A STUDY OF SELECTIVITY IN THE REACTIONS OF UNSYMMETRICAL TRIALKYLBORON COMPOUNDS

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by

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Abstract

The reaction of disiamylborane with enol acetates derived from an aldehyde bearing two α-hydrogen atoms involves a slow anti-Markownikoff hydroboration followed by rapid elimination and re-hydroboration reactions. Selectivity between reaction of the cis and trans isomers is far smaller than for the corresponding olefinic hydrocarbons. Enol acetates derived from ketones are generally unreactive to disiamylborane.

The extent of reaction of propionic acid with a representative series of trialkylboranes depends on the steric resistance of the borane to the initial co-ordination of the acid. The extent of protonolysis decreases with an increase in the total number of alkyl substituents at the α - and β - carbon atoms to boron. With an unsymmetrical trialkylborane the selectivity between the breaking of secondary - and primary - carbon to boron bonds is small. A very large selectivity is found in favour of the removal of a primary - rather than a tertiary-alkyl group. This is thought to be due to steric and not electronic factors.

The stepwise oxidation of several unsymmetrical boranes, using small aliquots of aqueous alkaline hydrogen peroxide, shows an anomalous selectivity. Thus the secondary alcohol, 2-methylbutan-3-ol, is produced more readily from disiamyl-n-hexylborane than is the tertiary alcohol, 2,3-dimethylbutan-2-ol, from thexyldi-n-hexylborane. The relative reactivity is suggested to be controlled by the overall steric (rather than electronic) requirements of the organoborane-hydroperoxide complex.

Trialkylboranes decompose by two competing mechanisms in the presence of neutral aqueous hydrogen peroxide. A fast reaction involving the homolytic fission of the carbon to boron bonds, yields hydrocarbons. The second slower mechanism yields an alcohol but probably not via a free radical mechanism. The importance of the free radical mechanism declines inversely as the number of oxygen atoms bonded to the boron atom. Selectivity in the hydrogen peroxide dealkylation of an unsymmetrical trialkylborane is masked by the competition between the two reactions. In carbon tetrachloride solution the yield of alkane is replaced by alkyl chloride, and in the presence of iodine an alkyl iodide is obtained.

The oxidation of unsymmetrical trialkylboranes by molecular oxygen leads to the predominant formation of the corresponding alcohols. Only a very small selectivity is found between the breaking of the different carbon to boron bonds.

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ABBREVIATIONS USED IN THE TEXT

Mol. — mole equivalent

T.H.F. — tetrahydrofuran

Diglyme — diethylene glycol dimethyl ether

G.l.c. — gas liquid chromatography

P.m.r. — proton magnetic resonance

Disiamyl-* — bis-(1,2-dimethylpropyl)-

Thexyl-* — 1,1,2-trimethylpropyl-

* As far as possible chemical nomenclature and quantities follow the recommendations made in the Chemical Society's Handbook for Authors (1961 Ed.). The two abbreviated names above are used as suggested in 'Hydroboration', by H.C. Brown, W.A. Benjamin, New York, 1962.

CONTENTS

/Contents - continued/ page

2. The reaction of Propionic Acid with Representative Symmetrical and Unsymmetrical Trialkylboranes

3. The Selective Protonolysis of Representative Unsymmetrical Trialkylboranes

SECTION III. The Selective Oxidation of Unsymmetrical Trialkylboranes using Alkaline Hydrogen Peroxide Solution

SECTION IV. The Reaction of Neutral Aqueous Hydrogen Peroxide with Representative Trialkylboranes, a New Reaction

2. The Reaction of Neutral Aqueous Hydrogen Peroxide with Tri-n-hexylborane

/Contents - continued/ page

Experimental Section.

GENERAL INTRODUCTION

Although the reactions of trialkylboron compounds leading to fission of the carbon to boron bond have been described in many reports in the literature since 1938, the studies have generally been confined to boranes containing a single alkyl group. The present study attempts to discover any selectivity between the breaking of carbon to boron bonds when two different alkyl groups are bound to the same boron atom.

Three different preparative routes to unsymmetrical trialkylboranes are used. The main technique is hydroboration.[1] In the presence of an ether diborane adds readily to a tri-substituted olefin, yielding a dialkylborane. The subsequent addition of a less alkylated olefin leads to the formation of an unsymmetrical trialkylborane. Thus the reaction of diborane with two equivalents of 2-methylbut-2-ene, followed by one equivalent of hex-1-ene, produces bis-(1,2-dimethylpropyl)-n-hexylborane. A tetrasubstituted olefin yields a monoalkylborane with diborane. Thus diborane gives

1,1,2-trimethylpropyldi-n-hexylborane with one equivalent of 2,3-dimethylbut-2-ene, followed by two equivalents of hex-l-ene. To avoid the necessity for continued repetition in the text of the full systematic names of the above two organoboranes, the abbreviations used by Brown have been followed, the former borane being referred to as disiamyl-n-hexylborane, and the latter borane as thexyldi-n-hexylborane.

For the other unsymmetrical boranes examined, Hennion and McCusker's method[2] and Hawthorne's method[3] are used. The former preparation proceeds via the selective alkylation of boron trifluoride by t-butylmagnesium chloride in the presence of hex-l-ene to give di-t-butyl-n-hexylborane. Hawthorne's method for t-butyldi-n-hexylborane via the reaction of the amine-borane, trimethylamine:t-butylborane, with hex-l-ene, is followed.

The use of gas-liquid chromatography under carefully chosen conditions allowed the experiments to be carried out on a small scale, 10-15 mmoles oforganoborane being used generally. Lengthy isolation and purification procedures, necessitating larger scale experiments, were avoided by this method. The chromatographic estimations used are described fully in the Appendix.

Five reactions of the unsymmetrical boranes have been studied and the thesis is divided into four Sections. The first Section describes the reaction of disiamylborane with representative enol acetates. The second Section describes the reaction of propionic acid with a series of unsymmetrical trialkylboranes. The final two Sections describe the oxidation of representative unsymmetrical boranes, in the first using alkaline hydrogen peroxide solution. The final Section includes the results of oxidations using neutral aqueous hydrogen peroxide, and also the complementary study using molecular oxygen. An introduction to the relevant reaction precedes each Section.

The first part of the Experimental Section contains details of the experimental techniques common to all Sections of the study, including the purification of solvents and reagents. Also included is a description of the apparatus used in a typical hydroboration experiment, together with the procedure followed during (a) an external, and (b) an internal, generation of diborane.

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[1] H.C. Brown, 'Hydroboration', W.A. Benjamin, New York, 1962.

[2] G.F. Hennion, P.A. McCusker and J.V. Marra, J. Amer.Chem. Soc., 1959, 81, 1768.

[3] M.F. Hawthorne, J. Amer. Chem. Soc., 1961, 83, 831.

SECTION I.

THE REACTION OF DISIAMYLBORANE WITH ENOL ACETATES.

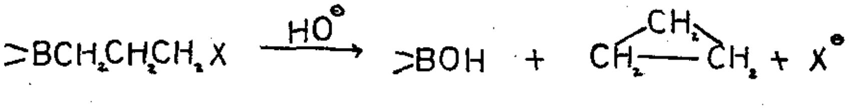
1) Introduction

An extensive study has been made of organoboranes containing a functional group in the α, β, or γ position to the boron atom.[1,2,5-14,16-19,21-26] These compounds are readily available through the hydroboration of olefins containing a substituent in the vinylic or allylic position.

A systematic study of the hydroboration of allyl derivatives has been made by Brown.[2] The allyl substituent was found to influence the direction of addition of the B-H bond to the olefinic double bond.

The overall directive influence was explained in terms of an inductive (I) effect. The proportion of boron added at the secondary (β) position reflected the degree of polarisation of the double bond induced by the I effect of the functional group. Thus hydroboration of allyl ethyl ether placed 18% of the boron at the secondary position (small -I effect),[2] allyl chloride, 40%,[2] and 1,1,1-trifluoropropene, 74% (large-I effect).

Under hydroboration conditions the boranes with a γ substituent were found generally to be stable to further reaction, although with boranes containing a chlorine or p-toluene sulphonyl group in the γ position, subsequent addition of aqueous base caused a cyclisation reaction providing a cyclopropane derivative in good yield as in SchemeI.[2,6]



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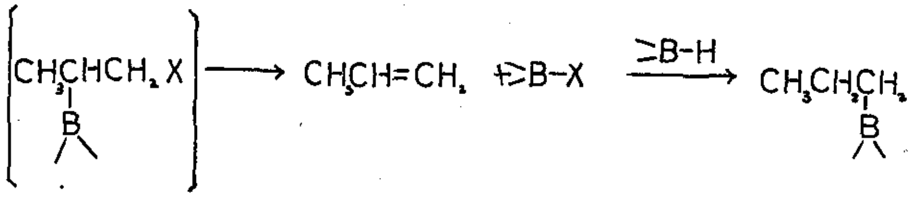
$X = OTs, Cl, etc.$

The stability of the boranes with a β functional group depended on the particular functional group. The secondary boron derivative from allyl tosylate,[2] chloride,[2,6,8] acetate,[2] and from 3-chlorocyclohexene[7] suffered a spontaneous uncatalysed elimination reaction as in Scheme 2.



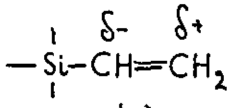
$$\left[CH_3\underset{\underset{\wedge}{B}}{C}HCH_2X\right] \longrightarrow CH_3CH{=}CH_2 + {>}B{-}X \xrightarrow{\geq B-H} CH_3CH_2\underset{\underset{\wedge}{B}}{C}H_2$$

2

At 0^0 the secondary boron derivative from allyl borate,[2] phenoxide,[2] and ethoxide,[2] allyl trimethyl silane,[9] and allyl trichlorosilane[9] were stable to further reaction, although all but the silane derivatives suffered elimination in refluxing tetrahydrofuran (T.H.F.) solution. In addition, a base catalysed elimination was noted for the phenoxide derivative.[2] The hydroboration of allyl phenyl sulphide at 25° during 3 days yielded only 5% of n-propanol, the product which would be expected from a β elimination reaction of the intermediate borane. This result might suggest that a sulphur containing group in the allyl position exerts only a small directive effect.[10] This need not be so, however, as the reaction here was complicated by "transfer reactions" which reduced the overall yield of hydroxysulphides and made it difficult to assess the relative importance of the elimination reaction.

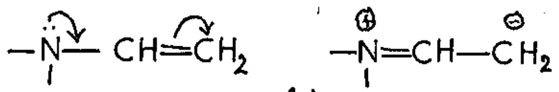
Several workers have hydroborated vinyl compounds including the vinyl silanes[11,12] vinyl halides,[8] enol ethers,[13,14,15] ene thiols,[10,16] and ene-amines.[17,24] Here the hydroboration reaction can produce either an α or β substituted borane. With vinyl compounds, the inductive (-I) effect of an electronegative group on the double bond should be stronger than with the allylic substituents as examined by Brown. Hydroboration of such a compound should therefore lead predominantly to the formation of an α- substituted borane.[18] Conversely, mesomeric interaction of the lone pair electrons of the vinyl substituent with the olefinic double bond is possible in all the derivatives studied above (with the exception of the silanes) and would polarise the double bond in the opposite direction to that favoured by an inductive (- I) effect.

It is significant that whereas vinyl trimethyl silane was hydroborated to place 37% of the boron at the secondary position,[11] the eneamine derived from cyclohexanone added diborane to place boron only in the β position to the amine function.[17] The silicon containing group cannot participate in mesomeric interaction with the double bond, and the electronegativity of the silicon atom would explain the large proportion of boron placed in the α position to the silicon atom, as in (a). The analogous carbon compound, t-butyl ethylene, gives only 6% of the secondary boron derivative.[20] In the case of the eneamine, inductive polarisation of the double bond is clearly outweighed by another factor, the most feasible being mesomeric donation of the lone pair electrons on nitrogen, as in (b).



$-\underset{|}{\overset{|}{Si}}-\overset{\delta-}{CH}=\overset{\delta+}{CH_2}$

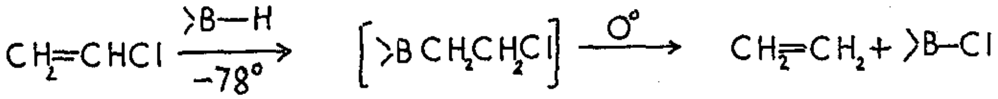
(a)



$-\underset{|}{\ddot{N}}-CH=CH_2 \qquad -\underset{|}{\overset{\oplus}{N}}=CH-\overset{\ominus}{CH_2}$

(b)

Hawthorne was unable to obtain an organoborane stable at ice temperature from the hydroboration of vinyl chloride.[8] Instead, a violent exothermic reaction took place on warming the mixture to 0°. The production of a large yield of ethylene was interpreted as evidence for the formation of a thermally unstable β- halo organoborane, which underwent a spontaneous elimination reaction, as in Scheme 3.



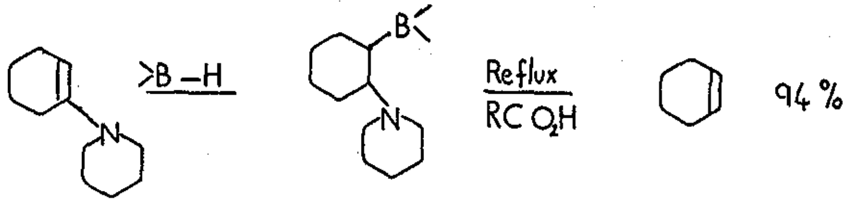
$$CH_2{=}CHCl \xrightarrow[-78^\circ]{>B-H} \left[>BCH_2CH_2Cl\right] \xrightarrow{0^\circ} CH_2{=}CH_2 + >B-Cl$$ 3

Pasto, studying the hydroboration of ω -ethoxystyrene, observed a similar elimination reaction.[14] Here, however, the reaction was less vigorous and consequently more readily studied. At 0^0, hydroboration of the enol ether and subsequent oxidation of the borane using alkaline hydrogen peroxide solution yielded several products including 1-phenyl-2-ethoxyethanol. When the experiment was repeated at 25°, however, this alcohol was replaced by a mixture of 1-, and 2-phenyl-ethanol in a total yield similar to that of the ethoxy alcohol, and in the proportions (80:20, respectively) which would be expected from the hydroboration/oxidation of styrene.[26] This result could be explained most reasonably in terms of a temperature sensitive four centre cis β -elimination of an intermediate organoborane. This conclusion is reinforced by the subsequent observation[14] that the hydroboration of 1-ethoxycyclohexene produced a borane which was stable to elimination in refluxing T.H.F. solution. Here hydroboration was demonstrated to produce a trans β-ethoxy boron compound, suggesting that the uncatalysed elimination cannot proceed with trans stereochemistry. The addition of a Lewis acid, boron trifluoride, to the reaction mixture after hydroboration, caused an exothermic reaction producing both cyclohexene and, after alkaline oxidation, a much increased yield of cyclohexanol. Clearly an acid catalysed β elimination was now occurring, but with trans stereochemistry. The cis elimination reaction observed with ω-ethoxystyrene is clearly related to those observed by Brown and other workers to be important for the β-substituted boron derivative obtained from the hydroboration of allyl derivatives.

A further example of a temperature dependent elimination reaction was found when di-isobutylaluminium hydride was added to a simple vinyl ether. On warming the reaction mixture from 0° to 25° a reaction occurred, liberating a substantial yield of ethylene.[15]

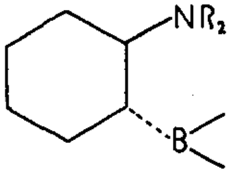
When a series of ene thiols was treated with diborane, Pasto obtained a mixture of several products in varying yields. The products here were explained on the basis of "transfer" reactions involving the boron and sulphur atoms,[21] however, rather than by elimination, re-addition reactions.[10,16] The mechanism proposed has not found overall acceptance.[2]

A further example of the acid catalysed β-elimination reaction was found in the case of the product from the hydroboration of an eneamine.[17] When N-cyclohex-1-enylpiperidene was treated with diborane, and then refluxed in diglyme solution in the presence of a carboxylic acid, an almost quantitative yield of cyclohexene was obtained as in Scheme 4. J. W. Lewis[17] used the known stereochemistry (trans) of the addition of diborane to an eneamine[19]

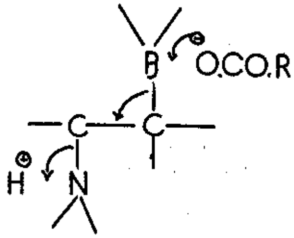


4

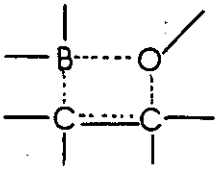
(c), and the necessity for acid catalysis, as evidence for the formation of cyclohexene proceeding via a trans β - elimination, as in (d).



(c)



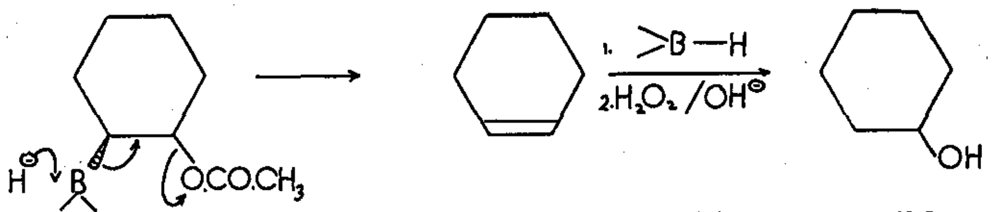
(d)



(e)

In general, therefore, it has been found that a borane with an oxygen substituent in the β position will undergo a temperature sensitive, uncatalysed, cis elimination, provided that the stereochemistry of the borane is suitable. When a cis elimination is not allowed owing to stereochemical factors, a trans elimination reaction can occur, with either acidic,[14,17] or basic,[2] catalysis, and for both oxygen- and nitrogen-containing functions.

Prior to this study, two reports in the literature had described the hydroboration of enol acetates. Cagliotti et al. hydroborated the enol acetate of cholestan-3-one with diborane and, on treatment of the reaction products with acetic anhydride, obtained a good yield of cholest-2-ene.[22] The olefin formation is analogous to that noted by Lewis,[17] and by Pasto,[14] requiring acid catalysis. The intermediate borane has a stereochemistry which would favour an elimination step similar to that in fig.(d) above. Hassner and Braun treated 1-acetoxycyclohexene with an excess of diborane and obtained cyclohexanol (38%) and trans cyclohexan-1,2,-diol (41%), after alkaline hydrogen peroxide oxidation.[23] The production of cyclohexanol was explained on the basis of a hydride-catalysed trans elimination of the β-acetoxyborane followed by the addition of B-H to the resulting cyclohexene, as in Scheme 5. This explanation is unusual in that it is the only trans elimination so far proposed to occur under hydroboration conditions, rather than with a catalyst added during work-up. The situation is further complicated by the possible presence of boron trifluoride during the experiment using "disiamylborane" (internal generation of diborane, using boron fluoride etherate). Pasto[14] found that the presence of boron fluoride during hydroboration



5

of enol ether altered the course of the reaction. Supporting evidence for the importance of the presence of a Lewis acid is found in the hydroboration of the morpholine eneamine of 2-ethylbutanal, where hydroboration used only 1.0 mol. of B-H bond, but occurred only when more than 1.3 mol. of borane was present.[24]

It had been observed[25] that the reaction of isopropenyl acetate with disiamylborane required 2.0 mol. of the borane. The hydroboration of a series of representative enol acetates was therefore undertaken, using disiamylborane in order to attempt to resolve the surprising absence of a report of the uncatalysed elimination reaction of the organoborane obtained from the hydroboration of the enol acetate structure. Such an absence is in contrast with the enol ether structure where both catalysed and uncatalysed eliminations are known. It was hoped that the use of unambiguously prepared disiamylborane might lead to a more selective olefin synthesis than obtainable by the use of diborane, on account of the dialkylborane's greater bulk, and its lower Lewis acidity.[26]

2. Results and Discussion

a) Scope of the Reaction

The reaction of an approximately fourfold excess of disiamylborane with a series of enol acetates was carried out in T.H.F. solution at 0° (Table I). After 24 hr. the residual hydride was estimated by hydrolysis of the reaction mixture with water. Residual enol acetate was estimated by g.l.c. The reaction mixture was then oxidised with an excess of aqueous alkaline hydrogen peroxide, and estimated by g.l.c. for alcohols and any olefin produced. In a control experiment the internal standard, chlorobenzene, was found to be stable under hydroboration conditions (Experimental Section).

The enol acetates derived from the ketones reacted very slowly to give undetectable amounts of alcohols. Symmetrical ketones were used in order to limit isomerism to cis-trans isomers about the olefinic group. The enol acetates derived from the aldehydes with an α-methylene group reacted rapidly,

Table I

Reaction of Enol Acetates with an Excess of Disiamylborane in T.H.F. Solution at 0° (24 hr.)

Enol Ester Derived From	Initial Enol Ester (mmoles)	Initial R_2BH (mmoles)	Residual Enol Ester (mmoles)	Residual R_2BH (mmoles)	Alcohol (mmoles)
n-Butyraldehyde	11.5	45.5	0.0	20.5	7.9
n-Hexaldehyde	10.9	45.0	0.0	23.0	7.3
n-Octaldehyde	9.3	42.8	0.0	17.7	5.5
Isobutyraldehyde	7.6	29.8	6.3	25.7	-
Acetone	11.2	37.2	0.0	15.0	8.4
3-Pentanone	10.9	42.8	9.8	38.0	0.0
4-Heptanone	11.5	38.2	9.8	31.9	0.0
Cyclohexanone	9.5	38.1	9.1	33.8	0.0

however, with the absorption of two equivalents of disiamylborane, producing no detectable amount of olefin, but a good yield of the n-alcohol, on oxidation.

As a confirmatory experiment the hydroboration of 1-acetoxyhex-1-ene was repeated on a preparative scale (using 27.5 mmoles enol acetate). The n-hexanol was isolated (67% yield) after the alkaline hydrogen peroxide oxidation, and identified by the preparations of its phenylurethane which had a melting point identical with that of the derivative prepared from a known sample of n-hexanol.

There were two anomalous cases. The ester derived from iso-butyraldehyde behaved like those derived from the ketones, only 17% reacting during 24 hr., while the enol acetate derived from acetone reacted rapidly to completion, behaving more like an aldehyde enol acetate.

The relative reactivity of the enol esters is readily correlated with their structure. Disiamylborane has been shown to react easily with a di-substituted olefin, but only very slowly with a tri-substituted double bond.[26] The aldehyde enol acetates all have a 1,2-disubstituted double bond, while the acetates from iso-butyraldehyde and the ketones have a 1,1,2-trisubstituted double bond. Iso-propenyl acetate is unusual in having a 1,1-disubstituted double bond, and would therefore be expected to react readily with a dialkylborane.

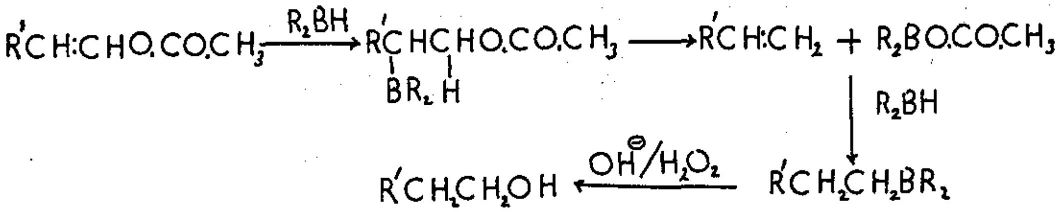
At 0° cyclohexenyl acetate did not react significantly with disiamylborane, during 48 hr. The loss of hydride from the reaction mixture was similar to that from a solution of disiamylborane in the absence of cyclohexenyl acetate (see Experimental Section, Table III). Hassner and Braun achieved over 60% reaction with this system,[23] however, but here the temperature was allowed to rise to 60°. Furthermore the experimental data given describe the production of a monoalkylborane (2 moles. of 2-methylbut-2-ene with 1 mole. of diborane), rather than disiamylborane. Apart from any increase in reactivity on raising the temperature, disiamylborane isomerises readily in refluxing T.H.F. solution (66°), to give a less hindered borane which yielded 3-methylbutan-1-ol on oxidation (as in Table II, Experimental Section). Either factor might explain the difference in the results reported here from those obtained by Hassner.

The formation of n-alcohols and with no detectable amount of the parent aldehyde, suggests that boron is not added at the carbon atom in the α position to the acetoxy function, during the initial hydroboration. Small amounts of ketone detected were probably produced through some hydrolysis of the enol acetate during the alkaline oxidation. If addition of the B-H bond had occurred to place boron α to the acetoxyl group, then the subsequent alkaline oxidation should produce a 1,1-diol which would lose water to regenerate the parent aldehyde.

A more satisfactory explanation, which also accounts for the necessity for two equivalents of the dialkylborane, is that the boron is added at the β-carbon to the acetoxy group. This would explain both the ready reaction of isopropenyl acetate, and the low reactivity of the enol acetate from iso-butyraldehyde. The former contained only hydrogen at the β-carbon, while the latter ester had two β-alkyl substituents. Thus the inductive withdrawal of electrons by the acetoxy group, as described by Brown for the hydroboration of allyl acetate,[2] is not important here.

In the case of enol esters it appears that inductive withdrawal is outweighed by the mesomeric donation of a lone pair from the ethereal oxygen atom, an effect operating in the opposite direction. A similar explanation has been offered in the case of enol ethers.[14]

A β-elimination reaction of the intermediate borane, producing an olefin and disiamylboron acetate, would then explain the necessity for the second equivalent of disiamylborane. Subsequent hydroboration of the olefin as in Scheme 6, below, would produce a borane capable of giving the n-alcohol on alkaline oxidation.



6

The eliminated dialkylboron acetate has been shown to be unreactive to disiamylborane,[31] and the second equivalent of hydride cannot therefore be spent in reducing the ester group.

