ACID CATALYSED DIMERISATION
OF
2,3-DIMETHYLBUTADIENE

BY

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THIS THESIS IS SUBMITTED IN PARTIAL FULFILMENT
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"أهداء ..."

"الى والداى العزيزان ..."

أهدى هذه الرسالة الى والداى العزيزان تعبيراً عن شكرى لهم وتقديرى لصبرهم واحتمالهم عدم رؤياى طوال فترة دراستى فى انجلترا ، وبقدر مابذلت من مجهود فى انجاز وجمع مادة هذه الرسالة بقدر ما أعتز بها فهى بالنسبة لى كفاح سنين طويلة وأغلى وأعز ما أملك بين يدى حاليا وللحق فان والداى هما أحق الناس بالاهداء وأكرر شكرى لهم على تشجيعهم وتعضيدهم لى ودعواتهم المستمرة مع تمنياتى لهما بحياة طويلة مديدة كلها سعادة وصحة وهناء .

جورج

"Dedication"

To Mum and Dad

This Thesis is dedicated to my beloved parents;in which I should like to thank them for being very patient in not seeing me during the years of my doing the work in this thesis, and for their endless encouragement and prayers for me. I wish them a very happy and long life.

George

ABSTRACT

The acid catalysed dimerisation of 2,3-dimethylbutadiene has been carried out using sulphuric acid in acetic acid as solvent.

Analysis by gas chromatography, mass spectroscopy revealed that the product, b.p. 46 - 120° at 0.5 mm consisted of at least thirteen compounds. Of the eight major components (hydrocarbons), five have a molecular weight of 164 and three 162.

No acetates appeared to be formed during the reaction and only one compound was found to be a solid (m.p. 87°).

The major compounds were separated in a pure state using preparative G.l.c. and their molecular structure investigated using ^{1}H and ^{13}C n.m.r. and open-chain, mono-cyclic, bicyclic, tricyclic and aromatic structures have been found in these compounds.

The following compounds were suggested: 3-methylene-2,6,7-trimethyl-1,6-octadiene or 4-methylene-2,3,7-trimethyl-2,7-octadiene, 1,2,4-trimethyl 4-isopropenyl cyclohex-1-ene, 2-methylene-1,3,3,4-tetramethyl-bicyclo[2,2,1]heptane, 2-methylene-1,4,7,7-tetramethylbicyclo [2,2,1] heptane (solid), 2,4-dimethyltricyclene or 1,2,4,7,7-pentamethyltricyclo $(2,2,1,0^{2-6})$ heptane, 2,4-2,5- and 3,4-dimethyl t-butylbenzene.
The kinetic study of the reaction has shown that it is second order in 2,3-dimethyl-1,3-butadiene.

Acknowledgements

I wish to express my deep gratitude and indebtedness to Professor T G Bonner for his encouragement, support and advice. His kindness and help, which words can hardly express, have enabled me to carry on with my studies at Royal Holloway College.

I would like to thank Dr R A Hancock for supervision and acknowledge his guidance throughout this project and for his help with interpreting the results reached as well as for many useful discussions.

I also wish to express my appreciation to Mrs E Summers at King's College (London University) for recording the ^{13}C n.m.r. spectra, and the staff of the n.m.r. laboratory at the Physical Chemical Measurements Unit (Harwell) for recording the ^{1}H n.m.r. spectra.

Special thanks are also extended to Miss J L Hurn the Registrar of the Royal Holloway College, to the administration and to the Bourne Laboratory staff for unfailing help and the British Council for financial assistance.

Finally I wish to thank Mrs E I Kearsey for her neat typing of the present Thesis.

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"Chapter 1."

"Introduction"

Introduction

I. The Chemistry of Acyclic Hydrocarbons Containing Two Double Bonds

Diolefins or Dienes, (C_nH_{2n-2}) can be divided into three classes according to the relative positions of their double bonds: A) those containing cumulated double bonds, in which two double bonds are attached to the same carbon atom, as in allene, $CH_2 = C = CH_2$, B) those containing conjugated double bonds, in which the double bonds are separated by one single bond, as in butadiene $CH_2 = CH-CH=CH_2$ and C) those containing isolated double bonds, in which one or more saturated carbon atoms separate the olefinic systems as in 1,4-pentadiene $CH_2=CH-CH_2-CH=CH_2$.

The substance of this thesis is concerned with a reaction of 2,3-dimethylbutadiene, so the chemistry of conjugated dienes is now reviewed.

II. Conjugated Dienes

The simplest of the conjugated dienes is 1,3-butadiene; some derivatives of which are of great industrial importance in the manufacture of synthetic elastomers.

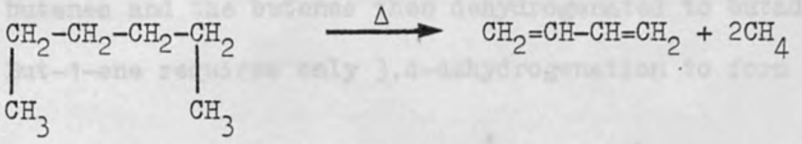
II.A Methods of Formation

(i) From hydrocarbons

As early as 1913 it was stated[1] that: "butadiene is obtainable from any organic compound by thermal treatment alone". The statement was justified by listing twenty one methods for preparing alkadienes, principally butadiene.

In a review,[2] published in 1944, Egloff and Hulla indicated that over eightyfive distinct, if somewhat unusual, organic reactions can yield butadiene e.g. the elimination of methane by the thermolysis of hexane (II.1).

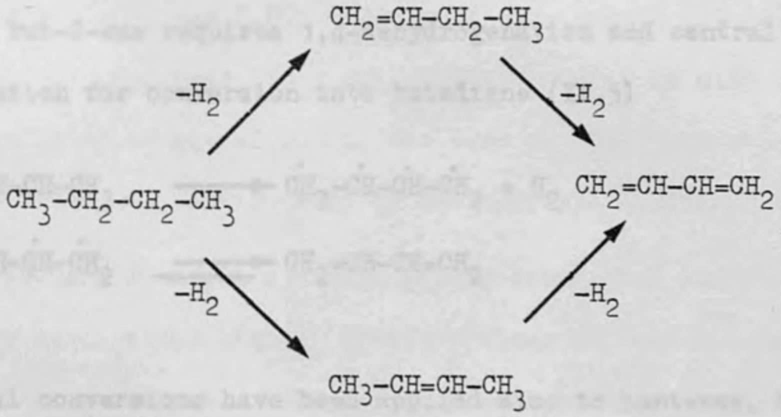
The yields reported were often low and less than 5%



$$\underset{CH_3}{\underset{|}{CH_2}}-CH_2-CH_2-\underset{CH_3}{\underset{|}{CH_2}} \xrightarrow{\Delta} CH_2=CH-CH=CH_2 + 2CH_4$$

(II.1)

Egloff and Hulla also referred to the conversion of alkanes to butadiene catalytically e.g. the dehydrogenation of n-butane into butadiene in (a) a single-stage (400-650°C) or in (b) a two-stage catalytic process (482 - 650°C) (II.2).



(II.2)

In this, good yields (70 - 80%) may be approached by a recycling operation;but with deposition of carbon upon the catalyst.

Dunstan, Hague,and Wheeler are exponents of a polymerisation - dehydrogenation route e.g. the polymerisation of ethene to butene and then its dehydrogenation to butadiene[2]:

$$2C_2H_4 \longrightarrow CH_2=CH-CH=CH_2 + H_2$$

(II.3)

Propene can be thermally decomposed into a mixture of ethene and butenes and the butenes then dehydrogenated to butadiene.

But-1-ene requires only 3,4-dehydrogenation to form butadiene (II.4).

$$\mathrm{CH_2{=}CH{-}CH_2{-}CH_3 \longrightarrow CH_2{=}CH{-}\dot{C}H{-}CH_3 + \dot{H}}$$

$$\mathrm{CH_2{=}CH{-}\dot{C}H{-}CH_3 \longrightarrow CH_2{=}CH{-}\dot{C}H{-}\dot{C}H_2 + \dot{H}}$$

$$\mathrm{2\dot{H} \longrightarrow H_2}$$

$$\mathrm{CH_2{=}CH{-}\dot{C}H{-}\dot{C}H_2 \rightleftharpoons CH_2{=}CH{-}CH{=}CH_2} \qquad \text{(II.4)}$$

whereas but-2-ene requires 1,4-dehydrogenation and central bond activation for conversion into butadiene (II.5)

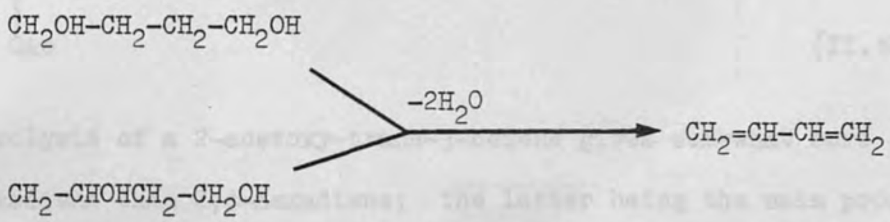
$$\mathrm{CH_3{-}CH{=}CH{-}CH_3 \longrightarrow \dot{C}H_2{-}\dot{C}H{-}\dot{C}H{-}\dot{C}H_2 + H_2}$$

$$\mathrm{\dot{C}H_2{-}\dot{C}H{-}\dot{C}H{-}\dot{C}H_2 \rightleftharpoons CH_2{=}CH{-}CH{=}CH_2} \qquad \text{(II.5)}$$

Thermal conversions have been applied also to pentenes, hexadecene, alkadienes, alkynes, alkenynes and alkadiynes as well as alicyclic hydrocarbons. In all cases if hydrogen has to be removed, catalytic dehydrogenation gives superior results compared to simple thermal treatments. When 1-butene is converted to 1,3-butadiene, the competing process, (II.6) giving the isomeric but-1-yne, occurs only to a small extent.[3]

$$\mathrm{CH_2{=}CH{-}CH_2{-}CH_3 \longrightarrow CH{\equiv}C{-}CH_2{-}CH_3} \qquad \text{(II.6)}$$

(ii) <u>By dehydration of the saturated 1,2-, 1,3-, or 1,4-diols and by pyrolysis of their diesters</u>



(II.7)

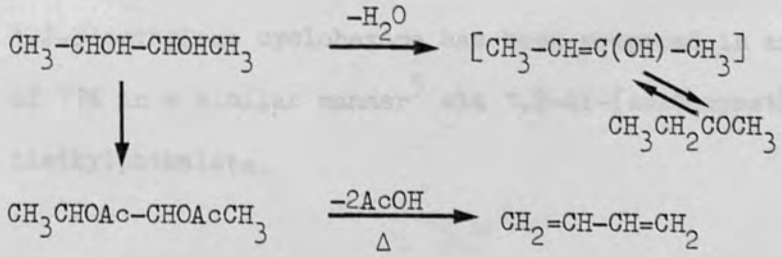
Reactions carried out catalytically, or by the action of a dehydrating agent e.g. H_2SO_4 and H_3PO_4 have found wide use in the laboratory as well as for important technical applications. As with the dehyration of simple alcohols, the ease of the dehydration process for diols varies with the environment of the hydroxyl functions.

Tertiary alcohols are most easily dehydrated and primary usually require the highest concentrations of dehydrating agent and highest temperatures. Reduction of some acetylenic glycols with lithium aluminium hydride, dehydrates the glycol to diene.[4]

$$CH_3CH(OH)C \equiv CCH(OH)CH_3 \xrightarrow[-H_2O]{LiAlH_4} CH_3CH{=}CHCH{=}CHCH_3$$

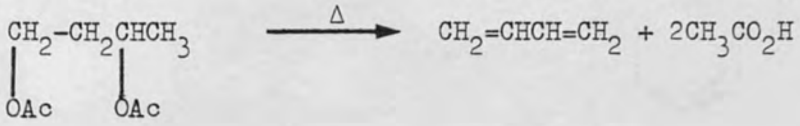
(II.8)

The dehydration of 2,3-butanediol gives largely ethyl methyl ketone whereas pyrolysis of the corresponding dicacetate gives butadiene in good yield:



(II.9)

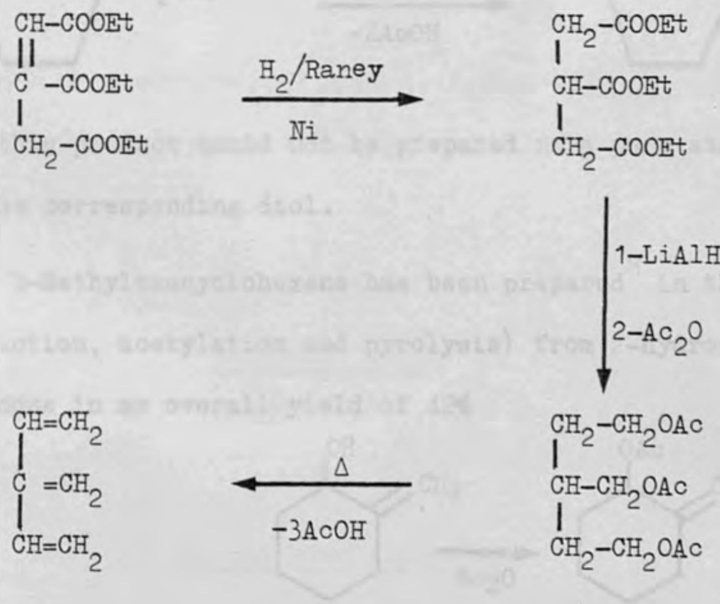
Similarly 1,3-butanediol diacetate also forms 1,3-butadiene on catalytic pyrolysis:



$$CH_2(OAc)-CH_2CH(OAc)CH_3 \xrightarrow{\Delta} CH_2=CHCH=CH_2 + 2CH_3CO_2H$$

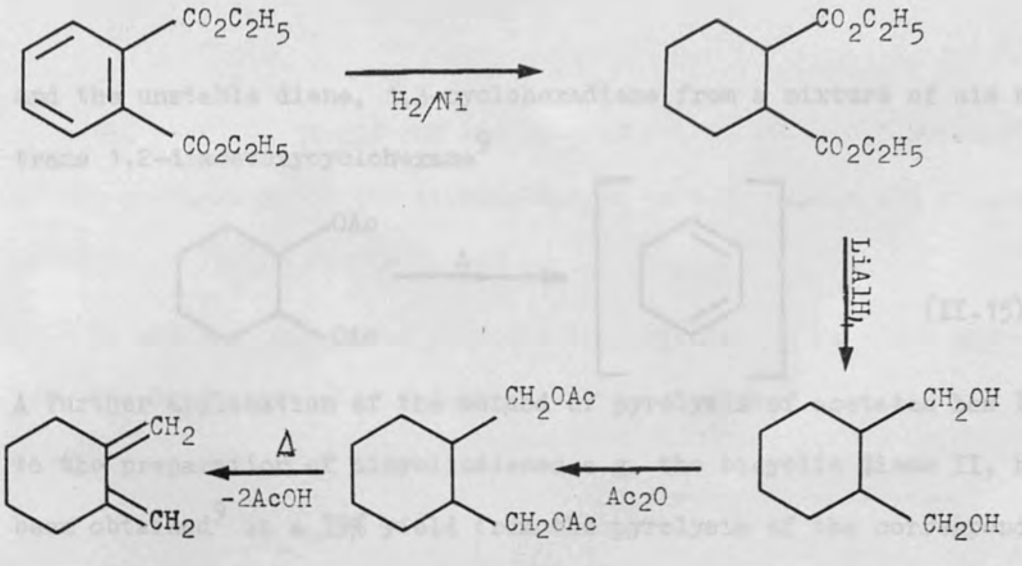
(II.10)

The pyrolysis of a 2-acetoxy-trans-3-hexene gives somewhat more 1,3-hexadiene than 2,4-hexadiene; the latter being the main product of the pyrolysis of 4-acetoxy trans-2-hexene. Ester pyrolyses have been used by Bailey and co-workers[5] for the synthesis of dienes which cannot easily be obtained by other methods e.g. strained dienes and highly unsaturated compounds. The pyrolysis of a triacetate has been used to produce 2-vinyl 1,3-butadiene in an overall yield of 40% from the triethyl ester of aconitic acid,[6] (II.11).



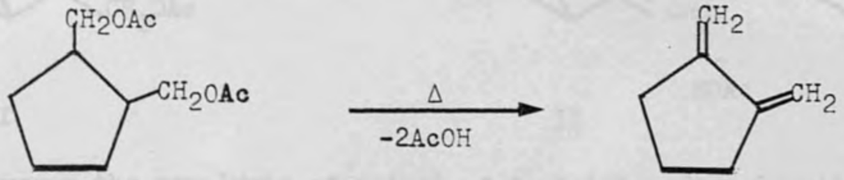
(II.11)

1,2-Dimethylene cyclohexane has been prepared in an overall yield of 77% in a similar manner[5] via 1,2-di-(acetoxymethyl)cyclohexane from diethylphthalate.



(II.12)

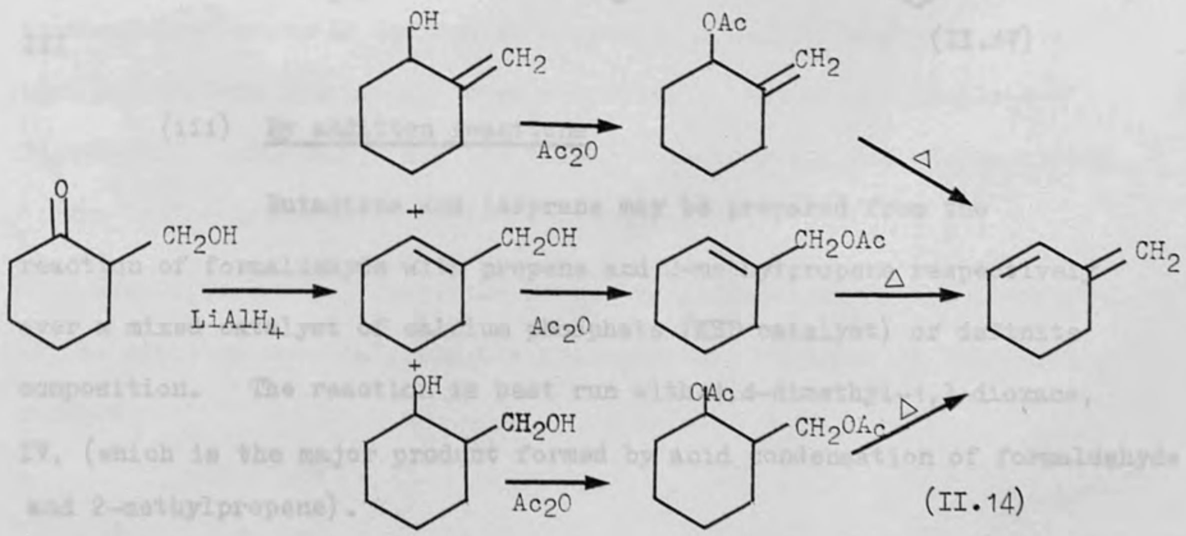
The pyrolysis of 1,2-di (acetoxymethyl)-cyclopentane, has produced 1,2-dimethylenecyclopentane in a 44% yield[7]



(II.13)

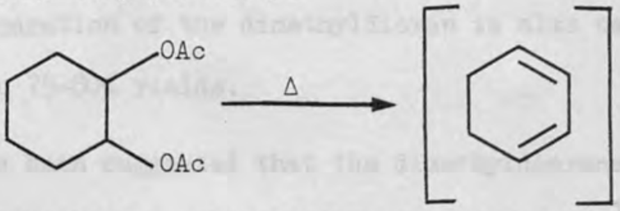
but this product could not be prepared in a pure state by dehydration of the corresponding diol.

3-Methylenecyclohexene has been prepared[8] in three steps, (reduction, acetylation and pyrolysis) from 2-hydroxymethylcyclohexanone in an overall yield of 42%



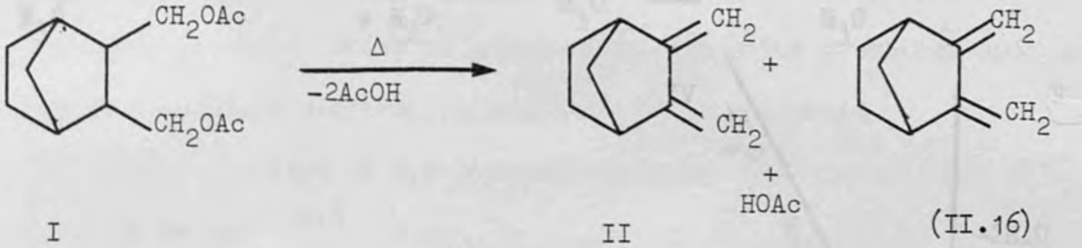
(II.14)

and the unstable diene, 1,3-cyclohexadiene from a mixture of cis and trans 1,2-diacetoxycyclohexane[9]



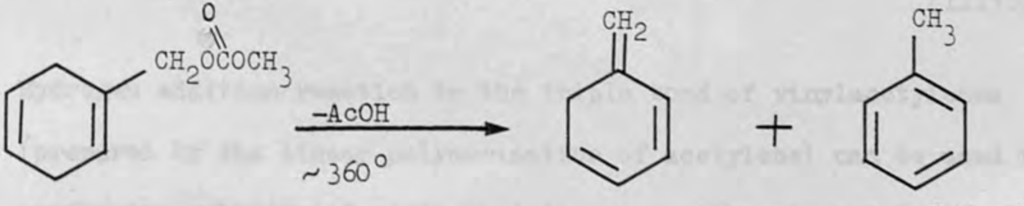
(II.15)

A further application of the method of pyrolysis of acetates has led to the preparation of bicyclicdienes e.g. the bicyclic diene II, has been obtained[9] in a 79% yield from the pyrolysis of the corresponding acetate, I.



I II (II.16)

However the pyrolysis of methyl, 1,4-cyclohexadienyl methylcarbonate III, yields 5-methylene-1,3-cyclohexadiene which appears to be quite stable at -80° [10]



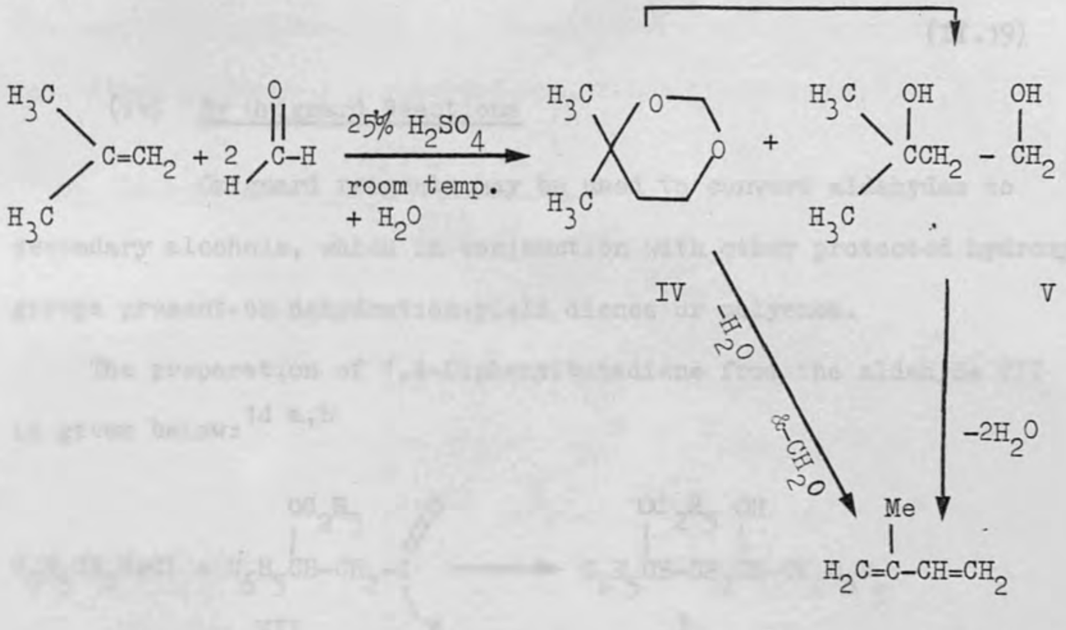
III (II.17)

(iii) By addition reactions

Butadiene and isoprene may be prepared from the reaction of formaldehyde with propene and 2-methylpropene respectively over a mixed catalyst of calcium phosphate (KSD catalyst) of definite composition. The reaction is best run with 4,4-dimethyl-1,3-dioxane, IV, (which is the major product formed by acid condensation of formaldehyde and 2-methylpropene).

The yield is 39-44% but the by-product, V, (2-methyl butan-2,4-diol) of the preparation of the dimethyldioxan is also usable and yields isoprene in 75-80% yields.

It has been suggested that the dimethyldioxane is first converted into the diol which itself dehydrates to isoprene[11 a,b] in 1 or 2 steps.



(II.18)

Hydrogen addition reaction to the triple bond of vinylacetylenes (prepared by the linear polymerisation of acetylene) can be used to synthesise substituted conjugated dienes. Alkenyl acetylenes of the type RCH=CH-C≡CH hydrogenate more selectively than do the isomeric CH_2=CH-C≡CR, compounds; and the former readily yield the corresponding dienes in the presence of palladium in methanol.[12 a,b]

The difference in behaviour is due to differences in the adsorbability of the starting materials and the hydrogenation products on the catalyst surface.

Isoprene can be prepared from the unsaturated alcohol, VI, by hydrogenolysis; VI, can be prepared from acetone and acetylene[13]

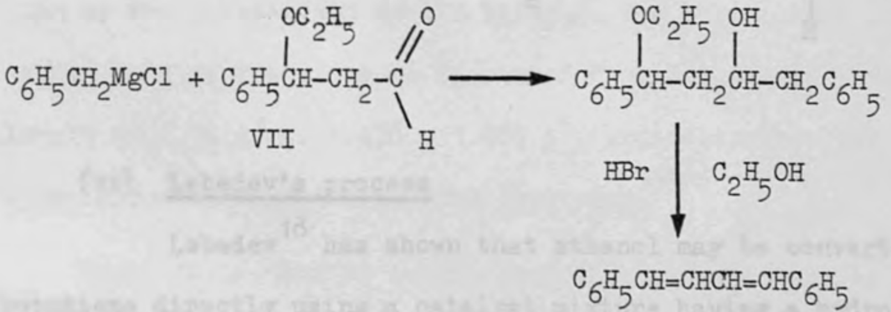
$$\begin{tikzcd}
Me_2CO + CH{\equiv}CH \arrow[r, "NaNH_2"] & Me_2C(OH)C{\equiv}CH \arrow[d, "H_2\ Pd"] & VI \\
 & CH_2{=}CMe{-}CH{=}CH_2 &
\end{tikzcd}$$

(II.19)

(iv) By Grignard Reactions

Grignard reagents may be used to convert aldehydes to secondary alcohols, which in conjunction with other protected hydroxyl groups present, on dehydration, yield dienes or polyenes.

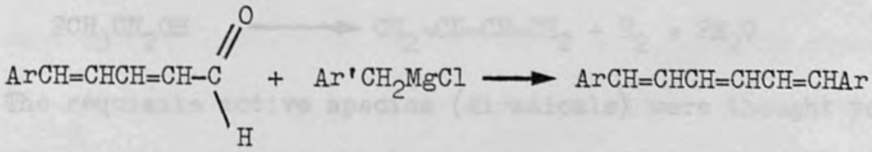
The preparation of 1,4-Diphenylbutadiene from the aldehyde VII is given below:[14 a,b]



$$C_6H_5CH_2MgCl + \underset{VII}{C_6H_5CH(OC_2H_5)-CH_2-CHO} \longrightarrow C_6H_5CH(OC_2H_5)-CH_2CH(OH)-CH_2C_6H_5 \xrightarrow{HBr\ \ C_2H_5OH} C_6H_5CH{=}CHCH{=}CHC_6H_5$$

(II.20)

1,6-Diaryl-substituted 1,3,5-hexatrienes have been prepared by a similar method.[15 a,b]



$$ArCH{=}CHCH{=}CH{-}CHO + Ar'CH_2MgCl \longrightarrow ArCH{=}CHCH{=}CHCH{=}CHAr'$$

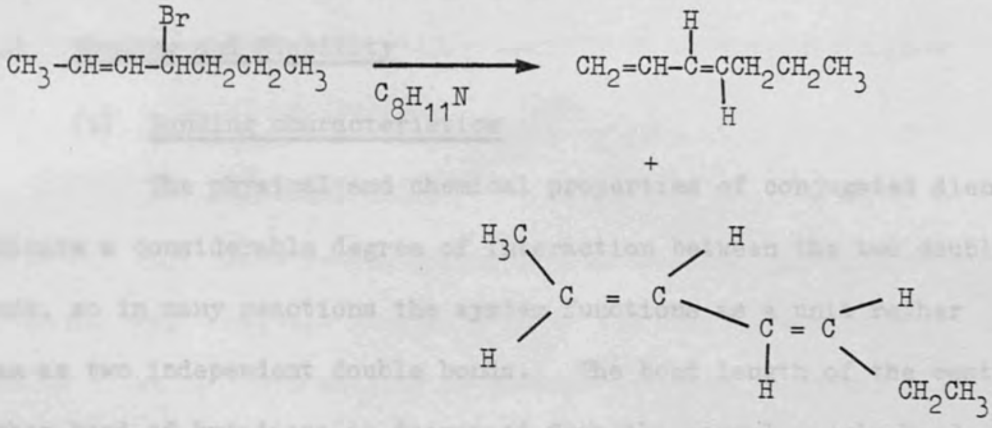
(II.21)

(v) By 1,4-elimination reactions

Butadiene is obtained by the action of zinc on 1,4-dibromobut-2-ene[16 a,b]

$$BrCH_2CH{=}CHCH_2Br \xrightarrow{Zn} CH_2{=}CH{-}CH{=}CH_2 + ZnBr_2 \qquad (II.22)$$

The dehydrobromination[17] of 4-bromohept-2-ene by refluxing with collidine, produces a 1,3-heptadiene, 2,4-heptadiene mixture.



(II.23)

(vi) Lebedev's process

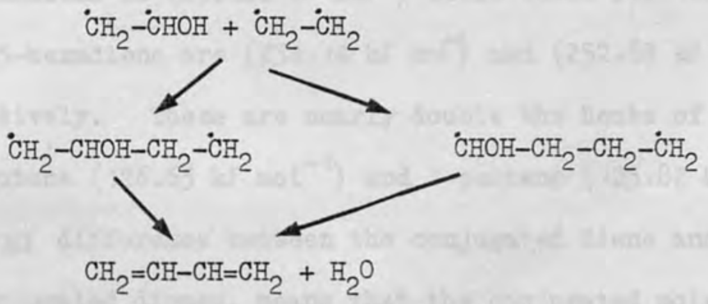
Lebedev[18] has shown that ethanol may be converted into butadiene directly using a catalyst mixture having a hydrogenating component and dehydrating component. The process follows the overall equation

$$2CH_3CH_2OH \longrightarrow CH_2{=}CH{-}CH{=}CH_2 + H_2 + 2H_2O \qquad (II.24)$$

The requisite active species (diradicals) were thought to arise through both the dehydrogenation and dehydration of ethanol.

$$CH_3-CH_2OH \longrightarrow \dot{C}H_2-\dot{C}HOH + H_2$$

$$CH_3CH_2OH \longrightarrow \dot{C}H_2-\dot{C}H_2 + H_2O$$



(II.25)

II.B Bonding and Stability

(i) Bonding characteristics

The physical and chemical properties of conjugated dienes indicate a considerable degree of interaction between the two double bonds, so in many reactions the system functions as a unit rather than as two independent double bonds. The bond length of the central-carbon bond of butadiene is decreased from the normal single bond length of 1.54 A° to 1.476 - 1.483 A°, indicating that it possesses a certain amount of double bond character.[19]

These facts, can be interpreted wave-mechanically by delocalization of the 2 p_z electrons in π-molecular orbitals extending over the four carbon atoms. The delocalization means that the central carbon-carbon bond gains some double bond character by having some π-electron density above and below the plane of the molecule, so that it is shorter than a single σ carbon-carbon bond.

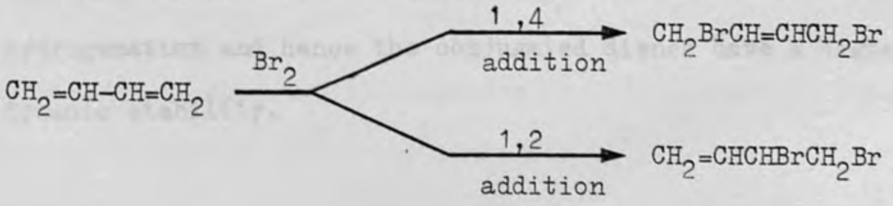
The delocalization energy or resonance energy is one of the most remarkable features of butadiene and conjugated molecules in general; this delocalization of the electron produces extra stability for the conjugated dienes. The heat of hydrogenation of 1,3-butadiene is (238.68 kJ mol^{-1}) while those for 1,4-pentadiene and 1,5-hexadiene are (254.14 kJ mol^{-1}) and (252.89 kJ mol^{-1}) respectively. These are nearly double the heats of hydrogenation of 1-butene (126.65 kJ mol^{-1}) and 1-pentene (125.82 kJ mol^{-1}). The 15 KJ difference between the conjugated diene and the non-conjugated dienes, means that the conjugated molecules have a lower energy than the non-conjugated molecues; that is to say, the conjugated dienes are more stable than the non-conjugated dienes due to electron delocalization.

(ii) 1,2- and 1,4-Addition

Substances having conjugated double bonding, in particular 1,3-diene compounds, are generally noted for their great reactivity. This is shown by their ability to undergo addition reactions and as a consequence to polymerise easily.

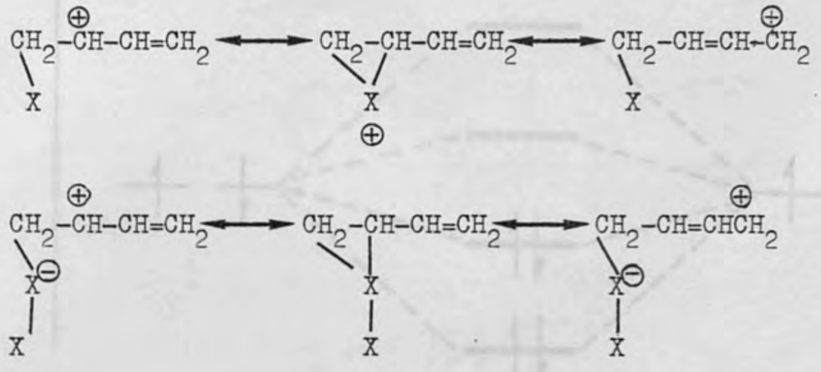
An example of the addition reactions of butadiene is its bromination producing 1,4-dibromo-2-butene and 3,4-dibromo-1-butene.

1,4-Addition[20] is accompanied by the migration of the double bonding to the 2,3-position.



(II.26)

Addition of halogens to conjugated systems is generally regarded as a two-stage process: electrophilic attack by halogen or halonium ion, followed by nucleophilic attack by halide ion.[21]

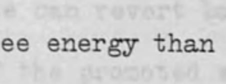


(iii) Valence Bond Approach and Thermodynamic Stability

Butadiene may be regarded as a resonance hybrid of the classical structure (VIII — XI); VIII marking the greatest contribution and with much smaller contributions from the structures IX, X, and XI.

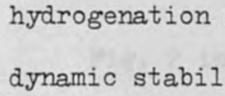
$CH_2=CH-CH=CH_2$

VIII



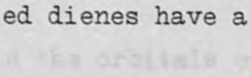
$\overset{|\text{- - - - - - -}|}{CH_2-CH=CH-CH_2}$

IX



$\overset{\oplus}{C}H_2-CH=CH-\overset{\ominus}{C}H_2$

X



$\overset{\ominus}{C}H_2-CH=CH-\overset{\oplus}{C}H_2$

XI

The conjugated dienes have a lower free energy than the isomeric unconjugated dienes, as illustrated above with their lower heat of hydrogenation and hence the conjugated dienes have a higher thermodynamic stability.

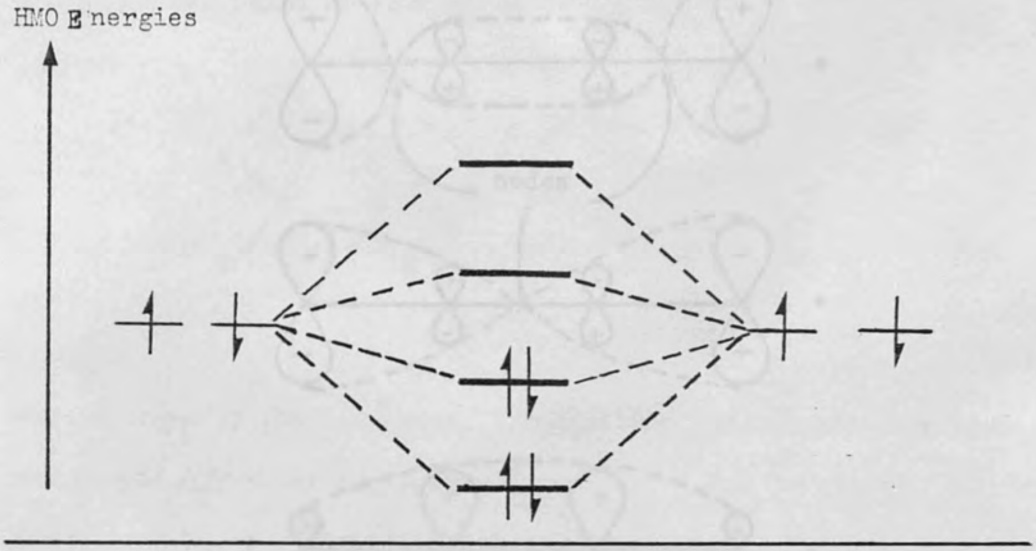


Fig. 1

Fig. 1 indicates the relative energy levels of the four π-molecular orbitals of butadiene. It shows that the lowest energy state occurs when the two lowest orbitals are completely filled with paired electrons.

In the lowest excited state, one electron becomes promoted to the next lowest energy level $(\alpha - 0.618\beta)$ to produce either a singlet or a triplet state. By losing the energy that was absorbed in the excitation process, the singlet state can revert back to the ground state very easily. If the spin of the promoted electron is inverted a triplet state results.

Fig. 2 indicates the symmetry in the orbitals of butadiene using the common plus - minus notation.[22]

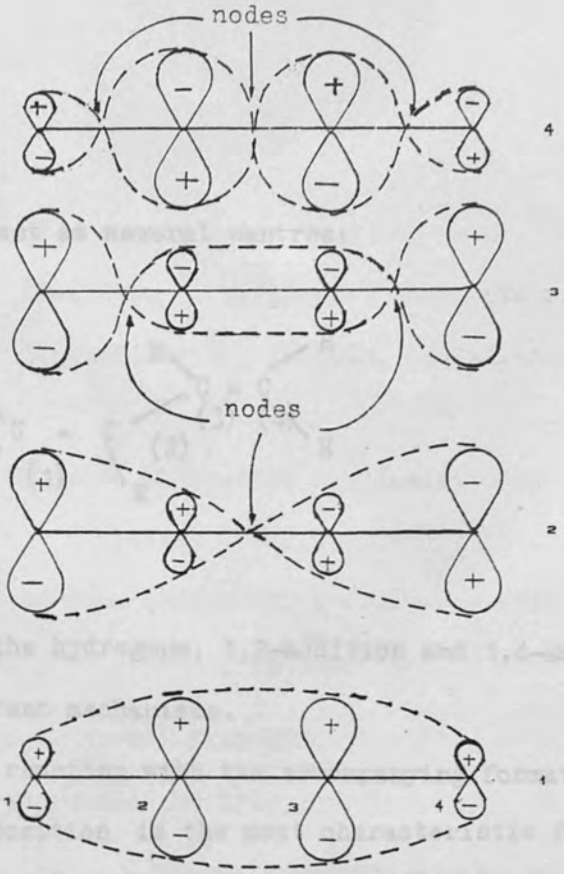
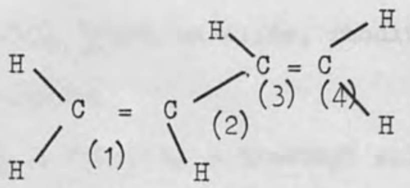


Fig. 2 Nodes in the LCAO molecular orbitals of butadiene .

III. Addition Reactions of 1,3-Butadiene:

Conjugated dienes, are generally more reactive than mono-olefins or unconjugated dienes, owing to those factors which lower the energy of the molecule and which often operate still more effectively to lower the energy of the transition states of reactions. As well as being the simplest conjugated diene, butadiene is an inexpensive industrial chemical, highly reactive, and has been probably one of the most investigated of all organic compounds. A number of its more recent reactions, are included in the following section.

Butadiene can react at several centres:



Substitution of the hydrogens, 1,2-addition and 1,4-addition each by several different mechanisms.

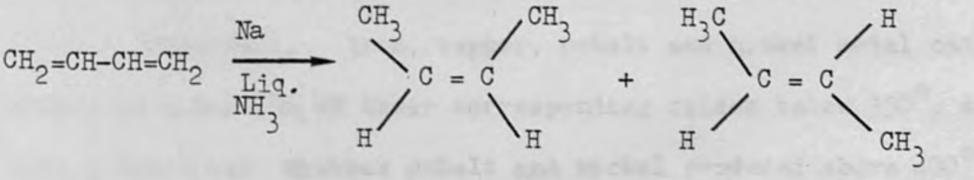
The 1,4-addition reaction with the accompanying formation of a double bond in the 2,3-position is the most characteristic feature of the chemistry of conjugated dienes.

Butadiene is able to form linear dimers, trimers, and polymers and undergo a variety of reactions to give three-, four-, five-, six-, eight-, and higher membered rings.

Examples of the more important of these reactions are now discussed briefly:

III.A <u>Addition of Hydrogen</u>:

Conjugated dienes undergo 1,4-addition of hydrogen when reduced by dissolving metals e.g. sodium in liquid[23 a,b] ammonia. Thus, butadiene affords a mixture of E and Z-but-2-enes.



(III.1)

Many catalysts, mostly transition metals and their compounds have been used for the reduction of butadiene, among the most effective are Raney nickel, platinum oxide, rhodium, palladium-on-charcoal,[24] and copper chromite.

A palladium chloride - dimethyl sulphoxide complex catalyses the reduction of 1,3-butadiene and 2,3-dimethyl butadiene to a non-equimolar mixture of the corresponding alk-1-ene and alk-2-ene,[25 a,b] with the alk-2-ene predominating in each case.

In comparison, a nickel phosphide catalyst gives mainly 1-butene when it catalyses the hydrogenation of 1,3-butadiene.[26 a,b]

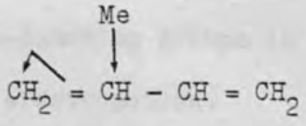
Nickel metal itself exhibits poor selectivity for butene formation i.e. it gives simultaneously 66% butane when the hydrogenation is carried out in ethanolic solution at -8°.

The gas phase hydrogenation of 1,3-butadiene using iron, cobalt or nickel has been shown to be highly **selective**, giving almost exclusively butenes with very little butane; but-1-ene and trans-but-2-ene predominate over cis-but-2-ene. It is proposed that the but-1-ene product is formed by hydrogen atom addition to the chemisorbed (through only one π-bond) alkadiene (type A behaviour), whereas the cis and trans but-2-ene[27] arise by additions to first the di π-bonded chemisorbed species and then to the π-allyic species (type B behaviour). Iron, copper, cobalt and nickel metal catalysts formed by reduction of their corresponding oxides below 350°, show type A behaviour, whereas cobalt and nickel produced above 400° give products from a type B behaviour. The cobalt and nickel catalysts could be changed from one type to the other by re-exposing to the reduction conditions.[28]

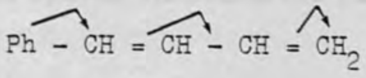
Hydrogenation in most cases is carried out at room temperature and just above atmospheric pressure and has been shown to be affected by the structure of the initial diene.

III.B Electrophilic Addition

It is convenient to sub-divide electrophilic addition to conjugated dienes into two classes: (i) acids as electrophiles for addition and (ii) additions with other electrophiles. If the two ends of the diene are made non-equivalent by alkyl or aryl substitution, then that end at which the substituent itself can contribute a hyperconjugative or conjugative +E effect will be preferred as the point of initiation of addition. Thus in isoprene it is expected that attack by the electrophile should occur at the 1-position but that in 1-phenylbutadiene at the 4-position.[28]



$CH_2 = C(Me)H - CH = CH_2$



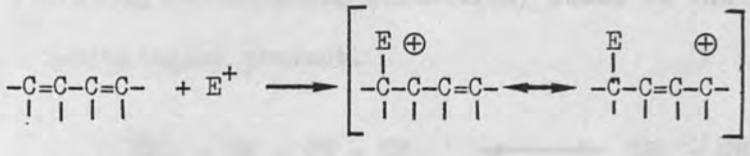
$Ph - CH = CH - CH = CH_2$

Electron withdrawing groups inhibit the electrophilic reactions because they lower the electron density of the double bond, but for electron releasing substituents the situation is reversed.

(i) Acids as electrophiles for addition

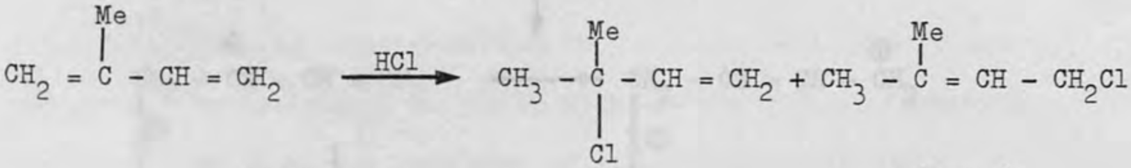
With the addition of the strong acids, one always obtains 1,2-, and 1,4-addition products, and often the latter in the much larger yield. The competition between the two types of products comes about because the carbonium ion resulting from attack by E^+, is a resonance hybrid, with partial positive charge at the 2- and 4-position, since E^+ always attacks at the end of the conjugated system to give the most stable carbonium ion.

The nucleophile (Nu^-) may complete the reaction[29] by attack at either the 2 or 4 positions.



$$-C{=}C{-}C{=}C- + E^+ \longrightarrow \left[-\overset{E}{C}{-}\overset{\oplus}{C}{-}C{=}C- \longleftrightarrow -\overset{E}{C}{-}C{=}C{-}\overset{\oplus}{C}- \right]$$

Isoprene, treated with HCl gives the two products (III.2).



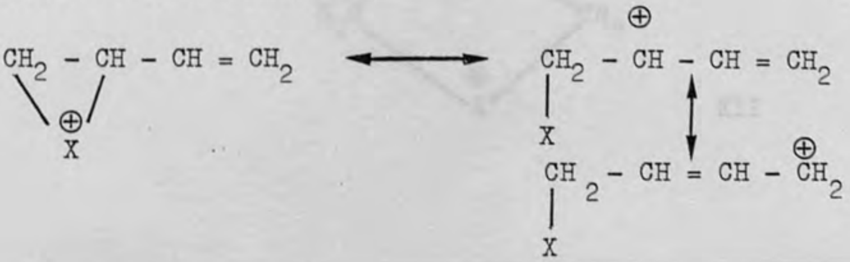
$$CH_2 = \overset{Me}{C} - CH = CH_2 \xrightarrow{HCl} CH_3 - \underset{Cl}{\overset{Me}{C}} - CH = CH_2 + CH_3 - \overset{Me}{C} = CH - CH_2Cl$$

(III.2)

Whereas $PhCH{=}CH{-}CH{=}CH_2$ gives only $PhCH{=}CH{-}CHClCH_3$ since this is the only one of the possible products to have a double bond in conjugation with the ring and results from an initial attack by H^+ at an end of the conjugated system. In general the presence of electron-donating groups in the diene system increases the reactivity towards electrophiles.

