# The Reactions of Nitrogen Dioxide With Conjugated and Non Conjugated Alkenes.

By

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Submitted for the degree
Doctor of Philosophy

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September 1993.

# ABSTRACT

The reactions between nitrogen dioxide and 2,5-dimethyl-2,4-hexadiene, 2,4-hexadiene and 2,3-dimethyl-1,3-butadiene were investigated in various organic solvents. The major products isolated were where the nitrogen dioxide had added at each end of the conjugated system *i.e.* 2,5-dimethyl-2,5-dinitro-3-hexene (78%), 2,5-dinitro-3-hexene (56%) and 2,3-dimethyl-1,4-dinitro-3-butene (68%). X-ray crystal structures were obtained for 2,5-dimethyl-2,5-dinitro-3-hexene and *t*-2,3-dimethyl-1,4-dinitro-3-butene. *t*-2,3-Dimethyl-1,4-dinitro-3-butene was found to isomerise to *c*-2,3-dimethyl-1,4-dinitro-3-butene when a catalytic excess of nitrogen dioxide was present.

*c,t,t*-1,5,9-Cyclododecatriene reacted with nitrogen dioxide to form the 1,2-dinitro-*t,t,*-5,9-cyclododecadiene (35%) and 5,6-dinitro-*c,t,*-1,9-cyclododecadiene (32%) predominantly. Tetranitrocyclododecene (10%) was also isolated.

1,6-Heptadiene reacted with nitrogen dioxide to form the straight chain adducts 1,2-dinitro-6-heptene (51%) and 2-hydroxy-1-nitro-6-heptene (37%) predominantly. *Cis* and *trans* 1,2-(nitromethyl)-cyclopentane (19%) were isolated when slow addition times (6h or longer) of nitrogen dioxide were employed.

Allyl ether reacted with nitrogen dioxide to form *cis* and *trans* 2,3-(nitromethyl)-tetrahydrofuran (59%) and traces of the straight chain adducts 1,2-dinitropropyl-3,3'-oxy-1'-propene and 2-hydroxy-1-nitropropyl-3,3'-oxy-1'-propene. This reaction was also investigated using $^{15}$N labelled nitrogen dioxide and the reaction studied using $^{15}$N n.m.r. spectroscopy. Chemically induced dynamic nuclear polarisation (C.I.D.N.P.) effects were observed in the spectra for the formation of both the tetrahydrofuran, and the straight chain

adducts. The C.I.D.N.P. effects were consistent with the attack of two separate nitrogen dioxide radicals.

*To My Parents.*

# ACKNOWLEGEMENTS

I would like to thank my supervisor Professor J. H. Ridd for his help, encouragement, and enthusiasm during the completion of this work.

I would also like to thank the technical staff, especially Jill Maxwell, Steve Corker, and Alan Stones for the chemical analysis and h.p.l.c.

I would also like to thank Professor Deeming and Dr. Tocher for the X-ray crystal determinations.

My thanks are extended to all those postgraduates who admit to knowing me, especially Ems, Joe, Rup, Stu 'Yeah', Elliot, Bruce, Vern, Navjot, Paula and Duncan.

My thanks are also extended to my industrial supervisors Norman Paul and Dr. Ross Millar, and to the Procurement Executive, Ministry of Defence for funding the project.

I would like to thank my family for their support and help during my years at University. Finally my thanks are extended to my Mum, Dad and Ems again for making me write up so 'soon' after leaving University!

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## Abbreviations

| | |
|---|---|
| (A) | d$^6$-Acetone |
| (ACN) | d$^3$-Acetonitrile |
| bs | broad singlet |
| (C) | d-Chloroform |
| C.I.D.N.P. | Chemically Induced Dynamic Nuclear Polarisation. |
| C.I.M.S. | Chemical Ionisation Mass Spectrometry |
| d | chemical shift in ppm |
| d | doublet |
| dd | doublet of doublets |
| ddd | doublet of doublet of doublets |
| dh | doublet of heptets |
| h.p.l.c. | high performance liquid chromatography |
| I.R. | Infra-red |
| J | coupling constant in Hz |
| m | multiplet |
| n.m.r. | nuclear magnetic resonance |
| q | quartet |
| s | singlet |
| t | triplet |
| t.l.c. | thin layer chromatography |

# CHAPTER ONE

# INTRODUCTION

## 1.1 Introduction.

Initially this chapter deals with the formation and physical properties of nitrogen dioxide and its dimer dinitrogen tetroxide. The reactions of nitrogen dioxide in solution with various alkenes are then described followed by the reactions with conjugated and non-conjugated polyalkenes. An outline is then given of the aims of this thesis.

## 1.2 Preparation Of Nitrogen Dioxide.

Nitrogen dioxide can be made in a number of ways. The most common methods are outlined below.

### 1.2.1 From Concentrated Nitric Acid and Copper.

On mixing concentrated nitric acid with copper metal, copper nitrate and water are formed and nitrogen dioxide is liberated as a brown gas (**Eqn. 1.1**).

$$4HNO_3\ (l) + Cu\ (s) \longrightarrow Cu(NO_3)_2\ (s) + 2H_2O\ (g) + 2NO_2\ (g)$$

**Eqn. 1.1**

### 1.2.2 From Lead Nitrate.

On heating lead nitrate breaks down to evolve nitrogen dioxide and oxygen, while leaving a pale yellow solid of lead oxide (**Eqn. 1.2**).

$$2Pb(NO_3)_2\ (s) \longrightarrow 2PbO\ (s) + 4NO_2\ (g) + O_2\ (g)$$

**Eqn. 1.2**

### 1.2.3 From the Nitrosonium and Nitrate Ions[1].

$$KNO_3\,(s) + NOHSO_4\,(l) \longrightarrow KHSO_4\,(s) + 2NO_2\,(g) \qquad \textbf{Eqn. 1.3}$$

$$NO_3^- + NO^+ \longrightarrow 2NO_2\,(g) \qquad \textbf{Eqn. 1.4}$$

Addition of nitrosonium hydrogen sulphate to potassium nitrate evolves nitrogen dioxide. The nitrosonium salt is ionised to form the nitrosonium cation and the potassium salt is ionised to form the nitrate anion; these then combine to form nitrogen dioxide (**Eqn. 1.3** and **Eqn. 1.4**).

### 1.2.4 Industrial Scale Production.[2]

Nitrogen dioxide is made on a large scale by one main route, the oxidation of nitric oxide by air. The nitric oxide is prepared from two sources (a) the oxidation of nitrogen in the air or (b) the catalytic synthesis and oxidation of ammonia (**Eqn. 1.5** and **Eqn. 1.6**).

$$N_2\,(g) + 3H_2\,(g) \xrightarrow{Ni\,(s)} 2NH_3\,(g) \qquad \textbf{Eqn. 1.5}$$

$$4NH_3\,(g) + 5O_2\,(g) \longrightarrow 4NO\,(g) + 6H_2O\,(g) \qquad \textbf{Eqn. 1.6}$$

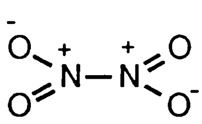
## 1.3 The Physical Properties Of Nitrogen Dioxide.

### 1.3.1 Solid Nitrogen Dioxide.

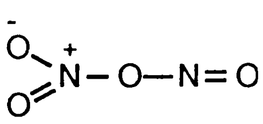
Nitrogen dioxide exists as a dimer in the crystalline form with a melting point of -11.2 °C. Between -11.2 and -30 °C it exists as a pale yellow crystalline solid and, if cooled to temperatures below -30 °C, it becomes white in colour.

X-ray crystallography techniques have shown that the crystal is based on a body centred cubic lattice[3,4] with twelve nitrogen dioxide molecules in the unit cell. These are paired into six sets of dinitrogen tetroxide molecules.

The bonding possible in the dinitrogen tetroxide had been of particular interest in the prediction of its physical and chemical properties. To explain the properties obtained, four structures had been postulated for the dimer:-



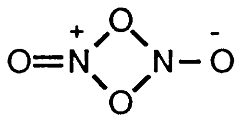
**I**



**II**

O=N–O–O–N=O

**III**



**IV**

Structures **I**, **II** and **III** were thought to exist in equilibrium[5], and structure **IV** had been devised from chemical indications[6]. However, the work by Broadley[4], Hendricks[3] and Smith[7] clearly pointed towards structure **I** with the N-N bond connecting the two nitrogen dioxide molecules (**Figure 1.1**).

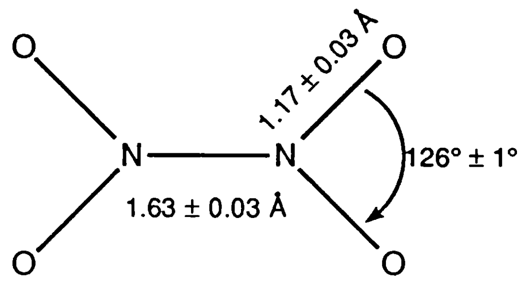


**Figure 1.1** Bond lengths and angles of dinitrogen tetroxide determined by X-ray crystallography[4].

Structure **I** was found to exist in two forms when gaseous nitrogen dioxide was cooled rapidly to liquid helium temperatures in an argon matrix[8,9]. The most stable form was that of planar dinitrogen tetroxide where all the atoms are in the same plane; this was characterised by stretching frequencies from its I.R. spectrum[8] (**Table 1.1**). The second form was that of staggered dinitrogen tetroxide which was also identified by I.R. stretching frequencies[8] (**Table 1.1**). The staggered form is not as stable as the planar molecule although steric interactions would be minimised in this orientation. The stabilisation is an electronic effect and this is discussed in more detail later.

**Table 1.1** Spectral data for the nitrogen dioxide and the isomers of dinitrogen tetroxide at liquid helium temperatures.

| Compound | Absorption Frequencies ($cm^{-1}$) |
|---|---|
| $NO_2$ (monomer)[a] | 1829, 1645, 1611. |
| $N_2O_4$ (planar)[b] | 1751, 1742, 1260, 755, 740. |
| $N_2O_4$ (staggered)[a] | 1718, 1282, 752. |
| $ONONO_2$[a] | 1829, 1645, 1290, 787. |

a: Carried out in an argon matrix.

b: Carried out in a carbon dioxide matrix.

A third form (**II**) was also discovered in an argon matrix by Bent[8,10] and co-workers. This was the asymmetric molecule of the nitro nitrite where instead of an N-N bond connecting the two nitrogen dioxide molecules together a N-O bond joins them. This form of dinitrogen tetroxide is the least stable form. Its I.R. bands are summarised in **Table 1.1**. Parts and Miller[11] have studied this structure in more detail and concluded that two polymorphs exist, one between 79 K and 205 K corresponding to the ionic nitrosonium-nitrate ($NO^+NO_3^-$) form, and one at or above 205 K corresponding to the covalent form ($ONONO_2$).

There is no evidence for the structures **III** and **IV** in crystalline dinitrogen tetroxide and these forms are not thought to exist.

As mentioned earlier, the most stable form of the dinitrogen tetroxide molecule is when all the atoms are in the same plane. This would not be expected as this would increase the amount of steric interaction occurring between the adjacent oxygen atoms. The dinitrogen tetroxide structure had to be explained and also three apparent anomalies.

(1) From electron diffraction measurements[7,12] it was found that the N-N bond was longer than expected at 1.78 Å compared with hydrazine (**Figure 1.2a**) which has an N-N bond of 1.47 Å.

(2) The O-N-O angle was also found to be larger than expected at 126° compared with the OSO angle in sulphuryl fluoride (**Figure 1.2b**); this would therefore increase the steric interactions of the neighbouring oxygen atoms.

(3) The barrier to rotation about the N-N bond was higher than expected and also the stability of the planar structure I compared to the skewed structure I and the nitro nitrite structure II.

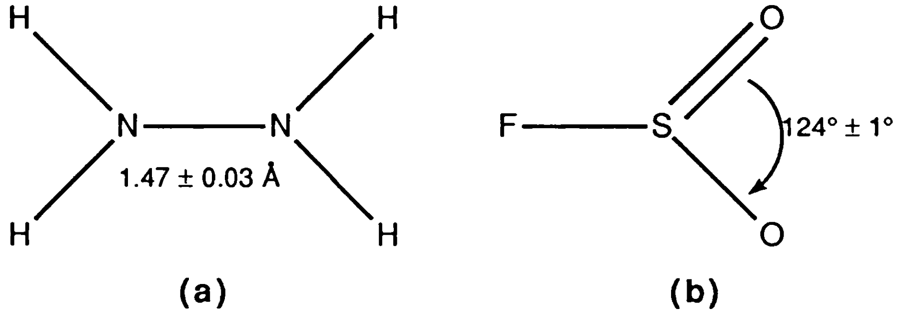


**Figure 1.2** **(a)** hydrazine; **(b)** sulphuryl fluoride

Various explanations were put forward for the long N-N bond length. Bent[8] described it as a splayed σ bond which would not account for the planar nature of the molecule. Smith and Hedberg[7] described it as a "π only" bond, and stated that there was no contribution from the σ electrons. The latter theory has been discarded by Pauling[13] as the odd electron of nitrogen dioxide occupies a $\sigma$ orbital which, when combined with another nitrogen dioxide molecule, would form a $\sigma$ bond.

Studies carried out by Ahlrichs[14] and Howell[15] have attempted to clarify some of these anomalies by *ab initio* calculations. Their work concluded that dinitrogen tetroxide was planar and that this structure derived its stabilisation from weak bonding interactions between the oxygen atoms at adjacent ends of the molecule. They also found that due to this interaction there was a shift of electron distribution from the nitrogen atom to the oxygen atoms; this would have the effect of weakening the N-N bond and account for the longer bond observed. Also the weak bonding interactions between the oxygen atoms at either end of the molecule should lead to an increase in the O-N-O bond angle. The overall result is that the nitrogen electrons are effectively delocalised throughout the molecule and this would explain the higher barrier to rotation about the N-N bond.

### 1.3.2 Liquid Nitrogen Dioxide.

In the solid form nitrogen dioxide exists predominately as its dimer dinitrogen tetroxide, however, when the crystalline solid melts, the dinitrogen tetroxide can dissociate in three possible ways:-

$$N_2O_4 \rightleftharpoons NO_2^+ + NO_2^- \qquad \textbf{Eqn. 1.7}$$

$$N_2O_4 \rightleftharpoons NO^+ + NO_3^- \qquad \textbf{Eqn. 1.8}$$

$$N_2O_4 \rightleftharpoons 2\ NO_2^{\cdot} \qquad \textbf{Eqn. 1.9}$$

In the pure liquid phase, the equilibrium lies to the left hand side of the above equations; hence there is little dissociation. The equilibrium represented by **Eqn. 1.7** is not a large contributor in the pure liquid phase and studies of liquid dinitrogen tetroxide solutions by I.R.[16] and Raman[17] spectroscopy have shown no evidence for the nitrite ion ($NO_2^-$) or the nitronium ion ($NO_2^+$) being present as free ions.

Evidence for their existence has been observed as the ion pair [$NO_2^-$ .$NO_2^+$] in the presence of Lewis acid halides[5]. Work by Olah[18] and co-workers also identified ionic species present when boron trifluoride and dinitrogen tetroxide were complexed (**Figure 1.3**).

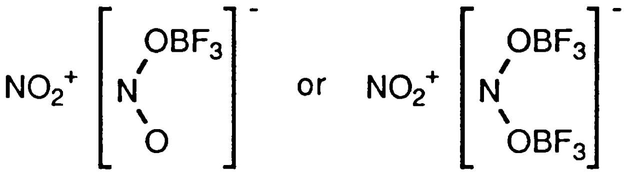


**Figure 1.3** Postulated structures for the ionic species present between boron trifluoride and dinitrogen tetroxide.

The equilibrium represented by **Eqn. 1.8** is not a large contributor in pure liquid nitrogen dioxide solutions, and there has been no evidence of the nitrate [$NO_3^+$] ion or the nitrosonium [$NO^+$] ion being present from either infra-red or Raman spectroscopy. On mixing nitrogen dioxide with a high dielectric constant solvent such as nitric acid, Millen and Goulden[19] found strong evidence for the nitrosonium ion with a strong signal at 2240 $cm^{-1}$, and no evidence for the dimer dinitrogen tetroxide. Dinitrogen tetroxide is fully ionised to the nitrate and nitrosonium ions in strong acidic electrolyte solutions.

Evidence for self ionisation of dinitrogen tetroxide has been observed. Clusius and Vechi[20] found by dissolving tetramethylammonium $^{15}N$-nitrate in excess dinitrogen tetroxide that complete exchange of the $^{15}N$ occurred.

The third equilibrium (**Eqn. 1.9**) is thought to be the major contributor in dinitrogen tetroxide solutions, and even this is small with homolytic dissociation to nitrogen dioxide being less than 1%. From measurements of the magnetic susceptibility Sone[21] concludes that pure liquid dinitrogen tetroxide contains 0.7% nitrogen dioxide. Evidence for a small contribution of the ionised forms was obtained by Faraday[22] and Addision[23] who measured the specific conductivity ($1.3 \times 10^{-12}$ mho$^{-1}$cm$^{-1}$) and the dielectric constant ($\varepsilon$ 2.4) of the pure dry liquid. If a heterolytic dissociation were occurring (**Eqn. 1.7** and **Eqn. 1.8**), then a much larger specific conductivity and dielectric constant should have been observed when a potential difference was placed across the dinitrogen tetroxide solution. Due to the low values obtained for the specific conductivity and the dielectric constant, the dissociation occurring in dry dinitrogen tetroxide must involve neutral species and this would imply the homolytic dissociation (**Eqn. 1.9**).

Liquid dinitrogen tetroxide when completely dry is a good solvent for most organic compounds[24], and is inert in anhydrous conditions. Saturated hydrocarbons, halogen and nitro derivatives, carboxylic acids, ketones and quinones were all found to be soluble and stable in liquid nitrogen dioxide and could be recovered unreacted; this was not true for hydroxy or amino substituted compounds which reacted readily with the solvent. If the liquid nitrogen dioxide was wet then the organic compounds generally reacted[24]. Inorganic salts did not dissolve in dry liquid dinitrogen tetroxide[24] which is further evidence that **Eqn. 1.8** is not a large contributor in pure liquid dinitrogen tetroxide.

### 1.3.3 Gaseous Nitrogen Dioxide.

In the gas phase, the equilibrium between dinitrogen tetroxide and nitrogen dioxide (**Eqn. 1.9**) is an important factor. At temperatures just above the boiling point of dinitrogen tetroxide the equilibrium lies to the left with an equilibrium constant[25] $K_e$(298 K) $1.51 \times 10^{-1}$ mol dm$^{-3}$, and dissociation of dinitrogen tetroxide becomes effectively complete at temperatures exceeding 413 K[26].

When nitrogen dioxide is heated to higher temperatures it undergoes homolytic dissociation into nitric oxide and oxygen (**Eqn. 1.10**). A similar reaction occurs if nitrogen dioxide is irradiated by light[27,28] with a wavelength of 313 nm or 316 nm. Baxter[29] found that nitrogen dioxide exhibited fluorescence when irradiated with light of wavelength 600 nm.

$$2NO_2\ (g) \xrightarrow{\Delta} 2NO\ (g) + O_2\ (g) \qquad \textbf{Eqn. 1.10}$$

## 1.4 Nitrogen Dioxide in Organic Solvents.

Redmond and Wayland[30] found that the degree of dissociation of dinitrogen tetroxide to nitrogen dioxide was considerably less in cyclohexane and carbon tetrachloride than in the gas phase (**Table 1.2**). They attributed the difference to the decrease in free volume on going from the gas phase to the solvent as the solvent would be exerting large internal pressures on the solute which would therefore inhibit the dissociation process. The degree of dissociation fell on going from a non co-ordinating to a co-ordinating solvent. For acetonitrile, the low dissociation was

**Table 1.2** Equilibrium constants $K_e$ for the dissociation of Dinitrogen Tetroxide in various organic solutions and the gas phase at 298 K

| Solvent | Dissociation Constant of Dinitrogen Tetroxide. $K_{e(298\ K)}$ mol dm$^{-3}$ |
|---|---|
| Cyclohexane | $1.77 \pm 0.1 \times 10^{-4}$ |
| Carbon Tetrachloride | $1.78 \pm 0.1 \times 10^{-4}$ |
| Acetonitrile | $0.30 \pm 0.1 \times 10^{-4}$ |
| No solvent (gas phase) | $1.51 \pm 0.1 \times 10^{-1}$ |

attributed to the high degree of co-ordination between dinitrogen tetroxide and acetonitrile compared to that of nitrogen dioxide and acetonitrile; this implies that dinitrogen tetroxide is a stronger Lewis acid than nitrogen dioxide.

Earlier work by Addison and Sheldon[31] classified solvents into two main types:-

1) Onium donors which were solvents such as ethers which contained an atom which had one or more lone pairs of electrons available to co-ordinate to dinitrogen tetroxide.

2) π-Donors which were solvents such as benzene which contained electrons in a π molecular orbital and which were able to co-ordinate with dinitrogen tetroxide.

A third class of solvent was added later this being the non donor solvents[32] such as aliphatic hydrocarbons and chlorinated aliphatic hydrocarbons.

It was found that, with onium donors such as ether and 1,4-dioxane, complex formation occurred which in dioxane is strong enough for crystal formation. The classification of addition compounds between dinitrogen tetroxide/nitrogen dioxide and solvents was broken down into two main categories; molecular compounds with onium and aromatic solvents, or ionic compounds between onium and aromatic solvents. As mentioned earlier, there is little evidence for the heterolytic dissociation of dinitrogen tetroxide (**Eqn. 1.7**), however work by Comyns[33,34] found evidence for ionic co-ordination in tertiary amines and dinitrogen tetroxide mixtures and therefore the heterolytic dissociation may occur. Addison and Sheldon[31] concluded that molecular dinitrogen tetroxide and onium donors complex in a ratio of

1:2 where the lone pairs of electrons on the donor co-ordinate with the nitrogen atoms in dinitrogen tetroxide. 1,4-Dioxane behaves as a chelating agent and donates two lone pairs of electrons to the dinitrogen tetroxide.

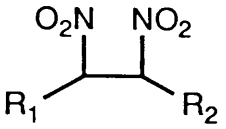
In molecules with π-systems such as benzene and other aromatic hydrocarbons, the compound formation was found to be layered[35,36], with an aromatic layer followed by a dinitrogen tetroxide layer. This has been attributed to the planarity of both the aromatic ring and dinitrogen tetroxide. Both have a π-system of a similar size and can therefore overlap in the solid state. However in the liquid state there is no evidence of any compound formation even though there is an association between the solute and solvent.

In non co-ordinating solvents there is no evidence of any complex formation.

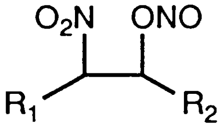
It can therefore be seen that by carrying out reactions with dinitrogen tetroxide in different solvents it may be possible to alter the course of the reaction. In onium and π donor solvents, molecular dinitrogen tetroxide is complexed to the solvent and the probability of dissociation occurring is reduced, but in non donor solvents there is no co-ordination and the possibility of dissociation increases.

## 1.5 Reaction of Nitrogen Dioxide and Alkenes.

The reactions between nitrogen dioxide and alkenes have been well documented and several reviews[37,38] have appeared in the literature with work dating back to 1864 by Semenoff[39] who described the reactions between nitrogen dioxide and ethene. Three main products were isolated corresponding to the dinitro, nitro-alcohol and the nitro-nitrate adducts of ethane.



V



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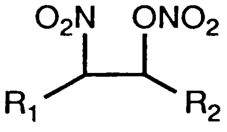
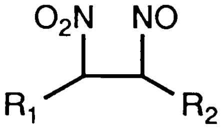
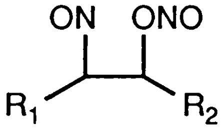


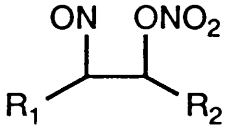
VII



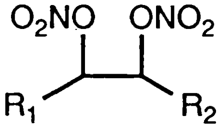
VIII



IX



X



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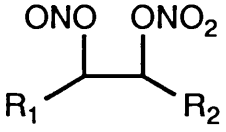
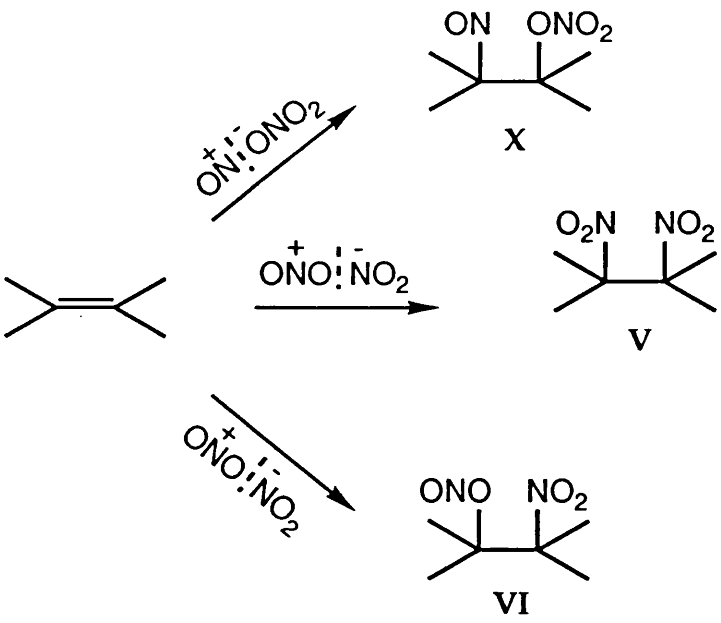


XII

The reactions between nitrogen dioxide and alkenes when first studied were found to give complex reaction products which were reported to be dinitro (**V**), nitro-nitrite (**VI**), nitro-nitrate(**VII**), nitro-nitroso (**VIII**), nitroso-nitrite (**IX**), nitroso-nitrate (**X**), dinitrate(**XI**), and nitrito-nitrate (**XII**) adducts. As a result of the number of reaction products formed, a number of mechanistic studies have been carried out to simplify the reaction mixtures.

Levy[40,41,42] and co-workers found that the number of products isolated was dependent upon the purity of the nitrogen dioxide used. They found that other oxides of nitrogen such as nitrous oxide and dinitrogen trioxide were responsible for a number of the products. Also the presence of water and oxygen were found[43] to add to the complexity of the reaction mixture.

Once nitrogen dioxide had been prepared in a dry pure form the complexity of the reaction mixture decreased dramatically and the predominant products isolated were the dinitro (**V**), nitro-nitrite (**VI**) and nitro nitrate (**VII**).

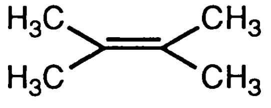


**Scheme 1.1**

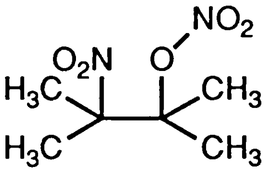
The mechanism of the addition was of particular interest and led to many conflicting publications. The addition of nitrogen dioxide was initially thought to proceed via the dinitrogen tetroxide molecule which could add across the double bond by electrophilic attack. Dinitrogen tetroxide was thought to exist as structures **I** and **II** but to account for the products obtained during the reaction between nitrogen dioxide and alkenes structure **II** was thought to be the major contributor. This would account for the formation of **V**, **VI** and **X** (**Scheme 1.1**).

Levy[40] suggested that the attack of the nitroniun ion ($NO_2^+$) was brought about by a solvent dinitrogen tetroxide association

The idea of the solvent solute interaction appeared to account for the products obtained. Work by Parts[43] at low temperatures suggested that the ionic form of dinitrogen tetroxide was responsible for the addition products obtained with isobutylene. Parts worked in the temperature range 77 to 195 K in which the ionic form of dinitrogen tetroxide was known to exist[11]. The 'nitrosonium nitrate' was prepared *in situ* by allowing oxygen to react with nitric oxide in the presence of excess olefin. At temperatures above 195 K no reaction occurred between dinitrogen tetroxide and isobutylene and they concluded that above this temperature the symmetrical structure of dinitrogen tetroxide (**I**) existed which did not react with the olefin.



**XIII**

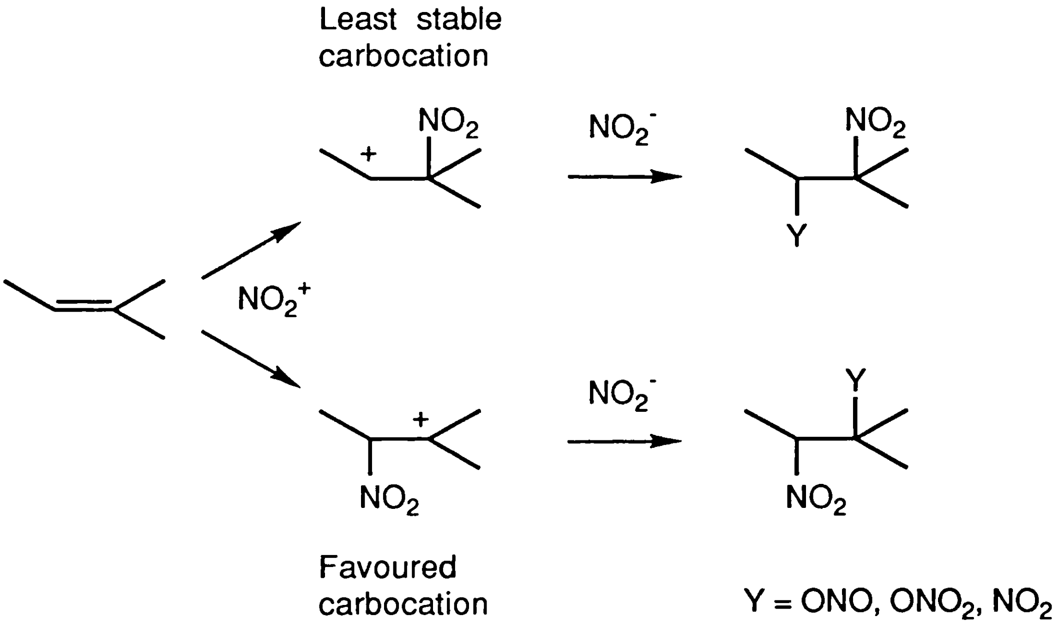


**XIV**

Work by Duynstee[44] found evidence for the addition of the ionic form of dinitrogen tetroxide to alkenes. The main difference from the work of Parts[43], was that he was studying the reaction in carbon tetrachloride which is a non polar solvent and would therefore not polarise the dinitrogen tetroxide. Duynstee also carried out the reaction at low temperature (-20 °C) but bubbled dinitrogen tetroxide through 2,3-dimethyl-2-butene (**XIII**) and nitrogen dioxide. He claims that 2,3-dimethyl-2-nitroso-3-nitrato-butane (**XIV**) was the only product formed and attributes this to the dinitrogen tetroxide adding heterolytically as $NO^+NO_3^-$.

Further evidence for the heterolytic addition of dinitrogen tetroxide to alkenes was obtained by Schoenbrunn and Gardner[45], who found that the addition of dinitrogen tetroxide exhibited some nitrosonium and nitrate ion characteristics. These were observed when the reaction was carried out in a nitric acid medium which was known to bring about the heterolytic dissociation of dinitrogen tetroxide[15]. However they also found that dinitrogen tetroxide added homolytically as a nitrogen dioxide radical if ether solvents were used which was in agreement with earlier work[46,47]. Schoenbrunn concluded that the formation of the nitroso-nitrate adducts was a direct consequence of the acidity of the solvent used. Ether being basic produced the homolytic dissociation and hence two nitrogen dioxide radicals.

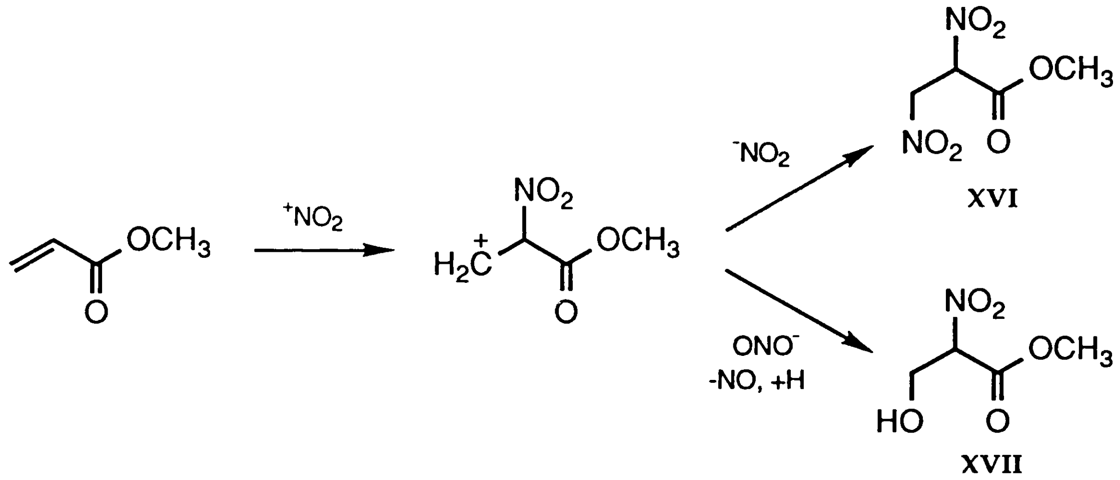
Previous chemists[37,40,41,42] had believed that the addition of dinitrogen tetroxide to alkenes had always occurred by the heterolytic dissociation route (**Eqn. 1.7**), but work in the 1950's began to find serious flaws in this hypothesis.



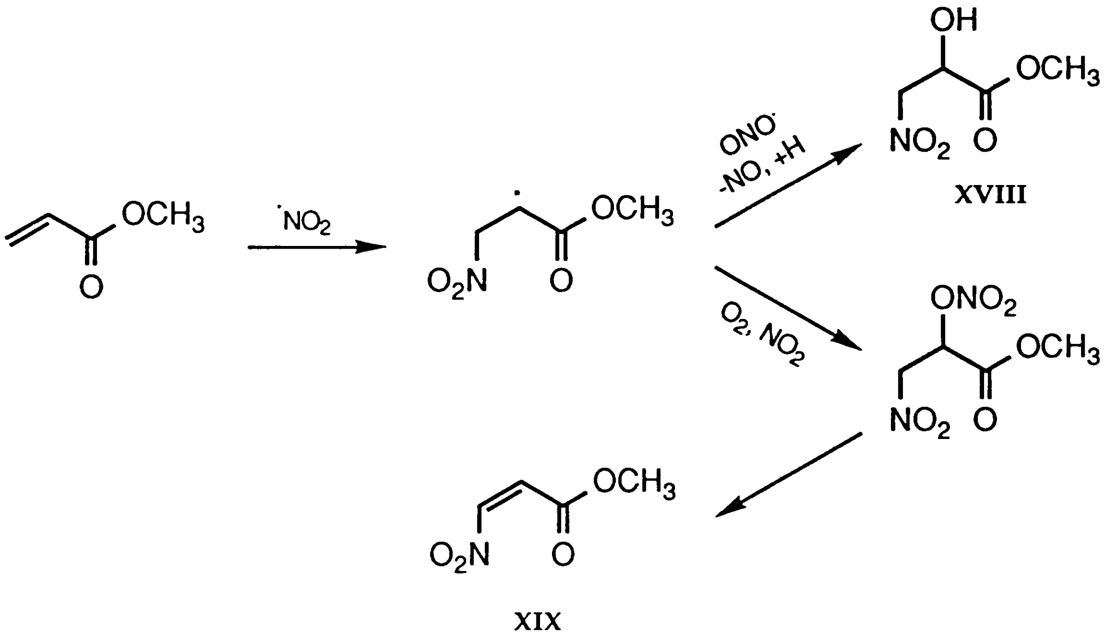
**Scheme 1.2**

Levy[40,41,42] noticed that the dinitro, the nitro-nitrate, and the hydroxy-nitro adducts always had the nitro group on the least substituted carbon centre. This would be consistent with the addition of the nitronium ion ($NO_2^+$) as the carbocation formed would be the most stable (**Scheme 1.2**).

Levy and co-workers however had only studied unsaturated alkenes with no polar substituents. Schecter and Conrad[46] looked at the addition of dinitrogen tetroxide to methyl acrylate (XV) as this was an electronegatively substituted olefin and would therefore polarise the addition of the dinitrogen tetroxide if it occurred heterolytically. Therefore the nitro group should always appear on the most substituted carbon (**Scheme 1.3**), however the isolation of XVI or the corresponding alcohol (XVII) were never obtained. Instead methyl-2-hydroxy-3-nitroacrylate (XVIII) and methyl-3-nitroacrylate (XIX) were isolated after work up. They attributed these compounds to the radical attack of nitrogen dioxide to the alkene (**Scheme 1.4**).

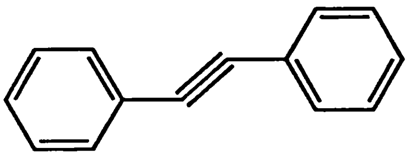


**Scheme 1.3**

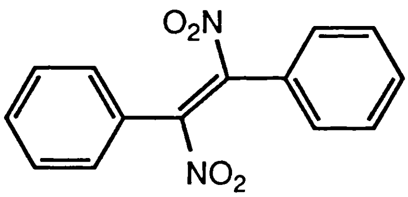


**Scheme 1.4**

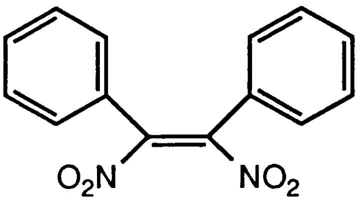
During the same period, reactions of dinitrogen tetroxide and tolane (XX) were being investigated[48] and the results obtained here were also in disagreement with the addition of the nitronium and nitrite ions. Products isolated included *trans* and *cis* 1,2-dinitrostilbene (**XXI**) and (**XXII**) respectively. Ionic addition to alkynes generally gives rise to *trans* adducts[49]. Rearrangement of **XXI** to **XXII** could not be induced so they concluded that part of the addition of dinitrogen tetroxide was occurring via a radical mechanism.



XX



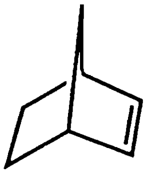
XXI



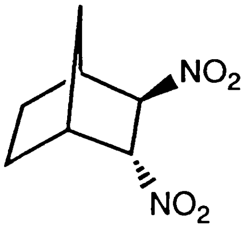
XXII

Further evidence to support the results of Schecter[46] and Campbell[48] came soon afterwards by the work of Brand and Steven[47,50]. They followed the reaction between cyclohexene and dinitrogen tetroxide in the presence of the radical trap bromotrichloromethane. The products isolated from the reaction were found to contain bromo and nitro substituents even when the reaction was carried out in the dark. The fact that halogen extraction had occurred in the dark implied that the bromine must have been removed by a radical and not by photolysis.

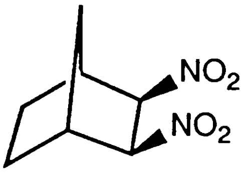
Work by Stevens and Emmons[51] also found a radical mechanism to be present by the use of iodine as a radical trap and they obtained good yields of β-nitro iodides from the reactions between dinitrogen tetroxide and alkenes. They also found that the addition of dinitrogen tetroxide to alkynes occurred via a radical mechanism in agreement with earlier work[48].



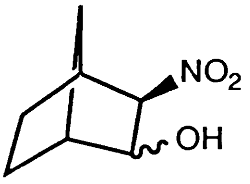
XXIII



XXIV

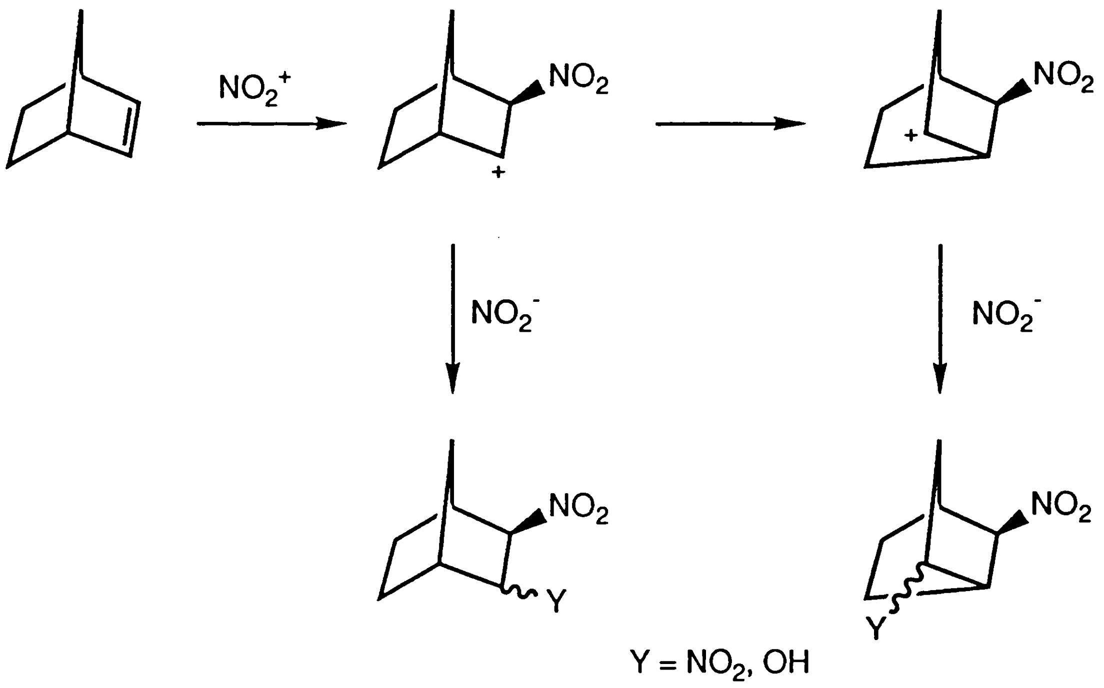


XXV



XXVI

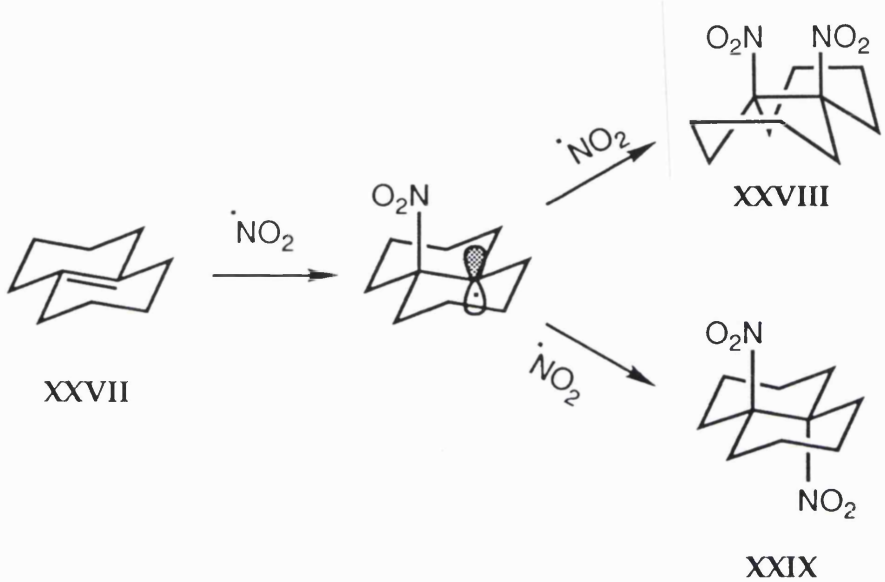
Further evidence for the radical addition of dinitrogen tetroxide to alkenes was obtained by Schecter[52]. On reacting norbornene (XXIII) with dinitrogen tetroxide the major products obtained were the *exo*, *trans* and *exo*, *cis*-2,3-dinitrobicyclo-[2,2,1]-heptanes, XXIV and XXV respectively, and 3-hydroxy-3-nitro-bicyclo-[2,2,1]-heptane (XXVI). There was no evidence of any carbon skeleton rearrangement[52] known to occur if the reaction produces a carbocation on the carbon skeleton (**Scheme 1.5**). On adding nitrogen dioxide to $\Delta^{9,10}$ octalin (XXVII), again *cis* and *trans* dinitro adducts



**Scheme 1.5**

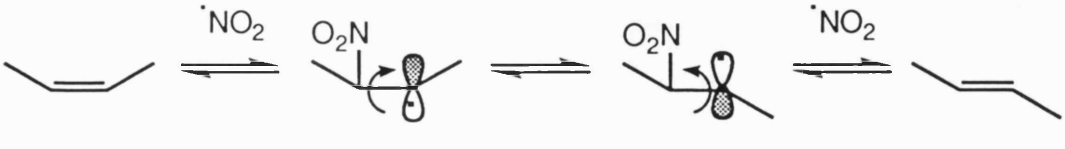
were obtained, XXVIII and XXIX respectively. For the *trans* adduct to be formed two separate attacks of nitrogen dioxide must occur. Initially the 10-

nitro-9-decalyl radical would form and this could then react with a second nitrogen dioxide molecule or extract nitrogen dioxide from dinitrogen tetroxide (**Scheme 1.6**).



**Scheme 1.6**

The fact that the addition of dinitrogen tetroxide may occur as molecular dinitrogen tetroxide or as the free nitrogen dioxide radical had now been recognised as two distinct mechanistic routes. Evidence for the molecular addition of dinitrogen tetroxide had been obtained by Pryor[53] who had found kinetic evidence to support both the addition of dinitrogen tetroxide and nitrogen dioxide. Recent kinetic work by Coombes[54] also supports the results of Pryor[53].



**Scheme 1.7.**

Khan[55] found further evidence for the attack of nitrogen dioxide on alkenes. He found that it was possible for *cis, trans* isomerisation to occur and this was explained by the attack of a nitrogen dioxide radical on the double bond followed by bond rotation then elimination of the nitro group to reform the double bond (**Scheme 1.7**). Work by Powell[56] also found strong evidence of the nitrogen dioxide radical being the attacking species. By using $^{15}N$ n.m.r. spectrometry to study the reactions between nitrogen dioxide and alkenes, chemically induced dynamic nuclear polarisation (C.I.D.N.P.) effects were observed which were interpreted as the attack of the nitrogen dioxide radical and not dinitrogen tetroxide.

## 1.6 Reactions Between Nitrogen Dioxide and Diene Systems.

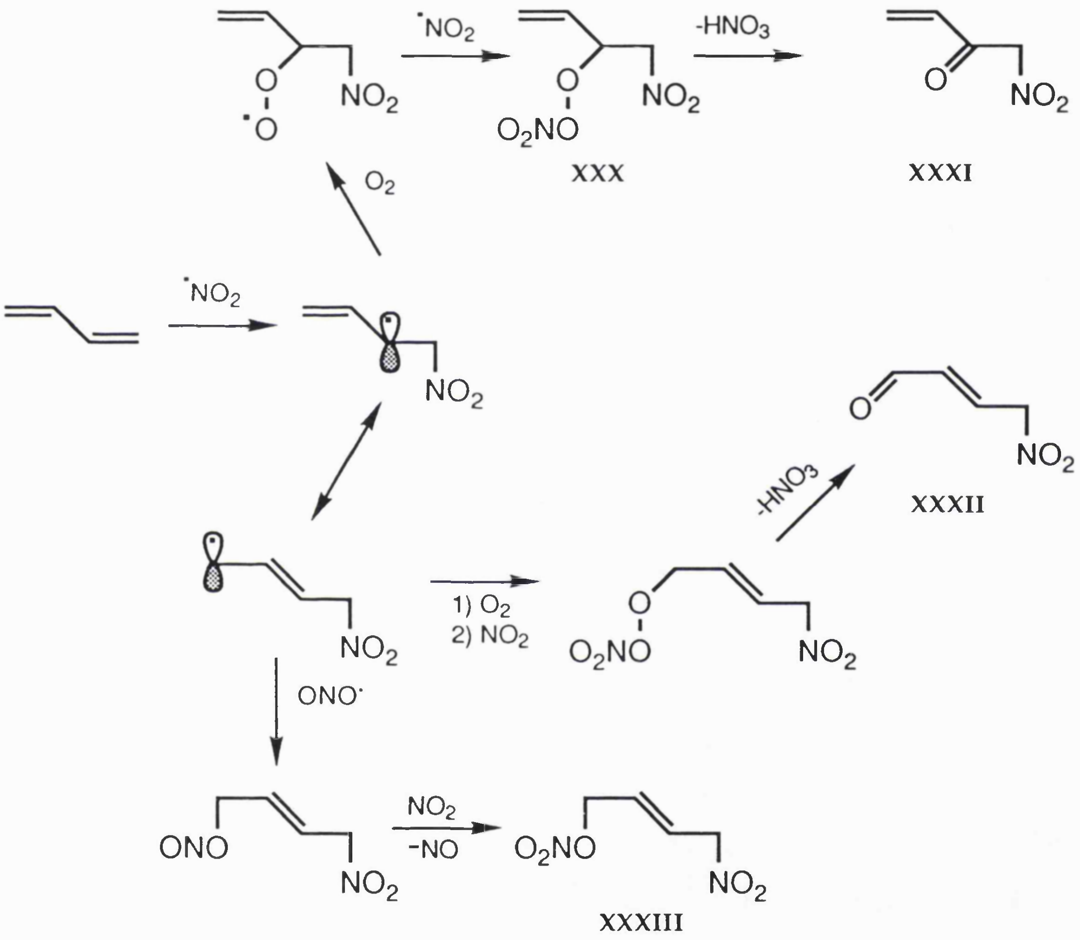
Little work has been published on the reactions between nitrogen dioxide and straight chain conjugated dienes[57]. Pryor[53] considered the mechanism of addition of nitrogen dioxide to 2,5-dimethyl-2,4-hexadiene and found that the reaction was first order with respect to the concentration of the nitrogen dioxide present. The general rate equation for addition to alkenes is given by **Eqn. 1.11** but for 2,5-dimethyl-2,4-hexadiene $k_1 = 18500 \pm 800\ M^{-1}s^{-1}$ with no reported value for $k_2$.

$$\frac{dP}{dt} = k_1[NO_2][Alkene] + k_2[NO_2]^2[Alkene] \qquad \textbf{Eqn. 1.11}$$

These results were in agreement with those obtained by Atkinson[58] whom found that the disappearance of the dienes 1,3-cyclopentadiene and 1,3-cyclohexadiene was first order with respect to nitrogen dioxide and the diene. At low concentrations of nitrogen dioxide **Eqn. 1.12** is followed.

$$\frac{-d[Alkene]}{dt} = k_1[NO_2][Alkene] \qquad \textbf{Eqn. 1.12}$$

The main difference between the work of Pryor[53] and Atkinson[58] was that Pryor had carried out his reactions in the liquid phase whereas Atkinson had carried out his reactions in the gas phase. The reaction products were not investigated although a radical mechanism was proposed by both authors. Atkinson[58] found that when oxygen was present in the reaction mixture, it reacted with the radical centre formed after the initial attack of nitrogen dioxide with the double bond (**Scheme 1.8**); this led to the formation of peroxy nitrates (**XXX**) in the reaction mixture, which ultimately decompose to give nitro ketones (**XXXI**).



**Scheme 1.8.**

The formation of **XXXI** only in the work of Atkinson was in contrast to work carried out by Brindley and Nicholson[59] who studied the reactions between conjugated dienes and nitric oxide in the liquid phase. They found that the conjugated dienes gave predominantly 1,4-adducts (**XXXIII**) which were the most thermodynamically favoured products (**Scheme1.8**).

In these reactions there was no evidence of any proton extraction by the nitrogen dioxide radical which would result in the formation of nitro substituted allylic compounds. This is a common path in the nitration of benzyl derivatives[60]. Pryor[61] using gaseous nitrogen dioxide found that hydrogen abstraction occurred in cyclohexane and that allylic substituted products were formed. By decreasing the concentration of the nitrogen dioxide the amount of allylic substitution increased.

The aims of this thesis were to study the reactions between nitrogen dioxide solutions and various conjugated and non conjugated dienes, to determine the reaction products, and to account for their formation. From this work it should be possible to determine the mode of addition of the nitrogen dioxide *i.e.*, whether the attacking species present was the dimer dinitrogen tetroxide or the monomer radical nitrogen dioxide. The following chapters are therefore concerned with the identification of the products and mechanistic implications that can be derived from them.

# CHAPTER TWO

# REACTIONS BETWEEN CONJUGATED DIENES AND NITROGEN DIOXIDE.

## 2.1 Introduction.

This chapter deals with the identification of the products formed in the reactions between the conjugated dienes 2,5-dimethyl-2,4-hexadiene, 2,4-hexadiene, 2,3-dimethyl-1,3-butadiene and nitrogen dioxide. The reaction between nitrogen dioxide and hexachlorobutadiene was also studied. The formation of the products obtained is then discussed in more detail.

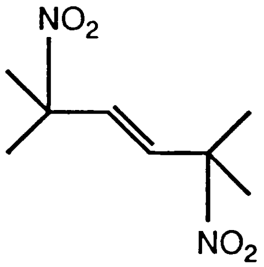
The products were isolated using normal phase h.p.l.c., and then identified by their $^{1}H$ n.m.r., $^{13}C$ n.m.r., and C.I.M.S. spectra. Where possible chemical analysis was obtained on the samples. In some cases, the chemical analyses given are poor *i.e.* the C:H:N ratios calculated and observed are not within 0.5%. This has been attributed to the incomplete combustion of the sample which is common with nitrogen containing compounds.

The experimental details for the reactions between nitrogen dioxide and 2,5-dimethyl-2,4-hexadiene, 2,4-hexadiene, 2,3-dimethyl-1,3-butadiene and hexachlorobutadiene are described in Chapter 8 sections 8.4, 8.5 ,8.6.and 8.7 respectively.

In section 2.3 concerning the identification of the products from the reactions between nitrogen dioxide and 2,4-hexadiene, the products obtained contained chiral centres and these centres are denoted by an asterisk (*). The diastereoisomers isolated contained the DL and *meso* forms, and these were separated using h.p.l.c. These isomers had similar $^{1}H$ n.m.r. spectra and absolute configuration was not possible to determine so the diastereoisomers are classified under how fast they were eluted off the h.p.l.c. column.

## 2.2 Products from the reaction between 2,5-Dimethyl-2,4-hexadiene and Nitrogen Dioxide.

### 2.2.1 *trans*-2,5-Dimethyl-2,5-dinitro-3-hexene.



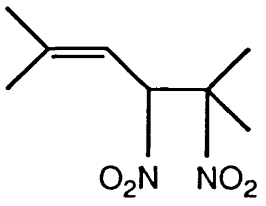
The $^1H$ n.m.r. spectrum recorded (Figure 2.1) consisted of two signals, δ 1.72 and δ 6.14 corresponding to the methyl and olefinic protons respectively; this also showed that the molecule was symmetrical.

The $^{13}C$ n.m.r. spectrum showed that the molecule was symmetrical with only three signals being present. The low field signal at δ 132.4 corresponded to the olefinic carbons, and the signal at δ 87.17 is due to the nitro substituted carbon. The remaining signal is from the methyl groups.

To determine the stereochemistry of the central double bond, an X-ray analysis was performed on a slowly grown crystal. The calculated structure showed that the double bond was of the *trans* conformation (Figure.2.2).

| | |
|---|---|
| $^1H$ n.m.r.(C) δ: | 1.72(12H) s; 6.14(2H) s. |
| $^{13}C$ n.m.r.(C) δ: | 25.79, 87.17, 132.41. |
| C.I.M.S. m/e: | 220($M.NH_4^+$), 109($M^+$-93). |
| Analysis: | Calculated for $C_8H_{14}N_2O_4$: C, 47.52; H, 6.69; N, 13.72.<br>Found: C,47.64; H, 7.23; N, 13.72. |
| M. pt.: | 103 °C. |

### 2.2.2 2,5-Dimethyl-2,3-dinitro-4-hexene.



From the $^1$H n.m.r. spectrum (Figure 2.3), the predominant feature was that there were four distinct methyl signals. The two higher field methyl signals at δ 1.82 and δ 1.85 were split into doublets due to long range coupling through the double bond to the olefinic proton $H_c$. The methyl protons $H_e$ and $H_f$ are diastereotopic and are seen as two separate signals.

Proton $H_c$ (δ 5.36) appears as a doublet of multiplets which approximates to a doublet of heptets. A perfect heptet is not observed as there is a slight difference between the coupling constants $J_{a,c}$ and $J_{b,c}$. Finally proton $H_d$ (δ 5.90) appears as a doublet due to coupling with proton $H_c$.

The $^{13}$C n.m.r. spectrum confirms the asymmetry of the molecule as eight signals are observed. A large chemical shift difference was observed between the two olefinic carbons; this is brought about by the substituent effect of the methyl groups attached to $C_1$ which has the effect of moving the signal to a lower field. Two signals were observed for the nitro substituted carbons at δ 88.49 and δ 88.57. The four high field signals are due to the four methyl carbons.

$^1$H n.m.r.(C) d: 1.57 (3H) s; 1.72 (3H) s; 1.82 (3H) d, $^4J_{b,c}$ 1.37 Hz; 1.85(3H) d, $^4J_{a,c}$ 1.40 Hz; 5.36 (1H) dm, $^3J_{c,d}$ 10.39 Hz, $^4J_{a,c}$ 1.40 Hz, $^4J_{c,b}$ 1.37 Hz; 5.90 (1H) d, $^3J_{d,c}$ 10.39 Hz.

