# STUDIES ON
# ENDO-2,4-ETHYLENETETRABORANE

BY

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A THESIS SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF

MASTER OF SCIENCE
in the Department
of
Chemistry

Accepted for the
Faculty of Graduate
Studies

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We accept this thesis as conforming
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## ABSTRACT

The results of the thermal decomposition and the reactions of endo-2,4-ethylenetetraborane are described. About 40% endo-2,4-ethylenetetraborane decomposes when left at 30 °C for one hour. The main products of the thermal decomposition are diborane and hydrogen. The reactions of endo-2,4-ethylenetetraborane with diethylether, tetrahydrofuran, ammonia and trimethylamine are described. The results are discussed and compared with the corresponding tetraborane reactions. It is concluded that reactions of endo-2,4-ethylenetetraborane with these Lewis bases result in B-C bond cleavage followed by intermolecular reactions to yield polymeric compounds and n-butane. The boron-hydrogen framework cleaves to give products analogous to those formed in the corresponding reactions of tetraborane.

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* From designs by Dr. S.G. Gibbins, Department of Chemistry, University of Victoria, Victoria, British Columbia, Canada.

## ACKNOWLEDGEMENTS

I wish to express my appreciation to Dr S G Gibbins for his encouragement and guidance.

Many thanks are due to Dr Keith Dixon for his generous assistance and many useful discussions,especially in the preparation of this thesis.

I am indebted to the technicians and other staff of the department; particularly the glassblowers who were often called at very short notice.

The contributions of other faculty members and fellow graduate students are gratefully recognized.

I would like to acknowledge the financial support of the University of Victoria.

Thank you,Liz-Love Minus Zero/No Limit

# CHAPTER 1 : INTRODUCTION

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## 1.1. Nomenclature

The compound represented by the structure shown in Fig 1

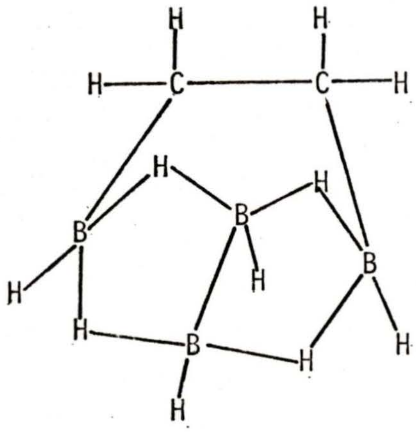


Fig 1 : Endo-2,4-ethylenetetraborane

was called dimethylenetetraborane by Harrison et al(1). Shapiro et al(2) called the compound 2,4,dimethylenetetraborane. In 1968(3) the American Chemical Society approved the name endo-2,4-ethylenetetraborane. Recent communication with the American Chemical Society has indicated that the name of the compound will probably be changed in the near future to endo-2,4-(1,2-ethanediyl)tetraborane. In this thesis the compound will be called endo-2,4-ethylenetetraborane.

## 1.2. History of the Boranes

In 1809, Davy published a paper which included the first description of a borane(4). He was studying the reaction of dilute hydrochloric acid on the mass obtained from the reduction of boric oxide by potassium. Davy obtained a gas which was mainly hydrogen but had a disagreeable odour and burnt with a blue flame, tinged with green. In the next one hundred years many workers, including two Nobel laureates, investigated the gases produced by similar reactions. Various formulae were assigned to the boranes and some speculations on the structure were made.

The chemistry of the boranes really began with the work of Alfred Stock. It has been said that before Stock everything written about the boranes was incorrect. In a series of papers from 1912 to 1936, Stock and his co-workers prepared and chemically characterized the following boranes : $B_2H_6$, $B_4H_{10}$, $B_5H_9$, $B_5H_{11}$, $B_6H_{10}$ and $B_{10}H_{14}$. Stock is credited with the development of the glass vacuum line and the techniques for using it. His pioneering work has, without doubt, made him the 'father of borane chemistry'. Stock reviewed his work in 1933(5).

In 1930, Schlesinger started to investigate boranes. The discovery of aluminium borohydride, in 1939, led to the first relatively quantitative synthesis of a borane. Schlesinger and Burg reviewed this work in 1942(6).

Immediately following World War II, the Americans initiated studies on the use of boranes as potential fuels for air-breathing engines. The boranes $B_6H_{12}$, $B_8H_{12}$, $B_8H_{18}$, $B_9H_{15}$, $B_{10}H_{16}$, $B_{18}H_{22}$, iso-$B_{18}H_{22}$ and $B_{20}H_{16}$ were prepared and characterized.

It soon became apparent that to obtain the desired physical characteristics the fuel would probably have to be alkylated derivatives of boranes. Although most of the work was carried out on pentaborane(9) and decaborane(14), almost every aspect of boron chemistry was studied. In the late 1950's,undesirable properties of borane fuels, such as difficulty in handling, high cost and a solid oxidation product ($B_2O_3$), caused the programs to end. The use of boranes as fuels was abandoned.

Since then the pace of borane research has slowed. At the present time most emphasis is being placed on the mechanisms of the reactions in the hope that our understanding of borane chemistry will, one day, be more systematic.

## 1.3. Chemistry of the Boranes

### 1.3.1. Introduction

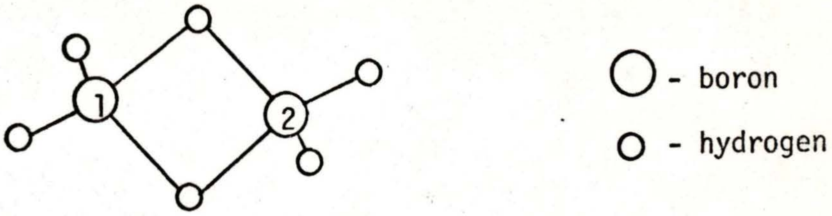
Boron can be viewed as a rare element; there are 3 ppm boron in the earth's crust, compared with 28 ppm yttrium, 6.4 ppm gadolinium and 4.5 ppm dysprosium. Fortunately, geochemical processes have greatly concentrated boron, and, from the standpoint of economic availability, boron is not a rare element. The major boron reserves are in California, United States of America. The principal ores of economic importance are borax ($Na_2B_4O_5(OH)_4 \cdot 8H_2O$) and kernite ($Na_2B_4O_5(OH)_4 \cdot 2H_2O$).

Although boron has a $2s^2 2p^1$ electronic structure, it is always trivalent and never monovalent. This is because the total energy released in the formation of three bonds in a $BX_3$ compound exceeds the energy of formation of one bond in a BX compound by more than enough to provide for promotion of boron to a hybridized valence state of the $sp^2$ type. Examples of $BX_3$ compounds are the trihalides, boric acid and alkylboranes of the type $BR_3$. This leaves one low energy orbital vacant owing to a shortage of electrons. A consequence of this is the ability of $BX_3$ compounds to behave as Lewis acids; this is achieved by approximately $sp^3$ hybridization. The vacant orbital also plays a part in another important aspect of boron chemistry, namely in the bonding of electron deficient compounds. The simplest example of this phenomenon is diborane which has a dimeric structure, $B_2H_6$, having electron deficient hydrogen bridges. This is explained more fully in Section 1.3.2. Free borane, $BH_3$, has not been shown to exist.

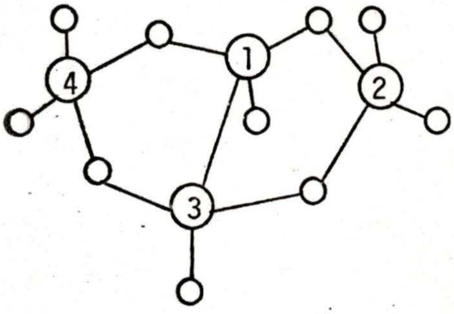
The inorganic and organic chemistry of boron has been extensively investigated as has the chemistry of the carboranes - these are borane cage molecules containing carbon in the skeletal framework. Most work has, however, been carried out on the hydrides of boron (boranes) and their derivatives.

### 1.3.2. Structure and Bonding in the Boranes

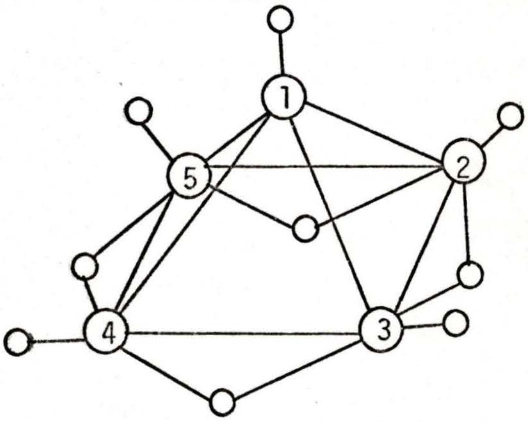
The structures of some boranes are shown in Fig 2. It is common practice to consider the borane structures as fragments of an icosahedron (Fig 3); these include $B_4H_{10}$, $B_5H_{11}$, $B_6H_{10}$, $B_6H_{12}$, $B_8H_{12}$ and $B_9H_{15}$. It should be noted that five faces of an icosahedron with a common vertex form a pentagonal pyramid. Bridge hydrogens generally lie above the edges of the icosahedral fragment, each hydrogen being bonded to two borons at adjacent vertices. Each boron is attached to



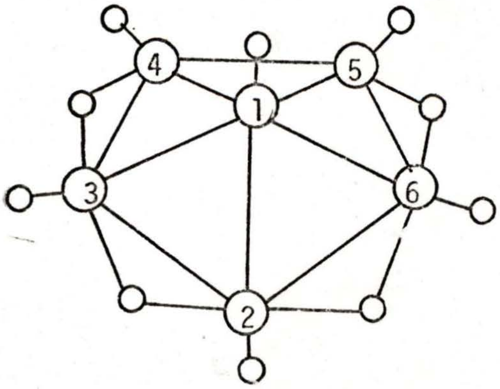
Diborane



Tetraborane



Pentaborane(9)



Hexaborane(10)

Fig 2 : The Structures of some Boranes
(taken from 'Boron Hydrides' by W. N. Lipscomb)

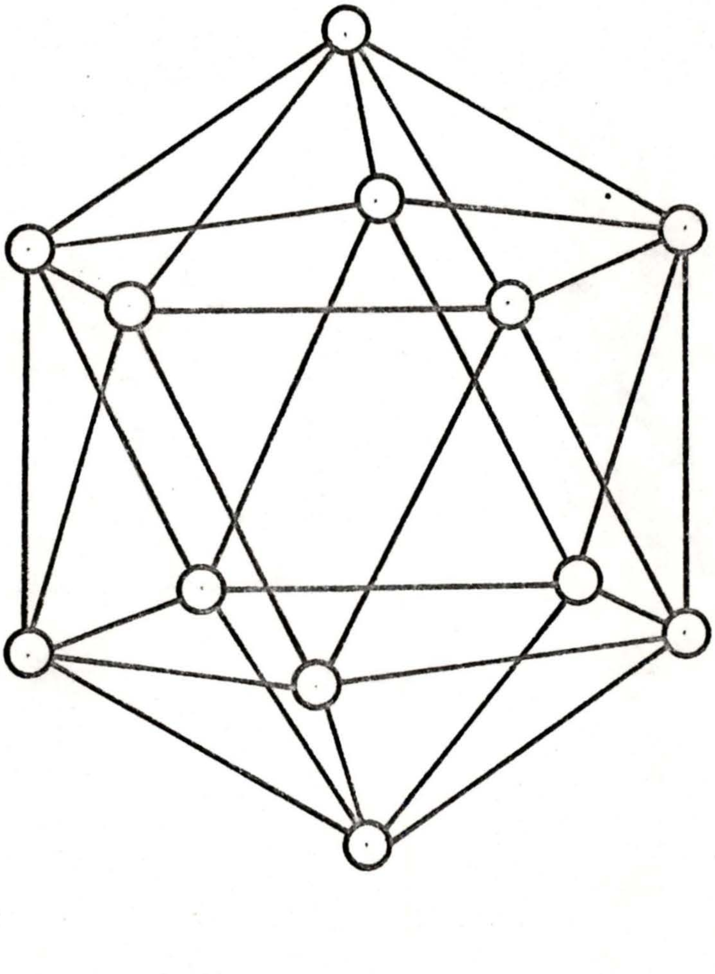


Fig 3 : Icosahedron

a singly-bonded hydrogen which points directly away from the centre of the icosahedron. Boron atoms with one or two other boron atoms as near neighbours have a second singly-bonded hydrogen. Pentaborane(9) is an exception in that it has a square pyramidal structure (which is a segment of an octahedron).

Boranes have been termed electron-deficient compounds because there are more adjacent pairs of atoms, close enough together that they must be regarded as bonded, than there are electrons necessary to provide an electron-pair bond for each pair of atoms. This arises from the fact that each boron atom has four available orbitals (2s, $2p_x$, $2p_y$ and $2p_z$) which it seeks to use in bonding but only three valence electrons. In boranes the two-electron two-centre bond concept requires modification. From a suggestion by Longuet-Higgins, Lipscomb(7) developed the concept of the two-electron three-centre bond. In such a bond the three component atomic orbitals may combine to form a bonding orbital, a nonbonding orbital and an antibonding orbital (Fig 4).

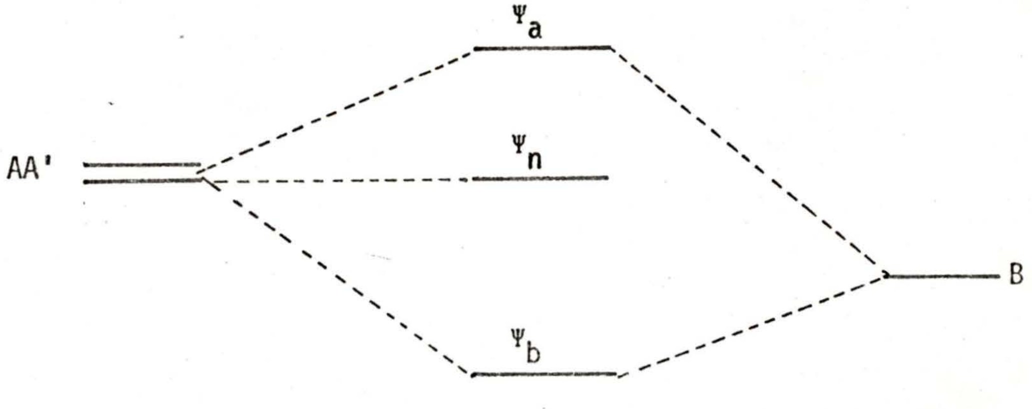


Fig 4 : Energy Level Diagram for 3-centre Molecular Orbitals

The two electrons occupy the bonding orbital. There is no a priori reason to limit multicentre bonding to three centres. In fact, multicentre bonding is necessary to describe the bonding in the more symmetrical species. However, in the simpler boranes it is more convenient to think of bonding in these compounds as arrays of localized two or three-centre bonds. Lipscomb postulated three idealized types of three-centre bonds, these are shown in Fig 5 :-

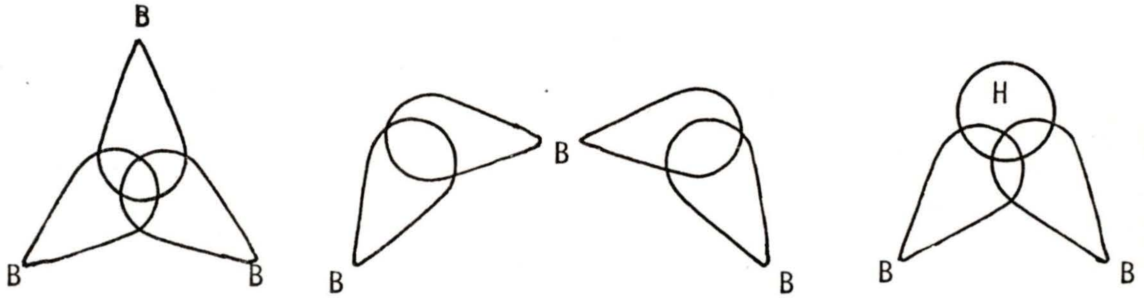


Fig 5 : Atomic Orbital Arrangements that Constitute 3-centre Bonds

The boron atoms employed in these formulations are normally considered to be $sp^2$ or $sp^3$ hybridized as the geometry of the system demands. Lipscomb pointed out that the approximate charge distribution can be obtained by placing one electron of the bonding pair on the hydrogen atom of the B-H-B bridge or the $sp^2$ hybridized boron atom of the 'open' three-centre B-B-B bond. The other electron is equally distributed between the terminal boron atoms. In the case of the closed three-centre bond, the electron pair is distributed equally between the three boron atoms.

In tetraborane, the $B_2$ and $B_4$ atoms each form two external B-H bonds and two B-H-B three-centre bridge bonds. These four bonds completely account for the four $sp^3$ hybrids and the three valence electrons of $B_2$ and of $B_4$. The $B_1$ and $B_3$ boron atoms each form only one external B-H bond and two B-H-B three-centre bonds. These bonds account for three of the boron orbitals and two valence electrons of $B_1$ and of $B_3$, and hence leave a single orbital and one electron which may be used to form essentially a normal single bond between $B_1$ and $B_3$. The configuration of the three hydrogens surrounding borons $B_1$ and $B_3$ is approximately trigonal. To a first approximation each boron in tetraborane may be considered electrically neutral. The angle $B_2B_1B_4$ is $98^o$.

Dickerson and Lipscomb$^{(8)}$ developed a topological method to provide a solution to the problems of describing the best bonding scheme for a particular species and allowing an a priori prediction of boranes and their derivatives. The basis of their method lies in the recognition of similar and almost invariant structural features that are often present in borane species. All possible bonding schemes are obtained in terms of two and three-centre orbital interactions. Finally, certain of the bonding schemes are rejected on the grounds of geometrical considerations or from the fact that known molecular geometries have not established a precedent for the interaction. This method has been successful in dealing with molecules of low symmetry since these molecules provide the best models for localized bonding. As the complexity or the symmetry of the boranes increases, the localized three-centre bond description becomes less adequate and finally fails to give useful results. This problem has been circumvented with both the valence bond and the molecular orbital methods. A third method which may be described as an approximate molecular orbital method has proved to be useful in describing highly symmetrical species such as $B_{10}H_{10}^{2-}$ and $B_{10}H_{12}^{2-}$(7).

### 1.3.3. Reactions of the Boranes

A detailed review of the chemistry of the boranes would be much too long for inclusion here; a brief summary will suffice. It must be pointed out that the following account of the chemistry of the boranes is designed primarily to aid the discussion section and the emphasis is placed with this in mind.

The reactions of the boranes are divided into six types - substitution, cleavage, loss of a proton, loss of molecular hydrogen, reactions with alkenes and other reactions. The reactions of boranes with alkenes are really special types of substitution reactions. Substitution reactions involve a boron-terminal hydrogen bond, whereas the remaining reactions involve the boron-hydrogen framework. The present work is concerned mainly with cleavage reactions.

### 1.3.4. Substitution Reactions

Most work in this field was in attempts to produce alkylated boranes(9). The replacement of a terminal hydrogen atom by an alkyl group in the presence of aluminium chloride is well established. The position of substitution is as expected from charge distribution calculations. Substitution of a terminal hydrogen by a halogen atom has been observed. In the chemistry of tetraborane, a chloro(10) and a 2-bromo(11) derivative have been made but both are too unstable to characterize. Various mono and dimethyltetraboranes have been made in small amounts(12, 13, 14, 15). The above plus endo-2,4-ethylenetetraborane comprise all the substitution products of tetraborane known at the present time.

### 1.3.5. Cleavage Reactions

Cleavage reactions are discussed in greater detail in section 3.3.1. The term 'cleavage' in regard to the reactions of the boranes was first used by Shore and Parry(16). They applied this term to the breaking of the double bridge hydrogen bond in diborane. Shore and Parry noted that Lewis bases cleaved diborane in one of two ways which they termed symmetrical and unsymmetrical cleavage.

In symmetrical cleavage the molecule is split to yield two $BH_3$ fragments as shown in Fig 6, ie :-

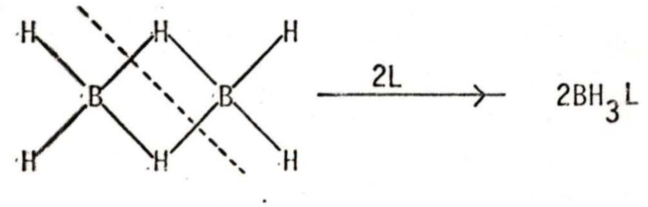


Fig 6 : Symmetrical Cleavage of Diborane

In the unsymmetrical cleavage of diborane the bonds are broken as shown giving rise to a dihydroboron (1+) ion ($BH_2^+$) and a tetrahydroborate ion ($BH_4^-$) as shown in Fig 7, ie :-

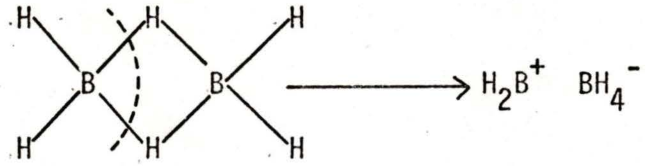


Fig 7 : Unsymmetrical Cleavage of Diborane

This terminology was extended to tetraborane. Symmetrical cleavage results in borane ($BH_3$) and triborane(7) ($B_3H_7$) fragments and unsymmetrical cleavage results in the formation of dihydroboron (1+) and octahydrotriborate (1-) ($B_3H_8^-$) ions. Cleavage, both symmetrical and unsymmetrical(17), has been observed in the reactions of pentaborane(11). Symmetrical cleavage produces borane and triborane(7) fragments and unsymmetrical cleavage produces the dihydroboron (1+) ion and the nonahydrotetraborate (1-) ion ($B_4H_9^-$).

Kodama and Parry(18) describe the cleavage of pentaborane(9). Symmetrical cleavage results in the formation of borane and tetraborane(6) ($B_4H_6$) fragments and unsymmetrical cleavage produces dihydroboron (1+) and heptahydrotetraborate (1-) ($B_4H_7^-$) ions. Kodama and Parry suggest that the term 'symmetrical cleavage' and 'unsymmetrical cleavage' be applied to reactions which produce borane fragments and dihydroboron (1+) respectively. They also propose a new term 'anomalous cleavage' which is that combination of the above processes or another process which generates products containing other borane fragments.

Most Lewis bases including ethers, amines, thiophene, alkyl sulphides and phosphines cleave boranes symmetrically; ammonia and metal hydrides and amides cleave them unsymmetrically.

### 1.3.6. Reactions Involving Loss of a Proton

Many of the early attempts to account for the electron deficiency of diborane involved the suggestion that the molecule contains potentially acidic hydrogens culminating in Pitzer's bridge model(19). Lipscomb(20) cited n.m.r. and theoretical calculations as evidence that the bridge hydrogens in diborane are more negatively charged than the terminal hydrogens. Lipscomb stated that the bridge hydrogens of other boranes appear to be more acidic but remarked that it is because a much less drastic change in structure will result if a bridge proton is lost than if a terminal proton is removed. Edwards and Hough, in an unpublished work quoted in Ref 7, pg 172, showed that decaborane(14) has acidic hydrogens by preparing $NaB_{10}H_{13}$. That bridge hydrogens are involved has been shown by many independent groups of which only Hawthorne(21) published his findings in the literature. Parry(22) slowly reacted diborane and ammonia at -120 $^{o}C$ and noted a drop in the diborane pressure resulting from compound formation. As some diborane and ammonia could be separated from the mixture he concluded that the compound was not the conventional ammoniate of diborane. Parry and Shore(23) pictured such an addition as resulting from ammonia co-ordination to the weakly acidic hydrogen located in the bridge. Kodama(24) made similar postulates concerning the tetraborane-ammonia system.

In 1967, Gaines and Iorns published a note(25) which described the preparation of the octahydropentaborate (1-) ion ($B_5H_8^-$) by reacting pentaborane(9) with methyl or n-butyllithium. Reaction of lithium octahydropentaborate (1-) with deuterium chloride generated μ-deuteropentaborane(9). The octahydropentaborate (1-) ion was also produced by Onak et al(26) by the reaction of pentaborane(9) and metal hydrides and by Shore et al(27) using a reaction similar to that of Gaines. It appears that pentaborane(9) will readily lose a bridge hydrogen, indicating that the bridge hydrogen is acidic. In 1969, Shore et al(28) reported the formation of the nonahydrohexaborate (1-) ($B_6H_9^-$) ion from the reaction of hexaborane(10)and potassium or sodium hydride, or methyllithium. In 1970, Parry and Edwards' suggestion(22) concerning the interaction of bridge hydrogens and ammonia was supported by the paper of Shore et al(29) which showed that hexaborane(10) and ammonia reacted at low temperatures to form the nonahydrohexaborate (1-) ion. Bond and Pinsky(30) reported in 1970 the formation of lithium nonahydrotetraborate (1-) ($B_4H_9^-$) from the low temperature reaction of methyllithium and tetraborane. Ammonia has been shown by Johnson and Shore to deprotonate tetraborane at low temperatures(31). Shore also gives evidence for the deprotonation of pentaborane(11) by ammonia. Kodama and Parry(28) have deprotonated pentaborane(11) using lithium alkyls.

It seems clear that the bridge protons of the lower boranes are acidic but there is no evidence for the deprotonation of diborane.

### 1.3.7. Reactions Involving Loss of Molecular Hydrogen

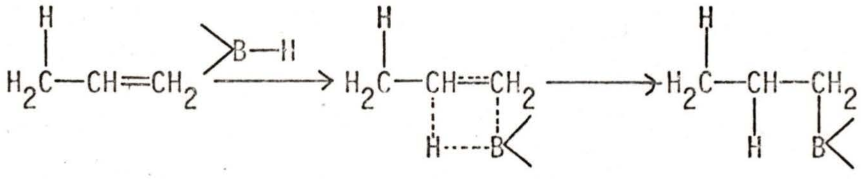
All the boranes will lose hydrogen if the temperature is raised sufficiently. In general, boranes with the formula $B_nH_{n+6}$ lose hydrogen easier than those represented by $B_nH_{n+4}$. Hydrogen loss usually becomes more difficult as the size of the boron framework increases.

### 1.3.8. Reaction of Boranes with Alkenes

Where no reference is given in this section, the reader is referred to Ref 9, Chapter VIII.

Stock found that an explosion occurred when ethylene and diborane were heated to 100 °C. He noticed, however, that products could be condensed when the reactants were moderately heated. It was found later that diborane does not react with ethylene at room temperature but the addition of Tygon shavings does cause a pressure drop. Many methods were later used to accelerate this reaction. The typical product consisted of various ethyldiboranes and triethylborane. Triethylborane was formed by a process which Brown called 'hydroboration'(32).

