STUDIES OF NORBORNYL COMPOUNDS

by

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A thesis submitted to the School of Graduate Studies
in partial fulfillment of the requirements for the
degree of Doctor of Philosophy

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Preface

The original object of this work was to investigate the kinetics of the gas phase pyrolysis of exo-2-norbornyl chloride. The stereospecific placing of deuterium on the 3-carbon atom would allow one to determine whether the unimolecular elimination of halogen acid to produce norbornene was a *cis* or *trans* process and whether the transition state was sufficiently polar for a Wagner-Meerwein isomerisation to take place therein. The problem proved more complex than expected, partly due to the surprising production of nortricyclene (also by a unimolecular elimination of hydrogen chloride) and partly because of interest in the mass spectral fragmentation mechanisms of norbornyl compounds. This interest developed through the use of mass spectrometry as a tool to discover the fate of deuterium in the pyrolysis of the labelled norbornyl chlorides.

Acknowledgement

The author wishes to express his deepest appreciation and thanks to Dr. J. Holmes for his continuing support and encouragement throughout the course of these investigations. The author also wishes to thank Dr. F. Lossing for the determination of appearance potentials, Dr. R. Rye for metastable defocusing and many stimulating discussions, Dr. N. Isaacs for proposing the initial problem and for preparing some of the labelled compounds, Dr. R. Pottie for metastable defocusing, Dr. N.H. Werstiuk for supplying the norbornene-endo-5-endo-6-d_2 , and Mr. A. Philpot, Mr. R. Capoor, Mr. P. Coulombe and Miss N. Lee for invaluable experimental assistance.

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Abstract

The gas phase pyrolyses of exo-2-norbornyl chloride and some deuterium labelled analogues have been studied and the 1,2 elimination yielding the major product (norbornene) was shown to occur by a cis process. The other major product nortricyclene, was shown to arise from a 1,3 elimination involving the 6-endo H atom.

The use of the relative abundance of metastable ion peaks in labelled compounds to isolate and examine a particular mass spectral fragmentation has been developed. This technique has been used to determine the extent of Wagner-Meerwein reaction in the preparation of exo-2-norbornyl chloride by various methods and to elucidate the mass spectral fragmentation mechanisms of exo-2-norbornyl chloride, exo-2-norbornyl bromide, norbornene, nortricyclene, exo-2-norborneol, endo-2-norborneol and norbornane.

The addition reaction between hydrogen chloride and norbornene has been investigated using deuterium labelling and mass spectrometric analysis. The results indicate that the norbornyl cation intermediate is captured in an asymmetric state.

Some of the above work has been published as shown in the following list:

1. J.L. Holmes and D. McGillivray, Advances in Mass Spectrometry, The Institute of Petroleum, London, 5, 706 (1971).
2. J.L. Holmes, D. McGillivray and N.S. Isaacs, Can. J. Chem., 48, 2791 (1970).
3. J.L. Holmes and D. McGillivray, Org. Mass Spectrom., 5, 1339 (1971).
4. J.L. Holmes and D. McGillivray, Org. Mass Spectrom., 5, 1349 (1971).
5. J.L. Holmes and D. McGillivray, Org. Mass Spectrom., 7, in press (1973).

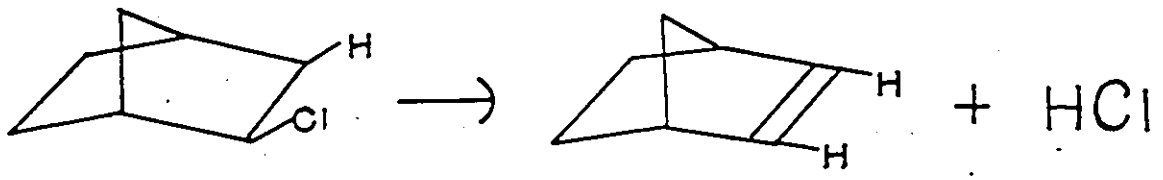
PART I

Gas Phase Pyrolysis of exo-2-Norbornyl Chloride.

INTRODUCTION

Object of the Investigation

To determine whether loss of halogen acid from halogen containing hydrocarbons in the gas phase occurs by a 1,2 *cis* or *trans* process. For this purpose the gas-phase pyrolysis of *exo*-2-norbornyl chloride (*exo*-2-chloro-bicyclo (2,2,1) heptane) was undertaken. *exo*-2-Norbornyl chloride was chosen because of its rigid geometry and its presumed ability to form only one elimination product, norbornene (bicyclo (2,2,1) hept-2-ene).



By labelling the *exo*-2-norbornyl chloride with deuterium in the *exo*-3 or *endo*-3 position and determining the deuterium content of the pyrolysis product (norbornene), it should be possible to deduce the extents of *cis* and *trans* elimination of hydrogen chloride.

A possible interesting complication would arise if the elimination proceeded via a transition state capable of undergoing the Wagner-Meerwein reaction. This feature is

discussed in detail later.

No attempt will be made here to cover all aspects of the kinetics of chemical reactions, only a brief background will be presented, sufficient to allow discussion of the results from the pyrolysis of exo-2-norbornyl chloride.

Kinetics, the study of reaction rates, is used as a probe to investigate the mechanisms of chemical reactions.

(1) Mathematical treatment of results [1a,2a]

The rate of reaction is described as the amount of reactant (dx) which changes in a definite period of time (dt) . Expressing the rate's dependence on the concentration of the species present we obtain:-

$$\frac{dC_A}{dt} = k\, C_A^{\alpha} C_B^{\beta} C_C^{\gamma} \ldots\ldots$$

where k is a numerical constant, defined as the rate constant; α,β,γ ..... are usually integers and C_A, C_B, C_C ..... refer to the concentration of the chemical species A,B,C ..... present in the system at a given time. Similar expressions can be written for the rate of change of the concentrations of the other species dC_B/dt, dC_C/dt ..... and so on. The individual derivatives

dC_A/dt, dC_B/dt, and dC_C/dt are referred to as the rate of reaction with respect to A, B, and C respectively and are related by the stoichiometry of the chemical reaction.

The rates of reactions are classified into simple categories, that is a reaction is said to have an order with respect to each individual reactant, for example α is the order with respect to A, β is the order with respect to B etc., the overall order of the reaction being given by the sum of the individual orders i.e. $\alpha + \beta + \gamma + \ldots\ldots$.

First Order Reaction

A reaction is said to be first order when the rate of reaction depends only on the first power of the concentration of one reactant species as shown below:-

$$\frac{dC}{dt} = kC$$

where C is the concentration of the reacting species

k is the first order rate constant ($time^{-1}$)

this can be re-expressed as

$$-\frac{d(C_o - x)}{dt} = k(C_o - x)$$

where C_o is the initial concentration of the reacting species

x is the amount of the reacting species which has been consumed in a period of time dt

or

$$\frac{dx}{dt} = k(C_o - x)$$

From the practical viewpoint of handling experimental data the integrated form of the above expression is more useful, when t is 0 the amount changed x is 0 , whereas after time t it is x ; on integration this yields:-

$$k = \frac{1}{t} \ln \frac{C_o}{(C_o - x)}$$ First Order Rate Equation

For a reaction to be first order a plot of $\ln C_o/(C_o-x)$ against t must be linear, the slope of the line being equal to 1/k, thus allowing the measurement of k , the first order rate constant which has units of reciprocal time only.

Second Order Reaction

A reaction is said to be second order when the rate of reaction depends on the first power of the concentrations of each of two reactant species or the second power of the concentration of one reacting species. An example of the mathematics of the former is shown below:-

A + B = products

$\frac{dx}{dt} = k(a-x)(b-x)$ where a and b are the initial concentrations of A and B respectively

k is the second order rate constant

x is the amount of reacting species consumed in a period of time dt

dx/dt is equivalent to either $-d(a-x)/dt$ or $-d(b-x)/dt$.

Integration, taking into account that x is 0 when t is 0 and x is x when t is t, gives

$$k = \frac{1}{t(a-b)} \ln \frac{b(a-x)}{a(b-x)}$$ Second Order Rate Equation

this can be rearranged to

$$k = \frac{1}{t(a-b)} \ln\left(\frac{b}{a}\right) - \frac{1}{t(a-b)} \ln\left(\frac{a-x}{b-x}\right)$$

In this form it can be observed that for a reaction to be second order a plot of $\ln (a-x)/(b-x)$ against t must be linear and the slope is equal to $1/k(a-b)$ allowing the determination of k, the second order rate constant which has units of reciprocal concentration and reciprocal time.

Third and higher order reactions are treated in a similar manner; however in practice very few examples have

been found due to the low probability of having a collision between three or more particles.

Use of the integrated form of the rate equation is only one way of determining the order of a reaction, other mathematical methods of treating the results can be found in any text book on kinetics, e.g. Benson[1b].

Although reaction rates can generally be classified as simple first or second order reactions, several factors may be present such as reverse, concurrent and consecutive reactions which will complicate the interpretation of the experimental data.

(a) Reverse Reactions[2b]

Some point in a simple reaction may be reached when the reverse reation rate becomes significant, resulting in a non-linear rate plot. Consider the simple case of a first order reaction with a reverse first order reaction:-

$$A \underset{k'}{\overset{k}{\rightleftharpoons}} B$$

If a is the concentration of A initially and there is no B present at the commencement of the reaction, then after a time t the concentration of A and B are given by $(a-x)$ and x respectively

$$\frac{dx}{dt} = k(a-x) - k'x$$

where k and k' are the forward and reverse rate constants (time^{-1})

the presence of the latter term will cause an apparent reduction in x, resulting in a curved rather than a linear first order rate plot, the curve starting at a point in the reaction where the reverse reaction becomes significant. At equilibrium

$k(a-x_e) = k'x_e$ where x_e is the amount of B formed or A changed at equilibrium

rearranging and substituting for k' in the above equation gives

$$\frac{dx}{dt} = k(a-x) - \frac{kx}{x_e}(a-x_e)$$

or $$\frac{dx}{dt} = \frac{ka}{x_e}(x_e-x)$$

On integration, noting that x is 0, when t is 0 and x is x when t is t, we obtain

$$\frac{kt}{x_e} = \frac{1}{t} \ln \frac{x_e}{(x_e-x)}$$

From a plot of $\ln x_e/(x_e-x)$ against t and a knowledge of a and x_e, k, the rate constant for the forward reaction can be determined.

Reverse reactions involving higher order reactions are treated in a similar manner, however if some of the

products are initially present the integration of the rate equation becomes complex.

(b) Consecutive Reactions [1c]

No particular problem is present when one of the consecutive reactions is considerably slower than the rest, the assumption can then be made that the other reactions will not effect the kinetics of the over all reaction. The difficulty arises when the consecutive reactions have similar rates. The simplest case is where the consecutive processes are first order; for example:-

$$A \xrightarrow{k_a} B \xrightarrow{k_b} C$$

If B is considered as intermediate in the over all reaction $A \rightarrow C$ then the following set of rate equations can be written:-

$$\frac{da}{dt} = -k_a a \qquad \ldots\ldots(1)$$

$$\frac{db}{dt} = k_a a - k_b b \qquad \ldots\ldots(2)$$

$$\frac{dc}{dt} = k_b b \qquad \ldots\ldots(3)$$

where a, b and c represent the concentrations of A, B and C respectively

Equation (1) is treated as a simple first order equation, the solution being

$$a = a_o e^{-k_A t} \qquad \ldots\ldots(4)$$

substituting this value for a in equation (2) we obtain the following expression:-

$$\frac{db}{dt} + k_B b = k_A a_o e^{-k_A t} \qquad \ldots\ldots(5)$$

This is identified as a linear differential equation of the first order [3] and its solution is obtained as the sum of a particular solution, given by making the right hand side equal to zero and solving the equation, plus a general solution, obtained by solving the equation obtained when the left hand side is made equal to zero. The general solution is equal to e^{-kBt} and the particular solution equals e^{-kAt}. The total solution written as a linear combination is shown below:-

$b = a_1 e^{-kBt} - a_2 e^{-kAt}$ ....(6) where a_1 and a_2 are constants

By substituting back into equation (5) it can be shown that

$$a_2 = \frac{k_A A_o}{k_B - k_A}$$

which on substituting into the general solution equation (6)

gives

$$B = a_1 e^{-k_B t} - \frac{k_A A_o}{k_B - k_A} e^{-k_A t}$$

substituting the initial conditions that $B = B_o$ at $t = 0$ yields

$$a_1 = B_o - \frac{k_A A_o}{k_B - k_A}$$

which on substitution for a_1 yields the following expression for B

$$B = B_o e^{-k_B t} - \left[\frac{k_A A_o}{k_B - k_A} \left(e^{-k_A t} - e^{-k_B t} \right) \right]$$

The concentration of C at any time t is given by the relationship provided by the chemical equation:-

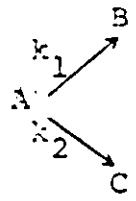
$$A + B + C = \text{constant} = A_o + B_o + C_o$$

such that

$$C = C_o - A_o(1 - e^{-k_A t}) - B_o\left(1 - e^{-k_B t} - \frac{A_o/B_o}{1 - k_B/k_A} \left(e^{-k_B t} - e^{-k_A t} \right)\right)$$

(c) Concurrent Reactions

Considering the simplest case where the concurrent processes are first order, for example



At time 0 $(A) = (A_0)$, $(B) = (C) = 0$, at any time t $(A)_t + (B)_t + (C)_t = A_0$. With these conditions the following rate equation can be set up for the concentration of A at any time t.

$$\frac{-d(A)_t}{dt} = (k_1 + k_2)(A)_t \equiv k'(A)_t \quad \ldots\ldots(1)$$

where $k' = k_1 + k_2$

$$\frac{-d(A)_t}{(A)_t} = k'dt$$

On integration the following solution is obtained

$$-\ln(A)_t = k't + \text{const.}$$

when $t = 0$

$$-\ln(A)_0 = \text{const.}$$

$$-\ln(A)_t = k't + \ln(A)_0$$

$$(A)_t = (A)_0 e^{-k't} \qquad \ldots\ldots(2)$$

For the concentration of product B, the following rate expression can be considered

$$\frac{d(B)_t}{dt} = k_1(A)_t \qquad \ldots\ldots\ldots(3)$$

Substituting expression (2) for the concentration of A at any time t in expression (3) we obtain the following equation

$$\frac{d(B)_t}{dt} = k_1(A)_0 e^{-k't}$$

therefore $(B)_t = k_1(A)_0 e^{-k't} dt$

which on integration yields

$$(B)_t = \frac{-k_1}{k'}(A)_0 e^{-k't} - \text{const.}$$

when time = 0 $(B) = 0$ and $e^{-k't} = 1$

$$\frac{-k_1}{k'}(A)_0 = \text{const.}$$

$$(B)_t = \frac{k_1}{k'}(A)_0 - \frac{k_1}{k'}(A)_0 e^{-k't} \quad \ldots\ldots(4)$$

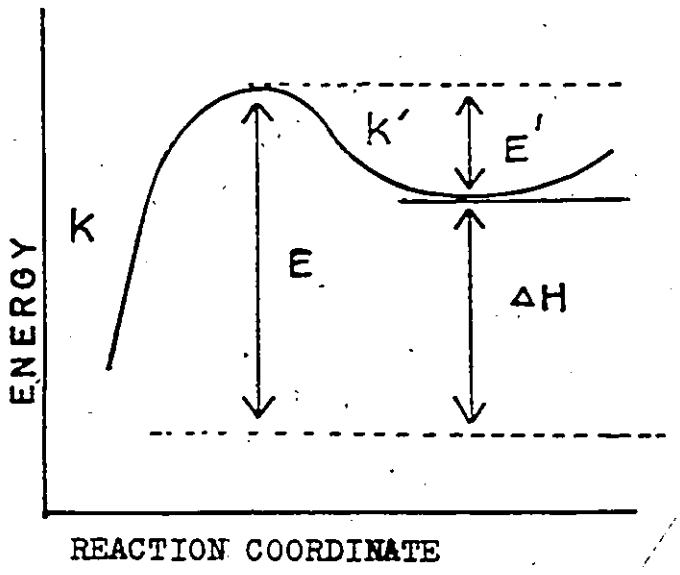
An identical expression can be derived for the concentration of product C at any time t, except k_1 is replaced by k_2.

Effect of Temperature on the Rate of Reaction

The effect of temperature on the rate constant can be most simply expressed in terms of the van't Hoff isochore

$$\frac{d\ln K}{dt} = \frac{\Delta H}{RT^2}$$

where K is the equilibrium constant
ΔH is the enthalpy change
R is the gas constant (calories per mole)
T is temperature (absolute)



Substituting k/k' for K where k and k' are the rate constants for the forward and reverse reactions respectively and $E-E'$ for H where E and E' are the activation energies for the forward and reverse reactions respectively. The equation can then be split into two as shown below:-

$$(1)\quad \frac{d\ln k}{dt} = \frac{E}{RT^2} \quad \text{and} \quad (2)\quad \frac{d\ln k'}{dt} = \frac{E'}{RT^2}$$

On integration, equation (1) gives:-

$$\ln k = \frac{-E}{RT} + A' \qquad \text{where } A' \text{ is an integration constant}$$

or $$k = Ae^{\frac{-E}{RT}} \qquad \text{where } A \text{ is the frequency factor}$$
E is the activation energy.

The integrated equation is known as the Arrhenius equation and A and E are referred to as the Arrhenius parameters. These parameters can be determined by measuring the rate constant at a series of temperatures. By plotting $\ln k$ against $1/T$, the activation energy E can be determined from the slope of the straight line plot.

If the Arrhenius plot is not linear this may indicate that the reaction is occuring in more than one phase. For example if the plot is concave upwards this

could indicate participation of a (low activation) surface energy reaction together with the homogeneous (high activation) reaction.

(2) Reaction Mechanisms in Gas Phase Pyrolysis

Homogeneous gas phase pyrolyses can proceed by two different types of mechanism (a) by a process involving free radicals or (b) by a molecular process.

(a) Radical Mechanism

Radical mechanisms are generally complex and involve a series of consecutive reactions which can be split into three groups (1) initiation reactions which produce free radicals by a homolytic bond dissociation (2) propagation reactions; those in which the free radicals react to produce intermediates and result in the removal of reactants (3) termination reactions, which remove the active intermediates. Radical reactions can be separated into two classes, non-chain and chain reactions.

(a.1) Non-Chain Reaction

The reaction scheme shown below is an example of a non-chain reaction:-

(1) $M_1 \rightarrow R_1^{\bullet} + R_2^{\bullet}$ Initiation

(2) $M_1 + R_1^{\bullet} \rightarrow R_1H + R_3^{\bullet}$ Propagation

(3) $R_2^{\bullet} + R_3^{\bullet} \rightarrow M_1 + M_2$ Termination

This type of reaction is rare since as pointed out by Maccoll[4] the activation energy must be equal to the homolytic bond strength of the bond ruptured in the initiation reaction, the rate determining step. Some of the few examples of this type of reaction are the gas phase pyrolyses of allylic halides or esters[5,6]

(a.2) Chain Reactions

The reaction scheme shown below is a typical example of a chain reaction:-

(1) $M_1 \xrightarrow{k_1} R_1^{\bullet} + R_3^{\bullet}$ — Initiation

(2) $R_1^{\bullet} + M_1 \xrightarrow{k_2} R_1H + R_2^{\bullet}$ — Propagation

(3) $R_2^{\bullet} \xrightarrow{k_3} R_1^{\bullet} + M_2$ — Propagation

(4) $R_1^{\bullet} + R_2^{\bullet} \xrightarrow{k_4} M_3 + M_4$ — Termination

(5) $R_1^{\bullet} + R_1^{\bullet} \xrightarrow{k_5} M_5$ — Termination

(6) $R_2^{\bullet} + R_2^{\bullet} \xrightarrow{k_6} M_6$ — Termination

This is defined as a chain reaction because radical $R_1^{\bullet}$ required in reaction (2) is produced in reaction (3) in addition to that supplied by the slow initiation reaction (1), that is, after the initial induction period the reaction

proceeds independently of reaction (1). The kinetics of this reaction scheme cannot be solved directly but the approximation is made that once the extremely small steady state concentration of the active intermediates has been obtained, their concentration will not change during the course of the reaction. The kinetics can be investigated as follows: if the reaction scheme is terminated by step (4) then the following equations can be drawn up for the concentration of the intermediate species $R_1^\bullet$ and $R_2^\bullet$

$$\frac{d(R_1^\bullet)}{dt} = k_1(M_1) + k_3(R_2^\bullet) - k_2(R_1^\bullet)(M_1) - k_4(R_1^\bullet)(R_2^\bullet) = 0$$

$$\frac{d(R_2^\bullet)}{dt} = k_2(R_1^\bullet)(M_1) - k_3(R_2^\bullet) - k_4(R_1^\bullet)(R_2^\bullet) = 0$$

From the above equations it can be shown that

$$(R_1^\bullet) = \left(\frac{k_1 k_3}{2k_2 k_4}\right)^{1/2}$$

The rate at which the reactant is consumed is given by:-

$$-\frac{d(M_1)}{dt} = k_1(M_1) - k_2(R_1^\bullet)(M_1)$$

If k_1 is very small relative to k_2 then

$$-\frac{d(M_1)}{dt} = k_2(R_1)(M_1)$$

$$= M_1 \times \left(\frac{k_1 k_2 k_3}{2k_4}\right)^{1/2}$$

From the final expression it can be observed that it is first order in M_1, the reactant.

If the reaction scheme is terminated by step (5) instead of step (4) then the following expression is obtained:-

$$-\frac{d(M_1)}{dt} = k_1(M_1)^{3/2} - \left(\frac{k_2}{k_5}\right)^{1/2}$$

in this case the reaction is 3/2 order in M_1, the reactant. Finally if step (6) is the termination process it can be shown in a similar manner that the rate is of 1/2 order with respect to M_1, the reactant.

In practice all three termination steps may occur to various degrees resulting in some unpredictable fractional order of reaction.

Some radical reactions can be inhibited by means of compounds like cyclohexene and cyclopentene which readily react with the free radicals present in the system. In the case of alkyl halides they can be used to separate radical and molecular reactions.

(b) Unimolecular Elimination Reactions

Unimolecular elimination reactions have no induction period and are not affected by initiators or inhibitors; the reactions are first order at high pressure becoming second order at very low pressure (a theoretical requirement[7]). Good examples of unimolecular elimination reactions are the pyrolyses of the alkyl chlorides[8a] and alkyl esters[9].

(c) Mixed Mechanisms

Gas phase reactions often occur by mixed mechanisms i.e., both molecular and chain reactions. In order to study the molecular reaction it is necessary to remove the chain reactions by the addition of inhibitors such as cyclohexene which removes the free radicals. Examples of mixed mechanisms can be found in the gas phase pyrolysis of alkyl bromides[10,11].

(d) Surface Reactions

Gas phase pyrolyses carried out in clean pyrex reaction vessels have been observed to give irreproducible results and can be extremely rapid[12]. However if several pyrolysis runs are carried out in the reaction vessel the rate of reaction is often reduced by each run and finally becomes reproducible[12]. This is due to the presence of a pyrolytic carbon coating which builds up on the walls of the reaction vessel. An alternative method of coating the reaction vessel is to pyrolyse allyl bromide or

cis butene-2 in the vessel[13] . The surface reaction on the clean pyrex walls of the reaction vessel is due to the polar surface which directs cis elimination[14] . The carbon coated surface can be made reactive towards radical reactions by small quantities of oxygen, which can act as a source of free radicals. If for some reason oxygen should enter the reaction vessel then the surface must be retreated with allyl bromide or cis butene-2.

In order to test for a heterogeneous reaction; the (normal) unpacked reaction vessel is replaced by one packed with glass tubing in order to increase the surface to volume ratio. (Both vessels being coated with pyrolytic carbon). The rate will be observed to increase in proportion to the surface to volume ratio if a significant proportion of the reaction is heterogeneous. No rate change will be observed if the reaction is homogeneous.

At sufficiently low temperatures even in the presence of a carbon coating a heterogeneous reaction may become significant. This can be detected in at least two ways. (1) the Arrhenius plot will start to curve when a significant part of the pyrolysis reaction is occuring by the (low Activation Energy) heterogeneous route and (2) on going from an unpacked reaction vessel to one packed with glass tubing, the rate will be observed to increase in proportion to the change of surface to volume ratio.

(3) Brief Review of Gas Phase Pyrolysis of Alkyl Chlorides and Alkyl Bromides

In the gas phase pyrolysis of alkyl halides both molecular and radical reactions have been observed[8b,8c], as well as mixed molecular and radical reactions[11,15a,15b]. The radical reactions have been observed in the case of dichlorides where the chlorine atoms are on different carbon atoms and some mono bromides[8c,8d]. Molecular reactions are observed for the mono chlorides, and the dichlorides where the two chlorine atoms are on the same carbon atom[8a]. The results for the alkyl chlorides are in excellent agreement with the principles pointed out by Barton et al.[12] for predicting whether a reaction will be molecular or radical. These authors stated "a chloro compound will decompose by a radical chain mechanism only so long as neither the compound itself nor the reaction products are inhibitors for the chain reactions", see Table I 3.1.

Molecular elimination of hydrogen chloride from alkyl chlorides proceeds by a 1,2 elimination, this is inferred from three sets of experimental data. The first is that only olefin products are observed in the pyrolyses alkyl halides, no ring compounds are observed[16]. Secondly in the pyrolysis of 1-bromo-butane only 1-butene is

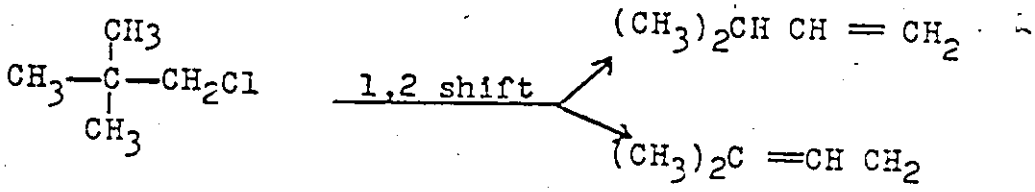
Table I 3.1. [12, 8e]

Predicted Mode of Decomposition of Chloroalkanes

Compound	Unimolecular	Radical Chain
C_2H_5Cl	X	
CH_3CHCl_2	X	
CH_2ClCH_2Cl		X
$CH_2ClCHCl_2$		X
CH_2ClCCl_3		X
$CHCl_2CHCl_2$		X
$CH_3CH_2CH_2Cl$	X	
$CH_3CHClCH_3$	X	
$CH_3CHClCH_2Cl$	X	
$CH_3(CH_2)_2CH_2Cl$	X	
$(CH_3)_3CCl$	X	
$CH_2ClCH_2OCH_2CH_2Cl$		X
$C_6H_5CHClCH_3$	X	
$C_6H_5CH_2CH_2Cl$		X

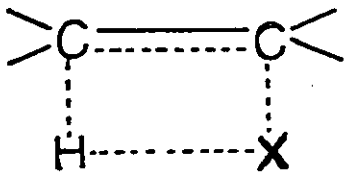
obtained when inhibitors were present (to remove the free radical reactions[11]). The final set of data comes from the pyrolysis of neopentyl chloride which has no

β carbon-hydrogen bonds, if elimination occurs only by a 1,2 process then only rearranged products should be observed. After the radical reactions are removed by means of inhibitors it has been shown [15a] that the molecular elimination of hydrogen chloride involves a 1,2 shift of a methyl group leading to 2-methyl-1-butene and 2-methyl-2-butene .



(a) Transition State in the Molecular Pyrolysis of Alkyl Chlorides and Bromides

Prior to the 1950's it was generally accepted that the transition state for unimolecular elimination of hydrogen halide involved a planar four centre transition state.



Green et al. [17] pointed out that for a series of alkyl bromides, although the frequency factors A for the thermal decomposition were essentially the same ($\sim 10^{13}$) the

activation energies for the process decrease in the order primary (50 kcal.mole^{-1}) > secondary (46 kcal.mole^{-1}) > tertiary (42 kcal.mole^{-1}) . From this trend the authors concluded that a correlation existed between the activation energies and the heterolytic carbon-bromine bond strength.

Table I 3.a.1. [8f,18]

Activation Energies for a Series of α Methyl Substituted Alkyl Halides with the Homolytic and Heterolytic Bond Dissociation Energies for the Carbon Halogen Bond.

		C_2H_5	i C_3H_7	t C_4H_9
Cl	$E^{\neq}$ kcal.mole^{-1}	37.3	30.9	23.3
	Rate Const.Ratio	1	150	25,000
	Homolytic	79	77	75
	Heterolytic	200	181	155
Br	$E^{\neq}$ kcal.mole^{-1}	33.0	27.5	21.3
	Rate Const.Ratio	1	140	46,000
	Homolytic	65	63	61
	Heterolytic	191	172	144
I	$E^{\neq}$ kcal.mole^{-1}	30.5	25.5	17.6
	Rate Const.Ratio	1	102	35,000
	Homolytic	52	50	48
	Heterolytic	190	171	139

Table I 3.a.1 [8f,18] contains the activation energies for a series of α methyl substituted alkyl halides together with homolytic and heterolytic bond dissociation energies for the carbon-halogen bond. From these results Thomas and Maccoll [18] concluded that while little correlation existed

between the activation energy and the homolytic bond dissociation energies D(R-X), a clear correlation existed between the activation energy for elimination and the heterolytic bond dissociation energy $D(R^+X^-)$.

Evidence that the transition state is affected by the β carbon-hydrogen bond, but only to a limited extent, can be observed from the effect of β methyl substitution (see Table I 3.a.2). Here the rate only changes by a factor of three or four when a β hydrogen is replaced by a methyl group whereas in the case of α methyl substitution the rate changed by a factor of several hundreds for each hydrogen replaced.

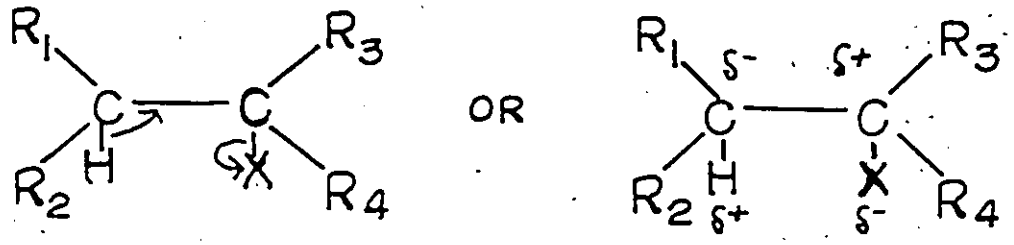
Table I 3.a.2. [8g]

Activation Energy and Rate Constant Ratios for a Primary β-Methylated Series

		C_2H_5	$n\text{-}C_3H_7$	$i\text{-}C_4H_9$
Cl	$E^{\ddagger}$ kcal.mole^{-1}	57.8	55.1	56.1
	Rate Const.Ratio	1	3.6	4.7
Br	$E^{\ddagger}$ kcal.mole^{-1}	53.0	51.1	50.4
	Rate Const.Ratio	1	3.4	7.3

Thomas and Maccoll[18] suggested that a possible description of the transition state is a primary elongation with polarization of the carbon-halogen bond with some

limited assistance from a polarized carbon-hydrogen bond. It was proposed that the β-hydrogen atoms played a similar role to the solvent in liquid phase reactions in stabilizing the transition state. Maccoll[19] has termed his above description of the transition state for the elimination of hydrogen halides as the "Ion Pair Theory".



A plot of the activation energies for the elimination of hydrogen halide from a series of alkyl halides against their heterolytic bond strengths yields a reasonably straight line, from which the following relationship can be deduced:

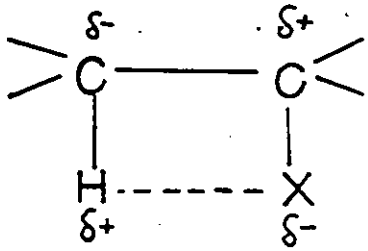
$$E(HX) = 0.29D(R^+X^-)$$

where $E(HX)$ is the activation energy for elimination

$D(R^+X^-)$ is the heterolytic bond dissociation energy.

The activation energies for a simple elimination can be calculated to within ± 1 kcal.mole^{-1} from this expression, the limitation being the lack of accurate heterolytic bond strengths.

Benson[20] interprets the transition state in a slightly different manner which he refers to as the "Semi-Ion Pair Theory". He visualizes the hydrogen halide approaching the double bond (see below) and partial bonds forming between



the β carbon atom and hydrogen atom of the hydrogen halide; and the α carbon atom and the halogen. Using this as a representation of the transition state Benson developed the following expression to calculate the minimum activation energy for the elimination reaction:

$$E_o = E^o - \tfrac{1}{2}(e^2 \mu_1^2 r_{HX}^2 / \alpha_{HX})(1 - \alpha_C r_{HX}/2r_a^6)$$

where E^o is the enthalpy of heterohalogenation, r_{HX} and α_{HX} are the H-X distance and polarization of the H-X in the transition state, α_C is the polarizability of the olefin in the transition state and r_a is the distance between the hydrogen halide molecule and the olefin.

The results obtained from the above equation for a series of α methyl substituted chlorides[8h] are shown in Table I 3.a.3 together with the values found by experiment. The trend is correct but the effect of the α methyl

Table I 3.a.3.[8h]

Activation Energies for a Series of α-Methylated Substituted Alkyl Halides Calculated on the Basis of the Semi-Ion-Pair Theory

Halogen	Alkyl		
	C_2H_5	$i\text{-}C_3H_7$	$t\text{-}C_4H_9$
Cl	58 (58)	47 (51)	47 (45)
Br	58 (53)	47 (48)	47 (41)
I	45 (51)	45 (46)	42 (38)

Values in parentheses are experimental results.

Table I 3.a.4.[8h]

Activation Energies for a Series of α-Methylated Substituted Alkyl Halides Calculated on the Basis of a Modified Semi Ion Pair Theory

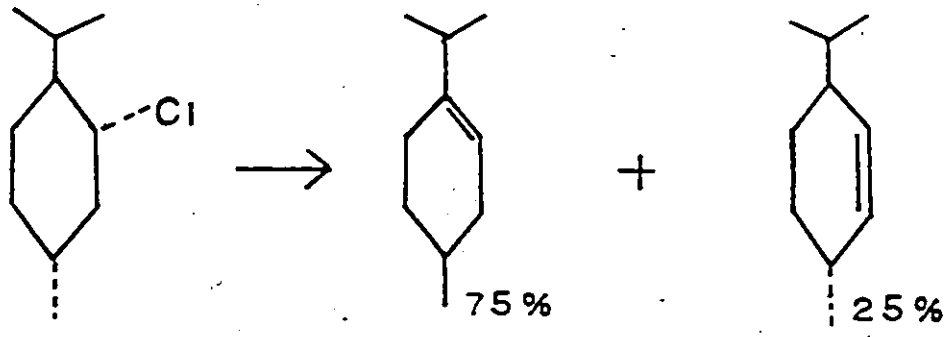
Halogen	Alkyl		
	C_2H_5	$i\text{-}C_3H_7$	$t\text{-}C_4H_9$
Cl	56 (58)	52 (51)	48 (45)
Br	56 (53)	52 (48)	45 (41)
I	54 (51)	50 (46)	44 (38)

Values in parentheses are experimental results.

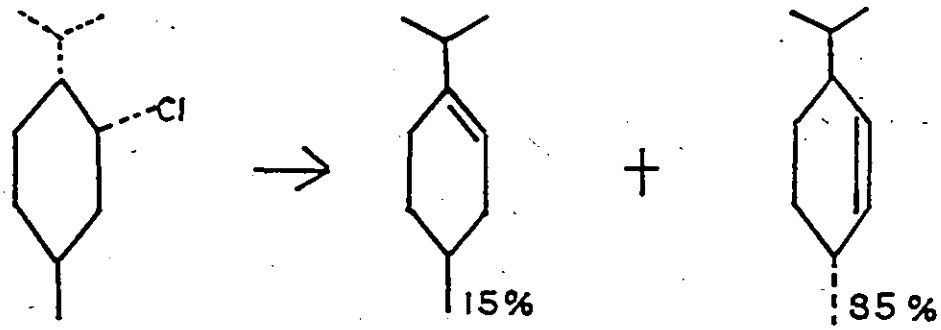
substitution is underestimated. Benson[8h,20] considered an alternative model in which both the olefin and the hydrogen halide are initially polarized parallel to their reacting bonds by the equivalent of $\pm \frac{1}{2}$ e formal charge. The results obtained for the same set of α methyl substituted halides on the basis of this model are shown in Table I 3.a.4 [8h], the agreement is better but there is still present an underestimation of the effect of the α methyl substitution.

In terms of the "Ion Pair Theory" it is possible that if the carbon-halogen bond is sufficiently elongated in the transition state, then the hydrogen atoms both cis and trans to the halogen in the ground state may be lost. Conversely in terms of the "Semi-Ion Pair Theory" a planar four centre transition state allows cis elimination only with symmetrical displacement of the departing hydrogen halide.

The first investigation into the sterospecificity of alkyl halide pyrolysis was reported by Barton [21] who pointed out that a planar four centre transition state will require a cis elimination. He and others [22] undertook the gas phase pyrolysis of menthyl chloride and they observed



a predominance in the yield of menthene-3 over menthene-2 which these authors claimed was evidence for cis elimination. However, Harding and Maccoll [23] have pointed out that this is the ratio one would anticipate, since the hydrogen eliminated to give the menthene-3 is tertiary while that eliminated to give menthene-2 is secondary. Maccoll and Bamkole [24] confirmed Barton's results and then investigated the pyrolysis of neomenthyl chloride.



They found an 85% yield of menthene-2 which is consistent with a predominantly cis elimination.

The simplest mono halogen compounds which can yield more than one product are the secondary butyl halides and pyrolysis of these compounds yield 1-butene and cis and trans 2-butene. Maccoll and Stone [25] observed that 42%, 34% and 17% 1-butene was obtained from the secondary chloro, bromo and iodo compounds respectively. In the case of the former two, ammonia was added to try to prevent isomerisation by the halogen acids; the ratio of cis to trans 2-butene was observed to be very close to the thermodynamic value. Other authors[26,27] have investigated the pyrolysis of secondary

butyl chloride on different surfaces and have concluded that an alkyl bromide surface in the presence of halogen acids catalyses the isomerisation of the butenes. The present trend of results[25,26,27] indicates (in the absence of any catalysed isomerisation) that although the cis:trans ratio is very close to the thermodynamic value the butene-1 to cis or trans ratio is clearly not thermodynamically controlled.

It has been pointed out that if co-planarity is a requirement in the transition state then the trans isomer should predominate,[25] indeed Heydtmann and Rinck [26] observed this in the pyrolysis of secondary butyl chloride.

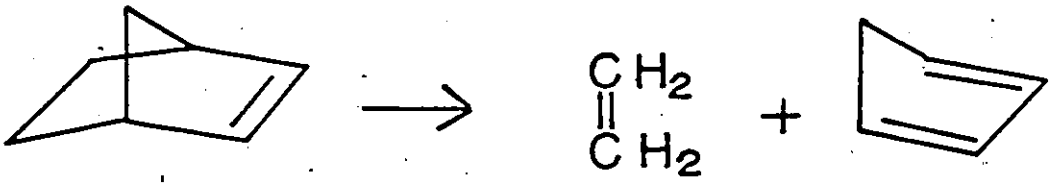
Clearly absolute determinations as to whether the elimination from alkyl halides occurred by a cis or trans mechanism would be of considerable help in postulating the transition state for the elimination of hydrogen halide as discussed in the preceeding pages.

(4) Gas Phase Pyrolysis of exo-2-Norbornyl Chloride

(a) Review

The gas phase pyrolysis of this material has been briefly mentioned by Herndon et al.[28,29], they reported that the rate for the elimination of hydrogen chloride from exo-2-norbornyl chloride relative to that of cyclohexyl chloride at 400 and 500 °C was 0.67 and 0.77 respectively. They also reported that the olefin

formed, norbornene, rapidly underwent a retro Diels-Alder reaction yielding ethylene and cyclopentadiene.



A second paper by Herndon et al.[30] in the same year reported the kinetics for the gas phase retro Diels-Alder reaction of norbornene in the temperature range 300 to 440 °C; the following Arrhenius expression was presented covering that temperature range.

$$\log k = 13.78 \pm 0.19 \exp(-42{,}750 \pm 560/4.573T)\ sec^{-1}$$

(b) Experimental

Chemicals: exo-2-Norbornyl chloride used in the gas phase pyrolysis was prepared by bubbling hydrogen chloride through a solution of norbornene in methylene chloride at -78 °C and it was purified by distillation. The preparation of exo-2-norbornyl chloride- (56% exo-3 and 44% syn-7)-d_1, exo-2-norbornyl chloride-3,3-d_2, exo-2-norbornyl chloride-exo-5-exo-6-d_2 and nortricyclene (tricyclo (1,1,1) heptane) are described in Part IV of this thesis.

Apparatus: The pyrolysis was performed using a typical static vacuum system as shown in Fig. I 4.b.1. The reaction vessel* was heated by a furnace thermostatically controlled to ± 1 °C and the temperature was measured by a chromel-aluminum thermocouple and a potentiometer. The gas chromatographic unit shown in Fig. I 4.b.2 consists of a Gowmac thermal conductivity detector (using a Trygon D.C. power supply) and a 1 meter column at room temperature containing 10% by weight diisodecylphthalate on Chromasorb P; helium was used as the carrier gas.

Procedure: A typical pyrolysis was carried out by freezing a sample† of exo-2-norbornyl chloride into the side arm of the reaction vessel (see Fig. I 4.b.3) using liquid nitrogen, the sample was then flashed into the reaction vessel (of known volume, previously treated with pyrolysis products to eliminate surface catalysed reactions) at a specific temperature, by flaming the side arm, covering it with an electrically heated tube and then measuring the initial pressure using a null glass-diaphragm gauge (see Fig. I 4.b.3); the reaction kinetics were then studied by one of the following techniques. (I) By continually monitoring the pressure of the reaction mixture: the null glass-diaphragm gauge shown in Fig. I 4.b.3 operates by adding a balancing pressure to the side of the gauge external to the reaction vessel such that zero deflection of the

* Reaction Vessel 200 c.c. † Sample Size ~150 μ moles

light beam is observed, the pressure in the reaction vessel is then equal to the external pressure applied. (II) By titration of the hydrogen chloride produced in the pyrolysis: the reaction was stopped after a given time by freezing out the reaction mixture in a side tube cooled to liquid nitrogen temperature (see Fig. I 4.b.1) which is then sealed under vacuum. The tube was then broken under ice-cold water and the resulting solution titrated with a standard borax solution (all glassware and solutions involved in the titrations were chilled to 0 °C to prevent hydrolysis of the chloride, which occurs at a slow but measurable rate at room temperature). (III) By gas phase chromatography: the analytical apparatus is as shown in Fig. I 4.b.2; the hydrogen chloride produced in the pyrolysis must be removed from the sample before it can be passed through the diisodecylphthalate column (hydrogen chloride decomposes the ester); this was achieved by allowing the sample from the reaction vessel to pass through a U-tube cooled to -119 °C (ethyl bromide slush bath) where the pyrolysis products were frozen out, except for hydrogen chloride and ethylene which were removed by pumping. The reaction mixture was then warmed to room temperature and swept into the gas chromatograph unit by the helium carrier gas.

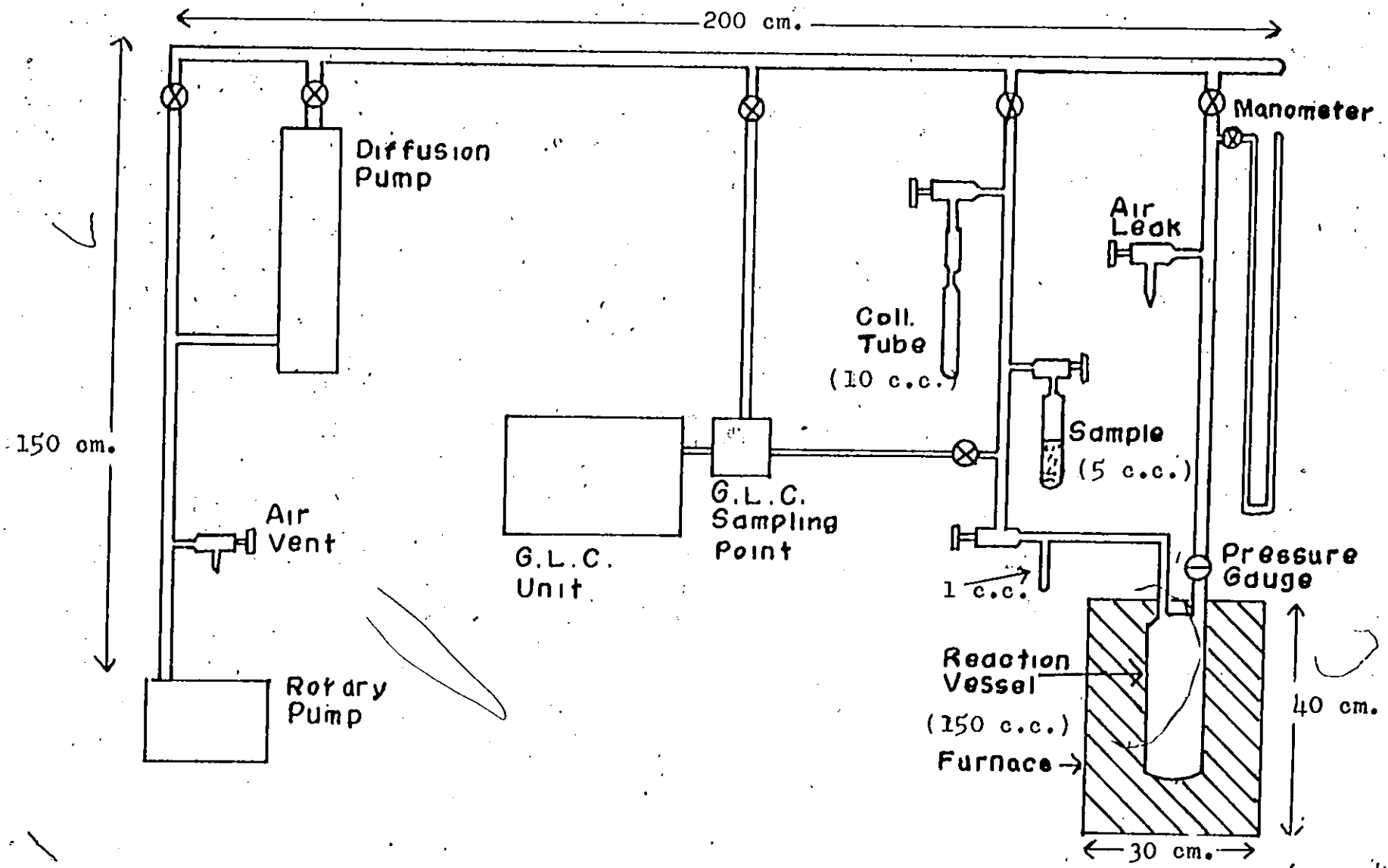


Fig. I 4.b.1. Vacuum System.

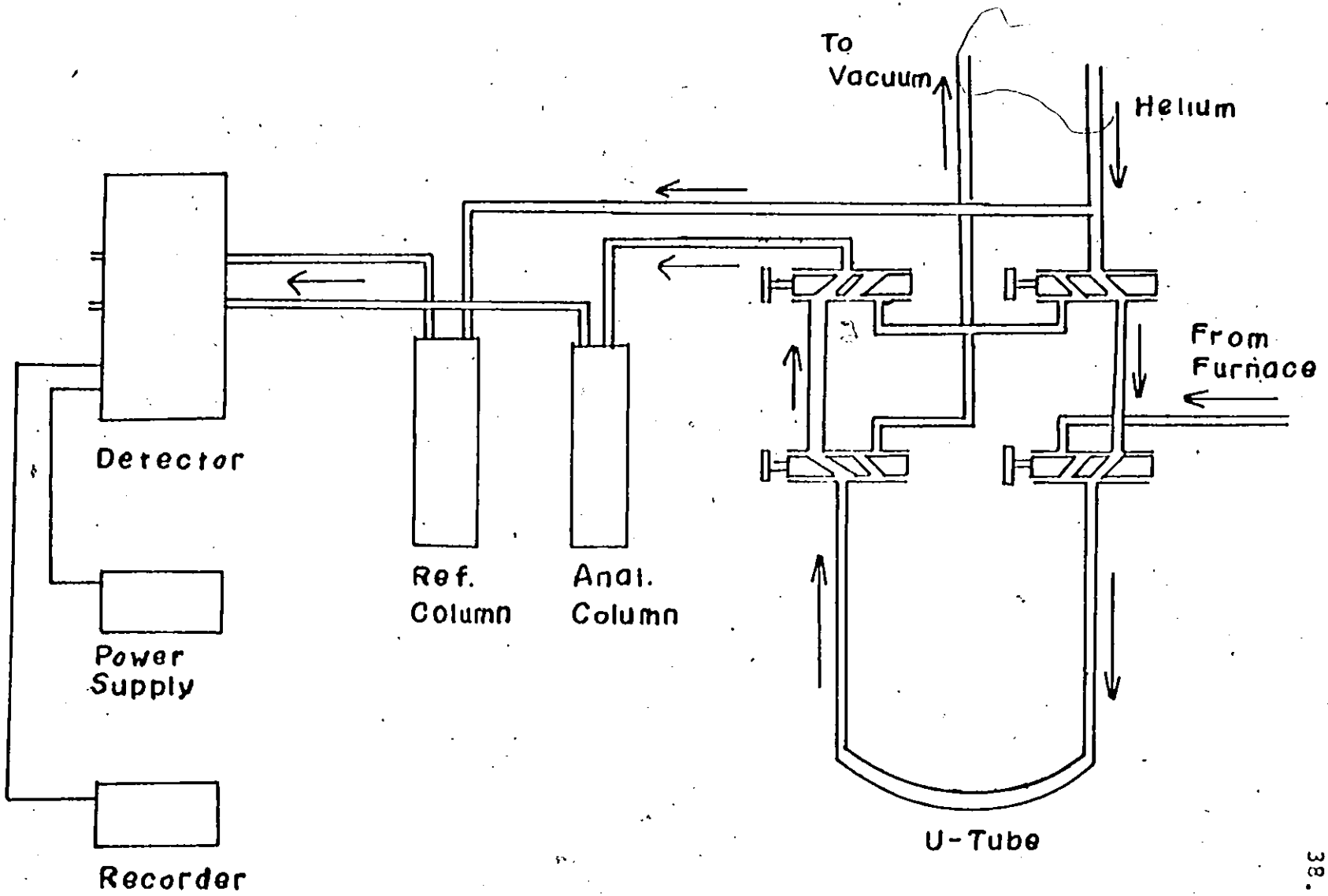


Fig. I 4.b.2. Gas Chromatographic Unit.

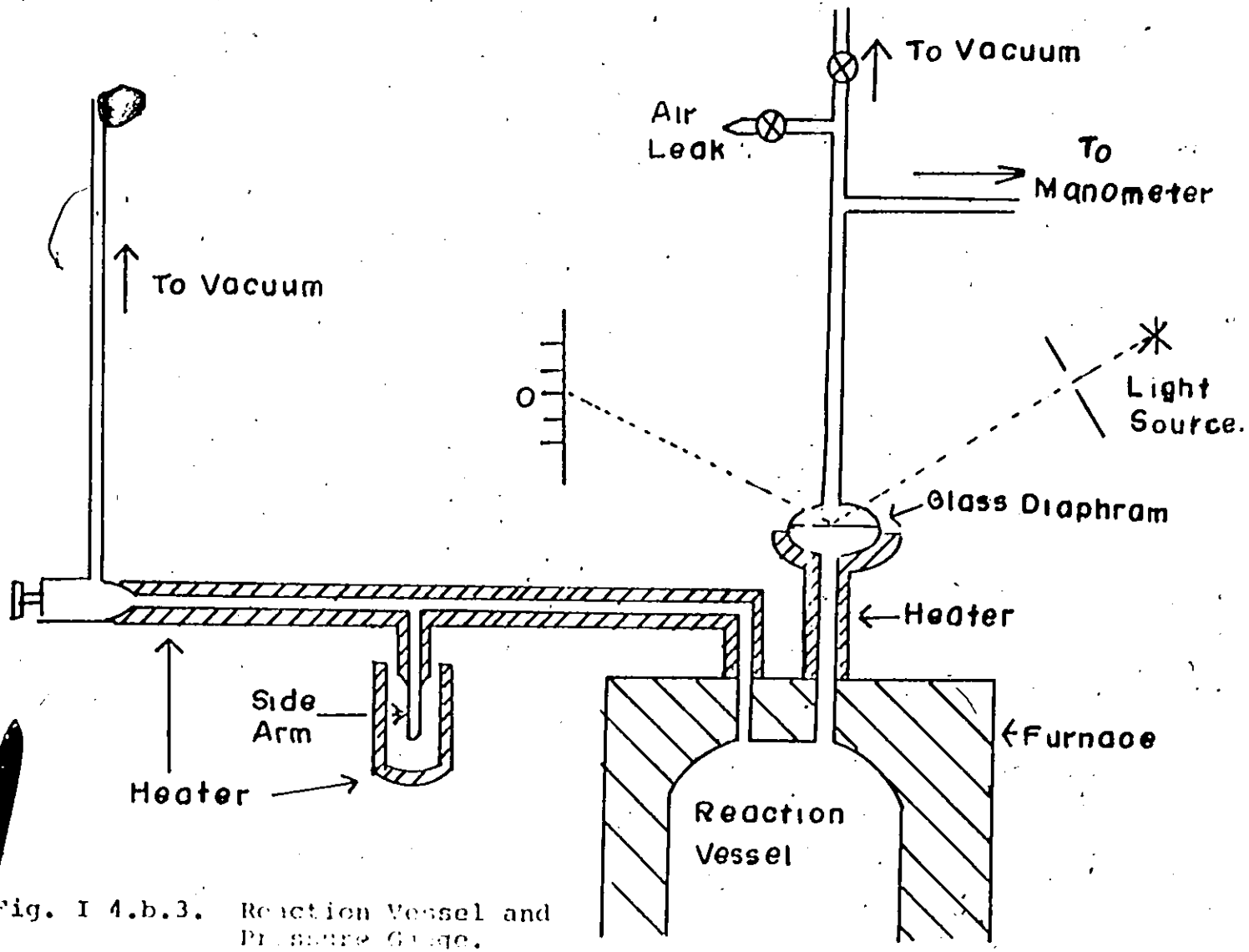


Fig. I 4.b.3. Reaction Vessel and Pressure Gauge.

(c) Results

A typical first order rate plot for the formation of hydrogen chloride is shown in Fig. I 4.c.1. The remainder of the experimental results in the temperature range 300-370°C are to be found in the Appendix on page 72 , Table I 4.c.1 contains the rate of formation of hydrogen chloride at these temperatures. The Arrhenius plot for the formation of hydrogen chloride in the above temperature range is shown in Fig. I 4.c.2 and the Arrhenius parameters derived from the plot yield the following equation:-

$$k = 13.79 \pm 0.70 \exp(-49,000 \pm 2000/RT)\,sec^{-1}$$

The products expected from the gas phase pyrolysis of exo-2-norbornyl chloride are hydrogen chloride, ethylene, cyclopentadiene and any undecomposed norbornene. However, on substituting the rate of formation of hydrogen chloride (k_A) (determined by titration) and the rate of the retro-Diels-Alder reaction (k_B) reported by Herndon et al. at a specific temperature into the following expression:

$$B_t = B_o e^{-k_B t} - \frac{k_A A_o}{k_B - k_A} (e^{-k_A t} - e^{-k_B t})$$

where B_o and A_o are the initial concentrations of norbornene and exo-2-norbornyl chloride, and where B_t is the concentration of norbornene at any time t.

which represents the concentration of the first product in a

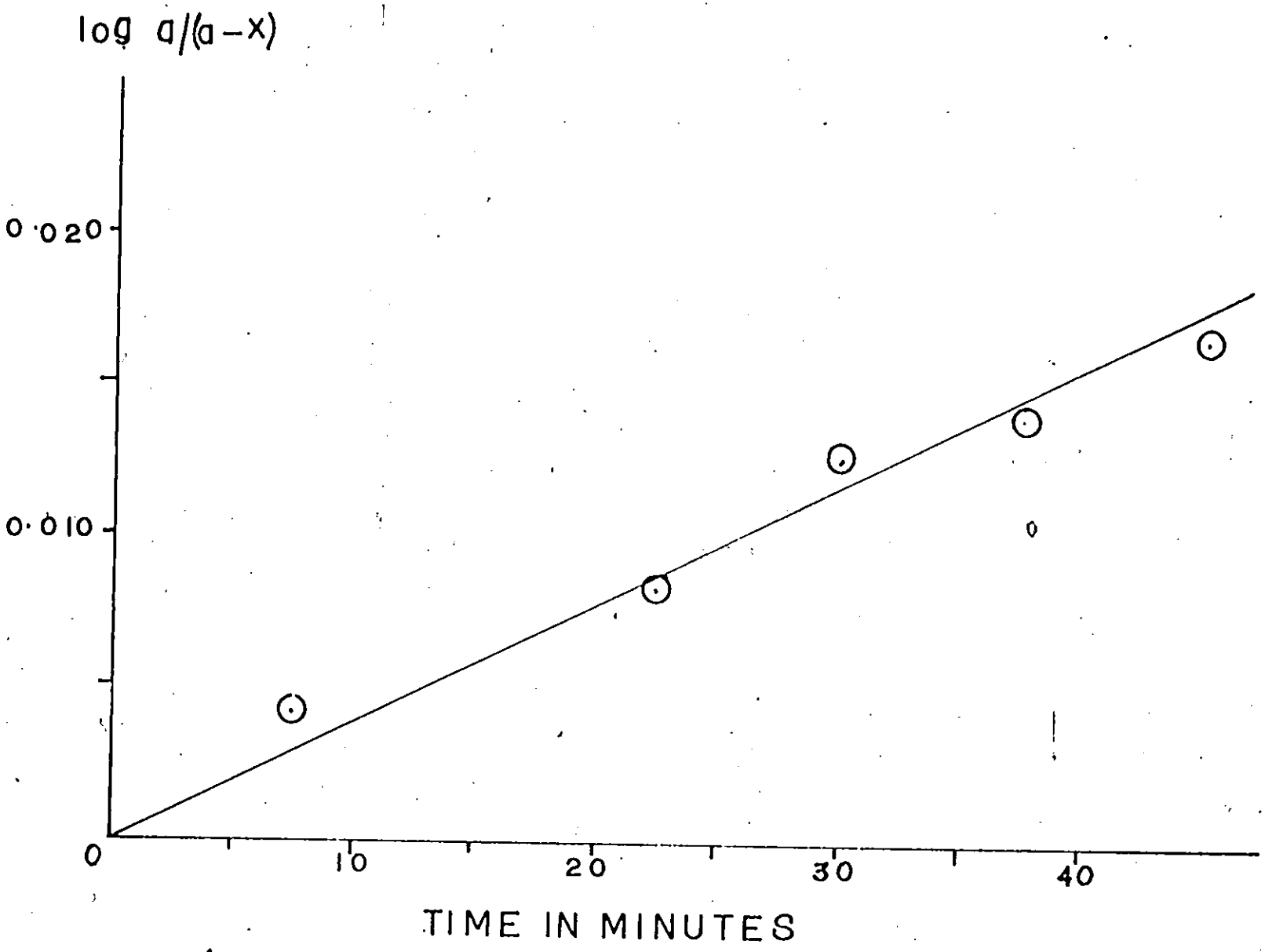


Fig. I 4.c.1. Typical First Order Rate Plot for the Formation of Hydrogen Chloride. Temp. 310 C.

Table I 4.c.1.