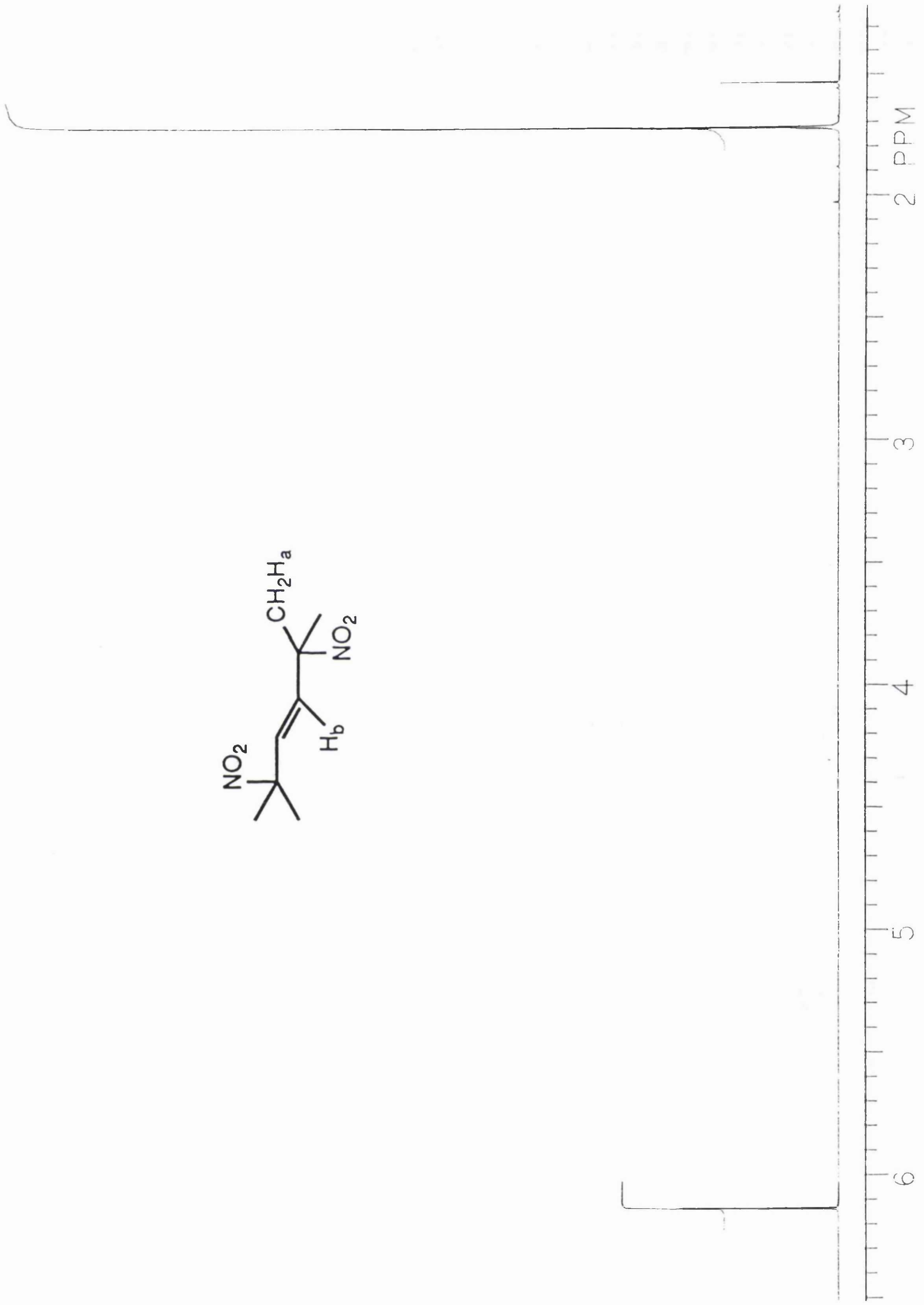


**Figure 2.1** $^1H$ n.m.r. spectrum for 2,5-dimethyl-2,5-dinitro-3-hexene

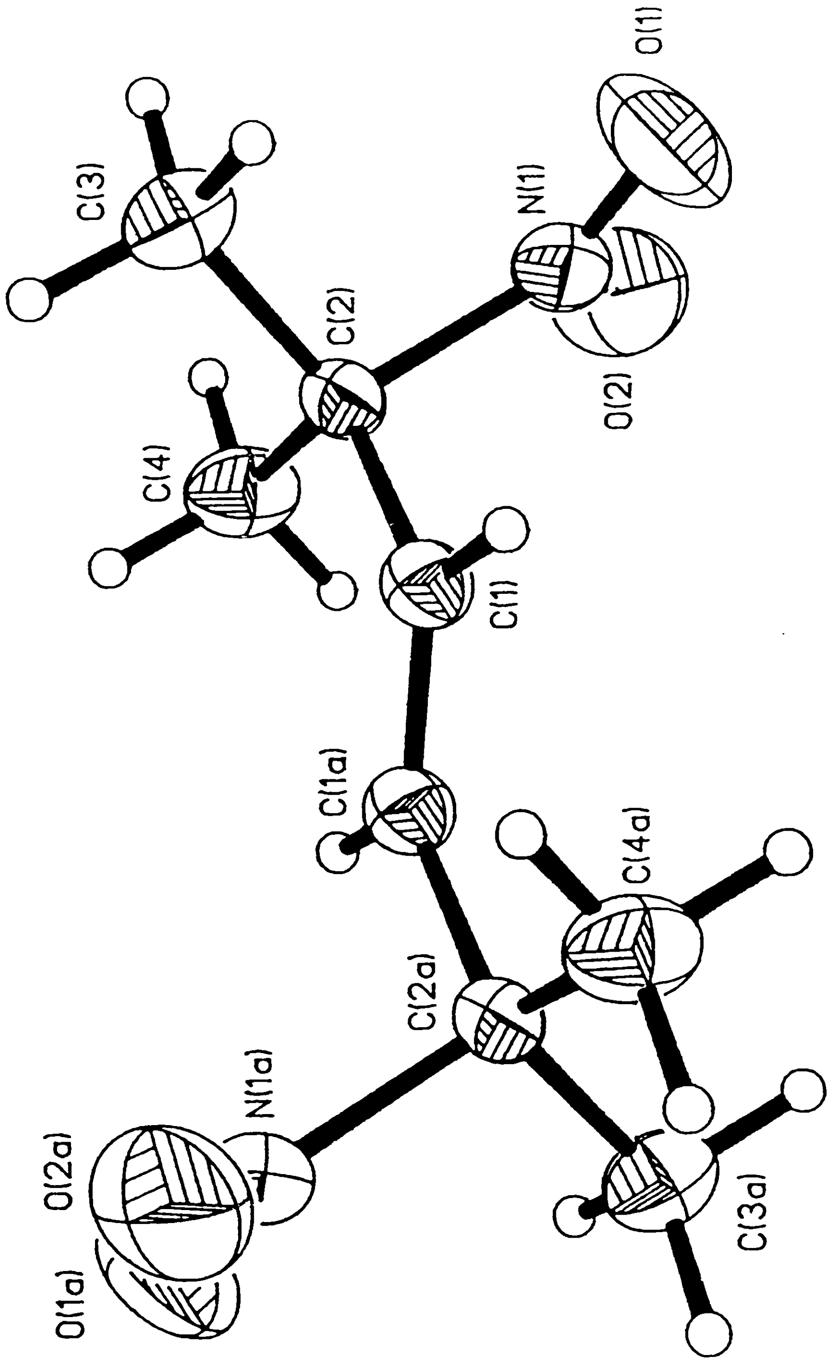


**Figure 2.2** Structure of *trans* 2,5-dimethyl-2,5-dinitro-3-hexene from X-ray analysis

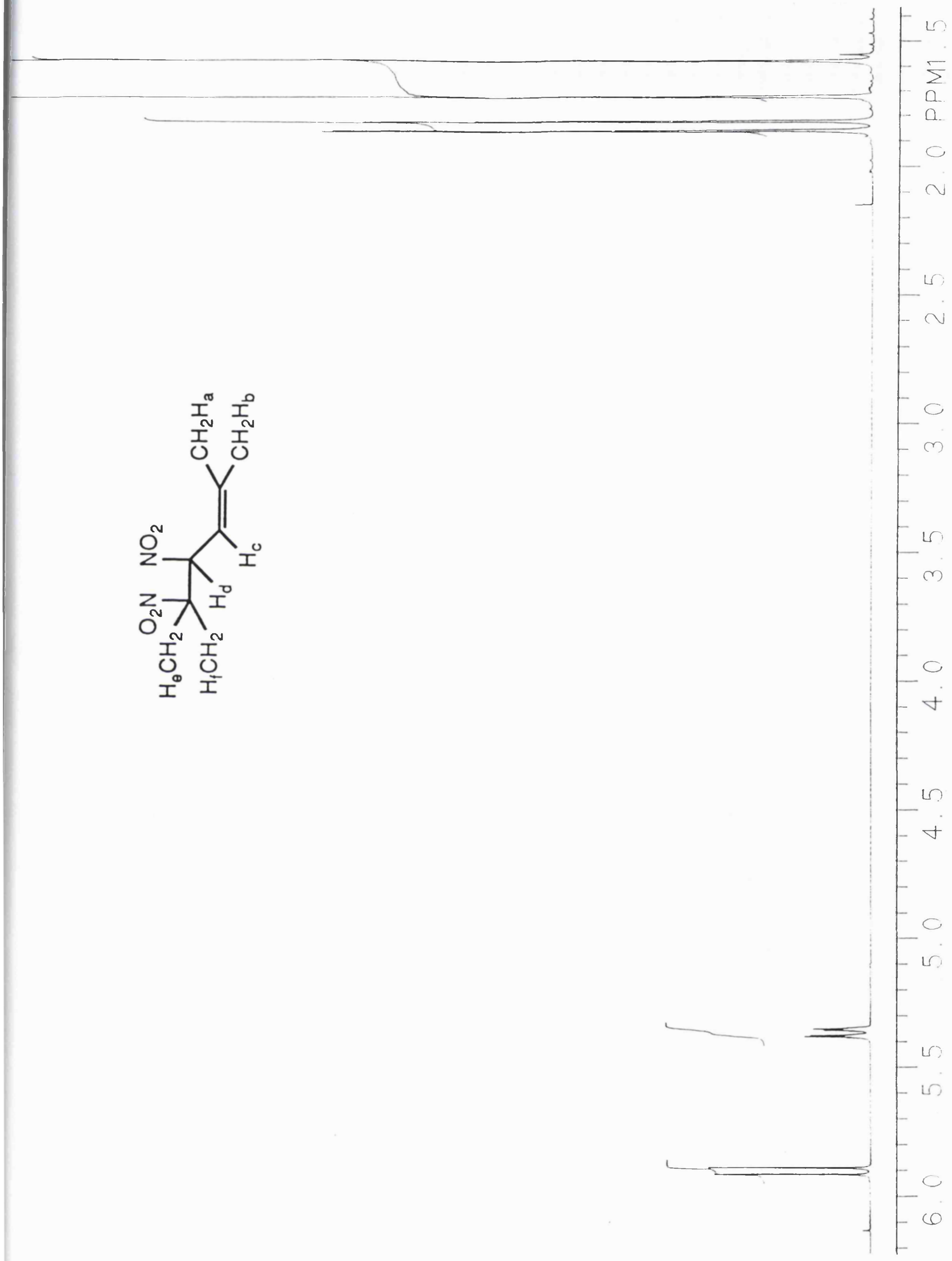
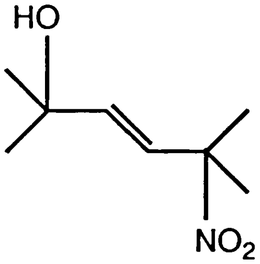


**Figure 2.3** $^1$H n.m.r. spectrum for 2,5-dimethyl-2,3-dinitro-4-hexene.

| | |
|---|---|
| $^{13}$C n.m.r.(C) δ: | 18.77, 21.43, 24.45, 26.26, 88.49, 88.57, 113.40, 146.61. |
| C.I.M.S. m/e: | 220 ($M.NH_4^+$), 109 ($M^+$-93). |
| Analysis: | Insufficient sample. |

### 2.2.3 2-Hydroxy-2,5-dimethyl-5-nitro-3-hexene.



The $^1$H n.m.r. spectrum obtained (Figure 2.4) was simple, two methyl signals were observed, with no splitting, thus implying that asymmetric addition had occurred at either end of the molecule. Two low field doublets were also seen and these arose from the coupling of the two olefinic protons. There was no evidence of the hydroxy proton in the spectrum.

From the $^{13}$C n.m.r. spectrum recorded, there were six peaks. This was consistent with the asymmetric addition at either end of the molecule. In the methyl region of the spectrum two signals were observed, corresponding to the methyl groups at either end of the molecule. The signals at δ 79.75 and δ 87.55 are consistent with the chemical shifts expected for hydroxy and nitro substituted carbon centres respectively. Finally the two low field peaks are due to the two olefinic carbons.

The C.I.M.S. spectrum confirmed the hydroxy adduct as a molecular ion for $C_8H_{15}NO_3$ was observed, and also a signal corresponding to the dimer was seen in the spectrum.

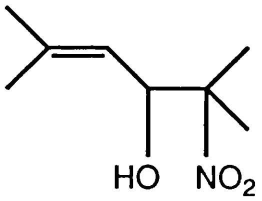
$^1$H n.m.r. (C) δ: 1.27 (6H) s; 1.69 (6H) s; 5.85 (1H) d, $^3$J 16.19 Hz; 5.90(1H) d, $^3$J 16.19 Hz.

$^{13}$C n.m.r. (C) δ: 24.82, 25.94, 79.75, 87.55, 129.23, 137.24.

C.I.M.S. m/e: 362 ($2M.NH_2^+$); 172 ($M^+$-1); 126 ($M^+$-47); 110 ($M^+$-63); 97($M^+$-75).

Analysis: Insufficient sample.

### 2.2.4 3-Hydroxy-2,5-dimethyl-2-nitro-4-hexene.



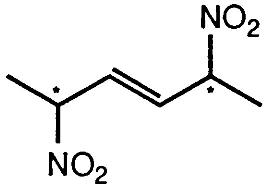
In the $^1$H n.m.r. spectrum (Figure 2.5) four methyl signals are clearly visible. The two high field signals at δ 1.48 and δ 1.56 correspond to the protons $H_f$ and $H_g$. The two lower field signals are split into doublets and this arises from long range coupling between the methyl protons $H_a$, $H_b$ and the olefinic proton $H_c$. The hydroxy proton $H_e$ has a chemical shift δ 2.08, and this appears as a doublet due to coupling with proton $H_d$. Proton $H_d$ appears as a doublet of doublets centred on δ 4.81 as it couples to the olefinic and the hydroxy proton. The low field doublet of heptets is produced by the olefinic proton $H_c$, as it couples to the protons $H_a$, $H_b$ and $H_d$. Due to the methyl protons $H_a$ and $H_b$ being *cis* and *trans* to $H_c$ the coupling constants are slightly different, however as the coupling constants are similar the splitting pattern observed approximates to a heptet.

The $^{13}$C n.m.r. spectrum consisted of eight peaks. Four signals were observed in the methyl region and this again confirms addition at the 2 and 3 position, as all the methyl groups had become non equivalent. The hydroxy and nitro substituted carbons appear at δ 72.56 and δ 91.87 respectively. The two low field signals are due to the olefinic carbons.

| | |
|---|---|
| $^1$H n.m.r.(C) δ: | 1.48 (3H) s; 1.56 (3H) s; 1.74 (3H) d, $^4J_{a,c}$ 1.27 Hz; 1.76(3H) d, $^4J_{b,c}$1.28 Hz; 2.08 (1H) d, $^3J_{e,d}$ 4.99 Hz; 4.81(1H) dd, $^3J_{d,c}$ 9.34 Hz, $^3J_{d,e}$ 4.99 Hz; 5.09 (1H) dh, $^3J_{d,c}$ 9.34 Hz, $^4J$ 1.27 Hz. |
| $^{13}$C n.m.r.(C) δ: | 18.83, 19.83, 23.82, 26.18, 72.76, 91.87, 121.09, 140.16. |
| C.I.M.S. m/e: | 191 ($M.NH_4^+$), 173 ($M^+$), 127 ($M^+$-46), 109 ($M^+$-64). |
| Analysis: | Insufficient sample. |

## 2.3 Products from the reaction between 2,4-Hexadiene and Nitrogen Dioxide.

### 2.3.1 2,5-Dinitro-3-hexene (First Diastereoisomer).



This molecule had a complex $^1$H n.m.r. spectrum initially as the molecule existed as a mixture of two diastereoisomers one as the *meso* form, the other as a mixture of two enantiomers. These were separated using h.p.l.c. (Section 8.5). The enantiomers gave the same general splitting pattern as the diastereoisomers, just different chemical shifts.

The $^1$H n.m.r. spectrum of the separated diastereoisomers consisted of three main regions, the methyl region, the olefinic region, and the nitro-

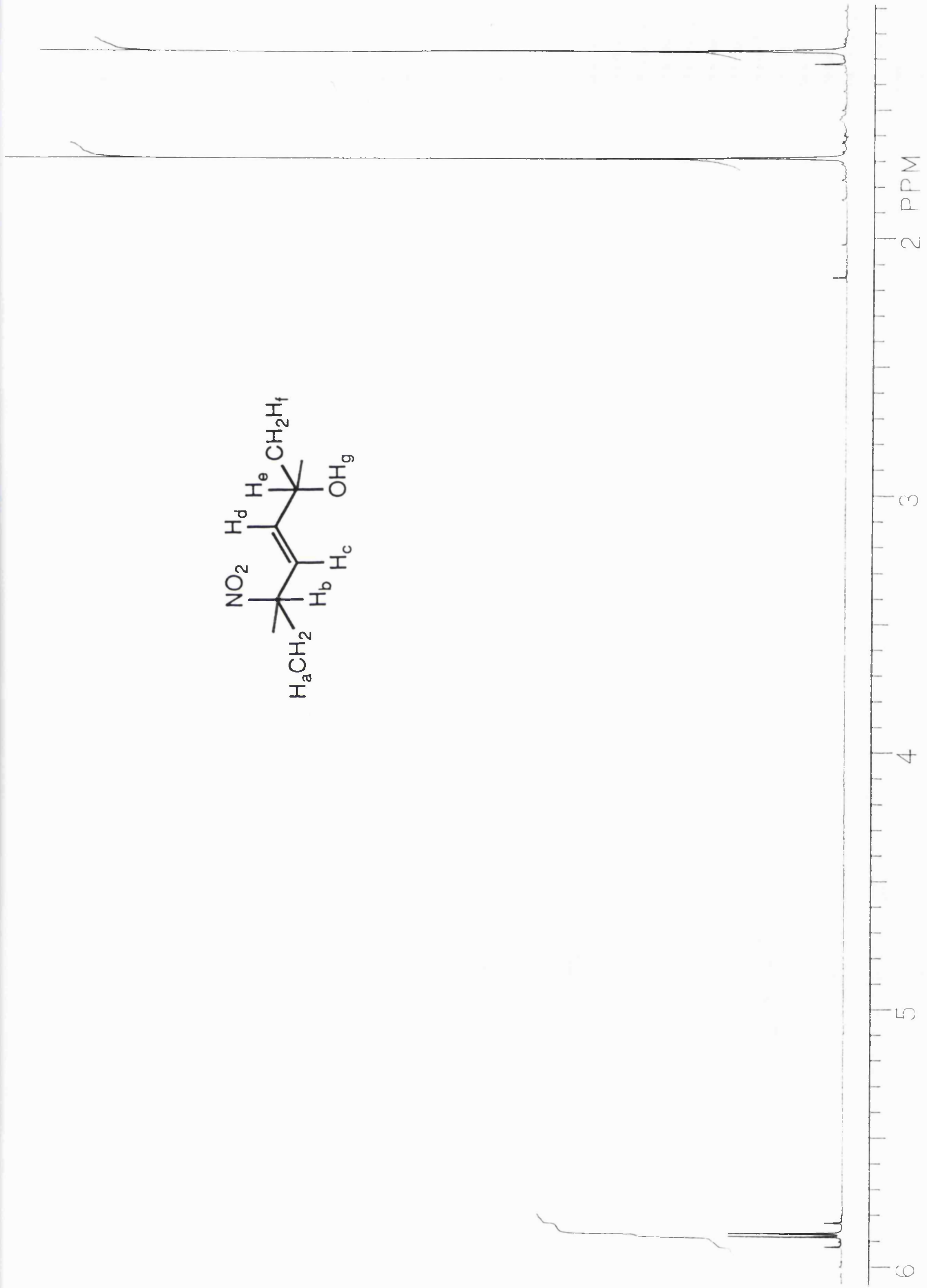


**Figure 2.4** $^1$H n.m.r. spectrum for 2-hydroxy-2,5-dimethyl-5-nitro-3-hexene

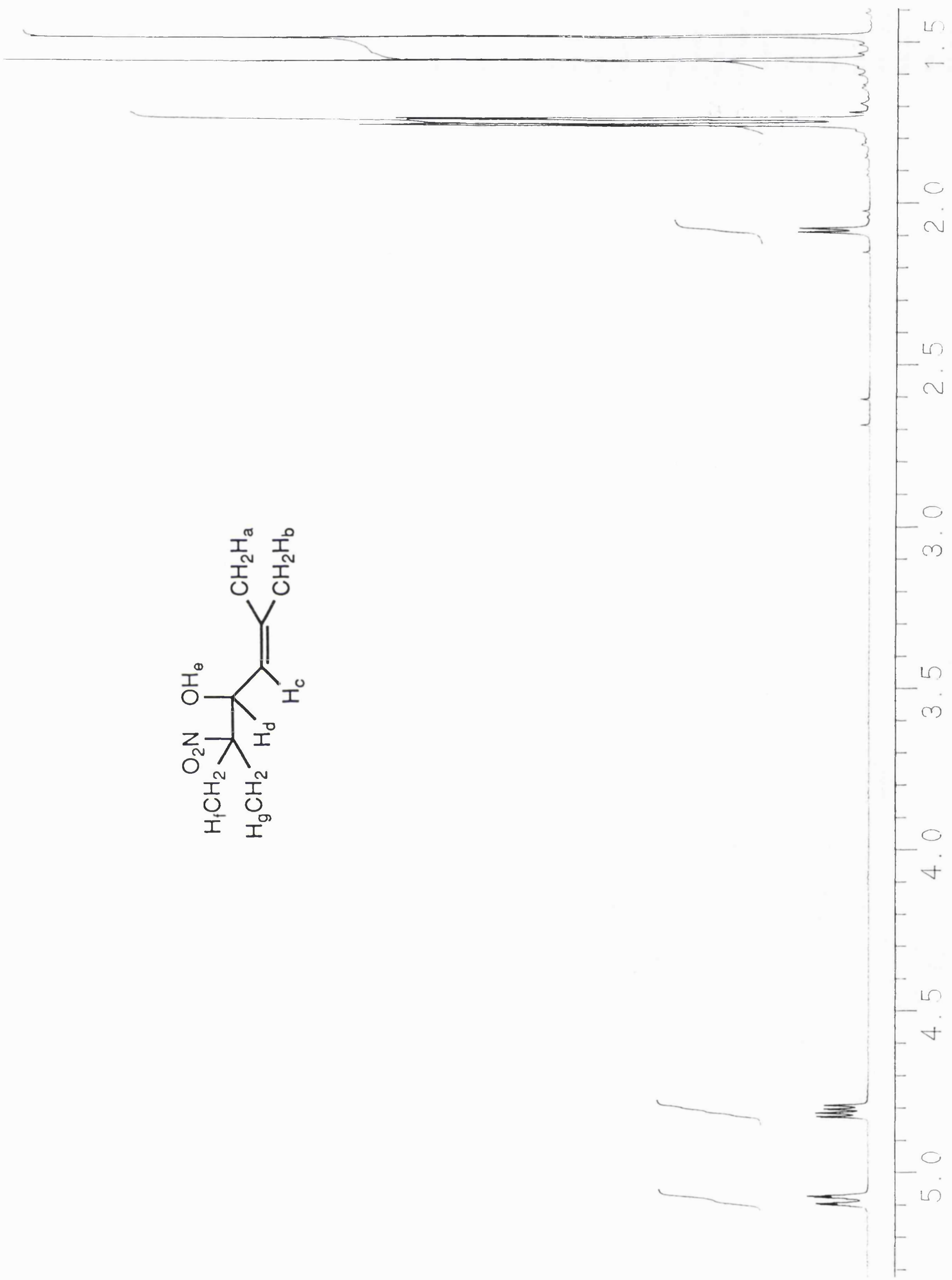


**Figure 2.5** $^1$H n.m.r. spectrum for 3-hydroxy-2,5-dimethyl-2-nitro-4-hexene

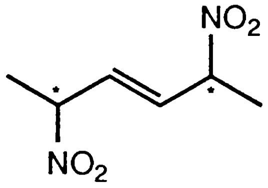
substituted region (Figure 2.6). The methyl signal appeared as a doublet due to coupling between protons $H_a$ and proton $H_b$. The olefinic region consisted of a doublet of doublets brought about by proton $H_c$ coupling to $H_b$ with a large coupling constant, and this was split further by a long range coupling of proton $H_c$ to proton $H_e$. No coupling is observed between protons $H_c$ and proton $H_d$ as they are equivalent.

The nitro substituted region of the spectrum consisted of a complex multiplet centred on δ 5.09. This multiplet was due to proton $H_b$ coupling to the methyl protons $H_a$ to produce a quartet. This was split further into a quartet of doublets by coupling to $H_c$, and then split further by a long range coupling to $H_d$ to produce the observed multiplet. The multiplet was simulated, and can be compared in Figure 2.7.

The $^{13}C$ n.m.r. spectrum consisted of three signals as would be expected by the symmetry of the molecule. The high field signal corresponded to the methyl groups, the low field signal to the olefinic carbons and the remaining signal to the nitro-substituted carbon.

| | |
|---|---|
| $^1H$ n.m.r.(C) δ: | 1.70 (3H) d, $^3J_{a,b}$ 6.80 Hz; 5.09 (1H) m, $^3J_{b,a}$ 6.80 Hz, $^3J_{b,c}$ 4.40 Hz, $^4J_{b,d}$ 2.12 Hz; 6.10 (1H) dd, $^3J_{c,b}$ 4.40 Hz, $^4J_{c,e}$ 2.12 Hz. |
| $^{13}C$ n.m.r.(C) δ: | 19.20, 83.25, 131.19. |
| C.I.M.S. m/e: | 192 ($M.NH_4^+$), 127 ($M^+$-46). |
| Analysis: | Calculated for $C_6H_{10}N_2O_4$: C, 41.38; H, 5.79; N, 16.08<br>Found: C, 40.71; H, 6.02; N, 15.19 |

### 2.3.2 2,5-Dinitro-3-hexene (Second Diastereoisomer).



Like its diastereoisomer (section 2.3.1) the $^1H$ n.m.r. spectrum consisted of three main regions. Similar splitting patterns were observed, however they all appeared at higher fields implying that they were more shielded.

The $^{13}C$ n.m.r. spectrum consisted of three signals which was consistent with the symmetry of the molecule.

$^1H$ n.m.r.(C) $\delta$: 1.66 (3H) d, $^3J_{a,b}$ 6.85 Hz; 5.05 (1H) m, $^3J_{b,a}$ 6.85 Hz, $^3J_{b,c}$ 4.90 Hz, $^4J_{b,d}$ 2.40 Hz; 6.07 (1H) dd, $^3J_{c,b}$ 4.90 Hz, $^4J_{c,e}$ 2.40 Hz.

$^{13}C$ n.m.r.(C) $\delta$: 18.89, 82.92, 130.82.

C.I.M.S. m/e: 192 ($M.NH_4^+$).

Analysis: Calculated for $C_6H_{10}N_2O_4$: C, 41.38; H, 5.79; N, 16.08

Found: C, 41.62; H, 5.77; N, 15.63

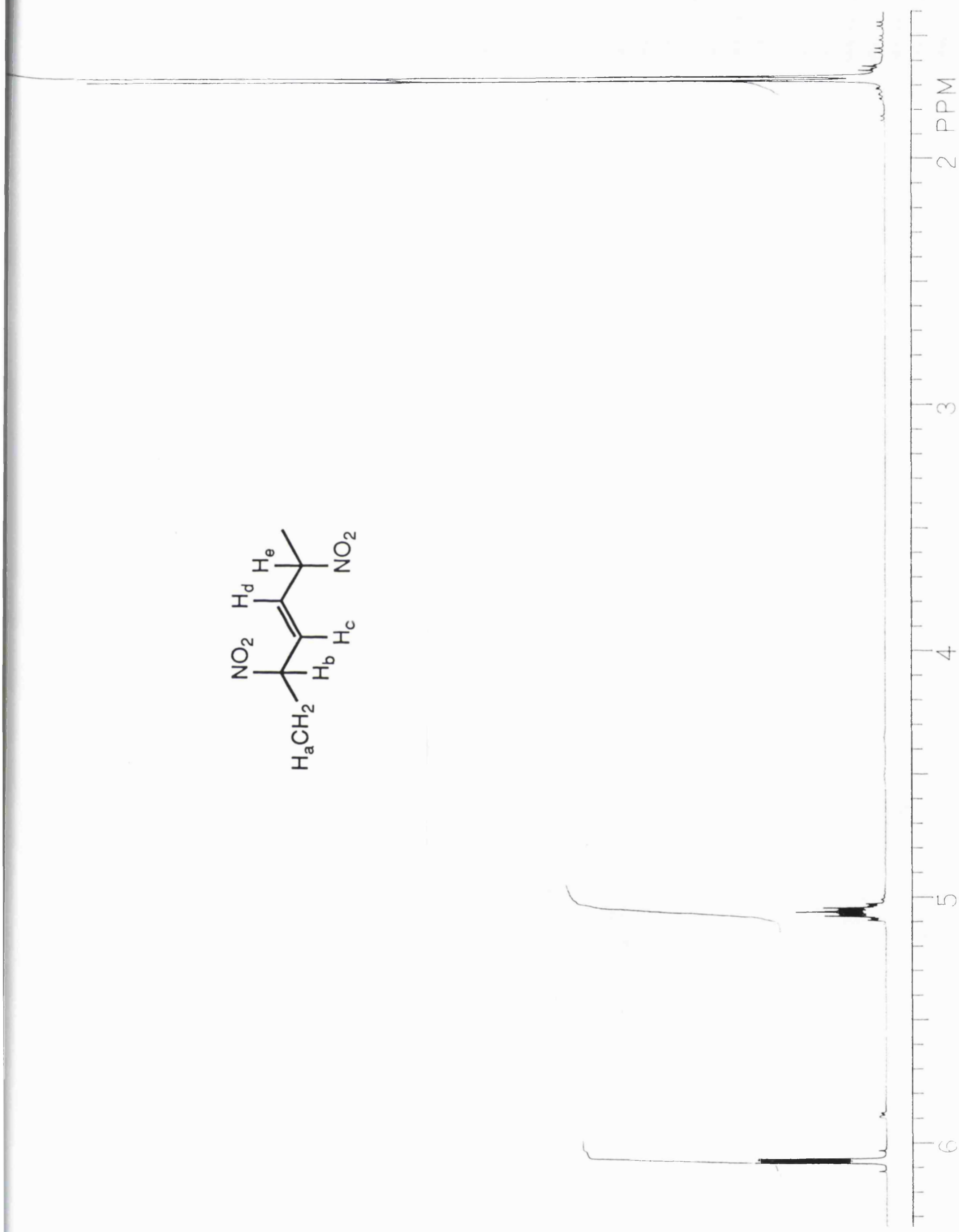


**Figure 2.6** $^1H$ n.m.r. spectrum for 2,5-dinitro-3-hexene

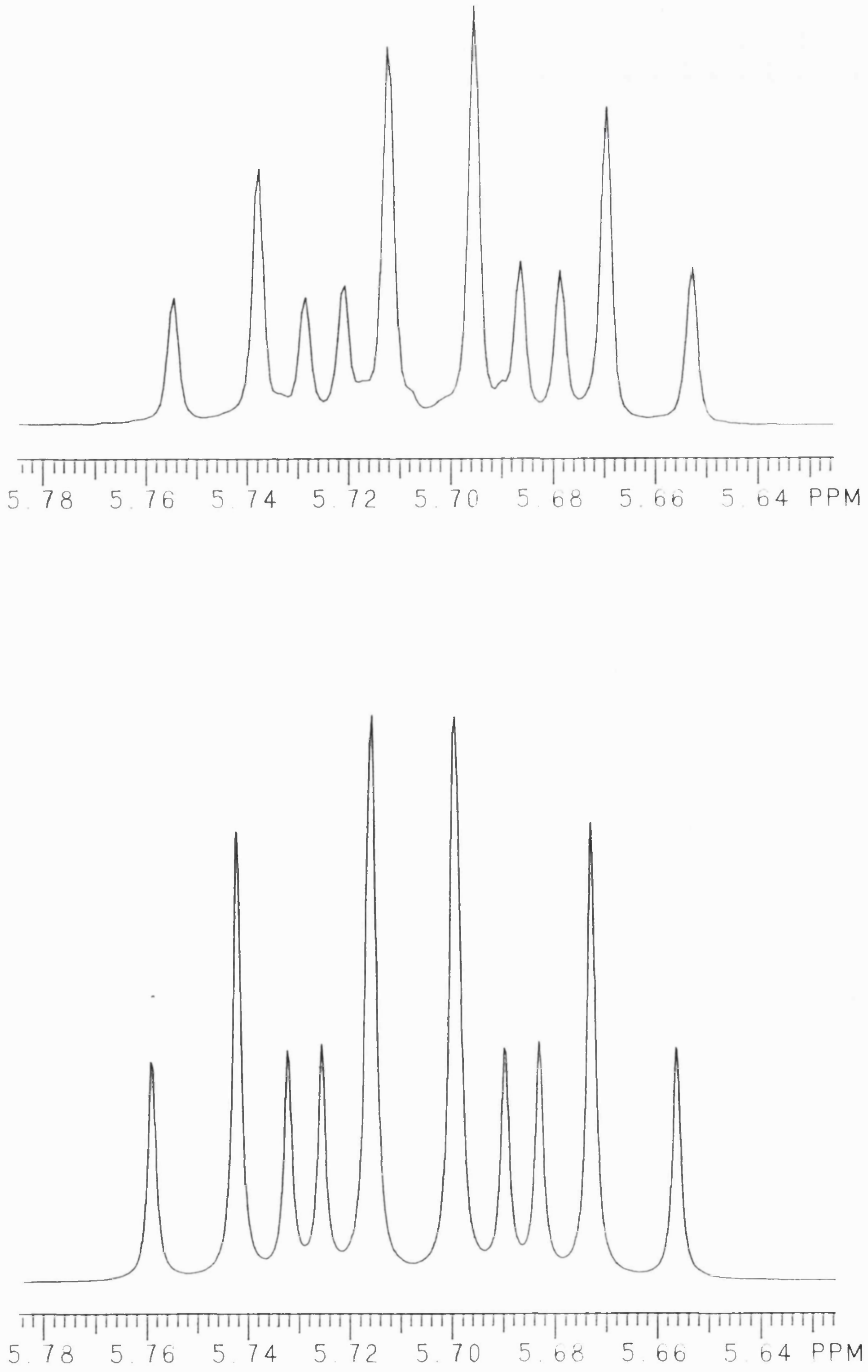


**Figure 2.7** Comparison of the multiplet centred on $\delta$ 5.09 for:-

a) $^1$H n.m.r. spectrum for 2,5-dinitro-3-hexene (first diastereoisomer)

b) the computer simulated multiplet.

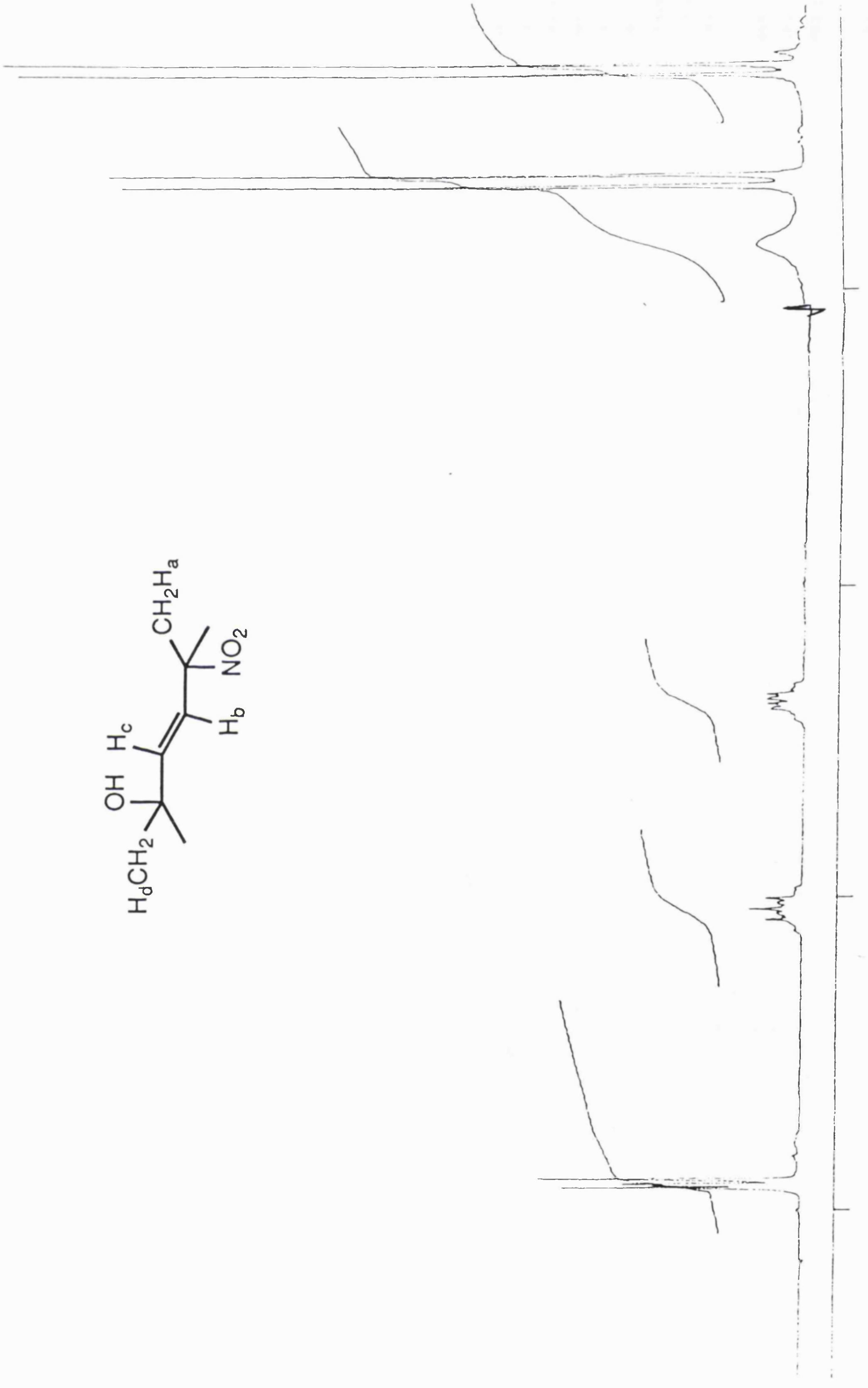
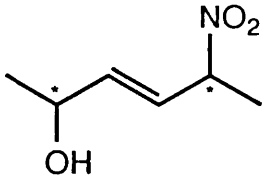


**Figure 2.8** $^1$H n.m.r. spectrum for 2-hydroxy-5-nitro-3-hexene

### 2.3.3 2-Hydroxy-5-nitro-3-hexene (First Diastereoisomer).



The $^1H$ n.m.r. spectrum (Figure 2.8) was complicated and consisted of six main regions. The methyl region comprised of two sets of doublets, arising from the methyl groups at either end of the molecule coupling with their neighbouring proton $H_b$ or $H_e$. From proton decoupling experiments it was possible to assign $H_g$ as the high field doublet. The multiplet centred on δ 5.02 was due to proton $H_b$, which was brought about by coupling to the protons $H_a$, $H_c$ and $H_d$. The splitting pattern obtained was consistent with that observed for the similar proton in 2,5-dinitro-3-hexene (section 2.3.1). Proton $H_e$ appeared as a complex multiplet centred on δ 4.38. This had a more complex splitting pattern than $H_b$ because of the additional coupling to the hydroxy proton $H_g$, which appeared as a broad singlet at δ 1.60. The signals from the olefinic protons $H_c$ and $H_d$ were overlapping and appeared as a complex multiplet δ 5.02.

The $^{13}C$ n.m.r. spectrum consisted of six signals which was consistent with the assignment of an asymmetric addition at either end of the molecule. The two high field signals correspond to the methyl groups, while the two low field signals correspond to the olefinic carbons. The signals at δ 74.67 and δ 87.12 are due to the hydroxy-substituted and nitro-substituted carbons respectively.

$^1H$ n.m.r.(C) δ: 1.28 (3H) d, $^3J_{f,e}$ 6.56 Hz; 1.62 (3H) d, $^3J_{a,b}$ 6.84 Hz; 1.60 (1H) bs; 4.28 (1H) m; 5.02 (1H) m; 5.90 (2H) m.

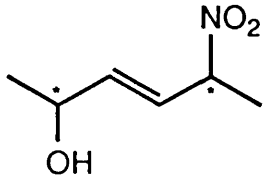
$^{13}C$ n.m.r.(C) δ: 13.11, 17.82, 74.67, 87.12, 127.61, 132.20.

C.I.M.S. m/e: 162 ($M.NH_3^+$), 81 ($M^+$-64)

Analysis : Calculated for $C_6H_{11}NO_3$: C, 49.65; H, 7.64; N, 9.65.

Found: C, 49.40; H, 7.56; N, 9.67.

### 2.3.4 2-Hydroxy-5-nitro-3-hexene (Second Diastereoisomer).



The $^1H$ n.m.r. spectrum was similar to its diastereoisomer (section 2.3.3), with the same splitting patterns being observed, except that they appeared at a slightly higher field.

$^1H$ n.m.r.(C) $\delta$: 1.28 (3H) d, $^3J_{f,e}$ 6.56 Hz; 1.62 (3H) d, $^3J_{a,b}$ 6.84 Hz; 1.60 (1H) bs; 4.28 (1H) m; 5.02 (1H) m; 5.90 (2H) m.

$^{13}C$ n.m.r.(C) $\delta$: 13.11, 16.18, 73.38, 86.21, 127.28, 131.21.

C.I.M.S. m/e: 163 ($M.NH_4^+$), 98 ($M^+$-47), 80 ($M^+$-65)

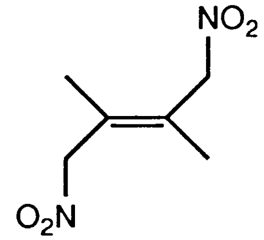
Analysis : Calculated for $C_6H_{11}NO_3$: C, 49.65; H, 7.64; N, 9.65.

Found: C, 49.90; H, 7.81; N, 9.32 .

## 2.4 Products from the reaction between 2,3-Dimethyl-1,3-Butadiene and Nitrogen Dioxide.

All reactions were carried out in the liquid phase in standard organic solvents. Full experimental details for this set of reactions are given in Chapter 8 (Section 8.4).

### 2.4.1 *trans*-2,3-Dimethyl-1,4-dinitro-3-butene.



*trans*-2,3-Dimethyl-1,4-dinitro-2-butene exists as a white crystalline solid, and was recrystallised from cold hexane to produce needle like crystals. An X-ray analysis was carried out on the crystal.

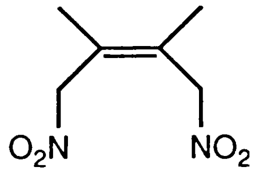
The $^1H$ n.m.r. spectrum (Figure 2.9) observed consisted of two singlets; one due to the methyl protons and the other from the protons attached to the nitro-substituted carbon. As only two signals were observed it showed that the molecule was symmetrical.

The $^{13}C$ n.m.r. spectrum consisted of three signals. The high field signal corresponded to the methyl carbons, the low field signal to the olefinic carbons, while the signal at δ 78.2 was due to the nitro-substituted carbon.

The conformation of the molecule was determined by the X-ray analysis. The double bond was found to be of the *trans* orientation (Figure 2.10).

| | |
|---|---|
| $^1H$ n.m.r.(C) δ: | 1.99 (6H) s; 5.08 (4H) s. |
| $^{13}C$ n.m.r.(C) δ: | 18.1, 78.2, 129.5. |
| C.I.M.S. m/e: | 192 ($M.NH_4^+$), 35 ($M^+$-149). |
| Analysis: | Calculated for $C_6H_{10}N_2O_4$: C, 41.38; H, 5.79; N, 16.07.<br>Found: C, 41.29; H, 5.73; N, 15.51. |

### 2.4.2 *cis*-2,3-Dimethyl-1,4-dinitro-2-butene.



This compound existed as a pale yellow oil and like its isomer (section 2.4.1) the $^1H$ n.m.r. spectrum was simple and consisted of only two signals; the high field signal corresponding to the methyl protons, and the low field signals to the methylene protons.

$^{13}C$ n.m.r. spectrum had three signals, with the low and high field signals corresponding to the olefinic and methyl carbons respectively, and the signal at $\delta$ 78.00 corresponding to the nitro substituted carbon.

| | |
|---|---|
| $^1H$ n.m.r.(C) $\delta$: | 1.95 (6H) s; 5.12 (4H) s. |
| $^{13}C$ n.m.r.(C) $\delta$: | 18.4, 78.0, 129.9. |
| C.I.M.S. m/e: | 192 ($M.NH_4^+$). |
| Analysis: | Calculated for $C_6H_{10}N_2O_4$: C, 41.38; H, 5.79; N, 16.07.<br>Found: C, 40.86; H, 5.44; N, 15.95. |

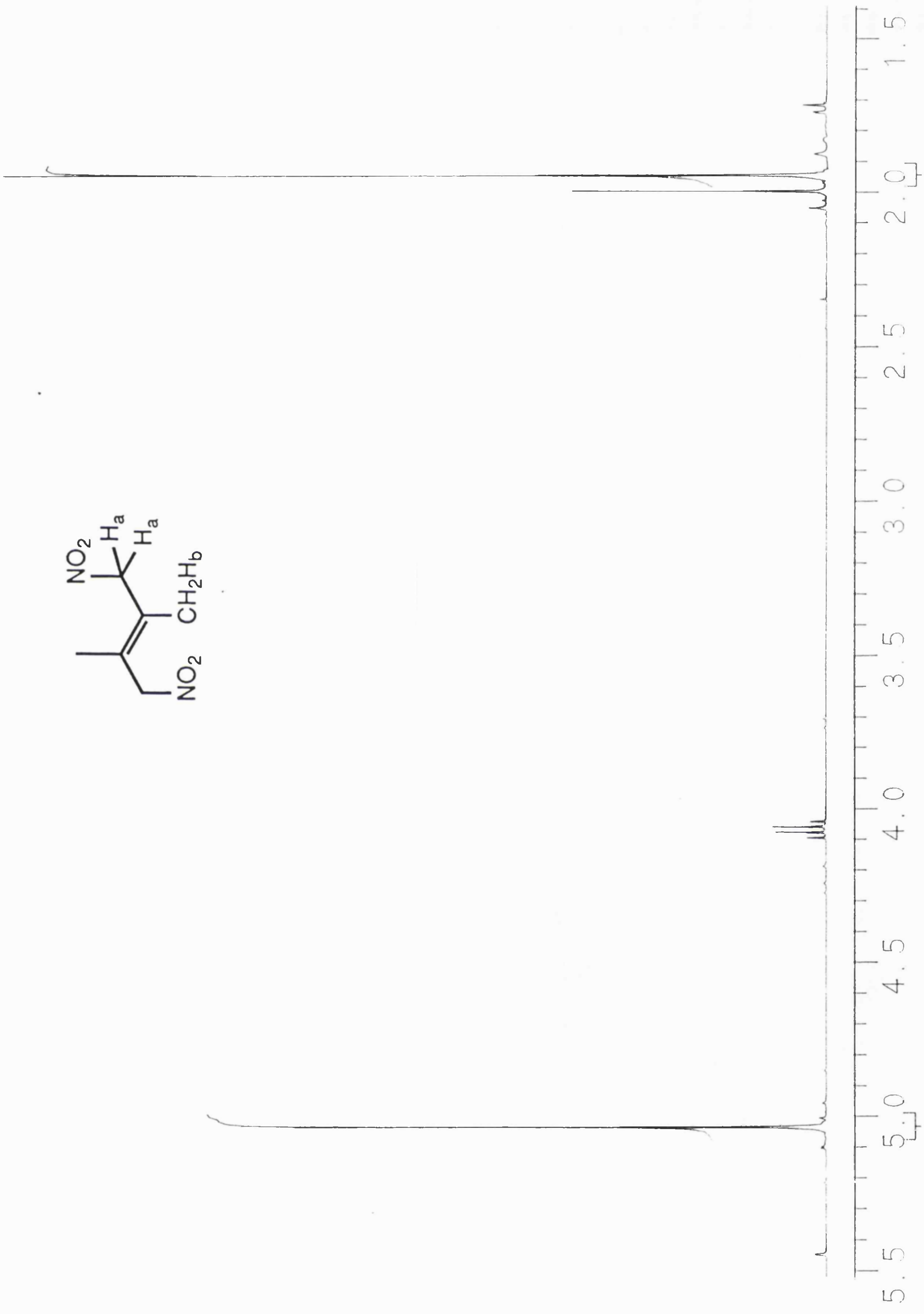


**Figure 2.9** $^{1}H$ n.m.r. spectrum for *trans*-2,3-dimethyl-1,4-dinitro-3-butene

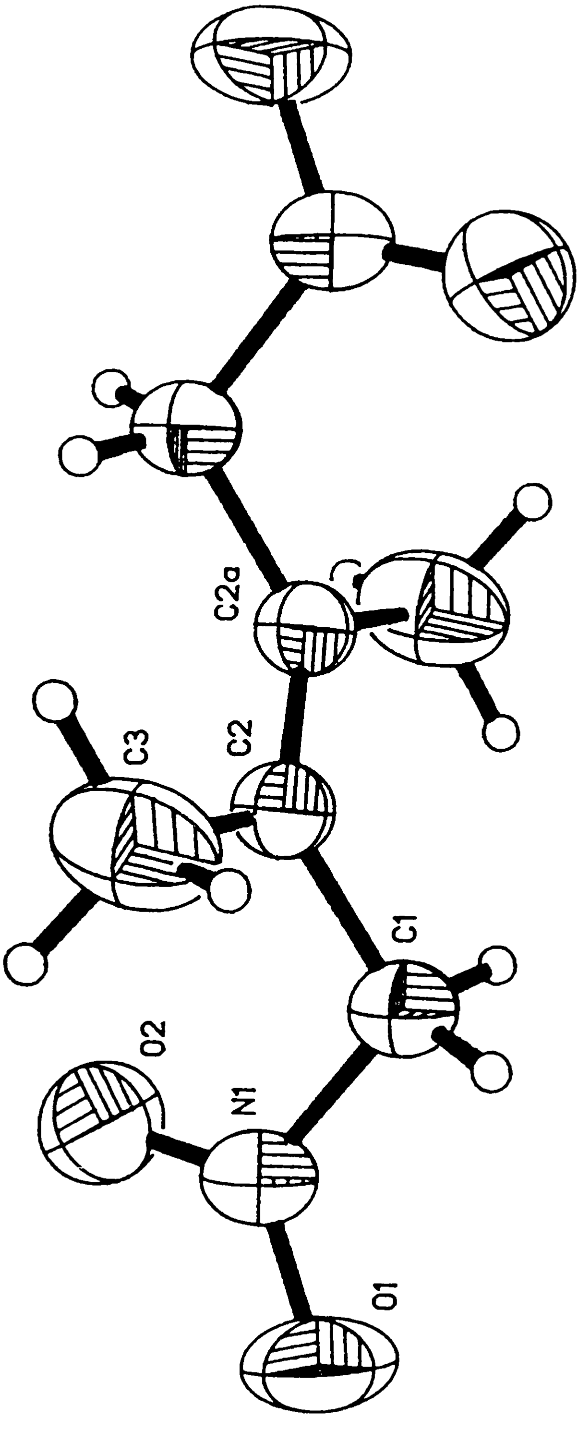
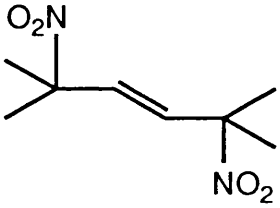


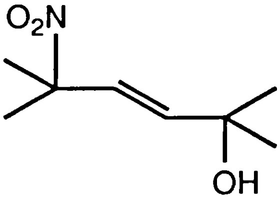
**Figure 2.10** Crystal structure for *trans*-2,3-dimethyl-1,4-dinitro-3-butene.

## 2.5 Discussion.

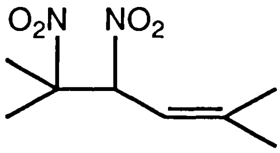
From the reactions between 2,5-dimethyl-2,4-hexadiene and nitrogen dioxide, one main product was isolated, 2,5-dimethyl-2,5-dinitro-3-hexene (**1**), which was formed in an approximate yield of 80%. From the remaining 20% three other compounds were positively identified: 2-hydroxy-2,5-dimethyl-5-nitro-3-hexene (**2**), 2,5-dimethyl-2,3-dinitro-4-hexene (**3**), and 3-hydroxy-2,5-dimethyl-2-nitro-4-hexene (**4**).



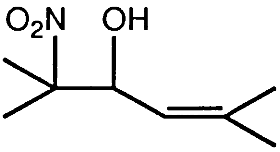
**1**



**2**

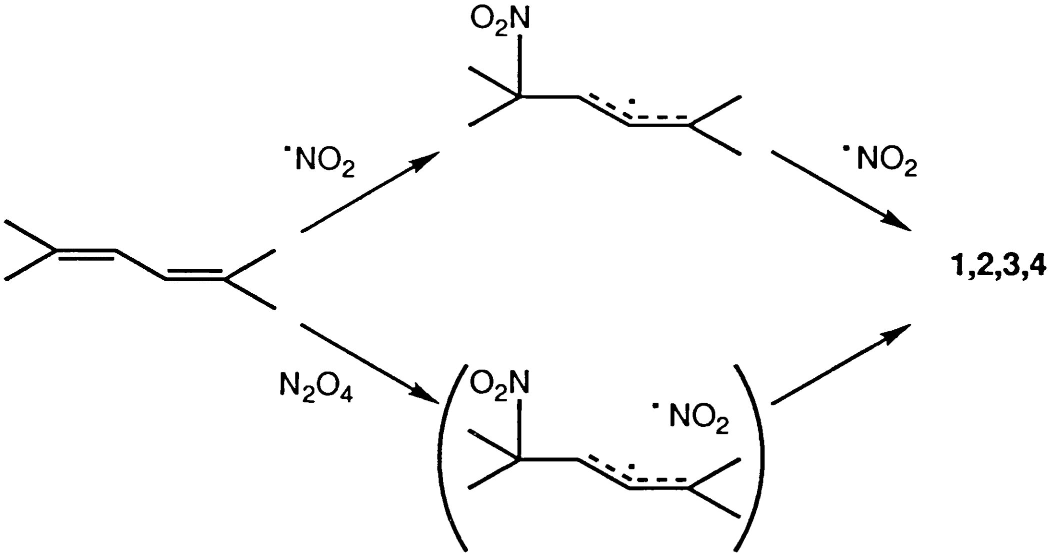


**3**



**4**

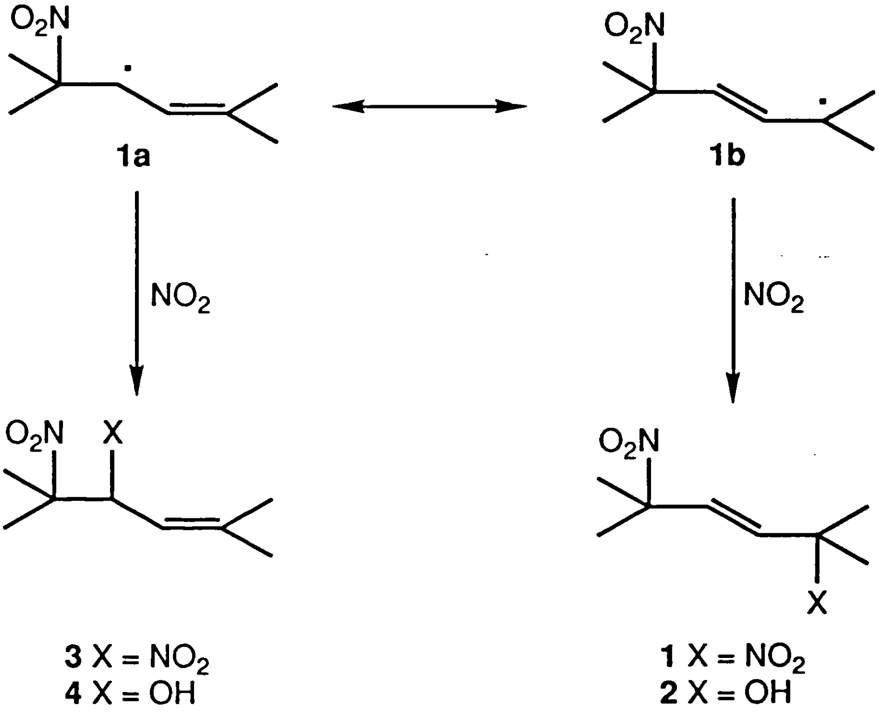
The formation of these compounds was consistent with the products expected from the attack of nitrogen dioxide on dimethylhexadiene (Scheme 2.1). The formation of **1** and **3** result from attack of two nitrogen dioxide molecules with reaction occurring on the nitrogen. Compounds **2** and **4** are formed by the initial attack via the nitrogen centred radical, then attack of a second nitrogen dioxide molecule via the oxygen. The resultant compound produced is the nitro-nitrite adduct, but these are unstable and decompose to the hydroxy-nitro adducts before they can be isolated. The decomposition of the nitrite occurs by the attack of water and acid to produce the alcohol and nitrous acid. There is evidence of their formation during the course of the reaction as the reaction mixture turns a pale green/blue colour which is characteristic of nitro-nitrite products. The colour disappears on standing.



**Scheme 2.1**

The reaction products were independent on the mode of addition of the reactants. Two modes of addition were employed: the normal mode of addition, which involves the addition of the nitrogen dioxide solution to that of the diene solution, and the reverse mode which involves adding the diene solution to the nitrogen dioxide solution.

Under normal mode conditions, where the ratio of $NO_2$ : diene was 2:1 the products **1**-**4** were produced, with 80% of **1** and trace amounts of **2-4**; similar yields were also observed for the reverse mode of addition. It was hoped that by changing the mode of addition we could alter the product distribution such that under normal modes of attack **1** and **2** would predominate, and under reverse mode **3** and **4** would predominate. This was thought because under normal mode addition, the diene would be in an excess to that of the nitrogen dioxide; therefore the concentration of nitrogen dioxide and dinitrogen tetroxide would be low. With low concentrations of nitrogen dioxide addition via two separate nitrogen dioxide radicals was envisaged which would favour the formation of **1** and **2** as these are derived from the most stable radical intermediate (Scheme 2.2 **1b**). At high concentrations of nitrogen dioxide *i.e.*, the reverse mode of addition, the amount of dinitrogen tetroxide present is greater. If dinitrogen tetroxide were adding across the double bond then a concerted reaction may occur with **1a** (Scheme 2.2) reacting immediately with another nitrogen dioxide radical to produce **3** and **4**.

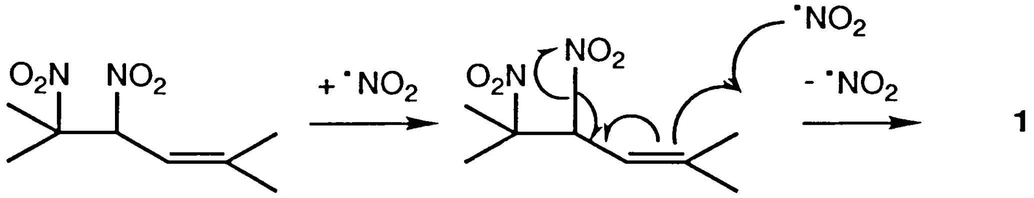


**Scheme 2.2**

As mentioned previously there was no discrimination between the two modes of attack, and this can be explained in two possible ways:-

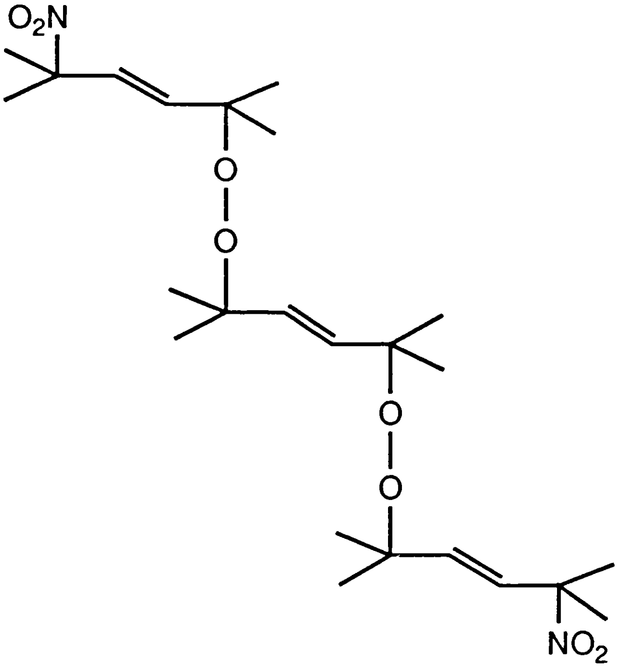
1. Reaction occurs always through the separate addition of two $NO_2$ radicals with no contribution from $N_2O_4$ which would favour compounds **3** and **4**.

2. That in the reverse mode of addition, **3** and **4** are formed, but **3** can react further with nitrogen dioxide (Scheme 2.3), and β-elimination of a nitro alkane occurs[55]. The resulting product being **1**.

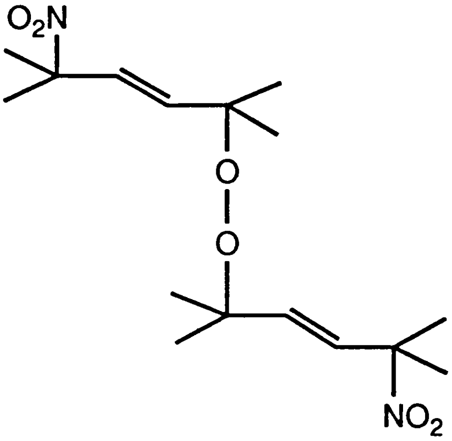


Scheme 2.3

The unidentified products from the reactions appeared to be polymeric species from their mass spectra. Two of the spectra (Figure 2.11 and Figure 2.12) have had tentative structures assigned to them. In Figure 2.11 the peak at 504 has been attributed to the empirical formula $C_{24}H_{48}N_2O_8[NH_4^+]$, which may represent structure **5**. The signal at 362 amu in Figure 2.12 corresponds to the structural formula $C_{16}H_{28}N_2O_6[NH_4^+]$, and may have the structure **6**. Fragmentation of **5** and **6** would account for the peaks at 315, 127 and 109 amu.