(ii) Additions with other electrophiles

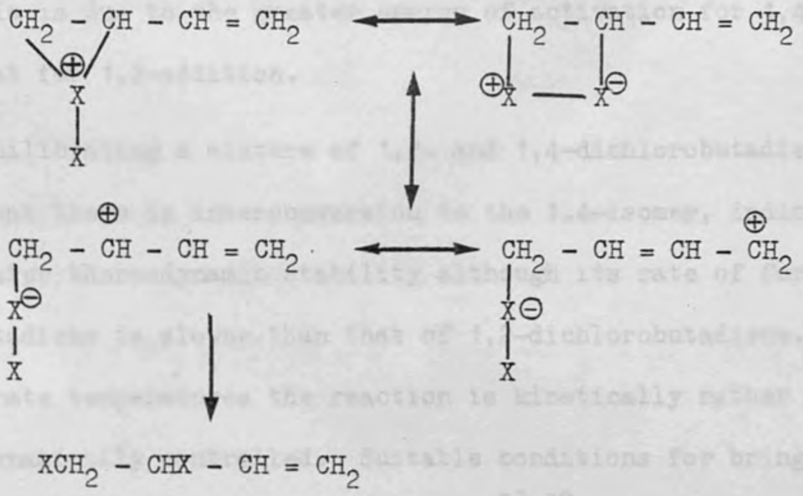
Many reactions are promoted by electrophilic attack at one end of the diene system, see (III.3 and III.4). The addition of halogens is a two-stage process with electrophilic attack by halogen or halonium ion followed by nucleophilic attack by the halide ion.[21] The intermediate can have the following contributing structures when the attacking reagent coordinates with one of the terminal double bonds.



$$\underset{\overset{\oplus}{X}}{CH_2 - CH} - CH = CH_2 \longleftrightarrow \underset{X}{CH_2} - \overset{\oplus}{CH} - CH = CH_2 \longleftrightarrow \underset{X}{CH_2} - CH = CH - \overset{\oplus}{CH_2}$$

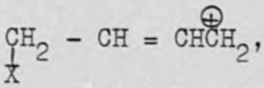
(III.3)

The subsequent association of halide ion (represented by the following contributing structures) leads to the formation of the 1,2-dihalogeno product.

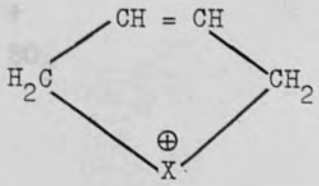


mainly

(III.4)

Stereochemically most 1,2-additions are anti with the groups approaching from opposite sides. If the attack by halide ion takes place with the allyl carbonium ion  $\underset{X}{CH_2} - CH = CH\overset{\oplus}{C}H_2$, i.e. with the charge localised on C(4), then the 1,4-dihalogens product results.

It has been demonstrated[21] that the 1,4-addition of chlorine to butadiene is an anti addition - that is, the chloromethyl groups in the product lie trans to each other, which indicates that the 1,4-addition mechanism does not go through an intermediate such as XII which would lead to the cis product.



XII

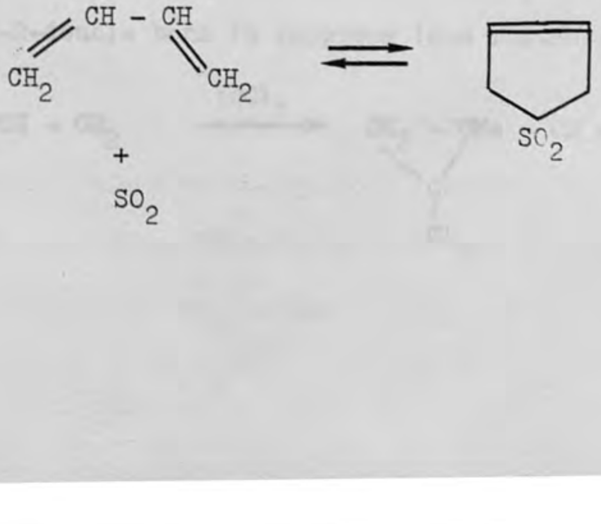
The rates of 1,2-addition are generally greater than those of 1,4-addition thus the 1,2-addition of chlorine to butadiene at room temperature predominates but as the reaction temperature is raised, 1,4-addition becomes increasingly important.

This is due to the greater energy of activation for 1,4-addition than that for 1,2-addition.

Equilibrating a mixture of 1,2- and 1,4-dichlorobutadienes has shown that there is interconversion to the 1,4-isomer, indicating its greater thermodynamic stability, although its rate of formation from butadiene is slower than that of 1,2-dichlorobutadiene. At moderate temperatures the reaction is kinetically rather than thermodynamically controlled. Suitable conditions for bringing about the interconversion of the isomers[28,30] have been by heating to 200° with zinc chloride. The mixture obtained first at room temperature (75% 1,2-dichlorobutadiene) is transformed to 75% 1,4-dichlorobutadiene.

III.C Addition of Sulphur Dioxide

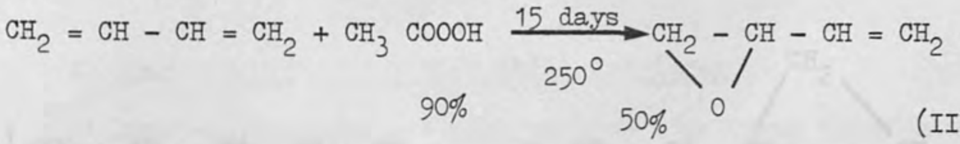
Many 1,3-dienes undergo reversible cyclo 1,4-addition of sulphur dioxide giving cyclic sulphones. These cheleotropic reactions are used in the purification of dienes.[20]



(III.5)

III.D Reaction with Organic Peracids

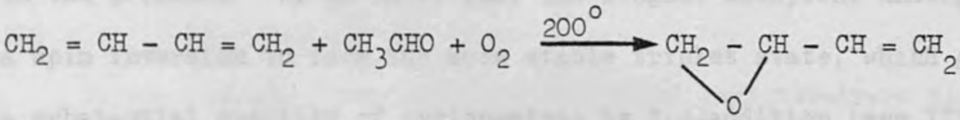
Organic peracids convert 1,3-dienes into unsaturated epoxides by 1,2-addition.[31 a,b,c,d] Butadiene reacts quite slowly with peracetic acid, as indicated in the following equation.



$$CH_2 = CH - CH = CH_2 + CH_3\,COOH \xrightarrow[250^{\circ}]{15\ days} \underbrace{CH_2 - CH}_{O} - CH = CH_2$$

90% 50% (III.6)

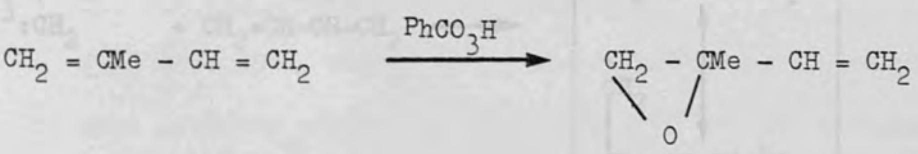
The peracetic acid can be generated in situ during the cooxidation of butadiene and acetaldehyde:



$$CH_2 = CH - CH = CH_2 + CH_3CHO + O_2 \xrightarrow{200^{\circ}} \underbrace{CH_2 - CH}_{O} - CH = CH_2$$

(III.7)

Isoprene is preferentially attacked at the double bond to which the methyl group is bonded in these epoxide forming 1,2-addition reactions.

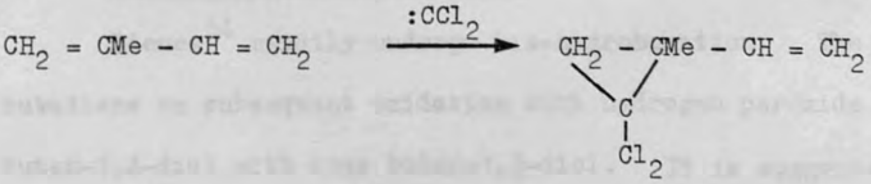


$$CH_2 = CMe - CH = CH_2 \xrightarrow{PhCO_3H} \underbrace{CH_2 - CMe}_{O} - CH = CH_2$$

(III.8)

III.E Addition of Carbenes

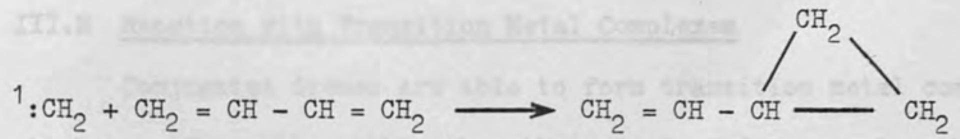
These occur at C_1 and C_2 giving vinyl cyclopropanes e.g. Methylene[32 a,b,c,d] and dichlorocarbene ($:CCl_2$) preferentially attack the 1-2-double bond in isoprene (see III.10).



$$CH_2 = CMe - CH = CH_2 \xrightarrow{:CCl_2} \underbrace{CH_2 - CMe}_{\underset{Cl_2}{C}} - CH = CH_2$$

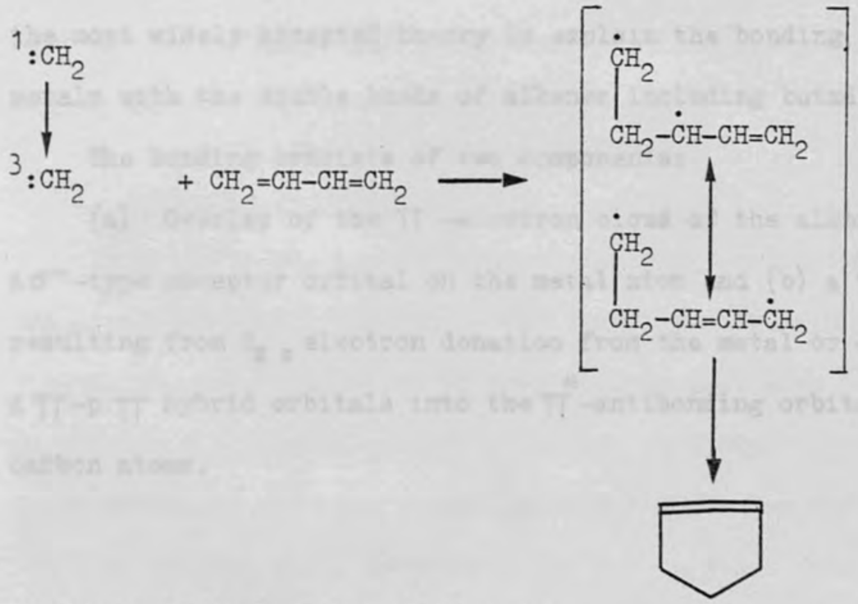
(III.9)

The reaction with (: CH_2), the simplest carbene, is thought to take place in the singlet state when it is produced by the photolysis of diazomethane. In the absence of diluents, it gives almost exclusively vinylcyclopropane on reaction with butadiene.



(III.10)

In the presence[33] of an inert gas, the singlet methylene undergoes a spin inversion to form the more stable triplet state, which gives a substantial quantity of cyclopentene by 1,4-addition (see III.12)



(III.11)

III.F The Hydroboration of Dienes

Dienes[34] readily undergo bis-hydroboration. The adduct from butadiene on subsequent oxidation with hydrogen peroxide gives mainly butan-1,4-diol with some butan-1,3-diol. It is suggested here that the hydroboration does not proceed through a single simple reaction path.

III.G Coupling with Diazonium Salts

1,3-Dienes[35,36] can couple with the more reactive diazonium salts, e.g. when butadiene or isoprene (R : H or CH_3) react with $XC_6H_4N_2Cl$ (X electron withdrawing) X $C_6H_4CH_2CR = CHCH_2Cl$ is obtained.

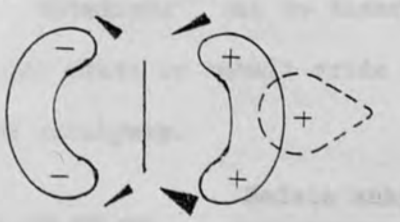
III.H Reaction with Transition Metal Complexes

Conjugated dienes are able to form transition metal complexes which are often more stable than those derived from simple alkenes. The complexes of butadiene, in particular those with copper salts, are important not only for modifying the reactivity of butadiene, but also in recovery and purification procedures.

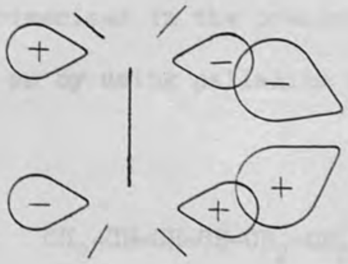
Silver nitrate forms crystalline solids with butadiene having a 1:1 or 2:1 molar ratio. Dewar[37] has suggested what has become the most widely accepted theory to explain the bonding of transition metals with the double bonds of alkenes including butadiene.

The bonding consists of two components:

(a) Overlap of the π-electron cloud of the alkene with a σ-type acceptor orbital on the metal atom and (b) a "back-bond" resulting from d_{xz} electron donation from the metal or other $d\pi$-$p\pi$ hybrid orbitals into the π^*-antibonding orbital on the carbon atoms.

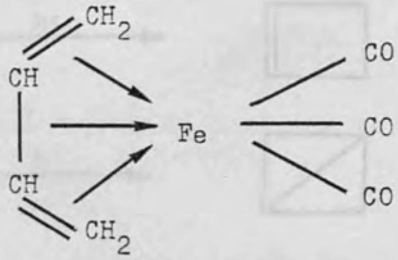


(a)



(b)

In 1958, Hallam[38] and Pauson, by analogy with the carbon-metal bonding in Ferrocene, proposed that the butadiene-metal bond in e.g. iron-butadiene complex, results from the overlap of a bonding π-orbital of the diene with an empty orbital of the metal.



Similar π-complexes have been prepared with Cobalt, Nickel, Manganese, Platinum and Palladium compounds.

III.I Addition to other Dienes

As referred to previously, butadiene can undergo addition reaction with itself to form linear dimers and trimers. This process is usually promoted by some reagent that adds to butadiene to produce a carbonium ion, free radical or coordination compound to which one or more additional butadiene molecules add before a termination step gives destruction of the reactive centre.

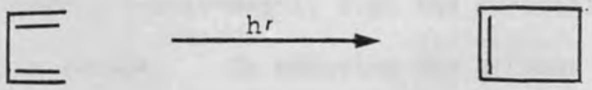
Butadiene[31e] can be dimerised or trimerised in the presence of nickel oxide or cobalt oxide complexes or by using palladium or iron catalysts.

$$CH_2{=}CH{-}CH{=}CH_2 \xrightarrow[(\phi_3P)_2/\,Pd\,/\,Benzene.]{Maleic\ anhydride\ /} CH_2{=}CH{-}CH{=}CH{-}CH_2{-}CH_2{-}CH{=}CH_2$$

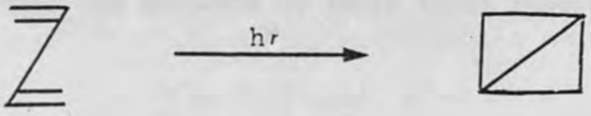
(III.13)

III.J Ring Forming Reactions of Dienes

One of the most unusual characteristics of diene, especially butadiene, is its ability to form rings of various sizes. Butadiene can probably produce, conveniently, more different sized rings in high yields than any other simple compound e.g.



(III.14)



(III.15)

Its reaction with triplet carbene giving cyclopentenes was discussed previously (III.E). Diels-Alder type of cycloaddition with dienophiles gives 6-membered ring compounds.

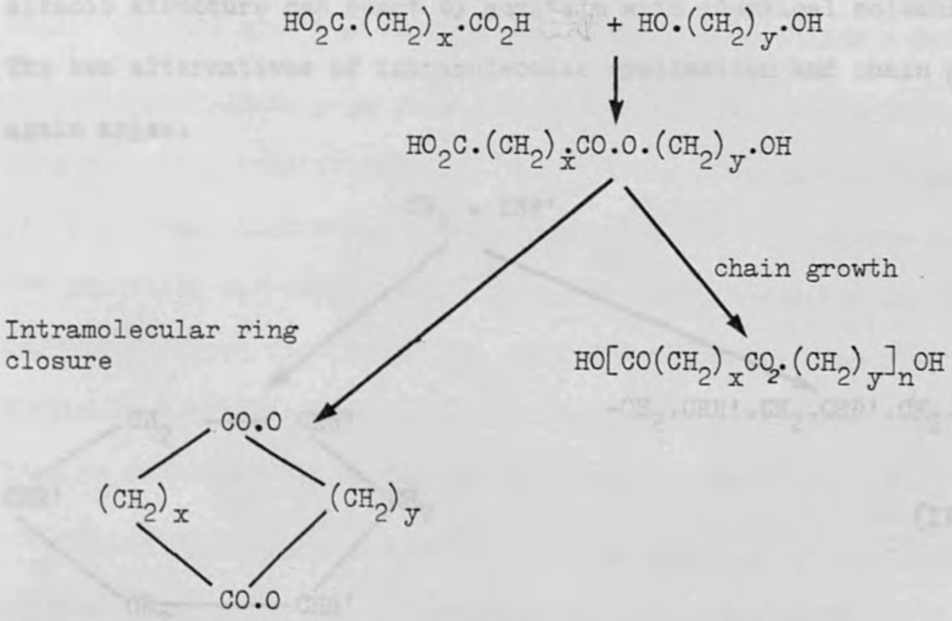
IV. The Polymerisation of Conjugated Dienes

The formation[39] of dimers can be achieved by the use of catalysts, viz acids (both Brønsted acids and Lewis acids) some transition metals, organometallic compounds e.g. Ziegler catalysts. Alternatively it may have been achieved photochemically or simply by thermal induction.

Of all polymerisation processes dimerisation is the simplest and is the limiting example of oligomerisation. Carothers has classified the polymerisation into (i) addition polymerisation, and (ii) condensation polymerisation. The essential difference between these two types lies in the mechanism of polymerisation, since the first proceeds by stepwise condensation of reactive groups, while the second type proceeds by chain mechanisms involving active centres.

Somewhat different structures for the polymers result from the application of these two different processes. Inter-unit groupings (cross links) are found in condensation polymers but not usually in addition polymers.

In either type of polymerisation the monomer or monomers must meet certain requirements, e.g. the possession of two or more reactive groups. In addition the monomer or monomers must be such that the products of their first reactions should be acyclic.



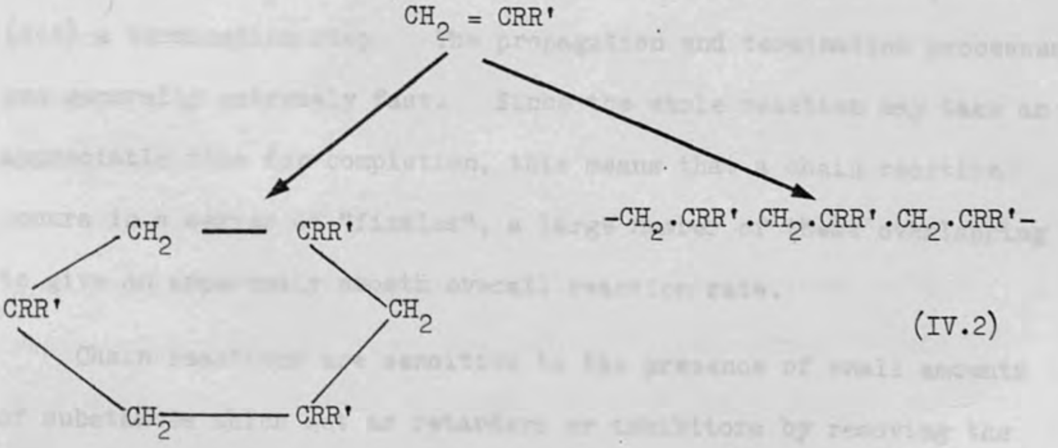
(IV.1)

The cyclic product has no longer any functional groups available for further reaction with other molecules in the reaction mixture.

The linear polymer still possesses two functional groups and can react with other difunctional molecules present to increase the length of the polymer chain still further.

The formation of ring or chain products depends on the size of the ring which may be formed. If the formation of a ring will involve less than five or more than seven atoms, linear polymers are likely to be formed. However since five-membered rings are essentially free from strain, if their formation is possible, then linear chains are unlikely to be formed; but if six- and seven-membered rings are possible their formation may compete with that of linear chains and either or both products may be formed.

Polymerisation can also occur with unsaturated molecules possessing no other functional group. Molecules containing the alkenic structure can react by addition with identical molecules. The two alternatives of intramolecular cyclisation and chain growth again arise:



(IV.2)

If the formation of strain-free rings cannot occur, linear polymer chain are produced.

The tendency of such unsaturated compounds to polymerise depends very much on the nature and position of the substituents.

The ease of polymerisation is often increased by the introduction of groups such as halogen, CN, CHO, CO_2H and C_6H_5. If more than one substituent is introduced the reactivity varies with the relative positions of the substituents.

The polymerisability of dienes depends on the relative position of the double bonds. Conjugated dienes, such as 1,3-butadiene are easily polymerised but 1,2-alkadienes such as allene, $CH_2:C:CH_2$ are difficult to polymerise.

The oligomerisation by chain addition mechanisms can be initiated by (a)free-radicals (b) cations or (c) anions and the chain carriers are then free radicals, cations or anions respectively.

General addition polymerisation proceeds through three distinct stages (i) an initiation step, (ii) chain propagation steps and (iii) a termination step. The propagation and termination processes are generally extremely fast. Since the whole reaction may take an appreciable time for completion, this means that a chain reaction occurs in a series of "fizzles", a large number of these overlapping to give an apparently smooth overall reaction rate.

Chain reactions are sensitive to the presence of small amounts of substances which act as retarders or inhibitors by removing the chain carriers either partially or completely.

During cationic polymerisation, the π-electrons of the unsaturated monomers become shared with the initiating electrophilic reagents giving rise to a carbocation. This then undergoes addition with the unsaturated monomer. The cationic polymerisation of 1,3-dienes, such as butadiene and isoprene, may result in the formation of polymers of differing structures according to whether their addition occurs at the 1- and 4- or 1- and 2-positions. Both types of addition may occur together in a random manner and the unit resulting from 1,4-addition may have a cis or transgeometry provided there is no methyl substituent on C2.

Lebeder[40] started a systematic study of the thermal polymerisation of isoprene, butadiene and 2,3-dimethyl butadiene in 1907. He concluded that "the ability to polymerise is exhibited by those dienic hydrocarbons which possess a conjugated system of double bonds". The reaction proceeds in two directions: the formation of cyclic dimers and the formation of linear polymers. Later studies on the kinetics[41, 42 a,b] of dimerisation have shown that this reaction is a bimolecular homogeneous process. It was found that the rate of the dimerisation reaction shows only little dependence on the nature of the solvent but with substituted butadienes the rate depends to a considerable extent on the position and nature of the substituents.

Substitution at the 2- and 3-positions of butadiene by electron donating groups causes an increase in the dimerisation reaction rate, while substitution at the terminal carbon atoms (1- and 4-positions) has the reverse effect.

The dimerisation of conjugated dienes can be considered to be a reaction in which a second molecule of the diene reacts as a dienophile.

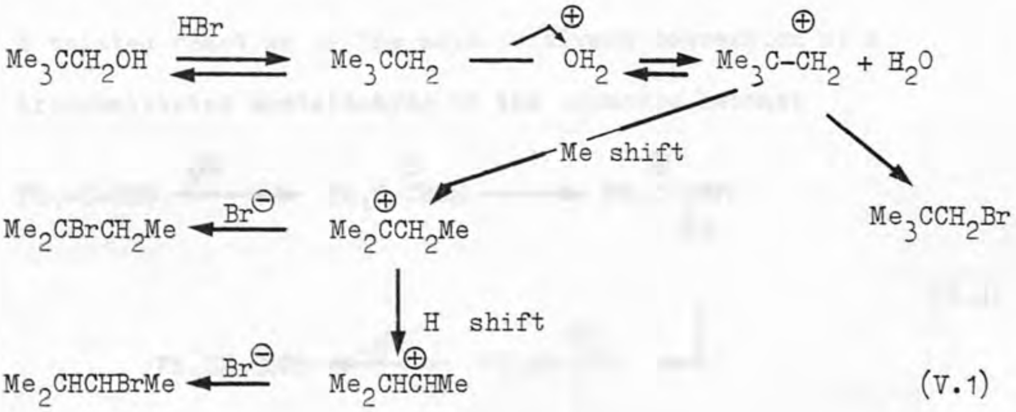
At the same time, dimerisation of dienes can also be regarded as a special case of polymerisation, in which the reaction is concluded after the first step due to stabilization of the growing chain by ring closure.

V. Carbocations and their Rearrangements

A. Simple Rearrangement of Carbocations

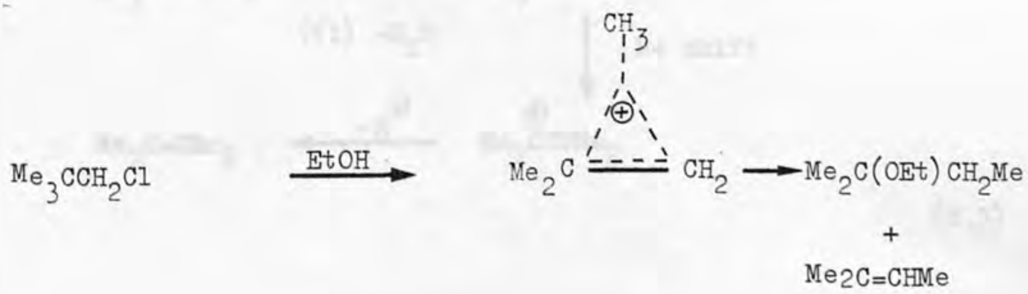
Acid catalysed dehydration of alcohols may sometimes be accompanied by carbonium ion rearrangements involving methyl and/or hydride ion 1,2-shifts. This was suggested by Whitmore (1932) and thereafter was often referred to as the Whitmore mechanism.

Neopentyl alcohol (2,2-dimethylpropanol) reacts with HBr, following a carbonium ion mechanism giving some neopentyl bromide but mainly, 2-bromo-2-methyl butane and 2-bromo-3-methyl butane, as a result of 1,2-methyl and hydride shifts.



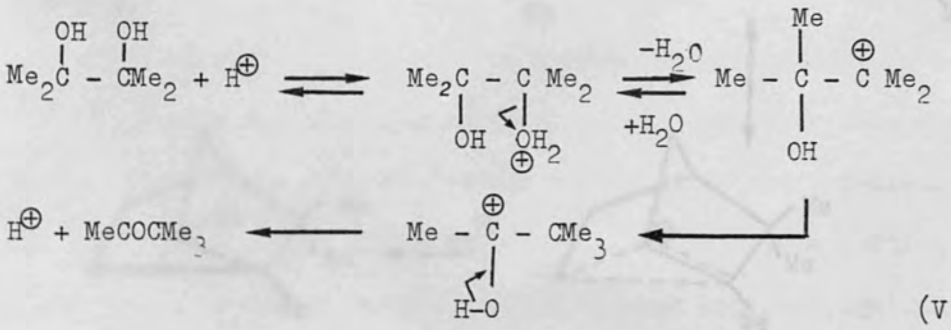
(V.1)

The driving force, for the rearrangement results from the relative stabilities of the carbonium ions. A similar rearrangement[43] occurs in the reaction of neopentyl chloride with ethanol.



(V.2)

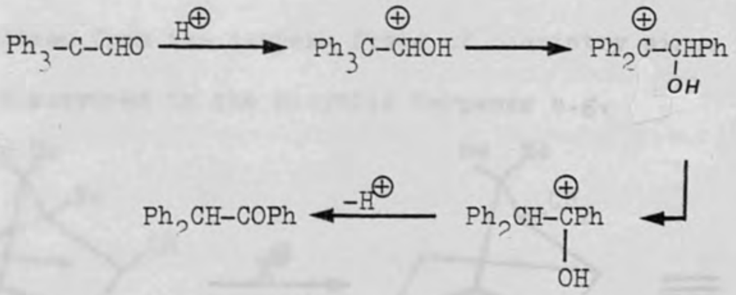
When[44] pinacol is treated with cold, concentrated sulphuric acid, pinacolone is produced by losing a molecule of water and a methyl group having shifted from one of the central carbons to another. The conversion of pinacol into pinacolone is known as the pinacol-pinacolone rearrangement.



(V.3)

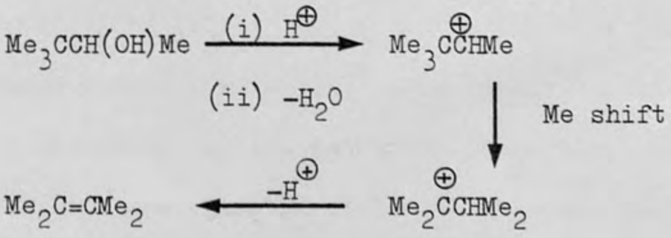
This mechanism was suggested by Bunton (1959).

A related reaction is the acid-catalysed conversion of a trisubstituted acetaldehyde to the isomeric ketone:



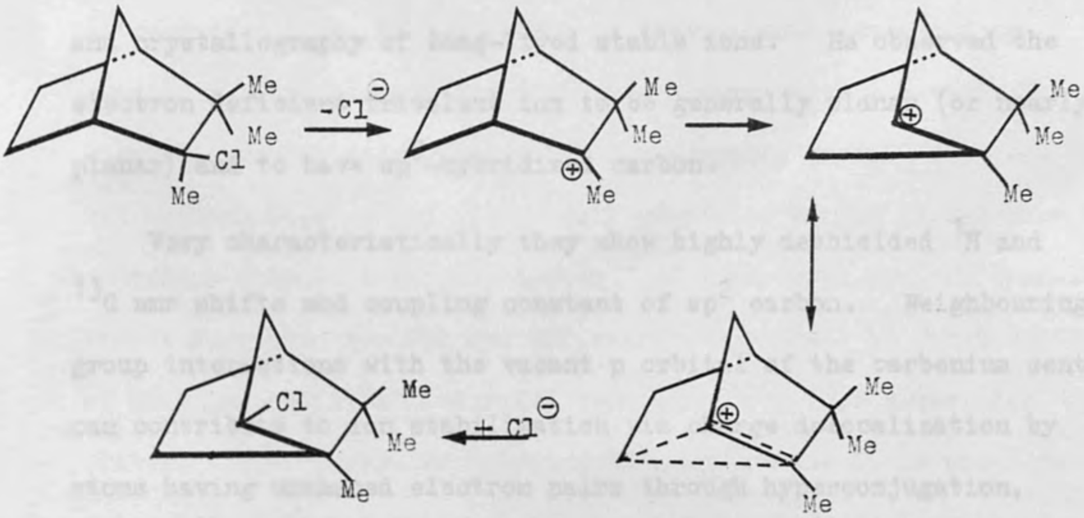
(V.4)

When an alkene bond is formed as a product following a 1,2-shift reaction, it is said to be a retropinacol rearrangement e.g.



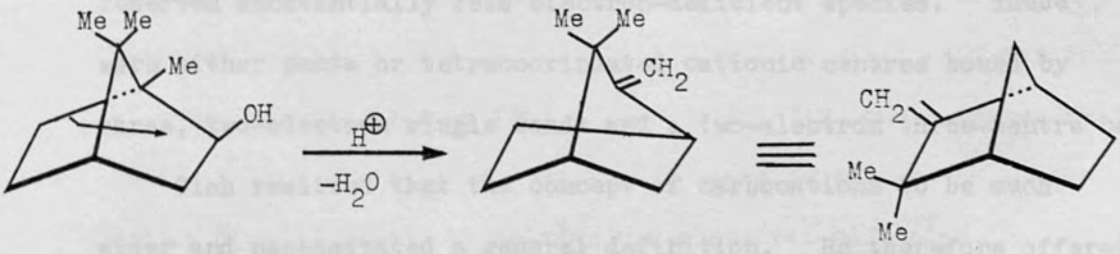
(V.5)

The[45] conversion of camphene hydrochloride into isobornyl chloride follows the so-called Wagner-Meerwein rearrangement.



(V.6)

Wagner-Meerwein rearrangements are often illustrated with examples drawn from the terpene field of chemistry since it was first discovered in the bicyclic terpenes e.g.



Isoborneol

Camphene

(V.7)

B. General Concepts of Carbocations

George A. Olah[46] based his continuing study of carbocations on direct observation by nmr, ir, Raman, x-ray induced spectroscopy and crystallography of long-lived stable ions. He observed the electron deficient trivalent ion to be generally planar (or nearly planar) and to have sp^2-hybridized carbon.

Very characteristically they show highly deshielded ^1H and ^{13}C nmr shifts and coupling constant of sp^2 carbon. Neighbouring group interactions with the vacant p orbital of the carbenium centre can contribute to ion stabilization via charge delocalization by atoms having unshared electron pairs through hyperconjugation, conjugation with bent σ-bonds, and π electron systems, thus trivalent ions can show varying degrees of delocalization.
In connection with the study of structural problems, related to the so-called "non-classical" nature of ions, e.g. norbornyl, 7-norbornenyl, 7-norbornadienyl, cyclopropylcarbinyl and cyclobutyl cations, Olah observed substantially less electron-deficient species. These[47] were either penta or tetracoorindated cationic centres bound by three, two-electron single bonds and a two-electron three-centre band.

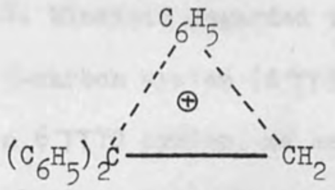
Olah realized that the concept of carbocations to be much wider and necessitated a general definition. He therefore offered such a definition based on the realization that two distinct classes of carbocations exist; one class consists of trivalent ("classical") carbenium ions, of which CH_3^+ is a parent. Skeletal rigidity or steric hindrance can prevent their planarity, vinyl cations and acyl cations are examples of trivalent ions, having linear (or close to linear) sp-hybridized cationic centres. A second class consists of three-centre bound penta- or tetracoordinated ("non-classical") carbonium ions of which CH$_5^+$ is the parent.

C. Non-Classical Ions

There can be only eight valence electrons in the outer shell of carbon. Thus, the covalency of carbon cannot exceed four. Penta- or tetracoordination describes a species with five or four ligands, respectively, being within reasonable bonding distance from the central atom, a definition well adaptable to the carbon atom in carbonium ions. A representation[48] of such cases are the transition states suggested for SN2 and SE2 reactions as well as for 1,2-alkyl or hydrogen shifts in saturated hydrocarbons.[49] However, the observation of penta- or tetracoordinated species in solution had never been reported until recent studies relating to long-lived "non-classical ions" in superacid solvent systems.

In contrast to the rather well-defined trivalent "classical" carbocations "non-classical" ions have been more loosely defined. In recent years, a lively controversy has centred on the "classical-non-classical carbonium ion" problem. The literature contains numerous contributions to the topic. A frequently used definition of non-classical ions is that of Bartlett: "an ion is non-classical if its ground state has delocalized σ-bonding electrons". The use of "dotted lines" in writing non-classical carbonium ion structure has been strongly[50] criticized by Brown.

The term "non-classical ions" was first applied to cations in which it was postulated that unorthodox bonds, as represented with dotted lines are to mean partial covalent bonding betwen carbon atoms e.g.

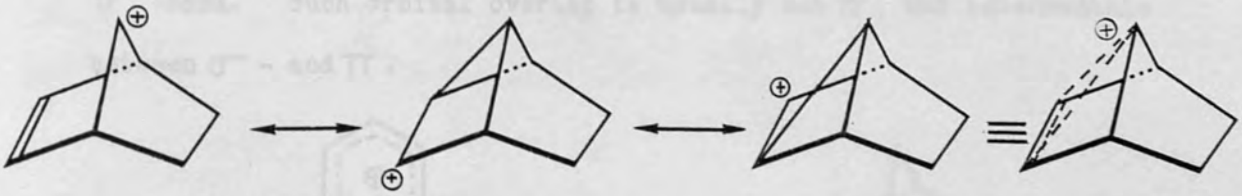


I

and

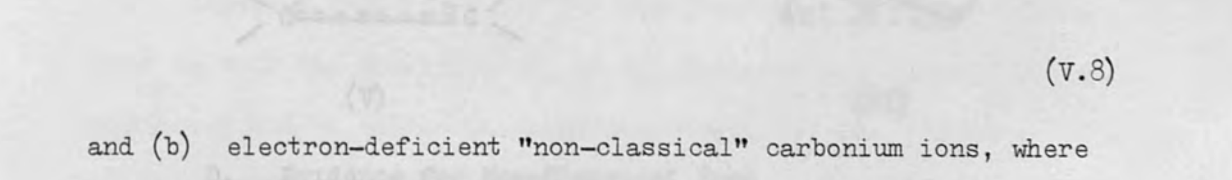
II

The essential feature of such formulae is the presence of "bridges" creating unusually disposed rings. Such ions are described as "bridged carbonium ions". These "non-classical ions" may be classified into two classes: (a) electron sufficient "non-classical" carbonium ions, having unsaturation that is not adjacent to the atom carrying the positive charged formed i.e. homoallylic carbonium ions



(V.8)

and (b) electron-deficient "non-classical" carbonium ions, where the canonical forms do not involve unsaturation at all. These forms involve overlap with the σ-orbitals of carbon-carbon single bonds e.g.



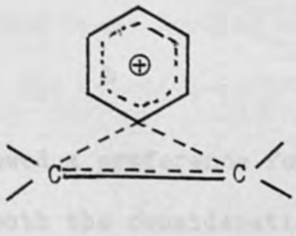
(V.9)

S. Winstein regarded the benzenonium ion (III), which 4π-electrons 5-carbon system (4π5C), and the tropylium ion (IV) representing a 6π7C system, as examples of "classical ions" which involve electron delocalization by normal conjugation employing pπ-orbital overlap.

(III)

(IV)

He illustrated "non-classical cations" by the phenonium ion (V) and the norbornyl cation (VI). Each[51] involves "non-classical" electron delocalization employing, at least in part, overlap of orbitals on carbon atoms between which there was not originally a σ-bond. Such orbital overlap is usually not π, but intermediate between σ- and π.



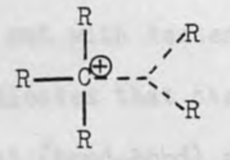
(V)

(VI)

D. Evidence for Non-Classical Ions

Unequivocal experimental evidence has been obtained, based on direct spectroscopic observation for non-classical ions, such as (a) the methonium ion, CH_5^+. This was originally only known from mass spectrometric studies.

The bonding involves three, two-electron covalent bonds with the fourth bond being a two-electron, three centre bond. The latter can be bound either to two additional atoms (penta coordinated) or involve a carbon atom to which there is already a single bond (tetracoordinated).

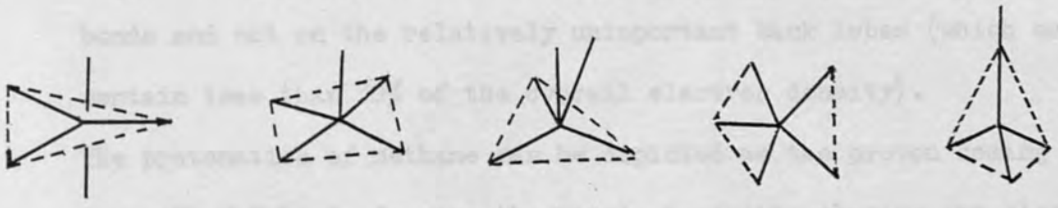


(VII)
Pentacoordinated

(VIII)
Tetracoordinated

R = H or alkyl

Several structures have been suggested for the methonium ion.



(IX)

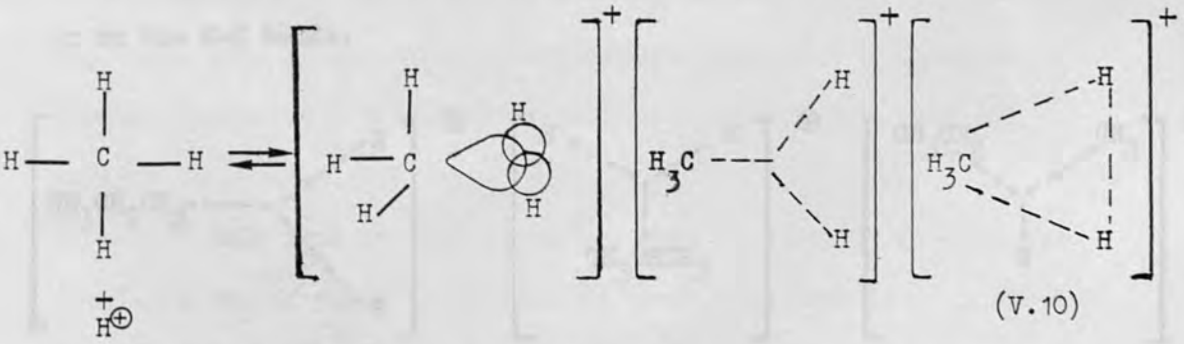
a b c d e

Olah[52] showed a preference for (C) the front-side protonated form, based on both the consideration of the chemistry of methane in superacids and on self-consistent field calculation. Chemical evidence and the results of more sophisticated calculation, make the trigonal bipyramidal form (a) the least favourable.

Muetterties recognized that ready interconversion of stereoisomeric forms of CH_5^+ is possible by a pseudo-rotational type process, or as Muetterties[53] recently suggested a "polytopal rearrangement" (also called sometimes "polyhedral rearrangement");

Olah nevertheless prefers to call such intramolecular carbonium ion rearrangements "bond to bond rearrangements". The scrambling of hydrogen-deuterium of deuterated methane in superacid solutions, provides strong evidence of such processes. It is suggested[52] that BH_5, an intermediate proposed in the acid hydrolysis of borohydrides, is a suitable model for CH_5^+. When the hydrolysis of borohydrides is carried out with deuterated acid not only HD but also H_2 is formed. This indicates that the attack of D^+ is on the B-H bond, followed by polytopal (bond-bond) rearrangement, before cleavage takes place.[54] The mechanism of electrophilic attack on saturated hydrocarbons, will usually take place on the C-H or C-C bonds; the electrophilic reagent will seek out the region of highest electron density. Thus, if there is no hindrance, the attack generally will occur on the main lobes of the bonds and not on the relatively unimportant back lobes (which usually contain less than 10% of the overall electron density).

The protonation of methane can be depicted as the proton coming in onto the C-H bond, forcing the single bond into sharing its electron pair with the electron-deficient reagent.

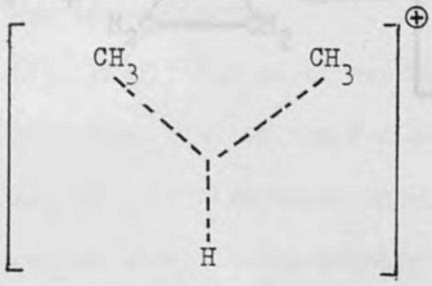


(V.10)

The dotted branched lines joining the three atoms have been suggested to be used instead of drawing the orbitals to depict the three-centre bonds. In comparison with the general usage of straight lines to represent two-centre bonds (full lines usually meaning two-electron bonds and dotted lines one-electron bonds), the three-centre bonds can also be written by a triangle of dotted lines joining all three atoms, to avoid misunderstanding of an atom at the "junction" of the branched dotted line symbols.

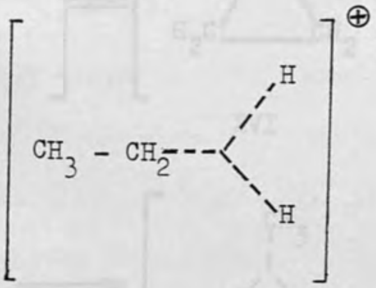
The preferred direction of attack by the electrophile may well vary from one compound to another, depending on the reaction conditions involved.

(b) Ethane can be protonated either on the C-C or C-H bonds; thus, the isomers of $C_2H_7^+$ are the C- and H-ethonium ions



C-ethonium ion

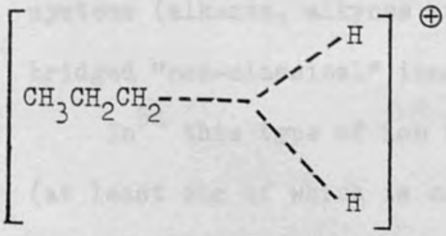
(X)



H-ethonium ion

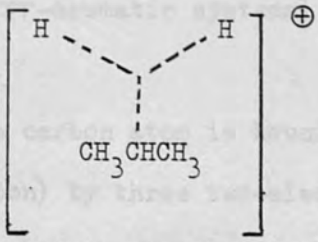
(XI)

and propane can be protonated on the secondary or primary C-H bonds or on the C-C bonds.



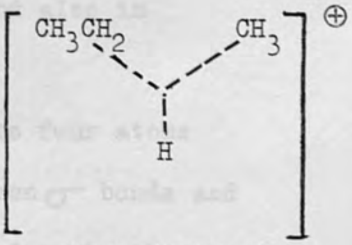
H-1-proponium ion

(XII)



H-2-proponium ion

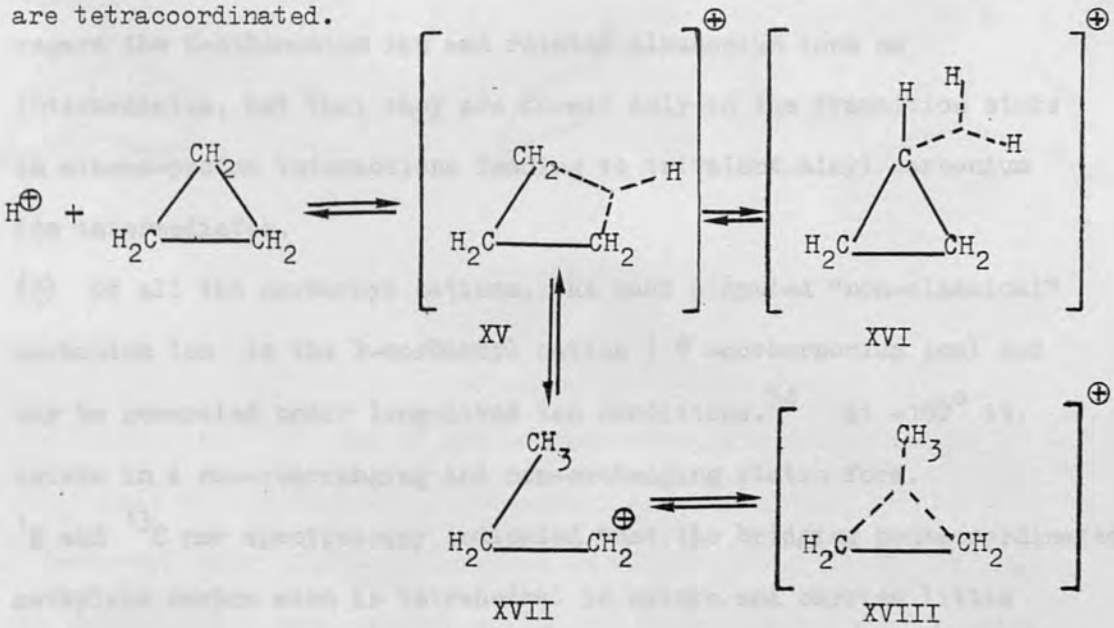
(XIII)



C-proponium ion

(XIV)

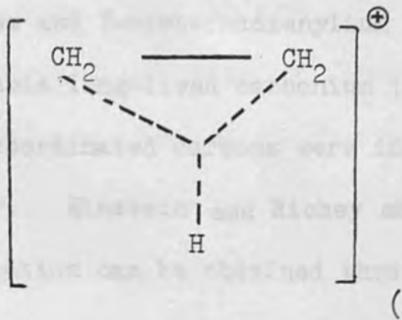
The protonation of cyclopropane can be C-cycloproponium (XV) and H-cycloproponium (XVI) ions; the methyl-bridged form (XVIII) of the protonation is not considered to be directly formed, but results from a rearrangement of XVII. The three-centre carbon bond, formed by methyl bridging involves C–C bond delocalization. The bridging methyl group is pentacoordinated and the methylene carbons are tetracoordinated.



(V.11)

The tetra-coordinated carbonium ions are considered to play an important role in the usual electrophilic reactions of π-donor systems (alkenes, alkynes and π-aromatic systems) and also in bridged "non-classical" ions.