Further confirmation of the importance of an olefinic intermediate comes from a comparison of the results of the hydroboration of 1-acetoxyhex-1-ene, and isopropenyl acetate. The former enol acetate gives a good yield of n-hexanol, the hydroxyl group being placed in the same position as the original acetoxy group. The latter enol ester gives a good yield of n-propanol, the hydroxyl group appearing at the terminal position rather than at the site of the acetoxy function. This result would be expected if the reaction proceeded through the hydroboration/oxidation of prop-1-ene and hex-1-ene. The use of disiamylborane explains the absence of small amounts of hexan-2-ol, and isopropanol.[38]

b) Attempted Separation of the Two Steps of Reaction

As the elimination reaction of the intermediate borane occurred readily at 0° during this study, it was not possible to use the method of Cagliotti,[22] where an excess of the hydroborating agent was used, and followed by the hydrolysis of residual B-H bonds before an acid catalysed elimination step. In order to isolate the olefin, therefore, it was necessary to add one equivalent of disiamylborane to the enol acetate. Table IV summarises the overall results obtained when the more reactive enol acetates were treated with 1.0 equivalent of disiamylborane at ice temperature.

Samples were withdrawn periodically from the reaction mixture, quenched with an excess of hex-1-ene, and the residual enol ester estimated by g.l.c. The results obtained from reactions using the enol acetates of n-butyraldehyde, n-hexaldehyde, and n-octaldehyde are shown in Tables V-VII. In all cases the enol-ester loss followed a smooth curve, with a stoicheiometry of two moles of dialkylborane reacting with one mole of enol ester. The curves obtained from a typical experiment are shown in Fig. 1. It is evident that the initial hydroboration is considerably slower than the subsequent two stages, making isolation of an olefinic intermediate impossible. Similar rapid β-eliminations have been reported, as described in the introduction to this section.[2,6-8,14]

Experimental difficulties were encountered in the estimation of residual enol acetates derived from n-hexaldehyde and n-octaldehyde. Here, other compounds were eluted simultaneously

Table IV

Reaction of Enol Acetates with Equimolar Quantities of Disiamylborane in T.H.F. Solution at 0° (24 hr.)

Enol Ester Derived From	Initial Enol Ester (mmoles)	Initial R_2BH (mmoles)	Residual Enol Ester (mmoles)	Residual R_2BH (mmoles)
n-Butyraldehyde	45.0	45.0	22.9	0.0
n-Hexaldehyde	38.5	42.0	15.1	0.0
n-Octaldehyde	34.4	34.7	19.0	0.0
Acetone	24.9	23.0	13.1	0.0

Table V (Fig. 1.)

The Reaction of 1-Acetoxybut-1-ene (47.2 mmoles) with Disiamylborane (19.6 mmoles, 0.5M.) in T.H.F. Solution at O°.

Time (hr.)	0.0	0.5	1.1	2.0	4.3	6.0	7.0	9.0	11.6	13.0	23.6
Enol acetate unreacted											
Cis isomer (mmoles)	21.5	19.5	19.0	17.3	15.8	15.0	15.0	14.9	15.1	15.2	15.6
Trans isomer (mmoles)	25.7	24.7	25.0	23.5	21.9	22.0	22.3	22.1	22.1	22.2	22.4

Table VI

The Reaction of 1-Acetoxyhex-1-ene (35.2 mmoles) with Disiamylborane (20.4 mmoles) in T.H.F. Solution at 0°

Time (hr.)	0	0.5	1.0	2.5	4.0	5.5	7.5	14.1	22.5
Enol Acetate unreacted									
Cis isomer (mmoles)	15.6	15.4	14.2	13.4	11.6	11.9	10.7	10.1	10.1
Trans isomer (mmoles)	19.6	19.8	18.6	17.2	16.2	16.7	15.1	15.1	14.9

Table VII

The Reaction of 1-Acetoxyoct-1-ene (33.1 mmoles) with Disiamylborane (24.2 mmoles) in T.H.F. Solution at 0°

Time (hr.)	0	0.9	1.8	3.3	5.0	7.0	8.2	19.7
Enol Acetate unreacted								
Cis isomer (mmoles)	14.6	12.2	11.1	8.9	8.9	8.1	8.4	7.6
Trans isomer (mmoles)	18.5	17.5	16.5	15.4	14.9	13.6	14.1	13.4

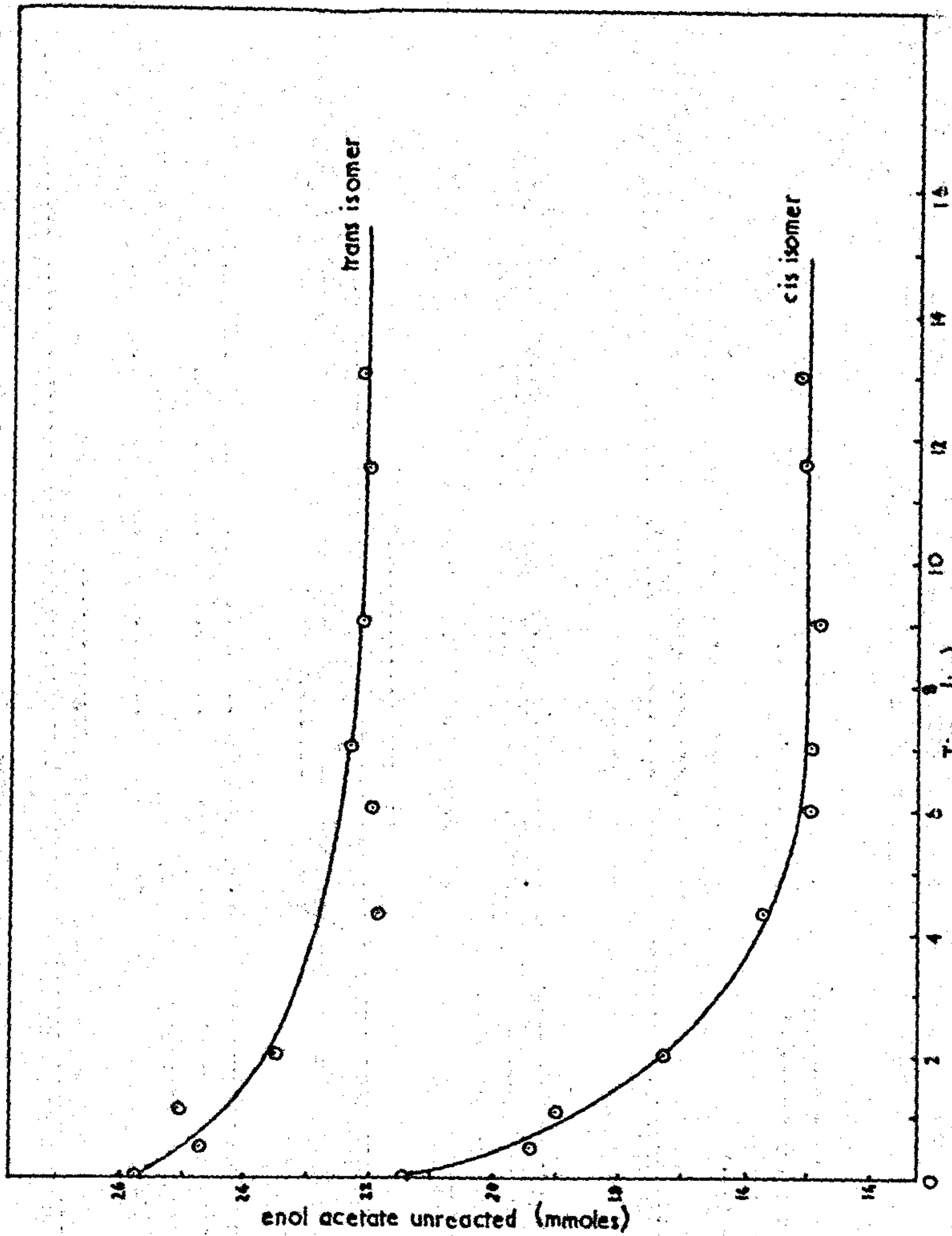


FIGURE I. Residual Enol Acetate During the Reaction of 1-Acetoxybut-1-ene (47·2 mmoles) with Disiamylborane (19·6 mmoles, 0·5 M.) in T.H.F. Solution, at 25°. (Table V.)

with the enol esters during g.l.c. analysis, giving an unreliable estimation. The contaminant in the n-hexaldehyde case was found to be water, probably introduced during quenching of the samples with hex-1-ene. Use of carefully dried syringes and sample bottles overcame the difficulty. In the case of the n-octaldehyde enol acetates, the contaminant appeared to be an organoboron compound, as the alkaline hydrogen peroxide oxidation of the sample caused the peak to disappear.

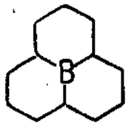
A small scale oxidation of each sample withdrawn was not suitable as a method of estimation, however, because some of the ester was hydrolysed under the oxidation conditions, as shown by the appearance of some n-octaldehyde. The alkaline oxidation of the reaction mixture obtained from the hydroboration of 1-acetoxyoct-1-ene did not lead to the production of n-octaldehyde, however, when an excess of disiamylborane had been present.

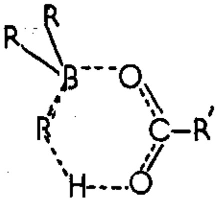
When dec-1-ene was used in place of hex-1-ene to quench the samples, the contaminant peak was eluted later than the enol acetates, allowing a reproducible estimation of the residual esters.

The change in elution time was surprisingly small, however, for a probable increase of four carbon atoms in the unknown compound.

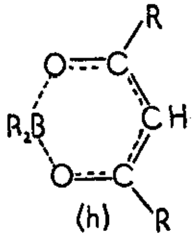
The β-acetoxy borane structure undergoes elimination more readily than the β-ethoxy boranes studied by Pasto.[14] With the latter structure the elimination reaction only became important on increasing the reaction temperature to 25°. Pasto was able to demonstrate that the thermal elimination proceeded through a cis transition state as in (1) below. Owing to the limited reactivity of enol acetates derived from a cyclic ketone, it was unfortunately not possible to hydroborate an enol ester which would demonstrate the stereochemistry of the elimination step in this study. It is probably significant, however, that all the trans elimination reactions of β-functional boranes which have so far been reported, have required additional acidic or basic catalysis and relatively vigorous conditions.

The electron withdrawing carbonyl group might be expected to make the ethereal oxygen atom of the acetoxy group less basic than that of an enol ether, and therefore less ready to participate in a cis elimination process of type (1). Several reports have described the ready inclusion of boron as a substituent in six-member alicyclic systems, as in (f).[32] In addition, strong evidence has been presented for a six-centre cyclic transition state for the protonolysis reaction of trialkylboron compounds, as in (g).[33] Another report describes the ready formation of cyclic compounds as in (h) below, through the reaction between a β-diketone and a trialkylborane.[34] Taking into account that the carbonyl oxygen atom has been shown to be the most basic site of the carboxyl group,[35] therefore, it is probable that the elimination reaction of the β-acetoxyboron structure proceeds through a

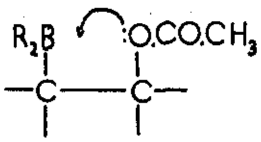

(f)



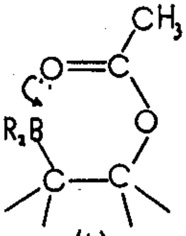
(g)



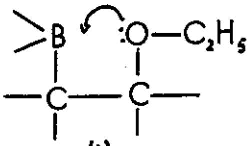
(h)



(j)



(k)



(l)

six-centre intermediate as in (k), similar to that proposed for a pyrolytic ester elimination rather than via a four-centre reaction as in (j).

More information on the nature of the elimination reaction might be obtained by examining the hydroboration of an enol ester whose acid function contained a strongly electron withdrawing group which would reduce the basicity of the carbonyl oxygen atom. Duncanson and Gerrard found that the infra-red spectrum of di-n-butyl boron trifluoroacetate was unusual in that the shift to a lower wave number, observed for the absorption frequency of the carbonyl group of a dialkyl boron acetate, propionate, etc., did not occur.[36] This anomaly was explained on the basis of the quenching of a mesomeric equilibrium, as in (m) below, through the inductive withdrawal of charge from the carbonyl group by the trifluoromethyl group.


(m)

An attempt was made therefore to prepare 1-trifluoroacetoxyhex-1-ene, using the method of Bedoukian.[28] No enol trifluoroacetate could be detected in the reaction mixture, however, possibly because the boiling point of the trifluoro-acetic acid anhydride (39°) was too low to allow enolisation of the hexaldehyde to compete successfully with polymerisation.

c) Selectivity

Disiamylborane has been used to remove the more reactive cis-isomer from a mixture of cis- and trans-olefins. Of the enol acetates examined above, only cyclohexenyl acetate, isopropenyl acetate, and the enol acetate of isobutyraldehyde show a single isomer. The enol acetates prepared from pentan-3-one and heptan-4-one are a mixture of cis and trans isomers. The remaining aldehyde enol esters studied show only cis, trans isomerism. The preparative methods used gave an approximately equimolar mixture of the two isomers (by g.l.c. analysis).[27-30]

The results of the experiments where an insufficiency of disiamylborane was added to the reactive aldehyde enol acetates (Tables V-VII; Fig. 1) can therefore be used to calculate a relative-rate factor for the competition between the two isomers for the available dialkylborane. The method of Ingold and Smith[37] gave the following results:

1-acetoxybut-1-ene, k_{cis}/k_{trans} = 1.3

1-acetoxyhex-1-ene, k_{cis}/k_{trans} = 1.3

1-acetoxyoct-1-ene k_{cis}/k_{trans} = 1.2

Reported values[38] for the hydroboration of olefins by disiamylborane are: but-2-ene, $k_{cis}/k_{trans} = 6$; hex-3-ene, $k_{cis}/k_{trans} = 9.5$, a far larger selectivity.

An experiment was therefore carried out to find out whether isomerisation of the enol acetates occurred under the reaction conditions. 1-acetoxyhex-1-ene was separated into the cis and trans isomers by preparative g.l.c. A sample of the purified cis isomer was then treated with a small amount of disiamylborane, and allowed to stand at ice temperature for 24 hr. After a small initial drop in the amount of the cis isomer as the disiamylborane reacted (Fig. 2, Experiment Section Table VIII), no further change in the relative amounts of the two isomers occurred. The enol acetates were therefore stable to isomerisation under hydroboration conditions.

Reaction of 1-acetoxyhex-1-ene with the very hindered di-isopinocampheylborane resulted in a small increase in selectivity ($^{k_{cis}}/_{k_{trans}} = 1.6$). The experimental conditions were arranged to be similar to those in the competition experiments using disiamylborane. The results are shown in Table IX. Again the behaviour of the enol acetate isomers is in contrast to the cis-trans mixture of the corresponding olefin, which shows such selectivity that the trans-olefin reacts only by a displacement reaction.[39]

This final observation indicates that the acetoxy group is exerting very little effect on the course of the addition. It is surprising that the enol acetate of pentan-3-one, which has one extra substituent at the double bond, and at the carbon atom bonded to the acetoxy group, should be so unreactive to disiamylborane. On steric grounds, therefore, it might be expected that the dialkylborane would add its

Table IX

The Reaction of 1-Acetoxyhex-1-ene (13.6 mmoles) with ~~Di-iso~~pinocampheylborane (11.4 mmoles, 0.5 M.) in Diglyme Solution

Time (hr)	0.00	2.65	15.1	17.7	25.8
Enol acetate unreacted (mmoles)					
Cis isomer ...	6.2	4.8	2.9	2.7	2.7
Trans isomer ..	7.4	6.7	5.4	5.3	5.2

Table X

The Reaction of 1-Pivaloyloxyhex-1-ene (4.70 mmoles) with Disiamylborane (4.84 mmoles, 0.5 M.) in T.H.F.Solution.

Time (hr).	0.0	0.90	2.50	5.00	8.1
Enol pivalate unreacted (mmoles)					
Cis isomer..	2.10	1.70	1.32	0.83	0.53
Trans isomer..	2.60	2.30	2.13	1.90	1.75

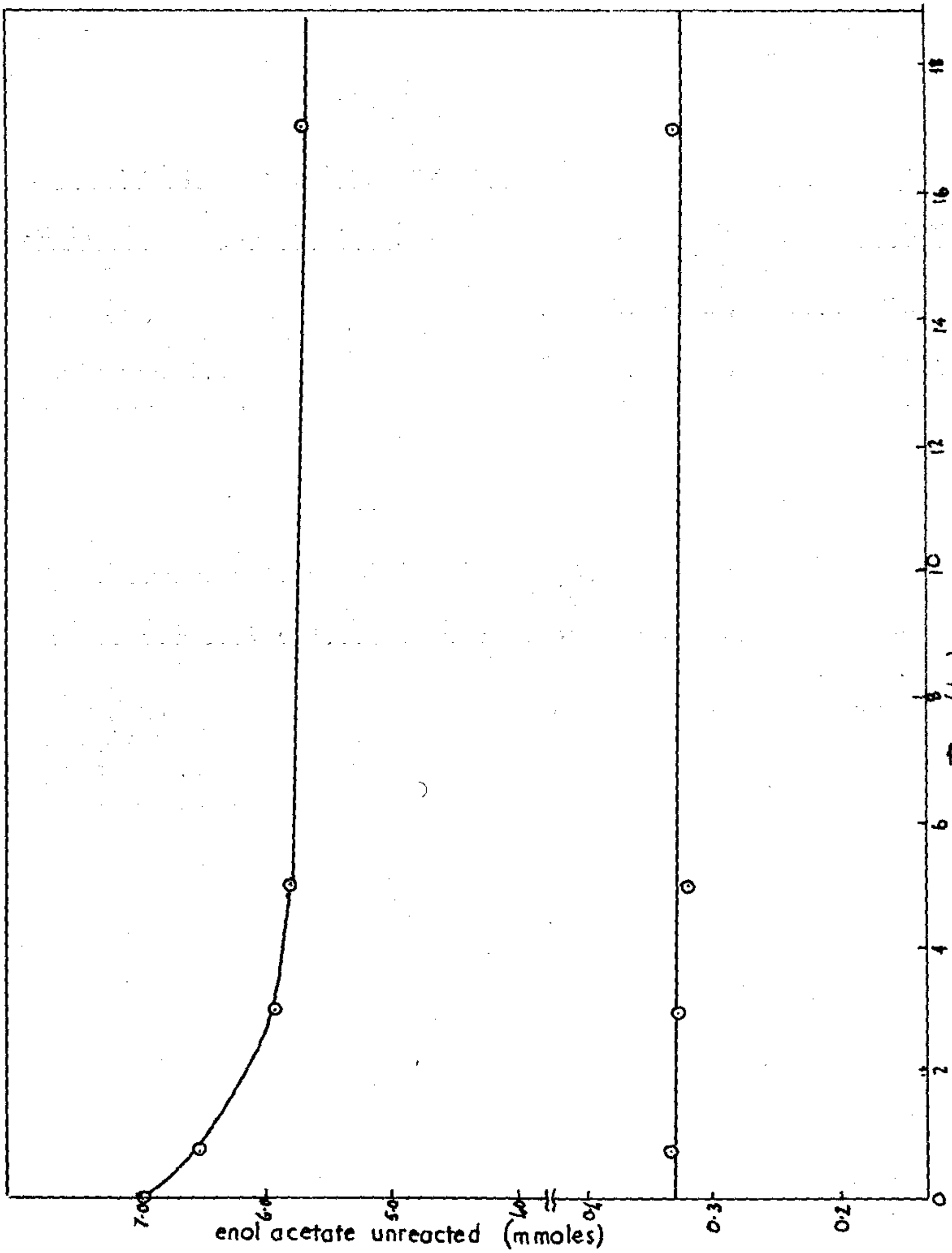
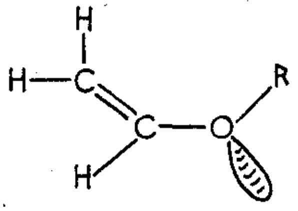


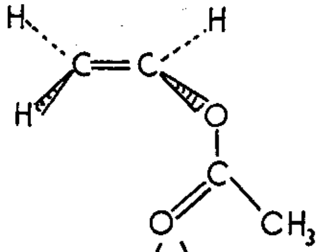
FIGURE 2. The Reaction of Disiamylborane (1·25 mmoles) with cis-1-Acetoxyhex-1-ene (7·23 mmoles) in THF Solution at 0°.

boron atom to the acetoxy-end of the double bond. The fact that addition is in the opposite sense appears to confirm the electronic nature of the control of the reaction.

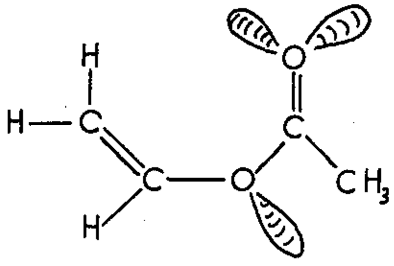
Some doubt exists as to the configuration of the enol acetate group. Sheppard and Owen, studying methyl vinyl ether, used the rotational fine structure of certain infra-red absorptions to demonstrate the existence of two rotational isomers about the oxygen-vinyl carbon bond.[40] One isomer was more stable than the other by 1.5 kcal., suggesting that the $C=C-O$ group is planar. The cis isomer (n) was identified as the more stable. Methyl formate was similarly found to have a planar configuration.



(n)



(p)



(q)

Yogev and Mazur, however, examined the ultra-violet spectrum of the more closely analogous compound, vinyl acetate, and found that the double bond makes little contribution to the electronic transition of the acetate chromophore.[41] It was therefore assumed that the plane of the $CH_3CO.O-$ group was perpendicular to the plane of the double bond, as in (p), rather than in the same plane (q) as would be assumed from Sheppard's results. If the enol acetate adopts the configuration (p), then the small cis/trans selectivity of hydroboration would be explained by the ready attack of the organoborane from the less hindered side. Equally, the presence of a strongly hindered acid group in the enol ester should have little influence on the selectivity. A sample of 1-pivaloyloxyhex-1-ene, $C_4H_9\,CH{=}CH.O.CO.C(CH_3)_3$, was therefore prepared and separated by preparative g.l.c. A mixture of the cis and trans isomers was treated with disiamylborane in a competition experiment, and gave a competition factor $^{k}\mathrm{cis}/k_{\mathrm{trans}} = 1.7$ (Table X). A sample of the trans isomer was hydroborated also with an excess of disiamylborane in order to check that the overall reaction of an enol pivalate with disiamylborane was similar to that of an enol acetate. The results were:

	Quantities (mmoles)	
	Initial	Final
Enol Pivalate (trans)	4.9	1.2
Disiamylborane	16.1	6.5
n-Hexanol obtained	3.15 mmoles (85%)	
Hex-1-ene	(undetected)	

showing that the overall reaction is similar to the enol acetate case.

The selectivity between cis and trans enol pivalates parallels that shown during the reaction of aldehyde enol acetates with di-isopinocampheylborane. Thus the bulky pivaloyloxy-group is able to influence the selectivity of the reaction. If the acid group is not in the plane of the double bond, very little difference from the selectivity of the enol acetates case would be expected. It is possible, therefore, that the enol ester group has a planar configuration, as in (q).

The small selectivity observed in the reaction of aldehyde enol acetates with disiamylborane may therefore be a reflection of the smaller size of the ethereal oxygen atom of the ester, compared with the alkyl group of a hydrocarbon.

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SECTION II

THE REACTION OF PROPIONIC ACID WITH REPRESENTATIVE SYMMETRICAL AND UNSYMMETRICAL TRIALKYLBORANES

Introduction

Trialkylboron compounds have proved resistant to hydrolysis by water and alcohols except under forcing conditions of temperature and pressure.[1] Aqueous hydrochloric and hydrobromic acids react readily to liberate one equivalent of alkane, but further hydrolysis of the dialkylborinic acid formed is very slow.[2] The presence of alkali generally increases resistance to hydrolysis except in the case of an isolated report by Weinheimer and Marisco, who found that the monoalkyl borane obtained by the hydroboration of 1,2-dimethyl-1,2-diphenylethylene was readily hydrolysed by aqueous sodium hydroxide, giving overall a stereospecific hydrogenation of the olefinic double bond.[3] This unusual behaviour was explained in terms of the ability of the 1,2-dimethyl-1,2-diphenylethyl group to sustain a negative charge, allowing migration of the alkyl group from boron to hydrogen. The general behaviour of trialkylboron compounds therefore contrasts with that of trialkylaluminium compounds, which tend to be very unstable to hydrolysis by water.[4]

The more weakly acidic carboxylic acids are more effective agents in the hydrolysis of organoboranes. The protonolysis of a trialkylborane by a carboxylic acid was first reported by Meerwein _et al._ in 1936,[5] and has since been used preparatively by Goubeau,[6] and Brown,[7] to achieve the complete dealkylation of trialkylboranes. Kolesnikov _et al._ studied the reaction of tri-n-butylborane with mono- and di-carboxylic acids,[14] and M. Kumada _et al._ developed the reaction using formic acid as a preparative route to tri-n-butylboroxine.[15] A further report by Lang mentions the preparation of boron-nitrogen heterocycles through the protonolysis reaction using an α-amino acid.[16]

A.K. Holliday _et al._ developed the reaction as an analytical method for trialkylboranes.[8] Goubeau made a careful study of the course of the reaction of trimethylborane with acetic acid under mild conditions, and found that the dialkylboron acetate product is polymeric at low temperatures, and that the boron containing product after removal of the last equivalent of methane under more vigorous conditions contains a B-O-B bond.[9] H.C. Brown proposed a six-centre cyclic mechanism for the protonolysis reaction,[10] and was subsequently able to demonstrate that the implied condition of retention of configuration was followed during the protonolysis of tri-2-norbornylborane.[11] During the course of the present study Toporcer et al. reported an exhaustive kinetic study of the reaction of triethylborane with several carboxylic acids.[12] An inverse relationship was found between the pKa of the acid, and the rate of dealkylation. Support was also obtained for the six-centre reaction mechanism proposed by Brown, both by demonstrating the importance of the configuration of the carboxyl group, and by the synthesis of compounds of similar structure to that proposed for the protonolysis reaction intermediate.

