METATHESIS OF EPOXY ALKENES

By

MJ Motaung

Thesis submitted in fulfilment of the requirements for the degree Master of Science at the Mafikeng Campus of the North-West University



North-West University
Mafikeng Campus Library

NWU LIBRARY

Supervisor: **Dr BB Marvey**

Co-supervisor: **Prof HCM Vosloo**

April 2008

MAFIKENG CAMPUS
2008 -08- 25
08/A0429
NORTH-WEST UNIVERSITY

DECLARATION

"I hereby declare that the thesis for the degree of Master of Science, at the North-West University hereby submitted, has not previously been submitted by me for a degree at this or any other university, that it is my own work in design and execution, and that all material contained herein has been duly acknowledged."



MAJOROBELA JOSEPH MOTAUNG

NWU LIBRARY

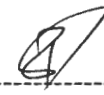
I further authorize the North-West University to reproduce this thesis by photocopying or by other means, in total or in part, at the request of other institutions or individuals for the purpose of scholarly research.



MAJOROBELA JOSEPH MOTAUNG

CERTIFICATION OF ACCEPTENCE FOR EXAMINATION

This thesis entitled "Metathesis of epoxy alkenes" written by Majorobela Joseph Motaung, Student Number 10444246 of the Department of Chemistry in the Faculty of Agriculture, Science and Technology is hereby recommended for acceptance for examination.



Supervisor	: Dr BB Marvey
Co-supervisor	: Prof HCM Vosloo (Potchefstroom Campus)
Department	: Chemistry
Faculty	: Agriculture, Science and Technology
University	: North-West University (Mafikeng campus)

ACKNOWLEDGEMENTS

I am grateful to my supervisor Dr Bassie Marvey for giving me an opportunity to do this highly demanding, but yet exciting project. I also gratefully acknowledge the assistance of my co-supervisor Professor Manie Vosloo for his valuable advice and discussions, as well as his critical assessment of this work.

I am thankful to Mr. Fanyana Mtunzi; Ms. Naledi Seheri; Ms. Keitumetse Segakweng; Ms. Minah Lebogo; Ms. Mpho Tlotleng; Ms Selinah Makhele and Ms Sofie Setshedi, for their emotional support throughout my study. I am also thankful to Mr. Jacob Rakosa; Mr. Enoch Malatji; Mr. Madoda Ngam, Ms Mamokete Mokoko and Mr. Aubrey Khunong for their technical support. I am sincerely grateful to Mr Johan Jordaan for his assistance with the MS analysis.

I thank Dr. Seloka Phirwa for his help with the interpretation of some of the strange results.

I am sincerely thankful to the Science Foundation department for supporting me emotionally, as well as financially, especially for funding my trips to the two CATSA conferences, where I presented two papers on my work.

I am sincerely thankful to the HOD of the chemistry department Dr. David Isabirye, for his intervention during my crisis.

My appreciations go to Mr Moletsane for editing this manuscript.

I am sincerely grateful to the Faculty of Agriculture, Science and Technology for their financial support.

I am grateful to the Almighty God for his Grace; Love; Care and above all His everlasting protection during my entire study.

Last but not least, I am truly grateful to my wife Lizzey and my two boys Itumeleng and Oreratile for their support and encouragement, but above all their forbearance throughout my study.

NWU LIBRARY

ACKNOWLEDGEMENTS

I am grateful to my supervisor Dr Bassie Marvey for giving me an opportunity to do this highly demanding, but yet exciting project. I also gratefully acknowledge the assistance of my co-supervisor Professor Manie Vosloo for his valuable advice and discussions, as well as his critical assessment of this work.

I am thankful to Mr. Fanyana Mtunzi; Ms. Naledi Seheri; Ms. Keitumetse Segakweng; Ms. Minah Lebogo; Ms. Mpho Tlotleng; Ms Selinah Makhele and Ms Sofie Setshedi, for their emotional support throughout my study. I am also thankful to Mr. Jacob Rakosa; Mr. Enoch Malatji; Mr. Madoda Ngam, Ms Mamokete Mokoko and Mr. Aubrey Khunong for their technical support. I am sincerely grateful to Mr Johan Jordaan for his assistance with the MS analysis.

I thank Dr. Seloka Phirwa for his help with the interpretation of some of the strange results.

I am sincerely thankful to the Science Foundation department for supporting me emotionally, as well as financially, especially for funding my trips to the two CATSA conferences, where I presented two papers on my work.

I am sincerely thankful to the HOD of the chemistry department Dr. David Isabirye, for his intervention during my crisis.

My appreciations go to Mr Moletsane for editing this manuscript.

I am sincerely grateful to the Faculty of Agriculture, Science and Technology for their financial support.

I am grateful to the Almighty God for his Grace; Love; Care and above all His everlasting protection during my entire study.

Last but not least, I am truly grateful to my wife Lizzey and my two boys Itumeleng and Oreratile for their support and encouragement, but above all their forbearance throughout my study.

ABSTRACT

This study investigated the metathesis of epoxy alkenes using the $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalytic system by (1) investigating the influence of various parameters such as the Sn:Re molar ratio, Re_2O_7 loading, reaction temperature, type of solvent, and substrate concentration on the activity, selectivity and stability of the $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalytic system; (2) investigating the influence of the epoxy and ester groups on the activity, selectivity and stability of the $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalytic system, with a view of understanding how the epoxy and ester groups, affect the activity and selectivity; (3) investigating the activity and selectivity of the $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalytic system in the cross-metathesis of (a) 1,2-epoxy-9-decene with 1-pentene, (b) 1,2-epoxy-9-decene with 1-hexene, (c) methyl-12,13-epoxy-9-octadecenoate with methyl oleate, (d) methyl-12,13-epoxy-9-octadecenoate with 1-pentene and methyl-12,13-epoxy-9-octadecenoate with 1-hexene.

Samples were collected at regular time intervals and analysed on GC using Ackman's method of molecular responses, and the corresponding peaks were characterised by GC-MS. The reaction mixture was also characterised by FTIR, and the spectra of both the pure substrates and the reaction mixtures were collected and analysed for any presence of hydroxylated products.

The 1 wt.% $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalytic system was highly active (ca. 99.8%) and selective (>95.5%) towards the diepoxy olefins in the metathesis of 1,2-epoxy-9-decene, which is a terminal epoxy olefin. However, the 2 wt.% Re_2O_7 system, with the second highest activity (ca. 99.0%), was optimised since it required less amount of the catalyst, which did not interfere with the mechanical stirring. Generally, the activity and selectivity of the $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalytic system decreased with increase in the Re_2O_7 loading. The double bond migration due to Brønsted acid sites on the $SiO_2{\cdot}Al_2O_3$ support, led to formation of dimerization products.

The activity of the 2 wt.% $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalytic system increased with increase in the Bu_4Sn content from Sn:Re molar ratio of 1 (ca. 50.0%) up to 3 (ca. 84.6%). However, the catalytic system was the most active at the Sn:Re molar ratio of 0.5 (ca. 99.0%). The selectivity of the catalytic system decreased with increase in the Bu_4Sn content. The 2 wt.% $Re_2O_7/SiO_2{\cdot}Al_2O_3/Bu_4Sn$ catalytic system was the most active (ca. 99.2%) and selective (>95.5%) at 20 °C. The 2 wt.% $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalytic system was the most active in chlorobenzene (ca. 99.2%) followed by hexane (ca. 60.0%). The selectivity of the 2 wt.%

$Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalytic system was higher in polar solvents such as dichloromethane (ca. 82%) and chlorobenzene (ca. 98.2%). The selectivity decreased with increase in the substrate loading.

In the cross-metathesis of 1,2-epoxy-9-decene with linear alkenes, The 2 wt.% $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$/ED/alkene catalytic system deactivated relative to the $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$/ED catalytic system. Furthermore, the activity increased with increase in the linear alkene chain length: $ED/C_5^{1=} < ED/C_6^{1=} < ED$. The selectivity of the $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalytic of the
$Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalytic system towards PMP also increased in the order: $ED/C_5^{1=} < ED/C_6^{1=} < ED$.

The 2 wt.% $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalytic system was also highly active (ca. 94.2%) in the metathesis of methyl vernolate, which is an internal epoxy alkene. However, the catalytic system was equally selective towards both isomerisation (ca. 44.8%) and secondary metathesis products (ca. 44.8%). The 2 wt.% $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$/MV catalytic system was deactivated relative to the 2 wt.% $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$/ED system. The deactivation was attributed to the interference of the epoxy group, due to its close proximity to the double bond; as well as competing reactions between the double bond, epoxy group, as well as the carboxylic acid group; for the metal carbene species responsible for metathesis reaction.

In the cross-metathesis of methyl vernolate with linear alkenes and methyl oleate, the activity of the 2 wt.% $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalytic system increased in the order: $MV/MO < MV/C_5^{1=} < MV/C_6^{1=} < MV$. The selectivity of the $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalytic system towards PMP decreased in the order: $MV/MO < MV/C_5^{1=} < MV < MV/C_6^{1=}$. Generally, there seemed to be a strong interaction between the epoxy group of MV and the double bond of the linear alkenes, which may have possibly led to the formation of high molecular compounds, which may have contributed to the deactivation of the $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalytic system, by clogging of the surface pours on the support.

TABLE OF CONTENTS

	PAGE
Title Page	i
Declaration	ii
Certification of Acceptance for Examination	iii
Acknowledgements	iv
Abstract	v
Table of Contents	vii
Abbreviations	xii
CHAPTER 1 INTRODUCTION AND AIM OF STUDY	**1**
1.1 Introduction	**1**
1.2 Problem statement	**3**
1.3 Aim of study	**4**
CHAPTER 2 LITERATURE SURVEY	**5**
2.1 Metathesis Reaction And Mechanism	**5**
2.1.1 Metathesis reaction	5
2.1.2 General mechanism	9
2.2 Catalyst Systems	**10**
2.2.1 Heterogeneous catalyst systems	12
2.2.2 $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnR_4$ catalytic systems	15
2.3 Chemistry of epoxides	**16**
2.3.1 Preparation of epoxides	17

2.3.2 Epoxy fatty acids 17

2.3.3 Reactions of epoxides 18

2.4 Metathesis of unsaturated fatty acid esters 21

2.5 Summary 29

CHAPTER 3 EXPERIMENTAL 30

3.1 Materials 30

3.2 Apparatus 30

3.3 Preparation and activation of catalysts 30

3.3.1 3 wt% $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalyst 31

3.3.2 2 wt% $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalyst 31

3.3.3 1 wt% $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalyst 31

3.3.4 0.5 wt% $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalyst 31

3.4 Metathesis reactions 32

3.4.1 Metathesis of 1,2-epoxy-9-decene 32

3.4.2 Cross-metathesis of 1,2-epoxy-9-decene with 1-pentene 32

3.4.3 Cross-metathesis of 1,2-epoxy-9-decene with 1-hexene 32

3.4.4 Metathesis of methyl oleate 32

3.4.5 Metathesis of methyl vernolate 33

3.4.6 Cross-metathesis of methyl vernolate with methyl oleate 33

3.4.7 Cross-metathesis of methyl vernolate with 1-pentene 33

3.4.8 Cross-metathesis of methyl vernolate with 1-hexene 33

3.5 Analysis 33

3.5.1 GC Analysis of reaction mixture 33

3.5.2 Characterisation of the reaction products by GC/MS 35

3.5.3 Characterisation of the reaction products by FTIR 35

CHAPTER 4 RESULTS AND DISCUSSIONS 36

4.1 METATHESIS OF EPOXY ALKENES 36

4.1.1 Metathesis of 1,2-epoxy-9-decene 36

4.1.2 The influence of the Sn:Re molar ratio 43

4.1.3 The influence of the Re_2O_7 loading 47

4.1.4 The influence of reaction temperature 50

4.1.5 The influence of solvent type 53

4.1.6 The influence of substrate concentration 57

4.2 CROSS-METATHESIS OF 1,2-EPOXY-9-DECENE WITH 1-PENTENE 59

4.3 CROSS-METATHESIS OF 1,2-EPOXY-9-DECENE WITH 1-HEXENE 69

4.4 METATHESIS OF METHYL OLEATE 77

4.4.1 Reaction products 78

4.4.2 The influence of Re_2O_7 loading 80

4.4.3 The influence of reaction temperature 82

4.5 METATHESIS OF METHYL VERNOLATE 85

4.6 CROSS-METATHESIS OF METHYL VERNOLATE WITH METHYL OLEATE 94

4.7 CROSS-METATHESIS OF METHYL VERNOLATE AND 1-PENTENE 99

4.8 CROSS-METATHESIS OF METHYL VERNOLATE AND 1-HEXENE 107

CHAPTER 5: CONCLUSIONS AND DISCUSSIONS 114

5.1 Metathesis of 1,2-epoxy-9-decene (ED) 114

5.1.1 Proposed mechanisms of reactions 114

5.1.1.1 Proposed mechanisms for SM of ED 114

5.1.1.2 Proposed mechanism for the dimerisation of ED 115

5.1.1.3 Proposed mechanisms for other reactions 117

5.1.1.4 Deactivation of $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$/ED 119

5.1.2 Influence of the Sn:Re molar ratio 119

5.1.3 Influence of Re_2O_7 loading 120

5.1.4 Influence of the reaction temperature 124

5.1.5 Influence of solvent type 124

5.1.6 Influence of substrate concentration 125

5.2 MECHANISMS FOR THE CM OF ED WITH 1-PENTENE ($C_5^{1=}$) AND 1-HEXENE ($C_6^{1=}$) 126

5.2.1 Proposed mechanism for the SM of $C_5^{=}$ and $C_6^{=}$ 126

5.2.2 Proposed mechanism for the CM of ED with $C_5^{1=}$ and $C_6^{1=}$ 127

5.2.3 Proposed mechanism for CM of $C_5^{1=}$ with $C_5^{2=}$ and $C_6^{1=}$ with $C_6^{2=}$ 127

5.2.4 Proposed mechanism for SM of $C_5^{2=}$ and $C_6^{2=}$ 129

5.2.5 Proposed mechanism for the reaction, which lead to the formation of other products 129

5.2.6 Proposed mechanism for the deactivation of the $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalytic system in the CM of ED with $C_p^{1=}$ (p = 5 or 6) 132

5.3 PROPOSED MECHANISM FOR THE SM OF MO 134

5.4 METATHESIS OF METHYL VERNOLATE 134

5.4.1 Proposed mechanism for isomerization of MV 134

5.4.2 Proposed mechanism for SM of MV and its isomers 135

5.4.3 Proposed mechanism for CM reactions 137

5.4.4 Proposed mechanism for the deactivation of the $Re_2O_7/SiO_2{\cdot}Al_2O_3/Bu_4Sn$/MV 141

5.5 CROSS-METATHESIS OF METHYL VERNOLATE WITH METHYL

NWU LIBRARY

OLEATE **143**

5.6 CROSS-METATHESIS OF MV WITH $C_5^{1=}$ AND $C_6^{1=}$ **143**

5.6.1 Proposed mechanism for the CM of MV with $C_5^{1=}$ or $C_5^{1=}$ 143

5.6.2 Proposed mechanism for the CM of MV with $C_5^{2=}$ or $C_6^{2=}$ 145

5.6.3 Proposed mechanism of CM of methyl-12,13-epoxy-10-octadecenoate and $C_5^{1=}$ 146

5.6.4 Proposed mechanism of CM of $C_6^{2=}$ and $C_6^{3=}$ 146

5.7 SUMMARY **147**

5.8 RECOMMENDATIONS **149**

REFERENCES **150**

APPENDICES **154**

ABBREVIATIONS

ADMET	Acyclic diene metathesis
amu	Atomic mass unit
bipy	Bipyridyl
Bu	Butyl
Bu_4Sn	Tetrabutyltin
$C_5^{1=}$	1-pentene
$C_6^{1=}$	1-hexene
$C_6^{2=}$	2-hexene
$C_5^{3=}$	3-hexene
CM	Cross-metathesis
DMP	Dimerisation products
ECR	Effective carbon responses
ED	1, 2-epoxy-9-decene
EIM	Electron impact mode
FID	Flame ionising detector
FTIR	Fourier transform infrared
GC	Gas chromatograph
m-CPBA	m-Chloroperoxy-benzoic acid
MO	Methyl oleate
MOT	Methyltrioxorhenium
MRF	Molecular response factor
MS	Mass spectroscopy
MV	Methyl vernolate
m/z	Mass to charge ratio
NHC	N-heterocyclic carbene
PMP	Primary metathesis products
R	Alkyl
RCM	Ring-closing metathesis
R & D	Research and development
ROM	Ring-opening metathesis
ROMP	Ring-opening metathesis polymerisation

RT	Room temperature
She	soluble epoxide hydrolase
SM	Self-metathesis
SMP	Secondary metathesis products
TFA	Trifluoroacetic acid
TON	Turnover number
XPS	X-ray photoelectron spectroscopy

CHAPTER 1

INTRODUCTION AND AIM OF STUDY

1.1 INTRODUCTION

With the continuing increase in global population, the increasing use of petroleum and petroleum products results in a progressive increase in the amount of carbon dioxide in the atmosphere, and the acidification of soil and water. Preservation of the environment is regarded as one of the most critical issues facing the global community.[1,2] For example, the extreme weather conditions being experienced by the global community are believed to be linked to carbon dioxide and other gases which contributes to global warming.[3]

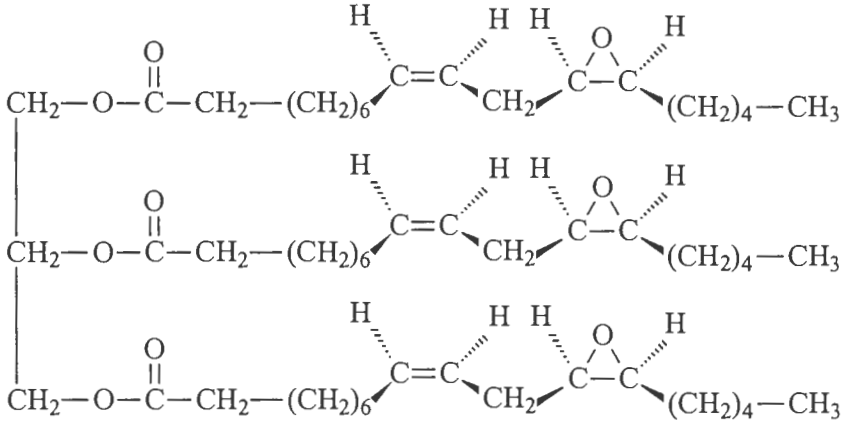
There are strong incentives for developing chemical processes from bio-sustainable resources to meet the demand for energy and other chemical products that do not have adverse effect on the environment. Fats and oils, which are produced from bio-sustainable resources and are easily biodegradable, offer more advantages, in contrast to petroleum-derived feedstock.[4] Catalytic processes can be used to convert these bio-sustainable resources, which consist of highly functionalised molecules, into highly priced derivatives used as food additives, commodities and fine chemicals.[5]

There is recognition of the importance of natural fats and oils as the main biological raw materials for chemical and technical applications, and many countries are supporting R&D activities along the whole production and processing chain. Chemists and other scientists are already exploiting renewable resources to meet the demand for energy and other chemical products, without adverse effect on the environment.[6]

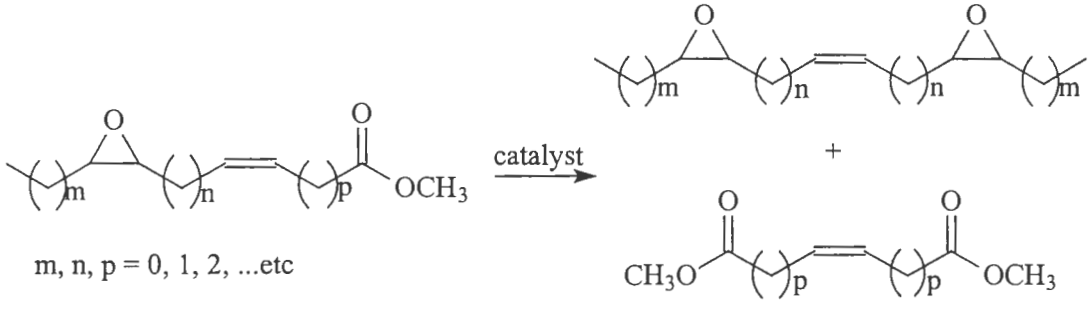
Metathesis chemistry is rapidly developing into one of the more powerful tools for converting natural fats and oils into highly priced derivatives, which could then be used to synthesise products including pharmaceuticals, cosmetics, polymers and fine chemicals.[4] There have been numerous advances in metathesis-based synthesis due to the development of structurally defined metathesis-competent alkylidene complexes.[7] With the discoveries of new, well-defined and mild catalysts, olefin metathesis has transcended its original application to polymer chemistry and has become a powerful synthetic tool used in the preparation of many target molecules.[8] For example, ring-closing metathesis (RCM) has become a proven way of generating various heterocycles and cycloalkenes, as well as providing numerous applications toward natural product synthesis.[7]

Epoxidised compounds are generally among the most important building blocks in synthesis owing to their chemical reactivity.[9] For example, epoxidised vegetable oils have become a rich source of epoxy-fatty acids that are potential raw materials for plasticizer and stabilizer.[10] Other products made from epoxidised vegetable oil are degradable lubricants and lubricant additives, epoxy resins, adhesives, insecticides and insect repellents, crop-oil concentrates, and carriers of slow-release pesticides.[10]

For example, Vernonia oil (structure shown below) is a feedstock for oleochemicals, whose major application is in the surfactant industry for the manufacture of soaps, detergents and is also used in research laboratories for the synthesis of chemical intermediates:[11]

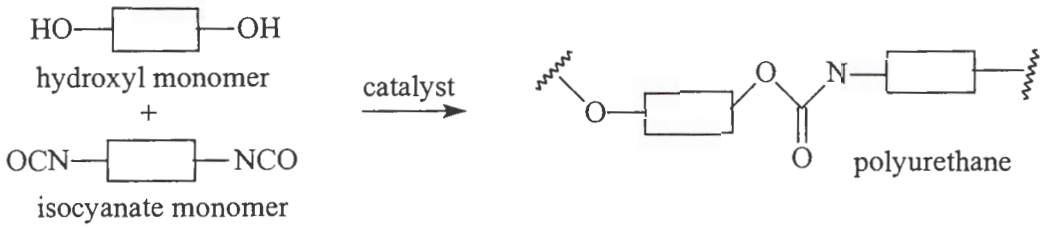


Olefin metathesis is a powerful synthetic tool in synthesising these highly priced epoxidised derivatives, which are often difficult to synthesise by other methods. For example, metathesis of epoxidised olefins presents a useful technique for a one step synthesis of unsaturated diepoxy olefins and dicarboxylic esters, as illustrated by reaction (1).



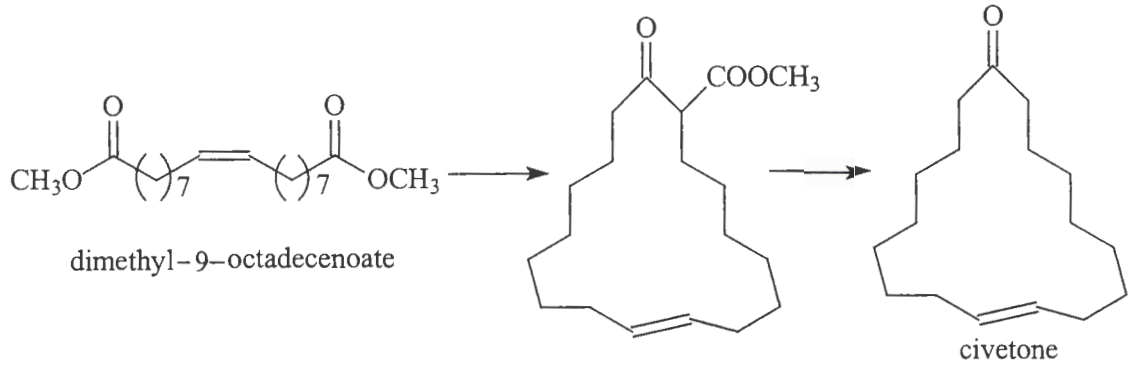
(1)

Diepoxy olefins can be converted to hydroxylated monomers, for the synthesis of polyurethane (reaction (2)), via an acid-catalysed ring opening reaction.[12]



(2)

Dicarboxylic esters are intermediates for the synthesis of polyesters, polyamides, macrocyclic compounds such as civetone, which have application in the perfume industry.[13] For example, the diester that can be obtained by metathesis of methyl-12,13-epoxy-9-octadecenoate (methyl vernolate) could be subjected to a Dieckmann condensation, followed by hydrolysis and decarboxylation, to give civetone as illustrated by reaction (3).



(3)

NWU LIBRARY

The use of olefin metathesis in organic synthesis has been directly correlated to improvements in metal-carbene catalysts.[14] The quest for highly active olefin metathesis catalysts has prompted considerable research efforts to develop olefin metathesis systems capable of tolerating a variety of highly functional groups, such as the epoxy group contained in the two substrates investigated in this study. However, selectivity issues have remained important challenge in the development of new and synthetically useful olefin metathesis catalysts,[15] because selectivity and reactivity in these types of reactions are dictated by the nature of the intermediates involved in the catalytic cycle.[16]

1.2 PROBLEM STATEMENT

In this study the activity and selectivity of the $Re_2O_7/SiO_2 \cdot Al_2O_3/Et_4Sn$ catalytic system for the metathesis of epoxy alkenes including 1,2-epoxy-9-decene and methyl-12,13-epoxy-9-octadecenoate (methyl vernolate) were investigated. Rhenium oxide supported on silica-alumina is a well-known catalyst for metathesis of simple alkenes.[17] When promoted with a suitable cocatalyst such as R_4M (see Figure 1), the $Re_2O_7/SiO_2 \cdot Al_2O_3$ catalyst is also suitable for the

metathesis of highly functionalised alkenes.[14,17] However, the selectivity still remains the main problem.[16]

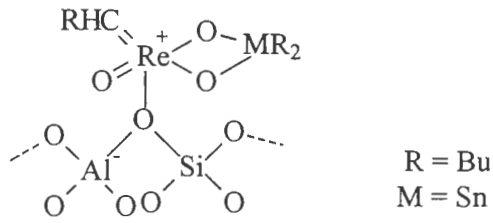


Figure 1. Structure of the promoted rhenium oxide catalyst supported on $SiO_2 \cdot Al_2O_3$.

The highly reactive epoxy group, which is contained in both the substrates studied, can open under acidic conditions presented by the $SiO_2 \cdot Al_2O_3$ support. This may lead to the catalyst being selective towards other products such as hydroxylated compounds, instead of the highly priced derivatives, as illustrated by reaction 1. The epoxy group may also deactivate the catalyst by interacting with the rhenium-carbene species, due to the induced positive charge on the rhenium metal.

1.3 AIM OF STUDY

This study aims to understand how the epoxy group affects the activity, selectivity and stability of the $Re_2O_7/SiO_2 \cdot Al_2O_3/Bu_4Sn$ catalytic system. The primary objectives are the following:

- To identify the best reaction conditions by investigating the influence of various parameters such as the Sn:Re molar ratio, Re_2O_7 loading, reaction temperature, type of solvent, and substrate concentration on the activity, selectivity and stability of the $Re_2O_7/SiO_2 \cdot Al_2O_3/SnBu_4$/1,2-epoxy-9-decene catalytic system.
- To investigate the activity and selectivity of the $Re_2O_7/SiO_2 \cdot Al_2O_3/SnBu_4$ catalytic system in the cross-metathesis of 1,2-epoxy-9-decene with (1) 1-pentene, (2) 1-hexene.
- To investigate the influence of parameters such as the Re_2O_7 loading and reaction temperature on the activity, selectivity and stability of the $Re_2O_7/SiO_2 \cdot Al_2O_3/SnBu_4$/ Methyl oleate catalytic system, in order to identify the best reaction conditions for the metathesis of methyl vernolate using $Re_2O_7/SiO_2 \cdot Al_2O_3/SnBu_4$.
- To investigate the activity and selectivity of the $Re_2O_7/SiO_2 \cdot Al_2O_3/SnBu_4$ catalytic system in the cross-metathesis of methyl vernolate with (1) methyl oleate, (2) 1-pentene and (3) 1-hexene.

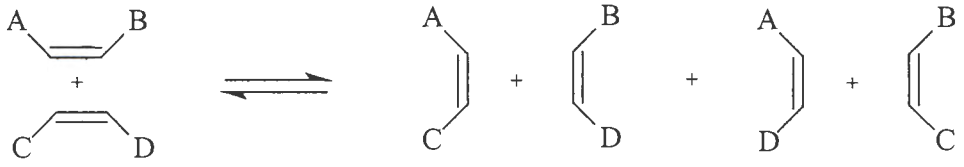
CHAPTER 2

LITERATURE SURVEY

2.1 METATHESIS REACTIONS AND MECHANISMS

2.1.1 Metathesis Reactions

Olefin metathesis was first observed in the 1950s by industrial chemists.[18] It refers to the metal-catalysed redistribution of carbon-carbon double bonds,[19] that is the carbon-carbon double bonds are rearranged in the presence of metal-carbene complexes. The general olefin metathesis reaction is illustrated by reaction (4).



(4)

It is clear from this reaction that olefins exchanging groups around the double bond can result in several outcomes. For example, straight swapping of groups between different acyclic olefins, is known as cross-metathesis (CM), if the olefins are the same, it is known as self-metathesis (SM); closure of terminal dienes to form large rings is known as ring-closing metathesis (RCM); formation of dienes from cyclic and acyclic olefins is known as ring-opening metathesis (ROM); polymerisation of cyclic olefins is known as ring-opening metathesis polymerisation (ROMP); and polymerisation of acyclic dienes is known as acyclic diene metathesis polymerisation (ADMET).[18]

2.1.1.1 Self-metathesis reactions

Self-metathesis is a reaction involving the interchange of atoms or groups of atoms between two similar molecules. Self-metathesis of propylene, for example, once found practical applications in the petrochemical industry as a means of converting surplus propylene into useful products (see reaction (5)).[20]



propylene ethylene butene

(5)

Eleuterio[18] obtained a mixture of propylene, ethylene, and butene from a propylene feed passed over a molybdenum-on-alumina catalyst at DuPont's petrochemicals department, in 1956. Chemists at other petrochemical companies obtained similar results. For example, Peters and Evering of Stanford Oil Co. reported similar results using molybdenum oxide-on-alumina treated with triisobutyl aluminium, in 1960. Banks and Baily of Phillips Petroleum (1964) used molybdenum hexacarbonyl supported on alumina.[18]

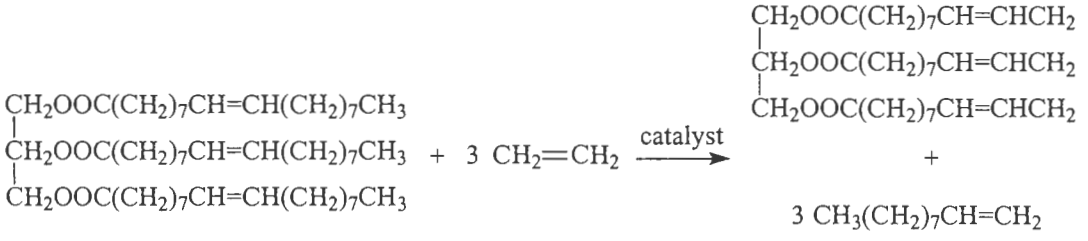
2.1.1.2 Cross-metathesis reactions

Cross-metathesis reaction is a reaction involving the interchange of atoms or groups of atoms between two different molecules. A cross metathesis reaction can either involve only acyclic compounds known as acyclic cross-metathesis or involve both cyclic and acyclic compounds.[20] A simple example of acyclic cross metathesis is the reversed Phillips Triolefin Process for the production of polymerisation-grade propylene from ethylene and 2-butene:[21]



butene ethylene propylene (6)

Reaction (6) is also known as ethenolysis since one of the reactants is ethene.[20] An example of a cross-metathesis involving both cyclic and acyclic compounds is the metathesis with ethylene of soybean oil (a mixture of unsaturated fatty acids) about the C_9-C_{10} double bond, which produces a triglyceride. This product is used as a feedstock for a detergent with good lather properties.[5]



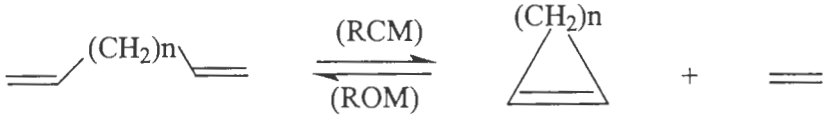
(7)

Reaction (7) illustrates the metathesis reaction between an oleic acid triglyceride molecule and an ethylene molecule; to produce a value added shorter-chain triglyceride. This detergent feedstock can be converted to a linear-chained detergent which is believed to be more environmentally friendly than branched-chained, or benzene based detergents.[22] An inspection of the mixture of these unsaturated fatty acid chains found in soybean oil suggests that any or all of the following chemicals can be synthesised: 1-decene; 1-heptene; 1-butene; 1,4,7-decatriene; and

1,4-decadiene. Vernonia oil also contains a similar triglyceride molecule. However, there are epoxy groups on carbons 12 and 13. This shows that vernonia oil can undergo a similar metathesis reaction with ethylene, to produce the same shorter-chain triglyceride. However, the reaction will produce epoxidised olefins instead of normal olefins that are produced from soybean oil.

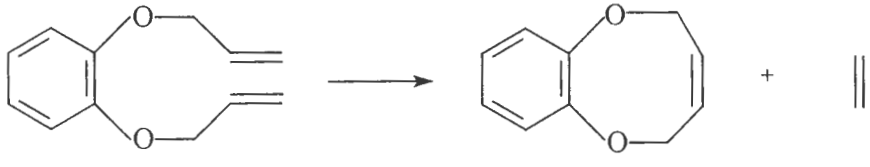
2.1.1.3 Ring-closing and ring-opening metathesis reactions

Ring-closing metathesis represents a process in which an acyclic diene is cyclised to produce a cycloalkene.[23]



(8)

Many useful cyclic intermediates containing functional groups or hetero-atoms (Si, O, N) have been prepared by application of the ring-closing metathesis reactions.[18] RCM is favoured for the production of unstrained rings and is driven both entropycally and by the elimination of a volatile alkene.[24] Since RCM and ROMP processes involve equilibria, the RCM reaction is more favoured by running the experiment at low dilution so that most of the reactions are intra-molecular rather than intermolecular. In addition, the catalysts should be selected that have good reactivity with terminal alkenes, but low reactivity with internal alkenes.[24] Intra-molecular RCM reactions tend to be favoured when the product is a 5-, 6-, 7-, or sometimes an 8- or higher-membered, ring compound,[3] as illustrated by reaction (9):

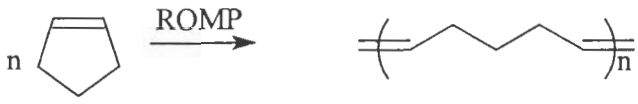


(9)

The reverse of reaction (8) results in ROM, and this is only favoured at very high alkene concentrations, or more commonly with strained alkenes.

2.1.1.4 Ring-opening metathesis polymerisation (ROMP)

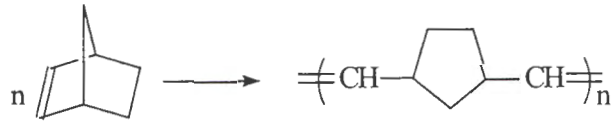
Ring-opening metathesis polymerisation describes metathesis of strained cycloalkenes to produce unsaturated polymers.[7] Reaction (10) below illustrates a ROMP reaction:



(10)

Care must be exercised in selecting a catalyst for ROMP, because if the catalyst is too active it can metathesise the unstrained alkene bonds in the polymer growing chain (back biting), and thus reduce the molecular weight and increase the molecular weight distribution (polydispersity).[20,24] A cyclic dimer of cyclooctene, an intermediate in the perfume industry, can be prepared by lowering the concentration of monomer, which favours intra-molecular metathesis reactions (back biting) .[20]

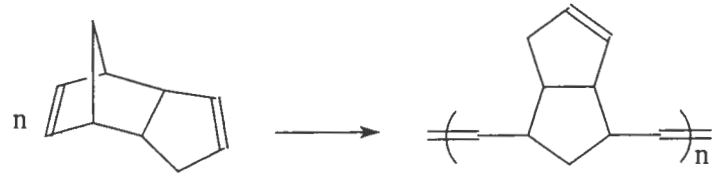
The high-trans polymer of cyclopentene formed in reaction (10) was once expected to find use as an all-purpose elastomer, because raw materials are cheap and the product had properties similar to those of natural rubber.[20] However, other high-trans polymers such as those formed from norbornene, reaction (11), and cyclooctene, reaction (12), have penetrated the market as components of elastomeric products. Also the ROMP of endo-dicyclopentadiene, reaction (13), is used to produce large objects by reaction injection moulding.[20]



(11)



(12)



(13)

2.1.1.5 Acyclic diene metathesis

Acyclic diene metathesis involves the metathesis of α,ω-dienes to produce polymers,[24] as illustrated by reaction (14):

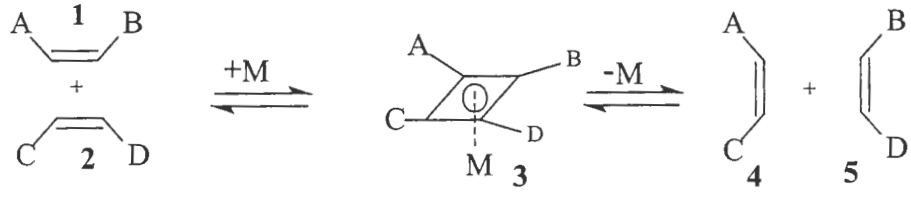


(14)

Intermolecular metathesis reactions, such as reaction (14), lead to high polymers and proceed very cleanly when initiated by metal carbene complexes.[16] This method was pioneered by Wagener and Boncella at the University of Florida, and uses α,ω-dienes to produce polymers.[18] The reaction is also driven by the removal of ethylene from the reaction mixture, with a nitrogen purge. A possible means of recycling automobile tyres involves the reverse of reaction (14), i.e. the reaction of an unsaturated polymer with excess ethylene in the presence of a metathesis catalyst. However, it is still not clear if the method will be commercially viable, because a highly active catalyst is needed that can tolerate the functional groups in tyres (e.g. sulphur, carbon black, etc.).[24]

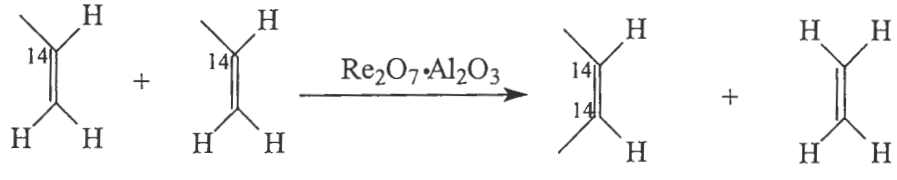
2.1.2 General mechanisms of olefin metathesis

In 1967, Calderon[25] performed experiments with butene and deuterated 2-butene in the presence of a homogeneous catalyst. He proposed that the mechanism involved a cyclobutane intermediate (**3**) complexed to the metal.[26]



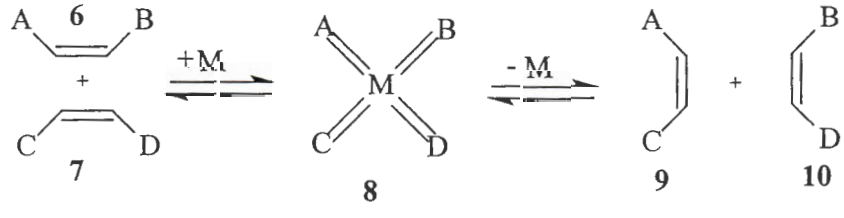
(15)

In 1968, Mol[27] provided independent evidence about the nature of the cleavage and the rearrangement of the double bonds, by using propylene and (^{14}C) propylene in the presence of a heterogeneous catalyst.



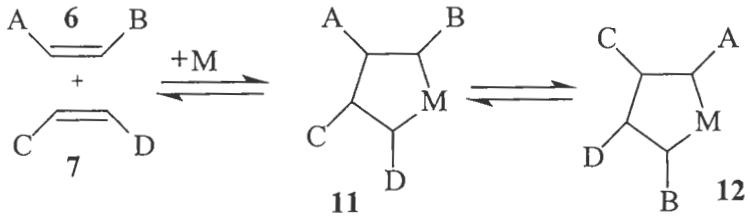
(16)

In 1971, Pettit[28] proposed that a tetramethylene complex (**8**) is formed as an unstable intermediate in which four methylene groups are bonded to a central metal atom.



(17)

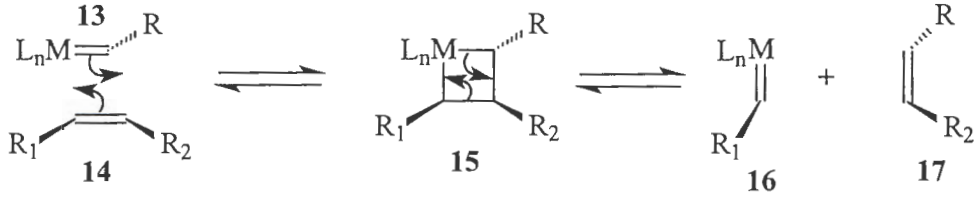
In the early 1970s, Grubbs,[29] proposed a different mechanism. He suggested that the redistribution of groups around the double bonds was due to a rearranging metallacyclopentane intermediate (**11**):



(18)

He later suggested that one mode of rearrangement could lead to the formation of a cyclobutane complexed to a metal carbene.[30]

In 1971, Herrison and Chauvin[20,31] suggested a metal carbene or metallacyclobutane mechanism for olefin metathesis. They proposed that the reaction involved a [2+2]- cycloaddition reaction between an initiating metal carbene (**13**) and the olefin (**14**) to give a metallacyclobutane intermediate (**15**), which then rearranges to form a new olefin (**17**) and a new metal carbene (**16**) that propagates the reaction, as illustrated below:[22]



(19)

Since such cycloaddition reactions between two alkenes to give cyclobutanes is symmetry forbidden and occurs only photochemically,[24] this mechanism was disputed for a long time because of lack of information in the organometallic literature to support it. However, it was suggested that this symmetry is broken by the presence of d-orbitals on the metal carbene and the reaction thus become quite facile.[24] By 1975 the evidence in favour of the metal carbene mechanism had become so compelling that the earlier mechanisms were discarded.[20]

2.2 CATALYST SYSTEMS

This section deals with different types of catalyst systems. Alkene metathesis is initiated by a large number of catalyst systems, which consist mainly of two, three or more components that may be heterogeneous or homogeneous.[3] However, it is difficult to know whether the catalytic activity resides in the homogeneous or the heterogeneous part. The activity of a particular catalyst system was found to be dependent on a number of factors including:[20]

1. The proportion of the components: the activity over rhenium oxide-based catalysts supported on silica-alumina was found to increase with Re_2O_7 loading since not only the Lewis acid sites interact with the ReO_4 groups, but also the surface hydroxyls are substituted by ReO_4 groups.[32]
2. Pretreatment procedures, especially for catalysts supported on Al_2O_3 or SiO_2. The Lewis acidity, Brønsted acidity or both depend on the pretreatment conditions of the $SiO_2 \cdot Al_2O_3$ support.[33] During the activation of the rhenium oxide-based catalysts, the ReO_4^- ions attach to the centres formerly occupied by the bridge OH groups.[33,34] This pre-treatment is also presumed to bring the supported catalyst into the most favourable oxidation state for the formation of the initial metal carbene.[20]
3. The order in which the components are mixed. In the case of rhenium oxide-based catalysts supported on silica-alumina, the best catalyst is obtained when ReO_4^- species react with the Brønsted acid sites on the support followed by promotion with Bu_4Sn.[35]
4. In the case where the alkene is added last, the period of incubation before adding the alkene. Catalyst systems such as $WCl_6/EtAlCl_2/EtOH$ reach maximum activity very quickly after mixing. The alkene should therefore be added before the cocatalyst ($EtAlCl_2$). Other systems, like $MoCl_2(NO)_2(py)_2/Et_3Al_2Cl_3$, require an hour or so to develop their full activity; here one should premix the catalyst components and wait before adding the alkene.[20]

NWU LIBRARY

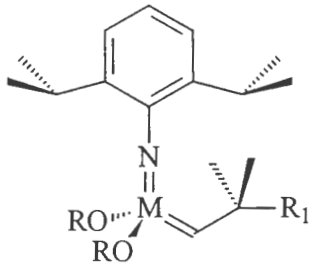
The most important catalyst systems for alkene metathesis are derived from compounds of the transition elements shown in Table 1:[20]

Table 1. Elements used for preparation of compounds used in catalyst systems for alkene metathesis.

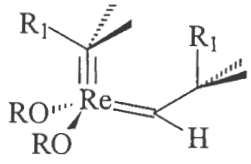
IVA	VA	VIA	VIIA	VIII	
Ti	V	Cr			Co
Zr	Nb	**Mo**	Tc	**Ru**	Rh
	Ta	**W**	**Re**	Os	Ir

The elements shown in bold type are generally regarded the most effective.[20] The most important homogeneous catalysts are the "third generation" Schrock catalyst systems, which are known as Schrock carbenes and the "fourth generation" Grubbs catalyst systems. These Schrock carbenes are typically found on high oxidation state metal complexes (early to mid transition metals), and

tend to be nucleophilic at the alpha carbon atom because of the polarised metal-carbon double bond, whereby a partial negative charge is assigned to the alpha carbon atom.[24] The most important of these Schrock catalyst systems are the commercially available, highly active Mo, W and Re-based catalysts shown in Figure 3.[22,36] The W complex is very reactive, but the Mo complex is more versatile.[36] The molybdenum complex is very sensitive to oxygen and moisture as well as protic compounds (alcohols, ketones, aldehydes, etc.).



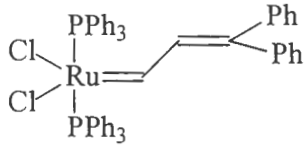
18



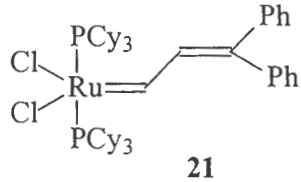
19

M = Mo, W
R = alkyl, aryl
R_1 = Me, Ph

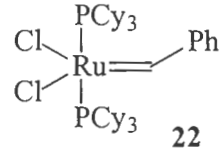
In the early 1990's Grubbs[37,38] developed a series of Ru catalysts that differ from the previous generation catalysts in several ways. First, the metal is not in its highest oxidation state and is supported by phosphine ligands. Secondly, these catalysts are so tolerant of functional groups that they can operate in the presence of water. However, such functional group tolerance comes at the expense of lower metathesis rates than Schrock catalysts.[37,38] The lower-valent, late transition metal complexes are expected to be more tolerant of electrophilic and protic functional groups because the carbene would be less nucleophilic.



20



21



22

2.2.1 Heterogeneous catalyst systems

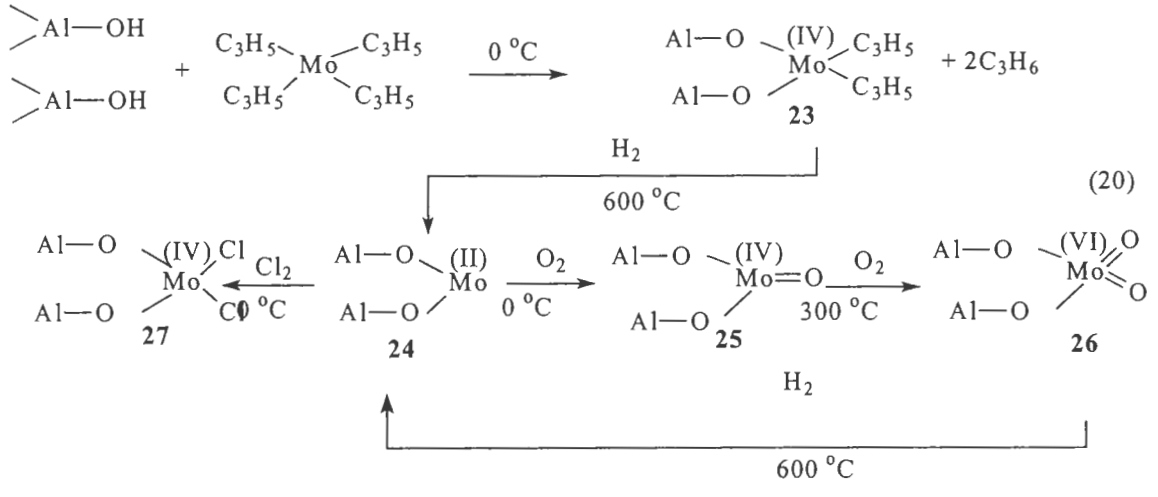
Heterogeneous metathesis catalysts are generally derived from a transition metal oxide, or an organometallic complex, which is fixed on a porous inorganic support. Many examples of heterogeneous catalysts are derived from the metals in Table 1, for example, MoO_3/SiO_2; WO_3/SiO_2; Re_2O_7/Al_2O_3 and $Re_2O_7/SiO_2{\cdot}Al_2O_3$. TiO_2 is included in a MoO_3/Al_2O_3 catalyst to increase its activity for the metathesis of propylene and 1-butene, although not without a concurrent double-bond shift reaction.[20] Alkema, in 1970, brought about the metathesis of pent-2-ene using an Al_2O_3-supported zirconium catalyst.[20]

Banks, in 1969, showed that supported vanadium oxide catalyses alkene metathesis reactions but they are not selective.[20] But both Nakamura and Xu[20] showed in 1977 and 1985, respectively, that vanadium oxide, in combination with Re_2O_7, can produce a very active catalyst system, with alumina as the support. In 1993, Ahn[3] showed that when V_2O_5/Al_2O_3 is preheated to about 575 °C and treated with Me_4Sn it is an effective catalyst system for propene metathesis at 25 °C. In 1957, Eleutrio[20] initiated the ROMP of cycloalkenes by chromium oxide catalysts supported on Al_2O_3 and activated by $LiAlH_4$; the yields are however very low.

Supported MoO_3 catalysts have received much attention because of their wide application in industrial petrochemical processes, including the Shell Higher Olefin Process (SHOP).[20] Their surface properties and catalytic activity are strongly influenced by the specific oxide support, surface Mo-oxide content, calcination temperature, etc. These catalysts are prepared in one of the following ways:[20]

1. by impregnation of the support (Al_2O_3, SiO_2, TiO_2) with molybdate solution,
2. by treatment of the support with $Mo(CO)_6$, and
3. by treatment of the support with organomolybdenum compound.

In each case the supported Mo compound is subjected to an appropriate heat treatment coupled with oxidation (O_2) or reduction (CO, H_2, C_2H_6) to bring it into an active state. A widely used supported catalyst is $(\pi\text{-}C_3H_5)_4Mo$, whose activity is attributed to Mo being present entirely in its highest valence. The Mo catalyst attaches itself to the support by replacing two hydroxyl groups on the surface, thereby generating two molecules of propene as shown by reaction (20).

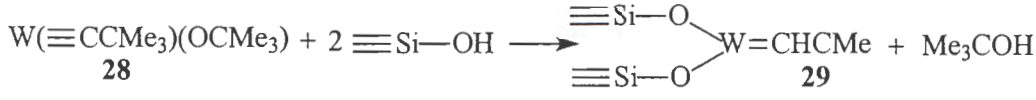


Of these compounds, only those in oxidation state IV, namely **23**, **25** and **27**, which have been characterised by X-ray photoelectron spectroscopy (XPS) as having binding energies of 235.3 and 232.5 eV, show appreciable metathesis activity for propene at 0 °C.[20] Neither **24** nor **26** is active.

Reaction (20) is more facile when the support is more acidic. For example, the following order is observed for the rate of metathesis of propene: $SiO_2 \cdot Al_2O_3 > Al_2O_3 >> SiO_2$, which corresponds to the decreasing Bronsted acidity of the support. The silica analogue of **26** is a highly active and stable catalyst for the metathesis of hex-2-yne at 350 °C with a selectivity of 90-100%, and the activity is several times greater than that of a catalyst prepared by impregnation method.[20]

These catalyst systems for alkene metathesis are more widely used than all the others together.[20, 39] These catalysts are especially effective for internal and cyclic alkenes, and W-based catalysts for the metathesis of terminal alkenes are comparatively few in number.

Tungsten(IV) carbyne complexes exhibit varying degree of metathesis activity, depending on the ligands.[20] For example, W (≡$CCMe_3$)$(Cl)_3$(dme) catalyses the metathesis of linear and cyclic alkenes at 20 °C, whereas W(≡$CCMe_3$)$(OCMe_3)$ only becomes active for the metathesis of oct-1-ene in hexane at 69 °C after reaction with SiO_2.[20] Reaction (21) illustrates the reaction of the carbyne complex **28** with the weakly Bronsted-acidic Si-OH protons, resulting in a Schrock-type carbene complex **29**.



(21)

Al_2O_3 as a support also gives good activity. However, the highest conversions are observed with $SiO_2 \cdot Al_2O_3$ as a support, but the selectivities are poor because of the double-bond migration in the substrate. This results in the cross-metathesis of the substrate with its isomers.[20] WO_3/Al_2O_3 has a much lower activity towards alkene metathesis than MoO_3/Al_2O_3 owing to the fact that WO_3/Al_2O_3 is more difficult to reduce. Also, after standard activation, the performance of WO_3/Al_2O_3 is not as good as than that of MoO_3/SiO_2.[20]

Rhenium based catalyst systems are generally based on Re_2O_7, $ReCl_5$, or a carbonyl or other complex compounds.[20] Propylene metathesis by Re_2O_7 supported on Al_2O_3, is best achieved by pre-treating the catalyst with H_2 or CO at 500 °C followed by exposure to O_2 at room

temperature.[20] This pre-treatment is presumed to bring the surface compound into the most favourable oxidation state for the formation of the initial metal carbene.[20] Both Nakamura in 1982, and Xu in 1986, showed an alternatively route whereby, the catalyst is treated first with propylene at 450 °C and then with oxygen at 80 °C. [20]

Methyltrioxorhenium (MOT, $MeReO_3$), which can be used as heterogeneous (MOT supported on a Al_2O_3 or SiO_2) and homogeneous catalysts, catalyses the metathesis of functionalised alkenes such as oleate at room temperature in methylene chloride.[36] MOT catalyst can be prepared from Re(IV) oxide and Me_4Sn as shown by reactions (22) and (23) respectively.

$$ClSiMe_3 \xrightarrow{Re_2O_7} 2\,ClReO_3 \xrightarrow{Me_4Sn} 2\,MeReO_3 + Me_3SnCl \qquad (22)$$

$$Re_2O_7 + Me_4Sn \longrightarrow 2\,MeReO_3 + Me_3SnOReO_3 \qquad (23)$$

When the oxide is supported on Al_2O_3, the reaction may be carried out at 20-100 °C with the substrate alkene either in the gas phase or in solution. This reaction takes place with high selectivity and the products can be easily recovered.[20] For example, this catalyst brings about the metathesis of soybean oil at 100 °C and 15 atm and is used as a feedstock for the detergent industry.[21]

2.2.2 $R_2O_7/SiO_2{\cdot}Al_2O_3/SnR_4$ catalytic system

Rhenium-based metathesis catalysts are the most active heterogeneous catalysts in olefin metathesis and have many practical applications.[40] Re_2O_7 supported on $SiO_2{\cdot}Al_2O_3$ is a highly active metathesis catalyst.[34] In the presence of a suitable cocatalyst, such as R_4Sn, it is an excellent metathesis catalyst for functionalised olefins.[34]

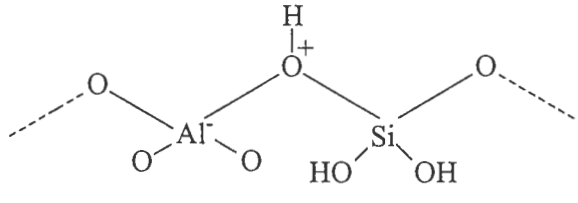


Figure 2. The structure of silica-alumina, $SiO_2{\cdot}Al_2O_3$.

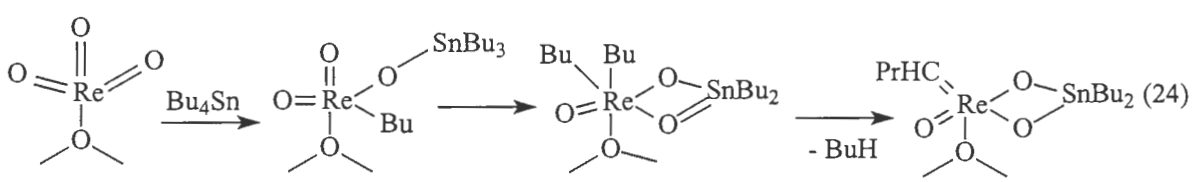
Figure 2 shows that there are two types of OH groups on the silica-alumina support, which leads to Brønsted acid character.[34,41] One type of OH is directly attached to silicon, while the other is bridged between silicon and aluminium.[34,41] The presence of these strong acid sites on the

catalyst is responsible for the double bond isomerisation of alkenes, and the migration of double bonds occurs on both Brønsted and Lewis acids.[44]

Xiaoding et al. [34,41] showed in 1986, that the ReO_4^- ions attach to the centres formerly occupied by the bridged OH groups during the activation of the $Re_2O_7/SiO_2{\cdot}Al_2O_3$ system. Although the use of silica-alumina as support leads to a higher activity, the selectivity is however lower.[14] The improvement in the catalytic activity is further enhanced by promotion with R_4Sn.[42] The catalytic activity of supported rhenium complexes can also be increased by treating the support with phosphate ions prior to impregnation with rhenium complexes.[32,45] However, in 1999, Mathew et al.[46] found that the addition of phosphate ions on the silica-alumina before calcinations did not show any marked influence in the self-metathesis products resulting from metathesis of 1-octene.

Although the selectivity of self-metathesis reactions can be improved by the addition of cesium ions to the support, this addition lowers total activity due to an decrease in side reactions.[47,48] These findings were confirmed by the results obtained by Mathew et al.[46] in the metathesis of 1-octene.

The metal carbene species formed by the interaction of Re_2O_7 with tetrabutyltin, as proposed by Buffon et al.,[43] is illustrated by reaction (24).



(24)

Buffon et al.[42] suggested that the promoter is involved in the formation of new initiating metal-alkylidene species (**30**) via double bond alkylation of the rhenium, followed by α-H elimination.

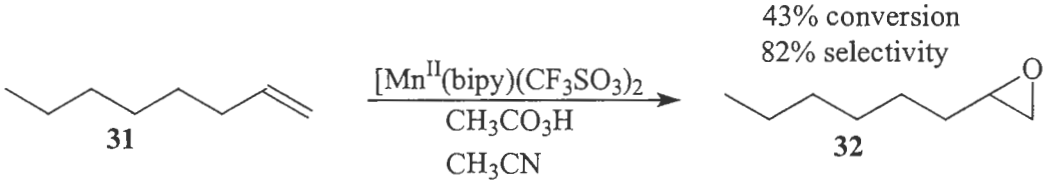
2.3 CHEMISTRY OF EPOXIDES

Epoxy chemistry was first reported in 1859 when Wurtz synthesised ethylene oxide from ethylene chlorohydrin using aqueous base.[49] The "epoxy" name generally refers to a ring containing oxygen. This section deals with the general chemistry of epoxides. For example, the methods of preparation of epoxides, the occurrence of natural epoxy fatty acids and the reactions

of epoxides are discussed. The chemistry of vernonia oil is of interest since it is one of the substrates that will be used in this project.

2.3.1 Preparation of epoxides

Although there are many methods for preparation of epoxides, but an important preparative methodology that has developed rapidly over the last few years is the Mn mediated epoxidation of alkenes (the Jacobsen-Katsuki epoxidation).[50] For example, 1-octene (**31**) is converted to its corresponding epoxide (**32**) in practically quantitative yield within 5 min when it is exposed to peracetic acid in the presence of the Mn(II)-bipyridyl complex at 0.1 mol% catalyst loading, as illustrated by reaction (25).



31 **32** (25)

2.3.2 Epoxy fatty acids

Epoxy fatty acids are valuable as industrial feedstocks and may also be of significance to plant pest defence.[51] Certain wild plants are known to have epoxygenases that transform fatty acids into epoxy fatty acids that accumulate in seed oil. The natural species are all C18 compounds, saturated or unsaturated.[51] For example, vernonia galamensis and lagscae contain an epoxy fatty acid known as vernolic acid, which is also known as 12,13-epoxy-9-octadecenoic acid.

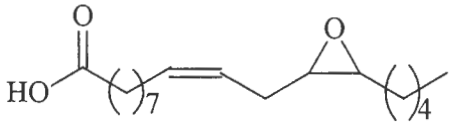
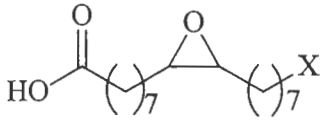


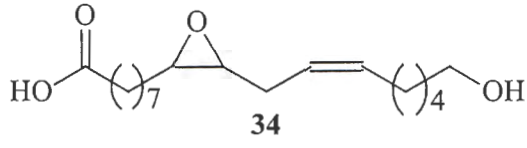
Figure 3. The structure of vernolic acid.

On prolonged storage, these epoxy fatty acids can be transformed into hydroxy derivatives such as 9,10-epoxystearic (**33**) and 9,10-epoxy-12-octadecenoic (**34**) acids. These are found in sunflower seeds.



33

X = CH_2OH, CHO, COOH



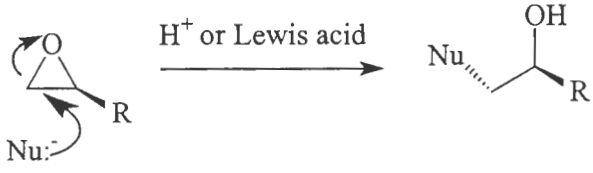
34

Vernonia seed contains a very active lypolytic enzyme, lipase, which breaks down the triacylglycerols to give free fatty acids.[11] Epoxy oils are widely used in plasticiser and additives in flexible polyvinyl chloride resins. A potential market use might be as a drying agent in reformulated oil-based or alkyd-resin paints.[52] The composition of vernonia oil has superior qualities compared to these other oils, since the drying agents currently used are major pollutants. Vernonia has "reactive dilutant" oil properties that reduce these pollutants.[52] It is characterised by very low viscosity, low melting point, homogeneous molecular structure, low drying temperature, and potentially low price.[53]

2.3.3 Reactions of epoxides

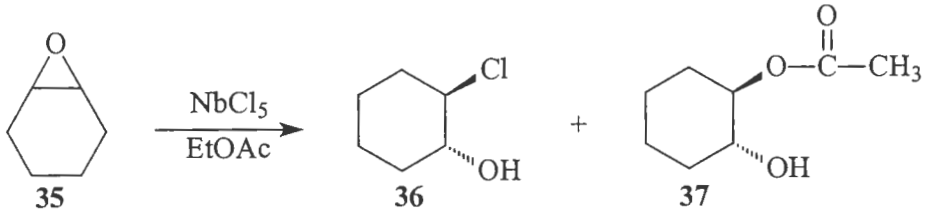
Epoxy groups, even hindered ones such as those in vernonia oil, are known to have a relatively high degree of reactivity when compared with many other functional groups.[1] This is due to a highly strained epoxy ring.

The epoxy ring may open under acidic conditions, leading to a Wittig type reaction as illustrated by reaction (26).



(26)

Opening of epoxides is frequently involved in the synthesis of natural products when boron trifluoride etherate or niobium pentachloride (which is a stronger acid) are used as Lewis acids.[54] For example, Constantino et al.[54] reacted 1,2-epoxycyclohexane (**35**) with $NbCl_5$ dissolved in anhydrous ethyl acetate, at room temperature under N_2 atmosphere, and obtained a mixture of products (**36** & **37**) as illustrated by reaction (27).

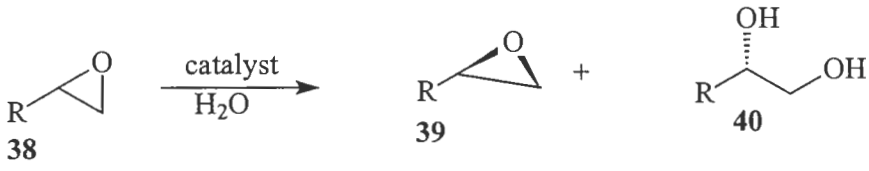


35 **36** **37**

(27)

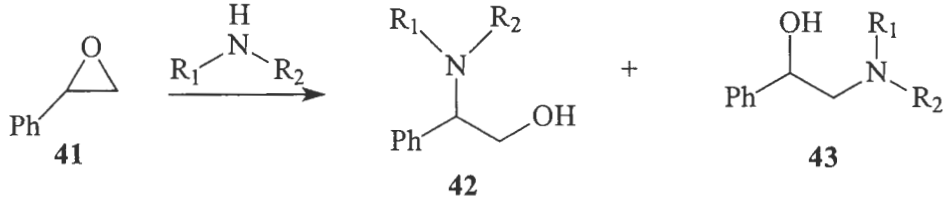
Epoxides also undergo hydrolysis, which is a well-known reaction that has been exploited for various syntheses. For example, racemic epichlorohydrin (**38**) was resolved in the presence of a

suitable catalyst and excess water to form compounds **39** and **40** as illustrated by reaction (28).[50,55]



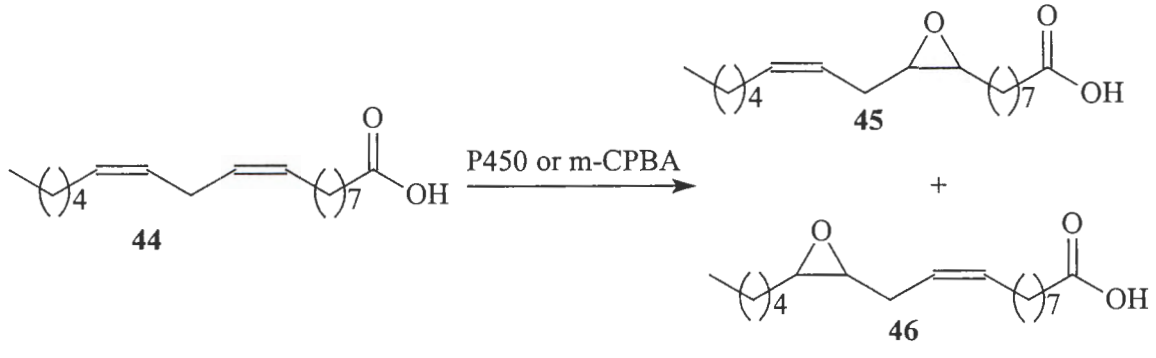
(28)

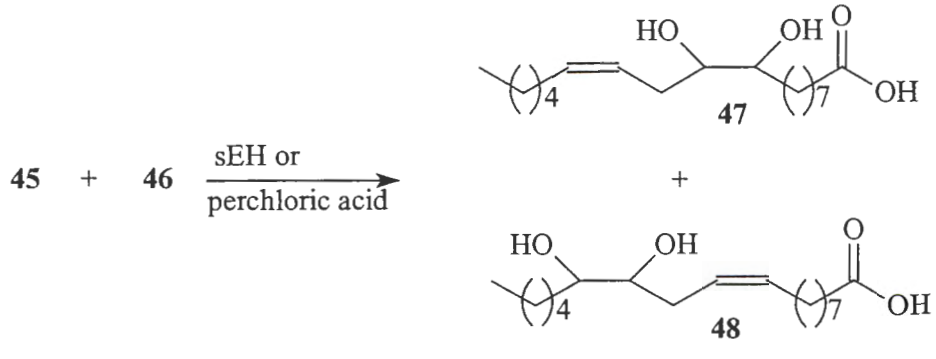
Epoxides also undergo nucleophilic reactions with amines, forming ethanolamine derivatives. For example, styrene oxide (**41**) undergoes ring opening in the absence of catalyst under strictly thermal conditions (90 °C in a sealed tube) to give predominantly the amino-alcohol (**42**), as illustrated by reaction (29).[50]



(29)

Long-chain epoxy fatty acid methyl esters are potential pro-toxins; they are metabolised by soluble epoxide hydrolase (sEH) to more toxic diols.[56]

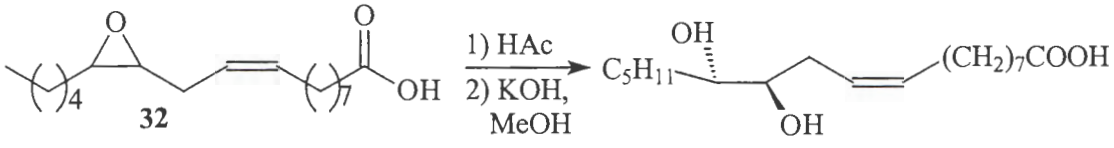




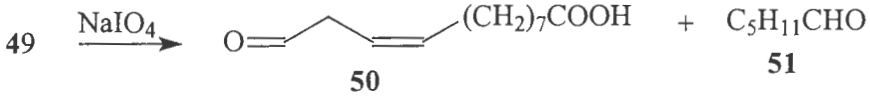
(30)

For example, leukotoxin, (Z)-9,10-epoxy-12-octadecenoic acid (**45**) and isoleukotoxin, (Z)-12,13-epoxy-9-octadecenoic acid (**46**), which are associated with acute respiratory distress syndrome, were synthesised using m-chloroperoxy-benzoic acid (m-CPBA).[57,58] The more toxic diols were synthesised using m-CPBA or dimethyldioxirane, as regioisomeric mixtures (**47** & **48**) by Green et al.[56] These diols were found to be toxic whether or not functional sEH was present. Reaction (30) illustrates the synthesis of these diols.

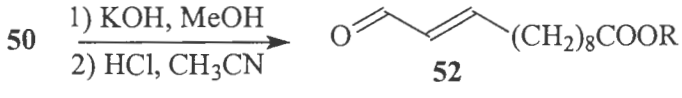
Several synthesis routes for the production of selected speciality chemicals in which the vernolic acid (**32**) epoxy group serves as a key functionality are illustrated by reactions (31-37). Bombykol (**54**), has been identified as a sex pheromone of the silkworm Bombyx mori and can be used in pest control.[59] As illustrated by reactions (31)-(35), it is synthesised starting from vernolic acid (**32**) by ring-opening of the epoxy ring, resulting in a diol product (**49**). This diol could be selectively cleaved to the aldehyde (**50**) without affecting the C-C double bond and leaving hexanal (**51**) as a side-product, that in itself may find useful applications in the flavour industry. Protecting the carboxylic acid group and isomerisation of the double bond yielded a reactive intermediary product (**52**), which is 12-oxo-(E)-10-dodecenoic acid, which contained a carboxylic ester and also an aldehyde functionality in conjugation with the C-C double bond. Subsequent Wittig olefination of (**52**) leads to product (**55**), which is selectively reduced to bombykol (**54**).



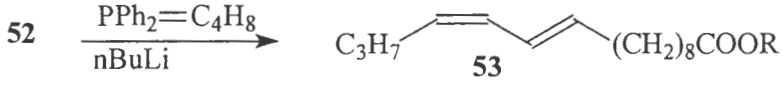
32 **49** (31)



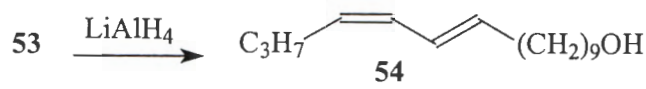
50 **51** (32)



52 (33)

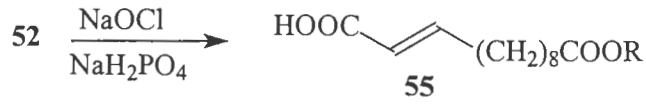


53 (34)

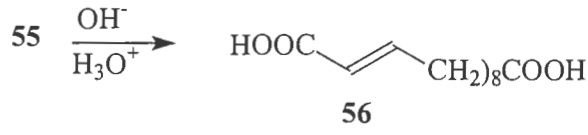


(36)

Mild oxidation of the reactive aldehyde (**52**) leads to the formation of a carboxylic acid functionalty product (**55**), while leaving the C-C double bond unaffected. Cleavage of the ester part of product (**55**) yields traumatic acid (**56**), a base for certain pharmaceuticals. For example, traumatic acid ((E)-2-dodecenoic acid) is active as wound hormone of plants and can be used as an intermediate in prostaglandine synthesis.



(36)

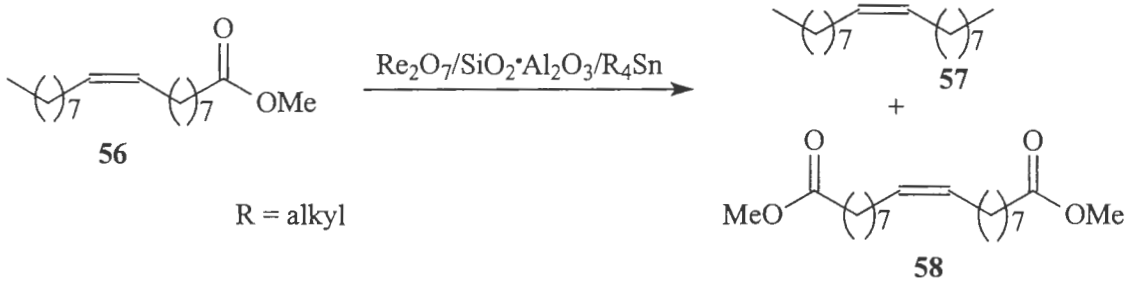


(37)

2.4 METATHESIS OF UNSATURATED FATTY ACID ESTERS

There are no examples of metathesis of epoxy olefins reported in the literature to date. However, there are numerous examples of metathesis of compounds that have a variety of other functional groups that have been reported in the literature.

Olefin metathesis of seed oils and their fatty acid methyl esters has been an active area of research for some time. For example, Mol showed that supported rhenium catalysts activated with tetraalkyltin species, are active in the homometathesis of methyl oleate.[59] This is illustrated by reaction (38).



(38)

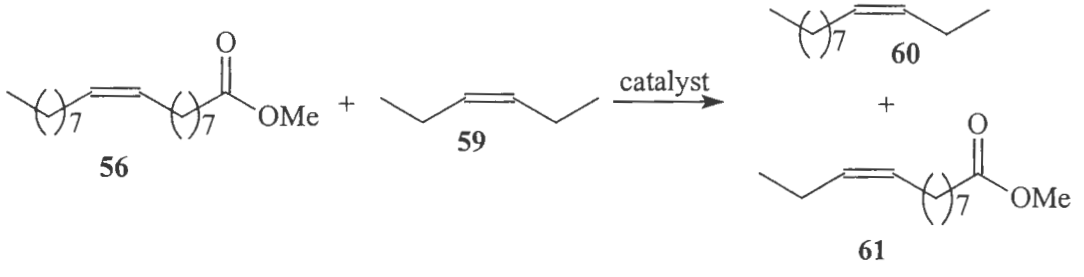
This reaction has interesting possibilities in oleochemistry. In the presence of these catalysts, the reaction takes place at room temperature. The use of silica-alumina as support led to a higher activity, but the selectivity was poor. Buffon et al.[14] investigated the possibility of replacing tin by germanium and silicon compounds as promoters, with a view to evaluating both their reactivity towards Re_2O_7-based catalysts and the catalytic performance of the resulting systems

in the metathesis reaction. They established that, after appropriate treatment, germanium and silicon alkyl compounds are active promoters for supported rhenium catalysts. However, they found that both of these promoters induced a lower activity.