The reaction of borane with alkenes offers many useful synthetic routes to the organic chemist. The mechanism for the initial hydroboration reaction is thought to be :-



The borane is generated from the reaction of lithium tetrahydroborate and trifluoroborane. The boron fragment attaches itself to the least substituted carbon. G.l.c. examination of the products of pyrolysis of diborane and ethylene indicate the presence of mono-to pentaethylpentaboranes and mono-to tetraethyldecaboranes. Diborane was found to react with 2-butene to give 2-butylborane. The reaction of diborane with butadiene gives various products, depending upon the conditions when the reaction is performed. In the vapour phase(33) the major product was 1,2-tetramethylenediborane :- (Fig 8)

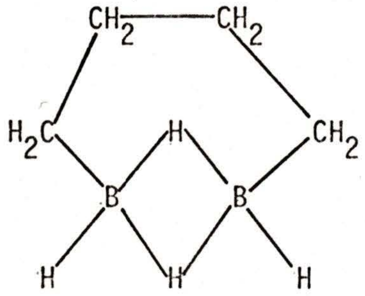


Fig 8 : 1,2-tetramethylenediborane

and the minor product was 1,2-(1'-methyltrimethylene)diborane, Fig 9 :-

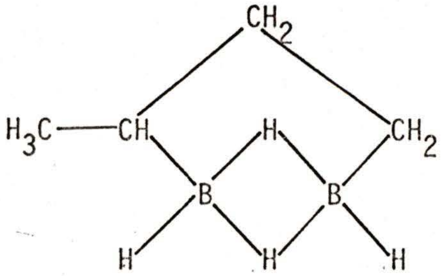


Fig 9 : 1,2-(1'-methyltrimethylene)diborane

The only reported reaction of tetraborane and an alkene is the one resulting in the formation of endo-2,4-ethylenetetraborane(1). Ethylene and pentaborane(9) do not react at temperatures up to 100 °C and pressures up to 1,000 psi. If, however, aluminium chloride was present reaction did occur at 140 °C leading to the formation of an ethylpentaborane. Various alkenes were reacted using a Friedel-Craft catalyst; only monoalkylated derivatives were obtained. Ethylene and pentaborane(11) react at 25 °C to give ethylpentaborane(11)(34) and various by-products including endo-2,4-ethylenetetraborane. As endo-2,4-ethylenetetraborane was not found to be a product of the decomposition of ethylpentaborane(11) it was postulated to have been formed via the following reaction :-

$$B_5H_{11} \longrightarrow B_4H_8 + BH_3$$

Decaborane reacts with ethylene at 100 °C with aluminium chloride as a catalyst and at 232 °C without a catalyst to give ethylated decaborane.

### 1.3.9. Other Reactions

This classification includes rearrangements, disproportionations, oxidation-reduction reactions and various reactions of the B-B bond. A more detailed account is found in Ref 7.

## 1.4. The Problem

In 1960, Harrison et al reported that they had prepared a new compound, later named endo-2,4-ethylenetetraborane, from the reaction of tetraborane and ethylene in a hot-cold reactor(1). From wet analysis and infrared data they concluded the compound contained a dimethylene bridge between borons 2 and 4 in, essentially, a tetraborane skeleton. Hydrolysis of this compound yielded ethylene glycol and methanolysis yielded the already known compound $(CH_3O)_2B(CH_2)_2B(CH_3O)_2$. Harrison gave two equations for the formation of these compounds and stated that the amount of hydrogen evolved supported the stoichiometry of one of them :-

$$C_2H_4B_4H_8 + 10H_2O \longrightarrow HOCH_2CH_2OH + 9H_2$$

$$C_2H_4B_4H_8 + 10CH_3OH \longrightarrow (CH_3O)_2B(CH_2)_2B(OCH_3)_2 + 9H_2$$

As neither equation was balanced this support was rather weak. Harrison pointed out that boranes which contain a $BH_2$ group have a doublet at about 4μ in the infrared spectrum, whereas boranes which contain only BH groups have a singlet. Thus, tetraborane has a doublet at ~4μ and endo-2,4-ethylenetetraborane should have a singlet. The spectrum in Harrison's paper shows "... the small indication of a doublet ...". Harrison chose to interpret this as arising from the two different types of B-H bonds. Absorption in the 8-9μ region in tetraborane arises from the $BH_2$ groups. This absorption was absent in the spectrum of endo-2,4-ethylenetetraborane. Later work confirmed the structure through mass spectrometric and n.m.r. data(2, 37, 38). The mass spectrum indicated that there were four borons in the molecule; it also showed very small peaks at p and (p - 1) mass numbers. This, the authors noted, is a characteristic of tetraborane. This feature is also found in the mass spectrum of pentaborane(11) and is usually considered to be a property of boranes containing a $BH_2$ group. Endo-2,4-ethylenetetraborane does not contain any $BH_2$ groups. The $^{11}B$ n.m.r. spectrum was similar to that of tetraborane. The triplet (arising from $BH_2$ groups) of the tetraborane spectrum was absent and was replaced by a doublet (indicating BH groups) which was shifted downfield. The downfield shift is characteristic of alkyl substitution. The proton n.m.r. consisted mainly of a large singlet which was believed to have arisen from the methylene protons.

Although nearly every text on the boranes includes a description of endo-2,4-ethylenetetraborane, calling the compound 'unusual', 'intriguing' and 'curious', very little is known about it. A carbon bridge between boron atoms in a borane skeleton is quite rare in borane chemistry. Shapiro et al reported the formation of 1,2-tetramethylenediborane and 1,2(1'-methyltrimethylene) diborane from the vapour phase reaction of diborane and butadiene(33). Thermal decomposition of these diborane derivatives resulted in diborane; little else is known about them.

Endo-2,4-ethylenetetraborane is considered to be an alkylated derivative of tetraborane because the tetraborane skeleton remains intact. If endo-2,4-ethylenetetraborane is a derivative of tetraborane then it is reasonable to compare its chemistry with that of tetraborane. The chemistry of tetraborane is considered to be, in many ways, analogous to the chemistry of diborane.

One purpose of this work was to find out how the dimethylene bridge would affect what is fundamentally a tetraborane molecule. As the B-C-C-B moiety remained intact upon methanolysis, it was possible that at low temperatures the bridge would inhibit the complete cleavage of the compound by Lewis bases and that some intermediates might be detected which would help in our understanding of cleavage. It was conceivable that, if the $B_2$-C-C-$B_4$ moiety remained intact, it would provide a means of distinguishing borons 1 and 3 from borons 2 and 4. In general terms the work was carried out to help answer the question, 'how does endo-2,4-ethylenetetraborane react?'

Before reacting endo-2,4-ethylenetetraborane with Lewis bases it was necessary to ascertain how quickly the compound thermally decomposed and what were the products of the decomposition. Without such information there would be considerable doubt as to how long reaction mixtures could be left at various temperatures without significant decomposition of the endo-2,4-ethylenetetraborane. There would also be great uncertainty as to whether a reaction product was the result of a reaction with a Lewis base or was the result of decomposition of the endo-2,4-ethylenetetraborane.

An example of the complexity of the reactions of boranes is shown by the reaction of diborane and ammonia in Fig 10. It is often difficult to predict the products of borane reactions and unwise to discuss reactions unless the conditions are rigidly specified.

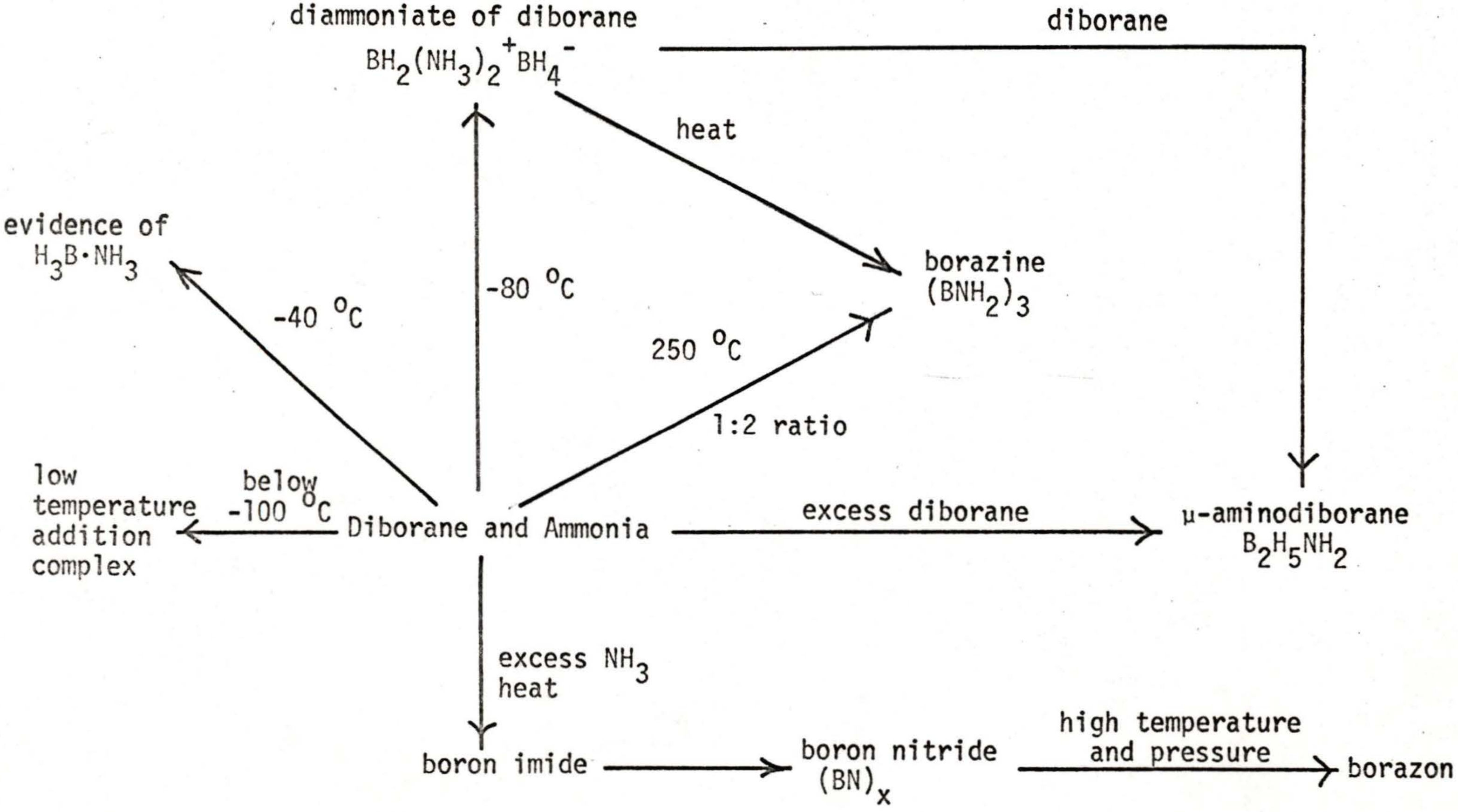


Fig 10: Reactions of Diborane and Ammonia

# CHAPTER 2 : EXPERIMENTAL

# Chapter 2 : Experimental

## 2.1. Introduction

Most of the work was carried out in a standard glass vacuum system(39) equipped with greased stopcocks and mercury float valves. The amounts of volatile materials were determined by pressure measurements in calibrated volumes. In general, a background pressure of about $10^{-4}$ mmHg was adequate for the reactions. The specialized pieces of apparatus will be described in sections on the relevant preparations.

## 2.2. Techniques Employed

### 2.2.1. Boron N.M.R.

$^{11}B$ n.m.r. spectra were recorded on a Varian HA-60 spectrometer equipped with a variable temperature controller. The shifts were measured from trifluoroborane diethyletherate (used as an external standard). It was found that the signal of the trifluoroborane diethyletherate, in some cases, overlapped the resonance of the sample and could make interpretation of the spectrum difficult. In these instances another spectrum was run with no standard. In one experiment a tube interchange technique was used.

### 2.2.2. Proton N.M.R.

The proton n.m.r. spectra were recorded on a Perkin-Elmer R12A spectrometer. This instrument operates at 60 MHz and incorporates a permanent magnet. Tetramethylsilane was used as a standard. A tube interchange technique was employed.

### 2.2.3. Mass Spectrometry

All the spectra were recorded on a Hitachi Perkin-Elmer RMU-6E double-focusing spectrometer at an ionization potential of 70 eV. In most cases the samples were gaseous.

### 2.2.4. Infrared Spectrometry

The spectra were recorded on Beckman IR4 and Perkin-Elmer 337 spectrophotometers using a 100 mm gas cell with sodium chloride windows. Spectra were recorded between 1 and 15μ and were calibrated against a polystyrene film. The pressure in the cell was generally about 10-50 mmHg.

### 2.2.5. Gas Liquid Chromatography

A Varian Aerograph Autoprep 700 chromatograph with a gas sampling valve was used to separate the boranes and to check their purity. The column was 5' x 3/8" stainless steel, the stationary phase was 20% Apiezon L (Varian Aerograph) on Chromosorb P (Varian Aerograph) and the carrier gas was helium at a flow rate of 200 ml/min. The column temperature was 30 °C, the inlet temperature and detector temperature both were 50 °C. Under these conditions endo-2,4-ethylenetetraborane was eluted in about forty minutes; diborane was eluted in about five minutes; tetraborane in about fifteen minutes and the pentaboranes in about twenty-five minutes.

In preparative g.l.c. the impure sample was held in a special tube (Fig 11). The separated compounds were retained in special collection tubes (Fig 12) cooled to -196 °C.

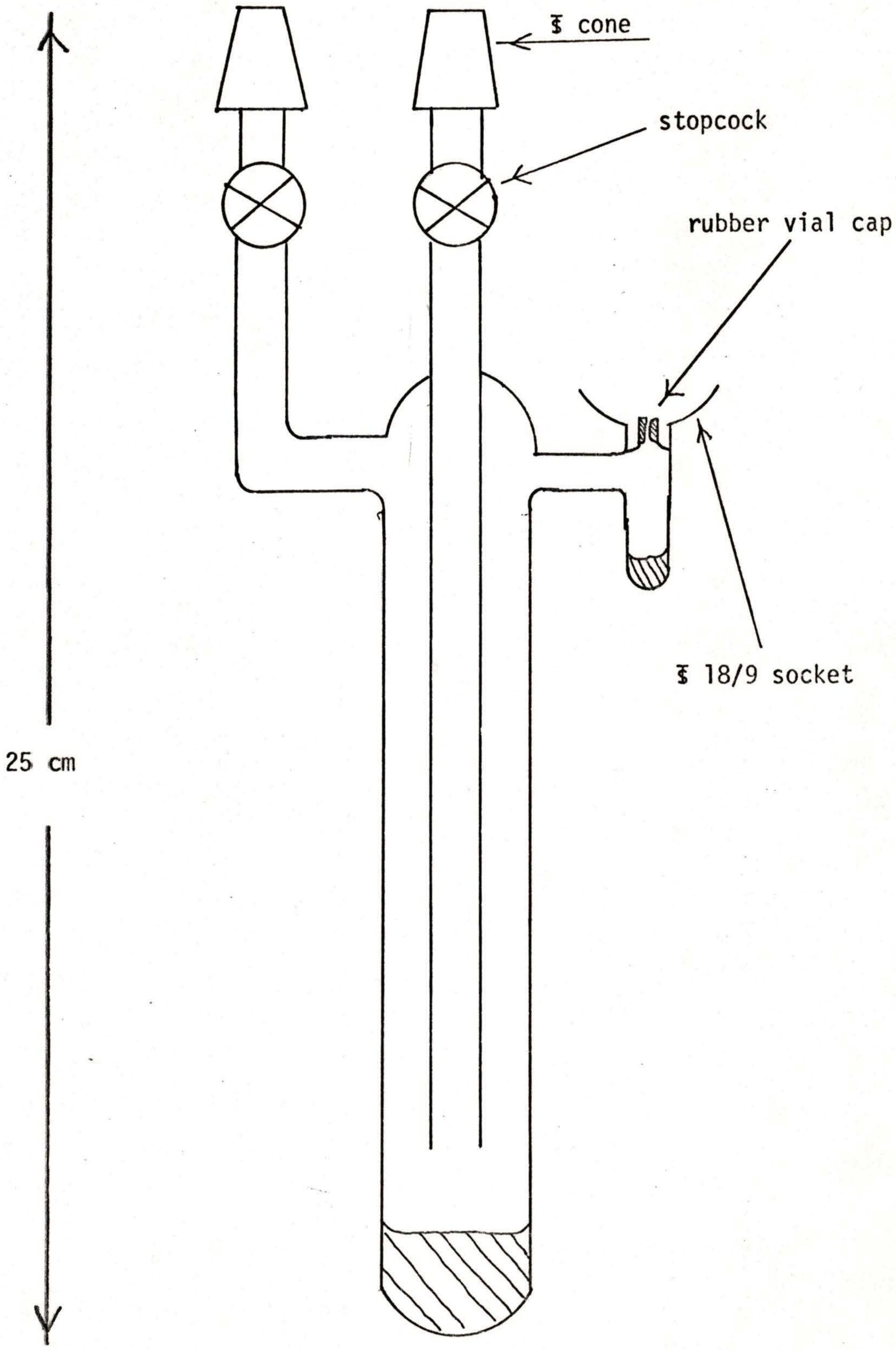


Fig 11 : Tube for Taking Liquid Samples for G.C.

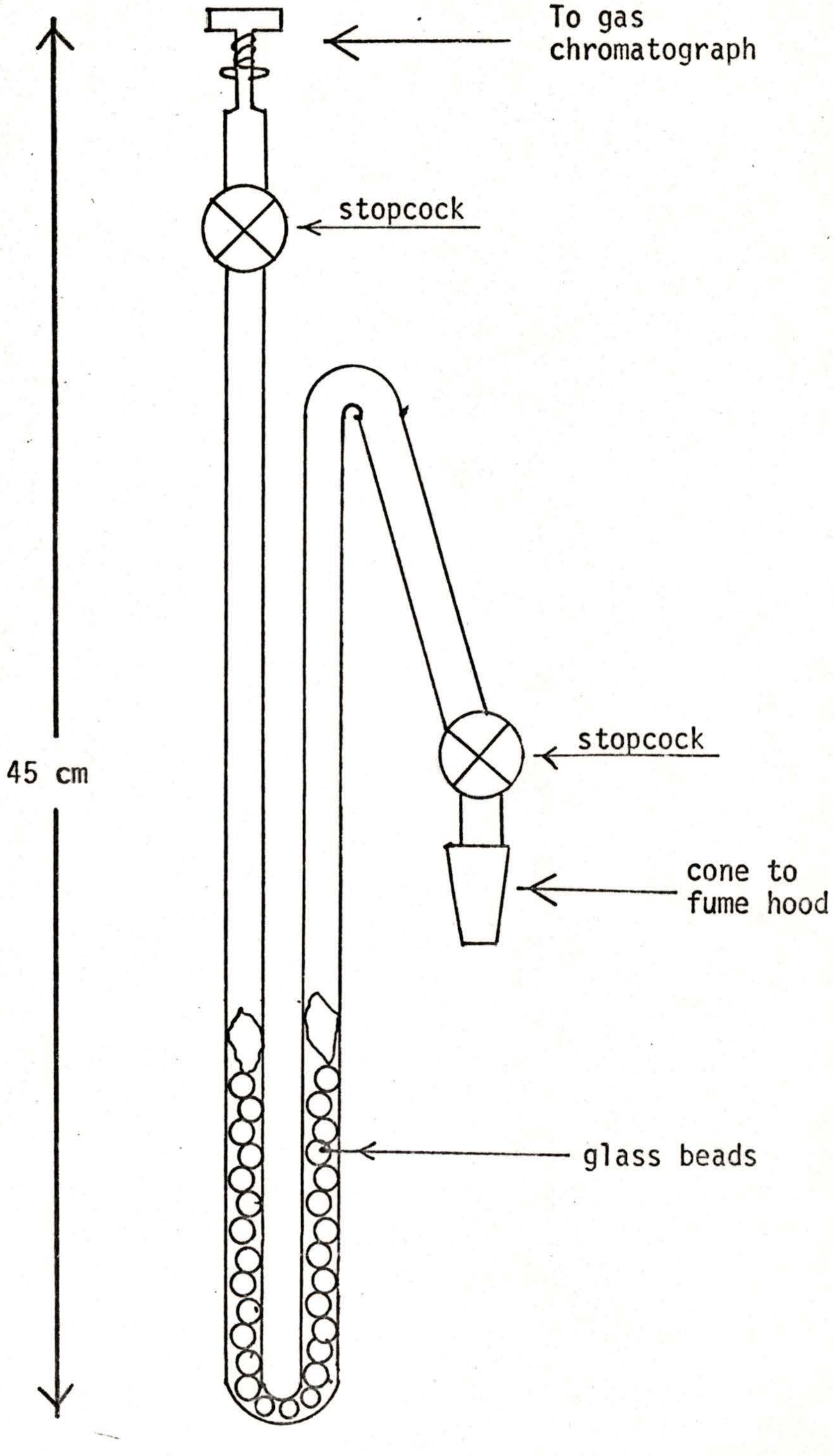


Fig 12 : Collection Tube for Gas Chromatograph

### 2.2.6. Vapour Pressure Measurements

Vapour pressure measurements have been widely used as a criterion of purity. At the present time, vapour pressure measurements are still used to check the purity of the boranes and some of their derivatives. Vapour pressure measurements were made using a system consisting of a U-tube equipped with a Stock valve and a Torricelli manometer. Vapour pressures were measured to ± 0.5 mm using a metre rule.

### 2.2.7. Fractional Condensation

Fractional condensation is a means of separating compounds of significantly different volatility by passing the vapours through a series of traps cooled to temperatures which will selectively condense the components. It has been found experimentally, that, if the vapour pressures of two compounds differ by a factor of $10^4$, a good separation can be expected; if the ratio is $10^2$, repeated and careful fractionations will be necessary to obtain a good separation. Any chemical interaction will invalidate the above guidelines. It is also important to note that a slow distillation can lead to accumulation of the less volatile component in the more volatile. This is caused by the finite volatility of the less volatile component. If a distillation is carried out too quickly there is a possibility of the less volatile component being entrained by the more volatile. This is a particular danger if a non-condensible gas is being passed through the system. Thus, in many cases, a compromise must be made.

A further complication can arise when the components are mutually soluble and their vapour pressures are similar. The vapour pressure of a compound, in a mixture, is a function of its mole fraction. As a distillation proceeds, the mole fraction of a component, and therefore its vapour pressure, will change; this change in vapour pressure can ruin a separation. When separating compounds of similar volatility it is useful to distil the unseparated mixture from a temperature that is 5-10 °C above the temperature of the first trap and to pump on the distillation train. This allows a fast fractionation and reduces entrainment, as there is only a small amount of vapour present at any one time.

It is difficult to lay down hard and fast rules for successful fractional condensation; the technique is an art.

## 2.3. Preparation of Endo-2,4-Ethylenetetraborane

### 2.3.1. Introduction

The preparation of endo-2,4-ethylenetetraborane can be divided in four parts. Firstly, diborane was prepared. It was then polymerized to tetraborane. Tetraborane was reacted with ethylene to produce endo-2,4-ethylenetetraborane. The product was then purified.

### 2.3.2. Preparation of Diborane

Although in industry diborane was often prepared from the reaction of trichloroborane and lithium hydride or by heating dimethoxyborane, in the laboratory diborane is often prepared from the reaction of lithium tetrahydroborate or lithium tetrahydroaluminate on trifluoroborane. The method of Shapiro et al(40) was followed with some modifications. This method utilized the reaction of lithium tetrahydroaluminate and trifluoroborane diethyletherate. The reaction is in two stages :-

$$BF_3 + LiAlH_4 \longrightarrow LiBH_4 + AlF_3$$

$$BF_3 + 3LiBH_4 \longrightarrow 2B_2H_6 + 3LiF$$

The yield was found to be essentially 100%. After some practice it was possible to make 0.5 mol diborane per batch, although this is not to be recommended; it is rather a large quantity to handle conveniently in a vacuum line. The apparatus was set up as in Fig 13 and flushed with dry hydrogen. Fifty grams of lithium tetrahydroaluminate and 200 ml dry ether were placed in the flask and 140 ml trifluoroborane diethyletherate were placed in the funnel. The flask was kept cool and the trifluoroborane diethyletherate was slowly added over a period of two to three hours. Shapiro used dry nitrogen to carry the diborane from the flask to the U-tube train. It was found that this causes a great deal of ether to be carried past the dry ice-acetone traps. Less ether was carried over when diborane was allowed to move under its own pressure alone. At the end of the reaction the whole system was flushed by gently passing hydrogen through it. Ether was removed from the diborane by fractional condensation. A pet. ether slush (-135 $^{o}$C) was used. At this temperature the vapour pressure of diborane is ~ 30 mmHg and the vapour pressure of diethylether is < 0.01 mmHg: diborane will pass a trap at -135 $^{o}$C but diethylether will be retained. The diborane was condensed at -196 $^{o}$C (liquid nitrogen). After one pass at -135 $^{o}$C the diborane

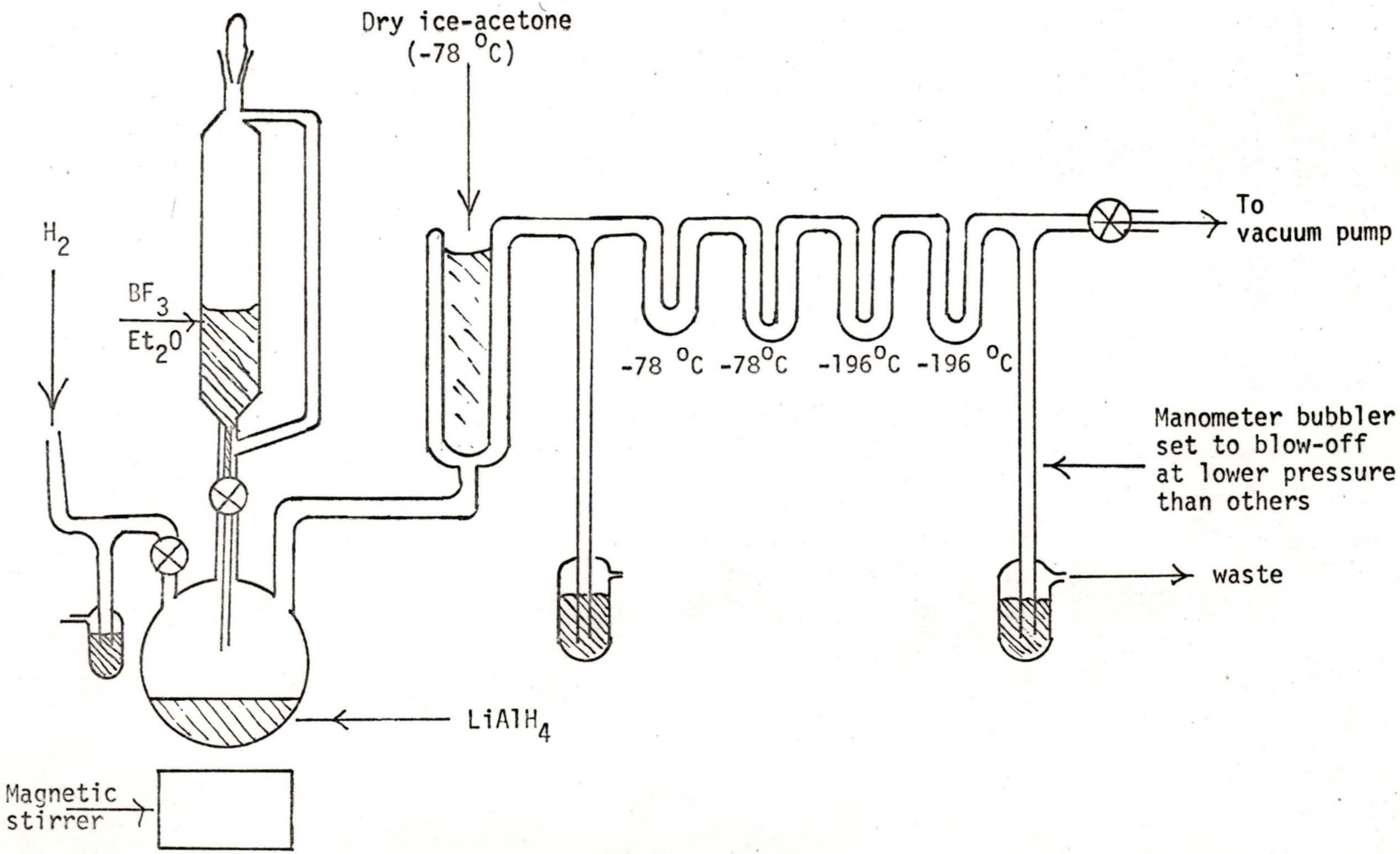


Fig 13 : Apparatus for the Preparation of Diborane was found by mass spectrometry and infrared spectrometry to be free from impurities. Gas liquid chromatography did indicate the presence of ethane but the amount was so small (~0.05%) that it was ignored.