In only one isolated case[11] was mention made of the protonolysis of trialkylboranes which were not straight chain tri-n-alkylboranes. In the present study, therefore, the aim was to estimate the importance of structure of the alkyl groups bound to boron on the rate of protonolysis, and then to attempt to discover any selectivity between the removal of the different alkyl groups of an unsymmetrical trialkylborane.

During the course of the study on selectivity, a parallel series of experiments became known,[13] but the results obtained in the other work, under more vigorous conditions, disagreed markedly with those found here, and it was therefore decided to proceed. In the present work the approximate rates, and the hydrocarbon products of the reaction were studied. Since the organoboranes produced via hydroboration are not completely pure (93-99%),[10] and cannot be purified without the risk of extensive isomerisation and disproportionation, no attempt at a kinetic study was made.[17-19] Rather, portions were withdrawn from a standard concentration of the reactants in diglyme (diethylene glycol dimethyl ether) solution, quenched with aqueous sodium hydroxide, and then the extent of reaction was estimated by measurement of the hydrocarbon products by gas liquid chromatography (g.l.c.).

The study was therefore divided into three parts: (i) an initial survey using tri-n-hexylborane, to determine the most convenient conditions for the study, and then (ii) a comparative study of the overall rates of protonolysis of representative trialkylboranes. Finally, (iii), a series of unsymmetrical boranes were protonolysed by propionic acid to estimate the selectivity of removal of different alkyl groups.

1. The Reaction of Tri-n-hexylborane with Propionic Acid, under Conditions of Different Solvent, Temperature and Concentration of the Reactants.

Results and Discussion

Before experiments could be carried out to assess the relative stability of various trialkylboranes to propionic acid, it was necessary to explore the reaction of a simple trialkylborane with propionic acid, in order to find out the most convenient conditions for a comparative study. A series of samples of tri-n-hexylborane was therefore treated with varying amounts of propionic acid at several different temperatures.

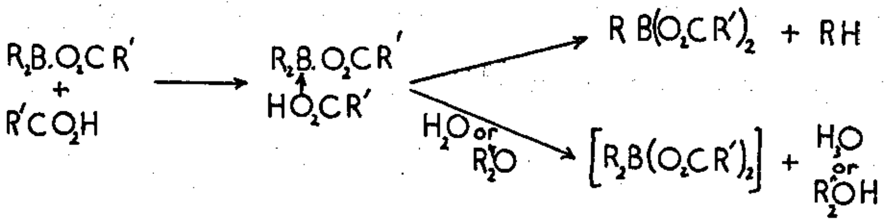
The curves in Fig. 1 show that at 0°, the reaction of tri-n-hexylborane with propionic acid, using a concentration of 3.0 moles of propionic acid per mole of trialkylborane, proceeds readily to give one equivalent of n-hexane in 20 hr. A large excess of propionic acid should greatly accelerate the dealkylation, and with 15.0 mol. of propionic acid, one equivalent of n-hexane was liberated in 4.0 hr. The second B-C bond was more resistant to protonolysis, and anomalous results were obtained. The reaction with 3.0 moles of propionic acid per mole of borane gave a slow reaction to produce 7% of the second equivalent within 115 hr., whereas 15.0 mol. of propionic acid (a five-fold excess) failed to react beyond the first stage. A similar trend was found when the borane, in diglyme solution, was protonolysed with 3.0 mol., and 15.0 mol., of propionic acid at 25° (Figs. 2 and 3). Here the first equivalent of n-hexane was produced within 3 hr. and with 3.0 mol. propionic acid, 60% of the second equivalent in 42.5 hr. With 15.0 mol. propionic acid liberation of the first equivalent of alkane was very fast, but no further reaction was found within 110 hr.

Fig. 3 also shows the relative rates of protonolysis of tri-n-hexylborane in tetrahydrofuran (T.H.F.) solution, and in petrol ether (100-120° boiling fraction). The protonolysis with 3.0 mol. acid in T.H.F. solution was slower than that in diglyme ($k_{\text{diglyme}}/k_{\text{T.H.F.}} = 2.1$ approximately, at 60.0 hr.), while the reaction in petrol ether was faster ($k_{\text{petrol}}/k_{\text{diglyme}} = 1.26$ approx.

at 40.0 hr.) When a sample of tri-n-hexylborane was protonolysed in T.H.F. solution with 15.0 mol. of the acid (Fig. 2), the rate of protonolysis of the second B-C bond was similar to that in diglyme solution using 3.0 mol. of acid. The behaviour here contrasts with that in diglyme solution, where an excess of acid appeared to inhibit the protonolysis.

The most convenient solvent for a comparative study of the reaction was therefore diglyme, where an internal generation of diborane in the presence of an olefin, produced the trialkylborane *in situ.*[20] T.H.F. was rejected as a possible solvent as, although an internal preparation of the borane was possible, diglyme solution gave a more useful rate of protonolysis. Petrol ether solution gave a small increase in rate over diglyme, but here the organoborane had to be isolated after its preparation in an ethereal solvent, with the attendant danger of oxidation during transfer, and of isomerisation and disproportionation during distillation.

Further experiments were carried out to attempt to obtain an explanation of the inhibition of the second stage of protonolysis in the presence of an excess of propionic acid. A. K. Holliday *et al.*[8] found that the presence of water inhibited the second stage of dealkylation of trimethylborane by acetic acid in ether solution at 40°. Dissociation of a complex between the solvent and the dialkylboron acetate was not thought to be rate determining, as acetate ion, in a dry ether solution, was also able to inhibit the second dealkylation. Proton loss to the solvent (or to the acetate ion in the latter case) from the second co-ordinated acid molecule was suggested as a possible explanation (Scheme 1).



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Diborane is more soluble in T.H.F. than in diglyme, and in solution is in the dissociated form (BH_3), when it can co-ordinate with the solvent as $R_2O:BH_3$. T.H.F. is therefore a more basic solvent than diglyme, and the slower rate of protonolysis of the second alkyl group in the former solvent was probably due to the more ready solvation of a proton. A Karl Fischer estimation of the propionic acid used showed that redistillation of the acid before use had allowed the retention of 0.39% (w/v) H_2O. The large excess of propionic acid used in the protonolyses in diglyme solution may therefore have introduced sufficient water to allow the type of inhibition observed by Holliday. Fig. 2 shows that the inhibition is not merely a concentration effect as the subsequent addition of sufficient dry diglyme to reduce the concentration of the acid to the molarity present during the less concentrated protonolysis only allowed breaking of the second B-C bond to proceed very slowly. Inhibition is therefore only a function of the relative proportions of the reagents. A sample of propionic acid was therefore dried to contain only 0.04% H_2O (w/v) (Fischer determination), and the experiment using a large excess of the acid at 25° repeated, using the dried acid. Fig. 4 shows that a rapid dealkylation of the dialkylboron propionate occurred at 25°, producing 70% of the second equivalent of n-hexane within 13 hr. A second reaction was carried out under similar conditions, but in the absence of $NaBF_4$, the by-product of an internal generation of diborane (Fig.4).

The second equivalent of n-hexane was released a little more rapidly (^{k}diglyme$/k_{NaBF_4}$ = 1.5 approx. at 9.0 hr.) showing that the presence of $NaBF_4$ can inhibit the second stage of dealkylation to a small extent. Presumably, therefore, the borofluoride ion can act as a proton acceptor, similarly to acetate ion, in the study reported above,[8] but only to a small extent.

The protonolysis in T.H.F. solution using an excess of acid was an anomalous case (Fig. 2). Here, the wet acid was able to protonolyse the dialkylboron propionate slowly, although the more basic solvent, T.H.F., together with the water introduced with the acid, should be a more effective proton accepting system, causing strong inhibition of the reaction. No reasonable explanation for this feature could be found.

Brown and Murray[7,10] have reported that trialkylboranes containing secondary carbon to boron bonds protonolyse less readily than those with primary carbon to boron bonds. As a preparative procedure for alkanes they suggested that an initial thermal isomerisation of the borane should be carried out, allowing the subsequent protonolysis of a more reactive structure. Tri-n-hexylborane was probably therefore among the more reactive boranes of the present series and, with less reactive trialkylboranes, comparison of extents of protonolysis would be most conveniently based on the first stage of dealkylation. Torporcer et al.[12] in a kinetic study of the mono-dealkylation of triethylborane by various organic acids, found that protonolysis was approximately one order of magnitude faster in xylene solution than in diglyme. It was of interest therefore to compare the extent of protonolysis of the first alkyl group in diglyme solution with that in a non-polar solvent. The sterically hindered borane, thexyldi-n-hexylborane, reacted with propionic acid at a convenient rate for this comparison.

An attempt to isolate the borane by vacuum distillation (0.05mm) was unsuccessful, yielding 2,3-dimethylbut-2-ene, and tri-n-hexylborane. The procedure recommended by Hawthorne[19] was therefore followed, whereby the borane was prepared in T.H.F. solution. The solvent, and excess olefins from the preparation were then removed under reduced pressure. It was possible, in this way, to prepare solutions of the borane in diglyme, and petrol ether ($100-120^{\circ}$ boiling fraction). Treatment with dried propionic acid (3.0 mol.) slowly produced n-hexane, but only a very small amount of 2,3-dimethylbutane. The rate of n-hexane production was similar in the two solvents (Fig. 5), giving an approximate value for ${}^{k_{petrol}}/_{k_{diglyme}}$ of 1.4-1.5, a much smaller value than found by Toporcer for triethylborane. Clearly, therefore, the initial dissocation of a co-ordination complex between a more branched borane and the solvent diglyme is not important under the conditions of this study.

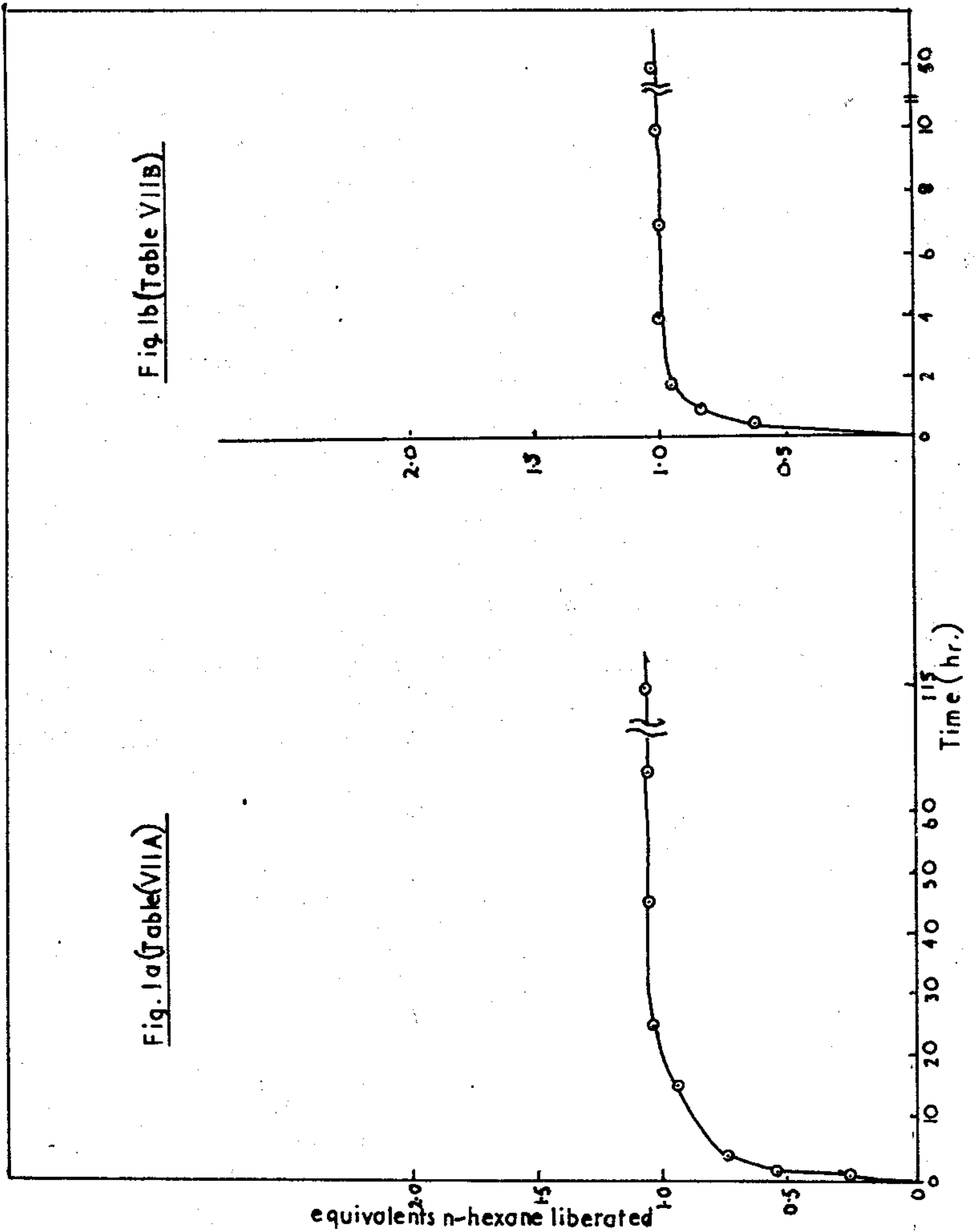


FIGURE 1a. The Reaction of Propionic Acid (38·50 mmoles) with Tri-n-hexylborane (12·0 mmoles, 0·65M.) in Diglyme Solution, at 0°. FIGURE 1b. The Reaction of Propionic Acid (145·0 mmoles) with Tri-n-hexylborane (12·20 mmoles, 0·65M.) in Diglyme Solution, at 0°.

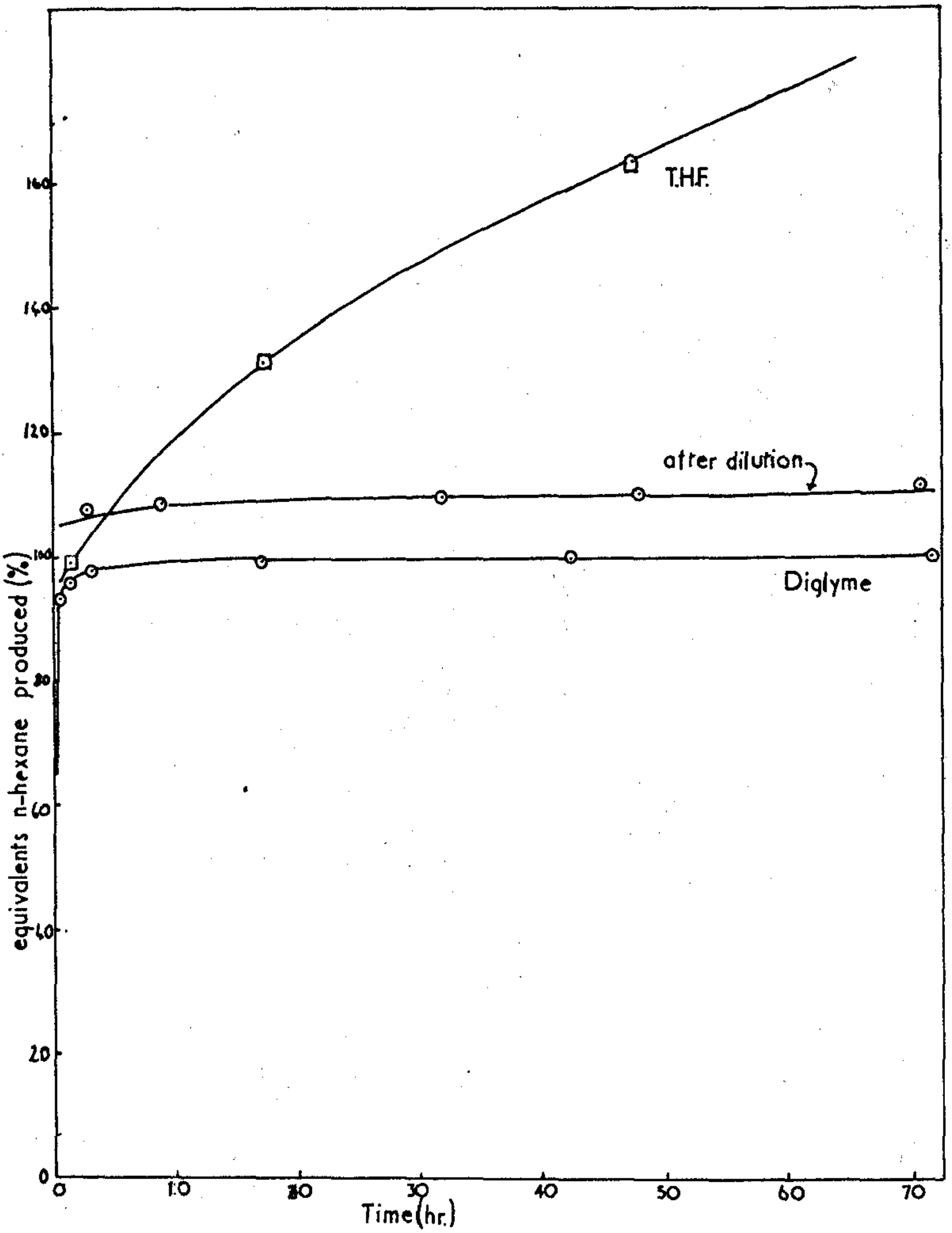


FIGURE 2. n-Hexane Production During the Reaction of an Excess of Propionic Acid with Tri-n-hexylborane, a) in T.H.F. Solution (0·65 M.)(Table VIII a), and b) in Diglyme Solution (0·65 M.)(Table VIII b.)

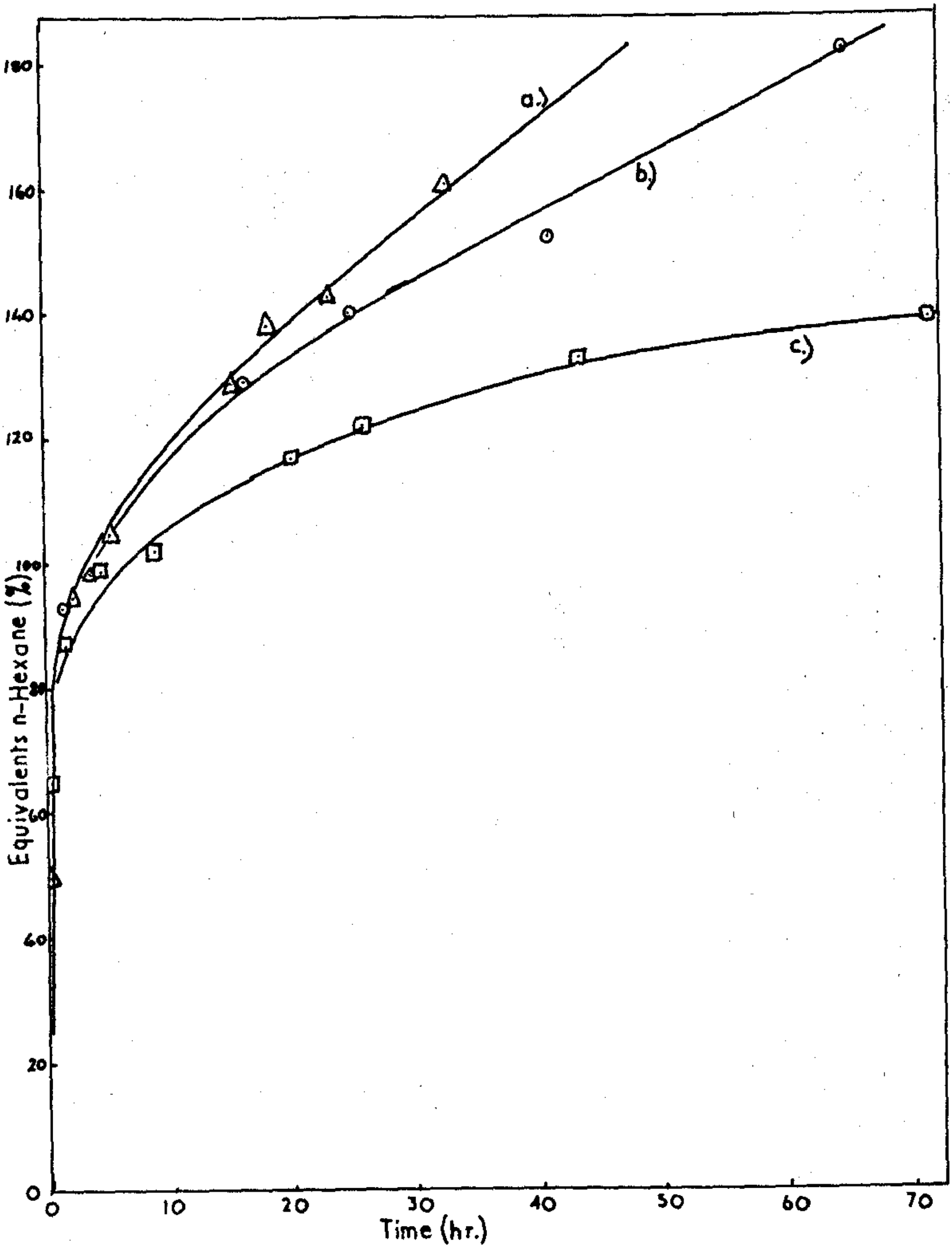


FIGURE 3. Production of n-Hexane During the Reaction of Propionic Acid with Tri-n-hexylborane Solutions (0·65 M.) in a) Petrol Ether (Table IXa), b) Diglyme (Table IX b), and c) T.H.F (Table IX c), at 25°.

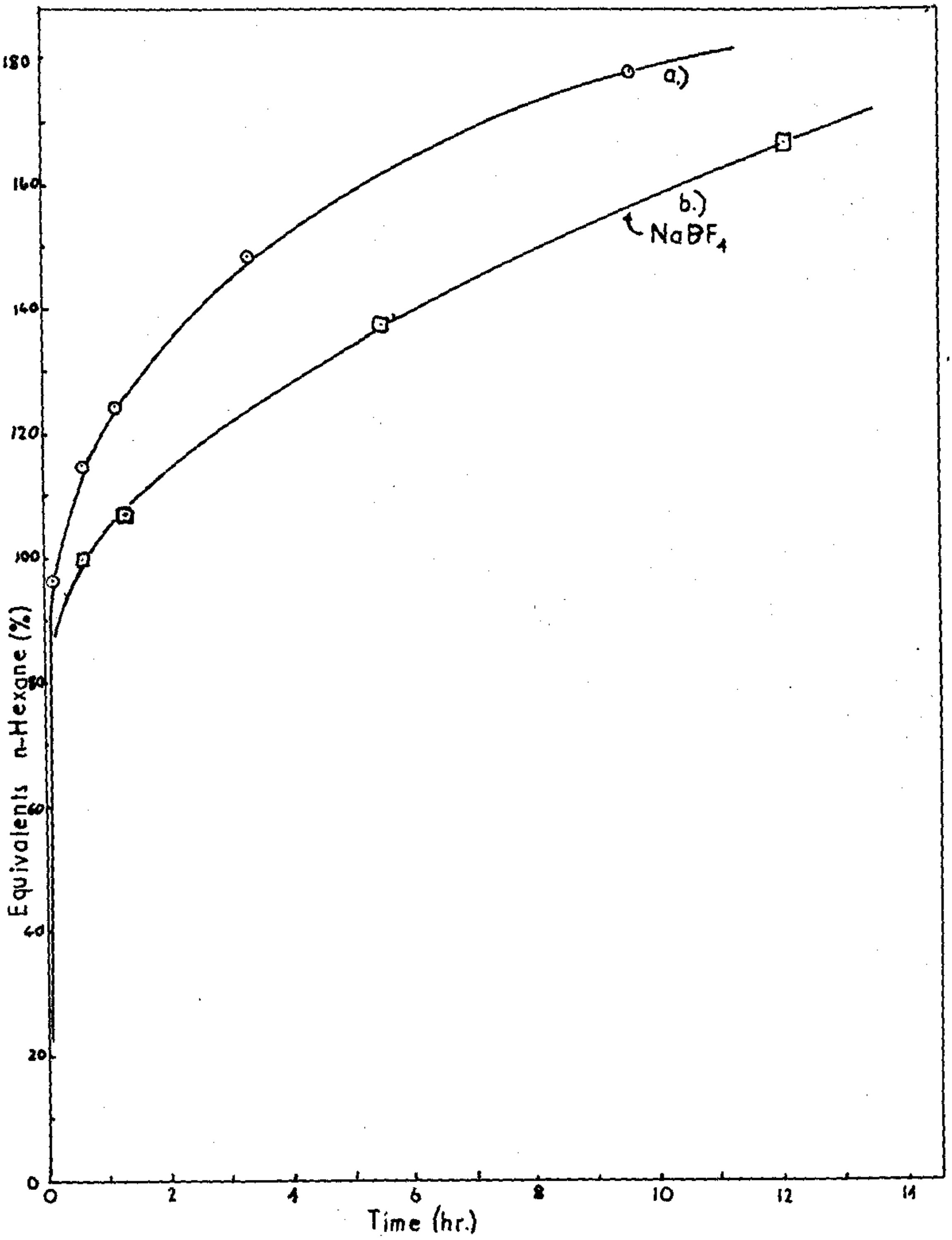


FIGURE 4. Production of n-Hexane During the Reaction of an Excess of Propionic Acid with Tri-n-hexylborane a) in Diglyme Solution (0·65 M.)(Table XIb), and b) in Diglyme Solution (0·65 M.) in the Presence of Sodium Borofluoride, at 25°(Table XIa).