Buffon et al.[42] investigated metatheses of methyl oleate using $B_2O_3/SiO_2{\cdot}Al_2O_3$ as support, after treatment with different promoters. The results obtained showed that the catalytic activity is not only promoted by R_4M (M = Ge, Si, Sn), but also by mono-hydride derivatives ($HMBu_3$) (M = Ge, Si, Sn). Best reaction conditions are 41 ± 1 °C, with selectivities of >70% toward primary metathesis products. With the tetraalkyl-metal used as a promoter, the cis/trans ratio of the diester is ~0.22, which is a thermodynamic equilibrium value. However, when the hydride is used, a higher cis/trans ratio of 0.85 was obtained.

Sibeijn and Mol[60] reported the conversion of ca. 47.2% after 1 h in the metathesis of methyl oleate with $R_2O_7/SiO_2{\cdot}Al_2O_3$ catalytic system, with the selectivity of >95%. The best reaction conditions are molar ratio methyl oleate/Re/$SnBu_4$ = 120/1/0.6, at 24 °C (297 K). The $R_2O_7/SiO_2{\cdot}Al_2O_3$ catalytic system seems to perform better than a homogeneous catalyst in the metathesis of methyl oleate. Nakurama et al.[61,62] reported metathesis conversion (ca. 50%) of methyl oleate with WCl_6-$(CH_3)_3Al_2Cl_3$ catalyst, which was reached after 17 h. However, this catalyst could only be applied at lower temperatures (<30 °C), resulting in limited reaction rates. The best reaction conditions were a molar ratio methyl oleate/W/Al = 30/1/2, at 28 °C.

In 1977, Verkuijlen demonstrated new synthetic routes to homologous esters generated from co-metathesis of unsaturated esters with olefins, which were often difficult to obtain by other methods.[63] For example, the cross-metathesis of methyl oleate (**56**) with 3-hexene (**59**) in the presence of WCl_6-$Sn(CH_3)_4$ catalyst gives 3-dodecene (**60**) and methyl 9-dodecenoate (**61**), as shown by reaction (39).

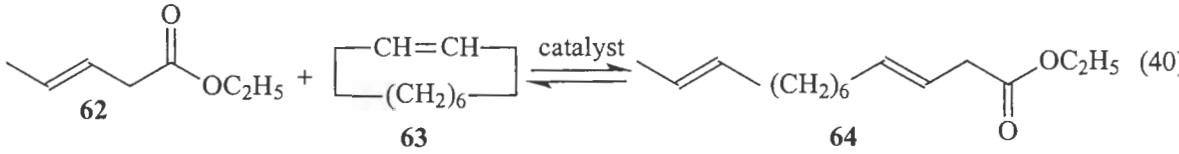


(39)

However, products of self-metathesis of methyl oleate were also formed. For example, with ester/3-hexene/WCl_6-$Sn(CH_3)_4$ ratio = 50/50/1, a conversion of 38% via cross-metathesis

and 32% via self-metathesis of methyl oleate was obtained after 18 h at 70 °C.

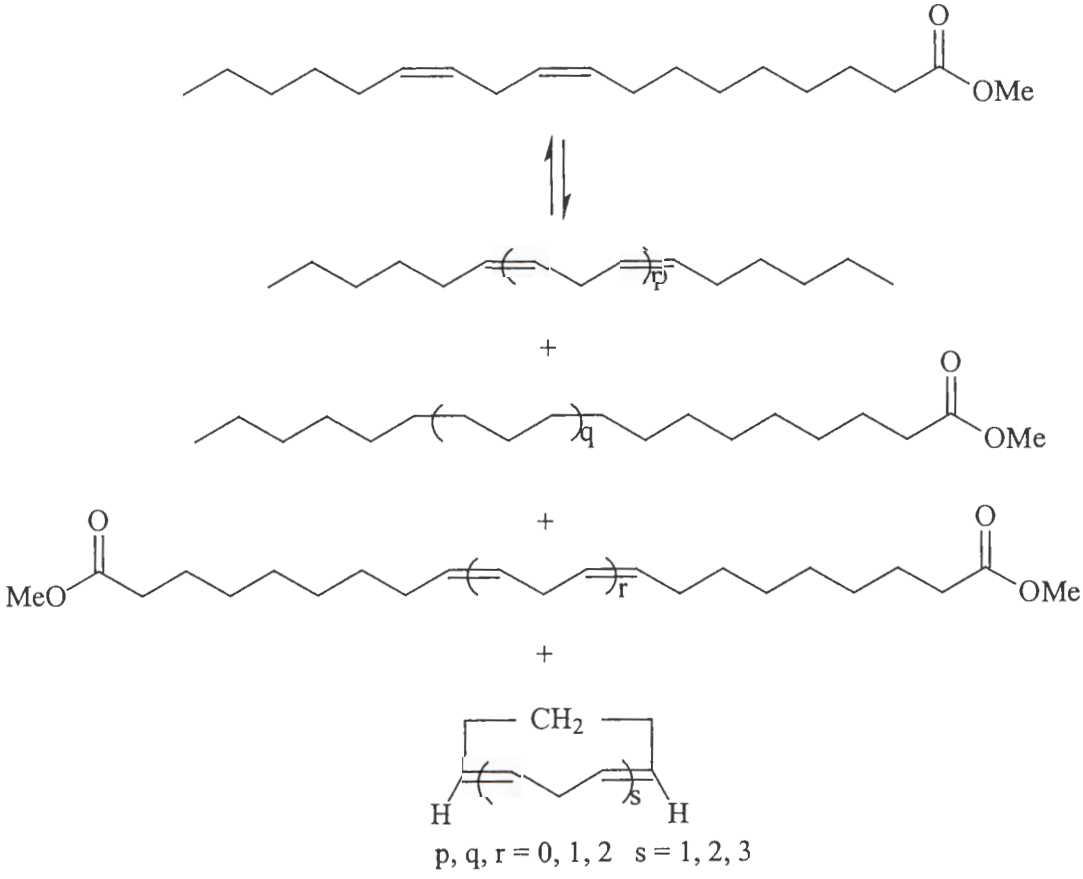
Otton et al.[64] showed that long-chain linear di-unsaturated monoesters can be prepared from co-metathesis of unsaturated monoester with a cyclic olefin in the presence of WCl_6-$Sn(CH_3)_4$ catalyst, as shown by reaction (40).



(40)

With carefully chosen conditions, a good selectivity for the monoesters was achieved. For example, with ester/cyclo-octene/W/Sn = 30/10/1/1, a 25% conversion of ethyl-3-pentenoate was obtained with a selectivity of ca. 46% for the C_{13}-monoester, and 34% for the C_6-diester.

Marvey et al.[6,65] carried out metathesis of unsaturated fatty acid esters derived from South African sunflower oil.



(41)

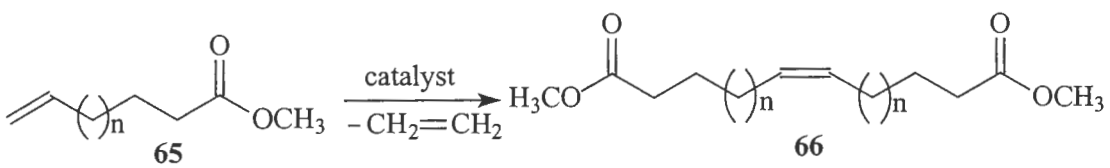
p, q, r = 0, 1, 2 s = 1, 2, 3

For example, metatheses of cis, cis-9,12-Octadecanoate (Linoleate) with both a heterogeneous $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalyst and a homogeneous W $(O\text{-}2,6\text{-}C_6H_3X_2)_2Cl_4$/ Me_4Sn (X=Cl,

Ph) catalytic system yield alkenes, monoesters and diesters as shown by reaction (41).

The metathesis activity of the Re-based catalyst is comparably higher than that reported in literature for a homogeneous $WCl_6/SnMe_4$ catalytic system, with methyl linoleate conversions of ca. 86.1% and ca. 84% respectively. The selectivity of the Re-based catalyst towards primary metathesis products is >95%, and the best reaction condition are 60 °C. Secondary metathesis products were not obtained.

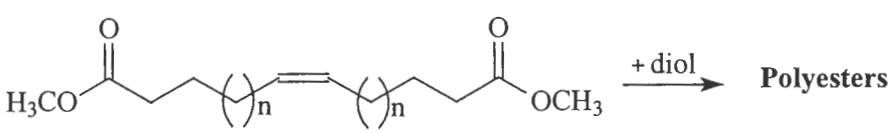
Metathetical dimerisation of ω-unsaturated fatty acid methyl esters using the highly efficiently $Re_2O_7/B_2O_3/SiO_2{\cdot}Al_2O_3/Bu_4Sn$ has been used by Warwel et al.[66] to prepared long chain dicarboxylic acid esters. This reaction (42) was carried in vacuum to enable the removal of ethylene so that the equilibrium was shifted towards the dicaborxylic esters.



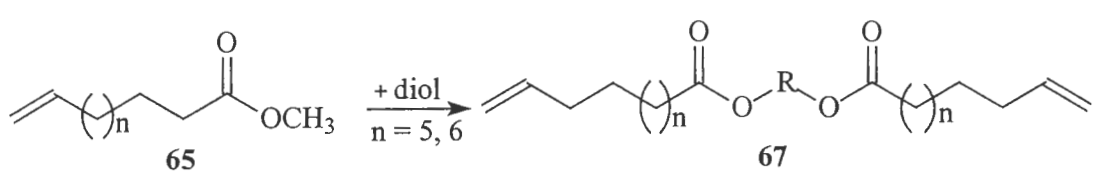
65 66 (42)

n = 1, 2, 5, 6, 9

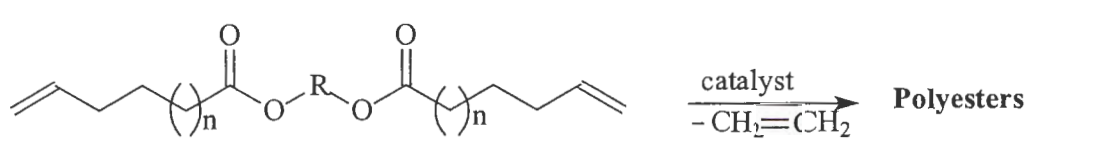
Transesterification of polycondensation of C_{18}, C_{20} and C_{26} dicarboxylic acid dimethylesters was carried out with ethylene glycol, 1,4-butanediol and 1,4-(bishydroxymethyl)cyclohexane using catalysts such as titanium tetrabutylate and calcium acetate/antimony trioxide, as illustrated by reactions (43 - 45).



66 (43)

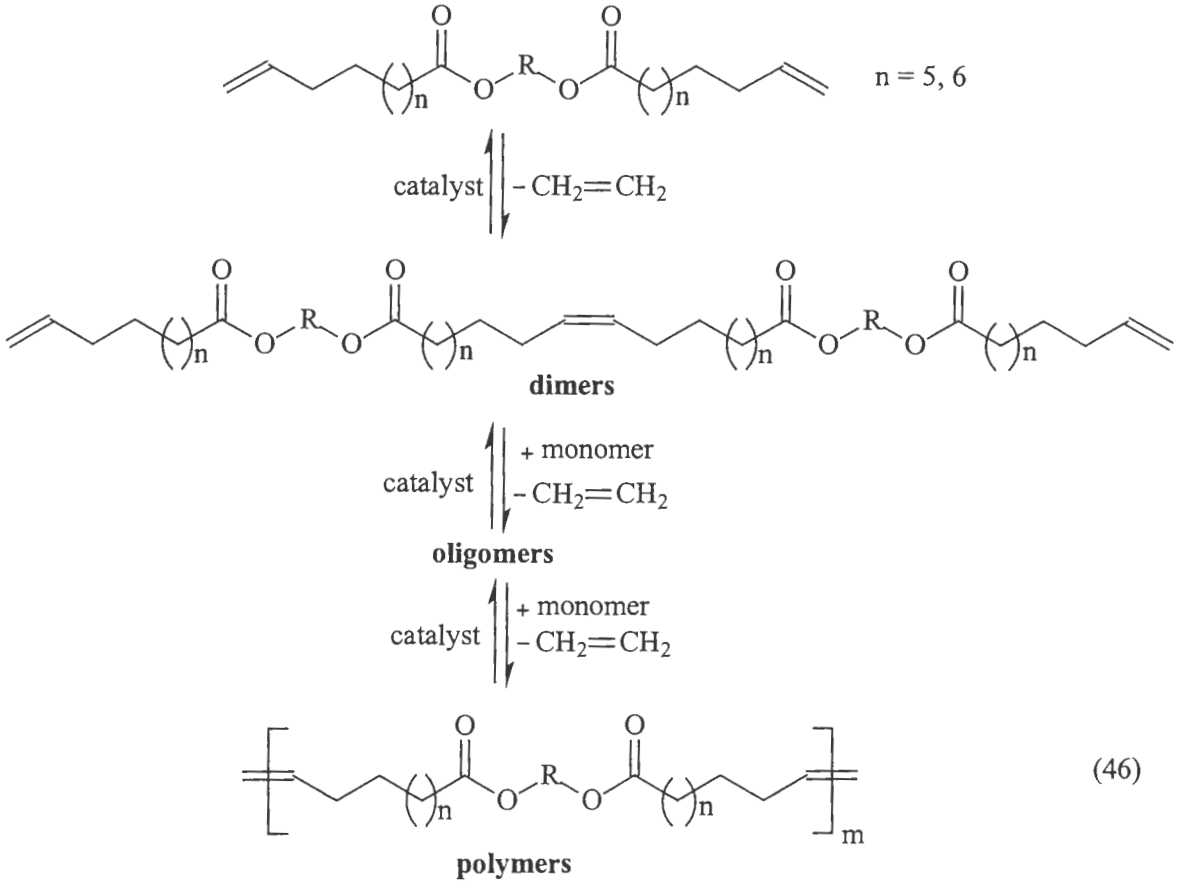


65 67 (44)



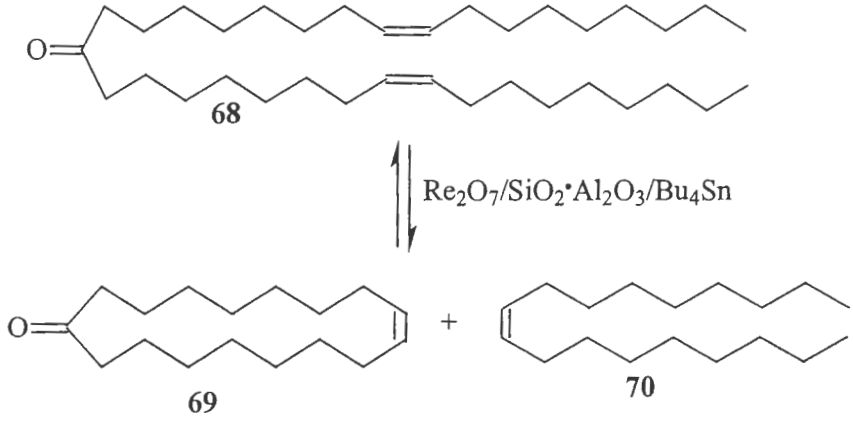
67 (45)

Structurally identical polyesters were also prepared by ADMET-polymerisation of α,ω-alkylene dialkenoates using $Re_2O_7/B_2O_3/SiO_2{\cdot}Al_2O_3/Bu_4Sn$, as illustrated by reaction (46).



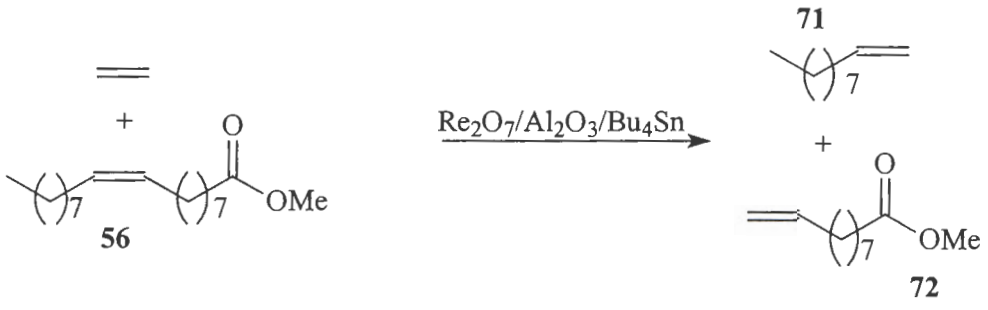
(46)

A convenient new synthetic route to civetone has been developed, where methyl oleate is first converted via a Claisen condensation to the doubly unsaturated ketone oleon, 9,26-pentatriacontadien-18-one (**68**).[67] Oleon is then converted into 9-octadecene (**69**) and a cis-trans mixture of 9-cycloheptadecen-1-one (**70**), also known as civetone. This metathesis reaction is illustrated by reaction (47).



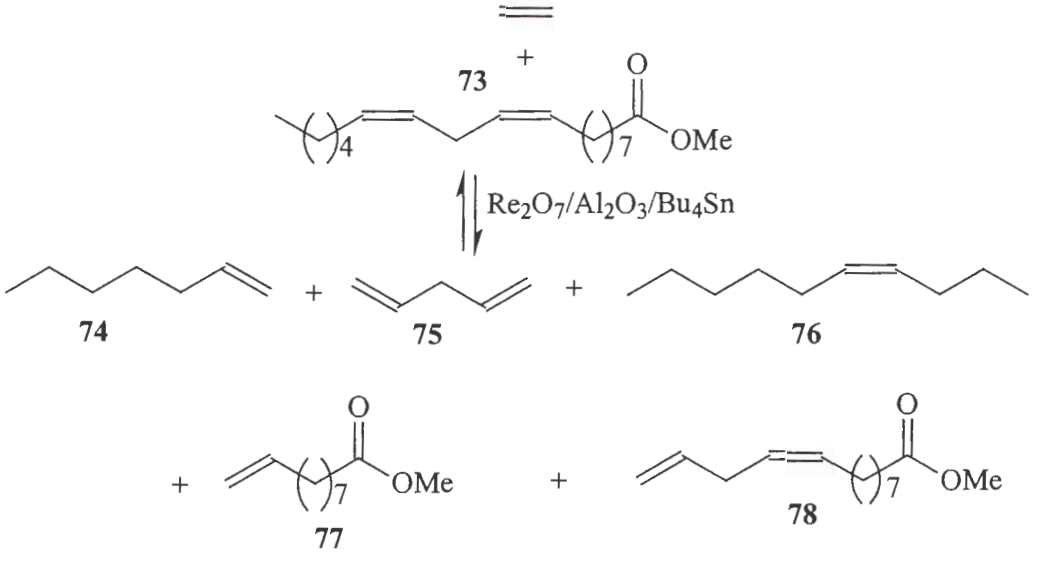
(47)

Cross- metathesis of unsaturated fatty acid esters with ethylene, which is also known as ethenolysis, allows the synthesis of short-chain ω-unsaturated esters, which have a wide range of applications.[67] For example, ethenolysis of methyl oleate produces methyl-9-decenoate and 1-decene,[68] as illustrated by reaction (48).



(48)

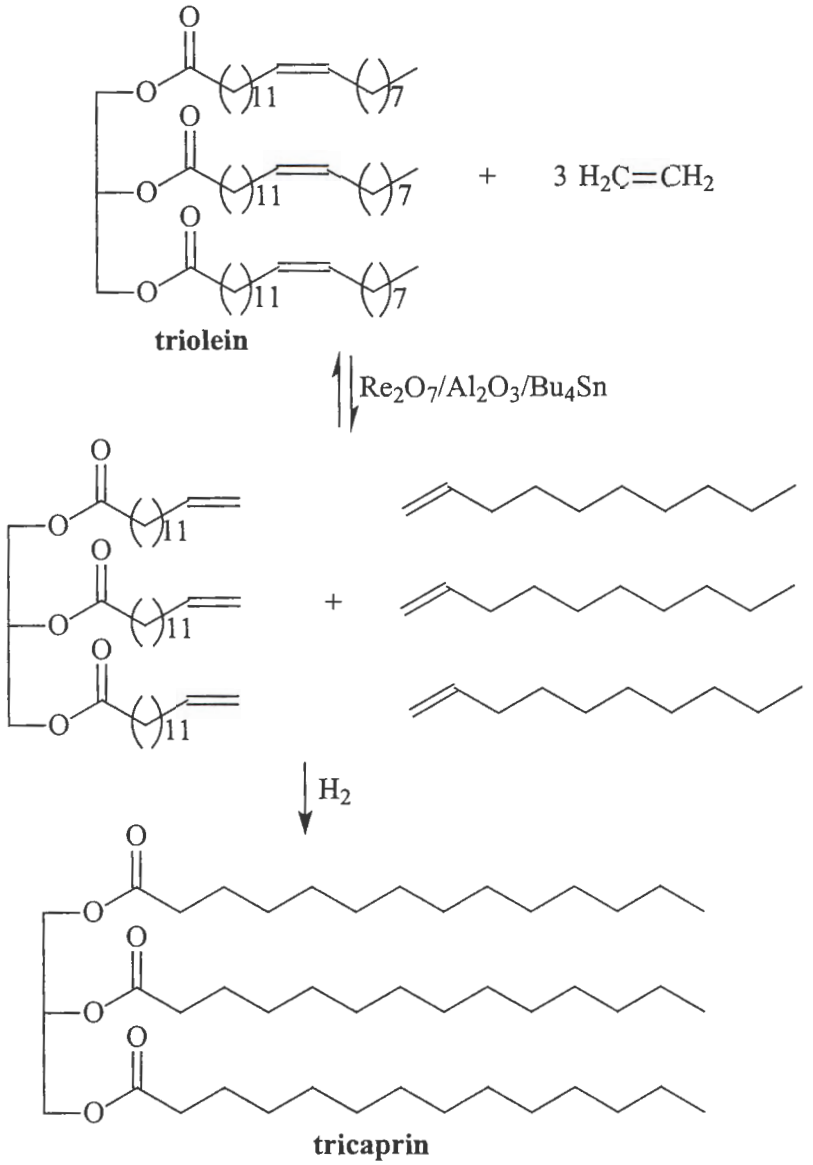
Another example is ethenolysis of methyl linoleate, which produces various short-chain unsaturated olefins, as well as olefini esters, and is illustrated by reaction (49).



(49)

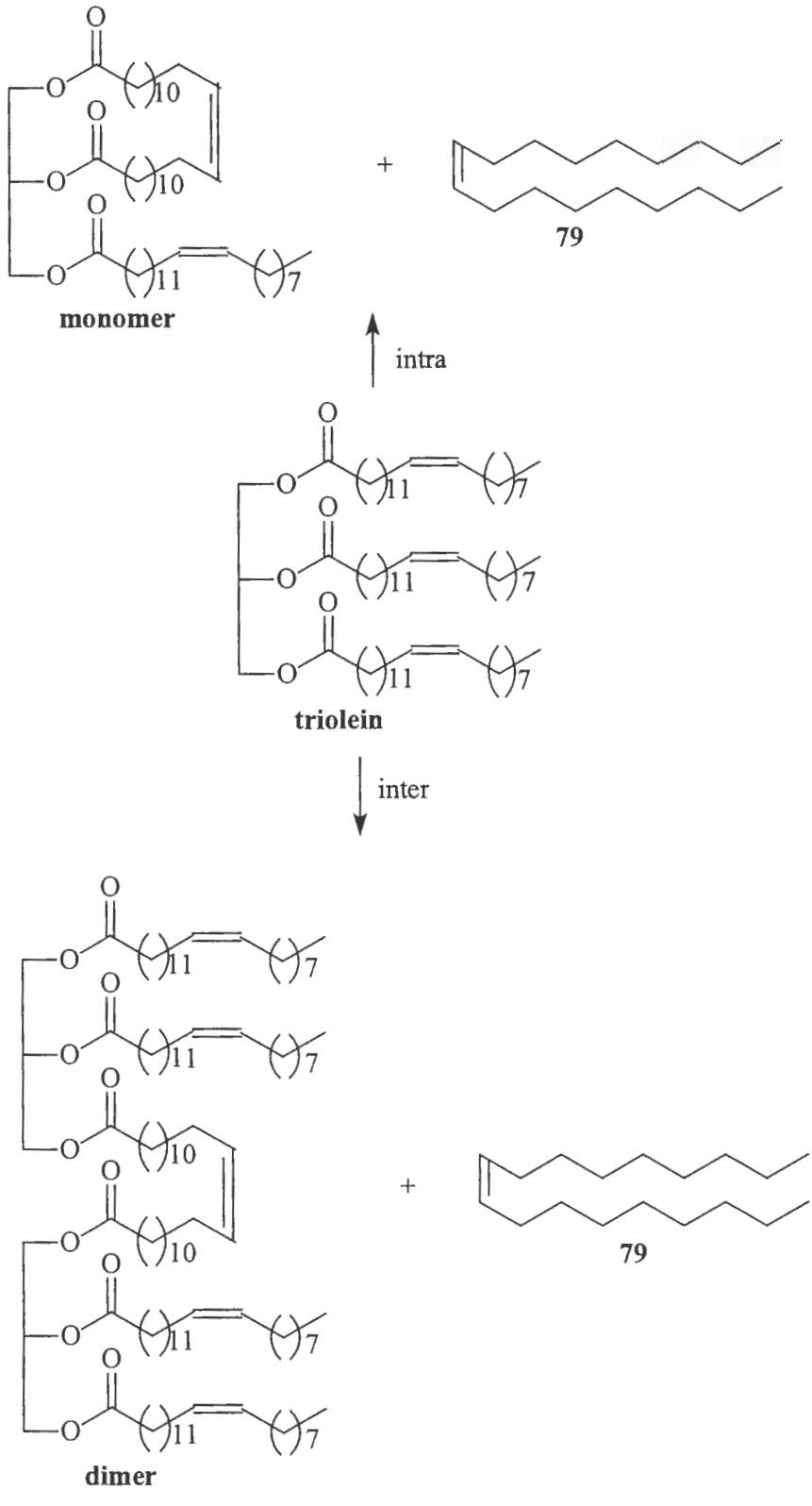
Cross-metathesis of distinct fatty oils consisting of long-chain unsaturated fatty acid triglycerides, with lower olefins allows the transformation of natural fatty oils into fatty oils of lower molecular weight.[68] For example, tricaprin can be prepared by ethenolysis of olive oil, which contains the triolein triglyceride, and subsequent hydrogenation, as illustrated by reaction (50).

NWU LIBRARY



(50)

The triolein triglycerides also undergo self-metathesis, which may proceed intramolecularly as well as intermolecularly, as illustrated by reaction (51), but the latter reaction is strongly predominating.[68]



(51)

Self-metathesis of olive oil, as can be seen in reaction (51), yields 9-octadecene (**79**) and polymeric triglycerides, which are mainly dimmers and trimers. Metathesis of these oils results in high-molecular weight oils, also known as stand oils (i.e. drying oils of high viscosity). These

high-molecular weight oils have drying properties that are more pronounced than those of thermally polymerised oils where the polymerisation process has already considerably reduced the number of double bonds available for cross-linking during the drying process.[69]

2.5 SUMMARY

Literature survey was conducted to gather information on the following aspects:

- Metathesis reactions and mechanisms,
- Catalyst systems,
- Chemistry of epoxides,
- Metathesis of unsaturated fatty acids esters.

This information assists me in understanding the concept of metathesis, as well as the mechanisms involved in metathesis reactions. This knowledge is essential to predicting the expected products. Knowledge of catalyst systems is critical for identifying the best catalyst system for metathesis of unsaturated fatty acid esters, e.g. 1,2-epoxy-9-decene and 12,13-epoxy-9-octadecenoate.

The chemistry of epoxides enables me to obtain a better understanding of the reactivity of the epoxy group. Generally, epoxides are known to undergo Wittig type reactions leading to the opening of the epoxy ring under acidic conditions. The rhenium-based metathesis catalysts when supported on $SiO_2 \cdot Al_2O_3$ and used in the presence of a suitable cocatalyst such as R_4Sn (R = alkyl), were found to be the most active in olefin metathesis. However, due to the acidity of the support, the epoxy group may undergo Wittig type reactions, leading to hydroxylate epoxy alkenes, instead of primary metathesis products.

The literature survey revealed that there are currently numerous examples of metathesis of unsaturated fatty acid esters that have a variety of other functional groups. However, there are no examples of metathesis of epoxy alkenes reported in literature. Metathesis of epoxy alkenes presents a useful technique for a one step synthesis of unsaturated diepoxyolefins and dicarboxylic esters. Diepoxyolefins can be converted to hydroxylated monomers, for the synthesis of polyurethane, *via* an acid-catalysed ring opening reaction. Dicarboxylic esters are intermediates for the synthesis of polyesters; polyamides, macrocyclic compounds such as civetone, which have application in the perfume industry.

CHAPTER 3
EXPERIMENTAL

3.1 MATERIALS

Chlorobenzene (SAARCHEM) was dried by refluxing over P_2O_5, distilled and stored under N_2. Benzene (SAARCHEM) was distilled from calcium hydride under N_2 atmosphere, and then dried over activated aluminium oxide. Hexane was dried by refluxing over sodium under N_2 for about 4 hours, followed by distillation under N_2. Dichloromethane was pre-dried with calcium chloride, followed by refluxing for 2 hours over phosphorus pentoxide and then distilled onto fresh phosphorus pentoxide under N_2. Dichloromethane was then stored over phosphorus pentoxide.

Ammonium perrhenate, NH_4ReO_4 (Fluka); silica alumina, $SiO_2 \cdot Al_2O_3$ (particle size: extrudate, Aldrich); phosphorus pentoxide, P_2O_5 (Aldrich) and tetrabutyl tin, Bu_4Sn (Aldrich), aluminium oxide (Aldrich) were used as purchased. Methyl oleate (99%, Aldrich), 1,2-epoxy-9-decene (97%, Aldrich), methyl vernolate (99%, Aldrich), 1-pentene (99.5%, Fluka) and 1-hexene (99.8%, Fluka) were stored under nitrogen, and kept in the refrigerator.

3.2 APPARATUS

The two-necked pear-shaped glass reactors were used as reactors. All glass reactors were dried at 100 °C and purged with nitrogen before reagents were introduced. The two necks were each fitted with a rubber septum, and were initially used as gas inlet and gas outlet (during purging). These were later used as sample inlet for introducing the liquid reagents, and sample outlet for sampling by means of syringes.

3.3 PREPARATION AND ACTIVATION OF CATALYSTS

Figure 4 shows a schematic diagram illustrating the apparatus used for the preparation of the Re_2O_7 catalyst.

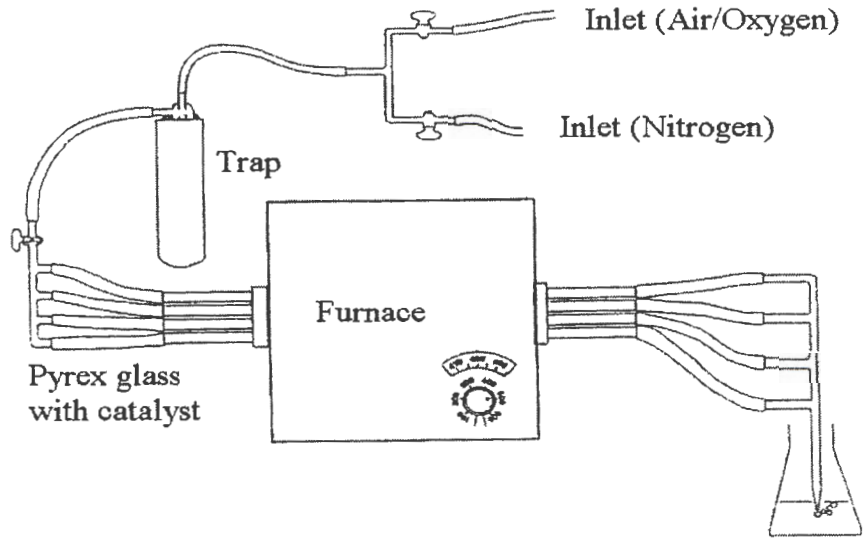


Figure 4. Schematic diagrams illustrating the activation of the $Re_2O_7/SiO_2{\cdot}Al_2O_3$ catalyst.

3.3.1 3 wt% $Re_2O_7/SiO_2{\cdot}Al_2O_3/Bu_4Sn$ catalyst (particle size: extrudate)

The 3 wt% $Re_2O_7/SiO_2{\cdot}Al_2O_3$ catalyst was prepared as described by Marvey et al.[28] $SiO_2{\cdot}Al_2O_3$ (0.97 g) in extrudate form was impregnated with an aqueous solution of NH_4ReO_4 (0.0332 g dissolved in about 2 cm^3 of distilled water), and then dried in the oven at 120 °C. The catalyst was activated as illustrated in Figure 4, by placing it inside a borosilicate glass tube and calcined at 550 °C in a tube furnace under a stream of air/O_2 for 3 h and subsequently under a stream of N_2, for 2 h.

3.3.2 2 wt% Re_2O_7/ $SiO_2{\cdot}Al_2O_3/Bu_4Sn$ catalyst

$SiO_2{\cdot}Al_2O_3$ (0.98 g) in extrudate form was impregnated with an aqueous solution of NH_4ReO_4 (0.0232 g in about 2 cm^3 of distilled water), and then dried in the oven at 120 °C. The catalyst was activated as in 3.3.1 above.

3.3.3 1 wt% Re_2O_7/ $SiO_2{\cdot}Al_2O_3/Bu_4Sn$ catalyst (particle size: extrudate)

$SiO_2{\cdot}Al_2O_3$ (0.99 g) in extrudate form was impregnated with an aqueous solution of NH_4ReO_4 (0.0132 g in about 2 cm^3 of distilled water), and then dried in the oven at 120 °C. The catalyst was activated as in 3.3.1 above.

3.3.4 0.5 wt% Re_2O_7/ $SiO_2{\cdot}Al_2O_3/Bu_4Sn$ catalyst (particle size: extrudate)

$SiO_2{\cdot}Al_2O_3$ (0.995 g) in extrudate form was impregnated with an aqueous solution of NH_4ReO_4 (0.0053 g in about 2 cm^3 of distilled water), and then dried in the oven at 120 °C. The catalyst was activated as in 3.3.1 above.

3.4 METATHESIS REACTIONS

Figure 5 shows a schematic diagram illustrating the apparatus used for the metathesis reaction.

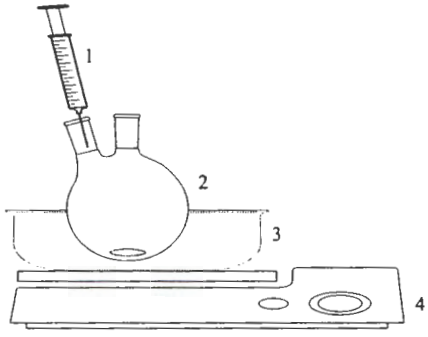


Figure 5. Schematic diagrams illustrating the apparatuses used for metathesis reactions: syringe (1), pear-shaped glass reactor fitted with rubber septum (2), sand/water bath (3) and magnetic stirrer/hot plate (4).

3.4.1 Metathesis of 1,2-epoxy-9-decene

Chlorobenzene (2 cm^3) was added to 0.73 g of a calcined 2 wt% Re_2O_7/ SiO_2·Al_2O_3 (5.47 x 10^{-5} mol Re) catalyst in a two-necked pear-shaped glass reactor, which was allowed to cool to room temperature under a stream of N_2. Then 9.0 x 10^{-3} cm^3 of Bu_4Sn (2.74 x 10^{-5} mol Sn) was then added, followed by 5 min of stirring, after which 0.1 cm^3 of 1,2-epoxy-9-decene (5.47 x 10^{-4} mol) was added. The reaction mixture was allowed to stir for 18 h.

3.4.2 Cross-metathesis of 1, 2-epoxy-9-decene and 1-pentene

The same procedure as in 3.4.1 was used to metathesise 50:50 mixture of 1,2-epoxy-9-decene/1-pentene (v/v, i.e. 5.0 x 10^{-2} cm^3 of 1,2-epoxy-9-decene/5.0 x 10^{-2} mL of 1-pentene dissolved in 1 mL of chlorobenzene).

3.4.3 Cross-metathesis of 1,2-epoxy-9-decene and 1-hexene

The same procedure as in 3.4.1 was used to metathesise 50:50 mixture of 1,2-epoxy-9-decene /1-hexene (v/v, i.e. 5.0 x 10^{-2} cm^3 of 1,2-epoxy-9-decene/5.0 x 10^{-2} cm^3 of 1-hexene dissolved in 1 cm^3 of chlorobenzene).

3.4.4 Metathesis of methyl-9-Octadeceneoate (methyl oleate)

Chlorobenzene (2 cm^3) was added to 0.2 g of a calcined 2 wt% Re_2O_7/ SiO_2·Al_2O_3 (2.48 x 10^{-5} mol Re) catalyst in a two-necked pear-shaped glass reactor, which was allowed to cool to room temperature under a stream of N_2. Then 4.9 x 10^{-3} cm^3 of Bu_4Sn (1.44 x 10^{-5} mol Sn) was added, followed by 5 min of stirring, after which 8.3 x 10^{-2} cm^3 of methyl oleate (2.48 x 10^{-4} mol) was added. The reaction mixture was allowed to stir for 18 h, with periodic sampling.

3.4.5 Metathesis of methyl-12,13-epoxy-9-octadeceneoate (methyl vernolate)

Chlorobenzene (2 cm^3) was added to 0.06 g of a calcined 2 wt% $Re_2O_7/ SiO_2{\cdot}Al_2O_3$ (4.65×10^{-6} mol Re) catalyst in a two-necked pear-shaped glass reactor, which was allowed to cool to cool to room temperature under a stream of N_2. Then 9.1×10^{-4} cm^3 of Bu_4Sn (2.79×10^{-6} mol Sn) was then added, followed by 5 min of stirring, after which 16.0×10^{-3} cm^3 of 1,2-epoxy-9-octadecenoate (4.64×10^{-5} mol) was added. The reaction mixture was allowed to stir for 18 h, with periodic sampling.

3.4.6 Cross-metathesis of methyl vernolate and methyl oleate

The same procedure as in 3.4.5 was used to metathesise 50:50 mixture of methyl vernolate/methyl oleate (v/v, i.e. 8.0×10^{-3} cm^3 of methyl vernolate/8.0×10^{-3} cm^3 of methyl oleate dissolved in 1 cm^3 of chlorobenzene).

3.4.7 Cross-metathesis of methyl vernolate and 1-pentene

The same procedure as in 3.4.5 was used to metathesise 50:50 mixture of methyl vernolate/1-pentene (v/v, i.e. 8.0×10^{-3} cm^3 of methyl vernolate/8.0×10^{-3} cm^3 of 1-pentene dissolved in 1 cm^3 of chlorobenzene).

3.4.8 Cross-metathesis of methyl vernolate and 1-hexene

The same procedure as in 3.4.5 was used to metathesise 50:50 mixture of methyl vernolate/1-hexene (v/v, i.e. 8.0×10^{-3} cm^3 of methyl vernolate/8.0×10^{-3} cm^3 of 1-hexene dissolved in 1 cm^3 of chlorobenzene).

3.5 ANALYSIS

3.5.1 GC analysis of reaction mixture

Samples were collected at regular time intervals and analysed on a Varian GC 3400 equipped with a cold on-column injector, a DB 624 fused silica capillary column (30 m x 0.530 mm x 3.00 µm, J & W Scientific) and FID using the following conditions: carrier gas (N_2, 300 kPa), Air/H_2 mixture (400/300 kPa), detector temperature (300 °C), injector temperature (270 °C), oven programmed at 150 °C for 1 min, 150 to 250 °C at 15 °C/min and then maintained at 250 °C for 10 min. Hydrogen provides the combustion gas, whilst oxygen is used as an oxidant for FID.

3.5.2 Calculations for conversion, yield and selectivity

The substrate conversion, product yield and selectivity were calculated from the peak areas of

the GC analyses, excluding that of the solvent (PhCl), corrected for the molecular response by Ackman's method:[52]

$$\% \text{ Conversion} = (1 - C_s / \sum C_i) \times 100$$

$$\% \text{ Yield} = (C_i / \sum C_i) \times 100$$

$$\text{Selectivity} = (C_i / (1 - C_s)) \times 100$$

Where:

$i = 1, 2, \ldots \xi$;

C_s is the corrected peak area for the substrate

C_i is the corrected peak areas for the component i in the product mixture with ξ components (i.e. including the substrate);

Corrected peak areas (C_i) were calculated from molecular response factors (MRF) as follows:

$$C_i = MRF_s / MRF_i \times A_i$$

Where:

MRF_s is the molecular response factor of the substrate;

MRF_i is the molecular response factor of component i in the product mixture with ξ components; and

A_i is the uncorrected peak areas for any component i in the product mixture

Molecular response factors (MRF) were estimated by Ackman's method[52] using the effective carbon response (ECR) values of some functional groups (Table 2). The methylene group ($-CH_2-$) was chosen as a unit of effective carbon response, where hundred response units were assigned for each carbon atom. The calculated molecular response factors for some selected unsaturated olefins are given in Table 3.

Table 2. Effective carbon responses (ECR).

ECR	Units
C	100
C–C	200
C=C	178
O=C–O	0

Table 3. Molecular response factors for selected unsaturated olefins.

Component	Carbon chain	MRF
1,2-epoxy-9-decene	COC-C_6-C=C-C_6-COC	978
1,2,17,18-diepoxy-9-octadecene	COC-C_6-C=C-C_6-COC	1778
Methyl-12,13-epoxy-9-octadecenoate	C_5-COC-C-C=C-C_7-COOC	1778
Dimethyl-9-octadecenoeate	COOC-C_7-C=C-C_7-COOC	1978

3.5.3 Characterisation of the reaction products by GC/MS

The corresponding peaks were characterised by GC/MS equipped with cold on-colunm injector, a DB 5MS fused silica capillary column (30 m x 0.250 mm x 0.25 μm, minimum temperature – 20 °C, maximum temperature 260 °C, J & W Scientific) and the mode of breaking the molecule is the electron impact mode (EIM).

3.5.4 Characterisation of reaction mixtures by FTIR

The infrared spectra of the reaction mixture, between sodium chloride windows were measured with an FTIR Impact 410 spectrometer in the range between 500 and 4000 cm^{-1}, in order to identify functional groups present in the reaction mixtures. Chlorobenzene was used as a blank.

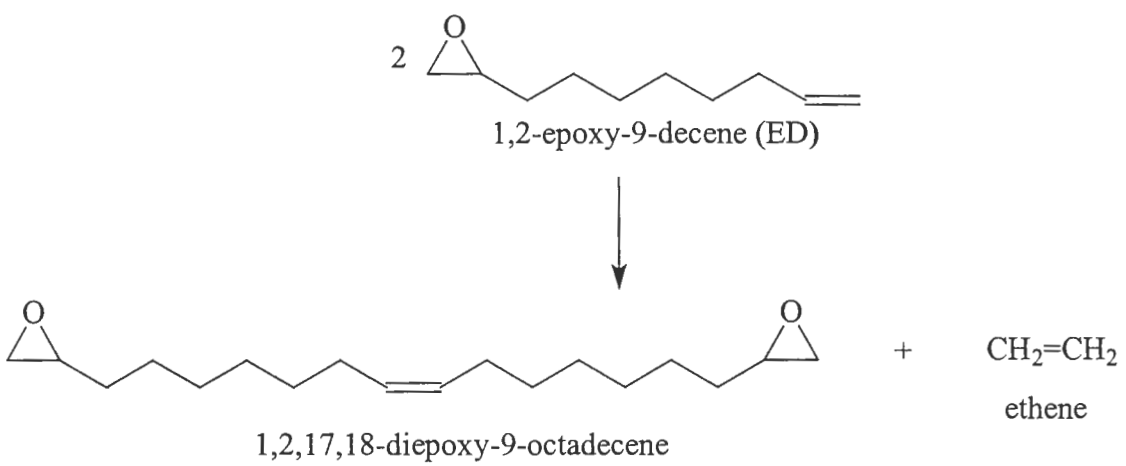
CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 METATHESIS OF 1,2-EPOXY-9-DECENE (ED)

Metathesis activity, selectivity and stability of $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalytic systems were investigated for ED (1,2-epoxy-9-decene). The influence of various reaction parameters such as the Sn:Re molar ratios, Re_2O_7 loading, reaction temperature, type of solvent, and substrate concentration on the activity, selectivity and stability of the $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalytic system, were studied as a function of time. A substrate:Re molar ratio of 10 was used throughout all experiments.

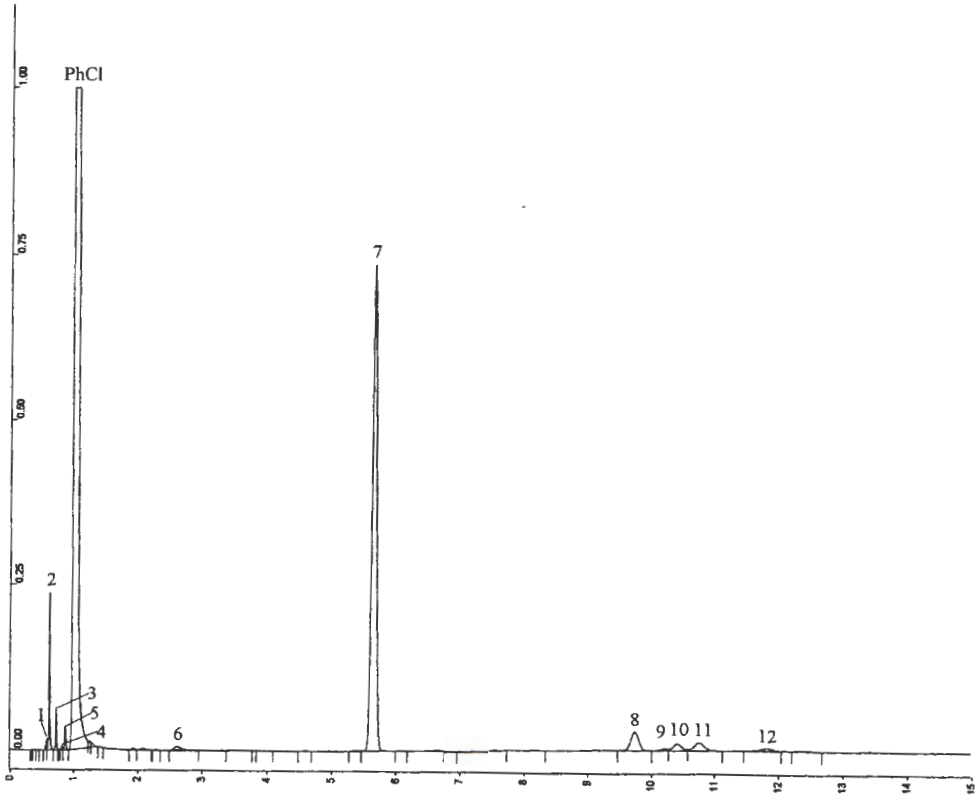
ED was metathesised with 2 wt.% Re_2O_7 catalyst at room temperature and the Re:Sn:ED used was 1:0.5:10. Scheme 1 illustrates the formation of the primary metathesis products (PMP), which are 1,2,17,18-diepoxy-9-decene and ethene, upon metathesis of ED.



Scheme 1. The metathesis of ED to give PMP.

4.1.1 Reaction products

Figure 6 shows a typical chromatogram of the product mixture obtained when ED is metathesised with 2 wt.% $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalyst. According to the reaction Scheme 1, only one peak should be expected in Figure 6 since the gaseous product (ethene) is removed during purging with nitrogen. However, the presence of more peaks suggests formation of other products, possibly from side reactions or polymerisation reactions.



NWU LIBRARY

Figure 6. GC of metathesis products of 1,2-epoxy-9-decene: ED (Peak 6); 1,2,17,18-diepoxy-9-octadecene (Peak 7), C_{20} dimers (Peaks 8 – 12, see Table 4) and other (Peaks 1 – 5, see Table 4). PhCl = chlorobenzene solvent.

4.1.1.1 IR of reaction mixture

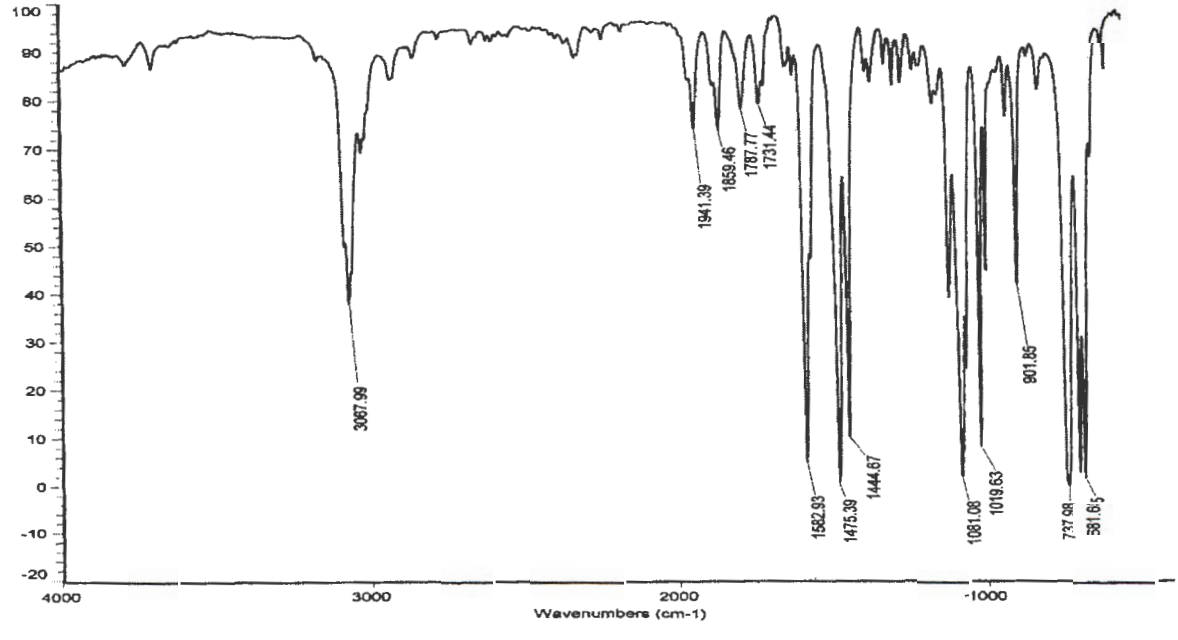


Figure 7. An FTIR spectrum of pure ED.

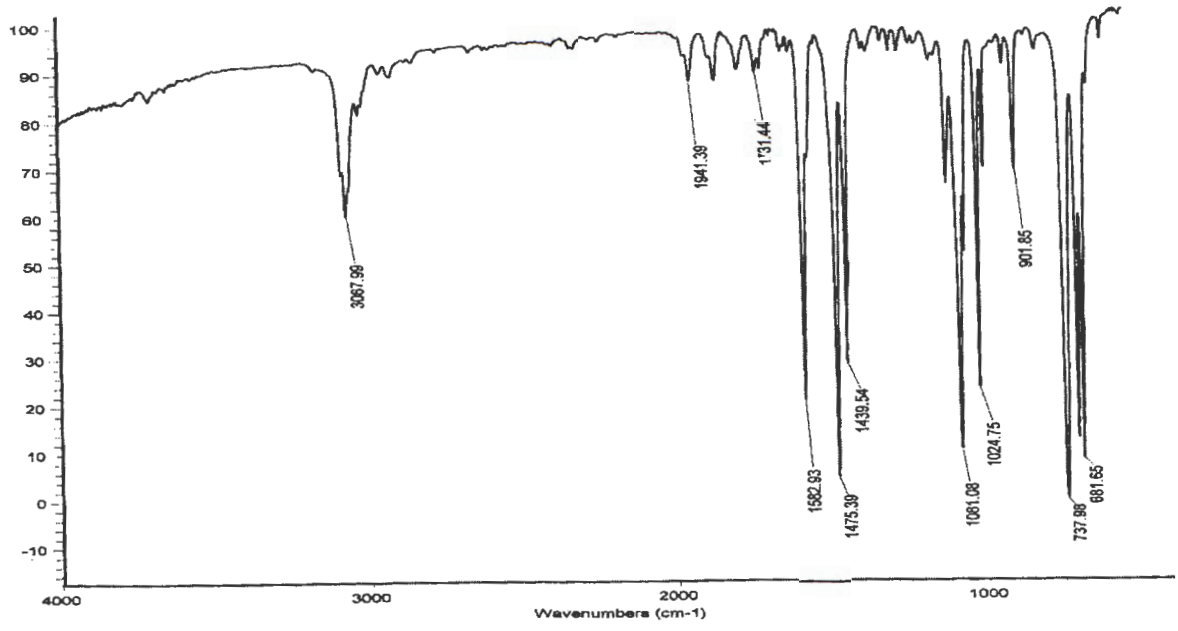


Figure 8. A typical FTIR spectrum of metathesis reaction mixture of ED obtained after 6 h reaction time.

Figures 7 and 8 show respectively the IR spectra of pure ED and the reaction mixture. The absence of a broad OH peak (Figure 7), which is expected in the region 3000 to 3700 cm^{-1}, as well as the presence of the epoxy peak (Figures 7 and 8) in the region 901 to 1122 cm^{-1}, does not suggest the presence of hydroxylated products but suggests that the epoxy ring was retained during the metathesis reaction.

4.1.1.2 Mass spectrum (MS) of primary metathesis products

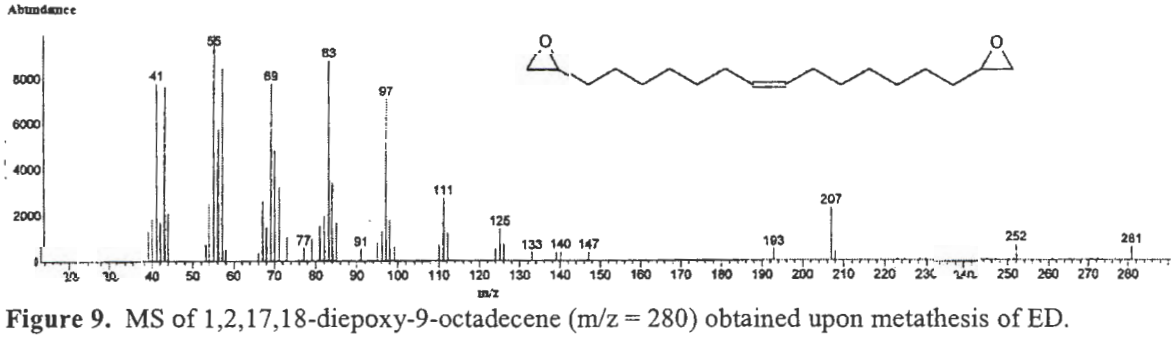


Figure 9. MS of 1,2,17,18-diepoxy-9-octadecene (m/z = 280) obtained upon metathesis of ED.

Figure 9 represents a typical mass spectrum (MS) of 1,2,17,18-diepoxy-9-octadecene (Peak 6), which is a primary metathesis product obtained upon metathesis of ED (Appendix 1). The molecular ion m/z = 280 is not detectable. The ion at m/z = 252 reflects fragmentation of the first epoxy ring, with the subsequent loss of oxygen. It is presumed that the epoxy rings open under bombardment by electrons. The ion at m/z = 140 reflects fragmentation of the double

bond. The ions at m/z = 125 and 111 reflect, respectively, fragmentations at the alpha and beta carbon atoms to the double bond. The ions at m/z = 55 and 41 are due, respectively, to the fragmentations at the beta and alpha carbon atoms to the second epoxy ring. This may explain why m/z = 55 is also a base peak. The gap of 112 amu between m/z = 252 and 140 suggests that the double bond is in position 9 and that the first epoxy ring is in positions 1 and 2. The gap of 97 amu between m/z = 140 and 43 indicates that the second epoxy ring is in positions 17 and 18.

4.1.1.3 Mass spectrum (MS) of dimerisation products (DMP)

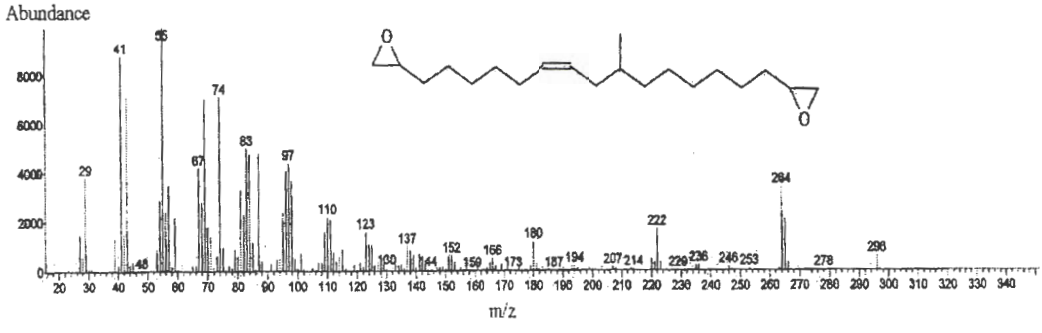


Figure 10. MS of 1,2,18,19-diepoxy-11-methyl-8-nonadecene (m/z = 308).

The compound associated with peak 8 is a dimer and has a spectrum consistent with 1,2,18,19-diepoxy-11-methyl-8-nonadecene (Figure 10). This dimer is formed by the cross-metathesis of a molecule of ED with another molecule, which is one of its isomers. These isomers are obtained as a result of the double bond migration in ED. Although the compound corresponding to peak 7 (Figure 9) is also a dimer, it is formed from self-metathesis of ED and the associated removal of ethene gas by purging of the reaction mixture with nitrogen. The molecular ion m/z = 308 of this dimer was not detected. The ions at m/z = 296 and 278 reflect fragmentations of the epoxy ring, and the subsequent loss of oxygen. The ion at m/z = 264 reflects fragmentation alpha to the epoxy ring. The ions at m/z = 194 and 207 reflect fragmentations alpha and beta to the double bond. The ion at m/z = 180 reflects fragmentation of the double bond itself. The ions at m/z = 166 and 152 reflect fragmentations, respectively, at the alpha and beta carbon atoms to the double bond. The ion at m/z = 137 reflects fragmentation of the methyl group attached to the chain. The abundant ion at m/z = 123 reflects fragmentation at the alpha carbon atom to the carbon attaching the methyl group. The abundant ions at m/z = 55 and 41 reflect fragmentations, respectively, at the beta and alpha carbon atoms to the epoxy ring. While the abundant ion at m/z = 29 reflects fragmentation of the epoxy ring. The gap of 70 amu between m/z = 264 and 194 suggests that the double bond is in position 8 from the first epoxy ring. The gap of 139 amu between m/z = 180 and 41 indicates that the second epoxy ring is in position 9 from the double

bond, but in position 18 from the other epoxy ring. The gap of 111 amu between m/z = 152 and 41 indicates that the methyl group is in position 9 from the second epoxy ring, but in position 11 from the first epoxy ring.

The compounds corresponding to peaks 9 – 12 have spectra consistent, respectively, with 1,2-epoxy-9-methyl-nonoxy-1,8-decadiene (Appendix 2); 3-(1,2-epoxy-heptyl)-11,12-epoxy-4-methyl-2-dodecene (Appendix 3); 3-(1,2-epoxy-heptyl)-11,12-epoxy-4-methyl-1-dodecene (Appendix 4) and 1,2,17, 18-diepoxy-9,10 dimethyl-7-octadecene (Appendix 5).

4.1.1.4 Mass spectrum (MS) of other products

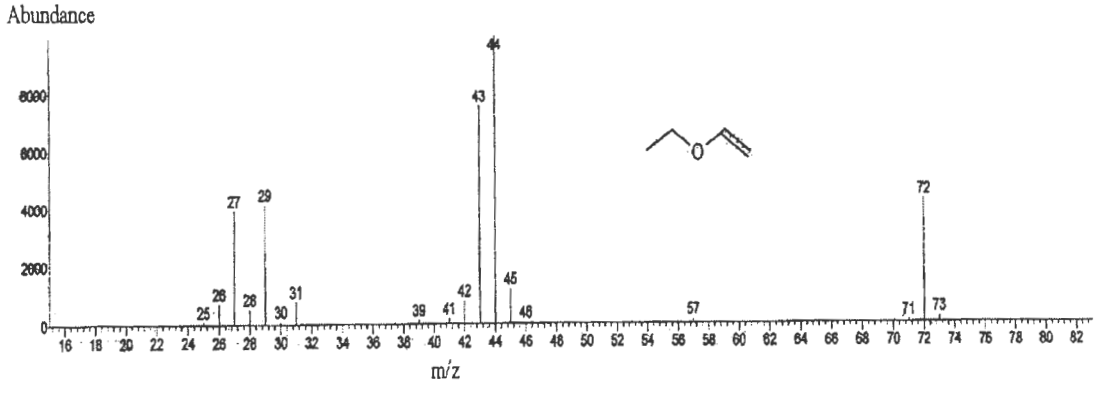


Figure 11. MS of ethoxy-ethene (m/z = 72).

The compounds corresponding to peaks 2 - 5 are consistent, respectively, with ethoxy-ethene (Figure 11), methylene chloride (Appendix 6), 1-hexene (Appendix 7) and benzene (Appendix 8).

Table 4. Products obtained when ED is metathesised using 2 wt.% $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalyst at room temperature.

Peak no	C_x	Product	Carbon skeleton	m/z	Yield	Selectivity
					%	%
Substrate						
6	C_{10}	1,2-epoxy-9-decene	$COC_8{=}C$	154	1.0	
Primarymetathesis products						
7	C_{18}	1,2,17,18-diepoxy-9-octadecene	$COC_8{=}C_8OC$	280	97.4	98.4
Dimerization products						
8	C_{20}	1,2,18,19-diepoxy-11-methyl-8-nonadecene	$COC_7{=}C_3(C)C_7OC$	308	-	-
9	C_{20}	1,2-epoxy-9-methyl-nonoxy-1,8-decadiene	$C{=}C_7{=}C_2OC(C)C_7OC$	308	0.6	0.6
10	C_{20}	3-(1,2-epoxy-heptyl)-11,12-epoxy-4-methyl-2-dodecene	$C_2{=}C(COC_6)C(C)C_7OC$	308	0.4	0.4
11	C_{20}	3-(1,2-epoxy-heptyl)-11,12-epoxy-4-methyl-1-dodecene	$C{=}C_2(COC_6)C(C)C_7OC$	308	0.3	0.3
12	C_{20}	1,2,17,18-diepoxy-9,10-dimethyl-7-octadecene	$COC_6{=}C_2(C)C(C)C_7OC$	308	0.3	0.3
Other						
1	C_3	Acetone	CCOC	58	-	-
2	C_4	ethoxy-ethene	$C{=}COC_2$	72	-	-
3	C	methylene chloride	ClCCl	84	-	-
4	C_6	1-hexene	$C{=}C_5$	84	-	-
5	C_6	benzene		78	-	-

Re:Sn:ED = 1:0.5:10, Reaction time = 2 h, Solvent = PhCl.

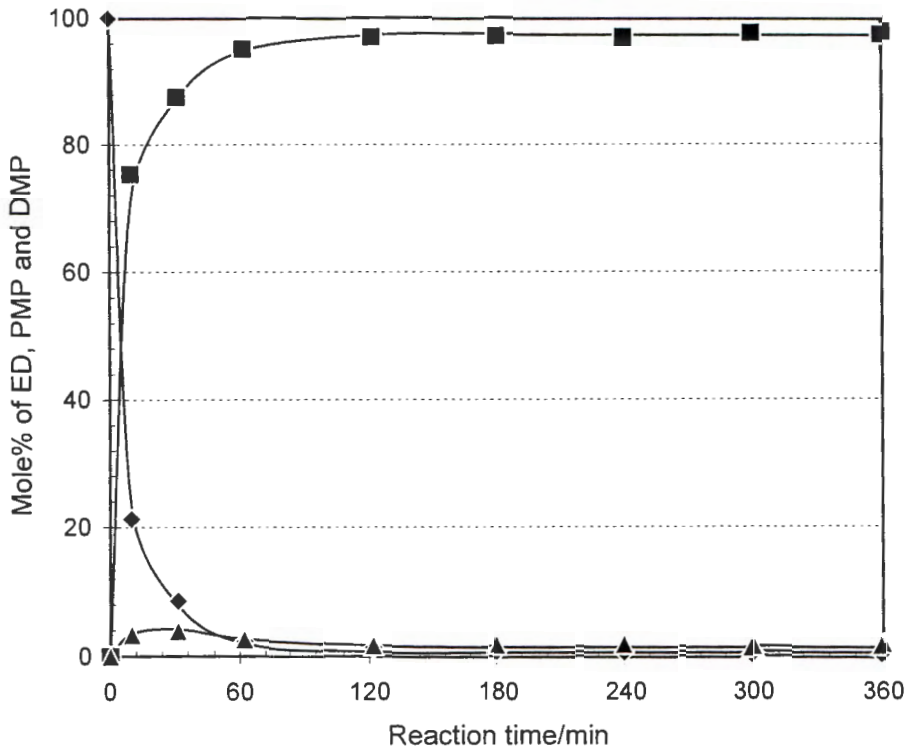


Figure 12. Amount of products and substrate (as mole%) as a function of reaction time, when ED is metathesised using 2 wt.% $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ at room temperature. [◆ : ED, ■ : PMP, ▲ : DMP]

Table 4 shows the product distribution, yields and selectivity when ED is metathesised with 2 wt.% Re_2O_7 catalyst. It can be seen that 1,2,17,18-diepoxy-9-octadecene was obtained in highest yield (ca. 97.4%), and also that the total DMP yield obtained was ca. 1.6%. The 2 wt.% $Re_2O_7/SiO_2{\cdot}Al_2O_3$ catalyst was therefore highly selective towards the primary metathesis product, 1,2,17,18-diepoxy-9-octadecene (ca. 98.4%). Other products obtained from side reactions were in traces. Although it has been reported[14] that the use of silica-alumina support leads to lower selectivity, Table 4 suggests that $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalyst, which is highly active, is also highly selective in the metathesis of a terminal epoxy olefin.

This high selectivity could be explained in terms of the removal of ethene from the reaction mixture, which was achieved by purging with nitrogen. The removal of ethene would lead to the equilibrium shifting towards the diepoxy olefin (see reaction (42) in chapter 2, page 25). In the case of α,ω-dienes, the removal of ethene led to the formation of polymers, as illustrated by reaction (46) in chapter 2, page 26.

The primary metathesis product was 1,2,17,18-diepoxy-9-octadecene (m/z = 280), whilst the dimers were an ether type product 1,2-epoxy-9-methyl-nonoxy-1,8-decadiene (m/z = 308) and the following diepoxy alkenes: 1,2,18,19-diepoxy-11-methyl-9-nonadecene (m/z = 308); 3-(1,2-epoxy-heptyl)-11,12-epoxy-4-methyl-2-dodecene (m/z = 308); 3-(1,2-epoxy-heptyl)-11,12-epoxy-4-methyl-1-dodecene (m/z = 308) and 1,2,17,18-diepoxy-9,10-dimethyl-7-octadecene (m/z = 308). Other products formed were ethoxy ethene, methylene chloride, 1-hexene and benzene. Although acetone was also found to be present in the reaction mixture, it could have been accidentally introduced during sampling.

Figure 12 shows the change in substrate and products amounts (as mole%) with time. It can be seen that the reaction almost went to completion. The conversion of ED was ca. 99.0% and this suggests that the 2 wt.% Re_2O_7/ SiO_2·Al_2O_3 catalyst was highly active in the metathesis of ED. Products (PMP and DMP) and substrate (ED) reached their steady state after 2 hours. The total DMP yield was 4.2% after 30 minutes, and this decreased to ca. 1.6% after 2 hours.

4.1.2 The influence of the Sn:Re molar ratio

The influence of the molar ratio of Sn:Re on the activity, selectivity and stability of Re_2O_7/SiO_2·$Al_2O_3/SnBu_4$ catalytic system when ED (1,2-epoxy-9-decene) was metahesised, was also investigated. ED was metathesised in chlorobenzene, in the presence of 2 wt.% Re_2O_7 catalyst, at room temperature. Re:Sn:ED = 1:x:10 , where x = 0, 0.5, 1, 2, 3.

Table 5. Conversion, yield and selectivity for ED using 2 wt.% Re_2O_7/SiO_2·$Al_2O_3/SnBu_4$ catalyst.

Sn:Re	Conversion (%)	Yield (%)		Selectivity (%)
		PMP	DMP	PMP
0	20.4	15.2	5.2	74.5
0.5	99.0	97.4	1.6	98.4
1	50.0	40.0	10.0	80.0
2	57.5	39.3	18.2	68.4
3	84.6	51.1	33.5	60.4

Reaction temperature = room temperature. Reaction time = 4 h, Solvent = PhCl.

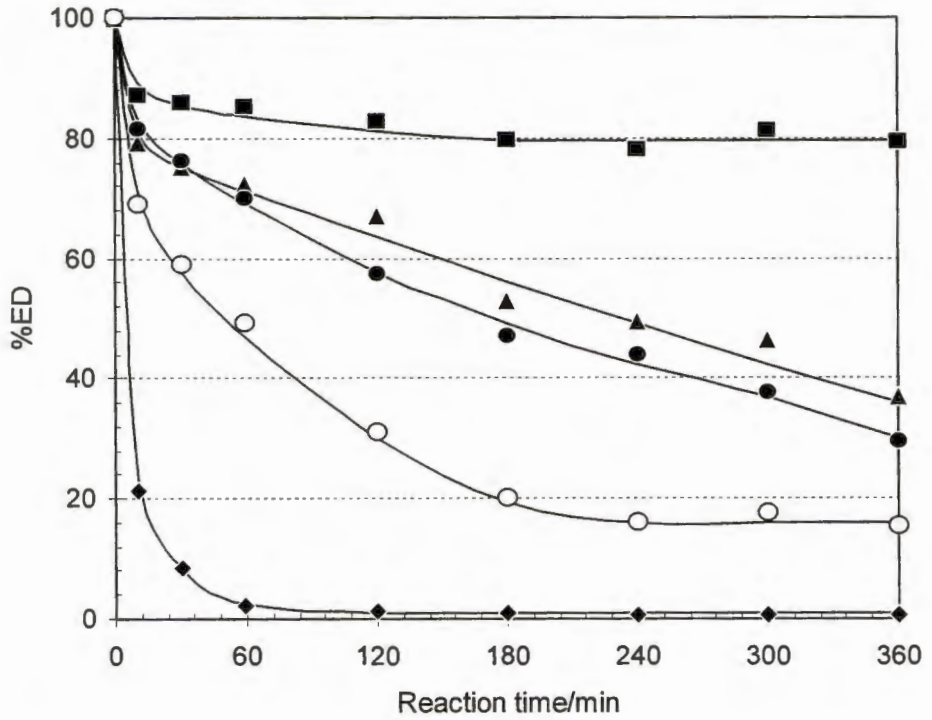


Figure 13. %ED converted at various Sn:Re molar ratios, as a function of reaction time, using 2 wt.% $Re_2O_7/SiO_2 \cdot Al_2O_3/SnBu_4$ at room temperature. [■ : Sn:Re = 0, ◆ : Sn:Re = 0.5, ▲ : Sn:Re = 1, ● :Sn:Re = 2, ○ : Sn:Re = 3]

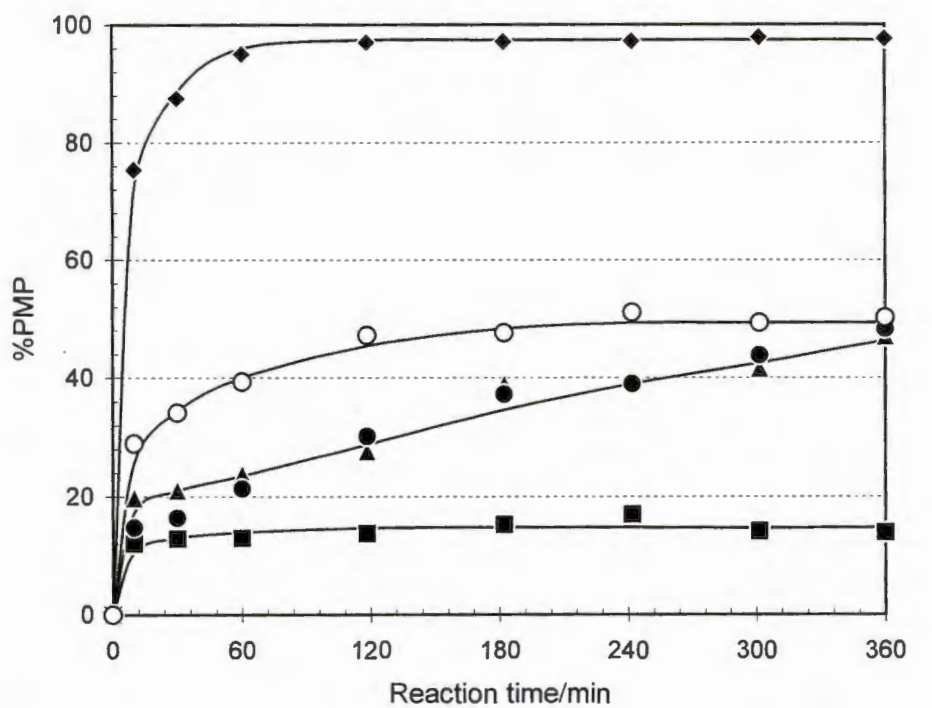


Figure 14. %PMP (1,2,17,18-diepoxy-9-octadecene) yield, at various Sn:Re molar ratios, as a function of reaction time, using 2 wt. % $Re_2O_7/SiO_2 \cdot Al_2O_3/SnBu_4$ at room temperature. [■ : Sn:Re = 0, ◆ :Sn:Re = 0.5, ▲ : Sn:Re = 1, ● : Sn:Re = 2, ○ : Sn:Re = 3]

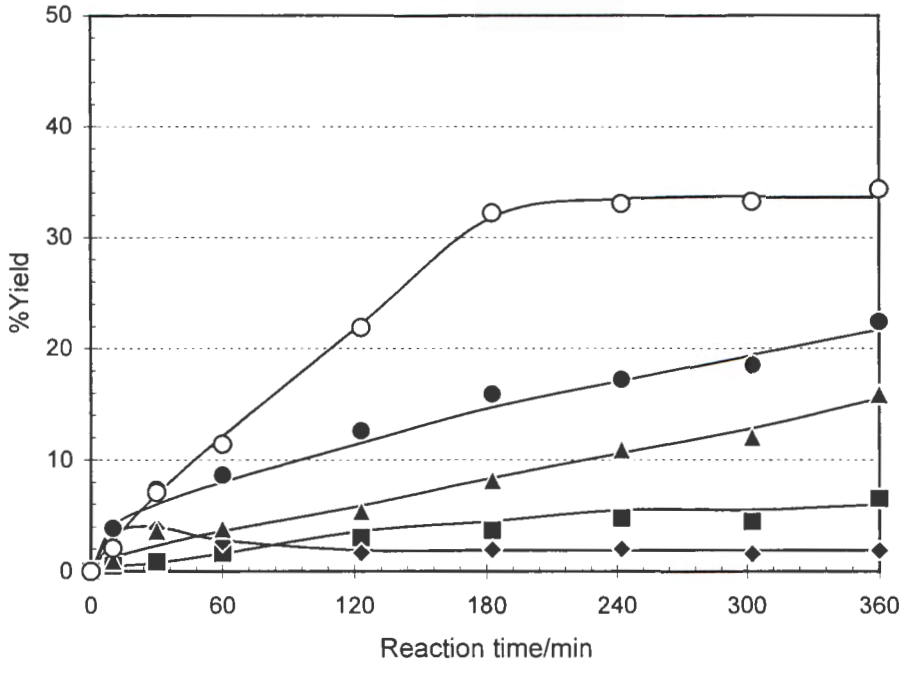


Figure 15. %DMP (dimers) yield at various Sn:Re molar ratios, as a function of reaction time using 2 wt. % $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ at room temperature. [■ : Sn:Re = 0, ◆ : Sn:Re = 0.5, ▲ :Sn:Re = 1, ● : Sn:Re = 2, ○ : Sn:Re = 3]

Table 5 shows conversions, yields and selectivity when ED was metathesised at different Sn:Re molar ratios, after 4 h. It can be seen that the 2 wt.% $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalyst gave the highest conversion (ca. 99.0%) at a Sn:Re molar ratio of 0.5. Generally, the conversion increased with increase in Sn:Re molar ratio from Sn:Re molar ratio of 0 to 3, with the exception of Sn:Re molar ratio of 0.5.