### 2.3.3. Preparation of Tetraborane

The hot-cold reactor (Fig 14) is used to prepare a less volatile unstable compound from a more volatile unstable compound. The starting compounds are condensed into the cup and allowed to warm and evaporate slowly. The compounds will touch the hot surface where the reaction will occur. Before the product can decompose it touches the cold surface and condenses to run back into the cup. Klein et al have used this method to prepare tetraborane from diborane(41). Klein used a hot-side temperature of 120 °C and a cold-side temperature of -78 °C. He prepared tetraborane in 1-2 mmol quantities (80-95% yield).

Klein reported the total pressure in his system as 1400 mmHg (the vapour pressure of diborane at -78 °C). If the pressure in the system is calculated from the amount of diborane present (about 5 mmol), the volume of the system (at least 500 ml) and the temperature (-78 °C), the pressure should be ~122 mmHg. To reach a pressure of 1400 mmHg would require ~57 mmol diborane. This inconsistency is not explained. The volume of the system used for this work is ~1L. To reach a pressure of 1400 mmHg would require about 116 mmol diborane.

In practice 250 mmol of diborane were condensed into the cup using a liquid nitrogen bath. This Dewar was replaced by a dry ice-

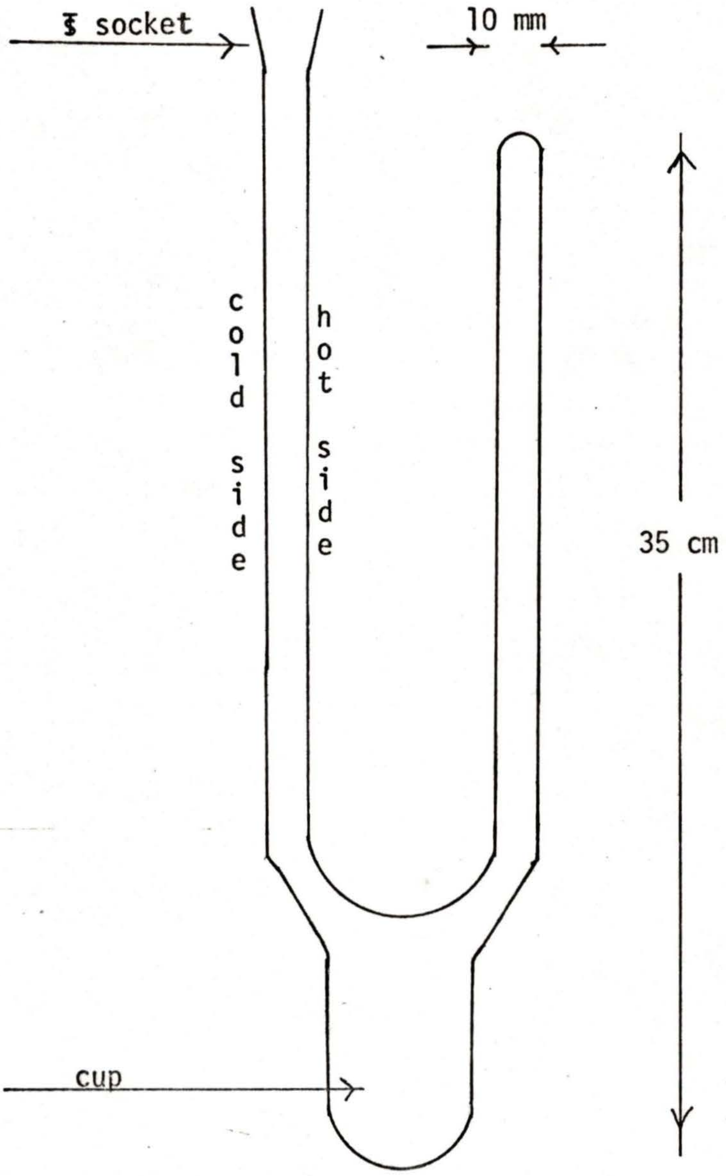


Fig 14 : Hot-Cold Reactor

acetone Dewar (-78 °C). The inner tube was filled with ethylene glycol and the temperature was brought to 120 °C by means of an immersion heater. The ethylene glycol was stirred. The vapour pressure of diborane at -78 °C is ~1400 mmHg. The pressure was monitored on a 2000 mm blow-off manometer (Fig 15). The manometer was designed to blow-off when the pressure in the system reached 2000 mmHg. Tube A was kept narrow to minimize the amount of mercury that would be moved. There were constrictions to eliminate oscillation of the mercury and various expansion bulbs and return tubes. In preliminary tests the manometer worked very well but in practice was not needed as a blow-off. The reaction in the hot-cold reactor can be represented by the equation :-

$$2B_2H_6 \longrightarrow B_4H_{10} + H_2$$

While liquid diborane is present the pressure in the system should rise due to hydrogen evolution but when all the diborane is in the vapour phase, the pressure should drop as 2 mole diborane are consumed for every mol of hydrogen formed. Decomposition of the tetraborane would cause hydrogen evolution and the pressure should increase. Klein's paper indicates the pressure rose from 1400 mmHg to 1700 mmHg, but he does not say whether the pressure remained at 1700 mmHg or not. In practice the pressure rose to 1573 mmHg and remained there. This took over twelve hours, compared with Klein's times of between one and three hours. The reaction was stopped by syphoning the ethylene glycol out and replacing the dry ice-acetone bath with a liquid nitrogen bath. The hydrogen was pumped off.

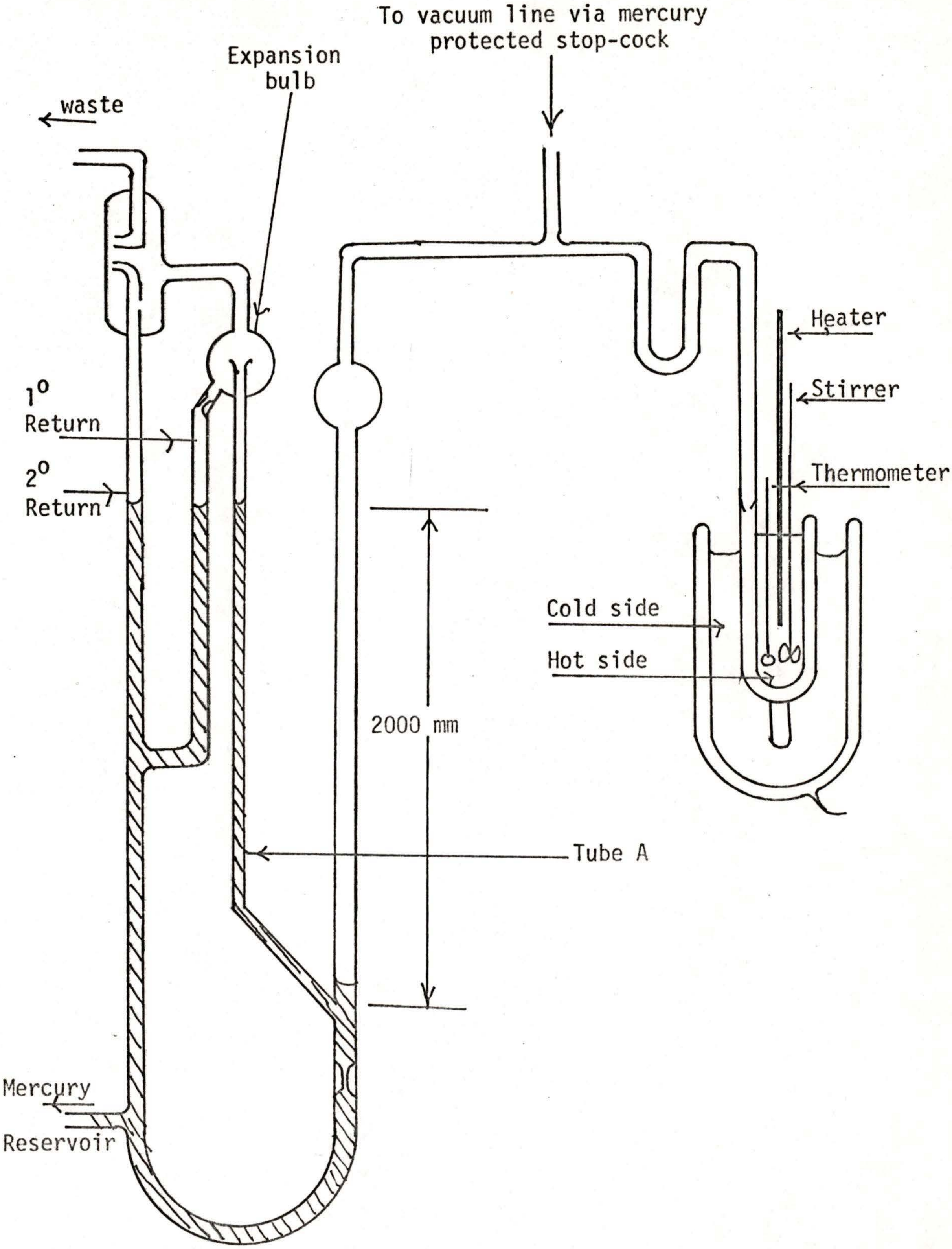


Fig 15 : Hot-Cold Reactor System Showing 2000 mm Manometer just Before Blow-off

There was less than a 10% yield of tetraborane. The tetraborane was purified by fractional condensation. Diborane was removed by passing the mixture through or to a -135 $^{o}$C trap (pet. ether) at which temperature tetraborane, but not diborane, is retained. Impurities less volatile than tetraborane were removed by a -78 $^{o}$C trap.

The purity of the tetraborane was checked by mass spectrometry and infrared spectrometry. Gas liquid chromatography showed traces of diborane and pentaborane but these could have been due to decomposition.

The preparation was repeated twice. In one attempt the temperature of the hot side of the reactor was raised to 160/180 $^{o}$C. This attempt produced pentaborane(11) rather than tetraborane. In another run the system was left for thirty-six hours after which the pressure slowly fell (1 mm/hr); again the yield of tetraborane was small and this method of preparing tetraborane was abandoned.

Conversations with Dr D. Ritter (University of Washington, Seattle) have led this worker to believe that the condition of the surface of the reactor is of great importance. Yields of tetraborane are improved when the surface is scrupulously clean. Other workers(42) have used a similar apparatus and method but with poor yields of tetraborane. It has been suggested that this is due to the pressure in the reactor being less than one atmosphere. Indeed, pressure is important in the pyrolysis of diborane to tetraborane(43), but it is difficult to see how Klein reached a pressure of two atmospheres using 5 mmol of gas in a volume of at least 500 ml.

Kotlensky and Schaeffer subjected diborane to a silent electric discharge(44) and isolated tetraborane (40% yield), pentaborane(9) (20% yield), pentaborane(11) (30% yield) and small amounts of hexaborane(10) and nonaborane(15). Nigon obtained up to 86% yields of tetraborane(45) (based on 44% conversion of diborane) by circulating diborane at 225 mmHg pressure for four hours through a silent discharge chamber at 0 °C. Cromwell(46) circulated diborane at 100-1000 mmHg through a silent electric discharge tube. He obtained a 90% yield of tetraborane with about 8% conversion of diborane. Other studies(47) showed tetraborane could be obtained in 73% yield with 29% conversion of diborane. The following method gave 77-83% yields of tetraborane with about 90% conversion of diborane in six hours, which makes this method a significantly better method of preparing tetraborane than those mentioned above.

The silent electric discharge apparatus is shown in Fig 16. The apparatus consists of a discharge section, a pump, a trap, a manometer and a ballast section.

The discharge section consisted of two concentric tubes about 1 m in length. The outer tube was 20 mm in diameter and the inner tube 15 mm. The outer tube was wrapped with brass shim and the inner tube was filled with 1 M cupric sulphate solution. An a.c. potential of 15 kV was maintained between the brass shim electrode and the cupric sulphate solution by an Allanson Luminour Tube Transformer (Allanson Manufacturing Corporation Limited, Toronto, Canada). The inner tube had to be steadied by a number of small

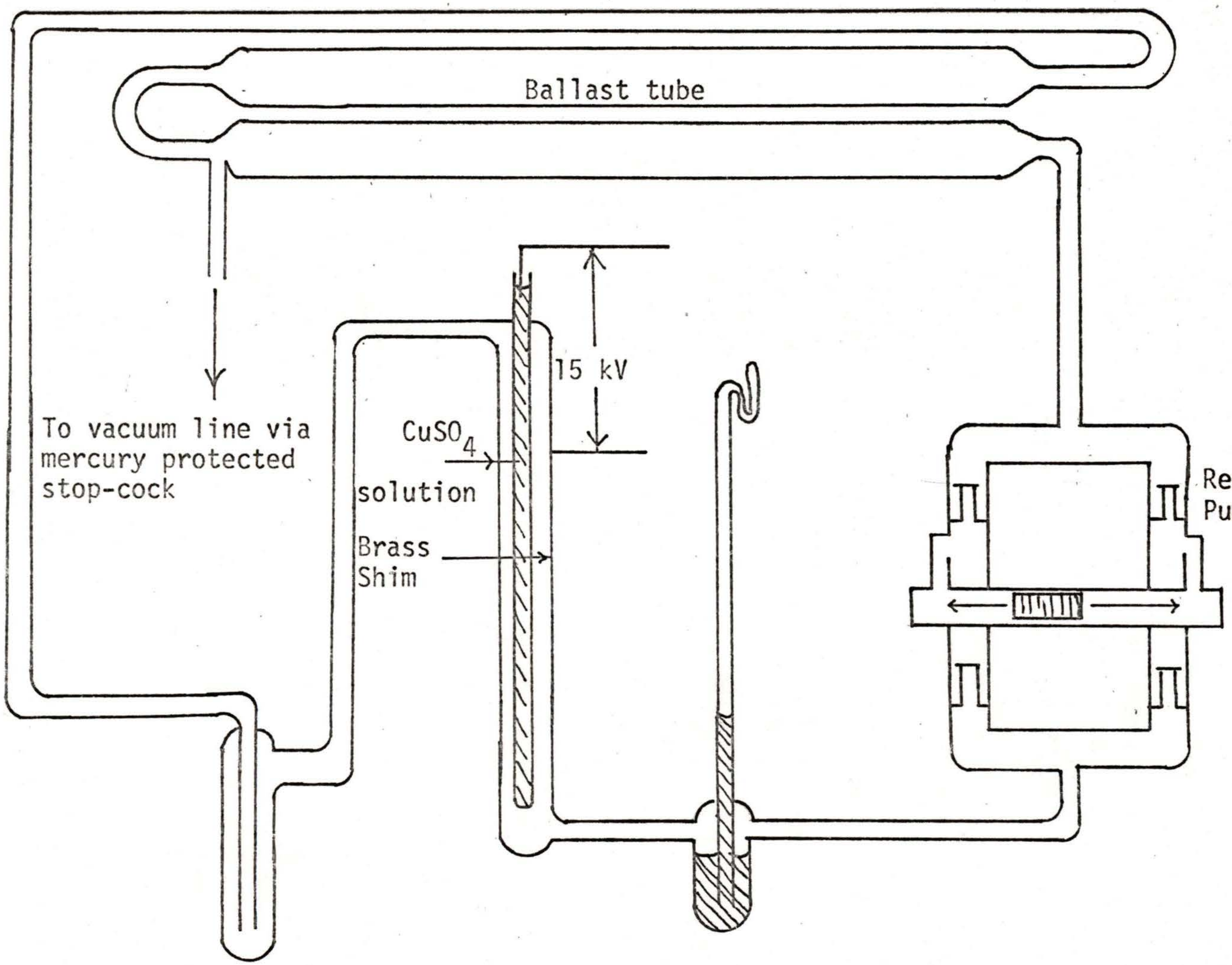


Fig 16 : High Voltage Silent Electric Discharge System indentations in the outer tube, as there was a great deal of vibration.

The pump was an all glass double stroke type driven by an electric motor. The piston was a cylinder of iron enclosed in glass, moved by a permanent magnet attached to the motor, and the valves were microscope cover slips.

A Torricelli manometer and a trap were built into the system; it is an advantage to have the pump, the discharge tube and the trap fitted with joints so they can be removed easily and cleaned. Two tubes, 2.5 m long and 60 mm diameter, acted as ballast tubes. They increased the volume of the system and promoted mixing. The silent electric discharge apparatus was connected to the rest of the vacuum line by means of a mercury protected stop-cock.

About 250 mmol diborane were condensed into the silent electric discharge apparatus using a liquid nitrogen bath. The liquid nitrogen was replaced by dry ice-acetone causing the pressure to rise to about 650 mmHg. At -78 $^{o}$C (dry ice-acetone) tetraborane has a vapour pressure of ~3 mmHg. To reduce this figure, and consequently to more efficiently trap tetraborane, air was blown through the dry ice-acetone. The procedure lowered the temperature of the bath to -92 $^{o}$C at which temperature the vapour pressure of tetraborane is ~0.9 mmHg. Simultaneously, the silent electric discharge and the pump were started. The pressure in the system was recorded at intervals. The reaction for the preparation of tetraborane is :-

$$2B_2H_6 \longrightarrow B_4H_{10} + H_2$$

This reaction should and did cause the pressure to decrease. The reaction was stopped at minimum pressure. A graph of pressure in the system versus time for a typical run is shown in Fig 17. The graph shows that most of the pressure drop occurs in the first two hours and that this method of preparing tetraborane is not only relatively efficient but also quick. The hydrogen was pumped off. Unreacted diborane was separated from the mixture by passing it through a -135 °C (pet. ether) bath. Tetraborane was separated from less volatile compounds by a series of rapid distillations through a -78 °C (dry ice-acetone) bath. Neither mass spectral nor infrared examination indicated any impurity in the tetraborane. Its vapour pressure at 0 °C was found to be 390 mmHg (literature value is 388 mmHg). There was some yellow solid left in the apparatus. At the end of the reaction there were ~20-25 mmol diborane left, (90-92% conversion), and between 96 and 104 mmol tetraborane were isolated, (77-83% yield).

### 2.3.4. Reaction of Tetraborane with Ethylene

In 1954, De Lorenzo and Chick reacted tetraborane and ethylene at 105 °C in a flow system using hydrogen as a diluent(48). The reaction product contained 52% boron - the boron content of ethyltetraborane is 53.2%. As the boron content of endo-2,4-ethylenetetraborane is 54.4% it is possible that they prepared this compound.

Endo-2,4-ethylenetetraborane was prepared by Harrison from the reaction of tetraborane and ethylene in a hot-cold

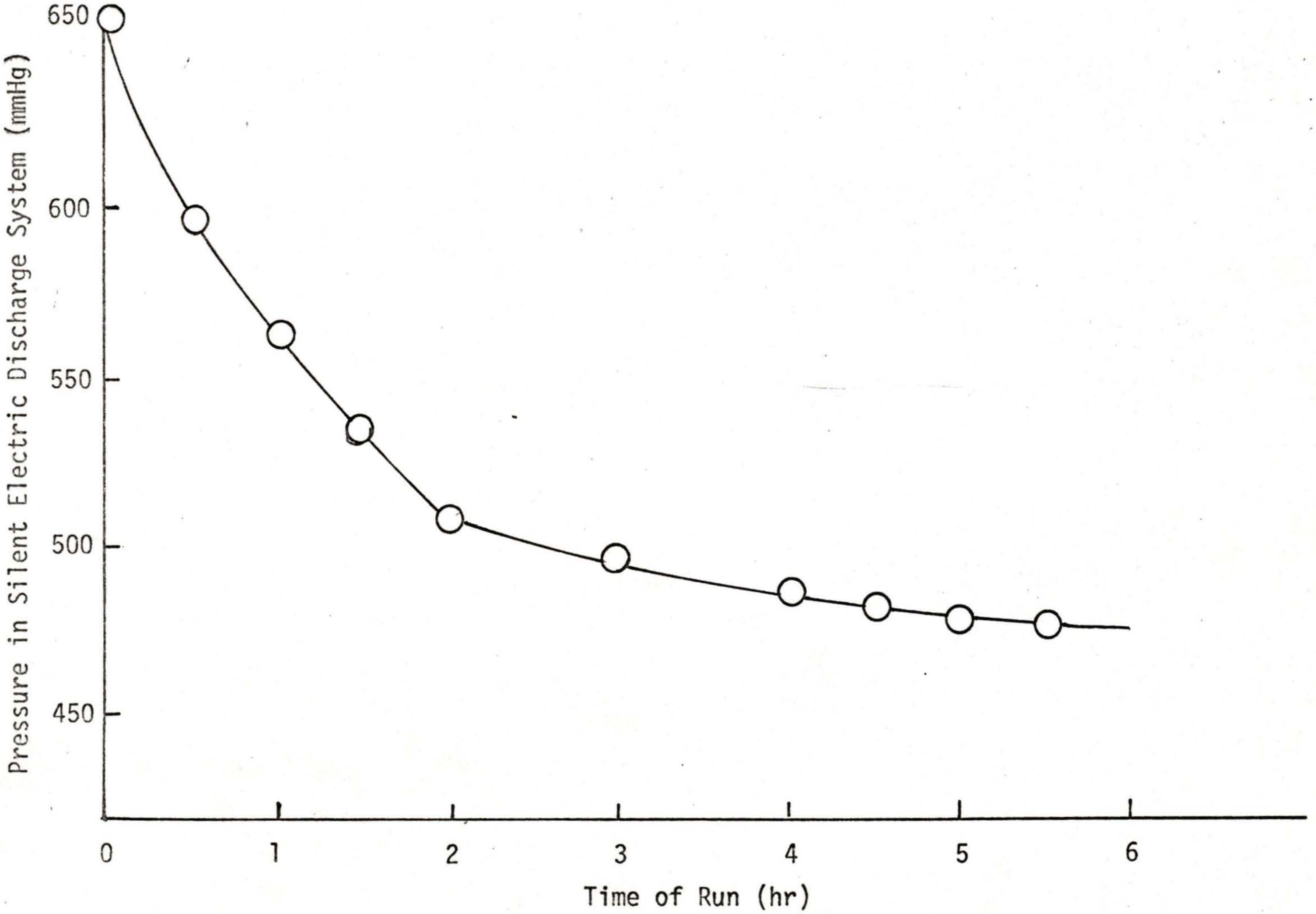


Fig 17 : A Graph of Pressure in Silent Electric Discharge System versus Time reactor(1). Aluminium chloride was used as a catalyst but in later experiments its use was discontinued, since the increase in conversion did not appear to justify the handling difficulties. Harrison found the optimum temperatures for the reactor to be 100 °C for the hot side and 0 °C for the cold side. Lowering either temperature led to a reduced conversion, whilst raising either temperature led to decomposition. Harrison reported an overall yield of endo-2,4-ethylenetetraborane of ~70%. The reaction can be represented by the equation :-

$$B_4H_{10} + C_2H_4 \longrightarrow B_4H_8C_2H_4 + H_2$$

At 0 °C tetraborane has a vapour pressure of 388 mmHg and the product a vapour pressure of 14.5 mmHg. As the reaction proceeded for 1 mol of ethylene consumed, 1 mol of hydrogen was evolved. Thus the pressure should drop slightly as tetraborane was converted into endo-2,4-ethylenetetraborane. Harrison found that as subsequent hydrogen producing decomposition reactions began, the pressure started to rise. He terminated his runs at minimum pressure. It was found that the per cent conversion was directly related to the initial pressure which could be raised by adding more ethylene. In a typical reaction Harrison used 21 mmol tetraborane and 5.8 mmol ethylene and obtained 'good results'.

In this work ethylene C.P. was distilled into the vacuum line and purified by a slow distillation through a -135 °C bath (pet. ether) to remove less volatile impurities; the distillate was distilled to a -196 °C trap with pumping, to remove more volatile impurities. Infrared, mass spectral and gas chromatographic examination of the ethylene indicated no impurities. Equal quantities of tetraborane and ethylene (about 150 mmol) were condensed into the hot-cold reactor which was then shut off from the vacuum line. The liquid nitrogen bath was replaced with an ice bath. The inner tube was filled with ethylene glycol which was heated to 100 °C. The pressure was followed and plotted against time (Fig 18). The graph shows that even after twenty-four hours the pressure had not reached a minimum. Most of the pressure drop occurred in the first five hours, indicating that the reaction is quite rapid. The reaction was stopped by replacing the ice bath with a liquid nitrogen bath and syphoning the hot ethylene glycol from the inner tube.

The first time this reaction was attempted there was a loud bang accompanied by an increase in pressure and the appearance of a considerable quantity of a buff colour solid. Mass spectral and infrared examination of the resulting mixture indicated the presence of tetraborane, ethylene, diborane, ethane and hydrogen. A very small quantity of endo-2,4-ethylenetetraborane was produced. It was at first thought that this very rapid reaction was caused by local overheating; subsequent work has shown this to not be the case. Rapid reactions termed 'flash reactions' have been observed by Gaines in the reactions of tetraborane or pentaborane(11) and acetylenes(49). He found that by altering the mole ratio of the mixture, the flash reaction temperature could be altered by more than one hundred degrees. Subsequent attempts to prepare endo-2,4-

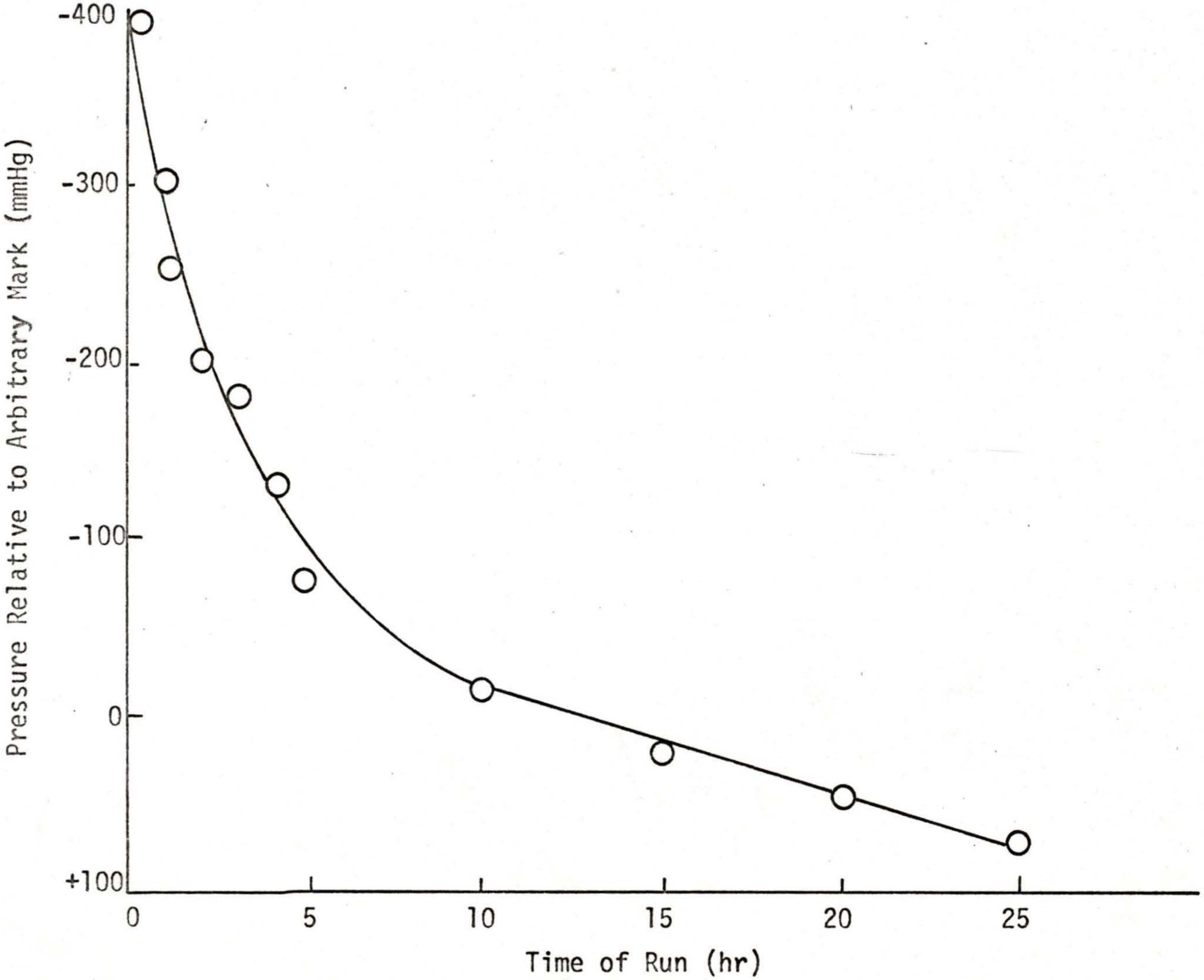


Fig 18 : A Graph of Pressure in the Hot-Cold Reactor System versus Time ethylenetetraborane under identical conditions as before were successful.