Rate Constants for Formation of Hydrogen Chloride, Cyclopentadiene and Nortricyclene* at Various Temperatures in the Range 300-370°C

Temp. °C	Rate Constant for the Formation of Hydrogen Chloride (sec^{-1})	Rate Constant for the Formation of Cyclopentadiene (sec^{-1})	Rate Constant for the Formation of Nortricyclene* (sec^{-1})
296	6.3×10^{-6}	——	——
310	1.5×10^{-5}	1.0×10^{-5}	0.5×10^{-5}
322	3.3×10^{-5}	—	—
330	7.1×10^{-5}	4.7×10^{-5}	2.4×10^{-5}
335	1.2×10^{-4}	—	—
338	1.1×10^{-4}	—	—
341.5	1.8×10^{-4}	—	—
346	1.6×10^{-4}	—	—
346.5	2.1×10^{-4}	—	—
350	2.3×10^{-4}	1.4×10^{-4}	0.9×10^{-4}
352	2.9×10^{-4}	—	—
360	5.2×10^{-4}	—	—
370	7.0×10^{-4}	4.5×10^{-4}	2.5×10^{-4}

* Determined by the difference between the rate of formation of hydrogen chloride and cyclopentadiene.

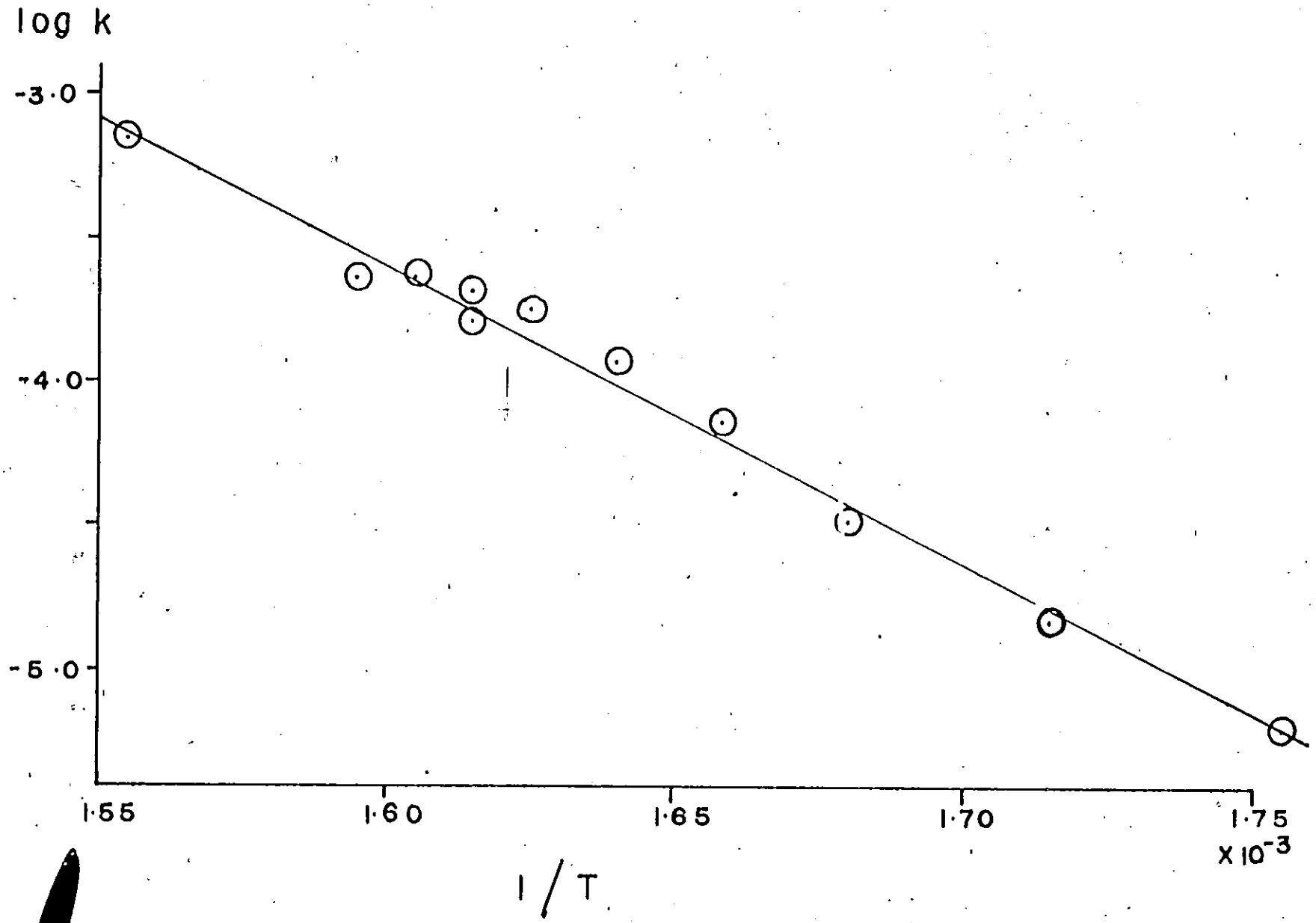


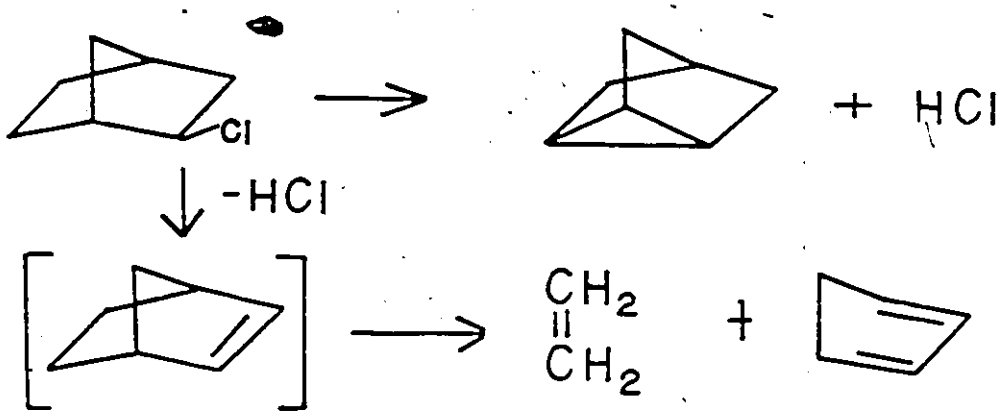
Fig. I 4.c.2. Arrhenius Plot for the Formation of Hydrogen Chloride in the Temperature Range 330-370°C .

set of consecutive first order reactions (see page 10 for derivation), it soon became clear that the amount of norbornene was effectively zero. However the amount apparently determined by gas phase chromatography was substantial. The mass spectrum of this material obtained from the pyrolyses showed that its molecular weight was 94 but it had relative abundances for many of the ions significantly different from those observed in the mass spectrum of pure norbornene. It was concluded that the isomer nortricyclene possibly was being produced in the pyrolysis and therefore some nortricyclene was prepared by a Bamford-Stevenson reaction[31] on the tosyl-hydrazone of norcamphor (see Part IV for details). It was found to be thermally stable at pyrolysis temperatures and to have the same retention time and mass spectrum as the recovered pyrolysis product. No other product could be detected at the limits of the g.l.c.

When pure norbornene was placed in the reaction vessel the sample pressure was observed to increase very rapidly as the fast retro Diels-Alder reaction proceeded; after the pressure rise was complete no C_7H_{10} isomers could be detected by gas phase chromatography or mass spectrometry. Nortricyclene placed in the reaction vessel under the same conditions was found to yield no pressure change and the mass spectrum of the recovered material corresponded to nortricyclene with no indication of ethylene or cyclopentadiene.

These results show that the isomerization of norbornene to nortricyclene and vice-versa does not occur under these conditions.

Thus the gas phase pyrolyses of exo-2-norbornyl chloride can be represented as shown below.



A typical first order rate plot for the formation of cyclopentadiene is shown in Fig. I 4.c.3. The remainder of the results in the temperature range 300-370° are shown in the Appendix on page 81 . Table I 4.c.1 contains the rate of formation of cyclopentadiene at these temperatures. The Arrhenius plot for the formation of cyclopentadiene in the above temperature range is shown in Fig. I 4.c.4 and the Arrhenius parameters derived from the plot yield the following Arrhenius equation:

$$k = 12.97 \pm 0.70 \exp(-48{,}000 \pm 2000/RT)\,sec^{-1} .$$

It was not possible to measure all the products in one sample. However at each temperature studied it was

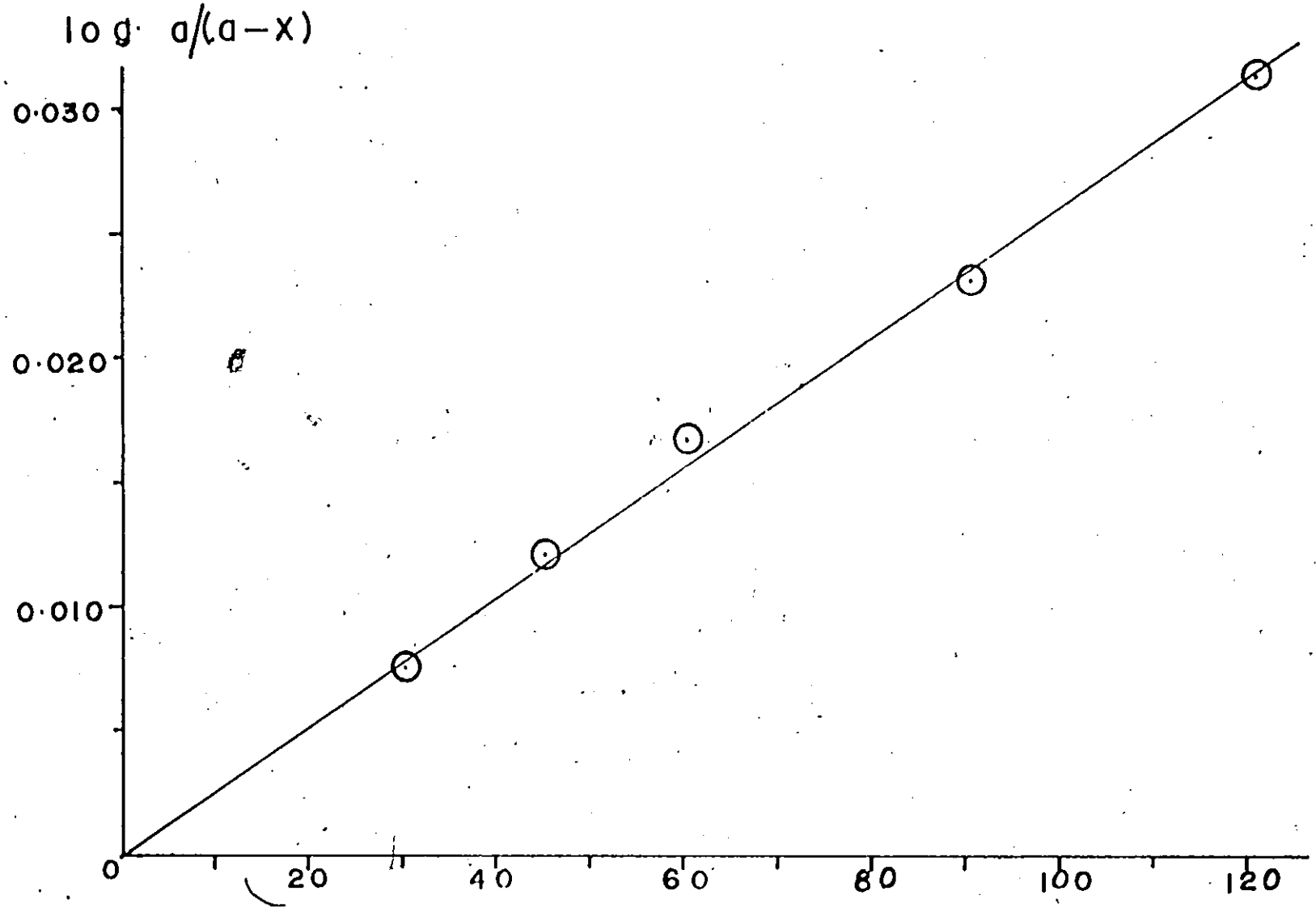


Fig. I 4.c.3. Typcial First Order Rate for the Formation of Cyclopentadiene. Temp. 310 °C.

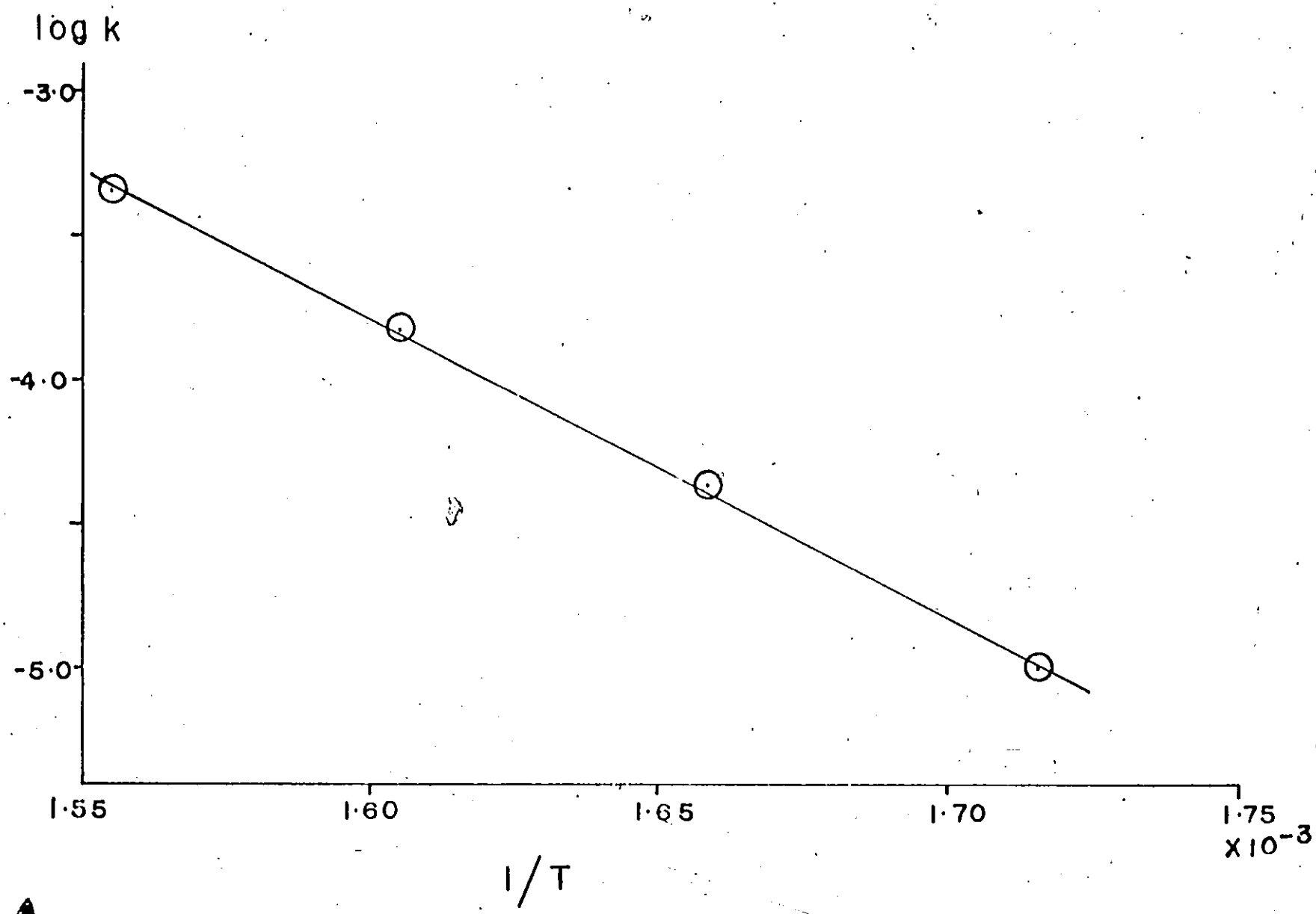


Fig. I 4.c.4. Arrhenius Plot for the Formation of Cyclopentadiene in the Temperature Range 300-370°C .

observed that the rate of formation of cyclopentadiene (which necessarily represents the rate of formation of norbornene since the rate of the retro Diels-Alder reaction is very much greater than the rate of formation of norbornene) is virtually a constant fraction of the rate of formation of hydrogen chloride (see Table I 4.c.1). Owing to the solubility of nortricyclene in the unpyrolysed exo-2-norbornyl chloride and the difficulty of sweeping the chloride from the U-tube (see Fig. I 4.b.2) onto the gas chromatograph column it was not possible directly to measure the absolute rate of formation of nortricyclene. In order to establish that the problem lay in the analysis of the nortricyclene the following investigation was carried out. An injection port was fitted between the sample collection U-tube and the gas chromatograph column; the ratio of nortricyclene to cyclopentadiene in a pyrolysis sample was then obtained (I) by injecting the sample onto the column and (II) by sweeping a similar pyrolysis product mixture directly from the U-tube (N.B. the injection port was present for these experiments only). In the latter case the ratio of nortricyclene : cyclopentadiene was found to be 1:5 while in the former the value was 1:3, substantiating the source of the analytical problem. The rate of formation of nortricyclene was measured by the difference between the rate of formation of hydrogen chloride and cyclopentadiene

(which represents the rate of formation of norbornene) at each temperature. Table I 4.c.1 contains the rate of formation of nortricyclene in the temperature range 300-370 °C and the Arrhenius plot constructed from the data is shown in Fig. I 4.c.5. From this plot the Arrhenius parameters were obtained

$$k = 13.29 \pm 0.70 \exp(-49{,}000 \pm 2000/RT)\,sec^{-1} .$$

Owing to the complexity of the system one cannot determine the rates of the individual reactions from the pressure data alone, but by using the rates of formation of hydrogen chloride measured by titration, cyclopentadiene measured by gas chromatography and nortricyclene determined by the difference in rates between the hydrogen chloride and cyclopentadiene (see Table I 4.c.1) one can calculate the expected pressure changes using the equation shown below for two first order concurrent reactions (see page 13 for derivation).

$$(B \text{ or } C)_t = \frac{-k_{(1 \text{ or } 2)}}{k'} (A_o) e^{-k't} + \frac{k_{(1 \text{ or } 2)}}{k'} (A_o)$$

where k_1 is the rate of formation of nortricyclene

k_2 is the rate of formation of cyclopentadiene (which represents the rate of formation of norbornene)

A_o is the initial concentration (pressure) of exo-2-norbornyl chloride

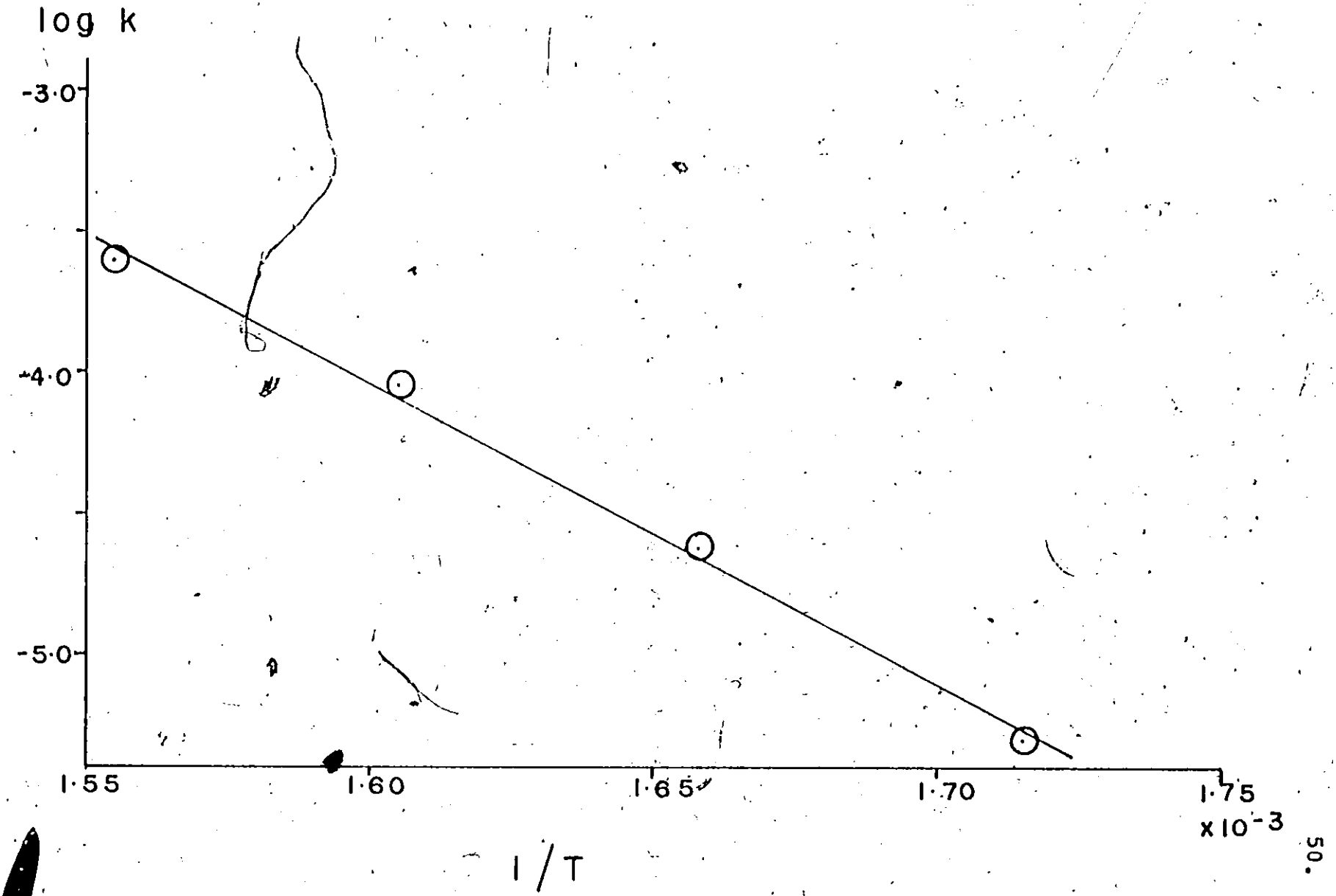


Fig. I 4.c.5. Arrhenius Plot for the Formation of Nortricyclene in the Temperature Range 300-370°C .

B_t is the concentration of nortricyclene or the hydrogen chloride produced in this reaction at time t .

C_t is the concentration of ethylene or cyclopentadiene or hydrogen chloride produced in this reaction at time t .

k' is equal to the sum of k_1 and k_2

It is assumed that the concentration of norbornene at any time t is zero.

The total pressure change is determined by calculating the individual pressures of the different species at a particular time t and summing them to give the total pressure at that time; this was repeated for a series of times and a pressure-time plot constructed. The experimental and calculated curves for the pressure change during the pyrolyses at several temperatures in the temperature range 325-385 °C are shown in Figs. I 4.c.6 to 11 . The good to excellent agreement provides additional support for the assumption that the discrepancy in the mass balance lies in the determination of the rate of formation of nortricyclene. The curves are compatible up to 60% reaction in the case of the pyrolyses carried out at 385 °C .

In order to check that no surface reaction was occuring, the gas phase pyrolysis was carried out in a packed reaction vessel (s/v 5:1) in the temperature range 340-370 °C , the kinetics being followed by hydrogen

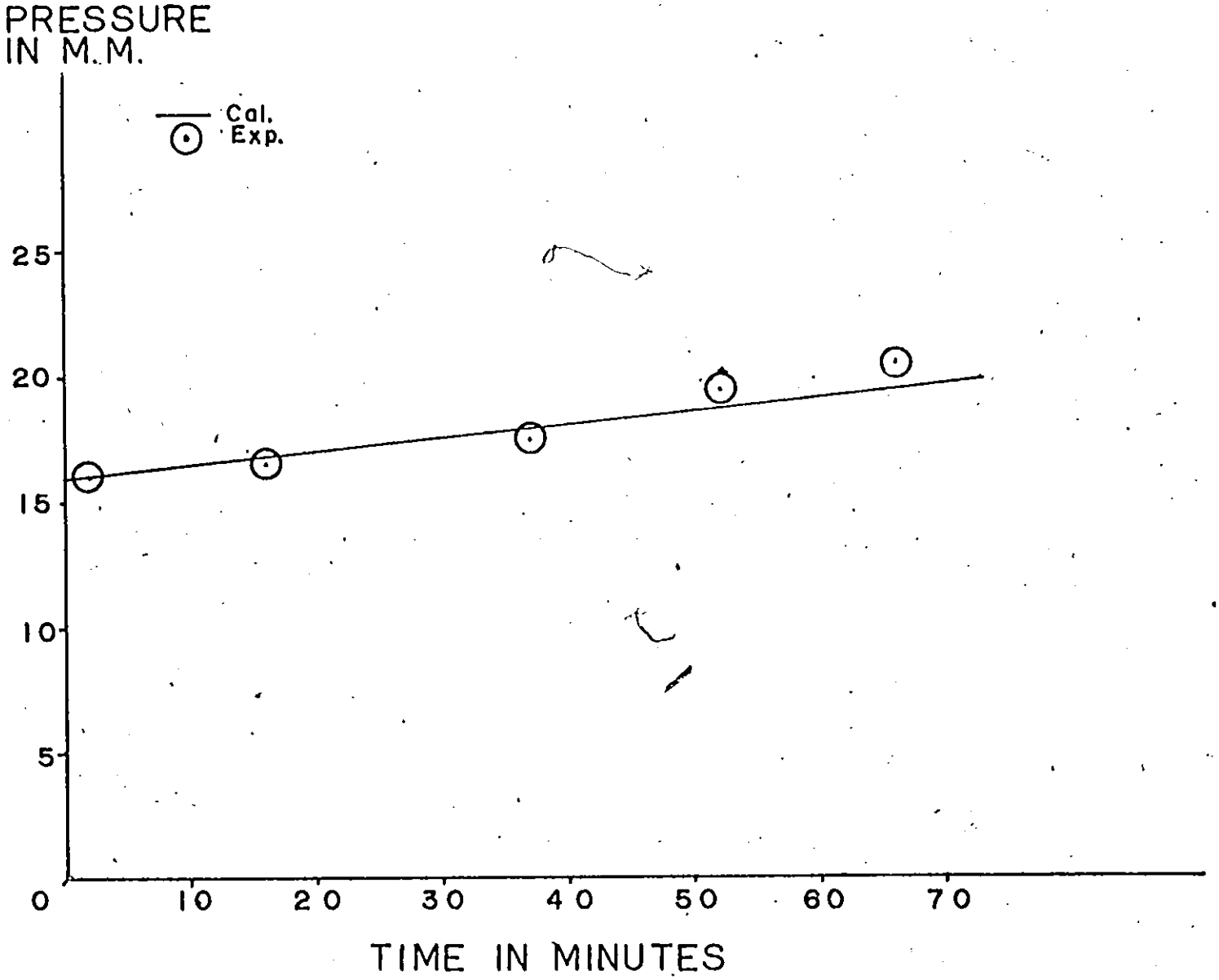


Fig. I 4.c.6. Pressure-Time Plot for the Gas Phase Pyrolysis of exo-2-Norbornyl Chloride at 325°C .

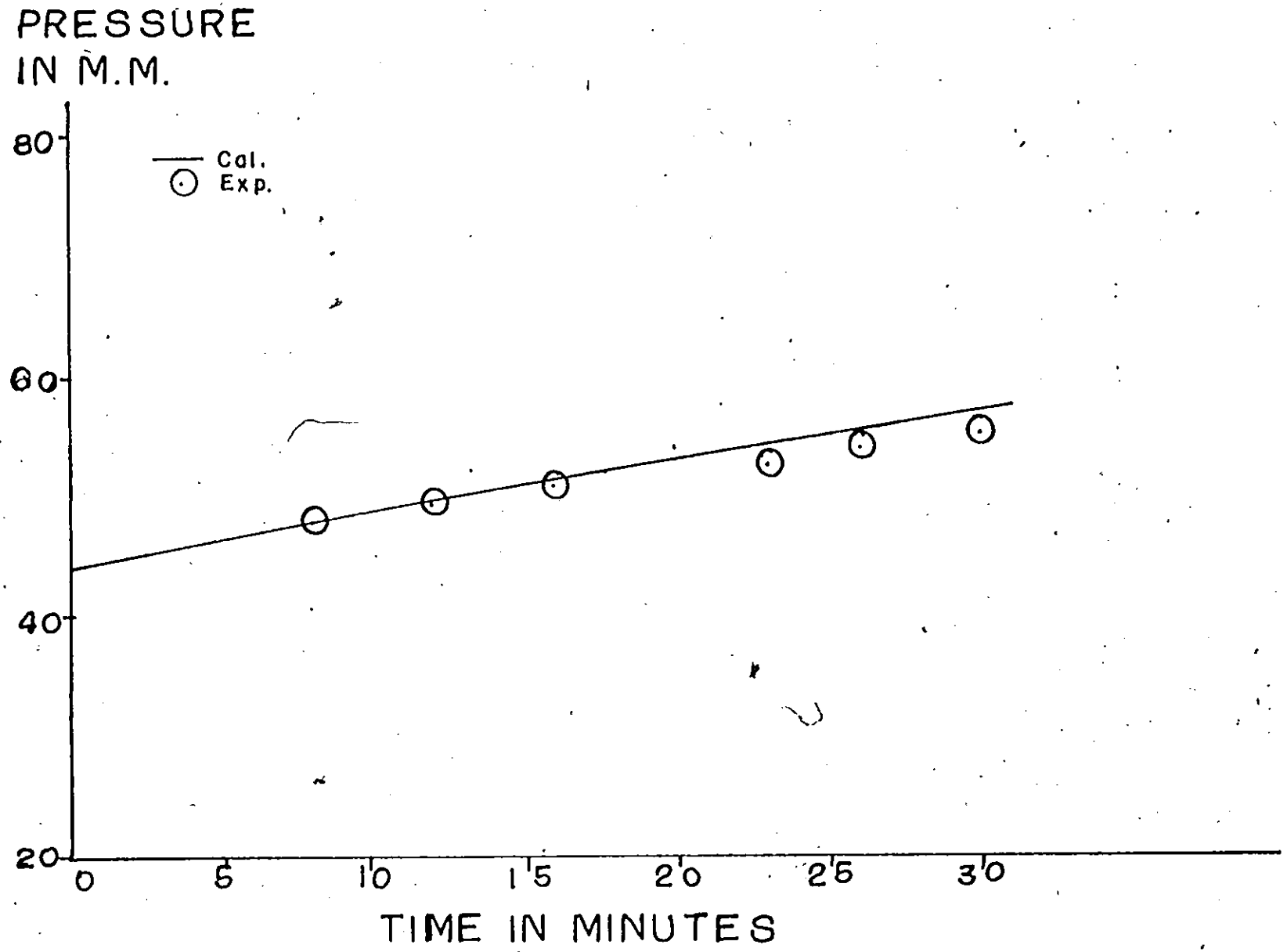


Fig. I 4.c.7. Pressure-Time Plot for the Gas Phase Pyrolysis of exo-2-Norbornyl Chloride at 339°C .

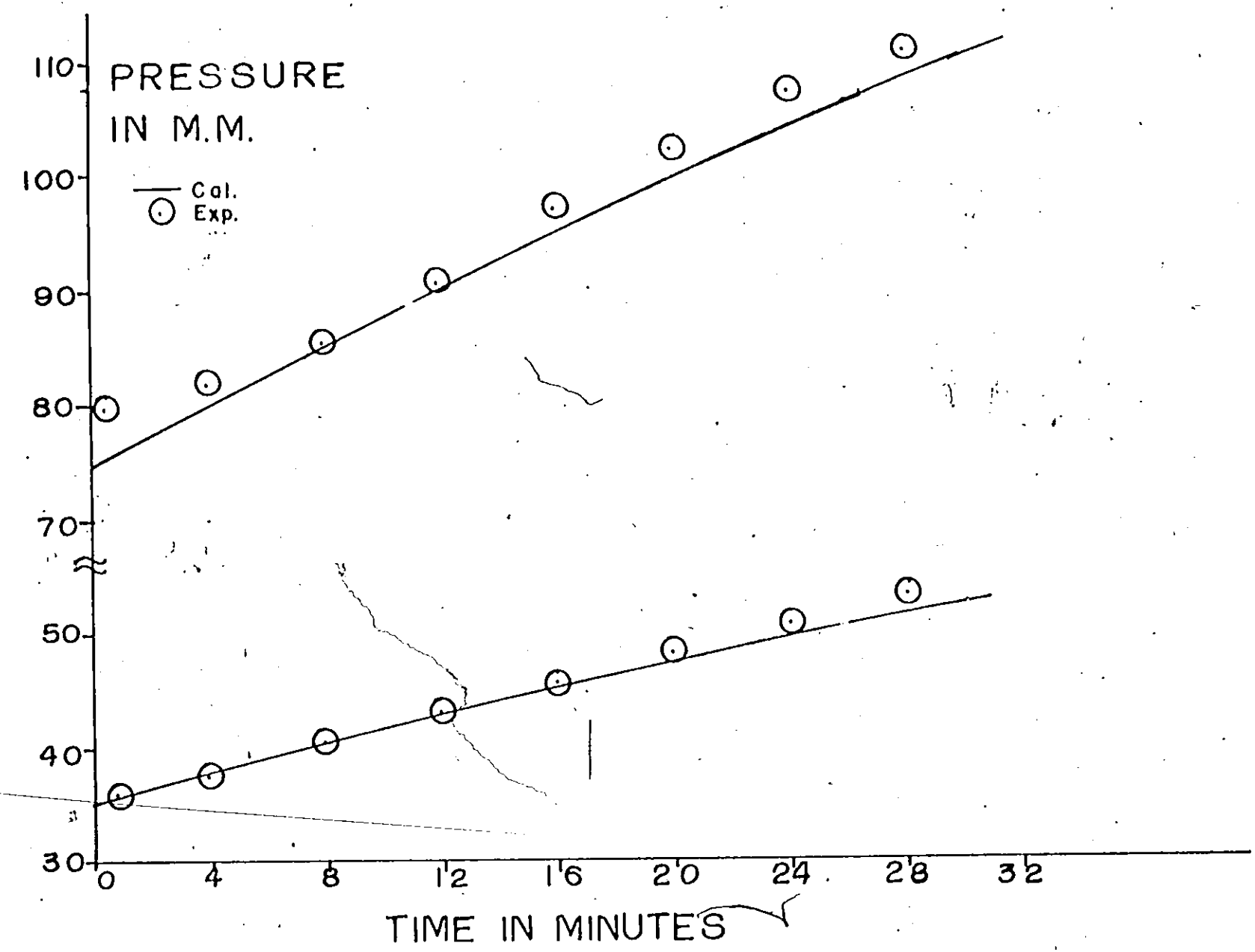


Fig. I 4.c.8. Pressure-Time Plot for the GasePhas Pyrolysis of [illegible]-Norbornyl Chloride at 346°C .

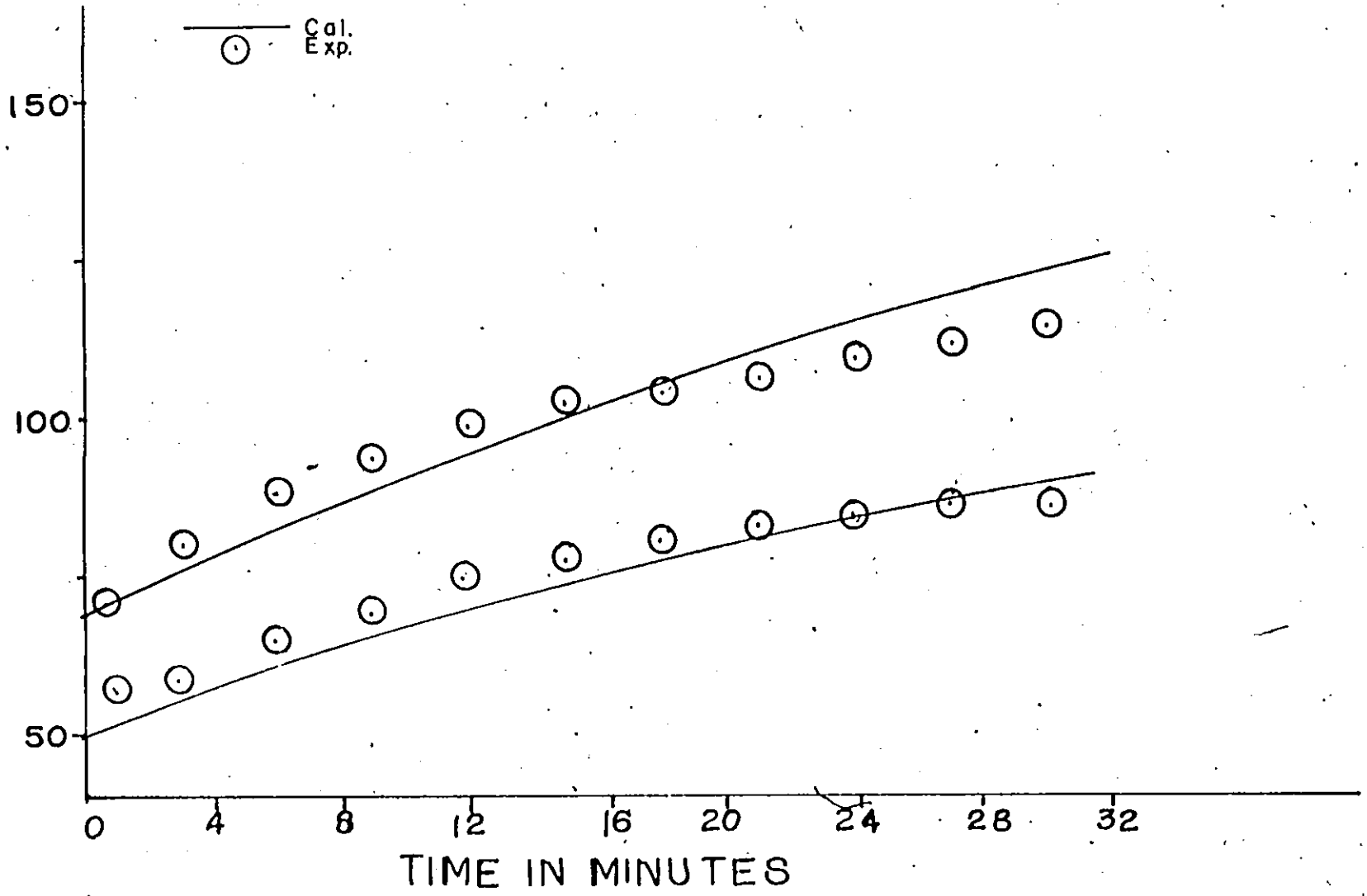


Fig. I 4.c.9. Pressure-Time Plot for the Gas Phase Pyrolysis of exo-2-Methallyl Chloride at 355°C .

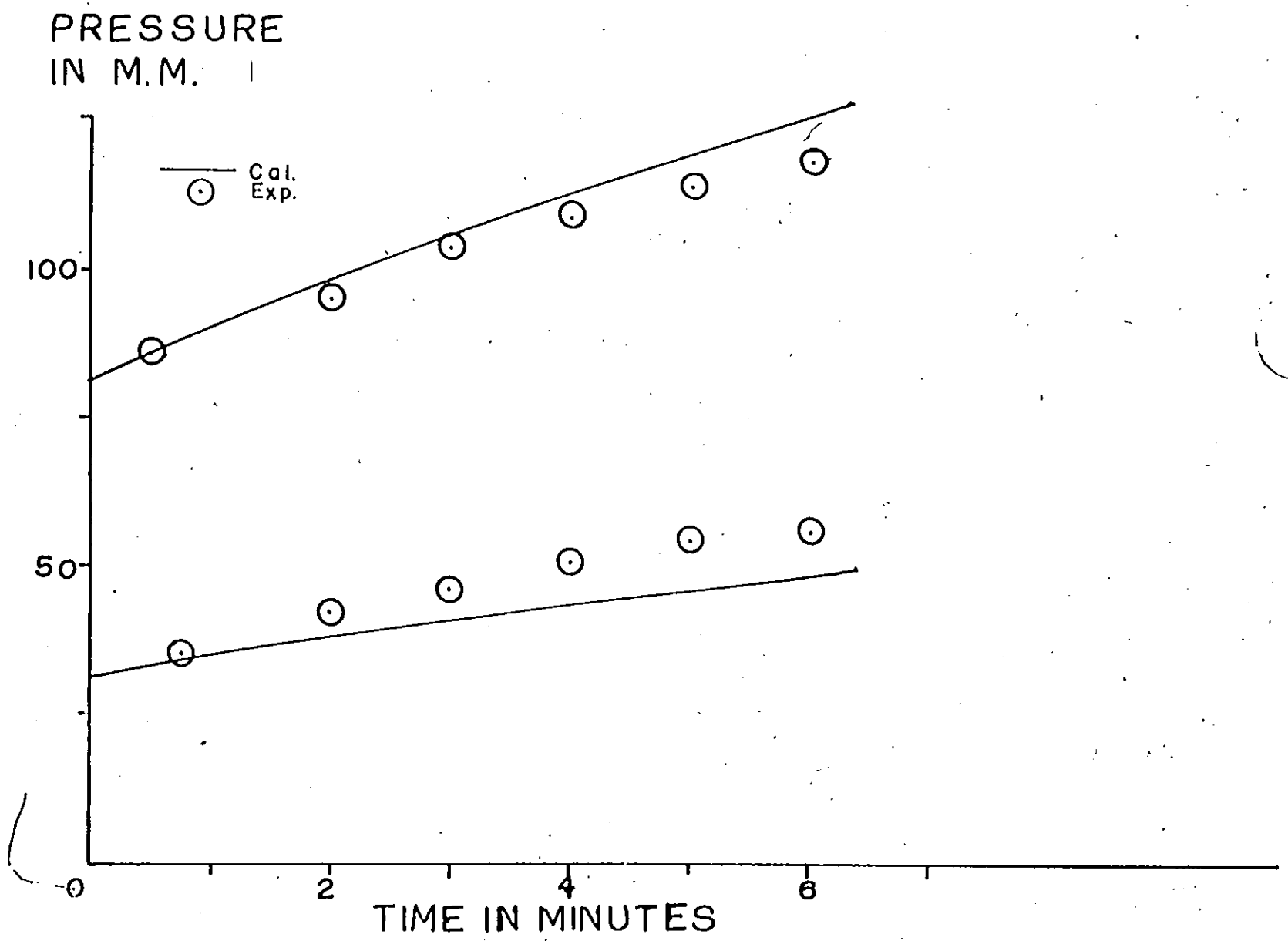


Fig. I 4.c.10. Pressure-Time Plot for the Gas Phase Pyrolysis of exo-2-Norbornyl Chloride at 373.5°C .

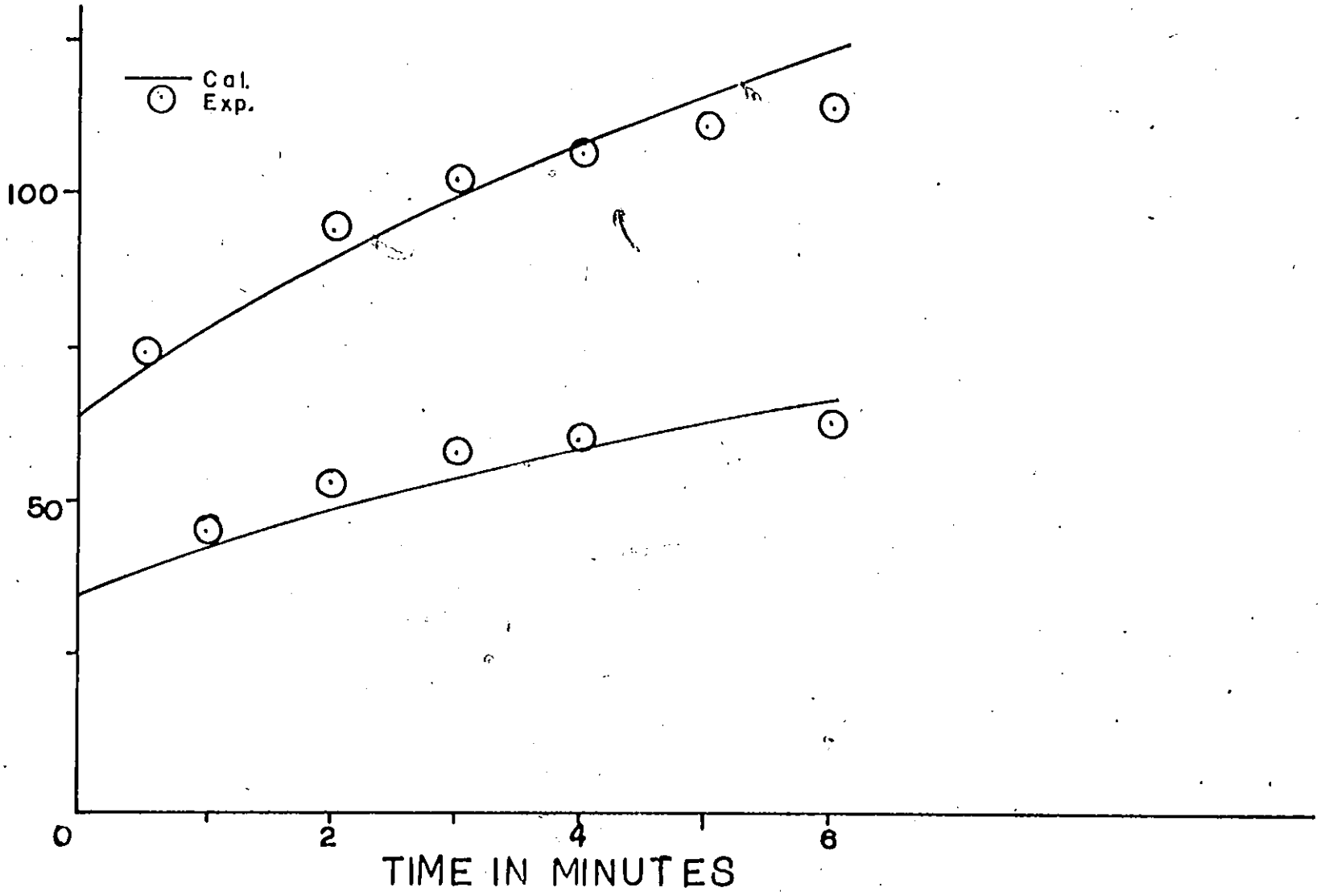


Fig. I 4.c.11. Pressure-Time Plot for the Gas Phase Pyrolysis of exo-2-Norbornyl Chloride at 385.5°C .

chloride titrations. The results are shown in Table I 4.c.2 and are in good agreement with those reported in Table I 4.c.1 for the formation of hydrogen chloride in the unpacked reaction vessel (s/v 1.1:1) thus confirming the absence of a surface reaction.

Table I 4.c.2.

Rate of Formation of Hydrogen Chloride in a Packed Reaction Vessel (s/v ratio 5:1) in the Temperature Range 340-370°C

Temperature 0 °C	Rate Constant for the Formation of Hydrogen Chloride (sec^{-1})
339	1.3×10^{-4}
339.5	1.4×10^{-4}
341	1.9×10^{-4}
366	1.0×10^{-3}

(d) Discussion of Results

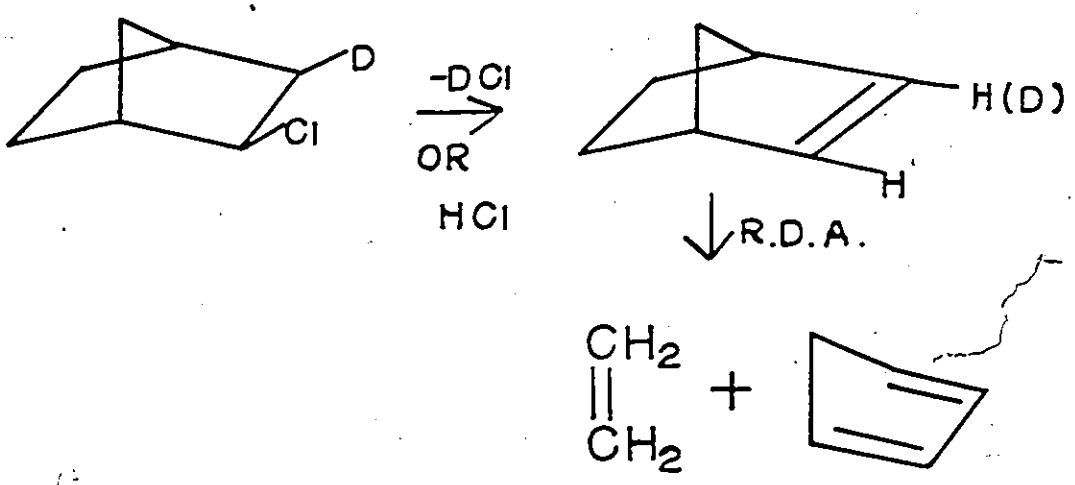
Inspection of the rate plots (see Figs. I 4.c.1 and 3) indicate that all the reactions involved in the gas phase pyrolyses of exo-2-norbornyl chloride are first order and unimolecular, any significant amount of a free radical reaction present would be inhibited by the build up of cyclopentadiene. Thomas and Maccoll[32] showed cyclopentadiene to be an efficient inhibitor but stated that it should not

be used owing to the possibility of dimerisation; this seems an unreasonable statement considering the temperatures involved.

The Arrhenius plots shown in Figs. I 4.c.2,4 and 5 for the formation of hydrogen chloride, cyclopentadiene and nortricyclene are linear also indicating that the reactions are homogeneous and occuring only in the gas phase.

5. Labelling Experiments

The gas phase pyrolysis of exo-2-norbornyl chloride was undertaken in order to determine, quantitatively, whether hydrogen chloride was eliminated by a cis or trans mechanism. This chloride was chosen for its rigid structure which prevents rotation about the C-C bonds and the belief that it formed only one product, norbornene, which rapidly decomposed by a retro Diels-Alder reaction to yield ethylene and cyclopentadiene.



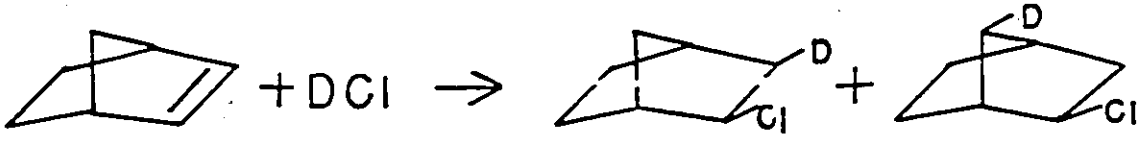
If, for example, the norbornyl chloride was specifically labelled in the exo-3 position (as shown above) then simply by measuring the deuterium content of the cyclopentadiene one can determine the extent of cis or trans elimination in the formation of norbornene. The kinetic experiments however showed that significant quantities of nortricyclene were produced. By using the appropriate labelled chlorides and measuring the deuterium content of the nortricyclene produced it should therefore, also be possible to determine which hydrogen atom(s) are involved in the formation of the nortricyclene.

(a) Preparation of Compounds and Method of Analysis

The pyrolysis products of the labelled compounds (see Part IV of this thesis for methods of preparation) were swept through the g.l.c. column using helium as carrier gas, the separated compounds were then trapped in a U-tube by means of liquid nitrogen, after they leave the column, whilst the helium flowed on over the detector. The helium was then pumped off under vacuum and the samples were transferred to small gas bulbs. These were then attached to the mass spectrometer and the deuterium content of the products determined by comparing the relative abundance of appropriate molecular ion peaks at low eV.

(b) Results and Discussion

It has been observed that when deuterium chloride[79] is added to norbornene two products are obtained as a result of a Wagner-Meerwein reaction, namely exo-2-norbornyl chloride-exo-3-d_1 and exo-2-norbornyl chloride-syn-7-d_1.



In order to determine if a Wagner-Meerwein reaction is taking place during the gas phase pyrolysis, exo-2-norbornyl chloride-3,3-d_2, was prepared by reacting endo-2-norborneol-3,3-d_2 with triphenyl phosphine in excess carbon tetrachloride and the product was analysed for the extent of Wagner-Meerwein reaction and deuterium content. The Wagner-Meerwein analysis is carried out by comparing the relative abundance of the metastable ion peaks for the chloroethyl radical loss to the dideuterated chloroethyl radical loss from the molecular ion, (it has been shown (see page 130 for details) that the chloroethyl radical loss involves the 2 and 3 carbon atoms and their attached hydrogen atoms, with the fourth hydrogen atom coming from the endo-6 position) the results indicated that 11.5% Wagner-Meerwein reaction occurred. The deuterium content of the halide was 92% d_2 and 8% d_1.

The compound was then pyrolysed and the deuterium content of the pyrolysis products determined, the results are shown in Table I 5.1. The theoretical deuterium content of the cyclopentadiene was then calculated (assuming a cis elimination) using the deuterium content and Wagner-Meerwein analysis of the starting material. An isotope effect of 3 was assumed for HCl:DCl relative elimination rates[81,33].

	Position of label in exo-2-norbornyl chloride-3,3-d_2				
	-3,3-d_2,	-7,7-d_2,	exo-3-d_1,	endo-3-d_1,	-7-d_1
% Label	81.5	10.5	3.5	3.5	1.0
Species lost in pyrolysis	DCl	HCl	DCl	HCl	HCl
Predicted % label left in the cyclopentadienes (Isotope effect of 3 used)	27.2-d_1	10.5-d_2	1.2-d_0	3.5-d_1	1.0-d_1

Sum of d_2,d_1 and d_0 cyclopentadienes left:-

d_2	d_1	d_0	
10.5	31.7	3.0	Total = 43.3

Thus the calculated percentages of the labelled cyclopentadiene obtained from the pyrolysis of exo-2-norbornyl chloride-3,3-d_2 are

24% - d_2 73% - d_1 3% - d_0 .

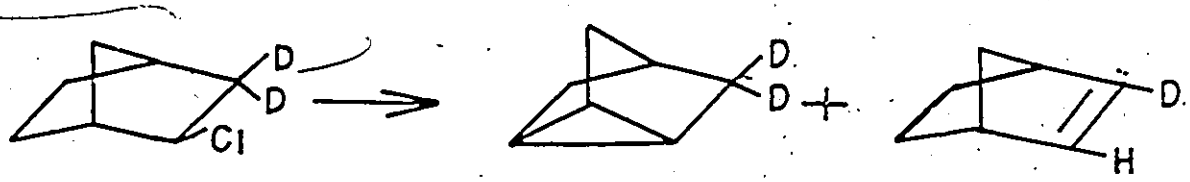
Table I 5.1.

Deuterium Content of the Pyrolysis Products of Various Labelled exo-2-Norbornyl Chlorides

Compound	% Label	% Wagner-Meervein	Pyrolysis Products		% Label	
exo-2-Norbornyl Chloride-3,3-d_2	92% d_2 8% d_1	11.5%	Cyclopentadiene	24% d_2	71% d_1	5% d_o
			Ethylene	0% d_2	2.5% d_1	97.5% d_o
			Nortricyclene	92% d_2	5% d_1	3% d_o
exo-2-Norbornyl Chloride-exo-3-d_1	94% d_1 6% d_o	44%	Cyclopentadiene		62% d_1	38% d_o
			Ethylene		0% d_1	100% d_o
			Nortricyclene		94% d_1	6% d_o
exo-2-Norbornyl Chloride-exo-5-exo-6-d_2	30% d_2 40% d_1 30% d_o	0%	Cyclopentadiene	0% d_2	0% d_1	100% d_o
			Ethylene	31% d_2	40% d_1	29% d_o
			Nortricyclene	28% d_2	41% d_1	31% d_o
exo-2-Norbornyl Chloride-exo-5-exo-6-d_2	72% d_2 22% d_1 6% d_o	15% †	Cyclopentadiene	4% d_2	7% d_1	89% d_o
			Ethylene	63% d_2	24% d_1	13% d_o
			Nortricyclene	57% d_2	34% d_1	10% d_o

† From metastable analysis of the chloride it is clear that at least 5% of the d_2 is in the 2 and 3 positions, which, with the Wagner-Meervein reaction probably means that there is another 5% d_2 in the 1, and 7 positions, which is contributing to the discrepancy in the results.

The good agreement between the above results and the experimental values (see Table I 5.1) indicates that only the hydrogen atoms on the 3 carbon atom are involved in the elimination of hydrogen chloride which yields norbornene, and therefore proving the absence of a Wagner-Meervein reaction in the gas phase pyrolysis. The nortricyclene formed in the above pyrolyses was found to have the same deuterium content as its parent chloride indicating that the hydrogen atoms on the 3 carbon atom were not involved in its formation.



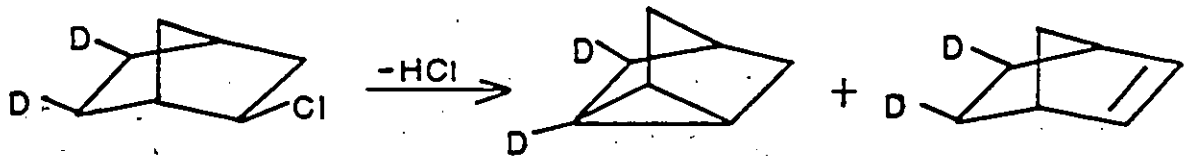
Exo-2-norbornyl chloride, prepared by the addition of deuterium chloride to norbornene (shown by metastable ion analysis* of the chloroethyl radical loss to contain 56% exo-2-norbornyl chloride-exo-3-d_1 and 44% exo-2-norbornyl chloride-syn-7-d_1) was pyrolysed and the deuterium contents of the products were as reported in Table I 5.1. The expected deuterium content of the cyclopentadiene was calculated in exactly the same manner as for the exo-2-norbornyl chloride-3,3-d_2. The calculated result was 65% d_1 and 35% d_o which is in good agreement with the

*Combined with 220 MHz N.M.R. analysis[79] (see also page 279)

experimental result (see Table I 5.1) and is compatible with cis elimination in the formation of norbornene. Again the deuterium content of the nortricyclene was the same as the parent chloride indicating that the hydrogen atoms in the exo-3 and syn-7 positions are not involved in the formation of nortricyclene.

In order to determine whether both the exo and endo 6 hydrogen atoms are involved in the formation of nortricyclene the pyrolysis of exo-2-norbornyl chloride-exo-5-exo-6-d_2 was undertaken and the deuterium contents of the pyrolysis products determined. These are reported in Table I 5.1. The ethylene had the same deuterium content as the parent chloride indicating that the hydrogen atoms on the exo 5 and 6 positions were not involved in the formation of norbornene. Similarly the deuterium content of the nortricyclene was the same as that of the chloride indicating that only the endo-6 hydrogen atom can be involved in the formation of the nortricyclene. This indicates that a trans elimination was involved in this case and again confirms that no Wagner-Meerwein reaction occurs during the pyrolysis (a Wagner-Meerwein reaction would invert the exo and endo hydrogen atoms on the 5 and 6 carbon atoms). This pyrolysis was repeated using a sample of exo-2-norbornyl chloride-exo-5-exo-6-d_2 which was richer in deuterium and these results are also reported in Table I 5.1. They substantiate the

previous results.



Discussion of the Transition State in the Unimolecular Gas Phase Pyrolysis of Alkyl Halides

The kinetic results obtained in this work indicate that exo-2-norbornyl chloride behaves as a typical secondary halide insofar as the elimination activation energy is concerned. Labelling experiments show that in the formation of norbornene, a cis 1,2 elimination is involved while in the formation of nortricyclene an apparent trans 1,3 process is occuring, in neither case is a Wagner-Meerwein reaction observed.

These results place exo-2-norbornyl chloride between alkyl halides (bearing a β hydrogen atom) and isobornyl and bornyl chlorides as follows:

(1) Simple (Unsubstituted) Aliphatic and Monocyclic Halides; Primary, Secondary and Tertiary [89]

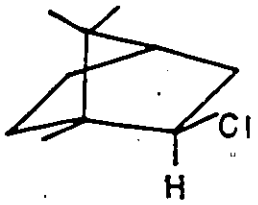
In this group β hydrogen atoms are available and the various products obtained in the case of secondary and tertiary aliphatic halides can be explained by simple

rotation about the carbon-carbon single bond.