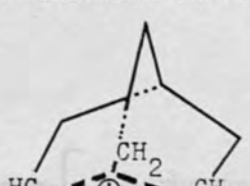
In[54] this type of ion the carbon atom is bound to four atoms (at least one of which is carbon) by three two-electron σ bonds and a two-electron, three centre bond, which involves bonding to the same carbon atom to which there is also single bonding. The parent of this type of tetracoordinate carbonium ion can be considered to be the C-ethenonium ion; the structure of which has been confirmed



(XIX)

by several spectroscopic methods. Olah and his co-workers do not regard the C-ethenonium ion and related alkanonium ions as intermediates, but that they are formed only in the transition state in alkene-proton interactions leading to trivalent alkyl carbenium ion intermediates.

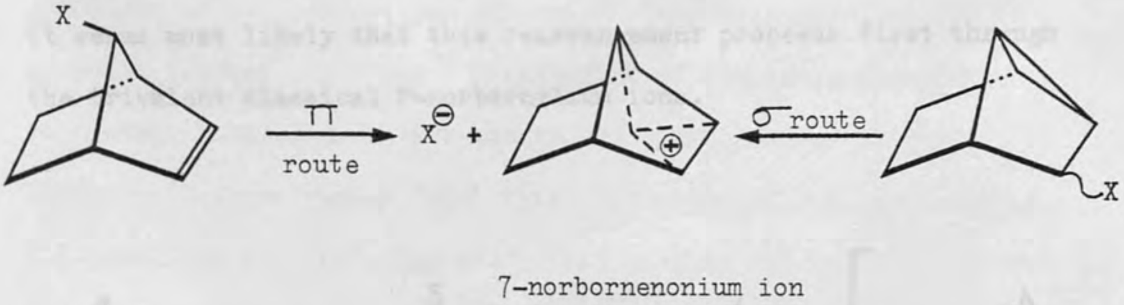
(c) Of all the norbornyl cations, the most disputed "non-classical" carbonium ion is the 2-norbornyl cation (6 -norbornonium ion) and may be generated under long-lived ion conditions.[54] At -150° it exists in a non-rearranging and non-exchanging static form. ^1H and ^{13}C nmr spectroscopy indicated that the bridging pentacoordinated methylene carbon atom is tetrahedral in nature and carries little charge. X-ray induced[52] photoelectron spectroscopy, also gave clear indication of this non-classical carbonium ion structure.



(XX)

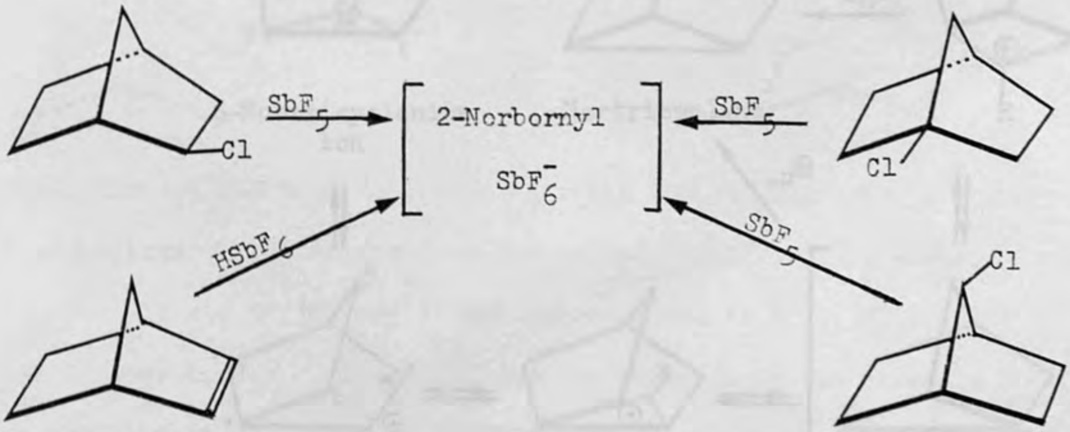
The methine carbons to which bridging takes place are tetracoordinated and the charge is delocalized mostly into the methine methylene bonds. This "non-classical" carbonium ion may be formed by C-C σ-bond delocalization, i.e. the σ-route to the symmetrical delocalized ion.[55,56]

The 7-norbornenylium and 7-norbornadienylium ions are other examples of directly observable long-lived carbonium ions in which the tetra and/or pentacoordinated carbons were identified by ^{13}C and ^{1}H nmr spectroscopy. Winstein and Richey showed that the 7-norbornenyl cation can be obtained through both the σ and π routes.



(V.12)

The 2-norbornyl[57,58] cation can be generated in solution as the SbF_6^- salt from a variety of precursors e.g. when 2-exo or 1-norbornyl chlorides are dissolved in a solution of $AgSbF_6$ in liquid SO_2 containing a small amount of SbF_5 or when norbornene is treated with $HSbF_6$ ($HF + SbF_5$) in SbF_5.

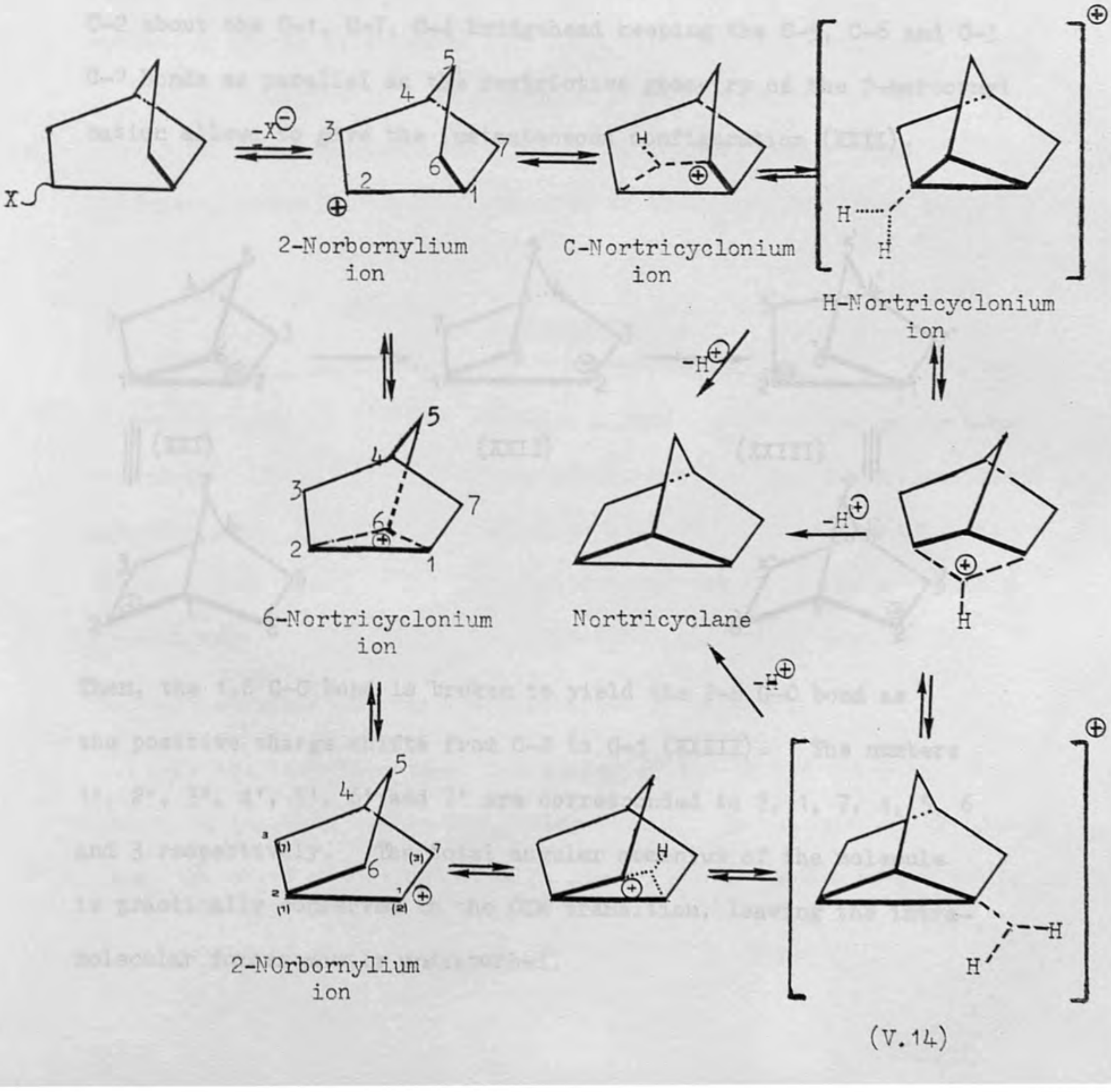


(V.13)

In addition it is obtained from exo-2-norborneol in $FSO_3H - SbF_5$

(SO_2, SO_2ClF) or in SbF_5 - SO_2 (SO_2ClF), and from norbornane, norbornylene or nortricyclene in FSO_3H - SbF_5 or HF-SbF_5 (SO_2, SO_2ClF); Jensen and Beck have also prepared the ion from exo-2-norbornyl chloride in $GaBr_3$-SO_2.

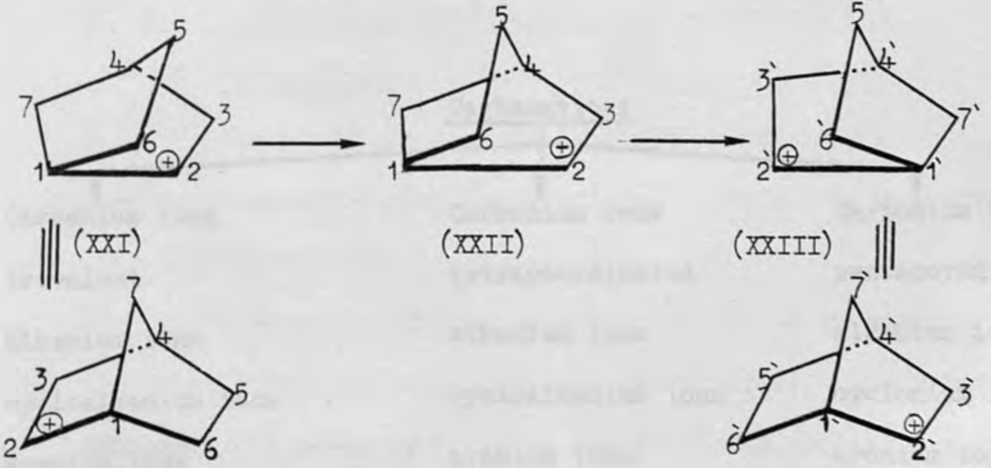
The 2-norbornyl[52] system and related precursors can be interconverted to the corresponding protonated nortricyclanes. However it seems most likely that this rearrangement proceeds first through the trivalent classical 2-norbornylium ions.



(V.14)

Interconversions of the 2-norbornylium ions may occur through a 6-2-1-6 hydride shifts and involve various nortricyclonium ions. However they may also be interconverted directly by a Wagner-Meerwein shift through C-C-bond delocalization i.e. the 6-norbornonium ion.

It has been accepted that the 2-norbornyl cation rearrangement and those of its derivatives follow the intramolecular Wagner-Meerwein route. A close[59] examination of the intramolecular shift is useful. The 2-norbornyl cation (XXI) can undergo first a concerted intramolecular (CIM) twist vibration of C-5, C-6 and C-3, C-2 about the C-1, C-7, C-4 bridgehead keeping the C-5, C-6 and C-3 C-2 bonds as parallel as the restrictive geometry of the 2-norbornyl cation allows to give the instantaneous configuration (XXII).



Then, the 1,6 C-C bond is broken to yield the 2-6 C-C bond as the positive charge shifts from C-2 to C-1 (XXIII). The numbers 1', 2', 3', 4', 5', 6' and 7' are corresponded to 2, 1, 7, 4, 5, 6 and 3 respectively. The total angular momentum of the molecule is practically conserved in the CIM transition, leaving the intramolecular forces mostly undisturbed.

E. The Naming of Carbocations

The use of the word carbenium for some carbocations is in accordance with IUPAC rules. Its use should be used only for trivalent ions and not as a generic name for all carbocations.

Jennen, discussing in 1966 the naming of ions, pointed out that the carbenium ion (methyl cation) can be looked at as a protonated carbene (i.e. singlet carbene). Thus there is a logical relationship between carbene and carbenium ion. The word carbonium should relate to the highest valency state carbocations, i.e. those that are penta coordinated cations of the CH_5^+ type, and strictly the word carbanium should be reserved for the tetracoordinated cations.

Olah[52] originally differentiated trivalent carbenium ions from both penta and tetracoordinated "carbonium" ions. The systematic names for several types of carbocations are shown below.

Carbocations

Carbenium ions	Carbanium ions	Carbonium ions
trivalent	tetracoordinated	pentacorddinated
alkenium ions	alkanium ions	alkonium ions
cycloalkenium ions	cycloalkanium ions	cyclonium ions
arenium ions	aranium ions	aronium ions

The carbocationic centres are identified by numbers.

For the carbenium ions, the number of the carbon carrying the charge is inserted before the ending "ium". In the case of carbonium ions, the three-centre bond can be formed either by C-H or C-C bond coordination with an electrophile, so the prefix H or C is used to denote the participating bond.

Carbon bridged alicyclic carbonium ions (the most studied "non-classical" ions) represent a more severe naming problem; the number of the bridging carbon i.e. with highest coordination number, viz penta, should precede the skeleton name and to which is added the "onium" suffix. The carbons to which the bridging takes place (generally tetracoordinated) are indicated by the usual numbering system employed for identifying specific bonds, e.g. in unsaturated systems. The rules of IUPAC nomenclature of organic compound are expounded in "Pure and Applied Chemistry" and those particularly for the carbocations are in volume 11 page 63, (1965).

VI Nuclear Magnetic Resonancy Spectroscopy

A. Proton ('H)n.m.r. Spectroscopy

(i) Introduction

The proton n.m.r. spectroscopy is one of the most important developments regarding structural elucidation of organic molecules in modern times.

Nuclear[60] resonance effects were first detected in bulk matter in 1945, using simple materials such as solid paraffin and water.

NMR spectra depends upon making use of the nucleus as a magnetic probe to investigate local magnetic effects inside a molecular system. The local magnetic field near a particular nucleus depends on its chemical environment and is determined by a number of factors including: the polarization of remote parts of the molecule, magnetic moments of neighbouring molecules, and intramolecular effects due to other nuclei and electrons in the same molecule.

Considering nuclei, with a spin number I and magnetic moment μ, not equal to zero, placed in a static uniform magnetic field H_0, the nucleus behaves as a very tiny bar magnet. According to Quantum mechanical arguments it can be shown that the proton, $I = \frac{1}{2}$, is restricted to just two possible orientations $[(2I + 1) = 2]$, in the applied field; (a) a low energy or parallel orientation in which the magnet is aligned with the field, (b) a high energy or anti-parallel orientation in which it is aligned against the field. These two orientations correspond to two energy states. To induce transitions between them it is necessary to irradiate with the appropriate frequency of the electromagnetic radiation. The absorption or emission of the quantum of energy causes turning over or "flipping" of the nuclear magnet from one orientation to the other. Accordingly the nucleus in the static field is subjected to electromagnetic radiation in a plane perpendicular to the direction of the static field H_0. The absorption of energy may be accomplished either by varying the frequency of the electromagnetic radiation or by varying the strength of the applied magnetic field. A radiofrequency receiver "detector" indicates when energy from the source is being absorbed by the sample. The process of varying the magnetic field or frequency over a small range corresponds to scanning the spectrum and determines the position of absorption lines in terms of frequency or field strength.

The chemical shift is the most important parameter to be dervied from an NMR spectrum. Since the NMR signals of nuclei of different elements in a fixed magnetic field normally occur in very different regions of the spectrum, so also hydrogen atoms of the same molecule which are not chemically equivalent will experience different diamagnetic electron screening in a magnetic field and give rise to separate resonance signals. The equivalent nuclei in a given molecule will give rise to identical chemical shifts. Such nuclei normally also occupy chemically equivalent positions in the molecule. The number of protons giving rise to each signal can be derived from the relative intensities of their resonance signals when their chemical shifts are sufficiently different.

(ii) Spin-Spin Coupling

When a number of liquids were first examined by nmr spectroscopy it was found that certain substances showed more lines than were required by simple considerations of the number of non-equivalent nuclei. Some molecules gave symmetrical multiplet signals (triplets, quartets etc.). These multiplets arise from an interaction between neighbouring nuclear spin. The first[61] interpretation of these interactions was given by Ramsey and Purcell who showed that they arise from an indirect coupling mechanism via the electrons in the molecule. Thus[60] a nuclear spin tends to orient the spins of electrons nearby, which in turn orient spins of other electrons and consequently spins of other nuclei. The magnitudes of the spin interaction energies are usually expressed in cycles per second or Hertz. So for molecules having two different sets of equivalent nuclei, the spectrum may become complex since in addition to the two distinguished signals each of these signals may be split into further components due to spin-spin interaction between non-equivalent nuclei. The HD molecule could be considered as the simplest case of two non-equivalent nuclei to explain the interaction of the bonding electrons. The interaction of one nucleus with the electron of its atom will make the electron spin lie more frequently antiparallel than parallel to the nuclei spin. The two electron spins in the covalent bond must be antiparallel to each other so that the electron spin of the other atom will tend to be more frequently parallel to the spin of the first nucleus. However, the electron of the second atom interacts magnetically with the nucleus of this atom and consequently the spin of the second nucleus tends to be antiparallel to that of the first. The combination of these coupling effects therefore provides a spin interaction between the two nuclei. The interaction energy has the form $J_{1,2}$; it is independent of temperature and of the applied field. and it has the dimensions of energy. Since the magnetic fields responsible for the interaction are regarded as arising within the molecule itself the interaction is independent of the applied field. The electron coupled spin-spin interaction between members of an equivalent group of nuclei does not give rise to multiplet splitting. In the general case for a set of n_A equivalent nuclei of type A interacting with n_X equivalent nuclei of type X, the A signal has $2n_XI_X + 1$ components and the X signal has $2n_AI_A + 1$ components. The relative intensities of each group of signals are in the ratio of the corresponding binomial coefficients.

(iii) Field-frequency Lock Systems

Most spectrometers are equipped with a "field frequency" stabilization (lock) system. It could be either the locked "field sweep" or the locked "frequency sweep" mode.

TMS is used for the internal lock and the reference signal; alternative reference compounds are cyclopentane or hexamethyldisiloxane. It is necessary to have only a small quantity of an internal standard in solution to eliminate bulk susceptibility corrections to the chemical shifts.

External references, either a small sealed capillary placed in the solution or a coaxial capillary system are also used. The chemical shifts of the hydrogens in reference compounds normally change with solvent.

When working with the coaxial capillary both the inner tube and the standard 5 mm nmr tube must be of high precision to minimize spinning side bands.

The larger range of sample-tube sizes now permissible enables an improvement in the signal-to-noise factor for all nuclei and this is especially important for natural abundance ^{13}C nmr. For an[62] additional improvement in the signal-to-noise ratio spectrometers now have the Fourier transform pulse capability as opposed to the continuous wave. These spectrometers are interfaced with small, digital computers which accumulate the time-domain signal from the pulse experiment, transform it to a standard "frequency domain" absorption spectrum and allow the spectrum to be recorded in the conventional manner.

(iv) Nuclear Magnetic Double Resonance

Nuclear magnetic double resonance refers to a spectroscopic experiment in which a system is simultaneously irradiated at two different frequencies. The multiplet structure arising from the coupling of certain nuclei can be made to disappear since the spin of these nuclei are decoupled from the remainder of the spin system.

Double resonance experiments can be subdivided into two categories (a) homonuclear, where the irradiated and the observed nuclei belong to the same nuclear species and (b) heteronuclear where two different nuclei are involved, one of them will be observed, while the other will decouple.

Nuclear magnetic double resonance experiments include "selective irradiation" and "spin tickling". In a "selective irradiation" technique the transitions involved in a particular spectral splitting are irradiated simultaneously. This results in the collapse of associated transitions in another region of the spectrum. This method is most useful in the analysis of weakly coupled systems. With strong or intermediate coupling, applications to the system are not possible to prevent more than one spin coupling from being disturbed by the strong irradiating field. The spin tickling technique may be performed for tightly coupled spectra but this will not be discussed further here.

The application of the above techniques to analyse and simplify nmr spectra and to determine the relative signs of coupling constants on systems having at least three mutually coupled spins, such as an ABC system, may be found in the article by Abraham, Ray J., "The Analysis of high resolution NMR Spectra", Amsterdam Elsevier, 1971.

B. Carbon ^{13}nmr

The first report of successful determination of nuclear magnetic resonance of ^{13}C nuclei in natural abundance appeared in 1957 but the utilisation of the technique as a regular feature of structure determination was delayed until the early seventies owing to problems associated with obtaining good quality reproducible ^{13}C spectra.

Since the natural abaundance of the ^{13}C isotope is only 1.1% compared to 99.98% for the proton low sensitivity has been one of the difficulties associated with obtaining ^{13}C spectra. Accordingly larger samples relatively are required for obtaining the maximum signal to compensate for the low sensitivity and long relaxation times. Relaxation is the process whereby nuclei in higher energy states return to the low energy state. This can occur in two ways (a) by transferring or emitting energy to some electromagnetic vector having the proper orientation and correct dimension to absorb the energy. These are to be found in the surrounding environment e.g. neighbouring nuclei or solvent molecules. This so called spin-lattice relaxation has a time constant that determines the rate of net abosrption of energy.

The mean half-life of the spin-lattice relaxation is designated T_1 and it is large in nonviscous liquids and for solutions of solids, since their molecular orientations are random and the transfer of energy by spin-lattice relaxation is inefficient. (b) The alternative process of transferring energy to a nucleus is termed spin-spin relaxation and here one nucleus loses energy whilst the other gains it. Net change in the populations of the two spin states is involved. The mean half-life of the spin-spin relaxation process is designated T_2.

If T_1 and T_2 are small, then the lifetime of an excited nucleus is short, and this gives rise to very broad absorption bands in the nmr spectrum. However if T_1 and T_2 are large, sharp spectral lines arise.

In the ^{13}C spectrum the signal:noise (S/N) ratio is less than that obtained with ^{1}H; but sharp signals are expected if spin-coupling with other nuclei are removed. This can be achieved by irradiating the sample with a second radio frequency with a band width covering the frequency ranges of the protons.

In the absence of ^{13}C-H spin-spin coupling each magnetically unique carbon atom in an organic molecule will give rise to a single line in the ^{13}C spectrum of that molecule; these spectra are known as "broad band decoupled" or "decoupled" ^{13}C spectra. ^{13}C spectra obtained when ^{13}C-H coupling are observed are known as "undecoupled" spectra.

^{13}C-^{13}C spin-spin couplings are not observed in the low natural abundance spectra so splittings of the lines do not appear in the spectra.

The undecoupled are more complex than the decoupled spectra owing to second order effects arising from ^{13}C-^{1}H splitting.

A third type of ^{13}C spectra are obtained by using a decoupling frequency a few hundred Hertz outside the range of the Larmor frequencies of the protons. This causes geminal and longer range couplings to collapse and this type of ^{13}C spectrum is called an "off resonance decoupled" spectrum.

The chemical shifts of ^{13}C lines were originally relative to carbon disulphide or benzene as standards but are now quoted to be relative to TMS as for protons. The deshielding of nuclei are indicated as increasing positive numbers on the scale. The chemical shifts range of ^{13}C nuclei are from 0 to 200 for most organic molecules. The $^{13}C-^{1}H$ coupling constants are much larger than $^{1}H-^{1}H$ coupling constants e.g. a range of 100 - 250 Hz is observed. Geminal ($^{13}C-C-H$) and Vicinal ($^{13}C-C-C-H$) couplings are also observable but the latter are dependent upon the dihedral angles between the coupled nuclei.

Further information on the use of ^{13}C nmr is available in the review by Wilson[53] and Stothers (stereochemical approach[64])and the monograph by Stothers (theory and background).

Chapter 2

Results and Discussion

Results and Discussion

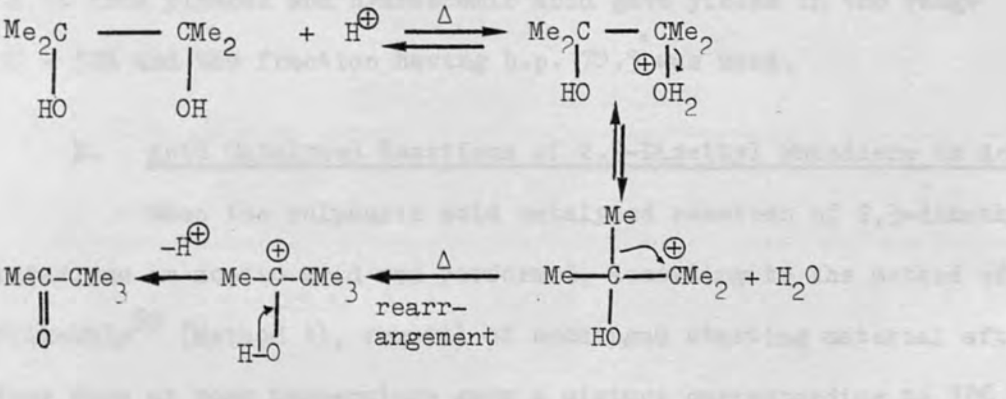
I. The Reaction of 2,3-Dimethyl Butadiene with Sulphuric Acid in Acetic Acid Solution

A. The preparation of 2,3-Dimethyl Butadiene by Acid Dehydration of Pinacol

Commercially 2,3-dimethylbutadiene can be prepared from pinacol by acid (hydrobromic[65] or sulphuric acid), dehydration. Fitting[66] however, discovered conversion by sulphuric acid of pinacol to the ketone, pinacolone

$$Me_2C(OH) — CMe_2(OH) \longrightarrow MeCO.CMe_3$$

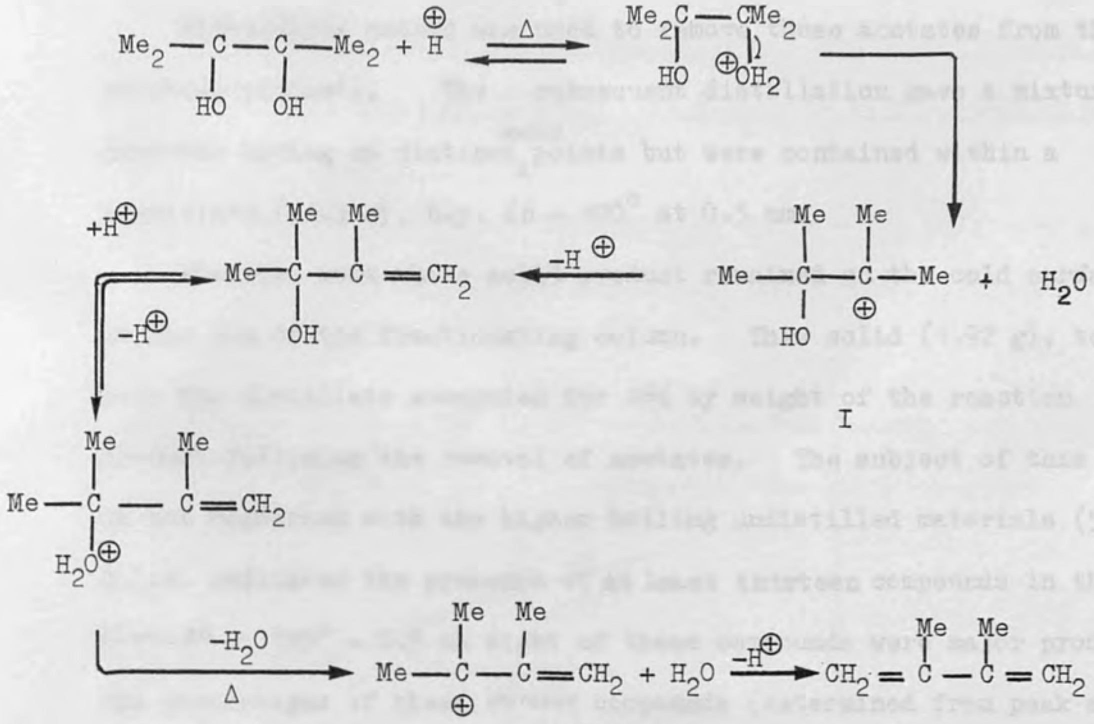
The feature of this change is the shifting of a methyl group from one of the "glycol carbon" atoms to the other. 2,3-Dimethylbutadiene is a by-product of this acid dehydration of pinacol.[65] The formation of pinacolone is suggested to proceed through the following mechanism:[67]



I

(I.1)

The formation of 2,3-Dimethylbutadiene cannot involve the rearrangement mechanism, but probably occurs through the common cationic intermediate I that can lose a proton to give the dimethylbutenol.(68 a,b)



(I.2)

For investigating the reactions of 2,3-dimethylbutadiene preparation of it from pinacol and hydrobromic acid gave yields in the range 47 - 52% and the fraction having b.p. 70.5° was used.

B. <u>Acid Catalysed Reactions of 2,3-Dimethyl Butadiene in Acetic Acid</u>

When the sulphuric acid catalysed reaction of 2,3-dimethylbutadiene in acetic acid was performed, according to the method of Pitkethly[69] (Method 1), removal of unchanged starting material after four days at room temperature gave a mixture corresponding to 78% reaction. It was supposed that this would contain compounds corresponding to hydrocarbon oligomers $(C_6H_{10})_n$ of 2,3-dimethylbutadiene and acetate esters.

Pitkethly's method was used to remove these acetates from the reaction products. The subsequent distillation gave a mixture of products having no distinct boiling points but were contained within a distillate (31.3 g), b.p. 46 - 120° at 0.5 mm.

However, some white solid product remained on the cold surfaces at the top of the fractionating column. This solid (1.92 g), together with the distillate accounted for 46% by weight of the reaction product following the removal of acetates. The subject of this thesis is not concerned with the higher boiling undistilled materials (54%). G.l.c. indicated the presence of **at least thirteen** compounds in the distillate 46 - 120° - 0.5 mm eight of these compounds were major products. The percentages of these thirteen compounds (determined from peak areas), for various stages in the collection of the distillate are given in table 1. It was subsequently shown that the major component of the solid material retained in the fractionation column corresponded to compound E.

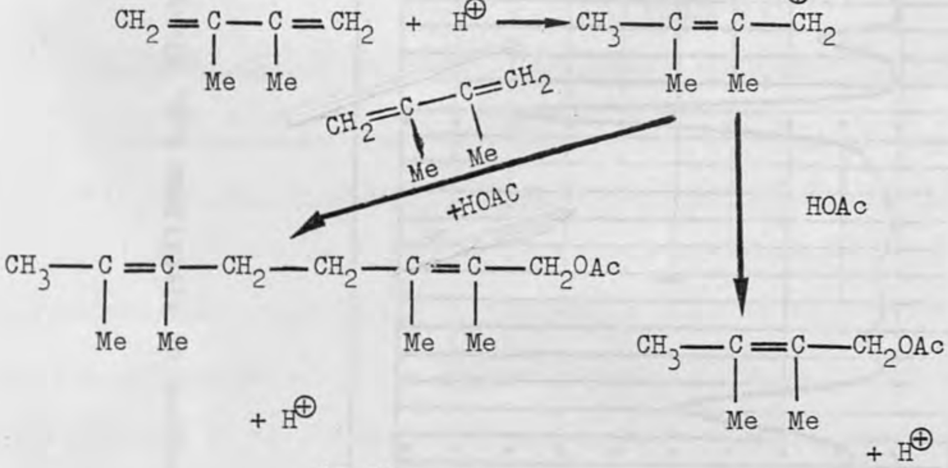
Table 1

Distillate Compositions

Compound	Initial (46–52° 0.5 mm)	Intermediate (52 - 70° 0.5 mm)	Final (110 - 120° 0.5 mm)	Crude solid (52 - 57° 0.5 mm)
				%
A	22.3	17.2	0.8	12.0
B	2.9	4.2	1.3	2.6
C			0.3	
D	13.0	11.4	2.5	15.1
E	43.2	45.9	15.3	60.0
F	6.5	5.7	17.5	6.7
G			16.0	
H	11.9	15.3	42.4	3.6
I			3.2	
others			0.7	

C. Alternative method of Examination of Reaction Products from the Reaction of 2,3-Dimethyl Butadiene with Sulphuric Acid in Acetic Acid

In method 1 it was assumed that there could be formed acetate esters resulting from solvent capture by carbocations produced in the reaction mixture



(I.3)

Accordingly saponification was carried out with alcoholic potassium hydroxide of the total reaction mixture. The alcohols thus produced from any acetates were reacted with boric acid to give the corresponding borates. These would have been insufficiently volatile to be distilled along with the hydrocarbon fraction b.p. 120° at 0.5 mm.

In method 2 the saponification reaction was omitted following the removal of unreacted 2,3-dimethyl butadiene in a typical experiment using 100 g of 2,3-dimethylbutadiene separation of the acetic acid from the reactants and products left a residue of 88 g. Of this about 10 g was unreacted starting material. The distillation procedure gave 34.0 g of liquid distillate and 2.3 g of solid product. The g.l.c. examination showed the presence of **thirteen** compounds as found previously. Their percentages in the distillate b.p. 46 – 120° at 0.5 mm are given in table 2.

Figure 3 . G.L.C. Chromatogram of distillate b.p. 57--94°C / 0.5 mm.

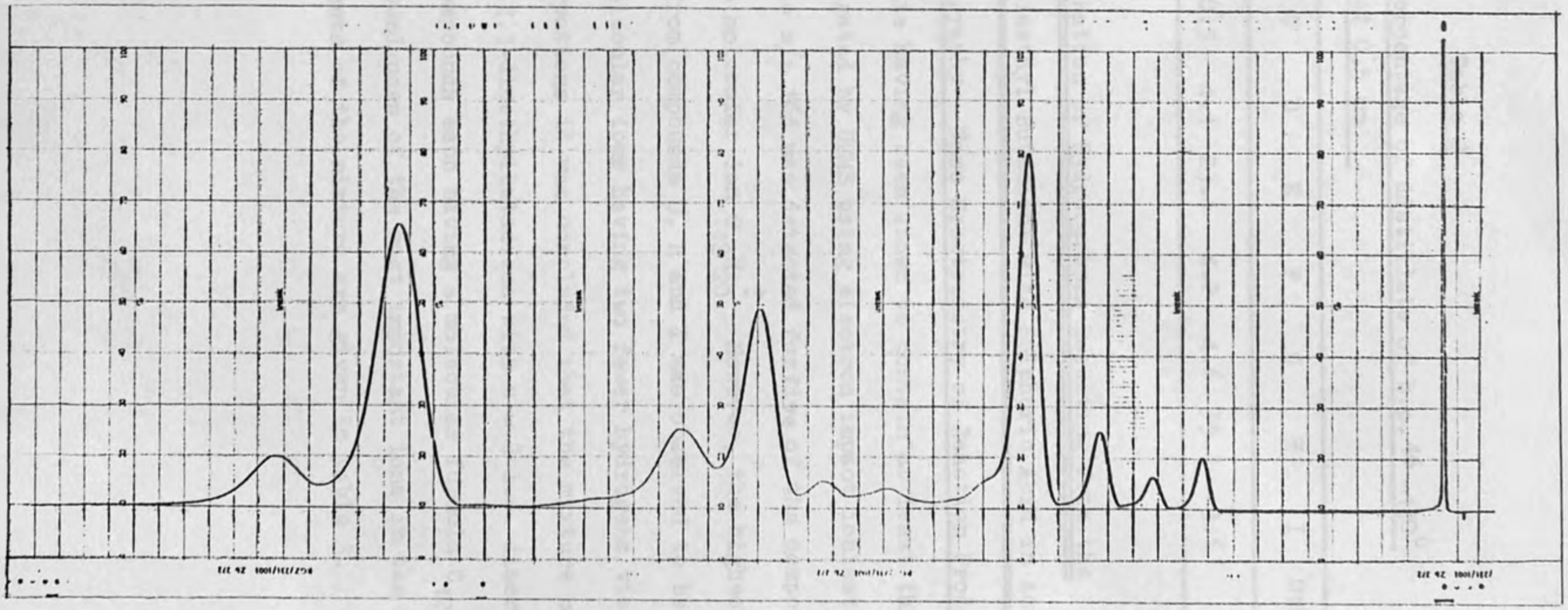


Table 2

Composition by percentage of distillate of b.p. 46 –120°
at 0.5 mm

Compound	A	B	C	D	E	F	G	H	I	Other compounds
%	2.9	0.8	0.5	4.1	23.4	4.2	4.6	55.1	3.6	0.8

II. Structure Determination of Hydrocarbons Resulting from the Reaction of 2,3-Dimethyl Butadiene with Sulphuric Acid in Acetic Acid

A. Gas chromatography - Mass Spectrometry of Reaction Products

The distillate having been shown to contain at least **thirteen** components was investigated by GCMS using electron impact ionisation. An ion corresponding to m/z 164 was detected for **five** of the compounds and presumed to be the molecular ion $C_{12}H_{20}^{\overset{+}{\bullet}}$ However, the highest value of m/z of ions from compounds G, H and I was observed to be 162. This corresponds to molecular ions having two fewer hydrogens viz. $C_{12}H_{18}^{\overset{+}{\bullet}}$.

For these observations it was concluded that the mixture contained oligomers $(C_6H_{10})_n$ of 2,3-dimethylbutadiene with n = 2 i.e. dimers together with three compounds each having a molecular formula $C_{12}H_{18}$.

The relative abundances of the most important ions in the mass spectra of the components of the mixture are given in table 3.

Table 3

Ions and relative abundances of fragments produced by electron impact mass spectrometry of reaction products

A			B			D			E		
m/e	R.A.%	Fragments	m/e	R.A.%	Fragments	m/e	R.A.%	Fragments	m/e	R.A.%	Fragments
164	51.3	$C_{12}H_{20}^{+}$	164	46.6	$C_{12}H_{20}^{+}$	164	41.5	$C_{12}H_{20}^{+}$	164	51.6	$C_{12}H_{20}^{+}$
149	59.7	$C_{11}H_{17}^{+}$	149	50.0	$C_{11}H_{17}^{+}$	149	53.8	$C_{11}H_{17}^{+}$	149	25.8	$C_{11}H_{17}^{+}$
121	90.2	$C_9H_{13}^{+}$	147	56.6	$C_{11}H_{17}^{+}$	135	36.9	$C_{10}H_{15}^{+}$	135	10.0	$C_{10}H_{15}^{+}$
107	100	$C_8H_{11}^{+}$	134	73.3	$C_{10}H_{14}^{+}$	121	87.7	$C_9H_{13}^{+}$	121	83.8	$C_9H_{13}^{+}$
91	19.4	$C_7H_7^{+}$	119	100	$C_9H_{11}^{+}$	107	100	$C_8H_{11}^{+}$	107	100	$C_8H_{11}^{+}$
79	13.5	$C_6H_7^{\mp}$	107	76.6	$C_8H_{11}^{+}$	93	55.4	$C_7H_9^{+}$	93	71.0	$C_7H_9^{+}$
67	10.8	$C_5H_7^{+}$	93	30.0	$C_7H_9^{+}$	79	23.0	$C_6H_7^{+}$	79	38.7	$C_6H_7^{+}$
			79	23.3	$C_6H_7^{+}$	67	23.0	$C_5H_7^{+}$	67	16.1	$C_5H_7^{+}$
			66	23.3	$C_5H_6^{+}$						

Table 3 (continued)

F			G			H			I		
m/e	R.A.%	Fragments	m/e	R.A.%	Fragments	m/e	R.A.%	Fragments	m/e	R.A.%	Fragments
164	51.5	$C_{12}H_{20}^+$	162	49.2	$C_{12}H_{18}$	162	25.0	$C_{12}H_{18}^+$	162	28.5	$C_{12}H_{18}^+$
149	87.8	$C_{11}H_{17}^+$	147	100	$C_{11}H_{15}^+$	147	13.4	$C_{11}H_{15}^+$	147	28.9	$C_{11}H_{15}^+$
						145	100	$C_{11}H_{13}^+$			
135	9.0	$C_{10}H_{15}^+$	133	9.5	$C_{10}H_{13}^+$	131	3.8	$C_{10}H_{11}^+$	145	42.8	$C_{10}H_{15}^+$
121	69.6	$C_9H_{13}^+$	119	47.7	$C_9H_{11}^+$	119	17.3	$C_9H_{11}^+$	119	17.8	$C_8H_{11}^+$
107	100	$C_8H_{11}^+$	105	67.1	$C_8H_9^+$	107	15.3	$C_8H_{11}^+$	117	14.3	$C_0H_9^+$
91	30.3	$C_7H_7^+$	91	16.4	$C_7H_7^+$	106	38.3	$C_8H_{10}^+$	106	14.5	C_8H_{10}
79	15.1	$C_6H_7^+$	89	23.8	$C_7H_5^+$	105	5.7	$C_8H_9^+$	105	100	$C_8H_9^+$
67	15.1	$C_5H_7^+$	79	40.3	$C_6H_7^+$	91	7.6	$C_7H_7^+$	104	21.4	$C_8H_8^+$
						89	14.8	$C_7H_5^+$	103	14.8	$C_8H_7^+$
						77	7.8	$C_6H_5^+$	91	15.0	$C_7H_7^+$
									89	29.0	$C_7H_5^+$
									77	10.7	$C_6H_5^+$

Table 4

The principal ions produced by fragmentation of compound A.

	A	
	m/z	R.A.(%)
M^+	164	51.3
(M-15)	149	59.7
(M-43)	121	90.2
(M-57)	107	100

Table 5

Comparison of principal ions produced by fragmentation of compound B with nortricyclene

	Nortricyclene*		B	
	m/z	R.A.(%)	m/z	R.A.(%)
M^+	94	37.5	164	50
$[M-15]^+$	79	100	149	50
$[M-17]^+$	77	29.1	147	56.6
$[M-28]^+$	66	77.7	-	

Nortricyclene base peak is $[M-15]^+$

Compound B base peak is $[M-45]^+$

* Reference No.70

Table 6

Comparison of principal ions produced by fragmentation of compounds D and E with camphene

	Camphene*		D		E	
	m/z	R.A.(%)	m/z	R.A.(%)	m/z	R.A.(%)
M^+	136	3.	164	41.5	164	51.6
$[M-15]^+$	121	10	149	53.8	149	25.8
$[M-43]^+$	93	100	121	87.7	121	83.8
$[M-57]^+$	79	10	107	100	107	100

Camphene base peak is $[M-43]^+$

Compound D base peak is $[M-57]^+$

Compound E base peak is $[M-57]^+$

* Reference No.71

Table 7

Comparison of principal ions produced by fragmentation of compound F with δ-limonene

	δ-limonene*		F	
	m/z	R.A.(%)	m/z	R.A.(%)
M^+	136	11	164	51.5
$[M-15]^+$	121	15	149	87.8
$[M-29]^+$	107	15	135	12.1
$[M-68]^+$	68	100	-	
$[M-82]^+$	-			

Limonene base peak is $[M-68]^+$

Compound F base peak is $[M-57]^+$

* Reference No.71

Table 8

Comparison of principal ions produced by fragmentation of compounds G, H and I with t-butylbenzene and p-xylene

	t-butylbenzene*		p-xylene		G		H		I	
	m/z	R.A.(%)	m/z	R.A.(%)	m/z	R.A.%	m/z	R.A.%	m/z	R.A.%
M^+	134	24.5	106	24.5	162	49.2	162	25.0	162	28.5
$[M-15]^+$	119	100			147	100	147	13.4	147	28.9
$[M-29]^+$	105		77		133	9.5				
$[M-43]^+$	91	53.2			119	47.7	119	17.3	119	17.8
$[M-55]^+$	79				107		107	15.3		
$[M-57]^+$	77				105	67.1		5.7	105	100
$[M-71]^+$	-				91	16.4	91	7.6	91	15.0

Metastable ion observed for compound H $m^* = 96.3$

$$96.3\ (147^+) \longrightarrow (119^+) + 28$$

* References No . 72,73.

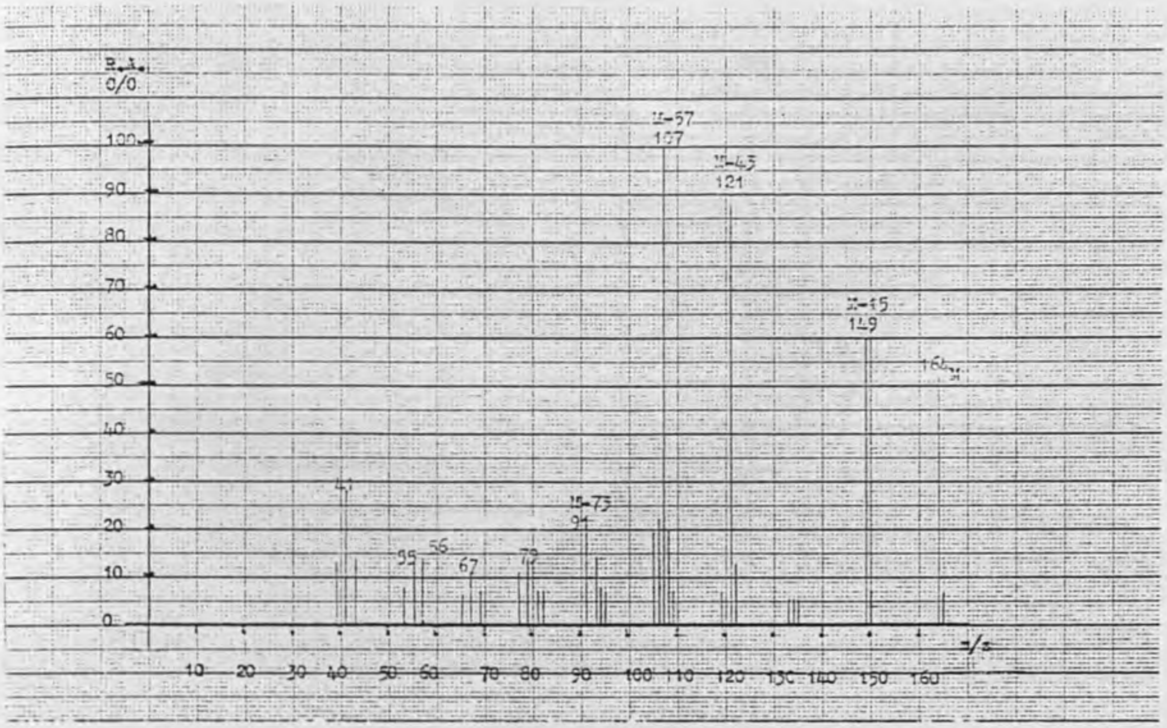


Figure 4. The mass spectrum of compound A.