**5**



**6**

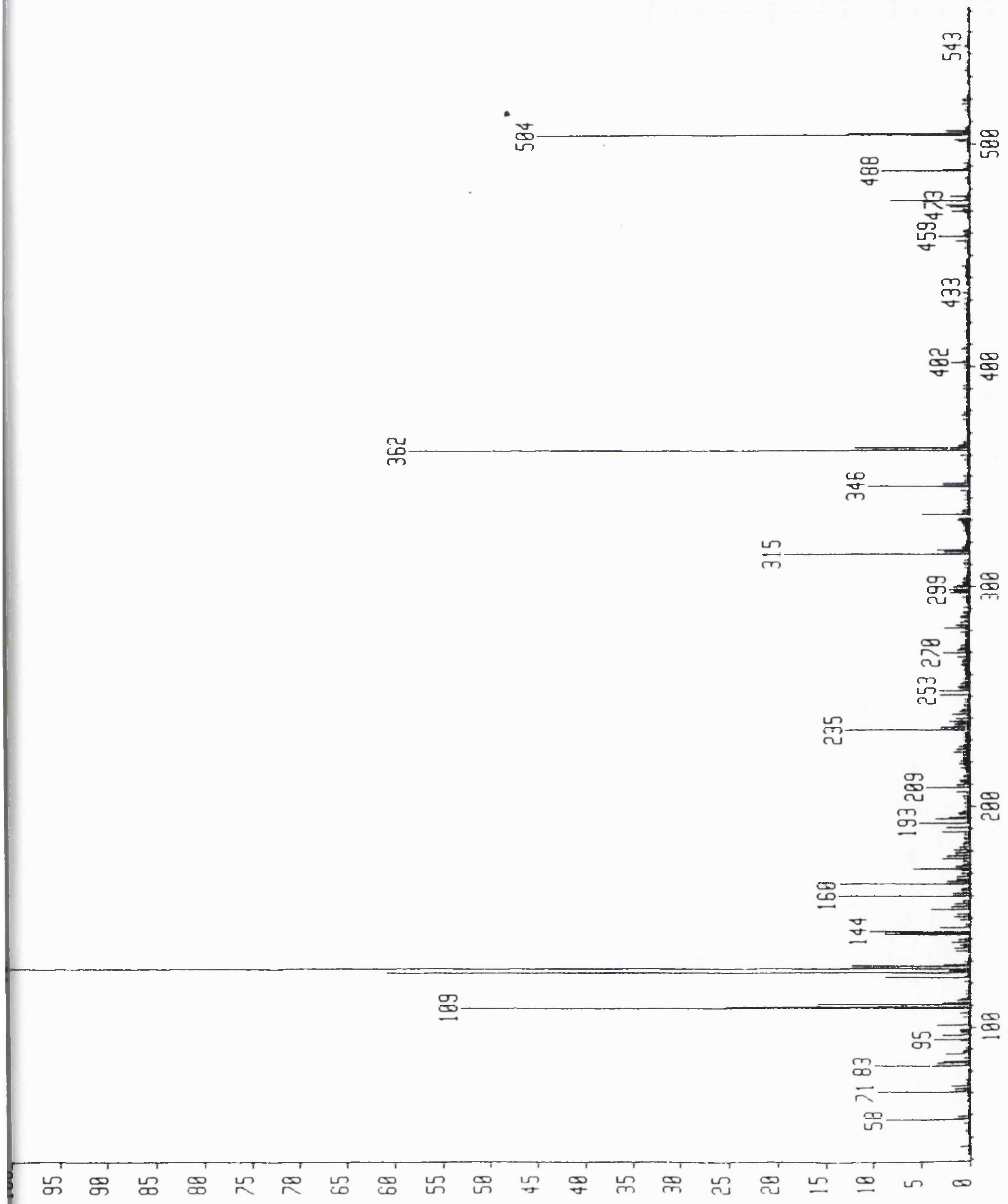


**Figure 2.11** C.I.M.S. spectrum for the postulated structure **5** ($C_{24}H_{48}N_2O_4$)

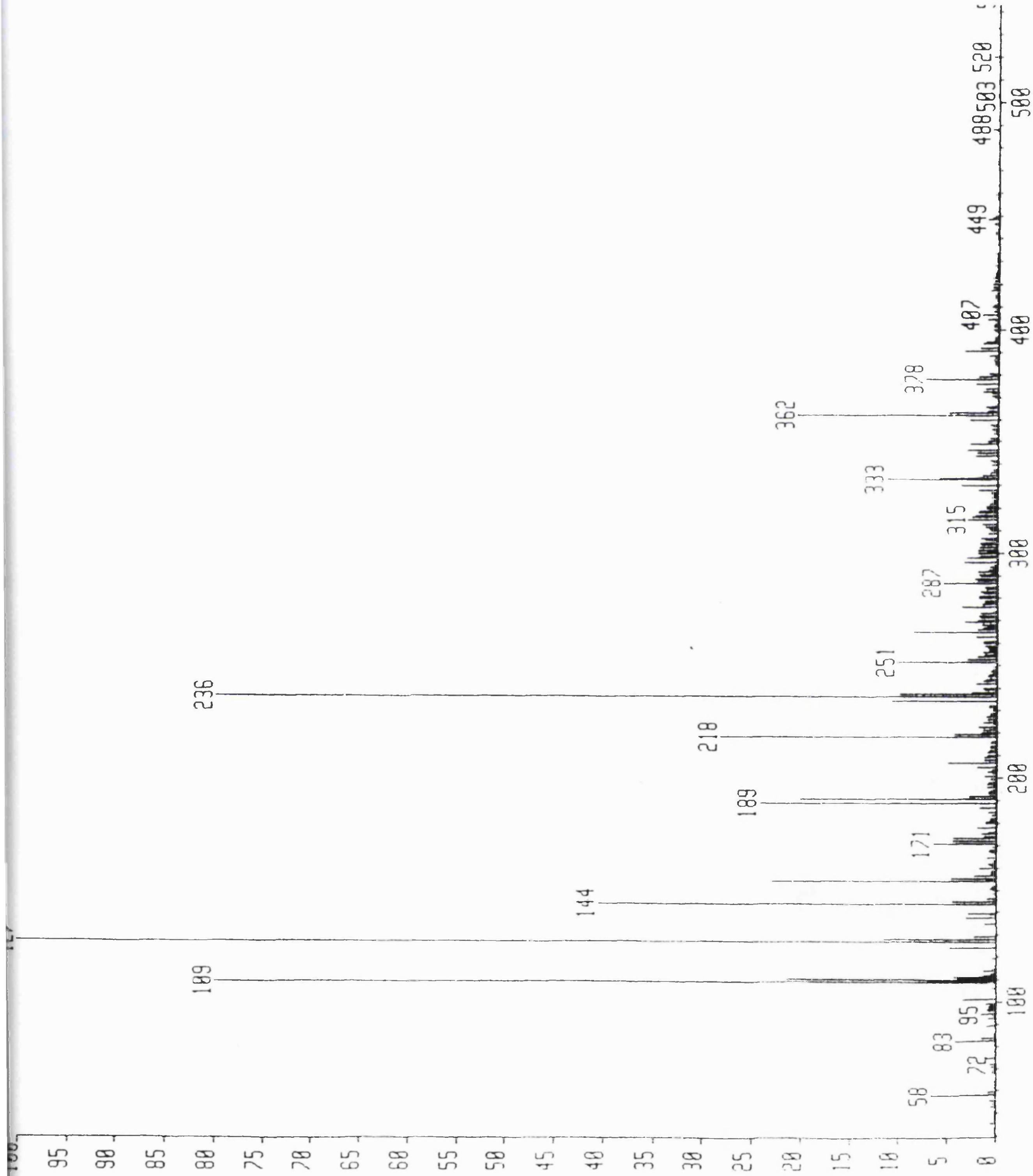
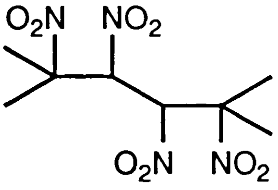


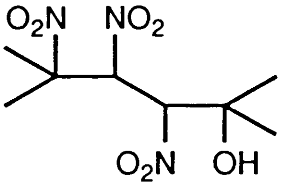
**Figure 2.12** C.I.M.S. spectrum for the postulated structure **6** ($C_{16}H_{28}N_2O_4$)

Other mass spectra obtained from minor h.p.l.c. fractions showed numerous peaks above 200 amu, and were attributed to polymeric species which remained unidentified.

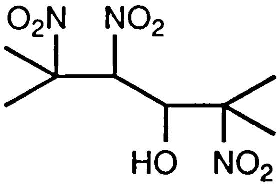
The reactions between 2,5-dimethyl-2,4-hexadiene and excess nitrogen dioxide were also investigated, as it was hoped that both double bonds would undergo addition by $NO_2$ to produce the tetra adducts **7**, **8**, **9**, **10**, and **11** However none of these compounds were isolated from the reaction mixture, and **1** was the predominant product.



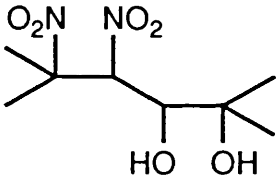
**7**



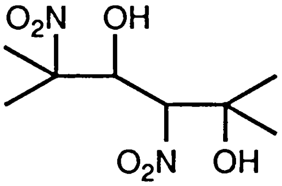
**8**



**9**



**10**



**11**

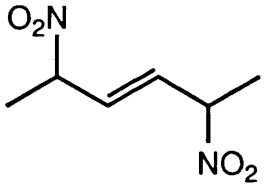
The reactions between **1** and nitrogen dioxide were carried out in both the normal and reverse modes of addition. Under both conditions there was no evidence of any reaction occurring, and **1** was fully recovered.

The inertness of the central double bond towards the attack of nitrogen dioxide could be brought about in two ways:-

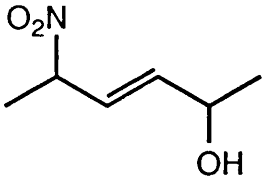
1. The double bond is too sterically hindered for nitrogen dioxide to add across it.
2. Due to the nitro groups being electronegative, the nitro groups at the 2 and 5 positions in **1** would have an electron withdrawing

effect on the double bond; this effect would make the double bond less susceptible to attack by the nitrogen dioxide since nitrogen dioxide is considered to be an "electrophilic" radical.

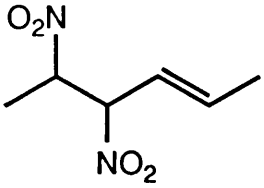
The first reason was not thought to be an important factor as addition of nitrogen dioxide to more sterically hindered alkenes has been reported[40], however to make certain we studied the reactions of 2,4-hexadiene with nitrogen dioxide.



**12**



**13**

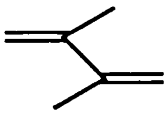


**14**

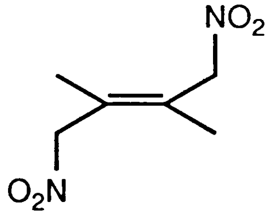
The reaction between 2,4-hexadiene and nitrogen dioxide was similar to that between 2,5-dimethyl-2,4-hexadiene and nitrogen dioxide, the major products being 2,5-dinitro-3-hexene (**12**), and 2-hydroxy-5-nitro-3-hexene (**13**). The products **12** and **13** both consisted of two diastereoisomers, which were split by h.p.l.c.(section 8.5). The two diastereoisomers were produced in approximately equal yields.

The reaction between 2,3-dimethyl-1-3-butadiene (**15**) and nitrogen dioxide was studied. This reaction was of particular interest as the methyl substituents at the 2 and 3 position would be electron donating to the central double bond if addition occurred at the 1 and 4 position. It was therefore hoped that higher adducts would be observed.

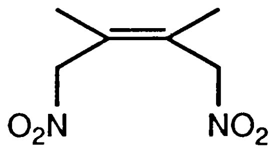
Under the normal mode of addition with a 1:2 molar ratio of **15**:nitrogen dioxide the expected 2,3-dimethyl-1,4-dinitro-3-butene adduct was observed. Unlike the reactions with 2,5-dimethyl-2,4-hexadiene and 2,4-hexadiene here there was evidence for both the *trans* and cis isomers, **16** and **17** respectively. 1–Hydroxy-4-nitro-3-butene (**18**) was not isolated.



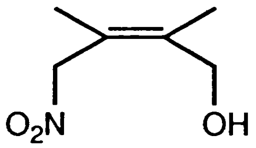
**15**



**16**



**17**



**18**

The isomers **16** and **17** were studied further and it was found that the amount of **16**:**17** could be greatly altered by the polarity of the solvent media and the ratio of **15**:nitrogen dioxide used in the reaction.

When the reactions were carried out such that the ratio of **15**:nitrogen dioxide was 1:2, the results obtained by changing the solvent are summarised in table 2.1. The reactions were all carried out in the 'normal' mode of addition.

From table 2.1 it can be seen that as the polarity of the solvent increases so the formation of the *trans* product becomes more favourable, increasing from 50% in non polar solvents such as n-hexane to 90% in acetonitrile. The only discrepancy is with 1,4-dioxane which favours the formation of the *trans* product although it has no dipole moment. This can be explained as overall there is no nett dipole moment, but locally each end of the dioxane molecule has a dipole moment associated with it, which will enhance the formation of the *trans* product.

This was consistent with molecular modelling predictions which calculated that the *trans* product would have a larger dipole moment, and hence the transition state would be stabilised to a greater extent by a polar solvent than that of the *cis* isomer.

If the reactions were now repeated but this time using a catalytic excess of nitrogen dioxide then over a 24 h period the amount of **16** and **17** produced was independent of the polarity of the solvent used, and the final composition was equal for both isomers. The composition does not change on leaving for longer periods.

**Table 2.1 Dependence of the formation of *cis*-2,3-dimethyl-1,4-dinitro-3-butene and *trans*-2,3-dimethyl-1,4-dinitro-3-butene on solvent polarity.**

| Solvent | Dipole Moment $\mu$/D | % *cis* isomer | % *trans* isomer |
|---|---|---|---|
| n-hexane | 0.0 | 50 | 50 |
| Benzene | 0.0 | 50 | 50 |
| Carbon tetrachloride | 0.0 | 50 | 50 |
| 1,4-dioxane | 0.0 | 36 | 64 |
| Diethyl ether | 1.15 | 21 | 79 |
| Dichloromethane | 1.60 | 29 | 71 |
| Acetonitrile | 3.85 | 10 | 90 |

a: The percentages quoted are the percentages of each isomer relative to the total amount of 2,3-dimethyl-1,4-dinitro-3-butene formed.

b: dipole moments recorded in the gas phase[62].

Increasing the amount of nitrogen dioxide further, had no effect on the final ratio of **16** and **17**, they were always equal, all that changed was the rate at which the equilibrium composition was reached.

Reverse mode of addition results mirrored those of the excess nitrogen dioxide results for the normal mode.

From these results some conclusions can be made about the reaction products and the reaction mechanism.

1. As **17** is formed in excess initially when the reaction is carried out in a polar medium then this must be the kinetically controlled product, as on

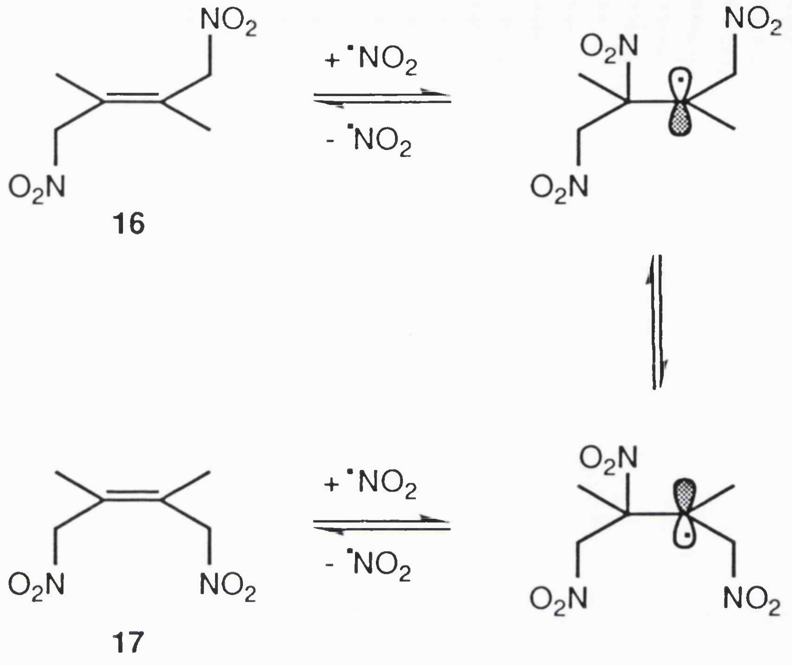
leaving with a catalytic excess of nitrogen dioxide equal amounts of **16** and **17** are formed.

2. As equal amounts of **16** and **17** exist when there is an excess of nitrogen dioxide present, and this does not change over time, both **16** and **17** must have similar energies of formation.

3. The conversion of **17** to **16** by the catalytic excess of nitrogen dioxide, implies that the central double bond must be broken, and the mechanism is outlined in Scheme 2.4. Nitrogen dioxide attacks the double bond, this produces a tertiary radical which will be relatively stable. The stability of this radical enables bond rotation to occur before the double bond can reform and expel the nitrogen dioxide molecule, hence regenerating the catalyst. Work carried out by Khan[55] found a similar isomerisation occurring in fatty acids.

The third conclusion is important as it implies that the central double bond can be attacked further by nitrogen dioxide, and therefore it may be possible to produce the tetra adduct compounds. As there was no evidence of any *cis* and *trans* isomerisation in **1** and **12** with a catalytic excess of nitrogen dioxide, then this would imply that the methyl groups at the 2 and 3 positions in **16** and **17** were activating the central double bond towards electrophilic attack.

The reaction of **17** with nitrogen dioxide was studied. These reactions gave some evidence for tetra nitro adducts being formed. A white crystalline solid was isolated, and had an $^1$H n.m.r. spectrum (Figure 2.13) which was consistent with that of 2,3-dimethyl-1,2,3,4-tetranitrobutane (**19**). The $^1$H n.m.r. spectrum would be expected to have a high field singlet due to the methyl protons, and a doublet of doublets corresponding to the diastereotopic protons attached to the nitro substituted carbon. However the sample was impure and could not be recrystallised so more accurate analysis could not be carried out.

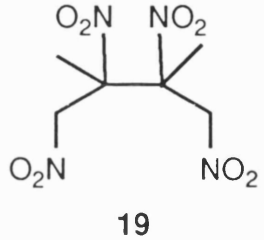


Scheme 2.4

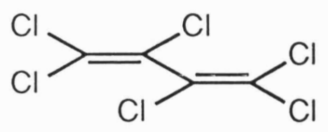
On extracting the starting material from the reaction mixture there was almost a quantitative recovery of the dinitro adduct, except that isomerisation of **17** had occurred and **16** was also recovered.

Further attempts to produce **19** were unsuccessful, the set of doublet of doublets could be seen in the $^1H$ n.m.r. spectrum of the crude reaction mixture, but it could not be isolated by h.p.l.c.

As there appeared to be a large electronic effect on the central double bond in the products **1**, **12**, **16** and **17** then the reactions between nitrogen dioxide and hexachlorobutadiene were studied.



**19**



**20**

From the experiments carried out there was no evidence of any reaction occurring between **20** and nitrogen dioxide, and **20** was fully recovered. These results were expected as the Cl group like the $NO_2$ group is electronegative, and has the effect of deactivating double bonds towards electrophilic addition. In **20** the double bonds are so deactivated that no electrophilic addition could occur.

## 2.6 Conclusion.

From the results obtained in this chapter it would appear that the nature of the substituents on the starting diene play an important role in the course of the reaction. In the case of 2,5-dimethyl-2,4-hexadiene, 2,4-hexadiene and 2,3-dimethyl-1,4-butadiene addition of the nitrogen dioxide occurred extensively at the ends of the molecule, to produce the dinitro adducts predominantly

For further additions to occur at the central double bond electron donating substituents are necessary as shown by the isomerisation of *cis* and *trans* 2,3-dimethyl-1,4-dinitro-2-butene. Where electron withdrawing substituents are present as in hexachlorobutadiene, in 2,5-dimethyl-2,5-dinitro-3-hexene and 2,5-dinitro-3-hexene, these are sufficient to reduce the activity of the double bond, and render it unreactive to further attack by nitrogen dioxide.

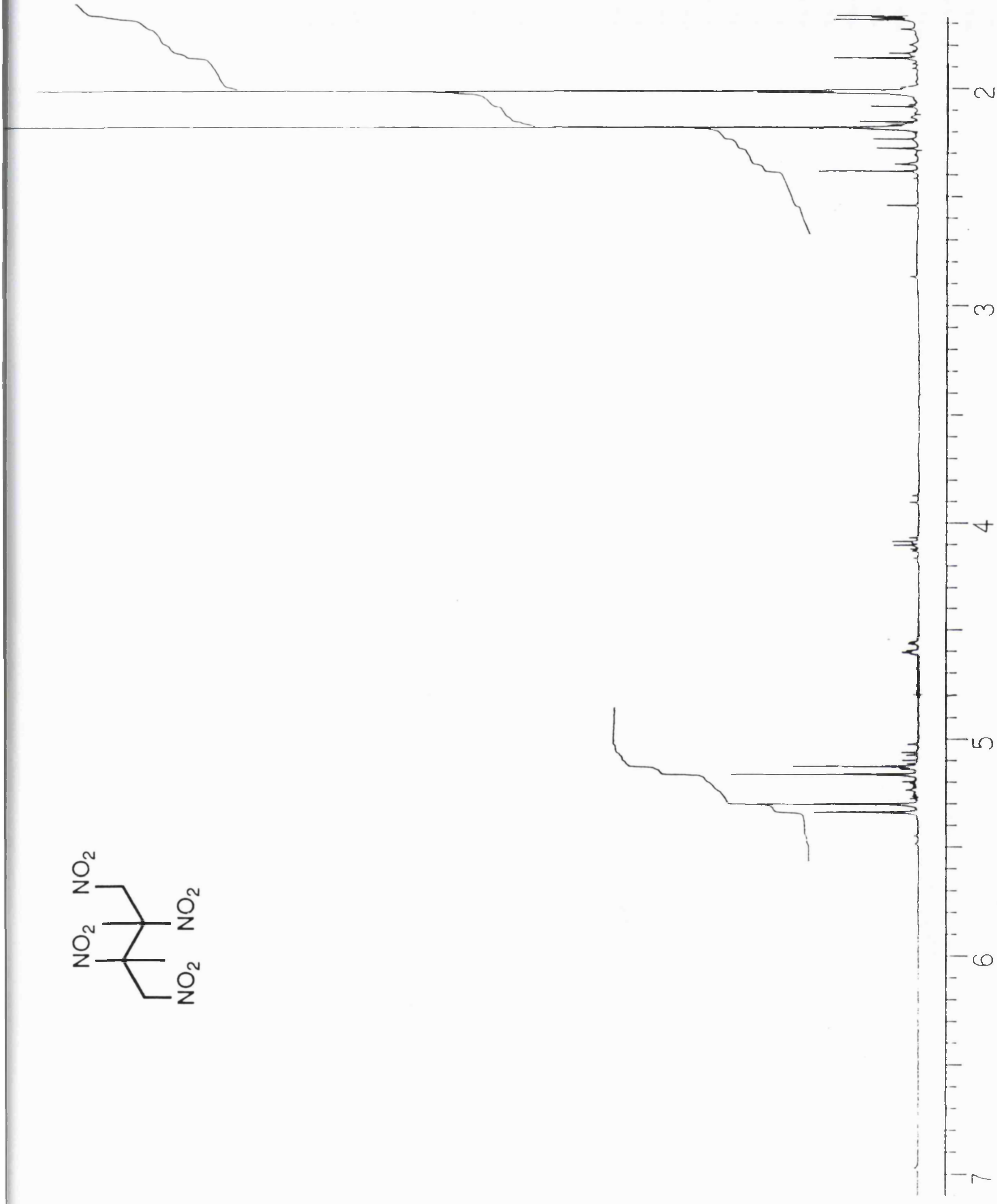


**Figure 2.13** $^1$H n.m.r. spectrum consistent with the assignment for the compound 2,3-dimethyl-1,2,3,4-tetranitrobutane.

# CHAPTER THREE

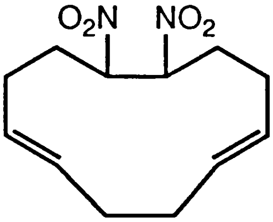
# REACTIONS OF NITROGEN DIOXIDE WITH CONJUGATED AND NON CONJUGATED TRIENES

## 3.1 Introduction.

This chapter deals with the reactions between nitrogen dioxide and the conjugated triene 1,3,5-hexatriene and also those of nitrogen dioxide with the nonconjugated triene *cis,trans,trans*-1,5,9-cyclododecatriene. The chapter starts with the identification of the products obtained from the reactions between the cyclododecatriene and nitrogen dioxide, followed by a discussion of the products formed. Due to the reactivity of the 1,3,5-hexatriene no monomeric products were isolated and the products formed appeared to be complex polymers which could not be identified. Attempts were made to reduce the amount of polymer formed by changes in the reaction conditions.

## 3.2 Products formed in the Reaction between *cis,trans,trans*-1,5,9-Cyclododecatriene and Nitrogen Dioxide.

### 3.2.1 1,2-Dinitro-*trans,trans*-5,9-Cyclododecadiene.



Owing to the symmetry of the molecule, the $^1H$ n.m.r. spectrum (Figure 3.1) is simple. It consists of three regions: the olefinic region, the nitro region and the methylene region. The signals in the methylene region are complex and consist of two multiplets which could not be resolved. The olefinic region of the spectrum was also complex and this consisted of a two multiplets which could not be resolved centred on δ 5.02 and δ 5.25. These are brought about by the proton at either end of the double bond coupling to three other protons. The nitro region of the spectrum overlaps the low field multiplet of the olefinic region. A doublet of doublets is observed for the hydrogen $H_a$ due to the proton coupling with the two diastereotopic protons in $H_b$ and $H_c$.

The $^{13}C$ n.m.r. spectrum (Figure 3.2) reflects the symmetry of the molecule by the presence of only six signals. Three are observed in the methylene region of the spectrum due to the unsubstituted ring carbons. One signal is observed in the nitro region of the spectrum at δ 83.56 confirming that both the nitro substituted carbons are equivalent and finally two signals are present in the olefinic region corresponding to the carbons at either end of the double bond.

The C.I.M.S. spectrum confirms the molecular weight with a molecular ion at 272 amu corresponding to the molecular formula $[C_{12}H_{18}N_2O_4.NH_4^+]$.

$^1H$ n.m.r. (C) δ: 2.12(6H) m; 2.21(6H) m; 5.02 (2H) m; 5.20(2H) dd, $^3J_{a,b}$ 6.58 Hz, $^3J_{a,c}$ 15.41 Hz; 5.25(4H) m.

$^{13}C$ n.m.r. (C) δ: 27.99, 29.42, 31.47, 83.56, 129.07, 133.99.

C.I.M.S. m/e: 272 $(M.NH_4^+)$; 225 $(M.NH_4^+-47)$; 161$(M^+-93)$.

Analysis: Calculated for $C_{12}H_{18}N_2O_4$ : C, 56.68; H, 7.14; N, 11.01.
Found: C, 56.30; H, 7.17; N, 10.68.

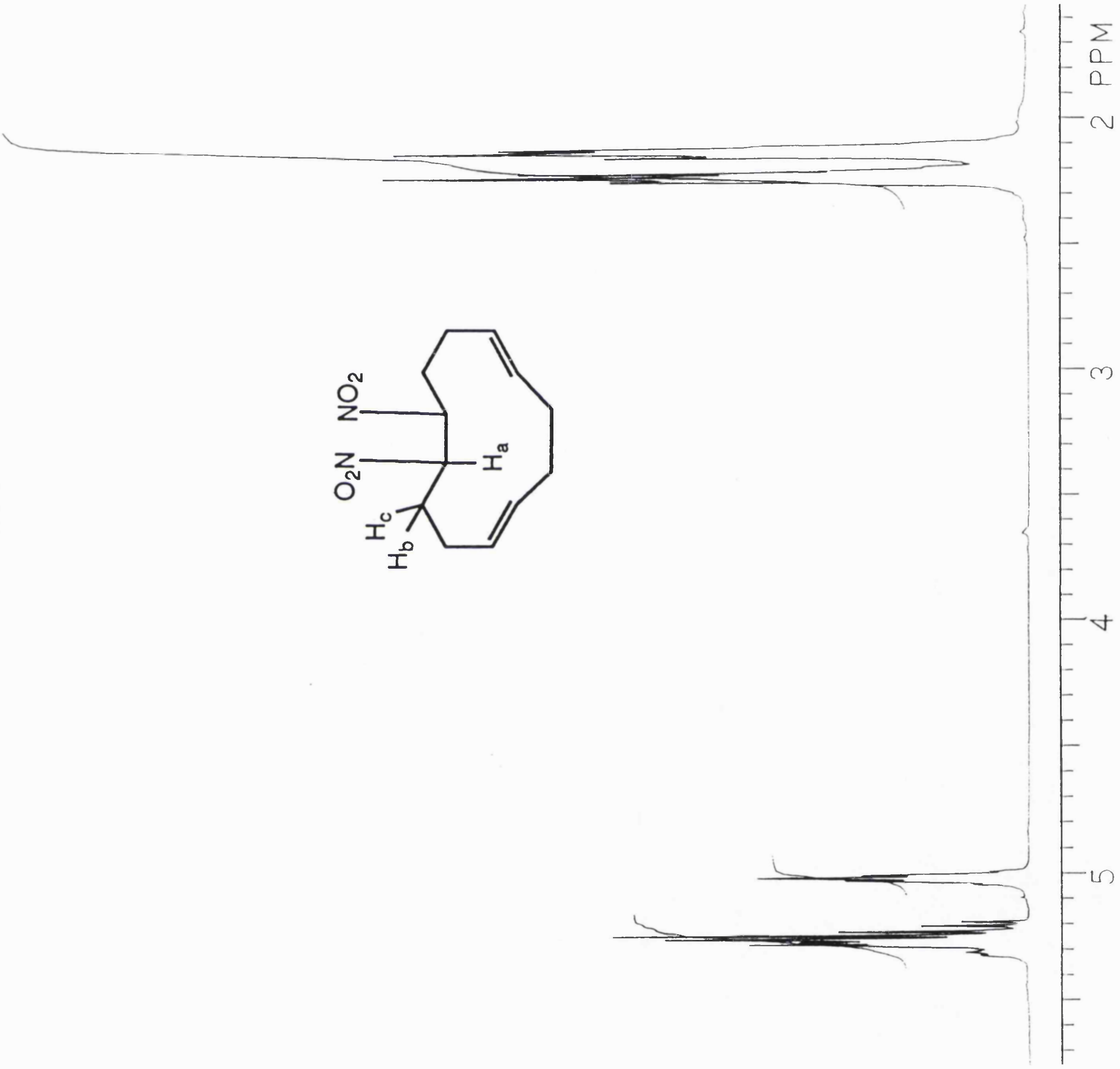


**Figure 3.1** $^1H$ n.m.r. spectrum of 1,2-dinitro-*trans,trans*-5,9-cyclododecadiene

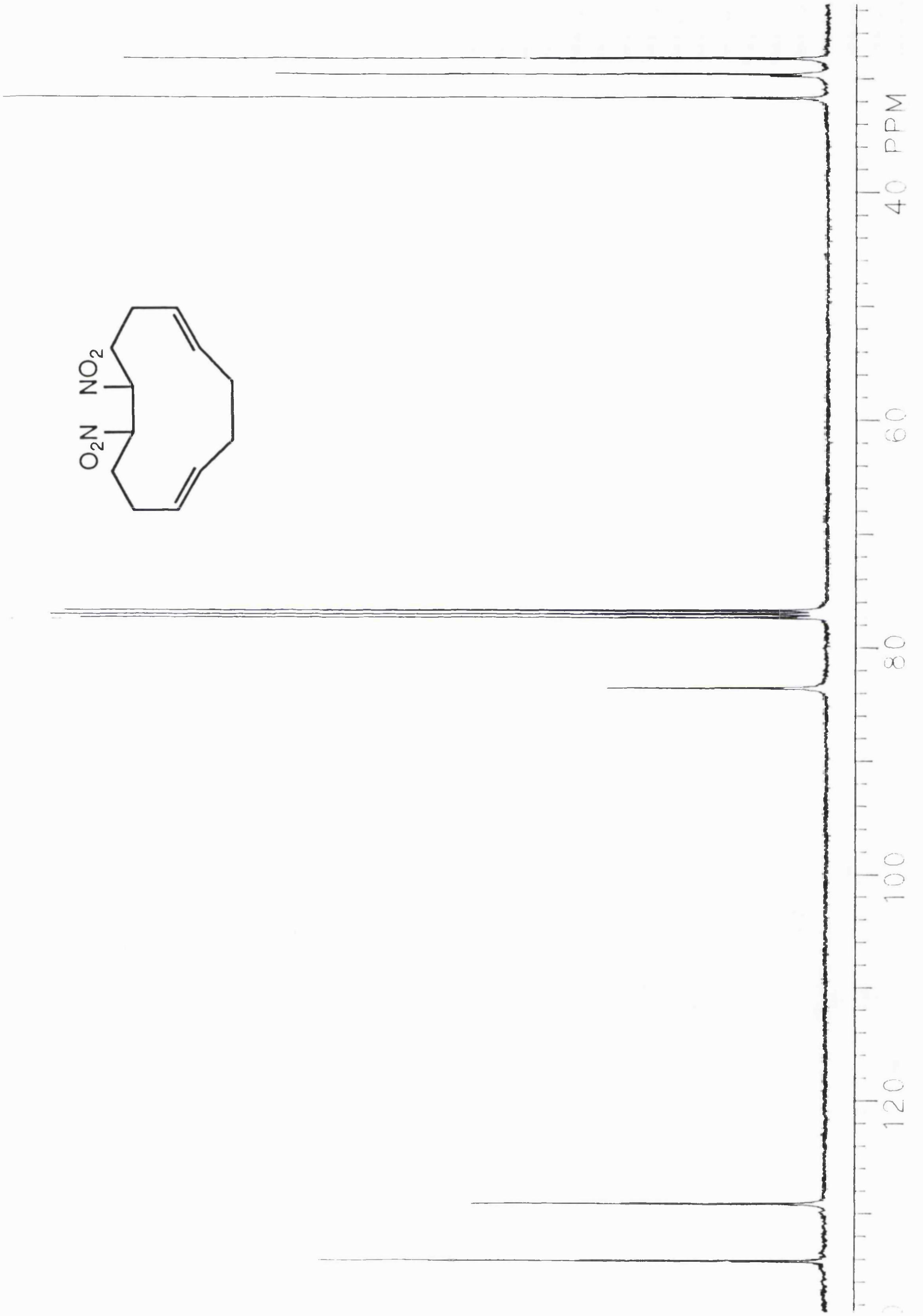
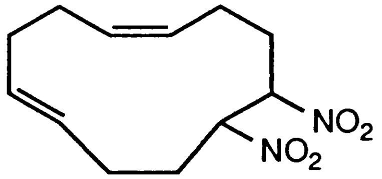


**Figure 3.2** $^{13}$C n.m.r. spectrum of 1,2-dinitro-*trans,trans*-5,9-cyclododecadiene.

### 3.2.2 5,6-Dinitro-*cis,trans*-1,9-cyclododecadiene.



The $^1H$ n.m.r. spectrum for this dinitro adduct was more complex than the adduct in section 3.2.1 due to the asymmetry of this compound brought about by the *cis* and *trans* bonds being present.

The methylene protons give rise to complex multiplets which could not be resolved between δ 2.02-2.40. The olefinic protons and the four hydrogens attached to the nitro substituted carbons all give rise to complex multiplets which could not be resolved in the region δ 4.70-5.50.

The most conclusive evidence for the formation of this adduct comes from the $^{13}C$ n.m.r. spectrum (Figure 3.3) which consists of twelve signals, implying an asymmetric molecule. The important feature is the two signals in the C-$NO_2$ region of the spectrum at δ 82.95 and δ 83.34, which clearly show that the two nitro groups are attached to two carbons which are in a different environment. Further evidence is from the olefinic region of the spectrum which has four signals present showing that the two remaining double bonds are in the *cis* and *trans* orientations. The remaining six signals are the low field methylene carbons in the ring.

The C.I.M.S. spectrum gave a molecular ion corresponding to the molecular formula [$C_{12}H_{18}N_2O_4.NH_4^+$].

$^1H$ n.m.r. (C) δ: 2.02-2.40(12H) m; 4.77(1H) m; 5.07(1H) m; 5.26(1H)m; 5.44(3H) m.

$^{13}C$ n.m.r. (C) δ: 22.58, 27.61, 28.06, 28.31, 28.69, 30.83, 82.95, 83.34, 127.77, 127.92, 131.40, 133.86.

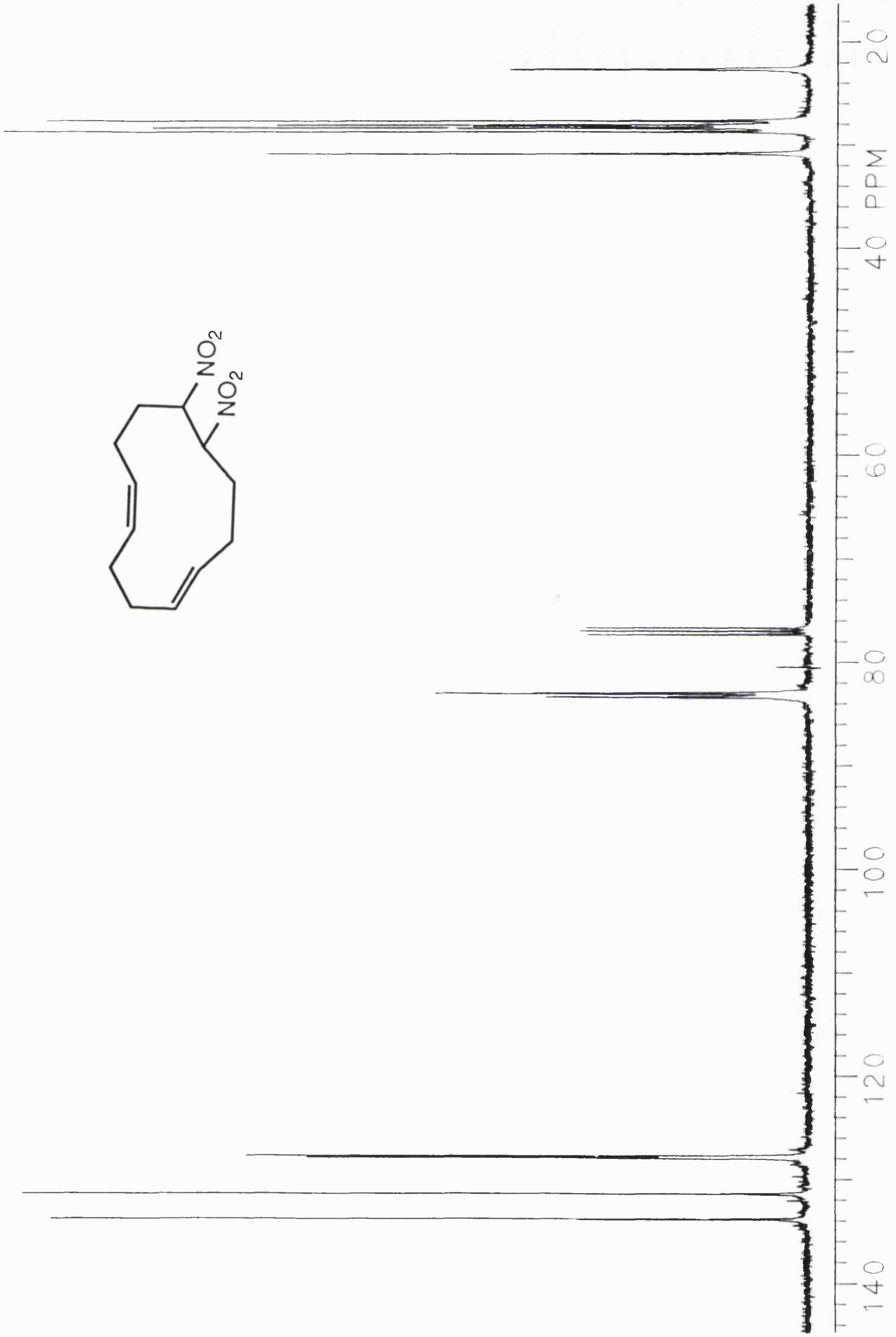


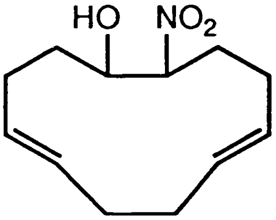
**Figure 3.3** $^{13}C$ n.m.r. spectrum of 5,6-dinitro-*cis,trans*-1,9-cyclododecadiene.

C.I.M.S. m/e: 272(M .$NH_4^+$); 208($M^+$-46); 161($M^+$-93); 149($M^+$-105).

Analysis: Calculated for $C_{12}H_{18}N_2O_4$: C, 56.68; H, 7.14; N, 11.01.

Found: C, 56.40; H, 7.14; N, 10.80.

### 3.2.3 2-Hydroxy-1-nitro-5,9-cyclododecadiene.



These white crystals gave a complex $^1H$ n.m.r. spectrum. The methylene region of the spectrum consisted a very complex multiplet between δ 1.80-2.40. A broad signal was observed at δ 2.6 corresponding to the hydroxy proton. Signals at δ 3.85 and δ 4.72 correspond to the H-COH and H-$CNO_2$ protons respectively, these were both complex multiplets. The multiplet at δ 3.85 was broadened; this was due to the coupling between the nuclei of the hydroxy proton and the hydrogen attached to the carbon. The multiplet at δ 4.72 was a doublet of doublets of doublets due to coupling of three non equivalent nuclei. A large multiplet centred on δ 5.16 corresponds to the olefinic hydrogens.

The $^{13}C$ n.m.r. spectrum (Figure 3.4) consisted of twelve signals as expected for the asymmetry of the molecule. Six signals were observed in the methylene region of the spectrum corresponding to the saturated ring carbons. The important feature of this spectrum is the signal at δ 66.88 which is clearly due to the hydroxy substituted carbon. The lower field signal at δ 86.01 arises from the nitro substituted carbon. In the olefinic region of the spectrum four signals are clearly present which confirms the presence of two double bonds.

The C.I.M.S. confirms the molecular weight with a molecular ion at 243 amu which is in agreement with the molecular ion [$C_{12}H_{19}NO_3$.$NH_4^+$].

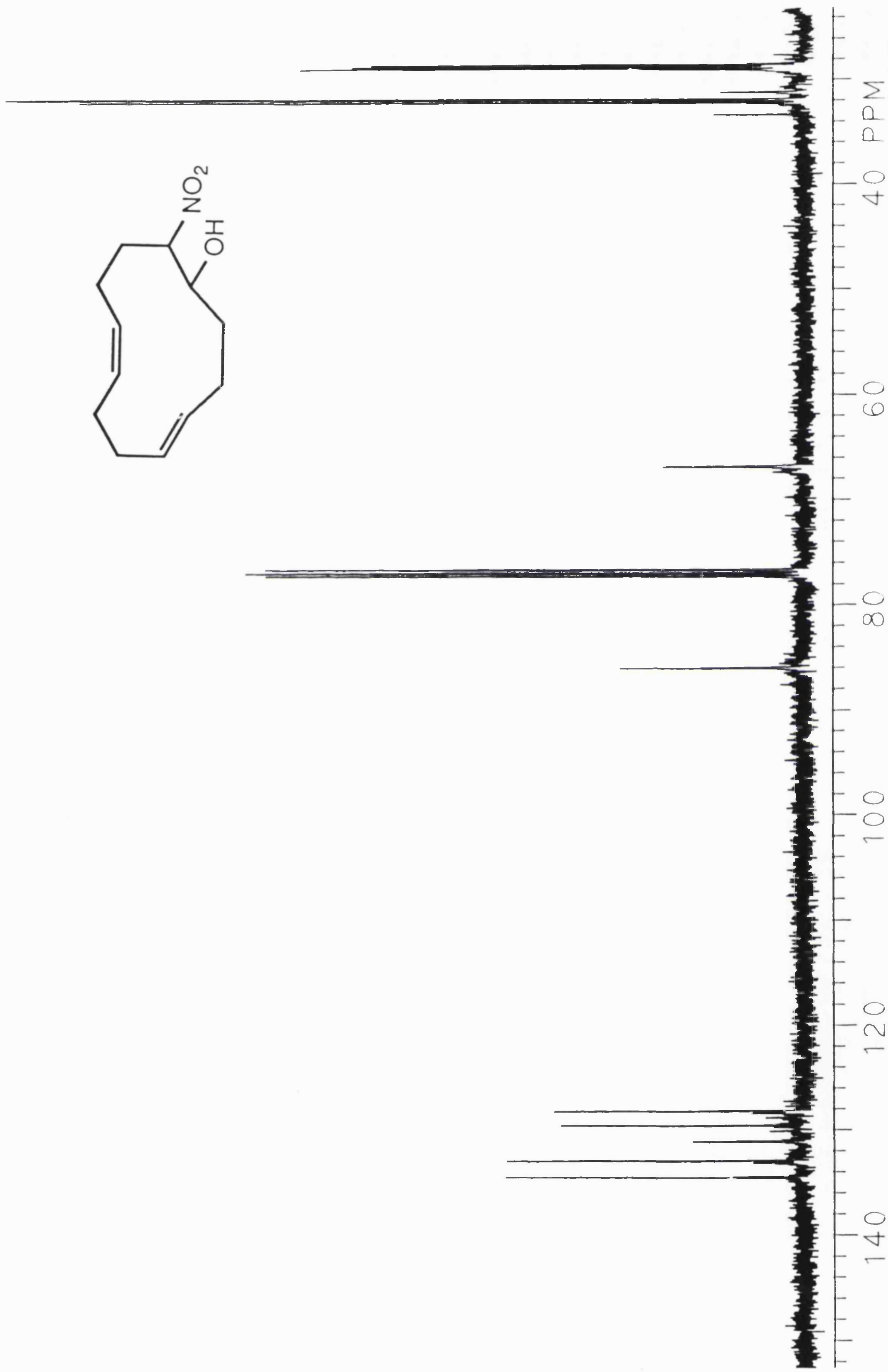


**Figure 3.4** $^{13}C$ n.m.r. spectrum for 1-hydroxy-2-nitro-5,9-cyclododecadiene.

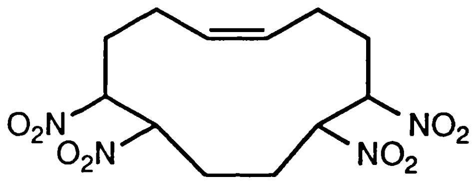
$^1$H n.m.r. (C) $\delta$: 1.80-2.40(12H) m; 2.6(1H) bs; 3.85(1H) m; 4.72(1H) ddd, $^3$J 2.59 Hz, $^3$J 4.65 Hz, $^3$J 10.60 Hz; 5.16(4H) m.

$^{13}$C n.m.r.(C) $\delta$: 28.50, 28.69, 28.90, 31.84(2C), 32.17, 66.88, 86.01, 128.18, 129.54, 132.89, 134.49.

C.I.M.S. m/e: 243($M.NH_4^+$); 179($M.NH_4^+$-46); 161($M^+$-64); 149($M^+$-76).

Analysis: Calculated for $C_{12}H_{19}NO_3$: C, 63.97; H, 8.50; N, 6.22.
Found: C, 63.85; H, 8.57; N,6.36.

### 3.2.4 1,2,5,6-Tetranitro-9-cyclododecene.



This compound was a white crystalline solid which was recrystallised from hot methanol. Pure crystals could not be obtained as a yellow oil was always formed with it, and no method of separation could be found to remove this.

The formation of this compound has been assigned on the basis of its $^1$H n.m.r. spectrum,$^{13}$C n.m.r. spectrum and also its chemical analysis. No C.I.M.S. spectrum was obtained on this sample.

From the $^1$H n.m.r. spectrum (Figure 3.5) only three signals were observed. One is the high field multiplet between $\delta$ 2.00-2.40 corresponding to the methylene protons. Another is the broad signal at $\delta$ 5.22 due to the hydrogens attached to the nitro substituted carbons. This would be expected to be a complex multiplet and may explain its broadness. Similarly a broad low field signal is also observed and this corresponds to the two remaining olefinic protons. An important feature is that the integral associated with the signal a $\delta$ 5.22 is approximately twice that of the signal at $\delta$ 5.75 which implies that there

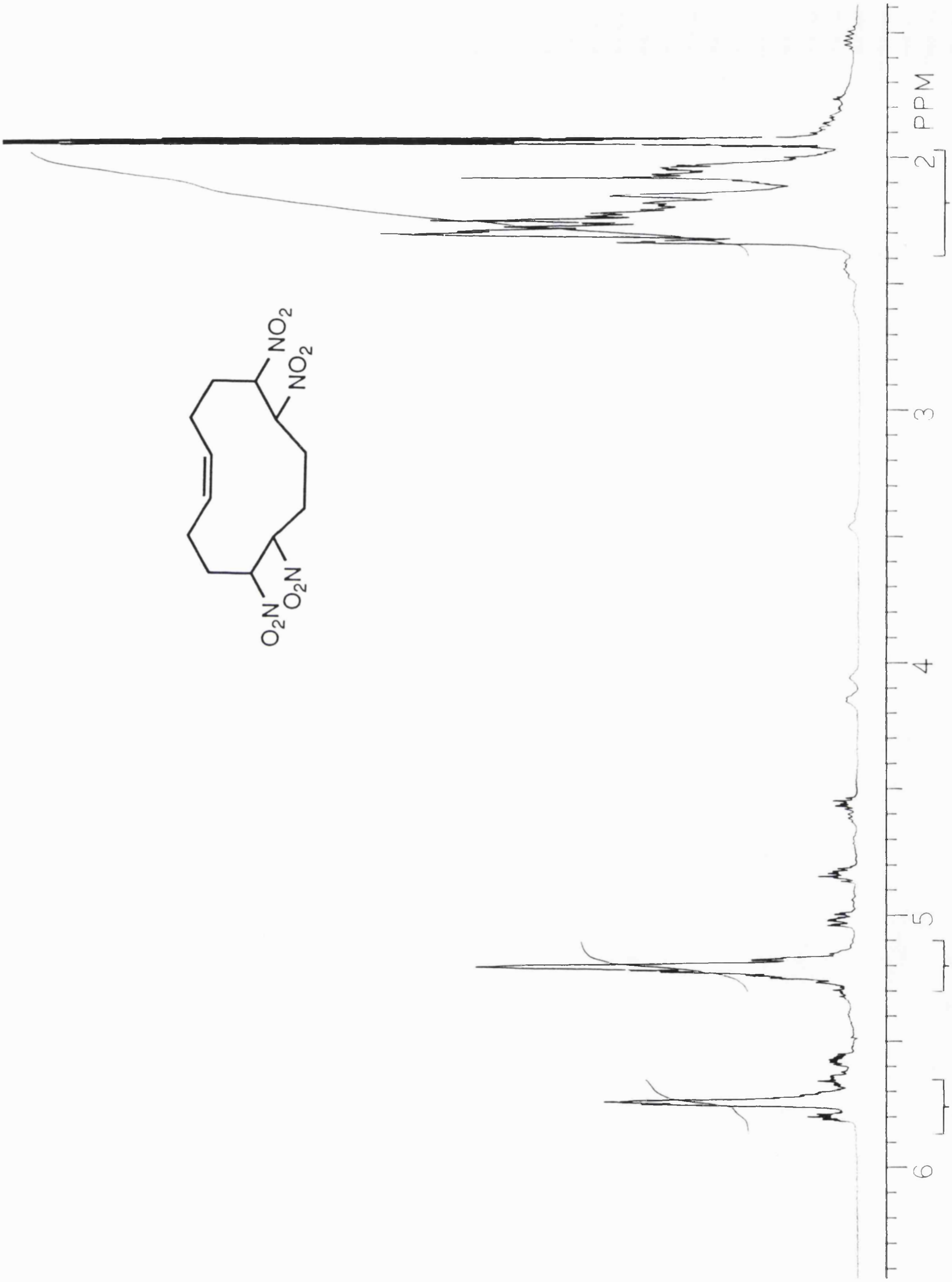


**Figure 3.5** $^1$H n.m.r. spectrum for 1,2,5,6-tetranitro-9-cyclododecadiene.

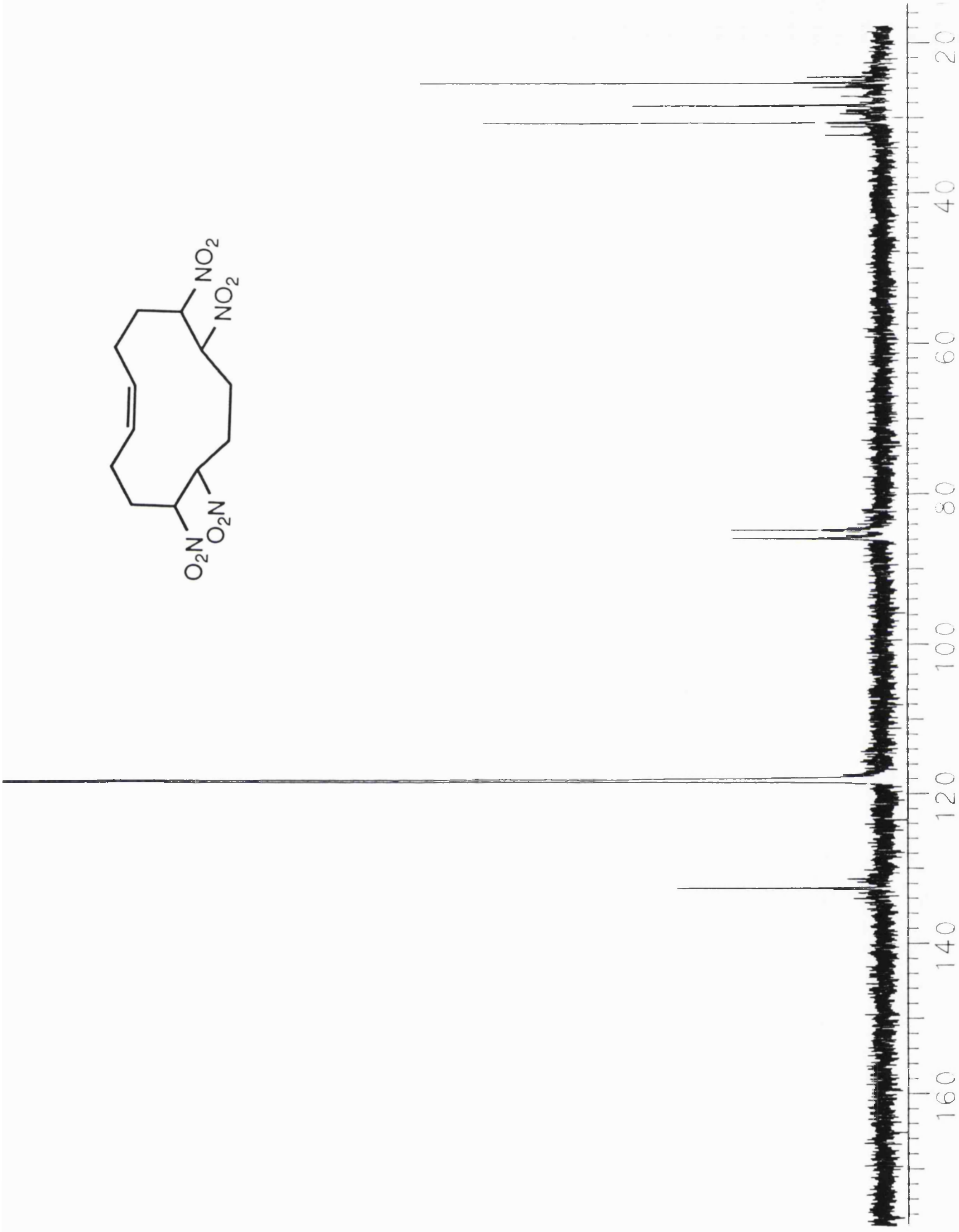


**Figure 3.6** $^{13}$C n.m.r. spectrum for 1,2,5,6-tetranitro-5,9-cyclododecadiene.

are twice as many hydrogens attached to nitro substituted carbons as there are olefinic carbons.

The $^{13}C$ n.m.r. spectrum (Figure 3.6) consisted of six signals which would imply that the molecule was symmetrical. Three signals are observed in the high field region of the spectrum and these are due to the methylene carbons in the ring. At lower field, two signals are observed in the nitro region of the spectrum at $\delta$ 84.21 and $\delta$ 85.22, which would be consistent with the assignment as there are two different environments for the nitro substituted carbons. Finally in the olefinic region there is only one signal at $\delta$ 132.00 corresponding to the two equivalent carbons in the olefinic bond.

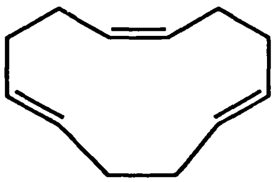
$^1H$ n.m.r. (ACN) $\delta$: 2.00-2.40(12H) m; 5.22(4H) bs; 5.75(2H) bs.

$^{13}C$ n.m.r. (ACN) $\delta$: 24.50, 27.66, 29.92, 84.21, 85.22, 132.00.

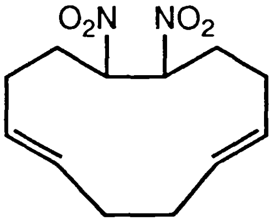
Analysis: Calculated for $C_{12}H_{18}N_4O_8$: C, 41.62; H 5.24; N, 16.18.
Found: C, 41.79; H, 5.16; N, 15.43.

## 3.3 Discussion.

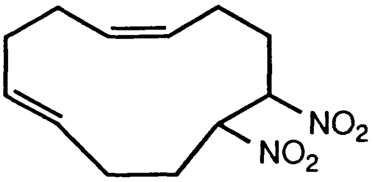
### 3.3.1 Reactions involving *c,t,t*,-1,5,9-Cyclododecatriene.



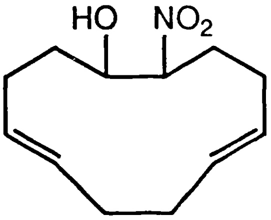
**21**



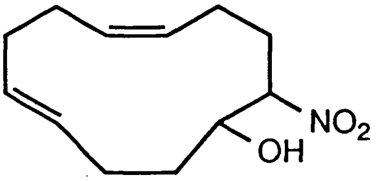
**22**



**23**



**24**

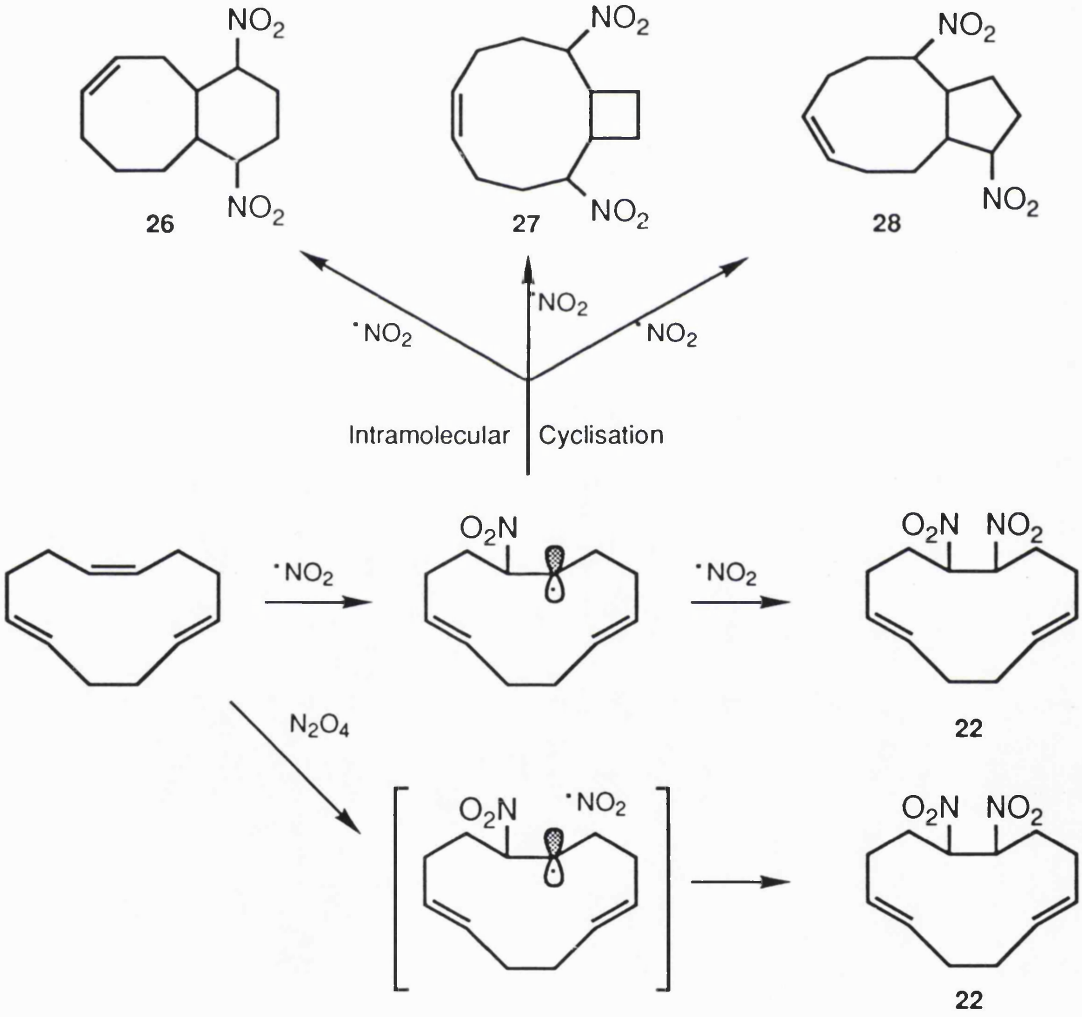


**25**

From the reaction between *c,t,t*-1,5,9-cyclododecatriene (**21**) and nitrogen dioxide four major products were isolated after h.p.l.c.; 1,2-dinitro-*t,t*-5,9-cyclododecadiene (**22**), 5,6-dinitro-*c,t*-cyclododecadiene (**23**), 1-hydroxy-2-nitro-*t,t*-cyclododecadiene (**24**), and 5-hydroxy-6-nitro-*c,t*-cyclododecadiene (**25**). These four compounds accounted for 85% of the reaction products with the dinitro adducts accounting for 68% of the total products. The remaining 15% of the products were not identified as insufficient samples were obtained for analytical work. These samples may have been bicyclic products which may have formed during the course of the reaction because of intramolecular cyclisation. This is discussed in more detail later in this section.

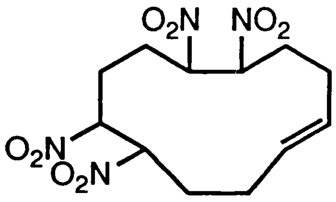
Reaction conditions were examined to see if the total yield of the dinitro products could be enhanced. Various methods were attempted by varying the mode of addition , *i.e.* adding the $NO_2$ solution to the cyclododecatriene so that the triene was always in excess, or adding the triene to the $NO_2$ solution such that the nitrogen dioxide was always in excess. The majority of the reactions were carried out in n-hexane as this was a non-polar solvent. The advantage of using n-hexane was that once addition had occurred across one of the double bonds the product fell from solution and would therefore have less chance of reacting further; this probably simplified the reaction products.

The mode of addition or the rate of addition of the reagents had little or no effect on the distribution of the reaction products and no method was found to increase the formation of **22** or **23**.