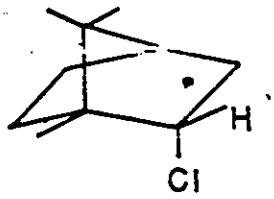
(2) exo-2-Norbornyl Chloride

In this compound β hydrogen atoms are available. However, one of the products obtained, nortricyclene, apparently involves a 1,3 elimination. No Wagner-Meerwein reaction occurs during the pyrolysis.

(3) Isobornyl and Bornyl Chlorides[35]



ISOBORNYL CHLORIDE



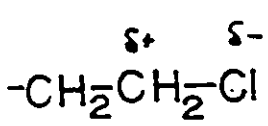
BORNYL CHLORIDE

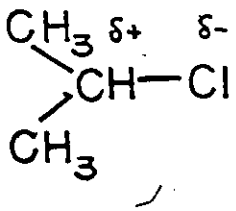
These reactants also contain β hydrogen atoms; products requiring a 1,2 elimination, a 1,3 elimination and a Wagner-Meerwein reaction are observed.

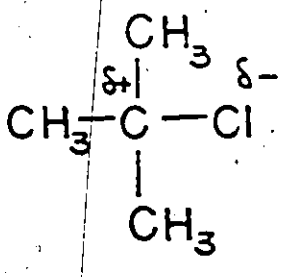
(4) Neopentyl Chloride

This compound has no β hydrogen atoms, a Wagner-Meerwein reaction is believed to take place[15a] but the unusually complex mechanism invoked for this pyrolysis (a mixed free radical chain and molecular process) makes this conclusion uncertain.

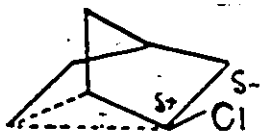
In the case of the simple aliphatic and monocyclic halides the (partial) positive charge is already on the preferred site and there is no other equivalent site in the molecule.

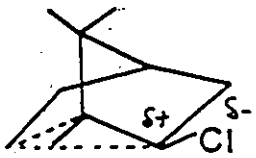


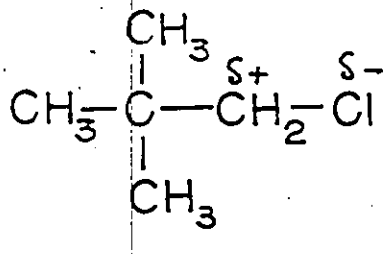




Considering the 1,2 Eliminations in Norbornyl Chloride, Isobornyl (and Bornyl) Chloride and Neopentyl Chloride. (This argument is presented in terms of non-classical carbonium ions, a similar scheme can be drawn up using classical carbonium ions).







In each of the above molecules there are two possible locations for the (partial) positive charge. For norbornyl chloride the sites (1 and 2 carbon atoms) are equivalent and because of this the presence of the chlorine may be sufficient to prevent migration of the charge, explaining the absence of the Wagner-Meerwein products. In the case of isobornyl (and bornyl) chloride the 1 carbon atom (which is tertiary) is preferred over the 2 carbon atom (which is secondary) for the site of the (partial)

positive charge, similarly for neopentyl chloride the preferred site of the charge is the 2 carbon atom, assuming that the proposed methyl migration[15a] takes place. (In the case of isobornyl (and bornyl) chloride and neopentyl chloride the "chloride could be said to follow the positive charge".)

In the next step, the 1,2 elimination of the halogen acid occurs from the rearranged and unrearranged molecules, provided β hydrogen atoms are available. Thus (1) for norbornyl chloride (no migration of the (partial) positive charge) where β hydrogen atoms are available, the elimination proceeds to yield norbornene, (2) for isobornyl (and bornyl) chloride where β hydrogen atoms are available at both possible locations of the positive charge (1 and 2 carbon atoms) the elimination yields both rearranged and unrearranged products, (3) for neopentyl chloride there are only β hydrogen atoms available at the preferred site of the charge, the 2 carbon atom, and thus only rearranged products are obtained in the elimination.

The activation energies for the eliminations are typical for secondary chlorides in the case of norbornyl chloride, and isobornyl (bornyl) chloride; this is reasonable when one considers that the secondary chloride transition state must be formed first before any rearrangement can occur.

Considering the 1,3 Elimination in Norbornyl Chloride and Isobornyl (and Bornyl) Chloride.

The products obtained from this elimination are probably derived from a transition state involving a slightly more polarised carbon-halogen bond relative to that in the case of the 1,2 elimination (the difference may not be large, due to the geometry of the molecules). This difference is exemplified in the case of norbornyl chloride where the rate of formation of nortricyclene (1,3 elimination product) is half that of norbornene (1,2 elimination product). There is no similar kinetic information available in the case of isobornyl and bornyl chlorides.

APPENDIX

Kinetic Data for the Formation of Hydrogen Chloride in the Gas Phase Pyrolysis of exo-2-Norbornyl Chloride

Temperature Range 300 - 370 °C

Unpacked Reaction Vessel.

Temperature 296°C.

Time (min.)	Norbornyl Chloride Pressure (cm of Hg)	(moles) x 10^{-6}	Hydrogen Chloride (moles) x 10^{-6}	log a/(a-x)
15	2.20	105.0	2.20	0.0090
30	2.20	105.0	4.25	0.0174
45	2.20	105.0	5.80	0.0249
60	2.20	105.0	7.10	0.0311
75	2.20	105.0	7.90	0.0338
90	2.20	105.0	8.30	0.0367

Rate Constant 6.3×10^{-6} sec^{-1}

Temperature 310°C.

Time (min.)	Norbornyl Chloride Pressure (cm of Hg)	(moles) x 10^{-6}	Hydrogen Chloride (moles) x 10^{-6}	log a/(a-x)
7.5	5.10	231.7	2.2	0.0042
15	5.70	258.7	8.9	0.0152
22.5	4.50	204.4	3.9	0.0083
30	4.00	181.7	5.2	0.0126
37.5	4.45	202.3	6.4	0.0140
45	4.75	215.8	8.1	0.0167

Rate Constant 1.51×10^{-5} sec^{-1}

Temperature 322°C.

Time (min.)	Norbornyl Chloride Pressure (cm of Hg)	(moles) x 10^{-6}	Hydrogen Chloride (moles) x 10^{-6}	log a/(a-x)
5	2.30	104.0	0.7	0.0029
15	2.15	97.4	2.0	0.0090
20	2.75	124.5	5.0	0.0178
30	3.00	136.0	7.0	0.0229
37.5	2.50	113.0	9.0	0.0360
45	3.00	136.0	10.5	0.0349

Rate Constant 3.3×10^{-5} sec^{-1}

Temperature 330°C.

Time (min.)	Norbornyl Chloride Pressure (cm of Hg)	Norbornyl Chloride (moles) $\times 10^{-6}$	Hydrogen Chloride (moles) $\times 10^{-6}$	log a/(a-x)
5	5.45	239.5	2.4	0.0044
10	4.85	213.1	6.8	0.0141
15	5.45	239.1	13.1	0.0244
20	5.45	239.1	14.4	0.0269
25	5.00	219.7	20.5	0.0425
30	4.90	215.0	23.6	0.0505
35	3.95	173.6	22.6	0.0603
40	3.70	162.6	26.5	0.0771
45	4.50	197.8	34.9	0.0843
45	4.15	182.2	30.9	0.0807
50	3.50	153.6	29.6	0.0926
55	3.70	162.3	34.7	0.1045
55	3.95	173.3	35.8	0.1005
60	5.45	239.1	58.2	0.1211
60	3.65	160.4	35.9	0.1101

Rate Constant 7.1×10^{-5} sec^{-1}

Temperature 335°C.

Time (min.)	Norbornyl Chloride Pressure (cm of Hg)	Norbornyl Chloride (moles) $\times 10^{-6}$	Hydrogen Chloride (moles) $\times 10^{-6}$	log a/(a-x)
5	1.40	62.0	2.0	0.0142
10	2.95	130.6	9.0	0.0310
15	2.00	88.5	8.5	0.0438
20	1.55	68.6	9.0	0.0610
25	2.15	95.2	17.0	0.0854
30	2.40	106.4	23.0	0.1058

Rate Constant 1.2×10^{-4} sec^{-1}

Temperature 338°C.

Time (min.)	Norbornyl Chloride Pressure (cm of Hg)	Norbornyl Chloride (moles) x 10^{-6}	Hydrogen Chloride (moles) x 10^{-6}	log a/(a-x)
10	2.30	145.4	17.6	0.0557
15	3.55	156.8	26.7	0.0810
20	2.15	94.4	20.4	0.1064
25	2.85	125.8	35.7	0.1364
30	3.15	138.7	42.7	0.1584

Rate Constant 1.1×10^{-4} sec^{-1}

Temperature 341.5°C.

Time (min.)	Norbornyl Chloride Pressure (cm of Hg)	Norbornyl Chloride (moles) x 10^{-6}	Hydrogen Chloride (moles) x 10^{-6}	log a/(a-x)
2.5	2.05	89.7	2.7	0.0133
5.0	2.25	98.4	6.0	0.0273
7.5	2.05	89.7	8.2	0.0416
10.0	2.05	89.7	9.6	0.0492
12.5	1.95	85.3	11.0	0.0600
15.0	1.85	80.9	14.1	0.0832
17.5	1.50	65.6	8.6	0.0587
20.0	1.95	85.3	15.1	0.0846
25.0	1.15	50.3	10.6	0.1028

Rate Constant 1.8×10^{-4} sec^{-1}

Temperature 346°C.

Time (min.)	Norbornyl Chloride Pressure (cm of Hg)	Norbornyl Chloride (moles) x 10^{-6}	Hydrogen Chloride (moles) x 10^{-6}	log a/(a-x)
5	3.10	134.9	8.0	0.0266
10	4.45	193.7	17.5	0.0411
15	5.50	239.4	33.8	0.0661
20	4.20	182.7	32.0	0.0836
25	6.15	267.7	58.2	0.1065
30	2.55	111.0	28.5	0.1288

Rate Constant 1.6×10^{-4} sec^{-1}

Temperature 346.5°C.

Time (min.)	Norbornyl Chloride Pressure (cm of Hg)	Norbornyl Chloride (moles) x 10^{-6}	Hydrogen Chloride (moles) x 10^{-6}	log a/(a-x)
5	2.35	102.5	4.0	0.0173
10	2.35	102.5	12.0	0.0541
15	1.80	78.5	13.0	0.0786
20	2.00	81.0	17.7	0.1071
25	2.10	91.5	22.4	0.1227
30	1.55	67.5	19.3	0.1463

Rate Constant 2.1×10^{-4} sec^{-1}

Temperature 350°C.

Time (min.)	Norbornyl Chloride Pressure (cm of Hg)	Norbornyl Chloride (moles) x 10^{-6}	Hydrogen Chloride (moles) x 10^{-6}	log a/(a-x)
5	5.45	237.6	17.3	0.0337
10	4.85	206.1	25.7	0.0579
15	4.90	208.2	35.4	0.0808
20	3.45	146.8	36.2	0.1229
25	5.05	214.9	62.4	0.1489
30	4.65	197.6	70.5	0.1916

Rate Constant 2.3×10^{-4} sec^{-1}

Temperature 352°C.

Time (min.)	Norbornyl Chloride Pressure (cm of Hg)	Norbornyl Chloride (moles) x 10^{-6}	Hydrogen Chloride (moles) x 10^{-6}	log a/(a-x)
2.5	1.85	79.7	6.1	0.0346
5.0	2.45	105.8	14.3	0.0630
7.5	1.50	64.6	11.8	0.0875
10.0	1.80	77.6	17.1	0.1081
12.5	1.70	73.1	18.9	0.1299
15.0	1.50	64.6	18.1	0.1427

Rate Constant 2.9×10^{-4} sec^{-1}

Temperature 360°C.

Time (min.)	Norbornyl Chloride Pressure (cm of Hg)	Norbornyl Chloride (moles) $\times 10^{-8}$	Hydrogen Chloride (moles) $\times 10^{-6}$	log a/(a-x)
10	2.25	95.6	28.1	0.1514
15	4.90	209.5	89.2	0.2409
20	3.10	132.1	54.8	0.2327
25	2.20	93.6	49.8	0.3298
30	2.75	116.9	70.8	0.4041

Rate Constant 5.2×10^{-4} sec^{-1}

Temperature 370°C.

Time (min.)	Norbornyl Chloride Pressure (cm of Hg)	Norbornyl Chloride (moles) $\times 10^{-8}$	Hydrogen Chloride (moles) $\times 10^{-6}$	log a/(a-x)
2.5	4.70	194.8	20.2	0.0477
5	4.15	172.0	35.9	0.1014
7.5	4.75	196.3	51.3	0.1015
10	6.15	254.5	96.2	0.2059
10	4.25	175.5	55.1	0.1636
12.5	4.25	175.3	71.9	0.2294
15	3.90	161.6	73.2	0.2620
20	4.20	174.2	93.1	0.3311
30	2.60	107.8	69.0	0.4438

Rate Constant 7.0×10^{-4} sec^{-1}

Kinetic Data for the Formation of Hydrogen Chloride in the Gas Phase Pyrolysis of exo-2-Norbornyl Chloride

Temperature Range 335 - 370 °C

Packed Reaction Vessel.

Temperature 339°C.

Time (min.)	Norbornyl Chloride Pressure (cm of Hg)	Norbornyl Chloride (moles) x 10^{-8}	Hydrogen Chloride (moles) x 10^{-8}	log a/(a-x)
5	2.30	89.2	1.0	0.0049
10	2.60	100.8	6.0	0.0266
15	2.50	97.0	10.0	0.0472
20	2.15	83.4	11.3	0.0632
25	2.15	83.4	16.5	0.0958
30	2.50	97.0	21.5	0.1088

Rate Constant 1.3×10^{-4} sec^{-1}

Temperature 339.5°C.

Time (min.)	Norbornyl Chloride Pressure (cm of Hg)	Norbornyl Chloride (moles) x 10^{-6}	Hydrogen Chloride (moles) x 10^{-6}	log a/(a-x)
10	3.15	122.0	8.7	0.0327
15	3.50	135.6	15.5	0.0464
21	3.30	127.9	24.4	0.0989
25	3.20	124.0	21.0	0.0812
30	2.50	116.0	28.6	0.0123

Rate Constant 1.4×10^{-4} sec^{-1}

Temperature 341°C.

Time (min.)	Norbornyl Chloride Pressure (cm of Hg)	Norbornyl Chloride (moles) x 10^{-6}	Hydrogen Chloride (moles) x 10^{-6}	log a/(a-x)
5	4.00	155.0	5.5	0.0154
10	3.95	152.5	16.8	0.0508
15	4.30	166.5	28.8	0.0795
20	3.90	149.5	31.5	0.1021
30	2.80	108.0	30.9	0.1464

Rate Constant 1.9×10^{-4} sec^{-1}

Temperature 366°C.

Time (min.)	Norbornyl Chloride Pressure (cm of Hg)	Norbornyl Chloride (moles) x 10^{-6}	Hydrogen Chloride (moles) x 10^{-6}	log a/(a-x)
5	3.35	124.4	34.1	0.1391
10	3.55	131.9	65.8	0.3001
15	3.55	131.9	77.4	0.3839
30	2.90	107.7	82.9	0.6378

Rate Constant 1.0×10^{-3} sec^{-1}

Kinetic Data for the Formation of Cyclopentadiene in the Gas Phase Pyrolysis of exo-2-Norbornyl Chloride

Temperature Range. 300 - 370 °C

Unpacked Reaction Vessel.

Temperature 310°C.

Time (min.)	Norbornyl Chloride Pressure (cm of Hg)	Norbornyl Chloride (moles) x 10^{-6}	Cyclopentadiene (moles) x 10^{-6}	log a/(a-x)
30	4.60	208.8	3.6	0.0075
30	3.60	163.4	2.8	0.0074
45	3.80	172.3	4.7	0.0121
60	2.95	134.1	5.2	0.0170
60	3.05	138.6	5.2	0.0168
90	2.40	109.2	5.7	0.0231
120	3.45	156.7	10.9	0.0312

Rate Constant 1.0×10^{-5} sec^{-1}

Temperature 330°C.

Time (min.)	Norbornyl Chloride Pressure (cm of Hg)	Norbornyl Chloride (moles) x 10^{-6}	Cyclopentadiene (moles) x 10^{-6}	log a/(a-x)
10	5.40	237.1	5.7	0.0106
15	5.50	241.5	8.8	0.0145
20	4.50	197.5	9.3	0.0210
25	4.05	178.1	12.2	0.0314
30	4.60	202.0	16.4	0.0378
30	4.10	180.2	16.1	0.0407
35	4.75	208.8	21.8	0.0479
40	4.45	195.6	22.4	0.0528
45	4.20	184.6	23.1	0.0581
50	4.35	191.0	25.2	0.0614
55	4.45	195.6	26.7	0.0637
60	4.75	208.6	32.4	0.0730
65	4.45	195.6	33.6	0.0818

Rate Constant 4.7×10^{-5} sec^{-1}

Temperature 350°C.

Time (min.)	Norbornyl Chloride Pressure (cm of Hg)	Norbornyl Chloride (moles) x 10^{-6}	Cyclopentadiene (moles) x 10^{-6}	log a/(a-x)
5	4.85	206.4	6.0	0.0128
5	6.65	283.0	11.8	0.0185
10	5.50	233.7	24.2	0.0475
10	4.00	170.1	18.5	0.0500
15	3.95	168.1	20.8	0.0573
15	4.00	170.2	18.4	0.0497
20	5.10	217.1	33.3	0.0723
25	4.55	193.5	37.4	0.0936
25	3.80	161.9	24.8	0.0726
30	4.75	201.8	45.2	0.1101
35	3.95	167.9	39.6	0.1168
40	3.80	161.6	40.3	0.1246

Rate Constant 1.4×10^{-4} sec^{-1}

Temperature 370°C.

Time (min.)	Norbornyl Chloride Pressure (cm of Hg)	Norbornyl Chloride (moles) x 10^{-6}	Cyclopentadiene (moles) x 10^{-6}	log a/(a-x)
2	4.20	173.0	14.3	0.0378
3	5.00	206.5	18.5	0.0369
4	4.65	191.8	23.6	0.0570
5	4.95	204.1	25.4	0.0577
6	6.05	249.8	35.7	0.0669
7	5.40	222.8	35.5	0.0755
8	4.90	202.2	37.8	0.0899
9	4.35	179.5	31.7	0.0844
10	3.90	160.9	31.9	0.0960
12	4.15	171.5	39.0	0.1121
14	2.20	90.8	23.1	0.1275
16	2.80	115.5	28.7	0.1240

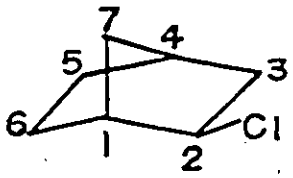
Rate Constant 4.5×10^{-4} sec^{-1}

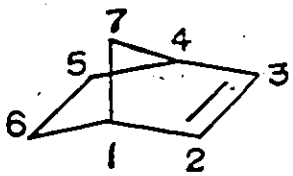
PART II

MASS SPECTRAL STUDIES OF SOME NORBORNYL COMPOUNDS

OBJECT OF THE INVESTIGATION

The initial object of the mass spectral investigation was to determine the fragmentation mechanism of exo-2-norbornyl chloride (exo-2-chloro-bicyclo(2,2,1)heptane) and norbornene (bicyclo(2,2,1)hept-2-ene); in order to help locate the position and amount of deuterium in the reactants and products of the gas phase pyrolysis of exo-2-norbornyl chloride.





In the course of the investigation of the mass spectral fragmentation of exo-2-norbornyl chloride a new technique was developed, namely the use of the relative intensities of the metastable ion peaks, for a particular fragmentation in the labelled compounds, to deduce the fragmentation mechanism. This technique was also used in the investigation of the fragmentation mechanisms of the norbornene nortricyclene (tricyclo(1,1,2.6,0)heptane) and norborneol (bicyclo(2,2,1)heptanol) molecules. The metastable ion studies were combined with accurate determinations of appearance potentials. In order to help determine which of the fragmentations arose from the bicyclic structure

(bicyclo(2,2,1)heptane) and which resulted from the effect of the substituents, the mass spectral fragmentation mechanism of norbornane was investigated.

INTRODUCTION

Material in this section will consist only of a general discussion of principles, of use of apparatus and interpretation of results. Detailed considerations of many phenomena will appear in discussion of the present results.

(a) General Discussion of Mass Spectrometry

(1) The main direction of research by the organic chemist in the field of mass spectrometry, has been towards obtaining a set of rules whereby a compound can be identified and its molecular structure deduced by inspection of the mass spectrum. The mass spectrometer has been used by the physical chemist as a means of measuring heats of formation of ions, bond dissociation energies and other energetic information, but advances in this field have been restricted until recently by the lack of electron impact ion sources in which a monoenergetic electron beam can be produced. Attempts by theoretical chemists to predict the fragmentation mechanisms of molecules by the quasi-equilibrium theory [35]. have been successful in the case of some small molecules, but the

agreement between theory and experiment declines with increase in molecular size and the presence of a hetero-atom.

The above paragraph briefly outlines the direction of research in the field of organic mass spectrometry to the present day. Although a great deal of information has been obtained in the form of catalogues of spectra of organic molecules [36] and tables of ionisation and appearance potentials [37], the interpretation of mass spectra still owes much to empirical rules.

(2) Brief Outline of Processes and Instrumentation in Mass Spectrometry [38, 39a]

The material under investigation is passed into the ion chamber of the mass spectrometer (the instrument being under high vacuum, see Fig. II(a) 2.1.) in the form of a vapour or gas. The molecules in the ion chamber are bombarded

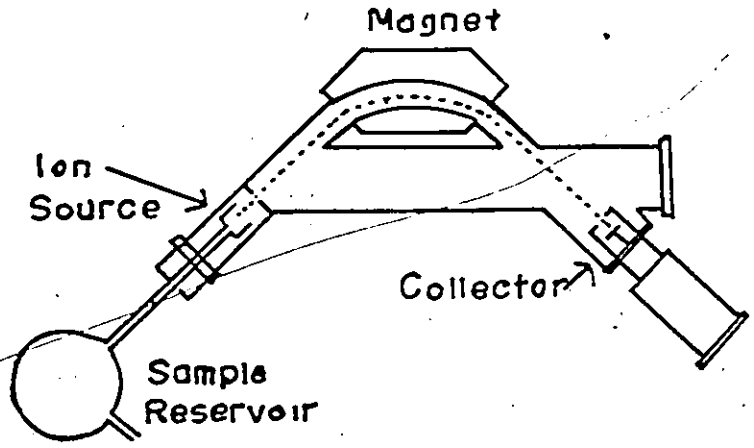


Fig. II(a) 2.1. Single Focusing Mass Spectrometer.

by a stream of electrons having 70eV. energy. When an electron passes close enough to a molecule an electron is expelled therefrom yielding a molecular ion.

$$M + e = M^{+} + 2e$$

Molecular Ion

70eV. is approximately equivalent to 1,600 K cal mole^{-1} A:B = A$^{\cdot}$ + B$^{\cdot}$ Homolytic Bond Fission requires 50-120 k cal mole^{-1} [40] A:B = A:$^{-}$ + B^{+} Heterolytic Bond Fission requires 150-250 k cal mole^{-1} [40]. Thus there is sufficient excess energy in many of the molecular ions for them to undergo fragmentations by many different processes. The molecular ion fragments either (a) by the loss of a radical to yield an even electron ion, or (b) by the loss of a neutral molecule giving an odd electron ion

(a) $(A\text{-}B)^{+\cdot} = A^{+} + B^{\cdot}$ or $A^{\cdot} + B^{+}$

(b) $(A\text{-}B)^{+\cdot} = A^{+\cdot} + B$

The molecular and fragment ions are pushed towards the exit slit by repeller plates, where they are accelerated by a large potential drop (2-8 k V) into the field free region and on into the curved analyser tube where a magnetic field is applied at right angles to the flight path. Ions of low mass are deflected by a greater amount than ions of higher mass by

the imposed magnetic field. By varying the strength of the magnetic field it is possible to sweep the spectrum of ions over the collector slit and determine the relative abundances of each ionic species present in the spectrum. The spectrum is generally presented in the form of a bar graph (see Fig. II(a) 2.2) or table (see Table II(a) 2.1) with the relative intensities of the ion peaks expressed as a percentage of the most intense peak (base peak).

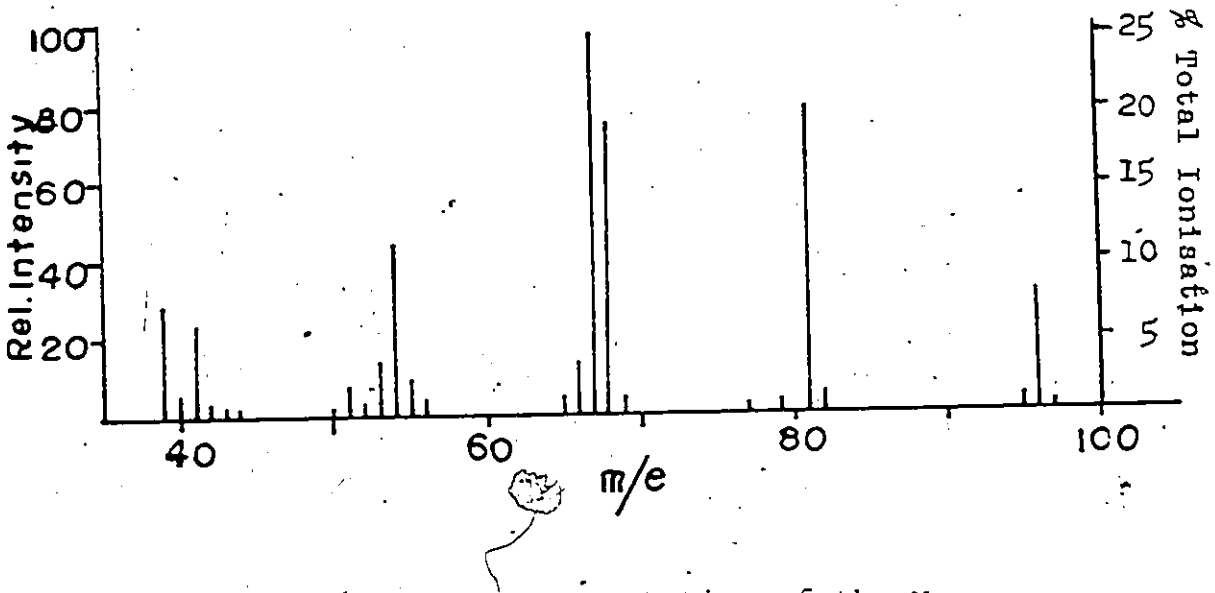


Fig. II(a) 2.2. Bar Graph Representation of the Mass Spectrum of Norbornane.

Table II(a) 2.1

List of Relative Intensities of Ion Peaks in Norbornane Expressed as a Percentage of the Most Intense Peak (Base Peak).

M/e	RI	M/e	RI	M/e	RI
39	29	53	14	69	5
40	6	54	44	77	3
41	23	55	9	79	4
42	4	56	2	81	80
43	3	65	5	82	6
44	3	66	14	95	5
51	4	67	100	96	31
52	2	68	76	97	2

(b) Production and Study of Ions

(1) Formation of Ions in the Mass Spectrometer (See Fig. II(b) 1.1.)[41a]

Ions are generally produced by bombarding the molecules with a stream of electrons. The electrons are emitted from a hot wire filament and repelled across the ion chamber by means of a small potential negative, with respect to the ion chamber, to a positive target. The electrons follow a spiral path which is induced by a small external magnet; this is to increase the residence time of the electrons in the source. The molecular and fragment ions are repelled towards the exit slit by one

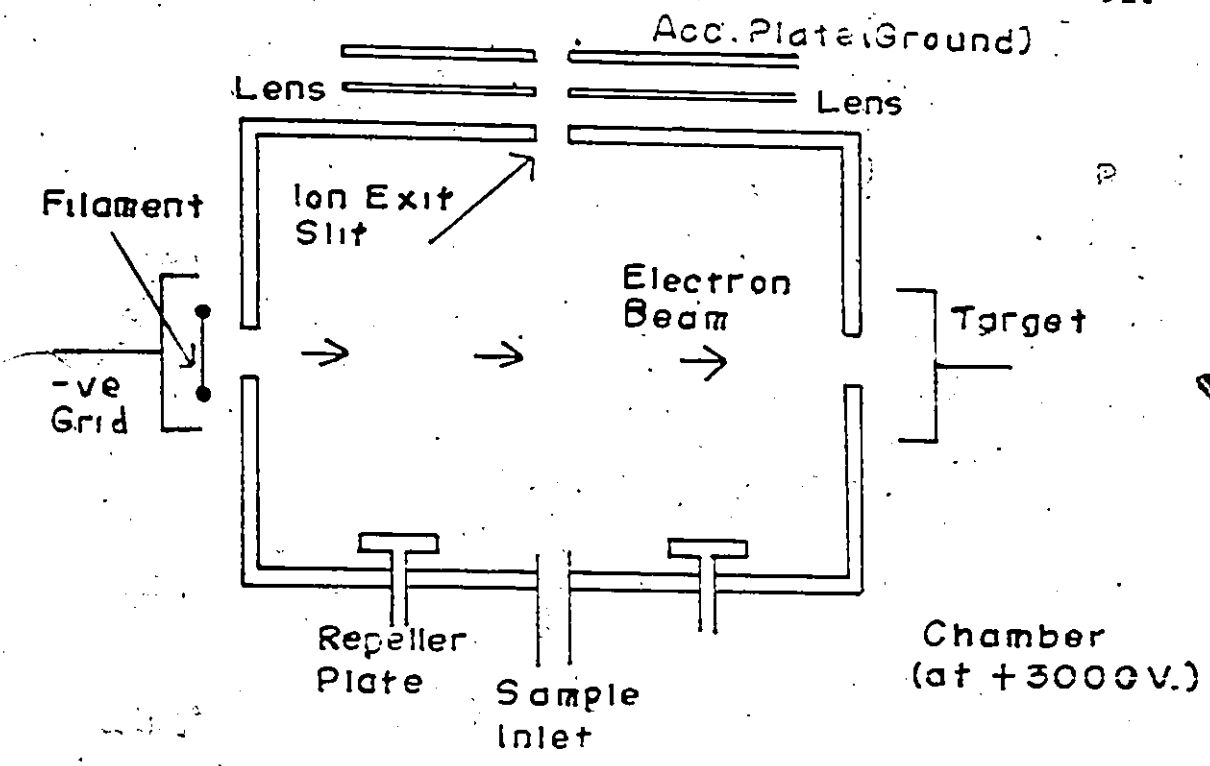


Fig. II(b) 1.1. Schematic of Ion Chamber.

or two repeller plates at a small positive potential relative to the ion chamber. By varying the potential on the repeller plates it is possible to focus the ions on the source exit slit. The resulting ion beam is then collimated by means of two electrostatic lenses prior to acceleration into the field free region. The period of time the electron is in the vicinity of the molecule is considerably less than one vibration and therefore the excitation must be of the Franck-Condon Type[41b]. In Fig. II(b) 1.2 (a) the molecular ion (M^+) is stable in the ionisation potential region therefore a molecular ion peak should be observed; (b) at the ionisation potential mixed processes will be present

(M^{+}, A^{+} and $B^{\cdot}$), the molecular ion peak will be present but it will not be the base peak (the most intense peak in the spectrum); (c) the molecular ion (M^{+}) is unstable at its ionisation potential and will not be observed, only ion A^{+} and the neutral molecule $B^{\cdot}$ will exist, both in an excited state.

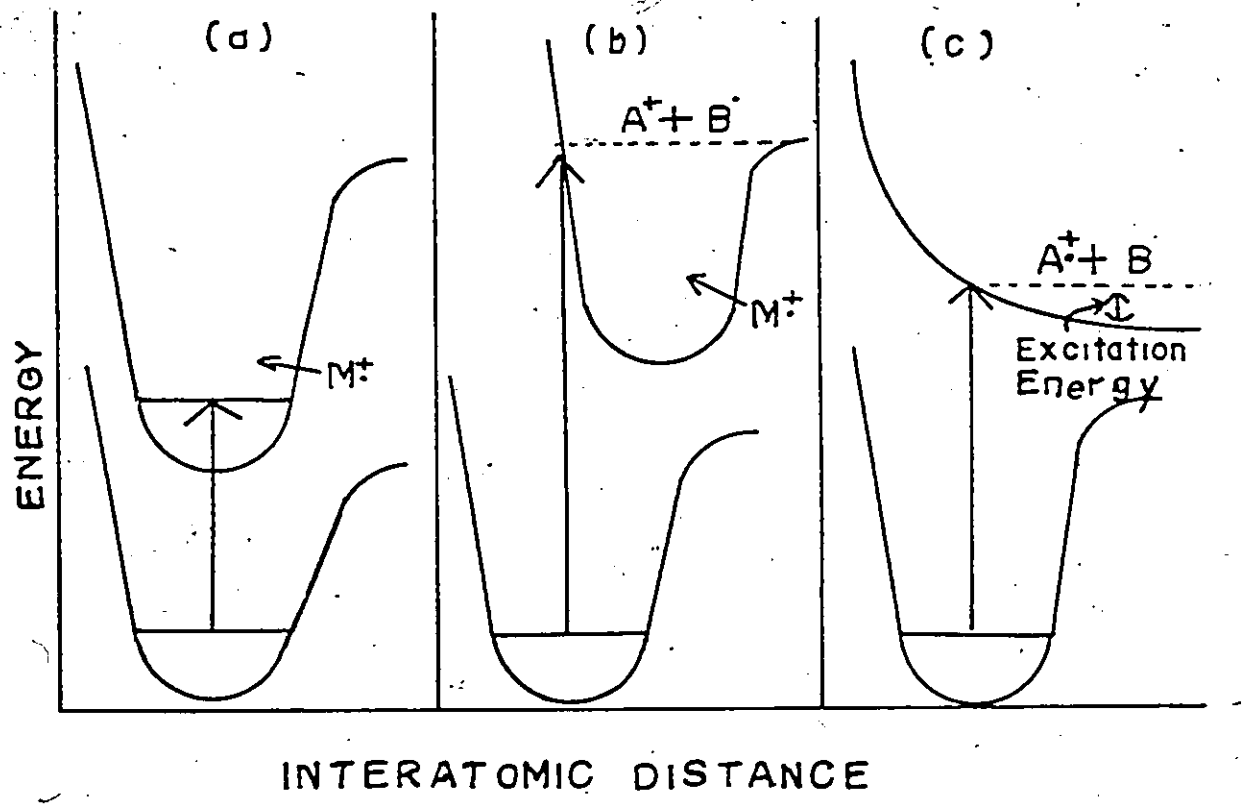


Fig. II(b) 1.2. Franck-Condon Diagrams.

(2) Focusing and Resolution of Ions

(2.1) Magnetic or Direction Focusing.[41c] (Fig. II(b) 2.1.1)

After acceleration all ions with the same charge have the same kinetic energy which is given by the expression

$eV = (1/2)mv^2$ (ergs) ..... (1) where e = charge (esu)
V = acceleration potential (erg/esu)
m = mass (g)
v = velocity (cm/sec)

The magnetic field is at right angles to the flight path, this results in a sideways force being applied to the ions, this force is given by the expression

Force from Magnetic Field $= \frac{Hev}{C}$ (dynes) where H = magnetic field strength (oersted)
e = charge (esu)
v = velocity of the ions (cm/sec)
C = velocity of light (cm/sec)

This force will be balanced by the centrifugal force acting on the ions

Centrifugal force = $\frac{mv^2}{r}$ where m = mass (g)

v = velocity of the ions (cm/sec)

r = radius of curvature of flight path (cm)

On combining the expressions for the two opposing forces the resulting expression is obtained

$$\frac{mv^2}{r} = \frac{Hev}{C}$$

which on rearrangement gives

$$v^2 = \frac{H^2e^2r^2}{m^2}$$

Substitution for v^2 in (1) gives

$$\frac{m}{e} = \frac{H^2r^2}{2VC^2}$$

where m = mass (g)

H = magnetic field strength (gauss)

V = potential drop (volts)

e = number of electronic charges

$$\frac{m}{e} = \frac{kH^2}{V} \quad \ldots\ldots\ldots (2)$$

where $k = \frac{r^2}{2C^2}$

From the expression it can be observed that to achieve focusing of an ion of a particular m/e value at the collector slit, one can either vary the magnetic field strength or the acceleration potential. In practice the magnetic field strength is generally scanned at a fixed acceleration potential.

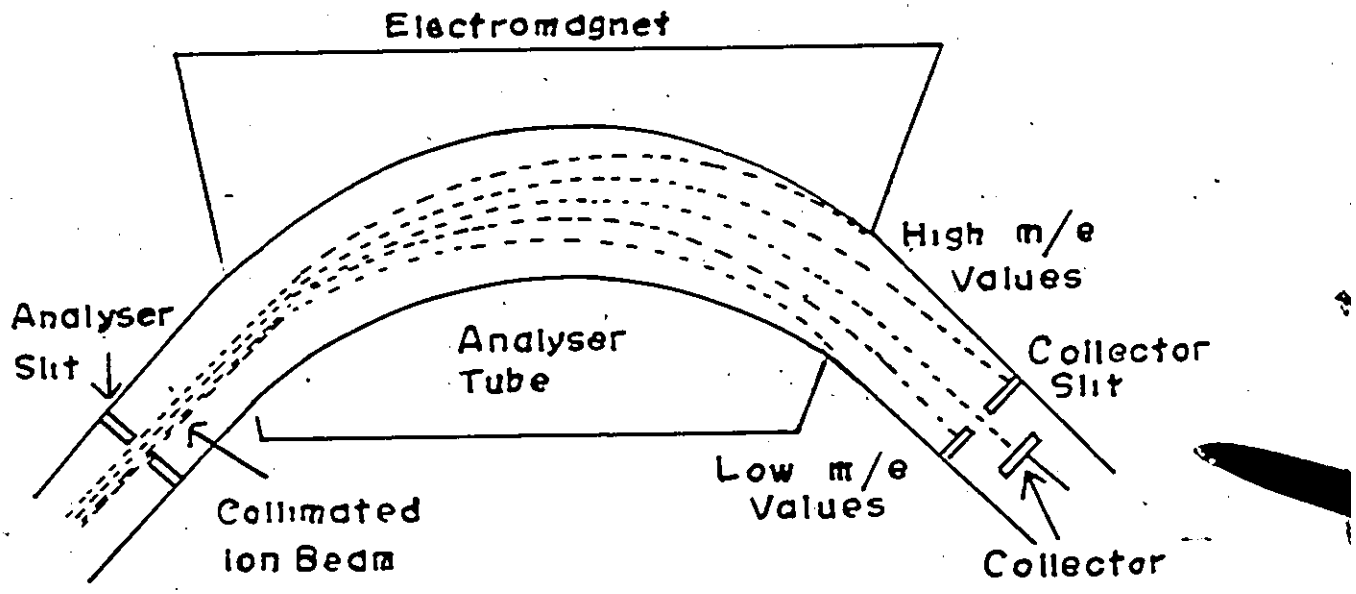


Fig. II(b) 2.1.1 Analyser Tube

(2.2) Velocity or Energetic Ion Focusing [41d]

(Fig. II(b) 2.2.1)

Ions are not formed at one point in the ion chamber and as a result those ions closer to and travelling towards the exit slit will have slightly higher post-acceleration velocities than those further away or travelling

away from the exit slit. This results in the ion beam having a small energy spread approximately representative of thermal translational energies (the mean value being $eV = (1/2)m_x V_x^2$ which depends on the average acceleration potential experienced by the ions). Energy focusing is achieved by passing the ion beam between two curved plates under an electrostatic potential. The radius of curvature of the electrostatic field is given by

$$r_e = \frac{2V}{F}$$

where r_e = radius of electrostatic field (cm)

F = electrostatic field (esu-volts/cm)

V = acceleration potential (esu)

N.B. mass is not a factor of energy focusing

By varying the electrostatic field the radius of curvature of a beam of ions of a particular energy can be adjusted so that the beam passes through the exit slit of the electrostatic analyser to yield a monoenergetic beam of ions. Energy focusing is used in double focusing mass spectrometers to enable high resolution of ion peaks.

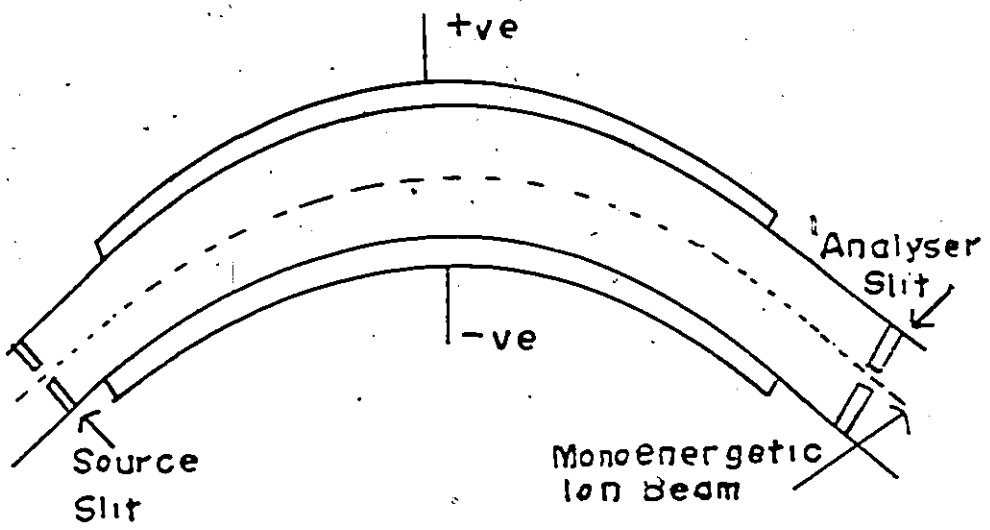


Fig. II(b) 2.2.1 Sector Analyser

(2.3) Double Focusing

Using magnetic focusing it is possible easily to separate ions of approximately integral mass. However, the mass of isotopes are not integral (based on $^{12}C=12.0000$). For example N_2, CO and C_2H_4 have the same nominal mass of 28 u. , but their absolute masses are different. The exact masses can be determined by combining energetic and magnetic focusing giving the double focusing mass spectrometer (Fig. II (b) 2.3.1).

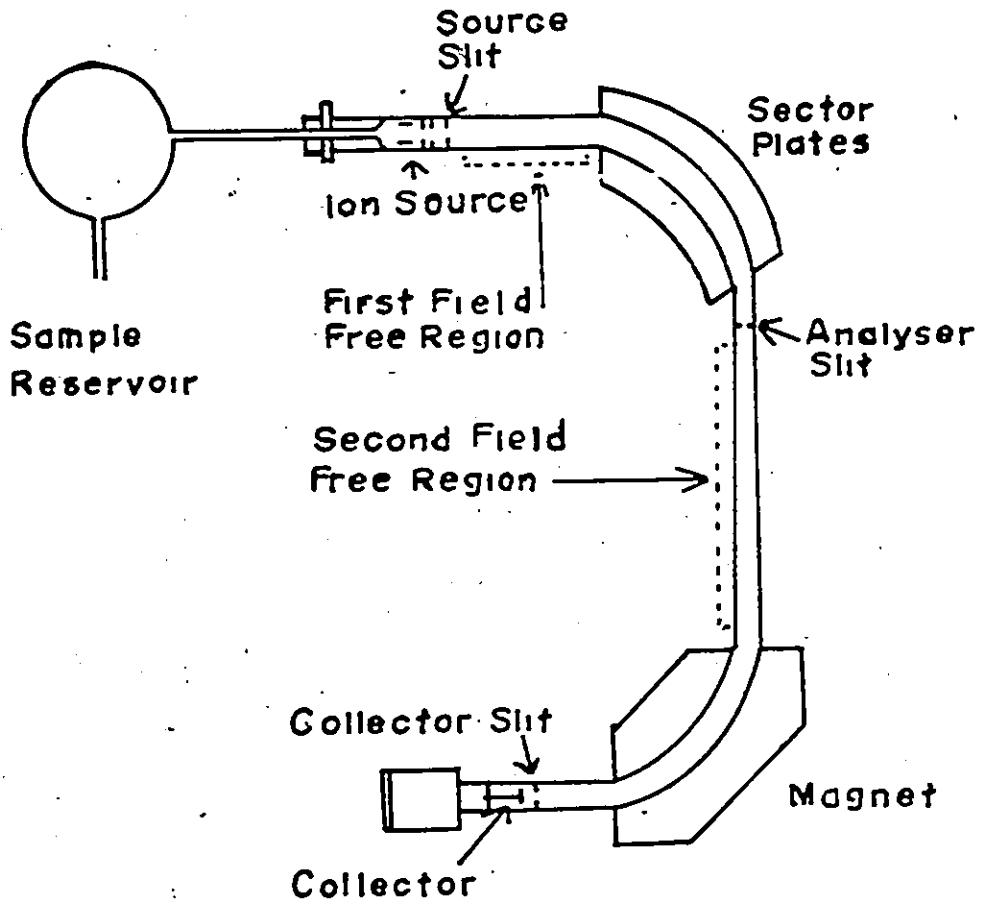


Fig. II (b) 2.3.1. Double Focusing Mass Spectrometer.

The magnetic analyser receives only a monoenergetic ion beam from the energy analyser, and as a result is able to resolve ions which differ in mass by 10 p.p.m.

The ability to separate ions of different mass is measured in terms of resolving power[41e]. Resolving power is a measure of the difficulty of ion separation, and is given by the expression

$$r = \frac{m}{\Delta m}$$

where m = mass of the ion peak

Δm = difference in mass between the peak of mass m and its nearest distinguishable neighbour, the peaks are said to be separated when overlap of the peaks is 5 or 10 percent.

Single focusing instruments have a resolving power of up to ~ 8,000. Double focusing instruments can have resolving power of 200,000 and greater

(3) Detection of Ions[41f]

(3.1) Photographic Plate

With this method of mass spectrometry the magnet is set at a predetermined value and (there is no collector slit) one simply photographs the spectrum using a photographic plate.

(3.2) Faraday Cup

The Faraday cup is used when large samples are available. It operates by measuring the potential built up

between ground and a collector cup. The sensitivity of the Faraday cup is fairly low and as a result high sample pressures are used; this may cause ion-molecule reactions in the source.

(3.3) Electron Multiplier (preamplifier)

The electron multiplier is the most commonly used detector, it is extremely sensitive and hence only very low sample pressures are necessary, thus reducing the possibility of ion-molecule reactions. Spectra have been easily obtained on commercial instruments from nanogram samples.

(4) Interpretation of the Fragmentation Pattern

Fragmentation processes are generally studied in an empirical manner. One approach has been to study the spectra of an homologous series containing a common functional group or structural unit and to observe general trends. Empirical rules are then proposed to fit such observations. For example with simple aliphatic hydrocarbons, as the length of the chain increases from methane through butane the molecular ion is seen to be the most intense peak in the spectrum. Beyond butane the intensity of the molecular ion drops off rapidly as the chain length increases and the spectra are similar in general appearance to that shown in Fig. II.(b) 4.1.[39b] irrespective of the chain length.

If there is a branch in the chain then an abundant peak will be present due to a bond rupture at the site of the branch. Thus from the mass spectrum it is possible to deduce the structure of an aliphatic hydrocarbon.

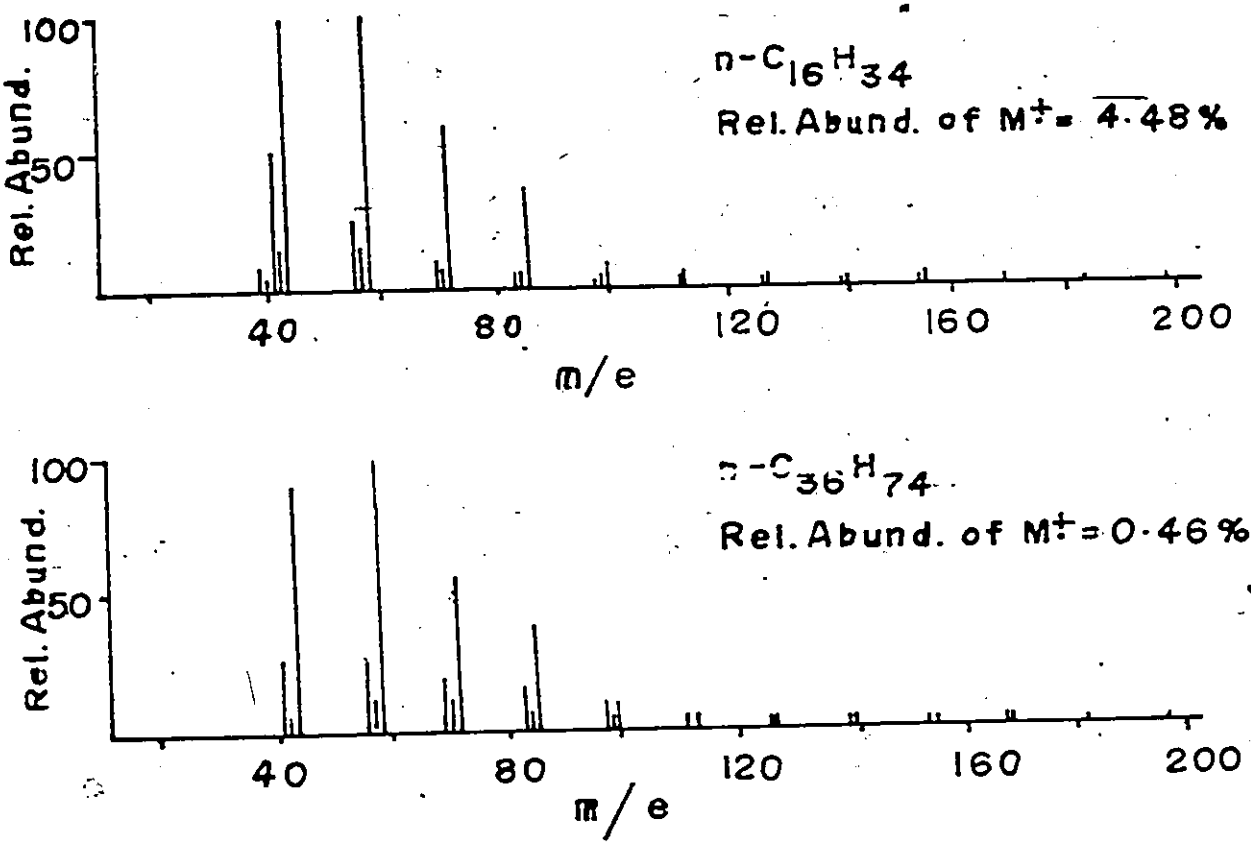
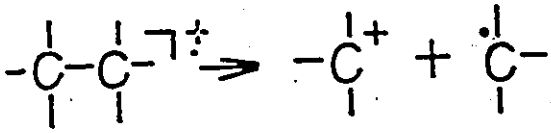


Fig. II(b) 4.1. Mass Spectra of Straight Chain Hydrocarbons.

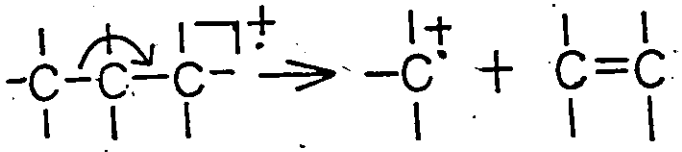
Some fragmentation types which are frequently observed are shown in Fig. II(b) 4.2. Fragmentations 1 and 2 involve cleavage of a single bond with retention of the positive charge at a carbon atom stabilized by hydrocarbon groups. In the first mechanism a free radical is formed, while in the second case an olefin is produced.

In the third mechanism the carbonium ion is stabilized

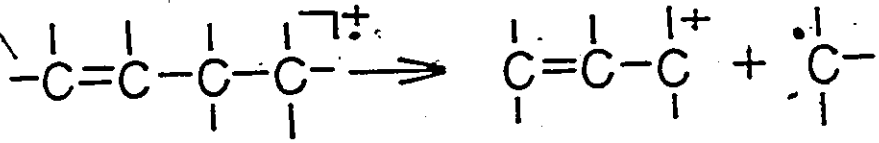
1.



2.



3.



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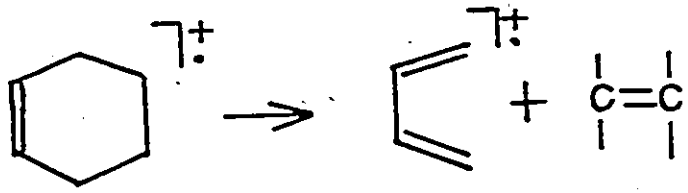

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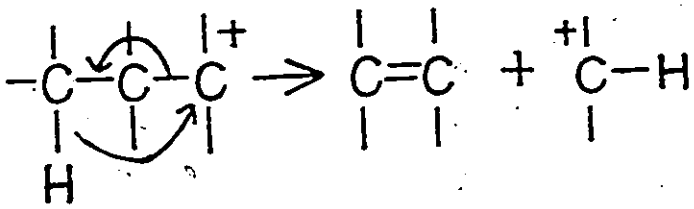


6.

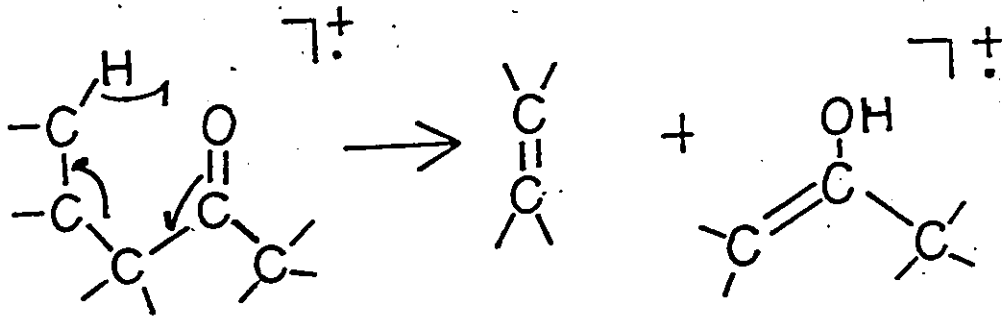


Fig. II (b) 4.2. Fragmentation Mechanisms.

through resonance by the formation of an allylic carbonium ion. The formation of this stable ion provides a particularly strong driving force for the fragmentation leading to it. The fourth mechanism is a prominent fragmentation process in the mass spectra of some cyclic olefins. Commonly called the retro-Diels Alder fragmentation, the fragmentation is characterised by the cleavage of two bonds with the formation of two stable unsaturated fragments.

The fifth mechanism shows that a hydrogen atom transfer can occur allowing formation of a fragment ion and a stable neutral molecule.

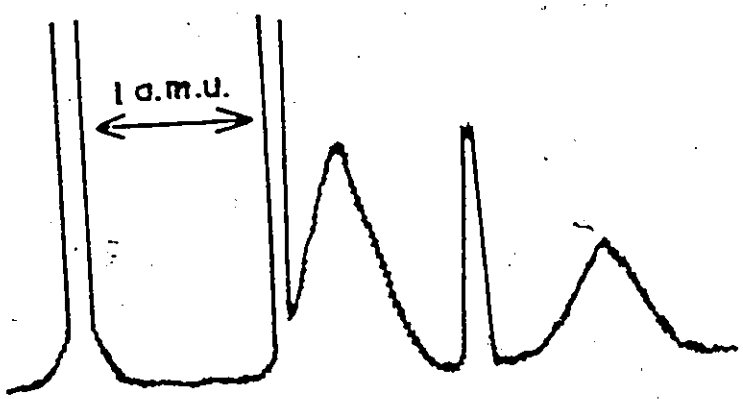
The McLafferty rearrangement[42] is shown in the sixth mechanism and involves a six membered intermediate, observed for example, in many compounds containing carbonyl groups.

(c) Methods of Elucidating Fragmentation Mechanisms

In the previous section it was very briefly indicated how some principles for the interpretation of mass spectra were developed from observations of molecular and fragment ion peaks in normal mass spectra (example: aliphatic hydrocarbons). However when two or more functional groups are present these simple principles may fail. This section deals briefly with the four standard methods of investigation used to study fragmentation mechanisms.

(1) Metastable Ion Peaks

Small weak diffuse peaks are often observed in the mass spectrum of a compound, these peaks are termed metastable ion peaks. They arise from ions of long life time which fragment in the field free region between the ion source exit slit and the magnetic analyser (single focusing machine).



All ions leaving the ion source have the same kinetic energy as shown by the following equation (single focusing instrument).

$$e.V. = K.E. = \frac{1}{2} m_1 v_1^2 = \frac{1}{2} m_2 v_2^2 \quad \text{.... etc.} \qquad (2)$$

where e.V. = electron volts

If ion m_1 with velocity v_1 decomposes in the first field free region giving ion m_2 it can be shown that the velocity of m_2 will be v_1 and not v_2.

thus the K.E. of $m_2 = \frac{1}{2} m_2 v_1^2$ ..... (3)

as a result the ion will not be observed at an m/e value equal to either m_1 or m_2.

$$\text{From (2)} \qquad v_1^2 = \frac{m_2 v_2^2}{m_1}$$

on substituting this expression into (3) the following equation is obtained

$$\text{K.E.}_{m^*} = \frac{1}{2} \frac{m_2 m_2}{m_1} v_2^2 \qquad \ldots\ldots\ldots\ldots\ldots (4)$$

From equation (4) it can be observed that the metastable ion peak (m*) will come to focus at an apparent mass given by the following expression

$$m/e\ m^* = \frac{m_2^2}{m_1}$$

In a double focusing instrument a metastable ion formed in the first field free region (see Fig. II(b) 2.3.1) will not pass through the electric sector because its kinetic energy is not that of the main beam of ions (the beam containing the "normal" ions all having the same kinetic

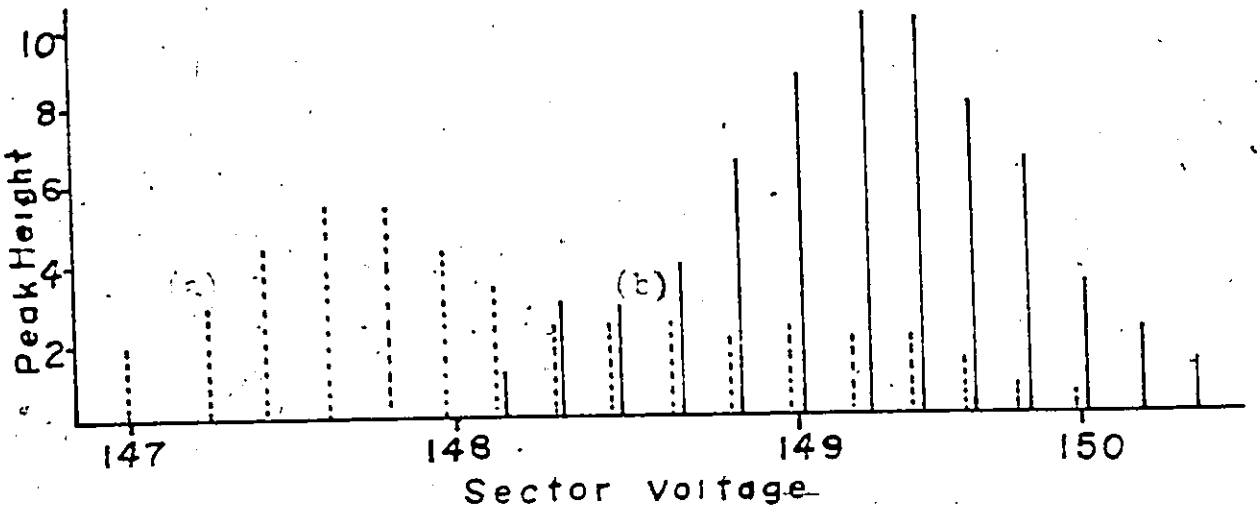
energy, shown in equation (2)). Equation (4) can be rewritten in the following manner

$$K.E._{m*} = \frac{m_2}{m_1} \frac{1}{2} m_2 v_2^2$$

Now if the sector potential is reduced from E_o, that which allows the main beam to pass through the sector analyser, in the ratio m_2/m_1, only those metastable ions having a daughter to precursor ion mass ratio m_2/m_1 will be transmitted through the energy analyser and will be detected at a m/e value of m_2^2/m_1.