A similar trend was also observed with respect to the PMP yield, whereby the Sn:Re molar ratio of 0.5 gave the highest PMP yield (ca. 97.4%). The DMP yield was lowest at Sn:Re molar ratio of 0.5 (ca. 1.6%). Although there was a general increase in the PMP yield with increase in Sn:Re molar ratio between 0 and 3, there was no significant difference in the PMP yield at Sn:Re molar ratios of 1 and 2. Generally, the DMP yield increased with increase in the Sn:Re molar ratio between 0 and 3, with the exception at Sn:Re molar ratio of 0.5.

The selectivity towards PMP decreased with increase in the Sn:Re molar ratio between 0.5 and 3. In the absence of a cocatalyst, the 2 wt.% $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalyst was also still highly selective towards PMP.

The highest activity at Sn:Re molar ratio of 0.5 suggests that all the $SnBu_4$ added to the catalytic system is not needed to produce the active sites responsible for metathesis reaction. A sharp decrease in the conversion between an Sn:Re molar ratio of 0.5 and 1 suggests deactivation of the rhenium catalytic system. This indicates a possible interaction between the extra $SnBu_4$ molecules with the rhenium-carbene species. A sharp decrease in the conversion in the absence of $SnBu_4$ suggests that a co-catalyst is essential for enhancing the activity of the rhenium catalyst, for the metathesis of epoxy alkenes.

Figure 13 compares the conversions of ED at various Sn:Re molar ratios as a function of reaction time. It can be seen that the conversion of ED increased with increase in Sn:Re molar ratio from 0 to 0.5, then decreased from 0.5 to 1. The conversion increased again between Sn:Re molar ratios of 1 and 3. The reaction at a Sn:Re molar ratio of 0.5 was faster than at other molar ratios. For example, the equilibrium was reached after 2 h. For Sn:Re molar ratio of 3 the equilibrium was reached after 4 h, with a conversion of ca. 84.6%. In the absence of a cocatalyst (Sn:Re molar ratio = 0), the reaction equilibrium was reached after 3 h of reaction with a conversion of ca. 20.4%. For both the Sn:Re molar ratio of 1 and 2, the reaction equilibrium could not be reached within 6 h.

Figure 14 shows the change in the PMP yield with reaction time. It can be seen that the yield for a Sn:Re molar ratio of 0.5 reached equilibrium after 2 h, with the highest yield of ca. 97.4%. This was followed by a Sn:Re molar ratio of 3 where equilibrium was reached after 4 h of reaction, with an optimum yield of ca. 51.1%. For both Sn:Re molar ratios of 1 and 2, PMP yield increased with time without attaining equilibrium within 6 h of reaction.

Figure 15 shows the change in the DMP yield as a function of reaction time. It can be seen that the Sn:Re molar ratio of 3 gave the highest DMP yield (ca. 33.5%), with equilibrium reached after 4 h of reaction. For Sn:Re molar ratios of 1 and 2, the DMP yield continued to increase without reaching equilibrium within the 6 h. For an Sn:Re molar ratio of 0, DMP yield increased with time without reaching equilibrium. The Sn:Re molar ratio of 0.5 gave the lowest DMP yield, with the yield increasing for the first 30 minutes and then gradually decreasing until it reached equilibrium after 2 h of reaction.

Since PMP and the DMP yields increased with increase in the $SnBu_4$ content within the Sn:Re molar ratio of 1and 3 (see Table 3), the decrease in selectivity cannot be attributed to the deactivation of the catalytic system. Examination of Figures 14 and 15 shows that the rate of

dimerisation was slightly higher than the rate of self-metathesis. This clearly suggests that the increased activity of the catalytic system was due to the increased rate of the dimerisation reaction. This was possibly initiated by an increased interaction between the remaining $SnBu_4$ and the support, which increased the Brønsted acid sites responsible for isomerization via double bond migration. These findings are in agreement with the results reported by Rodella et al. [35] for the metathesis of methyl oleate over Re_2O_7-based catalysts supported on borated silica-alumina. They reported that the selectivity of Re_2O_7-based catalysts depends on the concentration of $SnBu_4$ concentration.

4.1.3 Influence of Re_2O_7 loading

The influence of Re_2O_7 content on the activity of $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalytic system was investigated. ED (1,2-epoxy-9-decene) was metathesised in chlorobenzene at room temperature, with wt. %Re_2O_7 = 0.5, 1, 2, 3. Re: Sn:ED = 1:0.5:10.

Table 6. Conversion, product yield and selectivity of ED at room temperature; using different Re_2O_7 loadings.

Re_2O_7 (wt. %)	Conversion (%)	Yield (%)		Selectivity (%)
		PMP	DMP	PMP
0.5	99.0	97.3	1.7	98.3
1	99.8	98.7	1.1	98.9
2	99.0	97.4	1.6	98.4
3	93.7	87.2	6.5	93.1

Re:Sn:ED = 1:0.5:10, Reaction time = 4 h, Solvent = PhCl.

NWU LIBRARY

Table 6 shows conversions, yields and selectivity of ED at different Re_2O_7 loadings, after 4 h of reaction. The catalytic system was most active in the range 0.5 to 2 wt.% Re_2O_7 loading. The highest conversion of ca. 99.8% was obtained with a 1 wt.% Re_2O_7 loading. Generally, conversions decreased with increase in Re_2O_7 loading from 1 to 3 wt.% Re_2O_7 loading. There was also a decrease in conversion below 1 wt.% Re_2O_7 loading. PMP yield was most optimum in the range 0.5 to 2 wt.% Re_2O_7 loading. The highest yield of ca. 99.8% was obtained with a 1 wt.% Re_2O_7 loading. Whilst there was a decrease in PMP yield from 1 to 3 wt.% Re_2O_7 loading, there was corresponding increase in DMP yield. The catalytic system was most selective in the range 0.5 to 2 wt.% Re_2O_7 loading. The highest selectivity of ca. 98.9% was obtained with a 1 wt.% Re_2O_7 loading. Generally, the selectivity decreased with increase in Re_2O_7 loading from 1 to 3 wt.% Re_2O_7 loading.

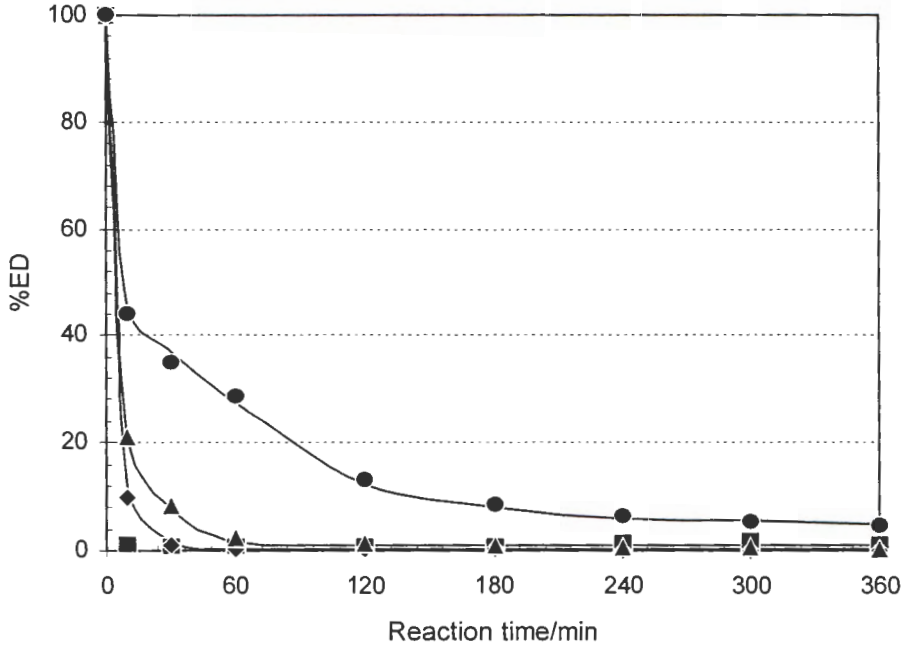


Figure 16. %ED converted at different Re_2O_7 loadings, as a function of reaction time at room temperature temperature. Re:Sn:ED = 1:0.5:10. [■ : 0.5 wt.% Re_2O_7, ◆ : 1 wt.% Re_2O_7, ▲ : 2 wt.% Re_2O_7, ● : 3 wt.% Re_2O_7]

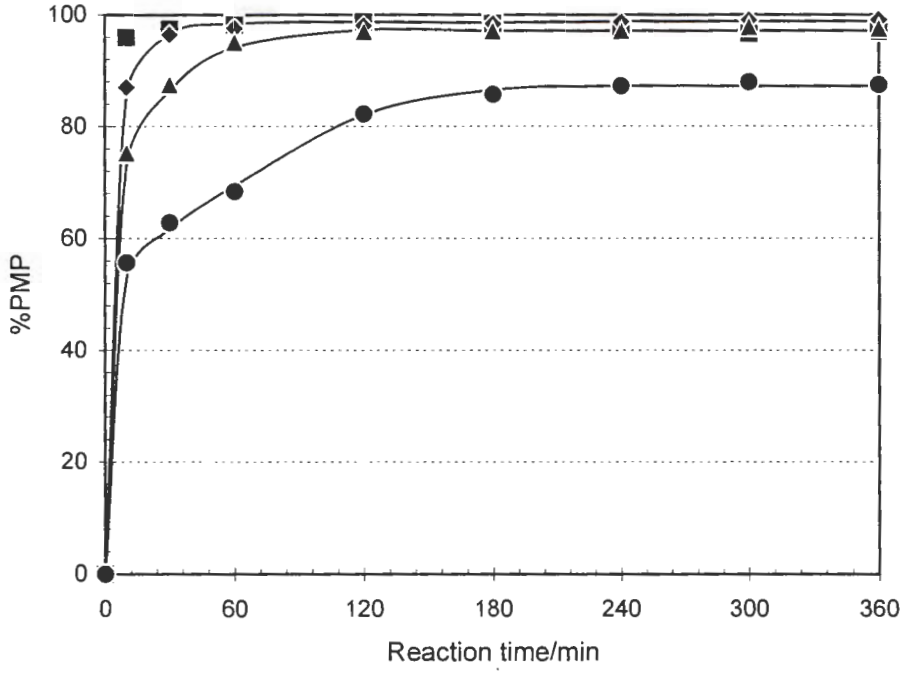


Figure 17. %PMP yield at different Re_2O_7 loadings, as a function of reaction time, at room temperature. Re: Sn:ED = 1:0.5:10. ■ : 0.5 wt.% Re_2O_7, ◆ : 1 wt.% Re_2O_7, ▲ : 2 wt.% Re_2O_7, ● : 3 wt.% Re_2O_7]

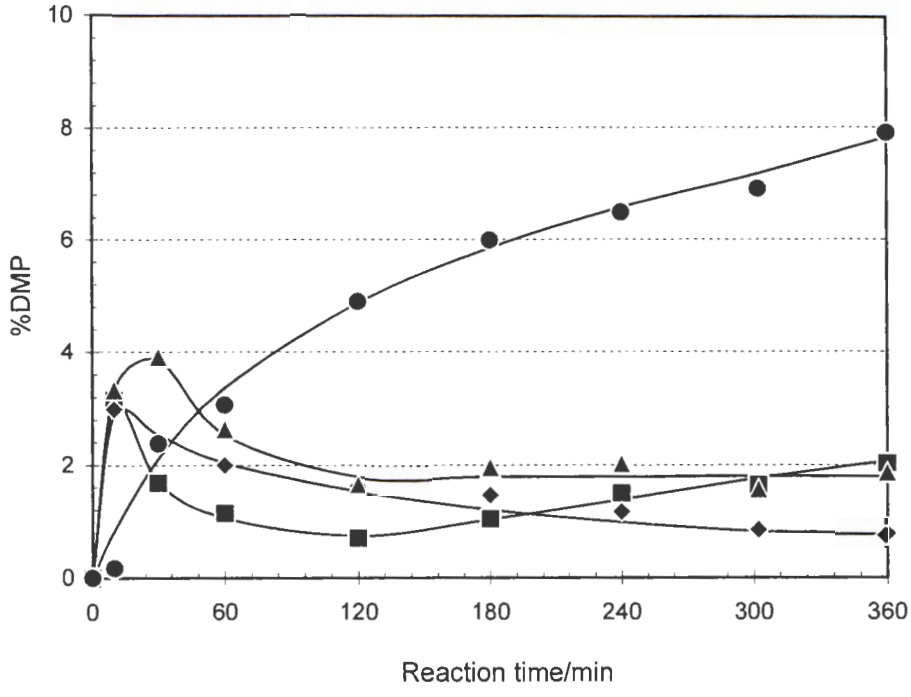


Figure 18. %DMP yield at different Re_2O_7 loadings, as a function of reaction time at room temperature. Re: Sn:ED = 1:0.5:10. ■ : 0.5 wt.% Re_2O_7, ◆ : 1 wt.% Re_2O_7, ▲ : 2 wt.% Re_2O_7, ● : 3 wt.% Re_2O_7]

Figure 16 shows the conversions of ED at different Re_2O_7 loadings. It can be seen that equilibrium in the metathesis reaction is achieved faster with decrease in Re_2O_7 loading. Figures 17 and 18 show, respectively, the change in PMP and DMP yields as a function of reaction time. Examination of Figure 17 shows that at 0.5 wt.% Re_2O_7 loading the PMP yield reached an optimum value after 2 h of reaction. This was followed by a gradual decrease in the yield. Figure 18 shows that there was a corresponding increase in the DMP yield after 2 h of reaction. This suggests that the rate of dimerisation reaction increased when that of self-metathesis reaction decreased. At lower Re_2O_7 loadings, there is possibly an interaction of the $SnBu_4$ molecules with the support. This may lead to increase in Brønsted acidity of the support and therefore to double bond isomerisation of substrate molecules. This would increase DMP yield.

At higher Re_2O_7 loadings, most of the OH groups on the support are replaced by ReO_4^- species. This would lead to an increase in the Brønsted acid sites on the support, and therefore to the double bond isomerisation of substrate molecules. Hence to an increase in DMP yield. The deactivation of the catalytic system at both lower and higher Re_2O_7 loadings may be attributed to the adsorption of dimerisation products and polymeric products onto the surface of the support. This would block the surface pores on the support and would also decrease the selectivity of the

catalytic system (see Table 4).

4.1.4 Influence of reaction temperature

The influence of temperature on the activity, selectivity and stability of $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalytic system was investigated by metathesising ED (1,2-epoxy-9-decene) using 2 wt.% $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalyst in chlorobenzene at Re:Sn:ED = 1:0.5:10. Temperatures used were 20, 40, 60, 80, 100 °C.

Although a 1 wt.% Re_2O_7 loading gave the highest activity and selectivity, it had the disadvantage of requiring large amounts of catalyst which interfered with the mechanical stirring of the solution: frequent physical agitation was needed to resume stirring. This problem was due to the large particle size of the catalyst. This problem could be resolved by diluting the reaction mixture with chlorobenzene solvent: dilution however, would reduce the amounts of products formed. Since there was no significant difference in the catalytic activity between the 1 and 2 wt.% Re_2O_7 loadings, a 2 wt.% Re_2O_7 loading was used in my studies.

Table 7. Conversion, product yield and selectivity for ED at different reaction temperatures using 2 wt.% $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalyst.

Re_2O_7 (wt. %)	Conversion (%)	Yield (%)		Selectivity (%)
		PMP	DMP	PMP
0	68.7	43.1	25.6	62.7
20	99.2	97.4	1.8	98.2
40	90.5	39.2	51.3	43.3
60	91.7	44.5	47.2	48.5
80	83.6	39.9	43.7	47.7
100	85.2	34.3	50.9	40.3

Re:Sn:ED = 1:0.5:10, Reaction time = 4 h, Solvent = PhCl.

Table 7 shows the conversions, yields and selectivity for ED in the temperature range 0 – 100°C. It can be seen that, the highest conversion of ca. 99.2% was obtained at 20 °C. Generally, conversions decreased with increase in temperature from 20 – 100 °C. $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalytic system also showed high activity even at the very low temperature of 0 °C (ca. 68.7%), with high selectivity towards PMP (ca. 62.7%). Although PMP yield decreased above 20 °C, there was corresponding increase in DMP yield above this temperature. The catalytic system was most selective at 20 °C. The selectivity decreased with increase in temperature between 20 – 100 °C. The catalytic system was also selective towards PMP (ca. 62.7%) below 20 °C.

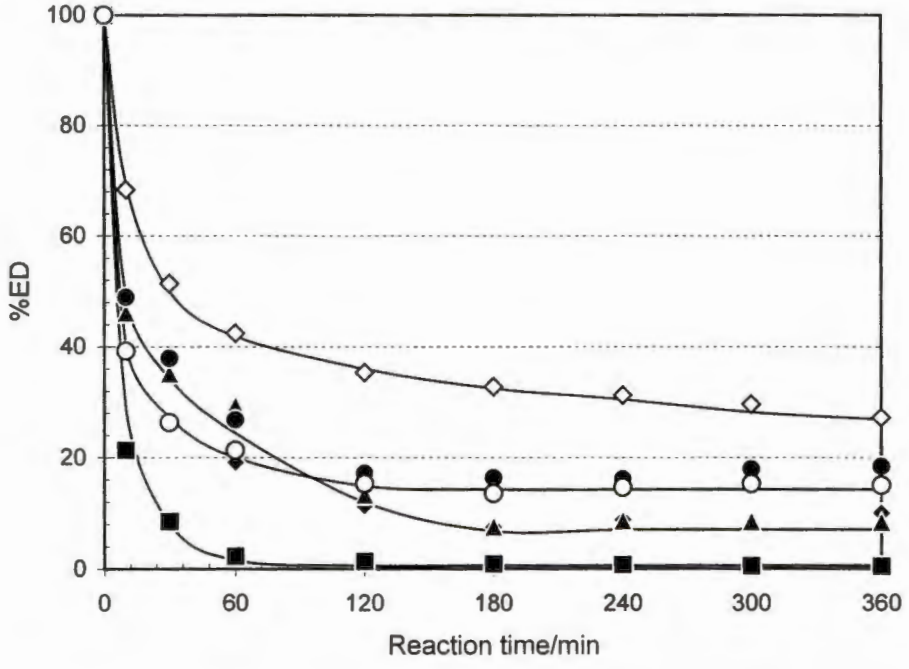


Figure 19. % ED at different temperatures, as a function of reaction time, using 2 wt. % $Re_2O_7/SiO_2 \cdot Al_2O_3/SnBu_4$. [◇ : 0 °C, ■ : 20 °C, ◆ : 40 °C, ▲ : 60 °C, ● : 80 °C, ○ : 100 °C]

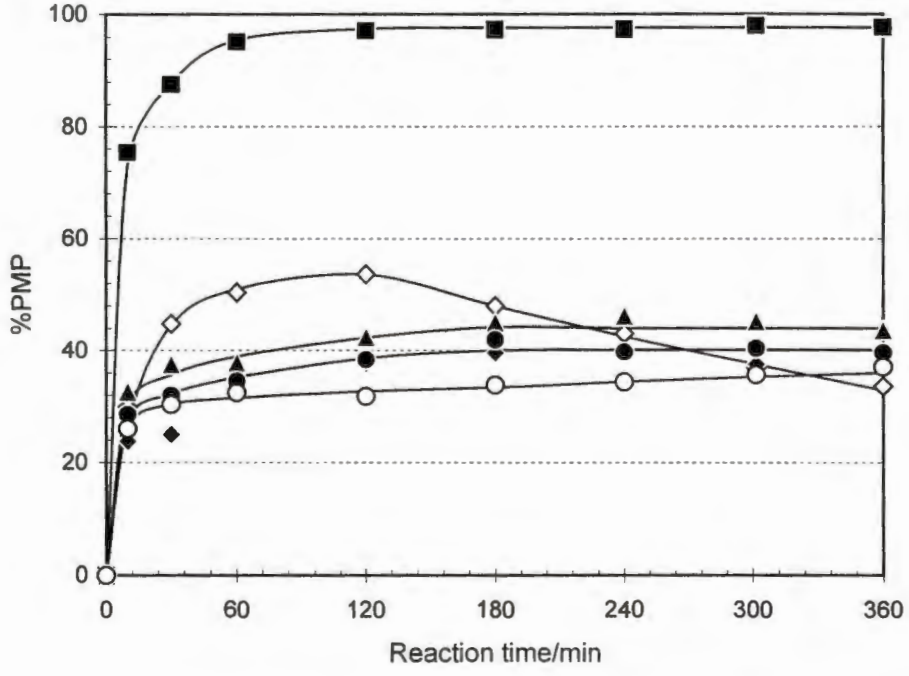


Figure 20. %PMP yield at different temperatures, as a function of reaction time, using 2 wt. % $Re_2O_7/SiO_2 \cdot Al_2O_3/SnBu_4$. [◇ : 0 °C, ■ : 20 °C, ◆ : 40 °C, ▲ : 60 °C, ● : 80 °C, ○ : 100 °C]

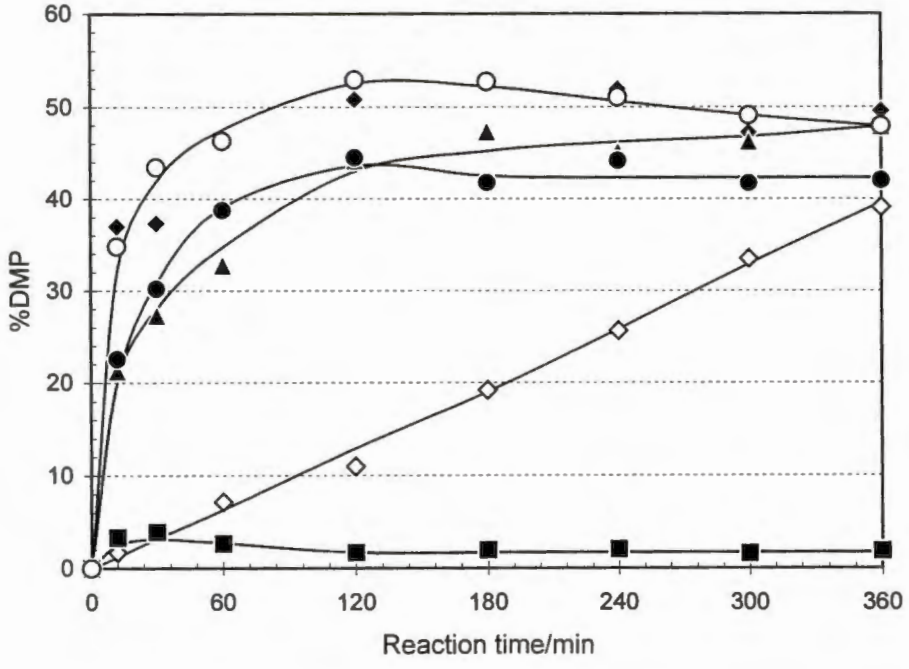


Figure 21. %DMP yield at different temperatures, as a function of reaction time, using 2 wt. % Re_2O_7/ SiO_2·Al_2O_3/$SnBu_4$. [◇ : 0 °C, ■ : 20 °C, ◆ : 40 °C, ▲ : 60 °C, ● : 80 °C, ○ : 100 °C]

Figure 19 shows the conversions of ED as a function of reaction time at different temperatures. $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalytic system gave the highest conversion (ca. 99.2%) at 20 °C, with equilibrium attained after just 2 h of reaction. The equilibrium at both 40 and 60 °C was reached after 3 h of reaction, and there was no significant difference in the conversions. A similar trend was also observed in the conversions between 80 and 100 °C. At 0 °C, the reaction did not attain equilibrium.

Figure 20 shows the change in the PMP yield as a function of time. The $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalytic system gave the highest PMP yield (ca. 97.4%) at 20 °C, with equilibrium reached after 2 h. At 0 °C, the optimum yield (ca. 53.6%) was obtained after 2 h; the yield then decreased with time. At 60 °C, the optimum PMP yield of ca. 46.2%, was obtained after 3 h of reaction. At both 40 and 80°C, the maximum PMP yield was obtained after 3 h of reaction. At 100 °C, the PMP yield continued to increase with time.

Figure 21 shows the change in DMP yield as a function of time at various temperatures. It can be seen that the highest yields were obtained at 40 °C and 100 °C. At 100 °C, the optimum DMP yield of ca. 52.5% was obtained after 2 h, and it then decreased with time. At 40 °C, the optimum DMP yield of ca. 52.9% was obtained after 2 h. At 80 °C, the maximum DMP yield of

ca. 44.5% was obtained after 2 h, and it then decreased to ca. 42.0%. At 60 °C, the maximum DMP yield of ca. 47.3% was obtained after 3 h of reaction. At 0 °C, the DMP yield continued to increase with time.

The decrease in conversion (see Table 7 and Figure 19) and PMP yield (see Table 7 and Figure 20) above 20 °C, suggests deactivation of the $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalytic system. This deactivation could be due to the clogging of the surface pores on the support by DMP and polymeric products. This is illustrated by high DMP yield at temperatures above 20 °C (see Table 7 and Figure 21). This would lead to blockage of substrate molecules from reaching the rhenium-carbene species. These species are responsible for metathesis reaction. These finding are contrary to the previous studies reported in literature. For example, Marvey et al.[6] achieved metathesis conversions of 86.1 to 86.9%, respectively, between 20 – 60 °C, in the metathesis of methyl linoleate. Kawai et al. [72] also obtained optimum metathesis conversion at 60 °C, for metathesis of halogen-containing olefins over Re_2O_7/Al_2O_3 catalyst promoted with an alkyl-metal as a cocatalyst.

4.1.5 The influence of solvent type

The influence of solvent type on the activity, selectivity and stability of $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalytic system was investigated by metathesising ED (1,2-epoxy-9-decene) using a 2 wt.% $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalyst at 20 °C. Re:Sn:ED = 1:0.5:10. The various solvents used were PhCl, C_6H_{14}, C_6H_6 and $CHCl_2$.

Table 8. Conversion, product yield and selectivity of ED in different solvents using 2 wt.% $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$.catalyst.

Solvent	Conversion (%)	Yield (%)		Selectivity (%)
		PMP	DMP	PMP
Chlorobenzene	99.2	97.4	1.8	98.2
Hexane	60.0	46.3	13.7	77.2
Benzene	35.8	24.3	11.5	67.9
Dichloromethane	24.7	20.4	4.3	82.3

Re:Sn:ED = 1:0.5:10, reaction time = 2 h. Reaction temperature = 20 °C.

Table 9. Solvent polarity values according to Reichardt[74].

Solvent	E_T^N value
n-Hexane	0.009
Carbon tetrachloride	0.052
Benzene	0.111
Chlorobenzene	0.188
Chloroform	0.259

Table 8 shows the conversions, yields and selectivity of ED using different solvents, after 2 h of reaction. Table 9 gives the normalised E_T^N values of solvent polarity according to Reichardt.[74] Although the polarity of dichloromethane is not shown, it can be estimated that its E_T^N value would be between that of chlorobenzene and chloroform. Therefore, the polarity of the solvent would increase in the order: dichloromethane > chlorobenzene > benzene > hexane.

It can be seen from Table 8, that the highest conversion (ca. 99.2%) was obtained using a moderately polar chlorobenzene solvent, followed by the least polar hexane solvent (ca. 60%). The lowest conversion (ca. 24.7%) was obtained using a highly polar dichloromethane solvent. Conversions generally decreased in the order: chlorobenzene > hexane > benzene > dichloromethane. This suggests that there was no correlation between the activity and solvent polarity. The activity generally increased with increase in solvent polarity.[6]

The PMP yield also decreased in the order: chlorobenzene > hexane > benzene > dichloromethane. Chlorobenzene and dichloromethane gave, respectively, the lowest DMP yields of ca. 1.8% and ca. 4.3%. The highest DMP yields were obtained when hexane (ca. 13.7%) and benzene (ca. 11.5%) were used. Highly polar solvents such as dichloromethane and chlorobenzene gave, respectively, the highest selectivity towards the PMP. Selectivity decreased in the order chlorobenzene > dichloromethane > hexane > benzene. Oikawa et al.[40] also reported conversion of up to 50.0%, with high selectivity towards primary metathesis products (>95%) in the metathesis of 7-hexadecene in hexane.

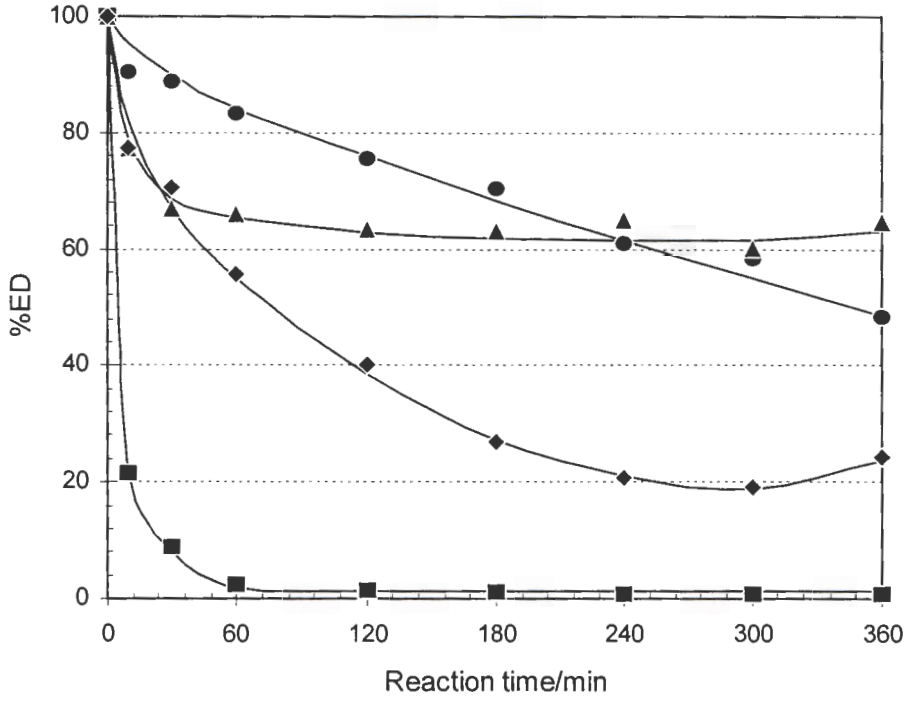


Figure 22. %ED for various solvents, as a function of reaction time using 2 wt. % $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ at 20 °C. [■ : chlorobenzene, ◆ : hexane, ▲ : benzene, ● : dichloromethane]

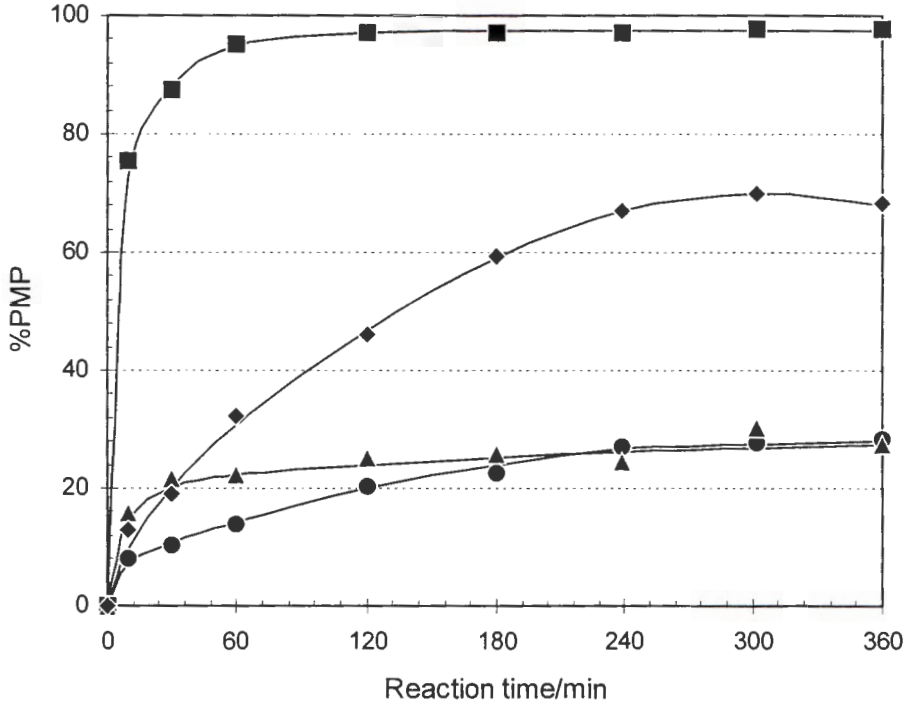


Figure 23. %PMP yield for various solvents, as a function of reaction time using 2 wt. % $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$, at 20 °C. [■ : chlorobenzene , ◆ : hexane, ▲ : benzene, ● : dicholoromethane]

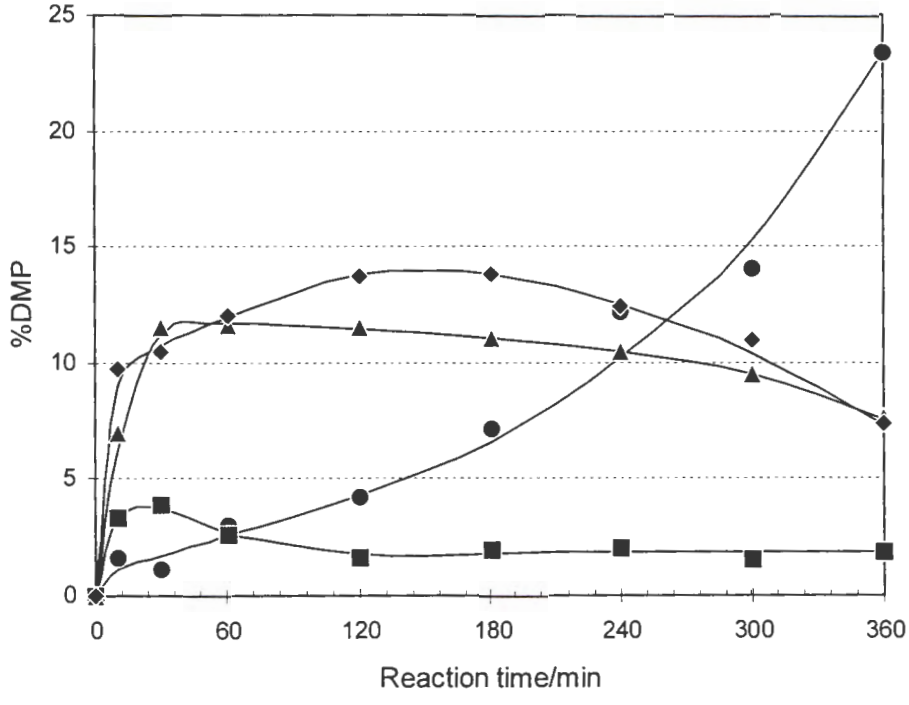


Figure 24. %DMP yield for various solvents, as a function of reaction time using 2 wt. % $Re_2O_7/SiO_2 \cdot Al_2O_3/SnBu_4$, at 20 °C. [■: chlorobenzene , ◆: hexane, ▲: benzene, ●: dicholoromethane]

Figure 22 shows the conversions of ED for various solvents, as a function of time. It can be seen that chlorobenzene solvent gave the highest conversion of ca. 99.2% after 2 h. A non-polar hexane solvent gave the second highest conversion (ca. 80%) after 5 h of reaction. However, the conversion decreased after 5 h. Benzene solvent gave a conversion of ca. 35.8% after 2 h of reaction. For dichloromethane, the conversion increased with time.

Figure 23 shows the change in PMP yield as a function of time. The $Re_2O_7/SiO_2 \cdot Al_2O_3/SnBu_4$ catalytic system gave the highest PMP yield (ca. 97.4%) in chlorobenzene, with equilibrium attained after 2 h of reaction. Hexane gave the optimum PMP yield of ca. 70.0% after 5 h of reaction, and it then decreased. The PMP yield in dichloromethane reached the optimum of ca. 26.9%, with equilibrium reached after 4 h. The PMP yield in benzene continued to gradually increase.

Figure 24 shows the change in DMP yield as a function of time. Chlorobenzene solvent gave the lowest yield of ca. 1.8% after 2 h. In hexane, the optimum DMP yield of ca. 13.8% was obtained after 2 h of reaction. However, the yield then decreased without equilibrium being attained. A

similar trend was also observed with benzene, where the optimum DMP yield of ca. 11.5% was obtained after 30 minutes of reaction. In dichloromethane, DMP yield increased with time without equilibrium being attained.

4.1.6 The influence of substrate concentration

The influence of substrate concentration on the activity, selectivity and stability of $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalytic system was also investigated. ED (1,2-epoxy-9-decene) was metathesised with a 2 wt.% $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalyst at 20 °C. Solvent = PhCl. Re:Sn:ΔED = 1:0.5:x, where x = 10, 25, 50, 100, 200, 300, 400.

Table 10. Conversion, product yield and selectivity for ED using 2 wt.% $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalyst, at different Re:ED molar ratios.

Re_2O_7 (wt. %)	Conversion (%)	Yield (%)		Selectivity (%)
		PMP	DMP	PMP
1: 10	99.2	97.8	1.8	98.2
1: 25	96.4	38.2	58.2	39.6
1: 50	96.4	48.8	51.7	50.6
1: 100	98.5	46.3	41.2	47.0
1: 200	96.7	56.3	40.4	58.2
1: 300	95.1	34.0	61.1	35.8
1: 400	93.4	43.0	50.4	46.0

Re:Sn = 1:0.5, Reaction time = 4 h, Solvent = PhCl.

Table 10 shows conversions, yields and selectivity of ED for different substrate concentrations. It can be seen that the highest conversion of ca. 99.2% was obtained using an ED:Re molar ratio of 10. Although there was a slight decrease in conversion within ED:Re molar ratios of 10 to 400, the $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalytic system was still very active. This is probably due to an increase in the number of moles of ED converted by the catalyst. The rhenium catalyst was found to be stable even when the substrate concentration was increased forty times.

There were no patterns between the PMP yield, DMP yield, selectivity and substrate concentration. The DMP yield, however, increased with increase in substrate concentration; selectivity then decreased.

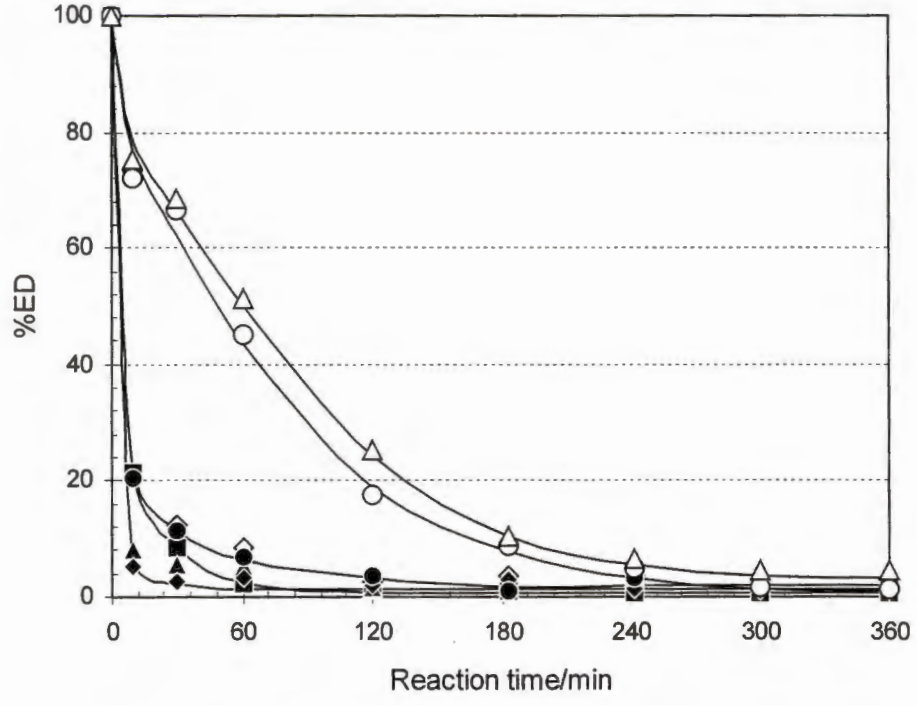


Figure 25. %ED converted for different ED/Re ratios, as a function of reaction time using 2 wt. % $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$. [■ : ED/Re = 10, ▲ : ED/Re = 25, ◇ : ED/Re = 50, ◆ : ED/Re = 100, ● : ED/Re = 200, ○ : ED/Re = 300, △ : ED/Re = 400]

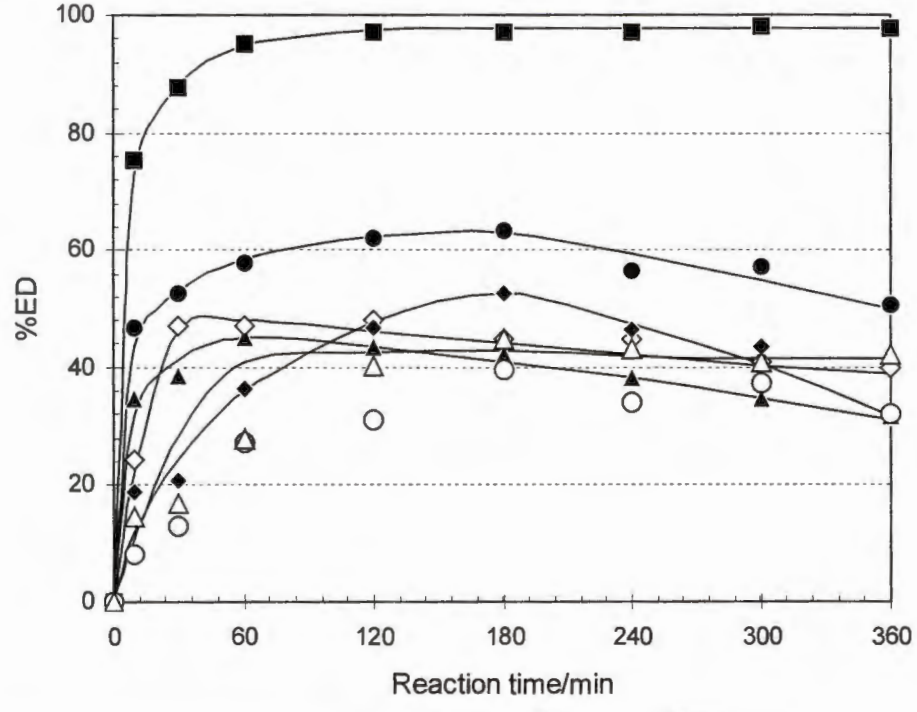


Figure 26. %PMP yield for different ED/Re ratios, as a function of reaction time using 2 wt. % $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$. [■ : ED/Re = 10, ▲ : ED/Re = 25, ◇ : ED/Re = 50, ◆ : ED/Re = 100, ● : Substrate/Re = 200, ○ : Substrate/Re = 300, △ : Substrate/Re = 400]

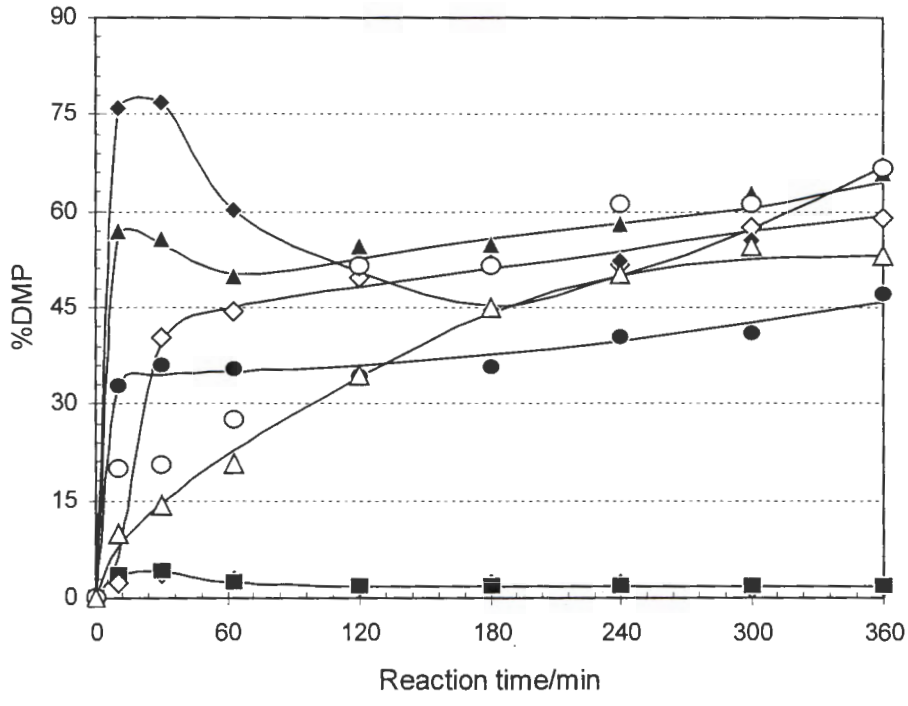


Figure 27. %DMP yield for different ED/Re ratios, as a function of reaction time using 2 wt. % Re_2O_7/ SiO_2·Al_2O_3/$SnBu_4$. [■ : ED/Re = 10, ▲ : ED/Re = 25, ◇ : ED/Re = 50, ◆ : ED/Re = 100, ● :Substrate/Re = 200, ○ : Substrate/Re = 300, △ : Substrate/Re = 400]

Figure 25 shows the conversion of ED for different substrate concentrations, as a function of time. It can be seen that equilibrium was attained faster at lower substrate concentrations. Figure 26 shows the change in PMP yield as a function of reaction time. The highest PMP yield was obtained when using an ED:Re ratio of 10, with equilibrium attained after 2 h. There was an initial increase in the PMP yield for other ED:Re ratios, and then decreased. For example, for an ED:Re ratio of 200, the PMP yield reached a maximum of ca. 63.5% after 3 h of reaction and then decreased.

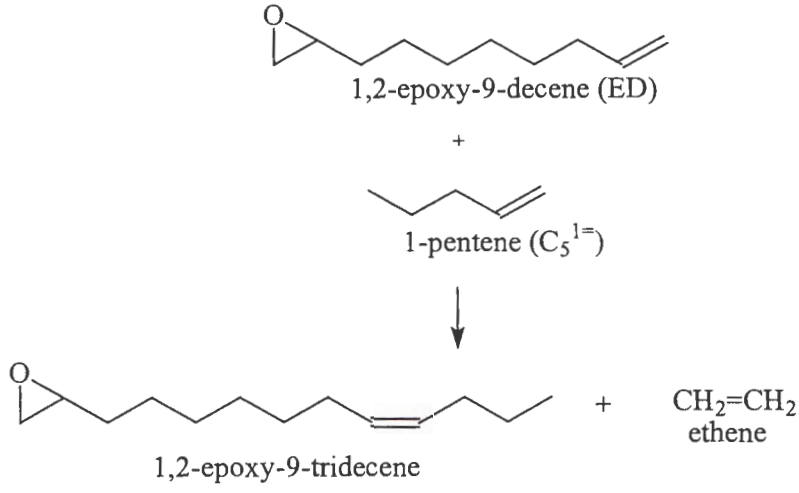
Figure 27 shows the change in DMP yield as a function of. The lowest DMP yield was obtained when using an ED:Re ratio of 10. The DMP yield increased within the first 30 minutes and then decreased to ca. 1.8% after 2 h. The DMP yield continued to increase for the following ED:Re ratios: 50; 200; 300 and 400. Figure 26 shows, however, that there was corresponding increase in PMP yield for ED:Re ratios of 50; 200; 300 and 400.

4.2 CROSS-METATHESIS OF 1,2-EPOXY-9-DECENE WITH 1-PENTENE ($C_5^{1=}$)

Metathesis activity, selectivity and stability of Re_2O_7/SiO_2·$Al_2O_3/SnBu_4$ catalyst were investigated for the cross-metathesis of ED (1,2-epoxy-9-decene) with $C_5^{1=}$ (1-pentene). ED and

$C_5^{1=}$ were metathesised in chlorobenzene at 20 °C, using a 2 wt.% $Re_2O_7/SiO_2{\cdot}Al_2O_3$/ $SnBu_4$ catalyst. Re:Sn:ED: $C_5^{1=}$ = 1:0.5:5:10.

Scheme 2 illustrates the formation of the primary metathesis products (PMP), 1,2-epoxy-9-tridecene and ethene, during the cross-metathesis of ED with $C_5^{1=}$. The gaseous product (ethene) is removed during purging with nitrogen.



Scheme 2. The cross-metathesis of ED with $C_5^{1=}$ to give PMP.

4.2.1 Reaction products

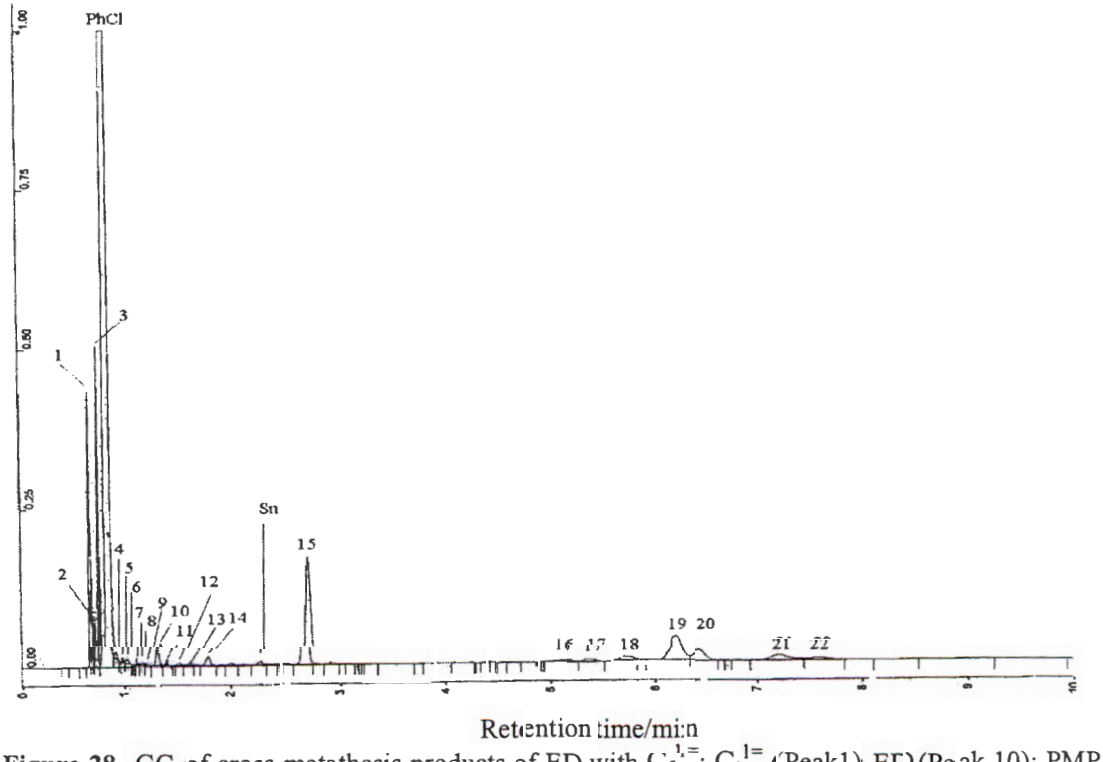


Figure 28. GC of cross-metathesis products of ED with $C_5^{1=}$: $C_5^{1=}$ (Peak1); ED (Peak 10); PMP (Peak: 5, 14-15; see Table 11); DMP (Peak 16 – 22, see Table 11) and other (Peak: 2 – 4, 6-9, 11-13; see Table 11). PhCl = chlorobenzene solvent.

Figure 28 shows a typical chromatogram of the product mixture obtained when ED is cross-metathesised with $C_5^{1=}$, using a 2 wt.% $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalyst. Although, according to the reaction Scheme 2, only one peak should be expected in Figure 28, the presence of more peaks suggests formation of other products, possibly from self-metatheis of ED and $C_5^{1=}$, side reactions and polymerisation reactions.

4.2.1.1 Mass spectrum (MS) of primary metathesis products (PMP)

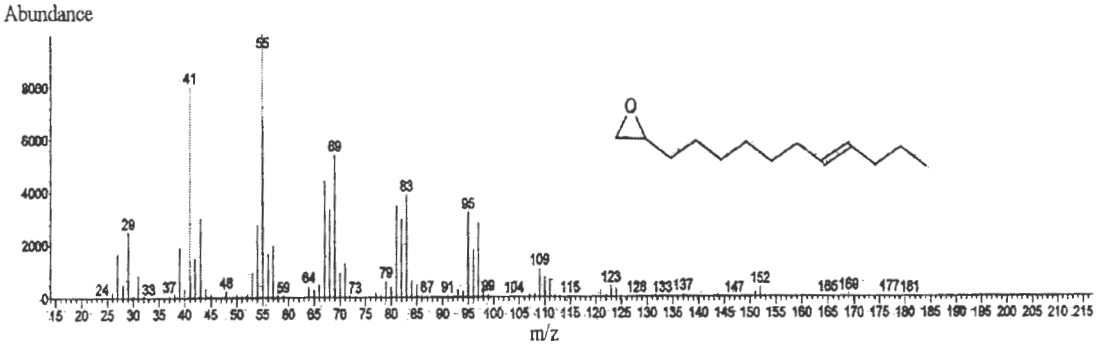


Figure 29. MS of 1,2-epoxy-9-tridecene (m/z = 196) obtained upon cross-metathesis of ED with $C_5^{1=}$.

Figure 29 represents a typical mass spectrum (MS) of 1-epoxy-9-tridecene (Peak 14), which is a primary metathesis product (PMP). This compound is obtained upon cross-metathesis of ED (Appendix 1) with $C_5^{1=}$ (Appendix 10). The molecular ion m/z = 196 is not detectable. The ion at m/z = 152 reflects fragmentation either at the alpha carbon atom to the double bond or alpha carbon atom to the epoxy ring. Examination of the MS shows abundant ions at m/z = 55, 41 and 29. The ions at m/z = 55 and 41, respectively, are more likely to reflect fragmentations at the carbon atoms beta and alpha to the epoxy ring. The ion at m/z = 29 would reflect fragmentation of the epoxy ring. This suggests that fragmentation of the molecular ion initially occurs at the methyl group rather than at the epoxy ring. This explains why the ion at m/z = 55 is also a base peak. The gap of 111 amu between m/z = 152 and 41, and of 82 amu between m/z = 123 and 41 serve to locate the double bond at position 9 from the epoxy ring.

The compound associated with peak 5 has a spectrum consistent with (Z)-4-octene (Appendix 11), which is a PMP obtained upon self-metathesis of $C_5^{1=}$ (Appendix 10). While the compound associated with Peak 15 has a spectrum consistent with 1,2,17,18-diepoxy-9-octadecene (Figure 11), which is a PMP obtained when ED self-metathesise.

4.2.1.2 Mass spectrum (MS) of dimerisation products (DMP)

The compounds corresponding to Peaks 16-22 have spectra consistent, respectively, with 1,2,18,19-diepoxy-11-methyl-8-nonadecene (Figure 10); 1,2,18,19-diepoxy-11-methyl-9-nonadecene (Appendix 21); 1,2-epoxy-9-methyl-nonoxy-1,8-decadiene (Appendix 2); 3-(1,2-epoxy-heptyl)-11,12-epoxy-4-methyl-2-dodecene (Appendix 3); 3-(1,2-epoxy-heptyl)-11,12-epoxy-4-methyl-1-dodecene (Appendix 4); 1,2,17,18-diepoxy-9,10-dimethyl-8-octadecene (Appendix 22); 1,2,17,18-diepoxy-9,10-dimethyl-7-octadecene (Appendix 5). These compounds are dimers obtained by the double bond migration in ED.

4.2.1.3 Mass spectrum (MS) of other products

The compounds associated with Peaks 2-4 have spectra consistent, respectively, with 2-hexene (Appendix 12); 3-hexene (Appendix 13) and (E)-3-heptene (Appendix 14). These compounds are secondary metathesis products obtained as a result of cross-metathesis of $C_5^{1=}$ with its isomers. The compound associated with Peak 13 has a spectrum consistent with 1,2-epoxy-9-undecene (Appendix 15). This compound is also a secondary metathesis product, but is obtained by the cross-metathesis of ED with isomers of $C_5^{1=}$.

The compounds corresponding to Peaks 7-9 and 11-12 have spectra consistent, respectively, with trans-2,2-dimethyl-3-heptene (Appendix 16); 1,8-nonadiene (Appendix 17); trans-4-nonene (Appendix 18); 2-(1-methylethyl)-1-chlorobenzene (Appendix 19) and 2,2,3,5,6-pentamethyl-3-heptene (Appendix 20). These compounds are possibly obtained from side reactions.

NWU LIBRARY

Table 11. Products obtained when ED is cross-metathesised with $C_5^{1=}$ using 2 wt.% $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalyst.

Peak no	C_x	Product	Carbon skeleton	m/z	Yield %	Selectivity %
Substrate						
1	C_5	1-pentene	C_4=C	70	50.3	
10	C_{10}	1,2-epoxy-9-decene	COC_8=C	154	11.3	
Primary metathesis products						
5	C_8	(Z)-4-octene	C_4=C_4	112	0.3	0.2
15	C_{18}	1,2,17,18-diepoxy-9-octadecene	COC_8=C_8OC	280	44.0	32.0
14	C_{13}	1,2-epoxy-9-tridecene	COC_8=C_4	196	0.6	0.4
Dimerization products						
16	C_{20}	1,2,18,19-diepoxy-11-methyl-8-nonadecene	COC_7=C_3(C)C_7OC	308	2.1	1.5
17	C_{20}	1,2,18,19-diepoxy-11-methyl-9-nonadecene	COC_8=C_2(C)C_7OC	308	1.3	0.9
18	C_{20}	1,2-epoxy-9-methyl-nonoxy-1,8-decadiene	C=C_7=C_2OC(C)C_7OC	308	0.7	0.5
19	C_{20}	3-(1,2-epoxy-heptyl)-11,12-epoxy-4-methyl-2-dodecene	C_2=C(COC_6)C(C)C_7OC	308	18.4	13.4
20	C_{20}	3-(1,2-epoxy-heptyl)-11,12-epoxy-4-methyl-1-dodecene	C=C_2(COC_6)C(C)C_7OC	308	10.9	7.9
21	C_{20}	1,2,17,18-diepoxy-9,10-dimethyl-8-octadecene	COC_7=C (C)C(C)C_7OC	308	7.3	5.3
22	C_{20}	1,2,17,18-diepoxy-9,10-dimethyl-7-octadecene	COC_6=C_2(C)C(C)C_7OC	308	3.0	2.2
Secondary metathesis products						
2	C_6	2-hexene	C_2= C_4	84	5.1	3.7
3	C_6	3-hexene	C_3=C_3	84	36.8	26.8
4	C_7	3-heptene	C_3=C_4	98	1.1	0.8
6	C_8	(Z)-3-octene	C_3 =C_5	112	0.9	0.6
13	C_{11}	1,2-epoxy-9-undecene	COC_8=C_2	168	0.3	0.2

Peak no	C_x	Product	Carbon skeleton	m/z	Yield %	Selectivity %
Side reactions						
7	C_9	Trans-2,2-dimethyl-3-heptene	$C_2(C)_2C=C_4$	126	0.13	0.1
8	C_9	1,8-nonadiene	$C=C_7=C$	124	0.5	0.4
9	C_9	trans-4-nonene	$C_4=C_5$	126	0.4	0.3
11	C_9	2-(1-methyl)-1-chlorobenzene		154	2.1	1.7
12	C_{12}	2,2,3,5,6-pentamethyl-3-heptene	$C_2(C)C(C)C=C(C)C(C)_2C$	168	1.5	1.1

Re:Sn:ED:$C_5^=$ = 1:0.5:5:10, Reaction temperature = 20 °C, Reaction time = 4 h, Solvent = PhCl.

Table 12. Diepoxy alkenes, epoxy esters and diesters obtained when ED is cross-metathesised with $C_5^{1=}$ using 2 wt.% $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalyst.

C_x	Product	m/z	Yield	Selectivity
			%	%
Alkenes				
C_8	(Z)-4-octene	112	0.3	0.2
C_8	(Z)-3-octene	112	0.9	0.6
C_6	2-hexene	84	5.1	3.7
C_6	3-hexene	84	36.8	26.8
C_7	3-heptene	98	1.1	0.8
C_9	1,8-nonadiene	124	0.5	0.4
C_9	trans-4-nonene	126	0.4	0.3
C_9	trans-2,2-dimethyl-3-heptene	126	0.1	0.1
C_9	2-(1-methylethyl)-1-chlorobenzene	154	2.1	1.7
C_9	2,2,3,5,6-pentamethyl-3-heptene	168	1.5	1.1
Epoxy alkenes				
C_{13}				
C_{11}	1,2-epoxy-9-tridecene	196	0.6	0.4
	1,2-epoxy-9-undecene	168	0.3	0.2
Diepoxy alkenes				
C_{18}				
C_{20}	1,2,17,18-diepoxy-9-octadecene	280	44.0	32.0
C_{20}	1,2,18,19-diepoxy-11-methyl-8-nonadecene	308	2.1	1.5
C_{20}	1,2,18,19-diepoxy-11-methyl-9-nonadecene	308	1.3	0.9
C_{20}	3-(1,2-epoxy-heptyl)-11,12-epoxy-4-methyl-2-dodecene	308	18.4	13.4
C_{20}	3-(1,2-epoxy-heptyl)-11,12-epoxy-4-methyl-1-dodecene	308	10.9	7.9
C_{20}	1,2,17,18-diepoxy-9,10-dimethyl-8-octadecene	308	7.3	5.3
	1,2,17,18-diepoxy-9,10-dimethyl-7-octadecene	308	3.0	2.2
Ethers				
C_{18}	1,2-epoxy-9-methyl-nonoxy-1,8-decadiene	308	0.7	0.5

Re:Sn:ED: $C_5^{=}$ = 1:0.5:5:10, Reaction temperature = 20 °C, Reaction time = 4 h, Solvent = PhCl.

Table 11 shows the product distribution, yields and selectivity when ED is cross-metathesised with $C_5^{1=}$, using a 2 wt.% $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalyst. It can be seen from the spectrum that the products are PMP and DMP. There are also secondary metathesis products (obtained from isomerisation of $C_5^{1=}$) and other products due to side reactions. The PMP ranged from C_5 to C_{18} and their molecular weights ranged from 70 to 280. Secondary metathesis products

(SMP) ranged from C_6 to C_{11}, while their molecular weights ranged from 84 to 168. There was only one cross-metathesis product (C_{13}), which had a molecular weight of 196. All the C_{20} DMP had a molecular weight of 308. Other products that were formed possibly from side reactions ranged from C_7 to C_{11}, and their molecular weights ranged from 98 to 168.

The highest PMP (1,2,17,18-diepoxy-9-decene) yield of ca. 44.0% was obtained from self-metathesis of ED. The cross-metathesis of ED with $C_5^{1=}$ also gave a PMP (1,2-epoxy-9-tridecene) with a yield of only ca. 0.6%. This suggests that in the cross-metathesis of ED with $C_5^{1=}$, the self-metathesis of ED is more favoured than cross-metathesis reaction (as illustrated by scheme 2).

DMP obtained during isomerisation of ED gave a combined yield of ca. 43.7% (Table 11). This yield was much higher than the yield obtained in the self-metathesis of ED (see Table 4). This suggests that the presence of $C_5^{1=}$promoted dimerisation of ED. It can be seen from Table 11 that the total selectivity towards PMP was ca. 32.6%. Table 12 shows the yield and selectivity in terms of the functional groups present in products. It can be seen that the product spectrum consisted mainly of alkenes, epoxy alkenes, diepoxy alkenes and the ether type products. The total selectivity towards diepoxy alkenes was ca. 63.2%.

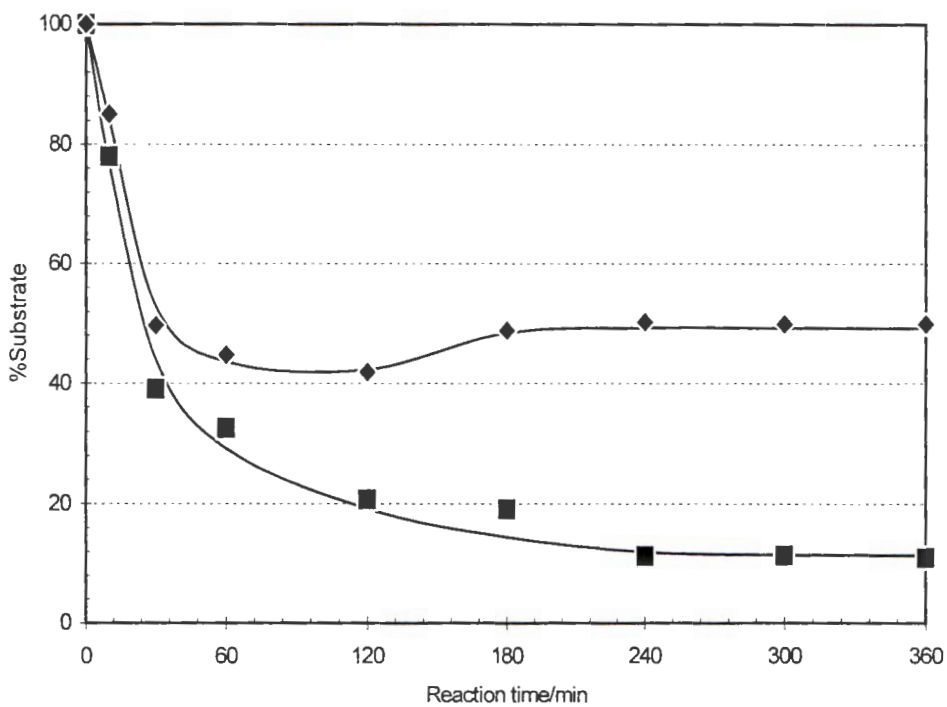


Figure 30. %Substrate (ED and $C_5^{1=}$) converted when ED is metathesised with $C_5^{1=}$, as a function of reaction time using 2 wt. % $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalyst. [■ : ED, ◆ : $C_5^{1=}$]

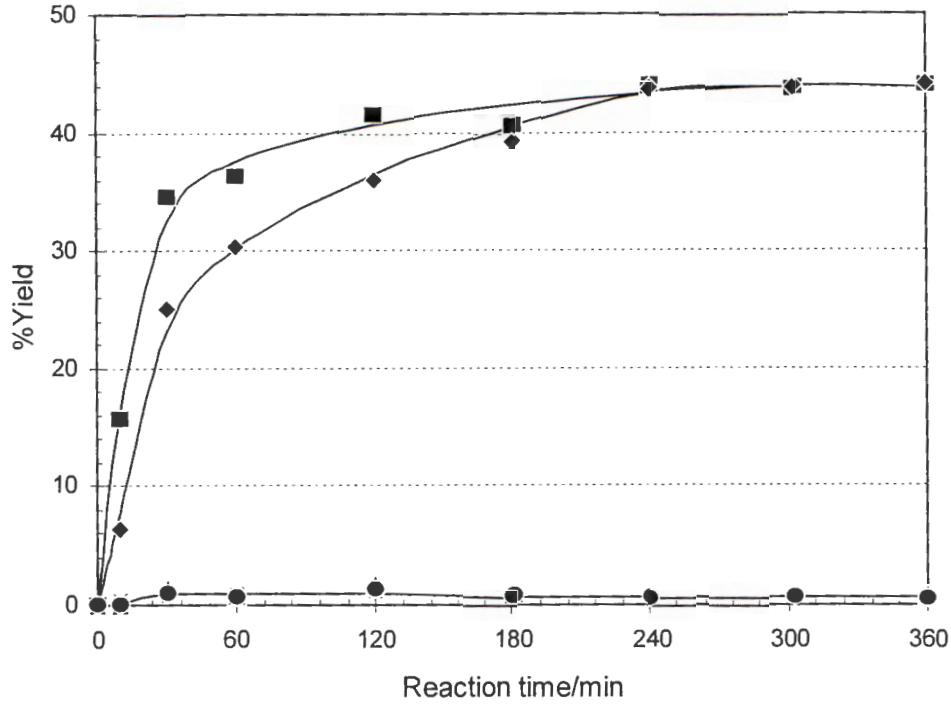


Figure 31. %Yield (relative to ED) as a function of reaction time, when ED is cross-metathesised with $C_5^{1=}$ using 2 wt. % $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalyst. [■ : PMP obtained from self-metathesis of ED, ◆ : DMP obtained from isomerisation of ED, ▲ : SMP obtained from cross-metathesis of ED with $C_5^{1=}$ and ● : PMP obtained from cross-metathesis of ED with $C_5^{1=}$]

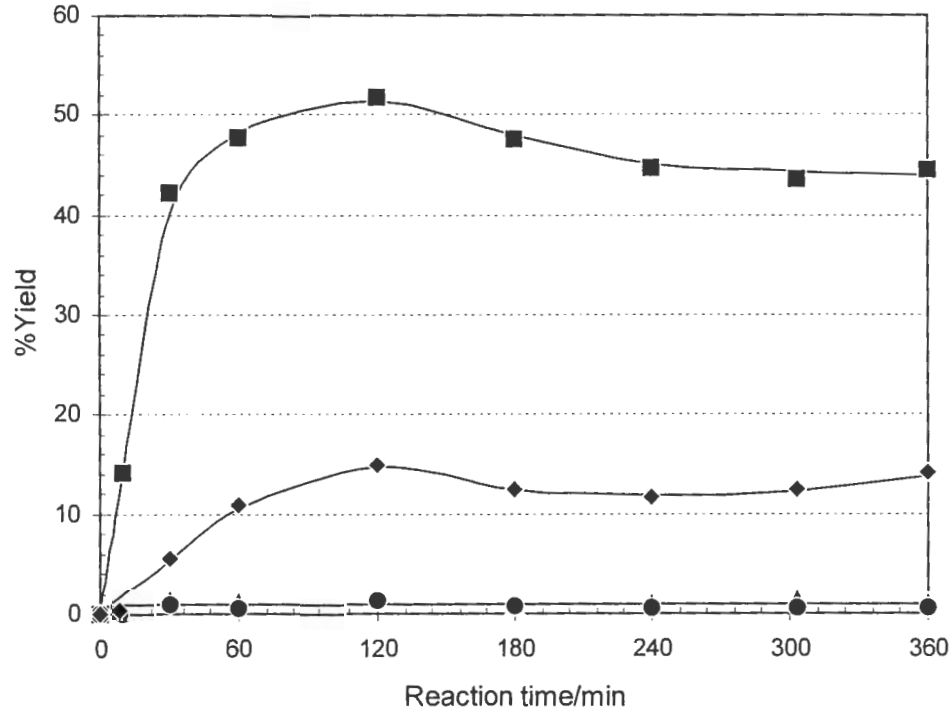


Figure 32. %Yield (relative to $C_5^{1=}$) as a function of reaction time when ED is cross-metathesised with $C_5^{1=}$ using 2 wt. % $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalyst. [■ : SMP resulting from cross-metathesis of ED with $C_5^{1=}$, ◆ : other products from side reactions, ▲ : PMP resulting from self-metathesis of $C_5^{1=}$, ● : PMP resulting from cross-metathesis of ED with $C_5^{1=}$]

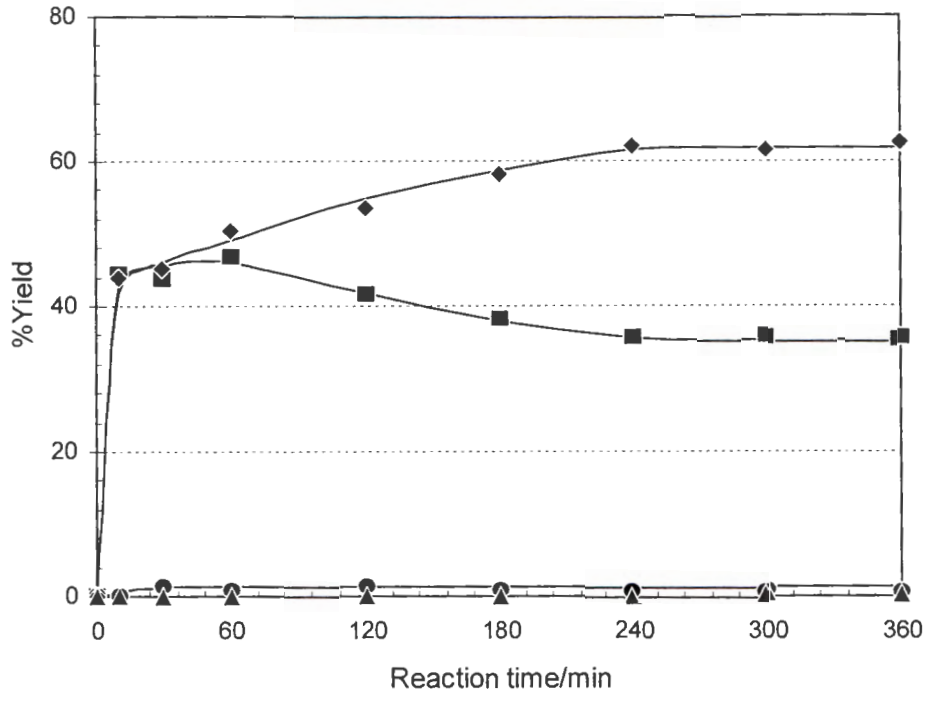


Figure 33. %Yield in terms of functional groups, as a function of reaction time from cross-metathesis of ED with $C_5^{1=}$ using 2 wt. % $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalyst. [■ : simple alkenes, ◆ : diepoxy alkenes, ▲ : ethers, ● : epoxy alkenes]

Figure 30 shows the conversions of ED and $C_5^{1=}$ obtained when ED was cross-metathesised with $C_5^{1=}$. It can be seen that ED gave the highest conversion (ca. 88.7%), and equilibrium attained after 4 h of reaction. The equilibrium for $C_5^{1=}$ was also attained after 4 h, with the conversion of ca. 49.3%. $C_5^{1=}$, however, attained an optimum conversion of ca. 58% after 2 h, and it then decreased.

