Synthesis and characterisation of novel organophosphorus polymers for specific surface interactions

Jones, Mark Stuart

Jones, Mark Stuart (1992) *Synthesis and characterisation of novel organophosphorus polymers for specific surface interactions*, Durham theses, Durham University. Available at Durham E-Theses Online: http://etheses.dur.ac.uk/6168/

Synthesis and Characterisation of Novel Organophosphorus Polymers for Specific Surface Interactions.

by

Mark Stuart Jones, B.Sc. (Hons). G.R.S.C.
(Graduate Society)

A thesis submitted
for the Degree of Doctor of Philosophy
to the University of Durham
1992.

to Vicki.

ACKNOWLEDGEMENTS.

I would like to express sincere thanks to Professor W.J. Feast for his continual advice and encouragement throughout the supervision of this work.

Thanks must also go to several members of the academic and technical staff at the University of Durham. Those I am particularly grateful to are, Mrs. J.M. Say for recording the high quality NMR spectra, Dr. A.M. Kenwright and Professor R.K. Harris for many NMR analysis discussions, Mr. D. Hunter for his assistance in the High Pressure Laboratory, Dr. M. Jones for recording the mass spectra and Mr. G.M. Forest for his assistance in GPC analysis.

I am also very grateful to all my colleagues at the Interdisciplinary Research Centre at the University of Durham, especially Dr. B. Wilson and Dr. E. Khosravi-Babadi for many helpful discussions and John Holland and Paul Richardson for their friendship and sense of humour.

A mention must also go to Barbara, John-Paul and Jane Hadfield and Billy and Valerie Jewson, whose friendship and generosity throughout my stay in Durham has been greatly appreciated.

The author acknowledges the funding from Ciba-Geigy Industrial Chemicals.

Finally, very special thanks go to my parents for their love, support and encouragement throughout my education, my brother Gavin and Vicki for her continual love, patience and understanding.

MEMORANDUM.

The work in this thesis was carried out in the Chemistry and IRC Laboratories of the University of Durham between October 1989 and September 1992. This work has not been submitted for any other degree and is the original work of the author except where acknowledged by references.

ABSTRACT.

The work described in this thesis was concerned with the synthesis and attempted Ring Opening Metathesis Polymerisations (ROMP) of a series of monocyclic phospholenes and organophosphorus derivatives of bicyclo[2.2.1]heptene using a variety of catalysts and conditions.

This thesis comprises five chapters. The first chapter deals with the background of fire retardancy, industrial water treatment and ROMP. Chapter two describes the synthesis and characterisation of some potential organophosphorus monomers. Chapter three gives details of the attempted ROMP of the potential monomers prepared in chapter two. Investigations into the possible preparation of oligomers using a variety of chain transfer agents are described in chapter four. The conclusions and proposals for future work are outlined in the final chapter.

CONTENTS.

ABBREVIATIONS.

The following abbreviations have been used in this thesis:-

ROMP - Ring Opening Metathesis Polymerisation.
CTA - Chain Transfer Agent.
NMR - Nuclear Magnetic Resonance.
COSY - Correlated Spectroscopy.
HETCOR - Heteronuclear Correlation Spectroscopy.
DEPT - Distortionless Enhancement by Polarisation Transfer.
GC - Gas Chromatography.
HPLC - High Performance Liquid Chromatography.
GPC - Gel Permeation Chromatography.
M_n - Number average molecular weight.
M_w - Weight average molecular weight.
DP - Degree of Polymerisation.
DMVP - Dimethylvinylphosphonate.
DME - 1,2-Dimethoxyethane.
TMSBr - Trimethylsilyl bromide.

Chapter One:
Introduction.

1.1 Introduction.

The objective of the work described in this thesis was to investigate the possibility of preparing phosphorus containing polymers by Ring Opening Metathesis Polymerisation (ROMP). Such polymers are of potential interest in a number of fields of application, such as water treatment (i.e. scale prevention), surface coating applications related to corrosion inhibition and in the general area of flame retardancy.[1] In this chapter the motivation and objectives of the work will be set in context.

1.2 The use of flame retardants.

The flammability of organic polymers, including those occurring naturally, has been a problem for several hundred years and this has led to the detailed investigation into fire retardancy.[2,3] The first known fire retardants were used by the Egyptians and later by the Romans, who used alum (potassium aluminium sulphate) and vinegar to decrease the ease of combustion of wood and other natural organic polymers. The first patent to describe a method for treating wood to reduce its flammability was issued to Wild in 1735,[4] the substrate was exposed to a mixture of alum, borax and vitriol. In 1783 the Montgolfier brothers coated their balloons with alum to reduce the fire hazards from the fabric. The first phosphorus containing fire retardants, comprising a mixture of ammonium phosphate, ammonium chloride and borax, were used by Gay-Lussac to protect the wood and textiles used in theatres.[5]

Today as the use of synthetic organic polymers becomes more widespread the flammability risks increase and more fire retardants have to be used, not only to prevent flaming combustion but also to inhibit the production of toxic fumes.[6]

The burning of a polymer is a highly complex process involving a series of interrelated and/or independent stages. Three phases are involved, the condensed phase, the gaseous phase and the interface between the condensed and gaseous phases.[3] In order to reduce the flammability of a material it is essential to break into this complex series of processes at one or more stages and reduce the rate and/or change the mechanism at that point.[2,7]

The first and most important step in the combustion of a polymer is the fuel production stage in which an external heat source causes an increase in temperature, which results in the dissociation of chemical bonds and the evolution of volatile materials. These diffuse into the surrounding air creating a flammable mixture and combustion starts when this mixture reaches the ignition temperature. Once initiated the combustion reaction is exothermic. The third stage is flaming combustion, which only proceeds if the heat is sufficient to decompose the polymer and the temperature is high enough to ignite the decomposition products and the amount of heat transferred back to the polymer is high enough to maintain the cycle (*Figure 1.1*).[6]

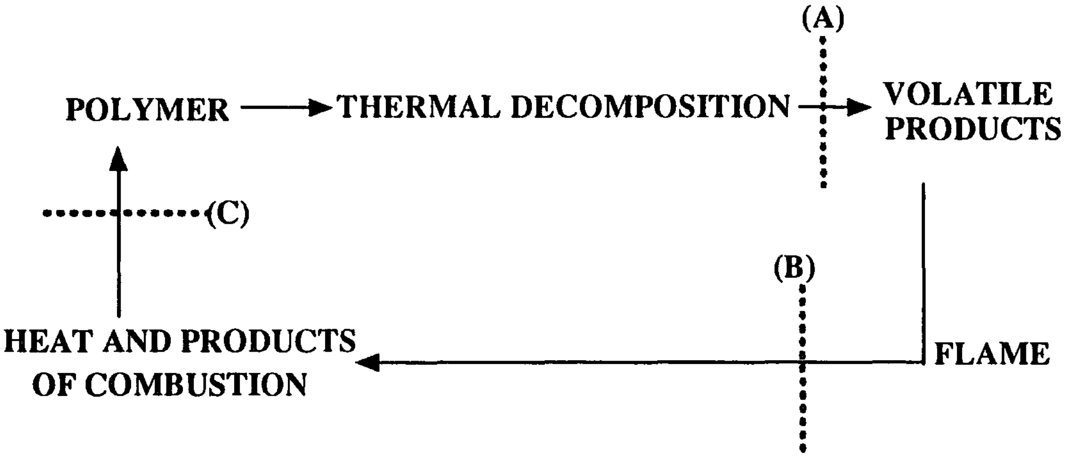


Figure 1.1: The combustion of a polymer.

Fire retardants therefore have to interrupt the cycle at one of the three points (A) -by modifying the thermal decomposition, (B) -quenching the flame or (C) -reducing the heat supply from the flame back to the decomposing polymer.

Smouldering or non-flaming combustion occurs with high surface area polymers which break down to form chars. The first stage involves thermal or oxidative breakdown followed by ignition and the burning of the char, occurring at much lower temperatures than the ignition temperatures of the volatiles, and non-flaming combustion occurs if there is no local ignition source or if the rate of production of the volatiles is too low.

There are two main types of fire retardant namely, reactive and additive retardants. A reactive fire retardant chemically binds to the polymer structure so that it effectively forms a copolymer, whereas an additive retardant is added to the polymer and blended by physical means. The additive type is more widely used as it is more flexible, is less likely to alter the physical properties of the original polymer and can be incorporated in the final stages of production.[3]

There are, in principle, several modes of action by which a fire retardant can act.

(a) Both additive and reactive types may change the mechanism of breakdown of the polymer in such a way that the rate of evolution and type of gaseous decomposition products are altered so that when the gases interdiffuse with the air the resulting mixture is no longer flammable.

(b) The flame retardant may cause the chemical termination of the free radical chain reactions in the condensed phase, which are responsible for the thermal decomposition of the polymer.

(c) Inert solids, known as fillers, are often incorporated into the polymers to act as heat sinks, conducting heat away in order to prevent the polymers reaching their decomposition temperatures.

(d) If the flame retardants decompose endothermically they may have a cooling effect on the system by consuming some of the heat and the temperature can be kept below the ignition point.

(e) The surface of the polymer can be coated with a non-flammable protective layer, which insulates the polymer from the external heat source preventing either the formation of the volatile decomposition gases or their liberation into the gas phase. The coating may also exclude oxygen from the system.

(f) Some flame retardants incorporated into or coated on the polymer react or decompose in the condensed phase to form a highly insulating protective char coating which is non-flammable at normal oxygen concentrations. Inorganic acids, such as phosphoric acid and polyphosphoric acid are examples of good char promoters. If the intermediates of the char forming reaction are kept in a viscous elastic state at the final decomposition stage, the volatile gases can be trapped in the char layer to form an intumescent foam coating.[2,3]

Other methods of fire retardancy involve the inhibition of combustion:

(a) The additive may reduce the spread of the flame by releasing reactive gases, which subsequently participate in the flame reactions by quenching the highly active free radicals.

(b) By the release of small mists of particles a flame inhibitor may interfere with propagation of the flame by inducing chain termination by catalytic recombination of the free radicals created from the thermal decomposition of the polymer on the mist particle surface.

(c) Inert gases can also be released by the additives on decomposition of the polymer. These alter the composition of the gaseous products, which after interdiffusion with oxygen are no longer capable of sustaining the flame reactions.

(d) Certain additives are released as a heavy vapour when the polymer burns. This vapour smothers the flame.

(e) In some systems the fire retardant additive has the effect of depolymerisation of the polymer to lower the molecular weight, which eases melting. As the melted polymer drips it carries away some of the heat which would have been used to decompose the polymer, hence decreasing the flammability. The major drawback with this method is that the flame may be spread by the polymer drips.

(f) The inhibition of flame production can also be achieved by coating the polymer so that when it burns incandescent sections disintegrate from the original polymer and remove heat with them from the combustion region.[3] This process is known as ablation and is the solid phase analogue of liquid phase melt/dripping.[8] If a surface char layer is formed, the polymeric bulk is isolated from the external heat source and the disintegration, involving melting, vaporization, oxidation or pyrolysis, takes place underneath.[7]

Unambiguous identification of fire retardant mechanisms is difficult although it is possible to identify in which phase a particular kind of mechanism occurs. It is also believed that several mechanisms may be brought about by one retardant and that some of these mechanisms may be acting simultaneously. If the flame retardant acts by the interference with the decomposition mechanism of the polymer, it is generally believed that the effect is independent of the nature of the oxidant but depends on the polymer structure, and if the additive interferes with the flame reactions, the effect is dependent on the oxidising atmosphere but, to a large degree independent of the structure of the polymer.

Smouldering combustion can not be inhibited by the same flame retardants that prevent flaming combustion, although the mechanisms of prevention are similar. Flame retardants affecting non-flaming combustion include borates and phosphates, which act in the condensed phase by affecting the polymer decomposition, and halogen and sulphur compounds, which affect the gas phase reactions.

Fire retardants in general may be useful in the ignition, flame spread and growth phases of a fire, where the heat flux on the bulk of the fuel is low, but they are ineffective in the later stages of burning when the heat fluxes are higher.[7]

1.3 Phosphorus containing flame retardants.

1.3.1 General Details.

Most flame retardant additives contain heteroelements from Groups (III), (V) or (VII), with six elements being particularly associated with fire retardancy in polymers, namely boron, aluminium, phosphorus, antimony, chlorine and bromine.[3,9] Generally boron and aluminium containing additives inhibit heat flow, chlorine, bromine and antimony act by quenching the flame and phosphorus tends to change the thermal degradation mechanism.

Both inorganic and organic phosphorus containing flame retardants are useful for fire retardancy, especially those containing phosphorus salts and esters.[2] These phosphorus containing species act as precursors to phosphoric acids, which have significant effects on the thermal degradation of the polymers.[3]

1.3.2 Inorganic phosphorus flame retardants.

Ammonium polyphosphate is an effective flame retardant for polyurethanes and poly(methylmethacrylate), producing polyphosphoric acid on decomposition (*Figure 1.2*) and altering the degradation mechanism in such a way that decomposition occurs 30°C lower than in the untreated polymer.[10]

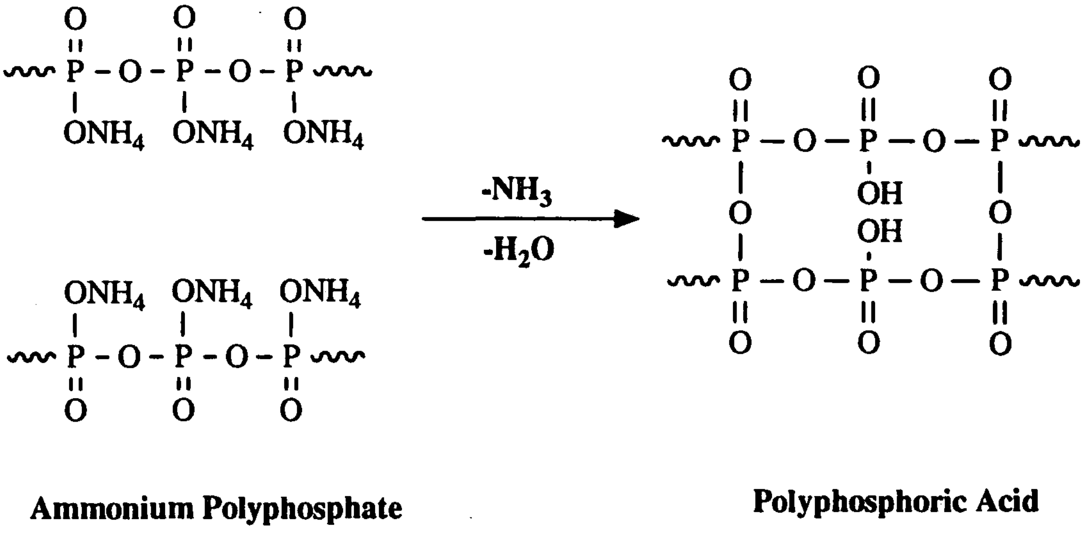


Figure 1.2: Formation of polyphosphoric acid from ammonium polyphosphate.

The decomposition of polyurethanes is accelerated by the presence of the ammonium polyphosphate, but it is directed in such a way that the volatile products of the reaction are changed dramatically and become less flammable.[11] The ease of ignition of common polyurethane foams is associated with the evolution of butadiene, the production of which is inhibited if ammonium polyphosphate is used as a fire retardant.[10] A layer of char, which protects the undecomposed material by impeding the transfer of heat to the bulk of the polymer, is also produced during the degradation. The major disadvantage of using ammonium polyphosphate as a flame retardant for polyurethanes is that ammonia, aniline and other toxic compounds are by-products of the degradation. Similar effects are seen if ammonium polyphosphate is used in conjunction with poly(methylmethacrylate).[10] The primary effect is the conversion of ester groups to anhydride rings which affect the depolymerisation process, so that monomer production (i.e. fuel production) is decreased.

1.3.3 Red phosphorus.

Although red phosphorus burns under certain conditions and is used in safety matches, it has been claimed that it can be used as an effective flame retardant in a specified concentration range. During combustion red phosphorus (*Figure 1.3*) can be a very concentrated source of phosphoric acids and hence an effective flame retardant for polyolefins, polystyrene, polyesters and epoxy resins, although occasionally coadditives are required to achieve a desirable flame retardancy.[12]

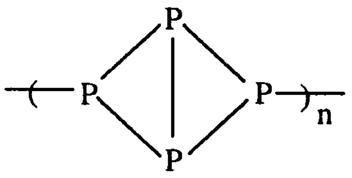


Figure 1.3: Red phosphorus.

Despite these claims there is a major inhibition to using red phosphorus in as much as it can be flammable and it does revert slowly to white phosphorus (*Figure*

1.4), which is spontaneously flammable.[9,13]

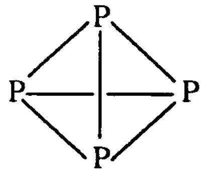


Figure 1.4: White phosphorus.

1.3.4 Organophosphorus flame retardants.

1.3.4a Additive flame retardants.

Phosphorus additive fire retardants have the greatest utility with highly oxygenated polymers such as cellulose, where the phosphoric acids that are formed in the additive/cellulose degradation reaction, esterify the hydroxyl groups.[6] This results in char, which protects the polymer from the heat of combustion, and water being formed at the expense of flammable volatiles, hence altering the fuel production step. Additives can also work by catalysing thermal depolymerisation of the polymer melt, facilitating the flow/drip of the melt away from the combustion zone. Some additives, for example phosphate esters, are stable under flame conditions,[3] they are released as a heavy vapour and may inhibit the combustion of non-hydroxylated polymers by blanketing the flame.

Examples of additive flame retardants include:-[12]

a) Tricresyl phosphate {$P(OC_6H_4CH_3)_3$}, the first major commercial organophosphorus fire retardant, is used in PVC and cellulosic formulations.

b) Alkyl acid phosphates {$P(OH)(OR)_2$/$P(OH)_2(OR)$, where R= Me, Bu}, which have a high phosphorus content and originate from low cost starting materials and are used in many commercial plastics.

c) Trialkylphosphates {$P(OR)_3$, where R= Et, Oct), which also are low cost additives with a high phosphorus content, and are used in cellulosics and polyester laminates. Due to their water-solubility there is a weathering disadvantage.

d) Dimethyl methylphosphonate {$CH_3P(O)(OCH_3)_2$}, which is a high phosphorus containing additive, is very effective in the flame retardancy of thermosets because of its high volatility. It is also used to increase the phosphorus content of other fire retardants in rigid foams.

e) Halogenated alkyl phosphates and phosphonates are used in conjunction with polyurethanes, eg. tris-(2-chlorethyl)phosphate {$P(O)(OCH_2CH_2Cl)_3$}, which can also be reacted with dimethyl methylphosphonate to form oligomeric halogen-free phosphorus esters (*Figure 1.5*).[12]

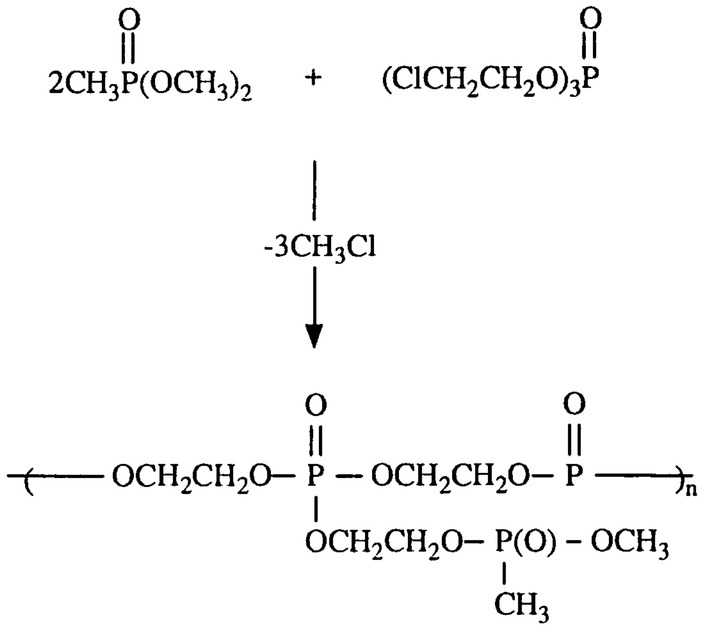


Figure 1.5: Preparation of oligomeric phosphorus esters.

These oligomers, which are used in air filters, have a high phosphorus content, low volatility and are water soluble. Introducing halogens into phosphorus retardants often produces synergistic behaviour. This occurs when the combined effect of two or more retardants is greater than the sum of each of the two components on their own. It has been suggested that this behaviour may be due to the presence of phosphorus halides produced during polymer decomposition, which may inhibit the flames.[15]

1.3.4b Reactives flame retardants.

Reactive compounds are generally more effective than additives as they are incorporated into the polymeric structure and hence are not lost through evaporation or leaching with solvents.[3] They are also immediately available to protect the polymer in a fire since they are liberated as the polymer decomposes, whereas the decomposition temperature of an additive has to be matched with that of the polymer, so that it is not available before it is required or after the polymer has degraded. The disadvantages of reactive retardants are that they are more expensive and affect the chemical stability of the polymer and therefore may affect the mechanical strength and the electrical and optical properties of the polymer as well. They may also be more susceptible to thermal and photolytic oxidation.[15]

As with all reactive retardants, reactive phosphorus compounds alter the pyrolysis of the polymer and the fuel production processes. They cause the break up of polymer chains and loss of pendant groups at lower temperatures than normal. This effect may result in:

a) Reduced flammability of volatile materials,

b) The mixture of air and flammable gases being outside the flammable limits for sustained burning,

c) The ignition temperature of the flammable mixture being raised above the temperature of the external heat source.

A secondary effect can be char formation from dehydration and elimination reactions. Although the phosphorus can be volatilised during burning,[16] a substantial amount remains behind in the char, increasing its mechanical strength.[17]

The effect of phosphorus on the polymer depends on the position and type of bonds present, for example a main chain phosphorus atom will have a different effect than a phosphorus atom in a side chain. Other differences will arise from whether the phosphorus is bonded to oxygen or carbon atoms.[2]

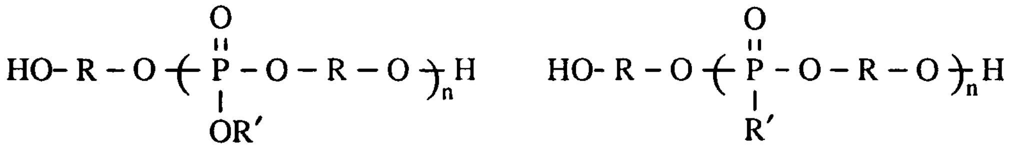
i) A main chain P-C bond is a weak point in a polymer chain because it is readily broken by thermal and thermal oxidative processes.

ii) A P-C bond in a side chain may result in the elimination of a P-H compound if a β-hydrogen is present.

iii) If the phosphorus atom occurs in the side chain, bonded to an oxygen atom, the β-hydrogen should facilitate the elimination of a P-OH compound.

The polymer degrades as a result of these processes producing low molecular weight phosphorus compounds, which in turn produce one or more phosphonic acids.

Reactive phosphorus compounds may be prepared by several methods. The copolymerisation of vinyl and/or allyl phosphonates with vinyl monomers, the addition of phosphines to unsaturated polymers and the condensation polymerisation of hydroxyalkylphosphates and phosphonates (*Figure 1.6*) in polyesters and polyurethanes are all methods that have been used commercially.[10,12]



$HO-R-O\left(\overset{O}{\overset{\|}{\underset{\underset{OR'}{|}}{P}}}-O-R-O\right)_{n}H$

$HO-R-O\left(\overset{O}{\overset{\|}{\underset{\underset{R'}{|}}{P}}}-O-R-O\right)_{n}H$

Hydroxyalkyl Phosphate **Hydroxyalkyl Phosphonate**

Figure 1.6: Hydroxyalkylphosphates and phosphonates.

Reactions of these phosphates and phosphonates with diisocyanates and varying amounts of non-phosphorus polyols, produces polyurethanes with a range of phosphorus contents (*Figure 1.7*).[10]

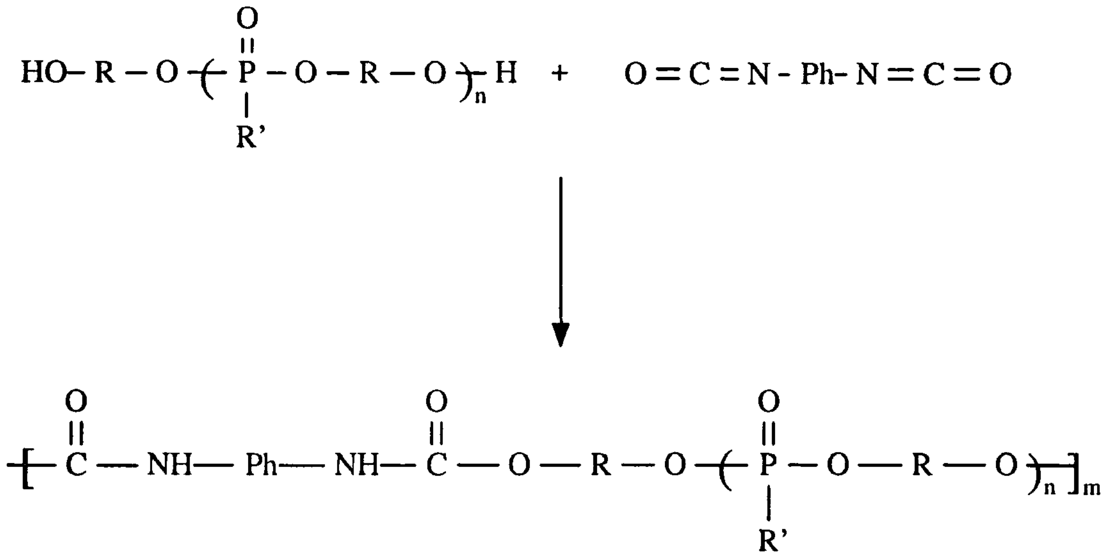


Figure 1.7: Condensation polymerisation of an hydroxyalkyl phosphonate with a diisocyanate.

1.4 Summary.

Phosphorus based flame retardants act mainly in the condensed phase encouraging the formation of char, especially with highly hydroxylated polymers such as cellulose, or polymers that become so, for example epoxy resins. If phosphorus fire retardants are used with hydrocarbon thermoplastics, then the retardant mechanism acts in the gas phase either by chemical or physical methods.

The recent development of phosphorus flame retardants has led to the production of less volatile materials and the question of inhibition of smoke and toxic by-products eg. phosphorus retardants decrease the amount of hydrogen cyanide evolved in the burning of polyurethanes.[18]

1.5 Treatment of industrial water.

Industrial plants use vast amounts of water every year in manufacturing processes, most of which comes from reservoirs and contains dissolved salts, which may interfere with the plant operation.[19] These unsuitable "hard waters" can cause several problems in industrial water systems, notably deposition of scale and corrosion, which in turn may lead to leakage and bulging of heating pipes and boilers. Scale formation is a major problem because it reduces heat transfer due to its poor thermal conductivity and this may well result in the unit being shutdown for scale removal, causing a costly loss of production.[20] Scale is also a large problem in the petroleum industry since large amounts of water are brought to the surface during primary recovery of crude oil. Many of the pipes become clogged and the removal of the scale is often an expensive process.

The dissolved salts creating most concern are:-[21]

(i) *Calcium and magnesium chlorides*, which can be a source of HCl resulting in the corrosion and pitting of metal pipes.

(ii) *Sodium chloride*, which can contribute to the corrosion of nonferrous metals.

(iii) *Calcium and magnesium bicarbonates*, which cause temporary hardness scales. This type of scale is deposited in boiler systems as a soft sludge and can be removed by a "blown down" process (i.e. high pressure flushing) or with wire brushing.

(iv) *Barium sulphate, calcium sulphate, calcium phosphate and calcium carbonate*, which are known as hard scales.[21] These inorganic precipitates adhere firmly to the walls of pipes and can be removed by the addition of acids, but since this increases the rate of corrosion of the pipes, such scales are preferably chipped away.[21,22]

Calcium carbonate occurs in many forms from pearls to limestone. Any deposit of calcium carbonate can be dissolved by water, particularly if the water is slightly acidic. Rainwater exists as carbonic acid, formed as water dissolves the carbon dioxide in the air (*Figure 1.8a*), and this weak acid readily dissolves calcium carbonate in the form of calcium hydrogen carbonate (*Figure 1.8b*), allowing calcium carbonate to be transported in aqueous solution.

$$CO_2 + H_2O \longrightarrow H_2CO_3 \qquad (a)$$

$$H_2CO_3 + CaCO_3 \longrightarrow Ca^{2+} + 2HCO_3^- \qquad (b)$$

Figure 1.8: Formation of calcium hydrogen carbonate.

Calcium carbonate is the most common scale forming salt and exists in three forms, calcite, vaterite and aragonite.[23,24] Calcite, occurring at temperatures below 50°C, has a trigonal crystal structure and is the chief constituent of limestones and marbles. It is also a major component of inorganic scales. Vaterite is hexagonal in structure and being metastable is the least common form, readily converting to the calcite structure. Aragonite, the orthorhombic form, occurs above 50°C [25] and is harder and denser than the other two structures, because of this is the most troublesome form of scale.[26] It is the most common industrial scale found in boilers, desalination plants and heating systems where operating temperatures are above 70°C. As the temperature increases the solubility of calcium carbonate and calcium sulphate decreases and this unusual behaviour means that scale readily precipitates on metal surfaces, especially heating pipes, where the temperature is the highest.[22]

Scale inhibits the flow of heat through boiler plates and pipes preventing direct contact between the water and the metal surfaces, which subsequently become overheated and strained. Overheating may result in corrosion or the occurrence of chemical changes in the water constituents. The corrosive compounds, formed from these changes, then adhere to the metal pipes, and because they are shielded from the water by the scale deposits they are not washed away but remain in situ to attack the metal.[20]

When grease is present in the system overheating can be so severe that the metal surfaces soften and deformation of the pipes can result. Tubes may become so clogged that rivets are sheared and seams opened leading to rupture and collapse of the system.[20]

In most arid countries sea water has to be distilled in desalination plants to provide a potable water supply and this creates similar problems to those encountered in boiler systems. Although brackish water, which has a lower salinity than sea water,[22] can be treated by ion exchange,[27] the salt content of sea water is too high to make this process economically viable. Scale deposits are produced as the brine is heated in the boiler and in the cooling pipes of the condenser. These act as heat exchangers, preheating the inlet water before it reaches the boiler hence minimising the heating costs. The inorganic scale precipitates in the metal pipes, reducing the heat transfer and flow, adversely affecting the efficiency and economics of the desalination process.[27]

In order to reduce the rate of deposition of the industrial scales in all of the water systems mentioned, pretreatment of the water is required to remove or alter the constituents to make the water suitable for use.[20] Some industrial steam generating plants use sophisticated treatments before the water is fed into the boiler, including softening, coagulation and filtration techniques, but these are only partially effective. It is therefore necessary to delay or inhibit the formation of scale by the use of water soluble polymers and other compounds,[28] which maintain the dissolved salts in solution or suspension by modifying the crystal growth, thus inhibiting attachment to the walls of the metal pipes. Additives can do this in four ways:-

(i) *Preventing homogeneous nucleation.*[29-31]

As calcium and carbonate ions are transported in solution highly concentrated regions, known as supersaturated regions, are formed. The ions are electrostatically attracted to each other forming thermodynamically unstable clusters called critical nuclei. The nuclei may either undergo a phase change and become solid crystal nuclei or may diperse to relieve the thermodynamically unstable situation. When an antiscalant polymer is introduced into the system the functional groups on the polymer interact electrostatically with the calcium ions reducing the electrostatic attraction between the calcium cations and the carbonate anions and this results in the radius of the critical nucleus being increased. This radial increase maybe too energetically unfavourable for the critical nucleus to be produced and homogeneous nucleation is prevented.

(ii) *Preventing heterogeneous nucleation.*

Coating of the metal pipe with an antiscalant polymer, containing carboxylic acid or phosphoric acid functional groups, prevents scale nucleating and adhering at the metal surface.

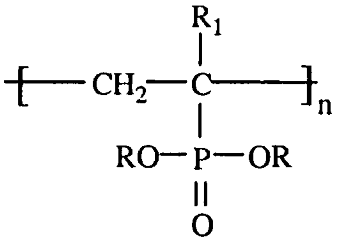
(iii) *Complexation.*[28,32]

In this case functional groups on a polymeric additive complex with the calcium ions reducing the concentration of cations available to form the aragonite structure. Large concentrations of polymer must be used to complex significant amounts of the calcium ions in order to prevent crystallisation.

(iv) *Crystal surface modification.*[28,30,33]

If nucleation has already occurred the antiscalant polymer may interact with one of the faces of the growing crystal preventing further growth and limiting the amount of aragonite precipitated.

The commercial polymers currently used for inhibiting the formation of aragonite are predominantly poly(acrylic acid) and its derivatives and the reaction products of the free radically initiated polymerisation of maleic acid in the presence of xylene.[34] Recent work has led to the use of simpler polycarboxylic acids of fairly uniform structure for the inhibition of aragonite,[28] but such materials are ineffective against other forms of scale such as calcium and barium sulphate.[19] Phosphates and polyphosphates are also capable of removing preformed scale and residual hardness in the water and also can be used as corrosion inhibitors.[35-37] For example; the poly(alkenylphosphonic acid)s (*Figure 1.9*),[38] the most useful polymer was found to be poly(2-isopropenylphosphonic acid (R_1= Me in *Figure 1.9*), usually known as poly(isoprenylphosphonic acid).



R = H or metal cation.
R_1 = alkyl group containing 1-6 carbon atoms.

Figure 1.9: The poly(alkenyl)phosphonic acids.

The monomer is prepared from acetone and PCl_3 followed by the addition of acetic acid and hydrochloric acid and dehydrochlorination (*Figure 1.10*).

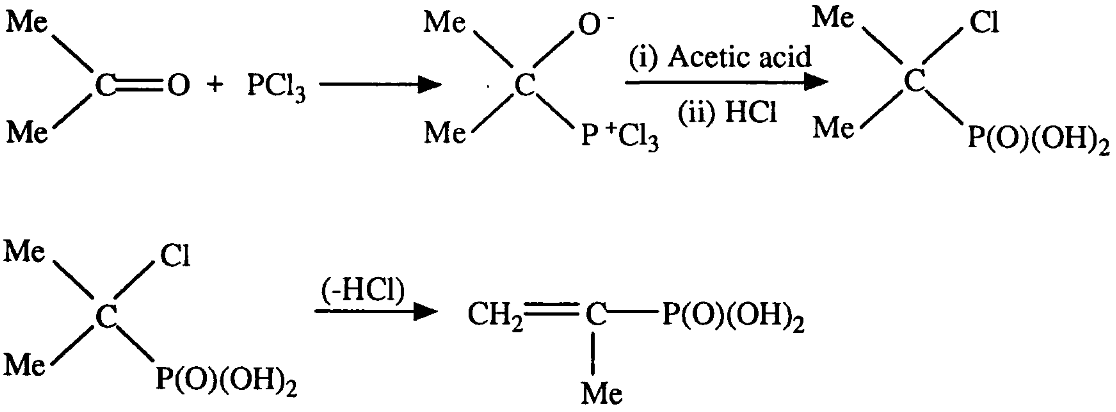


Figure 1.10: Synthesis of 2-propenyl phosphonic acid.

Poly(2-propenylphosphonic acid) is prepared by radical chain addition polymerisation.

Tests on the phosphonic acid polymers have been carried out in simulated boiler and cooling water systems and these polymers have been shown to be reasonably effective in the inhibition of calcium sulphate, calcium carbonate and calcium phosphate formation. They can also be used in conjunction with a variety of organic and inorganic, phosphonic and phosphoric acids and their derivatives to increase the activity of the polymers.[38] The amount of polymer added to any system depends on a variety of factors such as, the area of pipe subjected to corrosion, the quantity of water present and the pH and temperature of the system.[38]

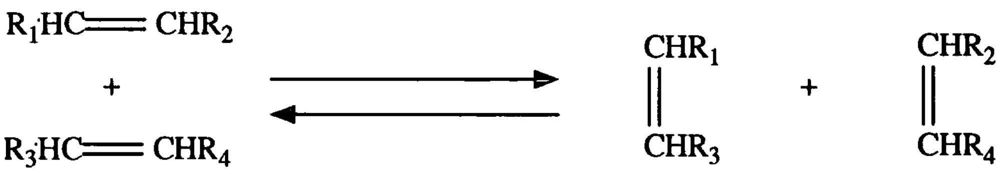
1.6 The olefin metathesis reaction.

1.6.1 Historical background.

The olefin metathesis reaction is defined as a catalytically induced bond reorganisation reaction involving the making and breaking of carbon-carbon double bonds. The total number and type of bonds remains unchanged during the process.

The reaction has proved useful in three kinds of process, all of which proceed via a chain mechanism, involving metal carbenes and metallacyclobutanes as the chain carrying species.[39]

(a) *Olefin disproportionation/exchange reaction* involving acyclic olefins (*Figure 1.11*).



1.11: The olefin disproportion reaction.

(b) *Ring Opening Metathesis Polymerisation (ROMP)* involving cyclic or polycyclic olefins (*Figure 1.12*).

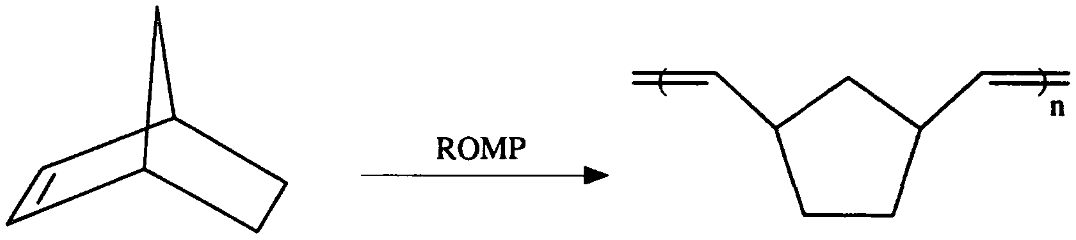


Figure 1.12: Ring Opening Metathesis Polymerisation of norbornene.

(c) *Degradative metathesis*. Unsaturated networks may be degraded after swelling with an acyclic olefin.

Probably the first citation of a metathesis reaction was reported by Anderson and Merckling of Du Pont[40] in 1955 with the ROMP of norbornene (*Figure 1.12*) using $TiCl_4$ and EtMgBr at 50°C. However, it was not until 1960 that the polymer was identified as a poly(alkylene vinylene) by Truett.[41] In 1964 Banks and Bailey,[42] whilst attempting to develop a new heterogeneous catalyst for olefin alkylation, reported that in the presence of heterogeneous catalysts, prepared from tungsten and molybdenum carbonyls supported on alumina, acyclic olefins gave rise to higher and lower molecular weight fractions. They analysed the process as proceeding via an exchange of alkylidene units and named the reaction olefin disproportionation. Although over the next few years a series of patents and papers reported a number of catalysed exchange/disproportionation and ROMP reactions,[43-49] it was not until 1967 that the term olefin metathesis was first introduced, when Calderon realised that the mechanisms of the ROMP of cyclic and polycyclic olefins and the exchange reaction of acyclic olefins were identical. The history and development of the ROMP reaction has been reviewed in a series of recent publications.[39,51-54]

1.6.2 Olefin metathesis initiator systems.

Olefin metathesis can be initiated by a variety of transition metal catalysts from groups (IVA) to (VIII).[39]

IVA	VA	VIA	VIIA	VIII
Ti	V	Cr		
Zr	Nb	Mo		Ru Rh Pd
Hf	Ta	W	Re	Os Ir Pt

Table 1.1: Metals active in the catalysis of metathesis.

The most widely used catalysts are compounds of W,Mo and Re, which are capable of initiating the metathesis of acyclic olefins[42] as well as less strained cyclic olefins such as cyclopentene.[39] Metathesis of strained rings, such as norbornene, can be achieved by the use of Ti, V, Ru, Os and Ir. Some non transition metal catalyst systems have been reported to be capable of initiating metathesis, for example $Al_2O_3/EtAlCl_2$.

The catalysts can initially be classified into two types, heterogeneous and homogeneous systems.

(a) Heterogeneous catalysts are generally transition metal oxides, sulphides or carbonyls absorbed onto a high surface area refractory support such as alumina or silica; examples are listed in *Table 1.2*.

Oxides	Sulphides	Carbonyls
Mo W Re V Sn Te Nb Ta La Ru Os Ir Rh Sr Ba	Mo W	Mo W Re

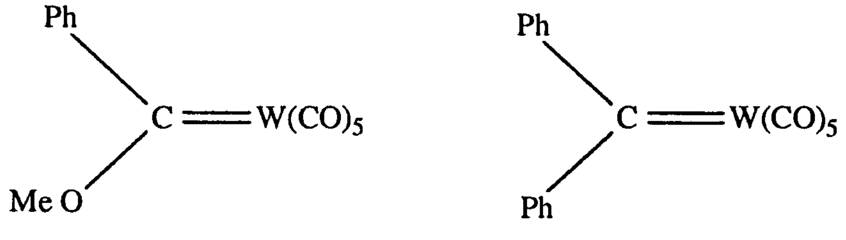
Table 1.2: Heterogeneous metal catalysts.

The three main methods of preparing the catalysts are:- (i) dry mixing, (ii) coprecipitation and (iii) impregnation of the support with a compound that decomposes at high temperatures to leave the catalyst precursor. The catalysts are activated in an inert atmosphere and used with cocatalysts and/or promoters. The selectivity of these reactions is always below 100% due the numerous side reactions that occur eg. polymerisation and isomerisation, which can be minimised to a certain extent by the addition of alkali[56] or alkaline earth[57] metals or copper or silver[58] before catalyst activation. Heterogeneous catalysts can initiate metathesis of acyclic olefins but they are rarely used for ROMP.

(b) Homogeneous catalysts are usually used in the liquid phase, either in neat monomer or dissolved in a solvent, and although they are termed homogeneous catalysts, some of them may react giving finely divided heterogeneous catalysts.

The classical supposedly homogeneous catalyst systems can be divided into three main categories:-

I) *Single component systems which already comprise a metallocarbene (Figure 1.13).*[59-65] The initial Fischer carbenes $(CO)_5M{=}C(OR)R'$, where $M = Cr$, $R = Me$ and $R' = Ph$, had disappointing activity as organometallic catalysts and only reacted with strained olefins such as cyclobutene and monomers similar in structure to norbornene. Their activity is increased on addition of Lewis Acid cocatalysts. However Casey carbenes are more reactive and can initiate less strained cyclic olefins.



Fischer Carbene **Casey Carbene**

Figure 1.13: Metal carbenes used to initiate metathesis.

(II) *Two or three component systems involving cocatalysts and/or promoters.* This type of classical initiator usually contains a transition metal compound (eg. a halide) and an alkyl, aryl or allyl containing cocatalyst, eg. $MoCl_5/SnMe_4$ and $WCl_6/SnPh_4$. The metal carbene is generated by the reaction of the two components.[66] Ultra-violet spectroscopic studies of the $WCl_6/SnMe_4$ system led to the following proposed mechanism for metallocarbene formation (*Figure 1.14*).[67-69] The reaction is complex and many side reactions are possible.

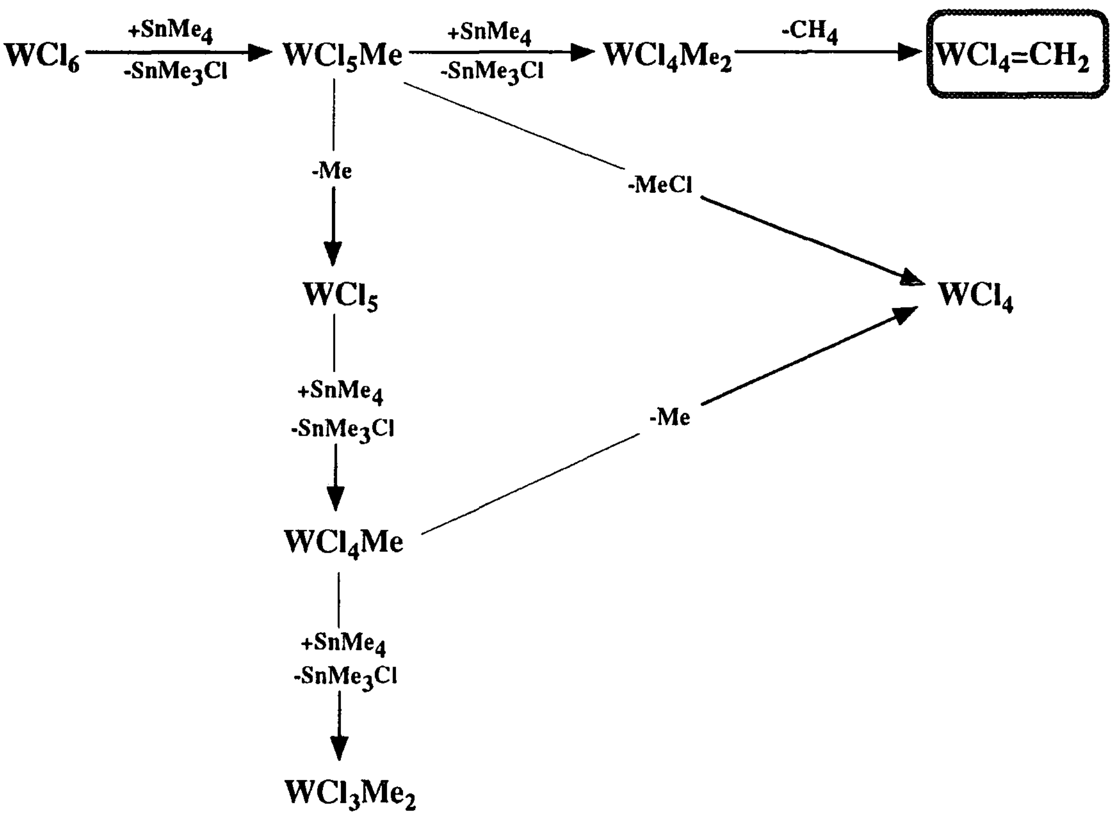


Figure 1.14: Mechanism for metallocarbene generation using $WCl_6/SnMe_4$.

Grubbs,[70] using $WCl_6/SnMe_4$, and Muetterties,[71] with $WCl_6/ZnMe_2$, later confirmed the production of methane during the reaction. Sometimes the reaction will not proceed and a third component, known as a promoter or activator is required eg.

water[72] or ethanol.[73]

(III) *Compounds that contain neither a pregenerated metallocarbene nor an alkyl, aryl or allyl containing species.* Examples of this kind of system are the transition metal halides:- WCl_6, $ReCl_5$, $RuCl_3$, $OsCl_3$ and $IrCl_3$. This kind of initiator generates the metallocarbene in situ by reaction of the transition metal halide with the first monomer unit, although activators are sometimes required, eg. oxygen, water or ethanol.

Ruthenium, osmium and iridium hydrated trichlorides ($XCl_3.3H_2O$) are somewhat unique in that they initiate ROMP in protic media (water and ethanol), unlike most other metathesis catalysts, which are destroyed by such solvents. These aqueous initiators are capable of ring opening strained monocyclic rings (eg. cyclobutene[75] and 3-methylcyclobutene[76]) substituted norbornenes[77-86] and oxanorbornenes, in alcoholic and aqueous emulsified systems between 20-100°C.

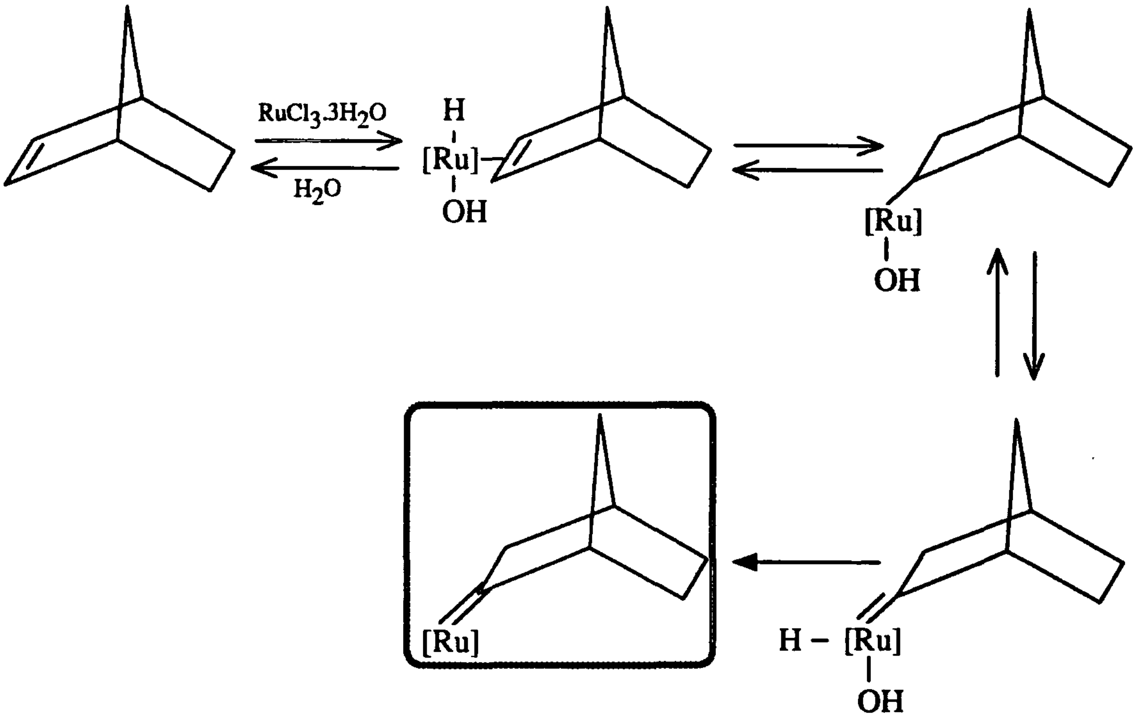


Figure 1.15: Mechanism for metallocarbene generation using $RuCl_3.3H_2O$.

The ROMP mechanism involving the group VIIIA transition metal chlorides, such as ruthenium trichloride, is not fully understood but is believed to generate a metallocarbene via the initial formation of Ru-H bonds (*Figure 1.15*).[87-88] Generally ruthenium catalysts polymerise monomers at a faster rate in water than the osmium and iridium initiators,[86] whereas the behaviour is reversed and iridium trichloride is more active if ethanol is used as the solvent.[77]

The ill-defined classical catalysts have a few disadvantages:-

(i) There is a lack of molecular weight control when they are used, due to the activity of the M=C bond which tends to react with the C=C bonds in the polymer chain producing linear and cyclic oligomers (see section 1.6.4).

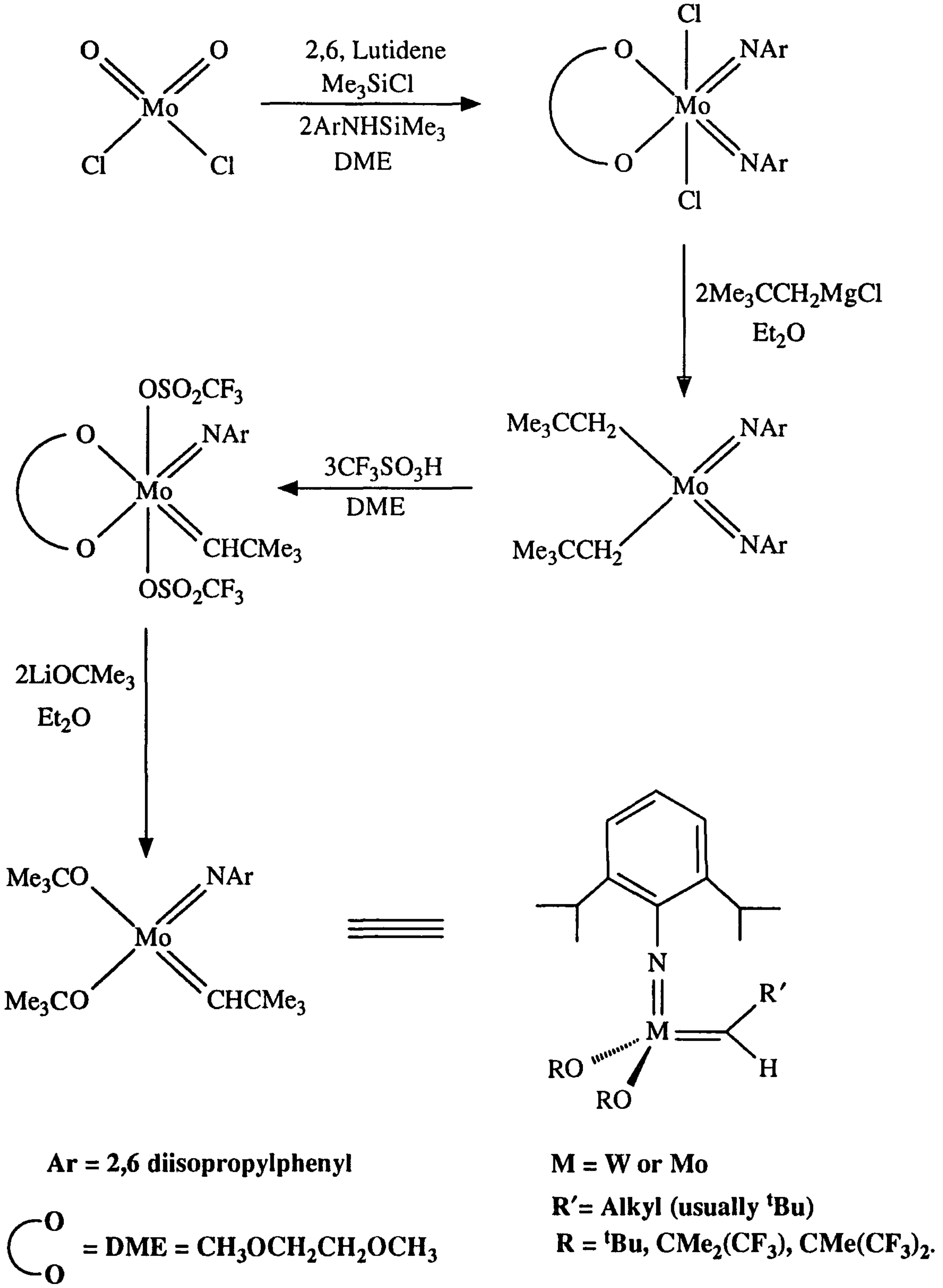
(ii) There is an element of irreproducibility because the production of the initiating carbene tends to be dependant on physical parameters such as temperature,[89] concentration and mixing rates.[90]

(iii) Stereoregular polymers are rarely produced.

(iv) Alkylidene complexes are produced only in low yield and decompose easily.

(v) They also have a limited tolerance towards functional groups. Most classical tungsten, molybdenum and rhenium initiators, for example, are destroyed by oxygen, water and oxygen containing monomers and solvents. Difficulties often arise if heterocyclic compounds are used, the heteroatom, which has donor properties, reacts with the carbene initiator and occupies the active acceptor sites on the initiator thus destroying it. However there are numerous cases where monomers containing heteroatoms have been polymerised.[86,91-99]

In recent years Schrock,[100-102] Grubbs[103,104] and Osborn[105] have reported a series of transition metal carbenes or metallacyclobutanes, which are able to initiate "living" ROMP of cyclic olefins, such species are generally referred to as well defined initiators. An outline of one such synthesis is shown in Figure 1.16.



Ar = 2,6 diisopropylphenyl

= DME = $CH_3OCH_2CH_2OCH_3$

M = W or Mo

R'= Alkyl (usually ^{t}Bu)

R = ^{t}Bu, $CMe_2(CF_3)$, $CMe(CF_3)_2$.

Figure 1.16: Metathesis initiators prepared by Schrock.

Highly stereoregular monodisperse polymers and well defined block copolymers can be prepared from cyclic olefins, in favourable cases, using these catalysts. The living system allows addition of a second monomer after the first has been consumed hence producing the block copolymer. Examples of these initiators include Schrock's four coordinate tungsten and molybdenum alkylidene complexes (*Figure 1.16*);[106,107] and Grubbs' titanacyclobutane/titanium carbene complex[104] derived from Tebbe's reagent (*Figure 1.17*)[108] and related tantalum compounds.[100]

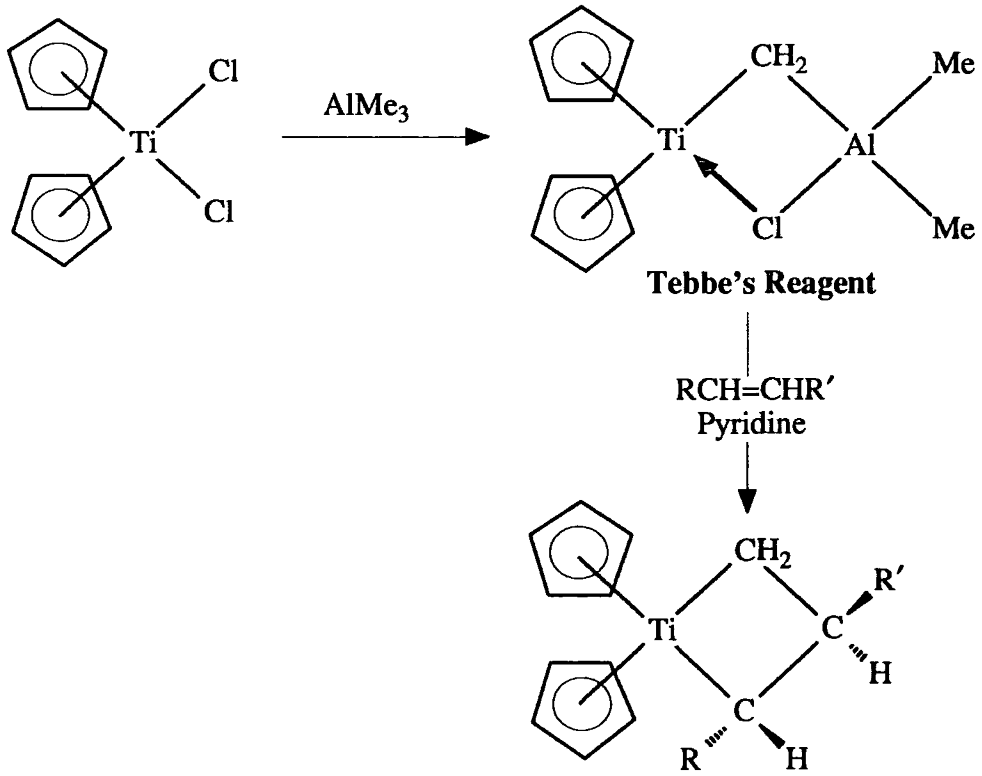


Figure 1.17: Metathesis initiator derived from Tebbe's reagent.

The molybdenum and tungsten initiators are more active than the titanium and tantalum catalysts, showing a greater tolerance towards polar functional groups.[109,110]

The most recent development in this area has been reported by Grubbs,[104] who observed that a stable ruthenium metallocarbene was capable of initiating "living"

ROMP of strained olefins in organic media, both in the absence and in the presence of protic solvents by preparing block copolymers of norbornene and 2,3-dideuterionorbornene in the presence of ethanol and water. The stable carbene was prepared from the reaction of 3,3-diphenylcyclopropene with either $RuCl_2(PPh_3)_3$ or $RuCl_2(PPh_3)_4$ (*Figure 1.18*).

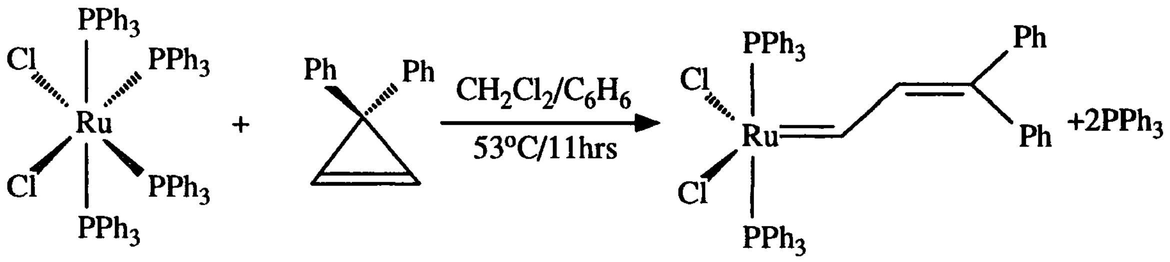


Figure 1.18: Preparation of the Grubbs ruthenium metallocarbene.

1.6.3 Mechanistic rationalisation of metathesis reactions.

There have been several attempts to provide a mechanistic rationalisation for the metathesis reaction. The non-pairwise mechanism of polymerisation, which is generally accepted now, was initially proposed by Hérrison and Chauvin[111] in 1970 after studying the products of cross metathesis between a series of cycloalkenes and linear unsymmetrical alkenes. The mechanism involves transalkylidenation via the cleavage of the C=C double bond and the production of a transition metal carbene, which possesses a vacant coordination site and acts as the chain carrier. In the scheme outlined in Figure 1.19, the C=C double bond first coordinates to the vacant site on the metal carbene forming a metal π-complex, this is followed by the formation of a metallacyclobutane intermediate via a [2+2] cycloaddition. The metallacyclobutane cleaves either degeneratively or productively resulting in the formation of a new metal carbene and a new π-complexed C=C double bond, which then decoordinates from the metal carbene to regenerate the active species. Several of the steps are reversible and the outcome in the metathesis of acyclic alkenes and in ROMP depends on reaction conditions (temperature, concentration), the nature of the chain carrier and the olefin.

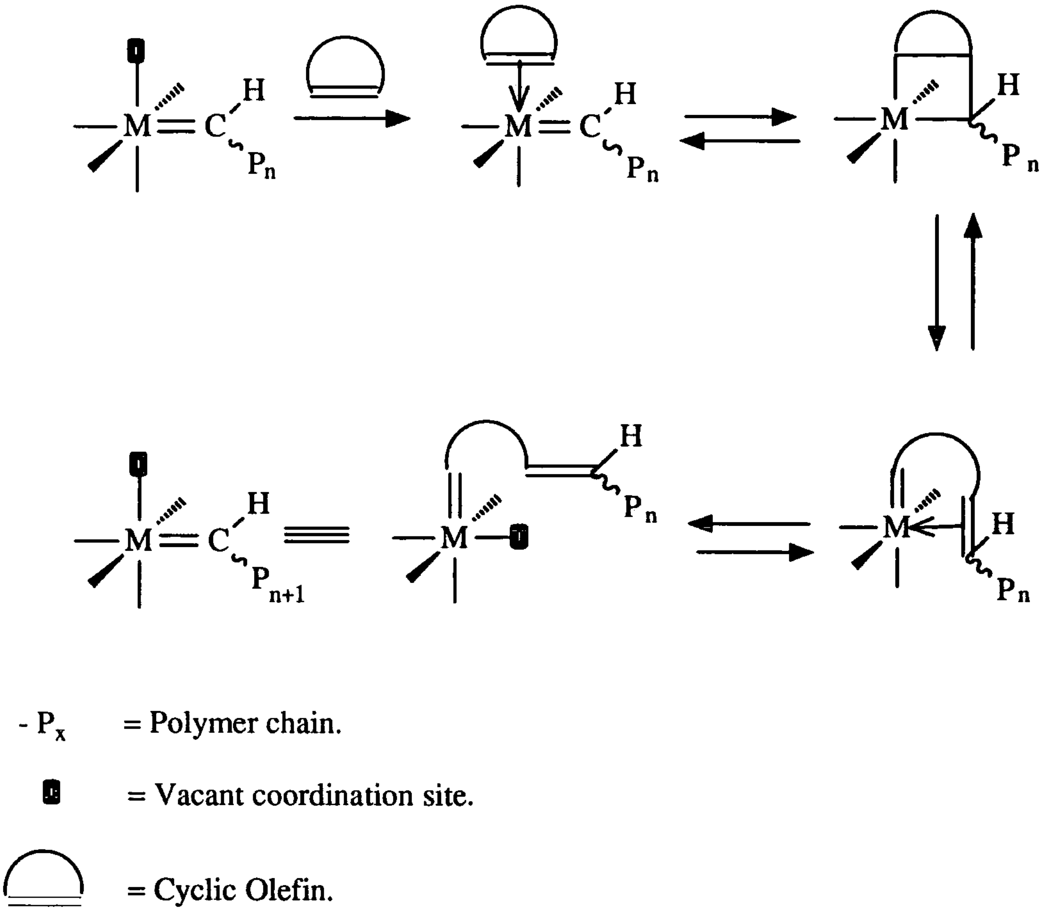


Figure 1.19: Propagation mechanism for Ring Opening Metathesis Polymerisation.

The scheme is supported by existence of stable metallocarbenes at low temperatures, such as the Casey[59-61] and the Fisher[62-65] carbenes, and the isolation of stable metallacyclobutanes derived from Tebbe reagent (*Figure 1.17*),[104,108] both of which will initiate metathesis polymerisation of strained cyclic olefins. Further evidence of a metallacyclobutane intermediate was reported by Green,[112] who stated that stable metallacyclobutanes produced metal carbenes and alkenes on thermolysis or photolysis. Osborn produced the final confirmation when he observed the simultaneous occurrence and interconversion of a W=C metal carbene and tungsten metallacyclobutane during the ROMP of norbornene with the Osborn catalyst (*Figure*

1.20).[113] More recently Schrock and co-workers have also isolated metallacyclobutanes from the reaction of molybdenum carbenes (*Figure 1.16*) and substituted norbornene derivatives.[106,107]

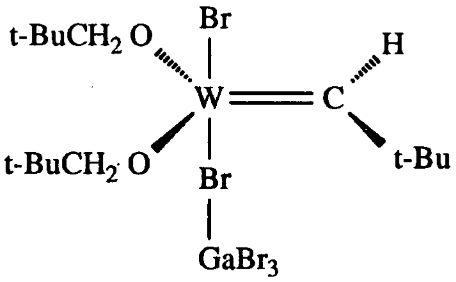
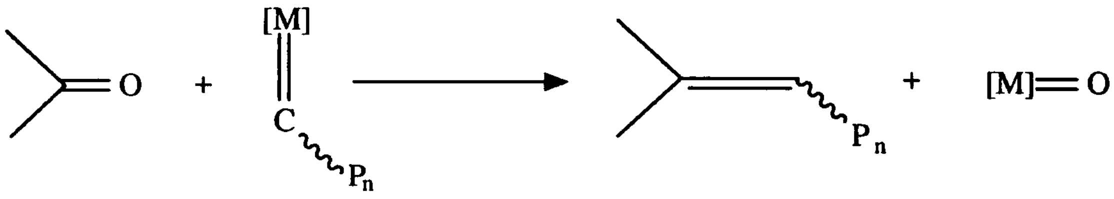


Figure 1.20: The Osborn catalyst.

1.6.4 Termination of ROMP.

The termination of the ROMP reaction can occur in a number of ways, which can be divided into two main types; (i) reactions where the propagating metallocarbene is destroyed and (ii) metathesis reactions, which do not destroy the chain carrier.

(i) Although alcohols and water destroy some active initiators presumably by adding to the reactive metal carbene, some initiators are inert towards protic solvents. Wittig-type reactions involving other oxygen containing species, notably benzaldehyde and acetone, are often used in controlled termination of both "living" and "classical" metathesis reactions (*Figure 1.21*).[114]



P_n = Polymer chain.

$[M]{=}O$ = Unreactive transition metal oxide.

Figure 1.21: Termination of metathesis using acetone.

Two other "destructive" termination reactions observed are the formation of cyclopropanes (*Figure 1.22*) and β-hydrogen abstraction (*Figure 1.23*).

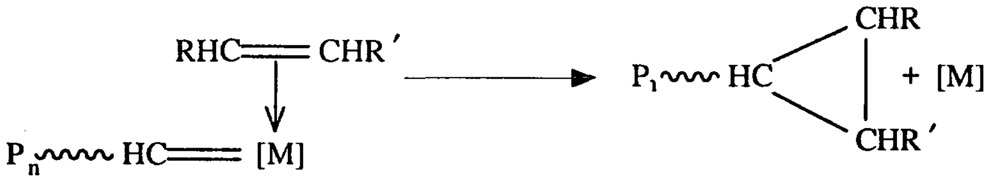


Figure 1.22: Termination of metathesis by the formation of cyclopropanes.

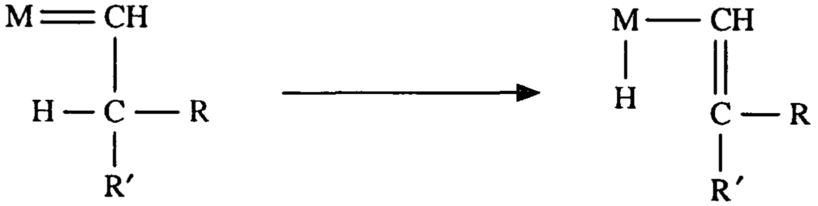


Figure 1.23: Termination of metathesis by β-hydrogen abstraction.

(ii) Chain transfer reactions can occur between the propagating metallocarbene and a C=C double bond in another polymer chain. The polymer C=C double bonds compete with those in the monomer for the active metallocarbene species, hence reducing the availability of these species (*Figure 1.24*).

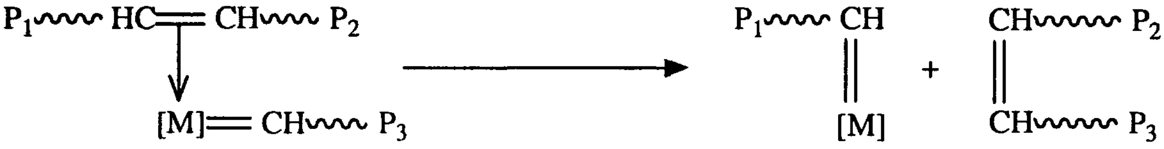


Figure 1.24: Chain transfer between propagating metallocarbene and the polymer chains.

A similar reaction can take place intramolecularly between the active metallocarbene and the C=C double bonds from the same polymer chain resulting in the formation of cyclic oligomers. This reaction is known as back biting and can result in a lower molecular weight and higher polydispersity of the resulting polymer (*Figure 1.25*). If the initial concentration of monomer $[M_0]$ is above a certain critical value then an equilibrium exists between the high molecular weight polymer and the low molecular weight cyclic oligomers. The higher the concentration of initiator the higher the proportion of high molecular weight polymer at equilibrium. If $[M_0]$ is below the critical value then no high molecular weight polymer is formed.[115,116]

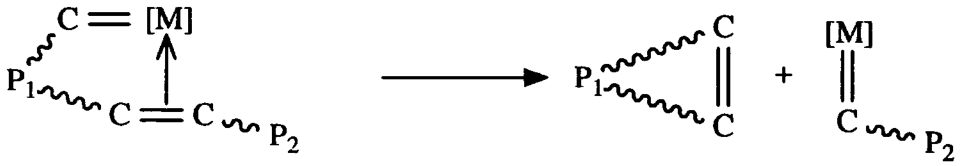


Figure 1.25: Formation of cyclic oligomers via back-biting.

Cross metathesis between acyclic olefins and the C=C double bonds in the polymer chain can also result in a lower molecular weight and broader molecular weight distributions as linear oligomers are produced. This type of reaction, where the acyclic olefin is known as a chain transfer agent, is often used in controlling the molecular weight of the polymer by the interruption of the chain growth (*Figure 1.26*). The new metallocarbene formed may induce further degenerative metathesis or initiate formation of a new polymer chain.

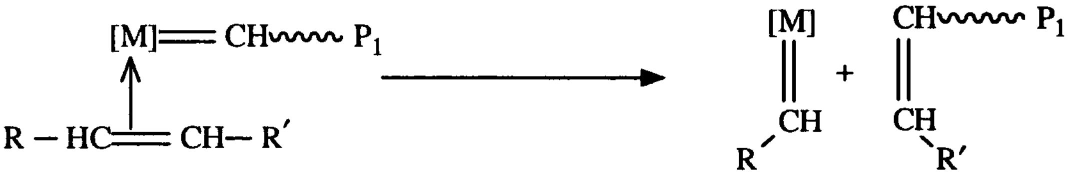


Figure 1.26: Chain transfer between acyclic olefins and the polymer chains.

Chain transfer between polymerising cyclic olefins and acyclic olefins can have two kinds of outcome. The first results from the effect small amounts of acyclic olefin (CTA) can have on the yield, molecular weight and *cis* content of a polymer produced from a cyclic monomer (M). The second concerns the use of larger amounts of chain transfer agent in attempts to produce telomers with well defined end groups. In the case of an unsymmetrical chain transfer agent ($R_1HC=CHR_2$) there is the possibility of three types of telomers, $[R_1HC=(M_n)=CHR_1]$, $[R_1HC=(M_n)=CHR_2]/[R_2HC=(M_n)=CHR_1]$ and $[R_2HC=(M_n)=CHR_2]$. For low molecular weight polymers (<5000) it is possible to detect polymer end groups using ^{13}C NMR.[86,111,117-120]

The prospect of molecular weight control of potential commercial polymers has resulted in several acyclic olefins being used as possible chain transfer agents for the ROMP of cyclic olefins, eg. norbornene and cyclopentene. Generally an increase in [CTA]/[M] reduces the molecular weight and if the ratio is high enough, telomers are produced. The structure of the acyclic olefin, the type of catalyst system used and the *cis* content of the resulting polymer all determine how effective the chain transfer agent is in reducing the molecular weight. The order of effectiveness is as follows:-

$$RCH=CH_2 > R^1CH=CHR^2(\textit{cis}) > R^1CH=CHR^2(\textit{trans}) >> R^1R^2C=CH_2.$$

It has also been observed that acyclic olefin additives have less effect on controlling the molecular weight when high *cis* polymers are produced,[122] which is rationalised in terms of the intramolecular coordination of the previously formed *cis* C=C double bond to the metallocarbene.[39,123] Certain olefins increase the *cis* content of the resulting ROMP polymer but have significant effects on the yield, allyl 2,4,6-tribromophenyl ether increases the amount of polymer recovered from cyclopentene,[124] whereas ethyl acrylate, diethyl maleate and diethyl fumarate decrease the yield of polynorbornene.[125,126]

The gradient of plots of 1/Mn against [CTA]/[M] give the chain transfer constant for a particular acyclic olefin (see appendix H), which is defined as the ratio of the chain transfer rate constant to the propagation rate constant. The constants give a reasonable indication of how effective the chain transfer agents are but the values are not entirely accurate due to experimental uncertainties, such as how the formation of cyclic oligomers affects M_n, and whether they are still present after recovery of the ROMP polymer.