Kiser et al.[43] have shown that metastable profiles can be examined in detail by varying the electric sector potential stepwise, in small increments of 0.1 to 0.2 V., above and below E_m (where $E_m = E_o m_2/m_1$) and scanning the magnetic field in the mass region m_2^2/m_1 at each sector potential. A plot of metastable peak height against sector potential gives a graphic representation of the metastable peak shape and relative intensity (as shown below), the maximum appearing at $E_m = m_2/m_1 E_o$.

An alternative method for examining metastable ions formed in the first field free region, described by Barber and Elliot[44], and by Jennings[45], is to hold the sector potential constant at E_o and vary the acceleration potential



Metastable Ion Peaks Obtained by Kiser's Method

Broken Line (a) represents (R-OD) - HDO
(b) represents $(R\text{-}OH)_{unlabelled}$ $-H_2O$] Norborneol

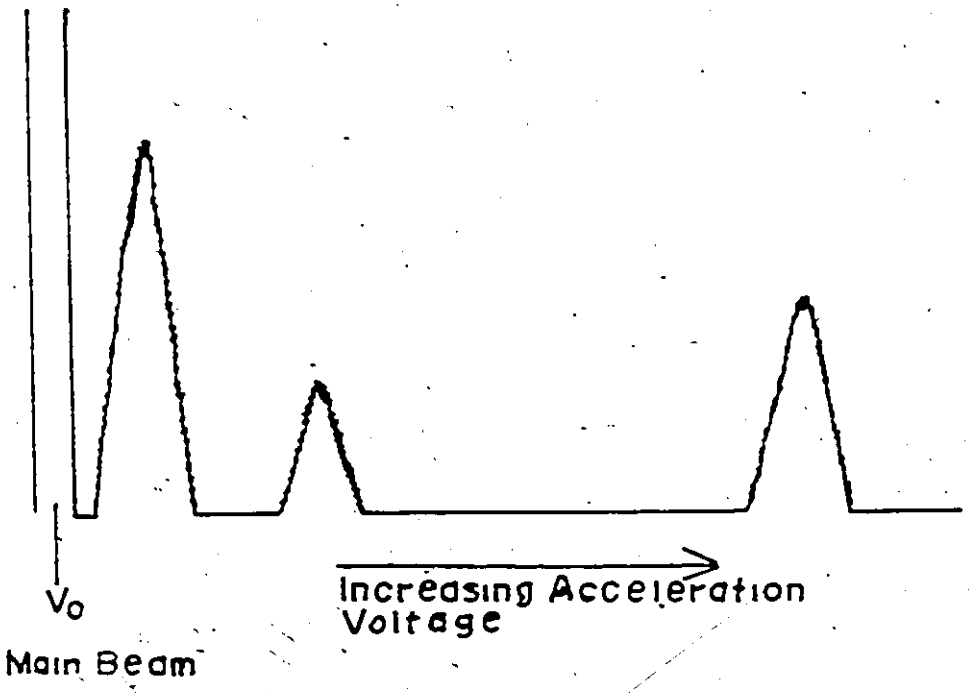
Solid Line represents (R-OD) - H_2O

upwards from V_o (that which allows the main beam to pass through the electrostatic sector) to V

where $V = V_o m_2/m_1$

then only daughter ions formed in the first field free region will have the required energy to pass through the electrostatic sector at its normal E_o. These ions will be observed at a mass corresponding to m_2. This is achieved by selecting the magnetic field appropriate to the mass of the daughter

ion m_2 and scanning the acceleration potential from V_o to V as shown below.



Metastable Ion Peaks Obtained by Jennings' Method

Kiser's method [43] is used when it is required to compare the relative intensities of different daughter ions produced from the same precursor, for example water and its labelled analogues lost from a labelled alcohol as shown on page 107. The Jennings method is a rapid and sensitive procedure for finding precursor to daughter ion relationship, but suffers from the disadvantage that the source conditions are changed whilst scanning.

A daughter ion formed in the second field free region (see Fig. II(b) 2.3.1) will be observed at its appropriate m/e value given by the expression m_2^2/m_1 and is independent of the sector analyser.

The unique features of a metastable ion peak are as shown above; it is therefore characteristic of a particular fragmentation and is positive evidence that the fragmentation occurs in the mass spectrum. The absence of a metastable ion peak does not mean that a fragmentation does not occur, the presence and abundance of a metastable ion is dependent on the precursor ion life time and the geometry and time scale of the instrument.

Ions which dissociate in the source are generally of high internal energy and have short life times, those which fragment in the field free regions (producing metastable ions) are of lower energy and longer life time. Processes which involve a simple bond rupture generally have weak or no metastable ions. Processes which give rise to metastable ions are often processes which involve considerable rearrangement prior to fragmentation.

Metastable ion peaks are diffuse as a result of some conversion of internal energy of the precursor ion into translational energy of the fragment products. The wider the diffuse peak the greater the energy conversion. The width of some very broad metastable ion peaks (called flat top

metastables) have been related to energy release by the equation of Beynon and Fontaine[46].

$$d = \frac{4m_2^2}{m_1}\left(\frac{uT}{eV}\right)^{1/2}$$

where d = width of flat top metastable in a.m.u.

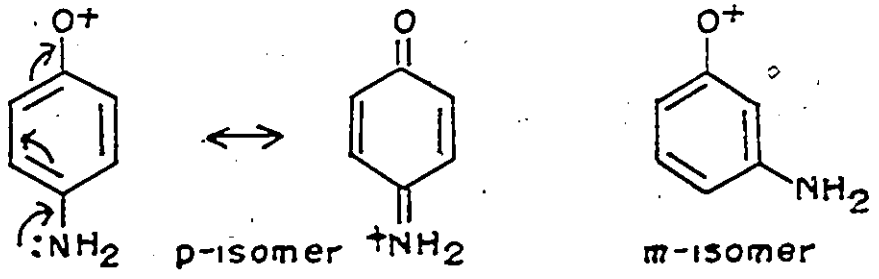
u = mass ratio $(m_1-m_2)/m_2$

eV = ion acceleration potential in electron volts

T = energy release in electron volts

An example of the use of flat top metastable ion peaks as a method of determining excess kinetic energy is the case of the o,m and p nitroanilines[47]. The o and p isomers yield a flat top metastable ion peak with the same energy release, for the loss of nitric oxide from the molecular ion; the m isomer does not. These results are compatible with the $(M - NO)^+$ ions in the ortho and para isomers being stabilized by resonance, which is not possible in the case of the meta isomer.

Ion formed by the loss of NO from the molecular ion of p- and m-



nitroanilines.

(2) High Resolution

As previously mentioned the exact mass of isotopes are not integral. For example while the nominal mass of CO, N_2 and C_2H_4 are 28 a.m.u. their exact masses are 27.9949, 28,0061 and 28.0109, therefore one requires enough resolution to be able to distinguish between these three in order to determine the molecular formula of the ion at m/e 28.A modest resolution of about 3,000 (see II,(b) 2.3) is sufficient for the separation to be achieved. At a m/e value around 300 there are about 150 combinations of C,N,O and H atoms which will give a nominal mass of 300 a.m.u. A resolution of the order of 50,000 giving m/e values to 6 significant figures is required to determine the molecular formula of a given species.

(3) Isotopic Labelling

Metastable ion peaks and high resolution studies give the origin and molecular formula of the species lost in the formation of an ion but give little or no information as to which atoms in the precursor ion are included in the species lost. Isotopic labelling is a possible route to determine which atoms are involved in the formation of a particular ion. Deuterium is the most widely used label, carbon ^{13}C and oxygen ^{18}O are useful but more expensive isotopes.

An example of the use of deuterium labelling is the

investigation of the water loss in aliphatic alcohols; the question that arises is that of the origin of the second hydrogen atom involved in the water loss. Deuterium labelling in butanols[48,49,50] and higher alcohols[51,52] showed that the process occurs predominantly by a 1,4 elimination through a six membered intermediate. This is in contrast with the 1,2 elimination observed in thermal dehydration, where a four centre transition state is involved [53].

A well documented example of isotopic labelling is the study of acetylene loss from the molecular ion of benzene. From a study of the relative abundance of the daughter ion peaks for loss of acetylene and its deuterated analogues from the molecular ion of benzene-1,2,3-d_3 McDonald and Shannon [54] were able to show that the hydrogen atoms were selected in a completely random manner. Jennings [55] has confirmed these results from a study of the relative abundance of the metastable ion peaks for the loss of acetylene and its deuterated analogues in benzene-1,4-d_2 and benzene-1,3,5-d_3. Horman, Yeo and Williams [56] prepared benzene-1,3,5-$^{13}C_3$ and studied the defocused first field free region metastable ion peaks corresponding to the loss of C_2H_2, $^{13}CCH_2$ and $^{13}C_2H_2$ from the molecular ion. After correction for incomplete labelling and contributions from the[(M-1)-acetylene] metastable ion peaks they observed a ratio of 21±4:61±4:18±2 which is in good agreement with the 1:3:1 value required for

completely random selection of the carbon atoms in the acetylene loss. Dickson and Williams[59] carried the investigation one step further by preparing benzene-1-^{13}C,-1-D and were able to show from the appropriate metastable ion peaks that the carbon and hydrogen atoms were completely scrambled in the acetylene loss. They concluded from their results that complete randomisation of the carbon and hydrogen atoms occurs prior to fragmentation of the molecular ion.

The presence of common ions has been detected in isomeric ions by comparing metastable abundance ratios for competing reactions. Shannon and McLafferty[58] and others[59-63] have concluded that isomeric ions which decompose by competing metastable reactions have the same structure if their metastable abundance ratios are the same, whereas isomeric ions of different structure show different metastable abundance ratios. However Yeo and Williams[64] have shown that the metastable abundance ratio for competing reactions will be a function of internal energy of the precursor ions and thus ions of the same structure need not necessarily display the same abundance ratio.

(4) Ionisation and Appearance Potentials

Metastable ion peaks, high resolution studies and isotopic labelling have yielded a great deal of information concerning the fragmentation of compounds in the mass spectrometer, however none of this information gives the structure of the ion formed. Just as isomers have the same molecular formula but different structures, ions in the mass spectrometer can have the same molecular formula but different structures.

The ionisation potential of a molecule is the minimum energy required to bring about the removal of one electron yielding the molecular ion. The appearance potential of a fragment ion is the minimum energy required to bring about its formation. For the reaction

$$e + M = A^{+} + B^{\cdot} + 2e$$

the appearance potential can be expressed as follows

$$A.P.(A^+) = \Delta H_f(A^+) + \Delta H_f(B^\cdot) - \Delta H_f(M)$$

where the ΔH_f's are the heats of formation, this can be re-expressed as

$$\Delta H_f(A^+) = A.P.(A^+) + \Delta H_f(M) - \Delta H_f(B^\cdot)$$

it follows that if the ΔH_f's of the compound M and that of the radical or neutral molecule B are known, then from the measurement of the appearance potential the heat of formation of the ion A^+ can be determined.

The measured appearance potential does not necessarily equal the true appearance potential. The difference between the two being the excess energy required to achieve a rate constant such that decomposition occurs in the source, this excess energy is termed the kinetic shift[65]. One measure of the kinetic shift is obtained from the difference between the appearance potential of the ions in the source and the metastable ions which are obtained from lower energy precursors. In terms of the quasi-equilibrium theory the lower appearance potential of the metastable ions can be explained by there being sufficient time for the energy to redistribute itself into the correct modes and fragmentation to occur before sampling (metastable ions are sampled at the end of the field free region). Difficulties arising from the kinetic shift

can be reduced to a negligible level by using a very small acceleration potential (of the order of ½ 50 v.) instead of the more usual values of 2 to 8 K.v. thereby increasing the time of the ions in the source and allowing time for energy redistribution.

An additional term must be considered, namely that at threshold A^+ and $B^\cdot$ may be formed with excess internal and or kinetic energy. This excess energy E^* corresponds to the energy of activation for the back reaction; at the present time little is known as to when E^* will have a significant value.

An example of the use and limitations of appearance potentials in structure determination is obtained from a discussion of the structure of the ion at m/e 31 in methanol. The reaction for the formation of the ion can be written as:-

$$CH_3OH + e \longrightarrow \underset{\text{m/e 32}}{CH_3OH^+\cdot} + 2e \longrightarrow \underset{\text{m/e 31}}{(M-H)^+} + H^\cdot$$

The structure of the $(M-H)^+$ ion can be formally written either as CH_3O^+ or CH_2OH^+. The appearance potential equals the heat of reaction (11.9e.V. = 274.5 k.cal/mole^{-1} 66) and can be expressed as follows

$$H(\text{reaction}) = 274.5 = H_f(M-H)^+ + H_f(H)^\cdot - H_f(CH_3OH)$$

$$\text{or } H_f(M-H)^+ = 274.5 + H_f(CH_3OH) - H_f(H)^\cdot$$

the heat of formation of methanol (g) and the hydrogen atom are -48.1 and +52.1 k.cal.mole^{-1} [66] respectively

$$\therefore H_f(M-H)^+ = 274.5 + (-48.1) - 52.1 \text{ k.cal.mole}^{-1}$$

$$H_f(M-H)^+ = 174 \text{ k. cal. mole}^{-1}$$

Thus, although the heat of formation of the $(M-H)^+$ ion in methanol is known, its structure is not known. Kiser[41g] has determined the heat of formation of the ion at m/e 31 for several alkanols from appearance potential data[67] and found the values to fall in the range 170 to 174 k.cal. mole^{-1} . This indicates that the same ion at m/e 31 is produced from the various alcohols.

The electron removed in the formation of the molecular ion of alcohols has been shown to be the nonbonding electron in the oxygen atom [66] , this can be represented as follows:-

$$R-\ddot{O}-H + e \longrightarrow R-\dot{\ddot{O}}^{+}-H + 2e$$

Fragmentations which give rise to an even electron species will be the energetically favoured process [5c] , in the case of alcohols α cleavage will yield the oxonium ion $(R = \overset{+}{O}H)$. Cummings and Bleakney [66] have shown from energetic considerations, that in the case of methanol the oxonium ion is formed by a carbon hydrogen bond break, the energy released in

forming the oxonium ion being great enough to compensate for the energy required to break the C-H bond.

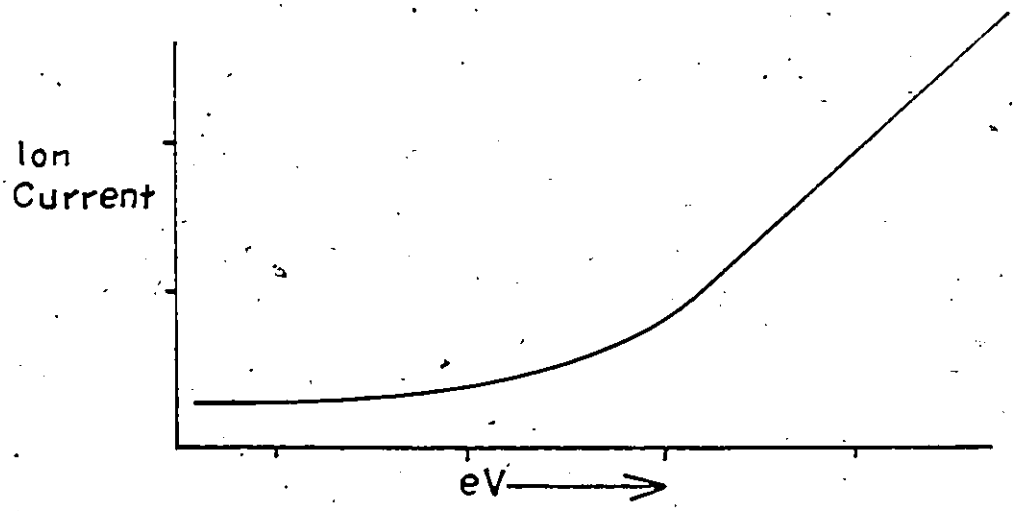
$$H\text{-}CH_2\text{-}\overset{\bullet\,+}{\underset{\bullet\bullet}{O}}\text{-}H \longrightarrow CH_2{=}\overset{+}{\underset{\bullet\bullet}{O}}H + H^{\bullet}$$

Supporting evidence for the above structural assignment is obtained from the value of 235 k.cal.mole^{-1} for the heat of formation of the ion at m/e 31 yielded by the $CH_3\text{-}\overset{\bullet\bullet}{\underset{\bullet\bullet}{O}}\text{-}NO$ molecule [7g], where the ion at m/e 31 is almost certainly the methoxy cation (CH_3O^+).

The above discussion has demonstrated that from heats of formation one can ascertain whether the same ion is present in different compounds, but it does not reveal the identity of the structure directly. It must be pointed out that at 70 e.V. more than one ion structure may be present for a particular m/e value, whereas the measured appearance potential will only be of the ion of the lowest appearance potential.

Ionisation (and appearance) potentials are determined by extrapolation of the ionisation curve (a plot of the ion current against electron energy) to zero ion current, the intercept being equated to the ionisation (or appearance) potential. In practice a calibrant gas, of known ionisation potential, must be run in series with the unknown compound since the voltmeter does not give a true potential and the

values vary slightly from day to day with source conditions. A much more serious problem is the tailing, at the foot of the ionisation curve, which arises from the Maxwell-Boltzmann distribution of energy of the electron beam, caused by thermionic emission from the hot filament. This results in an uncertainty of at least ±0.1 e.V. (±2.5 k.cal.mole^{-1}) in the determination of ionisation and appearance potentials.



The error in appearance potentials from the above sources plus that arising from the kinetic shift[65] has resulted in a wide range of heats of formation for given ions, making the comparison of the structure of ions unreliable. For example the heats of formation of CH_3^+ from propane are 301,273,263,273 and 269 k.cal.mole^{-1} as reported in the National Bureau of Standards, Tables of Ionization Potentials, Appearance Potentials and Heats of Formation of Gaseous Positive Ions[37a].

An early attempt to overcome the energy spread was to use a source described by Fox[68,69]. This source had a retarding potential which permitted only electrons of specific energy into the ion chamber. The use of calculations[70] to compensate for electron energy spread have been applied to the ionisation curve in order to more sharply define the appearance potential.

More recently sources have become available which allow appearance potentials to be measured to 0.05 e.V.

a) Hot-Filament electron source used to produce a mono-energetic electron beam. One method (used in this work) involves a two stage double hemispherical electron energy selector[71] which gives results equivalent to those obtained by photo-electron and photo ionisation sources (see below).

b) Photoelectron Emission[72] This type of ion source gives ionisation potentials of atoms and molecules by ionisation of the species using the light from a helium discharge lamp.

$$M + h\nu = M^{+} + e$$

A variable retarding potential is applied to the ejected electrons and from a plot of electron current against the retarding potential the value of the potential which just stops the electrons reaching the collector is determined. By subtracting this potential from the energy of the helium

radiation one obtains the energy required to produce ionisation of the species. This method gives first and higher order ionisation potentials but cannot be used for appearance potentials, since it only measures the energy required to remove the electron and gives no indication to the future of the ion.

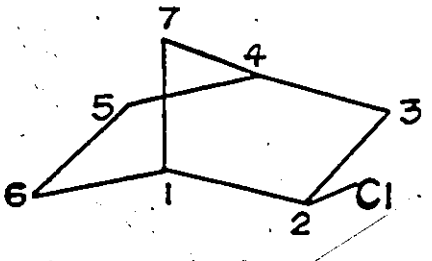
c) Photo Ionisation Source [73] A hydrogen lamp is used as the energy source coupled with a monochromator of bandwidth of 3Å, this gives an energy spread of 0.05 e.V. (1.25 k.cal. $mole^{-1}$). This type of source allows the measurement of both ionisation and appearance potentials.

With the advent of these new types of sources heats of formation of ions from appearance potential data are becoming much more reliable.

DISCUSSION

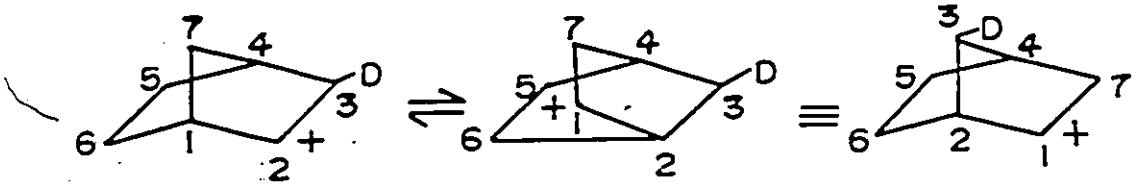
1. Mass Spectra of Norbornyl Halides

A. Mass Spectrum of Norbornyl Chloride ($C_7H_{11}Cl$ exo-2-chloro-bicyclo (2,2,1) heptane)



Review of previous mass spectral studies of norbornyl chloride. Bunton and Del Pesco [74] have reported the mass spectra of exo-2-norbornyl chloride and 12 of its methyl homologues. They proposed two fragmentation routes to explain the origins of the major ions in the mass spectrum of exo-2-norbornyl chloride. The $C_7H_{11}^+$ ion, formed by the loss of a chlorine atom from the molecular ion, subsequently fragments by the loss of ethylene giving the $C_5H_7^+$ ion at m/e 67. For the second fragmentation route they propose the loss of a $C_2H_3Cl^{\cdot}$ radical from the molecular ion to yield the $C_5H_8^{+\cdot}$ ion which subsequently fragments by the loss of a hydrogen atom giving the $C_5H_7^+$ ion at m/e 67. These authors did not carry out any labelling studies to substantiate

their proposed mechanisms and reported difficulty in detecting any metastable ion peaks. In addition they pointed out the possibility of a Wagner-Meerwein reaction prior to fragmentation in the methyl homologues on the basis of the



similarities of the spectra of the Wagner-Meerwein isomers; however, in many cases, particularly for the tertiary chlorides their spectra were contaminated by products of thermal decomposition.

The mass spectrum of exo-2-norbornyl chloride is shown in Fig. II 1.A.1; it is in good agreement with published data [74]. In contrast to Bunton and Del Pesco's work it was observed that the spectrum was rich in metastable ion peaks. Table II 1.A.1 lists the 12 most intense metastable ion peaks with their relative abundances and the fragmentations responsible for their genesis. Although the relative abundance of the most intense metastable ion peak was only 0.05% of the $C_5H_8^{+\cdot}$ ion, (the base peak), no difficulty was experienced in detecting metastable ion peaks.

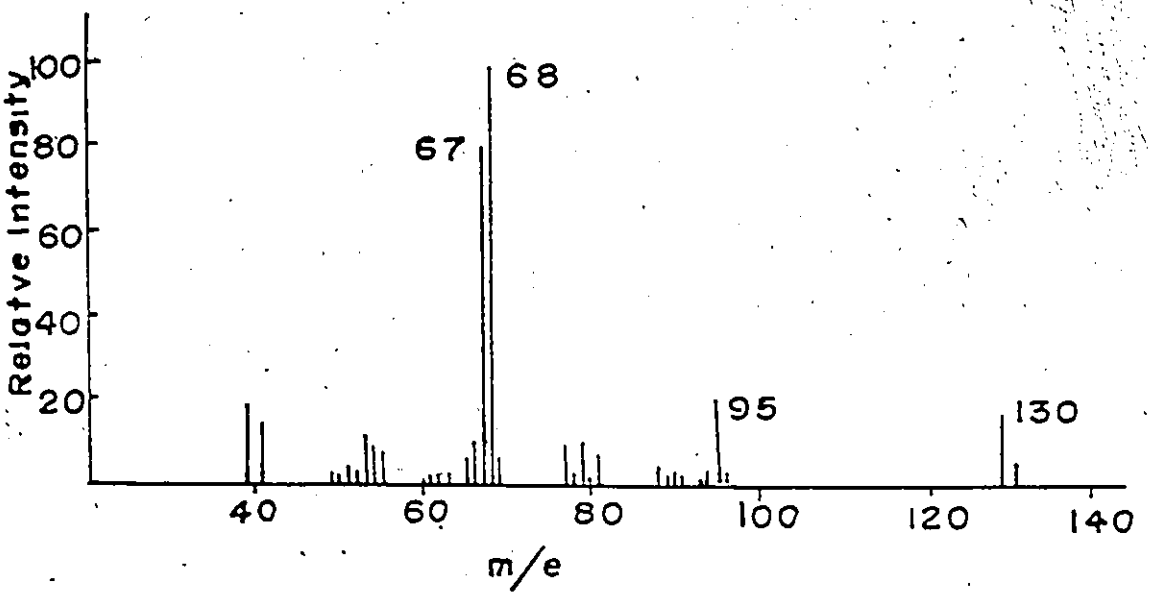


Fig. II 1.A.1. The Mass Spectrum of exo-2-Norbornyl Chloride.

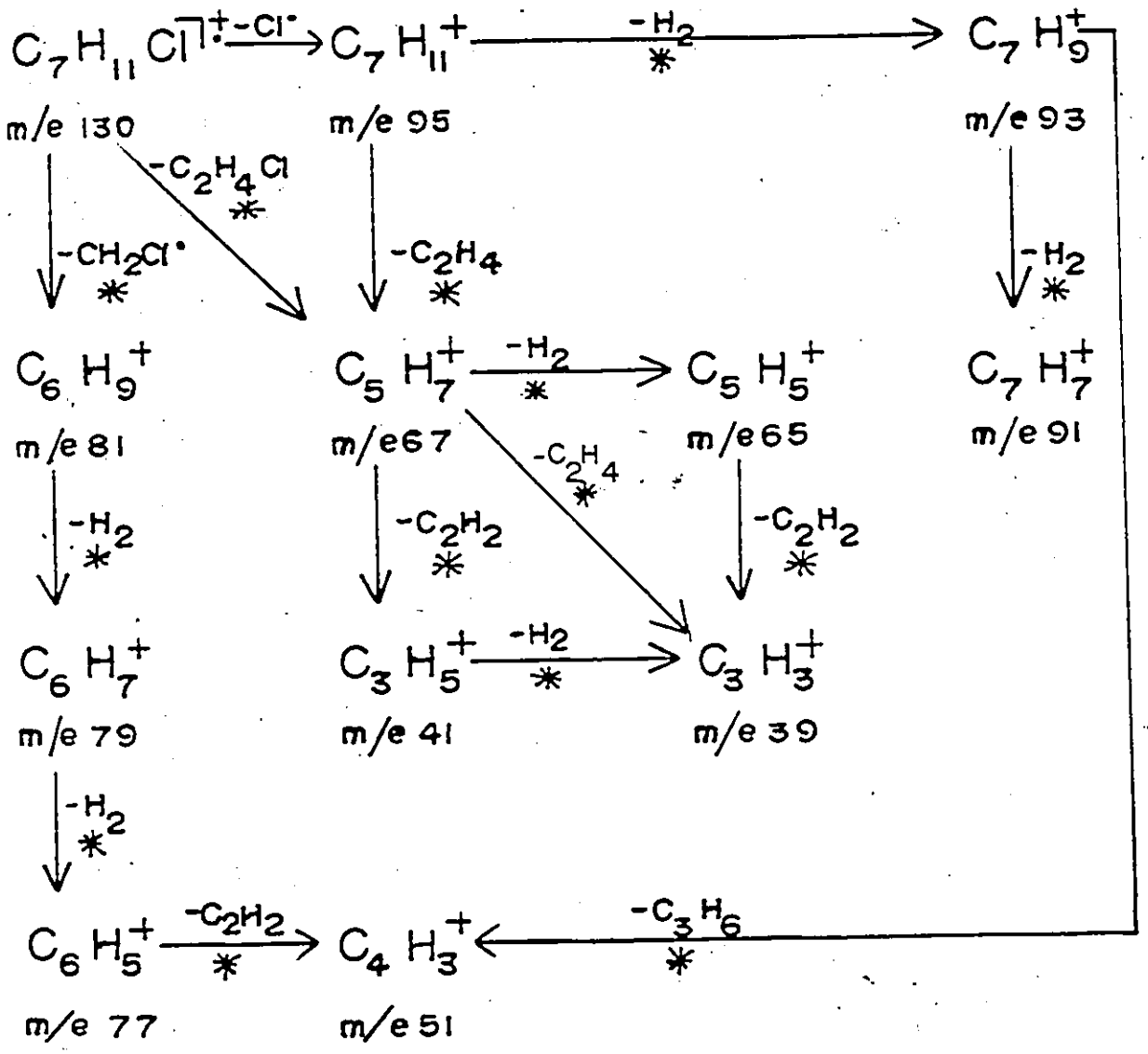
Table II 1.A.1.

Metastable Ion Peaks* Observed in the Mass Spectrum of exo-2-Norbornyl Chloride

Generating Fragmentation	m/e of m* (Observed)	Relative Intensity %
55 → 29	15.3	~5
67 → 41	25.15	10
132 → 67	34.0	32
130 → 67	34.6	100
131 → 68	35.3	~9
41 → 39	37.15	11
95 → 67	47.3	25
67 → 65	63.1	20
79 → 77	75.0	18
81 → 79	77.0	11
93 → 91	89.0(Flat-Top)	21
95 → 93	91.2(Flat-Top)	21

*Obtained from the normal spectrum run at 70 eV. (Hitachi RMU-6D)

Scheme II 1.A.1 shows the fragmentations of exo-2-norbornyl chloride for which metastable ion peaks were observed. The formation of the $C_6H_9^+$ ion at m/e 81 is shown to arise from the molecular ion by the loss of a $CH_2Cl^\bullet$ radical (the only alternative route for its formation involves the loss of a CH_2: diradical from the $C_7H_{11}^+$ ion, however the loss of a CH_2: has never been proven in mass spectrometry[75,76,77]).



Scheme II 1.A.1. Fragmentation Scheme for Exo-2-Norbornyl Chloride.

From Scheme II 1.A.1 it can be observed that the molecular ion fragments in three ways: (a) by the loss of a chlorine atom giving the $C_7H_{11}^+$ ion which further fragments by the loss of ethylene to give the $C_5H_7^+$ ion (as observed by Bunton and Del Pesco). (b) the $C_5H_7^+$ ion is also formed directly from the molecular ion by the loss of a chloroethyl radical (C_2H_4Cl). (c) the $C_6H_9^+$ ion is formed from the molecular ion by the loss of a $CH_2Cl^\cdot$ radical as discussed above, this species further fragments by two successive losses of a hydrogen molecule to give the $C_6H_5^+$ ion. Either or both of the $C_5H_7^+$ ions formed in (a) and (b) fragment by the loss of ethylene and acetylene.

From the information described thus far it is not possible to state how the base peak m/e 68 arises; it could come directly from the molecular ion by the loss of $C_2H_3Cl^\cdot$ and/or from the $C_7H_{11}^+$ ion by the loss of a $C_2H_3^\cdot$ radical. In order to investigate this point <u>exo</u>-2-norbornyl chloride-<u>exo</u>-3-d_1 was prepared by reacting deuterium chloride with norbornene (see Part III); from inspection of the relative intensities of the peaks in the 60's together with those of the $C_7H_{11}^+$ ion (see Table II.1.A.2) no firm conclusion could be drawn concerning the origin of the base peak.

Table II 1.A.2.

Relative Intensities of the Peaks m/e 67-70, the (M-Cl) and Molecular Ion

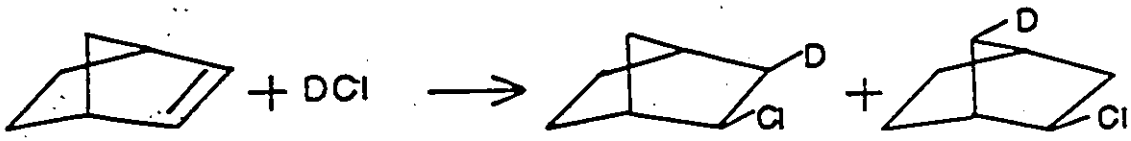
(Correction for ^{13}C)	m/e 67	m/e 68	m/e 69	(M-Cl)	M^+
exo-2-Norbornyl Chloride	82	95	0	20	19
exo-2-Norbornyl Chloride-exo-3-d_1	53	97	44	20	22

On examination of the metastable ion peaks in exo-2-norbornyl chloride-exo-3-d_1 two interesting groups of metastable ion peaks were observed. The first consisted of two metastable ions for the loss of ethylene and labelled ethylene from the $C_7H_{11}^+$ ion in the ratio of 64±2:36±2 respectively. The second group was a set of four metastable ions for the loss of a chloroethyl radical, labelled and unlabelled, from the molecular ion in the ratio 56±1:44±1 respectively for the ^{35}Cl pair. The presence of these metastable ion peaks in each group could arise in two separate ways or a combination of both (1) a Wagner-Meerwein reaction is occurring in the preparation of the labelled norbornyl chloride from norbornene (2) a Wagner-Meerwein reaction takes place in the mass spectrometer prior to fragmentation by (a) the loss of ethylene from the $C_7H_{11}^+$ ion and (b) the loss of a chloroethyl radical from the molecular ion.

In order to check the two possibilities, exo-2-norbornyl chloride-endo-3-d_1 was prepared from the endo-2-norborneol-endo-3-d_1 by the method of Stille and Sonnenberg[78], using thionyl chloride and pyridine. Analysis of the ethylene loss metastable ion peaks from the (M-Cl) species showed the loss of ethylene and mono-deuterated ethylene in the ratio 64±2:36±2 respectively; this is the same value as observed for the ethylene loss in exo-2-norbornyl chloride-exo-3-d_1 . Similarly two metastable ion peaks were observed for the chloroethyl radical loss from the molecular ion; however for these the ratio was the reverse of that observed in the exo-2-norbornyl chloride-exo-3-d_1 , that is $m^*(M-C_2H_4{}^{35}Cl):m^*(M-C_2H_3D^{35}Cl)$ appeared in the ratio of 56±1:44±1 .

About this time Brown and McIvor[79] reported the results of a 220MHz N.M.R. study on the products obtained from the addition of deuterium chloride to norbornene at -78° in chloroform. They observed that 55±3% of the product was exo-2-norbornyl chloride-exo-3-d_1 and 45±3% of the produce was exo-2-norbornyl chloride-7-syn-d_1 , these results are in remarkably good agreement with the metastable ion peak ratios for the loss of the chloroethyl radical from the molecular ion of the labelled exo-2-norbornyl chloride which was prepared in a similar manner. Brown and McIvor[79] explained the presence of the two products obtained in the

preparation of the exo-2-norbornyl chloride as arising from a Wagner-Meerwein reaction.



However it is still not possible to tell if a Wagner-Meerwein reaction is occurring in the molecular ion prior to its fragmentation.

Another attempt was made to achieve specific deuteration using the preparative method of Downie and Lee[80], this method involved reacting endo-2-norborneol-3, 3-d_2 with triphenylphosphine in excess carbon tetrachloride to yield (presumably) exo-2-norbornyl chloride-3,3-d_2 , this preparation was repeated starting with endo-2-norborneol-2,3,3-d_3 to yield (presumably) the exo-2-norbornyl chloride-2,3,3-d_3 .

In the chloroethyl radical loss from the molecular ion of the dideuterated norbornyl chloride only a metastable ion for the loss of $C_2H_2D_2Cl$ was observed, there being no metastable ion peak for any other chloroethyl radical loss; similarly in the trideuterated norbornyl chloride only a metastable ion peak for the loss of C_2HD_3Cl was observed. From these results it was concluded that a Wagner-Meerwein

reaction did not occur either in the preparation of the labelled norbornyl chloride (Downie and Lee's method) or in the mass spectrometer prior to fragmentation by the loss of a chloroethyl radical from the molecular ion.

The relative intensities of the metastable ion peaks for the loss of ethylene from the $C_7H_{11}^+$ ions in the labelled compounds are reported in Table II.1.A.3, clearly the ratios do not correspond to a specific fragmentation in any of the labelled compounds. In each case however the results correspond to the value for random selection of the hydrogen and deuterium atoms in the ethylene loss. Norbornyl chloride $-2-^{13}C$ was prepared (method-see page 288) and the ratio of $^{12}C_2H_4$: $^{12}C^{13}CH_4$ loss from the labelled $C_7H_{11}^+$ ion was determined and found to correspond to completely random selection of the carbon atoms in the ethylene loss.

Included in Table II 1.A.3 are the relative intensities of the metastable ion peaks for the loss of the chloroethyl radicals from the molecular ions of the labelled compounds. The results indicate that a specific process is occurring, that the chloroethyl radical lost contains the 2 and 3 carbon atoms with their attached hydrogen atoms. The origin of the fourth hydrogen atom in the chloroethyl radical was narrowed down by analysis of the metastable ion peaks in the mass spectrum of the products obtained when deuterium

Table II 1.A.3.

Relative Intensities of Metastable Ion Peaks* in Labelled Compounds

Ethylene Loss from (M-Cl).

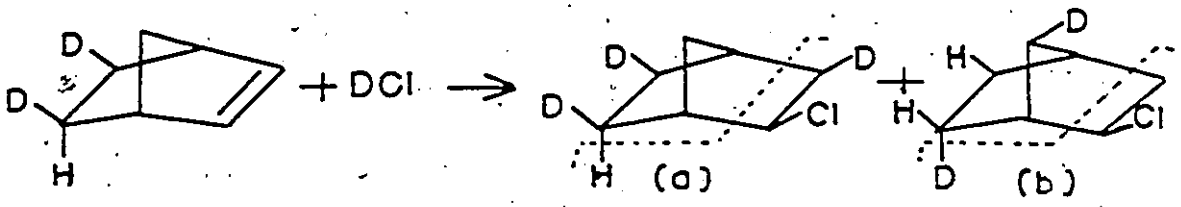
Compound	$(M-Cl)-C_2H_4$ m/e	$(M-Cl)-C_2H_4$ Rel.Abund.	$(M-Cl)-C_2H_3D$ m/e	$(M-Cl)-C_2H_3D$ Rel.Abund.	$(M-Cl)-C_2H_2D_2$ m/e	$(M-Cl)-C_2H_2D_2$ Rel.Abund.	$(M-Cl)-C_2HD_3$ m/e	$(M-Cl)-C_2HD_3$ Rel.Abund.
Norbornyl Chloride 6-d_1	48.2	64 ± 2 64(Calc.)	46.8	36 ± 2 36(Calc.)		———		———
Norbornyl Chloride (3-7)d_1	48.2	64 ± 2 64(Calc.)	46.8	36 ± 2 36(Calc.)		———		———
Norbornyl Chloride -3,3-d_2	49.1	40 ± 2 38(Calc.)	47.7	48 ± 2 51(Calc.)	46.3	12 ± 2 11(Calc.)		———
Norbornyl Chloride -2,3,3-d_3	50.0	22 ± 2 21(Calc.)		50 ± 2 51(Calc.)	47.2	25 ± 2 25.5(Calc.)	45.8	3 ± 2 2.5(Calc.)

Loss of Chloroethyl Radical from the Molecular Ion.

Compound	$M-C_2H_4Cl$ m/e	$M-C_2H_4Cl$ Rel.Abund.	$M-C_2H_3DCl$ m/e	$M-C_2H_3DCl$ Rel.Abund.	$M-C_2H_2D_2Cl$ m/e	$M-C_2H_2D_2Cl$ Rel.Abund.	$M-C_2HD_3Cl$ m/e	$M-C_2HD_3Cl$ Rel.ABund.
Norbornyl Chloride -6-d_1	35.3	49 ± 1	34.3	51 ± 1		———		———
Norbornyl Chloride -(3-7)d_1	35.3	44 ± 1	34.3	56 ± 1		———		———
Norbornyl Chloride -3,3-d_2		———		———	34.0	100		———
Norbornyl Chloride -2,3,3-d_3		———		———		———	33.8	100

* Obtained from the normal spectrum run at low eV.(Hitachi RMU-6D)

chloride was added to nortricyclene in a manner similar to that described by Brown and McIvor[79]; they had shown by N.M.R. analysis that the addition products were pure exo-2-norbornyl chloride with the deuterium atom 50±3% at the endo-6 position and 43±3% at the exo-6 position. The remaining 7% they believed to be in the anti-7 position (see Part III). In the present experiments it was observed that the loss of C_2H_3DCl and the loss of C_2H_4Cl from the molecular ion produced metastable ion peaks having a ratio of 49±1:51±1 respectively. This result is compatible with the fourth hydrogen atom originating from the 6 carbon atom; either the endo or exo hydrogen atoms are equivalent, or the loss involves specifically the endo-6 or exo-6 hydrogen atom. Both possibilities are within experimental error. Proof that the fourth hydrogen atom in the chloroethyl radical loss is specifically the endo-6 hydrogen atom was obtained from a similar experiment using the labelled norbornyl chloride obtained from the addition of deuterium chloride to norbornene-exo-5-exo-6-d_2. Only one metastable ion peak was observed, namely that for the loss of C_2H_3DCl. This can be explained by assuming the products are (a) and (b) (see Part III for details) (note the inversion of the exo and endo hydrogen atoms on the 5 and 6 carbon atoms as a result of the Wagner-Meerwein reaction).



The establishment of the chloroethyl radical fragmentation indicates that any Wagner-Meerwein detected, must occur in the preparation of the exo-2-norbornyl chloride (for example see page 128) and not in the mass spectrometer.

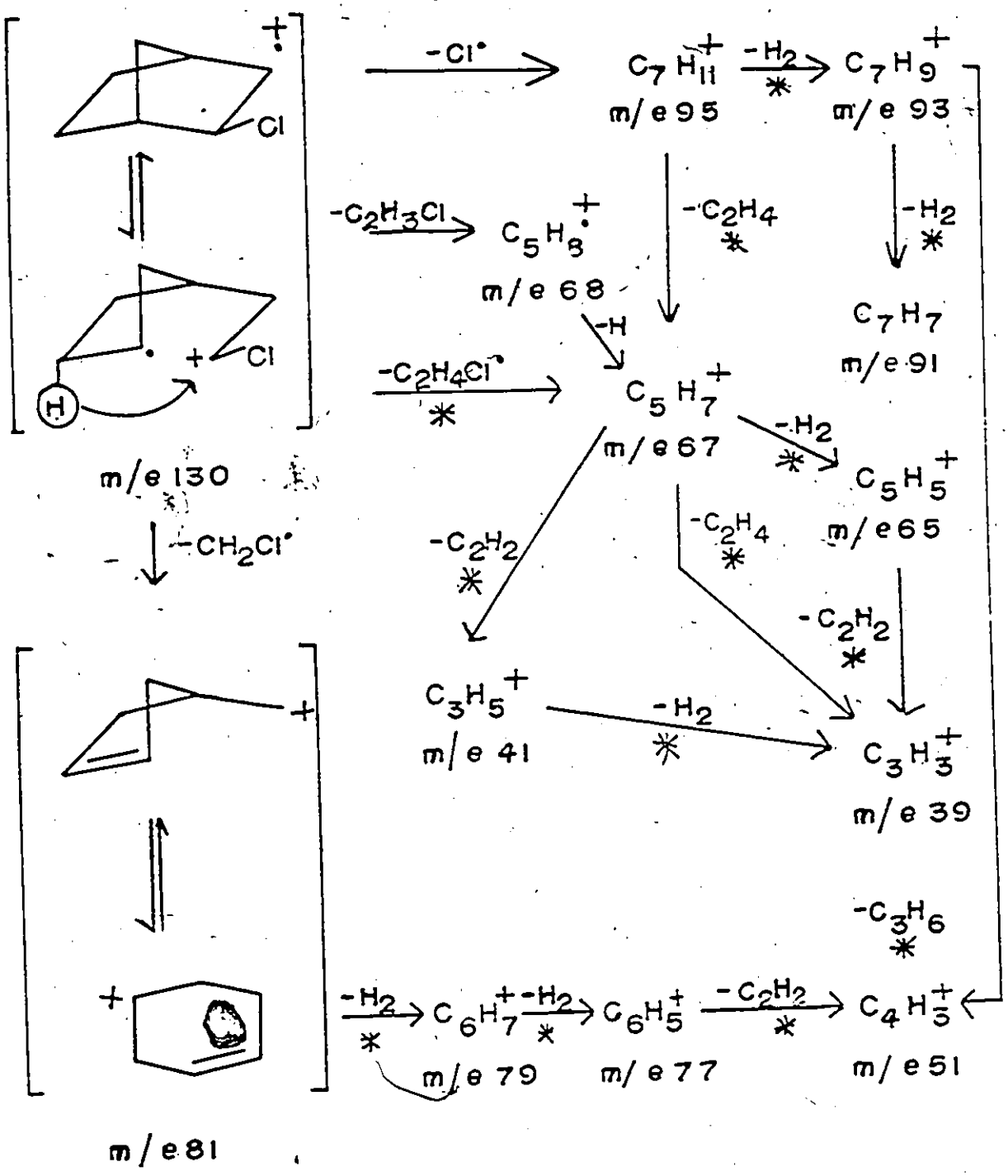
The results shown in Table II 1.A.4 show that the base peak in the mass spectra of the norbornyl chlorides studied remains at m/e 68 when the deuterium atoms are present on the 2 or 3 carbon atoms and is shifted to higher m/e values when deuterium is present on the 6 or 7 carbon atoms, it is therefore unlikely that the base peak $C_5H_8^+$ arises from the norbornyl cation (the $C_7H_{11}^+$ ion at m/e 95), where the carbon and hydrogen atoms are completely randomised prior to fragmentation by ethylene loss. It could be a fast, specific fragmentation of the $C_7H_{11}^+$ ion before scrambling but the base peak almost certainly proceeds directly from the molecular ion by the loss of C_2H_3Cl, the atoms involved in the fragmentation being the 2 and 3 carbon atoms and the attached hydrogen and chlorine atoms.

Table II 1.A.4.

Relative Intensities of the Peaks m/e 67-70.

Compound	Relative Intensities (corrected for ^{13}C)			
	m/e 67	m/e 68	m/e 69	m/e 70
exo-2-Norbornyl Chloride	82	95	0	0
exo-2-Norbornyl Chloride -3,3-d_2	68	96	10	0
exo-2-Norbornyl Chloride -2,3,3-d_3	72	96	18	8
exo-2-Norbornyl Chloride -6-d_1	40	59	97	0
exo-2-Norbornyl Chloride -(3-7)d_1	53	97	44	0

Scheme II 1.A.2 represents the complete fragmentation pattern of exo-2-norbornyl chloride as deduced from the analysis of metastable ion peaks in the unlabelled compound and a study of normal peaks and metastable ion peaks in the labelled compounds. The base peak ($C_5H_8^{+\cdot}$) is shown as being formed by the loss of C_2H_3Cl from the molecular ion; the fate of this daughter ion is uncertain; it may fragment by the loss of a hydrogen atom, but from a study of the labelled compounds this cannot occur to more than 15%. This makes proposals for the structure of this ion uncertain because molecular ions of this molecular formula[15a] either lose a hydrogen atom to yield an intense or base peak at m/e 67 or display an important fragment ion at m/e 53. Possibly it is a terminal ion, i.e. $C_5H_8^{+\cdot}$ ions formed from the molecular ion possess insufficient energy to fragment further (see results of appearance potential data for cyclopentadiene in norbornene and nortricyclene, page 173) The $C_5H_7^+$ ion is formed by two routes (a) directly from the molecular ion by the loss of the 2 and 3 carbon atoms with the attached chlorine and 3 hydrogen atoms, the fourth atom in the chloroethyl loss coming from the endo-6 position. (b) from the $C_7H_{11}^+$ ion (the norbornyl cation) by the loss of ethylene where the carbon and hydrogen atoms are selected at random. The norbornyl cation also fragments by two successive



Scheme II 1.A.2. Fragmentation Mechanism of Exo-2-Norbornyl Chloride.

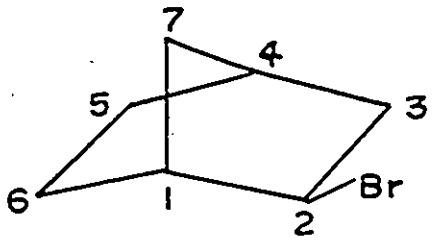
losses of a hydrogen molecule to yield (presumably) the tropyl cation, $C_7H_7^+$, the molecular hydrogen losses being accompanied by flat top metastable ion peaks which indicate energy release in the fragmentation (see page 109) Finally, the molecular ion loses a $CH_2Cl^\bullet$ radical to give the $C_6H_9^+$ ion at m/e 81 which fragments by two successive molecular hydrogen losses to give the $C_6H_5^+$ (phenyl) ion, which in turn decomposes by the loss of acetylene.

Having demonstrated the utility of comparing the relative intensities of metastable ion peaks in labelled compounds for studying a particular fragmentation mechanism, it is of interest to consider their advantages and limitations in deducing fragmentation mechanisms. There are four general limitations to studies of daughter ion peaks formed in the source (a) a particular peak can arise by more than route; for example the formation of the $C_5H_7^+$ ion in norbornyl chloride (b) two neighbouring daughter ion peaks could partially or completely overlap in the presence of a label for example the ion peaks at m/e 67 and 68 in norbornyl chloride (c) two neighbouring daughter ion peaks, where the daughter ion at higher mass further fragments by the loss of a hydrogen atom (d) in the case of incomplete labelling it is often extremely difficult to draw any meaningful results. Metastable ion peaks do not suffer from the disadvantages of the "normal" peaks as discussed above, because usually

they characterise a single process. Metastable ions detected in the normal spectrum are probably unique as indicated by the relationship $m^* = m_2^2/m_1$. However using the metastable ion defocusing technique of Kiser[43] a metastable ion can be uniquely catalogued by the two parameters m^* (where $m^* = m_2^2/m_1$) and E (where $E = m_2E_o/m_1$ and E_o is the electric sector potential which transmits the main beam) (see the introduction page 104 for a detailed discussion on metastable ions).

In very simple compounds no difficulty may be experienced in studying normal peaks in labelled analogues to deduce fragmentation mechanisms (e.g. benzene see page 112) However in compounds which are rich in fragmentation pathways it is unlikely that it will be possible to deduce fragmentation routes from "normal" peaks alone. If a metastable ion peak is present for a particular fragmentation then by metastable ion defocusing in conjunction with isotopic labelling it is possible to examine this fragmentation route uniquely. Norbornyl chloride is a relatively simple example.

B. Mass Spectrum of Norbornyl Bromide ($C_7H_{11}Br$, exo-2-bromo-bicyclo (2,2,1) heptane)



(a) Review of previous mass spectral studies of norbornyl bromide. De Jongh and Shrader [81] and De Jongh et al.[82] have reported the mass spectra of exo and endo-2-norbornyl bromide and found them to be closely similar except for the intensities of the molecular ions relative to the base peak. They indicated that the base peak, $C_7H_{11}^+$, arises by elimination of bromine from the molecular ion and they proposed that this species fragments in three ways (a) by the loss of ethylene giving the $C_5H_7^+$ ion (b) by the loss of methane giving the $C_6H_7^+$ ion (c) by the loss of a hydrogen molecule giving the $C_7H_9^+$ ion, which in turn fragments further by the loss of a hydrogen molecule to give the $C_7H_7^+$ ion. The other fragmentation pathway presented in their scheme was the loss of a C_2H_3Br from the molecular ion yielding the $C_5H_8^+$ ion at m/e 68.

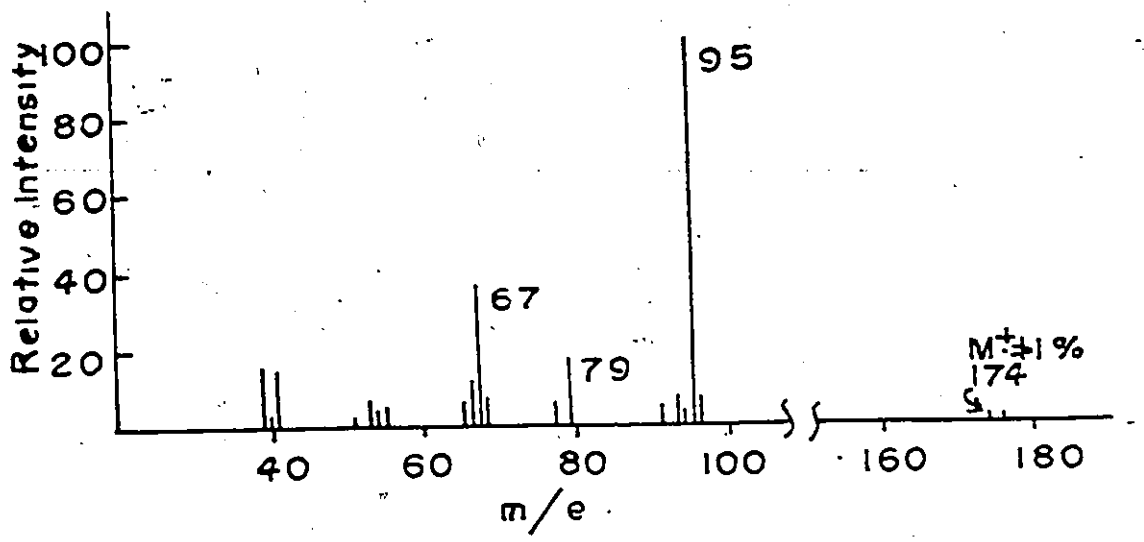


Fig. II 1.B.1. Mass Spectrum of exo-2-Norbornyl Bromide

Table II B.1.

Metastable (m*) Peaks† Observed in the Mass Spectrum of exo-2-Norbornyl Bromide.

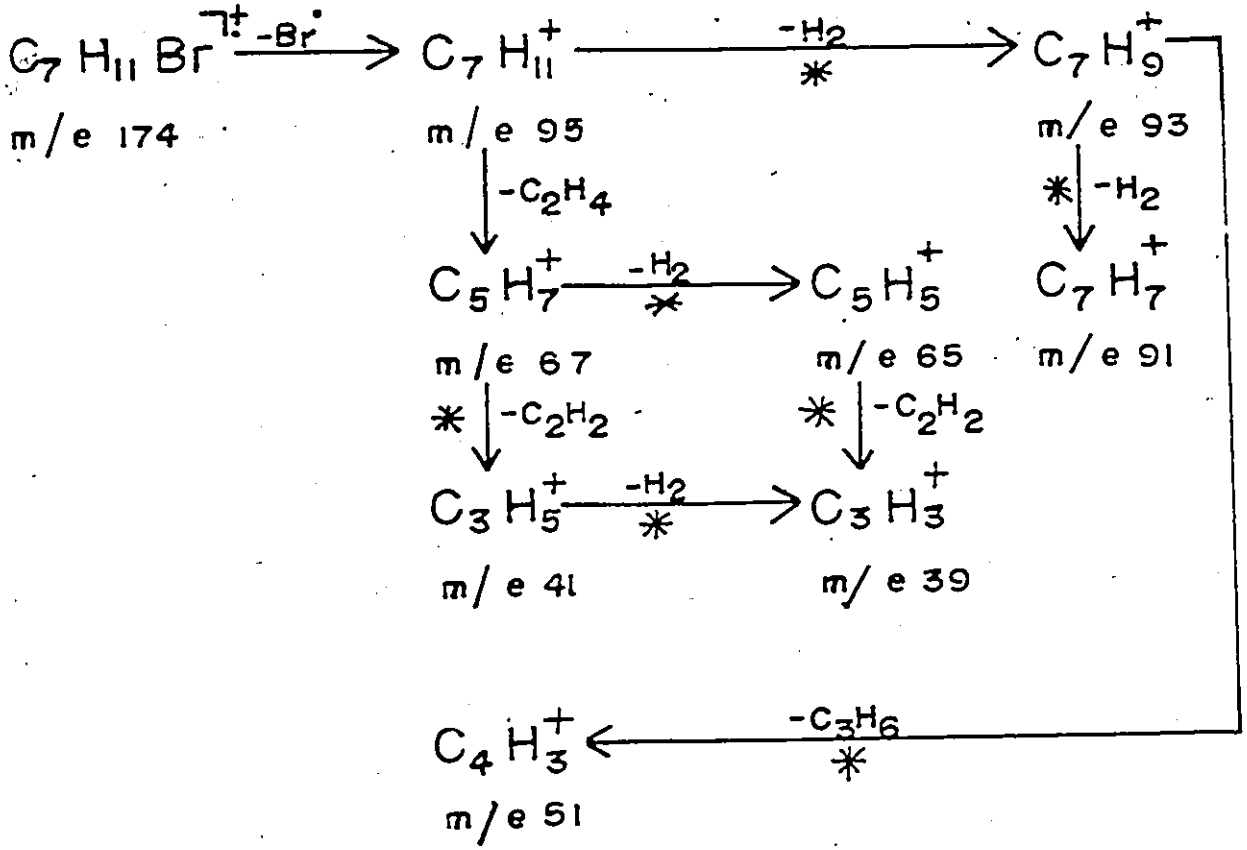
Generating Fragmentation	m/e of m* (Observed)	Relative Intensity %
53 → 27	13.8	9
67 → 41	25.10	6
93 → 51	28.10	7
41 → 39	37.2	100*
95 → 67	47.3	38
67 → 65	63.1	55
79 → 77	75.0	24
93 → 91	89.0 (Flat-Top)	87
95 → 93	91.2 (Flat-Top)	

* .1% of base peak.

†Obtained from the normal spectrum run at 70 eV. (Hitachi RMU-6D)

(b) The mass spectrum of exo-2-norbornyl bromide is shown in Fig. II 1.B.1. and is in fair agreement with published data [81,82]. Table II 1.B.1 lists the most intense metastable ion peaks, their relative abundances and the fragmentations responsible for their genesis.

Scheme II 1.B.1 shows the fragmentation breakdown for norbornyl bromide based on metastable ion peak observations.



Scheme II 1.B.1. Fragmentation Scheme for exo-2-Norbornyl Bromide.

From the above scheme it is observed that the molecular ion fragments by the loss of a bromine atom to yield the $C_7H_{11}^+$ ion at m/e 95 which fragments in two ways (a) by the loss of ethylene to yield the $C_5H_7^+$ ion at m/e 67 , this species decomposes by the loss of a hydrogen molecule and acetylene to give the $C_5H_5^+$ and $C_3H_5^+$ ions (b) by two successive losses of a hydrogen molecule to give the $C_7H_7^+$ ion.

Several deuterated norbornyl bromides were prepared from the corresponding alcohols using the method of Schafer and Weiberg [83] . Subsequent conversion of the labelled bromides into norbornenes (see page149) indicated that the upper limit of Wagner-Meerwein reaction occuring in the preparation of the norbornyl bromide was 11% .

Partial mass spectra of the above labelled compounds are shown in Table II 1.B.2 where the relative intensities of the peaks in the 60's and the norbornyl cation (m/e 95) are listed.

Table II 1.B.3. lists the relative intensities of the metastable ion peaks for the loss of ethylene and its labelled analogues from the $C_7H_{11}^+$ ion in the various labelled norbornyl bromides. Clearly the ratios of the metastable ion peaks correspond to the values for the random selection of the hydrogen atoms in the ethylene loss, in a manner similar to that observed in norbornyl chloride.

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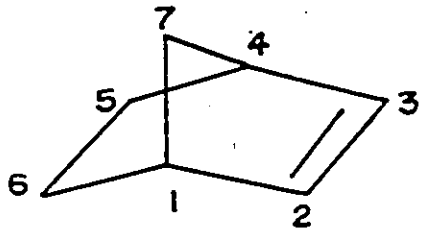
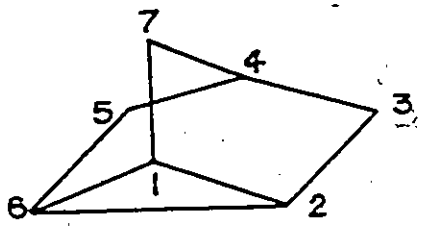
On comparing the mass spectra of norbornyl chloride Fig. II 1.A.1. with norbornyl bromide Fig. II.1.B.1, it was observed that although the relative intensities of the ions are different the same ions appear in the spectra of both compounds. From this conclusion and the identical behaviour of the $C_7H_{11}^+$ ion in both compounds, it is highly probable that the same fragmentations are occuring in each case.

2. Mass Spectra of Norbornene and Nortricyclene





Introduction

The mass spectra of the isomeric hydrocarbons norbornene and nortricyclene, are shown in Figs. II 2.A.1 and II 2.A.2. The major difference between the two spectra lies in the relative intensity of the ion peaks at m/e 66 and 79, produced by the loss of ethylene and a methyl radical respectively, from the molecular ion (see Table II 2.A.1).