Harrison purified the product by fractional condensation. The mixture was distilled through a -126 $^{o}$C trap; the distillate contained unreacted ethylene and traces of diborane. The condensate was distilled through a -95 $^{o}$C trap to remove the bulk of the unreacted tetraborane. The last traces of tetraborane were removed by repeated distillations through a -63 $^{o}$C trap. The condensate was then distilled through a -23 $^{o}$C trap to remove less volatile material. A repeat of the -63 $^{o}$C distillation gave pure endo-2,4-ethylenetetraborane (v.p. 14.5 mmHg at 0 $^{o}$C).

When the above procedure was followed, the resulting substance had an infrared spectrum similar to that given by Harrison(1). The mass spectrum was not similar to that given by Shapiro(2). The general contour was similar but showed some larger peaks around m/e 76 and m/e 55. The vapour pressure of endo-2,4-ethylenetetraborane at 0 $^{o}$C given by Harrison was 14.5 mmHg. Shapiro gave a formula from which the vapour pressure may be calculated; at 0 $^{o}$C the vapour pressure is 13.6 mmHg (Shapiro's observed vapour pressure was 13.9 mmHg). The vapour pressure of the substance prepared was 15.5 mmHg. A gas chromatographic examination of the purified endo-2,4-ethylenetetraborane was undertaken. Because the volatility of endo-2,4-ethylenetetraborane is rather low (53.5 mmHg at 25 $^{o}$C), a liquid injection had to be made. The endo-2,4-ethylenetetraborane was condensed in the evacuated tube (Fig 11) which was then filled with nitrogen. When the condensate had melted the liquid was poured into the side cup from which it was withdrawn using a Hamilton 50 μl micro-syringe. Immediately after injection the syringe had to be dismantled and washed in methanol to prevent seizure. Four fractions were collected in special collection tubes (Fig 12) which were cooled in liquid nitrogen. Each fraction was examined by mass spectrometry. The first fraction showed diborane, tetraborane, ethylene and possibly ethyldiborane. The second fraction showed pentaboranes and a little tetraborane and diborane. The third fraction showed pentaboranes and tetraborane but had a base peak of m/e 57. The fourth fraction which gave only one peak had a mass spectrum almost identical to that given by Shapiro et al (Appendix 1, m.s. 1, pg97 ). It is uncertain whether the sample decomposed before injection or within the gas chromatograph. The latter case was the more probable as the sample was kept cool until just prior to injection. G.l.c. cannot be used to determine the purity of endo-2,4-ethylenetetraborane.

Gas chromatography was considered as a method of separating endo-2,4-ethylenetetraborane from the crude reaction products. Two hundred microlitre samples were used. The gas chromatogram showed many peaks and was generally not reproducible. The last peak, which was always the biggest, was collected in one of the special collection tubes. The mass spectrum was identical with that shown in m.s. 1. The irreproducibility might have been due to decomposition of the sample before introduction or decomposition within the gas chromatograph. The viscosity of the sample increased so that in two hours it was too viscous to handle. It was apparent that the sample decomposed faster than it could be purified. The gas chromatographic separation of endo-2,4-ethylenetetraborane was abandoned and fractional condensation was re-examined.

The following procedure was found to result in endo-2,4-ethylenetetraborane which when examined by infrared spectrometry appeared to be pure. The mass spectrum had a m/e 55 peak that is bigger than that given in the literature(2). The crude product was distilled through a -23 °C trap (carbon tetrachloride) to remove less volatile impurities. There was only a small amount of such impurities, the bulk of which was hexaborane(10). The distillate was then passed through a -78 °C trap (dry ice-acetone). The distillate consisted of diborane and unreacted tetraborane and ethylene. The condensate was warmed to between -45 °C and -50 °C (acetone) and allowed to distil slowly through a -63 °C (chloroform) trap. The distillate consisted of pentaboranes and the condensate of endo-2,4-ethylenetetraborane.

The last step was repeated twice. The resulting endo-2,4-ethylenetetraborane had a vapour pressure of 14.5 mmHg at 0 °C (literature value 13.9 mmHg(2), 14.5 mmHg(1)). The overall yield of endo-2,4-ethylenetetraborane produced by the reaction of tetraborane and ethylene was 60-70%. Five hundred mmol diborane ultimately produced 120-130 mmol endo-2,4-ethylenetetraborane.

## 2.4. Thermal Decomposition of Endo-2,4-Ethylenetetraborane

### 2.4.1. Introduction

It was observed during the purification of endo-2,4-ethylenetetraborane by gas chromatography that the compound decomposed quite rapidly at room temperature. In air, samples became increasingly more viscous until, after ten to fifteen minutes, the substance appeared clear, colourless and immobile. Upon gentle heating a white solid was formed. This solid exploded upon touching with a spatula.

Samples left in sealed tubes became viscous more slowly than those left in air and a yellow precipitate appeared. Mercury (which was always present in the vacuum line) was found to catalyse the decomposition of endo-2,4-ethylenetetraborane. Care had to be taken to ensure that mercury did not condense in the n.m.r. tubes. The n.m.r. tubes were equipped with a wider tube at the top and a stop-cock (Fig 19). The material was quickly condensed on the wall of the wider tube. The stop-cock was closed and material was allowed to melt and run down into the n.m.r. tube. Mercury was not found to decompose endo-2,4-ethylenetetraborane during normal fractional condensation operations. In these cases the mercury formed a pool but in the n.m.r. tubes the mercury formed very small droplets which probably acted as centres for decomposition. It was possible to evaporate and condense endo-2,4-ethylenetetraborane only a finite number of times before it decomposed; one more evaporation after the critical number was reached caused a decomposition that was

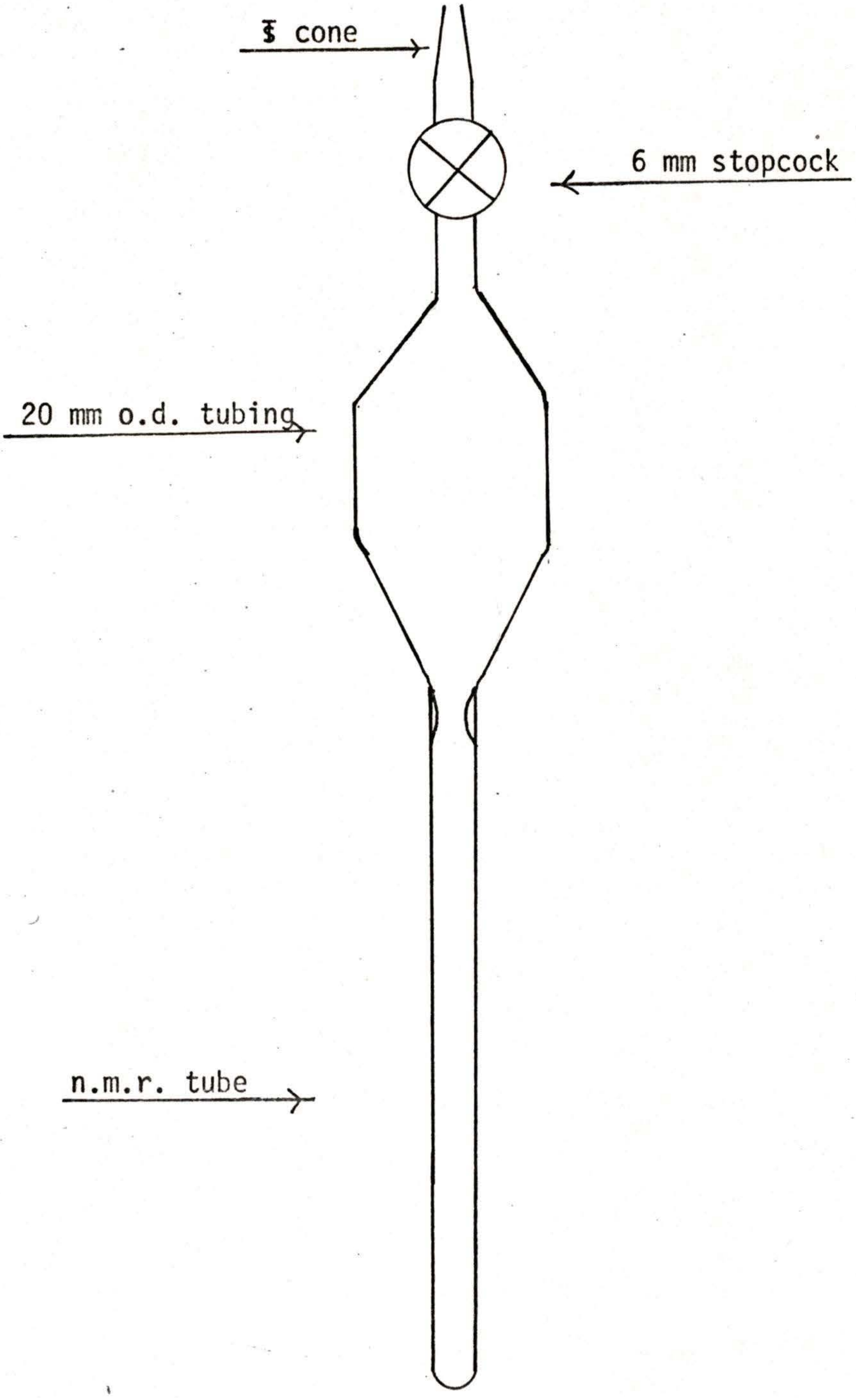


Fig 19 : Modification of N.M.R. Tubes

both rapid and complete. The liquid evolved hydrogen and turned darker until after about five minutes a brown involatile substance remained. The number is about 15-20. This suggests an auto-catalytic decomposition.

### 2.4.2. Sealed Tube Experiments

One mmol samples of endo-2,4-ethylenetetraborane were sealed into tubes (Fig 20) and left for one hour immersed in water at different temperatures. The temperatures chosen were 30, 50 and 100 °C. After one hour the tubes were connected to the vacuum line and opened. The contents of each tube were examined by mass spectrometry and infrared spectrometry. Attempts were made to measure the amount of hydrogen evolved but were unsuccessful because of the repeated mechanical failure of the Toepler pump.

### 2.4.3. Decomposition Monitored by Infrared Spectrometry

A gaseous sample of endo-2,4-ethylenetetraborane at 35 mmHg pressure and at room temperature was examined periodically over a period of 170 hours by infrared spectrometry.

### 2.4.4. Decomposition Monitored by N.M.R. Spectrometry

A sample of endo-2,4-ethylenetetraborane was sealed into a thick-walled n.m.r. tube. The $^{11}B$ n.m.r. spectrum was recorded periodically over a period of thirty-six hours. The tube was broken under vacuum (Fig 21) and the contents were examined by mass spectrometry and infrared spectrometry.

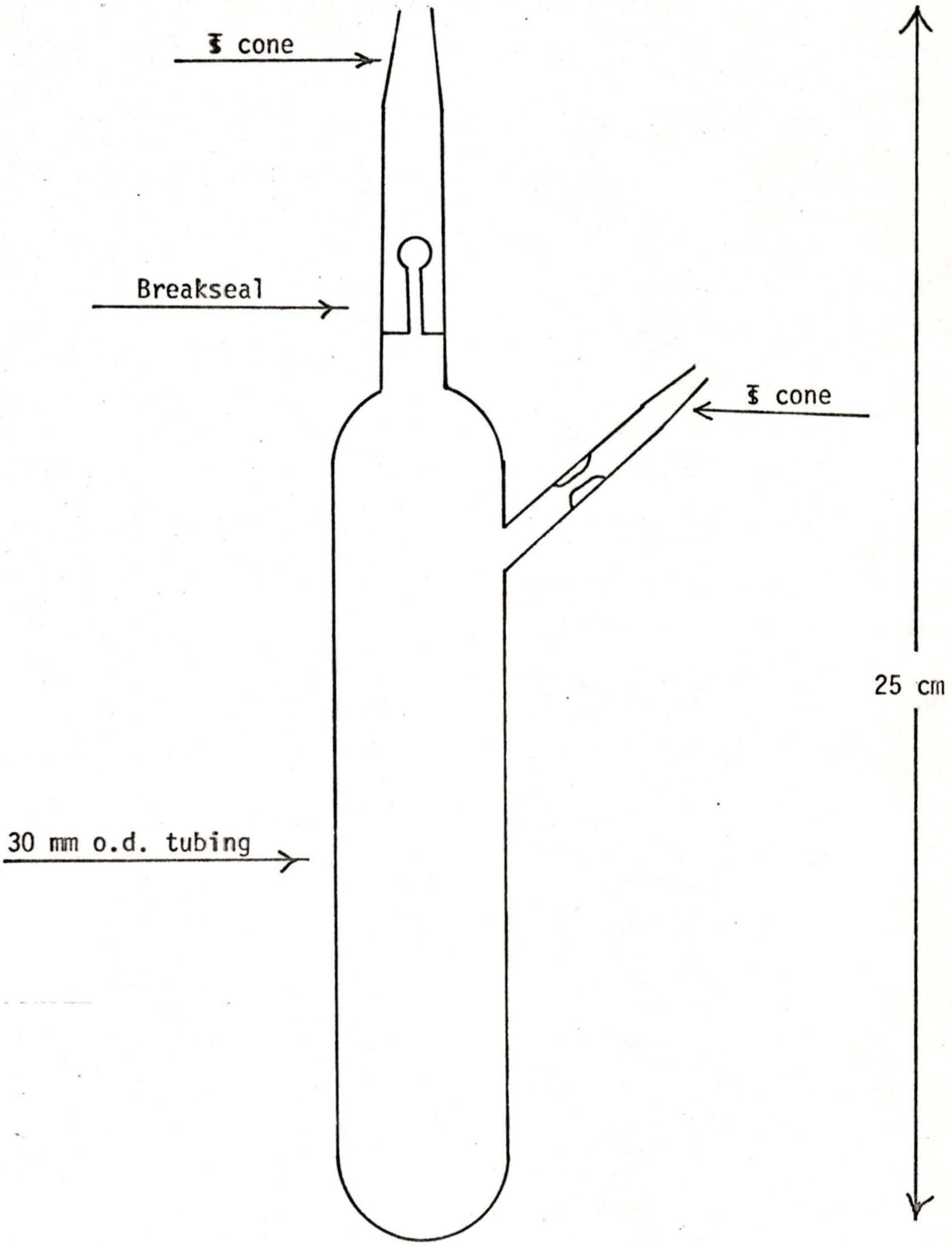


Fig 20 : Tube for Thermal Decomposition

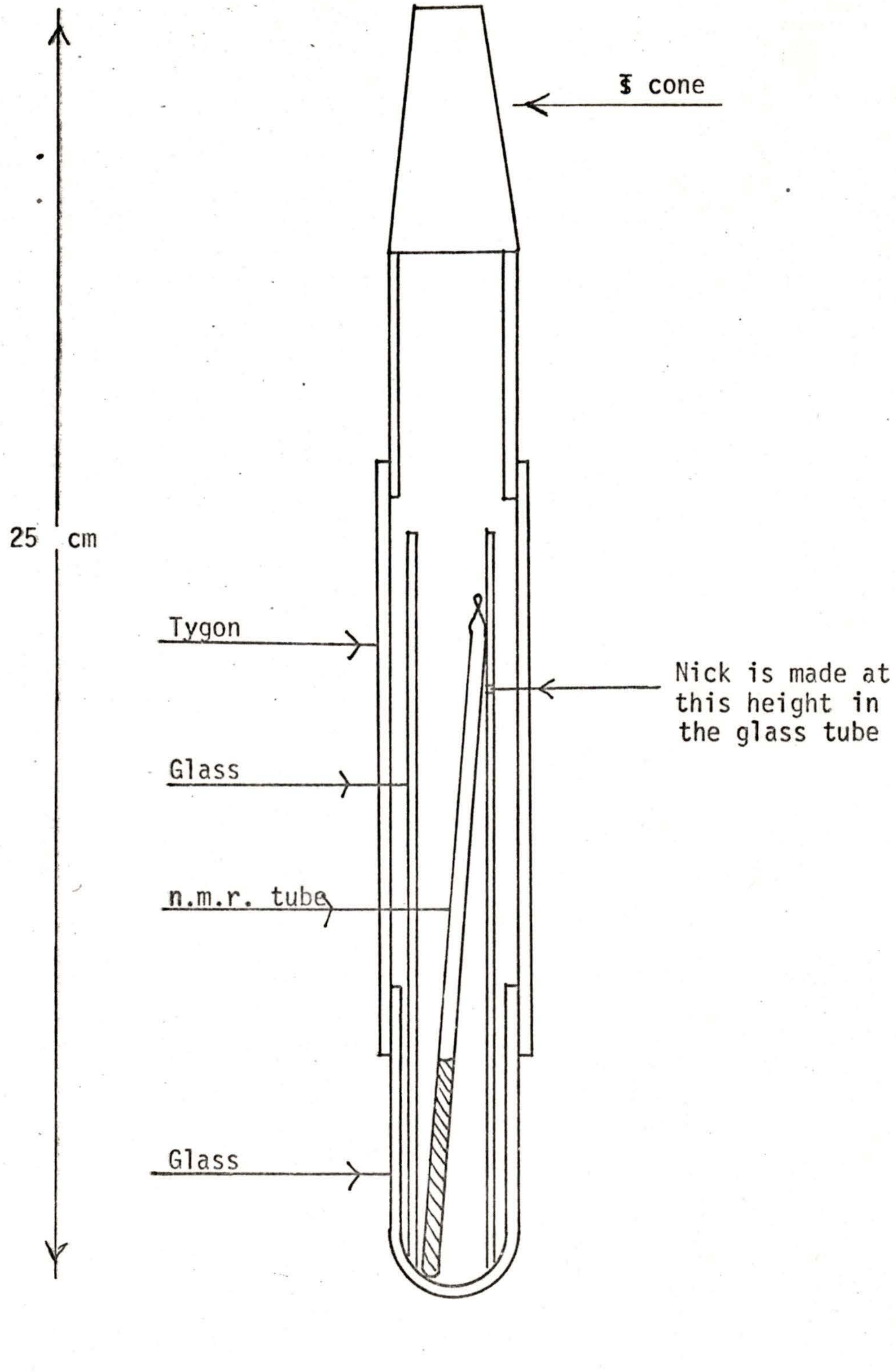


Fig 21 : System for Breaking N.M.R. Tubes Under Vacuum

## 2.5. Reaction of Endo-2,4-Ethylenetetraborane with Lewis Bases

### 2.5.1. Reaction of Endo-2,4-Ethylenetetraborane with Diethylether

The quantities of the reactants used were the same as those given by Schaeffer et al(50) in their paper on the reaction of tetraborane and ethers.

Commercial anhydrous diethylether was dried with sodium benzophenone and distilled into a vacuum line where it was stored in a bulb equipped with a mercury protected stop-cock. One mmol of endo-2,4-ethylenetetraborane and 5 mmol diethylether were quickly distilled into a medium-walled n.m.r. tube (Fig 19). The distillation was done quickly to reduce the amount of mercury which was condensed in the n.m.r. tube. The tube was sealed and stored at -196 $^{o}$C (liquid nitrogen). Upon warming to -78 $^{o}$C there was a vigorous reaction and a white solid was formed. The $^{11}$B n.m.r. spectrum was recorded at various temperatures from -60 $^{o}$C to room temperature and then periodically at room temperature over twenty-four hours. The sample was cooled to -50 $^{o}$C and the $^{11}$B n.m.r. spectrum was recorded. The proton n.m.r. spectrum was recorded when the sample first reached room temperature. The n.m.r. tube was placed in the system for breaking it under vacuum (Fig 21) and attached to the vacuum line. The system was pumped down and the tube was broken while the end was kept in liquid nitrogen. It was hoped to distil the liquid gently leaving the white solid behind. Because of a relatively high pressure of hydrogen in the n.m.r. tube, the contents of it were splattered over the tube and the tygon when it was broken. The volatile products were transferred to the vacuum line where they were condensed and the hydrogen was pumped off. To make the transfer, the volatile products had to be warmed to 50 °C for about two minutes. The volatile products were allowed to warm to room temperature in sufficient volume to ensure they were completely vapourized. Samples for mass spectrometry and infrared spectrometry were taken simultaneously. The tygon was cut open, in air, and the white solid was separated from the broken glass. The mass spectrum of the white solid was recorded. Attempts to dissolve the solid in order to record a proton n.m.r. spectrum were unsuccessful. The solvents used were deuterochloroform, deuterium oxide, deuterobenzene, deuteroacetone, deuterodimethylsulfoxide and deuteromethanol, but in no case did enough white solid dissolve to produce a proton n.m.r. spectrum.

### 2.5.2. Reaction of Endo-2,4-Ethylenetetraborane with Tetrahydrofuran

Reagent grade tetrahydrofuran was distilled from sodium benzophenone into the vacuum line where it was stored in a bulb equipped with a mercury protected stop-cock. One mmol of endo-2,4-ethylenetetraborane and 5 mmol of tetrahydrofuran were quickly distilled into a medium-walled n.m.r. tube. The tube was sealed and stored at -196 °C. After that the procedure was similar to that described in the reaction with diethylether and similar difficulties were encountered.

### 2.5.3. Reaction of Endo-2,4-Ethylenetetraborane with Ammonia in Diethylether

Ammonia gas (Linde) was passed into the vacuum line. The ammonia was slowly passed through a -78 °C trap (dry ice-acetone) to remove water and condensed at -196 °C (liquid nitrogen). Infrared examination showed no traces of impurities. The ether was dried as before. The procedure was similar to that described in the reaction with diethylether. One mmol of endo-2,4-ethylenetetraborane, 2 mmol of ammonia and 5 mmol diethylether were used. The rest of the procedure was similar to that of the reaction with tetrahydrofuran and similar difficulties were encountered.

### 2.5.4. Reaction of Endo-2,4-Ethylenetetraborane with Trimethylamine

Anhydrous trimethylamine (Eastman) was distilled into the vacuum line. Water was removed by slowly distilling the trimethylamine through a -78 °C (dry ice-acetone) trap. One mmol of endo-2,4-ethylenetetraborane and 5 mmol of trimethylamine were quickly distilled into a medium-walled n.m.r. tube. The procedure from then on was similar to that of the reaction with diethylether and similar difficulties were met.

# CHAPTER 3 : RESULTS AND DISCUSSION

# 3. Results and Discussion

## 3.1. Techniques Employed

### 3.1.1. Boron N.M.R.

There are many references to $^{11}B$ n.m.r. in the literature$^{(51)}$. Whilst a detailed account of boron n.m.r. would be out of place here, some basic principles and peculiarities associated with the study of boron compounds are included. In practice, what is studied is usually the boron-terminal hydrogen interaction; such a study is complicated by three factors :-

1. Normal boron is composed of two isotopes, $^{10}B$ and $^{11}B$ in about 1:4 ratio and both are n.m.r. active.
2. The nuclear spin of $^{10}B$ is 3 and the nuclear spin of $^{11}B$ is 3/2 leading to some complexity in the observed spectra.
3. Both $^{10}B$ and $^{11}B$ possess quadrupole moments resulting in substantial line broadening.

From the data in Table 1 the sensitivity at constant field for equal numbers of nuclei can be obtained using the relationship :-

$$\underset{(^1H = 1)}{\text{relative sensitivity}} = 7.652 \times 10^{-3}\frac{(I + 1)\mu^3}{I^2}$$

μ - magnetic moment
I - nuclear spin

the sensitivity for $^{11}B$ = 0.165
" " " $^{10}B$ = 0.0198

Table 1 : Nuclear Properties of $^{10}B$ and $^{11}B$

| ISOTOPE | PER CENT ABUNDANCE | NUCLEAR SPIN(I)* | MAGNETIC MOMENT ($\mu$)** | QUADRUPOLE MOMENT*** |
|---|---|---|---|---|
| $^{10}B$ | 19.46 | 3 | 1.8006 | 0.111 |
| $^{11}B$ | 80.4 | 3/2 | 2.6880 | $3.55 \times 10^{-2}$ |

* - in units of $\frac{h}{2\pi}$

** - in units of the nuclear magneton, $\frac{e\hbar}{2Mc}$

*** - in units of $10^{-24} cm^2.e$

Natural boron comprises of 80.4% $^{11}B$ and 19.6% $^{10}B$; when this is taken into account the sensitivity for $^{11}B/^{10}B = 34.2$ . Not only is the relative signal intensity lower for $^{10}B$, but $^{10}B$ also has the larger nuclear quadrupole moment. Although these factors make it difficult to obtain a good signal, $^{10}B$ n.m.r. has been used to study isotope effects. However, $^{11}B$ n.m.r. rather than $^{10}B$ n.m.r. is almost invariably used.

Various factors which offset the disadvantages result in the following generalizations :-

1. Boron atoms attached only to other boron atoms and one or more carbon, nitrogen, oxygen or halogen atoms give rise to only a single resonance.
2. In predicting the $^{11}B$ spectra the effect of the bridge protons may, in the first approximation, be ignored.
3. Principal spin coupling effects are observed only from the interaction of the particular atom with one or more hydrogens bonded directly to it.
4. In general, when n hydrogens are attached to a boron atom, the boron spectrum consists of (n + 1) lines with intensities in the ratio corresponding to the binomial coefficients of $(x + 1)^n$.
5. There appears to be a general relationship between the value of a coupling constant and the number of protons bound to a particular boron atom. In general the coupling constant decreases as the number of protons directly bound to the boron increases. This arises from the decreased s character of the B-H bond.

6. Although there is no theoretically sound reason for believing that a reliable relationship between electron density and chemical shift should exist for boron resonances, it has been found experimentally that a reasonably good correlation does exist. An increase in electron density around a boron atom tends to shift the resonance associated with that boron to higher field.

Exchange processes sometimes occur which can alter the observed spectrum. The octahydrotriborate (1-) ion ($B_3H_8^-$)offers a good example of intramolecular exchange. In a variety of solvents the $^{11}B$ spectrum is observed to be a septet which under favourable conditions can be resolved into a nonet. In the solid state the molecule contains two bridge hydrogens and six terminal hydrogens. The commonly accepted explanation is that in solution a rapid interchange of protons occurs between various boron atoms so that within a short time each boron atom has coupled to all eight hydrogen atoms. Intermolecular exchange is shown by $B_3H_7 \cdot Et_2O$ in diethylether. The $^{11}B$ n.m.r. spectrum is a poorly resolved sextet which has been shown to be the inner six lines of an octet. Not only does H tautomerism take place but also the intermolecular exchange of diethylether molecules.