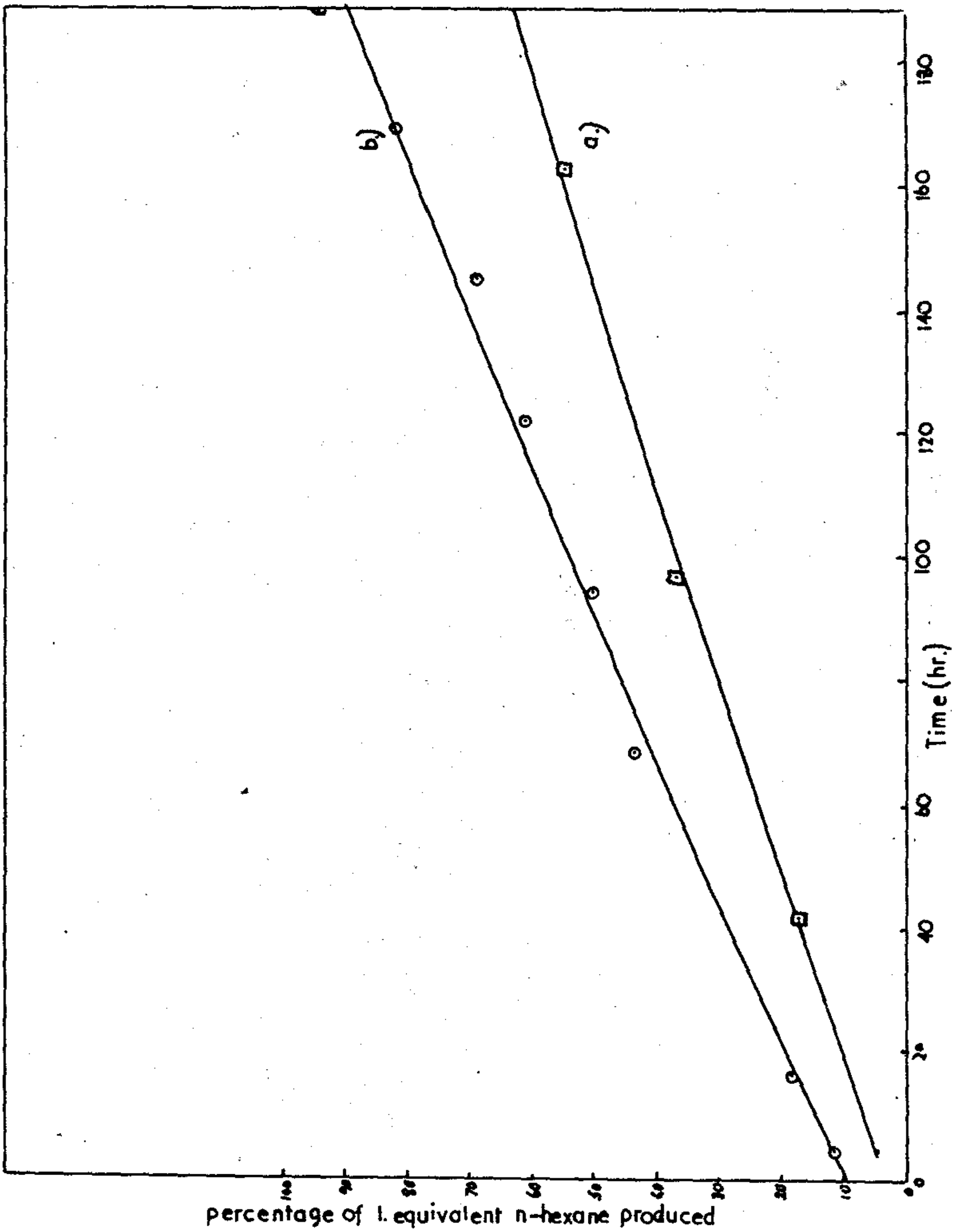


FIGURE 5. Production of n-Hexane During the Reaction of Propionic Acid with Thexyldi-n-hexylborane: a) in Diglyme Solution (0·65M.), and b) in Petrol Ether Solution (0·65M.), at 25°

2) The Reaction of Propionic Acid with Representative Symmetrical and Unsymmetrical Trialkylboranes

Results

The organoboranes studied were prepared by the hydroboration method, with the exception of the t-butylboranes which were prepared using the method of M. F. Hawthorne[21] and P. A. McCusker *et al.*[22] All protonolyses were carried out in diglyme solution (0.65M.), using the amount of dried propionic acid (3.0 mol.) necessary to break all B-C bonds present.

Experiments detailed in Part 1, above, showed the sensitivity of the protonolysis reaction to temperature. Only tri-n-hexylborane was reactive to propionic acid at 0°. The main comparison of the extent of protonolysis of the series of trialkylboranes was therefore carried out at 50°, the more reactive boranes also being compared at 25°.

J. Goubeau and H. Lehmann showed that the third stage of protonolysis of a trialkylborane is accompanied by a change in structure of the boron-containing residue, and does not proceed readily at low temperatures.[9] Experiments outlined in Part 1 above, together with the results of A.K. Holliday et al,[8] suggest the first stage of protonolysis to be more suitable than the second stage, as the basis of the comparative study. In addition, for an unsymmetrical borane, $R^fR^fBR^s$, which contains both an alkyl group (R^f) which is removed readily from boron and another (R^s) which is protonolysed slowly, the electronic nature of the boron containing compound would be different after the first stage of dealkylation. Thus if the extent of protonolysis is not allowed to proceed beyond approximately 75% of the removal of the first alkyl group, the substrate yielding the alkane may be assumed to be the trialkylborane. The assumption is supported by the relatively slow second dealkylation (see Part I, above), which is inhibited probably by electron donation from the propionyl group to the boron atom, lowering the Lewis acidity of the boron atom.[24]

The comparative data are therefore derived mainly from the first stage of protonolysis. This also allowed the use of a relatively low temperature, 50°, at which it was anticipated that isomerisation, etc., reactions of the boranes would not be important.

The isomerisation, disproportionation, etc., reactions possible under these conditions are considered more fully in Part 3 below.

The extent of protonolysis was estimated as described in the Introduction, above. The results obtained from a series of symmetrical and unsymmetrical boranes are summarised in Table I in order of the extent of protonolysis. The less reactive boranes were also protonolysed in sealed tubes as a precaution against possible contamination of the reaction mixture, or loss of volatile products, through the repeated puncture of the rubber Suba-Seal cap of the reaction flask.

For the unsymmetrical boranes, the total yield of saturated hydrocarbons is included in the table, and no account taken of selectivity between the different alkyl groups present.

The boranes studied included symmetrical tri-primary alkylboranes (reactions 1, and 4, in Table I), and tri-secondary alkylboranes (5,11). Unsymmetrical boranes examined included three boranes containing a tertiary, and two primary alkyl groups (2,6,7), and one containing a primary and two tertiary alkyl groups (3).

Table I

The Reaction of Propionic Acid with Representative Trialkylboranes in Diglyme Solution (0.65 M.)

	Total Yield of Alkanes Produced						Total Number of Alkyl Substituents		
	0°		25°		50°				
	Yield[a]	Time[b]	Yield[a]	Time[b]	Yield[a]	Time[b]	α	β	(α + β)
1. Tri-n-hexylborane	100	16-19	100	2-3	100	1.0	0	0	0
	117	110.0	173	110	140	3.2			
2. t-Butyldi-n-hexylborane	-	-	100	11.25	100	1.3	2	0	2
			126	75	114	3.2			
3. Di-t-butyl-n-hexylborane	-	-	74.1	11.25	76.6	1.3	4	0	4
			91.6	20.0	92.5	3.2			
4. Tri-(2-ethylhexyl)-borane	-	-	7.3	11.25	12.9	3.2	0	3	3
			16.3	48.0	95.9	48.0			
5. Tri-2-hexylborane	6.6	96.0	11.5	48.0	59.4	48.0	3	0	3
6. Thexyldi-n-hexylborane			67.0	240*	63.1	48.0*	2	1	3
7. Thexyldi-n-octylborane	-	-	-	-	66.3	48.0*	2	1	3
8. Disiamyl-n-hexylborane	-	-	12.1	123	52.5	66.0*	2	2	4
9. Disiamyl-n-octylborane	-	-	-	-	47.0	66.0*	2	2	4
10. Disiamyl-2-hexylborane	-	-	-	-	4.8	66.0*	3	2	5
11. Tri-siamylborane	-	-	-	-	2.4	46.2*	3	3	6
12. Dithexyl-n-octylborane)	Could not be prepared by hydroboration						4	2	6
13. Thexyldi-2-hexylborane)							5	2	7

* Sealed tube experiments   a % (100% = removal of one alkyl group from R_3B)   b hr.

Unsymmetrical trialkylboranes containing one primary and two secondary alkyl groups (8,9) and also a borane containing a mixture of two different secondary alkyl groups (10), were also examined. An attempt to prepare dithexyl-n-octylborane (12) by hydroboration failed, as did an attempt to prepare a trialkylborane containing both tertiary and secondary alkyl groups bonded to boron (13). The latter results (12,13) are in accordance with reports from H.C. Brown's laboratory.[23]

As it was not intended at this stage to distinguish between the alkyl groups removed during protonolysis, an attempt was made to follow the reaction spectroscopically through the change in the stretching frequency (infra-red region) of the carbonyl group of propionic acid, on reaction with a trialkylborane. W. Gerrard _et al._ have found that di-n-butyl acetylborinate shows only one C-O stretching frequency (1603cm.$^{-1}$) and at a lower frequency than that for the carbonyl group of free propionic acid, probably due to the sharing of lone pair electrons of the acid carbonyl group with the electron deficient boron atom, as in (a).[24]

When a sample of tri-n-hexylborane and propionic acid (1.0 mol.) in T.H.F. solution at ambient temperature was placed in an i.r.

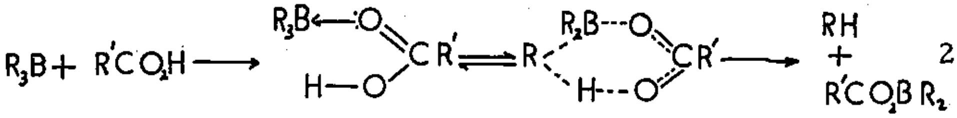
(a)

solution cell, the normal carbonyl stretching frequency of propionic acid could be distinguished (1725 cm^{-1}), together with a small absorption at 1630 cm^{-1}. The relative strength of the two absorptions did not change significantly within 5.0 hr., however, and no absorption was found in the region examined by Gerrard. The infra-red spectroscopic correlation of rates was not therefore pursued.

Table I also includes an analysis of the number of alkyl groups present at the carbon atoms α - , and β -, to boron in excess of those present in a straight chain trialkylborane. The rate of dealkylation, in general, decreases in accordance with the total number of α and β alkyl substituents present.

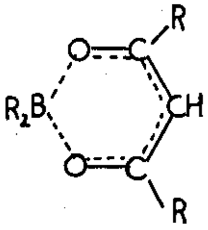
Discussion

A mechanism proposed for the protonolysis reaction by H.C. Brown involves the initial co-ordination of the carbonyl oxygen atom of the acid to the boron atom, followed by a six-centre bond rearrangement producing one mole of alkane and one mole of dialkyl acylborinate (Scheme 2).[10,11]



2.

The implied condition of retention of configuration at the carbon atom previously bonded to boron was verified experimentally.[11] Toporcer et al. were able readily to prepare derivatives of triethylborane, and a 1,3-diketone which had a configuration, as in (b), similar to that of the six-centre intermediate (in Scheme 2) proposed above.[12] They were also able to show that the acidity of the



(b)

reagent was not necessarily as important as its configuration. Thus 2-pyridone (pKa = 11.62) was able readily to protonolyse triethylborane, and with kinetics similar to the reaction with a carboxylic acid, but 4-pyridone (pKa = 11.09), of comparable acidity, was not. The protonation of a carboxylic acid has been demonstrated to place a proton on the carbonyl oxygen atom, suggesting this to be the most basic site of the carboxyl group.[25] The overall mechanism proposed by Brown is therefore reasonably substantiated.

On the basis of this mechanism, three factors may control the relative extents of protonolysis observed for the trialkylboranes in Table I. Such factors would be (i) the type of carbon to boron bond, (ii) the inductive effect of the alkyl groups bound to boron, and (iii) the combined steric requirements of the alkyl groups and the attacking acid. Considering the first factor, the order of thermodynamic stability for primary, secondary, and tertiary carbon to boron bonds has been estimated, from the behaviour of a branched borane under thermal equilibrating conditions, to be primary $>$ secondary $\gg$ tertiary.[17,26,27,28] Such an order is the reverse of that in Table I, where the primary borane (1) is the most unstable to protonolysis.

The inductive donation of charge from an alkyl group may be expected to influence the Lewis acidity of the boron atom, and thereby decrease the ease of co-ordination with the propionic acid. In the series of boranes (1,2,3) where n-hexyl groups are progressively replaced by t-butyl groups, the extent of protonolysis decreases as the inductive donation of the charge from t-butyl groups increases. When one n-hexyl group only is replaced by a 1,1,2-trimethylpropyl group, however, the extent of protonolysis is very greatly reduced. The inductive effect of the latter group would not be expected to be much larger than for a t-butyl group, as the inductive effect declines rapidly through one or more C-C bonds.[29] Similarly, in the results 4 and 5 (Table I), the extent of protonolysis of a tri-primary alkyl borane, tri-(2-ethylhexyl)-borane, was found to be similar to that of a tri-secondary alkylborane, tri-2-hexylborane. Such comparability could not readily be explained solely on the basis of donation of inductive charge from the alkyl groups to the boron atom.

Table I includes an analysis of the number of alkyl substituents at the carbon atoms at the α and β positions to boron, in excess of those present in a straight chain tri-n-alkylborane. The table is arranged to read from top to bottom in the order of decreasing extent of protonolysis, and inspection shows this order to correspond to the increase in the combined number of alkyl substituents ($\alpha + \beta$). If the mechanism proposed by Brown for the protonolysis reaction is accepted, then the formation of the intermediate complex requires the boron atom to change from a planar to a tetrahedral configuration, decreasing the separation of the alkyl groups.

Inspection of Dreiding molecular models suggests that the β-alkyl substituents increase the steric compression between the groups at boron to a similar, or greater extent than an α-substituent. Thus the approach of the large bidentate acid group will be resisted both on account of its own bulk, and also by internal strain generated in the borane. The rate-determining stage of protonolysis of a hindered borane may then possibly be either the initial co-ordination of the acid followed by a fast dealkylation, or an equilibrium (as in Scheme 3) which lies heavily to the left. The possible steric control of the reaction rate would be consistent with later results where the hydroperoxide anion, a

$$R_3B + R'CO_2H \rightleftharpoons R_3B.R'CO_2H \xrightarrow{fast} RH + R'CO_2B R_2 \qquad 3.$$

smaller but more active nucleophile, also gives results which are explained more satisfactorily on a steric, rather than an electronic basis (Section III; The Selective Oxidation of Unsymmetrical Trialkylboron Compounds using Aqueous Alkaline Hydrogen Peroxide).

3) The Selective Protonolysis of Representative Unsymmetrical Trialkylboranes

Results and Discussion

For reasons outlined in Part 2 of this Section (see above), the extent of protonolysis was not generally followed beyond the removal of the first 75% of one equivalent of alkyl group. A series of unsymmetrical trialkylboranes was therefore protonolysed in diglyme solution at 50°, using 3.0 mol. of dried propionic acid. The dealkylation was followed by the periodic withdrawal, and quenching, of small aliquots of reaction mixture which were then analysed for hydrocarbons by g.l.c. (as in Part 2 above). Initial protonolyses of the less reactive boranes gave erratic yields of alkane, and did not allow the calculation of reproducible selectivity factors. Clearly, repeated puncture of the rubber serum cap on the reaction flask had caused sufficient porosity of the seal to allow contamination of the reaction mixture from outside, and the possible escape of volatile hydrocarbons. The slower reactions were therefore repeated as sealed tube experiments, and analysed after a fixed time.

The results of the selective protonolyses are given in Table 2. The more rapid protonolysis of the t-butyl boranes was followed by the periodic analysis of the reaction flask contents, and curves plotted for the amounts of alkane produced (see figs. 6 and 7).

Results 1 and 2 in Table II show a small selectivity between the breaking of primary carbon to boron bonds, and secondary carbon to boron bonds, in the disiamyl-n-alkylboranes. Thus for disiamyl-n-hexylborane the statistically corrected selectivity is approximately 2.7 fold in favour of the breaking of the primary carbon to boron bond, and a little larger in the case of disiamyl-n-octylborane. When the unsymmetrical secondary borane, disiamyl-2-hexylborane (3), was protonolysed, the two alkanes 2-methylbutane, and n-hexane, were released slowly in a proportion very close to the statistical ratio.

Results 4,5,6 and 7 show the selectivity of dealkylation of trialkylboranes containing n-alkyl groups, and one or two tertiary alkyl groups. In all cases a very high selectivity was found in favour of the breaking of the primary carbon to boron bond. The relative rate factors are erratic because the amount of

Table II

Protonolysis of Unsymmetrical Trialkylboranes in Diglyme Solution (0.65 M.), at 50°. Selectivity of Dealkylation

	Percentage Yield of Alkane[b]			Time (hr.)	R = Straight chain / Branched chain	R, statistically Corrected
	Branched Alkyl Group	n-Alkyl Group	Total Alkyl Group			
1. Disiamyl-n-hexylborane	18. 2	24.4	42.6	48.0	1.34	2.7
2. Disiamyl-n-octylborane	23. 8	43.7	67.5	64.0	1.86	3.7
3. Disiamyl-2-hexylborane	5.7	2.8	8.5	78.0	0.49	1.0
4. Thexyldi-n-hexylborane	1.1[a]	73.5	74.6	43.0	>67	>34
5. Thexyldi-n-octylborane	0.4[a]	61.3	61.6	36. 0	165	. 83
6. t-Butyldi-n-hexylborane	<0.1[a]	93.5	93.6	1.0	>100	>50
7. Di-t-butyl-n-hexylborane	<0.1[a]	95.0	95.1	4.0	>100	>200
8. Thexyldi-2-hexylborane	Could not be prepared by hydroboration.					

* Sealed tube experiment

[a] Amount too small, relative to n-alkane, for accurate determination.

[b] 100% = removal of one alkyl group from boron.

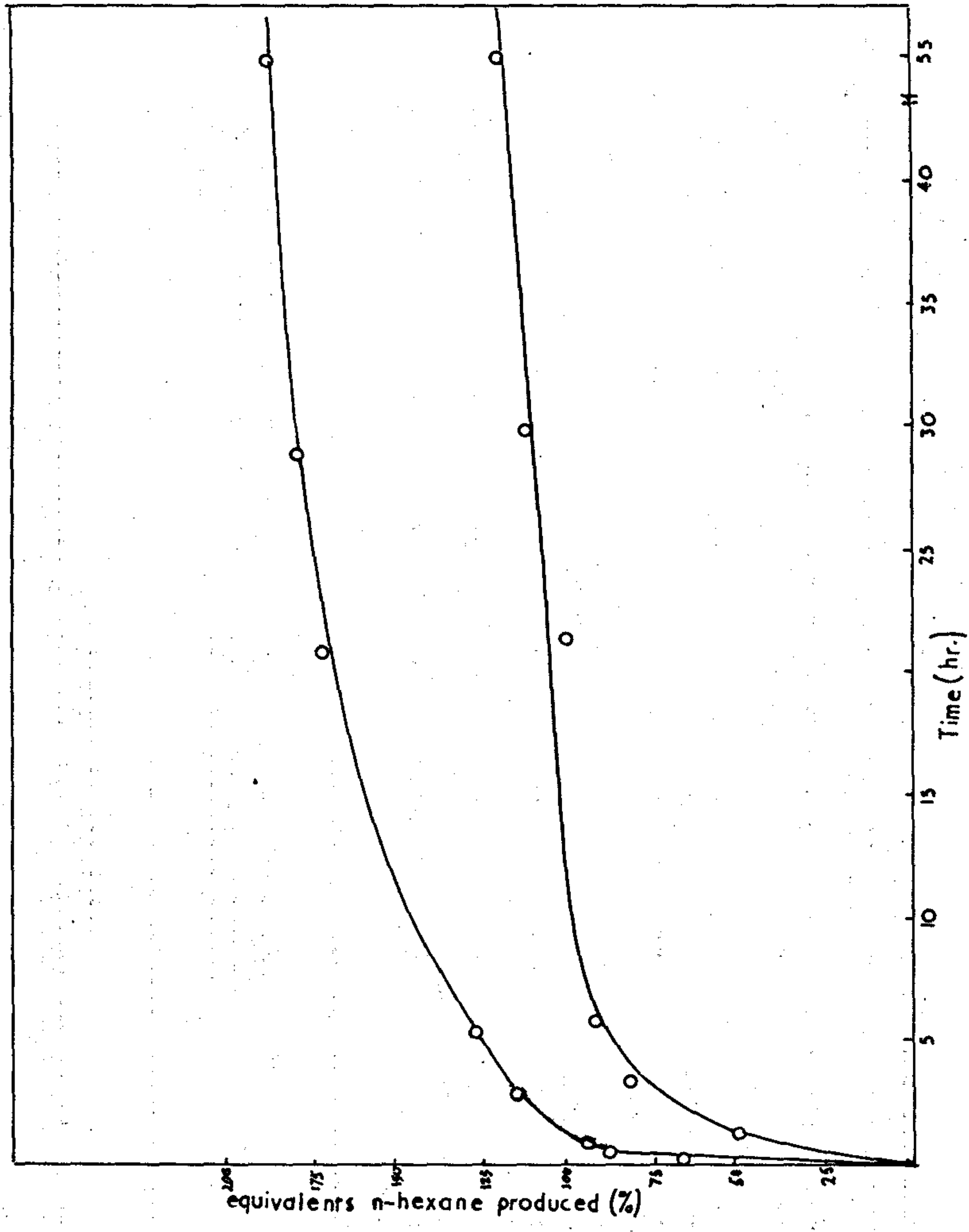


FIGURE 6. Production of n-Hexane During the Reaction of Propionic Acid with t-Butyldi-n-hexylborane in Diglyme Solution (0·65 M), a) at 25° (Table XIIa), and b) 50° (Table XIIb).

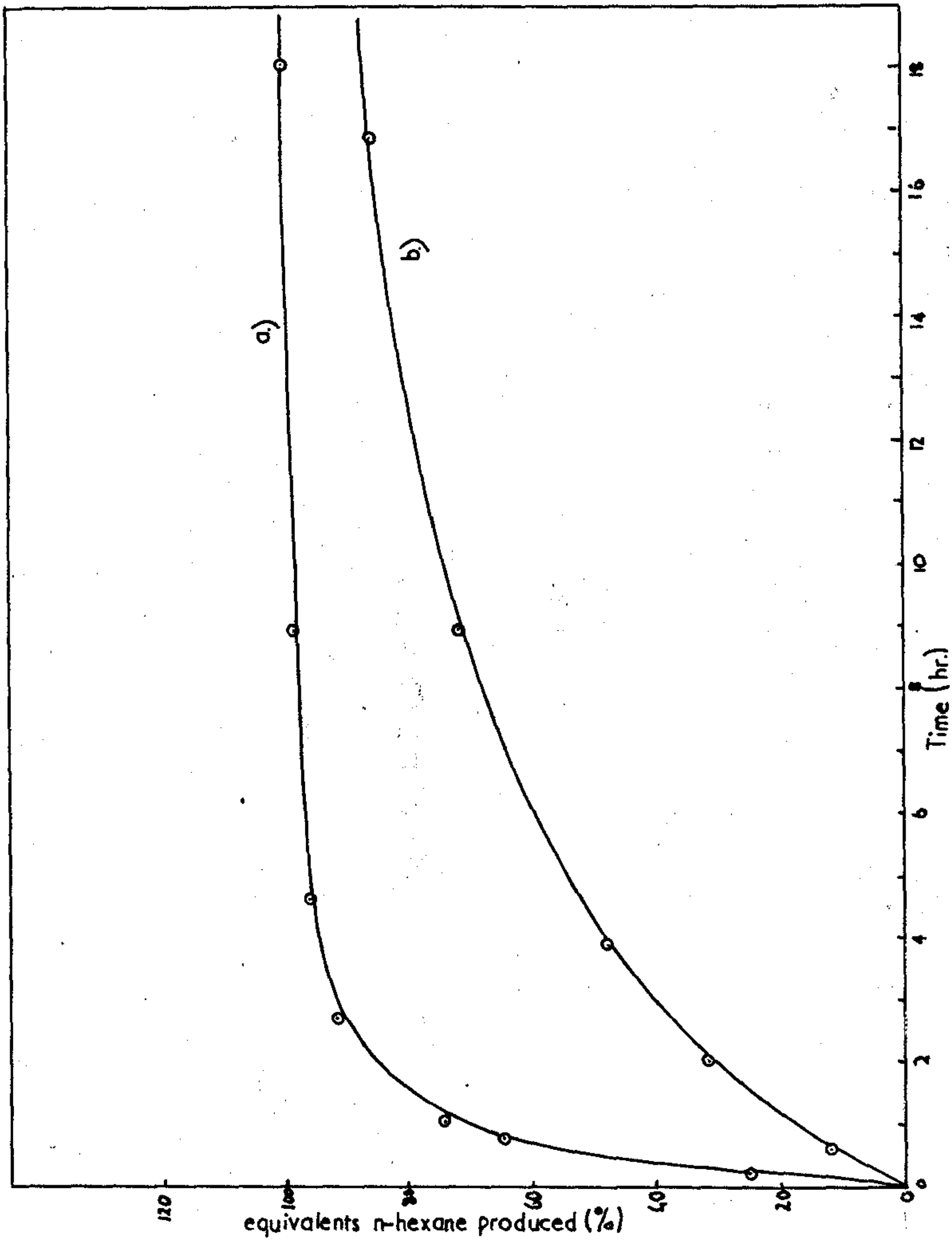


FIGURE 7. Production of n-Hexane During the Reaction of Propionic Acid with Di-t-butyl-n-hexylborane in Diglyme Solution at a), 25° (Table VI(b), and 50° (b) (Table VI(a).

2,3-dimethylbutane or isobutane released (0.05- 0.2 mmole) was too small to be related accurately by g.l.c. analysis to the large yield of n-alkane. A selectivity factor could not therefore be calculated with reasonable accuracy. For the boranes containing one tertiary carbon to boron bond, however, the relative ratio indicated a selectivity factor greater than 50 in favour of the breaking of the primary carbon to boron bond. For di-t-butyl-n-hexylborane, containing two tertiary groups, the selectivity may be a little smaller, but is greater than a 30 fold preference for the breaking of the primary carbon to boron bond.