1.6.5 Factors affecting the ROMP of cyclic olefins.

The thermodynamics and kinetics of ring opening play a large part in understanding ROMP, with effective metathesis requiring a low energy barrier between the metal carbene and the metallacyclobutane, and a negative Gibbs Free Energy of Ring Opening (ΔG_R) required for polymerisation.

$$\Delta G_R = \Delta H_R - T\Delta S_R.$$

ΔH_R is the enthalpy of ring opening, T the temperature(K) and ΔS_R is the entropy of ring opening. The entropy term ΔS_R is always negative due to the monomers being bound into macromolecules, hence reducing their freedom. Therefore $-T\Delta S_R$ is always positive and for a favourable reaction the ΔH_R term must be larger than the $T\Delta S_R$ term. As the temperature is increased the entropy term increases and the Gibbs Free Energy eventually becomes positive. So a temperature must exist where $\Delta G_R = 0$ ie. $\Delta H_R = T\Delta S_R$, this is known as the "ceiling temperature", above which polymerisation does not occur.[127]

Ring strain and ring size are important factors in determining whether monocyclic and bicyclic olefins undergo metathesis polymerisation. Generally in the case of 3,4 and 8-12 membered rings, metathesis occurs readily, whereas for 5,6 and 7 membered rings, where the ring strain is reduced, other physical factors will contribute, such as temperature, concentration and pressure.[39] The position, nature and size of substituents also influences ΔG_R. In general only substituents well separated from the C=C double bond can be tolerated, as the substituent gets closer to the double bond it has more effect on the polymerisability of the cyclic olefin, hence although 3-methylcyclopentene polymerises, 1-methylcyclopentene does not.[128] Exceptions occur in highly strained molecules such as 1-methylcyclobutene, which will undergo ROMP,[129] and in some strained bicyclic monomers, where a methyl substituent can be tolerated in any position.[130-135] The size of the substituent also has an effect on the outcome, if a substituent is too bulky the olefin may not polymerise, as is the case with 3-isopropylcyclopentene.[136] There is also the possibility of orbital interactions between distant substituents and the C=C double bond, which may reduce the electron density on the double bond and making coordination to the M=C metallocarbene less favourable.[137-138]

1.6.6 Microstructure and stereochemistry of ROMP polymers.

There are several ways of incorporating a monomer repeat unit into a polymer chain, altering the microstructure and morphology and hence the physical properties of the polymer. The microstructure can be controlled in certain circumstances by altering the catalyst system and the reaction conditions, so that it may be possible to synthesise a polymer with the required physical characteristics for a specific application. The three main factors which define the microstructure are:-

(a) the *cis/trans* vinylene frequency and distribution,

(b) the head/head and head/tail frequency and distribution

and (c) tacticity effects.

By altering each of the factors a large range of polymers can be obtained, in principle, from one monomer.

(a) Ring opened polymers resulting from norbornene-type structures are unsaturated and each C=C double bond can have *cis* or *trans* geometry (*Figure 1.27*).

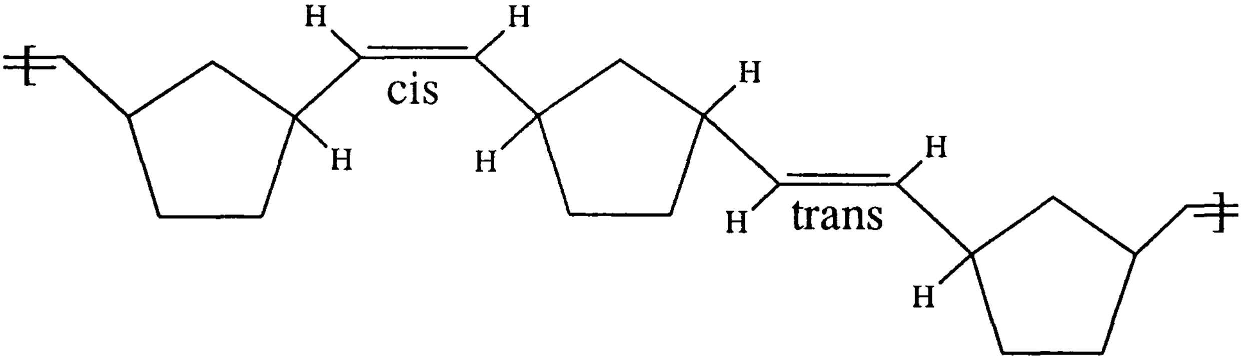


Figure 1.27: Cis/Trans geometry of double bonds in polynorbornene.

The proportion of *cis* double bonds in a particular polymer, denoted by σ_c, is primarily dependant on the catalyst system but concentration, temperature and the nature of the monomer may also have an influence. A polymer with σ_c= 1.0 has all *cis* double bonds and one with σ_c= 0 has all *trans* double bonds.

The model proposed by Ivin[131] for the formation of *cis* or *trans* double bonds is based on the hypothesis of a chain propagating species which is an octahedrally substituted metallocarbene with one vacant site. As the metal centre is chiral, the propagating metallocarbene has two enantiomeric forms P_r and P_l (*Figure 1.28*), each of which can attack the least hindered *exo*-face of the norbornene-type monomers in two ways depending on the orientation of the monomer.

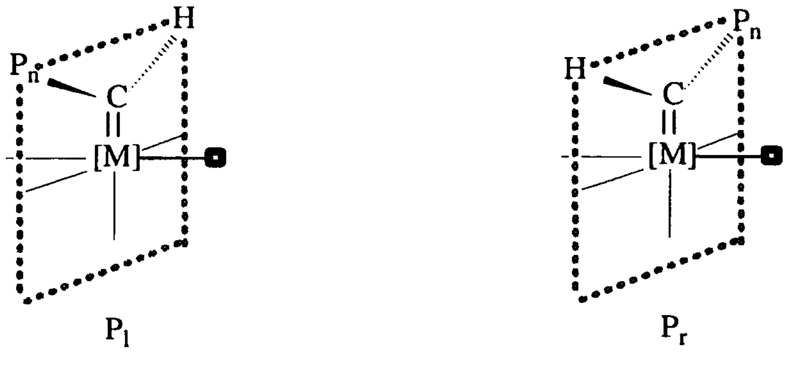
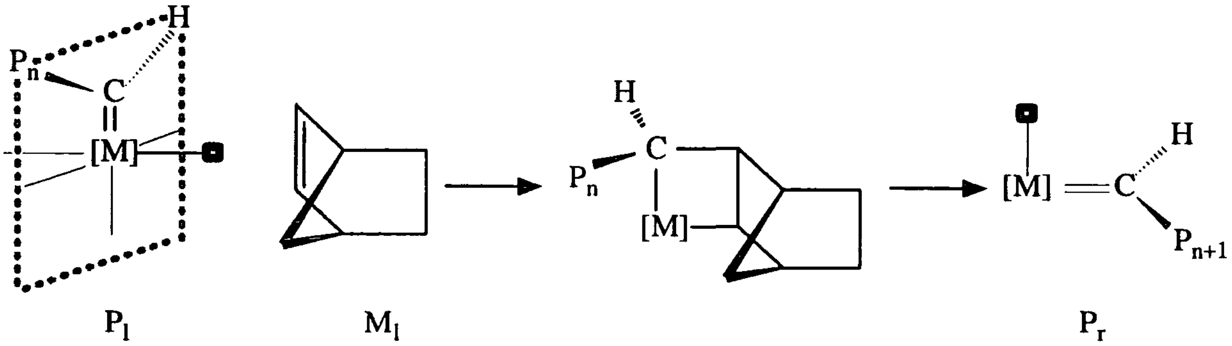


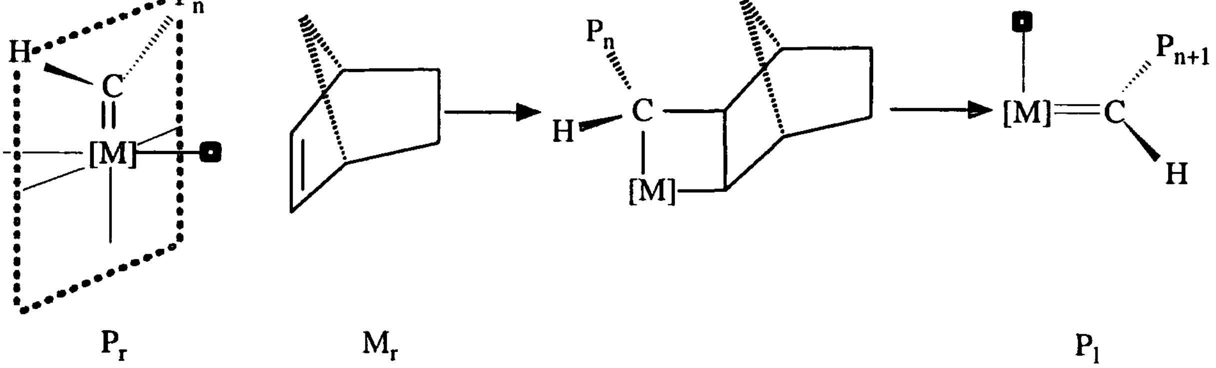
Figure 1.28: The two enantiomeric forms of the propagating metallocarbene.

The monomer may approach with the bridging methylene group orientated out of the paper (M_l) or into the paper (M_r) (*Figure 1.29*).

Figure 1.29: The possible orientations of norbornene.

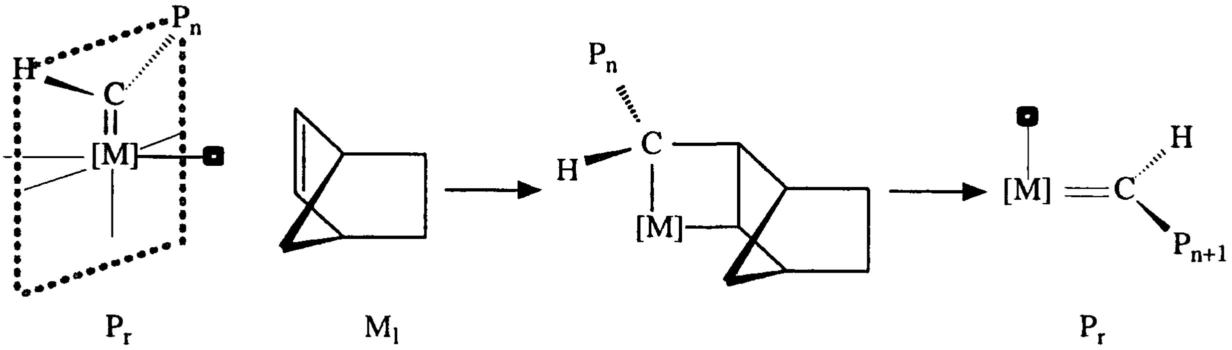


(1) CIS

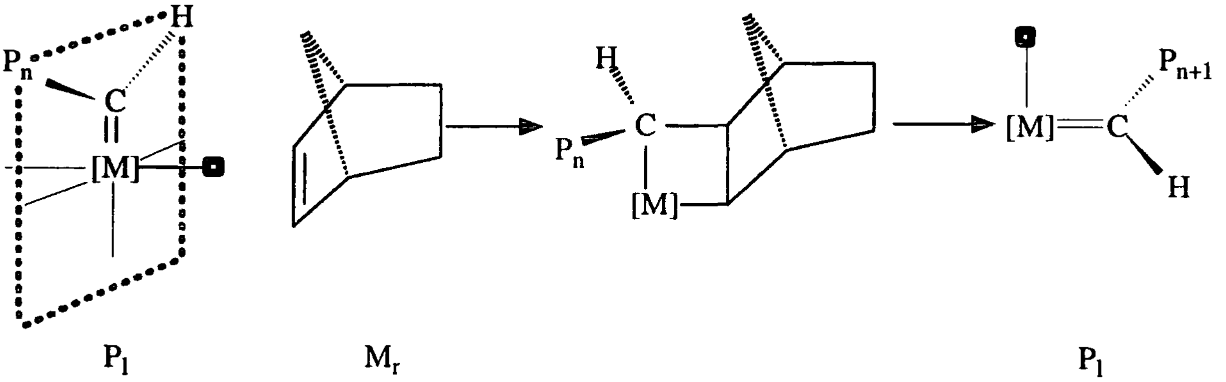


(2) CIS

Figure 1.30a: The two possible cis-forming additions of propagating metallocarbene and norbornene.



(3) TRANS



(4) TRANS

Figure 1.30b: The two possible trans-forming additions of propagating metallocarbene and norbornene.

In this picture the geometry of the C=C double bond is determined by the stereochemistry of the addition of monomer to the propagating species. The above schemes (*Figure 1.30a/b*) can therefore explain the possibility of preparing stereoregular polymers. The alternate repetition of schemes (1) and (2) result in a highly *cis*-syndiotactic polymer and the repetition of schemes (3) and (4) result in a *trans*-isotactic polymer. It is considered that atactic polymers originate from achiral propagating metallocarbene species, or those where stereochemistry is not retained between successive steps.

(b) In the case of unsymmetrically substituted monomers the possibility of head/head, head/tail effects exists. For example the polymer poly{2,5-[3-dimethylphosphonate]cyclopentylene}vinylene, of interest in the work reported in this thesis, has the numbering system illustrated in *Figure 1.31*, with carbons 2, 3, 7 and the phosphonate group ($P(O)(OMe)_2$) being the head part(H) of the polymer and carbons 4, 5 and 6 being the tail part(T).

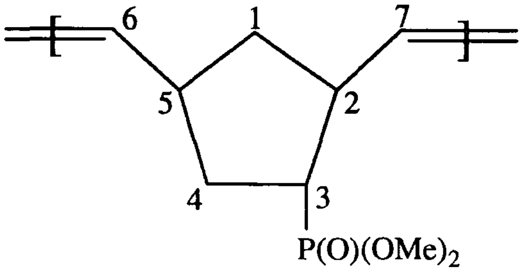


Figure 1.31: Poly{2,5-[3-dimethylphosphonate] cyclopentylene}vinylene.

Therefore the head part of the polymer can be in two possible environments, either HH or HT, depending on whether the adjacent repeat unit is in the head or tail configuration, this is illustrated in *Figure 1.32*.

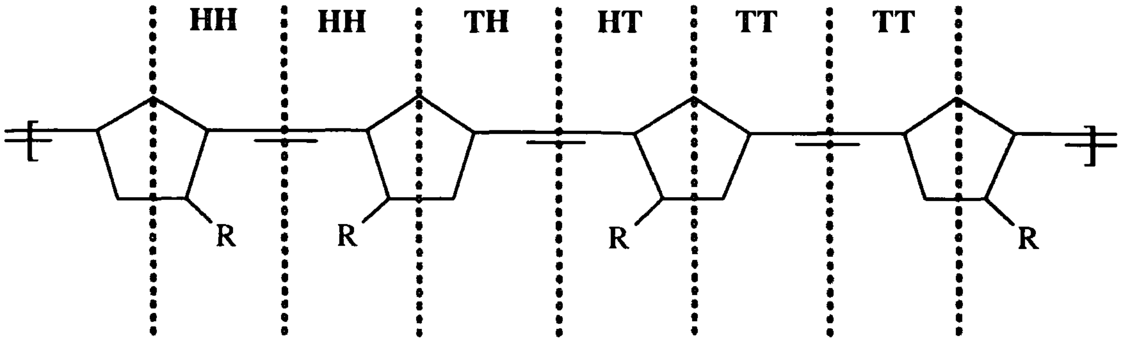


Figure 1.32: Head/Head, Head/Tail effects in poly{2,5-[3-dimethylphosphonate]cyclopentylene}vinylene.

Stereoregular polymers can be synthesised from unsymmetrically substituted monomers using a variety of initiator systems. In the case of the polymerisation of

1-methylnorbornene[130], for example, $ReCl_5$ gives an all *cis* all HT syndiotactic polymer, whereas with $OsCl_3$ an all *trans* HT polymer is observed. It has been suggested that the *cis* HH arrangement is not formed with 1-methylnorbornene due to steric hindrance in the metallocyclobutane intermediate. This is a subtle effect, for example, with 5,5-dimethylnorbornene there is less steric hindrance and the *cis* HH junction can be formed in polymerisations initiated with $ReCl_5$.[83]

The head/tail bias (B) is a measure of the likelihood of forming head/tail repeat units and is given by:-

$$B = \frac{HT + TH}{HH + TT}$$

If we consider an unsymmetrical monomer capable of forming head/tail repeat units, such as 1-methylnorbornene, there are two possible propagating species, one where the methyl substituent is adjacent to the propagating metallocarbene (P_H) and one where the methyl group is remote from the carbene (P_T).

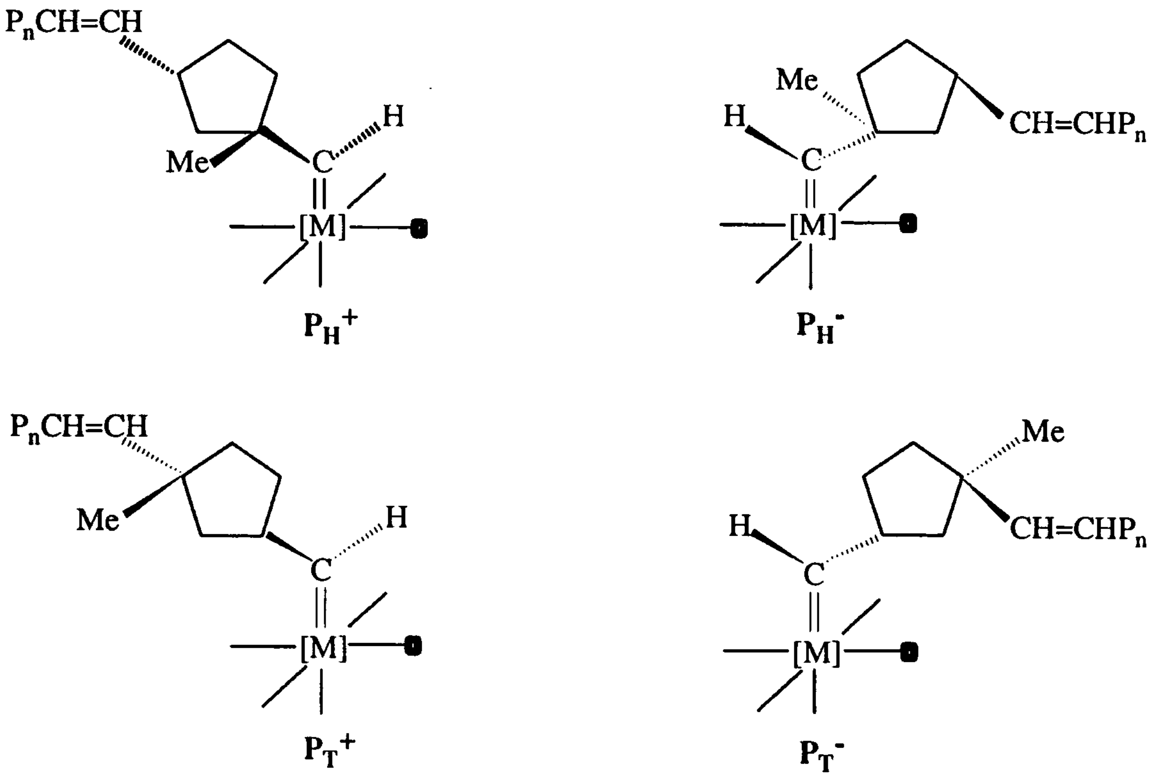


Figure 1.33: The four theoretically possible propagating species from 1-methylnorbornene.

As in the case of *cis/trans* double bond formation (*Section 1.6.6a*) the propagating metallocarbene centre is chiral and therefore two enantiomeric forms exist for each of the P_H and P_T species, arbitrarily labelled "+" and "-" (*Figure 1.33*).

The monomer also exists in two enantiomeric forms, again labelled "+" and "-". Each of these can approach the propagating metallocarbene in two ways, either with the bridging methylene directed into (r) or out of the plane (l) of the page, hence resulting in the four possible orientations (*Figure 1.34*).

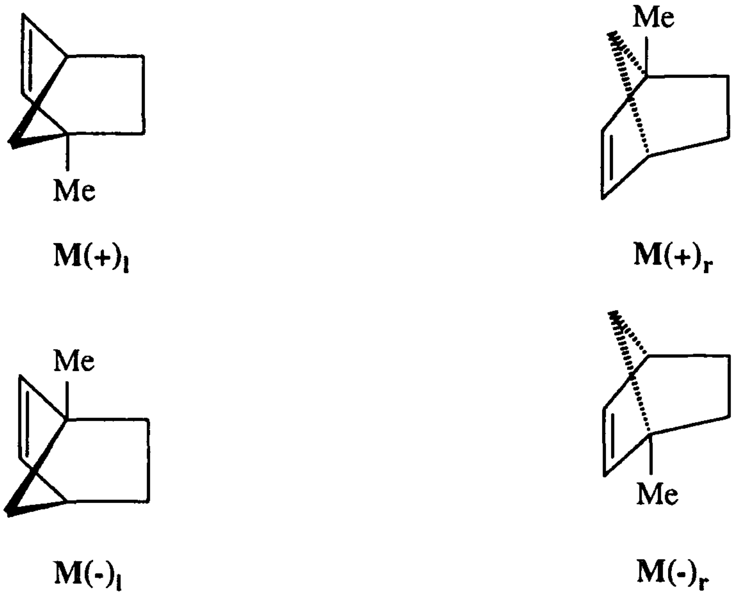


Figure 1.34: The four theoretically possible orientations of 1-methylnorbornene.

Catalysts that produce highly *cis* syndiotactic polymers also show a marked head/tail bias and the formation of such polymers can be explained by the alternate copolymerisation of the (+) and (-) 1-methylnorbornenes, which is illustrated in the reaction scheme in *Figure 1.35*.

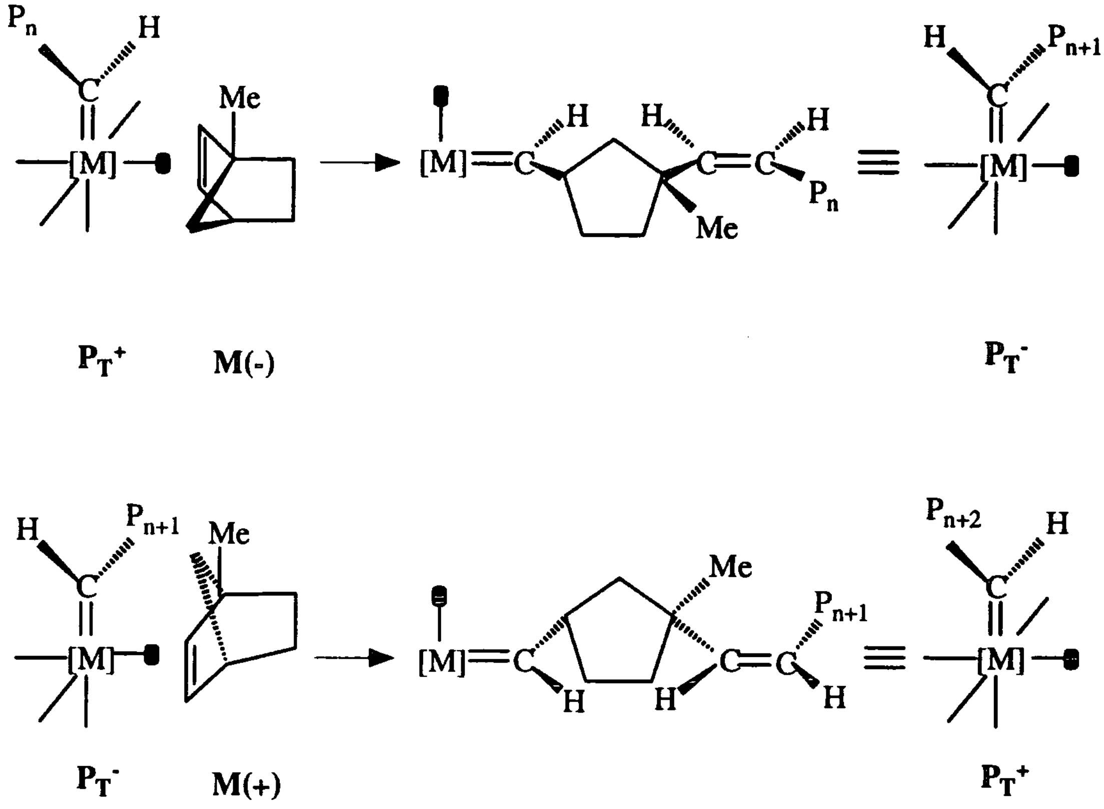
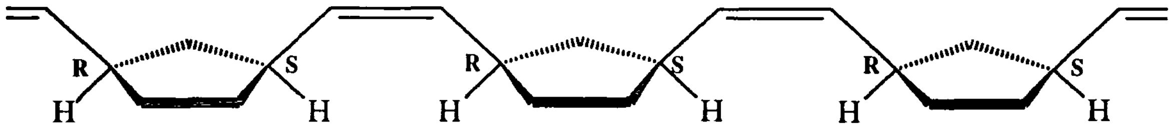


Figure 1.35: The formation of cis-HT syndiotactic poly(1-methylnorbornene).

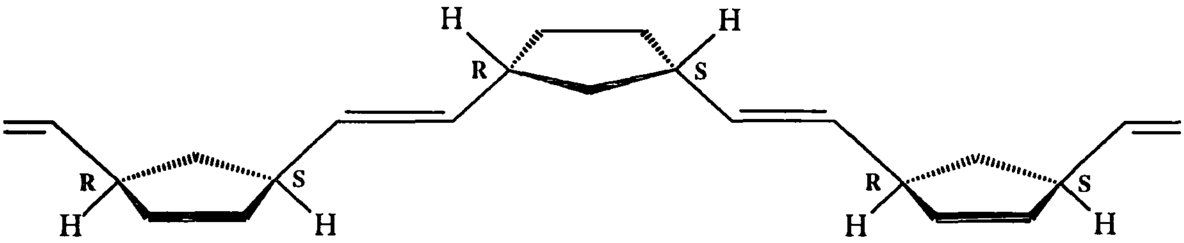
Both enantiomers are required for the polymerisation to continue, and the product is an entirely regio and stereospecific alternating copolymer of enantiomers. The steric fit with the C7 methylene and existing polymer chain syn with respect to each other and attack exclusively on the *exo* face of the monomer to give a *cis* cyclobutane provides a complete account of this remarkably specific reaction.

The reactions that lead to *trans* C=C double bonds do give head/head and tail/tail linkages, implying that the steric fit restrictions invoked to account for the polymer resulting from $ReCl_5$ initiation are relaxed with other initiators.

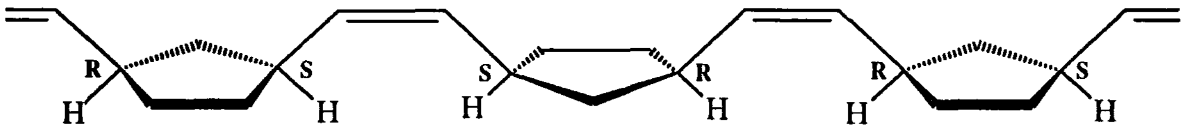
(c) The allylic carbons C2 and C5 are chiral and each can have *R* or *S* configuration. Therefore there is the possibility of the two carbons having the same chiralities, resulting in racemic (r) dyads, or different chiralities, giving meso (m) dyads. Sequences of racemic dyads give rise to syndiotactic polymers and sequences of meso dyads define isotactic polymers. Polymers with a random distribution of dyads are known as atactic. Each of the vinylic bonds can be *cis* or *trans* geometry, hence there are four possible tacticities for a stereoregular polymer as illustrated in *Figure 1.36.*



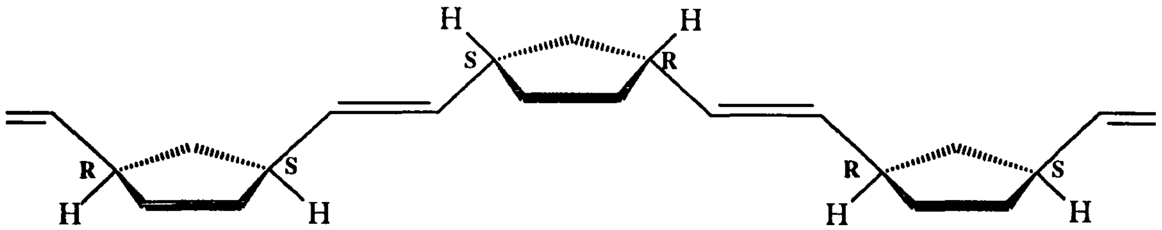
Meso dyads - *Cis* isotactic polymer



Meso Dyads - *Trans* isotactic polymer



Racemic Dyads - *Cis* syndiotactic polymer



Racemic Dyads - *Trans* syndiotactic polymer

Figure 1.36: The possible tacticities of polynorbornene.

Chapter Two:
Synthesis and Characterisation of Potential Monomers.

2.1 General Introduction.

This chapter describes the syntheses and characterisations of a series of monocyclic 1-hydroxy and 1-alkoxy-1-oxo-3-phospholenes and organophosphorus derivatives of bicyclo[2.2.1]heptene. The synthetic routes involve the formation of monocyclic and bicyclic compounds via cycloaddition reactions with butadiene and cyclopentadiene respectively.

2.2 General Background.

2.2.1 The Diels Alder reaction.[143]

The Diels Alder reaction is one of the most effective and widely used routes to six membered carbocyclic ring compounds. It involves a [4+2] cycloaddition reaction, so called since it takes place between a four π-electron system and a two π-electron system. An olefin or acetylene, known as the dienophile, adds to a conjugated diene in a one step process involving a cyclic transition state. The π-orbitals on the dienophile overlap with the termini of the π-orbitals on the diene, ie. carbons 1 and 4. These positions are rehybridised during reaction from sp^2 to sp^3 to form two new σ-bonds, whereas carbons 2 and 3 remain sp^2 hybridised and a new double bond is formed between them in the product (*Figure 2.1*).[144]

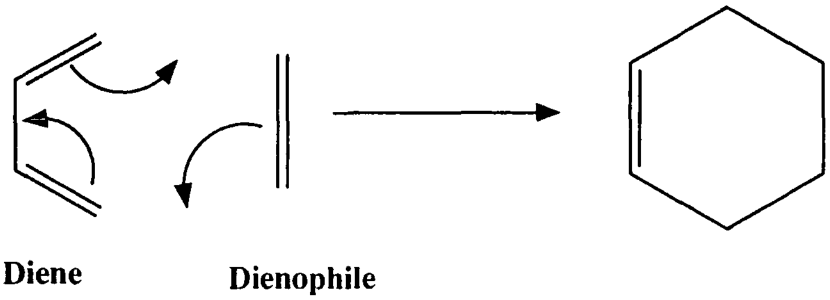


Figure 2.1: The Diels Alder reaction.

The reaction only occurs if the diene is capable of adopting a *cisoid* conformation about the single bond, where carbons 1 and 4 on the diene are close enough to allow reaction with the dienophile to occur. The π-orbitals at the ends of a *transoid* diene are too far apart to overlap those on the dienophile and no cycloaddition occurs. Some dienes can not adopt the *cisoid* conformation due to geometric constraints and steric hindrance and hence do not undergo Diels Alder reactions.

The cycloaddition is more favourable if there are electron withdrawing substituents on the dienophile and electron donating groups on the diene, this is known as a "normal" Diels Alder reaction. An inverse Diels Alder reaction, which is also a favourable reaction, involves electron withdrawing substituents on the diene and electron donating groups on the dienophile.

Cyclopentadiene is often used in the preparation of bicyclic compounds via Diels Alder reactions since the double bonds are "locked" in a coplanar, *cisoid* configuration. The addition of a substituted dienophile to the diene results in the formation of *endo* and *exo* isomers. The ratio of isomers is dependant on the reaction conditions, the *exo*-isomer being the product of thermodynamic control, and the *endo*-isomer being the kinetic product.

Other important features of the Diels Alder reaction are that it can be catalysed by Lewis Acids and it is a very stereospecific reaction. A cycloaddition between a *cis* dienophile and a diene results in the retention of traces of the *cis* stereochemistry in the product.[144] In this work the Diels-Alder reactions between cyclopentadiene and ethene phosphonates and ethene bisphosphonates have been used to prepare monomers for polymerisation studies.

2.2.2 Five membered phosphorus heterocycles.

Heterocycles containing phosphorus and carbon are of general interest because of their potential application to fire retardancy and biological chemistry. McCormack[145] in 1953, described a method using trivalent phosphorus halides and 1,3-dienes to prepare five membered phosphorus heterocycles (*Figure 2.2*).

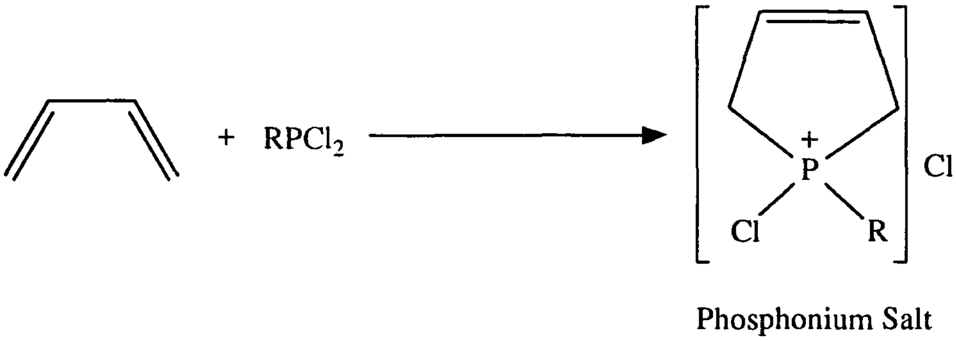


Figure 2.2: Preparation of phosphorus heterocycles.

The resulting compound is a useful precursor in the synthesis of new heterocyclic compounds, due to the presence of a double bond and a reactive phosphorus group. The 1,4 cycloaddition of trialkyl phosphites to α-dicarbonyl compounds has also been reported (*Figure 2.3*).[146-148]

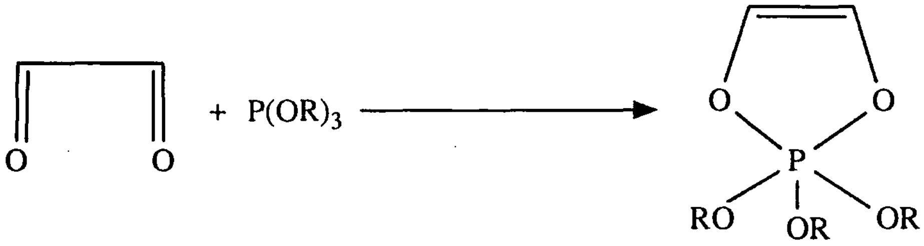


Figure 2.3: Preparation of oxyphosphoranes.

Obviously the diene must be capable of adopting a *cisoid* conformation as with Diels Alder reactions. The trivalent phosphorus in each of these reactions is capable of utilising its unpaired 3s electrons to form a higher covalency, usually tetravalent. It may therefore be regarded as an analogue of a dienophile in these 1,4 additions, which are sometimes described as Diels Alder type reactions. The 3s electrons are used in such a way that sp^3 bonds may be formed, resulting in a tetrahedral structure. In forming the tetrahedral arrangement the phosphorus may adopt a covalent structure, as in phosphorus oxides and acids, or an ionic structure as in the case of phosphonium salts (*Figure 2.2*). It is also possible that the 3d orbitals are utilised to create sp^3d pentacovalency, but this is relatively rare.[149]

The original aim of the research project was to prepare a number of 1-alkoxy-1-oxo-3-phospholene heterocycles (*Figure 2.4*) and then attempt to ring open them via Ring Opening Metathesis Polymerisation.

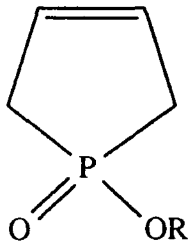


Figure 2.4: 1-Alkoxy-1-oxo-3-phospholenes.

Numerous routes have been proposed for the preparation of these compounds, but the simplest method seems to involve the preparation of 1-chloro-1-oxo-3-phospholene as an intermediate (*Figure 2.5*).[150]

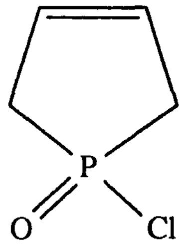


Figure 2.5: 1-Chloro-1-oxo-3-phospholene.

This compound is formed in the reaction between phosphordichlorodites and butadiene (*Figure 2.6*).[151,152] The initial product is a dihalophosphorane, which is unstable and subsequently undergoes dealkylation to the 1-chloro-1-oxo-3-phospholene via an Arbuzov type reaction.

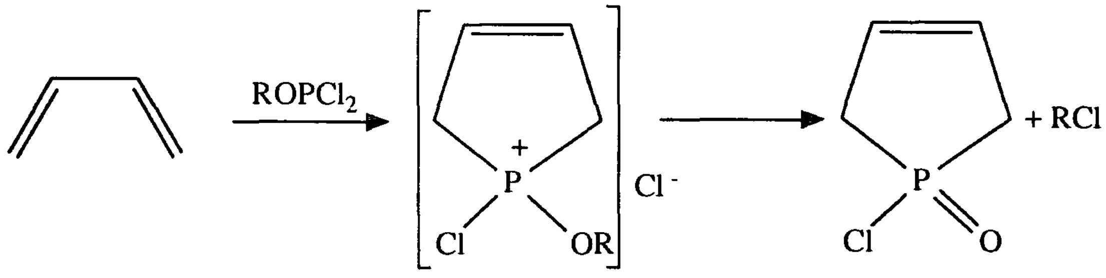


Figure 2.6: Preparation of 1-chloro-1-oxo-3-phospholene from the reaction between phosphordichlorodites and butadiene.

Moedritzer[150] observed that the reaction between phosphorus trichloride, butadiene and tris(chloroethyl) phosphite resulted in the 1:1 mixture of the two isomers of 1-chloro-1-oxo-phospholene. The phosphorus trichloride and tris(chloroethyl) phosphite react to form the (2-chloroethyl) phosphonic dichloride intermediate, which undergoes a 1,4-cycloaddition reaction with butadiene to yield the product. Although the synthesis is a one step, high yield procedure there is the problem of the separation of the two phospholene isomers. The synthesis of isomerically pure 1-chloro-1-oxo-3-phospholene can be achieved by the reaction between ethylene oxide, phosphorus trichloride and 1,3 butadiene (*Figure 2.7*). The ratio of the isomers can be controlled by altering the amount of ethylene oxide in the reaction mixture (*Table 2.1)*. As can be seen from the table a slight excess of ethylene oxide favours the production of the 3-phospholene isomer, so that n=3.[154] Since the ethylene oxide / PCl_3 and the tris(chlorethyl)phosphite / PCl_3 reagents are both believed to react via the same intermediate it is not clear why the latter reagent should give an isomerically pure product. However, the author has found the synthesis is effective as described.

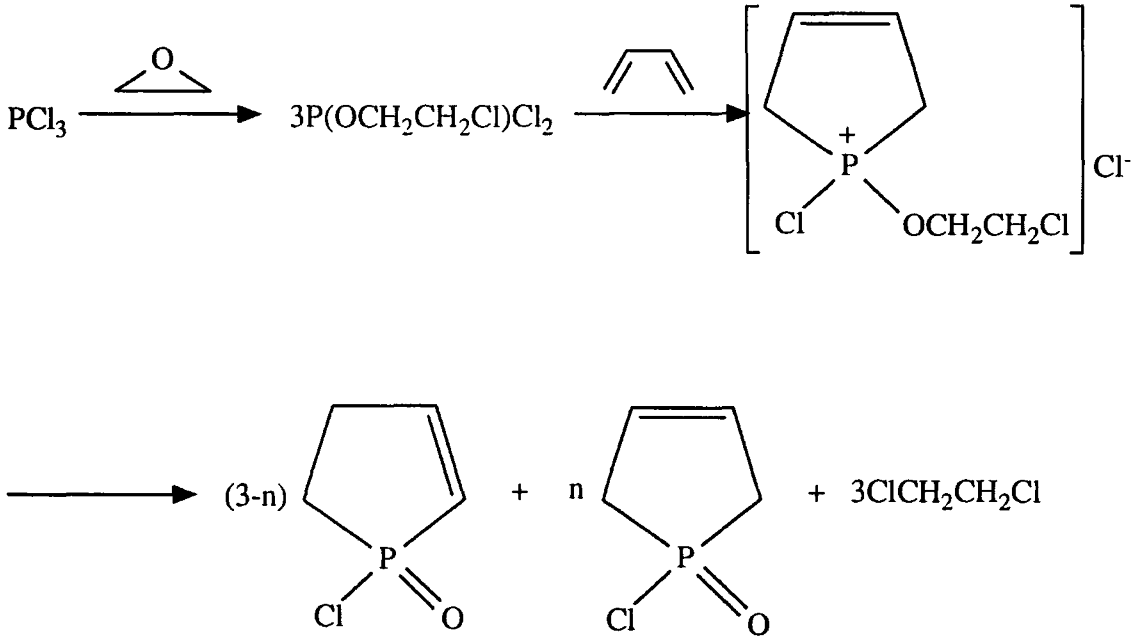


Figure 2.7: Synthesis of the 1-alkoxy-1-oxo-phospholene isomers.

Ethylene Oxide (Mol)	Ratio of 3-Isomer to 2-Isomer	Yield
1.10	100:0	92%
1.01	100:0	93%
1.00	73:27	83%
0.90	20:80	81%

Table 2.1: Variation of isomeric purity with differing amounts of ethylene oxide.

2.3 Experimental.

2.3.1 Reactants.

All reactants (Aldrich Chemical Co. Ltd. / Fluka Chemicals Ltd.) and solvents (May and Baker / BDH, laboratory grade) were used as supplied unless otherwise stated.

2.3.2 Characterisation.

All NMR spectra were recorded on a Varian VXR 400 NMR spectrometer, operating at 399.952 MHz for ^{1}H NMR, 100.577 MHz for ^{13}C NMR and 161.90 MHz for ^{31}P NMR, a Bruker AMX 500 NMR spectrometer operating at 125.770 MHz for ^{13}C NMR and 202.460 MHz for ^{31}P NMR or a Bruker AC250 FT NMR spectrometer operating at 97.15 MHz for ^{31}P NMR. Mass spectra were recorded on a VG Analytical Model 7070E mass spectrometer. Infrared spectra were recorded on a Perkin Elmer 1600 series Fourier Transform Infrared spectrometer or a Perkin Elmer 577 spectrometer.

2.3.3 The use of inhibitors.

To prevent the formation of polymeric adducts or butadiene polymers, inhibitors have to be used. Copper (II) Stearate and butyl pyrocatechol have been used extensively[145,149] for this purpose and so were used in the synthesis of 1-chloro-1-oxo-phosphol-3-ene.

2.4 Synthesis and characterisation of 1-chloro-1-oxo-phosphol-3-ene.

2.4.1 Synthesis of 1-chloro-1-oxo-phosphol-3-ene.

Phosphorus trichloride (204g/1.50 mol) and copper stearate (ca. 1.0g) were placed in a 2-litre glass lined stainless steel autoclave and ethylene oxide (67g/1.52 mol) and 1,3-butadiene (81g/1.50 mol) were introduced by vacuum transfer. The resulting mixture was then heated for 10 hours at 105°C. After the reaction was completed the volatiles were vented and trapped in a sodium hydrogen carbonate/ice bath and the excess phosphorus trichloride (b.p. 75°C) and the by-product dichloroethane (b.p. 83°C) were removed by distillation. The residue was distilled under vacuum (10cm Vigreaux column) and pure 1-chloro-1-oxo-phosphol-3-ene was collected as a colourless liquid (80-90°C/1mm), which crystallised in the receiver, 59%

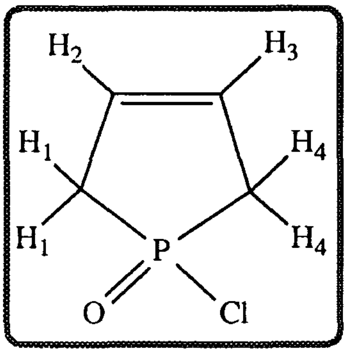
yield, white crystals (m.p. 52-53°C. Lit.[154] 52-53°C). This distillation was carried out using a Bunsen burner to ensure that it occurred rapidly to prevent decomposition of the 1-chloro-1-oxo-phosphol-3-ene product, which is heat sensitive and gives a lot of tarry residues when a conventional slow fractional distillation is attempted.

2.4.2 Characterisation of 1-chloro-1-oxo-phosphol-3-ene.

The ^1H-decoupled ^{31}P NMR spectrum (97.15 MHz/$CDCl_3$/ Appendix C1) shows one singlet at 76.61 ppm due to the presence of one phosphorus environment. The infrared spectrum of 1-chloro-1-oxo-phosphol-3-ene was recorded as a KBr disc and is shown in appendix D1. The peaks were consistent with the assigned structure with the most important diagnostic infrared bands being:- vinylic CH stretches at 3010 cm^{-1}, CH_2 stretch at 2960 cm^{-1}, a C=C stretch at 1595 cm^{-1} and P=O stretch at 1210 cm^{-1}.

The chemical ionisation mass spectrum (appendix E1) is somewhat equivocal due to the fragmentation of 1-chloro-1-oxo-phosphol-3-ene in the mass spectrometer. Although there is evidence of a mass peak at 102 (C_4H_6PO {+ H^+}) corresponding to the loss of a chlorine atom from the protonated parent ion, peaks at 182 and 184 could not be accounted for and may indicate the presence of higher molecular weight impurity in this compound or some complex process in the mass spectrometer source region.

The number and shifts of the signals in the ^1H NMR spectrum, and their integrations, are consistent with the assigned structure, 1-chloro-1-oxo-phosphol-3-ene (see appendix A1), with the assignments and chemical shifts summarised in Table 2.2.

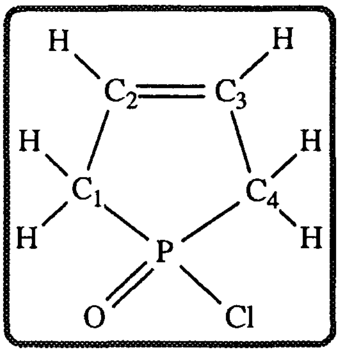


Assignment	Shift (ppm)	Multiplicity
H1,H4	2.92	Multiplet
H2,H3	6.02	Doublet $^3J_{PH}$ =38.51Hz

Table 2.2: ^1H NMR spectral assignments for
1-chloro-1-oxo-phosphol-3-ene (399.952 MHz/$CDCl_3$).

The signal at 2.92 ppm appears as a multiplet due to the two H_1 protons, and similarly the two H_4 protons, being non-equivalent. This creates an A_2B_2X environment with the phosphorus atom, one proton having a *syn* position with respect to the P=O bond and the other having a *anti* position. In low field spectra the allylic signal often appears as a doublet in phospholenes due to a deceptive simplification of the signal, but the observation of a multiplet in the higher field 400 MHz NMR spectrum of 1-chloro-1-oxo-phosphol-3-ene is in agreement with the expected non-equivalence of the protons in the 3-phospholenes.

The ^{13}C NMR spectrum is consistent with the assigned structure, 1-chloro-1-oxo-phosphol-3-ene (see appendix B1), with the assignments and chemical shifts summarised in Table 2.3.



Assignment	Shift (ppm)	Multiplicity
C1,C4	36.49	Doublet ${}^1J_{PC}$ =76.24Hz
C2,C3	126.17	Doublet ${}^2J_{PC}$ =17.50Hz

Table 2.3: ^{13}C NMR spectral assignments for 1-chloro-1-oxo-phosphol-3-ene (100.577 MHz/$CDCl_3$).

2.5 Synthesis and characterisation of 1-hydroxy-1-oxo-phosphol-3-ene.

2.5.1 Synthesis of 1-hydroxy-1-oxo-phosphol-3-ene.[150]

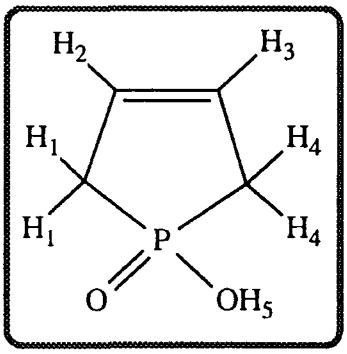
1-Chloro-1-oxo-phosphol-3-ene (10g/0.073 mol) was hydrolysed by slow addition to ice with constant cooling in an ice bath. The evolved HCl was vented into a sodium hydrogen carbonate/ice bath and the excess water was subsequently removed on a rotary evaporator (bath temperature 80°C). The resulting white crystals were dried in vacuo over potassium hydroxide pellets and finally recrystallised from hot toluene in 98% yield. (m.p. 84-85°C. Lit.[150] 86°C).

2.5.2 Characterisation of 1-hydroxy-1-oxo-phosphol-3-ene.

The ^1H-decoupled ^{31}P NMR spectrum (97.15 MHz/$CDCl_3$/ Appendix C2) shows one singlet at 75.53 ppm due to the presence of one phosphorus environment. The infrared spectrum of 1-hydroxy-1-oxo-phosphol-3-ene is shown in appendix D2 and is consistent with the assigned structure with the most important diagnostic infrared bands being:- vinylic CH stretches at 3040 cm^{-1}, CH_2 symmetric and unsymmetric stretches at 2960 cm^{-1} and 2900 cm^{-1}, a C=C stretch at 1605 cm^{-1} and a P=O stretch at 1235 cm^{-1}. The broad bands at ~3500 cm^{-1} and ~1700 cm^{-1} were indications of the probable retention of traces of water by the sample.

The electron impact mass spectrum (Appendix E2) is consistent with the assigned structure and contains a molecular ion at 118 and a base peak at 54 ($C_4H_6^+$) resulting from the extrusion of PO_2H from the molecular ion, a sort of retro-Diels Alder reaction.

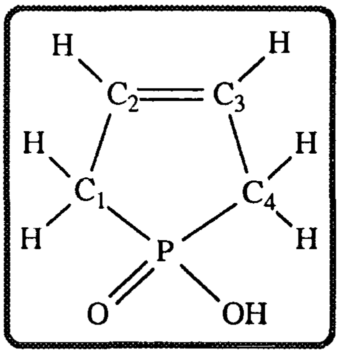
The number and shifts of the signals in the ^1H NMR spectrum, and their integrations, are consistent with the assigned structure (see appendix A2) with the assignments and chemical shifts summarised in Table 2.4.



Assignment	Shift (ppm)	Multiplicity
H1,H4	2.52	Doublet $^2J_{PH}$=13.84Hz
H2,H3	5.92	Doublet $^3J_{PH}$=33.68Hz
H5	10.13	Singlet

Table 2.4: ^1H NMR spectral assignments for 1-hydroxy-1-oxo-phosphol-3-ene (399.952 MHz/$CDCl_3$).

The ^{13}C NMR spectrum is consistent with the assigned structure (see appendix B2), with the assignments and chemical shifts summarised in Table 2.5.



Assignment	Shift (ppm)	Multiplicity
C1,C4	30.15	Doublet $^1J_{PC}$ =95.35Hz
C2,C3	126.90	Doublet $^2J_{PC}$ =15.19Hz

Table 2.5: ^{13}C NMR spectral assignments for 1-hydroxy-1-oxo-phosphol-3-ene (100.577 MHz/CDCl$_3$).

2.6 Synthesis and characterisation of 1-methoxy-1-oxo-phosphol-3-ene.

2.6.1 Synthesis of 1-methoxy-1-oxo-phosphol-3-ene.

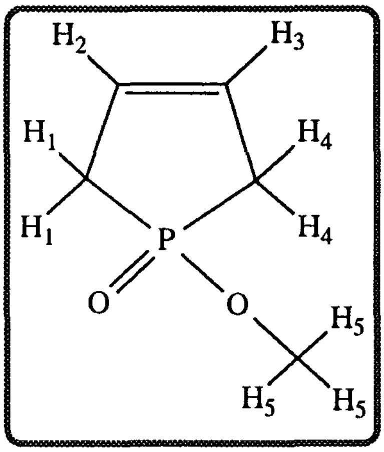
Dichloromethane, methanol and triethylamine were distilled and stored under nitrogen over 3A molecular sieves.

1-Chloro-1-oxo-phosphol-3-ene (10g / 0.073 mol), dissolved in dry dichloromethane (50ml), was added dropwise to a solution of dry methanol (2.53g/0.079 mol) and dry triethylamine (7.55g/0.075 mol), kept at 0°C. The resulting white slurry was allowed to warm to room temperature and was stirred for two hours.

The hydrochloride salts were removed by filtration, washed with dichloromethane and the low boiling materials were removed by distillation under nitrogen. The resulting brown residue was distilled in vacuo (10cm Vigreaux column) to give 1-methoxy-1-oxo-phosphol-3-ene as a colourless liquid (50-60°C/0.05 mm) in 45% yield.

2.6.2 Characterisation of 1-methoxy-1-oxo-phosphol-3-ene.[155]

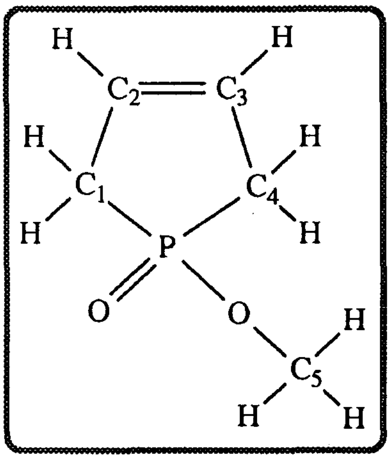
The number and shifts of the signals in the ^1H NMR spectrum, and their integrations, are consistent with the assigned structure (see appendix A3) with the assignments and chemical shifts summarised in Table 2.6.



Assignment	Shift (ppm)	Multiplicity
H1,H4	2.44	Doublet $^2J_{PH}$=12.20Hz
H2,H3	5.94	Doublet $^3J_{PH}$=32.81Hz
H5	3.77	Doublet $^3J_{PH}$=11.20Hz

Table 2.6: ^1H NMR spectral assignments for 1-methoxy-1-oxo-phosphol-3-ene (399.952 MHz/D_2O).

The ^{13}C NMR spectrum is consistent with the assigned structure (see appendix B3), with the assignments and chemical shifts summarised in Table 2.7.



Assignment	Shift (ppm)	Multiplicity
C1,C4	28.59	Doublet $^{1}J_{PC}$ =90.82Hz
C2,C3	127.02	Doublet $^{2}J_{PC}$ =15.29Hz
C5	51.33	Doublet $^{2}J_{PC}$ =6.94Hz

Table 2.7: ^{13}C NMR spectral assignments for 1-methoxy-1-oxo-phosphol-3-ene (100.577 MHz/D_2O).

The ^{1}H-decoupled ^{31}P NMR spectrum (97.15 MHz/$CDCl_3$/ Appendix C3) shows one singlet at 85.28 ppm due to the presence of one phosphorus environment. The infrared spectrum of 1-methoxy-1-oxo-phosphol-3-ene is shown in appendix D3 and is consistent with the assigned structure with the most important diagnostic infrared bands being:- vinylic CH stretches at 3040 cm^{-1}, CH_2/CH_3 stretches at 2940 cm^{-1} and 2900

cm^{-1}, a C=C stretch at 1615 cm^{-1} and a P=O stretch at 1243 cm^{-1}. The broad bands at ~3500 cm^{-1} and ~1700 cm^{-1} were indications of the probable retention of traces of water by the sample.

The electron impact mass spectrum (Appendix E3) is consistent with the assigned structure and contains a molecular ion at 132 and a base peak at 54 ($C_4H_6^+$).

2.7 Synthesis and characterisation of 1-phenoxy-1-oxo-phosphol-3-ene.

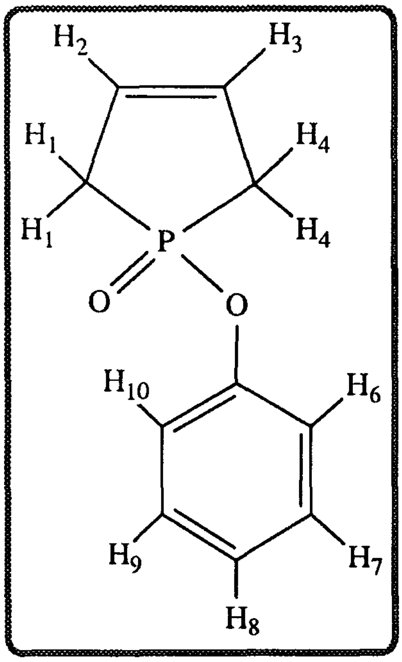
2.7.1 Synthesis of 1-phenoxy-1-oxo-phosphol-3-ene.[156]

Toluene and triethylamine were distilled and stored under nitrogen over 3A molecular sieves.

1-Chloro-1-oxo-phosphol-3-ene (10g/0.073 mol), dissolved in dry toluene (50ml), was added dropwise to a solution of dry triethylamine (7.78g/0.077 mol), phenol (6.89g/0.074 mol) and toluene (100ml), kept at 0°C. The resulting white slurry was then was allowed to warm to room temperature and was stirred for 48 hours. The hydrochloride salts were removed by filtration, washed with toluene and the low boiling fractions were removed by distillation under nitrogen. The residue was distilled under vacuum (10cm Vigreaux column) to produce a colourless liquid (80-90°C/0.07mm), which was left to recrystallise in the freezer. The white crystals of 1-phenoxy-1-oxo- phosphol-3-ene were recovered in 60% yield. (m.p.= 46-48°C. Lit.[156] 49-50°C).

2.7.2 Characterisation of 1-phenoxy-1-oxo-phosphol-3-ene.

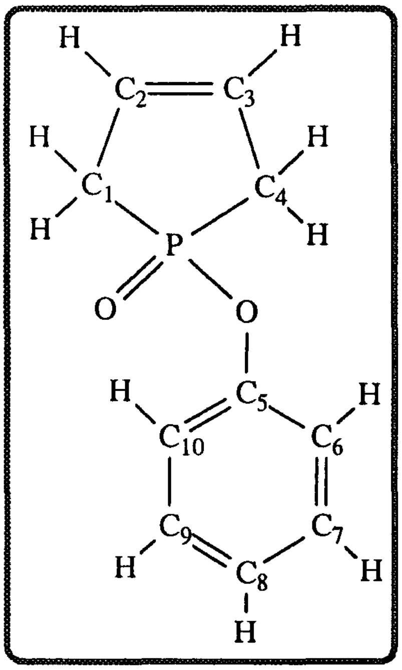
The number and shifts of the signals in the ^1H NMR spectrum, and their integrations, are consistent with the assigned structure (see appendix A4) with the assignments and chemical shifts summarised in Table 2.8.



Assignment	Shift (ppm)	Multiplicity
H1,H4	2.55	Multiplet
H2,H3	5.95	Doublet $^3J_{PH}$ =34.00Hz
H6-H10	7.25	Multiplet

Table 2.8: ^1H NMR spectral assignments for 1-phenoxy-1-oxo-phosphol-3-ene (399.952 MHz/$CDCl_3$).

The ^{13}C NMR spectrum is consistent with the assigned structure (see appendix B4), with the assignments and chemical shifts summarised in Table 2.9. The assignments of C5-C10 have been made with reference to $P(O)Ph_3$ data.[157]



Assignment	Shift (ppm)	Multiplicity
C1,C4	29.04	Doublet $^1J_{PC}$ =91.53Hz
C2,C3	126.99	Doublet $^2J_{PC}$=16.09Hz
C5	150.87	Doublet $^2J_{PC}$ =8.34Hz
C6,C10	120.32	Doublet $^3J_{PC}$ =4.53Hz
C7,C9	129.93	Singlet
C8	124.94	Singlet

Table 2.9: ^{13}C NMR spectral assignments for 1-phenoxy-1-oxo-phosphol-3-ene (100.577 MHz/$CDCl_3$).

The ^1H-decoupled ^{31}P NMR spectrum (97.15 MHz/$CDCl_3$/ Appendix C4) shows one singlet at 73.73 ppm due to the presence of one phosphorus environment.

The infrared spectrum of 1-phenoxy-1-oxo-phosphol-3-ene is shown in appendix D4 and is consistent with the assigned structure with the most important diagnostic infrared bands being:- vinylic CH stretches at 3060 cm^{-1}, 3010 cm^{-1}, CH_2 stretch at 2920 cm^{-1}, C=C stretches at 1620 cm^{-1} and 1595 cm^{-1} and a P=O stretch at 1243 cm^{-1}. The broad band at ~3500 cm^{-1} is probably due to the retention of traces of water by the sample.

The electron impact mass spectrum (Appendix E4) is consistent with the assigned structure and contains a molecular ion at 194 and a base peak at 140 (M^+-$C_4H_6^+$).

2.8 Synthesis and characterisation of 1-neopentoxy-1-oxo-phosphol-3-ene.

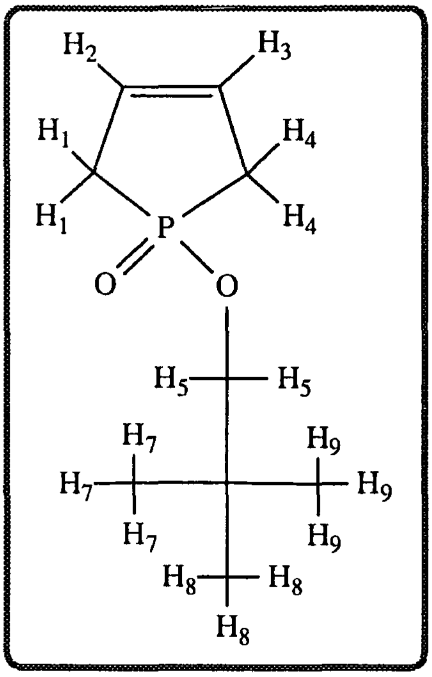
2.8.1 Synthesis of 1-neopentoxy-1-oxo-phosphol-3-ene.

Toluene and triethylamine were distilled and stored under nitrogen over 3A molecular sieves.

1-Chloro-1-oxo-phosphol-3-ene (10g/0.073 mol), dissolved in dry toluene (50 ml), was added dropwise to a solution of neopentanol (6.60g/0.074 mol), dry triethylamine (7.56g/0.075 mol) and dry toluene (100ml), kept at 0°C. The resulting white slurry was allowed to warm to room temperature and was stirred for 24 hours. The hydrochloride salts were removed by filtration, washed with toluene and the low boiling materials were removed by distillation under nitrogen. The residue was distilled under vacuum (10cm Vigreaux column) to produce a colourless liquid (80-85°C/0.05mm), which was left to recrystallise in the freezer. The white crystals of 1-neopentoxy-1-oxo-phosphol-3-ene were recovered in 66% yield. (m.p. 49-51°C).

2.8.2 Characterisation of 1-neopentoxy-1oxo-phosphol-3-ene.

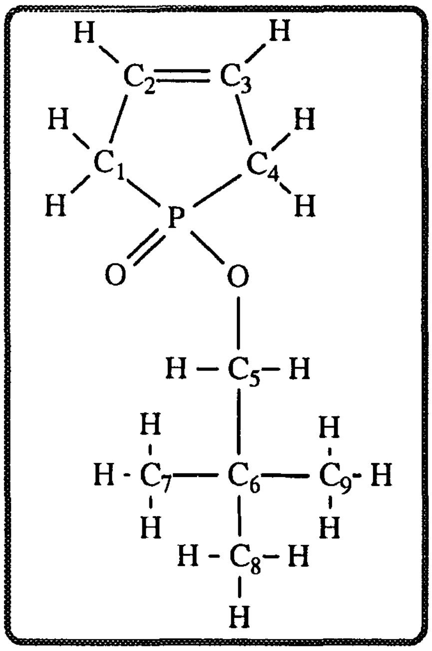
The number and shifts of the signals in the ^1H NMR spectrum, and their integrations, are consistent with the assigned structure (see appendix A5) with the assignments and chemical shifts summarised in Table 2.10.



Assignment	Shift (ppm)	Multiplicity
H1,H4	2.44	Doublet $^2J_{PH}$ =12.40Hz
H2,H3	5.93	Doublet $^3J_{PH}$ =33.20Hz
H5	3.67	Doublet $^3J_{PH}$ =5.60Hz
H7-H9	0.95	Singlet

Table 2.10: ^1H NMR spectral assignments for 1-neopentoxy-1-oxo-phosphol-3-ene (399.952 MHz/CDCl$_3$).

The ^{13}C NMR spectrum is consistent with the assigned structure (see appendix B5), with the assignments and chemical shifts summarised in Table 2.11.



Assignment	Shift (ppm)	Multiplicity
C1,C4	28.94	Doublet $^1J_{PC}$=91.53Hz
C2,C3	127.03	Doublet $^2J_{PC}$=15.28Hz
C5	74.09	Doublet $^2J_{PC}$ =6.84Hz
C6	31.99	Doublet $^3J_{PC}$ =6.84Hz
C7-C9	26.04	Singlet

Table 2.11: ^{13}C NMR Spectral Assignments for 1-Neopentoxy-1-oxo-phosphol-3-ene (100.577 MHz/CDCl$_3$).

The ^{1}H-decoupled ^{31}P NMR spectrum (97.15 MHz/CDCl$_3$/ Appendix C5) shows one singlet at 74.19 ppm due to the presence of one phosphorus environment. The infrared spectrum of 1-neopentoxy-1-oxo-phosphol-3-ene is shown in appendix D5 and is consistent with the assigned structure with the most important diagnostic infrared bands being:- vinylic CH stretches at 3060 cm^{-1}, 3010 cm^{-1}, CH$_2$/CH$_3$ stretches at 2960

cm^{-1} and 2880 cm^{-1}, a C=C stretch at 1595 cm^{-1} and a P=O stretch at 1252 cm^{-1}. The broad band at ~3500 cm^{-1} is probably due to the retention of traces of water by the sample.

The chemical ionisation mass spectrum (Appendix E5) is consistent with the assigned structure and contains a molecular ion peaks at 189 ($M + H^+$) and at 206 ($M + NH_4^+$).

2.9 Synthesis and characterisation of dimethylbicyclo[2.2.1]hept-2-ene-5-phosphonate.

2.9.1 Synthesis of dimethylbicyclo[2.2.1]hept-2-ene-5-phosphonate.[157-161]

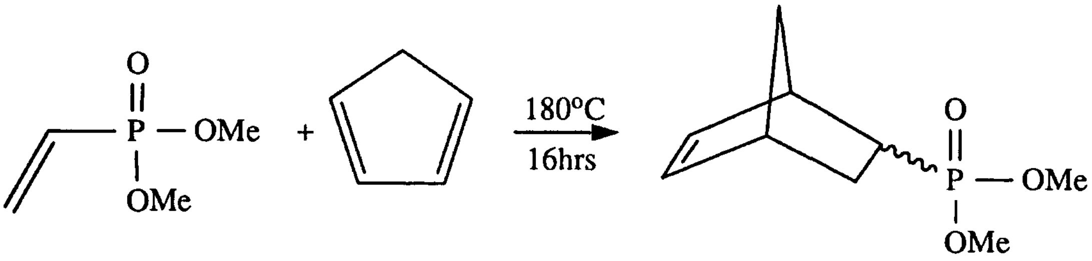
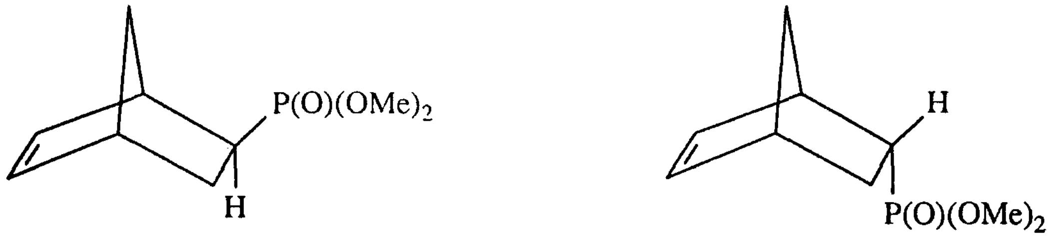


Figure 2.8: Synthesis of dimethylbicyclo[2.2.1]hept-2-ene-5-phosphonate.

Dimethyl vinyl phosphonate (50g/0.248 mol), cyclopentadiene (16.4g/0.248 mol) and hydroquinone (ca.0.1g) were sealed in a 160 ml Hastelloy autoclave and heated for 16 hours at 180°C. The brown reaction mixture was distilled in vacuo (10 cm Vigreaux column) to give two colourless fractions, dimethyl vinyl phosphonate (50-60°C/0.1mm) and dimethylbicyclo[2.2.1]hept-2-ene-5-phosphonate (80-90°C/0.1mm). The second fraction was redistilled in vacuo (10 cm Vigreaux column) to give a mixture of the *exo* and *endo* isomers of dimethylbicyclo[2.2.1]hept-2-ene-5-phosphonate in 70% yield, in an *exo/endo* ratio, based on NMR and g.l.c., of 1.11:1 (*Figure 2.9*). Detailed analysis of the NMR data (see later) shows the *exo* form to be the more abundant isomer.



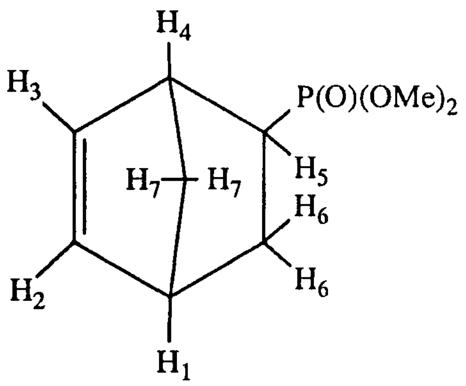
***Exo*-isomer** ***Endo*-isomer**

Figure 2.9: The exo and endo isomers of dimethylbicyclo[2.2.1]hept-2-ene-5-phosphonate.

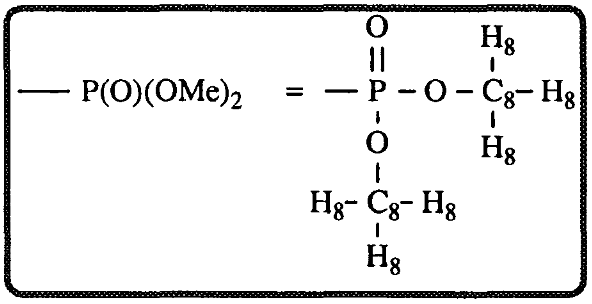
2.9.2 Characterisation of dimethylbicyclo[2.2.1]hept-2-ene-5-phosphonate.

Chromatography techniques were unsuccessful in separating the two isomers and therefore characterisation was carried out on the *exo/endo* mixture. A ^{1}H-decoupled ^{31}P NMR spectrum (97.15 MHz/$CDCl_3$/ Appendix C6) shows the presence of two peaks corresponding to the *endo* and *exo* environments:- *endo*-isomer 33.39 ppm (singlet), *exo*-isomer 34.48 ppm (singlet). The infrared spectrum of dimethylbicyclo [2.2.1]hept-2-ene-5-phosphonate is shown in appendix D6 and is consistent with the assigned structure with the most important diagnostic infrared bands being:- vinylic CH stretches at 3060 cm^{-1}, 3010 cm^{-1}, CH_2/CH_3 stretches at 3000 cm^{-1}, 2880 cm^{-1} and 2850cm^{-1}, a C=C stretch at 1570 cm^{-1} and a P=O stretch at 1236 cm^{-1}. The broad bands at ~3500 cm^{-1} and ~1700 cm^{-1} were indications of the probable retention of traces of water by the sample. The electron impact mass spectrum (Appendix E6) was consistent with the assigned structure with a small molecular ion being present at 202 and the base peak at 137 ($C_4H_{10}O_3P$) from a retro Diels Alder reaction accompanied by a hydrogen atom transfer.

The ^{1}H NMR spectrum (appendix A6) is summarized in Table 2.12. The assignments are based on a knowledge of the *exo/endo* ratio derived from analysis of the ^{13}C NMR (appendix B6), DEPT (appendix F1), COSY (appendix F2) and HETCOR (appendix F3) spectra. The overall shifts and integrations are self consistent.



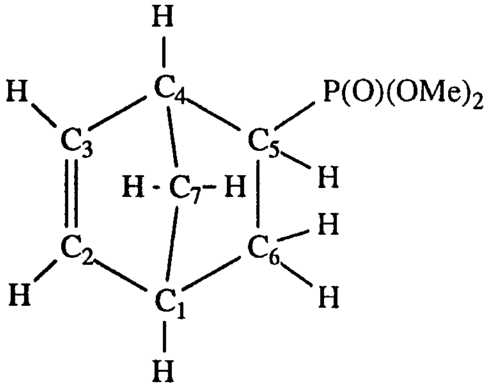
***Exo/Endo* Mixture.**



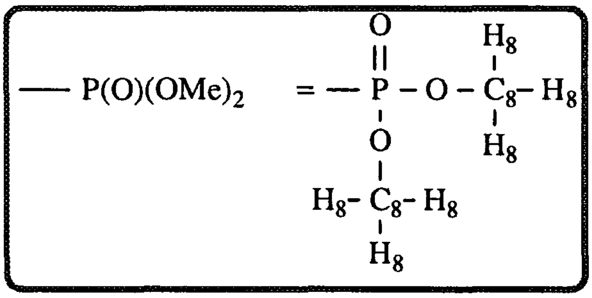
Assignment	Shift (ppm)	Multiplicity
H1 (endo/exo)	2.965	Broad Multiplet
H2/H3 (endo/exo)	6.120	Multiplet
H4 (exo)	3.148	Broad Multiplet
H4 (endo)	3.073	Broad Multiplet
H5 (endo)	2.316	Multiplet
H5 (exo)	1.561	Multiplet
H6 (endo/exo)	1.959 1.300	Multiplet Multiplet
H7 (exo)	1.643 1.214	AB Quartet
H7 (endo)	1.450 1.310	Multiplet Doublet
H8 (endo/exo)	3.720	Multiplet

Table 2.12: ^1H spectral assignments for dimethylbicyclo[2.2.1]hept-2-ene-5-phosphonate (399.952MHz/CDCl$_3$).

The ^{13}C NMR spectrum was more informative and is summarized in Table 2.13 with the phosphorus-carbon coupling constants listed in Table 2.14. DEPT spectra allowed easy assignment of the CH, CH_2 and CH_3 carbons and these are discussed in detail below.



Exo/Endo **Mixture.**



	EXO-ISOMER		ENDO-ISOMER	
	Shift (ppm)	Multiplicity	Shift (ppm)	Multiplicity
C1	41.07-41.04	doublet	41.54-41.48	doublet
C2	135.88	singlet	135.65	singlet
C3	135.84-135.68	doublet	132.04-131.99	doublet
C4	42.663-42.656	doublet	43.49-43.48	doublet
C5	33.92-33.53	doublet	34.57-33.05	doublet
C6	26.95	singlet	26.12-26.11	doublet
C7	45.49	singlet	49.44-49.27	doublet
C8	51.56-51.49	doublet	(a) 51.30-51.23 (b) 51.17-51.10	doublet doublet

Table 2.13: ^{13}C spectral assignments for dimethylbicyclo[2.2.1]hept-2-ene-5-phosphonate (100.577MHz/$CDCl_3$).

	EXO-ISOMER	ENDO-ISOMER
Carbon	P-C Coupling (Hz)	P-C Coupling (Hz)
C1	3.02	6.84
C2	--------	--------
C3	15.69	4.62
C4	0.70	1.91
C5	130.30	153.38
C6	--------	1.21
C7	--------	16.80
C8	6.84	(a) 6.93 (b) 6.54

Table 2.14: Phosphorus-carbon coupling constants for dimethylbicyclo[2.2.1]hept-2-ene-5-phosphonate.

A blank indicates that the coupling, if any, was too small to be detected under our measuring conditions.

C-H Carbons.

In the vinylic region there are six signals corresponding to two exo and two endo carbons. The presence of six signals can be explained by the fact that for both *exo*- and *endo*- isomers carbon C(3) is split by the phosphorus, whereas C(2) is not, hence a doublet and a singlet are observed for each of the two isomers. The major isomer appears to have the larger coupling constant between C(3) and phosphorus ($^3J_{P,C3}$ = 15.69 Hz compared to $^3J_{P,C3}$ = 4.62 Hz for the minor isomer) and using a Karplus-type relationship for 3-bond carbon-phosphorus coupling it can be deduced that the major isomer (135.839-135.683 ppm {doublet} and 135.653 ppm {singlet}) is the *exo* form.

Large coupling constants are normally observed between carbon and phosphorus when they are adjacent and this is the case for P-C(5). Two large coupling constants are observed for the major isomer at 33.924-32.529 ppm ($^1J_{P,C5}$ = 130.30 Hz) and the minor isomer at 34.573-33.048 ppm ($^1J_{P,C5}$ = 153.38 Hz). In similar compounds[162-165] the $^1J_{P,C}$ coupling constant in the *endo*-isomer is larger than that of the *exo*-isomer hence this strengthens the case for the major isomer being the *exo*-form.