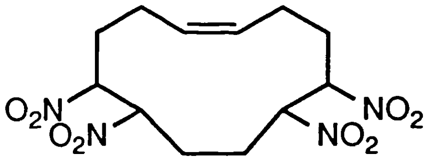


**Scheme 3.1**

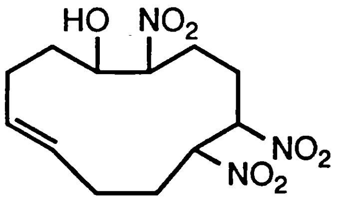
The reactions between **21** and nitrogen dioxide produced the expected compounds **22**, **23**, **24** and **25** which occurred from the addition of two nitro groups across the double bond or the addition of a nitro group and a nitrite group across the double bond with subsequent decomposition of the nitrite to the alcohol. However, if the addition rate of nitrogen dioxide to **21** had been slow such that the local concentration of $NO_2$ was low then three bicyclic products **26**, **27** and **28** may have formed (Scheme 3.1). The formation of these compounds would involve intramolecular cyclisation occurring, and for this to happen the concentration of $NO_2$ would have to be low to ensure that the rate of cyclisation $k_{cyclisation}$ was of a similar magnitude for the addition of the second $NO_2$ group. These products were not isolated from the reaction but they may account for some of the unidentified products. Formation of these products would have clearly indicated that $NO_2$ was an attacking species in nitrogen dioxide solutions, whereas products **22-25** may have been formed from dinitrogen tetroxide or nitrogen dioxide.



**29**



**30**



**31**

To produce higher adducts two methods were employed:- (1) the addition of nitrogen dioxide to **21** in chlorinated solvents so that the reaction would progress further to form the tetranitro adducts 1,2,5,6-tetranitro-*t*-9-cyclododecene (**29**) and 5,6,8,9-tetranitro-*c*-1-cyclododecene (**30**) or higher adducts still. (2) the addition of nitrogen dioxide to **22** and **23** in chlorinated solvents again to produce the tetranitro adducts.

The first method used did produce some tetranitro adducts but due to difficulty in separating the products formed in the reaction this method was abandoned. Difficulty arose because as many as sixteen products were formed which were all closely related in their polarities. It was thought that these were probably alcohols formed from nitrite addition. A tetranitro adduct was isolated in a small yield as this crystallised out during the course of the reaction (Section 3.2.4).

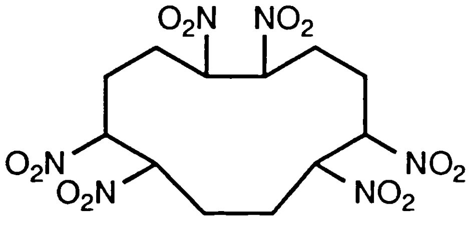
The second method tried was only slightly more successful, with again either **29** or **30** being isolated in a small yield.

The formation of **29** and **30** from **23** is straightforward with the addition of the nitrogen dioxide across either the *cis* or *trans* double bond. The formation of **30** is not expected to occur in the reaction between **22** and nitrogen dioxide as addition has already across the *cis* double bond. For **30** to be formed during the course of the reaction would require that the *trans* double bond was broken and reformed in the *cis* orientation.

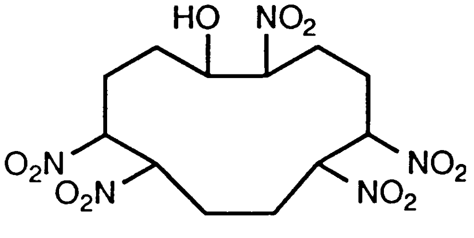
Structures **29** and **30** could not be distinguished by their $^1H$ n.m.r. or $^{13}C$ n.m.r. spectra as they are both symmetrical even though this is not immediately obvious for the structures shown; a specific assignment of which tetranitro product had been formed could not be made. As a white crystalline solid was isolated from the reactions of both **22** and **23** this was expected to be structure **29**.

Attempts were made to recrystallise the tetranitro product, and the most successful method was dissolving the compound in warm methanol and cooling. Colourless needlelike crystals grew but they were covered in a pale yellow oil which was thought to be a trinitroalcohol product such as **31** which would have formed from the decomposition of a nitrite. From the C.I.M.S. of the white crystals there was no evidence for the formation of a tetranitro adduct only the formation of the possible compound **31** or some other isomer thereof. This can be explained as the oil would be more volatile than the crystalline solid and would therefore be observed in the C.I.M.S. spectrum more readily. The $^1H$ and $^{13}C$ n.m.r. spectra and the chemical analysis in section 3.2.4 clearly supports the formation of the tetranitro adduct.

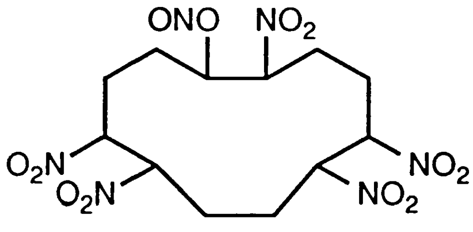
Attempts to produce higher adducts such as 1,2,5,6,9,10-hexanitro-cyclododecane (**32**) or 1-hydroxy-2,5,6,9,10-pentanitro-cyclododecane (**33**) from **30** were also attempted. Difficulty arose here in finding a suitable solvent and, as the tetra adducts were not soluble in chlorinated solvents, nitromethane was finally used.



**32**



**33**



**34**

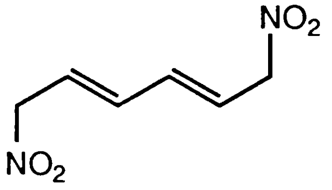
On addition of **30** to the nitrogen dioxide solution in nitromethane, the solution turned green in colour. On removal of the solvent, a dark green oil remained which, when dissolved in methanol, gave a white suspension and a green solvent layer. The suspension was removed and its n.m.r. spectrum was recorded; this was consistent with the starting material. The green oil from the methanol layer was inadequate for analysis but was thought to be the 1-nitrito-2,5,6,9,10-pentanitro-cyclododecane (**34**) as nitrite compounds have a blue/green colour associated with them; such nitrites may then decompose to the alcohol. There was no evidence for isolation of the hexanitro adduct **32**.

### 3.3.2. Reactions involving 1,3,5-hexatriene.

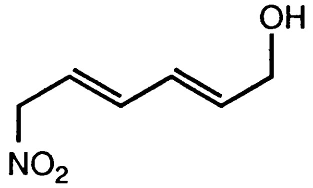
The reactions involving 1,3,5-hexatriene (**35**) and nitrogen dioxide were studied in the hope of isolating dinitro, tetranitro or possibly hexanitro adducts.

The reaction was carried out in n-hexane and both the 'normal' and 'reverse' modes of addition were tried. Formation of 1,6-dinitro-2,4-hexadiene (**36**) and 1-hydroxy-6-nitro-2,4-hexadiene (**37**) was expected to be straightforward by the addition of $NO_2$ to one end of the molecule, the delocalisation of the radical formed, and the addition of $NO_2$ or ONO to the other end (Scheme 3.2, route a). Formation of 1,2-dinitro-3,5-hexadiene (**38**) might also have been predicted if dinitrogen tetroxide were the attacking species with a concerted addition of two nitro groups (Scheme 3.2, route b). This was not the case and all that was obtained was a complex polymer independent of the mode of addition (Scheme 3.2, route c). It was hoped that by adding the triene to the nitrogen dioxide solution the polymerisation of the hexatriene would be stopped; as the $NO_2$ would be in excess and react faster than the addition of another hexatriene molecule. It was also thought that this method would probably produce 1,2,5,6-tetranitro-3-hexene (**39**) as the formation of **36** would then react further with nitrogen dioxide. From these reactions only polymeric products were obtained which could not be separated.

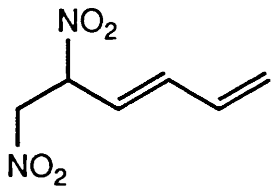
**35**



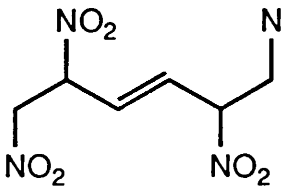
**36**



**37**

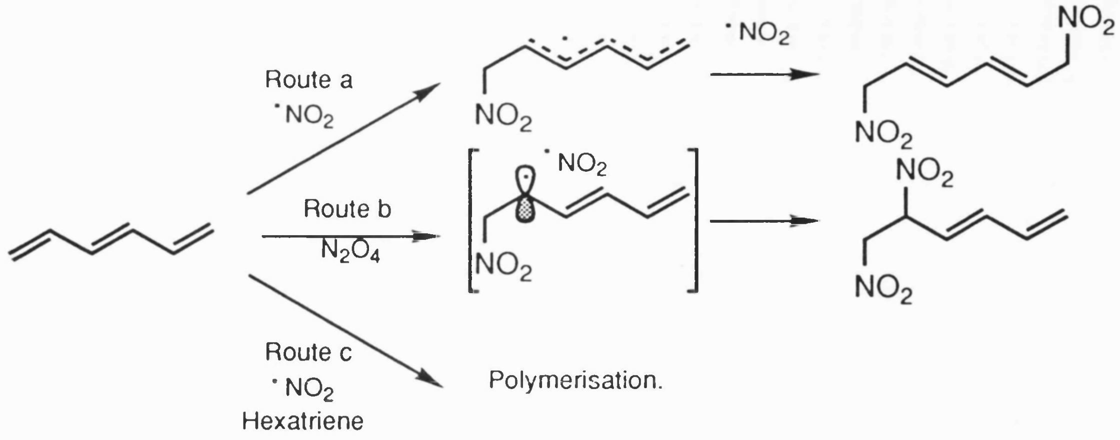


**38**



**39**

As the reaction in the liquid phase produced only complex polymers the reaction was attempted in the gas phase. It was hoped that in the gas phase the local concentration of **35** would be sufficiently low to stop the polymerisation.



**Scheme 3.2.**

Nitrogen was used as a carrier gas and **35** was passed into a nitrogen dioxide atmosphere. When the triene was passed into the chamber, a reaction took place and a brown oil formed on the sides of the vessel, this too gave a very complex $^1H$ n.m.r. spectrum and was also thought to be a polymer, with no evidence of **36**, **37** or **38** being formed.

Due to the unsuccessful isolation of any monomeric compounds the reactions of 1,3,5-hexatriene were not continued.

## 3.4 Conclusion.

The reactions of the two trienes studied varied a great deal. The reactions of *c,t,t*-1,5,9-cyclododecatriene with nitrogen dioxide were well behaved and the expected dinitro and hydroxy-nitro adducts were isolated quite readily. Formation of higher adducts such as the tetranitro adducts is also possible but separating the reaction products now becomes difficult probably due to the similarity in their physical properties such as solubility and dipole moment. From these reactions it also appears that nitrating the double bond becomes more difficult as one goes from the cyclic triene to the cyclic diene to the cyclic alkene. This is most likely to be caused by a steric interaction of the nitro groups being added rather than any electronic effects associated with the nitro group on the remaining double bonds (as seen for the conjugated dienes Chapter 2).

The reactions between hexatriene and nitrogen dioxide by contrast were totally different and no isolation of any monomeric species was obtained. This clearly shows the reactivity of the conjugated system to be much greater than that of the non-conjugated system. Attempts to produce monomeric species in the gas and liquid phase proved to be unsuccessful.

Information on the attacking species in nitrogen dioxide solutions was hard to come by in these sets of reactions but the formation of the polymers associated with 1,3,5-hexatriene would imply that $NO_2$ was the attacking species and not $N_2O_4$ as this should have produced the 1,2-dinitro-3,5-hexadiene adduct. Products from the reactions between cyclododecatriene and nitrogen dioxide do not permit a distinction to be made between $N_2O_4$ or $NO_2$ attack. Formation of bicyclic products was not observed which would have given conclusive evidence for $NO_2$ being the attacking species.

# CHAPTER FOUR

# THE REACTIONS BETWEEN 1,6-HEPTADIENE AND NITROGEN DIOXIDE.

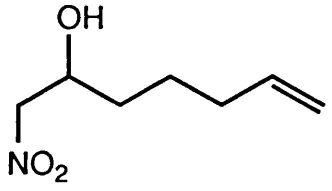
## 4.1 Introduction.

This chapter deals with the reactions between nitrogen dioxide and the non-conjugated diene 1,6-heptadiene. All the reactions carried out took place in the liquid phase, and the reaction procedures are outlined in section 8.10.

The products were isolated using h.p.l.c. (conditions in section 8.10), and then analysed using $^1H$ and $^{13}C$ n.m.r., C.I.M.S., and, where possible, chemical analysis. The first part of the chapter deals with the products that were formed in the course of the reaction and this is followed by a discussion on how these products may have arisen.

## 4.2 Products from the Reaction of Nitrogen Dioxide and 1,6-Heptadiene.

### 4.2.1 2-Hydroxy-1-nitro-6-heptene.



The $^1H$ n.m.r. spectrum (Figure 4.1) consisted of six regions, with strong evidence of a double bond being present by the characteristic multiplets observed at δ 5.75 and δ 4.97, corresponding to the olefinic proton $H_c$, and the protons $H_a$ ,$H_b$ respectively. Since the hydroxy group is attached at a chiral centre, this has the effect of making protons $H_h$ and $H_i$ diastereotopic with relation to proton $H_g$. This complicates the spectrum and accounts for the multiplet centred on δ 4.35. As the hydroxy group does not have a large anisotropic effect the field observed by the protons $H_h$ and $H_i$ is similar and therefore the signals appear at similar chemical shifts. The multiplet at δ 2.18 corresponds to the

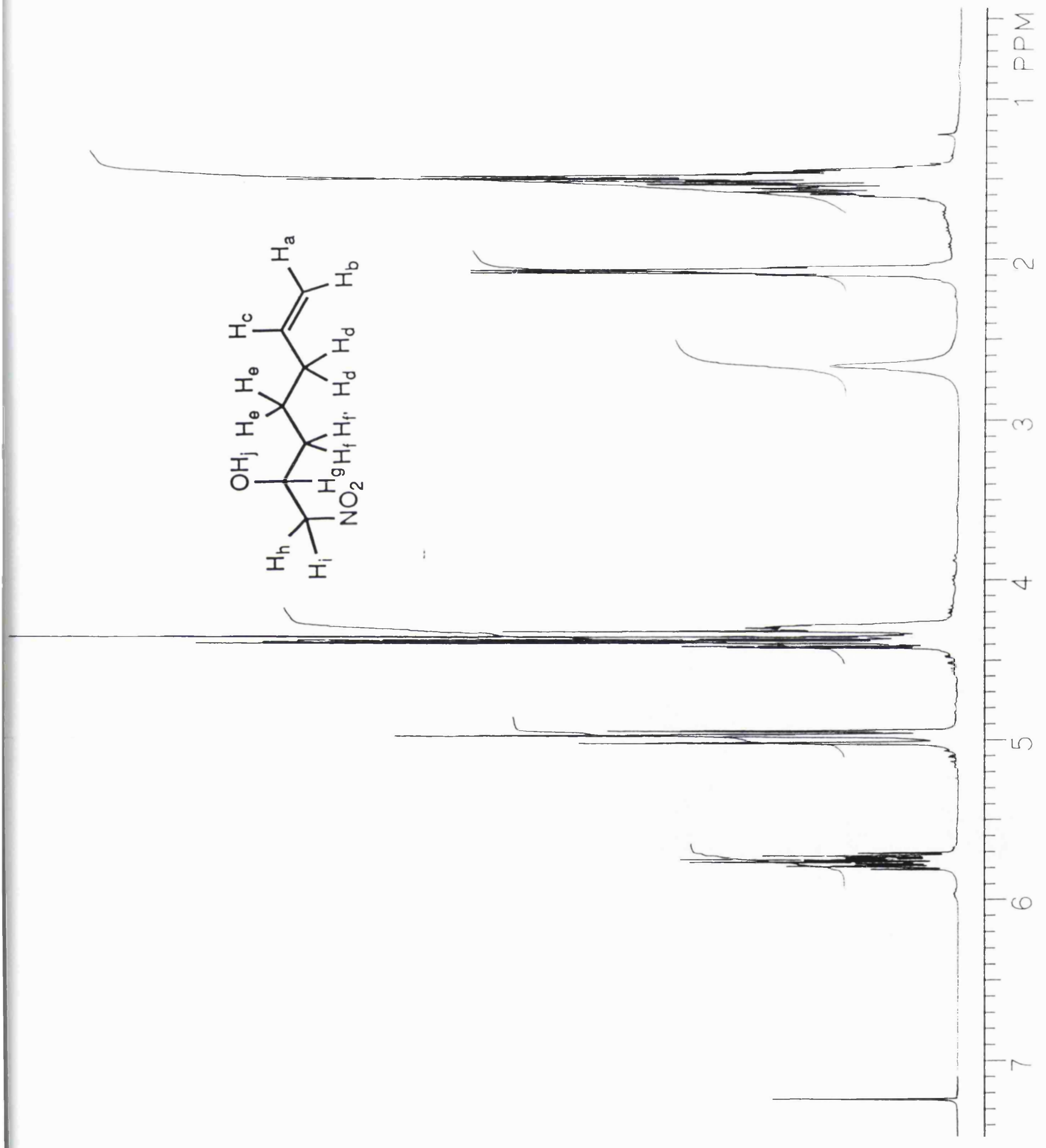


**Figure 4.1** $^1H$ n.m.r. spectrum for 2-hydroxy-1-nitro-6-heptene.

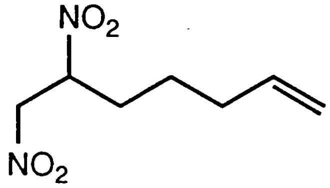
protons $H_d$, and the multiplet centred on δ 1.50 corresponds to the protons $H_e$ and the diastereotopic protons $H_f$, and $H_{f'}$. The broad singlet observed at δ 2.66 corresponds to $H_j$.

The $^{13}C$ n.m.r. spectrum has seven signals. The three high field signals correspond to the methylene carbons. The signals at δ 80.56 and δ 68.47 are characteristic of the chemical shifts for $C-NO_2$ and C-OH respectively. Finally the two low field signals at δ 115.23 and δ 137.85 correspond to the two olefinic carbons, the lower field signal resulting from the most substituted carbon.

The C.I.M.S. obtained was also consistent with this assignment with a molecular ion of 177 amu being observed.

| | |
|---|---|
| $^1H$ n.m.r. (C) δ: | 1.40-1.62 (4H) m; 2.07 (2H) q; 2.66 (1H) bs; 4.27-4.43 (3H) m; 4.94-5.02 (2H) m; 5.76 (1H) m, $^3J_{a,c}$ 10.33 Hz, $^3J_{b,c'}$ 17.06 Hz, $^3J_{c,d}$ 6.66 Hz, $^2J_{a,b}$ 1.56 Hz |
| $^{13}C$ n.m.r. (C) δ: | 24.31, 32.96, 33.19, 68.47, 80.58, 115.23, 137.85. |
| C.I.M.S m/e: | 177 ($M.NH_3^+$); 130 ($M.NH_3^+$ -47); 99 (M.-81); 52 (M-108). |
| Analysis: | Calculated for $C_7H_{13}NO_3$: C, 52.82; H, 8.23; N, 8.76.<br>Found: C, 52.22; H, 8.70; N, 8.31. |

### 4.2.2 1,2-Dinitro-6-heptene.



The assignment of the structure was based on the signals at δ 1.87, δ 1.98, δ 4.56 and δ 5.75 in the $^1H$ n.m.r. spectrum (Figure 4.2). In this molecule the secondary nitro group is attached to a chiral centre and as such the protons $H_f$,

$H_{f'}$, $H_h$, and $H_i$ become diastereotopic in relation to proton Hg. As a consequence of this a characteristic doublet of doublets is observed within the spectrum for protons $H_h$, and $H_i$,(δ 4.56 and δ 5.75) and complex multiplets are observed for the protons $H_f$, $H_{f'}$, and $H_g$.

Evidence for the double bond is given by the characteristic multiplet centred on δ 5.75 due to the proton $H_c$. Also the doublet of quartets at δ 2.05 is characteristic of the double bond. Due to the coupling of the $H_d$ protons with protons $H_e$, a triplet is observed for $H_d$; this is split further into doublets by coupling to proton $H_c$. As $^3J_{d,e} \approx {}^3J_{d,c}$ the splitting pattern becomes a quartet, this is itself split further by long range coupling to protons $H_a$ and $H_b$

The $^{13}C$ n.m.r. spectrum has seven signals, with the two low field signals corresponding to the olefinic carbons. The signals at δ 73.29 and δ 82.40 are due to the two nitro substituted carbons present in the molecule, and the remaining three high field signals correspond to the methine carbons.

This molecule was unstable and no C.I.M.S. spectrum could be obtained for this sample.

| | |
|---|---|
| $^1H$ n.m.r. (C) δ: | 1.48 (2H) q, $^3J$ 7.7 Hz; 1.87 (1H) m; 1.98 (1H) m; 2.05 (2H) dq, J 7.05 Hz, J 1.25 Hz; 4.56 (1H) dd, $^2J_{h,i}$ 14.43 Hz, $^3J_{g,h}$ 1.45 Hz; 4.9-5.2 (3H) m; 5.75 (1H) m, $^3J_{a,c}$ 10.64 Hz, $^3J_{b,c}$ 17.03 Hz, $^3J_{c,d}$ 6.77 Hz, $^2J_{a,b}$ 1.56 Hz. |
| $^{13}C$ n.m.r. (C) δ : | 24.25, 30.28, 32.51, 73.92, 82.40, 116.32, 136.50. |
| Analysis: | Sample decomposed. |

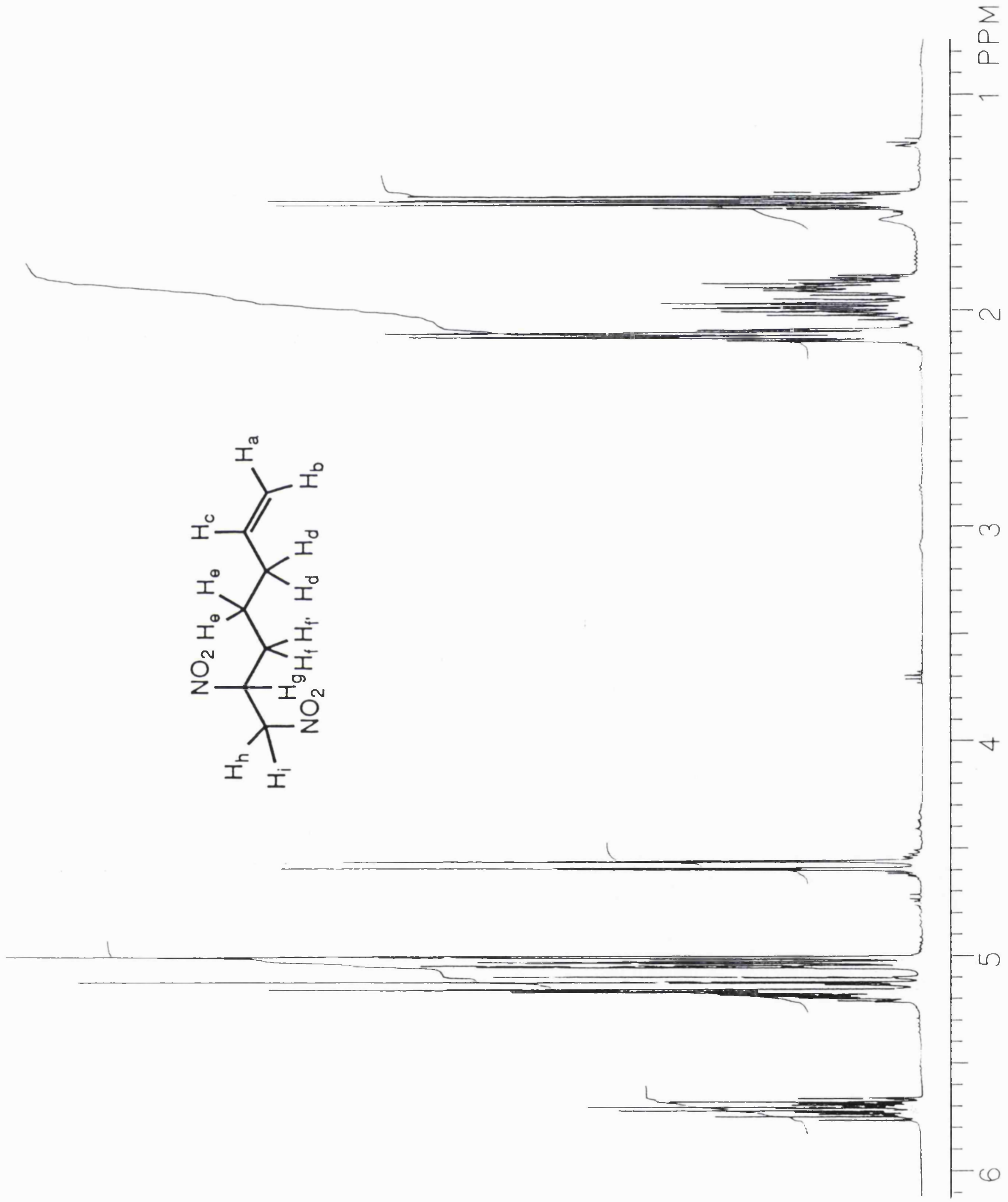
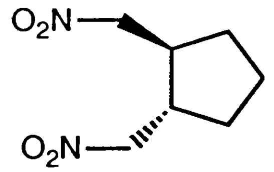


Figure 4.2 $^1H$ n.m.r. spectrum for 1,2-dinitro-6-heptene.

### 4.2.3 *trans*-1,2-(Nitromethyl)-cyclopentane.



From the $^{1}H$ n.m.r. spectrum obtained (Figure 4.3), it can be clearly seen that the characteristic multiplet associated with the double bond is no longer present. The spectrum observed is relatively simple due to the symmetry of the molecule.

The two high field doublets of doublets at δ 4.34 and δ 4.42 are brought about by the protons $H_a$ and $H_b$ which are diastereotopic to proton $H_c$. Proton $H_c$ gives rise to a complex multiplet due to coupling to protons $H_a$, $H_b$, $H_d$, and $H_e$ which are all diastereotopic. This multiplet is seen at a slightly higher field due to field effects from the nitro group. The low field multiplets are brought about by the protons $H_f$ , $H_d$ and $H_e$. The multiplet brought about by $H_f$ coupling to $H_d$ and $H_e$ is a quintet; this arises from the fast ring puckering which takes place and is described in more detail in section 4.3.

The $^{13}C$ n.m.r. spectrum consisted of four signals which was consistent with the cyclic assignment. There were no low field signals present corresponding to olefinic carbons and as only one low field signal was observed (δ 78.81) in the nitro substituted region of the spectrum this would imply that there was only one type of nitro substituted carbon present. This would not be the case if both double bonds had been added across to produce a tetra-nitro adduct. The nitromethyl substituted carbons (δ 41.01) in the cyclopentyl ring appear at a lower field than the three other carbons, and this is due to the substituent effect of the nitromethyl group. This signal is also of lower intensity than those for the remaining ring carbons since it is derived from a tertiary carbon centre, and therefore has a longer relaxation time associated with it.

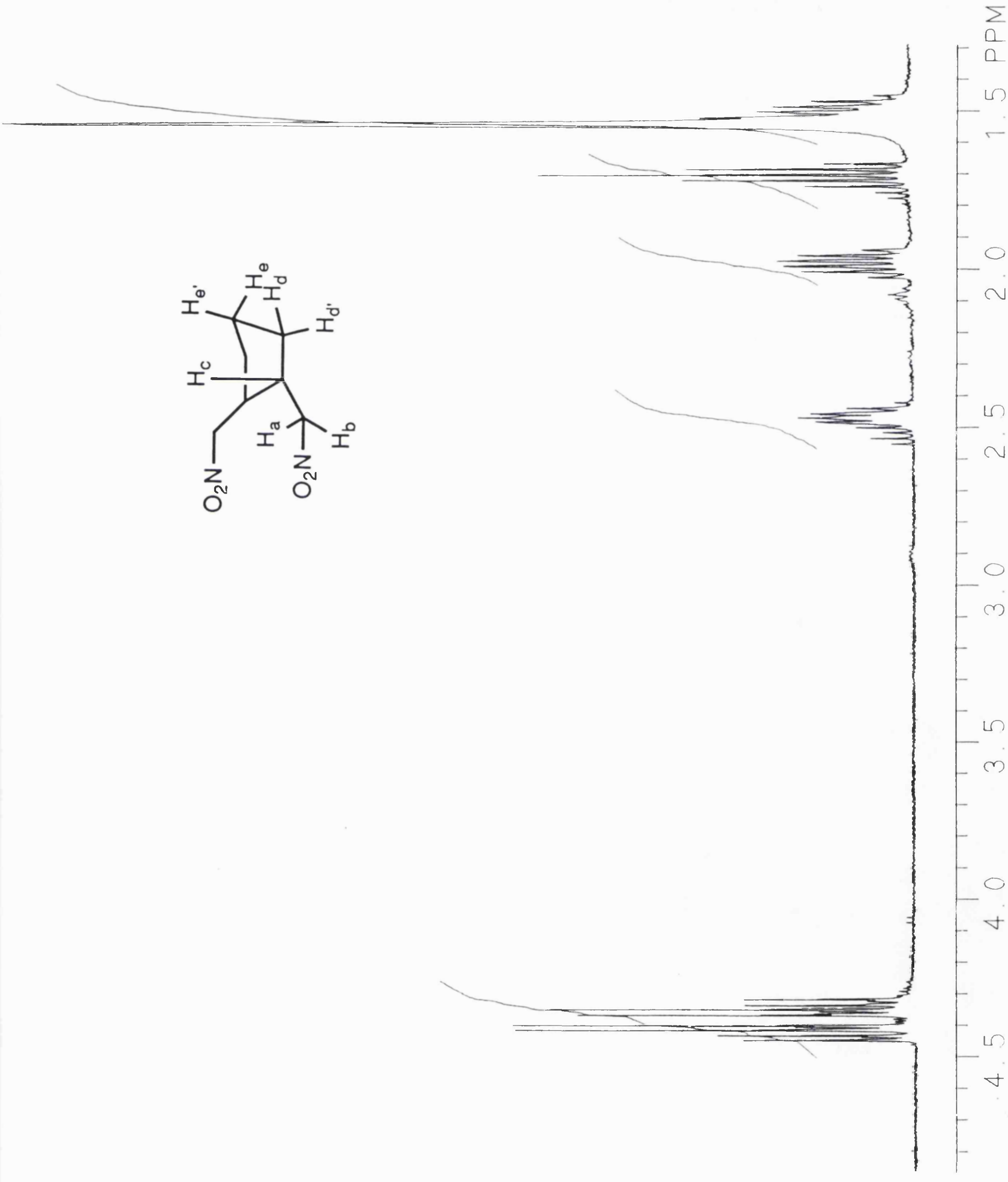


**Figure 4.3** $^1H$ n.m.r. spectrum for *trans*-1,2-(nitromethyl)-cyclopentane.

The C.I.M.S. gave a molecular ion of 206 amu which was in agreement with the empirical formula $C_7H_{10}N_2O_4.NH_4^+$. Also a fragmentation signal was observed at 67 amu which would be consistent for the cyclopentyl ring fragment.

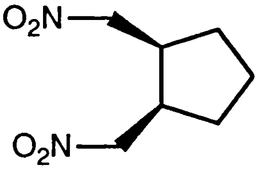
$^1$H n.m.r. (C) $\delta$: 1.49 (2H) m; 1.70 (2H) q, $^3J_{f,d}$ 7.13 Hz, $^3J_{f,e}$ 7.13 Hz; 1.98 (2H) m; 2.47 (2H) m; 4.34 (2H) dd, $^2J_{a,b}$ 12.63 Hz, $^3J_{a,c}$ 7.70 Hz; 4.42 (2H) dd, $^2J_{a,b}$ 12.63 Hz, $^3J_{b,c}$ 6.20 Hz.

$^{13}$C n.m.r. (C) $\delta$: 23.73, 30.33, 41.01, 78.81.

C.I.M.S. m/e: 206 ($M.NH_4^+$); 144 ($M.NH_4^+$-62); 126 ($M^+$-80); 95 ($M^+$-93); 81 ($M^+$-107); 67 ($M^+$-121).

Analysis: Insufficient sample.

### 4.2.4 *cis*-1,2-(Nitromethyl)-cyclopentane.



The $^1$H n.m.r. spectrum obtained (Figure 4.4) for this compound consisted of three main regions. The low field doublets of doublets at $\delta$ 4.27 and $\delta$ 4.43 are brought about by the diastereotopic protons $H_a$ and $H_b$ coupling, and then coupling to proton $H_c$. The multiplet centred on $\delta$ 2.95 corresponds to proton $H_c$ which is coupling to the four non equivalent protons $H_a$, $H_b$, $H_d$ and $H_{d'}$. The three multiplets in the high field region of the spectrum $\delta$ 1.4-2.0 are from the protons $H_d$, $H_{d'}$, $H_e$ and $H_{e'}$.

The $^{13}$C n.m.r. spectrum contained four signals, again with one low field signal from the nitro substituted carbon, two high field signals from the ring carbons, and one signal from the tertiary ring carbon at $\delta$ 42.00.

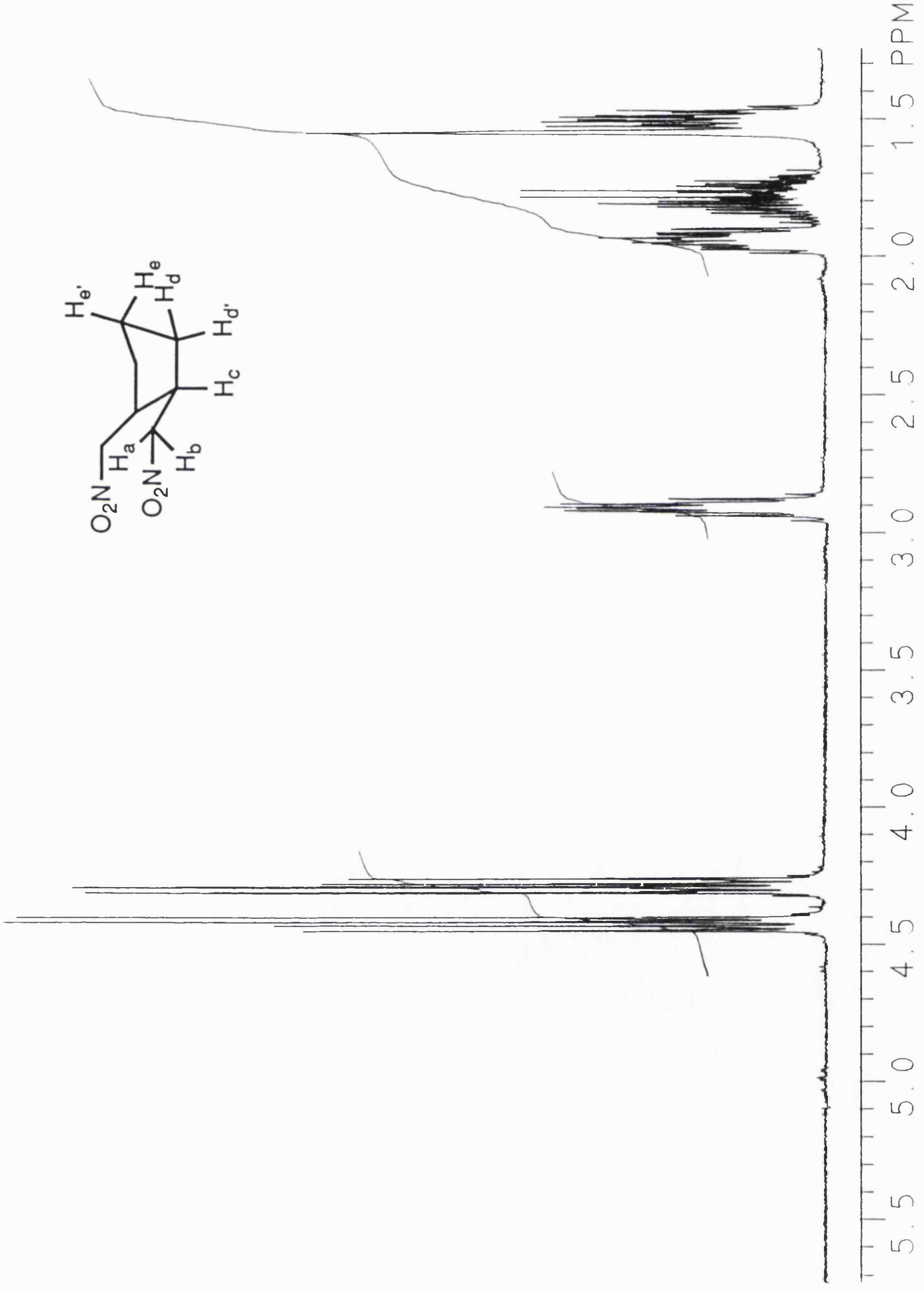


**Figure 4.4** $^1H$ n.m.r. spectrum for *cis*-1,2-(nitromethyl)-cyclopentane.

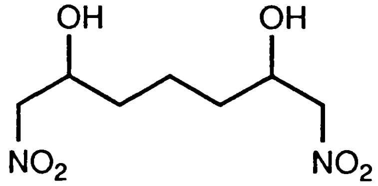
$^1$H n.m.r. (C) δ: 1.49(2H) m; 1.68-1.88(2H) m; 1.89-1.99(2H) m; 2.93(2H) m; 4.27(2H) dd, $^3J_{a,c}$ 8.18 Hz, $^2J_{a,b}$ 12.38 Hz,; 4.43(2H) dd, $^3J_{b,c}$ 6.73 Hz, $^2J_{b,a}$ 13.36 Hz.

$^{13}$C n.m.r. (C) δ: 21.87, 28.55, 40.01, 75.73.

C.I.M.S. m/e: 206($M.NH_4^+$); 144($M^+$-44); 126($M^+$-62); 95($M^+$-93).

Analysis: Insufficient sample.

### 4.2.5 2,6-Dihydroxy-1,7-dinitro-heptane.



The $^1$H n.m.r spectrum for this molecule was relatively simple (Figure 4.5), thus implying that the molecule was symmetrical. The splitting pattern observed in the region δ 4.25 to 4.45 was similar to that for 2-hydroxy-1-nitro-6-heptene (Section 4.2.1). The large multiplet at δ 1.58 corresponds to the diastereotopic protons $H_d$ and $H_{d'}$ coupling to proton $H_c$ and protons $H_e$. Overlapping this multiplet is the signal for the protons $H_e$. The $H_c$ protons are also diastereotopic and give rise to a complex multiplet centred on δ 4.3. Finally the protons $H_a$ and $H_b$ are also non equivalent and these produce a pair of doublets of doublets observed at δ 4.41 and δ 4.64.

The $^{13}$C n.m.r. spectrum was also consistent with the assignment as four signals were present within the spectrum, confirming that the molecule had undergone symmetrical addition. Unlike the cyclopentane derivatives, this spectrum had two high field signals and two low field signals. The low field signals at δ 82.15 and δ 69.21 correspond to the nitro substituted and the hydroxy

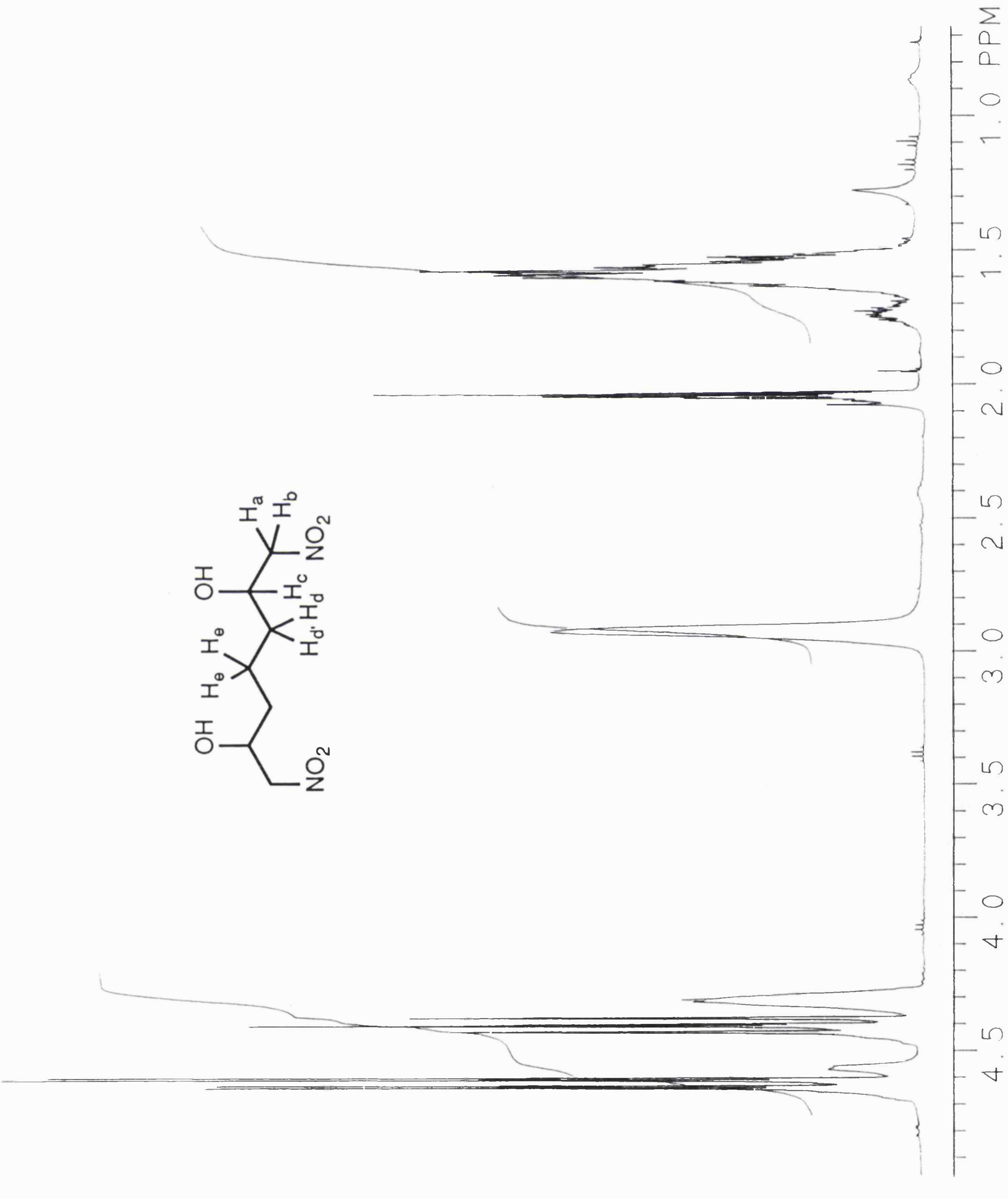


**Figure 4.5** $^1H$ n.m.r. spectrum for 2,6-dihydroxy-1,7-dinitro-heptane.

substituted carbons respectively. The two high field signals correspond to the central carbons in the molecule.

$^1H$ n.m.r. (A) δ: 1.58 (6H) m; 2.93 (2H) bs; 4.30 (2H) m; 4.41 (2H) dd, $^3J$ Hz, $^2J$ Hz; 4.64 (2H) dd, $^3J$ Hz, $^2J$ Hz.

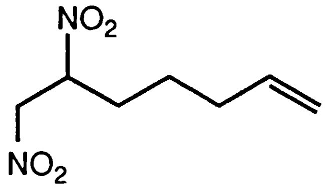
$^{13}C$ n.m.r. (A) δ: 21.77, 34.58, 69.21, 82.15.

C.I.M.S. m/e: 240($M.NH_4^+$); 222($M^+$); 204($M^+$-18); 175($M^+$-47); 128($M^+$-96).

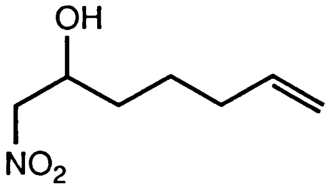
Analysis: Insufficient sample.

### 4.3 Discussion.

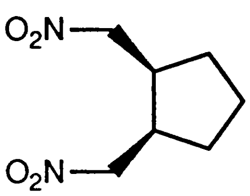
The reaction between nitrogen dioxide and 1,6-heptadiene proved to be quite an interesting reaction with the isolation of the straight chain adducts 1,2-dinitro-6-heptene (**40**), 2-hydroxy-1-nitro-6-heptene (**41**), the cyclic products *cis* and *trans* 1,2-(nitromethyl)-cyclopentane **42** and **43** respectively, and the tetra adduct 2,6-dihydroxy-1,6-dinitro-heptane (**46**).



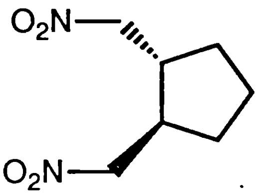
**40**



**41**



**42**

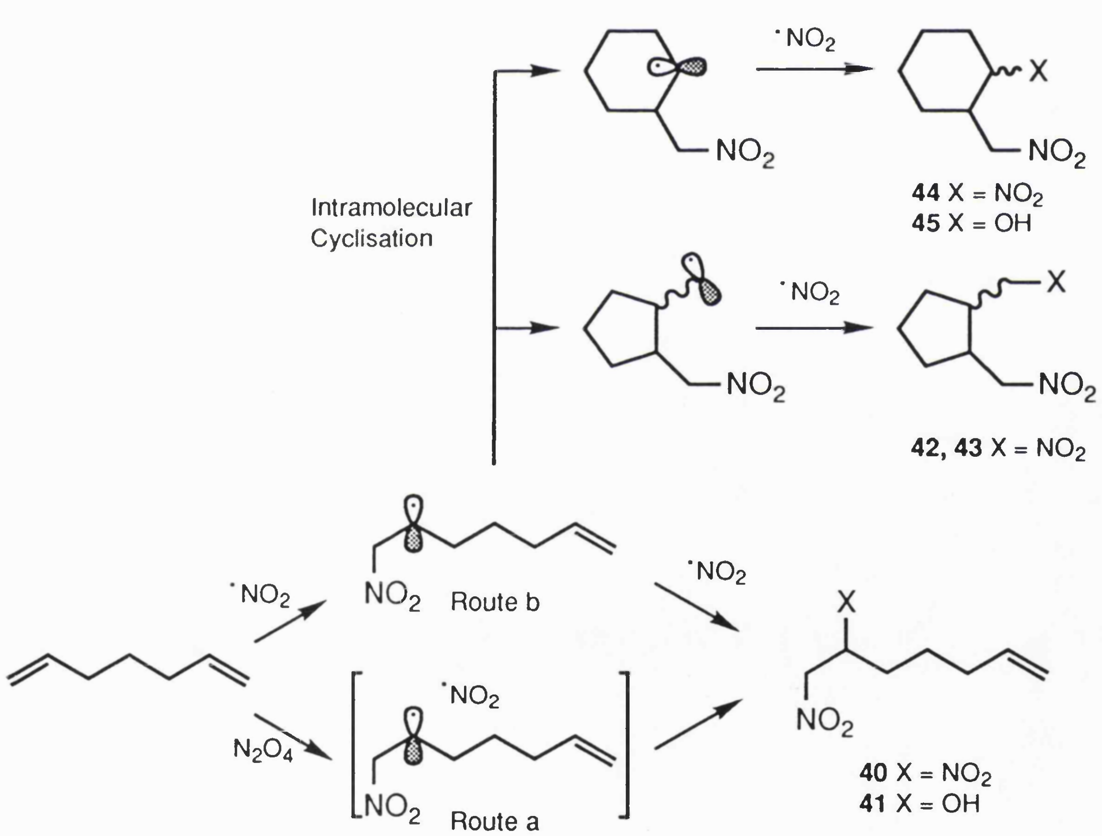


**43**

The straight chain adducts **40** and **41** were the predominant products from the reaction, and only trace amounts of **42** and **43** were isolated.

The reaction products from this reaction were dependant upon the mode of addition as well as the rate of addition, it was therefore hoped that by altering the conditions of the reaction we could alter the product distribution and increase the yield of the cyclic derivatives.

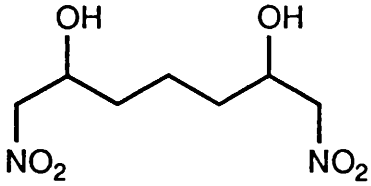
The normal mode of addition was studied predominantly as this was the most likely method of addition to obtain the cyclic compounds **42** and **43**. Under these conditions the diene would always be in excess compared to the nitrogen dioxide and it was envisaged that altering the rate of $NO_2$ addition would alter the reaction pathway (Scheme 4.1).



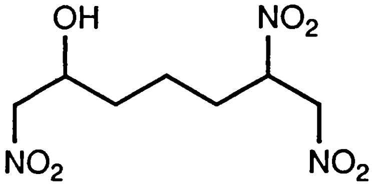
**Scheme 4.1**

When a fast addition rate of nitrogen dioxide to the 1,6-heptdiene solution was employed, it was envisaged that the reaction would proceed via routes **a** or **b** to produce the straight chain compounds **40** and **41**, as there would be a higher concentration of nitrogen dioxide present; the initial radical formed would react with another $NO_2$ radical before the intramolecular cyclisation could occur.

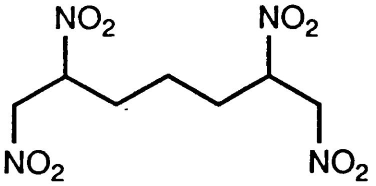
This was the case and there was no evidence for the formation of the cyclic products **42, 43, 44** or **45**. The yield of **40** and **41** was 27.4 % and 32.7 % respectively. The remaining products from the reaction showed ${}^{1}H$ and ${}^{13}C$ n.m.r. spectra characteristic of addition of nitrogen dioxide to both double bonds, as the characteristic olefinic signals in the ${}^{1}H$ and ${}^{13}C$ n.m.r. were no longer present. The chemical shifts of the ${}^{13}C$ n.m.r. signals were consistent with the addition of nitrogen dioxide at both double bonds as only two or three high field carbons were observed due to the methylene carbons or two and four carbons in the C-$NO_2$ and C-OH region of the spectrum depending on the symmetry of the product. These compounds were thought to be 2,6-dihydroxy-1,7-dinitro-heptane (**46**), 2-hydroxy-1,6,7-trinitro-heptane (**47**) or 1,2,6,7-tetranitro-heptane (**48**).



**46**

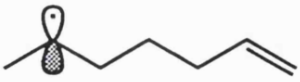


**47**



**48**

When the addition rate was slowed down such that the addition of 2 mmol of nitrogen dioxide in solution took 6 h or longer, the cyclic products **42** and **43** could be identified along with the straight chain products **40** and **41** which were still formed predominantly. There was no evidence of the cyclohexyl products **44** and **45**. This was consistent with the literature regarding the ring closure of 6-hepten-2-yl radicals[63,64,65,66,67] (**49**), and 5-hexen-1-yl radicals[68,69,70,71] (**50**). Under no conditions was the cyclohexane derivative observed, even though it is the thermodynamically favoured product[72]. This is consistent with Baldwins rules for ring closure[73].



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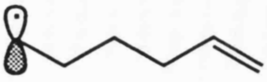


50

The rate of cyclisation for the 6-hepten-2-yl radical has not been determined, but results from molecular modelling[74,75] show the rate constants for the *cis* and *trans* products to be $1.1 \times 10^5\ s^{-1}$ and $4.2 \times 10^4\ s^{-1}$.

The determination of the configurations of **42** and **43** was done purely on their $^1H$ n.m.r. spectra. This was possible due to the ring puckering effect that takes place within the molecules. When in solution the cyclopentyl ring system can bend and this produces a marked difference in the spectra for **42** and **43**.

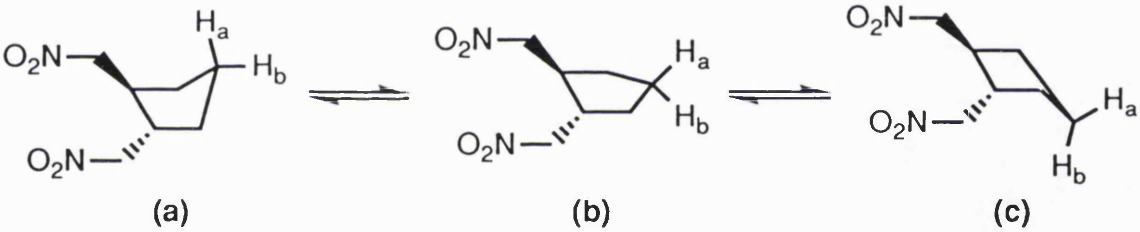


**Figure 4.6** Ring puckering in *trans*-1,2-(nitromethyl)-cyclopentane.

Considering compound **42** initially (Figure 4.6) then the ring puckering that occurs has three main conformations: (a) the molecule starts as a boat conformation with hydrogen $H_a$ in an axial position, and hydrogen $H_b$ occupies the equatorial position, (b) the ring becomes planar and hydrogens $H_a$ and $H_b$ become equivalent, (c) the ring becomes an 'inverted' boat with hydrogen $H_a$ now being equatorial and hydrogen $H_b$ becoming axial. Due to the substituents at the 1 and 2 positions being *trans*, the hydrogens $H_a$ in (a) is equivalent to hydrogen $H_b$ in (c) and likewise hydrogen $H_b$ in (a) is equivalent to hydrogen $H_a$ in (c). Therefore on the n.m.r. time scale the protons for $H_a$ and $H_b$ become equivalent and this leads to a quintet in the $^1H$ n.m.r. spectrum (Figure 4.8a).

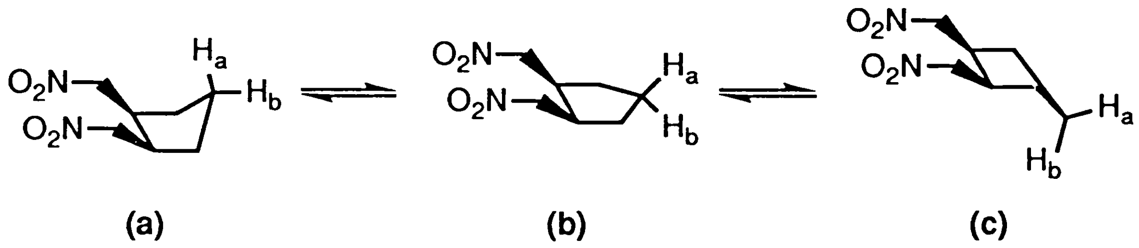


**Figure 4.7** Ring puckering in *cis*-1,2-(nitromethyl)-cyclopentane.

Considering **43**, the ring puckering still produces three main conformations (Figure 4.7): (a) the ring is in the boat conformation with hydrogen $H_a$ in the axial position, hydrogen $H_b$ in an equatorial position, (b) the cyclopentyl ring becomes planar but due to the substituents being on the same side of the ring hydrogens $H_a$ and $H_b$ are still non-equivalent, (c) the ring becomes an 'inverted' boat and now hydrogen $H_a$ becomes equatorial and $H_b$ axial. Here however hydrogen $H_a$ in (a) is not equivalent to $H_b$ in (b) because of the substituents. In conformation (a) hydrogen $H_a$ is in a *cis* orientation to the substituents and $H_b$ is in a *trans* orientation, this is also the case in conformations (b) and (c). Therefore the protons associated with $H_a$ and $H_b$ will always have a chemically different environment and this is reflected in the $^1H$ n.m.r. spectrum which becomes much more complicated (Figure 4.8b) due to the neighbouring protons becoming diastereotopic with respect to $H_a$ and $H_b$.

The formation and isolation of the higher adducts **46**, **47** and **48** proved difficult as they appeared to be unstable and to decompose on standing. Due to this instability, accurate analyses were not obtained for these compounds but $^1H$ and $^{13}C$ n.m.r. spectra for structures **46** and **47** were obtained. The isolation of **47** was not reported earlier in this chapter as no C.I.M.S. spectrum was obtained; the structure has been postulated from the comparison of the $^{13}C$ n.m.r. spectra for compounds **40** and **41** (Figure 4.9). From the comparison of the C-$NO_2$ and C-OH regions of **40** and **41** with **47** it can be seen that the spectrum fits well to

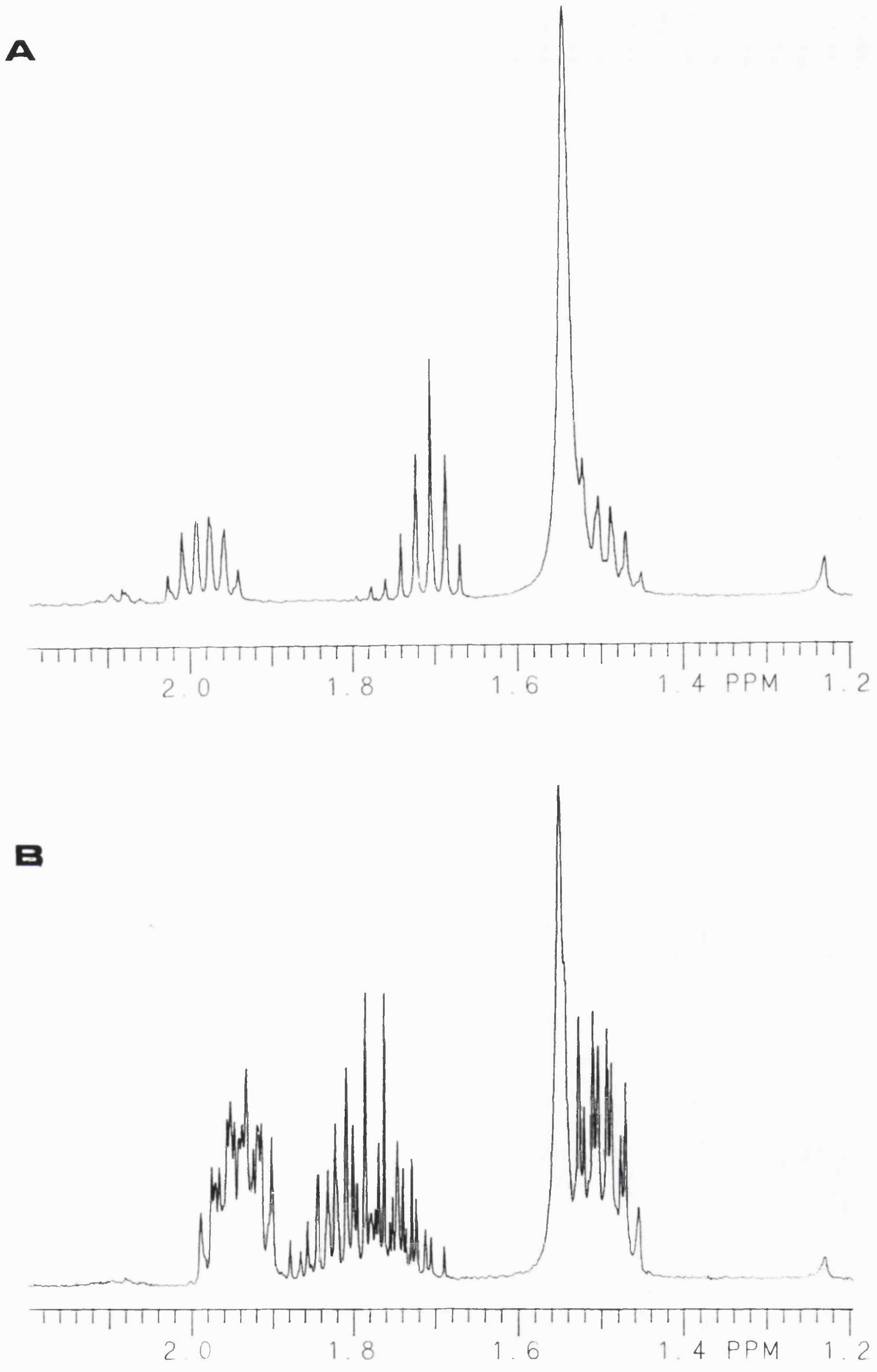


**Figure 4.8** Comparison of the methyl region of the $^1H$ n.m.r. spectrum for a) *trans*-1,2-(nitromethyl)-cyclopentane and b) *cis*-1,2-(nitromethyl)-cyclopentane.

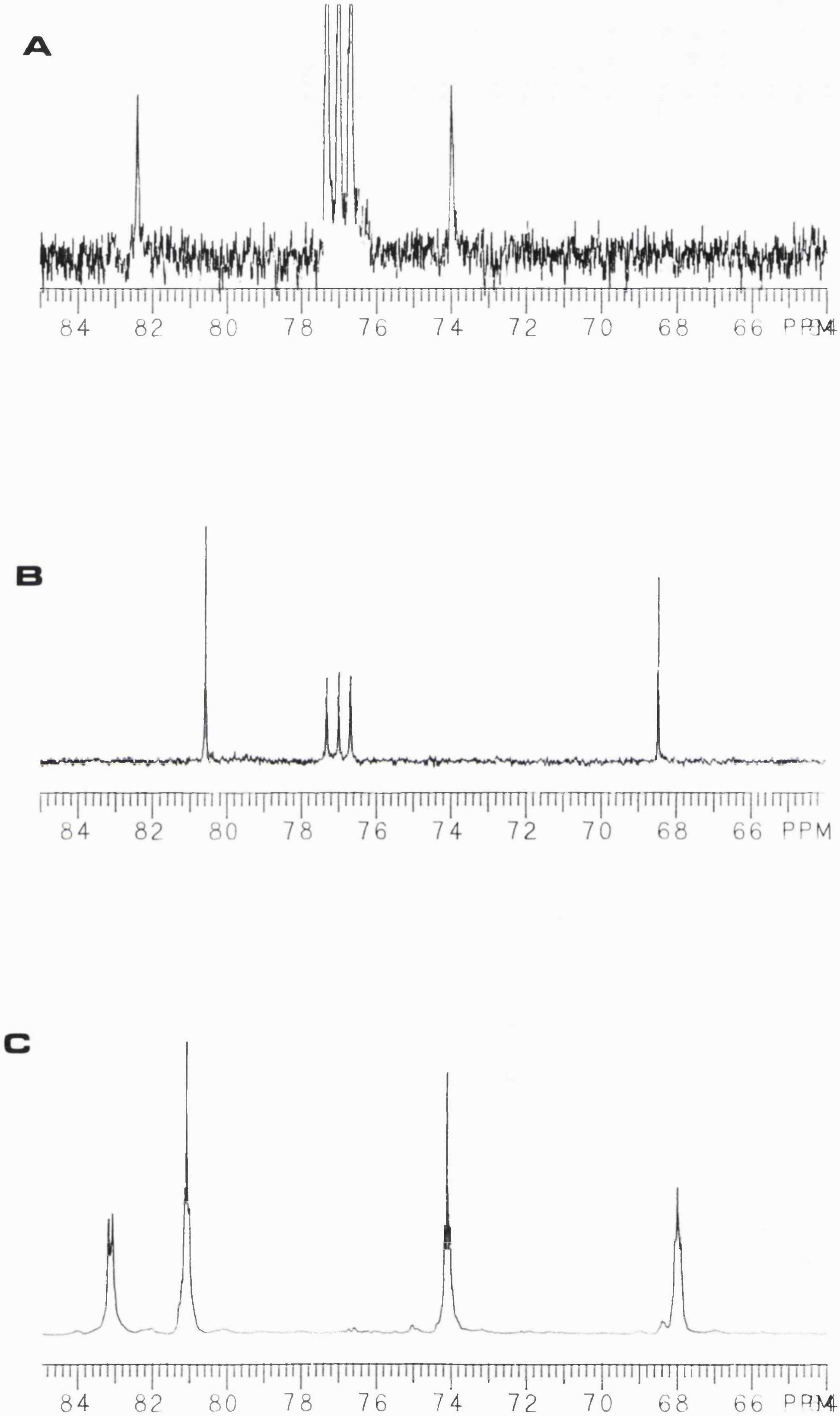


**Figure 4.9** Comparison of the $^{13}$C n.m.r. spectra in the C-NO2 and C-OH region for a) 1,2-dinitro-6-heptene; b) 2-hydroxy-1-nitro-6-heptene; c) the possible 2-hydroxy-1,6,7-trinitro-heptene.

that expected for **47**. The comparison of the $^1$H n.m.r. splitting patterns for **40** and **41** also approximated well to those observed for the spectrum obtained for **47**. No evidence for the formation of **48** was obtained.