Figures 31 and 32 show, respectively, the product yield with respect to ED and $C_5^{1=}$, obtained when ED was cross-metathesised with $C_5^{1=}$. The major products were PMP (obtained upon self-metathesis of ED), DMP (obtained during isomerisation of ED) and the SMP (obtained from isomerisation of $C_5^{1=}$) with yields reaching equilibrium after 4 h of reaction.

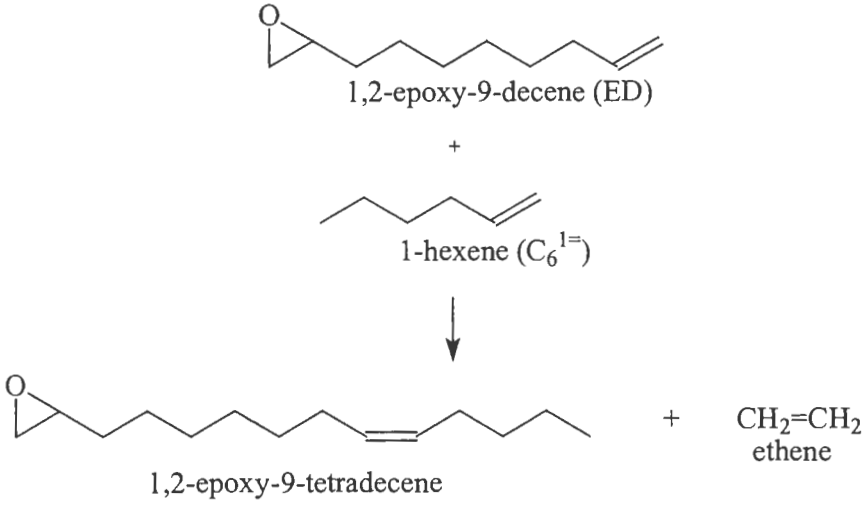
The optimum yield of ca. 52.0% of SMP was obtained after 2 h of reaction. This yield then decreased. The yield of other products, probably from side reactions, reached an optimum of ca. 14.7%. It then decreased for 4 h and then increased. The minor products were PMP obtained from self-metathesis of $C_5^{1=}$ and cross-metathesis of ED with $C_5^{1=}$. The equilibrium for minor products was reached after 3 h of reaction. The high DMP yield suggests that the degree of double bond isomerisation of ED was enhanced by the presence of $C_5^{1=}$. The decrease in

conversion of ED (Figure 30) suggests that there may be strong interactions between ED molecules and the rhenium metal. Furthermore, there may probably be a strong competition between ED and $C_5^{1=}$ for the active sites. This may be illustrated by a high SMP yield due to isomerisation of $C_5^{1=}$ (Figure 32). This may lead to the rate of dimerisation of ED increasing, probably due to the interaction of the epoxy group with the support.

Figure 33 shows the product yields as a function of the functional groups present. The simple alkenes obtained were mainly from self-metathesis of $C_5^{1=}$, as well as secondary metathesis products from isomerization of $C_5^{1=}$. The diepoxy alkenes and the ether type product were from self-metathesis, as well as dimerization of ED. The epoxy alkenes, which were produced in traces, were obtained from cross-metathesis of ED with $C_5^{1=}$. Simple alkenes reached an optimum yield of ca. 45.9% after 1 h of reaction. The yield then decreased until it reached equilibrium after 4 h of reaction, with the yield of ca. 35.6%. The diepoxy alkenes reached an optimum yield of ca. 61.9%, with equilibrium reached after 4 h.

4.3 CROSS-METATHESIS OF 1,2-EPOXY-9-DECENE WITH 1-HEXENE ($C_6^{1=}$)

ED and $C_6^{1=}$ were metathesised in chlorobenzene at 20 °C, using a 2 wt.% $Re_2O_7/SiO_2{\cdot}Al_2O_3$/ $SnBu_4$ catalyst. Re:Sn:ED:$C_6^{1=}$ = 1:0.5:5:10.



Scheme 3. The cross-metathesis of ED with $C_6^{1=}$ to give PMP.

Scheme 3 illustrates the formation of a PMP, which is 1,2-epoxy-9-tetradecene upon cross-metathesis of ED and $C_6^{1=}$. The gaseous product (ethene) is removed during purging with nitrogen.

4.3.1 Reaction products

Figure 34 shows a typical chromatogram of the product mixture obtained when ED is cross-metathesised with $C_6^{1=}$, using 2 wt.% $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalyst. Although, according to the reaction Scheme 3, only one peak should be expected in Figure 34, the presence of more peaks suggests formation of other products, possibly from self-metathesis of ED or $C_6^{1=}$, isomerisation of $C_6^{1=}$, side reactions and polymerisation reactions.

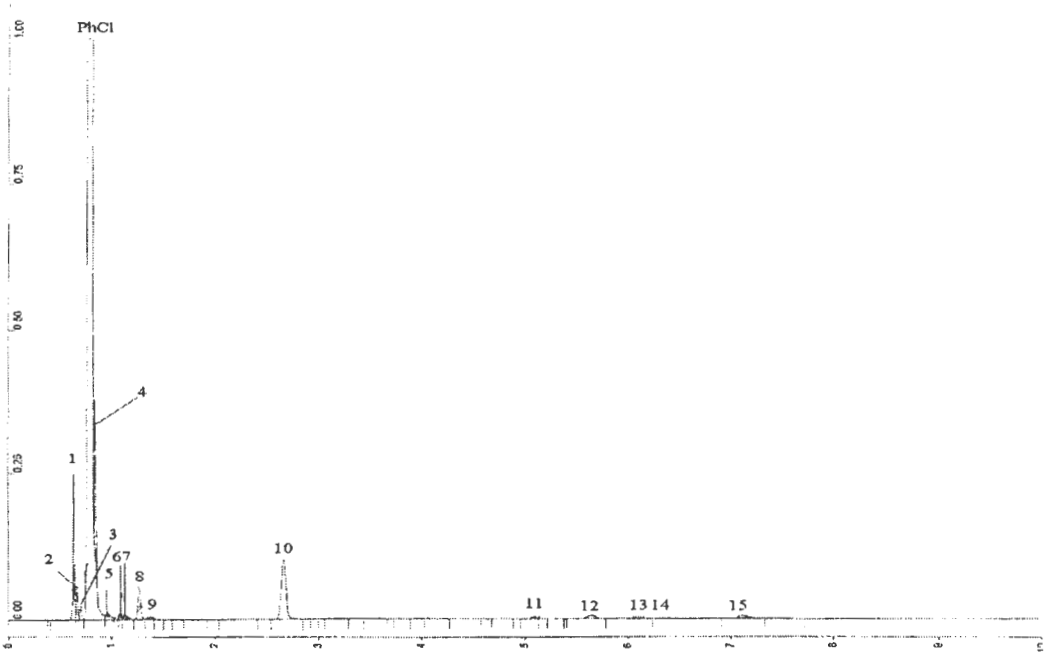


Figure 34. GC of cross-metathesis products of ED with $C_6^{1=}$: $C_6^{1=}$ (Peak1); ED (Peak 8); PMP (Peak: 7, 10; see Table 13); DMP (Peaks: 9 – 15, see Table 13); SMP (Peaks: 2; 4 – 6, see Table 13) and other (Peaks: 3 and 9; see Table 13). PhCl = chlorobenzene solvent.

4.3.1.1 MS of PMP

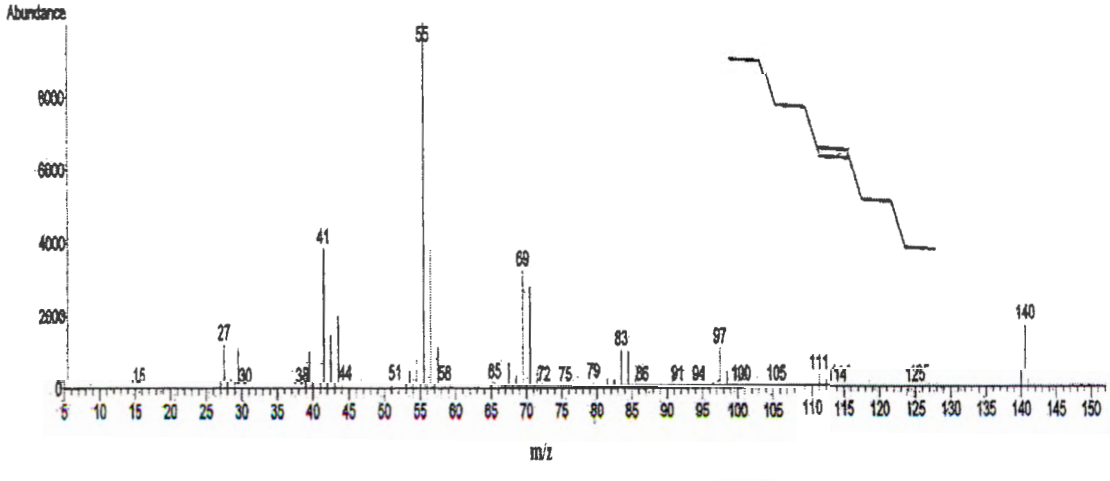


Figure 35. Mass spectrum of 5-decene (m/z = 112) obtained when ED is cross-metathesised with $C_6^{1=}$.

Figure 35 represents a typical mass spectrum (MS) of 5-decene (Peak 14), which is a primary metathesis product (PMP) of the self-metathesis of $C_6^{1=}$ (Appendix 7). Peak 10 in this spectrum is consistent with the compound 1,2,17,18-diepoxy-9-octadecene (Figure 9). This compound is also a PMP resulting from self-metathesis of ED (Appendix 1).

4.3.1.2 Mass spectrum (MS) of secondary metathesis products (SMP)

The compounds associated with Peaks 2 and 4 – 6 have spectra consistent, respectively, with 2-hexene (Appendix 12); 2-heptene (Appendix 24); (Z)-3-octene (Appendix 21) and trans-4-nonene (Appendix 18), respectively. These compounds were of the cross-metathesis of $C_5^{1=}$ with $C_5^{2=}$.

4.3.1.3 Mass spectrum (MS) of dimerisation products (DMP)

The compounds corresponding to Peaks 9 – 15 have spectra consistent, respectively, with 1,2,18,19-diepoxy-11-methyl-8-nonadecene (Figure 10); 1,2-epoxy-9-methyl-nonoxy-1,8-decadiene (Appendix 12); 3-(1,2-epoxy-heptyl)-11,12-epoxy-4-methyl-2-dodecene (Appendix 13); 3-(1,2-epoxy-heptyl)-11,12-epoxy-4-methyl-1-dodecene (Appendix 14); 1,2,17,18-diepoxy-9,10-dimethyl-8-octadecene (Appendix 15), respectively. These compounds are DMP obtained by the double bond migration in ED.

4.3.1.4 Mass spectrum (MS) of other products

The compounds associated with Peaks 3 and 9 have spectra consistent, respectively, with cyclohexene (Appendix 25) and 2-(1-methylethyl)-1-chlorobenzene (Appendix 19). These compounds could possibly be formed from side reactions, e.g. the interaction of chlorobenzene solvent with some short-chain alkenes.

Table 13. Products obtained when ED is cross-metathesised with $C_6^{1=}$ using 2 wt.% $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalyst.

Peak no	C_x	Product	Carbon skeleton	m/z	Yield	Selectivity
					%	%
Substrate						
1	C_6	1-hexene	C_5=C	84	28.9	
8	C_{10}	1,2-epoxy-9-decene	COC_8=C	154	3.6	
Primary metathesis products						
7	C_{10}	5-decene	C_4=C_4	112	1.3	0.8
10	C_{18}	1,2,17,18-diepoxy-9-octadecene	COC_8=C_8OC	280	94.0	56.1
Dimerization products						
11	C_{20}	1,2,18,19-diepoxy-11-methyl-8-nonadecene	COC_7=$C_3(C)C_7OC$	308	0.9	0.5
12	C_{20}	1,2-epoxy-9-methyl-nonoxy-1,8-decadiene	C=C_7=$C_2OC(C)C_7OC$	308	0.6	0.3
13	C_{20}	3-(1,2-epoxy-heptyl)-11,12-epoxy-4-methyl-2-dodecene	C_2=$C(COC_6)C(C)C_7OC$	308	0.6	0.3
14	C_{20}	3-(1,2-epoxy-heptyl)-11,12-epoxy-4-methyl-1-dodecene	C=$C_2(COC_6)C(C)C_7OC$	308	0.4	0.2
15	C_{20}	1,2,17,18-diepoxy-9,10-dimethyl-8-octadecene	COC_7=$C(C)C(C)C_7OC$	308	0.2	0.1
Secondary metathesis products						
2	C_6	2-hexene	C_2= C_4	84	13.4	8.0
4	C_7	3-heptene	C_3=C_4	98	42.2	25.2
5	C_8	(Z)-3-octene	C_3=C_5	112	3.1	1.8
6	C_9	trans-4-none	C_4 =C_5	126	0.3	0.2
Side reactions						
3	C_6	cyclohexene		82	9.7	5.8
9	C_9	2-(1-methylethyl)-1-chloro-benzene		154	1.1	0.7

Re:Sn:ED:$C_6^{=}$ = 1:0.5:5:10, Reaction temperature = 20 °C, Reaction time = 6 h, Solvent = PhCl.

Table 14. Diepoxy alkenes, epoxy esters and diesters obtained upon cross-metathesis of ED with $C_6^{1=}$ using 2 wt.% $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalyst.

C_x	Product	m/z	Yield	Selectivity
			%	%
Alkenes				
C_{10}	5-decene	112	1.3	0.8
C_6	2-hexene	84	13.4	8.0
C_7	2-heptene	98	42.2	25.2
C_8	(Z)-3-octene	112	3.1	1.8
C_9	trans-4-nonene	126	0.3	0.2
C_6	cyclohexene	82	9.7	5.8
C_9	2-(1-methylethyl)-1-chlorobenzene	154	1.1	0.7
Diepoxy alkenes				
C_{18}	1,2,17,18-diepoxy-9-decene	280	94.0	56.1
C_{20}	1,2,18,19-diepoxy-11-methyl-8-nonadecene	308	0.9	0.5
C_{20}	3-(1,2-epoxy-heptyl)-11,12-epoxy-4-methyl-2-dodecene	308	0.6	0.3
C_{20}	3-(1,2-epoxy-heptyl)-11,12-epoxy-4-methyl-1-dodecene	308	0.4	0.2
C_{20}	1,2,17,18-diepoxy-9,10-dimethyl-8-octadecene	308	0.2	0.1
Ethers				
C_{20}	1,2-epoxy-9-methyl-nonoxy-1,8-decadiene	308	0.6	0.3

Re:Sn:ED:$C_6^{=}$ = 1:0.5:5:10, Reaction temperature = 20 °C, Reaction time = 6 h, Solvent = PhCl.

Table 13 shows the product distribution, yields and selectivity obtained when ED is cross-metathesised with $C_6^{1=}$, using 2 wt.% Re_2O_7 catalyst. It can be seen that the product spectrum consisted of PMP, DMP, SMP (resulting from isomerisation of $C_6^{1=}$). Other products were obtained from side reactions. The PMP ranged from C_{10} and C_{18} and their molecular weights, respectively, ranged from 112 to 280. SMP ranged from C_6 to C_9 and their molecular weights, respectively, ranged from 84 to 126. PMP expected from cross-metathesis of ED with $C_6^{1=}$ were not identified. All the C_{20}- DMP had molecular weights of 308. Other products that were formed, possibly from side reactions, were C_6 and C_9. Their molecular weights ranged from 82 to 154, respectively.

5-decene, which is a PMP obtained from self-metathesis of $C_6^{1=}$, gave a yield of ca. 1.3%. It can be seen that 1,2,17,18-diepoxy-9-decene, which is a PMP obtained from self-metathesis of ED, was obtained in the highest yield (ca. 94.0%). This yield was more than twice the yield obtained from the cross-metathesis of ED with $C_5^{1=}$ (see Table 9). DMP obtained from ED gave a combined yield of ca. 2.9%, which is almost 15 times less than the yield obtained in the cross-

metathesis of ED with $C_5^{1=}$ (see Table 11). Combined SMP yield obtained from isomerization of $C_6^{1=}$ gave a combined yield of ca. 59.0%. This SMP yield was more than the combined yield obtained in the cross-metathesis of ED with $C_5^{1=}$ (see Table 11). Other products, which were obtained possibly from side reactions, gave a combined yield of ca. 10.8%. The catalyst was highly selective towards PMP (ca. 95.3%) when compared to the selectivity achieved in cross-metathesis of ED with $C_5^{1=}$ (32.6%). These results suggest that increased chain length of the linear alkenes enhances the interaction of the alkene with the support. The results also show that with shorter alkenes, the epoxy group of ED and the alkene interact equally with the support. This is illustrated by similar DMP and SMP yields obtained in the cross-metathesis of ED with $C_5^{1=}$ (see Table 11). These results further suggest that the selectivity towards PMP increases with increase in the chain length.

Table 14 shows the yield and selectivity in terms of the functional groups present in the products. It can be seen that the product spectrum consist mainly of alkenes, diepoxy alkenes and the ether type products obtained from cross-metathesis of ED with $C_6^{1=}$. The total selectivity towards the linear and cyclic alkenes was ca. 42.5%. The total selectivity towards the diepoxy alkenes was ca. 57.2%. It can be seen that 1,2,17,18-diepoxy-9-decene was the product obtained in highest yield (ca. 94.0%).

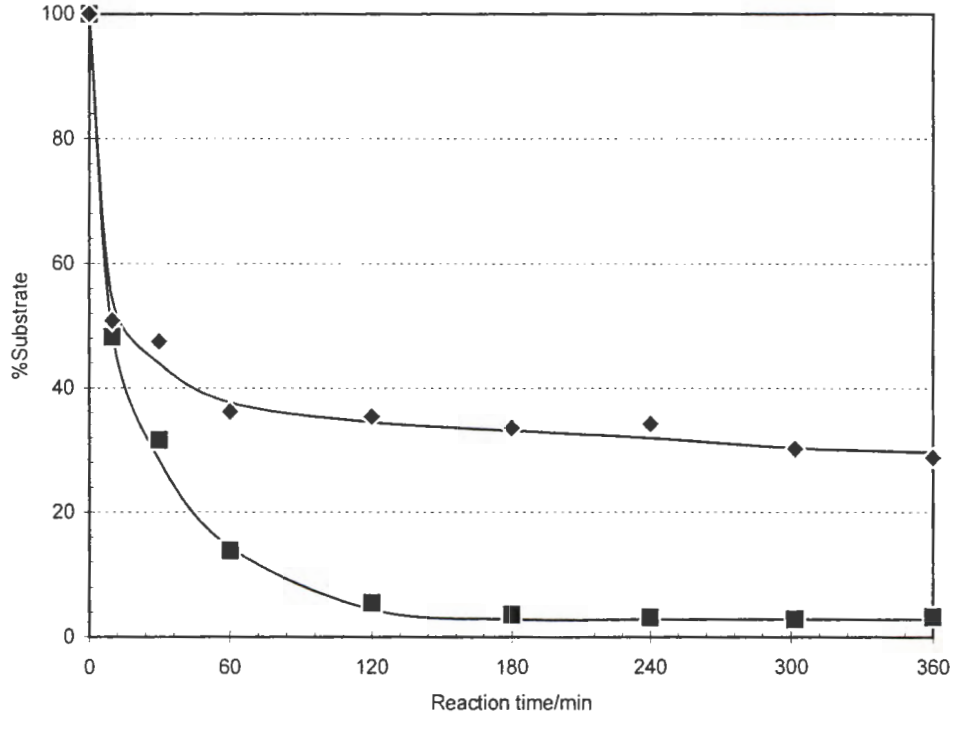


Figure 36. %Substrate (ED and $C_6^{1=}$) converted when ED is metathesised with $C_6^{1=}$, as a function of reaction time using 2 wt. % $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalyst. [■ : ED, ◆ : $C_6^{1=}$]

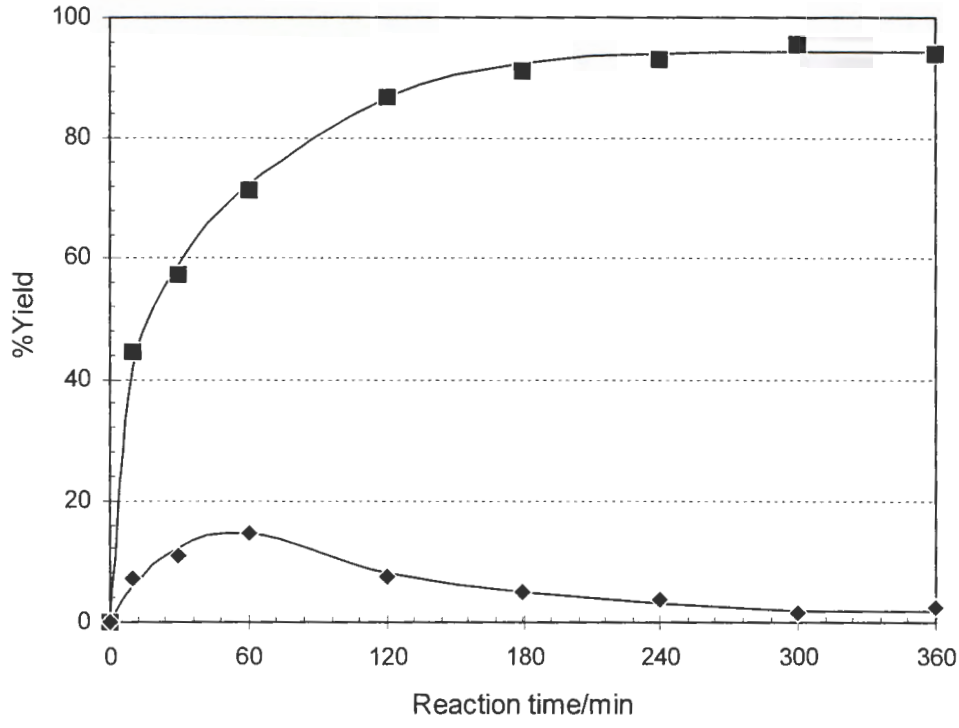


Figure 37. %Yield (relative to ED) as a function of reaction time, when ED is cross-metathesised with $C_6^{1=}$ using 2 wt. % $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalyst. [■ : PMP obtained from self-metathesis of ED, ◆ : DMP obtained from isomerisation of ED]

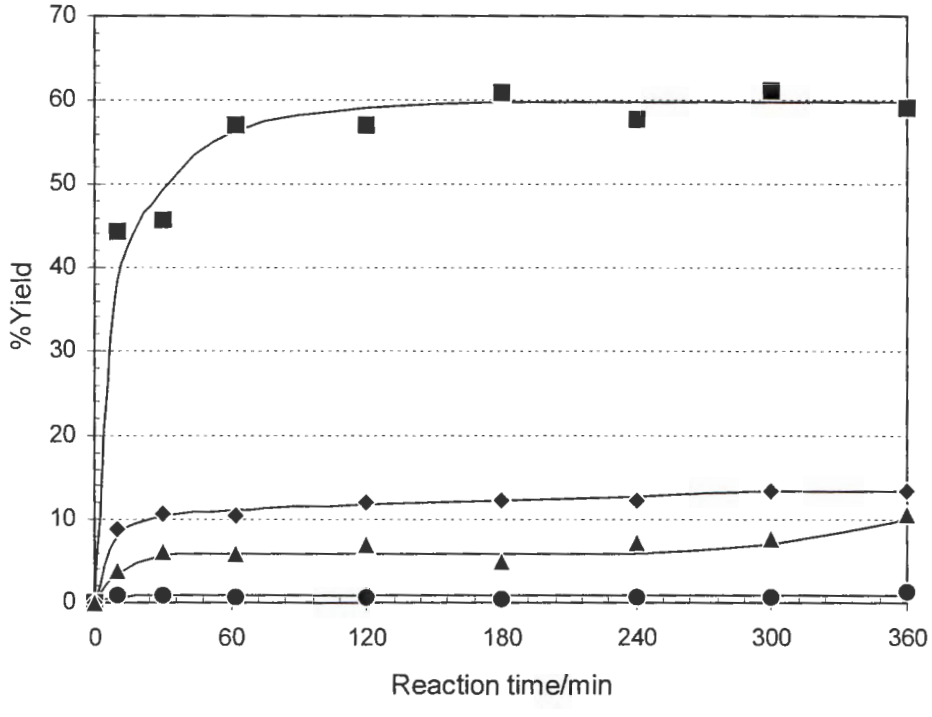


Figure 38. %Yield (relative to $C_6^{1=}$) as a function of reaction time, when ED is cross-metathesised with $C_6^{1=}$ using 2 wt. % $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalyst. [■ : SMP obtained from cross-metathesis of ED with $C_6^{1=}$, ◆ : Isomerisation products from $C_6^{1=}$, ▲ : PMP obtained from self-metathesis of $C_6^{1=}$, ● : Other products from side reaction]

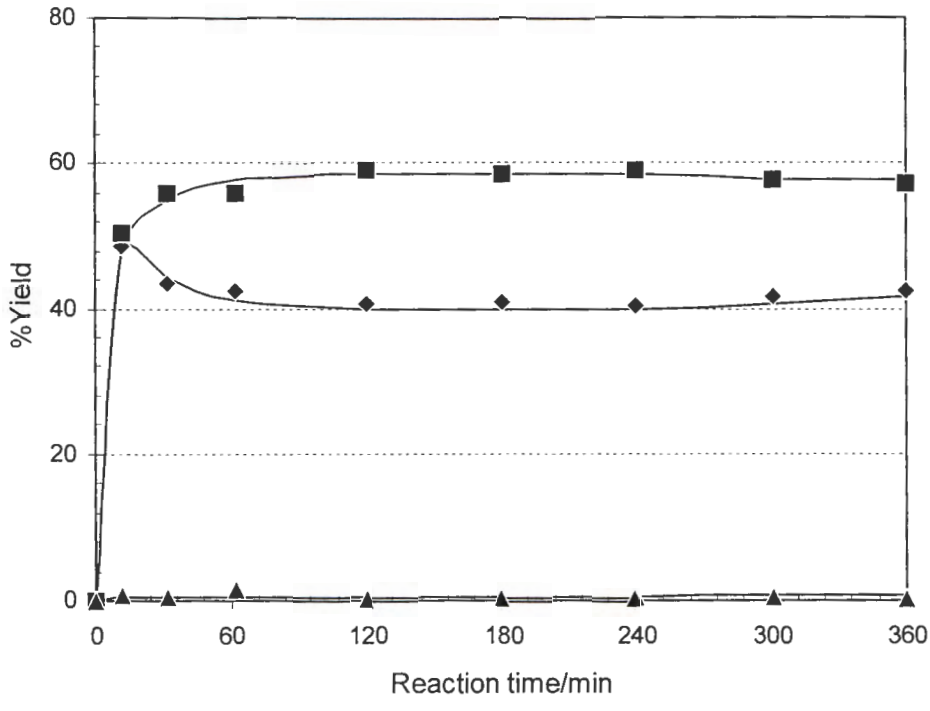


Figure 39. %Yield in terms of functional groups, as a function of reaction time for cross-metathesis of ED with $C_6^{1=}$, using 2 wt. % $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalyst. [■ : diepoxy alkenes, ◆ : simple alkenes, ▲: ethers]

Figure 36 compares the conversions of ED and $C_6^{1=}$ for the cross-metathesis of ED with $C_6^{1=}$. It can be seen that ED gave the highest conversion (ca. 96.4%), with equilibrium attained after 4 h of reaction. $C_6^{1=}$ gave a conversion of ca. 71.1%, but equilibrium was not attained within 6 h of reaction. These conversions were higher than the conversions obtained in the cross-metathesis of ED with $C_5^{1=}$ (see Figure 30).

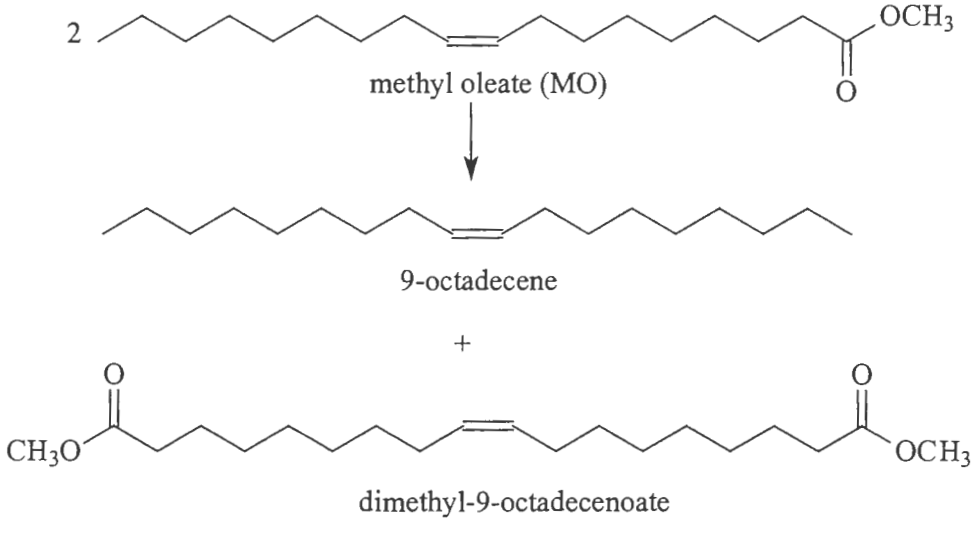
Figures 37 and 38 show, respectively, the product yield obtained when ED is cross-metathesised with $C_6^{1=}$, with respect to ED and $C_6^{1=}$. The major products were PMP (ca. 94.0%) obtained from self-metathesis of ED, with equilibrium attained after 4 h of reaction (Figure 37). DMP obtained from isomerisation of ED, occurred in traces (Figure 37). Figure 38 shows that SMP from isomerisation of $C_6^{1=}$ were products obtained in highest yield (ca. 60.0%), with equilibrium attained after 3 h of reaction. During the first 1 h of reaction, the epoxy group of ED and $C_6^{1=}$ were equally interacting with the support. This is illustrated by similar DMP yield (Figure 37) ad SMP yield (Figure 38). However, beyond 1 h of reaction the interaction of the epoxy group with the support decreased, while there was a slight increase in the interaction of $C_6^{1=}$ with the support.

Figure 39 shows the product yields in terms of the functional groups present, as a function of reaction time. The simple alkenes obtained were mainly from self-metathesis of $C_6^{1=}$, as well as SMP from isomerization of $C_6^{1=}$. The diepoxy alkenes and the ether type product were obtained from self-metathesis and dimerization of ED. The catalytic system was highly selective towards the diepoxy alkenes.

4.4 METATHESIS OF METHYL OLEATE (MO)

Metathesis activity, selectivity and stability of $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalytic systems were investigated for MO (methyl oleate). The influence of reaction parameters such as the Re_2O_7 loading and reaction temperature on activity, selectivity and stability of the $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalytic system, were studied as a function of reaction time. Metathesis of MO was investigated in order to identify the best reaction conditions that may be used for the metathesis of methyl vernolate, which has a similar structure to that of MO.

MO was metathesised with 3 wt.% Re_2O_7 catalyst in chlorobenzene at room temperature. The Re:Sn:MO molar ratio used was 1:0.5:10.



Scheme 4. The metathesis of MO to give the primary metathesis products, 9-octadecene and dimethyl-9-octadecenoate.

Scheme 4 illustrates the metathesis of MO to give the primary metathesis products, 9-octadecene and dimethyl-9-octadecenoate.

4.4.1 Reaction products

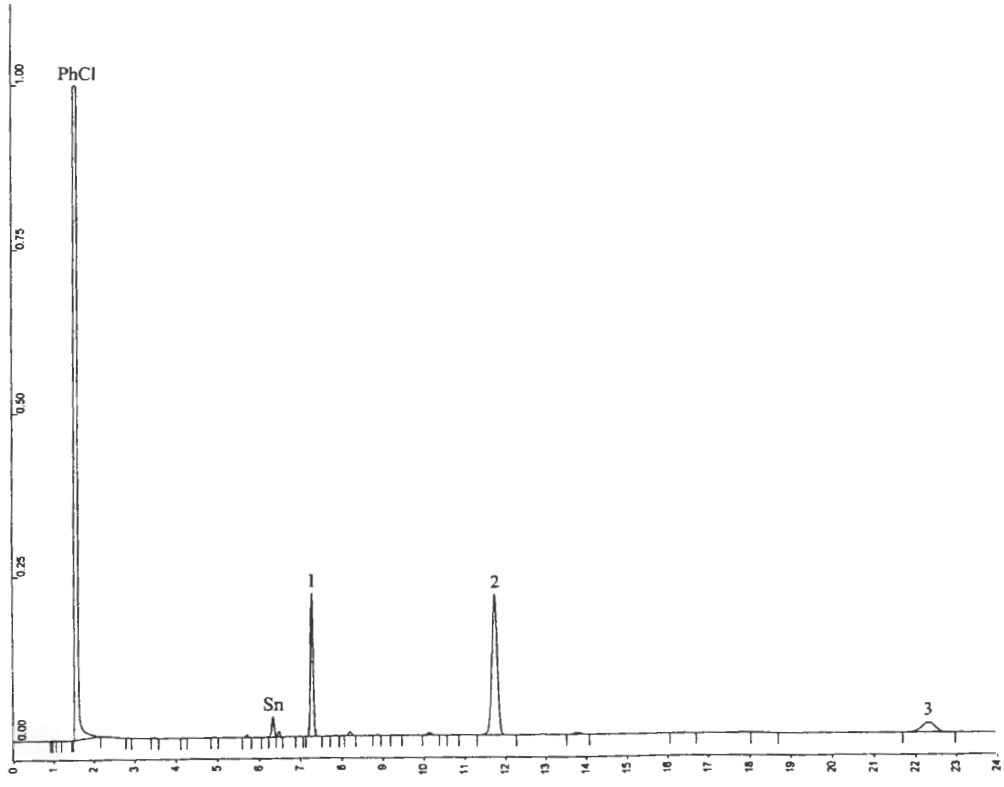


Figure 40. GC of metathesis products of methyl oleate: MO (Peak 2); 9-octadecene (Peak 1); dimethyl-9-octadecenoate (Peak 3). PhCl = chlorobenzene solvent and Sn = tetrabutyltin.

Figure 40 is a typical chromatogram of the product mixture obtained when MO is metathesised with 3 wt.% $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalyst. From Figure 40, it can be seen that the major products obtained are 9-octadecene and dimethyl-9-octadecenoate.

4.4.1.1 MS of 9-octadecene and dimethyl-9-octadecenoate

Appendices 26 and 27 are associated with mass spectra of 9-octadecene and dimethyl-9-octadecenoate, respectively. The compounds are PMP obtained upon metathesis of MO (Appendix 26).

Table 15. Products obtained upon metathesis of MO using 3 wt.% $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalyst.

Peak no	C_x	Product	Carbon skeleton	m/z	Yield	Selectivity
					%	%
Substrate						
2	C_{19}	methyl oleate	$C_9{=}C_9OOC$	296	51.8	
Primary metathesis products						
1	C_{18}	9-octadecene	$C_9{=}C_9$	280	32.0	66.4
3	C_{20}	dimethyl-9-octadecenoate	$COOC_9{=}C_9OOC$	340	16.2	33.6

Re:Sn:MO = 1:0.5:10, Reaction time = 4 h, Solvent = PhCl.

NWU LIBRARY

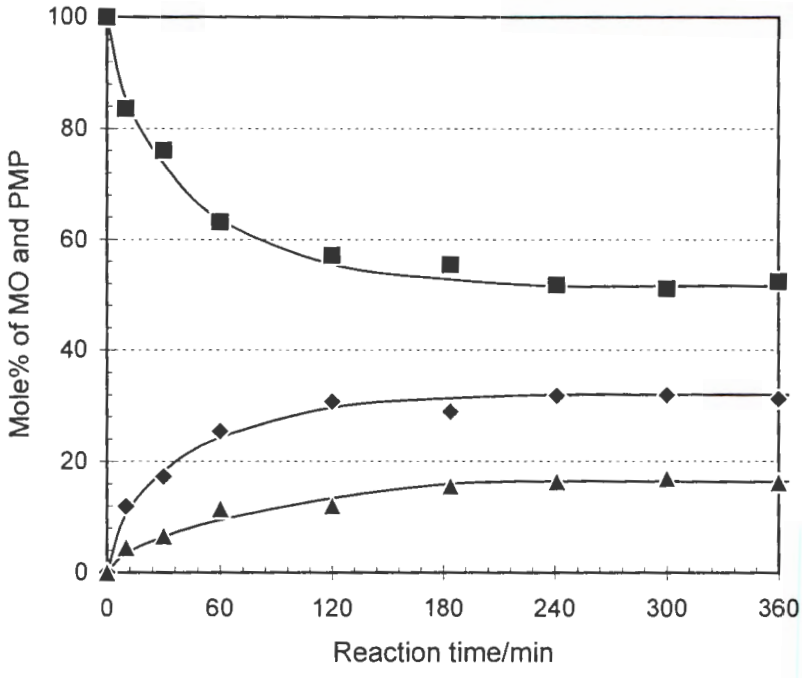


Figure 41. Amount of products and substrate (as mole%) as a function of reaction time, when MO is metathesised using 3 wt.% $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ at room temperature. ■ : MO, ◆ : 9-octadecene, ▲ : dimethyl-9-octadecenoate]

Table 15 shows the product distribution, yields and selectivity when MO was metathesised with 3 wt.% Re_2O_7 catalyst. The product obtained in highest yield was 9-octadecene (ca. 32.0%). Figure 41 shows the mole% of MO and the products. Equilibrium was attained after 4 h reaction time, with a conversion of ca. 48.2%.

4.4.2 Influence of Re_2O_7 loading

The influence of Re_2O_7 content on the activity of $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalytic system was investigated. MO was metathesised at room temperature, with wt. %Re_2O_7 = 0.5, 1, 2, 3 and Re:Sn:MO = 1:0.5: 10.

Table 17. Conversion, product yield and selectivity for MO at room temperature, using different Re_2O_7 loadings.

Re_2O_7 (wt. %)	Conversion (%)	Yield (%)		Selectivity (%)	
		Alkene	Diester	Alkene	Diester
0.5	50.4	34.4	16.0	68.3	31.7
1	52.4	39.5	12.9	75.4	24.6
2	50.1	36.8	13.3	73.5	26.5
3	48.2	32.0	16.2	66.4	33.6

Re:Sn:MO = 1:0.5:10, Reaction time = 4 h, Solvent = PhCl.

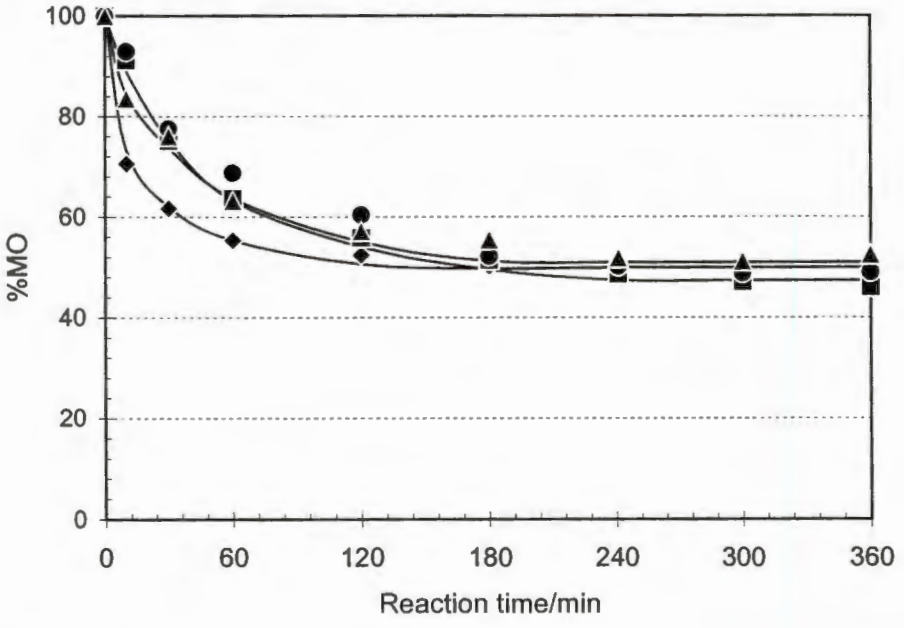


Figure 42. %MO converted at different Re_2O_7 loadings, as a function of reaction time, at room temperature. Re:Sn:MO = 1:0.5:10. [◆ : 0.5 wt.% Re_2O_7, ■ : 1 wt.% Re_2O_7, ● : 2 wt.% Re_2O_7, ▲ : 3 wt.% Re_2O_7]

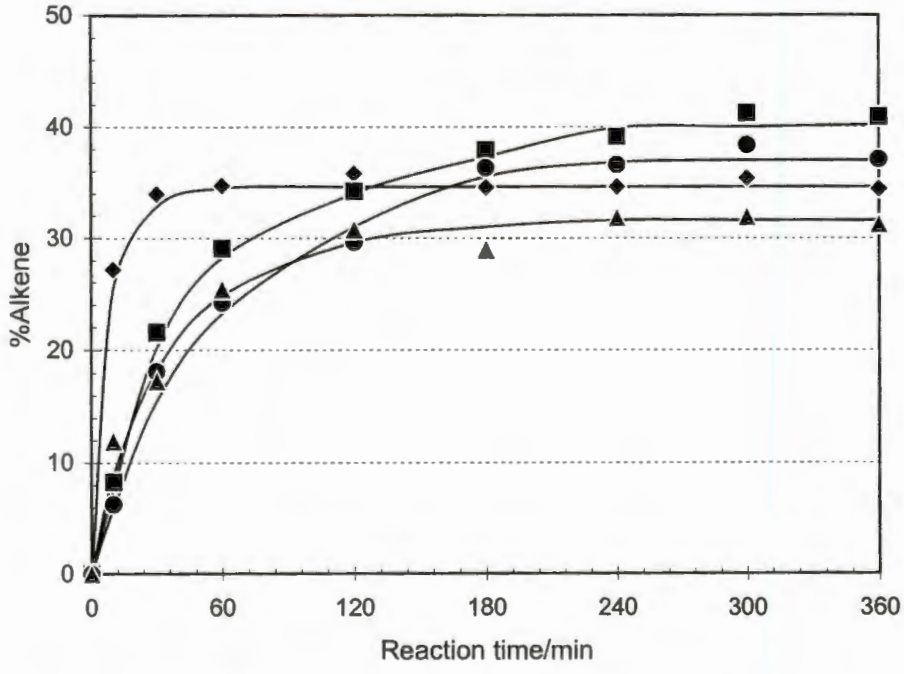


Figure 43. %Alkene yield at different Re_2O_7 loadings, as a function of reaction time, at room temperature. Re:Sn:MO = 1:0.5:10. [◆ : 0.5 wt.% Re_2O_7, ■ : 1 wt.% Re_2O_7, ● : 2 wt.% Re_2O_7, ▲ : 3 wt.% Re_2O_7]

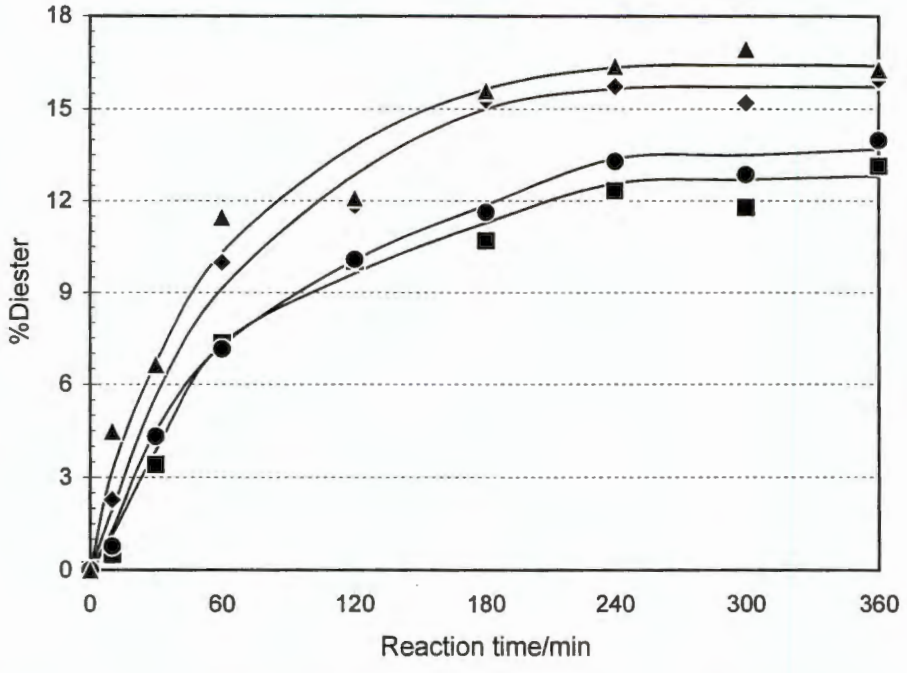


Figure 44. %Diester yield at different Re_2O_7 loadings, as a function of reaction time, at room temperature. Re:Sn:MO = 1:0.5:10. [◆ : 0.5 wt.% Re_2O_7, ■ : 1 wt.% Re_2O_7, ● : 2 wt.% Re_2O_7, ▲ : 3 wt.% Re_2O_7]

Table 17 shows conversions, yields and selectivity of MO at different Re_2O_7 loadings after 4 h of reaction. Figure 42 shows the conversions of MO at different Re_2O_7 loadings. It can be seen that the conversion and the linear alkene yield decreased with increase in Re_2O_7 loading within 1 to 3 wt.% Re_2O_7 loadings. The diester yield increased with increase in Re_2O_7 loading. The catalytic system was most active (ca. 52.4%) and selective (ca. 75.4%) towards the linear alkene at 1 wt.% Re_2O_7 loading. The selectivity towards the desired product (diester) increased with increase in Re_2O_7 loading within 1 to 3 wt.% Re_2O_7 loadings. The equilibrium for MO and the products in all four Re_2O_7 loadings was attained after 4 h of reaction.

Figures 43 and 44 show, respectively, the change in the linear alkene and diester yields as a function of reaction time. Both linear alkene and the diester yields attained their equilibriums after 4 h of reaction.

4.4.3 Influence of reaction temperature

The influence of reaction temperature on the activity, selectivity and stability of $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalytic system was investigated. MO (methyl oleate) was

metathesised in chlorobenzene, in the presence of a 2 wt.% $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalyst. Re:Sn:MO = 1:0.5:10 and ΔT = 20, 40, 60, 80, 100 °C.

Although 1 wt.% Re_2O_7 loading was most active, 2 wt.% Re_2O_7 loading had better selectivity towards the desired diester product (Table 17). For this reason, and for the purpose of comparison with the $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$/ED catalytic system, a 2 wt.% Re_2O_7 loading was used in my studies.

Table 18. Conversion, product yield and selectivity for MO at different temperatures, using 2 wt.% $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalyst.

Re_2O_7 (wt. %)	Conversion (%)	Yield (%)		Selectivity (%)	
		Alkene	Diester	Alkene	Diester
20	48.1	31.9	16.2	66.3	33.7
40	49.5	28.7	20.8	58.0	42.0
60	50.0	34.6	15.4	69.2	30.8
80	45.8	33.7	12.1	73.6	26.4
100	37.0	25.0	12.0	67.6	32.4

Re:Sn:MO = 1:0.5:10, Reaction time = 6 h, Solvent = PhCl.

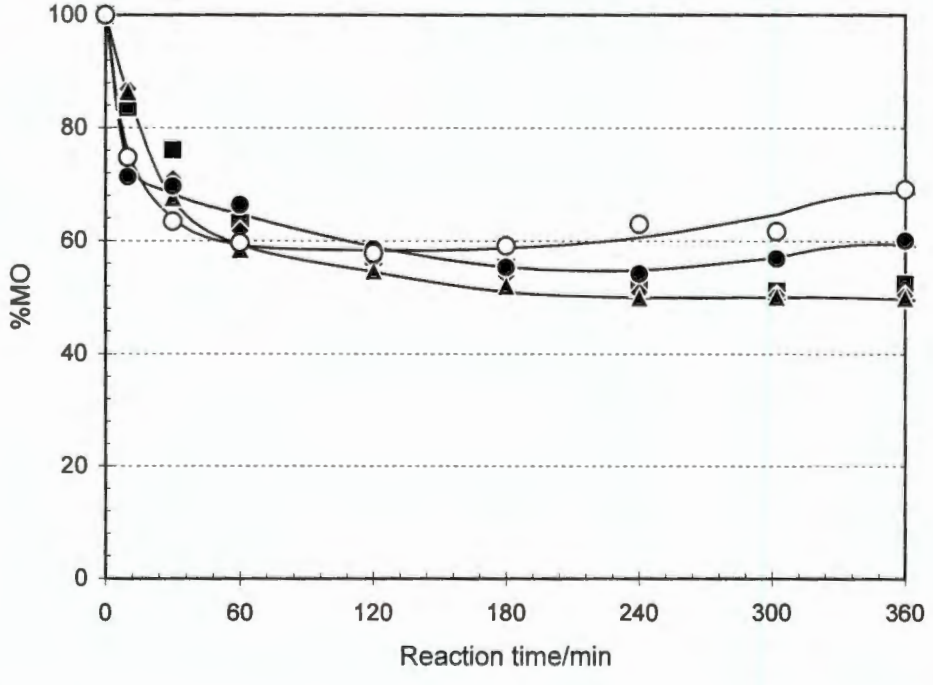


Figure 45. %MO at different temperatures, as a function of reaction time, using 2 wt. % $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$. [■ : 20 °C, ◆ : 40 °C, ▲ : 60 °C, ● : 80 °C, ○ : 100 °C]

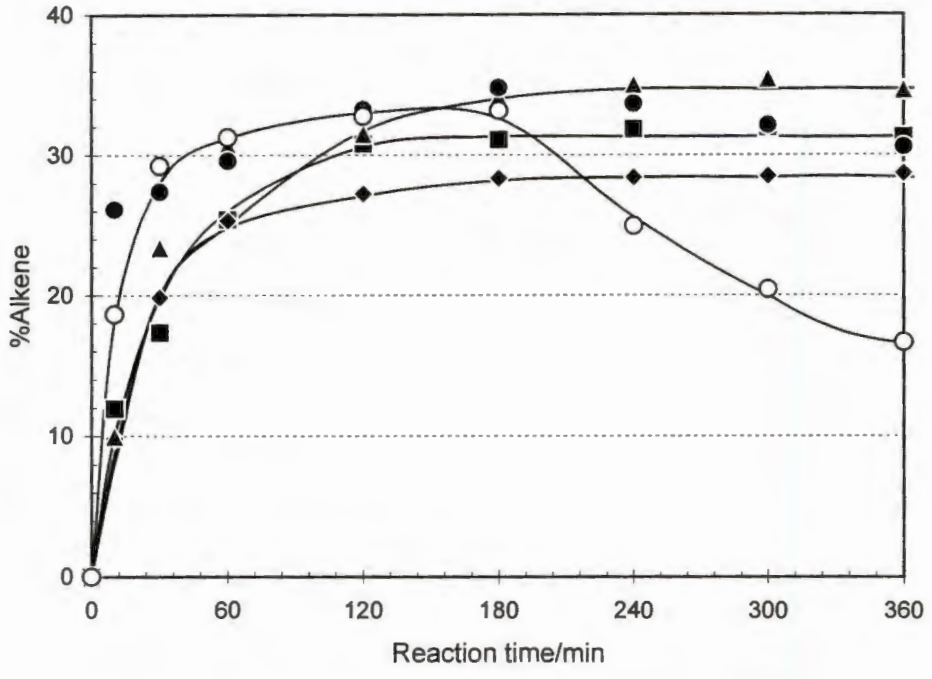


Figure 46. %Alkene yield at different temperatures, as a function of reaction time, using 2 wt. % Re_2O_7/ SiO_2·Al_2O_3/$SnBu_4$. [■ : 20 °C, ◆ : 40 °C, ▲ : 60 °C, ● : 80 °C, ○ : 100 °C]

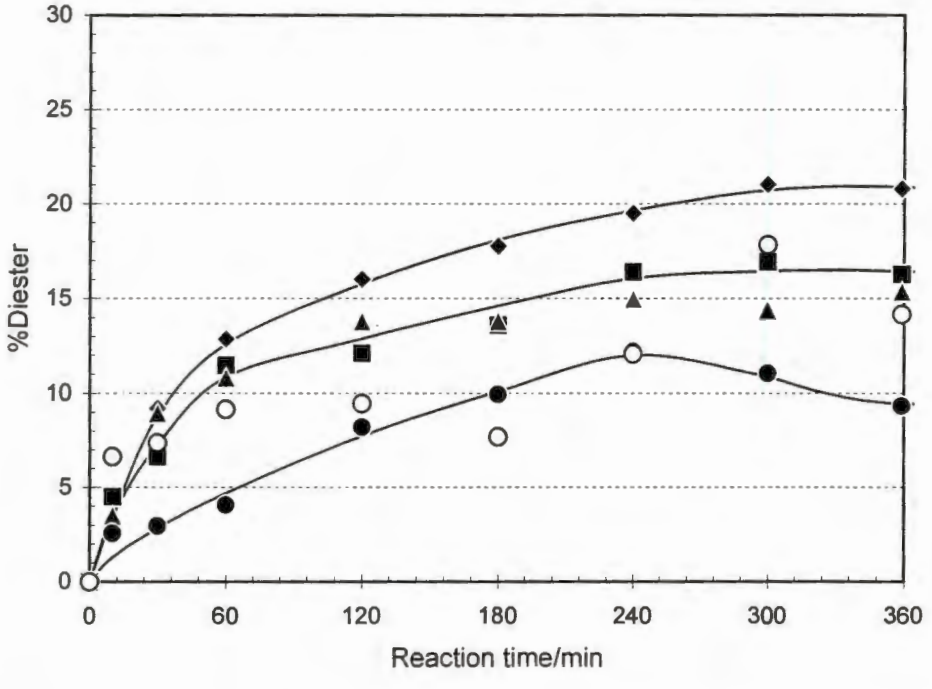


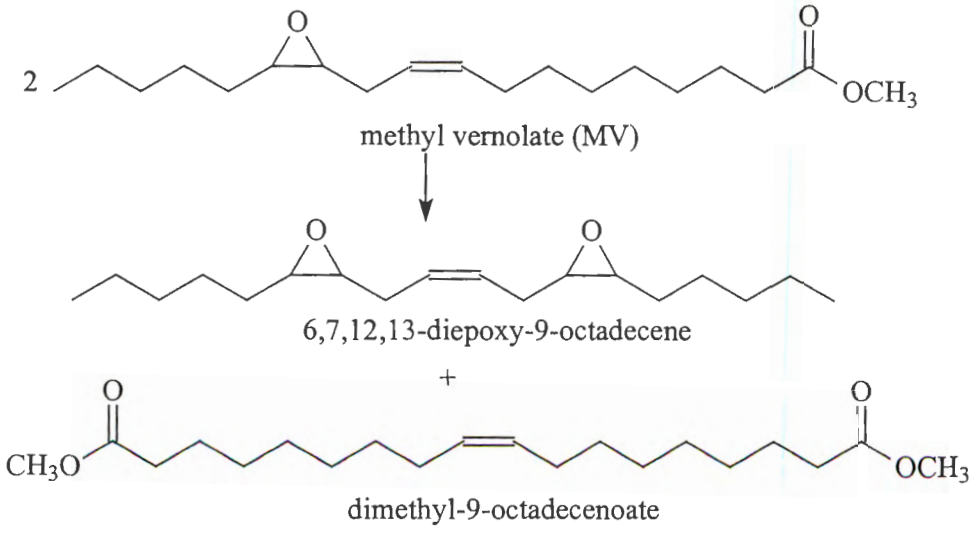
Figure 47. %Diester yield at different temperatures, as a function of reaction time, using 2 wt. % Re_2O_7/ SiO_2·Al_2O_3/$SnBu_4$. [■ : 20 °C, ◆ : 40 °C, ▲ : 60 °C, ● : 80 °C, ○ : 100 °C]

Table 1 8 shows t he c onversions, y ields and selectivity when MO is metatheised with 2 wt.% $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalytic system. Temperature ranged from 20 – 100 °C. Conversions and alkene yield increased with increase in temperature from 20 to 60 °C. The catalytic system, however, was deactivated above 60 °C. It can be seen that, the selectivity towards the diester was highest at 40 °C (ca. 42.0%).

Figure 45 compares the conversions of methyl oleate at different temperatures. Equilibrium between 20 to 60 °C was attained after 4 h of reaction. The $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalytic system was most active at 60 °C. Figures 46 and 47 show, respectively, the change in the alkene and diester yields with time. The highest alkene yield was obtained at 60 °C, and equilibrium was attained after 4 h of reaction. The highest diester yield, however, was obtained at 40 °C, with equilibrium attained after 5 h.

4.5 METATHESIS OF METHYL VERNOLATE (MV)

Metathesis a ctivity, s electivity a nd s tability of $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ c atalytic system were investigated for MV (methyl vernolate). This compound is also known as methyl-12,13-epoxy-9-octadecenoate. MV was metathesised with 2 wt.% Re_2O_7 catalyst in chlorobenzene at room temperature and Re:Sn:MV = 1:0.5:10. The $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalytic system was most active at 60 °C for metathesis of MO (see Table 18). The catalytic system, however, was deactivated at this temperature, in the metathesis of epoxy alkenes (see Table 7). The catalytic system was most active at 20 °C in the metathesis of ED. Since there was no significant difference between the activity at room temperature and 20 °C (see Tables 4 and 7), all metathesis reactions for MV were carried out at room temperature henceforth.



Scheme 5. The metathesis of MV to give PMP.

Scheme 5 illustrates the formation of primary metathesis products, 6,7,12,13-diepoxy-9-octadecene and dimethyl-9-octadecenoate when MV was metathesised. The diester obtained in this reaction is the same as the diester obtained in the metathesis of MO (see Scheme 4).

4.5.1 Reaction products

Figure 48 shows a typical chromatogram of the product mixture obtained upon metathesis of MV with 2 wt.% $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalyst.

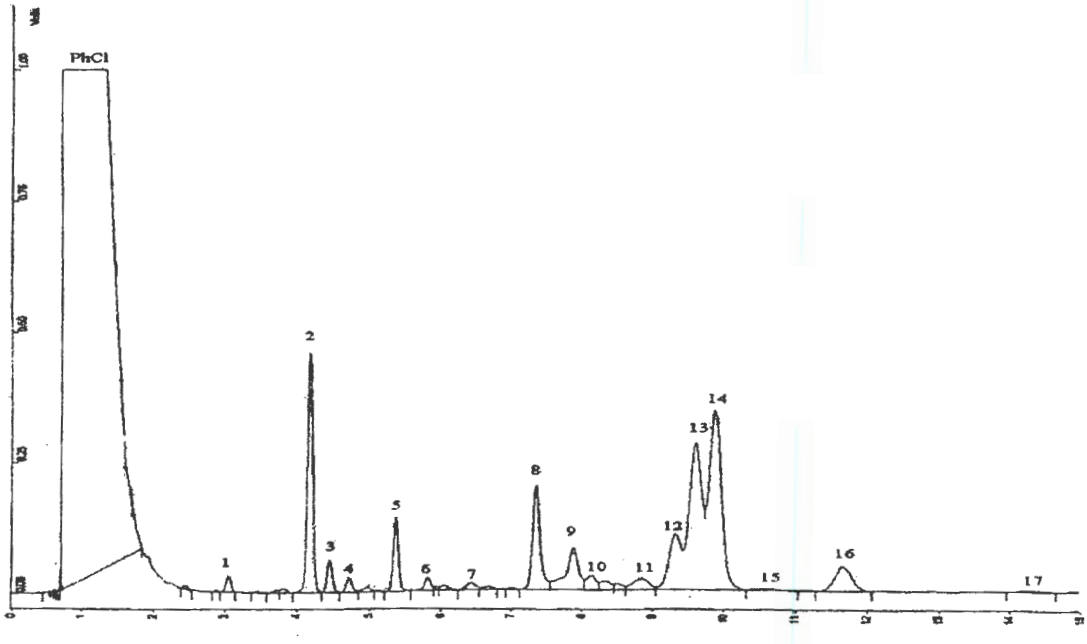


Figure 48. GC of metathesis products of methyl vernolate: MV (Peak 12); PMP (Peaks 5 and 16, see Table 19), SMP (Peaks 2 – 4; 6 – 11; 15 and 17, see Table 19); Isomerisation products (Peaks 13 and 14, see Table 19) and other (Peak 1, see Table 19). PhCl = chlorobenzene solvent.

Although, according to reaction Scheme 5, two peaks should be expected in Figure 48, the presence of more peaks suggests formation of other products. These are probably isomerisation products and SMP by the cross-metathesis of MV with its isomers.

4.5.1.1 IR of reaction mixture

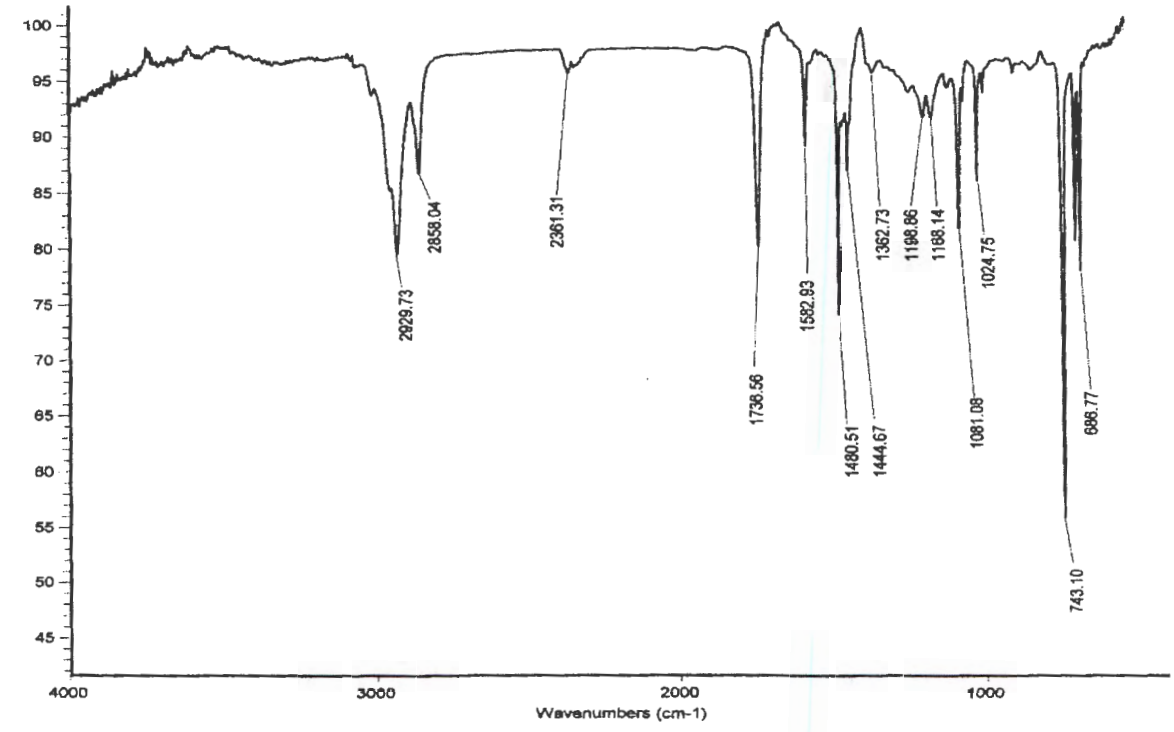


Figure 49. An FTIR spectrum of pure MV.

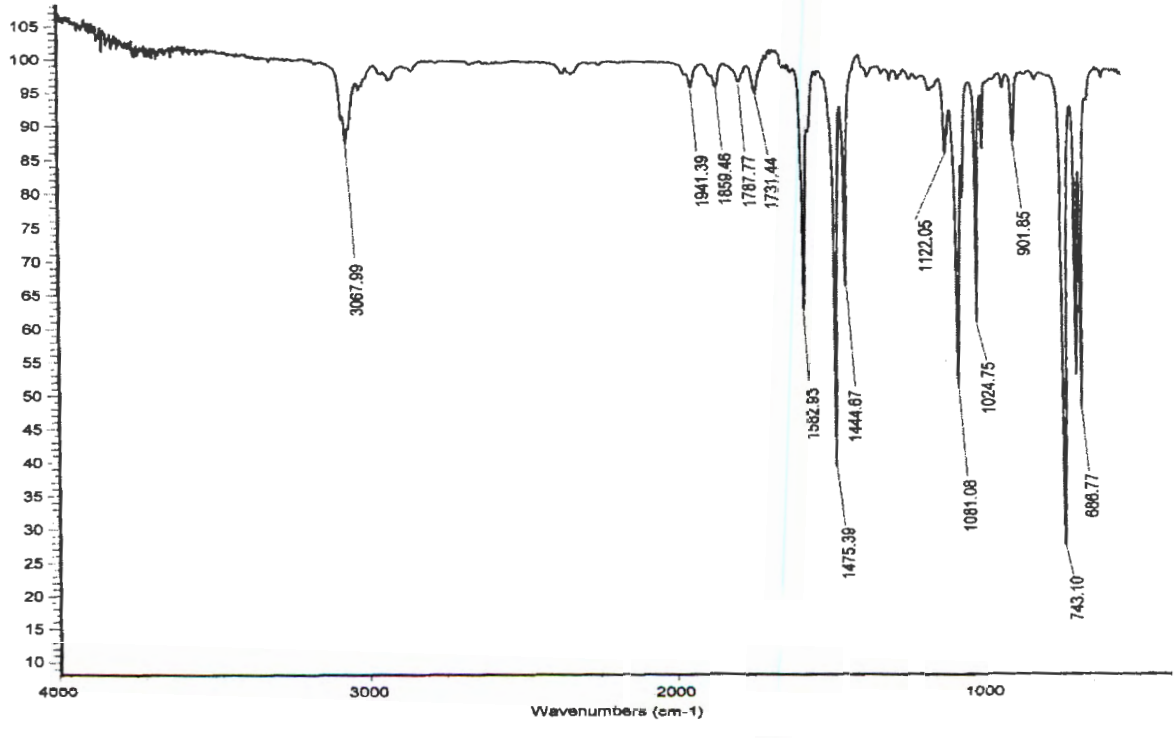


Figure 50. A typical FTIR spectrum of metathesis reaction mixture of MV obtained after 4 h reaction time.

Figures 49 and 50 show, respectively, the IR spectra of pure MV and the reaction mixture after 4 h. The absence of a broad OH peak (Figure 50), which is expected in the region 3000 to 3700 cm^{-1}, as well as the presence of the epoxy peak (Figures 49 and 50) in the region 901 to 1122 cm^{-1}, does not suggest the presence of hydroxylated products but suggests that the epoxy ring was retained during the metathesis reaction.

4.5.1.2 Mass spectrum (MS) of primary metathesis products (PMP)

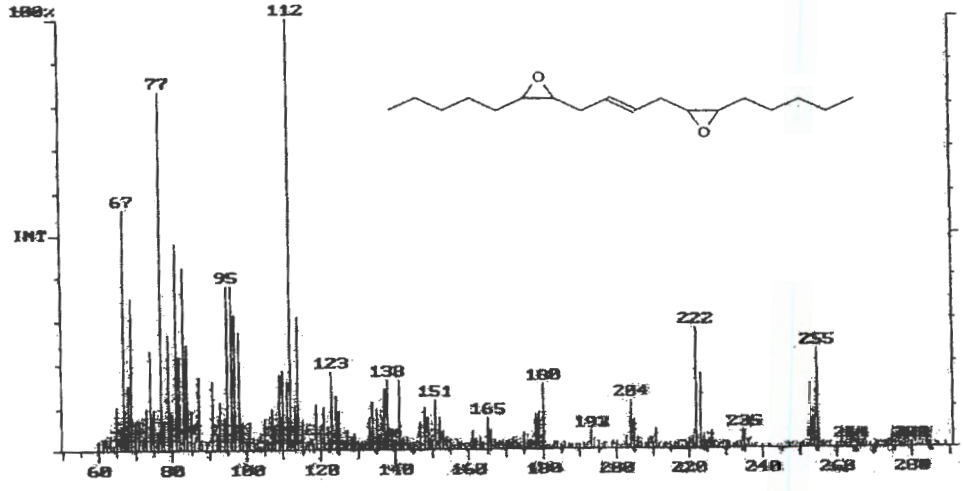


Figure 51. MS of 6,7,12,13-diepoxy-9-octadecene (m/z = 280) obtained upon metathesis of MV.

Figure 51 represents a typical mass spectrum of 6,7,12,13-diepoxy-9-octadecene (Peak 5), which is a PMP obtained upon metathesis of MV (Appendix 29). Another PMP obtained was dimethyl-9-octadecenoate (Appendix 28).

4.5.1.3 Mass spectrum (MS) of secondary metathesis products (SMP)

Peaks 2 – 11, 15 and 17 have mass spectra consistent, respectively, with the following compounds: 6,7,10,11-diepoxy-8-hexadecene (Appendix 30); 6,7,11,12-diepoxy-8-heptadecene (Appendix 31); methyl-9,10-epoxy-7-pentadecenoate (Appendix 32); methyl-10,11-epoxy-7-hexadecenoate (Appendix 33); dimethyl-7-tetradecenoate (Appendix 34); methyl-11,12-epoxy-9-heptadecenoate (Appendix 35); 6,7,14,15-diepoxy-9-cosene (Appendix 36); 6,7,16,17-diepoxy-11-docosene (Appendix 37); dimethyl-7-hexadecenoate (Appendix 38); methyl-13,14-epoxy-10-nonadecenoate (Appendix 39) and dimethyl-10-cosaenoate (Appendix 40).

4.5.1.4 Mass spectrum (MS) of isomerisation products

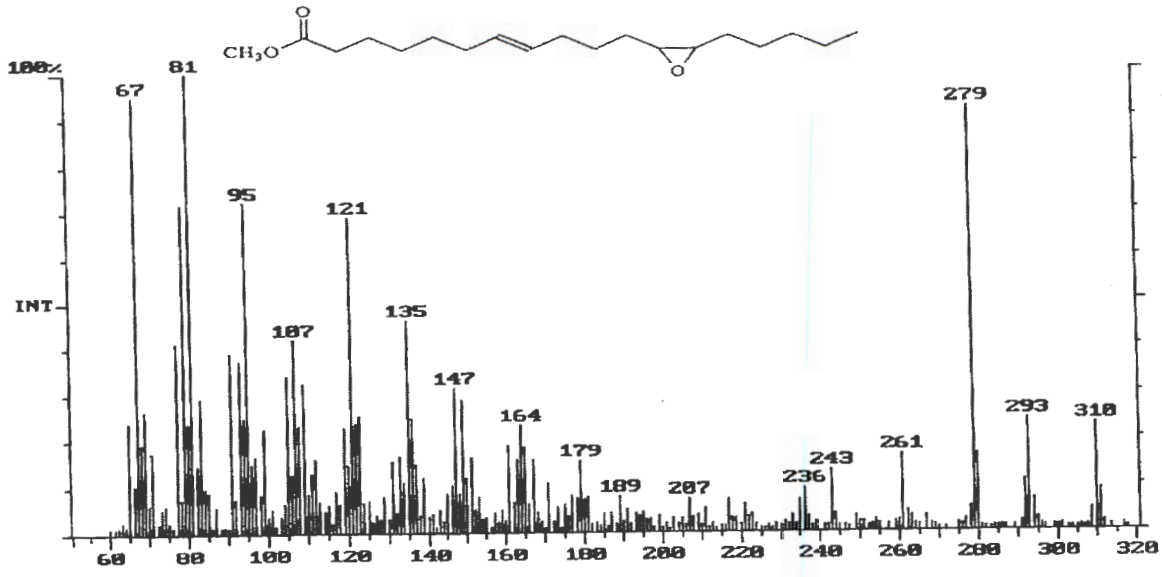


Figure 52. MS of methyl-12,13-epoxy-7-octadecenoate (m/z = 310).

The compound corresponding to Peak 13 has a mass spectrum consistent with methyl-12,13-epoxy-7-octadecenoate (Figure 52). The molecular ion m/z = 310 is detected. The abundant ion at m/z = 279 seem to reflect fragmentation of the methanol group rather than the ethyl group in the hydrocarbon chain. The ion at m/z = 261 then reflects fragmentation of the methyl group in the hydrocarbon chain, after the loss of the methanol group. The ion at m/z = 236 reflects fragmentation of the propyl group after loss of methanol group. The ions at m/z = 207 and 164, respectively, reflect fragmentations at carbon atoms alpha to the epoxy ring after loss of the methanol group. The abundant ion at m/z = 179 reflects fragmentation of the epoxy ring, with subsequent loss of oxygen atom. The abundant ions at m/z = 121 and 95, respectively, reflect fragmentations at carbon atoms alpha to the double bond. The abundant ions at m/z = 81 (base peak) and 135, respectively, reflect fragmentations at carbons beta to the double bond. The gap of 72 amu between m/z = 279 and 207, and of 115 between m/z = 279 and 164 suggests that the epoxy ring is in positions 12 and 13 from the carboxyl group. The gap of 158 amu between m/z = 279 and 121, and of 184 amu between m/z = 279 and 95 suggests that the double bond is in position 7 from the carboxyl group. The gap of 43 amu between m/z = 164 and 121 (i.e. loss of three carbon atoms) indicates the gap between the double bond and the epoxy ring.

The compound associated with Peak 14 has a spectrum consistent with methyl-12, 13-epoxy-10-octadecenoate (Appendix 41).

NWU LIBRARY

Table 19. Products obtained when MV is metathesis using 2 wt.% $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalyst.