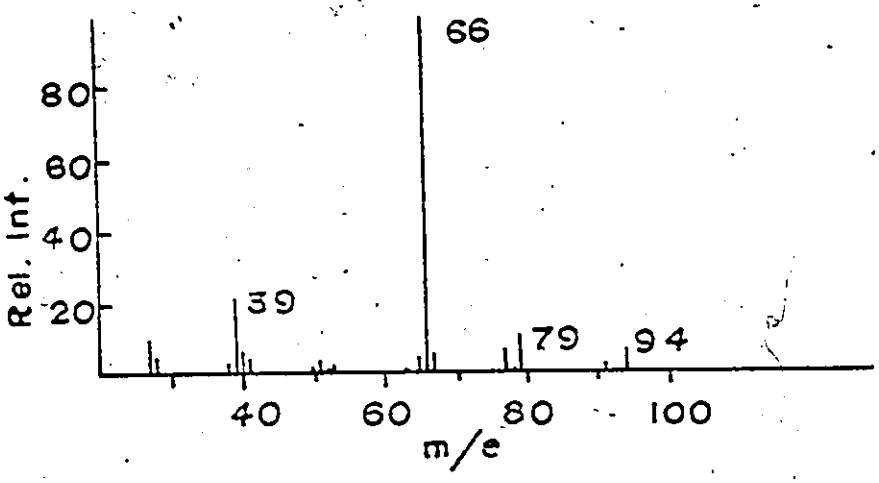


Fig. II 2.A.1. Mass Spectrum of Norbornene.

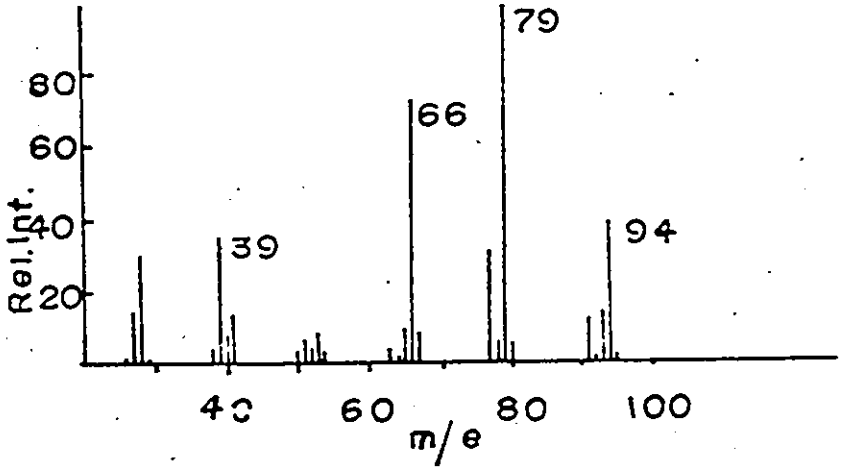


Fig. II 2.A.2. Mass Spectrum of Nortricyclene.

Recent publications[58-64] have indicated that many isomeric hydrocarbons undergo rearrangement to common intermediates before fragmentation. If this is the case for norbornene and nortricyclene, then a possible explanation for the difference in the relative intensities of major peaks in their spectra could be due to differences in the rates of formation and dissociation of common intermediates. It was therefore of some interest to examine in detail the similarities and differences in the mechanisms of formation of the various ions from the two isomeric hydrocarbons.

A. Mass Spectrum of Norbornene (C_7H_{10} bicyclo (2,2,1) hept-2-ene).

(a) Review of previous mass spectral studies of norbornene.

Goto et.al.[84], by analogy with the behaviour of 5,6-d_2-benzobicyclo (2,2,1) heptane, and Cristol et al.[85] from the behaviour of 5-norbornene-exo-2-acetate, proposed that the base peak in norbornene m/e 66, the $C_5H_6^+$ ion, was formed by a retro-Diels Alder reaction involving specifically carbon atoms 5 and 6 with the attached hydrogen atoms. Dorsey[86] showed the proposal to be correct using norbornene-exo-5-exo-6-d_2. (See Scheme II 2.A.2.) Biemann[87] suggested that the formation of the $C_6H_7^+$ ion, formed by the loss of methyl from the molecular ion, occurred by a 1,7 (or 4,7) bond break followed by migration of a hydrogen atom from the 5 or 6 carbon atom to the 7 carbon atom, (see Scheme II 2.A.4).

Biemann's scheme was subsequently shown to be correct by Dorsey's work with norbornene-exo-5-exo-6-d_2. The deuterium labelling showed no scrambling as feared by Biemann. Dorsey also presented a complete fragmentation scheme for norbornene but he did not discuss supporting evidence.

(b) The mass spectrum of norbornene is shown in Fig. II 2.A.1 and is in good agreement with published data (Steel et al.,[88] Goto et al.[84], Cornu and Massot,[36b] & Dorsey[86]). Table II 2.A.1 lists the eighteen most abundant metastable ion peaks observed in the spectrum, their relative abundance and the fragmentation responsible for their genesis.

Scheme II 2.A.1. shows the fragmentation break down for norbornene based on examination of the metastable ion peaks. From the scheme it can be observed that the molecular ion fragments in four ways:-

(a) by the loss of ethylene to yield the $C_5H_6^{\cdot+}$ ion at m/e 66, the base peak, which in turn fragments by the loss of hydrogen or acetylene.

(b) by the loss of methyl to give the $C_6H_7^+$ ion which undergoes subsequent fragmentation by the loss of hydrogen followed by acetylene.

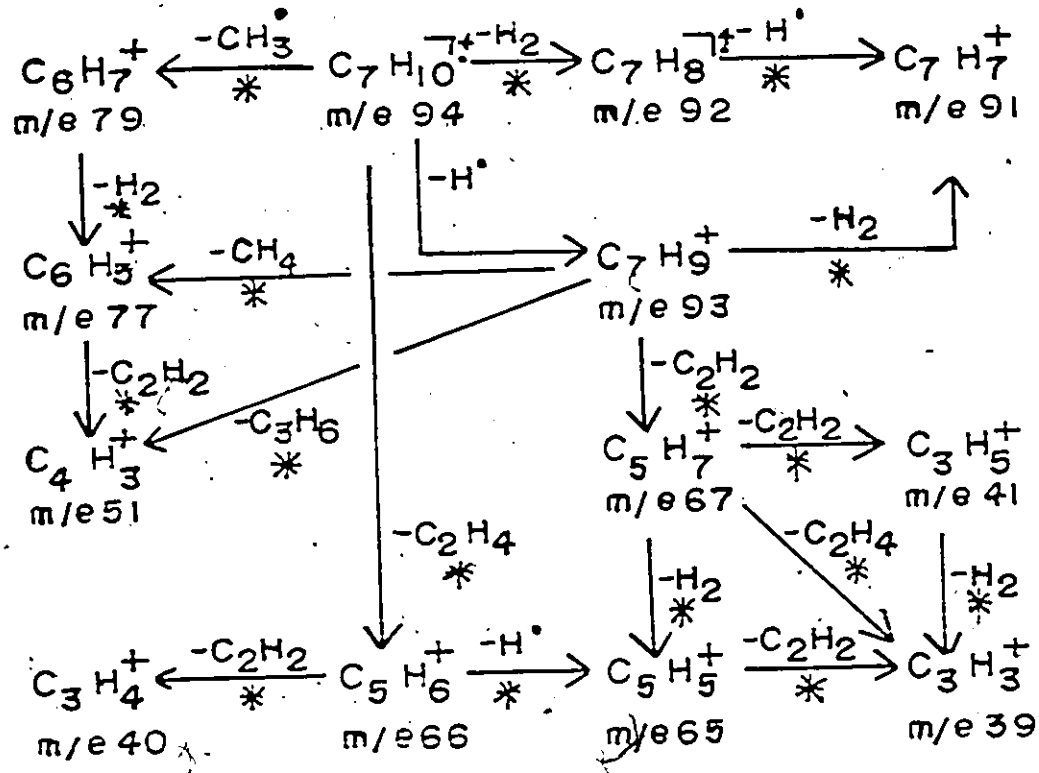
(c) by the loss of a hydrogen atom to yield the $C_7H_9^+$ ion which decomposes by four different pathways.

Table II 2.A.1.

Metastable Ion Peaks Observed in the Mass Spectra of Norbornene and Nortricyclene.

Generating Fragmentation	m/e of m*	Relative Abundance (70eV) Norbornene	Nortricyclene
$[C_5H_5]^+ \rightarrow [C_3H_3]^+ + H_2$	37.2	2.5	4.1
$[C_4H_5]^+ \rightarrow [C_4H_3]^+ + H_2$	49.2	1.1	3.5
$[C_4H_5]^+ \rightarrow [C_2H_3]^+ + C_2H_2$	13.8	1.2	1.0
$[C_5H_5]^+ \rightarrow [C_3H_3]^+ + C_2H_2$	23.4	1.6	2.3
$[C_5H_6]^{+\cdot} \rightarrow [C_5H_5]^+ + H^\cdot$	64.0	100	15
$[C_5H_5]^{+\cdot} \rightarrow [C_3H_4]^{+\cdot} + C_2H_2$	24.2	2.5	2.4
$[C_5H_7]^+ \rightarrow [C_5H_5]^+ + H_2$	63.1	6	7.0
$[C_5H_7]^+ \rightarrow [C_3H_3]^+ + C_2H_4$	22.7	0.5	0.7
$[C_5H_7]^+ \rightarrow [C_3H_5]^+ + C_2H_2$	25.1	1.3	2.7
$[C_6H_5]^+ \rightarrow [C_4H_3]^+ + C_2H_2$	33.8	11.6	2.4
$[C_6H_7]^+ \rightarrow [C_6H_5]^+ + H_2$	75.0	82.0	100[a]
$[C_7H_9]^+ \rightarrow [C_7H_7]^+ + H_2$	89.0	13[b,c]	15[c]
$[C_7H_9]^+ \rightarrow [C_6H_5]^+ + CH_4$	63.8	5	10
$[C_7H_9]^+ \rightarrow [C_4H_3]^+ + C_3H_6$	28.1	0.8	4.0
$[C_7H_9]^+ \rightarrow [C_5H_7]^+ + C_2H_2$	48.2	7.0	2.1
$[C_7H_{10}]^{+\cdot} \rightarrow [C_5H_6]^{+\cdot} + C_2H_4$	46.3	36	34
$[C_7H_{10}]^{+\cdot} \rightarrow [C_7H_8]^{+\cdot} + H_2$	90.0	3	not observed
$[C_7H_{10}]^{+\cdot} \rightarrow [C_6H_7]^+ + CH_3^\cdot$	66.4	<1	30

a Relative abundance in normal spectrum 0.5% bp.
b Relative abundance in normal spectrum 0.08% bp.
c "Flat-Top" metastable, see text for discussion.



Scheme II 2.A.1. Fragmentation Scheme for Norbornene and Nortricyclene.

Some or all of the above fragmentations may go via common intermediates. Several labelled norbornenes, (see Table II 2.A.2) were prepared from the corresponding labelled norbornyl bromides by dehydrobromination, using the method of Stille et al.[89] From Table II 2.A.2 it can be observed that in the case of norbornene-2,3-d_2 and norbornene-2-d_1 the base peak has moved completely from m/e 66 to m/e 68 and m/e 67 respectively, whereas in the case of norbornene-exo-5-exo-6-d_2 the base peak remains at m/e 66. These results confirm

Table II 2.A.2.

Normal and Metastable Ion Peak Intensities for Ethylene Loss in the Mass Spectra of Labelled Norbornenes.

Compound	Relative Intensity of Normal Peaks (corrected for ^{13}C and incomplete labelling)		
m/e	66	67	68
Norbornene	100	—	—
Norbornene-2-d_1 (a)	0	100	—
Norbornene-2,3-d_2 (b)	0	0	100
Norbornene-exo-5-exo-6-d_2 (c)	100	0	0

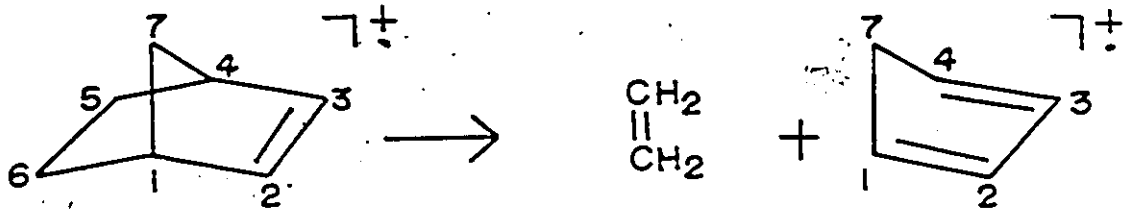
Compound	Relative Intensity of Metastable Ion Peaks*					
	m/e	Rel.Int.	m/e	Rel.Int.	m/e	Rel.Int.
Norbornene	46.3	100	———		———	
Norbornene-2-d_1	47.3	0	45.8	100	———	
Norbornene-2,3-d_2	48.2	0	46.8	0	45.4	100
Norbornene-exo-5-exo-6-d_2	48.2	100	46.8	0	45.4	0

(a) Contains 74% 2-d_1 ; 24% 7,7-d_2 ; 2% d_o

(b) Contains 91% 2,3-d_2 ; 9% 7,7,1-d_3

(c) Contains 79% 5,6-d_2 ; 17.5% 5d_1 ; 3.5% d_o .

*Obtained from the normal spectrum at low eV.(Hitachi RMU-6D)



Scheme II 2.A.2. Ethylene Loss from Norbornene

Dorsey's work, which indicated the formation of the $C_5H_6^{+\cdot}$ ion, m/e 66, from the molecular ion by expulsion of the 5 and 6 carbon atoms and the attached hydrogen atoms, by the retro-Diels Alder reaction (see Scheme II 2.A.2.). The appropriate metastable ion peaks for the ethylene and its labelled analogues lost from the molecular ions of the labelled compounds also further substantiate these results (see Table II 2.A.2.).

The determination of the mechanism for the formation of the $C_6H_7^+$ ion at m/e 79 is hampered in the 70 e.v. spectra by the presence of the neighbouring $C_6H_5^+$ ion peak at m/e 77 , which arises from two fragmentation routes; one involves the loss of a hydrogen molecule from the ion at m/e 79 (M* 75.1) and the loss of methane from the $(M-1)^+$ ion (M* 63.8). The presence of the above $C_6H_5^+$ ions introduces uncertainties into fragment peak height analysis of the deuterium labelled compounds. The metastable ion

peak for this process (M* 66.4) is very weak and in the normal spectrum is masked by the base peak. In the labelled compounds the metastable ions for the loss of methyl and its labelled analogues are too weak even in the defocused mode to allow accurate comparison of their relative intensities. Thus for labelled norbornenes the only available numbers are those for fragment ion peak heights (see Table II 2.A.3.), measured at low electron energies

Table II 2.A.3.

Relative Peak Intensities for Loss of Methyl and Its Deuterated Analogues from the Molecular Ions of Labelled Norbornenes.

Compound	Relative Intensities (corrected for ^{13}C contribution)			
m/e	82	81	80	79
Norbornene-2,3-d_2 [a]	5	60	28	7
Calc. (see text)	3	67.5	29	0.5
Norbornene-exo-5-exo-6-d_2 [b]	0	17	73	10
Calc. (see text)	0	17	71	12
Dorsey [c]	0	34	52	14
Norbornene-2-d_1 [d]	0	15	63	22
Calc. (see text)	0	11	68	22

(a) Contains 91% 2,3-d_2 9% 7,7,1-d_3

(b) Contains 79% 5,6-d_2 17.5% 5d_1 3.5% d_0

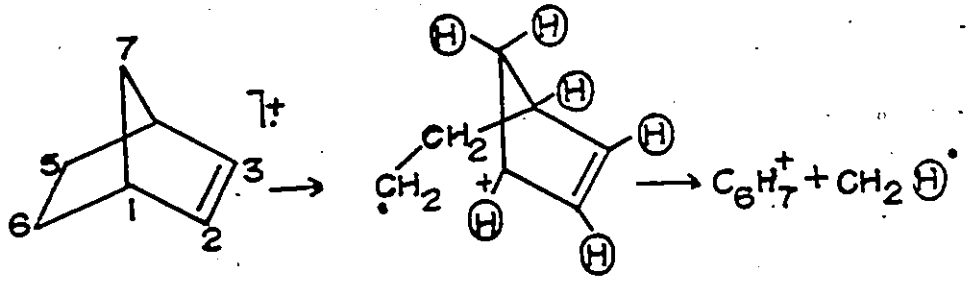
(c) Contains 73% 5,6-d_2 16.9% 5d_1 9.4% d_0

(d) Contains 74% 2d_1 24% 7,7-d_2 2% d_0

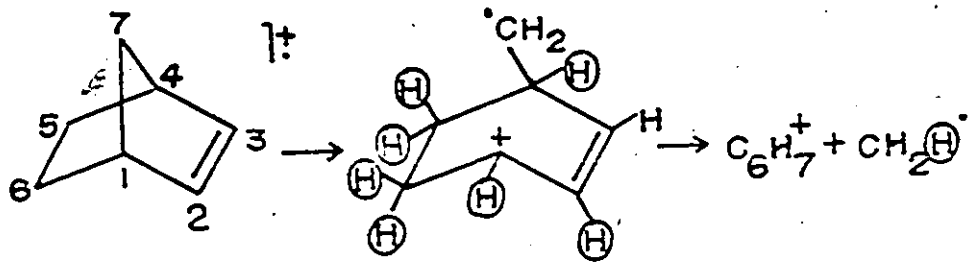
(NOTE: Normal spectrum peaks measured at nominal 12-15 eV corrected for ^{13}C abundance and normalized to 100 units.)

where the $C_6H_5^+$ ion and its labelled analogues are not produced. From these results we can rule out complete randomization of the hydrogen atoms before methyl radical loss. For the dideuterated norbornenes this would require $CH_3:CH_2D:CHD_2$ to be lost in the ratio 7:7:1. The mechanism which involves rupture of the bridge-head bond, C1-C7 (or C4-C7) and loss of the C7 carbon and hydrogen atoms with the third hydrogen atom coming from the 5 or 6 carbon atom, tentively proposed by Biemann[87] and supported by Dorsey[86] from his study on the norbornene-exo-5-exo-6-d_2 , is clearly incorrect. Such a mechanism does not predict CH_2D loss from norbornene-2,3-d_2 and norbornene-2-d_1 as observed here. Dorsey prepared his compound by partial deuteration of norbornadiene; his results for norbornene-exo-5-exo-6-d_2 are in poor agreement with the corresponding results in this work (see Table II 2.A.3).

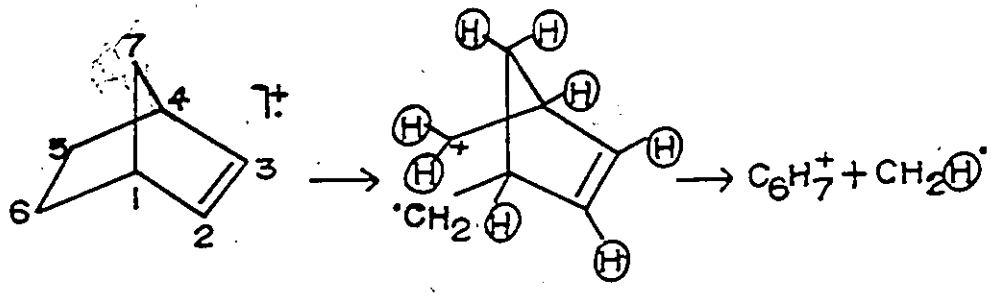
Clearly no single process will account for the relative intensities of the peaks at m/e 79,80 and 81 in the various labelled compounds. Schemes II 2.A.3, 4 and 5 show the three most likely mechanisms for the methyl loss from the molecular ion of norbornene. The first mechanism involves a C1-C6 (or C4-C5) bond break followed by random selection of a hydrogen atom from the cyclopentenyl ring by the departing CH_2 group (C5 or C6), the second involves C1-C7 (or C4-C7) bond break followed by random hydrogen selection by the departing CH_2 group (C7) from the cyclohexenyl ring and the third involves C5-C6 bond rupture followed by random



Scheme II 2.A.3 First Fragmentation Mechanism for Methyl Loss from the Molecular Ion of Norbornene.



Scheme II 2.A.4 Second Fragmentation Mechanism for Methyl Loss from the Molecular Ion of Norbornene.



Scheme II 2.A.5 Third Fragmentation Mechanism for Methyl Loss from the Molecular Ion of Norbornene.

The circled hydrogen atoms are those involved in the random selection.

selection of a hydrogen atom from the rest of the ion by the C5 or C6 methylene.

It could be argued that a summation of the above mechanisms is irrelevant and the mixed methyl and labelled methyl loss arise from an assemblage of ions of different energies which have undergone partial hydrogen scrambling. However in view of the successful analysis for the methyl loss in nortricyclene, (see page 161) it was felt worthwhile to attempt to relate the observations to a mechanism or mechanisms.

A summation of 15% , 55% and 30% of the three processes respectively gives good agreement (see Table II 2.A.3) with the experimental results for norbornene-exo-5-exo-6-d_2 and norbornene-2-d_1 , but poor agreement for norbornene-2, 3-d_2 . The limitation of this procedure is shown by the insensitivity of the calculated peak heights to quite large changes in the chosen proportions of each mechanism.

The third method of fragmentation of the molecular ion of norbornene is by the loss of a hydrogen atom to give the $C_7H_9^+$ ion at m/e 93 which is the precursor of many minor fragment ions. The process m/e 93 to m/e 91, yielding the $C_7H_7^+$ ion, gives rise to a prominent flat top metastable ion peak centered at m/e 89.1 (see page 170 for discussion on this point). Owing to the lack of a suitable mass spectrometer having a metastable defocusing facility and high

sensitivity it was not possible further to investigate this fragmentation route.

B. Mass Spectrum of Nortricyclene (C_7H_{10}, tricyclo (1,1,$1^{2,6}$,$0^{2,6}$)heptane)

The mass spectrum of nortricyclene has not been previously reported.

The mass spectrum of nortricyclene is shown in Fig. II 2.A.2. The eighteen most abundant metastable ion peaks observed in the spectrum, their relative abundance and the fragmentations responsible for their genesis are shown in Table II 2.A.1 together with those of norbornene for ease of comparison.

Scheme II 2.A.1 shows the fragmentations of norbornene and nortricyclene. The nortricyclene molecular ion, like that of norbornene, fragments in three ways: (a) by the loss of ethylene to yield the $C_5H_6^{\cdot+}$ ion (m/e 66), which in turn fragments further by the loss of hydrogen or acetylene. (b) by the loss of a methyl radical to give the $C_6H_7^+$ ion (m/e 79), the base peak, which undergoes subsequent fragmentation by the loss of hydrogen followed by acetylene. (c) by the loss of a hydrogen atom to yield the $C_7H_9^+$ ion which decomposes by four pathways as shown.

Nortricyclene was prepared from the tosyl-hydrazone of norcamphor by the Bamford-Stevens reaction (an elimination

process) under aprotic conditions.[31] Nortricyclene-3,3-d_2 was obtained from the corresponding norcamphor-3,3-d_2 prepared from norcamphor by exchange in basic deuterium oxide. This reaction has been investigated by Nickon and Werstiuk [31], who demonstrated by deuterium labelling on the 6 carbon atom, that a specific elimination reaction was involved. However it was observed here that the yield of nortricyclene-3,3-d_2 was unpredictable and retention of label was variable. Table II 2.B.1 contains the observed relative intensities of the daughter and metastable ion peaks for ethylene loss for a mixture of nortricyclene-3, 3-d_2 (77%) and nortricyclene-3-d_1 (23%); the latter peaks were observed to be independent of electron energy (in the range 12 to 30 e.V.) and acceleration potentials from 500 to 3,000V. This indicates that the fragmentation process is independent of energy and time. The five metastable ion peaks for the loss of ethylene and labelled ethylene [d_2-$(M-C_2H_4)$:$(M-C_2H_3D)$:$(M-C_2H_2D_2)$] and [d_1-$(M-C_4H_4)$: $(M-C_2H_3D)$] overlap only at their fringes and their relative abundances easily can be separately measured. Completely random selection of the hydrogen atoms in the ethylene loss does not occur (see Table II 2.B.1), this would require that in the dideuterated nortricyclene the metastable ion peaks for the loss of ethylene and its labelled analogues be in the ratio 5:8:1 . If the loss of ethylene from the

Table II 2.B.1.

Normal and Metastable[a] Peak Intensities for Ethylene Loss in the Mass Spectrum of Labelled Nortricyclene[b].

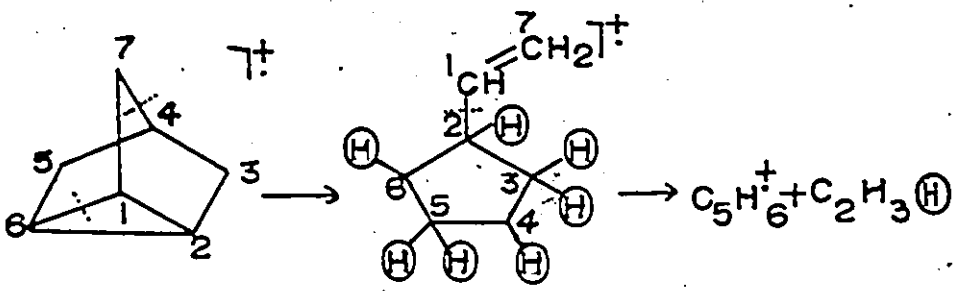
Relative Peak Heights (corrected for ^{13}C) m/e	68	67	66
70 eV	36	30	34
15 eV	38	28	34
12.5 eV	36	29	35
11 eV	38	28	34
Calculated peak heights (see Mechanism, Scheme II 2.B.1)	37	30	33

Relative metastable intensities for	$[M-C_2H_4]^+$	$[M-C_2H_3D]^+$	$[M-C_2H_2D_2]^+$
m/e	48.2	46.8	45.4
Nortricyclene-3,3-d_2	10	4.4	7
Predicted by Mechanism (Scheme II 2.B.1 and text)	10	4.0	7

	$[M-C_2H_4]^+$	$[M-C_2H_3D]^+$
m/e	47.3	45.8
Nortricyclene-3-d_1	22	15
Predicted by Mechanism (Scheme II 2.B.1 and text)	20	15

(b) Mixture of norticyclene-3,3-d_2 (77%) and nortricyclene-3-d_1 (23%).

(a) Measured in normal spectrum with electron energies 12-30V; the relative intensities were not affected by electron energy nor by acceleration potential (500-3,000 volts). The same results were observed for defocused metastables at 70 eV.



Scheme II 2.B.1 Fragmentation Mechanism for Ethylene Loss from the Molecular Ion of Nortricyclene.

molecular ions of norbornene and nortricyclene takes place via a common intermediate then nortricyclene must undergo isomerization to norbornene before it fragments by a retro-Dields Alder reaction. Two feasible mechanisms for the isomerization are: (a) fission of the C1-C2 bond followed by hydrogen migration from C7 to C2 or from C3 to C1; this process can (by symmetry) take place in three equivalent ways. The ethylene losses for the resulting intermediate, the molecular ion of norbornene-d_2, would be in the ratio $C_2H_4:C_2H_3D:C_2H_2D_2$ = 1:1:1 (likewise for the d_1 compound $C_2H_4:C_2H_3D$ = 1:1) (b) fission of the C1-C2 bond followed by hydrogen migration from C2 to C1 accompanied by a C3 to C2 hydrogen transfer. Fragmentation of the norbornene produced would yield the ratio $C_2H_4:C_2H_3D:C_2H_2D_2$ = 2:0:1 i.e., no loss of C_2H_3D .

A combination of two parts of (a) plus one part of

(b) gives numbers in good agreement with experiment. An alternative mechanism is that shown in Scheme II 2.B.1., which gives excellent agreement with experimental results. The tricyclic system is envisaged as opening (in three equivalent ways) to produce an ion which is shown as a vinyl cyclopentene; if the vinyl group then selects any one of the seven cyclopentene ring hydrogens before it departs as ethylene, then the predicted metastable ion peak abundance ratios for the two labelled compounds are as shown in Table II 2.B.1. The latter mechanism is to be preferred on grounds of simplicity, but at the time this work was carried out there was no well authenticated precedent for hydrogen scrambling in a hydrocarbon molecular ion which is restricted to some but not all of the hydrogen atoms. However more recent work on norborneol (described in this thesis) has provided supporting evidence for the above preference (see page 206 for discussion of this point).

Using the latter mechanism and summing the appropriate values for the mono- and dideuterated nortricyclenes, good agreement was obtained between the calculated and observed relative peak intensities (see Table II 2.B.1.). It is worth stressing that this problem could only be attacked by measurement of the relative abundances of the metastable ion peaks; normal ion peak abundances in these incompletely labelled compounds are impossible to relate to a fragmentation mechanism.

The "defocused" metastable ions for the formation of the $C_6H_7^+$ ion, the base peak, were intense and easily measured. The relative abundance of these metastable ion peaks for nortricyclene-3,3-d_2 and nortricyclene-3-d_1 are included in Table II 2.B.2, these results are compatible with completely random hydrogen selection in the methyl loss from the molecular ion in the first field free region.

Table II 2.B.2.

Normal and Metastable Ion Peak Intensities for the Loss of Methyl and its Deuterated Analogues from the Molecular Ions of Labelled Nortricyclenes.

Compound	Normal Peaks (corrected for ^{13}C contribution)		
m/e.	81	80	79
Nortricyclene-3,3-d_2 [e]	53 ± 1	34 ± 1	13 ± 1
Calc. (see text)	52	35	13
Nortricyclene-3-d_1 [e]	0	69 ± 1	31 ± 1
Calc. (see text)	0	69	31
Metastables	[M-CH_3]	[M-CH_2D]	[M-CHD_2]
m/e	68.3	66.7	65.2
Nortricyclene-3,3-d_2 [f]			
(defocused 70 eV)	7.0	6.8	1.5
(normal spectrum 15 eV)	7.0	7.0	1.5

(e) Values obtained by extrapolation, from Fig. II 2.B.1.

(f) Contains 77% 3,3-d_2; 23% 3-d_1. The defocused metastables for the d_1 compound were too small to be accurately measured. (Normal spectrum peaks measured at 12-15 eV and normalized to 100 units.)

The method of preparation always yielded a mixture of d_1 and d_2 nortricyclene. This made it difficult to draw conclusions from the relative abundances of the peaks at m/e 79, 80 and 81. The amounts of nortricyclene-3,3-d_2 in the mixtures were in the range 20 to 80%, the balance being mainly nortricyclene-3-d_1. Fig. II 2.B.1 shows the relative intensities of the fragment ion peaks m/e 79, 80 and 81 (corrected for ^{13}C natural abundance and small contributions from unlabelled nortricyclene) plotted against percentage nortricyclene-3,3-d_2 content for a variety of mixtures. These fragment ion peaks were measured at low electron energies (nominal voltages 12 to 15 eV) and within this range their relative abundances remained constant for a given mixture. At higher eV values the loss of hydrogen from the daughter ion peaks became apparent. By extrapolation of the straight line graphs a reasonably accurate estimate for the peak heights of the pure mono and di-deuterated compounds was obtained; these values are shown in Table II 2.B.2. For pure nortricyclene-3-d_1, the relative peak intensities are very close to the values for random selection of hydrogen and deuterium atoms in the methyl loss (CH_3:CH_2D = 7:3), observed 6.9:3.1. However, the results for pure nortricyclene-3,3-d_2 are far from the random selection values (CH_3:CH_2D:CHD_2 = 7:7:1), observed 4.1:2.6:1. That the ratios of daughter ion peaks and

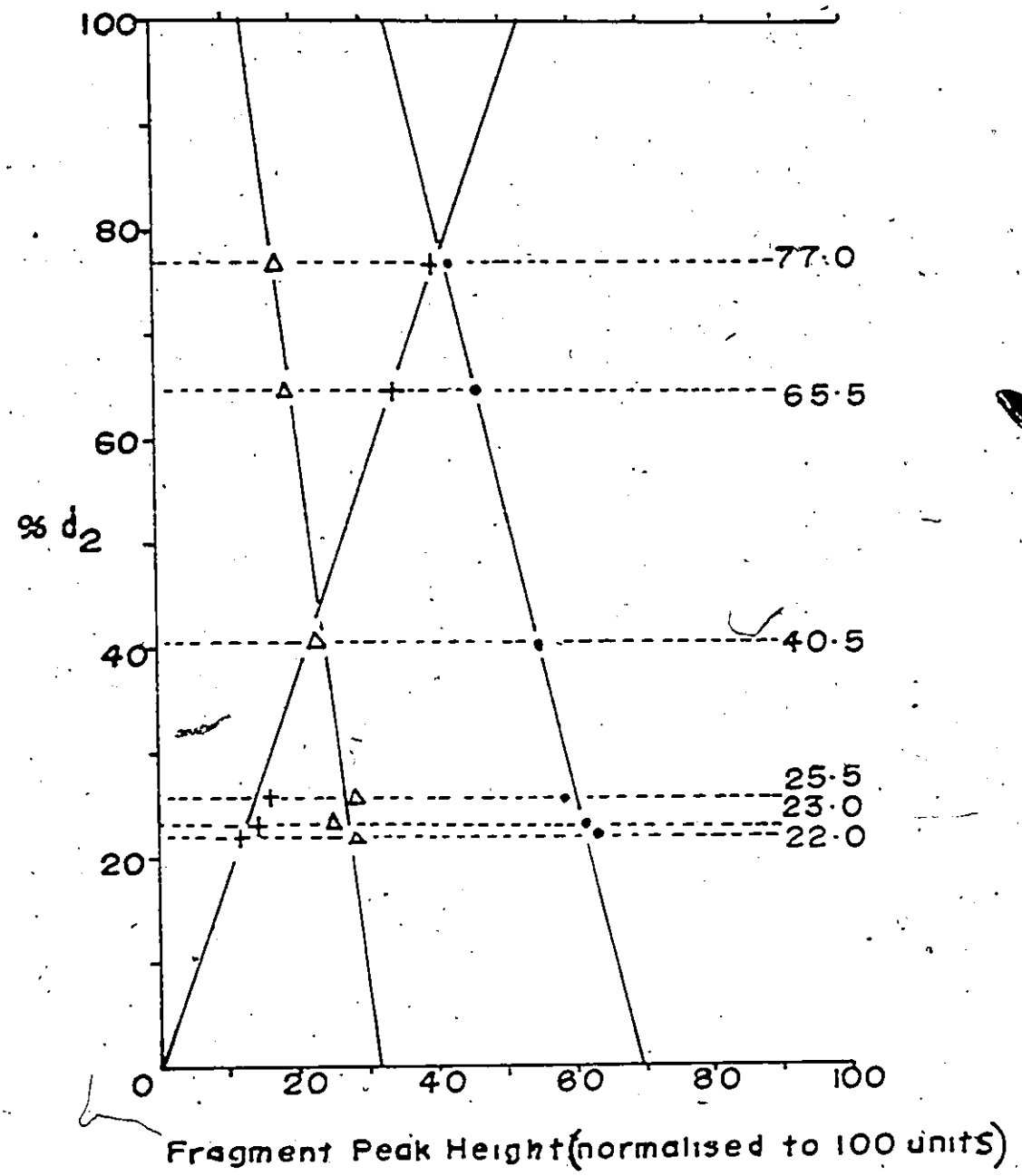


Fig. II 2.B.1. Relative Intensities of the Fragment Ion Peaks m/e 79,80 and 81, for Mixtures of 3,3-d_2 and 3-d_1 Nortricyclene. Δ = m/e 79; ● = m/e 80; + = m/e 81.

metastable ion peaks for 3,3-d_2 nortricyclene are not the same indicates that the same processes or ratio of processes which occur in the ion source do not occur in the first field free region. Therefore the methyl loss either arises from (1) at least two processes where the precursor ions have different life times or (2) a process involving incomplete randomisation occurring in the source (rapidly dissociating, high energy ions), tending towards complete randomisation in the first field free region (slowly dissociating, low energy ions). It has been previously shown from metastable ion analysis that in the first field free region the methyl loss involves completely random selection of the hydrogen atoms. Considering case (1), that at least two processes must be occurring in the source, a summation of three parts methyl loss involving completely random selection of the hydrogen atoms plus one part involving a specific loss of only CH_3 and CHD_2 for nortricyclene-3,3-d_2 gives good agreement with experimental results. It is proposed that in the latter process a methylene group 3 or 5 or 7 is lost with the third hydrogen atom coming from the 1,2,6 or 4 carbon atom (although the latter position is improbable). A similar treatment for nortricyclene-3-d_1 gives good agreement with the experimental data shown in Table II 2.B.2.

Although case (1) can be manipulated to give excellent agreement with the experimental results, at the time this work was carried out there was no direct evidence to support two distinct fragmentation processes. However the later work on norborneol has yielded some evidence in support of this argument (see page 202).

The molecular ion fragments by the loss of a hydrogen atom to give the $C_7H_9^+$ ion, at m/e 93, which is the precursor for many minor fragment ions (see Table II 2.A.1 and Scheme II 2.A.1). The process m/e 93 to m/e 91 yielding the $C_7H_7^+$ ion, gives rise to a prominent flat top metastable ion peak centered at m/e 99.1 , which is identical with the same metastable ion peak in norbornene. Owing to the lack of a mass spectrometer having suitable metastable ion defocusing facilities and high sensitivity it was not possible to investigate in detail by labelling experiments the fragmentations of the ion at m/e 93.

Secondary Fragmentations: the secondary fragmentations also were not examined in detail, but from the metastable ion study (in the unlabelled compound) it was observed that the $C_6H_7^+$ ion formed by the loss of methyl from the molecular ion further fragments as shown by Scheme II 2.A.1 in a similar manner to norbornene. Similarly, the secondary fragmentation processes of the $C_5H_6^{\cdot+}$ ion are shown in Scheme II 2.A.1 and correspond to those observed for the $C_5H_6^{\cdot+}$ ion in norbornene.

From the detailed investigation described above it is clear that a different mechanism operates for the loss of ethylene and methyl radical from each isomer. This result indicates that common intermediates cannot be formed prior to the fragmentation by loss of ethylene or methyl from these isomeric hydrocarbons. In the case of the hydrogen loss from the molecular ions no detailed investigation was possible; however since the $C_7H_9^+$ ions fragment by identical routes in both compounds (as shown by metastable ion studies on the unlabelled compounds, see Scheme II 2.A.1) and the formation of the $C_7H_7^+$ ion from $C_7H_9^+$ species in each compound is accompanied by identical energy releasing metastable ions, it is not unreasonable to propose that the $(M-1)^+$ ion is a common intermediate.

The appearance potentials and heats of formation of the $C_5H_6^+$, $C_6H_7^+$ and $C_7H_9^+$ ions in norbornene and nortricyclene were determined in order to see if the same ion is formed at threshold in each case.

The appearance potentials (A.P.) of the various ions are shown in Table II 2.B.3, these were measured on a quadrupole mass spectrometer fitted with an electron impact source having a double hemispherical electron monochromator[71].

The error due to the kinetic shift will be small because the repeller potential was only a few millivolts and the ion acceleration potential was small ~ 50 v.

Table II 2.B.3.

Appearance Potentials and Heats of Formation for the Ions $[C_7H_{10}]^+$, $[C_7H_9]^+$, $[C_6H_7]^+$ and $[C_5H_6]^+$ in the Mass Spectra of Norbornene and Nortricyclene.

Compound	Ion	Appearance Potential (eV ± 0.01)	ΔH_f (kcal.mole^{-1})
Norbornene	C_7H_{10}	——	28.9 (see text)
Nortricyclene	C_7H_{10}	——	23.8 (see text)
Norbornene	$[C_7H_{10}]^+$	8.80(8.95[88]; 8.81[90]; 8.82[72]; 8.83[91])	232
Nortricyclene	$[C_7H_{10}]^+$	8.92(9.02[91])	230
Norbornene	$[C_7H_9]^+$	11.0(11.5[88])[b]	232 ± 5 [b]
Nortricyclene	$[C_7H_9]^+$	11.3 [b]	233 ± 5 [b]
Norbornene	$[C_6H_7]^+$	10.46(11.2[88])	238
Nortricyclene	$[C_6H_7]^+$	10.17	226
Norbornene	$[C_5H_6]^+$	9.22(9.58[88])	229 [a]
Nortricyclene	$[C_5H_6]^+$	9.44	229 [a]
[Cyclopentadiene	$[C_5H_6]^+$	8.56(8.57[90]; 8.55[92])	229]

(a) It is assured that this ion is [cyclo-C_5H_6]$^+$ (see text)

(b) Appearance potentials determined by extrapolated voltage difference method, a less accurate method.

There may however be an error due to the kinetic shift in the case of the A.P. of the $C_7H_9^+$ and $C_7H_7^+$ ions which were measured on a conventional mass spectrometer, using the A.P. of the $C_6H_7^+$ ion, measured by the preceding method, as an internal standard (see discussion on measurement of I.P. and

A.P. on page 114). The value for the A.P. of the molecular ion of norbornene is in excellent agreement with the values obtained from photoionization[90] and photoelectron spectroscopy[72,91] for nortricyclene the agreement is fair[91].

In order to calculate the heat of formation of the molecular ions of the two compounds from their A.P. the heats of formation of the compounds are required.

$$\Delta H_f\ C_7H_{10}^{+\cdot} = A.P._{C_7H_{10}}^{+\cdot} + \Delta H_f(\text{norbornene})$$

$$\Delta H_f\ C_7H_{10}^{+\cdot} = A.P._{C_7H_{10}}^{+\cdot} + \Delta H_f(\text{nortricyclene})$$

For norbornene three values have been reported; 31 ± 4 kcal.mole^{-1} [88] 24.7 kcal.mole^{-1} [93] and 22.3 kcal.mole^{-1} [94]. Only the first of these leads to a reasonable value for the heat of formation of the fragment ion $C_5H_6^{+\cdot}$. This ion produced by the retro-Diels Alder reaction must almost certainly be the cyclo-$C_5H_6^{+\cdot}$, whose heat of formation is accurately known. The measured electron impact value for the A.P. of cyclo-$C_5H_6^{+\cdot}$ ion is in excellent agreement with those obtained by photoionization[90] and photoelectron spectroscopy[92]. The heat of formation of norticyclene has not been determined, but was estimated by Turner et al.[93] who used a value of -0.9 kcal.mole^{-1} (obtained from

equilibrium data [95]), for the free energy change for the isomerization of norbornene to nortricyclene. By assuming only a small entropy change for the isomerization, they estimated the heat of formation of nortricyclene by adding the free energy change for the isomerization to the heat of formation of norbornene. In view of the uncertainty of heats of formation of the isomeric hydrocarbons, norbornene and nortricyclene, their heats of formation were determined on the very reasonable assumption that the $C_5H_6^+$ ions are cyclo-$C_5H_6^+$ ions in both compounds. Using this assumption, the heat of formation of norbornene was found to be 28.9 kcal.mole^{-1} and that of nortricyclene was determined as 23.8 kcal.mole^{-1}.

If, as previously discussed, the $(M-1)^+$ ion is common to both compounds and the $C_5H_6^+$ ion is cyclopentadiene in each case, then the energetics for the $(M-1)^+$ and $[(M-1)-H_2]^+$ ions should be the same in both compounds. If the energetics for the $C_7H_9^+$ and $C_7H_7^+$ ions are the same, then this will be a check on the structure of the $C_5H_6^+$ ion and supporting evidence for a common intermediate.

The A.P. of the $C_7H_9^+$ and $C_7H_7^+$ ions were not determined using the electron monochromator (because of resolution difficulties in the quadrupole mass spectrometer to which it was attached), but were determined by the extrapolated voltage difference method of Warren[96], using

the A.P. of the $(M-CH_3)^+$ peak as an internal reference voltage. From the measured appearance potentials (Table II 2.B.3) the heat of formation of the $C_7H_9^+$ ions in norbornene and nortricyclene were calculated using the expression shown below:

$$\Delta H_f(C_7H_9^+) = A.P.(C_7H_9^+) + \Delta H_f(\text{isomer}) - \Delta H_f(H^+)$$

and the heats of formation were found to be 232±5 and 233±5 k cal.mole^{-1} respectively.

The appearance potentials of the $C_7H_7^+$ ions are the same as those of their precursor ions in their respective compounds; the energy release was determined from the width of the flat top metastable ions, making use of the equation of Beynon and Fontaine [46],

$$d = \frac{4m_2^2}{m_1}\left(\frac{uT}{eV}\right)^{1/2}$$

where d = width of flat top metastable ion in a.m.u.
u = mass ratio $(m_1-m_2)/m_2$
eV = ion acceleration potential in electron volts
T = energy release in electron volts

for the loss of a hydrogen molecule in the formation of the $C_7H_7^+$ ion from the $C_7H_9^+$ ion is 14±2 kcal.mole^{-1} in both compounds. The process $C_7H_9^+ \rightarrow C_7H_7^+ + H_2$ is remarkable in

that it is the only exothermic H_2 loss process yet observed for hydrocarbons. The heats of formation of the benzyl and cyclo-$C_7H_7^+$ cations have been determined as 212 and 213 kcal.mole^{-1} respectively [97]. The energy data for the formation of the $C_7H_7^+$ ion is summarised below:

$$C_7H_9^+ = C_7H_7^+ + H_2$$

	ΔH_f	ΔH_f
norbornene	232±5	212 or 213
nortricyclene	233±5	212 or 213

the energy release for both compounds is 14±2 kcal.mole^{-1}. It would therefore appear that much or all of the exothermicity of this dissociation is converted into translational kinetic energy and is observable as metastable ion peak broadening.

These results indicate that the $C_7H_9^+$ ion is indeed a common intermediate and provides additional support for the assumption that the $C_5H_6^{+\cdot}$ ions are cyclo-$C_5H_6^{+\cdot}$ in both compounds.

Using the calculated heats of formation for the isomeric hydrocarbons in conjunction with Bensons additivity data [98] the strain energies for norbornene and nortricyclene were calculated to be 29 and 46.2 kcal.mole^{-1} respectively.

The latter value is in fair agreement with Klopman's[99] estimated value of 40 kcal.mole^{-1}.

Using the above heats of formation of the hydrocarbons in conjunction with the appearance potentials of the $C_6H_7^+$ ions the heats of formation of these ions in norbornene and nortricyclene were found to be 238 and 226 kcal.mole^{-1} respectively.

The energetic studies are compatible with the same $C_5H_6^+$ and $C_7H_9^+$ ions being present in both norbornene and nortricyclene, but suggest the presence of different $C_6H_7^+$ ions in each of the compounds. Harrison et al.[100] have determined the heats of formation of $C_6H_7^+$ ions derived (by methyl loss) from a variety of C_7H_{10} molecules. Their results indicate that $C_6H_7^+$ ions produced from seven membered ring C_7H_{10} isomers have heats of formation of about 224 kcal.mole^{-1} some 10 kcal.mole^{-1} lower than those observed for methyl cyclohexadiene and dimethyl cyclopentadienes. The value for the $C_6H_7^+$ ion formed from norbornene falls in the latter group whereas the value for the ion formed from nortricyclene falls within the cycloheptyl group of compounds.

There has been considerable interest in comparing metastable abundance ratios for competing dissociations of isomeric ions. Shannon and McLafferty[58] and other workers[59-63] have concluded that isomeric ions which decompose by competing metastable reactions have the same

structure if their metastable abundance ratios are the same, whereas isomeric ions of different structure show different metastable abundance ratios. Yeo and Williams[64] have shown that the metastable abundance ratio for competing reactions will be a function of internal energy and thus ions of the same structure will not display the same metastable abundance ratios if they have widely different energy contents.

In Table II 2.A.1 it can be observed that the ratio of the (70 eV) metastable ions for the dissociation of the $C_5H_6^{+\cdot}$ ions by the loss of hydrogen and acetylene are approximately 40:1 for norbornene and ≯ 6:1 for nortricyclene. For cyclopentadiene the ratio was found to be 30:1 . This result also provides support for the proposal that the ion at m/e 66 in the norbornene mass spectrum is the cyclo-$C_5H_6^{+\cdot}$ ion, but no support for the same ion in nortricyclene.

In the mass spectrum of cyclopentadiene the base peak is the $(M-1)^+$ ion, but in the spectra of norbornene and nortricyclene there are only small peaks at m/e 65 . Therefore most of the $C_5H_6^{+\cdot}$ daughter ions have insufficient energy to dissociate in the source. The metastable ratios are different, but the ions are believed to be the same; the difference presumably therefore, lies in the energy content of the ions and thus the metastable abundance ratio rule is an inconclusive test.

The following conclusions have been drawn from the combined information obtained from metastable ions (unlabelled compounds), relative abundance of peaks and metastable ions in the labelled compounds and from the energetics for the three fragmentation pathways of the molecular ions of norbornene and nortricyclene:

(a) the $C_5H_6^{+\cdot}$ ion; (1) the $C_5H_6^{+\cdot}$ ions arise from different precursor ions, by different mechanisms. (2) the fragmentations of the $C_5H_6^{+\cdot}$ ions are similar but (3) metastable ion peak ratios are dissimilar. (4) their heats of formation are assumed to be the same. These ions are probably the cyclo-$C_5H_6^{+\cdot}$ ions with different energies.

(b) the $C_6H_7^+$ ions; (1) the $C_6H_7^+$ ions occur from different precursor ions, by different mechanisms in each isomer (2) the fragmentations of the $C_6H_7^+$ ions are similar (3) there are no measurable metastable ion peaks (4) the heats of formation are different. These ions are probably a mixture of different structures. Those which dissociate by hydrogen loss may be common to both norbornene and norticyclene.

(c) the $C_7H_9^+$ ion; (1) the fragmentations of the $C_7H_9^+$ ions are similar (2) metastable ratios are dissimilar (3) heats of formation are the same within experimental error (4) same exothermicity for H_2 loss. These ions probably have the same structure (a common intermediate) but different energy contents.

The results obtained in this work show that the difference in the relative ion abundances in the mass spectra of norbornene and nortricyclene are not due to the difference in the rates of formation and dissociation of common intermediates, but are due to the difference in rates of formation of the $C_5H_6^+$ ions relative to the $C_6H_7^+$ ions in the two isomers. In norbornene the ethylene loss occurs by the rapid retro-Diels-Alder process, which requires no rearrangement; whereas the methyl loss in norbornene, and the methyl and ethylene losses in nortricyclene occur via slower, low energy rearrangement processes. The metastable widths for the loss of ethylene from norbornene and nortricyclene were observed to be 0.4 amu and 0.5 amu which may be a reflection of the different mechanisms. The following general approach has been used in the interpretation of the mass spectral fragmentation mechanism of the isomeric hydrocarbons, norbornene and nortricyclene.

Daughter ion abundances sample all ions which dissociate in the source from their genesis to approximately 10^{-6} sec; these are made up of all short lived ions (probably specific fragmentations) and some relatively long lived ions. Metastable ion abundances sample all ions which dissociate within a narrow time interval (say 1-2μ sec) and are long lived ions only; many have relative abundances easily reconciled with simple mechanisms (e.g., McLafferty rearrangement[42], scrambling

etc). The general approach is to try a mechanism which fits the metastable ion abundances and "subtract" these from the daughter ion-intensities in some chosen proportions; then try to fit the residue to another simple or sensible mechanism.

3. Mass Spectrum of Norborneol ($C_7H_{11}OH$, bicyclo (2,2,1) heptane-2-ol)

Introduction

The initial reason for studying the fragmentation mechanism of norborneol was to try to locate the position of deuterium in the molecule from its mass spectrum, because it can be used as a precursor in the preparation of labelled norbornyl chlorides. It quickly became apparent that the mass spectrum was rich in fragmentation pathways of which only a few have been even partially studied[51,101,102] by deuterium labelling.

(a) Review of previous studies of the mass spectrum of norborneol: The mass spectra of exo and endo norborneol (Fig. II 3.1) have been previously reported by several authors[84, 101, 102, 103]. The base peak m/e 94, $C_7H_{10}^{+\cdot}$ arises from the loss of a water molecule from the molecular ion. Kwart and Blazer[101] proposed that the water loss involves extensive rearrangement of the molecular ion, but that the hydroxyl hydrogen is always lost; they suggest norbornene is the daughter ion formed, which then

undergoes its characteristic retro-Diels Alder fragmentation. This is in contrast with the proposals of Nurski and Klasinc[102], that the water loss occurs by a specific 1,3 elimination and possibly a 1,4 elimination.

The second most intense peak m/e 67, $C_5H_7^+$ Kwart and Blazer[101] suggest, results from a two step fragmentation involving the loss of a methyl radical (3-C) and then CH_2O (2-C). From high resolution studies these authors showed that the ion at m/e 57 contained oxygen and they proposed that it was formed by the loss of two hydrocarbon fragments without rearrangement of the carbon skeleton (i.e. a process similar to that observed in cyclohexanol[104a] and cyclopentanol[104b]).

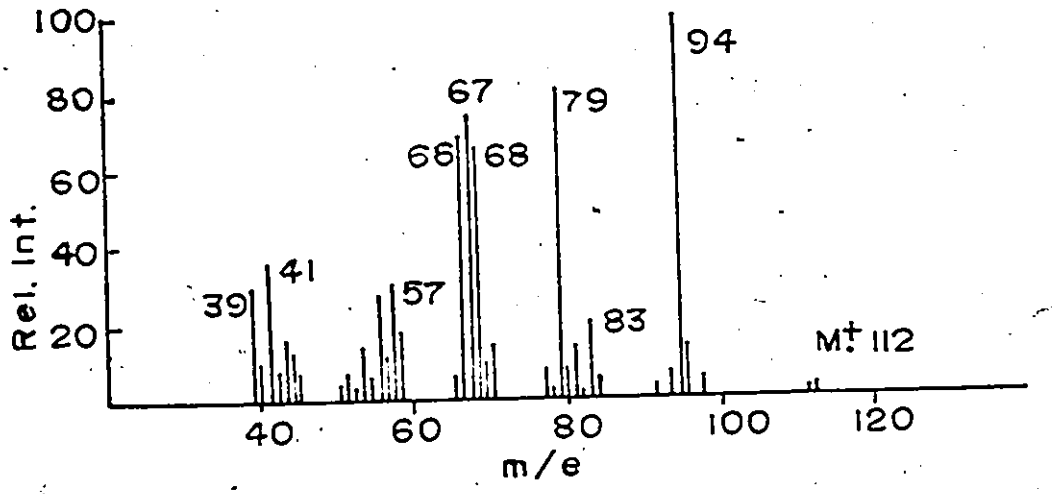


Fig. II 3.1. Mass Spectra of exo and endo Norborneol.

(b) The mass spectra of exo and endo norborneol are identical and are shown in Fig. II 3.1; they are in good agreement with previously published data[84,101,103]. Table II 3.1 lists the nineteen most intense metastable ion peaks in the normal mass spectrum of the compounds, their relative abundances (which are almost identical) and the fragmentations responsible for their genesis.

Schere II 3.1 (not a mechanistic scheme) shows the fragmentation of exo and endo norborneol based on metastable ion peaks. The presence of the ions at m/e 83 and 84 are included since they can only arise directly from the molecular ion.

From Scheme II 3.1 it can be observed that the molecular ion fragments in three or possible four ways: (a) by the loss of water to give a $C_7H_{10}^{+\cdot}$ ion (which further fragments by the loss of ethylene, acetylene and a methyl radical) (b) by the loss of 28 amu to yield an ion at m/e 84, (nothing further is known about this species) (c) by the loss of 29 amu to give the ion at m/e 83 (which decomposes by the loss of hydrogen, ethylene and acetylene) (d) the ion at m/e 67 (which fragments by ethylene and acetylene loss) may also arise directly from the molecular ion by loss of $C_2H_4OH^{\cdot}$ therefrom (by analogy with exo-2 norbornyl chloride).

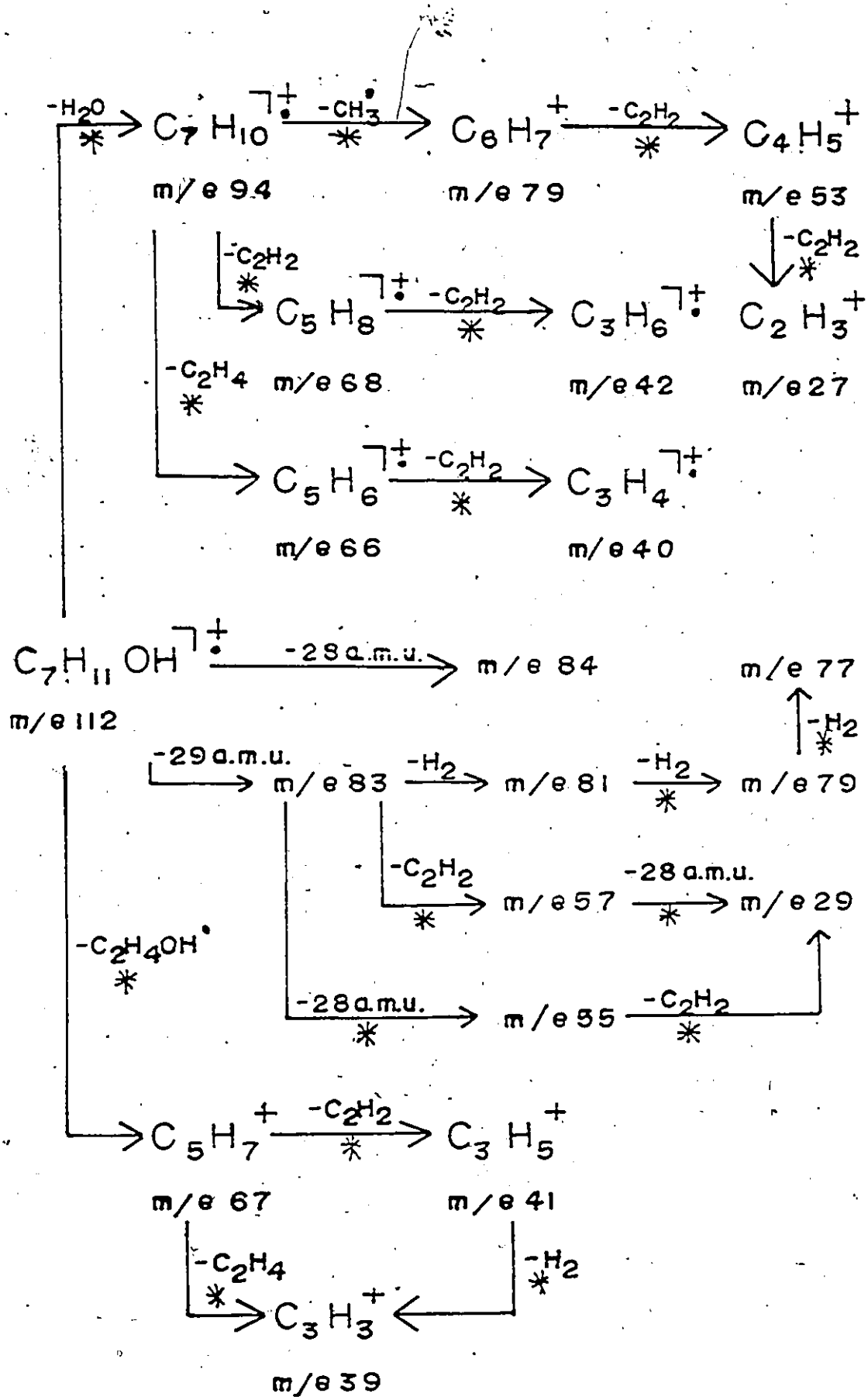
Table II 3.1

Metastable Ion Peaks† Observed in the Mass Spectra of exo and endo Norborneol.