## 4.4 Conclusions.

The reaction between 1,6-heptadiene and nitrogen dioxide yields both straight chain and cyclic adducts. The formation of the straight chain adducts could have been formed from either attack of molecular $N_2O_4$ or the $NO_2$ radical. The formation of the cyclic products would only be possible if the attack of the second $NO_2$ was slow compared to that of ring closing; this would not be the case if molecular $N_2O_4$ were attacking but would be characteristic of two separate additions of the $NO_2$ radical. Therefore $NO_2$ is present as an attacking species in nitrogen dioxide due to the formation of the cyclic products but the extent it plays in the formation of the straight chain adduct compared to that of molecular $N_2O_4$ it is not known.

# CHAPTER FIVE

# REACTIONS OF NITROGEN DIOXIDE WITH ALLYL ETHER AND DIALLYLAMINE.

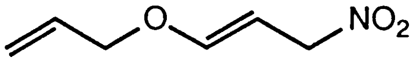
## 5.1 Introduction.

This Chapter deals with the reactions of allyl ether and diallylamine with nitrogen dioxide solutions. The aims of the work were to find out how the rate of addition of the nitrogen dioxide to the dienes altered the reaction products. It was hoped that both the substrates under consideration would undergo intramolecular cyclisation as this would give an insight into the reaction mechanism of nitrogen dioxide additions.

The chapter starts with the identification of the compounds isolated in the reactions between allyl ether and nitrogen dioxide and then diallyl amine and nitrogen dioxide. All of the proton spectra are shown and a representative selection of the $^{13}C$ n.m.r. spectra. The results obtained are then discussed and the Chapter closes with the conclusions that can be drawn from these results.

## 5.2 Products Formed in the Reactions Between Nitrogen Dioxide and Allyl Ether.

### 5.2.1 1-Nitro-2-propenyl-3,3'-oxy-1'-propene.



This compound was identified from its $^1H$ n.m.r. and $^{13}C$ n.m.r. spectra, however a mass spectrum could not be obtained for this molecule by C.I.M.S. The assignment as 1-nitro-2-propenyl-3,3'-oxy-1'-propene is not certain and there is the possibility it could be it its structural isomer 1-nitro-1-propenyl-3,3'-oxy-1'-propene.

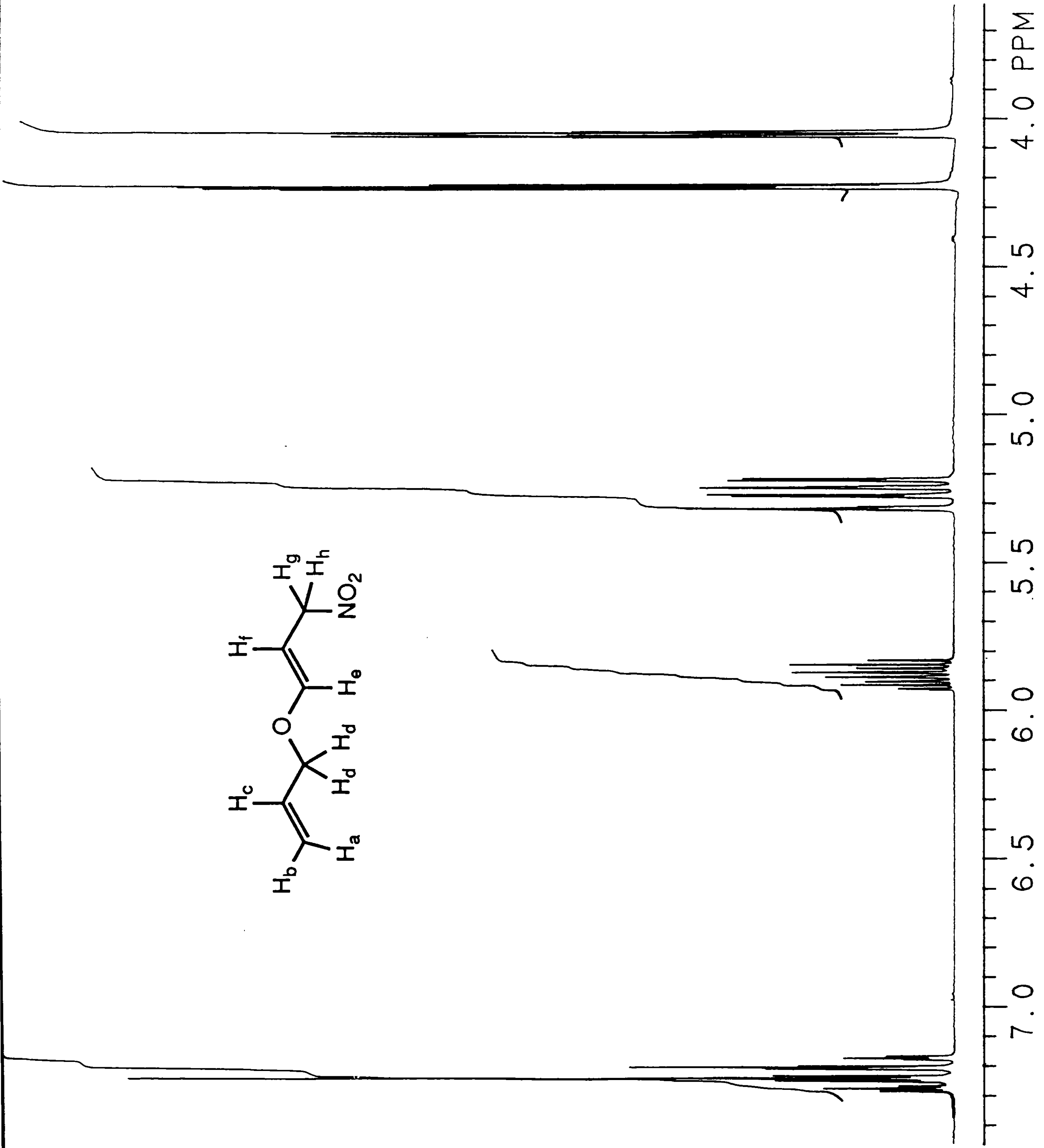


**Figure 5.1** $^1H$ n.m.r. spectrum for 1-nitro-2-propenyl-3,3'-oxy-1'-propene.

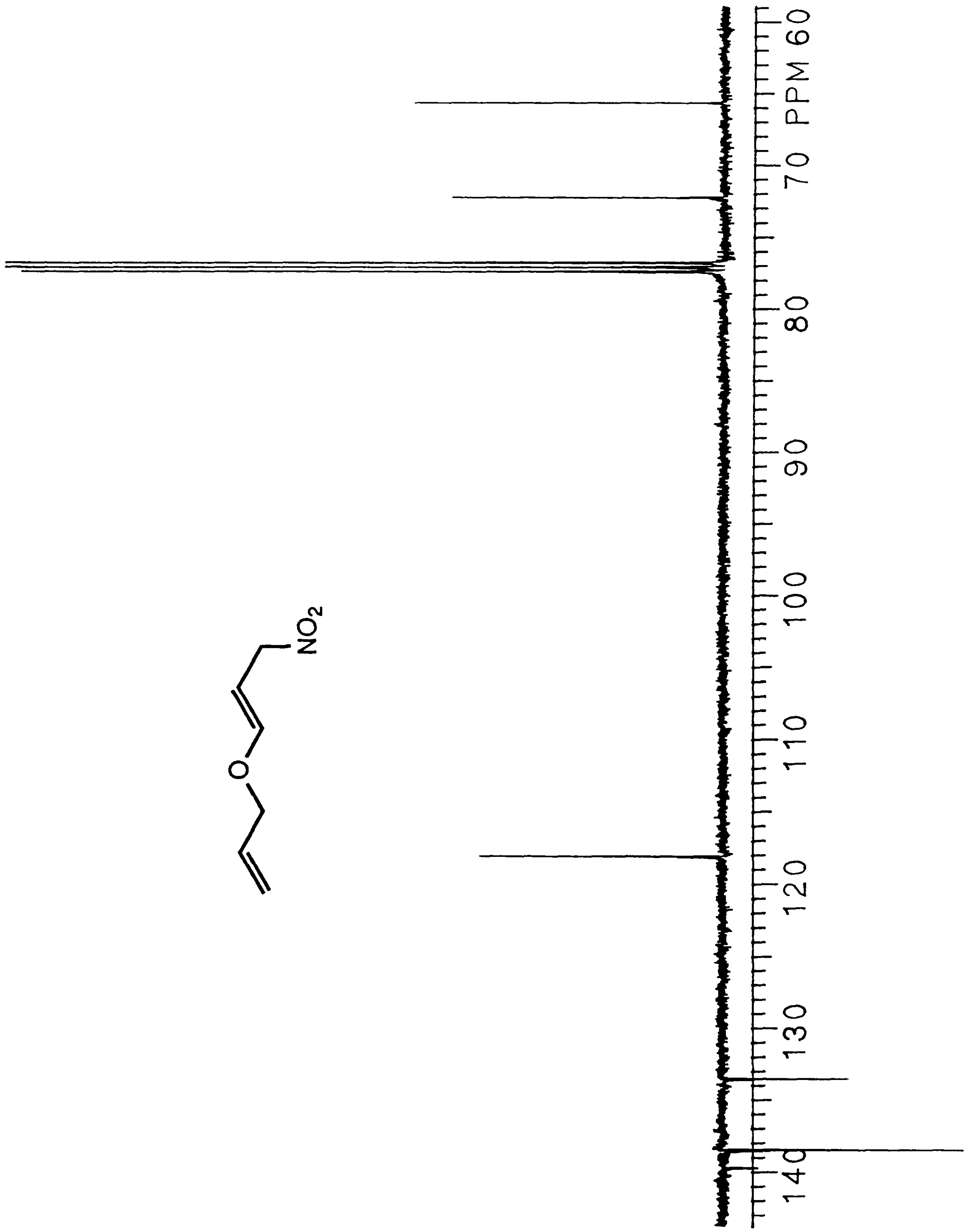


**Figure 5.2** $^{13}C$ n.m.r. spectrum for 1-nitro-2-propenyl-3,3'oxy-1'-propene.

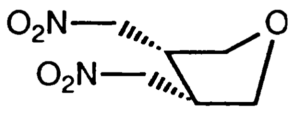
From the $^{1}H$ n.m.r. spectrum (**Figure 5.1**) there are five main regions present. The splitting patterns at δ 5.88, 5.29, 4.05 are characteristic of the starting diene. The low field multiplet corresponds to the olefinic protons $H_f$ and $H_e$. The nitro group has the effect of moving the methylene protons to a lower field and this can be seen by the multiplet at δ 4.23.

The $^{13}C$ n.m.r. spectrum (**Figure 5.2**) confirms this assignment too, as from the attached proton spectrum (A.P.T.) it can be seen that three of the olefinic carbons are of the nature CH, and only one is $CH_2$.

$^{1}H$ n.m.r. (C) δ: 4.05 (2H) dt, $^{3}J_{c,d}$ 5.62 Hz, $^{4}J_{d,b}$ 1.4 Hz, $^{4}J_{d,a}$ 1.4 Hz; 4.23 (2H) dd, $^{3}J_{e,f}$ 3.28 Hz, $^{4}J_{e,g}$ 1.96 Hz; 5.23 (1H) dq, $^{3}J_{b,c}$ 17.25 Hz, $^{2}J_{b,a}$ 1.5 Hz, $^{4}J_{b,d}$ 1.4 Hz; 5.29 (1H) dq, $^{3}J_{a,c}$ 10.38 Hz, $^{2}J_{a,b}$ 1.5 Hz, $^{4}J_{a,d}$ 1.4 Hz; 5.88 (1H) m, $^{3}J_{b,c}$ 17.25 Hz, $^{3}J_{a,c}$ 10.38 Hz, $^{3}J_{c,d}$ 5.62 Hz; 7.19 (1H) dt, $^{3}J_{f,g}$ 13.50 Hz, $^{4}J_{e,g}$ 1.95 Hz; 7.26 (1H) dt, $^{3}J_{f,g}$ 13.50 Hz, $^{3}J_{e,f}$ 3.54.Hz.

$^{13}C$ n.m.r. (C) δ: 65.55, 72.54, 118.05, 133.52, 138.47, 139.66.

### 5.2.2 *c*-2,3-(Nitromethyl)-tetrahydrofuran.



The identification of this molecule has been based on its $^{1}H$ n.m.r., $^{13}C$ n.m.r., I.R., and C.I.M.S. spectra.

From the $^{1}H$ n.m.r. spectrum (**Figure 5.3**) it can be clearly seen that there are four signals present. The high field multiplet corresponds to the protons attached to the tertiary carbons in the ring. The remaining hydrogens are all diastereotopic and give rise to doublet of doublet signals. The protons

$H_d$ and $H_e$ give rise to the signals at $\delta$ 3.63, 4.05 respectively. The low field doublet of doublets at $\delta$ 4.45, and $\delta$ 4.53 are brought about by the protons $H_a$ and $H_b$.

Owing to the symmetry of the molecule there are only three different carbon signals present within the $^{13}C$ n.m.r. spectrum (**Figure 5.4**). Two of the carbon signals are quite obvious; unfortunately the third signal lies directly under the solvent peak at $\delta$ 76.68, but it can be noticed by the enhancement of this signal relative to the signals at $\delta$ 77.01, 77.33.

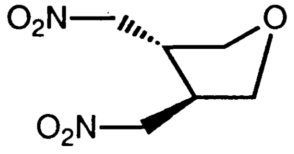
$^1H$ n.m.r. (C) $\delta$: 2.78 (2H) m; 3.63 (2H) dd, $^3J_{c,d}$ 4.96 Hz, $^2J_{d,e}$ 9.68 Hz; 4.05 (2H) dd, $^3J_{c,e}$ 6.78 Hz, $^2J_{d,e}$ 9.68 Hz; 4.45 (2H) dd, $^3J_{a,c}$ 7.77 Hz, $^2J_{a,b}$13.75 Hz; 4.53 (2H) dd, $^3J_{b,c}$ 6.71 Hz, $^2J_{b,a}$ 13.75 Hz.

$^{13}C$ n.m.r. (C) $\delta$: 40.75, 70.74,76.68.

I.R. cm$^{-1}$: 1557, 1376, 1094.

C.I.M.S. : 208 (M.$NH_4^+$); 161 (M.$NH_4^+$-47); 113 (M.$NH_4^+$-95).

### 5.2.3 *t*-2,3-(Nitromethyl)-tetrahydrofuran.



This molecule was characterised by its $^1H$ n.m.r., $^{13}C$ n.m.r., I.R., and C.I.M.S. spectra.

The $^1H$ n.m.r. spectrum (**Figure 5.5**) consisted of four main regions. The multiplet at $\delta$ 3.24 is characteristic of the protons attached to the tertiary carbons in the tetrahydrofuran ring, $H_c$. The doublet of doublets centred on $\delta$ 3.70 and $\delta$ 4.20 correspond to the diastereotopic protons $H_d$ and $H_e$

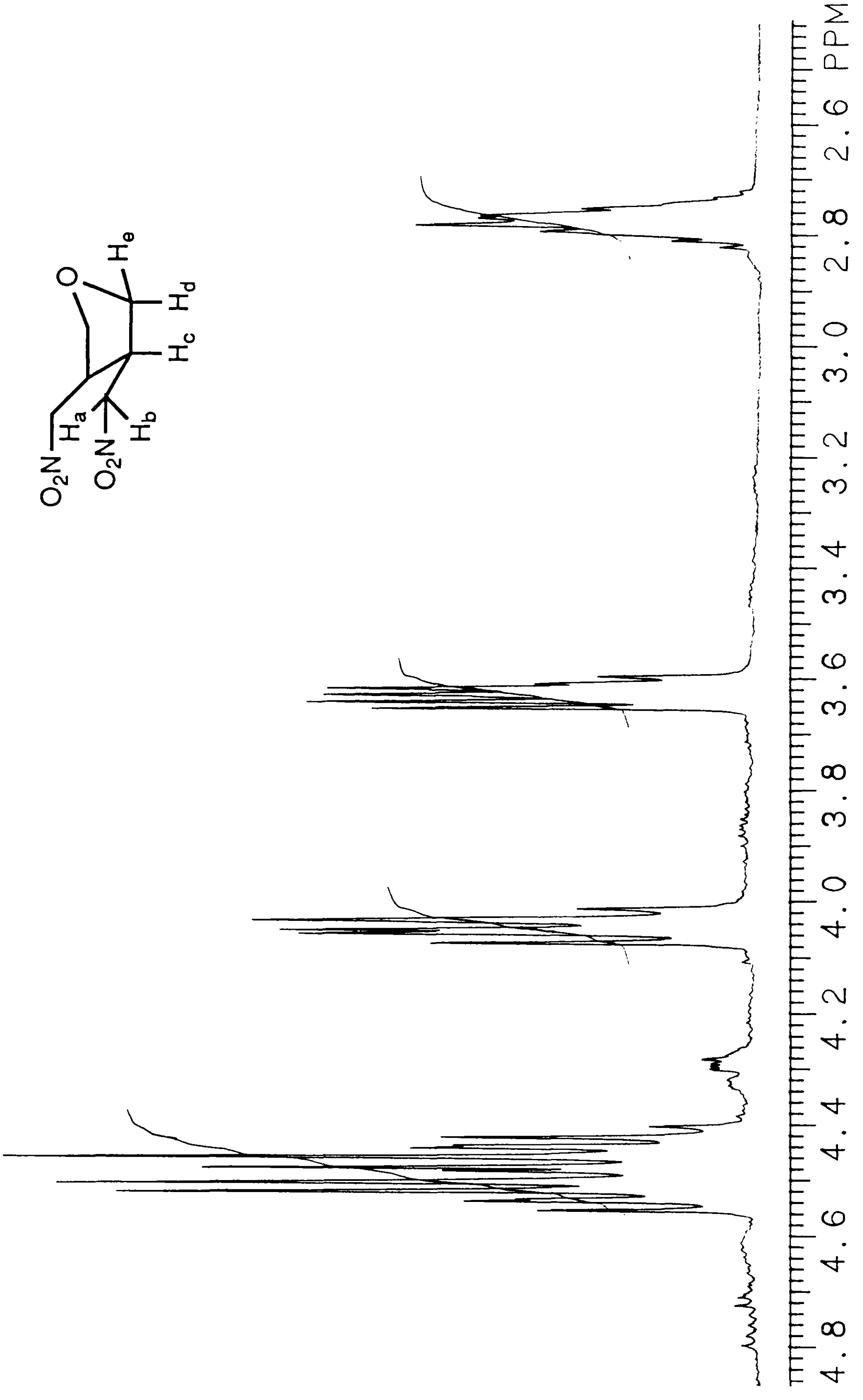


**Figure 5.3** $^1H$ n.m.r. spectrum for *c*-2,3-(nitromethyl)-tetrahydrofuran.

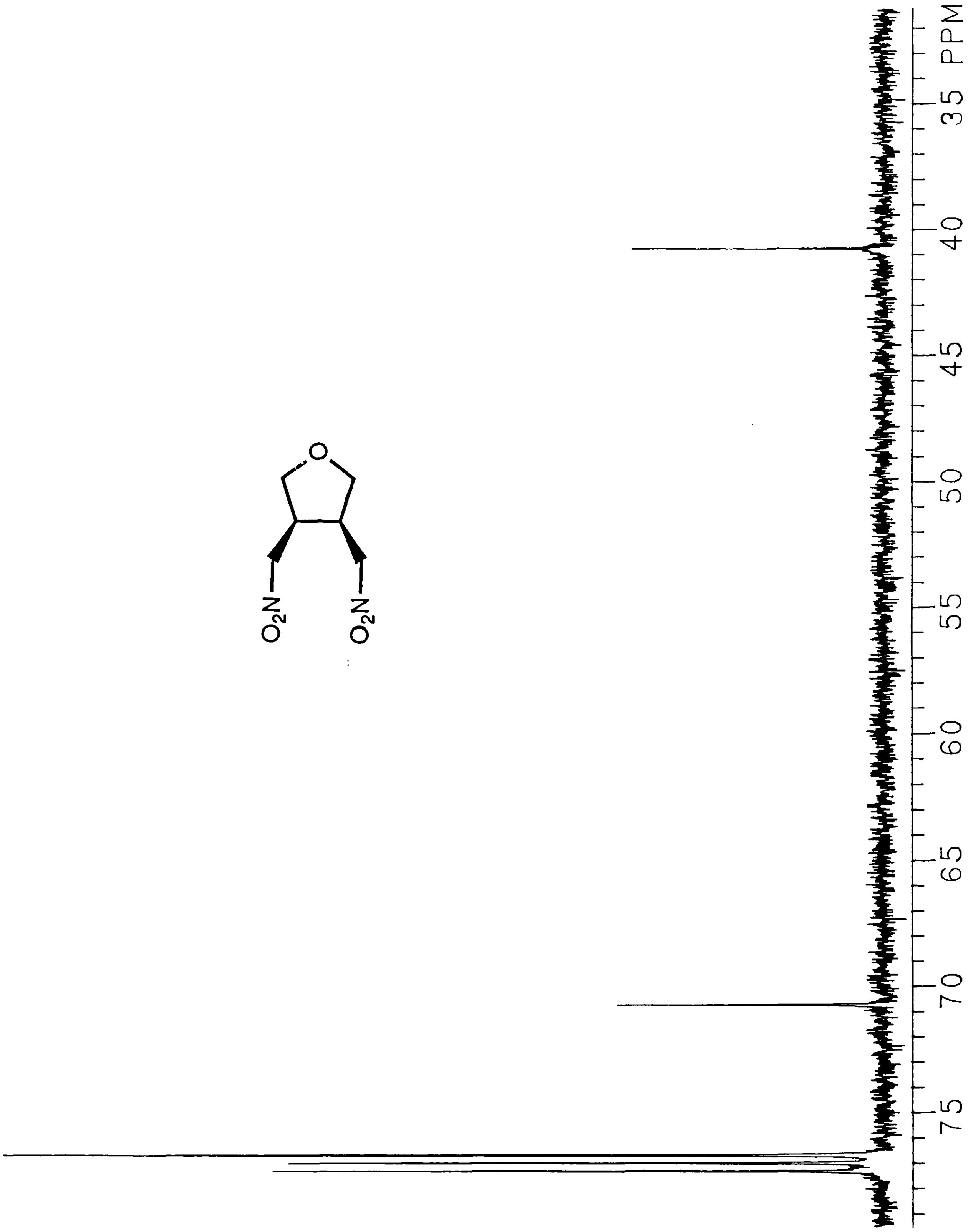


**Figure 5.4** $^{13}C$ n.m.r. spectrum for *c*-2,3-(nitromethyl)-tetrahydrofuran.

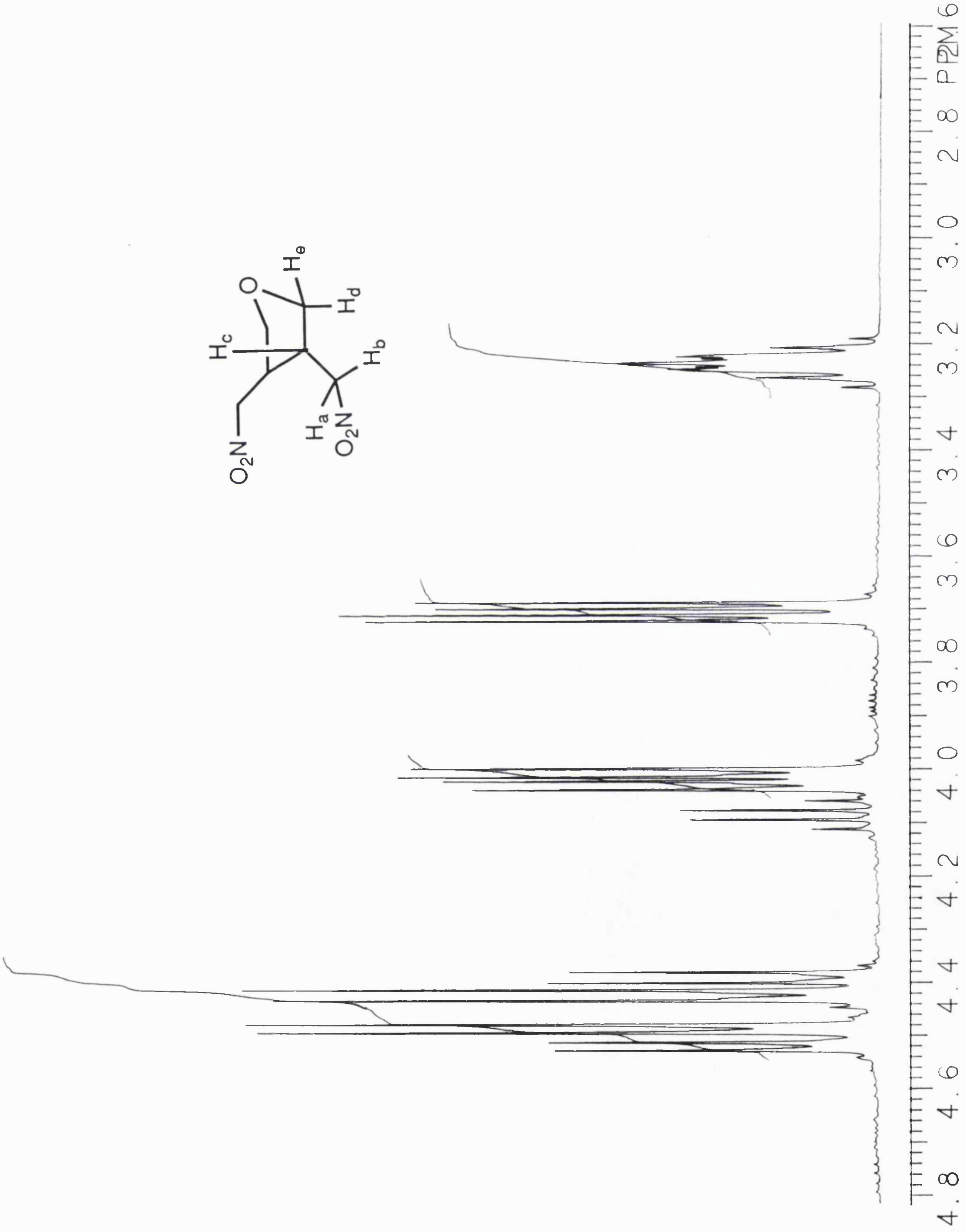


**Figure 5.5** $^1$H n.m.r. spectrum for *t*-2,3-(nitromethyl)-tetrahydrofuran.

respectively. Protons $H_a$ and $H_b$ are also diastereotopic and these give rise to the two sets of doublet of doublets at low field.

From the $^{13}C$ n.m.r. spectrum only three signals are observed due to the symmetry of the molecule. The high field signal corresponds to the tertiary carbons in the ring, the signal at $\delta$ 70.27 correspond to the carbons attached to oxygen while the low field signal is due to the nitro substituted carbon.

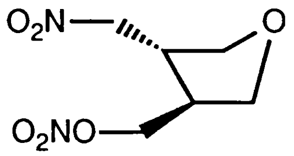
$^1H$ n.m.r. (C) $\delta$: 3.24 (2H) m; 3.71 (2H) dd, $^3J_{c,d}$ 5.08 Hz, $^2J_{d,e}$ 9.48 Hz; 4.02 (2H) dd, $^3J_{c,e}$ 6.53 Hz, $^2J_{d,e}$ 9.48 Hz; 4.41 (2H) dd,$^2J_{a,b}$ 13.29 Hz, $^3J_{b,c}$ 6.21 Hz; 4.51 (2H) dd, $^2J_{a,b}$ 13.29 Hz, $^3J_{a,c}$ 8.14 Hz.

$^{13}C$ n.m.r. (C) $\delta$: 39.28, 70.27, 73.39.

I.R. cm$^{-1}$: 1557, 1372, 1091.

C.I.M.S. : 208 ($M.NH_4^+$); 190 ($M^+$).

### 5.2.4 *t*-2-Nitratomethyl-3-nitromethyl-tetrahydrofuran.



From the $^1H$ n.m.r. spectrum (**Figure 5.6**), it can be seen that there are six regions. The important feature of the spectrum is that there are two high field multiplets at $\delta$ 2.85, and $\delta$ 3.19, due to protons $H_c$, and $H_h$ showing that the plane of symmetry is no longer present. The remaining protons on the molecule are all diastereotopic and should therefore all produce doublet of doublets. The multiplets at $\delta$ 3.72 and $\delta$ 4.01 correspond to the protons $H_d$, $H_e$ and $H_f$, $H_g$ respectively. The multiplet at $\delta$ 4.44 consists of a large doublet over laying

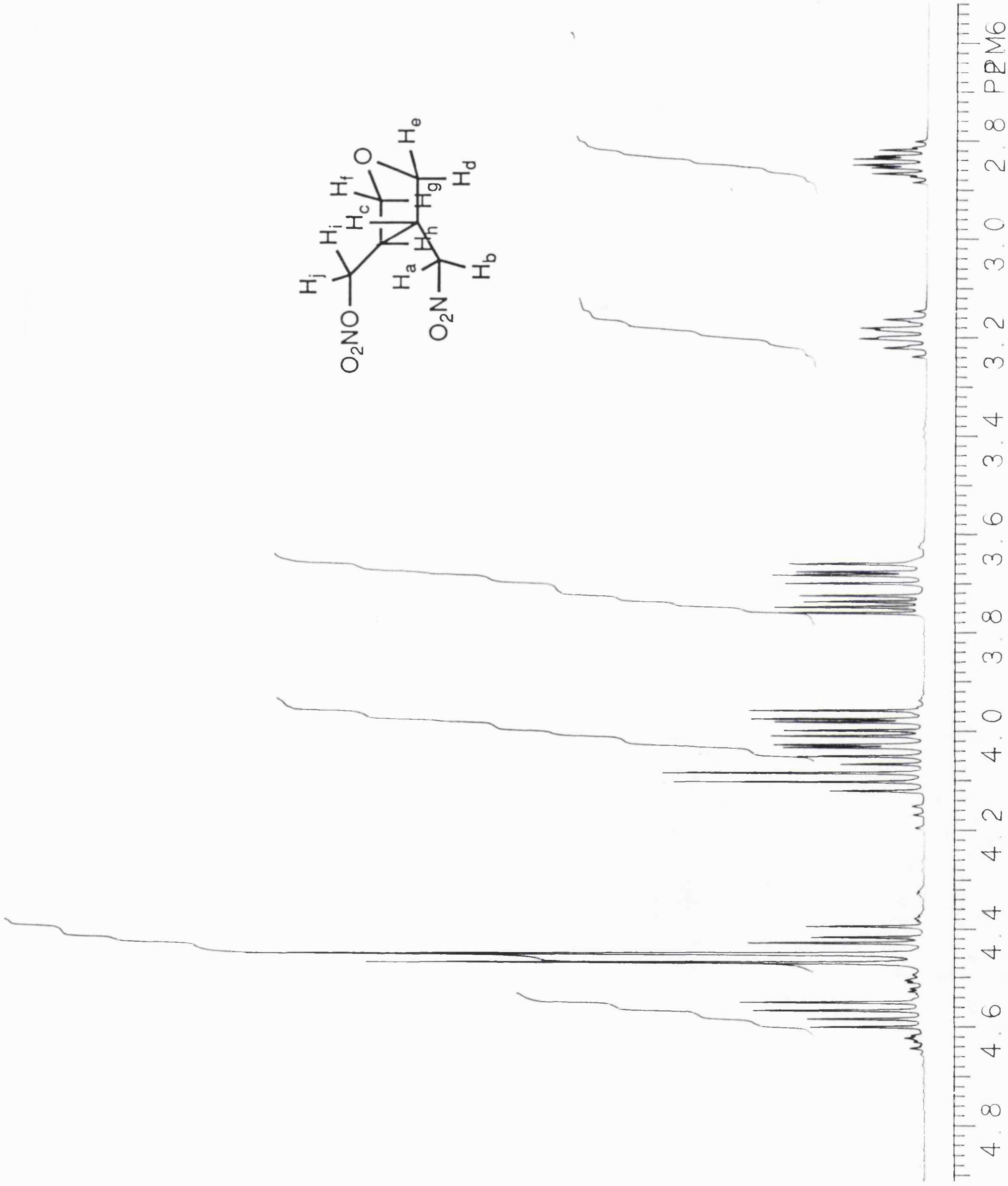


**Figure 5.6** $^1H$ n.m.r. spectrum for *t*-2-nitratomethyl-3-nitromethyl-tetrahydrofuran.

the doublet of doublets from proton $H_i$. This large doublet arises from accidental equivalence of protons $H_a$ and $H_b$.

Owing to the asymmetric nature of the molecule, the $^{13}C$ n.m.r. spectrum obtained contained six carbon signals. Evidence for the formation of the ring is given by the two high field signals in the spectrum at δ 38.53 and δ 39.14 as these correspond to the two tertiary carbons in the ring.

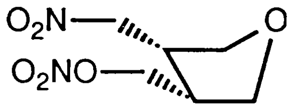
$^1H$ n.m.r. (C) δ: 2.85 (1H) m, $^3J_{a,c}$ 7.08 Hz, $^3J_{b,c}$ 7.08 Hz, $^3J_{c,d}$ 6.94 Hz, $^3J_{c,e}$ 4.8 Hz, $^3J_{c,h}$ 7.54 Hz; 3.20 (1H) m, $^3J_{h,j}$ 8.88 Hz, $^3J_{h,i}$ 6.56 Hz, $^3J_{f,g}$ 7.24 Hz, $^3J_{g,h}$ 6.68 Hz, $^3J_{c,h}$ 7.49 Hz; 3.68 (1H) dd, $^3J_{g,h}$ 6.68 Hz, $^2J_{f,g}$ 9.26 Hz; 3.75 (1H) dd, $^3J_{c,e}$ 4.8 Hz, $^2J_{d,e}$ 9.33 Hz; 3.98 (1H) dd, $^3J_{c,d}$ 6.94 Hz, $^2J_{d,e}$ 9.33 Hz; 4.03 (1H) dd, $^3J_{f,h}$ 7.24 Hz, $^2J_{f,g}$ 9.27 Hz; 4.43 (1H) dd, $^3J_{h,j}$ 8.88 Hz, $^2J_{i,j}$ 13.57 Hz; 4.46 (2H) d, $^3J_{a,c}$ 7.08 Hz; 4.57 (1H) dd, $^3J_{h,i}$ 6.56 Hz, $^2J_{i,j}$ 13.59 Hz.

$^{13}C$ n.m.r. (C) δ: 38.53, 39.14, 69.93, 70.20, 70.30, 73.66.

I.R. $cm^{-1}$: 1640, 1376, 1094.

C.I.M.S.: 224 ($M.NH_4^+$); 206 ($M^+$); 179 ($M.NH_4^+-45$); 113 ($M^+-91$); 82 ($M^+-124$).

### 5.2.5 *c*-2-Nitratomethyl-3-nitromethyl-tetrahydrofuran.



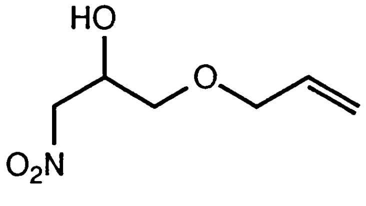
The $^1H$ n.m.r. spectrum (**Figure 5.7**) consists of five main regions. The multiplets at δ 2.41 and δ 2.81 correspond to the protons $H_c$ and $H_h$

respectively. The overlapping doublet of doublets centred on δ 3.64 and δ 4.02 are from the diastereotopic hydrogens $H_d$, $H_e$, $H_f$, and $H_g$. The large multiplet at δ 4.45 consists of four sets of doublet of doublets overlapping from the four remaining diastereotopic hydrogens $H_a$, $H_b$, $H_i$ and $H_j$, on the nitro and nitrato substituted carbons.

The asymmetry of the molecule is again apparent from the $^{13}C$ n.m.r. spectrum (**Figure 5.8**) as six signals are observed. The two high field signals are due to the tertiary ring carbons, while the two low field signals at δ 76.83, 72.90 are from the nitro and nitrato substituted carbons respectively. The two remaining signals are due to the carbons attached to oxygen.

| | |
|---|---|
| $^1H$ n.m.r. (C) δ: | 2.4 (1H) m; 2.80 (1H) m; 3.62 (2H) m, J 9.62 Hz, J 5.25 Hz, J 5.32 Hz; 3.98 (1H) dd, J 7.39 Hz, J 9.67 Hz; 4.05 (1H) dd, J 7.19 Hz, J 9.67 Hz; 4.45 (4H) m. |
| $^{13}C$ n.m.r. (C) δ: | 40.47, 40.50, 70.01, 70.81, 72.90, 76.83. |
| C.I.M.S.: | 224($M.NH_4^+$); 206 ($M^+$); 179 ($M.NH_4^+$-45); 113 ($M^+$-91); 82 ($M^+$-124). |

### 5.2.6 2-Hydroxy-1-nitro-propyl-3,3'-oxy-1'-propene.



From the $^1H$ n.m.r. spectrum (**Figure 5.9**) a couple of important features help to characterise this molecule; the multiplet centred on δ 5.85 has a splitting pattern which is characteristic for the olefinic proton $H_c$. The second feature is the doublet at δ 2.72 which has been attributed to the hydroxy proton $H_j$, which is coupling to proton $H_g$. The multiplets at δ 3.53 and δ 4.10 correspond to the

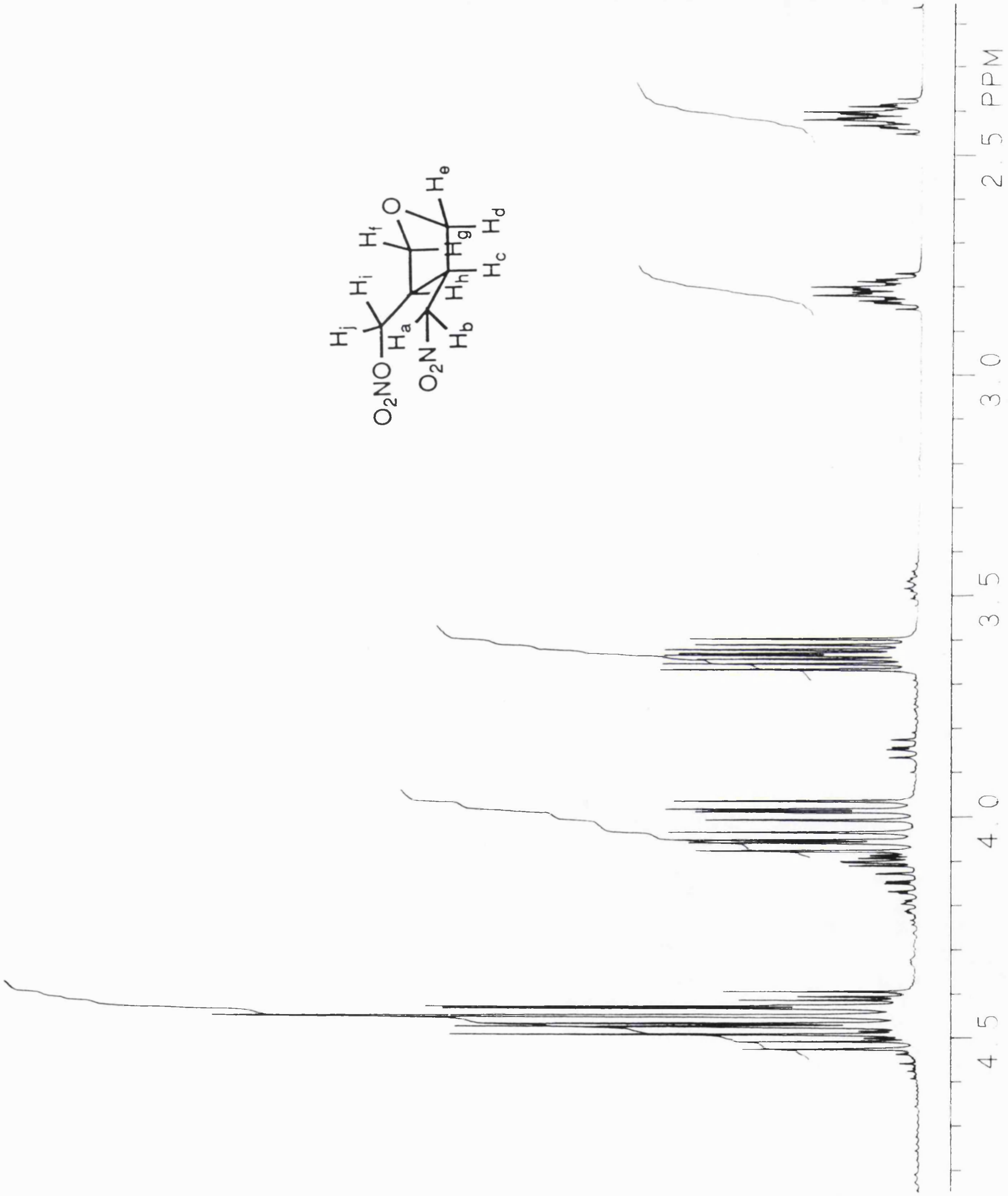


**Figure 5.7** $^1$H n.m.r. spectrum for *c*-2-nitratomethyl-3-nitromethyl-tetrahydrofuran.

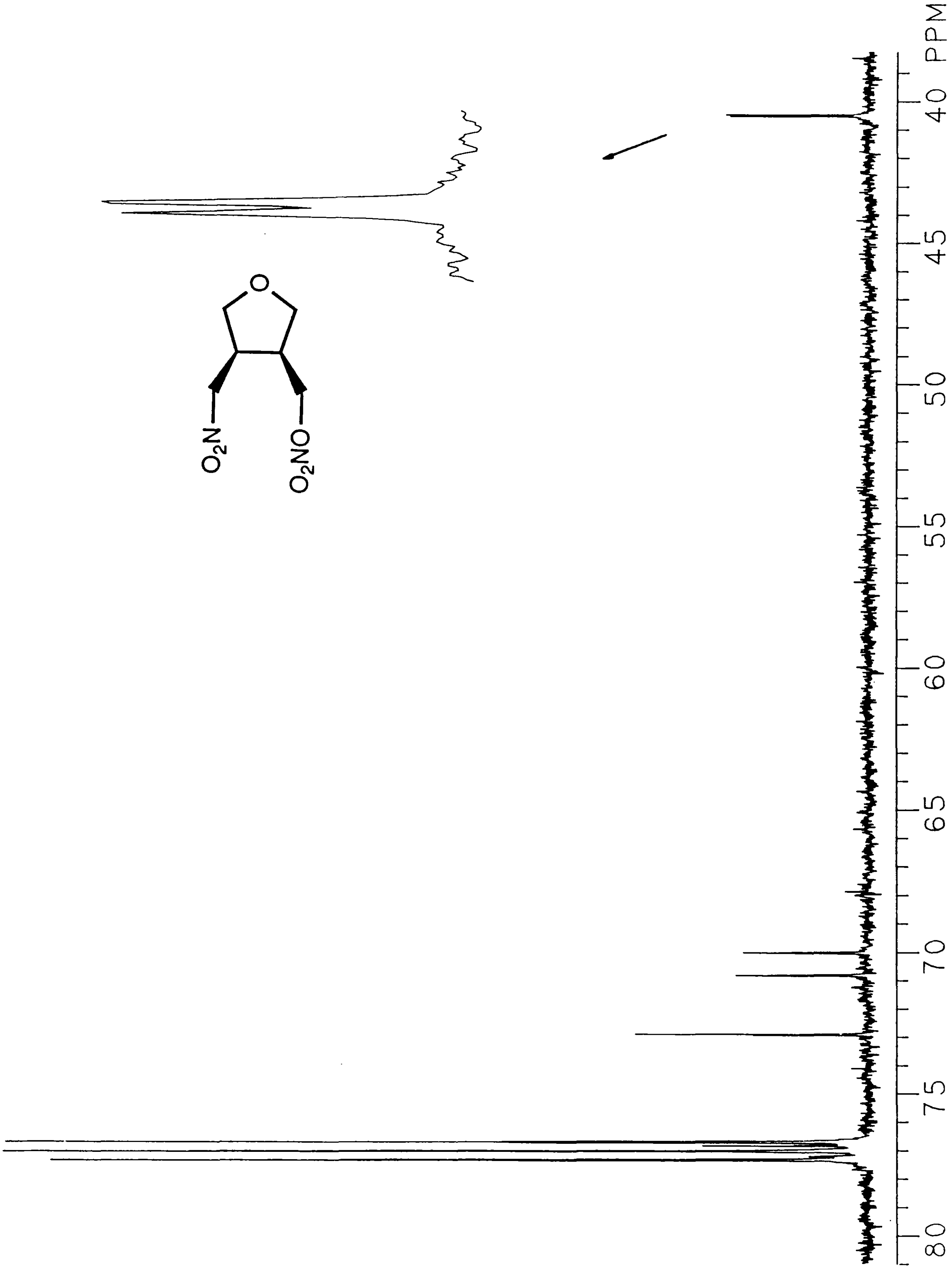


**Figure 5.8** $^{13}C$ n.m.r. spectrum for *t*-2-nitratomethyl-3-nitromethyl-tetrahydrofuran.

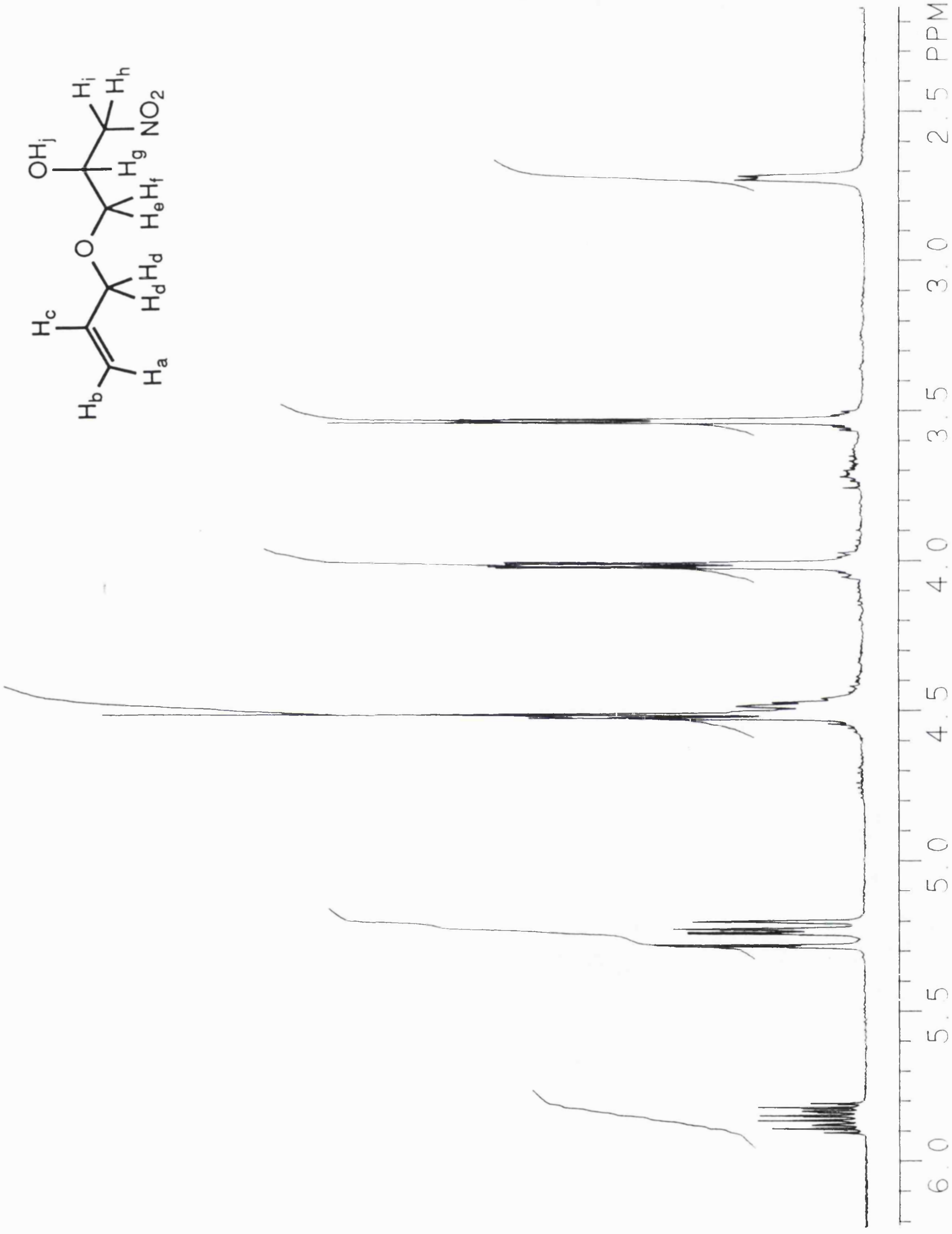


**Figure 5.9** $^1$H n.m.r. spectrum for 2-hydroxy-1nitro-propyl-3,3'-oxy-1'-propene.

protons $H_e$, $H_f$ and $H_d$ respectively. Due to the similar chemical shifts of the protons $H_g$, $H_h$, and $H_i$ they appear as a complex multiplet at δ 4.49. The remaining signals at δ 5.21 and δ 5.26 are due to the olefinic protons $H_b$ and $H_a$.

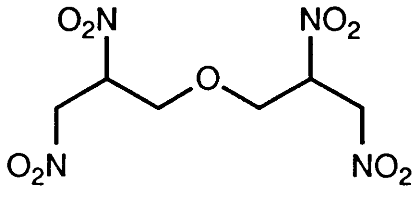
The $^{13}C$ n.m.r. spectrum also confirmed the presence of the double bond by the signals at δ 133.71 and δ 118.03 which are characteristic for a terminal alkene group. The signals from the nitro and hydroxy substituted carbons are at δ 78.04 and δ 72.44 respectively, the two remaining signals are from the ether carbons.

$^{1}H$ n.m.r. (C) δ: 2.72 (1H) d, $^{3}J_{g,j}$ 4.83 Hz; 3.53 (2H) m; 4.01 (2H) m, $^{3}J_{c,d}$ 5.75 Hz, $^{4}J_{a,d}$ 1.44 Hz, $^{4}J_{b,d}$ 1.44 Hz; 4.49 (3H) m; 5.21 (1H) dq, $^{3}J_{b,c}$ 10.39 Hz, $^{2}J_{a,b}$ 2.40 Hz, $^{4}J_{b,d}$ 1.44 Hz; 5.26 (1H) dq, $^{3}J_{a,c}$ 17.22 Hz, $^{2}J_{a,b}$ 1.40 Hz, $^{4}J_{a,d}$ 1.44 Hz; 5.86 (1H) m, $^{3}J_{a,c}$ 17.22 Hz, $^{3}J_{b,c}$ 10.39 Hz, $^{3}J_{c,d}$ 5.74 Hz.

$^{13}C$ n.m.r. (C) δ: 67.74, 70.24, 72.49, 78.04, 118.03, 133.71.

I.R. $cm^{-1}$ : 3152, 1640, 1464, 1377, 1093.

### 5.2.7 bis (2,3-Dinitropropyl) ether.



Evidence for this molecule has been based entirely on its $^{1}H$ n.m.r. and $^{13}C$ n.m.r. spectra.

From the $^{1}H$ n.m.r. spectrum (**Figure 5.10**) it can be seen that the spectrum is relatively simple, this is due to the symmetry of the molecule. The splitting patterns are all doublet of doublets except for the multiplet centred on δ 5.67 ($H_c$) as all the protons are diastereotopic. The two high field doublets of doublets correspond to the protons $H_d$ and $H_e$, while the two low field sets at δ 5.18 and δ 5.38 are from the protons $H_a$ and $H_b$ respectively.

The $^{13}C$ n.m.r. spectrum (**Figure 5.11**) clearly shows that there is symmetry present within the molecule as only three signals are present. This molecule could not be confused with a tetrahydrofuran derivative as there is no high field signal present due to the tertiary methine carbon.

A C.I.M.S. spectrum was recorded but unfortunately the sample underwent decomposition before it was obtained. Initially the compound was a white crystalline solid, however, prior to the spectrum being obtained, it had decomposed to a yellow oil. The C.I.M.S. recorded, however, was consistent with the hydroxy-trinitro derivative (**Section 5.2.8**).

| | |
|---|---|
| $^1H$ n.m.r. (A) δ: | 4.12 (2H) dd, $^3J_{c,d}$ 4.21 Hz, $^2J_{d,e}$ 11.09 Hz; 4.34 (2H) dd, $^3J_{c,e}$ 3.62 Hz, $^2J_{d,e}$ 11.09 Hz; 5.18 (2H) dd, $^3J_{a,c}$ 2.39 Hz, $^2J_{a,b}$ 16.57 Hz; 5.38 (2H) dd, $^3J_{b,c}$ 9.69 Hz, $^2J_{a,b}$ 16.56 Hz; 5.67 (2H) m, $^3J_{a,c}$ 2.29 Hz, $^3J_{b,c}$ 9.69 Hz, $^3J_{c,d}$ 4.21 Hz, $^3J_{c,e}$ 3.62 Hz. |
| $^{13}C$ n.m.r. (A) δ: | 70.08, 72.89, 82.59. |

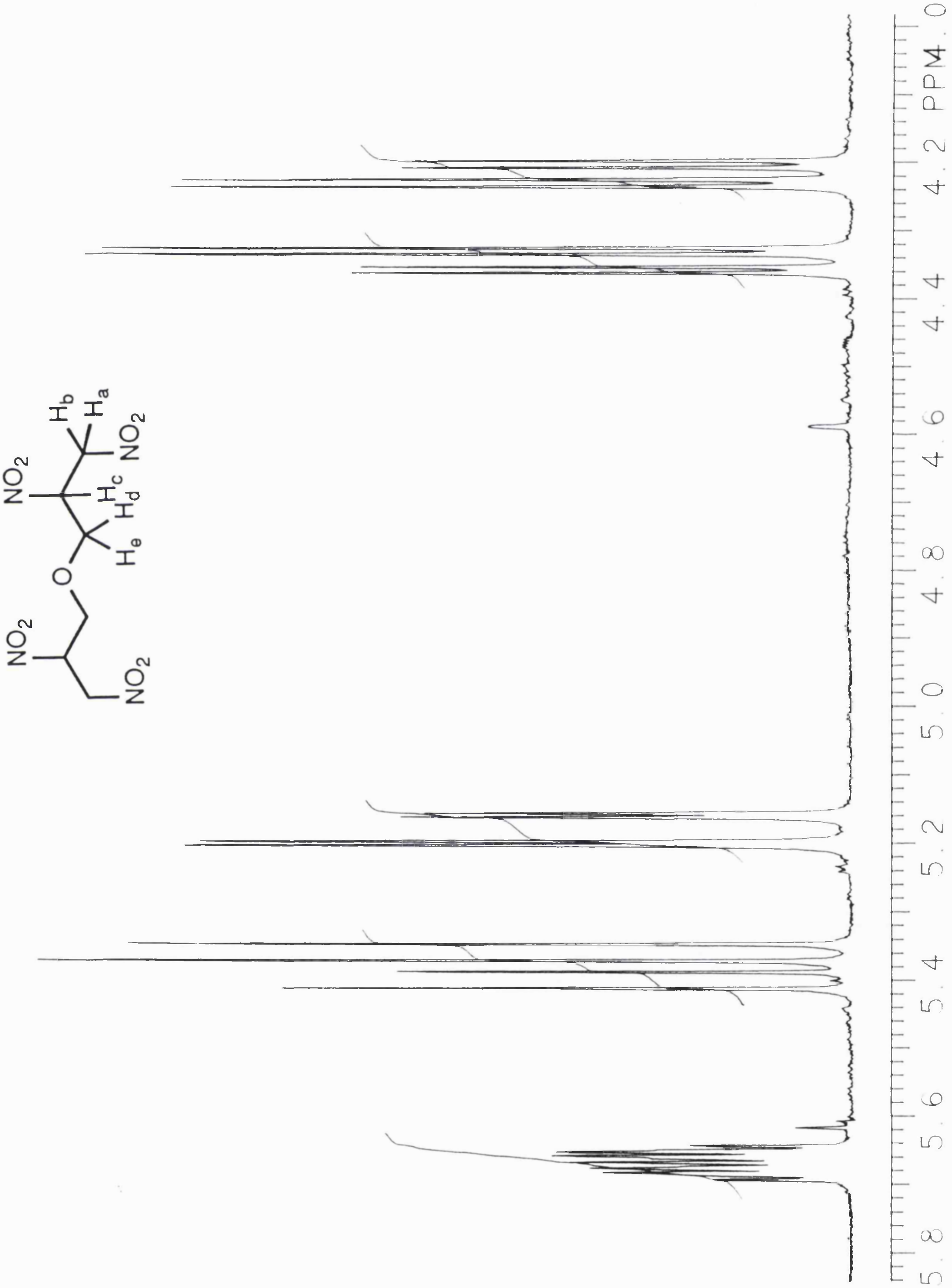


Figure 5.10 $^1H$ n.m.r. spectrum for bis (2,3-dinitropropyl) ether.

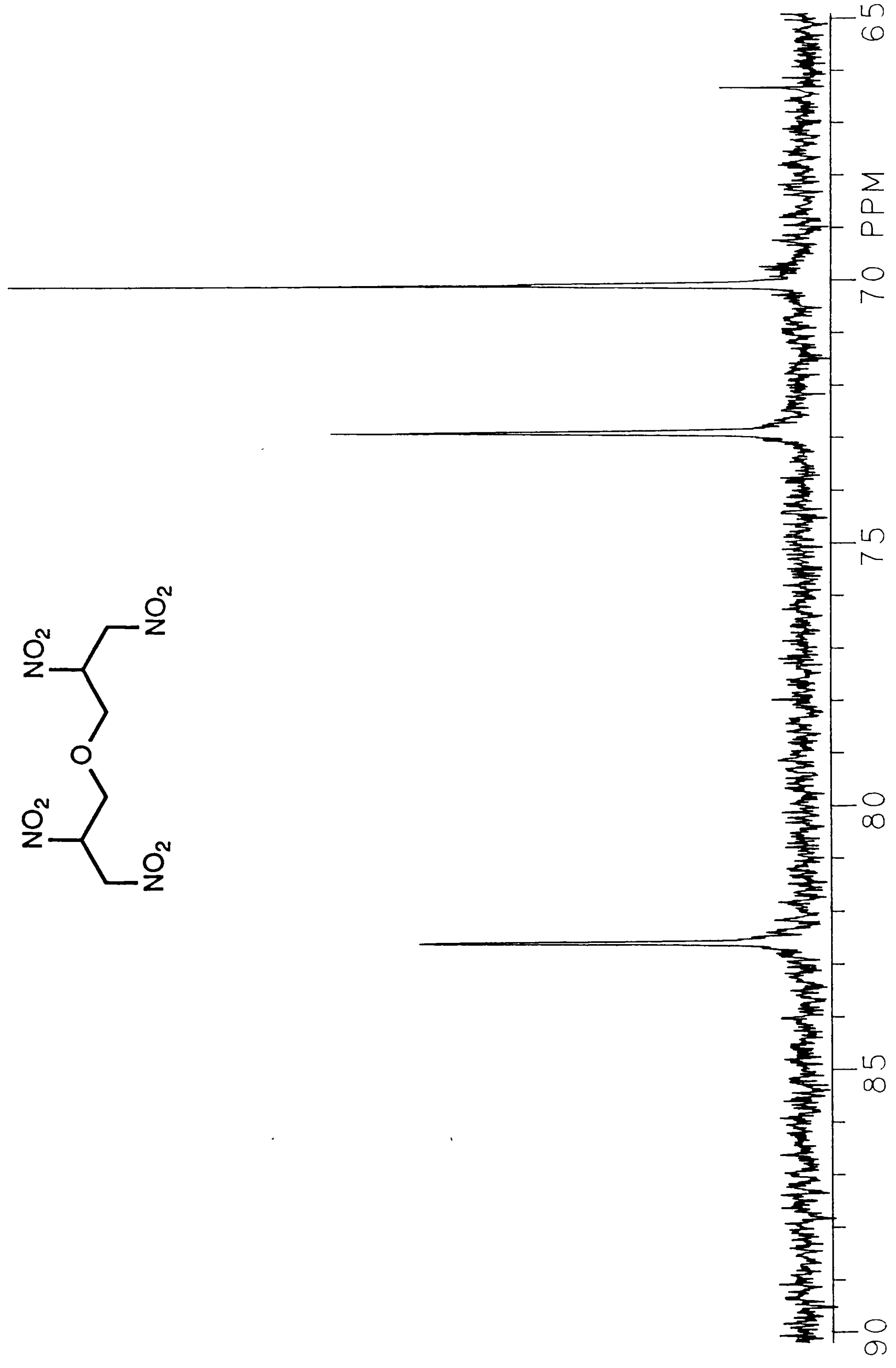
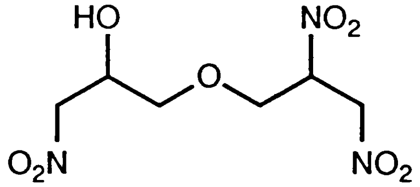


**Figure 5.11** $^{13}C$ n.m.r. spectrum for bis (2,3-dinitropropyl) ether.

### 5.2.8 2-Hydroxy-1-nitro-propyl-3,3'-oxy-1',2'-dinitropropane.



The $^1H$ n.m.r. spectrum (**Figure 5.12**) for this molecule was quite complicated with a total of nine different proton multiplets. The main evidence for the assignment of this molecule was the broad singlet at δ 4.88 due to the hydroxy proton. All the protons on the carbon skeleton are diastereotopic and should therefore all give doublets of doublets except for the protons $H_c$ and $H_h$ which will generate multiplets. The protons $H_f$ and $H_g$ are overlapping and give rise to the multiplet centred on δ 3.65, and proton $H_j$ is overlapping with the multiplet from proton $H_h$. The remaining doublet of doublets can be clearly observed.

