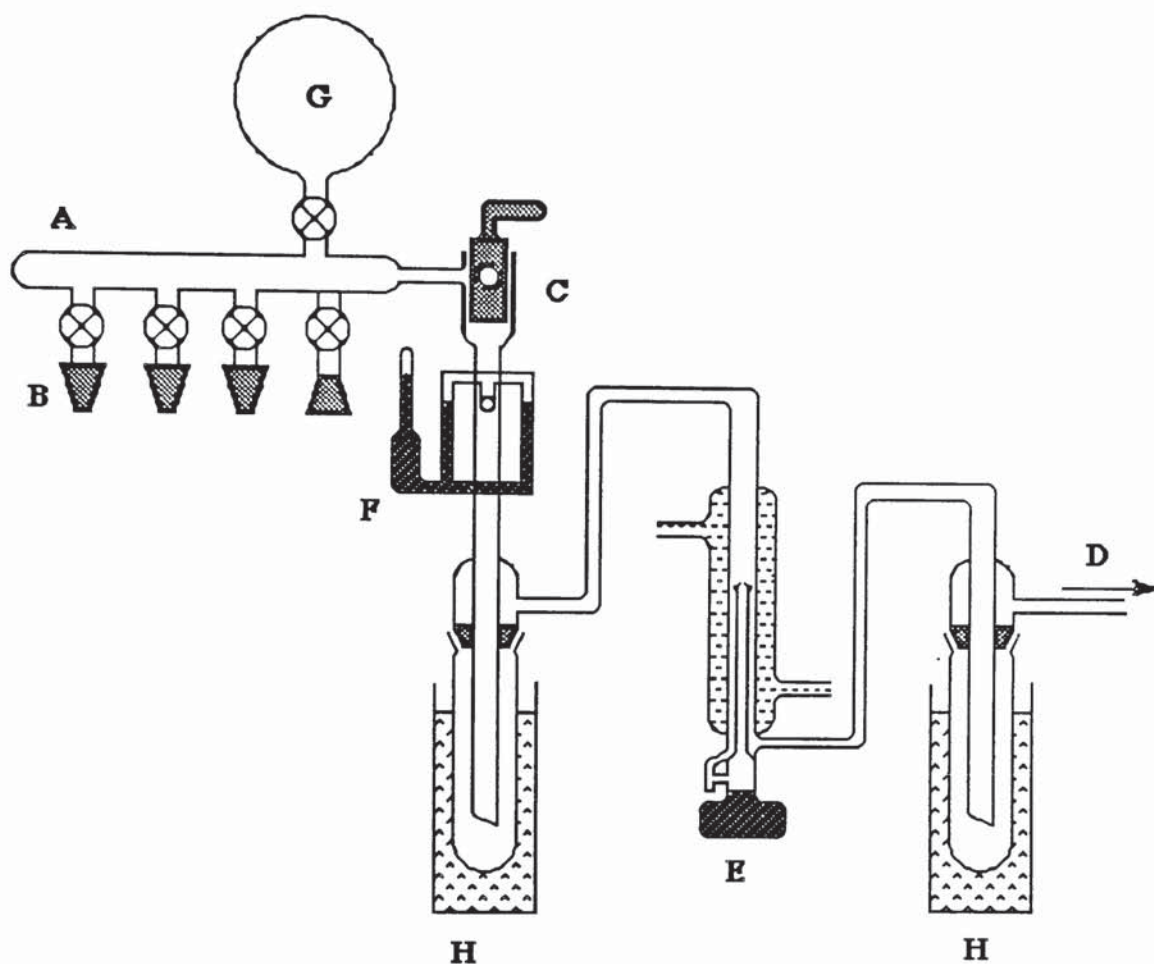
KEY

▨	Ground glass joints	▨	Mercury
▨	Liquid nitrogen	▨	Water
⊗	Greaseless tap		

2.1.2. Degassing the solvents

A flask containing solvent, fig 2.1.2, was attached to the vacuum line and the solvent was frozen by immersing the flask in liquid nitrogen. Tap(C) and the tap on the flask were then opened to evacuate the flask. When completely evacuated, tap (C) was closed and the contents

contents of the flask were allowed to warm up. During this period gas dissolved in the solvent out-gassed, and when visible signs of this process had ceased, the solvent was frozen again in liquid nitrogen. Tap (C) was opened, the flask evacuated and when a vacuum had been attained, the appropriate taps were closed and the contents of the flask were allowed to warm up. This cycle was repeated until there were no more visible signs of the solvent being degassed and a high vacuum was obtained immediately upon freezing the liquid.

Fig 2.1.2

The Solvent Flask
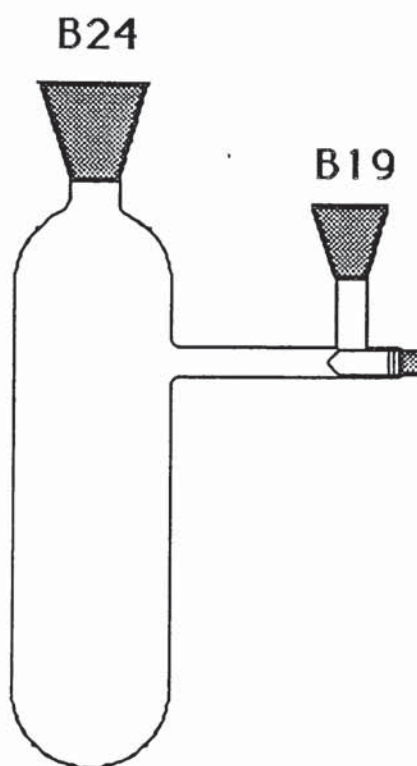
2.1.3. Distillation under vacuum

Two flasks, one of which contained degassed solvent, were connected to the vacuum line and evacuated. A flask containing sodium on benzophenone, into which the solvent was to be distilled, was cooled using liquid nitrogen. Tap (C) was closed from the manifold and the taps on both the flask and the manifold were opened and the solvent was distilled. The radical anion complex formed by heating sodium strips with benzophenone in the flask, fig 2.1.3, is very sensitive to moisture and oxygen and is used to indicate the efficiency of the degassing and

drying procedures. If the solvent is degassed and dry, the characteristic blue of the radical anion complex is observed. When the solvent contains air or moisture, the complex is green.

Fig 2.1.3.

The formation of the sodium/benzophenone radical complex
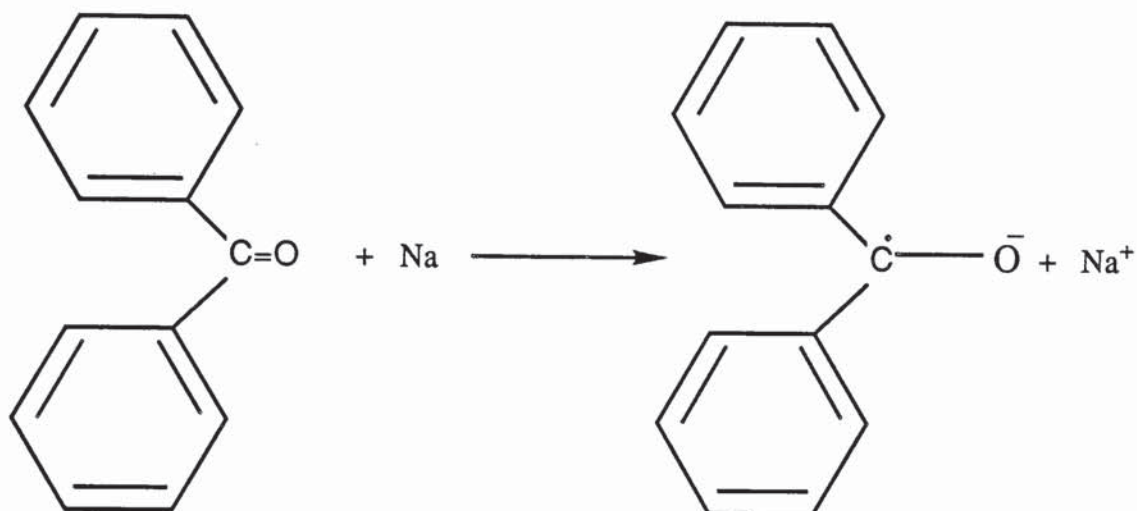
2.2. The chemicals

2.2.1. γ-Alumina

Catapal SB, obtained from BP Chemicals, a naturally occurring Boehmite alumina with a hydroxylated surface and a high surface area, was calcined at 580ºC to obtain the γ-alumina.

2.2.2. Ammonium perrhenate

Commercially available from Johnson Matthey, ammonium perrhenate was used without purification.

2.2.3 1-Hexene, 2-hexene and 4-nonene

1-Hexene from Fluka (98% pure) was dried over calcium hydride (Aldrich,95+%) for at least 24 hours. It was then degassed and distilled under vacuum into a flask containing sodium/benzophenone where it was stored, and from which it was distilled, as required. 2-Hexene and 4-nonene (98% pure, *cis* and *trans* mixture) were supplied by Aldrich and were used as supplied.

2.2.4. Cyclohexane

Technical grade cyclohexane was dried, degassed and distilled in the same way as 1-hexene.

2.2.5. Tetramethyl and tetrabutyl tin

Both compounds were obtained from Aldrich and were used as supplied.

2.2.6. Dichloromethane

Technical grade dichloromethane was dried over CaH_2 for 24h and purified by simple distillation. It was stored over molecular 4A sieve until use.

2.2.7. Diethylether

Technical grade diethylether was dried, purified and stored in the same way as dichloromethane.

2.2.8. 2-Amino-2-methyl-1-propanol

2-amino-2-methyl-1-propanol (95% pure) was obtained from Aldrich and was used as supplied.

2.2.9. Thionyl chloride

Thionyl chloride (>99% pure) was supplied by Fluka and was used as supplied.

2.2.10. 10-Undecenoyl chloride and 4-pentenoic acid

10-undecenoyl chloride (98% pure) and 4-pentenoic acid (97% pure) were supplied by Aldrich and were used as supplied.

2.2.11. Decahydronapthalene (Decalin)

Decahydronapthalene (98% pure) was supplied by Fluka as a *cis* and *trans* mixture and was used supplied.

2.3. Preparation of catalyst

A number of methods for preparing rhenium oxide supported on alumina catalysts are described extensively in the literature[2,6,32,103,104,105]. The method used throughout this research project involved the impregnation of the γ-alumina base with a solution of the precursor of the active component[32]. A catalyst with a rhenium loading of 6% was made up using the formula

$$y = 0.0707x$$

where y = the weight of ammonium perrhenate and

x = the weight of γ-alumina

The relative molecular masses of ammonium perrhenate and rhenium(VII) heptoxide are 268.2 and 484.4 respectively. In the preparation of the catalyst

$$2NH_4ReO_4 \longrightarrow Re_2O_7 + 2NH_3 + H_2O$$

1.107g NH_4ReO_4 is equivalent to 1g Re_2O_7. In order to prepare a catalyst that contains 6% Re_2O_7 on alumina, when x is the mass of alumina and y the mass of ammonium perrhenate, then

$$\frac{y/1.107}{x+y/1.107} = 0.06$$

This may be solved to give

$$y = 0.0707x$$

In a typical preparation, the γ-alumina was weighed into an evaporating dish which was placed over a steam bath at 80°C. The equivalent amount of ammonium perrhenate was dissolved with stirring in water on a hot plate and then poured slowly and carefully onto the alumina. The surface of the alumina was covered with water so that the perrhenate impregnated it evenly for 6 hours. The water was then evaporated from the slurry for 1 hour and the catalyst was dried for 18 hours at 110°C. The catalyst was then activated by calcining the material at 580°C for 18 - 24 hours under a steady stream of dry air. The apparatus used for this calcining procedure is shown in fig 2.3.1:

Fig 2.3.1

The Calcining Apparatus

catalyst   ground glass taps
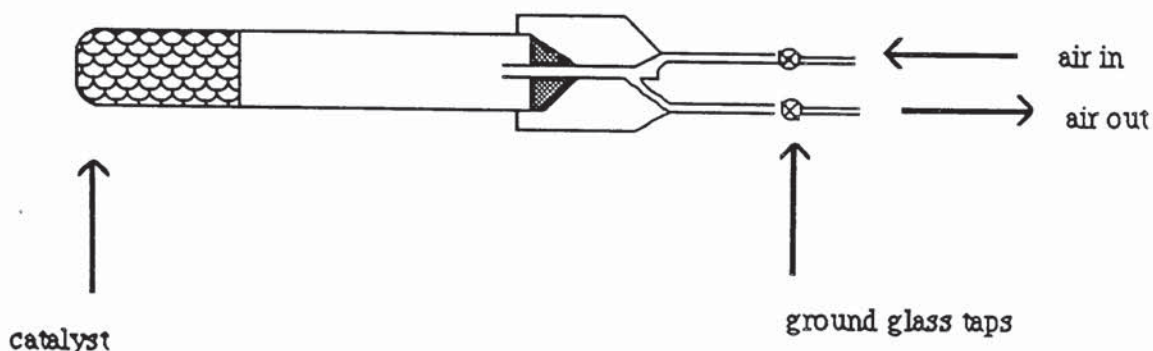
The catalyst was stored in the calcining apparatus under argon until it was required.

2.4. Preparation of a solution of 1-hexene in cyclohexane

1-Hexene and cyclohexane were distilled in turn from storage vessels into a sample glass vessel fitted with a tap and joint so that the final solution had a total volume of approximately $25cm^3$. The vessel was weighed before and after each distillation so that the concentration of 1-hexene could be determined. Cyclohexane also acted as an internal standard for analysis by gas liquid chromatography.

2.5. The metathesis of 1-hexene

The general equation for the metathesis reaction is:

$$2CH_2{=}CH(CH_2)_3CH_3 \longrightarrow CH_2{=}CH_2 + CH_3(CH_2)_3CH{=}CH(CH_2)_3CH_3$$

The reaction was performed in a specially constructed reaction vessel, shown in fig 2.5.1 Using this apparatus, the volume of ethene evolved could be measured as a function of time. The apparatus was attached to the vacuum line by joint (A) and tap (B) was opened to allow evacuation of the vessel. Once evacuated, the reaction vessel was placed, along with a weighed amount of catalyst, in a glove box filled with dry argon. The weighed amount of catalyst was transferred under argon, to the reaction vessel through tap (B). The apparatus was closed, removed from the glove box, attached to the vacuum line and evacuated again.   Tap (B) was

then closed and the glass vessel, containing the 1-hexene in the cyclohexane was placed on the apparatus at joint (C). Tap (D) was opened to evacuate the intervening space and, the gas collecting device (shown in fig 2.5.2) fixed at (G) was flushed out with argon. With tap (F) still closed, but the three way tap (G) positioned so that it connected the reaction vessel to the argon supply via the gas collecting device, the glass tube attached to tap (F) could be flushed out also, thus ensuring that no air entered the reaction vessel. Tap (D) was closed, tap (E) opened and the 1-hexene solution was released into the vessel. Tap (F) was opened and the timing of the reaction begun as ethene evolved on contact of the solution of 1-hexene with the catalyst. The reaction vessel and its contents were maintained at a constant temperature by circulating water from a constant temperature bath through the water jacket (H).

The gas evolved was collected in a gas collecting device, fig. 2.5.2, which was a simple manometer, consisting of a glass tube, approximately 100cm in length and radius of approximately 1.5cm). Fixed behind this tube was a 1m ruler, and the position of the meniscus was recorded as a function of the time of the experiment. The tube contained decalin which sparingly dissolved the ethene but the errors incurred were estimated to be small since the surface area in contact with ethene was small. A 1cm movement of the meniscus was estimated to be equivalent to the evolution of 7.1 cm^3 of ethene. Consequently the volume of gas evolved could be estimated using this approximate conversion. In order to estimate the errors involved in the measurement of the volume of ethene evolved during the metathesis of 1-hexene, the experiments were repeated until reproducible results were obtained.

Samples of the reaction mixture could also be removed for subsequent analysis. A sample tube was placed on (I) and tap (J) was opened in order for the tube to be evacuated. This tap was then closed and tap (K) was opened carefully to release some of the solution into the sample tube. The sample tube was removed whilst still under vacuum and the solution and any gaseous products collected were analysed by gas chromatography and other techniques.

Fig 2.5.1

The Reaction Vessel for Olefin Metathesis
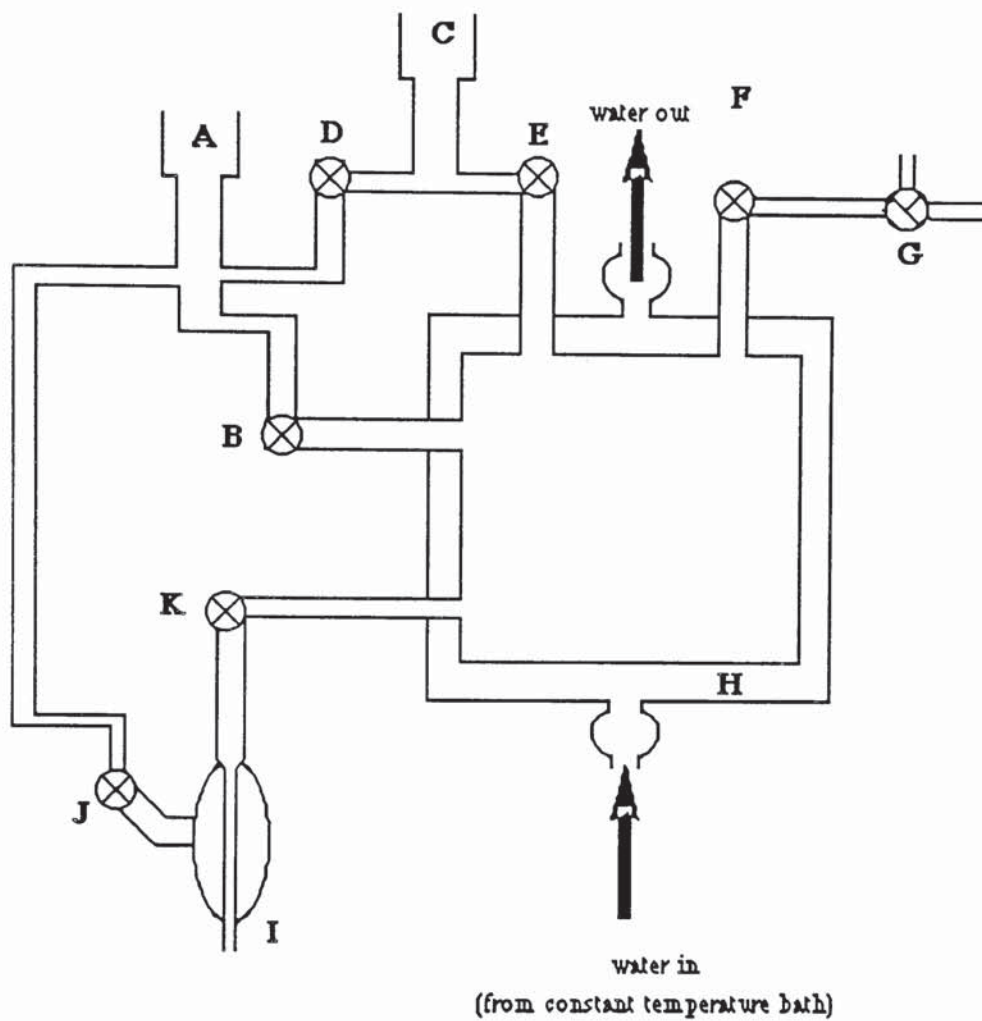
Fig 2.5.2

The Gas Burette
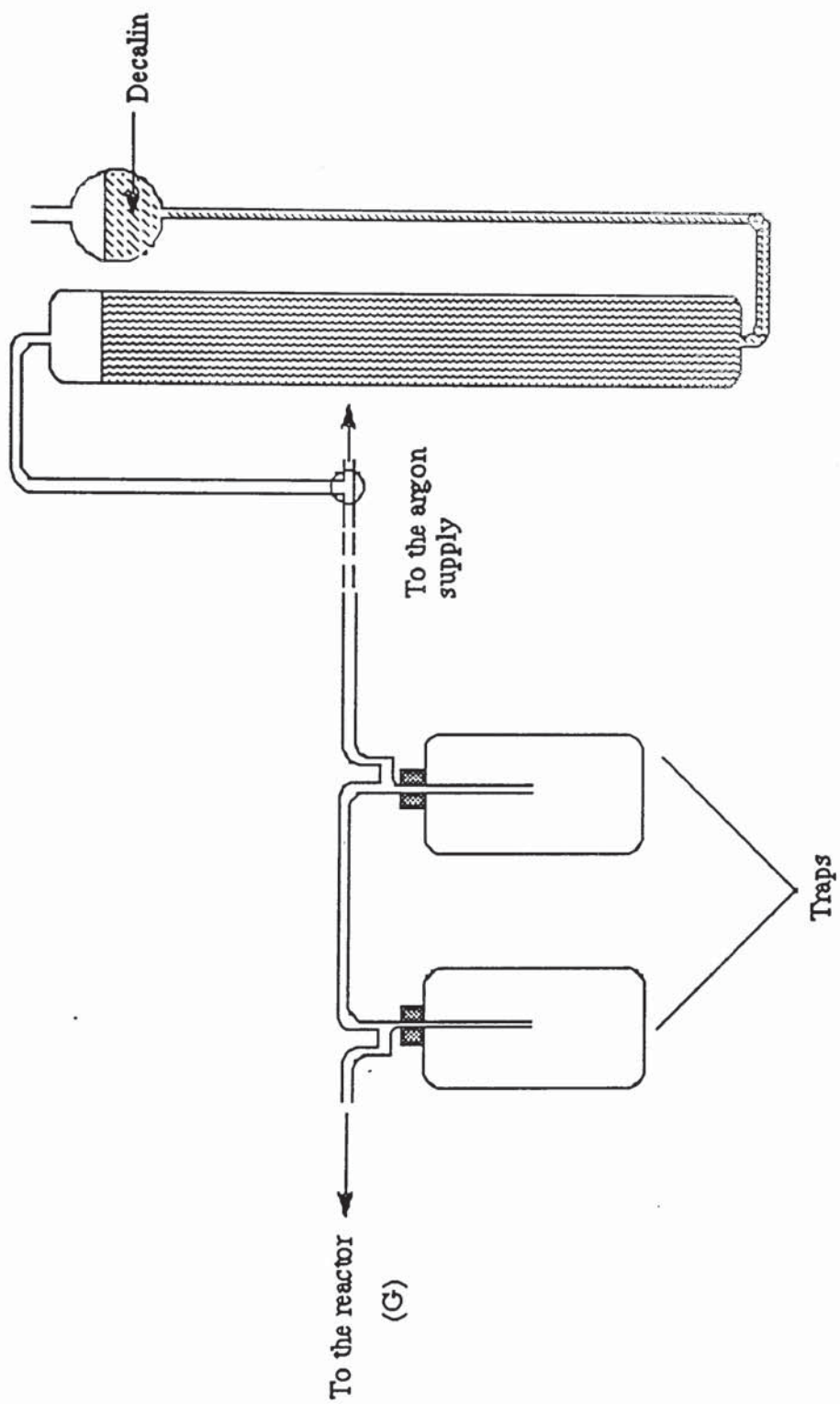
2.6. Preparation of the oxazolines

Oxazolines derived from 4-pentenoyl and 10-undecenoyl chloride were prepared according to the method established by Meyers[106]. The preparations are described in Chapter 6 and the products and intermediates were analysed by ^{1}H and ^{13}C nmr, ft-ir, tlc and mass spectroscopy.

2.7. Analytical techniques

A number of physical techniques were used to aid the analysis of reactions and to examine reactants and products.

2.7.1. Gas liquid chromatography (glc)

Gas liquid chromatography is an analytical technique used to separate and identify the components of a mixture[107,108]. In gas chromatography, the components of a mixture are partitioned between the gas and a stationary phase. Usually the stationary phase is a non-volatile liquid supported on an inert matrix such as silicon grease on diatomite and the mobile phase is an inert gas such as nitrogen. As the sample mixture descends the column, the various components are separated, according to their partition coefficients, and eluted at the end of the column where they are detected using a flame ionization detector. The conductivity of the flame is recorded and generates a peak as a component elutes from the column, fig 2.7.1.

Fig 2.7.1

A Schematic Diagram of a Gas Liquid Chromatography Machine
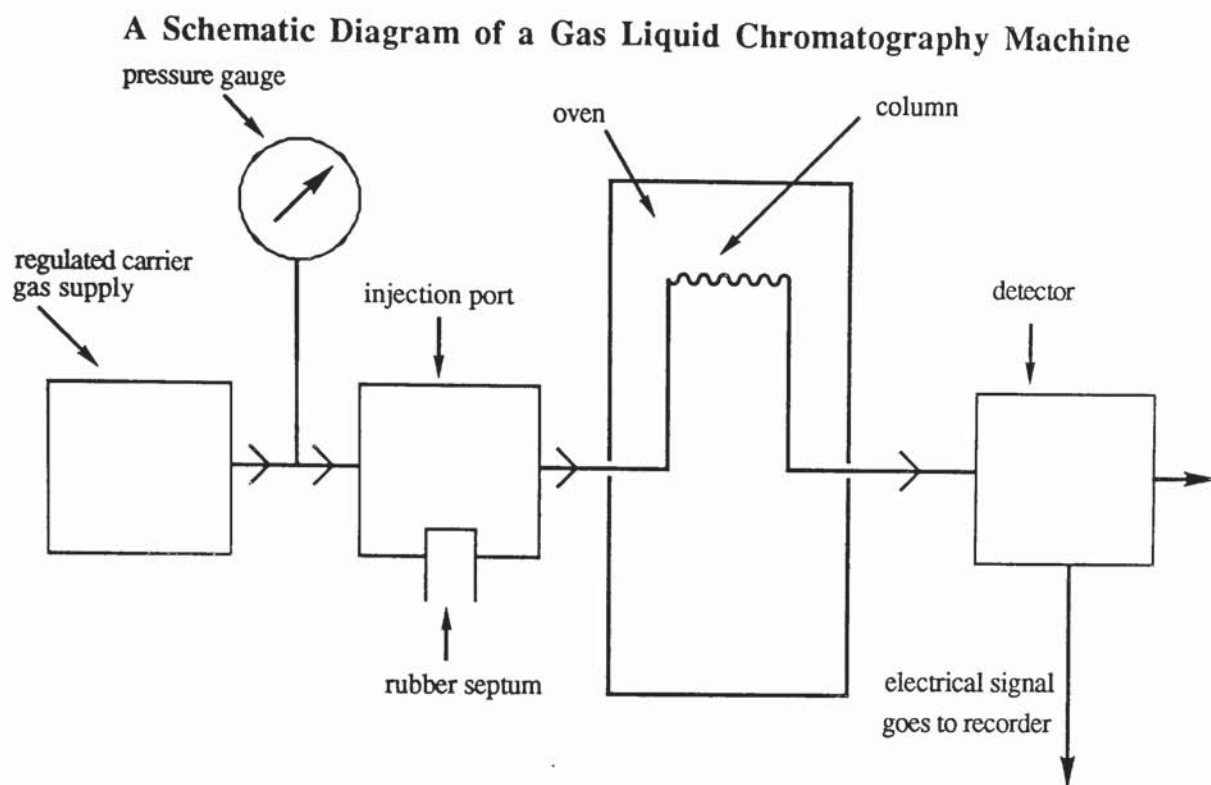
The gas liquid chromatograph used was a Pye Unicam GCD Chromatograph fitted with a Flame Ionization Detector. The column was composed of 25% Silicone Grease absorbed on diatomite. Connected to the Chromatograph was a Hewlett Packard 3396A computing integrator which recorded the peaks of the components along with their retention times and peak areas. The temperature of the column was set at 125°C and the sensitivity at 128×10^3. The technique was used principally to follow the extent of metathesis either by measuring the amount of 5-decene produced and the amount of 1-hexene consumed.

2.7.1.1. Calibration

Calibration curves were constructed in order to estimate the concentration of 1-hexene, 5-decene and 4-nonene in the reaction solutions during the metathesis of 1-hexene. For the construction of the 1-hexene calibration curve, solutions of 1-hexene were made up in cyclohexane so that the concentrations of 1-hexene varied between 0.73M and 4.4M. A typical gas chromatogram of a solution of 1-hexene in cyclohexane is shown in fig 3.6.1 in chapter 3. Each solution was analysed by gas chromatography and a calibration plot of log (% area cyclohexane)/(% area 1-hexene) against $\log \frac{[\text{cyclohexane}]}{[\text{1-hexene}]}$ generated as shown in fig 2.7.2.

Fig 2.7.2

Calibration plot for 1-hexene
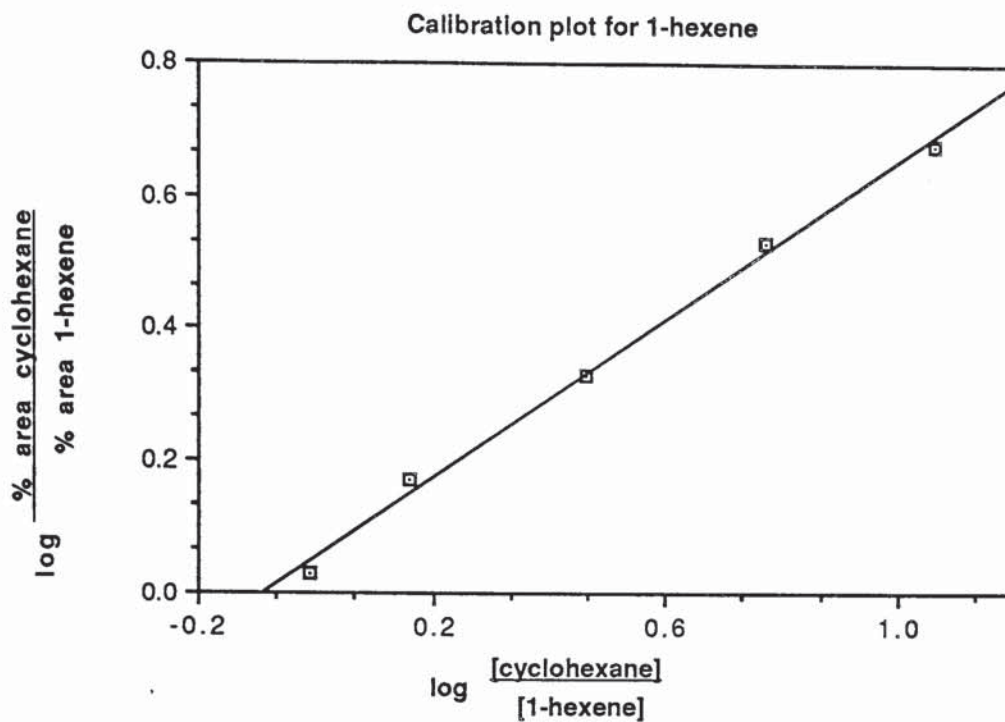
For the construction of the calibration plots for 5-decene and 4-nonene, each olefin was made up as a solution of 1-hexene. The initial solution was then diluted tenfold with 1-hexene and a further dilution of this second solution was also made with 1-hexene to form solutions of olefin such that the olefin to 1-hexene molar ratios were 1:0.07, 1:0.006 and 1:0.0006. The calibration curves for these materials are shown in figs 2.7.3 and 2.7.4.

Fig   2.7.3

Calibration plot for 5-decene

Calibration plot for 4-nonene
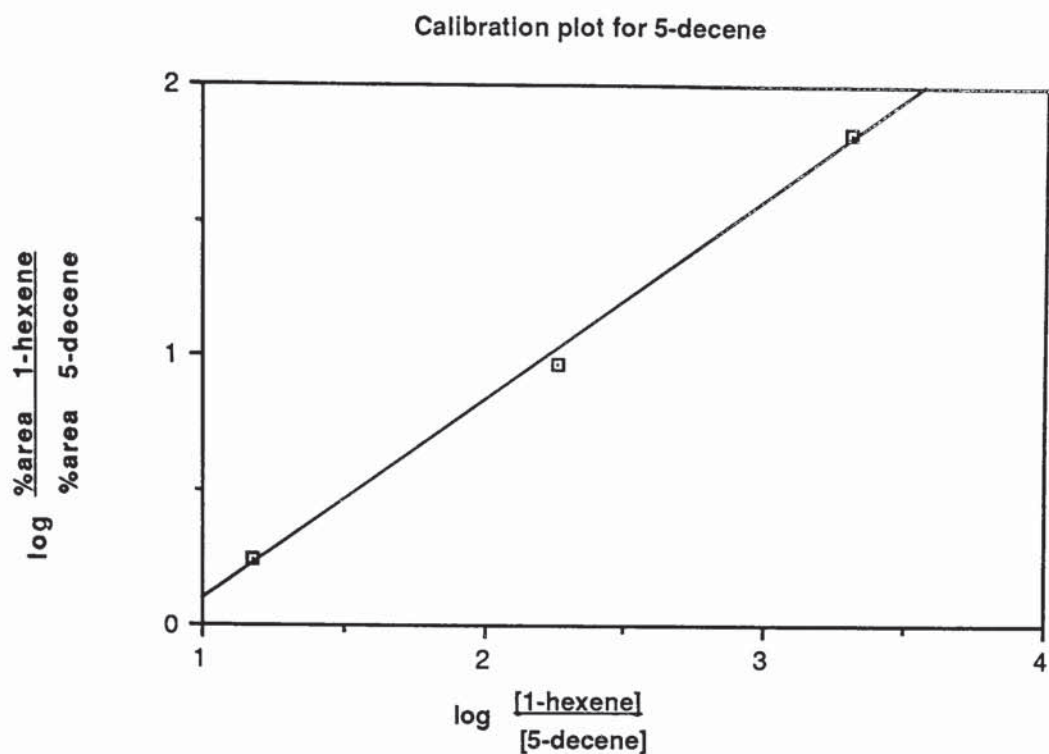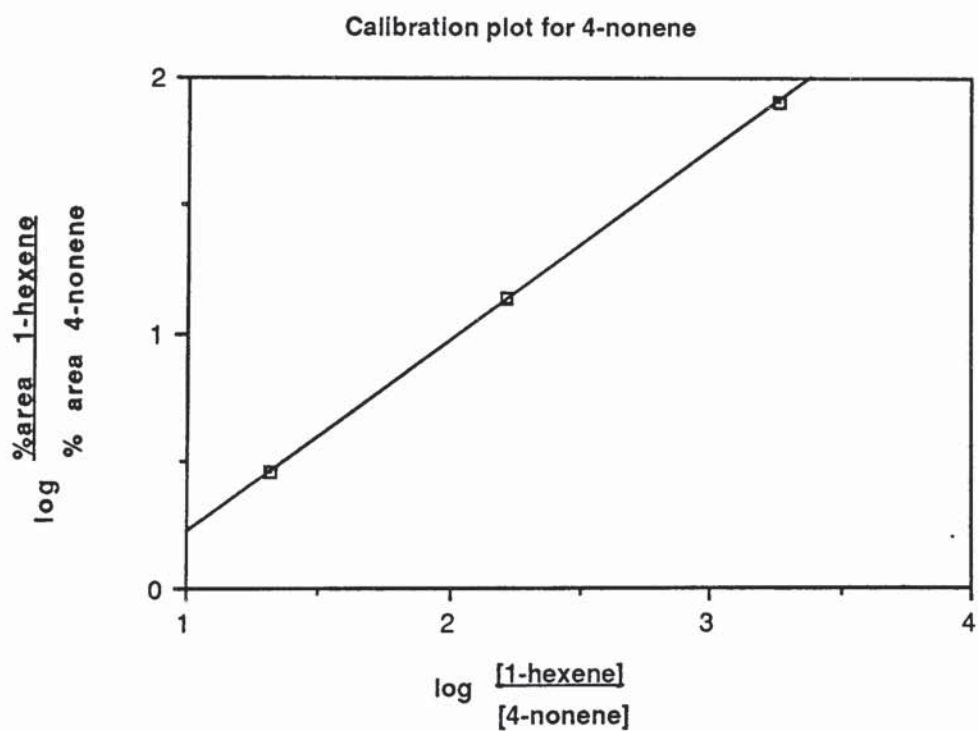
2.7.2. Thin layer chromatography (tlc)

Chromatography is a sensitive analytical technique which can detect the purity of a substance

and separate out the components of a solution[108]. This technique is particularly useful for

mixtures of non-volatile components. There are two phases involved; the stationary phase and the mobile phase. The stationary phase is the solid substance on which the solution to be separated is placed, and the mobile phase is the fluid which is allowed to ascend or descend the stationary phase. As the fluid flows over the stationary phase, the substances in the solution dissolve in the fluid to different degrees and travels different lengths of the stationary phase. The distance a component travels over the solid phase is dependent upon the partition coefficient of that component between the liquid and the solid. The components partition themselves between both phases and if the partition coefficients of the substances are different, good separation of the components will occur. The components in the solution undergoing analysis can be identified by comparing the solution alongside known samples or by measuring the R_f value of each component. The R_f value is a measure of the distance a substance travels from its origin and is calculated by dividing the distance travelled by the substance by the solvent front, fig 2.7.5. The R_f value for a particular substance in a particular solvent is constant at a given temperature.

Fig 2.7.5

A Thin Layer Chromatograph

origin marked with pencil

$$R_f = \frac{X}{Y}$$
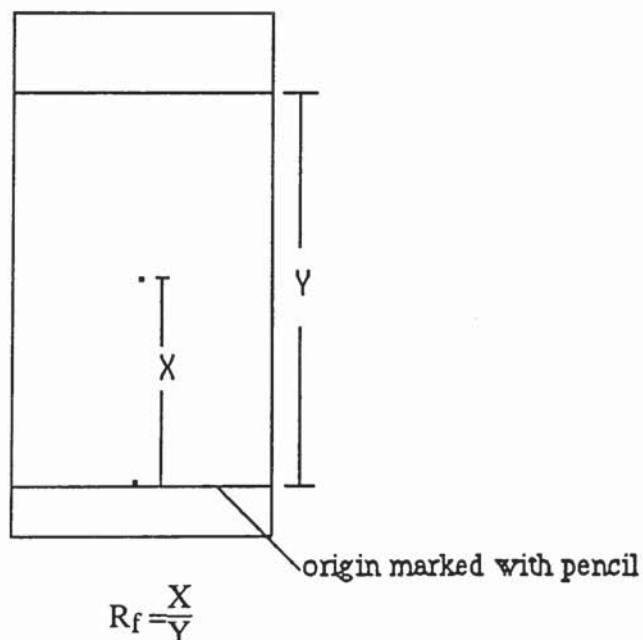
The stationary phase can be paper but in the case of TLC, it is silica gel, alumina or cellulose acetate. TLC is preferably used to paper chromatography because a quicker and more efficient separation is achieved.

In order for the R_f values to be calculated the spots relating to the various compounds must be visible. If the compounds are coloured then they are clearly visible to the naked eye but colourless compounds need to be developed using chemical or physical methods. Chemical methods of detection involve the use of a chemical known as the locating agent. The plate maybe sprayed or dipped into a solution of the locating agent and the application of heat helps to accelerate the process of the spots becoming visible. Locating agents include iodine vapour which is used to develop the spots of mainly organic unsaturated compounds. The spots appear brown. Physical methods are based on spectroscopic techniques involving ultra-violet light and fluorescence[108].

In this project silica gel tlc plates were used to ascertain the purity of the synthesised oxazolines and the related compounds and to determine whether metathesis of these compounds had occurred over Re_2O_7/Al_2O_3 catalysts. The solvent phase for 4,4-dimethyl-2-(9-decenyl)-1,3-oxazoline was cyclohexane and for 4,4-dimethyl-2-(3-pentenyl)-1,3-oxazoline methanol. The spots were developed in a closed vessel using iodine crystals.

2.7.3. Mass spectrometry

Mass spectrometry is a powerful, analytical technique which can be used to determine the molecular weight and the molecular structure of an organic compound[109]. A vapourized sample is introduced into an ion source, which is held at a pressure of between 10^{-5} 10^{-7} mmHg. The molecule is bombarded by an electron beam with energy of between 10 and 100eV, fig 2.7.6. Energy of the order of 10-15eV corresponds to the ionization potential range for many organic molecules. Ejection of an electron from the molecules by a repulsive interaction results in the formation of positive ions. Such ions are called molecular ions, M^+. Increasing the energy of the bombarding electrons beyond 15eV, results in the molecular ions having sufficient energy to undergo decomposition to fragment ions, which are characteristic of the molecular structure. 70eV has been found to give good fragmentation of reproducible intensity. Electrodes then accelerate these ions which are subjected to orthogonal magnetic and electric fields on entering a semi-circular chamber. The magnetic field causes the ions to follow a circular path, the radius of which depends on the mass to charge ratio, m/e. Variation of the electrostatic field causes the radius of the path executed by the ion to change. Scanning the field

strength causes various ions in turn to impinge on the detector. The width of the mark corresponds to the abundance of an isotope.

Fig 2.7.6

A Schematic Diagram of a Mass Spectrometer
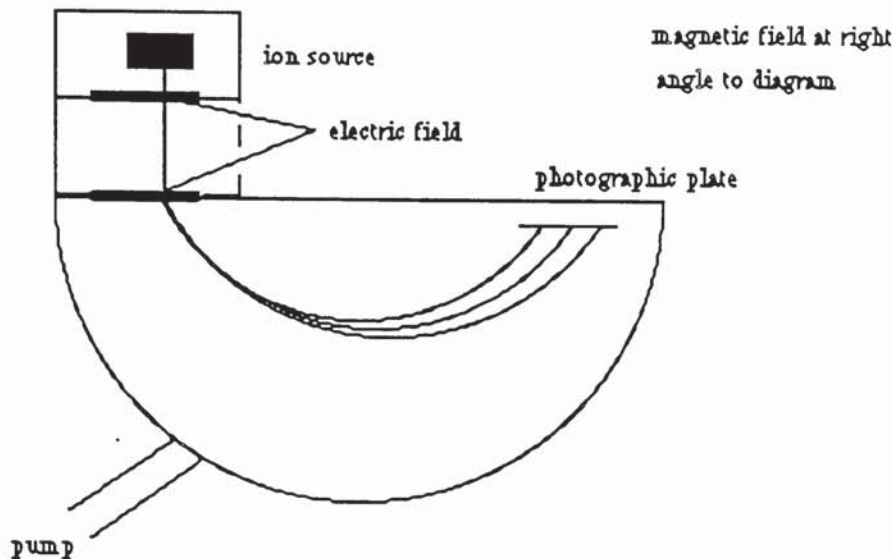
2.7.3.1. Ion production: volatile materials

Thermally volatile compounds are introduced into a chamber where they are ionized. Electron impact (EI) and chemical ionization (CI) are the two methods used to ionize thermally volatile compounds. In the EI technique the sample is bombarded by electrons so that it is ionized by the removal of an electron to produce a cation radical:

$$M \xrightarrow{-e} M^{+}_{\bullet}$$
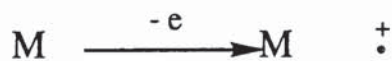
The primary disadvantage with this technique is that extensive fragmentation occurs so that the molecular ion is usually absent. Since one of the primary reasons for using mass spectrometry is to determine the molecular weight of the sample, this is not a desirable situation. CI overcomes this problem. In this technique a reagent gas, eg methane, is introduced into the ion chamber at pressures of around 10^2 Nm^{-2} and ionized by electrons. The ions produce fragments and because of the high pressures, collide with their neutral counterparts.

$$CH_4 + e \longrightarrow CH_4^+ + 2e$$

$$CH_4^+ \longrightarrow CH_3^+ + H^{\cdot}$$

$$CH_4^+ + CH_4 \longrightarrow CH_5^+ + \overset{\cdot}{C}H_3$$

$$CH_3^+ + CH_4 \longrightarrow C_2H_5^+ + H_2$$
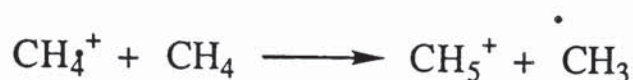
When the sample is volatized in this mixture of ions, the CH_5^+ acts as a strong acid and protonates the sample. Consequently the observed m/e is one unit higher than the actual molecular weight. Under these conditions the M+1 ion does not usually possess sufficient energy for fragment.

2.7.3.2. Ion production: involatile materials

It is very difficult to volatize compounds that have a low vapour pressure and a high molecular weight. Consequently alternative techniques are required for ion production. One of the more widely used techniques is fast atom bombardment (FAB). The sample is dissolved in a matrix of low volatility eg, glycerol, and then bombarded by a beam of of fast xenon atoms (Xe^*). These ions are produced when accelerating xenon ions (Xe^+) are neutralized by electron transfer as they pass almost stationary xenon atoms (Xe) at low pressure:

$$Xe^+ + Xe \longrightarrow Xe^* + Xe^+$$

After the fast xenon atoms have collided with the matrix, the sample is ionized and desorbed. Analysis occurs in the usual way.

2.7.4. Nuclear magnetic resonance spectroscopy (NMR)

This is a very powerful analytical technique used for elucidating the structure of compounds paticularly those containing carbon and hydrogen[109,110]. Atomic nuclei which have a nuclear spin I behave as bar magnets and in the presence of a magnetic field, they orientate themselves in 2I + 1 ways. Nuclei such as carbon and hydrogen have spins of $\frac{1}{2}$ and therefore can only occupy two orientations, a low energy orientation aligned with the applied field (the ground state) and a high energy orientation opposed to the field (the excited state). When the nuclei are

subjected to a weak oscillating magnetic field, produced by passing a radio frequency current, eg at 30MHz frequency, through a surrounding coil, the nuclei resonate with the field at definite frequencies and undergo transitions between the ground and excited energy levels. The resonance is detected, amplified and recorded to produce a spectrum. The information is classified into the chemical shift, δ, (the relative shift from a standard, eg tetramethylsilane) and the coupling constant, J. The significant feature of this technique is its ability to detect a nuclei and differentiate between its different electronic environments, eg ethanol has three different hydrogens and two different carbons corresponding to CH_3, CH_2, and OH and these are detected by ^{1}H and ^{13}C nmr respectively.

High resolution ^{13}C and ^{1}H nmr spectra were obtained using a Bruecker AC300 spectrometer. Samples were made up into solutions using a suitable deuterated solvent, eg deuterated chloroform ($CDCl_3$) and a small quantity of tetramethylsilane (TMS) was added as the reference material.

2.7.5. Infra-red spectroscopy (IR)

This technique makes use of the fact that vibrations within molecules show characteristic absorption bands in the infra-red region of the spectrum. and valuable information about molecular structure and symmetry is provided[109]. Infra-red spectra were recorded on a Perkin-Elmer FT-IR machine and all the analyses were done in the liquid phase on sodium chloride discs.

2.7.6. Electron spectroscopy for chemical analysis (ESCA)

ESCA is a technique used to measure the binding energies of valence and inner core electrons of elements and occurs when a sample is irradiated with X-rays of a certain energy[111]. The innermost electrons are bound with an energy that depends primarily on the nuclear charge of the atom to which they are held. The 1s electrons of the carbon atoms in a compound tend to have an ionization energy of about 1200eV (1.92×10^{-16}J) but this value is affected by the chemical environment of the carbon atoms. Consequently, measurement of the ionization energies of such inner electrons, reveals the various chemical environments of the atoms of a

given type in the molecules of the sample under study and therefore, the nature of the compound.

An ESCA Lab 200D machine by Vacuum Generators was used to analyse the surface of used and virgin $Re_2O_7/\gamma\text{-}Al_2O_3$ catalysts in order to try and ascertain its chemical environment before and after metathesis.

CHAPTER 3: THE KINETICS OF THE METATHESIS OF 1-HEXENE USING RHENIUM OXIDE ON γ - ALUMINA AS THE CATALYST

3.1. Introduction

Elucidating the kinetics of a reaction is a major step in determining the mechanism by which a reaction proceeds[112]. In the majority of reactions, the conversion of reactant to product is not a single-step procedure. A complex reaction may usually be broken down into a series of simple elementary steps and when one of these steps is slow compared to the others, this step may determine the rate of the overall reaction and become the rate determining step. The rate constant of a reaction is decided by the energy barrier, ie the activation energy, that reactants have to surmount in order to be converted into products, and the height of this barrier is determined by the mechanism of the reaction. A catalyst is a compound, or complex, that increases the rate of attainment of equilibrium in a reaction and provides the reactants with an alternative, lower energy route to the products, thereby increasing the rate of the reaction.

A spontaneous reaction is one which proceeds without the influence of outside forces, i.e. as soon as the reactants are in contact with one another, they react immediately to form products. The metathesis reaction is not a spontaneous reaction and requires a catalyst. The kinetics of the metathesis reaction will account for the effects of the catalyst as well as the reactants, temperature and promotors in the reaction.

The metathesis of 1-hexene over $CoO/MoO_3/Al_2O_3$, a heterogeneous catalyst, was first investigated by Banks and Bailey[1]. Propene, butene, pentene and heptene were obtained instead of the expected ethene and 5-decene because the rate of isomerization with this catalyst was greater than the rate of metathesis. Consequently co-metathesis between the isomerization products occurred to give a complex product mixture. The metathesis was carried out at temperatures in the range of 150-200^{0}C and conversions of 1-hexene of over 55% were attained. It was also noticed that the conversion of 1-hexene displayed an optimum temperature, hence showing the importance of temperature in the metathesis reaction, which was interesting because thermodynamically, the reaction is entropically controlled.