Generating Fragmentation	Metastable Peaks m/e Obs.	Relative Abundance exo	endo
$C_4H_5^+ \rightarrow C_2H_3^+ + C_2H_2$	13.3	0.7	1.5
$C_3H_5O^+ \rightarrow CHO^+ + C_2H_4$	14.8	Weak	
$C_4H_7^+ \rightarrow C_2H_5^+ + C_2H_2$	15.3	1.1	1.0
$C_5H_7^+ \rightarrow C_3H_3^+ + C_2H_4$	22.7	1.0	0.8
$C_5H_6^{+\cdot} \rightarrow C_3H_4^{+\cdot} + C_2H_2$	24.2	1.2	1.3
$C_5H_7^+ \rightarrow C_3H_5^+ + C_2H_2$	25.1	2.6	2.8
$C_5H_8^{+\cdot} \rightarrow C_3H_4^{+\cdot} + C_2H_4$	27.0	Very Weak	
$C_6H_7^+ \rightarrow C_4H_5^+ + C_2H_2$	35.6	0.7	0.8
$C_6H_{11}^+ \rightarrow C_4H_7^+ + C_2H_4$	36.4	6.6	6.9
$C_3H_5^+ \rightarrow C_3H_3^+ + H_2$	37.1	4.7	5.4
$C_5H_7O^+ \rightarrow C_3H_5O^+ + C_2H_2$	39.1	0.6	0.6
$C_7H_{12}O^{+\cdot} \rightarrow C_5H_7^+ + C_2H_5O^\cdot$	40.0	Very Weak	
$C_7H_{12}^{+\cdot} \rightarrow C_5H_8^{+\cdot} + C_2H_4$	46.3	2.3	1.7
$C_7H_{12}^{+\cdot} \rightarrow C_5H_8^{+\cdot} + C_2H_2$	49.2	Weak	
$C_5H_7^+ \rightarrow C_5H_5^+ + H_2$	63.1	8.3	9.5
$C_7H_{10}^{+\cdot} \rightarrow C_6H_7^+ + CH_3^\cdot$	66.4	100*	100*
$C_6H_7^+ \rightarrow C_6H_5^+ + H_2$	75.0	15.0	15.0
$C_7H_9^+ \rightarrow C_7H_7^+ + H_2$	89.0 (Flat Top)	3.0	3.1
$C_7H_{12}O^{+\cdot} \rightarrow C_7H_{10}^{+\cdot} + H_2O$	78.9	(only studied in the defocused mode)	

* 0.1% of base peak.

† Obtained from the normal spectrum run at 70 eV. (Hitachi RMU-6D)



Scheme II 3.1. Fragmentation Scheme for <u>exo</u> and <u>endo</u> Norborneol.

Several labelled norbornenols were prepared by the methods described in Part IV of this thesis involving commonly used reactions. In order to help identify the various ions formed in the fragmentation pathways, the primary fragment ions have been labelled $D_1, D_2, \ldots$ etc.

The following discussion on the relatively minor fragment ions D_3 m/e 83 and D_4 m/e 83 precedes the discussion on the formation of the base peak in order to prepare a suitable background for the development of the concepts used in the interpretation of the water loss from the molecular ion.

Formation of Ion D_3 at m/e 83 . The ion at m/e 83 arises by the loss of 29 amu , however it is not possible from the daughter ion peak heights in the labelled compounds (see Table II 3.2a) to determine how or what species is lost, in addition no metastable ion peak was observed for this fragmentation.

From a study of the ratios of the relative intensities of the metastable ion peaks in various labelled compounds for the secondary fragmentation of this ion (see Table II 3.3) :

$$m/e\ 83 - C_2H_4 = m/e\ 55$$

it is possible to deduce one route of formation of the ions

Table II 3.2.a.

Relative Intensities of Peaks for the Formation of the Ion's at m/e 57 and 83 (in the Unlabelled) for Labelled Norborneols.

Compound	Relative Intensities (Corrected for ^{13}C)					
Unlabelled and Nondeuterated	m/e	57	58	83	84	
exo and endo Norborneol		41	10	21	0	
endo Norborneol-(OD)		19	32	0	22	
exo-Norborneol-(OD)		23	36	0	23	
endo-Norborneol-exo-2-d_1		12	43	10	12	
exo-Norborneol-6-d_1		30	21	16	16	
exo-Norborneol-endo-3-d_1		51	16	11	18	
exo Norborneol-(exo-3-d_1 and syn-7-d_1)		32	20	7	15	
Dideuterated	m/e	57	58	33	84	85
endo-Norborneol-3,3-d_2		39	12	11	6	12
Norborneol-exo-3-exo-6-d_2		41	25	24	11	13
Trideuterated	m/e	57	58	83	84	85	86
endo-Norborneol-2,3,3-d_3		18	33	11	4	8	8
Norborneol-(OD)-exo-3-exo-6-d_2		24	41	16	15	20	10

Table II 3.2.b.

Relative Intensities of Peaks for the Formation of (M-HCO) Ion D_3[(a)] in Labelled Norborneols and ($M-C_2H_5$) Ion D_4[(b)].

Compound		Relative Intensities (Corrected for ^{13}C)			
Unlabelled and Nondeuterated	m/e	83	84		
exo and endo Norborneol		11(10)	0(0)		
endo-Norborneol-(OD)		0(0)	12(10)		
exo-Norborneol-(OD)		0(0)	13(10)		
endo-Norborneol-exo-2-d_1		0(10)	13(0)		
exo-Norborneol-6-d_1		16(0)	6(10)		
exo-Norborneol-endo-3-d_1		11(0)	8(10)		
exo-Norborneol-(56%-exo-3d_1 and 44%-syn-7-d_1)		7(0)	5(10)		
Dideuterated	m/e	83	84	85	
endo-Norborneol-3,3-d_2		11(0)	6(0)	2(10)	
Norborneol-exo-5-exo-6-d_2		24(0)	11(0)	2(10)	
Trideuterated	m/e	83	84	85	86
endo-Norborneol-2,3,3-d_3		11(0)	4(0)	0(-8)	8(0)
Norborneol-(OD)-exo-5-exo-6-d_2		16(0)	15(0)	20(0)	0(10)

(a) Values in parenthesis.

(b) Values obtained by subtracting values in parenthesis from values in Table II 3.2.a.

at m/e 83 , this ion will be labelled ion D_3 . It is observed that for endo-norborneol-exo-2-d_1 there is only one metastable ion peak for ethylene loss from ion D_3 (m/e 36.4) corresponding to the process (m/e 83), $D_3 - C_2H_4$, indicating that the deuterium on the 2 carbon atom is lost completely in the formation of ion D_3 . In exo and endo norborneol-OD there are only two metastable ion peaks observed (m/e 37.3 and 36.1) which correspond to the loss of C_2H_4 and C_2H_3D from m/e 84 (ion D_3), indicating complete retention of the hydroxyl hydrogen in the formation of ion D_3 . The relative intensities of these latter metastable ion peaks (m/e 37.3 and 36.1) are close to the value for random selection of the hydrogen atoms in the ethylene loss from 9 hydrogen atoms and 1 deuterium atom (the deviation from these values is certainly due to the metastable ions being taken from the normal spectrum, and their relative intensities are effected by the presence of nearby metastable ion peaks for the process m/e 41-H_2). Ion D_3 (m/e 83) can be formed in two ways from the molecular ion (a) by the loss of HCO (b) by the loss of $C_2H_5^{\cdot}$; in view of the above results (random selection of C_2H_4 from 9H and 1D), ion D_3 can only arise from loss of HCO . It is proposed that the precursor for ion D_3 is the cyclopentyl acetaldehyde cation (see Schemes II 3.2 and 3). Norborneol-exo-5-exo-6-d_2 and norborneol-2,3,3-d_3 show the same metastable

Table II 3.3.

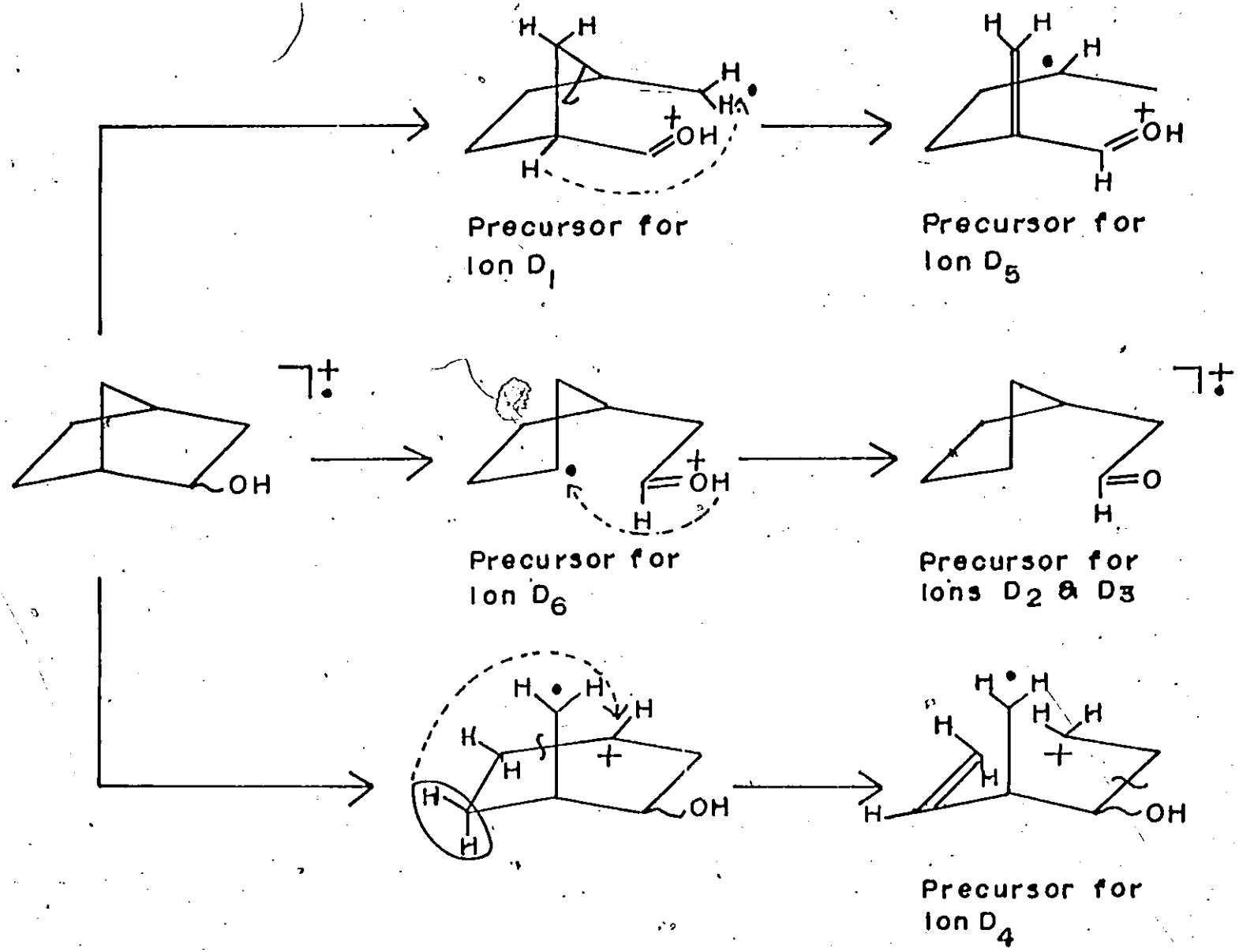
Metastable† Ion Peak Intensities for Ethylene Loss from (M-HCO) and (M-DCO) in the Mass Spectrum of Labelled Compounds:

Compound		Relative Metastable Ion Peak Intensities		
Monodeuterated	m/e	$[M-DCO]-C_2H_4$ 36.4		
endo-Norborneol-exo-2-d_1 (a)		100		
Calc.		(100)		
	m/e	$[M-HCO]-C_2H_4$ 37.4	$[M-HCO]-C_2H_3D$ 36.4	
exo and endo Norborneol-OD (b)		68±1.6	32±1.6	
Calc.		(64	36)	
exo-Norborneol (55%-exo-3-d_1 and 45%-syn-7-d_1) (b)		66±1.6	34±1.6	
Calc.		(64	36)	
Dideuterated	m/e	$[M-HCO]-C_2H_4$ 38.2	$[M-HCO]-C_2H_3D$ 36.9	$[M-HCO]-C_2H_2D_2$ 35.9
Norborneol-exo-5-exo-6-d_2		40±0.6	51±0.6	9±0.6
Calc.		(38	51	11)
Trideuterated	m/e	$[M-DCO]-C_2H_4$ 38.2	$[M-DCO]-C_2H_3D$ 36.9	$[M-DCO]-C_2H_2D$ 35.9
endo-Norborneol-2,3,3-d_3		43	47	10
Calc.		(38	51	11)

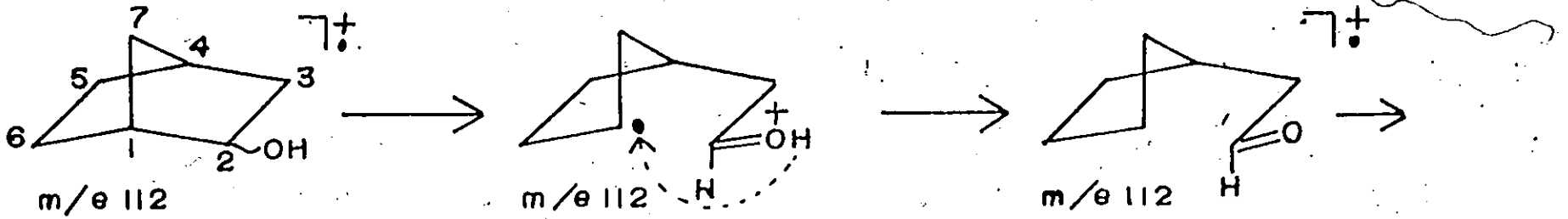
† Metastable ion peaks obtained from normal spectrum at low e.V.. the poor fit between experimental and random values is due to the presence of the metastable ion peak for the process m/e 41 - H_2 (see Table II 3.1).

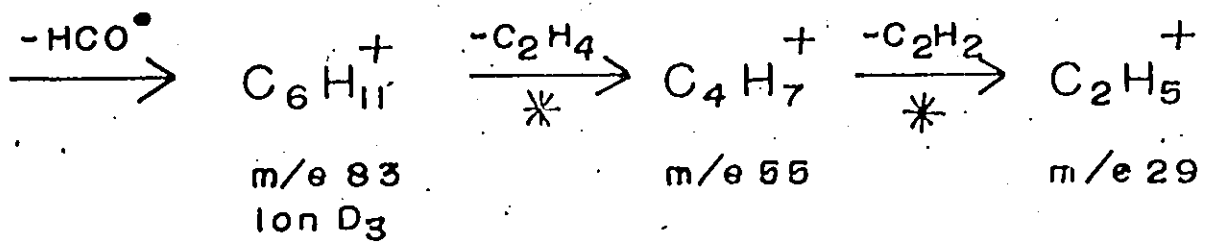
(a) Metastable ion peaks not observed for $(M-CHO)-C_2H_4$ and its labelled analogues.

(b) Metastable ion peak not observed for $(M-DCO)-C_2H_4$.



Scheme II 3.2. Rearrangements of the Norlorncol Molecular Ion.





Scheme II 3.3. Mechanism for the Formation and Decomposition of Ion D_3.

ion peaks for ethylene and labelled ethylene losses from ion D_3 (see Table II.3.3) and these peaks have similar relative abundances, close to the value for random hydrogen selection. Therefore norborneol-exo-5-exo-6-d_2 loses only HCO whereas norborneol-2,3,3-d_3 loses only DCO in the formation of ion D_3. These results prove that ion D_3 is formed by the loss of the 2 carbon atom and attached hydrogen and oxygen atoms (see Schemes II 3.2 and 3). Ion D_3 fragments (as has been shown) by the loss of ethylene in a random manner giving the $C_4H_7^+$ ion which in turn fragments characteristically by the loss of acetylene[62] (metastable at m/e 15.3).

Formation of Ion D_4 at m/e 83. It has been observed from high resolution studies[101] that the ion at m/e 57 contains oxygen, this in conjunction with a metastable ion peak (m/e 39.2), which corresponds to the loss of acetylene from m/e 83 yielding m/e 57, demonstrates that this ion (m/e 57) cannot arise from ion D_3. Kwart and Blazer[101], by analogy with the formation of the ion at m/e 57 in the mass spectrum of cyclohexanol[104a] and cyclopentanol[104b], proposed that the ion at m/e 57 in norborneol is $(CH_2{=}CHCHOH)^+$ and suggest that it is formed by the loss of a methyl radical (3-C) from the molecular ion followed by the loss of C_3H_4 (involving the 4, 5 and 7 carbon atoms).

The following alternative route is proposed for the formation of the $C_3H_5O^+$ ion (m/e 57)

$$C_7H_{11}OH^{+\cdot} \rightarrow C_2H_5^{\cdot} + C_5H_7O^+ \quad (1)$$
m/e 112 m/e 83 Ion D_4

$$C_5H_7O^+ \xrightarrow{*} C_2H_2 + C_3H_5O^+ \quad (2)$$
m/e 83 m/e 57

The $C_5H_7O^+$ ion is called ion D_4. Table II 3.2.a lists the relative abundances, in the labelled compounds, for the ion peaks at m/e 83, 84, 85 and 86 and the ion peaks at m/e 57, 58 and 59 corrected for ^{13}C, Table II 3.2.b lists the above peaks in the 80's after adjustment for the contribution for the formation of ion D_3. From these results several deductions can be made concerning the formation and decomposition of ion D_4. The hydrogen atoms attached to carbon atoms 3, 5 and 6 are involved in the ethyl loss from the molecular ion, while those on the 2, 7 and hydroxyl positions are not. From these results it is proposed that the precursor for ion D_4 arises by a 7-4 bond break followed by a hydrogen migration from the 6 carbon atom to the 4 carbon atom accompanied by a 4-5 bond rupture (see Scheme II 3.2). The precursor ion then loses an ethyl radical by migration of a hydrogen atom from the 5 to the 4 carbon atom followed by a 2-3 bond rupture giving

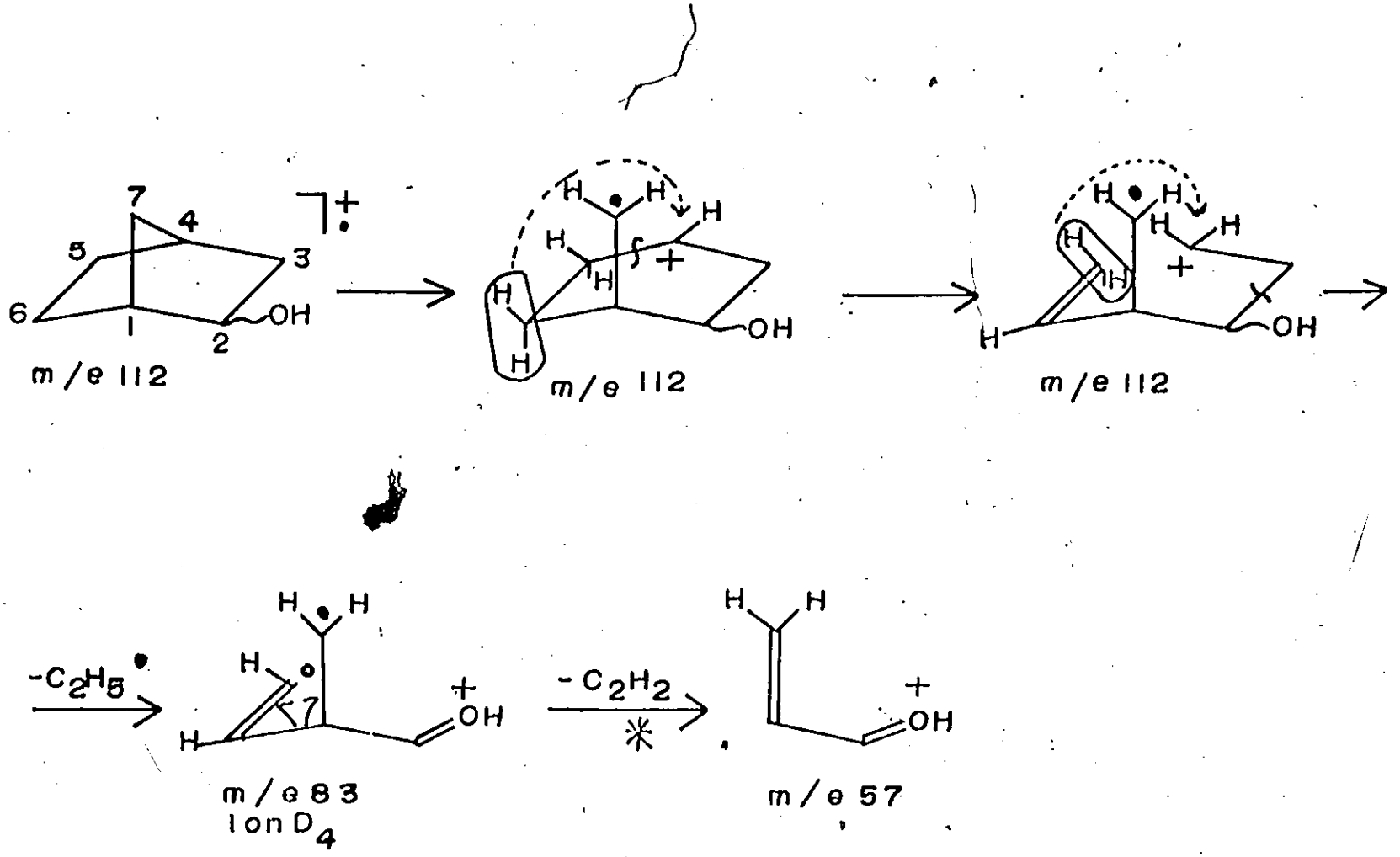
ion D_4 (see Scheme II 3.4). Only the hydroxyl hydrogen and that on the 2 carbon atom are completely retained in the formation of the $C_3H_5O^+$ ion at m/e 57 , this in conjunction with the above data indicates that the acetylene loss from ion D_4 occurs by a 1-6 bond break as shown in Scheme II 3.4.

High resolution studies of the ion peak at m/e 83 revealed a closely spaced doublet of approximately equal intensity, the doublet indicates the presence of both an oxygenated and a hydrocarbon species at m/e 83 . The oxygenated species being ion D_4 which arises by the loss of a hydrocarbon moiety, whilst ion D_3 is the hydrocarbon species produced by the loss of an oxygenated group.

The formation of ions D_3 and D_4 serve as an example to demonstrate how two ions of different structure, with the same mass, can be formed from the same molecular ion by two completely different mechanisms and also fragment by their own separate pathways.

Loss of Water from the Molecular Ion

Tables II 3.4 and 5 list the relative intensities of the normal and metastable ion peaks which correspond to the loss of H_2O, HDO and D_2O from the various labelled norborneols. These results confirm the observations of Kwart and Blazer[101], Rumski and Klasinc[102], and Benz and Biemann[51] that the hydrogen atoms on the 2 and 3 carbon atoms are not involved in the water loss. The values reported in



Scheme II 3.4. Mechanism for the Formation and Decomposition of Ion D_4 .

Tables II 3.4 and 5 indicate that the water loss involves partially the hydroxyl hydrogen, the syn-7 hydrogen atom and those on the 5 and 6 carbon atoms. It was not possible to show experimentally whether the hydrogens in the 1,4 or anti-7 position are involved.

Table II 3.4.

Normal Peak Intensities for Water Loss in the Mass Spectra of Labelled Norborneols*

Compounds	Relative Peak Heights (Corrected for ^{13}C)	
	$M-H_2O$	M-HDO
m/e	95	94
exo-Norborneol-OD	47	53
endo-Norborneol-OD	47	53
exo-Norborneol-6-d_1	85	15
(Calc. see text).	(87	13)
exo-Norborneol (45%-syn-7-d_1 + 55%-exo-3-d_1)	84	16
(Calc. see text)	(84	16)

* When deuterium is present on the 2 or 3 carbon atoms only H_2O loss is observed.

Table II 3.5.

Metastable† Ion Peak Intensities for Water Loss in the Mass Spectra of Labelled Norborneols*.

Compound	Relative Metastable Peak Intensities		
Monodeuterated		$M-H_2O$	M-HDO
	m/e	79.9	78.2
exo-Norborneol-(OD)		67	33
endo-Norborneol-(OD)		67	33
exo-Norborneol-7-d_1 (a)		61	39
(Calc. see text)		(58	42)
Dideuterated		$M-H_2O$	M-HDO	$M-D_2O$
	m/e	80.6	79.2	77.5
Norborneol-exo-5-exo-6-d_2		56	44	0
(Calc. see text)		(58	42	0)
exo-Norborneol (56% exo-5-exo-6-d_2 and 44% endo-5-endo-6-d_2)		63	37	0
(Calc. see text)		(58	42	0)
Trideuterated	m/e	81.0	80.1	78.5
Norborneol-(OD)-exo-5-exo-6-d_2		34	57	9
(Calc. see text)		(33	58	9)

† Metastable ion peaks obtained by defocusing technique Error is to ±2% .

* When deuterium is present on the 2 or 3 carbon atoms only H_2O loss is observed.

(a) Value for syn-7-d_1 norborneol calculated from (3-7)d_1 norborneol ($M-H_2O$: M-HDO = 83:17).

Exo and endo norborneol-OD were prepared by simple exchange in deuterium oxide. Several unexpected results were observed in the spectra of both compounds, which were identical; (1) both HOD and H_2O losses were observed, this indicates that the hydroxyl hydrogen atom is not always involved in the water loss. This is in contrast with the results obtained from aliphatic alcohols[48-51] where it has been shown that the water loss occurs by a simple 1,3 and 1,4 elimination via 5 and 6 membered rings.
(2) the ratio of $HOD:H_2O$ in the normal spectrum is 1:1 whereas the ratio for the metastable ion peaks for the same processes are 1:2 , this indicates that the water loss is not occurring by a simple mechanism (see discussion of ion life-times, page 175).

The change in the ratio of $HOD:H_2O$ in going from peaks to metastable ion peaks indicates that the same processes (which result in water loss) or ratio of processes which occur in the source do not occur in the first field free region (metastable ion peaks). This indicates that the water loss occurs by one of three pathways; (1) the water loss involves at least two processes where the precursor ions have different lifetimes (2) a process involving incomplete randomisation in the source, tending towards complete randomisation in the first field free region (3) a process involving incomplete localised randomisation occurring in the source, tending

towards complete localised randomisation in the first field free region.

Complete randomisation can be ruled out on two grounds. (i) The ratios of the relative abundances of the metastable ion peaks for water loss in the labelled compounds, do not correspond to the values for complete randomisation and (ii) the absence of involvement of the hydrogen atoms on the 2 and 3 carbon atoms. Of the two remaining processes, the first is preferred (at least two specific water losses) on the basis of observations on the secondary fragmentation, the loss of a methyl radical from the $C_7H_{10}^{+\cdot}$ ion ($M-H_2O$). The relative abundance for normal and metastable ion peaks for methyl loss from the $C_7H_{10}^{+\cdot}$ ion in the labelled compounds are reported in Tables II 3.6 and 7. In all the labelled compounds the values for the ratios of the methyl and its labelled analogues lost in the source and first field free region do not fit a single specific or random process but approach the random values. The metastable ions for the loss of methyl from exo and endo norborneol-OD are identical and show that methyl loss occurs from both the M-HDO and $H-H_2O$ species. However a very weak metastable ion peak was observed for the loss of deuterated methyl from the $M-H_2O$ species, representing about 3% of the total methyl loss. From the above results it was inferred that the loss of HDO from norborneol-OD was followed by methyl loss in

Table II 3.6.

Relative Peak Intensities for Methyl Loss from ($M-H_2O$) Species in Labelled Norborneols.

Compound	Relative Intensities (Corrected for ^{13}C)			
Mono-deuterated	m/e	79	80	
exo-Norborneol-(OD)		81	19	
endo-Norborneol-(OD)		85	15	
endo-Norborneol-exo-2-d_1		56	44	
(Calc. see text)		(44	56)	
exo-Norborneol-6-d_1		40	60	
(Calc. see text)		(34	66)	
exo-Norborneol-endo-3-d_1		49	51	
(Calc. see text)		(44	56)	
exo-Norborneol-(56% exo-3-d_1 and 44% syn-7-d_1)		42	58	
(Calc. see text)		(41	59)	
Dideuterated	m/e	79	80	81
endo-Norborneol-3,3-d_2		26	46	28
(Calc. see text)		(20	48	32)
Trideuterated	m/e	79	80	81	82
endo-Norborneol-2,3,3-d_3		13	44	27	11
(Calc. see text)		(8	36	36	20)

Table II 3.7.

Relative Intensities of Metastable Ion Peaks* for the Loss of Methyl from the $(M-H_2O)$ Species.

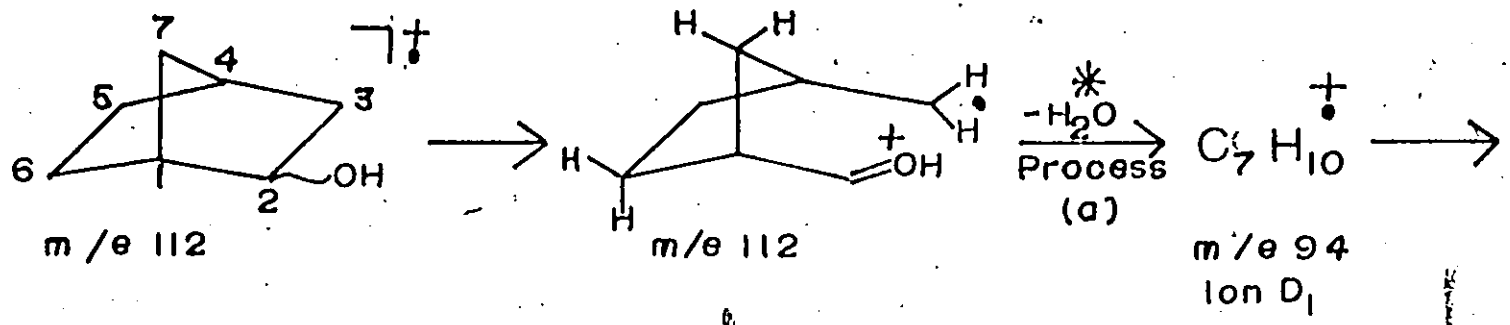
Compound	Relative Intensities		
Monodeuterated	$(M-HDO)-CH_3$	$(M-H_2O)-CH_3$	$(M-H_2O)-CH_2D$
m/e	66.4	67.4	65.7
endo-Norborneol-(OD)	67.5	30	2.5
exo-Norborneol-(OD)	67.5	30	2.5
endo-Norborneol-exo-2-d_1	0	55	45
(Calc. see text)	(0	56	44)
exo-Norborneol-endo-3-d_1	0	54	46
(Calc. see text)	(0	56	44)
exo-Norborneol-6-d_1	12	66	22
(Calc. see text)	(13	66	21)
exo-Norborneol-(44% syn-7-d_1 and 56% exo-3-d_1)	7	57	36
(Calc. see text)	(7	59	34)

Dideuterated	$(M-H_2O)-CH_3$	$(M-H_2O)-CH_2D$	$(M-H_2O)-CHD_2$
m/e	68.3	66.7	65.0
endo-Norborneol-3,3-d_2	31	46	23
(Calc. see text)	(32	48	20)
Norborneol-5,6-d_2 (a)	58	35	7
(Calc. see text)	(56	40	4)

Trideuterated	$(M-H_2O)-CH_3$	$(M-H_2O)-CH_2D$	$(M-H_2O)-CHD_2$	$(M-H_2O)-CD_3$
m/e	64.3	67.6	66.0	64.3
endo-Norborneol-2,3,3-d_3	20	28	42	10
(Calc. see text)	(20	36	36	8)

* "Defocused" metastable ion peaks, Kiser's method.

(a) Value for methyl loss and deuterated analogue from (M-HDO) 75% CH_3: 25 CH_2D (Calc. 76:24).



Scheme II 3.5. Mechanism for the Formation and Decomposition of Ion D_1 .

which the hydrogen atoms are probably selected in a completely random fashion. That which occurs by H_2O loss is followed by a specific methyl loss (discussed in detail later).

Although there is no well authenticated evidence for molecular ions rearranging to two different structures and then fragmenting by the loss of same species, it is proposed here that the water loss in norborneol occurs from two different forms of the molecular ion. The first route for water loss involves the hydroxyl hydrogen and gives rise to ion D_1, the second route does not involve the hydroxyl hydrogen and gives rise to ion D_2.

(a) Formation of Ion D_1

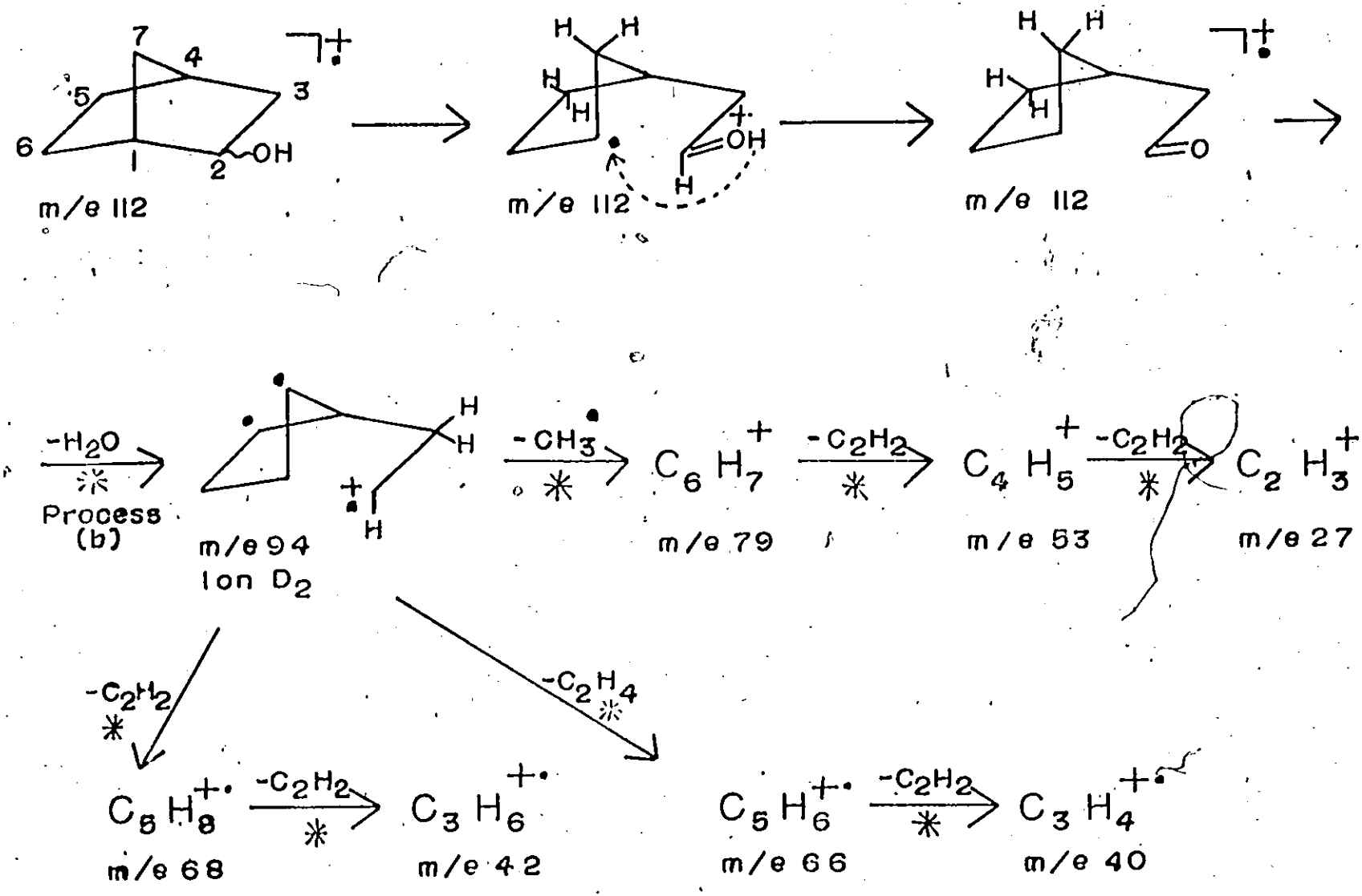
It is proposed that the formation of ion D_1 (see Schemes II 3.2 and 5) arises by a 2,3 bond break giving the precursor cation which then loses water. The hydrogen atoms involved are the hydroxyl hydrogen atom with the second hydrogen selected from one of those on the 6 or 7 carbon atoms. Supporting evidence for the formation of the cyclopentane cation is obtained from the $M-C_3H_6$ fragmentation which yields ion D_5.

(b) Formation of Ion D_2

The proposed precursor ion for the formation of ion D_2 arises in a similar manner to that proposed for the second water loss in cyclohexanol [50,105,106]. Its

formation is shown in Schemes II 3.2 and 6, it occurs by a 1,2 bond rupture followed by migration of the hydroxyl hydrogen atom to the 1 carbon atom yielding the cyclopentyl acetaldehyde cation, which then loses water, the hydrogen atoms being selected at random from the 5 and 7 positions. A similar type of random loss involving selected hydrogen atoms has been shown to occur in the water loss of cyclohexane-1,2-diol[107]. Supporting evidence for the formation of the cyclopentyl acetaldehyde cation is obtained from the M-HCO fragmentation which yields ion D_3 and the $M-C_2H_4OH$ fragmentation which gives rise to ion D_6.

The ratio of the daughter ion peak heights for the loss of $HOD:H_2O$ is 1:1 in exo and endo norborneol-OD. If one part of water loss (a), which gives rise to ion D_1 is added to one part of water loss (b), which gives rise to ion D_2, good agreement is observed with experimental results obtained from daughter ion peak heights of the various labelled compounds, as shown in Table II 3.4. The ratios of the metastable ion peaks for the loss of $HOD:H_2O$ was found to be 1:2 in norborneol-OD. If one part of water loss (a) is summed with two parts of water loss (b), good to excellent agreement with the experimental results is observed in the labelled norborneols (see Table II 3.5). The difference in the ratios between the daughter and metastable ion peaks arises from the slower rate of formation of ion D_2 over ion D_1.



Scheme II 3.6. Mechanism for the Formation and Decomposition of Ion D_2.

Fragmentation of Ions D_1 and D_2 by Loss of Methyl

As previously discussed, the results for methyl loss from the $M-H_2O$ species (see Table II 2.6 and 7) do not fit a single specific or random mechanism. The fact that ion D_2 in norborneol-OD loses methyl and no more than 3% methyl-d_1 (as observed from metastable ions), indicates a specific rather than a random process for the fragmentation. Since the values for the ratios of the methyl loss in the labelled norborneols tend towards random values and in view of the above results it is proposed that the methyl loss from ion D_1 involves completely random selection of the hydrogen atoms and the methyl loss from ion D_2 involves a localised process wherein the three hydrogen atoms of the methyl group are selected from four. Three of these hydrogen atoms are those attached to the 2 and 3 carbon atoms, the fourth being selected from the remainder of the molecule. There is no proven precedent for such a localised process in a hydrocarbon, but a similar hypothesis has been proposed to explain the ethylene loss from the molecular ion of nortricyclene (Part II 2.B). A summation of 67.5 parts of the random methyl loss from ion D_1 to 32.5 parts of the specific methyl loss from ion D_2 gives good to excellent agreement with the relative abundance of the metastable ion peaks (see Table II 3.7). The chosen proportions of the two processes were those observed in exo and endo norborneol-OD

(which were identical). An example of the summation of the two methyl losses is shown below in the case of norborneol-3,3-d_2 :-

	CH_3	CH_2D	CHD_2		CH_3	CH_2D	CHD_2
Complete Random	47	47	6 × .675	=	32	32	4
Localised Random	0	50	50 × .325	=	0	16	16
				$\leq$	32	48	20

In a similar manner, using the ratio of the daughter ion peak abundances for methyl loss from ion D_1 to methyl loss from ion D_2 in exo and endo norborneol-OD, (which were identical), for the summation of the random methyl loss from ion D_1 to the specific methyl loss from ion D_2, fair agreement was obtained between calculated and observed daughter ion peak heights in the labelled compounds (see Table II 3.6). As can be observed from the table more label is lost than predicted by the mechanism.

These results indicate that not only are ions D_1 and D_2 formed by different mechanisms, but they also fragment by different mechanisms, by the loss of a methyl radical in each case, to yield $C_6H_7^+$ ions differing in structure and/or energy content. This correlates with the observation in norbornene and nortricyclene (Part II 2) where the same species was shown to be lost from the two isomers by different mechanisms.

For ions D_1 and D_2, in addition to having different structures, they will probably have different internal energies. The energies will only cover a narrow range since the ions in question (D_1 and D_2) are fragment ions and not molecular ions which are produced directly from electron bombardment. It is proposed that ions D_1 and D_2 fragment by the loss of a methyl radical by different mechanisms as a result of their having different structures and internal energies.

Fragmentation of Ions D_1 and D_2 by Ethylene and Acetylene Loss (the $C_5H_8^{+\cdot}$ ion m/e 68, $(M-H_2O)-C_2H_2$ and the $C_5H_6^{+\cdot}$ ion m/e 66, $(M-H_2O)-C_2H_4$)

Kwart and Blazer[101] proposed that the ion at m/e 66, $C_5H_6^{+\cdot}$ arose by a retro-Diels Alder reaction of the $(M-H_2O)^{+\cdot}$ species, which they believed to be norbornene. This requires that in 2 d_1 and 3,3 d_2 - norborneols (see Table II 3.8) the peak at m/e 66 should be substantially reduced and the peaks at m/e 67 (in the case of 2 d_1- norborneol) and m/e 68 (in the case of the 3,3 d_2-norborneol) should be substantially increased, but this is not observed here (see Table II 3.8 and [101]). The proposed structures for ions D_1 and D_2 make the formation of norbornene as an intermediate very unlikely. In support, it is worth noting that the half height width for the ethylene loss metastable in norborneol is the same as that for nortricyclene (narrower than that for norbornene)

Table II 3.8.

Relative Intensities of the Peaks in the Upper 60's in Labelled Norborneols

Compound	m/e	Relative Intensity 66	67	68	69	70
exo and endo Norborneol		28	33	28	5	6
exo-Norborneol-endo-3-d_1		26	30	23	10	11
endo-Norborneol-exo-2-d_1		25	34	30	6	5
exo and endo Norborneol-(OD)		26	34	23	13	4
endo-Norborneol-3,3-d_2		31	32	25	6	5
endo-Norborneol-2,3,3-d_3		33	33	23	8	4
exo Norborneol-(56%-exo-3-d_1 and 44%-syn-7-d_1)		21	30	25	19	5
exo-Norborneol-6-d_1		23	25	26	21	5
Norborneol-exo-5-exo-6-d_2		6	15	31	29	18

Low eV. studies indicate that the ions at m/e 66 and m/e 68 arise from the "same precursor ion", this coupled with the presence of metastable ions at m/e 46.3 and m/e 49.2 corresponding to the processes $(M-H_2O)-C_2H_4$ and $(M-H_2O)-C_2H_2$ respectively, confirm that these ions arise from one or both of the $C_7H_{10}^{+\cdot}$ ions. From inspection of the peaks in the upper 60's (see Table II 3.8) in the labelled compounds one observes that when deuterium is

present on the 2 or 3 carbon atoms the position and relative intensities of the peaks are not substantially changed. However when deuterium is on the 5, 6 or 7 carbon atoms the peaks are displaced to higher mass. This indicates that the ethylene and acetylene losses from the $C_7H_{10}^{+\cdot}$ ion or ions involve the 2 or 3 carbon atoms with their attached hydrogen atoms. In view of the preceding statment it would seem reasonable that these fragmentations would arise from ion D_2, rather than ion D_1 wherein the 2 and 3 carbon atoms are shown as separated (see Schemes II 3.5 and 6).

The $C_5H_8^{+\cdot}$ and $C_5H_6^{+\cdot}$ ions both fragment by the loss of acetylene as indicated by metastable ion peaks at m/e 26.1 and m/e 24.5 (see Scheme II 3.6).

The structure of ion D_2, $C_7H_{10}^{+\cdot}$ raises an interesting point; it has the same structure as that proposed for the molecular ion of nortricyclene. The latter loses ethylene (see Scheme II 2.B.1) and the suggested mechanism involves the loss of the vinyl group with the fourth hydrogen atom selected at random from the cyclopentene ring. For the methyl loss from ion D_2, a mechanism similar to that discussed above for the ethylene loss from nortricyclene was proposed, namely a process wherein the three hydrogen atoms of the methyl group were selected at random from four; three of the hydrogen atoms are those

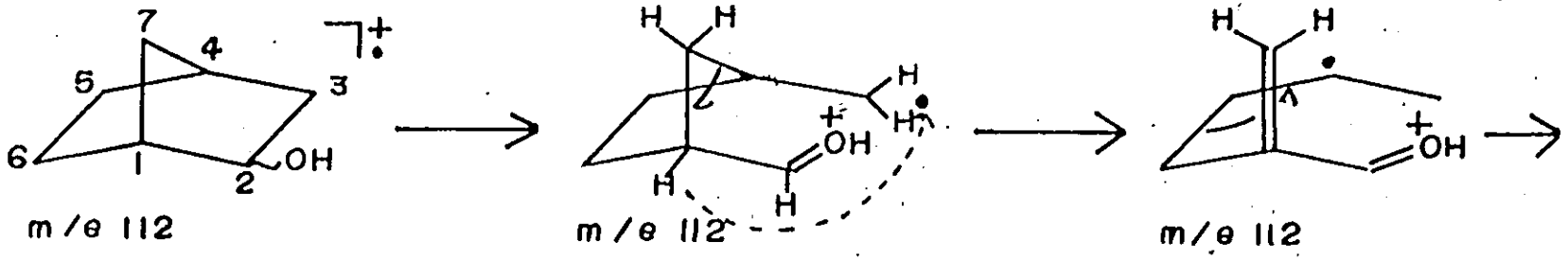
attached to the 2 and 3 carbon atoms, the fourth being selected at random from the cyclopentene ring (see Scheme II 3.6). The above points indicate that a similar process occurs for this ion in both nortricyclene and norborneol, it therefore seems reasonable to propose that the ethylene loss from ion D_2 in norborneol occurs in a manner identical to that in nortricyclene.

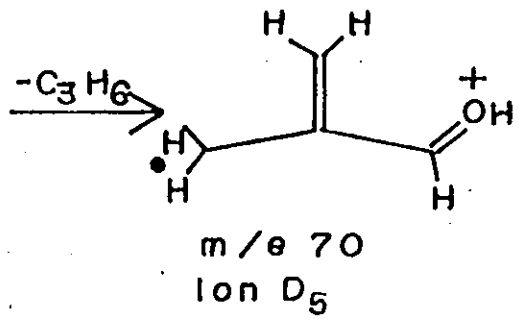
No methyl loss is observed from the vinylcyclopentene cation in nortricyclene, this is a result of the energy content of the ion and the kinetics of competing reactions.

Formation of Ion D_5 at m/e 70

By analogy with the fragmentation of the ions at m/e 57 and 71 in 4 methylcyclohexanol [104c] one can readily explain the formation of ion D_5 (see Schemes II 3.2 and 7). The precursor for ion D_5 is formed by a 2,3 bond break with a concurrent migration of the 1 hydrogen atom to the 3 carbon atom and a 7,4 bond break. The precursor ion then loses $C_3H_5^+$ by a single 5,6 bond rupture yielding ion D_5, $C_4H_6O^{+\cdot}$. This route of formation for the ion at m/e 70 is supported by high resolution studies which show that m/e 70 consists solely of $C_4H_6O^{+\cdot}$.

This fragmentation is in keeping with the proposed precursor ion for the formation of ion D_1.

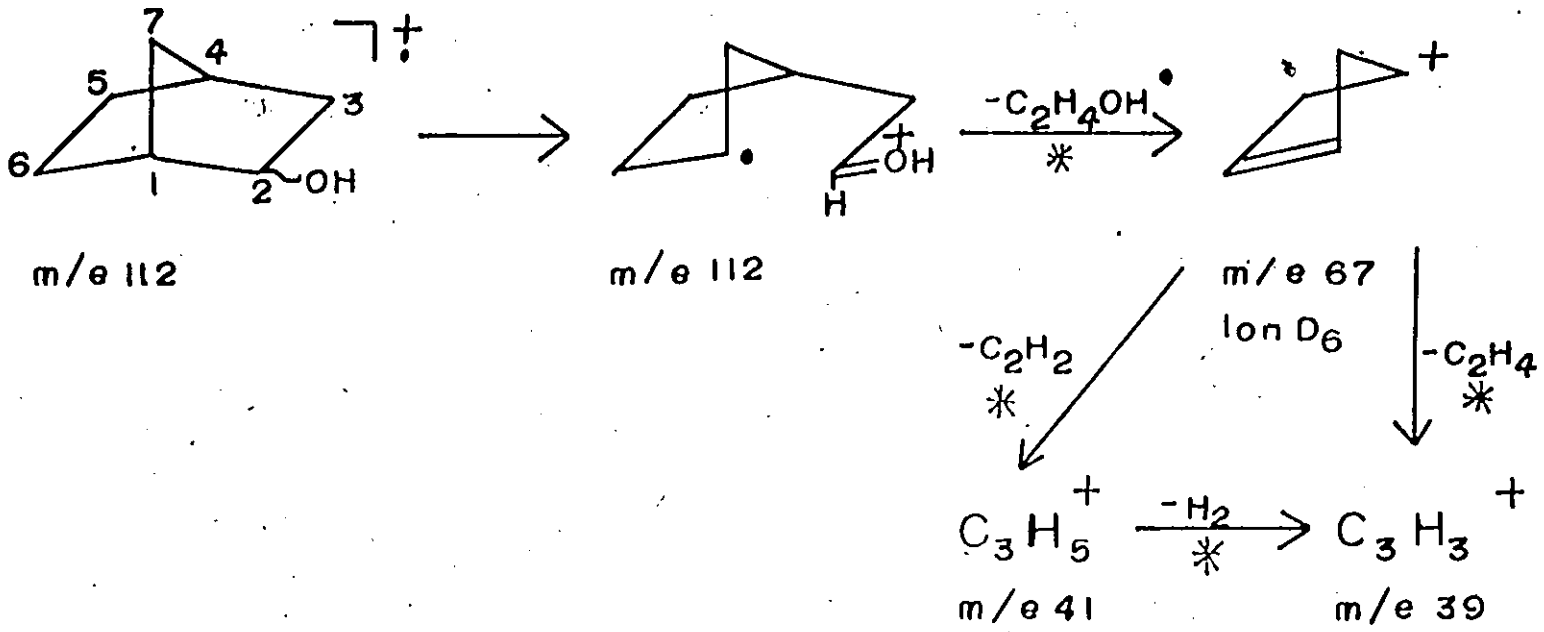




Scheme II 3.7. Mechanism for the Formation of Ion D_5.

Formation of ion D_6 at m/e 67

Kwart and Blaser[101] suggested that the ion at m/e 67, $C_5H_7^+$ occurs from a two step fragmentation involving the loss of a methyl radical (the 3 carbon atom) and then CH_2OH (the 2 carbon atom). In norborneol-OD;$3d_1$;$3d_1$;3,$3d_2$ and 2,3,$3d_3$ the ion remains at m/e 67 while in $6d_1$;(3-7)d_1 and 5,$6d_2$ norborneol this ion is displaced to higher mass (see Table II 3.8). From these results it is proposed (by analogy with the chloroethyl radical lost from the molecular ion of exo-2-norbornyl chloride (Part II 1.A)) that ion D_6 is formed in a one step fragmentation by the loss of $C_3H_4OH^\cdot$ from the molecular ion (see Scheme II 3.2 and 8) involving carbon atoms 2 and 3 with their attached hydrogen and oxygen atoms, the fourth hydrogen atom possibly comes from the 6 position (again by analogy with the chloroethyl loss from the molecular ion of exo-2-norbornyl chloride). Positive evidence for this fragmentation route was obtained in the form of a weak metastable in the unlabelled compound. Ion D_6 ($C_5H_7^+$) decomposes by the loss of ethylene and acetylene to give the $C_3H_3^+$ and $C_3H_5^+$ ions as indicated by the presence of metastable ion peaks at m/e 22.6 and 24.5 respectively. These are the same fragmentation processes that were observed for the $C_5H_7^+$ fragment ion in norbornyl chloride (Part II 1.A). The above fragmentation mechanism is in keeping with the proposal



Scheme II 3.8. Mechanism for the formation of Ion D_6 .

that the precursor for the formation of ion D_6 is the same as that for ion D_1 (see Scheme II 3.2).

Other Secondary Framentations

Ion D_3, $C_6H_{11}^+$ further fragments by three sucessive losses of a hydrogen molecule yielding the $C_6H_5^+$ ion; this parallels the loss of two hydrogen molecules from the $M-CH_2Cl$ species in norbornyl chloride (Part II 1.A). One or both of the $(M-H_2O)$ species loses a hydrogen atom to yield m/e 93 which in turn loses a hydrogen molecule to give the $C_7H_7^+$ ion, accompanied by energy release as indicated by a flat top metastable ion peak centered at m/e 89.1 (from the proposed structure and behaviour of ions D_1 and D_2 during fragmentation (see Schemes II 3.5 and 6), ion D_1 appears a more likely candidate for the loss of a molecule of hydrogen).

SUMMARY

Several attempts to interpret the fragmentation pattern of norborneol using labelled compounds and the relative abundance of daughter ion peaks have been unsuccessful owing to the large number of overlapping fragmentations present. However using the relative abundance of metastable ion peaks in conjunction with labelled compounds it has been possible to isolate and interpret individual fragmentations and then with this information return to the relative abundances

of the daughter ion peaks and undertake their interpretation. In this manner it was possible to start with the primary fragmentations and unravel much of the fragmentation pattern of exo and endo norborneols.

The results have indicated that exo and endo norborneol behave almost identically in all aspects of their fragmentations. The major fragmentation routes of norborneol can best be explained by postulating three primary rearrangements of the molecular ion (see Scheme II 3.2). Several interesting points have been observed; (1) two ions exist at m/e 83, one arises by the loss of a HCl radical from the molecular ion the second arises from the loss of $C_2H_5^{\cdot}$, the former fragments by the loss of ethylene whilst the latter fragments by acetylene loss. (2) the loss of water from the molecular ion to produce the base peak, occurs in two ways, producing two structurally and probably energetically different $C_7H_{10}^{+\cdot}$ ions which fragment by the loss of methyl, but by different mechanisms in each case. One of the ions (D_2) also fragments by the loss of acetylene and ethylene whilst the other (D_1) fragments by the loss of a hydrogen atom followed by the loss of a hydrogen molecule to give the $C_7H_7^+$ ion. (3) ion D_2 has been proposed to be the vinylcyclopentene cation, the same as observed in nortricyclene.

4. Mass Spectrum of Norbornane (C_7H_{12}, bicyclo (2,2,1) heptane)

Introduction

The mass spectral fragmentation mechanism of norbornane was studied in order to determine which, if any, of its fragmentations were characteristic of the bicyclic structure, and to compare these results with those obtained from the related molecules discussed in Part II.

(a) Previous studies of the mass spectrum of norbornane:

The mass spectrum of norbornane has been previously reported [84] but no comments or discussion have been recorded.

(b) The mass spectrum of norbornane is shown in Fig. II 4.1 and is in fair agreement with prevously published data [84]. Table II 4.1 lists the most intense metastable ion peaks in the normal spectrum of the compound and the fragmentation responsible for their genesis.

Scheme II 4.1 (not a mechanistic scheme) shows those fragmentations of norbornane for which metastable ion peaks were observed. From the scheme it can be seen that the molecular ion fragments in five ways: (a) by the loss of a hydrogen atom to give the $C_7H_{11}^+$ ion (which further fragments by two successive losses of a hydrogen molecule or the loss of a hydrogen molecule followed by C_3H_6). (b) by the loss of a methyl radical yielding the

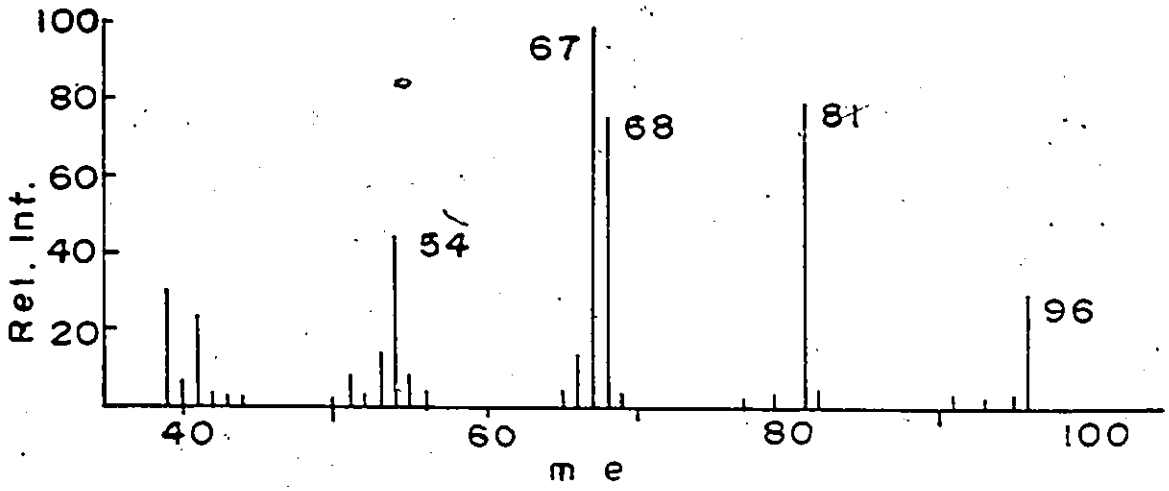
Table II 4.1.

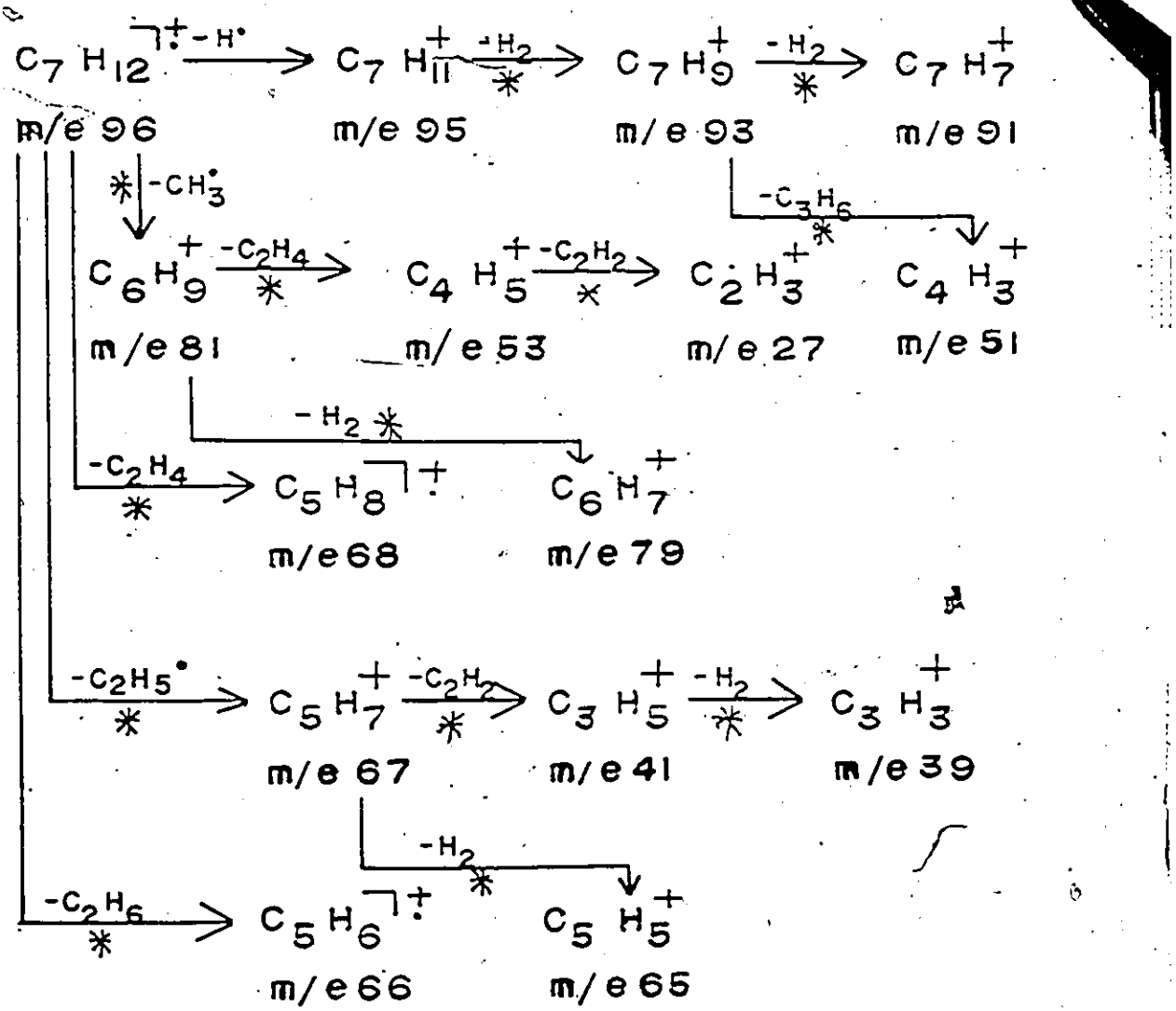
Metastable Ion Peaks* Observed in Norbornane

Genesis	M*
$C_3H_5^+ \rightarrow C_3H_3^+ + H_2$	37.2
$C_4H_5^+ \rightarrow C_2H_3^+ + C_2H_2$	13.8
$C_5H_7^+ \rightarrow C_3H_5^+ + C_2H_2$	25.2
$C_5H_7^+ \rightarrow C_5H_5^+ + H_2$	63.1
$C_6H_9^+ \rightarrow C_4H_5^+ + C_2H_2$	34.7
$C_6H_9^+ \rightarrow C_6H_7^+ + H_2$	77.1
$C_7H_9^+ \rightarrow C_4H_3^+ + C_3H_6$	28.1
$C_7H_9^+ \rightarrow C_7H_7^+ + H_2$	89.0
$C_7H_{11}^+ \rightarrow C_7H_9^+ + H_2$	91.0
$C_7H_{12}^{+\cdot} \rightarrow C_5H_6^{+\cdot} + C_2H_6$	45.4
$C_7H_{12}^{+\cdot} \rightarrow C_5H_7^+ + C_2H_5^{\cdot}$	46.8
$C_7H_{12}^{+\cdot} \rightarrow C_5H_8^{+\cdot} + C_2H_4$	48.3
$C_7H_{12}^{+\cdot} \rightarrow C_6H_9^+ + CH_3^{\cdot}$	68.4

* Obtained from the normal spectrum run at 70 eV. (Hitachi RMU-6D)

Fig. II 4.1. Mass Spectrum of Norbornane.