Peak no	C_x	Product	Carbon skeleton	m/z	Yield	Selectivity
					%	%
Substrate						
12	C_{19}	methyl-12,13-epoxy-9-octadecenoate	$C_5COCC_2{=}C_8COOC$	310	5.8	
Primary metathesis products						
5	C_{18}	6,7,12,13-diepoxy-9-octadecene	$C_5COCC_2{=}C_2COC_6$	280	5.4	5.7
16	C_{20}	dimethyl-9-octadecenoate	$COOC_9{=}C_9OOC$	340	3.9	4.1
Isomerisation products						
13	C_{19}	methyl-12,13-epoxy-7-octadecenoate	$C_5COCC_4{=}C_6COOC$	310	19.1	20.3
14	C_{19}	methyl-12,13-epoxy-10-octadecenoate	$C_5COCC{=}C_9COOC$	310	23.1	24.5
Secondary metathesis products						
2	C_{16}	6,7,10,11-diepoxy-8-hexadecene	$C_5COCC{=}CCOCC_5$	252	17.7	18.8
3	C_{17}	6,7,11,12-diepoxy-8-heptadecene	$C_5COCC_2{=}CCOCC_5$	266	2.3	2.4
4	C_{16}	methyl-9,10-epoxy-7-pentadecenoate	$C_5COCC{=}C_5COOC$	268	1.4	1.5
6	C_{17}	methyl-10,11-epoxy-7-hexadecenoate	$C_5COCC_2{=}C_6COOC$	282	1.1	1.2
7	C_{16}	dimethyl-7-tetradecenoate	$COOCC_6{=}C_6COOC$	284	2.3	2.4
8	C_{18}	methyl-11,12-epoxy-9-heptadecenoate	$C_5COCC{=}C_8COOC$	296	10.1	10.7
9	C_{20}	6,7,14,15-diepoxy-9-cosene	$C_5COCC_2{=}C_4COCC_5$	308	3.1	3.3
10	C_{22}	6,7,16,17-diepoxy-11-docosene	$C_5COCC_4{=}C_4COC_6$	336	1.7	1.8
11	C_{18}	dimethyl-7-hexadecenoate	$COOCC_8{=}C_6COOC$	312	2.3	2.4
15	C_{20}	methyl-13,14-epoxy-10-nonadecenoate	$COOCC_8{=}C_6COOC$	324	0.3	0.3
17	C_{22}	dimethyl-10-cosaenoate	$COOCC_8{=}C_6COOC$	368	-	-
1	C_{15}	methyl-9-tetradecenoate	$C_5{=}C_8COOC$	240	0.4	0.4

Table 20. Diepoxy alkenes, epoxy esters, diesters and esters obtained upon self-metathesis of MV using 2 wt.% $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalyst.

C_x	Product	m/z	Yield	Selectivity
			%	%
Diepoxy alkenes				
C_{16}	6,7,10,11-diepoxy-8-hexadecene	252	17.7	18.8
C_{17}	6,7,11,12-diepoxy-8-heptadecene	266	2.3	2.4
C_{18}	6,7,12,13-diepoxy-8-octadecene	280	5.4	5.7
C_{20}	6,7,14,15-diepoxy-9-cosene	308	3.1	3.3
C_{22}	6,7,16,17-diepoxy-11-docosene	336	1.7	1.8
Epoxy esters				
C_{16}	methyl-9,10-epoxy-7-pentadecenoate	268	1.4	1.5
C_{17}	methyl-10,11-epoxy-7-hexadecenoate	282	1.1	1.2
C_{18}	methyl-11,12-epoxy-9-heptadecenoate	296	10.1	10.7
C_{19}	methyl-12,13-epoxy-7-octadecenoate	310	19.1	23.3
C_{19}	methyl-12,13-epoxy-10-octadecenoate	310	23.1	24.5
C_{20}	methyl-13,14-epoxy-10-nonadecenoate	324	0.3	0.3
Diesters				
C_{16}	dimethyl-7-tetradecenoate	284	2.3	2.4
C_{18}	dimethyl-7-hexadecenoate	312	2.3	2.4
C_{20}	dimethyl-9-octadecenoate	340	3.9	4.1
C_{22}	dimethyl-10-cosaenoate	368	-	-
Ester				
C_{15}	methyl-9-tetradecenoate	240	0.4	0.4

Re:Sn:MV = 1:0.5:10, Reaction time = 4 h, Solvent = PhCl.

Table 19 shows the product distribution, yield and selectivity when MV is metathesised using 2 wt.% $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalytic system. It can be seen that the spectrum consists of PMP, isomerisation products, SMP (resulting from isomerisation of MV) and a side reaction product. The PMP consists of C_{18} and C_{20} and have molecular weights, respectively, of 280 and 340. SMP ranged from C_{16} to C_{22} and molecular weights, respectively, ranged from 252 to 368. There was only one side reaction product with a molecular weight of 240.

PMP obtained from self-metathesis of MV had a combined yield of ca. 9.3%, which was lower than the yield obtained in the metathesis of both ED (see Table 2) and MO (see Table 13). Both self-metathesis of MV and MO produced the same diester. The diester from self-metathesis of MO, however, was obtained in higher yield (ca. 16.2%) than the one obtained in the self-

metathesis of MV (ca. 4.1%). Although an internal diepoxy alkene was obtained in the self-metathesis of MV (see Scheme 5), a terminal diepoxy alkene with the same molecular weight (m/z = 280), was obtained in the self-metathesis of ED (see Scheme 1). The 2 wt.% $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalytic system was highly selective towards the terminal diepoxy alkene (ca. 98.4%) in the metathesis of ED. The catalytic system, however, was least selective towards the internal diepoxy alkene in the metathesis of MV. A combined SMP yield of ca. 42.7% was obtained from isomerisation of MV. Isomerisation products gave a combined yield of ca. 42.2%. It can be seen that the 2 wt.% $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalyst was selective towards SMP and isomerisation products equally, with the total selectivity of ca. 44.8% for each.

Table 20 shows the product distribution, yield and selectivity as a function of functional groups present in the products. The diepoxy alkenes had a combined yield of ca. 30.2%, while the total yield for the epoxy esters was ca. 55.1%. The total yield for the diesters was ca. 8.5% and the yield for normal esters was ca. 0.4%. The selectivity towards diepoxy alkenes, epoxy esters and the diesters, respectively, were ca. 32.0%, 58.5% and 8.9%. The high selectivity towards the epoxy esters may be due to high rate of isomerisation reaction.

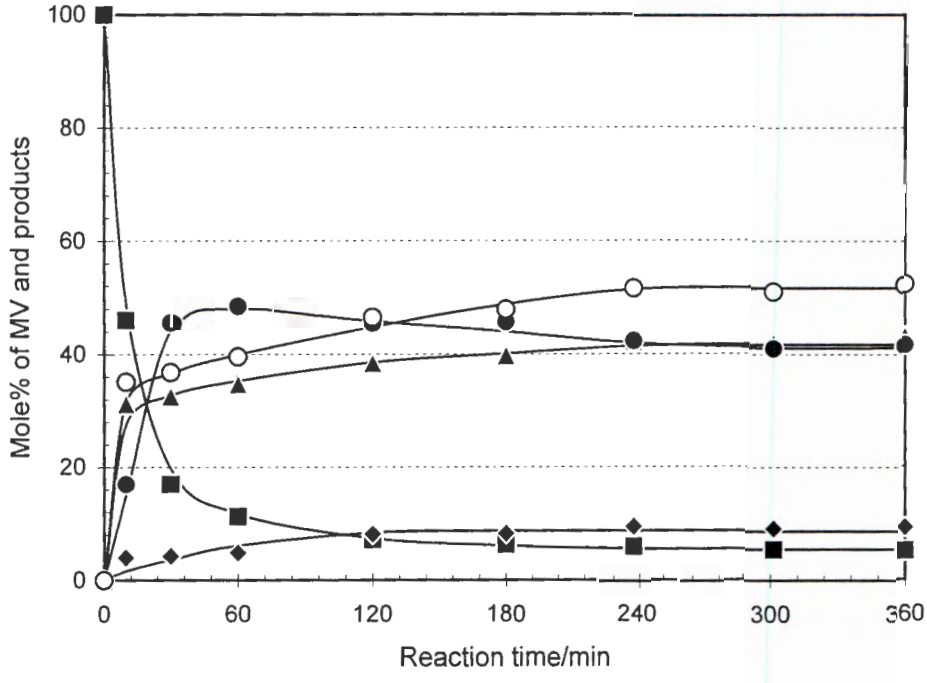


Figure 53. Amount of products and substrate (as mole%), as a function of reaction time for self-metathesis of MV using 2 wt. % $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalyst. [■ : MV, ◆ : PMP, ▲ : SMP, ● : Isomerisation products, ○ : Total metathesis]

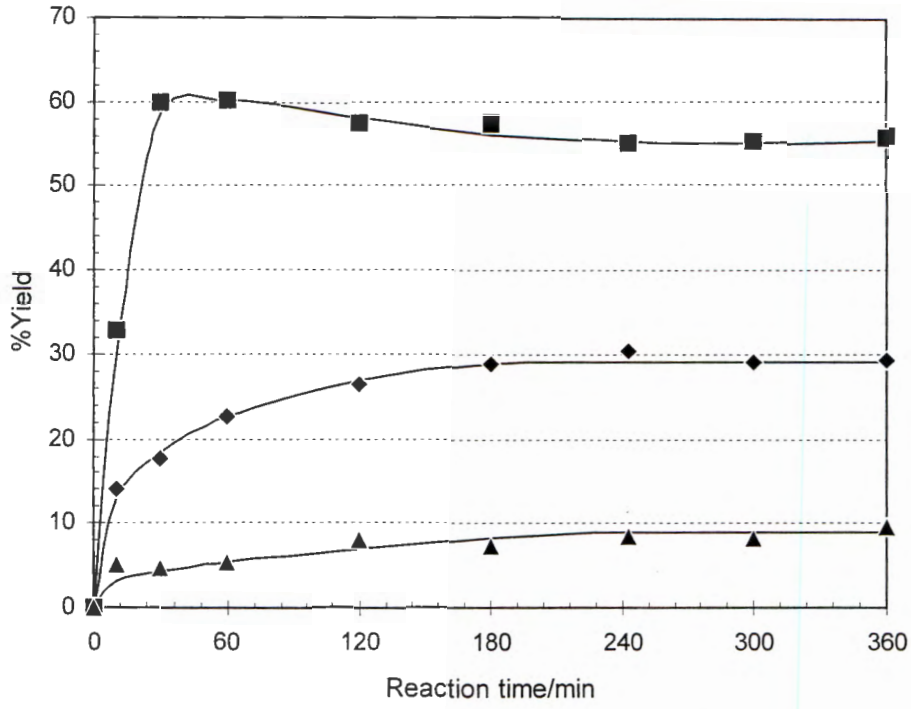


Figure 54. %Yield as a function of reaction time for self-metathesis of MV using 2 wt. % Re_2O_7/SiO_2·$Al_2O_3/SnBu_4$ catalyst. [■ : epoxy esters, ◆ : diepoxy alkenes, ▲ : diesters]

Figure 53 shows the amounts of MV, PMP, SMP, isomerisation products and the total metathesis products (TMP) with time. It can be seen that equilibrium was reached after 4 h of reaction. The substrate conversion was ca. 94.2%. Isomerisation product reached an optimum yield of ca. 48.0% after 1 h of reaction, and it then decreased to ca. 41.8% after 4 h. This decrease suggests cross-metathesis between the two isomers of MV, which may lead to increase in the SMP. The SMP yield reached an optimum value of ca. 42.3%. PMP yield was ca. 9.3%. The total metathesis product yield, which is the sum of PMP and SMP, was ca. 51.1%. This suggests that the Re_2O_7/SiO_2·$Al_2O_3/SnBu_4$ catalyst was highly selective towards metathesis products.

The close proximity of the epoxy group to the double bond (an active site in the metathesis reaction), may promote isomerisation of MV. The epoxy group probably blocks the catalyst molecules from interacting with the active sites on the substrate molecules. This leads to an increase in the rate of isomerisation reaction as compared to that of self-metathesis of MV. This blockage of active site by the epoxy group is further illustrated by higher yields of 6,7,10,11-diepoxy-8-hexadecene and methyl-11,12-epoxy-9-heptadecenoate (see Table 17). These two products are SMP derived, respectively, from self-metathesis of methyl-12,13-epoxy-10-octadecenoate (see Scheme 34) and cross-metathesis of MV with methyl-12,13-epoxy-10-

octadecenoate (see Scheme 35). The epoxy group and the double bond in methyl-12,13-epoxy-10-octadecenoate, are trans to each other, and hence the interference of the epoxy group with the catalyst molecules is expected to be minimal. This may also explain the high selectivity towards the PMP in the metathesis of ED, which is a terminal epoxy alkene (see Table 4).

The effect of the epoxy group on the activity and selectivity of the $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalyst can be illustrated by comparing the reactivity of MV and MO. In the metathesis of MO, SMP was not obtained. This suggests that the epoxy group interacts with the support in the isomerisation of MV. This leads to increased Brønsted acid sites, which are responsible for isomerisation reactions via the double bond migration. This then leads to high isomerisation product and SMP yields.

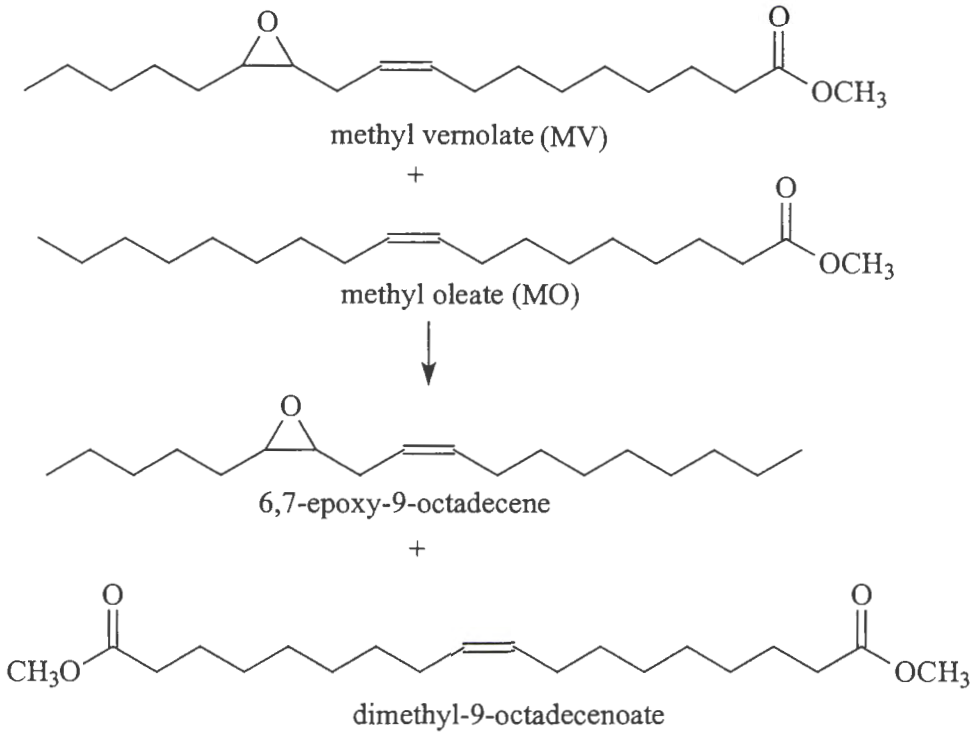
Both $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$/MV and $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$/MO catalytic systems were deactivated, possibly due to the interaction of the carboxylic acid group with the metal carbenes (see Scheme 37, Chapter 5). The deactivation in the case of $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$/MV catalytic system may be due to the interaction of the epoxy group with the metal carbene species (see Scheme 38, Chapter 5).

Figure 54 shows the product distribution in terms of the functional groups present in the products as a function of reaction time, when MV is metathesised. It can be seen that the catalytic system was highly selective towards the epoxy esters, and the yield reached an optimum value of ca. 60.0% after 30 min of reaction. The yield, however, decreased to ca. 55.1% after 4 h. The diepoxy alkenes reached an optimum value of ca. 29.0% after 3 h. The diester yield of ca. 8.5% was obtained after 4 h of reaction.

4.6 CROSS-METATHESIS OF METHYL VERNOLATE (MV) WITH METHYL OLEATE (MO)

MV was metathesised with MO in chlorobenzene at room temperature, using a 2 wt.% $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalyst. Re:Sn:MV: MO = 1:0.5:5:5.

Scheme 6 illustrates the formation of PMP, 6,7-epoxy-9-octadecene and dimethyl-9-octadecenoate, when MV is cross-metathesised with MO.



Scheme 6. The cross-metathesis of MV with $C_5^{1=}$ to give 6,7-epoxy-9-octadecene and dimethyl-9-octadecenoate.

4.6.1 Reaction products

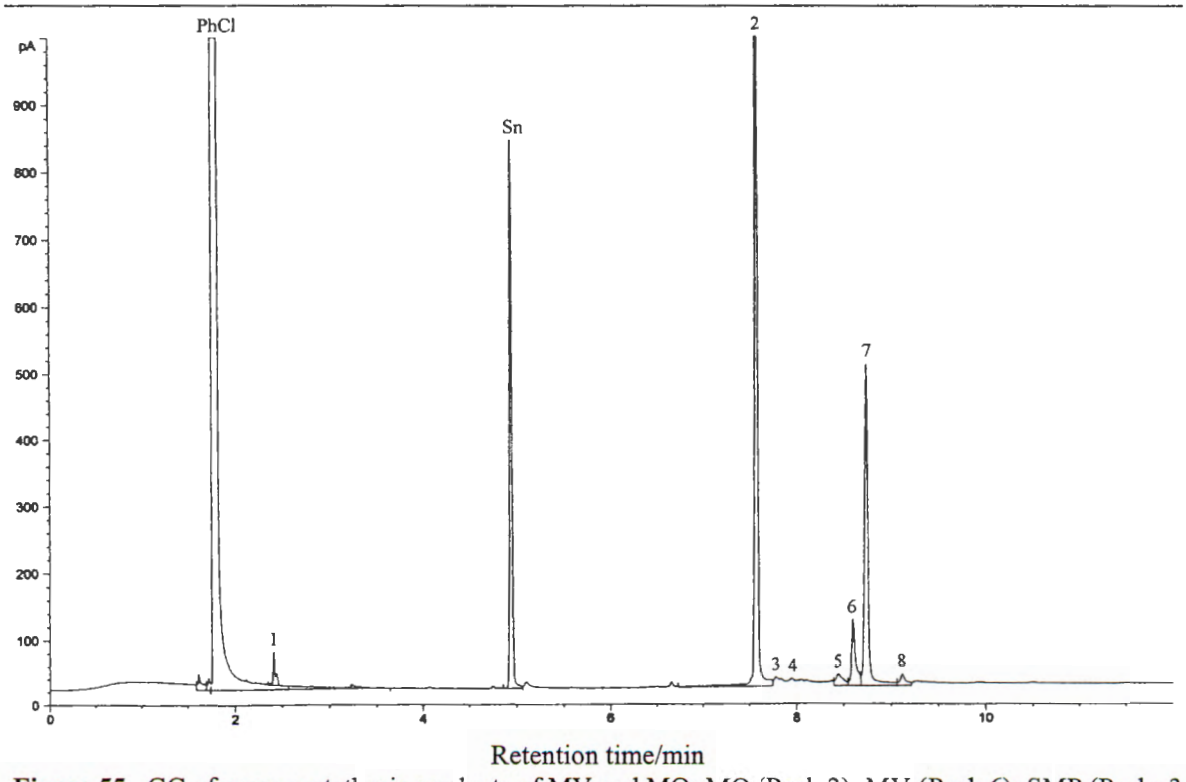


Figure 55. GC of cross-metathesis products of MV and MO: MO (Peak 2); MV (Peak 6); SMP (Peaks 3 – 5, 8; see Table 21); Isomerisation product (Peak 7, see Table 21) and other (Peak 1; see Table 21). PhCl = chlorobenzene solvent.

Figure 55 shows a typical chromatogram of the product mixture obtained when MV is cross-metathesised with MO, using 2 wt.% $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalyst. According to the reaction Scheme 6, only two peaks for the products should be expected in Figure 55. The presence of more peaks suggests formation of other products, probably from side reactions and isomerisation reactions. Two isomerisation products occurred in the self-metathesis of MV (see Figure 48 and Table 19). For the cross-metathesis of MV with MO (see Figure 55), however, only one isomerisation product was obtained.

4.6.1.1 Mass spectrum (MS) of primary metathesis products (PMP)

There were no PMP identified when MV was cross-metathesised with MO. The reason for the absence of PMP may be attributed to sterric factors. As both MV and MO are internal olefinic esters, the presence of the epoxy group near the double bond in MV may block the MO molecules from reaching the active sites in MV.

4.6.1.2 Mass spectrum (MS) of secondary metathesis products (SMP)

The compounds corresponding to Peaks 3 – 5; and 8 have mass spectra consistent, respectively, with 6,7,14,15-diepoxy-9-cosene (Appendix 36); 6,7,16,17-diepoxy-11-docosene (Appendix 37); dimethyl-7-hexadecenoate (Appendix 38) and methyl-13,14-epoxy-10-nonadecenoate (Appendix 39).

4.6.1.3 Mass spectrum (MS) of isomerisation products

Peak 7 has a mass spectrum consistent with methyl-12,13-epoxy-7-octadecenoate (Figure 52). This compound is an isomerisation product obtained from isomerisation of MV.

4.6.1.4 Mass spectrum (MS) of other products

The compound associated with Peak 1 has a mass spectrum consistent with 6,7-epoxy-8-tridecene (Appendix 43), which is a side reaction product (see Scheme 35).

Table 21. Products obtained upon cross-metathesis of MV with MO using 2 wt.% $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalyst.

Peak no	C_x	Product	Carbon skeleton	m/z	Yield %	Selectivity %
Substrate						
6	C_{19}	methyl-12,13-epoxy-9-octadecenoate	$C_5COCC_2{=}C_8COOC$	310	25.4	
2	C_{19}	methyl-9-octadecenoate	$C_9{=}C_8COOC$	296	100	
Isomerisation products						
7	C_{19}	methyl-12,13-epoxy-7-octadecenoate	$C_5COCC_4{=}C_6COOC$	310	64.2	86.1
Secondary metathesis products						
3	C_{20}	6, 7, 14, 15-diepoxy-9-cosene	$C_5COCC_2{=}C_4COCC_5$	308	2.8	3.7
4	C_{22}	6, 7, 16, 17-diepoxy-11-docosene	$C_5COCC_4{=}C_4COC_6$	336	-	-
5	C_{18}	dimethyl-7-hexadecenoate	$COOCC_8{=}C_6COOC$	312	4.6	6.2
8	C_{20}	methyl-13, 14-epoxy-10-nonadecenoate	$COOCC_8{=}C_6COOC$	324	3.0	4.0
Side reaction						
1	C_{16}	6, 7-epoxy-8-tridecene	$C_5COCC{=}C_5$	196	-	-

Re:Sn:MO:MV = 1:0.5:5:5, Reaction time = 4 h, Solvent = PhCl.

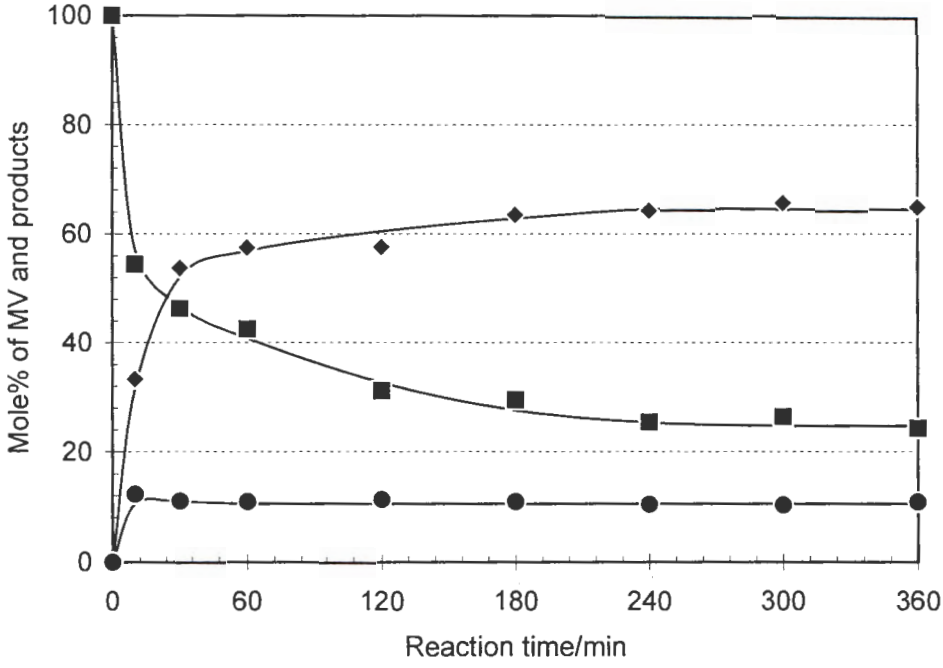


Figure 56. Amount of products and MV (as mole%) as a function of reaction time for cross-metathesis of MV with MO using 2 wt. % $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$. [■ : MV, ● : SMP, ◆ : Isomerisation products]

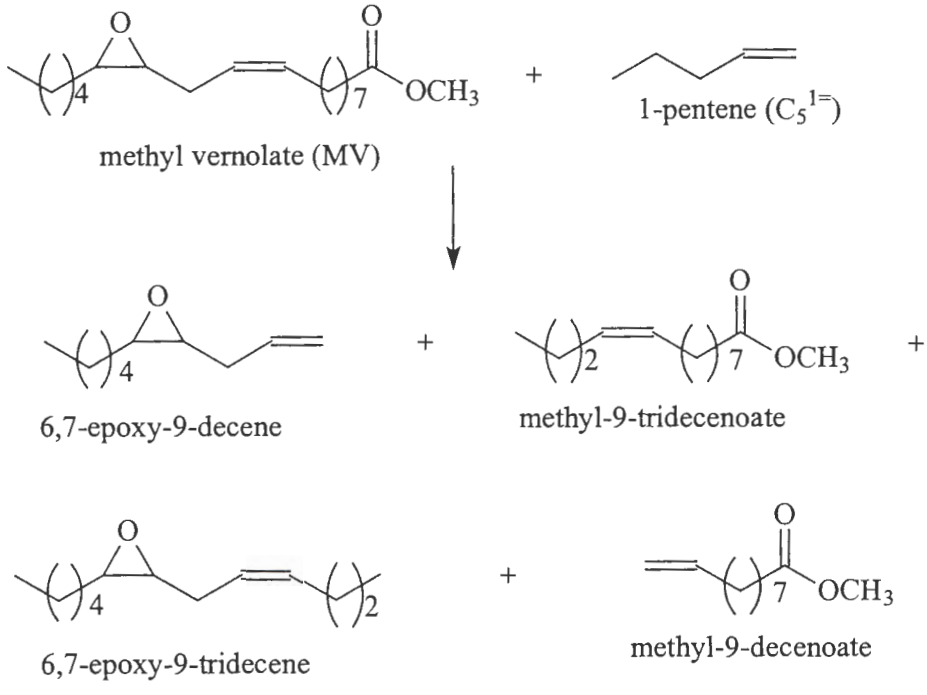
Table 21 shows the product distribution, yield and selectivity when MV is cross-metathesised with MO. The product spectrum is associated mainly of isomerisation products, and SMP (obtained from isomerisation of MV). Only one product was obtained from a side reaction. There were no PMP obtained from either cross-metathesis of MV with MO or self-metathesis of both MV and MO. MO was not metathesised. SMP ranged from C_{18} to C_{20}, respectively, and their molecular weights ranged from 308 to 324. The side reaction product had a molecular weight of 196. SMP obtained from isomerisation of MV gave a combined yield of ca. 10.4%, while isomerisation product gave the highest yield (ca. 64.2%). It can be seen that the $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalyst was highly selective towards an isomerisation product (ca. 86.1%).

Figure 56 shows the conversion of MV, SMP and isomerisation products as a function of time. It can be seen that equilibrium was attained after 4 h of reaction, and conversion was ca. 74.6%. An optimum isomerisation product yield of ca. 64.2% was obtained after 4 h. SMP yield obtained was ca. 10.4%. There was a decrease in the conversion of MV in the cross-metathesis of MV with MO, as compared to the conversion obtained in the metathesis of MV (see Figure53). This suggests that there was a deactivation of the $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$

catalyst in the cross-metathesis of MV with MO. This may be expected since there were now two carboxylic acid groups (from both MV and MO) interacting with the carbene species (see Scheme 37). The absence of PMP and the lower selectivity towards SMP (see Figure 56 and Table 19) indicates strong interaction of the two carboxylic acid groups with the carbene species.

4.7 CROSS-METATHESIS OF METHYL VERNOLATE (MV) WITH 1-PENTENE ($C_5^{1=}$)

MV (methyl vernolate) was metathesised with $C_5^{1=}$ (1-pentene) in chlorobenzene at room temperature, using 2 wt.% $Re_2O_7/SiO_2{\cdot}Al_2O_3$/ $SnBu_4$ catalyst. Re:Sn:MV: $C_5^{1=}$ = 1:0.5:5:15.



Scheme 7. The cross-metathesis of MV with $C_5^{1=}$ to give PMP.

Scheme 7 illustrates the formation of PMP when MV was cross-metathesised with $C_5^{1=}$. The products expected are the two epoxy alkenes, 6,7-epoxy-9-decene and 6,7-epoxy-9-tridecene and two esters, methyl-9-tridecenoate and methyl-9-decenoate.

4.7.1 Reaction products

Figure 57 shows a typical chromatogram illustrating the product mixture obtained when MV is cross-metathesised with $C_5^{1=}$, using 2 wt.% $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalyst.

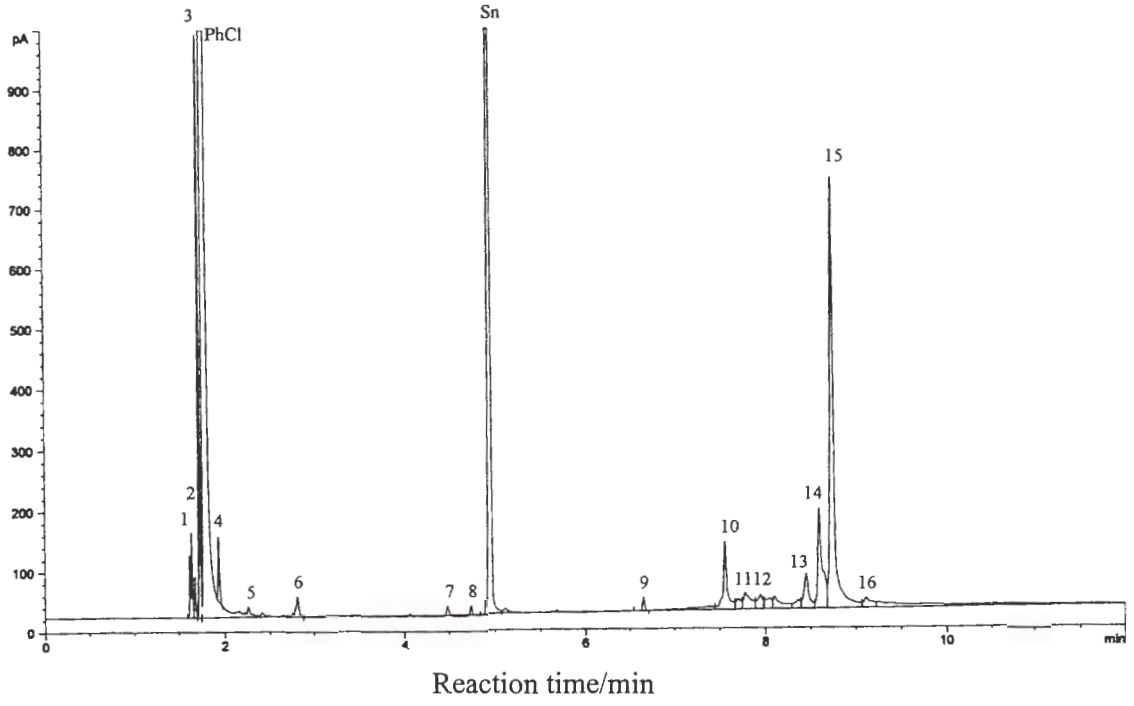


Figure 57. GC of cross-metathesis products of MV and $C_5^{1=}$: $C_5^{1=}$ (Peak 1); methyl MV (Peak 14); PMP (Peaks 5, 7 and 10; see Table 22); SMP (Peaks: 2 – 4, 6, 8 – 9, 11 – 13 and 16; see Table 22); Isomerisation product (Peak 15). PhCl = chlorobenzene solvent and Sn = tetrabutyltin.

As in the cross-metathesis of MV with MO (see Figure 55), only one isomerisation product is obtained in the cross-metathesis of MV with 1-pentene.

4.7.1.1 Mass spectrum (MS) of primary metathesis products (PMP)

The compounds corresponding to Peaks 5, 7 and 10 have mass spectra consistent, respectively, with (Z)-4-octene (Appendix 11); 6,7-epoxy-9-decene (Appendix 45) and 6,7,12,13-diepoxy-9-octadecene (Figure 51).

4.7.1.2 Mass spectrum (MS) of secondary metathesis products (SMP)

The compounds corresponding to Peaks 2 – 4 have mass spectra consistent, respectively, with 2-hexene (12); 3-hexene (Appendix 13) and 3-heptene (Appendix 14). All these compounds are the linear alkenes. Peak 6 has a mass spectrum consistent with 6,7, epoxy-8-nonene (Appendix 46), which is an epoxy alkene. The compound associated with Peak 8 has a mass spectrum consistent with methyl-9-dodecenoate (Appendix 47), which is an ester. The compounds associated with Peaks 9, 11 – 12 have mass spectra consistent, respectively, with 6,7,10,11-diepoxy-8-hexadecene (Appendix 30); 6,7,14,15-diepoxy-9-cosene (Appendix 36); 6,7,16,17-diepoxy-11-docosene (Appendix 37). These are diepoxy alkenes. The compound associated with Peak 13

has a spectrum consistent with dimethyl-7-hexadecenoate (Appendix 38), which is a diester. Peak 15 has a spectrum consistent with methyl-13,14-epoxy-10-nonadecenoate (Appendix 39), which is an epoxy ester.

4.7.1.3 Mass spectrum (MS) of isomerisation products

Peak 14 has a mass spectrum consistent with methyl-12,13-epoxy-10-octadecenoate (Appendix 41). This compound is an isomerisation product obtained from the double bond isomerisation in MV.

Table 22. Products obtained when MV is cross-metathesised with $C_5^{1=}$ using 2 wt.% $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalyst.

Peak no	C_x	Product	Carbon skeleton	m/z	Yield	Selectivity
					%	%
Substrate						
1	C_5	1-pentene	C_4=C	70	30.4	
14	C_{19}	methyl-12,13-epoxy-9-octadecenoate	C_5COCC_2=C_8COOC	310	9.8	
Primary metathesis products						
5	C_8	(Z)-4-octene	C_4=C_4	112	-	-
10	C_{18}	6,7,12,13-diepoxy-9-octadecene	C_5COCC_2=C_2COC_6	280	5.3	8.3
7	C_{10}	6,7-epoxy-9-decene	$COOC_9$=C_9OOC	154	-	-
Isomerisation products						
15	C_{19}	methyl-12,13-epoxy-10-octadecenoate	C_5COCC=C_9COOC	310	33.1	51.9
Secondary metathesis products						
2	C_6	2-hexene	C_2=C_4	84	0.9	1.4
3	C_6	3-hexene	C_3=C_3	84	11.1	17.4
4	C_7	3-heptene	C_3=C_4	98	4.4	6.9
6	C_9	6,7-epoxy-8-nonene	C_5COC_2=C	140	0.5	0.8
8	C_{13}	methyl-9-dodecenoate	C_3=C_8COOC	212	-	-
9	C_{16}	6,7,10,11-diepoxy-8-hexadecene	C_5COCC=$CCOCC_5$	252	1.1	1.7
11	C_{20}	6,7,14,15-diepoxy-9-cosene	C_5COCC_2=C_4COCC_5	308	0.9	1.4
12	C_{22}	6,7,16,17-diepoxy-11-docosene	C_5COCC_4=C_4COC_6	336	1.2	1.9
13	C_{18}	dimethyl-7-hexadecenoate	$COOCC_8$=C_6COOC	312	3.9	6.1
16	C_{20}	methyl-13,14-epoxy-10-nonadecenoate	$COOCC_8$=C_6COOC	324	1.4	2.2

Re:Sn:MV:$C_5^{1=}$ = 1:0.5:5:15, Reaction temperature = RT, Reaction time = 6 h, Solvent = PhCl.

Table 23. Diepoxy alkenes, epoxy esters, diesters and esters obtained when MV is cross-metathesised with $C_5^{1=}$ using 2 wt.% $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalyst.

C_x	Product	m/z	Yield	Selectivity
			%	%
Linear alkenes				
C_6	2-hexene	84	0.9	1.4
C_6	3-hexene	84	11.1	17.4
C_7	3-heptene	98	4.4	6.9
C_8	(Z)-4-octene	112	-	-
Ester				
C_{13}	methyl-9-dodecenoate	212	-	-
Epoxy alkenes				
C_9	6,7-epoxy-8-nonene	140	0.5	0.8
C_{10}	6,7-epoxy-9-decene	154	-	-
Diepoxy alkenes				
C_{16}	6,7,10,11-diepoxy-8-hexadecene	252	1.1	1.7
C_{18}	6,7,12,13-diepoxy-8-octadecene	280	5.3	8.3
C_{20}	6,7,14,15-diepoxy-9-cosene	308	0.9	1.4
C_{22}	6,7,16,17-diepoxy-11-docosene	336	1.2	1.9
Epoxy esters				
C_{19}	methyl-12,13-epoxy-10-octadecenoate	3 10	33.1	51.9
C_{20}	methyl-13,14-epoxy-10-nonadecenoate	324	1.4	2.2
Diesters				
C_{18}	dimethyl-7-hexadecenoate	312	3.9	6.1

Re:Sn:MV:$C_5^{1=}$ = 1:0.5:15, Reaction time = 6 h, Solvent = PhCl.

Table 22 shows the product distribution, yield and selectivity when MV is cross-metathesised with $C_5^{1=}$. PMP were obtained from both self-metathesis of MV and $C_5^{1=}$, and cross-metathesis of MV with $C_5^{1=}$. An isomerisation product was also obtained due to the double bond migration in MV. SMP were obtained from cross-metathesis of MV with isomers of $C_5^{1=}$. PMP consisted of C_8, C_{10} and C_{18} and their molecular weights were, respectively, 112, 154 and 280. SMP ranged from C_6 to C_{22}, and their molecular weights ranged from 84 to 336.

PMP yield obtained from cross-metathesis of MV with $C_5^{1=}$ was ca. 5.3%. This yield was lower than the PMP yield obtained in the cross-metathesis of ED with $C_5^{1=}$ (see Table 9). Combined SMP yield of ca. 25.4% was obtained from double bond isomerisation in both MV and $C_5^{1=}$.

The isomerisation product yield of ca. 33.1% was obtained from the double bond migration in MV. It can be seen that the 2 wt.% $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalyst was selective towards isomerisation product (ca. 51.9%). The catalytic system, however, was more selective towards the isomerisation products in the cross-metathesis of MV with MO (ca. 86.1%).

Table 23 shows the product distribution as a function of the functional groups present in the products. The yield for alkenes, epoxy alkenes, diepoxy alkenes, epoxy esters and diesters, respectively, were ca. 16.4; 0.5; 8.5; 34.5 and 3.9%. The catalytic system was most selective towards the epoxy ester (ca. 54.1%).

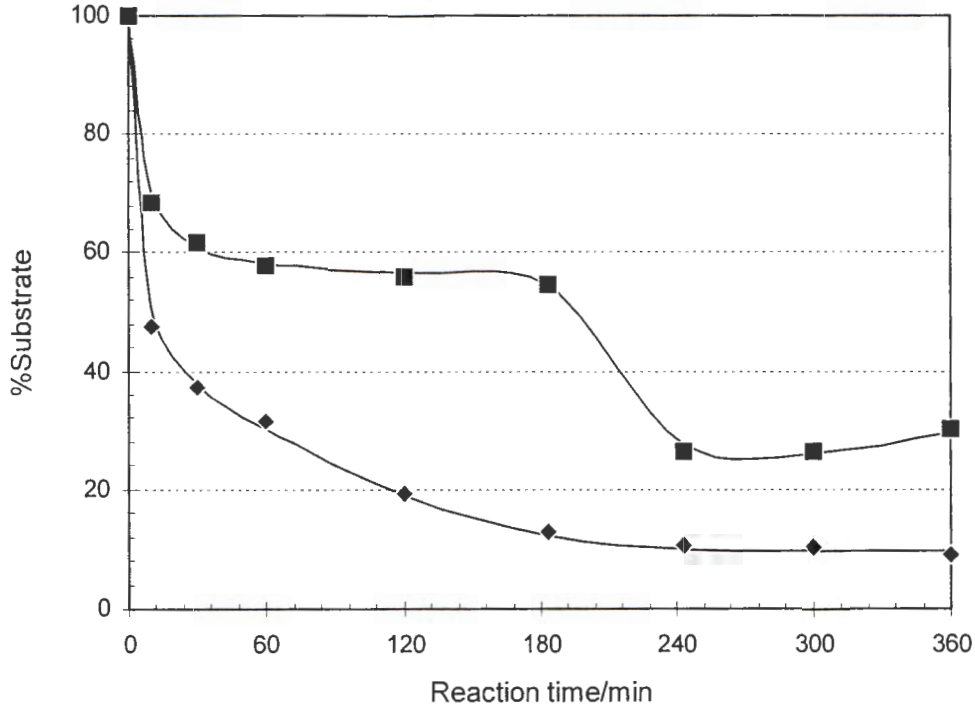


Figure 58. %Substrate (MV and $C_5^{1=}$) converted, as a function of reaction time, at room temperature. Re:Sn:MV: $C_5^{1=}$ = 1:0.5:5:15. [◆ : MV , ■ : $C_5^{1=}$]

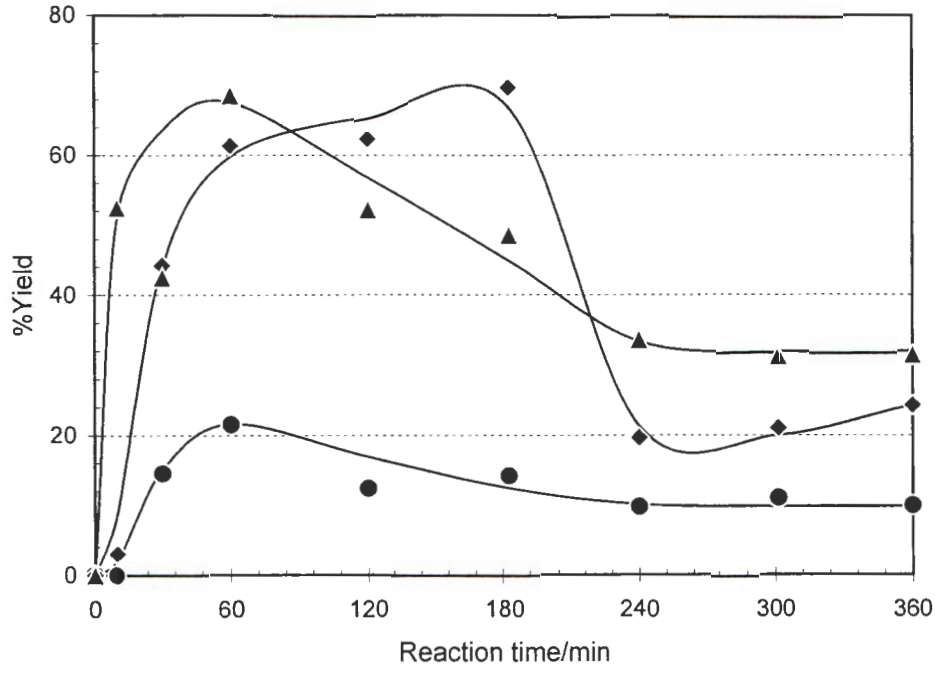


Figure 59. %Yield of products obtained for cross-metathesis of MV with $C_5^{1=}$, as a function of reaction time, at room temperature. Re:Sn:MV:$C_5^{1=}$ = 1:0.5:5:15. [● : PMP, ◆ : SMP, ▲ : isomerisation product]

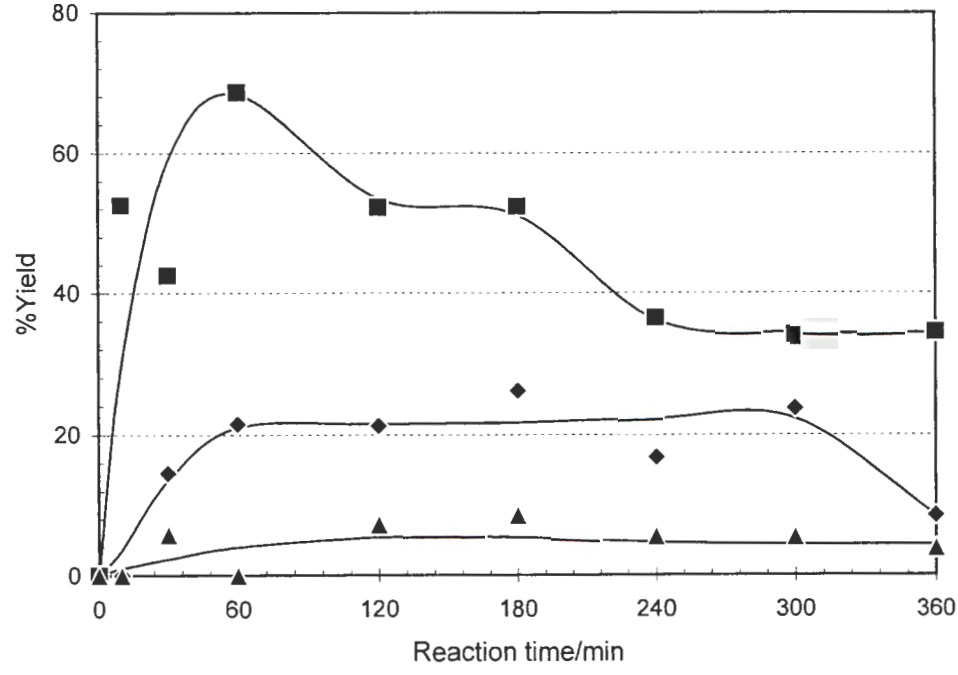


Figure 60. %Yield of products as a function of reaction time from cross-metathesis of MV with $C_5^{1=}$ using 2 wt. % $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$. Re:Sn:MV:$C_5^{1=}$ = 1:0.5:5:15. [■ : epoxy esters, ◆ : diepoxy esters, ▲ : diesters]

Figure 58 shows the conversions of MV and $C_5^{1=}$ as a function of reaction time. It can be seen that for MV system, equilibrium was attained after 4 h of reaction. Conversion was ca. 90.2%. The $C_5^{1=}$ system never reached equilibrium. The substrate conversion increased to an optimum of ca. 73.8% after 4 h, and then decreased.

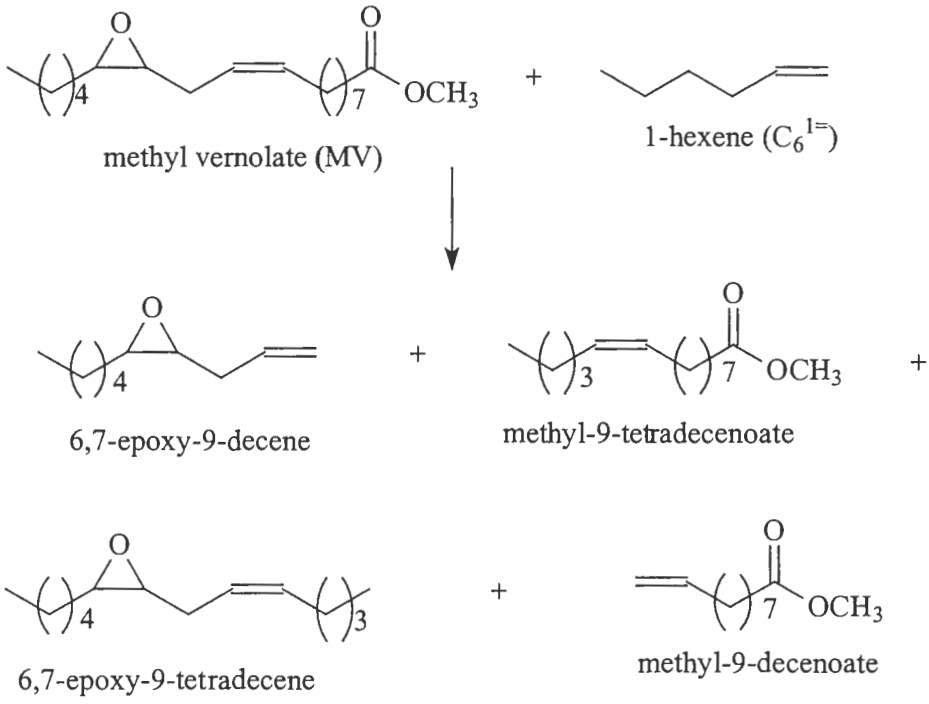
Figure 59 shows the change in PMP, SMP and isomerisation product yield as function of reaction time. Both PMP and isomerisation yield, respectively, increased to optimum of ca. 21.6 and 68.6% after 1 h of reaction. PMP and isomerisation product yield then decreased to ca. 9.8%, and ca. 32.0%, respectively, after 5 h and 4 h. SMP yield continued to increase until 3 h of reaction, and then followed by a decrease from 3 to 4 h of reaction. A slight increase in the SMP yield was again observed after 4 h.

The decrease in the isomerisation product yield between 1 and 3 h of reaction may be attributed to the cross-metathesis reaction between methyl-12,13-epoxy-10-octadecenoate and $C_5^{1=}$. This may be illustrated by an increase in the SMP. However, this decrease in isomerisation product yield may also suggest the probability of methyl-12,13-epoxy-10-octadecenoate undergoing other reactions. For example, it may suggest polymerisation reaction of methyl-12,13-epoxy-10-octadecenoate, which may be possible due to the close proximity of the epoxy group to the double bond. This may lead to the double bond isomerisation in methyl-12,13-epoxy-10-octadecenoate. This may be confirmed by a steady increase in the conversion of $C_5^{1=}$ between 1 and 3 h of reaction. This suggests that there may have been a minimal cross-metathesis reaction between methyl-12,13-epoxy-10-octadecenoate and $C_5^{1=}$. The epoxy ring may also open due to the acidity of the support leading to high molecular compounds, which may clog the pours on the support. The high conversion of MV with the corresponding lower PMP and SMP further supports the formation of high molecular compounds, which could be retained in the reaction mixture during sampling.

Figure 60 shows the product distribution as a function of the functional groups present. The catalytic system was selective towards the epoxy ester. Figure 60 suggests possible reactions between $C_5^{1=}$ (see Figure 58) and epoxy esters, diepoxy alkenes and the diesters, since there was a decrease in the conversion of MV, $C_5^{1=}$ and these compounds. The higher selectivity towards isomerisation products and SMP obtained from double bond isomerisation of $C_5^{1=}$, suggests the deactivation of the $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalyst.

4.8 CROSS-METATHESIS OF METHYL VERNOLATE (MV) WITH 1-HEXENE ($C_6^{1=}$)

MV was metathesised with $C_6^{1=}$ in chlorobenzene at room temperature, using a 2 wt.% $Re_2O_7/SiO_2{\cdot}Al_2O_3$/ $SnBu_4$ catalyst. Re:Sn:MV:$C_6^{1=}$ = 1:0.5:5:15.



Scheme 8. The cross-metathesis of MV with $C_6^{1=}$ to give PMP.

Scheme 8 illustrates the formation of PMP when MV is cross-metathesised with $C_6^{1=}$. The products expected are the two epoxy alkenes, 6,7-epoxy-9-decene and 6,7-epoxy-9-tetradecene and the two esters, methyl-9-tetradecenoate and methyl-9-decenoate. 6,7-epoxy-9-decene and methyl-9-decenoate are to be expected when MV is cross-metathesised with either $C_5^{1=}$ (Scheme 7) or $C_6^{1=}$ (see Scheme 8).

4.8.1 Reaction products

Figure 61 shows a typical chromatogram of the product mixture obtained when MV is cross-metathesised with $C_6^{1=}$, using 2 wt.% $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalyst. Although four peaks should be expected in Figure 61, the presence of more peaks suggests formation of other products. These products are probably obtained from self-metathesis of MV and $C_6^{1=}$, isomerisation of MV and $C_6^{1=}$, cross-metathesis of MV with its isomers or with isomers of $C_6^{1=}$, cross-metathesis of $C_6^{1=}$ with its isomers and side reactions.

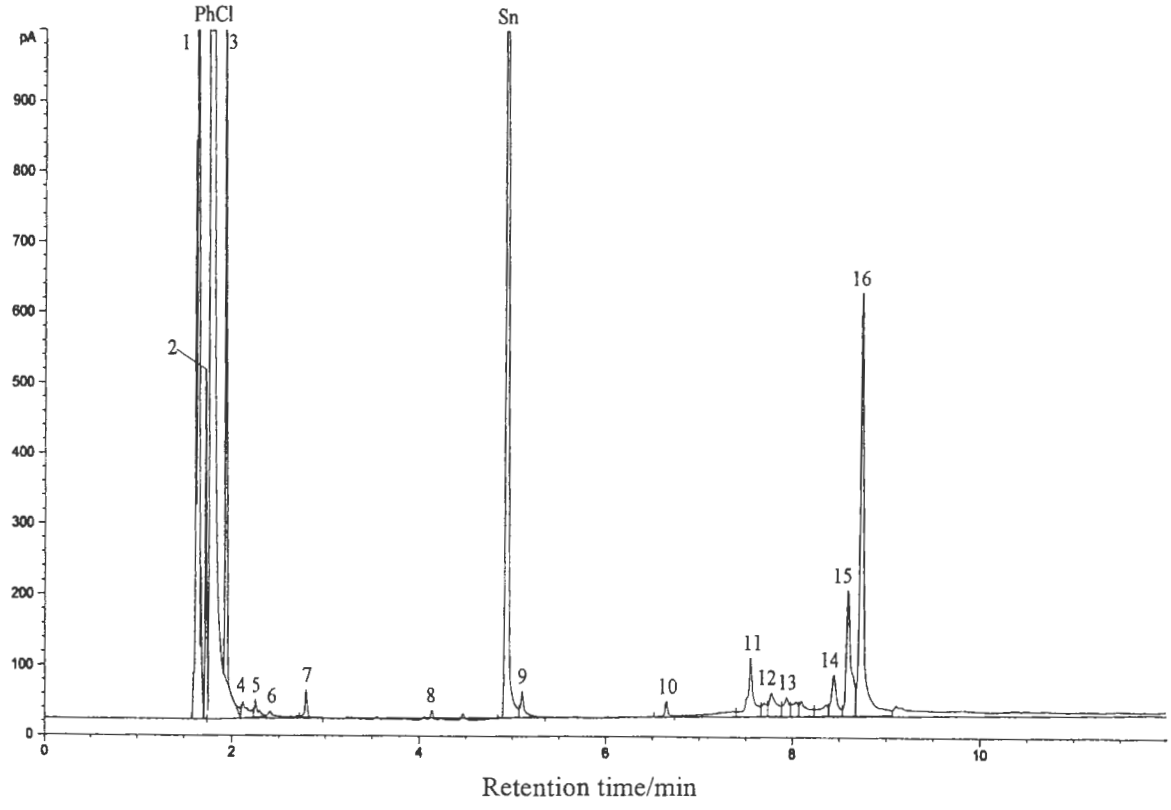


Figure 6 1. GC of cross-metathesis products of MV with $C_6^{1=}$: $C_6^{1=}$ (Peak 1); MV (Peak 15); PMP (Peaks 6, 8, 9 and 11; see Table 24); SMP (Peaks: 2 – 5, 7, 10, 12 – 14; see Table 24); Isomerisation product (Peak 16). PhCl = chlorobenzene and Sn = tetrabutyltin.

4.8.1.1 Mass spectrum (MS) of primary metathesis products (PMP)

Four PMP were identified in the cross-metathesis of MV with $C_6^{1=}$. The compounds corresponding to Peaks 6, 8, 9 and 11 have mass spectra consistent, respectively, with 5-decene (Figure 37), which is a linear alkene; 6,7-epoxy-9-decene (Appendix 44), which is an epoxy alkene; methyl-9-tetradecenoate (Appendix 45), which is an ester and 6,7,12,13-diepoxy-9-octadecene (Figure 51), which is a diepoxy alkene.

4.8.1.2 Mass spectrum (MS) of secondary metathesis products (SMP)

The mass spectra corresponding to Peaks 2 – 5 can be correlated with 2-hexene (Appendix 12); 3-hexene (Appendix 13); 3-heptene (Appendix 14) and trans-4-nonene (Appendix 18), which are all linear alkenes. Peak 7 has a spectrum correlating with 6,7-epoxy-8-nonene (Appendix 46), which is an epoxy alkene. Peaks 10; 12 – 14 have mass spectra consistent, respectively, with 6,7,10,11-diepoxy-8-hexadecene (Appendix 30); 6,7,14,15-diepoxy-9-cosene (Appendix 36); 6,7,16,17-diepoxy-11-docosene (Appendix 37), which are diepoxy alkenes. Peak 14 has a mass spectrum correlating with dimethyl-7-hexadecenoate (Appendix 38), which is a diester.

Table 24. Products obtained when MV is cross-metathesised with $C_6^{1=}$ using 2 wt.% $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalyst.

Peak no	C_x	Product	Carbon skeleton	m/z	Yield %	Selectivity %
Substrate						
1	C_6	1-hexene	$C_5{=}C$	84	21.1	
15	C_{19}	methyl-12,13-epoxy-9-octadecenoate	$C_5COCC_2{=}C_8COOC$	310	9.7	
Primary metathesis products						
11	C_{18}	6,7,12,13-diepoxy-9-octadecene	$C_5COCC_2{=}C_2COC_6$	280	10.0	14.5
6	C_{10}	5-decene	$C_5{=}C_5$	140	-	-
8	C_{10}	6,7-epoxy-9-decene	$C_5COC_3{=}C$	154	-	-
9	C_{15}	methyl-9-tetradecenoate	$C_5{=}C_8OOC$	240	1.4	2.0
Isomerisation products						
16	C_{19}	methyl-12,13-epoxy-10-octadecenoate	$C_5COCC{=}C_9COOC$	310	23.2	33.5
Secondary metathesis products						
2	C_6	3-hexene	$C_3{=}C_3$	84	-	-
3	C_7	3-heptene	$C_3{=}C_4$	98	26.0	37.6
4	C_8	(Z)-4-octene	$C_4{=}C_4$	112	-	-
5	C_9	trans-4-nonene	$C_4{=}C_5$	126	-	-
7	C_9	6,7-epoxy-8-nonene	$C_5COC_2{=}C$	140	0.2	0.3
10	C_{16}	6,7,10,11-diepoxy-8-hexadecene	$C_5COCC{=}CCOCC_5$	252	-	-
12	C_{20}	6,7,14,15-diepoxy-9-cosene	$C_5COCC_2{=}C_4COCC_5$	308	3.4	4.9
13	C_{22}	6,7,16,17-diepoxy-11-docosene	$C_5COCC_4{=}C_4COC_6$	336	-	-
14	C_{18}	dimethyl-7-hexadecenoate	$COOCC_8{=}C_6COOC$	312	5.0	7.2

Re:Sn:MV:$C_6^{=}$ = 1:0.5:5:15, Reaction temperature = RT, Reaction time = 6 h, Solvent = PhCl.

Table 25. Diepoxy alkenes, epoxy esters, diesters and esters obtained when MV is cross-metathesised with $C_6^{1=}$ using 2 wt.% $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalyst.

C_x	Product	m/z	Yield	Selectivity
			%	%
Linear alkenes				
C_6	3-hexene	84	0.9	1.4
C_7	3-heptene	98	26.0	37.4
C_8	(Z)-4-octene	112	-	-
C_9	trans-4-nonene	126	-	-
C_{10}	5-decene	140	-	-
Ester				
C_{15}	methyl-9-tetradecenoate	212	1.4	2.0
Epoxy alkenes				
C_9	6,7-epoxy-8-nonene	140	0.2	0.3
C_{10}	6,7-epoxy-9-decene	154	-	-
Diepoxy alkenes				
C_{16}	6,7,10,11-diepoxy-8-hexadecene	252	-	-
C_{18}	6,7,12,13-diepoxy-9-octadecene	280	10.0	14.5
C_{20}	6,7,14,15-diepoxy-9-cosene	308	3.4	4.9
C_{22}	6,7,16,17-diepoxy-11-docosene	336	-	-
Epoxy esters				
C_{19}	methyl-12,13-epoxy-10-octadecenoate	3 10	23.2	33.5
Diesters				
C_{18}	dimethyl-7-hexadecenoate	312	5.0	7.2

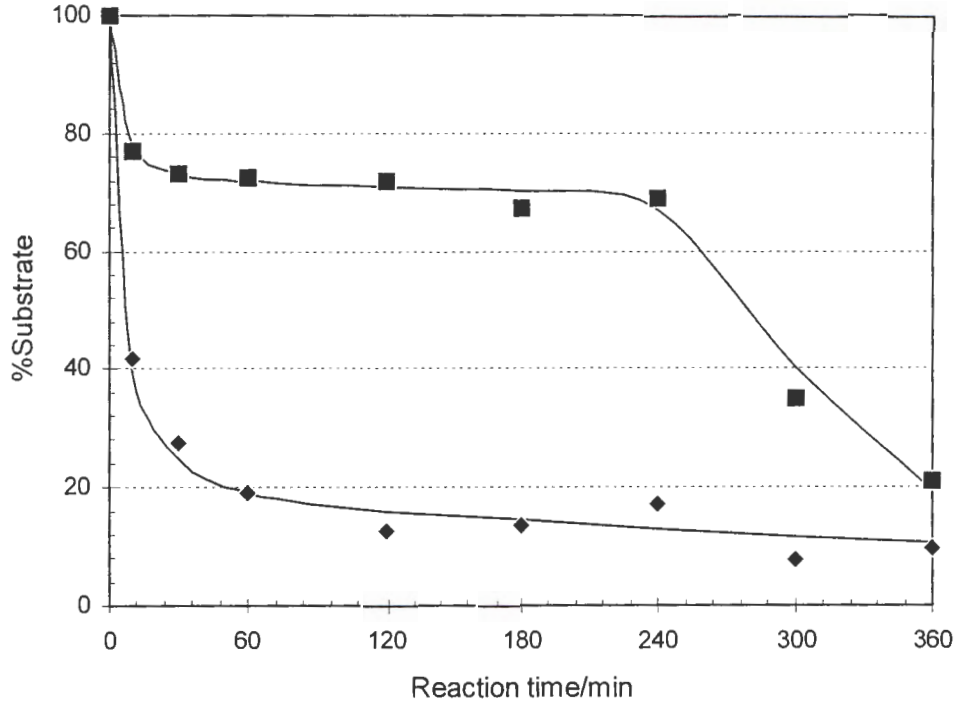
Re:Sn:MV:$C_6^{1=}$ = 1:0.5:5:15, Reaction time = 6 h, Solvent = PhCl.

Table 24 shows the product distribution, yield and selectivity obtained when MV is cross-metathesised with $C_6^{1=}$. It can be seen that the product spectrum is mainly PMP (obtained from self-metathesis of MV and $C_6^{1=}$), isomerisation products (obtained from double bond isomerisation of MV) and SMP (obtained from self-metathesis of both MV and $C_6^{1=}$, and cross-metathesis of MV with $C_6^{1=}$). The PMP ranged from C_{10} to C_{18}, and their molecular weights, respectively, ranged from 140 to 280. SMP ranged from C_6 to C_{22}, and their molecular weights, respectively, ranged from 84 to 336.

The combined yield of PMP obtained by the cross-metathesis of MV with $C_6^{1=}$ was ca. 11.4%. This is higher than the yield obtained in the cross-metathesis of MV with $C_5^{1=}$ (see Table 22), but lower than the yield obtained in the cross-metathesis of ED with $C_5^{1=}$ (see Table 9). The

combined yield of SMP was ca. 34.6%. This is also higher than the yield obtained in the cross-metathesis of MV with $C_6^{1=}$ (see Table 22). The isomerisation product yield was ca. 23.2%, and this is lower than in the cross-metathesis of MV with $C_5^{1=}$ (see Table 22). The selectivity towards PMP, isomerisation products and SMP, respectively, were ca. 16.5, 33.5 and 50.0%. This shows that the catalytic system was highly selective towards SMP. However, the catalytic system was highly selective towards isomerisation products in the cross-metathesis of MV with $C_5^{1=}$ (see Table 22). This suggests that in the cross-metathesis of MV with alkenes, the alkene chain length plays an important part in the selectivity of the $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalyst.

Table 25 shows the product distribution as a function of the functional groups present in the compounds. The $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalyst was equally selective towards both alkenes (ca. 39.0%) and the epoxy ester (ca. 33.5%. The compound that contributed the most towards the combined alkene yield was 3-heptene. This compound is obtained by the cross-metathesis between $C_5^{1=}$ and $C_6^{1=}$.



NWU LIBRARY

Figure 62. %Substrate (MV and $C_6^{1=}$) converted, as a function of reaction time, at room temperature. Re:Sn:MV:$C_6^{1=}$ = 1:0.5:5:15. [■ : $C_6^{1=}$, ◆ : MV]

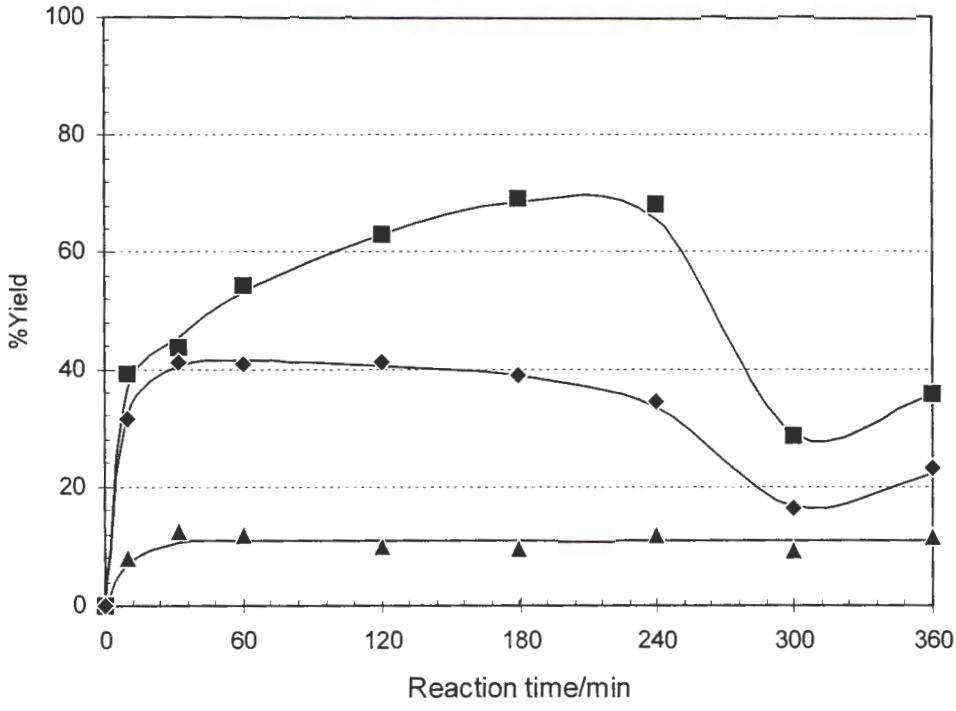


Figure 63. %Yield of products obtained for cross-metathesis of MV with 1-hexene, as a function of reaction time, at room temperature. Re:Sn:MV:$C_6^{1=}$ = 1:0.5:5:10. [▲ : PMP, ■ : SMP, ◆ : isomerisation product]

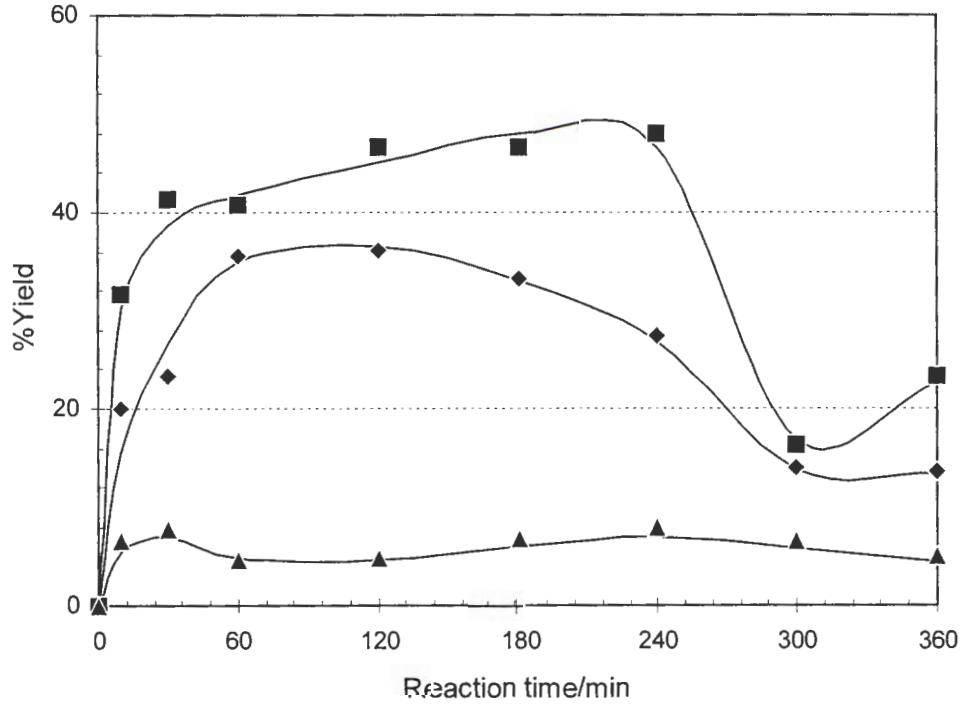


Figure 64. %Yield as a function of reaction time from cross-metathesis of MV with $C_6^{1=}$ using 2 wt. % $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalyst. Re:Sn:MV:$C_6^{1=}$ = 1:0.5:5:15. [■ : epoxy esters, ◆ : diepoxy alkenes, ▲ : diesters]

Figure 62 shows the conversions of MV and $C_6^{1=}$ as a function of time. Figure 64 shows the product distribution as a function of the functional groups present. Both MV and $C_6^{1=}$ systems never attained equilibrium within 6 h of reaction. The conversion of MV after 6 h was ca. 90.3%, while that of $C_6^{1=}$ was ca. 78.9%. There was not significant difference in the conversion of MV in the cross-metathesis of MV with $C_6^{1=}$ when compared to the conversion of MV in the cross-metathesis MV with $C_5^{1=}$ (ca. 90.2%).

Figure 63 shows the change in PMP; SMP and isomerisation product yields as function of reaction time. An optimum yield of ca. 10.9% was obtained for PMP after just 30 minutes of reaction. Although, there was a significant increase in the SMP yield after 30 minutes, there was a steady decrease in the yield of MV, $C_6^{1=}$ (see Figure 62) and isomerisaton product (methyl-12,13-epoxy-10-octadecenoate). This suggests that the major contribution towards the increase in SMP may be due to self-metathesis of methyl-12,13-epoxy-7-octadecenoate or cross-metathesis of MV with methyl-12,13-epoxy-7-octadecenoate. Since methyl-12,13-epoxy-7-octadecenoate peak was not identified in Figure 61, this suggests that it was immediately used up as it was formed.

A sharp decrease in the yields of SMP and isomerisation product (see Figure 63), associated with a sharp increase in the conversion of $C_6^{1=}$, suggests a cross-metathesis reaction between methyl-12,13-epoxy-10-octadecenoate and $C_6^{1=}$. This reaction may occur via the interaction of the epoxy group with the double bond in the alkene, resulting in high molecular compounds. These high molecular compounds may not be detected by GC/MS. This interaction of the epoxy group with the double bond is also illustrated by the decrease in the yield of the epoxy ester (see Figure 64). This type of reaction is also possible between MV and $C_6^{1=}$. The sharp decrease in the SMP yield suggests the deactivation of the $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalyst. This deactivation may be due to the clogging of the surface pours on the support by these high molecular compounds. This may result in both MV and $C_6^{1=}$ molecules failing to reach the metal carbene species, which are responsible for metathesis reaction.