An attempt was made to prepare a trialkylborane containing both tertiary and secondary carbon to boron bonds, in order to complete the series of different structures at the boron atom. The preparation of a borane of this structure has not been reported in the literature, however, and an attempt to prepare thexyldi-2-hexylborane (8) by the hydroboration method, failed.

K. J. Murray protonolysed disiamyl-n-octylborane and dicyclohexyl-n-hexylborane in diglyme solution at 100°, using a large excess of propionic acid.[13] Whereas n-octane was released from the former borane within 1 hr. in 100% yield, no 2-methylbutane was detected. The latter borane, however, yielded a mixture of n-hexane and cyclohexane in a 6:5 ratio, a very small selectivity. With disiamyl-n-octylborane, therefore, the use of more vigorous conditions than in the present study appeared to produce a higher selectivity. The apparatus used by Murray was a three-necked flask equipped with a pressure equalised funnel, rubber septum cap and a reflux condenser. It seems very possible that if 2-methylbutane (b.p. = 30°) were released during protonolysis, it would not be retained by such an apparatus at 100°, whereas n-octane (b.p. = 125.6°), n-hexane (b.p. = 68.7°), and cyclohexane (b.p. = 79°), would be. In a brief description of the selectivity of protonolysis of thexyldi-n-alkylboranes the yields of n-alkanes produced are recorded, but the fate of the 1,1,2-trimethylpropyl group is not described.

In general, therefore, the present study shows that the protonolysis of a secondary carbon to boron bond is a little slower than that of a primary carbon bond, within the same borane. The tertiary carbon to boron bond, however, was very resistant to protonolysis under the conditions of this study. The rapidity and selectivity of the protonolysis of t-butyldi-n-hexylborane, compared with that of disiamyl-n-hexylborane, shows that selectivity is not necessarily a function of overall rate. In Part 2 above, a close connection was demonstrated between steric hindrance of the borane and its rate of protonolysis. The strong steric hindrance of a t-alkyl group at boron has been shown to reduce the thermodynamic stability of the carbon to boron bond.[26]

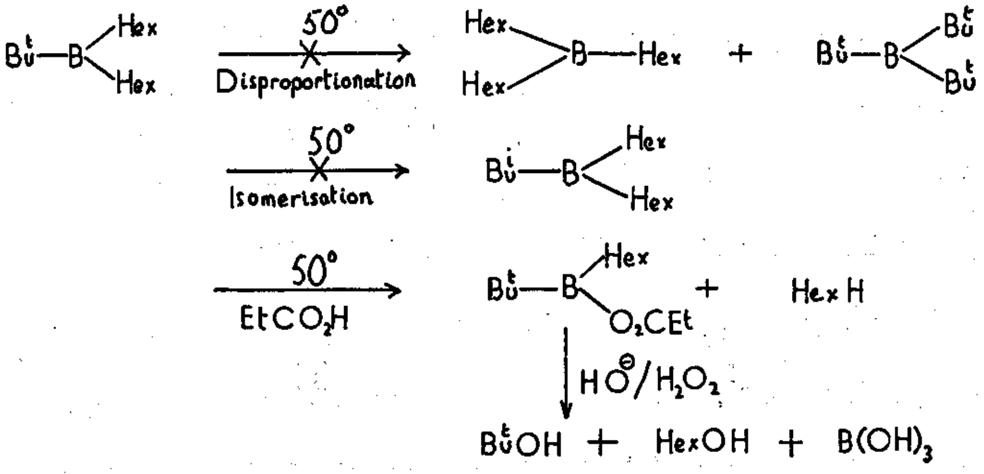
On the basis of an overall steric effect therefore the tertiary carbon to boron bond would be expected to be broken more readily than a secondary or primary bond. The results in Section III below (The Selective Oxidation of Unsymmetrical Trialkylboranes using Aqueous Alkaline Hydrogen Peroxide) are in accord with the control of selectivity by an overall steric effect but the order of reactivities is not the same as observed during the protonolyses. The smaller, more nucleophilic hydroperoxide anion gives a greater selectivity of dealkylation (in favour of the removal of the branched alkyl group) with disiamyl-n-hexylborane than with thexyldi-n-hexylborane.

Toporcer and Dessy[12] argued that co-ordination with the carboxylic acid simultaneously polarised and weakened the C-B bond, and increased the electrophilic character of the acid proton. Extension of this suggestion to the unsymmetrical boranes suggests that inductive donation to the α-carbon atom, as in a t-alkyl group, together with destabilisation of the C-B bond induced by the negatively charged boron atom, might make this group more unstable to protonolysis than a primary alkyl group.

A very close correlation of the relative reactivities of the tertiary, secondary and primary alkyl groups is found however with the Sn2 halide exchange reaction of the n-propyl-, isobutyl-, and neopentyl-halides in acetone solution.[32] Here a small decrease in rate was observed from the n-propyl- to the isobutyl-groups, but a very large decrease in rate for the neopentyl group.

The halide exchange results were interpreted as showing that whereas rotation of the C(α)-C(β) bond allows two methyl groups to avoid steric opposition with the approaching reagent, three methyl groups cannot avoid opposition by this method. The reagent can no longer attack the appropriate carbon atom along the preferred path, and consequently there is a low rate of reaction.

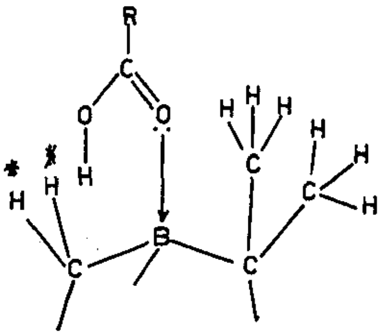
In the present study the propionyl group must approach close to one of the carbon atoms next to boron. Further, the hydroxyl group must attack the α-carbon atom from the same side as the boron atom to satisfy the condition of retention of configuration at the α-carbon atom.[11] For a primary alkyl group therefore, the acid hydroxyl group must be placed close to, or between, the two hydrogens marked with an asterisk in (c) below(p.84).With a secondary alkyl group (d), approach of the -OH group is a little more difficult as approach from one direction forces the -OH group close to a methyl group(p.84).The alternative orientation of approach is similar to that for the primary alkyl group, however, whereas with the tertiary alkyl group both directions of approach are blocked. This explanation has the advantage that whereas a consideration of inductive effects suggests that the 1,2-dimethylpropyl-, and hex-2-yl groups in disiamyl-2-hexylborane are not equivalent, the steric requirements at the α-carbon atom are very similar and would be expected to lead to the observed statistical dealkylation. The analogy is not complete as rotation of the C-B bonds would tend to be quenched by the approach of the propionyl group, and configurations similar to those shown in (c) and (d) may be the most favourable.



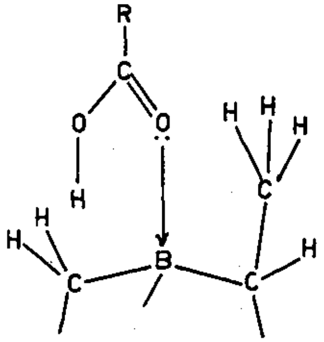
Disproportionation and Isomerisation of the Unsymmetrical Boranes under Protonolysis Conditions

During the reaction of propionic acid with disiamyl-n-hexylborane in a preliminary experiment, the release of some 2-methylbut-2-ene was observed. Likewise, some 2,3-dimethylbut-2-ene was produced during the protonolysis of thexyldi--n-hexylborane. Such breaking of secondary and tertiary carbon to boron bonds suggested the possibility that some disproportionation or isomerisation of the trialkylborane might occur before the reaction with propionic acid, causing any subsequent selectivity in hydrocarbon production to be an artifact.

For the boranes containing a tertiary carbon to boron bond any reaction of the borane which did not produce an alkane should be detected easily, as all the tertiary groups remained bound to boron during the protonolysis at 50°. The reaction mixtures after the protonolysis of the two t-butyl boranes (6 and 7) at 50°, were therefore neutralised and then treated with an excess of alkaline hydrogen peroxide solution. t-Butanol was released in a yield corresponding to at least 88% of the t-butyl group originally bound to boron, with each borane. It is clear, therefore, that no isomerisation of the butyl group had occurred during protonolysis.[30]



(c)



(d)

Disproportionation, as suggested by P. A. McCusker et al.,[17] is also unlikely to have occurred as the two t-butyl boranes protonolysed at different rates, suggesting that the species reacting were not the same. Also, disproportionation of di-t-butyl-n-hexylborane would imply the formation of tri-t-butylborane, although this borane has eluded all previous attempts at its synthesis.[31] The product from these attempts, t-butyldi-isobutylborane, did not arise here as only t-butanol was obtained in the final alkaline oxidation (see fig. p. 83).

The preparation of thexyldi-n-hexylborane requires the use of a small excess of the two olefins. To obtain more information on the behaviour of this borane under protonolysis conditions, two samples of the borane were prepared and each divided into two equal parts. One part of each of the preparations was treated with propionic acid (3.0 mol.) and then both of the flasks immersed in a constant temperature bath. Figs. 8 and 9 show the amounts of alkenes and alkanes present (against time) in the mixtures at 25° and 50° with and without the presence of propionic acid.

At 25^{o} (Fig. 8) the protonolysis flask showed the production of n-hexane and the release of a small amount of 2,3-dimethylbut-2-ene, while the blank flask showed little change during 154 hr. At 50^{o} (Fig. 9), however, the blank flask released 5.2 mmole of 2,3-dimethylbut-2-ene and absorbed 2.6 mmole of hex-1-ene (taken up from the excess present after the preparation) within 105 hr. Under protonolysis conditions, only 1.4 mmole of 2,3-dimethylbut-2-ene was released, while no hex-1-ene was absorbed. A very small amount of 2,3-dimethylbutane was formed, together with 10.9 mmole of n-hexane.

These results may be explained by a thermal elimination reaction, in diglyme solution, which favours the release of 2,3-dimethylbut-2-ene as temperature increases. When no propionic acid was present, hex-1-ene was able to add to the B-H bond formed to complete an elimination-addition reaction. In the presence of propionic acid, the elimination reaction was depressed, and no hex-1-ene was removed from solution. Propionic acid therefore competed successfully with hex-1-ene for reaction with any B-H bond formed. The rate of production

Table IIIA

Thexyldi-n-hexylborane (12.0 mmoles) in Diglyme Solution (0.65M.) Heated Alone at 50° for 39 hr. and then Protonolysed with Propionic Acid (38.00 mmoles)

	Time (hr)	Hydrocarbons Present (mmole)			
		2,3-dimethyl-butane	2,3-di-methyl-but-2-ene	n-hexane	hex-1-ene
Preparation	0.0	0.4	0.5	0.0	3.6
Sample after heating	39.0	0.5	2.7	0.1	3.0
Subsequent Protonolysis	3.1	0.5	2.7	1.7	2.9
Control protonolysis	27.3	0.4	0.9	1.7	4.2

Table IIIB

The Reaction of Propionic Acid (40.50 mmoles) with Disiamyl-n-octylborane (13.15 mmoles) in Diglyme Solution (0.65 M.) at 50°, with Subsequent Removal of Low-boiling Hydrocarbons

	Hydrocarbons Present (mmole)			
	2-methyl-butane	2-methyl-but-2-ene	n-octane	oct-1-ene
Before protonolysis	0.0	0.33	0.32	2.54
After Protonolysis (66.0 hr.)	2.56	2.52	3.30	2.48
After evacuation:-				
1) Vacuum trap	2.41	2.47	-	-
2) Reaction flask	0.0	0.0	-	-

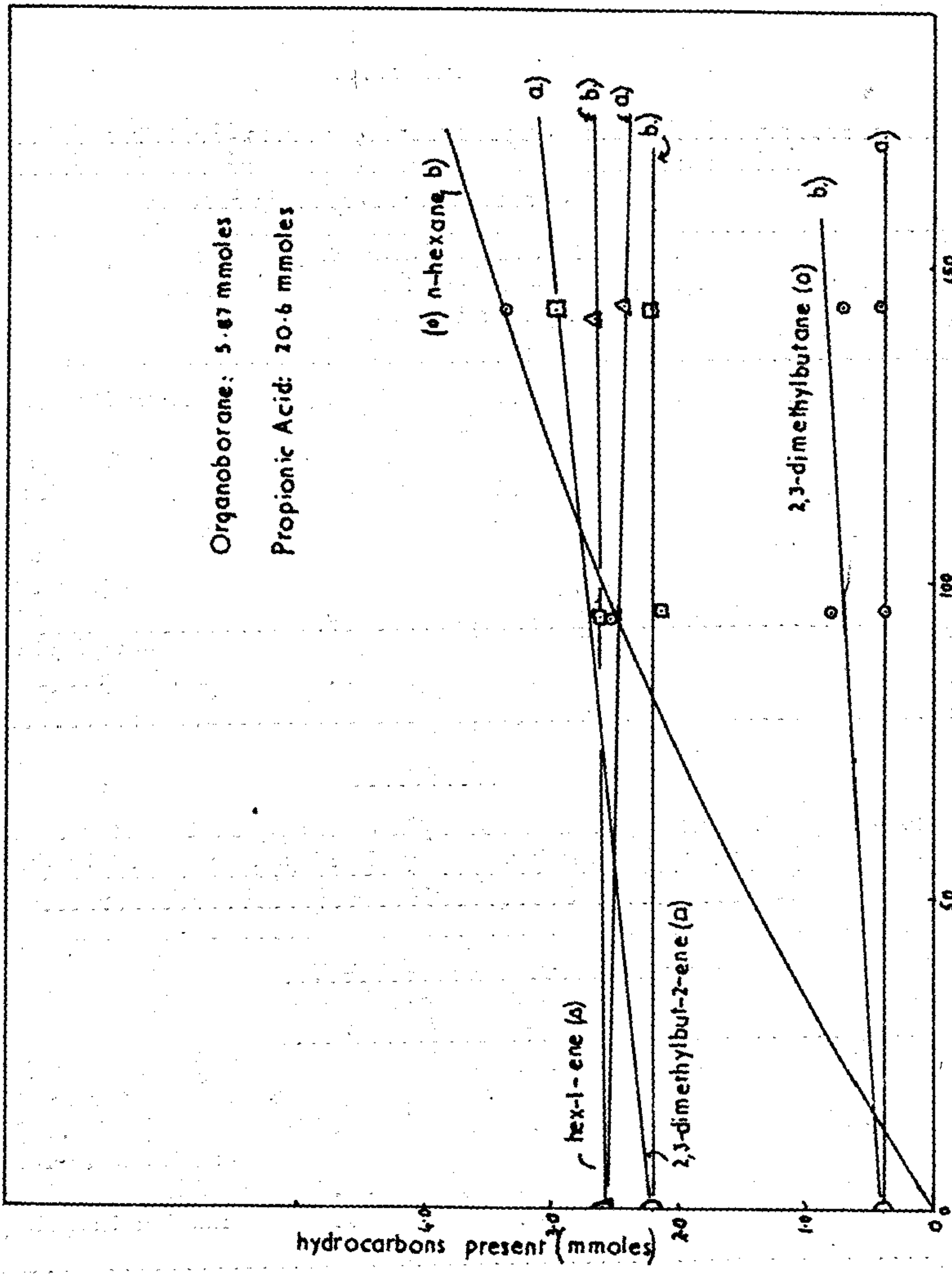


FIGURE 8. Hydrocarbons Present During the Heating of Thexyldi-n-hexylborane in Diglyme Solution (0·65 M.) at 25° a) Alone, and b) with Propionic Acid (Table XIII).

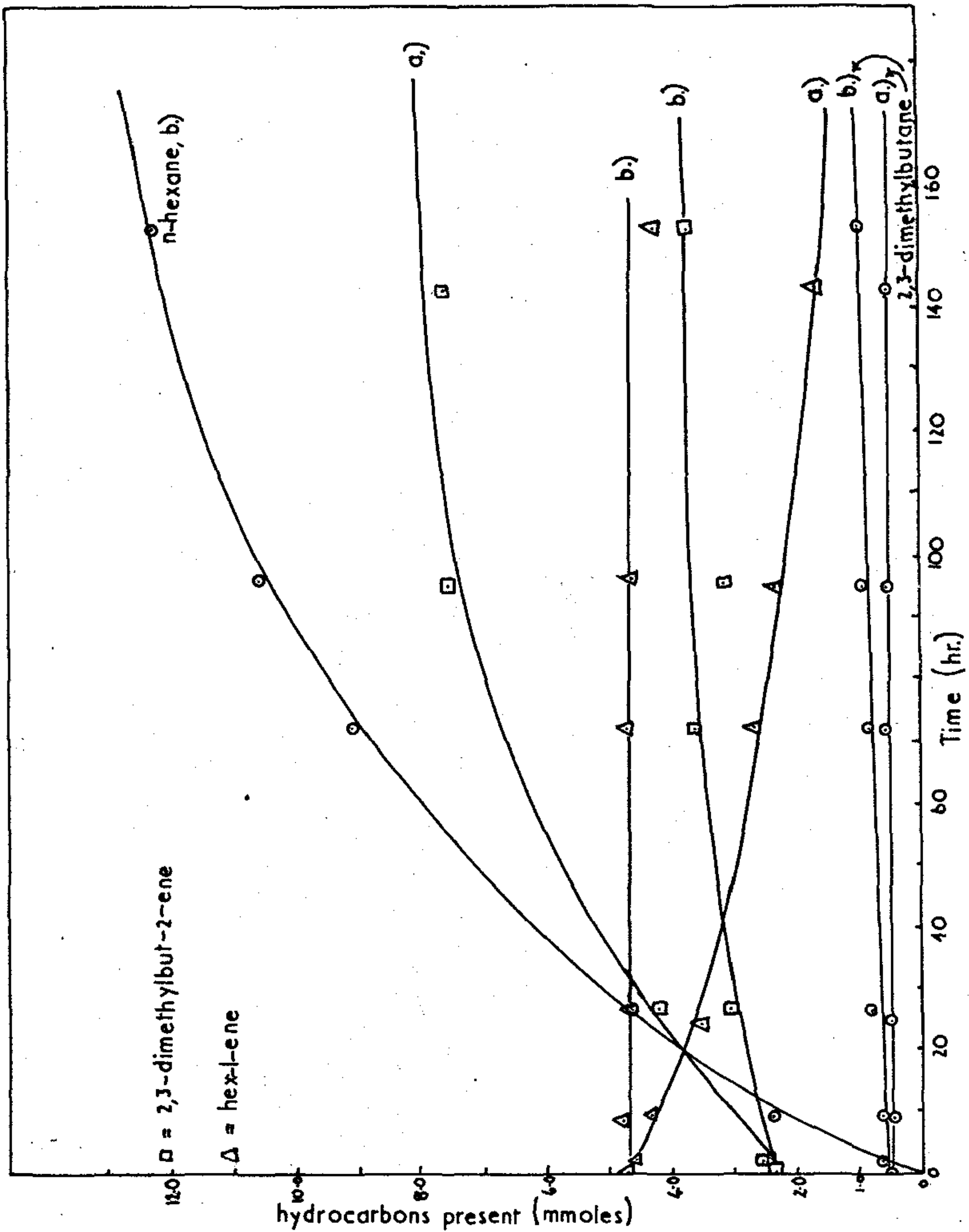


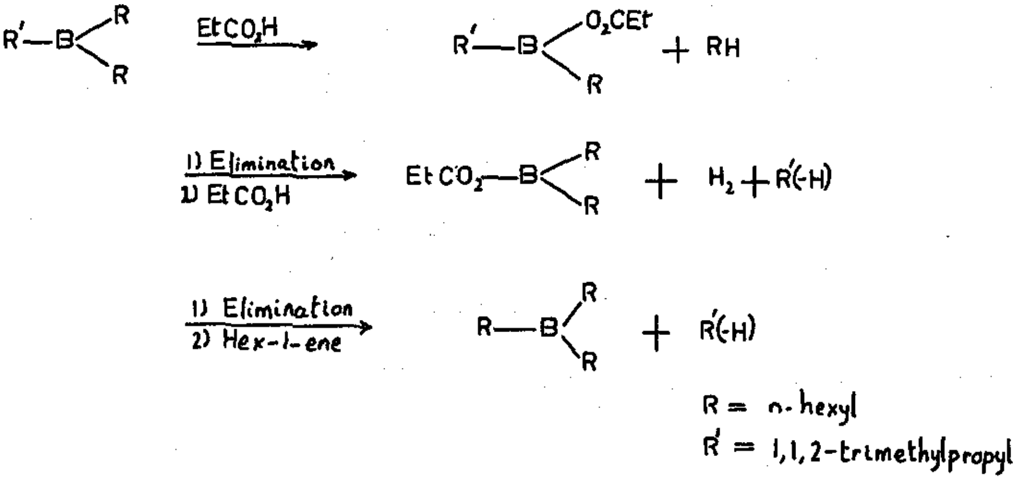
FIGURE 9. Hydrocarbons Present During the Heating of Samples of Thexyldi--n-hexylborane (5·96 mmoles) in Diglyme Solution (0·65M.) at 50° a) Alone, and b) with Propionic Acid (20·6 mmoles) (Table XIV).

of n-hexane was much greater than that of 2,3-dimethylbut-2-ene and it follows that protonolysis of the di-n-hexyl boron propionate (formed by the elimination-addition reaction) was not responsible for the main yield of n-hexane.

A further sample of thexyldi-n-hexylborane was divided into two equal parts, and one part heated at 50° for 48 hr. before protonolysis. The other part was protonolysed at 50°, as a control experiment. The results are shown in Table IIIA. The sample of borane heated in diglyme before protonolysis released the more alkylated olefin during the period of heating, and absorbed a corresponding quantity of hex-1-ene. The subsequent protonolysis of this sample produced n-hexane rapidly on subsequent protonolysis, in comparison with the control experiment. Clearly the borane responsible for the rapid production of n-hexane was now tri-n-hexylborane.

It is interesting that the elimination reaction produced the more thermodynamically stable olefin, 2,3-dimethylbut-2-ene, rather than 2,3-dimethylbut-1-ene. The mild conditions of the present study clearly did not allow migration of the boron-carbon bond to the terminal alkyl position, providing further evidence against the importance of an isomerisation reaction. Neutralisation of the reaction mixture, followed by oxidation with alkaline hydrogen peroxide solution, yielded only 2,3-dimethylbutan-2-ol.

In summary thexyldi-n-hexylborane appears to undergo the following three reactions under the conditions of this study, rather than an isomerisation reaction (Scheme 4).



4.

In the case of the disiamyl-n-alkylboranes, an experiment was carried out to ensure that the appearance of 2-methylbut-2-ene was not due to any pyrolysis induced under gas chromatography conditions. After analysis of the products of the 66 hr. protonolysis of disiamyl-n-octylborane, the flask was cooled to 0°, and evacuated at 0.5 mm.

Hydrocarbons volatile under these conditions were retained in a trap cooled by liquid nitrogen. The contents of the trap were found to be 2-methylbutane, and 2-methylbut-2-ene in substantially the same amounts as had been present during the original analysis (Table IIIB). G.l.c. analysis of the reaction flask showed no low boiling hydrocarbon fraction. Clearly, therefore, the chromatography conditions were not responsible for the production of 2-methylbut-2-ene.

Evaluation of any isomerisation or disproportionation which might have occurred could not be carried out by the same method as for the tertiary alkyl boranes, because comparable amounts of each group were removed from the borane. It was not possible to decide whether 2-methylbutane arose from the protonolysis of the 1,2-dimethylpropyl group, or from its isomer, the 3-methylbutyl group.

Three experiments were carried out in order to assess the extent of disproportionation of disiamyl-n-hexylborane at the temperature of the selective protonolyses. A sample of the borane was prepared and analysed for excess hydrocarbons, and from this were calculated the amounts of trisiamylborane, and of tri-n-hexylborane which would result from the complete disproportionation of the original sample of disiamyl-n-hexylborane. Quantities of two symmetrical boranes corresponding to a complete disproportionation of the sample were then prepared separately in diglyme solutions of the appropriate concentrations.

The sample of disiamyl-n-hexylborane was heated at 50° for 48 hr., cooled to ice temperature, and re-analysed for hydrocarbons (Table IV). The unsymmetrical borane was then treated with propionic acid (3.0 mol.). The same quantity of propionic acid was also added to each of the two symmetrical boranes, and then all three reaction mixtures were held at 50° for 3.0 hr. before re-analysis for hydrocarbons present. In the case of trisiamylborane, the amount of 2-methylbutane produced was too small for accurate measurement, and so the protonolysis at 50° was continued for 48 hr. in order to obtain a more measurable amount. The protonolysis of the sample of disiamyl-n-hexylborane was also continued, but for 18.6 hr.