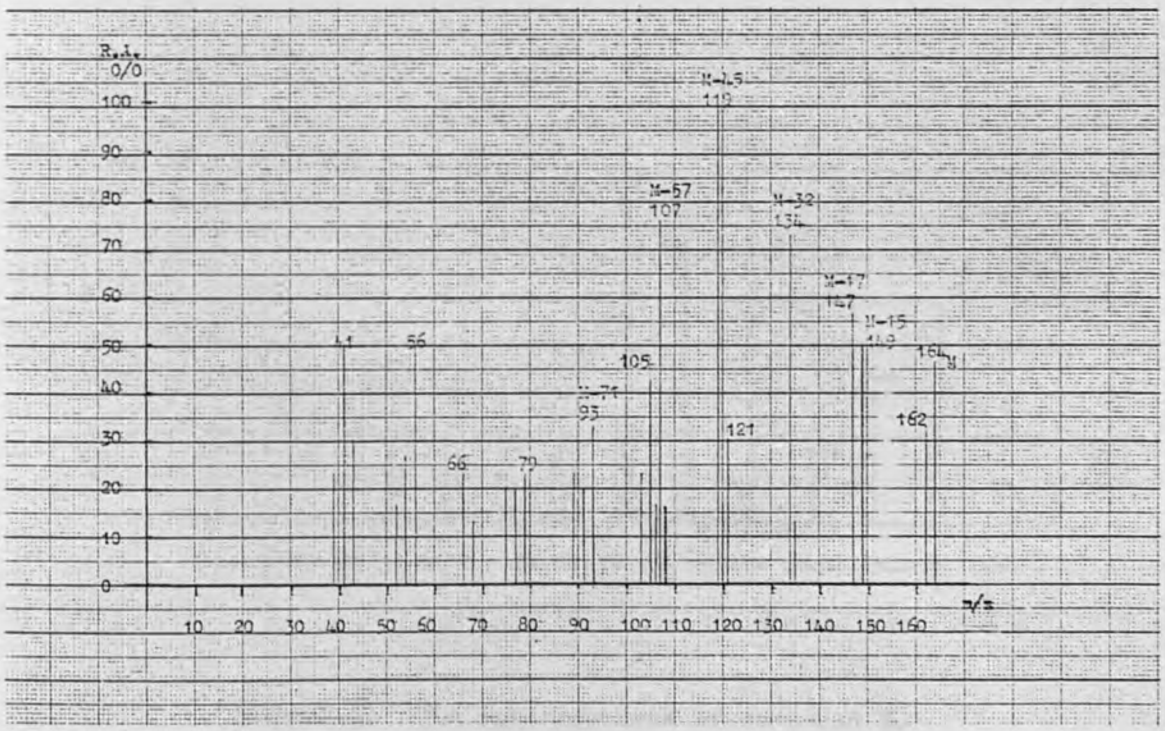


Figure 5. The mass spectrum of compound B.

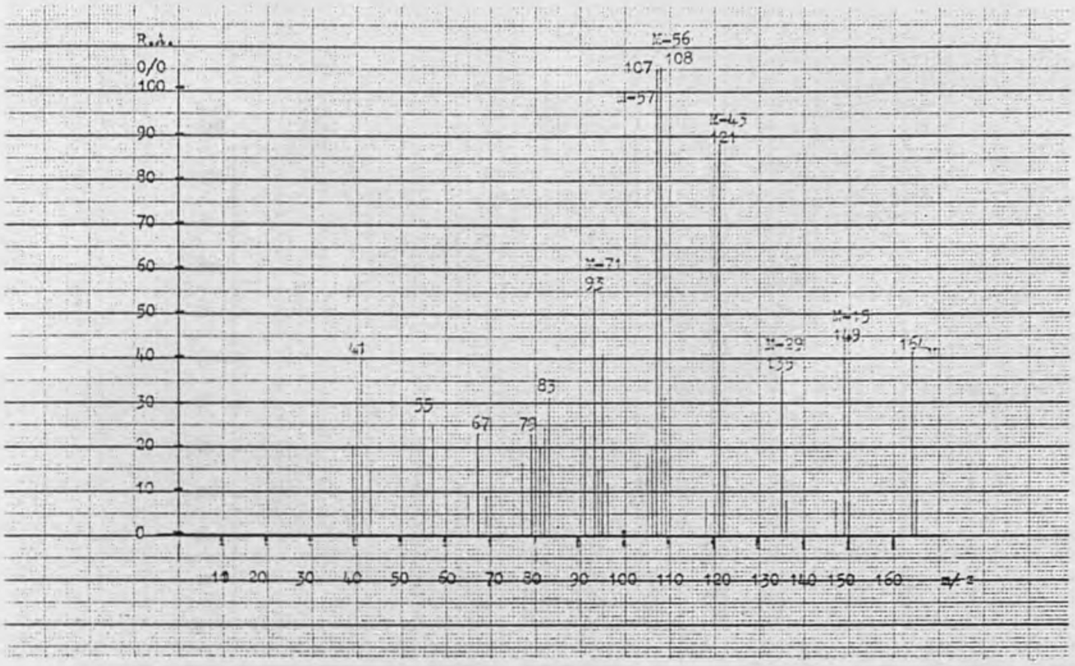


Figure 6. The mass spectrum of compound D.

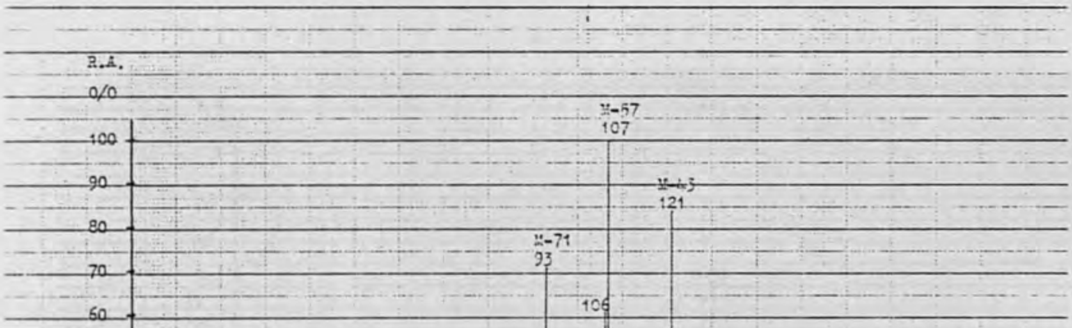


Figure 7. The mass spectrum of compound E.

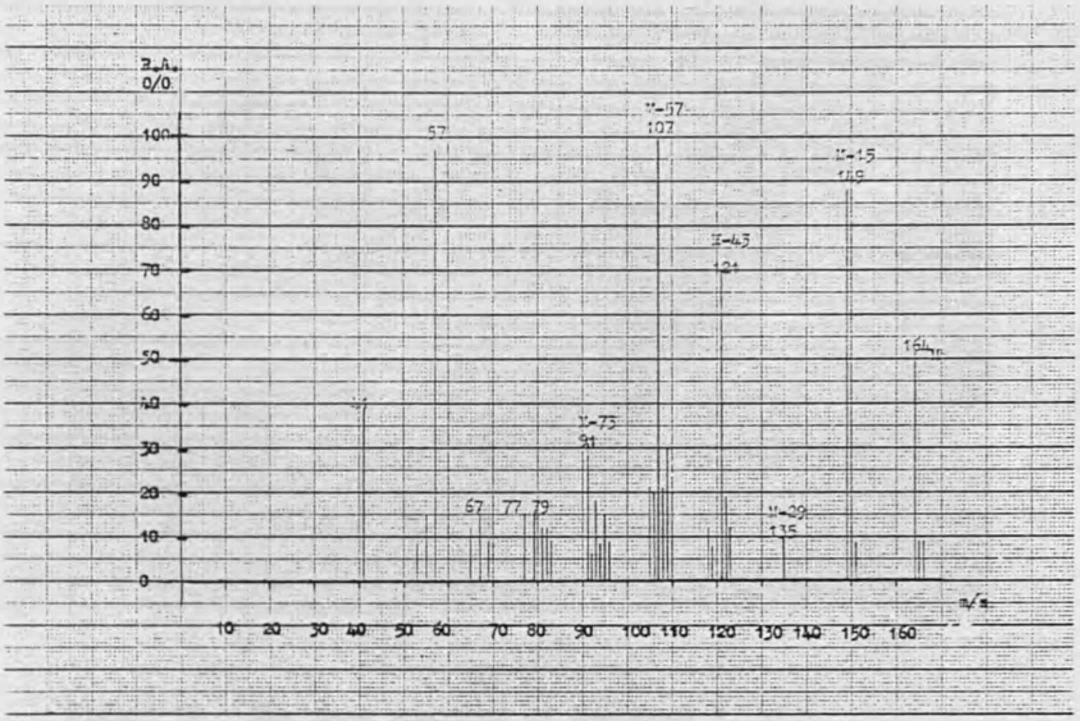


Figure 8. The mass spectrum of compound F.

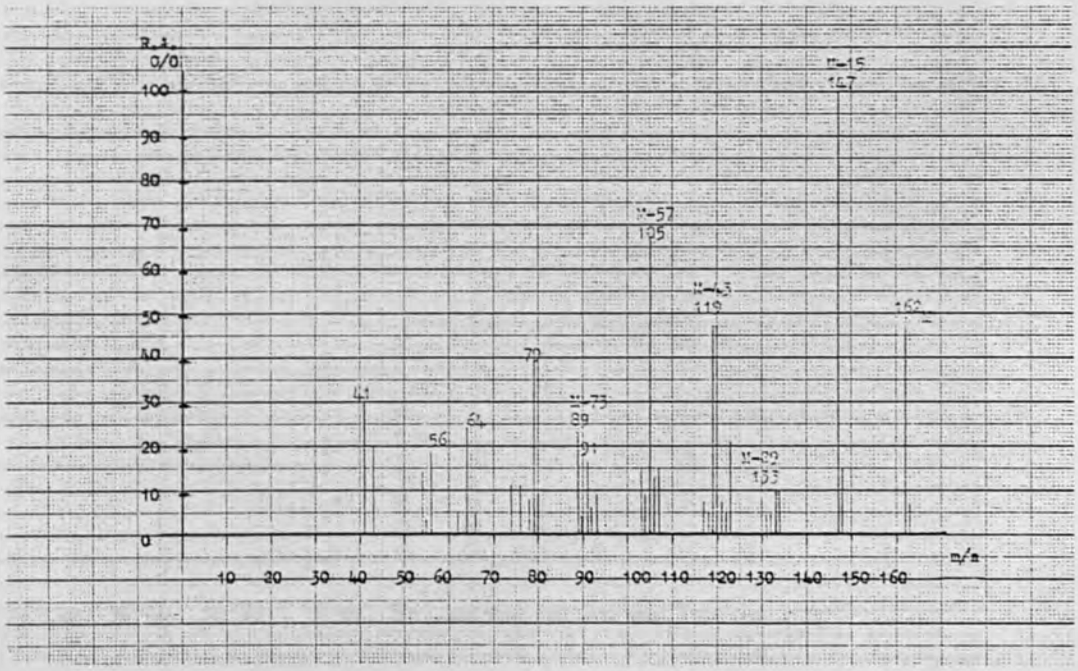


Figure 9. The mass spectrum of compound G.

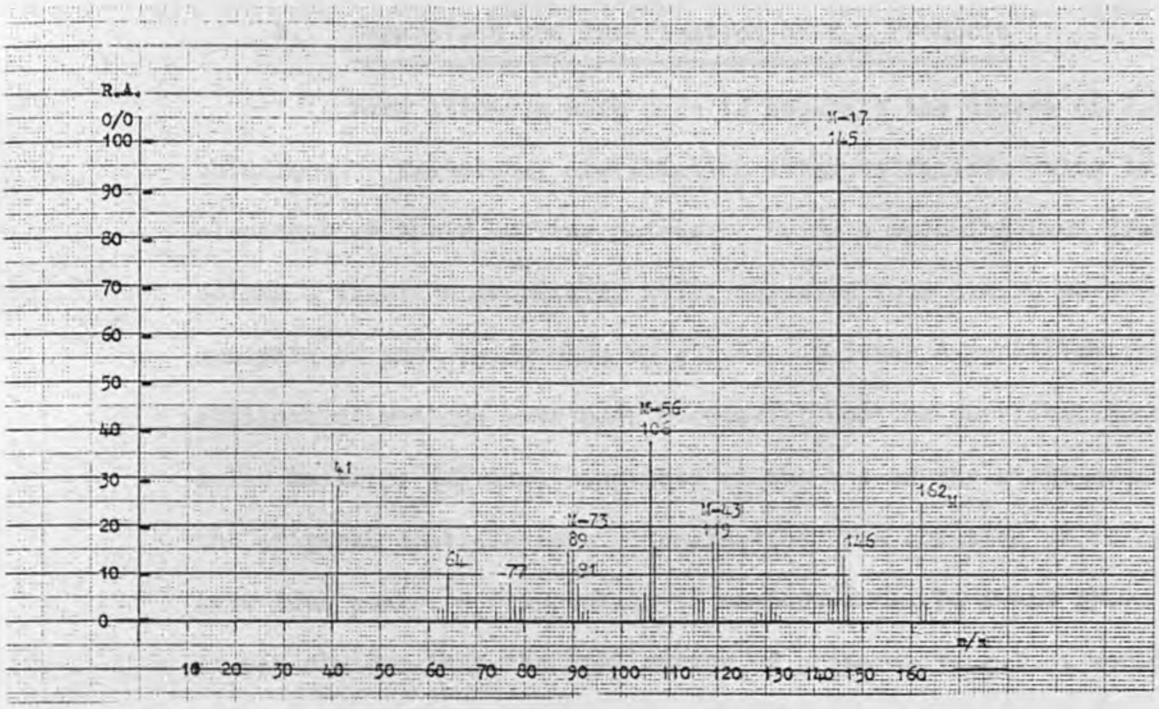


Figure 10. The mass spectrum of compound H.

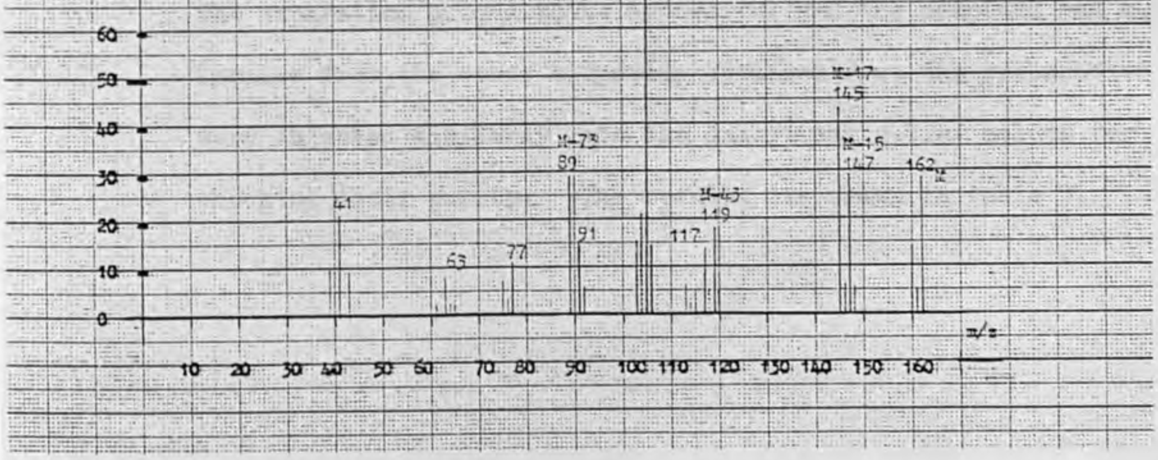


Figure 11. The mass spectrum of compound I.

B. Separation and Purification of C_{12} Products

Many attempts were made to separate the dimers of 2,3-dimethyl butadiene. Fractional distillation attempts failed, owing to the closeness of their boiling points. Using a spinning band distillation column a fraction containing still three or four dimers were collected analysis of them being made by g.l.c. Neither crystallisation nor sublimation methods have been successful for the purification of the solid material (E) that condensed at the top of the still-head during the original distillation. Examination of a solution of it by g.l.c. gave four peaks, corresponding to compounds (A, B, D and E). It was obvious that the application of preparative g.l.c. would be the best way of separation of these isomers in spite of being a very slow method.

Samples of 250 μl were injected repeatedly over several days to collect a few drops of each compound in the preparative cooled (-14°) g.l.c. traps.

A solid dimer (compound E) was the first dimer to be observed in sufficient quantity on the walls of the fifth trap. A sample of this solid dimer was dissolved in diethyl ether and injected into the analytical g.l.c. column to check its purity. The separation proved to be successful and the compound had m.p. 87°. Samples from the other compounds obtained from the preparative g.l.c. were injected similarly into the analytical g.l.c. column for checking their purity. The results are shown in table 9.

Table 9

Purities of the Products separated by the preparative G.L.C.

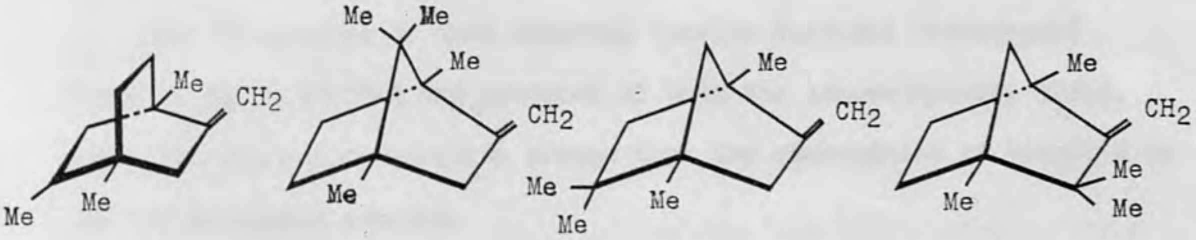
Compound number	Impurity (%)
A	D (0.04), E (0.7)
B	A (0.3), C(0.06), D (0.1), E (0.64) = 1.1%
D	B (0.02), C(0.05), E (0.3)
E	C (0.04), D (0.1)
F	E (0.3)
G	F (0.5)
H	D (0.02), E (0.1), F (0.1), G (1.7), I (1.8) = 3.7
I	other dimers (0.7)

C. N.M.R. Spectroscopy as an Aid to Structure Elucidation

After having obtained eight relatively pure samples arising from the dimerisation of 2,3-dimethylbutadiene methods for determining their structure were pursued, in particular ^{1}H and ^{13}C n.m.r. spectroscopy. Since the solid dimer (compound E) was the first and the easiest compound to be collected in the preparative g.l.c. traps, it was the first compound to be investigated from the structural point of view.

^{1}H n.m.r. spectra were obtained of a solution of E in carbon tetrachloride, using TMS as an external reference and ^{13}C n.m.r. spectra of a solution in chloroform-d. The ^{1}H n.m.r. chemical shifts data for compound **E** is given in table 10.

Pitkethly[69] and Martin[74] have suggested the following structures for the solid product obtained from the dimerisation of 2,3-dimethylbutadiene.



II III IV V

(Fig. 12)

These structures were advanced on the basis of it being (i) mono-olefinic, as determined by hydrogenation at atmospheric pressure and by reaction with perbenzoic acid; and (ii) bicyclic by its reaction with oxidising agents similar to those of camphene and α-fenchene. However they were unable to distinguish between the four different structures.

(i) Determination of the structure of compound E by ^1H and ^{13}C n.m.r. spectroscopy

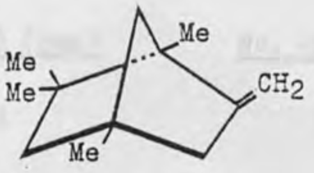
Examination of the ^1H n.m.r. showed the presence of twenty hydrogens. The exo-methylenic group was confirmed and seemed to be coupled with another CH_2 group (possible in structures II, III and IV).

The presence of four methyl groups uncoupled with any nearby hydrogens pointed to them being attached in such a way as to give quaternary carbons. This information alone confirmed that the solid dimer had a bicyclo heptane rather than a bicyclo octane structure i.e. structures(III,IV and V) and discounted compounds with tertiary carbons, one example of which is as VII. The existence of coupling between two alicyclic methylenes (see Fig. 12) $\delta = 1.25$ and $\delta = 1.54$ favours structures III and V.

The interpretation of the ^1H n.m.r. spectra suggested structure III for the solid dimer from the previously advanced possible structure.

The ^{13}C spectra of this compound (twelve distinct resonances) Table 11 has confirmed the presence of both the exo-methylenic group, and three alicyclic methylene groups from the observation of triplets in the off resonance spectra.

The low field resonance carbon atom with no coupling to hydrogen supports the presence of the exo-methylenic group, while the three quaternary carbons having resonances at $\delta = 46.1$, $\delta = 48.2$ and $\delta = 53.2$ assure the presence of the attachment of a methyl group at least to each bridgehead carbon; there being no tertiary carbons (i.e. no doublets observed in the off resonance spectra). The ^{13}C spectra indicate that there has to be,in addition to three quaternary carbon atoms having resonances at high field, three secondary carbon atoms (triplets in the off resonance spectra). Accordingly two methyl groups must be attached to the same ring carbon viz. C_3, C_5, C_7 or C_6 as in compounds V, IV, III and VI respectively.



VI

VII

The resonance due to the four methyl groups were distinct showing an absence of symmetry in the structure of the compound. By comparison with the ^{13}C n.m.r. spectra of several related compounds obtained by other[75, 76, 77] workers (see table 15) *the two high field methyls can be assigned to be attached to the 7- position of the bicycloheptane skeleton.* Structures IV and VI would be expected to have chemical shifts associated with two methyl groups c.a. δ = 27.0 - 32.0 ppm, i.e. attached to a non-bridging carbon but not adjacent to the exocyclic double bond. Similarly structure V would be expected to have resonance for two methyl groups c.a. δ = 23.0 - 30.0 ppm that are attached to a carbon adjacent to the exocyclic double bond. The presence of the two high field methyls can only be assigned if attached to the 7-position of the bicycloheptane skeleton. Of the remaining two methyl groups, their different chemical shifts (δ = 16.4 and δ = 17.2) result from their proximity or not to the unsaturation associated with the exocyclic methylene group. The one at the bridgehead closest to the unsaturation (position 1) will have δ = 17.2 (see table 15 compound (3)) and confirms that structure III, viz. 2-methylene-1,4,7,7-tetramethyl bicyclo [2,2,1] heptane best fits the data for compound E.

2-Methylene-1 4,7,7-tetramethyl bicyclo [2,2,1] heptane, (structure III) has been the subject of a study by Haseltine[78] and Soronsen the incorporation of deuterium into three of the methyl groups

Table 10

^{1}H n.m.r. chemical shifts of compound E

Shift (δ) (ppm)	No. of Hydrogens	Multiplicity
0.62	3H	singlet
0.74	3H	singlet
0.9	3H	singlet
0.93	3H	singlet
1.25	2H	doublet
1.54	2H	doublet
2.02	2H	multiplet
4.59	1H	singlet
4.67	1H	singlet

Table 11

^{13}C Chemical shifts of compound E

Carbon	Shift (δ ppm)	J_{C-H}(Hz)	Multiplicity
C-1	46.1	–	Singlet
C-2	198.4	–	Singlet
C-3	43.8	2.8	Triplet
C-4	48.2	–	Singlet
C-5	34.7	3.0	Triplet
C-6	35.6	3.0	Triplet
C-7	53.2	–	Singlet
C-7 Me(2)	13.2	2.6	
	16.0	2.6	Quartets
C-1 Me	17.2	2.8	Quartet
C-4 Me	16.4	2.6	Quartet
C-2 (CH_2=)	100.8	2.8	Triplet

permitted the ^1H n.m.r. resonance at highest field $\delta = 0.62$ ppm to be assigned to the syn-methyl at C-7.

The anti-methyl can accordingly be assigned to the resonance at $\delta = 0.74$ ppm and by analogy with the ^{13}C data the methyls at $\delta = 17.2$ and $\delta = 16.4$ correspond to the methyl groups at C-1 and C-4 respectively.

(ii) Determination of the structure of compound D by ^1H and ^{13}C spectroscopy

Examination of the ^1H n.m.r. of compound D showed the presence of twenty hydrogens with the presence of an exo-methylenic group but this time it appears to be uncoupled with any nearby protons which suggested the presence of only quaternary carbons around this exo-methylenic group, i.e. somewhat similar to the exo-methylenic group in camphene.

On the other hand the presence of four singlet resonances due to methyl groups again pointed to there being no nearby hydrogens and so they must be attached to quaternary carbons. Their attachment to carbons surrounding the exo-methylene group seems to incorporate the structural features of both the above observations (compound V). The coupling that does exist is between the three CH_2 groups in the high field of the bicyclic compounds considered previously as possibilities for compound E. Coupling between the hydrogens in adjacent methylene groups would be expected in II, III and V. If long range coupling are included i.e. between the hydrogens of the single methylene (C-7) and the hydrogens of other methylenes e.g. C_3, C_5 and C_6 then structures IV and VI must also be included as possibilities for compound D. Structure II is however not possible owing to the observation of resonances of four methyl groups and VII again dismissed since these signals are singlets.

With the inclusion of the long range coupling the compound expected to have most spin-spin interaction is that represented by structure V. A very complicated pattern of resonance signals was observed in the 200 m Hz spectrum for chemical shifts between δ - 1.2 and δ = 1.8 ppm. the presence of the type of long range interaction between the hydrogens of C-7, C-5 and C-6, referred to above, has been discussed by Bhacca and Williams.[80] The ^1H n.m.r. chemical shifts of compound D are shown in table 12. The ^{13}C spectra of this compound (twelve distinct resonances) table 13 has confirmed the presence of the exo-methylene group and three alicyclic methylene groups from the triplets in the off-resonance spectra.

The low field resonance carbon atom with no coupling to hydrogen supported the presence of the exo-methylenic group, while the three quaternary carbons assured the presence of the attachment of a methyl group to each bridgehead carbon, viz. the highest field methyls at δ = 16.4 ppm and δ = 18.7 ppm. The other two methyl groups must be attached to the same ring carbon as in structures IV, V and VI.

Further differentiation between these structures is not possible directly from examination of the ^{13}C chemical shifts but when these are used in conjunction with those of compound E and the additional compounds included in table 15, structure V seems most likely. This accords with the ^1H n.m.r. data. Compound D is therefore thought to be 2-methylene-1,3,3,4-tetramethylbicyclo[2,2,1] heptane.

Table 12

^{1}H n.m.r. Chemical shifts of compound D

Shift (δ)(ppm)	No. of hydrogens	Multiplicity
0.93	3H	Singlet
0.98	6H	Singlet
1.15	3H	Singlet
1.2 - 1.8	6H	Overlapping multiplets
4.56	1H	Singlet
4.62	1H	Singlet

Table 13

^{13}C Chemical shifts of compound D

Carbon	Shift δ (ppm)	J_{C-H}/Hz	Multiplicity
C-1	48.5	–	Singlet
C-2	170.2	–	Singlet
C-3	44.5	–	Singlet
C-4	49.4	–	Singlet
C-5	34.0	3.2	Triplet
C-6	37.8	3.2	Triplet
C-7	50.2	3.2	Triplet
C-3 Me(2)	27.4	3.2	
	23.8	2.8	Quartets
C-1 Me	18.7	3.2	Quartet
C-4 Me	16.4	3.2	Quartet
C-2 (CH_2=)	97.6	2.8	Triplet

Table 14

^{1}H n.m.r. Chemical shifts of camphene

This work[†]

Shift (δ) ppm	No. of Hydrogens	Multiplicity
1.01	3H	Singlet
1.05	3H	Singlet
1.17 - 1.32	2H	Multiplet
1.35 - 1.45	2H	Multiplet
1.58 - 1.75	2H	Multiplet
1.89	1H	Broad singlet
2.66	1H	Broad singlet
4.47	1H	Singlet
4.69	1H	Singlet
0.82	an impurity from Tricyclene	Singlet

Other workers[*]

Shift (δ) ppm	No. of Hydrogens	Multiplicity
0.82	2H	Singlet
1.02	3H	Singlet
1.07	3H	Singlet
1.10 - 1.85	4H (2 x 2H)	Multiplet
1.89	1H	Broad singlet
2.65	1H	Broad singlet
4.47	1H	Singlet
4.69	1H	Singlet

[†] purified by preparative GLC

[*] Reference No.79[a]

Table 15

^{13}C Chemical shifts of compounds D, E and their analogues

Compound	C-1	C-2	C-3	C-4	C-5	C-6	C-7	Me				=CH$_2$
(2)	45.6	154.3	38.4	37.0	28.6	29	39.2					102.0
(3)	48.8	157.5	39.8	36.2	30.4	36.9	46.3	1-Me	17.5			100.6
(5)^a	47.4	165.7	42.0	48.7	24.2	29.2	37.8	3-Me	29.7 - exo. 26.1 - endo.			99.8
(5)	47.0	166.0	41.8	48.2	29.4	28.9	37.4	3-Me	25.9 - exo. 23.8 - endo.			99.2
(5)^b	47.8	166.0	41.5	48.4	25.3	28.9	37.1	3-Me	28.5 - exo. 23.9 - endo.			100.0
(6)	49.9	169.2	42.8	47.4	25.5	35.6	44.3	3-Me	29.6 - exo. 26.1 - endo.	1-Me	18.3	96.8
(7)	46.9	37.3	29.4	46.9	29.4	37.3	45.5	1-Me	16.5	7-Me	19.9	
(D)	48.5	170.2	44.5	49.4	43.0	37.8	50.2	3-Me	27.4 - exo. 23.8 - endo.	1-Me 4-Me	18.7 16.4	97.6
(E)	46.1	198.4	43.8	48.2	34.7	35.6	53.2	1-Me 4-Me	17.2 16.4	7-Me	13.2 - anti. 16.0 - syn.	100.8

(5) This work

(5)^a Reference 64

(5)^b References 76, 81^{a,b}, 82.

(6) Reference 75

Table 16

The ^{13}C chemical shifts of Bornane and its methyl substituents*

Compound	C–1	C–2	C–3	C–4	C–5	C–6	C–7	Me	=CH_2
(1)	36.8	30.1	30.1	36.8	30.1	30.1	38.7		
(4)	42.6	43.3	161.3	45.8	28.8	28.8	35.3	2–Me 19.7	101.6
(8)	44.2	37.4	31.9	38.4	31.9	37.4	45.9	1–Me 21.4	
(9)	43.0	36.4	39.8	36.9	30.0	28.7	34.8	2–Me 22.3	
(10)	41.7	34.0	40.2	37.7	30.2	22.1	38.4	2–Me 17.4	
(12)	43.1	34.8	34.8	43.1	21.8	21.8	39.7	2,3–Me 11.8	
(13)	42.4	44.0	45.2	44.4	30.3	21.2	36.9	2–Me 15.9, 3– Me 21.1	
(14)	44.5	39.9	39.9	44.5	29.7	29.7	31.9	2,3–Me 15.7,	

* References 76, 81[a,b], 82.

(iii) Determination of the structure of compound B by ^{1}H and ^{13}C spectroscopy

The proton n.m.r. spectrum showed the presence of twenty hydrogens, all the peaks appearing at the high field region of the spectrum i.e. suggesting the absence of unsaturation in the molecule. The singlet peak (δ = 0.43 ppm) at very high field of the spectrum corresponded to just one hydrogen atom whilst five resonances (5 x 3H) appearing as singlets and points to their attachment to tertiary carbons.

The integration of the spectrum shows that two methylene groups are present and the low field (A-parts) of two AB splitting are centered at (δ = 1.42 and δ = 1.51 ppm). The corresponding high field portions are partially obscured by the methyl absorptions at δ = 1.0 and 1.13 ppm respectively; only two peaks are then **discernabel** and are most likely the highest for the methylene having the larger chemical shift (δ = 1.14 ppm) and the next to highest (δ = 1.04 ppm) for the methylene with the smaller chemical shift.

The chemical shift (δ = 0.43) is indicative of hydrogens attached to cyclopropyl ring systems[83] so a structure incorporating this, five methyls and no unsaturated carbons carrying hydrogen is consistent with the tricyclic structure.

Comparison of the chemical shifts and spin-spin interaction of compound B with those of 4-methyl **tricyclene**[84] confirm structure VIII.

Table 17 .

^{1}H n.m.r. Chemical shifts of compound B

Shift (δ) ppm	No. of Hydrogens	Multiplicity	J/H_Z
0.43	1H	Singlet	–
0.69	3H	Singlet	–
0.7	3H	Singlet	–
0.87	3H	Singlet	–
1.0	3H	Singlet	–
1.13	3H	Singlet	–
1.04	2H	AB pattern	11
1.42	2H	AB pattern	11

Table 18

^{1}H n.m.r. Chemical shifts of 4-Methyl Tricyclene*

Shift (δ) ppm	No. of Hydrogens	Multiplicity	J/Hz
0.7	6H	Singlet	–
0.82	2H	Singlet	–
0.89	3H	Singlet	–
1.04	3H	Singlet	–
1.45	2H	AB pattern	10
1.55	2H	AB pattern	10

* Reference 84

Table 19

^1H n.m.r. Chemical shifts of Tricyclene

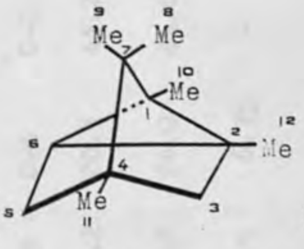
Shift (δ) ppm	No. of Hydrogens	Multiplicity	J/H_z
This work			
0.81	2H	Singlet	–
0.82	6H	Singlet	–
1.01	3H	Singlet	–
1.03	2H	AB pattern	10
1.66	2H	AB pattern	10
1.39	1H	Singlet	–
D.G. Morris and A.M. Murray*			
0.82	8H (2 x CH_3 and cyclo-propyl protons)	Singlet	
1.01	3H	Singlet	
1.66	2H	AB pattern	
1.03	2H	AB pattern	10.4
1.40	1H	Singlet	

* Reference 84.

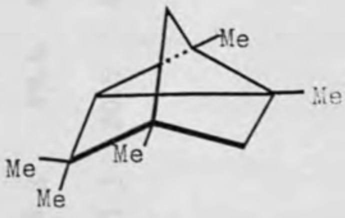
The ^{13}C spectrum of compound B showed twelve distinct resonances. All of them occurring with high field chemical shifts confirming the absence of unsaturation. Two alicyclic methylene groups were indicated by the observation of triplets in their off resonance spectra and only one douplet showed the presence of methine group.

Four resonances showing no coupling to hydrogen supported the presence of four quaternary carbons, which assured the attachment of a methyl group to three bridgehead carbons, and two methyl groups attached to a bridging carbon.

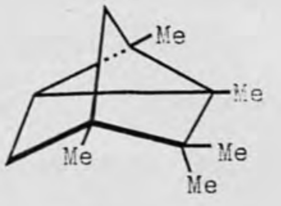
The resonances due to five methyl groups were distinct showing an absence of symmetry in the structure of compound B, although two of the methyl groups have very similar chemical shifts which suggests their attachment to the same ring carbon viz. at C-7, C-5, C-3 in compounds VIII, IX and X respectively.



VIII



IX



X

Compound IX would have two identical high field bridgehead methyls whereas X would be more likely to show the three in increasing chemical shifts in the order of attachment to C-2,C-4 and C-1. The assignments are made by comparison with the chemical shifts of similar compounds e.g. tricyclene (part of this study) or obtained by other workers[84] (see table 20). Compound B is suggested to have the structure shown by figure VIII orX and named as 2,4-dimethyltricyclene or 1,2,4,7,7-pentamethyl tricyclo(2,2,1,0^{2-6})heptane.

Table 20

^{13}C Chemical shifts of compound B and similar compounds

Compound	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-11	C-12
(15)[b]	28.8	20.3	38.2	43.3	38.2	20.3	44.2	17.7	17.7	11.5	12.2	
(B)	24.4	32.2	39.5	43.8	44.8	26.0	45.6	18.4	18.0	13.7	12.3	8.5
J_{C-H}/Hz	-	-	6.75	-	6.5	6.75	-	7.2	7.2	6.3	5.4	6.3
(16)[a]	26.3	19.4	31.3	41.8	31.3	19.4	43.1	20.6	20.6	9.4		
(16)[b]	26.2	20.5	31.3	41.9	31.3	20.5	43.0	19.4	19.4	10.5		

(16)[a] This work.

(16)[b] Reference 84

(iv) Determination of the structure of compound F by ^{1}H and ^{13}C Spectroscopy

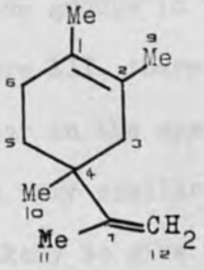
The ^{1}H n.m.r. spectrum of compound F showed that the sample contained traces of compounds E and G. The presence of these peaks effected the overall integration but did not prevent the assignment of some distinct groups.

An unsaturated methylene group appeared as a doublet at $\delta = 4.64$ ppm and four methyl groups appeared as three singlets.

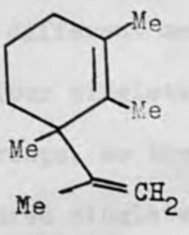
One singlet at $\delta = 0.98$ ppm suggested its attachment(70b) to a quaternary carbon atom, while the other three methyl groups appeared as two singlets at lower field indicating their attachment to unsaturated carbons.

The broad singlet at $\delta = 1.6$ ppm (6H) could arise from two methyl groups attached to either (a) the same unsaturated carbon atom or (b) two similar unsaturated carbon atoms. The fourth methyl group giving a singlet at $\delta = 1.74$ ppm points to a different invironment from that of $\delta = 1.6$ ppm methyls. The number of unsaturated carbon atoms consistent with the above could be a minimum of four or a maximum of six.

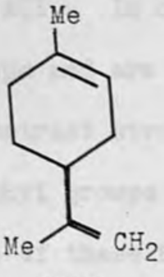
To be a dimer of 2,3-dimethylbutadiene the presence of two double bonds implies that compound F must be monocyclic with three saturated methylene groups as in structures XI or XII.



XI



XII



XIII

No open chain structure can be suggested for compound F that includes a methyl group attached to a quaternary carbon in the presence of three double bonds.

By comparing the spectrum of compound F with the spectrum of limonene XIII considerable similarity in the chemical shifts of the peaks were observed together with the definite absence of the peak at $\delta = 5.38$ ppm corresponding to the unsaturated methine group. Replacement of that hydrogen by a methyl group could give the resonance observed at $\delta = 1.6$ ppm. This singlet of six hydrogens at $\delta = 1.6$ ppm would then represent two similar methyl group; one of them is identical to that observed in the spectrum of limonene and corresponds to a methyl group attached to the ring.

The appearance of a methyl group at $\delta = 0.98$ ppm and attached to a quaternary carbon suggests that it has replaced the hydrogen atom of the saturated methine hydrogen in limonene at C-4. Since both limonene and compound F spectra show singlets corresponding to three hydrogens at $\delta = 1.72$ ppm and $\delta = 1.74$ ppm and doublets at $\delta = 4.68$ ppm and $\delta = 4.64$ ppm respectively corresponding to unsaturated methylene groups, the presence of a similar isopropenyl group to that in limonene is deduced for compound F. The multiplet at $\delta = 1.73 - 2.2$ ppm can arise from the three saturated methylene groups in the rings of structures XI and XII. In case of structure XII, there are four different methyl groups and are most likely to appear in the spectrum as four singlets. In contrast structure XI has two very similar methyl groups, so the four methyl groups would be more likely to give rise to three singlets with one of these having an integration corresponding to six hydrogens. This is exactly what is observed in the spectrum of compound F, it is concluded that F has structure XI.

Table 21

^{1}H nmr Chemical Shifts of compound F and limonene

	Shift (δ) ppm	No. of Hydrogens	Multiplicity
Compound F			
	0.98	3H	Singlet
	1.6	6H	Singlet
	1.74	3H	Singlet
	1.0 - 2.2	6H	Multiplet
	4.64	2H	Doublet
Limonene			
Reference 79[a]	1.38 - 1.6	2H	Multiplet
	1.64	3H	Singlet
	1.72	3H	Singlet
	1.74 - 2.07	4H	Multiplet
	2.10	1H	(br) Singlet
	4.68	2H	Singlet
	5.38	1H	(br) Singlet

Table 21 (continued)

	Shift (δ) ppm	No. of Hydrogens	Multiplicity
This work			
	1.64	3H	Singlet
	1.72	3H	Singlet
	1.74 - 2.07	6H	Multiplet
	2.10	1H	(br) Singlet
	4.68	2H	Singlet
	5.38	1H	(br) Singlet
	1.38 - 1.6	–	Multiplet (impurities)
Reference 79^c	1.57	3H	Singlet
	1.64	3H	Multiplet
	1.70 - 2.30	7H	Multiplet
	4.60	2H	Singlet
	5.25	1H	Multiplet

The ^{13}C n.m.r. spectrum of compound F showed eleven resonances, four of them at low field and seven at high field.

In the off-resonance spectrum three of the low field resonances are singlets indicating the presence of three unsaturated carbons bearing no hydrogens. The fourth signal was a triplet and arose from an unsaturated methylene group.

The presence of four unsaturated carbons in this dimer of 2,3-dimethylbutadiene implies a monocyclic structure with two double bonds one of which must bind the unsaturated methylene group.

Attachment of this methylene to a carbon bearing no hydrogens is supported by the presence of the lowest field carbon at δ = 152·0 ppm.

The seven high field resonances appeared in the off-resonance spectrum as follows: three quartets representing methyl groups, three triplets representing methylene groups and one singlet representing a quaternary carbon.

To accommodate 18 hydrogens as methyls and methylenes it is necessary to have four methyls and three methylenes present in structure F. Accordingly two of the methyl groups must either be attached to the same carbon or to two very similar carbons. The absence of doublets in the off-resonance spectrum of compound F indicates the presence of no methine groups in the structure of compound F and that means that the two methyl groups are either attached to (a) a quaternary carbon of the ring or (b) to two sp^2 carbons in the ring and these would have to be the only two sp^2 carbons in the ring.

The first possibility (a) might be expected to give a resonance at the very high field part of the spectrum and have the highest intensity of the methyl resonances. Second possibility (b) might be expected to give methyl resonances at lower fields compared to the other two methyl resonances. Also one of these other two methyl groups must be attached to the only quaternary carbon in the structure of compound F and the other methyl group to that sp^2 carbon atom having $\delta = 152.0$ ppm.

Alternative (b) leads to a structure with an isopropenyl group attached to a six membered ring and with three methyl substituents.

Structures XI and XII can be proposed for compound F but XII would be the one more likely to show four methyl resonances, XI therefore fits the data more satisfactorily i.e. 1,2,4-trimethyl 4-isopropenylcyclohex-1-ene.

Table 22

^{13}C Chemical shifts of compound F

Carbon	Shift	J_{C-H}	Multiplet
C-1	123.9	-	Singlet
C-2	124.2	-	Singlet
C-3	32.8	6.5	Triplet
C-4	42.9	-	Singlet
C-5	29.6	6.5	Triplet
C-6	37.9	4.0	Triplet
C-7	152.0	-	Singlet
C-8,9 Me	19.4	6.5	Quartet
C-10 Me	18.6	6.5	Quartet
C-11 Me	25.2	6.5	Quartet
C-12	108.6	6.5	Triplet

Table 23

^{13}C Chemical shifts of compound F and limonene

Compound	C-1	C-2	C-3	C-4	C-5	C-6	C-7		Me	=CH$_2$
XIII*	133.5	121.1	30.9	41.5	28.3	31.2	150.0		24.1 20.8	108.7
(F)	123.9	124.2	32.8	42.9	29.6	37.9	152.0	18.6	25.2 19.4	108.6
XIII†	133.4	120.6	30.6	41.1	27.9	30.8	149.8		23.3 20.7	108.4

* Reference 79[a]

† This work.

(v) Determination of the structures of compounds G, H and I by ^{1}H and ^{13}C spectroscopy

The ^{1}H n.m.r. spectra of each of these compounds showed the presence of eighteen hydrogens; indeed almost identical spectra were obtained for these three compounds.

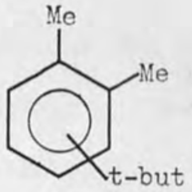
Each spectrum showed the presence of nine hydrogens having a singlet resonance in the region between $\delta = 1.28$ and $\delta = 1.32$ ppm indicating the presence of three identical methyl groups.

At $\delta = 2.16$ and $\delta = 2.27$ ppm, six hydrogens appeared as two singlets representing two methyl groups most probably attached to sp^2 carbon atoms.[79b, 85, 86]

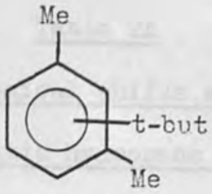
Multiplets representing three hydrogens on unsaturated carbons and showing some coupling to each other were observed for each of the three compounds between $\delta = 6.95$ and $\delta = 7.24$ ppm. The presence of two methyl groups having chemical shifts implying the presence of unsaturation must mean that two or four unsaturated carbons are present, the unsaturated carbons bearing three hydrogens must imply the presence of four or six unsaturated carbons. The resonances between $\delta = 6.95$ and $\delta = 7.24$ ppm point to the absence of terminal methylenic groups and exocyclic alkene groups. The only acceptable combinations of these two unsaturated systems are those in which there are either conjugated double bonds in an acyclic triene or else there is a benzene ring present.

The singlets for three similar methyl groups at $\delta = 1.3$, $\delta = 1.28$, $\delta = 1.32$ ppm in compounds G, H and I respectively, suggest the presence of the t-butyl group.[86]

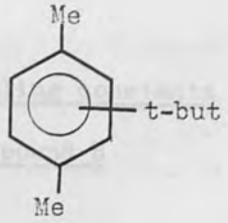
Aromatic structures consistent with $C_{12}H_{18}$ having two methyl groups and a t-butyl group are:



XIV



XV



XVI

These structural isomers will show only small differences in chemical shifts but will differ in the multiplets arising from the coupling of their aromatic hydrogens.

In structure XIV with the t-butyl group attached to C-1 and the methyl groups attached to C-2 and C-3 respectively would be two doublets of doublets as a result of coupling between the hydrogens attached to C-5 with C-4, C-6 with a coupling constant $J_{4,5}$, $J_{5,6}$ of 7.7 to 9.0 Hz; and $J_{4,6}$ of 1.4 - 3.0 Hz. In addition there will be two doublets due to the coupling between the hydrogen of C-5 with the hydrogens of C-4 and C-6. In the alternative structure XIV with the t-butyl group attached to C-1 and the methyl groups attached to C-3 and C-4 respectively, the multiplet would arise from the aromatic hydrogens as follows: a doublet with a meta coupling constant $J_{2,6}$ = 1.4 - 3.0 Hz and para coupling constant $J_{2,5}$ = 0.7 Hz for the hydrogen on C-2 and two doublets of doublets for the hydrogen atoms on C-5 and C-6, with coupling constants $J_{5,6}$ = 7.7 - 9.0 Hz, $J_{6,2}$ = 1.4 - 3.0 Hz and $J_{5,2}$ = 0.7 Hz.

The pattern of the aromatic hydrogens in the spectrum of compound H indicate that it has structure XIV with the t-butyl group at C-1 and methyl group at C-3 and C-4. See Table 24.

Table 24

^{1}H n.m.r. Chemical shifts and coupling constants

of the aromatic hydrogens of compound H

H-C	Multiplicity	Chemical shifts ppm	J/Hz
2	Doublet	7.11	3.0
6	Doublet of Doublets	7.06	8.0 2.0
5	Doublet	6.98	8.0

On the other hand a similar multiplet pattern could arise from couplings of the aromatic hydrogens in structure XVI where the methyl groups are attached to C-2 and C-5 and the t-butyl group in C-1; and also in structure XV where the methyl groups are attached to C-2 and C-4 and the t-butyl group to C-1.

These multiplets may be different only on the basis of slight change in chemical shifts of every individual hydrogen atom and these will be dependent on the effect of the substituents[87] affecting the π-electron density at a carbon atom to which hydrogen is bonded. With the three substituents in XIV, XV and XVI confined to the 1,2 and 4 positions of the rings the C-2 hydrogen pattern in XIV would show the lowest chemical shift of the three aromatic hydrogens while the C-5 hydrogen pattern would have the highest chemical shift with the C-6 hydrogen pattern between the previous two. A multiplet pattern corresponding to this appeared in the spectrum of compound H, Table 24.

In the case of structure XVI the chemical shift of the pattern arising from the C-6 hydrogen atom should be expected to appear at the lowest region of the spectrum as a consequence of the ortho t-butyl group, whereas the pattern arising from the C-4 hydrogen atom would appear at the highest chemical shift of the aromatic hydrogens multiplet; the pattern of the C-3 hydrogen will be in the middle of the multiplet. This pattern is observed in the spectrum of compound G. See Table 25.

Table 25

^{1}H n.m.r. Chemical shifts and coupling constants of the aromatic hydrogens of compound G

H-C	Multiplicity	Chemical shifts ppm	J/Hz
3	Doublet	7.14	2.0
6	Doublet of doublets	7.11	9.0 2.0
5	Doublet	7.02	8.0

In structure XV the splitting pattern for the C-3 hydrogen atom would be expected to have the lowest field chemical shift of the spectrum whereas the doublet of C-5 would be at highest chemical shift of the aromatic multiplet. The doublet of C-6 hydrogen atom would be in the middle of the aromatic multiplet. This pattern appeared in the spectrum of compound I. See Table 26.