Carbon (1) and carbon (4) were originally difficult to distinguish from each other as all four signals are doublets with very small coupling constants and appear in the same region of the spectrum. A HETCOR spectrum was required to correlate the C(1) and C(4) signals with their respective protons and a COSY spectrum was used to assign the proton regions. There is evidence from the COSY spectrum of coupling between the protons on C(6) and one of these unknown regions. This unknown region could now be assigned to the protons on C(1), as C(1) and C6) are adjacent it is more likely that H(6) protons would couple with the protons on C(1) than those on C(4). Therefore the doublets at 41.074-41.044 ppm ($^3J_{P,C1}$ = 3.02 Hz) and 41.544-41.476 ppm ($^3J_{P,C1}$ =

6.84 Hz) were assigned to the C(1) *exo*- and *endo*-isomers respectively, and the doublets at 42.663-42.656 ppm ($^2J_{P,C4}$ = 0.70 Hz) and 43.494-43.475 ppm ($^2J_{P,C4}$ = 1.91 Hz) correspond to C(4) *exo* and C(4) *endo* respectively. These assignments also agree with the literature[162-165] in that the *endo* coupling constants are larger than the corresponding *exo* values.

CH_2 Carbons.

In similar compounds the P-C coupling constants for the C(7) carbons in *endo*-isomers are considerably larger than the corresponding coupling constants in *exo*-isomers, which is consistent with a Karplus analysis. Indeed it is not uncommon for *exo*-isomers to show no P-C(7) coupling.[164,165] Using this information the doublet at 49.437-49.270 ppm ($^3J_{P,C7}$ = 16.80 Hz) and the singlet at 45.489 ppm are assigned to the C(7) *endo* and *exo* carbons respectively. Again the assignments are consistent with the *exo*-form being the major isomer.

The values of 2-bond P-C coupling constants can often be very small or even zero in some cases, and this is observed with the C(6) signals. The major and minor (*exo* and *endo*) isomers give rise to a singlet at 26.945 ppm and a doublet at 26.119-26.107 ppm ($^2J_{P,C6}$ =1.21 Hz) respectively.

HETCOR and COSY spectra were used to correlate the carbons with their respective protons and to observe the proton-proton couplings so that the C(7) and C(6) assignments could be confirmed.

CH_3 Carbons

The only CH_3 signals are those of carbon (8) which comprises a large doublet at 51.561-51.493 ppm ($^2J_{P,C8}$ = 6.84 Hz) and two smaller doublets at 51.296-51.227 ppm ($^2J_{P,C8}$ = 6.93 Hz) and 51.167-51.102 ppm ($^2J_{P,C8}$ = 6.54 Hz). The larger doublet is due to the major (*exo*) isomer with the minor (*endo*) form being represented by the two smaller doublets. This phenomenon can be explained by the fact that the two methyl groups are equivalent in the *exo*-compound, giving rise to one doublet, whereas they are non-equivalent in the *endo*-form hence producing two signals. The methyls in the major (*exo*) isomer can rotate freely but in the case of the minor (*endo*) isomer the methyls must experience steric constraints, which creates two environments and the two doublets. It is well known that *exo*-substituents are less crowded than *endo* substituents in norbornenes.

2.10 Synthesis and characterisation of diethylbicyclo[2.2.1]hept-2-ene-5-phosphonate.

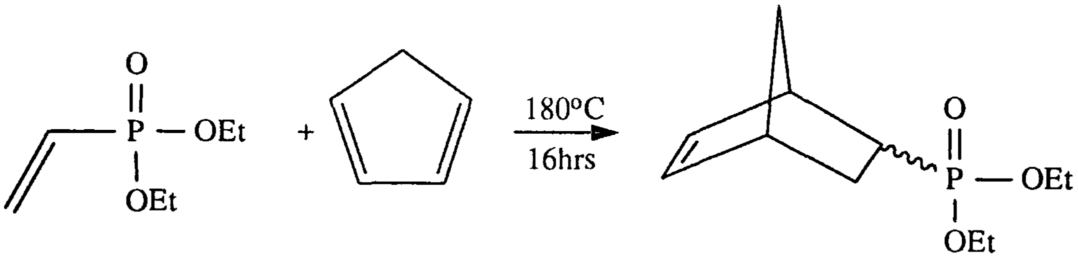


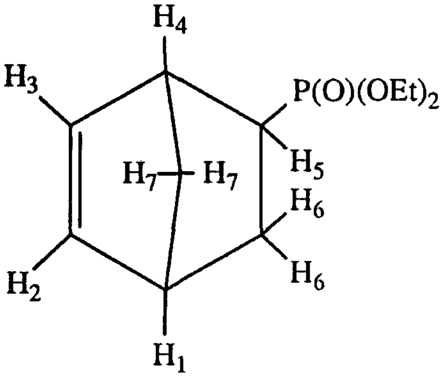
Figure 2.10: Synthesis of diethylbicyclo[2.2.1]hept-2-ene-5-phosphonate.

2.10.1 Synthesis of diethylbicyclo[2.2.1]hept-2-ene-5-phosphonate.[158-159]

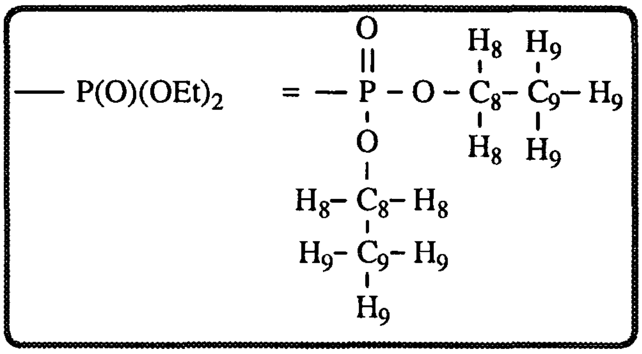
Diethyl vinyl phosphonate (25.g/0.152mol), cyclopentadiene (10g/0.152mol) and hydroquinone (0.1g) were sealed in a 160 ml Hastelloy autoclave and heated for 16 hours at 180°C. The brown liquid product was distilled in vacuo to give two colourless fractions, diethyl vinyl phosphonate (50-60°C/0.1mm) and diethylbicyclo[2.2.1] hept-2-ene-5-phosphonate (80-90°C/0.1mm). The second fraction was redistilled in vacuo (10 cm Vigreaux column) to give a mixture of the *exo* and *endo* isomers of diethylbicyclo[2.2.1]hept-2-ene-5-phosphonate in 66% yield in an *exo*/*endo* ratio, based on NMR and g.l.c. analysis, of 1.13:1.

2.10.2 Characterisation of diethylbicyclo[2.2.1]hept-2-ene-5-phosphonate.

The ^1H NMR spectrum (appendix A7) is summarised in Table 2.15. The assignments are based on a knowledge of the *exo/endo* ratio derived from comparative analysis of the ^{13}C NMR, DEPT, COSY and HETCOR spectra of dimethylbicyclo[2.2.1]hept-2-ene-5-phosphonate. The overall shifts and integrations are self consistent.



***Exo/Endo* Mixture.**

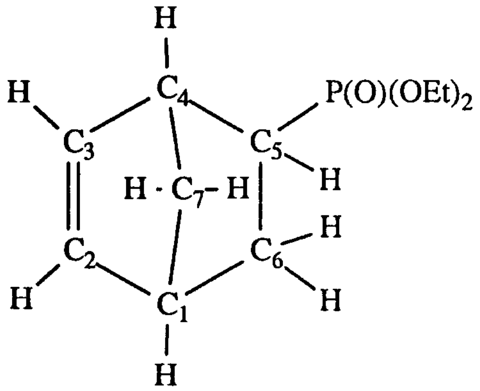


Assignment	Shift (ppm)	Multiplicity
H1 (endo/exo)	2.971	Broad Multiplet
H2/H3 (endo/exo)	6.114	Multiplet
H4 (exo)	3.148	Broad Multiplet
H4 (endo)	3.069	Broad Multiplet
H5 (endo)	2.309	Multiplet
H5 (exo)	1.557	Multiplet
H6 (endo/exo)	1.986 1.300*	Multiplet Multiplet
H7 (exo)	1.686 1.204	AB Quartet
H7 (endo)	1.457 1.300*	Multiplet Doublet
H8 (endo/exo)	3.720	Multiplet
H9 (endo/exo)	1.314	Multiplet

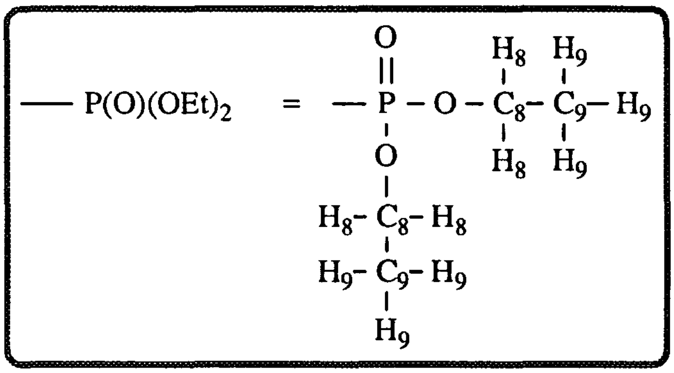
** - peak obscured by (H9) multiplet.*

Table 2.15: ^1H spectral assignments for diethylbicyclo[2.2.1]hept-2-ene-5-phosphonate (399.953MHz/CDCl$_3$).

The ^{13}C NMR spectrum (appendix B7) is assigned by comparison with the dimethylbicyclo[2.2.1]hept-2-ene-5-phosphonate ^{13}C spectrum and is summarised in Table 2.16.



***Exo/Endo* Mixture.**



	EXO-ISOMER		ENDO-ISOMER	
	Shift (ppm)	Multiplicity	Shift (ppm)	Multiplicity
C1	41.98-41.95	doublet	42.47-42.40	doublet
C2	136.75*	singlet	136.43	singlet
C3	136.88-136.74	doublet	132.98-132.93	doublet
C4	43.62	doublet	44.45	singlet
C5	35.52-34.12	doublet	36.06-34.53	doublet
C6	27.91	singlet	27.15	singlet
C7	46.34	singlet	50.37-50.21	doublet
C8	61.49-61.42	doublet	(a) 61.26-61.19 (b) 61.11-61.04	doublet doublet
C9	16.53	singlet	16.59	singlet

* - *peak obscured by (C3) doublet.*

Table 2.16: ^{13}C spectral assignments for diethylbicyclo[2.2.1]hept-2-ene-5-phosphonate (100.577MHz/$CDCl_3$).

The phosphorus-carbon coupling constants are as follows:-

	EXO-ISOMER	ENDO-ISOMER
Carbon	P-C Coupling (Hz)	P-C Coupling (Hz)
C1	2.71	6.84
C2	--------	--------
C3	13.78	4.53
C4	--------	--------
C5	140.71	153.80
C6	--------	--------
C7	--------	16.39
C8	6.84	(a) 6.84 (b) 6.84
C9	--------	--------

Table 2.17: Phosphorus-carbon coupling constants for diethylbicyclo[2.2.1]hept-2-ene-5-phosphonate.

A blank indicates that the coupling, if any, was too small to be detected under our measuring conditions.

The ^{13}C NMR assignments are consistent with those of dimethylbicyclo[2.2.1] hept-2-ene-5-phosphonate (Section 2.9.2), but the small P-C4 coupling present in the dimethyl phosphonate monomer is not observed in diethylbicyclo[2.2.1] hept-2-ene-5-phosphonate. The carbon (C8) signals again appear as a large doublet at 61.45ppm ($^2J_{PC}$= 6.84 Hz) and two smaller doublets at 61.22ppm ($^2J_{PC}$= 6.84 Hz) and 61.07ppm ($^2J_{PC}$= 6.84 Hz). The larger doublet is due to the *exo*-isomer with the *endo*-isomer being represented by the two smaller doublets. This can be explained by the two methyl groups being equivalent in the *exo*-isomer, giving rise to one doublet. However, the *endo*-isomer experiences steric constraints and the two methyl groups are non-equivalent creating two methyl environments and hence the two doublets. Therefore it would be expected that the C9 signals show a similar effect but the splitting is unresolved and the signals appear as two singlets at 16.53ppm and 16.59ppm, corresponding to the *exo* and *endo*-isomers respectively.

A ^{1}H-decoupled ^{31}P NMR spectrum (97.15 MHz/$CDCl_3$/ Appendix C7) shows the presence of two peaks corresponding to the *endo* and *exo* environments:- *endo*-isomer 33.32 ppm (singlet), *exo*-isomer 34.42 ppm (singlet). The infrared spectrum of diethylbicyclo[2.2.1]hept-2-ene-5-phosphonate is shown in appendix D7 and is consistent with the assigned structure with the most important diagnostic infrared bands being:- vinylic CH stretches at 3070 cm^{-1}, 3010 cm^{-1}, CH_2/CH_3 stretches at 3000 cm^{-1}, 2880 cm^{-1} and 2850cm^{-1}, a C=C stretch at 1570 cm^{-1} and a P=O stretch at 1240 cm^{-1}. The broad bands at ~3500 cm^{-1} and ~1700 cm^{-1} were indications of the probable retention of traces of water by the sample.

The electron impact mass spectrum (Appendix E7) was consistent with the assigned structure with the small molecular ion being present at 230 and the base peak at 165 ($C_6H_{14}O_3P$) arising from a retro Diels Alder reaction with hydrogen transfer to the charge carrying fragment.

2.11 Synthesis and characterisation of *exo,endo*-5,6-bis(dimethylphosphonate)bicyclo[2.2.1]hept-2-ene.

2.11.1 Synthesis of *trans*-ethene-1,2-bis(dimethylphosphonate).[166-168]

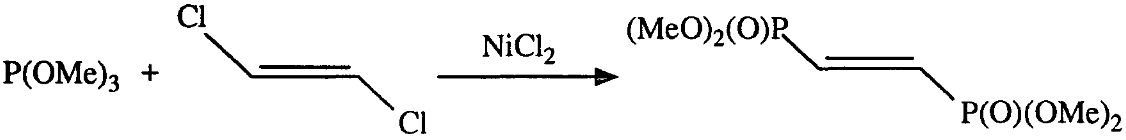


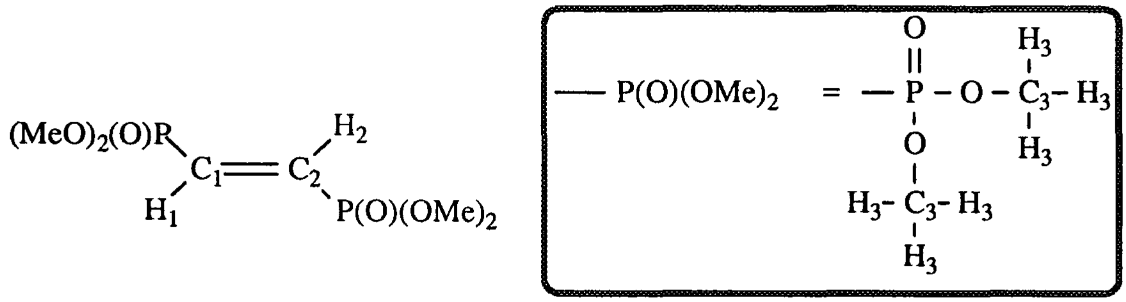
Figure 2.11: Synthesis of trans-ethene-1,2-bis(dimethylphosphonate).

Trimethyl phosphite (25g/0.20 mol), *trans*-1,2-dichloroethene (10g/0.10 mol), and nickel (II) chloride (ca. 0.5g) were sealed in a 160 ml Hastelloy autoclave and heated for 4 hours at 190°C. The brown reaction product was distilled to remove the low boiling fractions and the distillation was continued in vacuo (10cm Vigreaux column) to produce *trans*-ethene-1,2-bis(dimethylphosphonate) as a colourless liquid (140-145°C/0.1mm) in 65% yield.

2.11.2 Characterisation of *trans*-ethene-1,2-bis(dimethylphosphonate).

The ^1H-decoupled ^{31}P NMR spectrum (202.46 MHz/$CDCl_3$/Appendix C8) shows the presence of one peak at 16.40 ppm corresponding to one phosphorus environment. The infrared spectrum of *trans*-ethene-1,2-bis(dimethylphosphonate) (appendix D8) is consistent with the assigned structure with the most important diagnostic infrared bands being:- vinylic CH stretches at 3010 cm^{-1}, CH_2/CH_3 stretches at 2990 cm^{-1} and 2850cm^{-1} and a P=O stretch at 1255 cm^{-1}. The broad bands at ~3500 cm^{-1} and ~1700 cm^{-1} were indications of the probable retention of traces of water by the sample. The electron impact mass spectrum (Appendix E8) was consistent with the assigned structure with the small molecular ion being present at 244 and the base peak at 135 ($C_4H_8O_3P$) resulting from the loss of one of the $P(O)(OMe)_2$ groups.

The number and shifts of the signals in the ^1H NMR spectrum, and their integrations, are consistent with the assigned structure (see appendix A8) with the assignments and chemical shifts summarised in Table 2.18. The ^{13}C NMR spectrum is consistent with the assigned structure (see appendix B8), with the assignments and chemical shifts summarised in Table 2.19. The detailed analysis leading to these assignments is explained in appendix G.



Assignment	Shift (ppm)	Multiplicity
H1/H2	6.80	multiplet
H3	3.79	multiplet

Table 2.18: ***^{1}H spectral assignments for trans-ethene-1,2-bis(dimethylphosphonate) (399.952MHz/$CDCl_3$).***

Assignment	Shift (ppm)	Multiplicity
C1/C2	136.18	multiplet $^1J_{PC}$=179.0 Hz $^2J_{PC}$ = 2.35 Hz $^3J_{PP}$ = 94.1 Hz
C3	53.00	multiplet $^2J_{PC}$ = 5.90 Hz

Table 2.19: ***^{13}C spectral assignments for trans-ethene-1,2-bis(dimethylphosphonate) (125.77MHz/$CDCl_3$).***

2.11.3 Synthesis of *exo,endo*-5,6-bis(dimethylphosphonate)bicyclo[2.2.1]hept-2-ene.[170]

Cyclopentadiene (14g/0.21 mol) and *trans*-ethene-1,2-bis(dimethylphosphonate) (23g/0.1 mol) were heated in a 160 ml Hastelloy autoclave for 3 hours at 115°C followed by 7 hours at 125°C. The low boiling fractions were removed by Kugelrohr distillation (40°C/0.1mm) to give as a pot residue *exo,endo*-5,6-bis(dimethyl phosphonate)bicyclo[2.2.1]hept-2-ene in 90% yield. An attempted vacuum distillation of the product resulted in a retro Diels Alder reaction; consequently characterisation was carried out on the undistilled product.

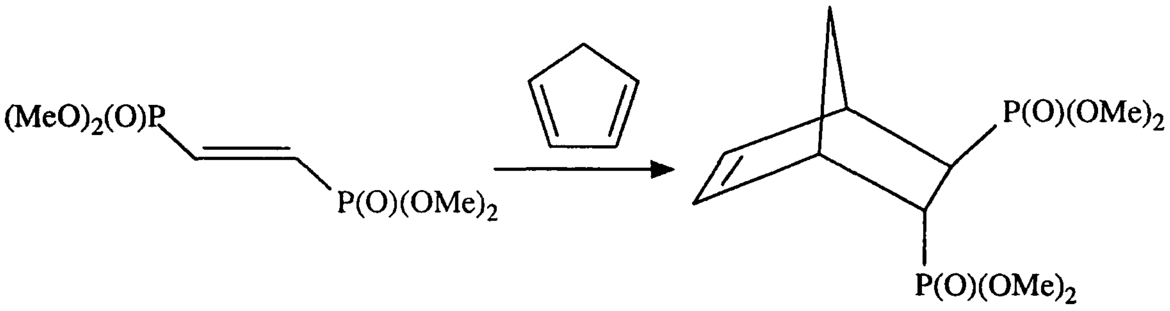
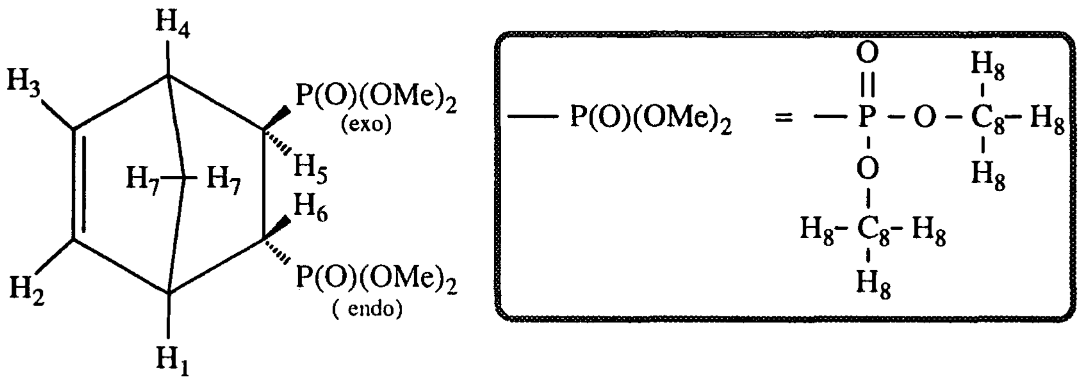


Figure 2.12: Synthesis of exo,endo-5,6-bis(diethylphosphonate)bicyclo[2.2.1]hept-2-ene.

2.11.4 Characterisation of *exo,endo*-5,6-bis(dimethylphosphonate) bicyclo[2.2.1]hept-2-ene.

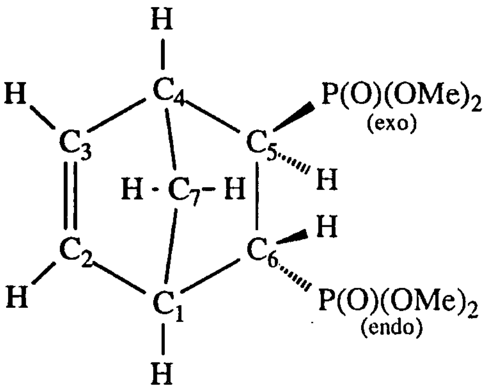
The number and shifts of the signals in the ^1H NMR spectrum, and their integrations, are consistent with the assigned structure (see appendix A9) with the assignments and chemical shifts summarised in Table 2.20. The assignments are based on a comparative analysis of the ^{13}C NMR, DEPT (Appendix F4), COSY (Appendix F5) and HETCOR (Appendix F6) spectra with those of dimethylbicyclo[2.2.1] hept-2-ene-5-phosphonate.

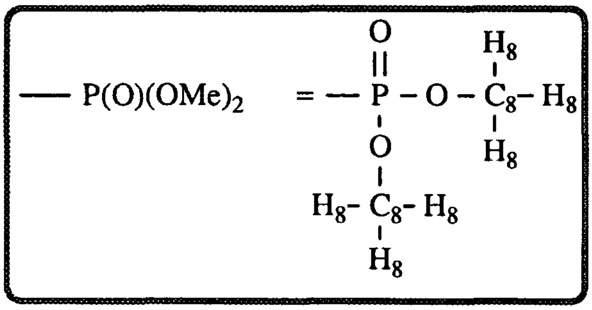


Assignment	Shift (ppm)	Multiplicity
H2	6.28	multiplet
H3	6.19	multiplet
H8	3.75	multiplet
H4	3.27	broad multiplet
H1	3.22	broad multiplet
H5/H6	2.65 1.98	multiplet multiplet
H7	1.74 1.41	doublet multiplet

Table 2.20: ^1H spectral assignments for exo,endo-5,5-bis(dimethylphosphonate)bicyclo[2.2.1]hept-2-ene ($399.952 MHz/CDCl_3$).

The ^{13}C NMR spectrum (see appendix B9) is assigned by comparative analysis of the ^{13}C NMR, DEPT (Appendix F4), COSY (Appendix F5) and HETCOR (Appendix F6) spectra with those of the *exo/endo* mixture of dimethylbicyclo[2.2.1] hept-2-ene-5-phosphonate, with the assignments and chemical shifts summarised in Table 2.21.





Assignment	Shift (ppm)	Multiplicity
C3	136.22	doublet $^3J_{PC}$ = 14.54 Hz
C2	135.15	doublet $^3J_{PC}$ = 4.22 Hz
C8	52.64	multiplet $^2J_{PC}$ = 6.84 Hz
C7	47.98	doublet $^3J_{P(endo)C}$ = 15.59 Hz
C1	45.51	multiplet $^3J_{PC}$ = 3.52 Hz $^2J_{PC}$ = 1.91 Hz
C4	45.25	multiplet $^3J_{PC}$ = 6.64 Hz $^2J_{PC}$ = 1.11 Hz
C6	37.25	doublet $^1J_{PC}$ =140.81 Hz
C5	37.00	multiplet $^1J_{PC}$ =153.13 Hz $^2J_{PC}$ = 2.62 Hz

Table 2.21: ^{13}C spectral assignments for exo,endo-5,6-bis(dimethylphosphonate)bicyclo[2.2.1]hept-2-ene ($100.577 MHz/CDCl_3$).

DEPT spectra allowed easy assignment of the CH, CH_2 and CH_3 carbons and these are discussed in detail below.

C-H Carbons.

In the vinylic region there are two doublets corresponding to the two olefinic carbons C(2) and C(3). Carbon C(2) is split by the *endo* phosphorus atom and similarly the C(3) carbon is split by the *exo* phosphorus atom, and each case, as with the dimethylbicyclo[2.2.1]hept-2-ene-5-phosphonate monomer, there is no four bond P-C coupling. By comparing the assignments of the *endo/exo* mixture of dimethylbicyclo [2.2.1]hept-2-ene-5-phosphonate and using a Karplus-type relationship for three bond coupling, it can be deduced that the larger coupling constant ^3J= 14.54 Hz, centred at 136.22ppm, corresponds to the P(exo)-C(3) coupling and the ^3J= 4.22 Hz, centred at 135.15ppm, corresponds to P(endo)-C(2) coupling.

Large coupling constants are normally observed between carbon and phosphorus when they are adjacent and this is the case for P(*exo*)-C(5) and P(*endo*)-C(6). There are two large coupling constants observed for the doublet at 37.25ppm and the doublet of doublets at 37.00ppm. The smaller coupling in the doublet of doublets arises from two bond P-C coupling. The values of two bond coupling constants can often be small or even zero in some cases, and this is observed for the case of the doublet. In similar compounds[164,165] *endo* substituents are more likely to undergo two bond coupling than *exo* substituents. It was therefore concluded that the doublet of doublets corresponds to carbon C(5) and carbon C(6) gives rise to the doublet. This is again consistent with the observations made in the characterisation of the *endo/exo* mixture of dimethylbicyclo [2.2.1]hept-2-ene-5-phosphonate (see section 2.9.2).

Carbons C(1) and C(4) were again difficult to distinguish from each other as both signals are doublets of doublets with small coupling constants and they appear in the same region of the spectrum. HETCOR and COSY spectra were again required to correlate the C(1) and C(4) signals with their respective protons and to assign the proton regions. There is evidence on the COSY spectrum of coupling between the H(6) protons and one of these unknown regions. This unknown region can now be assigned to the protons on C(1), as C(1) and C(6) are adjacent and it is more likely that the H(6) protons would couple with the H(1) protons than those on C(4). Therefore the doublet of doublets at 45.25ppm ($^3J_{PC}$ = 6.64 Hz, $^2J_{PC}$ = 1.11 Hz) was assigned to carbon C(4) and the doublet of doublets at 45.51ppm ($^3J_{PC}$ = 3.52 Hz, $^2J_{PC}$ = 1.91 Hz) was assigned to carbon C(1). It can be seen that the three bond coupling constants are larger than the two bond coupling constants and that the P(*endo*)-C(1) and P(*endo*)-C(4) coupling constants are larger than the corresponding *exo* values. These observations are consistent with the assignments of dimethylbicyclo [2.2.1]hept-2-ene-5-phosphonate and with the literature.[164-165]

CH$_2$ Carbons.

In similar compounds the P-C coupling constants for C(7) carbons for *endo* substituents are considerably larger than those for *exo* substituents, which is in agreement with a Karplus-type relationship, and it is not uncommon for there to be no P(*exo*)-C(7) coupling.[164,165] It was therefore deduced that coupling constant for the doublet at 47.98ppm ($^3J_{PC}$ = 15.59 Hz) arises from P(*endo*)-C(7) coupling.

CH$_3$ Carbons.

The multiplet, centred at 52.64ppm, comprises four doublets (all $^2J_{PC}$= 6.84 Hz) corresponding to the four C(8) carbons. This phenomenon can be explained by the fact that the two methyl groups on each phosphonate substituent must be non-equivalent due to steric constraints, hence creating four different environments in all. Each of the four carbons is therefore split by a phosphorus atom and this results in the four doublets. This differs slightly to the assignments for the *endo*/*exo* mixture of dimethyl bicyclo[2.2.1]hept-2-ene-5-phosphonate, where methyl groups on the *exo* substituent were equivalent and could rotate freely resulting in one phosphorus environment and one doublet (section 2.9.2). The presence of two phosphonate groups on the *exo,endo*-5,6-bis(dimethylphosphonate)bicyclo[2.2.1]hept-2-ene creates further steric hindrance and accounts for this difference.

The ^1H-decoupled ^{31}P NMR spectrum shows a doublet of doublets at 17.72 ppm resulting from the two phosphorus environments giving rise to an AB spin system. The infrared spectrum of *exo,endo*-5,6-bis(dimethylphosphonate)bicyclo[2.2.1]hept-2- ene (appendix D9) is consistent with the assigned structure with the most important diagnostic infrared bands being:- vinylic CH stretches at 3070 cm^{-1}, 3010 cm^{-1}, CH_2/CH_3 stretches at 2990 cm^{-1}, 2880 cm^{-1} and 2850cm^{-1}, a C=C stretch at 1570 cm^{-1} and a P=O stretch at 1230 cm^{-1}. The broad bands at ~3500 cm^{-1} and ~1700 cm^{-1} were again due to the retention of traces of water by the sample.

The electron impact mass spectrum (Appendix E9) was consistent with the assigned structure with the molecular ion being present at 310 and the base peak at 244 ($C_6H_{14}O_6P_2$) from the retro Diels Alder reaction.

2.12 Synthesis and characterisation of *exo,endo*-5,6-bis(diethylphosphonate)bicyclo[2.2.1]hept-2-ene.

2.12.1 Synthesis of *trans*-ethene-1,2-bis(diethylphosphonate).[166-168]

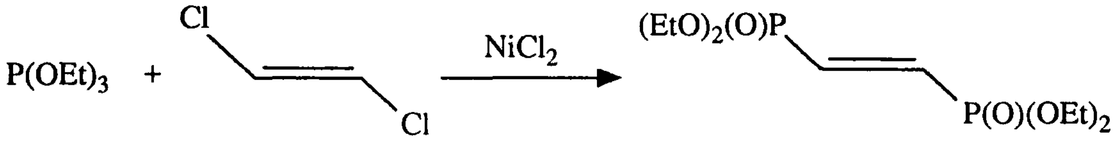
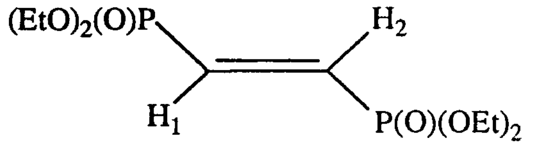


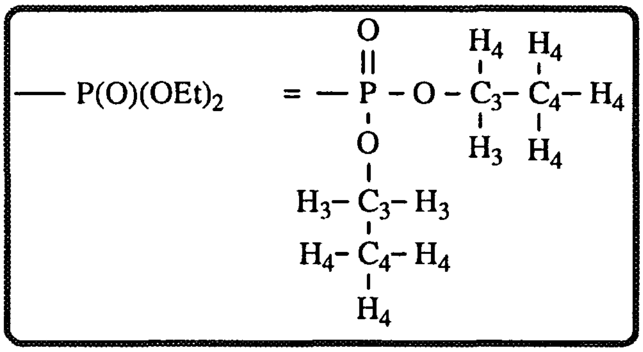
Figure 2.13: Synthesis of trans-ethene-1,2-bis(diethylphosphonate).

Triethyl phosphite (33g/0.20 mol), *trans*-1,2-dichloroethene (10g/0.10 mol) and nickel (II) chloride (ca. 0.5g) were sealed in a 160 ml Hastelloy autoclave and heated for 4 hours at 190°C. The brown reaction product was distilled to remove the low boiling fractions and the distillation was continued in vacuo (10cm Vigreaux column) to produce *trans*-ethene-1,2-bis(diethylphosphonate) as a colourless liquid (140-145°C/0.1mm) in 61% yield.

2.12.2 Characterisation of *trans*-ethene-1,2-bis(diethylphosphonate).

The ^1H NMR spectrum is consistent with the structure of *trans*-ethene-1,2-bis (diethylphosphonate) and is shown in appendix A10 with the chemical assignments and chemical shifts summarised in Table 2.22.



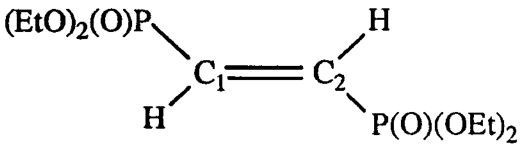


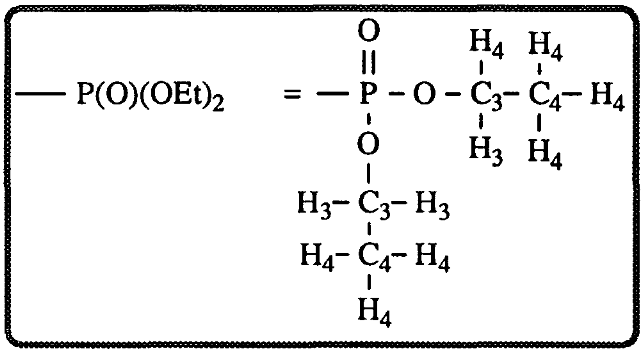
Assignment	Shift (ppm)	Multiplicity
H1/H2	6.80	multiplet
H3	4.13	multiplet
H4	1.35	multiplet

Table 2.22: ^1H spectral assignments for trans-ethene-1,2-bis(diethylphosphonate) (399.952MHz/$CDCl_3$).

The ^1H-decoupled ^{31}P NMR spectrum (202.46 MHz/$CDCl_3$/Appendix C10) shows the presence of one peak at 13.97 ppm corresponding to one phosphorus environment. The infrared spectrum of *trans*-ethene-1,2-bis(diethylphosphonate) (appendix D10) is consistent with the assigned structure with the most important diagnostic infrared bands being:- vinylic CH stretches at 3010 cm^{-1}, CH_2/CH_3 stretches at 2880 cm^{-1} and 2850cm^{-1} and a P=O stretch at 1260 cm^{-1}. The broad bands at ~3500

cm^{-1} and ~1700 cm^{-1} were indications of the probable retention of traces of water by the sample. The electron impact mass spectrum (Appendix E8) was consistent with the assigned structure with the small molecular ion being present at 300 and the base peak at 163 ($C_6H_{12}O_3P$) resulting from the loss of one of the $P(O)(OEt)_2$ groups.





Assignment	Shift (ppm)	Multiplicity
C1/C2	135.59	multiplet $^1J_{PC}$ =178.3 Hz $^2J_{PC}$ = 2.04 Hz $^3J_{PP}$ = 93.3 Hz
C3	62.54	multiplet $^2J_{PC}$ = 5.55 Hz
C4	16.38	multiplet $^3J_{PC}$ = 6.24 Hz

Table 2.23: ^{13}C spectral assignments for trans-ethene-1,2-bis(diethylphosphonate) (125.77MHz/$CDCl_3$).

2.12.3 Synthesis of *exo,endo*-5,6-bis(diethylphosphonate)bicyclo[2.2.1]hept-2-ene.[170]

Cyclopentadiene (14g/0.21 mol) and *trans*-ethene-1,2-bis(diethylphosphonate) (23g/0.1 mol) were heated in a 160 ml Hastelloy autoclave and heated for 3 hours at 115°C followed by 7 hours at 125°C. The low boiling fractions were removed by Kugelrohr distillation (40°C/0.1mm) to produce *exo,endo*-5,6-bis(diethylphosphonate) bicyclo[2.2.1]hept-2-ene in 88% yield. Vacuum distillation resulted in a retro Diels

Alder reaction and so characterisation was carried out on the undistilled product.

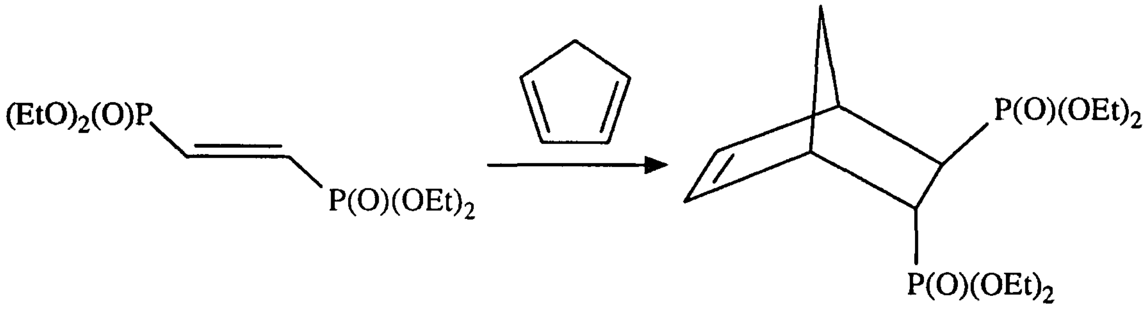


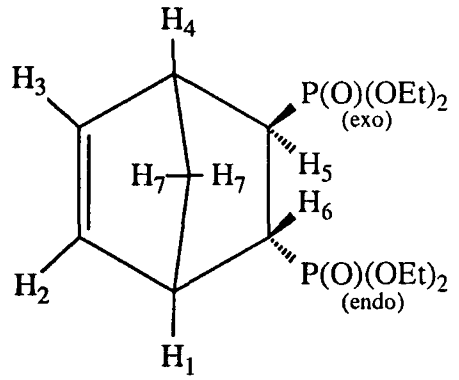
Figure 2.14: Synthesis of exo,endo-5,6-bis(diethylphosphonate)bicyclo[2.2.1]hept-2-ene.

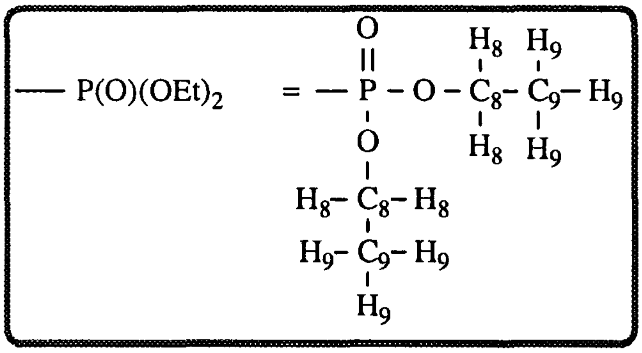
2.12.4 Characterisation of *exo,endo*-5,6-bis(diethylphosphonate) bicyclo[2.2.1]hept-2-ene.

The ^{1}H-decoupled ^{31}P NMR spectrum shows a doublet of doublets at 15.14 ppm resulting from the two phosphorus environments giving rise to an AB spin system. The infrared spectrum of *exo,endo*-5,6-bis(diethylphosphonate)bicyclo[2.2.1]hept-2-ene (Appendix D11) is consistent with the assigned structure with the most important diagnostic infrared bands being:- vinylic CH stretches at 3070 cm^{-1}, 3010 cm^{-1} and a C=C stretch at 1570 cm^{-1}, CH_2/CH_3 stretches at 3000 cm^{-1}, 2950 cm^{-1} and 2880cm^{-1} and a P=O stretch at 1250 cm^{-1}. The broad bands at ~3500 cm^{-1} and ~1700 cm^{-1} were again due to the retention of traces of water by the sample.

The electron impact mass spectrum (Appendix E11) was consistent with the assigned structure with the small molecular ion being present at 366 and the base peak at 229 ($C_{11}H_{18}O_3P$) due to the loss of a P(O)(OEt)$_2$ group.

The number and shifts of the signals in the ^{1}H NMR spectrum, and their integrations, are consistent with the assigned structure (see appendix A11) with the assignments and chemical shifts summarised in Table 2.24. The assignments are based on a comparative analysis of the ^{1}H NMR spectrum of *exo,endo*-5,6-bis(dimethyl phosphonate)bicyclo[2.2.1]hept-2-ene.





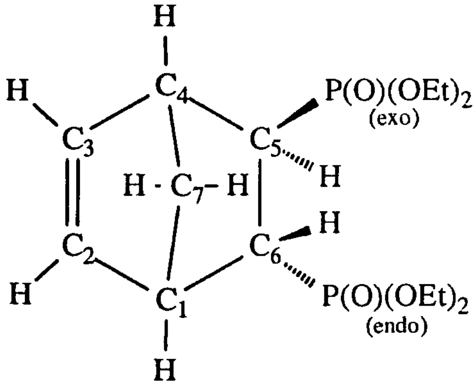
Assignment	Shift (ppm)	Multiplicity
H2	6.26	multiplet
H3	6.21	multiplet
H8	4.11	multiplet
H4	3.27	broad multiplet
H1	3.21	broad multiplet
H5/H6	2.64 1.97	multiplet multiplet
H7	1.76 1.33	doublet multiplet*
H9	1.33	multiplet

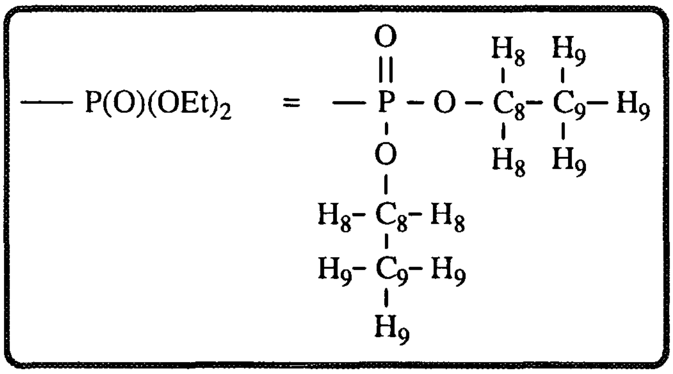
** - peak obscured by H9 multiplet.*

Table 2.24: ^{1}H spectral assignments for exo,endo-5,5-bis(diethylphosphonate)bicyclo[2.2.1]hept-2-ene (399.952MHz/$CDCl_3$).

The ^{13}C NMR spectrum was assigned by comparison with the ^{13}C NMR spectrum of *exo,endo*-5,6-bis(dimethylphosphonate)bicyclo[2.2.1]hept-2-ene. The assignments, chemical shifts and P-C coupling constants are consistent with those of *exo,endo*-5,6-bis(dimethylphosphonate)bicyclo[2.2.1]hept-2-ene (Section 2.11.4). The carbon C(8) signals again appear as four doublets (all $^{2}J_{PC}$= 6.84 Hz). This can be explained by the two methyl groups in each phosphonate substituent being non-equivalent due to steric constraints and this creates four carbon environments in all. Each carbon is split by a phosphorus atom resulting in the four doublets. This phenomenon is not observed in the *endo/exo* mixture of diethylbicyclo[2.2.1] hept-2-ene-5-phosphonate. Although the two carbon C(8) CH_2 groups on the *endo*-isomer experience steric constraints and are non-equivalent giving rise to two doublets, the carbon C(8) CH_2 groups on the *exo*-isomer are equivalent and can rotate freely, resulting in one phosphorus environment and one doublet (Section 2.10.2). The presence of two phosphonate groups on the *exo,endo*-5,6-bis(diethylphosphonate) bicyclo[2.2.1]hept-2-ene creates further steric hindrance and accounts for this difference. Therefore it would be expected that the C9 signals show a similar effect but the splitting is unresolved and the signals appear as two singlets at 16.25ppm and 16.19ppm, corresponding to the *exo* and *endo* phosphonate substituents respectively.

The ^{13}C NMR spectrum is shown in appendix B11 with the chemical assignments and chemical shifts summarised in Table 2.25.





Assignment	Shift (ppm)	Multiplicity
C3	136.79	doublet $^3J_{PC}$ = 14.48 Hz
C2	135.10	doublet $^3J_{PC}$ = 4.22 Hz
C8	61.46	multiplet $^2J_{PC}$ = 6.84 Hz
C7	47.65	doublet $^3J_{P(endo)C}$ = 15.59 Hz
C1	45.41	multiplet $^3J_{PC}$ = 3.22 Hz $^2J_{PC}$ = 2.31 Hz
C4	45.17	multiplet $^3J_{PC}$ = 6.49 Hz $^2J_{PC}$ = 0.70 Hz
C6	37.71	doublet $^1J_{PC}$ =140.71 Hz
C5	37.41	multiplet $^1J_{PC}$ =153.18 Hz $^2J_{PC}$ = 1.91 Hz
C9(exo) C9(endo)	16.19 16.25	singlet singlet

Table 2.25: ^{13}C spectral assignments for

exo,endo-5,6-bis(diethylphosphonate)bicyclo[2.2.1]hept-2-ene (100.577MHz/$CDCl_3$).

2.13 Attempted preparation of bicyclo[2.2.1]hept-2-ene-5-phosphonic acid.

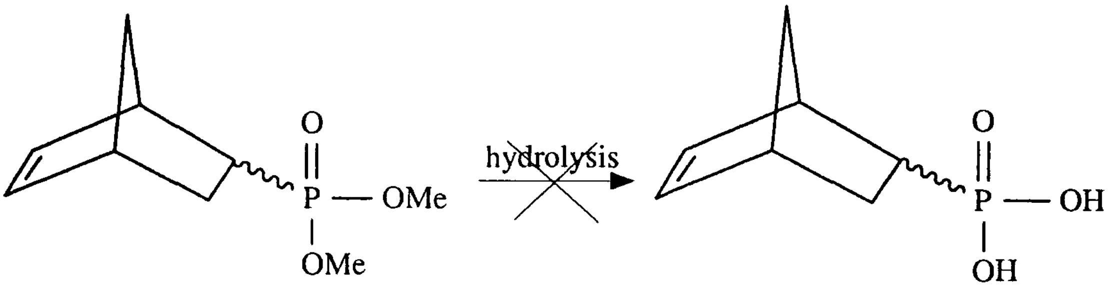


Figure 2.15: Attempted hydrolysis of dimethylbicyclo[2.2.1]hept-2-ene-5-phosphonate.

The hydrolysis of dimethylbicyclo[2.2.1]hept-2-ene-5-phosphonate was carried out in attempts to obtain monomers with pendant phosphonic acid groups. The objective being to increase the water solubility of the resulting polymers. In principle hydrolysis can be carried out by three methods, acid catalysed hydrolysis, base catalysed hydrolysis and by the reaction with bromo-trimethylsilane. It is reported that both of the alkyl groups are removed by acid catalysed hydrolysis and by the reaction with bromo-trimethylsilane,[171-173] whereas only one is cleaved by base catalysed hydrolysis.[171]

2.13.1 Acid catalysed hydrolysis.

Dimethylbicyclo[2.2.1]hept-2-ene-5-phosphonate (5.0g/0.025 mol) was dissolved in an 18% HCl solution (50ml) and refluxed for 6 hours. Analysis of the resulting mixture revealed that although partial hydrolysis had occurred, evident from the reduction of the P-OR infrared signal and the decrease of the methyl signals in both ^{1}H and ^{13}C NMR, the conditions used were appropriate for acid catalysed addition of water across the double bond, consequently a complex intractable mixture of products was obtained.

2.13.2 Base catalysed hydrolysis.

Dimethylbicyclo[2.2.1]hept-2-ene-5-phosphonate (5.0g/0.025 mol) was dissolved in a saturated solution of sodium hydroxide (50ml) and refluxed for 6 hours. Analysis again revealed that the conditions were suitable for promoting addition of water across the double bond and the reaction product was a complex intractable mixture

2.13.3 Attempted hydrolysis via initial reaction with bromotrimethylsilane.[172-173]

In an attempt to find a milder more specific reagent bromo-trimethylsilane was investigated.

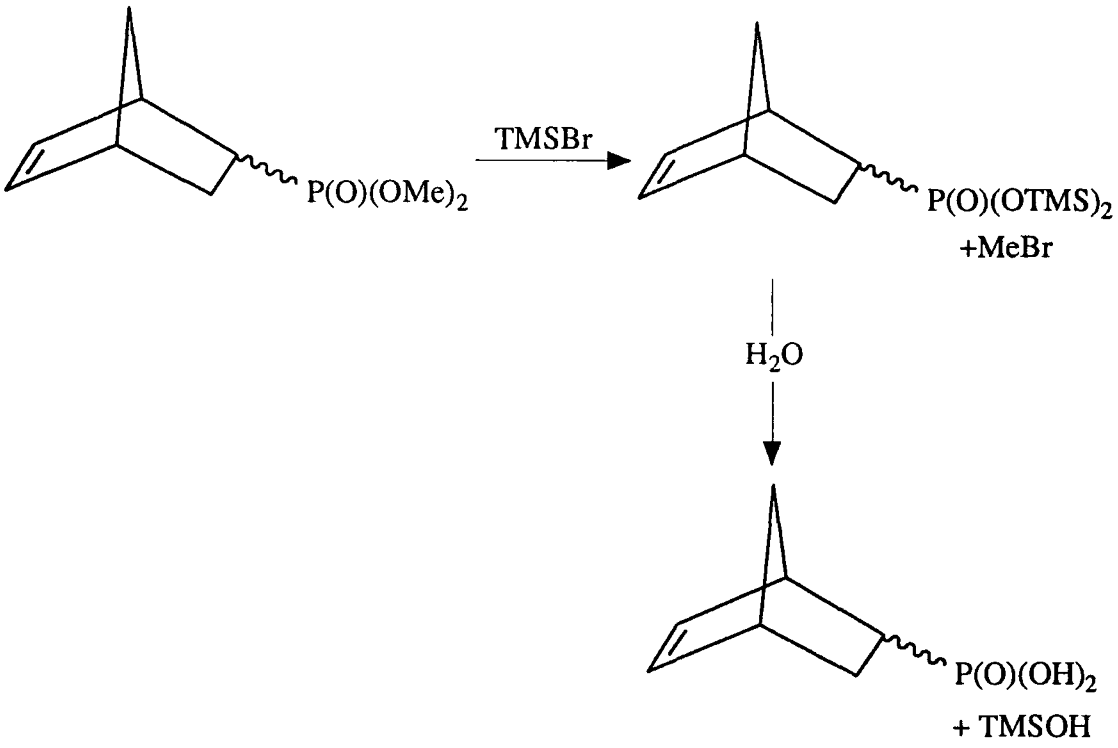


Figure 2.16: Attempted synthesis of bicyclo[2.2.1]hept-2-ene-5-phosphonic acid using bromotrimethylsilane.

Bromotrimethylsilane (50g/0.33 mol) was added dropwise to dimethylbicyclo [2.2.1]hept-2-ene-5-phosphonate (20g/0.10 mol) kept at 0°C, and the mixture was stirred for 30 minutes. Water (15ml/0.83 mol) was then added dropwise and the resulting slurry was stirred for a further 30 minutes and allowed to warm up to room temperature. The hydroxytrimethylsilane was filtered off and the water was removed on a rotary evaporator (bath temperature 80°C). The product was dried in vacuo for 24 hours to give a brown viscous semi-solid.

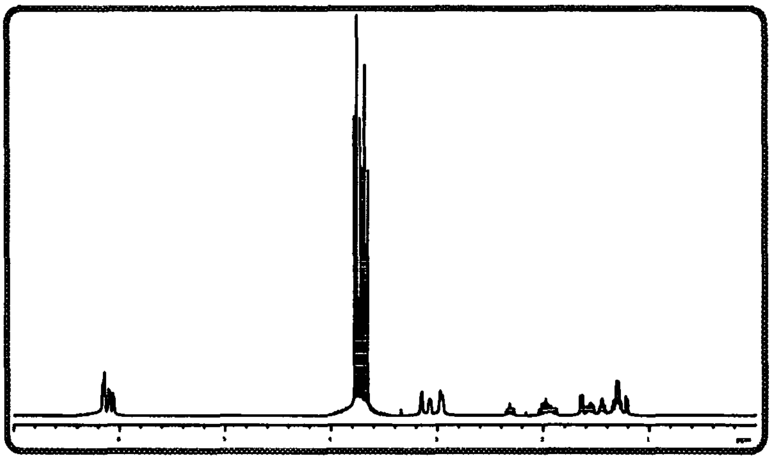


Figure 2.17: ^1H spectrum of dimethylbicyclo[2.2.1]hept-2-ene-5-phosphonate (399.952 MHz/$CDCl_3$).

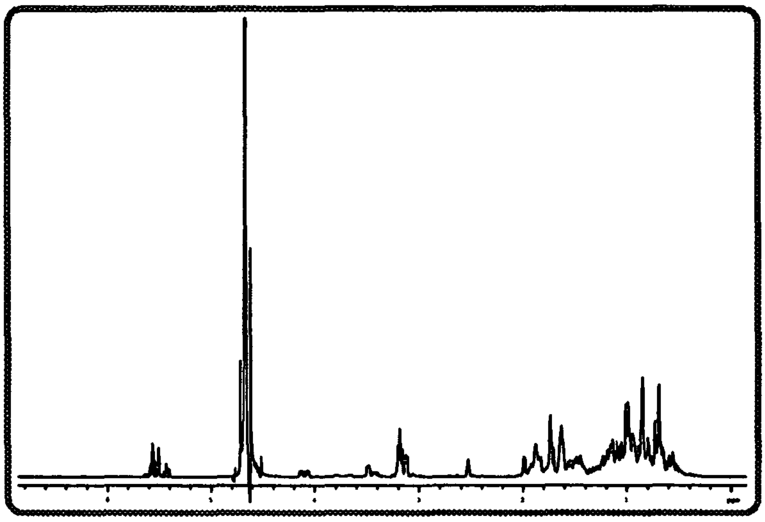


Figure 2.18: ^1H spectrum of hydrolysis product (399.952 MHz/D_2O).

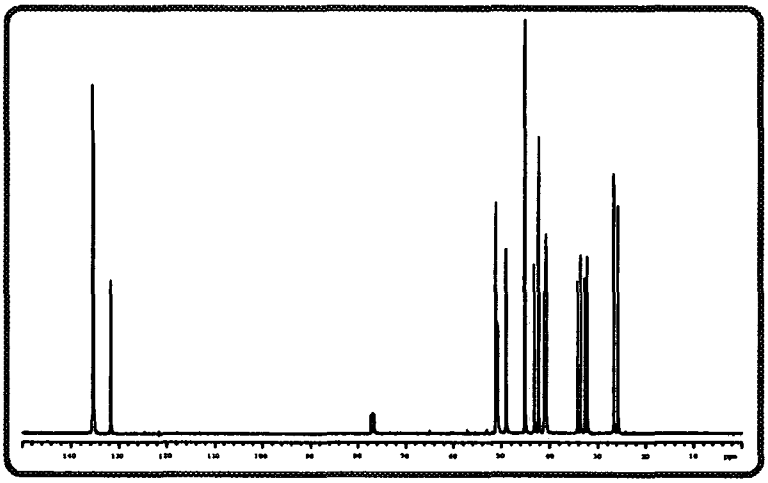


Figure 2.19: ^{13}C spectrum of dimethylbicyclo[2.2.1]hept-2-ene-5-phosphonate (100.577 MHz/CDCl$_3$).

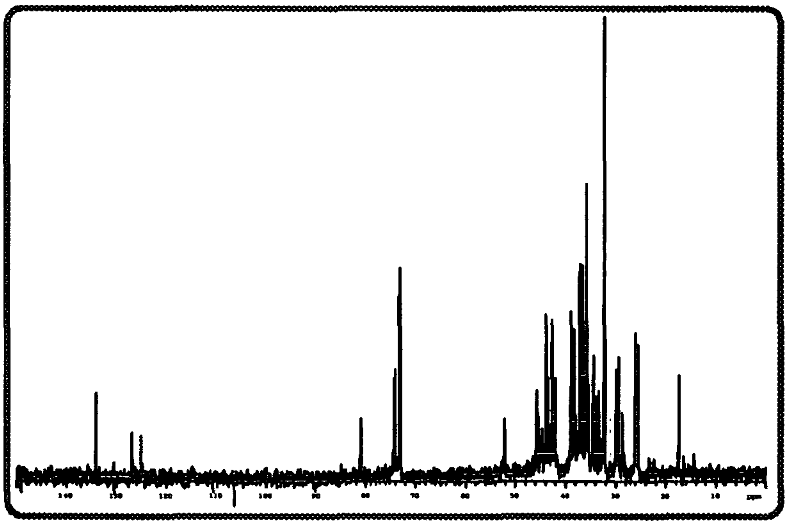


Figure 2.20: ^{13}C spectrum of hydrolysis product (100.577 MHz/D$_2$O).

Analysis of the product reveals that the methyl group signals disappear from the ^1H NMR (3.720 ppm)and ^{13}C NMR ($\approx$ 50-51 ppm) spectra, the relative intensity of the vinylic carbon signal is decreased and the vinylic to aliphatic ratio of protons is decreased from 2:7 in the starting material (excluding the methyl groups) to 2:65 in the product. There is also a slight difference in the spectral shifts between the product and starting material and an increased complexity of signals in the spectra of the product.

On the basis of these data it is concluded that the TMSBr method is effective in the removal of the methyl groups and a water soluble acid product is obtained. This is supported by the evolution of a gas during the reaction which was presumed to be CH_3Br. The norbornene vinylic region of the product is involved in an uncharacterised reaction leading to a water soluble product which gives peaks in its aqueous GPC analysis at masses corresponding to approximately $23x10^3$, $12x10^3$ and $3x10^3$.

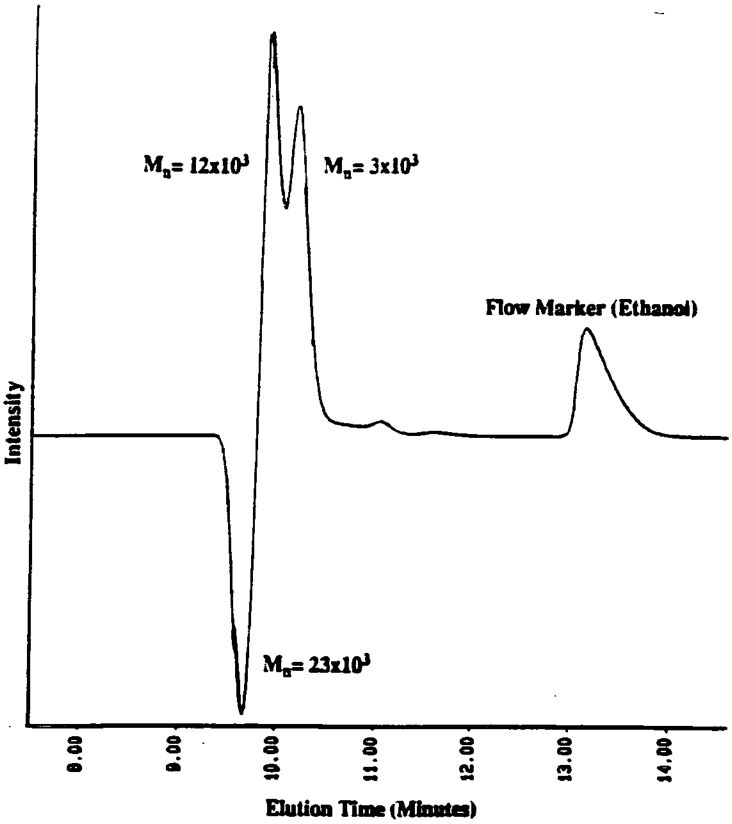


Figure 2.21: Aqueous GPC of hydrolysis product.

There is probably some error in the absolute values of the masses, due to the presence of three peaks close to each other, but it is clear that we do not have a simple *exo/endo* mixture of bicyclo[2.2.1]hept-2-ene-5-phosphonic acid as the product of this reaction. It seems reasonable to assume that some "polymerisation" of the norbornene structure is caused by the strong protic acid. Using this procedure the author has successfully made vinyl phosphonic acid from the demethylation of dimethyl vinylphosphonate, and the product was isolated in good yield.[173] The failure to obtain the analogous norbornene product must therefore be attributed to the enhanced susceptibility of the norbornene double bond to cationic reactions. The only plausible route to polymers with pendant $P(O)OH)_2$ units would therefore appear to be via demethylation of the polymers containing pendant esters using TMSBr, such an approach is unfortunately prohibitively expensive for conventional polymer syntheses and in any event the free $P(O)(OH)_2$ groups might be expected, in light of this experience, to react with or catalyse reactions of the main chain double bonds.

Chapter Three:
Syntheses and Attempted Syntheses of ROMP Polymers.

3.1 General Introduction.

This chapter describes the syntheses and characterisations of high molecular weight polymers via Ring Opening Metathesis Polymerisation (ROMP) of bicyclic organophosphorus monomers in organic and aqueous solvents using various transition metal chlorides as the precursors to the initiating and propagating species. The initiating species, which are presumed to contain a metallocarbene, are formed in situ and are ill defined with respect to structure.[39] Unsuccessful attempts to polymerise monocyclic 3-phospholenes via ROMP are also described.

3.2 Experimental.

3.2.1 Reactants.

All transition metal chlorides, WCl_6, $MoCl_5$, $RuCl_3.3H_2O$, $IrCl_3.3H_2O$, $OsCl_3.3H_2O$ and $PdCl_2$ (Aldrich Chemical Co. Ltd.) and solvents (May and Baker / BDH, laboratory grade) were used as supplied unless otherwise stated. The attempted aqueous ROMP of the monomers prepared in chapter 2 used distilled water.

3.2.2 Characterisation.

Polymer characterisation was performed using the apparatus described in Section 2.3.2. The molecular weights of the ring opened polymers were measured by Gel Permeation Chromatography (GPC) using chloroform as the eluent. The equipment comprised a Waters model 590 HPLC pump, a Waters R401 Refractive Index (RI) detector, a Waters U6K injection valve with 200μl injection loop and a three column set (5μ 10^5Å 30cm + 5μ 10^3Å 30cm + 5μ 100Å 30cm from Polymer Laboratories Ltd.). The calculation of molecular weights from the raw data was performed using the Polymer Laboratories Ltd. software package and the equipment was calibrated using polystyrene standards (Polymer Laboratories Ltd.).

3.3 Attempted ROMP of 1-hydroxy- and 1-alkoxy-1-oxo-3-phospholenes.

3.3.1 Attempted ROMP of 1-hydroxy-1-oxo-phosphol-3-ene using $WCl_6/SnMe_4$ and $MoCl_5/SnMe_4$.

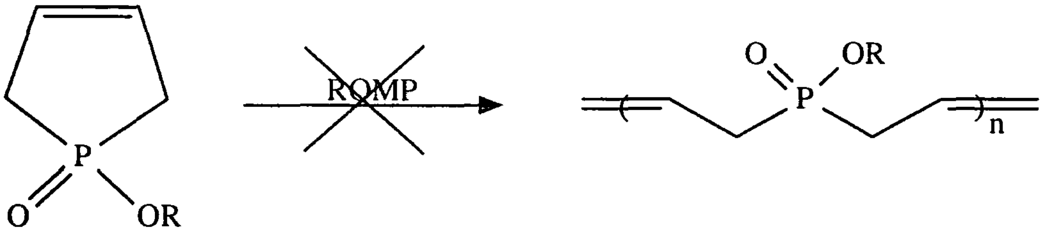


Figure 3.1: Attempted ROMP of the 1-hydroxy-1-oxo-3-phospholene.

1-Hydroxy-1-oxo-3-phospholene (1.0g/0.005-0.008 mol) was dissolved in dried toluene in a dry oxygen free reaction vessel connected directly to the vacuum/nitrogen manifold. The solution was degassed by a freeze/thaw procedure and eventually let down to a dry nitrogen atmosphere. A toluene solution of $WCl_6/SnMe_4$ was prepared by dissolving tungsten hexachloride and tetramethyl tin in dried, degassed toluene under nitrogen in a vessel connected to a vacuum/nitrogen line. The resulting solution was a deep chocolate brown/red colour, characteristic of an active initiator derived from this catalyst/co-catalyst mixture. The premixed $WCl_6/SnMe_4$ solution was injected into the monomer solution using a syringe, yielding a blue/black colour immediately on addition, indicating the destruction of the active initiator species. Spectroscopic analysis of the solution revealed the monomeric starting material. The experiment was repeated using molybdenum pentachloride/tetramethyl tin as the catalyst/co-catalyst system and using chlorobenzene as the solvent, but no polymerisation resulted. Control reactions were performed with norbornene to verify that the initiators were active and the experimental technique adopted was satisfactory in each case. The P(O)(OH) group on the 1-hydroxy-1-oxo-phosphol-3-ene results in this material being very hygroscopic and the moisture free conditions required for the $WCl_6/SnMe_4$ and $MoCl_5/SnMe_4$ classical initiator systems almost certainly were not obtained, thus accounting for the rapid quenching of the active initiator. The infra-red spectrum (Appendix D2) of the monomer suggests that it retains moisture despite our attempts to dry it.

3.3.2 Attempted ROMP of the 1-alkoxy-1-oxo-phosphol-3-enes using $WCl_6/SnMe_4$ and $MoCl_5/SnMe_4$.

The experimental procedure outlined in section 3.3.1 was repeated for each of the three 1-alkoxy-1-oxo-3-phospholenes with the results tabulated below (*Table 3.1*).

3.3.3 Attempted aqueous ROMP of 1-hydroxy-1-oxo-phosphol-3-ene.

The aqueous ROMP of 1-hydroxy-1-oxo-phosphol-3-ene was attempted using several transition metal chlorides as the precursors to the initiating and propagating species. In each reaction the 1-hydroxy-1-oxo-phosphol-3-ene (1.0g,0.008 mol) was placed in a test tube, dissolved in solvent (6.5ml) and stirred for 30 minutes with a magnetic stirrer at 55°C. Transition metal chloride (70mg) was then added and the resulting solution was stirred at 55°C for seven days. The resulting solution was freeze dried to recover a dark solid, which was extracted with diethyl ether to separate organic material from the catalyst residues, in each case the monomeric starting material was recovered ($\geq$ 0.93g).

The same experiment was repeated several times at different temperatures between 25°C and 85°C and left for times varying between two days and one week. Polymerisation was not observed under any of the conditions investigated.

Control reactions were performed in each case with *exo,exo*-7-oxabicyclo[2.2.1.] hept-5-ene-2,3-dicarboxylic acid (*Figure 3.2*) to verify that the initiators were active and the experimental technique adopted was satisfactory. Although the polymerisation of the 1-hydroxy-1-oxo-3-phospholene proved to be unsuccessful, the control experiment produced the expected ring opened polymer in every case.

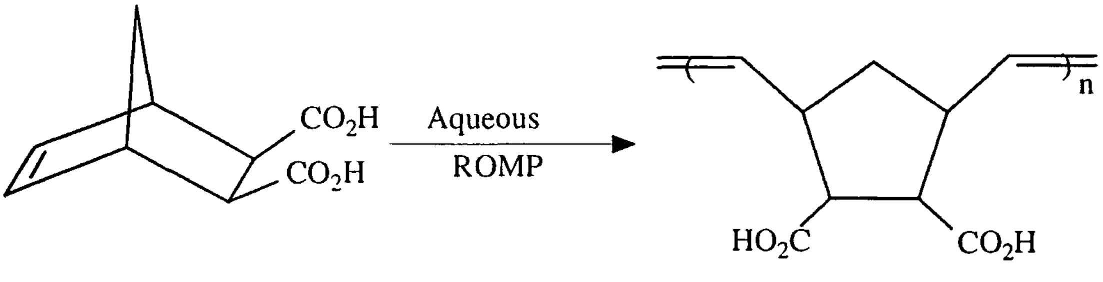
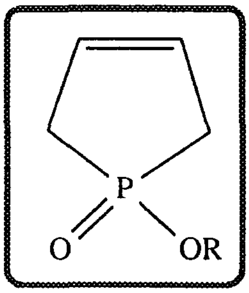


Figure 3.2: Aqueous ROMP of

exo,exo-7-oxabicyclo[2.2.1.]hept-5-ene-2,3-dicarboxylic acid

3.3.4 Attempted aqueous ROMP of the 1-alkoxy-1-oxo-phosphol-3-enes.

The experimental procedure outlined in section 3.3.3 was repeated for each of the three 1-alkoxy-1-oxo-3-phospholenes with the results tabulated below (*Table 3.1*), where R = H, Me, Ph or neopentyl and X indicates a failed polymerisation attempt.



Solvent	Initiator	H	Me	Ph	Neopentyl
H_2O	$RuCl_3$	X	X	X	X
EtOH	$RuCl_3$	X	X	X	X
Ph-Cl	$RuCl_3$	X	X	X	X
H_2O/EtOH	$RuCl_3$	X	X	X	X
Ph-Cl/EtOH	$RuCl_3$	X	X	X	X
H_2O	$IrCl_3$	X	X	X	X
EtOH	$IrCl_3$	X	X	X	X
Ph-Cl	$IrCl_3$	X	X	X	X
H_2O/EtOH	$IrCl_3$	X	X	X	X
Ph-Cl/EtOH	$IrCl_3$	X	X	X	X
H_2O	$OsCl_3$	X	X	X	X
EtOH	$OsCl_3$	X	X	X	X
Ph-Cl	$OsCl_3$	X	X	X	X
H_2O/EtOH	$OsCl_3$	X	X	X	X
Ph-Cl/EtOH	$OsCl_3$	X	X	X	X
Ph-Cl	$WCl_6/SnMe_4$	X	X	X	X
Ph-Me	$WCl_6/SnMe_4$	X	X	X	X
Ph-Cl	$MoCl_5/SnMe_4$	X	X	X	X
Ph-Me	$MoCl_5/SnMe_4$	X	X	X	X

Table 3.1: Results of attempted ROMP experiments with 3-phospholenes.

3.3.5 Discussion of observations on non-polymerisability of 3-phospholenes.

In order to investigate why the 3-phospholenes and cyclopentene fail to undergo ROMP with aqueous initiators we must take into account the important factors affecting the free energy of polymerisation, which are (see section 1.1.3):

(i) *Size and nature of the ring, hence the ring strain.*

(ii) *Substituents on the monomer.*

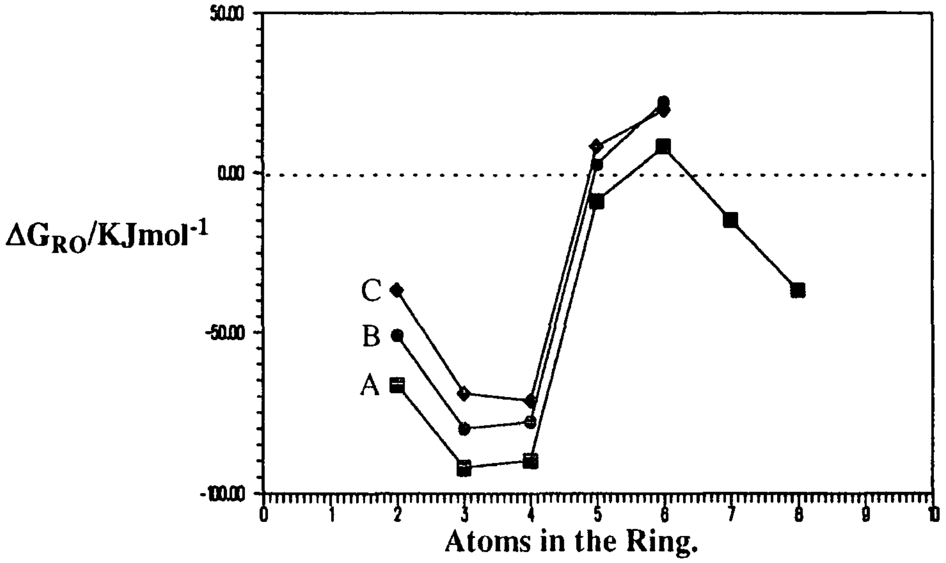
(iii) *The cis/trans geometrical isomerism of the polymer.*

(iv) *Tacticity of the polymer.*

The ring size and substitution are the two major factors in this set. Dainton and Ivin[127] considered the hypothetical ring opening polymerisation of a series of cycloalkanes by estimating the Gibbs Free Energy of Ring Opening (ΔG_{RO}) from thermodynamic data (*Table 3.2*) and plotting the results against the size of the ring (*Figure 3.3*).[53]

Cyclic Hydrocarbon	ΔG_{RO}	Polymerises
Cyclobutane	Large negative	No
Cyclopentane	Small negative	No
Cyclohexane	Small positive	No
Cycloheptane	Small negative	No
Cyclooctane	Large negative	No
Cyclobutene	Large negative	Yes
Cyclopentene	Small negative	Yes
Cyclohexene	Small positive	No
Cycloheptene	Small negative	Yes
Cyclooctene	Large negative	Yes

Table 3.2: Polymerisability of cycloalkanes and cycloalkenes.



A = Unsubstituted Cycloalkane.
B = Methyl Substituted Cycloalkane.
C = 1,1-Dimethyl Substituted Cycloalkane.

Figure 3.3: Free energy of polymerisation of cycloalkanes as a function of the number of atoms in the ring.

Although it is not possible to polymerise cycloalkanes by metathesis the ΔG_{RO} values for cycloalkanes are approximately equal to those of the cycloalkenes and therefore direct comparisons can be made. All the values are negative except for that of cyclohexene, which is the only cycloalkene that will not undergo ROMP. The ΔG_{RO}- ring strain relationship is emphasised by the fact cyclobutene and cyclooctene have large negative ΔG_{RO} values and undergo ROMP to completion, whereas cyclopentene has a small negative ΔG_{RO} value and stops short of completion. This suggests that the polymerisations of cyclobutene and cyclooctene are irreversible reactions, whereas the polymerisation of cyclopentene is essentially an equilibrium process. When the ΔG_{RO} value is small, slight changes in the chemical structure (eg. substitution - see Figure 3.3) and physical conditions may render the monomer unpolymerisable. This is the case for cyclopentene, where the monosubstituted compounds undergo ROMP but the disubstituted cyclopentenes do not. From this we can see that the polymerisation of five membered rings is very dependant on the nature of the ring and it has been concluded that the bond lengths and angles result in a low ring strain. Therefore it is believed that the aqueous initiators, which are less electrophilic than the tungsten and molybdenum initiators, are unable to offset the small free energy of ring opening.[53]

It would therefore seem there is a delicate balance between ring strain and conditions as to whether the five membered rings polymerise or not. Thus favourable conditions have not yet been met for the case of the ring opened polymerisations of the 3-phospholenes. This is emphasised by the fact that 1,1-dimethylsilacyclopent-3-ene (*Figure 3.4*)[174] and cyclopentene undergo ROMP with classical and "living" initiators and a wide range of phosphorus heterocycles such as 2-alkoxy-2-oxo-1,3,2-dioxaphospholane[175] ring open polymerise via anionic and cationic polymerisation (*Figure 3.5*).

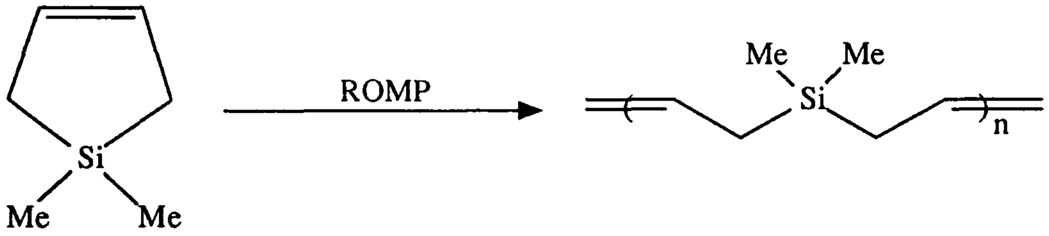


Figure 3.4: ROMP of 1,1-dimethylsilacyclopent-3-ene.