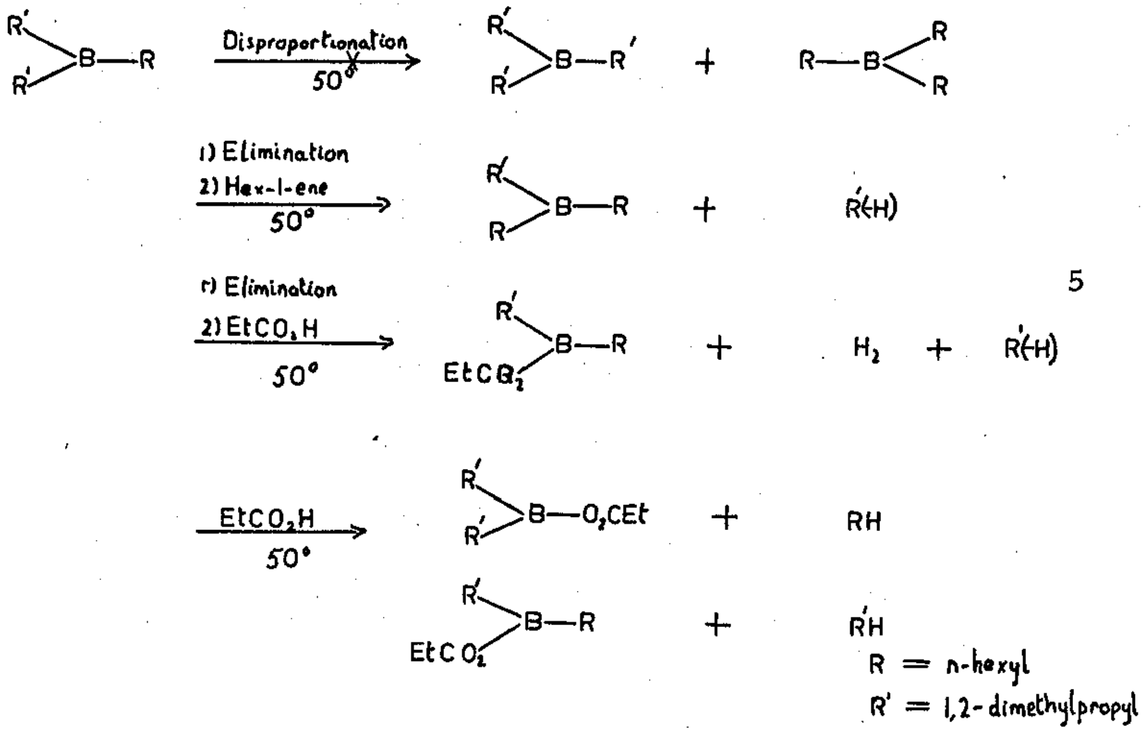
TABLE IV

Protonolysis of Disiamyl-n-hexylborane (0.65 M.), Tri-n-hexylborane (0.22 M.), and Trisiamylborane (0.44 M.) in Diglyme Solution at 50°. Investigation of Possible Disproportionation.

	Hydrocarbons Present (mmole)			
	2-methyl-butane	2-methyl-but-2-ene	n-hexane	hex-1-ene
Disiamyl-n-hexylborane (12.30 mmoles)				
Before heating	0.0	0.0	0.0	4.1
After heating at 50° for 48 hr.	0.0	3.3	0.0	0.8
Protonolysis for				
3.0 hr. at 50°	0.7	3.3	1.0	0.8
18.6 hr. at 50°	1.6	3.3	3.7	0.8
Trisiamylborane (12.40 mmoles)				
Before protonolysis	0.0	2.7		
After protonolysis for 48 hr.				
a) Sealed tube	0.3	3.2		
b) reaction flask	0.3	3.4		
Tri-n-hexylborane (4.15 mmoles)				
Before protonolysis			0.0	0.0
After protonolysis for 3.18 hr. at 50°			5.8	0.0

The results in Table IV indicate that different species are being protonolysed in the three reaction flasks. As expected, the sample of tri-n-hexylborane was dealkylated rapidly, and to a stage beyond the removal of one equivalent of n-hexyl group, while the trisiamylborane suffered very little attack during three hours. A far longer period of protonolysis (48 hr.) was unable to release the amount of 2-methylbutane obtained from the protonolysis of disiamyl-n-hexylborane. The initial period of protonolysis of the unsymmetrical borane produced a surprisingly large, although selective, amount of the two saturated hydrocarbons, but the subsequent period of reaction proceeded more slowly.

Clearly, therefore, although the unsymmetrical borane was protonolysed more rapidly at first than was normal for disiamyl-n-hexylborane, the results are not consistent with any disproportionation of the borane, as a considerable amount of 2-methylbutane was produced. Inspection of the amounts of olefin present after the preliminary period of heating of the sample of disiamyl-n-hexylborane shows that 3.3 mmoles of 2-methylbut-2-ene had been displaced from the borane by hex-1-ene. The behaviour ofthexyldi-n-hexylborane in diglyme solution, at 50°, is therefore followed also by the secondary borane. The rapid initial rate of protonolysis may then be due to the presence of a small amount of siamyldi-n-hexylborane (3.3 mmoles, approximately), which also shows some selectivity in the breaking of carbon to boron bonds in favour of the primary carbon bond. Inspection of Table IIIA shows that although depressed by the presence of propionic acid, the elimination reaction releasing 2-methylbut-2-ene still occurs, but is not accompanied by absorption of oct-1-ene (hex-1-ene). Overall behaviour is therefore similar to that of the thexyldi-n-alkylboranes in the presence of propionic acid. The behaviour of a disiamyl-n-alkylborane under the conditions of this study may therefore be summarised by the series of reactions in Scheme 5.



5

A survey was made of the behaviour of a series of trialkylboranes when heated in diglyme solution at 50°, in the presence of oxygen-free water. Results in Table V show that tri-n-hexylborane was almost unaffected by the presence of water during 48 hr. Tri-2-hexylborane also yielded only a small amount of hex-2-ene in 48 hr., although a further period of heating in the presence of propionic acid produced a larger amount (3.9 mmole) of hex-2-ene. Trisiamylborane did not eliminate 2-methylbut-2-ene to a significant extent. Both of the unsymmetrical trialkylboranes, disiamyl-n-hexylborane and thexyldi-n-hexylborane eliminated significant amounts of olefin, particularly in the case of the secondary borane. The latter result was consistent with a relationship between steric compression between the alkyl groups bound to boron, and ease of the elimination reaction. This is not so in the case of the very hindered borane, trisiamylborane, however, which showed little tendency to elimination.

An explanation of this anomalous case may lie in the nature of the elimination reaction. If the elimination reaction is the reverse of the hydroboration reaction, then the hydrogen atom involved in the incipient B-H bond formation, must become hydridic in order to attack the boron atom. The presence of secondary or tertiary alkyl substituents would tend to place inductive charge at the boron atom, making hydridic attack less favourable. Thus, in the case of disiamyl-n-hexylborane, the steric compression of the alkyl groups encouraging elimination is countered by the inductive effect of a 1,2-dimethylpropyl group, and a n-hexyl group, whereas with trisiamylborane, the compression is countered by the larger inductive effect of the two 1,2-dimethylpropyl groups.

In general, a higher selectivity was observed between the breaking of tertiary- and primary-carbon to boron bonds than between secondary- and primary-carbon to boron bonds. It was possible to remove the n-hexyl group almost to the exclusion of the t-butyl, or 1,1,2-trimethylpropyl group. The protonolysis reaction should, therefore, offer a route to the synthesis of the acyl derivatives of unsymmetrical borinic acids, a class of compounds which has not been available previously. A useful selectivity was not found between the breaking of secondary and primary carbon to boron bonds.

TABLE V

The Reaction between Water (25.0 mmoles) and Representative Trialkylboranes in Diglyme Solution (0.65 M.) during 48 hr. at 50°

	Hydrocarbons Present (mmole)						
	n-hexane	hex-1-ene	hex-2-ene	2-methylbutane	2-methylbut-2-ene	2,3-dimethylbut-2-ene	2,3-dimethylbutane
Tri-n-hexylborane (12.5 mmoles)							
After preparation	0.0	2.3					
After heating	0.0	2.3					
Tri-2-hexylborane (12.5 mmoles)							
After preparation	0.3	0.7	3.1				
After heating	0.3	0.7	3.3				
Protonolysis 46.0 hr.	7.9	0.9	7.2				
Trisiamylborane (12.5 mmoles)							
After preparation				0.0	2.7		
After heating				0.0	3.0		
Disiamyl-n-hexylborane (11.3 mmoles)							
After preparation	0.0	3.1		0.0	0.7		
After heating 96.9 hr.	0.0	3.2		0.0	7.5		
Thexyldi-n-hexylborane (12.0 mmoles)							
After preparation	0.0	3.6				0.4	0.5
After heating	0.0	4.0				2.6	0.5

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SECTION III

THE SELECTIVE OXIDATION OF UNSYMMETRICAL TRIALKYLBORANES USING ALKALINE HYDROGEN PEROXIDE SOLUTION

Introduction

The cleavage of trialkylboranes by basic solutions of aqueous hydrogen peroxide was reported in 1938 by J.R. Johnson *et al.*,[1] who observed a rapid quantitative dealkylation of tri-n-butylborane to n-butanol and boric acid. Subsequently, in 1952, R. Belcher *et al.*[2] reported the reaction as an analytical technique for organoboranes. Forcing conditions were used, i.e. excess H_2O_2, and concentrated NaOH, under reflux. Winternitz and Carrotti[3] used substantially similar conditions to oxidise boron heterocycles.

During development of the Hydroboration technique, H.C. Brown (1956), who at first used the vigorous oxidation conditions,[4,5] found that mild conditions (0°C, and aqueous reagents (3N.NaOH, and 30% w/v H_2O_2)) allowed vigorous and quantitative reaction.[6,8] He later (1960)[7] quoted still unpublished work where it was to be shown that the oxidation was most efficient in diglyme and T.H.F. solutions and less so in diethyl ether. The reaction in ether was improved by the addition of ethanol (giving up to 95% yields) and it was concluded that immiscibility of the reagents was the reason for the previous disappointing results.

Brown compared his results with those of H.G.Kuivila and his co-workers[9-12] who established that phenylboronic acid was oxidised by hydrogen peroxide under basic conditions by the mechanism outlined in the reaction schemes shown in Fig. I (see Discussion). Rate functions were calculated which were (a) first order, and (b) second order, in boronic acid concentration. He suggested that an identical mechanism, in three separate stages, might be applicable to trialkylboranes. A.G. Davies et al.[13] have provided supplementary evidence from ^{18}O labelling experiments. When $PhB(^{18}OH)_2$ was oxidised by isotopically normal H_2O_2 in $H_2{}^{18}O$, only normal PhOH was produced, showing that it derives its oxygen only from the peroxide group. T.G. Traylor et al. carried out the complementary study using a series of alkylboronic acids.[19] Here, however, the rate function second order in boronic acid concentration was absent. The rate of oxidation was found to depend on the structure of the alkyl group. The oxidation was fastest with t-butylboronic acid, and became slower as the branching of the substituent decreased. The experimental order was t-Butyl > but-2-yl > n-butyl > methyl.

The only information available on the H_2O_2 oxidation of mixed organoboranes is the neutral H_2O_2 oxidation of t-butyldi-isobutylborane reported by Davies et al.[14] Here H_2O_2(100%, 1 mol.) was added slowly in ether solution, to the organoborane, also in ether solution, and stirred for 3 hr. at 0°. The products were subjected to molecular distillation at room temperature yielding a volatile fraction containing only t-butanol and ether; the boron containing products did not distil and contained only isobutyl groups. Under neutral conditions therefore alkyl groups with a tertiary carbon atom bound to boron are removed far more easily by H_2O_2 than groups bound via a primary carbon atom. The estimation of alcohols in Davies' work was by gas-liquid chromatography (g.l.c.). Alcohols produced from oxidations by Brown[4-7] were estimated by g.l.c. and also by fractional distillation (especially in his earlier work). P.A. McCusker et al.[15,16] used fractional distillation for separation and estimation of the alcohols produced during their earlier work, and g.l.c. during their later work.[17]

The stepwise dealkylation of a series of representative mixed boranes was therefore undertaken using small aliquots of alkaline

H_2O_2, in order to find out whether selectivity of oxidation can be found between primary and secondary and between primary and tertiary alkyl groups. Studies with neutral H_2O_2 indicate that with the trialkylboranes oxidised in this work, a different reaction from that noted by Davies occurs (See Section IV, below; The Reaction of Neutral Aqueous Hydrogen Peroxide with Symmetrical and Unsymmetrical Trialkylboranes). It was hoped that the alkaline reagent added under mild conditions would give a minimum of side reactions, and possibly indicate a route to unsymmetrical borinic acid derivatives.

Results and Discussion

A representative series of unsymmetrical organoboranes was prepared containing (a) two secondary carbon atoms and one primary carbon atom bound to boron,

i) Disiamyl-n-hexylborane
ii) Disiamyl-n-octylborane

(b) one tertiary carbon atom, and two primary carbon atoms,

iii) Thexyldi-n-hexylborane
iv) Thexyldi-n-octylborane
v) t-Butyldi-n-hexylborane

(c) two tertiary carbon atoms, and one primary carbon atom

vi) Di-t-butyl-n-hexylborane

Mixed organoboranes containing tertiary and secondary carbon atoms bound to boron have not been isolated free of disproportionation products, and so were not studied.

If a small difference only in the rate of oxidation is displayed between primary, secondary, and tertiary alkyl groups, then the relative rate of removal of two different groups may be expected to change progressively during an oxidation as the amount of the more readily oxidised group present decreases compared with the more stable group. The organoboranes oxidised were therefore treated with successive small aliquots of the oxidising agent, and analysed by g.l.c. for alcohol released after each addition. In this way it was hoped to observe continuously any change in selectivity. Preliminary experiments showed that the oxidation was very fast, allowing analysis to be made within ten minutes of the addition of an aliquot of oxidising agent. Concentration of the organoboranes in T.H.F. solution was approximately 0.5 M. Disiamyl-n-hexylborane and thexyldi-n-hexylborane were oxidised also in 0.25 M solution to test for any dependence of selectivity on concentration. Diglyme was used as solvent for the t-butyl boranes owing to the difficulty of g.l.c. estimation of t-butanol in the presence of T.H.F. A sample of thexyldi-n-hexylborane was also oxidised in diglyme solution to ensure compatibility of the results. The oxidising agent was added below the surface of the vigorously stirred reaction mixture in order to minimise local concentration gradients, which might also affect selectivity. All oxidations were carried out at ice temperature. Gas-liquid chromatography using a polar column, either of polypropylene glycol on chromosorb W, or polyethylene glycol adipate on silocel was found to be suitable for periodic analysis when an 8 in. forerun of diglycerol on Chromosorb W was employed to retain the oxidised boron residues (see Appendix).

If no selectivity is displayed the percentage of each of the two different groups oxidised, and hence of the two alcohols liberated, should be the same. A plot of percentage alcohol liberated against amount of oxidant added should therefore be a straight line for each of the two alcohols present. Curves showing the percentage of alcohol produced (based on total of the individual alkyl group bound originally to boron), were therefore plotted for the oxidation of each of the six boranes examined (Figs. I-VIII).

The Table summarises the reaction conditions and the ratio of the amounts of the two alcohols produced when (a) 33%, and (b) 66% of the total amount of the secondary (or tertiary) carbon to boron bond present had been oxidised. In order to obtain an accurate

Organoborane oxidised	Solvent	Organoborane concentration (M.)	Ratio of percentages[a] of R^1OH[b] to ROH[c] observed		No. of alkyl substituents	
			A) After the production of 33% R^1OH	B) After the production of 66% R^1OH	C(α)	C(β)
Disiamyl-n-hexylborane	T.H.F.	0.26	4.71	2.36	2	2
Disiamyl-n-hexylborane	T.H.F.	0.51	3.14	2.32	2	2
Disiamyl-n-octylborane	T.H.F.	0.52	2.54	2.40	2	2
Thexyldi-n-hexylborane	T.H.F.	0.26	1.65	1.50	2	1
Thexyldi-n-hexylborane	T.H.F.	0.52	1.27	-	2	1
Thexyldi-n-octylborane	T.H.F.	0.51	1.25	-	2	1
Thexyldi-n-hexylborane	Diglyme	0.26	1.94	1.61	2	1
t-Butyldi-n-hexylborane	Diglyme	0.28	1.50	1.42	2	0
Di-t-butyl-n-hexylborane	Diglyme	0.26	1.69	1.67	4	0

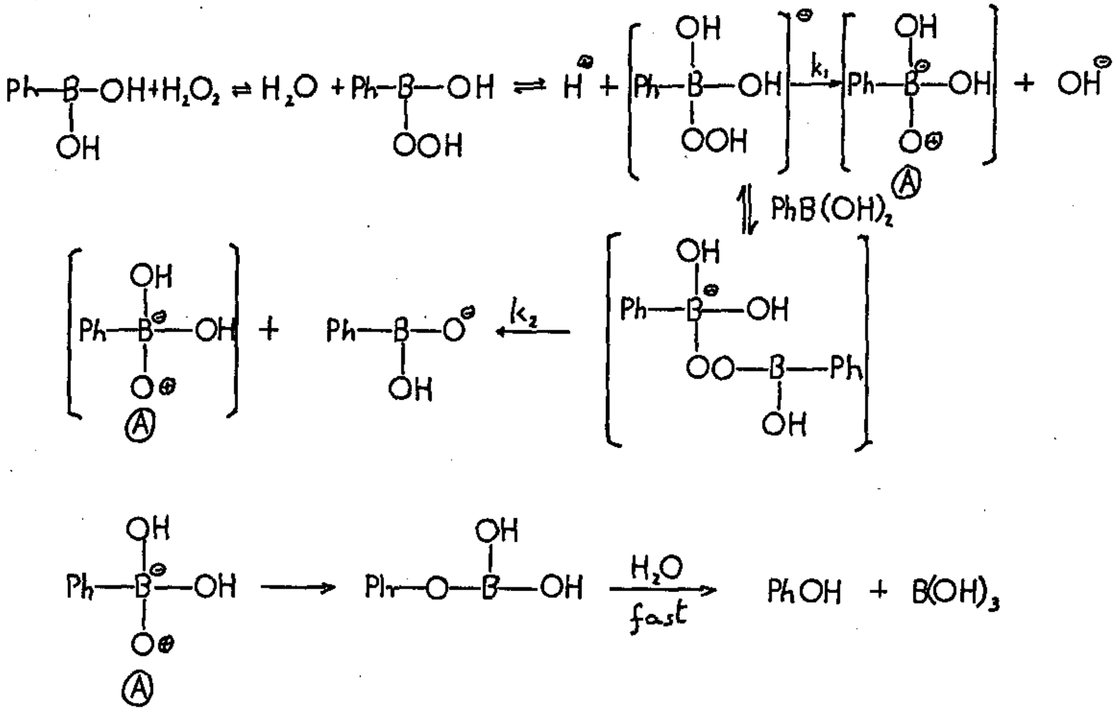
[a] Percentages based on the total amount of each alkyl group bound originally to boron.

[b] R^1OH = 2-methylbutan-3-ol, 2,3-dimethylbutan-2-ol, or t-butanol.

[c] ROH = n-hexanol or n-octanol.

assessment of selectivity, the ratios shown in columns A and B are expressed in terms of the divergence from random oxidation using the quotient obtained from the percentage of the two alkyl groups oxidised (as found from the percentage yield of the alcohols produced), rather than directly from mmoles of alkyl group oxidised (from mmoles alcohols produced). The table shows that concentration of the organoborane solution, and the choice between diglyme and T.H.F. as solvent, have little effect on the selectivity of dealkylation under alkaline hydrogen peroxide oxidation conditions. Some selectivity between tertiary and primary, and between secondary and primary alkyl groups, is shown by each of the boranes examined, although it is small in some cases. Surprisingly, the order of reactivity of the various alkyl groups examined is secondary > tertiary > primary, in contrast to the progressive gradation of thermodynamic stability of B-C bonds (primary > secondary > tertiary)[15] as obtained from the tendency to de-hydroboration (discussed in Section II: Protonolysis, above), in the susceptibility to isomerisation (tertiary > secondary > primary),[20] and disproportionation (primary > secondary > tertiary).[15,16]

Two possible effects may contribute to the selectivity observed during alkaline hydrogen peroxide oxidation, the first being the widely different magnitude of the inductive effect of the various alkyl groups and hence of the charge density at the carbon atom adjacent to boron, and the second being a change in the stability to oxidation of the C-B bonds on formation of the four-coordinate complex between the borane and the hydroperoxide group. Kuivila[12] made a systematic study of the effect of meta, and para substituents on the rates of reaction between benzeneboronic acid, and hydrogen peroxide. He established that the pH-dependent reaction consisted of two components, one of which (k_1) is first order, and the other (k_2) is second order, in boronic acid concentration.



Hammett curves ($\log (k_{1,2} + 3)$ vs. σ) plotted from the rate constants of the reactions of ten representative meta, and para substituted benzeneboronic acids, had very small slopes (ρ values), 0.071 for k_1 and 0.28 for k_2, indicating little dependence of overall reaction rate on the electron density at the carbon bonded to the boron atom. This result was explained by the existence of counterbalancing electronic demands during the slow steps of the reaction. Intermediate A increases in concentration as the electron density at boron decreases (positive ρ), but both the ionic cleavage of the peroxide group, with hydroxide ion leaving, and the subsequent migration of the aryl group to oxygen should be favoured by high electron density (negative ρ). Thus the formation of A and its subsequent transformation to products have essentially equal but opposite electronic demands. H.C. Brown[8] suggested that this mechanism, presumably with similar electronic features, may operate during the alkaline oxidation of trialkylboranes. The small selectivities observed generally during this study would be satisfactorily explained on the basis of such an argument, but the anomalously high selectivity found with the disiamyl-n-alkylboranes is incompatible.

A. G. Davies[14], using neutral hydrogen peroxide in the oxidation of t-butyldi-isobutylborane, found that only the t-butyl group was attacked when one mole of hydrogen peroxide was added, giving t-butanol but no isobutanol. The specificity was explained in terms of the known mobilities of different alkyl groups in the Baeyer-Villiger oxidation. Under Baeyer-Villiger oxidation conditions,[21] t-alkyl groups are more mobile than secondary and primary groups. When neutral hydrogen peroxide was allowed to react with the boranes examined in this study, however, a different group of products was obtained (see Section IV: The Reaction of Neutral Hydrogen Peroxide Solution with Symmetrical and Unsymmetrical Trialkylboranes). Davies' work suggests that the most reactive group should be the t-alkyl group. On this basis di-t-butyl-n-hexylborane followed by t-butyldi-n-hexylborane and the thexyldi-n-alkylboranes should show greater selectivity than the disiamyl-n-alkylboranes. Again this was not found to be the case. Clearly the factors controlling oxidation under the conditions of this study must be different.

Columns C and D of the table contain an analysis of the number of alkyl substituents at the α, and β carbon atoms to boron, in excess of those present in a long chain tri-n-alkylborane. The number of alkyl substituents at the β-carbon atom can be seen in general to correspond to the degree of selectivity shown during the alkaline oxidation. It is probable therefore that the migratory aptitudes operating in Davies' work are not important here. In that study the t-butyl group appears to migrate from boron to oxygen in accordance with the higher inductive charge at the α-carbon atom to boron in comparison with the isobutyl group. Clearly the branching at the β-carbon atom makes a smaller contribution to the inductive charge at the α-carbon atom, than branching at the α-carbon atom. In addition, the species attacking the boron atom in the present study is unlikely to be the un-ionised species operating in Davies' work. In the presence of base the attacking species is more likely to be the much more nucleophilic hydroperoxide anion, as judged by the relative speeds of oxidation in the two studies. Thus the migratory aptitudes observed by Davies are outweighed by the more active, less specific reagent as used in the present study.

Thus the selectivity of dealkylation by the hydroperoxide anion is probably controlled by different factors from those operating in the protonolysis reaction (Section II, above). This difference is satisfactorily explained by the nature of the two reagents. Whereas the large bidentate carboxylic acid group can attack a sterically hindered borane only with difficulty, the smaller hydroperoxide ion readily attacks even a hindered boron atom and selectivity of the subsequent dealkylation reaction must depend on the relative mobilities of the alkyl groups bound to boron. In the protonolysis reaction therefore the carboxyl group, once co-ordinated to boron, attacks the α-carbon atom which presents the least steric opposition to approach of the hydroxyl group. The decreasing order of reactivity of alkyl groups is therefore primary > secondary > tertiary, and β-alkyl branching of each alkyl group has little effect on the observed selectivity. With the easy attack on boron of the hydroperoxide anion, substitution of the α-carbon atom is less important than the overall steric properties of the borane.

Inspection of Dreiding molecular models suggests that the overall steric requirements of the thexyl group are similar to those of the siamyl group, and each sweeps out an approximately hemispherical volume about the boron atom if free rotation of the B-C, C(α)-C(β), and C(β)-C(γ) bonds is allowed. By comparison the t-butyl groups are less sterically demanding, rotation of the C(α)-C(β) bonds leading to little increased steric compression between the alkyl groups at boron. Thus the most sterically hindered boranes, on the basis of bulk steric factors, are the disiamyl-n-alkylboranes, which have a steric requirement which is approximately twice as large as that of the thexyldi-n-alkylboranes.

The relative stability to oxidation of the siamyl (or thexyl) and n-alkyl groups may then be related to the relief of the bulk steric hindrance on removal of a siamyl (or thexyl) group compared with a n-alkyl group. Thus the apparent inconsistency of the results from the disiamyl-n-alkylboranes is accounted for by the great reduction in the steric compression between the alkyl groups at boron following the removal of a siamyl group. The alkyl-alkyl repulsions are correspondingly smaller with a thexyldi-n-alkylborane, and a t-butyl borane, and a selectivity closer to the statistical dealkylation is accordingly observed.

In the present study the two specificity ratios tabulated show a change in magnitude from the 33% reaction point to the 66% reaction point where oxidation of a second equivalent of C-B bond is substantially complete. On the basis of the arguments above it is reasonable to expect that the specificity in the latter case will be altered as a different boron species is being oxidised. As there is no evidence from the curves of products obtained (Figs. I-VIII), that the rates of the second dealkylation of a given boron atom is very much slower than the first (unlike the neutral hydrogen peroxide oxidation of t-butyldi-isobutylborane[14]), it must be supposed that the second reaction becomes an increasingly important factor in the observed selectivity as the reaction progresses.

Alkaline hydrogen peroxide oxidation can therefore have only limited use for the preparation of borinic acids and their derivatives from trialkylboranes, except in the case of the disiamyl-n-alkyl boranes where reasonable yields of an unsymmetrical borinic acid might be achieved.

The order of stability to oxidation of the boron to carbon bonds (primary > secondary > tertiary) as predicted by Traylor,[19] was not therefore observed. This prediction was based on the assumption that only electronic factors were operative. The present results suggest that with the organoboranes studied here, steric factors assume a dominant role in deciding the order of stability to oxidation.