The $^{13}C$ n.m.r. spectrum consists of six signals which is consistent with the asymmetry of the molecule. The important signal is at δ 68.48 which corresponds to the hydroxy substituted carbon.

| | |
|---|---|
| 1H n.m.r. (A) δ: | 3.64 (1H) dd, $^3J_{h,f}$ 7.66 Hz, $^2J_{f,g}$ 17.16 Hz; 3.67 (1H) dd, $^3J_{g,h}$ 8.99 Hz, $^2J_{f,g}$ 17.16 Hz; 4.15 (1H) dd, $^3J_{c,d}$ 4.11 Hz, $^2J_{d,e}$ 11.05 Hz; 4.33 (1H) dd, $^3J_{c,e}$ 3.62 Hz, $^2J_{d,e}$ 11.05; 4.48 (2H) m; 4.68 (1H) dd, $^3J_{h,i}$ 5.15 Hz, $^2J_{i,j}$ 10.05 Hz; 4.88 (1H) bs; 5.20 (1H) dd, $^3J_{b,c}$ 9.90 Hz, $^2J_{a,b}$ 16.45 Hz; 5.45 (1H) dd, $^3J_{a,c}$ 2.31 Hz, $^2J_{a,b}$ 16.45 Hz; 5.63 (1H) m. |
| $^{13}C$ n.m.r. (A) δ: | 68.48, 70.24, 73.03, 73.55, 79.31, 82.88. |
| C.I.M.S.: | 271 ($M.NH_4^+$), 253 ($M^+$), 224 ($M.NH_4^+$-47), 204 ($M^+$-47), 179 ($M.NH_4^+$-96). |

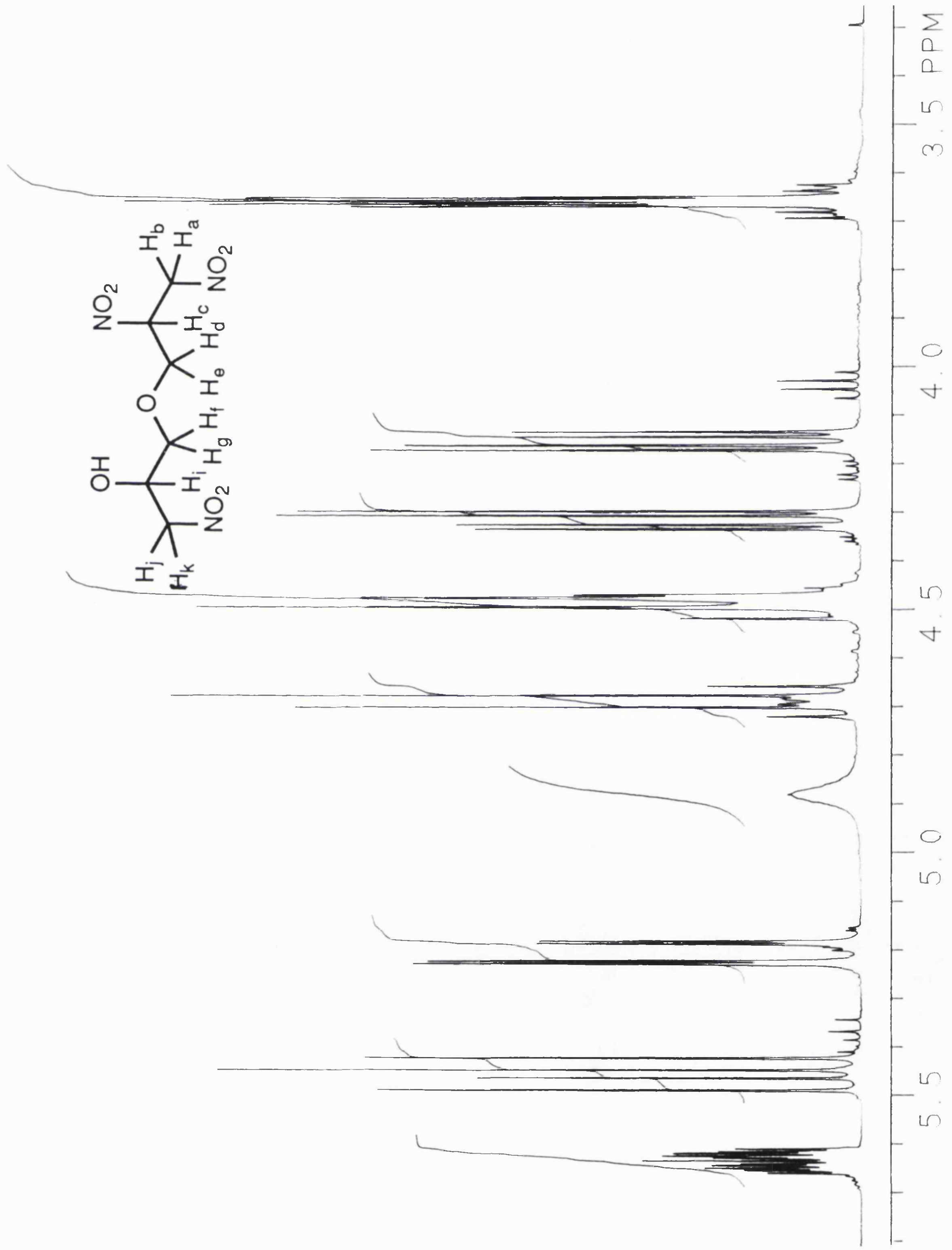
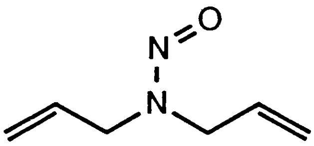


**Figure 5.12** $^1H$ n.m.r. spectrum for 2-hydroxy-1-nitro-3,3'-oxy-1',2'-dinitro-propane.

## 5.3 Products Formed in the Reaction Between Nitrogen Dioxide and Diallylamine

### 5.3.1 N-Nitroso-diallylamine.



The identification of this compound was based mainly on the $^{1}H$ and $^{13}C$ n.m.r. spectra recorded and to a lesser extent on the chemical analysis obtained on the sample.

The $^{1}H$ n.m.r. spectrum (**Figure 5.13**) consists of seven regions. The two high field multiplets centred on δ 5.58 and δ 5.87 are characteristic for the two protons $H_c$ and $H_f$ respectively. These appear as complex multiplets due to coupling to three sets of non equivalent protons. The multiplet centred on δ 5.06 corresponds to proton $H_b$ and appears as a sets of doublet of quartets. This is due to a proton $H_b$ having a large coupling constant with proton $H_c$ to produce a doublet. This signal is then split further by the long range coupling of proton $H_b$ with the two protons $H_d$ to give rise to a set of doublet of triplets. These signals are then split further by the short range coupling between the protons $H_b$ and $H_a$ into doublets. Due to the coupling constant $^{4}J_{b,d} \approx {}^{2}J_{b,a}$ the proton $H_b$ sees the three protons $H_a$ and $H_d$ as equivalent so a quartet is observed. The same explanation holds for the multiplets brought about by the protons $H_a$, $H_h$ and $H_g$ centred on δ 5.16, δ 5.29 and δ 5.30. The splitting patterns due to $H_g$ and $H_h$ overlap and this gives rise to the larger intensity quartet centred on δ 5.32. The doublet of triplets observed at δ 4.14 and δ 4.68 correspond to the protons $H_d$ and $H_e$ respectively.

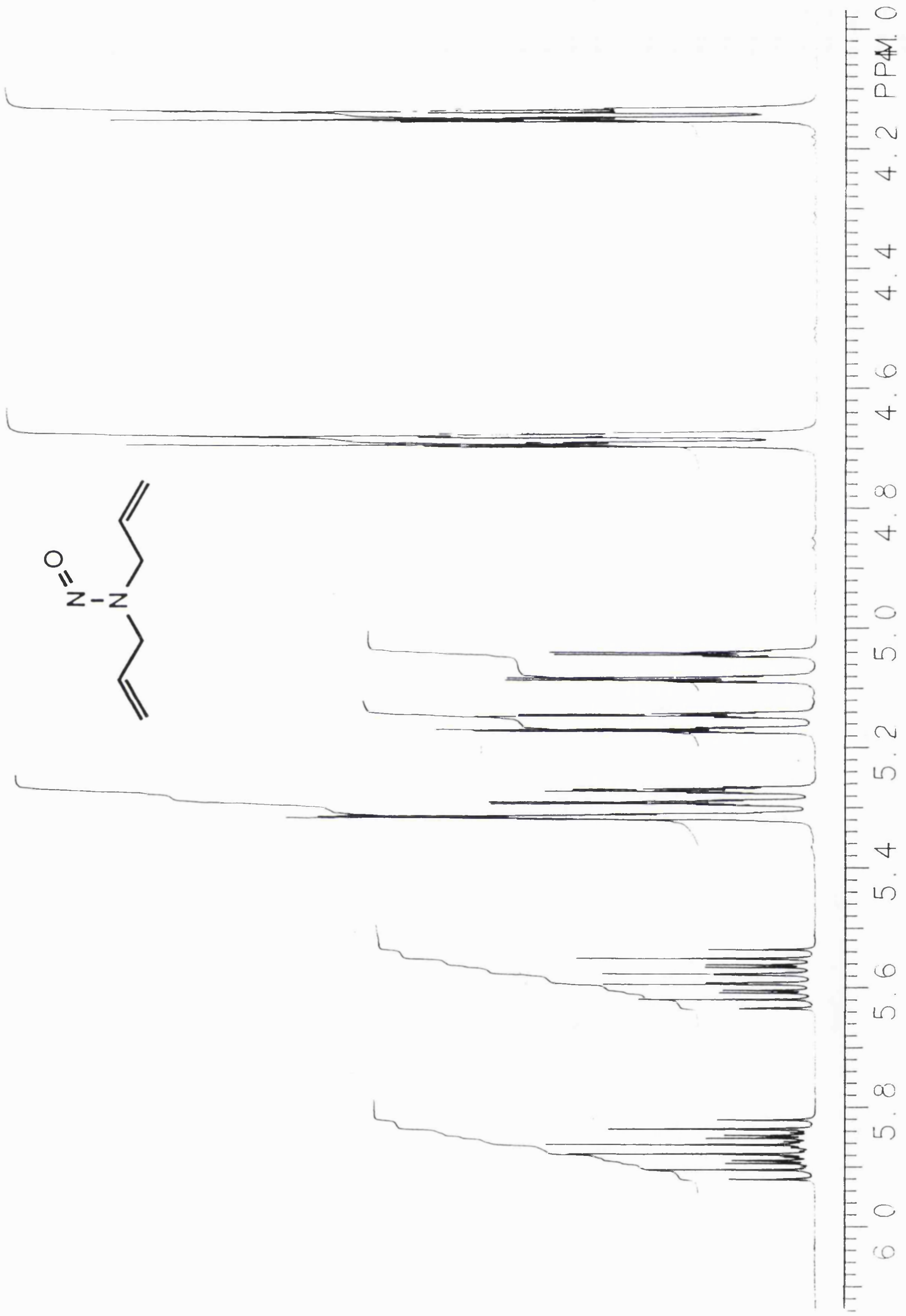


**Figure 5.13** $^{1}H$ n.m.r. spectrum for N-nitroso-diallylamine.

The $^{13}C$ n.m.r. spectrum also shows strong evidence that both the double bonds are intact due to four high field signals being present in the olefinic region. The two low field signals at δ 45.11 and δ 54.09 correspond to the carbons either side of the central amine. There are no sample signals in the range δ 75-85 which is characteristic for the C-$NO_2$ carbon.

The chemical analysis was obtained after several days and some sample decomposition may have occurred before it was run. Also, due to the delay, hydration may have occurred partially and that explains why the empirical formula that best fits the results contains some water.

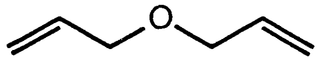
$^{1}H$ n.m.r. (C) δ: 4.14 (2H) dt, $^{3}J_{d,c}$ 5.99 Hz, $^{4}J_{d,a}$ 1.40 Hz, $^{4}J_{d,b}$ 1.40 Hz; 4.68 (2H) dt, $^{3}J_{e,f}$ 6.22 Hz, $^{4}J_{e,g}$ 1.37 Hz, $^{4}J_{e,h}$ 1.37 Hz; 5.06 (1H) dq, $^{3}J_{d,c}$ 17.13 Hz, $^{4}J_{b,d}$ 1.40 Hz, $^{2}J_{b,a}$ 1.44 Hz; 5.16 (1H) dq, $^{3}J_{a,c}$ 10.17 Hz, $^{4}J_{a,d}$ 1.40 Hz, $^{2}J_{a,b}$ 1.44 Hz; 5.29 (1H) dq, $^{3}J_{h,f}$ 16.78 Hz, $^{4}J_{h,e}$ 1.37 Hz, $^{2}J_{h,g}$ 1.21 Hz; 5.30 (1H) dq, $^{3}J_{g,f}$ 10.54 Hz, $^{4}J_{g,e}$ 1.37 Hz, $^{2}J_{g,h}$ 1.21 Hz; 5.58 (1H) m, $^{3}J_{c,b}$ 17.13 Hz, $^{3}J_{c,a}$ 10.17 Hz, $^{3}J_{c,d}$ 5.99 Hz; 5.87 (1H) m, $^{3}J_{f,h}$ 16.78 Hz, $^{3}J_{f,g}$ 10.54, $^{3}J_{f,e}$ 6.22 Hz.

$^{13}C$ n.m.r. (C) δ: 45.11, 54.09, 119.09, 120.16, 129.11, 131.76.

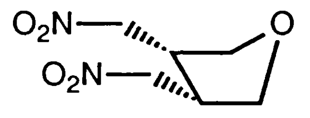
Analysis: calculated for$C_6H_{10}N_2O\,{}^{1}/_{2}[H_2O]$:
C, 53.33; H, 8.20; N, 20.70; O, 17.77.
Found: C, 54.99; H, 8.27; N, 20.70; O, 16.04.

## 5.4 Discussion.

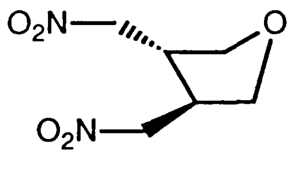
In the reactions between allyl ether (**51**) and nitrogen dioxide the main products isolated were *c*-2,3-(nitromethyl)-tetrahydrofuran (**52**), *t*-2,3-(nitromethyl)-tetrahydrofuran (**53**), *c*-2-nitromethyl-3-nitratomethyl-tetrahydrofuran (**54**), *t*-2-nitromethyl-3-nitratomethyl-tetrahydrofuran (**55**), and small amounts of 2-hydroxy-1-nitro-3,3'-oxy-1'-propene (**56**). The formation of these products was again consistent with the addition reactions of nitrogen dioxide to olefinic double bonds and the mechanisms are outlined in **Scheme 5.1**.



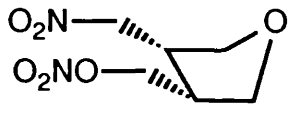
**51**



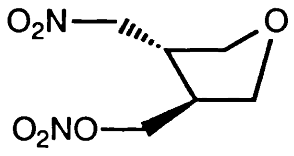
**52**



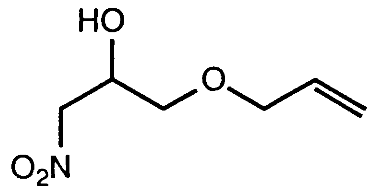
**53**



**54**



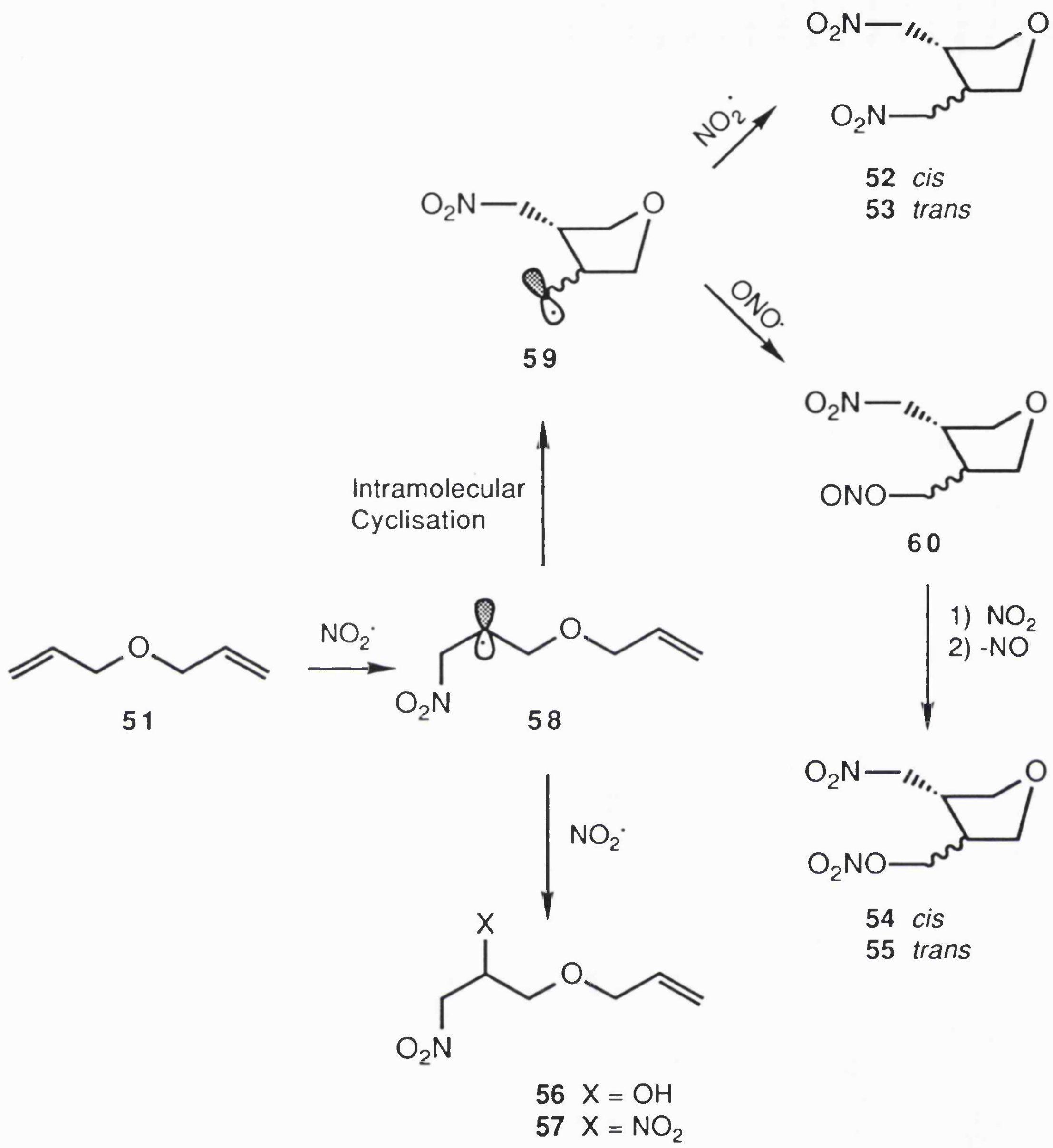
**55**



**56**

The formation of the derivatives **52** to **56** can be envisaged as attack by a nitrogen dioxide radical at the least substituted end of the double bond to form the 1-nitro-prop-2-yl-3,3'-oxy-1'-propene radical (**58**). This radical can now react along two distinct reaction pathways:-

a) it can undergo rapid intramolecular cyclisation to form the tetrahydrofuran radical (**59**) which can then react further with the nitrogen of a nitrogen dioxide radical to form **52** and **53**; or it can react with the oxygen of a nitrogen dioxide radical which would form the 2-nitromethyl-3-nitritomethyl-tetrahydrofuran (**60**). Compound **60** could then react further with the nitrogen of another nitrogen dioxide radical followed by the loss of nitric oxide to form the adducts **54** and **55**.



**Scheme 5.1**

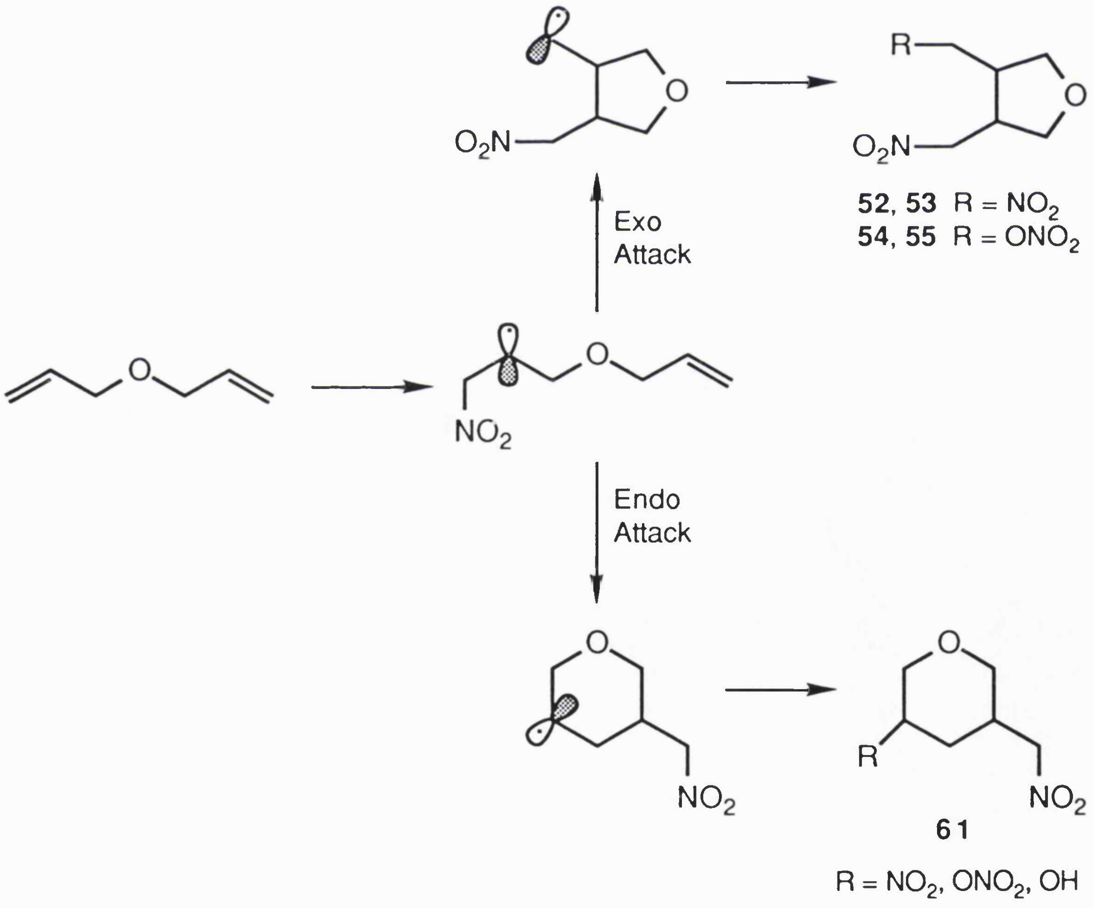
b) it can react with nitrogen dioxide to form the straight chain adducts **56** and **57**.

The mechanistic implication of the reactions between nitrogen dioxide and allyl ether are discussed in more detail in Chapter 6 where Chemically induced Dynamic Nuclear Polarisation (C.I.D.N.P.) effects were observed; these imply that a radical reaction was taking place to form the tetrahydrofuran derivatives in agreement with reported work[77].

The rate of addition of nitrogen dioxide was varied to see how this would effect the product distribution as it was envisaged that the slower addition rates would favour the formation of the tetrahydrofuran derivatives. This would decrease the concentration of nitrogen dioxide in the solution and therefore increase the probability of intramolecular cyclisation occurring, and also the probability of dimerisation occurring. As mentioned in Chapter 4, the addition times had played an important part in the formation of the cyclopentane derivatives from 1,6-heptadiene.

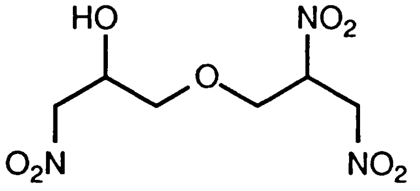
As we were interested in cyclising the allyl ether, initial investigations were carried out using long addition times, where the addition of the nitrogen dioxide solution was in excess of 6 h. These reactions yielded the cyclic products **52-55** in total yields of 80%, and very little evidence of the straight chain adduct **56**. This was in contrast to the reactions of 1,6-heptadiene where only small amounts of the cyclopentane derivatives were isolated. The addition times were decreased to 30 min and the effect on the product distribution was unaltered with the tetrahydrofuran derivatives still accounting for upto 80% of the overall yield of products. This immediately implied that the rate of cyclisation for the allyl ether was faster than that of the 1,6-heptadiene, and this was in accord with work carried out by Beckwith and Schiesser[78,79], who carried out molecular modelling experiments on various ether systems. The reason for the faster intramolecular cyclisation for the allyl ether system compared with the 1,6-heptadiene system has been attributed to the smaller CO bond length, and the smaller C-O-C bond angle[78], compared to that of the C-C bond length and the C-C-C bond angle in the central carbons in 1,6-heptadiene systems.

Even though the formation of the tetrahydrofuran derivatives was predominant and the experimental conditions employed favoured the intramolecular cyclisation as the relative concentration of the nitrogen dioxide was very low, there was no evidence for the formation of any tetrahydropyran derivatives (**61**); tetrahydropyran derivatives would be expected if the intramolecular attack occurred at an *endo* position (**Scheme 5.2**), also they would be thermodynamically favoured compared to the tetrahydrofuran derivatives. Brace[80] and Reed[81] also found that the intra-molecular cyclisation products of allyl ether by various free radicals produced the tetrahydrofuran derivatives exclusively.

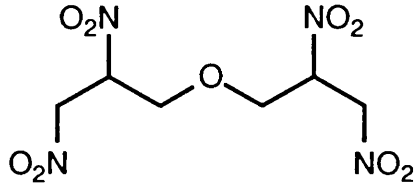


**Scheme 5.2**

The experimental conditions employed as mentioned previously were to favour the formation of the cyclic products. This was achieved by adding nitrogen dioxide to dilute solutions of allyl ether. The concentration of the allyl ether was approximately 0.1 M $dm^{-3}$ and this was sufficiently low to reduce the amount of intermolecular collisions which may have brought about polymerisation. No polymerisation products were isolated from the reactions but polymerisation of allyl ether has been reported in the literature[82].

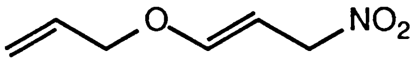


**62**



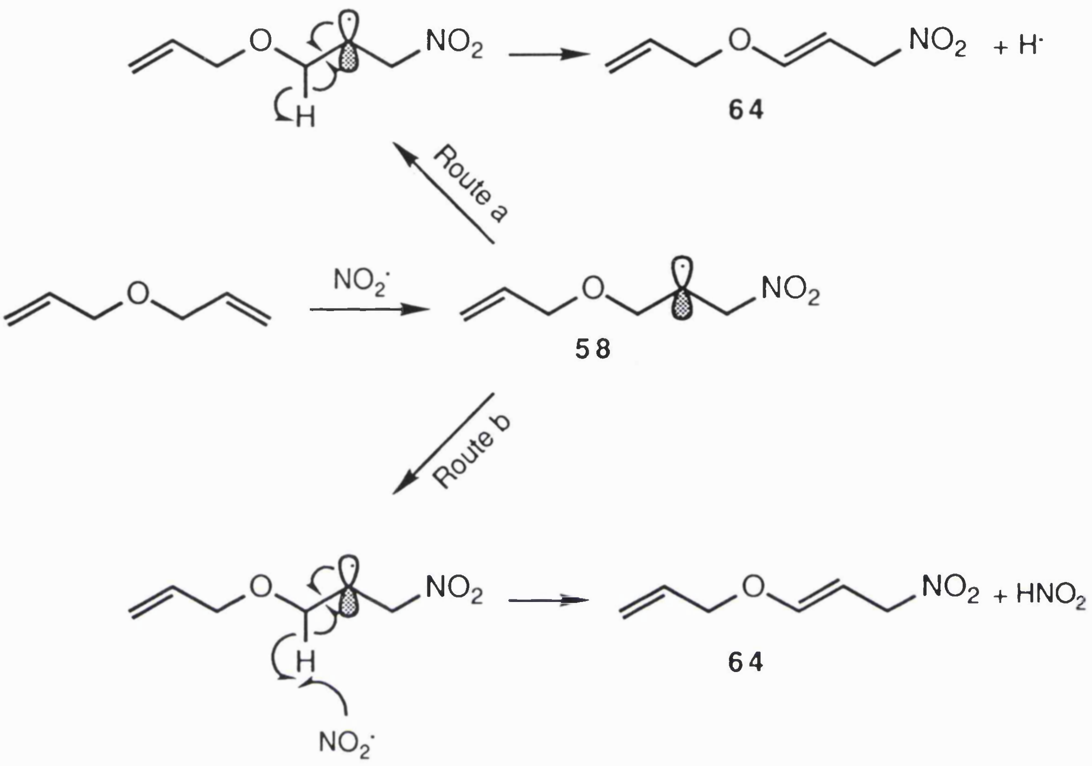
**63**

The formation of the tetra substituted adduct 2-hydroxy-1-nitro-propyl-3,3'-oxy-1',2'-dinitro-propane (**62**) was derived from the further reaction of **56** with nitrogen dioxide. Again the initial attack was by the nitrogen of nitrogen dioxide on the least substituted end of the double bond followed by the attack by the nitrogen of another nitrogen dioxide radical to form **62**. The isolation of bis(2,3-dinitropropane)ether (**63**) can only be formed from the further reaction of 1,2-dinitro-propyl-3,3'-oxy-1-propene (**57**) with nitrogen dioxide. Isolation of compound **57** was never obtained and this may imply that the molecule undergoes decomposition. This would be in accord with the results for 1,2-dinitro-6-heptene in Chapter 4 which underwent decomposition on standing.



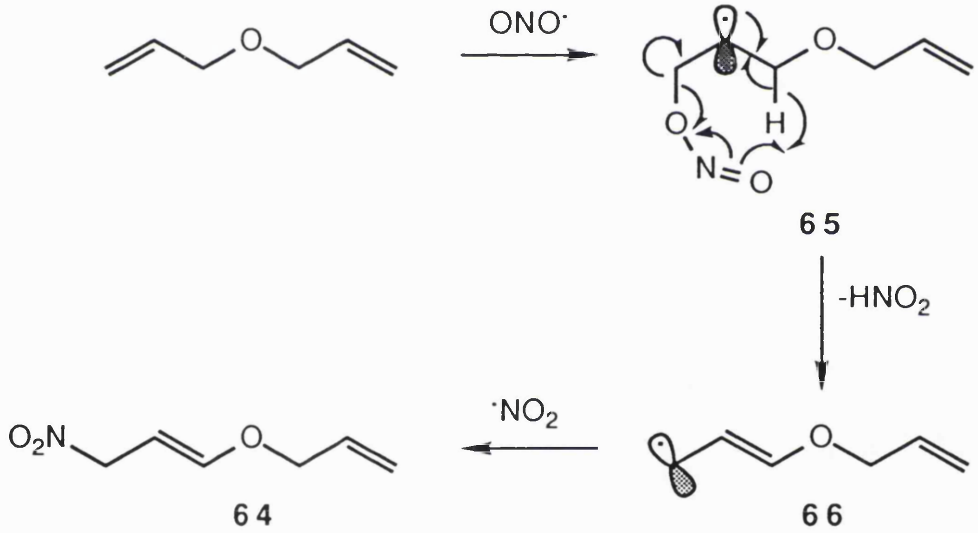
**64**

The reaction between allyl ether and nitrogen dioxide was carried out in darkness to see if this had any effect on the reaction as the allyl ether was light sensitive. The reaction was carried out in the normal mode so the nitrogen dioxide solution was added to that of the ether over a period of 6.5 h. One main product was isolated from this reaction and this was identified as 1-nitro-2-propenyl-3,3'-oxy-1'-propene (**64**). The formation of this compound must again have been brought about by the initial attack of a nitrogen dioxide molecule an the least substituted end of the double bond to produce the 1-nitro-prop-2-yl-3,3'-oxy-1'-propene radical (**58**). In previous reactions, **58** had either reacted with another nitrogen dioxide molecule to produce the straight chain adducts or undergone intramolecular cyclisation to form the tetrahydrofuran derivatives; here, however, a different reaction path way was observed and hydrogen abstraction occurs at the β position. The abstraction of this hydrogen can be brought about by two ways (**Scheme 5.3**): a) where the radical combines with an electron in the neighbouring methine group to form a double bond and eliminate a hydrogen radical or b) where a second nitrogen dioxide molecule



**Scheme 5.3**

reacts with a hydrogen atom at the β position to form nitrous acid and the double bond forms in a concerted reaction to form (**64**). Route b would be more favourable than route (a) as this does not result in the formation of a highly reactive hydrogen radical which would be unfavourable. The third possibility would involve the initial attack by an oxygen of a nitrogen dioxide radical (**Scheme 5.4**); this would react with a double bond in **58** to form the 1-nitrito-prop-2-yl-3,3'-oxy-1'-propene radical (**65**). This radical then undergoes intramolecular cyclisation with the end oxygen in the nitrite functionality to expel nitrous acid and form the prop-2-en-1-yl-3,3'-oxy-1'-propene radical (**66**), this can then react with a nitrogen of a nitrogen dioxide radical to form **61**.

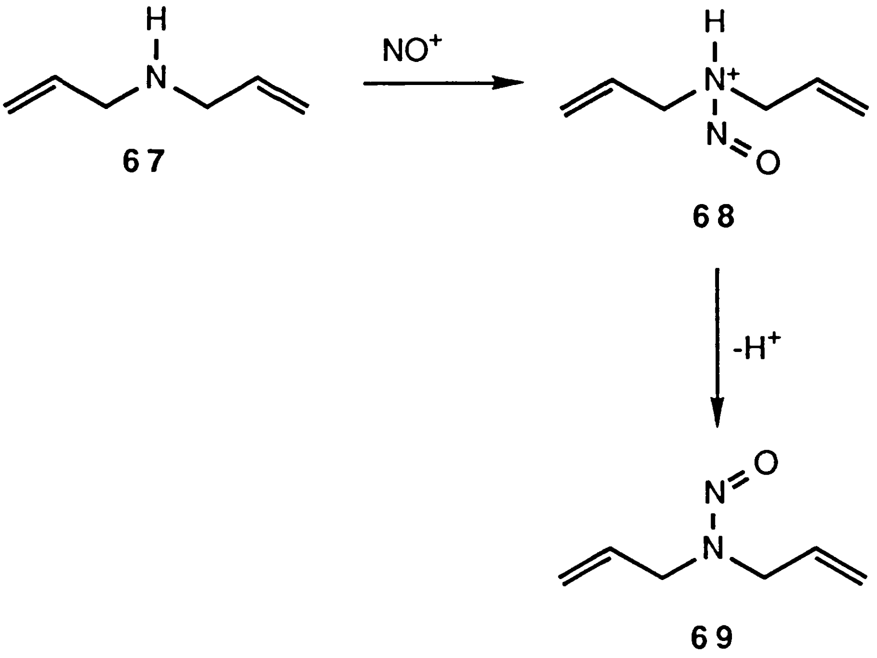


**Scheme 5.4.**

Jenkins[83] also found that allyl ether undergoes hydrogen abstraction when allowed to react with t-butyl radicals with the predominant products showing hydrogen abstraction at the 3'-position (69%) and at the 1'-position (27%) when carried out in the presence of a radical trap.

H-abstraction has been documented in allylic systems[84,85]. For the allyl ether moiety, the high proportion of H-abstraction documented at the 3'-positions has been attributed to the presence of the ether oxygen. The lone pairs of electrons present on the oxygen donate electron density into the anti bonding orbital of the C-H bonds[83] and thus weaken the bond and making it more susceptible to H-abstraction; this is also consistent with the gas phase bond dissociation energies[86] where that for the 3-position is the lowest. H-abstraction has also been investigated in a range of other ethers[87,88] and similar results were obtained.

The H-abstraction would tend to imply that the attacking species present in nitrogen dioxide solutions is the nitrogen dioxide radical and not the dimer dinitrogen tetroxide as the dimer attack would result in addition of two nitro groups at the 1- and 2-position. Kwart[84,85] *et al* described the mechanism of hydrogen abstraction as going through a 'pericyclic transition structure'. The addition of a nitrogen dioxide radical would fulfil this requirement **(Scheme 5.4)**.



**Scheme 5.5**

The reactions of diallylamine **(67)** with nitrogen dioxide resulted in complex reaction mixtures which proved hard to separate using h.p.l.c. (Section 8.13). The amine functionality was not protected prior to the reactions with nitrogen dioxide and this added to the complexity of the reaction mixtures as the acid amine proton was removed readily in the nitrogen dioxide mixtures. The only product isolated from these reactions was N-nitroso-diallylamine (**69**). The formation of this compound can be envisaged as shown in (**Scheme 5.5**). Nitrosonium ion ($NO^+$) or a carrier of the nitrosonium ion attacks the amine to form the nitroso-diallylamine cation (**68**) followed by elimination of the proton to form **69**. This would imply that the nitrogen dioxide is attacking as dinitrogen tetroxide which takes the form of the nitrosonitrate structure ($ONONO_2$).

## 5.4 Conclusions.

This Chapter implies that, in the reactions of allyl ether with nitrogen dioxide solutions, the reactive species present is the nitrogen dioxide free radical. The products formed were predominantly tetrahydrofuran derivatives which resulted from the radical cyclisation after the initial attack of nitrogen dioxide. Evidence for hydrogen abstraction was also obtained by the isolation of 1-nitro-2-propenyl-3,3'-oxy-1'-propene. The mechanism here was again thought to be free radical in nature.

The reaction of diallylamine and nitrogen dioxide solutions point more to reactions via the dimer and particularly to that form of the dimer with the structure $ONONO_2$

# CHAPTER SIX

# CHEMICALLY INDUCED DYNAMIC NUCLEAR POLARISATION EFFECTS

## 6.1 Introduction.

This chapter deals with the Chemically Induced Dynamic Nuclear Polarisation (C.I.D.N.P.) Effects encountered in the reaction between nitrogen dioxide and allyl ether. The effects were studied on a Varian XL-400 MHz n.m.r. spectrometer.

Initially the chapter deals with the theory behind the C.I.D.N.P. effects especially in relation to the $^{15}N$ nucleus, and then follows a short discussion on how to interpret the spectrum from Kaptein's rules (Section 3.6.1). Identification of the products formed from the reaction between $^{15}N$ enriched nitrogen dioxide and allyl ether then follows. The C.I.D.N.P. spectrum obtained is then interpreted with the aid of Kaptein's rules, and possible mechanisms for the reaction in terms of the attack of $NO_2$ and molecular $N_2O_4$ on allyl ether are outlined.

## 6.2 C.I.D.N.P. Effects.

### 6.2.1 What is a C.I.D.N.P. Effect?[89,90]

A C.I.D.N.P. effect may be seen when following a reaction by nuclear magnetic resonance, and when the products formed during the reaction were obtained from a pair of free radicals. The effect is observed by a polarised spectrum containing enhanced absorption or enhanced emission signals.

### 6.2.2 Theory of the C.I.D.N.P. Effects[91,92].

The C.I.D.N.P. effects described in this chapter are those observed using the $^{15}N$ nucleus. The $^{15}N$ nucleus has a quantum number $I = {}^{1}/_{2}$, and is therefore similar to a proton. Unfortunately the natural abundance of $^{15}N$ is very low, 0.36%, and the nucleus is also much less sensitive to radio frequency radiation than a proton. It was therefore necessary to use $^{15}N$ enriched nitrogen dioxide.

The $^{15}N$ nucleus has one major difference from a proton, and that is in the sign of the magnetogyric ratio. This is the relationship between the angular momentum and the magnetic moment of the spinning nucleus. If a classical picture is considered, a spinning positive charge (Figure 6.1a) has a magnetic field associated with if (Figure 6.1b), which would correspond to a bar magnet (Figure 6.1c).

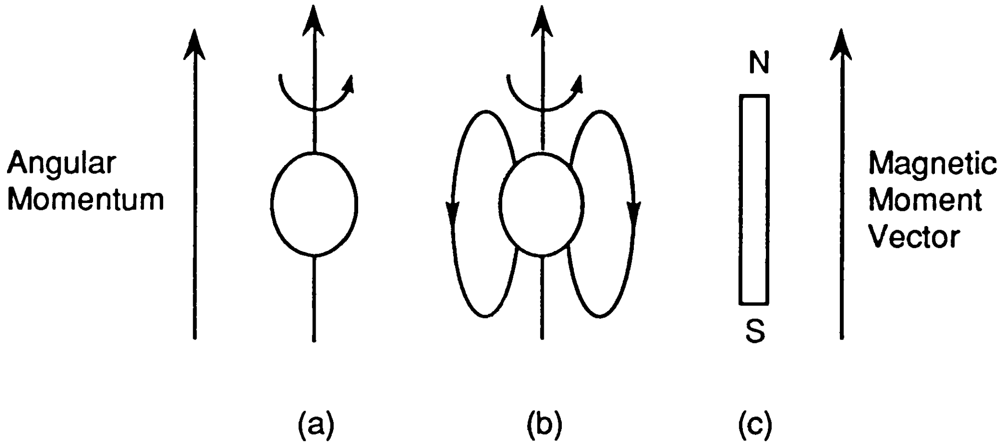


**Figure 6.1** a) spinning positive charge. b) spinning positive charge in a magnetic field. c) Bar magnet giving a corresponding field.

Angular momentum is a vector quantity and is colinear with the axis of spin. The magnetic moment is colinear too with the axis of spin with the positive end taken as north. Classically for a positive spinning charge the angular momentum vector and the magnetic moment vector are in the same direction, as in the proton, and so the magnetogyric ratio between the two quantities is positive. However in the $^{15}N$ nucleus this is not the case and the angular momentum and the magnetic moment vectors are in opposite directions (Figure 6.2), hence the magnetogyric ratio is negative.

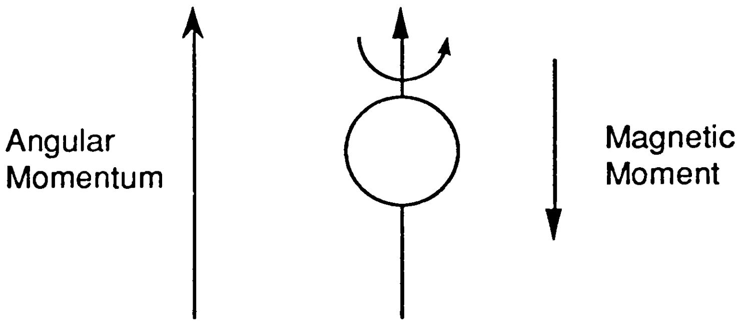


**Figure 6.2** $^{15}N$ nucleus showing the angular momentum and the magnetic moment opposing each other.

The mathematical relationship for the magnetogyric ratio $\gamma$, spin quantum number I and the magnetic moment $\mu$ (in the direction of the field) is given by equation 6.1.

$$\mu = \gamma Ih/2\pi \qquad \textbf{Eqn. 6.1}$$

The energy states of a nucleus in a magnetic field are governed by the magnetic quantum number $M_I$ which can take the values given by equation 6.2.

$$M_I = I, I-1, I-2, \ldots, -I \qquad \textbf{Eqn. 6.2}$$

Therefore for the $^{15}N$ nucleus the allowed quantum numbers are $M_I=+{}^1/_2$ and $M_I=-{}^1/_2$. If a magnetic field of strength B is applied then the energy of the system is given by equation 6.3.

$$E = -M_I\gamma Bh/2\pi \qquad \textbf{Eqn. 6.3}$$

Now from equation 6.3 for a $^{15}N$ nucleus where the magnetogyric ratio is negative the lowest energy level is when $M_I=-{}^1/_2$ (Figure 6.3), and absorption takes place when the energy difference $E=h\upsilon$ where $\upsilon$ is the frequency of the incident radiation.

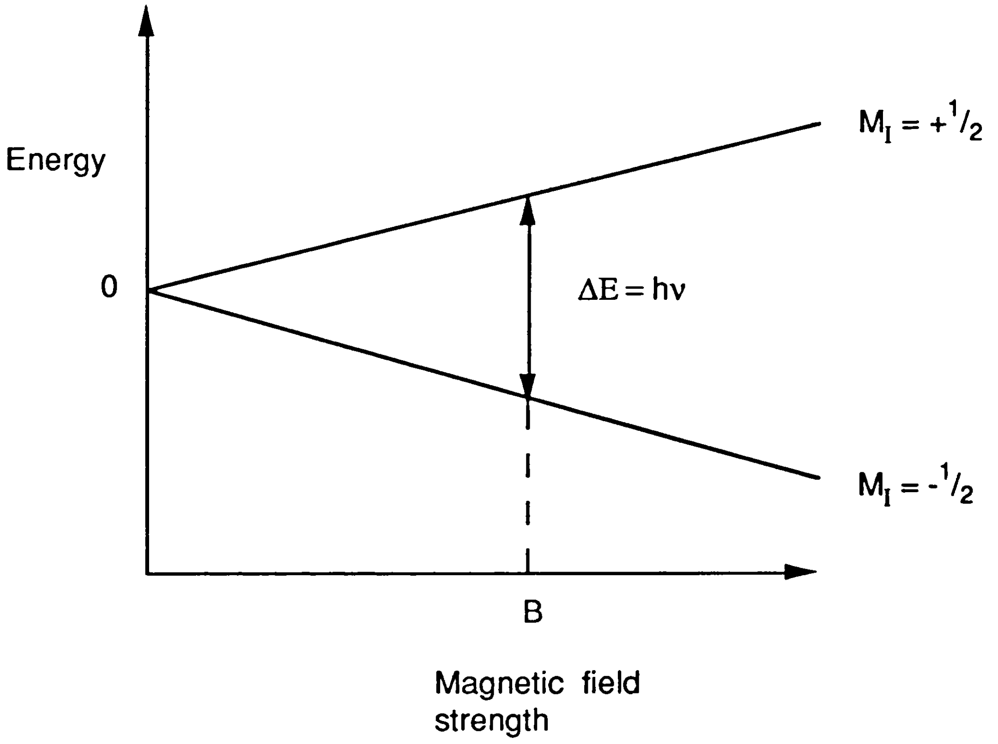


**Figure 6.3** Energy levels of a $^{15}N$ nucleus in an applied field.

### 6.2.3 Interaction of the $^{15}N$ Nucleus with One Electron.

An electron is also a spinning charge and as such has a spin quantum number $S={}^1/_2$ and a magnetic quantum number $M_S=\pm{}^1/_2$ associated with it. The energy levels of an electron in a magnetic field are given by equation 6.4, where B is the applied field strength, g the Lande g-factor (2.002319 for a free electron) and $\beta$ is the Bohr magnetron.

$$E = M_s g B \beta \qquad \textbf{Eqn. 6.4}$$

When there is coupling between nuclear and electron spins, the energy term for the electron is modified to take account of both spins (equation 6.5). The energy is governed by how large the interaction between the spins is, and this is determined by the hyperfine coupling constant a, and the energy levels are shown schematically in figure 6.4.

$$E = M_s g B \beta + a M_I M_s \qquad \textbf{Eqn. 6.5}$$

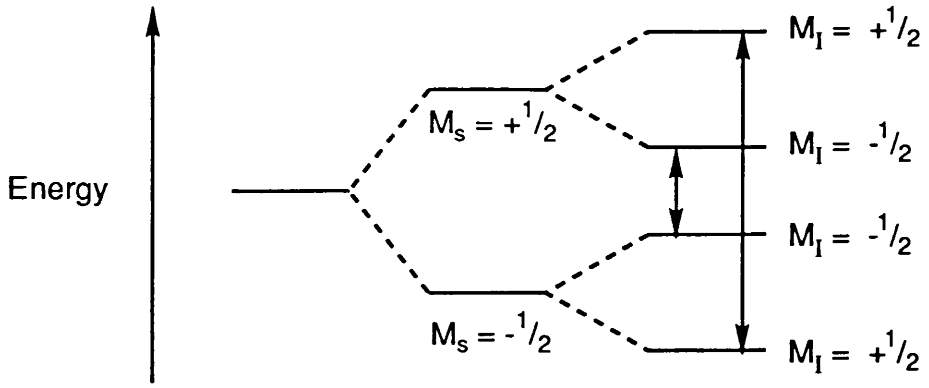


**Figure 6.4** Energy levels of a $^{15}N$ nucleus with one electron.

When the electronic spin changes the nuclear spin does not change and the electronic transitions permitted are indicated by the vertical lines.

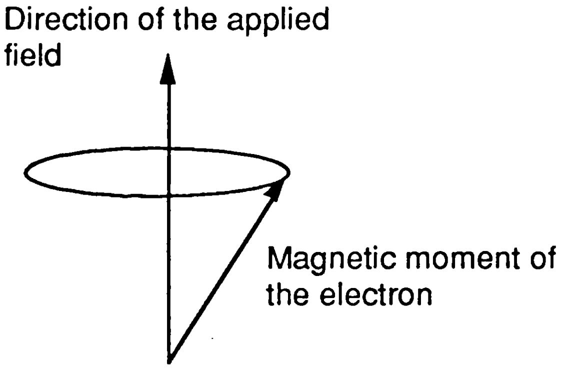


**Figure 6.5** Path of precession of an electron coupled to a nucleus in an applied field.

When an electron is subjected to a magnetic field, the electron spin does not align with the magnetic field, instead it precesses around the direction of the applied field (Figure 6.5). The velocity of this precession is related to the energy of the electron, and if no coupling is present then the angular velocity ω is given by equation 6.6.

$$\omega = 2\pi g B \beta / h \qquad \textbf{Eqn 6.6}$$

However if there is nuclear and electron spin coupling then equation 6.6 is modified by a term including the hyperfine coupling constant and the nuclear quantum number $M_I$, equation 6.7. It is this precession which is important in the C.I.D.N.P. effects.

$$\omega = 2\pi(gB\beta + aM_I)/h \qquad \textbf{Eqn 6.7}$$

### 6.2.4 Interaction of a $^{15}N$ Nucleus with Two Electrons.

If we have two radicals close to each other then their electron spins can arrange themselves in four ways. The spin quantum number S can take the values S=0, 1, and as such they can align themselves in four ways in an applied field (Figure 6.6).

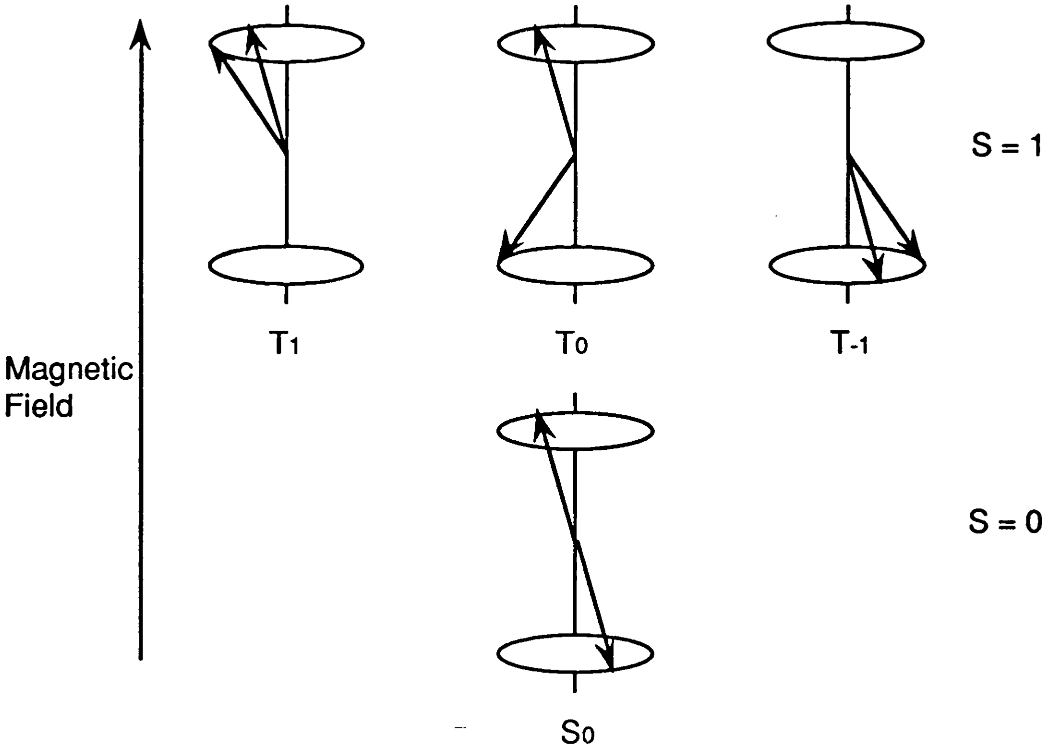


**Figure 6.6** Orientations of a two electron system in an applied magnetic field.

In the S=0 case, this is the singlet state and the magnetic moments of the two electrons are in opposite directions, and as such there is no magnetic moment associated with this state. In the S=1 case, three possibilities arise, and these are known as the triplet states. In the $T_1$ state, both the electron spins are aligned with the field and therefore there is a net magnetic moment component in the direction of the field. In the $T_{-1}$ state both the electron spins are opposing the applied magnetic field ($H_0$) and this produces a magnetic moment component in the direction opposing $H_0$.

In the $T_0$ case there is an electron with a spin component with the field and an electron with a spin component opposing the field. Unlike the singlet state the orientations of the electron spins in the $T_0$ state is such that the magnetic moments do not cancel, and therefore the $T_0$ state has a magnetic moment associated with it.

If the two radicals present were the same then the precession frequency of the two electrons would be the same, i.e. they would have the same Lande g-factor, and as such would stay in the initial spin state. If the two radicals were different then they would have different g-factors and as a consequence they would have different precession frequencies. The different precession frequencies allow for inter-system crossing to occur between the S state and the $T_0$ state. The rate of interconversion is dependent upon the relative rates of precession of the two electrons.

$$\omega_1-\omega_2 = 2\pi B\beta(g_1-g_2)/h \qquad \textbf{Eqn. 6.8}$$

This rate is given by equation 6.8 assuming there is no nuclear and electron coupling, where $\omega_1$ and $\omega_2$ are the rates of precession of the two electrons, and $g_1$ and $g_2$ are the Lande g-factors for electron 1 and 2 respectively.

When there is nuclear and electron coupling equation 6.8 is modified to account for this and the new rate of interconversion is given by

$$\omega_1-\omega_2 = 2\pi(B\beta(g_1-g_2) + aM_I)/h \qquad \textbf{Eqn. 6.9}$$

where one electron is coupled to the nucleus with a hyperfine coupling constant a. From equation 6.9 it can be seen that the relative rate of precession is related to the spin state of the nucleus, hence the value of $M_I$ will determine the rate of interconversion of the singlet to triplet states and vice versa.

Since the singlet and triplet states can give rise to different products there can be a non-Boltzmann distribution of the nuclear levels in these products, and this is known as polarisation. If the lower energy state is more populated than the higher energy state then the nett movement of nuclei is from the lower energy state to the higher energy state and an enhanced absorption signal will be observed in the spectrum. If the higher energy state is more populated then the lower energy state then the nett movement of nuclei is from the higher energy level to the lower energy level and an enhanced emission signal would be observed in the spectrum.

## 6.3 Interpretation of C.I.D.N.P. Effects.

C.I.D.N.P. effects were first observed when following a benzoyl peroxide induced polymerisation reaction on a $^1$H n.m.r. spectrometer[93]. Within the spectrum an emission peak was observed in the aromatic region which disappeared once the decomposition was complete and the normal benzene absorption occurred.

It is the escape of certain radical species from a solvent cage that gives rise to the C.I.D.N.P. effect. The radicals can escape if their spin states are not compatible for recombination. The effective separation[94] of the radical pair is thought to occur at distances greater than 5 Å.

The C.I.D.N.P. effects observed will be opposite for products derived from singlet precursors or triplet precursors[95]. Then for products resulting from the original radical cage (in which singlet-triplet mixing occurs) will have a polarisation which will be opposite to that which are brought about by escape from the cage.

### 6.3.1 Kaptein's Rules[96].

To determine the polarisation expected within the C.I.D.N.P. spectrum Kaptein[96] devised an expression which would calculate the phase depending on the type of radical encounter taking place. Kaptein's Rule for net polarisation with the hydrogen nucleus is given by equation 6.10.

$$\Gamma_n = \mu\varepsilon\Delta g a_i \qquad \textbf{Eqn. 6.10}$$

When considering the C.I.D.N.P. effects associated with the $^{15}N$ nucleus equation 6.10 has to be modified to account for the magnetogyric ratio of $^{15}N$ being negative (Equation 6.11).

$$\Gamma_n = -\mu\varepsilon\Delta g a_i \qquad \textbf{Eqn. 6.11}$$

If $\Gamma_n$ is positive then you observe net absorption, A.

If $\Gamma_n$ is negative then you observe net emission, E.

The factors governing $\Gamma_n$ :-

$\mu$ = + for a radical pair formed from a triplet precursor, or from the encounter of two radicals (free precursor).

$\mu$ = - for a radical pair formed from a singlet precursor.

$\varepsilon$ = + for products from recombination within the original cage, *i.e.* collapse of a radical pair.

$\varepsilon$ = - for products formed from recombination of radicals which have escaped from the solvent cage.

Finally two criteria for C.I.D.N.P. effects to occur are:-

1. A radical pair should occur on the reaction pathway.
2. The rate of singlet-triplet interconversion of this radical pair must influence the product composition.

## 6.4 Results.

The reaction studied was that between allyl ether and $^{15}N$ enriched nitrogen dioxide in deuterochloroform. Owing to the speed of the reaction the reactants were added to a n.m.r. tube separately and then frozen immediately in liquid nitrogen to stop the reaction. An internal reference tube was used containing $^{15}N$-nitrobenzene as the reference.

The n.m.r. spectrometer was tuned for the $^{15}N$ probe using a $^{15}N$-nitrobenzene sample, and the coil was shimmed using a previous sample of the same volume. The frozen n.m.r. tube was then placed in the spectrometer and allowed to warm to room temperature while spectra were being collected.

This technique ensured that we would observe any C.I.D.N.P. effects at the beginning of the reaction as the reaction mixture melted.

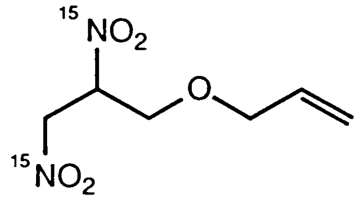
To identify the products giving rise to the C.I.D.N.P. signals, a large scale reaction was carried out and the products separated by h.p.l.c. (Section 8.12). The $^{15}N$ n.m.r. spectra of these products were then recorded and compared to those in the C.I.D.N.P. spectra.

### 6.4.1 Identification of the Products.

The products were identified by comparing the $^{1}H$ n.m.r. spectra of the $^{15}N$ labelled compounds, with the $^{1}H$ n.m.r. spectra of the unlabelled compounds.

The $^{15}N$ n.m.r. chemical shifts quoted below were measured against an internal reference of $^{15}N$-nitrobenzene, which was assigned a chemical shift of $\delta = 0$. Chemical shifts at lower field were measured as positive.

### 6.4.2 1,2-[$^{15}N_2$]-Dinitro-propyl-3,3'-oxy-1'-propene.



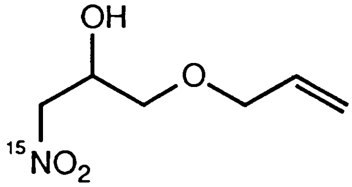
The $^1H$ n.m.r. spectrum observed consisted of five regions. The signals at δ 3.99 and δ 5.78 were characteristic for the starting material. The signals at δ 4.11 and δ 4.70 showed additional coupling, this is due to the proton coupling between the $^{15}N$ nucleus and the $^1H$ nucleus.