Table 26

^{1}H n.m.r. Chemical shifts and coupling constants of the aromatic hydrogens of compound I

H-C	Multiplicity	Chemical shifts ppm	J/Hz
3	Doublet	7.24	1.0
5	Doublet of Doublets	7.13	9.0 2.5
6	Doublet	7.06	8.0

Table 27

^{1}H n.m.r. Chemical shifts of compounds G, H, I and similar compounds*

17a	17b	17c				18
o-xylene	m-xylene	p-xylene	compound G	H	I	t-but.benzene
Me,s, δ = 2.20	Me, s, δ = 2.28	Me, s, δ = 2.27	Me, s, δ = 2.24	Me, s, δ = 2.16	Me, s, δ =2.24	
			δ = 2.21	δ = 2.2	δ = 2.27	
CH, s, δ = 6.95	CH, m, δ = 6.62 - 7.08	CH, s, δ = 6.90	CH, m, δ = 7.04 - 7.24	CH, m, δ = 6.95 - 7.12	CH, m, δ = 7.04 - 7.24	CH, m, δ = 7.28 - 7.13
			t-but., s, δ = 1.32	t-but., s, δ = 1.28	t-but., s, δ = 1.32	t-but., s, δ = 1.32

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* References 79[b], 86 and 87.

The ^{13}C spectra of each of the three compounds were almost identical; each spectrum showing the presence of ten distinct resonances, (a) four resonances at high field, (b) six resonances at low field. The high field resonances include one carbon resonance corresponding to quaternary carbon due to the absence of coupling with hydrogen in the off-resonance spectra. The other three resonances are methyl groups since each of them couples with three hydrogens as indicated by quartets in the off-resonance spectra.

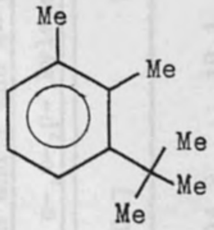
One of these methyl resonances represents more than one similar methyl group owing to its higher intensity when compared to the other two methyl resonances.

The six low field unsaturated resonances were distinguished as three unsaturated carbon atoms and three unsaturated-CH-groups by singlet and doublets respectively in the off-resonance spectra. These six low field resonances support the presence of three double bonds in each compound.

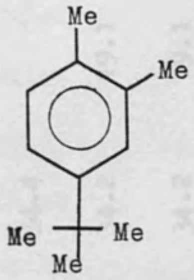
On the basis of expecting twelve carbon resonances for compounds G, H and I, derived from two molecules of 2,3-dimethylbutadiene, the presence of some similar groups amongst the ten resonances is indicated. The presence of a high intensity for one of the methyl resonances pointed to three similar methyl groups present in the structure and attached to the high field quaternary carbon.

These structures with five methyl groups, three-CH-groups and four quaternary carbons atoms correspond to $C_{12}H_{18}$.

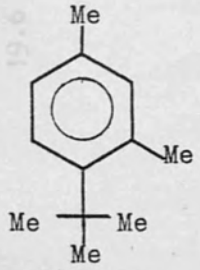
This molecular formula can only be consistent with an acyclic tetraene if (i) less than five methyl groups are included or (ii) less than four quaternary carbon are present or (iii) methylene groups are included. If however monocyclic trienes are considered then the following benzene derivatives (XVII - XXII) are possible structures for G, H and I. The dimethyl t-butyl benzenes XXI and XXII have identical methyl groups and can be rejected.



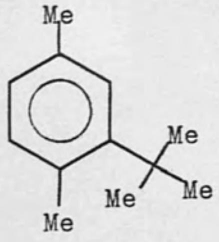
XVII



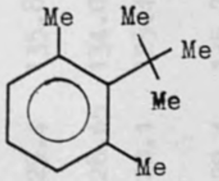
XVIII



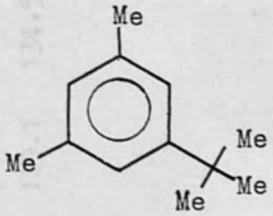
IXX



XX



XXI



XXII

Table 28

^{13}C Chemical Shifts of Compounds G, H and I and 4- t-Butyl toluene , benzene and o-,m-,p- Xylene.

Compound	C-1	C-2	C-3	C-4	C-5	C-6	C-7	Me		t-but
G	148.5	122.6	129.4	135.8	133.3	126.5	34.2	19.1	20.0	31.4
19^{*}	147.6	124.8	128.65	134.0	128.6	124.8	34.1		20.7	31.4
	150.5	125.0	128.1	125.4	128.1	125.0	34.4		21.3	31.4
H	148.5	122.6	129.4	135.7	133.2	126.5	34.2	19.1	20.0	31.4
I	148.6	122.6	129.3	135.8	133.4	126.6	34.2	19.1	20.0	31.4
18	149.2	125.4	128.4	125.9	128.4	125.4				
17^{a}	136.4	136.4	129.9	126.1	126.1	129.9		19.6		
+ 17^{b}	137.5	130.1	137.5	126.4	128.3	126.4			21.3	
17^{c}	134.5	129.1	129.1	134.5	129.1	129.1			21.3	

* References 88 and 89[a].

\+ Reference 89[b].

Table 29

^{13}C Chemical Shifts of Compounds G.

Chemical Shifts ppm	Multiplicity	$J_{C-H/Hz}$	Assignment
19.1	Quartet	4.95 Hz	Methyl group
20.0	Quartet	4.95 Hz	Methyl group
31.4	Quartet	5.85 Hz	Methyl group
34.2	Singlet	2.7 Hz	$-\overset{\vert}{\underset{\vert}{C}}-$
122.6	Doublet	4.5	=CH-
126.5	Doublet	4.05	=CH
239.4	Doublet	4.5	=CH-
133.3	Singlet		=C
135.8	Singlet		=C
148.5	Singlet		=C

vi) Determination of the structure of compound A by ^{1}H and ^{13}C spectroscopy

The integration of the ^{1}H n.m.r. spectra of compound A to account for the presence of twenty hydrogens showed: nine hydrogens as a singlet resonance at 1.72 ppm and three hydrogens as a singlet resonance at 1.76 ppm. At 2.06 ppm a singlet resonance represented four hydrogens and in addition another four hydrogens appeared as a singlet with a chemical shift corresponding to hydrogen on unsaturated carbons at 4.61 ppm.

From the integration and the chemical shifts of the resonances the presence of three similar methyl groups and a fourth different methyl group are suggested. Since the three similar methyl group appear down field from that of the chemical shifts associated with the tertiary butyl group, it indicates(79b, 85, 86) that they are not attached to the same carbon atom but are found in similar environments and most likely bonded to sp^2 carbons. The downfield chemical shift of the fourth methyl group also points to its attachment to unsaturated carbon.

The presence of four methyl groups attached to unsaturated carbons can be consistent with the presence of a minimum of four and a maximum of eight unsaturated carbons.

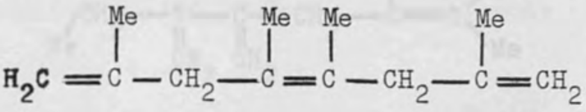
The singlet representing four hydrogen atoms at 2.06 ppm implies the presence of two very similar if not identical CH_2-groups.

The four most downfield hydrogens have a chemical shift corresponding to unsaturated CH_2 groups and not to unsaturated CH nor aromatic CH groups.

The two unsaturated CH_2 groups indicate the presence of four unsaturated carbons.

The maximum number of unsaturated carbons that could be accommodated in this dimer of 2,3-dimethylbutadiene is six. This dimer of 2,3-dimethylbutadiene having three double bonds must be acyclic. Compound A therefore is an open chain compound having three similar methyl groups attached to unsaturated carbons, another methyl group attached to an unsaturated carbon atom, two saturated CH_2 groups in addition to two unsaturated groups.

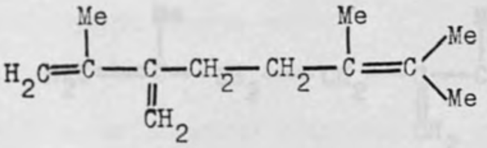
Structure XXIII has these features



$$H_2C{=}\overset{Me}{C}{-}CH_2{-}\overset{Me}{C}{=}\overset{Me}{C}{-}CH_2{-}\overset{Me}{C}{=}CH_2$$

XXIII

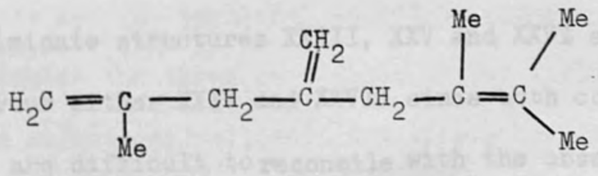
but because the four methyl groups should give two n.m.r. resonances having equal integrations of their areas this formula can be rejected. If compound A, has structure XXIV



XXIV

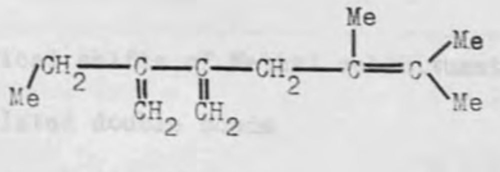
the spectra would show resonances having similar chemical shifts for the saturated CH_2 groups as well as similar resonance for the unsaturated CH_2 groups.

In the case of structure XXV, integrations of the methyl resonances might be the ratio 3:1



XXV

the unsaturated CH_2 groups might appear at different chemical shifts owing to slight differences in their environments. If structure XXVI is proposed for compound A

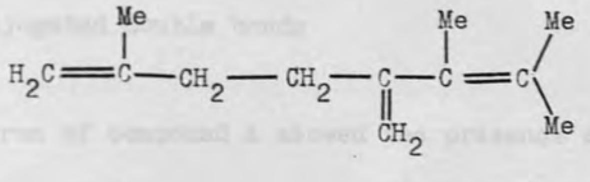


$\mathrm{MeCH_2{-}C({=}CH_2){-}C({=}CH_2){-}CH_2{-}C(Me){=}CMe_2}$

XXVI

then this can be rejected through the absence of a multiplet for the terminal ethyl group.

If structure XXVII is proposed for compound A,



$\mathrm{H_2C{=}C(Me){-}CH_2{-}CH_2{-}C({=}CH_2){-}C(Me){=}CMe_2}$

XXVII

the two saturated CH_2 groups might be expected to have similar chemical shifts and similarly the two unsaturated CH_2 groups might give overlapping resonances.

However the methyl groups might not be expected to give two singlets with integrations in the ratio 3:1. From the above considerations it is possible to eliminate structures XXIII, XXV and XXVI as alternative but not easy to favour either XXIV and XXVII since both contain structural features which are difficult to reconcile with the observed spectrum.

Josey[90] observed non-typical resonances in both conjugated and unconjugated dienes and trienes. In particular there is often observed no apparent spin-spin interactions between hydrogens on adjacent carbons.

Table 30 shows the chemical shifts and multiplicities of some linear dimers of conjugated dienes in which there are some absences of spin-spin interaction between certain groups as in compound A. The functionabilities are given below:

(1) The Chemical shifts of Methyl substituents on unsaturated carbons in:
  (a) isolated double bonds
  (b) conjugated double bonds
(2) Adjacent - saturated methylene groups, with no spin-spin interaction.
(3) Unsaturated methylene groups, with no vicinal coupling and no chemical shift difference between the hydrogens of the methylene group in:
  (a) isolated double bonds
  (b) conjugated double bonds

^{13}C nmr spectrum of compound A showed the presence of seven separate resonances, four of them appearing at the high field region of the spectrum and three at the unsaturated low field region.

The four resonances corresponding to saturated were shown three different methyl groups to be associated with (quartets in the off resonance spectrum) and a methylene group (triplet in the off resonance spectrum).

Integration of the decoupled spectra suggested that there were two identical methyls and two identical methylene groups.

From the above the three resonances at low field had to arise from six unsaturated carbons as follows; one triplet in the off resonance spectrum from two identical unsaturated methylene groups, two singlets each representing two tertiary carbon atoms. Again the evidence for

Table 30

Selected ^{1}H n.m.r. chemical shifts of acyclic Trienes*

Compound No.	Functionality				
	1		2	3	
	a	b		a	b
20	δ = 1.70 s.	δ = 1.78 s.	δ = 2.12 br.s.	δ = 3.69 s.	δ = 4.80 s.
21	δ = 1.70 s.		δ = 2.12 br.s		
22		δ = 1.80 s.	δ = 2.12 br.s		
23	δ = 1.65 s.	δ = 1.85 s.		δ = 4.68 s.	δ = 4.90 s. δ = 5.00 s.
24		δ = 1.72 br.s			
25 & 26				δ = 4.72 s.	δ = 4.83 s.

Table 31

^{1}H n.m.r. Chemical shifts of compound A

Shift (δ) (ppm)	No. of Hydrogens	Multiplicity
1.72	9	Singlet
1.76	3	Singlet
2.06	4	Singlet
4.61	4	Singlet

* Reference 90

six unsaturated carbons points to three double bonds in compound A and that in turn implies an open chain structure. The absence of unsaturated methine groups was inferred from the absence of doublet in the low field region. No one structure (XXIV - XXVII) can be assigned without difficulty to the ^{13}C nmr spectral information.

The presence of two tertiary carbons giving resonances at δ = 162.8 ppm may be those attached to the two terminal unsaturated CH_2 groups δ = 122.6 ppm.

This compound could be named as

1) 3-methylene-2,6,7-trimethyl-1,6-octadiene as in structure XXIV

or

2) 4-methylene-2,3,7-trimethyl-2,7-octadiene as in structure XXVII.

Table 32

^{13}C Chemical shifts of compound A

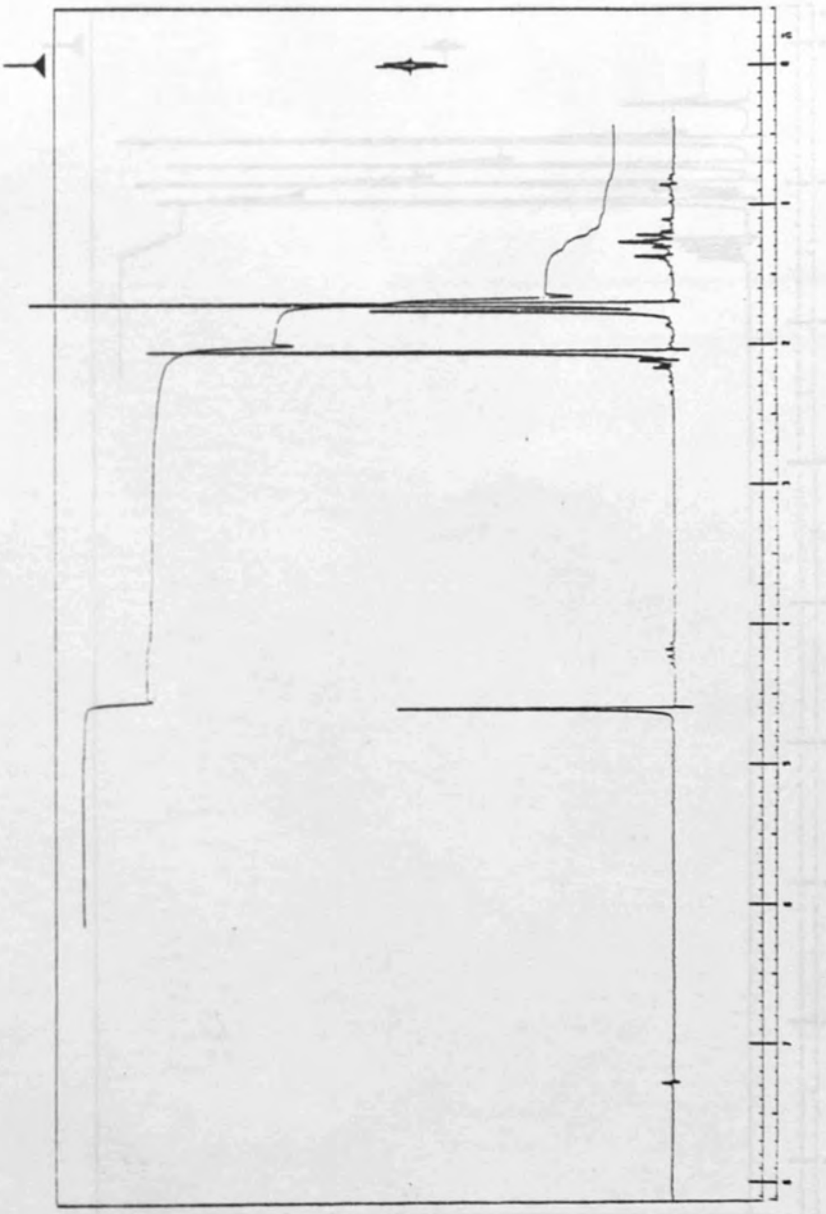
Carbon No.	Shift (δ) ppm	J_{C-H}/Hz	Multiplicity
C-2,3	171.4	–	Singlet
C-6,7	132.0	–	Singlet
C-1,12	122.8	2.0	Triplet
C-4,5	65.8	2.5	Triplet
C-8,11	20.9	2.4	Quartet
C-9	20.2	2.4	Quartet
C-10	16.7	2.5	Quartet

(vii) ^1H and ^{13}C n.m.r. spectra of compounds D,
E, F, G, H and I.

"Spectra"

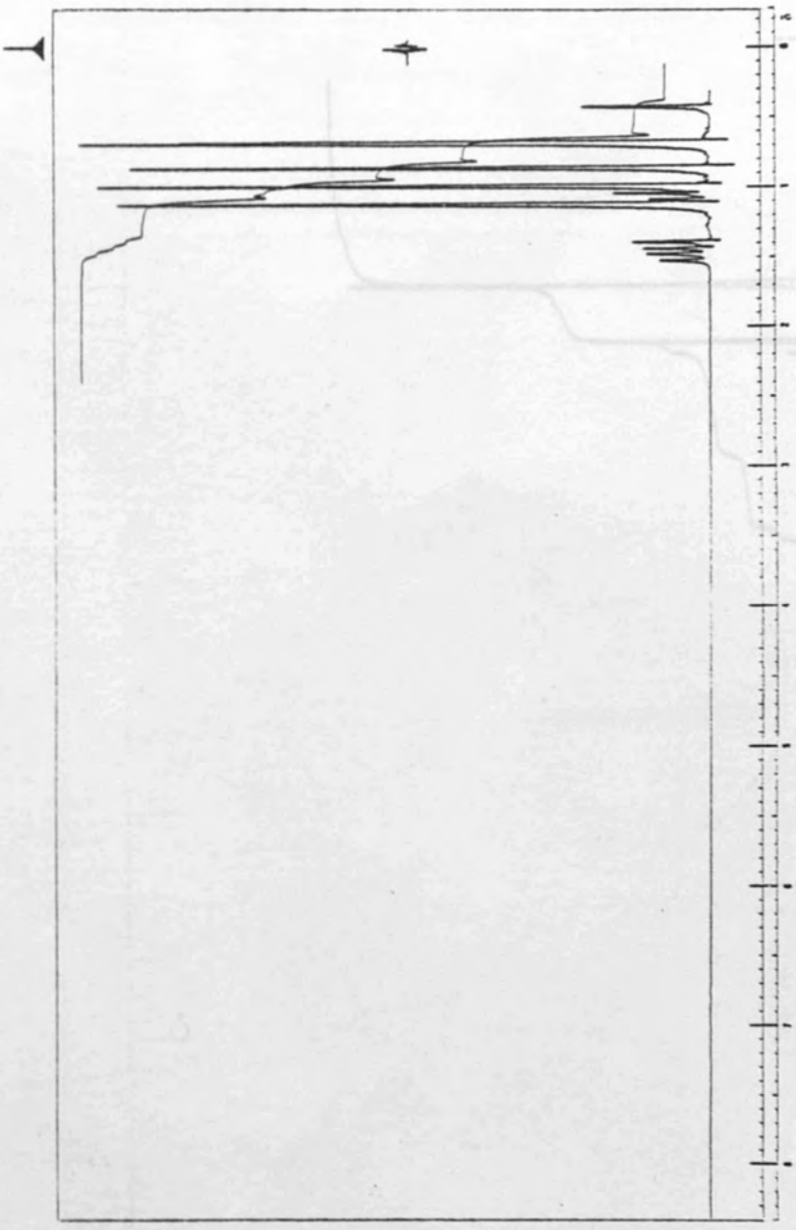
Spectrum (1) ^1H n.m.r. of compound "A"

(vii) ^{1}H and ^{13}C n.m.r. spectra of compounds A, B, C, E, F, G, H and I.

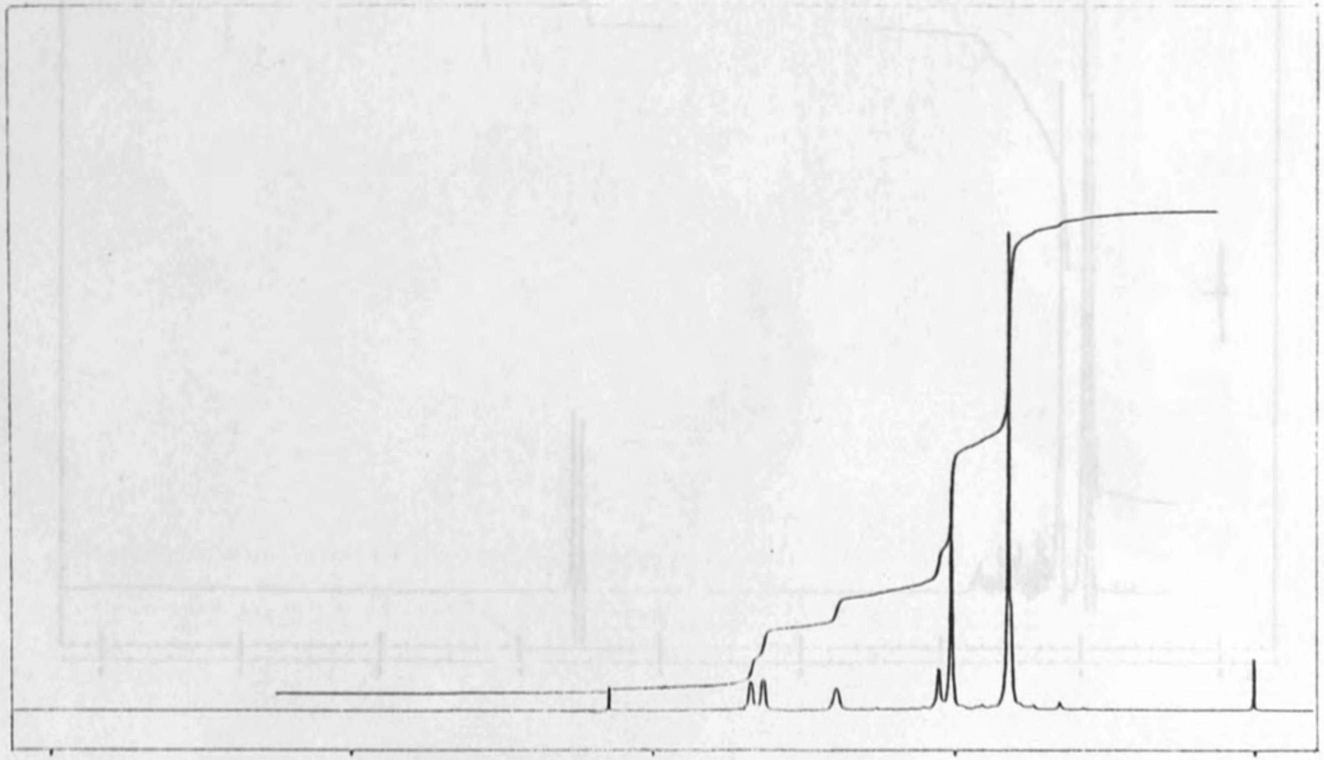


Spectrum (1) ^{1}H. n.m r. of compound " A ".

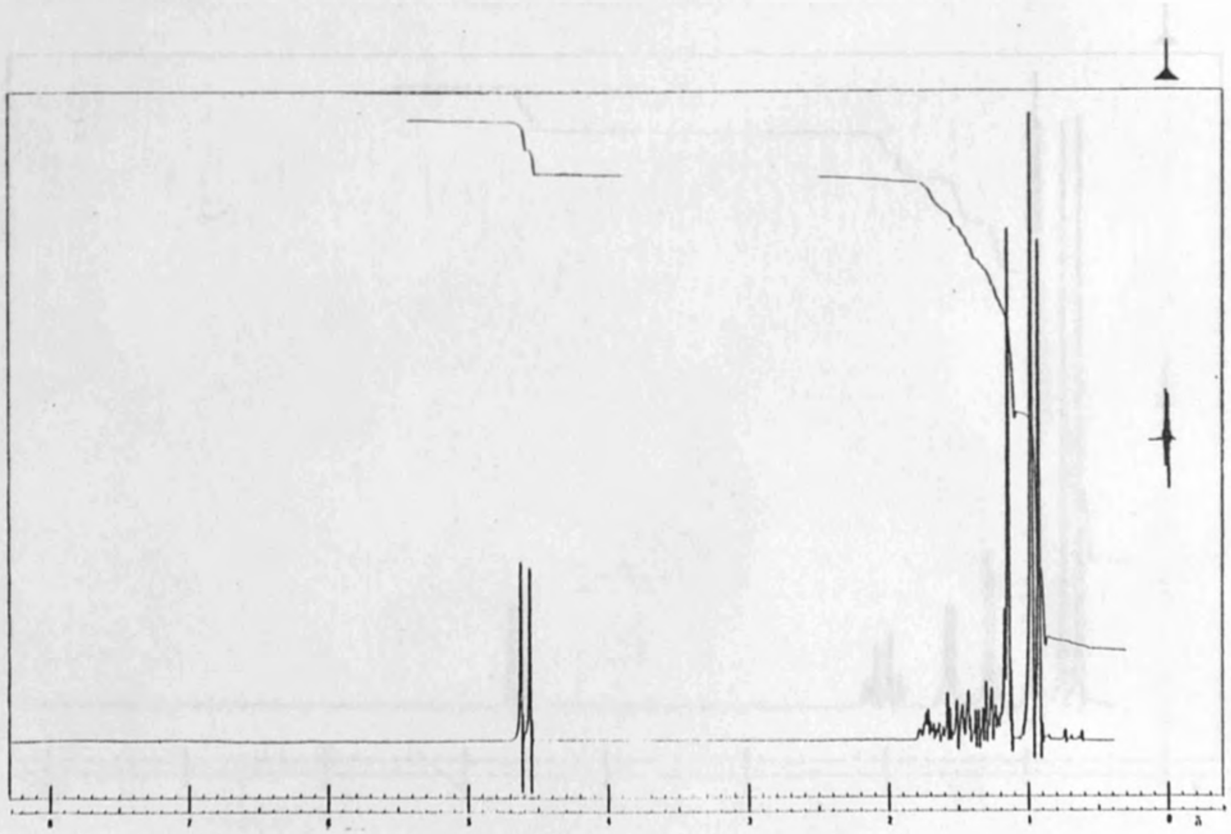
Spectrum (2) ^{1}H.n.m.r. of compound " B "



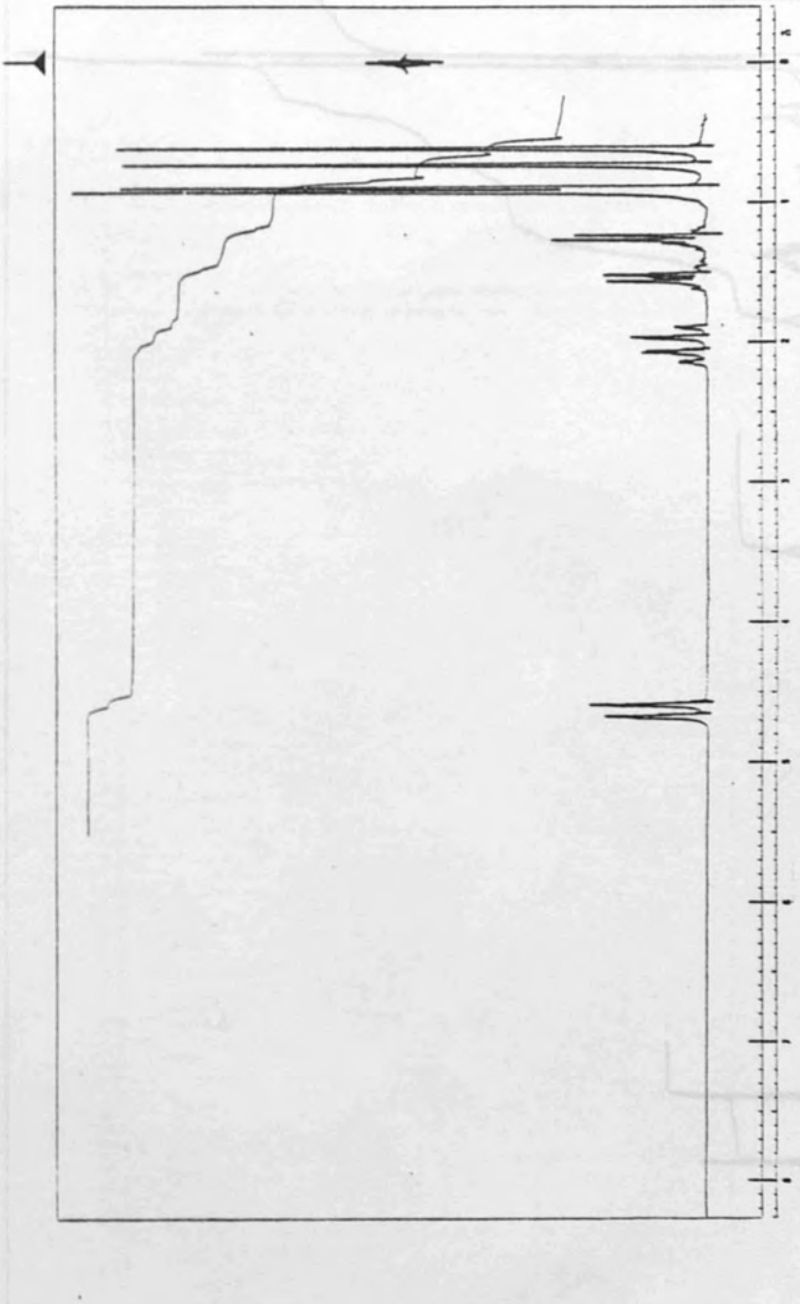
Spectrum (3) ^{1}H. n.m.r. of Tricyclene



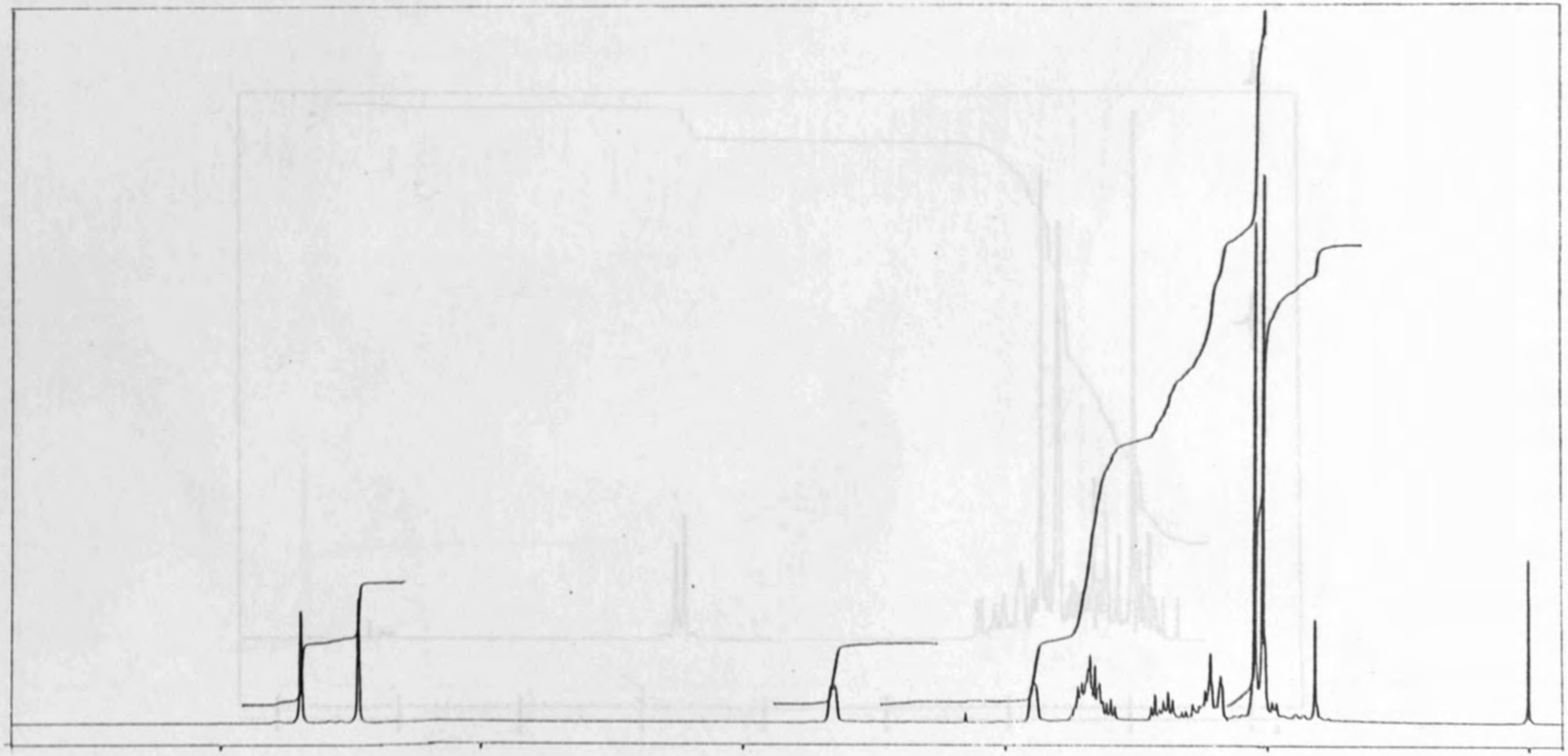
Spectrum (4) ^{1}H . n.m.r. of compound " D " .



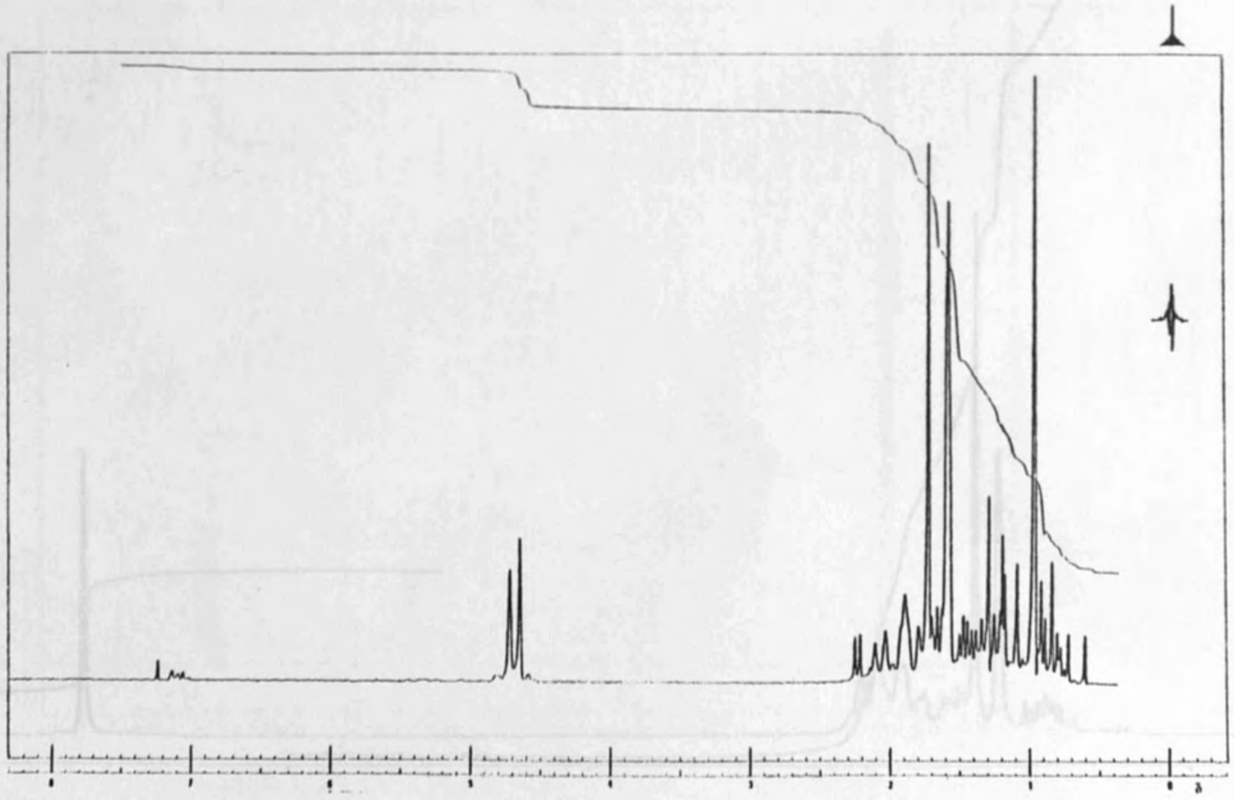
Spectrum (5) ^{1}H.n.m.r. of compound " E "



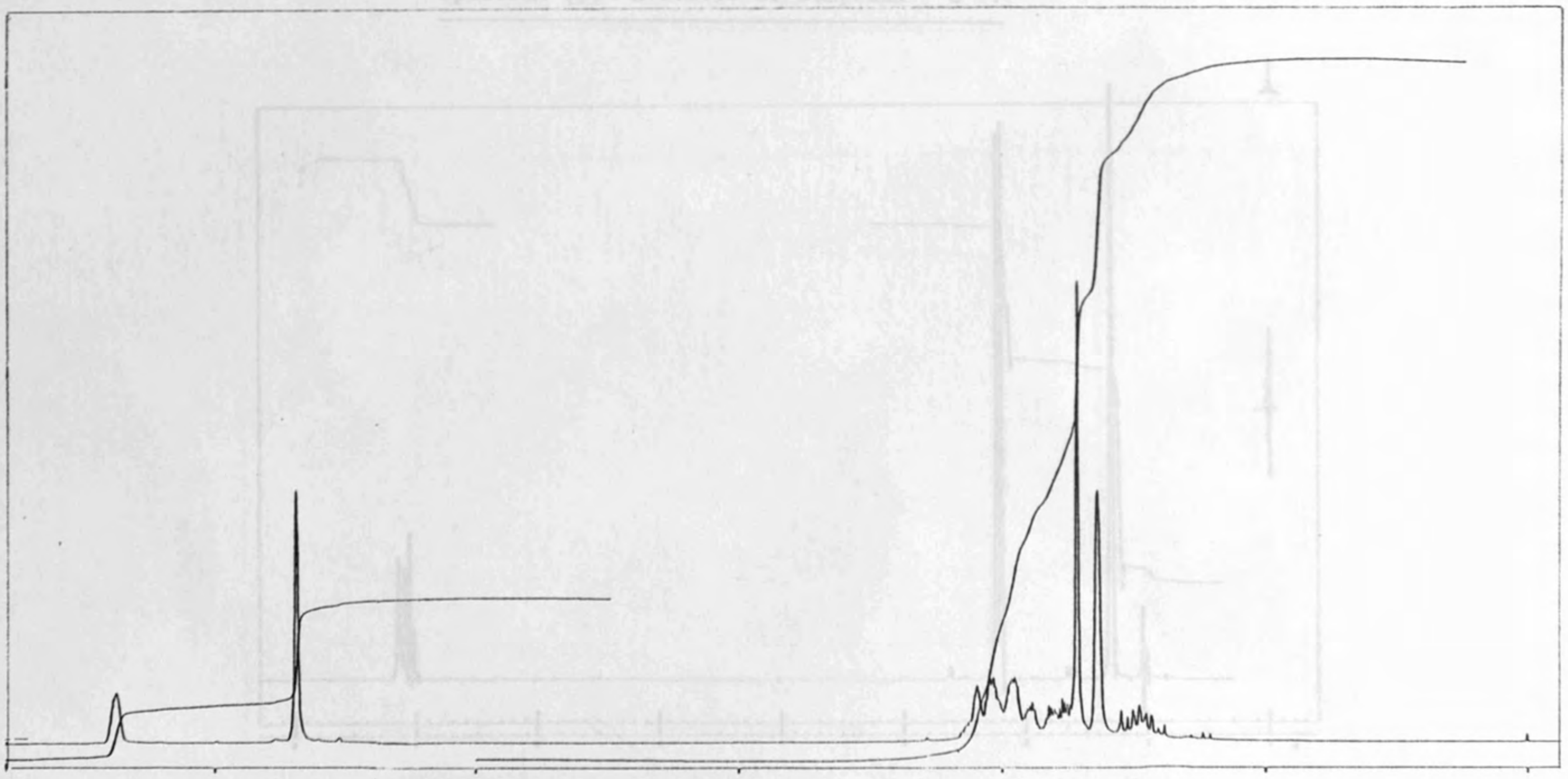
Spectrum (6) ^{1}H.n.m.r. of **Ca**mphene



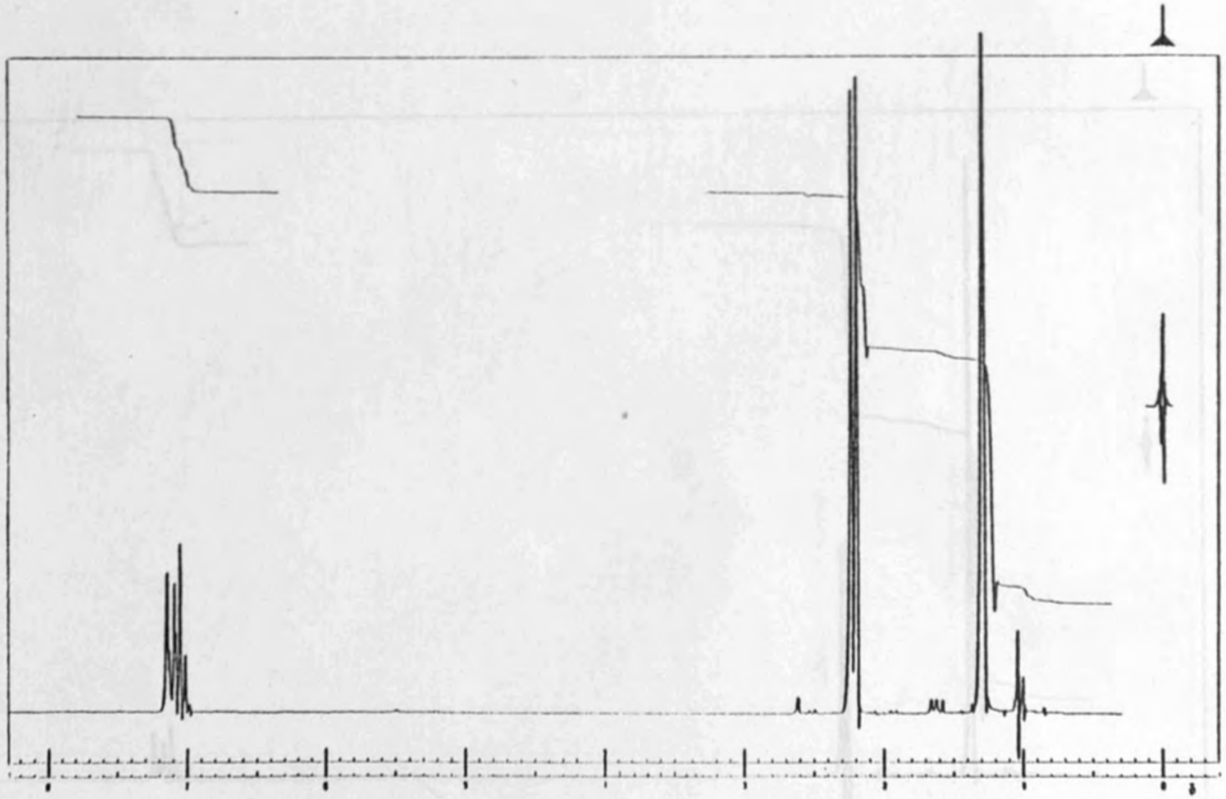
Spectrum (7) ^{1}H.n.m.r. of compound " F "



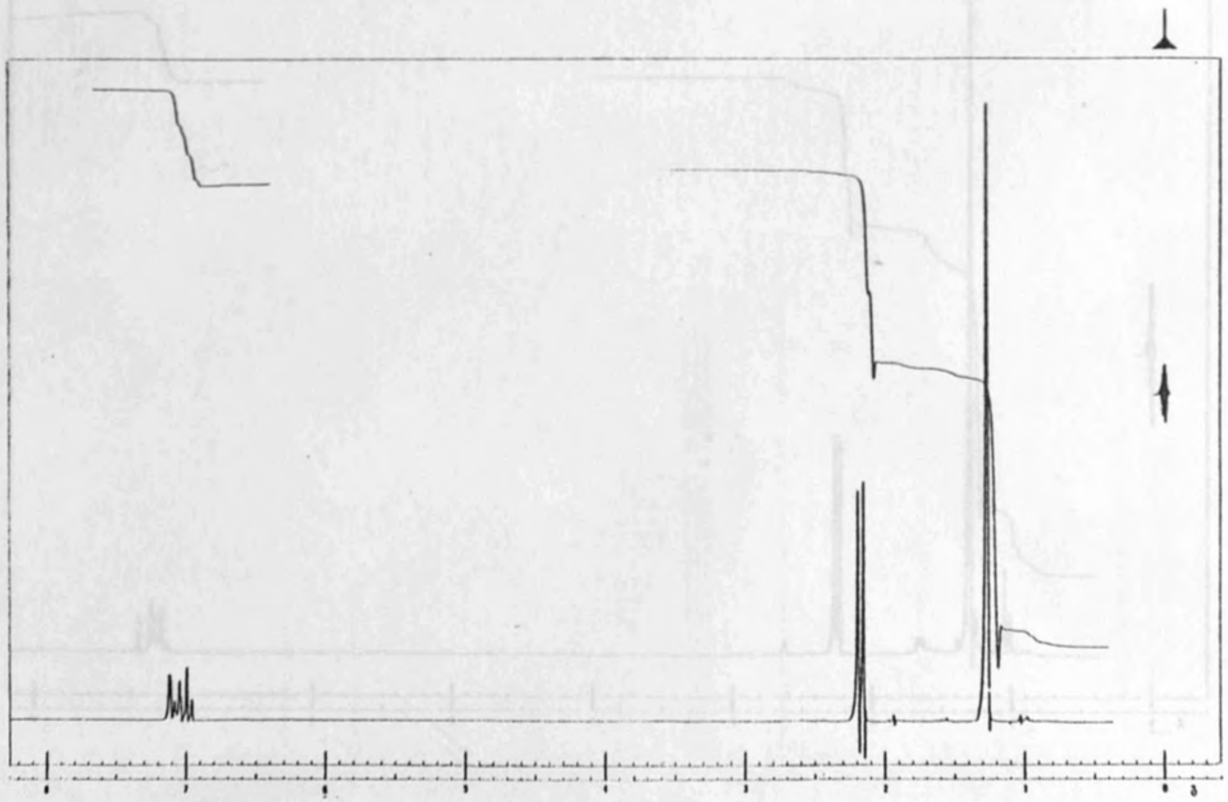
Spectrum (8) ^{1}H.n.m.r. of Limonene



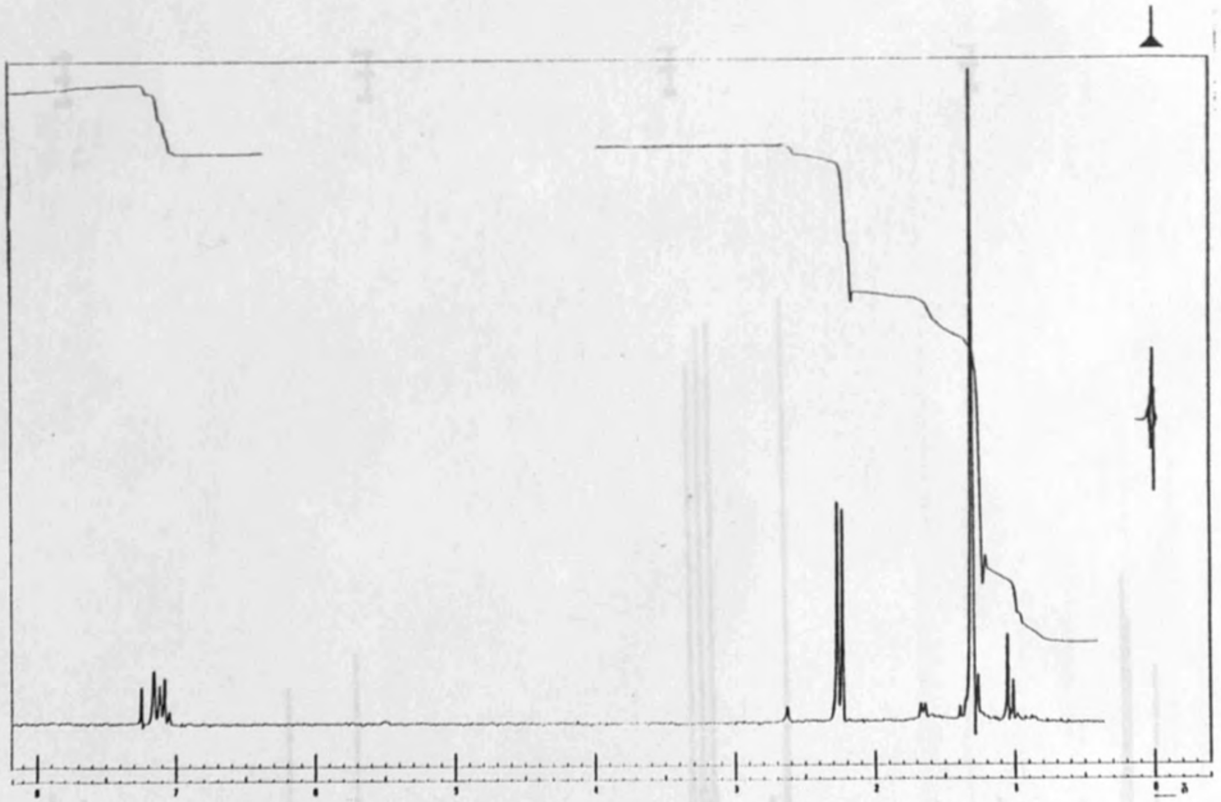
Spectrum (9) ^{1}H.n.m.r. of compound " G ".