1-hexene is of particular interest because of its metathesis product, 5-decene. C_{10}-C_{18} olefins are used extensively in the manufacture of detergents, polymer materials, oils and additives and therefore, the increased production of these olefins is desirable.

To date, a complete and unambiguous understanding of the kinetics of olefin metathesis has not been achieved. In this project, the activity of 1-hexene metathesis over rhenium (VII) oxide/γ-alumina catalyst with respect to 1-hexene concentration, catalyst weight and temperature was investigated. The effects of cocatalysts and the life time of the catalyst on the rate of metathesis were also examined.

3.2. The effect of 1-hexene concentration on the rate of metathesis

Many different kinetic models have been postulated to account for the mechanism of the metathesis reaction but considerable disagreement exists[73-78]. The kinetic models either support a mechanism that is unimolecular or bimolecular with respect to the olefin substrate. The aim of this section is hopefully to shed some light on this controversial area.

The metathesis of 1-hexene was carried out as described in section 2.5 using 6% rhenium (VII) oxide on γ-alumina catalyst. In a typical experiment, 700mg of catalyst was reacted with 25ml of 6.8M 1-hexene solution in cyclohexane at a temperature of 35°C. Ethene was collected in the gas burette and its volume estimated as described previously (see section 2.5). Fig. 3.2.1 shows a typical plot of the volume of ethene evolved as a function of time. The experiment was repeated using the same quantity of catalyst and different concentrations of 1-hexene solution; the volume of 1-hexene solution was kept constant at 25ml. The effect of the concentration of 1-hexene on the rate of evolution of ethene is shown in fig 3.2.2.

The kinetic data of the conversion of 1-hexene to ethene may be analysed either by considering the individual reactions and generating integrated rate equations that fit the data obtained or by comparing the initial rates of reaction of 1-hexene at different concentrations. The initial rates could be determined from the plotted data and were most conveniently obtained using the

MacIntosh Cricket Graph software. The plots shown in figures 3.2.1 and 3.2.2 were obtained using this software and a close fit of the data was obtained using the quadratic relation

$$v = a_0 + a_1t + a_2t^2$$

where v is the volume of ethene generated and a_1 is a measure of the initial rate of evolution of ethene. The values of the coefficient a_1, which were significantly larger than the corresponding values of a_2, are shown in table 3.1 for the series of 1-hexene concentrations:

Table 3.1

The value of the coefficients of the linear term for the dependence of volume of ethene with respect to time at different concentrations of 1-hexene.

1-hexene concentration mol dm^{-3}	a_1/cm^{3}min^{-1}	a_2/cm^{3}min^{-1}
6.8	4.23	-0.76
4.0	1.72	-0.20
3.7	1.88	-0.25
2.3	0.91	-0.15
1.6	0.73	-0.10

Fig 3.2.1

Plot to show the rate of ethene evolution

using a 6.8M solution of 1-hexene
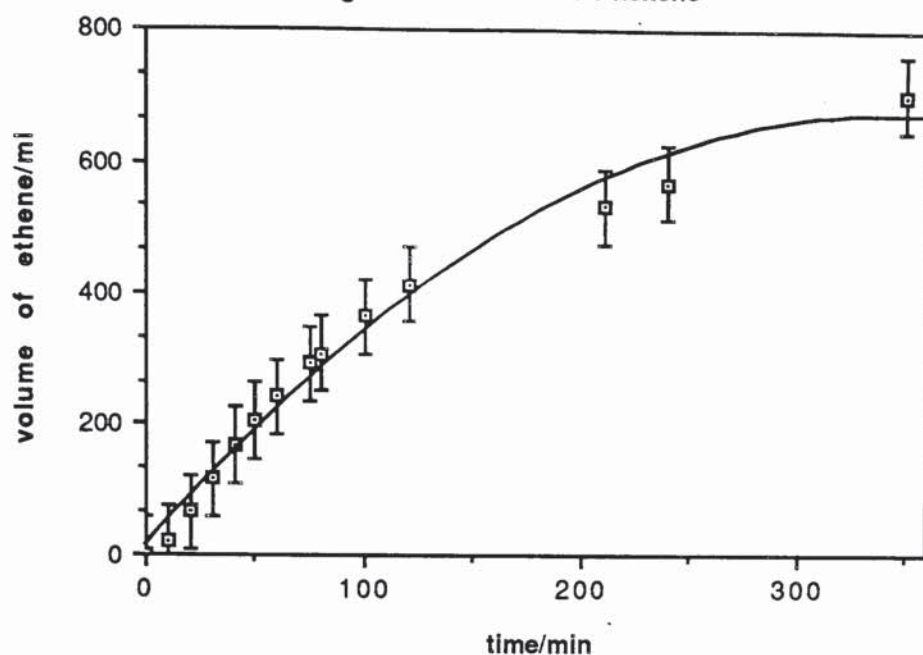
Fig 3.2.2

Effect of 1-hexene concentration on the

rate of evolution of ethene
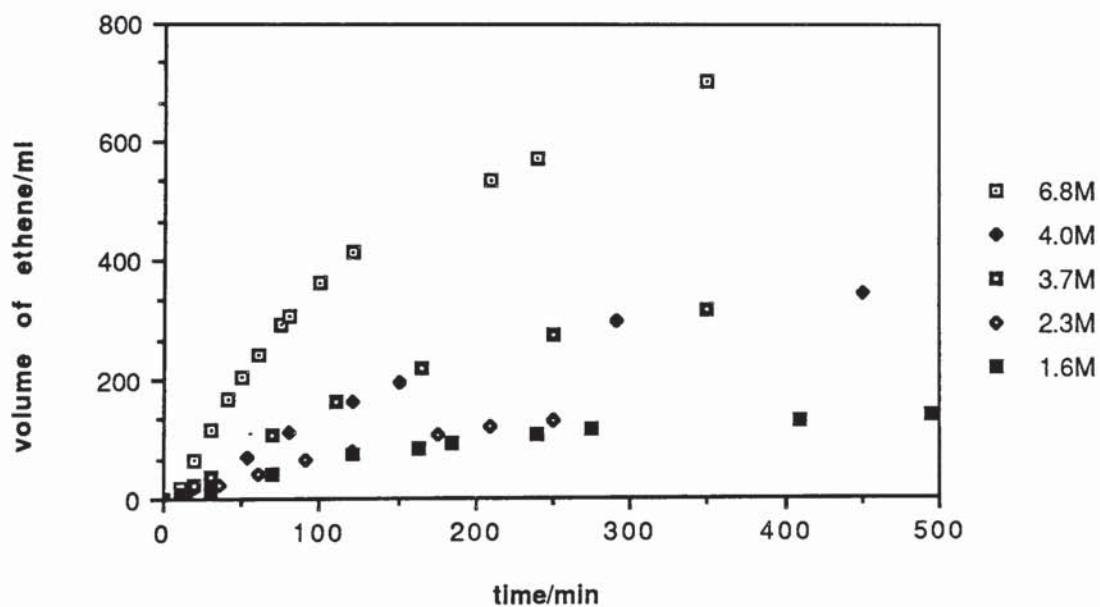
A plot of rate of evolution of ethene against $[hex]^2$ produced a reasonably linear dependence, within experimental error, as shown in fig. 3.2.3, which implies that the order of reaction is second order with respect to 1-hexene concentration.

Fig 3.2.3

**Plot to show the order of the reaction
with respect to 1-hexene**
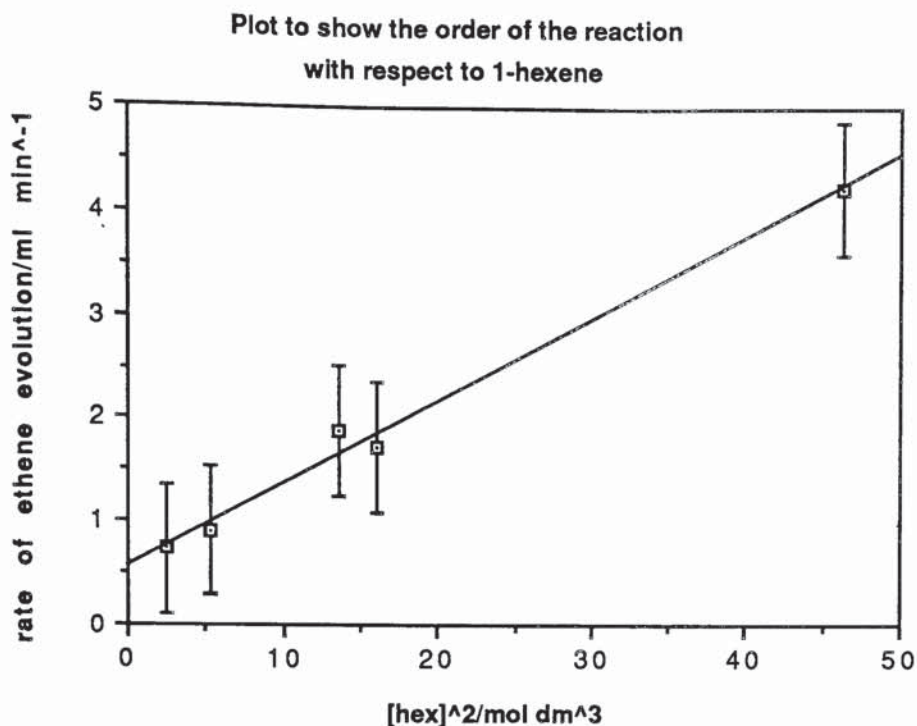
3.3. The effect of catalyst concentration on the rate of metathesis of 1-hexene solution

Catalysts provide favourable energetic pathways for reactions that might otherwise not be possible. The elucidation of the mode by which the catalyst interacts with a substrate is a prerequisite to a full determination of the mechanism of a reaction. In the case of the metathesis of olefins, the mechanism proposed by Herisson and Chauvin has been generally accepted and accordingly, any kinetic model ought to be consistent with this mechanism.

The metathesis of 1-hexene was carried out as before, using various weights of the catalyst (6% $Re_2O_7/\gamma\text{-}Al_2O_3$) and 25 ml of 3.7M solution of 1-hexene in cyclohexane. The volume of ethene evolved as a function of time using different weights of catalysts is shown in fig 3.3.1:

111

Fig 3.3.1

The effect of catalyst weight
on the rate of metathesis of 3.7M 1-hexene solution
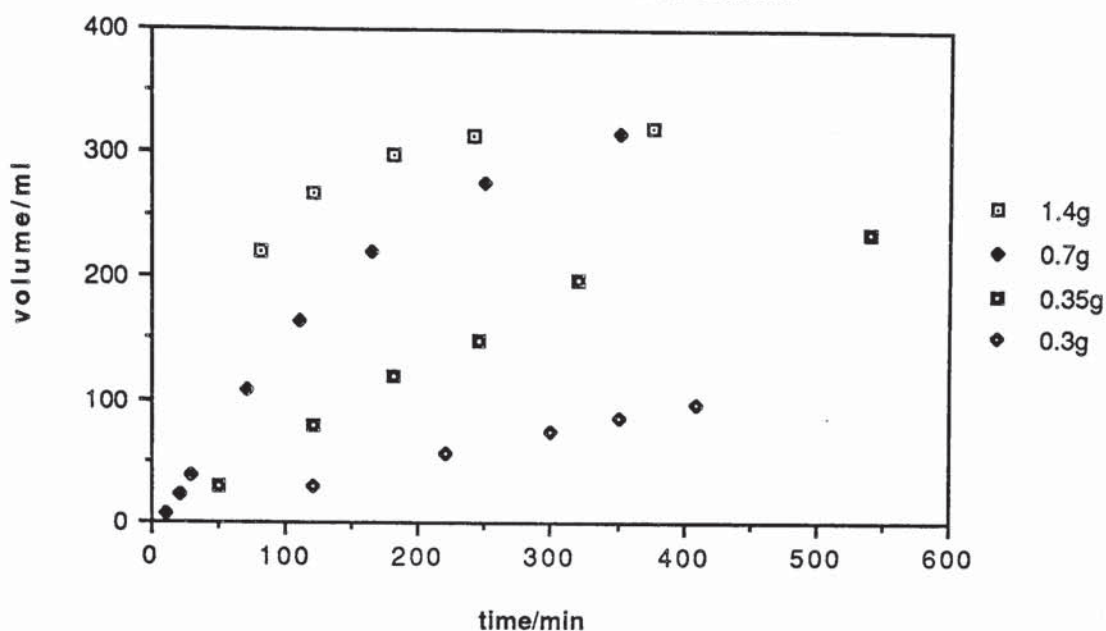
The initial rate of ethene formation depended on the weight of catalyst used. The initial rate of ethene formation was determined as described in section 3.2 and the values of the coefficients obtained from a quadratic fit of the experimental points, was used as a measure of the rate of the reaction, table 3.2.

A plot of log(rate) versus log(weight of catalyst) gave an order of reaction of 1.3 with respect to catalyst concentration. Inspection of the first order and second order plots showed that the first order plot produced the better linear fit, fig 3.3.2. This implied that the order of the reaction with respect to the weight of the catalyst was approximately one.

Table 3.2.

The value of the coefficients of the linear term for the dependence of volume of ethene with respect to time at different weights of catalyst.

weight of catalyst/g	a_1/cm^3min^{-1}	a_2/cm^3min^{-2}
1.40	3.02	-0.660
0.70	1.88	-0.250
0.35	0.35	0.033
0.30	0.30	-0.016

Fig 3.3.2

Order of reaction with respect to the catalyst
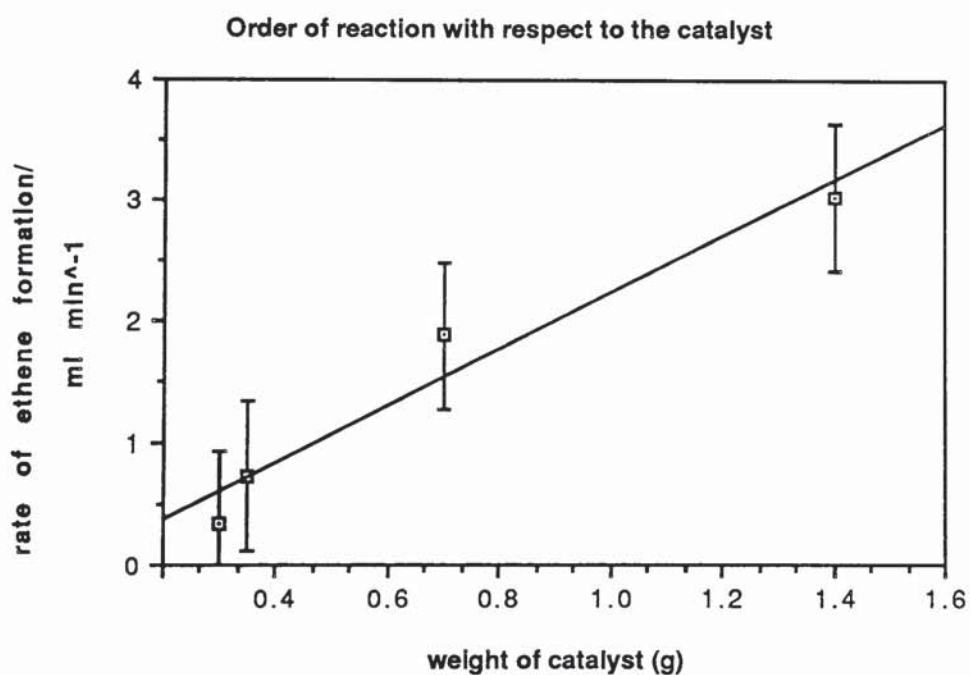
Within experimental error, the dependence of the rate of reaction on weight of catalyst extrapolates to the origin which is typical of a first order plot.

3.4. Effects of 1-hexene concentration on % conversion to ethene at constant catalyst weight

According to the initial rate studies the rate of reaction would appear to be second order in the concentration of 1-hexene and first order in the concentration of the catalyst. If that is so then the rate equation may be stated simply as

$$\frac{-d[\text{1-hexene}]}{dt} = k[\text{1-hexene}]^2[\text{catalyst}]$$

The concentration of 1-hexene at any time is given by

$$[\text{1-hexene}] = (1-x)[\text{1-hexene}]_o$$

where $[\text{1-hexene}]_o$ is the initial concentration of 1-hexene and x is the fractional conversion.

The rate equation for the reaction then becomes:

$$-\frac{d[\text{1-hexene}]}{dt} = [\text{1-hexene}]_o \frac{dx}{dt} = k(1-x)^2[\text{1-hexene}]^2_o[\text{catalyst}]$$

therefore,

$$\frac{dx}{dt} = k(1-x)^2[\text{1-hexene}]_o[\text{catalyst}]$$

integrating between the limits of x and 0 gives

$$\frac{1}{(1-x)} - 1 = k[\text{1-hexene}]_o[\text{catalyst}]t$$

therefore,

$$\frac{x}{1-x} = k[\text{1-hexene}]_o[\text{catalyst}]t$$

Data from fig 3.2.2 was analysed to produce the dependence of $\frac{x}{(1-x)}$ after 120min of reaction on the initial concentration of 1-hexene. The data shown in fig 3.4.1 confirms that during the initial period of the reaction, the rate of ethene formation is second order in the concentration of 1-hexene.

114

Fig 3.4.1

Effect of 1-hexene concentration on the

fractional conversion to ethene after 120 min
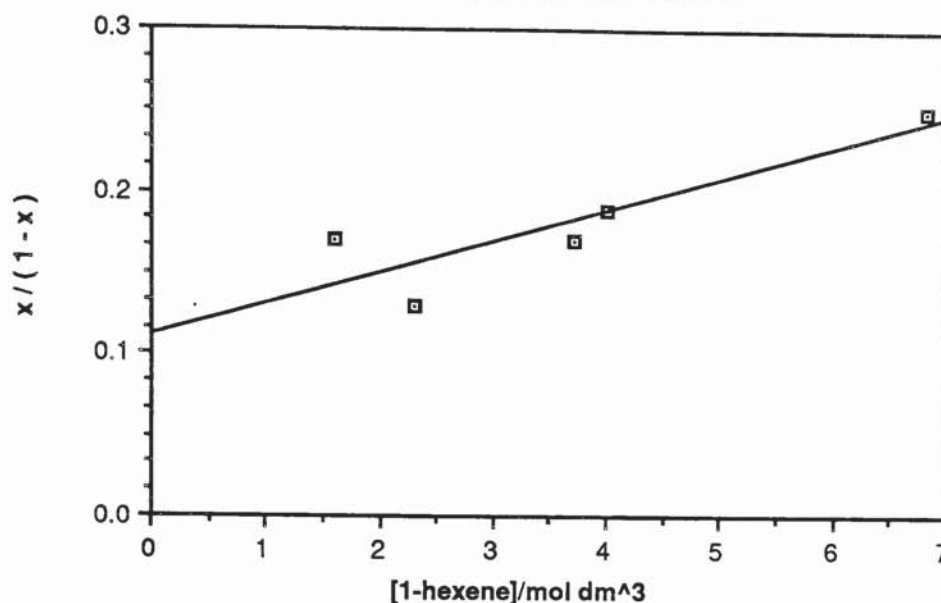
Similarly the plot shown in fig 3.4.2 confirms that the reaction is also first order in the concentration of catalyst used. In this case the fraction $\frac{x}{(1-x)}$, calculated from experimental data, is plotted against the weight of catalyst used in the reaction. According to this simple kinetic treatment the value of the overall rate constant k may be calculated from two plots. When these values are compared, 0.6 and 13×10^{-5} dm^3 mol^{-1} g^{-1} s^{-1}, significant differences are obtained. This difference is believed to be associated with the fact that the concentration of the catalyst is constant over this period and independent of concentration of 1-hexene. That the rate of reaction decreases to zero at a rate dependent on the concentration of 1-hexene would indicate that the concentration, if constant, may be a function of the fact that 1-hexene plays a role in the formation of the active site. Such complications are not allowed for in the above treatment.

Fig 3.4.2

**Effect of catalyst weight on the fractional
conversion of 1-hexene to ethene**
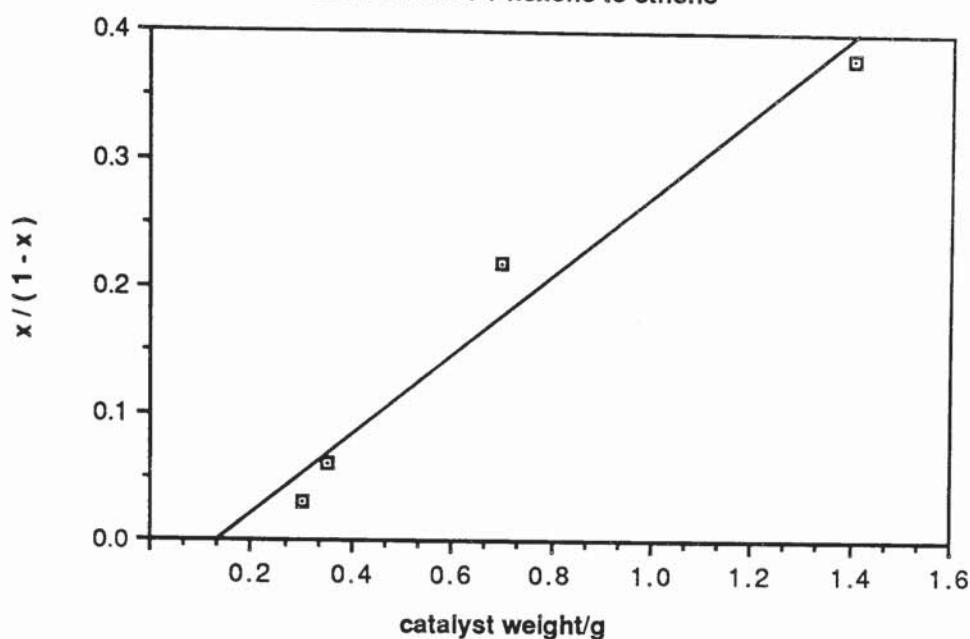
3.5. Gas liquid chromatograph (glc) studies on the metathesis of 1-hexene

The principle method used for the measurement of the extent of the metathesis of 1-hexene was the determination of the volume of ethene generated during the reaction. Obviously, one of the problems involved in the use of a single technique for the estimation of the extent of reaction is the reliability of the information gained from those measurements. It was decided therefore to apply a confirmatory method of analysis, glc, to the metathesis of 1-hexene because the effects of solubility of ethene in the solvent were unknown.

3.5.1. Detection of primary products

The metathesis of 1-hexene was carried out as described in section 2.5. 25ml of 4.8M 1-hexene solution was metathesised using $Re_2O_7/\gamma-Al_2O_3$ as the catalyst at 35°C. Samples of the reaction solution were removed at predetermined times and retained in closed vessels before analysis, thus making it impossible for any gases present to escape. Fig 3.5.1 shows the glc of the product obtained after 16h reaction. It can be seen that there are three major peaks in the chromatogram, corresponding to 1-hexene, retention time 1.469min, cyclohexane, 2.155min and 5-decene, 6.189min. 1-Hexene, cyclohexane and 5-decene were separately injected into the chromatograph to confirm the retention time of these materials.

116

A series of chromatograms were obtained during the course of a metathesis experiment and these were analysed to determine the rates of consumption of 1-hexene and the formation of 5-decene during the course of the reaction. Fig 3.5.2 shows a plot of the number of moles of 1-hexene consumed and the number of moles of 5-decene produced during the reaction. It was possible to determine these values from calibration curves shown in section 2.7. The amount of ethene produced as a function of time in another experiment carried out under the same conditions is plotted for comparison, fig 3.5.3.

START

.548
.615
.740
0.995
1.112
1.869
2.565
2.906
3.686
4.810
5.524

1.469

2.155

6.189

11.055

STOP
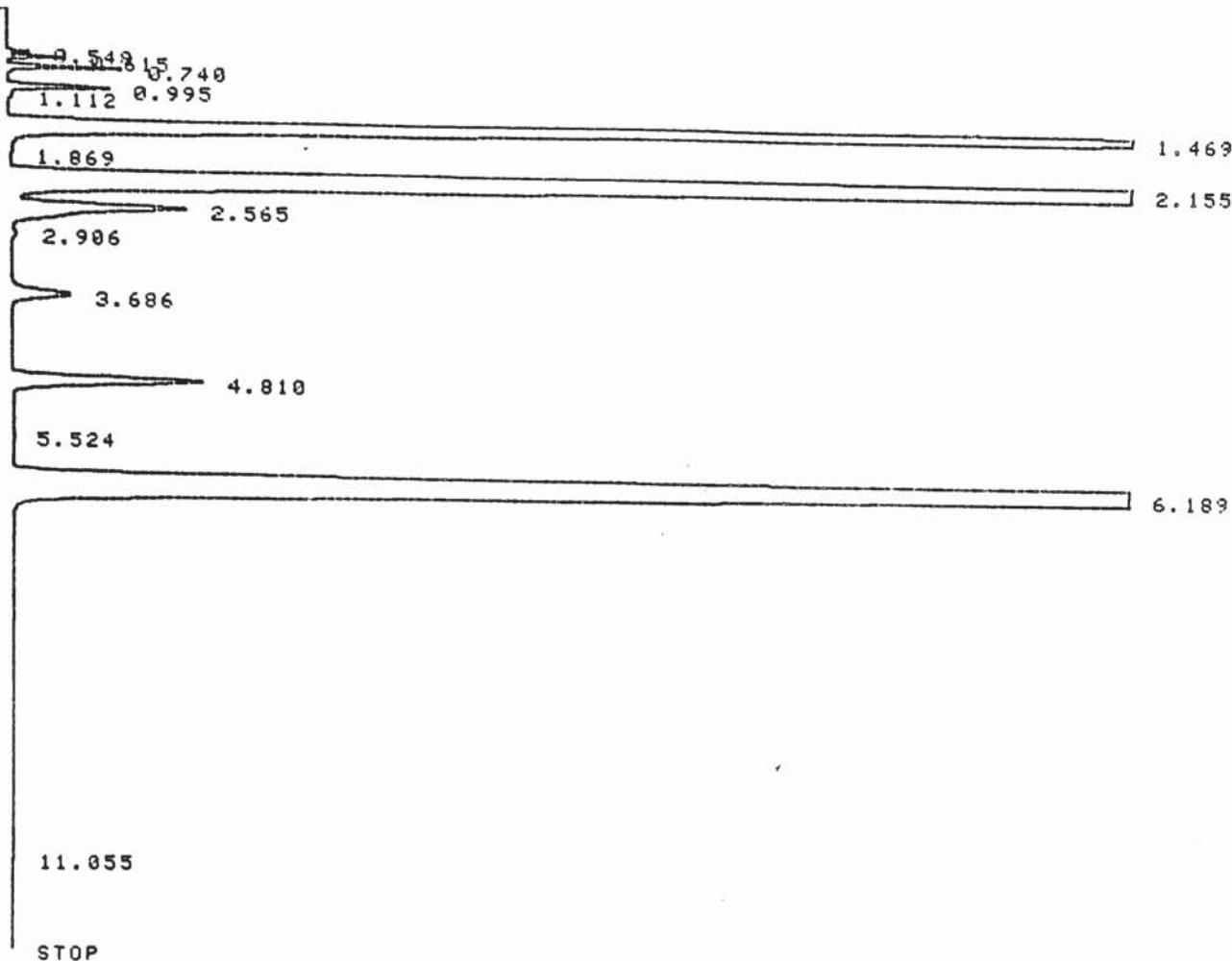
Closing signal file M:SIGNAL .BNC
Storing processed peaks to M:Q128285D.PRO

RUN#   20   AUG 8, 1990 15:23:08

SIGNAL FILE: M:SIGNAL.BNC
PEAK FILE : M:Q128285D.PRO
AREA%

RT	AREA	TYPE	WIDTH	AREA%
.548	4642	PV	.031	.04990
.615	13086	VP	.034	.14066
.740	31229	PB	.041	.33568
.995	38090	BV	.055	.40943
1.112	2036	VB	.058	.02189
1.469	1854879	PB	.100	19.93814
1.869	1407	BP	.077	.01512
2.155	3685150	PV	.150	39.61176
2.565	165512	VV	.138	1.77909
2.906	6524	VB	.119	.07013
3.686	52736	PB	.129	.56686
4.810	150825	PB	.116	1.62122
5.524	2456	PP	.150	.02640
6.189	3287634	PB	.195	35.33883
11.055	6968	VB	.360	.07490

TOTAL AREA=9.3032E+06
MUL FACTOR=1.0000E+00

Fig 3.5.1

GIC chromatograph of the product of the metathesis of 1-hexene

Fig 3.5.2

Plot to compare the decrease in 1-hexene concentration

with the increase in 5-decene concentration
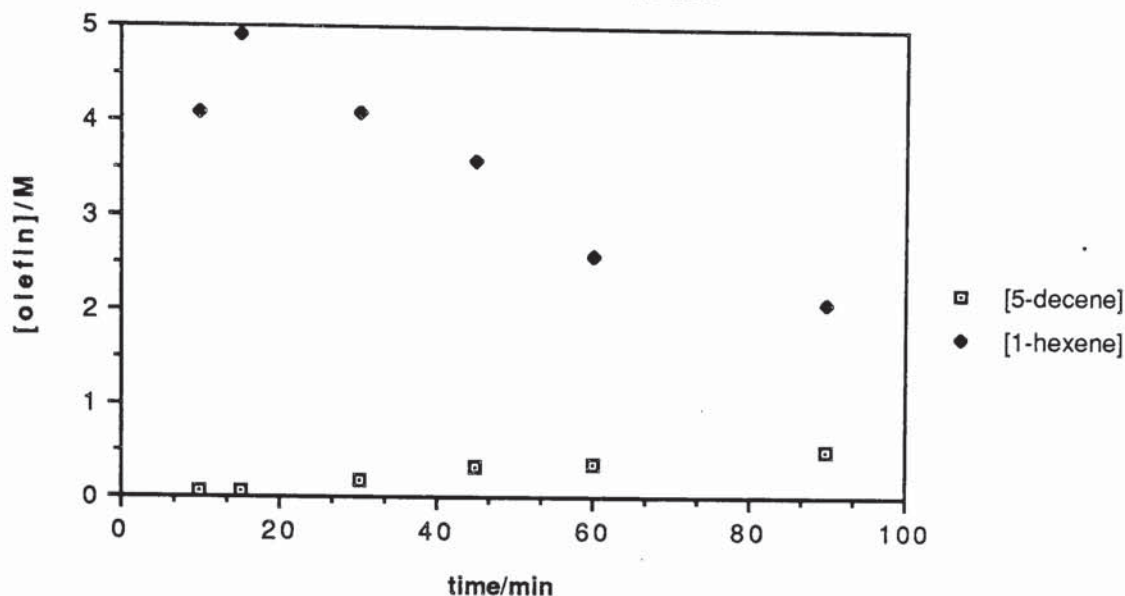
Fig 3.5.3

Plot to show the volume of ethene evolved
during the metathesis of 4.8M 1-hexene
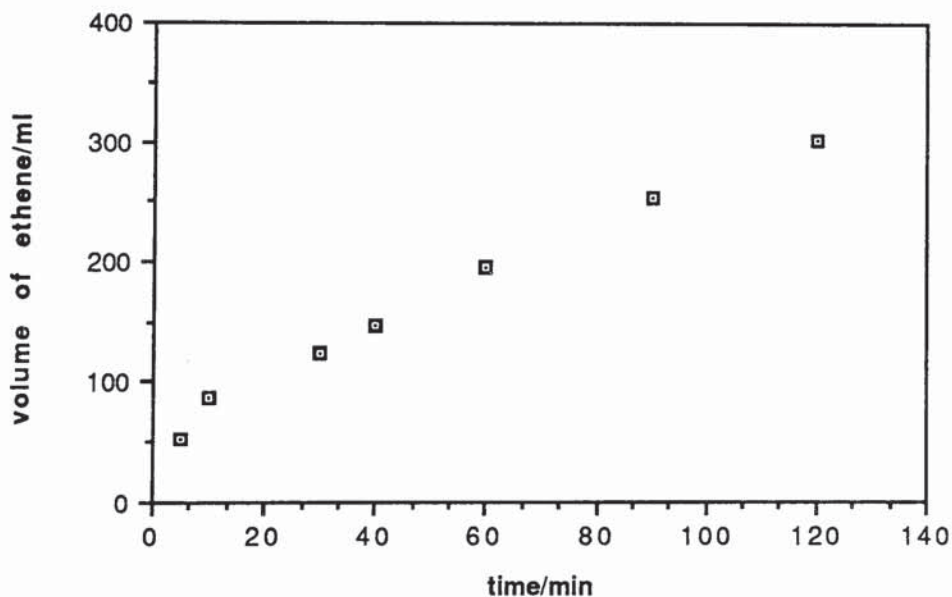
3.6. GLC-Mass spectroscopic (gc-ms) analysis of the products of the metathesis of 1-hexene

Gas chromatographic analysis, as shown in fig 3.5.1, showed that a number of minor products, not present in 1-hexene or the solvent, were formed in the reaction. The quantities of

these materials produced were extremely small; typically, the total area under these peaks was only 3% of the total area, and attempts to separate and characterise them individually were unsuccessful. Analysis of these minor products was attempted by glc/mass spectroscopy. The analyses were carried out on a VG-Mass Lab 12-250 GC-MS instrument.

3.6.1 Detection of secondary products

Gas chromagraphic analysis of the product shown in fig 3.5.1 revealed that at least two peaks, excluding 5-decene, were not present in the gas chromatograph of the reactant, 1-hexene, and the solvent, cyclohexane, fig 3.6.1. The retention time of these peaks are 2.565min and 4.810 min. In order to try to identify these peaks, gc-ms analysis was performed on the product and the results are found in Appendix 1. The peak at 537 on the gc-ms chromatograph, corresponds to the peak on the gc chromatograph with the retention time of 2.565min and was identified as 2-heptene, mass number 98. The peak at 648 corresponds to the peak with the retention time 4.810min and has been identified as 4-nonene, mass number 126.

Many of the other minor peaks found in fig 3.5.1 can be accounted for in fig 3.6.1 but there does appear to be an abundance of peaks with retention times less than that of 1-hexene, namely those appearing at 0.548min, 0.615min and 1.112min in fig 3.5.1; these will need to be characterised in the future.

3.6.2. 4-Nonene

Analysis of the glc data showed that one of the minor peaks, retention time 4.778 minutes, changed in concentration as a function of time and was identified by gc-ms as 4-nonene. As a confirmation, pure 4-nonene was injected into the gc and the retention time of the peak was found to be close to 4.810min, as shown in fig 3.6.2. A scheme suggesting its formation will be given later.

```
START
        0.735
        1.030
        1.325
        1.885

        2.922
       3.261
        3.583

        4.195

      STOP
```
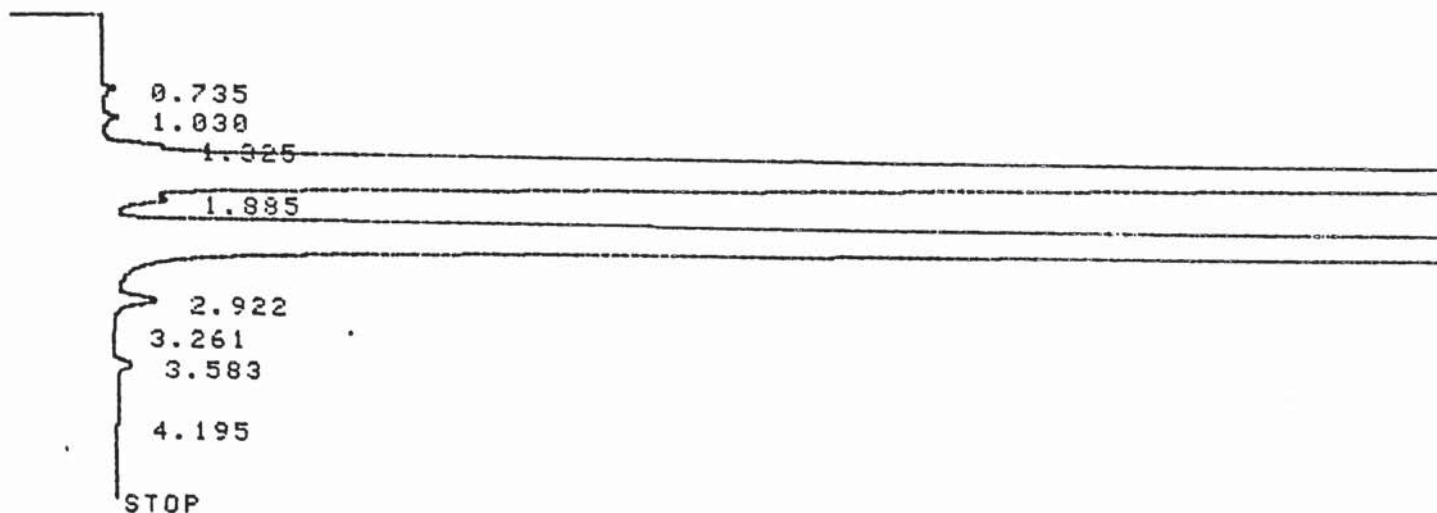
Closing signal file M:SIGNAL .BNC
Storing processed peaks to M:Q1EA7796.PRO

RUN#   3   JAN 1, 1901 00:40:53

SIGNAL FILE: M:SIGNAL.BNC
PEAK FILE : M:Q1EA7796.PRO
AREA%

RT	AREA	TYPE	WIDTH	AREA%
.735	3472	VV	.046	.00635
1.030	5921	VV	.073	.01082
1.325	18452	VH	.056	.03372
1.446	27736912	SHH	.128	50.68994
1.885	8737	TBP	.070	.01597
2.177	26897216	SHB	.147	49.15536
2.922	23818	TBP	.107	.04353
3.261	1067	TPB	.102	.00195
3.583	11175	PV	.114	.02042
4.195	12035	VV	.536	.02199

TOTAL AREA=5.4719E+07
MUL FACTOR=1.0000E+00

Fig 3.6.1

GLC chromatograph of 1-hexene/cyclohexane
solution

121

START

1.208

3.090

4.596

5.470
STOP
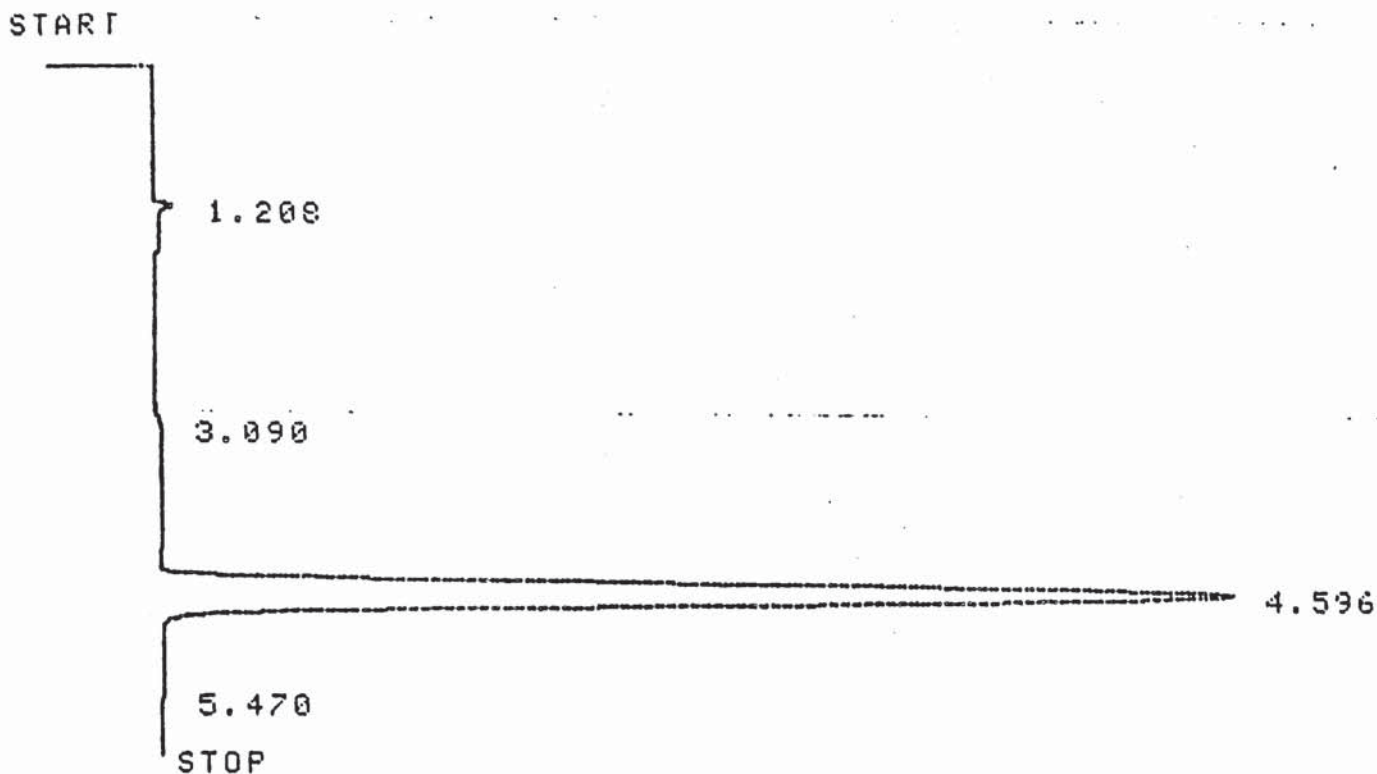
Closing signal file M:SIGNAL   .BNC
Storing processed peaks to M:Q1D1F05C.PRO

RUN#   4   DEC 13, 1990 10:09:31

SIGNAL FILE: M:SIGNAL.BNC
PEAK FILE : M:Q1D1F05C.PRO
AREA%

RT	AREA	TYPE	WIDTH	AREA%
1.208	5218	PB	.066	.51729
3.090	7518	PV	.412	.74530
4.596	989575	PB	.197	98.10205
5.470	6409	BV	.504	.63536

TOTAL AREA=1008720
MUL FACTOR=1.0000E+00

Fig 3.6.2

GLC chromatograph of pure 4-nonene

The change in concentration with time of 4-nonene is shown in fig 3.6.3. The concentration of 4-nonene increases as a function of time but when compared with that of 5-decene, its concentration is very low, as would be expected for a minor product, fig 3.6.4. If the ratios of the concentrations of 4-nonene and 5-decene are compared, there is found to be virtually no variation in the ratios with time, fig 3.6.5. This suggests that the mechanistic pathways for the formation of these products are interdependent and this will be discussed later on in more detail.

Fig 3.6.3

Plot to show the rate of formation of 4-nonene
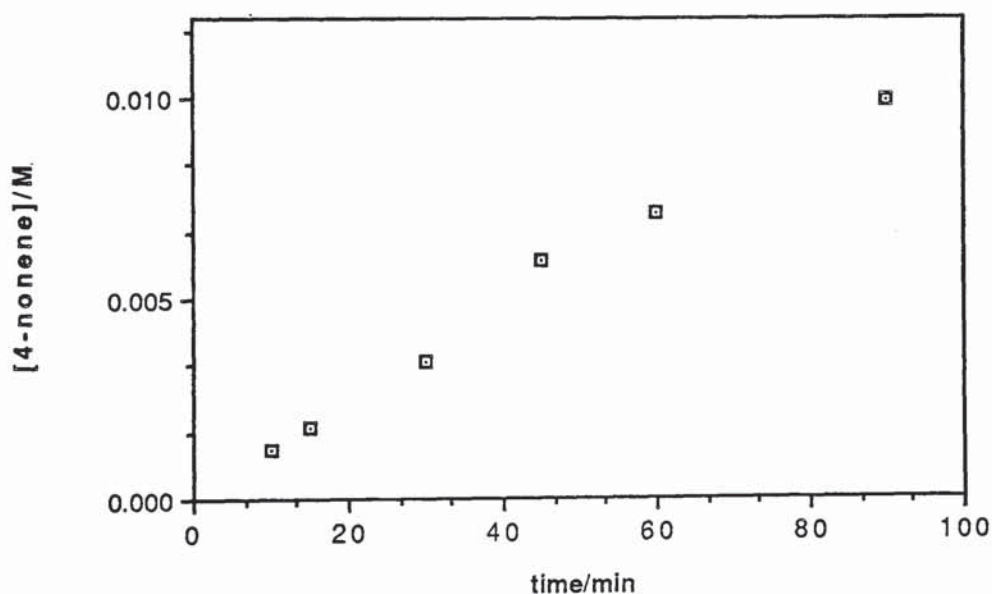
Fig 3.6.4

**Plot to compare the rate of formation of 4-nonene
with the rate of formation of 5-decene**
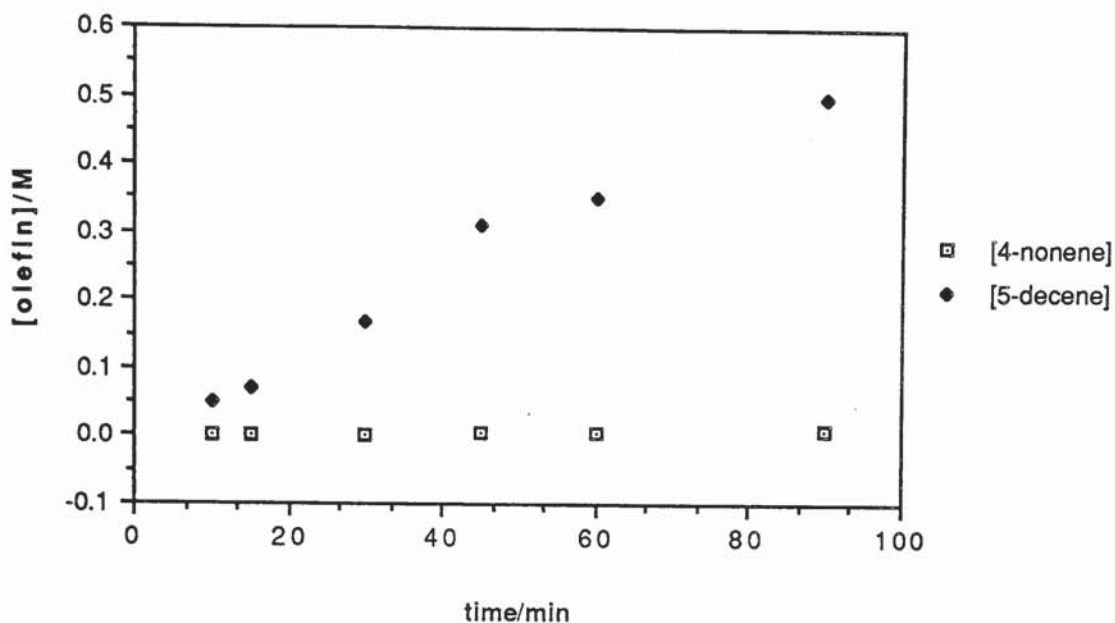
Fig 3.6.5

**Plot to show the ratio of 4-nonene concentration to that
of 5-decene concentration as a function of time**
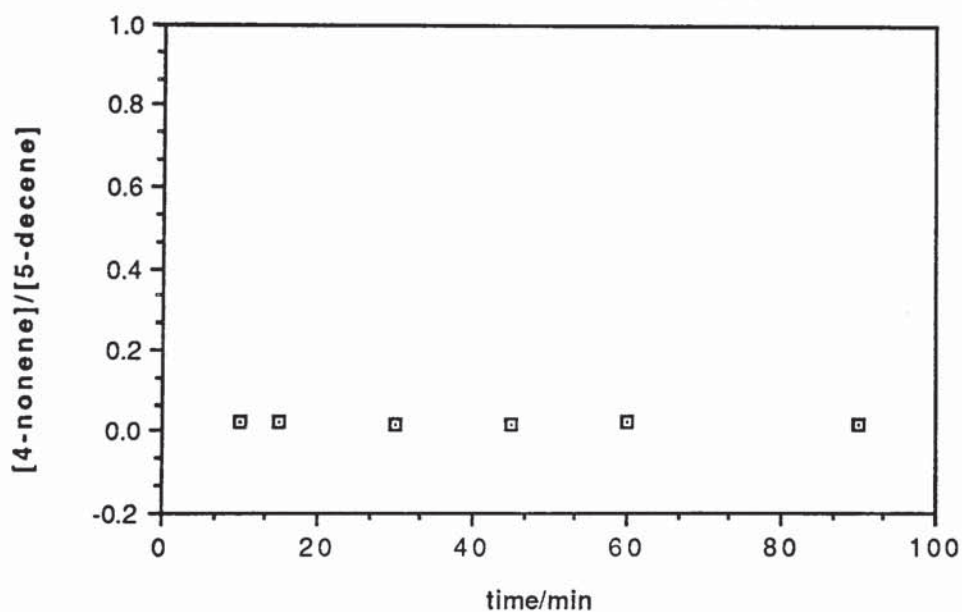
3.7. % Conversion of 1-hexene to ethene and 5-decene

Another method employed to determine the extent of dissolution of ethene in cyclohexane was

to compare the % conversion of ethene with that of 5-decene. Since stoichiometrically, 2 moles

of 1-hexene react to give 1mole of ethene and 1mole of 5-decene, it therefore follows that the

relative % conversions of 1-hexene to ethene and 5-decene should be close to unity. If ethene were soluble in cyclohexane to any significant degree, the extent of conversion of 1-hexene to ethene, as measure by gas evolution, would be expected to be less than that for 5-decene. Tables 3.3 and 3.4 compares the conversion of 1-hexene to ethene and 5-decene at the end of a series of metathesis reactions, under a range of reaction conditions. For the series of reactions shown in table 3.3, the metatheses of 25ml samples of different concentrations of 1-hexene solution in cyclohexane were performed using 0.70g of $Re_2O_7/\gamma-Al_2O_3$ as the catalyst at 35°C.