$^{11}B$ n.m.r. has been very useful for studying boron compounds especially boranes and related ions and compounds. However, quadrupolar relaxation and exchange processes make the application of n.m.r. to boron chemistry less straightforward than in the case of carbon chemistry. Apart from the qualitative analytical aspect,

$^{11}$B n.m.r. is used to help solve two problems in borane chemistry. Firstly, it can indicate how many types of boron atoms are in a molecule and secondly, it can show how many hydrogen atoms are attached to each boron atom.

### 3.1.2. Proton N.M.R.

Proton n.m.r. has been of relatively minor importance in the study of boranes. Proton n.m.r. of boron compounds is complicated by the fact that $^{11}$B has a nuclear spin of 3/2 and $^{10}$B has a nuclear spin of 3. Thus an $^{11}$B-H interaction results in a quartet and a $^{10}$B-H leads to a septet. Bridge hydrogen resonances produce a broad unresolved band or a poorly split multiplet. In boron compounds the line widths are larger than are normally found in the resonances of hydrogen attached to carbon, due to the large quadrupole moment of $^{11}$B. In practice, the proton n.m.r. signals of boron-hydrogen interactions usually have a width at half height ($W_{\frac{1}{2}}$) about 30-60 Hz whereas the line widths of the resonances of carbon-hydrogen interactions are usually less than a few Hz wide. Thus the proton n.m.r. spectra of boron compounds are poorly resolved relative to the proton n.m.r. of organic compounds.

### 3.1.3. Mass Spectrometry

Mass spectrometry has been used extensively(37, 52, 53) in the study of boranes and their derivatives.

When a molecule contains several boron atoms in natural isotopic abundance, its mass spectrum has a characteristic pattern and is fairly easy to identify. A mass spectrum of elemental boron in its natural isotopic abundance would show a statistical distribution of $^{11}B$ and $^{10}B$. Thus, in the parent group spectrum of, say, pentaborane(9) there is a large spread caused by distribution of the various $^{11}B$ and $^{10}B$ species such as $^{11}B_5H_9$, $^{11}B_4{}^{10}BH_9$, $^{11}B_3{}^{10}B_2H_9$ and $^{11}B_2{}^{10}B_3H_9$, as well as by successive abstractions of hydrogen from these species. Because hydrogen atoms are lost readily from the parent group, the fragment ions overlap and give the spectrum its pronounced spread. In the mass spectra of the boranes the parent group is always larger than any other and the height of the groups becomes less as the number of boron atoms in the group decreases. By this means it is possible to analyse a mixture of boranes. Using a high quality mass spectrometer and a stripping technique, it is possible to analyse a mixture of boranes and various other compounds. The relative heights of the peaks must be reproducible before the contributions of different components to any one peak can be subtracted. The reproducibility of the Hitachi Perkin-Elmer RMU-6E mass spectrometer used in the present work is not sufficiently high to permit the use of these procedures.

### 3.1.4. Infrared Spectrometry

Infrared spectrometry has been widely used to study the boranes and their derivatives(54). In general, infrared spectrometry is used as a means of identification of boranes and as a quick method of qualitatively examining a mixture of boranes.

### 3.1.5. Gas Liquid Chromatography

There are a few references to the use of gas liquid chromatography in borane chemistry(55). The lower boranes have been separated using Octoil S, tricresyl phosphate and paraffin oil as stationary phases(56). Ritter has used g.l.c. to separate mixtures of alkyl boranes(12, 13, 57).

## 3.2. Thermal Decomposition of Endo-2,4-Ethylenetetraborane

### 3.2.1. Introduction

Upon preparing endo-2,4-ethylenetetraborane it soon became apparent that the compound was less stable than had been expected. An investigation of the thermal decomposition of endo-2,4-ethylenetetraborane was made to find out how quickly it did decompose and what were the products of decomposition. Pyrolysis of diborane is still the most common method of preparing other boranes and many papers have been published on the pyrolysis of boranes. The mechanisms of pyrolysis and interconversions of the boranes are unsettled. A recent paper by Long(58) is an attempt to reinterpret the evidence and provide an all-embracing mechanism. Whilst there are many reports on the pyrolysis of the boranes there are few on the pyrolysis of the alkylboranes and none on the pyrolysis of alkyltetraboranes.

### 3.2.2. Sealed Tube Experiments

All attempts to measure the hydrogen evolved were unsuccessful because of repeated mechanical failure of the Toepler pump. After one hour at 30 °C about sixty per cent of the endo-2,4-ethylenetetraborane remained. Decomposition is virtually complete if the sample is left for one hour at 50 °C; at 100 °C for one hour decomposition is complete. The mass spectra of the products obtained at the different temperatures are similar. The mass spectrum of the products obtained from the run at 50 °C are shown in Appendix 1, m.s. 2, pg 98 , along with the mass spectrum of diborane. The spectrum is mainly that of diborane. There is evidence for the presence of endo-2,4-ethylenetetraborane (peaks up to m/e 78) and a trace of tetraborane (peaks around m/e 50). Absence of a peak at m/e 69 precludes the formation of triethylborane or di- or triethyldiboranes. Ethyldiborane has m/e 41 and 51 peaks and might be present. The infrared spectrum of the products is shown in Appendix 2, i.r. 2, pg 110. The principal peaks are shown below alongside the principal peaks of diborane.

| i.r. 2 | diborane |
|---|---|
| 2.7μ | 2.7μ |
| 3.4 | |
| 3.7 | 3.7 |
| 3.8 | 3.8 |
| 3.9 | 3.95 |
| 4.8 | |
| | 6.15 |
| 6.2 | 6.25 |
| 6.3 | 6.3 |
| 8.3 | 8.3 |
| 8.6 | 8.5 |
| 8.7 | 8.7 |
| 9.0 | |
| 9.8 | |
| 10.4 | 10.25 |

I.r. 2 is similar to the spectrum of diborane. The peaks in i.r. 2 not in the diborane spectrum are probably due to endo-2,4-ethylenetetraborane and tetraborane. There is no evidence of either ethylene or ethane.

### 3.2.3. Decomposition Monitored by Infrared Spectrometry

In the interests of clarity only two infrared spectra are shown in Appendix 2, i.r. 3, pg 110. They are those obtained at time zero and after 170 hr at room temperature. The major peaks in i.r. 3 are shown below. The peaks which diminish are shown alongside those of endo-2,4-ethylenetetraborane and those which increase are shown alongside those of diborane.

| Peaks diminishing in i.r. 3 | Endo-2,4-ethylene-tetraborane | Peaks increasing in i.r. 3 | Diborane |
|---|---|---|---|
| 3.4µ | 3.42µ | 2.7µ | 2.7µ |
| | 3.85 | | 3.7 |
| | 3.95 | | 3.8 |
| | | | 3.95 |
| 4.7 | 4.7 | | |
| | | 6.15 | 6.15 |
| | 7.0 | | 6.25 |
| | | 6.4 | 6.3 |
| 9.5 | 9.5 | | |
| | | 8.4 | 8.3 |
| | 10.3 | 8.5 | 8.5 |
| | | 8.6 | 8.7 |
| 11.5 | 11.4 | | |
| | | | 10.25 |
| | 13.5 | | |

There are peaks at 3.8, 3.95 and 10.3µ which remain at about the same intensity; these peaks are common to the infrared spectra of both diborane and endo-2,4-ethylenetetraborane. The results of this experiment show that while the peaks corresponding to endo-2,4-ethylenetetraborane steadily decrease those corresponding to diborane steadily increase. A rise in pressure in the infrared cell is observed due to hydrogen evolution. On the basis of infrared data it appears that endo-2,4-ethylenetetraborane decomposes to only diborane and hydrogen.

### 3.2.4. Decomposition Monitored by N.M.R. Spectrometry

The $^{11}B$ n.m.r. spectra are shown in Appendix 3, n.m.r. 1, pgs 115 and 116. At -50 °C the spectrum is similar to that in the literature(2, 37). In n.m.r. 1 at -50 °C there are doublets at -3.7 ppm (J = 130 Hz) and at 38.5 ppm (J = 147 Hz). The literature lists doublets at -4.0 ppm (J = 130 Hz) and at ~39 ppm (J = 145 Hz). There is also a small peak at 53.5 ppm which is probably due to an impurity. After one hour at room temperature the peaks become smaller but a new peak appears at -16 ppm. This is probably due to diborane which has a signal at -17 ppm.(51) After twenty-four hours at room temperature the peaks are small and there is a broad absorption centred at ~0 ppm. By thirty-six hours this broad absorption is sufficiently well resolved to observe a doublet at 38.8 ppm and a number of other signals centred at ~-4.6 ppm. Some of the above signals are from endo-2,4-ethylenetetraborane and diborane but the cause of the rest is not known. The broadening and diminishing of the signals is due, in part, to the increased viscosity of the liquid. Cooling the sample to -50 °C has no significant effect on the signal.

The proton n.m.r. spectrum is shown in Appendix 3, n.m.r. 2, pg 117 . The spectrum is consistent with the qualitative description given in the literature(2). Using the 50 ppm scale a broad absorption ($W_{\frac{1}{2}}$ ~540 Hz) is observed with a sharp singlet slightly upfield of centre at 9.1τ. Below the singlet are some small bumps on the broad absorption.

The mass spectrum of the volatile products is tabulated in Appendix 1, m.s. 3, pg 99 along with the mass spectra of diborane and ethylene. The mass spectrum has a cut off at m/e 64. Peaks around m/e 50 probably indicate the presence of tetraborane and around m/e 60 a trace of either, or both, pentaboranes. The peaks from m/e 29 to m/e 22 indicate the presence of diborane and ethylene. There is no m/e 30 peak so ethane is absent. Unfortunately, little else can be said about the spectrum as the accuracy of the spectrometer does not permit the investigation of mixtures.

The infrared spectrum taken after thirty-six hours at room temperature, Appendix 2, i.r. 4, pg 111 , contains no peaks indicating the presence of endo-2,4-ethylenetetraborane. In the most part, peaks corresponding to those in the diborane spectrum are observed. Some peaks in the spectrum, while occurring at the wavelength expected, have a different shape from those in the diborane spectrum. This coupled with the 3.4μ peak made ethyldiborane a possibility.

### 3.2.5. Conclusions

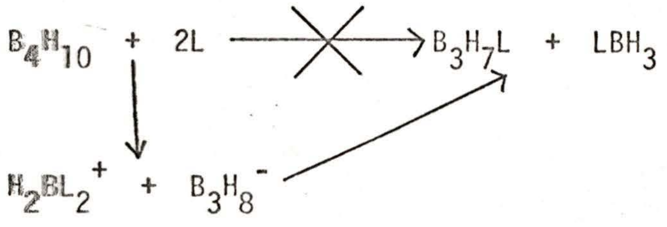
Endo-2,4-ethylenetetraborane is much less stable than was anticipated. Its $^{11}$B n.m.r. spectrum is recognisable after one hour at room temperature but not after twenty-four hours. The volatile products of the thermal decomposition were diborane and hydrogen. Traces of tetraborane and pentaboranes were found. As diborane was a major product of the thermal decomposition of 1,2-tetramethylenediborane(33), by analogy tetraborane might be expected to be a product of the thermal decomposition of endo-2,4-ethylenetetraborane. There is a possibility that ethyldiborane was formed and there was mass spectral evidence for the formation of ethylene. There was no evidence for the formation of ethane.

## 3.3. Reaction of Endo-2,4-Ethylenetetraborane with Lewis Bases

### 3.3.1. Introduction

It was widely believed that diborane and tetraborane were symmetrically cleaved by all Lewis bases except ammonia which cleaved the boranes unsymmetrically. This statement, quite naturally, raises two questions - why is this? and how does cleavage occur? As symmetrical cleavage is much more common than unsymmetrical cleavage, it might be thought that symmetrical cleavage is the principal reaction and unsymmetrical cleavage will occur where symmetrical cleavage is impossible. It was also implicit in the earlier papers, before 1964, that the reaction of a borane with a Lewis base proceeds in an either/or manner. Either there is symmetrical cleavage or there is unsymmetrical cleavage. Parry, in his far-seeing paper in 1959$^{(22)}$, stated that the nature of the bridge cleavage process is determined by both the nature of the base and the nature of the hydride. For example, a borane such as diborane with double hydrogen-bridged bonds, and thus an easily removed $BH_2$ group, would be expected to react differently from pentaborane(9) which does not have this feature. Parry also stated that the type of cleavage process occurring in a given borane is governed primarily by the base and secondarily by the experimental conditions. It was apparent that the bases which cleaved boranes unsymmetrically were smaller than those which cleaved boranes symmetrically. The fragment produced in unsymmetrical cleavage is $BH_2L_2^+$ and it is clear that steric factors will be more important than in reactions which produce fragments which have only one base attached to a boron.

In 1964, Schaeffer et al published a paper on the cleavage of tetraborane by ethers$^{(50)}$. Using nuclear magnetic resonance to examine the course of tetraborane reactions, Schaeffer found evidence that the overall symmetrical cleavage reaction takes place by a nonsymmetrical cleavage process followed by the exchange of an ether molecule in $H_2BL_2^+$ and a hydride ion from the octahydrotriborate(1-) ion. This is represented below :-



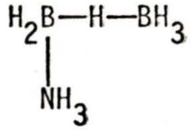
This conclusion was based on the observation of the octahydrotriborate(1-) n.m.r. signal from a mixture of tetraborane and tetrahydrofuran at -20 °C. At higher temperatures the triborane(7) complex forms. The data were weak in accounting for the other boron atom which was assumed to form $BH_2L_2{}^+$ and there was a chance that only a single bridge bond was broken. Schaeffer eliminated this possibility by the isolation of octahydrotriborate(1-). He also reacted tetraborane with ammonia in ether at low temperatures and his data are similar to those of Shore et al(31) who showed that this reaction deprotonated tetraborane.

The reactions of diborane with methylamines are well known to yield the symmetrical cleavage products, amine boranes. Shore et al in 1965 reported the unsymmetrical cleavage of diborane by methylamine, dimethylamine and trimethylamine(59). They monitored the reactions between diborane and amines at -80 to -90 °C by $^{11}B$ n.m.r. The relative amounts of the reaction products are listed below :

| | unsymmetrical cleavage product | | symmetrical cleavage product |
|---|---|---|---|
| $CH_3NH_2$ | $H_2B(NH_2CH_3)_2{}^+BH_4{}^-$ | $\gg$ | $H_3BNH_2CH_3$ |
| $(CH_3)_2NH$ | $H_2B(NH(CH_3)_2)_2{}^+BH_4{}^-$ | $<$ | $H_3BNH(CH_3)_2$ |
| $(CH_3)_3N$ | | | $H_3BN(CH_3)_3$<br>(only product) |

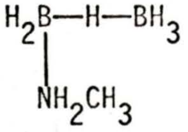
These results indicate that the smaller Lewis bases produce unsymmetrical cleavage products.

Later, Shore and Hall(60) announced that they had prepared and then obtained $^{11}B$ n.m.r. spectra of some singly hydrogen-bridged boranes which are shown below :



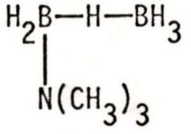
$\underset{NH_3}{H_2B}-H-BH_3$

I



$\underset{NH_2CH_3}{H_2B}-H-BH_3$

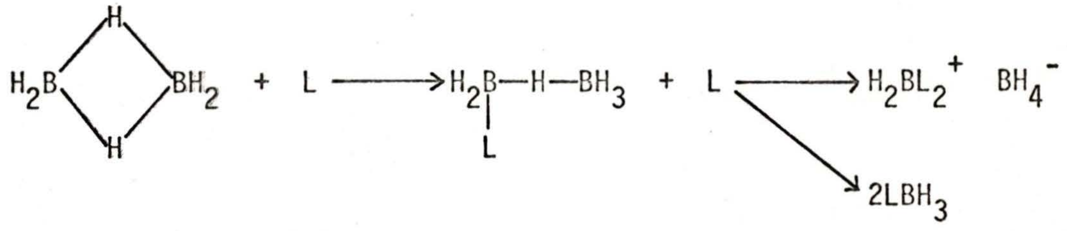
II



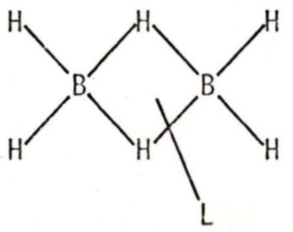
$\underset{N(CH_3)_3}{H_2B}-H-BH_3$

III

The addition of a second molecule of amine at -78 °C resulted in unsymmetrical cleavage products in the case of I and II and the symmetrical cleavage product in the case of III. In view of this and evidence of analogous intermediates in other systems Shore concluded that the reaction of diborane with a ligand takes place in a stepwise fashion thus :

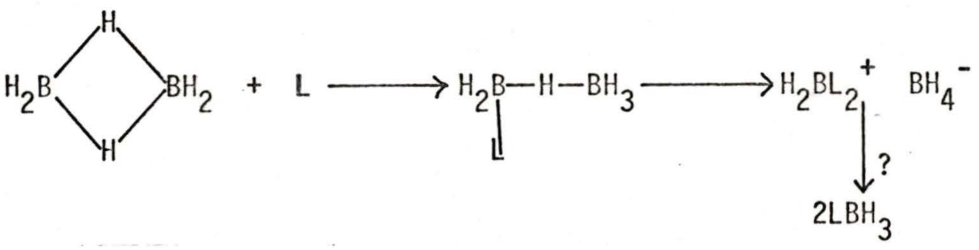


Eastham(61) interpreted Shore's work in a different way. He suggested that the initial reaction of a Lewis base and diborane resulted in the formation of a π bonded complex :

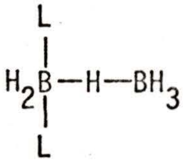


Additional base might or might not dissociate the complex. He used Gaines'(62) observation that the $^{11}$B n.m.r. spectrum of diborane in glycol ethers at room temperature consisted of a septet indicating a rapid intermolecular exchange of protons but no dissociation to show that a $B_2H_6$-L complex of diborane is quite stable to dissociation. Shore et al(63) refuted Eastham's structure on thermodynamical grounds and on the evidence of some isotope exchange work.

Beachley(64) suggested that the reactions of diborane with Lewis bases at low temperatures might involve unsymmetrical cleavage but that the product could readily rearrange to form the symmetrical cleavage product depending upon which form is more stable at that particular temperature. The process Beachley suggested might be represented thus :

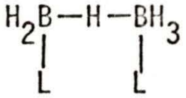


He observed that ammonia borane (which can be made indirectly) decomposes to form $H_2B(NH_3)_2{}^+BH_4^-$ but $H_2B(NH_2CH_3)_2{}^+BH_4^-$ decomposes to methylamineborane. Beachley speculated that perhaps there is only one type of cleavage of diborane - unsymmetrical cleavage. This is nearly the opposite of some earlier ideas. It is apparent that unsymmetrical cleavage is much more common that at first thought but whether symmetrical cleavage is really unsymmetrical cleavage followed by a hydride ion transfer is still in doubt. Probably the initial attack of a Lewis base produces a singly hydrogen-bridged species but the crux of this problem is - at which boron does the second Lewis base attack? If Beachley is correct, then the second Lewis base will always attack at the same boron as the first to give an intermediate such as :-



$$H_2\underset{L}{\overset{L}{B}}-H-BH_3$$

It is, however, possible that the second Lewis base might attack the boron at the other end of the bridge hydrogen bond to give an intermediate such as :-

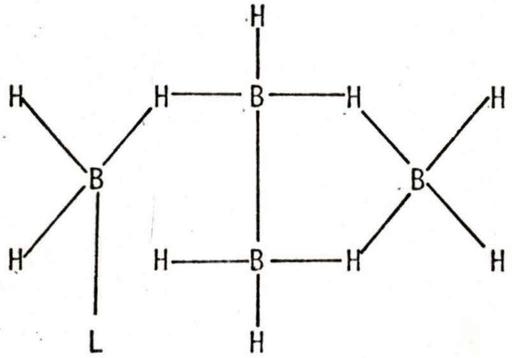


$$H_2\underset{L}{B}-H-\underset{L}{B}H_3$$

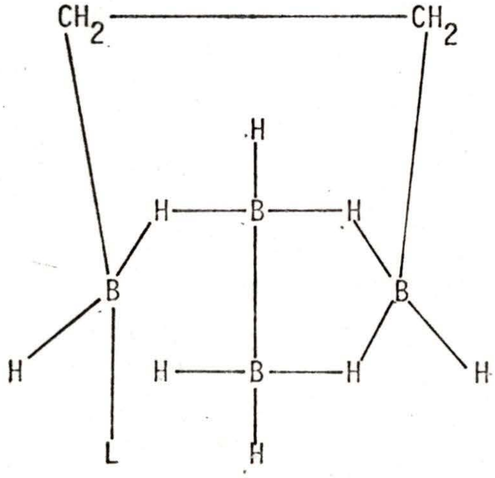
which might have a transitory existence breaking down to give two $H_3BL$ molecules. It is, of course, possible that the size of the Lewis base might control the site of attack of the second molecule of the base.

Beachley's suggestion is of value in that it intimates, as does Schaeffer(50), that the products of a cleavage reaction might rearrange. If this is correct then Parry's simple definitions of symmetrical and unsymmetrical cleavage (see Section 1.3.5.) are not useful in clarifying reaction mechanisms.

Not much work has been reported on the reactions of tetraborane with Lewis bases at low temperatures. Kodama(24) suggested that the attack of ammonia on tetraborane might give the intermediate :



A second molecule of ammonia would give the unsymmetrical cleavage product. Such an intermediate has never been isolated in the case of tetraborane. If, in the case of endo-2,4-ethylenetetraborane, a similar mechanism occurs the intermediate would be :



How this would break down or react with another molecule of Lewis base is difficult to say. The B-H-B bonds in $B_3H_8^-$ are resistant to attack by ammonia but the B-H-B bonds in $(CH_3)_3N\text{-}B_3H_7$ can be broken by more trimethylamine to give $H_3B\cdot x(CH_3)_3N$ where $x = 0.37\text{-}0.54$(65).

In 1969, Ritter et al(66) elaborated on an earlier communication in which they reported the formation of a $B_2H_4L_2$ species by the reaction of the ether adduct of $B_3H_7$ and a substituted phosphine. Graybill and Ruff(67) recognised that the stronger the ligand bond in $LB_3H_7$, then the greater the extent of the degradation of the triborane upon reaction with a stronger Lewis base. Ritter listed three types of reactions :-

(a) the formation of another triborane

(b) transformation to a diborane(4) adduct

(c) degradation to a borane adduct and a polymer.

Obviously the chemistry of tetraborane is more complicated than that of diborane and less well studied. It is difficult to make accurate predictions concerning the reactions of endo-2,4-ethylenetetraborane and Lewis bases.

### 3.3.2. Reaction of Endo-2,4-Ethylenetetraborane with Diethylether

The reactions of tetraborane and diethylether were summarized in a technical report by Hough et al(68). At room temperature tetraborane is cleaved symmetrically by diethylether. The borane-ether adduct is unstable and decomposes to give diborane.

$$2B_4H_{10} + 2(C_2H_5)_2O \longrightarrow 2(C_2H_5)_2O\cdot B_3H_7 + B_2H_6$$

With excess tetraborane a further reaction occurs to give pentaborane(9) :

$$5B_4H_{10} \xrightarrow{(C_2H_5)_2O\cdot B_3H_7} 2B_5H_9 + 5B_2H_6 + H_2$$

Immediately, the endo-2,4-ethylenetetraborane and diethylether melt there is a vigorous reaction and hydrogen is evolved. A small amount of white solid is formed. Four $^{11}B$ n.m.r. spectra are shown in Appendix 3, n.m.r. 3, pg 118 . The spectrum at -60 $^{o}C$ is that of endo-2,4-ethylenetetraborane with a doublet centred at -3.1 ppm (J = 142.5 Hz) and one centred at 37.5 ppm (J = 145 Hz). As the mixture warms to room temperature, the signals collapse and become broader. This is probably caused by an increase in the viscosity of the solution. After twenty-four hours at room temperature there are peaks just below 0 ppm and between 35 and 40 ppm probably indicating the presence of endo-2,4-ethylenetetraborane. There is a larger peak at 7.4 ppm. This signal arises from $B_3H_7\cdot O(C_2H_5)_2$. The literature value given by Phillips et al(69) is 7.6 ppm. Phillips reported that the $^{11}B$ n.m.r. spectrum of $B_3H_7\cdot O(C_2H_5)_2$ appeared to be a symmetrical sextet of ~30 Hz spacing. Lipscomb(70) pointed out that it was probably the inner six lines of an octet. Ring et al(71) showed that both hydrogen tautomerism and Lewis base exchange were taking place. There is a signal at 17.5 ppm, the cause of which is not known. It is significant that there is no peak at 30 ppm - the position of the $B_3H_8^-$ resonance.

Cooling to -50 °C improves the signal. The $B_3H_7 \cdot O(C_2H_5)_2$ peak and the endo-2,4-ethylenetetraborane peaks are still present. Peaks at 15.2 ppm and at -36 ppm are of unknown origin but could be significant.

The proton n.m.r. of the sample shows peaks corresponding only to those of diethylether - a quartet at 5.68τ (J = 6.7 Hz) and a triplet at 7.82τ (J = 7.0 Hz) - and is not shown.

The mass spectrum of the volatile products is tabulated in Appendix 1, m.s. 4, pg 100 . The spectrum is similar to the mass spectrum of diethylether. The large m/e 28 peak is probably caused by air.

The infrared spectrum of the volatile products, Appendix 2, i.r. 5, pg 111 , is shown below alongside that of ether. I.r. 5 shows mainly ether peaks with unidentified peaks at 3.8μ and 6.2-6.3μ:

| i.r. 5 | ether |
|---|---|
| 3.3μ | 3.35μ |
| 3.45 | 3.47 |
| 3.80 | 5.05 |
| 6.22 | |
| 6.27 | |
| 6.95 | 6.90 |
| 7.22 | 7.20 |
| 8.80 | 8.80 |
| 9.35 | 9.30 |
| 10.70 | 10.75 |

The mass spectrum of the solid has peaks above m/e 150 but all the peaks above m/e 101 are very small, as was the m/e 11 peak.

Most peaks in the spectrum are in groups and the groups are generally separated by 14 mass units. The spectrum below m/e 101 is shown in Appendix 1, m.s. 5, pg 101 , along with that of ether. Even if all the m/e 74 peak in m.s. 5 were due to ether, it is an indication that ether is only present in a relatively small amount. Many of the larger peaks, eg. m/e 101, 72, 43, are separated by 29 mass units. The m/e 29 peak is large, as is the m/e 45 peak (14 mass units above m/e 31). It is probable that the white solid is hydrocarbon in nature.

The reaction of 1 mmol endo-2,4-ethylenetetraborane and 5 mmol diethylether results in the ether-triborane adduct but not diborane. The mass spectrum and infrared spectrum show mainly ether. There is no evidence for unsymmetrical cleavage. A number of peaks in the $^{11}B$ n.m.r. cannot be explained and the identity of the white solid is not known but it is probably hydrocarbon in nature. Although excess ether was used there is no evidence of pentaborane(9).

### 3.3.3. The Reaction of Endo-2,4-Ethylenetetraborane with Tetrahydrofuran

Hough et al$^{(68)}$ described the reaction of tetraborane and tetrahydrofuran. At room temperature symmetrical cleavage occurs. The borane-tetrahydrofuran adduct is unstable and decomposes to give diborane :-

$$2B_4H_{10} + 2C_4H_8O \longrightarrow 2C_4H_8O\cdot B_3H_7 + B_2H_6$$

If there is an excess of tetraborane, pentaborane(9) is obtained by the following reaction :

$$5B_4H_{10} \xrightarrow{C_4H_8O\cdot B_3H_7} 5B_2H_6 + 2B_5H_9 + H_2$$

As previously noted, studies by Schaeffer et al(50) have indicated that at low temperatures tetrahydrofuran cleaves tetraborane unsymmetrically to give the octahydrotriborate(1-) ion, $B_3H_8^-$.