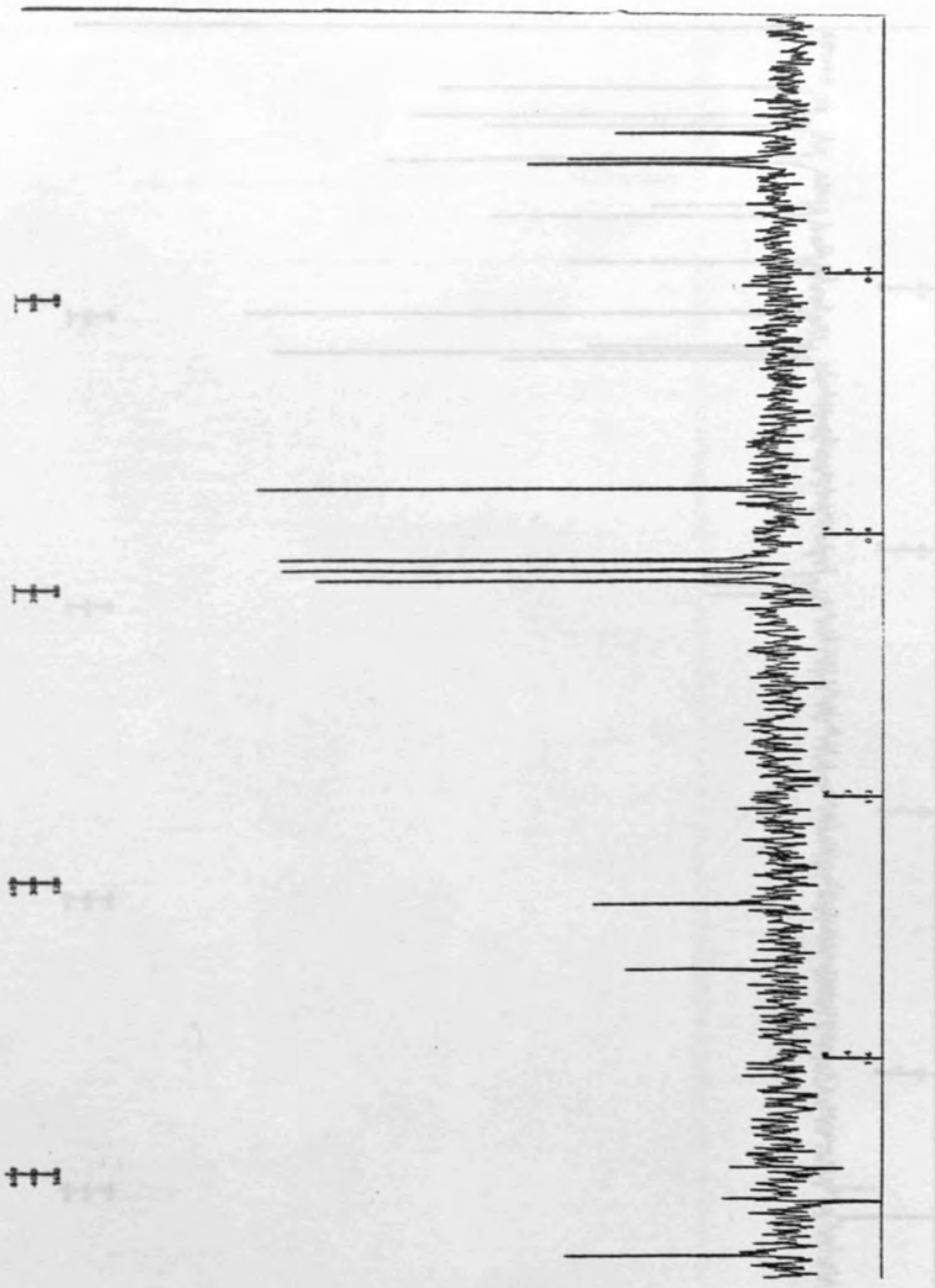
Spectrum (10) ^{1}H. n.m.r. of compound " H "



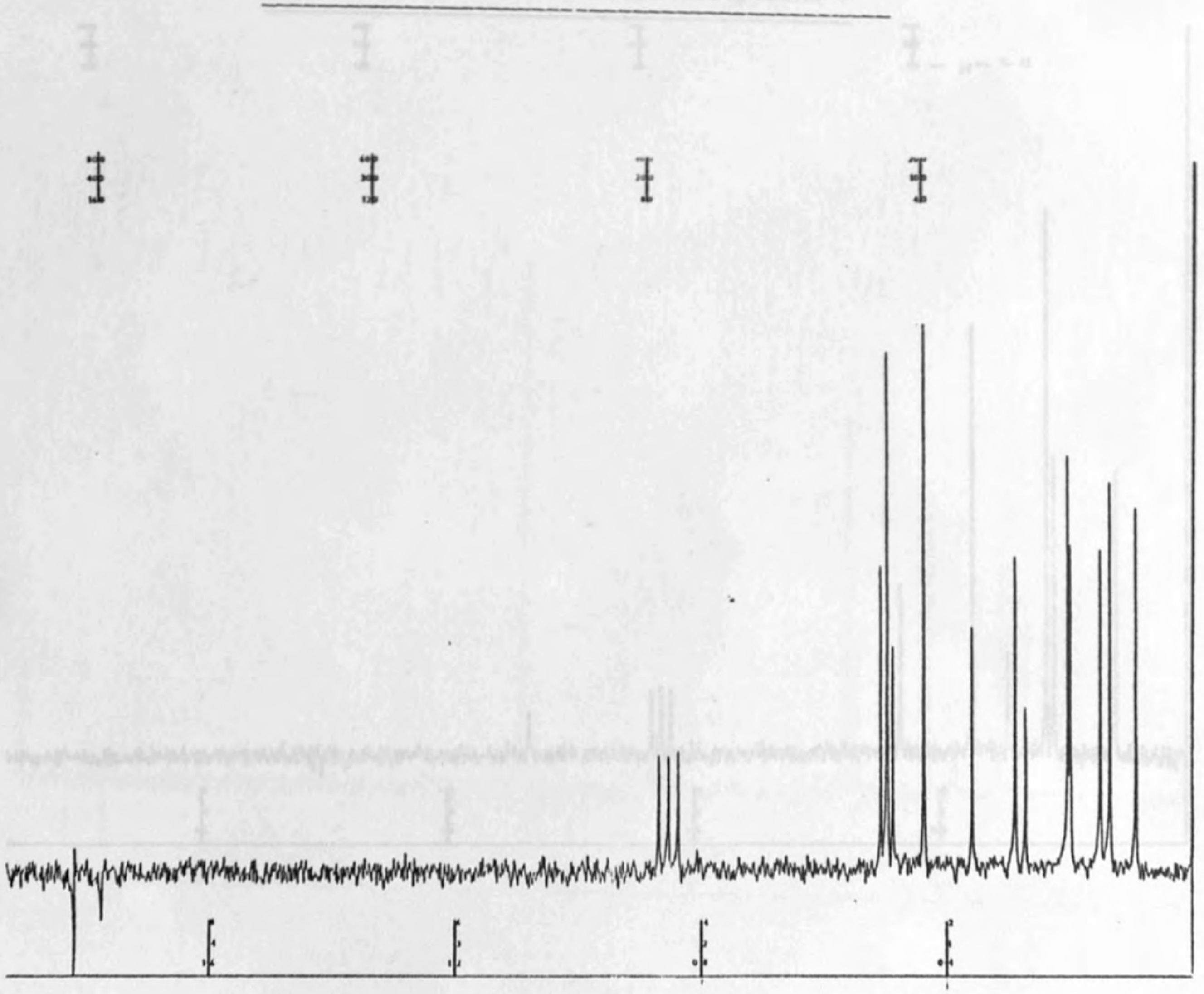
Spectrum (11) ^{1}H. n.m.r. of compound " I "



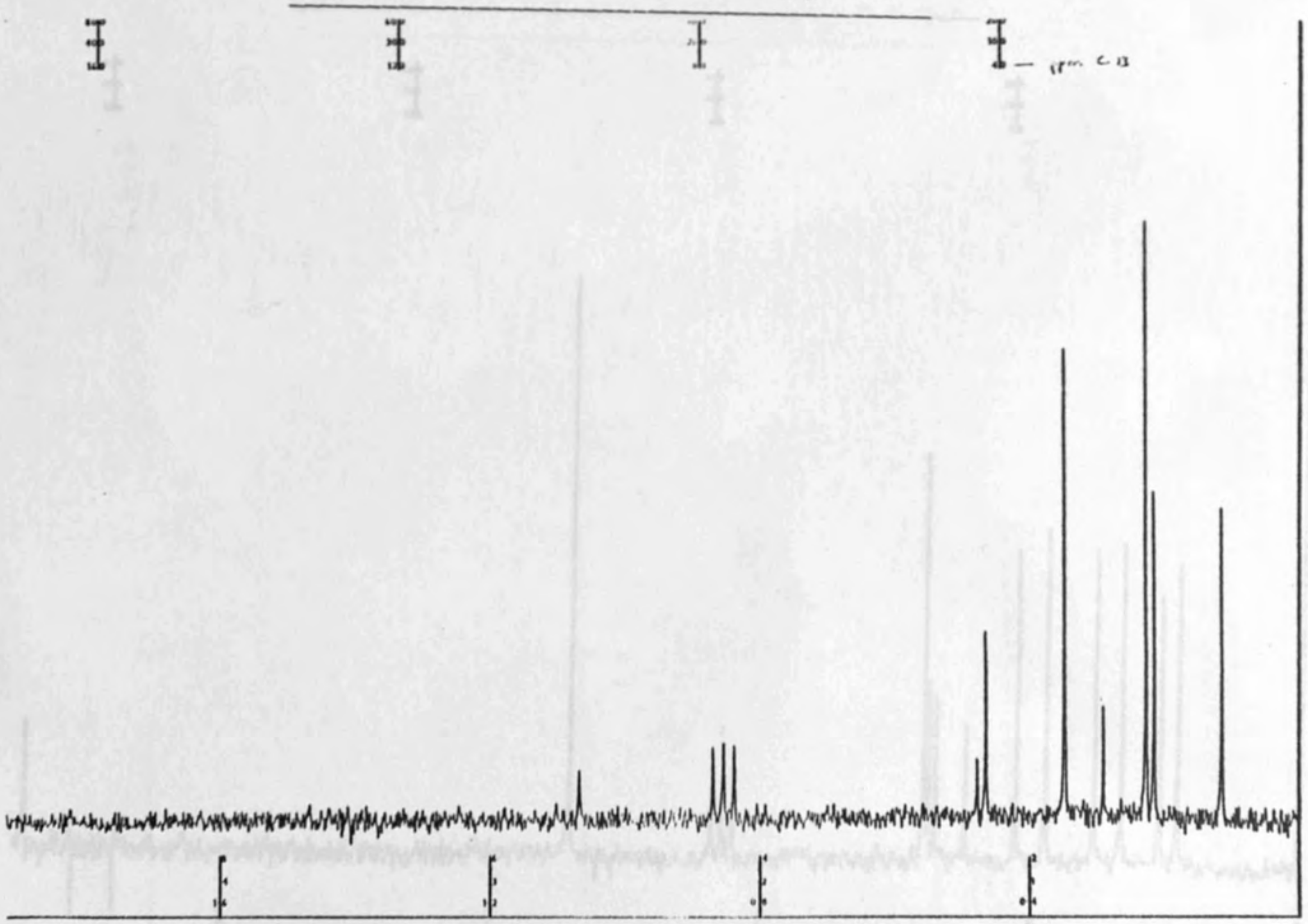
Spectrum (12) ^{13}C.n.m.r. of compound " A "



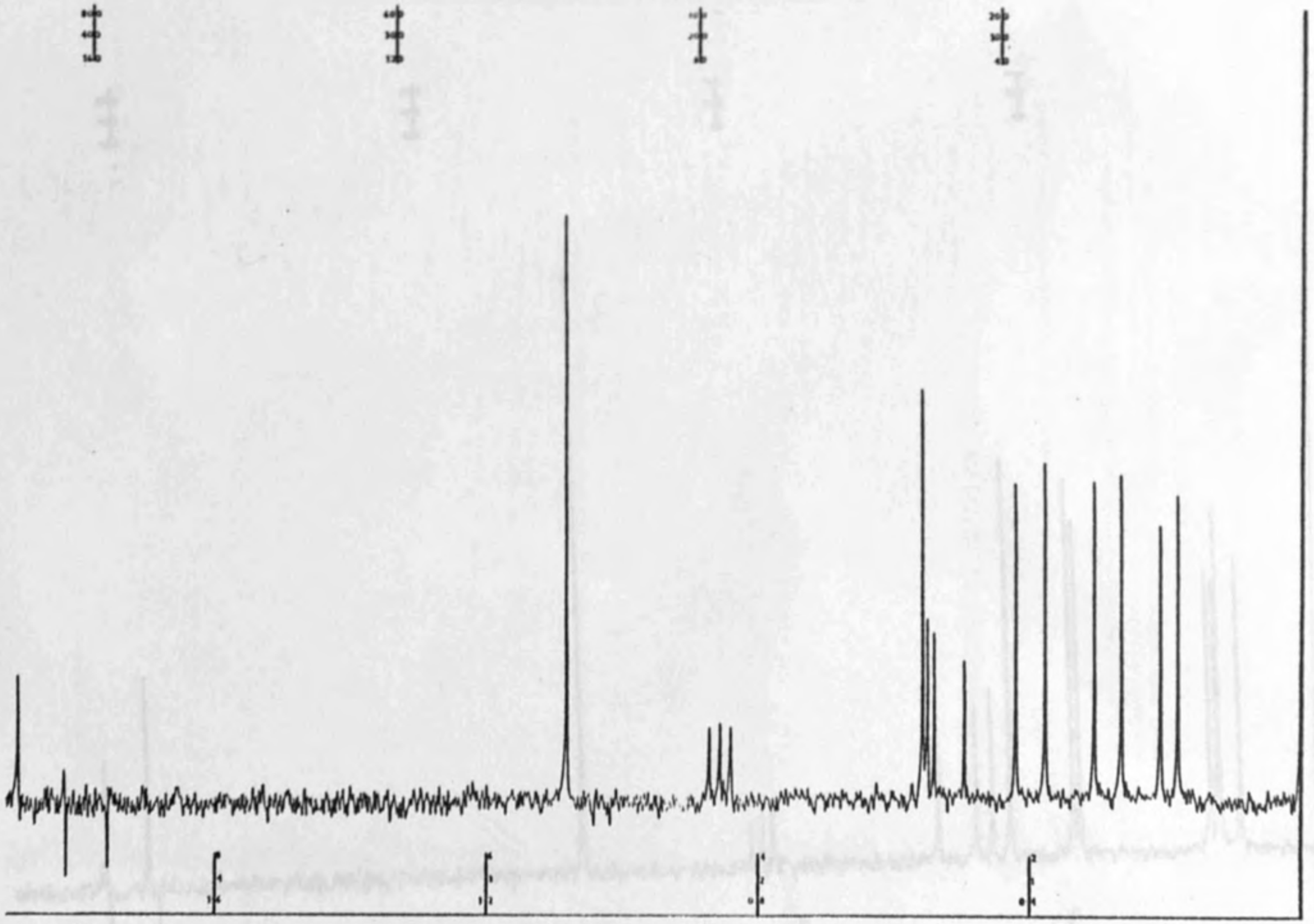
Spectrum (13) ^{13}C. n.m.r. of compound " B "

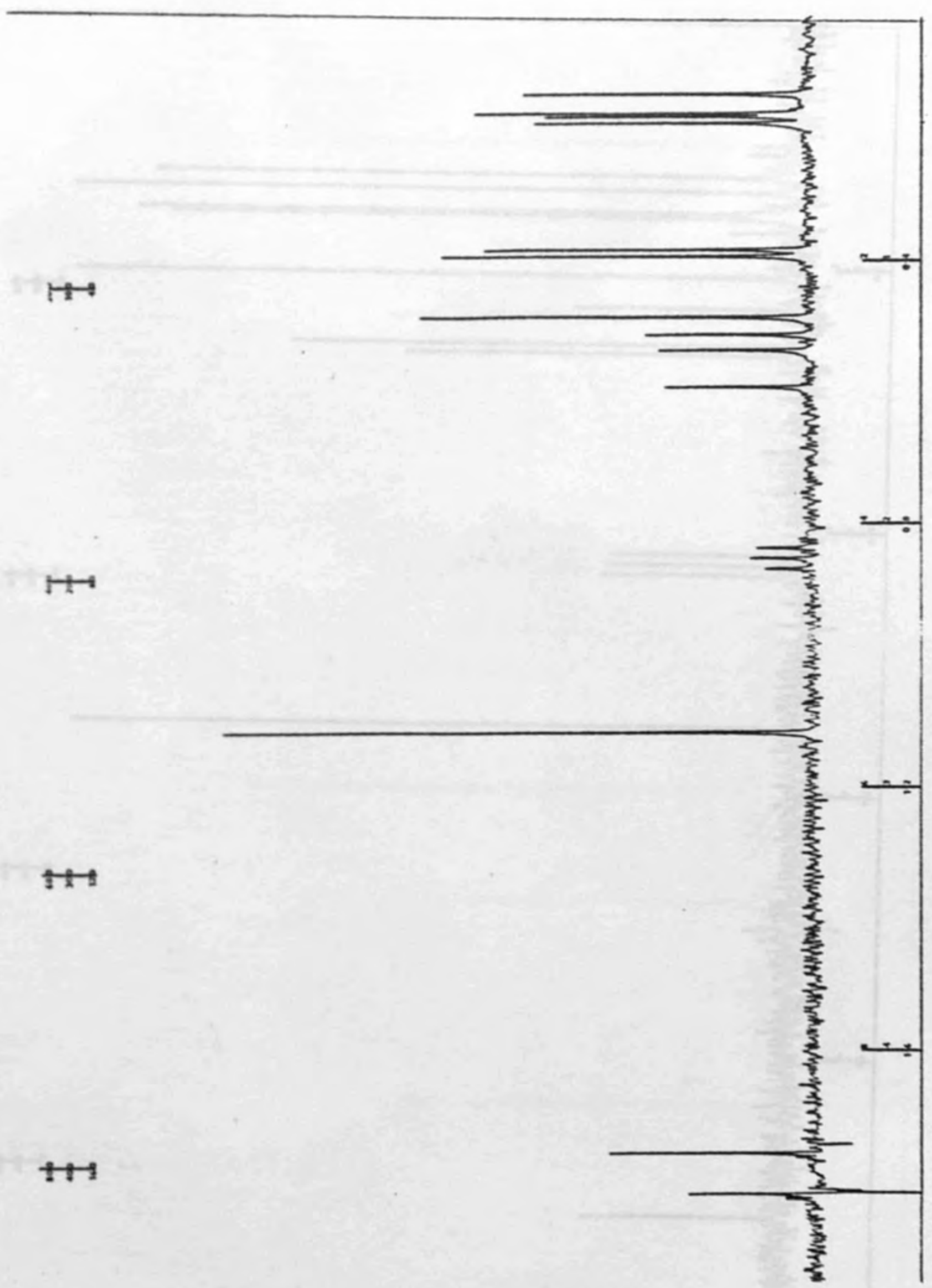


Spectrum (14) ^{13}C. n.m.r. of Tricyclene



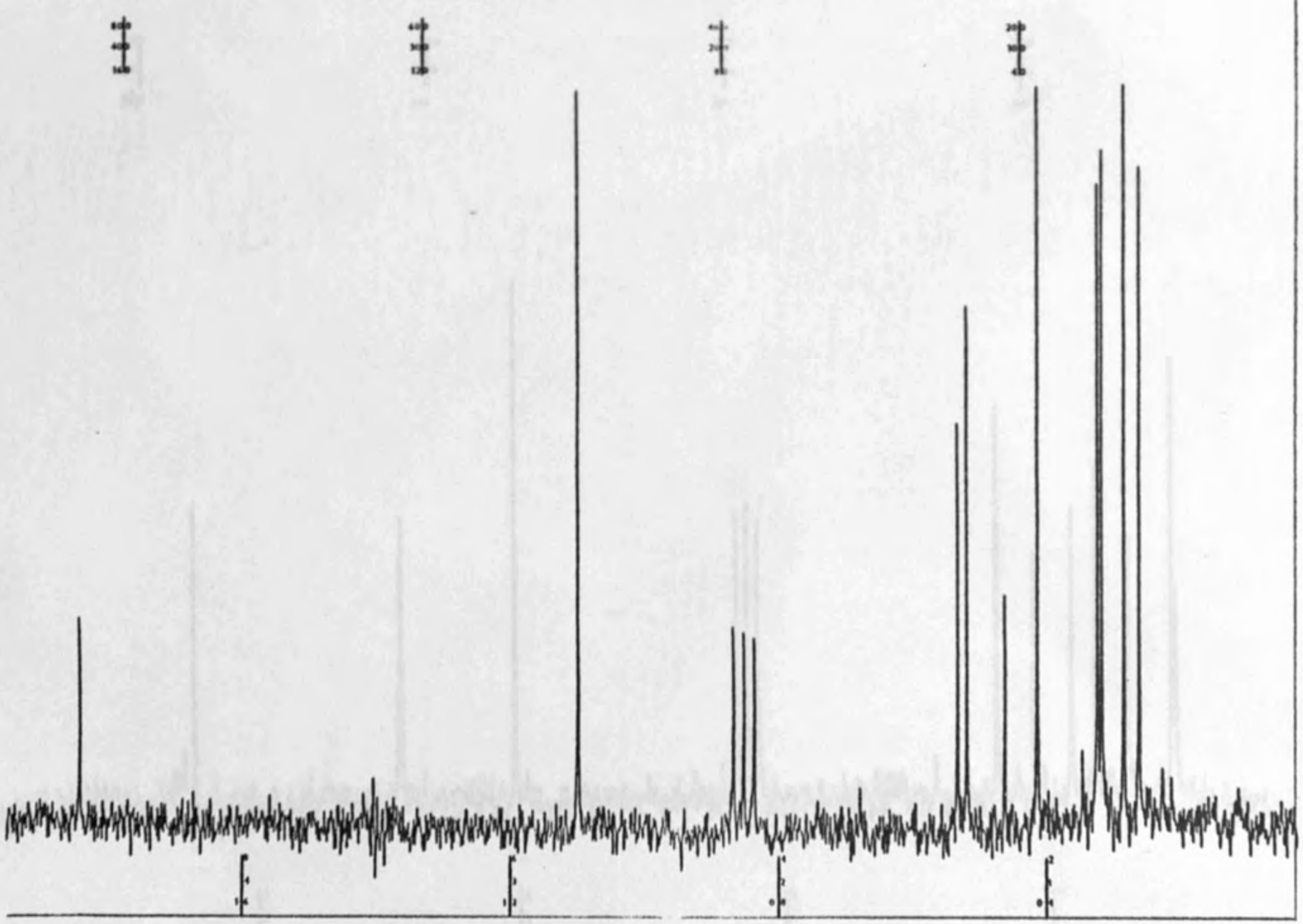
Spectrum (15) ^{13}C.n.m.r. of compound " D ".



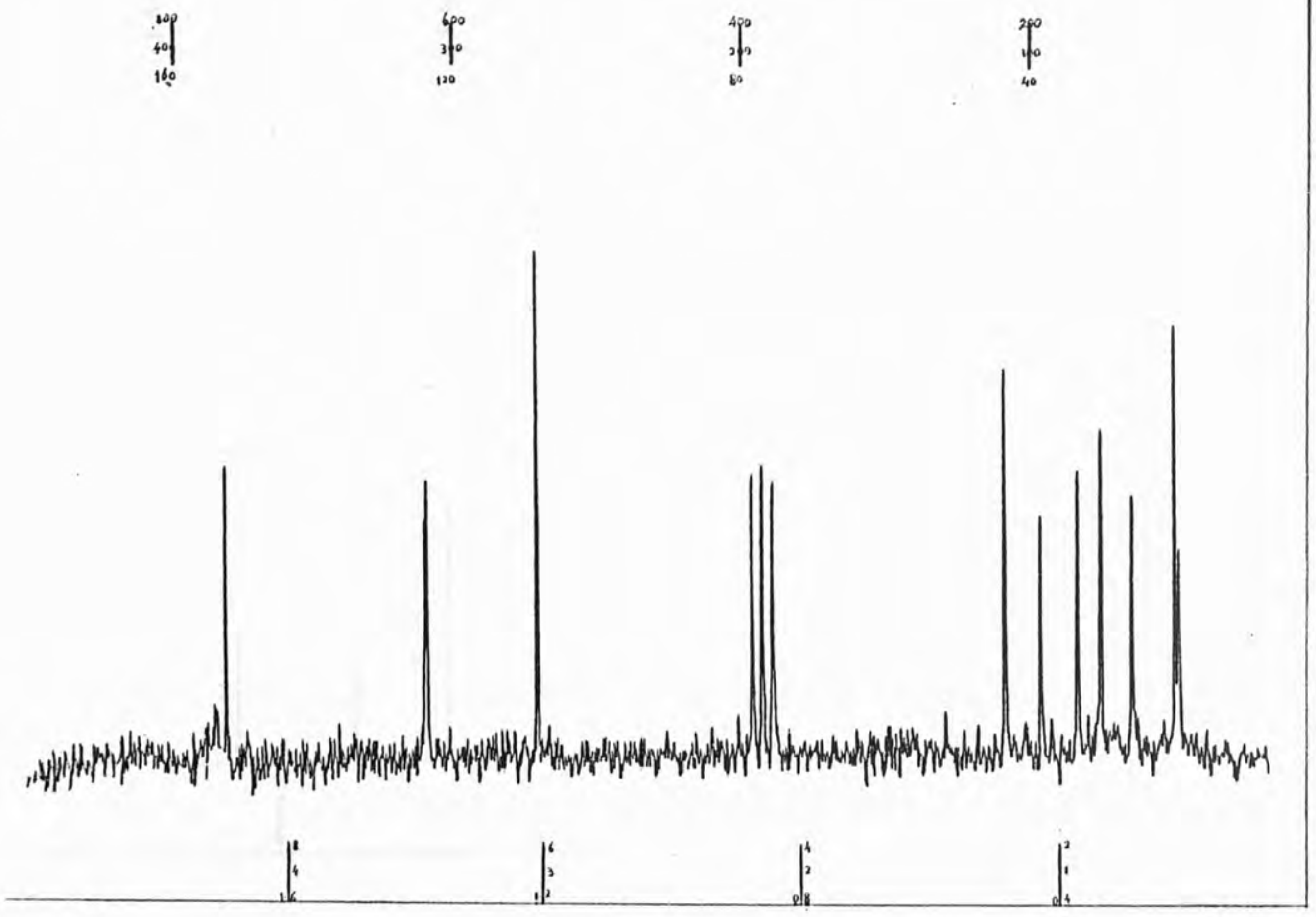


Spectrum (16) ^{13}C. n.m.r. of compound " E ".

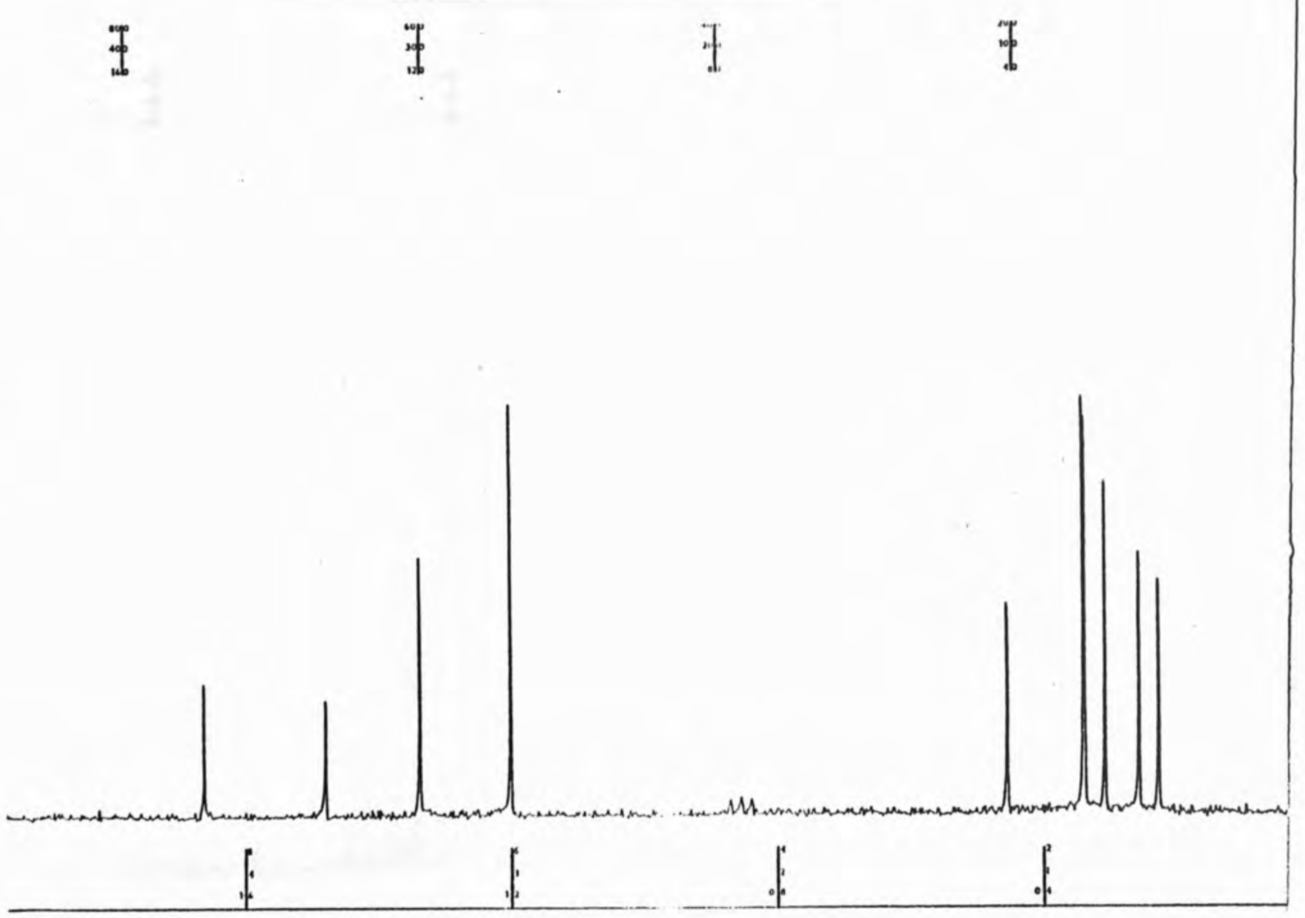
Spectrum (17) ^{13}C . n.m.r. of Camphene



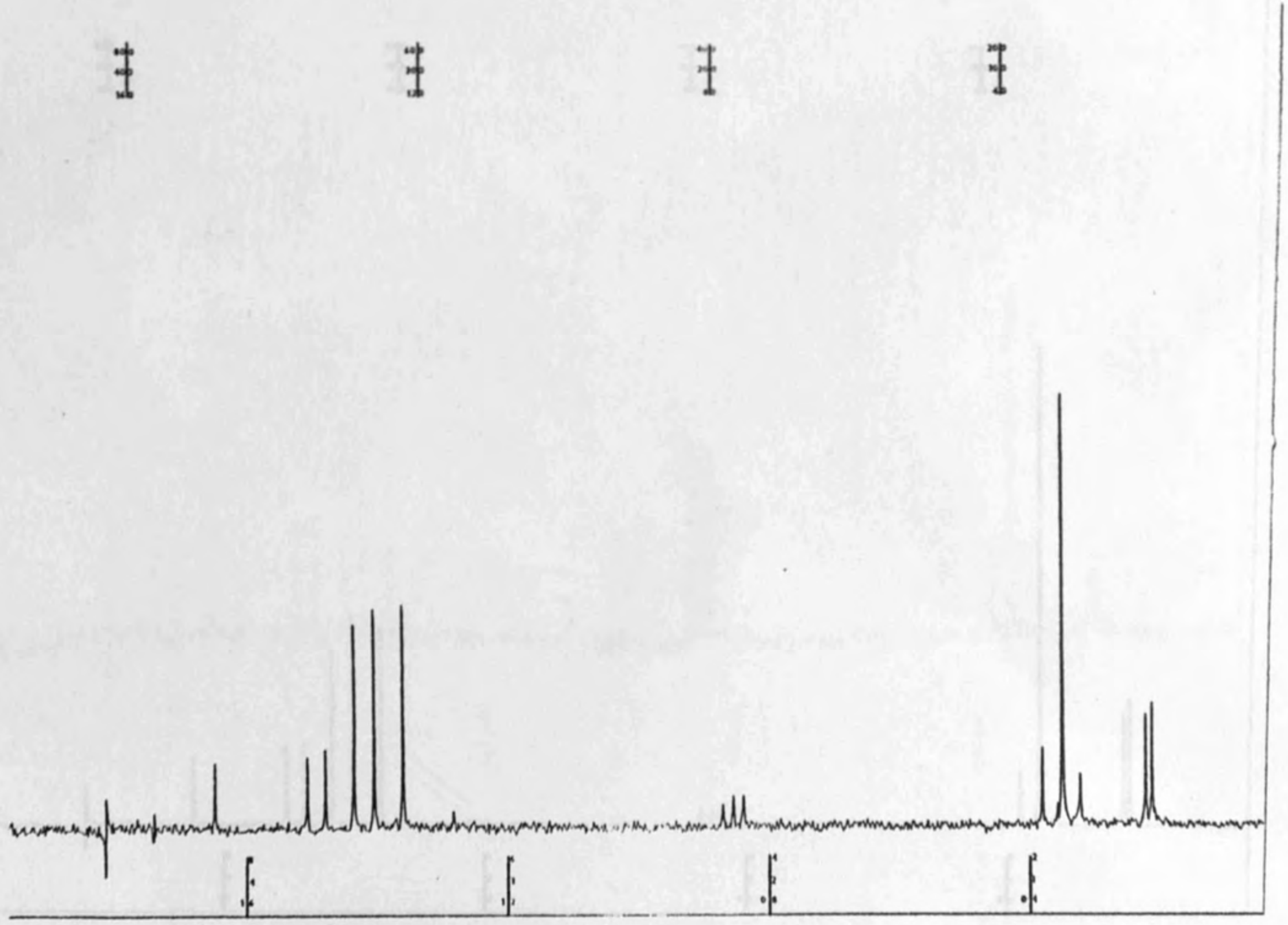
Spectrum (18) ^{13}C.n.m.r. of compound " F "



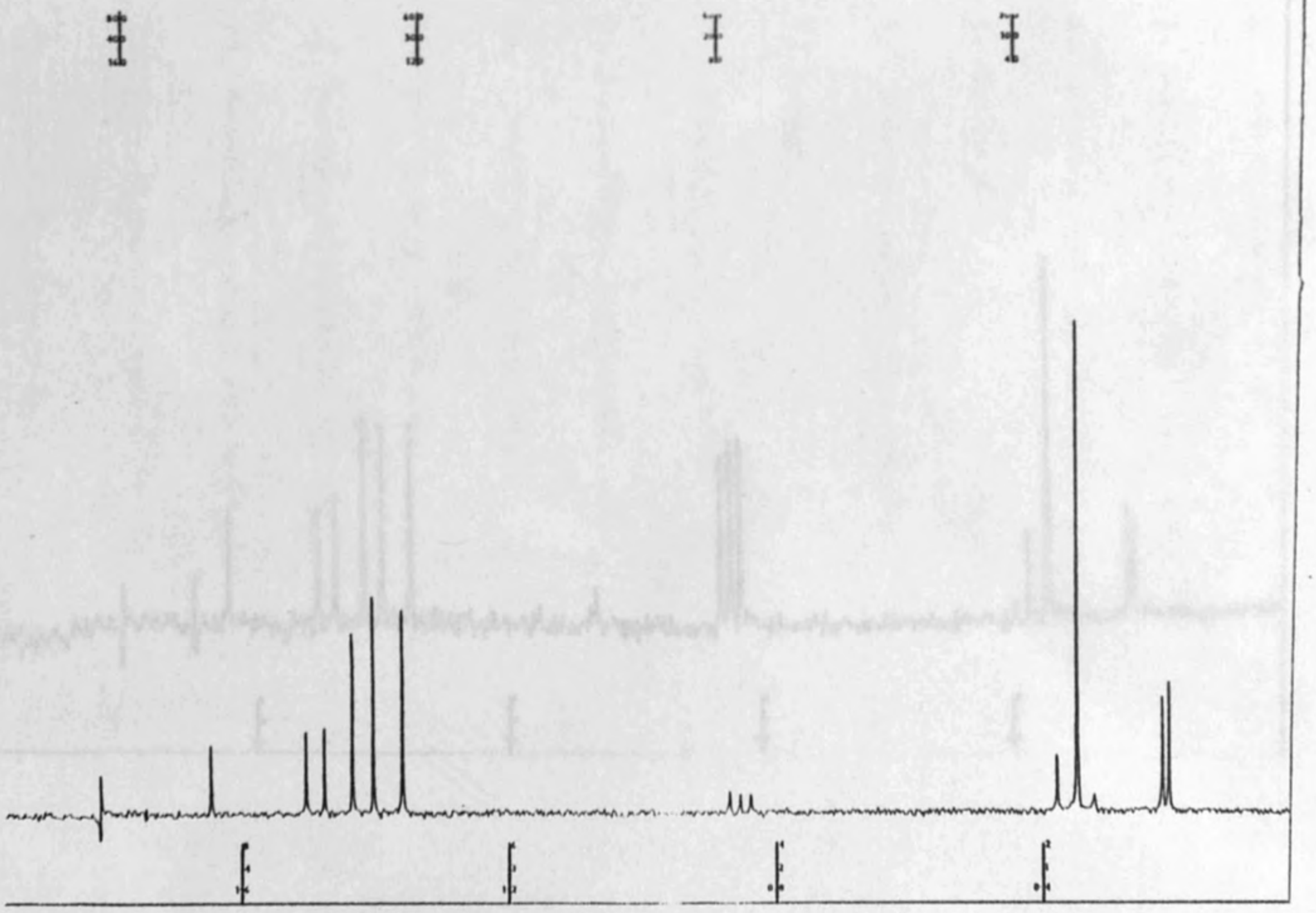
Spectrum (19) ^{13}C.n.m.r. of L~~i~~monene

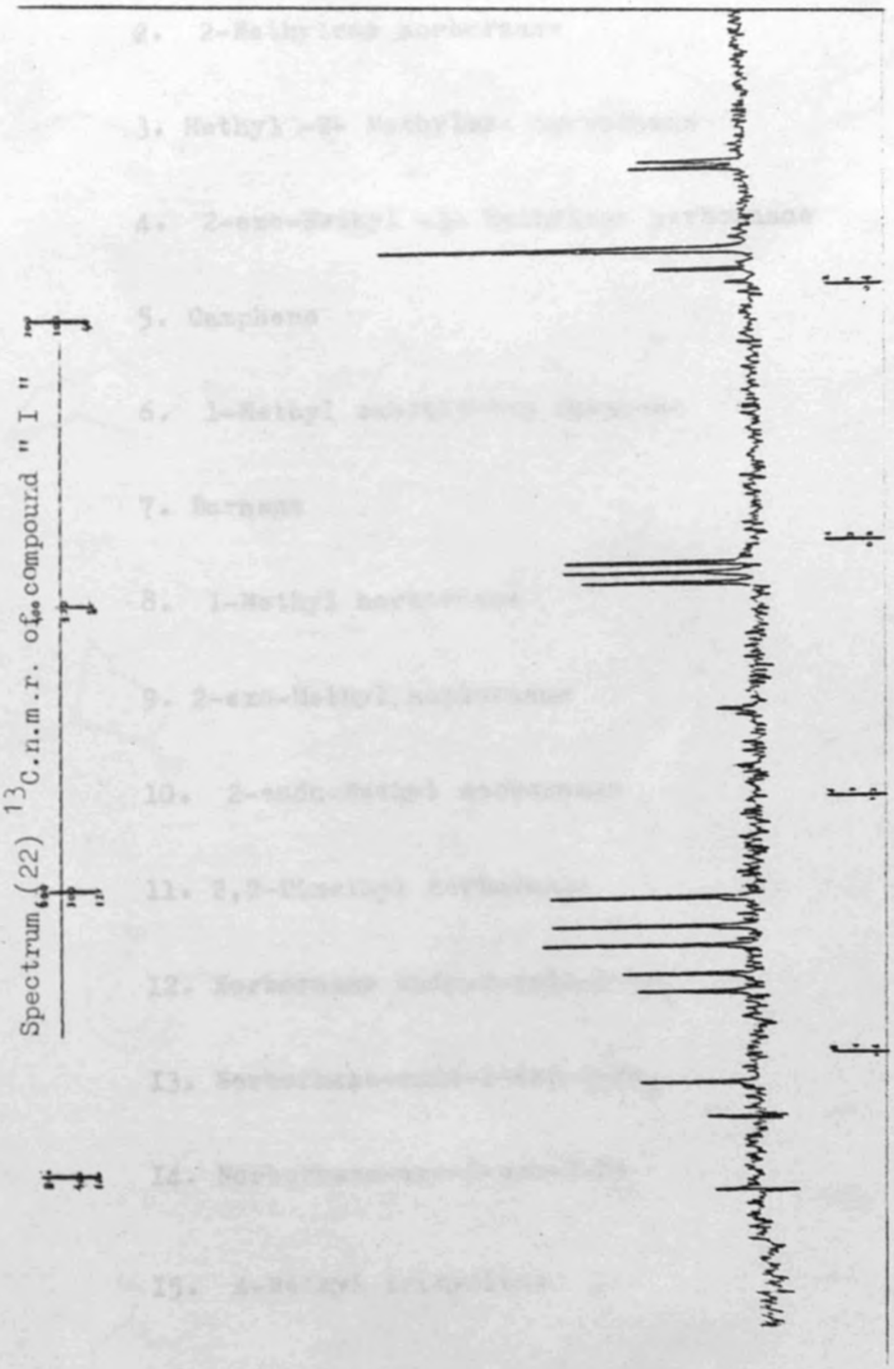


Spectrum (20) ^{13}C. n.m.r. of compound " G "



Spectrum (21) ^{13}C.n.m.r. of compound " H ".