Table 3.3

Comparison of the molar ratios of ethene to 5-decene at different concentrations of 1-hexene

Concentration of 1-hexene/mol dm^{-3}	Moles of ethene produced x 10^3	Moles of 5-decene produced x 10^3	$\dfrac{\text{moles of ethene}}{\text{moles of 5-decene}}$
1.6	5.6	2.0	2.8
2.3	8.5	2.8	3.0
3.7	13	6.0	2.2
4.0	14	9.5	1.5
6.8	29	16	1.8

Analysis showed that, within experimental error, the ethene/5-decene molar ratio decreased as the 1-hexene concentration increased but the molar ratios of the products were significantly different from those expected. Complete analysis of the material cannot account for this difference in terms of the concentrations of minor products.

The experiments in table 3.4 were carried out using 25ml of 3.7M 1-hexene solution in cyclohexane at 35°C and with different weights of $Re_2O_7/\gamma-Al_2O_3$. Within experimental error, the ethene/5-decene ratio remained a constant as the catalyst concentration increases.

Table 3.4

Comparison of the molar ratios of ethene to 5-decene at different weights of catalyst

Weight of catalyst/g	moles of ethene x 10^3	moles of 5-decene x 10^3	$\dfrac{\text{moles of ethene}}{\text{moles of 5-decene}}$
0.30	8.3	4.8	1.7
0.35	13	7.3	1.8
0.70	13	6.0	2.2
1.40	13	7.5	1.7

The results in tables 3.3 and 3.4 show that almost twice as much ethene as 5-decene is formed and this ratio is dependent upon the concentration of 1-hexene and is independent of the catalyst weight.

As will be seen later in section 3.9, a scheme is set out as a possible route to the formation of 4-nonene and 5-decene. One of the products of the reaction is propene which would be expected to be gaseous. In a typical experiment the cumulative percentage area under the peaks of the by-products is 1.3% and that under 5-decene is 7.4%. Even allowing for the fact that propene is also produced the amount of missing 5-decene is still substantial. It would seem unlikely that the difference can be accounted for by evaporation of the 5-decene because it is the least volatile of the products. It can only be concluded therefore that 5-decene participates in other reactions that lead to higher molecular weight materials that are not detected by glc.

3.7.1. The cross metathesis between 1-hexene and 2-hexene

Analysis of the product from the metathesis of 1-hexene by glc and gc-ms revealed the formation of 2-heptene and 4-nonene as minor products, and it could be that the formation of these products is responsible for the lower yield of 5-decene. It is believed that both these products arise from the involvement of 2-hexene in the metathesis of 1-hexene. 2-hexene is either present as an impurity of 1-hexene or it is formed by the isomerization of 1-hexene during the metathesis reaction. In order to assess if 2-hexene is involved in the reaction, 1-

hexene was cross-metathesised with 2-hexene and the formation of products followed as a function of time.

10ml of 3.7M 1-hexene solution in cyclohexane was metathesised with $Re_2O_7/\gamma\text{-}Al_2O_3$ at 35°C for 5min before removing a sample. 10ml of 3.7M 2-hexene in cyclohexane was then added to the reaction solution and samples were removed after 10 and 60min. The solutions were subsequently analysed by glc and table 3.5 shows the results obtained.

<div align="center">

Table 3.5

The conversions to 4-nonene and 2-heptene

</div>

Time/min	$\dfrac{\% \text{ area 5-decene}}{\% \text{ area 4-nonene}}$	$\dfrac{\% \text{ area 5-decene}}{\% \text{ area 2-heptene}}$
5	25	24
10	10	11
60	6	5
1080	4	4

From table 3.5 it is clear that the concentrations of 4-nonene and 2-heptene are increasing as a function of time. On addition of 2-hexene after 5min, there is a pronounced decrease in the ratios which is a result of the increase in concentration of both 2-heptene and 4-nonene. It was also observed that there was no significant change in 5-decene concentration after the addition of 2-hexene and that the ratios for 4-nonene and 2-heptene were virtually identical. This provides confirmatory evidence for the fact that 4-nonene and 2-heptene could arise from 2-hexene; a kinetic scheme suggesting the formation of 2-hexene and these minor products will be given later.

3.8. The effect of multi-additions of 1-hexene solution on the activity of rhenium oxide catalysts

During the investigations of the kinetics of the metathesis of 1-hexene, it was found that the rate of reaction went to zero before all the 1-hexene was consumed. The results suggested that the

active metathesis sites on the surface of the catalyst were either destroyed by poisons or decayed after taking part in the metathesis reaction. Experiments were carried out to ascertain whether the active sites were destroyed by poisons in the reaction solution; the reaction solution was removed from the catalyst and a fresh aliquot of 1-hexene solution was added. If the poisons were removed with the reaction solution, then fresh 1-hexene was expected to undergo metathesis readily at a rate comparable to that of the first addition whereas, if the catalyst sites were completely destroyed, no metathesis would be expected on the addition of the second aliquot of 1-hexene.

Rhenium is a very expensive metal which makes the industrial use of rhenium oxide metathesis catalysts very costly and one way to minimize the costs is to reuse the catalysts for successive metathesis reactions. It has been reported that rhenium oxide/γ-alumina catalysts can be reactivated by calcining them at high temperatures[113] but this is a high energy process and therefore costs money. To maximize the use of the catalyst, it is desirable that the catalyst should be able to metathesise several solutions of an olefin, preferably without having to recalcine it.

3.8.1. The effect of drying the catalyst under vacuum between successive additions of 1-hexene solution

The metathesis reaction was carried out as previously described in section 2.5. 25ml of 3.7M 1-hexene solution was metathesised using 0.70g of Re_2O_7/γ-Al_2O_3 at 35°C. After 30 min the apparatus was closed to the gas burette and the reaction solution was removed under vacuum and analysed by glc. The apparatus was then evacuated and the catalyst was dried under vacuum for 30 min. Another 25ml of the 1-hexene solution was subsequently added to the catalyst and this was allowed to react for 60 min, after which time it was removed. The catalyst was not dried and another 25ml of 1-hexene solution was added 15 min after the second aliquot had been removed. Fig 3.8.1 is a plot of the effect of several additions of 1-hexene solution on the activity of the catalyst in a metathesis reaction and it can be clearly seen that compared to the first experiment, the activity of the dried catalyst with the second aliquot of 1-hexene is very much reduced. For the third addition of 1-hexene, the catalyst had not been dried and the

metathesis occurred at a rate which was fairly close to that of the second experiment. For the second addition of 1-hexene solution, the induction period prior to the commencement of the metathesis reaction, was longer compared to the first experiment but on the third addition of 1-hexene, when the catalyst remained wet, the induction period was found to be of the same order as when the catalyst was first used. These results suggests that on drying the catalyst by using the vacuuming technique, the active sites on the catalysts are either destroyed or removed. To assess the above possibilities, the experiments were repeated but this time the catalyst was not dried between successive additions.

Fig 3.8.1

The effect of successive additions of 1-hexene on the activity of the rhenium oxide/alumina catalyst
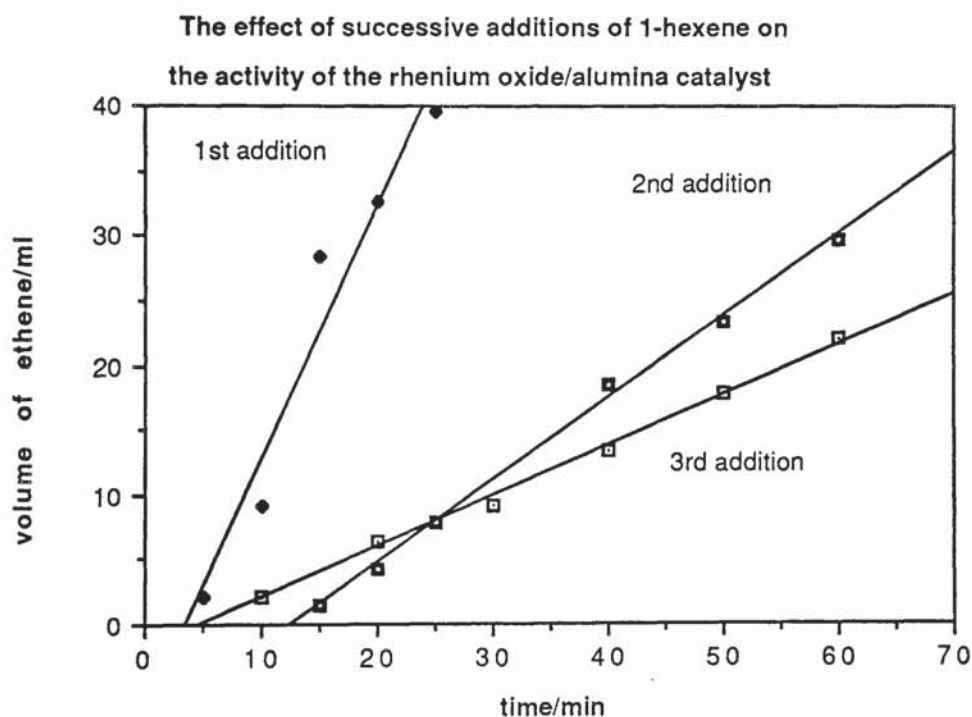
Fig 3.8.2 shows that the activity of the catalyst between the first and second additions of 1-hexene has not decreased substantially whereas by the third addition, the decrease in the activity of the catalyst is more pronounced. Also, the induction period for all three experiments is very similar. The main problem with both set of experiments was that for the first and second addition, the metathesis of 1-hexene was only allowed to proceed for no more than 60min. Consequently, the experiments were repeated but before the addition of the next aliquot, the reactions were allowed to proceed until the activity of the catalyst started to decrease. The reaction solution was then removed and after 15min, 25ml of 3.7M 1-hexene solution was

added to the dried catalyst. Fig 3.8.3 shows that the activity of the catalyst was retained for the second addition of 1-hexene with both the induction periods being similar.

Fig 3.8.2

The effect of successive additions of 1-hexene on the activity of the rhenium oxide/alumina catalyst
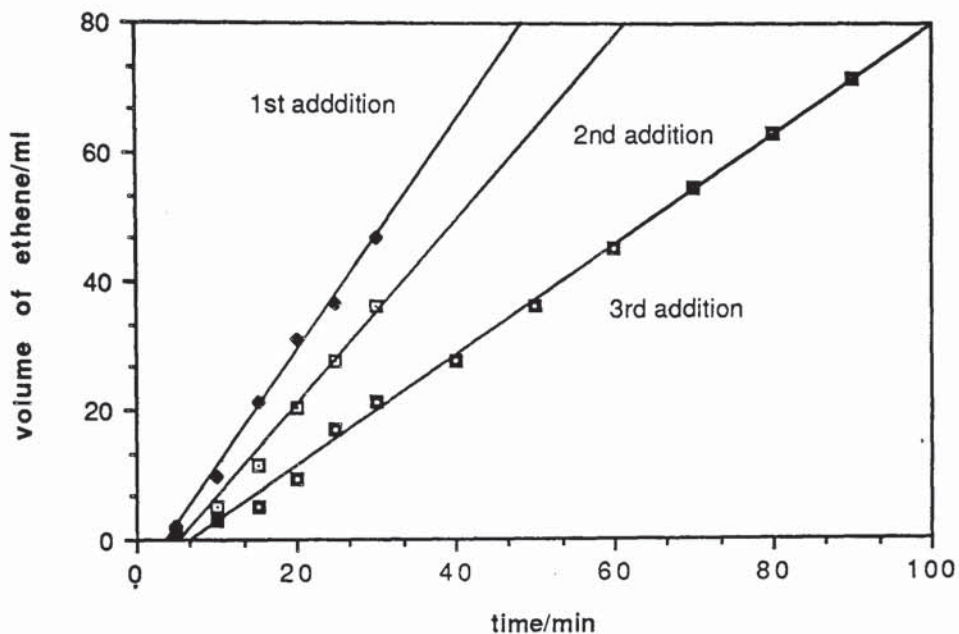
Fig 3.8.3

The effect of successive additions of 1-hexene on the activity of rhenium oxide/alumina catalyst

130
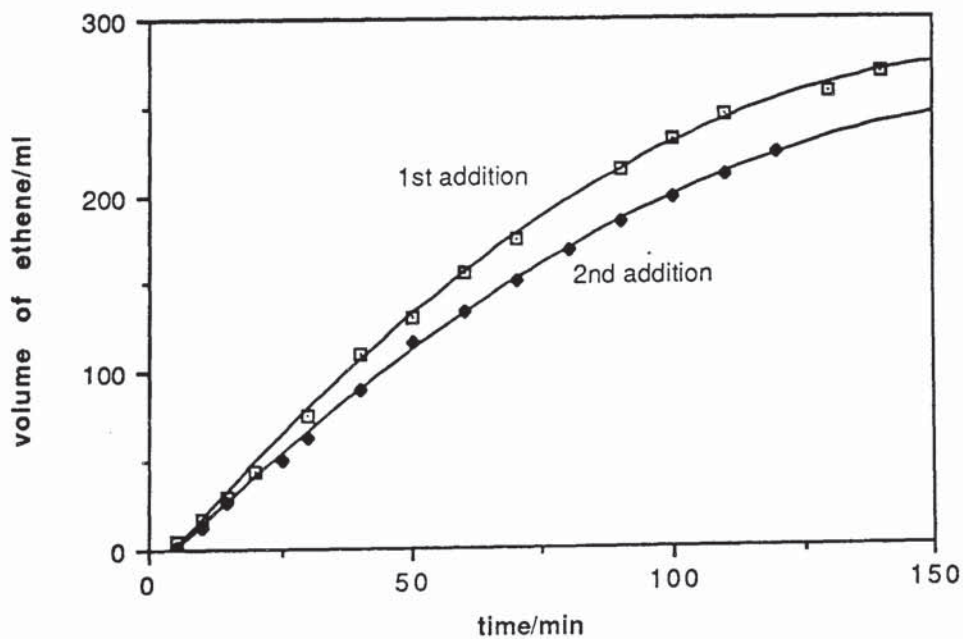
3.8.2. Gas liquid chromatography studies

It has been shown that the activity of the $Re_2O_7/\gamma\text{-}Al_2O_3$ catalyst towards metathesis decreases when several fresh solutions of 1-hexene are added to it. In previous experiments it has been observed that the % yield of 5-decene is much less than that of ethene. Consequently, the effect of reusing the catalyst to metathesise fresh solutions of 1-hexene was investigated to see if the activity of the catalyst towards 5-decene production decreased by a magnitude comparable to that of ethene.

25ml of 3.7M solution of 1-hexene was metathesised using 0.70g of the rhenium catalyst at 35^oC. Samples of the reaction solution were removed at predetermined times and after 18h the final reaction solution was removed. The catalyst was not dried and 25ml of fresh 1-hexene solution was added to the catalyst and the experiment repeated. The samples obtained were analysed by glc.

Fig 3.8.4

**The effect of successive additions of
1-hexene on the production of 5-decene**

131
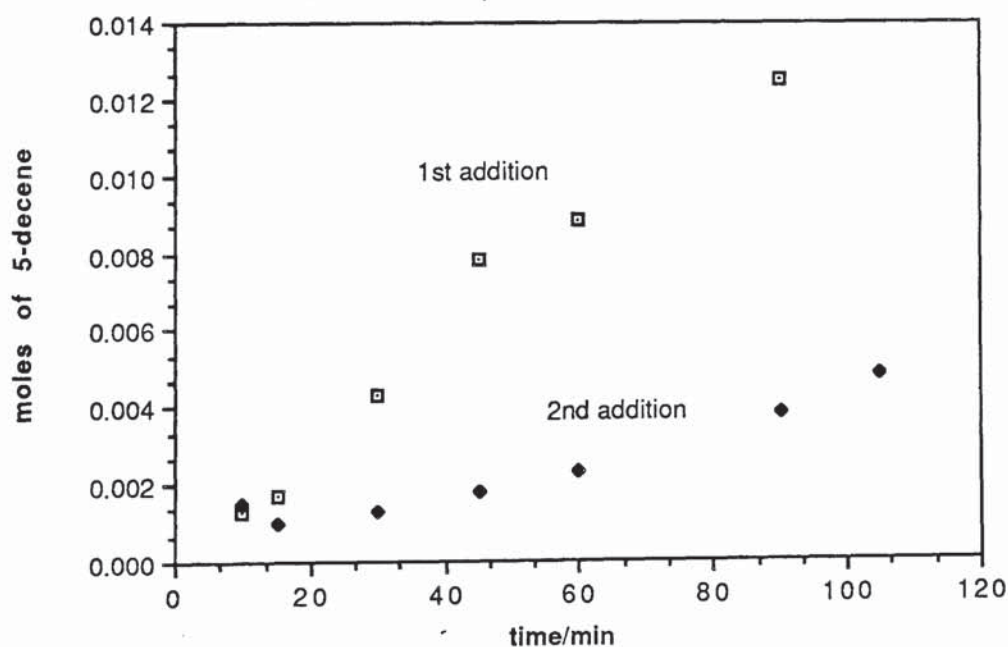
Fig 3.8.5

The effect of successive additions of
1-hexene on the production of 4-nonene
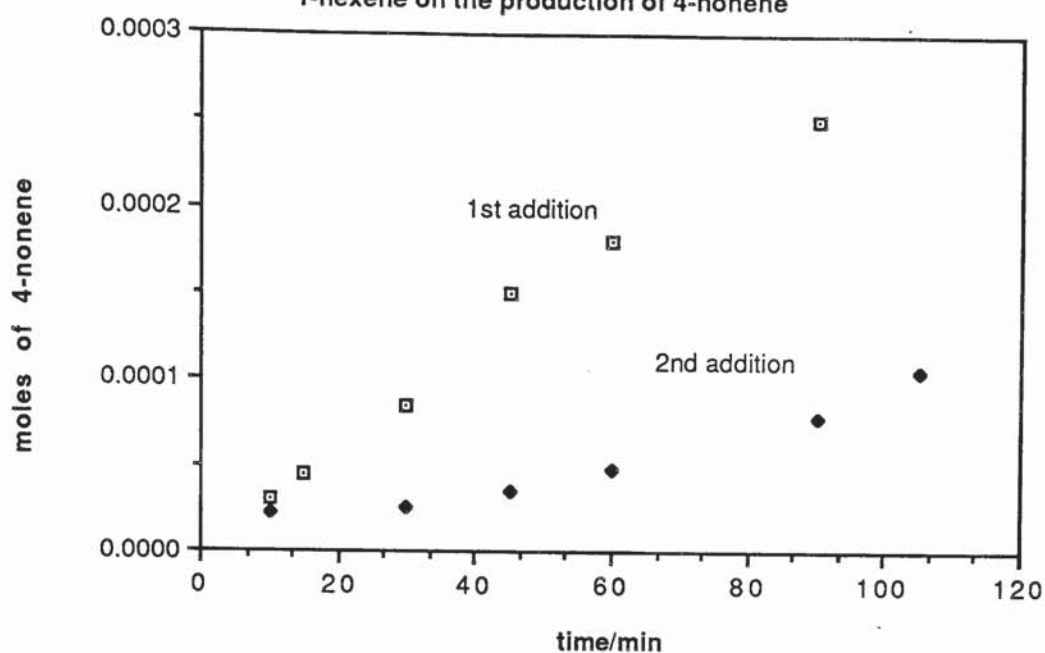
Figs 3.8.4 and 3.8.5 show the increase in concentration of 5-decene and 4-nonene as a function of time for sequential additions of 1-hexene. The rate of formation of both products for the second addition of 1-hexene is very much slower than that for the first. In fact both products appear to exhibit the same kinetics and this promotes the theory that their formations are interdependent which will be discussed in section 3.9.

3.9. Discussion

Most of the kinetic studies on the metathesis of olefins in the heterogeneous phase have been carried out on propene using various catalyst systems and the results corresponded to either a unimolecular or bimolecular model with respect to the olefin[73-78]. The current investigation into the kinetics of the metathesis of 1-hexene over $Re_2O_7/\gamma\text{-}Al_2O_3$ has revealed that the order of the reaction with respect to 1-hexene is two and the catalyst one. Furthermore, the fractional conversion of 1-hexene to ethene increases in the expected manner with 1-hexene concentration and weight of catalyst. It is possible to generate a scheme (scheme 3.1) that correlates the experimental kinetics for the metathesis of 1-hexene and the carbene mechanism put forward by Herisson and Chauvin, scheme 1.7. In the initial reaction, $Re_2O_7/\gamma\text{-}Al_2O_3$ reacts with 1-

hexene to produce a metallocarbene, which can be of two types, but only one, (a), will be considered here. The metallocarbene reacts with a molecule of 1-hexene to produce the other metallocarbene, (b), and ethene as one of the major products via a metallocyclobutane intermediate. The new metallocarbene reacts with another molecule of 1-hexene to complete the kinetic chain and the product, 5-decene, is generated together with the original metallocarbene. These alternating reactions continue until a termination reaction occurs:

Scheme 3.1

A Mechanistic Scheme of the Metathesis of 1-Hexene

$$Re^* + CH_2=CH(CH_2)_3CH_3 \xrightarrow{k_i} \underset{(a)}{Re^*=CH_2}$$

$$Re^*=CH_2 + CH_2=CH(CH_2)_3CH_3 \xrightarrow{k_{m1}} CH_2=CH_2 + \underset{(b)}{Re^*=CH(CH_2)_3CH_3}$$

$$Re^*=CH(CH_2)_3CH_3 + CH_2=CH(CH_2)_3CH_3 \xrightarrow{k_{m2}}$$

$$CH_3(CH_2)_3CH=CH(CH_2)_3CH_3 + Re^*=CH_2$$

$$Re^* \xrightarrow{k_t} Re_{inactive}$$
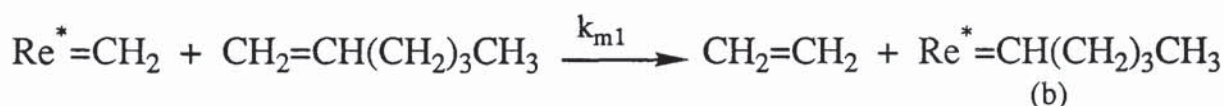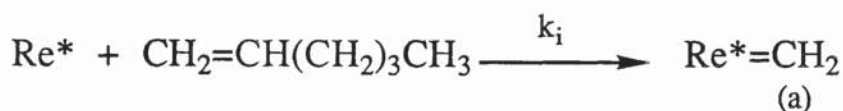
where Re^* is the rhenium complex

k_i is the rate constant for the formation of the initial carbene species

k_{m1} is the rate constant for the formation of ethene

k_{m2} is the rate constant for the formation of 5-decene and

k_t is the rate constant for the termination reaction

During the investigation into the effects of 1-hexene concentration and catalyst weight on the rate of metathesis of 1-hexene, it was found that in all cases the reaction rate went to zero after several hours without all the 1-hexene being consumed. According to the carbene mechanism

for olefin metathesis, the catalyst components react to form a carbene species which initiates the metathesis reaction. In this case there is only one type of transition metal component present and this must be in a satisfactory form to react with the olefin to form the active metathesis site. As the reaction rate tends to zero during the course of the reaction, the active centres either decay or are destroyed by impurities or other reaction products. Indeed, it is known that air and moisture are means by which to deactivate metathesis catalyst but when the reaction is carried out under conditions that exclude these two components, other methods which could be responsible for the deactivation of the catalyst need to be considered. Furthermore the kinetic model is based upon the fact that the active centre for metathesis is formed steadily in a kinetic chain and is not completely generated at the outset.

In some instances the rate of the reaction decays with time even though the maximum conversion of 1-hexene to products is less than 30%. If the active centre is generated by reaction of the catalyst with 1-hexene, since there is still 1-hexene present when the rate has declined to zero, either the metal site is no longer able to react with 1-hexene to generate an active centre or the catalyst has been poisoned. Workers such as Nakamura and Echigoya have shown that the metathesis of olefins, using $Re_2O_7/\gamma-Al_2O_3$ as the catalyst, occurs on the surface of the catalyst at specific sites and it has been calculated that less than 1% of the Re atoms present are active in the metathesis reaction[114]. However, during the investigation into the effect of the multi-addition of 1-hexene on catalyst activity, it was found that fresh solutions of 1-hexene were capable of re-generating new active sites on the catalyst surface so that metathesis of 1-hexene could occur when the catalyst was dried under vacuum. This led to the belief that poisons generated in the reaction solution during the metathesis reaction were responsible for inhibiting the metathesis of unreacted 1-hexene and that these were removed when the catalyst was dried under vacuum. However, when the original reaction solution was removed without drying the catalyst under vacuum, and a fresh solution of 1-hexene was added, metathesis occured, albeit at a slower rate. It is possible that a diffusion gradient may exists between the surface of the catalyst and the reaction solution; so if poisons are generated during the reaction, it is possible that they diffuse from the surface of the catalyst to the reaction solution.

It is expected that ethene and 5-decene are produced in the molar ratio of 1:1 as dictated by the stoichiometric equation

$$2CH_2=CH(CH_2)_3CH_3 \longrightarrow CH_2=CH_2 + CH_3(CH_2)_3CH=CH(CH_2)_3CH_3$$

However, it was found that more ethene than 5-decene was formed and minor products were also detected. These products were identified as 4-nonene and 2-heptene and their formation can be explained by the following reaction scheme:

Scheme 3.2

A Mechanistic Scheme showing the Formation of Secondary Products during the Metathesis of 1-Hexene

$$CH_2=CH(CH_2)_3CH_3 \xrightarrow[\text{catalysed}]{k_s} CH_3CH=CH(CH_2)_2CH_3$$

$$Re^*=CH(CH_2)_3CH_3 + CH_3CH=CH(CH_2)_2CH_3 \xrightarrow{k_n}$$

$$CH_3CH_2CH_2CH=CH(CH_2)_3CH_3 + Re^*=CHCH_3$$

$$Re^*=CHCH_3 + CH_2=CH(CH_2)_3CH_3 \xrightarrow{k_p}$$

$$Re^*=CH(CH_2)_3CH_3 + CH_2=CHCH_3$$

$$Re^*=CH(CH_2)_3CH_3 + CH_3CH=CH(CH_2)_2CH_3 \xrightarrow{k_h}$$

$$CH_3CH=CH(CH_2)_3CH_3 + Re^*=CH(CH_2)_2CH_3$$
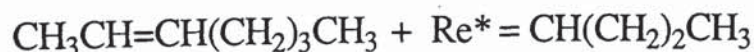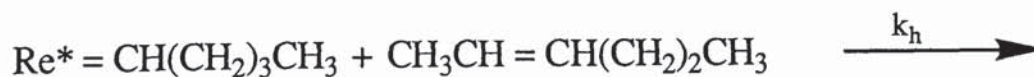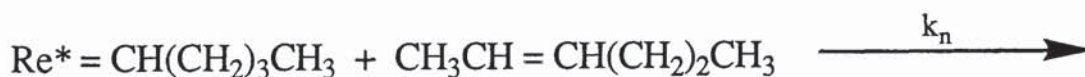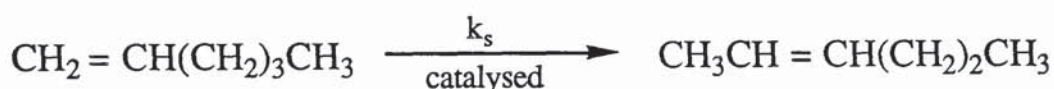
where k_s is the rate constant for the isomerization of 1-hexene to 2-hexene, k_n and k_p are the rate constants for the reaction between 1-hexene and 2-hexene to form 4-nonene and propene, and k_h is the rate constant for the formation of 2-heptene.

2-hexene which is either present as an impurity in 1-hexene or is formed by the isomerization of 1-hexene, gives rise to 4-nonene according to scheme 3.2. The molar ratio of [4-nonene]/[5-decene] has a constant value of 0.02 for the metathesis of 1-hexene at different concentrations of 1-hexene and weights of catalyst. This suggests that 4-nonene and 5-decene are produced at the same active site, one by reaction of the site with 2-hexene and the other by reaction with 1-hexene. However, much more 4-nonene is formed than one would expect from the starting concentration of 2-hexene. The chromatograph of pure 1-hexene shows that its composition is 99.3% 1-hexene, fig 3.9.1, and if 2-hexene is present, its concentration is very low. The carbene responsible for the production of 5-decene is also responsible for the production of 4-nonene and 2-heptene, and it is possible that this could contribute to the low conversion of 1-hexene to 5-decene. However, the low concentration of these minor products in the reaction solution shows that their formation is not a significant factor in affecting the concentration of 5-decene. It is possible that 5-decene could undergo self metathesis but because it is a symmetrical olefin, the products themselves would be 5-decene. Therefore, as mentioned in section 3.7, it is possible that the 5-decene undergoes other reactions which would lead to the synthesis of higher molecular weight oligomeric materials which have not been detected.

RT

0.710

1.247   1.339

1.997
2.154

3.517

4.752

STOP
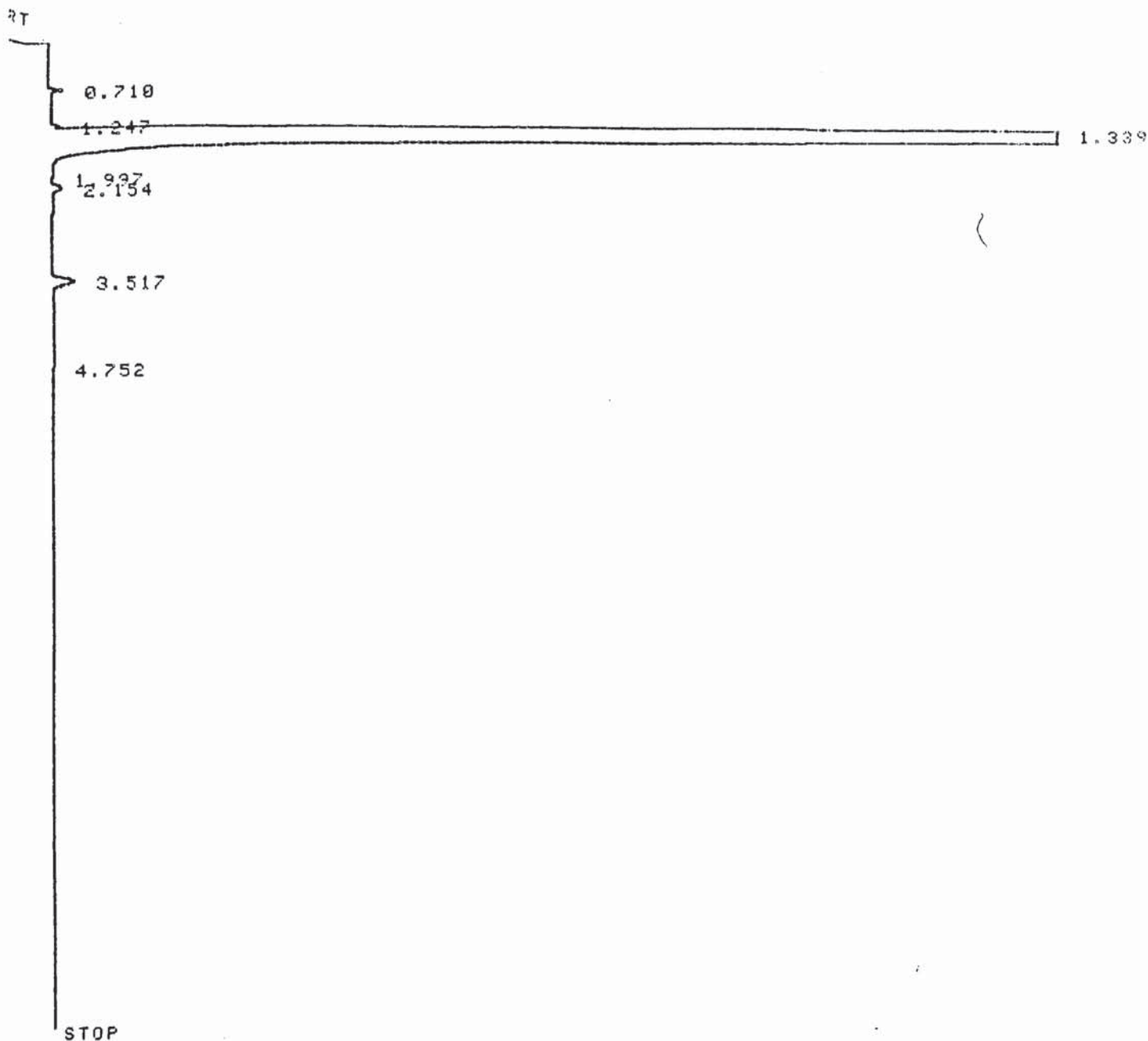
Using signal file M:SIGNAL   .BNC
Using processed peaks to M:Q127EF33.PRO

6   AUG 8, 1990 11:19:14

SIGNAL FILE: M:SIGNAL.BNC
PEAK FILE : M:Q127EF33.PRO
IN%

RT	AREA	TYPE	WIDTH	AREA%
.710	4200	BB	.040	.07618
1.247	3320	PV	.050	.06022
1.339	5471808	VB	.150	99.25296
1.997	950	BV	.089	.01723
2.154	8144	VB	.103	.14772
3.517	19228	PB	.110	.34878
4.752	5343	BV	.582	.09692

TOTAL AREA=5512992
FACTOR=1.0000E+00

137

GLC chromatograph of pure 1-hexene

Fig 3.9.1

3.9.1. A kinetic analysis of the mechanism of olefin metathesis

It has been well established that olefin metathesis proceeds via a chain mechanism involving metallocarbene and metallacyclobutane intermediates. However, the mechanism of formation of the initial catalytic species from many systems has not been established. Consequently analysis of the results of the kinetic investigation into the metathesis of 1-hexene over Re_2O_7/γ-Al_2O_3 will now be undertaken and it is believed that some light will be thrown on this particular system. Particularly, an in-depth analysis of the initiation, propagation and termination steps will be carried out in order to correlate the results obtained in the experimental work with the mechanisms postulated in the literature, especially the carbene mechanism by Herisson and Chauvin[12].

3.9.1.1. Initiation

Previous work has shown that the acidity of the alumina support, particularly the Bronsted acidity, is important in determining the activity of the catalyst in the metathesis reaction. The acidity is believed to be associated with sites with the chemical structure Al-O-H and that these are the sites at which Re_2O_7 is bound after the catalyst has been calcined at 580°C. It is quite possible that the rhenium atom is bound to the catalyst by way of an Al-O-Re type bond. In order to initiate the metathesis, a metal (Re) carbene must form, probably by reaction with the olefin itself. The mechanism suggested here relies on the fact that the active centre precursor consists of -Re=O and a vacant site. The suggested vacant site would have a structure similar to

$$\diagdown \underset{\displaystyle \underset{\square}{|}}{\overset{\delta+}{-}} \mathrm{Re} \overset{\delta-}{=} \mathrm{O}$$
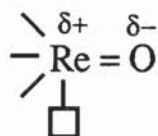
The vacant site can co-ordinate a molecule of 1-hexene to form a complex. This complex could then rearrange to form a metalloxacyclobutane complex which undergoes a slow decomposition reaction to the initiating metallocarbene:

$$\text{Re} = O \ + \ C_4H_9CH=CH_2 \ \longrightarrow \ \underset{C_4H_9CH=CH_2}{\overset{\text{Re} = O}{\uparrow}}$$

$$\underset{C_4H_9CH=CH_2}{\overset{\text{Re} = O}{\uparrow}} \ \longrightarrow \ \underset{C_4H_9CH\text{---}CH_2}{\text{Re---O}} \ \longrightarrow \ \underset{CHC_4H_9}{\text{Re--}\square}$$
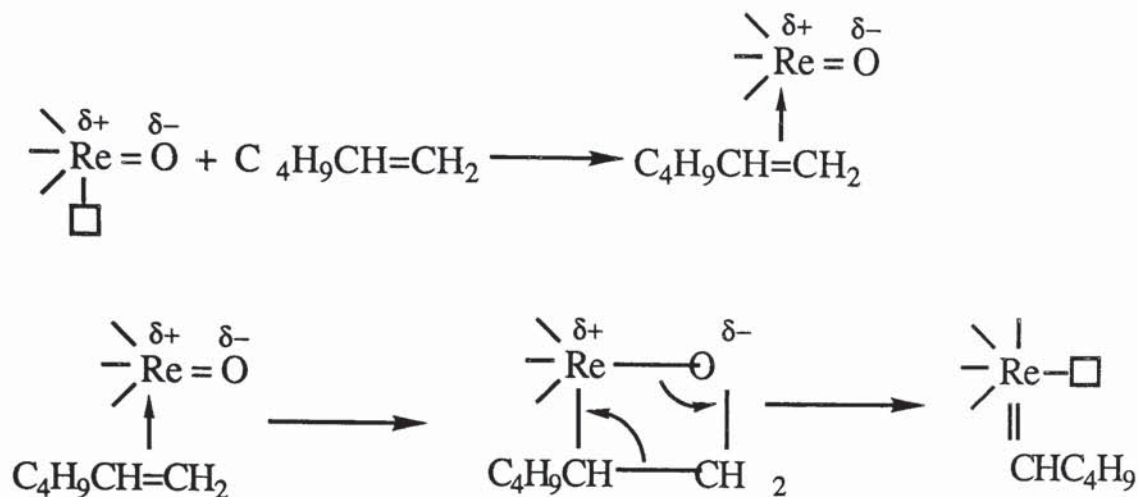
The formation and decomposition of the metalloxacyclobutane is thought to be manifested as the slow build up in the rate of ethene evolution after the addition of the catalyst to the solution of 1-hexene.

Close analysis of the kinetics of the evolution of ethene show the volume time curves to be sigmoidal in shape and that the rate of ethene evolution builds up slowly to a maximum. This is believed to be indicative of the fact that the active centres are formed slowly over a period of time. Kinetic analysis of the initial rates of reaction showed that the reaction was second order in 1-hexene and first order in the catalyst. This effect could be explained by the mechanistic scheme shown earlier in section 3.9 in which 1-hexene played a significant role in the formation of the active centre, as well as participating in the propagation reaction.

3.9.1.2. Propagation

Having generated active centres on the surface of the catalyst, propagation involves these active centres in reactions of the Herisson-Chauvin type. The initial rate studies have shown that the reaction is first order in catalyst concentration. Since the catalysts used in these systems are heterogeneous, it seems reasonable that the principle of heterogeneous catalysis developed by Langmuir and Hinshelwood should be applied to this system. According to the Langmuir-type adsorption isotherm, the adsorption of 1-hexene molecules can be considered to be a chemical reaction, i.e.

$$\text{Molecule + Active site} \ \underset{k_d}{\overset{k_a}{\rightleftharpoons}} \ \text{Adsorbed molecule} \ \longrightarrow \ \text{Ethene}$$

139

An equilibrium will be established between 1-hexene in solution and that adsorbed on the surface, such that rate of adsorption = rate of desorption.

Thus: k_a[1-hexene][free active sites] = k_d[complexed active sites]

Let θ be fraction of active sites that are complexed, then

[complex active sites] = θ[active sites]

[free active sites] = 1-θ[active sites]

Hence, k_a[1-hexene][1-θ][active sites] = $k_d\theta$[active sites]

$$K = \frac{k_a}{k_d} = \frac{\theta}{(1-\theta)[1\text{-hexene}]}$$

∴

$$\theta = \frac{K[1\text{-hexene}]}{1+K[1\text{-hexene}]}$$

Since the rate of formation of ethene is k[complex active sites]

$$\text{Rate} = k\theta[\text{catalyst}] = k\frac{K[M]}{1+K[M]}[\text{catalyst}] \qquad\qquad \text{x}$$

where [M] is the concentration of 1-hexene.

The concentration of the catalyst refers to the number of active sites on the surface, which will be unknown. A substitution can be made for this term if it is assumed that at anytime

$$\frac{d[\text{catalyst}]}{dt} \simeq 0$$

i.e., there is a stationary state in the concentration of such sites. According to scheme 3.1

$$\frac{d[\text{catalyst}]}{dt} = k_i[\text{Re}]_{\text{surface}}[1\text{-hexene}] - k_t[\text{Re}{=}CH_2]$$

and $\quad [\text{Re}{=}CH_2] = \frac{k_i}{k_t}[\text{Re}]_{\text{surface}}[1\text{-hexene}] \qquad\qquad \text{y}$

Substitution of y into x leads to

$$\text{Rate} = \frac{d[CH_2{=}CH_2]}{dt} = \frac{kK[Re]_{surface}[\text{1-hexene}]^2}{1+K[\text{1-hexene}]}$$

The observed experimental data show first order in weight of catalyst and second order in 1-hexene concentration. If the above model is applied, this behaviour can be explained if the olefin is only weakly adsorbed on the catalyst surface. That this should be so is in agreement with the fact that although the olefin forms a reactive complex with the active site, the product of the reaction, which is also an olefin, desorbs rapidly from the active centre, or is displaced by the incoming olefin quite readily. Then $K[\text{1-hexene}] \ll 1$, but it is possible that this situation may change according to the type of catalyst system used. K is important because

$$K = \frac{k_a}{k_d} \quad \text{and if } K \ll 1, \text{ then } k_a \ll k_d.$$

This means that when complexes form they are unstable and

$$\theta = \frac{K[M]}{1+K[M]} \; \tilde{} \; K[\text{1-hexene}]$$

and $\qquad\qquad$ $\text{rate} = kK[Re]_{surface}[\text{1-hexene}]^2$

Since $K[\text{1-hexene}] \ll 1$, only a small fraction of available sites ($\theta = K[\text{1-hexene}]$) is active at any one time. This appears at first sight to be a disadvantage but olefin metathesis relies upon exchange reactions taking place rapidly. Thus, although the first step in the Herisson-Chauvin mechanism involves formation of a complex between olefin and active centre, the last stage requires that a similar complex between the new olefin and catalyst breaks down readily. The kinetic treatment given above would appear to provide evidence for exactly this situation. Complexes between active centres and olefins are unstable but are able to form. Only a fraction of the potential sites are active kinetically at any one time.

3.9.3. Termination

The evidence for termination processes occurring comes from the fact that 1-hexene is not consumed completely before the rate of evolution of ethene goes to zero. This is believed to be due to the fact that the number of active sites is decaying with reaction time. According to scheme 3.1 this is a first order process and therefore involves the decomposition of the active centre which could occur when it is uncomplexed, complexed or in the form of a metallocyclobutane.

(i) **The decomposition of uncomplexed active sites**

One of the ligands of the active centre, eg =O, could react with the carbene

$$-Re = CHR$$
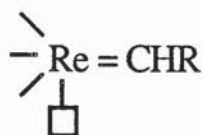
to form a stable structure. The existence of such a structure on the surface of the catalyst would have to be confirmed by techniques such as ESCA, but the ESCA investigations carried out during this project did not provide sufficient detail for this to be decided.

(ii) **The decomposition of complexed active sites**

$$RCH=CH_2$$
$$-Re = CHR$$
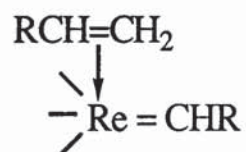
Reactions involving this complex cannot be ruled out at this stage, but it is felt that if they occur they compete with the propagation reaction. Thus one could envisage such reactions occuring if the complexed olefin reacted with another ligand instead of the carbene ligand. However if reactions of this type occur it is difficult to see how the catalytic activity can be regenerated when the second aliquot of 1-hexene is added.

(iii) **The decomposition of metallacyclobutanes**

One of the intermediates formed during the metathesis reaction is known to be a metallacyclobutane and according to the carbene mechanism, scheme 1.7, this decomposes to form a metallocarbene and a product olefin. It is possible that the metallacyclobutane could also decompose via another mechanism to form a cyclopropane derivative and an inactive Re complex.

$$
\begin{array}{ccc}
RCH\text{------}CH_2 & & RCH\text{------------}CH_2 \\
| \qquad\quad | & \longrightarrow \quad Re_{inactive} \;+\; & \diagdown\qquad\diagup \\
Re\text{------}CH_2 & & CH_2
\end{array}
$$

Indeed, Casey and Burkhardt proposed a mechanism in which the metallacyclobutane formed could undergo reductive elimination to give a cyclopropane derivative or undergo cleavage to produce a metal-olefin complex (section 1.5.3.2). Support for the postulate that the metallacyclobutane intermediate could undergo cleavage to produce a cyclopropane derivative in a chain termination step came from Grubbs, who noted that less active metathesis catalysts tended to be better at catalysing the cyclopropanation reaction and vice versa[115]. This implies that the formation of cyclopropanes inhibits the metathesis of reactant olefins to produce product olefins.

Cyclopropanes have properties similar to olefins, eg addition of HBr, and therefore, once they are formed they could react like olefins with the active centre to form more stable complexes. Indeed, one of the particular features of the metathesis of 1-hexene is that the rate of reaction decreases after a few hours and this is believed to be related to the decrease in the available number of Re atoms that are potentially active sites.

If cyclopropanes do form more stable complexes with the active centres, then in the multi-addition work, these complexes are probably broken down to release the active centres as the catalyst is dried by evacuation. This could account for the return in activity of the catalyst with a subsequent addition of 1-hexene. However, the number of active centres is less than the original because some have already been destroyed.

CHAPTER 4: EFFECTS OF TEMPERATURE ON THE RATE OF METATHESIS OF 1-HEXENE

4.1. Effects of temperature on the rate and extent of metathesis

The extent of olefin metathesis has been shown to be dependent on temperature when other heterogeneous catalyst systems such as Co-MoO$_3$/Al$_2$O$_3$[1] are used. Banks and Bailey studied the metathesis of propene over Co-MoO$_3$/Al$_2$O$_3$ using a temperature range of 90-300°C. It was found that optimum yields of products were obtained at lower temperatures even though the conversion increased with increasing temperature. As the temperature was increased the concentration of minor products such as propane also increased whilst that of the major products decreased. The amount of residue and coke deposition also increased with temperature. Some of the products detected in the final reaction solution are shown in table 4.1.

Table 4.1

Metathesis of propene over Co-MoO$_3$/Al$_2$O$_3$ at various temperatures

Temperature °C	% propene	% ethene	% trans -2-butene	% cis -1-butene
93	82.1	6.0	7.3	3.4
163	62.8	10.0	14.6	7.5
205	57.4	11.6	13.9	7.8
300	85.4	1.9	2.7	1.5

Bradshaw et al. studied the metathesis of 1-butene using the catalyst CoO$_3$-MoO$_3$-Al$_2$O$_3$ in the temperature range 122-245°C[5]. The conversion to products increased with temperature, reaching a maximum of 41.4% at 180°C whilst the selectivity towards the primary products, ethene and 3-hexene, decreased with increasing temperature. The decrease in selectivity was explained by the increase in isomerization to 2-butene.

In the homogeneous phase, the metathesis reaction proceeds readily at room temperature but variations in temperature do affect the conversion to products. Wang and Menapace found that in the metathesis of 2-pentene using the catalyst system WCl_6/n-BuLi, high conversions were obtained if temperatures greater than room temperature were used, with maximum conversions occurring in the temperature range of 61-130°C[18]. Temperatures greater than this resulted in the catalyst losing its activity.

The effect of temperature on the metathesis of 1-hexene over the rhenium oxide/γ-alumina catalyst has been investigated in detail in this work using the gas evolution technique. A batch of 1-hexene was produced that was sufficient for all the experiments in this series and the same sample of catalyst was also used. In this way attempts were made to eliminate extraneous variables that could affect the metathesis reaction. In addition, the following precautions were taken:

(i) A higher purity sample of cyclohexane (99% pure) was employed.

(ii) The dry air used during the calcination of the catalyst was dried over a combination of calcium chloride and silica gel prior to use.

(iii) The high purity argon used to flush out the manometer was dried over alumina prior to use.

25ml of 3.7M 1-hexene solution was metathesised at different temperatures according to the procedure in section 2.5 using 0.70g of catalyst. The rate of the reaction was followed by monitoring the volume of ethene evolved. The results obtained in these studies highlighted the difficulties associated with measuring the rate of ethene production within acceptable limits of experimental error. As shown in figs 4.1.1-4.1.5, the problems of reproducibility were greatest at the lower temperatures of metathesis close to ambient conditions. Thus, the principal source of error would appear to be the effectiveness of controlling the temperature of the reaction which is difficult at temperatures close to ambient. The range of temperatures that could be used was limited by the fact that boiling point of 1-hexene was 64°C. Temperatures close to this value would have resulted in serious problems associated with evaporation.