The reaction between endo-2,4-ethylenetetraborane and tetrahydrofuran is extremely vigorous, even at a temperature just above the melting point of endo-2,4-ethylenetetraborane (about -78 °C). A small amount of white solid separates out. A mass spectrum of the white solid was recorded but there was too little for a successful infrared spectrum. The solid was insoluble in the solvents listed on pg 54

$^{11}B$ n.m.r. spectra are shown in Appendix 3, n.m.r. 4, pg 119 . The spectrum at -60 °C is similar to the spectrum of endo-2,4-ethylenetetraborane in the literature(2). As the sample is warmed the peaks collapse until at -10 °C only a broad hump is present, mainly upfield of 0 ppm. By ten minutes at room temperature the $B_3H_7\cdot OC_4H_8$ signal appears at 8.5 ppm (literature values 8.4±1.5 ppm(50), 10±1 ppm(72). There is a shoulder on the upfield side of the peak. No signal at 30 ppm ($B_3H_8^-$) is observed. After one hour at room temperature the $B_3H_7\cdot OC_4H_8$ signal is much stronger. There is a broad signal at lower field.

After twenty-four hours at room temperature more signals appear. There is a peak at -27.8 ppm, the origin of which is unknown. This region of the spectrum could be caused by ethyldiborane, the boron-11 n.m.r. spectrum of which is similar in this region. The peak at 9.5 ppm could be the $B_3H_7{\cdot}OC_4H_8$ signal. The peak at 17.2 ppm is unexplained. The doublet at 38.5 ppm is probably due to unreacted endo-2,4-ethylenetetraborane, the low field doublet is probably obscured by the peaks at about 0 ppm.

Upon cooling to -50 $^{o}$C, the low field signals collapse, the upfield signals are enhanced and a new peak appears at 51 ppm. It is possible that the peak at 51 ppm is due to a trace of pentaborane(9) (doublets at 13.3 ppm and 51.5 ppm(51)) with the peaks at lower field obscured.

The proton n.m.r. is shown in Appendix 3, n.m.r. 5, pg 120 The positions of the peaks are shown below compared with those of n-butane, tetrahydrofuran and 1 -butanol :-

| | | | | |
|---|---|---|---|---|
| Reaction Products | 6.32τ | 8.57τ | 9.02τ | 9.12τ |
| n-butane | | 8.75 | 9.00 | 9.15 |
| tetrahydrofuran | 6.42 | 8.22 | | |
| 1-butanol | 6.42/6.60 | 8.50/8.61 | 8.99/9.10 | 9.10/9.18 |

There is a range given for the position of the peaks in the spectrum of 1-butanol as the position of peaks varies depending upon how much water and acid are present. The contour of the spectrum is characteristic of 1-butanol rather than n-butane. The absence of the tetrahydrofuran peak at 8.22τ is puzzling as an excess of tetrahydrofuran is used in the reaction. From the above data it is reasonable to conclude that 1-butanol is present in the n.m.r. tube.

The mass spectrum of the volatile products is shown in Appendix 1, m.s. 6, pg 102 . The mass spectrum is very similar to that of n-butane. Tetrahydrofuran has a base peak at m/e 42 and so there is no indication of that compound. The peaks around m/e 50 could be due to the presence of tetraborane. The peaks at m/e 25 and 24 are probably due to diborane.

The infrared spectrum between 3μ and 15μ of the volatile products is shown in Appendix 2, i.r. 6, pg 112 . The stronger peaks are shown below along with those of diborane :

| i.r. 6 | diborane |
|---|---|
| 3.35μ | |
| | 3.70μ |
| 3.8 | 3.80μ |
| 3.95 | 3.95 |
| 6.17 | 6.15 |
| 6.22 | 6.24 |
| 6.29 | 6.30 |
| 8.35 | 8.30 |
| 8.50 | 8.50 |
| 8.70 | 8.70 |
| 10.27 | 10.25 |
| 11.95 | |

Although diborane is probably present, the large peak at 3.35μ could be due to an alkyldiborane, the spectra of which are similar to the parent diborane(54). There is no indication of n-butane, tetrahydrofuran or 1-butanol.

The mass spectrum of the solid is shown in Appendix 1, m.s. 7, pg 103 , along with the mass spectrum of 1-butanol. The mass spectrum of the solid does show small peaks up to about m/e 200. The spectrum below m/e 74 is very similar to that of 1-butanol. 1-butanol is a liquid at these temperatures but the sample is a white, insoluble solid. The solid is probably hydrocarbon in nature (there is no m/e 11 boron peak in the mass spectrum) and is mixed with 1-butanol. The solid does, however, burn with the green flame characteristic of boron.

There is no explanation why the proton n.m.r. shows 1-butanol, while the mass spectrum of the volatile products shows n-butane and the infrared spectrum shows diborane or an alkylated derivative. It is possible that the liquid in the n.m.r. tube was, in part, 1-butanol but the separation removed the volatile products from it. Mass spectrometry is more sensitive than infrared spectrometry for the detection of compounds. It is possible that mass spectrometry would detect traces of n-butane in the volatile products but infrared spectrometry would not.

There is no evidence of unsymmetrical cleavage. The origin of the n-butane and 1-butanol is obscure in this reaction. It is possible that they might arise from decomposition of tetrahydrofuran as no tetrahydrofuran is present in the products; this is, however, unlikely.

Sufficient hydrogen to explode a sealed n.m.r. tube was generated. The main boron containing product after twenty-four hours appears to be triborane(7). This species is formed in the analogous reaction of tetraborane.

### 3.3.4. Reaction of Endo-2,4-Ethylenetetraborane with Ammonia in Diethylether

In ether solution tetraborane is unsymmetrically cleaved by ammonia according to the well known reaction :-

$$B_4H_{10} + 2NH_3 \longrightarrow BH_2(NH_3)_2^+ \; B_3H_8^-$$

At low temperatures ammonia has been found to deprotonate tetraborane according to the reaction (31) :-

$$B_4H_{10} + NH_3 \longrightarrow B_4H_9^- + NH_4^+$$

Reaction between ammonia and endo-2,4-ethylenetetraborane occurs as soon as the borane derivative melts (about -78 °C). A small amount of white solid forms. As in the case of the previous reactions, the solid is insoluble. The $^{11}B$ n.m.r. spectra for this reaction are shown in Appendix 3, n.m.r. 6, pg 121 . The spectrum at -60 °C shows the literature spectrum of endo-2,4-ethylenetetraborane. There is no evidence of the nonahydrotetraborate(1-) ion ($B_4H_9^-$) which at -60 °C has resonances at 0.4 ppm, 9.7 ppm and 53.2 ppm(31). As the sample is warmed the peaks collapse until at 0 °C the spectrum is two broad humps, the upfield one barely split into a doublet. The collapse of the peaks is probably due to an increase in viscosity of the mixture. After one and a half hours at room temperature the spectrum shows a strong signal at 30 ppm. The octahydrotriborate(1-) ion ($B_3H_8^-$) has an $^{11}B$ n.m.r. resonance at 30 ppm(50). There is a broad resonance centred downfield from the octahydrotriborate(1-) ion signal.

This is probably due to the $BH_2(NH_3)_2^+$ ion which has an $^{11}B$ n.m.r. signal of a triplet at 14.6 ppm(50). There is no evidence of the nonahydroborate(1-) ion which has $^{11}B$ n.m.r. signals at 9.7 ppm and 26.5 ppm at room temperature(31). The n.m.r. spectrum does not alter upon leaving the sample at room temperature for thirty-six hours. Subsequent cooling to -50 °C causes all the peaks to collapse. The $^{11}B$ n.m.r. spectra shows that endo-2,4-ethylenetetraborane is unsymmetrically cleaved by ammonia to give the products of the unsymmetrical cleavage of tetraborane.

The proton n.m.r. spectrum shows peaks corresponding to those of diethylether and a very small peak at 5.57τ. No ammonia resonance can be observed.

The mass spectrum of the volatile products is shown in Appendix 1, m.s. 8, pg 104 , along with mass spectrum of diethylether. The two spectra are very similar.

The infrared spectrum of the volatile products is shown in Appendix 2, i.r. 7, pg 112 . The prominent peaks are shown below, alongside those of diethylether :-

| i.r. 7 | diethyl-ether |
|---|---|
| 3.30μ<br>3.40 | 3.35μ<br>3.47 |
| 7.12<br>7.27 | 6.90<br>7.20 |
| 7.60 | 7.65 |
| 8.66 | 8.80 |
| 9.15 | 9.30 |
| 10.60 | 10.75 |

I.r. 7 is very similar to the i.r. spectrum of diethylether.

The mass spectrum of the solid below m/e 100 is shown in Appendix 1, m.s. 9, pg 105 . There is no cut-off up to ~ m/e 250. There are very large water and ammonia peaks. Above m/e 100 there are small groups of peaks separated by 14 mass numbers. In any group of peaks two, separated by two mass numbers, are more prominent than the rest. This trend continues below m/e 100 with two sets of peaks offset by two mass numbers. There are relatively large peaks at the following mass numbers ; 97, 95, 83, 81, 69, 67, 55, 53, 41, 39, 27. There is a very large peak at m/e 71 and this is the heaviest peak of another series which includes m/e 71, 57, 43,29. The large peak at m/e 30 is characteristic of amines. There is no evidence of boranes (no m/e 11 peak) or diethylether (no m/e 74 peak). The solid does burn with a green flame which is indicative of boron. The solid appears to be hydrocarbon in nature and is possibly a mixture of higher amines. Perhaps it is significant that the base peak of many high cycloalkanes occurs at m/e 55 and the mass spectra of these compounds include many of the above peaks. There is no evidence of water in the mass spectrum of the volatile products and so water must have got onto the solid during the transfer to the mass spectrometer after the n.m.r. tube was broken.

The presence of the high molecular weight compounds in the solids indicates that endo-2,4-ethylenetetraborane might break down to form a radical. There is no evidence of proton abstraction as from tetraborane. The tetraborane fragments react with ammonia to form the unsymmetrical cleavage products of tetraborane.

### 3.3.5. Reaction of Endo-2,4-Ethylenetetraborane with Trimethylamine

Tetraborane reacts with trimethylamine to form the symmetrical cleavage products trimethylamineborane and trimethylaminetriborane :-

$$B_4H_{10} + (CH_3)_3N \longrightarrow (CH_3)_3N\cdot BH_3 + (CH_3)_3N\cdot B_3H_7$$

In this case the Lewis base is strong enough to form a stable borane adduct. If excess trimethylamine is present it further cleaves the trimethylaminetriborane(65) according to the equation :-

$$B_4H_{10} + (3 + x)(CH_3)_3N \longrightarrow 3(CH_3)_3N\cdot BH_3 + BH\cdot x(CH_3)_3N$$

$$x = 0.37\text{-}0.54$$

A reaction occurs upon mixing endo-2,4-ethylenetetraborane and trimethylamine at about -78 °C. A white insoluble solid forms which burns with a green flame.

The $^{11}B$ n.m.r. spectra are shown in Appendix 3, n.m.r. 7, pg 122 . The signal does not alter upon warming the sample nor upon leaving it at room temperature for thirty-six hours. The spectrum consists of a quartet superimposed over a broad singlet :-

| | | |
|---|---|---|
| quartet shift | - 7.4 ppm | J ~ 100 Hz |
| $(CH_3)_3N\cdot BH_3$ shift | - 7.8 ppm | J ~ 100 Hz(72) |

The singlet is centred at ~1 ppm and is probably caused by $BH\cdot x(CH_3)_3N$. The signals collapse to a broad resonance ($W_{\frac{1}{2}}$ ~ 279 Hz) when the sample is cooled to -50 °C.

The proton n.m.r. is shown in Appendix 3, n.m.r. 8, pg 123 The main feature is a large singlet at $7.90\tau$ which is due to trimethylamine (literature value $7.88\tau$)(73). There is a doublet at $7.46\tau$, J = 4.7 Hz). The literature value for the shift of methyl protons in $(CH_3)_3N\cdot BH_3$ is given as $7.40\tau$(73). If the doublet is caused by $(CH_3)N\cdot BH_3$ a quartet of peaks equal in height would be expected from the borane protons but no quartet is observed. There are two very small peaks at $5.52\tau$ and $5.54\tau$ and with high sensitivity small broad resonances at $9.00\tau$ and $9.83\tau$ can just be observed.

The mass spectrum of the volatile products is shown in Appendix 1, m.s. 10, pg 106 , along with the mass spectra of n-butane and trimethylamine. The mass spectrum of the liquid products indicates the presence of both these compounds but mainly n-butane. There is only a very small m/e 11 peak.

The infrared spectrum of the liquid products is shown in Appendix 2, i.r. 8, pg 113 . The major peaks are tabulated below and shown along with the infrared spectra of trimethylamine :

| i.r. 9 | trimethylamine |
|---|---|
| $3.35\mu$ | $3.40\mu$ |
| 3.55 | 3.46 |
| 3.65 | 3.56 |
| 6.75 | 6.75 |
| 6.77 | |
| 6.82 | |
| 6.92 | 6.92 |
| | 6.96 |
| 7.80 | 7.88 |
| 7.92 | 7.93 |
| 8.43 | 8.46 |
| | 8.50 |
| 9.00 | |
| 9.67 | 9.66 |
| | 9.73 |
| 12.10 | 12.10 |

In the infrared spectrum there are no peaks at ~4μ (B-H stretch) which indicates the absence of $(CH_3)_3N{\cdot}BH_3$. It is evident that trimethylamine is present. There is also a possibility of the presence of n-butane (peaks at 3.43, 6.84, 7.66, 10.22 and 10.33μ).

The mass spectrum of the solid, Appendix 1, m.s. 11, pg 107 shows no clear cut off but all the peaks above m/e 72 are small. The m/e 72 is not prominent in the mass spectra of the butylamines but is a feature of the mass spectra of many higher amines.

The reaction of endo-2,4-ethylenetetraborane and trimethylamine yields the ultimate products of symmetrical cleavage of tetraborane, ie. trimethylamineborane $(CH_3)_3N{\cdot}BH_3$ and the compound $BH{\cdot}x((CH_3)_3N)$, and the products of, presumably, a free radical reaction resulting in the formation of a white solid and n-butane.

### 3.4.6. Conclusions

The main purpose of this work was to study the effect of the dimethylene bridge on the mode of reaction of the boron-hydrogen framework during cleavage reactions of endo-2,4-ethylenetetraborane. To achieve this, endo-2,4-ethylenetetraborane was reacted with a variety of Lewis bases in an attempt to establish the mechanism of the cleavage processes.

As described earlier in this chapter most Lewis bases including ethers and amines (but not ammonia, see over) cleave tetraborane symmetrically to yield $B_3H_7L$ and $BH_3L$ as the primary products. Various subsequent reactions might occur, for example in the reactions of tetraborane with diethylether or tetrahydrofuran, the $BH_3L$ adduct decomposes to produce diborane. If excess tetraborane is reacted with diethylether or tetrahydrofuran, a reaction occurs resulting in the formation of pentaborane(9) and diborane. If excess trimethylamine is reacted with tetraborane the $(CH_3)_3N \cdot B_3H_7$ is further cleaved to give $H_3B \cdot x(CH_3)_3N$. In the case of the reaction of tetraborane and ammonia unsymmetrical cleavage occurs yielding the 'diammoniate of tetraborane', $H_2B(NH_3)_2^+ \; B_3H_8^-$.

The reactions of endo-2,4-ethylenetetraborane with Lewis bases produced cleavage products which were similar to the products of the analogous tetraborane reactions. The reaction of endo-2,4-ethylenetetraborane with diethylether produced $B_3H_7 \cdot Et_2O$ and the reaction with tetrahydrofuran yielded $B_3H_7 \cdot C_4H_8O$. The 'diammoniate of tetraborane' $(BH_2(NH_3)_2^+ \; B_3H_8^-)$ was a product of the reaction of endo-2,4-ethylenetetraborane with ammonia in ether. The reaction of endo-2,4-ethylenetetraborane with trimethylamine yielded $BH_3 \cdot (CH_3)_3N$ and $H_3B \cdot x(CH_3)_3N$. In addition to these products derived from the boron framework, each reaction gave a white polymeric solid and the reactions of endo-2,4-ethylenetetraborane with tetrahydrofuran and with trimethylamine yielded n-butane. The white solids and the n-butane were presumably derived from the dimethylene bridge.

Schaeffer et al (50) found evidence for the unsymmetrical cleavage of tetraborane upon reaction with tetrahydrofuran. No evidence for unsymmetrical cleavage was observed in the analogous endo-2,4-ethylenetetraborane reaction although there were peaks in the $^{11}B$ n.m.r. spectra that were not explained. Johnson and Shore$^{(31)}$ have shown that ammonia will deprotonate tetraborane at low temperatures. There was no evidence for an analogous reaction in the case of endo-2,4-ethylenetetraborane.

These results suggest that the effect of the dimethylene bridge in endo-2,4-ethylenetetraborane is not to hold the boron atoms $B_2$ and $B_4$ together since most of the boron containing products are the same as those of analogous tetraborane reactions. Evidently the B-C bond cleavage occurs generating free radicals which react to produce the polymeric white solids, n-butane and 1-butanol. It is improbable that a $CH_2$-$CH_2$ species leaves a molecule of endo-2,4-ethylenetetraborane as such a moiety would yield ethylene. Consequently the polymeric white solids, n-butane and 1-butanol must have resulted from intermolecular reactions. The reaction of the remaining boron-hydrogen framework yielded products similar to the analogous tetraborane reaction.

Although the mechanism of the cleavage processes will probably be discovered by the systematic investigation of diborane, tetraborane and then endo-2,4-ethylenetetraborane, it is possible that extensions of the present work as described in the next section will be rewarding.

### 3.3.7. Suggestions for future work

The reactions of endo-2,4-ethylenetetraborane with the Lewis bases employed in this work should be repeated using different mole ratios of the reactants and under other conditions. The products of such reactions might be quite different from those described here. An example is shown in Fig 10 which indicates the products of the reaction of diborane and ammonia are highly dependent upon the conditions of reaction. There were unexplained peaks in the $^{11}B$ n.m.r. spectra of all the reactions (except with ammonia); it is necessary to identify the species causing these peaks. There are no reports of the reactions of Lewis bases with 1,2-tetramethylenediborane, such reactions might prove interesting. Finally, the reactions involving the B-C bond cleavage with the possible subsequent formation of free radicals might be modified to produce new organo-boron compounds.

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# APPENDIX 1 : MASS SPECTRA

## Mass Spectrum 1

| m/e | Intensity % of m/e 41 | Ref. 2 |
|---|---|---|
| 80 | 1.3 | 0.7 |
| 79 | 2.5 | 1.9 |
| 78 | 29.6 | 28.6 |
| 77 | 36.4 | 33.4 |
| 76 | 58.7 | 57.9 |
| 75 | 50.1 | 50.0 |
| 74 | 29.3 | 34.0 |
| 73 | 25.4 | 29,0 |
| 72 | 16.7 | 19.8 |
| 71 | 11.5 | 13.7 |
| 70 | 8.1 | 9.5 |
| 69 | 9.1 | 10.8 |
| 68 | 6.6 | 8.2 |
| 67 | 2.9 | 3.6 |
| 66 | 4.8 | 5.5 |
| 65 | 5.5 | 6.1 |
| 64 | 42.0 | 47.5 |
| 63 | 51.9 | 54.8 |
| 62 | 44.5 | 49.0 |
| 61 | 33.9 | 37.6 |
| 60 | 18.8 | 20.6 |
| 59 | 14.1 | 15.6 |
| 58 | 10.2 | 12.0 |
| 57 | 5.5 | 6.6 |
| 56 | 3.1 | 2.6 |
| 55 | 3.5 | 1.2 |
| 54 | 2.0 | 0.5 |
| 53 | 4.2 | 4.0 |
| 52 | 12.9 | 14.6 |
| 51 | 34.6 | 33.4 |
| 50 | 30.7 | 35.9 |
| 49 | 33.9 | 45.4 |
| 48 | 32.8 | 43.7 |
| 47 | 25.8 | 35.2 |
| 46 | 16.0 | 21.6 |
| 45 | 7.9 | 10.7 |
| 44 | 17.1 | 4.8 |
| 43 | 4.2 | 2.0 |
| 42 | 3.1 | 2.7 |
| 41 | 100 | 100 |
| 40 | 30.0 | 31.0 |
| 39 | 13.9 | 19.8 |
| 38 | 11.5 | 17.7 |
| 37 | 30.5 | 55.0 |
| 36 | 21.2 | 34.5 |
| 35 | 9.9 | 17.2 |
| 34 | 4.5 | 7.6 |
| 33 | 1.5 | 2.4 |
| 32 | 1.2 | 0.6 |
| 28 | 4.7 | 2.4 |
| 27 | 10.2 | 19.5 |
| 26 | 8.5 | 14.0 |
| 25 | 13.1 | 6.9 |
| 24 | 18.2 | 6.0 |
| 23 | 9.2 | 2.9 |
| 22 | 2.1 | 1.0 |
| 13 | 8.0 | 31.8 |
| 12 | 3.1 | 13.0 |
| 11 | 8.6 | 28.1 |
| 10 | 2.5 | |

There are doubly charged ions giving peaks in both spectra at m/e 36.5, 35.5, 34.5.

## Mass Spectrum 2

| m/e | Intensity % of m/e 27 | m.s. diborane |
|---|---|---|
| 78 | 1.2 | |
| 76 | 2.3 | |
| 75 | 1.9 | |
| 74 | 1.3 | |
| 73 | 1.0 | |
| 64 | 2.6 | |
| 63 | 3.1 | |
| 62 | 3.0 | |
| 61 | 2.8 | |
| 60 | 2.5 | |
| 59 | 2.4 | |
| 58 | 1.8 | |
| 57 | 1.2 | |
| 56 | 1.0 | |
| 55 | 2.1 | |
| 54 | 1.5 | |
| 53 | 1.0 | |
| 52 | 1.2 | |
| 51 | 3.2 | |
| 50 | 6.0 | |
| 49 | 6.8 | |
| 48 | 6.2 | |
| 47 | 5.3 | |
| 46 | 3.6 | |
| 45 | 2.3 | |
| 44 | 1.5 | |
| 41 | 5.6 | |
| 40 | 2.6 | |
| 39 | 2.1 | |
| 38 | 2.0 | |
| 37 | 4.3 | |
| 36 | 3.1 | |
| 35 | 2.4 | |
| 34 | 1.5 | |
| 27 | 100 | 100 |
| 26 | 93.7 | 99.9 |
| 25 | 47.6 | 57.5 |
| 24 | 79.9 | 86.7 |
| 23 | 38.2 | 42.2 |
| 22 | 9.8 | 9.5 |
| 21 | 1.9 | 1.4 |
| 13 | 23.0 | 17.2 |
| 12 | 12.6 | 10.7 |
| 11 | 22.3 | 17.4 |
| 10 | 5.6 | 3.8 |

## Mass Spectrum 3

| m/e | Intensity % of m/e 27 | m.s. diborane | m.s. ethylene |
|---|---|---|---|
| 64 | 2.0 | | |
| 63 | 2.3 | | |
| 62 | 3.5 | | |
| 61 | 2.7 | | |
| 60 | 2.9 | | |
| 59 | 2.7 | | |
| 58 | 2.5 | | |
| 57 | 6.0 | | |
| 56 | 9.4 | | |
| 55 | 4.5 | | |
| 54 | 3.5 | | |
| 53 | 4.0 | | |
| 52 | 16.0 | | |
| 51 | 25.0 | | |
| 50 | 22.0 | | |
| 49 | 15.5 | | |
| 48 | 10.8 | | |
| 47 | 6.5 | | |
| 46 | 3.5 | | |
| 45 | 2.7 | | |
| 44 | 1.5 | | |
| 43 | 1.0 | | |
| 42 | 8.9 | | |
| 41 | 12.5 | | |
| 40 | 9.5 | | |
| 39 | 4.5 | | |
| 38 | 2.5 | | |
| 29 | 2.2 | | 2.6 |
| 28 | 65.0 | | 100 |
| 27 | 100 | 100 | 55.2 |
| 26 | 72.0 | 99.9 | 50.8 |
| 25 | 27.4 | 57.5 | 9.4 |
| 24 | 31.6 | 86.7 | 3.0 |
| 23 | 13.5 | 42.2 | |
| 22 | 10.9 | 9.5 | |
| 21 | 3.0 | 1.4 | |
| 18 | 3.5 | | |
| 13 | 3.5 | | |
| 12 | 1.5 | | |
| 11 | 3 | | |

## Mass Spectrum 4

| m/e | Intensity % of m/e 31 | diethyl-ether |
|---|---|---|
| 75 | 2.0 | 1.6 |
| 74 | 34.0 | 30.4 |
| 73 | 4.6 | 4.0 |
| 64 | 2.2 | |
| 63 | 2.0 | |
| 62 | 4.1 | |
| 61 | 3.2 | |
| 60 | 7.0 | |
| 59 | 60.1 | 53.0 |
| 58 | 2.0 | |
| 57 | 3.0 | |
| 56 | 3.2 | |
| 55 | 3.0 | |
| 54 | 3.5 | |
| 50 | 4.0 | |
| 49 | 2.0 | |
| 48 | 2.4 | |
| 47 | 2.4 | |
| 46 | 2.7 | |
| 45 | 43.0 | 37.5 |
| 44 | 4.2 | 3.5 |
| 43 | 10.7 | 6.9 |
| 42 | 4.5 | 1.3 |
| 41 | 8.2 | 5.2 |
| 32 | 1.4 | |
| 31 | 100 | 100 |
| 30 | 2.7 | 1.8 |
| 29 | 43.2 | 39.5 |
| 28 | 56.1 | 6.0 |
| 27 | 22.6 | 17.7 |
| 18 | 4.7 | |
| 17 | 1.2 | |
| 13 | 6.9 | |
| 12 | 4.7 | |
| 11 | 2.1 | |

## Mass Spectrum 5

| m/e | Intensity % of m/e 43 | diethyl-ether |
|---|---|---|
| 101 | 43.4 | |
| 100 | 42.4 | |
| 99 | 30.3 | |
| 86 | 18.2 | |
| 85 | 46.4 | |
| 84 | 40.4 | |
| 74 | 10.2 | 30.4 |
| 73 | 9.1 | 4.0 |
| 72 | 71.7 | |
| 71 | 61.6 | |
| 70 | 58.6 | |
| 69 | 32.3 | |
| 60 | 22.2 | |
| 59 | 16.4 | 53.0 |
| 58 | 25.5 | |
| 57 | 32.3 | |
| 56 | 78.8 | |
| 55 | 47.6 | |
| 46 | 30.3 | |
| 45 | 98.0 | 37.5 |
| 44 | 44.4 | 3.5 |
| 43 | 100 | 6.9 |
| 42 | 76.8 | |
| 41 | 55.6 | 1.3 |
| 40 | 20.2 | 5.2 |
| 39 | 15.2 | |
| 32 | 11.1 | |
| 31 | 66.7 | 100 |
| 30 | 17.2 | 1.8 |
| 29 | 63.6 | 39.5 |
| 28 | 97.0 | 6.0 |
| 27 | 79.8 | 17.7 |
| 26 | 58.6 | |
| 25 | 26.2 | |
| 24 | 18.2 | |
| 15 | 36.3 | 3.2 |
| 14 | 10.1 | |
| 13 | 4.0 | |