Spectrum (22) ^{13}C.n.m.r. of compound " I "

List of Compounds

1. Norbornane

2. 2-Methylene norbornane

3. Methyl -2- Methylene norbornane

4. 2-exo-Methyl -3- Methylene norbornane

5. Camphene

6. 1-Methyl substituted Camphene

7. Bornane

8. 1-Methyl norbornane

9. 2-exo-Methyl norbornane

10. 2-endo-Methyl norbornane

11. 2,2-Dimethyl norbornane

I2. Norbornane endo-2-endo-3-Me_2

I3. Norbornane-endo-2-exo-3-Me_2

I4. Norbornane-exo-2-exo-3-Me

I5. 4-Methyl tricyclene

I6. Tricyclene

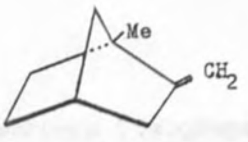
I7. a) o-Xylene b) m-Xylene c) p-Xylene

I8. t-Butyl benzene I9. 4-t-butyl toluene

20. Limonene

(1)

(2)



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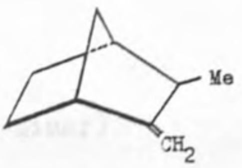

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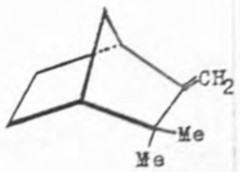

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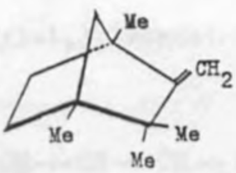

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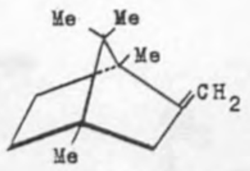

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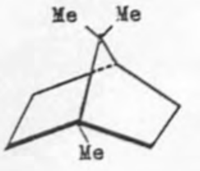

(7)

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(9)

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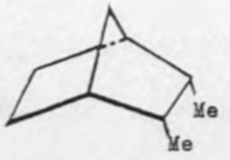
(11)



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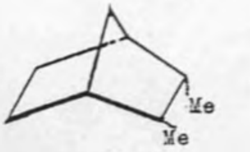

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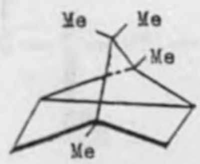
(14)



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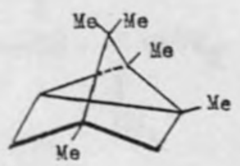

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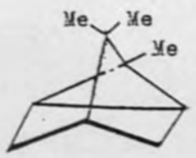

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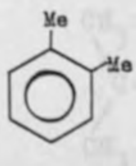
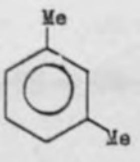
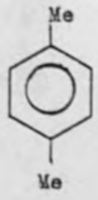


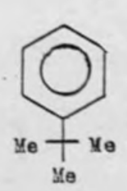
(17^{a})



(17^{b})



(17^{c})



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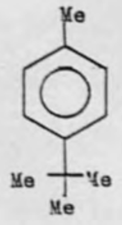

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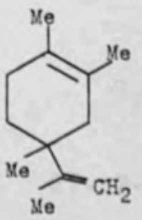

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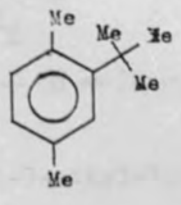

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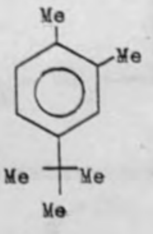

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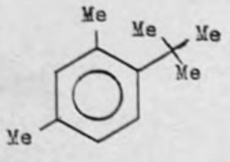

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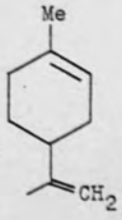
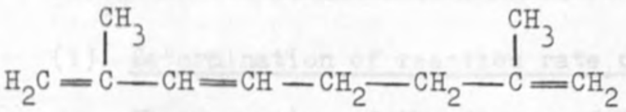


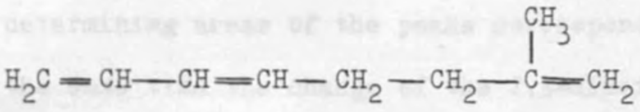
(20)

21. 2,7-Dimethyl-1,3,7-octatriene (Isoprene dimer)



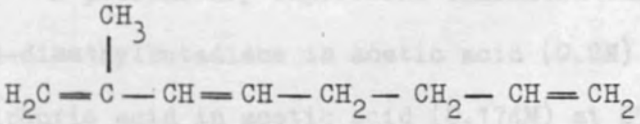
$$H_2C{=}C(CH_3){-}CH{=}CH{-}CH_2{-}CH_2{-}C(CH_3){=}CH_2$$

22. 7-Methyl-1,3,7-octatriene



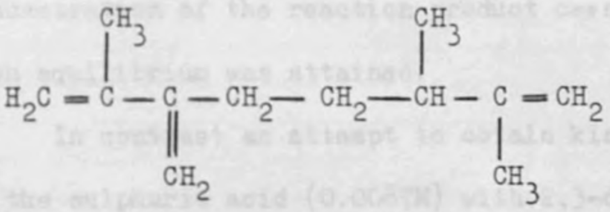
$$H_2C{=}CH{-}CH{=}CH{-}CH_2{-}CH_2{-}C(CH_3){=}CH_2$$

23. 2-Methyl-1,3,7-octatriene



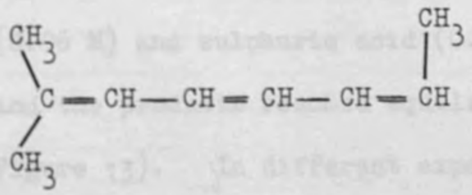
$$H_2C{=}C(CH_3){-}CH{=}CH{-}CH_2{-}CH_2{-}CH{=}CH_2$$

24. 2,6-Dimethyl-3-methylene-1,7-octadiene



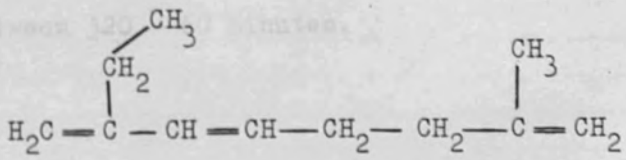
$$H_2C{=}C(CH_3){-}C({=}CH_2){-}CH_2{-}CH_2{-}CH(CH_3){-}C(CH_3){=}CH_2$$

25. 2-Methyl-2,4,6-octatriene



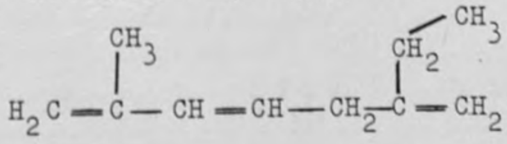
$$(CH_3)_2C{=}CH{-}CH{=}CH{-}CH{=}CH(CH_3)$$

26. 2-Ethyl-7-methyl-1,3,7-octatriene



$$H_2C{=}C(CH_2CH_3){-}CH{=}CH{-}CH_2{-}CH_2{-}C(CH_3){=}CH_2$$

27. 2-Methyl-7-ethyl-1,3,7-octatriene



$$H_2C{=}C(CH_3){-}CH{=}CH{-}CH_2{-}C(CH_2CH_3){=}CH_2$$

III Kinetics of the formation of dimers of 2,3-Dimethylbutadiene

(i) Determination of reaction rate of Acid catalysed Dimerisation

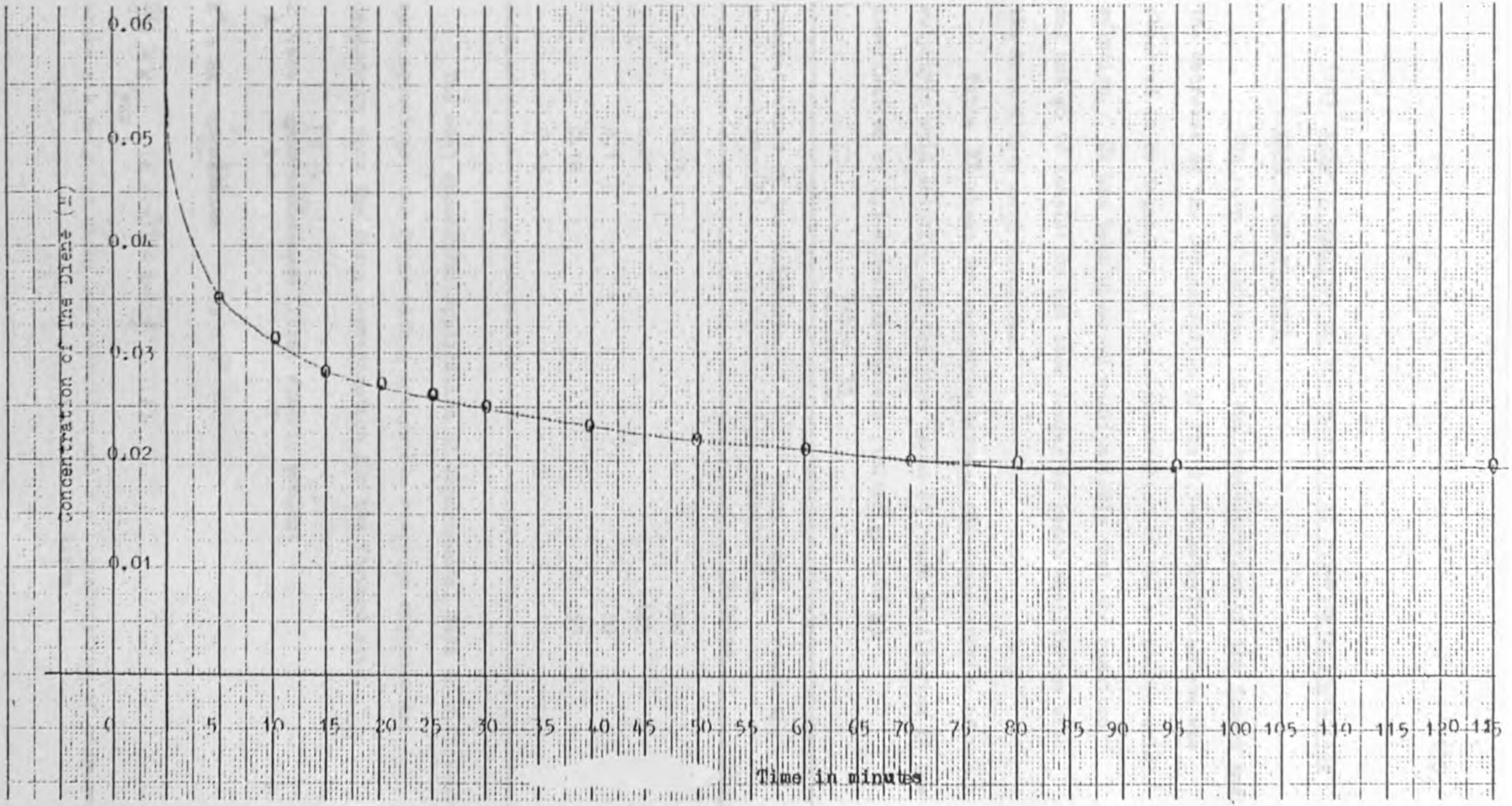
The formation of the dimers of 2,3-dimethylbutadiene was monitored at different times during the reaction by using g.l.c. and by determining areas of the peaks corresponding to the different dimers. At the same time the change of the 2,3-dimethylbutadiene concentration was similarly recorded.

A preliminary experiment indicated that when a solution of 2,3-dimethylbutadiene in acetic acid (0.2M) reacted with a solution of sulphuric acid in acetic acid (0.174M) at 25° the decrease in the concentration of 2,3-dimethylbutadiene and the increase in the concentration of the reaction product ceased after about seven minutes when equilibrium was attained.

In contrast an attempt to obtain kinetic data using a solution of the sulphuric acid (0.0087M) with 2,3-dimethylbutadiene (0.2 M) in acetic acid failed since the reaction was too slow.

When a reaction mixture consisting of 2,3-dimethylbutadiene (0.06 M) and sulphuric acid (0.1 M) in acetic acid was used, the diene and the products reached equilibrium after eighty minutes (see Figure 13). In different experiments the concentrations of sulphuric acid in acetic acid was varied between (0.03 M and 0.12 M) and reacted with 2,3-dimethylbutadiene (0.06 M) equilibrium was observed between 320 - 60 minutes.

Figure 13 The decrease in the concentration of 2,3- Dimethyl butadiene with time.



(ii) Kinetic analysis of the reaction of 2,3-Dimethylbutadiene with sulphuric Acid

The rate of increase in the concentration of the dimers and the decrease of the concentration of the 2,3-dimethylbutadiene was observed to be dependent on the concentration of the sulphuric acid solution. It has been observed qualitatively that the reaction did not go to completion but took longer to reach equilibrium with the more dilute acid solutions.

Table 33 shows the variation between the concentration of sulphuric acid solution and the time taken to reach equilibrium in the dimerisation of 2,3-dimethylbutadiene (initially 0.06 M)

Table 33

Concentration of the sulphuric acid solution. (M)	Time taken to reach the equilibrium minutes
0.03	320
0.07	140
0.1	80
0.12	55
0.13	17

The most successful application of experimental data to different rate equations, was found with a reversible reaction second-order dependence upon the diene concentration for the forward step.

$$\underset{A}{\text{2 Diene}} \underset{k-1}{\overset{[H^+]k_{exp}}{\rightleftharpoons}} \underset{X}{\text{First dimeric product}}$$

$$H^+ + 2A \underset{k-1}{\overset{k_{1\,exp}}{\rightleftharpoons}} X + H^+$$

$$\frac{dx}{dt} = k_{1_{exp}} (a - x)^2 - k\text{-}1\,\frac{x}{2} \qquad (I)$$

where a = original diene concentration and x = concentration of consumed diene

At equilibrium $\frac{dx}{dt} = 0$

$$\therefore \quad 0 = k_{1_{exp}} (a - x_e)^2 - k-1 \; \frac{x_e}{2} \qquad \text{(II)}$$

where x_e is the concentration of the consumed diene at equilibrium

$$\therefore \quad k_{-1} = \frac{{}^{2}k_{exp} (a - x_e)^2}{x_e} \qquad \text{(III)}$$

and by substituting III in I

$$\therefore \quad \frac{dx}{dt} = k_{1_{exp}} (a - x)^2 - \frac{2k_{1_{exp}} (a - x_e)^2 x}{2x_e}$$

By using partial fractions, the integrated equation is:

$$k_{1_{exp}} \; t = \frac{x_e}{a^2 - x_e^2} \left[\ln \frac{x_e}{a^2} + \ln \frac{(a2 - xx_e)}{(x_e - x)} \right]$$

$$\ln \left(\frac{a^2 - xx_e}{x_e - x} \right) = k_1 \; \exp \left(\frac{a^2 - x_e{}^2}{x_e} \right) t + \ln \; \frac{a^2}{x_e} \qquad \text{(IV)}$$

Since the extraction of the diene into the methylene chloride solution for g.l.c. analysis is not achieved with 100% efficiency but ~ 90% a common extraction coefficient factor (f) for a and (a - x) is assumed making the extracted concentration fa and f (a - x) respectively.

Assuming that $fx = \bar{x}$ and $fa = \bar{a}$

then $x = \frac{\bar{x}}{f}$ and $a = \frac{\bar{a}}{f}$

If similarly $fx_e = \bar{x}_e$ then $x_e = \frac{\bar{x}_e}{f}$

By substituting for a, x and x_e in equation (IV)

$$\ln \left(\frac{\bar{a}^2 - \bar{x}\bar{x}_e}{\bar{x}_e - \bar{x}} \right) = \left[k_{exp} \frac{1}{f} \left(\frac{{}^{1}a^{2} - \bar{x}_e^{2}}{\bar{x}_e} \right) \right] t + \ln \; \frac{\bar{a}^2}{\bar{x}_e}$$

Figure 14 The increase of Dimeric products with time

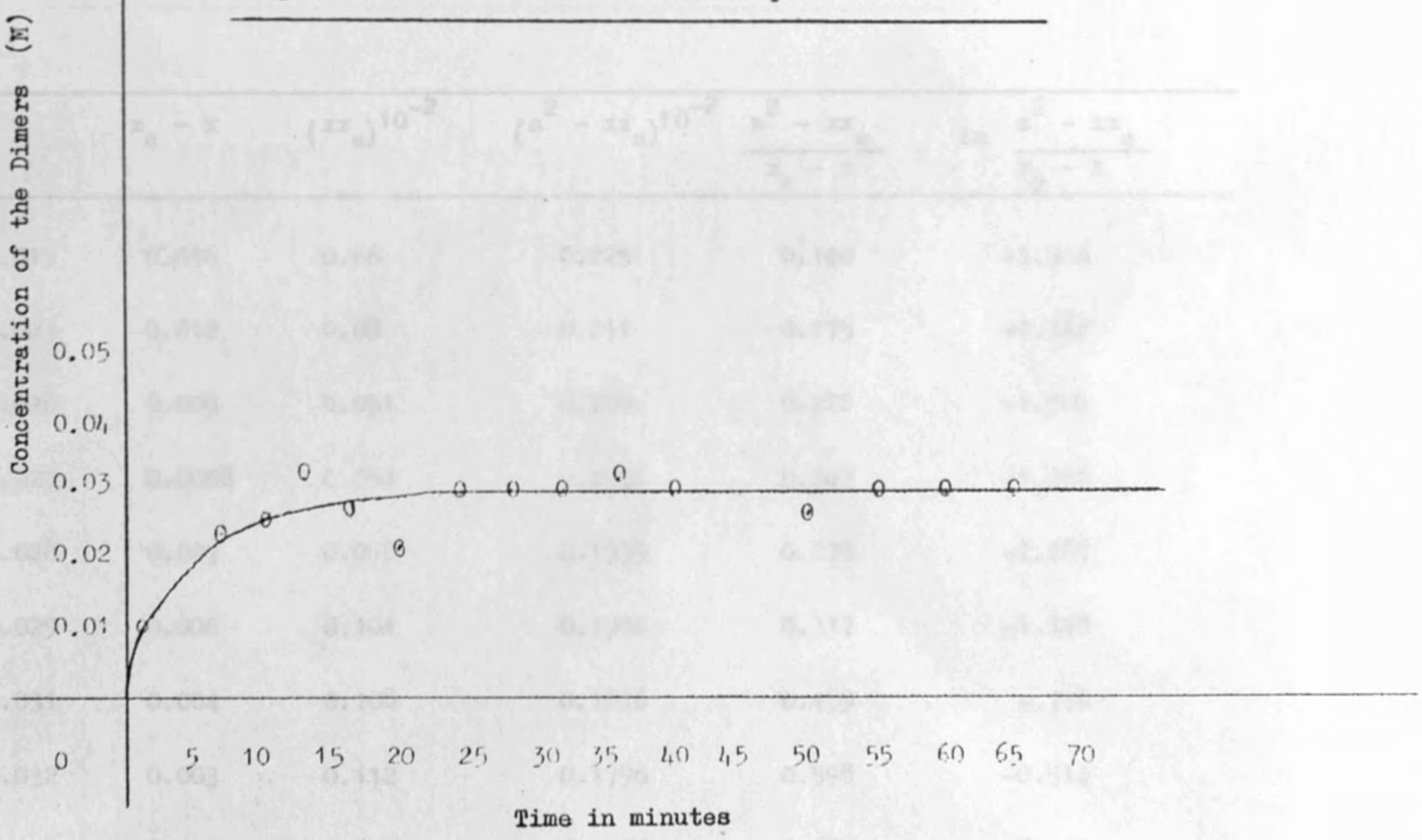


Table 34 Typical set of data for kinetic plot, (Diene concentration 0.06 M) catalysed by Sulphuric Acid (initial concentration 0.1 M)

t_{min}	$a - x$	x	$x_e - x$	$(xx_e)10^{-2}$	$(a^2 - xx_e)10^{-2}$	$\frac{a^2 - xx_e}{x_e - x}$	$\ln \frac{a^2 - xx_e}{x_e - x}$
5	0.035	0.019	0.016	0.66	0.225	0.140	-1.966
10	0.031	0.023	0.012	0.08	0.211	0.175	-1.742
15	0.028	0.026	0.009	0.091	0.200	0.222	-1.505
20	0.027	0.027	0.0008	0.094	0.1976	0.247	-1.398
25	0.026	0.028	0.007	0.098	0.1935	0.276	-1.287
30	0.025	0.029	0.006	0.101	0.1906	0.317	-1.148
40	0.023	0.031	0.004	0.108	0.1836	0.459	-.778
50	0.022	0.032	0.003	0.112	0.1796	0.598	-0.514
60	0.021	0.033	0.002	0.115	0.1766	0.883	-0.124
70	0.02	0.034	0.001	0.119	0.1726	1.726	0.545
80	0.019	0.035	0				

Figure 15 Kinetic plot for disappearance of Diene (initial concentration o.o6 M)

catalysed by Sulphuric Acid (initial concentration 0.03 M)

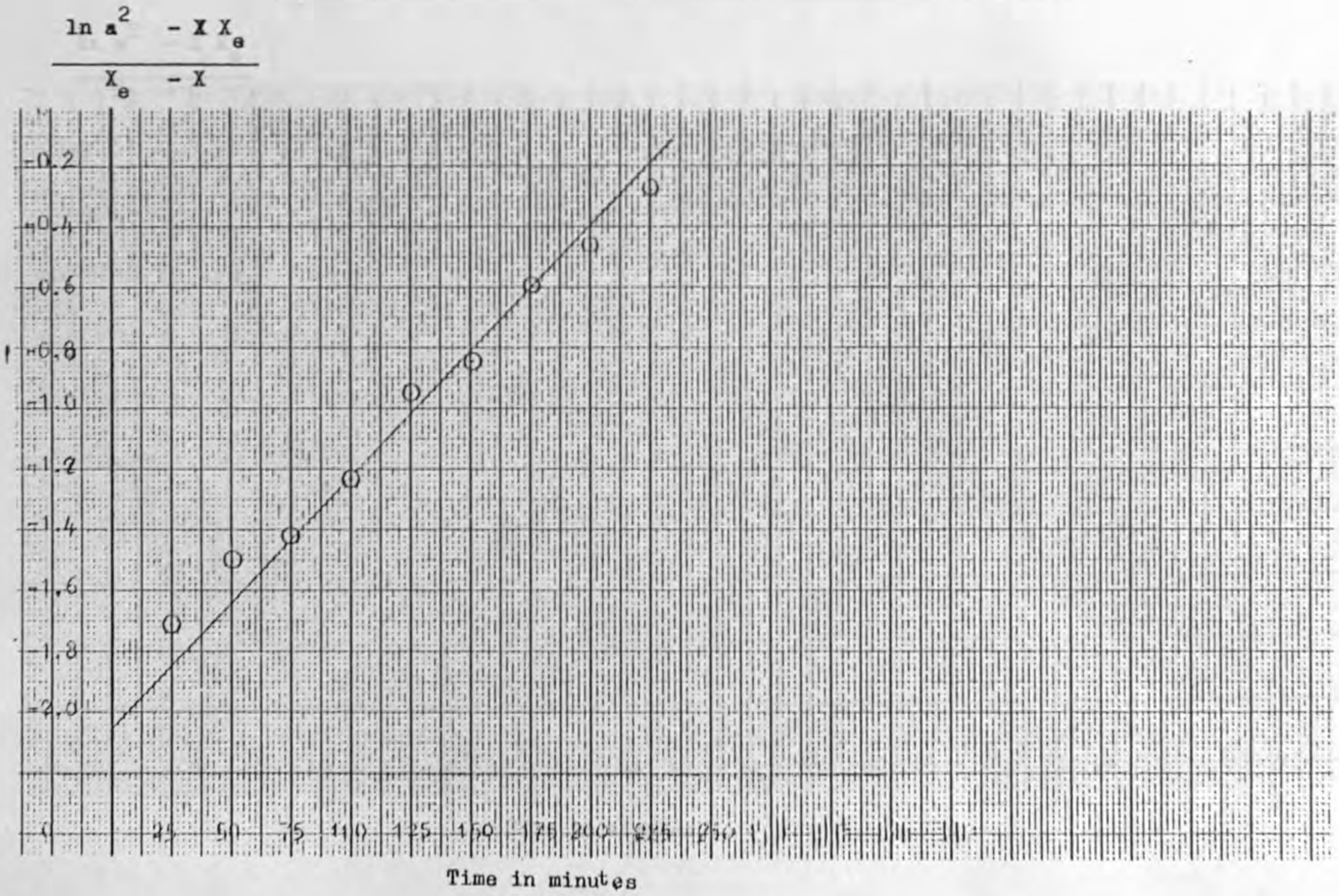


Figure 16 Kinetic plot for disappearance of Diene (initial concentration 0.06 M) catalysed by Sulphuric Acid (initial concentration 0.07 M)

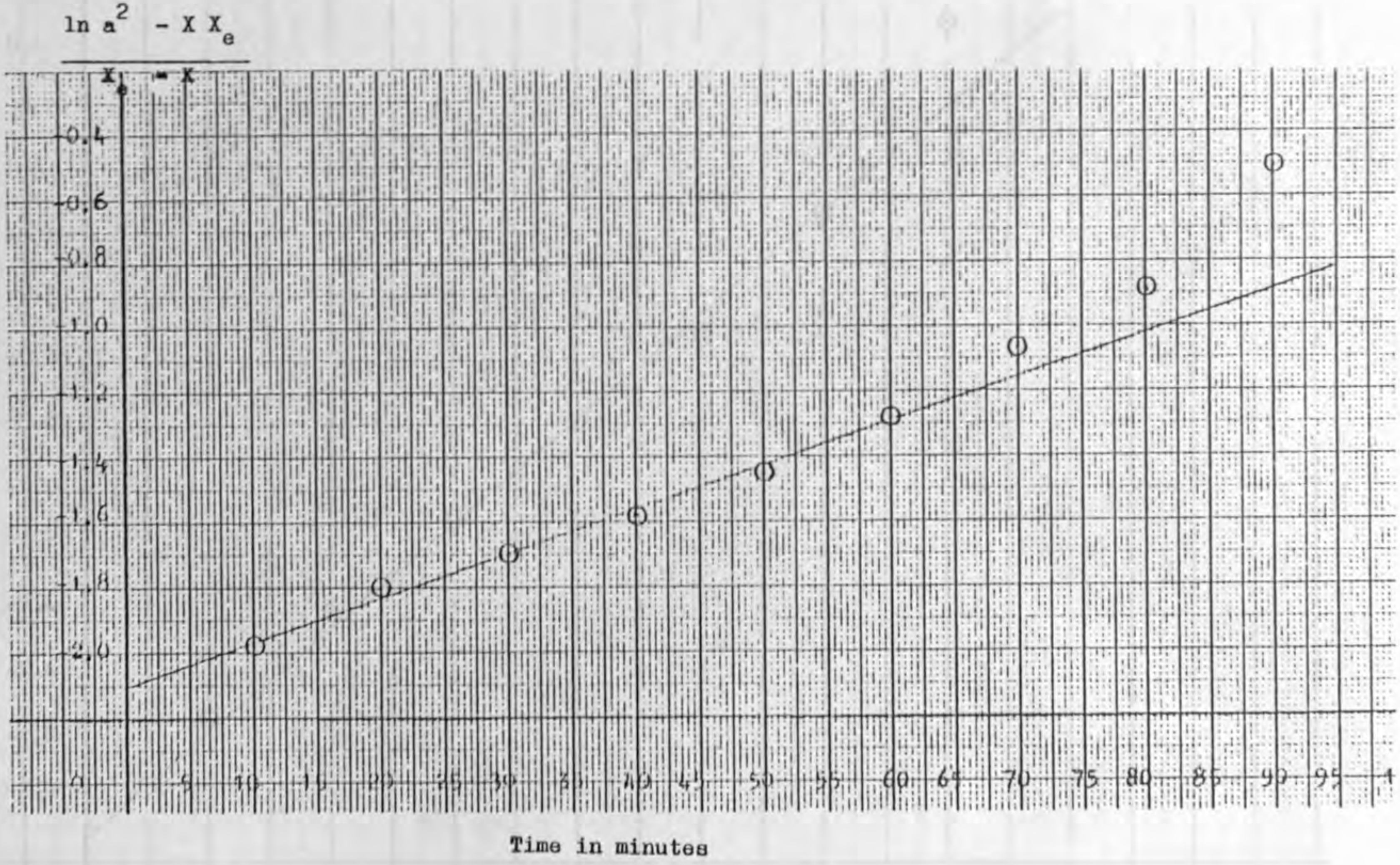


Figure 17 Kinetic plot for disappearance of Diene (initial concentration 0.06 M)

catalysed by Sulphuric Acid (initial concentration 0.1 M)

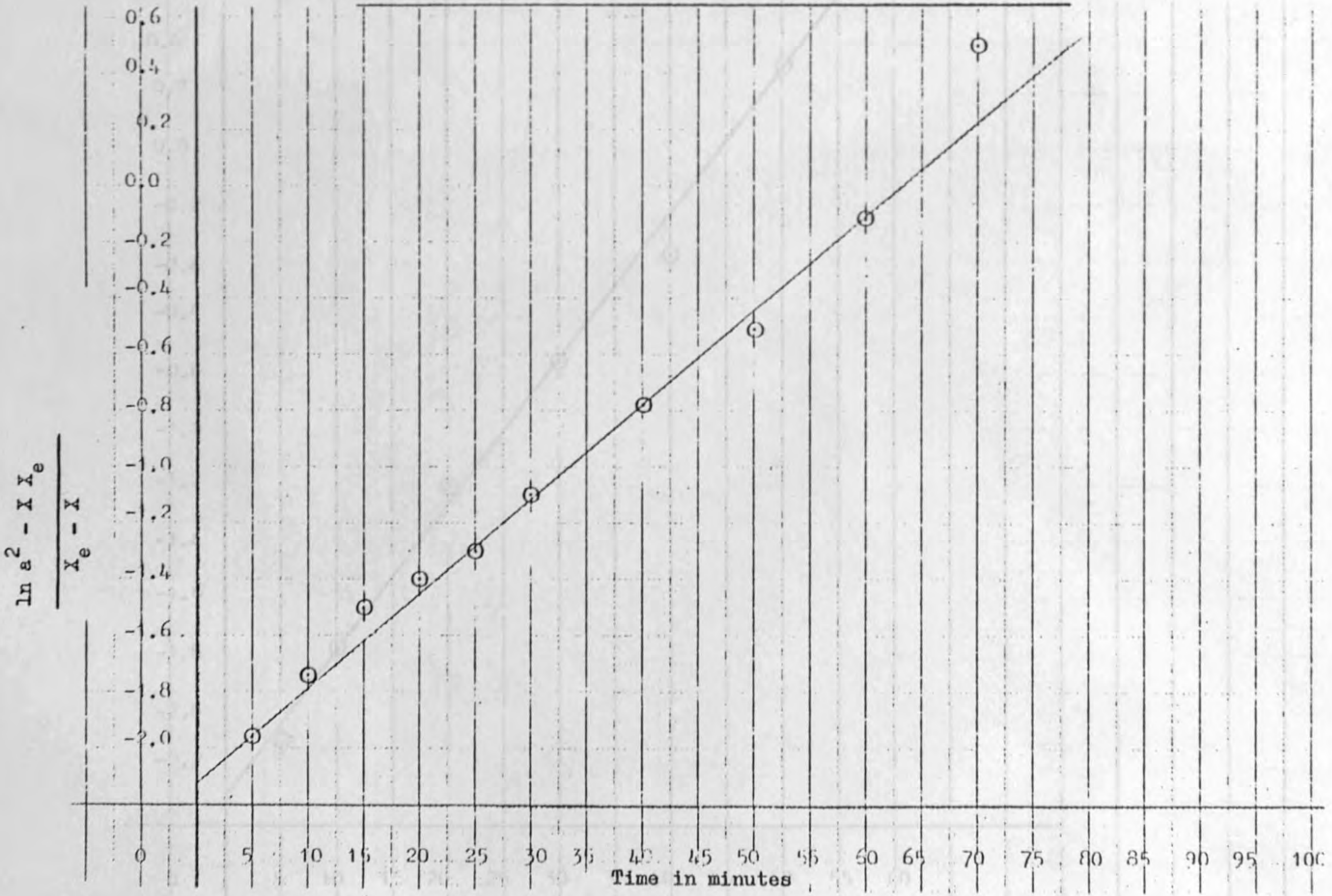


Figure 18 Kinetic plot for disappearance of Diene (initial concentration 0.06 M) catalysed by Sulphuric Acid (initial concentration 0.12 M)

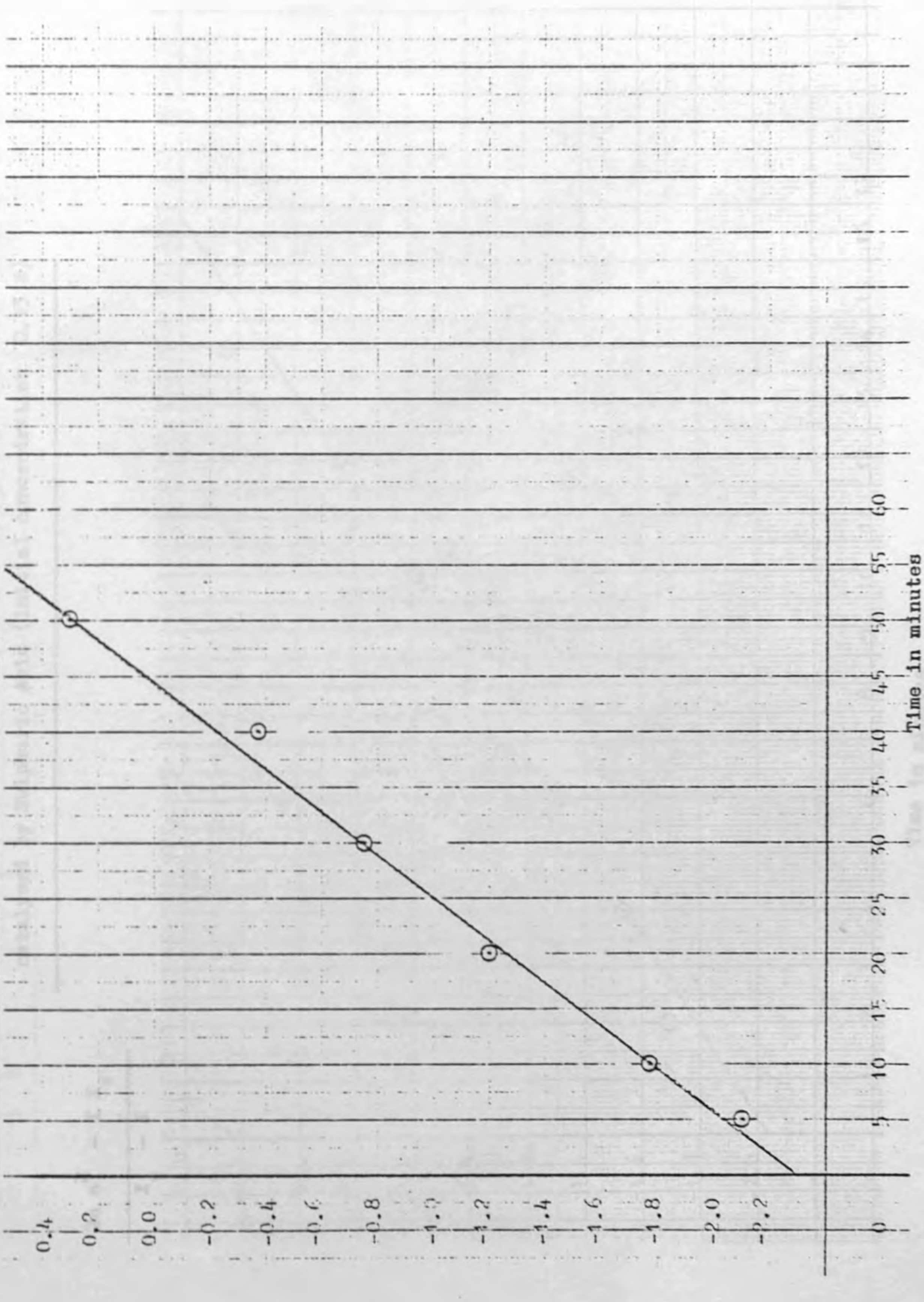


Figure 19 Kinetic plot for disappearance of Diene (initial concentration 0.06 M) catalysed by Sulphuric Acid (initial concentration 0.13 M)

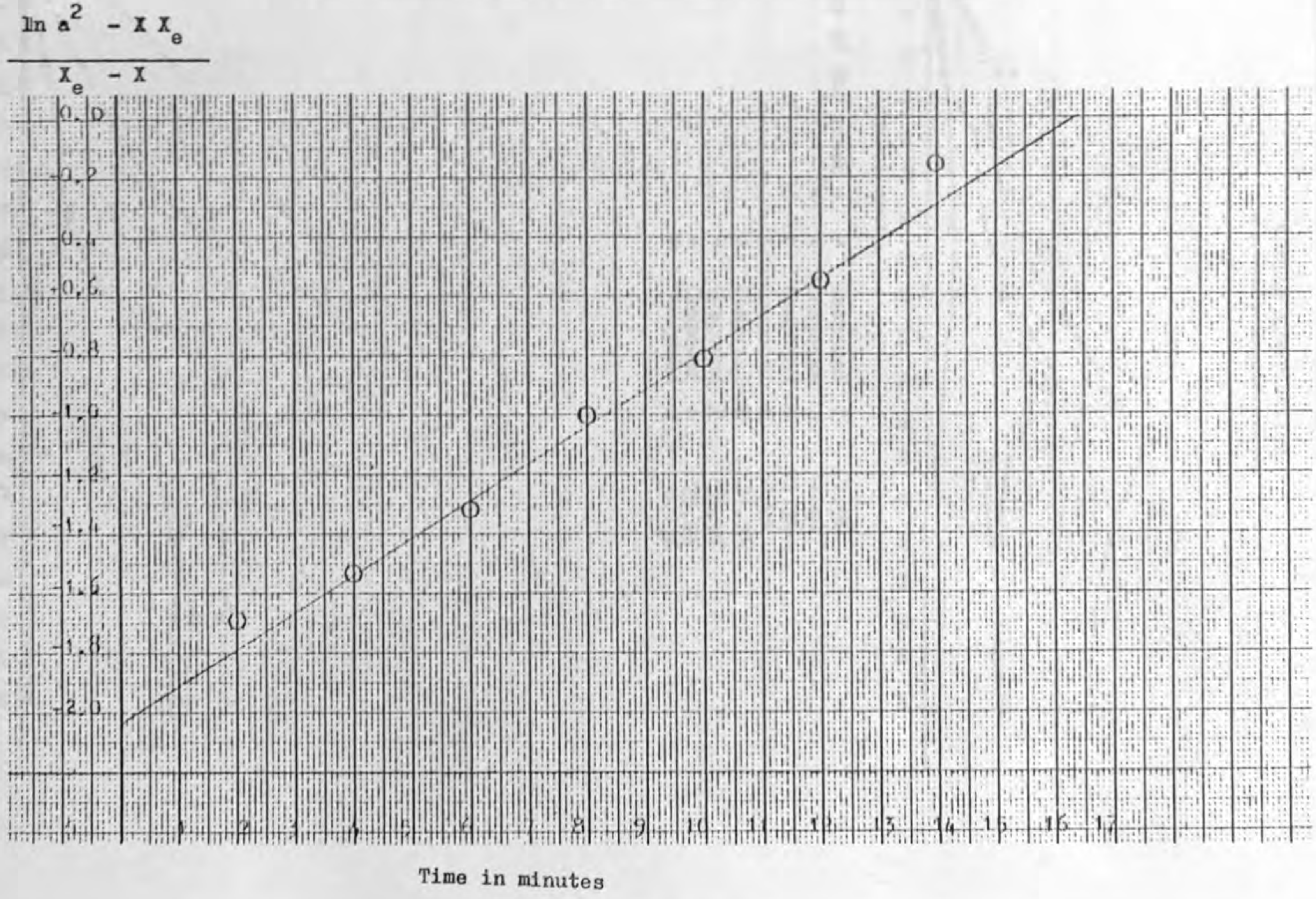
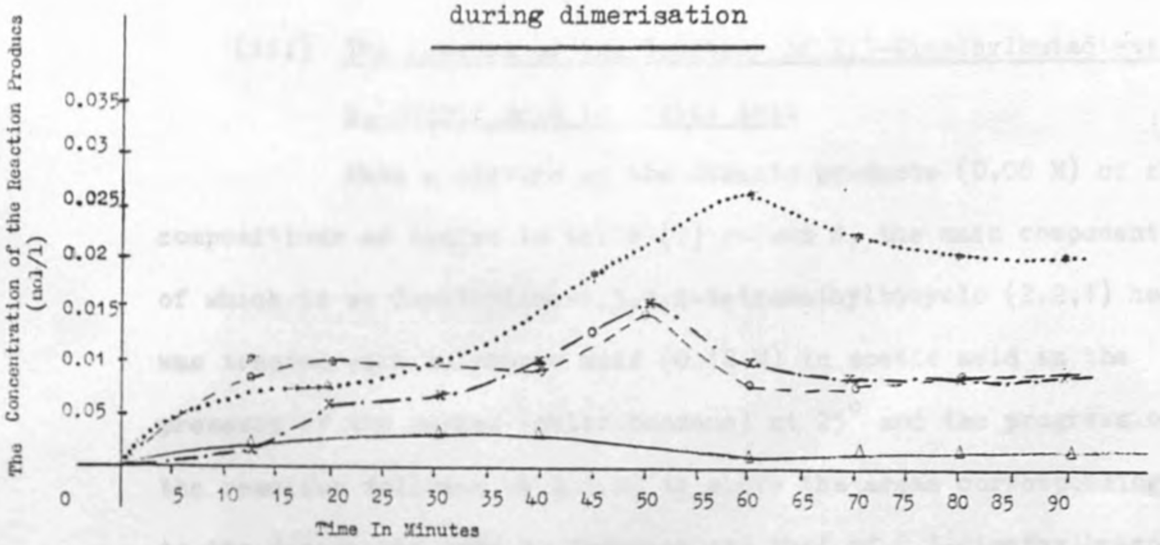
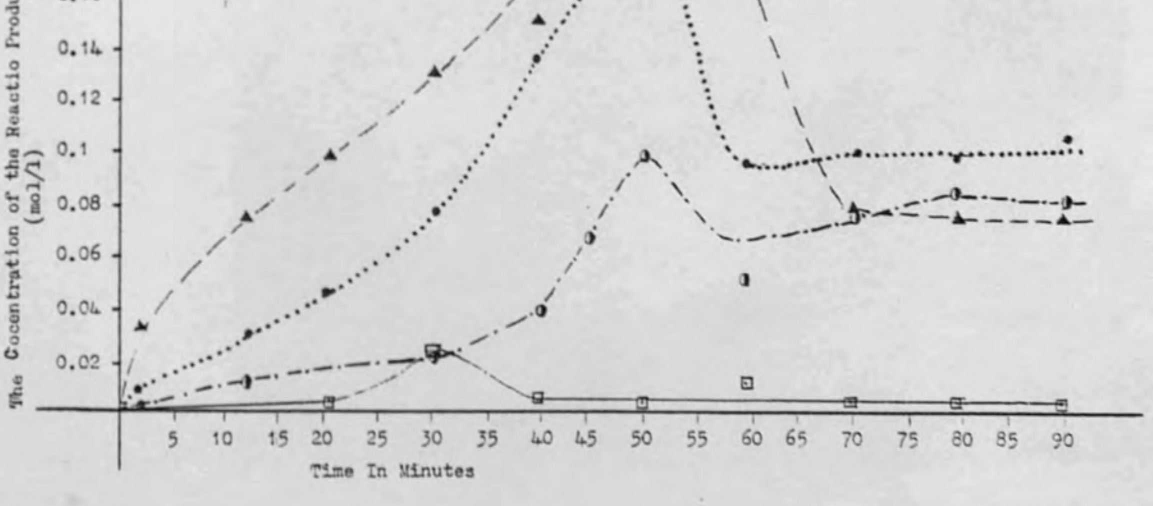


Figure 20 Variation in concentration of individual Dimers during dimerisation



Key of the graph ;			
*	Compound	I	7.5%
X	Compound	D	2.4%
o	Compound	G	2.3%
△	Compound	H	0.9%
▲	Compound	E	24.3%
●	Compound	F	35.9%
◐	Compound	A	25.6%
◻	Compound	B	0.73%



(iii) The Reverse of the Reaction of 2,3-Dimethylbutadiene and Sulphuric Acid in Acetic Acid

When a mixture of the dimeric products (0.06 M) of relative compositions as listed in table (1) column 4, the main component (60%) of which is as 2-methylene-1,3,3,4-tetramethylbicyclo (2,2,1) heptane was treated with sulphuric acid (0.12 M) in acetic acid in the presence of the marker (chlorobenzene) at 25° and the progress of the reaction followed by g.l.c. as above the areas corresponding to the dimers was seen to decrease and that of 2,3-dimethylbutadiene increase with time. The reaction appeared to reach equilibrium after 30 minutes. Another mixture of the dimeric products shown in table (2) when treated similarly produced the same result.

(iv) Variation of Experimental Rate constants with Concentration of Acid

Figure 21 shows that the experimental rate constant of the dimerisation of 2,3-dimethylbutadiene shows a linear dependence on acid for concentration up to ~ 0.08 M but increased rapidly with the higher concentrations of acid.

This graph is represented without any comment.

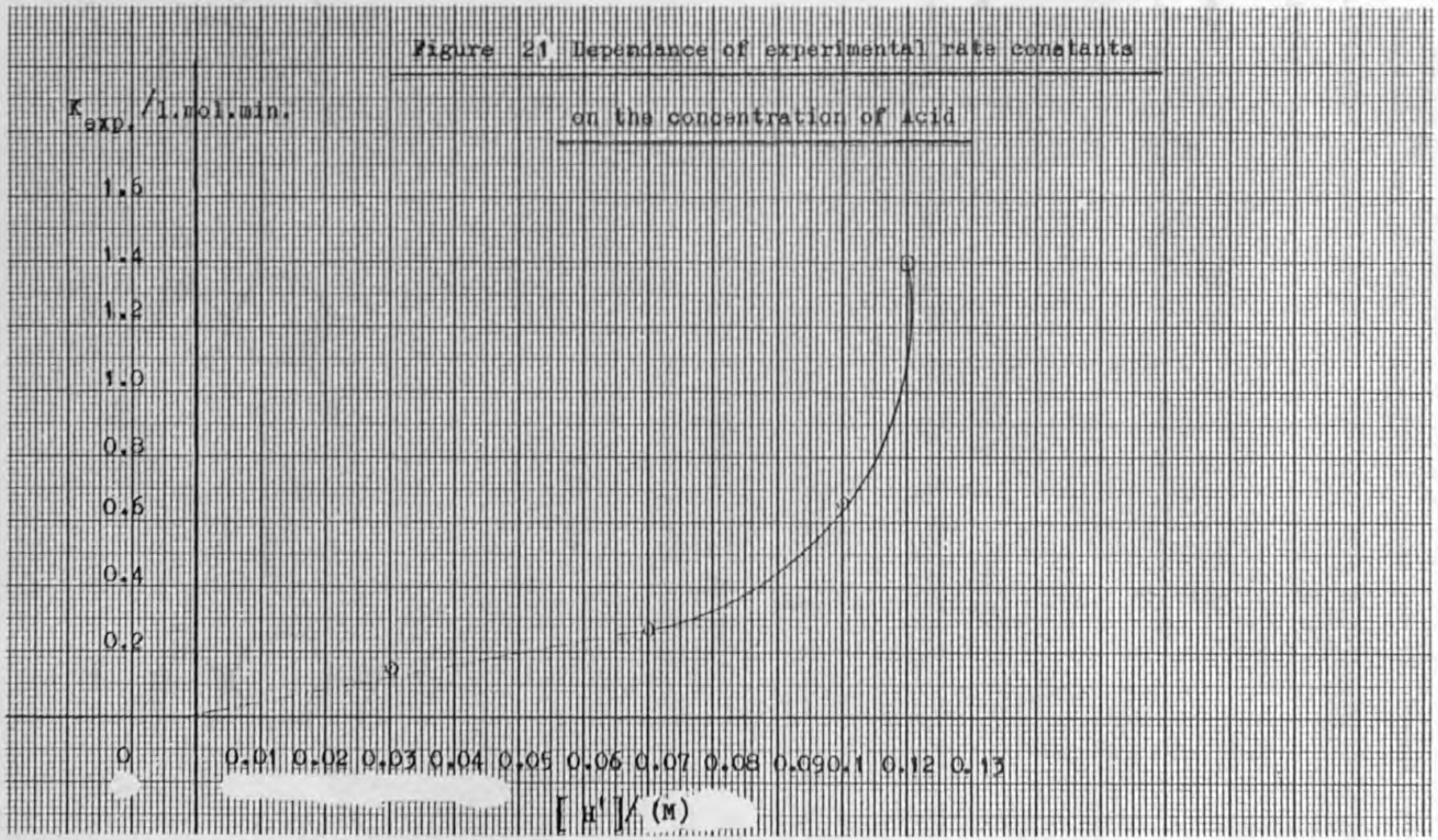
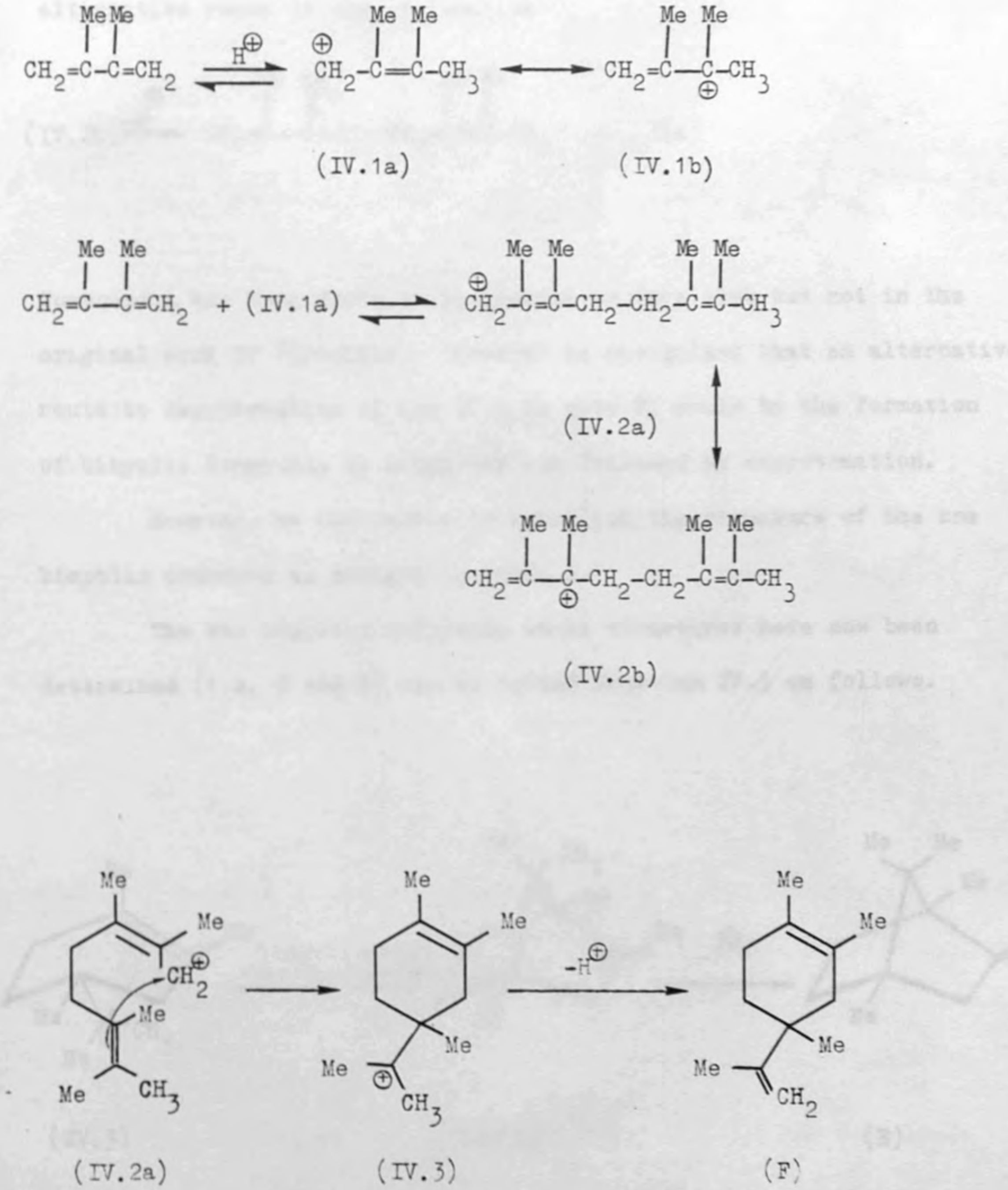


Figure 21 Dependance of experimental rate constants on the concentration of Acid

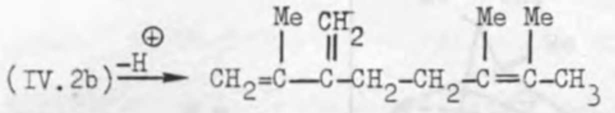
IV. Suggested Mechanism of the Formation of $C_{12}H_{20}$ and $C_{12}H_{18}$ Products

Pitkethly[69] has already suggested a scheme for the formation of 1,2,4-trimethyl 4-isopropenylcyclohex-1-ene from 2,3-dimethylbutadiene as follows:



Scheme IV.1

Catalysis of oligomerisation[91] of Isoprene by some cobalt chelate complexes gives limonene 20 which differs only by the absence of two methyl groups from compound F. Deprotonation of the carbenium ion IV.2b would give 3-methylene-2,6,7-trimethyl-1,6-octadiene(A) as an alternative route to the cyclisation



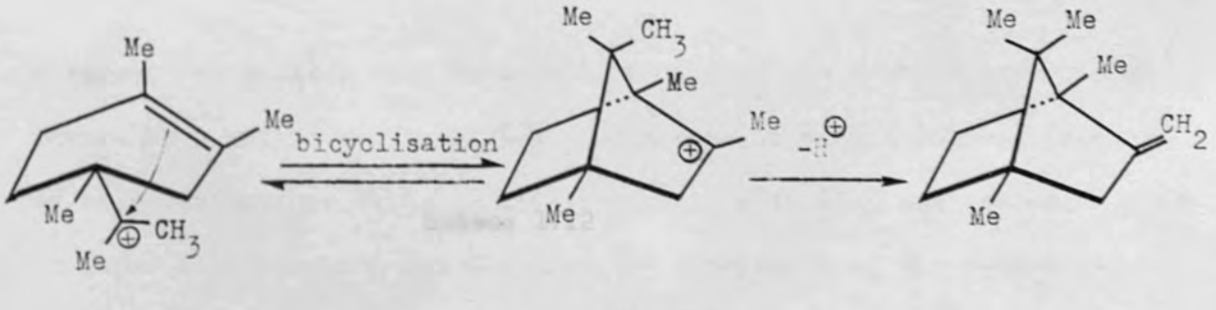
$$(IV.2b)\xrightarrow{-\overset{\oplus}{H}} CH_2{=}\overset{\overset{Me}{|}}{C}{-}\overset{\overset{CH_2}{\|}}{C}{-}CH_2{-}CH_2{-}\overset{\overset{Me}{|}}{C}{=}\overset{\overset{Me}{|}}{C}{-}CH_3$$

(A)

Compound A has been shown to be present in this work but not in the original work of Pitkethly. However he recognised that an alternative route to deprotonation of ion IV.3 to give F, would be the formation of bicyclic compounds by bicyclisation followed by deprotonation.