Fig 4.1.1

Plot to compare the rate of metathesis of 3.7M 1-hexene

solution in different experiments at 30 C

Fig 4.1.2

Plot to compare the rate of metathesis of 3.7M 1-hexene
solution in different experiments at 35 C

Fig 4.1.3

Plot to compare the rate of metathesis of 3.7M 1-hexene
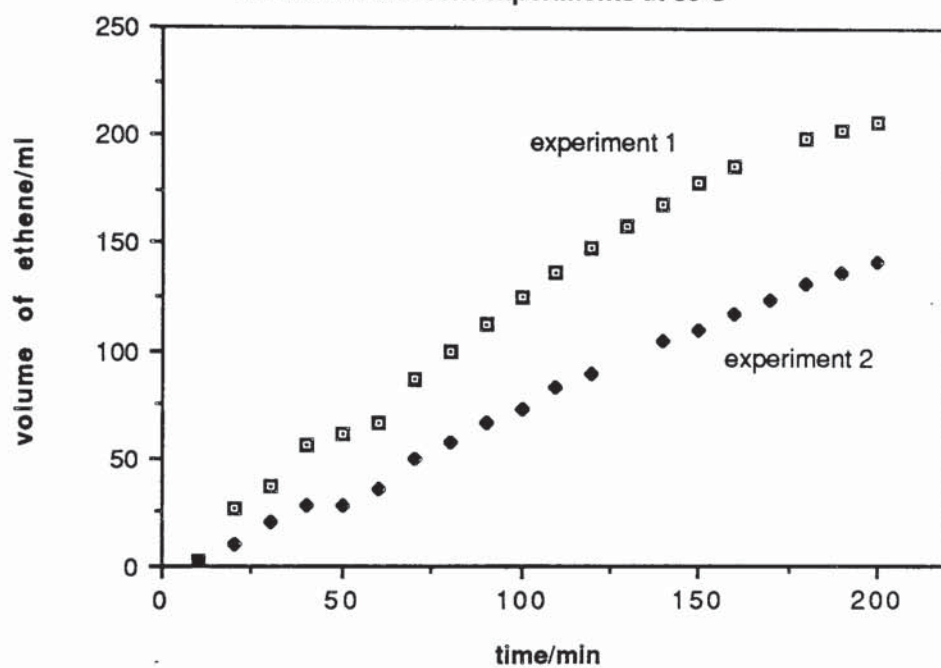
solution in different experiments at 40 C
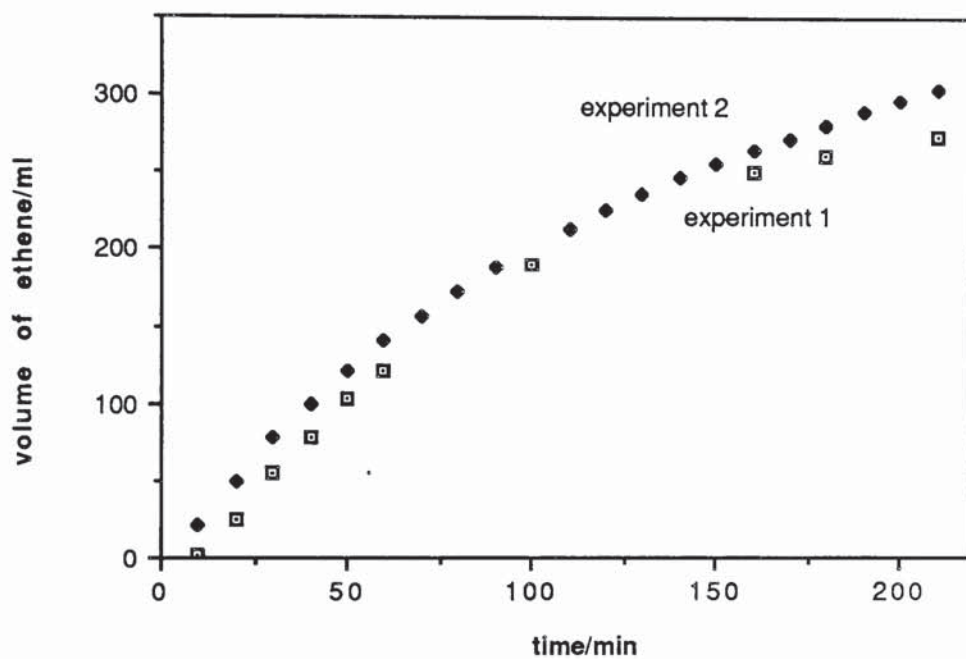
Fig 4.1.4

Plot to compare the rate of metathesis of 3.7M 1-hexene
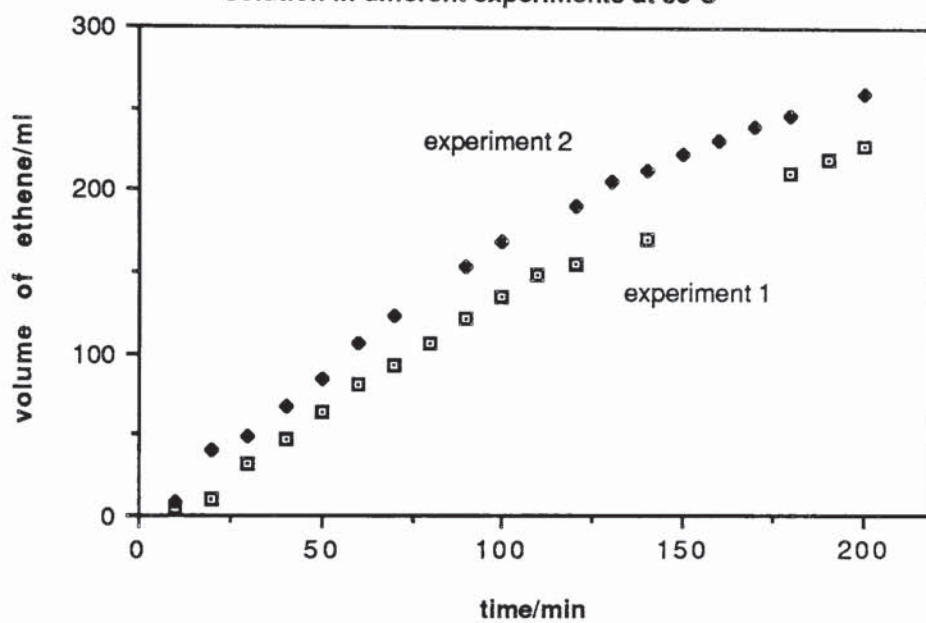solution in different experiments at 45 C
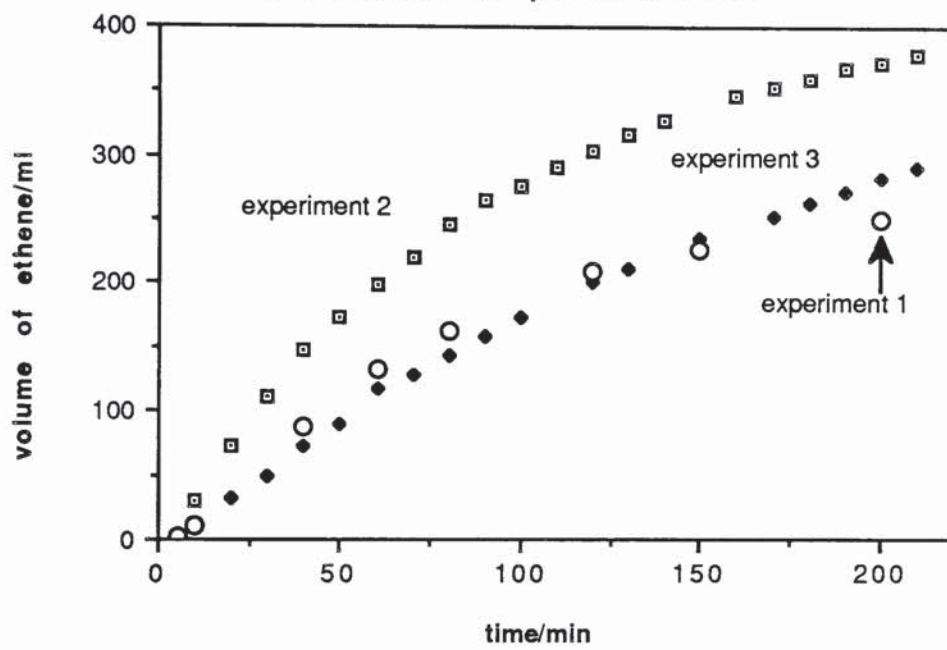
Fig 4.1.5

Plot to compare the rate of metathesis of 3.7M 1-hexene solution in different experiments at 50 C and 55 C
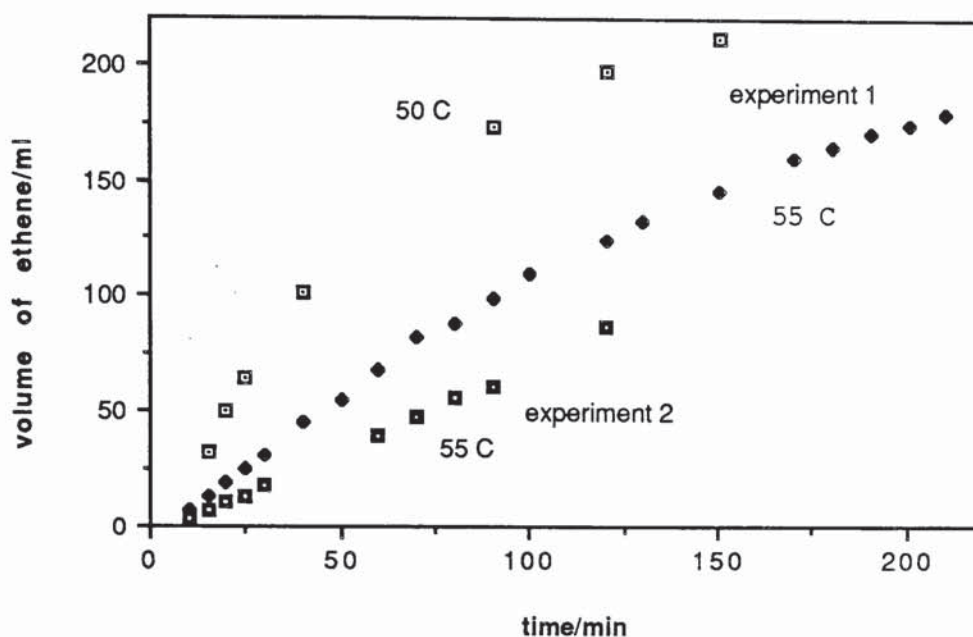
The effect of temperature may be summarised by comparing the fastest rates of metathesis as a function of temperature as shown in fig 4.1.6. This plot shows that an optimum temperature for the metathesis of 1-hexene is obtained at 45^0C. Therefore, it is reasonable to assume that to maximise the metathesis of 1-hexene over rhenium oxide/γ-alumina catalyst, an operating temperature between 40-45^0C needs to be employed. This conclusion is drawn from the fact that the error in the reproducibility of 1-hexene metathesis is greatest at those temperatures close to ambient. The effect of temperature on the rate of metathesis is unusual in that the rate appears to decrease above 45^oC. The increase in rate below this temperature can be ascribed to the normal Arrhenius dependence of rate of chemical reactions. The decrease in rate above 45^oC can be explained by the fact that the metathesis reaction involves an unstable intermediate and the rates of the reactions leading to the destruction of this species increases also, so that the concentration of the intermediate decreases more rapidly with temperature.

Fig 4.1.6

The effect of temperature on the rate of metathesis of 1-hexene
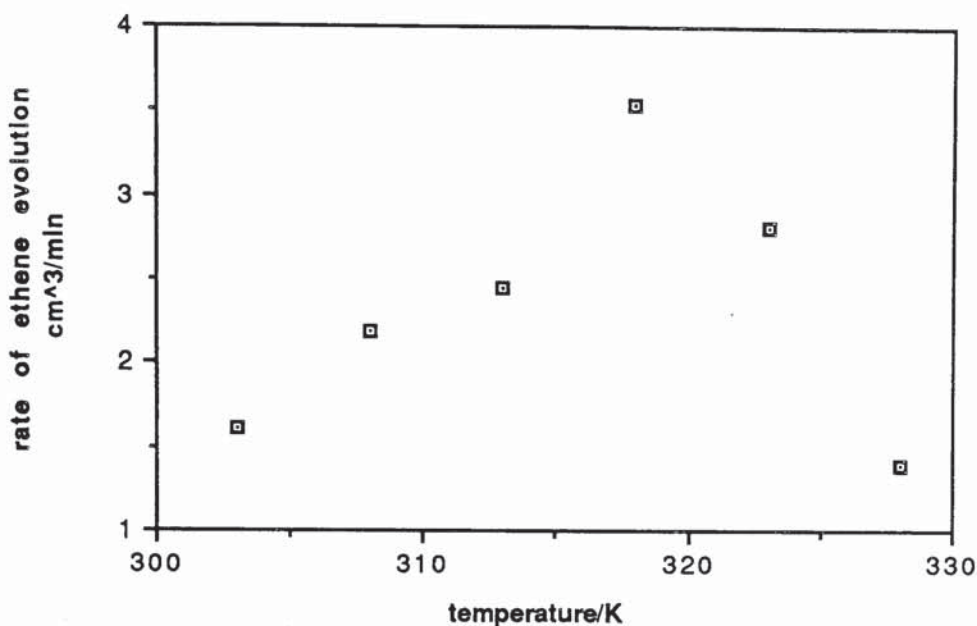
4.2. Determination of the activation energy

For many chemical processes the reaction rate varies greatly with temperature; typically the rate doubles for a 10°C rise in temperature. The metathesis of 1-hexene can be stated as

$$2A \xrightarrow{\quad k \quad} B$$
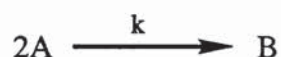
where A = 1-hexene, B = product of metathesis and k = the rate constant.

The rate constant k is the temperature dependent term in the above equation and Arrhenius has shown that the rate constant can be expressed as

$$\log k = \log A - \frac{E}{2.303RT}$$

This equation is known as the Arrhenius equation and can also be expressed as

$$k = A \exp(-E/RT)$$

where A = frequency factor (a constant which measures the frequency of collisions between reactant molecules), E = the activation energy, R = molar gas constant and T = the absolute temperature[112].

The Arrhenius equation shows that the rate constant for a reaction is dependent upon the activation energy and the frequency factor. If log k is plotted against 1/T, a linear plot is obtained if the Arrhenius equation is obeyed and the slope will then be equal to -E/2.303R. Thus, the activation energy can be determined from the slope. Fig 4.2.1 is a plot to determine the activation energy for the metathesis of 1-hexene and it covers the temperature range of 30-45°C, the temperatures tending to the maximum rate for the metathesis of 1-hexene (see fig 4.1.6). Using the Cricket Graph software pertaining to the Apple MacIntosh Computer, the slope is found to correspond to a value of $-2077K^{-1}$. This value is equal to (-E/2.303R). E, the activation energy, was calculated to have a value of 39kJ mol^{-1}. Begley and Wilson obtained a value of 78kJ mol^{-1} for the metathesis of propene over a tungsten/silica catalyst[76] and Clark et al a value of 32kJ mol^{-1} for the metathesis of propene over Co-MoO$_3$/Al$_2$O$_3$[116]. The main problem with this calculation is that the rate of reaction used to calculate the activation energy pertains only to the composite rate constant for the chain reaction which would include the rate constants for the initiation, propagation and termination steps. Separation of the contributions of the individual rate constants to the overall constant is difficult to achieve without knowledge of the complete kinetic analysis.

Fig 4.2.1

Plot to determine the activation energy for the metathesis of 1-hexene
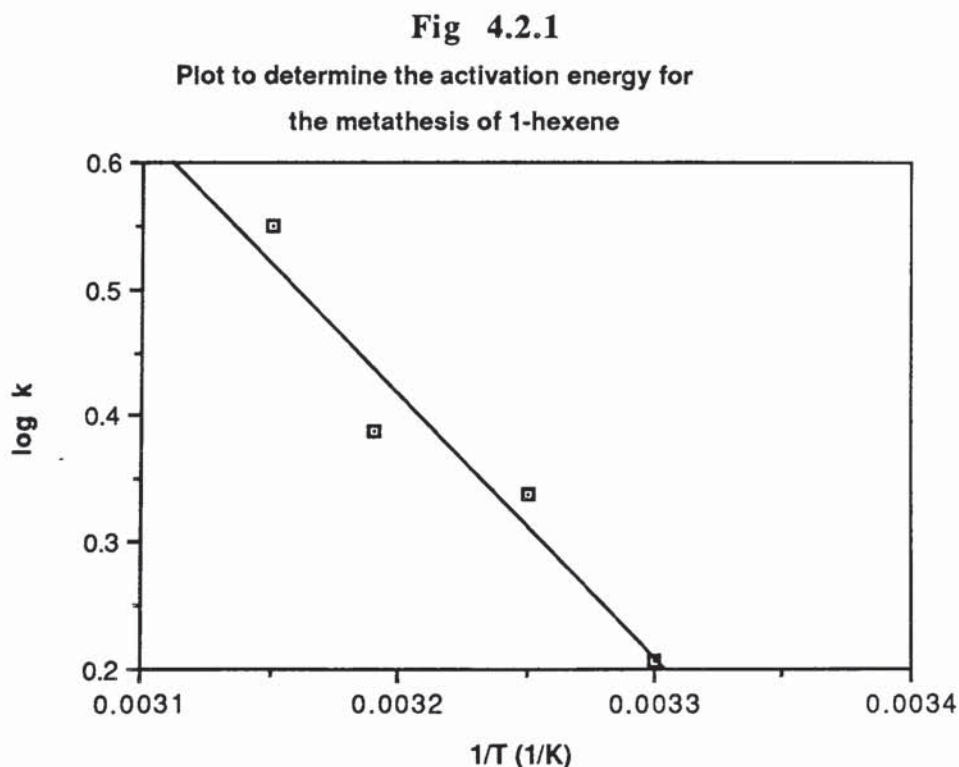
CHAPTER 5: THE EFFECT OF ADDITION OF COCATALYST ON THE RATE OF METATHESIS OF 1-HEXENE

Rhenium is very expensive so effective Re_2O_7/Al_2O_3 catalysts with a low rhenium content are desirable. Increased efficiency of metathesis can be achieved by the addition of co-catalysts to such catalyst systems. Co-catalysts are compounds which are used to enhance the activity of a catalyst. In terms of the olefin metathesis reaction, the co-catalyst can be regarded as a reducing agent, an alkyl donor, or a Lewis acid, which can coordinate to the metal in order to alter its electron density. This change is responsible for enhancing the activity of the catalyst with respect to metathesis. In homogeneous metathesis a co-catalyst is almost always used, particularly for the binary and ternary catalysts. The classical metathesis catalyst first used by Calderon et al, $WCl_6/EtAlCl_2/EtOH$, used ethanol as the promotor[9]. Nakamura and Echigoya have reported the use of a modified heterogeneous catalyst, Re_2O_7/Al_2O_3[41]. Metal oxides such as V_2O_5, MoO_3 and WO_3 were found to promote the activity of the catalyst for the metathesis of oleyl chloride and its co-metathesis with linear olefins such as 1-hexene and 5-decene. Higher activity was particularly noticeable at low rhenium content. These catalysts were also found to be effective for the metathesis of linear olefins.

Tetraalkyl tin compounds were first used as co-catalysts by van Dam et al for the metathesis of methyl oleate using $WCl_6/SnMe_4$ as the catalyst[10]. Verkuijlen first reported on the heterogeneous metathesis of methyl esters of unsaturated fatty acids using $Re_2O_7/Al_2O_3/Sn(CH_3)_4$ as the catalyst[11]. Since then, tetramethyltin has been used as a co-catalyst in the metathesis of other functional and non-functional olefins[94,96,97]. In this project, a variety of experiments were carried out using tetramethyl tin ($Sn(CH_3)_4$) and tetrabutyl tin ($SnBu_4$) as co-catalysts for the rhenium oxide/γ-alumina catalyst in the metathesis of 1-hexene. The effect of multiple additions of co-catalysts and substrate was investigated and the reaction solutions were analysed by gas liquid chromatography.

5.1. The effect of tetramethyl tin concentration on the rate of metathesis

SnMe$_4$ was prepared as a 0.66M solution in cyclohexane and flushed with argon. 2ml of the solution was added under an argon atmosphere to the evacuated reaction vessel, fig 2.5.1 containing 0.70g of Re$_2$O$_7$/γ-Al$_2$O$_3$. The vessel was returned to the vacuum line and 23ml of a 3.7M solution of 1-hexene in cyclohexane was added so that the total volume of the reaction solution was 25ml. The volume of ethene evolved on contact with the catalyst was followed as before and all the experiments were carried out in duplicate or triplicate. This experiment was repeated using different concentrations of the SnMe$_4$ and the rate of evolution of ethene is shown in fig 5.1.1. It was found that increasing the concentration of SnMe$_4$ had no consistent effect on the rate of metathesis.

Fig 5.1.1

Plot to compare the rate of metathesis of 1-hexene at different concentrations of SnMe4
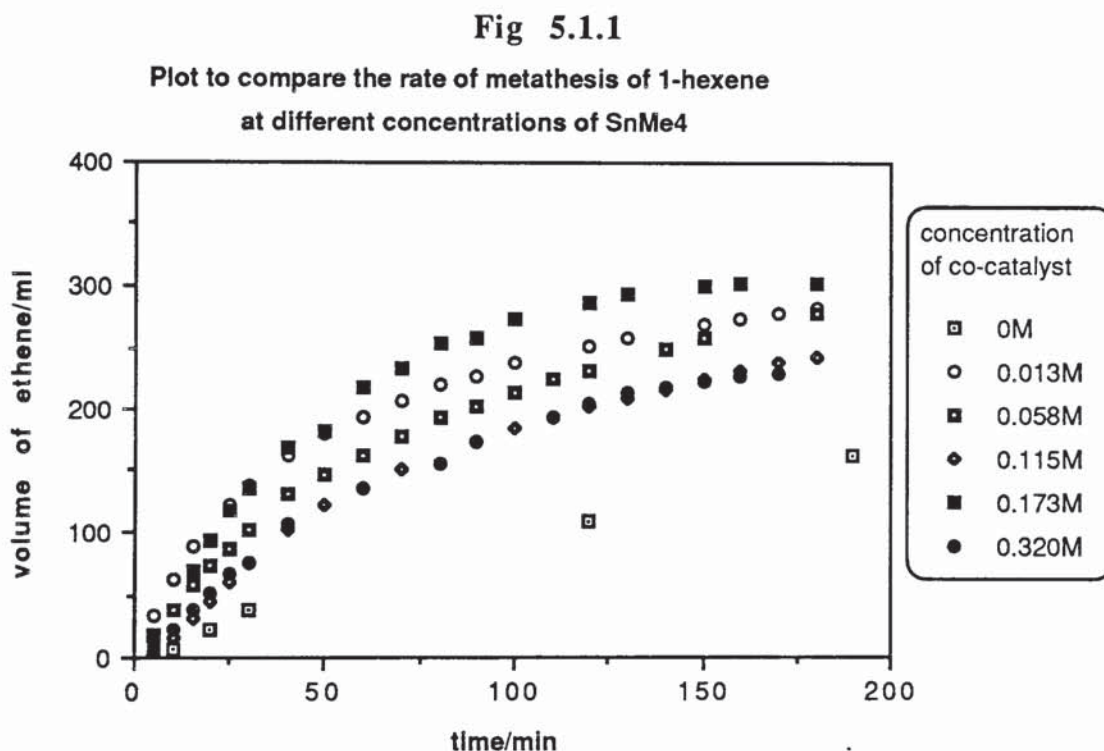
Also shown in fig 5.1.1 is the dependence of rate of evolution of ethene for the experiment in which no SnMe$_4$ was used. It can be seen from fig 5.1.1 that the use of SnMe$_4$ as a co-catalyst

(i) increases the overall rate of metathesis,

(ii) increases the overall yield of product and

(iii) the decrease in the rate of metathesis with conversion seems to be faster for those reactions in which the initial rate of metathesis is fastest.

In doing an experiment at a particular concentration of SnMe4, the apparent irreproducibility in the volume of ethene recorded between different experiments, was thought to be due to the time delay between the addition of SnMe4 and 1-hexene solution. The time taken to transfer the reaction vessel from the dry box to the vacuum line varied from experiment to experiment and consequently, the mode of addition of SnMe4 was altered. The effect of the time difference between the addition of SnMe4 and 1-hexene was investigated.

5.2. The effect of the length of time between the addition of SnMe4 and 1-hexene

The experiments were carried out using the same procedure described in section 5.1. The reaction vessel was returned to the vacuum line and specified periods of time between the mixing of the catalyst components and admission of the 1-hexene were allowed to elapse. 2ml of 0.66M solution of SnMe4 and 0.70g of $Re_2O_7/\gamma\text{-}Al_2O_3$ were used throughout and the effect of mixing times on the rate of ethene evolution was investigated, fig 5.2.1.

Fig 5.2.1

Plot to show the effect of the length of time on the rate of metathesis between the addition of SnMe4 and 1-hexene

155
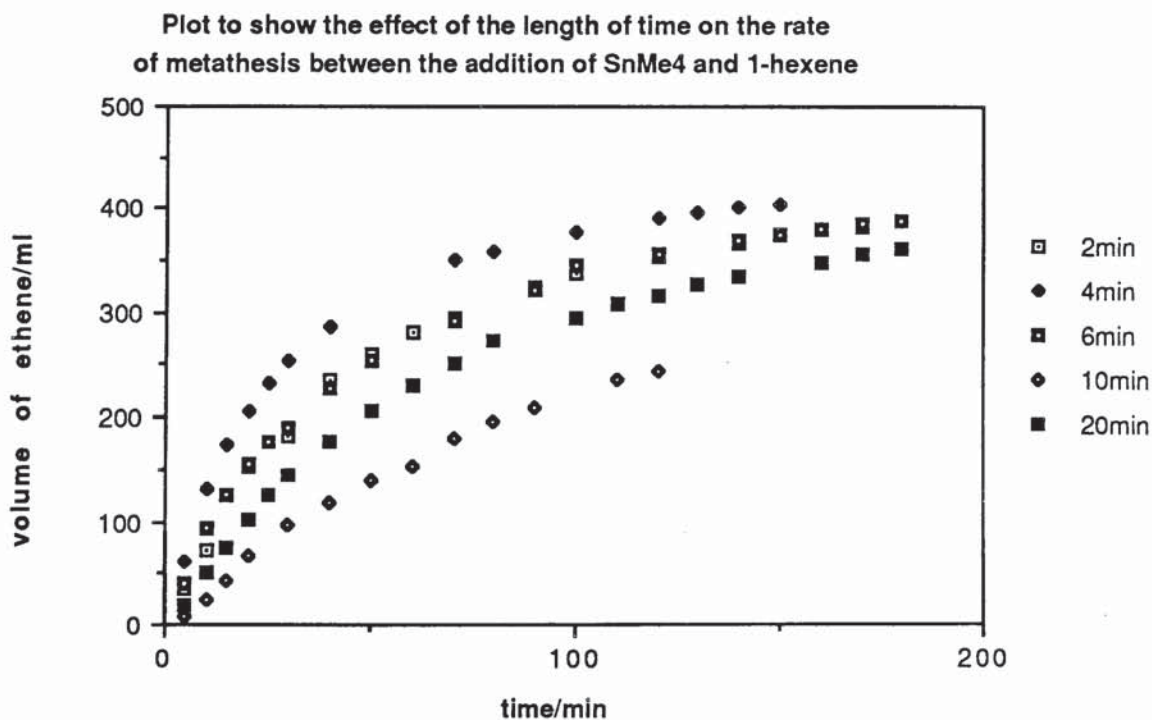
Fig 5.2.1 shows that the length of time (the pre-mixing time) between the addition of SnMe$_4$ and 1-hexene solution to the catalyst does not appear to affect the rate of the reaction in any systematic manner except that an optimum time of 4 minutes would appear to apply. Consequently the mode of addition of SnMe$_4$ was altered to try to obtain a relationship between the rate of metathesis of 1-hexene and the pre-mixing time.

In a separate series of experiments, the solution of SnMe$_4$ was added by syringe through a suba-seal attached at joint C (fig 2.5.1). It was believed that in this way the error involved in measuring the quantities of co-catalyst solutions into the reactor were minimised. The dependence of rate of evolution of ethene on pre-mixing time in this set of experiments is shown in fig 5.2.2.

Fig 5.2.2

Plot to compare the effects of the length of time between the addition of SnMe4 and 1-hexene
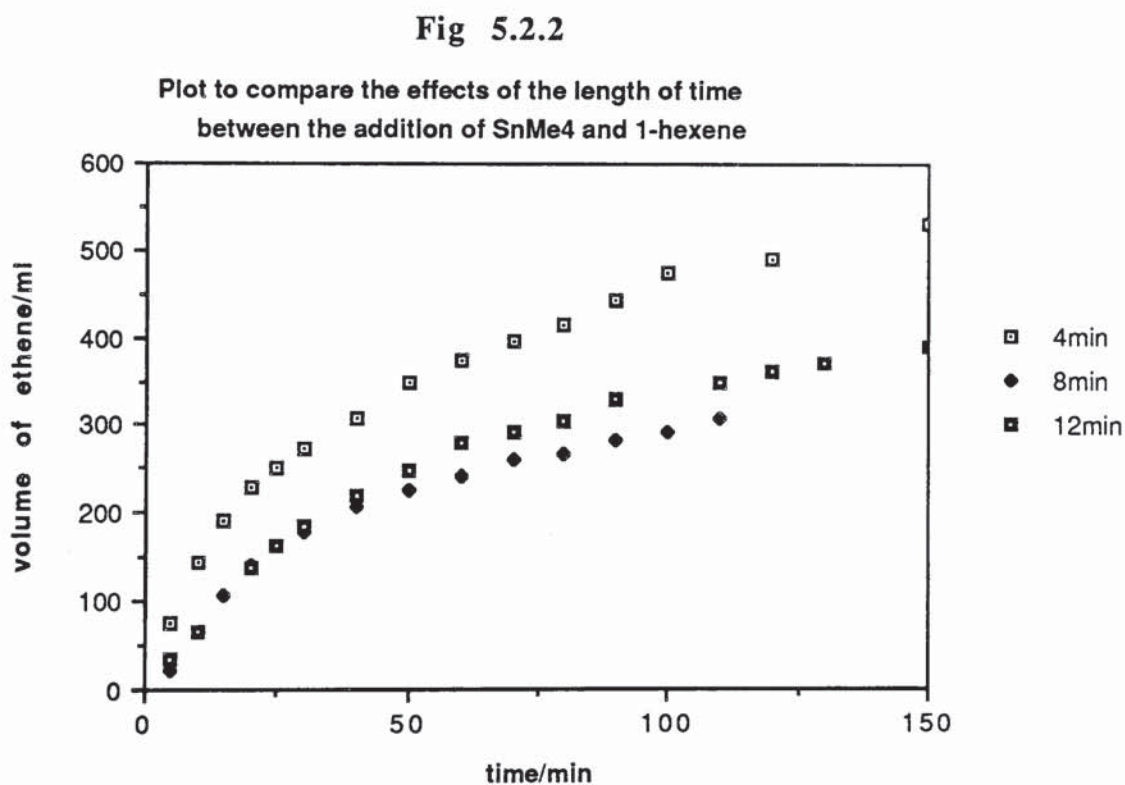
5.3. The effect of tetrabutyl tin concentration on the rate of metathesis

Tetramethyl tin is one of a range of tetraalkyl tin compounds that have been used as co-catalysts for olefin metathesis and ring opening metathesis polymerization. Others including tetrabutyl and tetraphenyltin have also been used for reactions of this type. Reactions were carried out to

compare the activity of tetrabutyl tin and tetramethyl tin as co-catalysts for various times between addition of the co-catalyst and olefin to the catalyst (Re_2O_7/γ-Al_2O_3).

The effect of the length of time between the addition of $SnBu_4$ and 1-hexene was investigated using the same procedure in section 5.2. 2ml of a 0.66M solution of $SnBu_4$ in cyclohexane was added to 0.70g of the catalyst using a syringe followed by the addition of 23ml of 3.7M solution of 1-hexene and the effect of varying the mixing time is shown in fig 5.3.1.

Fig 5.3.1

Plot to compare the effects of the length time between the addition of SnBu4 and 1-hexene
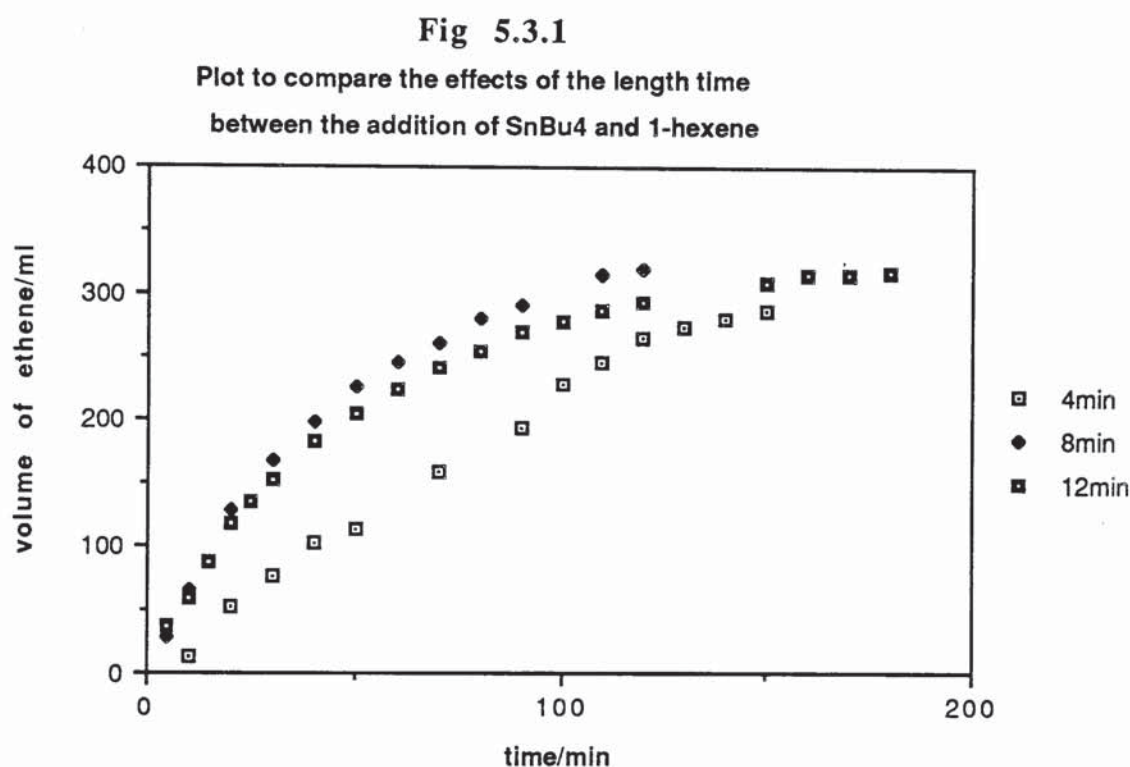
Fig 5.3.1 shows that varying the mixing time between $SnBu_4$ and 1-hexene does not produce any consistent trends and when the results are compared with those in fig 5.2.2, it is evident that $SnMe_4$ promotes the conversion to ethene more effectively than $SnBu_4$. It is also interesting that after approximately three hours of reaction, the rate of evolution of ethene tends to zero. This is also observed when $SnMe_4$ is used and suggests that the number of active metathesis centres are being reduced either by decay processes or by extraneous influences.

5.4. Effect of the multi-addition of 1-hexene using co-catalysts

The previous results showed that the promoted rhenium (VII) oxide/γ-alumina catalyst was much more active towards the metathesis of 1-hexene than the unpromoted. It was also observed that the rate of decrease in the rate of metathesis with conversion is greater for the promoted catalyst than for the unpromoted, which suggests that less active metathesis sites are available for the reaction. It is not known how or why these active centres are reduced in number, so experiments were carried out to investigate whether the catalyst could be reactivated towards metathesis by the addition of a fresh solution of 1-hexene. This was carried out in order to ascertain if the species responsible for the decay of catalyst was produced during the reaction and was present in the reaction solution. If a poison was present in the reaction solution then the fresh batch of 1-hexene should undergo metathesis at a rate comparable to that of the first batch of 1-hexene since the poison would be removed on draining the catalyst after the first metathesis.

The investigation into the activity of the catalyst was twofold:

(i) After the co-catalyst had been added, 1-hexene was added, metathesised, removed and another aliquot of 1-hexene was added.

(ii) After the first aliquot of 1-hexene had been removed, a further aliquot co-catalyst was added to the catalyst again followed by another aliquot of 1-hexene solution.

5.4.1. Effect of SnBu₄ and SnMe₄ on the multi-addition of 1-hexene

The experiment was carried out according to the method described in section 5.1. A 0.174M solution of co-catalyst in cyclohexane was used so that the Re:Sn ratio was 1:1. 2ml of this solution was added to 0.70g catalyst and 4min later, 23ml of 3.7M 1-hexene solution was added. The reaction rate was followed by monitoring the rate of evolution of ethene and as the reaction rate started to tend to zero, the reaction solution was removed and 25ml of fresh 1-hexene solution was added to the wet catalyst almost immediately and the volume of ethene evolved was measured.

Figs 5.4.1 and 5.4.2 show the activity of the catalyst for both additions of 1-hexene solution using SnMe$_4$ and SnBu$_4$ respectively. In both cases the activity of the catalyst is substantially reduced with respect to metathesis of the second 1-hexene solution. Both plots show that the kinetics of the evolution of ethene for the first addition is different from that of the second addition but more significantly, there is no indication of decaying processes occurring with the second addition.

Fig 5.4.1

**Effect of SnMe4 on the activity of the catalyst
for the multi-addition of 1-hexene**
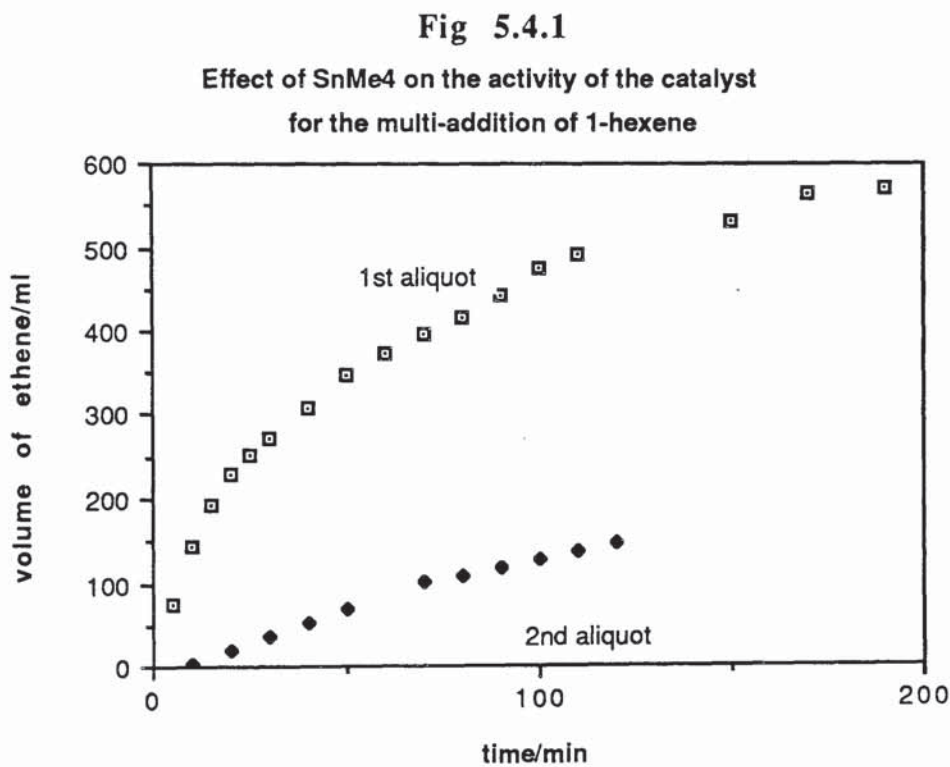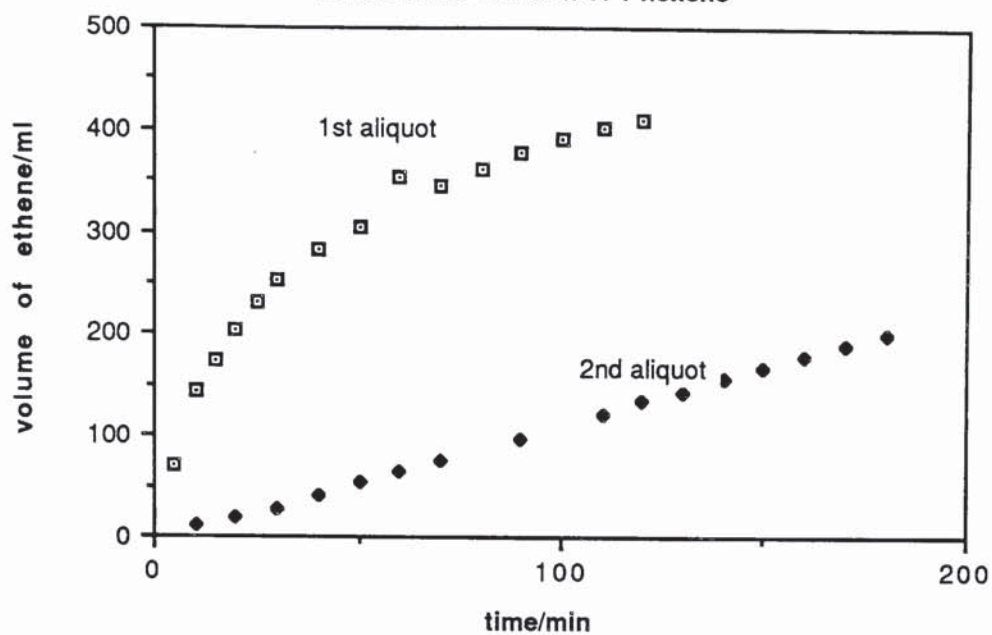
Fig 5.4.2

Effect of SnBu4 on the activity of the catalyst

for the multi-addition of 1-hexene

If the volume of ethene evolved on the promoted catalysts is compared with the volume evolved on an unpromoted catalyst, it becomes evident that the co-catalysts are helping to deactivate the catalyst towards the metathesis of subsequent additions of 1-hexene, fig 5.4.3.

Fig 5.4.3

Effect of co-catalysts on the activity of the rhenium (VII) oxide/alumina catalyst

KEY (chart legend): 1a, 1b, 2a, 2b, 3a, 3b
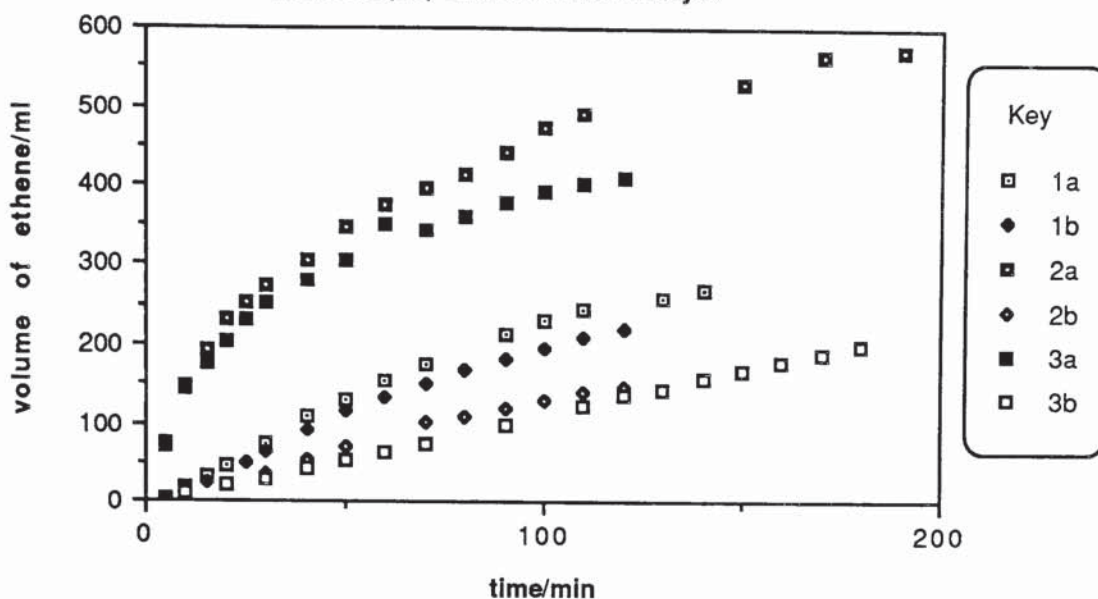
KEY

1a: 1st aliquot of 1-hexene (no co-catalyst)   1b: 2nd aliquot of 1-hexene (no co-catalyst)

2a: 1st aliquot of 1-hexene (with SnMe$_4$)   2b: 2nd aliquot of 1-hexene (no SnMe$_4$)

3a: 1st aliquot of 1-hexene (with SnBu$_4$)   3b: 2nd aliquot of 1-hexene (no SnBu$_4$)

5.4.2. Effect of the multi-addition of SnBu$_4$ and SnMe$_4$ on the activity of the rhenium(VII) oxide/γ-alumina catalyst

The previous results showed that after the catalyst had been treated with a co-catalyst, a subsequent addition of 1-hexene underwent metathesis at a much slower rate than before. This indicated that the catalyst had been deactivated towards the metathesis reaction and simply adding fresh 1-hexene did not help it to regain its original activity. Consequently, the experiments were repeated but this time, fresh co-catalyst was added to the wet catalyst after the first reaction solution had been removed. 2ml of 0.74M solution of co-catalyst was added to 0.70g catalyst and 4min later, 23ml of 3.7M 1-hexene solution was added. As the reaction rate started to tend to zero, the reaction solution was removed leaving the catalyst wet. 10min later 2ml of co-catalyst was added to the catalyst followed 4min later by the second addition of 1-hexene solution. Figs 5.4.4 and 5.4.5 show that the rate of evolution of ethene for the second

161

addition of 1-hexene is still very slow compared to the first experiment, even though fresh co-catalyst had been added.

Fig 5.4.4

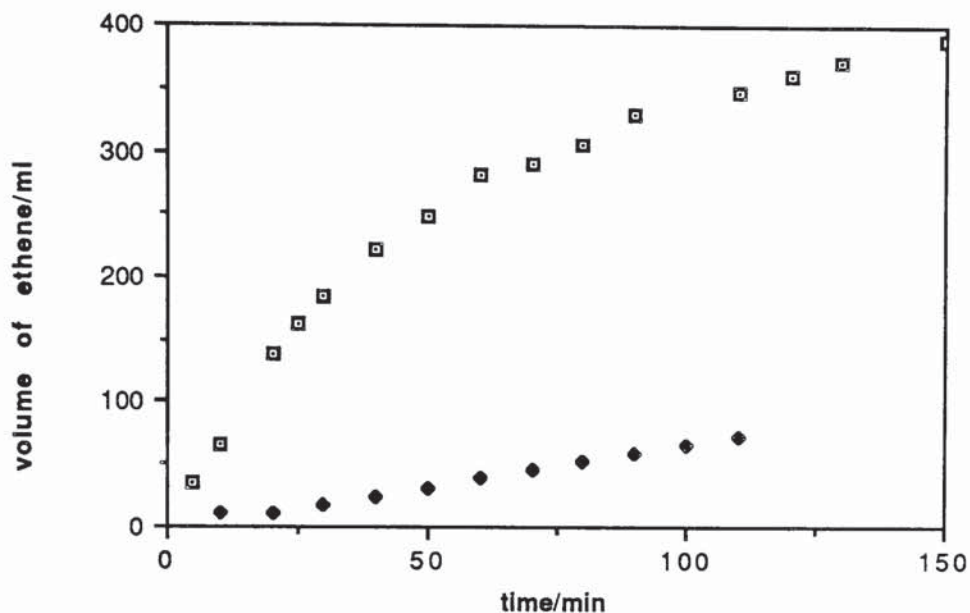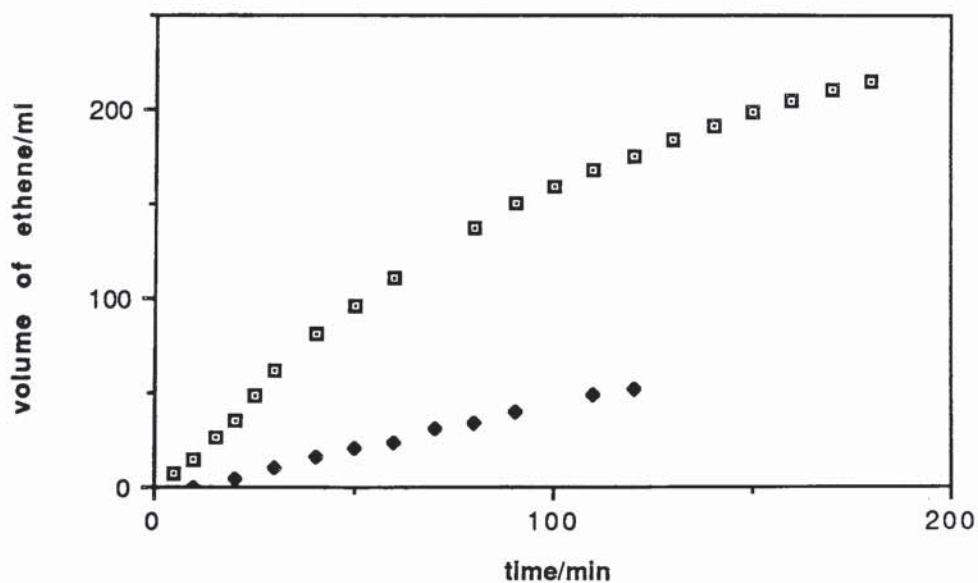**Effect of the multi-addition of SnMe4 on a wet catalyst**

Fig 5.4.5

Effect of the multi-addition of SnBu4 on a wet catalyst

The experiment using co-catalysts was repeated without removing the first aliquot of 1-hexene solution from the catalyst. Towards the end of the reaction, a fresh solution of the co-catalyst

was added to the reaction mixture to see if the catalyst could be reactivated, but nothing was observed to happened, ie the evolution of ethene did not recommence. It would appear therefore that the decay in activity is not simply associated with the consumption of SnMe$_4$.