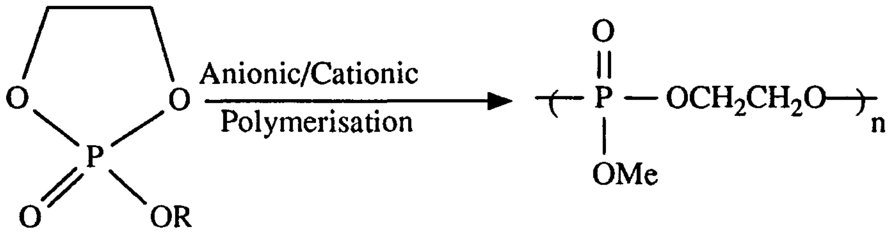


Figure 3.5: The polymerisation of 2-alkoxy-2-oxo-1,3,2-dioxaphospholane.

3.4 Synthesis and characterisation of poly{2,5[3-dimethylphosphonate]cyclopentylene}vinylene.

3.4.1 Attempted ROMP of dimethylbicyclo[2.2.1]hept-2-ene-5-phosphonate using $WCl_6/SnMe_4$ and $MoCl_5/SnMe_4$.

Dimethylbicyclo[2.2.1]hept-2-ene-5-phosphonate (1.0g, 0.005 mol) was dissolved in dried toluene in a dry oxygen free reaction vessel connected directly to the vacuum/nitrogen manifold. The solution was then degassed by a freeze/thaw procedure and eventually let down to a dry nitrogen atmosphere. A toluene solution of $WCl_6/SnMe_4$ was prepared by dissolving tungsten hexachloride and tetramethyl tin in dried, degassed toluene under nitrogen in a vessel connected to a vacuum/nitrogen line. The resulting solution was a deep chocolate brown/red colour, characteristic of an active initiator derived from this catalyst/co-catalyst mixture. The premixed $WCl_6/SnMe_4$ solution was injected into the monomer solution using a syringe, yielding a blue/black colour immediately on addition, indicating the destruction of the active initiator species. Work up of the solution, as described earlier, gave the monomeric starting material in good yield. The experiment was repeated using molybdenum pentachloride/tetramethyl tin as the catalyst/co-catalyst system and using chlorobenzene as the solvent, but no polymerisation resulted. Control reactions were performed in each case with norbornene to verify that the initiator was active and the experimental technique adopted was satisfactory. The $P(O)(OMe)_2$ group on the dimethylbicyclo [2.2.1]hept-2-ene-5-phosphonate monomer results in this material being very hygroscopic and the moisture free conditions required for the $WCl_6/SnMe_4$ and $MoCl_5/SnMe_4$ classical initiator systems almost certainly were not obtained, thus accounting for the rapid quenching of the active initiator. The infra-red spectrum (Appendix D6) of the monomer suggests that it retains moisture despite our attempts to dry it.

3.4.2 Aqueous ROMP of dimethylbicyclo[2.2.1]hept-2-ene-5-phosphonate.

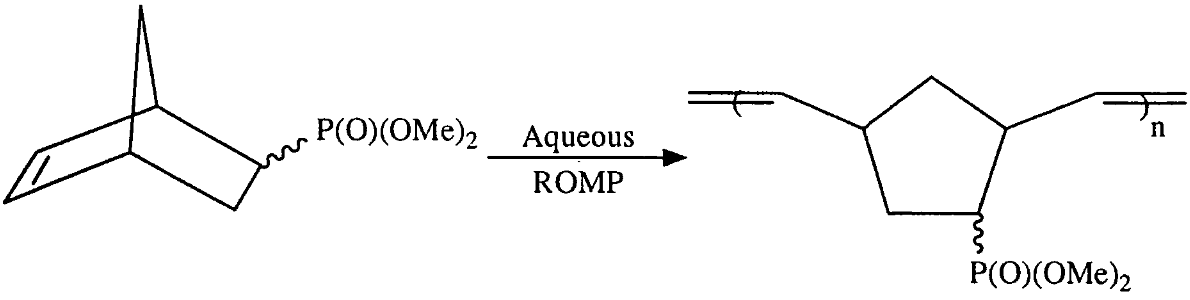


Figure 3.6: Aqueous ROMP of dimethylbicyclo[2.2.1]hept-2-ene-5-phosphonate.

The aqueous ROMP of dimethylbicyclo[2.2.1]hept-2-ene-5-phosphonate was attempted using various transition metal chlorides as the precursors to the initiating species in a variety of solvent systems. In each reaction the dimethylbicyclo[2.2.1] hept-2-ene-5-phosphonate monomer (1g, 0.005 mol) was placed in a test tube, dissolved in solvent (6.5ml) and stirred for 30 minutes with a magnetic stirrer at 55°C. Transition metal chloride (70mg) was then added and the resulting solution was stirred at 55°C for two days. Polymerisation occurred, as was evident from the precipitation of a rubbery gel. The polymers (poly{2,5-[3-dimethylphosphonate]cyclopentylene} vinylenes) were recovered by decantation and/or filtration, dissolved in ethanol and reprecipitated into water. This process was repeated twice and the polymers were obtained as stringy, solvent swollen materials, which were dried in vacuo for 24 hours. Successful polymerisations were achieved with $IrCl_3.3H_2O$, $RuCl_3.3H_2O$ and $OsCl_3.3H_2O$ but no polymers were formed with $PdCl_2$. A series of reactions were performed to discover how yield and molecular weight varied with variations in solvent composition and the results are tabulated below (*Tables 3.3-3.7*). Plots of reciprocal number average weight against ethanol volume concentration (%), for each set of results, are presented in Figures 3.7-3.11. All sets of experiments were performed using the same batches of initiator, monomer, distilled water and ethanol, in the same water bath and worked up and analysed in the same way.

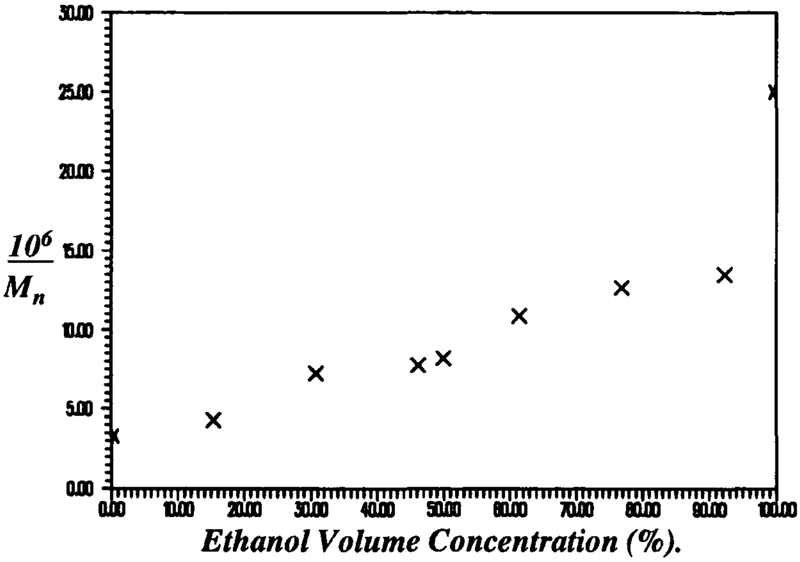


Figure 3.7: Graph of reciprocal number average molecular weight against ethanol volume concentration (%) for the ROMP of dimethylbicyclo[2.2.1]hept-2-ene-5-phosphonate using $IrCl_3.3H_2O$ and ethanol/water.

Ethanol (ml)	Water (ml)	Mn	Mw	Mw/Mn	Yield
6.5 ml	0 ml	40000	195000	4.872	75 %
6.0 ml	0.5 ml	74000	204000	2.757	68 %
5.0 ml	1.5 ml	79000	264000	3.346	69 %
4.0 ml	2.5 ml	92000	276000	3.002	70 %
3.25 ml	3.25 ml	122000	318000	2.606	72 %
3.0 ml	3.5 ml	129000	234000	1.820	68 %
2.0 ml	4.5 ml	138000	330000	2.394	71 %
1.0 ml	5.5 ml	233000	501000	2.141	74 %
0 ml	6.5 ml	304000	493000	1.620	81 %

Table 3.3: Aqueous ROMP of dimethyl bicyclo[2.2.1]hept-2-ene-5-phosphonate using $IrCl_3.3H_2O$ and ethanol/water.

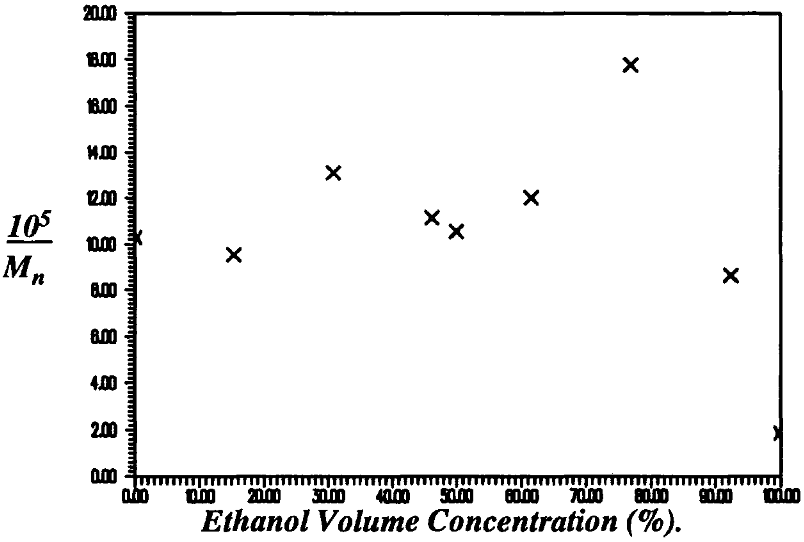


Figure 3.8: Graph of reciprocal number average molecular weight against ethanol volume concentration (%) for the ROMP of dimethyl bicyclo[2.2.1]hept-2-ene-5-phosphonate using $IrCl_3.3H_2O$ and ethanol/chlorobenzene.

Ethanol (ml)	Ph-Cl (ml)	Mn	Mw	Mw/Mn	Yield
6.5 ml	0 ml	40000	195000	4.872	75 %
6.0 ml	0.5 ml	12000	40000	3.429	66 %
5.0 ml	1.5 ml	6000	18000	3.152	67 %
4.0 ml	2.5 ml	8000	13000	1.558	64 %
3.25 ml	3.25 ml	9000	18000	1.912	60 %
3.0 ml	3.5 ml	9000	17000	1.848	62 %
2.0 ml	4.5 ml	8000	11000	1.442	61 %
1.0 ml	5.5 ml	10000	17000	1.638	63 %
0 ml	6.5 ml	10000	22000	2.259	61 %

Table 3.4: Aqueous ROMP of dimethyl bicyclo[2.2.1]hept-2-ene-5-phosphonate using $IrCl_3.3H_2O$ and ethanol/chlorobenzene.

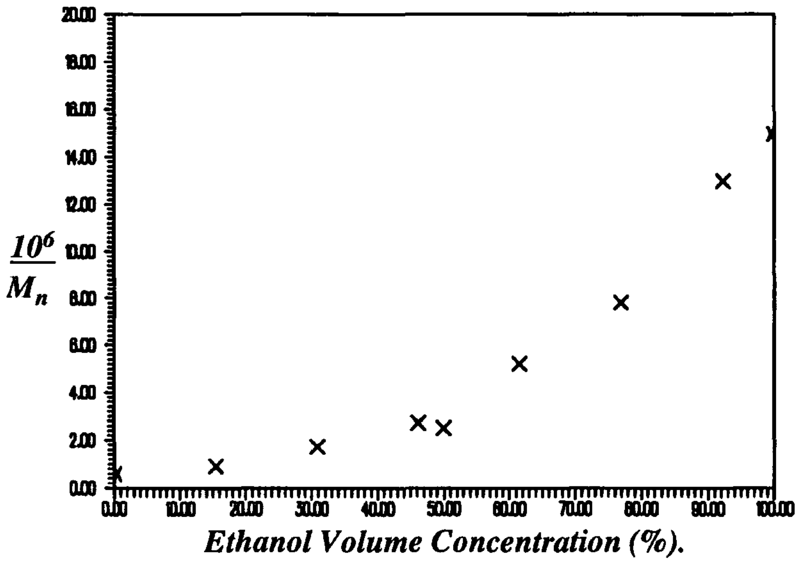


Figure 3.9: Graph of reciprocal number average molecular weight against ethanol volume concentration (%) for the ROMP of dimethyl bicyclo[2.2.1]hept-2-ene-5-phosphonate using $RuCl_3.3H_2O$ and ethanol/water.

Ethanol (ml)	Water (ml)	Mn	Mw	Mw/Mn	Yield
6.5 ml	0 ml	7000	37000	5.588	11 %
6.0 ml	0.5 ml	8000	21000	2.782	11 %
5.0 ml	1.5 ml	13000	45000	3.520	30 %
4.0 ml	2.5 ml	19000	55000	2.848	72 %
3.25 ml	3.25 ml	40000	103000	2.567	73 %
3.0 ml	3.5 ml	37000	92000	2.509	69 %
2.0 ml	4.5 ml	58000	195000	3.352	70 %
1.0 ml	5.5 ml	109000	209000	1.909	78 %
0 ml	6.5 ml	173000	491000	2.841	91 %

Table 3.5: Aqueous ROMP of dimethyl bicyclo[2.2.1]hept-2-ene-5-phosphonate using $RuCl_3.3H_2O$ and ethanol/water.

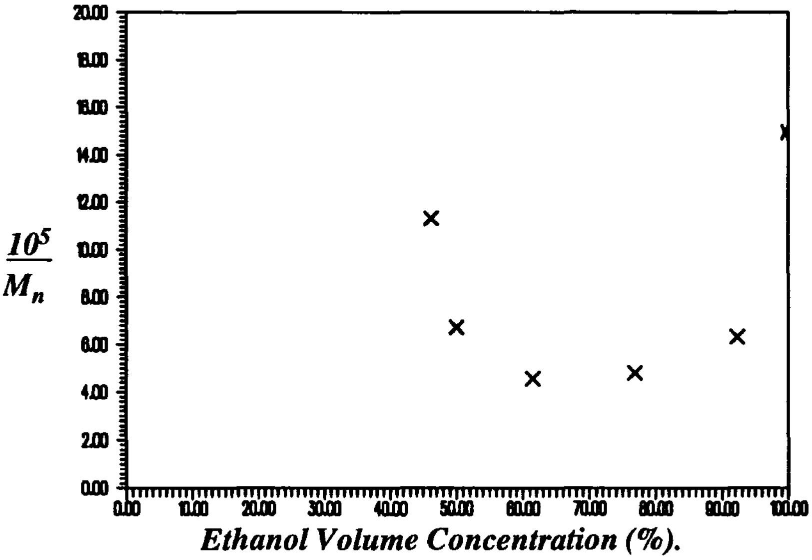


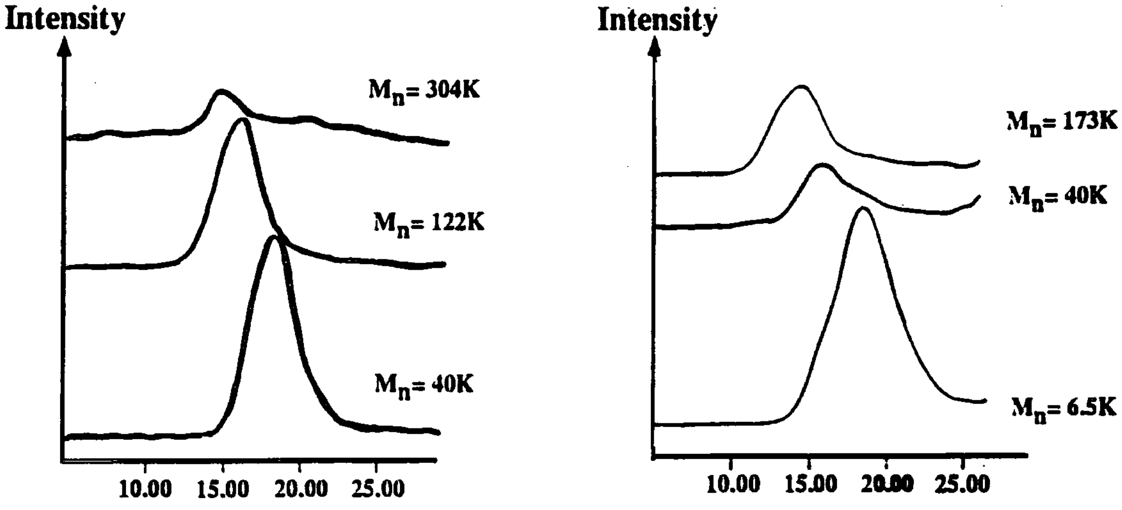
Figure 3.10: Graph of reciprocal number average molecular weight against ethanol volume concentration (%) for the ROMP of dimethylbicyclo[2.2.1]hept-2-ene-5-phosphonate using $RuCl_3.3H_2O$ and ethanol/chlorobenzene.

Ethanol (ml)	Ph-Cl (ml)	Mn	Mw	Mw/Mn	Yield
6.5 ml	0 ml	7000	37000	5.588	11 %
6.0 ml	0.5 ml	16000	98000	6.198	30 %
5.0 ml	1.5 ml	21000	71000	3.426	26 %
4.0 ml	2.5 ml	22000	91000	4.158	15 %
3.25 ml	3.25 ml	15000	49000	3.294	2 %
3.0 ml	3.5 ml	9000	28000	3.174	1 %
2.0 ml	4.5 ml	-----	-----	-----	0 %
1.0 ml	5.5 ml	-----	-----	-----	0 %
0 ml	6.5 ml	-----	-----	-----	0 %

Table 3.6: Aqueous ROMP of dimethyl bicyclo[2.2.1]hept-2-ene-5-phosphonate using $RuCl_3.3H_2O$ and ethanol/chlorobenzene.

Ethanol (ml)	Water (ml)	Yield
6.5 ml	0 ml	0 %
6.0 ml	0.5 ml	1 %
5.0 ml	1.5 ml	2 %
4.0 ml	2.5 ml	10 %
3.25 ml	3.25 ml	14 %
3.0 ml	3.5 ml	15 %
2.0 ml	4.5 ml	17 %
1.0 ml	5.5 ml	23 %
0 ml	6.5 ml	26 %

Table 3.7: Aqueous ROMP of dimethyl bicyclo[2.2.1]hept-2-ene-5-phosphonate using $OsCl_3.3H_2O$ and ethanol/water.



(a) $IrCl_3.3H_2O$ (b) $RuCl_3.3H_2O$

Figure 3.11: GPC chromatograms showing variation in molecular weight distribution with ethanol/water solvent composition with (a) $IrCl_3.3H_2O$ and (b) $RuCl_3.3H_2O$.

The variations in molecular weight with the proportion of ethanol in an ethanol/ water solvent mixture using $IrCl_3.3H_2O$ and $RuCl_3.3H_2O$ are illustrated in Figures 3.11a and 3.11b respectively.

The ^1H decoupled ^{31}P NMR spectra (eg. 97.15 MHz/$CDCl_3$/Appendix C12) of the polymers produced by the route described above, indicated the presence of two phosphorus peaks at 34.18 ppm and 31.75 ppm corresponding to the environments of phosphorus nuclei in repeat units derived from the *endo* and *exo* monomers. It is evident from the spectrum that the *exo* derived peak is larger than the *endo* derived peak and as the ratio has increased from 1:1 in the monomer mixture to 2:1 in the polymer, it would seem that the *exo* isomer preferentially undergoes ROMP. This observation would explain all the yields being less than 100% since all the *endo* isomer is not consumed during the reaction, probably due to the bulky *endo*-phosphonate group being too close to the C=C double bond on the norbornene and hence inhibiting the ROMP reaction. This result is as expected since *exo* substituted norbornenes have been found to undergo ROMP more readily than the corresponding *endo* substituted compounds. The infrared spectrum of the polymer is shown in appendix D12 and is consistent with the assigned structure with the most important diagnostic infrared bands being:- vinylic CH stretches at 3010 cm^{-1}, CH_2/CH_3 stretches at 2990 cm^{-1}, 2880 cm^{-1} and 2850 cm^{-1}, a C=C stretch at 1620 cm^{-1} and a P=O stretch at 1240 cm^{-1}. The ^1H NMR (399.952 MHz/$CDCl_3$/Appendix A12) and ^{13}C NMR spectra (100.577 MHz/$CDCl_3$/Appendix B12) are very complex due to the presence of *cis*/*trans* and *endo*/*exo* derived residues and the further complication of ^{31}P coupling and complete analyses could not be achieved. The C1, C4, C5 and C7 carbon signals, which were resolved in the monomer spectrum, coalesce in the polymer spectrum, giving the very complicated signals centred at 42 ppm. The vinylic carbons also coalesce and there is a noticeable upfrequency shift for carbon 6 (CH_2). The methyl groups on the phosphonate remain in the same position as the monomer.

3.4.3 Discussion of Results.

Analysis of the results using the $IrCl_3.3H_2O$ derived initiator and the ethanol/water solvent system suggested that molecular weight control was possible by varying the proportion of ethanol in the solvent for the ROMP reaction without a significant influence on the yield of polymer. Several further reactions were carried out and the trends recorded in Table 3.3 were reasonably reproducible. In an attempt to analyse the data, the reciprocal number average molecular weight (Mn) was plotted against volume percentage of ethanol in the reaction solvent. Apart from the 100 % point a reasonably good straight line plot was obtained. This analysis is analogous to that used for determining chain transfer constants for chain growth polymerization, which are given by the gradient of a plot of $^{1}/_{M_n}$ versus $^{[CTA]}/_{[M]}$ (where [CTA] and [M] are the concentrations of chain transfer agent and monomer respectively). In this case [M] is kept constant and the water and ethanol contents are changing. However, tempting as it may be to suggest that transfer to solvent is occurring, we have to keep in mind that this reaction is non-ideal. The initial problem is that we do not know whether the mixture was a solution, suspension or a dispersion due to the dark colour of the initiator, but the major problem was that the polymer separates fully as a rubbery precipitate in water, whereas as the percentage of ethanol increases it becomes more like a swollen viscous gel. The graph does at least indicate the promise of reasonably well controlled molecular weight regulation with this system but if the polydispersity is analysed it can be seen that it is variable. It is difficult to measure the polydispersity because the base-lines were noisy and the exact position of the base-line could not be defined with any precision.

A different situation arose when an ethanol/chlorobenzene mixture was used, the yield of polymer was largely unaffected by the variation of ethanol concentration in the solvent, as was the case with ethanol/water, but results in Table 3.4 suggest there is no direct relationship between the solvent composition and the molecular weight of the resultant polymer.

For the $RuCl_3.3H_2O$ system as the precursor to the initiator in the ethanol/water solvent system, a similar relationship to that observed for $IrCl_3.3H_2O$ was found but the results were not as convincing and the yield of polymer was severely reduced with increasing ethanol concentration (*Table 3.5*). The graph of $^1/_{M_n}$ versus ethanol concentration shows a fairly smooth curve and the linear form seen for the $IrCl_3.3H_2O$ case is not evident casting doubt on any analysis in terms of chain transfer to solvent, but again indicating the possibility of reasonably well controlled molecular weight regulation.

The ethanol/chlorobenzene solvent mixture proved to be very poor with $RuCl_3.3H_2O$ as the precursor to the initiator, yields were all low and there seemed to be no obvious relationship between molecular weight and the concentration of ethanol present in the solvent (*Table 3.6*).

The use of $OsCl_3.3H_2O$ as the precursor to the initiator, in an ethanol/ chlorobenzene mixture, yielded no polymer, whereas in the ethanol/water series of reactions, polymeric material was recovered. However these polymers were insoluble in water and the common organic solvents investigated (variety of aromatic and aliphatic hydrocarbons, alcohols, amines, esters, ethers and halogenated solvents), suggesting that they were probably crosslinked (*Table 3.7*).

By observation of the colour changes occurring during the ROMP reactions an approximate indication of the time of initiation of each reaction can be obtained. When $IrCl_3.3H_2O$ was used as the initiator in water the initial red/brown colour of the solution turned to yellow after approximately 2 hours but there was no detectable change in viscosity. The colour became red/orange after 36 hours and this process was accompanied by separation of a rubbery polymer. Using $RuCl_3.3H_2O$ the initial brown colour changed to red after 6 hours and green after 2 days, the first evidence of polymerisation occurred as the green colour appeared. There were no colour changes observed with the black $OsCl_3.3H_2O$ catalyst solution but crosslinked polymeric material was recovered in low yield after two days. If we assume that the colour changes are an indication of the formation of an active propagating species it would appear that the aqueous ROMP of dimethylbicyclo[2.2.1]hept-2-ene- 5-phosphonate occurs more readily with the iridium initiator than with ruthenium. The characteristics of the reaction using osmium in water are more difficult to measure as there is no colour change and a more complex reaction appears to be occurring, which results in crosslinked polymer being precipitated. These results contrast with the findings of Harrison,[86] who reported that aqueous ROMP was faster with a series of disubstituted oxanorbornene monomers using $OsCl_3.3H_2O$ and slowest for $IrCl_3.3H_2O$ with the ruthenium initiator being of intermediate activity.

When $IrCl_3.3H_2O$ was used as the initiator for the polymerisation of dimethylbicyclo[2.2.1]hept-2-ene-5-phosphonate in ethanol the initial red/brown colour of the solution turned to yellow after approximately 1 hour and to a red/orange solvent swollen gel after 1 day, and the use of chlorobenzene resulted in colour changes after 5 hours and 2 days respectively. Using $RuCl_3.3H_2O$ the initial brown colour changed to red after 24 hours and to a green gel after approximately 2 days but no polymerisation occurred using $RuCl_3.3H_2O$ in chlorobenzene. No polymer was recovered using $OsCl_3.3H_2O$ in either ethanol or chlorobenzene. By again assuming the colour changes are an indication of the presence of active propagating species, it can be seen that the initiation of ROMP of dimethylbicyclo[2.2.1]hept-2-ene- 5-phosphonate with the iridium initiator is accelerated by using ethanol as the solvent but decelerated by the presence of chlorobenzene. These results are consistent with the work of Michelotti[77], who suggested that iridium chlorides are considerably more active initiators in ethanolic solvents than the ruthenium and osmium chlorides.

The colour changes do not necessarily correspond to the formation of the metal carbene and hence only give a vague indication of events in the polymerisation process

As the aqueous metathesis initiators are generated in situ from transition metal chlorides, which are a mixture of chlorides and oxychlorides,[176] the precise form of the initiator is not known and neither are the factors involved in carbene production.

Therefore there are many variables in the experimental procedure, such as slight changes in temperature and solvent which can affect the reaction, to come to unambiguous conclusions about the reaction mechanism of aqueous ROMP, on the basis of the presently available data and systems, is not possible.

3.5 Synthesis and characterisation of poly{2,5[3-diethylphosphonate]cyclopentylene}vinylene.

3.5.1 Aqueous ROMP of diethylbicyclo[2.2.1]hept-2-ene-5-phosphonate.

Diethylbicyclo[2.2.1]hept-2-ene-5-phosphonate (1g, 0.004 mol) was placed in a test tube (diameter 13mm), dissolved in solvent (6.5ml) and stirred for 30 minutes with a magnetic stirrer at 55°C. Transition metal chloride (70mg) was then added and the resulting solution was stirred for four days at 55°C. The resulting polymers (poly{2,5[3-diethylphosphonate]cyclopentylene}vinylenes) were recovered by decantation and/or filtration then dissolved in ethanol and reprecipitated into water. This process was repeated twice and the polymers were dried in vacuo for 24 hours.

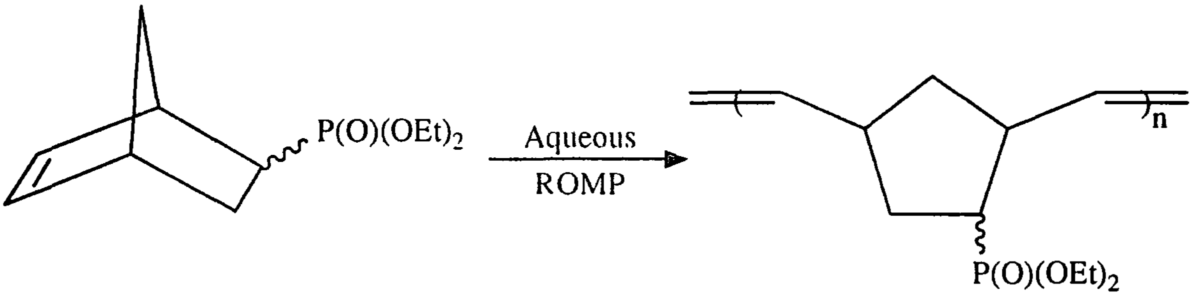


Figure 3.12: Aqueous ROMP of diethyl bicyclo[2.2.1]hept-2-ene-5-phosphonate.

A ^1H-decoupled ^{31}P NMR spectra (eg. 97.15 MHz/$CDCl_3$/Appendix C13) of the polymers indicated the presence of two phosphorus peaks at 35.58 ppm and 33.35 ppm, corresponding to the two phosphorus nuclei in repeat units derived from the *exo* and *endo* monomers. It is again evident that the *exo* derived peak is larger than the *endo* derived peak, the *exo*:*endo* ratio has increased from 1:1 in the monomer to 7:3 in the polymer and hence the *exo* isomer again seems to preferentially undergo ROMP, presumably for similar reasons to the dimethyl ester case. The infrared spectrum of the polymer is shown in appendix D13 and is consistent with the assigned structure with the most important diagnostic infrared bands being:- vinylic CH stretches at 3010 cm^{-1}, CH_2/CH_3 stretches at 2990 cm^{-1}, 2870 cm^{-1} and 2850 cm^{-1}, a C=C stretch at 1620 cm^{-1} and a P=O stretch at 1210 cm^{-1}. The ^1H NMR (399.952 MHz/$CDCl_3$/Appendix A13) and ^{13}C NMR spectra (100.577 MHz/$CDCl_3$/Appendix B13) were again very complicated and complete analyses could not be achieved.

A limited number of polymerisation studies were attempted with the transition metal chlorides, which resulted in successful reactions in the cases recorded in Tables 3.8-3.9. Plots of reciprocal number average weight against ethanol volume concentration (%), for each set of results, are presented in Figures 3.13-3.14.

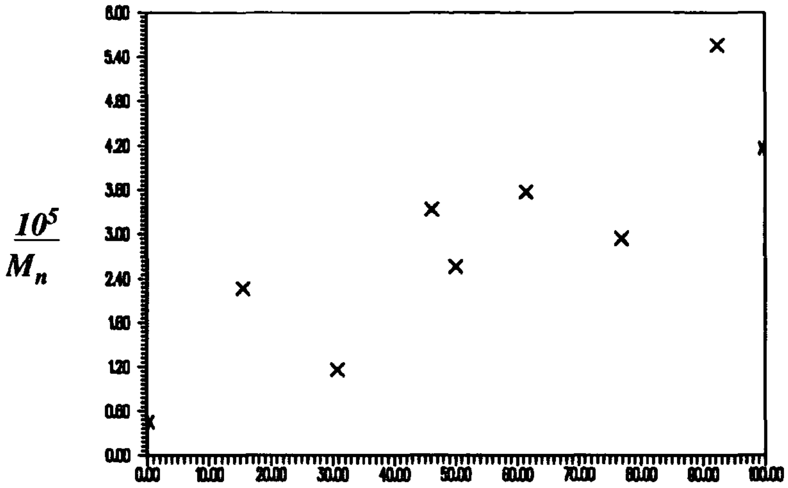


Figure 3.13: Graph of reciprocal number average molecular weight against ethanol volume concentration (%) for the ROMP of diethylbicyclo[2.2.1]hept-2-ene-5-phosphonate using $IrCl_3.3H_2O$ and ethanol/water.

Ethanol (ml)	Water (ml)	Mn	Mw	Mw/Mn	Yield
6.5 ml	0 ml	24000	88000	3.637	63 %
6.0 ml	0.5 ml	18000	68000	3.734	59 %
5.0 ml	1.5 ml	34000	152000	4.424	63 %
4.0 ml	2.5 ml	28000	89000	3.217	46 %
3.25 ml	3.25 ml	39000	191000	4.917	47 %
3.0 ml	3.5 ml	30000	125000	4.212	41 %
2.0 ml	4.5 ml	86000	272000	3.177	45 %
1.0 ml	5.5 ml	44000	237000	5.436	29 %
0 ml	6.5 ml	222000	551000	2.482	32 %

Table 3.8: Aqueous ROMP of diethyl bicyclo[2.2.1]hept-2-ene-5-phosphonate using $IrCl_3.3H_2O$ and ethanol/water.

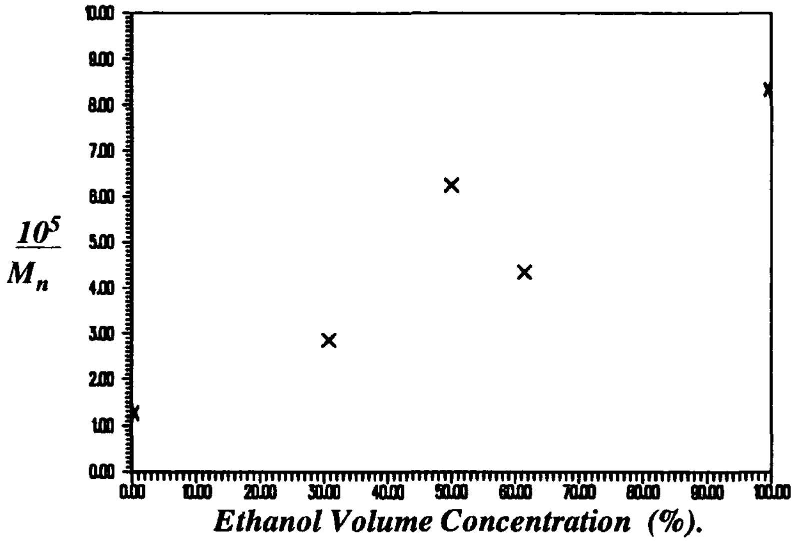


Figure 3.14: Graph of reciprocal number average molecular weight against ethanol volume concentration (%) for the ROMP of diethylbicyclo[2.2.1]hept-2-ene-5-phosphonate using $RuCl_3.3H_2O$ and ethanol/water.

Ethanol (ml)	Water (ml)	Mn	Mw	Mw/Mn	Yield
6.5 ml	0 ml	12000	29000	2.48	16 %
4.0 ml	2.5 ml	23000	61000	2.65	18 %
3.25 ml	3.25 ml	16000	62000	3.89	22 %
2.0 ml	4.5 ml	35000	105000	2.99	19 %
0 ml	6.5 ml	79000	266000	3.37	22 %

Table 3.9: Aqueous ROMP of diethylbicyclo[2.2.1]hept-2-ene-5-phosphonate using $RuCl_3.3H_2O$ and ethanol/water.

3.5.2 Discussion of Results.

The diethylbicyclo[2.2.1]hept-2-ene-5-phosphonate is not as soluble in water as the dimethyl analogue and this affects the results considerably. Although the graph of

$^1/_{M_n}$ versus ethanol concentration shows again indicates the possibility of reasonable control of molecular weight using $IrCl_3.3H_2O$, the yields of polymer were significantly less than those obtained using dimethylbicyclo[2.2.1]hept-2-ene-5-phosphonate.

For the $RuCl_3.3H_2O$ system as the precursor to the initiator in the ethanol/water solvent system a similar relationship to that observed for $IrCl_3.3H_2O$ was found but the results were again not as convincing. The yields are all low due to the combination of the poor activity of $RuCl_3.3H_2O$ in ethanol and the poor solubility of the monomer in water. The graph of $^1/_{M_n}$ versus ethanol concentration shows a fairly straight line and again there are indications of the possibility of reasonably well controlled molecular weight regulation.

The use of $OsCl_3.3H_2O$ in the ethanol, water, ethanol/water, chlorobenzene and ethanol/chlorobenzene solvent systems and $IrCl_3.3H_2O$ or $RuCl_3.3H_2O$ in chlorobenzene yielded no polymeric material.

The observation of colour changes occurring during the ROMP reaction again give some indication of the time at which active propagating species were formed. When $IrCl_3.3H_2O$ was used as the initiator in water, the initial red/brown colour of the solution turned to yellow after approximately 6 hours and red/orange after two days, accompanied by the precipitation of polymer. Using $RuCl_3.3H_2O$ the initial brown colour changed to red after approximately 12 hours and green after 2/3 days, the first sign of polymerisation occurring as the green colour appeared. Again the use of ethanol favours the reaction using $IrCl_3.3H_2O$ as the initiator, with the analogous colour changes taking place after 4 hours and 36 hours respectively. However the use of ethanol is disadvantageous with $RuCl_3.3H_2O$ as the initiator and the colour changes take place after 24 hours and 48 hours respectively. These findings are again consistent with the work of Michellotti,[77] who reported the increased activity of $IrCl_3.3H_2O$ in ethanolic solvents. Comparison of these results with those in section 3.4.3 reveal that the ROMP of diethylbicyclo[2.2.1]-hept-2-ene-5-phosphonate is considerably less favourable than the ROMP of the dimethylphosphonate analogue. This may be attributed to the increased size of the phosphonate substituent. Functionalised monomers can coordinate to the metathesis initiator but large side groups are believed to affect the rate of polymerisation and the subsequent reactivity and this would account for the differing rates of reaction. As the diethylbicyclo[2.2.1]-hept-2-ene-5-phosphonate is less soluble in water than dimethylbicyclo[2.2.1]-hept-2-ene-5-phosphonate this would also affect the rates of the two reactions.

3.6 Attempted synthesis and characterisation of poly(2,5-(3,4-bis(dimethylphosphonate)cyclopentylene)vinylene.

3.6.1 Aqueous ROMP of *exo,endo*-5,6-bis(dimethylphosphonate)-bicyclo[2.2.1]hept-2-ene.

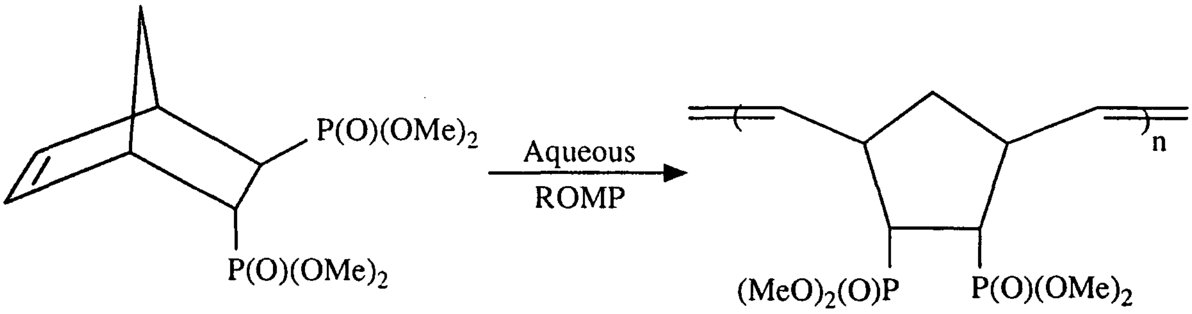


Figure 3.15: Aqueous ROMP of exo,endo-5,6-bis(dimethylphosphonate)-bicyclo[2.2.1]hept-2-ene.

exo,endo-5,6-Bis(dimethylphosphonate)-bicyclo[2.2.1] hept-2-ene (1.0g/0.003 mol) was placed in a test tube (diameter 13mm), dissolved in solvent (6.5ml) and stirred for 30 minutes with a magnetic stirrer at 55°C. Transition metal chloride (70mg) was then added and the resulting solution was stirred for two days at 55°C. The solvent was removed by rotary evaporation and the resulting oligomers (poly(2,5-(3,4-bis(dimethylphosphonate)cyclopentylene)vinylenes) were dissolved in ethanol, reprecipitated into pentane and dried in vacuo for 24 hours. The results are discussed in Section 3.8.

The product in each of the successful reactions was a series of oligomers in very low yields (≤ 10%). GPC analysis indicated that these mainly consisted of trimers and dimers (eg. *Figure 3.16*). It can be seen from the chromatogram that there is a considerable amount of unreacted monomer present in the samples, which could not be removed during the work up of the oligomers.

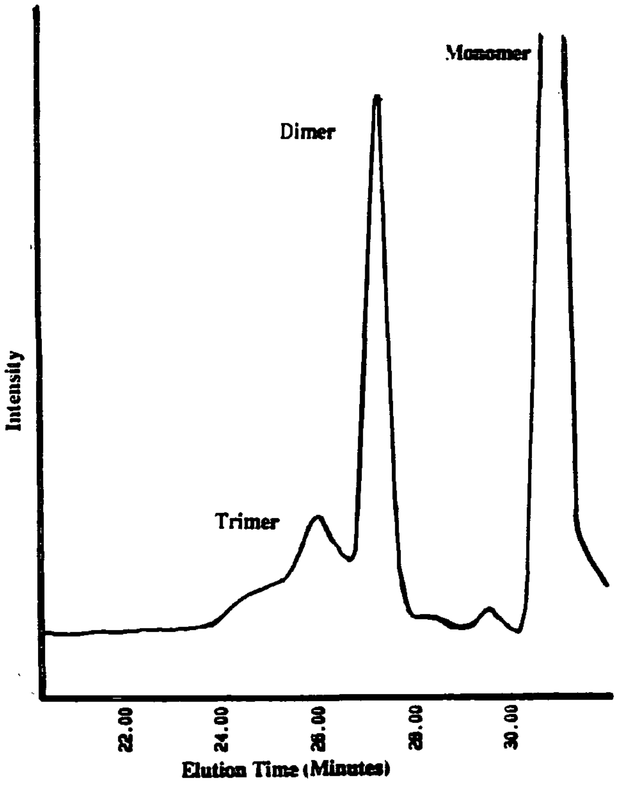


Figure 3.16: GPC chromatogram showing oligomers formed from the ROMP of the exo,endo-5,6-bis(dialkylphosphonate)- bicyclo[2.2.1]hept-2-enes.

The ^1H decoupled ^{31}P spectrum (202.46 MHz/$CDCl_3$/Appendix C14) shows the presence of two peaks at 29.85 ppm and 29.07 ppm probably corresponding to the two phosphorus environments in the dimer. There is also a series of smaller peaks probably corresponding to the higher molecular weight oligomers.

The infrared spectrum of the product is shown in appendix D14 and is consistent with the assigned structure with the most important diagnostic infrared bands being:- vinylic CH stretches at 3010 cm^{-1}, CH_2/CH_3 stretches at 2990 cm^{-1}, 2950 cm^{-1} and 2850 cm^{-1}, a C=C stretch at 1600 cm^{-1} and a P=O stretch at 1260 cm^{-1}.

The ^{1}H NMR (399.952 MHz/$CDCl_3$/Appendix A14) and ^{13}C NMR spectra (100.577 MHz/$CDCl_3$/Appendix B14) are very complex due to the presence of *cis/trans* and *endo/exo* derived repeat units and the further complication of ^{31}P coupling and unreacted monomer being present and therefore complete analyses could not be achieved. The C1, C4, C5 and C7 carbon signals, which were resolved in the monomer spectrum, coalesce in the polymer spectrum, giving the very complicated signals centred at 40 ppm.

3.7 Attempted synthesis and characterisation of poly(2,5-(3,4-bis(diethylphosphonate)cyclopentylene)vinylene.

3.7.1 Aqueous ROMP of *exo,endo*-5,6-bis(diethylphosphonate)-bicyclo[2.2.1]hept-2-ene.

exo,endo-5,6-Bis(diethylphosphonate)-bicyclo[2.2.1]hept-2-ene (1.0g/0.003 mol) was placed in a test tube (diameter 13mm), dissolved in solvent (6.5ml) and stirred for 30 minutes with a magnetic stirrer at 55°C. Transition metal chloride (70mg) was then added and the resulting solution was stirred for two days at 55°C. The solvent was removed by rotary evaporation and the resulting oligomers (poly(2,5-(3,4-bis(diethylphosphonate)cyclopentylene)vinylenes) were dissolved in ethanol, reprecipitated into pentane and dried in vacuo for 24 hours. The results are discussed in Section 3.8.

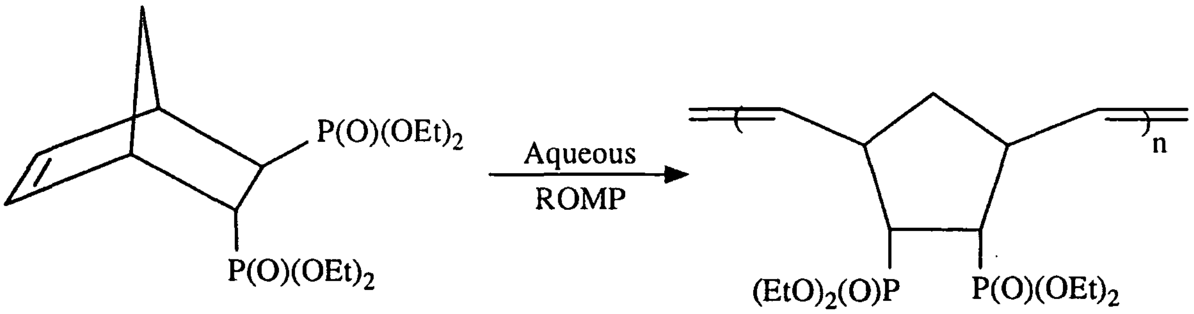


Figure 3.17: Aqueous ROMP of

exo,endo-5,6-bis(diethylphosphonate)-bicyclo[2.2.1]hept-2-ene.

The product in each of the successful reactions was again a series of oligomers in very low yields (≤ 10%). GPC analysis again indicated that these mainly consisted of trimers and dimers (eg. *Figure 3.16*).

The ^1H decoupled ^{31}P spectrum (202.460 MHz/$CDCl_3$/Appendix C15) shows the presence of two peaks at 27.45 ppm and 26.62 ppm probably corresponding to the two phosphorus environments in the dimer. There is also a series of smaller peaks probably corresponding to the higher molecular weight oligomers. The infrared spectrum of the polymer (Appendix D15) is consistent with the assigned structure with the most important diagnostic infrared bands being:- vinylic CH stretches at 3020 cm^{-1}, CH_2/CH_3 stretches at 2990 cm^{-1}, 2900 cm^{-1} and 2850 cm^{-1}, a C=C stretch at 1600 cm^{-1} and a P=O stretch at 1260 cm^{-1}. The ^1H NMR (399.952 MHz/$CDCl_3$/Appendix A15) and ^{13}C NMR spectra (100.577 MHz/$CDCl_3$/Appendix B15) are again complex and complete analyses could not be achieved.

3.8 Discussion of results obtained from ROMP of *exo,endo*-5,6-bis(dialkylphosphonate)-bicyclo[2.2.1]hept-2-enes.

Several reactions were performed to discover how yield and molecular weight varied with solvent composition and the results are tabulated below (*Table 3.11*). All sets of experiments were performed using the same batches of monomer, distilled water, ethanol and initiator in the same water bath and worked up and analysed in the same way. No colour changes were observed during the reaction and with the yields being very low no information concerning the rates of the ROMP reaction was obtained.

Solvent	Initiator	Me	Et
H_2O	$RuCl_3$	oligomers	oligomers
EtOH	$RuCl_3$	X	X
Ph-Cl	$RuCl_3$	X	X
H_2O/EtOH	$RuCl_3$	oligomers	oligomers
Ph-Cl/EtOH	$RuCl_3$	X	X
H_2O	$IrCl_3$	oligomers	oligomers
EtOH	$IrCl_3$	oligomers	oligomers
Ph-Cl	$IrCl_3$	X	X
H_2O/EtOH	$IrCl_3$	oligomers	oligomers
Ph-Cl/EtOH	$IrCl_3$	oligomers	X
H_2O	$OsCl_3$	X	X
EtOH	$OsCl_3$	X	X
Ph-Cl	$OsCl_3$	X	X
H_2O/EtOH	$OsCl_3$	X	X
Ph-Cl/EtOH	$OsCl_3$	X	X

Table 3.11: Results of ROMP attempts using exo,endo-5,6-bis(dialkylphosphonate)-bicyclo[2.2.1] hept-2-enes.

The results again indicate that $IrCl_3.3H_2O$ is a more effective initiator than $RuCl_3.3H_2O$ and $OsCl_3.3H_2O$ in organic solvents such as ethanol and chlorobenzene by initiating polymerisation of *exo,endo*-5,6-bis(dimethylphosphonate)bicyclo[2.2.1] hept-2-ene in these solvents. The low yields in each case can be explained by the presence of the large *endo* dialkylphosphonate groups on the monomers, which are close to the C=C double bond in the norbornene structure and, as we noted in the monosubstituted norbornene case, inhibit ROMP. These results are consistent with the earlier findings, as is the restricted polymerisation of the *exo,endo*-5,6-bis(diethyl phosphonate)bicyclo[2.2.1]hept-2-ene monomer.

Chapter Four.

Attempted Syntheses of Oligomers Using Chain Transfer Agents.

4.1 General Introduction.

The objective of the work described in this chapter was to prepare oligomers of (poly{2,5[3-dimethylphosphonate]cyclopentylene}vinylene) of varying molecular weight by aqueous Ring Opening Metathesis Polymerisation. The oligomers were formed by the cross metathesis of the chain propagating species with a series of acyclic olefins, known as chain transfer agents, a method that has been successful in reducing the molecular weight in previous studies.[86,177-182] The olefins used as potential chain transfer agents in this chapter are *cis*-but-2-ene-1,4-diol, dimethylvinylphosphonate and *trans*-ethene-1,2-bis(dimethylphosphonate).

4.2 Experimental.

4.2.1 Reactants and characterisation.

The transition metal chlorides $RuCl_3.3H_2O$ and $IrCl_3.3H_2O$ (Aldrich Chemical Co. Ltd.) and solvents (May and Baker / BDH, laboratory grade) were used as supplied unless otherwise stated. The preparations of monomers was described in chapter 2 and the polymerisations were carried out in distilled water or distilled ethanol.

The characterisation of the polymers was performed using the techniques and apparatus described in section 3.2.2.

4.3 Control of molecular weight using chain transfer agents.

4.3.1 Attempted synthesis of oligomers of (poly{2,5[3-dimethylphosphonate] cyclopentylene}vinylene) using *cis*-but-2-ene-1,4-diol as a potential chain transfer agent.

Dimethylbicyclo[2.2.1]hept-2-ene-5-phosphonate monomer(1g / 0.005 mol) was placed in a test tube, dissolved in a water/*cis*-but-2-ene-1,4-diol solvent mixture(6.5ml) and stirred for 30 minutes with a magnetic stirrer at 55±0.1°C. Transition metal chloride (70mg) was then added and the resulting solution was stirred for two days at 55±0.1°C. The resulting polymers (poly{2,5[3-dimethylphosphonate]cyclopentylene} vinylenes) were recovered as described previously, dissolved in ethanol and reprecipitated into water. The reactions were all carried out using the same batches of distilled water, monomer and transition metal chloride in the same water bath. The intended process is indicated in Figure 4.1. The results and graphs of the reciprocal of the number average molecular weight ($^{1}/_{M_n}$) against the ratio of the chain transfer agent concentration to the monomer concentration ($^{[CTA]}/_{[M]}$) are tabulated in Tables 4.1 and 4.2 and Figures 4.2-4.3 respectively.

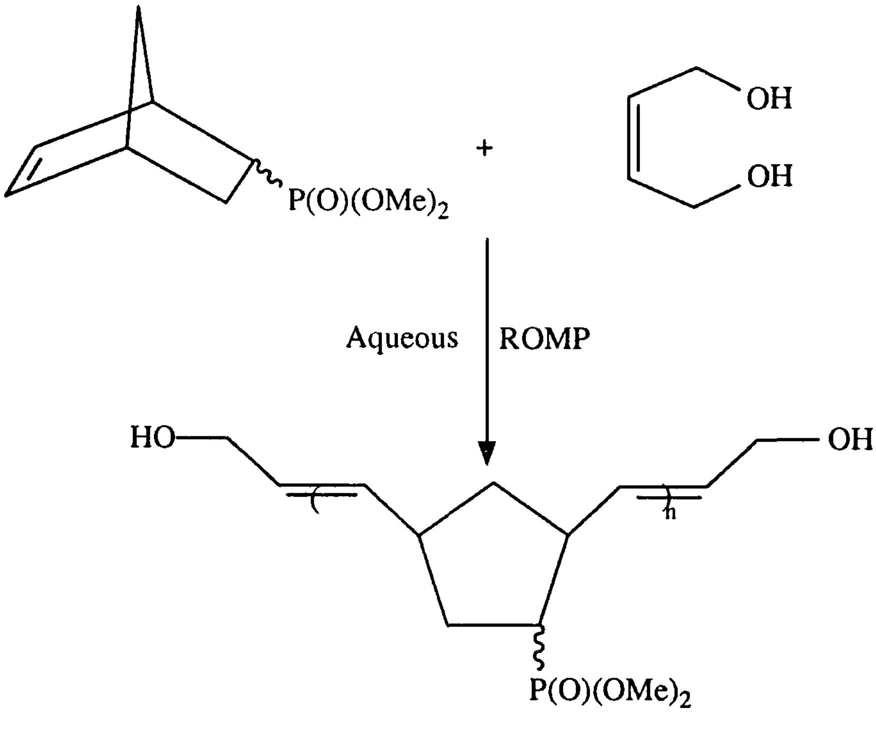


Figure 4.1: ROMP of dimethylbicyclo[2.2.1]hept-2-ene-5-phosphonate using cis-but-2-ene-1,4-diol as a potential chain transfer agent.

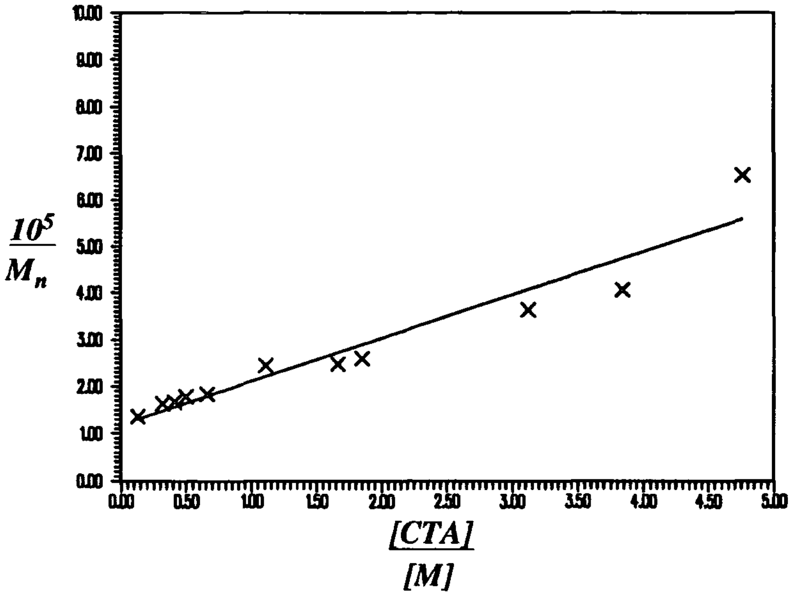


Figure 4.2: Graph of $^{1}/_{Mn}$ against $^{[CTA]}/_{[M]}$ the ROMP of dimethylbicyclo[2.2.1] hept-2-ene-5-phosphonate in water using $IrCl_3.3H_2O$ and cis-but-2-ene-1,4-diol as a potential chain transfer agent.

$\frac{[CTA]}{[M]}$	Mn	$\frac{10^5}{Mn}$	$\frac{Mw}{Mn}$	Yield
0.133	74000	1.36	2.19	71%
0.323	61000	1.63	2.62	55%
0.412	60000	1.67	2.08	57%
0.500	56000	1.78	3.39	43%
0.662	54000	1.84	2.98	40%
1.11	41000	2.44	4.79	21%
1.66	41000	2.48	2.33	12%
1.85	38000	2.60	1.53	10%
3.13	27000	3.64	2.90	5%
3.85	25000	4.06	2.59	6%
4.76	15000	6.53	2.10	2%

Table 4.1: ROMP of dimethylbicyclo[2.2.1]hept-2-ene-5-phosphonate in water using $IrCl_3.3H_2O$ and cis-but-2-ene-1,4-diol as a potential chain transfer agent.

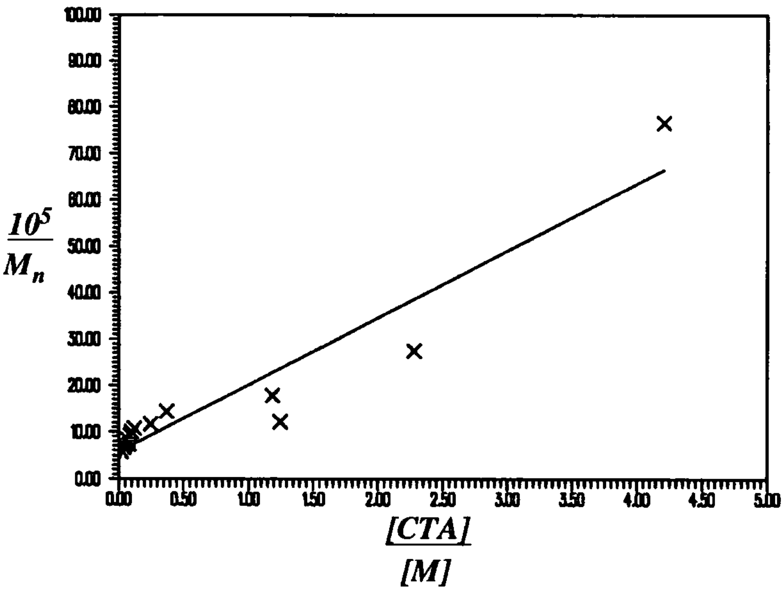


Figure 4.3: Graph of $^1/_{M_n}$ against $^{[CTA]}/_{[M]}$ for the ROMP of dimethylbicyclo[2.2.1] hept-2-ene-5-phosphonate in water using $RuCl_3.3H_2O$ and cis-but-2-ene-1,4-diol as a potential chain transfer agent.

$\frac{[CTA]}{[M]}$	Mn	$\frac{10^5}{Mn}$	$\frac{Mw}{Mn}$	Yield
0.020	17000	5.72	2.67	52%
0.041	15000	6.56	2.99	53%
0.050	14000	7.19	2.23	51%
0.070	12000	8.32	2.13	49%
0.082	14000	7.27	2.82	49%
0.089	11000	9.28	2.20	47%
0.100	10000	9.98	1.83	42%
0.123	9000	10.75	2.12	39%
0.249	9000	11.65	2.81	26%
0.373	7000	14.38	2.68	27%
1.19	6000	17.84	1.80	21%
1.25	8000	12.17	1.98	20%
2.28	4000	27.50	1.48	11%
4.21	1000	76.63	3.21	10%

Table 4.2: ROMP of dimethylbicyclo[2.2.1]hept-2-ene-5-phosphonate in water using $RuCl_3.3H_2O$ and cis-but-2-ene-1,4-diol as a potential chain transfer agent.

The ROMP of dimethylbicyclo[2.2.1]hept-2-ene-5-phosphonate using *cis*-but-2-ene-1,4-diol as a chain transfer agent was attempted with $IrCl_3.3H_2O$ and $RuCl_3.3H_2O$ in ethanol. Using $IrCl_3.3H_2O$ as the initiator a series of low molecular weight oligomers (dimers, trimers and tetramers) were produced in very low yields (<10%) if low concentrations of the chain transfer agent were used. No polymeric material was recovered in the case of the $RuCl_3.3H_2O$ initiator, even with very small concentrations of the acyclic olefin.

4.3.2 Discussion of results obtained using *cis*-but-2-ene-,1,4-diol as a potential chain transfer agent.

It can be seen from Tables 4.1 and 4.2 that similar sets of results were obtained for $IrCl_3.3H_2O$ and $RuCl_3.3H_2O$. GPC analysis shows that the molecular weight of the polymers and oligomers are related to the concentration of *cis*-but-2-ene-1,4-diol used in each ROMP reaction. However the yield of polymer is considerably affected by the presence of the diol and although it is possible to obtain low molecular weight oligomers with high concentrations of the diol, there is very poor recovery of these materials. This suggests that the metallocarbene formed from chain transfer of the diol with dimethylbicyclo[2.2.1]hept-2-ene-5-phosphonate is unable to initiate further metathesis. However it is more likely that the *cis*-but-2-ene-1,4-diol deactivates the metallocarbene and in high concentrations prevents the ROMP reaction occurring altogether. These results differ slightly from those of Harrison,[86] who reported that *cis*-but-2-ene-1,4-diol is an effective chain transfer agent in the presence of dicarboxylic acid- and dimethoxymethyl- substituted oxanorbornenes, but has no effect on the yield of polymer. Harrison also reported, on the basis of the observation of colour and physical state changes occurring during the reaction, that ROMP appeared to be faster in the presence of high concentrations of the diol. These observations were attributed to solvent effects causing changes in the polarity of the system. In the work carried out for this thesis, the ROMP of dimethylbicyclo[2.2.1]hept-2-ene-

5-phosphonate was not found to be accelerated by the use of *cis*-but-2-ene-1,4-diol.

It can be shown that the gradients of plots of reciprocal number average molecular weight ($^1/_{M_n}$) against the ratio of the chain transfer agent concentration to the monomer concentration ($^{[CTA]}/_{[M]}$) give the chain transfer constant (*Appendix H*).[184] This constant is defined as the ratio of the chain transfer rate constant to the propagation rate constant.[39] The plots for chain transfer using *cis*-but-2-ene-1,4-diol, shown in Figures 4.2 and 4.3, are reasonably straight lines and the chain transfer constants using $IrCl_3.3H_2O$ and $RuCl_3.3H_2O$ as initiators were calculated as $9.72x10^{-6}$ and $1.46x10^{-4}$ respectively. However these numerical values have little quantitative significance since the chain transfer agent has a considerable effect on the recovery of the polymer and there is an uncertainty concerning the M_n values, as fractionation may have occurred during the isolation of product. Although the results show that in the $RuCl_3.3H_2O$ system the diol appears to be a more effective chain transfer agent than in the $IrCl_3.3H_2O$ initiator system, it may be the case that slight changes in solvent composition contribute to the reduction of molecular weight (see section 3.4.3).

In the absence of the diol the $IrCl_3.3H_2O$/ ethanol initiator system gives a polymer with a molecular weight of approximately M_n= 40,000, but in the presence of small concentrations of the diol oligomers are found to be the only product. It appears that the chain transfer mechanism involving *cis*-but-2-ene-1,4-diol is more favourable in ethanol than in water with small amounts of the diol considerably affecting the results. This may be a result of the polymer being soluble in ethanol and not precipitating during the reaction as in the $IrCl_3.3H_2O$/ water situation.

The ROMP of dimethylbicyclo[2.2.1]hept-2-ene-5-phosphonate with $RuCl_3.3H_2O$ in ethanol, in the absence of a chain transfer agent, gives a poor yield of a low molecular weight polymer (M_n= 6500 - see section 3.4.3). The presence of *cis*-but-2-ene-1,4-diol results in only the monomer being recovered. This can be attributed to a combination of low yields of polymer being formed in $RuCl_3.3H_2O$/ ethanol systems, a very effective chain transfer reaction taking place and the diol deactivating the catalyst or monopolising activity through preferred degenerate exchange of the chain transfer agent.

4.3.3 Attempted synthesis of oligomers of (poly{2,5[3-dimethylphosphonate] cyclopentylene}vinylene) using dimethylvinylphosphonate as a potential chain transfer agent.

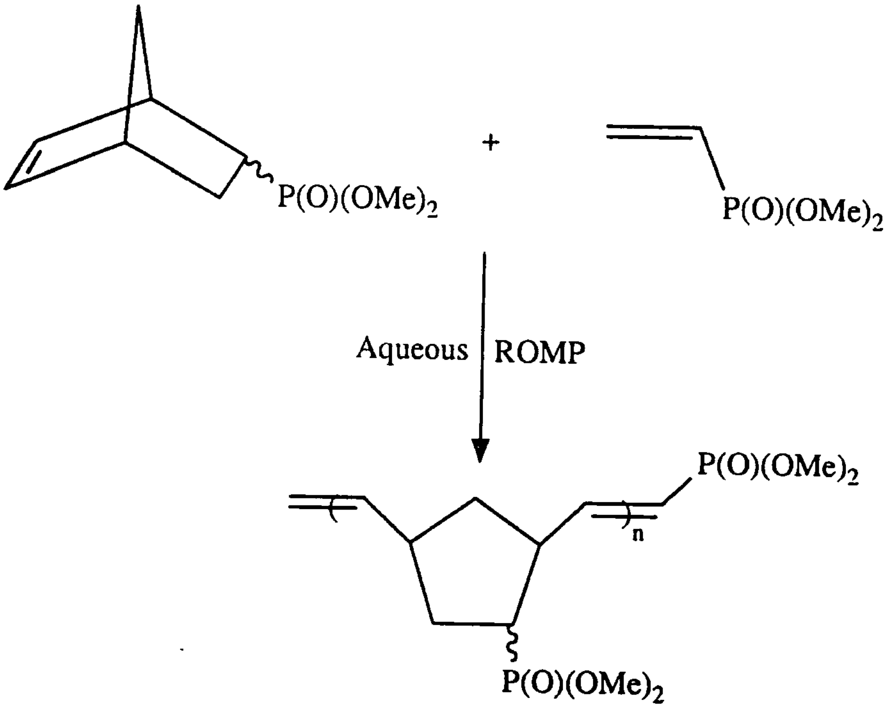


Figure 4.4: ROMP of dimethylbicyclo[2.2.1]hept-2-ene-5-phosphonate using dimethylvinylphosphonate as a potential chain transfer agent.

Dimethylbicyclo[2.2.1]hept-2-ene-5-phosphonate monomer(1g / 0.005 mol) was placed in a test tube, dissolved in a water/dimethylvinylphosphonate solvent mixture(6.5ml) and stirred for 30 minutes with a magnetic stirrer at 55±0.1°C. Transition metal chloride (70mg) was then added and the resulting solution was stirred for two days at 55±0.1°C. The resulting polymers (poly{2,5[3-dimethylphosphonate] cyclopentylene}vinylenes) were recovered as described previously, dissolved in ethanol and reprecipitated into water. The reactions were all carried out using the same batches of distilled water, monomer and transition metal chloride in the same water bath. The intended process is outlined in Figure 4.4 and the results and graphs of the reciprocal of the number average molecular weight ($^1/_{M_n}$) against the ratio of the chain transfer agent concentration to the monomer concentration ($^{[CTA]}/_{[M]}$) are tabulated in Tables 4.3-4.5 and Figures 4.5,4.7 and 4.8 respectively (see page 139 for the discussion).

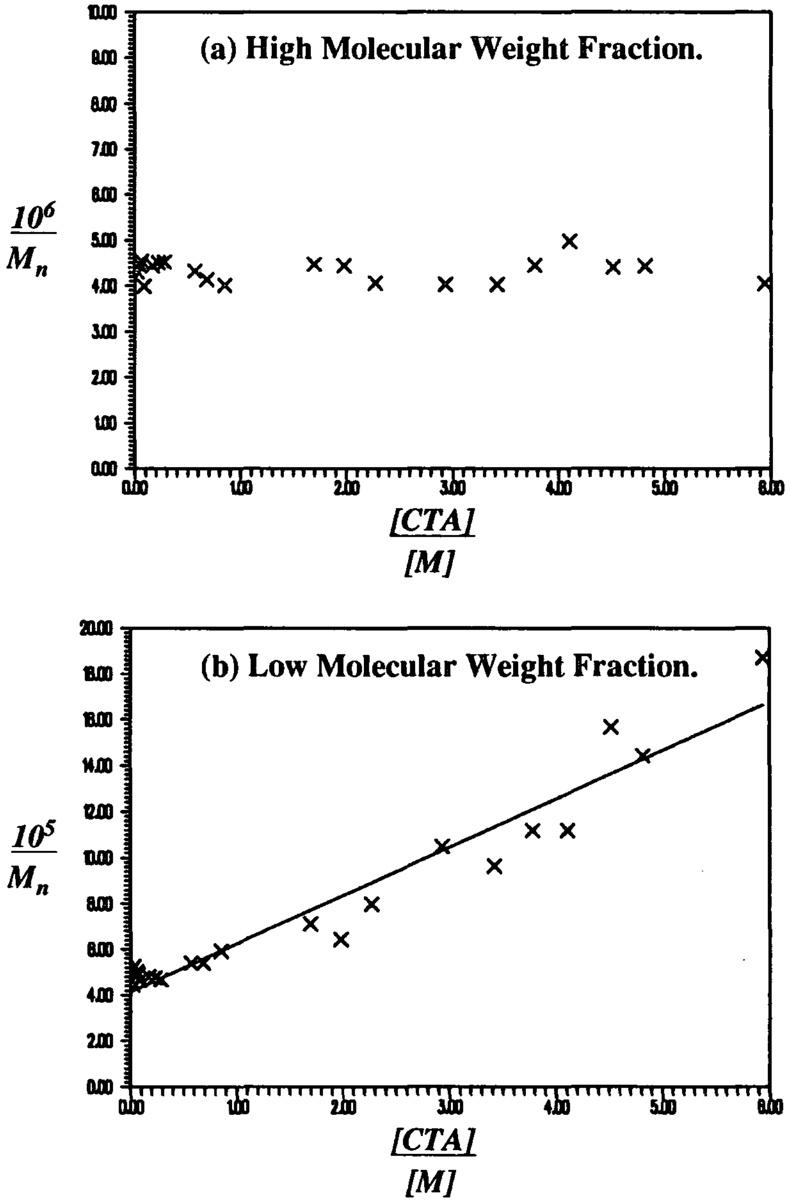


Figure 4.5: Graphs of $^1/_{M_n}$ against $^{[CTA]}/_{[M]}$ for the ROMP of dimethylbicyclo[2.2.1] hept-2-ene-5-phosphonate in water using $IrCl_3.3H_2O$ and dimethylvinylphosphonate as a potential chain transfer agent.

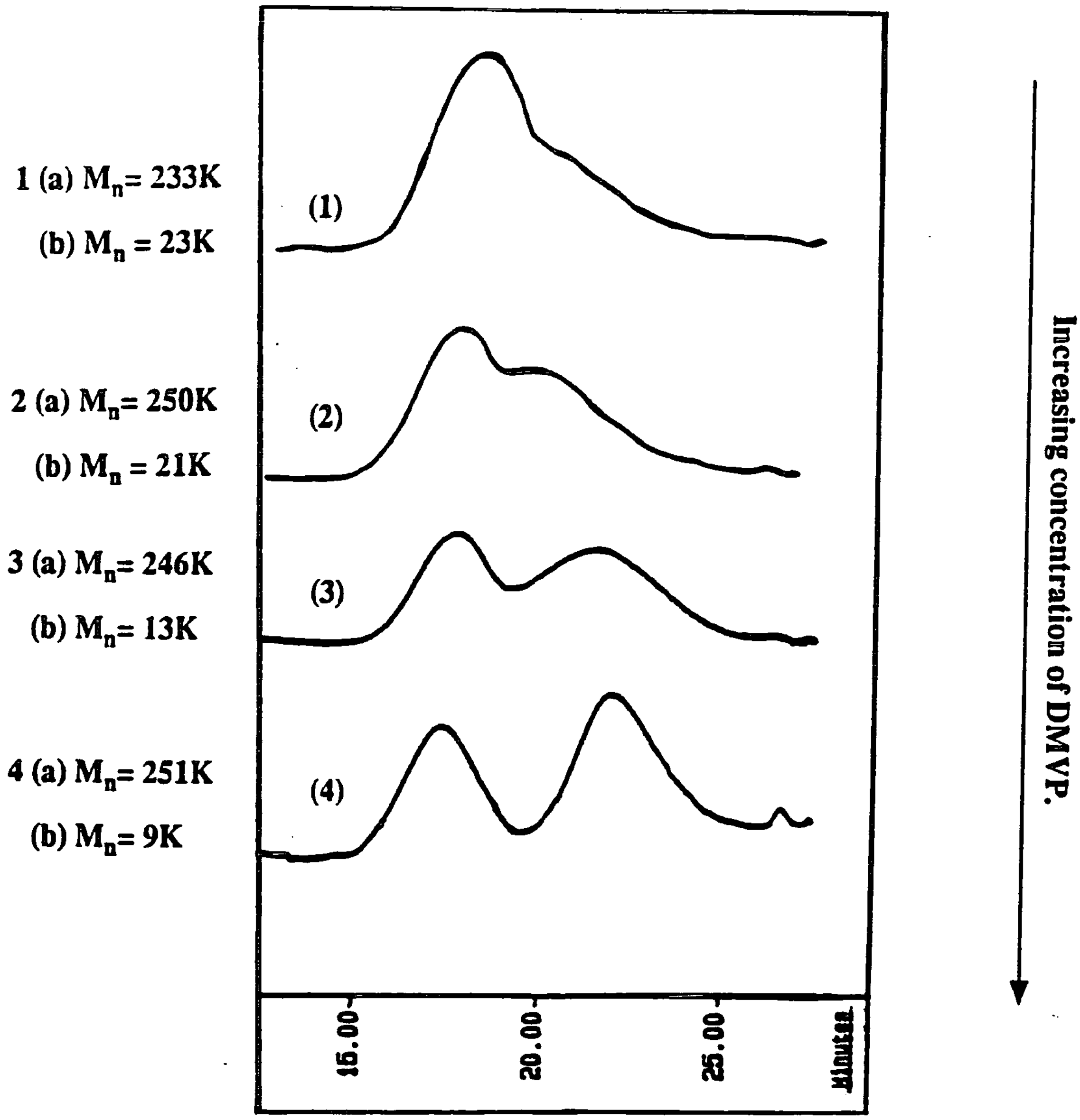


Figure 4.8: GPC chromatograms to show the two fractions formed from the ROMP of dimethylbicyclo[2.2.1]hept-2-ene-5-phosphonate in water using $IrCl_3.3H_2O$ and dimethylvinylphosphonate as a potential chain transfer agent.

In the following table:-

(a) and (b) correspond to the high molecular weight and low molecular weight fractions respectively.

$\frac{[CTA]}{[M]}$	(a)Mn	(a)$\frac{10^6}{Mn}$	(a)$\frac{Mw}{Mn}$	(b)Mn	(b)$\frac{10^5}{Mn}$	(b)$\frac{Mw}{Mn}$	Yield
0.017	233000	4.30	1.37	23000	4.45	1.87	57%
0.026	224000	4.47	1.75	19000	5.25	1.69	53%
0.057	225000	4.45	1.65	20000	5.03	1.37	48%
0.068	220000	4.54	1.62	20000	4.91	1.58	45%
0.085	250000	3.99	2.14	21000	4.66	1.88	39%
0.170	225000	4.44	1.73	21000	4.81	1.32	44%
0.226	222000	4.51	1.66	21000	4.76	1.33	41%
0.284	221000	4.52	2.13	21000	4.68	1.26	32%
0.566	231000	4.33	1.72	19000	5.40	1.22	22%
0.680	242000	4.14	1.79	19000	5.40	1.76	23%
0.850	249000	4.02	1.54	17000	5.93	1.50	20%
1.70	224000	4.47	1.89	14000	7.11	1.45	12%
1.98	225000	4.44	2.44	16000	6.43	1.36	14%
2.27	246000	4.06	1.56	13000	7.99	1.14	11%
2.93	248000	4.03	1.71	10000	10.48	1.26	8%
3.42	248000	4.03	1.64	10000	9.63	1.23	3%
3.78	224000	4.45	1.98	9000	11.18	1.36	6%
4.11	251000	4.98	1.55	9000	11.19	1.19	2%
4.52	227000	4.41	1.55	6000	15.67	1.27	1%
4.82	226000	4.43	1.94	7000	14.43	1.13	1%
5.94	247000	4.05	1.59	5000	18.70	1.21	1%

Table 4.3: ROMP of dimethylbicyclo[2.2.1]hept-2-ene-5-phosphonate in water using $IrCl_3.3H_2O$ and dimethylvinylphosphonate as a potential chain transfer agent.