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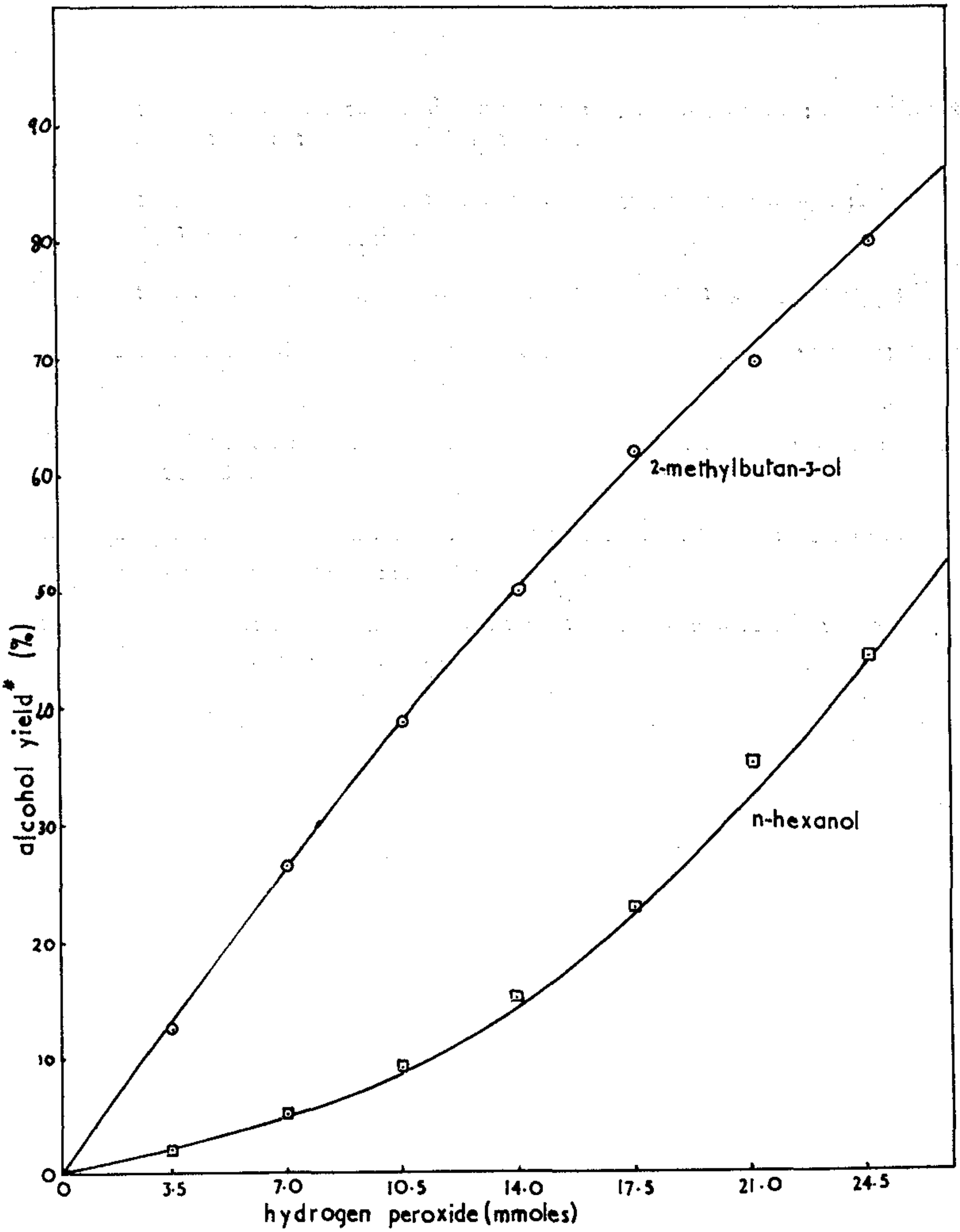


FIGURE 1. Production of 2-Methylbutan-3-ol and n-Hexanol During the Alkaline Hydrogen Peroxide Oxidation of Disiamyl-n-hexylborane (11·30 mmoles) in T.H.F. Solution (0·26M.) at 0°. (Table 1).

* see Discussion.

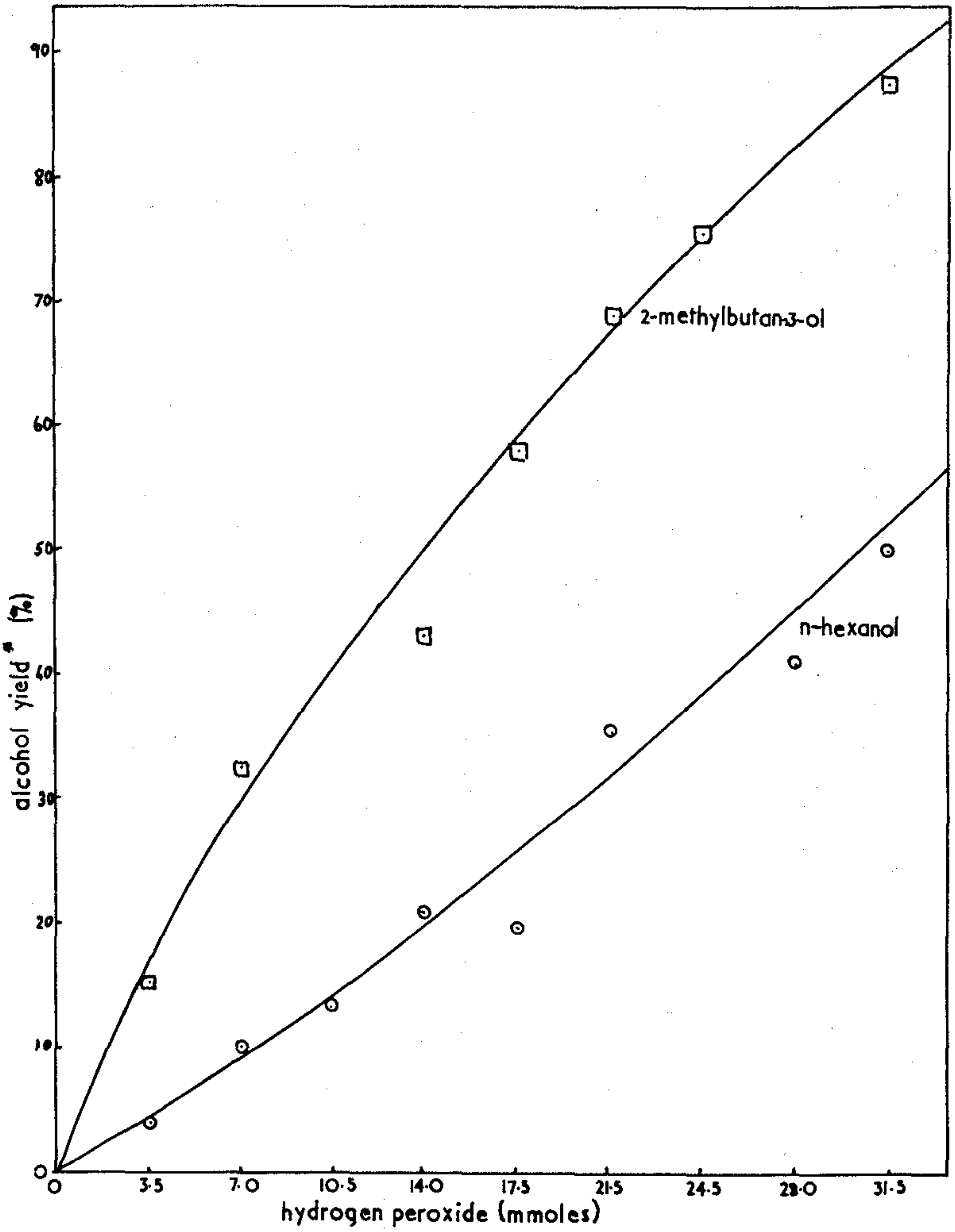


FIGURE 2. Production of 2-Methylbutan-3-ol and n-Hexanol During the Alkaline Hydrogen Peroxide Oxidation of Disiamyl-n-hexylborane (12·55 mmoles) in T.H.F. Solution (0·51 M.), at 0° (Table II).

*see Discussion

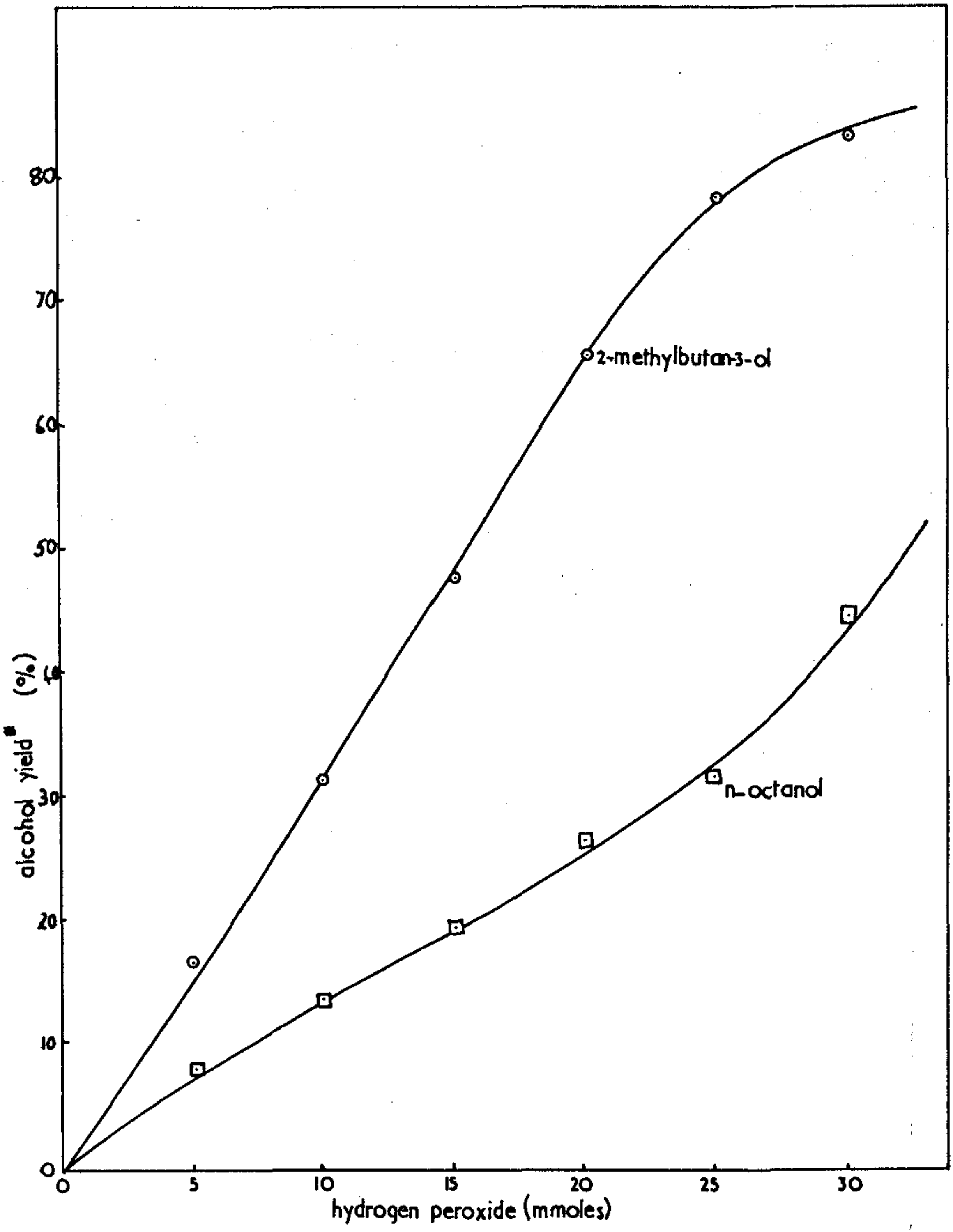


FIGURE 3. Production of 2-Methylbutan-3-ol and n-Octanol During the Alkaline Hydrogen Peroxide Oxidation of Disiamyl-n-octylborane (13·11 mmoles) in T.H.F. Solution (0·52 M), at 0° (Table III).

\# see Discussion

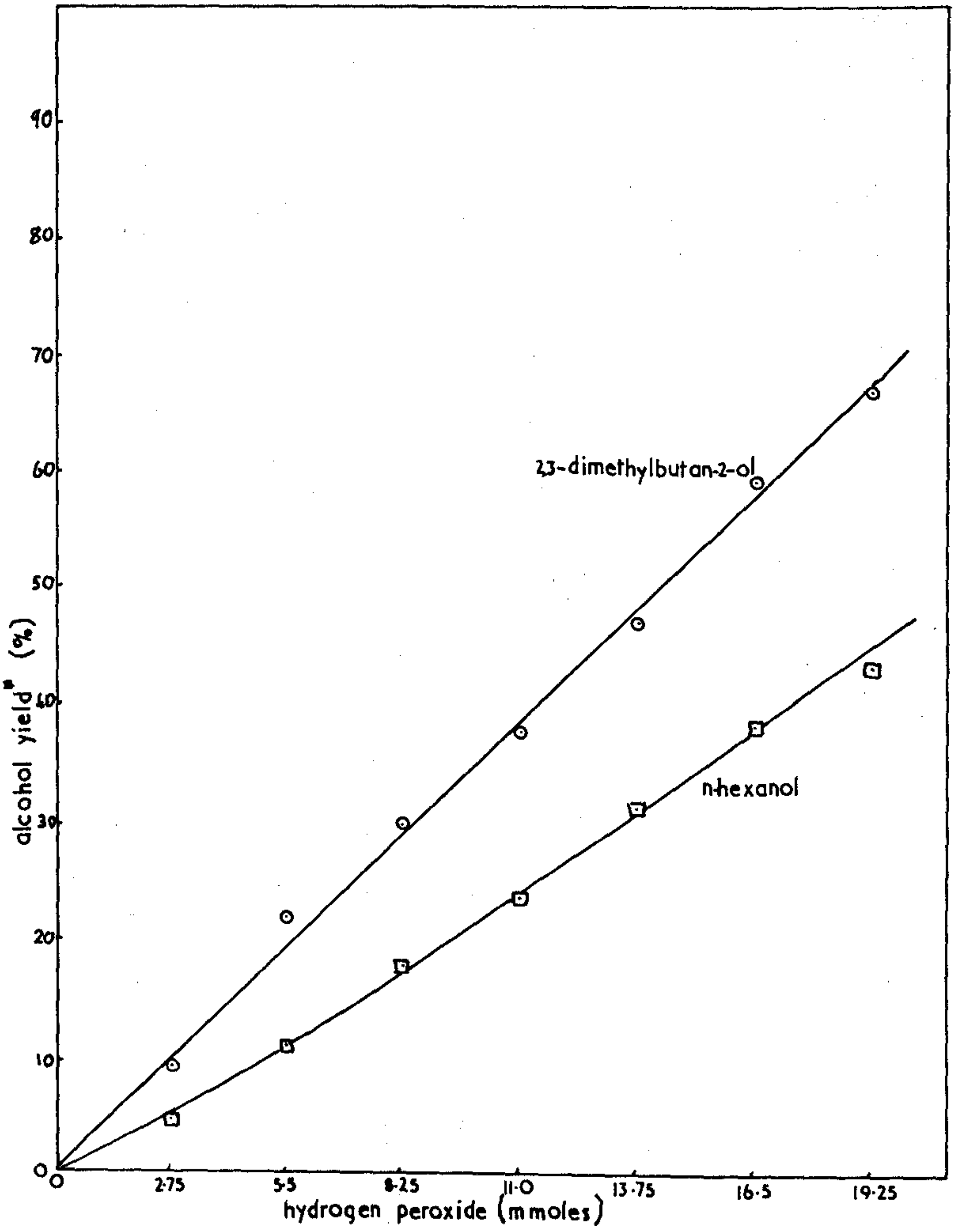


FIGURE 4. Production of 2,3-Dimethylbutan-2-ol and n-Hexanol During the Alkaline Hydrogen Peroxide Oxidation of Thexyldi-n-hexylborane (12·00 mmoles) in T.H.F. Solution (0·26 M), at 0° (Table IV).

*see Discussion

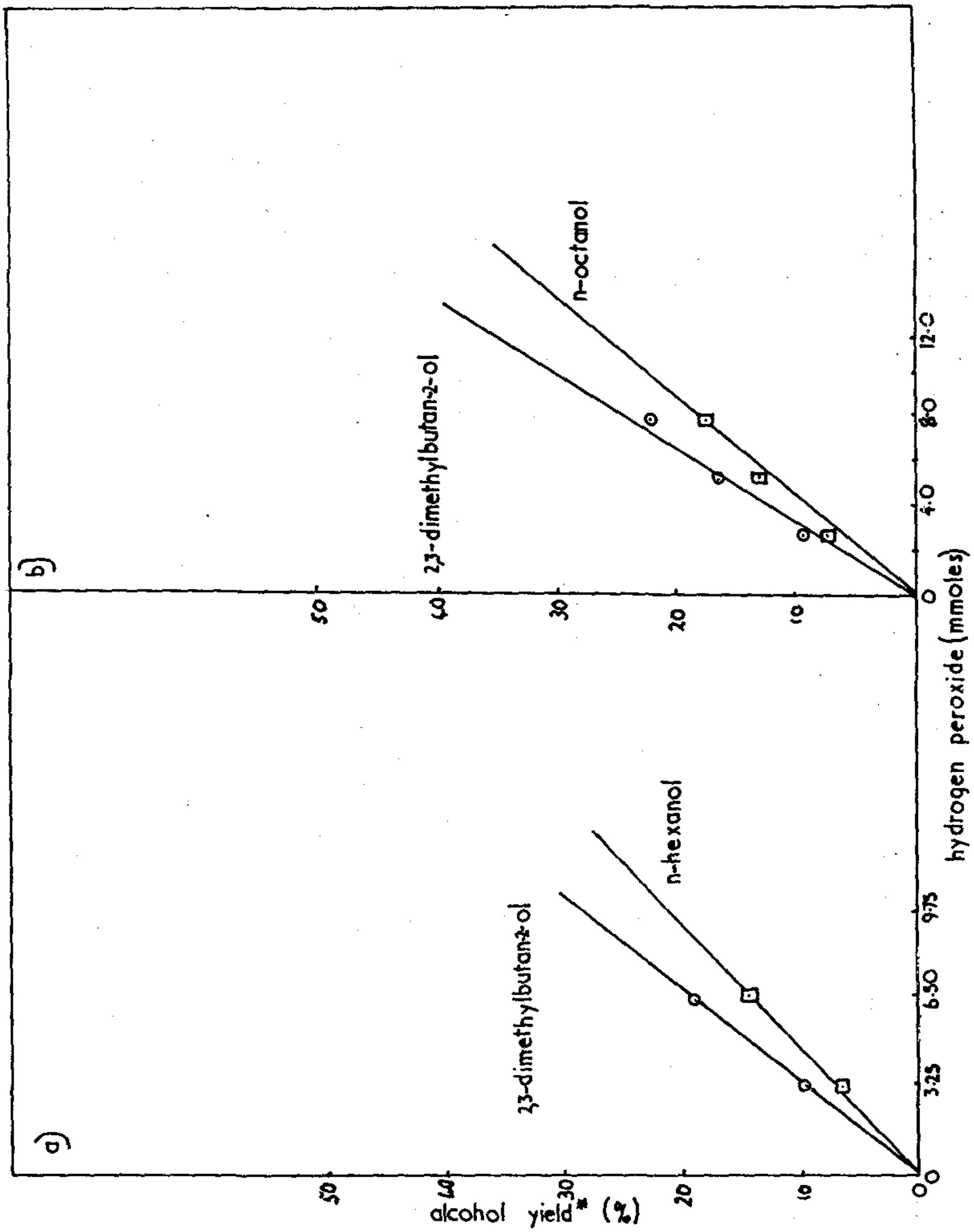


FIGURE 5. Production of 2,3-Dimethylbutan-2-ol, n-Hexanol, and n-Octanol During the Alkaline Hydrogen Peroxide Oxidation of a) Thexyldi-n-hexylborane (13·00 mmoles, 0·52 M) and b) Thexyldi-n-octylborane (12·31 mmoles, 0·51 M.) in T.H.F. Solution, at 0° (Tables V & VI).

* see Discussion

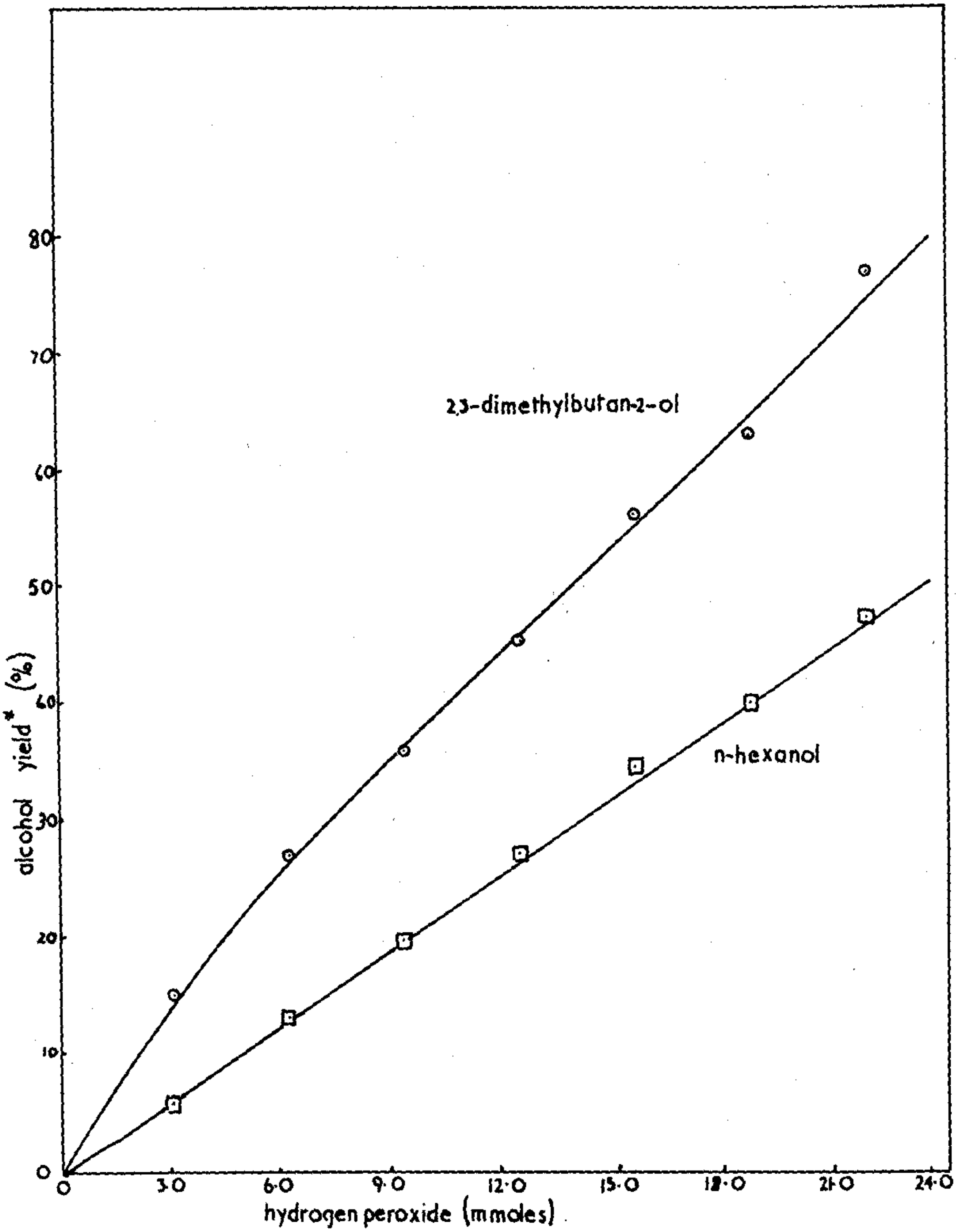


FIGURE 6. Production of 2,3-Dimethylbutan-2-ol and n-Hexanol During the Alkaline Hydrogen Peroxide Oxidation of Thexyldi-n-hexylborane (12·40 mmoles) in Diglyme Solution (0·26M.), at 0° (Table VI).