Scheme II 4.1. Fragmentation Scheme for Norbornane.

$C_6H_9^+$ ion (which decomposes by the loss of acetylene or H_2).
(c) by the loss of ethylene to produce the $C_5H_8^+$ ion (no further dissociations of this species were observed).
(d) by the loss of an ethyl radical giving the $C_5H_7^+$ ion (which fragments by the loss of acetylene or a hydrogen molecule)
(e) by the loss of ethane to yield the $C_5H_6^+$ ion (no further dissociations of this species were observed).

Several labelled norbornanes, see Table II 4.2, were prepared by reduction of the unsaturated compounds with deuterium gas over platinum oxide catalyst or by reduction of various labelled norbornyl tosylates with lithium aluminium hydride or deuteride.

The order of presentation of the fragmentation processes is chosen for the sake of clarity.

Ethylene Loss The daughter ion peaks for the ethylene and ethyl fragmentations overlap in the labelled compounds. Table II 4.2 contains the relative abundance of these daughter ion peaks in the labelled compounds, split into ethylene and ethyl losses on the basis of the ratio observed for these fragmentations in the unlabelled compound. Since in the mono labelled compounds the ethylene and ethyl losses show almost equal abundance of labelled and unlabelled, a similar split was used in the dideuterated compounds.

For ethylene loss from the molecular ion, the results (based on the split in Table II 4.2) are compatible

Table II 4.2.

(a) Relative Abundance of Daughter Ion Peaks for Ethylene and Ethyl Loss.

Compound	Peaks (Corrected for ^{13}C and normalized to 100)			
m/e	67	68	69	70
Norbornane	58	42		
exo-2-d_1 Norbornane	28	49	23	
endo-2-d_1 Norbornane	29	46	25	
exo-2-exo-3-d_2 Norbornane	21	32	29	18
2,2-d_2 Norbornane	20	29	29	22

(b) Relative Abundance of Daughter Ion Peaks for Ethylene Loss

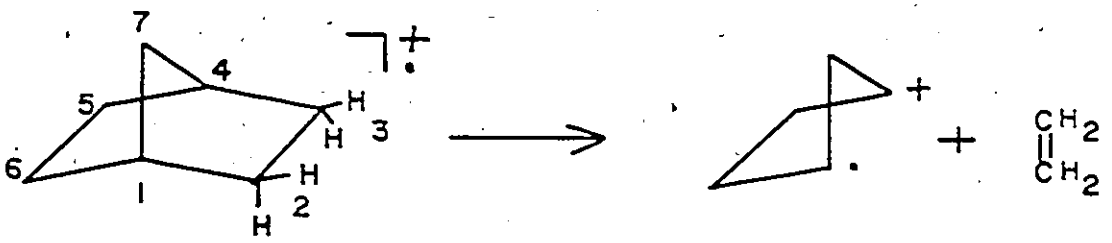
Compound	$M-C_2H_4$	$M-C_2H_3D$	$M-C_2H_2D_2$
Norbornane	100(42)	—	—
exo-2-d_1 Norbornane	55(23)	45(19)	—
endo-2-d_1 Norbornane	59(25)	41(17)	—
exo-2-exo-3-d_2 Norbornane	47(18)	0 (0)	53(24)
2,2-d_2 Norbornane	52(24)	0 (0)	48(20)

(c) Relative Abundance of Daughter Ion Peaks for Ethyl Loss

Compound	$M-C_2H_5$	$M-C_2H_4D$	$M-C_2H_3D_2$
Norbornane	100(58)	—	—
exo-2-d_1 Norbornane	52(30)	48(28)	—
Calc.[1]	(50.5	49.5)	
endo-2-d_1-Norbornane	50(29)	50(29)	—
Calc.	(50.5	49.5)	
exo-2-exo-3-d_2 Norbornane	55(32)	9 (5)	34(21)
Calc.	(49	16	35)
2,2-d_2 Norbornane	50(29)	15.5(9)	34.5(20)
Calc.[2]	(47	16	37)

Values in parenthesis are the actual values obtained from Table (a) after being split into ethylene and ethyl losses.

with a process involving either the 2 and 3 or 5 and 6 carbon atoms and their attached hydrogen atoms.



The metastable ion peak for ethylene loss from the (unlabelled) molecular ion was too weak to be of mechanistic value.

Ethyl Loss In the case of the ethyl radical lost from the molecular ion no mechanism or summation of mechanisms could be found which will yield an excess of $C_2H_5^{\bullet}$ loss over the $C_2H_3D_2^{\bullet}$ loss in the dideuterated compounds as observed in the daughter ion peaks. For example if the ethyl fragment is formed by a 1,2 bond break followed by loss of the 2 and 3 carbon atoms and their attached hydrogen atoms with the fifth hydrogen atom being randomly selected from the cyclopentane ring (cf. nortricyclene and norborneol) the following results are obtained for 2,2-d_2-norbornane:

	$M-C_2H_5$	$M-C_2H_4D$	$M-C_2H_3D_2$
1,2 bond break	0	0	8
4,3 bond break	0	0	8
4,5 bond break	6	2	0
1,6 bond break	6	2	0
Sum	12	4	16
Normalized	37.5	12.5	50
Exp	50	15.5	34.5

If an attempt is made to explain the results by an isotope effect favoring hydrogen over deuterium selection for the fifth hydrogen atom, it is found that even if the value of the isotope effect is very large the results would be $50C_2H_5 : 0C_2H_4D : 50C_2H_3D_2$ i.e., no major loss of $C_2H_5^{\bullet}$ and no loss of $C_2H_4D^{\bullet}$. Thus if the results are to be explained through an isotope effect it must be applied to the ring opening step, e.g. the presence of deuterium on the 2 carbon atom making the 1,2 carbon-carbon bond stronger than the 1,6 bond. Similar bond strengthening has been proposed in the fragmentation of deuterium labelled aliphatic hydrocarbons [104d]; 1,1,1-d_3-pentane has been shown to lose more CH_3 than CD_3 for example.

$$CD_3-CH_2-CH_2-CH_2-CH_3$$

1,1,1-d_3-pentane

Isotope effects for ring opening (listed below) were applied to our above example, 2,2-d_2-norbornane.

Table II 4.3.

No. of deuterium atoms	Type of secondary effect	Value used
1	β	1.25
2	β	1.50
1	α	1.50
2	α	2.00

and the results calculated as shown below:

	$M-C_2H_5$	$M-C_2H_4D$	$M-C_2H_3D_2$				
1,2 bond break	0	0	8	× 0.5	0	0	4
4,3 bond break	0	0	8	× 0.66	0	0	5.3
4,5 bond break	6	2	0	× 1	6	2	0
1,6 bond break	6	2	0	× 1	6	2	0
				Sum	12	4	9.3
				Normalized	47	16	37
				Exp	50	15.5	34.5

The agreement here observed between calculated and experimental daughter ion abundances and for the other labelled compounds (see Table II 4.2) is fair to good, supporting the proposed mechanism in conjunction with the isotope effect. The isotope effect was applied to other possible fragmentation processes for ethyl loss but without similar success.

Ethane Loss Strong metastable ion peaks were observed for ethyl (C_2H_5) and ethane (C_2H_6) losses from the molecular ion; these overlapped in the labelled compounds. The relative abundance of these metastable ion peaks in the labelled compounds were split into ethyl and ethane metastables on the basis of their observed ratios in the unlabelled compound; these are shown in Table II 4.4. At the time of writing no mechanism with or without an isotope effect has been deduced which can explain the relative abundance of the metastable ion peaks for ethyl or ethane losses from the molecular ion.

The relative intensity of the daughter ion peak for ethane loss is extremely small (6 % B.P.) and in the presence

Table II 4.1.

(a) Relative Abundance of Metastable Ion Peaks* for Ethyl and Ethane Loss.

Compound	$M-C_2H_5$	$M-C_2H_6$
m/e	46.8	45.4
Norbornane	66	34

	$M-C_2H_5$	$M-(C_2H_4D/C_2H_6)$	$M-C_2H_5D$
m/e	47.7	46.3	45.9
exo-2-d_1 Norbornane	46	41	13

	$M-C_2H_5$	$M-(C_2H_4D/C_2H_6)$	$M-(C_2H_3D_2/C_2H_5D)$	$M-C_2H_4D_2$
m/e	48.6	47.2	45.8	44.4
exo-2-exo-3-d_2-Norbornane	31	38	24	7
2,2-d_2-Norbornane	32	35	24	9

(b) Relative Abundance of Metastable Ion Peaks for Ethyl Loss.

Compound	$M-C_2H_5$	$M-C_2H_4D$	$M-C_2H_3D_2$
Norbornane	100(66)	—	—
exo-2-d_1 Norbornane	70(46)	30(20)	—
exo-2-exo-3-d_2-Norbornane	47(31)	17(11)	36(24)
2,2-d_2 Norbornane	49(32)	15(10)	36(24)

(c) Relative Abundance of Metastable Ion Peaks for Ethane Loss.

Compound	$M-C_2H_6$	$M-C_2H_5D$	$M-C_2H_4D_2$
Norbornane	100(34)	—	—
exo-2-d_1 Norbornane	62(21)	38(13)	—
exo-2-exo-3-d_2-Norbornane	76(26)	0(0)	24(7)
2,2-d_2 Norbornane	74(25)	0(0)	26(9)

* Defocused Metastable Ion Peaks, Kiser's Method[43].

Values in parentheses are the actual values obtained from Table (a) above, after being split into Ethyl and Ethane losses.

of the strong $M-C_2H_5$ and $M-C_2H_4$ peaks no mechanistic information could be obtained from the corresponding peaks in the labelled compounds.

Methyl Loss The relative abundance of the daughter and metastable ion peaks for methyl loss from the molecular ion are sensitive to repeller plate potentials (ion residence time in the source). In the Hitachi R.M.U.-6D mass spectrometer the $M-CH_3$ daughter ion peak is base peak jointly with the $M-C_2H_5$ daughter ion peak and no metastable ion peak is observed (under normal scanning conditions) for methyl loss from the molecular ion with a nominal repeller plate potential of zero. However at a repeller plate potential of about 30 volts (max. value obtainable) the $(M-CH_3)$ daughter ion peak abundance drops to 60% of base peak $(M-C_2H_5)$, and the metastable ion intensity for methyl loss is now 3% of base peak. This observation can be used to test whether the same process or sum of processes is occurring for methyl loss leading to daughter ion peaks (fragmentations occurring in the field free region). The relative abundance of daughter ion peaks for methyl and its deuterated analogues lost from the molecular ion of 2,2-d_2-norbornane were compared at repeller plate potentials of 0 and 27 volts.

Repeller plate potential	$M-CHD_2$	$M-CH_2D$	$M-CH_3$
0 volts	14	26	60
27 volts	15	25	60

Recalling that some of the ions which fragment in the source at low repeller plate potential will fragment in the field free region at higher potential (and thus be recorded as metastable ions peaks) we can infer from the above results that the same process (or sum of processes) which occur in the source also occur in the field free region.

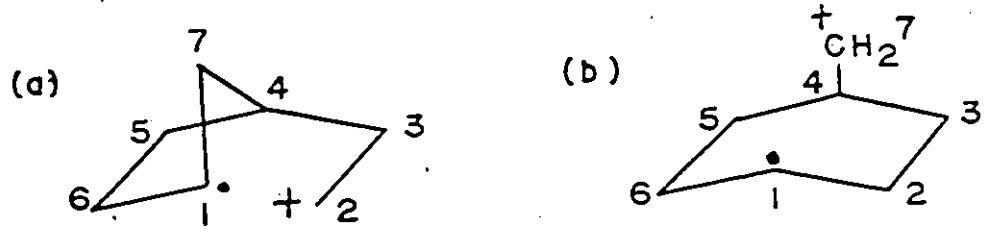
Ion residence times in the source are affected in a similar manner by the acceleration potential. The relative abundance of the metastable ion peaks (obtained by metastable defocusing, Kiser's method [43]) for the loss of a methyl radical and its labelled analogues from the molecular ion of 2,2-d_2-norbornane were compared at acceleration potentials of 2 and 8 Kv. in the M.S.902S mass spectrometer.

Acceleration potential	$M-CHD_2$	$M-CH_2D$	$M-CH_3$
2 Kv.	7	24	69
8 Kv.	7	27	66

The ratios are again almost independent of the ion source residence time indicating that the same process or sum of processes are occuring in the source and first field free region. It can be observed however that the results for daughter ion peaks and metastable ion peaks are significantly different which may indicate that more than one process is occurring involving ions of slightly different life times.

This small difference between daughter and metastable ion peaks is also observed for the other deuterated norbornanes (see Tables II 4.5 and .6).

It is proposed that the methyl loss occurs by the two processes described below. (a) In a manner similar to the ethyl radical and involving the same isotope effects (see Table II 4.3). That is, a 1,2 bond break followed by the loss of the 2 carbon atom and its attached hydrogen atoms, the third hydrogen atom being selected at random from the cyclopentane ring (this can occur similarly for the 3,5 and 6 carbon atoms). (b) A 1,7 (or 4,7) bond break followed by the departure of the 7 methylene group, the third hydrogen atom being selected at random from the cyclohexene ring.



A summation of two parts of process (a) with one part of process (b) gives good to fair agreement with the relative abundance of the daughter ion peaks observed in the labelled compounds for the loss of methyl radicals (see Table II 4.5). Similarly a summation involving equal parts

Table II 4.5.

Relative Abundance of Daughter Ion Peaks for Methyl Loss (^{13}C Corrected).

Compound	$M-CH_3$	$M-CH_2D$	$M-CHD_2$
exo-2-d_1 Norbornane	77	23	—
Calc.	78	22	—
endo-2-d_1 Norbornane	76	24	—
Calc.	78	22	—
exo-2-exo-3-d_2 Norbornane	51	37	12
Calc.	59	41	0
2,2-d_2 Norbornane	64	25	11
Calc.	72	17	11

Table II 4.6.

Relative Abundances of Metastable Ion Peaks* for Methyl Loss and its Labelled Analogues.

Compound	$M-CH_3$	$M-CH_2D$	$M-CHD_2$	$M-CD_3$
exo-2-d_1 Norbornane	82	18	—	—
Calc.	80	20	—	—
exo-2-exo-3-d_2 Norbornane	72	28	0	—
Calc.	66	34	0	—
2,2-d_2 Norbornane	66	27	7	—
Calc.	74	18	8	—
exo-2,3,5,6-d_4 Norbornane	30	57	13	0
Calc.	34	51	15	0

* Defocused Metastables obtained by Kiser's Method[43].

of processes (a) and (b) yields good to fair agreement with the relative intensities of the metastable ion peaks for methyl loss (see Table II 4.6).

The relative abundance of the methyl losses are fairly insensitive to large changes in the amounts of processes (a) and (b) taken and there is little to be gained from adjusting the mix in a attempt to obtain closer agreement with the experimental results. What these results do show is that by invoking an isotope effect, reasonable mechanisms can be found to explain the loss of a methyl radical from the molecular ion of norbornane (without an isotope effect no mechanism specific or random, or summation of mechanisms, could be found to account for the experimental data.

The $C_7H_{11}^+$ ion formed by the loss of a hydrogen atom from the molecular ion fragments by two successive losses of a hydrogen molecule, each loss being accompanied by a flat-top metastable ion peak. The $C_7H_9^+$ ion formed in this fragmentation route also loses C_3H_6 . This particular fragmentation pathway is observed in all the norbornyl compounds studied in this work.

Conclusion of Mass Spectrometry Section

The main conclusions to be drawn from this section of the work, are that by using the methods listed below it is possible to interpret mass spectral fragmentation mechanisms in considerable detail.

(1) Observations of the relative abundance of metastable ion peaks in labelled compounds allows one to isolate a particular fragmentation irrespective of the degree of labelling, this is rarely possible using the relative abundance of daughter ion peaks.

(2) Metastable ions arise by slow, low energy, routes and as a result their formation can generally be explained by one or two simple mechanisms. Daughter ions on the other hand are formed by fast, high energy, processes with contributions from slower low energy processes thus causing difficulty in interpretation. By subtracting the mechanism(s) which explain the metastable ion peak abundance in some chosen proportion from the daughter ion peak abundance, it is often possible to fit a simple mechanism(s) to the remainder.

(3) Knowing the mechanism of a primary fragmentation will often lead to an understanding of subsequent fragmentations in the same route; the inverse is also true (that is the mechanism by which an ion decomposes is related to the ion's formation and correlates with the decomposition of the daughter ion produced).

(4) It has been shown that a compound containing a hetero-atom can lose the same species by more than one mechanism to form ions of the same empirical formula but with different structures and probably different energies. These isomeric daughter ions may also be identified if they fragment by different fragmentation pathways.

Characteristics of Mass Spectrometers Used

Two instruments were used in this work. Normal spectra, relative peak intensities in labelled compounds and undefocused metastable ion peaks were obtained using the Hitachi R.M.U.-6D single focusing mass spectrometer while defocused metastable ion peaks were obtained on the A.E.I. MS 902s double focusing instrument.

The Hitachi R.M.U.-6D mass spectrometer consists of an electron impact ion source, magnetic analyser and a choice of two detection systems, either the Faraday Cup or the electron multiplier. The energy of the bombarding electrons can be varied from 8 to 80 eV.. The acceleration voltage can be adjusted in a stepwise fashion from 900 to 3,600 volts, enabling ions in the mass range 0 to 1,800a.m.u. to be investigated. The source slit is fixed at 0.6 mm., but the collector slit can be varied from 0 to 1 mm., allowing a resolving power of up to 2,000. The electron multiplier detector system has a gain of up to 10^4, so that spectra can be obtained from sample sizes as small as 1 μ mole. The inlet systems are capable of being heated up to 200°C..

The A.E.I. MS902s mass spectrometer consists of an electron impact ion source, an electrostatic analyser, a magnetic analyser and a detection system of either a Faraday Cup or electron multiplier. The energy of the bombarding electrons can be varied from 5 to 100 eV. Acceleration voltages of 2,4,6 and 8 kV. are available allowing a large

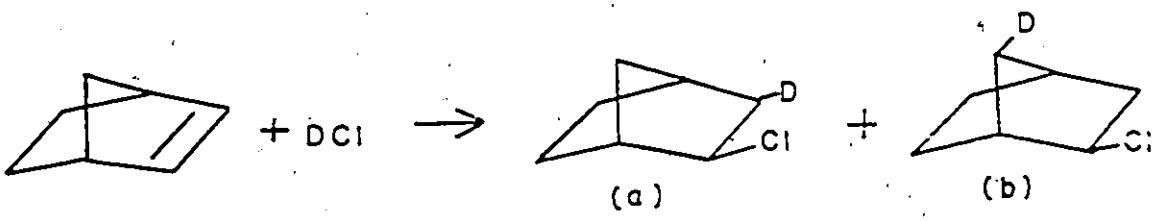
mass range to be covered(up to about 2,000 a.m.u.). Three variable slits are present on the instrument; one is present on the source exit , another at the exit of the electrostatic sector and the last one is at the collector. A dynamic resolving power of 10,000 is possible , whilst static resolving power can be up to 100,000. The electron multiplier has a gain of up to 10^6. The inlet systems are capable of being heated up to 250°C.. This instrument has been modified to allow defocusing of metastable ions by Kiser's [43] and Jenning's [45] methods.

Part III

Some Observations on the Addition Reaction Between Hydrogen Chloride and Norbornene.

Object of Investigation

During the initial attempts to prepare specifically mono-deuterated norbornyl chloride (for gas phase pyrolysis see Part I 5.b) one of the preparative methods used was the addition of deuterium chloride to norbornene at -78°C in chloroform. Subsequent mass spectral and N.M.R. analysis[79] of the exo-2-norbornyl chloride produced indicated that the deuterium had almost an equal probability of being located in one of two positions.

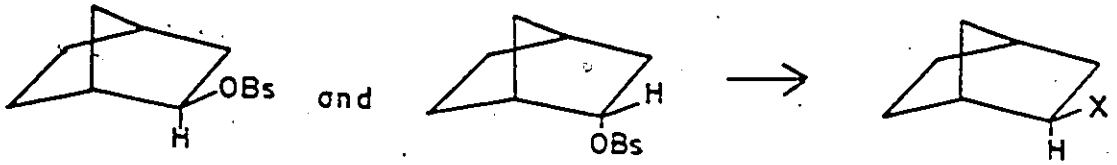


The percentage of the two products obtained at -78°C [(a) and (b) above] were observed to be 56 ± 2% and 44 ± 2% respectively. The mass spectrometric analytical technique, which requires very little sample, is quick, accurate and easy to perform (see Part II 1.A). It was also simple to add deuterium chloride to norbornene under controlled conditions and so it was considered to be of some interest to carry out a temperature study to observe if any effect was involved. The second point of interest was whether the

presence of the deuterium in the 3 position produced the 56:44 product ratio through an isotope effect, or whether the possible intermediate, the norbornyl cation, is captured in an asymmetric state.

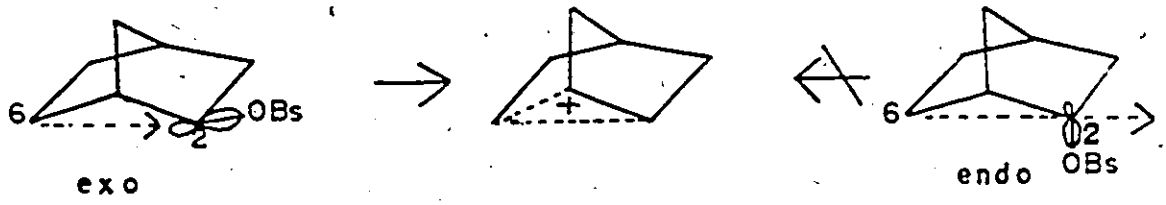
Introduction

Winstein and Trifan[108] observed that the hydrolysis and acetolysis of exo and endo norbornyl brosylates yielded only the exo-products



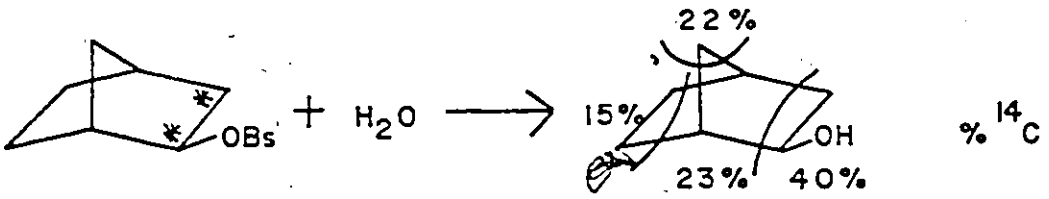
where X = AcO^- or OH^-

Winstein et al.[109] showed that the exo-norbornyl brosylate hydrolysed 10^4 times faster than the endo-norbornyl brosylate. He[108,109] explained the difference in rates by postulating that rear attack of the exo-2 substituent by the 6 carbon atom (which is clearly not possible in the case of the endo-substituent) enhanced the removal of the exo substituent. Winstein represented the intermediate as the non-classical carbonium ion shown below.

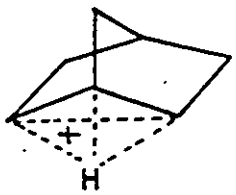


It can be seen that in Winstein's non-classical carbonium ion, carbon atoms 1 and 2 are identical, as are carbon atoms 3 and 7. Attack on the non-classical carbonium ion intermediate by the hydroxyl ion can therefore occur with equal probability at carbon atoms 1 or 2. The Wagner-Meerwein isomer is the product obtained when the attacking species adds to the 1 carbon atom.

Roberts et al.[110,111] pointed out however, that the non-classical carbonium ion could not explain the presence of ^{14}C in the 5 and 6 positions which they observed in the hydrolysis products of norbornyl-2,3-^{14}C-brosylate.

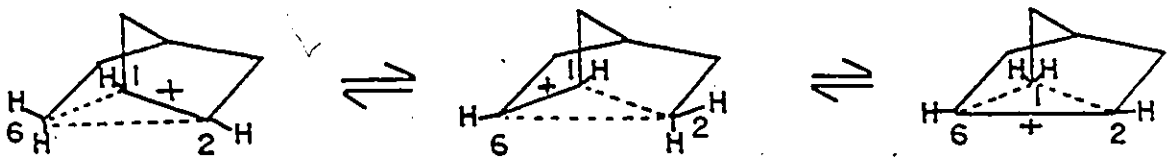


Roberts et al.[110,111] explained their results by proposing that the reaction proceeded via the non-classical nortricyclonium ion 45% of the time

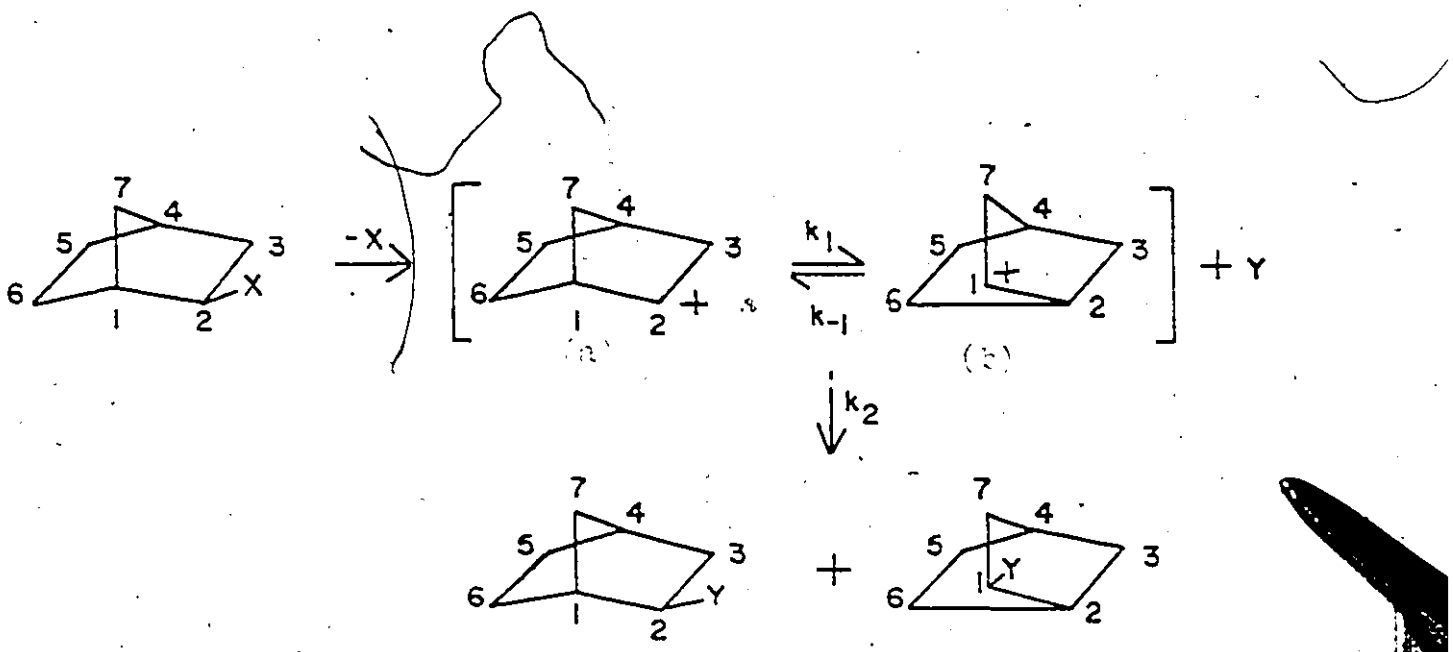


and via Winstein's non-classical carbonium ion[108,109] 55% of the time.

Winstein[112] suggested that an alternative explanation for Roberts' results could be obtained from three forms of the non-classical carbonium ion, the inter conver ion being achieved by hydride migration implying carbons 6,2 and 1.



H.C. Brown[113] stated that there is insufficient evidence for non-classical ions and that the results can best be explained in terms of an equilibrating pair of classical carbonium ions. In this case the product distribution will be kinetically controlled and will depend on the rate of establishment of the equilibrium (k_1/k_{-1}) relative to the rate of attack of the anion (k_2). In this case the Wagner-Meervein reaction occurs when the attacking anion adds to the rearranged classical carbonium ion (b), see page 234. The classical carbonium ion pair in conjunction with a 6,2 hydride shift can equally well explain the results of Roberts et al.[110,111].



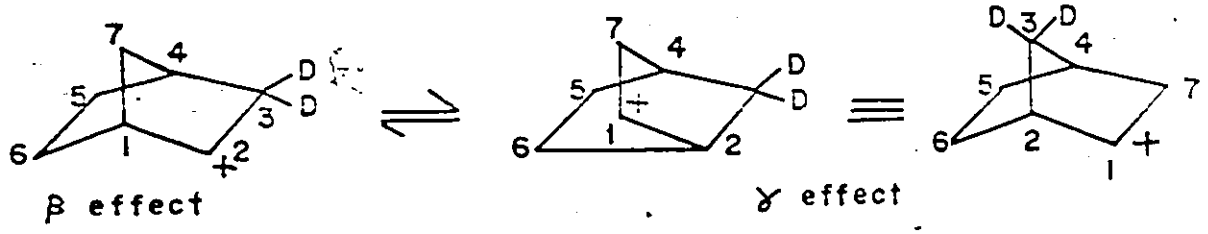
The question as to whether the structure is classical or non-classical has been keenly pursued over the last 20 years. One approach to the problem has been to study the kinetic isotope effects on solvolysis and acetolysis of various norbornyl compounds[114,115]. For example in the acetolysis of norbornyl brosylates [115], the results of which are presented in Table III 1.[115], the secondary kinetic isotope effects in endo-brosylates were observed to have the predicted value for a classical carbonium ion, but in the case of the exo-brosylates the kinetic isotope effects

Table III.1.

Secondary Deuterium Isotope Effects in the Acetolysis of 2-Norbornyl Brosylates[115]

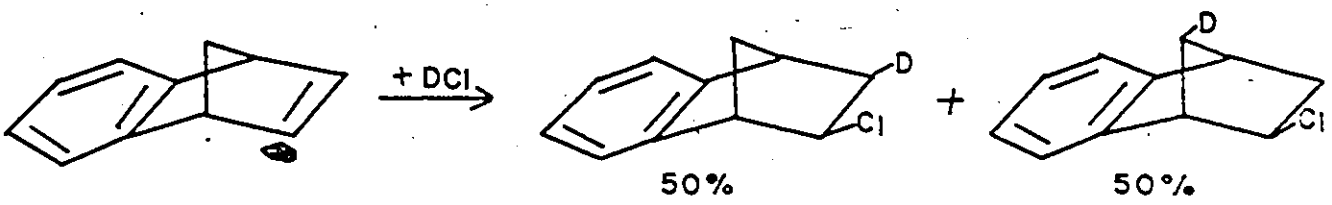
Compound	Transition State	Expected k_H/k_D	Observed k_H/k_D
exo-2-Norbornyl Brosylate-endo-2-d_1	Classical	1.15-1.20	
	Bridged	1.10	1.10
endo-2-Norbornyl Brosylate-exo-2-d_1	Classical	1.15-1.20	1.20
exo-2-Norbornyl Brosylate-3,3-d_2	Classical	1.30	
	Bridged	1.10	1.014
endo-2-Norbornyl Brosylate-3,3-d_2	Classical	1.30	1.26

are observed to be lower than those for the classical carbonium ion. In terms of the non-classical carbonium ion it is argued that the low kinetic isotope effect for the exo-brosylate is due to the presence of the rear attack of the exo-2-substituent by the 6 carbon atoms. However, the results can be explained equally well in terms of Brown's classical carbonium ion pair if it is noted that the deuterium atoms will occupy different positions in each of the equilibrating carbonium ions



and thus would result in a reduced secondary kinetic isotope effect!

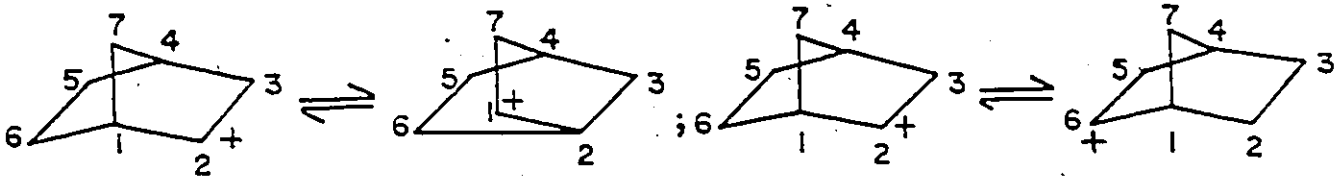
This problem, the structure of the norbornyl cation has also been investigated by the addition of hydrogen and deuterium chloride to various norbornenes (substituted; labelled and unlabelled[79,116-118]). An example is the addition of deuterium chloride to benzo-norbornadiene [119], the resulting products were found to be a 50:50 mixture of the two deuterochlorides. These results can be explained either by the non-classical carbonium ion or by a fully equilibrated pair of classical carbonium ions.



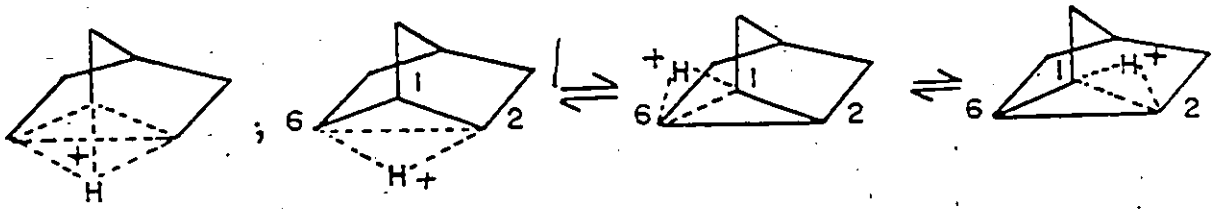
50% 50%

The stable norbornyl cation has been detected in strong acid solutions such as SbF_5, SO_2 [120], $HF-SbF_5SO_2$ [120], $FSO_3-H-SbF_5-SO_2$ [121] and $GaBr_3-SO_2$ [122] so-called "magic" and "super" acids. The low temperature (-60°C) N.M.R. spectrum of the norbornyl cation in SbF_5 or SbF_5-SO_2 [120] was shown to consist of three peaks at δ 5.35, 3.15 and 2.20 (relative to external T.M.S.) in the ratio 4:1:6 respectively; on warming the acid solution to a temperature of -5°C [120] the three peaks were observed to collapse to a singlet.

These results can again be explained equally well by both the classical and non-classical interpretations. Classical, if the Wagner-Meerwein reaction and the 6,2 hydride shift is rapid, with a slow 3,2 hydride shift, then the four hydrogen atoms on the 6,2 and 1 carbon atoms will be identical, similarly the six hydrogen atoms on the 3,5 and 7 carbon atoms. The hydrogen on the 4 carbon atom is unique



Non-classically, the results can be explained in terms of the face or equilibrating edge protonated nortricyclene (a non-classical carbonium ion where the hydrogen atoms on the 6,2 and 1 carbon atoms are migrating round the cyclopropane ring)



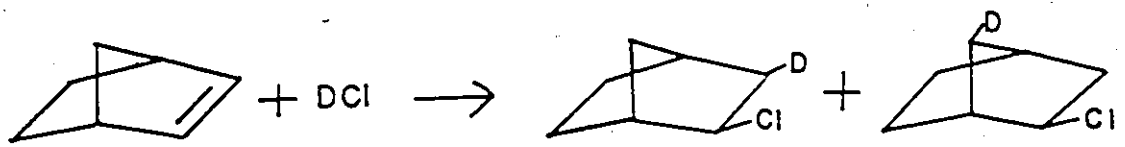
Olah et al.[123] used Raman spectra to study the norbornyl cation on a very short time scale, vibration transition rates are faster than hydride shifts or Wagner-Meerwein reactions. On comparison of the low temperature Raman spectra of the norbornyl cation in "magic" acid with protonated nortricyclene, identical spectra were obtained showing that the structure of the norbornyl cation was protonated nortricyclene in these media. Further studies by Olah et al.[124] on carbon ^{13}C N.M.R. and low temperature

N.M.R. indicated that in strong acid solution the structure of the norbornyl cation is best represented as corner protonated nortricyclene.

The Norbornene Addition Reaction

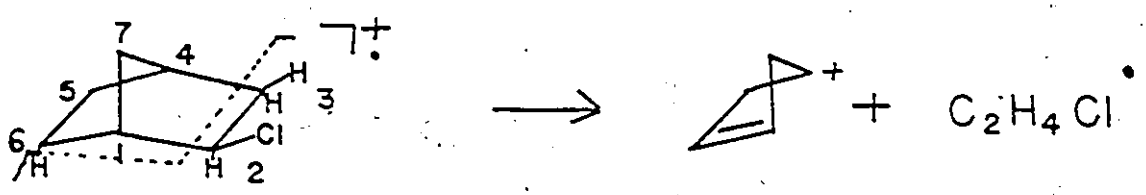
Results and Discussion

Brown and McIvor [79] have shown by a 220 M.Hz. N.M.R. study that the addition products obtained by reacting deuterium chloride with norbornene at -78°C in chloroform were 55 ± 3% exo-2-norbornyl chloride-exo-3-d_1 and 45 ± 3% exo-2-norbornyl chloride-syn-7-d_1 .



It has been shown (Part II 1.A) in the mass spectrum of Brown and McIvor's reaction products, that the ratio of the abundances of the metastable ion peaks for the loss of mono-deuterated and unlabelled chloroethyl radicals from the molecular ion is 56 ± 2% C_2H_3DCl:44 ± 2% C_2H_4Cl . It has also been shown that in the mass spectrum of exo-2-norbornyl chloride the loss of a chloroethyl radical

($C_2H_4Cl^+$) from the molecular ion involves specifically carbon atoms 2 and 3 and their attached hydrogen atoms with the fourth hydrogen atom coming from the endo-6 position.



It was decided to use the ratio of the labelled chloroethyl:unlabelled chloroethyl metastable ion peaks as a measure of the product ratio resulting from the Wagner-Meerwein reaction during the addition of hydrogen or deuterium chloride to norbornene and deuterated norbornenes. A typical set of metastable ion peaks for the chloroethyl loss from the molecular ion of mono-deuterated exo-2-norbornyl chloride prepared by deuterium chloride addition to norbornene, are shown in Fig. III.1, these metastable ion peaks were obtained using a single focusing mass spectrometer. Fig. III.2 shows the same set of metastable ion peaks but obtained in the defocused mode using Jennings[44,45] method on a double focusing mass spectrometer.

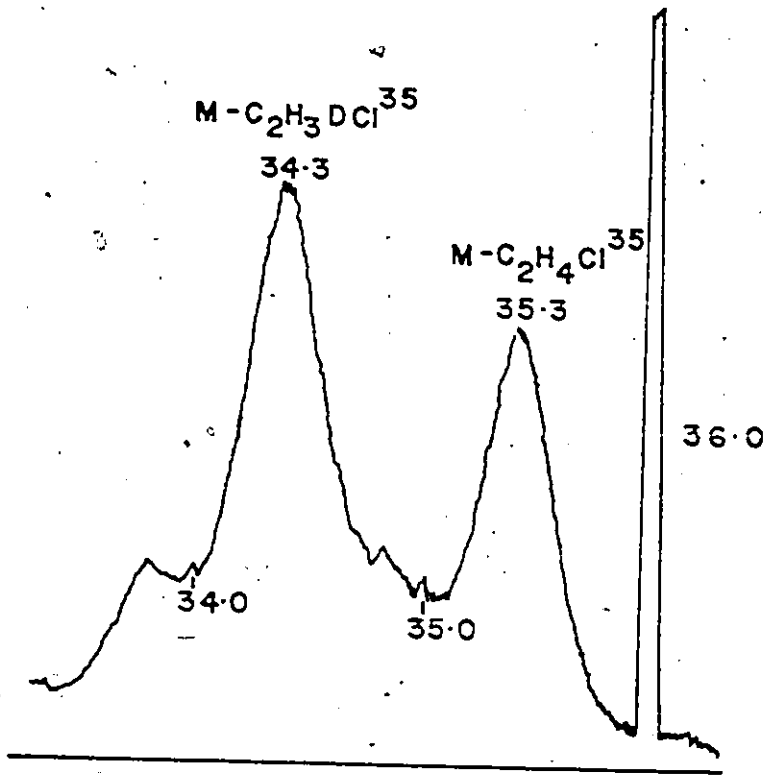


Fig. III 1. Metastable-Ion Peaks for Chloroethyl Radical Loss from the Molecular Ions of the Addition Products of Norbornene and Deuterium Chloride.

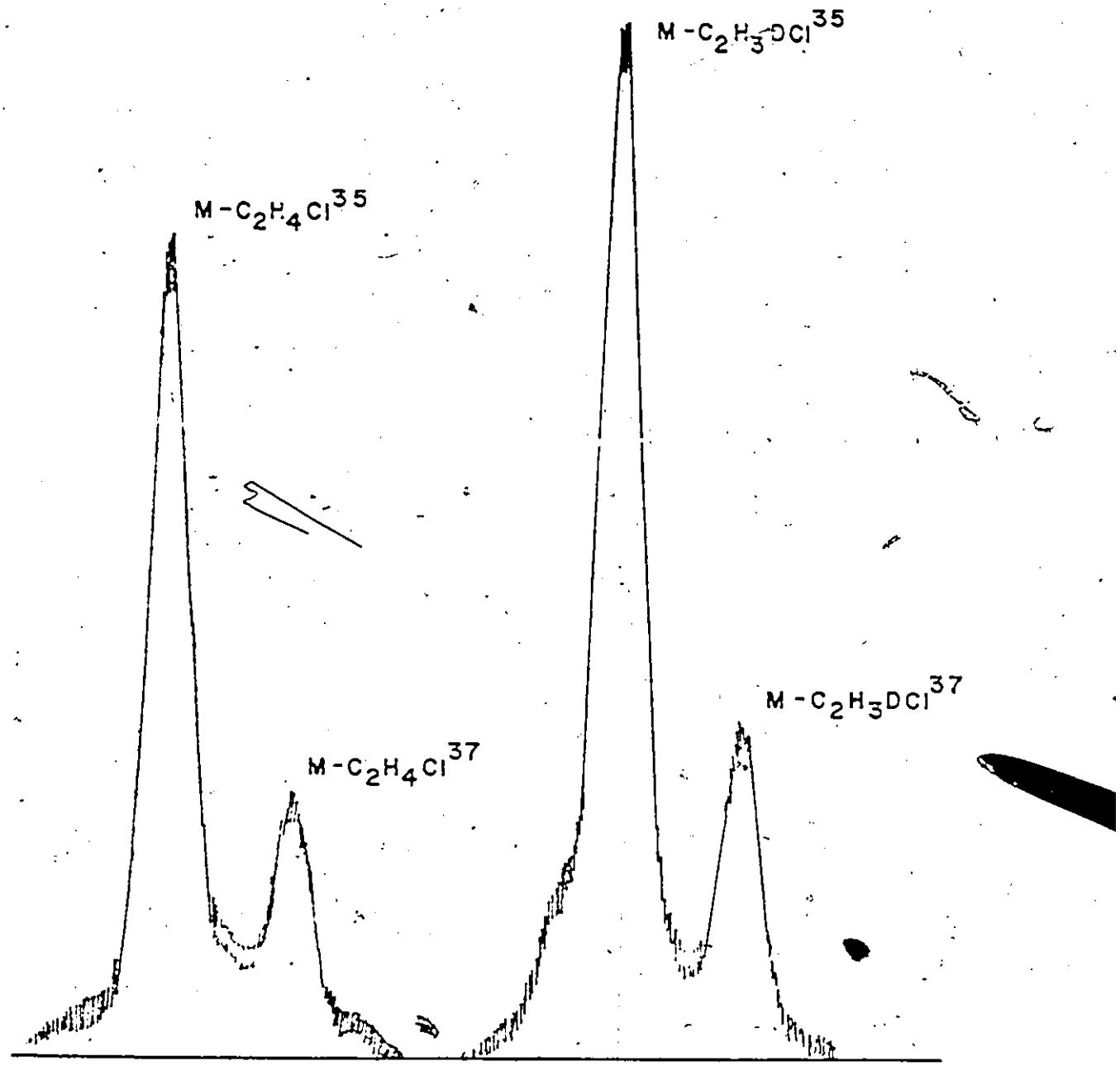


Fig. III 2. Unfocused Metastable Ion Peaks for Chloroethyl Neutral Loss from the Molecular Ions of the Addition Products of Norbornene and Deuterium Chloride.

Deuterium chloride was added to norbornene in two ways: (1) in the absence of solvent by admitting the deuterium chloride gas into a cooled evacuated tube containing the norbornene, (2) by bubbling deuterium chloride through a chilled solution of norbornene in methylene chloride.

Table III.2 contains the results for the product ratios obtained when deuterium chloride was added to norbornene in the presence and absence of methylene chloride solvent at -21°, -78°, -95° and -119°C. As observed from Table III.2 identical results were obtained in each case, the mass spectral analysis showing that 44 ± 2% of the deuterium is in the syn-7 position and 56 ± 2% of the deuterium is in the exo-3 position, giving a product ratio of 0.79 which is independent of temperature over a range of ~100°C .

In order to check that no secondary reaction involving positional change of the label was occuring on warming the reaction mixture to room temperature, a sample of exo-2-norbornyl chloride-2,3,3-d_3 was treated with deuterium chloride under conditions identical with those of the addition reaction at -119°C. Examination of the metastable ion peaks for the loss of the chloroethyl radicals in the labelled norbornyl chloride before and after the above

Table III.2.

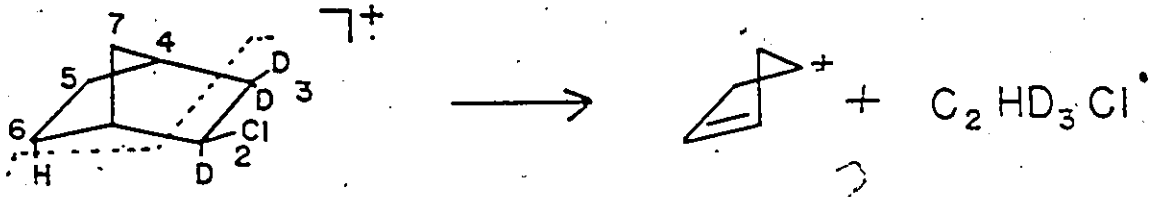
Percentage† of Exo-3-d_1-Exo-2-Norbornyl Chloride and Syn-7-d_1-Exo-2-Norbornyl Chloride Obtained When Deuterium Chloride is Added to Norbornene at Various Temperatures.

Temperature °C	Percentage exo-3-d_1	Percentage syn-7-d_1
-21	56 ± 2%	44 ± 2%
-78	57 ± 1%*	43 ± 1%*
	57 ± 2%	43 ± 2%
-95	55 ± 2%	45 ± 2%
-119	54 ± 2%	46 ± 2%

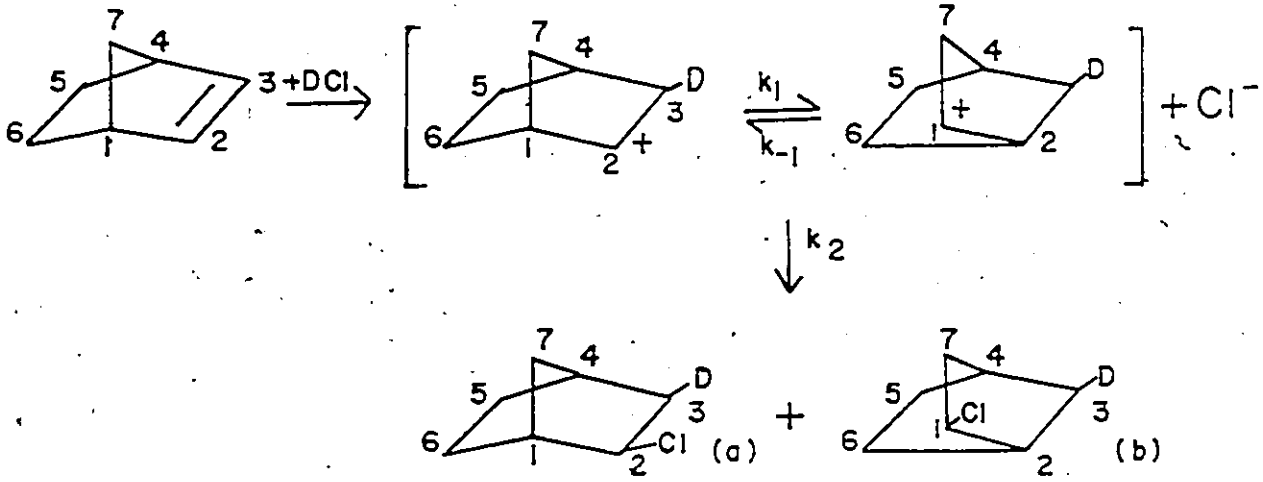
† Percentages measured using metastable ion peaks obtained at low eV on a single focusing mass spectrometer.

* Percentages measured by defocused metastables obtained on a double focusing instrument.

treatment showed only one metastable ion peak, corresponding to the loss of C_2HD_3Cl from the molecular ion, proving that neither deuterium position nor isotope content had changed as a result of the treatment with deuterium chloride.



In terms of the classical carbonium ion pair the greater yield of exo-2-norbornyl chloride-exo-3-d_1 over exo-2-norbornyl chloride-syn-7-d_1 could arise as a result of k_2 (rate of Cl^- attack on the norbornyl cation) being slightly greater than k_1 (rate of formation of the

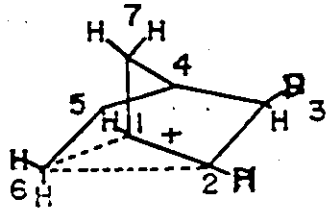


rearranged secondary carbonium ion). The results recorded in Table III.2 show that the product ratio (b/a) is independent of temperature; thus, either both k_1 and k_2

have the same (or no) temperature coefficient, or if the equilibrium k_1, k_{-1} is achieved and lies, by virtue of an isotope effect, in favour of (a) then the equilibrium constant too must have no temperature coefficient.

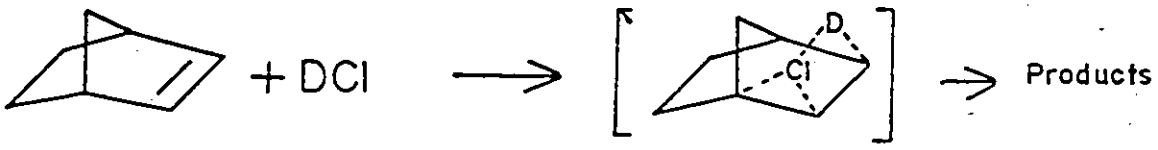
A β secondary isotope effect could be an alternative explanation for the product ratio being independent of temperature and the deviation of a/b from unity. The reciprocal of the product ratio, 1.21 is a measure of the isotope effect and it is similar in magnitude to the observed kinetic isotope effects for the solvolysis[125] of labelled endo-2-norbornyl bromides and brosylates but greater than the value obtained from the exo-derivatives. This is in direct contrast with the statements of Brown et al.[116] and Kwart et al.[126] who claim that the effect of a β deuterium substituent on the 3 carbon atom (in the classical carbonium ion pair) in directing the halogen ion to the alternate sites would be negligible.

The observed deviation of the product ratio from unity and its temperature independence could be explained by a β secondary isotope effect operating in a non-classical carbonium ion

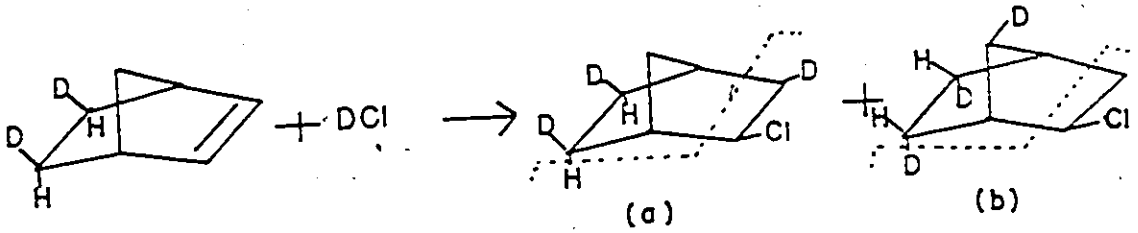


The isotope effect can be envisaged as resulting from a reduction in the hyperconjugation between the delocalized positive charge and the hydrogens on the 3 carbon atom due to the presence of the deuterium, this will result in more positive charge being present on the 1 and 7 carbon atoms relative to the 2 and 3 carbon atoms. However, the charge on the 7 carbon atom is obtained at the expense of the 1 carbon atom (hyperconjugation) and the reduction in charge at the 3 carbon atom will result in a slightly greater charge on the 2 carbon atom, thus the 2 carbon atom will be more positive relative to the 1 carbon atom, inspite of the greater total positive charge over the 1 and 7 carbon atoms mentioned above.

A third explanation which must also be considered is that the ion is captured in an asymmetric state possibly as shown below (the classical explanation is really another form of asymmetric capture)



There are several reports in the literature concerning isotope effects which occur when deuterium is present on the 6 carbon atom in the norbornyl structure [127, 128]. These authors have observed that the kinetic isotope effect (k_h/k_d) for the solvolysis of exo-2-norbornyl brosylate is of the order of 1.10, but for the endo-2-norbornyl brosylate there is no isotope effect. It was thus deemed of some interest to investigate the effect on the product ratio of a deuterium atom located at the 6 carbon atom, in order to distinguish between the above explanations. This was studied by adding deuterium chloride to norbornene-exo-5-exo-6-d_2 in the absence of solvent at -131.5°C and -86°C. Metastable peak analysis of the products obtained at each temperature showed only one metastable ion, namely that for the loss of a monodeuterated chloroethyl radical from the molecular ion of the trideuterated norbornyl chloride. If the two species obtained from norbornene-exo-5-exo-6-d_2 are (a) and (b) shown below:

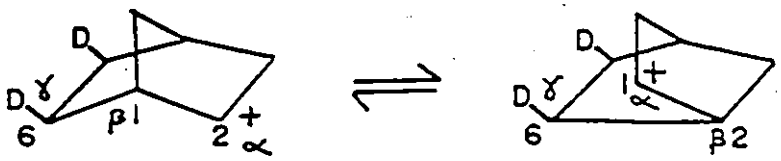


then in each case only a monodeuterated chloroethyl radical can be lost. Products (a) and (b) arise from chloride addition to the norbornyl cation at positions 1 and 2. Note the inversion of configuration (exo-d_1 to endo-d_1 at positions 5 and 6) when the chloride anion adds to the 1 position.

The addition of deuterium chloride to norbornene-exo-5-exo-6-d_2 shows the presence of the Wagner-Meerwein reaction but not its extent. In order to obtain a measure of the product ratio the addition reaction was repeated using hydrogen chloride and norbornene-exo-5-exo-6-d_2 at -131.5°C and -86°C in the absence of solvent and at -78°C using methylene chloride as solvent. For the addition at each temperature the metastable ion peak analysis of the chloroethyl radicals lost from the products showed 44 ± 2% loss of C_2H_3DCl and 56 ± 2% loss of C_2H_4Cl giving a product ratio of 0.79 . This ratio is thus independent of temperature and within experimental error, the same as that obtained in the addition of deuterium chloride to norbornene.

These results can be explained in terms of the classical carbonium ion pair in the same manner as the product ratio obtained from DCl addition to norbornene. The greater yield of exo-5-exo-6-d_2-exo-2-norbornyl chloride arising from k_2 (rate of chloride ion attack on the norbornyl cation) being slightly greater than k_1 (rate of

formation of the rearranged secondary carbonium ion). No isotope effect can be invoked with the classical carbonium ion pair because cancellation of the equivalent γ effects would yield a product ratio of unity.



We will now briefly consider these experimental results in terms of the non-classical carbonium ion [113]. Winstein explained the faster rate of reaction for solvolysis [129a] and acetolysis [129b] of the exo over the endo compounds in terms of the rear attack from the 6 carbon atom to the exo-2-substituent, an effect which is not possible in the case of the endo-2-substituent.

The rear attack may arise from the rear lobe of the exo-6-hydrogen carbon bond; as this interaction occurs a corresponding weakening of the 1,6 bond must also occur

to give the resultant non-classical carbonium ion. When the deuterium carbon bond can interact (along the 6,2 partial bond) with the delocalized charge, see above, it makes the 2 carbon atom more positive relative to the 1 carbon atom. This could explain the observed yield of exo-5-exo-6-d_2-exo-2-norbornyl chloride.

The product ratio obtained when deuterium is in the exo-6-position can also be explained by the ion being captured in an asymmetric state (see page 247). This agrees exactly with the results obtained on adding deuterium chloride to norbornene.

In order to investigate the effect of deuterium in the endo-6-position, hydrogen chloride was added to norbornene-endo-5-endo-6-d_2 [130] at -78°C in the absence of solvent. Metastable ion analysis of the products indicated a product ratio of 0.85 (46.5 ± 2% C_2H_4Cl to 54.4 ± 2% C_2H_3DCl loss). These results must be interpreted with some caution since the label in this norbornene was not positionally pure as shown by a careful mass spectrometric study of the olefin (see Appendix, page 276). However these results (see Appendix, page 277 for details) are compatible with a product ratio of 0.79 (44 ± 2% exo-5-exo-6-d_2-exo-2-norbornyl chloride : 56 ± 2% endo-5-endo-6-d_2-exo-2-norbornyl chloride). These results can be explained in terms of the classical carbonium ion pair in a similar

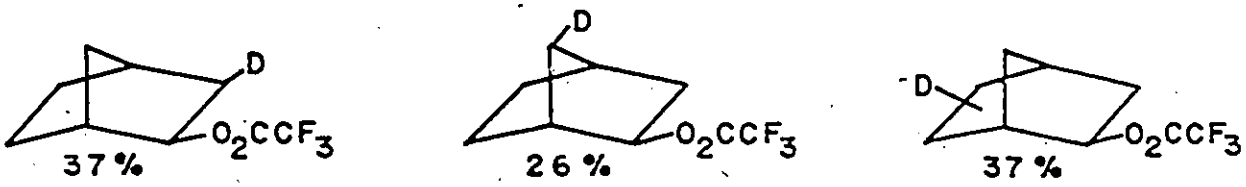
manner to the product ratios obtained in the DCl addition to norbornene and HCl addition to norbornene-exo-5-exo-6-d_2.