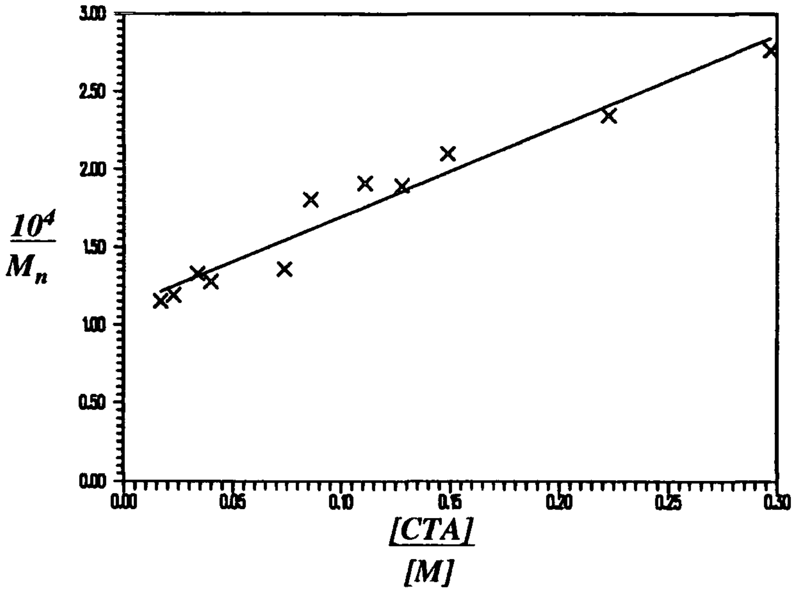


Figure 4.7: Graph of $^1/_{M_n}$ against $^{[CTA]}/_{[M]}$ for the ROMP of dimethylbicyclo[2.2.1] hept-2-ene-5-phosphonate in water using $RuCl_3.3H_2O$ and dimethylvinyl phosphonate as a potential chain transfer agent.

$\frac{[CTA]}{[M]}$	Mn	$\frac{10^4}{Mn}$	$\frac{Mw}{Mn}$	Yield
0.017	8700	1.15	2.19	19%
0.023	8400	1.19	2.21	17%
0.034	7500	1.33	2.13	17%
0.040	7800	1.28	2.42	16%
0.074	7400	1.36	1.36	12%
0.086	5500	1.81	1.98	10%
0.111	5200	1.91	1.88	5%
0.128	5300	1.89	1.92	9%
0.149	4800	2.10	1.93	8%
0.223	4300	2.35	1.71	4%
0.297	3600	2.76	2.02	1%

Table 4.4: ROMP of dimethylbicyclo[2.2.1]hept-2-ene-5-phosphonate in water using $RuCl_3.3H_2O$ and dimethylvinylphosphonate as a potential chain transfer agent.

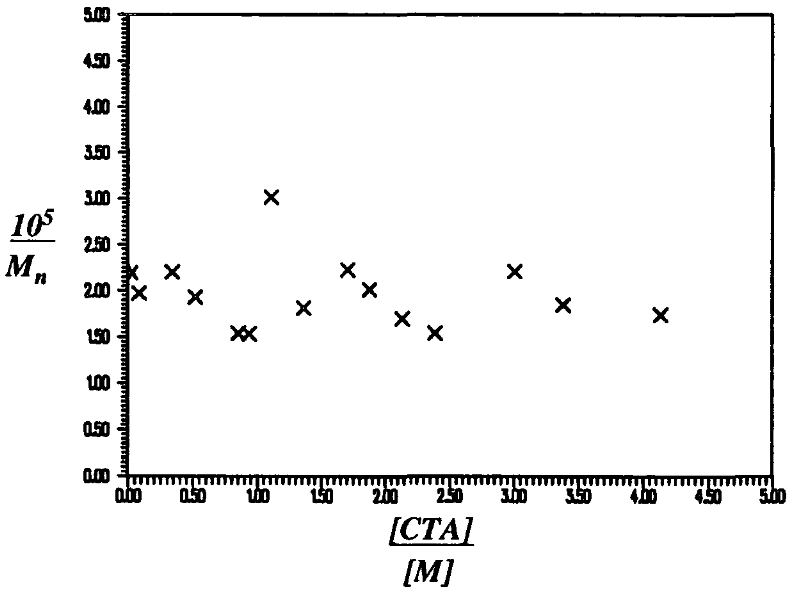


Figure 4.8: Graph of $^1/_{M_n}$ against $^{[CTA]}/_{[M]}$ for the ROMP of dimethylbicyclo[2.2.1]hept-2-ene-5-phosphonate in ethanol using $IrCl_3.3H_2O$ and dimethylvinyl phosphonate as a potential chain transfer agent.

$\frac{[CTA]}{[M]}$	Mn	$\frac{10^5}{Mn}$	$\frac{Mw}{Mn}$	Yield
0.017	46000	2.19	3.88	51%
0.086	51000	1.97	3.91	53%
0.343	45000	2.20	3.79	38%
0.523	52000	1.93	3.69	36%
0.854	65000	1.54	3.06	29%
0.940	65000	1.53	3.29	30%
1.11	33000	3.01	4.52	25%
1.37	55000	1.81	3.13	19%
1.71	45000	2.23	3.48	18%
1.88	50000	2.01	3.28	12%
2.14	59000	1.69	3.33	10%
2.39	65000	1.54	2.29	11%
3.01	45000	2.21	3.88	8%
3.39	54000	1.85	3.69	3%
4.14	58000	1.74	3.75	4%

Table 4.5: ROMP of dimethylbicyclo[2.2.1]hept-2-ene-5-phosphonate in ethanol using $IrCl_3.3H_2O$ and dimethylvinylphosphonate as a potential chain transfer agent.

4.3.4 Discussion of results obtained using dimethylvinylphosphonate as a potential chain transfer agent.

The use of dimethylvinylphosphonate (DMVP) as a potential chain transfer agent in an $IrCl_3.3H_2O$/ water initiator system results in two fractions being formed. GPC analysis reveals that the high molecular weight fraction is unaffected by the presence of dimethylvinylphosphonate (*Figure 4.8*). This fraction has a molecular weight approximately equal to that found using $IrCl_3.3H_2O$ in water in the absence of any chain transfer agent (section 3.4.3). The molecular weight of the second fraction is related to the concentration of dimethylvinylphosphonate used in the ROMP of dimethylbicyclo [2.2.1]hept-2-ene-5-phosphonate. The lowest molecular weight polymers being formed with the highest concentrations of dimethylvinylphosphonate. However the recovery of polymer is considerably affected by the olefin and again the metallocarbene is deactivated by the chain transfer agent, as in the case of *cis*-but-2-ene-1,4-diol. Using the $RuCl_3.3H_2O$/ water initiator system and dimethylvinylphosphonate as a potential chain transfer agent, only one fraction is produced, indicated by the presence of one peak on the GPC. The molecular weight of this fraction is again related to the concentration of the phosphonate, but again the yield is also affected as the olefin deactivates the metallocarbene.

These phenomena can be explained by two processes, the ROMP of dimethylbicyclo[2.2.1]hept-2-ene-5-phosphonate and the chain transfer reaction, competing with each other. In the case of the $IrCl_3.3H_2O$/ water/DMVP system the ROMP reaction is considerably more effective than the chain transfer process. This result could be rationalised on the assumption that the high molecular weight polymer is formed relatively rapidly at the beginning of the reaction, and this process is followed by a chain scission reaction occurring between the polymer and DMVP. Hence the high molecular weight polymer is cleaved to form the lower molecular weight fraction and the appearance of the two peaks on the GPC. Using $RuCl_3.3H_2O$/ water/DMVP, the ROMP reaction is less favourable (section 3.4.3) and the chain transfer process competes effectively from the start. As the polymer is formed, chain transfer occurs between the polymer and dimethylvinylphosphonate resulting in a reduction in the molecular weight of the polymer. As the concentration of the phosphonate is increased the chain transfer process is more effective, but unfortunately so is the deactivation of the catalyst, hence the decrease in yield. The result of this process is the formation of one fraction and the presence of one peak on the GPC.

The dimethylvinylphosphonate has no effect on the molecular weight of the polymer formed during the ROMP of dimethylbicyclo[2.2.1]hept-2-ene-5-phosphonate using $IrCl_3.3H_2O$ in ethanol, but again appears to deactivate the initiating species, hence affecting the polymeric yield. The use of DMVP produces polymers with a molecular weight ($M_n \approx 45,000$) comparable to that formed in the absence of a chain transfer system ($M_n \approx 40,000$). In this case the ROMP reaction is considerably more favourable in ethanol than in water (section 3.4.3) and the high molecular weight polymer is formed but the subsequent chain transfer reaction is not observed, as with water, before the DMVP deactivates the metallocarbene.

In the $RuCl_3.3H_2O$/ ethanol/ DMVP system the chain transfer reaction appears to be more favourable and the results are comparable to those found using *cis*-but-2-ene-1,4-diol as a chain transfer agent. In the absence of a chain transfer agent a low molecular weight polymer ($M_n = 6500$) is produced in low yield, but the use of dimethylvinylphosphonate results in only the monomer being recovered (section 3.4.3). This is a consequence of a combination of low yields of polymer being formed in $RuCl_3.3H_2O$/ ethanol systems, a very effective chain transfer reaction taking place and the DMVP deactivating the catalyst.

The chain transfer constants for the $IrCl_3.3H_2O$/ H_2O/ DMVP and $RuCl_3.3H_2O$/ H_2O/ DMVP systems were calculated as 2.11×10^{-5} and 6.01×10^{-4} respectively. These values again have little quantitative significance as the yield is affected by the chain transfer agent and fractionation may be occurring during recovery of the polymer.

As with the diol, the ROMP of dimethylbicyclo[2.2.1]hept-2-ene-5-phosphonate was not found to be accelerated by the use of DMVP, which contrasts with Harrison's results.[86]

4.3.5 Attempted synthesis of oligomers of (poly{2,5[3-dimethylphosphonate] cyclopentylene}vinylene) using *trans*-ethene-1,2-bis(dimethylphosphonate) as a potential chain transfer agent.

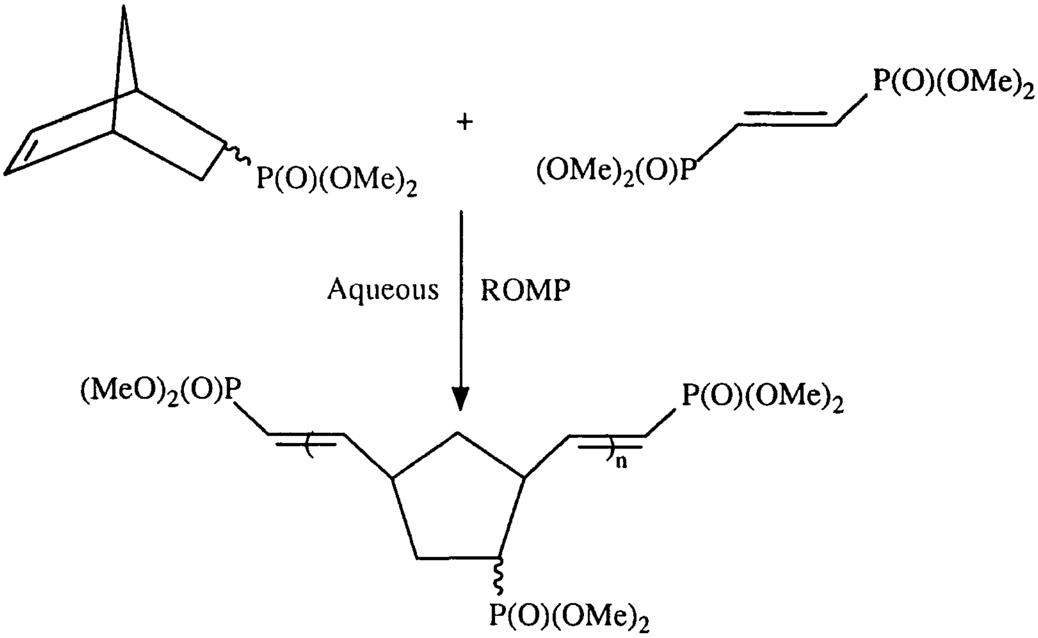


Figure 4.9: ROMP of dimethylbicyclo[2.2.1]hept-2-ene-5-phosphonate using trans-ethene-1,2-bis(dimethylphosphonate) as a potential chain transfer agent.

Dimethylbicyclo[2.2.1]hept-2-ene-5-phosphonate monomer(1g / 0.005 mol) was placed in a test tube, dissolved in a water / *trans*-ethene-1,2-bis(dimethylphosphonate) solvent mixture(6.5ml) and stirred for 30 minutes with a magnetic stirrer at 55±0.1°C. Transition metal chloride (70mg) was then added and the resulting solution was stirred for two days at 55±0.1°C. The resulting polymers (poly{2,5[3-dimethylphosphonate] cyclopentylene}vinylenes) were recovered as described previously, dissolved in ethanol and reprecipitated into water. The reactions were all carried out using the same batches of distilled water, monomer and transition metal chloride in the same water bath. The intended process is indicated in Figure 4.9. The results and graphs of the reciprocal of the number average molecular weight ($^1/_{Mn}$) against the ratio of the chain transfer agent concentration to the monomer concentration ($^{[CTA]}/_{[M]}$) are tabulated in Tables 4.6-4.8 and Figures 4.11-4.13 respectively.

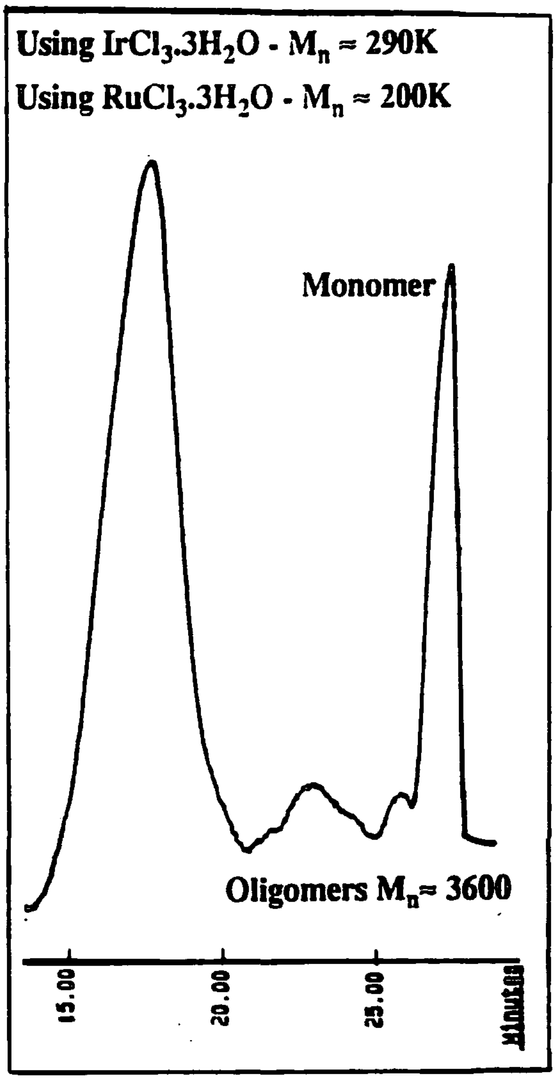


Figure 4.10: GPC chromatogram to show the high molecular weight fraction and the series of oligomers formed from the ROMP of dimethylbicyclo[2.2.1] hept-2-ene-5-phosphonate in water using $IrCl_3.3H_2O$ or $RuCl_3.3H_2O$ and dimethylvinylphosphonate as a potential chain transfer agent.

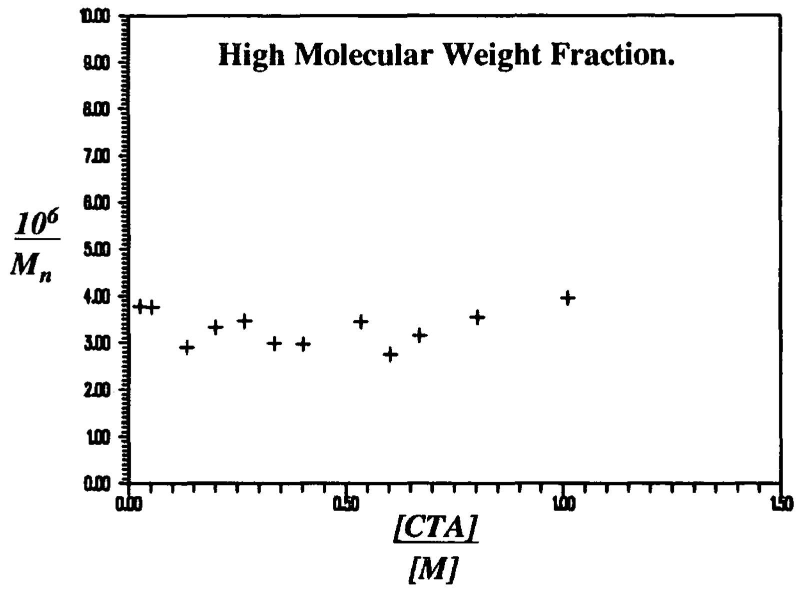


Figure 4.11: Graph of $^1/_{M_n}$ against $^{[CTA]}/_{[M]}$ for the ROMP of dimethylbicyclo[2.2.1] hept-2-ene-5-phosphonate in water using $IrCl_3.3H_2O$ and trans-ethene-1,2-bis(dimethylphosphonate) as a potential chain transfer agent.

$\frac{[CTA]}{[M]}$	Mn	$\frac{10^6}{Mn}$	$\frac{Mw}{Mn}$	Yield
0.027	265000	3.78	1.86	57%
0.054	266000	3.77	2.78	49%
0.134	344000	2.91	1.63	37%
0.201	300000	3.33	1.81	29%
0.268	289000	3.46	2.46	22%
0.335	335000	2.99	1.72	19%
0.402	338000	2.96	1.46	10%
0.536	290000	3.45	2.01	13%
0.603	362000	2.76	1.39	10%
0.670	317000	3.15	1.58	2%
0.804	282000	3.55	1.71	2%
1.01	253000	3.96	2.61	1%

Table 4.6: ROMP of dimethylbicyclo[2.2.1]hept-2-ene-5-phosphonate in water using $IrCl_3.3H_2O$ and trans-ethene-1,2-bis(dimethylphosphonate) as a potential chain transfer agent.

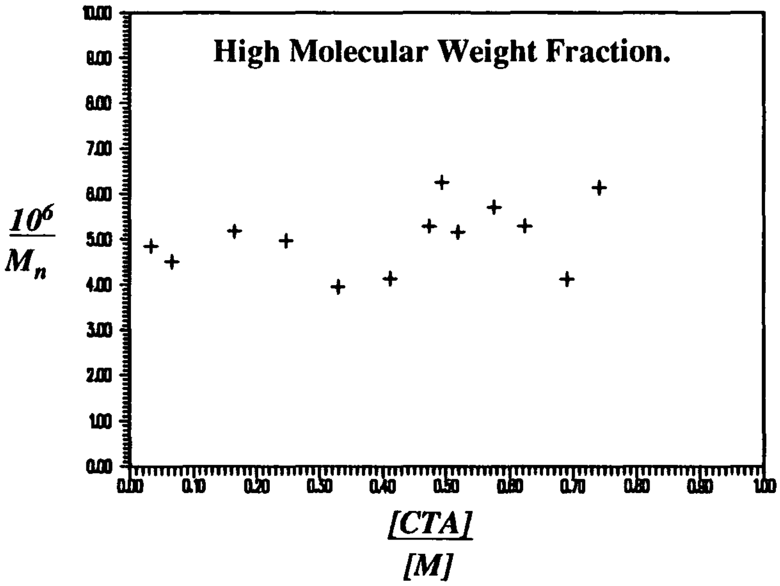


Figure 4.12: Graph of $^{1}/_{M_n}$ against $^{[CTA]}/_{[M]}$ for the ROMP of dimethylbicyclo[2.2.1] hept-2-ene-5-phosphonate in water using $RuCl_3.3H_2O$ and trans-ethene-1,2-bis(dimethylphosphonate) as a potential chain transfer agent.

$\frac{[CTA]}{[M]}$	Mn	$\frac{10^6}{Mn}$	$\frac{Mw}{Mn}$	Yield
0.033	206000	4.85	1.91	39%
0.066	222000	4.51	2.44	36%
0.165	193000	5.18	2.14	29%
0.247	201000	4.98	2.11	25%
0.330	253000	3.95	2.63	21%
0.412	242000	4.13	2.83	17%
0.473	189000	5.29	2.47	13%
0.494	160000	6.25	2.51	12%
0.519	194000	5.16	2.62	9%
0.576	175000	5.71	2.33	7%
0.623	189000	5.29	1.99	2%
0.691	243000	4.12	2.17	1%
0.742	163000	6.14	2.47	1%

Table 4.7: ROMP of dimethylbicyclo[2.2.1]hept-2-ene-5-phosphonate in water using $RuCl_3.3H_2O$ and trans-ethene-1,2-bis(dimethylphosphonate) as a potential chain transfer agent.

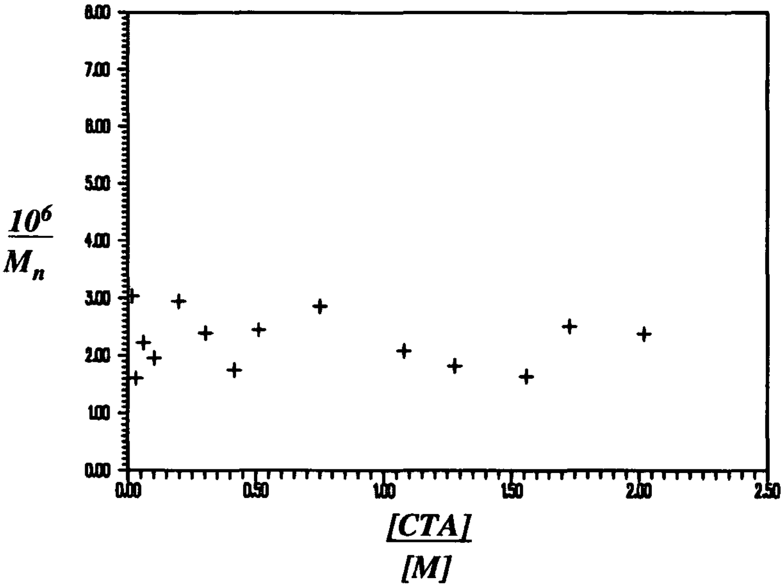


Figure 4.13: Graph of $^1/_{M_n}$ against $^{[CTA]}/_{[M]}$ for the ROMP of dimethylbicyclo[2.2.1] hept-2-ene-5-phosphonate in ethanol using $IrCl_3.3H_2O$ and trans-ethene-1,2-bis(dimethylphosphonate) as a potential chain transfer agent.

$\frac{[CTA]}{[M]}$	Mn	$\frac{10^5}{Mn}$	$\frac{Mw}{Mn}$	Yield
0.015	33000	3.03	3.67	59%
0.031	62000	1.61	3.58	53%
0.060	45000	2.22	3.91	49%
0.103	51000	1.95	3.87	31%
0.198	34000	2.95	3.71	28%
0.304	42000	2.39	3.86	21%
0.416	57000	1.75	3.91	23%
0.511	41000	2.44	3.68	21%
0.751	35000	2.86	4.02	15%
1.08	48000	2.08	3.89	12%
1.28	55000	1.82	3.63	11%
1.56	61000	1.64	3.65	9%
1.73	40000	2.50	3.99	2%
2.02	42000	2.38	4.11	1%

Table 4.8: ROMP of dimethylbicyclo[2.2.1]hept-2-ene-5-phosphonate in ethanol using $IrCl_3.3H_2O$ and trans-ethene-1,2-bis(dimethylphosphonate) as a potential chain transfer agent.

Similar sets of results to those obtained with *trans*-ethene-1,2-bis(dimethylphosphonate), as described above were obtained when *trans*-ethene-1,2-bis(diethylphosphonate) was used as a potential chain transfer agent. They add nothing to the account and are not discussed in this thesis.

4.3.6 Discussion of results obtained using *trans*-ethene-1,2-bis(dimethylphosphonate) as a potential chain transfer agent.

The use of *trans*-ethene-1,2-bis(dimethylphosphonate) as a potential chain transfer agent in the ROMP of dimethylbicyclo[2.2.1]hept-2-ene-5-phosphonate in water gave similar results for both the iridium and ruthenium initiator systems. In each case GPC analysis (*Figure 4.10*) revealed the presence of a high molecular weight fraction (*see Tables 4.6-4.7*) and a series of oligomers ($M_n \approx$ 3000). Intermediate molecular weights were not observed. This may be rationalised if the chain transfer process is more favourable than the ROMP reaction and the series of oligomers are formed at the beginning of the reaction. When the phosphonate transfer agent is consumed the monomer is polymerised to high dp with no interference from the oligomers. If this is the case, an increase in the intensity of the oligomer peaks and a decrease in the intensity of the main polymer peak would be expected with increasing amounts of chain transfer agent. Although GPC analysis indicated a slight increase in the intensity of the oligomer peaks with increasing transfer agent concentration, the effect is not convincingly demonstrated as high concentrations of the transfer agent, *trans*-ethene-1,2-bis(dimethylphosphonate), deactivates the initiating species and yields drop.

The use of *trans*-ethene-1,2-bis(dimethylphosphonate) in the ROMP of dimethylbicyclo[2.2.1]hept-2-ene-5-phosphonate using $IrCl_3.3H_2O$ in ethanol gives similar results to those found using dimethylvinylphosphonate as a potential chain transfer agent. There is no effect on the molecular weight of the polymer formed in the ROMP reaction but again the yield is affected, presumably as a result of the phosphonate deactivating the catalyst.

As a result of low yields of polymer being formed in $RuCl_3.3H_2O$/ ethanol systems, a very effective chain transfer reaction taking place and the chain transfer agent deactivating the initiating species, no polymer is recovered for the $RuCl_3.3H_2O$/ ethanol/ *trans*-ethene-1,2-bis(dimethylphosphonate) system.

These results are comparable to those found using *cis*-but-2-ene-1,4-diol (section 4.3.2) and dimethylvinylphosphonate (section 4.3.4) as potential chain transfer agents.

The ROMP of dimethylbicyclo[2.2.1]hept-2-ene-5-phosphonate does not appear to be accelerated by the use of *trans*-ethene-1,2-bis(dimethylphosphonate) in any of these systems.

4.4 Summary.

The work outlined in this chapter shows that low molecular weight polymers and oligomers of poly{2,5[3-dimethylphosphonate]cyclopentylene}vinylene can be prepared by the aqueous ROMP of dimethylbicyclo[2.2.1]hept-2-ene-5-phosphonate using *cis*-but-2-ene-1,4-diol or dimethylvinylphosphonate as chain transfer agents and $IrCl_3.3H_2O$ or $RuCl_3.3H_2O$ as the initiator. However in each case the yield of polymer/oligomer is severely affected by the chain transfer agents, which appear to deactivate the initiating species. Although *trans*-ethene-1,2-bis(dimethylphosphonate) also appears to act as a chain transfer agent in the aqueous ROMP of dimethylbicyclo[2.2.1]hept-2-ene-5-phosphonate, the low molecular weight oligomers that are formed can not be isolated. The work has also shown that low molecular weight polymers/oligomers can not be prepared using the chain transfer agents in ethanol. Therefore if high yields of low molecular weight polymers are required, a more effective chain transfer agent is needed, which does not deactivate the initiating species or monopolise the initiator activity through preferred degenerate exchange of the chain transfer agent.

Chapter Five.
Conclusions and Future Work.

5.1 Introduction.

The original aims of the work described in this thesis were:-

(a) to prepare a series of organophosphorus polymers by Ring Opening Metathesis Polymerisation (ROMP), which may be of potential interest in water treatment, fire retardancy and/or surface corrosion inhibition;

(b) to see how the ROMP process was affected by the use of different catalysts and changes in solvent composition;

(c) to investigate the possibility of preparing low molecular weight polymers/oligomers by ROMP using a series of chain transfer agents.

The work has shown that:-

(i) the monocyclic 1-hydroxy- and 1-alkoxy-1-oxo-phospholenes do not undergo ROMP with aqueous initiators ($RuCl_3.3H_2O$, $OsCl_3.3H_2O$, $IrCl_3.3H_2O$);

(ii) the monosubstituted organophosphorus derivatives of bicyclo[2.2.1] hept-2-ene undergo ROMP using $IrCl_3.3H_2O$ and $RuCl_3.3H_2O$ as precursors to the initiating species, whereas only low yields of oligomers are formed from the ROMP of disubstituted organophosphorus derivatives of norbornene using these initiator systems;

(iii) solvent composition and the type of initiator used both have a considerable effect on the yield and molecular weight of the polymer formed from the ROMP of the dialkylbicyclo[2.2.1]hept-2-ene-5-phosphonates;

(iv) low molecular weight polymers can be prepared by the aqueous ROMP of dialkylbicyclo[2.2.1]hept-2-ene-5-phosphonate using chain transfer agents, such as *cis*-but-2-ene-1,4-diol and dimethylvinylphosphonate, but the yield is affected by the presence of the chain transfer agents since they are believed to deactivate or monopolise the activity on the catalyst.

The proposals for future work, which are presented below, are put forward in the light of these findings.

5.2 Proposals for future work.

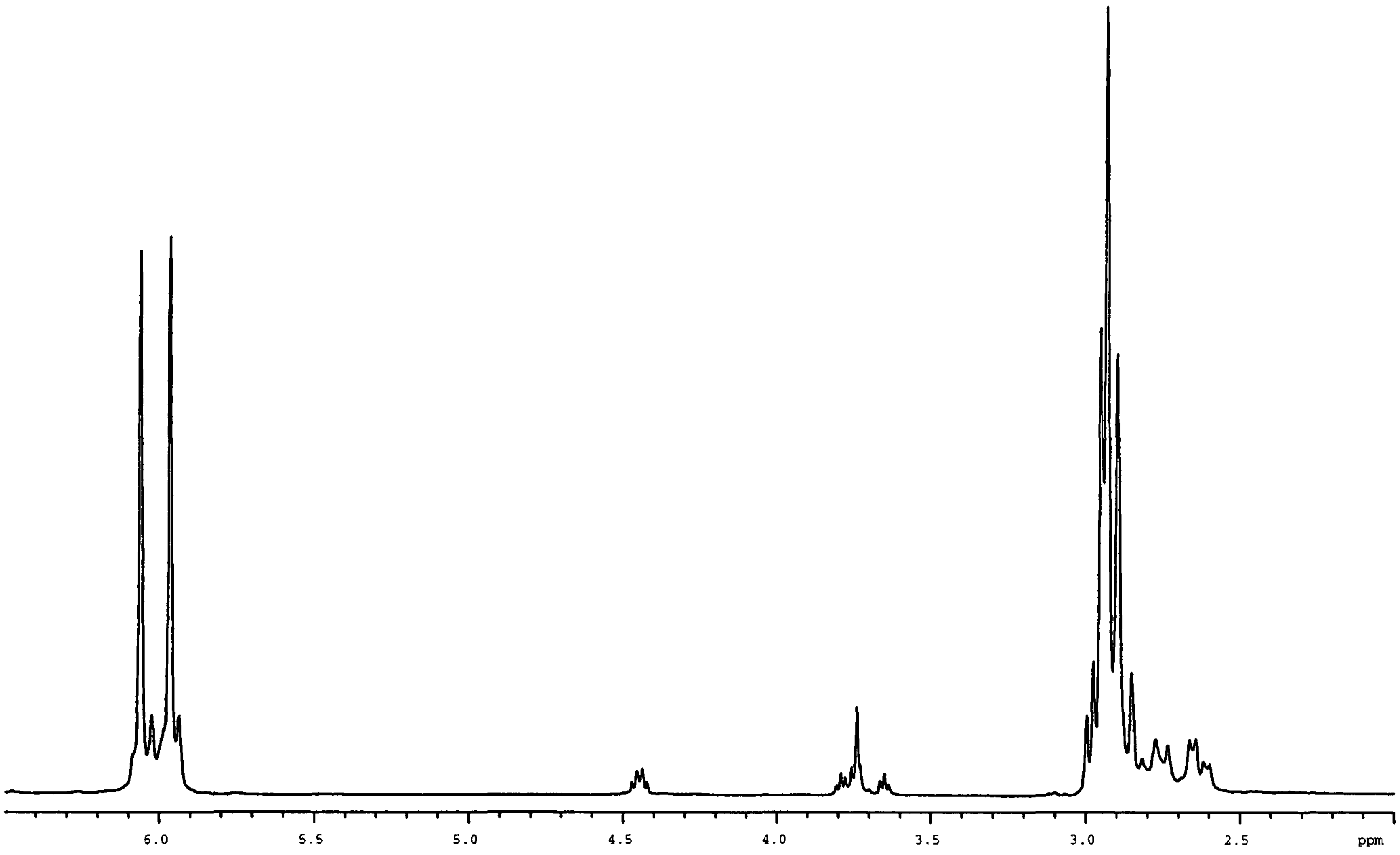
Some unexpected results have arisen during the course of this work, notably the molecular weight variation with ethanol concentration during the ROMP of the dialkylbicyclo[2.2.1]hept-2-ene-5-phosphonates in the water/ ethanol/ $IrCl_3.3H_2O$ and water/ ethanol/ $RuCl_3.3H_2O$ systems and the unusual chain transfer results obtained with *cis*-but-2-ene-1,4-diol, dimethylvinylphosphonate and *trans*-ethene-1,2-bis (dimethylphosphonate). These phenomena need to be investigated further. A kinetic investigation into the chain transfer reaction may reveal whether the theories proposed in chapter four are correct or not. This would also include a detailed study of the polymer product formed as the ROMP reaction proceeds. The problem of initiator deactivation by the chain transfer agents may be overcome by further studies of the chain transfer mechanism and finding an alternative more effective chain transfer agent.

One other problem arising from the work is that the poly{2,5-[3-dialkyl phosphonate]cyclopentylene}vinylene polymers are insoluble in water and obviously are no use in the water treatment. It may be possible to overcome this problem by increasing the water solubility by preparing random copolymers with a monomer that undergoes ROMP to yield a water soluble polymer, such as dicarboxylic acid-, dimethoxymethyl- and dihydroxymethyl- substituted oxanorbornenes. It may also be possible to synthesise block copolymers of the two monomers by using a well-defined initiator which can tolerate the presence of moisture. One example of an initiator, which may possibly be of value in such work is Grubbs' ruthenium metallocarbene (see section 1.6.2).

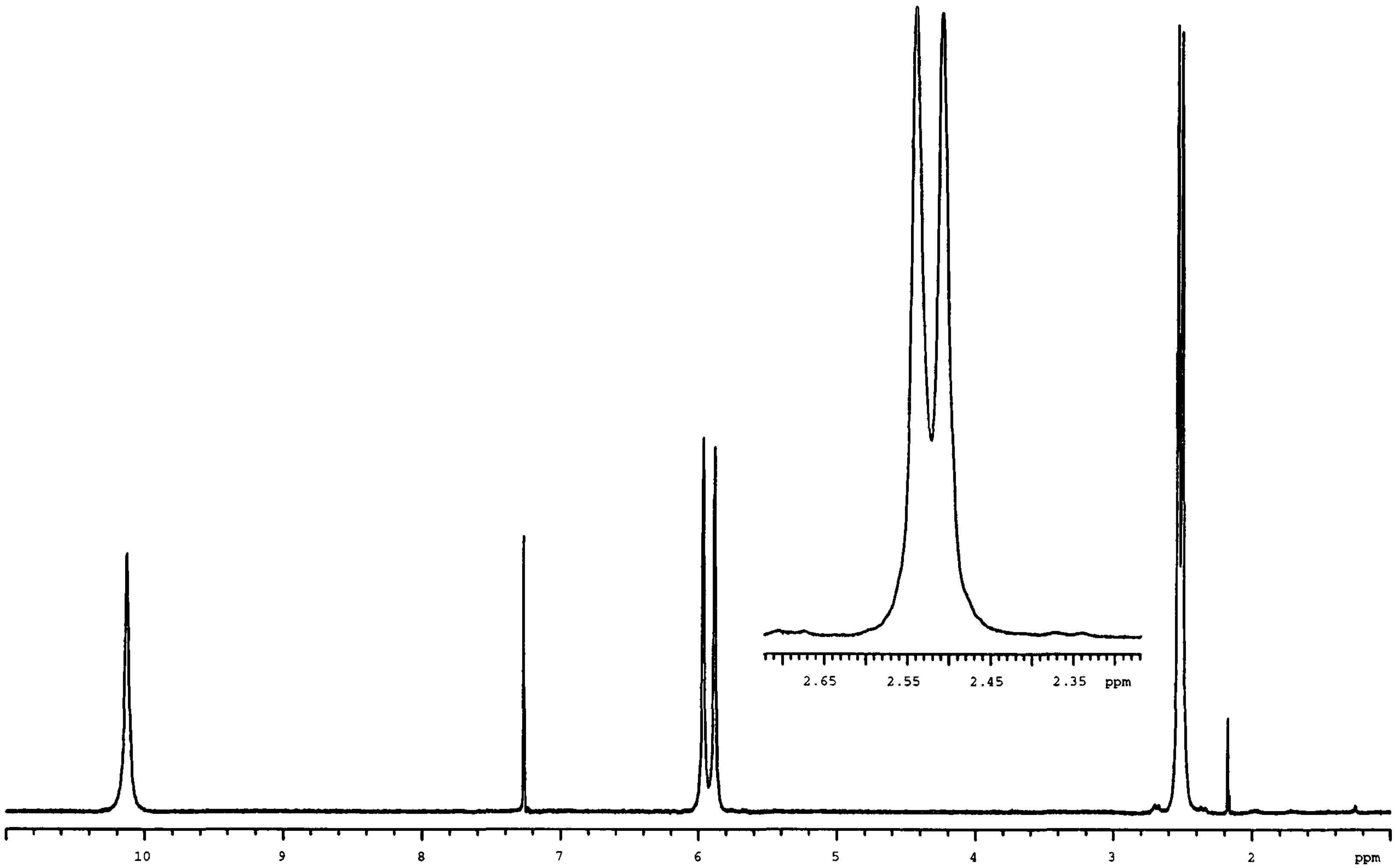
The fire retardancy of the polymers may be enhanced by increasing the amount of phosphorus in the polymers or by incorporating the phosphorus atom in the main polymer chain, as opposed to having pendant groups such as phosphonate groups. Design synthesis and polymerisation of other phosphorus containing monomers therefore merits further thought.

The exact nature of the initiating and propagating species formed from the aqueous initiators, $RuCl_3.3H_2O$, $OsCl_3.3H_2O$ and $IrCl_3.3H_2O$, were not investigated and further studies, designed to illuminate the nature of the chain carrying species might be useful and help to clarify the reaction mechanism taking place. Part of the problem for work in this area is defining what species are present in the ill-defined systems currently used in aqueous ROMP. The advances made in ROMP following the introduction of well-defined and single metal centre initiators may indicate that the primary objective for aqueous ROMP should be the design and synthesis of well-defined initiators capable of working in water.

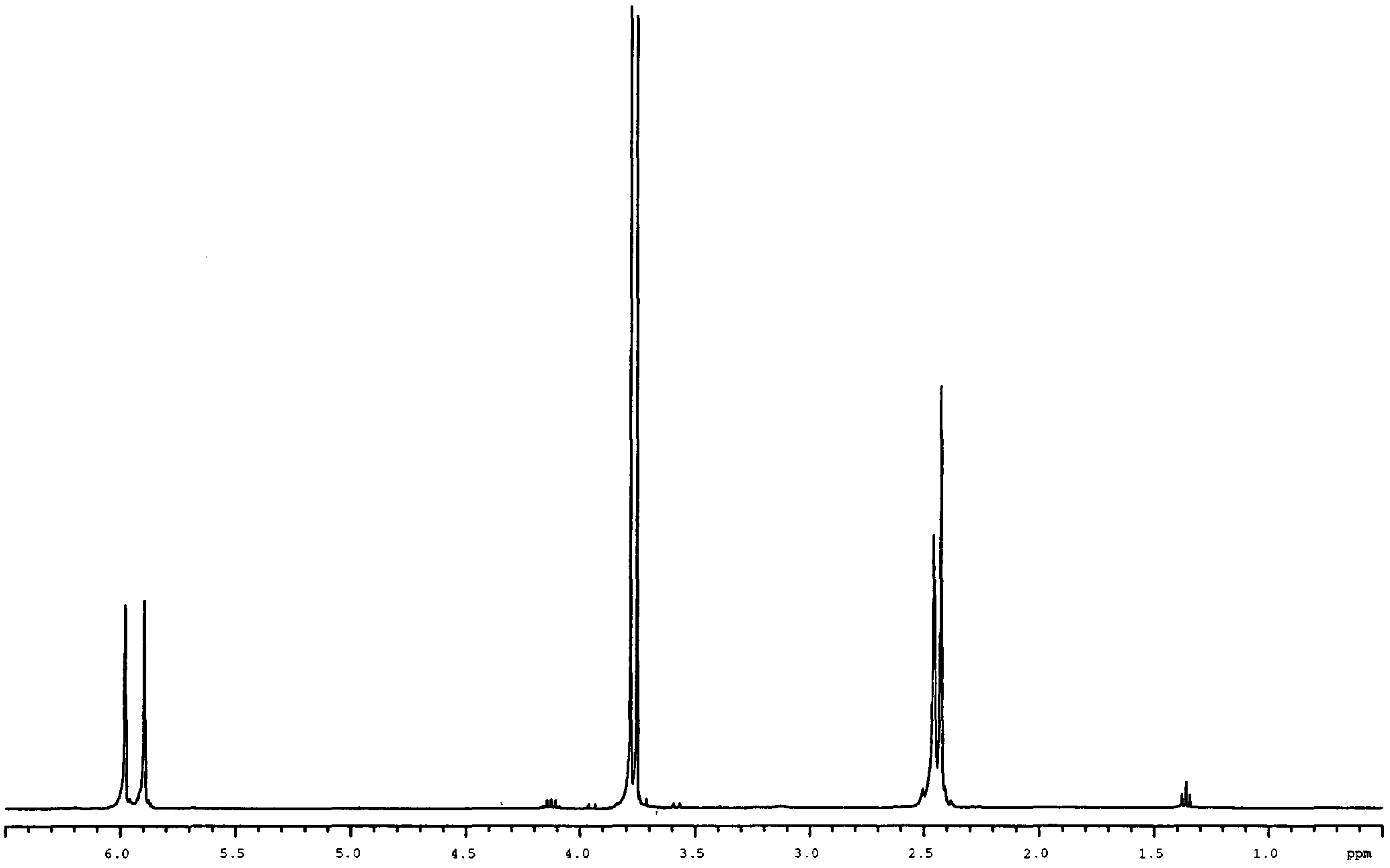
Appendix A:
^1H NMR Spectra.



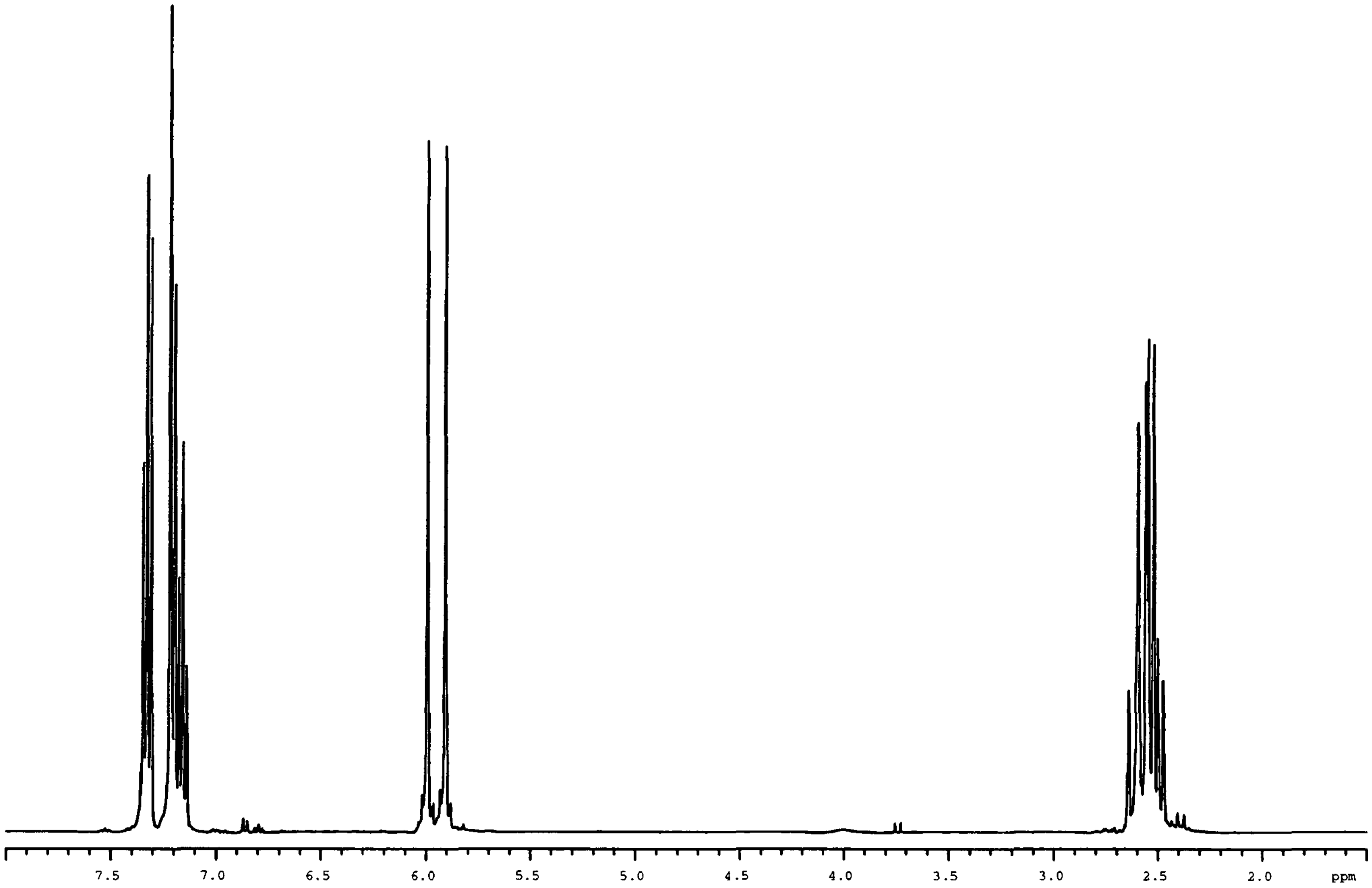
Appendix A1: ^{1}H NMR Spectrum (399.952MHz) of1-Chloro-1-oxo-3-phospholene.



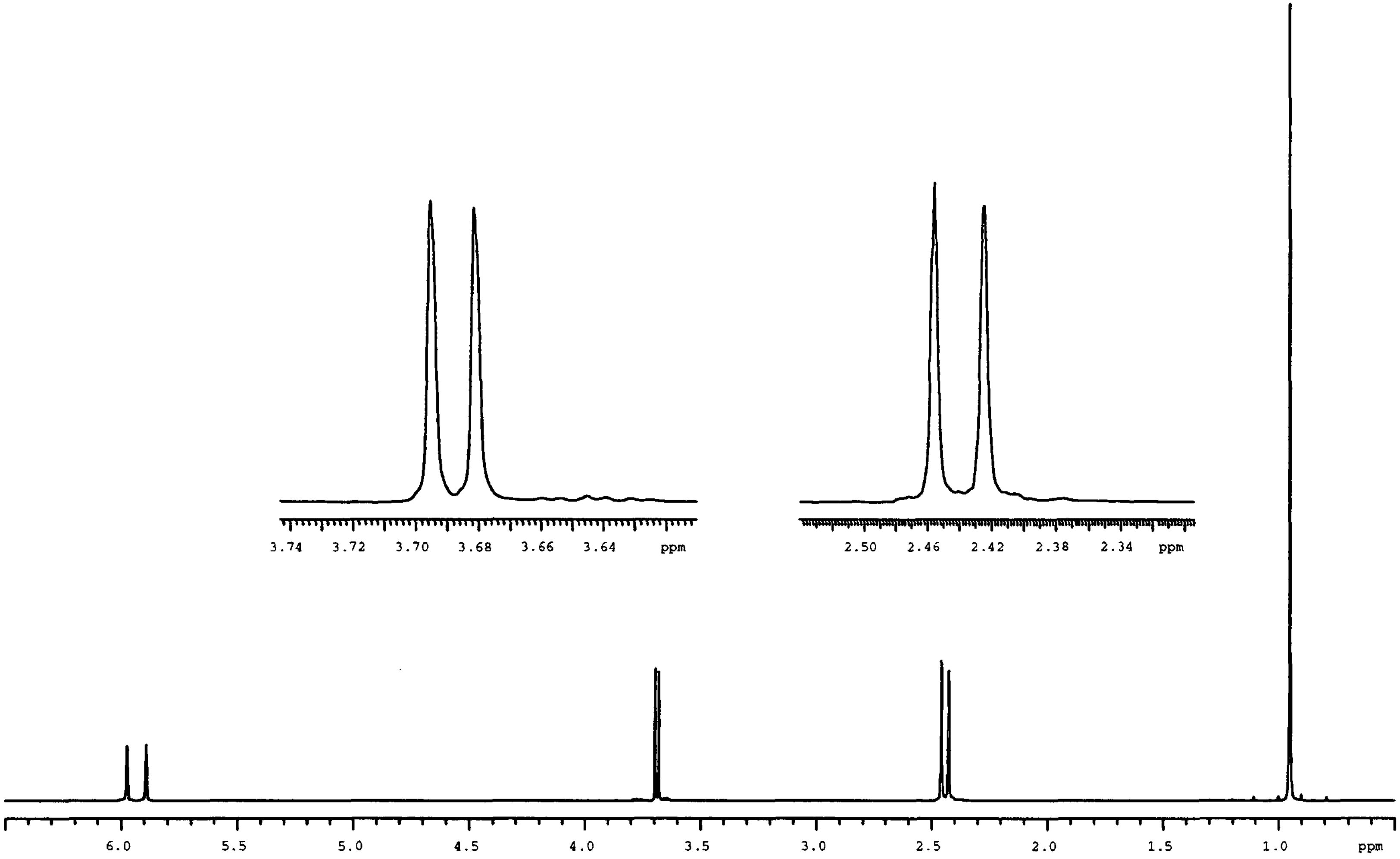
Appendix A2: ^1H NMR Spectrum (399.952 MHz) of 1-Hydroxy-1-oxo-3-phospholene.



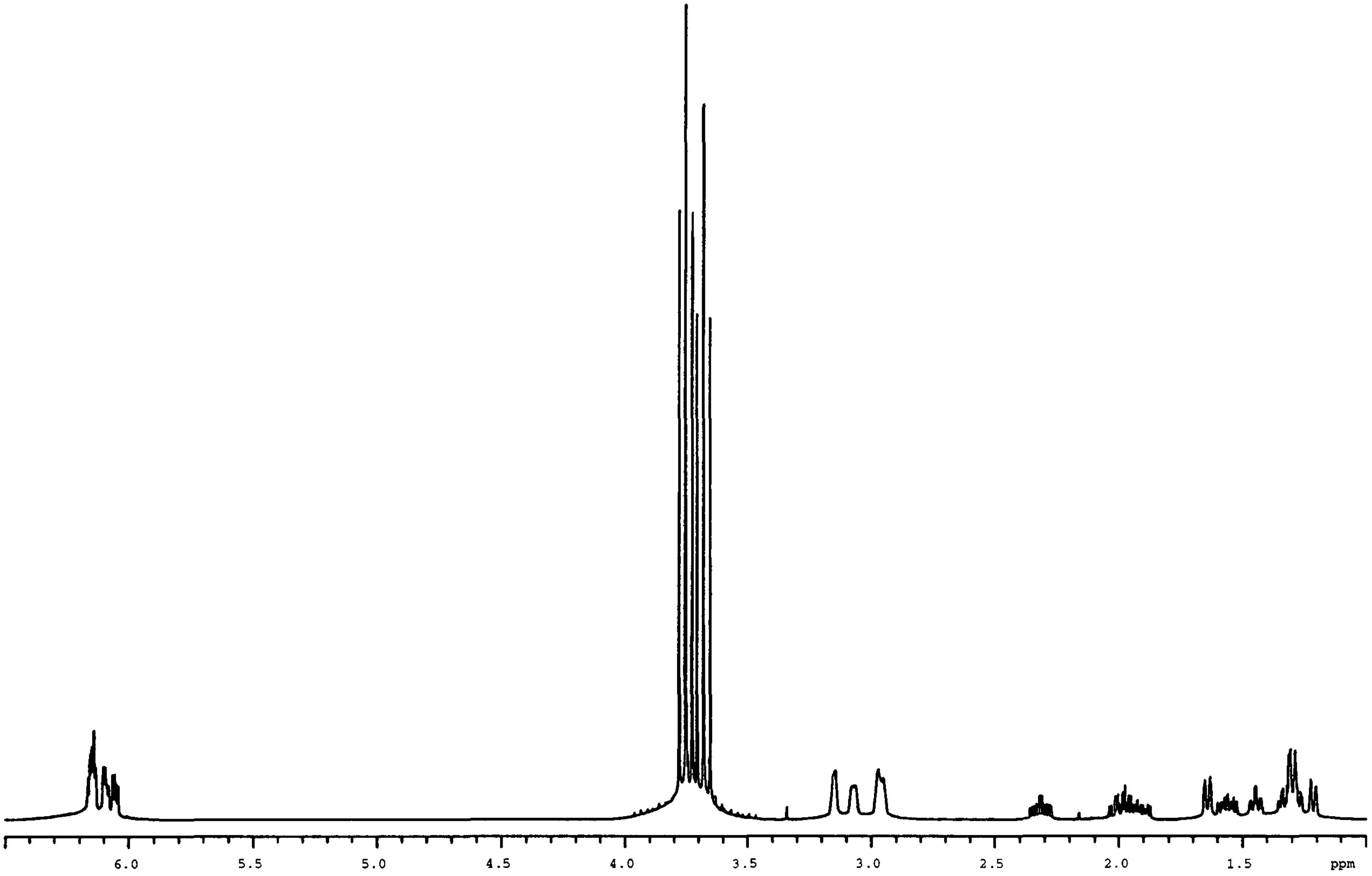
Appendix A3: ^{1}H NMR Spectrum (399.952 MHz) of 1-Methoxy-1-oxo-3-phospholene.



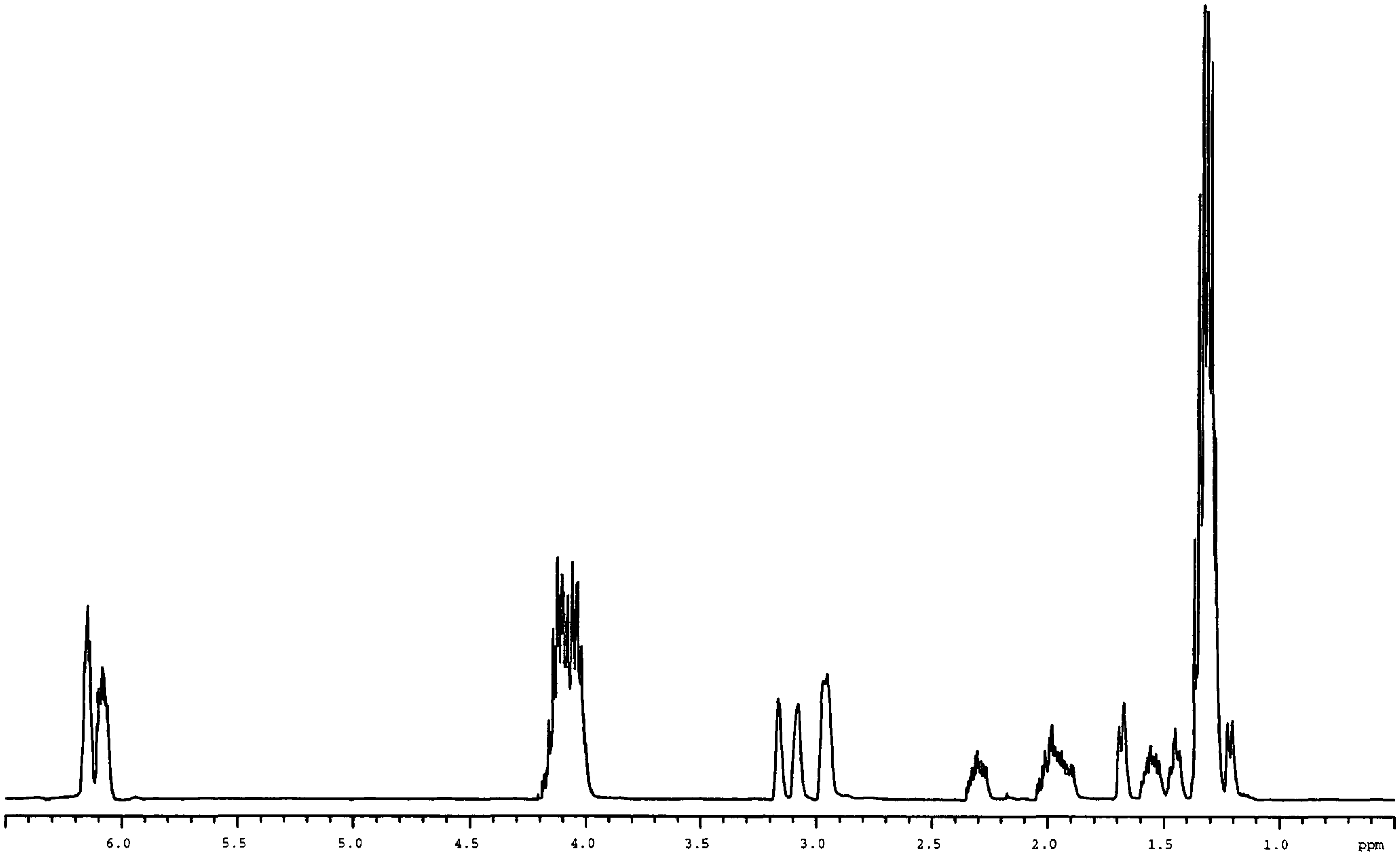
Appendix A4: ^1H NMR Spectrum (399.952 MHz) of 1-Phenoxy-1-oxo-3-phospholene.



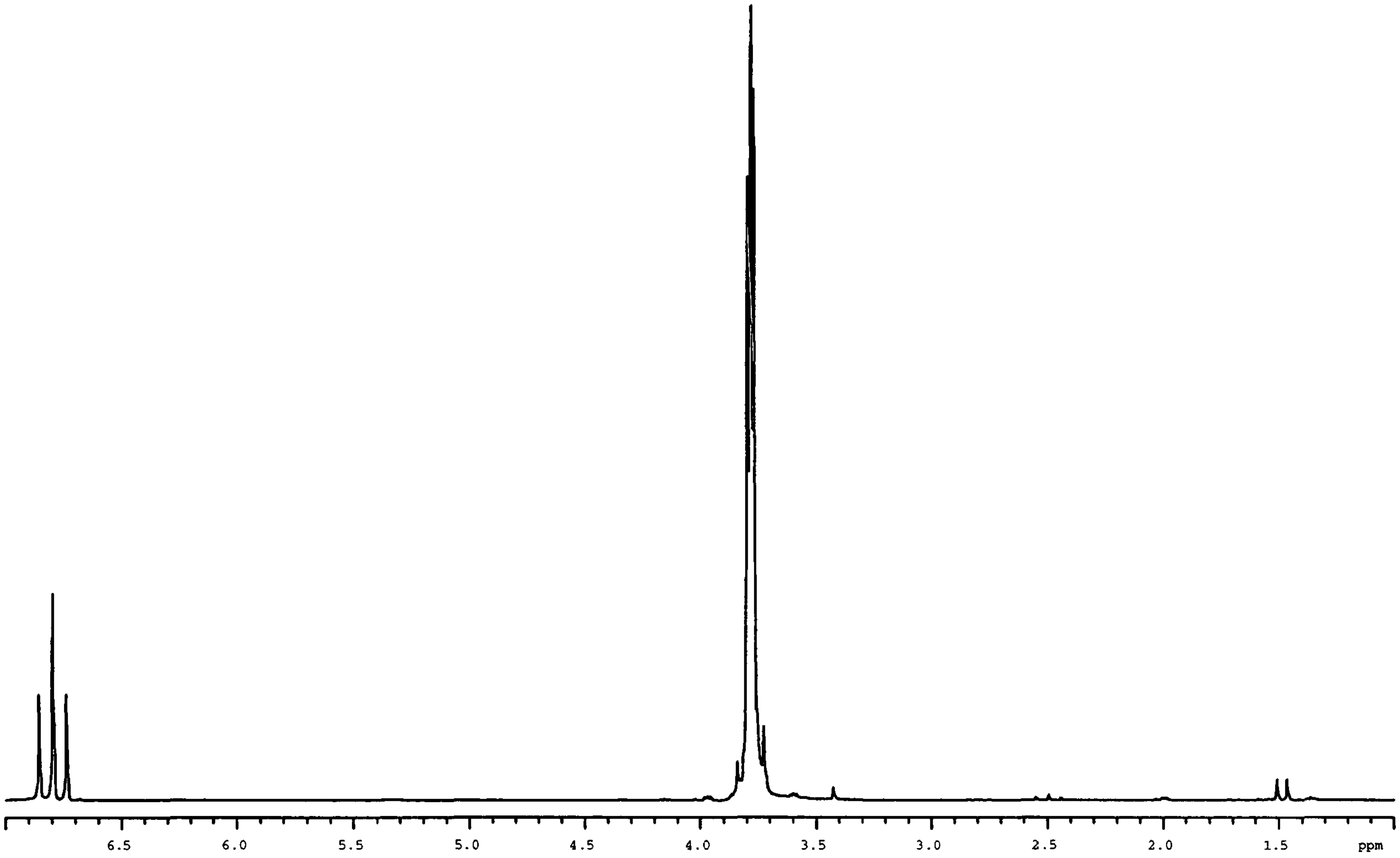
Appendix A5: ^{1}H NMR Spectrum (399.952 MHz) of 1-Neopentoxy-1-oxo-3-phospholene.



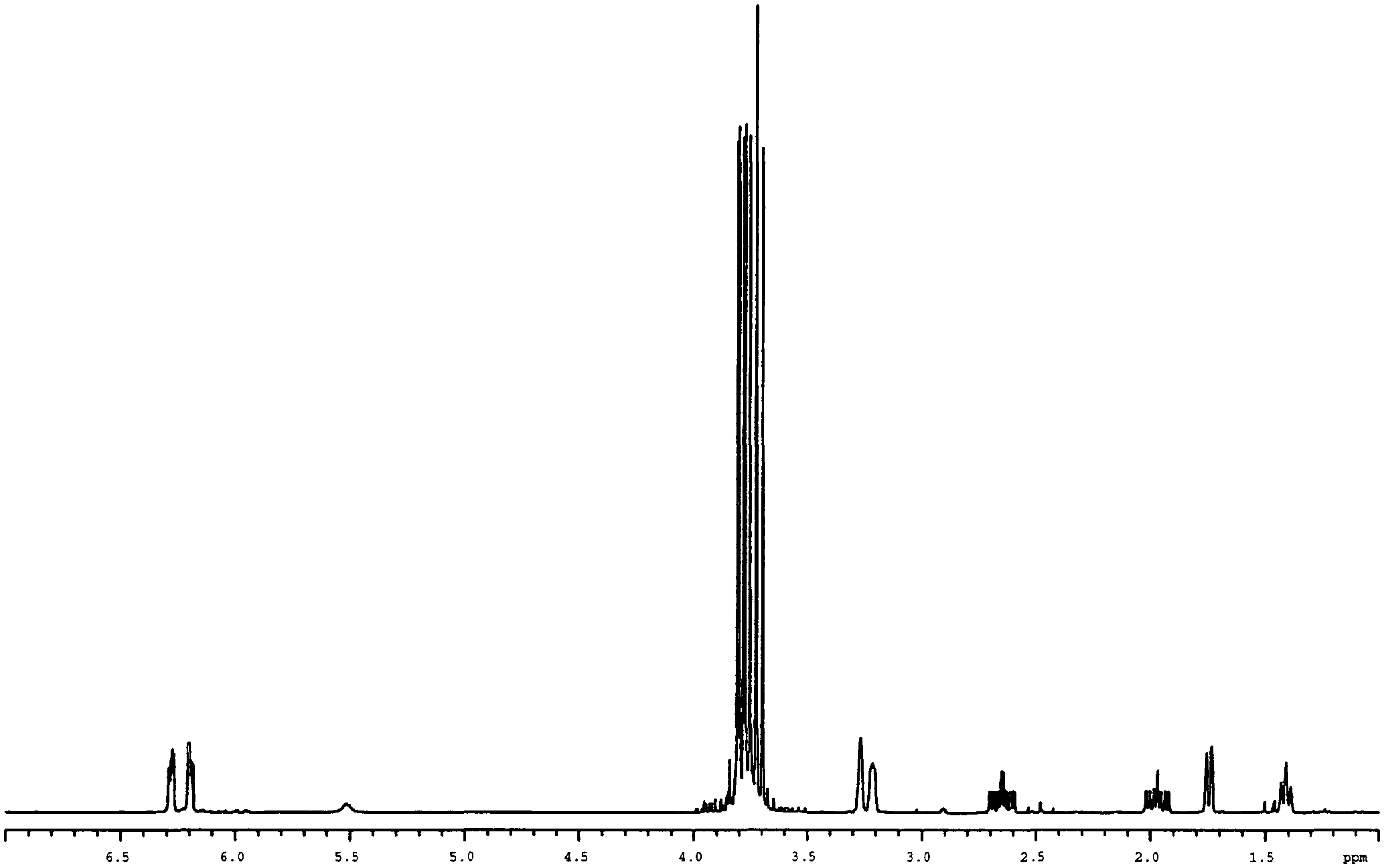
Appendix A6: ^1H NMR Spectrum (399.952 MHz) of Dimethylbicyclo[2.2.1]hept-2-ene-5-phosphonate.



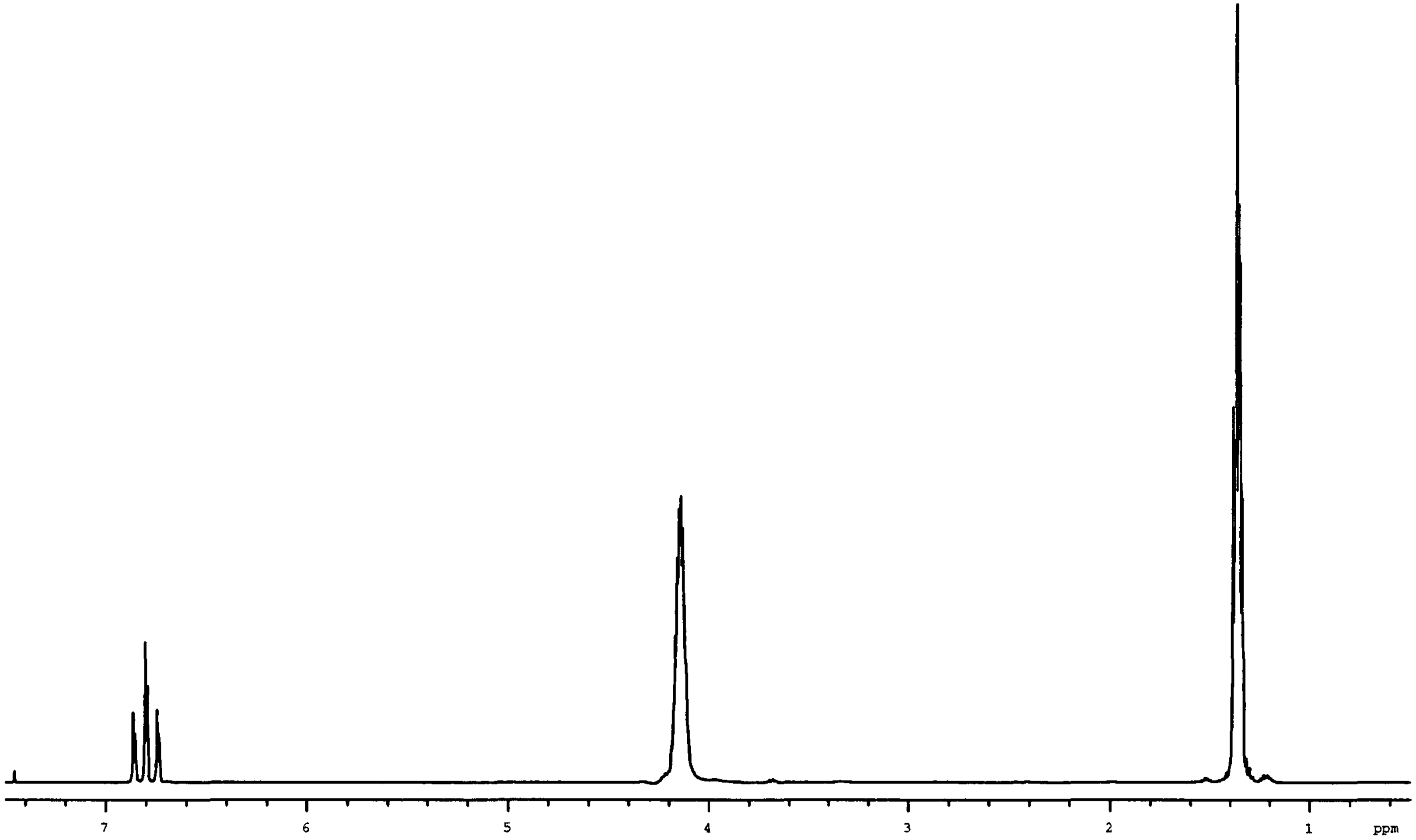
Appendix A7: ^{1}H NMR Spectrum (399.952 Mhz) of Diethylbicyclo[2.2.1]hept-2-ene-5-phosphonate.



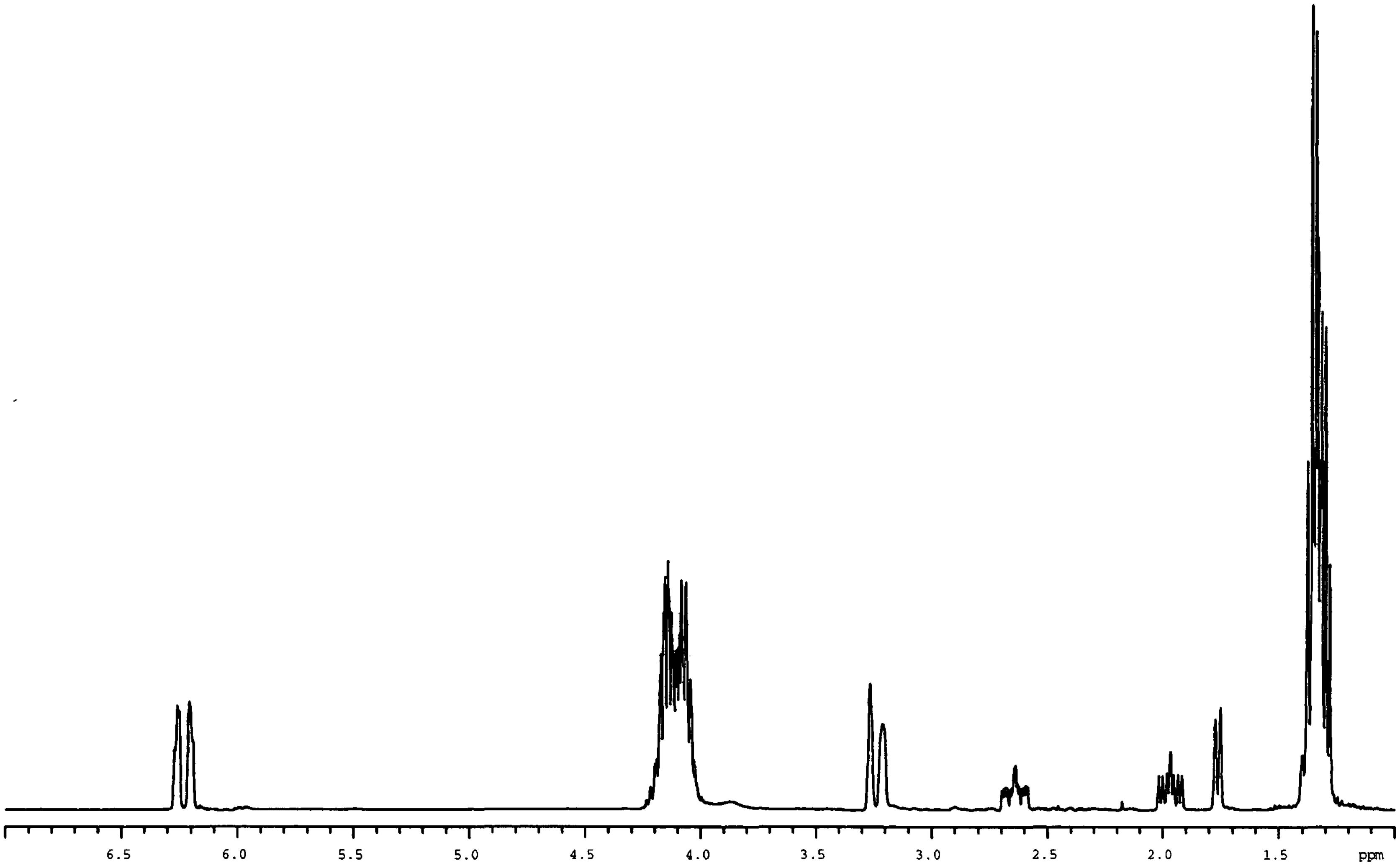
Appendix A8: ^{1}***H NMR Spectrum (399.952 MHz) of trans-Ethene-1,2-bis(dimethylphosphonate).***



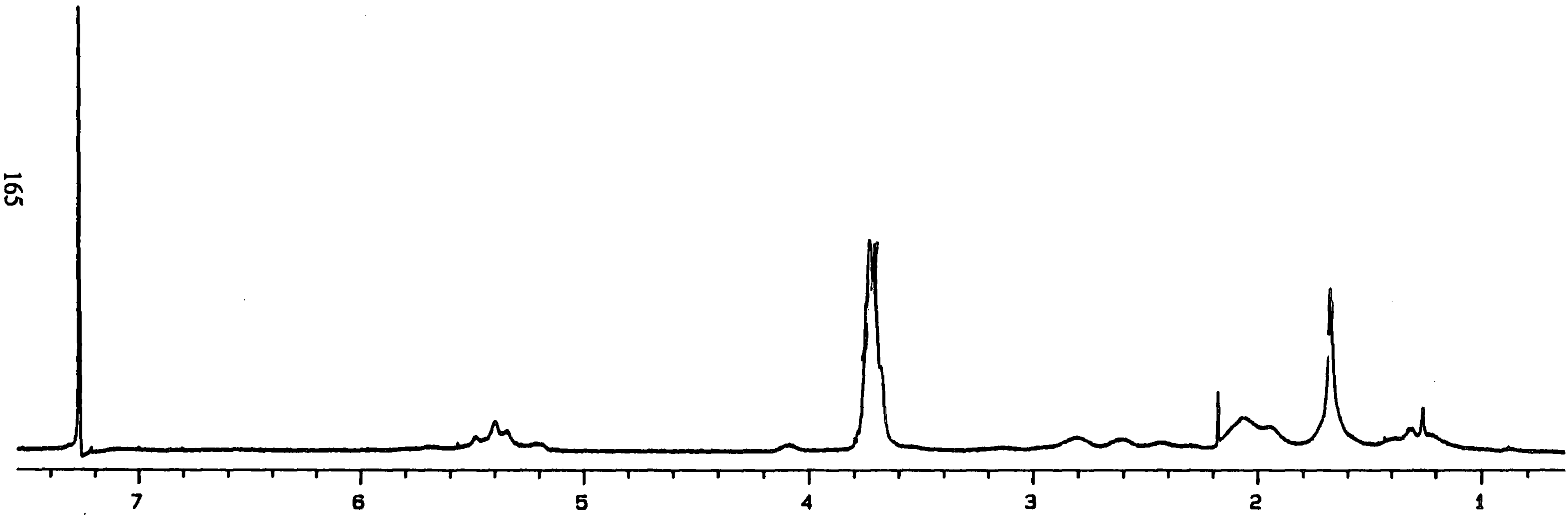
Appendix A9: ^{1}H NMR Spectrum (399.952 MHz) of exo,endo-5,6-bis(dimethylphosphonate)bicyclo[2.2.1]hept-2-ene.