CHAPTER 5

PROPOSED MECHANISMS AND CONCLUSIONS

5.1 METATHESIS OF 1,2-EPOXY-9-DECENE (ED)

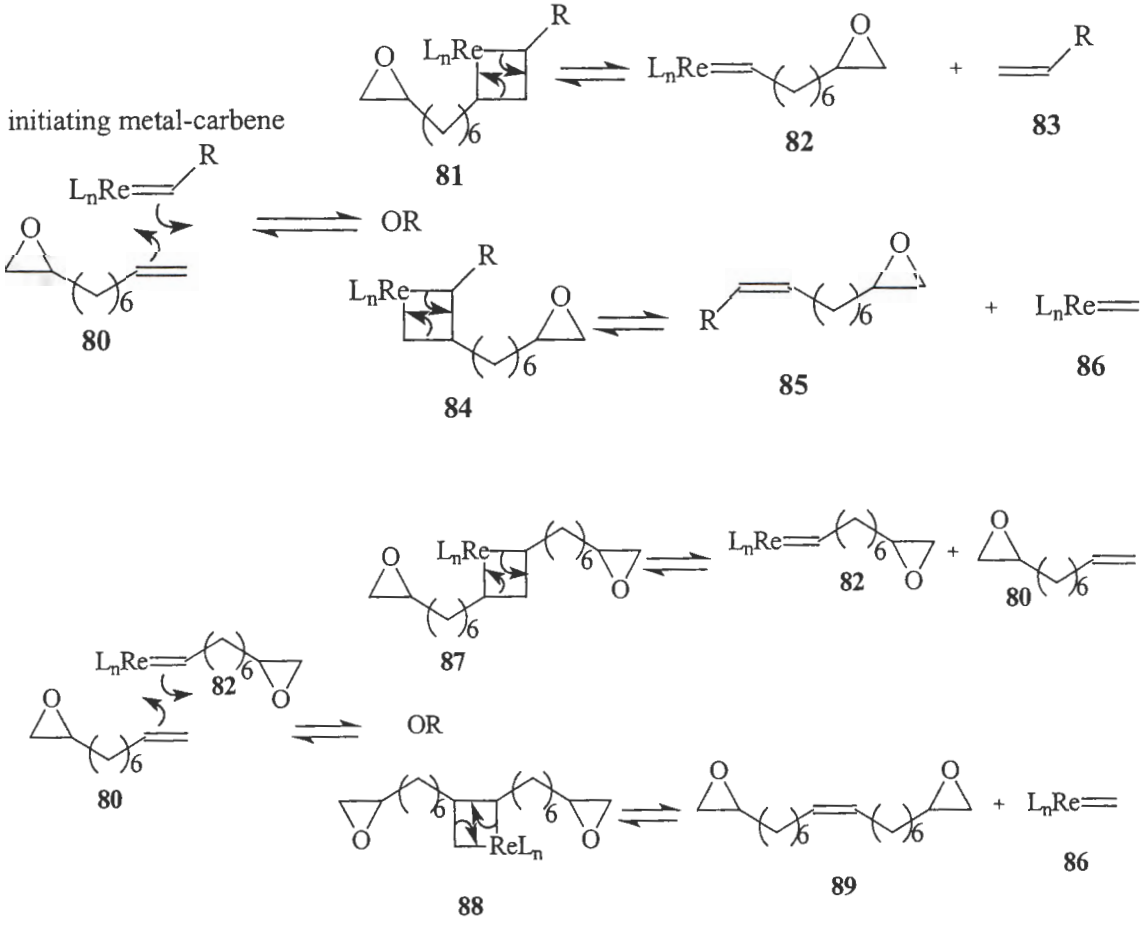
The high activity (ca. 99.2%) and selectivity (ca. 98.2%) of $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalytic system towards primary metathesis products (PMP), suggests that the reaction follows the 'carbene' mechanism proposed by Chauvin and Hérrison.[31]

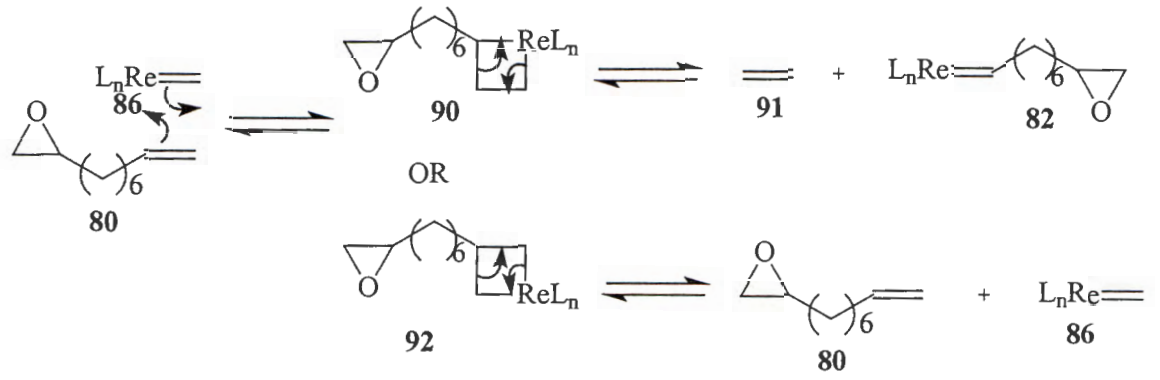
5.1.1 Proposed mechanisms of reactions

Apart from the PMP formed from the self-metathesis of ED, there were also dimerization products (DMP) formed. Other products were also obtained from side reactions.

5.1.1.1 Proposed mechanism for the self-metathesis of ED

Scheme 9 illustrates the mechanism for the self-metathesis of ED.





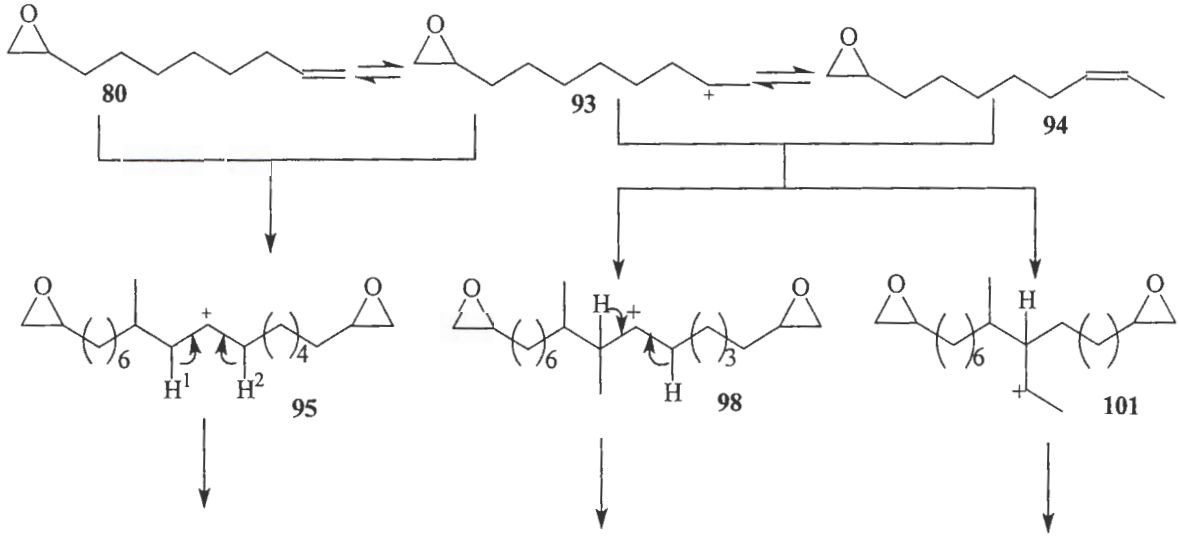
Scheme 9. Mechanism for self-metathesis of ED to give PMP.

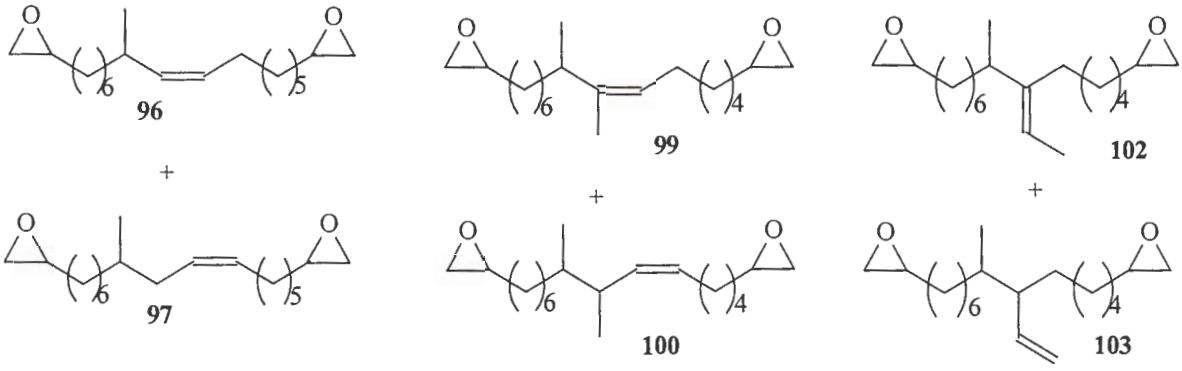
The primary metathesis product was compound **89**, which is 1,2,17,18-diepoxy-9-octadecene. This compound was generated by a reaction between a propagating metal carbene **82** and another molecule of ED. The MS did not detect other products.

5.1.1.2 Proposed mechanism for the dimerization of ED

High molecular products corresponding to peaks 8 to 12 (Table 4 and Figure 6, Chapter 4, pages 37 and 41) suggest dimerization of ED. Normal terminal alkenes are known to undergo double bond isomerization, which is caused by the Brønsted acidity of the support.[44]

Two possible mechanisms for the dimerization of ED are outlined in Scheme 10. Dimerization mechanism on Brønsted acid catalysts occurs through the carbocation intermediate. One possible mechanism is via the reaction between the two double bonds, as illustrated by Scheme 10.

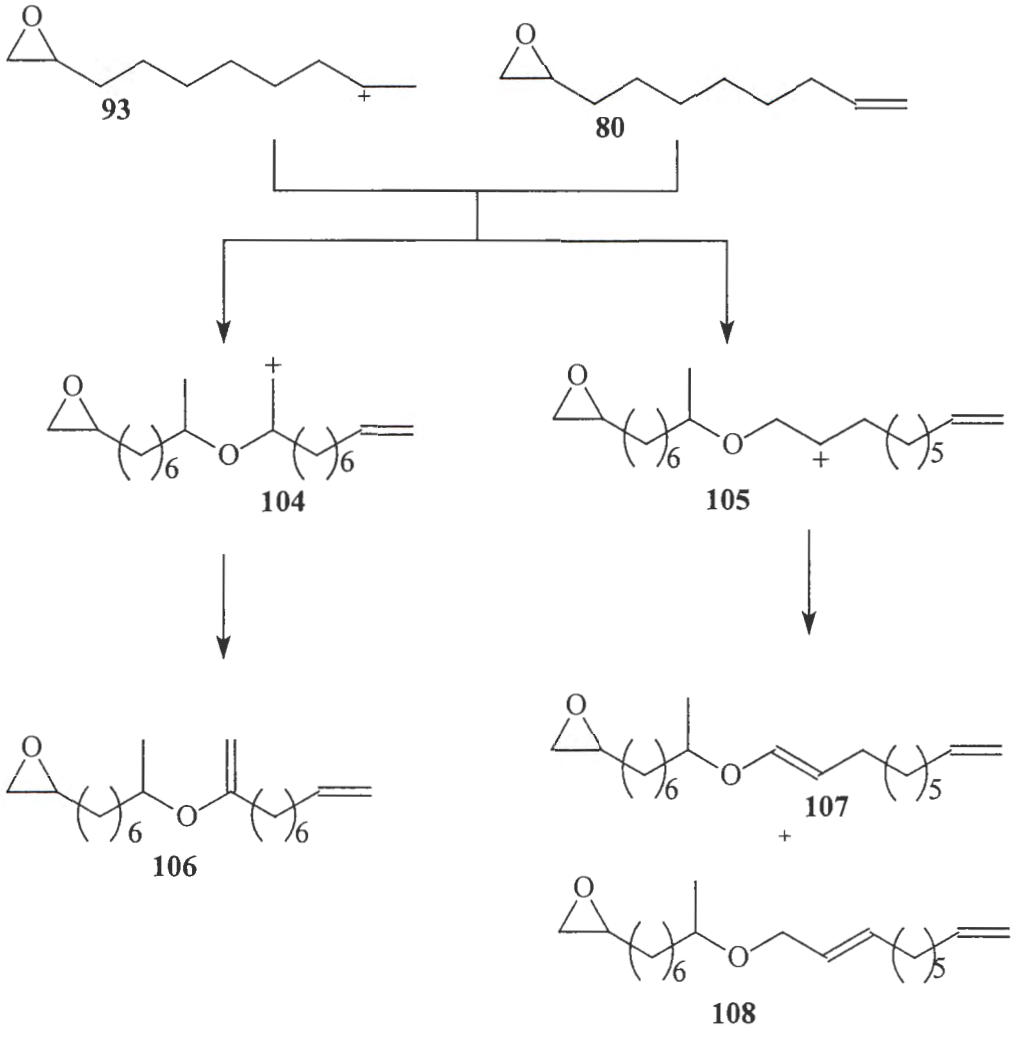




Scheme 10. Mechanism for the dimerization of ED via the reaction between the C=C double bonds.

The carbocation intermediate **93** may react with ED (**80**) to generate the carbocation intermediate **95**. This intermediate rearranged to form compound **96** and **97** (1,2,18,19-diepoxy-11-methyl-8-nonadecene. The MS did not detect compound **96**. The intermediate **93** may also react with 1, 2-epoxy-8-decene (**94**) to generate carbocation intermediates **98** and **101.** Intermediate **98** rearranged to form compounds **99** (not detected by MS) and 1,2,17,18-diepoxy-9,10-dimethyl-7-octadecene (**100**), Intermediate **101** rearranged to form 3-(1,2-epoxy-hepty)-11,12-epoxy-4-methyl-2-dodecene (**102**) and 3-(1,2-epoxy-hepty)-11,12-epoxy-4-methyl-1-dodecene (**103**). All these compounds are shown in Table 4.

An alternative mechanism is one involving a reaction between the C=C double and the epoxy ring. Scheme 11 illustrates the formation of dimerisation products via this mechanism. The presence of an ether type product (Peak 11) suggests the opening of the epoxy ring, with subsequent reaction between the carbocation and the epoxy ring, which is possible under Lewis acidic conditions (see Reaction 27).



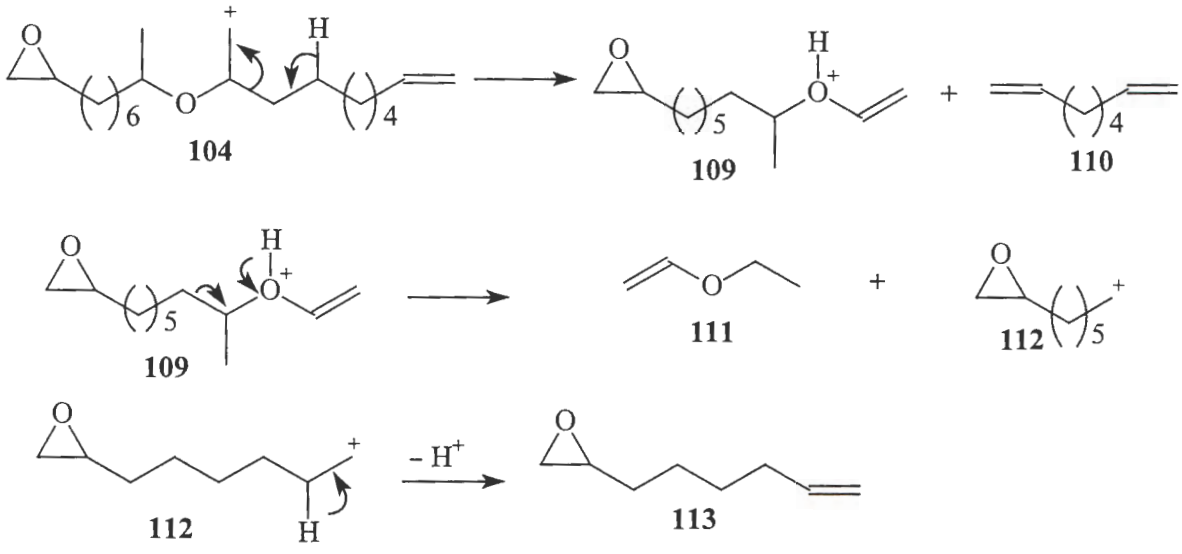
Scheme 11. Mechanism for dimerization of ED via the reaction between the C=C double bond and the epoxy ring (C – O – C).

The carbocation intermediate **93** reacts with the electron rich epoxy ring to generate the two carbocation intermediates **104** and **105**. These intermediates then rearrange to form the diene-compounds **106**; **107** (not detected by MS) and **108**. Compound **108**, which is 1,2-epoxy-9-methyl-nonoxy-1, 8-decadiene was detected by MS (see Table 4).

5.1.1.3 Proposed mechanisms for other reactions

Mechanism for a reaction, which leads to the formation of ethoxy-ethene:

The presence of ethoxy-ethene (Peak 2) suggests an opening of a highly strained epoxy ring due to the acidity of the support, which then leads to the interaction of the epoxy ring with the double bond. The mechanism of this epoxy ring opening and subsequent interaction with the double bond is illustrated in Scheme 12.

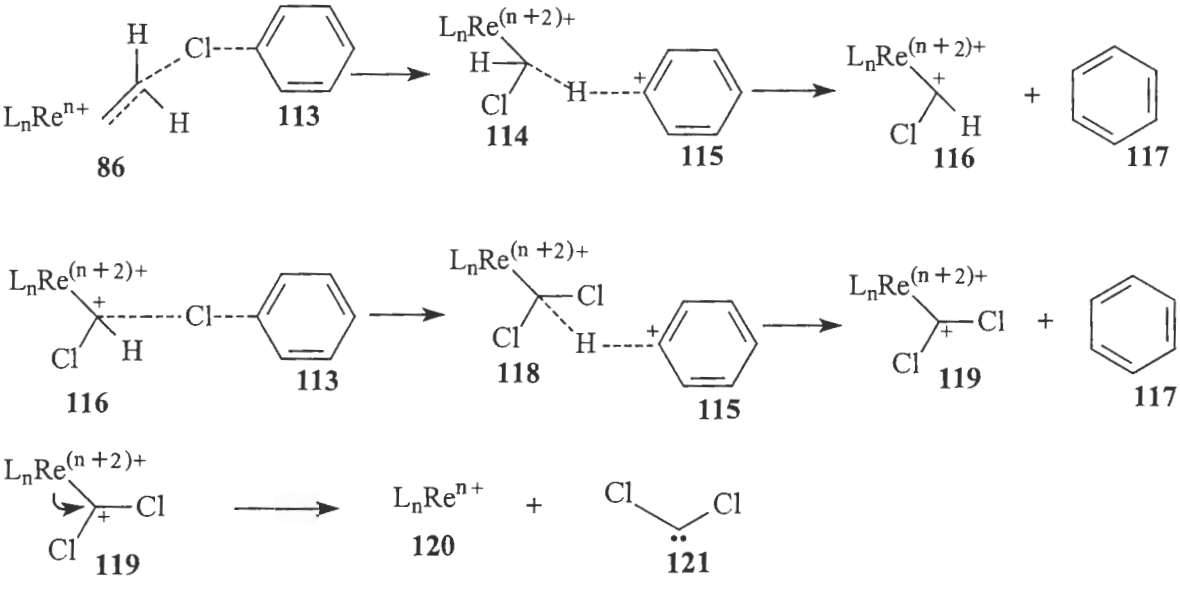


Scheme 12. Mechanism for a reaction, which leads to the formation of ethoxy-ethene.

Carbocation **104** instead of rearranging to form compound **106** (see scheme 11), rearranged to form compound **110** and intermediate **109**. Intermediate **109** then rearranged to form ethoxy-ethene (**111**) and 1, 2-epoxy-7-octene (**113**). The MS did not detect compounds **110** and **113**. Compound **110** may undergo ADMET-polymerisation to form poly-olefins, as illustrated by reaction (47).

Mechanism for reactions, which lead to the formation of methylene chloride and benzene:

The presence of methylene chloride (Peak 3) and benzene (Peak 5) suggests an interaction between chlorobenze solvent and metal carbene **86**. Scheme 13 illustrates this reaction.



Scheme 13. Mechanism for reactions, which lead to the formation of methylene chloride and benzene.

The metal carbene generated in the SM of ED (see scheme 2), interacted with chlorobenzene solvent to generate two benzene molecules (**117**) and intermediate **119**. This intermediate then rearranged to form methylene chloride (**120**) and the rhenium species **120**.

Mechanism for a reaction, which leads to the formation of 1-hexene:

1-hexene (**83**) was generated by self-metathesis of ED (see scheme 9).

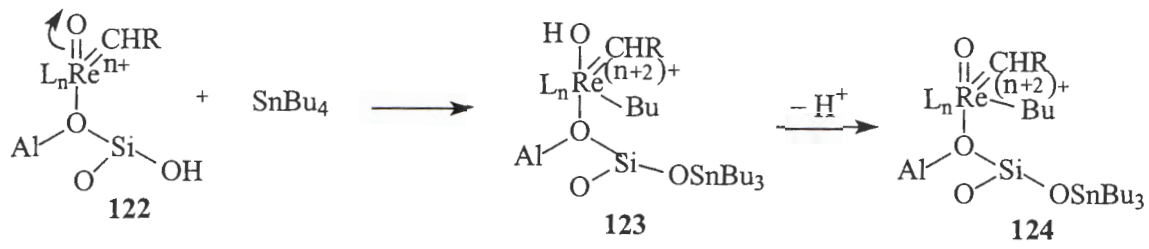
5.1.1.4 Deactivation of the $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$/ED catalytic system

The fact that the reaction did not go to completion suggests that the catalytic system was deactivated. The deactivation may be attributed to the presence of minor products. For example, there may be (1) coordination of benzene molecules around the high valent rhenium metal, due to the electron cloud being dispersed around the benzene molecule; or (2) competing reactions between other compounds and the substrate, for the active sites on the metal carbene; or (3) the interaction between products such as methylene chloride and the rhenium metal or (4) the clogging of surface pours on the support by high molecular products such as DMP.

The benzene coordination as mentioned in (1) above may be eliminated due to the chemical inertness of benzene.[70] Methylene chloride is known to be a very weakly coordinating compound. However, it is not totally unreactive since it is known to undergo chloride extraction in the presence of certain highly oxidized or highly reduced inorganic or organometallic complexes.[71] The deactivation of the catalytic system is therefore attributed to either (2) or (4). The detection of benzene and methylene chloride by he GC/MS (see Table 4 and Scheme 13) supports the assertion in (2).

5.1.2 Influence of the Sn:Re molar ratio

The deactivation of the $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalytic system between Sn:Re molar ratios of 0.5 and 1 (see Table 5, Chapter 4, page 43), may be attributed to the interaction of the $SnBu_4$ molecules with (1) the rhenium-carbene species and (2) the support. Scheme 14 illustrates a mechanism to explain this strange observation, i.e. the anomaly at Sn:Re molar ratio of 0.5, as well the decrease in selectivity.



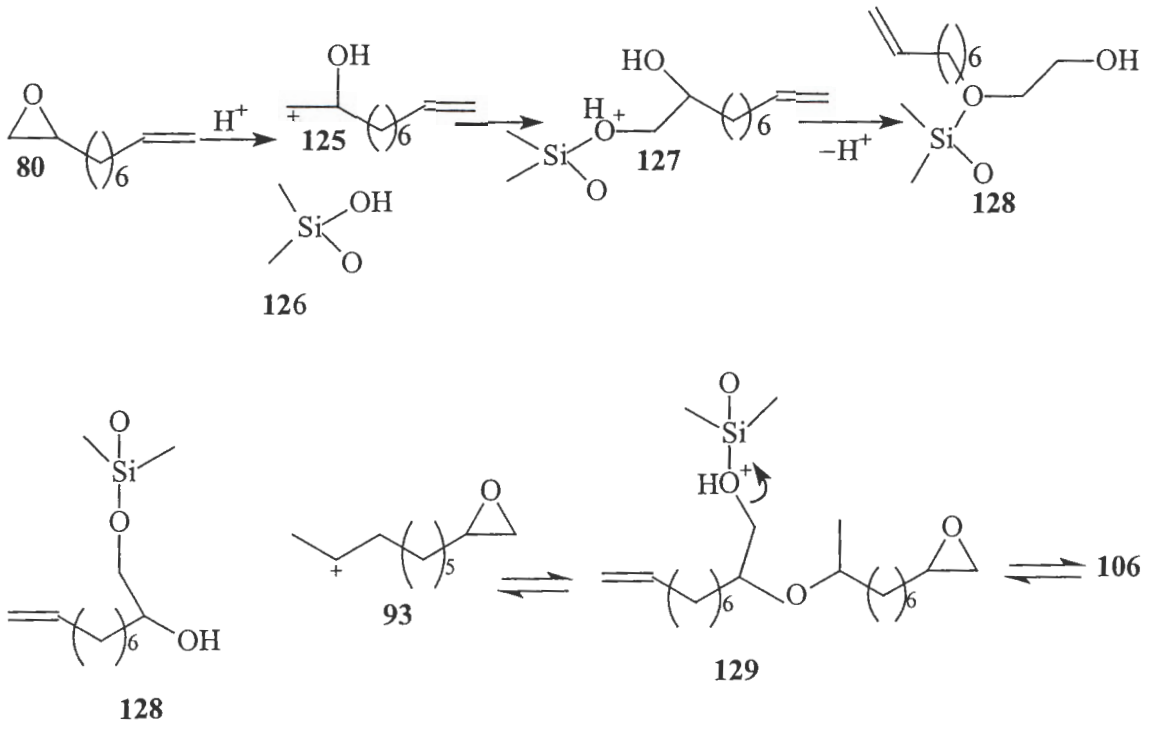
Scheme 14. Mechanism for the deactivation of the $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalytic system due to $SnBu_4$.

First, the SnB_4 interact with the acidic OH groups on silica (**122**). The H^+ ion produced is then attracted to the electron rich oxygen of the rhenium species, which increases the oxidation state of rhenium metal. This led to the attachment of the bulky butyl group onto the metal, which then increased the coordination on the metal, resulting in a bulky metal carbene species (**123** and **124**). This may further block the substrate molecules from reaching the active sites, which are responsible for metathesis reaction. The H^+ ion regenerated will then initiate the double bond isomerization, as proposed in Schemes 10 and 11.

5.1.3 The influence of Re_2O_7 loading

The mechanism for the deactivation of the catalytic system at lower Re_2O_7 loadings, due to the interaction of the extra $SnBu_4$ molecules is similar to the one outlined in scheme 14.

Figure 18 (Chapter 4, page 49) shows that the DMP yield continued to increase while the PMP yield reached a steady state. This also suggests that at lower Re_2O_7 loadings the substrate molecules interact with the support, via the epoxy group. The highly strained epoxy ring makes it to be highly reactive, and thus will be susceptible to H^+ ion attack, and lead to the opening of the ring. Schemes 15 and 16 illustrate the interaction of the substrate molecules with the support, which then led to the formation of ether type products.

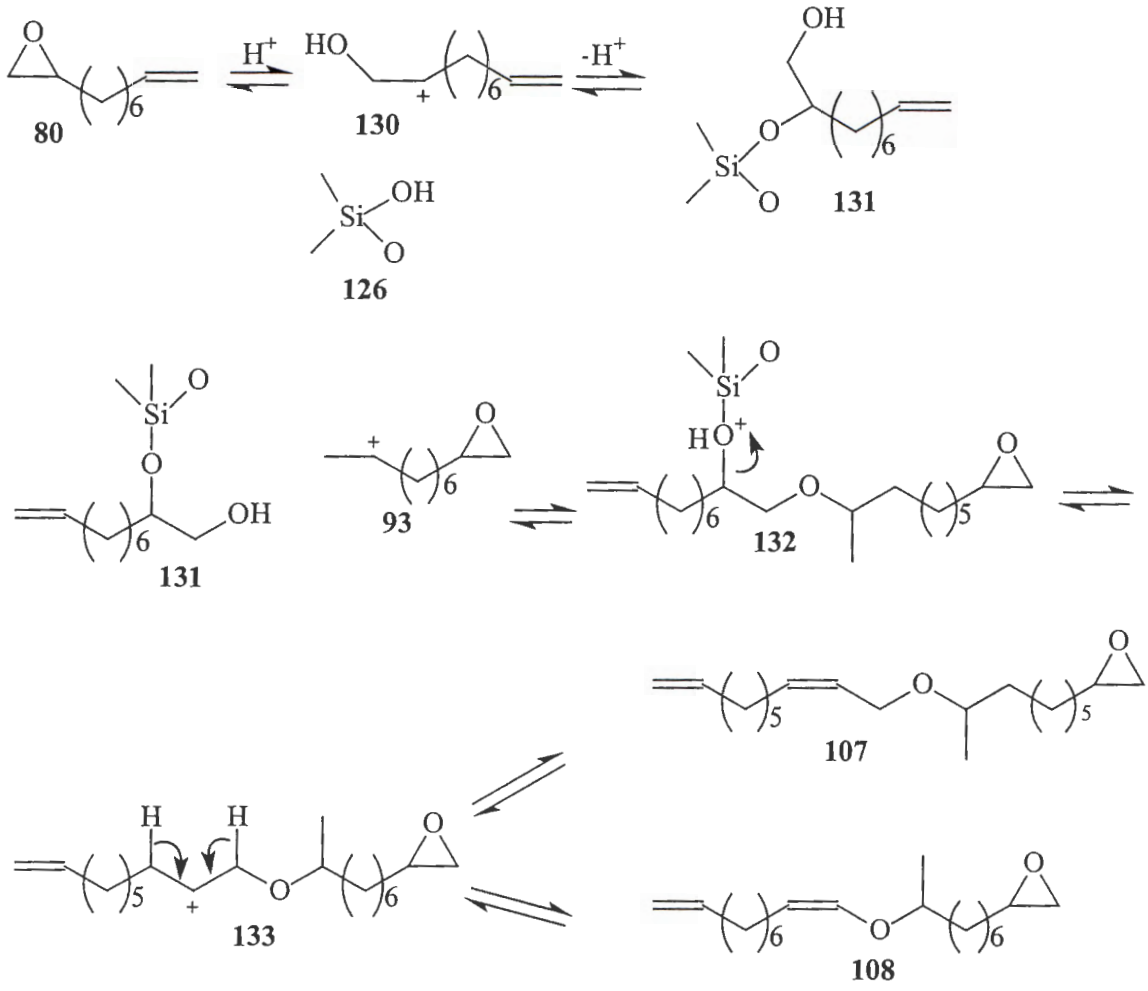


NWU LIBRARY

Scheme 15. Mechanism for dimerization of ED via the reaction between the C=C double bond and the epoxy ring (C – O – C), which leads to the formation of compound **106.**

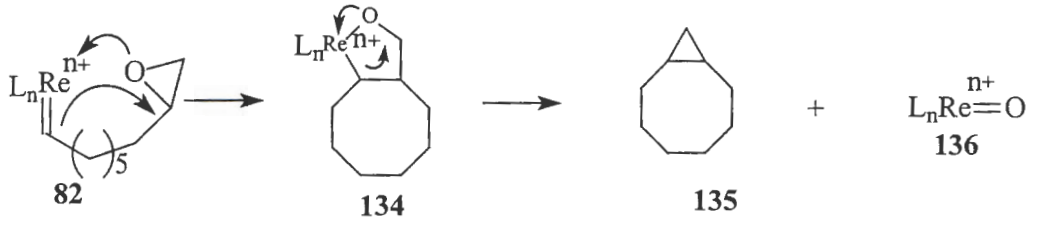
The epoxy ring was protonated and led to a carbocation intermediate **125**, which then reacted with the OH group attached to silicon (**50**) to form a complex compound **127**. This complex then rearranged via a loss of proton, to form another complex compound **128**, which reacted with carbocation **93** and thereby generating another complex **129**. Complex **129** then detached from the support to form compound **106**. The opening of the epoxy ring under acidic conditions is a well-known reaction. For example, toxic diols were prepared by Green et al.[56] using soluble epoxide hydrolase or perchloric acid (see reaction (30)). Cuperus and Derksen[59] also prepared speciality chemicals from vernolic acid by ring-opening of the epoxy ring (see reaction (31)).

An alternative mechanism for the formation of other two ether type products is illustrated by scheme 17.



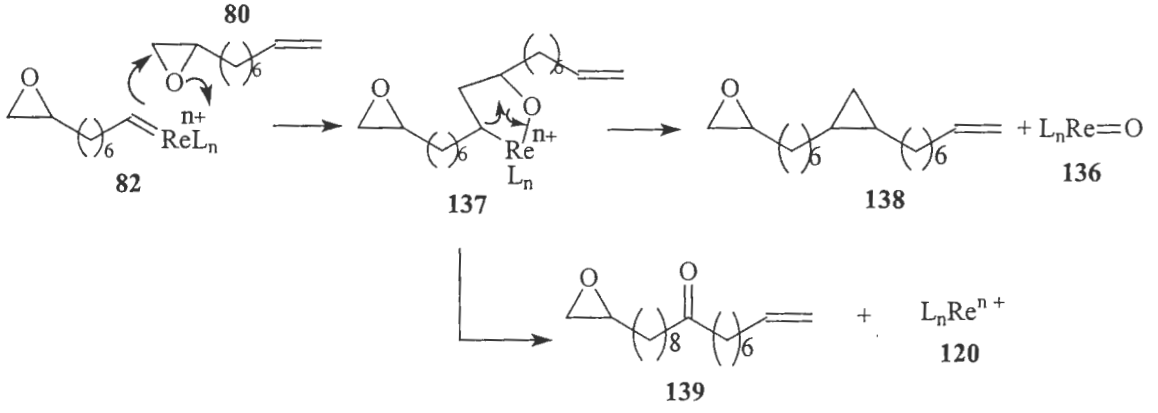
Scheme 16. Mechanism for the dimerization of 1,2-epoxy-9-decene via the reaction between the C=C double bond and the epoxy ring (C – O – C), which leads to the formation of compounds **107** and **108**.

Another possible reason for the deactivation at 0.5 wt.% Re_2O_7 loading may be attributed to the interaction of the substrate molecules with the rhenium-carbene species. Marvey et al.[65] found in their studies that, for homogeneous catalytic systems containing Cl substituents, there was a deactivation of the catalytic system. They attributed this deactivation to (1) an intramolecular interaction of chlorine atom with the metal-carbene and (2) an intermolecular interaction of chlorine of a different molecule with the metal carbene. Kawai et al.[72] also arrived at the same conclusion regarding metathesis of 2-bromo-1-butene with Re_2O_7/Al_2O_3 catalyst. In my study, the rapid deactivation may be caused by the interaction of the metal carbene with the electron rich oxygen of the epoxy ring, and this is illustrated by schemes 17 and 18.



Scheme 17. Mechanism for the deactivation of the catalytic system via the intramolecular interaction between Re and the epoxy ring (of the carbene species).

In Scheme 17, there was an intramolecular interaction between the epoxy ring and the rhenium metal, which led to the formation of cyclic intermediate **134**. This intermediate rearranged to form a cyclic compound **135** and an oxy-rhenium species **136**. This oxy-rhenium species is not active for metathesis reactions



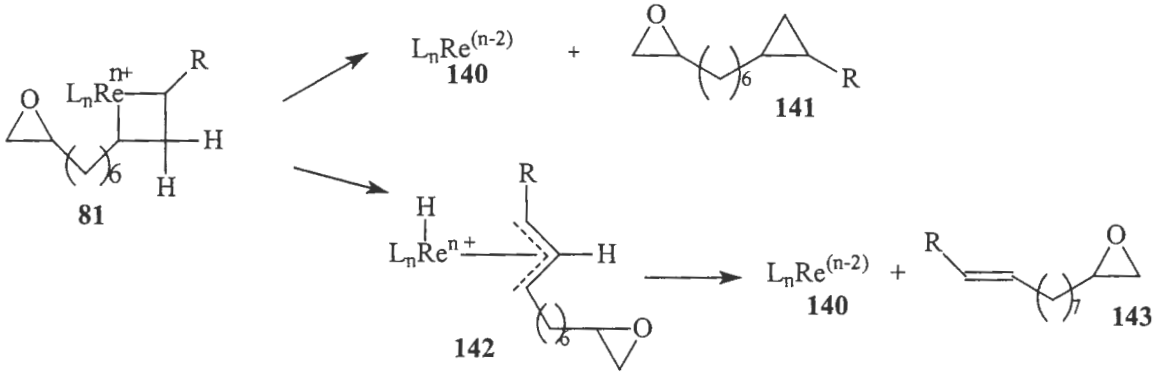
Scheme 18. Mechanism for the deactivation of the catalytic system via the intermolecular interaction between Re and the epoxy ring from another molecule of ED.

In Scheme 18, there was an intermolecular interaction between the epoxy ring of another ED molecule (**80**) and the metal carbene species **82**, to form an intermediate **137**. This intermediate may rearrange in two ways. One way may lead to the formation of compound **138** and an oxy-rhenium species **136**. Another way may involve the formation of compound **139** and the rhenium species **120**.

At higher Re_2O_7 loadings, the hydroxyl groups attached to a Si atom are also replaced, and resulting in the double bond migration that causes the isomerisation reaction (scheme 10 & 11). However, the replacement of the hydroxyl groups attached to Si atom results in inactive rhenium centres of the type $\equiv Si–O–ReO_3$ (or rhenium clusters), as is known that Re_2O_7/SiO_2 has no activity in olefin metathesis.[73] Mol[73] suggested that the inactivity of the Re_2O_7/SiO_2 might be due to the fact that SiO_2 does not stabilise the necessary intermediate oxidation state of rhenium.

5.1.4 The influence of reaction temperature

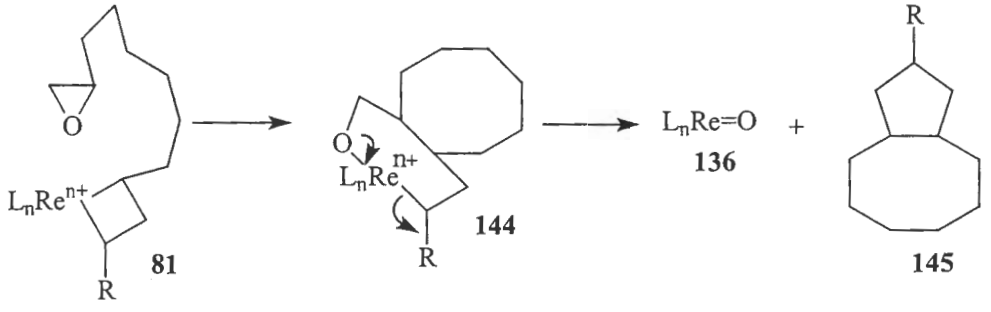
The deactivation of the catalytic system at higher temperatures may be attributed to several factors. Firstly, it may be attributed to the reductive elimination of the metallacyclobutane intermediate[6], whose mechanism is outlined in Scheme 19.



Scheme 19. Mechanism illustrating the reductive elimination of the metallacyclobutane intermediate due to increase in reaction temperature.

The deactivation, as shown by Scheme 19, may be via the formation of an epoxy cyclopropane compound **141**, or ß-elimination leading to the formation of an epoxy compound **143**.

Secondly, the deactivation may be attributed to an interaction of a highly strained epoxy ring with the high valent rhenium atom, as shown by Scheme 20. A higher temperature is likely to make the ring highly unstable and thus make the epoxy group highly reactive.



Scheme 20. Mechanism for the deactivation of the catalytic system via the intramolecular interaction between Re and the epoxy ring.

The interaction of the epoxy ring with the high valent rhenium metal leads to the formation of a cyclic compound **145** and an oxy-rhenium species **136**. Thirdly, the deactivation could be attributed to the interaction of the epoxy ring with the support (see Schemes 15 and 16).

5.1.5 The influence of solvent type

The low activity of the $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalytic system in dichloromethane may

suggest an interaction of the solvent molecules with the metal centre. This may lead to the blockage of the active sites responsible for metathesis. However, due to the inertness of dichloromethane, as well as the increase in the activity of the catalytic system (see Figure 22), this possibility is ruled out. There was a corresponding increase in the DMP yield (see Figure 24), with increase in the activity of the catalytic system. This suggests an increased reactivity of the epoxy group, which could lead to the interaction of the epoxy group with the support and thus increasing the Brønsted acidity of the support. This could in turn lead to increased DMP yield, as illustrated by schemes 10; 11; 15 and 16. The deactivation could also be related to the reactivity of the epoxy group, with possible interaction of the epoxy group with the rhenium species, as illustrated by schemes 17 and 18.

In the case of a non-polar solvent hexane, the active sites on the metal are available for reaction with alkene molecules. The non-polar solvent also reduces the reactivity of the epoxy group, thus limiting side reactions involving the epoxy group.

The electron withdrawing inductive effect of the chlorine atom in chlorobenzene, may result in the positive charge being dispersed around the benzene part of the molecule. The highest activity of chlorobenzene could be attributed to this positive charge being spread over a large surface area on benzene. Therefore, this may lead to repulsion between the positive rhenium metal and the benzene part of the solvent molecules. There is also a likelihood of the epoxy ring, which is rich in electrons interacting with chlorobenzene molecules as the result of high deposit of a positive charge on benzene, which was induced by highly electron-withdrawing chlorine atom. This will reduce the probability of the epoxy ring interacting with the metal carbene species responsible for metathesis reaction. Figure 24 shows that the dimerization product yield increases initially, i.e. in the first 10 minutes and then drops with reaction time when benzene solvent was used.

The low activity of the $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalytic system in benzene may be attributed to a larger coordination effect of the solvent molecules towards the metal atom, which may be due to high electron density on benzene. This may lead to benzene molecules competing with the substrate molecules for the active sites on the catalyst.

5.1.6 The influence of substrate concentration

The slight reduction in conversion at ED:Re molar ratio of 25 may be attributed to an interaction between the substrate molecules with the active rhenium species, as illustrated by Schemes 11

and 12. However, at higher substrate concentrations, the substrate molecules, in addition to interacting with the rhenium carbene species, may also interact with the surface hydroxyl groups, thus promoting the double bond isomerisation. This may lead to blockage of the pours on the support, thus blocking substrate molecules from reaching the active sites.

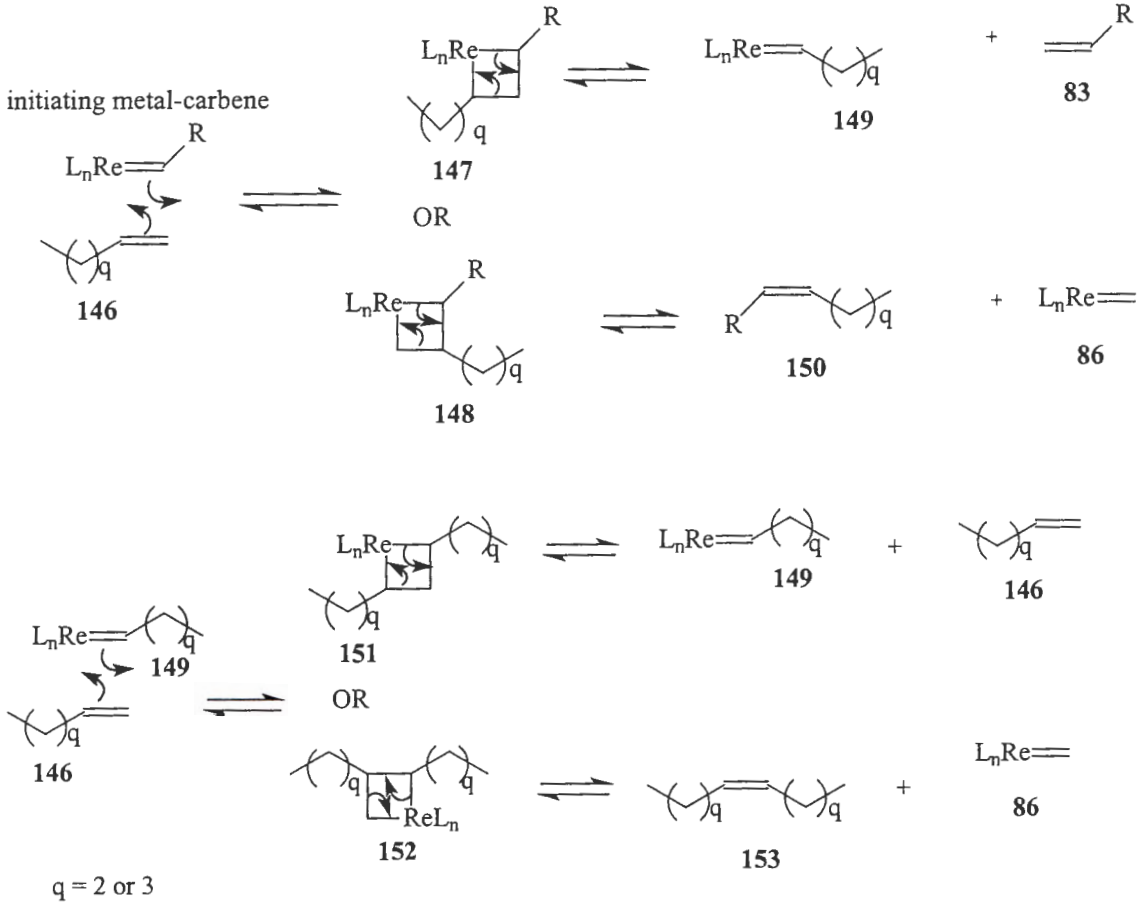
5.2 Proposed mechanisms for the cross-metathesis of ED with 1-pentene ($C_5^{1=}$) and 1-hexene ($C_6^{1=}$)

The high SMP yield in the cross-metathesis of ED with both $C_5^{1=}$ and $C_6^{1=}$ suggests that there was a high degree of double bond isomerization of both $C_5^{1=}$ and $C_6^{1=}$. This resulted to the following possibilities:

- SM of $C_p^{1=}$
- CM of $C_p^{1=}$ + $C_p^{2=}$
- CM of ED + $C_p^{1=}$
- CM of ED + $C_p^{2=}$

Where p = 5 and 6.

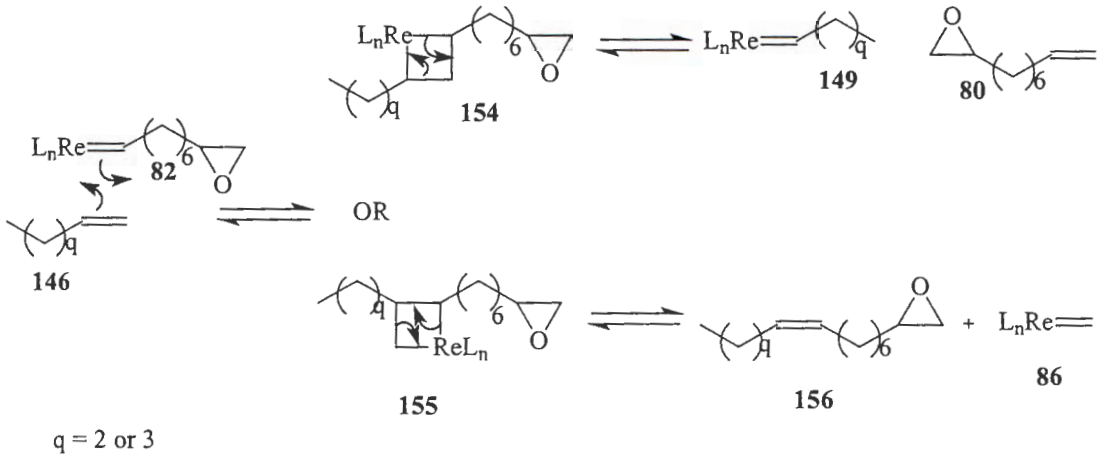
5.2.1 Proposed mechanism for the SM of $C_5^{=}$ and $C_6^{=}$



Scheme 21. Mechanism for the self-metathesis of $C_5^{1=}$ and $C_6^{1=}$.

Compound **153** for self-metathesis of $C_5^{1=}$ was (Z)-4-octene (see Table 11, Chapter 4, page 63). However, for self-metathesis of $C_6^{1=}$, it was 5-decene (see Table 13, Chapter 4, page 72). The MS did not detect 1-hexene (**83**).

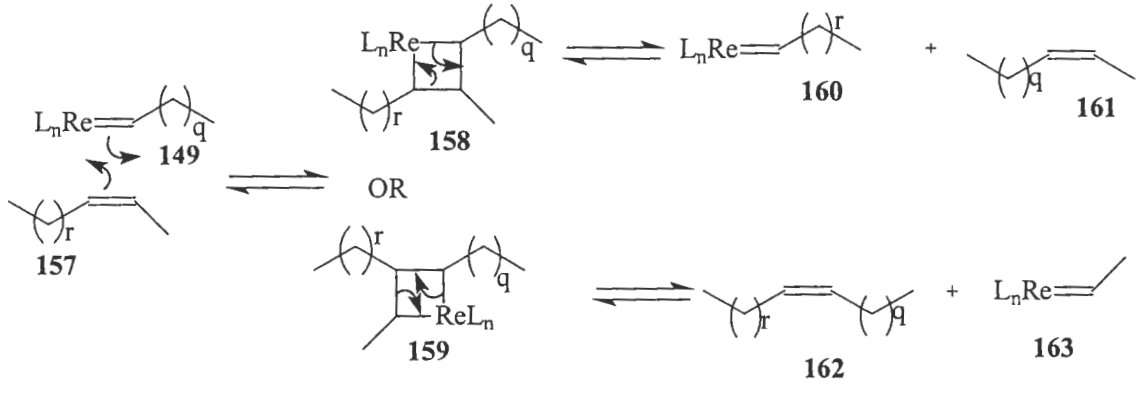
5.2.2 Proposed mechanism for the CM of ED with $C_5^{1=}$ and $C_6^{1=}$

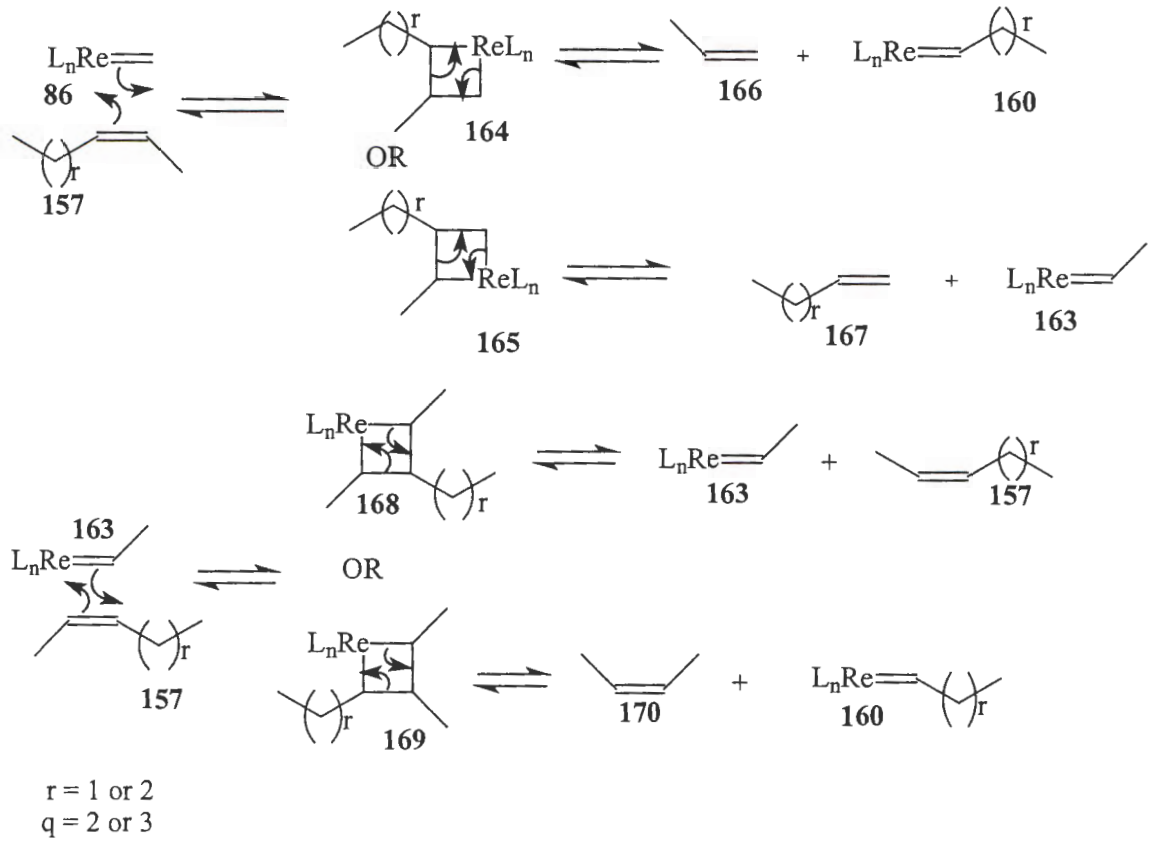


Scheme 22. Mechanism for the CM of ED with $C_5^{1=}$ and $C_6^{1=}$.

Compound **156** in the cross-metathesis of ED with $C_5^{1=}$, was 1,2-epoxy-9-tridecene (see Table 11). However, in the cross-metathesis of ED with $C_6^{1=}$, compound **156** was 1,2-epoxy-9-tetradecene. The initial step that generated metal carbene **82** has been omitted since it is similar to the one discussed in Scheme 9. Although the MS detected 1,2-epoxy-9-tridecene, 1,2-epoxy-9-tetradecene was not detected.

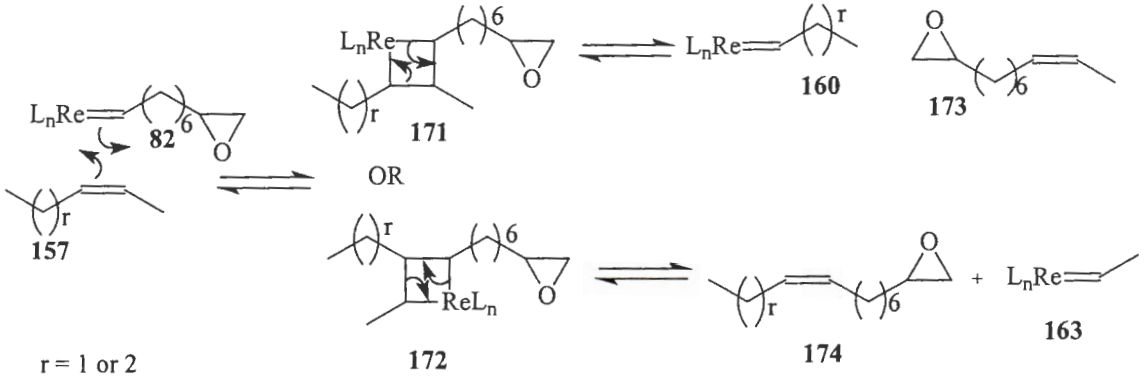
5.2.3 Proposed mechanism for CM of $C_5^{1=}$ with $C_5^{2=}$ and $C_6^{1=}$ with $C_6^{2=}$





Scheme 23. Mechanism for the cross-metathesis of $C_5^{1=}$ with $C_5^{2=}$ and $C_6^{1=}$ with $C_6^{2=}$.

The initiating step that generated metal carbene **149** is similar to the one in scheme 21, therefore was omitted. In the cross-metathesis of $C_5^{1=}$ with $C_5^{2=}$ compounds **161** and **162**, respectively, were 2-hexene and 3-heptene (see Table 11). Metal carbene **86** also generated short-chain alkenes such as propene (**166**) and 1-butene (**167**). However, the MS did not detect these compounds. In the case of the cross-metathesis of $C_6^{1=}$ with $C_6^{2=}$, compounds **161** and **162**, respectively, were 2-heptene and trans-4-nonene (see Table 13). The MS did not detect compounds **146**, **166** and **170**. These compounds were propene, $C_5^{1=}$ and 2-butene, respectively.

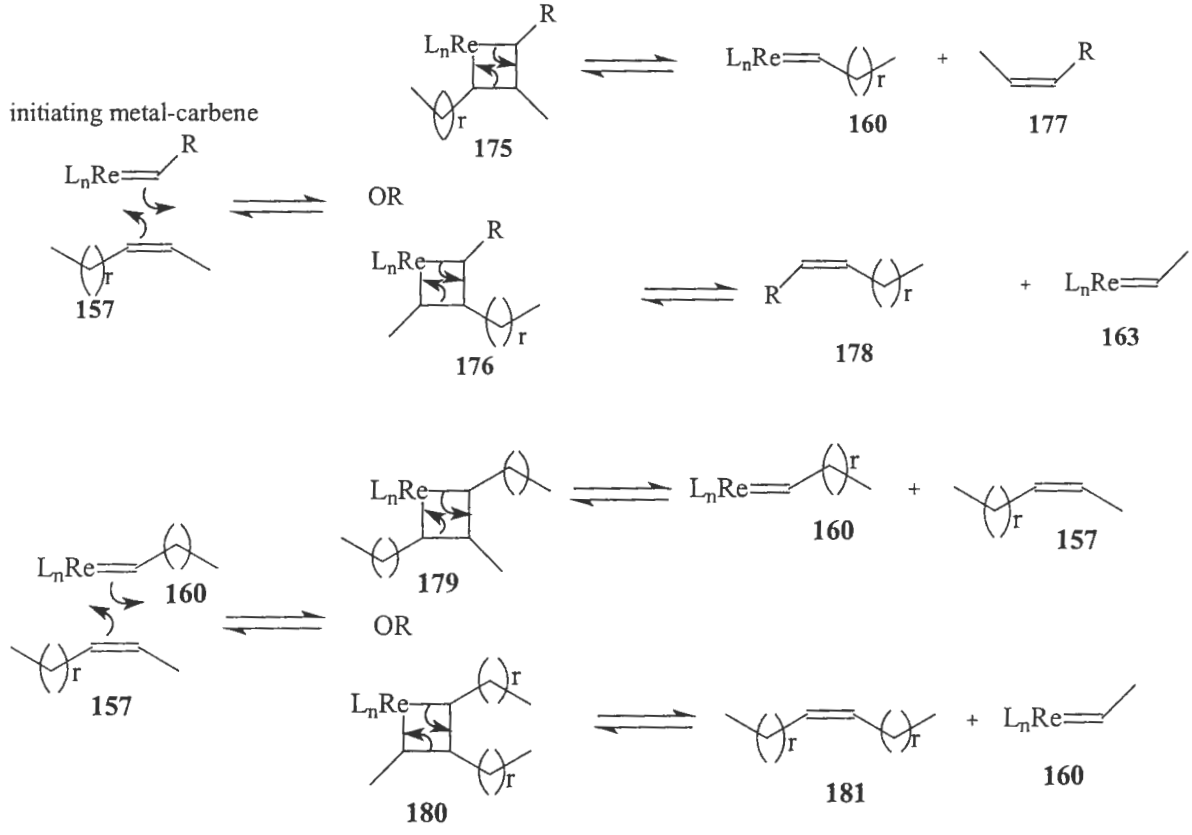


Scheme 24. Mechanism for the cross-metathesis of ED with $C_5^{2=}$ or $C_6^{2=}$.

The MS detected compound **173**, which wass 1,2-epoxy-9-undecene in the cross-metathesis of ED with $C_5^{2=}$. However, this compound was not detected in the cross-metathesis of ED with $C_6^{2=}$. Compound **174** in the case of the cross-metathesis of ED with $C_5^{2=}$, was 1,2-epoxy-9-dodecene. This compound in the cross-metathesis of ED with $C_6^{2=}$, was 1,2-epoxy-9-tridecene. The MS did not detect both compounds.

.

5.2.4 Proposed mechanism for SM of $C_5^{2=}$ and $C_6^{2=}$



r = 1 or 2

Scheme 25. Mechanism for the self-metathesis of $C_5^{2=}$ and $C_6^{2=}$.

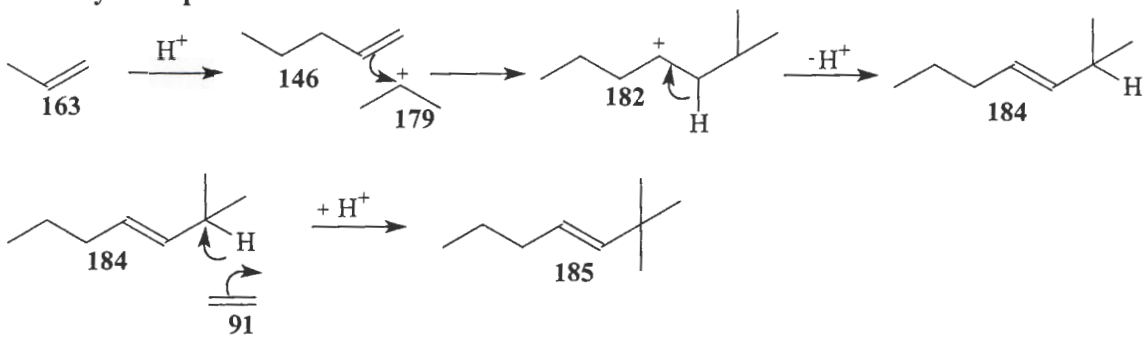
In the self-metathesis of $C_5^{2=}$, compounds **178** and **181**, respectively, were (Z)-3-octene and 3-hexene (see Table 11, Chapter 4, page 63). The MS did not detect compound **174**, which was 2-heptene. In the self-metathesis of $C_6^{2=}$, compounds **178** and **181**, respectively, were trans-4-nonene (see Table 13, chapter 4, page 72) and (Z)-4-octene. The MS did not detect (Z)-4-octene.

5.2.5 Proposed mechanism for the reaction, which lead to the formation of other products

The presence of other products that were not derived from metathesis reactions, suggests the possibility of side reactions. These reactions could involve short-chain alkenes or even the

the solvent.

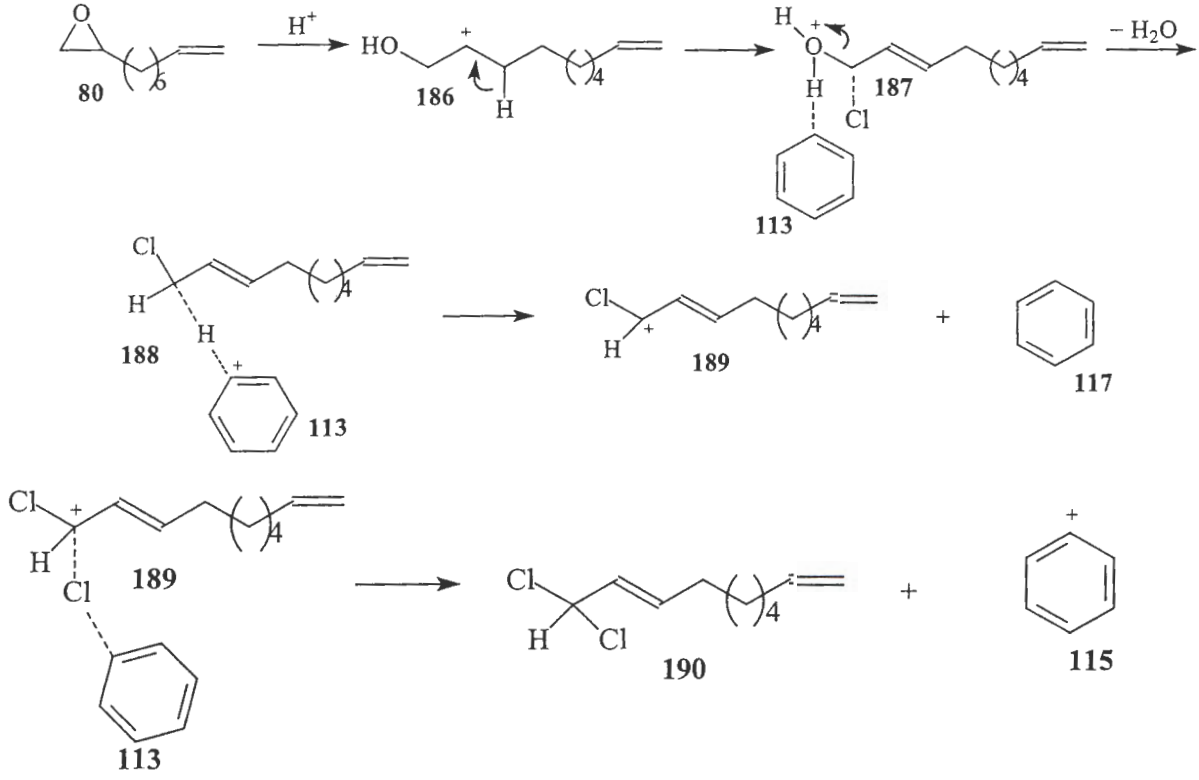
5.2.5.1 Proposed mechanism for a reaction, which leads to the formation of trans-2, 2-dimethyl-3-heptene

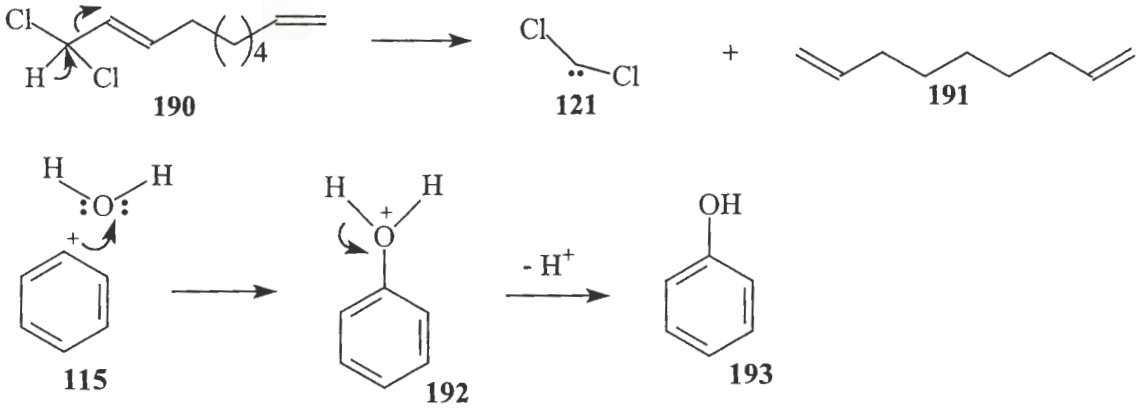


Scheme 26. Mechanism for a reaction, which leads to the formation of trans-2,2-dimethyl-3-heptene.

A highly reactive propene molecule (**163**) in acidic conditions (due to the support) was likely to react with 1-pentene via carbocation **179** to form carbocation **180**. This carbocation then rearranged to form compound **181**, which then reacted with a highly reactive gaseous ethene molecule (**91**) to generate compound **183**. Compound **183** was trans-2,2-dimethyl-3-heptene (see Table 11, Chapter 4, page 63).

5.2.5.2 Proposed mechanism for a reaction, which leads to the formation of 1,8-nonadiene



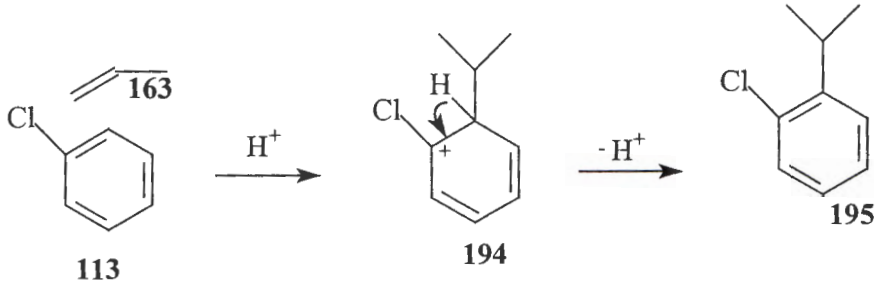


Scheme 27. Mechanism for a reaction, which leads to the formation of 1,8-nonadiene (**191**).

Scheme 26 illustrates a possible mechanism for a reaction, which leads to the formation of 1,8-nonadiene, **191** (see Table 11, Chapter 4, page 63). Water and phenol are also possible undesired products, as they are known to deactivate the rhenium-based catalysts. This may also explain the decrease in the conversion of ED. The deactivation was attributed to the protonation of the active rhenium species by these polar compounds. For example, Du Plessis et al.[15] found that the Re_2O_7/SiO_2-$Al_2O_3/SnMe_4$ was deactivated by the presence of H_2O in the metathesis of 1-octene. The degree of deactivation was higher when 1-butanol was present. This was attributed to a proton that could easily react with the rhenium intermediate. The deactivation in the case of Re_2O_7/SiO_2-$Al_2O_3/SnBu_4$/ED/$C_5^{1=}$ catalytic system could be attributed to the presence of phenol. Its proton can easily react with the rhenium intermediates responsible for propagating the metathesis reaction.

5.2.5.3 Proposed mechanism for a reaction, which leads to the formation of 2-(1-methylethyl)- 1-chlorobenzene

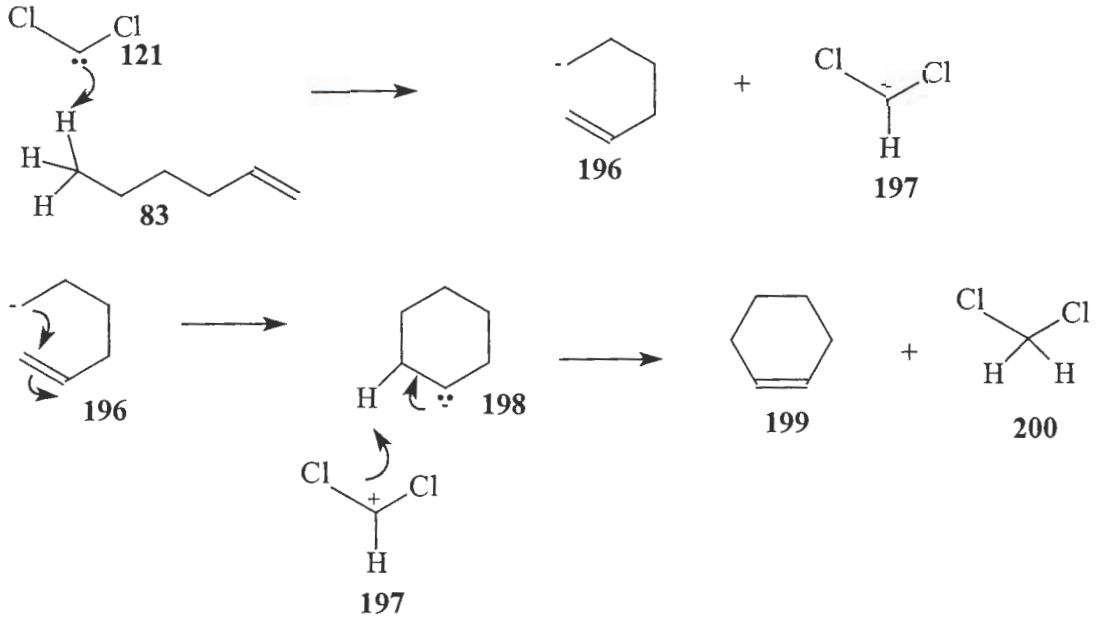
The presence of 2-(1-methylethyl)-1-chlorobenzene (see Table 11, Chapter 4, page 63) suggests the interaction of chlorobenzene solvent with short chain alkene products, possibly generated from side reactions.



Scheme 28. Mechanism for a reaction, which leads to the formation of 2-(1-methylethyl)-1-chlorobenzene

Chlorobenzene reacted with propene (**163**) under acidic conditions due to the support, to generate carbocation **194**. This carbocation then rearranged to form 2-(1-methylethyl)-1-chlorobenzene (**195**).

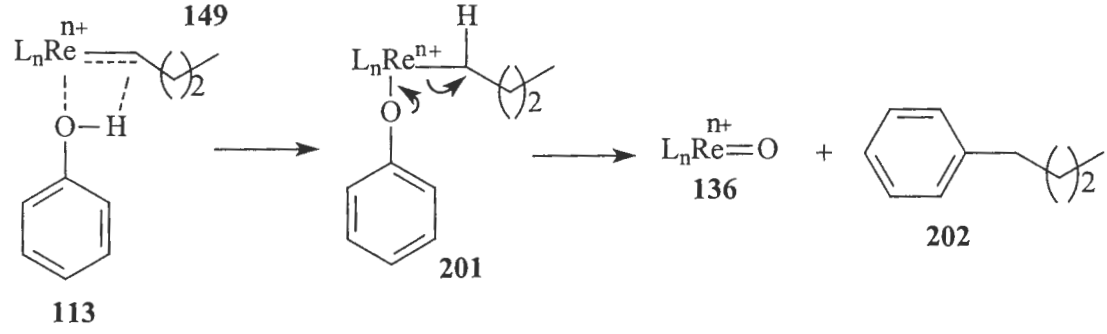
5.2.5.4 Proposed mechanism for the cyclization of $C_6^{1=}$



Scheme 29. Mechanism for the cyclization of $C_6^{1=}$.

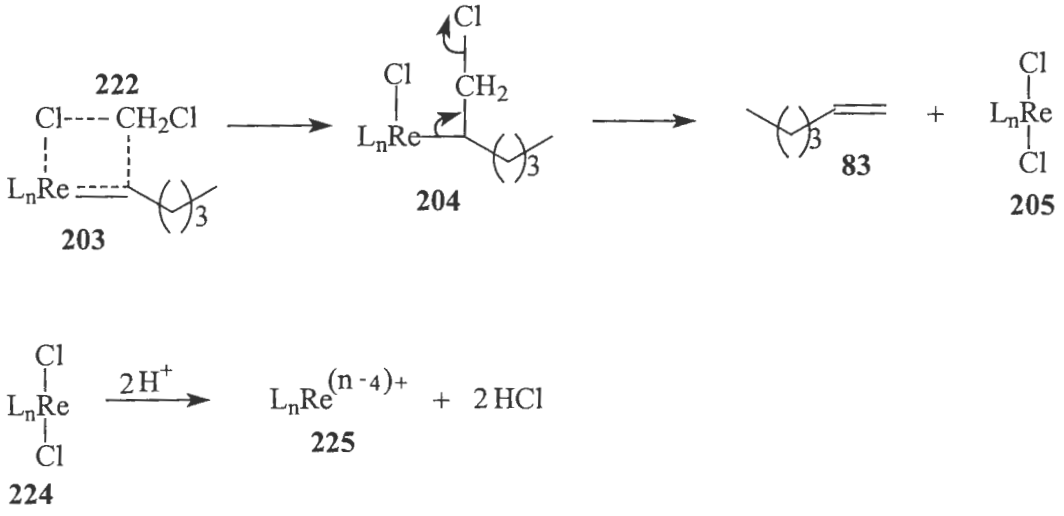
The presence of cyclohexene, **199** (see Table 13, Chapter 4, page 72) suggests the cyclization of 1-hexene, possibly by the interaction with methylene chloride (**121**). Scheme 33 illustrates the mechanism of this reaction. Traces of dichloromethane (**200**) were also generated, but the MS did not detect it.

5.2.6 Proposed Mechanism for the deactivation of the $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalytic system in the CM of ED with $C_p^{1=}$ (p = 5 or 6)



Scheme 30. Deactivation mechanism for $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnMe_4/ED/C_5^{1=}$ catalytic system due to phenol.

Scheme 30 illustrates the deactivation of the $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalytic system for the cross-metathesis of ED with $C_5^{1=}$. This deactivation was possibly due to the interaction of phenol and the metal-carbene **149**, which led to the formation of an intermediate **201**. This intermediate rearranged to generate an oxy-rhenium species **136** and compound **202**. However, the MS did not detect compound **202**.



Scheme 31. Mechanism for the deactivation of the $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4/ED/C_6^{1=}$ catalytic system.

Scheme 31 illustrates the deactivation of the $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalytic system for the cross-metathesis of ED with $C_6^{1=}$. These highly acidic conditions due to HCl could be attributed to the high degree of isomerization of $C_6^{1=}$, as indicated by the presence of 2-hexene. Although the presence of SMP in the cross-metathesis of ED with $C_5^{1=}$ suggested isomerization of $C_5^{1=}$, the MS did not detect 2-pentene. These findings suggest that the degree of isomerization in the cross-metathesis of ED with $C_6^{1=}$ was higher than in the cross-metathesis of ED with $C_5^{1=}$.

The influence of the bromo-containing olefins over Re_2O_7/Al_2O_3 catalyst promoted with alkylmetal as a cocatalyst, was investigated by Kawai et al.[75] They established that although the selectivity was always nearly 100%, the catalytic activity decreased fairly faster as compared to 1-hexene.

In the study of 1-octene, H_2O also gave the highest yield of cross-metathesis products.[15] This was attributed to the fact that H_2O may have interacted more with the $SiO_2{\cdot}Al_2O_3$ support to form Brønsted acid sites, with fewer interactions with the rhenium species. Figure 34 also indicate that the catalytic system gave the highest yield of the secondary metathesis products, which resulted from the cross-metathesis of 1-pentene with its isomer (2-pentene). This was indicative of the interaction of H_2O with the $SiO_2{\cdot}Al_2O_3$ support to increase Brønsted acid sites.