Two signals were observed in the $^{15}N$ n.m.r. (Figure 6.7) which was consistent with the assignment of the dinitro adduct. The nitro group attached to the primary carbon has been assigned the signal at δ 3.39, and the nitro group attached to the secondary carbon the signal at δ 7.59. The assignments were based the proton coupled $^{15}N$ n.m.r. spectrum. The signal at δ 3.39 appears as a quartet and this is due to the $^{15}N$ nucleus coupling with the protons $H_a$ and $H_{a'}$ to form a triplet which is split further by proton $H_b$ to give a multiplet which appears as a quartet. The signal at δ 7.59 is a complex multiplet due to the $^{15}N$ nucleus coupling to the five non equivalent protons $H_b$, $H_a$, $H_{a'}$, $H_c$, and $H_d$.

$^1H$ n.m.r. (C) δ: 3.87 (1H) J 3.57 Hz, J 4.62 Hz, J 10.70 Hz; 3.99 (2H) m, J 1.31 Hz, J 2.56 Hz, J 7.05 Hz; 4.11 (1H) m, J 1.75 Hz, J 4.16 Hz, J 10.85 Hz; 4.70 (1H) m, J 4.95 Hz, J 2.47 Hz, J 13.33 Hz; 5.21-5.35 (4H) m; 5.78 (1H) m.

$^{15}N$ n.m.r. (C) δ: 3.39, 7.59.

### 6.4.3 2-Hydroxy-1-[$^{15}N_1$]-nitro-propyl-3,3'-oxy-1'-propene.



The $^1$H n.m.r. spectrum was similar to that reported in section 5.2.6. Evidence of the addition of $^{15}$N nitrogen dioxide comes from the additional coupling seen in the region δ 4.46-4.53; this is again due to the $^1$H -$^{15}$N nuclear coupling.

The $^{15}$N n.m.r. spectrum (Figure 6.8) was also in accord with the assigned structure with only one signal being observed.

From the $^{13}$C n.m.r. spectrum, three signals were observed in the nitro-hydroxy region; one signal corresponds to the hydroxy substituted carbon, while the two other signals are from the nitro substituted carbon. This signal is a doublet due to the $^{13}$C and $^{15}$N nuclear coupling.

$^1$H n.m.r.(C) δ: 2.74 (1H) bs; 3.53 (2H) m; 4.01 (2H) m; 4.46-4.53 (3H) m; 5.21 (1H) m, $^3J_{a,c}$ 10.37 Hz, $^2J_{a,b}$ 2.90 Hz, $^4J_{a,d}$ 1.23 Hz; 5.26 (1H) m, $^3J_{b,c}$ 17.23 Hz, $^2J_{a,b}$ 2.90 Hz, $^4J_{b,d}$ 1.57 Hz; 5.86 (1H) m, $^3J_{c,b}$ 17.22 Hz, $^3J_{c,a}$ 10.39 Hz, $^3J_{c,d}$ 5.73 Hz.

$^{15}$N n.m.r. (C) δ: 10.63.

$^{13}$C n.m.r. (C) δ: 67.74, 70.24, 72.50, 78.00 d $J_{13C,15N}$ 8.2 Hz; 118.04, 133.74.

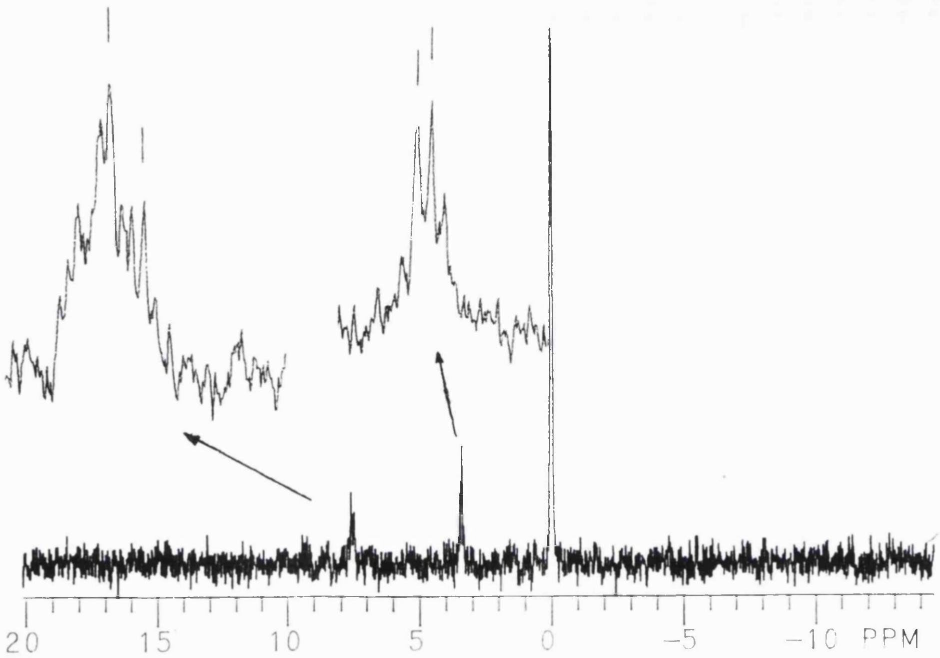


**Figure 6.7** $^{15}N$ n.m.r. spectrum for 1,2-[$^{15}N_2$]-dinitro-propyl-3,3'-oxy-propene.

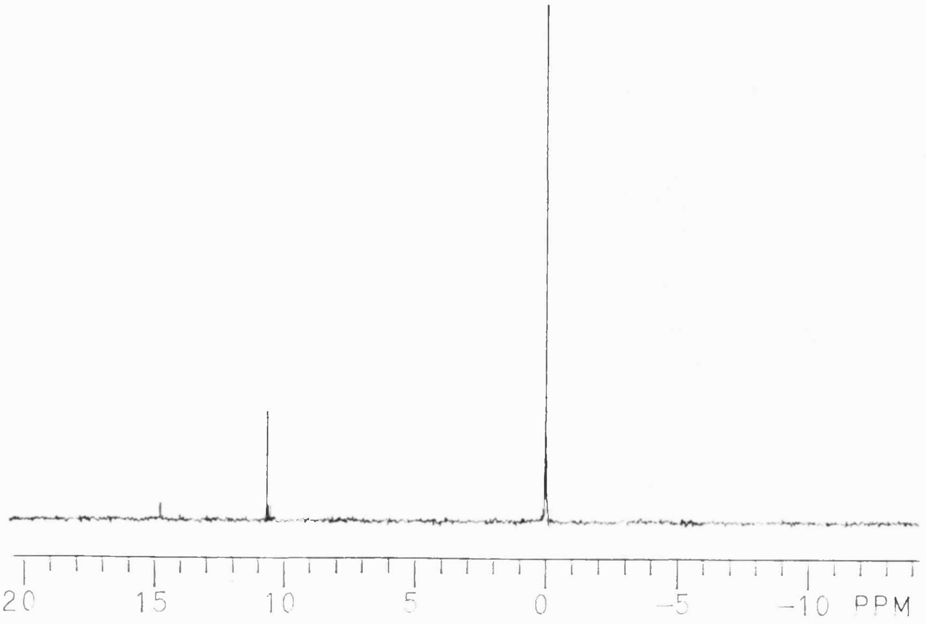
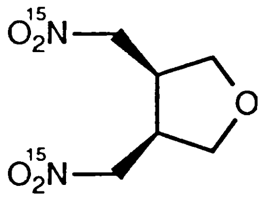


**Figure 6.8** $^{15}N$ n.m.r. for 2-hydroxy-1-[$^{15}N_1$]-nitro-propyl-3-3'-oxy-1'-propene.

### 6.4.4 *cis* 2,3-([$^{15}N_1$] -nitromethyl)-tetrahydrofuran.



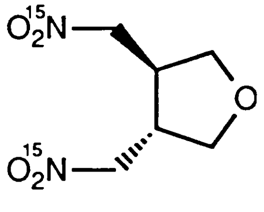
The $^1H$ n.m.r. spectrum obtained corresponded to that in section 5.2.2 The only difference observed was that the multiplicity of the signals at δ 4.45 and δ 4.53 had increased from being doublet of doublets to doublet of doublet of doublets (Figure 6.9); this was again brought about by the extra coupling between the hydrogen proton and the $^{15}N$ nucleus.

The $^{15}N$ n.m.r. spectrum consisted of only one signal (Figure 6.10).

$^1H$ n.m.r. (C) δ: 2.78 (2H) m; 3.63 (2H) dd, $^3J_{c,d}$ 4.97 Hz, $^2J_{d,e}$ 9.68 Hz; 4.05 (2H) dd, $^3J_{c,e}$ 6.78 Hz, $^2J_{e,d}$ 9.68 Hz; 4.44 (2H) ddd, $^2J_{a,15N}$ 2.03 Hz, $^3J_{a,c}$ 7.77 Hz, $^2J_{a,b}$ 13.73 Hz; 4.52 (2H) ddd, $^2J_{b,15N}$ 1.97 Hz, $^3J_{b,c}$ 6.74 Hz, $^2J_{b,a}$ 13.70 Hz.

$^{15}N$ n.m.r. (C) δ: 11.23.

### 6.4.5 *trans* -2,3-([$^{15}N_1$]-nitromethyl)-tetrahydrofuran.



The $^1H$ n.m.r. spectrum obtained for this molecule was again similar to that reported in section 5.2.3. Again the multiplicity of the signals observed for the hydrogens attached to the nitro substituted carbon had increased from sets of doublet of doublets to sets of doublet of doublet of doublets because of the additional coupling.

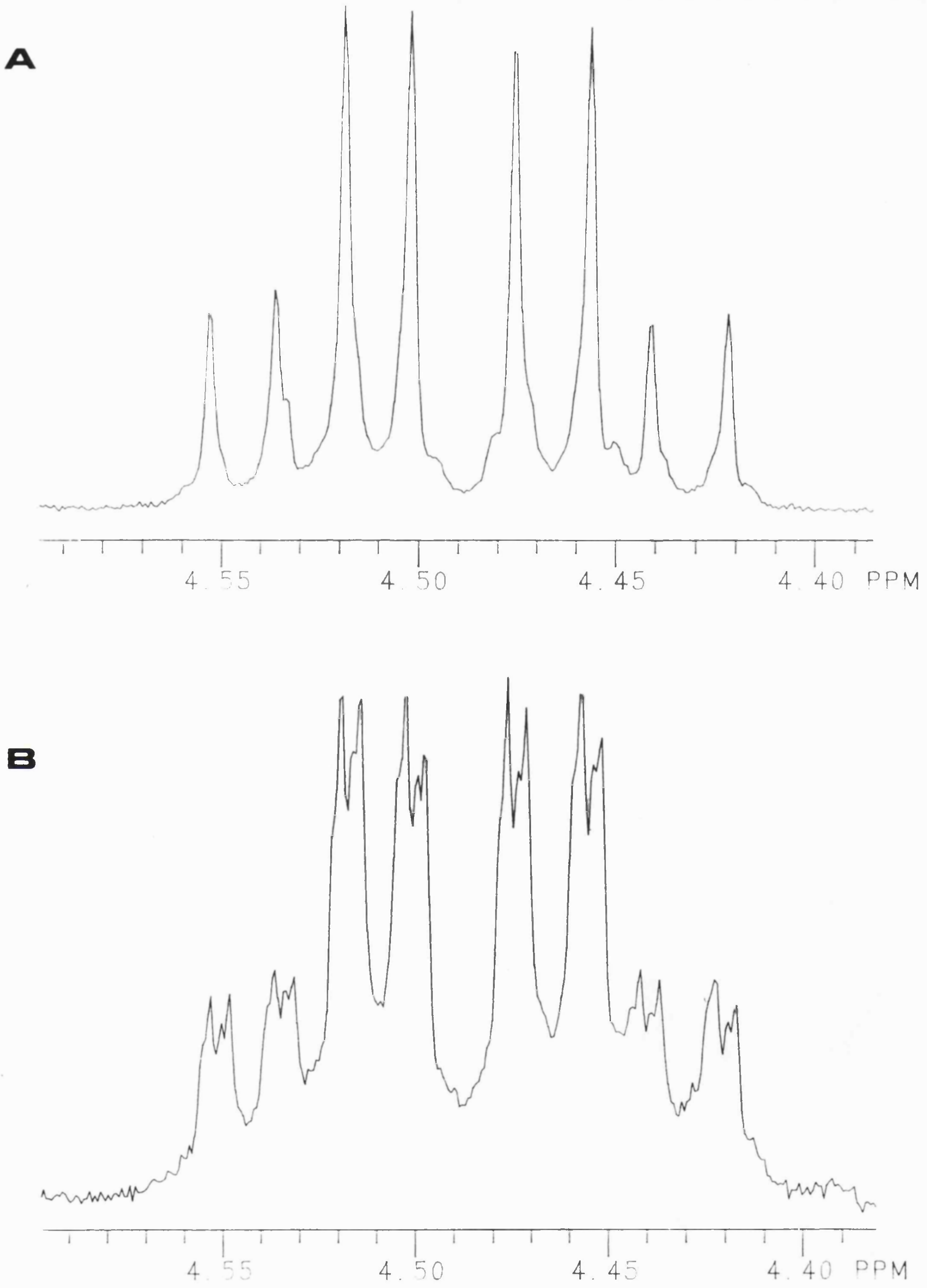


**Figure 6.9** a) $^{1}H$ n.m.r. signal for hydrogen attached to the nitro substituted carbon in *cis*-2,3-(nitromethyl)-tetrahydrofuran. b) $^{1}H$ n.m.r signal for hydrogen attached to the $^{15}N$-nitro substituted carbon in *cis*-2,3-([$^{15}N_1$]-nitromethyl)-tetrahydrofuran.

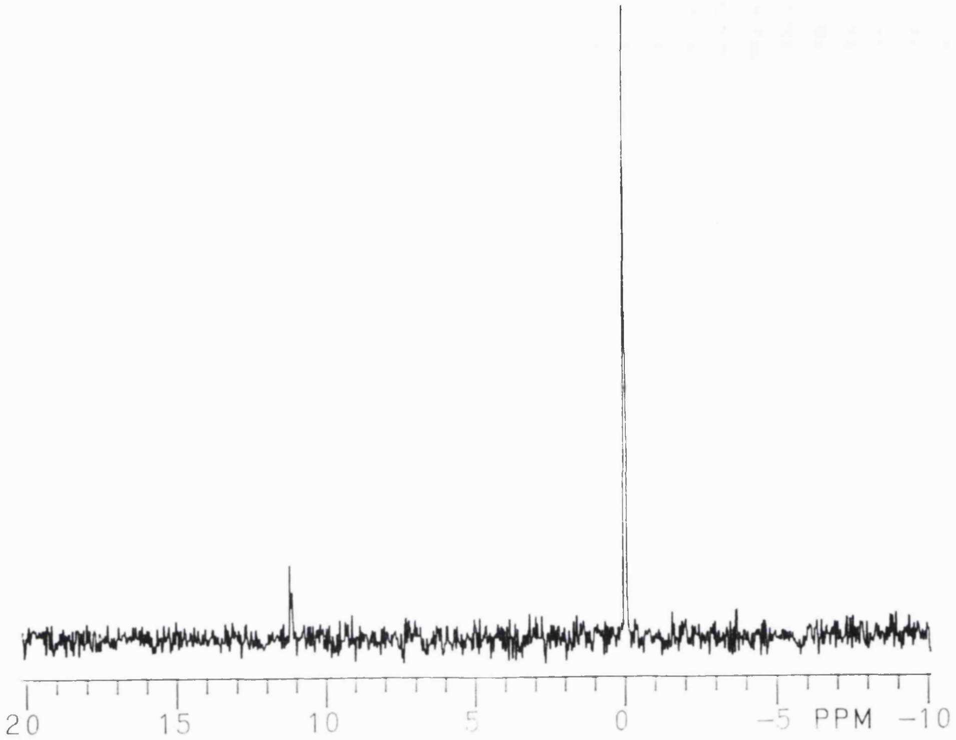


**Figure 6.10** $^{15}N$ n.m.r. spectrum of *cis*-2,3-([$^{15}N_1$]nitromethyl)-tetrahydrofuran.

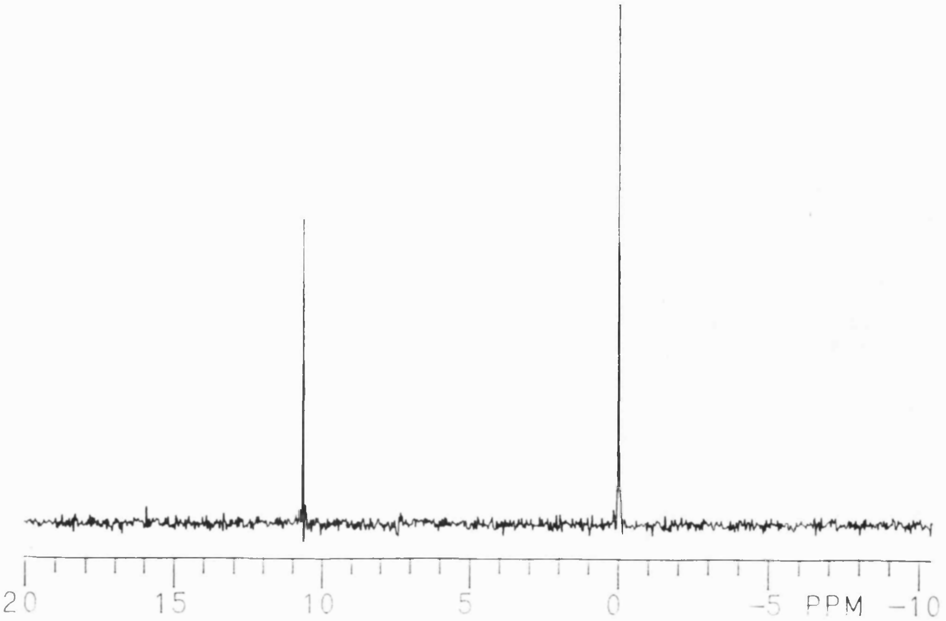


**Figure 6.11** $^{15}N$ n.m.r. spectrum of *trans* -2,3-([$^{15}N_1$]nitromethyl)-tetrahydrofuran

Again the $^{15}N$ n.m.r. spectrum obtained had one signal (Figure 6.11).

| | |
|---|---|
| $^{1}H$ n.m.r. (C) δ: | 3.34 (2H) m; 3.71 (2H) $^{3}J_{d,c}$ 5.09 Hz, $^{2}J_{d,e}$ 9.45 Hz; 4.02 (2H) dd, $^{3}J_{e,c}$ 6.58 Hz, $^{2}J_{e,c}$ 9.45 Hz; 4.40 (2H) ddd, $^{2}J_{a,15N}$ 2.16 Hz, $^{3}J_{a,c}$ 8.19 Hz, $^{2}J_{a,b}$ 13.31; 4.50 (2H) ddd, $^{2}J_{b,15N}$ 2.11 Hz, $^{3}J_{b,c}$ 6.28 Hz, $^{2}J_{b,a}$ 13.24 Hz. |
| $^{15}N$ n.m.r. (C) δ: | 10.66. |

## 6.5 Observed C.I.D.N.P. Effects.

From the infinity spectrum (Figure 6.12) recorded 24h after the start of the reaction, and consisting of approximately 6000 transients four important features must be noticed:-

1. The relative intensities of the product signals to that of the internal nitrobenzene reference at δ = 0.

2. The presence of both signals corresponding to 1,2-[$^{15}N_2$]-dinitro-propyl-3,3'-oxy-1'-propene at δ = 3.40 and δ = 7.70.

3. The identification of *cis* 2,3-([$^{15}N_1$]-nitromethyl)-tetrahydrofuran at δ = 11.23.

4. The identification of *trans* 2,3-([$^{15}N_1$]-nitromethyl)-tetrahydrofuran at δ = 10.66

A few minor products can be observed within the spectrum but these have remained unidentified and are thought to be the cyclic nitro-nitrates which were observed in Chapter 5 (Sections 5.2.4 and 5.2.5).

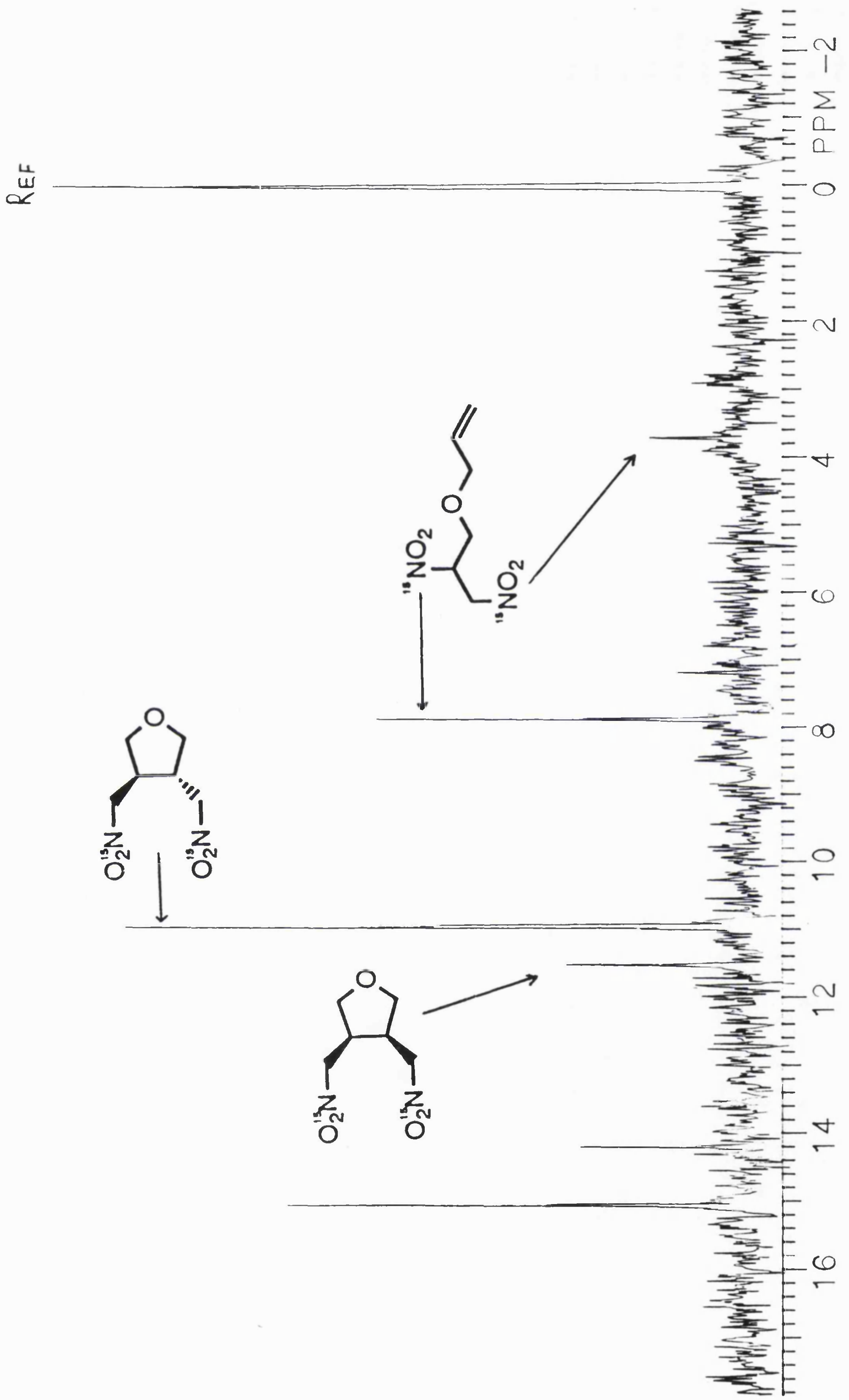


**Figure 6.12** Infinity $^{15}N$ n.m.r. spectrum for the reaction between $^{15}N$-nitrogen dioxide and allyl ether.

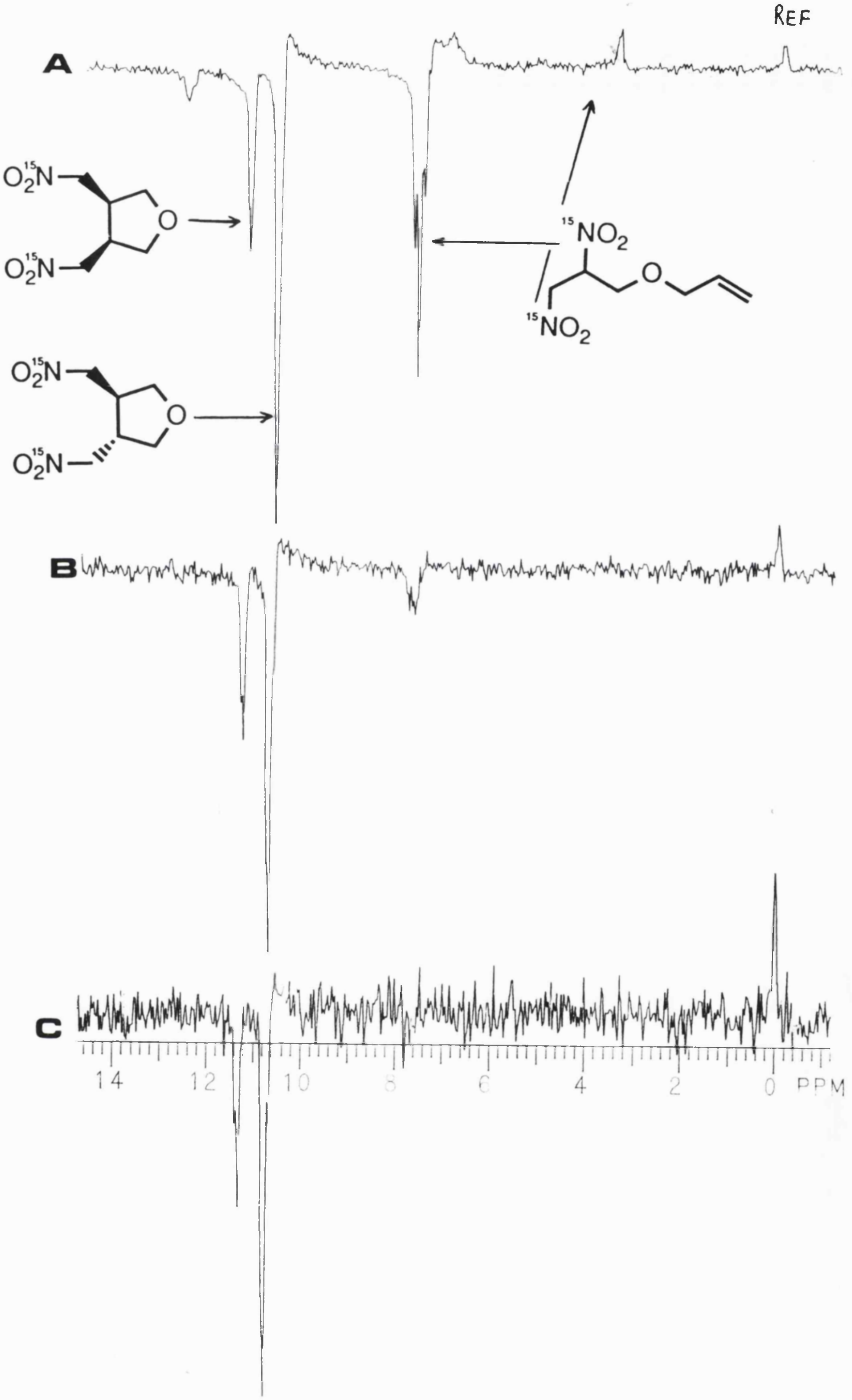


**Figure 6.13** $^{15}$N-C.I.D.N.P. spectrum obtained during the course of the reaction between $^{15}$N-nitrogen dioxide and allyl ether. a) 1 min. b) 3 min. c) 5 min.

Three of the C.I.D.N.P. spectra are shown in figure 6.13. Important features to note are:-

1. The relative intensity of the product signals to that of the $^{15}$N-nitrobenzene reference in figure 6.13a.

2. The presence of enhanced emission and absorption signals in the formation of 1,2-[$^{15}N_2$]-dinitro-propyl-3,3'-oxy-1'-propene.

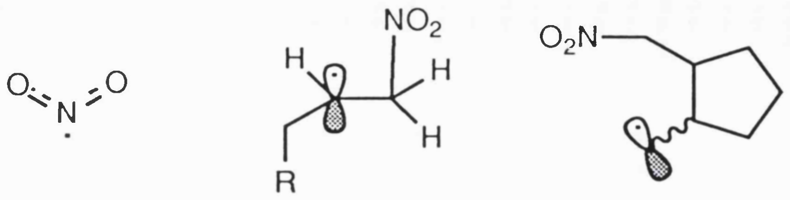
3. The presence of only enhanced emission signals in the formation of *cis* and *trans* 2,3-([$^{15}N_1$]-nitromethyl)-tetrahydrofuran.

4. The decrease in the relative intensities of the signals to the $^{15}$N-nitrobenzene reference and the noise as the reaction proceeds.

### 6.5.1 C.I.D.N.P. Effects in the Formation of 1,2-[$^{15}N_2$]-dinitro-propyl-3,3'-oxy-1'-propene.

In the formation of this product from the reaction between allyl ether and $^{15}$N labelled nitrogen dioxide a large C.I.D.N.P. effect was observed, clearly showing that a radical process was occurring during its formation. Two signals were observed for this product at $\delta$ 3.40 and $\delta$ 7.70 (Figure 6.13).

From figure 6.13a it can be seen that the signal at $\delta$ 3.40 is an enhanced absorption signal, and this corresponds to the primary nitro group (Section 6.4.2), while the signal at $\delta$ 7.70 is from the secondary nitro group which has a large enhanced emission signal. From Kaptein's Rules (6.3.1) and equation 6.11 it is possible to rationalise these results.



$g_{NO2} = 2.00$ $g_{straightrad} > 2$ $g_{cyclicrad} > 2$

(a) (b) (c)

**Figure 6.14** g-values for a) nitrogen dioxide radical b) β-nitro radical c) 1-nitromethyl-tetrahydrofuran-2-yl radical

Now considering initially the $^{15}N$ nucleus in the β-nitro-alkyl radical (Figure 6.14b) then on combining with the nitrogen dioxide radical a small enhanced emission signal was observed on the formation of 1,2-[$^{15}N_2$]-dinitro-propyl-3,3'-oxy-1'-propene. Therefore from Kaptein's Rule for nett polarisation (Equation 6.10)

For the β-nitro radical, $\Delta g$ is positive since $g_{straightrad} - g_{NO2} > 0$.

For the coupling constant $a_i$, this will be negative due to the negative magnetogyric ratio associated with the $^{15}N$ nucleus.

$\mu = +$ as the product formed is from the encounter of two radicals.

$\varepsilon = +$ as the product formed is from the collapse of a radical pair.

Therefore $\Gamma_n = -(+)(+)(+)(-) = +$ Absorption.

Now considering the $^{15}N$ nucleus in the nitrogen dioxide radical;

For the nitrogen dioxide radical, $\Delta g$ is negative since $g_{NO2} - g_{straightrad} < 0$.

For the coupling constant $a_i$, this will be negative due to the negative magnetogyric ratio associated with the $^{15}N$ nucleus.

$\mu = +$ as the product formed is from the encounter of two radicals.

$\varepsilon = +$ as the product formed is from the collapse of a radical pair.

Therefore $\Gamma_n = -(+)(+)(-)(-) = -$ Emission.

### 6.5.2 C.I.D.N.P. Effects in the Formation of *trans*-2,3-([$^{15}N_1$]-nitromethyl)-tetrahydrofuran.

The formation of *trans*-2,3-([$^{15}N_1$]-nitromethyl)-tetrahydrofuran results from the recombination of a nitrogen dioxide radical and that of the 1-nitromethyl-tetrahydrofuran-2-yl radical (Figure 6.14 c).

Owing to the symmetry of the molecule only one signal was observed in the $^{15}N$ spectra, and this corresponds to the signal at $\delta$ 10.66 (Figure 6.12). This signal showed a large enhanced emission in the C.I.D.N.P. spectra (Figure 6.13). The signal was assigned as the C.I.D.N.P. effect derived from the nitrogen dioxide radical as the coupling constant between the electrons and the $^{15}N$ nucleus in the $^{15}N$ nitrogen dioxide will be much larger than that of the coupling constant between the electrons and the $^{15}N$ nucleus in 1-[$^{15}N_1$]-nitromethyl-tetrahydrofuran-2-yl radical.

Applying Kaptein's Rules to the $^{15}N$ nucleus in the nitrogen dioxide radical

For the nitrogen dioxide radical, $\Delta g$ is negative since $g_{NO2} - g_{straightrad} < 0$.

For the coupling constant $a_i$, this will be negative due to the negative magnetogyric ratio associated with the $^{15}N$ nucleus.

$\mu = +$ as the product formed is from the encounter of two radicals.

$\varepsilon = +$ as the product formed is from the collapse of a radical pair.

Therefore $\Gamma_n = -(+)(+)(-)(-) = -$ Emission.

Considering the $^{15}N$ nucleus in the 1-[$^{15}N_1$]-nitromethyl-tetrahydrofuran-2-yl radical then applying Kaptein's Rules :-

For the cyclic radical $\Delta g$ is positive since $g_{cyclicrad} - g_{NO2} > 0$.

For the coupling constant $a_i$, this will be negative due to the negative magnetogyric ratio associated with the $^{15}N$ nucleus.

$\mu = +$ as the product formed is from the encounter of two radicals.

$\varepsilon = +$ as the product formed is from the collapse of a radical pair.

Therefore $\Gamma_n = -(+)(+)(+)(-) = -$ Absorption.

This enhanced absorption is not observed as it is swamped by the large emission signal due to the C.I.D.N.P. effect produced by the nitrogen dioxide radical.

### 6.5.3 C.I.D.N.P. Effects in the Formation of *cis* 2,3-([$^{15}N_1$]-nitromethyl)-tetrahydrofuran.

Again in the formation of this product only one signal was observed due to the symmetry of the molecule. This signal was an enhanced emission signal at $\delta$ 11.2 (Figure 6.12) and was assigned to the C.I.D.N.P. effect arising from the $^{15}N$ nucleus in the $^{15}N$ nitrogen dioxide radical.

Applying Kaptein's Rules to the $^{15}N$ nucleus in the nitrogen dioxide radical:-

For the nitrogen dioxide radical $\Delta g$ is negative since $g_{NO2} - g_{cyclicrad} < 0$.

For the coupling constant $a_i$, this will be negative due to the negative magnetogyric ratio associated with the $^{15}N$ nucleus.

$\mu = +$ as the product formed is from the encounter of two radicals.

$\varepsilon = +$ as the product formed is from the collapse of a radical pair.

Therefore $\Gamma_n = -(+)(+)(-)(-) = -$ Emission.

Considering the $^{15}N$ nucleus in the 1-[$^{15}N_1$]-nitromethyl-tetrahydrofuran-2-yl radical then applying Kaptein's Rules :-

For the cyclic radical, $\Delta g$ is positive since $g_{cyclicrad} - g_{NO2} > 0$.

For the coupling constant $a_i$, this will be negative due to the negative magnetogyric ratio associated with the $^{15}N$ nucleus.

$\mu = +$ as the product formed is from the encounter of two radicals.

$\varepsilon = +$ as the product formed is from the collapse of a radical pair.

Therefore $\Gamma_n = -(+)(+)(+)(-) = -$ Absorption.

This enhanced absorption is not observed as it is swamped by the large emission signal due to the C.I.D.N.P. effect produced by the nitrogen dioxide radical.

### 6.5.4 C.I.D.N.P. effects in the Formation of 2-hydroxy-1-[$^{15}N_1$]-nitro-propyl-3,3'-oxy-1'-propene.

No C.I.D.N.P. effects were observed for the formation of this product. This may be because the chemical shift of the $^{15}N$ nitro group in 2-hydroxy-1-[$^{15}N_1$]-nitro-propyl-3,3'-oxy-1'-propene is almost equivalent to the chemical shift of the nitro groups in *trans* 2,3-([$^{15}N_1$]-nitromethyl)-tetrahydrofuran. Therefore the peaks will be superimposed also.

## 6.6 Discussion.

The results of C.I.D.N.P. experiments indicate that the formation of 1,2-dinitro-propyl-3,3'-oxy-1'-propene and *cis* and *trans* 2,3-(nitromethyl)-tetrahydrofuran give rise to similar C.I.D.N.P. effects. This implies that the reaction with nitrogen dioxide is similar in the formation of both the straight chain adducts and the cyclic adducts. The presence of the C.I.D.N.P. effects indicates that much of the reaction occurs before the separation of the radical pair.

The lifetime of a radical pair[99] is in the order of $10^{-9}$-$10^{-10}$ s which equates to a first order rate coefficient of $10^{9}$-$10^{10}$ $s^{-1}$. The first order rate coefficient for the radical cyclisation of the 4-oxa-6-hepten-2-yl radical[100] (Figure 6.15) is $k_c \approx 3 \times 10^6$ s-1.

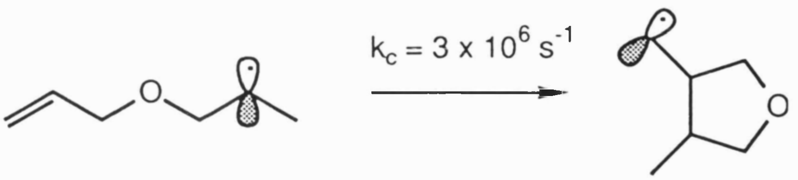


**Figure 6.15** Radical cyclisation for the 4-oxa-6-hepten-2-yl radical.

Therefore if the initial attack were occurring by molecular dinitrogen tetroxide, it would be expected that the addition of the second nitrogen dioxide molecule would take place almost immediately. However from the results obtained the initial β-nitro radical formed undergoes cyclisation to form the 1-[$^{15}N_1$]-nitromethyl-tetrahydrofuran-2-yl radical which is a much slower step.

This implies that the second nitrogen dioxide radical to add was not associated with the initial nitrogen dioxide that attacked. *i.e.* that the initial attack was by a solitary nitrogen dioxide radical.

The C.I.D.N.P. effects observed therefore point to the separate attack of two independent nitrogen dioxide radicals as the predominant pathway not the attack of the dimer dinitrogen tetroxide.

# CHAPTER SEVEN

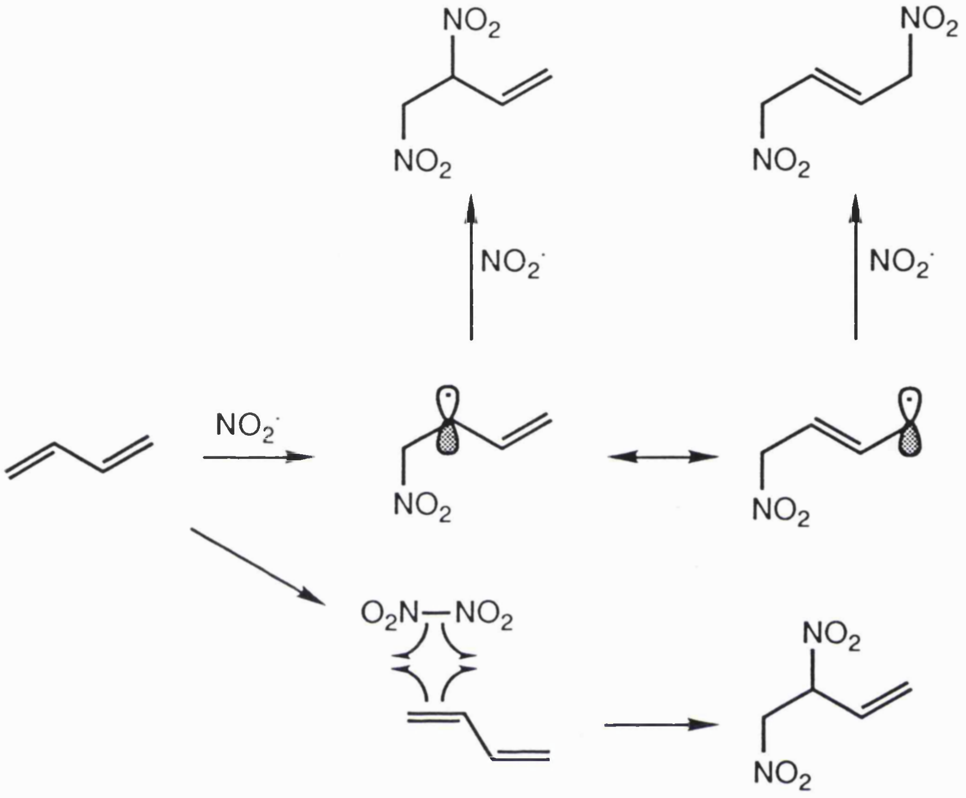
# CONCLUSION

## 7.1 Discussion.

The implication from the results described in the previous five chapters is that the attacking species is the nitrogen dioxide radical ($NO_2\cdot$).

In the work carried out on the reactions between nitrogen dioxide and the conjugated dienes (Chapter 2), the main compounds isolated were those where the nitrogen dioxide had added across the ends of the conjugated system. This would imply that the attack was brought about by the initial attack of a nitrogen dioxide radical at one end of the conjugated system. The radical produced then delocalises over the remaining double bond to form the allylic radical. This radical then reacts further with another nitrogen dioxide radical to form the 1,4-adducts with respect to the initial conjugated system (Scheme 7.1). A concerted addition of the dimer dinitrogen tetroxide would be expected to give rise to addition products across one double bond, so the resulting products would be 1,2-adducts with respect to the initial conjugated system. Evidence for the formation of 1,2-adducts was obtained only in the reactions of 2,5-dimethyl-2,4-hexadiene and nitrogen dioxide for the products then included 2,5-dimethyl-1,2-dinitro-4-hexene and 2,5-dimethyl-3-hydroxy-2-nitro-4-hexene.

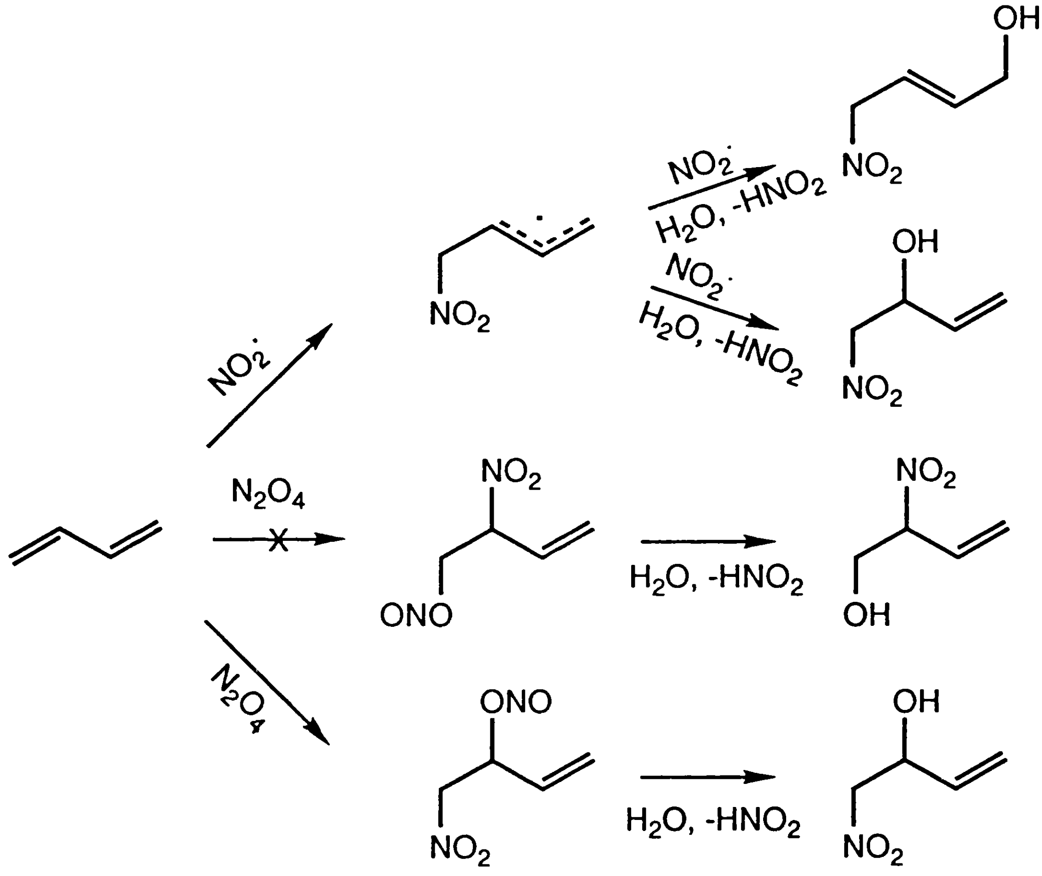
In all the products isolated, it appeared that from the reactions between nitrogen dioxide and the conjugated dienes the initial attack of the nitrogen dioxide radical occurred at the carbon to give the most stable radical *i.e.* by attacking the carbon at the end of the conjugated system to give the allylic radical. This again implies that the addition occurred via two separate nitrogen dioxide radicals as the products always had the nitro group at the 1-position with respect to the conjugated system. If the addition had occurred via the concerted addition of dinitrogen tetroxide then there would be no radical intermediate formed so the addition of the nitro group in hydroxy-nitro adducts would be expected to be equally distributed between the 1- and 2-positions however there was no isolation of any 1-hydroxy-2-nitro-adducts only 2-hydroxy-1-nitro adducts. The 2-hydroxy-1-nitro adducts are probably formed by the attack of the second nitrogen dioxide to the allylic system (Scheme 7.2).



**Scheme 7.1**

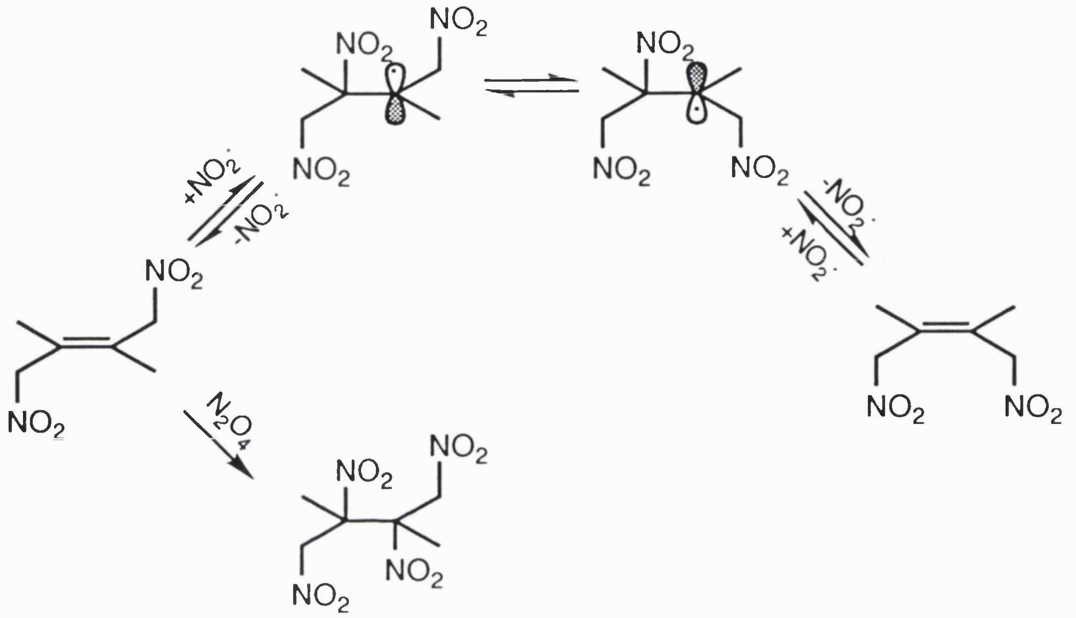
Further evidence for the attack occurring as two separate nitrogen dioxide radicals was obtained from the isomerisation of *cis* and *trans*-2,3-dimethyl-1,4-dinitro-3-butene. The *cis-trans* isomerisation occurred whether there was a catalytic excess or a large excess of nitrogen dioxide. The isomerisation would be expected to occur when there was a catalytic excess of nitrogen dioxide as the concentration of the nitrogen dioxide would be low; therefore once a nitrogen dioxide radical had attacked the double bond in

2,3-dimethyl-1,4-dinitro-3-butene then the resultant radical produced would be unlikely to react immediately with another nitrogen dioxide radical. Due to the long life of the radical compared to the time of bond rotation, isomerisation is able to occur. In solutions where there was a large excess of nitrogen dioxide the probability of the attacking species being dinitrogen tetroxide increases and this would then produce the 2,3-dimethyl-1,2,3,4-tetranitro-butane if the addition was concerted (Scheme 7.3). However as mentioned previously the isomerisation occurred predominantly and only trace amounts of the potential tetranitro adduct were isolated or observed in the $^1$H n.m.r. spectra of the crude reaction mixtures.



**Scheme 7.2**

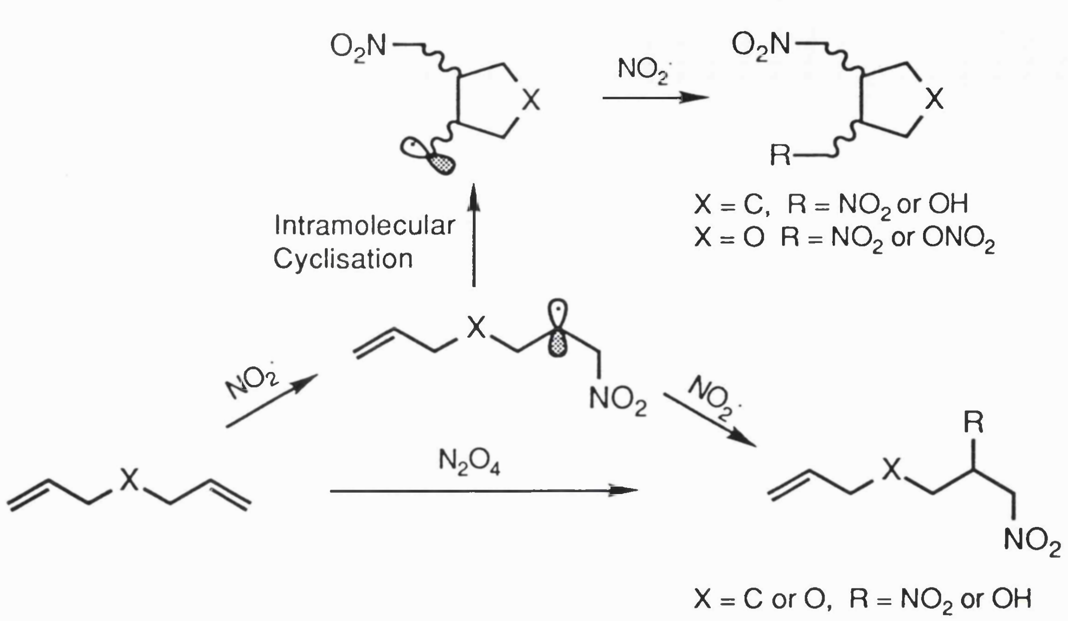
Further evidence for nitrogen dioxide and not dinitrogen tetroxide as the attacking species was obtained from the reactions between nitrogen dioxide and 1,3,5-hexatriene (Chapter 3). The only products to be formed were complex polymers which were brought about by the rapid reaction



Scheme 7.3

of a nitrogen dioxide molecule with that of the hexatriene molecule. The resulting radical then underwent rapid reaction with another hexatriene molecule to produce the dimer and so the chain began. If addition was occurring by the addition of dinitrogen tetroxide then the isolation of the 1,2-dinitro-3,5-hexadiene would have been expected or some isomer thereof. However no such class of compound was isolated.

The reactions between 1,5,9-cyclododecatriene and nitrogen dioxide did not produce any results that would give conclusive evidence for the addition of two separate molecules of nitrogen dioxide. The products isolated corresponded to attack across individual double bonds which would be consistent with attack by two separate nitrogen dioxide molecules or that of the dimer dinitrogen tetroxide. It was hoped that there would be evidence of some bicyclic adducts as these would be consistent with the addition of two separate nitrogen dioxide molecules, however no such compounds were isolated.

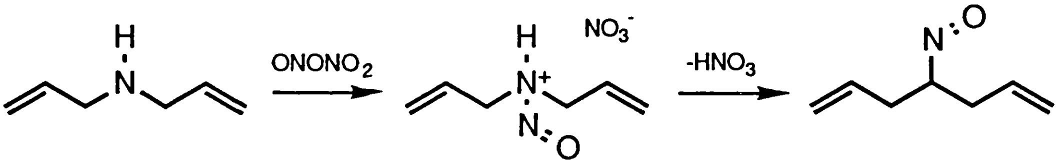


**Scheme 7.4**

From the reactions between the non conjugated diene 1,6-heptadiene and nitrogen dioxide (Chapter 4), strong evidence was obtained for the addition of two separate nitrogen dioxide molecules (Scheme 7.4). Products isolated contained some cyclopentane derivatives which would be consistent with intramolecular cyclisation occurring during the course of the reaction. This is consistent with the addition of the nitrogen dioxide radical at the least substituted end of one of the double bond to form the 1-nitro-6-hepten-2-yl radical which then attacks the remaining double bond to form the cyclopentyl radical which subsequently reacts with another nitrogen dioxide molecule to form the cyclopentane derivatives.

The reactions between nitrogen dioxide and allyl ether (Chapter 5) also gave strong evidence for the attack of the nitrogen dioxide radical. The major products isolated were tetrahydrofuran derivatives. These were consistent with the attack of a single nitrogen dioxide radical followed by intramolecular cyclisation to form the tetrahydrofuran derivatives (Scheme 7.4). If dinitrogen tetroxide were the attacking species then the formation of the tetrahydrofuran derivatives would not be expected as the addition of the second nitrogen dioxide radical would be fast compared to that of the cyclisation step and therefore only the straight chain adducts would be formed. Even when the addition times for the nitrogen dioxide solution were fast, the amount of straight chain adducts formed was negligible compared to that of the cyclised products.

The mechanistic conclusion was confirmed by the observation of C.I.D.N.P. effects in the $^{15}N$ n.m.r. spectra for the reaction between $^{15}N$ labelled nitrogen dioxide and allyl ether (Chapter 6). Enhanced absorption and emission signals were observed in both the formation of the straight chain dinitro adducts and those of the 2,3-(nitromethyl)-tetrahydrofuran derivatives. The C.I.D.N.P. effects observed were very similar for the straight chain adducts and the cyclic adducts, these being large emission signals derived from the nitrogen dioxide radical and small enhanced absorption signals for the nitroalkyl radical in the radical pair. These signals are consistent only with the addition of two separate nitrogen dioxide radicals to the allyl ether.



**Scheme 7.5**

The reactions between nitrogen dioxide and diallylamine (Chapter 5) showed that dinitrogen tetroxide may be responsible for some of the reaction products as the only compound to be isolated from these reactions was N-nitrosodiallylamine. The formation of this compound is consistent with dinitrogen tetroxide attacking (Scheme 7.5) in the form of the nitrosonitrate structure ($ONONO_2$).

## 7.2 Conclusion.

In the final analysis this thesis concludes that in organic solvents the reactions between nitrogen dioxide and conjugated or non-conjugated olefinic systems occurs predominantly by the addition of two separate nitrogen dioxide radicals. Our results do not rule out the attack of molecular dinitrogen tetroxide as an attacking species in the reactions with olefinic systems, but its contribution in the reaction is not as important as the reaction of the nitrogen dioxide radical.

# CHAPTER EIGHT

# EXPERIMENTAL

## 8.1 Introduction.

This Chapter outlines the experimental conditions employed on the reactions between nitrogen dioxide and the following substrates:- 2,5-dimethyl-2,4-hexadiene (section 8.4), 2,4-hexadiene (section 8.5), 2,3-dimethyl-1,3-butadiene (section 8.6), hexachloro-butadiene (section 8.7), *c,t,t*-1,5,9-cyclododecatriene (section 8.8), 1,3,5-hexatriene (section 8.9), 1,6-heptadiene (section 8.10), diallylamine (section 8.11) and allyl ether (section 8.12). Any further reactions carried out on products obtained from these reactions are described in the section concerning the starting substrate.

The identification and analysis of the products obtained in the reactions between the organic substrates and nitrogen dioxide are described in their relevant chapters:- 2,5-dimethyl-2,4-hexadiene, 2,4-hexadiene 2,3-dimethyl-1,3-butadiene and hexachlorobutadiene in Chapter Two, 1,5,9-*c,t,t*-cyclododecadiene and 1,3,5-hexatriene in Chapter Three, 1,6-heptadiene in Chapter Four, and allyl ether and diallylamine in Chapter Five.

## 8.2 Reagents and Solvents.

2,5-Dimethyl-2,4-hexadiene 99%, 2,4-hexadiene (mixture of isomers) 99%, *c,t*-2,4-hexadiene 98%, t,t-2,4-hexadiene 98% and 2,3-dimethyl-1,3-butadiene 98%, and hexachloro-1,3-butadiene 99% were all purchased from Aldrich Chemical Company Ltd and no subsequent purification was required before use.

*c,t,t*-1,5,9-Cyclododecatriene was purchased from Aldrich Chemical Company Ltd with a quoted purity of 98%. This was purified further by distillation (section 8.2.1). 1,3,5-Hexatriene was also purchased from Aldrich Chemical Company Ltd as a mixture of isomers with a quoted purity of 97%, this was not purified further. 1,6-Heptadiene 99% purity, allyl ether 99% purity, and diallyl amine 99% purity were all purchased from Aldrich Chemical Company Ltd and no subsequent purification was required.

Nitrogen dioxide was purchased from Argo International, and required purification before use (Section 8.2.2).

$^{15}N$-Labelled nitric acid (99.5 atom % $^{15}N$) was purchased from MSD Isotopes (a division of Merck Frosst Canada Inc.). Lead nitrate was purchased from Aldrich Chemical Company Ltd.

The solvents n-hexane, dichloromethane and ethyl acetate were high purity solvents purchased from Romil Chemicals, and were used for both h.p.l.c. and reactions. The solvents benzene, dioxane, diethyl ether and carbon tetrachloride were purchased from Aldrich Chemical Company Ltd.

Silica (particle size 0.040-0.063 mm) used in flash chromatography was purchased from Merck.

### 8.2.1 Purification of *c,t,t*-Cyclododeca-1,5,9-triene.

The *c,t,t*-1,5,9-cyclododecatriene provided was found to contain a large amount of impurity and was therefore redistilled before use.

*c,t,t*-1,5,9-cycododecatriene (15 cm$^3$) was added to a round bottomed flask (50 cm$^3$) fitted with vigreux column (10 cm x 1 cm$^2$) and a reflux condenser. The distillation apparatus was evacuated to 5 mmHg using an oil pump and the temperature increased using a graphite bath. Two minor fractions distilled over at 82 °C and 90 °C at 5 mmHg and these were discarded. The pressure was reduced further to 0.6 mmHg where a third component distilled over at 90 °C.

The first 1 cm$^3$ was discarded and the remainder collected. This was the *c,t,t*-1,5,9-cycododecatriene.

### 8.2.2 Purification of Nitrogen Dioxide.

Purification of the nitrogen dioxide purchased was essential due to the presence of other nitrogen oxides and traces of moisture.

Nitrogen dioxide from a cylinder was frozen out into a dry glass tube immersed in liquid nitrogen. The glass tube contained phosphorous pentoxide (2 g). This yielded a dark blue crystalline solid (≈5 g) which was allowed to warm to 0 °C, this gave a dark blue solution. Dry oxygen was bubbled through the blue solution and the fumes evolved were trapped in a second glass tube containing phosphorous pentoxide immersed in an acetone/cardice bath. This yielded a white crystalline solid of nitrogen dioxide. This was now stored in a deep-freeze at -16 °C where it became pale yellow in colour.

The tubes were connected by a ball and socket joint on two glass sidearms. Rubber piping could not be used to connect the tubes as the nitrogen dioxide caused it to perish.

### 8.2.3 Drying n-Hexane.

n-Hexane was dried by refluxing over calcium hydride for 1-2 h. The n-hexane was then allowed to distil over into oven dried glassware. The first 5 cm$^3$ collected was discarded and the remainder collected over activated 3 Å molecular sieves. The molecular sieves were activated by heating at 120 °C for 24 h under reduced pressure.

### 8.2.4 Drying Dichloromethane.

Dichloromethane was dried by refluxing over calcium hydride for 1-2 h. The dichloromethane was then allowed to distil over into oven dried glassware.

The first 5 $cm^3$ collected was discarded and the remainder collected over pre-activated 3 Å molecular sieves.

## 8.3 Experimental Procedures.

All glassware used was flame dried before use, and purged with dry nitrogen. The solvents were dried by standard laboratory techniques (sections 8.2.3 and 8.2.4) and were degassed using ultrasound for 5 min prior to use.

The addition of the reagents was carried out using a syringe pump to ensure the reproducibility of the addition times. The reactions were carried out in a nitrogen atmosphere.

### 8.3.1 High Performance Liquid Chromatography (h.p.l.c.).

High performance liquid chromatography (h.p.l.c.) was carried out using a Waters machine fitted with a refractive index detector. The apparatus used consisted of a Waters M6000 pump, Waters R401 refractive index detector and a Rheodyne injection valve. Normal phase separations were carried out using a stationary phase of two 250 x 10 mm silica columns (particle size 0.005 mm), and a mobile phase of ethyl acetate and n-hexane; the actual composition of the mobile phase will be defined in the experimental sections for each reaction carried out.