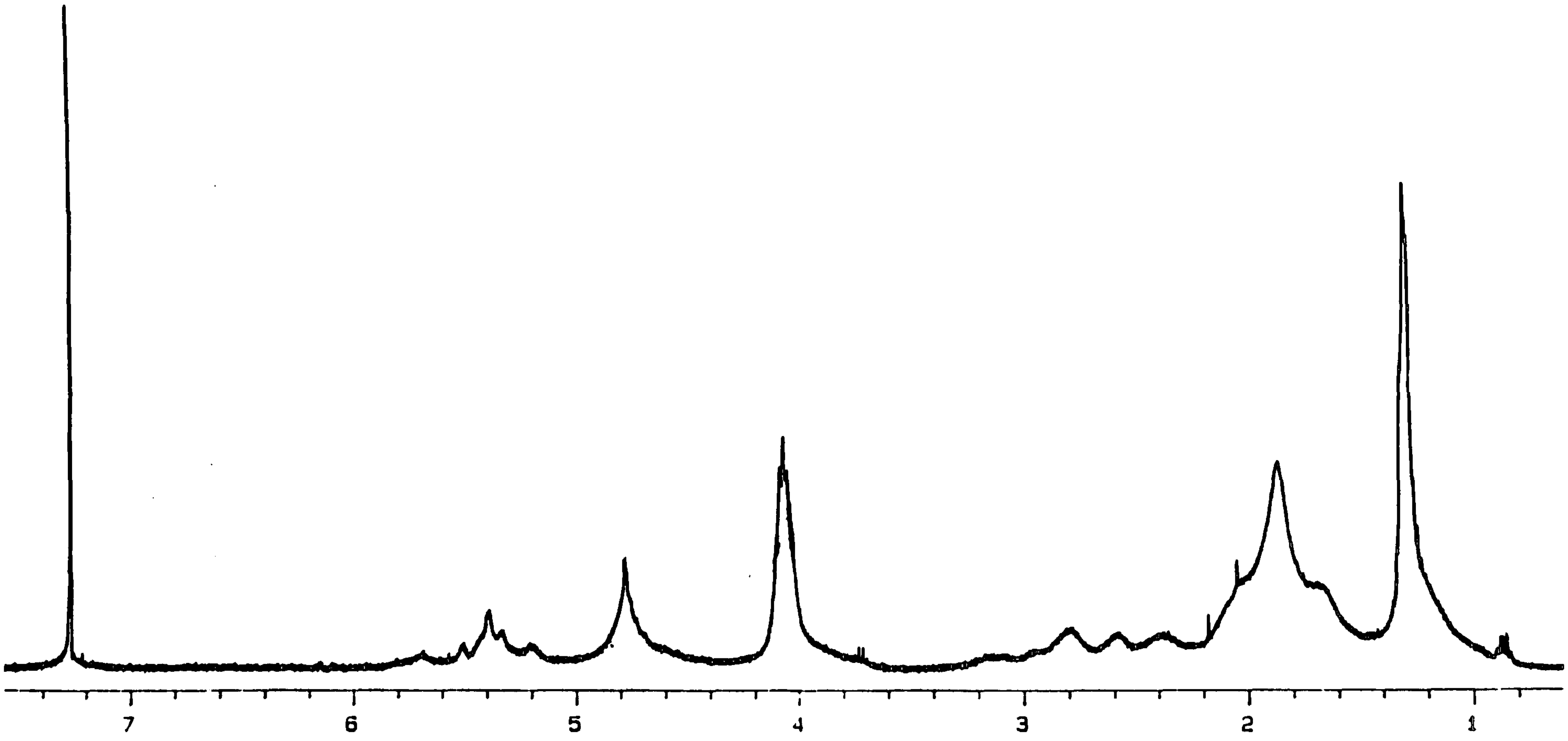
Appendix A10: ^{1}H NMR Spectrum (399.952 MHz) of trans-Ethene-1,2-bis(diethylphosphonate).



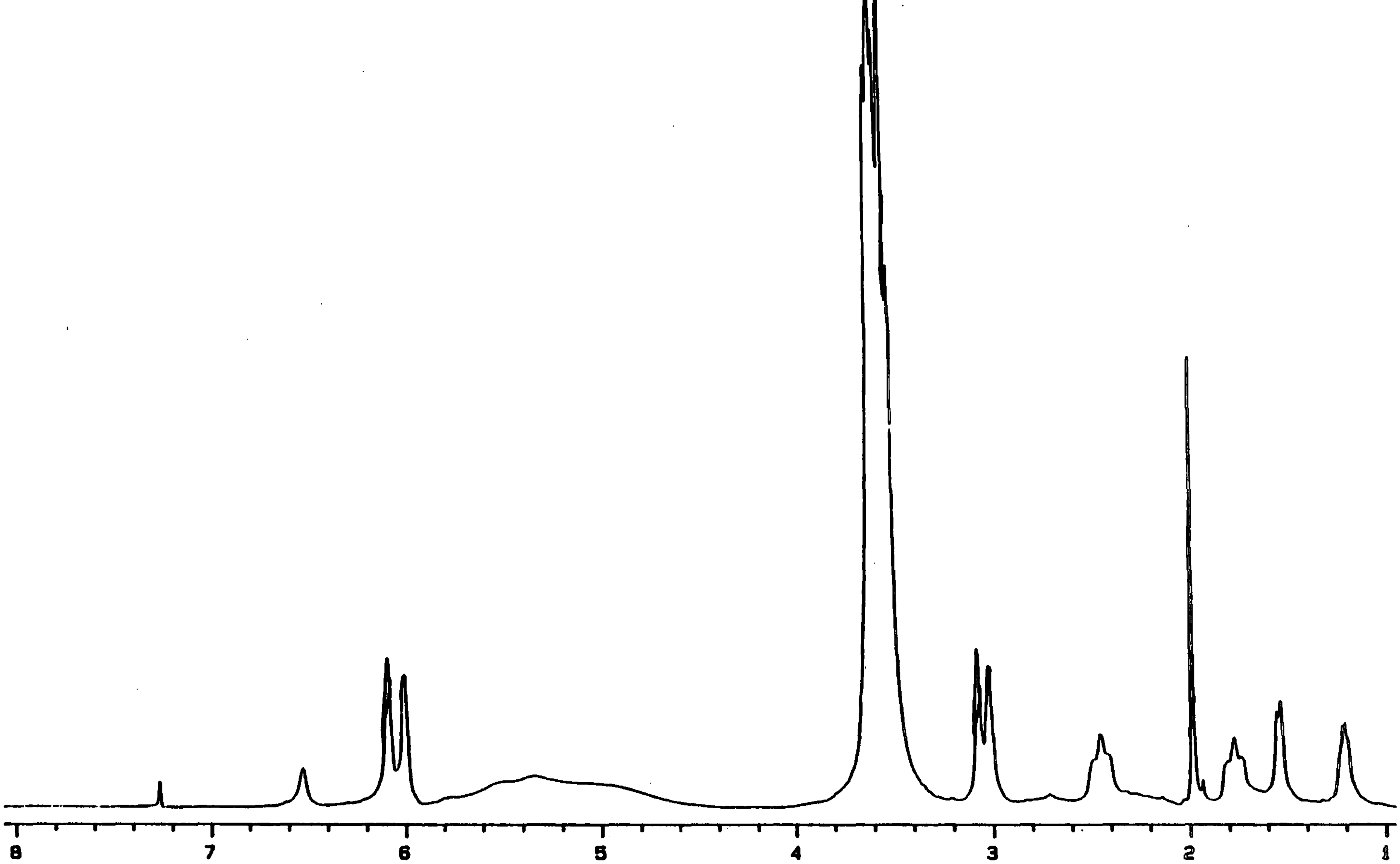
Appendix A11: ^{1}H NMR Spectrum (399.952 MHz) of exo,endo-5,6-bis(diethylphosphonate)bicyclo[2.2.1]hept-2-ene.



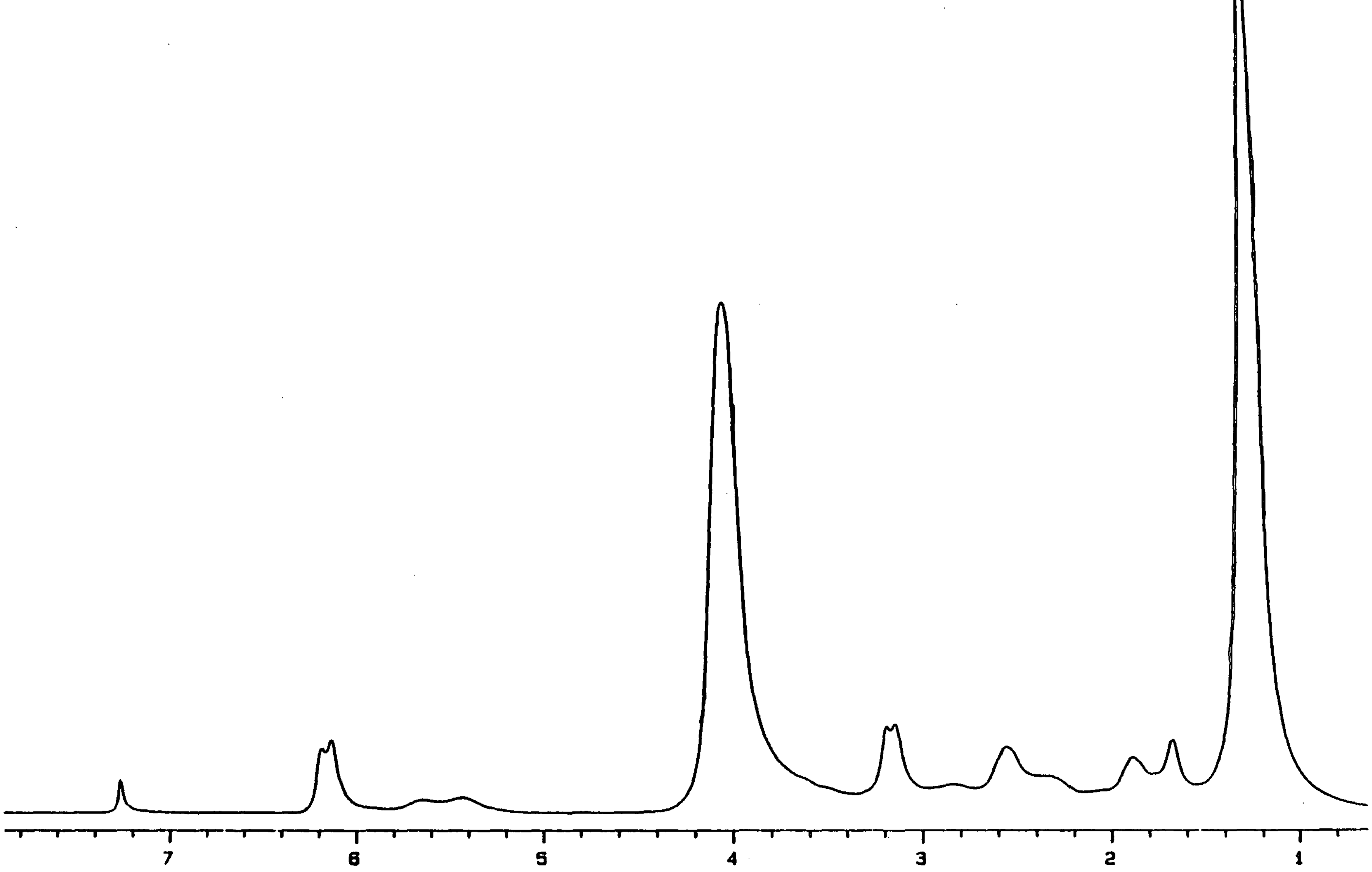
Appendix A12: ^{1}H NMR Spectrum (399.952 MHz) of Poly{2,5-[3-dimethylphosphonate]-cyclopentylene}-vinylene.



Appendix A13: ^1H NMR Spectrum (399.952 MHz) of Poly{2,5-[3-diethylphosphonate]-cyclopentylene}-vinylene.

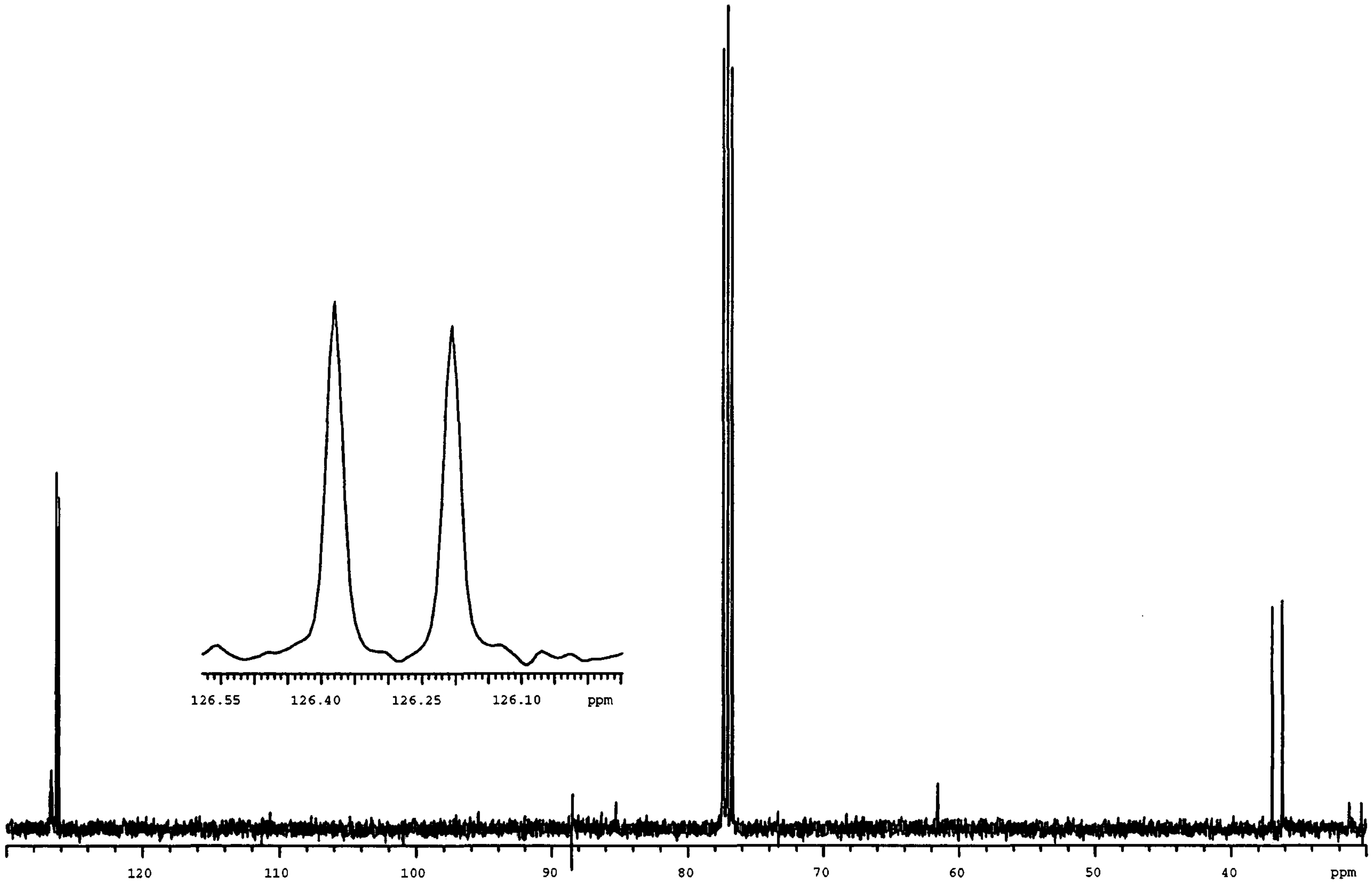


Appendix A14: ¹H NMR Spectrum (399.952 MHz) of Poly{2,5-[3,4-bis(dimethylphosphonate)]-cyclopentylene}-vinylene.

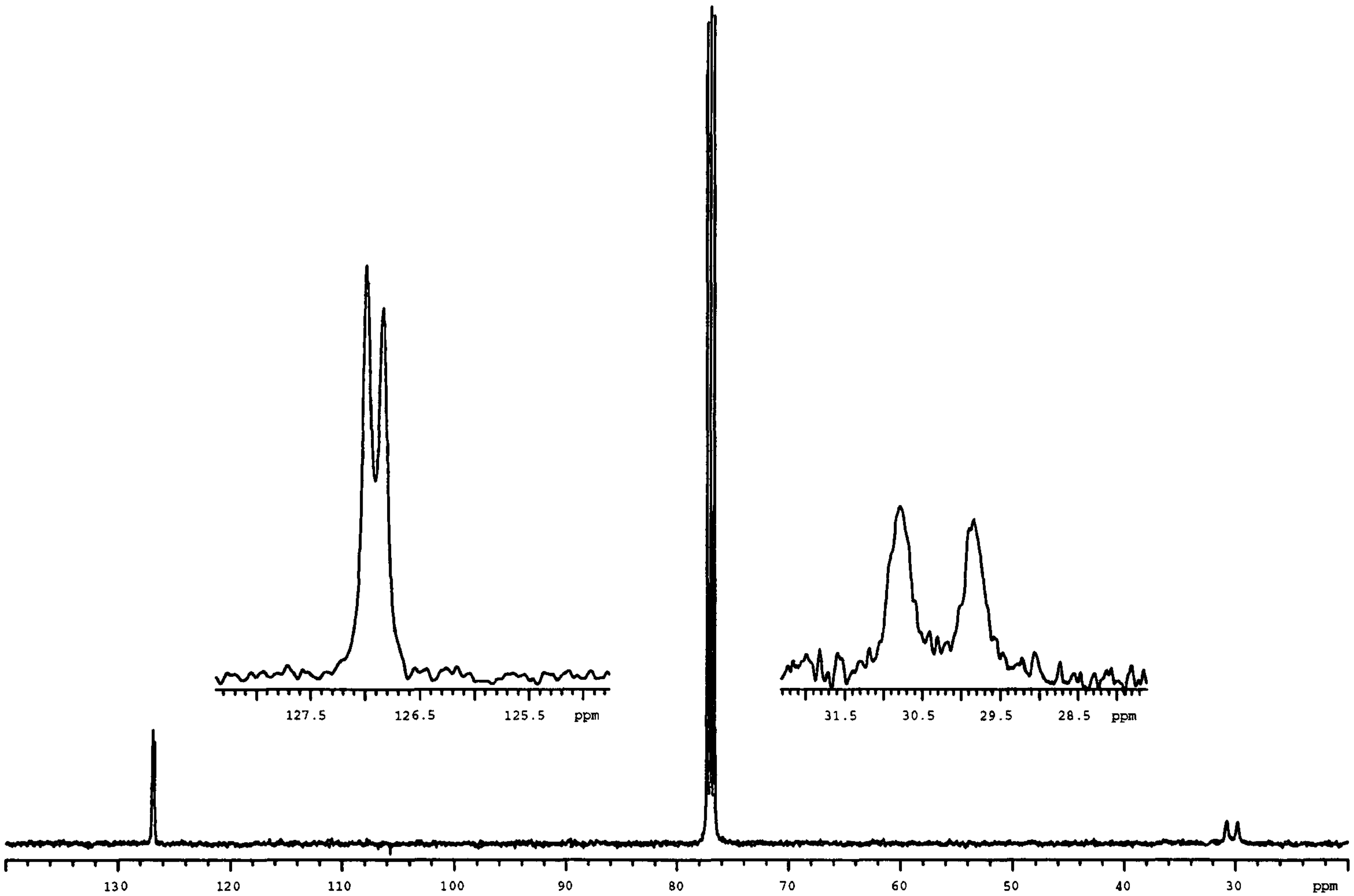


Appendix A15: ^{1}H NMR Spectrum (399.952 MHz) of Poly{2,5-[3,4-bis(diethylphosphonate)]-cyclopentylene}-vinylene.

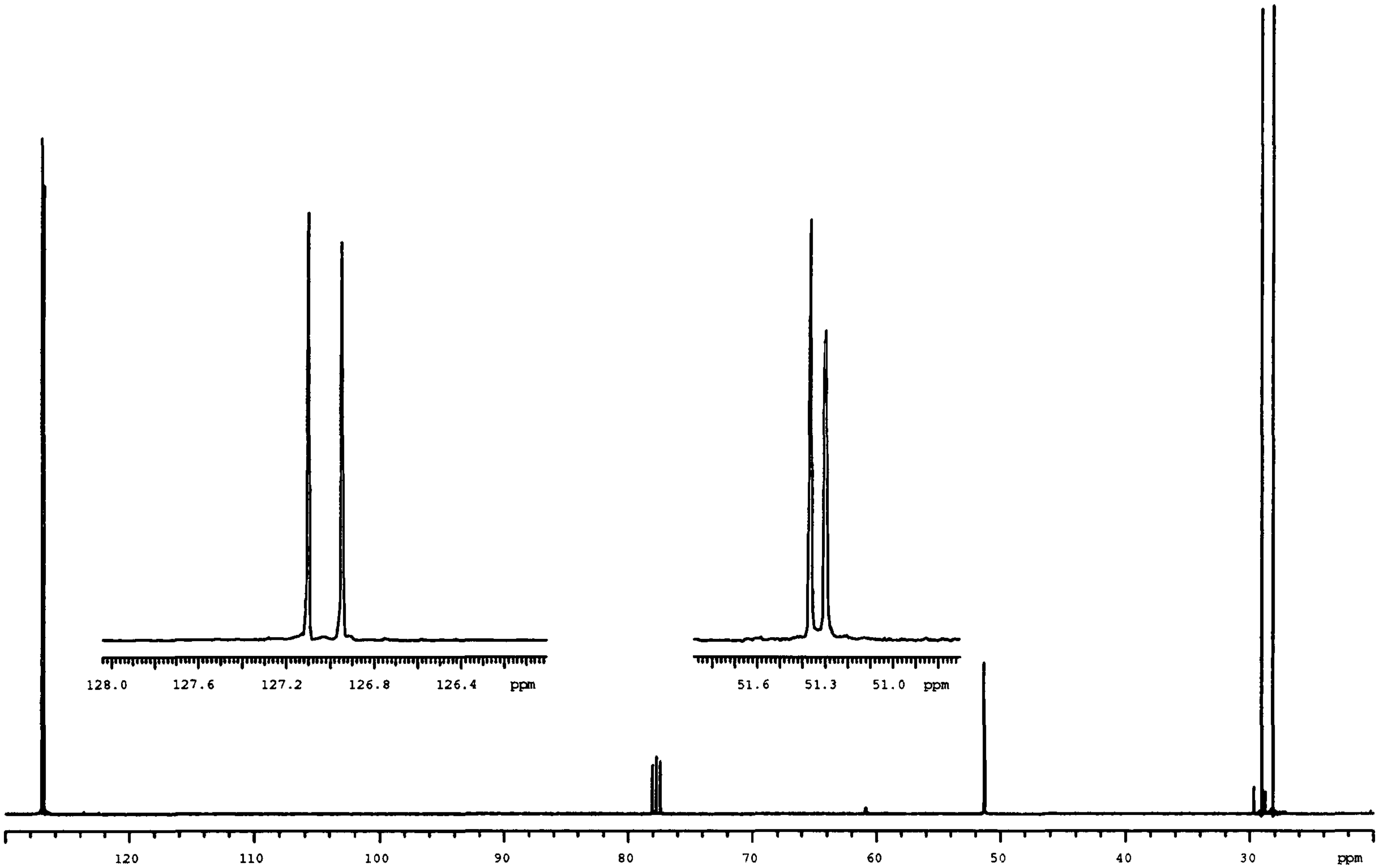
Appendix B:
^{13}C NMR Spectra.



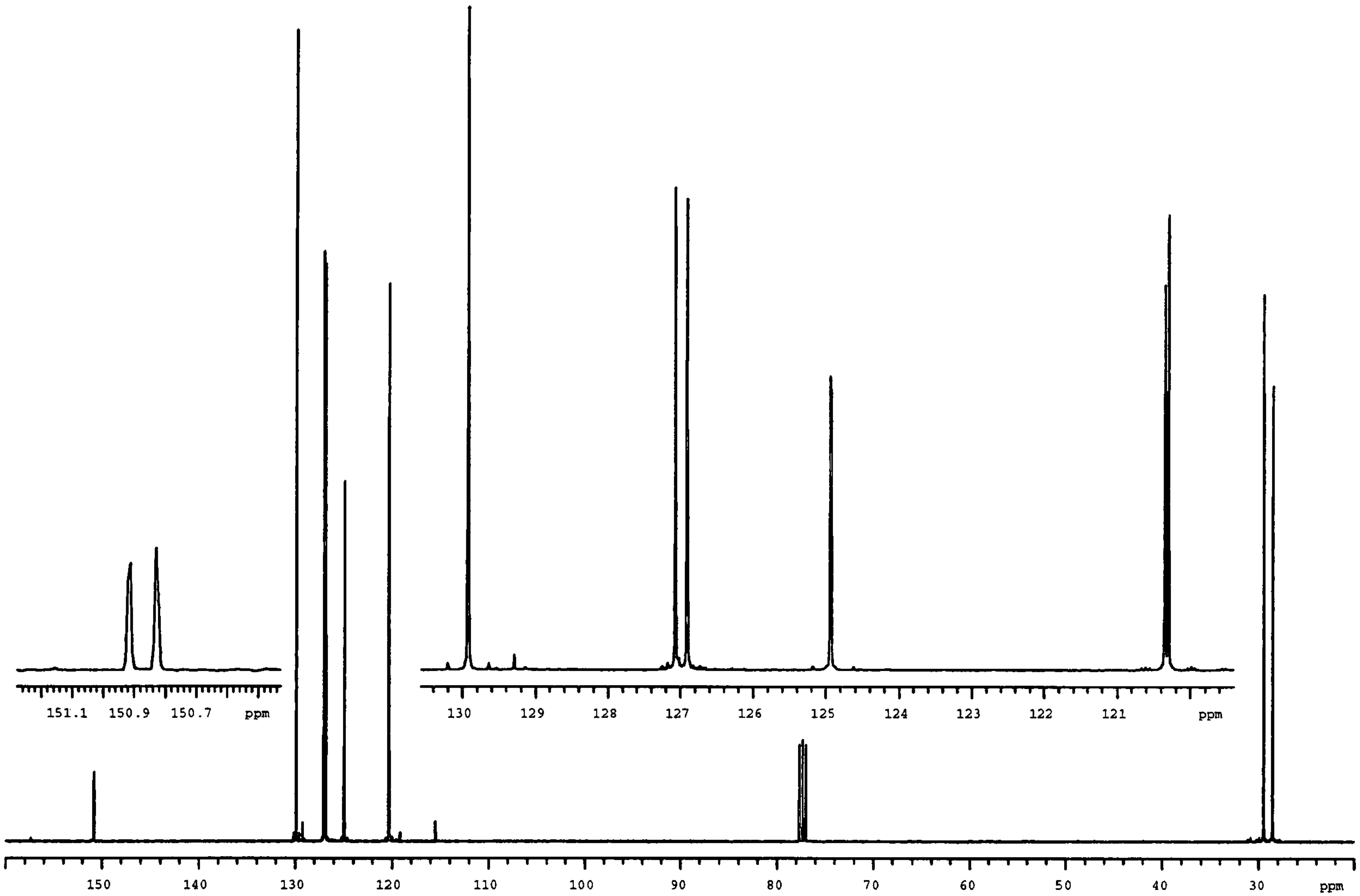
Appendix B1: ^{13}C NMR Spectrum (100.577 MHz) of 1-Chloro-1-oxo-3-phospholene.



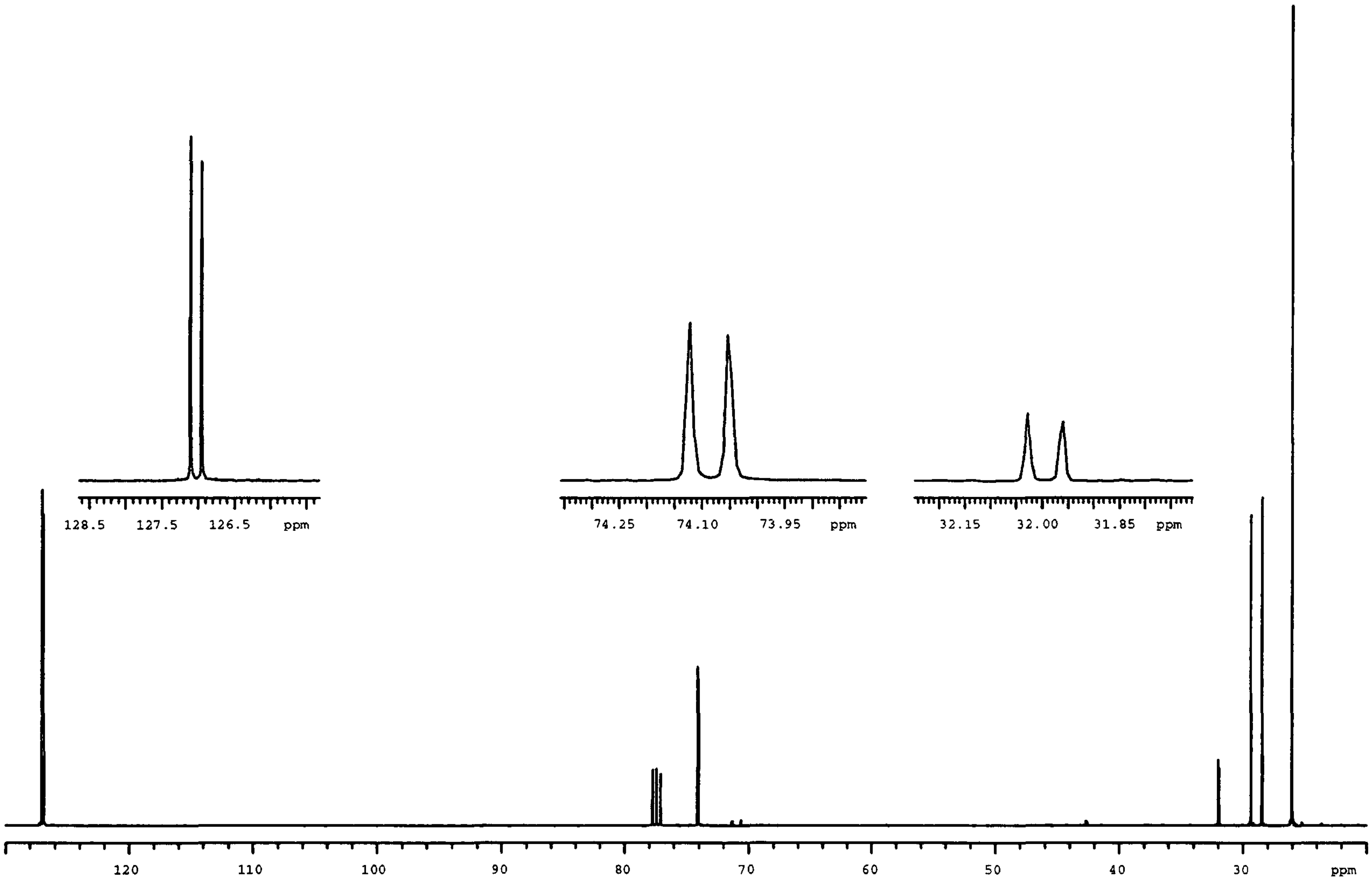
Appendix B2: ^{13}C NMR Spectrum (100.577 MHz) of 1-Hydroxy-1-oxo-3-phospholene.



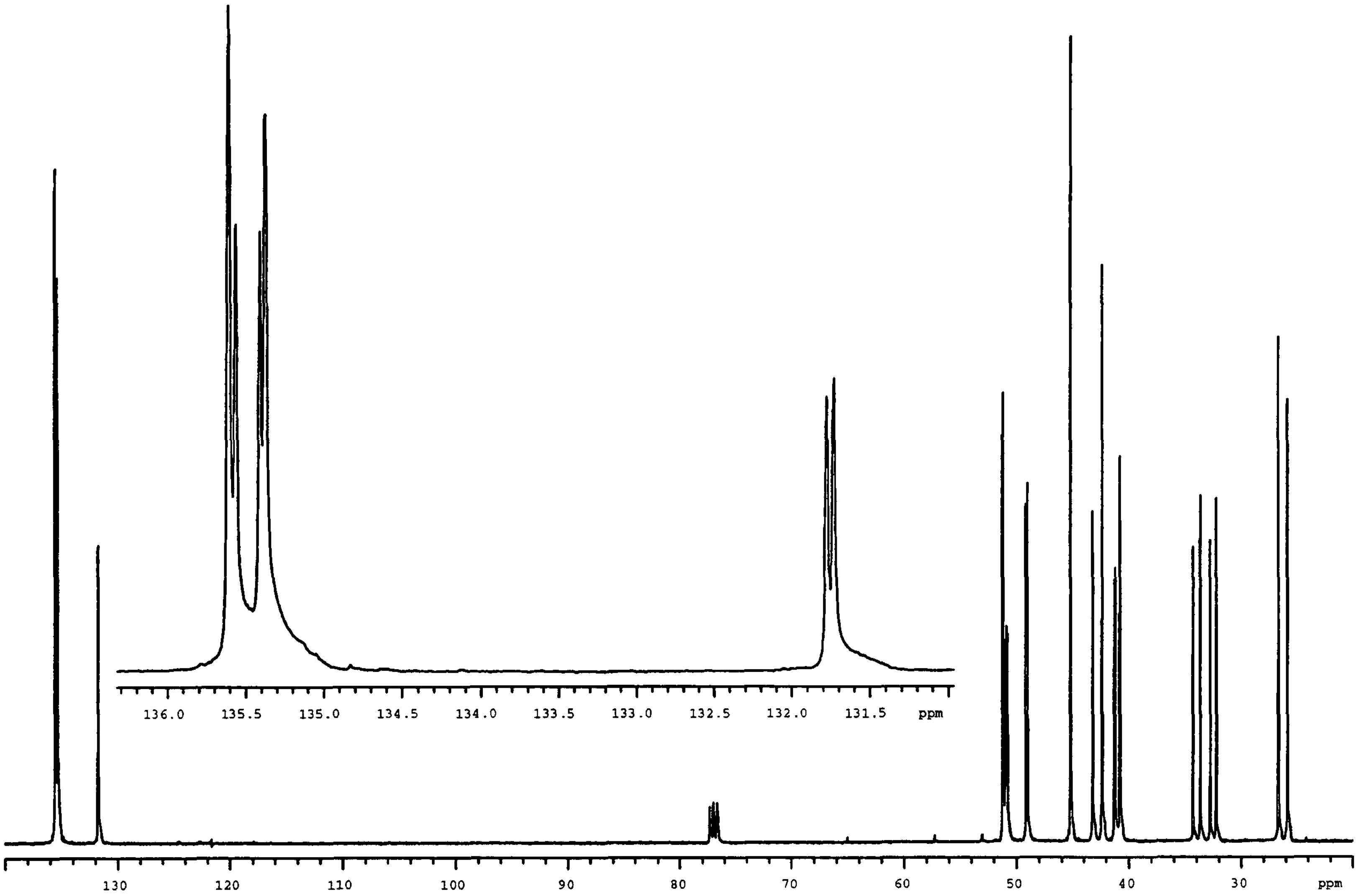
Appendix B3: ^{13}*C NMR Spectrum (100.577 MHz) of 1-Methoxy-1-oxo-3-phospholene.*



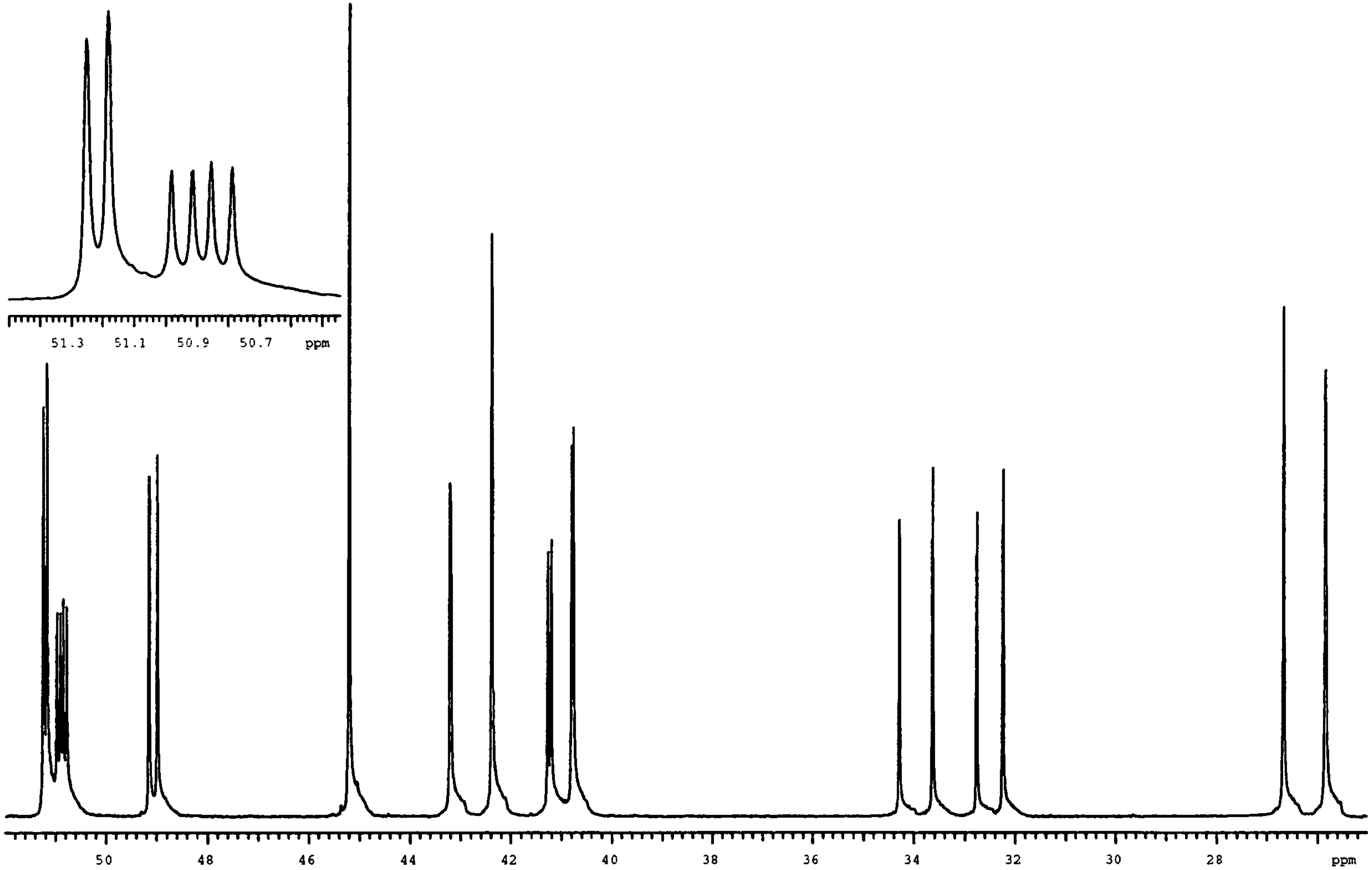
Appendix B4: ^{13}C NMR Spectrum (100.577 MHz) of 1-Phenoxy-1-oxo-3-phospholene.



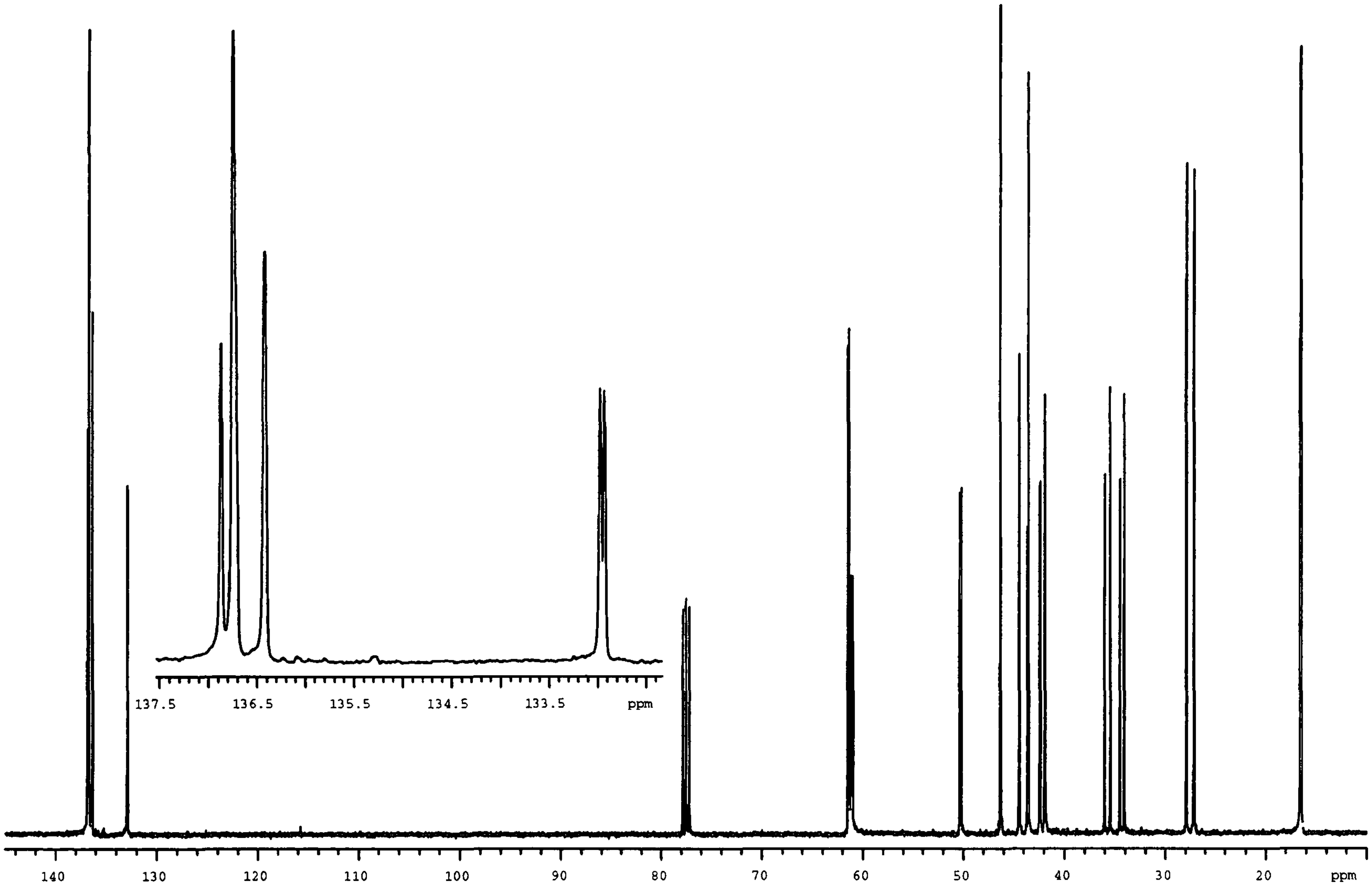
Appendix B5: ^{13}C NMR Spectrum (100.577 MHz) of 1-Neopentoxy-1-oxo-3-phospholene.



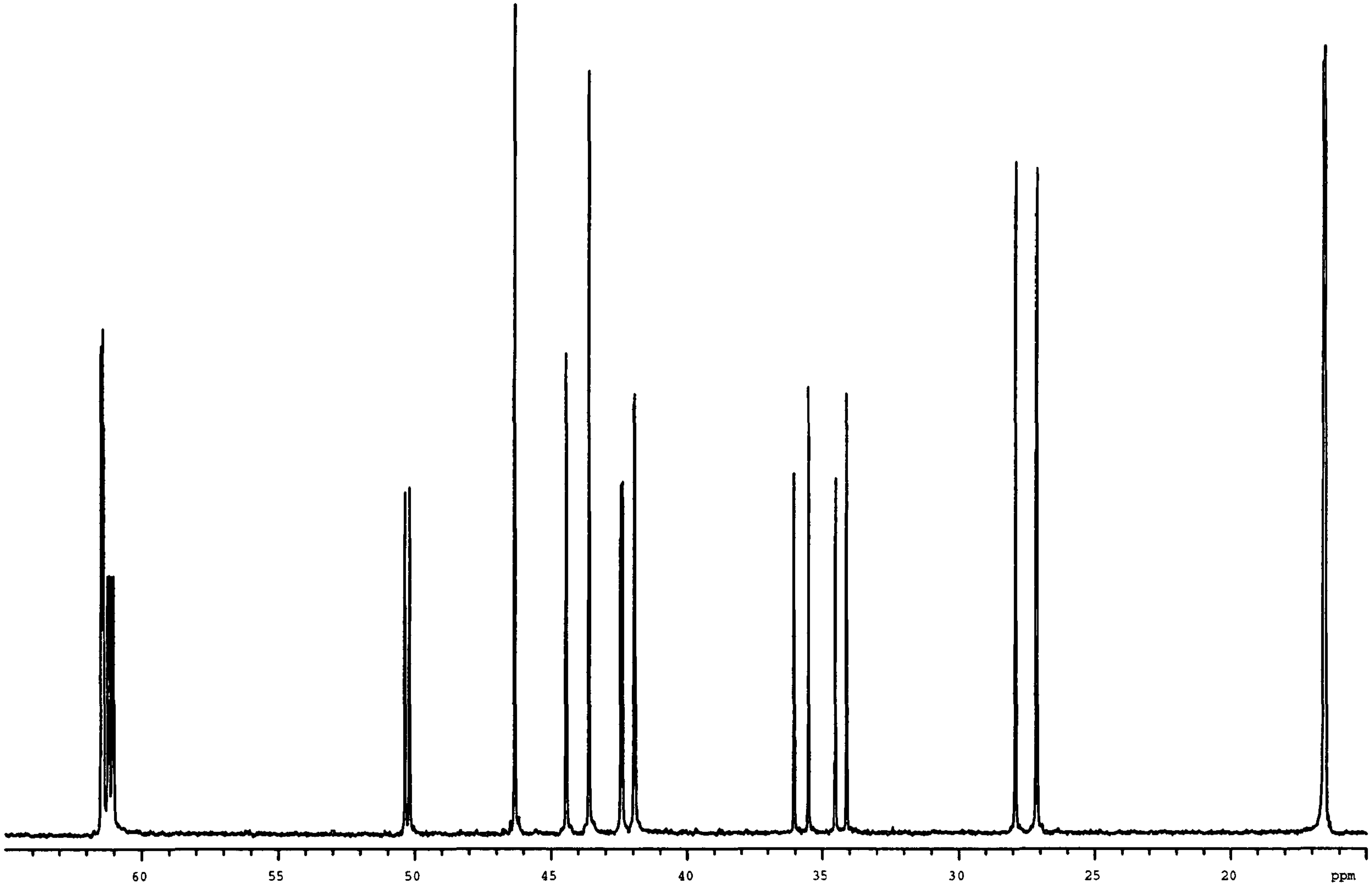
Appendix B6: ^{13}C NMR Spectrum (100.577 MHz) of Dimethylbicyclo[2.2.1]hept-2-ene-5-phosphonate.



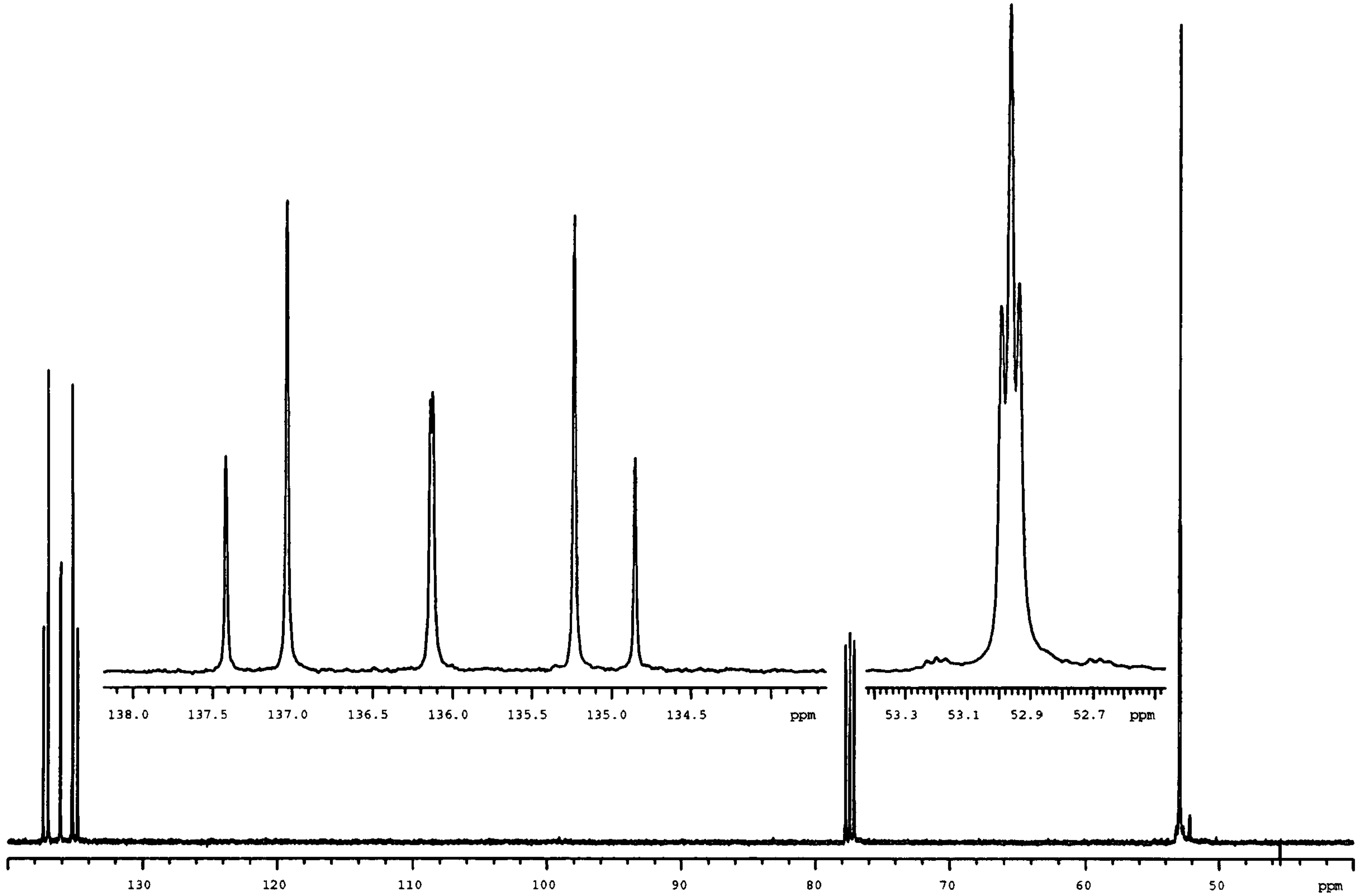
Appendix B6a: Expansions of the ^{13}C NMR Spectrum (100.577MHz) of Dimethylbicylo[2.2.1]hept-2-ene-5-phosphonate.



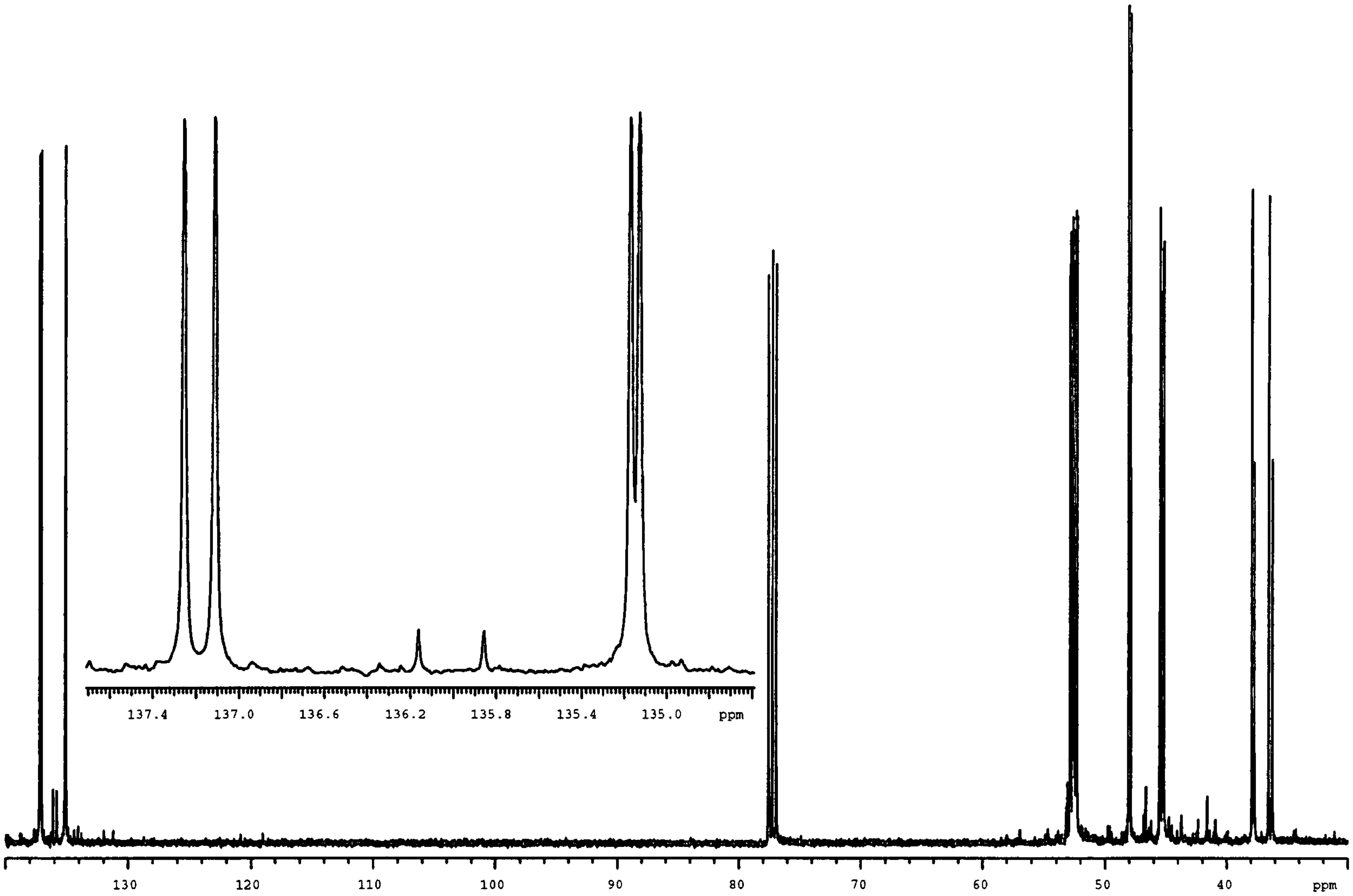
Appendix B7: ^{13}C NMR Spectrum (100.577 MHz) of Diethylbicylo[2.2.1]hept-2-ene-5-phosphonate.



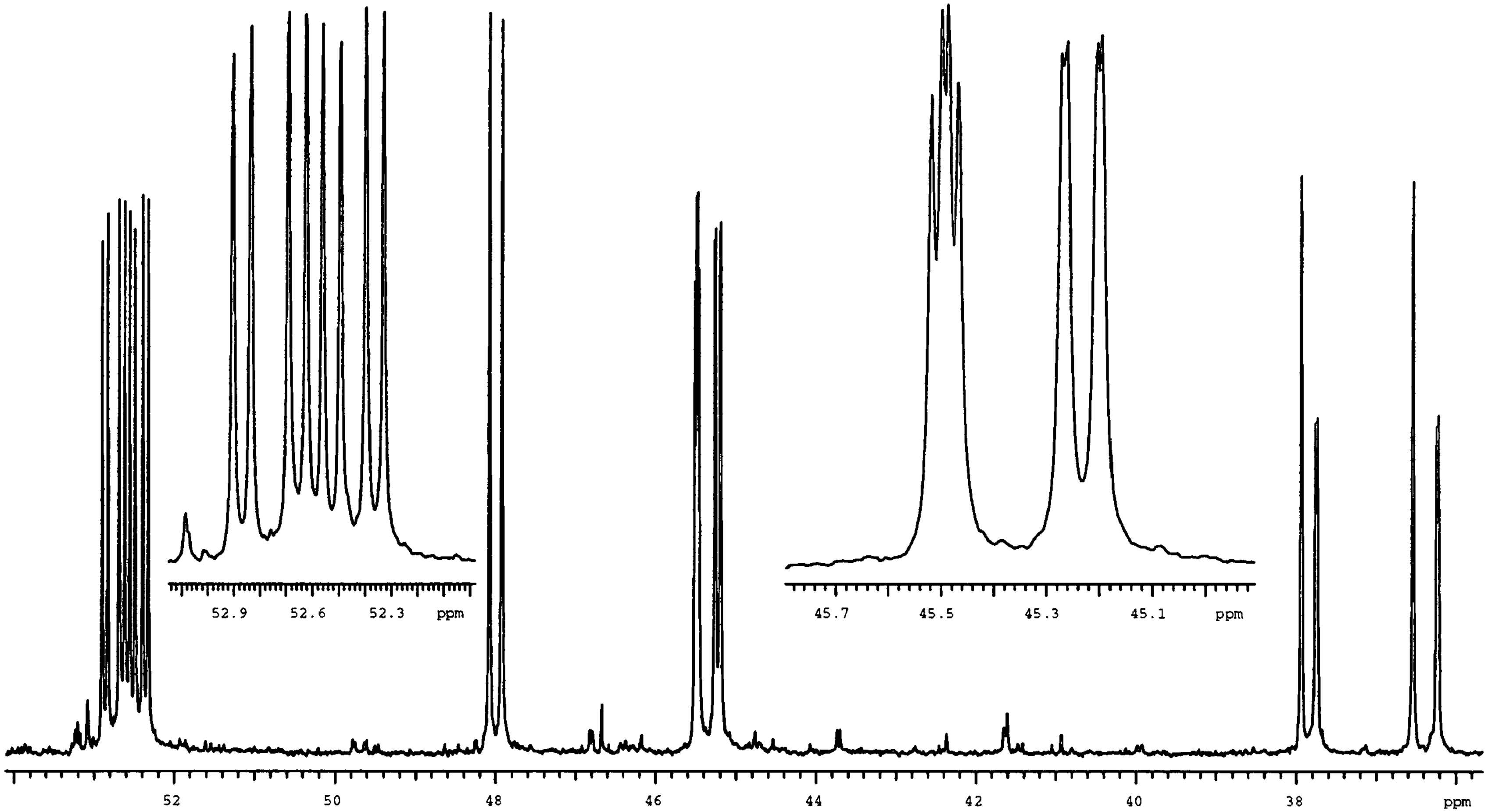
Appendix B7a: Expansions of the ^{13}C NMR Spectrum (100.577 MHz) of Diethylbicylo[2.2.1]hept-2-ene-5-phosphonate.



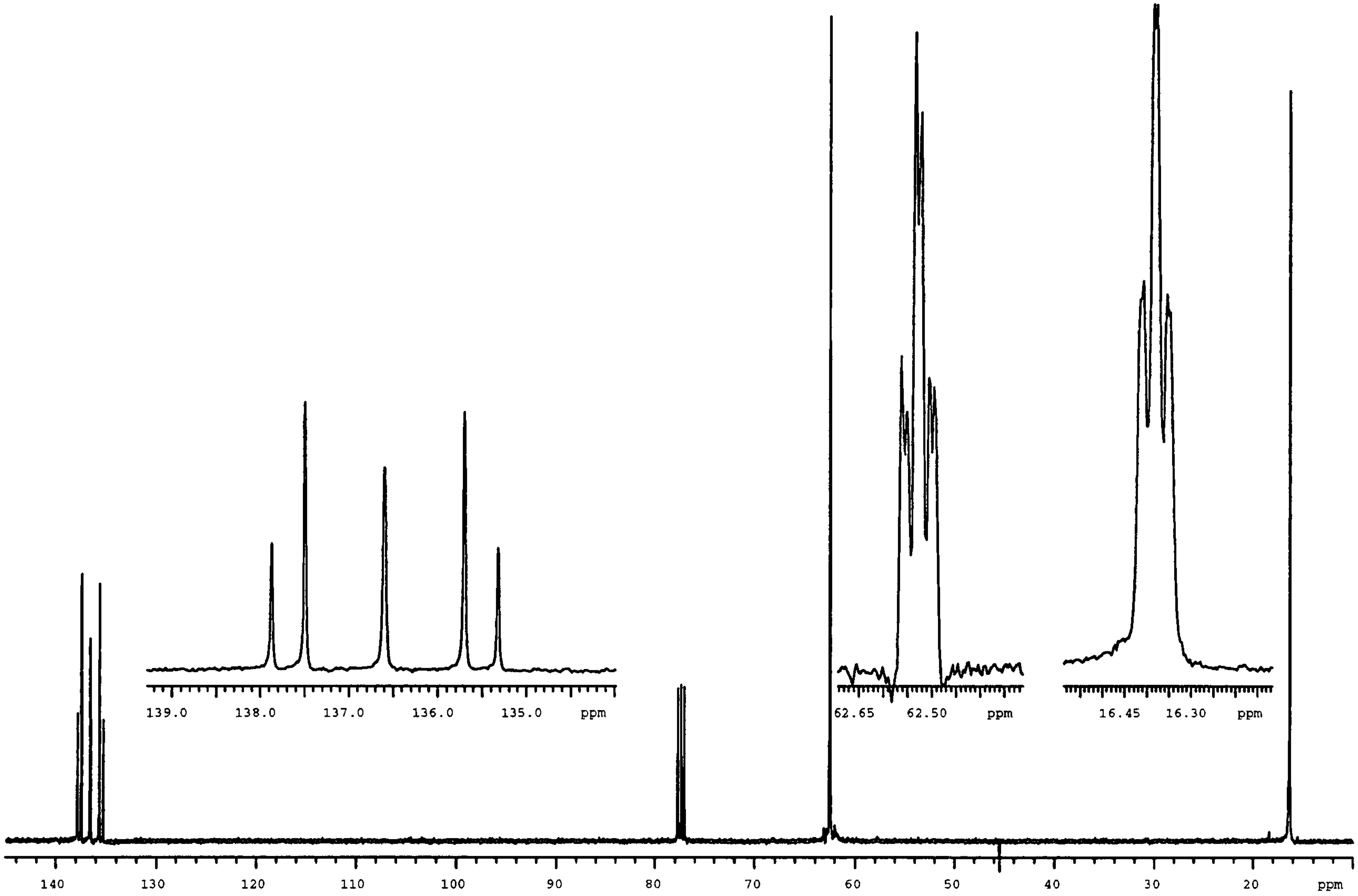
Appendix B8: ^{13}C NMR Spectrum (100.577 MHz) of trans-Ethene-1,2-bis(dimethylphosphonate).



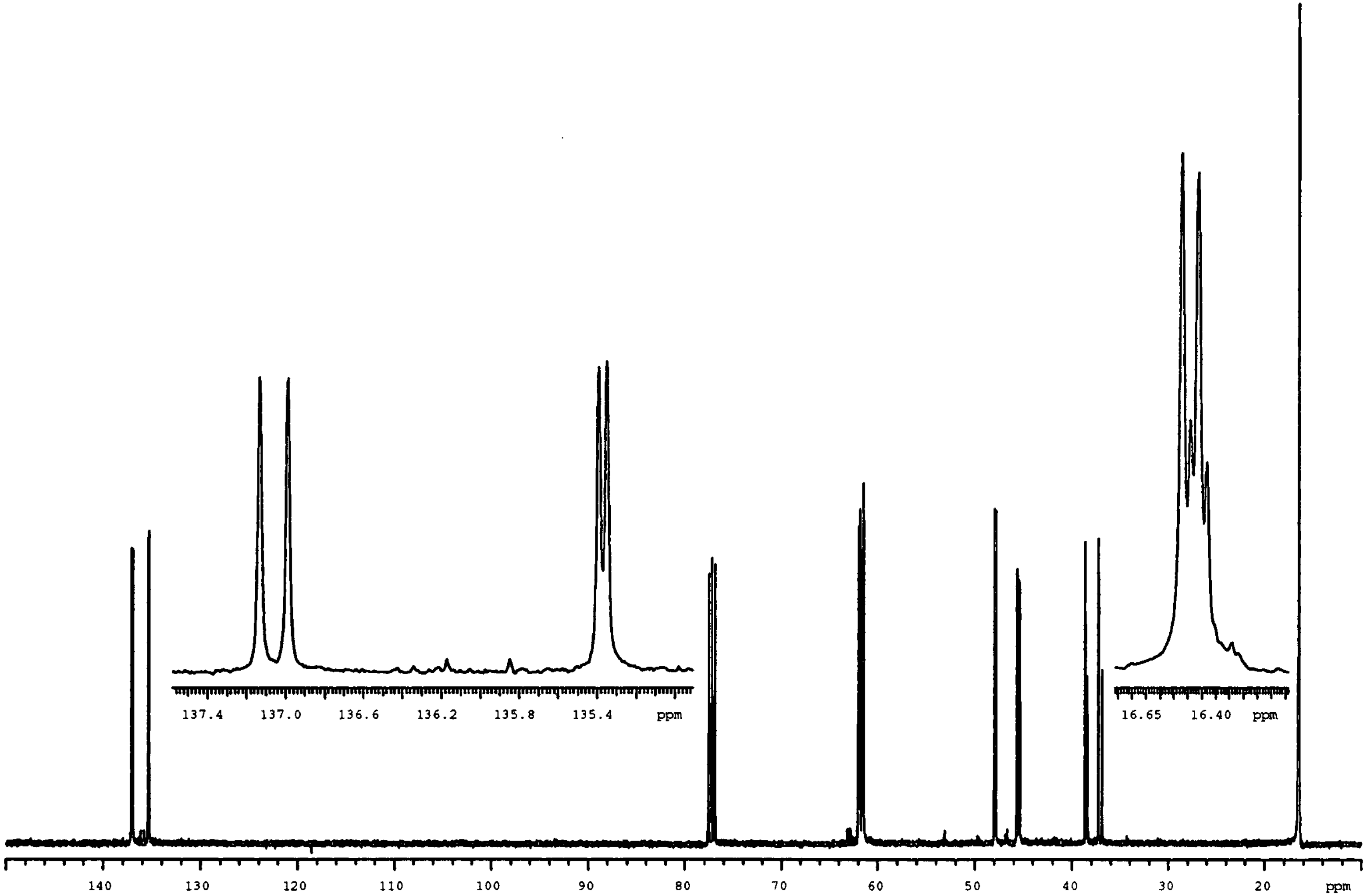
Appendix B9: ^{13}C NMR Spectrum (100.577 MHz) of exo,endo-5,6-bis(dimethylphosphonate)bicyclo[2.2.1]hept-2-ene.



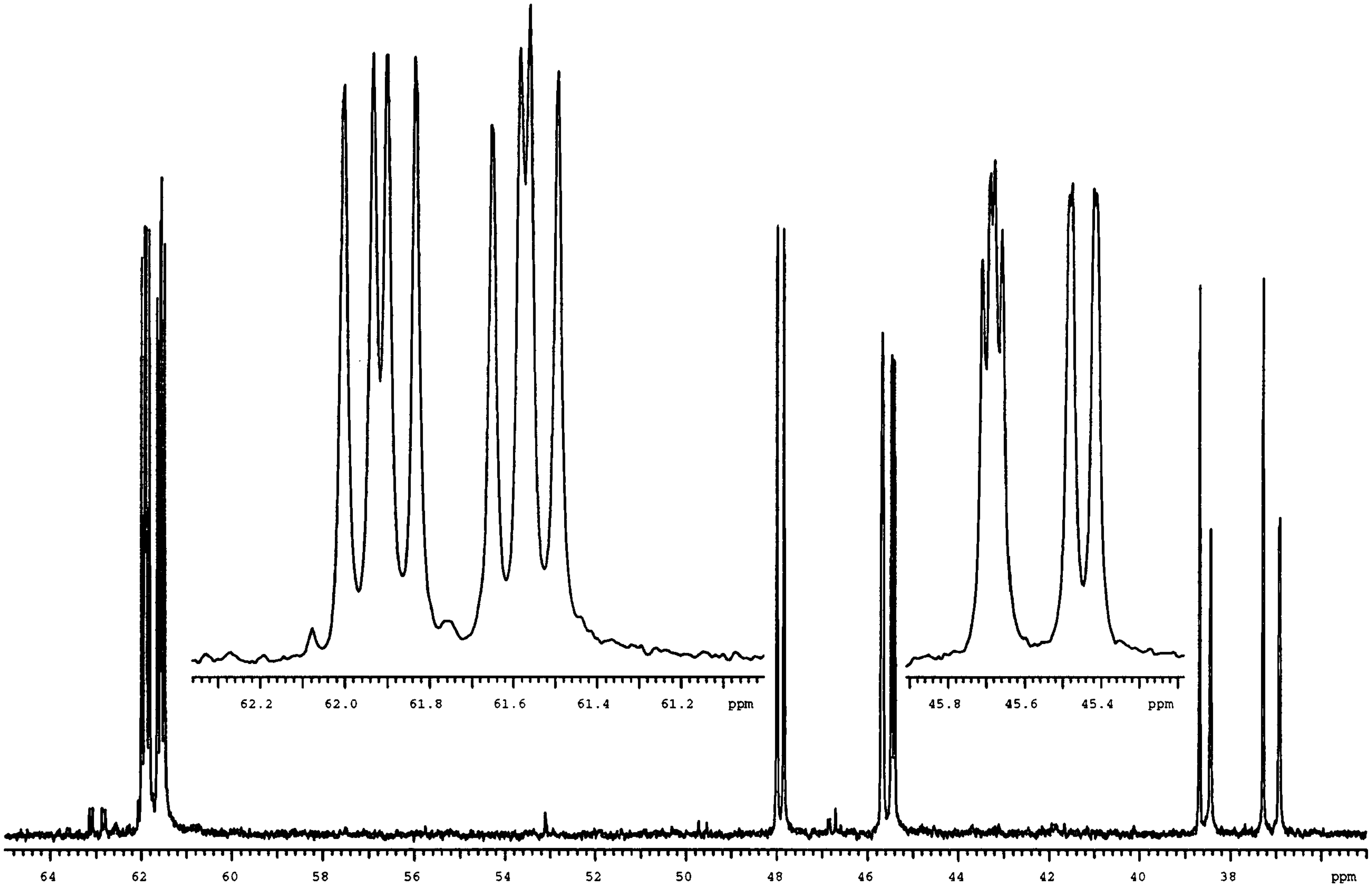
Appendix B9a: Expansions of the ^{13}C NMR Spectrum (100.577 MHz) of exo,endo-5,6-bis(dimethylphosphonate)bicyclo[2.2.1]hept-2-ene



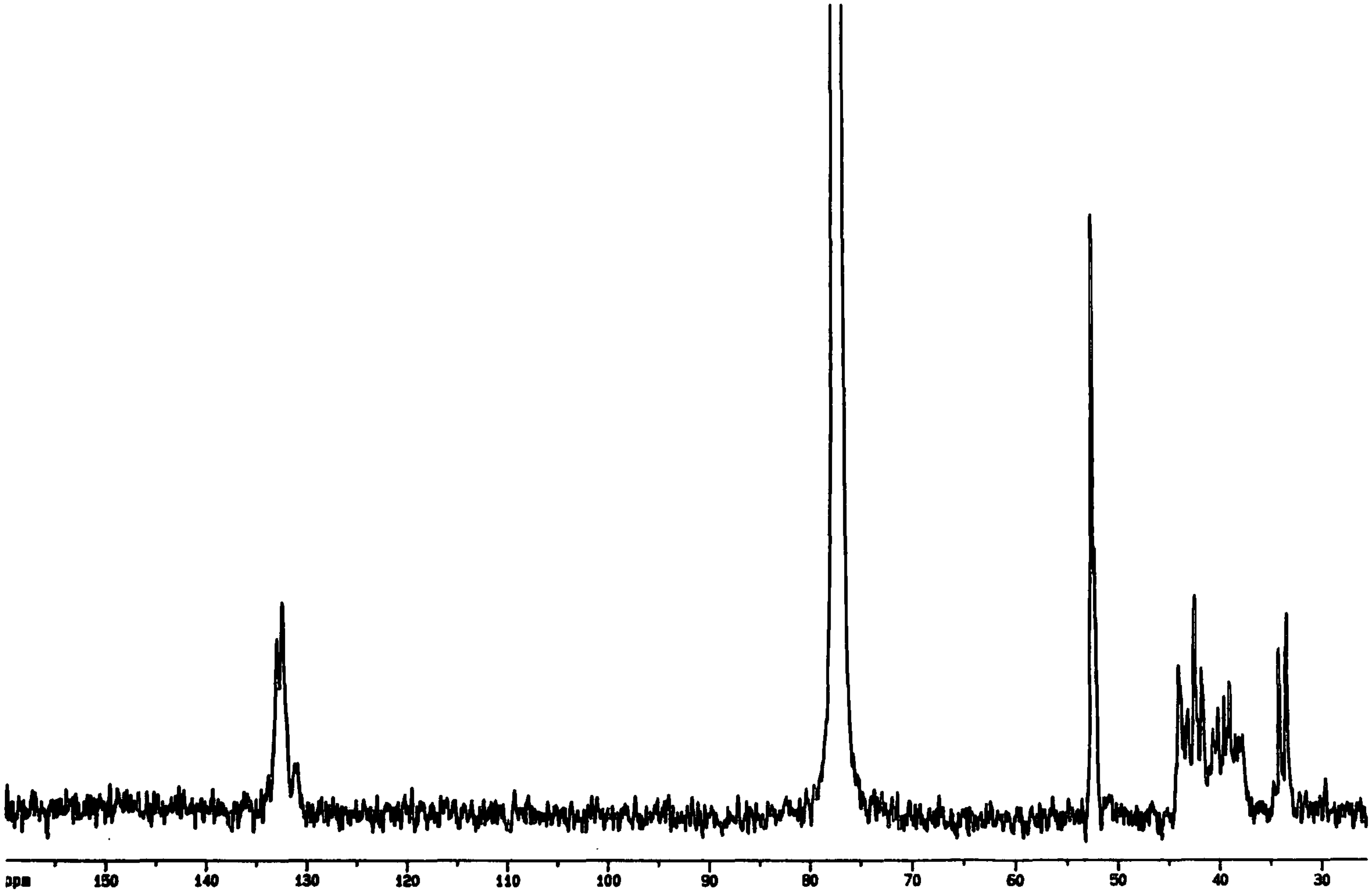
Appendix B10: ^{13}C NMR Spectrum (100.577 MHz) of trans-Ethene-1,2-bis(diethylphosphonate).