These results show that once the catalyst has been treated with co-catalyst, the configuration of the active sites for metathesis is altered such that when the sites are spent, it is not possible to reactivate the catalyst to its original activity; whereas reactivation is possible when no co-catalysts are used, fig 5.4.3.

5.5. Gas liquid chromatography studies

The reaction solutions at the end of the reactions discussed in sections 5.3 and 5.4 were analysed using glc. The chromatographs showed that the concentrations of the minor products, namely 2-heptene and 4-nonene, were much lower than when no co-catalyst was used. In previous experiments, when co-catalysts have not been used, the concentration of the minor products increased with time, albeit very slowly. However, when co-catalysts were used to help promote the metathesis of 1-hexene, a much cleaner conversion of 1-hexene to its primary products, ethene and 5-decene was achieved. The co-catalysts appear to improve the selectivity of the catalyst towards the metathesis of α - olefins by altering the active sites on the surface of the catalyst, so that isomerization of 1-hexene is reduced. A quantitative analysis of the glc results obtained from the final reaction solution of the experiments in sections 5.3 and 5.4 is shown in tables 5.1 and 5.2 respectively.

Table 5.1

The effect of sequential additions of 1-hexene on the activity of $Re_2O_7/\gamma\text{-}Al_2O_3$ promoted with co-catalysts

Aliquot of 1-hexene	Co-catalyst used	$\dfrac{\% \text{ area 5-decene}}{\% \text{ area 4-nonene}}$	$\dfrac{\% \text{ area 5-decene}}{\% \text{ area 2-heptene}}$
1st	SnMe$_4$	205	1109
2nd	-	190	522
1st	SnBu$_4$	244	1995
2nd	-	211	158

Table 5.2

The effect of sequential additions of co-catalysts on the metathesis of 1-hexene using $Re_2O_7/\gamma\text{-}Al_2O_3$

Aliquot of 1-hexene	Co-catalyst used	$\dfrac{\% \text{ area 5-decene}}{\% \text{ area 4-nonene}}$	$\dfrac{\% \text{ area 5-decene}}{\% \text{ area 2-heptene}}$
1st	SnMe$_4$	59	188
2nd	SnMe$_4$	58	118
1st	SnBu$_4$	66	73
2nd	SnBu$_4$	66	86

Table 5.1 shows that the concentration of the minor products, 4-nonene and 2-heptene is much lower than those obtained when no co-catalyst is used. The ratio decreases when a second aliquot of 1-hexene is added because less 5-decene is produced whilst the concentration of the minor products remains about the same. However, the situation is altered when sequential additions of co-catalyst are done as well. Table 5.2 shows that the concentration of 4-nonene and 2-heptene increases when a second aliquot of co-catalyst is used in the metathesis of a second aliquot of 1-hexene. Overall it is found that although the activity of the catalyst has decreased, the % conversion of a second aliquot of 1-hexene using a second aliquot of co-catalyst is of almost the same order as the first metathesis reaction, even though this second reaction occurs at very much slower rate.

Table 5.3 shows the ratio of 5-decene to 4-nonene and 2-heptene for the sequential addition of 1-hexene involving no co-catalyst, section 3.8. If these results are compared with those in tables 5.1 and 5.2, it can be seen that the selectivity of the catalyst has been increased in the presence of the co-catalyst. In particular, less 2-heptene than 4-nonene is formed.

Table 5.3

The effect of sequential additions of 1-hexene on the activity of $Re_2O_7/\gamma\text{-}Al_2O_3$

Aliquot of 1-hexene	$\dfrac{\% \text{ area 5-decene}}{\% \text{ area 4-nonene}}$	$\dfrac{\% \text{ area 5-decene}}{\% \text{ area 2-heptene}}$
1st	22	20
2nd	20	70

5.6. Discussion

It has been known for sometime now that tetraalkyltin compounds enhance the activity of $Re_2O_7/\gamma\text{-}Al_2O_3$ as a metathesis catalyst. The increase in activity is believed to be due to the fact that when tetramethyltin is added to $Re_2O_7/\gamma\text{-}Al_2O_3$, alkylation of the rhenium occurs followed by the formation of an active catalytic carbene species and methane[97]:

$$Re \xrightarrow{2Sn(CH_3)_4} Re\begin{matrix} CH_3 \\ CH_3 \end{matrix} \longrightarrow Re=CH_2 + CH_4$$

This carbenic species is believed to be responsible for enhancing the activity of metathesis catalysts. ESCA analysis of the surface of the catalyst has revealed that tin, as well as carbon is present but its molecular environment has yet to be determined, Appendix 2.

When the co-catalyst is added to the catalyst, it can activate the catalyst in one of two ways:

(i) Change the nature of the active centre to make it more active or

(ii) change the number of active centres without changing the nature of the sites.

It is highly likely that (i) rather than (ii) applies because the nature and distribution of the products is different. Fewer side products are present in the final reaction solution which suggests that side reactions, such as isomerization, have been reduced and this is probably due to the change in morphology of the active site. Another reason for ruling out (ii) is that the rate of decay of catalyst activity again seems to be faster for the most active catalysts.

As mentioned previously, promoted catalyst have improved selectivity in the reaction. Fewer side products are produced on the promoted catalyst than on the unpromoted catalyst and such side products are produced in lower yields; this is believed to be due to an alteration in the configuration of the active centres. Tanaka et al. found that treatment of the less active metathesis catalyst, MoO_3/SiO_2, with $SnMe_4$ led to it not only being 10^3 times more active towards the metathesis of propene at room temperature but that the inter- and intra- molecular hydrogen scrambling of the olefins was suppressed[117]. Therefore, only the products of the degenerate and productive metathesis of propene were obtained. The major side products of the metathesis of 1-hexene, 4-nonene and 2-heptene, are believed to arise from the cross metathesis between 1- and 2-hexene. 2-hexene could arise from the isomerization of 1-hexene and it is this reaction which is suppressed in the presence of co-catalysts. This therefore reduces the concentration of 2-hexene present in the reaction solution, thus reducing the likelihood of cross metathesis occurring between 1- and 2-hexene to give 4-nonene and 2-heptene.

Tanaka et al. examined the reaction time between $SnMe_4$ on MoO_3/SiO_2 and propene and found that the metathesis of propene increased as the reaction time was increased from 5min to 16h[116]. This was attributed to the fact that the number of active $Mo=CH_2$ species increased with reaction time. In the work carried out in this project, it was found that the effect of the length of time between the addition of the co-catalysts, $SnMe_4$ and $SnBu_4$ and 1-hexene gave inconsistent results and it was not possible to establish any such relationship. Why this inconsistency should occur has yet to be established.

The regeneration properties of the promoted catalyst differs vastly from that of the unpromoted catalyst. The active sites produced without the aid of co-catalysts can be regenerated, although not completely, when the catalyst is dried by evacuation; when a second aliquot of 1-hexene is added, it undergoes metathesis at a rate which is a little slower compared to the first reaction. In these experiments the activity was regenerated under two conditions - with and without co-catalyst. Without a second addition of co-catalyst, the activity of the catalyst is considerably reduced but when a second aliquot of $SnMe_4$ or $SnBu_4$ is added, an even lower activity associated with the second phase of metathesis is obtained. It appears that $SnMe_4$ and $SnBu_4$ react with the active centres to produce a stable intermediate which cannot be decomposed to regenerate active centres necessary for the metathesis reaction. Consequently, when a second aliquot of 1-hexene is added, the number of active centres have been considerably reduced and this manifests itself in the much lower activity of the catalyst.

6.1. Introduction

Oxazolines are five membered heterocyclic compounds having one double bond[118]. Three different types of oxazolines are known and they are distinguished by the positions of their double bonds:
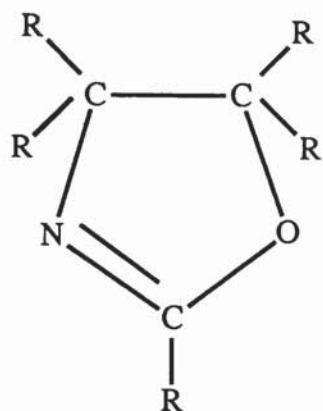
2-OXAZOLINE
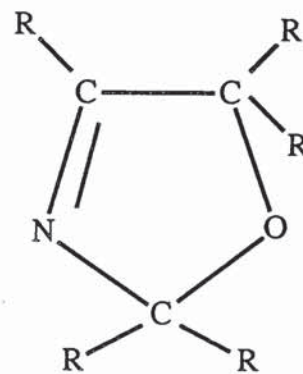
3-OXAZOLINE
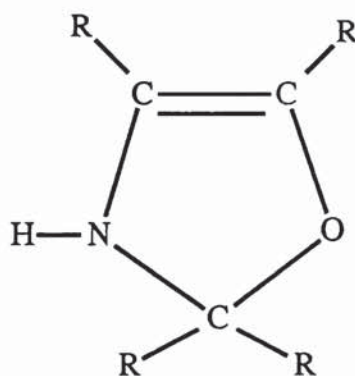
4-OXAZOLINE

Most of the work in the literature has been carried out using 2-oxazolines, so the rest of this review will be limited to them.

2-oxazolines, derived from the condensation of amino alcohols and carboxylic acids, have been of commercial interests because of their synthetic utility[119,120,121]. In 1937 Leffler and Adams reported on the use of aminophenyl-2-oxazolines as local anaesthetics[122], eg **XXIII**.

XXIII

These compounds were compared to the local anaesthetic Procaine and **XXIII** was found to have only a third of the toxicity of Procaine and was as efficient. There were several disadvantages in using these oxazolines as anaesthetics; namely the low solubility of the free base in water which was reduced further by additional substituents in either the be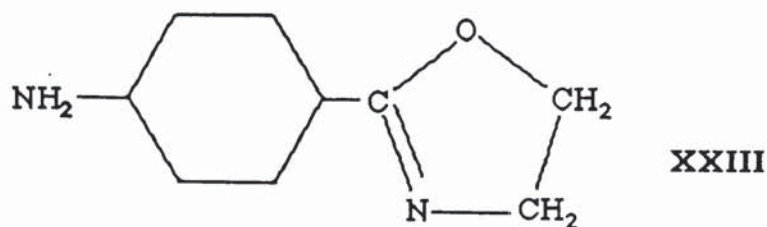nzene or oxazoline ring and the hydrochlorides of the aminophenyloxazolines were too acidic (pH 4-5) and underwent hydrolysis of the oxazoline ring in boiling water.

Optically active 2-alkylcarboxylic acids have been efficiently prepared from chiral 2-alkyloxazolines[120]. Metalation of the oxazoline with lithium diisopropylamide followed by alkylation with alkyl halides gave **XXIV**. **XXIV** was hydrolysed by 4N sulphuric acid to give either the (R) or (S) carboxylic acid, scheme 6.1.

Scheme 6.1

The preparation of optically active carboxylic acids
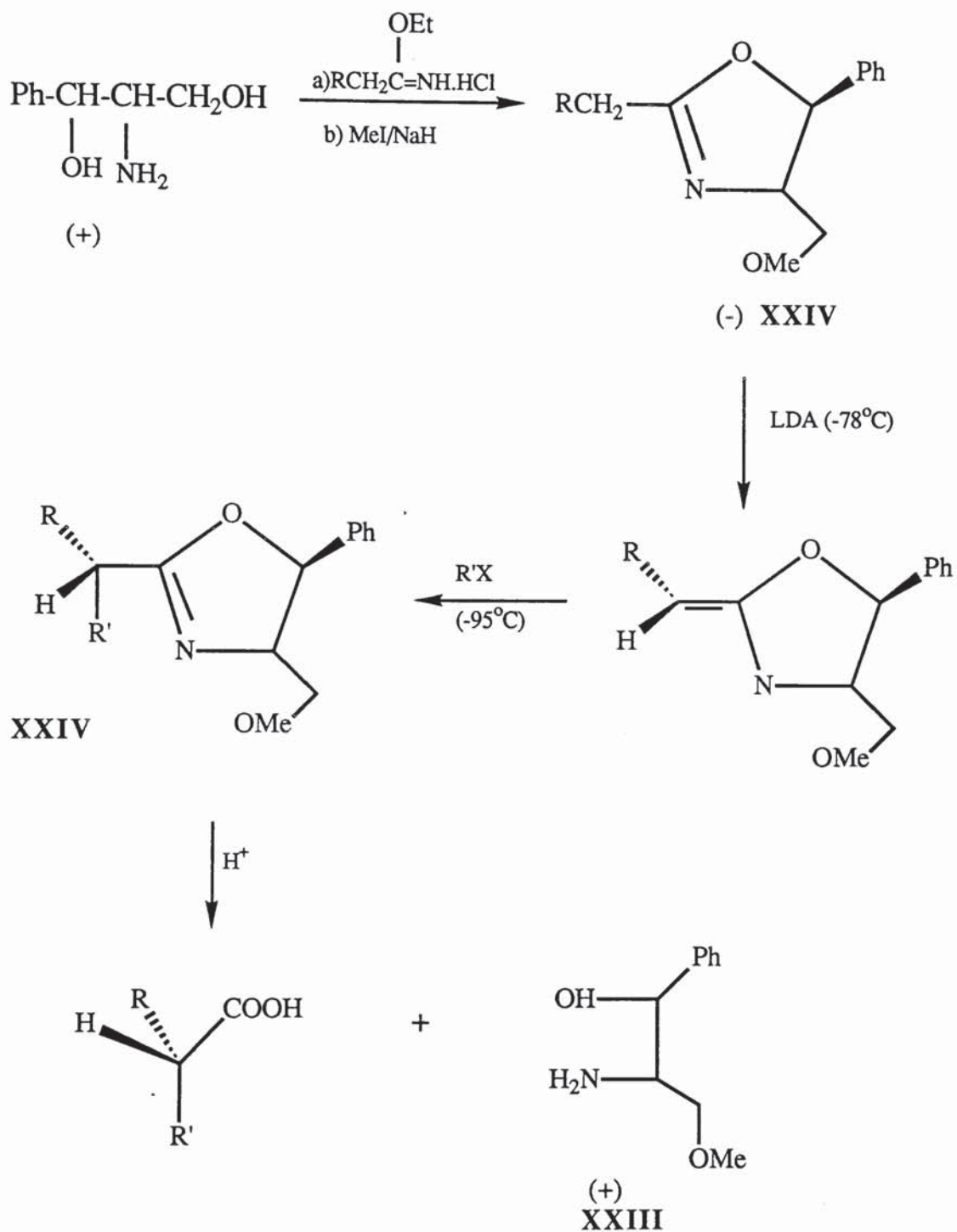
The method allows known enantiomers to be prepared by proper introduction of R and R', table 6.1.

Table 6.1

Preparation of optically active 2-alkylcarboxylic acids

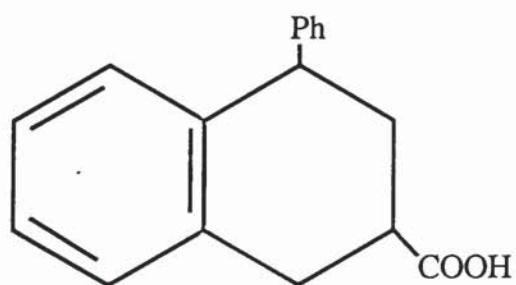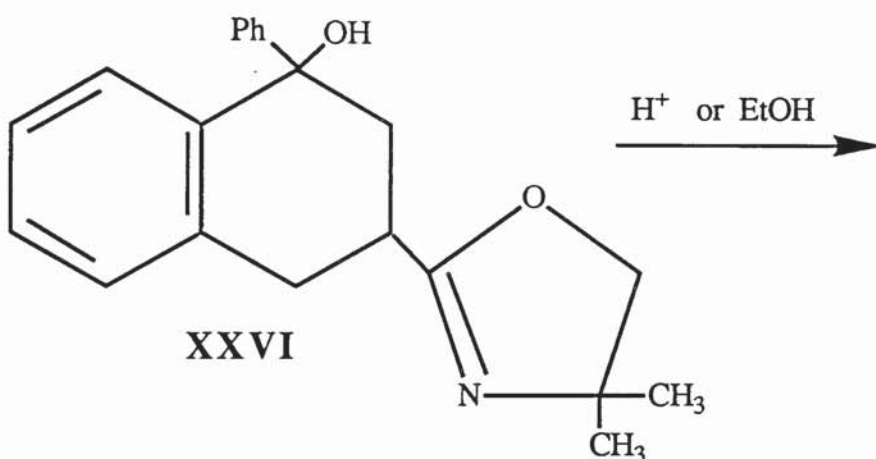| R	R'X	Overall yield %	Configuration
Me	EtI	84	S
Et	Me_2SO_4	83	R
Me	n-BuI	65	S
$PhCH_2$	Me_2SO_4	75	R

Optically active alcohols, carboxylic acids and esters can also be prepared using oxazolines[119-121].

One of the most significant properties of the oxazoline ring is its ability to withstand attack from a variety of reagents, eg Grignard reagents, mild acids, alkalis, oxidants and reductants, and consequently 2-oxazolines can be used as protecting groups for carboxylic acids during chemical reactions when reactions on other parts of the molecule involve such conditions. Meyers and Temple observed that the 2-oxazoline ring could be readily converted into the corresponding ethyl ester by heating in 5-7% ethanolic sulphuric acid; alternatively, when treated with an acidic aqueous medium, the carboxylic acid was produced[106,123]. Such procedures permit regeneration of the carboxylic acid after reaction, eg if a functionally substituted carboxylic acid is protected as an oxazoline (**XXV**) using 2-amino-2-methyl-1-propanol and is then treated with Grignard reagents, a tertiary alcohol (**XXVI**) is produced. This can be treated with either an aqueous acidic solution to regenerate the acid (**XXVII**) or an acidic solution of ethanol to produce the ethyl ester (**XXVIII**)[123].

$$+ \ H_2N\text{-}C(CH_3)_2CH_2)OH \ \rightleftharpoons$$

XXV

$$\xrightarrow[MgBr_2]{PhMgBr}$$

Ph OH

XXVI

$$CH_3$$
$$CH_3$$

$$\xrightarrow{H^+ \ \text{or} \ EtOH}$$

Ph

COOH

XXVII

or

Ph

COOEt

XXVIII
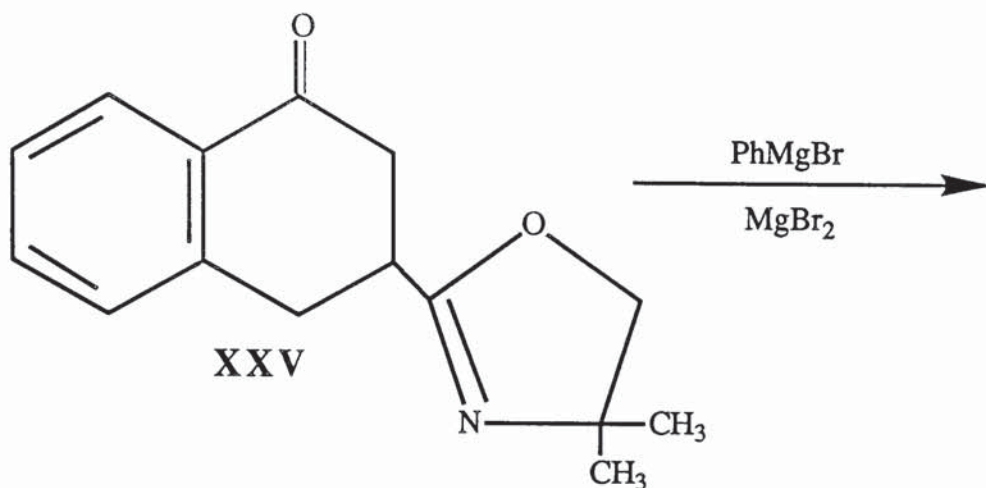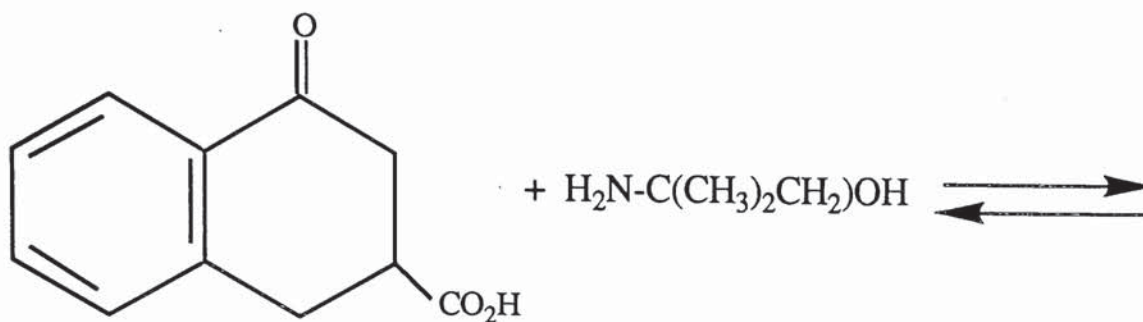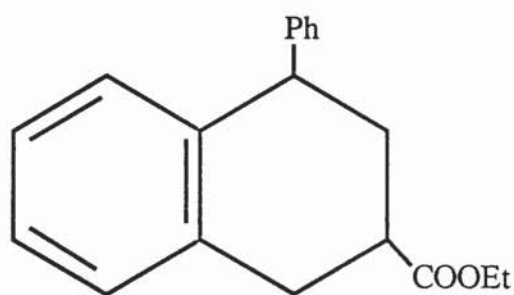
As mentioned previously, diesters are important in industry and one of the possible synthetic pathways of obtaining them is considered to be by the metathesis of an unsaturated ester. However, because of the high electron density associated with the heteroatom, the carbon-

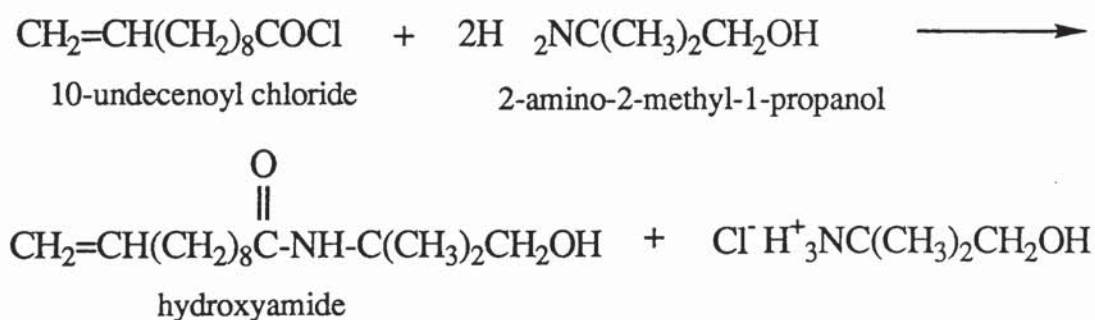carbon double bond is unable to compete effectively with the lone pair of electrons on the heteroatom for complexation to the active site on the catalyst. A possible means of overcoming this problem would be to protect the functional group in such a way that the carbon-carbon double bond could then compete for the active site on the catalyst.

It was decided that this approach to protection of the acid group would be adopted in this project. The unsaturated acid would be converted to the corresponding oxazoline and subsequently metathesised to produce the di-oxazoline. The product would then be treated with an alcoholic solution to yield the diester. If this method proved to be successful, it could provide a more productive route to the production of diesters by olefin metathesis. Consequently two oxazolines, 4,4-dimethyl-2-(9-decenyl)-1,3-oxazoline and 4,4-dimethyl-2-(3-pentenyl)-1,3-oxazoline were prepared. These were chosen because their metathesis would produce ethene as one of the products of metathesis and the reaction could be followed by monitoring the evolution of ethene.

6.1.1. Preparation of the hydroxyamide of 10-undecenoyl chloride[122,124]

$$CH_2=CH(CH_2)_8COCl \quad + \quad 2H_2NC(CH_3)_2CH_2OH \quad \longrightarrow$$

10-undecenoyl chloride   2-amino-2-methyl-1-propanol

$$CH_2=CH(CH_2)_8\overset{\overset{\displaystyle O}{\|}}{C}-NH-C(CH_3)_2CH_2OH \quad + \quad Cl^- H^+_3NC(CH_3)_2CH_2OH$$

hydroxyamide

In a typical preparation 50g (250mmol) of 10-undecenoyl chloride dissolved in 100ml of dichloromethane, was added dropwise, very slowly and with continuous stirring to 44g (500mmol) of 2-amino-2-methyl-1-propanol dissolved in 100ml of dichloromethane. During the course of this addition the temperature of the reaction was kept close to 0 ± 5°C. When the addition of the acid chloride was complete, the reaction temperature was allowed to rise to 25°C and the solution was stirred at this temperature for 2h. The ammonium salt that formed as a precipitate, was filtered off and the bronze coloured filtrate of the hydroxyamide, was washed

173

several times with distilled water to remove traces of the ammonium salt. The organic layer was then separated and dried over anhydrous magnesium sulphate overnight. When the solution was dry, the solution was filtered from the filtrate and the solvent was removed by distillaton and 55.5g (220mmol) of hydroxyamide were obtained as a viscous liquid (87%) yield.

I.R absorptions υ 3304 (O-H), 3077 (-CO-N), 2927-2855 (sat C-H), 1741cm^{-1} (N-H).

NMR data δ_C (CDCl$_3$) 24.08 (Me), 28.81(CH$_2$), 55.50 (CMe$_2$), 70.52 (CH$_2$O-), 113.94 (CH$_2$=), 138.80 (CH=), 174.49 (C=O).

FAB data m/e 256 (100% F), 238 (50.4% F).

Comparison of the IR spectra of the starting materials, 10-undecenoyl chloride and 2-amino-2-methyl-1-propanol, with that of the hydroxyamide showed that the peak, 1801cm^{-1}, pertaining to the acid chloride group, -COCl, had almost disappeared. The formation of a peak at 1741cm^{-1} was found to be consistent with the formation of an amide. ^{13}C nmr data identified all the carbon atoms pertaining to the structure of the hydroxyamide. The ir and nmr spectra can be found in Appendix 3.

The CI mass spectrum of the hydroxyamide in Appendix 3 shows that the M+1 ion at 256 corresponds to the molecular ion of the hydroxyamide (Mr = 255). The FAB data also shows that the principal peak at m/e of 237 corresponds to the mass of the oxazoline. This is probably formed by the loss of a water molecule, M-18, during fragmentation.

$$CH_2=CH(CH_2)_8 \overset{\overset{\text{O}}{\|}}{C}\text{-NH-}C(CH_3)_2CH_2OH \xrightarrow[\text{2) NaOH}]{\text{1) SOCl}_2}$$

$$CH_2=CH(CH_2)_8 \; C$$

oxazoline
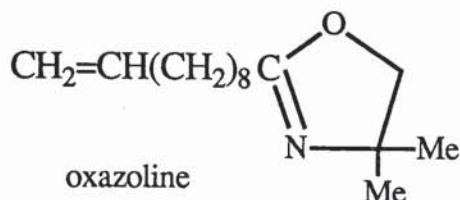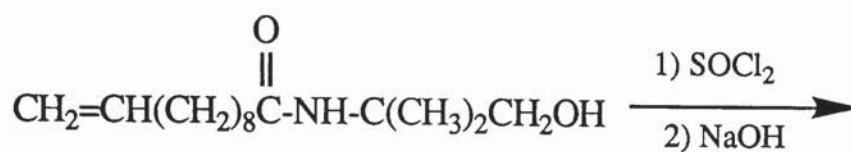
70.3g (600mmol) of thionyl chloride was added dropwise, with stirring, to 50.1g of hydroxyamide, prepared in section 6.1.2, at 0±5°C. After complete addition of the thionyl chloride, the solution was stirred at 0°C for 3h and then 40ml of 20% sodium hydroxide solution was added to effect the cyclization and to hydrolyse any unreacted thionyl chloride. The solution was stirred until there were no more signs of HCl production. The resulting solution was then extracted several times using ether (20ml) and the ether layer was dried over anhydrous magnesium sulphate. After the ether layer had been filtered through fluted filter paper, the ether was removed by distillation. 35.7g of a product was obtained.

IR absorptions υ 2916-2511 (sat C-H), 1641 (-C=N-), 1256cm^{-1} (-C-O-C-).

NMR data δ_C (CDCl$_3$) 28.09 (Me), 28.69 (CH$_2$), 55.04 (CMe$_2$), 77.14 (CH$_2$O-), 113.94 (CH$_2$=), 138.80 (CH=), 165.87 (C=N).

FAB data m/e 256 (100% F), 238 (4.5%).

The IR spectrum of the oxazoline showed the presence of the amide group at 1741cm^{-1}, the formation of an imine group at 1641cm^{-1} and the formation of an ether group at 1256cm^{-1}. A peak at 2057cm^{-1} was also formed but this has yet to be identified. One possibility is that the reaction forms an isothiocyanate as a by-product, since this group has an absorbance between 2140-1990cm^{-1}. A sensible mechanism for the formation of -N=C=S, consistent with the reactants present, cannot be suggested but if the reaction between the acid chloride and the

amino-alcohol formed the ester in preference to the amide then it is possible that a free amino group might subsequently react with the thionyl chloride to produce the -N=C=S.

The ^{13}C nmr spectrum showed the disappearance of the resonance pertaining to the C=O and the presence of the imino group, C=N which is present in the oxazoline ring.

The mass spectrum of the product in Appendix 3 shows that the sample contains only 4.5% of the oxazoline with the hydroxyamide being the principal constituent.

Several problems were encountered in the synthesis of the oxazoline with the initial problem being the control of the temperature . The addition of the acid chloride and the thionyl chloride had to be carried out very slowly because the temperature of the reaction solutions rose very quicky on addition of a few drops of the reagents. Sustained use of a mixture of cardice, acetone and salt ensured that the temperature was kept below zero provided the addition was carried out very slowly. Consequently the addition would sometimes take over 2h to complete.

Obtaining the final product in a pure form presented problems. Residues from the cyclization and the magnesium sulphate were dispersed throught out the product after removal of the ether. The product was dissolved therefore in dried cyclohexane to remove the insoluble material and filtered through fluted filter paper under an argon atmosphere. Cyclohexane was then removed by distillation to yield the product.

6.2. The metathesis of 4,4-dimethyl-2-(9-decenyl)-1,3-oxazoline

There was a long period between the synthesis and analysis of the product. On the assumption that the product was 4,4-dimethyl-2-(9-decenyl)-1,3-oxazoline, metathesis of the material was attempted.

A 1.08M solution of the product based on the molecular weight of the oxazoline, was made up in chlorobenzene and 20ml was placed in a reaction flask under an argon atmosphere. The flask was attached to joint C of the reaction vessel in fig 2.5.1 and the solution was added to

176

0.70g of $Re_2O_7/\gamma-Al_2O_3$ catalyst under vacuum. The reaction was followed by monitoring the gas evolved at 35°C. No changes in the height of the manometer were detected and analysis of the solution by tlc showed that the retention values of the product before and after the reaction were similar. Consequently the experiments were repeated using the co-catalysts $SnMe_4$ and $SnBu_4$ since it was believed that the oxazoline might have had difficulty in forming the initial propagating species by itself.

6.2.1. The effect of co-catalyst on the metathesis of 4,4-dimethyl-2-(9-decenyl)-1,3-oxazoline

2ml of the evacuated co-catalyst in chlorobenzene was added to 0.70g of $Re_2O_7/\gamma-Al_2O_3$ catalyst in the evacuated reaction vessel. 10min later 20ml of 1.08M oxazoline in cyclohexane was added and the reaction was followed as before at 35°C. The effect of co-catalyst concentration on the rate of metathesis of the oxazoline is shown in table 6.2.

Table 6.2

The effect of co-catalyst concentration on the rate of metathesis of the 4,4-dimethyl-2-(9-decenyl)-1,3-oxazoline

Re:SnMe₄	Comments	Re:SnBu₄	Comments
1:1	No reaction observed	1:1	25ml of a gas detected
1:7	No reaction observed	1:4	No reaction observed
1:10	No reaction observed	1:10	17ml of a gas detected

The greatest change in the height of the manometer occurred during the first 4h. In order to ascertain if the changes were due to the evolution of ethene, analysis of the product solution was undertaken to identify the compounds present which would provide information on the type of reaction occurring.

The product of metathesis was analysed by thin layer chromatography and a typical R_f value for the reactant was 0.46 and for the metathesis product 0.8, which indicated that the original

compound had disappeared. However, there did appear to be a significant amount of the hydroxyamide.

6.2.2. Effect of temperature

The metathesis of the oxazoline had not apparently been successful and even in the presence of co-catalysts, the reaction was rarely seen to happen. Consequently, it was decided to investigate the effect of using higher temperature.

The metathesis of 20ml of 1.08M oxazoline was carried out according to the method described in section 6.2 but this time the temperature was varied. The oxazoline was added to 0.70g of the catalyst in the reaction vessel without co-catalyst and the metathesis reaction was monitored for gas evolution. The reaction was carried out at temperatures of 35, 50 and 60°C but no signs of metathesis were observed in any of the experiments. In view of the absence of a reaction, it was decided to add a co-catalyst to assist in the initiation of the reaction at higher temperatures. 2ml of $SnBu_4$ was added to 0.70g of Re_2O_7/Al_2O_3 so that the Re:Sn ratio was 1:1. 5min later 20ml of the oxazoline solution was added and the reaction was monitored for gas evolution. The results are shown in table 6.3.

Table 6.3

The effect of temperature on the rate of metathesis of 4,4-dimethyl-2-(9-decenyl)-1,3-oxazoline

Temperature °C	Time/h	Volume of gas ml
35	2	6
50	1.5	8
60	6	8

Again, the greatest volume changes occurred during the first 3-4h and analysis of the solution was undertaken to identify the compounds present.

6.2.3. Analysis

Analysis of the final reaction solution proved to be very difficult because of the difficulty in separating the possible product, the di-oxazoline, from the reactants and other possible products. The FT-IR, ^{13}C and ^{1}H nmr spectra of the product solution were found to be very complex, which would seem to indicate that more than one product was present and no structurally sugnificant suggestions could be devised. The product was also analysed by mass spectrometry in order to determine the molecular weights of the compounds present in the solution and to try to determine the extent of the reaction by the amount of reactant remaining in the product solution.

Inspection of the mass spectrum shows that its composition is not much different from the spectrum of the starting reactant, Appendix 3. Fast atom bombardment data revealed that both the oxazoline and the hydroxyamide were present, the hydroxyamide being the major constituent.

6.3. Preparation of 4,4-dimethyl-2-(3-pentenyl)-1,3-oxazoline

The starting material for this synthesis is 4-pentenoyl chloride. However, it was not possible to purchase this reactant and consequently it had to be synthesised from 4-pentenoic acid. This is a very pungent substance and great care is needed when handling it and therefore the reactions were carried out in a well ventilated fume cupboard.

6.3.1. Synthesis of 4-pentenoyl chloride

$$CH_2=CHCH_2CH_2COOH \xrightarrow[\text{3 molar excess}]{SOCl_2} CH_2=CHCH_2CH_2COCl$$

4-pentenoic acid   4-pentenoyl chloride
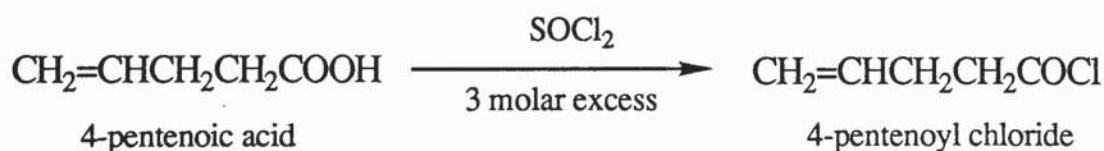
In a typical preparation, 10% excess of thionyl chloride, 50.16g (420mmol), was added dropwise to 25g (250mmol) of 4-pentenoic acid at a temperature below 10°C with stirring. After the addition of the thionyl chloride the solution was stirred at O°C for 1hr and then for a

further hour at 40°C. The solution was then fractionally distilled to remove the excess thionyl chloride and 4-pentenoyl chloride was obtained with a yield greater than 100%.

The high yield was due to the inefficient separation of the excess thionyl chloride from the acid chloride. It was estimated that their boiling points would be very close and this made separation by fractional distillation very difficult. Consequently, in subsequent preparations, a 1:1 molar ratio of 4-pentenoic acid to thionyl chloride was used and the reflux was performed for 2h instead of 1h, at 40°C.

In order to remove the HCl that was formed during the synthesis of 4-pentenoyl chloride, pyridine was incorporated into the synthesis. However, on addition of pyridine the reaction solution turned very deep red. When 2-amino-2-methyl-1-propanol was subsequently added to it, the solution went black and solidified. It appears that the carbonyl carbon atom of the acid chloride may have bonded to the pyridine to form a solid complex. Consequently, pyridine was not used in subsequent preparations.
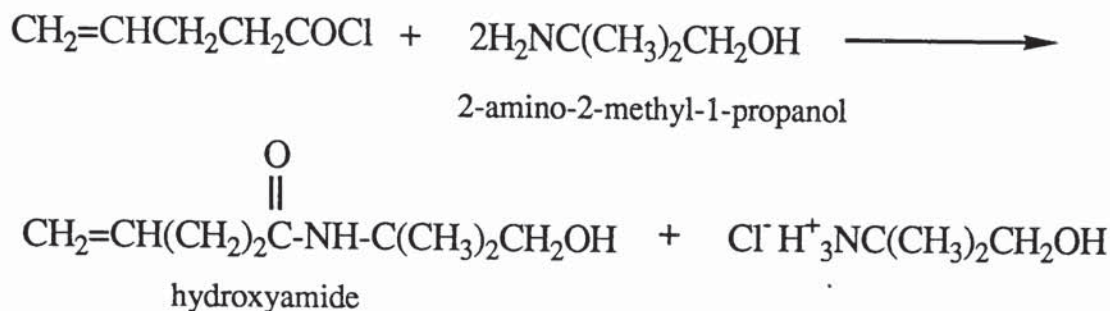
I.R absorptions υ 2984-2856 (sat C-H), 1796cm^{-1} (CO-Cl).

NMR data δ_C (CDCl$_3$) 28.47 (CH$_2$), 45.78 (CH$_2$), 116.42 (CH$_2$=), 134.73 (=CH), 172.63 (C=O).

NMR data δ_H (CDCl$_3$) 2.4 (CH$_2$), 2.9 (CH$_2$), 5.0 (CH$_2$=), 5.7 (=CH).

The IR spectrum of 4-pentenoyl chloride showed no peaks pertaining to 4-pentenoic acid and the nmr spectra showed that the 4-pentenoyl chloride had been produced in a very pure state, Appendix 4.

6.3.2. Preparation of the hydroxyamide of 4-pentenoyl chloride

$$CH_2=CHCH_2CH_2COCl \ + \ 2H_2NC(CH_3)_2CH_2OH \longrightarrow$$

2-amino-2-methyl-1-propanol

$$\overset{\displaystyle O}{\overset{\displaystyle \|}{CH_2=CH(CH_2)_2C}}\text{-NH-C}(CH_3)_2CH_2OH \ + \ Cl^-H^+_3NC(CH_3)_2CH_2OH$$

hydroxyamide

48.64g (410mmol) of 4-pentenoyl chloride dissolved in 50ml of dichloromethane, was added dropwise, very slowly and with continous stirring to 73.09g (820mmol) of 2-amino-2-methyl-1-propanol dissolved in 150ml of dichloromethane. During the course of this addition the temperature of the reaction was kept close to 0 ± 5^oC. When the addition of the acid chloride was complete, the reaction temperature was allowed to rise to 25^oC and the solution was stirred at this temperatue for 2h. The ammonium salt that formed as a precipitate was filtered off and the filtrate of the hydroxyamide, was washed several times with distilled water to remove traces of the ammonium salt. The remaining solution was then dried over anhydrous magnesium sulphate overnight. When the solution was dry the solvent was removed by distillation and 18.48g (110mmol) of hydroxyamide was obtained as a straw coloured viscous liquid.

I.R absorptions υ 3305 (O-H), 3079 (-CO-N), 2979-2928 (sat C-H), 1740cm^{-1} (N-H).

NMR data δ_C (CDCl$_3$) 23.5 (Me), 28-33 (CH$_2$), 52.5 (CMe$_2$), 64.9 (CH$_2$O-), 114 (CH$_2$=), 136.3 (CH=), 172 (C=O).

NMR data δ_H (CDCl$_3$) 1.1 (Me), 2.1 (CH$_2$), 3.2 (CH$_2$-O) 4.8 (CH$_2$=), 5.0 (N-H), 5.5 (=CH), 6.4 (OH).

FAB data m/e 172 (100% F), 154 (19% F).

The infra-red spectrum of the hydroxyamide showed that the acid chloride peak, 1796cm^{-1}, was no longer present and the peak at 1740cm^{-1} pertained to the amide group. The nmr spectra were very complex which indicated that the product contained impurities, which have not been identified as yet, but resonances pertaining to the hydroxyamide were present, Appendix 4.

The CI mass spectrum of the hydroxyamide in Appendix 4 shows that the M+1 ion at 172 corresponds to the molecular ion of the hydroxyamide (Mr = 171). The FAB data also shows that the presence of a species at mass 153, which is the relative molecular mass of the oxazoline formed by the loss of a water molecule, M-18, during the fragmentation of the amide.

6.3.3. Synthesis of 4,4-dimethyl-2-(3-pentenyl)-1,3-oxazoline

$$CH_2=CH(CH_2)_2\overset{\overset{\displaystyle O}{\|}}{C}-NH-C(CH_3)_2CH_2OH \quad \xrightarrow[\text{2) NaOH}]{\text{1) SOCl}_2}$$

oxazoline
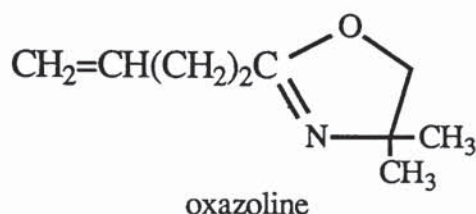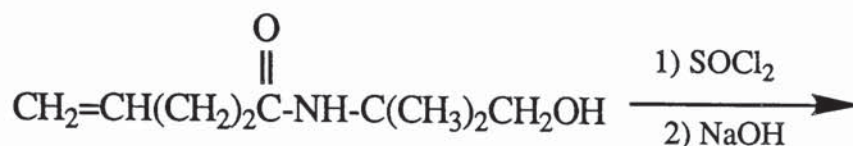
34.13g (288mmol) of thionyl chloride was added dropwise, with stirring, to 16.48g of hydroxyamide at ± 5ºC. After complete addition of the thionyl chloride, the solution was stirred at 0ºC for 3h and then 50ml of 20% sodium hydroxide was added to complete the cyclization to form the oxazoline and to hydrolyse any unreacted thionyl chloride. The solution was stirred until there were no more signs of HCl production. The resulting solution was then extracted several times using ether and the ether layer was dried over anhydrous magnesium sulphate. After the ether layer had been filtered through fluted filter paper, the ether was removed by distillation and 9.3g of the product was obtained.

I.R absorptions υ 3305 (O-H), 3079 (-CO-N), 2979-2927 (sat C-H), 1739 (N-H), 1643 (-C=N-), 1269cm^{-1} (C-O-C).

NMR data δ_C (CDCl$_3$) 24 (Me), 26-29 (CH$_2$), 52.4 (CMe$_2$), 65.1 (CH$_2$O-), 114.7 (CH$_2$=), 135.9 (CH=), 172.5 (C=O).

NMR data δ_H (CDCl$_3$) 1.1 (Me), 2.1 (CH$_2$), 3.9 (CH$_2$-O) 4.8 (CH$_2$=), 5.5 (=CH), 6.5 (OH).

FAB data m/e 172 (100% F), 154 (33.4% F).

The IR spectrum of the oxazoline showed the presence of the amide group at 1739cm^{-1} as well as the peaks at 1643cm^{-1} and 1269cm^{-1} which corresponded to the formation of an imine and ether group respectively. The nmr spectrum were very similar to those obtained for the hydroxyamide and resonances pertaining to the oxazoline were not identified. The mass spectrum of the oxazoline shows the fragmentation pattern of the hydroxyamide but there is no evidence that the oxazoline was produced. All the spectra can be found in Appendix 4.

6.4. Metathesis of 4,4-dimethyl-2-(3-pentenyl)-1,3-oxazoline

A 0.5M solution of the oxazoline was made up in chlorobenzene and 10ml was placed in a reaction flask under an argon atmosphere. The flask was attached to joint C of the reaction vessel in fig 2.4 and the solution was added to 0.70g of Re_2O_7/γ-Al_2O_3 catalyst under vacuum. The reaction was followed by monitoring the gas evolved at 35°C. No changes in the height of the manometer were detected and analysis of the solution by tlc, using methanol as the solvent, showed that the retention values of the materials before and after the reaction were 0.82 and 0.86 respectively. Consequently the experiment was repeated using the co-catalysts $SnMe_4$ and $SnBu_4$.

6.4.1. The effect of co-catalyst on the metathesis of 4,4-dimethyl -2-(3-pentenyl)-1,3-oxazoline

2ml of the evacuated co-catalyst in chlorobenzene was added to 0.70g of Re_2O_7/γ-Al_2O_3 catalyst in the evacuated reaction vessel. 5 min later 10ml of 0.5M oxazoline were added and the reaction was followed as before at 35°C. The effect of co-catalyst concentration on the rate of metathesis of the oxazoline is shown in table 6.4.

Table 6.4

The effect of co-catalyst concentration on the rate of metathesis of 4,4-dimethyl-2-(3-pentenyl)-1,3-oxazoline

Re:SnMe$_4$	Comments	Re:SnBu$_4$	Commemts
1:1	No reaction observed	1:1	No reaction observed
1:7	No reaction observed	1:4	No reaction observed
-	-	1:20	No reaction observed

Gas evolution was not detected so it appeared that the metathesis reaction had not occurred. However, other reactions might have occurred and therefore, the composition of the product was analysed.

6.4.2. Effect of temperature

Unlike 4,4,-dimethyl-2-(9-decenyl)-1-,3-oxazoline, the co-catalysts do not appear to have any effect on the metathesis of 4,4,-dimethyl-2-(3-pentenyl)-1,3-oxazoline and this led to an investigation into the effect of using higher temperatures.

The metathesis of 0.5M oxazoline was carried out according to the method described in section 6.3. 2ml of SnBu$_4$ was added to 0.70g of Re$_2$O$_7$/Al$_2$O$_3$ so that the Re:Sn ratio was 1:1. 5min later 10ml of the oxazoline solution was added and the reaction was monitored for gas evolution. The results are shown in table 6.5.

Table 6.5

The effect of temperature on the rate of metathesis of 4,4-dimethyl-2-(3-pentenyl)-1,3-oxazoline using a Re:Sn ratio of 1:1

Temperature °C	Time/h	% Conversion
35	-	no reaction
60	-	no reaction
70	-	no reaction

A Re:Sn ratio of 1:1 yielded no success in the metathesis of the oxazoline and so a higher Re:Sn ratio of 1:20 was used to see if this would help to initiate the reaction, table 6.6.

Table 6.6

The effect of temperature on the rate of metathesis of 4,4-dimethyl-2-(3-pentenyl)-1,3-oxazoline using a Re:Sn ratio of 1:20

Temperature °C	Time/h	Volume of gas ml
50	3	23
70	6	18
80	2	40

The greatest volume changes occurred during the first 3-4h of the reaction and the solutions were analysed to indentify the type of reactions which were taking place.

6.4.3.   Analysis

Analysis of the product solution was difficult because of the difficulty in separating the possible product from the reactants. The FT-IR, ^{13}C and ^{1}H nmr spectra of the product solution were

very complex and so the product was analysed by mass spectrometry in order to determine the molecular weight of the compounds present in the solution. .