The relative yields were normally obtained from $^1H$ n.m.r. spectra but where this was not practical, approximate yields were obtained by h.p.l.c. by calculating the area under each peak and comparing it to the total area of the whole trace. The percentage yields for the products from the reaction of allyl ether and nitrogen dioxide were determined using a Hewlett Packard Integrator Hp3396a.

### 8.3.2 Modes of Addition.

Two basic types of reaction were carried out, the normal mode of addition and the reverse mode of addition. The normal mode of addition will refer to the reactions involving the addition of the nitrogen dioxide solution to that of the substrate under consideration.

The reverse mode of addition will refer to all the reactions involving the addition of the alkene solution to that of the nitrogen dioxide solution.

## 8.4 Reactions Between 2,5-Dimethyl-2-4-hexadiene and Nitrogen Dioxide.

### 8.4.1 Reaction Between 2,5-Dimethyl-2,4-hexadiene and Nitrogen Dioxide; Normal Mode of Addition. (Experiment 1).

Nitrogen Dioxide (0.039 g, 0.847 mmol ) was added to n-hexane (2 $cm^3$) and the resulting solution stirred. This was then added dropwise to a stirred solution of 2,5-dimethyl-2,4-hexadiene (0.060 g, 0.541 mmol) in n-hexane (2 $cm^3$). On addition of the nitrogen dioxide solution, the reaction mixture became cloudy and a white crystalline solid fell out from the solution. The addition was complete after 5 min.

The crystals were removed by filtration and recrystallised from a minimum amount of hot n-hexane to yield white needlelike crystals of 2,5-dimethyl-2,5-dinitro-3-hexene (0.085 g)

The solvent was removed from the filtrate to yield a yellow oil which on standing crystallised and a yellow oil separated out. This consisted of trace amounts of 2,5-dimethyl-2,5-dinitro-3-hexene, and various unidentified products.

Percentage yield (by mass):-

| | |
|---|---|
| 2,5-dimethyl-2,5-dinitro-3-hexene (0.085 g) | 78% |

### 8.4.2 Reaction Between 2,5-Dimethyl-2,4-hexadiene and Nitrogen Dioxide; Reverse Mode of Addition (Experiment 1).

2,5-Dimethyl-2,4-hexadiene (0.058 g, 0.522 mmol) was added to n-hexane (2 cm$^3$) and the resulting mixture stirred. This was added dropwise to a stirred solution of nitrogen dioxide (0.050 g, 1.086 mmol) dissolved in n-hexane (2 cm$^3$). The addition was complete after 5 min. During the course of the addition a crystalline solid formed.

The crystalline solid was removed by filtration and then recrystallised from a minimum amount of hot n-hexane to yield white needlelike crystals of 2,5-dimethyl-2,5-dinitro-3-hexene (0.081 g).

Percentage yield (by mass):-

| | |
|---|---|
| 2,5-dimethyl-2,5-dinitro-3-hexene (0.081 g) | 76.7% |

### 8.4.3 Reaction Between 2,5-Dimethyl-2,4-hexadiene and Nitrogen Dioxide; Normal Mode of Addition (Experiment 2).

Nitrogen dioxide (0.162 g, 3.52 mmol) was added to n-hexane (2 cm$^3$) and the resultant solution added dropwise to a stirred solution of 2,5-dimethyl-2,4-hexadiene (0.064 g, 0.578 mmol) in n-hexane (2 cm$^3$). The addition was complete after 5 min; during the addition the reaction mixture became cloudy and a crystalline product fell from solution. The solvent was removed *in vacuo* to afford a yellow oil with some crystalline material.

Percentage yield (by $^1$H n.m.r.)

| | |
|---|---|
| 2,5-dimethyl-2,5-dinitro-3-hexene | 34.6% |
| 2,5-dimethyl-2,3-dinitro-4-hexene | 15.4% |
| 2-hydroxy-2,5-dimethyl-5-nitro-3-hexene | 10.8% |
| 3-hydroxy-2,5-dimethyl-2-nitro-4-hexene | 15.4% |
| Unidentified products | 23.8% |

### 8.4.4 Reaction Between 2,5-Dimethyl-2,4-hexadiene and Nitrogen Dioxide; Reverse Mode of Addition (Experiment 2).

2,5-Dimethyl-2,4-hexadiene (0.044 g, 0.401 mmol) was dissolved in n-hexane (2 cm$^3$). This solution was the added dropwise to a stirred solution of nitrogen dioxide (0.276 g, 6.005 mmol) in n-hexane (2 cm$^3$) over a period of 5 min. On addition of the diene there was no evidence of any product formation, and after several hours of stirring there was no evidence of the crystalline 2,5-dimethyl-2,5-dinitro-3-hexene being formed. On leaving overnight white crystals formed. The solvent was removed *in vacuo* to afford a crystalline solid and a pale yellow oil.

| Percentage yield (by $^1$H n.m.r.) | |
|---|---|
| 2,5-dimethyl-2,5-dinitro-3-hexene | 55.8% |
| 2-hydroxy-2,5-dimethyl-5-nitro-3-hexene | 13.8% |
| 3-hydroxy-2,5-dimethyl-2-nitro-4-hexene | 14.3% |
| Unidentified products | 16.1% |

### 8.4.5 Reaction Between 2,5-Dimethyl-2,4-hexadiene and Nitrogen Dioxide; Normal Mode of Addition (Experiment 3).

Nitrogen dioxide (0.149 g, 3.243 mmol) was added to diethyl ether (2 cm$^3$) and the resultant solution added dropwise to a stirred solution containing 2,5-dimethyl-2,4-hexadiene (0.160 g, 1.513 mmol) in diethyl ether (2 cm$^3$). During the addition of the nitrogen dioxide solution the reaction mixture became green in colour. The addition was complete after 7 min. The solvent was removed *in vacuo* to afford a crystalline solid in a green oil. The oil slowly changed colour to yellow on leaving in air for a few hours.

| Percentage yield (by $^1$H n.m.r.):- | |
|---|---|
| 2,5-dimethyl-2,5-dinitro-3-hexene | 22.7% |
| 3-hydroxy-2,5-dimethyl-2-nitro-3-hexene | 9.1% |

| | |
|---|---|
| 2-hydroxy-2,5-dimethyl-5-nitro-4-hexene | 54.5% |
| Unidentified products | 13.7% |

### 8.4.6 Reaction Between 2,5-Dimethyl-2,4-hexadiene and Nitrogen Dioxide; Normal Mode of Addition (Experiment 4).

A solution of nitrogen dioxide (0.144 g, 3.136 mmol) in benzene (2 $cm^3$) was added dropwise to an agitated solution of 2,5-dimethyl-2,4-hexadiene (0.163 g, 1.485 mmol) in benzene (2 $cm^3$). The addition was complete after 5 min. During the initial addition of the nitrogen dioxide solution the reaction mixture became pale green in colour. There was no evidence of any crystal formation. The excess nitrogen dioxide and the benzene were removed under reduced pressure to afford a crystalline solid in a pale green oil.

| Percentage yield (by $^1H$ n.m.r.) | |
|---|---|
| 2,5-dimethyl-2,5-dinitro-3-hexene | 66.7% |
| 2,5-dimethyl-2,3-dinitro-4-hexene | 11.7% |
| 3-hydroxy-2,5-dimethyl-2-nitro-4-hexene | 7.8% |
| 2-hydroxy-2,5-dimethyl-5-nitro-3-hexene | 7.8% |
| Unidentified products | 6.0% |

### 8.4.7 Reaction Between 2,5-Dimethyl-2,5-dinitro-3-hexene and Nitrogen Dioxide; Normal Mode of Addition (Experiment 1).

Nitrogen dioxide (0.124 g, 2.702 mmol) was added to benzene (2 $cm^3$) and the resultant solution added dropwise to a stirred solution of 2,5-dimethyl-2,5-dinitro-3-hexene (0.072 g, 0.356 mmol) in benzene (2 $cm^3$). The addition was complete after 5 min and the reaction mixture stirred at room temperature for a further 1 h. There was no decolouration of the reaction mixture. The solvent was removed under reduced pressure to afford a crystalline solid. A $^1H$ n.m.r. spectrum was recorded and it corresponded to unreacted starting material. There was no evidence of any product formation.

### 8.4.8 Reaction Between 2,5-Dimethyl-2,5-dinitro-3-hexene and Nitrogen Dioxide; Normal Mode of Addition (Experiment 2).

Nitrogen dioxide (0.170 g, 3.7 mmol) was added to dry diethyl ether (2 $cm^3$) and the resultant solution added to a solution of 2,5-dimethyl-2,5-dinitro-3-hexene (0.080 g, 0.395 mmol) in diethyl ether (2 $cm^3$). The addition was complete after 6 min. The reaction mixture became pale yellow in colour. The reaction was stirred for an additional 18 h. The solvent was removed *in vacuo* to afford a white crystalline solid. A $^1H$ n.m.r. spectrum was recorded and it corresponded to unreacted starting material. There was no evidence of any product formation.

## 8.5 Reactions Between 2,4-Hexadiene and Nitrogen Dioxide.

These reactions proved to be highly complex with a large number of products being formed in the course of the reaction. The best separations occurred when a mobile phase of 10% ethyl acetate / 90% n-hexane was employed. This however led to retention times in excess of 1h for some of the polar products. The retention times could be reduced by removing the more polar components first using a mobile phase of 30% ethyl acetate / 70% n-hexane, then separating the faster moving components with the initial mobile phase.

### 8.5.1 Reaction Between 2,4-Hexadiene (Mixture of Isomers) and Nitrogen Dioxide; Normal Mode of Addition.

Nitrogen dioxide (0.090 g, 1.966 mmol) was added to n-hexane (2 $cm^3$) and the resultant solution stirred. This solution was added dropwise to a stirred solution of 2,4-hexadiene (0.080 g, 0.973 mmol) in n-hexane (2 $cm^3$). The addition was complete after 5 min. During the addition the reaction mixture became white in colour and a suspension formed. The reaction was stirred for an additional 1 h. A pale yellow oil had formed. The solvent was removed *in vacuo* to afford a yellow oil.

Percentage yield (by $^1$H n.m.r.):-

| | |
|---|---|
| 2,5-dinitro-3-hexene (first diastereoisomer) | 29.7% |
| 2,5-dinitro-3-hexene (second diastereoisomer) | 25.9% |
| 2-hydroxy-5-nitro-3-hexene (first diastereoisomer) | 24.0% |
| 2-hydroxy-5-nitro-3-hexene (second diastereoisomer) | 10.1% |
| Unidentified products | 10.3% |

### 8.5.2 Reaction Between *t,t*-2,4-Hexadiene and Nitrogen Dioxide; Normal Mode of Addition (Experiment 1).

Nitrogen dioxide (0.096 g, 2.084 mmol) was added to n-hexane (2 cm$^3$) and then added dropwise to an agitated solution of *t,t*-2,4-hexadiene (0.091 g, 1.105 mmol) in n-hexane (2 cm$^3$). The addition was complete after 30 s. During the addition the reaction mixture became cloudy. On further stirring (1 h) a pale yellow oil formed on the sides of the reaction vessel. The solvent was removed *in vacuo* to afford a yellow oil.

The sample was kept in a deep-freeze at -38 °C over night and then h.p.l.c. performed on the sample the following day.

Percentage yields (by h.p.l.c.):-

| | |
|---|---|
| 2,5-dinitro-3-hexene (first diastereoisomer) | 27.5% |
| 2,5-dinitro-3-hexene (second diastereoisomer) | 23.5% |
| 2-hydroxy-5-nitro-3-hexene (first diastereoisomer) | 8.9% |
| 2-hydroxy-5-nitro-3-hexene (second diastereoisomer) | 8.9% |
| Unidentified products | 31.2% |

### 8.5.3 Reaction Between *t,t*-2,4-Hexadiene and Nitrogen Dioxide; Reverse Mode of Addition.

*t,t*-2,4-Hexadiene (0.077 g, 0.942 mmol) was dissolved in n-hexane (2 cm$^3$) and then added dropwise to a stirred solution of nitrogen dioxide (0.098 g, 2.120 mmol) in n-hexane (2 cm$^3$). The addition was complete after 2 min. Stirring was maintained for 1 h after the addition and a yellow oil precipitated out of the solution. The solvent was removed *in vacuo* to afford a yellow oil.

Percentage yields (by h.p.l.c.):-

| | |
|---|---|
| 2,5-dinitro-3-hexene (first diastereoisomer) | 27.5% |
| 2,5-dinitro-3-hexene (second diastereoisomer) | 23.5% |
| 2-hydroxy-5-nitro-3-hexene (first diastereoisomer) | 8.9% |
| 2-hydroxy-5-nitro-3-hexene (second diastereoisomer) | 8.9% |
| Unidentified products | 31.2% |

### 8.5.4 Reaction Between *t,t*-2,4-Hexadiene and Nitrogen Dioxide; Normal Mode of Addition (Experiment 2).

Nitrogen dioxide (0.089 g, 1.950 mmol) was dissolved in diethyl ether( 2 cm$^3$). The resultant solution was added dropwise to a stirred solution of *t,t*-2,4-hexadiene (0.079 g, 0.971 mmol) in diethyl ether (2 cm$^3$). The addition was complete after 2 min. The reaction was stirred for 1 h. The reaction mixture was left in a refridgerator at 5 °C for 48 h. The solvent was removed under reduced pressure to afford a yellow oil.

Percentage yields (by h.p.l.c.):-

| | |
|---|---|
| 2,5-dinitro-3-hexene (first diastereoisomer) | 25.1% |
| 2,5-dinitro-3-hexene (second diastereoisomer) | 23.1% |
| 2-hydroxy-5-nitro-3-hexene (first diastereoisomer) | 18.9% |
| 2-hydroxy-5-nitro-3-hexene (second diastereoisomer) | 20.8% |

| | |
|---|---|
| Unidentified products | 12.1% |

### 8.5.5 Reaction Between *c,t*-2,4-Hexadiene and Nitrogen Dioxide; Normal Mode of Addition.

Nitrogen dioxide (0.094 g, 2.041 mmol) was added to n-hexane (2 $cm^3$) and the solution agitated to ensure mixing. This solution was then added dropwise to a stirred solution of *c,t*-2,4-hexadiene (0.936 g, 1.140 mmol) in n-hexane (2 $cm^3$) at room temperature. The addition was complete after 5 min., and the stirring was continued for an additional 1.5 h. During the addition the reaction mixture became cloudy and after several minutes a yellow oil precipitated out of solution. The n-hexane was removed under reduced pressure to afford a yellow oil.

Percentage yields (by h.p.l.c.):-

| | |
|---|---|
| 2,5-dinitro-3-hexene (first diastereoisomer) | 24.5% |
| 2,5-dinitro-3-hexene (second diastereoisomer) | 23.2% |
| 2-hydroxy-5-nitro-3-hexene (first diastereoisomer) | 9.4% |
| 2-hydroxy-5-nitro-3-hexene (second diastereoisomer) | 8.7% |
| Unidentified products | 34.2% |

### 8.5.6 Reaction Between *c,t*-2,4-Hexadiene and Nitrogen Dioxide at -20 °C; Reverse Mode of Addition.

*c,t*-2,4-Hexadiene (0.051 g, 0.622 mmol) was dissolved in n-hexane (2 $cm^3$) and the mixture stirred thoroughly. This solution was then added dropwise to a stirred solution of nitrogen dioxide (0.057 g, 1.250 mmol) in n-hexane (2 $cm^3$) cooled to a temperature between -20 and -15 °C by an external acetone/cardice bath. The addition was complete after 5 min and stirring continued for an additional 1 h. A pale yellow oil formed on the sides of the reaction vessel. The sample was then placed in a deep-freeze at -28 °C until the reaction mixture was separated by h.p.l.c.. The solvent was removed *in vacuo* to afford a yellow oil immediately before h.p.l.c..

Percentage yields (by h.p.l.c.):-

| | |
|---|---|
| 2,5-dinitro-3-hexene (first diastereoisomer) | 10.5% |
| 2,5-dinitro-3-hexene (second diastereoisomer) | 16.1% |
| 2-hydroxy-5-nitro-3-hexene (first diastereoisomer) | 16.1% |
| 2-hydroxy-5-nitro-3-hexene (second diastereoisomer) | 21.6% |
| Unidentified products | 35.7% |

### 8.5.7 Reaction Between *c,t*-2,4-Hexadiene and Nitrogen Dioxide at -10 °C; Reverse Mode of Addition.

*c,t*-2,4-Hexadiene (0.051 g, 0.622 mmol) was dissolved in n-hexane (2 cm$^3$) and the mixture stirred thoroughly. This solution was then added dropwise to a stirred solution of nitrogen dioxide (0.057 g, 1.250 mmol) in n-hexane (2 cm$^3$) cooled to a temperature between -12 and -8 °C by an external acetone/cardice bath. The addition was complete after 5 min and stirring continued for an additional 1 h. A pale yellow oil formed on the sides of the reaction vessel. The sample was then placed in a deep-freeze at -28 °C until the reaction mixture was separated by h.p.l.c.. The solvent was removed *in vacuo* to afford a yellow oil immediately before h.p.l.c..

Percentage yields (by h.p.l.c.):-

| | |
|---|---|
| 2,5-dinitro-3-hexene (first diastereoisomer) | 22.4% |
| 2,5-dinitro-3-hexene (second diastereoisomer) | 19.6% |
| 2-hydroxy-5-nitro-3-hexene (first diastereoisomer) | 22.2% |
| 2-hydroxy-5-nitro-3-hexene (second diastereoisomer) | 13.8% |
| Unidentified products | 22.0% |

### 8.5.8 Reaction Between *c,t*-2,4-Hexadiene and Nitrogen Dioxide at 0 °C; Reverse Mode of Addition.

*c,t*-2,4-Hexadiene (0.051 g, 0.622 mmol) was dissolved in n-hexane (2 $cm^3$) and the mixture stirred thoroughly. This solution was then added dropwise to a stirred solution of nitrogen dioxide (0.057 g, 1.250 mmol) in n-hexane (2 $cm^3$) cooled to a temperature between -2 and 4 °C by an external acetone/cardice bath. The addition was complete after 5 min and stirring continued for an additional 1 h. A pale yellow oil formed on the sides of the reaction vessel. The sample was then placed in a deep-freeze at -28 °C until the reaction mixture was separated by h.p.l.c.. The solvent was removed *in vacuo* to afford a yellow oil immediately before h.p.l.c..

Percentage yields (by h.p.l.c.):-

| | |
|---|---|
| 2,5-dinitro-3-hexene (first diastereoisomer) | 24.9% |
| 2,5-dinitro-3-hexene (second diastereoisomer) | 31.2% |
| 2-hydroxy-5-nitro-3-hexene (first diastereoisomer) | 8.0% |
| 2-hydroxy-5-nitro-3-hexene (second diastereoisomer) | 8.2% |
| Unidentified products | 27.7% |

## 8.6 Reactions Between 2,3-Dimethyl-1,3-butadiene and Nitrogen Dioxide.

The reactions between 2,3-dimethyl-1,3-butadiene and nitrogen dioxide were carried out in a number of different solvents to see how the solvent affected the reaction products. In all the reactions where h.p.l.c. was employed to separate the reaction products the mobile phase used was 25% ethyl acetate and 75 % n-hexane. The percentage yields for these reactions was determined by the area of the h.p.l.c. trace. For those reactions where the products were not separated using h.p.l.c. the percentage yields were determined by the comparison of the integrals in the $^1H$ n.m.r. spectrum for the crude reaction mixture

### 8.6.1 Reaction between 2,3-Dimethyl-1,3-butadiene and Nitrogen Dioxide; Normal Mode of Addition (Experiment 1).

Nitrogen dioxide (0.092 g, 2.000 mmol) was added to dry n-hexane (2 $cm^3$) and the resultant solution added dropwise to a solution of 2,3-dimethyl-1,3-butadiene (0.082 g, 1.002 mmol) dissolved in n-hexane (2 $cm^3$). The addition was complete after 5 min, and the reaction mixture stirred at room temperature for a further 1 h. During the addition a white suspension formed which precipitated to form a green oil.

The solvent was removed under reduced pressure to yield a green oil, which on standing in an atmosphere of air for several hours crystallised. The reaction mixture was separated by h.p.l.c.

Percentage yields (by h.p.l.c.):-

| | |
|---|---|
| *t*-2,3-Dimethyl-1,4-dinitro-2-butene | 25.6% |
| *c*-2,3-Dimethyl-1,4-dinitro-2-butene | 22.2% |
| Unidentified products | 52.2% |

### 8.6.2 Reaction between 2,3-Dimethyl-1,3-butadiene and Nitrogen Dioxide; Reverse Mode of Addition (Experiment 1).

A solution of 2,3-dimethyl-1,3-butadiene (0.069 g, 0.842 mmol) in dry n-hexane (2 $cm^3$) was added dropwise to a stirred solution of nitrogen dioxide (0.088 g, 1.905 mmol) in n-hexane (2 $cm^3$) at room temperature. On initial addition of the diene the reaction mixture became cloudy and on further addition of the diene a green oil precipitated out of solution. The addition was complete after 5 min. Stirring was continued for 1 h by which time the oil had become yellow in colour.

The solvent was removed *in vacuo* to afford a green oil. A $^1H$ n.m.r. spectrum was recorded on the crude mixture. This reaction gave a set of doublet of doublets at δ 5.2 which may be due to the formation of 1,2,3,4-tetranitro-1,3-dimethyl-butane.

Percentage yields (by $^1$H n.m.r.):-

| | |
|---|---|
| *t*-2,3-Dimethyl-1,4-dinitro-2-butene | 23.4% |
| *c*-2,3-Dimethyl-1,4-dinitro-2-butene | 25.8% |
| Unidentified products | 50.2% |

### 8.6.3 Reaction between 2,3-Dimethyl-1,3-butadiene and Nitrogen Dioxide; Normal Mode of Addition (Experiment 2).

Nitrogen dioxide (0.177 g, 3.840 mmol) was dissolved in n-hexane (2 cm$^3$) and the resultant solution added dropwise to a stirred solution of 2,3-dimethyl-1,3-butadiene (0.050 g, 0.609 mmol) in n-hexane (2 cm$^3$). On addition a white suspension formed which on completion of the addition had become a yellow oil.

The n-hexane was removed under reduced pressure to afford a yellow oil. To this oil carbon tetrachloride (5 cm$^3$) was added and stirred for 10 min. A green immiscible oil formed on the surface of the organic layer. The immiscible oil was decanted off and the carbon tetrachloride removed under *vacuo* to afford a yellow oil. Diethyl ether (5 cm$^3$) was added to the residue and stirred for approximately 1 h, a yellow immiscible oil formed on the bottom of the flask on standing. The ether layer was decanted off and the ether removed *in vacuo*, this afforded a white powder which was recrystallised from the minimum amount of hot carbon tetrachloride. This corresponded to the *t*-2,3-dimethyl-1,4-dinitro-2-hexene. The immiscible oil form the diethyl ether wash corresponded to the *c*-2,3-dimethyl-1,4-dinitro-2-hexene plus a few minor impurities. The green oil separated off from the carbon tetrachloride and not identified was thought to be a mixture of several nitro-nitrites and nitro-alcohols formed during the course of the reaction.

### 8.6.4 Reaction between 2,3-Dimethyl-1,3-butadiene and Excess Nitrogen Dioxide; Reverse Mode of Addition (Experiment 2).

2,3-Dimethyl-1,3-butadiene (0.55 g, 0.672 mmol) was dissolved in n-hexane (2 cm$^3$) and the resultant solution was added dropwise to a stirred solution of nitrogen dioxide (0.363 g, 7.890 mmol) in n-hexane (2 cm$^3$). During the addition of the diene a white suspension formed, which on further stirring (24-h) became a yellow oil. The addition was complete after 3 min. The solvent was removed *in vacuo* to afford a yellow oil.

The reaction mixture was separated into its components using h.p.l.c. and proved to be extremely complex, with a large amount of minor products.

Percentage yields (by h.p.l.c.):-

| | |
|---|---|
| *t*-2,3-Dimethyl-1,4-dinitro-2-butene | 13.3% |
| *c*-2,3-Dimethyl-1,4-dinitro-2-butene | 12.1% |
| Unidentified products | 74.6% |

### 8.6.5 Reaction between 2,3-Dimethyl-1,3-butadiene and Nitrogen Dioxide; Normal Mode of Addition (Experiment 3).

Nitrogen dioxide (0.085 g, 1.843 mmol) was dissolved in diethyl ether (2 cm$^3$) and then added dropwise to a stirred solution of 2,3-dimethyl-1,3-butadiene (0.072 g, 0.874 mmol) in diethyl ether (2 cm$^3$). The addition was complete after 3 min. Stirring was maintained at room temperature for a further 1 h. The solution was pale green in colour. The solvent was removed *in vacuo* to afford a white crystalline solid and a pale green oil.

Percentage yields (by $^1$H n.m.r.):-

| | |
|---|---|
| *t*-2,3-Dimethyl-1,4-dinitro-2-butene | 58.3% |
| *c*-2,3-Dimethyl-1,4-dinitro-2-butene | 10.0% |
| Unidentified products | 31.7% |

### 8.6.6 Reaction between 2,3-Dimethyl-1,3-butadiene and Nitrogen Dioxide; Reverse Mode of Addition (Experiment 3).

Diethyl ether (3 $cm^3$) was added to 2,3-dimethyl-1,3-butadiene (0.093 g, 1.143 mmol) and the solution stirred. This solution was then added to an agitated solution of nitrogen dioxide (0.305 g, 6.635 mmol) in diethyl ether (3 $cm^3$) at room temperature. The addition was complete after 3 min and the reaction mixture stirred for an additional 1 h. The reaction mixture, after the addition of 2,3-dimethyl-1,3-butadiene, was brown but on standing became green in colour. On removal of the solvent under reduced pressure, a turquoise oil formed.

Percentage yields (by $^1H$ n.m.r.):-

| | |
|---|---|
| *t*-2,3-Dimethyl-1,4-dinitro-2-butene | 37.0% |
| *c*-2,3-Dimethyl-1,4-dinitro-2-butene | 11.0% |
| Unidentified products | 52.0% |

### 8.6.7 Reaction between 2,3-Dimethyl-1,3-butadiene and Nitrogen Dioxide; Reverse Mode of Addition (Experiment 4).

2,3-Dimethyl-1,3-butadiene (0.100 g, 1.220 mmol) was dissolved in 1,4-dioxane (3 $cm^3$) and the resultant solution added dropwise to a stirred solution of nitrogen dioxide (0.377 g, 8.198 mmol) in 1,4-dioxane (3 $cm^3$). The nitrogen dioxide/1,4-dioxane solution was a deep blue solution with a crystalline solid present due to the solvent/solute interaction. The addition was complete after 3 min. The reaction mixture was stirred for a further 1 h at room temperature and the reaction mixture became pale green in colour. The solvent was removed *in vacuo* to afford a green oil.

Percentage yields (by $^1H$ n.m.r.):-

| | |
|---|---|
| *t*-2,3-Dimethyl-1,4-dinitro-2-butene | 30.0% |
| *c*-2,3-Dimethyl-1,4-dinitro-2-butene | 16.2% |
| Unidentified products | 52.0% |

### 8.6.8 Reaction between 2,3-Dimethyl-1,3-butadiene and Nitrogen Dioxide; Normal Mode of Addition (Experiment 4).

2,3-Dimethyl-1,3-butadiene (0.035 g, 0.430 mmol) was dissolved in benzene (2 $cm^3$) and the resultant solution mixed thoroughly. This solution was then added dropwise to an agitated solution of nitrogen dioxide (0.289 g, 6.278 mmol) in benzene (2 $cm^3$) at room temperature. The addition was complete after 5 min. Stirring was continued for 12 h, after which time the resultant solution had turned a pale green. The solvent was removed under reduced pressure to afford a green oil.

Percentage yields (by $^1H$ n.m.r.):-

| | |
|---|---|
| *t*-2,3-Dimethyl-1,4-dinitro-2-butene | 16.5% |
| *c*-2,3-Dimethyl-1,4-dinitro-2-butene | 19.1% |
| Unidentified products | 64.4% |

### 8.6.9 Reaction between 2,3-Dimethyl-1,3-butadiene and Nitrogen Dioxide; Normal Mode of Addition (Experiment 5).

Nitrogen dioxide (0.098 g, 2.131 mmol) was dissolved in acetonitrile (2 $cm^3$) and the solution stirred. This was then added dropwise to an agitated solution of 2,3-dimethyl-1,3-butadiene (0.086 g, 1.052 mmol) in acetonitrile (2 $cm^3$) at room temperature. The addition was complete after 5 min. The solvent was removed under reduced pressure to yield a yellow oil.

From the $^1H$ n.m.r. there was evidence of polymerisation occurring in the reaction products.

Percentage yields (by $^1H$ n.m.r.):-

| | |
|---|---|
| *t*-2,3-Dimethyl-1,4-dinitro-2-butene | 7.6% |
| *c*-2,3-Dimethyl-1,4-dinitro-2-butene | 2.1% |
| Unidentified products | 92.3% |

### 8.6.10 Reaction between 2,3-Dimethyl-1,3-butadiene and Nitrogen Dioxide; Reverse Mode of Addition (Experiment 5).

Nitrogen dioxide (0.103 g, 2.239 mmol) was dissolved in acetonitrile (2 cm$^3$) and the resultant solution stirred vigorously. To this solution, 2,3-dimethyl-1,3-butadiene (0.079 g, 0.971 mmol) in acetonitrile (2 cm$^3$) was added. The addition was complete after 5 min. The solution became pale blue in colour on stirring for an additional 30 min. The solvent was removed *in vacuo* to afford a pale green oil.

Percentage yields (by $^1$H n.m.r.):-

| | |
|---|---|
| *t*-2,3-Dimethyl-1,4-dinitro-2-butene | 17.7% |
| *c*-2,3-Dimethyl-1,4-dinitro-2-butene | 6.1% |
| Unidentified products | 76.2% |

### 8.6.11 Reaction between 2,3-Dimethyl-1,3-butadiene and Nitrogen Dioxide; Reverse Mode of Addition (Experiment 6).

2,3-Dimethyl-1,3-butadiene (0.093 g, 1.140 mmol) in carbon tetrachloride (1 cm$^3$) was added dropwise to a stirred solution of nitrogen dioxide (0.218 g, 4.731 mmol) in carbon tetrachloride (1 cm$^3$). The addition was complete after 2 min. The reaction was exothermic and the carbon tetrachloride began to reflux an the sides of the reaction vessel. The reaction mixture was stirred for an additional 24 h. The solvent was removed *in vacuo* to afford a yellow oil.

Percentage yields (by $^1$H n.m.r.):-

| | |
|---|---|
| *t*-2,3-Dimethyl-1,4-dinitro-2-butene | 19.2% |
| *c*-2,3-Dimethyl-1,4-dinitro-2-butene | 20.8% |
| Unidentified products | 60.0% |

### 8.6.12 Reaction between 2,3-Dimethyl-1,3-butadiene and Nitrogen Dioxide; Reverse Mode of Addition (Experiment 7).

2,3-Dimethyl-1,3-butadiene (0.014 g, 0.179 mmol) was dissolved in dichloromethane (2 cm$^3$) and the solution mixed thoroughly. This was then added dropwise to a stirred solution of nitrogen dioxide (0.077 g, 1.684 mmol) in dichloromethane (2 cm$^3$). The addition was complete after 5 min. The resultant solution was pale yellow in colour. The solvent was removed under reduced pressure to afford a yellow oil.

| Percentage yields (by $^1$H n.m.r.):- | |
|---|---|
| *t*-2,3-Dimethyl-1,4-dinitro-2-butene | 19.2% |
| *c*-2,3-Dimethyl-1,4-dinitro-2-butene | 18.0% |
| Unidentified products | 62.8% |

## 8.7 Reactions Between Hexachloro-1,3-butadiene and Nitrogen Dioxide.

The reaction mixtures obtained from the following reactions were analysed by $^{13}$C n.m.r. spectroscopy only as the substrate and the potential products formed would be free from hydrogen. No h.p.l.c. was performed on the reaction products as there appeared to be no reaction from the $^{13}$C n.m.r. spectra obtained.

### 8.7.1 Reaction Between Hexachloro-1,3-butadiene and Nitrogen Dioxide; Normal Mode of Addition.

Nitrogen dioxide (0.119 g, 2.60 mmol) was dissolved in n-hexane (2 cm$^3$) and then added dropwise to an agitated solution of hexachloro-1,3-butadiene (0.196 g, 0.75 mmol) in n-hexane (2 cm$^3$). The addition was complete after 5 min. The reaction was left at room temperature for 1 h and then heated to 40-45 °C for 2 h. The solvent and the unreacted nitrogen dioxide were removed under reduced pressure to yield a colourless oil (0.174 g).

A $^{13}C$ n.m.r. spectrum was obtained on this sample and it compared exactly with that of the starting material hexachloro-1,3-butadiene. No reaction had occurred.

### 8.7.2 Reaction Between Hexachloro-1,3-butadiene and Nitrogen Dioxide; Reverse Mode of Addition.

Hexachloro-1,3-butadiene (0.216 g, 0.83 mmol) was added to n-hexane (2 $cm^3$) and then added dropwise to nitrogen dioxide (0.101 g, 2.12 mmol) in n-hexane (2 $cm^3$). The addition was complete after 5 min. The reaction mixture was heated to 40-45 °C for 1 h. The solvent was removed *in vacuo* to afford a colourless oil.

No reaction had taken place as the $^{13}C$ n.m.r. spectrum recorded on the oil corresponded exactly to that of the starting material.

## 8.8 Reactions Between *c,t,t*-1,5,9-Cyclododecatriene and Nitrogen Dioxide.

H.p.l.c. conditions employed for the separation of the reaction products for the following set of experiments were as follows: initially the reaction mixtures were separated into two components using the mobile phase 65% n-hexane/ 35% ethyl acetate. The first fraction was then separated further using the mobile phase 75% n-hexane / 25% ethyl acetate. The second fraction was separated into further components by using the mobile phase 87.5% n-hexane / 12.5% ethyl acetate.

### 8.8.1 Reaction Between *c,t,t*-1,5,9-Cyclododecatriene and Nitrogen Dioxide; Reverse Mode of Addition (Experiment 1).

*c,t,t*-1,5,9-Cyclododecatriene (0.135 g, 0.833 mmol) was dissolved in n-hexane (2.5 $cm^3$). This solution was then added dropwise to nitrogen dioxide (0.154 g, 3.34 mmol) in n-hexane (2.5 $cm^3$). Addition was complete after 5 min.

After addition of half the triene solution the reaction mixture grew cloudy. The reaction mixture was stirred for an additional 30 min. A green oil formed which crystallised on standing. The solvent was removed *in vacuo* to afford a yellow oil. This oil was submitted for h.p.l.c. analysis; there were four major products.

| Percentage yields (by h.p.l.c.):- | |
|---|---|
| 5,6-dinitro-*c,t*-1,9-cyclododecadiene | 32.7% |
| 1,2-dinitro-*t,t*-5,6-cyclododecadiene | 35.6% |
| hydroxy-nitro-cyclododecadiene (first h.p.l.c. fraction) | 8.8% |
| hydroxy-nitro-cyclododecadiene (second h.p.l.c. fraction) | 8.1% |
| Unidentified products | 14.8% |

### 8.8.2 Reaction Between *c,t,t*-1,5,9-Cyclododecatriene and Nitrogen Dioxide; Normal Mode of Addition.

Nitrogen dioxide (0.109 g, 2.382 mmol) was added to n-hexane (5 $cm^3$) and the resulting solution added dropwise for 6 min to a stirred solution of *c,t,t*-1,5,9-cyclododecatriene (0.193 g, 1.189 mmol) in n-hexane (5 $cm^3$). After the addition was complete the reaction mixture became cloudy. Stirring was continued for an additional 3 h. The hexane was removed *in vacuo* to afford a yellow oil. This was submitted for h.p.l.c. analysis.

H.p.l.c was carried out on the sample but the reaction consisted of many reaction products which could not be resolved. There were no major products.

### 8.8.3 Reaction Between *c,t,t*-1,5,9-Cyclododecatriene and Nitrogen Dioxide; Reverse Mode of Addition (Experiment 2).

*c,t,t*-1,5,9-Cyclododecatriene (0.106 g, 0.652 mmol) in acetonitrile (3 $cm^3$) was added rapidly to nitrogen dioxide (0.186 g, 4.05 mmol) in acetonitrile (3 $cm^3$). The addition was complete after 1 min, and the reaction mixture became warm and turned green in colour. Stirring was continued for 1 h. The solvent was removed *in vacuo* to afford a yellow gum.

The gum was submitted for h.p.l.c. but was too complex to analyse consisting of at least sixteen overlapping bands. There were no major components.

### 8.8.4 Reaction Between 1,2-Dinitro-*t,t*-5,9-cyclododecadiene and Nitrogen Dioxide; Normal Mode of Addition.

Nitrogen dioxide (0.031 g, 0.663 mmol) was dissolved in carbon tetrachloride (5 cm$^3$). This solution was then added dropwise to a stirred solution of 1,2-dinitro-*t,t*-5,9-cyclododecadiene (0.068 g, 0.268 mmol) in carbon tetrachloride (5 cm$^3$). Addition was complete after 2 h, and the reaction stirred for 1 h. On leaving to stand overnight a white crystalline solid formed which was removed by filtration and recrystallised from warm methanol. The carbon tetrachloride was removed *in vacuo* to afford a yellow oil. This was submitted for h.p.l.c.

From h.p.l.c. there was evidence of unreacted starting material and some minor components which could not be separated.

The crystals obtained corresponded to 1,2,5,6-tetranitro-9-cyclododecene (0.007 g, yield 8%).

### 8.8.5 Reaction Between 5,6-Dinitro-*c,t*-1,9-cyclododecadiene and Nitrogen Dioxide; Normal Mode of Addition.

5,6-Dinitro-*c,t*-1,9-cyclododecadiene (0.039 g, 0.153 mmol) was dissolved in warm n-hexane (5 cm$^3$) at 35-38 °C. Nitrogen dioxide (0.058 g, 1.267 mmol) in n-hexane (4 cm$^3$) was added over 1.75 h and the temperature maintained between 35-38 °C by a water bath. Stirring was continued for 2 h. On leaving overnight a white crystalline solid formed; this was removed by filtration and recrystallised from warm methanol.

The n-hexane was removed *in vacuo* and the residue submitted for h.p.l.c.. There were no major components, and products appeared to decompose on the column. A mobile phase of 80% n-hexane / 20% ethyl acetate was employed.

The crystals obtained corresponded to 1,2,5,6-tetranitro-9-cyclododecene (0.005 g, yield 10%).

### 8.8.6 Reaction Between 1,2,5,6-Tetranitro-9-cyclododecene and Nitrogen Dioxide; Reverse Mode of Addition.

1,2,5,6-Tetranitro-9-cyclododecene (0.014 g, 0.039 mmol) was dissolved in nitromethane (5 cm$^3$). This was then added dropwise to nitrogen dioxide (0.062 g, 1.347 mmol) in nitromethane (2 cm$^3$). The addition was complete after 2 h, and stirring continued for 1 h. The solvent was removed *in vacuo* to afford a green oil. Methanol (5 cm$^3$) was added to the oil and a white suspension formed; this was separated from the methanol layer by centrifuge (2000 revs/min, 4 °C, 15 min) and then decanting off the liquid. The methanol was removed *in vacuo* to afford a green oil.

A $^1$H n.m.r. spectrum of the white suspension showed it to be the unreacted 1,2,5,6-tetranitro-9-cyclododecene. There was insufficient sample for any analysis of the green oil but due to its colour it may have been 1-nitroso-2,5,6,9,10-pentanitrocyclododecane

## 8.9 Reactions Between 1,3,5-Hexatriene and Nitrogen Dioxide.

### 8.9.1 Reaction Between 1,3,5-Hexatriene and Nitrogen Dioxide; Reverse Mode of Addition (Experiment 1).

1,3,5-Hexatriene (0.073 g, 0.909 mmol) was dissolved in n-hexane (2.5 cm$^3$) and then added dropwise under nitrogen to an agitated solution of nitrogen dioxide (0.0797 g, 1.732 mmol) in n-hexane (2.5 cm$^3$). During the addition the reaction mixture became warm and a red viscous oil formed. Stirring was continued for 2 h. On standing the red oil solidified. The solvent was removed *in vacuo* to afford a red glasslike substance. The compound formed was insoluble in chlorinated solvents.

A $^1$H n.m.r. spectrum was obtained in d$^6$-DMSO; the spectrum was extremely complex and was thought to be of a complex polymer.

### 8.9.2 Reaction Between 1,3,5-Hexatriene and Nitrogen Dioxide; Reverse Mode of Addition (Experiment 2).

1,3,5-Hexatriene (0.102 g, 1.276 mmol) was added to n-hexane (3 cm$^3$) and then added dropwise to an excess amount of nitrogen dioxide (0.481 g, 10.455 mmol) in n-hexane (5 cm$^3$); the addition was complete after 5 min. During the addition the reaction mixture became warm and a red viscous oil formed. Excess nitrogen dioxide and the solvent were removed *in vacuo* to afford a red solid.

The $^1$H n.m.r. spectrum was complex, this was due to the formation of polymeric products.

### 8.9.3 Reaction Between 1,3,5-Hexatriene and Nitrogen Dioxide, in the Gas Phase; Normal Mode of Addition.

1,3,5-Hexatriene (0.115 g, 1.435 mmol) was put into a round bottom flask (25 $cm^3$), fitted with a gas inlet tube to a dry nitrogen source and a gas outlet tube to a second flask. Nitrogen dioxide (0.9854 g, 21.419 mmol) was added to the second flask which was immersed in an ice bath. Nitrogen gas was now passed through the first flask and the 1,3,5-hexatriene carried over into the second flask. On entering the second flask a mist formed and this condensed on the sides of the flask to form a red viscous oil. The transfer of the 1,3,5-hexatriene to the nitrogen dioxide was complete after 15 min.

The oil formed was dissolved in $d^6$-DMSO and a $^1H$ n.m.r. spectrum obtained. The spectrum was complex and was attributed to the formation of polymeric products.

## 8.10 Reactions Between 1,6-Heptadiene and Nitrogen Dioxide.

The reaction products in these reactions consisted of three types: the products derived from the addition across one double bond, or the addition across both double bonds, or the result of intramolecular cyclisation occurring. The initial reaction mixtures were separated using a mobile phase of 50% ethyl acetate / 50% n-hexane; this separated out the slow tetra adducts from the from the cyclic and di-adducts. The cyclic and di-adducts were then separated using a mobile phase of 15% ethyl acetate / 85% dichloromethane.

### 8.10.1 Reaction Between 1,6-Heptadiene and Nitrogen Dioxide; Normal Mode of Addition (Experiment 1).

Nitrogen dioxide (0.103 g, 2.238 mmol) was dissolved in n-hexane (5 $cm^3$) and added dropwise to an agitated solution of 1,6-heptadiene. 1,6-Heptadiene (0.092 g, 0.977 mmol) was dissolved in n-hexane (5 $cm^3$). The addition was carried out at room temperature and was complete after 1.5 min. Stirring was continued for 2 h. During this time the reaction mixture became cloudy and a green oil formed. The solvent was removed *in vacuo* to afford a yellow oil.

| Percentage yields (by h.p.l.c.):- | |
|---|---|
| 2-hydroxy-1-nitro-6-heptene | 24.2% |
| 1,2-dinitro-6-heptene | 26.8% |
| 2,6-dihydroxy-1,7-dinitro-heptane | 14.8% |
| Unidentified products | 34.2% |

### 8.10.2 Reaction Between 1,6-Heptadiene and Nitrogen Dioxide; Normal Mode of Addition (Experiment 2).

Nitrogen dioxide (0.115 g, 2.499 mmol) was dissolved in n-hexane (5 cm$^3$) and added dropwise to a vigorously stirred solution of 1,6-heptadiene (0.094 g, 0.977 mmol) in n-hexane (5 cm$^3$). The addition was complete after 1.5 h, and was carried out at room temperature. During the course of the reaction a yellow oil formed. The solvent was removed under reduced pressure to yield a yellow oil.

| Percentage yields (by h.p.l.c.):- | |
|---|---|
| 2-hydroxy-1-nitro-6-heptene | 37.4% |
| 1,2-dinitro-6-heptene | 51.5% |
| Unidentified products | 11.1% |

### 8.10.3 Reaction Between 1,6-Heptadiene and Nitrogen Dioxide; Normal Mode of Addition (Experiment 3).

Nitrogen dioxide (0.318 g, 6.912 mmol) was dissolved in n-hexane (10 cm$^3$) and added to a stirred solution of 1,6-heptadiene (0.118 g, 1.227 mmol) in n-hexane (10 cm$^3$). The addition was complete after 6.25 h, and stirring continued for 1 h. A yellow oil formed in the course of the reaction. The solvent was removed *in vacuo* to afford a yellow oil.

Percentage yields (by $^1$H n.m.r.):-

| | |
|---|---|
| 2-hydroxy-1-nitro-6-heptene | 19.2% |
| 1,2-dinitro-6-heptene | 21.3% |
| *cis*-1,2-(nitromethyl)-cyclopentane | 5.4% |
| *trans*-1,2-(nitromethyl)-cyclopentane | 4.6% |
| Unidentified products | 49.5% |

### 8.10.4 Reaction Between 1,6-Heptadiene and Nitrogen Dioxide; Normal Mode of Addition (Experiment 4).

Nitrogen dioxide (0.089 g, 1.934 mmol) was dissolved in n-hexane (10 cm$^3$) and added to a stirred solution of 1,6-heptadiene (0.098 g, 1.018 mmol) in n-hexane (10 cm$^3$). The addition was carried out at room temperature and was complete after 25 h. During the course of the addition a yellow oil formed. On completion of the addition, the solvent was removed under reduced pressure to afford a yellow oil.

Percentage yields (by h.p.l.c.):-

| | |
|---|---|
| 2-hydroxy-1-nitro-6-heptene | 17.1% |
| 1,2-dinitro-6-heptene | 17.9% |
| *cis*-1,2-(nitromethyl)-cyclopentane | 10.3% |
| *trans*-1,2-(nitromethyl)-cyclopentane | 8.9% |
| Unidentified products | 45.8% |

### 8.10.5 Reaction Between 1,6-Heptadiene and Nitrogen Dioxide; Normal Mode of Addition (Experiment 5).

1,6-Heptadiene (0.137 g, 1.424 mmol) was dissolved in carbon tetrachloride (10 cm$^3$). To this agitated solution, nitrogen dioxide (0.107 g, 2.323

mmol) in carbon tetrachloride (10 cm$^3$) was added dropwise for 3 min. A green oil formed during the course of the addition. Stirring was continued for 1 h, and the green oil changed to a yellow oil The solvent was removed *in vacuo* to afford a yellow oil.

Percentage yields (by h.p.l.c.):-

| | |
|---|---|
| 2-hydroxy-1-nitro-6-heptene | 10.7% |
| 1,2-dinitro-6-heptene | 14.9% |
| 2,6-dihydroxy-1,7-dinitro-heptane | 20.5% |
| Unidentified products | 53.9% |

### 8.10.6 Reaction Between 1,6-Heptadiene and Nitrogen Dioxide; Normal Mode of Addition (Experiment 6).

Nitrogen dioxide (0.088 g, 1.913 mmol) was dissolved to carbon tetrachloride (6 cm$^3$) and then added dropwise to a stirred solution of 1,6-heptadiene (0.090 g, 0.936 mmol) in carbon tetrachloride (5 cm$^3$). The reaction mixture was cooled in an ice bath. The addition was complete after 10 min. During the course of the reaction a yellow oil formed. The solvent was removed under reduced pressure to yield a yellow oil.

Percentage yields (by h.p.l.c.):-

| | |
|---|---|
| 2-hydroxy-1-nitro-6-heptene | 11.8% |
| 1,2-dinitro-6-heptene | 45.2% |
| Unidentified products | 43.0% |

### 8.10.7 Reaction Between 1,6-Heptadiene and Nitrogen Dioxide; Reverse Mode of Addition.

1,6-Heptadiene (0.108 g, 1.123 mmol) was dissolved in dichloromethane (10 cm$^3$) and added to a stirred solution of nitrogen dioxide (0.200 g, 4.347 mmol) in dichloromethane (10 cm$^3$). The reaction was maintained at 0 °C by the use of an ice bath. The addition was complete after 35 min, and the reaction stirred for an additional 30 min. The solution was yellow in colour. On removal of the solvent a pale blue oil remained.

Percentage yields (by h.p.l.c.):-

| | |
|---|---|
| 2-hydroxy-1-nitro-6-heptene | 10.7% |
| 1,2-dinitro-6-heptene | 9.6% |
| 2,6-dihydroxy-1,7-dinitro-heptane | 28.6% |
| Unidentified products | 51.1% |

## 8.11 Reactions Between Diallylamine and Nitrogen Dioxide.

The products obtained from the reaction between diallylamine and nitrogen dioxide proved to be very difficult to separate. The problem arose from the difficulty of selecting a suitable h.p.l.c. system to use. The normal phase h.p.l.c. conditions employed gave retention times that were to long to be viable as a separation technique. On changing to the reverse phase h.p.l.c., where polar solvents are used, the reaction mixture could not be retained sufficiently on the column for separation to occur. Owing to these difficulties, h.p.l.c. could not be used to separate the products and so the compounds isolated were obtained by flash chromatography. In some cases, it was then possible to separate or purify the products by h.p.l.c..

### 8.11.1 Reaction of Diallylamine with Nitrogen Dioxide; Normal Mode of Addition (Experiment 1).

Nitrogen dioxide (0.139 g, 3.017 mmol) was dissolved in dichloromethane (10 $cm^3$) and added dropwise to a stirred solution of diallylamine (0.105 g, 1.080 mmol) in dichloromethane (10 $cm^3$). The reaction was kept below 5 °C by use of an ice bath. The addition was complete after 5.5 h. A yellow opaque solution remained. The solvent was removed under reduced pressure to yield a yellow oil. This was then dissolved in ethyl acetate and the sample purified by flash chromatography.

Silica (15 g) was added to a mixture of n-hexane / ethyl acetate (3:1) and the slurry stirred. This was then poured into a column giving a column height of 10.5 cm. The sample was loaded onto the column by pipette and then eluted with n-hexane / ethyl acetate (3:1) solution. One fraction was eluted off the column and this was purified by h.p.l.c..

The mobile phase employed was 65% n-hexane / 35% ethyl acetate. One main product was isolated from the column. The solvent was removed *in vacuo* to afford a yellow oil.

| | |
|---|---|
| Percentage yield (by mass):- | |
| N-nitroso-diallylamine (0.032 g) | 23.7% |

### 8.11.2 Reaction of Diallylamine with Nitrogen Dioxide; Normal Mode of Addition (Experiment 2).

Diallylamine (0.105 g, 1.080 mmol) in dichloromethane (10 cm$^3$) was cooled to between 0-5 °C by an ice bath. To this stirred solution nitrogen dioxide (0.129 g, 2.802 mmol) in dichloromethane (10 cm$^3$) was added dropwise for 6 h. The solvent was removed *in vacuo* to afford a yellow oil.

An analysis by t.l.c. was carried out on this sample using silica plates and a mobile phase of 85% n-hexane / 15% ethyl acetate; it showed only one major product. The sample was cleaned by flash chromatography and purified by h.p.l.c. as described in section 8.11.1.

| | |
|---|---|
| Percentage yield (by mass):- | |
| N-nitroso-diallylamine (0.040 g) | 29.3% |

### 8.11.3 Reaction of Diallylamine with Nitrogen Dioxide, Reverse Mode of Addition.

Diallylamine (0.103 g, 1.060 mmol) was dissolved in dichloromethene (10 $cm^3$), and the resultant solution added dropwise to a stirred solution of nitrogen dioxide (0.550 g, 11.955 mmol) in dichloromethane (10 $cm^3$). The addition was complete after 26 min. The reaction was stirred for an additional 45 min at ice bath temperatures. A pale orange oil precipitated out on the sides of the reaction vessel. The solvent was reduced to a quarter of its original volume and then passed down a silica column. The mobile phase employed was 95% dichloromethane / 5% methanol. Three bands were collected which all consisted of numerous products which could not be separated cleanly from one another.

## 8.12 Reactions Between Allyl Ether and Nitrogen Dioxide.

The reaction products from the following reactions were separated using h.p.l.c.. For reactions involving 1:2 molar ratios of allyl ether:nitrogen dioxide the mobile phase employed was 20% ethyl acetate/80% n-hexane. Where the molar ratios of allyl ether:nitrogen dioxide was 1:4, a mobile phase of 50% ethyl acetate/50% n-hexane was used to remove the more polar components; the non polar products were separated as for a 1:2 molar ratio of reactants.

### 8.12.1 Reaction Between Allyl Ether and Nitrogen Dioxide; Normal Mode of Addition (Experiment 1).

Nitrogen dioxide (0.090 g, 1.956 mmol) was added to n-hexane (10 $cm^3$) and mixed thoroughly. This solution was then added dropwise to a stirred solution of allyl ether (0.073 g, 0.747 mmol) in n-hexane (10 $cm^3$). The addition took place in the dark and the addition was complete after 6.5 h. Stirring was continued for an additional 1 h. The solvent was removed *in vacuo* to afford a yellow oil.

Flash chromatography was carried out on the sample using a stationary phase of silica (10 g) and a mobile phase of 15% ethyl acetate / 85% n-hexane. Only one product was eluted from the column.

Percentage yield (by mass):-

| | |
|---|---|
| 1-nitro-1-propenyl-3,3'-oxy-1'-propene (0.014 g) | 13.3% |

### 8.12.2 Reaction Between Allyl Ether and Nitrogen Dioxide; Normal Mode of Addition (Experiment 2).

Nitrogen dioxide (0.135 g, 2.943 mmol) was added to n-hexane (10 cm$^3$). The resultant solution was added dropwise to a stirred solution of allyl ether (0.110 g, 1.123 mmol) in n-hexane (10 cm$^3$). The addition was complete after 30 min. The reaction temperature was maintained between 0-5 °C by placing the reaction flask in an ice bath. Stirring was maintained for an additional 3 h. The solvent was removed under reduced pressure to afford a yellow oil.

Percentage yields (by h.p.l.c.):-

| | |
|---|---|
| *t*-2,3-(nitromethyl)-tetrahydrofuran | 16.9% |
| *c*-2,3-(nitromethyl)-tetrahydrofuran | 29.7% |
| *t*-2-nitratomethyl-3-nitromethyl-tetrahydrofuran | 13.6% |
| *c*-2-nitratomethyl-3-nitromethyl-tetrahydrofuran | 25.5% |
| Unidentified | 14.3% |

### 8.12.3 Reaction Between Allyl Ether and Nitrogen Dioxide; Normal Mode of Addition (Experiment 3).

To a stirred solution of allyl ether (0.104 g, 1.056 mmol) in dichloromethane (10 cm$^3$) a mixture of nitrogen dioxide (0.139 g, 3.013 mmol) in dichloromethane (10 cm$^3$) was added dropwise for 30 min. Stirring was maintained for a further 3 h. The solvent was removed under reduced pressure to afford a green oil.

Percentage yields (by h.p.l.c.):-

| | |
|---|---|
| *t*-2,3-(nitromethyl)-tetrahydrofuran | 43.9% |
| *c*-2,3-(nitromethyl)-tetrahydrofuran | 15.0% |
| *t*-2-nitratomethyl-3-nitromethyl-tetrahydrofuran | 19.7% |
| *c*-2-nitratomethyl-3-nitromethyl-tetrahydrofuran | 5.7% |
| 2-hydroxy-1-nitro-propyl-3,3'-oxy-1'-propene | 4.3% |
| Unidentified | 11.4% |

### 8.12.4 Reaction Between Allyl Ether and Nitrogen Dioxide; Reverse Mode of Addition (Experiment 1).

Allyl ether (0.109 g, 1.112 mmol) in dichloromethane (10 cm$^3$) was added dropwise over a period of 30 min to a stirred solution of nitrogen dioxide (0.304 g, 6.608 mmol) in dichloromethane (10 cm$^3$). The temperature of the reaction was maintained between 0-5 °C by an ice bath. Stirring was continued for an additional 1 h. The solvent was removed *in vacuo* to afford a yellow oil.

Percentage yields (by h.p.l.c.):-

| | |
|---|---|
| bis (2,3-dinitropropyl) ether | 10.1% |
| 2-hydroxy-1-nitro-propyl-3,3'-oxy-1',2'-dinitropropane | 12.9% |
| bis (2-hydroxy-1-nitro-3,3'-oxy-propane) | 4.1% |
| 2,3-(nitromethyl)-tetrahydrofuran | 11.8% |
| Unidentified (tetrahydrofuran related) | 61.1% |

### 8.12.5 Reaction Between Allyl Ether and Nitrogen Dioxide; Reverse Mode of Addition (Experiment 2).

To a stirred solution of nitrogen dioxide (0.515 g, 11.192 mmol) in dichloromethane (10 cm$^3$) at ice bath temperatures, allyl ether (0.103 g, 1.049 mmol) in dichloromethane (10 cm$^3$) was added. The addition was complete after 30 min. Stirring was continued for an additional 2 h. The solvent was removed under reduced pressure to afford a yellow oil.

Percentage yields (by h.p.l.c.):-

| | |
|---|---|
| bis (1,2-dinitro-3,3,-oxy-propane) | 13.1% |
| 2-hydroxy-1-nitro-propyl-3,3'-oxy-1',2'-dinitropropane | 28.3% |
| bis (2-hydroxy-1-nitro-3,3'-oxy-propane) | 6.0% |
| 2,3-(nitromethyl)-tetrahydrofuran | 10.6% |
| 2-nitratomethyl-3-nitromethyl-tetrahydrofuran | 4.2% |
| Unidentified (linear adducts) | 23.6% |
| Unidentified | 14.2% |

## 8.13 Preparation of the $^{15}$N Labelled Compounds.

This section deals with the preparation of the $^{15}$N labelled compounds used in the C.I.D.N.P. reactions carried out in Chapter 6. The experimental details for these reactions are also given in this section.

### 8.13.1 Preparation of Labelled $^{15}$N-Lead Nitrate.

$^{15}$N-Nitric acid (1.000 g, 15.623 mmol in 1.68 g sol) was added to water (10 cm$^3$), and mixed vigorously to ensure that mixing had occurred. To this stirred solution lead oxide (1.797 g, 8.051 mmol) was added slowly over a period of 30 min. Stirring was continued for an additional 2.7 h until no more lead oxide had reacted. The reaction mixture was filtered to remove any unreacted lead oxide, and the residue was washed with water (3 x 5 cm$^3$) The water was then removed under reduced pressure at a temperature of 55 °C for 26 h. This yielded a white powder (2.617 g). This was labelled $^{15}$N-lead nitrate (yield 100%).

### 8.13.2 Preparation of labelled $^{15}$N-Nitrogen Dioxide.

$^{15}$N-Lead nitrate (0.1868 g, 0.560 mmol) was added to a round bottom flask (10 cm$^3$) fitted with a gas inlet, and a side arm to a trap with a gas outlet. The system was purged with argon for 30 min. The trap was then immersed in a cardice bath at -80 °C, and the lead nitrate heated strongly. Brown fumes of nitrogen dioxide were evolved and white crystals formed in the trap. Heating was stopped and a slow flow of argon allowed to flow through the system, this flushed out any nitrogen dioxide to the trap. The argon was turned off and the lead nitrate heated strongly again. The process was repeated until no more fumes were seen to evolve from the lead nitrate. A yellow solid remained of lead oxide. The trap was reweighed to determine the amount of nitrogen dioxide formed (0.043 g, 0.934 mmol, yield 83.4 %).

### 8.13.3 Preparation of $^{15}$N-Nitrobenzene.

Acetic anhydride (25 cm$^3$) was stirred in a round bottom flask cooled in a ice/water bath. $^{15}$N-Nitric acid (1.000 g, 15.623 mmol in 1.68 g sol) was added dropwise to the acetic anhydride to give a clear solution. To the resultant solution benzene (1.341 g, 17.167 mmol) was added followed by concentrated sulphuric acid (1.5 cm$^3$). The reaction was stirred overnight and allowed to warm to room temperature.

The reaction mixture was then poured into a beaker of iced water (≈10 cm$^3$). The aqueous layer was washed with dichloromethane (3 x 25 cm$^3$) and the organic layers combined and sodium hydrogen carbonate added until effervescence stopped. The organic layer was then dried over magnesium sulphate for 24h. The mixture was filtered and the solvent removed *in vacuo* to yield a pale yellow oil (1.634 g, 84.3%).

### 8.13.4 To Observe the C.I.D.N.P. Effects in the Reaction Between $^{15}$N-Nitrogen Dioxide and Allyl Ether.

$^{15}$N-Lead nitrate (0.061 g, 0.183 mmol) was added to a round bottom flask (5 cm$^3$) fitted with a tapped gas inlet and a side arm. The flask was purged with dry argon and then heated strongly. The $^{15}$N-nitrogen dioxide evolved was bubbled into deuterochloroform (0.25 cm$^3$) immersed in a acetone/cardice bath. The heating was stopped and the flask again purged with argon to remove any remaining $^{15}$N-nitrogen dioxide. This process of heating and purging was carried out three times.

Allyl ether (0.0153 g, 0.156 mmol) was added to deuterochloroform (0.25 cm$^3$) and added to a dry n.m.r. tube (507-pp). The n.m.r. tube now had an internal reference tube added containing ($^{15}$N)-nitrobenzene. The $^{15}$N-nitrogen dioxide solution was then added by syringe to the n.m.r. tube and the mixture shaken quickly (≈2 s) then immersed in liquid nitrogen to freeze out the reaction.

The n.m.r. tube was then placed while still frozen into a pre-shimmed and locked n.m.r. spectrometer. The n.m.r. tube was then allowed to warm up within the spectrometer and the acquisitions started immediately the tube had been inserted. The spectra were recorded on ten pulses using an acquisition time of 5 s and a pulse delay of 12 s.

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