## Mass Spectrum 6

| m/e | Intensity % of m/e 43 | m.s. n-butane |
|---|---|---|
| 59 | 2.0 | |
| 58 | 14.6 | 12.4 |
| 57 | 3.4 | |
| 56 | 1.9 | |
| 55 | 1.8 | |
| 54 | 1.0 | |
| 53 | 1.9 | |
| 52 | 1.0 | |
| 51 | 2.9 | |
| 50 | 3.9 | |
| 49 | 2.9 | |
| 48 | 1.9 | |
| 47 | 1.0 | |
| 46 | 1.1 | |
| 45 | 1.9 | |
| 44 | 3.9 | 3.4 |
| 43 | 100 | 100 |
| 42 | 11.1 | 12.5 |
| 41 | 24.3 | 27.6 |
| 40 | 1.9 | |
| 39 | 9.2 | 10.6 |
| 38 | 1.7 | |
| 37 | 1.3 | |
| 36 | 1.5 | |
| 35 | 1.5 | |
| 34 | 2.0 | |
| 33 | 1.3 | |
| 32 | 1.2 | |
| 31 | 1.7 | |
| 30 | 1.9 | |
| 29 | 36.9 | 39.4 |
| 28 | 47.6 | 28.7 |
| 27 | 33.0 | 28.5 |
| 26 | 20.8 | 4.1 |
| 25 | 8.7 | |
| 24 | 12.5 | |
| 23 | 6.0 | |
| 22 | 1.0 | |
| 21 | 2.2 | |
| 18 | 4.5 | |

## Mass Spectrum 7

| m/e | Intensity % of m/e 56 | m.s. 1-butanol |
|---|---|---|
| 74 | 1.6 | 1.0 |
| 73 | 2.0 | 2.3 |
| 72 | 1.6 | 7.6 |
| 71 | 1.2 | 0.9 |
| 69 | 1.6 | 0.5 |
| 59 | 1.6 | |
| 58 | 2.4 | |
| 57 | 16.7 | 9.8 |
| 56 | 100 | 100 |
| 55 | 23.8 | 15.6 |
| 53 | 3.2 | 1.1 |
| 46 | 1.6 | 0.5 |
| 45 | 7.9 | 6.7 |
| 44 | 4.0 | 29.5 |
| 43 | 45.6 | 64.8 |
| 42 | 25.8 | 31.8 |
| 41 | 53.2 | 69.6 |
| 40 | 4.0 | 4.1 |
| 39 | 12.3 | 16.8 |
| 38 | 1.6 | 3.6 |
| 37 | 1.0 | 1.5 |
| 33 | | 6.7 |
| 31 | 66.7 | 69.4 |
| 30 | 1.6 | 1.7 |
| 29 | 19.8 | 24.8 |
| 28 | 32.9 | 21.3 |
| 27 | 31.7 | 34.1 |
| 26 | 4.8 | 4.1 |

## Mass Spectrum 8

| m/e | Intensity % of m/e 31 | diethyl-ether |
|---|---|---|
| 75 | 1.6 | 1.6 |
| 74 | 33.7 | 30.4 |
| 73 | 3.1 | 4.0 |
| 59 | 51.0 | 53.0 |
| 46 | 1.1 | |
| 45 | 39.1 | 37.5 |
| 44 | 2.0 | 3.5 |
| 43 | 8.0 | 6.9 |
| 42 | 1.6 | 1.3 |
| 41 | 5.3 | 5.2 |
| 32 | 3.1 | |
| 31 | 100 | 100 |
| 30 | 1.6 | 1.8 |
| 29 | 46.8 | 39.5 |
| 28 | 14.7 | 6.0 |
| 27 | 20.8 | 17.7 |
| 26 | 3.7 | |
| 19 | 2.9 | |
| 18 | 2.9 | |
| 15 | 4.7 | 3.2 |
| 14 | 1.6 | |

## Mass Spectrum 9

| m/e | Intensity % of m/e 55 | m/e | Intensity % of m/e 55 |
|---|---|---|---|
| 99 | 9.3 | 53 | 32.7 |
| 98 | 7.5 | 52 | 7.5 |
| 97 | 31.8 | 51 | 7.5 |
| 96 | 12.1 | 50 | 5.6 |
| 95 | 26.1 | | |
| | | 45 | 38.3 |
| 92 | 7.5 | 44 | 13.1 |
| | | 43 | 54.2 |
| 90 | 12.1 | 42 | 11.2 |
| | | 41 | 43.0 |
| 85 | 21.0 | 40 | 13.1 |
| 84 | 20.6 | 39 | 12.1 |
| 83 | 35.5 | 38 | 12.1 |
| 82 | 16.8 | 37 | 12.5 |
| 81 | 21.5 | 36 | 7.5 |
| 80 | 3.7 | | |
| | | 32 | 3.7 |
| 71 | 39.2 | 31 | 18.7 |
| 70 | 22.4 | 30 | 89.7 |
| 69 | 39.2 | 29 | 55.1 |
| 68 | 8.4 | 28 | 87.9 |
| 67 | 15.0 | 27 | 38.3 |
| | | 26 | 7.5 |
| 58 | 5.6 | | |
| 57 | 71.0 | 18 | off-scale |
| 56 | 5.6 | 17 | off-scale |
| 55 | 100 | 16 | 35.5 |
| 54 | 52.3 | | |

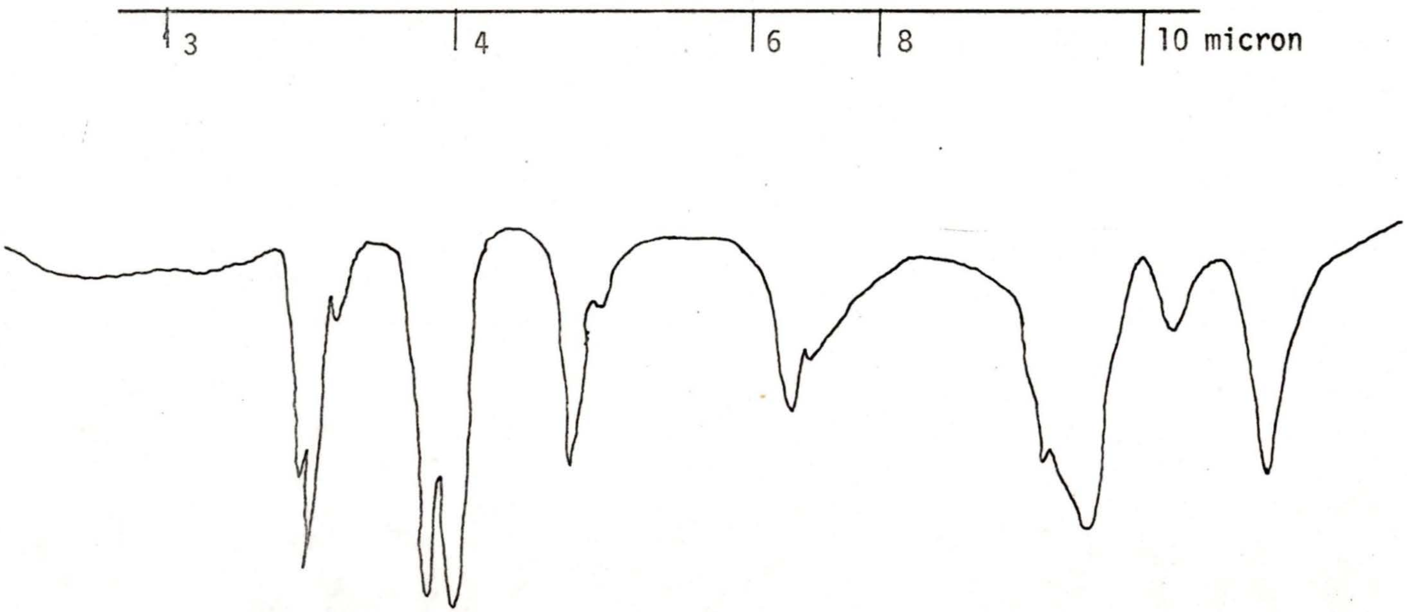
## Mass Spectrum 10

| m/e | Intensity % of m/e 43 | m.s. n-butane | m.s. trimethylamine |
|---|---|---|---|
| 72 | 11.3 | | |
| 71 | 4.8 | | |
| 70 | 3.0 | | |
| 69 | 1.2 | | |
| 59 | 4.2 | | 38.7 |
| 58 | 41.0 | 12.4 | 100 |
| 57 | 4.8 | | 7.4 |
| 56 | 6.0 | | |
| 55 | 3.6 | | |
| 44 | 4.8 | 3.4 | 7.7 |
| 43 | 100 | 100 | 9.7 |
| 42 | 15.4 | 12.5 | 46.3 |
| 41 | 31.1 | 27.6 | 8.0 |
| 40 | 2.4 | | |
| 39 | 12.0 | 10.6 | |
| 38 | 3.6 | | |
| 30 | 4.8 | | 17.6 |
| 29 | 34.6 | 39.4 | |
| 28 | off-scale | 28.7 | 13.3 |
| 27 | 28.6 | 28.5 | |
| 26 | 6.5 | 4.1 | |
| 17 | 5.6 | | |

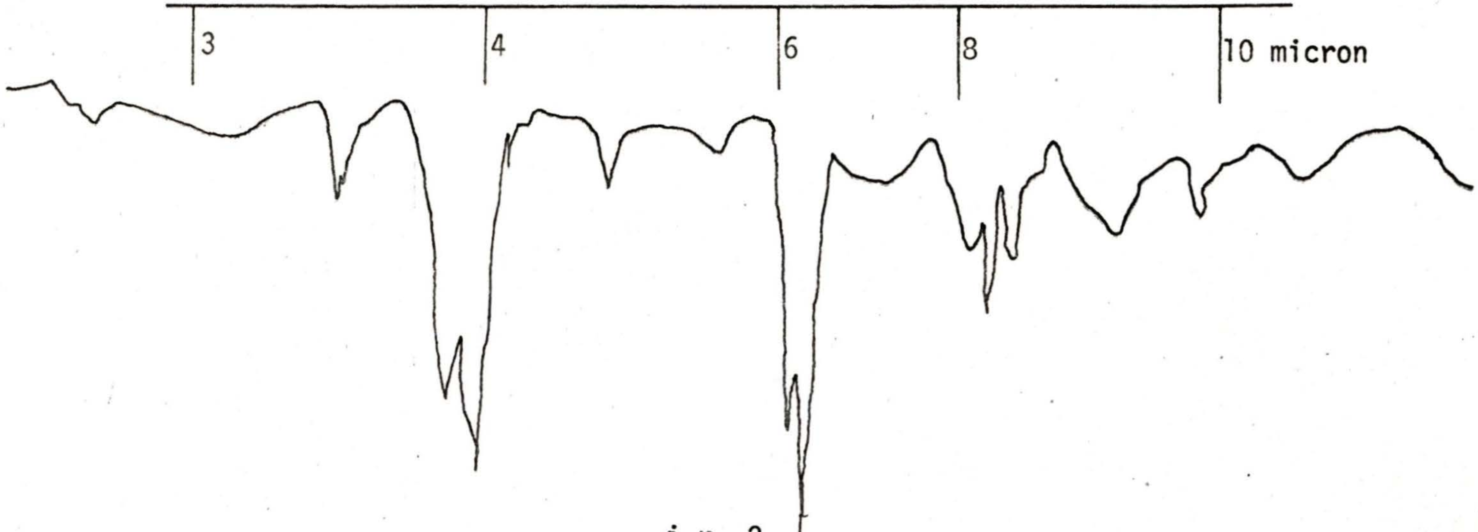
## Mass Spectrum 11

| m/e | Intensity % of m/e 58 | m.s. trimethylamine |
|---|---|---|
| 99 | 3.2 | |
| 98 | 1.7 | |
| 73 | 2.6 | |
| 72 | 54.3 | |
| 71 | 17.4 | |
| 70 | 11.8 | |
| 69 | 4.7 | |
| 68 | 2.6 | |
| 67 | 1.0 | |
| 60 | 2.0 | |
| 59 | 40.4 | 38.7 |
| 58 | 100 | 100 |
| 57 | 7.6 | 7.4 |
| 56 | 19.2 | |
| 55 | 4.5 | |
| 54 | 5.2 | |
| 53 | 2.0 | |
| 44 | 4.1 | 7.7 |
| 43 | 7.4 | 9.7 |
| 42 | 31.2 | 46.3 |
| 41 | 8.4 | 8.0 |
| 40 | 7.0 | |
| 39 | 2.9 | |
| 38 | 1.5 | |
| 30 | 17.8 | 17.6 |
| 29 | 6.1 | |
| 28 | 14.3 | 13.3 |
| 27 | 9.6 | |
| 26 | 3.2 | |
| 18 | 10.7 | |
| 17 | 2.6 | |
| 15 | 10.2 | |
| 14 | 1.2 | |
| 13 | 1.7 | |
| 11 | trace | |