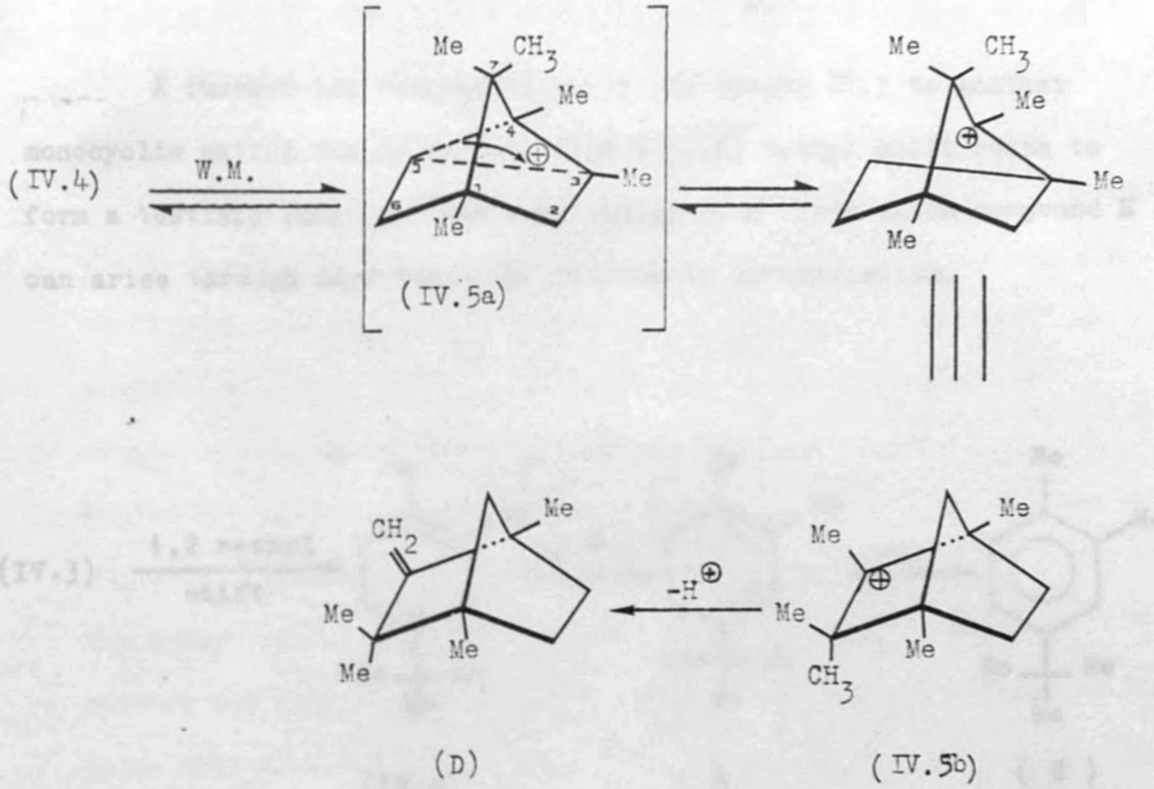
However, he was unable to establish the structure of the one bicyclic compound he managed to isolate.

The two bicyclic compounds whose structures have now been determined (i.e. D and E) can be formed from ion IV.3 as follows.



(IV.3) (IV.4) (E)

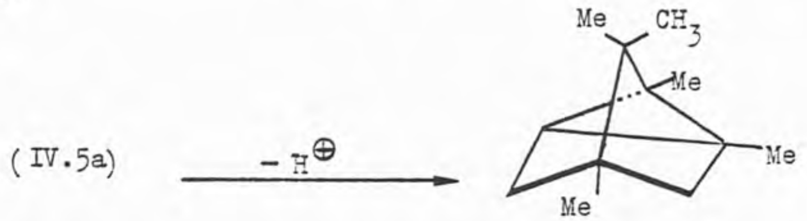
A Wagner-Meerwein rearrangement of IV.4 would give ion IV.5 a,b which on deprotonation would give compound D.



Scheme IV.2

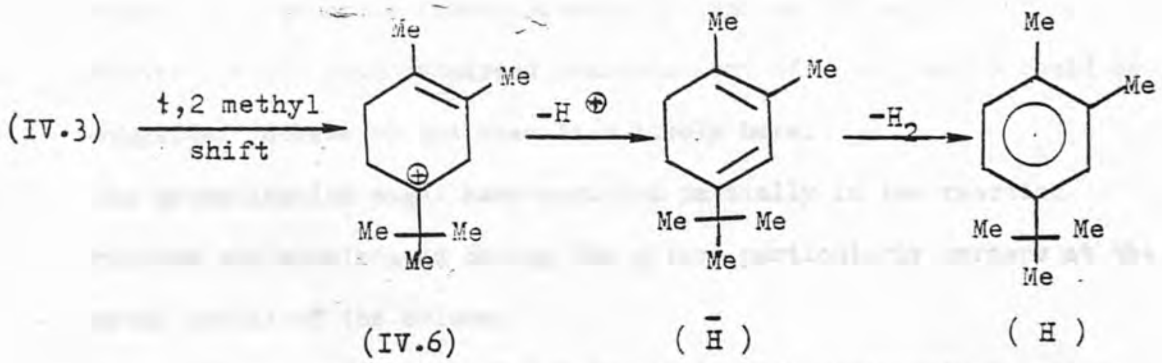
The facile rearrangement of the cation IV.4 to IV.5.b has been shown by Haseltine and Sorensen[78] in super acid by ^{1}H n.m.r. to be extremely fast, even at -120°C.

An alternative deprotonation of IV.5.a can lead to the tricyclic compound B.



(3)

A further ion rearrangement of the cation IV.3 to another monocyclic cation can be derived from a [1,2] methyl shift route to form a tertiary butyl cyclohexenyl cation IV.6 from which compound H can arise through deprotonation followed by aromatisation.



Sorensen[92] suggested that formation of ions of the type IV.6 should be formed by a methyl shift in IV.3 in competition with a pathway leading to bicyclic cations IV.4. This he studied with IV.3 and its homologues in super acid solution and assigned the structures of the rearranged ions by ^{1}H n.m.r.

If in the ion IV.4 there is a 3,2-hydride shift (see scheme IV. 3) to give IV.7 and this is followed by a retrobicyclisation (ring opening) then IV.8 is formed. The [1,2] methyl shift process (IV.3 → IV.6) if repeated here would give IV.9.

Subsequent deprotonation of IV.9 to $\bar{I}$ and aromatisation yields I. The occurrence of 3,2-hydride shifts is well known and it is expected therefore to be a fact process here.

Scheme IV.4 shows by a different series of rearrangements that ion IV.4 can be rearranged to IV.14. The ring opening (IV.14 — IV.15) methyl shift and aromatisation of $\bar{G}$ to G could be anticipated as above.

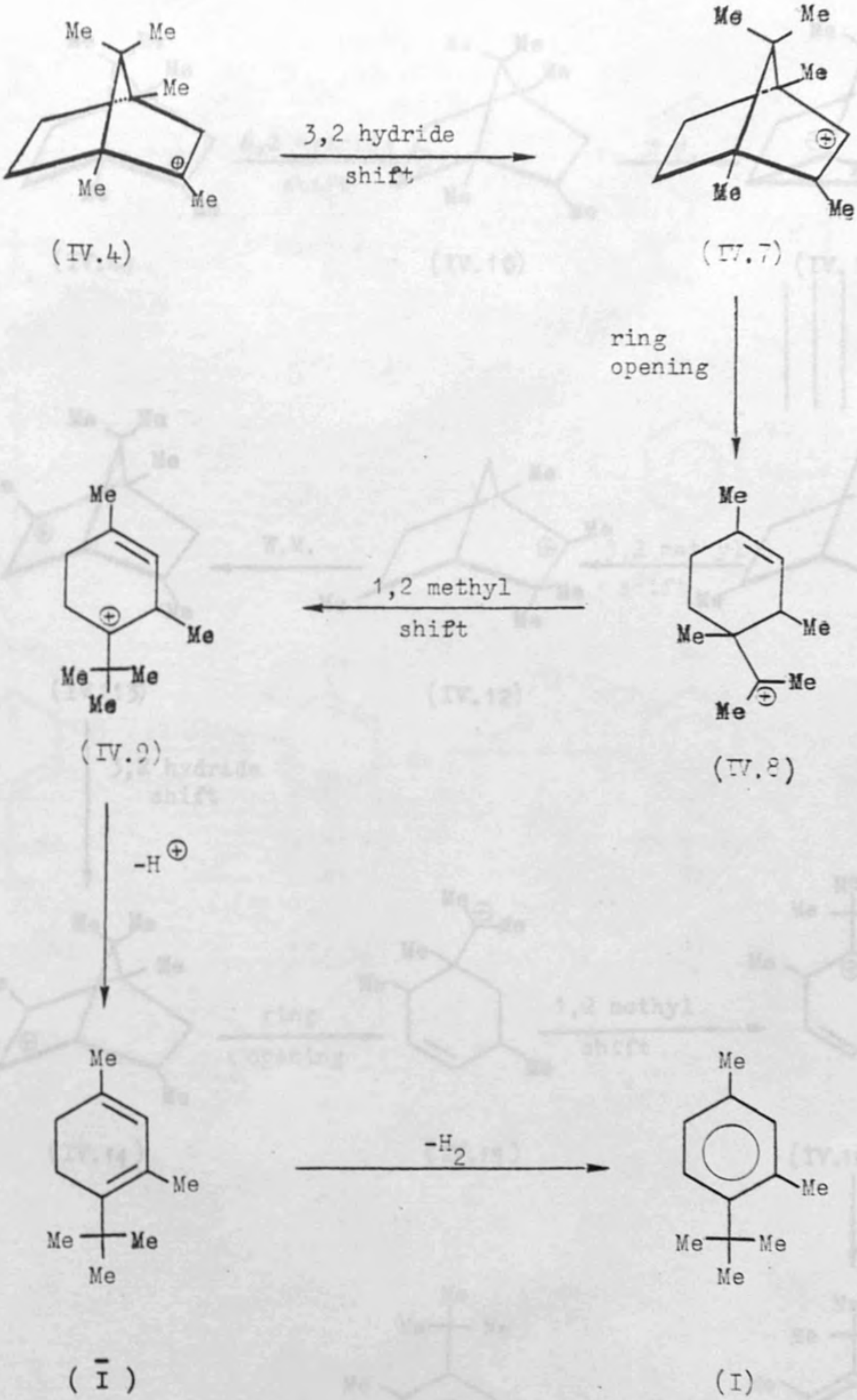
The sequence of rearrangement of IV.4 to IV. viz. 6,2-hydride shift, Wagner Merwein 3,2-methyl shift, Wagner Merwein, 3,2-hydride shift ring opening (retrobicyclisation) and [1,2] methyl shift is composed of steps, all of which have been suggested before in examining degenerate rearrangements by Deno and Houser.[93]
Routes for the acid catalysed rearrangement of H to I and G could be suggested (Scheme IV5) but seem less likely here.
The aromatisation might have occu red partially in the reaction mixture and accelerated during the g.l.c. particularly perhaps at the metal outlet of the column.

The aromatisation of 1,2-dimethylcyclohexadiene to o-xylene has been referred to by A. Cocks[94], H. Frey and R.H. Hopkins and shown to be accompanied by the formation of hydrogen at 296 - 354°C. The aromatisation confers more stability to the dimeric compounds $\bar{G}$, $\bar{H}$ and $\bar{I}$.

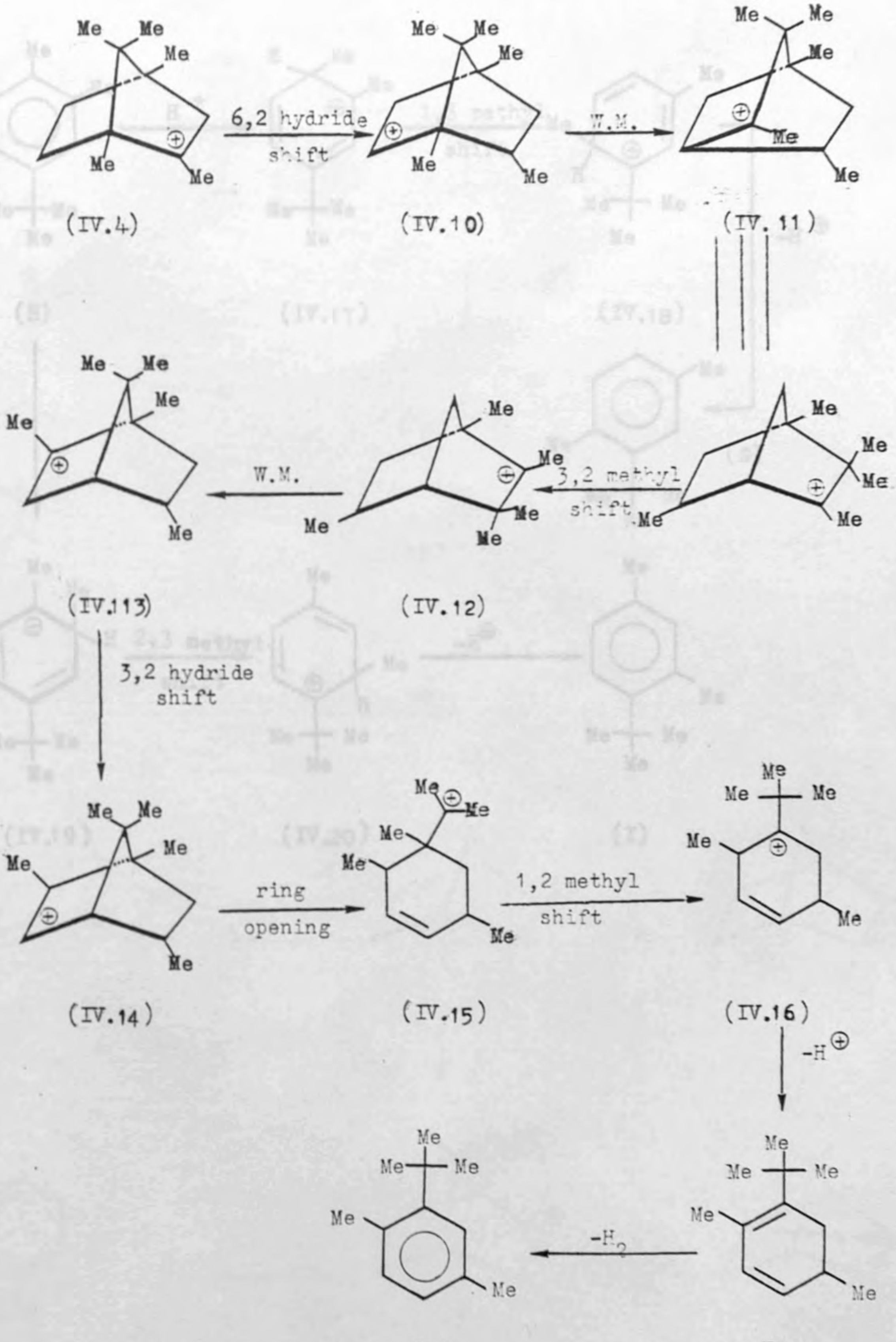
Also, F. Petit, M. Evrard and M. Blanchard[95 a,b] have suggested that the aromatisation of cyclohexadienes occurs with assistance of the cyclohexenyl cations. (IV. 21).

These aromatisations were observed in their vapour phase studies of the isomerisation of the bicyclic terpenes, camphene and fenchene over P_2O_5-SiO_2 (see scheme IV.6).
A mechanism advanced by these workers for the formation of isomers of camphene (scheme IV.7) shows considerable similarity to that suggested for the formation of compounds B, D, E, F observed in this work.

Scheme IV. 3

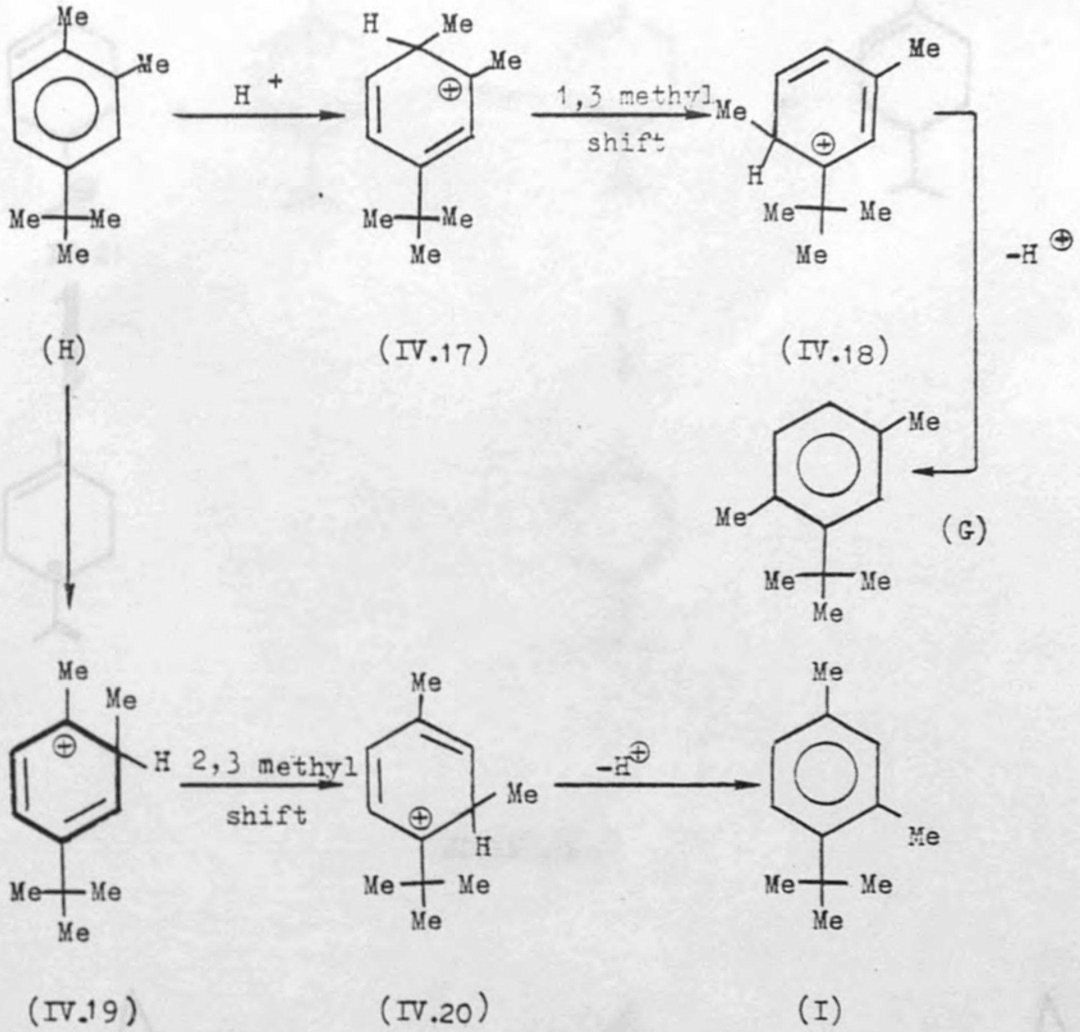

Me
Me
Me
Me
Me
(IV.4)
3,2 hydride
shift
(IV.7)
ring
opening
(IV.8)
1,2 methyl
shift
(IV.9)
-H ⊕
(Ī)
-H2
(I)

Scheme IV.4

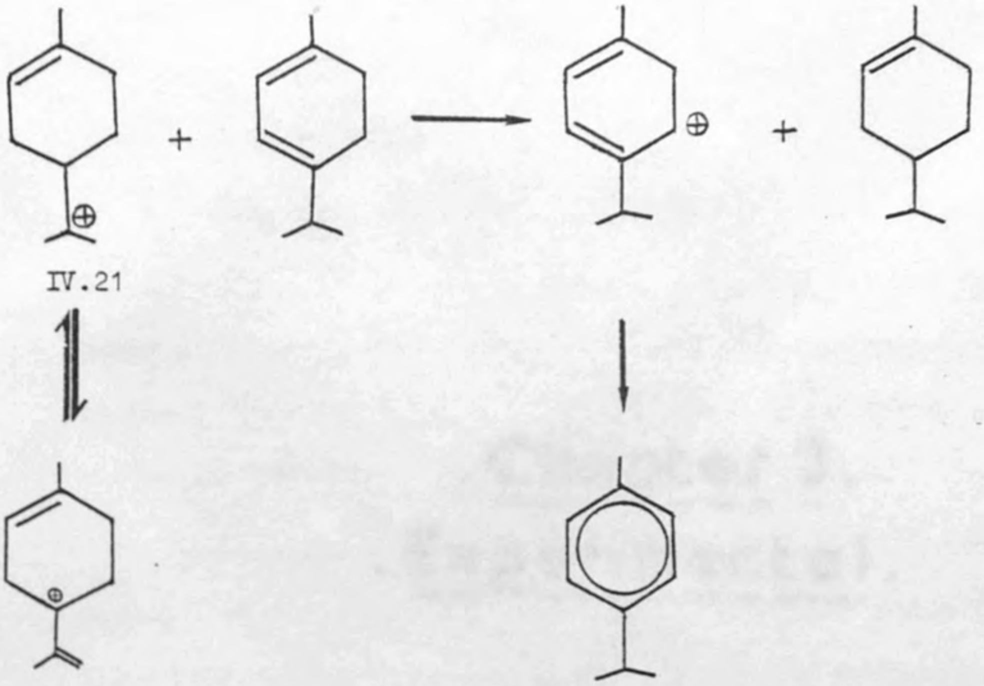


(IV.4)
6,2 hydride shift
(IV.10)
W.M.
(IV.11)
3,2 methyl shift
(IV.12)
W.M.
(IV.113)
3,2 hydride shift
(IV.14)
ring opening
(IV.15)
1,2 methyl shift
(IV.16)
-H⊕
-H2
(G)
(Ḡ)
Me

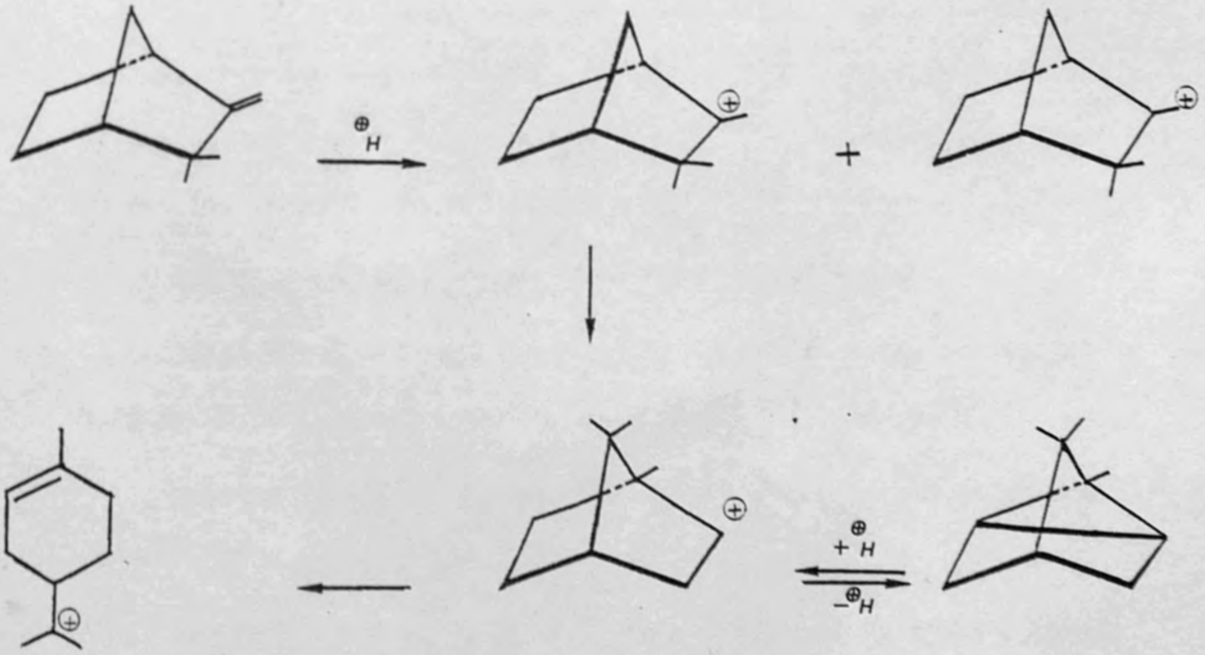
Scheme IV. 5


H +
1,3 methyl shift
-H ⊕
2,3 methyl shift
-H⊕
Me
H
(H)
(IV.17)
(IV.18)
(G)
(IV.19)
(IV.20)
(I)

Scheme IV.6



Scheme IV.7



. Chapter 3 .

. Experimental .

Experimental

I General Techniques

A. Gas-Liquid Chromatography (G.L.C.)

(i) Analytical gas-liquid chromatography was carried out using a Pye 104 double column gas liquid chromatograph with nitrogen as the carrier gas (flow rate = 40 cm^3/min^{-1}) and fitted with a flame ionisation detector.

Glass columns (4 mm diameter and lengths 3.5 and 7 m) were packed with 10, 15 and 20% Apiezon-L on chromosorb WHMDS (60 - 80 mesh). Temperature programming was carried out for the separations of the reaction products from 100° to 160° at 3° min^{-1}; the programming starting 15 minutes after injection of the sample.

Peak areas and retention times were measured using a Hewlett-Packard HP 3370 B.

(ii) A preparative gas liquid chromatograph (Pye 105) was used for the separation and purification of reaction products. It was equipped with a wide glass column (8 mm diameter and length 15 m), packed with 25% Apiezon-L on WHMDS (60 - 80 mesh).

The nitrogen carrier gas flow rate was 20 cm^3 min^{-1}.

Temperature programming was used after an isothermal period of 0.75 hr at 110°, with a heating rate of 2° min^{-1} to 160°.

For the completion of the separation the oven was maintained at 160° for a further 2 hours.

The outlet of the wide column was connected to 100:1 splitter to distribute the effluent between glass traps and the detector.

The glass traps were kept in a 10% glycerol-water mixture refrigerated cooling bath.

Repetition of injection of 250 µl samples was carried out every 4 hours.

B. Mass Spectrometry

G.l.c. - electron impact spectra were recorded in order to ascertain the relative molecular masses of the components in the 120°C 120 mm distillate.

The mass spectra were recorded on a VG micromass 12F spectrometer with an ionization potential of 70 eV, operating in with a jet separator interduce to Pye 104 gas chromatograph.

The carrier gas for the g.l.c. e.i. M.s. was helium at a flow rate of (40 cm^3/min^{-1}) and the temperature programming was as above for analytical gas chromatography.

C. Nuclear Magnetic Resonance (nmr).

60 MHz ^1H n.m.r. spectra were recorded on a Varian EM 360 spectrometer, 100 MHz ^1H spectra on a Varian HA 100 spectrometer and 220 MHz ^1H spectra were recorded at the Physico Chemical Measurements Unit (P.C.M.U.) at Harwell on a Varian HR 220 machine. The ^{13}C spectra were recorded on a Bruker HX 90E spectrometer operating at 22.63 MHz at Kings College, London. All spectra were run at ambient temperature and (T.M.S.) was used as an internal reference for both ^1H and ^{13}C spectra.

II Experiments

A. Synthesis of 2,3-Dimethylbutadiene[65]

48% Hydrobromic acid (2.5 cm^3) was added to pinacol (88.5 g) in a round-bottomed flask fitted with a condenser and a drying tube. After heating slowly in an oil bath the mixture was distilled in an oil bath and the distillate collected, having a boiling point up to 94°. The resulting upper non-aqueous layer was washed (2X) with water (25 cm^3) containing hydroquinone (0.12 g) and separated with separating funnel and dried overnight with calcium chloride.

Distillation through a simple fractionating column at 69 - 80.5° gave (29 g) of 2,3-dimethylbutadiene a yield of 48%.

B. The Oligomerisation of 2,3-Dimethylbutadiene

(i) Method 1

98% Sulphuric acid (1.0 cm^3) in glacial acetic acid (100 cm^3) was added to 2,3-dimethylbutadiene (43.14 g) in a brown bottle.

The mixture was stirred and left for 96 hours, the resulting solution was poured into water (600 cm^3) and the reaction products extracted with diethyl ether (3 x 150 cm^3).

The ethereal solution was neutralised by washing with sodium carbonate solution, dried overnight by sodium sulphate (5.0 g).

The ether was distilled off and then the unchanged 2,3-dimethylbutadiene (12%) separated from the reaction product by distillation through a 50 cm Vigreux column at 70°.

The product was hydrolysed with alcoholic potassium hydroxide (66 cm^3) and refluxed for 4 hours.

After distilling off most of the ethanol the mixture was poured into water (500 cm^3), extracted with diethylether (3 x 200 cm^3) and the ether layer dried with anhydrous sodium sulphate.

The residue, after removal of the ether, was heated on a steam bath for four hours with boric acid (3.0 g) to convert any alcohols to borate esters and then vacuum distilled.

A yellowish oily liquid (17.8 g) boiling point 46 - 120° (0.5 mm) was collected, in addition to a white solid product (0.5 g) which condensed at the head of the distillation column.

(ii) Method 2

In a similar experiment the product, freed from the unchanged diene was distilled under vacuum without the treatment to remove acetate esters. The same products were collected as in method 1.

C. Kinetic Experiments

(i) Materials

(a) 2,3-Dimethyl butadiene
Aldrich Chemical - 98% b.p. 68 - 69°.
Redistillation increased its purity to 99.5% (g.l.c.).

(b) Glacial Acetic Acid (BDH Analar 99.7%) was used without further purification.

(c) Sulphuric Acid (BDH Analar 98%) was used without further purification.

(d) Chlorobenzene (BDH Reagent grade)
G.l.c. showed it to be 99% pure.

(e) Dichloromethane (BDH Analar)
G.l.c. showed it to be 99.5% pure.

(f) Aqueous Potassium Bicarbonate Solution (BDH Analar)
Solid was dissolved in water to give solutions in the concentration range 0.83 - 1.66M.

(g) Aqueous Potassium Carbonate Solution (BDH Analar)

Solutions were prepared as above having conentrations 0.83 - 1.66M.

(ii) Determination of Calibration Graphs for 2-Methylene 1,4,7,7-Tetramethyl [2,2,1]-Bicyclo Heptane and 2,3-Dimethylbutadiene.

The pure solid dimer (2-methylene 1,4,7,7-tetramethyl [2,2,1]-bicyclo heptane was used as an example of a typical 2,3-dimethylbutadiene dimer for determination of a g.l.c. calibration graph for the dimers.

Solutions of it in dichloromethane (0.5 - 0.1M) were prepared using chlorobenzene as a marker at a constant concentration of 0.415M. These solutions were injected (2μl) into the gas liquid chromatograph fitted with an Apiezon-L (20%) column.

The areas of both dimer and chlorobenzene in each sample were obtained using the integrator and the ratios of areas were plotted against the concentrations of the dimer to give a calibration graph.

The same procedure was used for drawing a calibration graph for 2,3-dimethylbutadiene.

Samples of different strengths (0.2 - 0.01M) of 2,3-dimethylbutadiene in dichloromethane containing a constant concentration of the marker (0.041M) were injected as above into the gas liquid chromatograph.

(iii) Procedure for a Typical Kinetic Experiment

The rate of polymerisation of 2m3-dimethylbutadiene was followed by the "Sampling Method".

Stock solutions of 2,3-dimethylbutadiene together with chlorobenzene in glacial acetic acid and sulphuric acid also in glacial acetic acid were thermostatted at 25°, prior to the commencement of a kinetic experiment. In a specific kinetic experiment, 2,3-dimethylbutadiene (0.205 g) was dissolved in glacial acetic acid together with chlorobenzene, (0.28 g), and kept in a 25 cm^3 graduated flask. In another 25 cm^3 graduated flask, sulphuric acid, (0.49 g) in glacial acetic acid (25 cm^3), was kept at 25°. Both flasks were equilibrated for 15 minutes in the water bath before starting the reaction. Into an empty reaction flask at the water bath temperature were transferred equal volumes of the 2,3-dimethylbutadiene solution and the sulphuric acid solution. They were mixed rapidly, stirred, replaced in the water and the clock started.

After varying time intervals 5 cm^3 aliquots were removed. The reaction was quenched using a potassium carbonate solution (10 cm^3, 0.83M) to neutralise both the sulphuric and acetic acids.

The reaction products were extracted by shaking the neutralised mixture with dichloromethane, (5 cm^3), and the solvent layer separated off. This was dried with sodium sulphate (0.5 g).

[In some experiments potassium bicarbonate (6.2 cm^3 0.83M) was used as an alternative neutralising solution].

2 μL dichloromethane solution were injected into the gas liquid chromatograph and the areas of the unreacted 2,3-dimethylbutadiene and the dimer products were related to the marker area.

The calibration graphs were used for drawing plots of decreasing diene concentration against time and increasing dimers concentration with time for determining the rate of the reaction.

The kinetic experiment was repeated using different initial concentrations of the reactants.

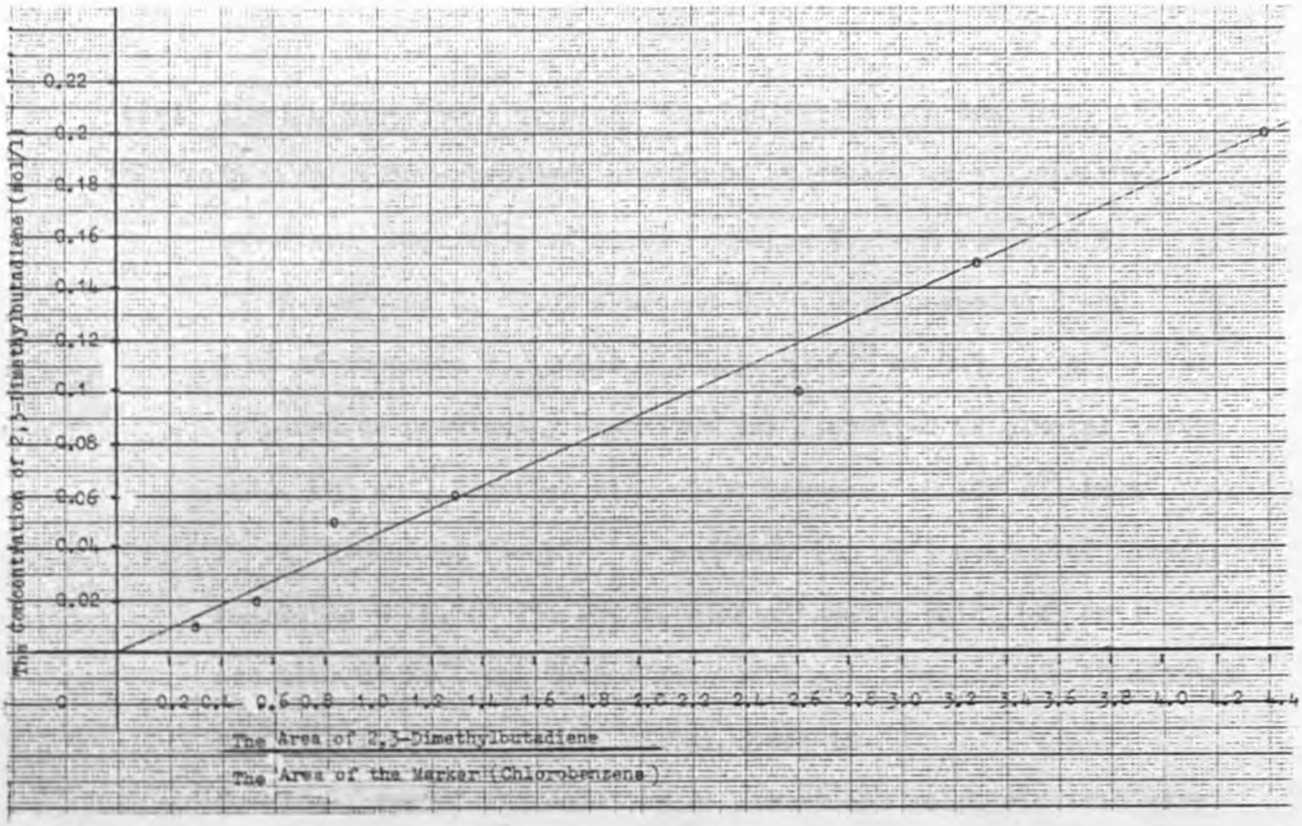


Figure 22 The calibration graph of 2,3-Dimethylbutadiene for GLC analysis

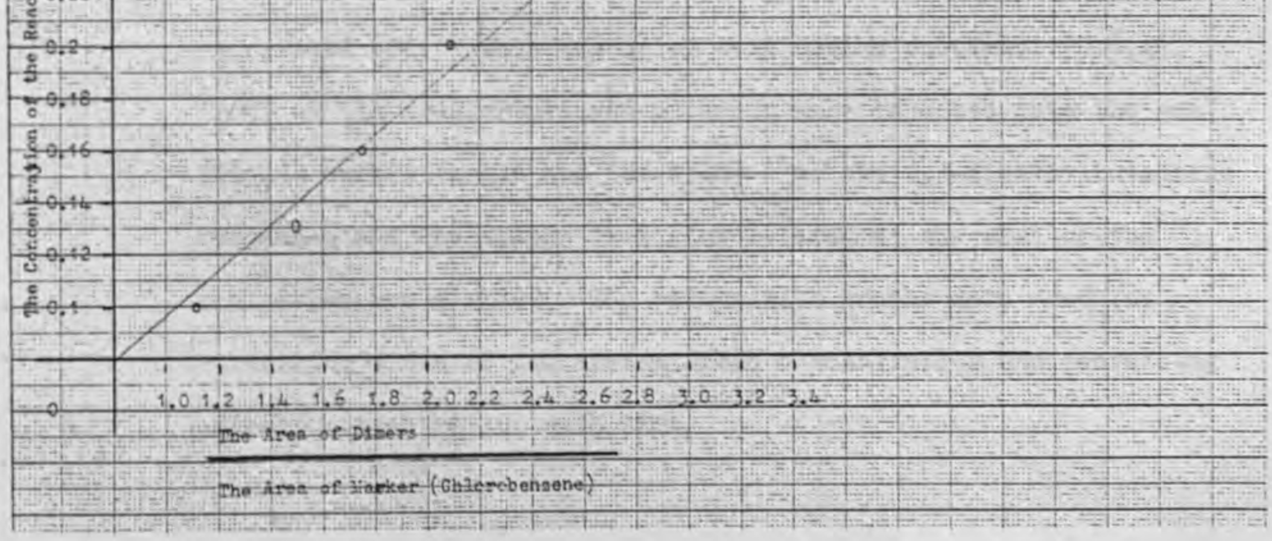


Figure 23 The calibration graph of the Dimers for GLC analysis.

(iv) Kinetic Experiment to study the Dedimerisation Reaction.

In a specific experiment a mixture of dimers of 2,3-dimethyl butadiene comprising of 12.0% compound A, 2.6% compound B, 15.1% compound D, 60.0% compound E, 6.7% of compound E and 3.6% of compound H, (0.246 g), b.p. 52-57° at 0.5 mm Hg obtained as previously described was dissolved in glacial acetic acid, (25 cm^3) together with chlorobenzene, (0.125 g), in a 25 cm^3 graduated flask. In another, (25 cm^3) graduated flask, sulphuric acid, (0.294 g), in glacial acetic acid, (25 cm^3) was kept at 25°, and both flasks were equilibrated for 15 minutes prior to the commencement of the reaction.

Equal volumes of the solution of dimers and sulphuric acid were transferred into an empty reaction flask maintained at 25°. The two solutions were mixed rapidly and then after varying time intervals (5 cm^3) aliquots removed. The reaction was quenched using a potassium carbonate solution, (10 cm^3, 1.66M), to neutralise both the sulphuric and acetic acids.

The reaction products were extracted by shaking the neutralised mixture with dichloromethane, (5 cm^3), and the solvent layer separated off. This was dried with sodium sulphate, (0.5 g), 2μl of the dichloromethane solution were injected into the gas liquid chromatograph and the areas of the 2,3-dimethylbutadiene produced and the dimers remaining related to the area of the chlorobenzene marker. The calibration graphs were used for obtaining plots of increasing diene concentration and decreasing dimers concentration with time.

The same experiment as above was carried out with a dimeric mixture (0.245 g) consisting of 2.9% compound A, 0.8% compound B, 0.5% compound C, 4% compound D, 23.4% compound E, 4.2% compound F, 4.6% compound G, 55.1% compound H 3.6% compound I and 0.8% of the other dimers.

(v) Determination of the loss of 2,3-Dimethylbutadiene during the experimental work

In order to determine the loss of 2,3-dimethylbutadiene during the extraction and drying process of solution of 2,3-dimethylbutadiene dimerisation a specific experiment was carried out by dissolving 2,3-dimethylbutadiene (0.246 g) in acetic acid (50 cm^3) together with chlorobenzene (0.25 g) in a 50 cm^3 graduated flask and kept at 25° for 30 minutes. The diene solution was neutralized with potassium carbonate solution (1.66M) (500 cm^3), the diene was extracted with dichloromethane (50 cm^3) and dried with sodium sulphate (5.0 g).

2 μl of the dichloromethane solution was injected into the gas liquid chromatograph and the area of the 2,3-dimethylbutadiene peak related to the area of the chlorobenzene marker peak. A previously determined calibration graph was used to obtain the concentration of 2,3-dimethylbutadiene.

(vi) Extraction coefficient of 2,3-Dimethylbutadiene from Acetic Acid solutions

In a specific experiment a solution of 2,3-dimethylbutadiene (0.06 M) in acetic acid (50 cm^3) and chlorobenzene as a marker (0.041 M) was neutralized with an accurate amount of saturated potassium carbonate solution. The diene and marker were extracted with dichloromethane (25 cm^3) and dried by sodium sulphate.

2 µl of the extracted solution was injected into the G.l.c. and then the area of 2,3-dimethylbutadiene related to the area of chlorobenzene.

The calibration graph was used to obtain the concentration of the diene and it was found to be 0.054 M, indicating a loss of 10% of the starting concentration.

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SUMMARY

2,3-Dimethyl-1,3-butadiene on treatment with sulphuric acid in acetic acid as a solvent gives rise to oligomeric products. Distillation between 46 to 120° at 0.5 mm Hg pressure gives a fraction having thirteen compounds; the principal eight members being liquids except for one having a m.p. 87°.

G.C.M.S. has shown that five,including the solid, have molecular weights of 164 and the other three have molecular weights of 162. There was no evidence for the formation of acetate esters. Preparative G.l.c. has successfully separated the eight major products in a pure state, and ^{1}H and ^{13}C n.m.r. spectroscopy has been used for the determination of the structure of these compounds.

The following structures are proposed: acyclictriene 3-methylene-2,6,7-trimethyl-1,6-octadiene or 4-methylene-2,3,7-trimethyl-2,7-octadiene, a derivative of tricyclene 2,4-dimethyltricyclene i.e. 1,2,4,7,7-pentamethyltricyclo (2,2,1,0$^{2-6}$)heptane, two bicyclo compounds 2-methylene-1,3,3,4-tetramethylbicyclo (2,2,1) heptane, 2-methylene-1,4,7,7-tetramethylbicyclo (2,2,1) heptane the solid product, a monocyclic compound 1,2,4-trimethyl 4-isopropenylcyclohex-1-ene, and three aromatic compounds 2,4- 2,5- and 3,4-dimethyl t-butyl benzene.

The kinetic study of the reaction has shown that the reaction is second order in 2,3-dimethyl-1,3-butadiene.

The dehydrogenation giving the substituted benzenes may arise during the preparative g.l.c. process since the aromatic compounds are more stable than their diene precursors.