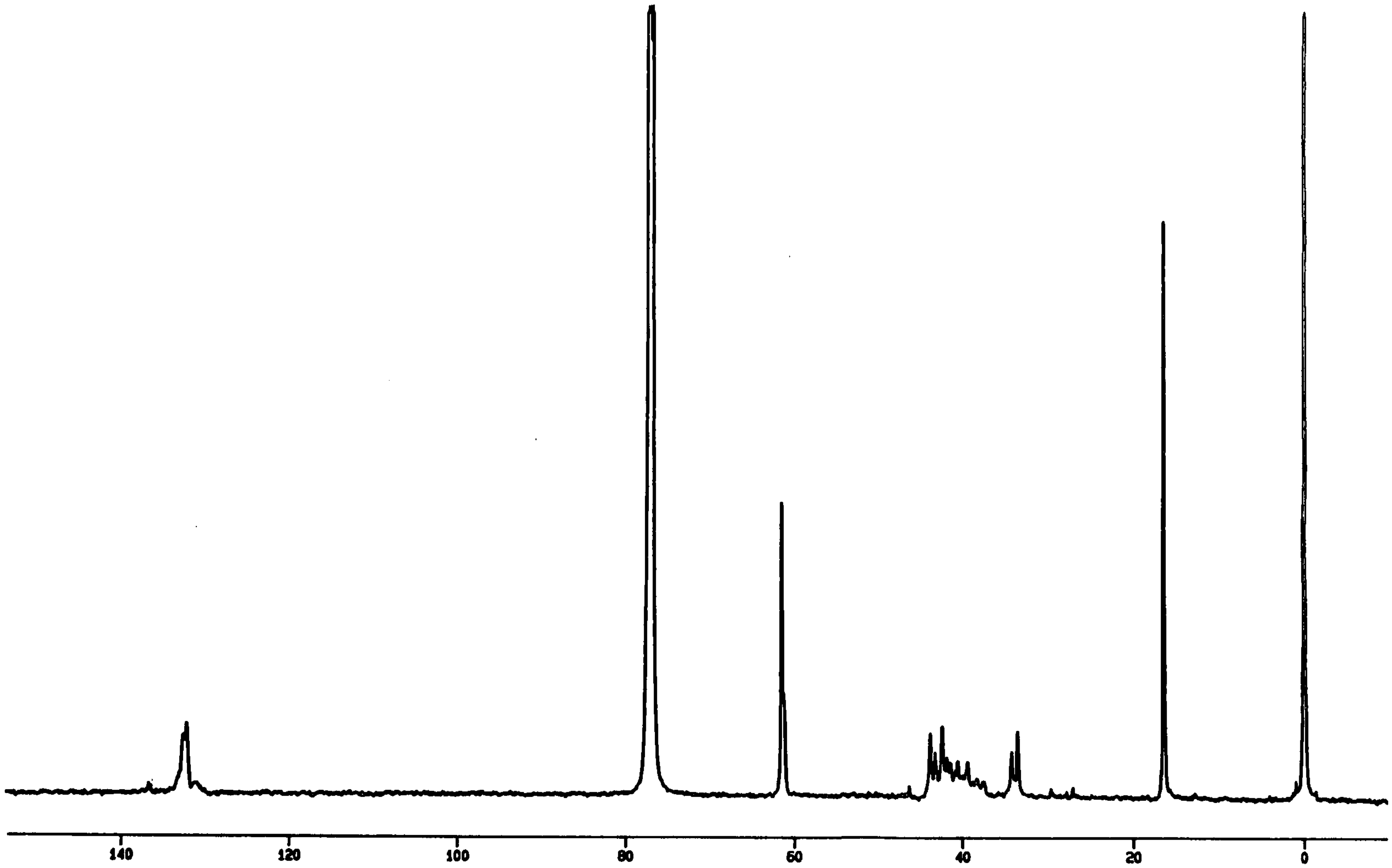
Appendix B11: ^{13}C NMR Spectrum (100.577 MHz) of exo,endo-5,6-bis(diethylphosphonate)bicyclo[2.2.1]hept-2-ene.



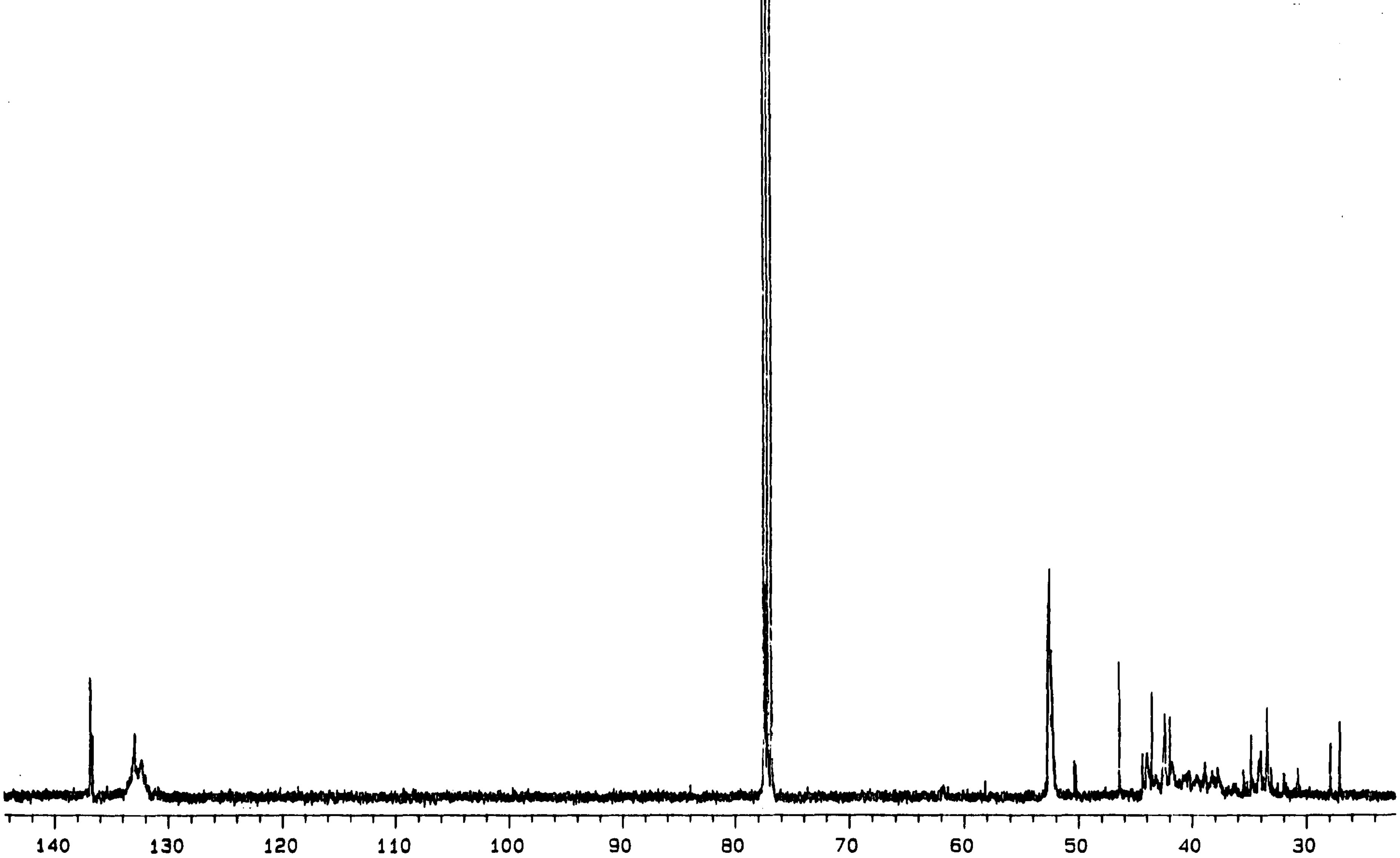
Appendix B11a: Expansions of the ^{13}C NMR Spectrum (100.577 MHz) of exo,endo-5,6-bis(diethylphosphonate)bicyclo[2.2.1]hept-2-en



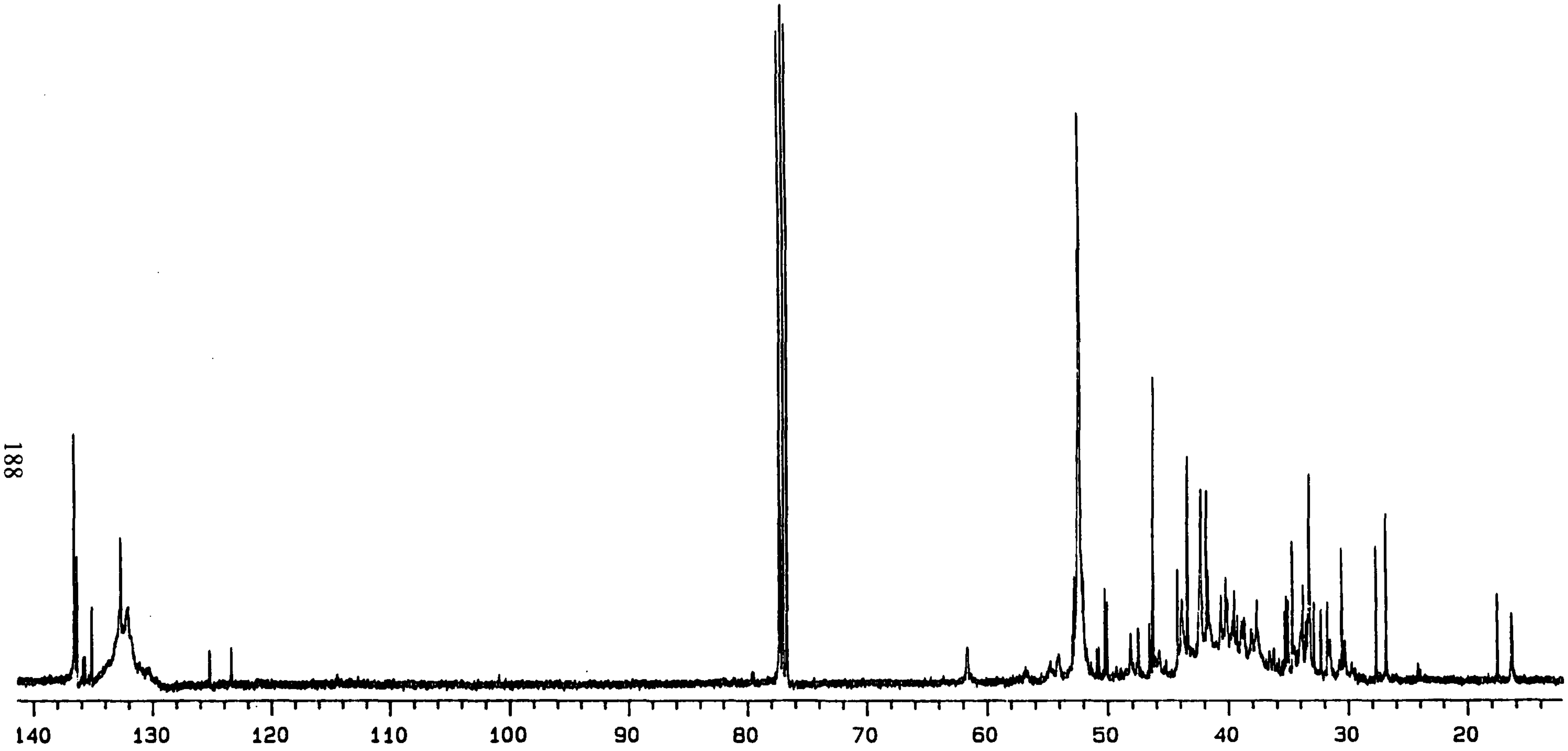
Appendix B12: ^{13}C NMR Spectrum (125.759 MHz) of Poly{2,5-[3-dimethylphosphonate]-cyclopentylene}-vinylene.



Appendix B13: ^{13}C NMR Spectrum (125.759 MHz) of Poly{2,5-[3-diethylphosphonate]-cyclopentylene}-vinylene.

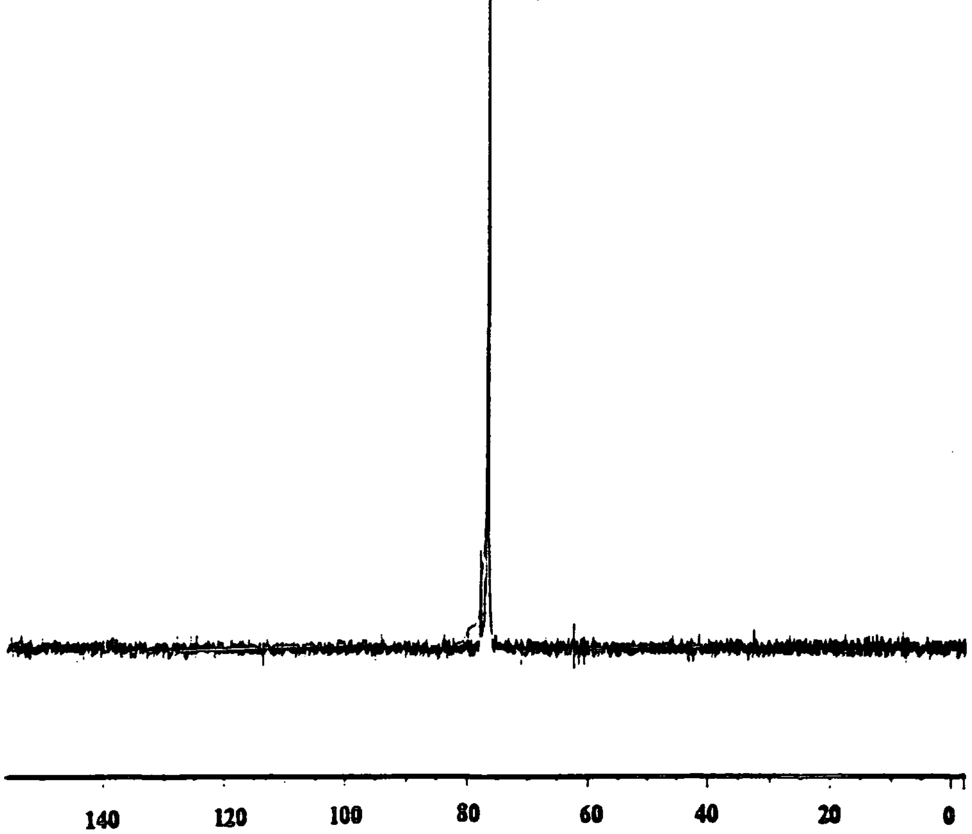


Appendix B14: ^{13}C NMR Spectrum (100.577 MHz) of Poly{2,5-[3,4-bis(dimethylphosphonate)]-cyclopentylene}-vinylene.

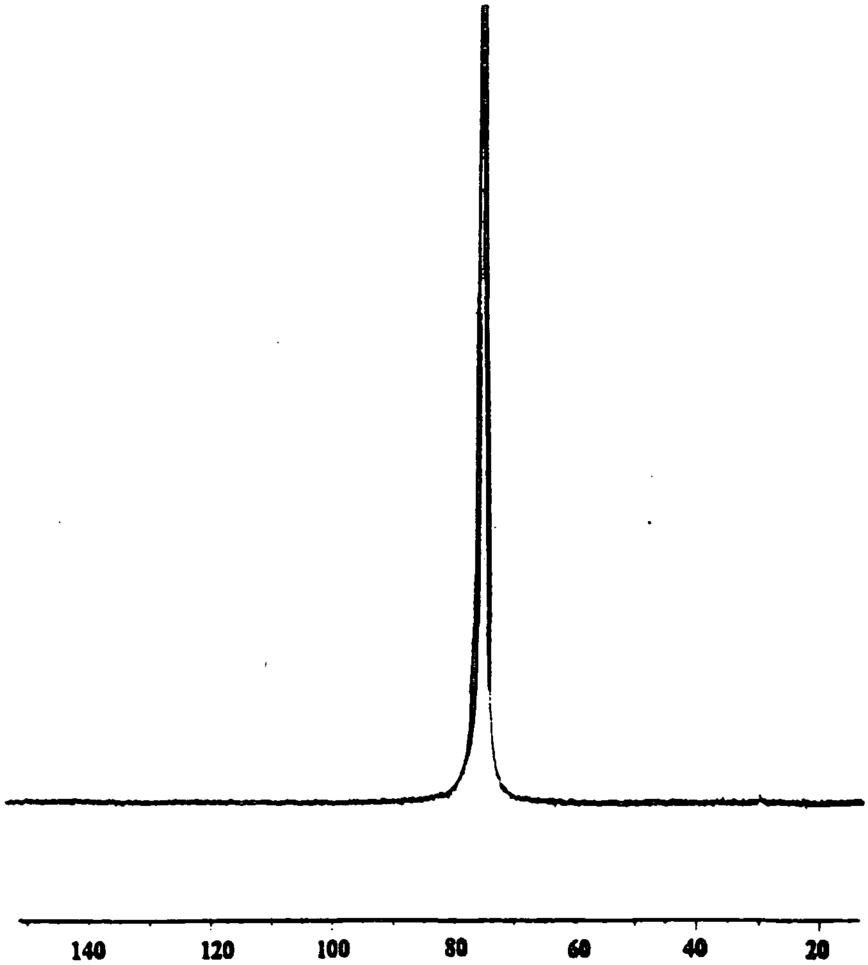


Appendix B15: ^{13} C NMR Spectrum (100.577 MHz) of Poly{2,5-[3,4-bis(diethylphosphonate)]-cyclopentylene}-vinylene.

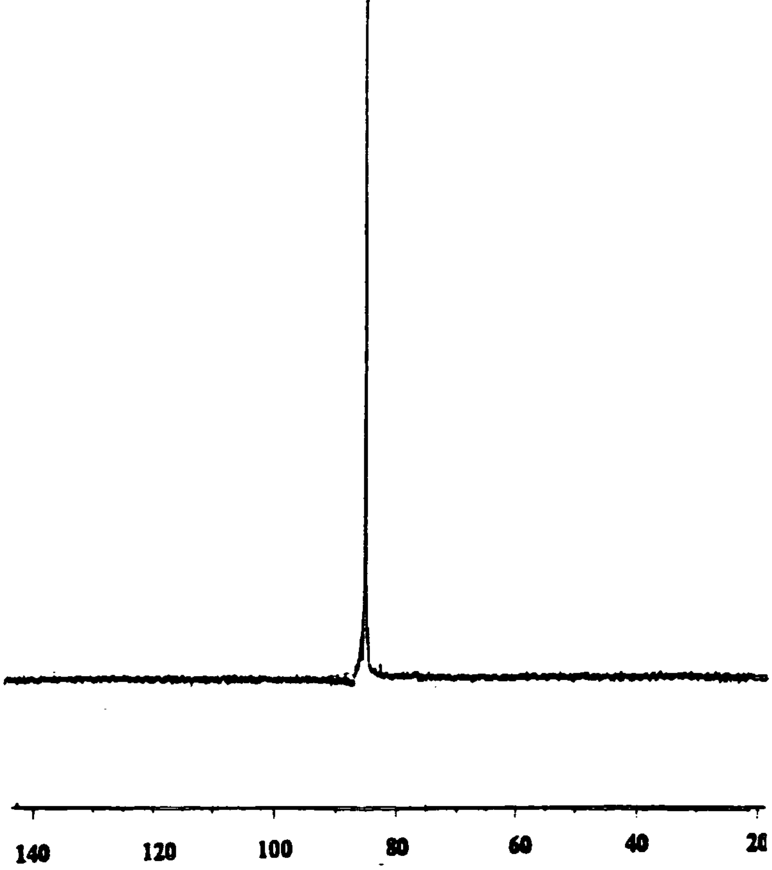
Appendix C:
^{31}P. NMR Spectra.



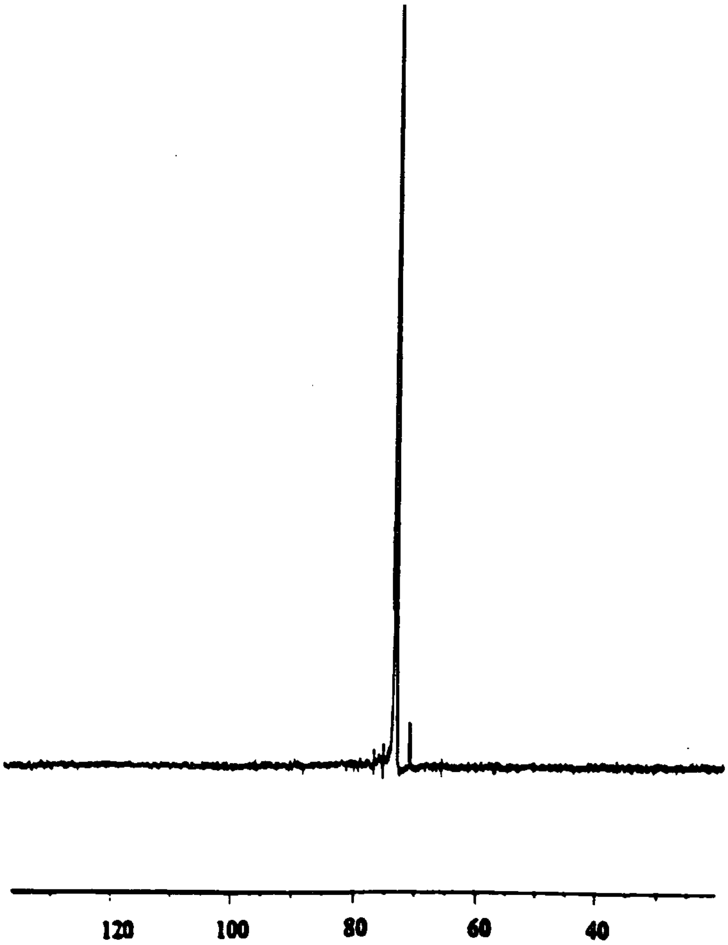
Appendix C1: 1-Chloro-1-oxo-3-phospholene.



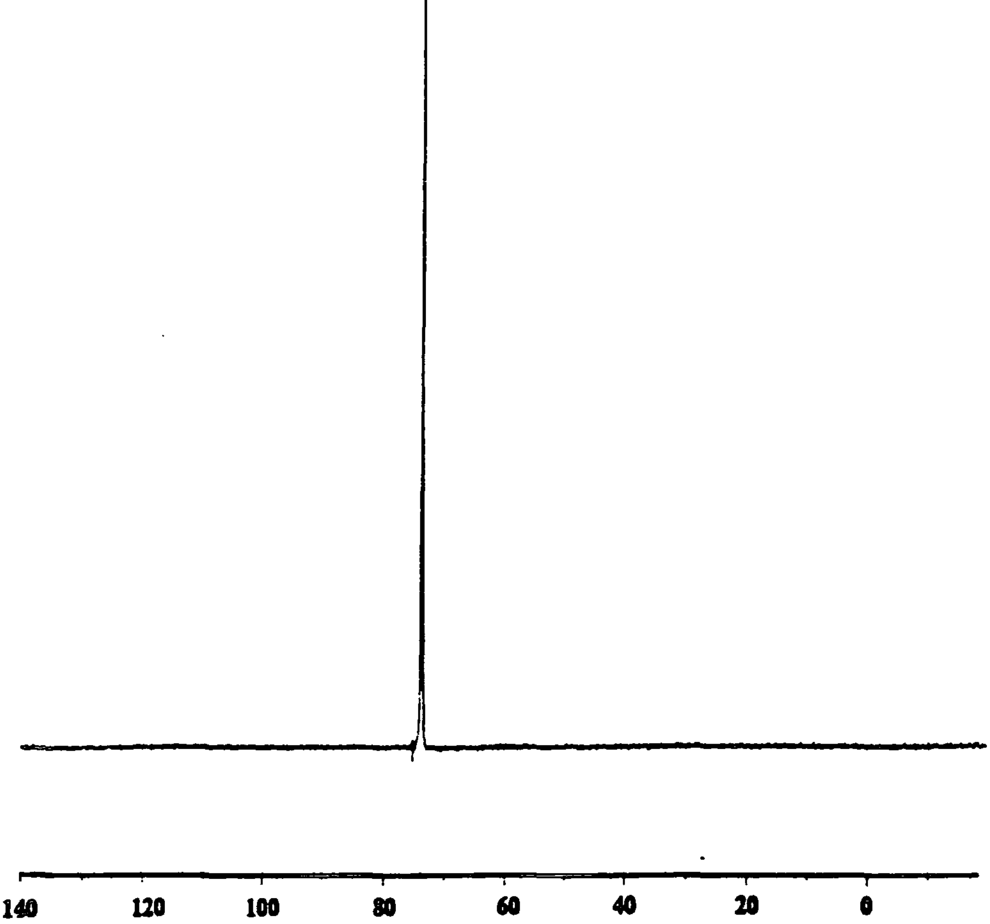
Appendix C2: 1-Hydroxy-1-oxo-3-phospholene.



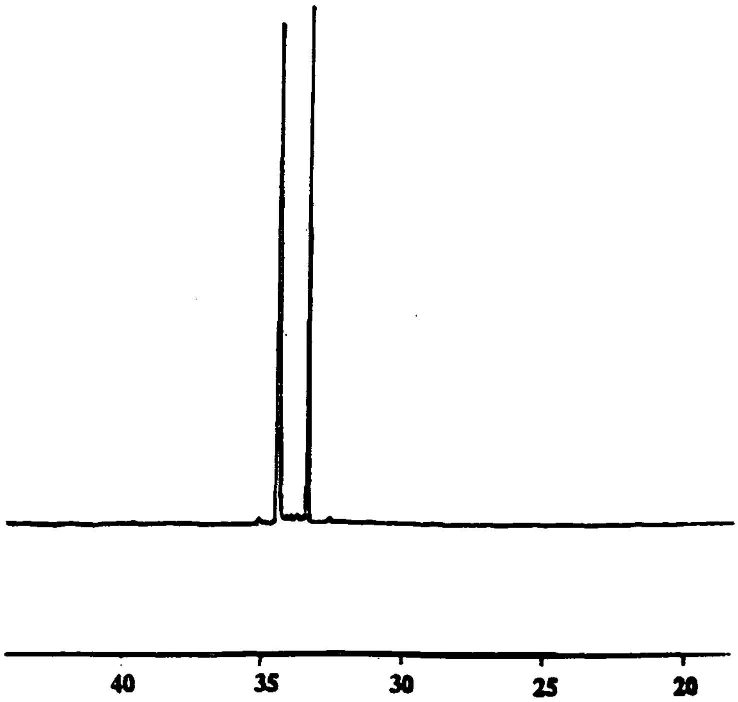
Appendix C3: 1-Methoxy-1-oxo-3-phospholene.



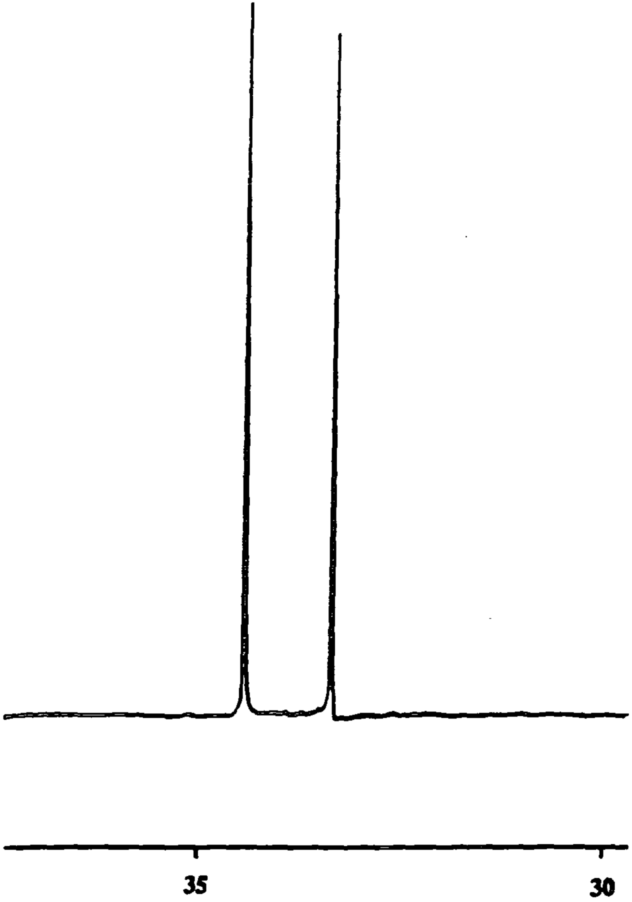
Appendix C4: 1-Phenoxy-1-oxo-3-phospholene.



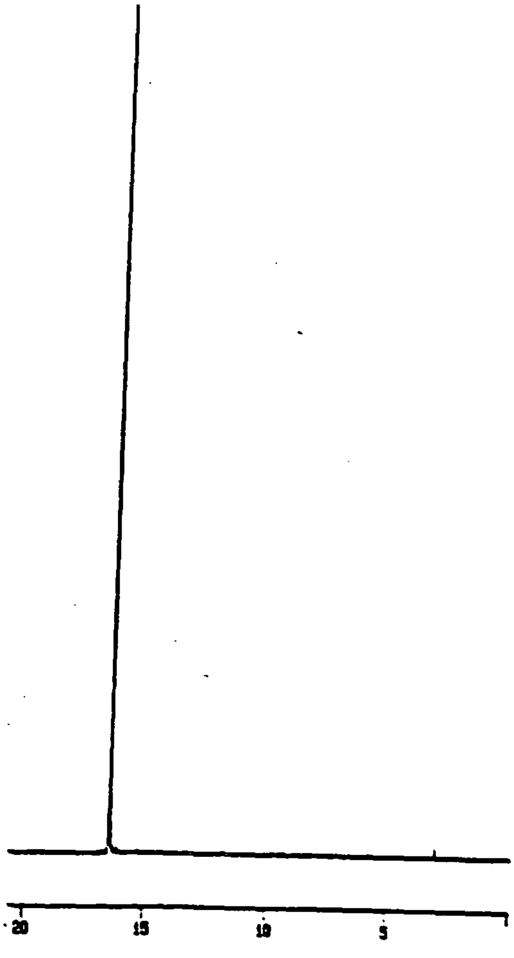
Appendix C5: 1-Neopentoxy-1-oxo-3-phospholene.



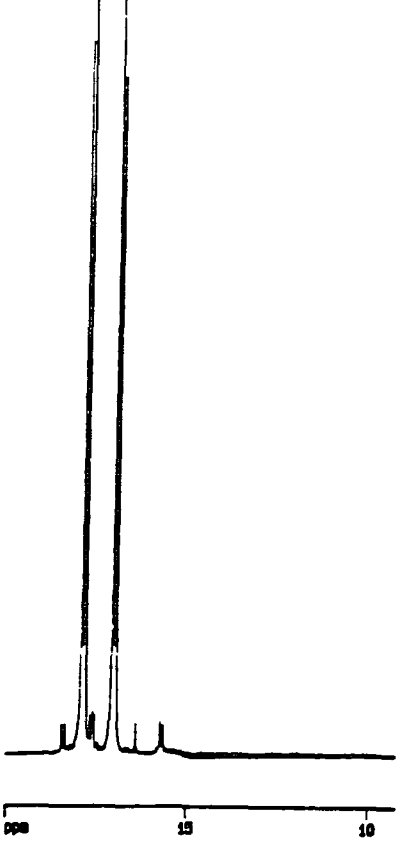
Appendix C6: Dimethylbicyclo[2.2.1]hept-2-ene-5-phosphonate.



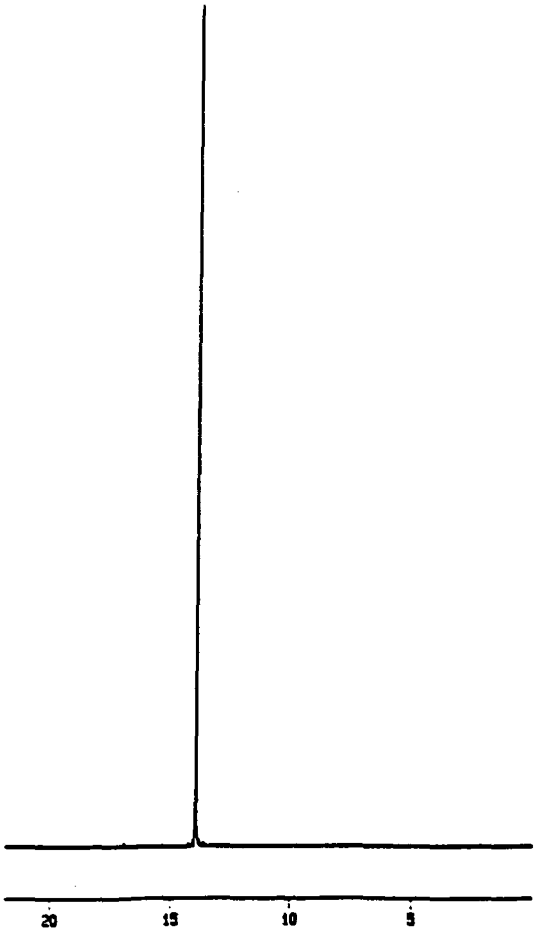
Appendix C7: Diethylbicyclo[2.2.1]hept-2-ene-5-phosphonate.



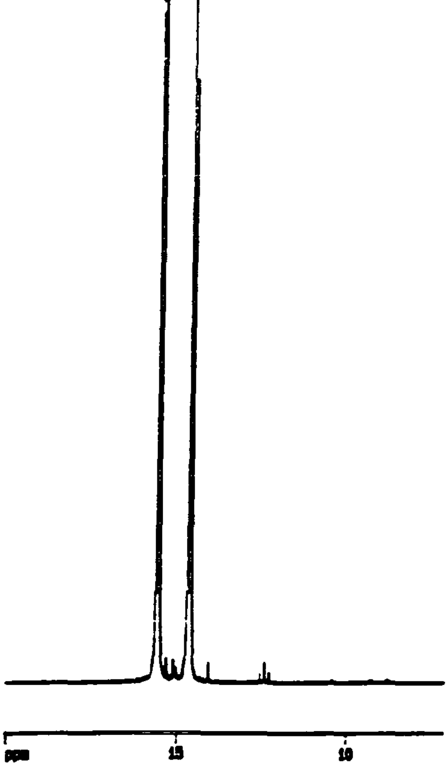
Appendix C8: trans-Ethene-1,2-bis(dimethylphosphonate).



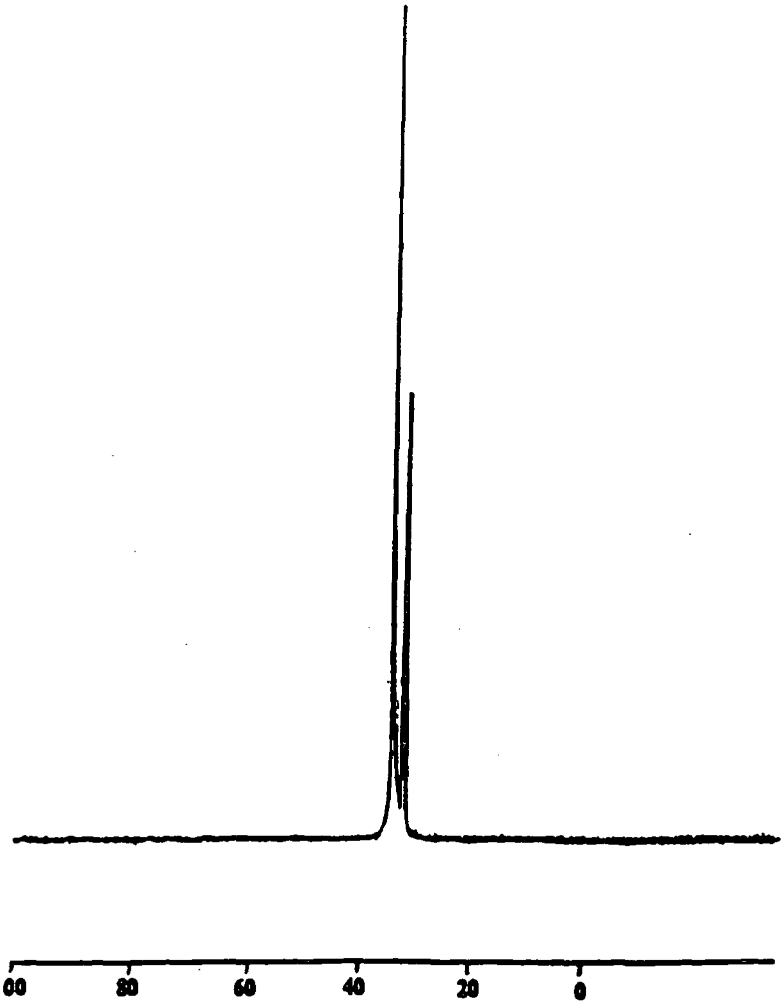
Appendix C9: exo,endo-5,6-bis(dimethylphosphonate)bicyclo[2.2.1]hept-2-ene.



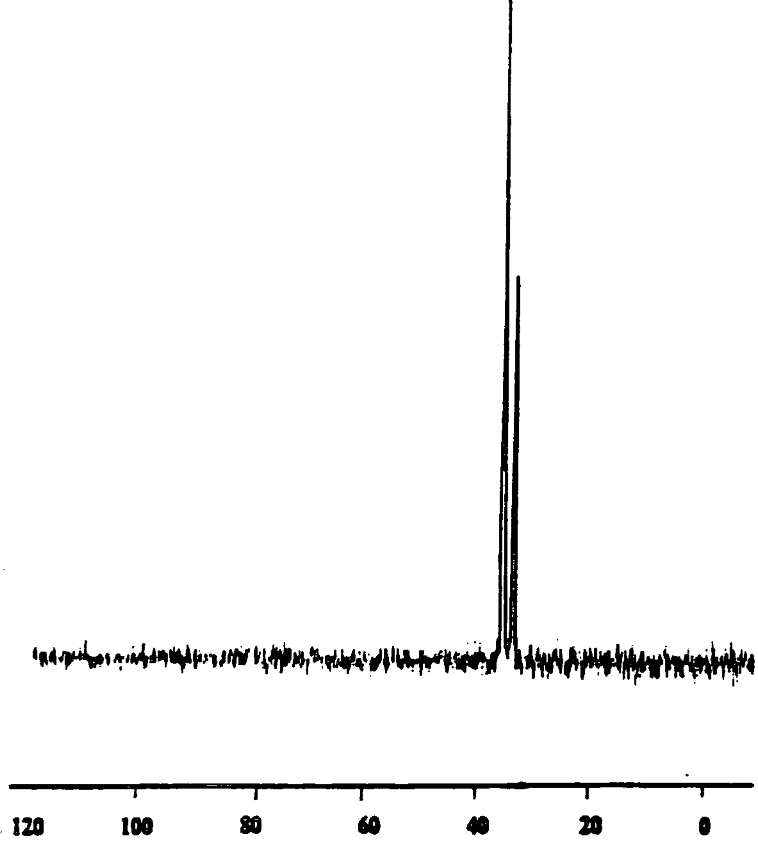
Appendix C10: trans-Ethene-1,2-bis(diethylphosphonate).



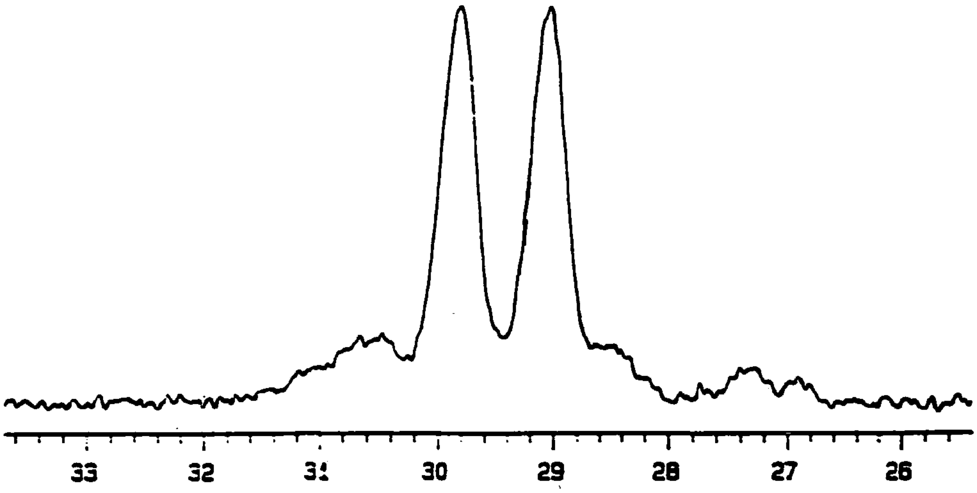
Appendix C11: exo,endo-5,6-bis(diethylphosphonate)bicyclo[2.2.1]hept-2-ene.



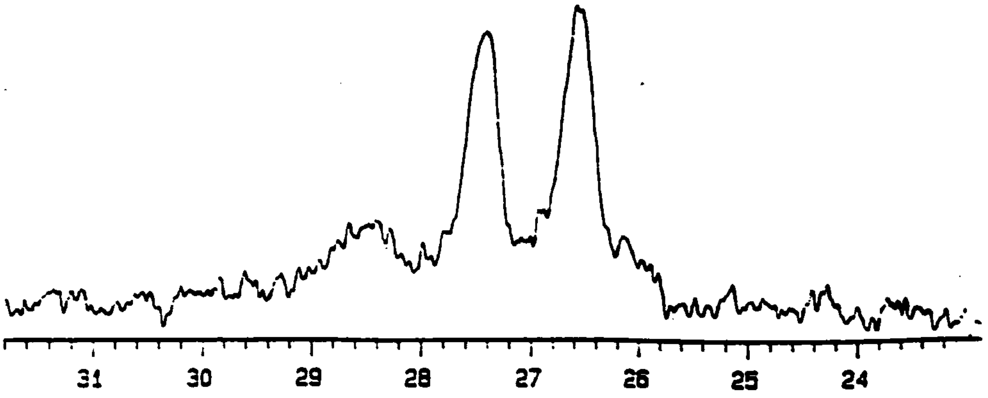
Appendix C12: Poly{2,5-[3-dimethylphosphonate]-cyclopentylene}-vinylene.



Appendix C13: Poly{2,5-[3-diethylphosphonate]-cyclopentylene}-vinylene.

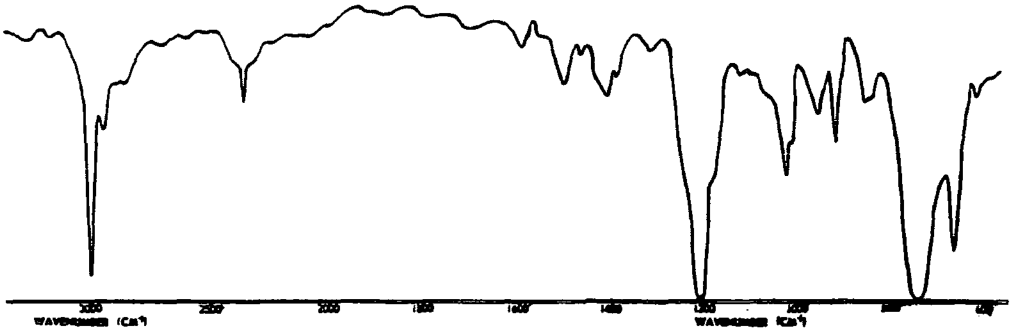


Appendix C14: Poly{2,5-[3,4-bis(dimethylphosphonate)-cyclopentylene}-vinylene.



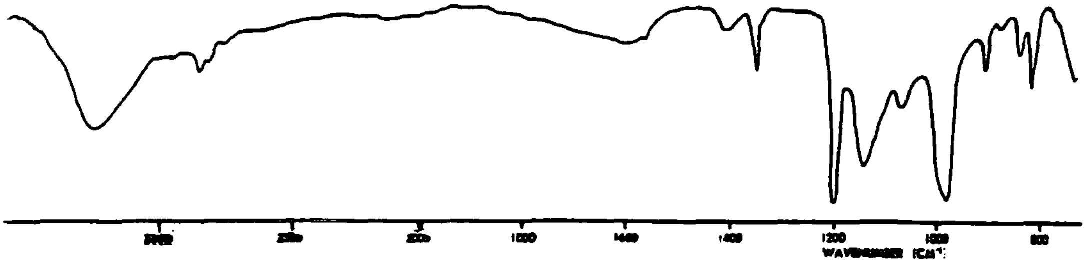
Appendix C15: Poly{2,5-[3,4-bis(diethylphosphonate)-cyclopentylene}-vinylene.

Appendix D:
Infra-red Spectra.

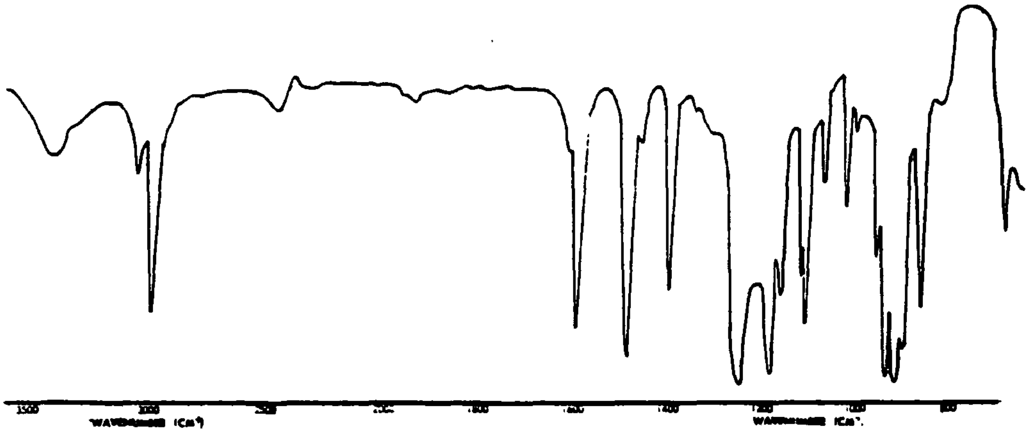


Appendix D1: 1-Chloro-1-oxo-3-phospholene.

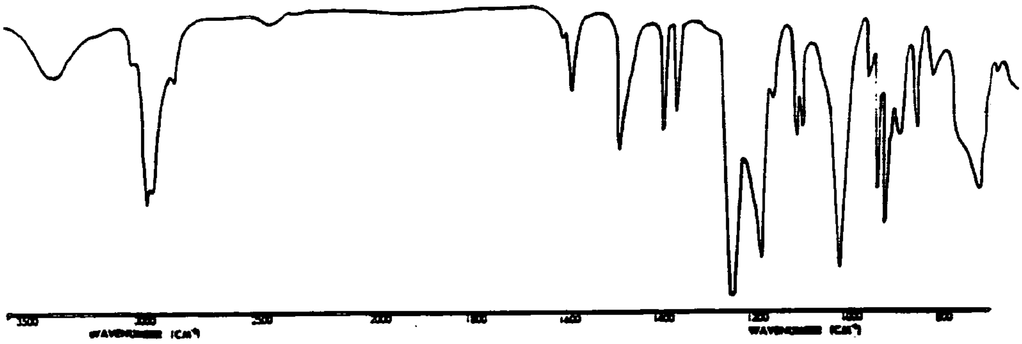
Appendix D2: 1-Hydroxy-1-oxo-3-phospholene.



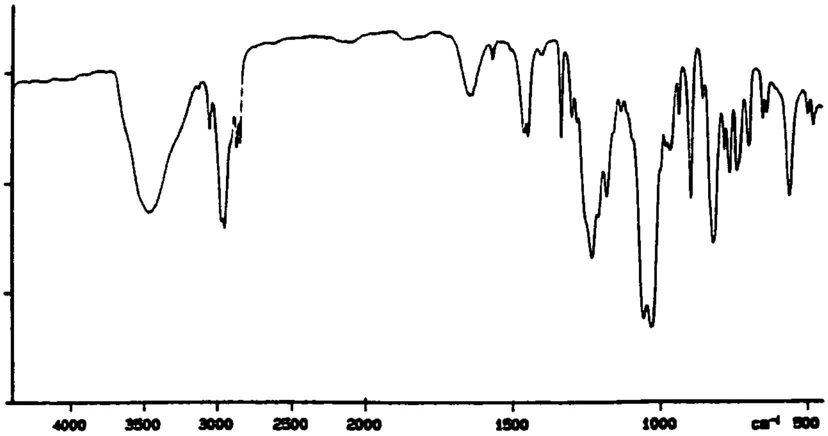
Appendix D3: 1-Methoxy-1-oxo-3-phospholene.



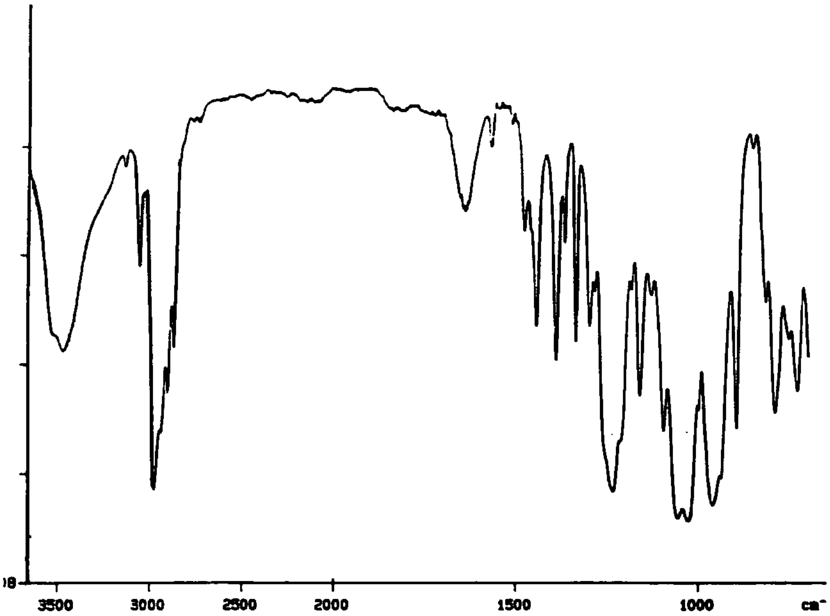
Appendix D4: 1-Phenoxy-1-oxo-3-phospholene.



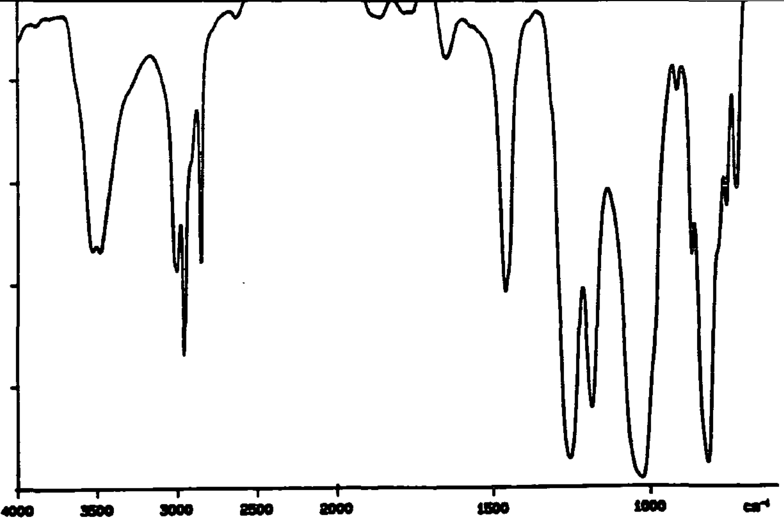
Appendix D5: 1-Neopentoxy-1-oxo-3-phospholene.



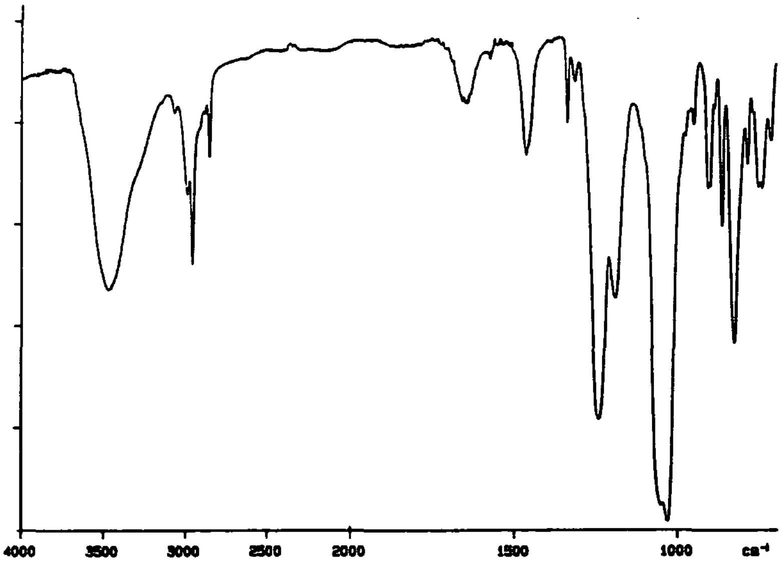
Appendix D6: Dimethylbicyclo[2.2.1]hept-2-ene-5-phosphonate.



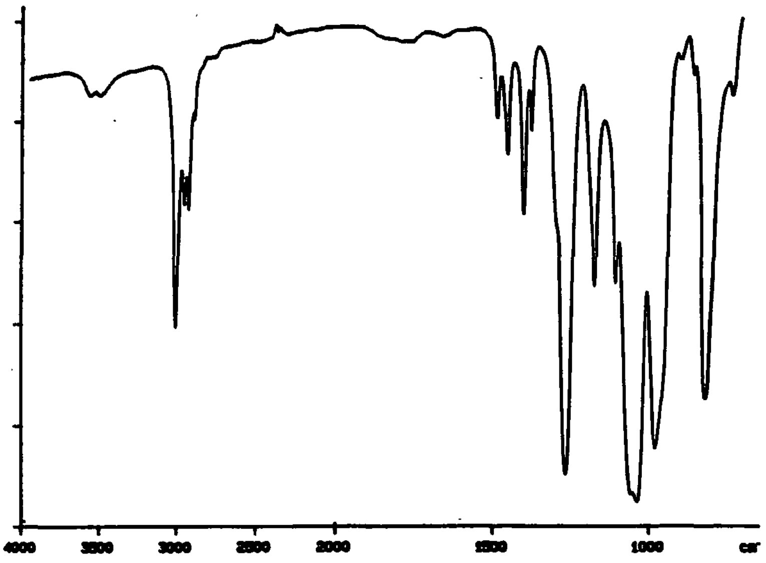
Appendix D7: Diethylbicyclo[2.2.1]hept-2-ene-5-phosphonate.



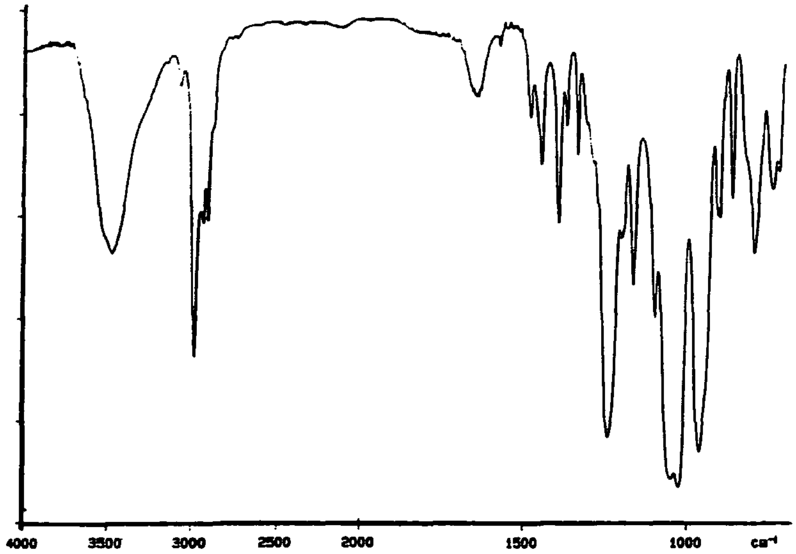
Appendix D8: trans-Ethene-1,2-bis(dimethylphosphonate).



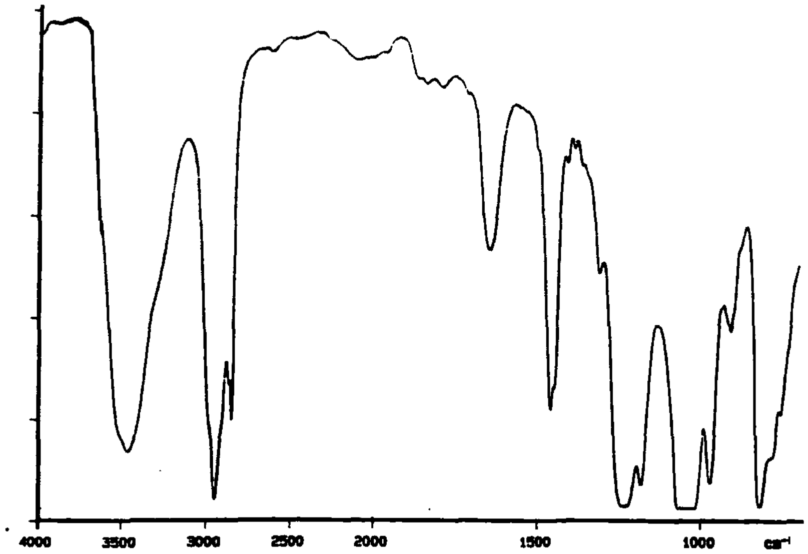
Appendix D9: exo,endo-5,6-bis(dimethylphosphonate)bicyclo[2.2.1]hept-2-ene.



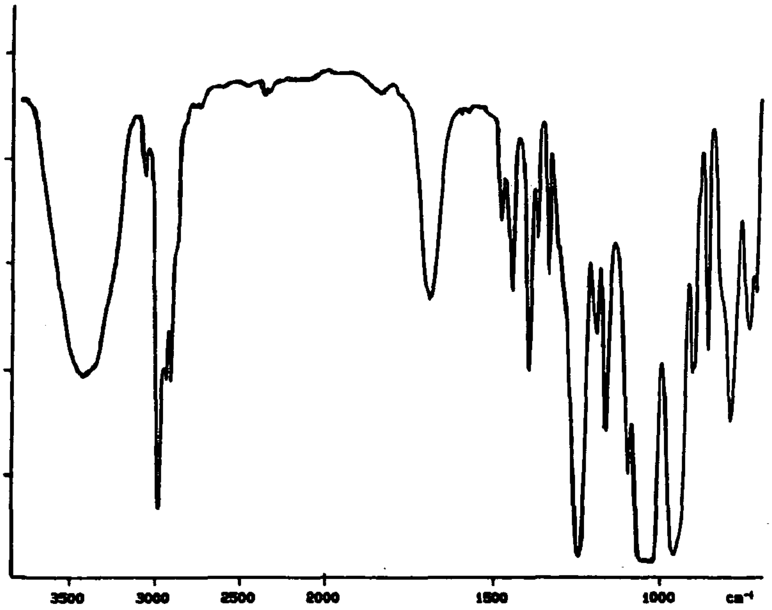
Appendix D10: trans-Ethene-1,2-bis(diethylphosphonate).



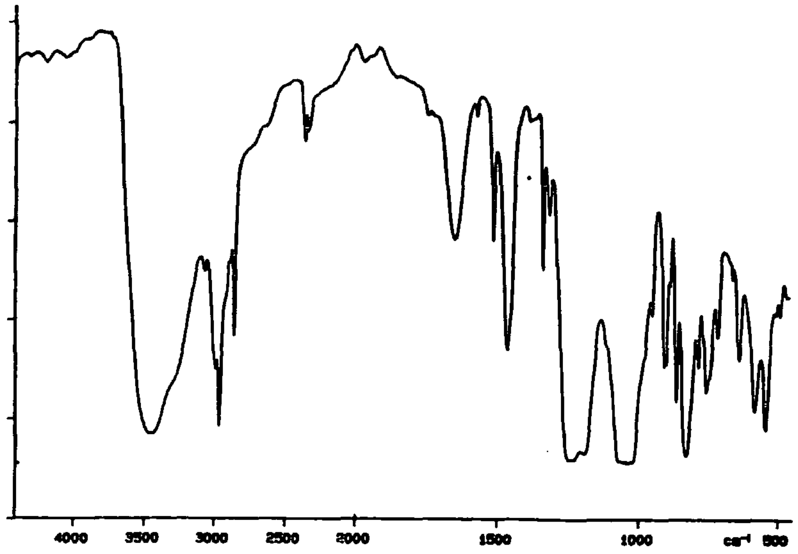
Appendix D11: exo,endo-5,6-bis(diethylphosphonate)bicyclo[2.2.1]hept-2-ene.



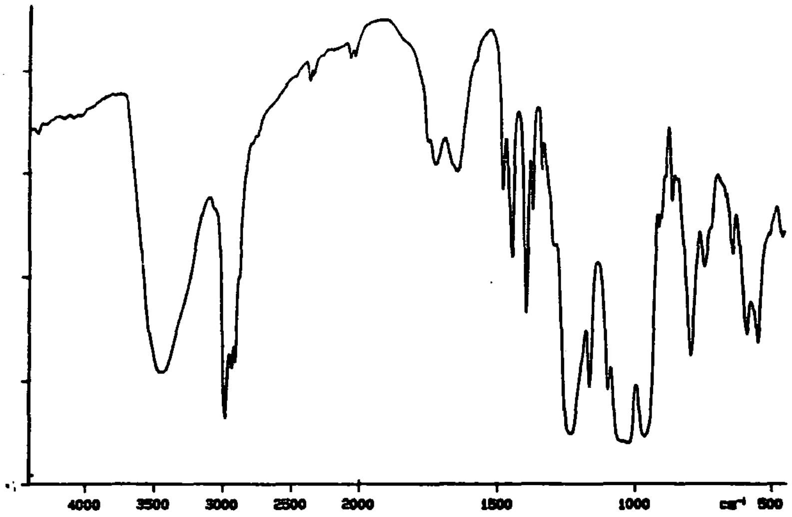
Appendix D12: Poly{2,5-[3-dimethylphosphonate]-cyclopentylene}-vinylene.



Appendix D13: Poly{2,5-[3-diethylphosphonate]-cyclopentylene}-vinylene.



Appendix D14: Poly(2,5-[3,4-bis(dimethylphosphonate)-cyclopentylene]-vinylene.



Appendix D15: Poly(2,5-[3,4-bis(dimethylphosphonate)-cyclopentylene]-vinylene.

Appendix E:

Mass Spectra.

The mass spectra of the compounds obtained during this work are recorded below. The ions are tabulated in the form:

119 (14%, $C_5H_{11}OP$, M-C_4H_6O).

In this example the ion has a mass of 119, its intensity is 14% of the base peak (B). The parent ion is denoted by M and therefore molecular ions in chemical ionisation spectra are denoted by either MNH_4^+ or MH^+.

Appendix E1. ***1-Chloro-1-oxo-3-phospholene.***

Chemical Ionisation (M = C_4H_6ClOP).

102 (23%, $C_4H_7O_2P$, MH^+-Cl).

Appendix E2. ***1-Hydroxy-1-oxo-3-phospholene.***

Electon Impact (M = C_4H_7OP).

118 (37%, $C_4H_7O_2P$, M): **54** (100%, C_4H_6, B): **47** (12%, PO, M-C_4H_7O).

Appendix E3. ***1-Methoxy-1-oxo-3-phospholene.***

Electon Impact (M = $C_5H_9O_2P$).

132 (44%, $C_5H_9O_2P$, M): **78** (10%, CH_3O_2P, M-C_4H_6): **54** (100%, C_4H_6, B).

Appendix E4. ***1-Phenoxy-1-oxo-3-phospholene.***

Electon Impact (M = $C_{10}H_{11}O_2P$).

194 (76%, $C_{10}H_{11}O_2P$, M): **140** (100%, $C_6H_5O_2P$, B):

94 (76%, C_6H_6O, M-$C_4H_6OP\{+H^+\}$): **77** (20%, C_6H_5, M-$C_4H_6O_2P$):

54 (11%, C_4H_6, M-B): **47** (12%, PO, M-C_4H_7O).

Appendix E5. ***1-Neopentoxy-1-oxo-3-phospholene.***

Chemical Ionisation (M = $C_9H_{17}O_2P$).

206 (15%, $C_9H_{21}NO_2P$, MNH_4^+): **189** (100%, $C_9H_{18}O_2P$, MH^+):

136 (10%, $C_4H_7O_2P$ {+NH_4^+}, MNH_4^+-C_5H_{11}{+H^+}):

119 (14%, $C_4H_7O_2P$ {+H^+}, MH^+-C_5H_{11}{+H^+}).

Appendix E6. ***Dimethylbicyclo[2.2.1]hept-2-ene-5-phosphonate.***

Electon Impact (M = $C_9H_{15}O_3P$).

202 (12%, $C_9H_{15}O_3P$, M): **137** (100%, $C_4H_{10}O_3P$, B):

105 (30%, $C_3H_6O_2P$, B-CH_3O-H^+): **92** (43%, C_7H_8, M-$C_2H_6O_3P$-H^+):

79 (14%, PO_3, M-C_9H_{15}): **66** (76%, C_5H_6, M-$C_4H_9O_3P$).

Appendix E7. ***Diethylbicyclo[2.2.1]hept-2-ene-5-phosphonate.***

Electon Impact (M = $C_{11}H_{19}O_3P$).

230 (4%, $C_{11}H_{19}O_3P$, M): **165** (100%, $C_6H_{14}O_3P$, B):

137 (32%, $C_4H_{10}O_3P$, M-C_7H_9): **109** (90%, $C_2H_6O_3P$, B-2C_2H_5{+2H^+}):

92 (20%, C_7H_8, M-$C_4H_{10}O_3P$-H^+): **66** (45%, C_5H_6, M-$C_6H_{13}O_3P$).

Appendix E8. ***trans-Ethene-1,2-bis(dimethylphosphonate).***

Electon Impact (M = $C_6H_{14}O_6P_2$).

244 (2%, $C_6H_{14}O_6P_2$, M): **150** (17%, $C_4H_8O_2P_2$, M-2CH_3O_2):

135 (100%, $C_4H_8O_3P$, B): **109** (14%, $C_2H_6O_3P$, M-B):

93 (35%, $C_2H_6O_2P$, M-$C_4H_8O_4P$): **79** (13%, PO_3, M-$C_6H_{14}O_3P$).

Appendix E9. ***exo,endo-1,2-bis(dimethylphosphonate)bicyclo[2.2.1]hept-2-ene.***

Electon Impact (M = $C_{11}H_{20}O_6P_2$).

310 (10%, $C_{11}H_{20}O_6P_2$, M): **244** (100%, $C_6H_{14}O_6P_2$, B):

135 (76%, $C_4H_8O_3P$, B-$C_2H_6O_3P$): **109** (90%, $C_2H_6O_3P$, 135-C_2H_2):

66 (34%, C_5H_6, M-B).

Appendix E10. ***trans-Ethene-1,2-bis(diethylphosphonate).***

Electon Impact (M = $C_{10}H_{22}O_6P_2$).

300 (6%, $C_{10}H_{22}O_6P_2$, M): **255** (10%, $C_8H_{17}O_5P_2$, M-C_2H_5O):

163 (100%, $C_6H_{12}O_3P$, B): **135** (60%, $C_4H_8O_3P$, B-C_2H_4).

Appendix E11. ***exo,endo-1,2-bis(diethylphosphonate)bicyclo[2.2.1]hept-2-ene.***

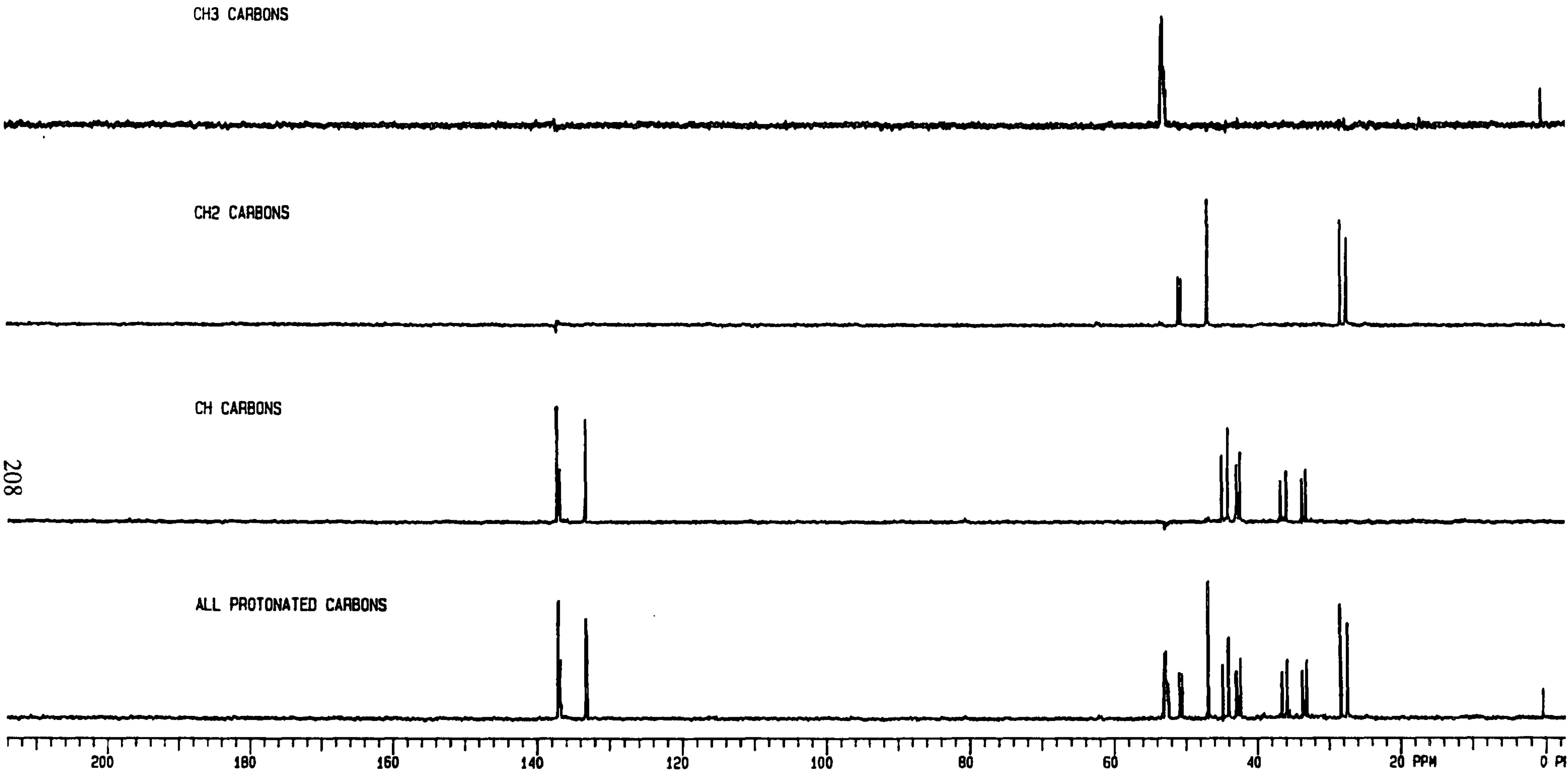
Electon Impact (M = $C_{15}H_{28}O_6P_2$)

366 (11%, $C_{15}H_{28}O_6P_2$, M): **301** (7%, $C_{10}H_{22}O_6P_2$, M-C_5H_5):

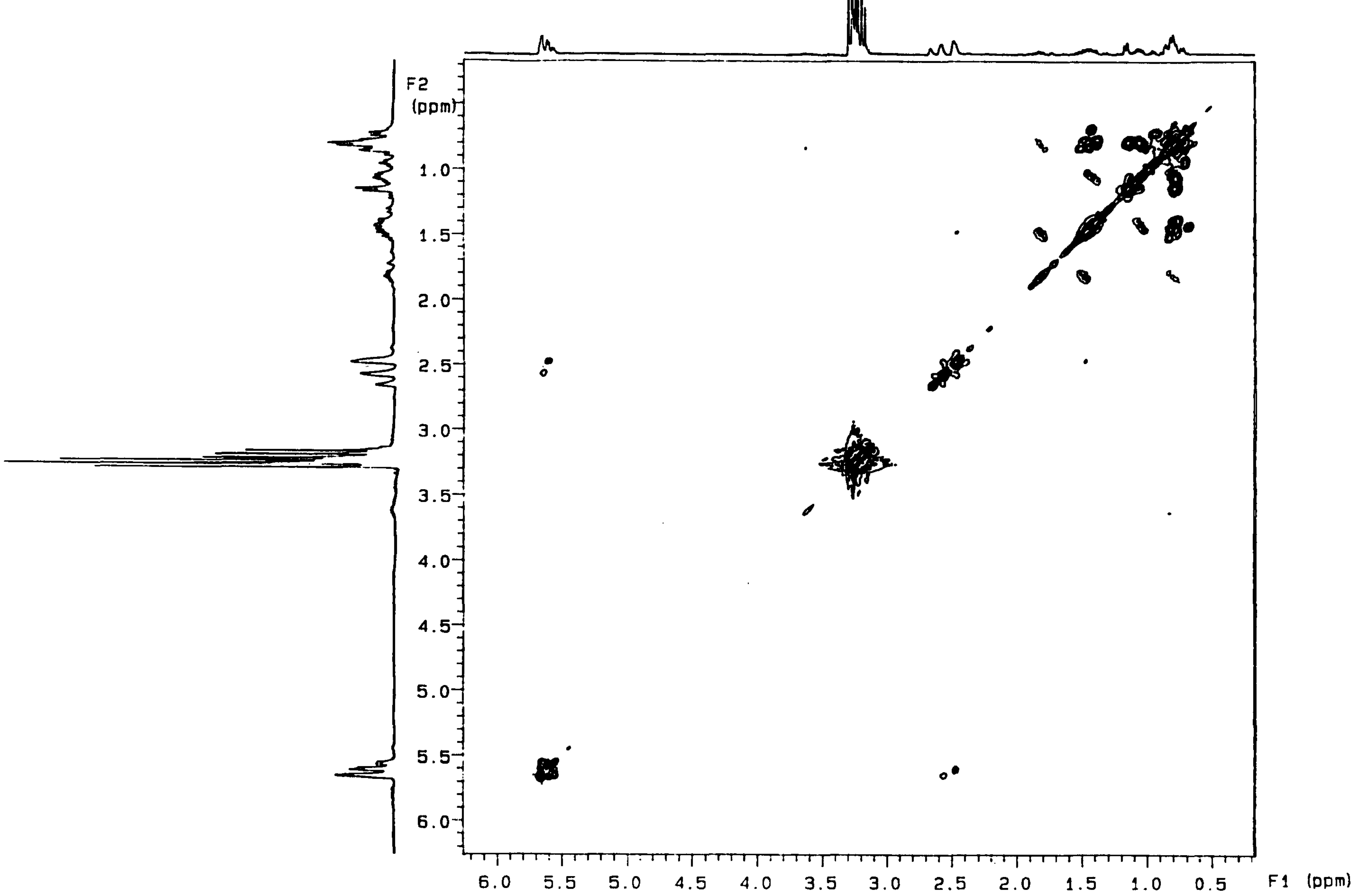
229 (100%, $C_{11}H_{18}O_3P$, B): **163** (67%, $C_6H_{12}O_3P$, 301-$C_4H_{10}O_3P$):

135 (54%, $C_4H_8O_3P$, 163-C_2H_4): **66** (39%, C_5H_6, M-$C_{10}H_{22}O_6P_2$).