Inspection of the mass spectrum showed that there was no difference between it and the spectrum of the starting material thus indicating that no reaction had occurred, Appendix 4.
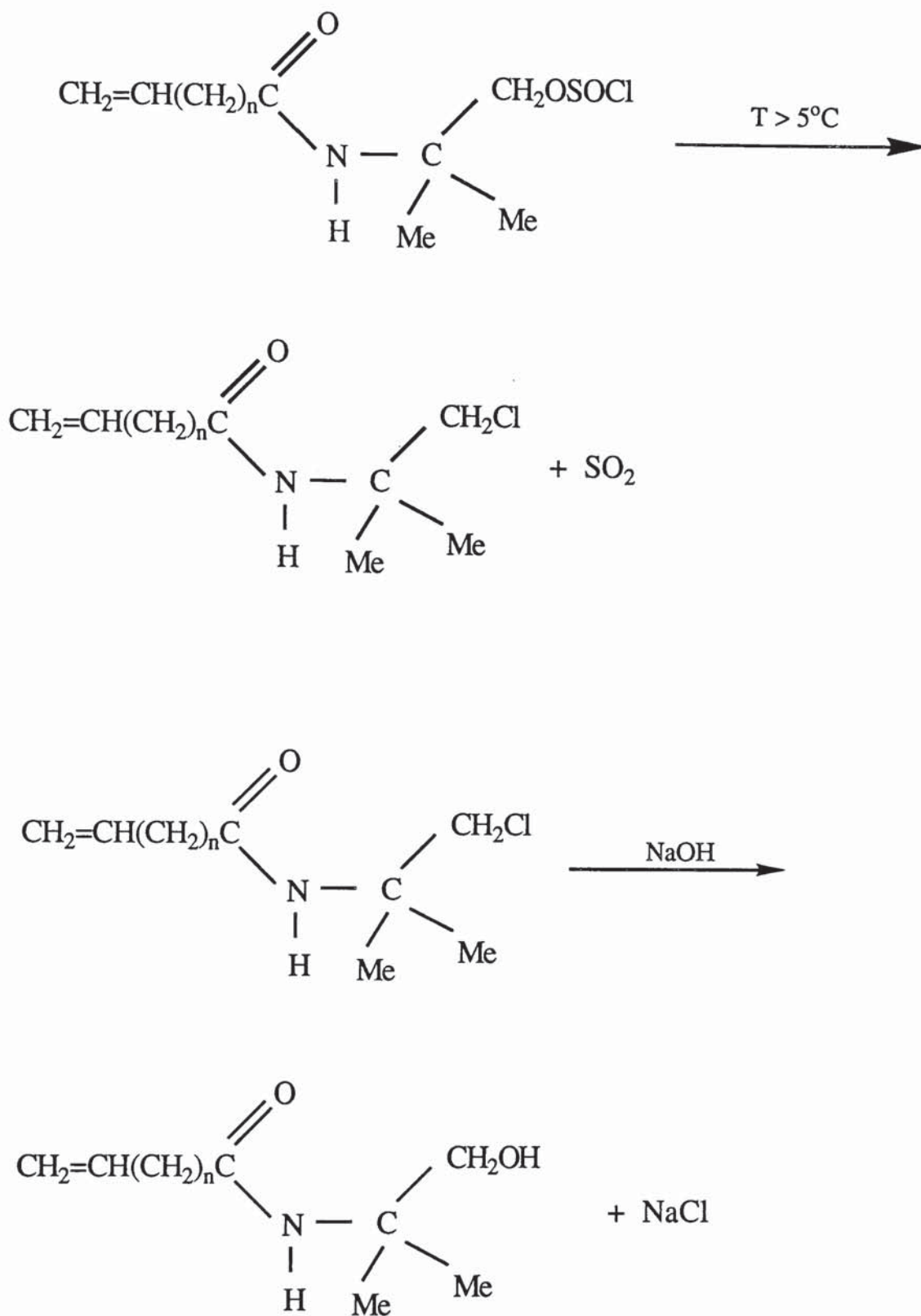
6.5. Discussion

4,4-Dimethyl-2-(9-decenyl)-1,3-oxazoline and 4,4-dimethyl-2-(3-pentenyl)-1,3-oxazoline would be expected to undergo the metathesis reaction in the presence of $Re_2O_7/\gamma\text{-}Al_2O_3$ as the catalyst but this was found not to be the case in the above work. The factors responsible for impeding the oxazolines from undergoing the metathesis reaction must therefore be analysed. The most important factor appears to be the impure nature of the compounds formed which can be attributed mostly to the low conversion of the intermediate hydroxyamides to the oxazolines. The method used to convert the hydroxyamide into the oxazoline involved the initial conversion of the primary alcohol group, $-CH_2OH$, into a chlorosulphite, $-CH_2OSOCl$, using thionyl chloride.
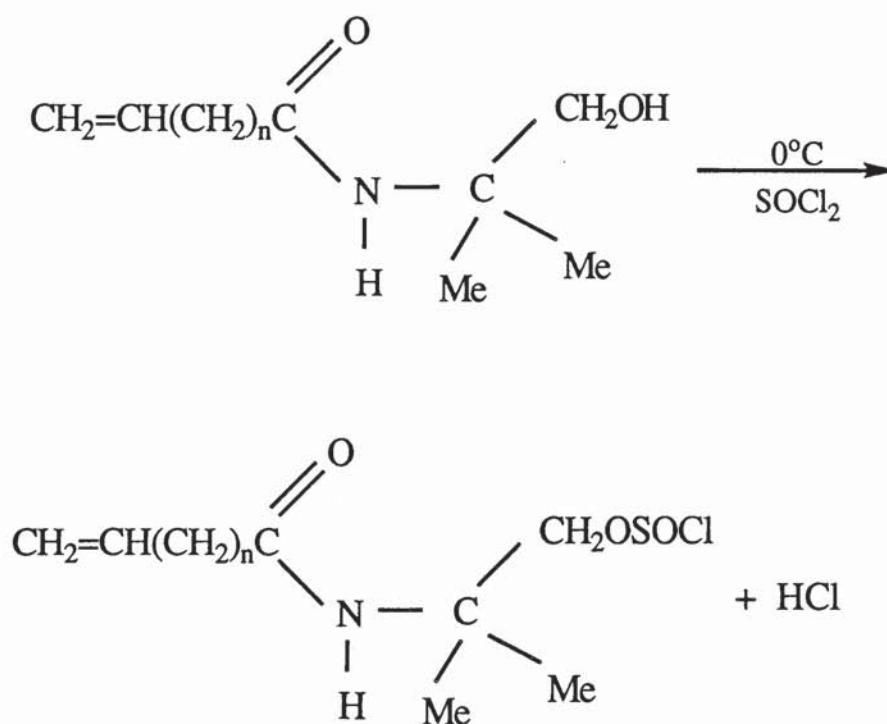
This was carried out at 0°C because the chlorosulphite group decomposes at higher temperatures. If the reaction solution is then treated with aqueous NaOH, the oxazoline is formed by attack of the carbonyl oxygen on the primary carbocation.
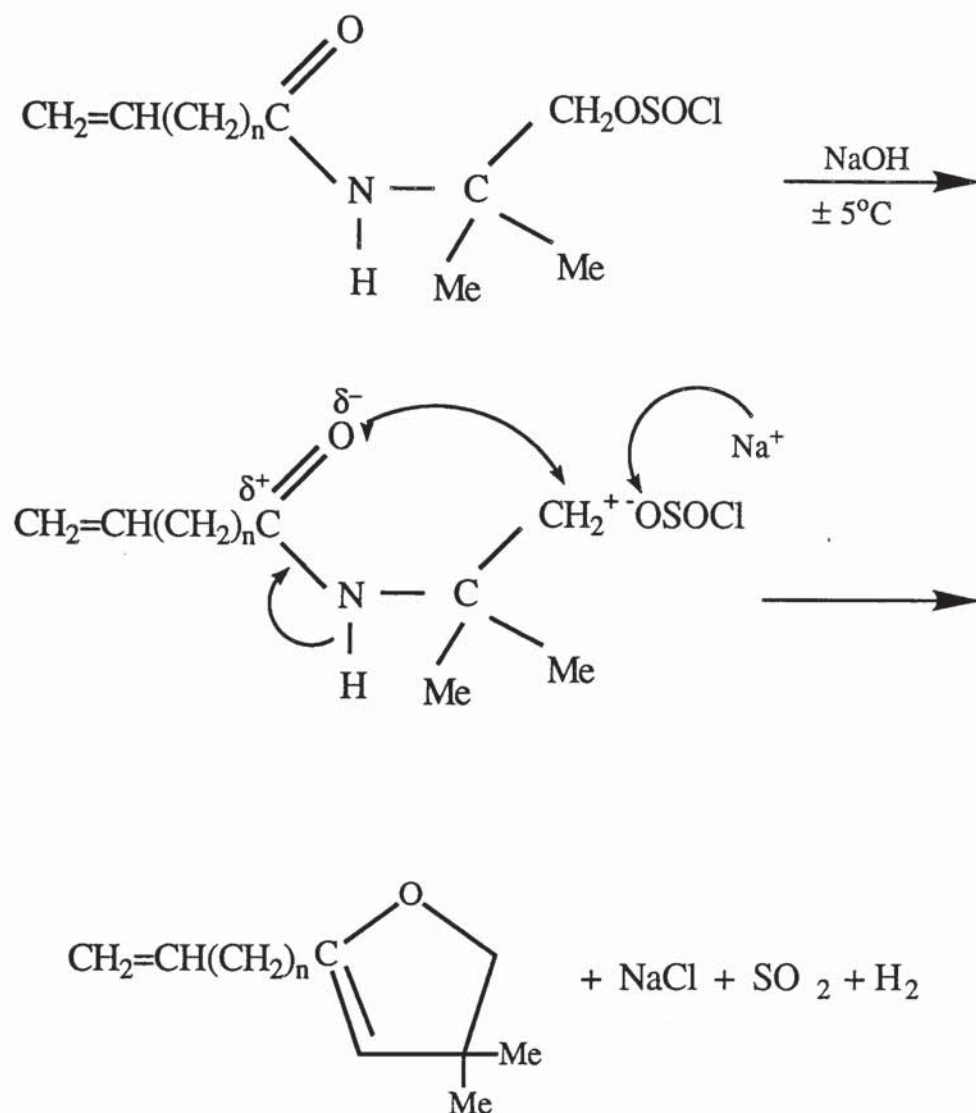

If, however, the temperature of the solution becomes too warm on addition of thionyl chloride, the chlorosulphite group decomposes to form the alkyl halide. When aqueous NaOH solution is then added, S_N2 nucleophilic substitution occurs and the hydroxyamide intermediate is reformed.

$CH_2=CH(CH_2)_nC(=O)$—NH—$C(CH_2OSOCl)(Me)(Me)$ $\xrightarrow{T > 5^\circ C}$

$CH_2=CH(CH_2)_nC(=O)$—NH—$C(CH_2Cl)(Me)(Me)$ $+ SO_2$

$CH_2=CH(CH_2)_nC(=O)$—NH—$C(CH_2Cl)(Me)(Me)$ $\xrightarrow{NaOH}$

$CH_2=CH(CH_2)_nC(=O)$—NH—$C(CH_2OH)(Me)(Me)$ $+ NaCl$

Obtaining 4,4-dimethyl-2-(9-decenyl)-1,3-oxazoline as a clear viscous liquid was a problem. White solids were suspended throughout the final product after it had been washed and dried. Consequently further washings followed by filtration were carried out. The white solids could

have been NaCl. The mass spectrographs showed that the final synthetic product contained 5% of oxazoline with the majority of the sample being the hydroxyamide.

The product obtained in the attempted synthesis of 4,4-dimethyl-2-(3-pentenyl)-1,3-oxazoline was a clear viscous liquid but the mass spectrographs and the FAB data showed no peak pertaining to the oxazoline. The peak of mass number 153, which is the molecular weight of the oxazoline, arises from the fragmentation of the hydroxyamide. Closer inspection of the FAB data in Appendix 4 of the hydroxyamide shows a peak of molecular weight 254. This is equivalent to the structure

$$CH_2=CH(CH_2)_2C \overset{\displaystyle O}{\diagup} \quad N-C \overset{\displaystyle CH_2OSOCl}{\diagup} \quad H \quad Me \quad Me$$
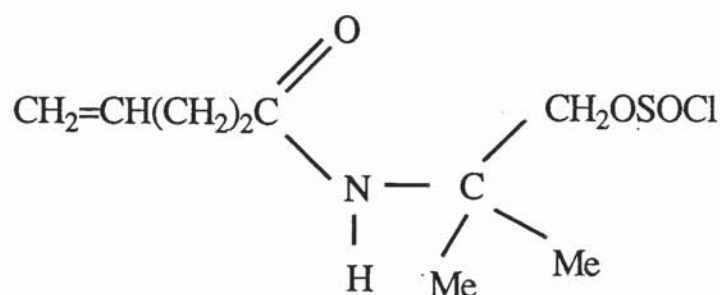
and it is also present in the sample of the oxazoline. This helps to corroborate the role of the thionyl chloride in the synthetic procedure and is a help in assessing how to improve the synthetic procedure to obtain the oxazoline.

Hydroxyamides would be expected to undergo the metathesis reaction with difficulty in the presence of $Re_2O_7/\gamma-Al_2O_3$ because of the two lone pair of electrons on the oxygen of the hydroxy group. These compete with the carbon-carbon double bond for complexation to the electrophilic metathesis active centres on the surface of the catalyst. The lone pair of electrons have a stronger nucleophilicity than the carbon carbon double bond and will therefore bind strongly and preferentially to the active site. This then ensures that no metathesis reaction will occur and therefore, the volume changes observed in the gas burette during the metathesis experiments were not due to the evolution of ethene from either the hydroxyamides or the oxazolines. Most of the volume changes occurred with the oxazoline of 4-pentenoyl chloride and was probably due to the decomposition of the chlorosulphite group to yield SO_2, a pungent gas. The hydroxyamide did have a very potent smell and this could have been due to the

chlorosulphite group. However, the mass spectrograph of the hydroxyamide of 10-undecenoyl chloride, which had a more pleasant smell, showed no peaks which would be consistent with a chlorosulphite group and this shows that the small changes in volume on the gas burette were due to another phenomenon which has yet to be deduced.

CHAPTER 7: CONCLUSIONS AND FURTHER WORK

7.1. The kinetics of the metathesis of 1-hexene over $Re_2O_7/\gamma\text{-}Al_2O_3$

The metathesis of 1-hexene over $Re_2O_7/\gamma\text{-}Al_2O_3$ was found to be first order in the weight of the catalyst and second order in the concentration of 1-hexene. It was possible to generate a kinetic scheme in which the experimental data was consistent with a chain mechanism such as that proposed by Herisson and Chauvin. This involved the application of the Langmuir-Hinshelwood theory to explain the kinetics of this particular system but combined with a realization that the surface active centre was itself formed in a kinetic chain process. This explained the second order nature of the reaction with respect to 1-hexene and did not involve, as proposed by other workers, the diffusion of species across the surface of the catalyst. The metallacyclobutane intermediates formed during the propagation stages of the reaction have to be fairly unstable to allow exchange reactions to occur with the incoming olefin on the active sites. The intermediates decompose to yield a product olefin and a propagating metallocarbene. In order for the exchange reactions of the reactant and product olefin to occur so that the chain mechanism is not disturbed, the product olefin must desorb from the active centre at a much faster rate than the rate at which the reactant olefin absorbs explaining the low efficiency of such catalyst.

It is possible that termination reactions are responsible for the incomplete conversion of 1-hexene to ethene and 5-decene. It is proposed that the termination step of the metathesis of 1-hexene is first order in the propagating species and it occurs by the decomposition of the metallacyclobutane intermediate to produce a cyclopropane derivative and an inactivated centre. This view is consistent with other workers who observed the presence of cyclopropane derivatives in their product solution and consequently a more detailed analysis of the product solutions from the metathesis of 1-hexene over $Re_2O_7/\gamma\text{-}Al_2O_3$ should be undertaken in the future. Locating and identifying cyclopropane derivatives would help in the complete elucidation of the kinetics of the reaction between 1-hexene and the catalyst. Indeed identification of the cyclopropane derivative could shed some light on its mode of formation

and provide information on whether it is involved in deactivating the active centres of metathesis.

The optimum temperature for the metathesis of 1-hexene over Re_2O_7/γ-Al_2O_3 was found to be 45°C. Above this temperature the rate of metathesis was found to decrease rapidly and this was attributed to the fact that the intermediates of the reaction became more unstable at higher temperatures. Whether their formation became more difficult or they decomposed more rapidly at these higher temperatures is not known as yet. If the rate of change in the rate of metathesis is directly proportional to the rate of cyclopropanation, it would appear that at higher temperatures the number of active centres for the metathesis of 1-hexene decreases because the cyclopropanation reaction becomes more dominant at higher temperatures. Experiments to confirm this postulate could be undertaken and the dependence of the rate of cyclopropanation on temperature investigated to see if any correlation with the present experimental data exists.

When 1-hexene undergoes metathesis using promoted Re_2O_7/γ-Al_2O_3 (the co-cotalyst used were $SnMe_4$ and $SnBu_4$) the reaction becomes more selective in the formation of the primary products ie, ethene and 5-decene. Other minor products are still present but their concentrations are much lower than when unpromoted catalysts are used. It is clear that the co-catalysts allow Re_2O_7/γ-Al_2O_3 to become selective in the metathesis of 1-hexene but how this occurs is not known. Another important feature of promoted catalysts is that it is not possible to regenerate their activity towards metathesis once they have been used, unlike unpromoted catalysts which can be readily reactivated when fresh solutions of 1-hexene are added. If cyclopropane derivatives are formed during metathesis, then it is possible that they react with the active centre to produce a more stable intermediate which can be decomposed to regenerate the active centre on evacuation of the catalyst. The termination reaction using promoted catalyst appears to occur by another mechanism which involves the formation of stable intermediates which do not undergo decomposition to regenerate the active centres necessary for metathesis. The role of the co-catalysts needs to be investigated in much greater detail, particularly their role in the initiation of the metathesis of 1-hexene on Re_2O_7/γ-Al_2O_3. Further investigations into

in the initiation of the metathesis of 1-hexene on $Re_2O_7/\gamma\text{-}Al_2O_3$. Further investigations into why the metathesis activity of promoted catalyst is very low could shed some light on how the co-catalysts affect the morphology of the surface of the catalyst, particularly the active centres.

7.2. The preparation and reactions of oxazolines

Preparing 4,4-dimethyl-2-(9-decenyl)-1,3-oxazoline and 4,4-dimethyl-2-(3-pentenyl)-1,3-oxazoline from their hydroxyamide precursors was very difficult. The difficulty lay in inducing ring closure in the hydroxyamide using $SOCl_2$ so that the ether linkage could be formed. Analysis of the products showed that 4,4-dimethyl-2-(3-pentenyl)-1,3-oxazoline was not obtained at all and that only 5% of 4,4-dimethyl-2-(9-decenyl)-1,3-oxazoline was obtained. The procedure used to prepare the oxazolines was that used by Meyers to prepare phenyl oxazolines. It appears that the preparation of alkyl oxzolines is much more difficult in the same way that alkyl diazonium compounds are more difficult to prepare than the phenyl derivatives. Improving the method of synthesis of the oxazoline so that it is obtained in a higher yield and greater purity is essential before investigations into its susceptibility to the metathesis reaction can be undertaken.

REFERENCES

1. Banks, R.L. and Bailey, G.C., Olefin Disproportionation, Ind. Eng. Chem. Prod. Res. Dev., 3, 170-173 (1964).

2. Dragutan, A.T. and Balaban, A.T., Dimonie, M., Olefin Metathesis and Ring Opening Polymerization of Cyclo-olefins, Wiley, New York (1985).

3. Schneider, V. and Frolich P.K., Mechanism of Formation of Aromatics from Lower Paraffins, Ind. Eng. Chem., 23, 1405- 1410 (1931).

4. McMurry, J., Organic Chemistry, Brookes and Cole, Calif. (1988).

5. Bradshaw, C.P.C., Howman, E.J. and Turner, L., Olefin Dismutation: Reactions of Olefins on Cobalt Oxide-Molybdenum Oxide-Alumina, J. Catal, 7, 269- (1967).

6. Ivin, K.J., Olefin Metathesis, Academic press, London (1983).

7. Natta, G., Dall'Asta., G., Mazzanti, G. and Motroni, G., Stereospecific Polymerization of Cyclobutene, Makromol. Chem., 69, 163-179 (1963).

8. Natta, G., Dall'Asta., Bassi, I.W. and Carella, G., Stereospecific Ring Cleavage Homopolymerization of Cycloolefins and Structural Examination of the Resulting Homologous Series of Linear Crystalline *trans* Polyalkenamers, Makromol. Chem., 91, 87-106 (1966).

9. Calderon, N., Chen, H.Y. and Scott, K.W., Olefin Metathesis - A Novel reaction For Skeletal Transformations of Unsaturated Hydrocarbons, Tet. Lett., 34, 3327-3329 (1967).

10. van Dam, P.B., Mrs Mittelmeijer, M.C. and Boelhouwer, C., Metathesis of Unsaturated Fatty Acid Esters by a Homogeneous Tungsten Hexachloride-tetramethyltin Catalyst, J.C.S. Chem. Comm., 1221-1222 (1972).

11. Verkuijlen, E., Kapteijn, F., Mol, J.C. and Boelhouwer, C., Heterogeneous Metathesis of Unsaturated Fatty Acid Esters, J.C.S. Chem. Comm., 198 (1977).

12. Herisson, J.L. and Chauvin, Y., Makromol. Chem, 141, 161- (1970).

13. Casey, C.P. and Burkhardt, T.J., (Diphenylcarbene)pentacarbonyltungsten, J. Am. Chem. Soc., 95 , 5833-5834 (1973).

14. Howard, T.R., Lee, J.B. and Grubbs, R.H., Titanium Metallacarbene-Metallocyclobutane Reactions: Stepwise Metathesis, J. Am. Chem. Soc., 102, 6876-6878 (1980).

15. Novak, B.M. and Grubbs, R.H., Catalytic Organometallic Chemistry in Water: The Aqueous Ring-Opening Metathesis Polymerization of 7-Oxanorbornene Derivatives, J. Am. Chem. Soc., 110, 7542-7543 (1988).

16. Parshall, G.W., Homogeneous Catalysis: the Applications and Chemistry of Catalysis by Soluble Transition Metal Complexes, Wiley-Interscience (1980).

17. Calderon, N., Ofstead, E.A., Ward, J.P., Judy, W.A. and Scott, K.W., Olefin Metathesis. I. Acyclic Vinylenic Hydrocarbons, J. Am. Chem. Soc., 90, 4133-4140 (1968).

18. Wang, J.L. and Menapace, H.R., Metathesis of 2-Pentene by a Binary Catalyst System of Tungsten Hexachloride and n-ButyllithiumJ. Org. Chem., 33, 3794-3787 (1968).

19. Greenlee, W.S. and Farona, M.F., Olefin Metathesis by Rhenium Carbonyl Halide-Alkylaluminium Halide Catalysts. Direct Evidence for a Coordinated Carbene Initiated Process, Inorg. Chem., 15, 2129-2143 (1976).

20. Muetterties, E.L., Mechanism for the Olefin Metathesis Reaction, Inorg. Chem., 14, 951-953 (1975).

21. Shahada, L.A. and Feast, W.J., Metathesis Ring Opening Polymerization of 5,6-bis(chloromethyl)bicyclo[2.2.1]hepta-2-ene, Eur. Polym. J., 26, 25-27 (1990).

22. Basset, J.M., Taarit, Y.B., Coudurier, G. and Praliaud, H., The Effects of Oxygen on Lewis Acidity of Aluminium Alkyl Compounds and its Promoting Effect on Cocatalysts in Metathesis, J. Organomet. Chem., 74, 167-173 (1974).

23. Mocella, M.T., Busch, M.A. and Muetterties, E.L., Olefin Metathesis Reaction. III. Mechanistic Considerations, J. Am. Chem. Soc., 98, 1283-1285 (1976).

24. Calderon, N and Chen, N.Y., Brit. 1, 125, 529, 28.08.68

25. Scott, K.W., Calderon, N., Ofstead, E.A., Judy, W.A. and Ward, J.P., Ring Opening Polymerization of Cycloolefins. Some mechanistic aspects, Chem. Abs. 21961r (1970).

26. Motz, V.W., and Farona, M.F., Olefin Metathesis by Pyridinepentacarbonyl-molybdenum and Related Catalysts: Reactions and Mechanisms, Inorg. Chem., 16, 2545-2549 (1977).

27. McGinnis, J., Katz, T.J. and Hurwitz, S., Selectivity in the Olefin Metathesis of Unsymmetrically Substituted Ethylenes, J. Am. Chem. Soc., 98, 605-606 (1976).

28. Katz, T.J., Lee, S.J. and Acton, N., Stereospecific Polymerizations of Cycloalkenes Induced by a Metal Carbene, Tet. Letts, 4247-4250 (1976).

29. Tebbe, F.N., Parshall, G.W.and Reddy, G.S., Olefin Homolgation with Titanium Methylene Compounds, J. Am. Chem. Soc., 100, 3611-3613 (1978).

30. Lee, J.B., Kinetics and Stereochemistry of the Titanacyclobutane- Titanamethylene. Interconversion. Investigation of a Degenerate Olefin Metathesis Reaction, J. Am. Chem. Soc., 104, 7491-7496 (1982).

31. Gilliom, L.R. and Grubbs, R.H., Titancyclobutanes Derived from Strained Cyclic Olefins: The Living Polymerization of Norbornene, J. Am. Chem. Soc., 108, 733-742 (1986).

32. U.K. Patent 1 414 488

33. Heckelsberg, L.F., Banks, R.L. and Bailey, G.C., Olefin Disproportionation Catalysts, Ind. Eng. Chem., Prod. Res. Deveolop., 8, 259-267 (1969).

34. Heckelsberg, L.F., Banks, R.C. and Bailey, G.C., A Tungsten Oxide on Silica Catalyst for Phillips Triolefin Process, 7, 29-31 (1968).

35. Danilyuk, A.F., Kuznetsov, V.L., Shmachkov, V.A. and Kochubey, D.I., J. Mol. Catal., 46, 209 (1988).

36. Casey, C.P., Tuinstra, H.E., and Saeman, M.C., Reactions of $(CO)_5WC(Tol)_2$ with Alkenes. A Model for Structural Selectivity in the Olefin Metathesis Reaction, J. Am. Chem. Soc., 98, 608-609 (1976).

37. Heckelsberg, L.F., Banks, R.L. and Bailey, G.C., Diene Disproportionation Reactions J. Catalysis, 13, 99-100 (1969).

38. Zuech, E.A., Hughes, W.B., Kubicek, D.H. and Kittleman, E.T., Homogeneous Catalysts for Olefin Disproportionations from Nitrosyl Molybdenum and Tungsten Compounds, J. Am. Chem. Soc., 92, 528-531 (1970).

39. Mol, J.C. and Woerlee, E.F.G., J. Chem. Soc., Chem. Commun., 330-331 (1979).

40. Bosma, R.H.A., Kouwenhoven, A.P. and Mol, J.C., Homogeneous Metathesis of Unsaturated Nitriles, J. Chem. Soc., Chem. Commun., 1081-1082 (1981).

41. Nakamura, R. and Echigoya, E., Metathesis of Oleyl Chloride, Chem. Lett., 1227-1230 (1977).

42. Warwel, V.S., Doring, S. and Biermanns, F.J., The Influence of Protecting groups in the Metathesis of Oleochemicals, Fett Wissen. Tech., 89, 335-338 (1987).

43. Pennella, R.L., Banks, R.L. and Bailey, G.C., Disproportionation of Alkynes, J. Chem. Soc., Chem. Commun., 1548 (1968).

44. Moulijn, J.A., Reitsma, H.J. and Boelhouwer, C., Disproportionation and Cyclotrimerization of Alkynes over Supported Tungsten Oxide, J. Catal., 25, 434-436 (1972).

45. Farona, M.F., Lofgren, P.A. and Woon, P.S., Polymerization of Phenylacetylene Catalysed by Arene-Group VIB Tricarbonyls, J. Chem. Soc., Chem. Commun., 240-247 (1974).

46. Scott, K.W., Calderon, N., Ofstead, E.A., Judy, W.A. and Ward, J.P., Ring Opening Polymerization of Cycloolefins-Some Mechanistic Aspects, Adv. Chem. Ser., 91, 399-418 (1969).

47. Gunther, P., Haas, F., Marwede, G., Nutzel, K., Oberkirc, W., Pampus, G., Schon, N. and Witte, J., Ring Opening Polymerization of Cyclopentene, (Catalysts Polymerization; Properties of Products) Angew. Makromol. Chem., 16/17, 27- (1971).

48. Ger. Offen. 2 058 198.

49. Truett, W.L., Johnson, D.R., Robinson, I. M., and Montague, B. A., Polynorbornene by Coordination Polymerization, J. Am. Chem. Soc., 82, 2337-2340 (1960).

50. Calderon, N., The Olefin Metathesis Reaction, Acc. Chem. Res., 5, 127-132 (1972).

51. Grubbs, R.H., The Olefin Metathesis Reaction, Prog. Inorg., 24, 1-50 (1978).

52. Mol, J.C., Carbon-14 Studies on the Mechanism of Disproportionation of Propene, J. Chem. Soc., Chem. Commun., 633 (1968).

53. Anderson, J.S., Complex Compounds of the Olefins with Metallic Salts. Part II. Homologues of Zeise's Salt, 139, 1042-1050 (1936).

54. Lewandos, G.S. and Pettit, R., On the Mechanism of the Metal-Catalysed Disproportionation of Olefins, J. Am. Chem. Soc., 93, 7087- 7088(1971).

55. Lewandos, G.S. and Pettit, A Proposed Mechanism for the Metal-Catalysed Disproportionation of Olefins R., Tet. Lett., 789-793 (1971).

56. Grubbs, R.H. and Brunck, T.K., A Possible Intermediate in the Tungsten-Catalysed Olefin Metathesis Reaction, J. Am. Chem. Soc., 94, 2538-2540 (1972).

57. Ofstead, E.A. and Calderon, N., Equilibrium Ring Opening Polymerization of Mono- and Multi-Cyclic Unsaturated Monomers, Makromol. Chem., 154, 21-34 (1972).

58. Reif, L. and Hocker, H., Oligomer Distribution in the Polymerization of 2-Norbornene via Metathesis, Makromol. Chem., Rapid Commun., 2, 183-185 (1981).

59. Katz, T.J. and McGinnis, J., Metathesis of Cyclic and Acyclic Olefins, J. Am. Chem. Soc., 99, 1903-1912 (1972).

60. Fischer, E.O. and Maasbol, A., On the Existence of a Tungsten Carbonyl Carbene Complex, Angew. Chem. Internat. Edit., 3, 580-581 (1964).

61. Schrock, R.R., An 'Alkylcarbene' complex of Tantalum by Intramolecular α-Hydrogen Abstraction, J. Am. Chem. Soc., 96, 6796- 6797 (1974).

62. Casey, C.P. and Burkhardt, T.J., Reaction of (Diphenylcarbene)pentacarbonyltungsten (O) with Alkenes. Role of Metal-Carbene Complexes in Cyclopropanation and Olefin Metathesis Reaction, J. Am. Chem. Soc., 96, 9808-9809 (1974).

63. Wengrovius, J.H, Schrock, R.R., Churchhill, M.R., Missert, J.R. and Youngs, W.J., Tungsten-Oxo Alkylidene Complexes as Olefin Metathesis Catalysts and the Crystal Structure of W(O)(CHCMe3)(PEt3)Cl2, J. Am. Chem. Soc., 102, 4515-4516 (1980).

64. Kress, J., Wesolek, M. and Osborn, J.A., Tungsten (VI) Carbenes for the Metathesis of Olefins. Direct Observation and Identification of the Chain Carrying Carbene Complexes in a Highly Active Catalyst System, J. Chem. Soc., Chem. Commun., 514-516 (1982).

65. Schrock, R.R., DePue, R.T., Feldman, J., Schaverien, C.J., Dewan, J.C. and Liu, A.H., Preparation and Reactivity of Several Alkylidene Complexes of the Type W(CHR')(N-2,6-C6H3-i-Pr2)(OR)2 and Related Tungstacyclobutane Complexes. Controlling Metathesis Activity through the Choice of Alkoxide Ligand, J. Am. Chem. Soc., 110, 1423-1435 (1988).

66. Lee, J.B., Gajda, G.J., Schaefer, W.P., Howard, T.R., Ikariya, T., Straus, D.A. and Grubbs, R.H., Structures of Titanocyclobutanes, J. Am. Chem. Soc., 103, 7358-7361(19881).

67. Bilhou, J.L., Basset, J.M., Mutin, R. and Graydon,W.F., A Stereochemical Study of Metathesis and Cis -Trans Isomerization of 2-Pentenes, J. Am. Chem. Soc., 99, 4083-4090 (1977).

68. Cowie, J.M.G., Polymers: Chemistry and Physics of Modern Materials, International Textbook Company LTD, Bucks (1973).

69. Green, R.M.E., Hamilton, J.G., Ivin, K.J. and Rooney, J.J., *Cis/Trans* Reactivity Ratios in the Ring Opening Polymerization of Bicyclo[2.2.1] hept-2-ene; The Nature of the Propagating Species in Olefin Metathesis, Makromol. Chem., 187, 619-632 (1986).

70. Ivin, K.J., Lapiensis, G., Rooney, J.J., Formation of Ring Opening Syndiotactic and Atactic Polynorbornenes using Metathesis Catalysts; Evidence for Retention of Configuration and Loss of Configuration of the Intermediate Metallocarbene, J. Chem. Soc., Chem. Commun., 1068-1070 (1980).

71. Amass, A.J., Metathesis Polymerization Chemistry, 109-134, Comprehensive Polymer Science, Pergamon Press, 4, (6) (1988).

72. Edreva-dardjieva, R.M. and Andreev, A.A., The Double Bond Migration Activity of Supported Rhenium Catalysts for Olefin Metathesis, J. Mol. Catal., 46, 201-207 (1988).

73. Hughes, W.B., Kinetics and Mechanism of the Homogeneous Olefin Disproportionation Reaction, J. Am. Chem. Soc., 92, 532-537 (1970).

74. Amass, A.J. and Tuck, C.N., The Kinetics of Polymerization of Cyclopentene by $WCl_6/AliBu_3$, Eur. Polym. J., 14, 817-822 (1978).

75. Amass, A.J. and Zurimendi, J.A., Kinetics of Metathesis Polymerization, J. Mol. Catal., 8, 243-248 (1980).

76. Begley, J.W. and Wilson, R.T., The Kinetics of Propylene Disproportionation, J. Catal., 9, 375-395 (1967).

77. Kapteijn, F., Bredt, H.L.G., Homberg, E. and Mol, J.C., Kinetics of the Metathesis of Propene Over Re_2O_7/Al_2O_3, Ind. Eng. Chem., Prod. Res. Develop., 20, 457-466 (1981).

78. Lewis, M.J. and Wills, G.B., Initial Rates of Propylene Disproportionation, J. Catal., 15, 140-143 (1969).

79. Davenport, W.H., Kollonitsch, V. and Kline, C.H., Advances in Rhenium Catalysts, Ind. and Eng. Chem., 60, 10-19 (1968).

80. Maksimov, Y.V., Kushnerev, M.Y., Dumesic, J.A., Nechitailo, A.E. and Fridman, R.A., Structural Investigation of Re_2O_7/Al_2O_3 Catalysts for Olefin Disproportionation, J.Catal., 45, 114-117 (1976).

81. Johnson, M.F.L. and Leroy, V.M., The State of Rhenium in Pt/Re/Alumina Catalysts, J. Catal., 35, 434- 440(1974).

82. Ellison, A., Coverdale, A.K. and Dearing, P.F., The Metathesis of Unsaturated Esters Over Re_2O_7/Al_2O_3 Catalysts, J. Mol. Catal., 28, 141-167 (1985).

83. Nakamura, R. and Echigoya, E., The Role of M_xO_y in theMetathesis of Olefins Over Modified Rhenium (VII) Oxide-Alumina with M_xO_y, Recl. Trav. Chim.Pays-Bas., 96, 31-43 (1977).

84. Duquette, L.G., Cieslinski, R. C., Jung, C.W. and Garrou, P.E., ESCA Studies on Silica-and Alumina Supported Rhenium Oxide Catalysts, J. Catal., 90, 362-365 (1984).

85. Nakamura, R., Abe, F and Echigoya, E., Structures of Rhenium (VII) Oxides on Alumina and their Catalytic Activities for Metathesis of Olefins, Chem. Lett., 51-54 (1981).

86. Moulijn, J.A. and Mol, J.C., Catalysts, J. Mol. Catal., 46, 1-14 (1988).

87. Kerkhof, F.P.J.M., Moulijn, J.A. and Thomas, R., Laser Raman Spectroscopy of the Alumina-Supported Re_2O_7 Metathesis Catalyst, J. Catal., 56, 279-283 (1979).

88. Herrmann, W.A., Kuchler, J.G., Felixberger, J.K., Herdtweck, E. and Wagner, W., Methylrhenium Oxides: Synthesis From R_2O_7 and Catalytic Activity in Olefin Metathesis, Angew. Chem. Int. Ed. Engl., 27, 394-396 (1988).

89. Rybak, W.K. and Ziolkowski, J.J., The Transformation of Oxo Rhenium Complexes used as Catalysts in Metathesis Reaction, J. Mol. Catal., 42, 347-352 (1987).

90. Toreki, R. and Schrock, R.R., a Well-Defined Rhenium (VII) Oldefin Metathesis Catalyst, J. Am. Chem. Soc., 112, 2448-449 (1990).

91. Xiaoding, X., Mol, J.C. and Boelhouwer, C., Surface Acidity of some Re_2O_7-Containing Metathesis Catalysts: An *in situ* Fourier Transform Infrared Study using Pyridine Adsorption, J. Chem.Soc., Faraday Trans. 1, 82, 2707-2718 (1986).

92. Xiaoding, X., PhD Thesis, University of Amsterdam (1985).

93. Xiaoding, X., Benecke J.I., Boelhouwer, C. and Mol, J.C., $Re_2O_7/SiO_2.Al_2O_3$ Catalysts for the Metathesis of Functionalized Alkenes, Appl. Catal. 28, 271-283 (1986).

94. Xiaoding, X. and Mol, J.C., $Re_2O_7/SiO_2.Al_2O_3-SnR_4$ or PbR_4, a Highly Active Catalyst for the Metathesis of Functionalized Alkenes, J.C.S. Chem. Comm., 631-633 (1985).

95. Xiaoding, X., Boelhouwer, C., Benecke J.I., Vonk, D. and Mol, J.C., $Re_2O_7/Al_2O_3.B_2O_3$ Metathesis Catalysts, J. Chem.Soc., Faraday Trans. 1, 82, 1945-1953 (1986).

96. Boelhouwer, C. and Mol, J.C., Metathesis Reactions of Fatty Acid Esters, Prog.Lipid Res., 24, 243-267 (1985).

97. Bosma, R.H.A., Van Den Aardweg, G.C.N. and Mol, J.C., Heterogeneous Metathesis of Unsaturated Esters using a Rhenium-Based Catalyst, J. Organomet. Chem., 255, 159-171 (1983).

98. U.S. Patent 3 340 332

99. Freitas, E.R. and Gum, C.R., Shell's Higher Olefin Process, Chem. Eng. Prog., 75, 73-76 (1979).

100. Banks, R.L. and Regier, R.B., Synthesis of Isoamylene Via Olefin Disproportionation, Ind. Eng. Chem. Prod. Res. Dev., 10, 46-51 (1971).

101. Le Delliou, P., Norsorex and Very Low Hardness, Rev. Gen. Caout. Plast., 54, 77-80 (1977).

102. Streck, R., Some Applications of that Olefin Metathesis Reaction to Polymer Synthesis, J. Mol. Catal., 15, 3-19 (1982).

103. U.K. Patent 1 121 806

104. U.S. Patent 3 424 812

105. U.S. Patent 3 448 163

106. Meyers, A.I. and Temple Jnr, D.L., Syntheses via 2-Oxazolines. III. The Formation of Substituted Benzoic Acids or Esters Utilizing the Grignard Reagent of 2-(Bromophenyl)-2-Oxzaolines, J. Am. Chem. Soc., 92, 6646-6647 (1970).

107. Pattison, J.B., A Programmed Introduction to Gas-Liquid Chromatography, 2nd Ed., Heydon and Son Ltd, London (1973).

108. Braithwaite, A. and Smith, F.J., Chromatographic Methods, 4th Ed., Chapman and Hall, N.Y. (1985).

109. Williams, D.H. and Fleming, I., Spectroscopic Methods in Organic Chemistry., 4th Ed., McGraw-Hill, Berk. (1987).

110. Akitt, J.W., NMR and Chemistry, 2nd Ed., Chapman and Hall, N.Y. (1983).

111. Hagstrom, S.B.M. and Fadley, C.S., X-Ray Photoelectron Spectroscopy, 379-444 X-Ray Spectroscopy, Azaroff, L.V., McGraw-Hill, U.S. (1974).

112. Avery, H.E., Basic Reaction Kinetics and Mechanisms, MacMillan Press, London (1982).

113. Personel Communication, 1990.

114. Nakamura, R. and Echigoya, E., Structure and Nature of Active Sites on an O_2^-/Re Oxide/Alumina Metathesis Catalyst, J. Mol. Catal., 15, 147-156 (1982).

115. Grubbs, R.H., Inorg. Chem., Mechanism of Olefin Metathesis and Cyclopropanation, 18, 2623 (1979).

116. Clark, A. and Cook, C., The Mechanism of Propylene Disproportionation, J. Catal., 15, 420-424 (1969).

117. Tanaka, K., Novel Supported Catalysts for Terminal Alkene Metathesis, 303-337 Olefin Metathesis and Polymerization Catalysts. Synthesis, Mechanism and Utilization., Proceedings of the NATO Advanced Study Institute on Olefin Metathesis and Polymerization Catalysts, Ackay, Turkey, Ed. Imamoglu, Y, Zumreoglu-Karan, B and Amass, A.J. (1989).

118. Frump, J.A., Oxazolines. Their Preparation, Reactions, and Applications, Chem. Rev., 71, 483-499 (1971).

119. Reuman, M and Meyers, A.I., The Synthetic Utility of Oxazolines in Aromatic Substitution, Tet., 41, 837-860 (1984).

120. Meyers, A.I. and Mihelich, E.D., The Synthetic Utility of 2-Oxazolines, Angew. Chem. Int. Ed. Engl. 15, 270-281 (1976).

121. Meyers, A.I. and Slade, J., Asymmetric Addition of Organometallics to Chiral Ketooxazolines. Preparation of Enantiomerically Enriched α- Hydroxy Acids, J. Org. Chem., 45, 2785-2791 (1980).

122. Leffler, M.T. and Adams, R., Aminophenyl-2-oxazolines as Local Anesthetics, J. Am. Chem. Soc., 59, 2252-2258 (1937).

123.   Meyers, A.I. and Temple Jnr, D.L., Syntheses via 2-Oxazolines. II. A Versatile Syntheses of Aliphatic Carboxylic Acids and Esters. Mono- and Dialkylation of Acids Masked by a Simple Protecting Group,J. Am. Chem. Soc., 92, 6644-6646 (1970).

124.   Hirao, A., Ishino,Y. and Nakahama, S., Protection and Polymerization of Functional Monomers. Synthesis of Well-Defined Poly(4-vinylbenzoic acid) by Means of Anionic Living Polymerization of 2-(4-Vinylphenyl)-4-,4-dimethyl-2-oxazoline, Macromol.,21, 561-565 (1988).