5.3 Proposed mechanism for self-metathesis of MO

Metathesis of MO has been studied extensively,[76] thus mechanism for this reaction will not be discussed in this study.

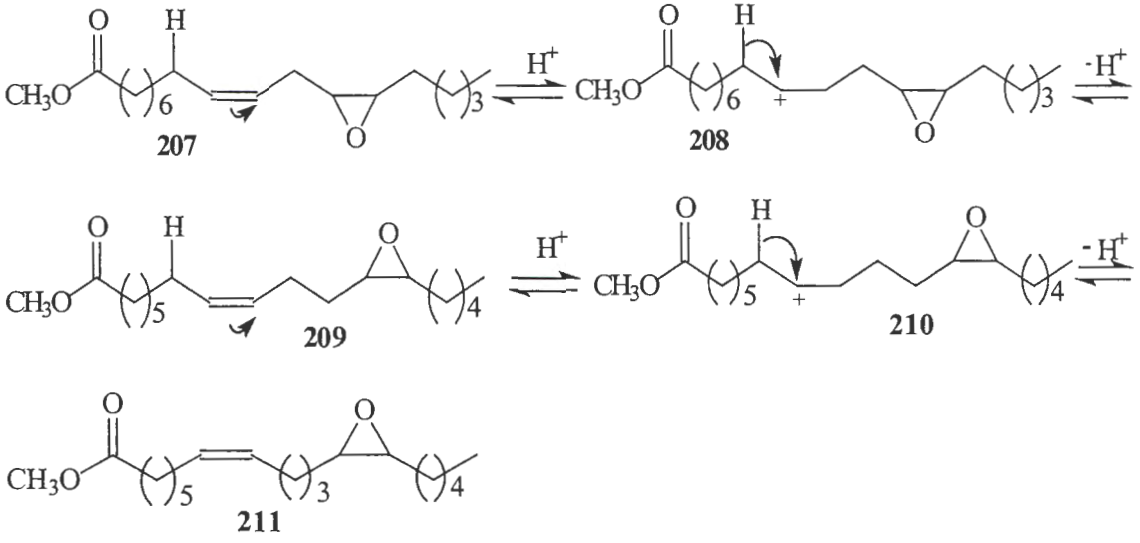
5.4 Metathesis of MV

The presence of isomerisation products and SMP in addition to PMP, suggests the possibilities of the following reactions:

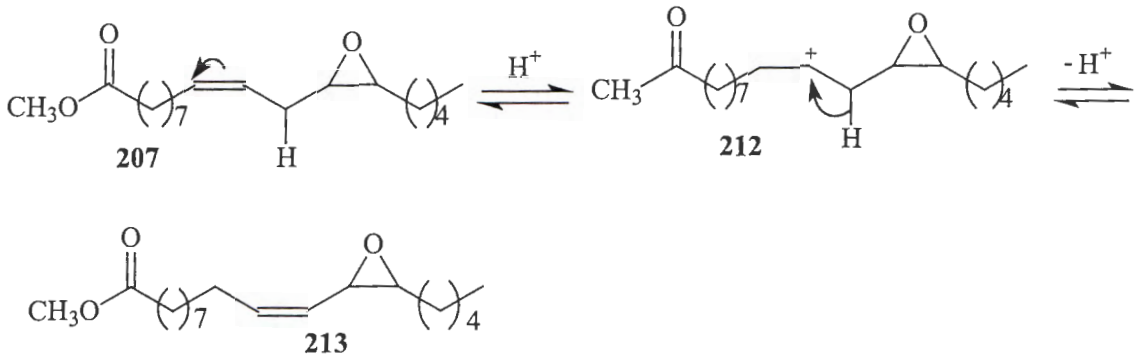
- SM of MV
- Isomerisation of MV to methyl-12,13-epoxy-7-octadecenoate and methyl-12,13-epoxy-7-octadecenoate
- SM of methyl-12,13-epoxy-7-octadecenoate
- CM of MV + methyl-12,13-epoxy-7-octadecenoate
- SM of methyl-12,13-epoxy-10-octadecenoate
- CM of MV + methyl-12,13-epoxy-10-octadecenoate
- CM of methyl-12,13-epoxy-7-octadecenoate + methyl-12,13-epoxy-10-octadecenoate

5.4.1 Proposed mechanism for isomerization of MV

The MS analysis of the reaction mixture obtained when MV was metathesised indicated the presence of two isomeric compounds. Schemes 32 and 33 illustrate mechanisms for the reactions which led to the formation of methyl-12,13-epoxy-7-octadecanoate and methyl-12,13-epoxy-10-octadecanoate, respectively.



Scheme 32. Mechanism for isomerization of methyl vernolate, which lead to formation of methyl-12,13-epoxy-7-octadecenoate.

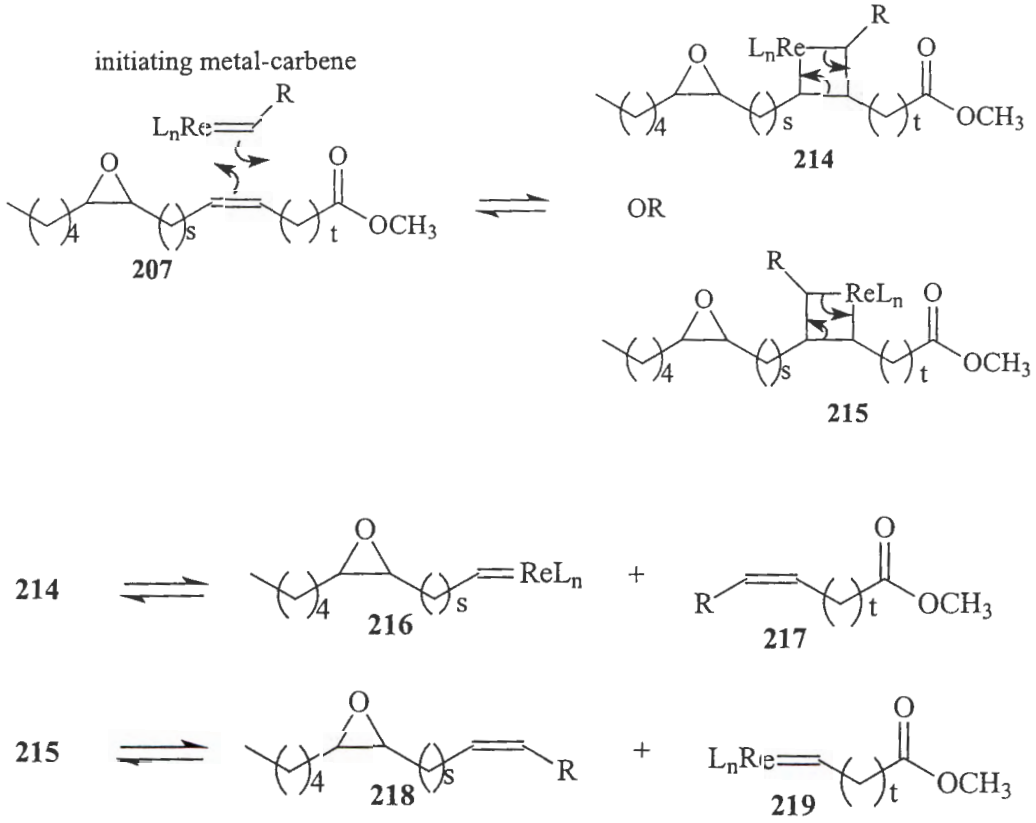


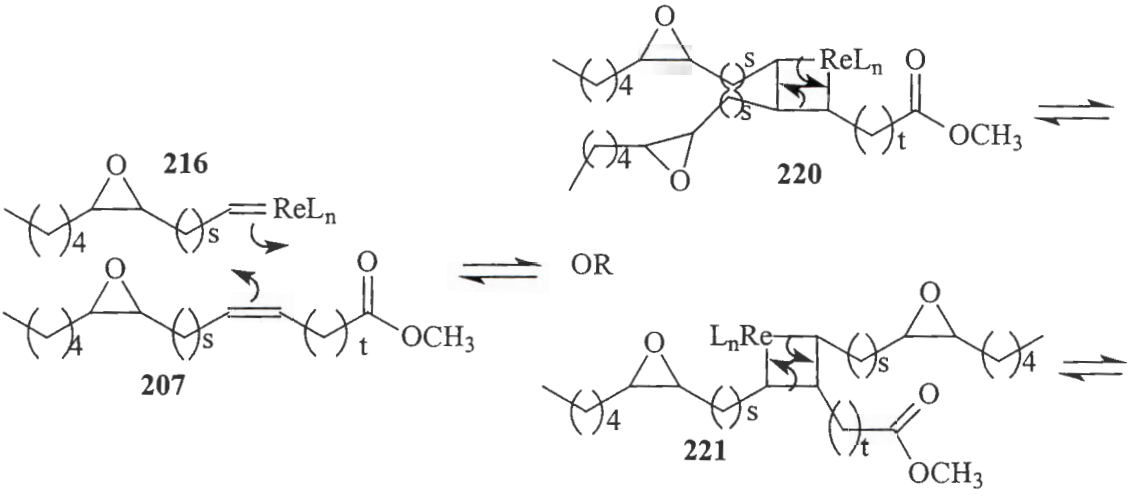
Scheme 33. Mechanism for isomerization of methyl vernolate, which lead to formation of methyl-12,13-epoxy-10-octadecenoate.

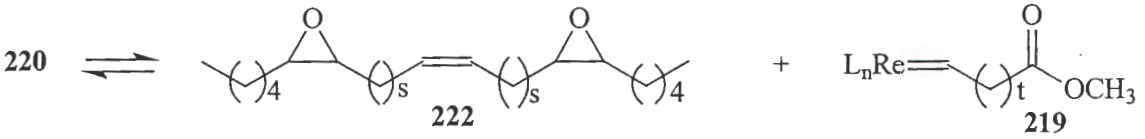
Compounds **211** and **213**, respectively, were methyl-12,13-epoxy-7-octadecenoate (Figure 52) and methyl-12,13-epoxy-10-octadecenoate (Appendix 41). The MS did not detect compound **209**, which suggests that it may also have undergone the double bond migration.

5.4.2 Proposed mechanism for SM of MV and its isomers

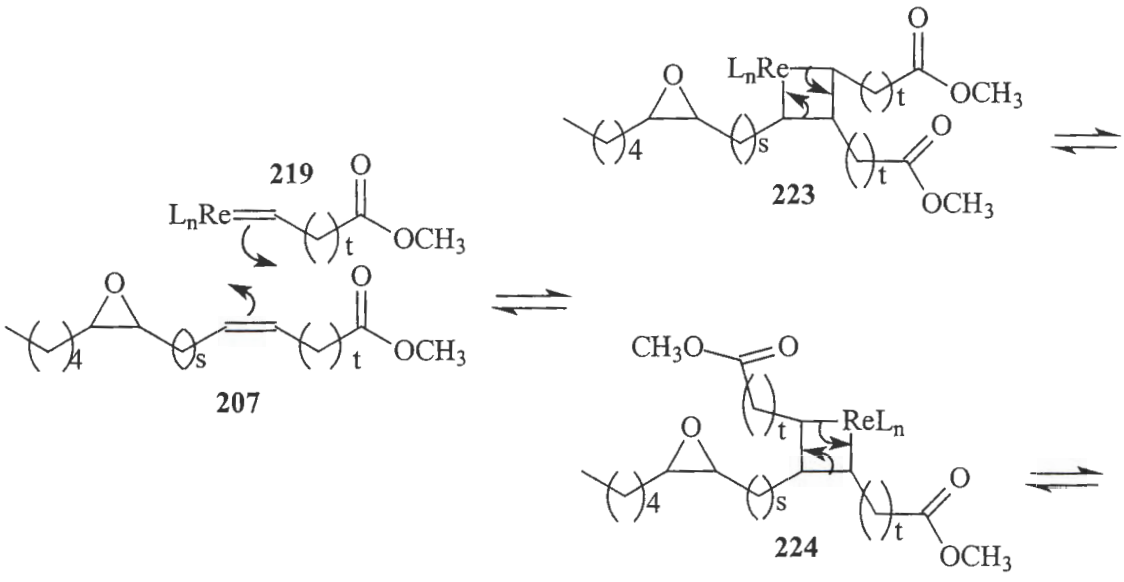
The presence of both PMP and SMP (see Table 19) suggests the self-metathesis of MV, methyl-12,13-epoxy-7-octadecenoate and methyl-12,13-epoxy-10-octadecenoate Scheme 34 illustrates the mechanism for self-metathesis reactions of these compounds.



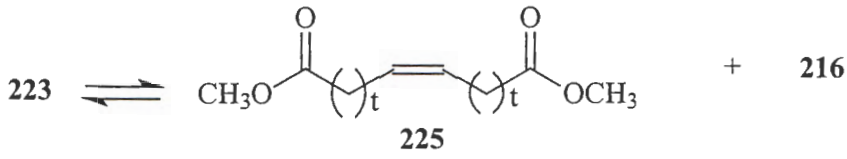




221 ⇌ 207 + 216



NWU LIBRARY



R = butyl group



MV: s = 1, t = 7
methyl-12,13-epoxy-7-octadecenoate: s = 3, t = 5
methyl-12,13-epoxy-10-octadecenoate: s = 0, t = 8

Scheme 34. Mechanism for self-metathesis of MV and its isomers.

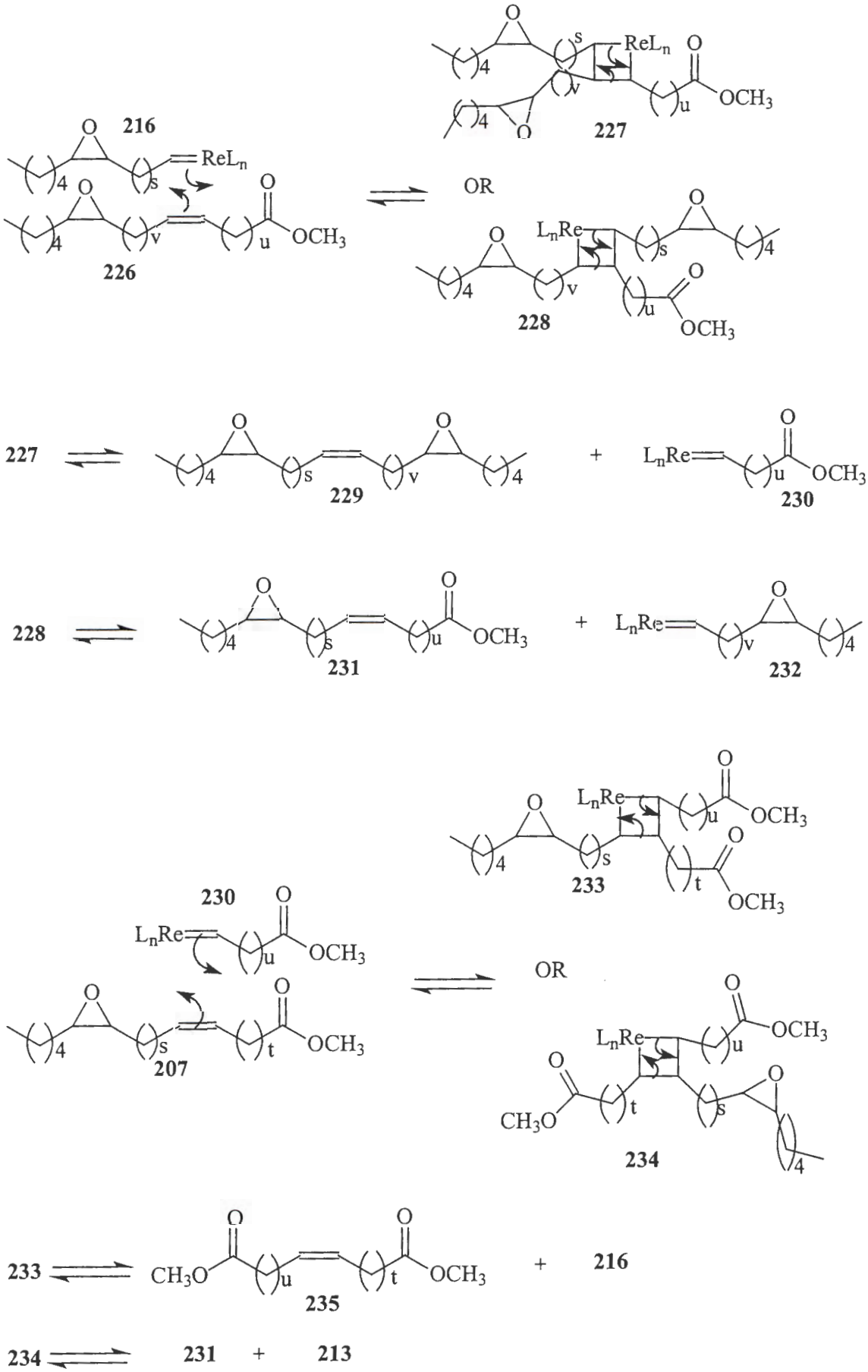
In the self-metathesis of MV, the PMP were compounds **222** and **225**. These compounds corresponded to 6,7,12,13-diepoxy-9-octadecene (Figure 53) and dimethyl-9-octadecenoate (Appendix 28), respectively. Both compounds **217** and **218**, respectively, were methyl-9-tetradecenoate (Appendix 43) and 6,7-epoxy-9-tetradecene. However, both compounds are not metathesis products but were obtained from side reactions (i.e. reaction between the initiating metal carbene and a molecule of MV. The MS did not detect compound **218**.

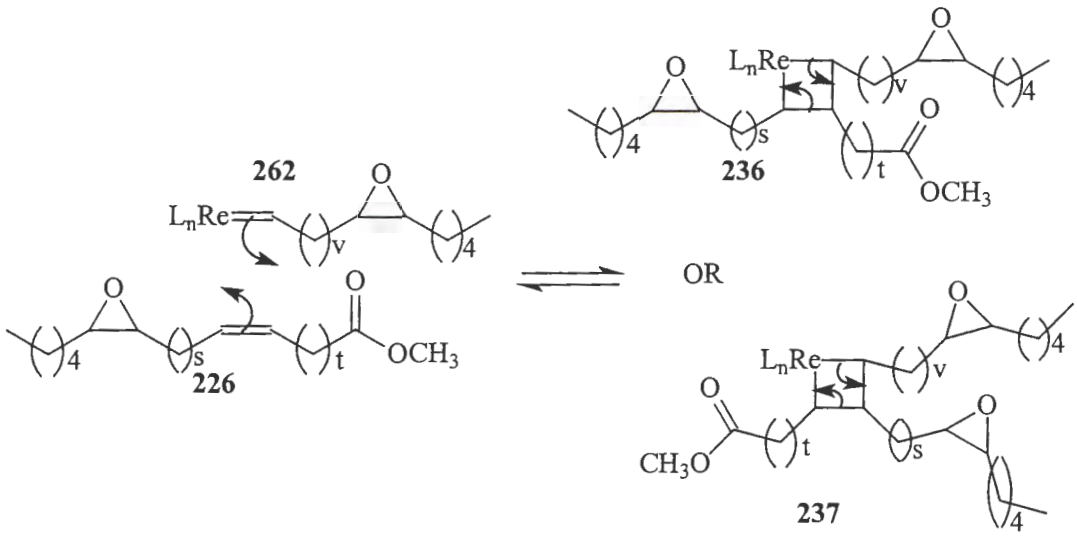
In the case of self-metathesis of methyl-12,13-epoxy-7-octadecenoate, compounds **222** and **225**, respectively, were 6,7,16,17-diepoxy-11-docosene (Appendix 33) and dimethyl-7-tetradecenoate (Appendix 38). The MS did not detect compounds **217** and **218**. For the self-metathesis of methyl-12,13-epoxy-10-octadecenoate, compounds **222** and **225**, respectively, were 6,7,10,11-diepoxy-8-hexadecene (Appendix 30) and dimethyl-10-cosaenoate (Appendix 40). However, the MS did not detect both compounds **217** and **218**.

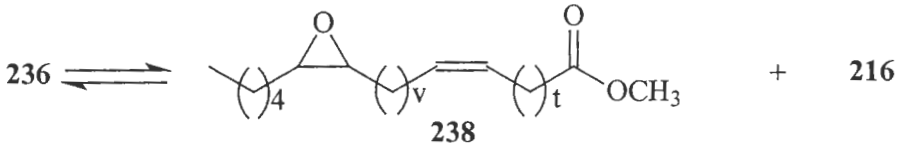
5.4.3 Proposed mechanism for CM reactions

5.4.3.1 Proposed mechanism for CM of MV with its isomers

Scheme 35 illustrates the mechanism of cross-metathesis of MV with methyl-12,13-epoxy-7-octadecenoate and methyl-12,13-epoxy-10-octadecenoate.


216
226
227
228
OR
227
229
230
228
231
232
230
207
233
OR
234
233
235
216
234
231
213







MV: s = 1, t = 7
methyl-12,13-epoxy-7-octadecenoate: u = 5, v = 3
methyl-12,13-epoxy-10-octadecenoate: u = 8, v = 0

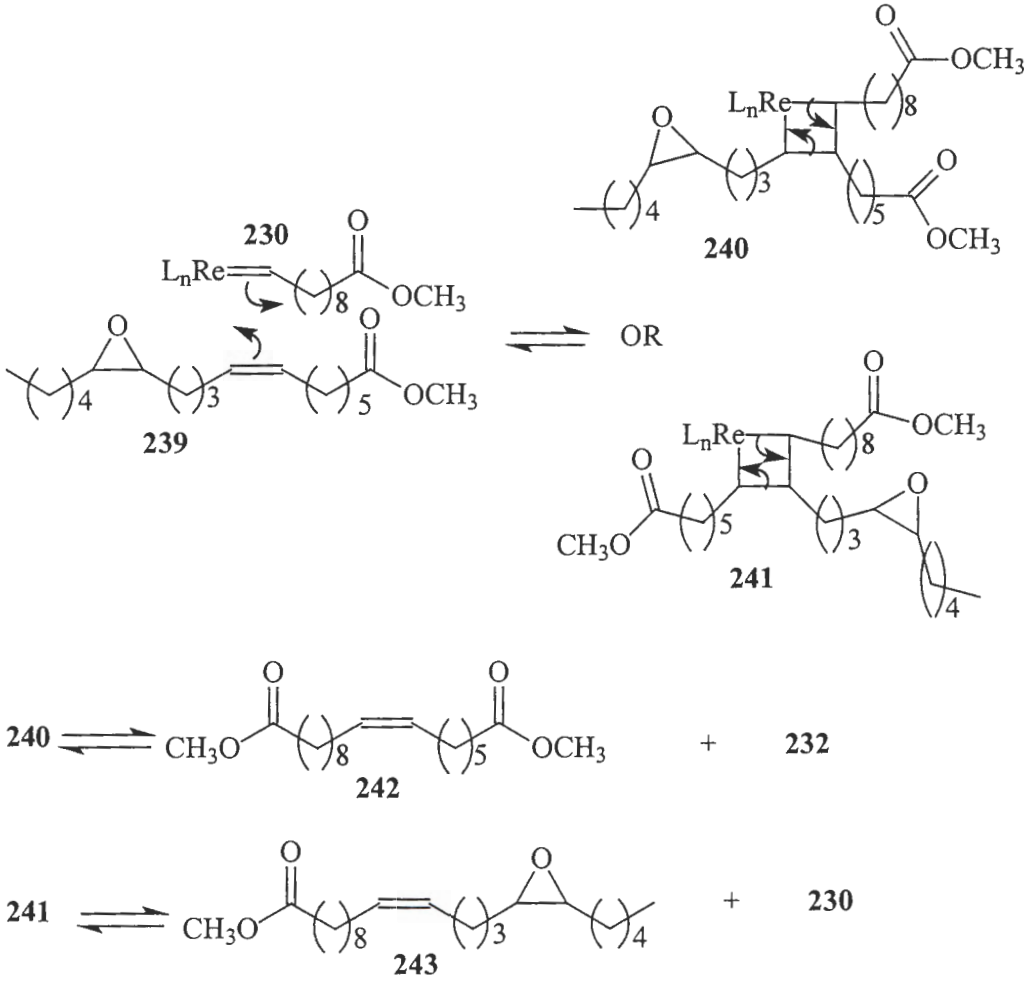
Scheme 35. Mechanism for cross-metathesis of MV with its isomers.

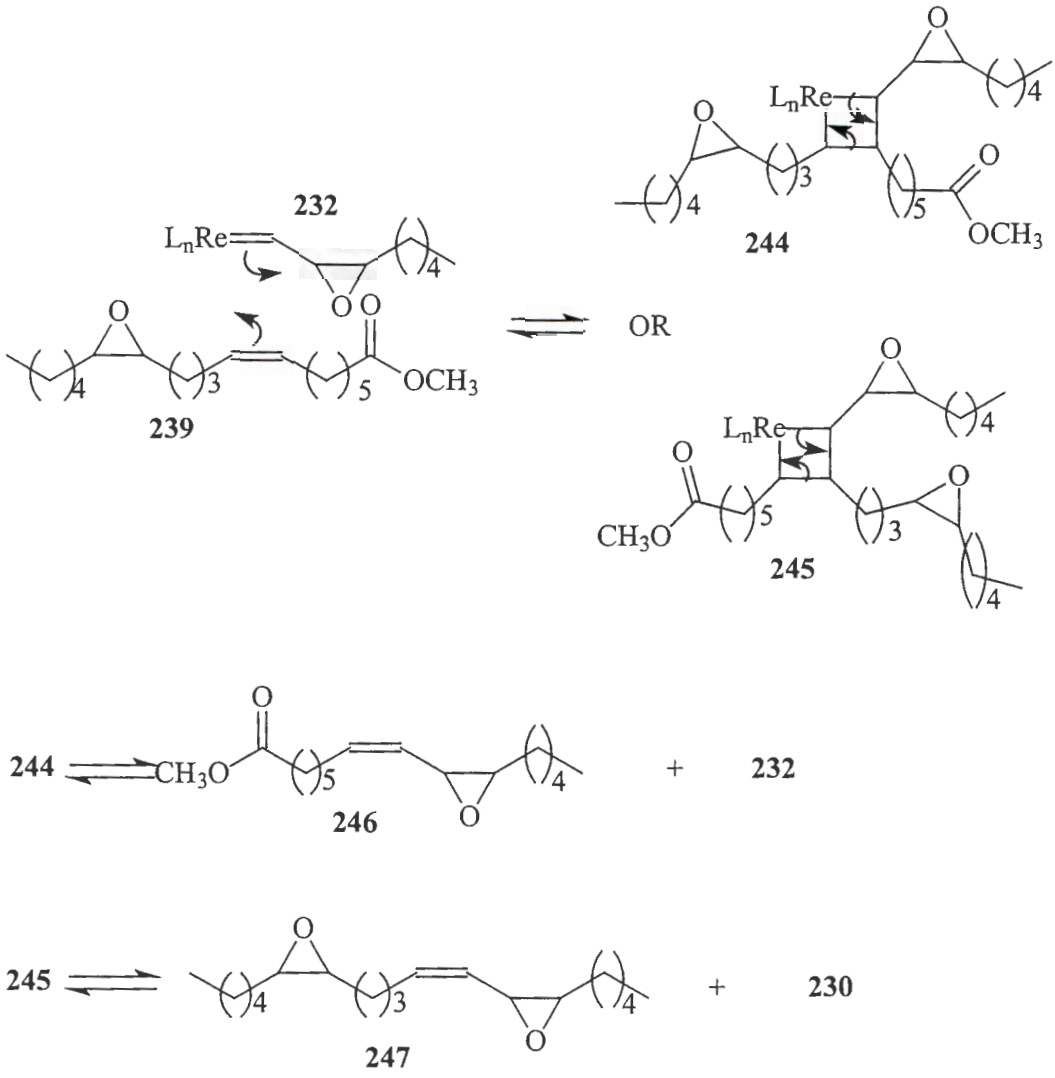
In the cross-metathesis of MV with methyl-12,13-epoxy-7-octadecenoate, compounds **229**, **231** and **235**, respectively, were 6,7,14,15-diepoxy-9-cosene (Appendix 32); methyl-10,11-epoxy-7-hexadecenoate (Appendix 35) and dimethyl-7-hexadecenoate (Appendix 39). The MS did not detect compound **238**.

For the cross-metathesis of MV with methyl-12,13-epoxy-10-octadecenoate, compounds **229**, **231** and **238**, respetively, were 6,7,11,12-diepoxy-8-heptadecene (Appendix 31); methyl-11,12-epoxy-9-heptadecenoate (Appendix 36) and methyl-13,14-epoxy-10-nonadecenoate (Appendix 37). The MS did not detect compound **235**.

5.4.3.2 Proposed mechanism for CM of methyl-12,13-epoxy-7-octadecenoate with methyl-12,13-epoxy-10-octadecenoate

Scheme 36 illustrates the mechanism for the cross-metathesis of methyl-12,13-epoxy-7-octadecenoate with methyl-12,13-epoxy-10-octadecenoate.





Scheme 36. Mechanism for CM of methyl-12,13-epoxy-7-octadecenoate with methyl-12,13-epoxy-10-octadecenoate.

The MS detected only compound **246**, which was methyl-9,10-epoxy-7-pentadecenoate (Appendix 34).

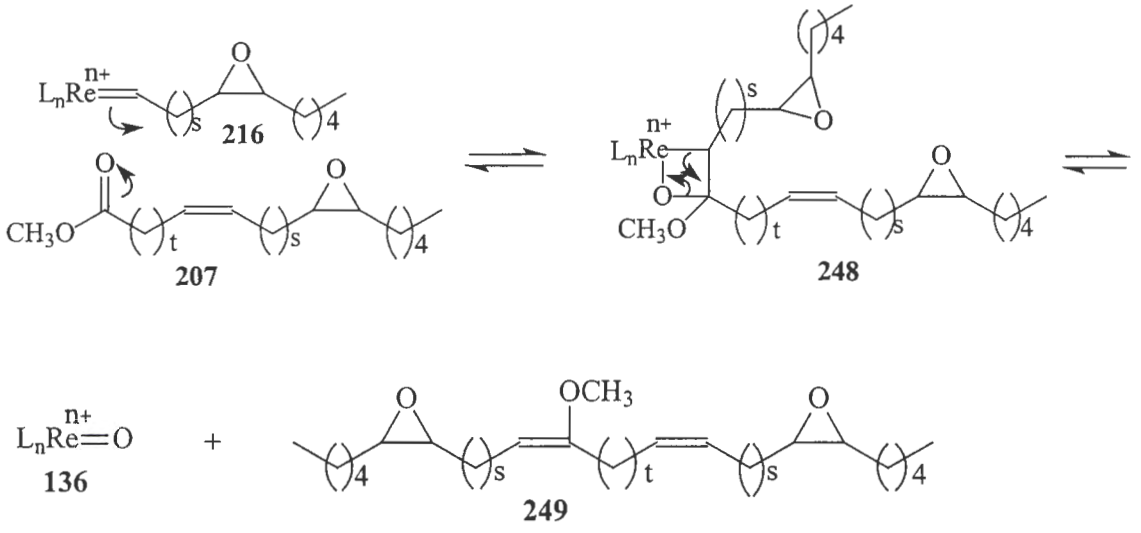
5.4.4 Proposed mechanism for the deactivation of the $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$/MV catalytic system

The conversion of MV (ca. 94.2%), which is an internal epoxy olefinic ester, was lower than that of ED (ca. 99.2%), an external epoxy olefin. The decrease in the conversion as suggested earlier, could be due to sterric as well as electronic effects. The epoxy ring in MV is closer to the double bond (see compound **226**, when v = 1 and u = 7), thus the metal-carbene could easily be blocked from reaching the active site on the alkene. The structure of MV also shows that there could be possibility of the double bond being enclosed within the two highly electron rich functional

groups, i.e. the epoxy and the ester groups. This could lead to the blockage of the rhenium-carbene species from reaching the double bond on the substrate molecule.

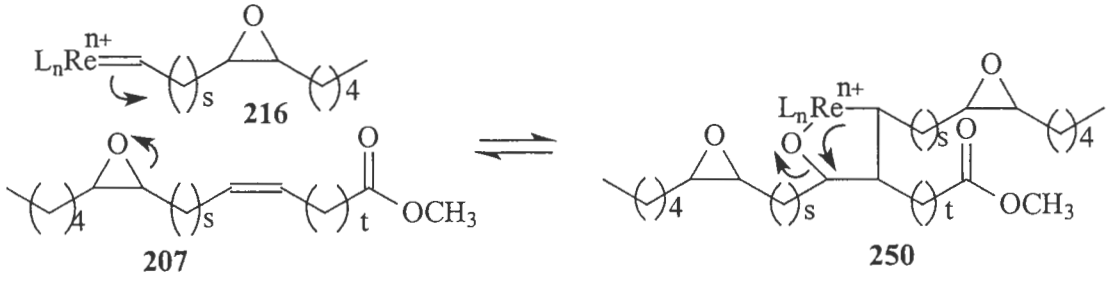
Both the epoxy and the ester group could interact with the rhenium-carbene intermediate in the following two ways:

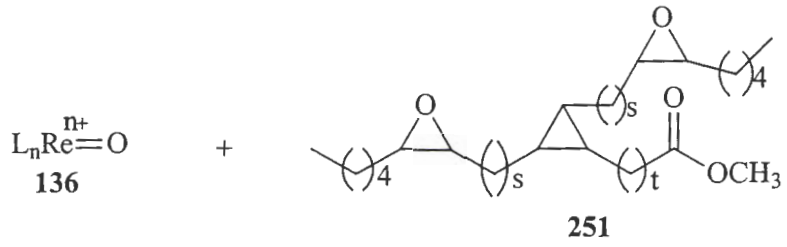
(1) The ester group could react with the rhenium-carbene intermediate, as illustrated by Scheme 37.



Scheme 37. Mechanism for the deactivation of the $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$/MV catalytic system via the interaction of the carboxylic acid group with the rhenium carbene species.

(2) The epoxy ring could also react with the rhenium-carbene species via the intermolecular interaction (Scheme 38). This could lead to overcrowding around the rhenium-carbene intermediate. The intramolecular interaction of the epoxy group with the rhenium-carbene species is not envisaged because of the close proximity of the epoxy ring to the double bond.





s = 1, t = 7

Scheme 38. Mechanism for the deactivation of the $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$/MV catalytic system via the interaction of the epoxy group with the rhenium carbene species.

5.5 Cross-metathesis of methyl vernolate with methyl oleate

Mechanisms for the isomerisation of MV and cross-metathesis of MV with its isomers, respectively, was discussed in Schemes 32 – 33 and 34 – 36. The mechanism for the possible deactivation of the catalytic system has been discussed in Scheme 37 and 38.

5.6 Cross-metathesis of MV with $C_5^{1=}$ and $C_6^{1=}$

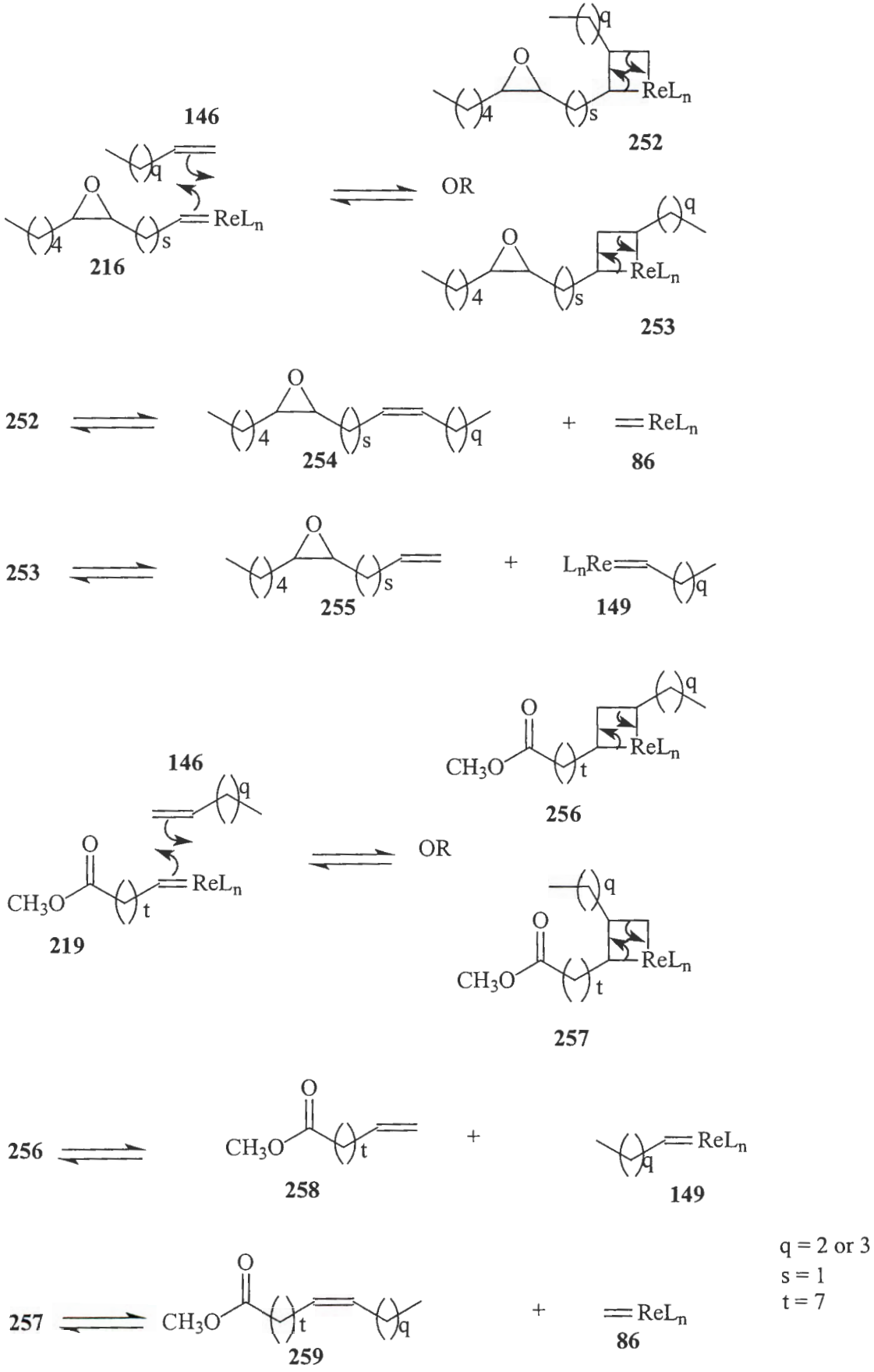
The presence of SMP in addition to PMP suggests the following reactions:

- Isomerisation of MV or $C_p^{1=}$
- SM of MV, $C_p^{1=}$, $C_p^{2=}$, methyl-12,13-epoxy-7-octadecenoate, methyl-12,13-epoxy-10-octadecenoate
- CM of MV with methyl-12,13-epoxy-7-octadecenoate, methyl-12,13-epoxy-10-octadecenoate, $C_p^{1=}$ or $C_p^{2=}$
- CM of methyl-12,13-epoxy-7-octadecenoate with methyl-12,13-epoxy-10-octadecenoate
- CM of $C_p^{1=}$ with $C_p^{2=}$
- CM of methyl-12,13-epoxy-7-octadecenoate with $C_p^{1=}$ or $C_p^{2=}$
- CM of methyl-12,13-epoxy-10-octadecenoate with $C_p^{1=}$ or $C_p^{2=}$

where p = 5 or 6.

5.6.1 Proposed mechanism for the CM of MV with $C_p^{1=}$

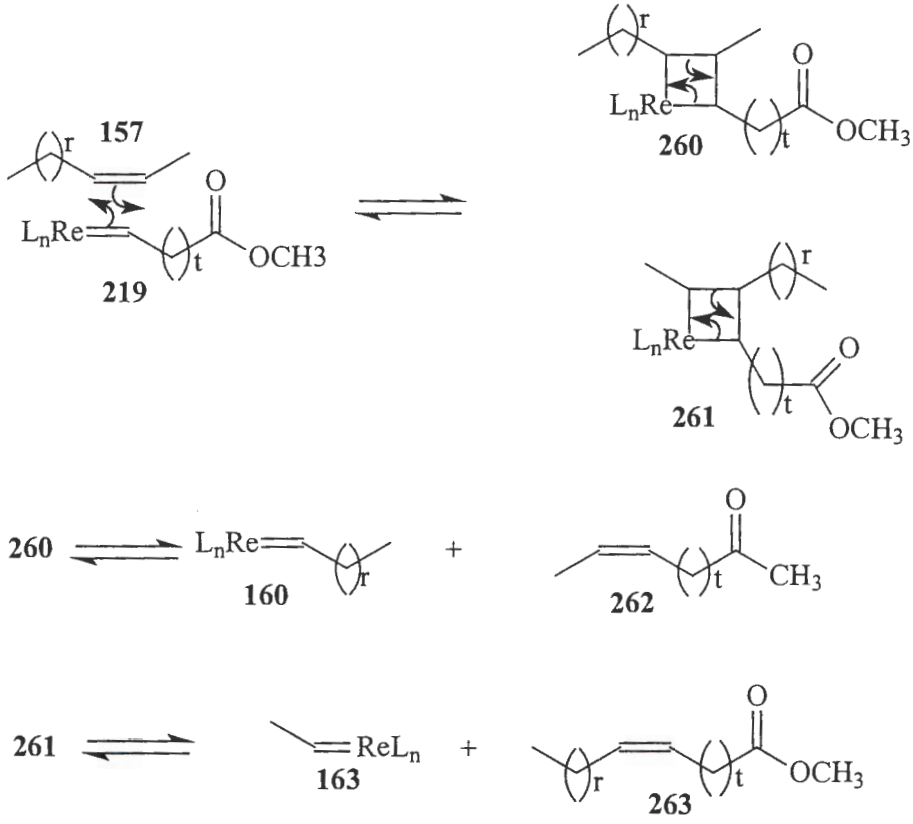
Scheme 39 illustrates the mechanism for the cross-metathesis of MV with either $C_5^{1=}$ or $C_6^{1=}$.



Scheme 39. Mechanism for CM of MV with $C_5^{1=}$ or $C_6^{1=}$.

Compound **255**, which is 6,7-epoxy-9-decene (Appendix 45), was obtained in both cross-metatheses of MV with $C_5^{1=}$ and MV with $C_6^{1=}$. However, the MS did not detect compound **254**. Compound **259**, which is methyl-9-tetradecenoate (Appendix 48), was obtained only in the cross-metathesis of MV with $C_6^{1=}$.

5.6.2 Proposed mechanism for the CM of MV with $C_p^{2=}$



$C_5^{2=}$: r = 1

$C_6^{2=}$: r = 2

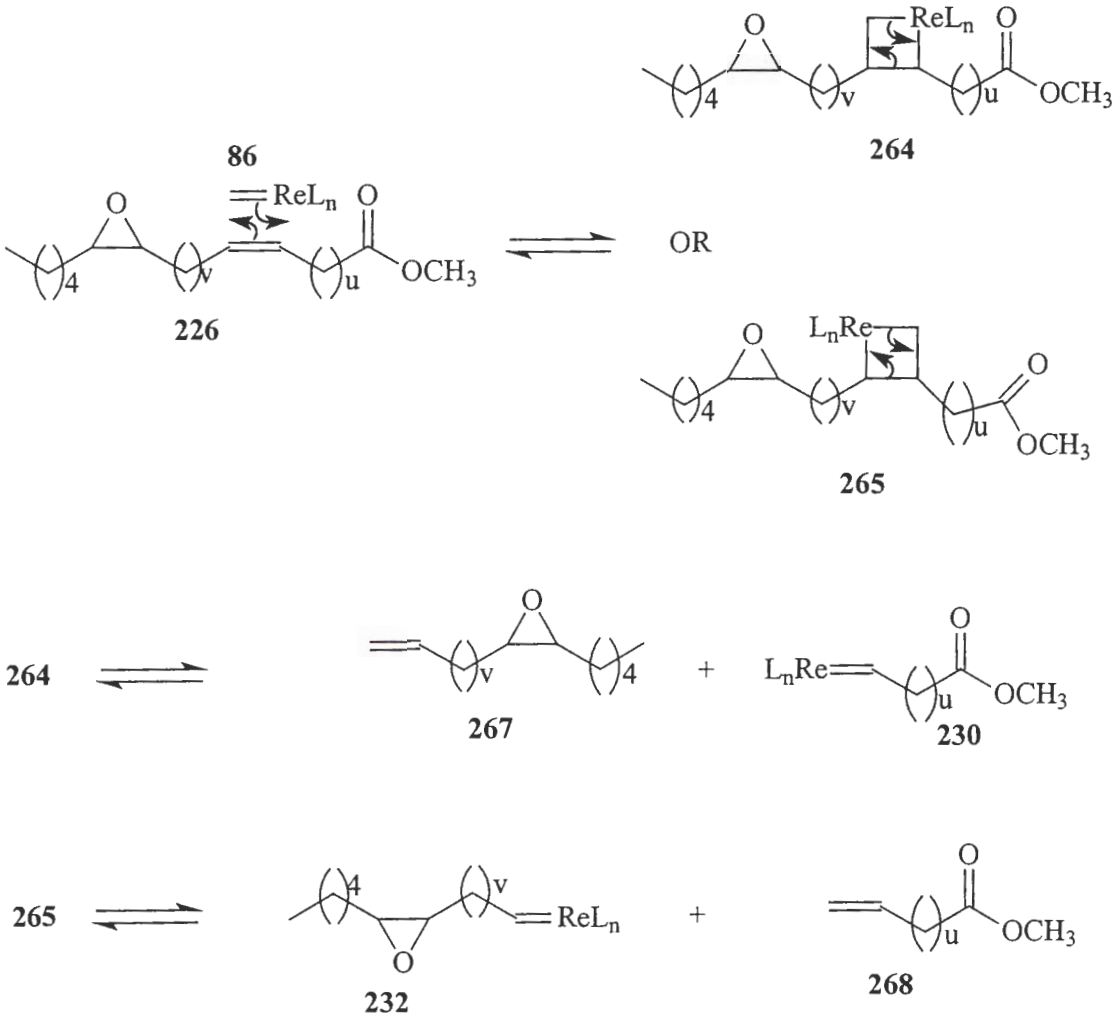
t = 7

Scheme 40. Mechanism for CM of MV with $C_p^{2=}$.

Compound **263**, which is methyl-9-dodecenoate (Appendix 47), was obtained in the cross-metathesis of MV with $C_5^{1=}$. However, the MS did not detect compound **262**.

5.6.3 Proposed mechanism of CM of methyl-12,13-epoxy-10-octadecenoate with $C_5^{1=}$

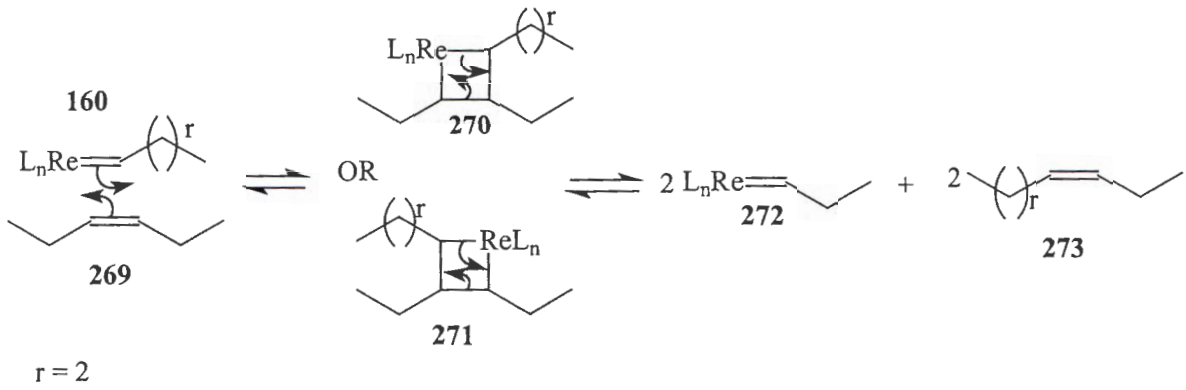
Scheme 41 illustrates the cross-metathesis of methyl-12,13-epoxy-10-octadecenoate with $C_5^{1=}$, which generated compound **267**.



Scheme 41. Mechanism for CM of methyl-12,13-epoxy-10-octadecenoate and $C_5^{1=}$.

5.6.4 Proposed mechanism for CM of $C_6^{2=}$ with $C_6^{3=}$

Scheme 42 illustrates the cross-metathesis of $C_6^{2=}$ with $C_6^{3=}$, which gave 3-heptene (**273**).



Scheme 42. Mechanism for the CM of $C_6^{2=}$ with $C_6^{3=}$.

5.7 SUMMARY

This study was primarily aimed at investigating the activity and selectivity of the $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ on epoxy alkenes, with a view of understanding how the epoxy group affects the activity and the selectivity of the $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalytic system. The following general remarks can be drawn from the study:

5.7.1 SM of MV, ED and MO

- The $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalytic system was both highly active and selective towards the PMP (i.e. diepoxy alkenes), in the metathesis of terminal epoxy alkenes such as ED (see Table 4 and Figure 12).
- The activity of the $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$/ED catalytic system generally increased with increase in the SnB_4 content (see Figure 13). However, the catalytic system was the most active at Re:Sn = 0.5. Although the selectivity decreased with increase in SnB_4 content (see Table 5), however, the catalytic system was the most selective at Re:Sn = 0.5.
- Both the activity and selectivity of the $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$/ED catalytic system generally decreased with increase in the Re_2O_7 loading (see Table 6 and Figure 16).
- The activity of the $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$/ED catalytic system generally decreased with increase in the reaction temperature (see Table 7 and& Figure 19).
- The $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$/ED catalytic system was the most active in chlorobenzene, followed by a non-polar hexane solvent (see Table 8 and Figure 22). The catalytic system was highly selective in polar solvents such as chlorobenzene and dichloromethane.

- Although the activity of the $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4/ED$ catalytic system generally decreased with increase in the substrate concentration, however, there was no clear pattern with regard to the selectivity (see Table 10 and Figure 25).
- Although the $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalytic system was still active in the metathesis of internal epoxy alkenes such as MV (see Table 19 and Figure 53), however, the catalytic system seemed to have been deactivated when compared to the ED system. This deactivation was attributed to sterric factors due to the close proximity of the epoxy group to the double bond. The deactivation was also attributed to competing reaction between the double bond, epoxy group, as well as the carboxylic acid group for the metal carbene species responsible for metathesis reaction.
- The catalytic system was less selective towards the PMP (i.e. diepoxy alkenes and the diesters).
- Although the $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4/MV$ catalytic system was highly active as compared to the $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4/MO$ catalytic system, however, the $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4/MO$ catalytic system was highly selective towards PMP.

5.7.2 CM reactions of epoxy alkenes with linear alkenes

5.7.2.1 CM of ED with linear alkenes

- The $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4/ED/C_5^{1=}$ and $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4/ED/C_6^{1=}$ catalytic systems deactivated when compared to the $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4/ED$ catalytic system. Furthermore, the activity seemed to increase with increase in the linear alkene chain length in the CM reactions (see Table 11 and 13). This suggests that the activity decreased in the order: $ED > ED/C_6^{1=} > ED/C_5^{1=}$.
- The selectivity of the $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalytic system towards PMP also decreased in the order: $ED > ED/C_6^{1=} > ED/C_5^{1=}$.

5.7.2.2 CM of MV with MO or linear alkenes

- The activity of the $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalytic system decreased in the order:

  $MV > MV/C_6^{1=} > MV/C_5^{1=} > MV/MO$ (see Table 19, 21 – 22 and 24)
- The selectivity of the $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalytic system towards PMP decreased in the order: $MV > ED/C_6^{1=} > ED/C_5^{1=} > MV/MO$.

Generally, there was a strong interaction between the epoxy group of MV and the double bond of the linear alkenes. This interaction led to the formation of high molecular compounds, which

may have attributed to the deactivation of the $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4$ catalytic system, by clogging of the surface pours on the support.

5.8 RECOMMENDATIONS

I recommend that another separate study be done in order to fully optimise the $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4/MV$ catalytic system, by investigating the influence of various parameters such as the Sn:Re molar ratio, Re_2O_7 loading, reaction temperature, type of solvent, and substrate concentration on the activity, selectivity and stability of the $Re_2O_7/SiO_2{\cdot}Al_2O_3/SnBu_4/MV$ catalytic system.

REFERENCES

1. D.L. Trumbo, J.C. Rudelich, B.E. Mote, Applications of Vernonia Oil in Coatings, 1999, p. 267. In: J. Janick (ed), Perspectives on New Crops and New Uses, 1999, ASHS Press, Alexandria, VA
2. L. Grandia, World Summit for Sustainable Development, The Star, August 21, 2002, 3
3. J. Charles, Extreme Weather Wrecks Havoc in Europe, The Star, August 14, 2002, 11
4. B.B. Marvey, Fats and Oils, Science in Africa, October 2002
5. P. Gallezot, Catalytic Transformation of Carbohydrates into Valuable Derivatives, 14th Symposium Proceedings, University of Limerich, 2002
6. B.B. Marvey, J.A.K. du Plessis, H.C.M. Vosloo, J.C. Mol, J. Mol. Catal. A: Chem. 201 (2003) 297
7. M.L. Randall, J.A. Tallarico, M.L. Snapper, J. Am. Chem. Soc. 117 (1995) 9610
8. A. Fürstner, Angew. Chem. Int. Ed. 39 (2000) 3012
9. M.I. Konaklieva, Tetrahedron Lett. 33 (1992) 7093
10. A.I. Mohamed, T. Mebrahtu, T. Andebrhan, Variability in Oil and Vernolic Acid Contents in The New Vernonia Galamensis Collection from East Africa, 1999; In: J. Janick (ed), Perspectives on New Crops and New Uses, 1999, ASHS Press, Alexandria, VA
11. F.O. Ayorinde, *What is Vernonia?*, Howard University, August 5, 2002, www.chem.howard.edu.html
12. A. Clark, Project report No OS47, University of Warwick, HGCA, March 2001
13. T. Tsuji, S. Hashiguchi, Tetrahedron Lett. 21 (1980) 2955
14. R. Buffon, I.J. Marochio, C. Rodella, J.C. Mol, J. Mol. Catal. A: Chem. 190 (2002) 171
15. J.A.K. du Plessis, A. Spamer, H.C.M. Vosloo. J. Mol. Catal. A: Chem. 133 (1998) 175
16. M.L. Snapper, J.A. Tallarico, M.L. Randall, J. Am. Chem. Soc. 119 (1997) 1478-1479
17. J.A. Tallarico, P.J. Bonitatebus, Jn., M.L. Snapper, J. Am. Chem. Soc. 119 (1997) 7157
18. A.M. Rouhi, Olefin metathesis: The Early Days, CENEAR. 80 No. 51 (2002) 29
19. J. Emsley, Ruthenium Runs Rings' Round Organic Reactions, ScienceWatch. 12. No. 1 (2001)
20. K.J. Ivin, J.C. Mol, Olefin Metathesis and Metathesis Polymerisation, Academic Press

(London). (1997) 3

21. R. Streck, Chemtech. 19 (1989) 498
22. K.G.T. Thich, M. Borene, E. Edwards, W.P. Tam, Metathesis of Soybean Oil, Geocities (31 Aug 2002) 1, www.geocities.com/gthich/soybean.htm
23. R.C. Larock, M.D. Refvik, K.W.C. Poon, Metathesis of Soybean Oil, Am. Oil. Chem. Soc. Archives: Meeting Abstracts (August 8, 2002), www.chem.iowa.ed.html
24. R. Toreki, Ring Opening Metathesis Polymerisation, Organometallic Hypertextbook. (August 13, 2002) 1-5, www.ilpi.com/organomet/alkylidene.html
25. N. Calderon, Tetrahedron Lett. 90 (1968) 4133
26. N. Calderon, J. Am. Chem. Soc. 90 (1968) 4133
27. J.C. Mol, Chem. Commun. (1968) 633
28. R. Pettit, J. Am. Chem. Soc. 93 (1971) 7087
29. R.H. Grubbs, J. Am. Chem. Soc. 94 (1972)
30. R.H. Grubbs, Inorg. Chem. 12 (1973) 2166
31. Y. Chauvin, J.L. Hérrison, Makromol. Chem. 141 (1971) 161
32. M. Sibeijn, J.A.R. Vanveen, A. Bliek, J.A. Moulijn, J. Catal. 145 (1994) 416
33. B.C. Gates, J.R. Katzer, G.C.A. Schuit, Chemistry of Catalytic Processes, McGraw-Hill, New York, 1979, p. 464
34. X. Xiaoding, J.I. Benecke, C. Boelhouwer, J.C. Mol. Appl. Catal. 28 (1986) 2767
35. C.B. Rodella, J.A.M. Cavalcante, R. Buffon. Appl. Catal. A: Gen. 274 (2004) 213
36. J. Tsuji, Transition Metal Reagents and Catalyst: Innovations in Organic Synthesis, Wiley (London) (2000) p5-35
37. P. Schwab, M.B. France, J.W. Ziller, R.H. Grubbs, Angew. Chem., Int. Ed Engl. 34 (1995) 2039
38. S.B.T. Nguyen, R.H. Grubbs, J. Am. Chem. Soc. 115 (1993) 9858
39. G. Natta, Angew. Chem., Int. Ed. 3 (1964) 723
40. T. Oikawa, T. Ookshi, T. Tanaka, T. Yamamoto, M. Onaka, Micropor. Mesopor. Mater. 74 (2004) 93
41. X. Xiaoding, J.C. Mol, C. Boelhouwer, J. Chem. Soc., Faraday Trans. 82 (1986) 2707
42. R. Buffon, U. Schuchardt, A. Abras, J. Chem. Soc., Faraday Trans. 91 (1995) 3511
43. R. Buffon, M.J.D.M. Jannini, A. Abras, J.C. Mol, J. Mol. Catal. A: Chem. 115 (1997) 173
44. T. Kawai, Y. Yamazaki, T. Taoka, K. Kobayashi, J. Catal. 89 (1984) 452
45. M. Sibeijn, R. Spronk, J.A.R. Vanveen, J.C. Mol, Catal. Lett. 8 (1991) 201
46. T.M. Mathew, J.A.K. du Plessis, J.J. Prinsloo, J. Mol. Catal. A: Chem. 148 (1999) 157

47. T. Kawai, T. Okada, T. Ishikawa, J. Mol. Catal. 76 (1992) 249
48. T. Kawai, H. Goto, Y. Yamazaki, T. Ishikawa, J. Mol. Catal. 46 (1988) 157
49. B. Ellis, Introduction to the chemistry, synthesis, manufacture and characterization of epoxy resins, Chemistry and Technology of Epoxy resins, 1st Edition, B. Ellis, Ed., 1993, Chapman & Hall, New York, p1-36
50. A. Padwa, S.S. Murphree, Arkivoc (2005) 4
51. D.F. Hildebrand, C. McCracken, C. Seither, Am. Soc. Plant Biol. 274 (1997) 1
52. D.A. Dierig, Water Consumption Laboratory Abstracts. (August 5, 2002) 1, http://www.uswcl.ars.ag.gov
53. H.R. Moyer, Compliance Coatings for Organic Finishing, Concurrent Technologies Corporation (5 Aug 2002) 1, http://www.dppr.ctc.com
54. M.G. Constantino, V. Lacerda Jr, V. Aragão, Molecules. 6 (2001) 770
55. D.E. White, E.N. Jacobsen, Tetrahedron Asym. 14 (2003) 3633
56. J.F. Green, J.W. Newman, K.C. Williamson, B.D. Hammock, Chem. Res. Toxic. 13 (2000) 213
57. H.M. Kosaka, Biochem. Int. 21 (1990) 573
58. T. Ozawa, M. Hayakawa, K. Kosaka, S. Sugiyama, T. Ogawa, K. Yokoo, H. Aoyama, Y. Izawa, Adv. Prostag, Thrombox, Leukotri. Res. 21 (1990) 569
59. J.C. Mol, R. Buffon, J. Braz. Chem. Soc. 9 (1998) 1
60. M. Sibeijn, J.C. Mol, Appl Catal. 67 (1990) 27995
61. R. Nakamura, S. Fukuhara, S. Matsumoto, K. Komatsu, Chem. Lett. (1976) 1019
62. R. Nakamura, S. Matsumoto, E. Echigoya, Chem. Lett. (1976) 1019
63. E. Verkuijlen, Metathesis of unsaturated esters, Ph.D. Thesis, University of Amsterdam. (1980)
64. J. Otton, Y. Colleuille, J. Varagnat, J. Mol. Catal. 8 (1980) 313
65. B.B. Marvey, J.A.K. du Plessis, H.C.M. Vosloo, J.C. Mol, J. Mol. Catal. A: Chem. 213 (2004) 151
66. S. Warwel, F. Brüse, C. Demes, and M. Kunz, M. Rausch gèn. Klaas, Chemosphere. 43 (2001) 39
67. J.C. Mol, Green. Chem. 4 (2002) 5
68. M. Sibeijn, J.C. Mol, J. Mol. Catal. 76 (1992) 345
69. C. Boelhouwer, J.C. Mol, Prog. Lipid Res. 242 (1985) 43
70. K.M. Kadish, X. Mu, J.E. Anderson. Pure Appl. Chem. 61 (1989) 1823
71. K.M. Kadish, J.E. Anderson. Pure Appl. Chem. 59 (1987) 703

72. T. Kawai, N. Maruoka, T. Ishikawa. J. Mol. Catal. 60 (1990) 209

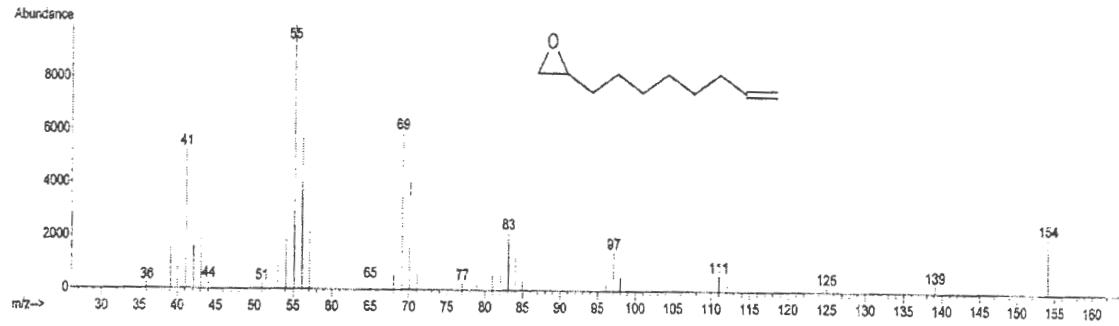
73. J.C. Mol, Catal. Today. 51 (1999) 289

74. H.C.M. Vosloo, J.A.K. du Plessis. J. Mol. Catal. A: Chem. 133 (1998) 205

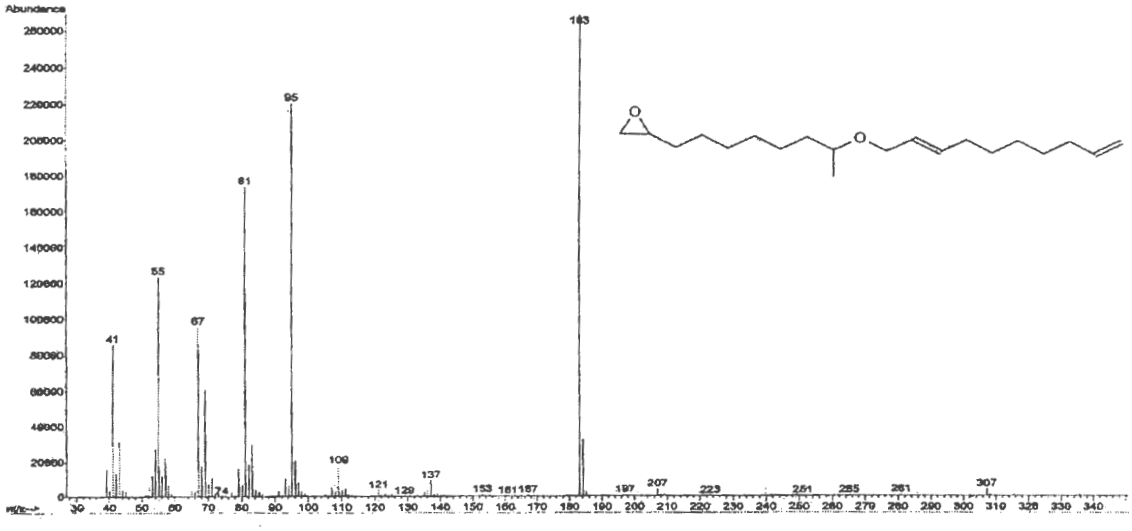
75. T. Kawai, S. Uejima, T. Suzuki, T. Iyoda. J. Mol. Catal. A: Chem. 133 (1998) 51

76. M. Sibeijn, Technological and economical aspects of the metathesis of unsaturated esters Ph.D. Thesis, University of Amsterdam. (1993)

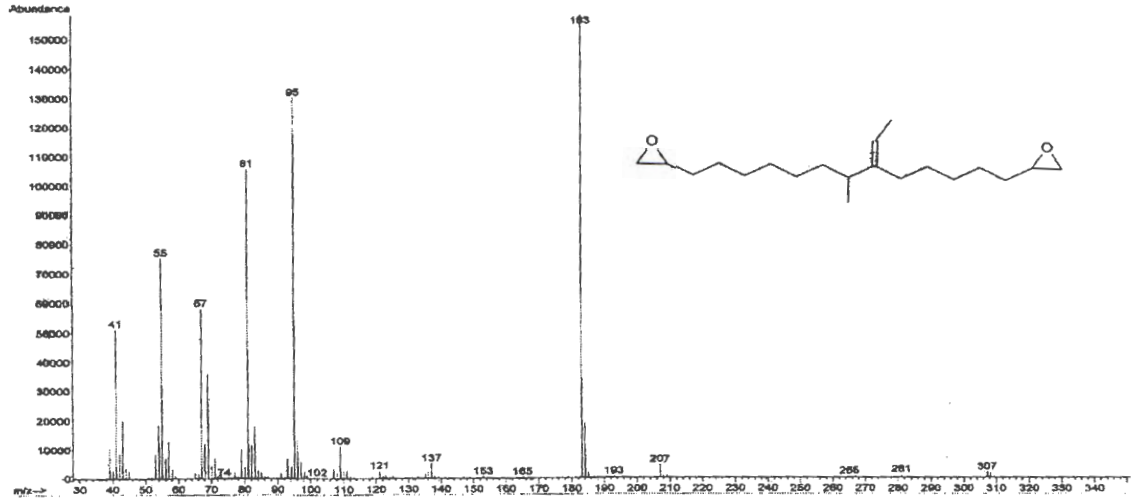
APPENDICES



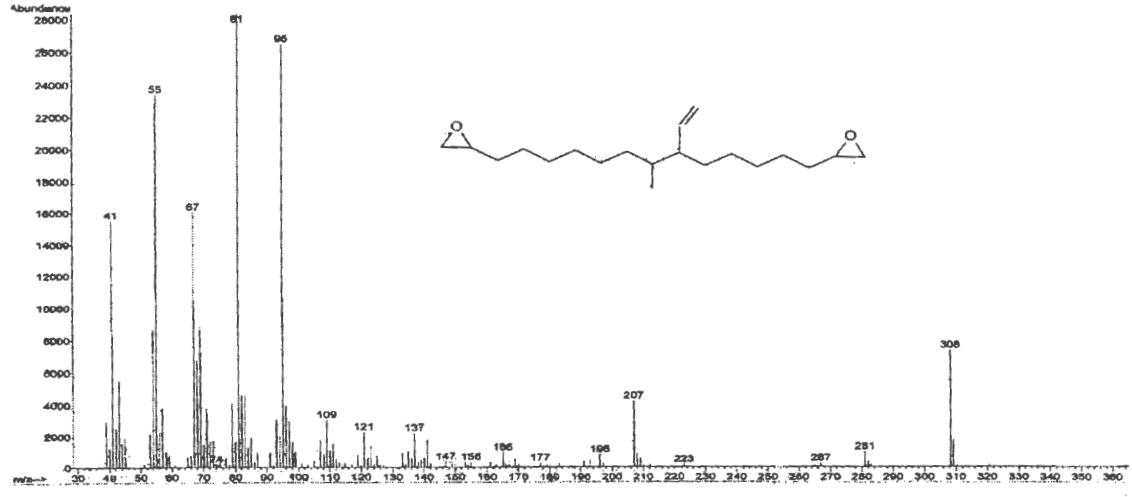
Appendix 1. Mass spectrum of 1,2-epoxy-9-decene.



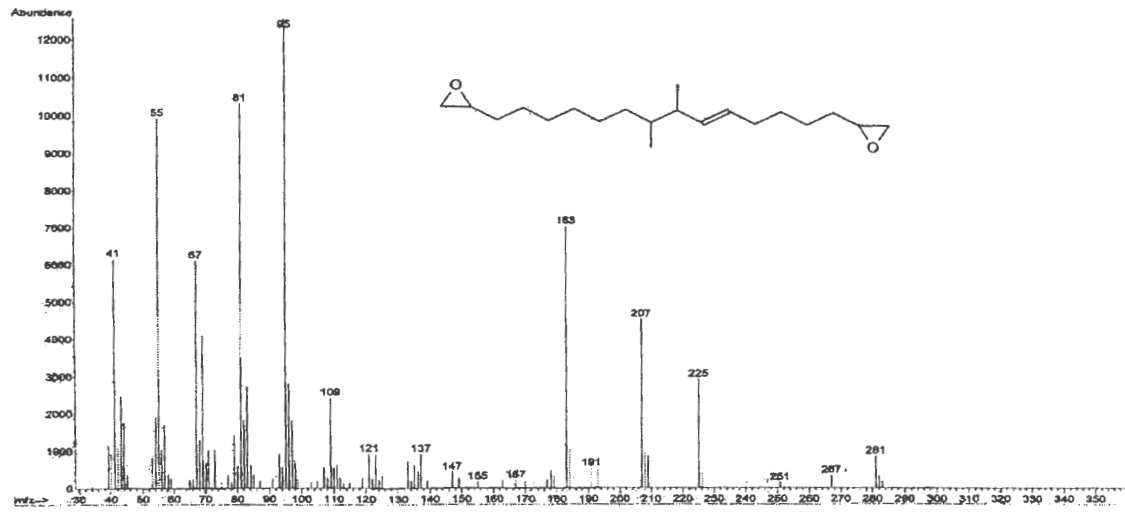
Appendix 2. Mass spectrum of 1,2-epoxy-9-methyl-nonoxy-1,8-decadiene.



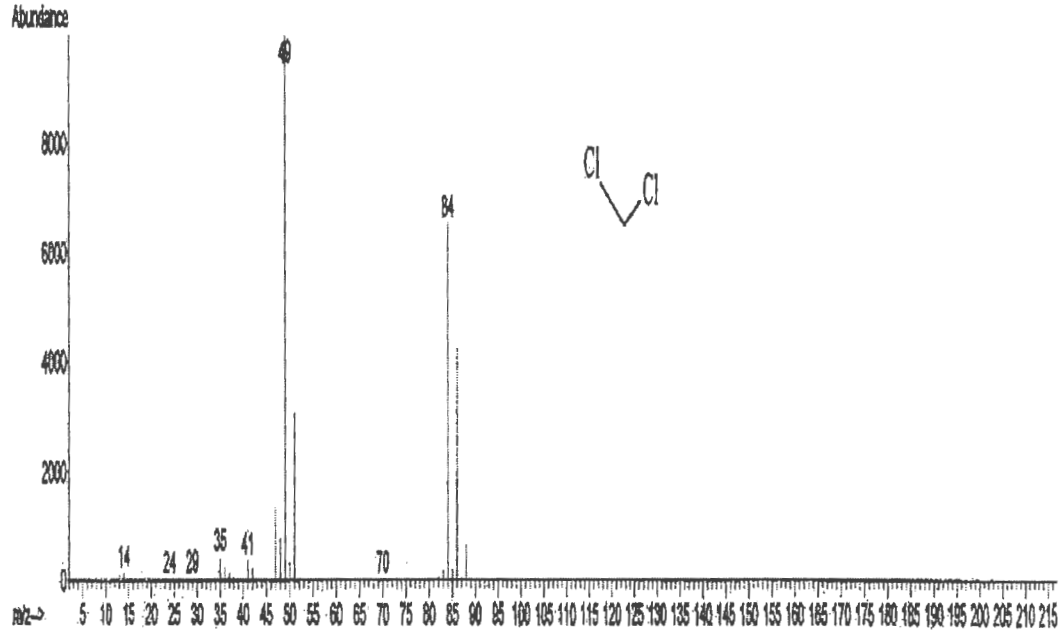
Appendix 3. Mass spectrum of 3-(1,2-epoxy-heptyl)-11,12-epoxy-4-methyl-2-dodecene.



Appendix 4. Mass spectrum of 3-(1,2-epoxy-heptyl)-11,12-epoxy-4-methyl-1-dodecene.

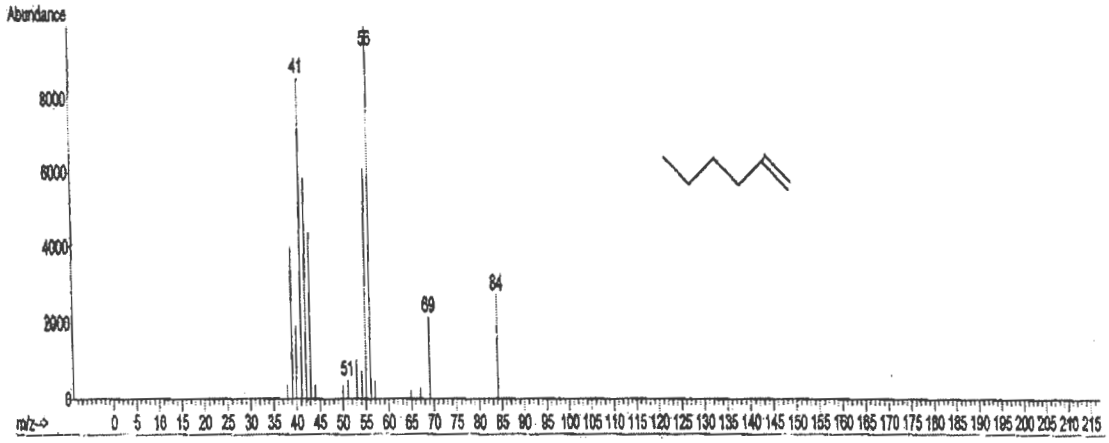


Appendix 5. Mass spectrum of 1,2,17,18-diepoxy-9,10-dimethyl-7-octadecenoate.