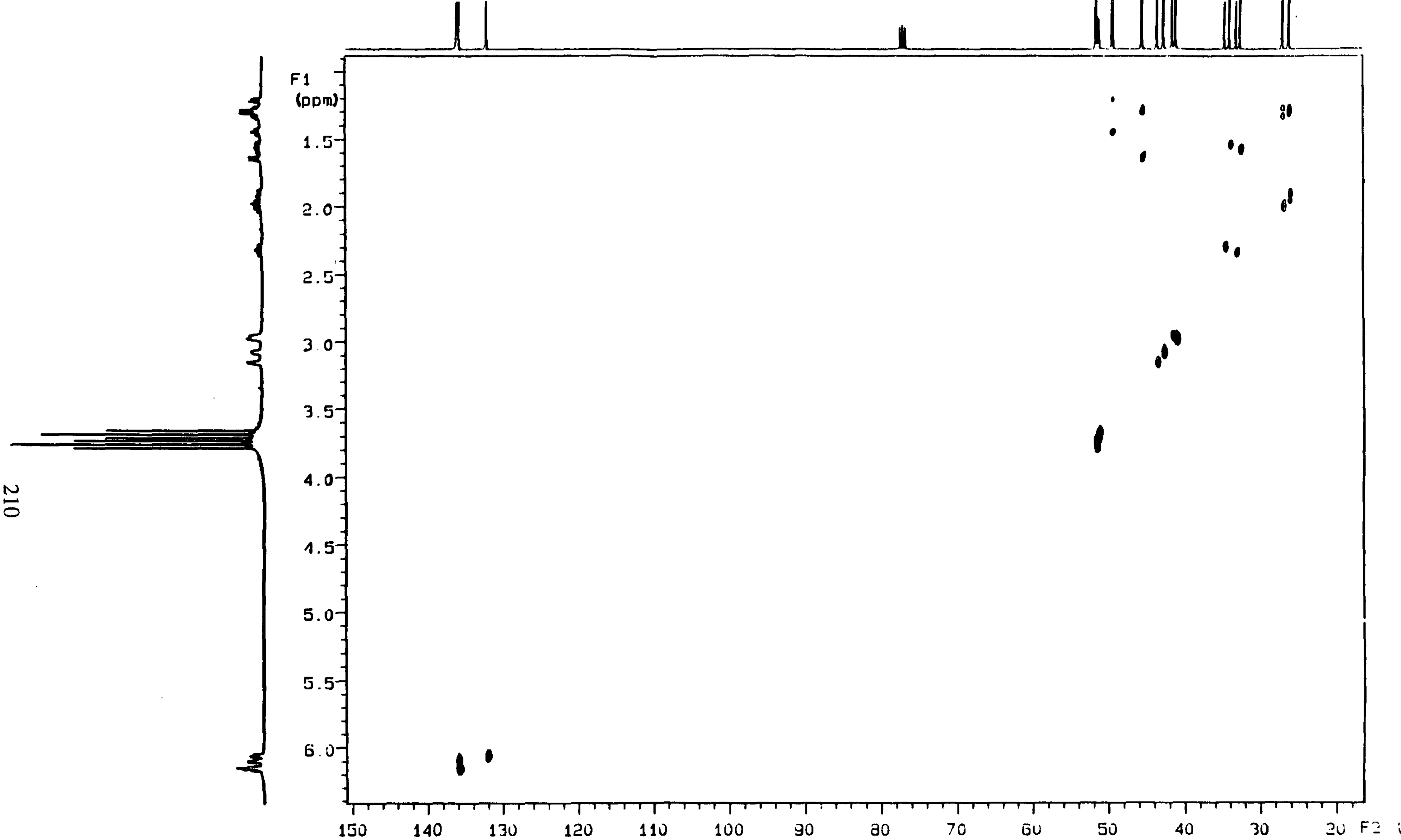
Appendix F:
DEPT, COSY and HETCOR Spectra.



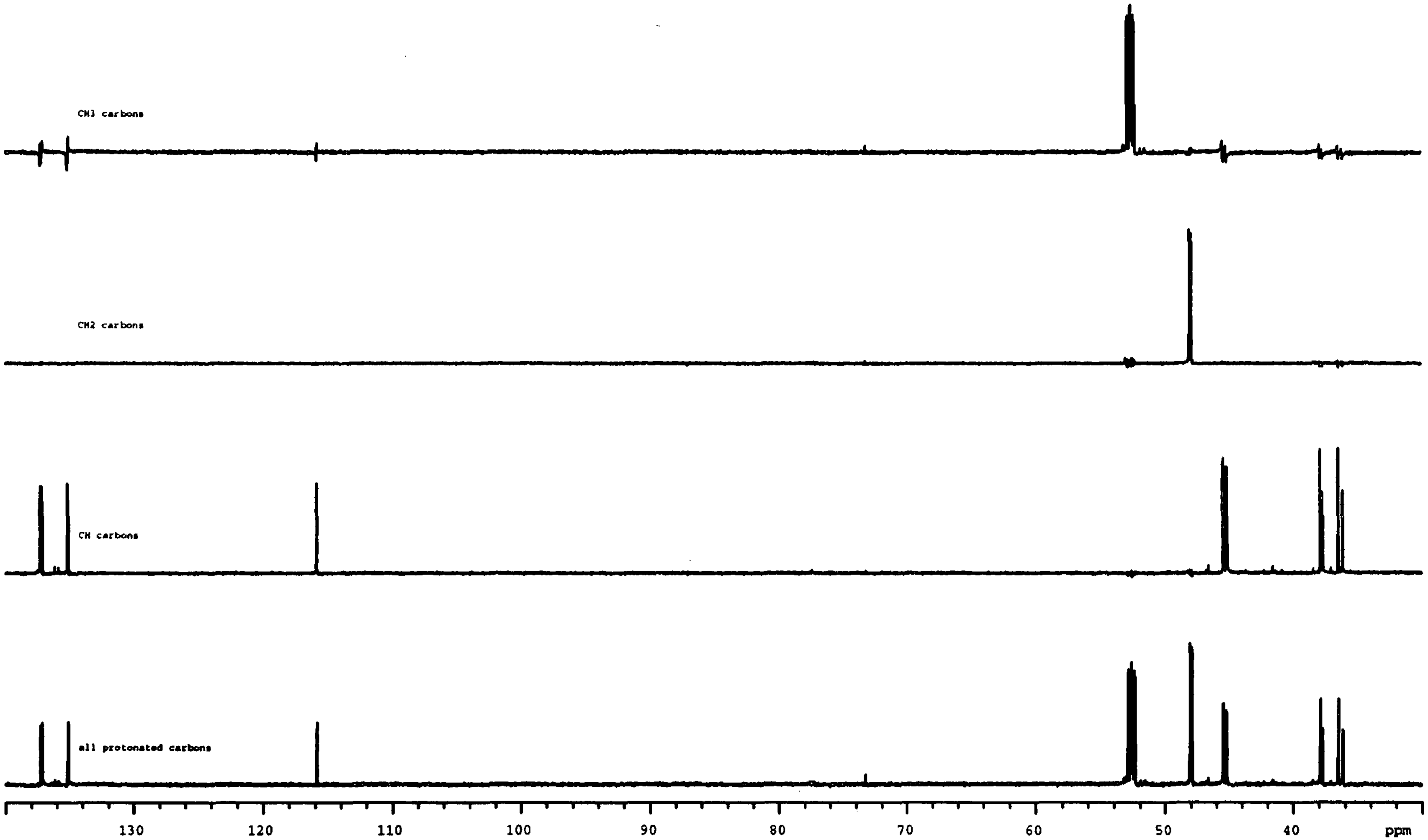
Appendix F1: DEPT Spectrum of Dimethylbicyclo[2.2.1]hept-2-ene-5phosphonate.



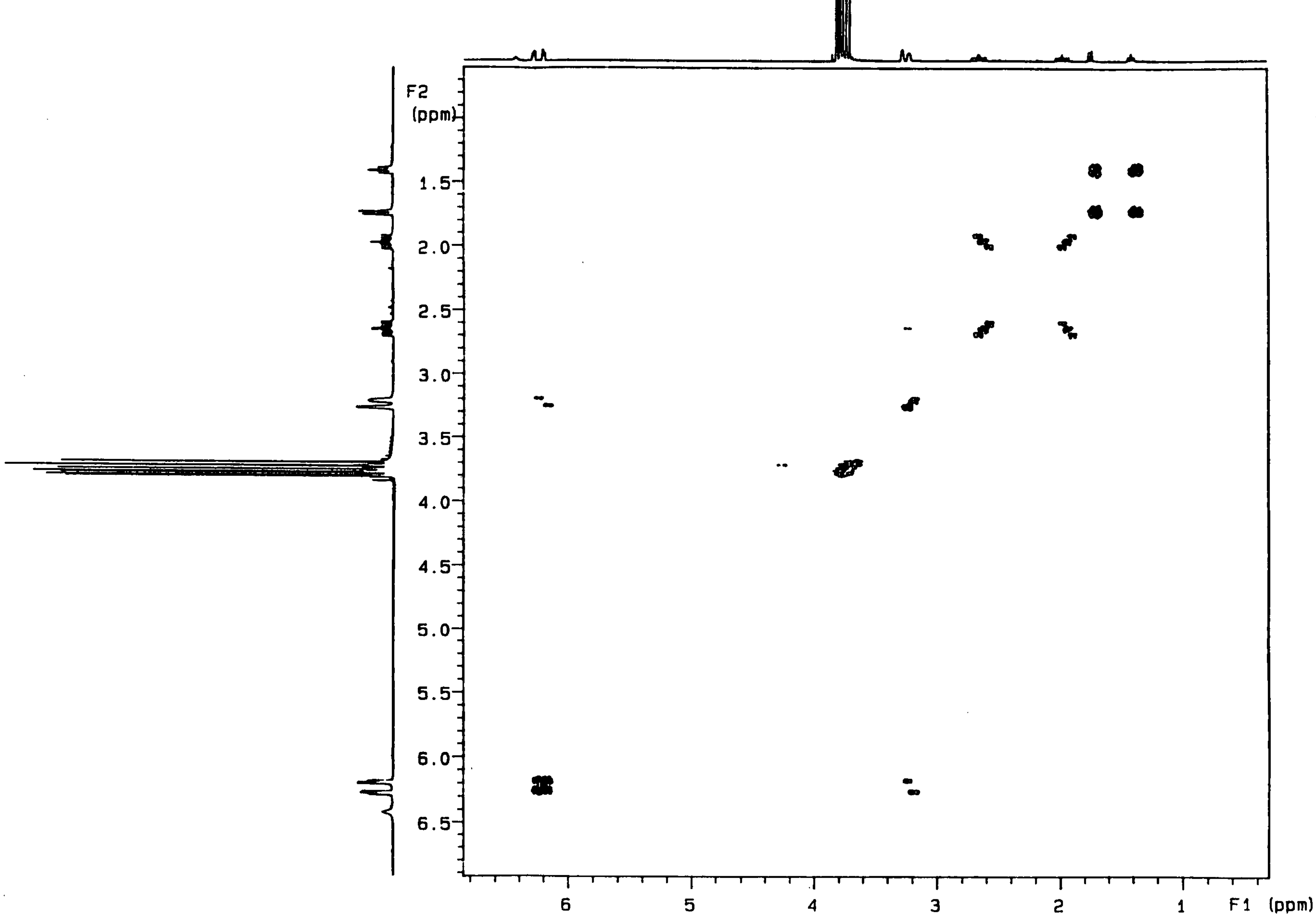
Appendix F2: COSY Spectrum of Dimethylbicyclo[2.2.1]hept-2-ene-5phosphonate.



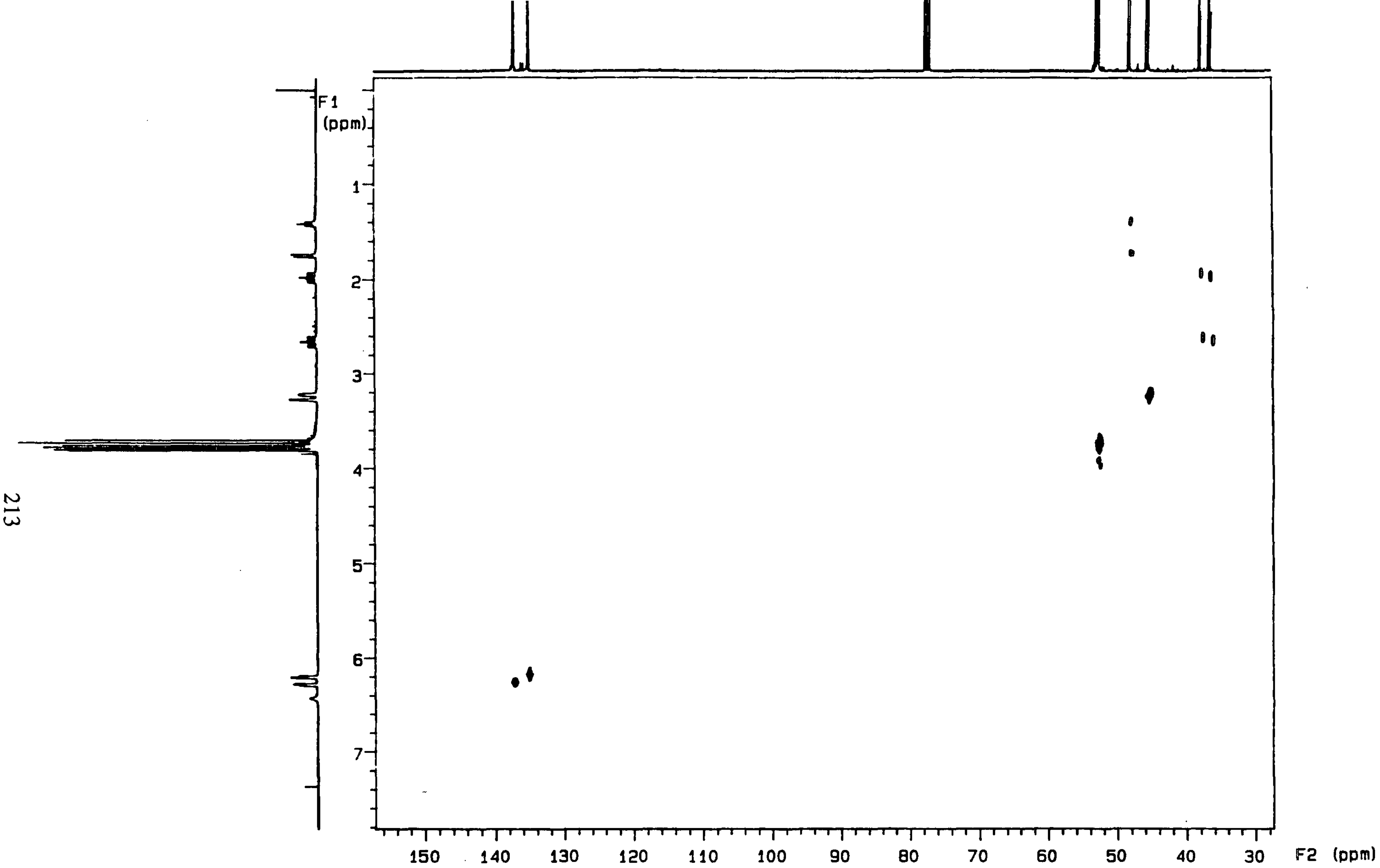
Appendix F3: HETCOR Spectrum of Dimethylbicyclo[2.2.1]hept-2-ene-5phosphonate.



Appendix F4: DEPT Spectrum of exo,endo-5,6-bis(dimethylphosphonate)bicyclo[2.2.1]hept-2-ene.



Appendix F5: COSY Spectrum of exo,endo-5,6-bis(dimethylphosphonate)bicyclo[2.2.1]hept-2-ene.



Appendix F6: HETCOR Spectrum of exo,endo-5,6-bis(dimethylphosphonate)bicyclo[2.2.1]hept-2-ene.

Appendix G:
ABX Spin System Analysis.

The ABX Spectrum.

All NMR spectra were recorded on a Bruker AMX 500 NMR spectrometer operating at 125.770 MHz for ^{13}C NMR and 202.460 MHz for ^{31}P NMR. The computer simulations were performed by the Varian NMR Fortran Program LAOCOON (LAME). For a thorough discussion of the mathematics, an explanation of the ABX spin system and an outline of the standard algorithms used in the computer simulations, the reader is directed to a number of publications.[185-189]

A) *trans*-Ethene-1,2-bis(dimethylphosphonate).

The ^{13}C NMR spectrum of *trans*-ethene-1,2-bis(dimethylphosphonate) can be assigned as an AA′X spin system, an ABX spin system, which occurs in symmetrical molecules containing two chemically equivalent nuclei of high natural abundance, such as ^{31}P, bound to a nucleus of low natural abundance, for example ^{13}C. The resultant spectrum of *trans*-ethene-1,2-bis(dimethylphosphonate) occurs as an ABX spin system due to an isotopic effect, where one of the vinylic carbons is a ^{13}C carbon and the other a ^{12}C carbon (*Figure G1*) giving an unsymmetrical molecule. There will also be signals arising from the symmetrical molecule where both carbons are ^{13}C, but due to the low abundance of the ^{13}C isotope the signals are very weak and are not observed under our measuring conditions.

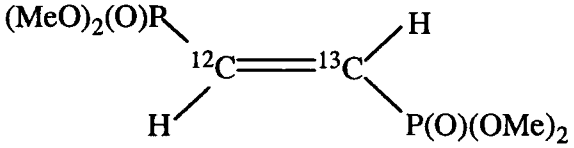


Figure G1: trans-Ethene-1,2-bis(dimethylphosphonate).

The $^{3}J_{PP}$ coupling constant can not be obtained from the conventional ^{31}P spectrum so observation of the ^{13}C satellites in the ^{31}P spectrum can be used to determine its value. The ^{13}C satellites comprise two subspectra which are almost symmetrical about the main ^{31}P peak. The two subspectra are not actually symmetrical due to the isotope effects. Observation of the spectrum reveals that the J_{PP} coupling constant can be measured at four points (*Figure G.2*) corresponding to the AB spacings. Values for D_+ and D_- the can also be measured from the spectrum.

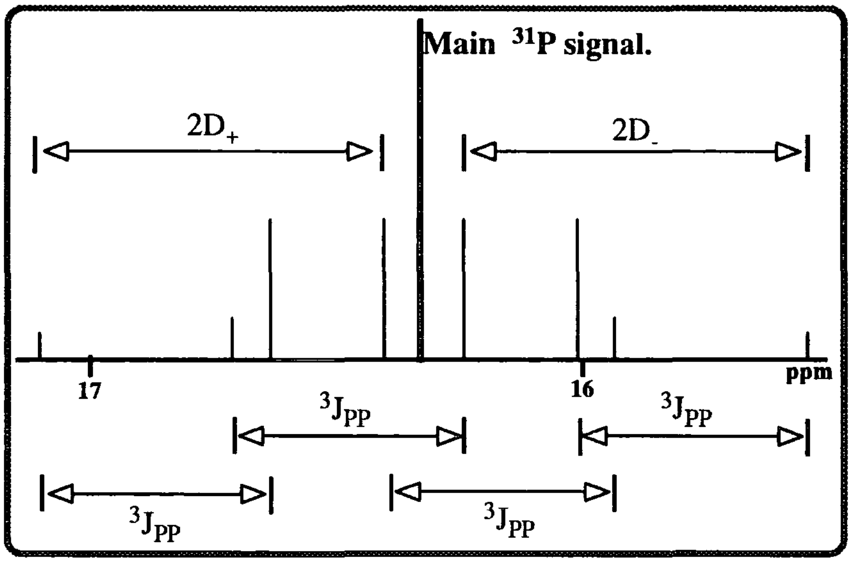


Figure G.2: The ^{13}C satellite peaks on the ^{31}P spectrum of trans-ethene-1,2-bis(dimethylphosphonate).

The values calculated from the ^{31}P spectrum (202.460 MHz) are:

D_+ = 64.06Hz, D_- = 65.01Hz (or vice versa)

and $^3J_{PP}$ = 94.10Hz.

As we are dealing with an isotopic effect the chemical shifts of the two phosphorus nuclei, ν_A and ν_B, are very similar so $\nu_A \approx \nu_B$ and so $D_+ \approx D_-$.

The vinylic region of the ^{13}C NMR spectrum comprises six signals (*Figure G.3*) and it has been shown that measurements taken from the spectrum can give a value for $|J_{AX} + J_{BX}|$ as well as D_+ and D_-, which confirm the values calculated from the ^{31}P spectrum.

The values calculated from the ^{13}C spectrum are:

$$\mathbf{D_+ = 65.02Hz,\ D_- = 63.99Hz\ (or\ vice\ versa)}$$

$$\mathbf{and\ |J_{AX} + J_{BX}| = 181.38Hz.}$$

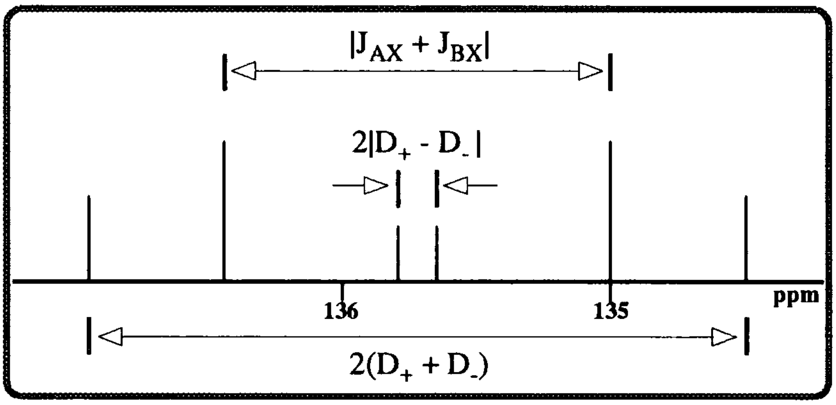


Figure G.3: The vinylic region of the ^{13}C spectrum of trans-ethene-1,2-bis(dimethylphosphonate).

Equations have been derived to calculate the coupling constants $^1J_{PC}$ and $^2J_{PC}$ (J_{AX} and J_{BX}) and all the correct chemical shifts in the ABX spin system using the information obtained from the ^{13}C satellite peaks on the ^{31}P spectrum and from the vinylic region of the ^{13}C NMR spectrum.

$$D_+ = \tfrac{1}{2}\{ [\nu_A - \nu_B + \tfrac{1}{2}(J_{AX} - J_{BX})]^2 + J_{AB}{}^2 \}^{1/2}$$

$$D_- = \tfrac{1}{2}\{ [\nu_A - \nu_B - \tfrac{1}{2}(J_{AX} - J_{BX})]^2 + J_{AB}{}^2 \}^{1/2}$$

The average values of D_+ and D_-, taken from the ^{31}P and the ^{13}C NMR spectra, were used in the following calculations.

We know the values of D_+, D_- and J_{AB} ($^3J_{PP}$) and substituting these into the above equations results in two simultaneous equations:

$$|\nu_A-\nu_B + {}^1/_2(J_{AX} - J_{BX})| = 86.84\text{Hz}$$

$$|\nu_A-\nu_B - {}^1/_2(J_{AX} - J_{BX})| = 89.75\text{Hz}$$

which gives two sets of roots:

$$|\nu_A-\nu_B| = 88.29\text{Hz} \quad \text{and} \quad |J_{AX} - J_{BX}| = 2.91\text{Hz}.$$

$$\text{or} \quad |\nu_A-\nu_B| = 1.46\ \text{Hz} \quad \text{and} \quad |J_{AX} - J_{BX}| = 176.58\ \text{Hz}.$$

but since we are dealing with an isotopic effect ν_A-ν_B is very small and so J_{AX} - J_{BX} >> ν_A-ν_B and making use of the known value for $|J_{AX} + J_{BX}|$, obtained from the ^{13}C spectrum, we can calculate the values for J_{AX} and J_{BX}:

$$|J_{AX}| = 178.98\text{Hz and } |J_{BX}| = 2.40\text{Hz}.$$

Double resonance experiments have to be used to determine the absolute signs of J_{AX} and J_{BX} and the relative sign of J_{AB}.

The centre of the eight ^{13}C satellite peaks gives a value for $^1/_2(\nu_A + \nu_B)$, this was calculated as 3317.39Hz, and since we have calculated that $(\nu_A - \nu_B)$ = 1.46Hz, we can therefore calculate the corrected shifts of the two phosphorus nuclei ν_A and ν_B.

$$\nu_A = 3318.12\text{Hz} = 16.389\text{ppm}.$$

$$\nu_B = 3316.66\text{Hz} = 16.382\text{ppm}.$$

Computer simulations have been performed using our calculated values of the shifts and coupling constants and the results have been compared to the vinylic region of the ^{13}C NMR spectrum (*Figure G.4*). As can be seen from the results the computer simulation fits well with the experimental data.

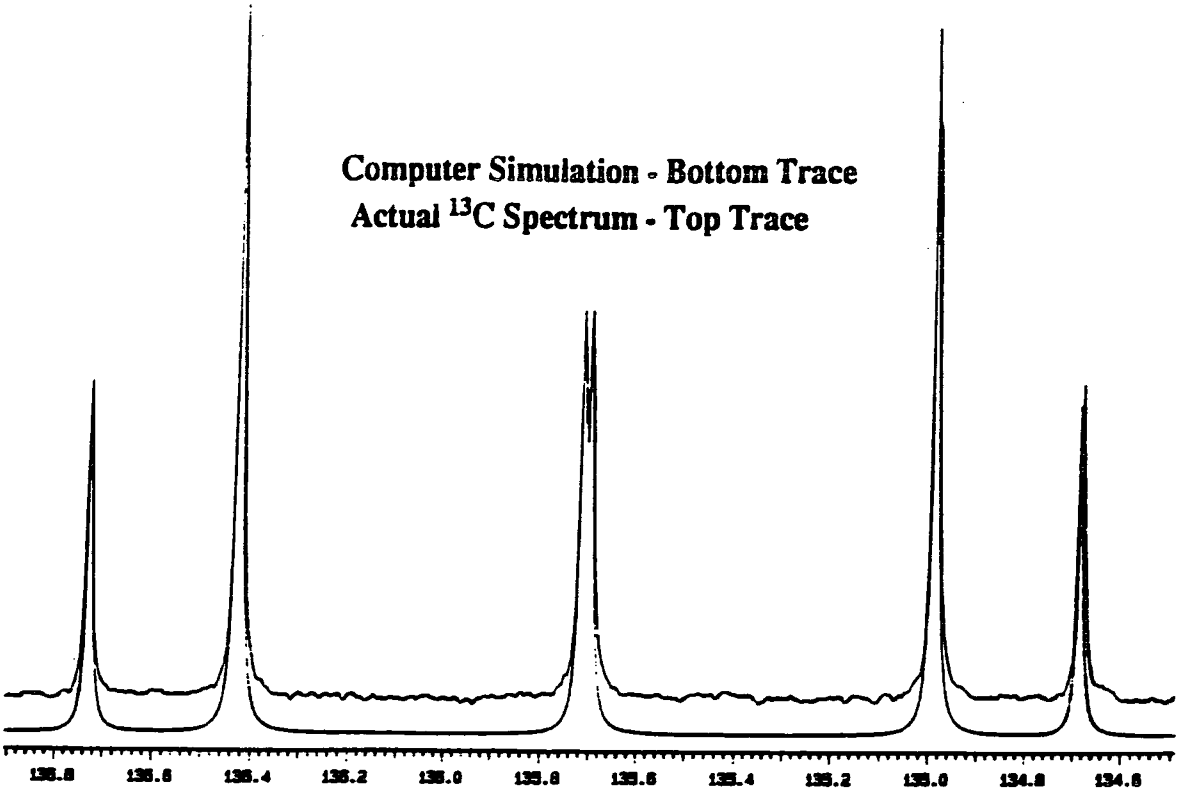
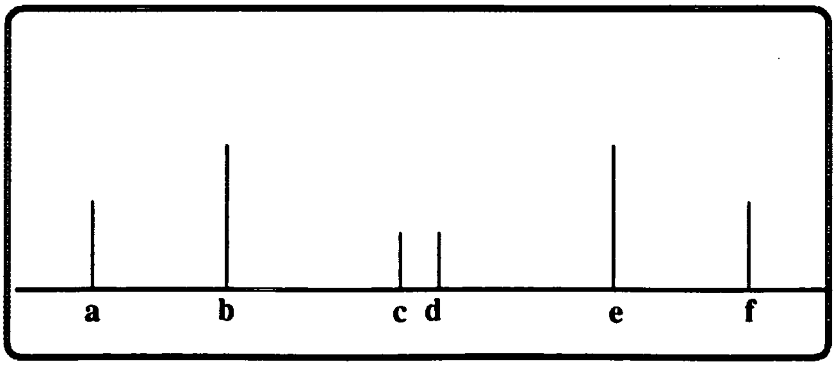


Figure G.4: Comparison of the vinylic region of the ^{13}C NMR spectrum of trans-ethene-1,2-bis(dimethylphosphonate) with the computer simulation results.

The phosphonate methyl signals appear as a triplet, which arises from there being no five bond P-C coupling, hence $J_{BX}= 0$.



This results in the peaks at c and d coalescing to form the centre peak of the triplet and the peaks at a and f disappearing. The peaks at b and e therefore form the outer peaks of the triplet with the coupling constant between them being $^2J_{PC}$ (J_{AX}). This value was measured as 5.9Hz.

B) *trans*-Ethene-1,2-bis(diethylphosphonate).

The same calculations can be used to determine the coupling constants $^1J_{PC}$ and $^2J_{PC}$ (J_{AX} and J_{BX}) and all the correct chemical shifts of *trans*-ethene-1,2-bis(diethylphosphonate).

The values calculated from the satellites on the ^{31}P spectrum and from the vinylic region of the ^{13}C NMR spectrum are:

$$\mathbf{D_+ = 63.63Hz,\ D_- = 64.70Hz\ (or\ vice\ versa)}$$

$$\mathbf{^3J_{PP} = 93.27Hz\ and}$$

$$\mathbf{|J_{AX} + J_{BX}| = 180.34Hz.}$$

The average values of D_+ and D_-, taken from the ^{31}P and the ^{13}C NMR spectra, were used in the calculations. These values can then be substituted in the following equations:

$$D_+ = \tfrac{1}{2}\{ [\nu_A - \nu_B + \tfrac{1}{2}(J_{AX} - J_{BX})]^2 + J_{AB}^2 \}^{1/2}$$

$$D_- = \tfrac{1}{2}\{ [\nu_A - \nu_B - \tfrac{1}{2}(J_{AX} - J_{BX})]^2 + J_{AB}^2 \}^{1/2}$$

this again results in two simultaneous equations:

$$|\nu_A - \nu_B + \tfrac{1}{2}(J_{AX} - J_{BX})| = \mathbf{86.60Hz}$$

$$|\nu_A - \nu_B - \tfrac{1}{2}(J_{AX} - J_{BX})| = \mathbf{89.63Hz}$$

which gives the two sets of roots:

$$|\nu_A - \nu_B| = \mathbf{88.11Hz} \quad \mathbf{and} \quad |J_{AX} - J_{BX}| = \mathbf{3.03Hz.}$$

$$\mathbf{or} \quad |\nu_A - \nu_B| = \mathbf{1.51\ Hz} \quad \mathbf{and} \quad |J_{AX} - J_{BX}| = \mathbf{176.23\ Hz.}$$

but since we are dealing with an isotopic effect ν_A-ν_B is very small and so J_{AX} - J_{BX} >> ν_A-ν_B and making use of the known value for $|J_{AX} + J_{BX}|$, obtained from the ^{13}C spectrum, we can calculate the values for J_{AX} and J_{BX}:

$$|J_{AX}| = 178.30\text{Hz and } |J_{BX}| = 2.04\text{Hz.}$$

Double resonance experiments have to be used to determine the absolute signs of J_{AX} and J_{BX} and the relative sign of J_{AB}.

The centre of the eight ^{13}C satellite peaks gives a value for $^1/_2(\nu_A+ \nu_B)$, this was calculated as 2825.23Hz, and since we have calculated that $(\nu_A- \nu_B)$ = 1.57Hz, we can therefore calculate the corrected shifts of the two phosphorus nuclei ν_A and ν_B.

$$\nu_A = 2826.02\text{Hz} = 13.958\text{ppm.}$$

$$\nu_B = 2824.45\text{Hz} = 13.951\text{ppm.}$$

The CH_2 and CH_3 groups on the phosphonate $[P(O)(OCH_2CH_3)_2]$ substituent both give rise to triplets as there is no four or five bond P-C coupling. These values were measured from the coupling between the two outer peaks of the triplet giving values of 5.55Hz and 6.24Hz respectively.

Appendix H:
Chain Transfer Kinetics.

Chain Transfer Kinetics.[39,184]

In the following discussion (*) indicates the chain initiating/propagating species (i.e. metallocarbene for ROMP).

Propagating Species Formation.

$$I \xrightarrow{k_f} R^* \qquad \textbf{(A)}$$

Initiation.

$$R^* + M \xrightarrow{k_i} RM^* \qquad \textbf{(B)}$$

Propagation

$$RM_n^* + M \xrightarrow{k_p} RM_{n+1}^* \qquad \textbf{(C)}$$

Termination

$$RM_n^* + RM_m^* \xrightarrow{k_t} \text{Dead Polymer} \qquad \textbf{(D}_\textbf{a}\textbf{)}$$

$$RM_n^* \xrightarrow{k_t'} \text{Dead Polymer} \qquad \textbf{(D}_\textbf{b}\textbf{)}$$

- where k_f, k_i, k_p and k_t are the rate constants for catalyst dissociation, initiation, propagation, bimolecular termination and unimolecular termination respectively and M represents the monomer molecule.

The termination steps are a combination of all termination reactions including disproportionation, coupling and any other process which gives a dead polymer. Dead polymer refers to cessation of growth from the propagating species.

The rate at which the monomer disappears is the same as the rate of polymerisation and this in turn is equal to the sum of the rates of initiation and propagation.

$$^{-d[M]}/_{dt} = R_i + R_p \qquad \text{(E)}$$

The number of monomer molecules reacting in the propagation step is much greater than the number in the initiation step, hence we can, to a first approximation, equate the rate of polymerisation to the rate of propagation.

$$^{-d[M]}/_{dt} = R_p \qquad \text{(F)}$$

The rate of propagation and hence the rate of polymerisation, is the sum of all the propagating steps and therefore can be expressed as:-

$$R_p = K_p[M^*][M] \qquad \text{(G)}$$

The kinetic chain length (υ) of a propagating species is defined as an average number of monomer molecules polymerised for each of the propagating species produced and is expressed as the ratio of the rate of propagation to the rate of initiation or indeed the rate of termination, since rate of initiation is equal to the rate of termination in a steady state approximation, which is assumed here.

$$v = \frac{R_p}{R_i} = \frac{R_p}{R_t} \qquad \text{(H)}$$

The number average degree of polymerisation (X_n) is the average number of monomer molecules in the polymer chain and is defined as the ratio of the molecular weight of the polymer (M_n) to the molecular weight of the monomer (M_o).

$$X_n = \frac{M_n}{M_o} \qquad \text{(I)}$$

If the propagating species are terminated by coupling X_n is related to the Kinetic Chain Length by:-

$$X_n = 2\upsilon \qquad (J)$$

If the propagating species are terminated by disproportionation or other processes leading to an uncoupled dead polymer then:-

$$X_n = \upsilon \qquad (K)$$

Chain transfer is a chain breaking reaction, resulting in a decreased propagating polymer chain size.

$$M_n^* + XA \xrightarrow{k_{ct}} M_n\text{-}X + A^* \qquad (L)$$

-where XA can be monomer, solvent, initiator or chain transfer agent and A is the transferred species.

$$R_{ct} = k_{ct}[M^*][XA] \qquad (M)$$

The new propagating species A^* can cause further polymerisation:-

$$A^* + M \xrightarrow{k_a} AM^* \qquad (N)$$

From equation (K) we can redefine X_n as the ratio of the rate of polymerisation to the sum of the rates of all chain breaking and chain terminating reactions.

$$X_n = \frac{R_p}{R_t + R_{ct,m} + R_{ct,z} + R_{ct,I}} \qquad (O)$$

-where R_t, $R_{ct,m}$, $R_{ct,z}$ and $R_{ct,I}$ are the rates of termination, chain transfer to monomer, chain transfer to chain transfer agent (z) and chain transfer to initiator reactions respectively.

Using $R_p=k_p[RM^*][M]$ from equation (G) and assuming termination has both bimolecular and unimolecular mechanisms, we can write $R_t=k_t[RM^*]^2+ k_t'[RM^*]$ from equations (D_a) and (D_b) and obtain:-

$$X_n = \frac{k_p[RM^*]\,[M]}{k_t[RM^*]^2 + k_t'[RM^*] + k_{ct,m}\,[M][RM^*] + k_{ct,z}[RM^*][Z] + k_{ct,I}[RM^*][I]} \tag{P}$$

If we simplify and take the reciprocal of equation (P) we obtain:-

$$\frac{1}{X_n} = \frac{k_t[M^*] + k_t'}{k_p[M]} + \frac{k_{ct,m}}{k_p\ [M]} + \frac{k_{ct,z}[Z]}{k_p[M]} + \frac{k_{ct,I}[I]}{k_p[M]} \tag{Q}$$

A Chain Transfer Constant (C_x) of a substance (X) is defined as the ratio of the rate constant for chain transfer of a propagating species with the substance (X) to the rate constant for propagation, where (X) can be monomer, initiator or chain transfer agent.

$$C_x = \frac{k_{ct,x}}{k_p} \tag{R}$$

If we then substitute this information into equation (Q) we obtain:-

$$\frac{1}{X_n'} = \frac{k_t[M^*] + k_t'}{k_p\,[M]} + C_m + C_z\frac{[Z]}{[M]} + C_I\frac{[I]}{[M]} \tag{S}$$

There is no transfer to monomer in ROMP hence C_m can be ignored and since the concentration of the initiator is very low and this process is inherently unlikely the last term can be considered negligible. The first term in equation (S) is the value of $^1/_{X_n}$ when there is no chain transfer agent present.

$$\frac{1}{X_{n'}} = \frac{k_t[RM^*] + k_t'}{k_p[M]} \qquad \text{(T)}$$

Hence:-

$$\frac{1}{X_n} = \frac{1}{X_{n'}} + C_z\frac{[Z]}{[M]} \qquad \text{(U)}$$

To obtain an expression for ${}^{1}/_{M_n}$ we can divide by M_o, the molecular weight of the monomer (equation (I)):-

$$\frac{1}{M_n} = \frac{1}{M_{n'}} + \frac{C_z\ [Z]}{M_o\ [M]} \qquad \text{(V)}$$

-where ${}^{1}/_{M_{n'}}$ is the value of ${}^{1}/_{M_n}$ in the absence of a chain transfer agent. Hence, if we define a new Chain Transfer Constant as $C_z' = {}^{C_z}/_{M_o}$, we obtain:-

$$\boxed{\frac{1}{M_n} = \frac{1}{M_{n'}} + C_z'\frac{[Z]}{[M]}} \qquad \text{(W)}$$

Appendix I.

Lectures / Conferences.

UNIVERSITY OF DURHAM
Board of Studies in Chemistry

Colloquia, Lectures and Seminars given by Invited Speakers.

1989.

October 17.	Dr. F. Palmer, (Nottingham University). Thunder and Lightning.
October 25.	Prof. C. Floriani, (University of Lausanne, Switzerland). Molecular Aggregates - A Bridge between Homogeneous and Heterogeneous systems.
November 1.	Dr. J.P.S. Badyal, (Durham University). Breakthroughs in Heterogeneous Catalysis.
November 9.	Prof. N.N. Greenwood, (Leeds University). Novel Cluster Geometries in Metalloborane Chemistry.
November 10.	Prof. J.E. Bercaw, (California Institute of Technology). Synthetic and Mechanistic Approaches to Ziegler-Natta Polymerisation of Olefins.
November 13.	Dr. J. Becher, (Odense University). Synthesis of New Macrocyclic Systems using Heterocyclic Building Blocks.
November 16.	Dr. D. Parker, (Durham University). Macrocycles, Drugs and Rock 'n' Roll.
November 29.	Prof. D.J. Cole-Hamilton, (University of St. Andrews). New Polymers from Homogeneous Catalysts.
November 30.	Dr. M.N. Hughes, (King's College, London). A Bug's Eye View of the Periodic Table.
December 4.	Dr. D. Graham, (B.P. Research Centre). How Proteins Absorb to Interfaces.
December 6.	Dr. R.L. Powell, (ICI). The Development of CFC Replacements.
December 7.	Dr. A. Butler, (University of St. Andrews). The Discovery of Penicillin: Facts and Fancies.
December 13	Dr. J. Klinowski, (Cambridge University). Solid State NMR Studies of Zeolite Catalysts.
December 15	Prof. R. Huisgen, (Universität München). Recent Mechanistic Studies of [2+2] Additions.

1990.

January 24	Dr. R.N. Perutz, (York University). Plotting the Course of C-H Activations with Organometallics.
January 31.	Dr. U. Dyer, (Glaxo). Synthesis and Conformation of C-Glycosides.
February 1.	Prof. J.H. Holloway, (University of Leicester). Noble Gas Chemistry.
February 7.	Dr. D.P. Thompson, (Newcastle University). The Role of Nitrogen in Extending Silicate Crystal Chemistry.
February 8.	Rev. R. Lancaster, (Kimbolton Fireworks). Fireworks - Principles and Practice.
February 12.	Prof. L. Lunazzi, (University of Bologna). Application of Dynamic NMR to the Study of Conformational Enantiomerism.
February 14.	Prof. D. Sutton, (Simon Fraser University, Vancouver B.C.) Synthesis and Applications of Dinitrogen and Diazo Compounds of Rhenium and Iridium.
February 15.	Prof. L. Crombie, (Nottingham University). The Chemistry of Cannabis and Khat.
February 21.	Dr. C. Bleasdale, (Newcastle University). The Mode of Action of Some Anti-tumour Agents.
February 22.	Prof. D.T. Clark, (ICI Wilton). Spatially Resolved Chemistry (Using Nature's Paradigm in the Advanced Materials Arena).
February 28.	Dr. R.K. Thomas, (Oxford University). Neutron Reflectometry from Surfaces.
March 1.	Dr. J.F. Stoddart, (Sheffield University). Molecular Lego.
March 8.	Dr. A.K. Cheetham, (Oxford University). Chemistry of Zeolite Cages.
March 21.	Dr. I. Powis, (Nottingham University). Spinning Off in a Huff: Photodissociation of Methyl Iodide.
March 23.	Prof. J.M. Bowman, (Emory University). Fitting Experiment with Theory in Ar-OH.
July 9.	Prof. V.E. Platonov, (USSR Academy of Sciences - Novosibirsk). Polyfluoroindanes: Synthesis and Transformation.

July 9.	Prof. I.N. Rozhkov, (USSR Academy of Sciences - Moscow). Reactivity in Perfluoroalkyl Bromides.
July 9.	Prof. L.S. German, (USSR Academy of Sciences - Moscow). New Syntheses in Fluoroaliphatic Chemistry: Recent Advances in the Chemistry of Fluorinated Oxiranes.
October 11.	Dr. W.A. Macdonald, (ICI, Wilton). Materials for the Space Age.
October 24.	Dr. M. Bochmann, (University of East Anglia.) Synthesis, Reactions and Catalytic Activity of Cationic Titanium Alkyls.
October 26.	Prof. L. Soulen, (South Western University, Texas). Preparation and Reactions of Bicycloalkenes.
October 31.	Dr. R. Jackson, (Newcastle University). New Synthetic Methods: α-Amino Acids and Small Rings.
November 1.	Dr. N. Logan, (Nottingham University). Rocket Propellants.
November 6.	Dr. P. Kocovsky, (Uppsala University). Stereo-Controlled Reactions Mediated by Transition and Non-Transition Metals.
November 7.	Dr. D. Gerrard, (British Petroleum). Raman Spectroscopy for Industrial Analysis.
November 8.	Dr. S.K. Scott, (Leeds University). Clocks, Oscillations and Chaos.
November 14.	Prof. T. Bell, (SUNY, Stoney Brook, U.S.A.). Functional Molecular Architecture and Molecular Recognition.
November 21.	Prof. J. Pritchard, (Queen Mary & Westfield College, London University). Copper Surfaces and Catalysts.
November 28.	Dr. B.J. Whitaker, (Leeds University). Two-Dimensional Velocity Imaging of State-Selected Reaction Products.
November 29.	Prof. D. Crout, (Warwick University). Enzymes in Organic Synthesis.
December 5.	Dr. P.G. Pringle, (Bristol University). Metal Complexes with Functionalised Phosphines.
December 13.	Prof. A.H. Cowley, (University of Texas). New Organometallic Routes to Electronic Materials.

1991.

January 15.	Dr. B.J. Alder, (Lawrence Livermore Labs., California. Hydrogen in all its Glory.
January 17.	Dr. P. Sarre, (Nottingham University). Comet Chemistry.
January 24.	Dr. P.J. Sadler, (Birbeck College, London). Design of Inorganic Drugs: Precious Metals, Hypertension and HIV.
January 30.	Prof. E. Sinn, (Hull University). Coupling of Little Electrons in Big Molecules. Implications for the Active Sites of (Metalloproteins and other) Macromolecules.
January 31.	Dr. D. Lacey, (Hull University). Liquid Crystals.
February 6.	Dr. R. Bushby, (Leeds University). Biradicals and Organic Magnets.
February 14.	Dr. M.C. Petty, (Durham University). Molecular Electronics.
February 20.	Prof. B.L. Shaw, (Leeds University). Syntheses with Coordinated, Unsaturated Phosphine Ligands.
February 28.	Dr. J. Brown, (Oxford University). Can Chemistry Provide Catalysts Superior to Enzymes.
March 6.	Dr. C.M. Dobson, (Oxford University). NMR Studies of Dynamics in Molecular Crystals.
March 7.	Dr. J. Markam, (ICI Pharmaceuticals). DNA Fingerprinting.
April 24.	Prof. R.R. Schrock, (Massachusetts Institute of Technology). Metal-Ligand Multiple Bonds and Metathesis Initiators.
April 25.	Prof. T. Hudlicky, (Virginia Polytechnic Institute). Biocatalysis and Symmetry Based Approaches to the Efficient Synthesis of Complex Natural Products.
June 20.	Prof. M.S. Brookhart, (University of North Carolina). Olefin Polymerisations, Oligomerisations and Dimerisations Using Electrophilic Late Transition Metal Catalysts.
July 29.	Dr. M.A. Brimble, (Massey University, New Zealand). Synthetic Studies Towards the Antibiotic Griseusin-A.
October 17.	Dr. J.A. Salthouse, (University of Manchester). Son et Lumiere - A Demonstration Lecture.

October 31.	Dr. R. Keeley, (Metropolitan Police Forensic Science). Modern Forensic Science.
November 6.	Prof. B.F.G. Johnson, (Edinburgh University). Cluster-Surface Analogies.
November 7.	Dr. A.R. Butler, (St. Andrews University). Traditional Chinese Herbal Drugs: A Different Way of Treating Disease.
November 13.	Prof. D. Gani, (St. Andrews University). The Chemistry of PLP Dependant Enzymes.
November 20.	Dr. R. More O' Ferrall,(University College, Dublin). Some Acid-Catalysed Rearrangements in Organic Chemistry.
November 28.	Prof. I.M. Ward, (IRC in Polymer Science, Leeds University). The SCI. Lecture: The Science and Technology of Orientated Polymer.
December 4.	Prof. R. Grigg, (Leeds University). Palladium Catalysed Cyclisation and Ion Capture Processes.
December 5.	Prof. A.L. Smith, (ex-Unilever). Soap, Detergents and Black Pudding.
December 11.	Dr. W.D. Cooper, (Shell Research). Colloid Science, Theory and Practice.

1992.

January 22.	Dr. K.D.M. Harris, (St. Andrews University). Understanding the Properties of Solid Inclusion Compounds.
January 29.	Dr. A. Holmes, (Cambridge University). Cycloaddition Reactions in the Service of the Synthesis of Piperidine and Indolizidine Natural Products.
February 12.	Prof. D.E. Fenton, (Sheffield University). Polynuclear Complexes of Molecular Clefts as Models for Copper Biosites.
February 19.	Prof. E.J. Thomas, (Manchester University). Application of Organostannanes to Organic Synthesis.
February 25.	Prof. J.F. Nixon, (University of Sussex). The Tilden Lecture: Phosphaalkynes, New Builing Blocks to Inorganic and Organometallic Chemistry.
February 26.	Prof. M.L. Hitchman, (Strathclyde University). Chemical Vapour Deposition.
March 11.	Dr. S.E. Thomas, (Imperial College). Recent Advances in Organoiron Chemistry.

March 18.	Dr. H. Maskill, (Newcastle University). Concerted or Stepwise Fragmentation in a Deamination-Type Reaction.
April 7.	Prof. D.M. Knight, (Philosophy Department, Durham University). Interpreting Experiments: The Beginning of Electrochemistry.
May 13.	Dr. J-C. Gehret, (Ciba-Geigy, Basel). Some Aspects of Industrial Agrochemical Research.

The author has attended the following lectures in the International Seminar Series 1991/1992.

1991.

18 March	Prof. G. Wegner, (Max-Planck-Institut fur Polymerforschung, Mainz) at Leeds University.
9 May	Prof. P.G. de Gennes, (Laboratoire de Physique de la Matiere Condensee, College de France, Paris) at Leeds University.
16 September	Dr. A. Griffin, (Melville Laboratory, University of Cambridge) at Durham University.

1992.

17 March	Prof. Sir S. Edwards, (Cavendish Laboratory, University of Cambridge) at Leeds University.
25 March	Prof. H. Cherdron, (Hoechst AG, Frankfurt am Main) at Durham University.
11 May	Prof. W. Burchard, (University of Freiburg) at Durham University.
21 September	Prof. E.L. Thomas, (MIT, Cambridge, Massachusetts) at Leeds University.

Conferences/Meetings Attended by the Author.

March 21 1990.
Macro Group (UK) Polymer Conference, Lancaster University.

March 26-28 1991.
Macro Group (UK) Polymer Conference, Lancaster University.

June 25 1991.
Macro Group (UK) Transition Metal Mediated Polymerisations Conference, SCI, London.

July 22-26 1992.
Polymer Surfaces and Interfaces Conference (II), Durham University.

March 26-28 1992.
Macro Group (UK) Polymer Conference, Durham University.

September 27 - October 2 1992.
European Polymer Federation: 4th Symposium on Polymeric Materials, Baden-Baden, Germany.

References:

1. Ciba-Geigy Industrial Chemicals, Private Communication 1.

2. D.L. Chamberlain, "Flame Retardancy of Polymeric Materials, Vol 4", eds. W.C. Kuryla and A.J. Papa, Marcel Dekker, New York (1978).

3. C.F. Cullis and M.M. Hirschler, "Combustion of Organic Polymers", Clarenden Press (1981).

4. J. Wyld, British Patent 551 (1735).

5. J.L. Gay-Lussac, Ann. Chim. Phys. **18** (2), 211, (1821).

6. N. Grassie and G. Scott, "Polymer Degradation and Stability", Cambridge University Press (1985).

7. G. Camino, L. Costa and M.P. Luda di Cortemiglia, Polymer Degradation and Stability, 33, 131, (1991).

8. D.L. Schmidt, "Ablative Plastics", eds. G.F. D'Alelio and J.A. Parker, Marcel Dekker, New York (1971).

9. M. Lewin and A. Basch, "Flame Retardant Polymeric Materials, Vol 1", eds. M. Lewin, S.M. Atlas and E.M. Pearce, Plenum Press, New York (1971).

10. I.C. McNeill, "Comprehensive Polymer Science Vol 6", eds. G. Allen and J.C. Bevington, Pergamon Press, Oxford (1989).

11. N. Grassie and M. Zulfiqar, "Developments in Polymer Stabilisation Vol1", ed. G. Scott, Applied Science, London (1979).

12. (a) E.D. Weil, "Flame Retardant Polymeric Materials, Vol 2", eds. M. Lewin, S.M. Atlas and E.M. Pearce, Plenum Press, New York (1978).

(b) I.J. Grunfest, E.M. Young, Prep. Am. Chem. Soc. Div. Org. Coat. Plast. Chem., 21(2), 113 (1961).

13. (a) F.A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", Interscience Publishers (1962).

(b) K.M. Mackay and R.A. Mackay, "Introduction to Modern Inorganic Chemistry, 4th ed.", Blackie and Son, Glasgow (1975).

14. B. Martel, J. Appl. Poly. Sci., 35, 1213 (1988).

15. E.D. Weil, "Flame Retardant Polymeric Materials, Vol 3", eds. M. Lewin, S.M. Atlas and E.M. Pearce, Plenum Press, New York (1975).

16. (a) H. Piechota, J. Cell. Plast, 1, 186 (1965).

(b) A.J. Papa and W.R. Proops, J. Appl. Poly. Sci., 16, 2361 (1972).

17. (a) D.W. Mitchell and E.M. Murphy, Proceedings of Conference on Foamed Plastics, PB181576, NASA, NRC, April (1973).

(b) M.A. Boult, R.K. Gamadia and D.H. Napier, Inst. Chem. Eng. (London) Symposium Series 33, 56 (1972).

18. K. Ashida, F. Yamauchi, M. Kotoh and T. Harada, J. Cell. Plast., 10, 181 (1974).

19. J.C. Cowan and D.J. Weintritt, "Water-Formed Scale Deposits", Gulf Publishing Company, Houston (1976).

20. G.V. James, "Water Treatment", 3rd ed. Technical Press Ltd., London (1966).

21. A.C. Twort, "Textbook of Water Supply", Edward Arnold Ltd., London (1965).

22. "Water Desalination in Developing Countries" - A United Nations Publication, New York (1964).

23. C. Palache et al., "The System of Mineralogy of J.D. and E.S. Dana", 7th ed. New York (1965).

24. L. Bragg and G.F. Claringbull, "Crystal Structures of Minerals vol. IV", Bell, London (1965).

25. J.L. Wray and F. Daniels, J.A.C.S., 79, 2031 (1957).

26. W.L. Roberts, T.J. Campbell and G.R.R. Rapp Jr, "Encyclopedia of Minerals", 2nd ed. Van Nostrand Reinhold, New York.

27. C.L. Boltz, "Desalination - Problems and Techniques", British Aqua Chem. Ltd., London (1967).

28. Skeist Laboratories INC, "Water-Soluble Polymers", (1983).

29. Ciba-Geigy Industrial Chemicals, Private Communication 2.

30. P. Hartman, "Crystal Growth - An Introduction", North Holland, Amsterdam (1973).

31. R.M. Garrels, "Mineral Equilibria", Harpers, New York (1960).

32. G. Wilkinson, "Comprehensive Polymer Science vol.3", eds. G. Allen and J.C. Bevington, Pergamon, Oxford (1987).

33. R.F. Stickland-Constable, "Crystallisation", Academic Press, London (1968).

34. Ciba-Geigy Industrial Chemicals, Private Communication 3.

35. Summers and Keevil, Power Plant Eng., 38, 219 (1934).

36. Hall, Power Plant Eng., 21, 277 (1933).

37. Neff and Brandes, European Patents, (a) 23123 (1909), (b) 26877 (1910), (c) 26878 (1910).

38. L.W. Becker, U.S. Patent, 4,446,046 (1984).

39. K.J. Ivin, "Olefin Metathesis", Academic Press, London (1983).

40. A.W. Anderson and N.G. Merckling, U.S. Patent, 2,721,189 (1955).

41. (a) I.M. Robinson and W.L. Truett, U.S. Patent, 2,932,630 (1960).
(b) W.L. Truett, D.R. Johnson, I.M. Robinson and B.A. Montague, J.A.C.S. 82, 2337 (1960).

42. R.L. Banks and G.C. Bailey, Ind. Eng. Chem. Prod. Res. Dev., 3, 170 (1964).

43. H.S. Eleuterio, U.S. Patent, 3,074,918 (1957), Chem. Abs. 55, 16005 (1961).

44. G. Dall'Asta, G. Mazzani, G. Natta and G. Mortoni, Makromol. Chem., 69, 163 (1964).

45. G. Dall'Asta, G. Mazzani and G. Natta, Angew. Chem, 76, 765 (1964).

46. N. Calderon et al, Chem. Eng. News, 45, 51 (1967).

47. N. Calderon, H.Yu. Chen and K.W. Scott, Tet. Lett. 3327 (1967).

48. N. Calderon, K.W. Scott, E.A. Ofstead, W.A. Judy and J.P. Ward,
(a) J.A.C.S., 90, 4133 (1968),

(b) A.C.S. Meeting, Abstract 155, L54 (1968),

(c) Adv. Chem. Ser., 91, 399 (1968).

49. N. Calderon and H.Yu. Chen, U.S. Patent, 3,535,401 (1970).

50. P. Blackmore, Ph.D. Thesis, Durham University (1986).

51. V. Drugatan, A.T. Balaban and M. Dimonie, "Olefin Metathesis and Ring Opening Polymerisation of Cyclo-Olefins", 2nd ed. Wiley Interscience (1985).

52. T. Saegusa and E. Goethals, "Ring Opening Polymerisation", A.C.S. Washington (1977).

53. K.J. Ivin and T. Saegusa, "Ring Opening Polymerisation", Elsevier, New York (1984).

54. A. Amass, "Comprehensive Polymer Science vol.4", eds. G. Allen and J.C. Bevington, Pergamon, Oxford (1989).

55. P. Dounis, M.Sc. Thesis, Durham University (1990).

56. C.P. Bradshaw, E.J. Howman and L. Turner, J. Catal. 7, 269 (1967).

57. T.P. Kobylinski and H.E. Swift, J. Catal. 26, 416 (1972).

58. (a) E.L. Muetterties and M.A. Busch, J. Chem. Soc. Chem. Commun., 75, 4 (1974).

(b) W.B. Hughes, Organomet. Chem. Synth., 1, 341 (1972).

59. C.P. Casey and T.J. Burkhardt, J.A.C.S., 95, 5833 (1973).

60. C.P. Casey and T.J. Burkhardt, J.A.C.S., 96, 7808 (1974).

61. T.J. Katz, S.J. Lee and N. Acton, Tett. Lett., 4247 (1976).

62. E.O. Fischer and A. Maasbol, Angew. Chem., Inter. Ed., 3, 580 (1964).

63. H.T. Ho, K.J. Ivin and J.J. Rooney, J. Mol. Cat., 15, 245 (1982).

64. T.J. Katz and N. Acton, Tett. Lett., 4251 (1976).

65. D. J. Cardin, B. Cetinkaya and M.F. Lappert, Chem. Rev., 72, 545 (1972).

66. R.H. Grubbs and C.R. Hoppin, J. Chem. Soc. Chem. Commun., 514 (1982).

67. E. Thorn-Csanyi, Angew. Makromol. Chem., 94, 181 (1981).

68. E. Thorn-Csanyi, J. Mol. Cat., 28, 49 (1985).

69. E. Thorn-Csanyi and H. Timm, J. Mol. Cat., 28, 37 (1985).

70. R.H. Grubbs and C.R. Hoppin, J. Chem. Soc. Chem. Commun., 634 (1977).

71. E.L. Muetterties, Inorg. Chem. 14, 951 (1975).

72. E. Thorn-Csanyi and M. Kessler, J. Mol. Cat., 36, 31 (1986).

73. K.J. Ivin, D.T. Laverty and J.J. Rooney, Makromol. Chem., 178, 1545 (1977).

74. A.J. Amass and T.A. Mc.Gourtney, Eur. Poly. J., 235 (1980).

75. G. Natta, G. Dall'Asta, and G. Mortoni, J. Poly. Sci. Polymer. Lett., B2, 349 (1964).

76. G. Natta, G. Dall'Asta and L. Porri, Makromol. Chem., 81, 253 (1965).

77. F.W. Michelotti and W.P. Keaveney, J. Poly. Sci., A3, 895 (1965).

78. J. Lahouste, M. Lemattie, J.C. Muller and C. Stern, Chem. Abs., 84, 122568 (1976).

79. U.S. Patent, 4,412,044 (1983).

80. British Patent, 1,487,185 (1977).

81. Uniroyal Inc., British Patent, 1,131,160 (1968).

82. B.M. Novak and R.H. Grubbs, J.A.C.S., 110, 960 (1988).

83. B.M. Novak and R.H. Grubbs, J.A.C.S., 110, 7542 (1988).

84. H.T. Ho, K.J. Ivin, B.S.R. Reddy and J.J. Rooney, Eur. Poly. J., 25, 805 (1989).

85. K.J. Ivin, J.J. Rooney, L. Bencze, J.G. Hamilton, L.M. Lam, G. Lapienis, B.S.R. Reddy and H.T. Ho, Pure Appl. Chem, 54, 447 (1982).

86. (a) D.B. Harrison, Ph.D. Thesis, Durham University (1990).

(b) D.B. Harrison and W.J. Feast, J. Mol. Cat., 65 (1-2), 63 (1991)

(c) D.B. Harrison and W.J. Feast, Polymer Bulletin, 25 (3), 343 (1991).

(d) D.B. Harrison and W.J. Feast, Polymer 32 (3), 558 (1991).

87. D.T. Laverty, M.A. McKervey, J.J. Rooney and A. Stewart, J. Chem. Soc. Chem. Comm., 193 (1976).

88. D.T. Laverty, J.J. Rooney and A. Stewart, J. Catal., 45, 110 (1976).

89. E. Ceausescu, A. Cornilescu, E. Nicolescu, M. Popescu, S. Coca, M. Cuzmici and C. Oprescu, J. Mol. Cat., 36, 163 (1986).

90. E.A. Ofstead and N. Calderon, Makromol. Chem., 154, 21 (1972).

91. S. Matsumoto, K. Komatsu and K. Igarashi, Polym. Prep., 18 (1), 110 (1977).

92. F.W. Michelotti and J.H. Carter, Am. Chem. Soc. Poly. Prep., 6, 224 (1965).

93. (a) B. Wilson, Ph.D. Thesis, Durham

(b) W.J. Feast and B. Wilson, Polymer, 20, 1182 (1979).

(c) W.J. Feast and B. Wilson, J. Mol. Cat., 8, 227 (1980).

94. W.J. Feast and K. Harper, Br. Poly. J., 18 (3), 161 (1986).

95. K.F. Castner and N. Calderon, J. Mol. Cat., 15, 47 (1982).

96. M.S. Jones and W.J. Feast, unpublished results.

97. K. Komatsu, S. Matsumoto and S. Aotani, Chem. Abs., 85: 78660 (1976).

98. T. Ueshima and S. Kobayashi, Jpn. Plast., 8, 11 (1974).

99. R.E. Rinehart, Chem. Abs. 68, 87750 (1968).

100. K.C. Wallace and R.R. Schrock, Macromolecules, 20, 448 (1987).

101. R.R. Schrock, Acc. Chem. Res., 19, 342 (1986).

102. R.R. Schrock, I.A. Weinstock, A.D. Horton, A.H. Liu and M.H. Schofield, J.A.C.S., 110, 2686 (1988).

103. L. Cannizzo and R.H. Grubbs, J. Org. Chem., 50, 2386 (1985).

104. L.R. Gillion and R.H. Grubbs, J.A.C.S., 108, 733 (1986).

105. M.T. Youinou, J. Kress, J. Fischer, A. Agero and J.A. Osborn, J.A.C.S. 110, 1488 (1988).

106. R.R. Schrock, R. DePue, J. Feldman, C.J. Schaverien, J.C. Dewan and A.H. Liu, J.A.C.S., 110, 1423 (1988).

107. R.R. Schrock, Acc. Chem. Res., 23, 158 (1990).

108. F.N. Tebbe, G.W. Parshall and G. Reddy, J.A.C.S., 100, 3611 (1978).

109. C.J. Schaverien, J.C. Dewan and R.R. Schrock, J.A.C.S., 108, 2271 (1986).

110. G. Bazan, E. Khosravi, R.R. Schrock, W.J. Feast and V.C. Gibson, Polymer Commun., 30, 258 (1989).

111. J. Hérrison and Y. Chauvin, Makromol. Chem., 141, 161 (1970).

112. M.L.H. Green, G.J.A. Adams, S.G. Davies, K.P. Ford, M. Ephritikhina and P.F. Todd, J. Mol. Cat., 8, 15 (1980).

113. J. Kress, J.A. Osborn, R.M.E. Greene, K.J. Ivin and J.J. Rooney, J.A.C.S., 109, 809 (1987).

114. Comprehensive Polymer Science vol.4, eds. G. Allen and J.C. Bevington, Pergamon, Oxford (1989).

115. K.J. Ivin, "Reactivity, Structure and Mechanism in Polymer Chemistry", eds. A.D. Jenkins and A. Ledwith, Wiley/Interscience, London (1974).

116. H. Jacobsen and W.H. Stockmeyer, J. Chem. Phys., 18, 1600 (1950).

117. J.M.G. Cowie, "Polymers: Chemistry and Physics of Modern Materials", ITC Ltd. (1973).

118. R. Rossi, P. Diversi, A Lucherini and L. Porri, Tet. Lett., 879 (1974).

119. W.J. Kelly and N. Calderon, J.Macromol. Sci. Chem., A9, 911 (1975).

120. J. Lal and R.R Smith, J. Org. Chem., 40, 775 (1975).

121. J.S. Murdzek and R.R. Schrock, Macromolecules 20, 2642 (1987).

122. R.J. Minchak and H. Tucker., Am. Chem. Soc. Poly. Prep., 13, 885 (1972).

123. E.A. Ofstead, J.P. Lawrence, M.L. Senyek and N. Calderon, J. Mol. Cat. 8, 227 (1980),

124. R. Streck and H. Weber, Chem. Abs. 85, 124699 (1976).

125. K.J. Ivin, D.T. Laverty, J.J. Rooney and P. Watt, Rec. Trav. Chim. Pays-Bas, 96, M54 (1977).

126. K.J. Ivin, J.H. O'Donnell, J.J. Rooney and C.D. Stewart, Makromol. Chem., 180, 1975 (1979).

127. F.S. Dainton and K.J. Ivin, Quart. Rev. Chem. Soc., 12, 61 (1958).

128. S.J. Lee, J. McGinnis and T.J. Katz, J.A.C.S., 98, 7818 (1976).

129. T.J. Katz, J. McGinnis and C. Altus, J.A.C.S., 98, 607 (1976).

130. J.G. Hamilton, K.J. Ivin, J.J. Rooney and L.C. Waring, J. Chem. Soc. Chem. Comm., 159 (1983).

131. J.G. Hamilton, K.J. Ivin and J.J. Rooney, Brit. Poly. J., 16, 21 (1984).

132. K.J. Ivin, Pure and Appl. Chem., 52, 1907 (1980).

133. K.J. Ivin, G. Lapienis and J.J. Rooney, Polymer, 21, 436 (1980).

134. K.J. Ivin, L.M. Lam and J.J. Rooney, Makromol. Chem., 182, 1847 (1981).

135. J.G. Hamilton, K.J. Ivin and J.J. Rooney, J. Mol. Cat., 28, 255 (1985).

136. T.J. Katz, S.J. Lee and M.A. Shippey, J. Mol. Cat., 8, 219 (1980).

137. P. Günther, F. Haas, G. Marwede, K. Nutzel, W. Oberkirch, G. Pampus, N. Schon and J. Witte, Angew. Makromol. Chem., 14, 87 (1970).

138. (a) R.A. Aitken, I. Gosney, H. Farries, M.H. Palmer, I. Simpson, J.I.G. Cadogan and E.J. Tinley, Tetrahedron, 41 (7), 1329 (1985).
(b) R.A. Aitken, J.I.G. Cadogan, H. Farries, I. Gosney, M.H. Palmer, I. Simpson and E.J. Tinley, J. Chem. Soc., Chem. Commun., 791 (1984).

139. "Polymer Handbook, 2nd ed.", eds. J. Brandup and E.H. Immergut, Wiley/Interscience, New York (1975).

140. R.C. Weast, "Handbook of Chemistry and Physics, 68th edition", CRC Press Inc. (1987).

141. "Vogel's Textbook of Practical Organic Chemistry, 5th ed.", revised by B.S. Furniss, A.J. Hannaford, P.W.G. Smith and A.R. Tatchell, Longman, New York (1989).

142. D.H. Williams and I. Fleming, "Spectroscopic Methods in Organic Chemistry, 4th ed.", McGraw-Hill, London (1987).

143. O. Diels and K. Alder, Ann., 460, 98 (1928).

144. J. McMurray, "Organic Chemistry", Brooks/Cole, Monterey, California (1984).

145. W.B. McCormack, U.S. Patent, 2,663,736 (1953).

146. G.H. Birum and J.L. Dever, Abstr. Am. Chem. Soc., 101p (1958).

147. V.A. Kukhtin, Dokl. Akad. Nauk. SSSR., 121, 466 (1958).

148. F. Ramirez and N.B. Desai, J.A.C.S., 85, 3752 (1953).

149. L.D. Quin, "Organic Chemistry- A series of Monographs, Vol. 8", ed. J.Hamer, Academic Press, New York (1967).

150. (a) K. Moedritzer, Synth. React. Inorg. Met. Org. Chem., 5 (1) 45 (1975).

(b) Shell Internationale Research, Belgian Patent 631,416 (1963).

(c) B.A. Arbuzov, A.O. Vizel, R.S. Giniyatullin, L.I. Shchukina and V.V. Pomazanov, Akad. Nauk. SSSR., 57 (1972).

(d) B.A. Arbuzov, A.O. Vizel, R.S. Giniyatullin and Yu.F. Tarenko, Izv. Akad. Nauk. SSSR. Ser. Khim., 8, 1847 (1972).

151. J. Goubeau and R. Baumgärtner, Z. Elektrochem., 64, 598 (1960).

152. K. Issleib and W. Seidel, Z. Anorg. Allgem. Chem., 288, 201 (1956).

153. U.H. Felcht to Hoechst, Chem. Abs., 94, 192456p (1982).

154. G. Crass and U.H. Felcht, Phosphorus and Sulfur, 13, 291 (1982).

155. B.A. Arbuzov, A.O. Vizel, Yu.Yu. Samitov and Yu.F. Tarenko, Izv. Akad. Nauk. SSSR. Ser. Khim., 3, 672 (1967).

156. K. Moedritzer and R.E. Miller, Phosphorus and Sulfur, 9, 293 (1981).

157. E. Breitmaier, G. Haas and W. Voelter, "Atlas of ^{13}C NMR Data", Heyden and Sons, London (1979).

158. A.C. Ladd to U.S. Rubber Co., Chem. Abs., 47, 9355.

159. W.M. Damiewski and C.E. Griffin, J. Org. Chem., 31, 3266 (1966).

160. H.J. Callot and C. Benezra, J. Chem. Soc., D, 485 (1970).

161. H.J. Callot and C. Benezra, Can. J. Chem., 48, 3382 (1970).

162. G.W. Buchanan and J.H. Bowen, Can. J. Chem., 55, 604 (1977).

163. G.W. Buchanan and C. Benezra, Can. J. Chem., 54, 231 (1976).

164. L.D. Quin, M.J. Gallagher, G.T. Cunkle and D.B. Chesnut, J.A.C.S., 102, 3136 (1980).

165. H.O. Kalinowski, S. Berger, S. Braun, "Carbon-13 NMR Spectroscopy, John Wiley and Sons, Chichester (1988).

166. P. Tavs, Chem. Ber., 100, 1571 (1967).

167. P. Tavs and H. Weitkamp, Tetrahedron, 26, 5529 (1970).

168. M.L. Honig and D.J. Martin, Phosphorus, 4, 63 (1974).

169. V. Kosolopoff and L. Maier, "Organic Phosphorus Compounds", Wiley (1963).

170. A.N. Pudovik and G.E. Vershinina, Z. Obshch. Khimi., 46, 11, 2492 (1976).

171. C.E. McKenna, M.T, Higa, N.H. Cheung and M.C. McKenna, Tet. Lett., 155 (1977).

172. C.E. McKenna and J. Schmidhauser, J. Chem. Soc. Chem. Commun., 739 (1979).

173. (a) Hoechst German Patent 1,023,033 (1960).

(b) Hoechst German Patent 1,023,034 (1960).

174. H. Lammens, G. Sartori, J. Siffert and N. Sprecher, J. Poly. Sci. Poly, Lett., 9, 341 (1971).

175. (a) E.J. Vandenberg, U.S. Patent 3,520,849 (1970).

(b) J. Liszowski, K. Kaluzynski and S. Penczek, J. Poly. Sci. Poly. Chem., 16, 1275 (1978).

(c) W.Vogt and R. Pflügler, Makromol. Chem. Suppl., 97, 1 (1975).

(d) J.P. Majoral, F. Mathis, A. Munoz, J.P. Vives and J. Navech, Bull. Soc. Chim. France, 4455 (1968).

176. E.A. Seddon and K.R. Seddon, "The Chemistry of Ruthenium", Elsevier, Amsterdam (1984).

177. G.C. Ray and D.L. Crain, Chem. Abs., 70, 114580 (1969).

178. E.A. Zuech, W.B. Hughes, D.H. Kubicek and E.T. Kittleman, J.A.C.S., 92, 528 (1970).

179. D.L. Crain and R.E. Reusser, Am. Chem. Soc. Div. Petr. Chem. Prep., 17, E80 (1972).

180. T.J. Katz and J. McGinnis, J.A.C.S., 99, 1903 (1977).

181. L. Porri, R. Rossi, P. Diversi and A. Lucherini, Makromol. Chem., 175, 3097 (1974).

182. L. Bencze, K.J. Ivin and J.J. Rooney, J. Chem. Soc. Chem. Commun., 834 (1980).

183. J. Otton, Chem. Abs., 90, 121028 (1979).

184. G.G. Odian, "Principles of Polymerisation, 2nd ed.", Wiley/Interscience (1981).

185. A.A. Bothner-by and S. Castellano, J. Chem. Phys., 41, 3863 (1964).

186. R.M. Stanley, D.W. Marquardt and R.C. Fergusson, J. Chem. Phys., 41, 2087 (1964).

187. "Progress in Nuclear Magnetic Resonance Spectroscopy, Vol. 1", eds. Emsley, Feeney and Sutcliffe, Pergamon, Oxford (1966).

188. "High Resolution Nuclear Magnetic Resonance Spectroscopy", eds. J.A. Pople, W.G. Schneider and H.J. Bernstein, McGraw-Hill, New York (1959).

189. H. Beckmann, G. Grossmann and G. Ohms, Mag. Res. Chem., 30, 860 (1992).

190. F.A. Bovey, "Nuclear Magnetic Resonance Spectroscopy", Academic Press, New York (1969).

191. P. Laszlo and P.V.R. Schleyer, J.A.C.S., 86, 1171 (1964).

192. P. Laszlo and P.V.R. Schleyer, J.A.C.S., 85, 2709 (1963).

193. N.A. Razumova and A.A. Petrov, Zh. Obshch. Khim., 33 (3), 783 (1963).

194. B.A. Arbuzov, A.O. Vizel, O.A. Raevskii, Yu.F. Tarenko and L.E. Petrova, Izv. Akad. Nauk. SSSR. Ser. Khim., 2, 460 (1969).

195. B.A. Arbuzov, A.O. Vizel, R.S. Giniyatullin, R.R. Shagidullin, I.A. Studentsova, R.R.Garaev and V.V. Pomazanov, Khim. Farm. Zh., 7 (11), 27 (1973).

196. G.M. Bogulyubov, L.I. Zubtsova, N.N. Grishin, N.A. Razumova and A.A. Petrov, Zh. Obshch. Khim., **41** (3), 527 (1971).

197. P.Haake, R.D. Cook, W. Schwarz and D.R. McCoy, Tet. Lett., **50**, 5251 (1968).