Fig A1.1

Gas chromatograph of metathesis solution of 1-hexene

Fig A1.2(a)

Mass spectra of product solution from the metathesis

of 1-hexene

Fig A1.2(b)

Mass spectra of product solution from
the metathesis of 1-hexene
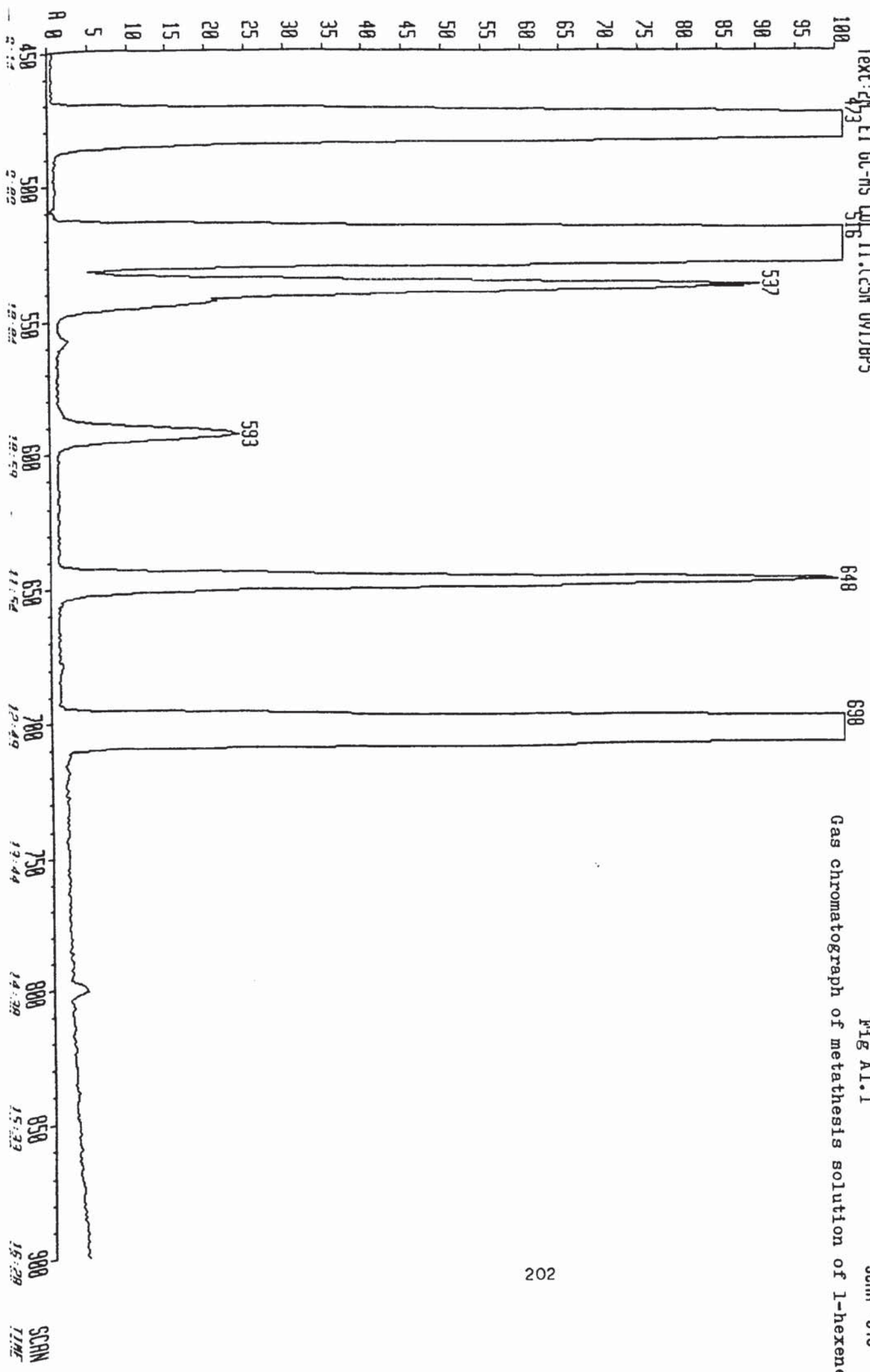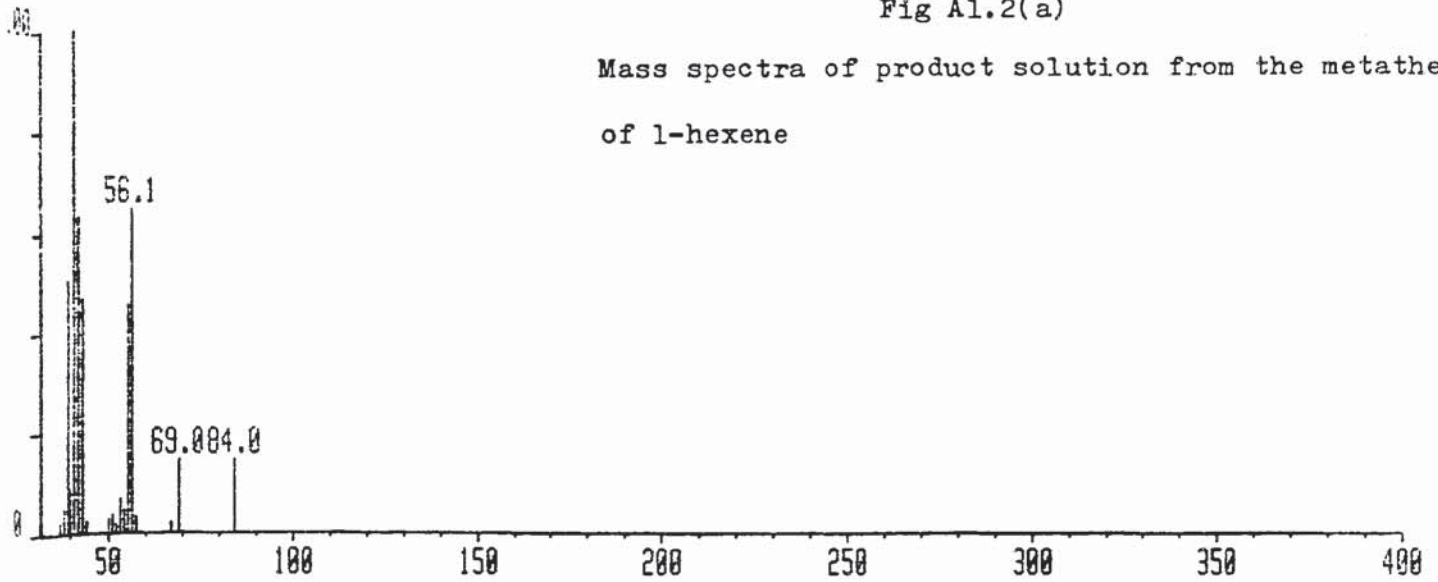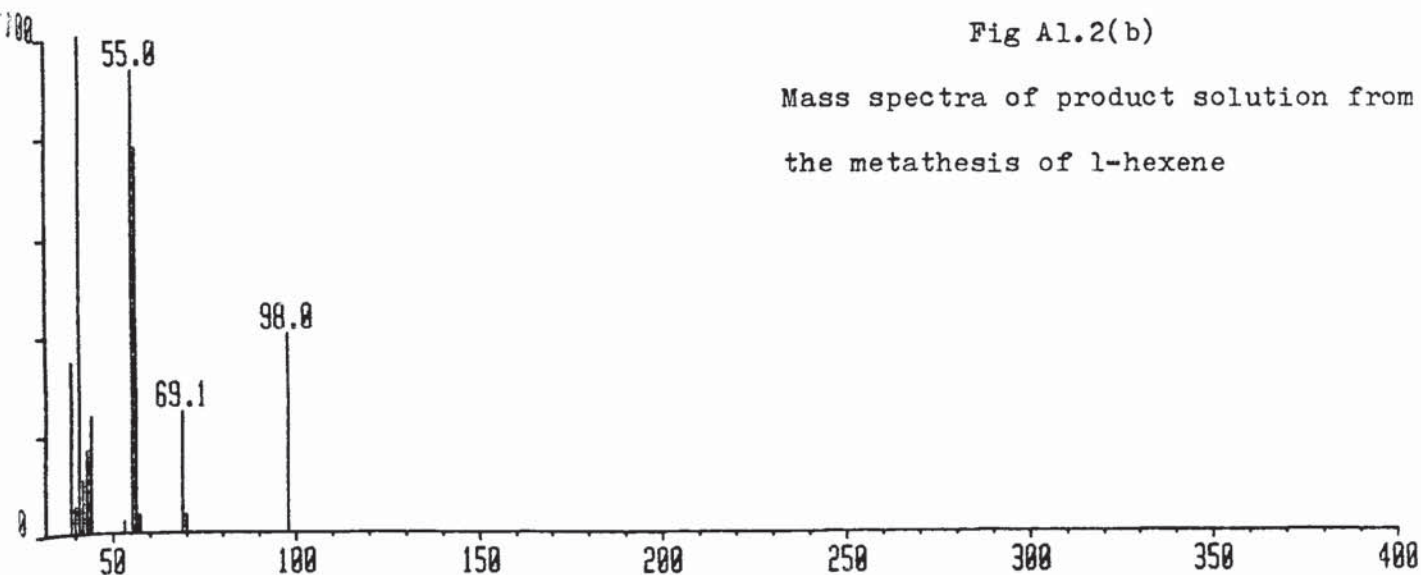
AST07IH2#698*   x10   12-253J   23-AUG-90 10:22+0:12:46 EI+
I=9.9v   TIC=31504300   Acnt:HOHN
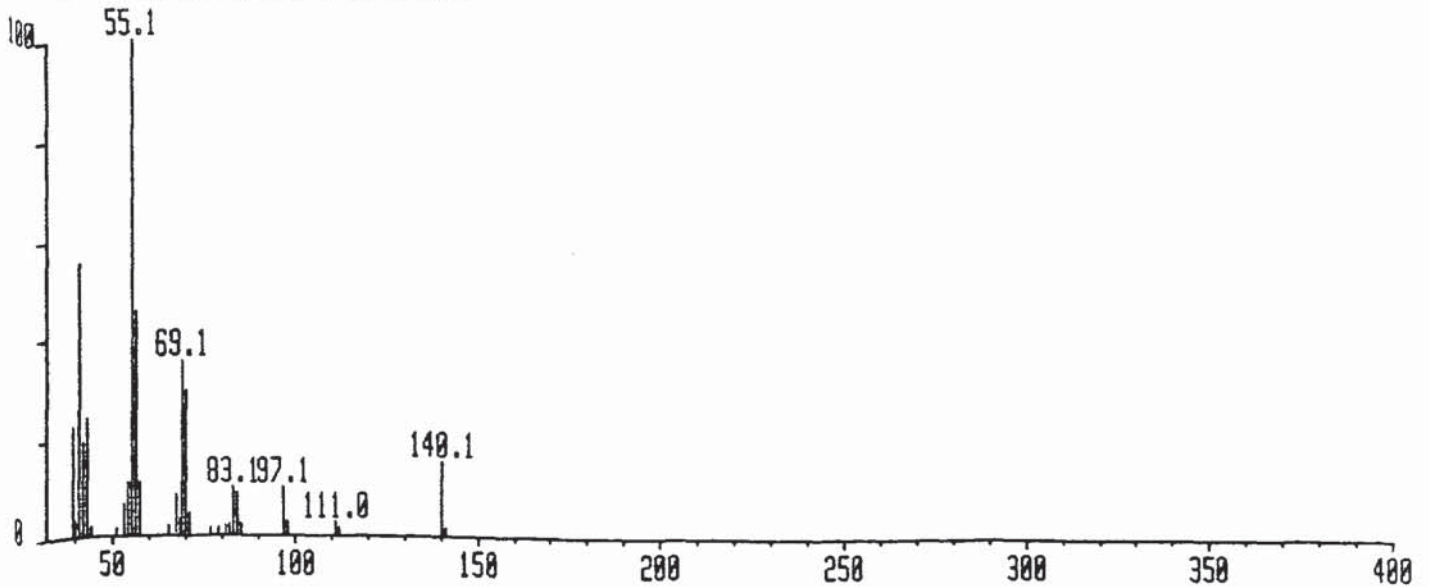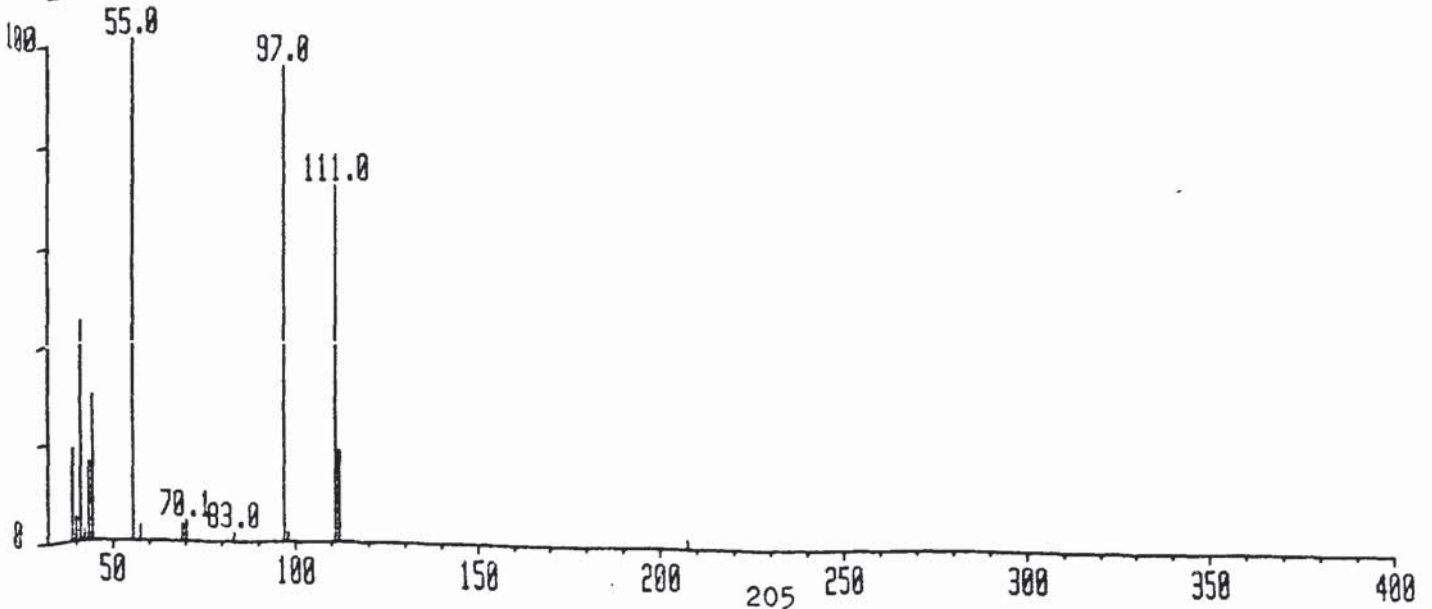2M EI GC-MS COL 11.(25M OV1)BP5

Fig A1.2(c)

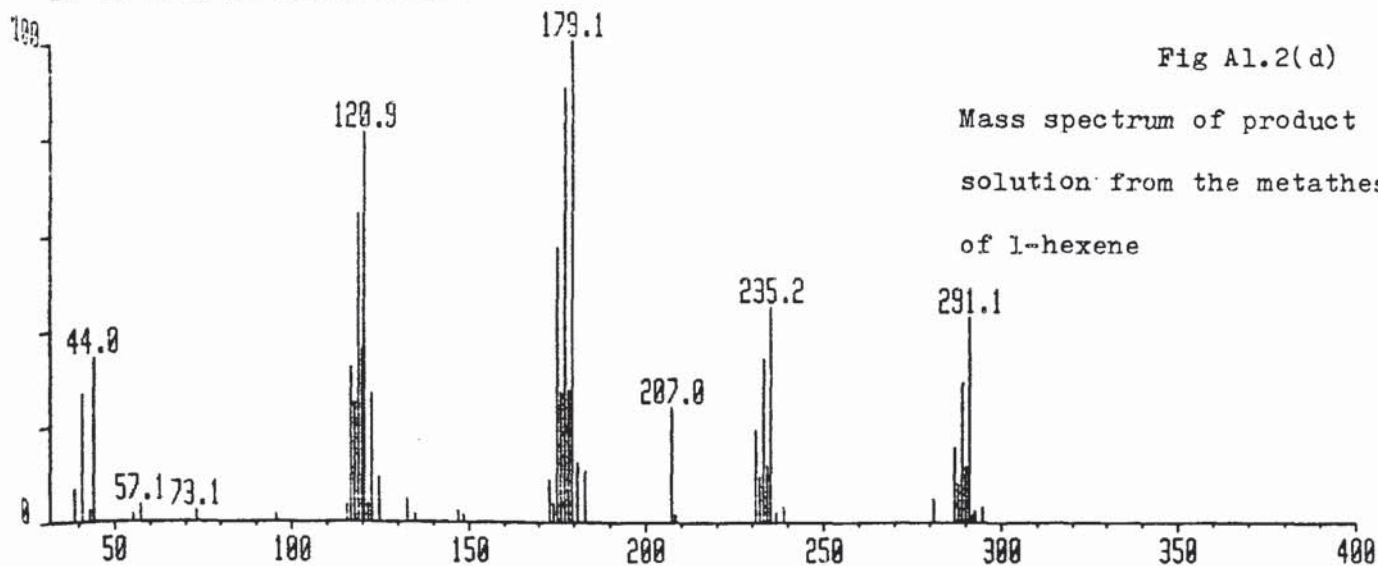Mass spectra of product solution from

the metathesis of 1-hexene

Fig A1.2(d)

Mass spectrum of product

solution from the metathesis

of 1-hexene

2262 Library spectra compared for BEST REVERSE FIT
    63   matched 5 or more of the   5 largest peaks in the unknown

t Entry Compound Name   Reference

  1182 2-HEPTENE, (E)-   14686-13-6
  1183 3-HEPTENE, (E)-   14686-14-7
  3923 PIPERIDINE, 2-METHYL-1-NITROSO-   7247-89-4
  9201 4-HEXENOIC ACID, 6-HYDROXY-4-METHYL-, METHYL ESTER, (Z)-   67884-44-0
  5943 CYCLOOCTANONE, 2-METHYL-   10363-27-6
  3838 2H-AZEPIN-2-ONE, HEXAHYDRO-3-METHYL-   2073-32-7
  1142 CYCLOHEXANE, METHYL-   108-87-2
 15600 PENTANE, 1-(2,2-DICHLORO-1-METHYLCYCLOPROPYL)-   24551-80-2
  3682 CYCLOHEPTANONE, 2-METHYL-   932-56-9
  1145 2-HEPTENE   592-77-8
 20685 2,5-CYCLOHEXADIEN-1-OL, 4-METHYL-4-(TRICHLOROMETHYL)-   13630-61-0
 15598 CYCLOPROPANE, 2-BUTYL-1,1-DICHLORO-2-ETHYL-   5685-44-9
  1179 2-HEXENE, 5-METHYL-, (E)-   7385-82-2
 20593 OXACYCLOTETRADECAN-2-ONE, 13-METHYL-   57092-32-7
  3705 CYCLOHEPTANONE, 3-METHYL-, (R)-   13609-58-0

t   Elements   Bpk   Mwt   pur   mix   REV

   C7.H14.   55   98   750   750   936
   C7.H14.   41   98   743   743   909
   C6.H12.N2.0.   56   128   438   438   899
   C8.H14.03.   41   158   473   482   897
   C9.H16.0.   55   140   472   472   887
   C7.H13.N.0.   127   127   392   392   885
   C7.H14.   83   98   506   506   885
   C9.H16.CL2.   41   194   512   512   882
   C8.H14.0.   55   126   470   470   882
   C7.H14.   41   98   791   840   880
   C8.H9.0.CL3.   55   226   377   377   879
   C9.H16.CL2.   56   194   586   586   879
   C7.H14.   56   98   700   700   878
   C14.H26.02.   41   226   362   362   868
   C8.H14.0.   41   126   599   599   868

Fig A1.3(a)

207

2262 Library spectra compared for BEST REVERSE FIT
    20   matched 5 or more of the   5 largest peaks in the unknown

t   Entry Compound Name   Reference

    3757 4-NONENE   2198-23-4
    3702 CYCLOHEXANONE, 4-ETHYL-   5441-51-0
   22698 HEXANOIC ACID, 1-METHYLOCTYL ESTER   55193-16-3
    3752 CYCLOHEXANE, 1,2,3-TRIMETHYL-   1678-97-3
    3750 CYCLOHEXANE, 1,2,3-TRIMETHYL-, (1.ALPHA.,2.BETA.,3.ALPHA.   1678-81-5
    3773 CYCLOHEXANE, 1,2,4-TRIMETHYL-, (1.ALPHA.,2.BETA.,4.BETA.)   7667-60-9
    3758 CYCLOHEXANE, 1,2,4-TRIMETHYL-   2234-75-5
    3780 CYCLOPROPANE, 1-METHYL-2-PENTYL-   41977-37-1
    3756 CYCLOPENTANE, BUTYL-   2040-95-1
    3772 CYCLOHEXANE, 1,2,3-TRIMETHYL-, (1.ALPHA.,2.ALPHA.,3.BETA.   7667-55-2
    3761 1-HEPTENE, 2,6-DIMETHYL-   3074-78-0
    3759 3-HEPTENE, 2,6-DIMETHYL-   2738-18-3
   11045 CYCLOBUTANE, 1-HEXYL-2,3-DIMETHYL-   55170-84-8
    3635 1,3-CYCLOPENTANEDIONE, 4-ETHYL-   57157-03-6
    6062 BORANAMINE, N-(1,1-DIMETHYLETHYL)-1,1-DIETHYL-   50612-53-8

t   Elements   Bpk   Mwt   pur   mix   REV

    C9.H18.   55   126   859   860   977
    C8.H14.O.   55   126   776   777   919
    C15.H30.02.   43   242   554   555   914
    C9.H18.   41   126   726   727   913
    C9.H18.   69   126   672   673   904
    C9.H18.   111   126   567   567   895
    C9.H18.   69   126   620   621   893
    C9.H18.   56   126   841   891   878
    C9.H18.   41   126   701   702   870
    C9.H18.   55   126   672   703   864
    C9.H18.   56   126   770   771   840
    C9.H18   41   126   620   660   835
    C12.H24.   56   168   713   714   813
    C7.H10.02   56   126   790   848   907
    C8.H20 N.B.   56   141   538   538   722

Fig A1.3(b)

WSH1.DAT | Region 3 / 3 | XPS – Spectrum | V.G. Scientific

WIDE 3 | Level 1 / 1 | Point 1 / 1

Fig A2.1(d)

ESCA spectrum of unused
rhenium heptoxide/alumina
catalyst

209
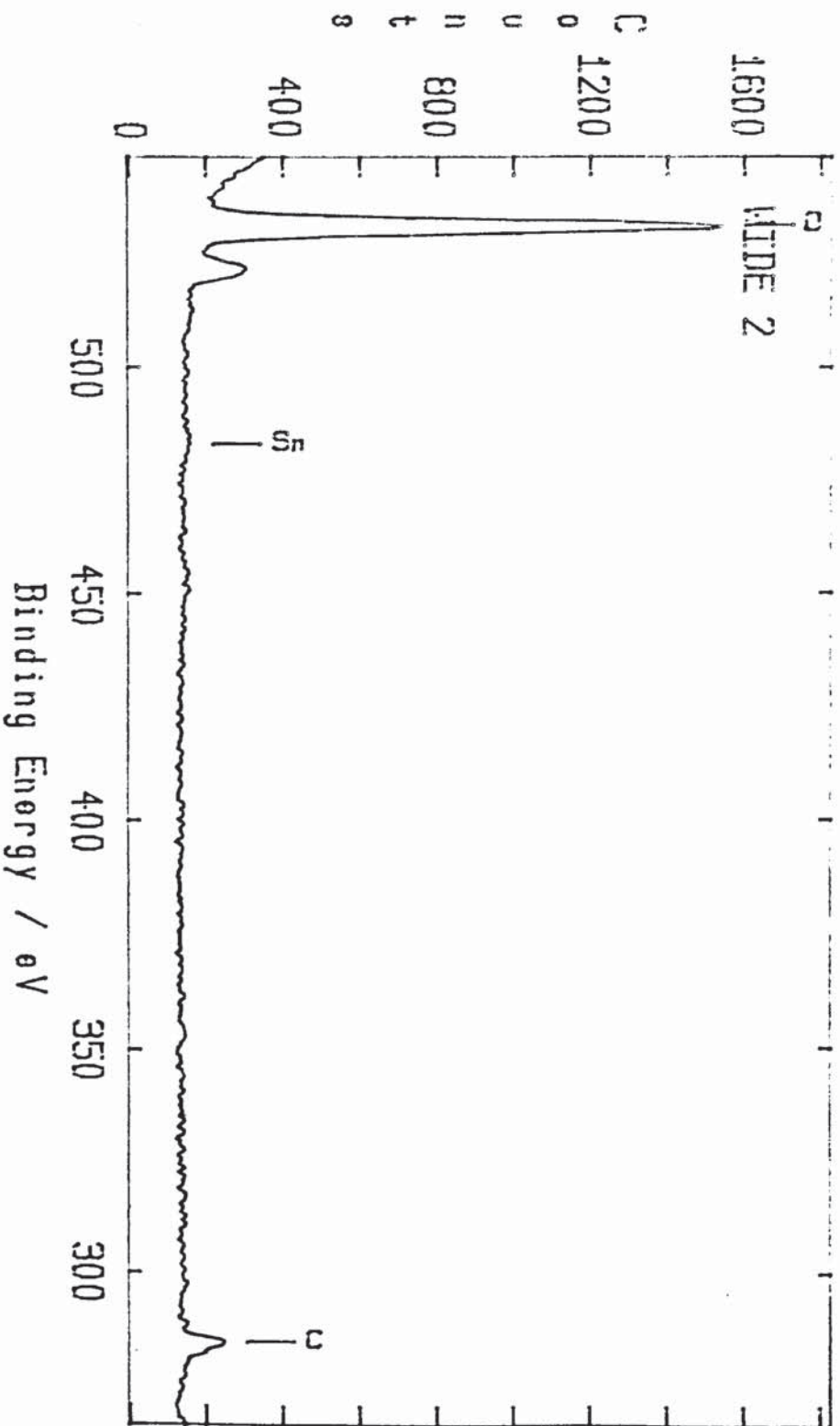
Fig A2.1(b)
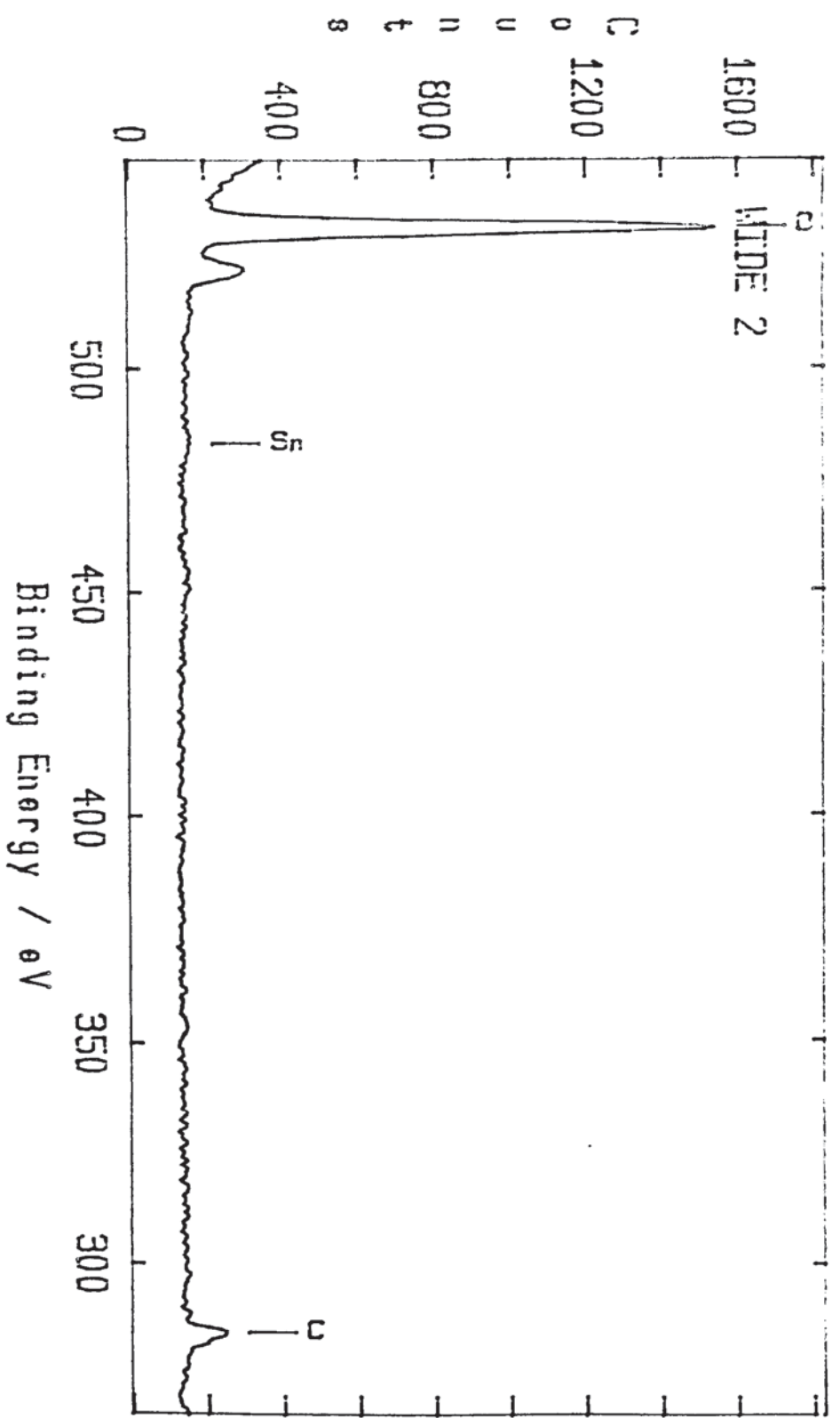
ESCA spectrum of unused rhenium heptoxide/alumina catalyst

Fig A2.1(a) ESCA spectrum of unused rhenium heptoxide/alumina catalyst

Fig A2.2(a)

ESCA spectrum of rhenium heptoxide/alumina catalyst used in the metathesis of 1-hexene
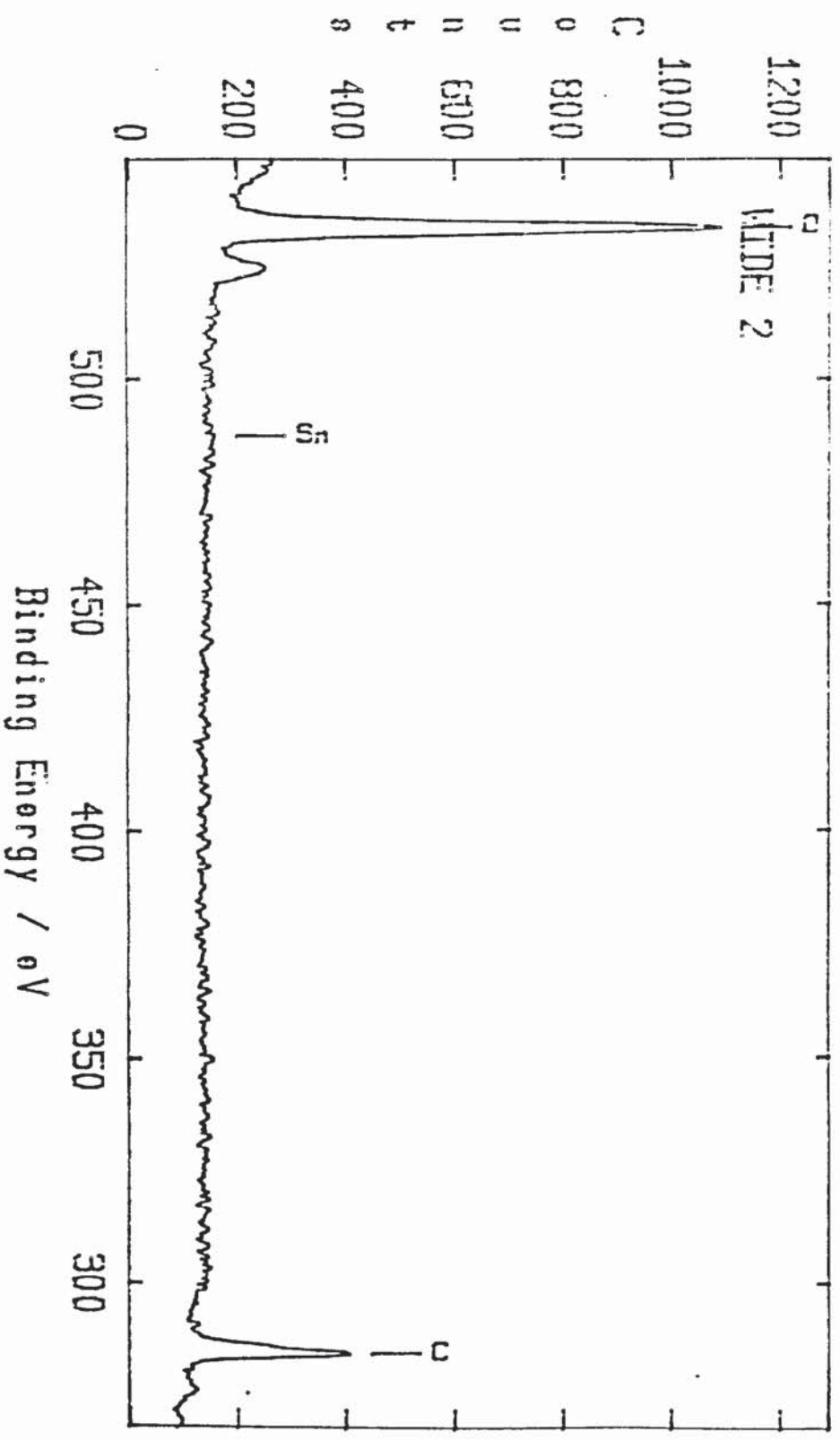
212
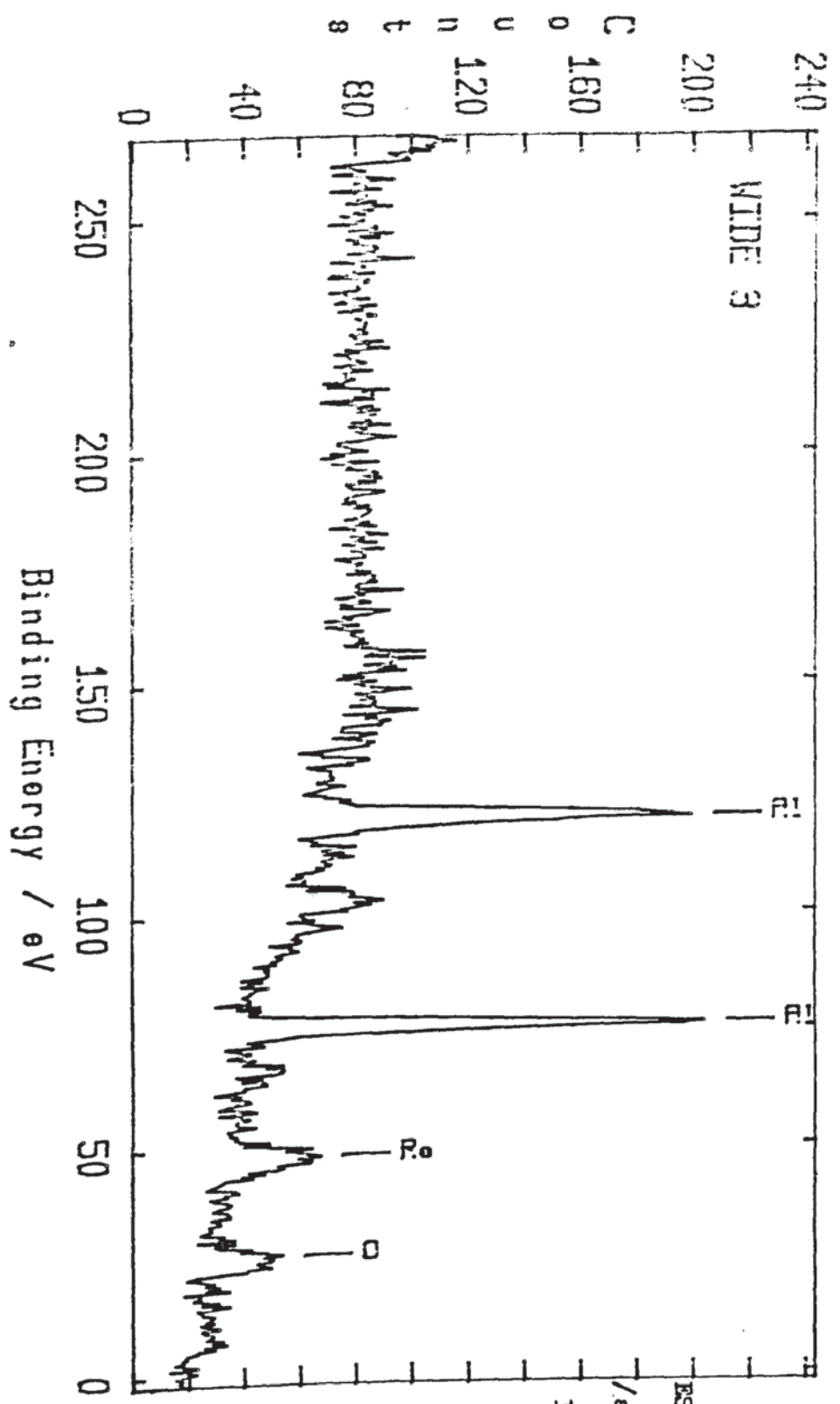
Fig A2.2(b) ESCA spectrum of rhenium heptoxide/alumina used in the metathesis of 1-hexene
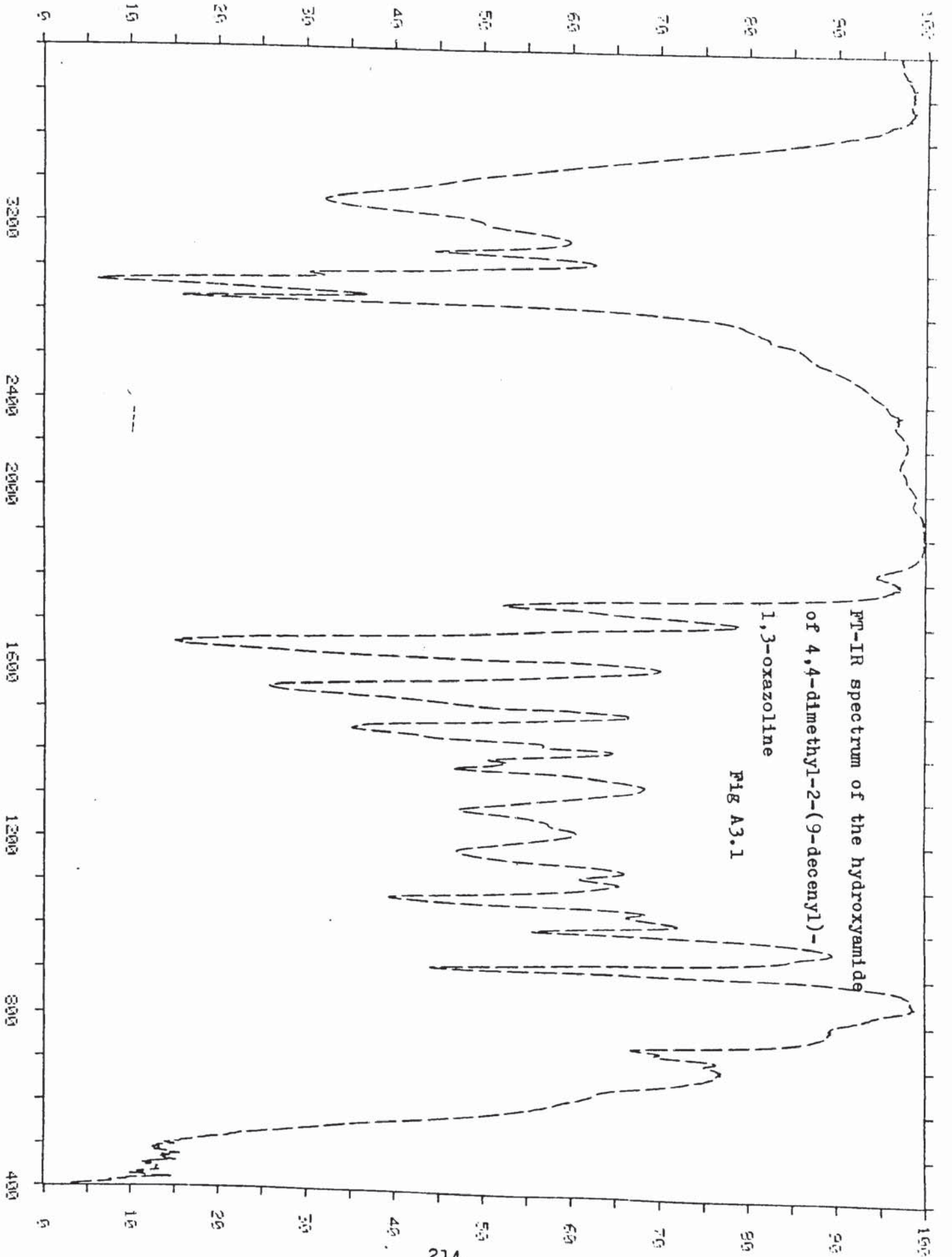
213

FT-IR spectrum of the hydroxyamide of 4,4-dimethyl-2-(9-decenyl)-1,3-oxazoline

Fig A3.1

214

^{13}C nmr spectrum of the hydroxyamide of 4,4-dimethyl-2-(9-decenyl)-1,3-oxazoline

Fig A.3.2
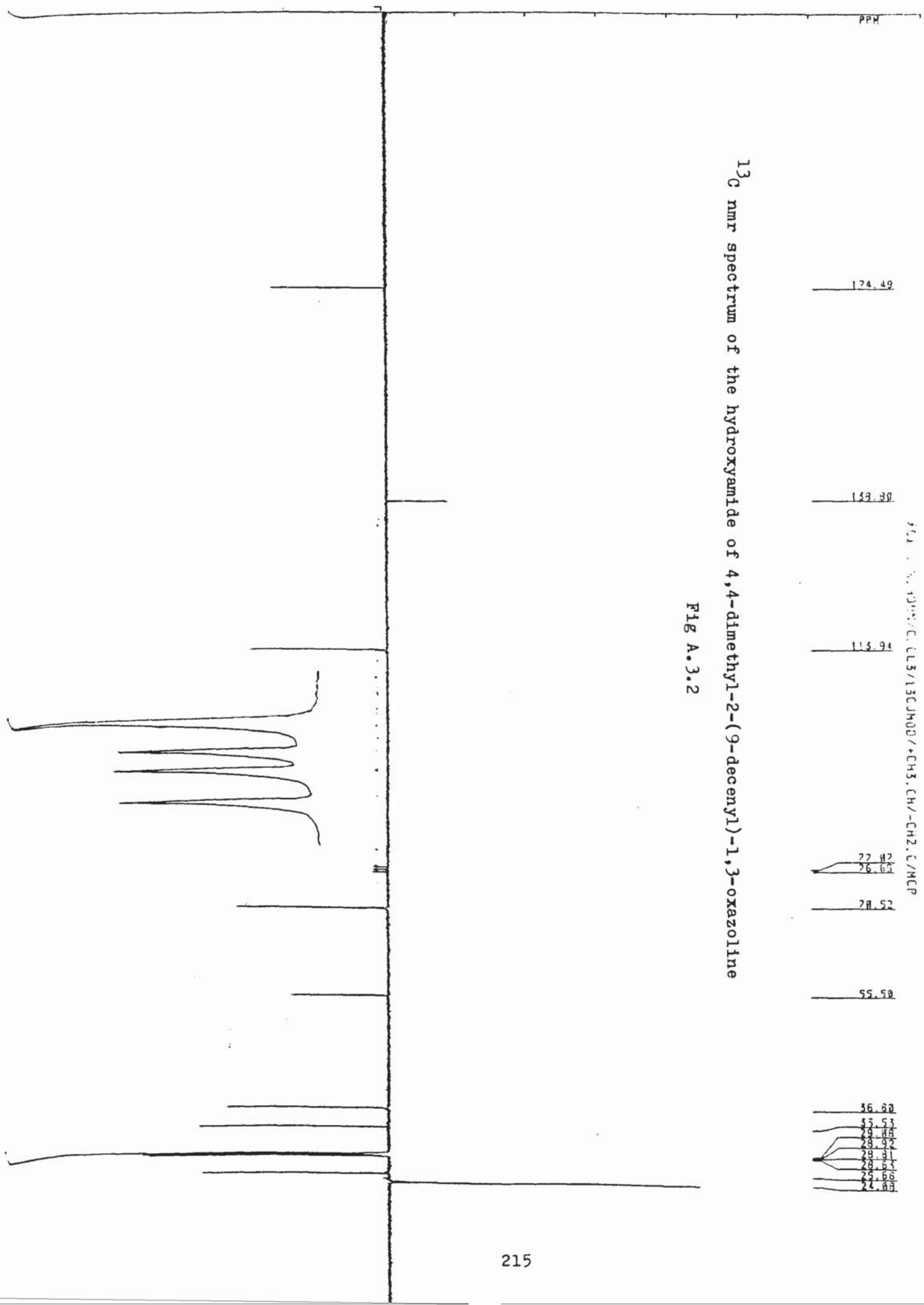
174.49

139.39

115.94

77.42 ... \\\ 13'\\'C, CL3/13CJM03/+CH3.CH/-CH2.C/MCP

77.42
76.65

78.52

55.58

56.69
53.53
49.49
29.92
29.91
28.63
25.66
24.89

PPM

FT-IR spectrum of
4,4-dimethyl-2-(9-decenyl)-1,3-oxazoline

Fig A.3.3

216

13C of 4,4-dimethyl-2-(9-decenyl)-1,3-oxazoline
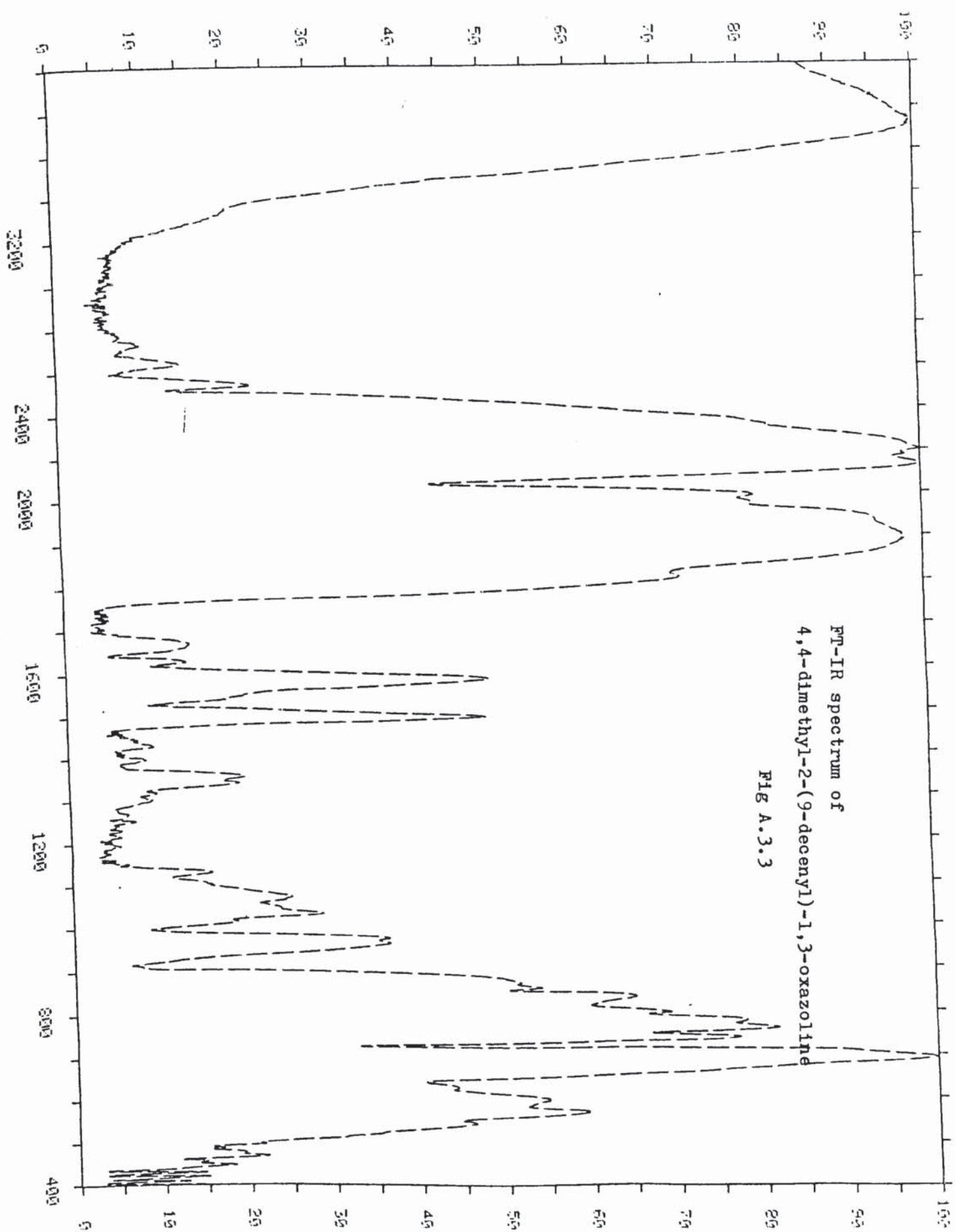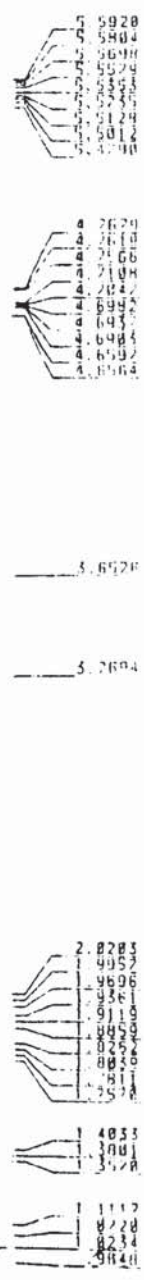
Fig A.3.4

Fig A.3.5

^{1}H nmr spectrum of 4,4-dimethyl-2-(9-decenyl)-1,3-oxazoline
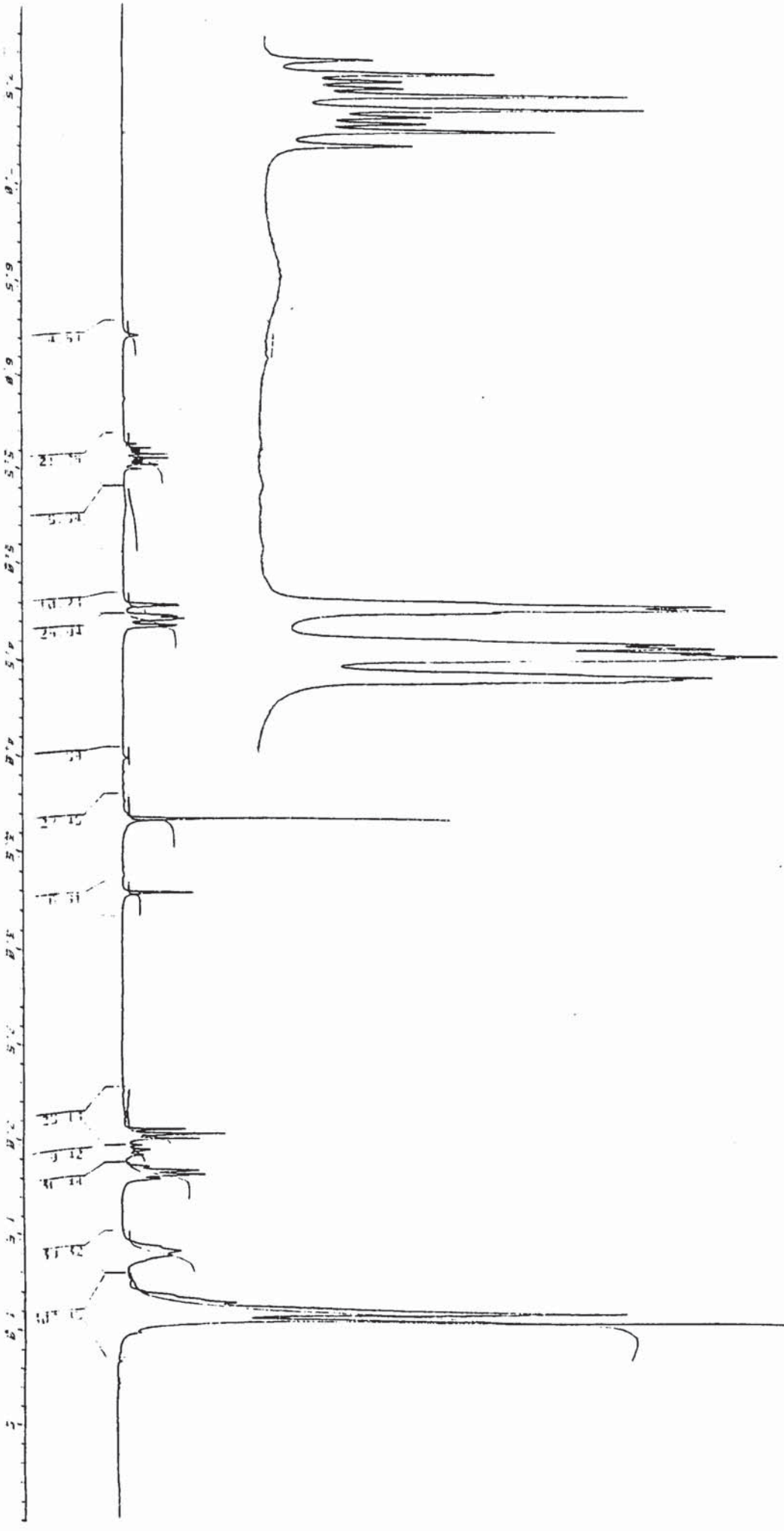
Fig A.3.6