The non-classical carbonium ion in conjunction with a β secondary isotope effect is ruled out by the preceding results, this would require that the inverse ratio be observed, namely 44 ± 2% endo-5-endo-6-d_2-exo-2-norbornyl chloride and 56 ± 2% exo-5-exo-6-d_2-exo-2-norbornyl chloride i.e. no difference in the product ratio regardless of whether the deuterium is in the exo or endo position.

The results of DCl addition to norbornene, HCl addition to norbornene-exo-5-exo-6-d_2 and HCl addition to norbornene-endo-5-endo-6-d_2 can be explained in terms of the non-classical carbonium ion in the same manner as the classical carbonium ion pair, i.e. that k_2 (the rate of chloride ion attack on the norbornyl cation) be slightly greater than k_1 (in this k_1 would be the rate of formation of the non-classical carbonium ion). This explanation in terms of the classical or non-classical carbonium ion requires that k_2/k_1 remains independent of temperature.

The above description of the results in terms of the non-classical carbonium ion and the similar description in terms of the classical carbonium ion pair (see page 245) could be termed capture of the norbornyl cation in an

asymmetric state. Brown et al.[117] explain their results for the addition of deuterotrifloroactetic acid to norbornene (see below) in terms of asymmetric capture of the norbornyl

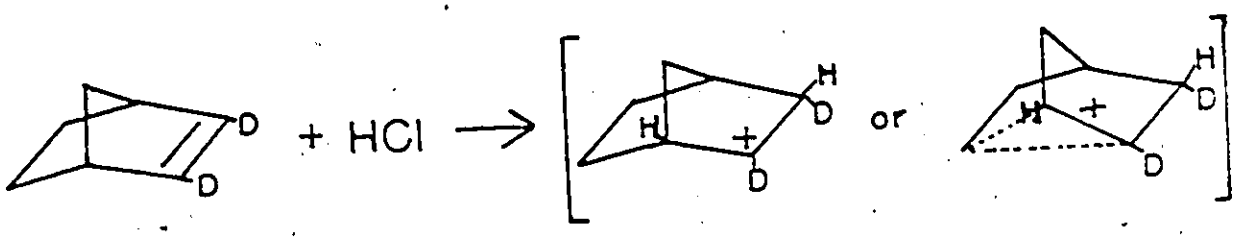


cation, which they show as occurring via the classical carbonium ion pair. An alternate form of asymmetric capture is shown on page 247 .

In order to confirm that no β secondary isotope effect is operating and the norbornyl cation is indeed captured in an asymmetric state, hydrogen chloride was added to a mixture of norbornene and norbornene-syn-7-d_1 in the absence of solvent. The mixture of norbornenes was obtained by the specifically cis dehydrobromination[89] of the addition products of deuterium bromide and norbornene which were a mixture of exo-2-norbornyl bromide-exo-3-d_1 and exo-2-norbornyl bromide-syn-7-d_1 . Metastable ion analysis of the final product (see Appendix for details of calculations, page 279) showed that the monodeuterated HCl addition product consisted of 55 ± 2% exo-2-norbornyl

chloride-syn-7-d_1 and 45 ± 2% exo-2-norbornyl chloride-exo-3-d_1 substantiating that in this reaction the norbornyl cation is indeed captured in an asymmetric state.

Having shown the absence of a β secondary isotope effect the possibility of an α isotope effect was investigated by adding hydrogen chloride to norbornene-2,3-d_2.



The addition reaction was carried out at -119°C. This gave the largest isotope effect, which also is temperature dependent. Metastable ion analysis showed that the product ratio is 1.15 [(1,7-d_2 (rearranged product))/(2,3-d_2 (unrearranged product))]. The addition was repeated under identical conditions using deuterium chloride; here the product ratio was found to be 1.52 . Clearly there is an α isotope effect which overrides the asymmetric capture and since the product ratio depends on whether hydrogen chloride or deuterium chloride is used it is suggested that a solvent isotope effect is also operating.

To obtain the rearranged products the chloride ion must add to the 1 carbon atom, for this to occur the ion must undergo a rearrangement, which we know (from the deuterium chloride addition to norbornene) is stopped before completion (i.e. capture in an asymmetric state). The

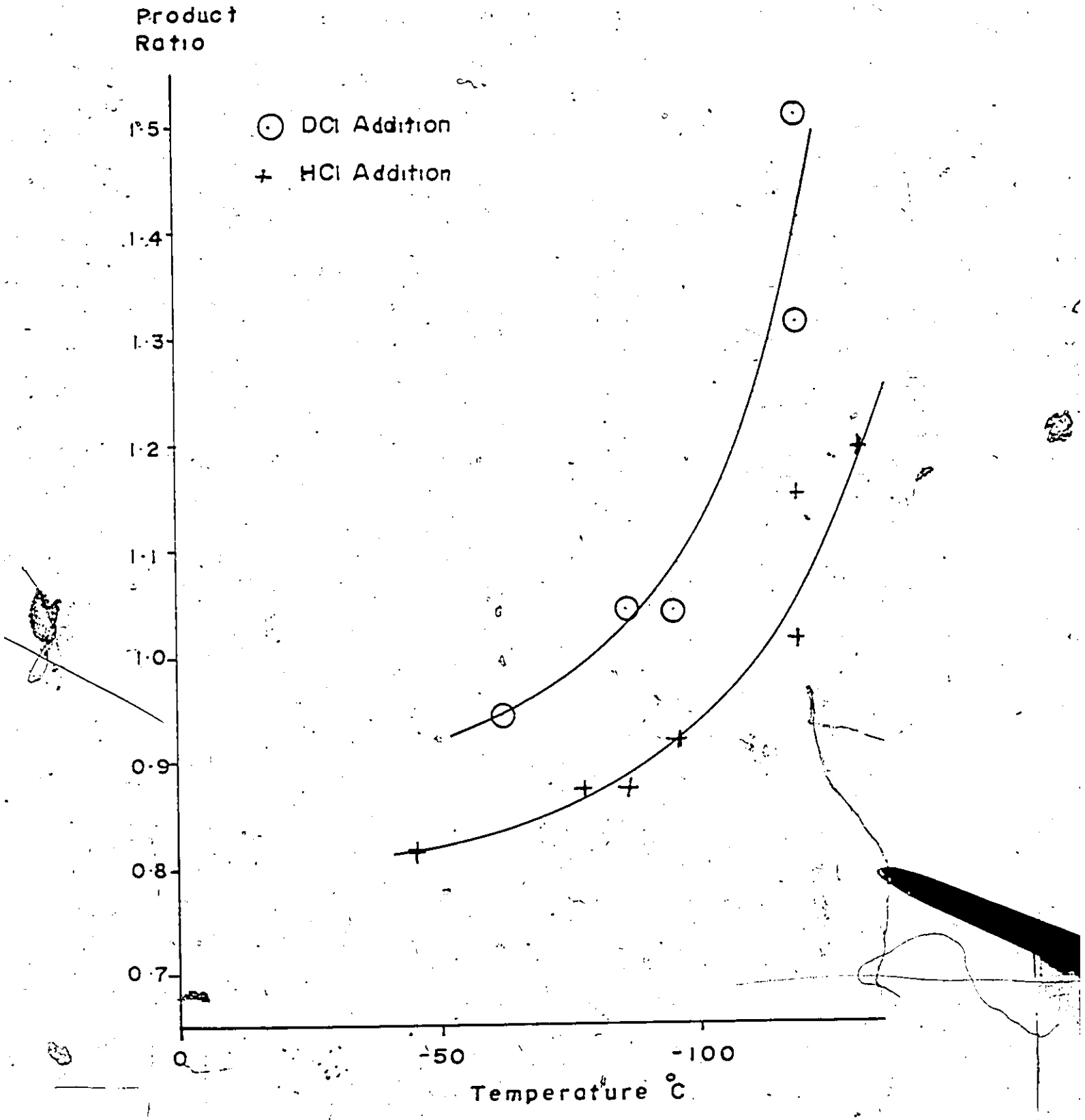


Fig. III.3. A Plot of Product Ratio Against Temperature.

observed results for the addition of hydrogen chloride and deuterium chloride to norbornene-2,3-d_2 (1.15 and 1.52 respectively) would seem to rule out the possibility of participation by the classical carbonium ion pair because for these a product ratio greater than unity [(rearranged products)/(unrearranged products)] is very unlikely.

Hydrogen chloride and deuterium chloride were added to norbornene-2,3-d_2 at a series of temperatures in order to investigate the temperature dependence of the α secondary isotope effect. Reasonable curves can be drawn through the points (see Fig. III 3) for the products from both the hydrogen and deuterium chloride addition products. For the hydrogen chloride addition products, the product ratio approaches the value for the deuterium chloride addition to norbornene at the higher temperatures, the product ratio for the deuterium chloride addition products approaches a higher asymptotic value at the higher temperatures.

It is observed from Fig. III.3 that a few points lie off the curve particularly at the lower temperatures; however every attempt was made to carry out the reactions under identical conditions and it was felt that the variation could be due to slight changes in the rate of addition of the halogen acid gas. To investigate this point, hydrogen

chloride was added extremely slowly (1 cm pressure every 2 min. for a period of 1 hour in the absence of solvent) to norbornene-2,3-d_2 cooled to -131.5°C, the product ratio was found to be 0.83 . The addition was repeated at -119° and -83°C with the same result. These values indicate that on slow addition of hydrogen chloride the product ratio is independent of temperature and the value is almost the same as the product ratio (0.79) obtained for deuterium chloride addition to norbornene. Apparently on slow addition of hydrogen chloride there is no α secondary isotope effect from the deuterium on the 2 carbon atom but only the product ratio which arises by the asymmetric capture of the cation.

Lee and Wong [131] observed very low α isotope effects in their investigation of the acetolysis of exo-2-norbornyl brosylate-endo-2-d_1 ; they presented two arguments to explain this result. The first was in terms of the non-classical carbonium ion; the low value was believed to arise from anchimeric assistance (rear attack of the exo-2 substituent by the 6 carbon atom) which confers SN_2 character to the reaction at the 2 carbon atom. SN_2 reactions have been shown to have no α isotope effect[132,133]. This proposal could explain the lack of an α isotope effect in the slow addition of hydrogen chloride to norbornene-2, 3-d_2. Their second explanation was in terms of the classical

carbonium ion pair; as a result of the charge migration, the deuterium atom effectively alternates between an α and β isotope substituent and would thus yield a reduced α secondary isotope effect.

The effect of adding hydrogen chloride rapidly (1 atmosphere instantaneously in the absence of solvent) to norbornene-2,3-d_2 was then investigated at several temperatures in the range 0° to -131.5°C. The results of these experiments are shown in Fig. III 4, clearly these values are temperature dependent. The observed temperature dependence appears to be a function of solvent: note the sharp rise near the liquifaction temperature of hydrogen chloride (-84.9°C); the presence of liquid hydrogen chloride would yield a highly polar solvent. In order to study the question of polarisability the addition reaction was carried out in a series of solvents of increasing dielectric constant. The results of the addition reactions carried out at -78°C, where the deviation from the slow value is small, are shown in Table III 3. The polarisability of the solvents clearly affects the product ratio, but the effect is too small to account for the deviation of the product ratio from the value obtained on slow addition. No temperature effect was observed in the deuterium chloride addition to norbornene (where only the value for asymmetric capture was observed). Therefore the temperature effect in the reaction must be

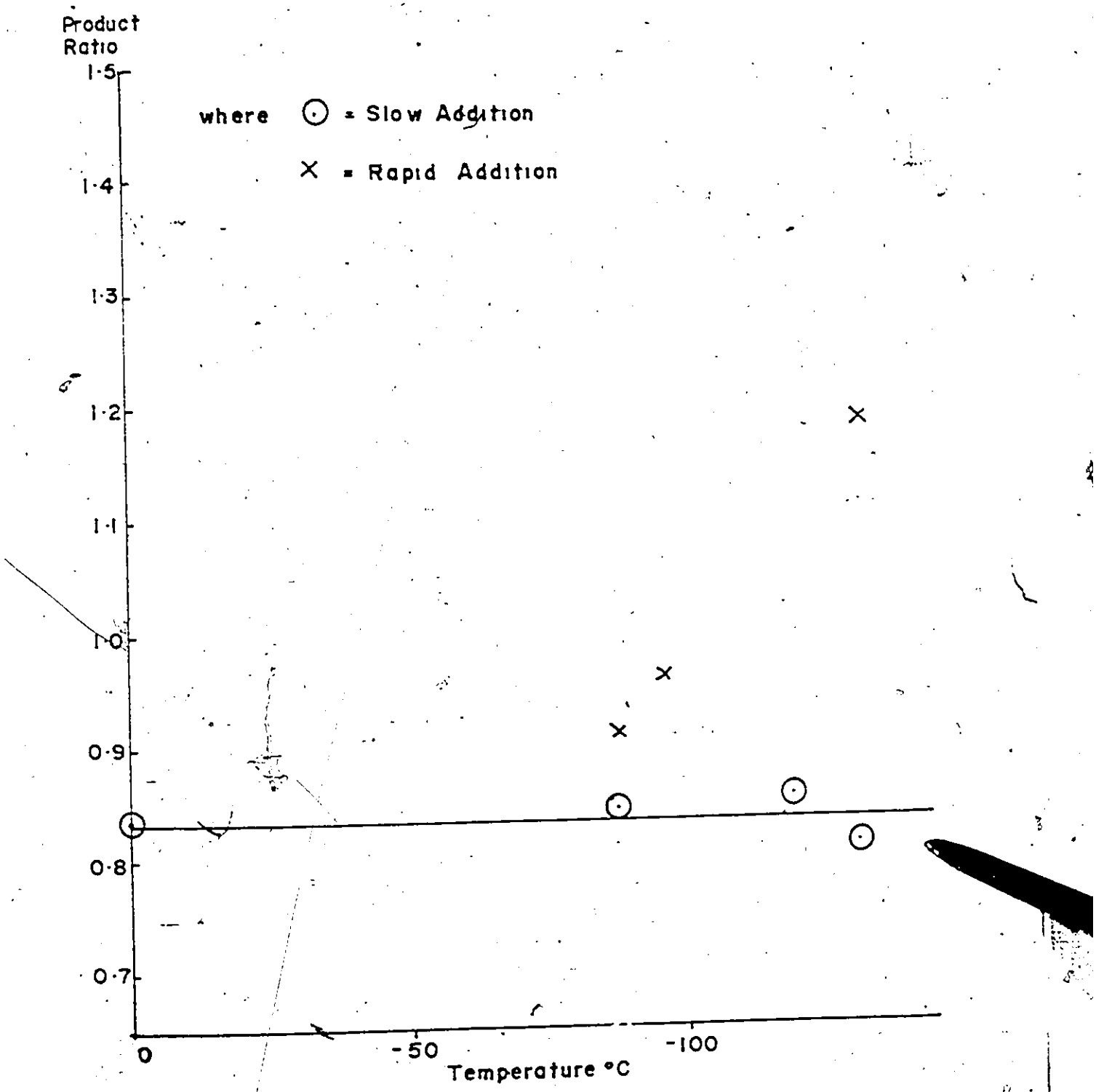


Fig. III 4. A Plot of the Product Ratio Obtained from the Hydrogen Chloride Addition to Norbornene-2,3-d_2 Against Temperature.

Table III 3.

Effect of Solvent Polarity on the Product Ratio of Hydrogen Chloride Addition to Norbornene-2,3-d_2 at -78 °C.

Solvent	Dielectric Constant	Dipole Moment (Debyes)	Product Ratio
Hydrogen Chloride	11.86	1.08	0.80 slow addition 0.87 fast addition
Ether	9.68 at -40°C 10.4 at -116°C	1.15	0.96
Methylene Chloride	115.23	1.60 (addition at -83°C)	1.00
Ethyl Bromide		2.03	1.00

linked with the deuterium on the 2 carbon atom; it is possibly due to an induced effect connected with the presence of excess hydrogen chloride.

Mayo et al.[134] have studied the kinetics of hydrogen chloride addition to isobutene in the absence of catalysts in non-ionizing solvents. They observed the rate to be third order in hydrogen chloride and first order in isobutene. They also observed a large increase in the rate if the reaction mixture was first cooled to the temperature of liquid nitrogen and then warmed to 0°C, after which the rate was measured. The third order in hydrogen chloride and the temperature effects were explained by the formation of a hydrogen chloride-isobutene complex at the lower temperatures which slowly decomposed on warming, at a rate lower than the rate of addition of the proton. It was proposed that the rate limiting step was the protonation of the double bond by the hydrogen chloride complex.

Pocker et al.[135,136] have more recently performed similar studies on the addition of hydrogen chloride to olefins and they observed a second order dependence in hydrogen chloride and first order dependence on olefin concentration. They also invoked the suggestion that the rate limiting step was the protonation of the double bond by a hydrogen chloride complex.

From the above work[134-6] it is reasonable to assume that in the initial protonation of the double bond a complex involving 2 or 3 molecules of hydrogen chloride and the norbornene would be formed, however after completion of the protonation the complex would be expected to break down[129c].

In the temperature range where hydrogen chloride will be in either the liquid or solid phase, it is likely that a halogen acid complex will be associated with each of the α carbon atoms in the norbornyl cation (one of which has a hydrogen atom attached to it and the other has a deuterium atom) and this may be the cause of the solvent induced α isotope effect.

The product ratios obtained at different temperatures when deuterium chloride is added both slowly and rapidly to norbornene-2,3-d_2 are shown in Fig III-5. Two main differences can be observed between the hydrogen and deuterium chloride additions to norbornene-2,3-d_2; (a) in the slow addition of deuterium chloride the asymptotic value at 0°C is 0.94 and not 0.83 as observed with hydrogen chloride and at lower temperatures there is a small change in the product ratio, (b) with rapid addition of deuterium chloride the product ratio changes more rapidly than in the case of hydrogen chloride. These differences in the product ratio for slow and fast addition could be due to a solvent isotope effect on going from hydrogen to deuterium chloride (there

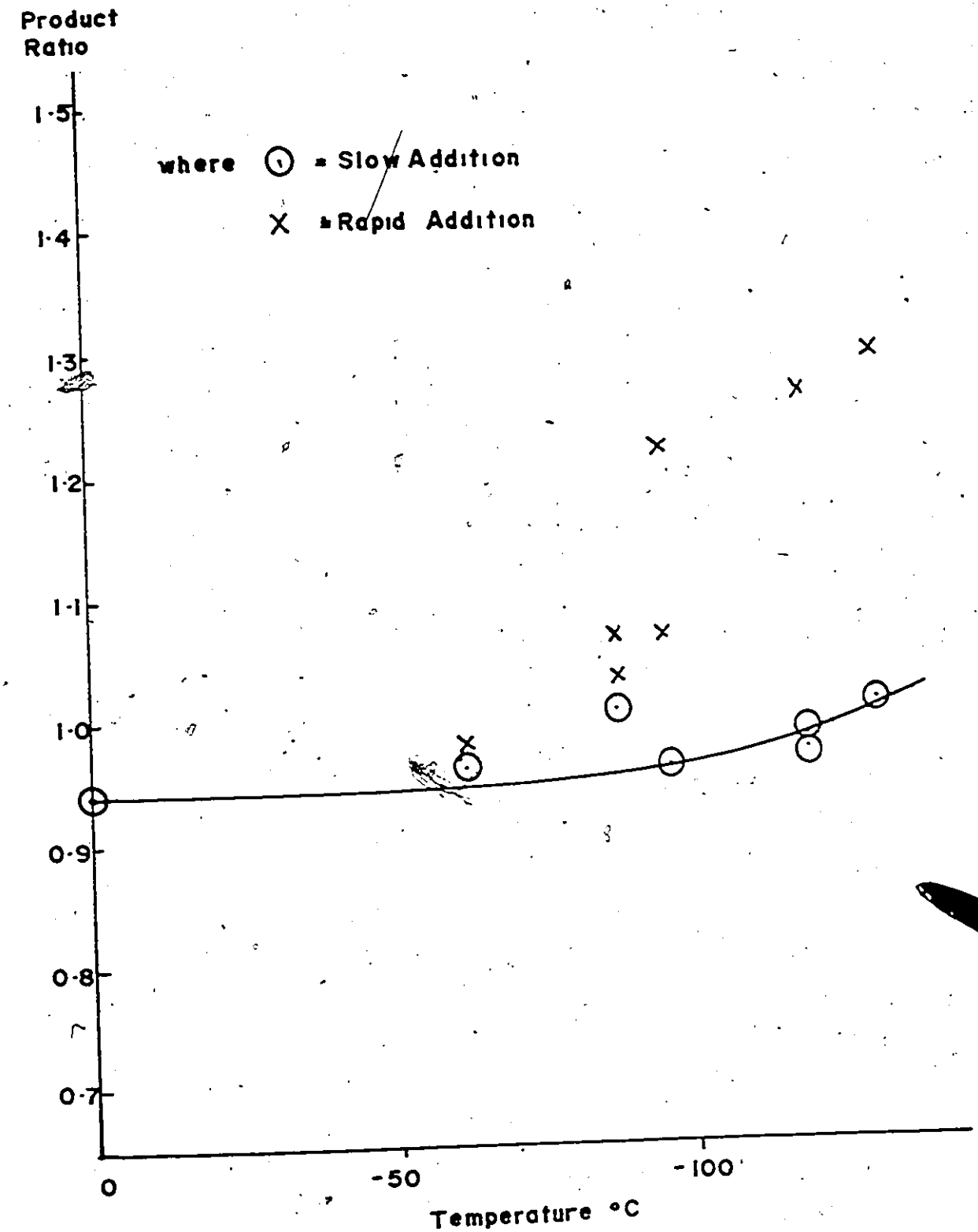


Fig. III 5. A Plot of the Product Ratio Obtained from the Deuterium Chloride Addition to Norbornene-2,3-d_2 Against Temperature.

is closer packing in the deuterium chloride in the liquid and solid phases relative to hydrogen chloride resulting from the stronger, shorter bonds in deuterium chloride[137]).

Summary

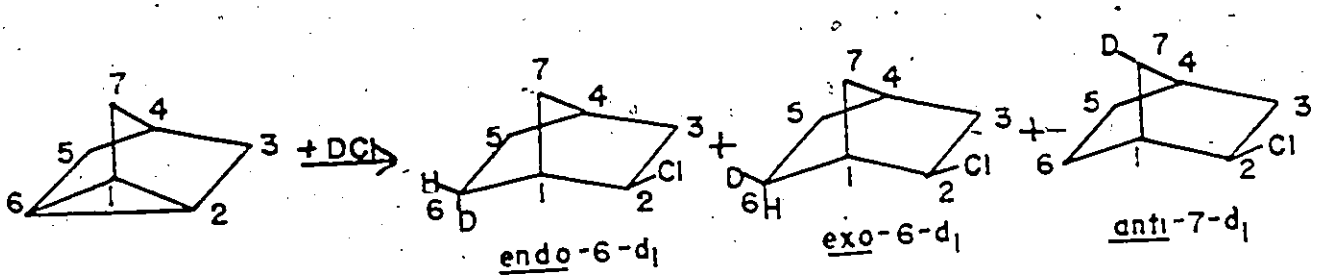
An investigation into the structure of the norbornyl cation intermediate in the hydrogen chloride addition reaction with norbornene in non-ionizing solvents (or media) has been performed. Deuterium atoms were placed in various positions of the bicyclic structure and their effect on the product ratio (which arises as a result of the Wagner-Meerwein reaction) was determined. It was observed when deuterium was present in the exo and endo-3- positions, exo and endo-6-positions and the syn-7-position, that within experimental error a constant product ratio (rearranged/unrearranged = 0.79) was obtained and thus was independent of temperature from -131.5 to 0°C. These results show that the deviation from unity for the product ratio is not due to a β isotope effect. The induced α- isotope effect (hydrogen and deuterium chloride addition to norbornene-2,3-d_2) is greater at lower temperatures, but the value also depends on the rate of addition of the halogen acid. When hydrogen chloride was added to norbornene-2,3-d_2 in the

presence of solvents of increasing polarisability at -78°C, the induced α isotope effect was again observed, indicating that the reaction is sensitive to reaction medium.

Nortricyclene Addition Reactions

Discussion

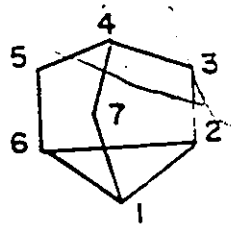
Brown and McIvor[79] investigated the addition of deuterium chloride to nortricyclene at -78°C in chloroform



and observed (from a 220 M.Hz N.M.R. study) that 50 ± 3% of the exo-2-norbornyl chloride product contained deuterium in the endo-6-position, 43 ± 3% in the exo-6-position and (they presumed) approximately 7% in the anti-7-position. Brown and McIvor[79] and Stille and Hughes[118] (on the basis of work carried out on protonated cyclopropane[138,139]) proposed that the addition reaction initially passes through the corner protonated nortricyclene which then undergoes an-

irreversible change to either the classical or non-classical carbonium ion before addition of the chloride ion. Theoretical calculations by Klopman[99] indicate that the protonated nortricyclene is more stable than either the classical or non-classical norbornyl cations.

The product of the addition of hydrogen chloride to nortricyclene has been shown to be only exo-2-norbornyl chloride[79], there is no experimental evidence for the production of endo-2-norbornyl chloride. This product is thus identical to that observed in the addition of hydrogen chloride to norbornene[79,116]. Nortricyclene is a highly symmetrical molecule[140]



and there are three equivalent bonds (1,2;2,6 and 6,1) which can be ruptured on the addition of deuterium chloride.

If the reaction goes initially via the corner protonated nortricyclene as suggested by Brown and McIvor[79] and Stille and Hughes[118], then the deuterium atom will have an equal probability of being found on either the 6,2 or 1 carbon atoms as a result of the hydrogen atoms at these positions migrating around the cyclopropane ring. Brown and McIvor's[79] results show that this is not so.

(see page 266). The location of the deuterium atom is relative to the position occupied by the chlorine atom.

If either the classical or non-classical carbonium ions are the structures involved, then on the addition of deuterium chloride to nortricyclene a product ratio of unity will be obtained, because if the deuterium goes in exo relative to the final position of the chlorine, the Wagner-Meerwein reaction will yield exo-6-d_1 and endo-6-d_1 in some ratio (see addition of hydrogen chloride to norbornene-exo-5-exo-6-d_2 , page 249), if on the other hand the deuterium goes in endo the inverse ratio will be obtained (see hydrogen chloride addition to norbornene-endo-5-endo-6-d_2, see page 251) but the net result will be a product ratio of unity since there is an equal probability of the deuterium entering either exo or endo. If an asymmetric addition is involved the summation of the different asymmetric products will also lead to a product ratio of unity.

Nortricyclene was prepared by the Bamford-Stevens reaction[31] on the tosyl-hydrazone of norcamphor under aprotic conditions. The resulting hydrocarbon was G.L.C. purified in order to remove some 6% norbornene, a bi-product of the reaction.

Deuterium chloride was added to nortricyclene at 0°C and -96°C in the absence of solvent and at -78°C using

methylene chloride as solvent. The metastable ions for the chloroethyl radicals lost from the molecular ion peaks of the addition products obtained at the various temperatures were analysed and found to be identical, a ratio of 51 ± 1% C_2H_4Cl : 49 ± 1% C_2H_3DCl being observed in every case. These values were interpreted as the distribution of the deuterium label in the exo-2-norbornyl chloride, that is 51 ± 1% of the deuterium is in the exo-6-position and 49 ± 1% is in the endo-6-position (remembering that the chloroethyl radical loss involves the hydrogen atoms on the 2 and 3 carbon atoms and the endo-6-hydrogen atom). It must be pointed out, however, that the 7% deuterium in the anti-7-position proposed by Brown and McIvor[79] will be included in the exo-6-deuterium count, thus the above results are in good agreement with those of Brown and McIvor[79]. We doubt however that deuterium is present in the 7-position in the products obtained from the addition of deuterium chloride to nortricyclene. The presence of deuterium in the 7-position could arise from traces of norbornene in Brown and McIvor's nortricyclene sample and furthermore their studies were carried out on products which were only 92% labelled. In view of the complexity of the N.M.R. spectrum (not completely resolved even at 220 M.Hz.) it is possible that the unlabelled product could be interfering with the N.M.R. analysis.

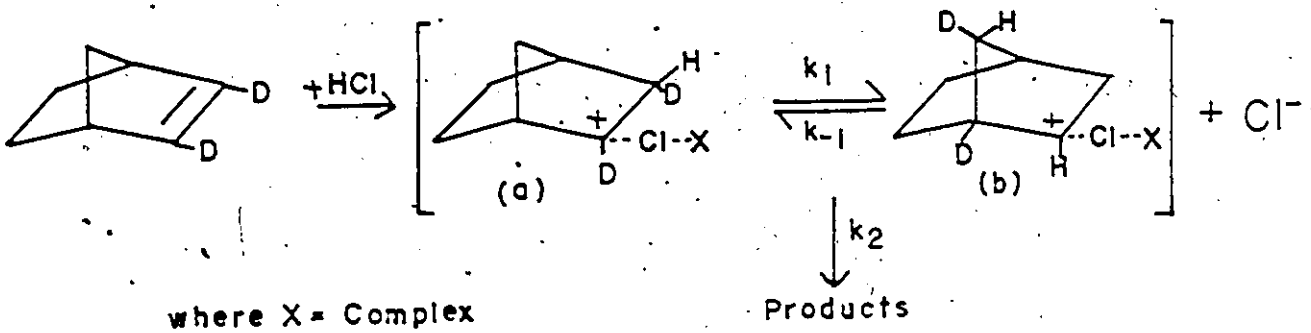
Summary

The results obtained from the addition of deuterium chloride to nortricyclene are as predicted. They convey no new information but confirm the results of Brown and McIvor[79] using an independent method.

Discussion of the Induced α Isotope Effect in the Addition of Halogen Acid to Norbornene-2,3-d_2

The induced α isotope effect only occurs when a deuterium atom is present on one of the α carbon atoms and the halogen acid is added rapidly at temperatures lower than -80°C. This suggests the presence of a complex between the halogen acid (involving 2 or 3 molecules of halogen acid[134-136]) and the α carbon atoms of the norbornyl cation.

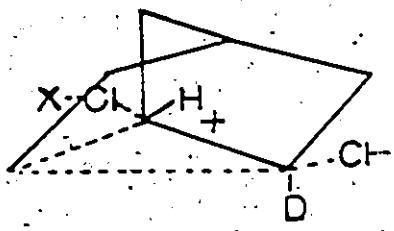
To explain the product ratio of 1.15 obtained when hydrogen chloride is added rapidly to norbornene-2,3-d_2 at -131.5°C in terms of the classical carbonium ion pair, k_1 must become greater than k_2 (by reduction of k_2 due to the presence of the complex and deuterium). This is required in order to explain the greater yield of rearranged product. However the maximum value one would expect would be unity where an equal concentration of both classical carbonium ions was present. To achieve a value greater than unity means that the complex and the presence of a deuterium



where X = Complex

atom on one of the α carbon atoms is causing some change in the equilibrium between the two classical carbonium ions. One would anticipate that the effect of the complex on the equilibrium between the classical carbonium ions would be greater than the α isotope effect since the complexed norbornyl cation (a) (see above) will be formed first and will reduce the rate of rearrangement (k_1) rather than enhance it, contrary to the observed results. Alternatively one would have to say that ion (b) was more reactive than (a) due solely to the presence of a deuterium atom on one of the α carbon atoms, however no change is observed in the product ratio when hydrogen chloride is added slowly to norbornene-2,3-d_2.

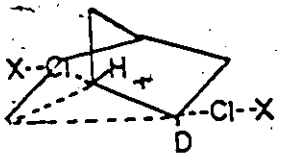
On examining the complexed non-classical carbonium ion which may be formed in the rapid addition of hydrogen chloride to norbornene-2,3-d_2, it can be observed that the difference between the complexed 2 carbon atom and the

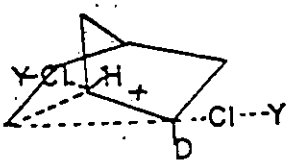


where X = Complex

complexed 1 carbon atom lies only in the α secondary isotope effect. When deuterium is present on <u>one</u> of the α carbon atoms two changes must occur in order to explain the product ratio of 1.15 . (1) the rate of formation of the non-classical carbonium ion must become relatively faster than the rate of attack of the chloride ion to allow time for (2) the charge density to increase at the 1 carbon atom at the expense of the 2 carbon atom. The change in charge density could be caused by the complexed hydrogen bearing α carbon atom (1 carbon atom) attracting the delocalized charge in one direction and the complexed

deuterium bearing carbon atom (2 carbon atom) pulling in the other direction, the former having the greater effect. The difference between the C-H and C-D bonds will become greater at lower temperatures ; this could explain the larger isotope effects observed at these temperatures. The isotope effect must operate through the complexes, other the no solvent isotope effect would be observed on going from hydrogen to deuterium chloride in the rapid addition. That is, from inspection of the complexed non-classical carbonium ion (shown below), the product ratio should be independent of whether hydrogen or deuterium chloride was used and depend only on the temperature.

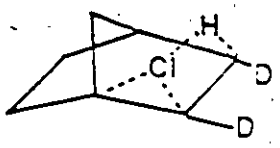




where X = HCl Complex
Y = DCl Complex

Considering the first step in the addition reaction to be protonation of the double bond, which is believed to occur through a complex involving 2 or 3 halogen acids molecules 134-136 (see page 262), it is unlikely in the rapid

addition at low temperatures that the norbornyl cation is captured in an asymmetric state as shown below:



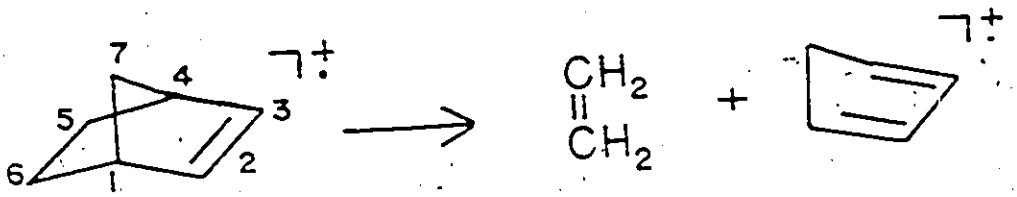
In addition, in the presence of the excess halogen acid it is difficult to visualize how an isotope effect would operate in the above cation.

The preceeding discussion indicates that the experimental results obtained in this work can best be explained in terms of the non-classical carbonium ion.

APPENDIX

Quantitative Mass Spectral Analysis of the Location of Deuterium in Norbornene-endo-5-endo-6-d_2.

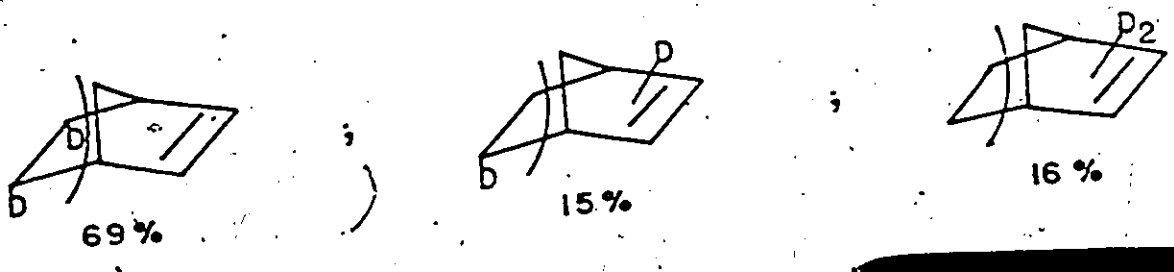
Norbornene is known to lose ethylene during its mass spectral fragmentation (see Part II 2.A) by a specific retro-Diels Alder reaction involving the 5 and 6 carbon atoms and their attached hydrogen atoms.



The relative abundance of the metastable ion peaks observed for norbornene-endo-5-endo-6-d_2 for loss of ethylene and its labelled analogues from the molecular ion are:

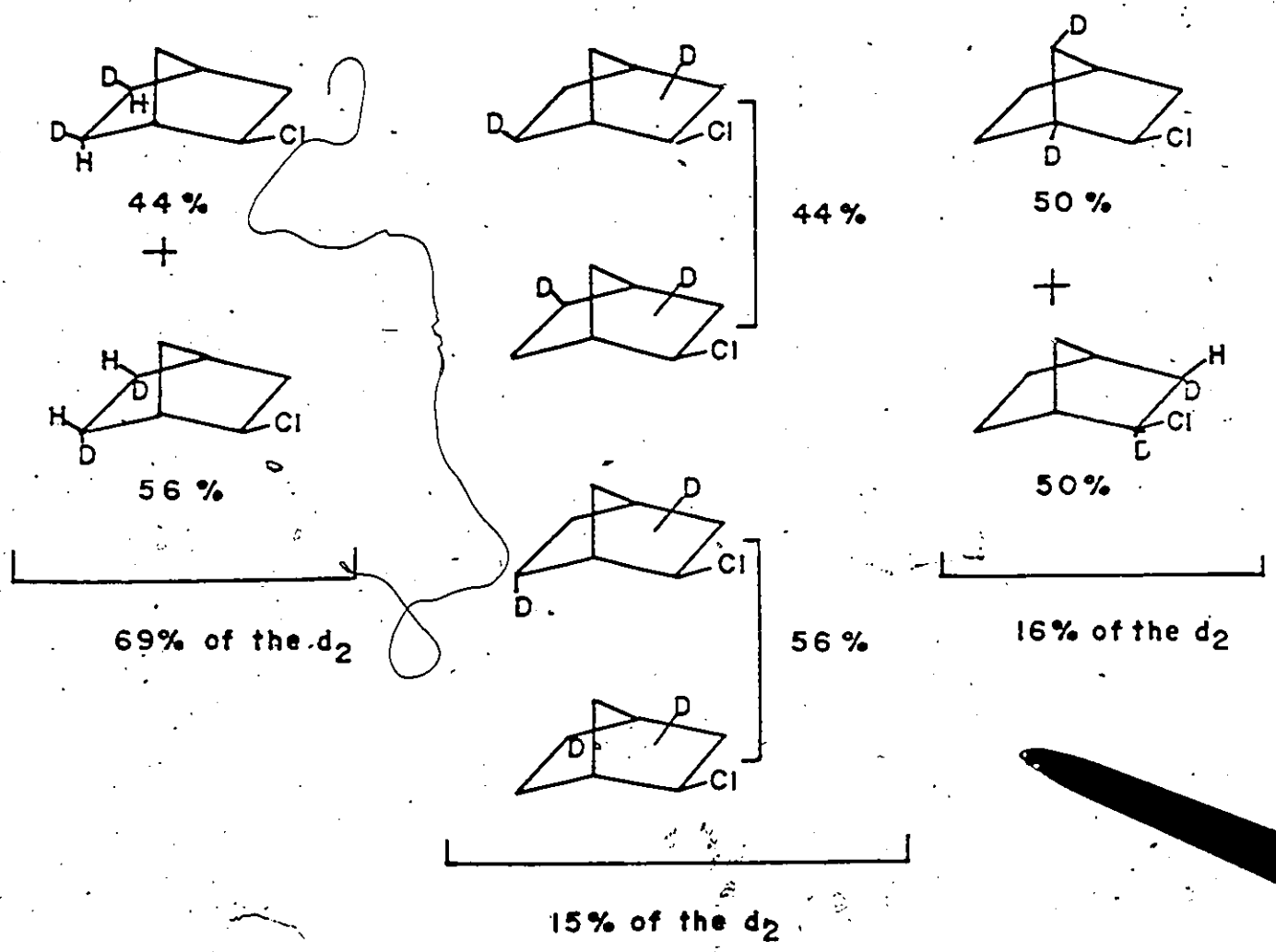
	$M-C_2H_2D_2$	$M-C_2H_3D$	$M-C_2H_4$
Relative Abundance	69	15	16

These results indicate that the deuterium distribution in the dideuterated compound is as follows:



Hydrogen Chloride Addition to Norbornene-endo-5-endo-6-d_2

On the basis of the metastable ion analysis of norbornene-endo-5-endo-6-d_2 (see page 276) and assuming a product ratio of 0.79 in the addition of hydrogen chloride the following product distribution will be obtained.



The above products will yield the following relative abundance of metastable ion peaks for the loss of chloroethyl and labelled chloroethyl radicals from the molecular ions.

$M-C_2H_4Cl$	29.6	$M-C_2H_4Cl$	6	$M-C_2H_4Cl$	8
$M-C_2H_3DCl$	39.4	$M-C_2H_3DCl$	8	$M-C_2H_2D_2Cl$	8
		$M-C_2H_2D_2Cl$	2		

$$\Sigma\ M-C_2H_4Cl = 29.6 + 6 + 8 = 43.6 \quad 48\%$$

$$\Sigma\ M-C_2H_3DCl = 39.4 + 8 + 0 = 47.4 \quad 52\%$$

Thus by calculation, the expected chloroethyl:monodeuterated chloroethyl loss will be in the ratio 48% : 52%. The observed experimental results, after correction of the relative abundance of the chloroethyl loss metastable for ^{13}C, were 46.5% : 54.5% for chloroethyl:monodeuterated chloroethyl loss. These results are compatible with a product ratio of 0.79 and asymmetric capture (see text for discussion, page 251).

Hydrogen Chloride Addition to a Mixture of Norbornene and Norbornene-syn-7-d_1.

From low eV studies of the molecular ion of the addition products the deuterium content was observed to be 30.5% d_1 and 69.5% d_o. The intensity of the metastable ion peak for the monodeuterated chloroethyl radicals lost from the molecular ion of the labelled compound was not measurable due to the presence of overlapping peaks; hence the intensity was calculated from the deuterium content and the abundance of the metastable ion peaks for the chloroethyl radicals lost from the molecular ions of the labelled and unlabelled compounds:

$M^*_{d_o} - C_2H_4Cl = 144.5$ units $\equiv 69.5 \pm 1.5\%$ Unlabelled

$\therefore M^*_{d_1} - (C_2H_4Cl + C_2H_3DCl)$ which equal 30.5% Monolabelled $\equiv 63.4 \pm 1.5$ units

$M^*_{d_1} - C_2H_4Cl = 34.9 \pm 1.5$ units = 55.2%

$\therefore M^*_{d_1} - C_2H_3DCl = 28.5 \pm 1.5$ units = 44.8%

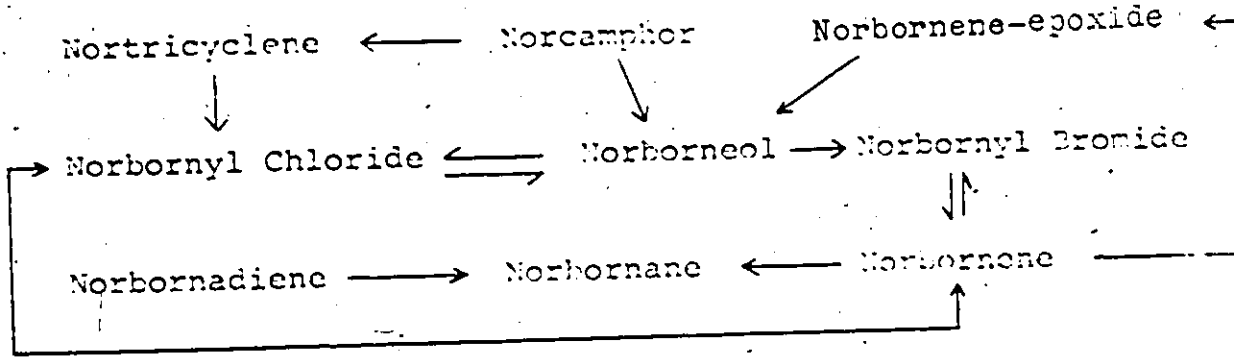
These results show that the addition products from the norbornene-syn-7-d_1 are 55% exo-2-norbornyl chloride-syn-7-d_1 and 45% exo-2-norbornyl chloride-exo-3-d_1.

Part IV

Preparation of Norbornyl Compounds

Introduction

Because of the interlinked nature of the synthetic routes leading to the various norbornyl compounds and their deuterated analogues, the methods involved are described together here in Part IV and are not included in the experimental section at the end of each chapter. The interlinking pathways are shown below:



Commercially Available Compounds

Norcamphor, norborneol (50% mixture of *exo* and *endo*), norbornene, norbornane, norbornadiene and 5-norbornene-2-ol (50% mixture of *exo* and *endo*) were obtained from Aldrich Chemical Co. Inc., Milwaukee, Wis. Hydrogen chloride (anhydrous) and deuterium (tech) were obtained from Matheson of Canada Ltd., Whitby, Ontario. Deuterium chloride was obtained from Merck, Sharp and

Dohme of Canada Ltd., Montreal, Quebec. Deuterium oxide was also obtained from Merck, Sharp and Dohme and from the Atomic Energy Commission.

Preparations

Deuterium content, location and identification of compounds was checked by mass spectrometry and N.M.R. where appropriate.

1. 3,3-d_2-Norcamphor Prepared by keto-enol tautomerism exchange of norcamphor (2g.) in alkaline D_2O (6g.) for three 24 hour periods, fresh D_2O being used for each period. The norcamphor was recovered after each exchange by extracting with sodium dried ether followed by evaporation of the solution to dryness. The deuterium content of the norcamphor was found to be better than 98% d_2 by mass spectrometry. The labelled norcamphor was used immediately and never stored for more than 1 hour in order to avoid back exchange with atmospheric water.

2. (a) endo-Norborneol Obtained from norcamphor by reduction with lithium aluminium hydride under anhydrous conditions using the method described by Stille and Sonnenberg[78]

2. (b) exo-2-d_1-endo-Norborneol Prepared from norcamphor by reduction with lithium aluminium deuteride under anhydrous conditions as described in 2(a). The deuterium content and the identity of the product was obtained from mass spectrometry.

2. (c) 3,3-d_2-endo-Norborneol Obtained by reduction of 3,3-d_2-norcamphor with lithium aluminium hydride using the conditions described in 2(a).

2. (d) 3,3,2-d_3-endo-Norborneol Prepared by reduction of 3,3-d_2-norcamphor using lithium aluminium deuteride as the reducing agent, the conditions are described in 2(a).

2. (e) exo-2-Norborneol Prepared by reacting norbornene with acetic anhydride giving norbornene epoxide which on reduction with lithium aluminium hydride gave the required alcohol

2. (f) endo-3-d_1-exo-2-Norborneol Obtained in the same manner as exo-2-norborneol but using lithium aluminium deuteride in the reduction step, see 2(e) for conditions.

2. (g) (exo-endo)6-d_1-exo-2-Norborneol A 50% mixture of exo-6-d_1 and endo-6-d_1-exo-2-norbornyl chloride was obtained by alkaline hydrolysis of (exo-endo)6-d_1-exo-2-norbornyl chloride (0.5g.) by refluxing the chloride in aqueous potassium hydroxide for about 6 hours or until the solid alcohol is observed on the walls of the condenser.

2. (h) (exo-3, syn-7)-d_1-exo-2-Norborneol A mixture of 57% exo-3-d_1 and 43% syn-7-d_1-exo-2-norborneol was obtained by alkaline hydrolysis of (exo-3,syn-7)-d_1-exo-2-norbornyl chloride using the conditions described in 2(g).

2. (i) exo,exo-5,6-d_2-Norborneol A 50% mixture of exo,exo-5,6-d_2-exo-norborneol and exo,exo-5,6-d_2-endo-norborneol was

obtained by reduction of 5-norbornene-2-ol (1 g.) with deuterium gas (30 lbs./sq.in.) over platinum oxide catalyst using ethyl acetate as solvent.

2. (j) (exo,exo,endo,endo)5,6-d_2-exo-Norborneol A mixture of 56% exo,exo-5,6-d_2-exo-2-norborneol and 44% endo,endo-5,6-d_2-exo-2-norborneol was obtained by conversion of exo,exo-5,6-d_2-norborneol to exo,exo-5,6-d_2-norbornene by the method of Stille, Sonnenberg and Kinstle[89]. On reaction with hydrogen chloride at -78°C (using methylene chloride as solvent) gives the mixture 56% exo,exo-5,6-d_2-norbornyl chloride and 44% endo,endo-5,6-d_2-norbornyl chloride which on alkaline hydrolysis yields the required alcohol.

3. (a) exo-2-Norbornyl Bromide Prepared by reacting either exo or endo norborneol with triphenyl phosphine and bromine under anhydrous conditions, and decomposing the triphenyl phosphine dibromide to give exo-2-norbornyl bromide. The preparation was carried out under the conditions described by Schafer and Weinberg[83].

3. (b) endo-2-d_1-exo-2-Norbornyl Bromide Obtained by treating exo-2-d_1-endo-2-norborneol with triphenyl phosphine and bromine as in 3(a) and decomposing the triphenyl phosphine dibromide complex.

3. (c) 3,3-d_2-exo-2-Norbornyl Bromide Obtained by reacting 3,3-d_2-endo-2-norborneol by the procedure described in 3(a).

3. (d) 3,3,2-d_3-exo-2-Norbornyl Bromide Yielded by the treatment of 3,3,2-d_3-endo-2-norborneol by the method

outlined in 3(a).

4. (a) 2-d_1-Norbornene The product was obtained from the dehydrobromination of 3,3-d_2-exo-2-norbornyl bromide by the method of Stille, Sonnenberg and Kinstle [89]. Norbornene was recovered from the reaction mixture by preparative G.L.C.

4. (b) 2,3-d_2-Norbornene By the method indicated in 4(a) but using 2,3,3-d_3-exo-2-norbornyl bromide in the dehydrobromination step.

4. (c) exo, exo-5,6-d_2-Norbornene Obtained by dehydrobromination of exo,exo-5,6-d_2-exo-2-norbornyl bromide as indicated in 4(a).

5. (a) Nortricyclene was prepared from the tosylhydrazone of norcamphor by the Bamford-Stevens reaction under aprotic conditions as described by Nickon and Werstiuk [31]. An alternative method for obtaining nortricyclene was to stir exo-2-norbornyl toluene-p-sulphonate [141] with activated alumina in carbon tetrachloride for 24 hours and extract the product by preparative G.L.C. using a carbowax 1500 column

5. (b) 3,3-d_2-Nortricyclene and 3-d_1-Nortricyclene A mixture of the two nortricyclenes was obtained when the tosyl derivative of 3,3-d_2-norcamphor was decomposed by the Bamford-Stevenson reaction [31] under aprotic conditions as described in 5(a). We were unable to decide which experimental conditions effected the ratio of mono and

di deuterated nortricyclenes.

6. (a) exo-2-Norbornyl Chloride Obtained by bubbling hydrogen chloride through a methylene chloride solution of norbornene at -78°C under anhydrous conditions. The chloride was identified by N.M.R. and mass spectrometry.

6. (b) (3-7)d_1-exo-2-Norbornyl Chloride A mixture of 56% exo-3-d_1-exo-2-norbornyl chloride and 44% syn-7-d_1-exo-2-norbornyl chloride was obtained by bubbling deuterium chloride through a methylene chloride solution of norbornene at -78°C under anhydrous conditions. The location of the deuterium was confirmed by N.M.R.[79] and mass spectral analysis.

6. (c) (exo-endo)-6-d_1-exo-2-Norbornyl Chloride A 50% mixture of exo-6-d_1-exo-2-norbornyl chloride and endo-6-d_1-exo-2-norbornyl chloride were obtained when deuterium chloride was added to nortricyclene by the method indicated in 6(a). The location of the deuterium in the 6 position was shown by N.M.R. analysis[79] and the amount in the exo and endo positions by mass spectrometry.

6. (d) endo-2-d_1-exo-2-Norbornyl Chloride Obtained by the reaction of exo-2-d_1-endo-2-norborneol with triphenyl phosphine in excess carbon tetrachloride under anhydrous conditions as described by Downie and Lee[80]. The location of the deuterium was confirmed by N.M.R. analysis.

6. (e) 3,3-d_2-exo-2-Norbornyl Chloride Prepared by treating 3,3-d_2-endo-norborneol by the procedure indicated in 6(d).

The location was again determined by N.M.R. analysis.

6. (f) 3,3,2-d_3-exo-2-Norbornyl Chloride Obtained by treating 3,3,2-d_3-endo-2-norborneol by the proceedure described in 6(d). Deuterium location confirmed by N.M.R. analysis.

6. (g) (exo,exo-endo,endo)5,6-d_2-exo-2-Norbornyl Chloride Aquired by adding hydrogen chloride to exo,exo-5,6-d_2-norbornene as described in 6(a)

7. (a) exo,exo-2,3-d_2-Norbornane Prepared by reduction of norbornene with deuterium gas (10 lbs./sq. in.) using platinium oxide as catalyst, the reaction was carried out in ethyl acetate solution and the labelled norbornene was recovered by preparative G.L.C.

7. (b) exo,exo,exo,exo-2,3,5,6-d_4-Norbornane Prepared in the same manner as 2,3-d_2-norbornane but using norbornadiene as starting material.

7. (c) 3,3-d_2-Norbornane Tosyl derivative of 3,3-d_2-norborneol obtained by adding the alcohol (in pyridine solution) dropwise to an equimolar quantity of p-toluene sulphonyl chloride also in dry pyridene, both solutions cooled to 0°C during the addition. The mixture was allowed to stand overnight at room temperature after which pyridinium chloride crystals were observed indicating formation of the tosylate. The mixture was poured into ice-water, which was then extracted with ether. The ether solution was washed with hydrochloric acid, sodium hydroxide solution and finally with distilled

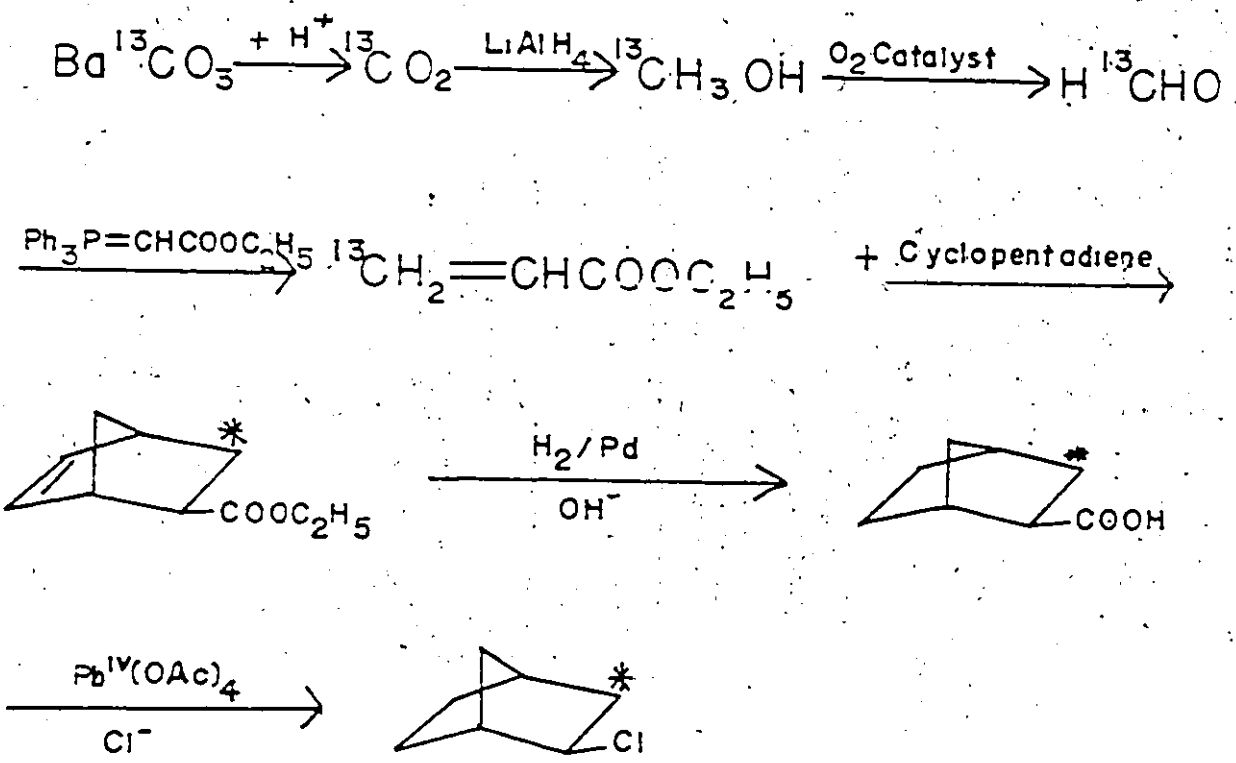
water. After drying overnight with anhydrous magnesium sulphate, the tosylate was reduced with lithium aluminium hydride to 3,3-d_2-norbornane. The reduction process was allowed to proceed overnight at room temperature to ensure completion of the reduction

7. (d) endo-2-d_1-Norbornane Prepared from exo-2-d_1-endo-2-norborneol by using the proceedure carried out in 7(c). Note inversion of position on reduction of tosylate.

7. (e) exo-2-d_1-Norbornane Prepared from endo-2-norborneol as in 7(c) but using lithium aluminium deuteride in the reduction step of the tosylate.

Norbornane-endo-5-endo-6-d_2 was obtained from Dr. N.H. Werstiuk[130], although N.M.R. analysis suggested that the label was positionally pure a careful mass spectral analysis (see page 276) indicated that the label also occupied other positions.

exo-2-Norbornyl chloride-3-^{13}C was obtained from Dr. N.S. Isaacs, The University, Whiteknights Park, Reading, England. The synthetic route involved is shown below. The position of the ^{13}C label was confirmed by mass spectrometric analysis.


Ba 13CO3 + H+
13CO2
LiAlH4
13CH3OH
O2 Catalyst
H 13CHO
Ph3P=CHCOOC2H5
13CH2=CHCOOC2H5
+ Cyclopentadiene
COOC2H5
H2/Pd
OH-
COOH
PbIV(OAc)4
Cl-
Cl

Claims to Original Research

1. The Arrhenius parameters and mechanism of the gas phase pyrolysis of exo-2-norbornyl chloride have been established.

2. The mass spectral fragmentation mechanisms of exo-2-norbornyl chloride has been determined and the atoms involved in the specific chloroethyl loss identified.

3. The use of the relative abundance of metastable ion peaks in labelled compounds to isolate a particular fragmentation pathway has been developed into a powerful mechanistic tool.

4. The mass spectral fragmentation pattern of exo-2-norbornyl bromide has been partially established.

5. The mass spectral fragmentation, mechanism and energetics of C_7H_{10} isomers norbornene and nortricyclene have been determined and compared in detail.

6. The mass spectral fragmentation mechanismsof exo and endo norborneol have been established. Detailed investigation has shown that the norborneols fragment by common pathways which can be traced to three primary bond breaks in the molecular ion.

7. The mass spectral fragmentation of norbornane has been partially determined. The results show the presence of an isotope effect in the ethyl and methyl loss from the molecular ion.

8. The combination of the relative abundance of metastable ion peaks and the chloroethyl fragmentation in norbornyl chloride has been developed as an analytical tool to determine the amount of deuterium label (and ^{13}C label) present in the 2 and 3 carbon atoms and in the 6 <u>endo</u> position.

9. Observations on the hydrogen chloride addition reaction to norbornene (by deuterium labelling and mass spectral analysis) has shown that the norbornyl cation is captured in an asymmetric state. The asymmetric capture is <u>not</u> effected by a β secondary isotope effect but <u>is</u> influenced by an α secondary isotope effect.

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