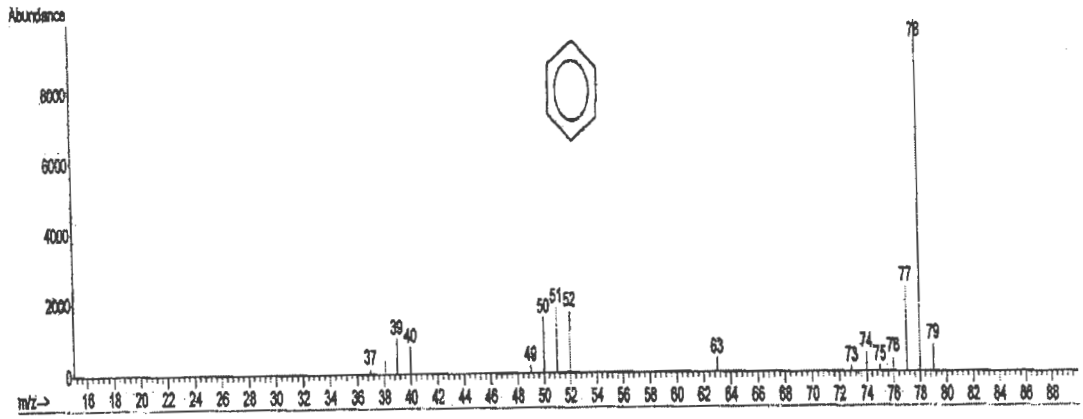


Appendix 6. Mass spectrum of methylene chloride.

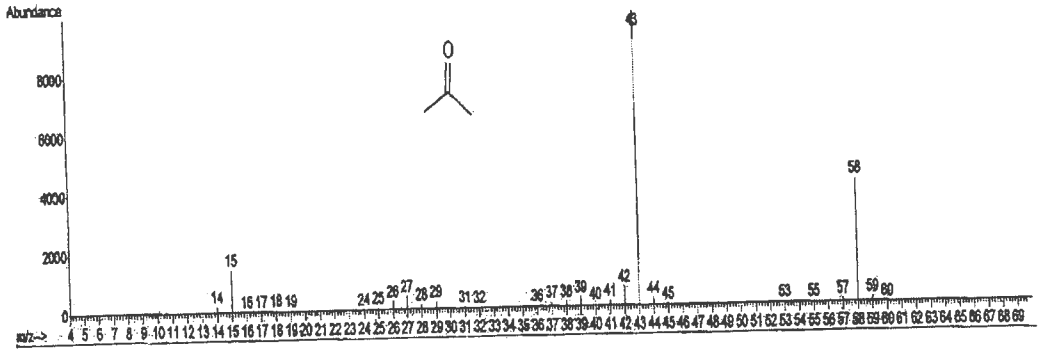
NWU LIBRARY



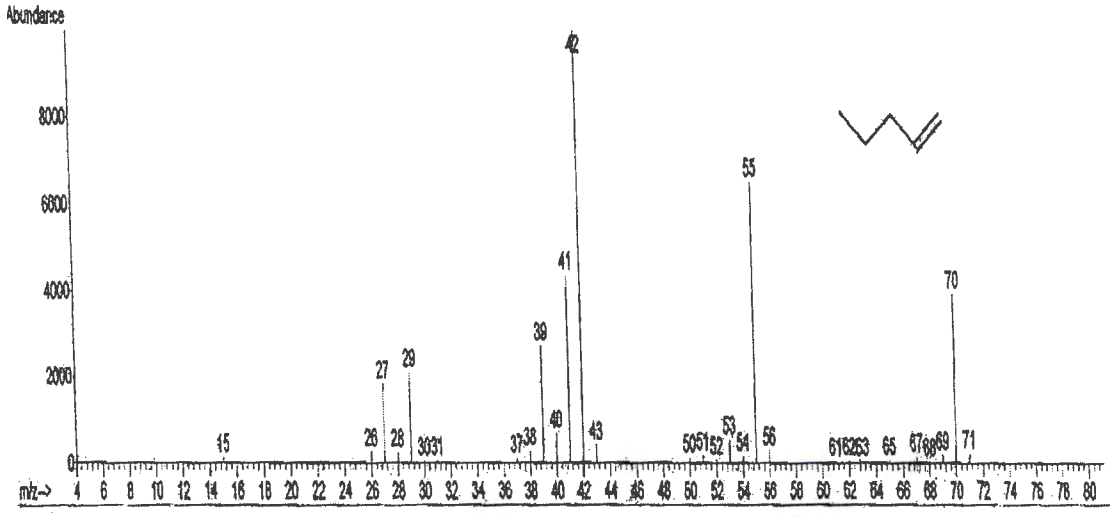
Appendix 7. Mass spectrum of 1-hexene.



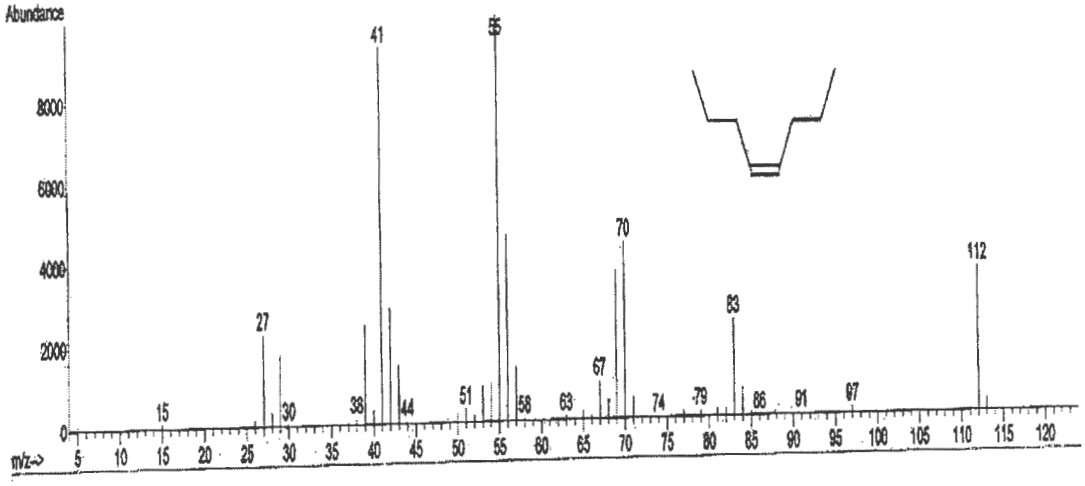
Appendix 8. Mass spectrum of benzene.



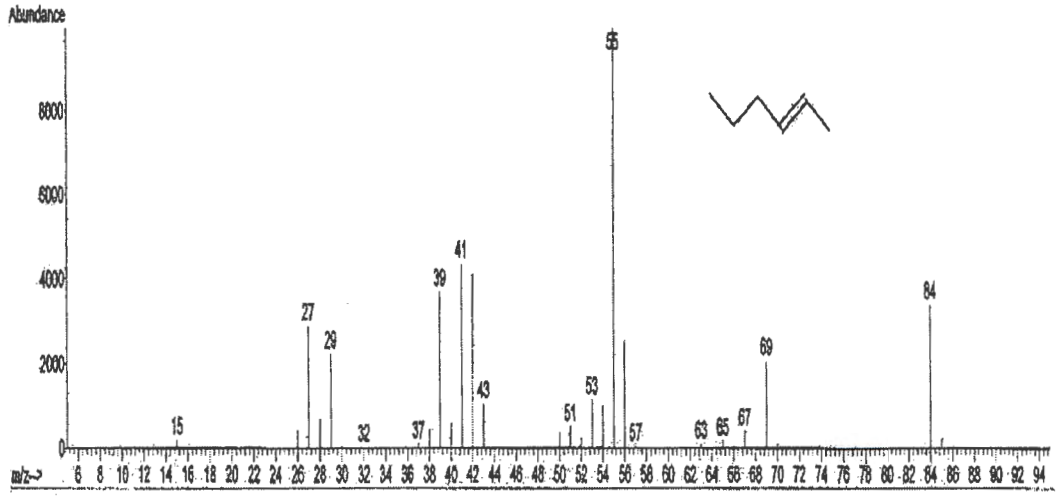
Appendix 9. Mass spectrum of acetone.



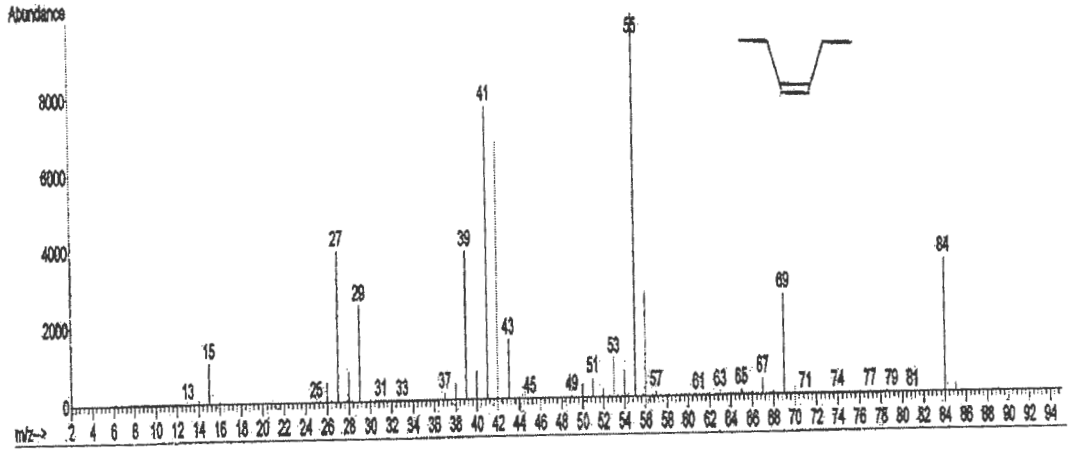
Appendix 10. Mass spectrum of 1-pentene.



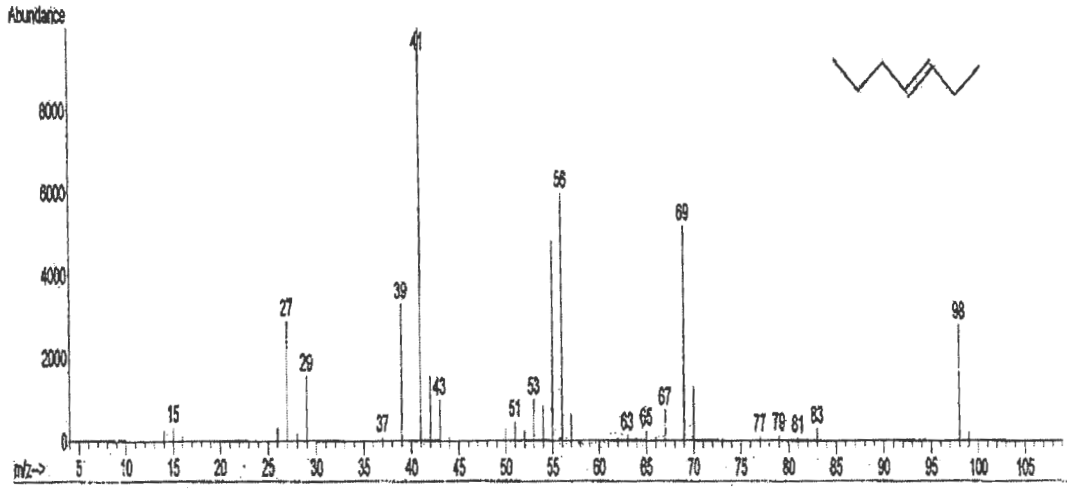
Appendix 11. Mass spectrum of (Z)-4-octene.



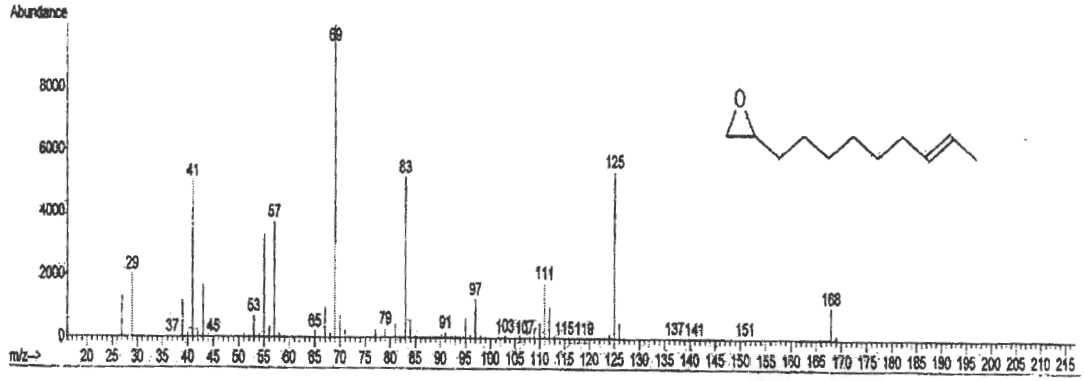
Appendix 12. Mass spectrum of (E)-2-hexene.



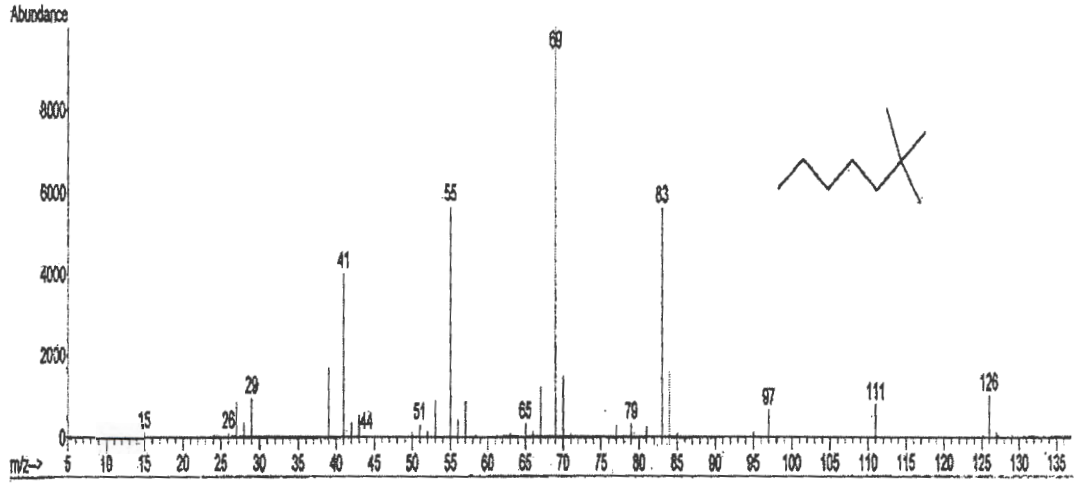
Appendix 13. Mass spectrum of (Z)-3-hexene.



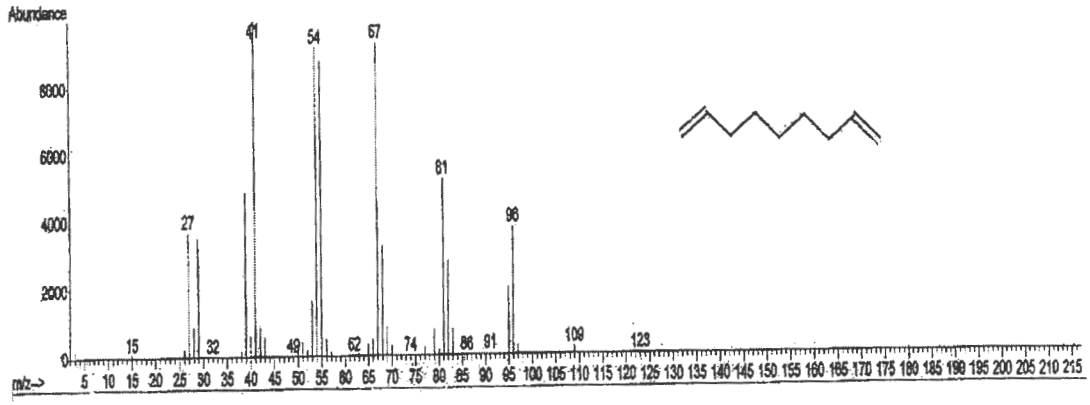
Appendix 14. Mass spectrum of (E)-3-heptene.



Appendix 15. Mass spectrum of 1, 2-epoxy-9-undecene.



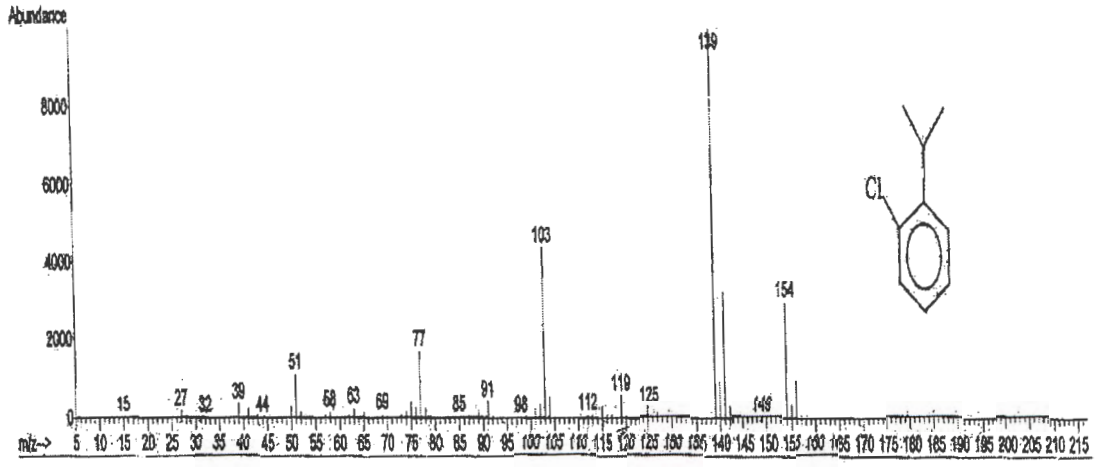
Appendix 16. Mass spectrum of trans-2, 2-dimethyl-3-heptene.



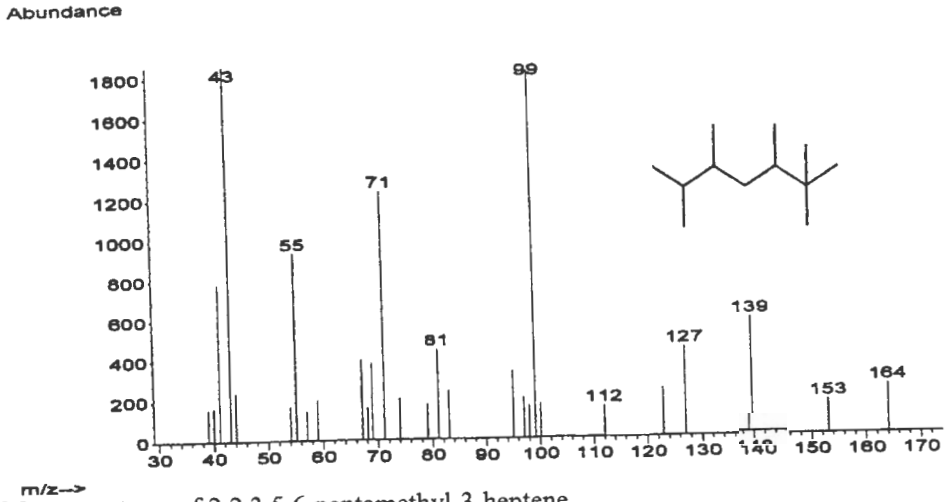
Appendix 17. Mass spectrum of 1, 8-nonadiene.



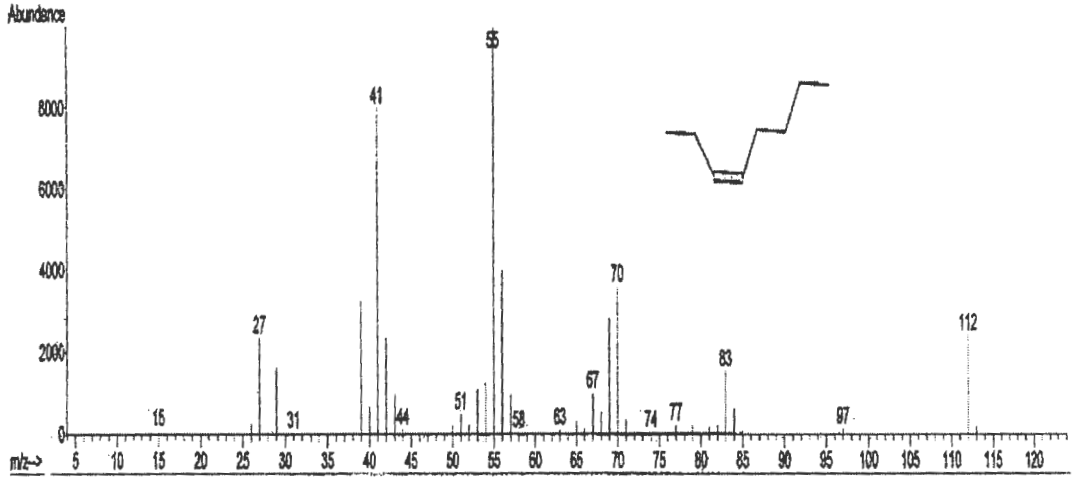
Appendix 18. Mass spectrum of trans-4-nonene.



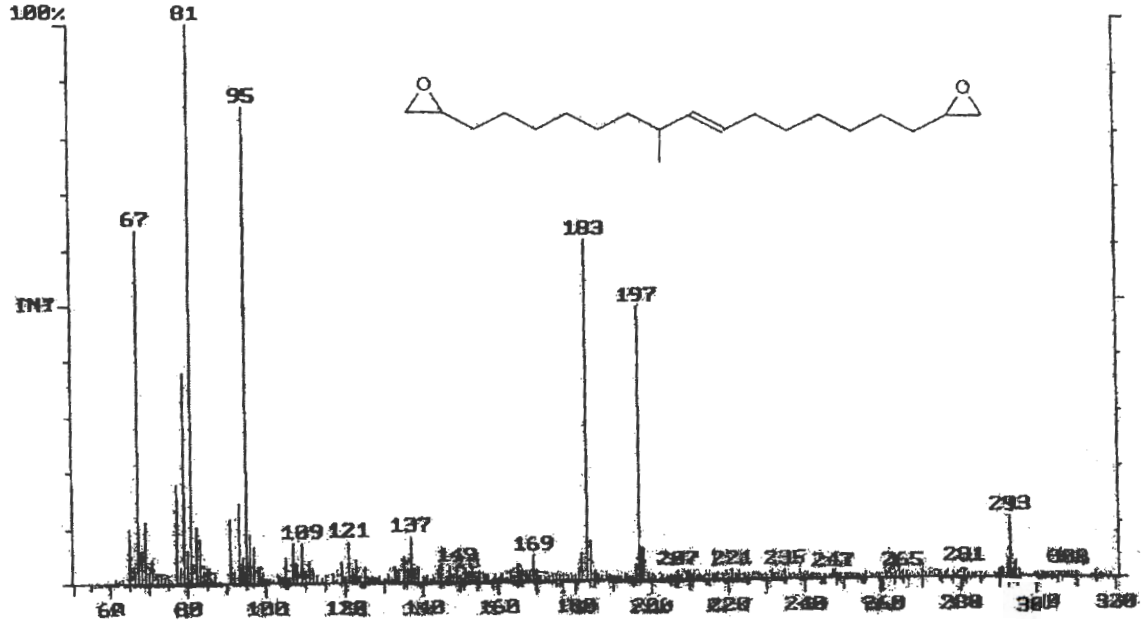
Appendix 19. Mass spectrum of 2-(1-methylethyl)-1-chlorobenzene.



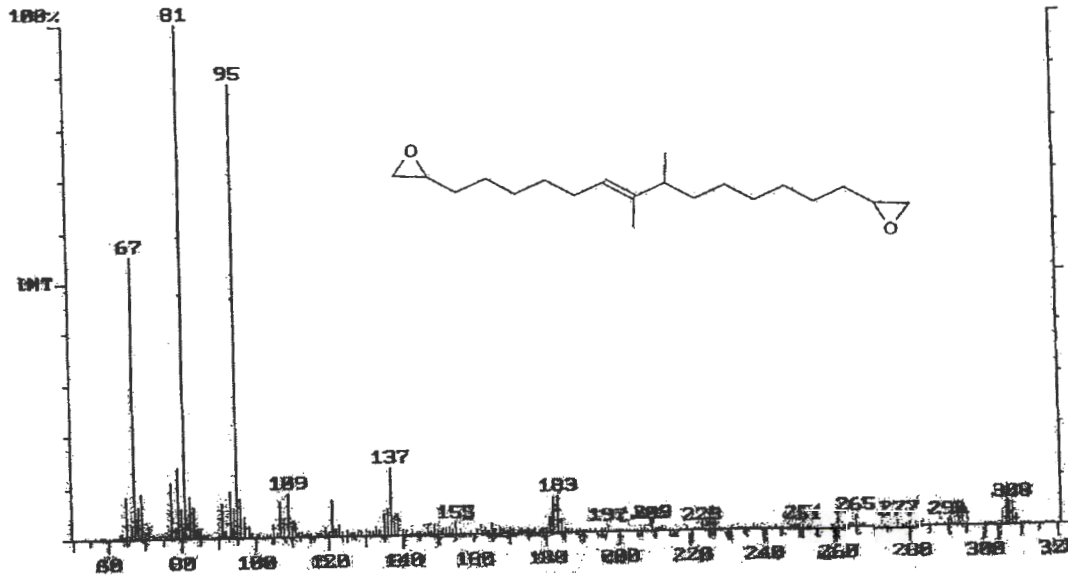
Appendix 20. Mass spectrum of 2,2,3,5,6-pentamethyl-3-heptene.



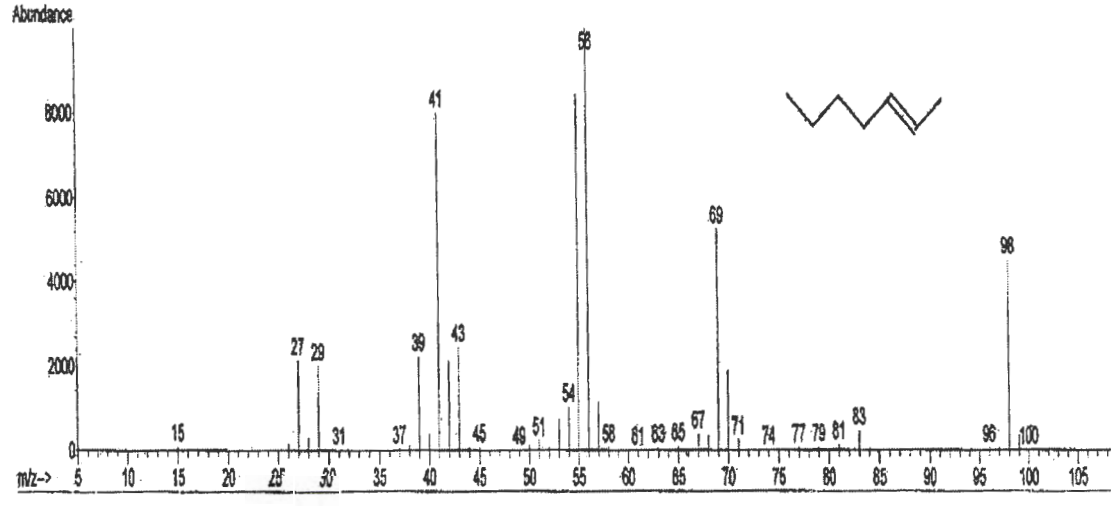
Appendix 21. Mass spectrum of (Z)-3-octene.



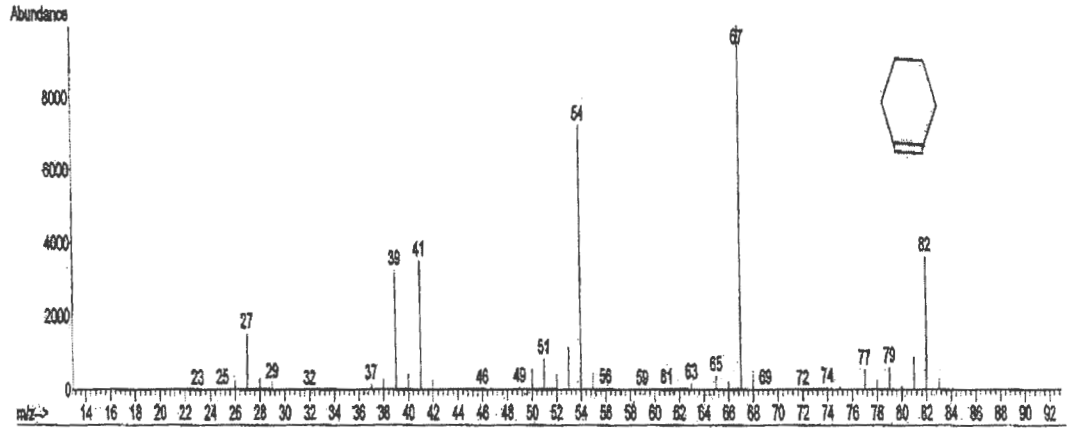
Appendix 22. Mass spectrum of 1,2,18,19-diepoxy-11-methyl-9-nonadecene.



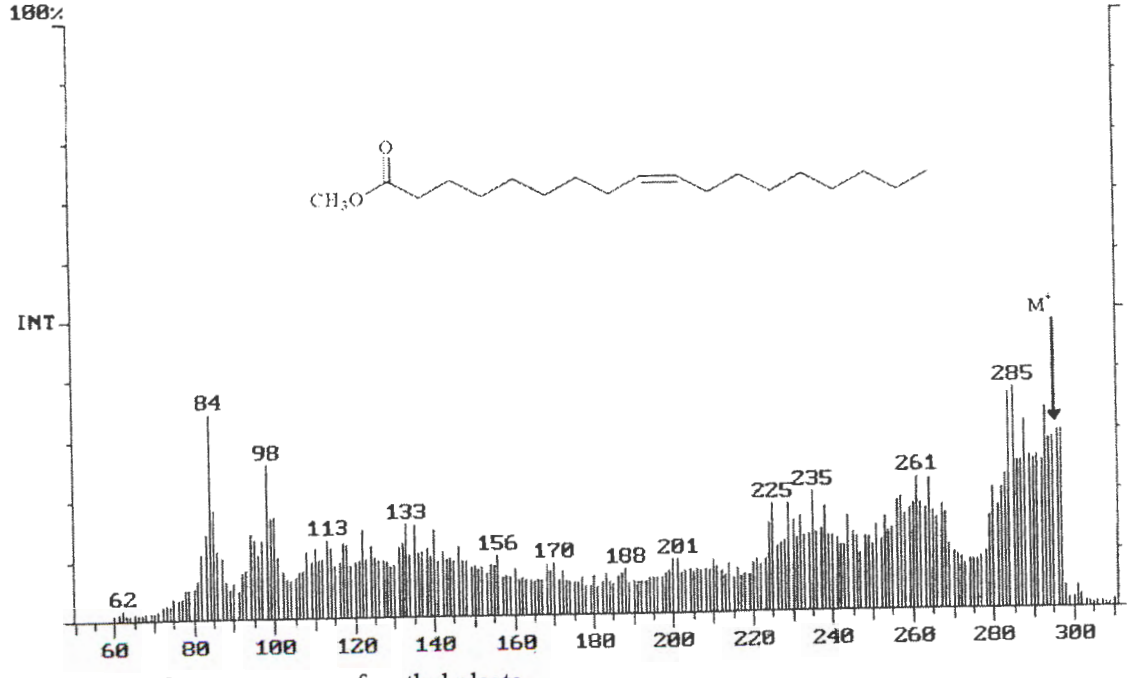
Appendix 23. Mass spectrum of 1,2,17,18-diepoxy-9,10-dimethyl-8-octadecene.



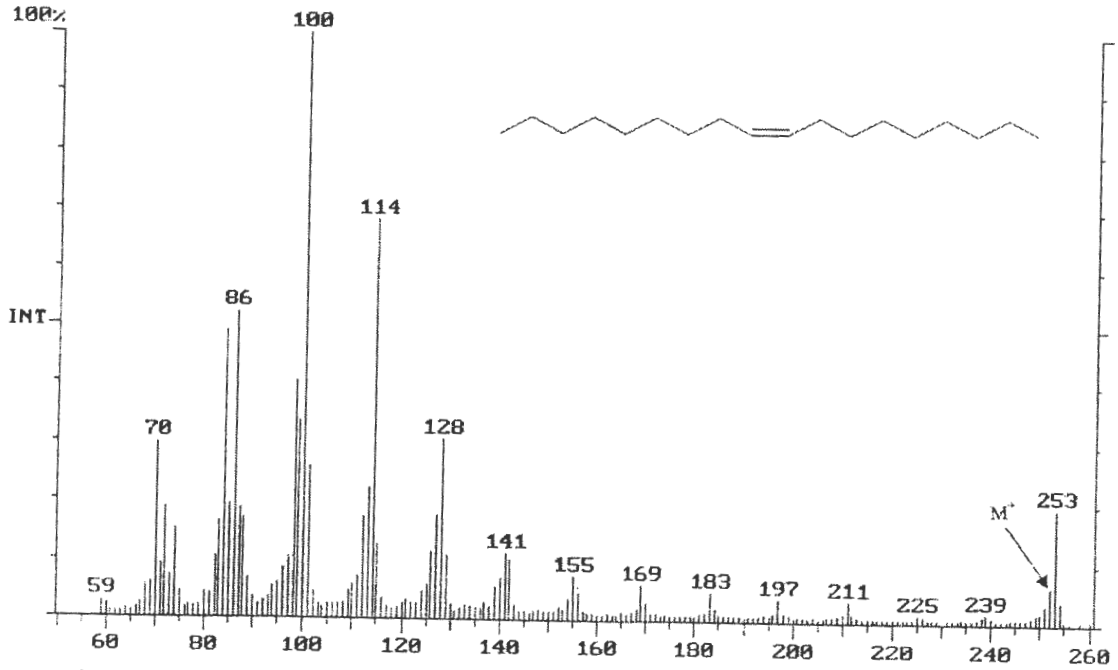
Appendix 24. Mass spectrum of 2-heptene.



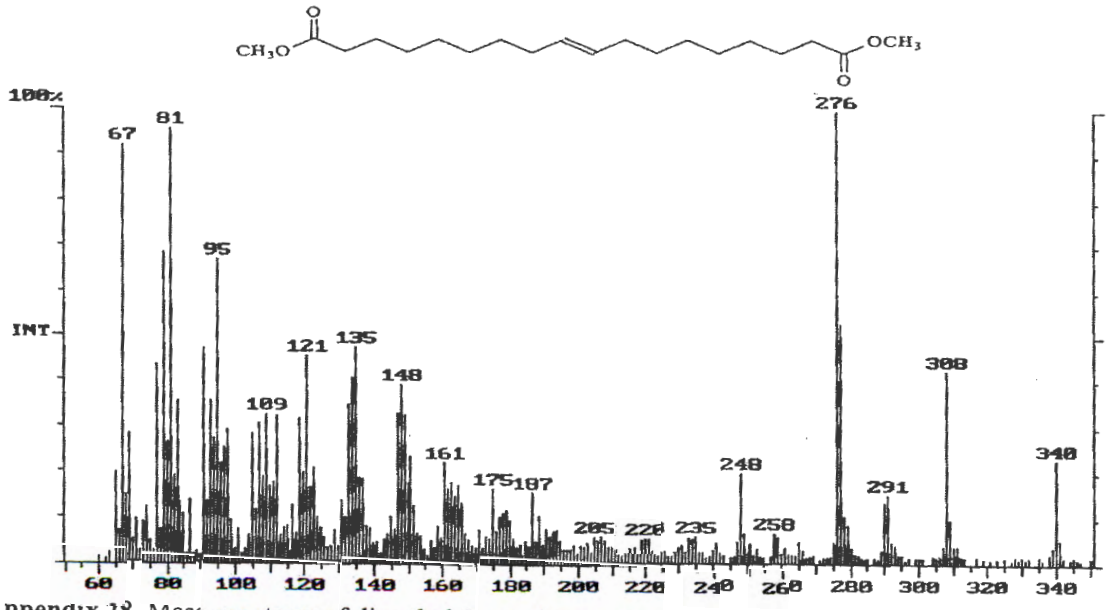
Appendix 25. Mass spectrum of cyclohexene.



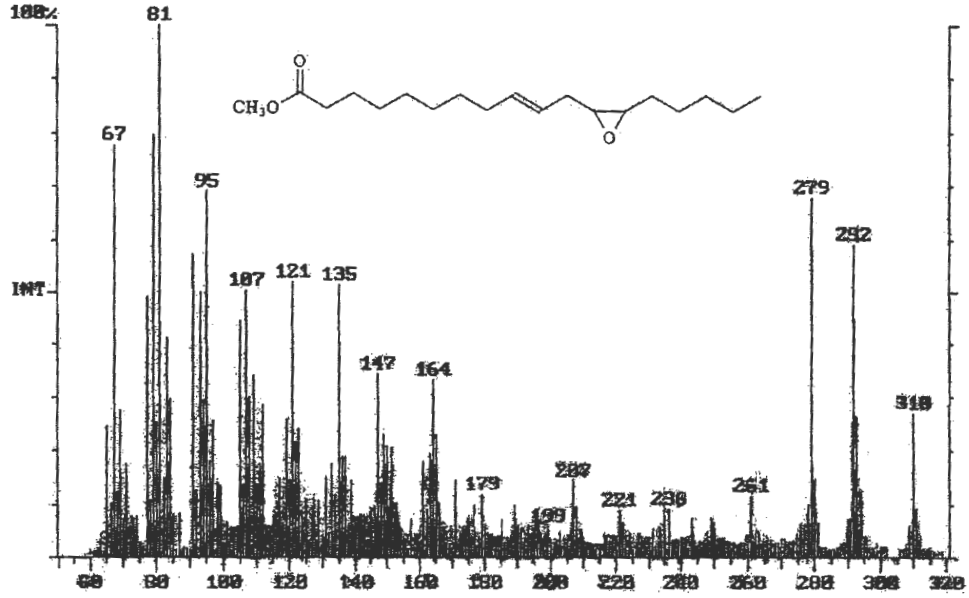
Appendix 26. Mass spectrum of methyl oleate.



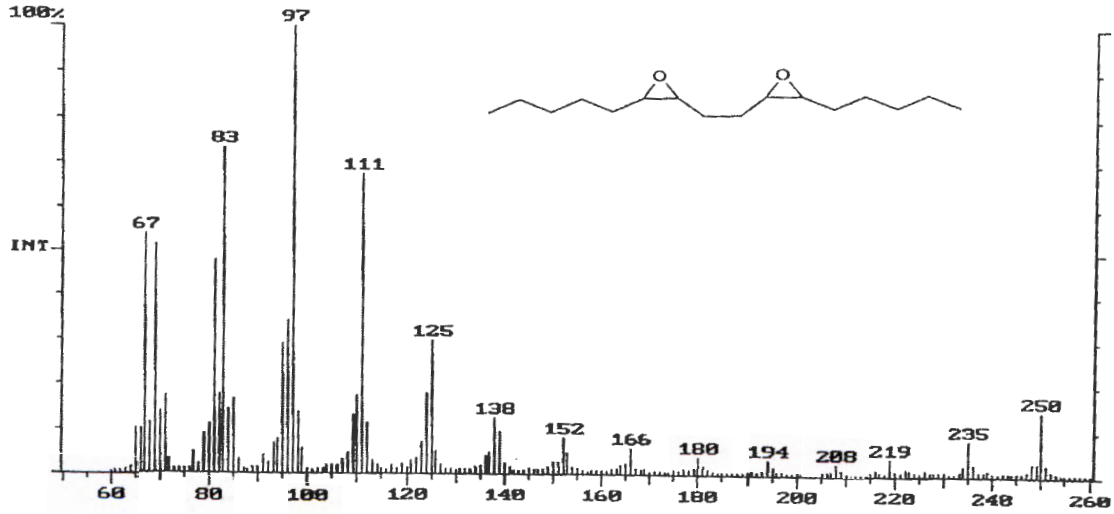
Appendix 27. Mass spectrum of 9-octadecene.



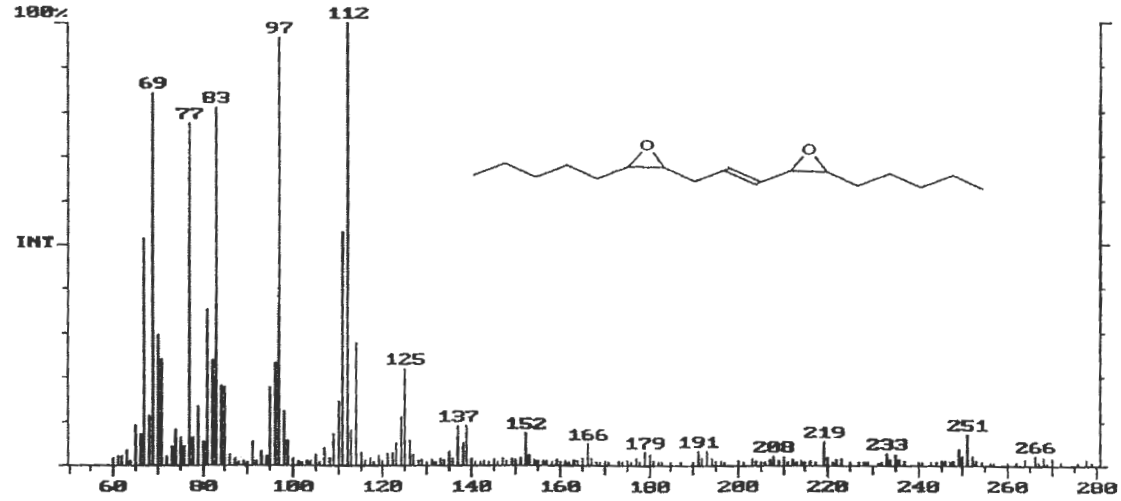
Appendix 28. Mass spectrum of dimethyl-9-octadecenoate.



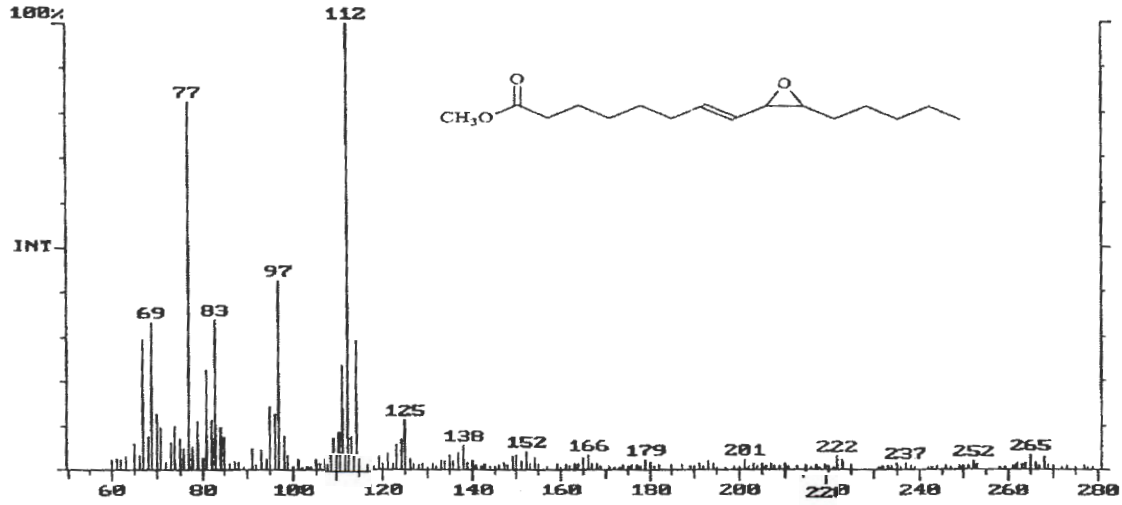
Appendix 29. Mass spectrum of methyl-12,13-epoxy-9-octadecenoate.



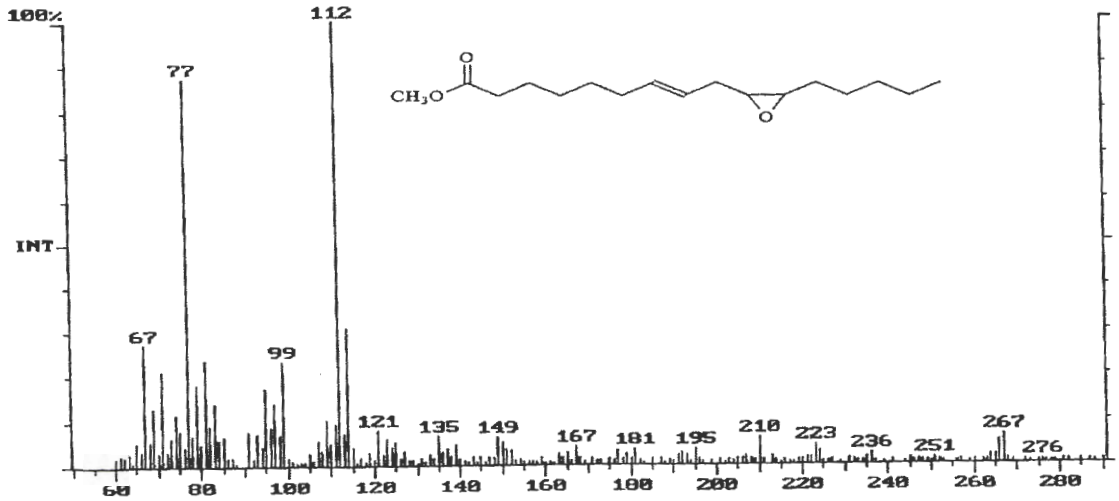
Appendix 30. Mass spectrum of 6,7,10,11-diepoxy-8-hexadecene.



Appendix 31. Mass spectrum of 6,7,11,12-diepoxy-8-heptadecene.

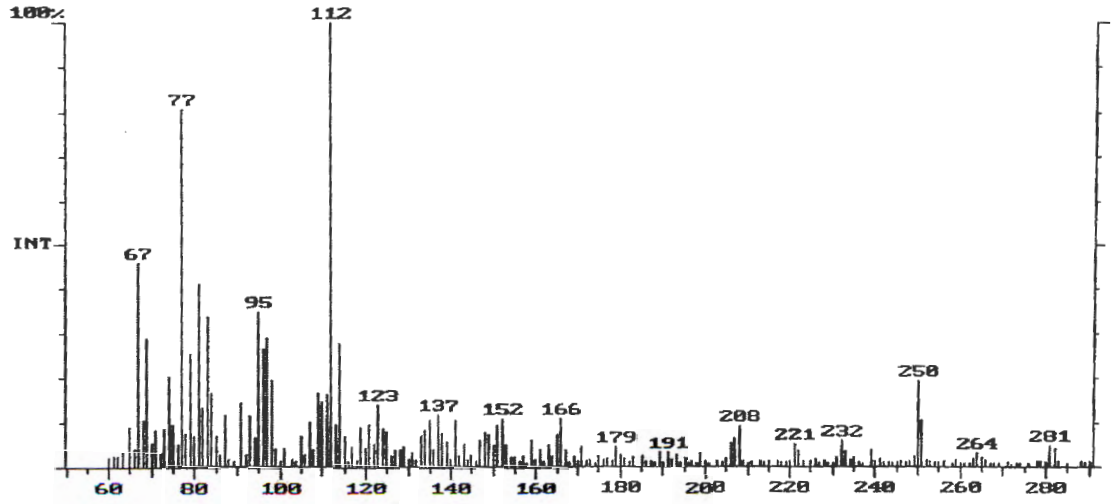


Appendix 32. Mass spectrum of methyl-9,10-epoxy-7-pentadecenoate.

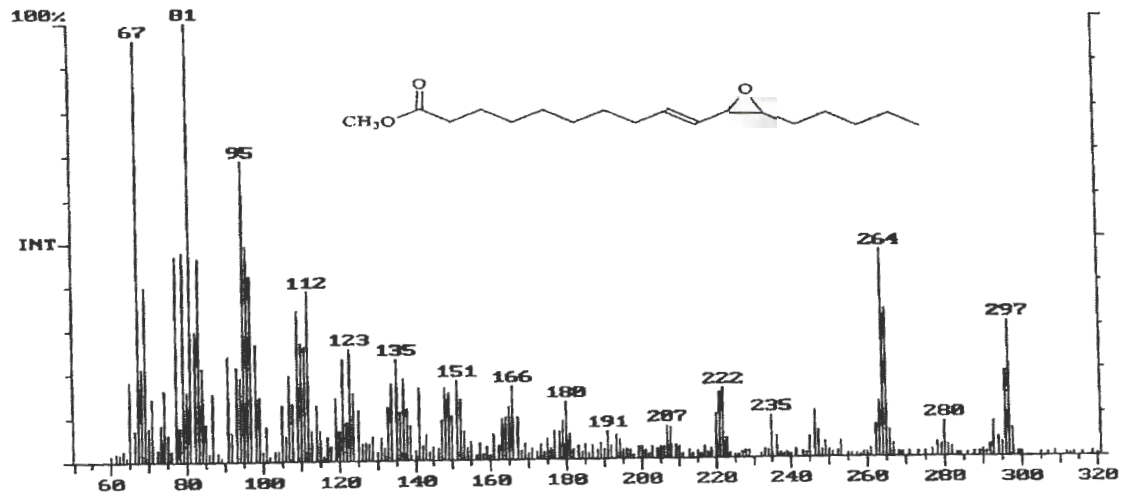


Appendix 33. Mass spectrum of methyl-10,11-epoxy-7-hexadecenoate.

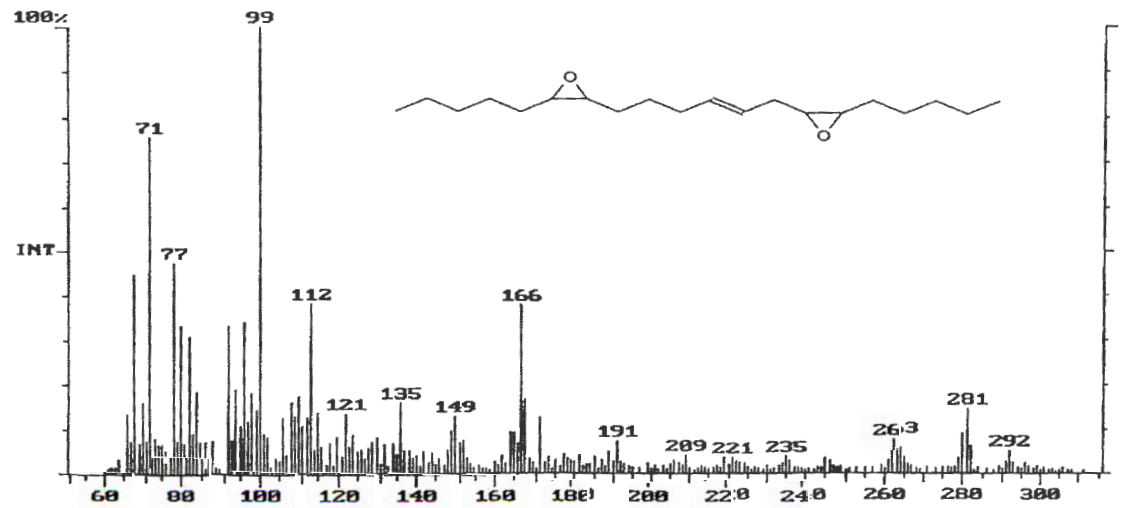
NWU LIBRARY



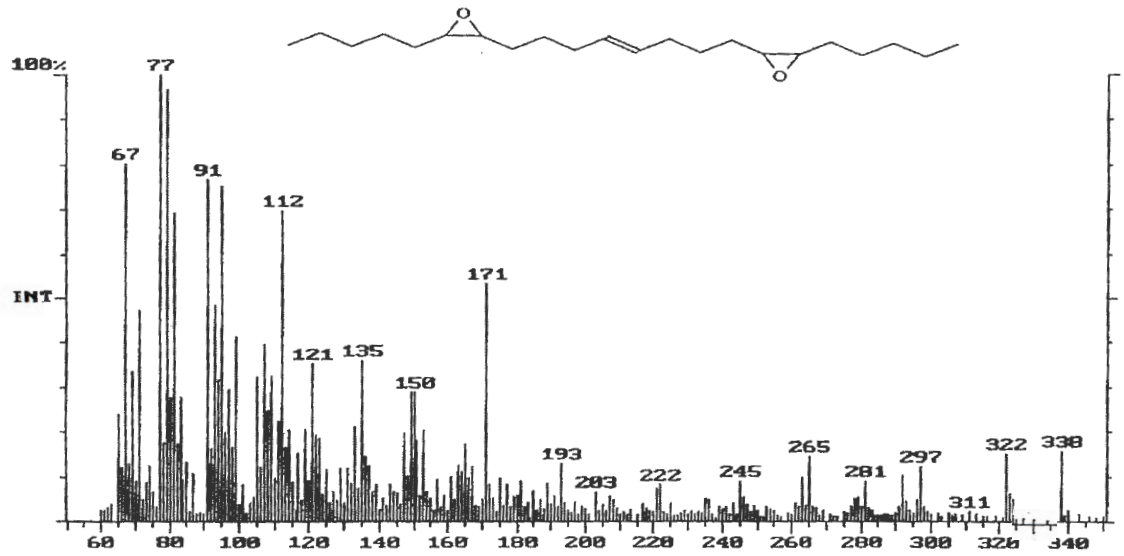
Appendix 34. Mass spectrum of dimethyl-7-tetradecenoate.



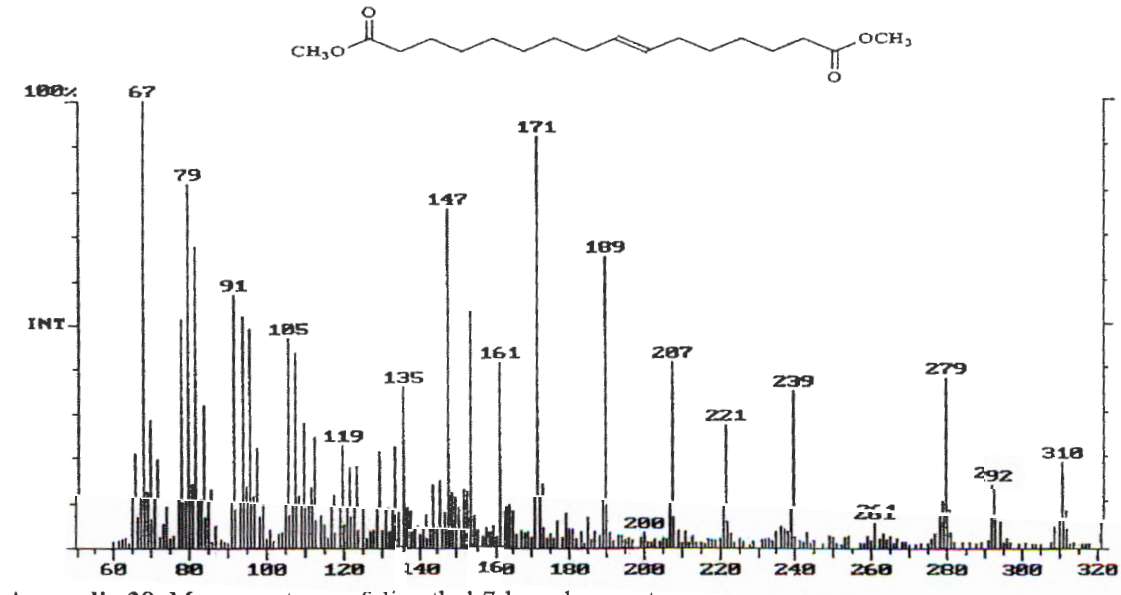
Appendix 35. Mass spectrum of methyl-11,12-epoxy-9-heptadecenoate.



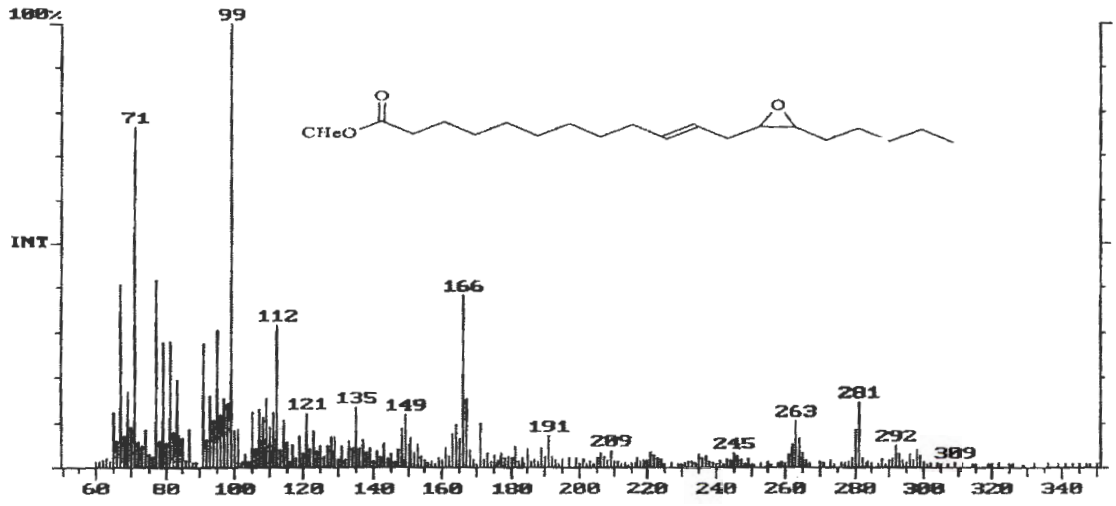
Appendix 36. Mass spectrum of 6,7,14,15-diepoxy-9-cosene.



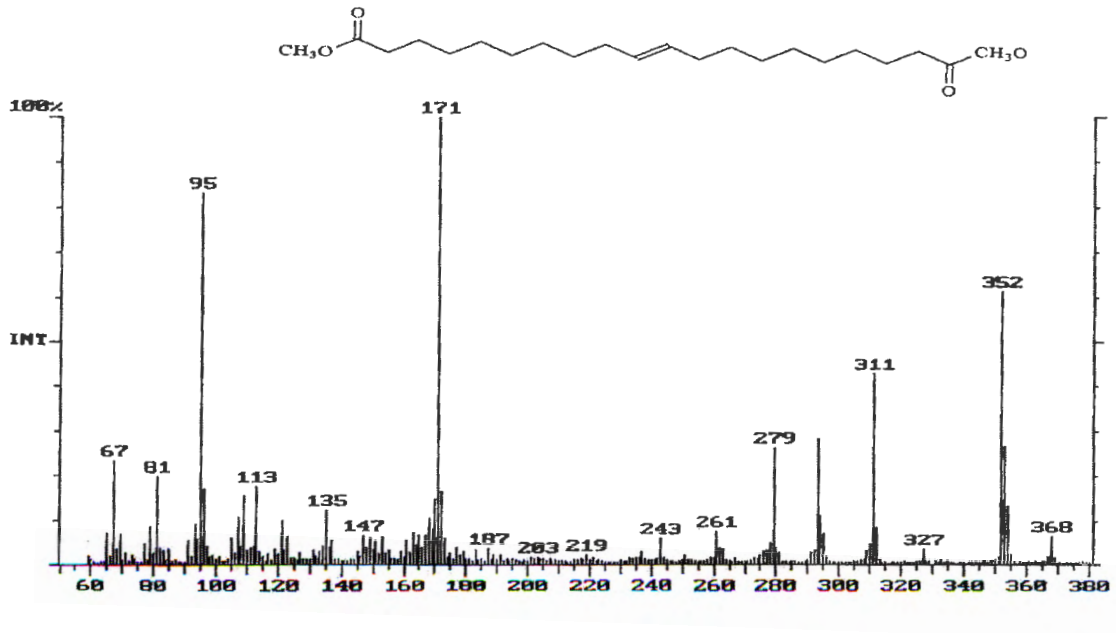
Appendix 37. Mass spectrum of 6,7,16,17-diepoxy-11-docosene.



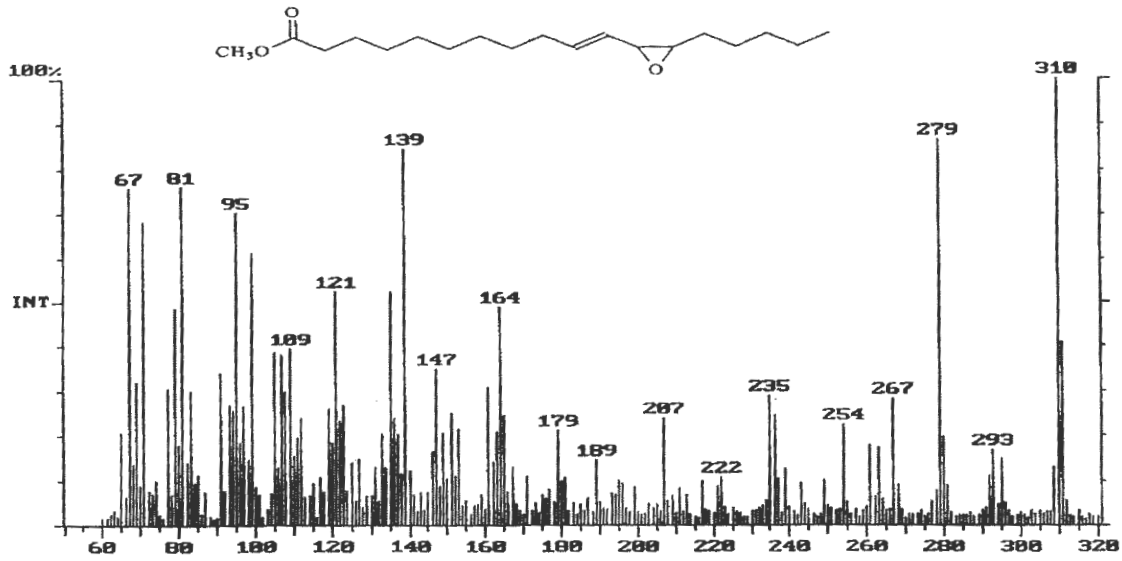
Appendix 38. Mass spectrum of dimethyl-7-hexadecenoate.



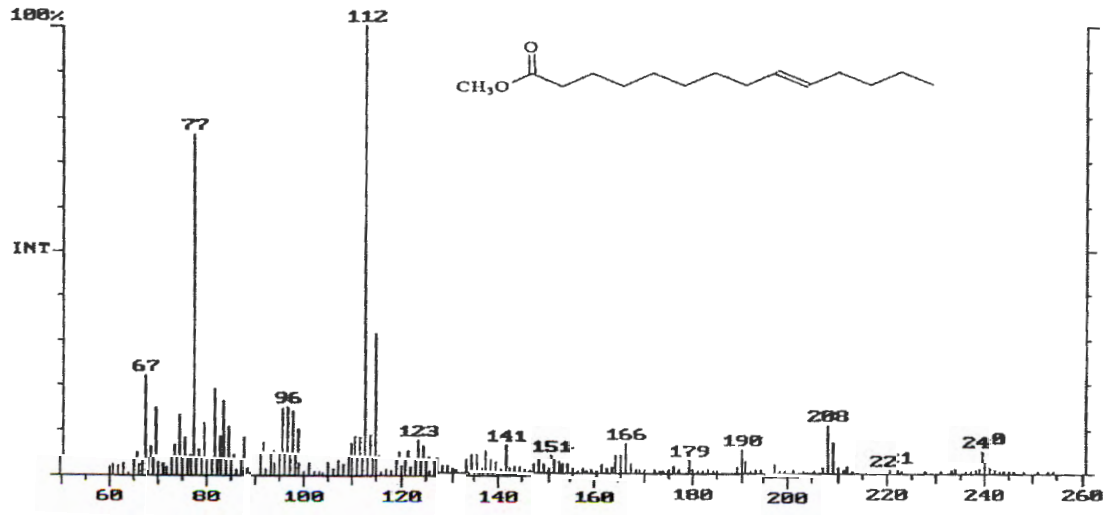
Appendix 39. Mass spectrum of methyl-13,14-epoxy-10-nonadecenoate.



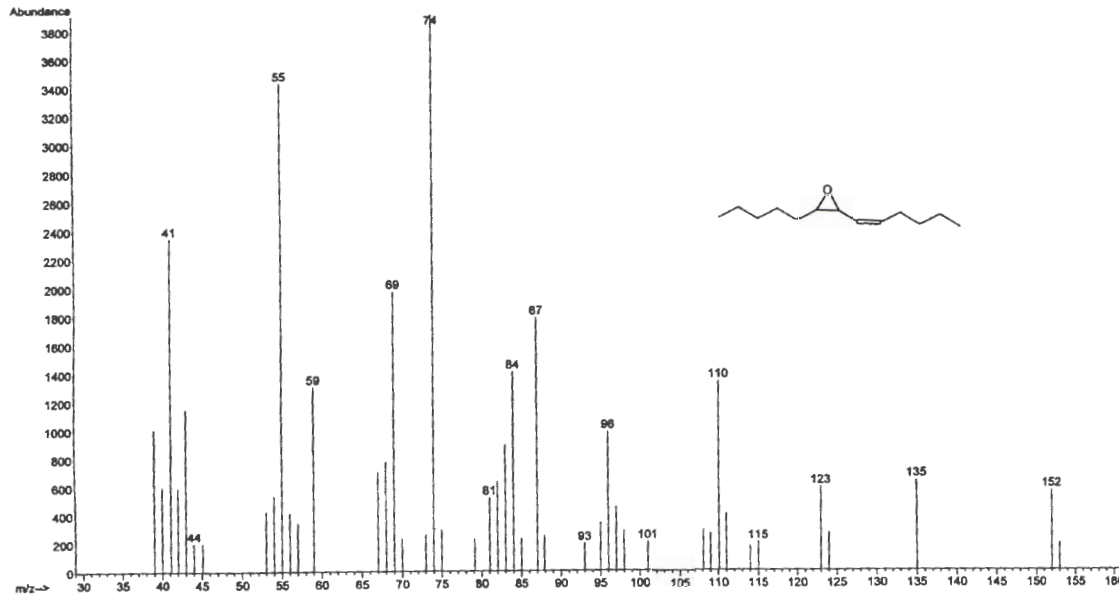
Appendix 40. Mass spectrum of dimethyl-10-cosaenoate.



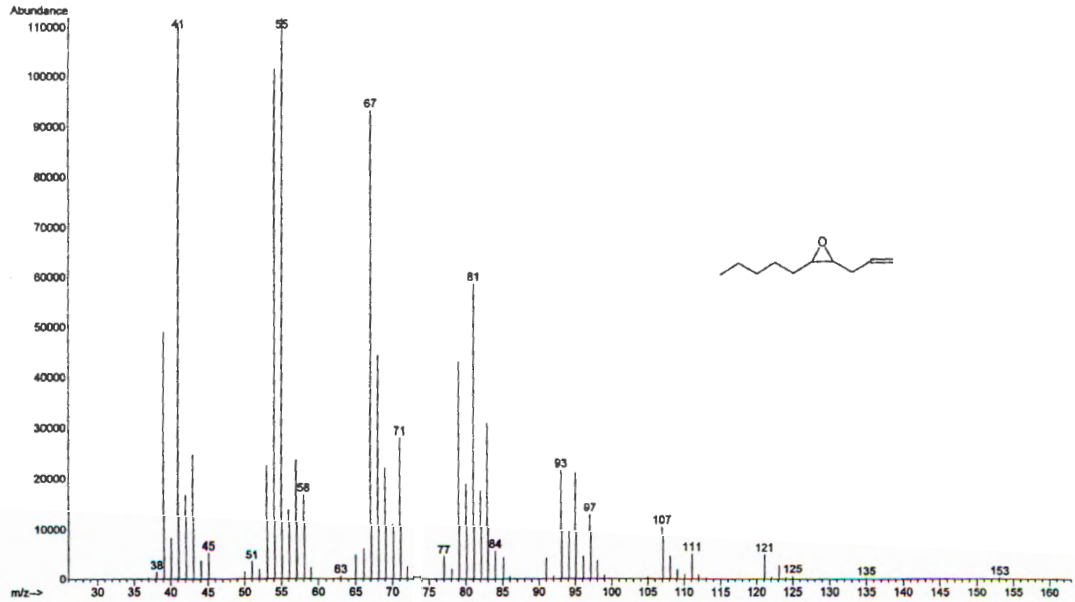
Appendix 41. Mass spectrum of methyl-12,13-epoxy-10-octadecenoate.



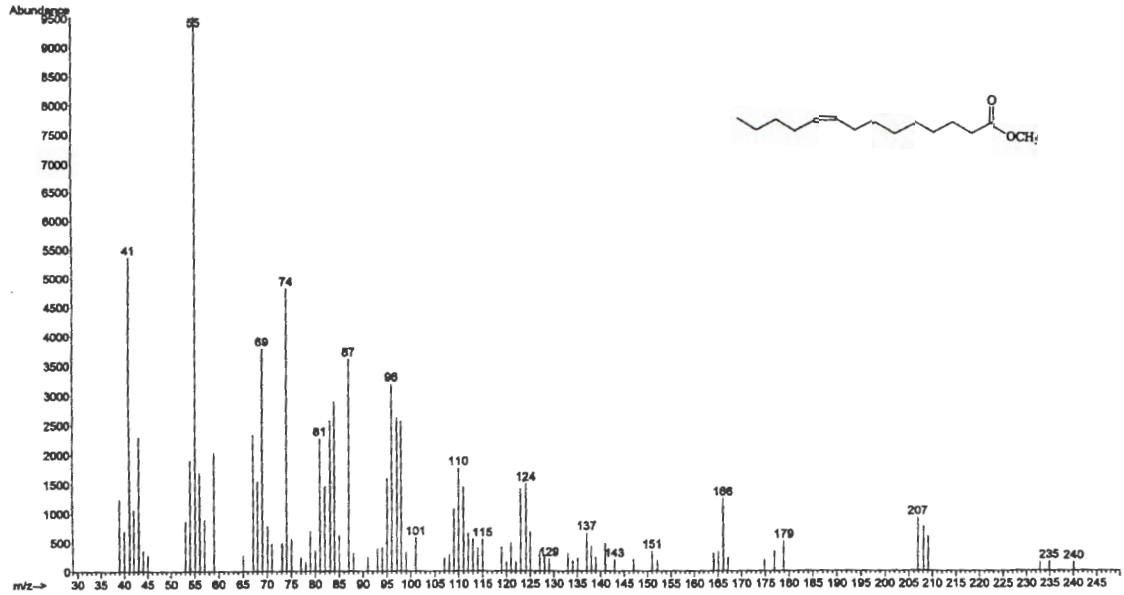
Appendix 42. Mass spectrum of methyl-9-tetradecenoate.



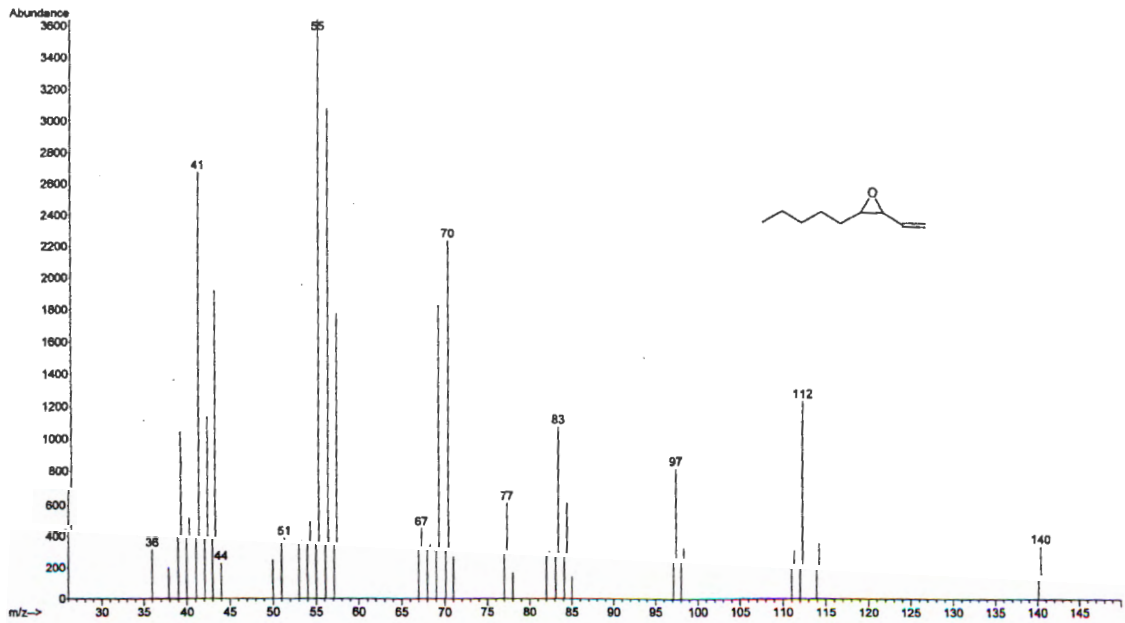
Appendix 43. Mass spectrum of 6,7-epoxy-8-tridecene.



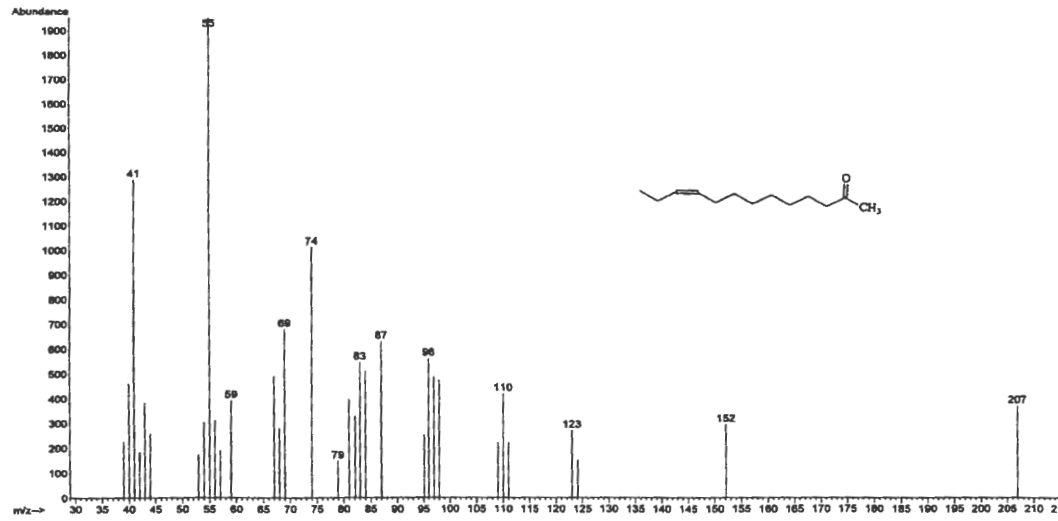
Appendix 44. Mass spectrum of 6,7-epoxy-9-decene.



Appendix 45. Mass spectrum of methyl-9-tetradecenoate.



Appendix 46. Mass spectrum of 6,7-epoxy-8-nonene.



Appendix 47. Mass spectrum of methyl-9-dodecenoate.