Mass spectrum of the hydroxyamide of 4,4-dimethyl-2-(9-decenyl)-
1,3-oxazoline

219
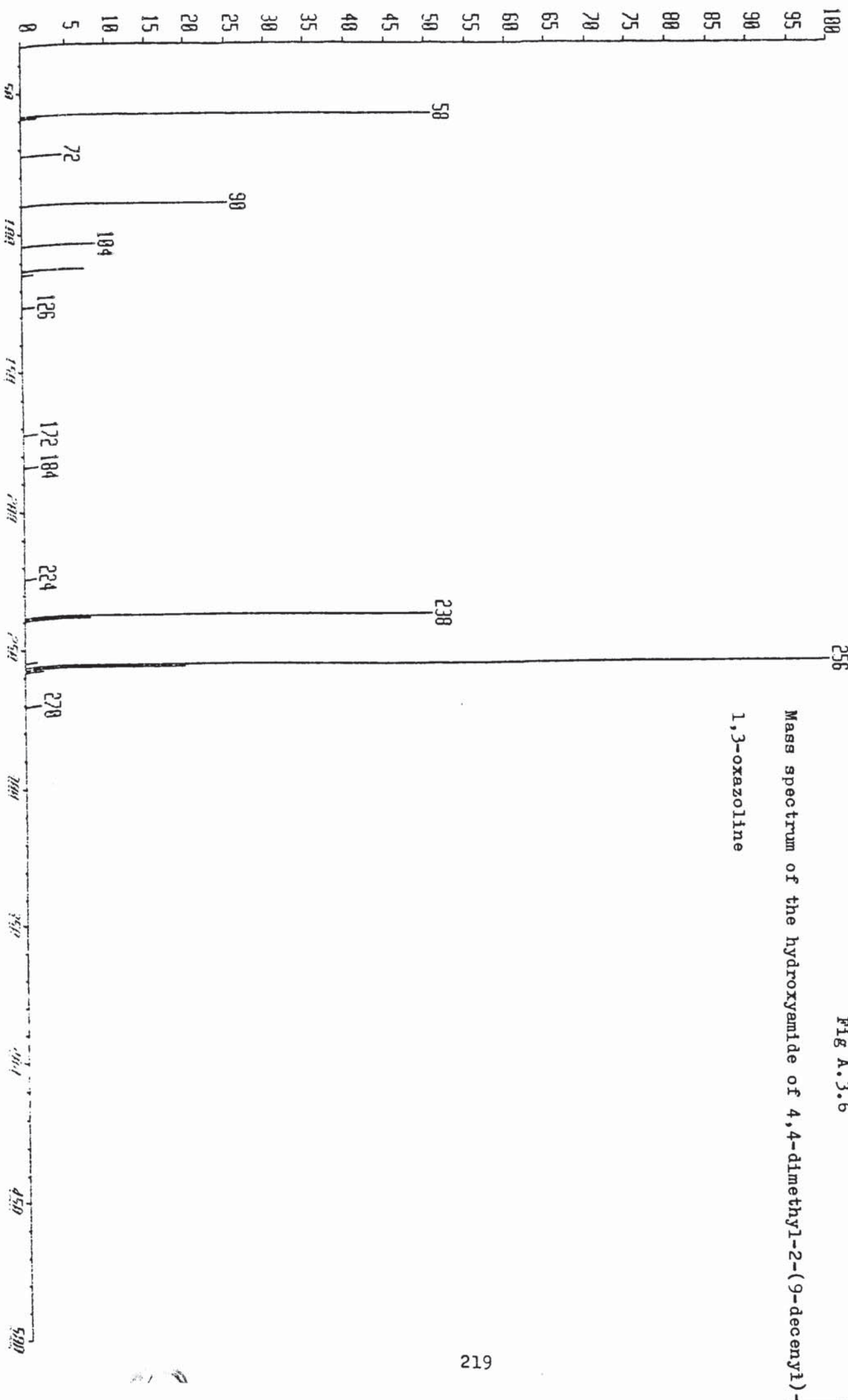
Mass	% Base	
58	50.6	F
59	1.5	F
72	4.5	
90	25.2	F
104	8.7	
113	7.2	F
114	1.1	F
126	1.3	
172	1.3	
184	1.3	
224	1.1	
238	50.4	F
239	7.6	F
254	1.1	
256	100.0	F
257	19.6	F
258	1.8	F
270	1.5	

Fast atom bombardment data of the hydroxyamide of 4,4-dimethyl-

2-(9-decenyl)-1,3-oxazoline

Fig A3.7

Mass spectrum of 4,4-dimethyl-2-(9-decenyl)-1,3-oxazoline

Fig A.3.8

Fig A.3.9

Mass spectrum of 4,4-dimethyl-2-(9-decenyl)-1,3-oxazoline

Mass	% Base	
58	40.4	F
72	6.0	
90	44.8	F
91	1.3	F
238	4.5	
254	1.4	
256	100.0	F
257	17.3	F
292	1.0	F
292	3.7	F
422	1.2	

Fast atom bombardment data of 4,4-dimethyl-2-(9-decenyl)-1,3-oxazoline

Fig A.3.10

Mass spectrum of the product of the metathesis of

4,4-dimethyl-2-(9-decenyl)-1,3-oxazoline
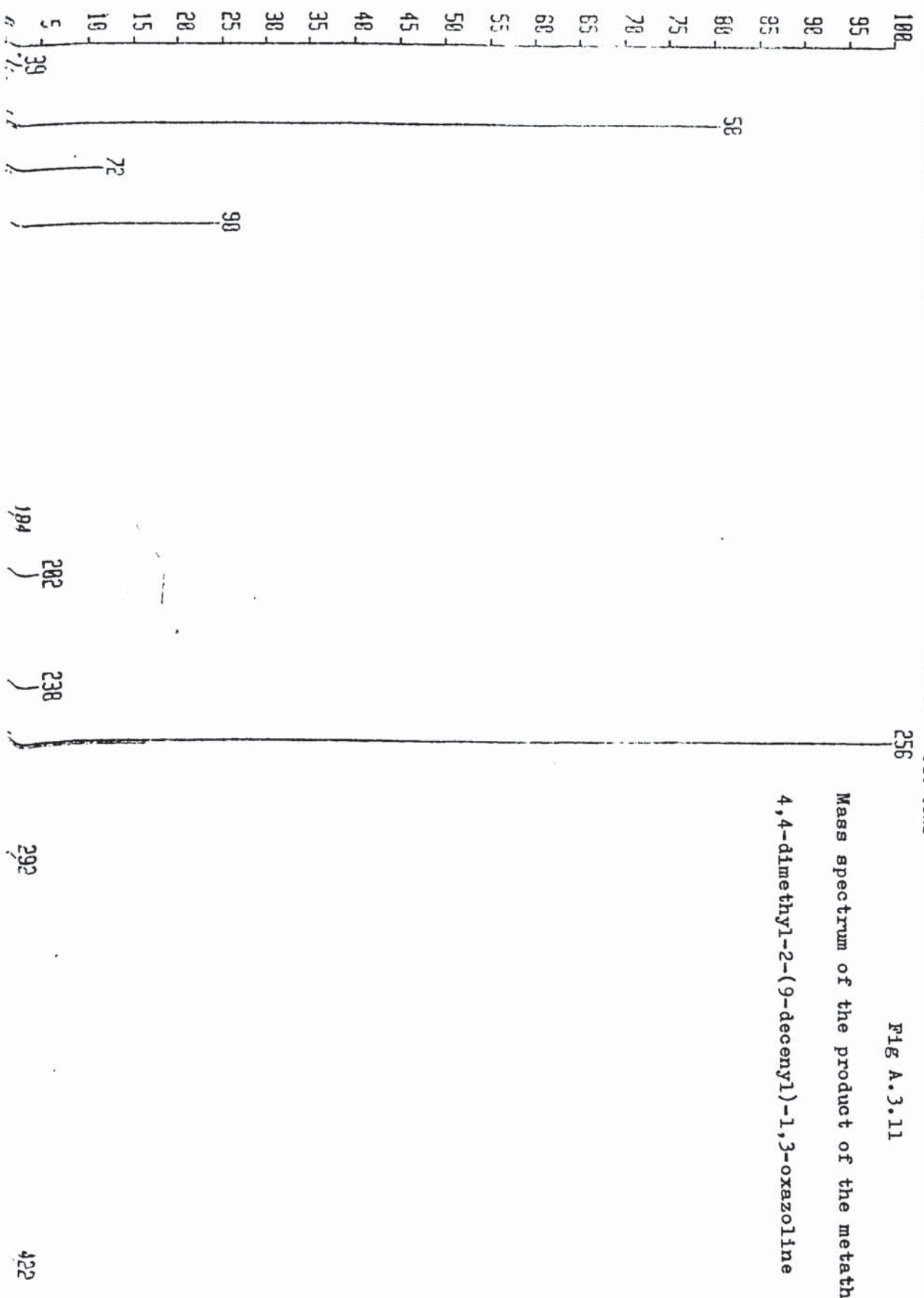
Fig A.3.11

Mass	% Base	
39	2.9	
41	1.5	
55	1.3	
58	80.5	F
59	2.2	F
72	11.6	F
74	1.1	
90	24.6	
184	1.6	
202	4.9	
238	5.0	
254	1.1	
256	100.0	F
257	16.6	F
292	2.3	
422	2.3	

Fast atom bombardment of the product of the metathesis of 4,4-dimethyl-2-
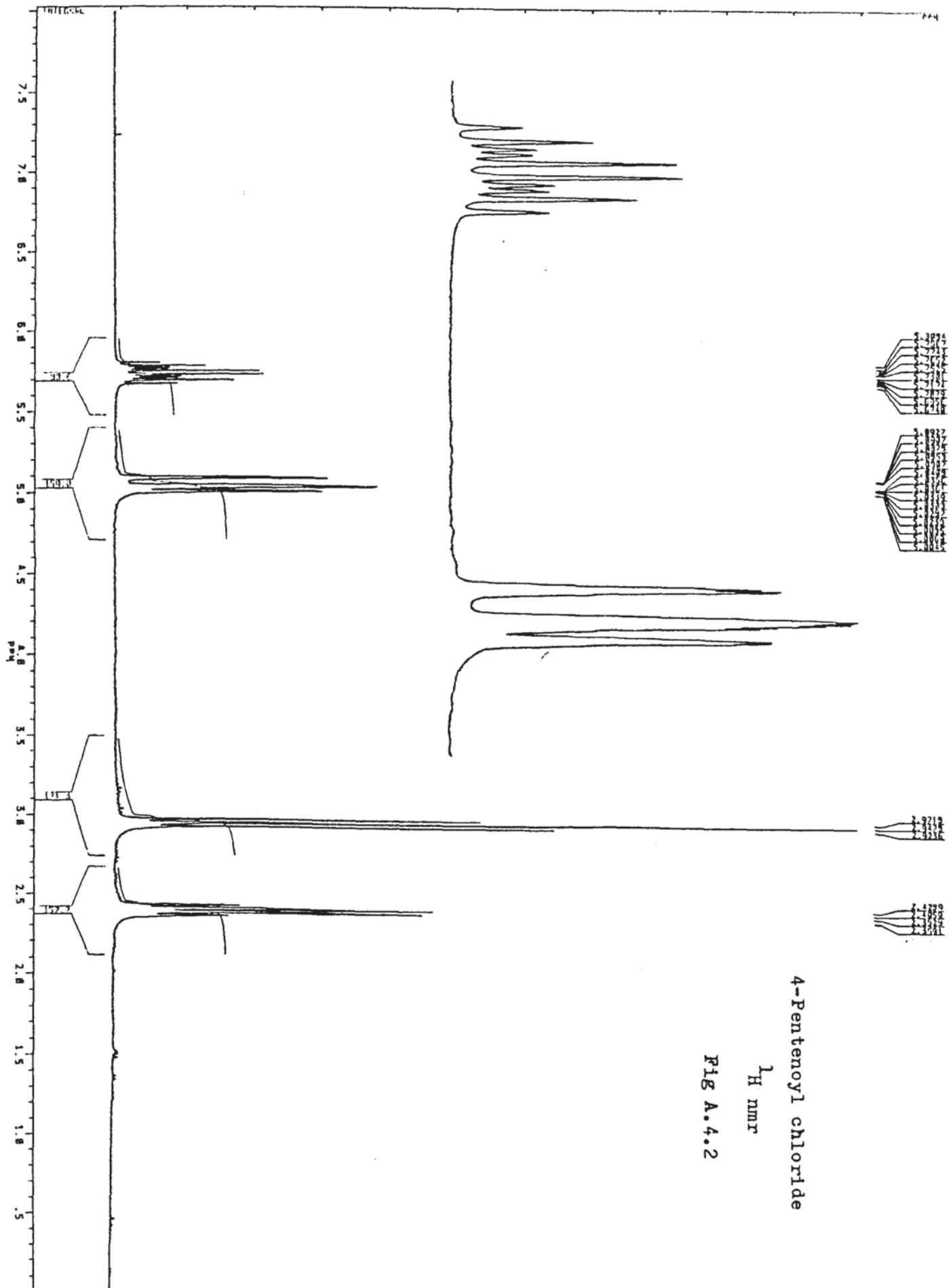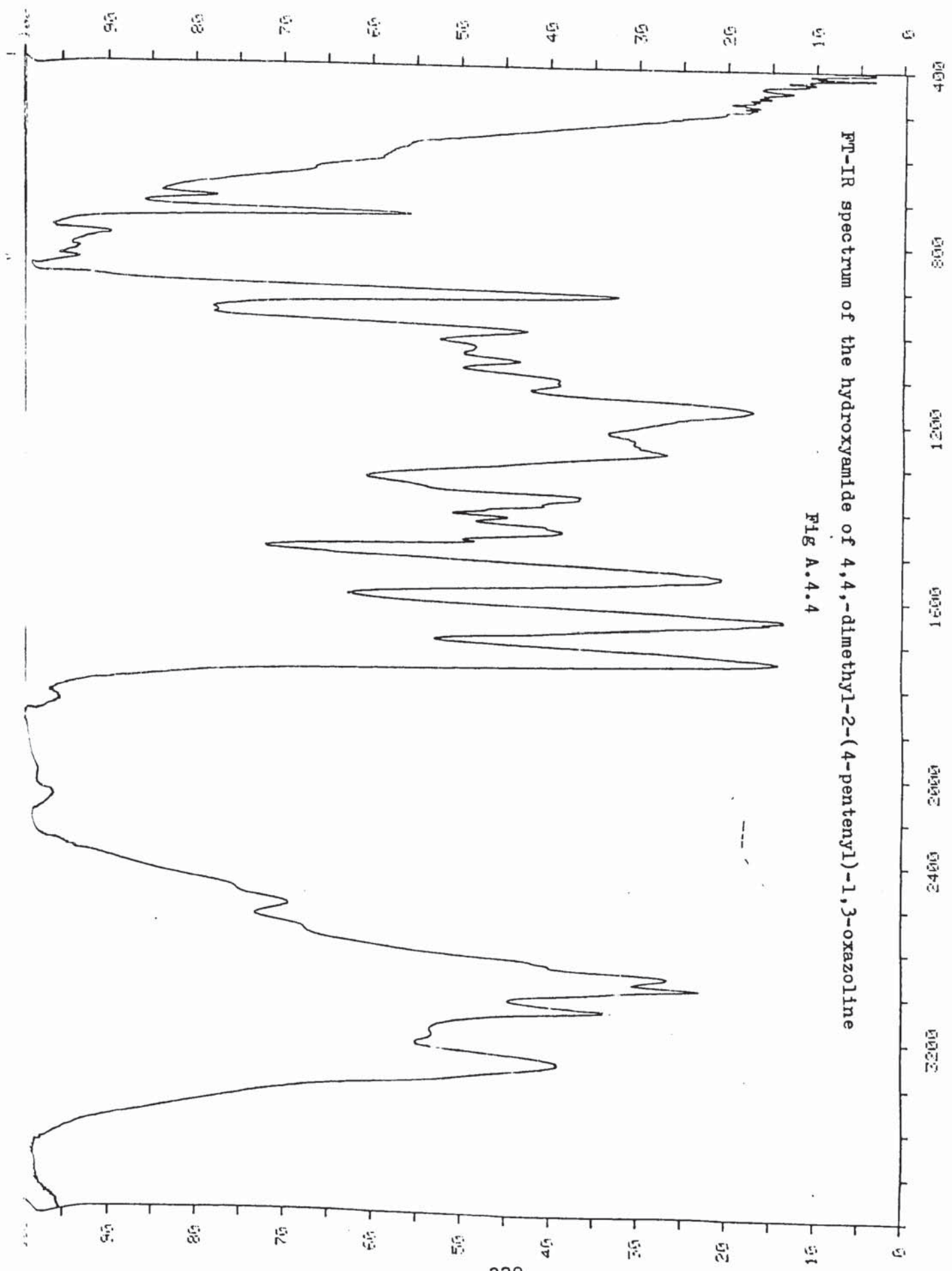
(9-decenyl)-1,3-oxazoline   Fig A.3.12
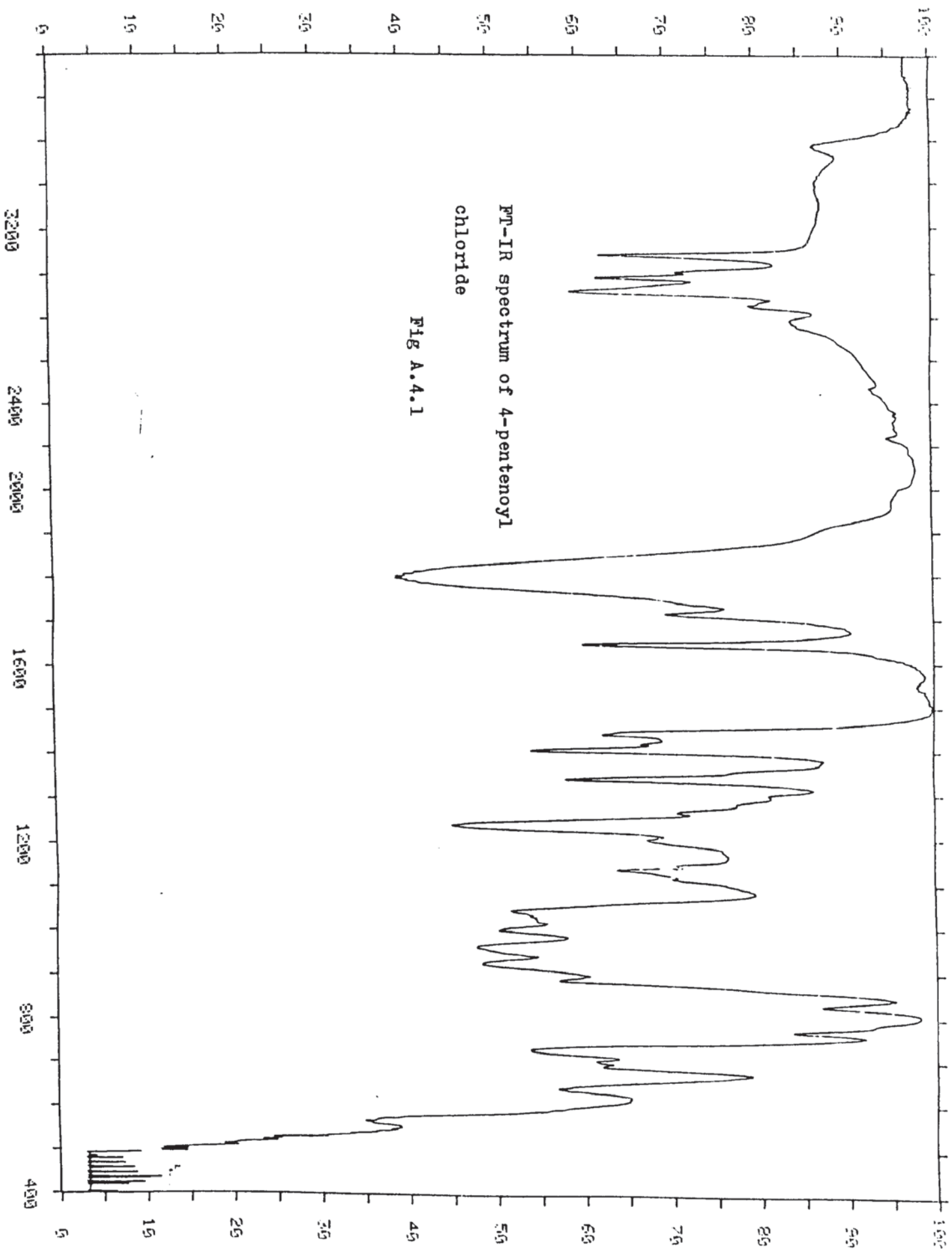
FT-IR spectrum of 4-pentenoyl chloride

Fig A.4.1

4-Pentenoyl chloride

^{1}H nmr

Fig A.4.2

FT-IR spectrum of the hydroxyamide of 4,4,-dimethyl-2-(4-pentenyl)-1,3-oxazoline

Fig A.4.4

229

^{13}C nmr spectrum of the hydroxyamide of 4,4-dimethyl-2-(4-pentenyl)-1,3-oxazoline

Fig A.4.5

Fig A.4.6

^{1}H nmr spectrum of the hydroxyamide of 4,4-dimethyl-2-(4-pentenyl)-1,3-oxazoline
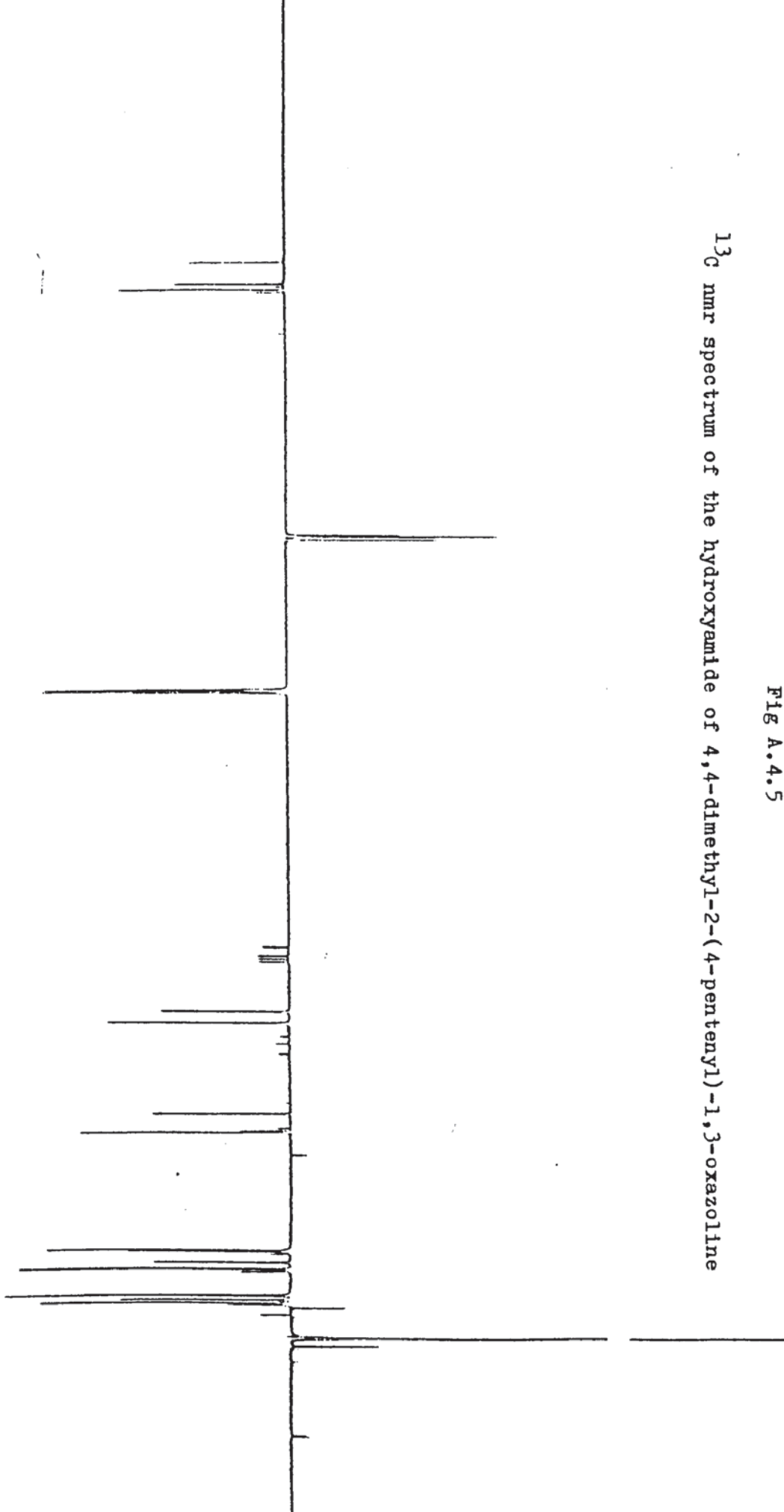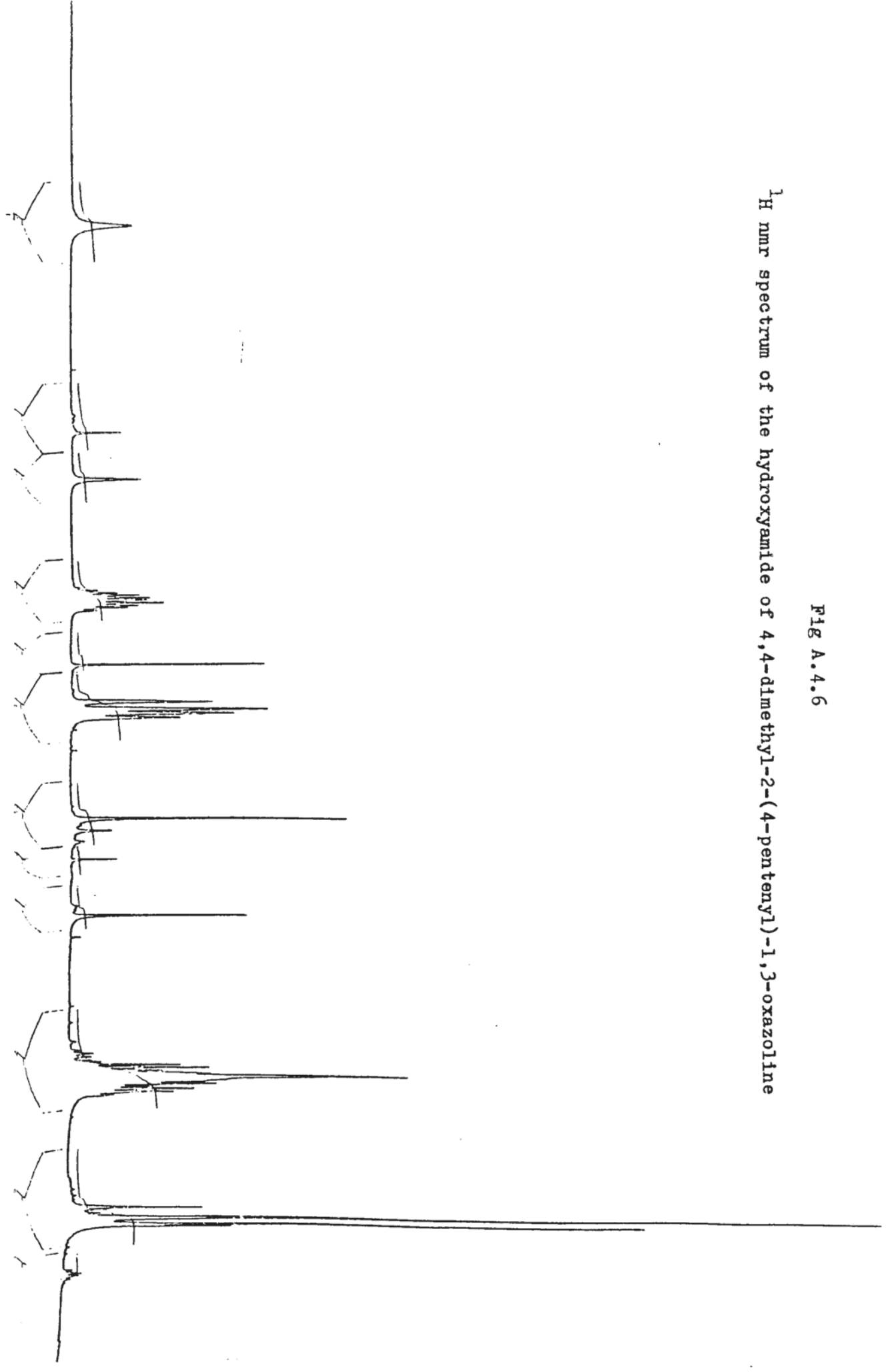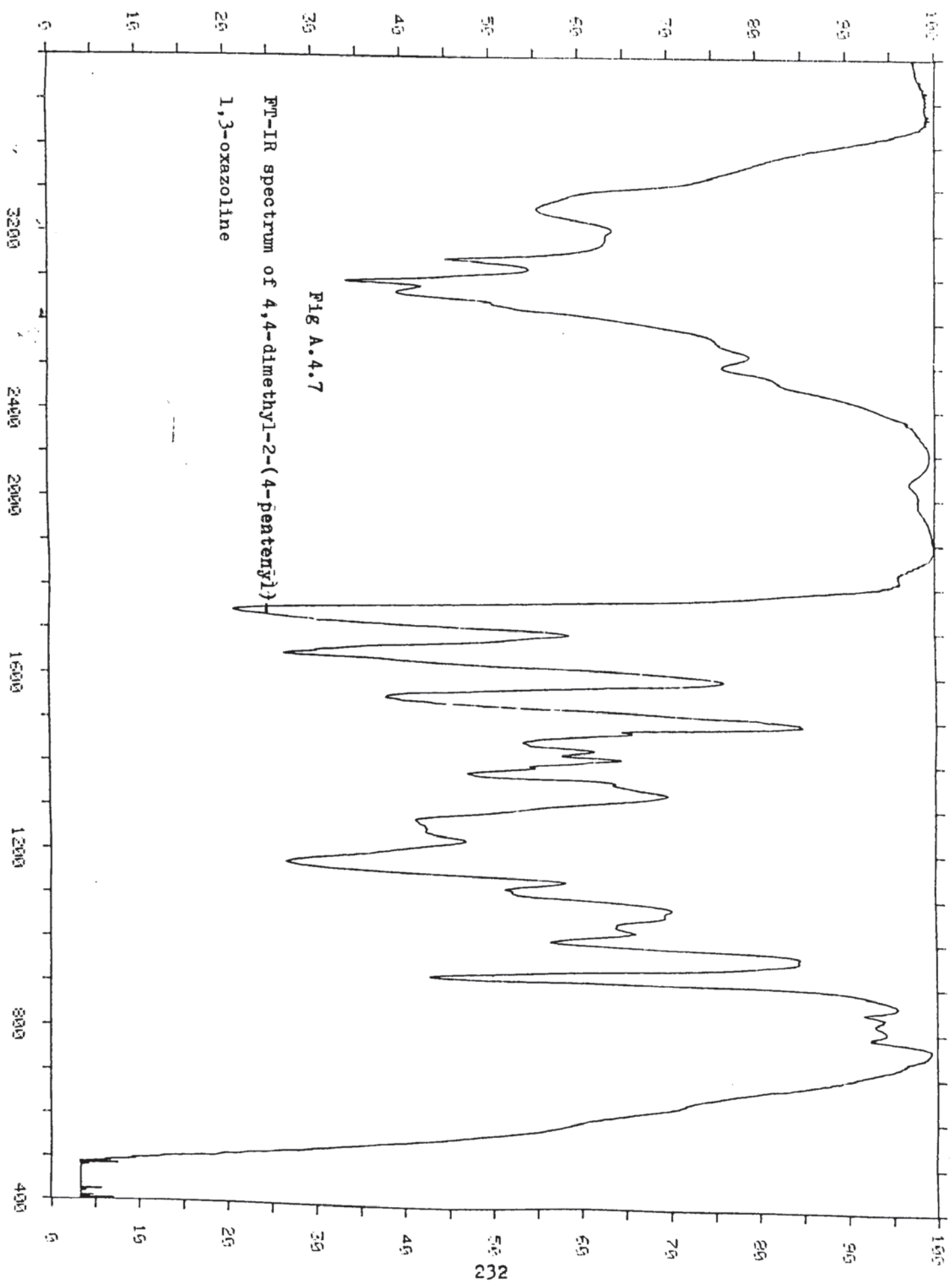
Fig A.4.7

FT-IR spectrum of 4,4-dimethyl-2-(4-pentenyl)
1,3-oxazoline

^{13}C nmr spectrum of 4,4-dimethyl-2-(4-pentenyl)-1,3-oxazoline

Fig A.4.8

^{1}H nmr spectrum of 4,4-dimethyl-2-(4-pentenyl)-1,3-oxazoline

Fig A.4.9

234
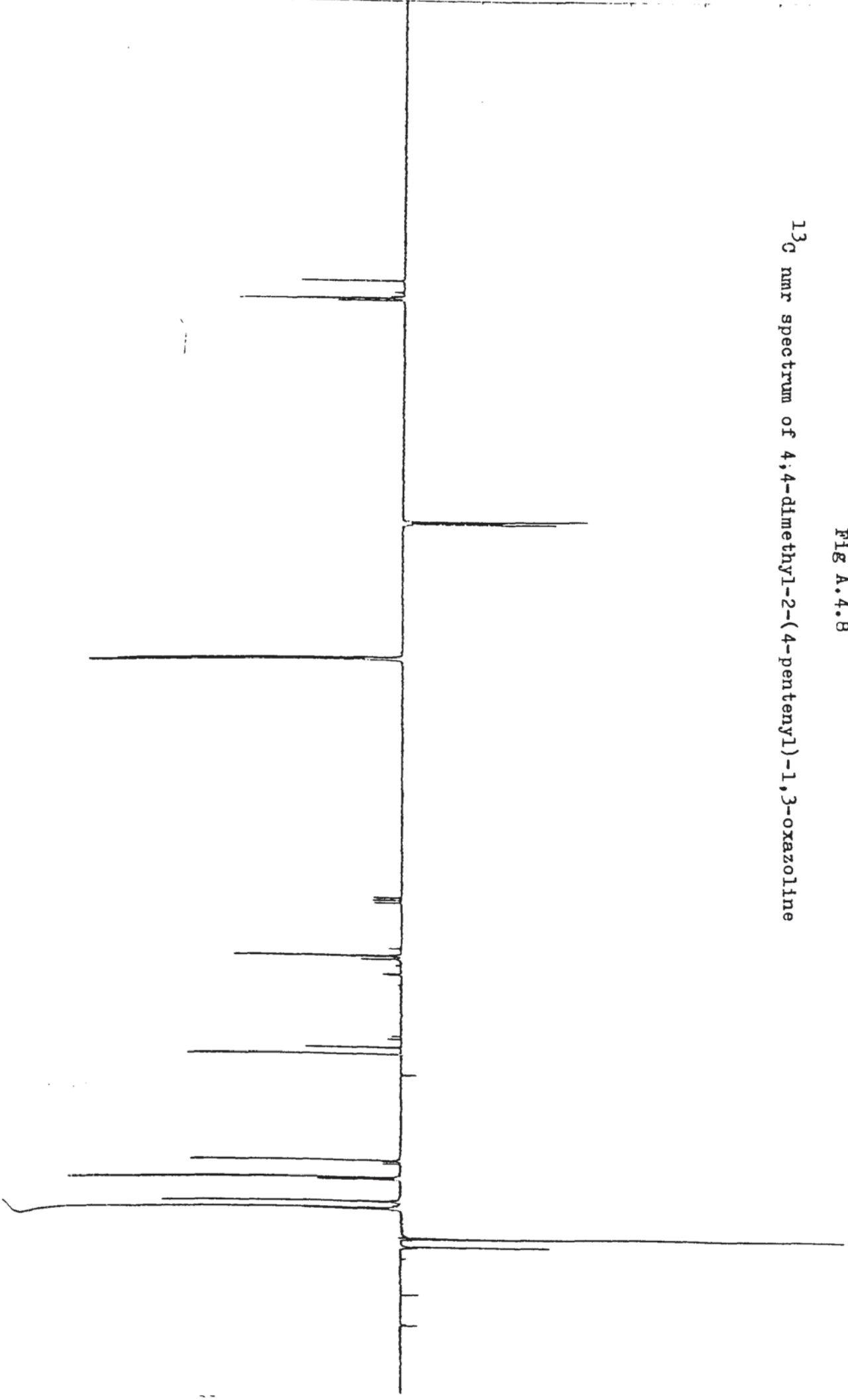
Mass spectrum of the hydroxyamide of 4,4-dimethyl-2-(4-pentenyl)-1,3-oxazoline

Fig A.4.10

HJ21HL14K   X10   Bgd-2   13-JUL-90 07.3470 00:31   12-2535   C14
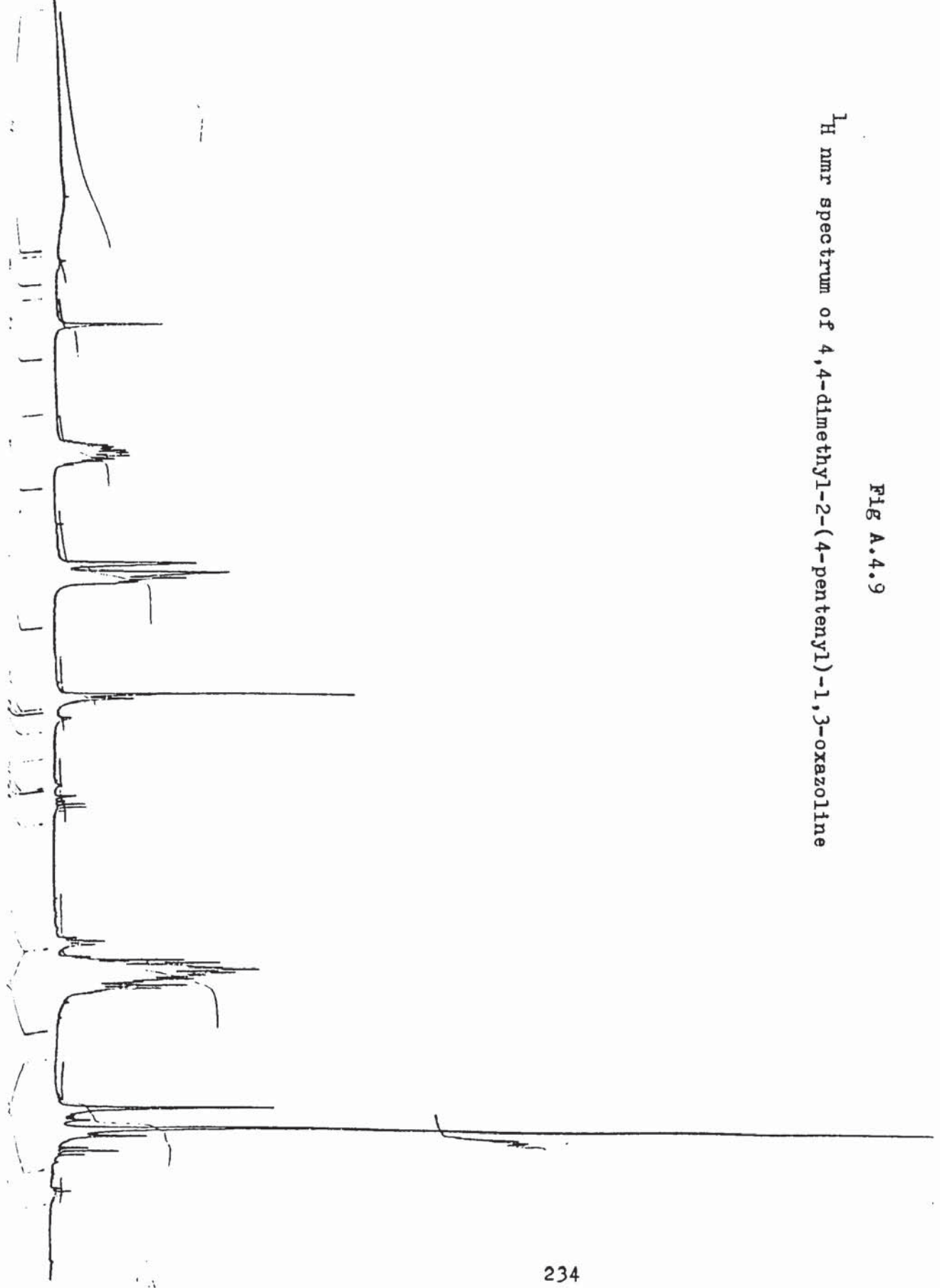
M=0   I=5.7v   Hm=0   TIC=9557600   Acnt: I.M. HOHN   Sys: ACE
  A.C.E. NH3   MW=171/100/89/119?   PT= 0   Cal: ICAL

Mass	% Base	
55	1.3	F
58	36.0	F
59	1.0	F
72	4.8	F
74	1.0	
90	1.8	
100	2.7	
140	5.7	F
153	1.2	F
154	19.0	F
155	2.4	F
172	100.0	F
173	10.1	F
186	1.5	F
186	3.3	F
254	46.2	F
255	6.9	F
311	1.2	

Fast atom bombardment data of the hydroxyamide of 4,4-dimethyl-2-(4-pentenyl)-

1,3-oxazoline   Fig A.4.11

Fig A.4.12

Mass spectrum of 4,4-dimethyl-2-(4-pentenyl)-1,3-oxazoline
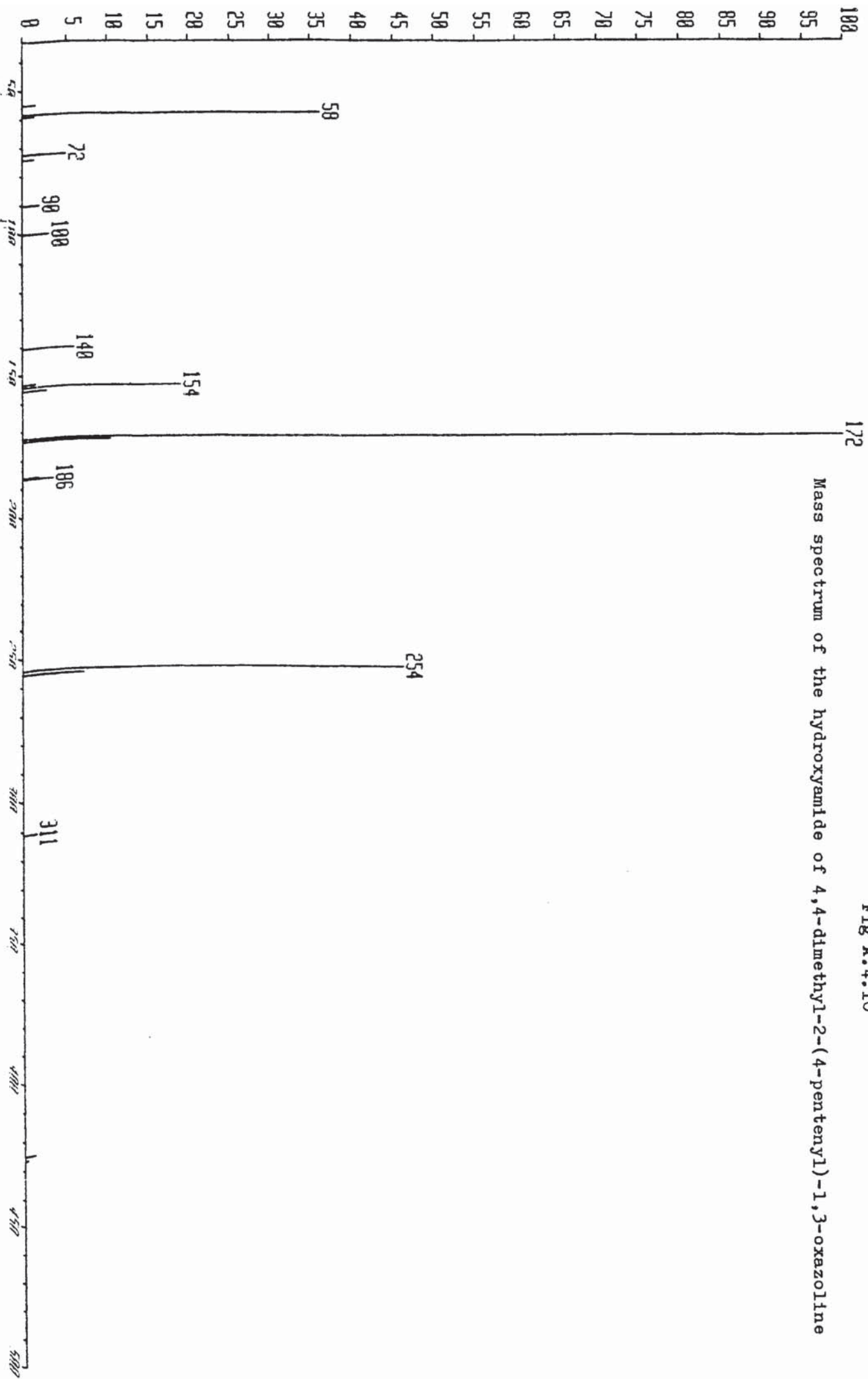
Mass	% Base	
39	1.3	
55	1.6	
58	49.7	F
59	1.1	F
71	1.2	F
72	5.5	F
100	2.9	
140	7.3	
153	1.9	F
154	33.4	F
155	4.0	F
172	100.0	F
173	10.5	F
186	3.2	
254	85.4	F
255	13.2	F
256	1.0	F
311	2.0	
425	2.9	
507	0.0	
766	0.0	

Fast atom bombardment of 4,4-dimethyl-2-(4-pentenyl)-1,3-oxazoline

Fig A.4.13
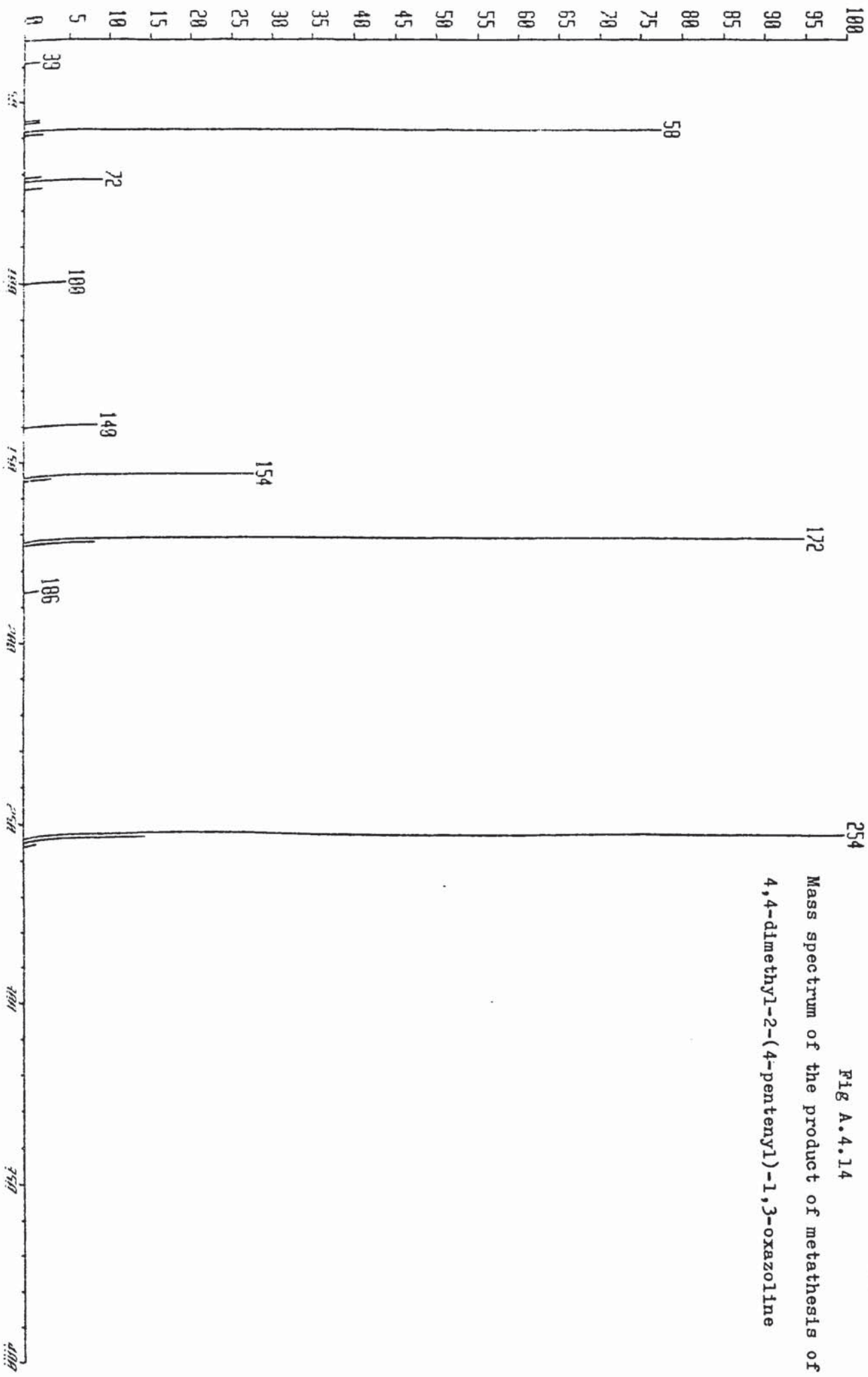
Fig A.4.14

Mass spectrum of the product of metathesis of
4,4-dimethyl-2-(4-pentenyl)-1,3-oxazoline

239

Mass	% Base	
39	1.4	
55	1.3	
56	1.3	
58	77.2	F
59	1.9	F
71	1.5	F
72	8.9	F
74	1.7	
100	4.5	
140	8.3	
154	27.5	F
155	2.8	F
172	94.9	F
173	8.0	F
186	1.4	
254	100.0	F
255	14.3	F
256	1.1	F

Fast atom bombardment of the product of the metathesis of 4,4-dimethyl-2-(4-pentenyl)-1,3-oxazoline

Fig A.4.15