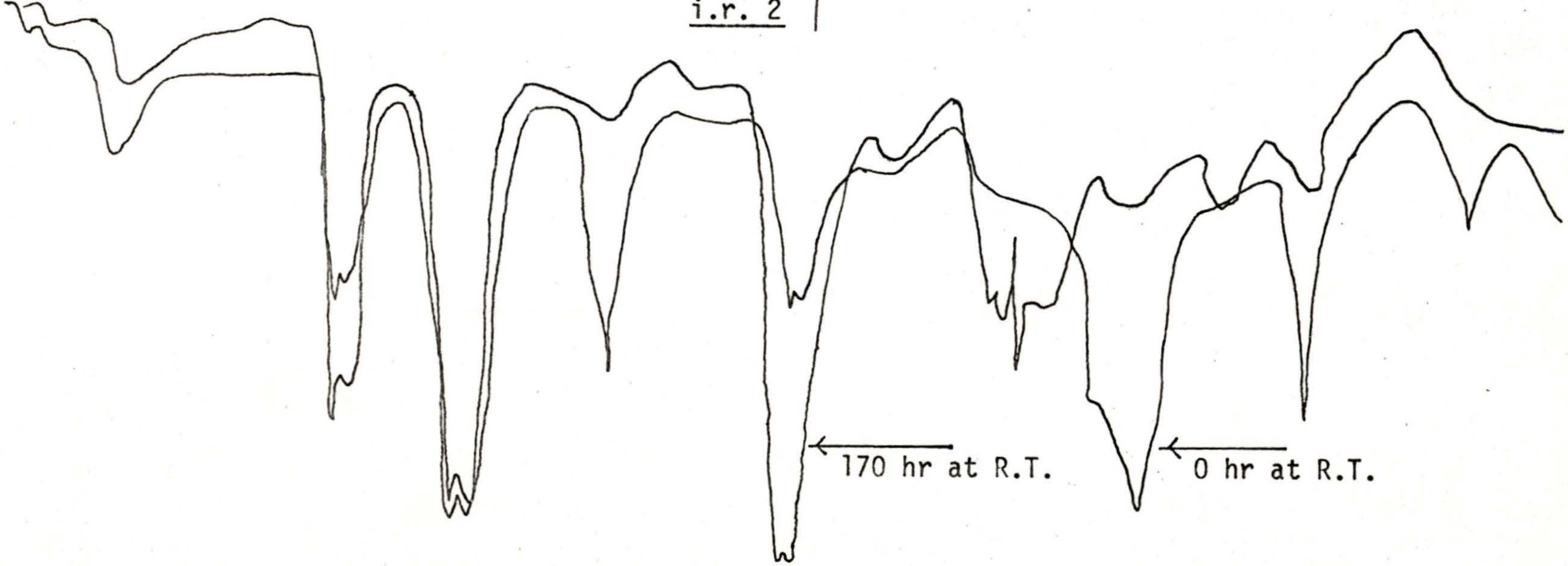
# APPENDIX 2 : INFRARED SPECTRA



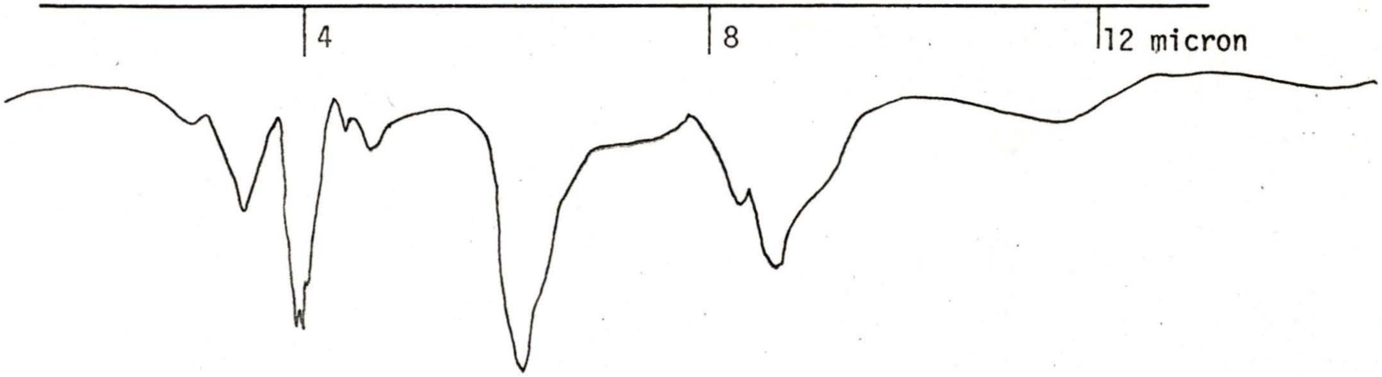
i.r. 1



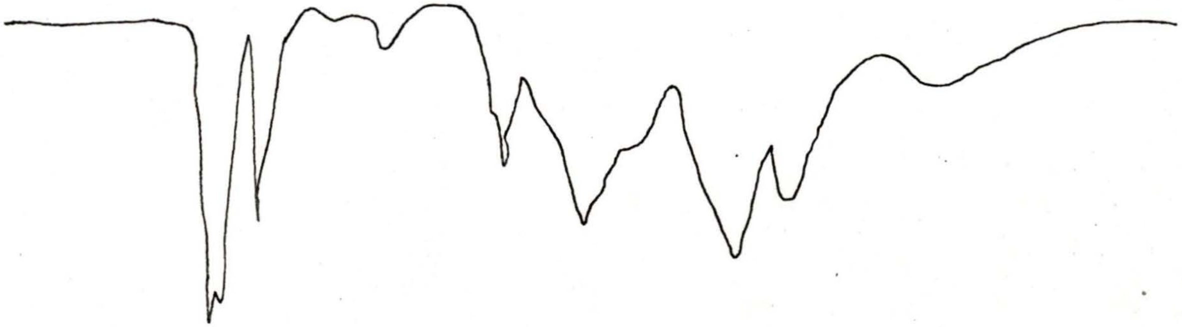
i.r. 2



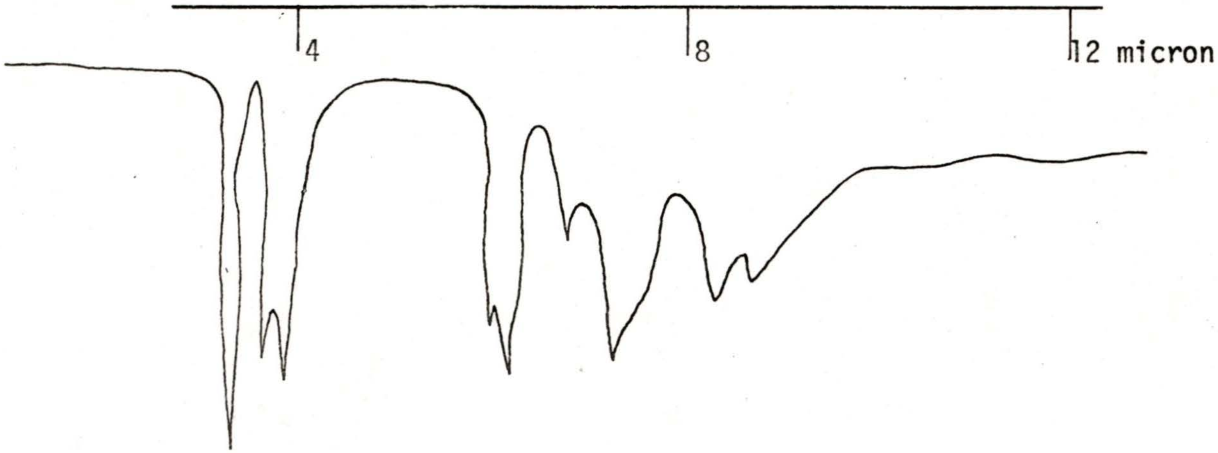
i.r. 3



i.r. 4

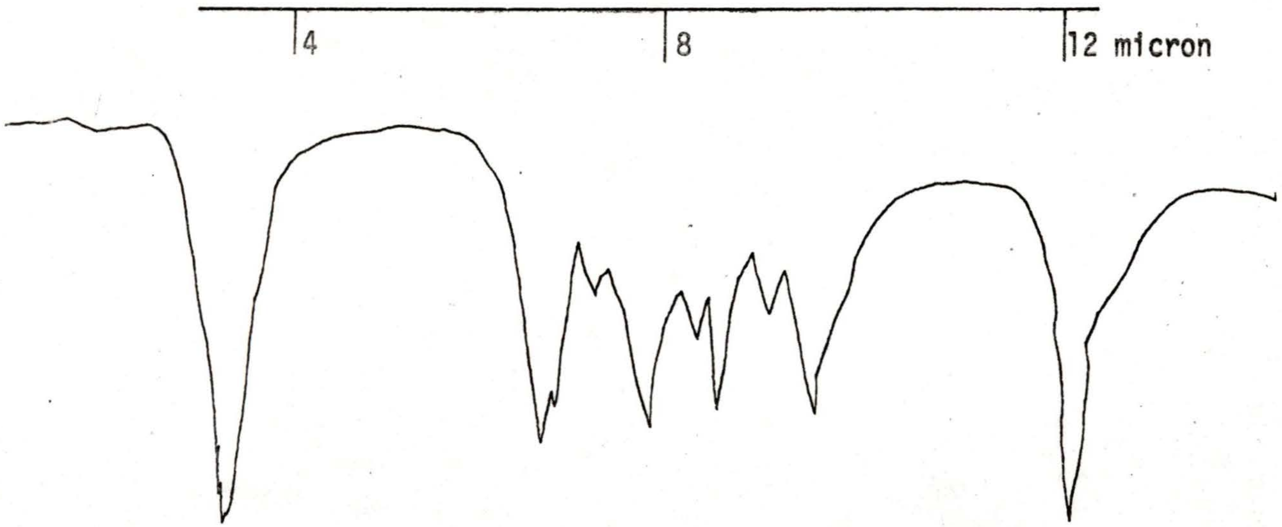


i.r. 5



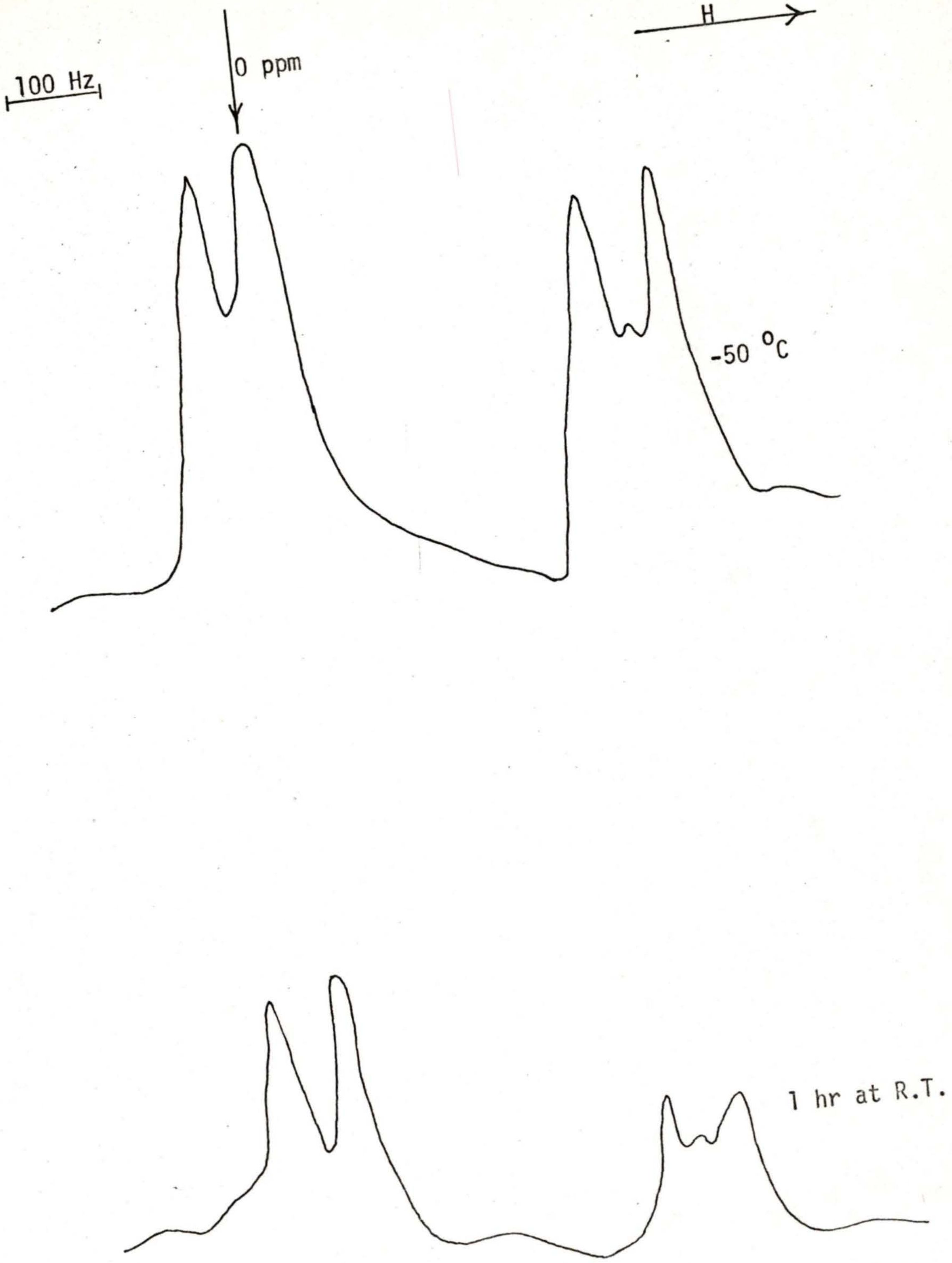
i.r. 6

i.r. 7

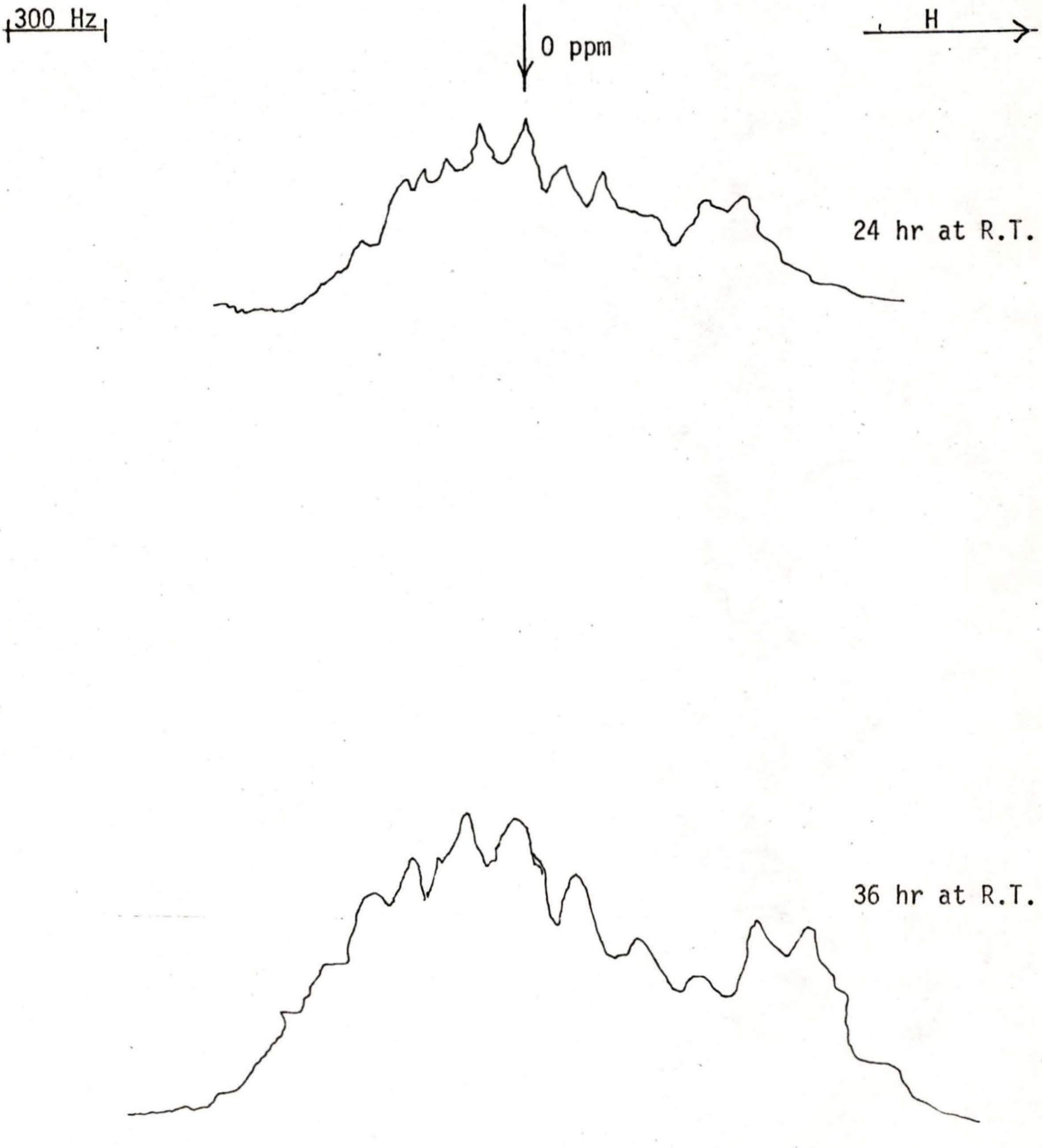


i.r. 8

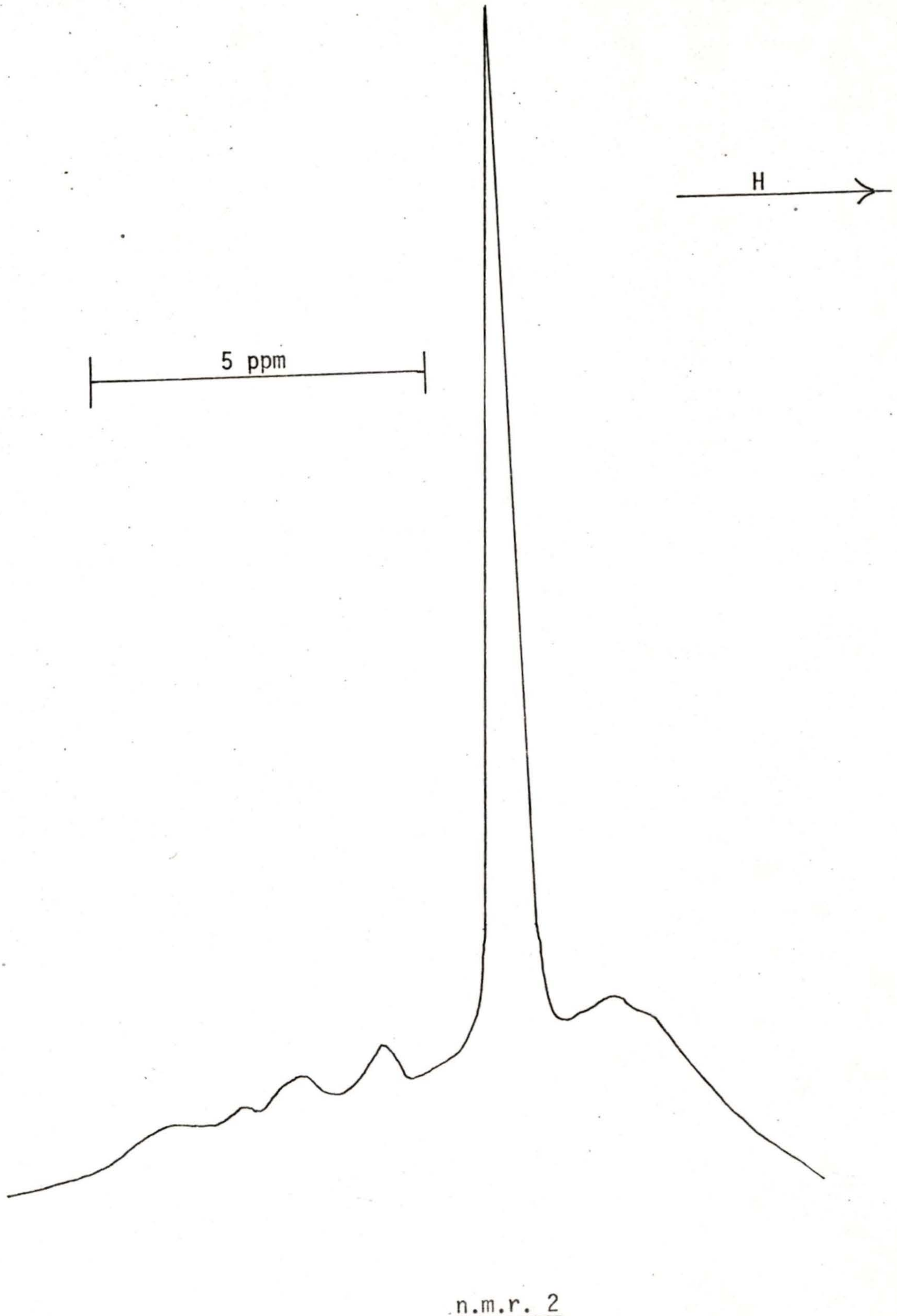
# APPENDIX 3 : NUCLEAR MAGNETIC RESONANCE SPECTRA



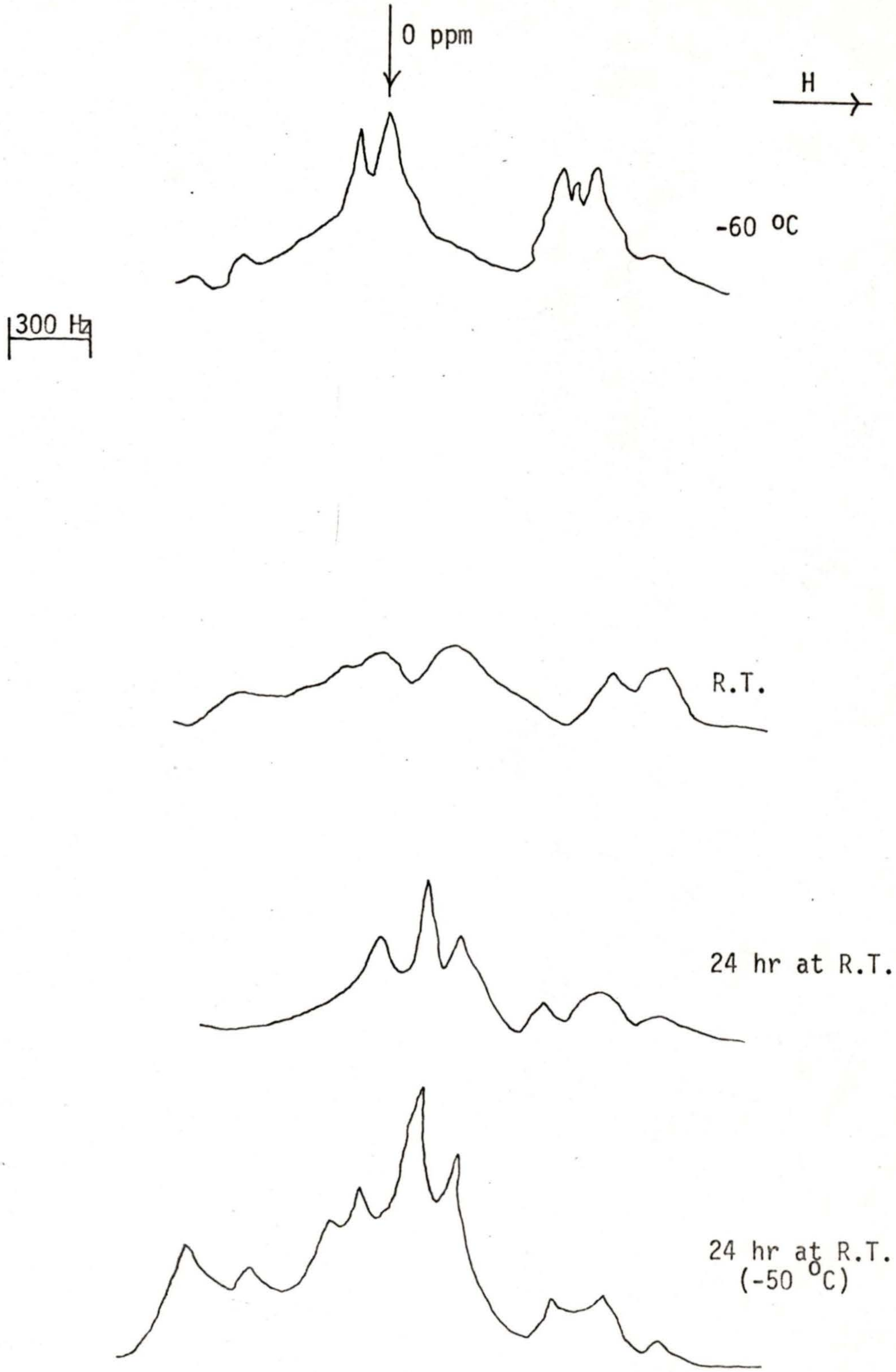
n.m.r. 1



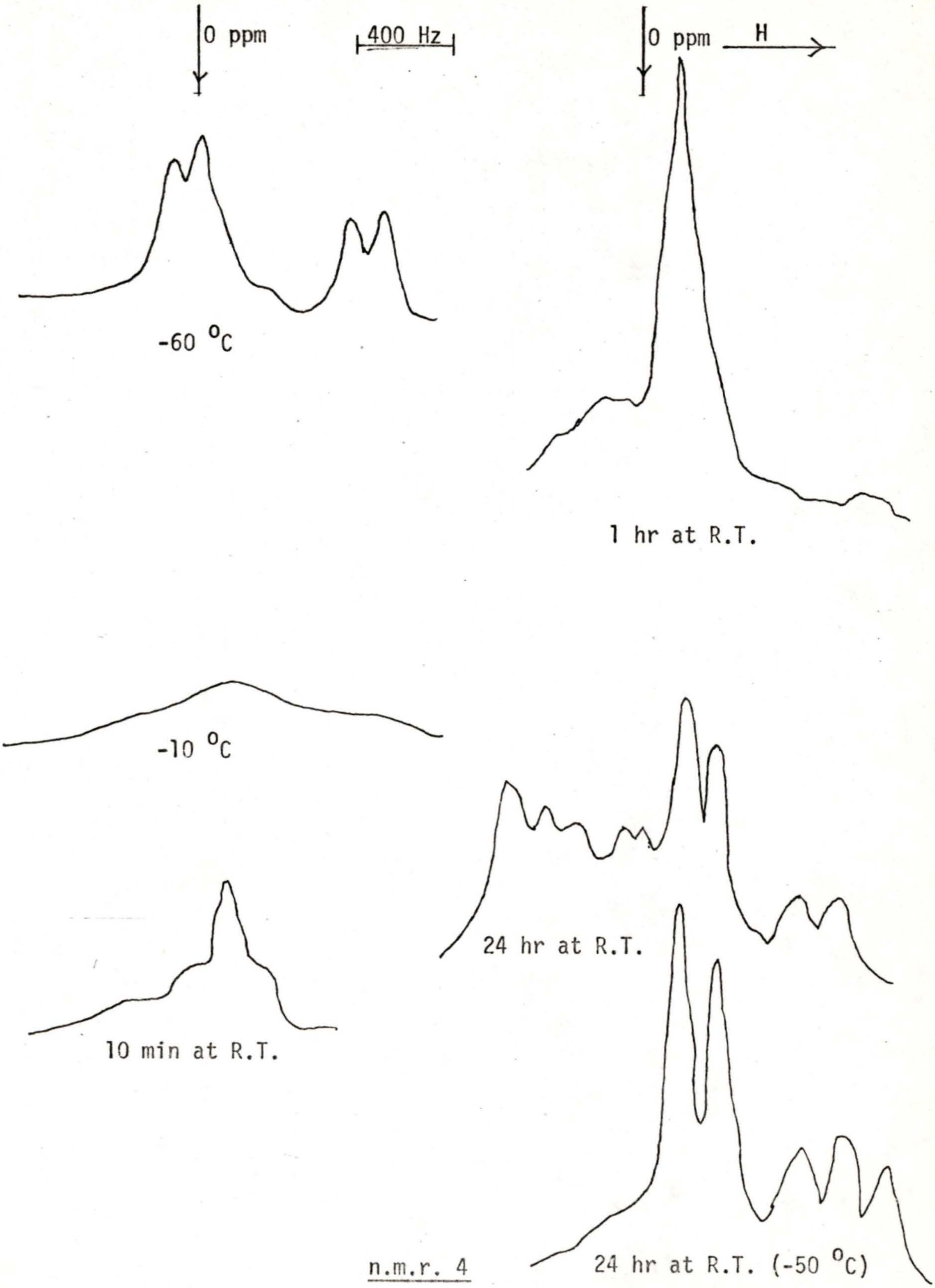
n.m.r. 1



n.m.r. 2



n.m.r. 3



-60 °C

1 hr at R.T.

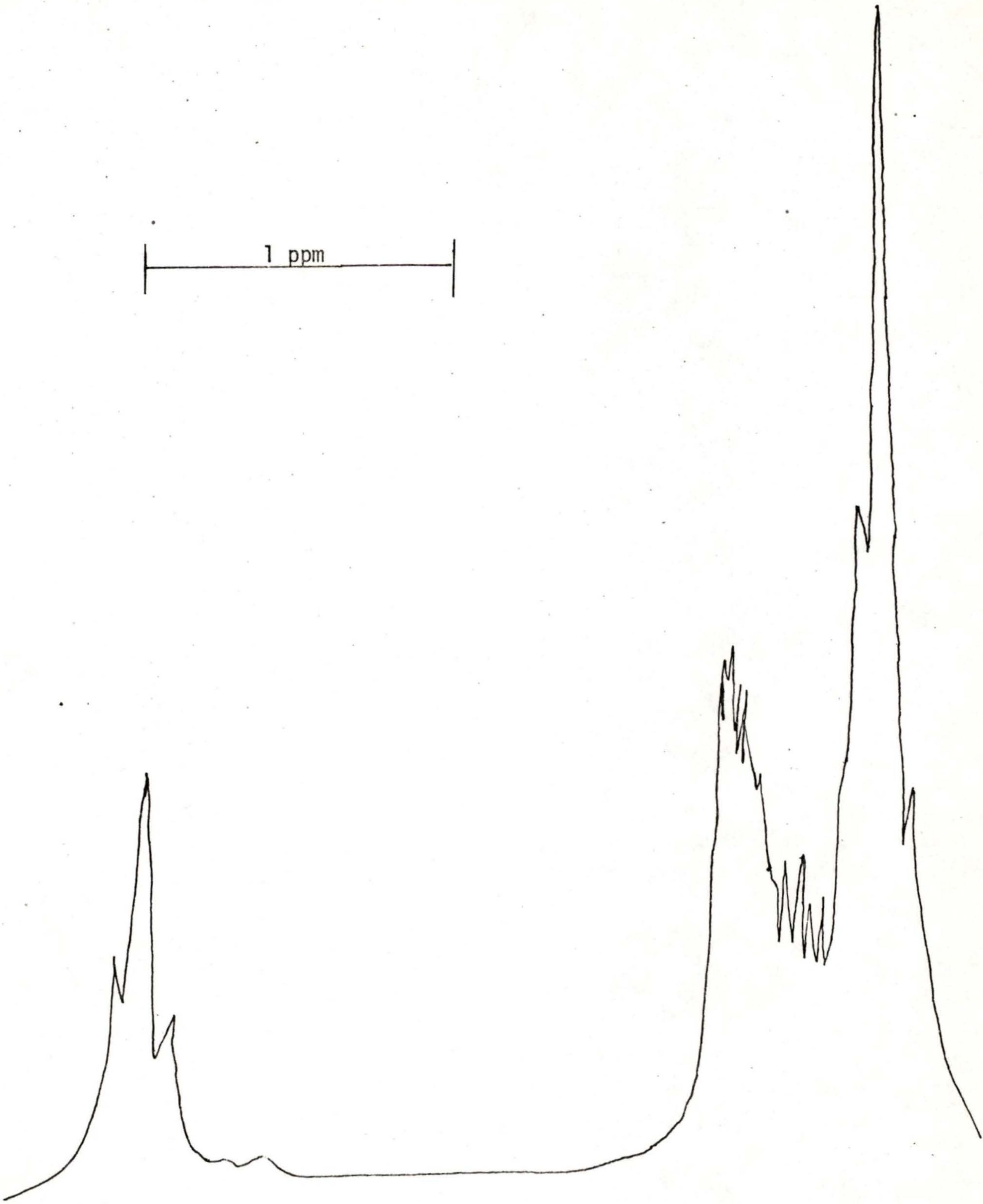
-10 °C

10 min at R.T.

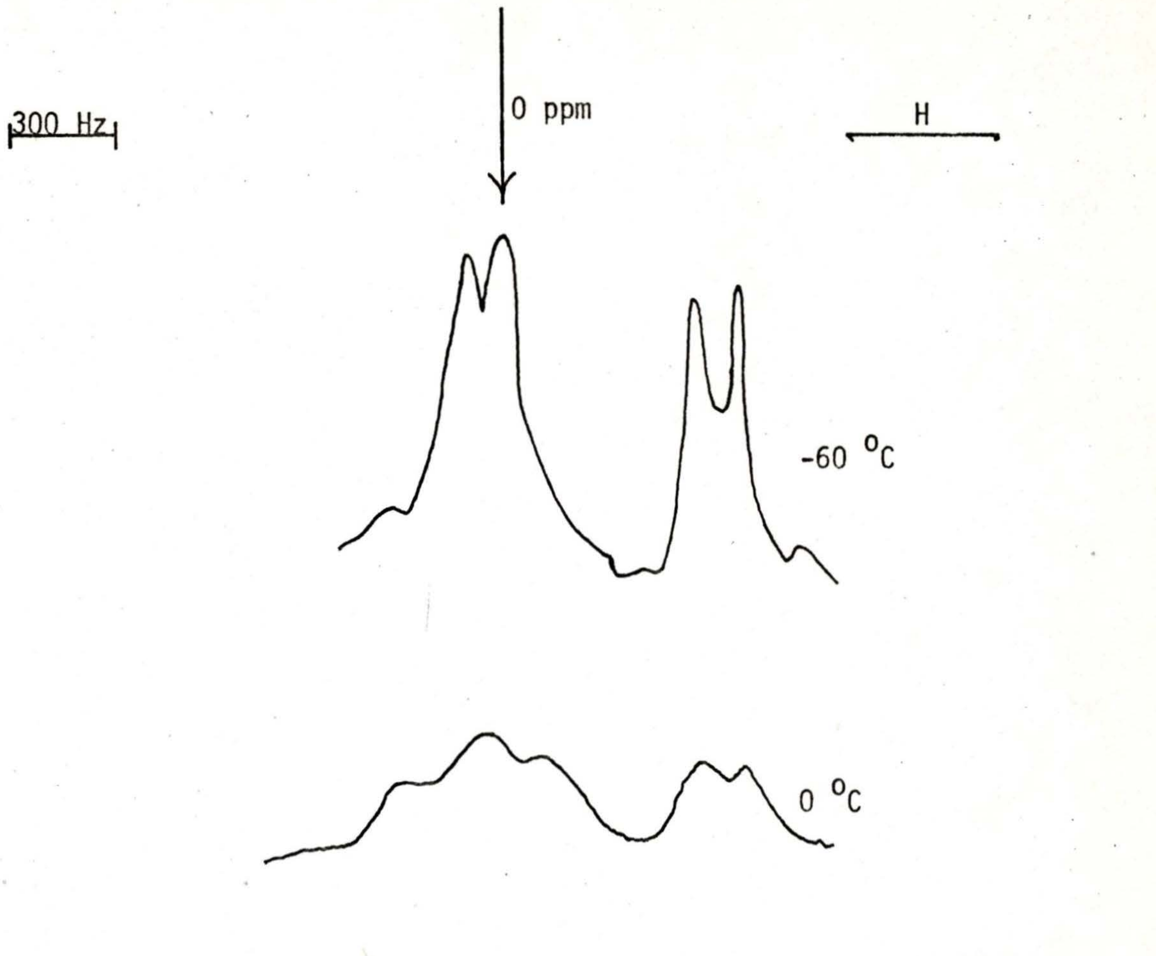
24 hr at R.T.

24 hr at R.T. (-50 °C)

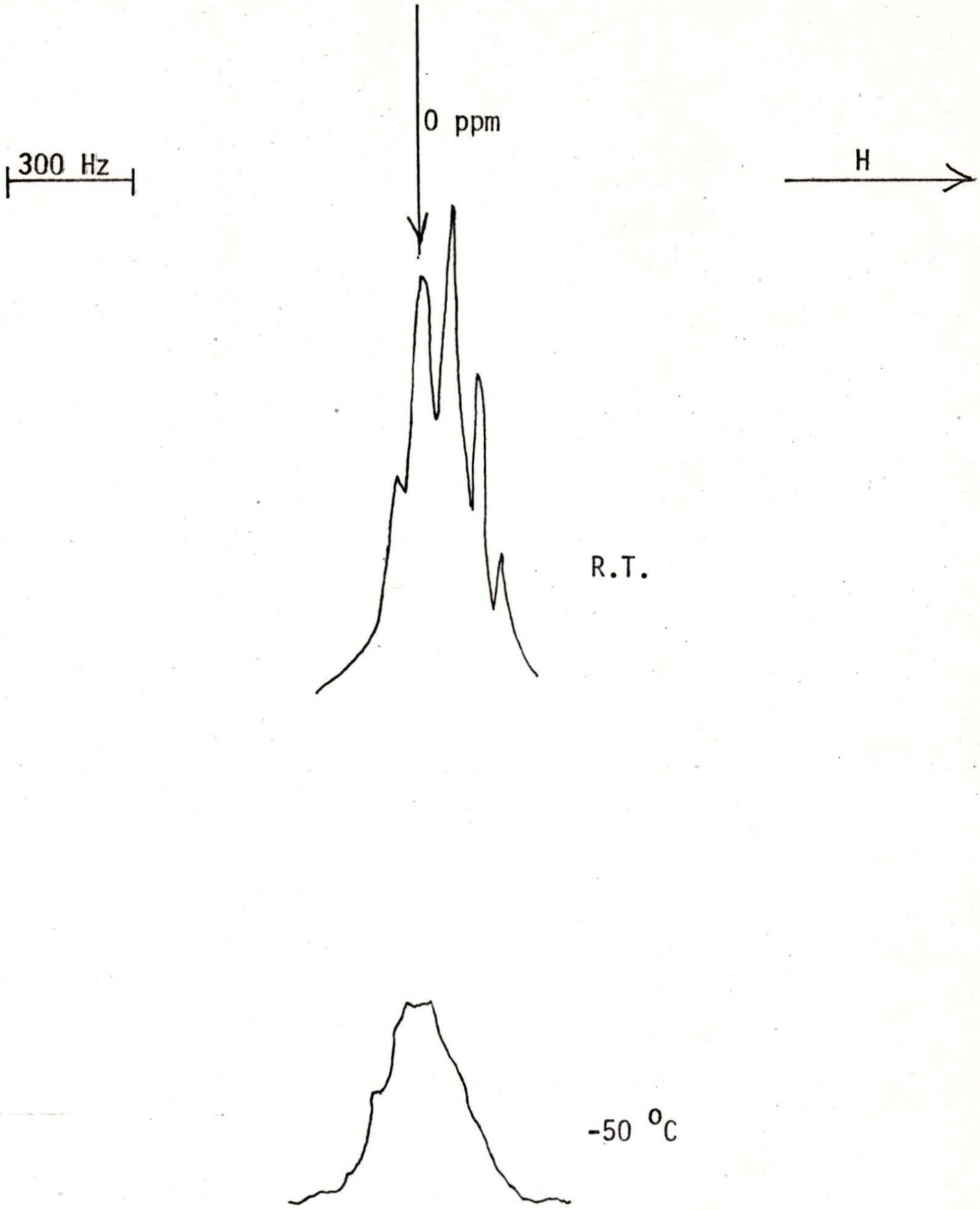
n.m.r. 4



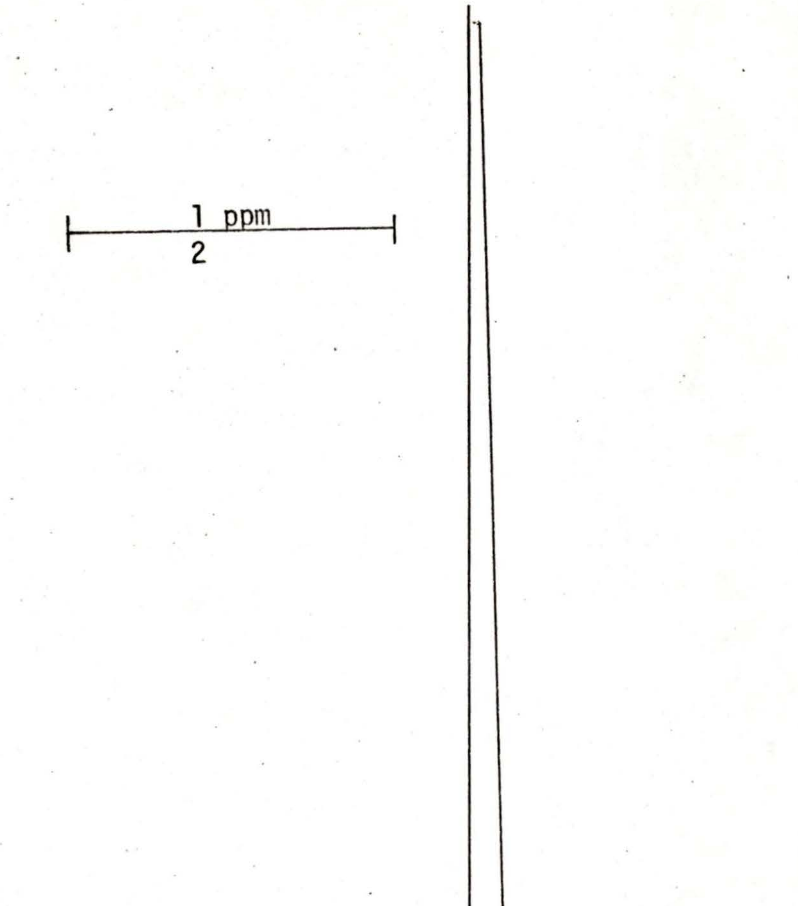
n.m.r. 5



n.m.r. 6



n.m.r. 7



n.m.r. 8

# VITA FORM

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Date of Birth : AUGUST 17, 1942.

Educational Institutions Attended, with Dates of Entering and Leaving:

| | |
|---|---|
| UNIVERSITY OF MANCHESTER | 1961 to 1964 |
| UNIVERSITY OF SALFORD | 1965 to 1968 |
| UNIVERSITY OF VICTORIA | 1968 to 1972 |

Degrees, Diplomas, &c, awarded, with Dates and Names of Institutions:

| | | |
|---|---|---|
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