* see Discussion

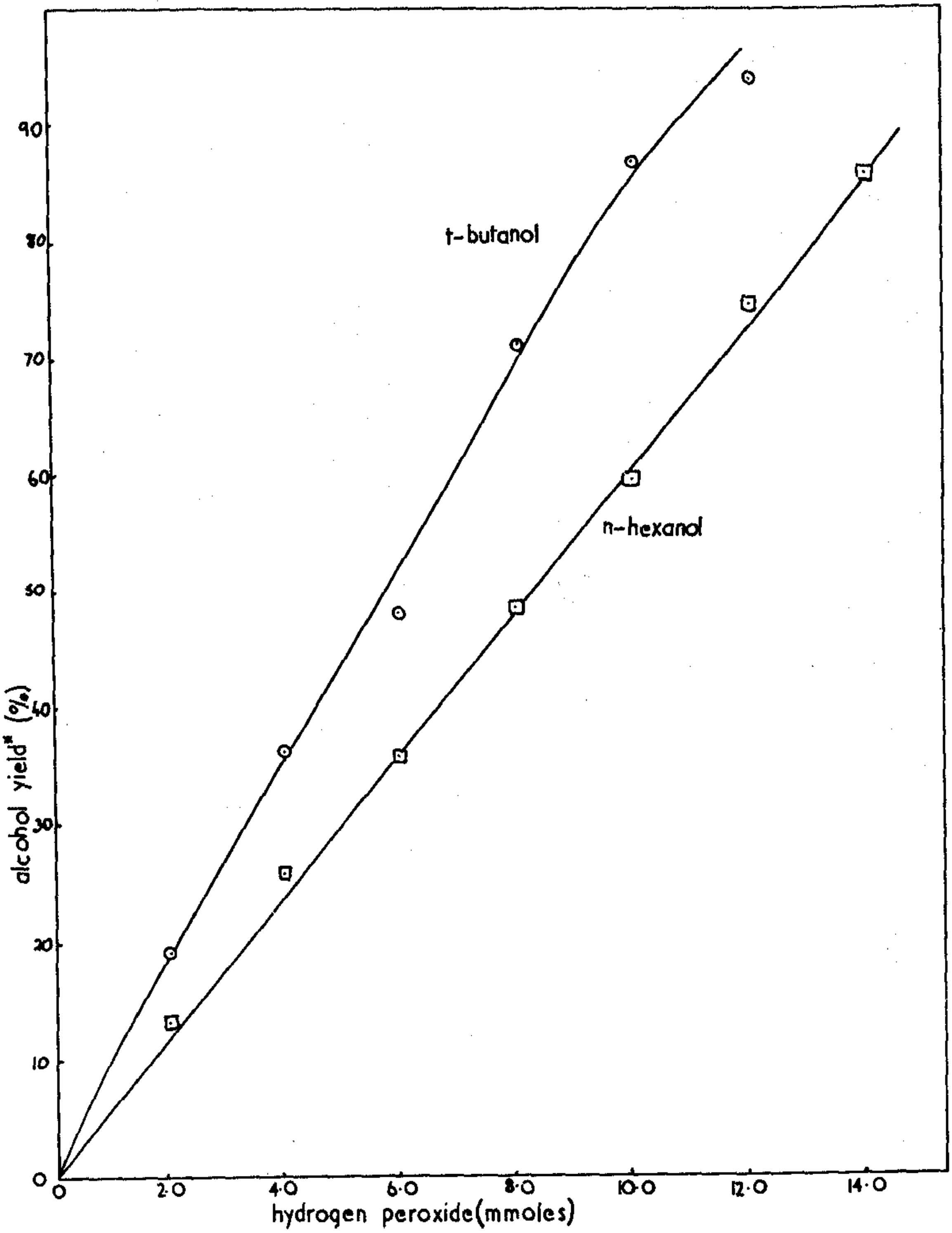


FIGURE 7. Production of t-Butanol and n-Hexanol During the Alkaline Hydrogen Peroxide Oxidation of t-Butyldi-n-hexylborane (4·30 mmoles) in Diglyme Solution (0·28 M.), at 0° (Table VIII).

*see Discussion

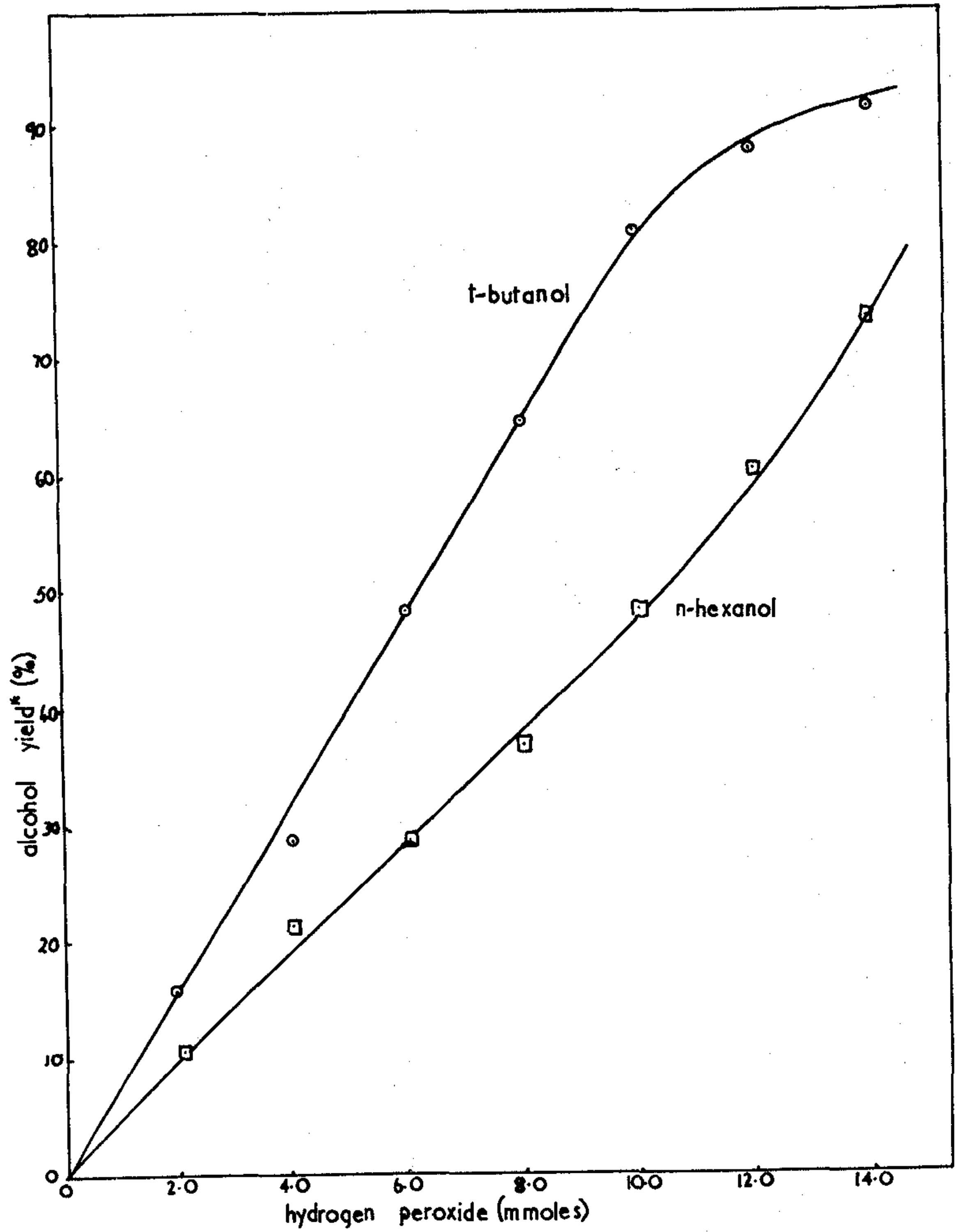


FIGURE 8. Production of t-Butanol and n-Hexanol During the Alkaline Hydrogen Peroxide Oxidation of Di-t-butyl-n-hexylborane (4·19 mmoles) in Diglyme Solution (0·26 M.), at 0° (Table IX).

*see Discussion

SECTION IV

THE REACTION OF NEUTRAL AQUEOUS HYDROGEN PEROXIDE WITH REPRESENTATIVE TRIALKYLBORANES, A NEW REACTION.

1.) Introduction

During an oxidation of tri-n-hexylborane, when aqueous solutions of sodium hydroxide, and hydrogen peroxide were added from two tap-funnels to a stirred T.H.F. solution of the organoborane, the sodium hydroxide solution failed to flow from the funnel. Reflux occurred, however, showing that reaction had taken place. Analysis of the oxidation products indicated the presence of n-dodecane, rather than n-hexanol. Further experiments when aqueous hydrogen peroxide was added to a carbon tetrachloride solution of tri-n-hexylborane, produced 1-chlorohexane, in a similar yield to that of n-dodecane from the oxidation in T.H.F. solution.

A search was made of the literature, but only a single isolated instance of this reaction could be found. The report was by Davies *et al.*[1,18] These authors treated t-butyldi-isobutylborane with 96% hydrogen peroxide (1.0 mol.) and obtained only an alcohol. Davies also oxidised the borane with molecular oxygen in carbon tetrachloride solution. The products were analysed by proton magnetic resonance spectroscopy and identified as t-butylchloride, and isobutylborinic acid.[1] Some phosgene was detected, also. If the 1-chlorohexane was produced by an autoxidation mechanism, then the oxidation using aqueous hydrogen peroxide might provide a convenient, and possibly selective in the case of an unsymmetrical trialkylborane, route to the preparation of alkyl chlorides by the dealkylation of an organoborane. Accordingly it was decided to investigate the scope of this reaction.

Considerable interest has been shown in the mechanism of autoxidation of trialkylboranes, principally because of the commercial use of these compounds as initiators in the polymerisation of olefins.[2] Earlier reports referred to the decomposition of a trialkylborane which leads to the production of free radicals which were able to start a chain polymerisation.[3,4] More careful work demonstrated that oxygen must be present in addition to the borane.[5-9] It was shown that oxidation of the trialkylborane led to the production of organoperoxyboranes which were thought to undergo a homolytic alkyl-oxygen, or alkoxy-oxygen, bond fission to produce free radicals.[9-11,22] Several kinetic studies have since been made of the polymerisation of olefins, using organoborane/air mixtures as initiator.[9,12-14]

Davies and co-workers have studied the air oxidation of trialkylboranes in the absence of readily polymerised materials.[1,15-18] Zutty and Welch supplied experimental evidence[19] since contested by Davies,[19a] that a long lived complex was formed between the trialkylborane and oxygen, and subsequently rearranged slowly to give the peroxide, $R_2B\cdot O-OR$. The rearrangement was later found to be fast at temperatures as low as -196°.[20] Bawn and co-workers supplied evidence that the presence of both the trialkylborane and its peroxide, was necessary to initiate polymerisation.[21] Mirviss conducted a kinetic study of the air oxidation of tri-n-butylborane, in various solvents, and was the first worker to report hydrocarbons among the reaction products.[22] A further kinetic study, by Hansen and Hamann, emphasised the necessity for the presence of both borane and peroxide to give free radicals.[23] They also confirmed the actual production of alkyl radicals in experiments using radical trapping agents, and suggested that a redox reaction between the organoboron peroxide, and a boron-carbon bond, led to the production of free radicals. The solubility of oxygen in hexane and benzene, the solvents used, limited the rate of the extremely fast oxidation of triethylborane during their work. Radicals were not produced in each reductive act, on the evidence of the yields of trapped radicals. Davies, and his co-workers, have made a study of the chemistry of organoboron peroxides and have provided strong evidence that an intramolecular redox rearrangement leading to the disappearance of the peroxide group is an important reaction of the organoboron peroxides studied.[1,17,18] A recent comprehensive review by Davies describes the chemistry of organoperoxyboranes.[19a]

A previous study by H.C. Brown has investigated the scope of the reaction of trialkylboranes with the noble metal oxides to produce dimeric hydrocarbons.[44,45,46a] The coupling reaction of the borane obtained by the hydroboration of hex-1-ene, using aqueous silver nitrate in the presence of excess sodium hydroxide, led to a 66% yield of n-dodecane, together with 5% of 5-methylundecane, and a mixture of hex-1-ene, and n-hexane. A non-terminal olefin, such as 2-methylbut-2-ene, formed a smaller yield of the coupled hydrocarbon, usually in the range 35-50%. The yield of monomeric hydrocarbons increased accordingly. H.C. Brown, in a side reference, recorded that the presence of carbon tetrachloride led to the production of an alkyl chloride, and hexachloroethane.[46b] The reaction was concluded from this evidence to be a free radical process. Sharefkin and Banks found that 30-40% of an alkyl chloride was obtained when a basic solution of the trialkylborane was treated with a dialkyl-N-chloroamine.[24] The yields of alkyl chlorides obtained from an organoborane formed by the hydroboration of a symmetrically disubstituted olefin, or a terminal olefin, were similar. The need for basic catalysis was interpreted as evidence against a free radical mechanism.

Mirviss found that the autoxidation of a trialkylborane yields a large number of non-boron containing products in small yields, in addition to the organoperoxyborane.[22] An essential difference with the present study was that here only a few hydrocarbon products could be detected, and in substantial yield, together with some alcohol. It was of interest, therefore, to explore the reaction and find out whether aqueous hydrogen peroxide behaved similarly to oxygen under these conditions. The reaction might also provide, in addition to the possible synthesis of alkyl chlorides mentioned above, a general route to coupled hydrocarbons.

A series of experiments was therefore undertaken to study the reaction of tri-n-hexylborane with aqueous hydrogen peroxide by varying the solvent, the concentration of the reagents, and their proportions. The yields of products obtained were measured using gas-liquid chromatography. In order to assess the scope and possible selectivity of the reaction, both in T.H.F., and carbon tetrachloride solutions, a representative series of symmetrical and unsymmetrical trialkylboranes was then oxidised by aqueous hydrogen peroxide under experimentally determined optimum conditions.

2. The Reaction of Neutral Aqueous Hydrogen Peroxide with Tri-n-hexylborane

Results and Discussion

A preliminary experiment, when a sample of tri-n-hexylborane in T.H.F. solution (0.5 M.) at ice temperature, was treated with aqueous hydrogen peroxide, showed that n-hexane, hex-1-ene, hexan-2-ol, and n-hexanol were produced in addition to the dimeric hydrocarbons n-dodecane, and 5-methylundecane. Reactions were accordingly carried out at 0°, in T.H.F. solution with varying amounts of 30% H_2O_2 solution, in order to establish the amount of oxidising agent necessary to give the maximum yield of dimeric hydrocarbons (see Table I). For convenience only the yields of the dodecanes produced were estimated. The results in Table I show that the reaction leading to hydrocarbon formation is complete within 3 hr., and that the maximum yield is obtained by the addition of one mole equivalent of hydrogen peroxide to the borane.

Table I

The Reaction of Tri-n-hexylborane, in T.H.F. Solution (0.52 M.) at 0°, with Varying Amounts of Aqueous Hydrogen Peroxide (30% w/v).

Time (hr.)	Percentage Yield of Hydrocarbons.[a]		Tri-n-hexyl-borane (mmole)	Hydrogen Peroxide (mmole)
	n-dodecane	5-methylundecane		
3	28.0	7.2	11.67	88.8
12	27.7	7.5	14.19	43.1
3	13.2	3.53	12.38	7.4
3	28.7	8.8	-	13.2

[a] Percentage calculated from amount C-B bond initially present.

Table II

The Reaction of Aqueous Hydrogen Peroxide (30% w/v.) with Tri-n-hexylborane (0.52 M.) in T.H.F. Solution. Subsequent Reaction of the Products with Excess Aqueous Alkaline Hydrogen Peroxide.

Time (hr.)	Percentage Yields of Oxidation Products[a]						Tri-n-hexylborane (mmole.)	Hydrogen Peroxide (mmole.)
	n-hexane	hex-1-ene	n-Dodecane	5-Methyl-undecane	n-Hexanol	Hexan-2-ol		
0.1	-	-	15.8	4.7	3.6	-	13.12	13.58
1.5			23.8	7.2	5.2			
3.2			27.2	8.1	5.6			
3.6			26.4	8.0	5.3			
8.3			25.0	7.6	5.2			
24	6.5	<0.1	27.0	8.1	5.4	-		
$^{\ominus}$OOH	6.5	<0.1	28.6	8.1	39.6	2.3		25.0
1.5			27.4	8.3	8.8	0.75	12.67	26.4
3.0			27.3	7.6	10.9	0.81		
4.0			27.2	8.2	10.5	0.79		
18.0	10.3	3.0	26.4	8.2	12.2	0.95		
$^{\ominus}$OOH	10.3	3.0	26.4	8.2	35.5	4.1		20.0
$^{\ominus}$OOH/1.0hr	0.67	<0.1	3.52	1.1	84.5	5.61	13.32	43.0

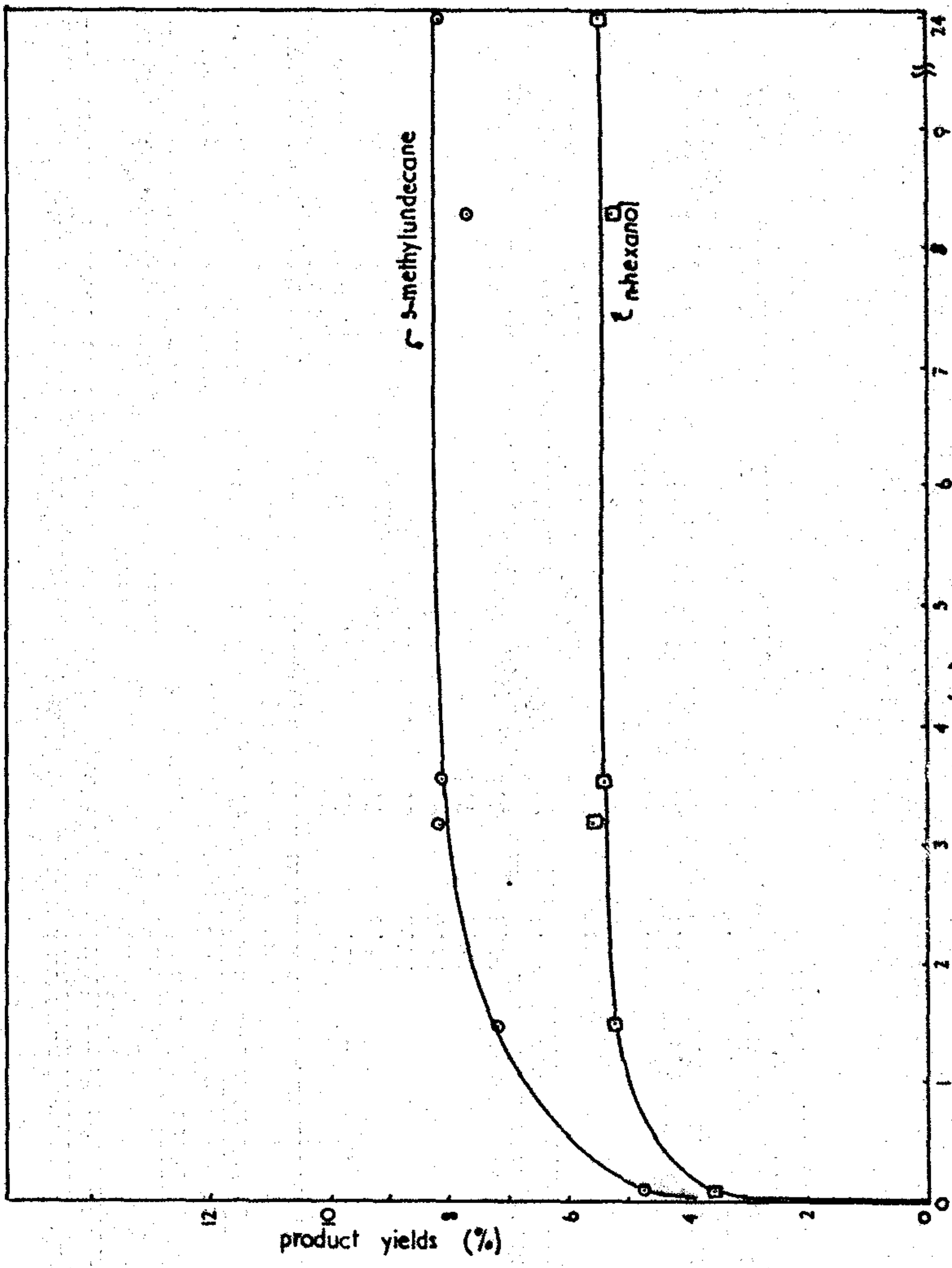


FIGURE I. Production of 5-Methylundecane and n-Hexanol During the Reaction of Tri-n-hexylborane in T.H.F. Solution (13·12 mmoles, 0·52 M.) with Neutral Aqueous Hydrogen Peroxide (13·58 mmoles, 30 %w/v), at 0° (Table II).

The reaction of tri-n-hexylborane with one mole equivalent of hydrogen peroxide was then repeated at 0°, and followed against time for the production both of n-hexanol and of isomeric dodecanes. The results are shown in Table II. The curves in Fig. 1 show that the production of n-hexanol and of the dodecanes was concurrent. After 24 hr. the reaction mixture was analysed again, with an additional estimation for n-hexane, and hex-1-ene, and then oxidised completely with an excess of alkaline hydrogen peroxide solution in order to estimate any residual carbon to boron bond. Only the yield of n-hexanol increased during the alkaline oxidation. The production of a small amount (2.3%) of hexan-2-ol was also observed. The increase in n-hexanol yield (34.2%) shows that one carbon to boron (C-B) bond was unaffected by the neutral peroxidation. It follows that the overall yield (47.6%) of n-hexanol, and of monomeric and dimeric hydrocarbons, is derived from a neutral H_2O_2 oxidation which breaks only two of the three available C-B bonds. A second experiment, using an excess of H_2O_2, was carried out with periodic estimation of the products during 18 hr. (Table II and Fig. 2). As expected, the yield of dimer was unchanged, but n-hexanol was obtained in increased yield. When excess aqueous alkaline hydrogen peroxide was added after 18 hr., to estimate the residual C-B bond, it was found that the increase in alcohol yield was only 26.6%. The n-hexanol, and hexan-2-ol, produced during the neutral oxidation must, therefore, be derived from oxidation of the third C-B bond, which previously was only attacked by the alkaline oxidising agent. As attack on the third C-B bond is very slow, and gives no additional dimer, it is probable that a different reaction path is being followed (see later discussion in Part 3: The Reaction of Neutral Hydrogen Peroxide Solution with Representative Organoboranes).

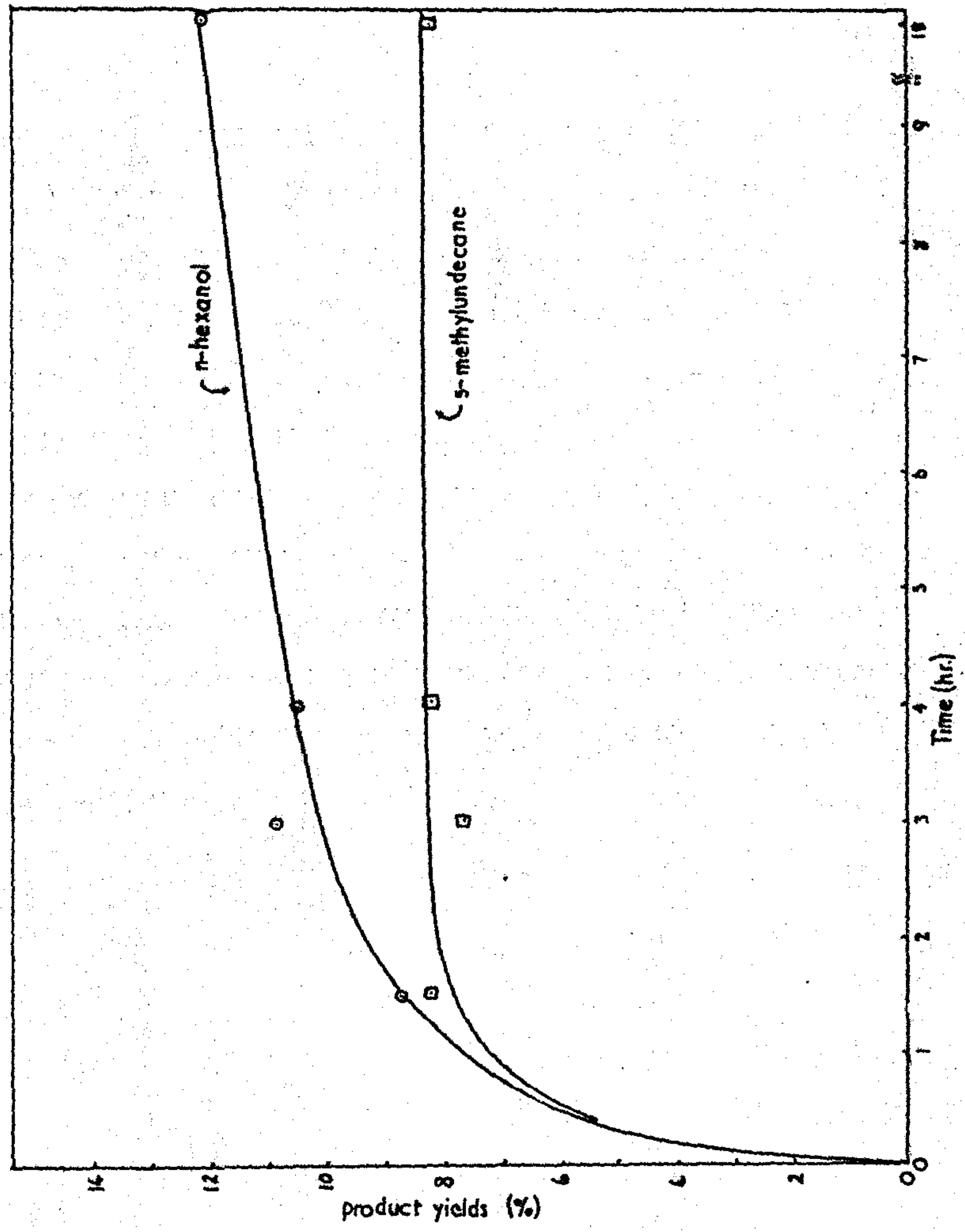


FIGURE 2. Production of 5-Methylundecane and n-Hexanol During the Reaction of Tri-n-hexylborane in T.H.F. Solution (12·67 mmoles, 0·52M) with Neutral Aqueous Hydrogen Peroxide (26·40 mmoles, 30 %w/v), at 0° (Table II).

H.C. Brown has reported that the yield of alcohols from the alkaline hydrogen peroxide (excess) oxidation of tri-n-hexylborane at 0° is 89%.[25] A similar oxidation was carried out in order to check that the synchronous addition of the sodium hydroxide and hydrogen peroxide solutions, from all-glass syringes, as used in this study, was capable of giving similar yields. An overall yield of 90.1% of hexanols was obtained (Table II), together with a small amount of isomeric dodecanes (4.62%), showing that the oxidation occurs efficiently under the experimental conditions of this study, and that imperfect mixing of the two aqueous reagents allows the neutral H_2O_2 reaction to proceed to a small extent.

In order to find out whether the products obtained were formed by a pyrolysis reaction during gas chromatographic analysis, a sample of tri-n-hexylborane was treated with hydrogen peroxide (1.0 mol.) at 0°. After stirring for 3 hr. the reaction mixture was estimated for monomeric and dimeric hydrocarbons, and then evacuated (0°, 0.5 mm.). Compounds volatile under these conditions were collected in a cold trap at -80°. The trap was then warmed to ice temperature and the contents analysed by g.l.c. The trap contained T.H.F., n-hexane, hex-1-ene, and the internal standard, 2,3-dimethylbutane (Table III). The amounts of n-hexane, and hex-1-ene, obtained were found to be substantially the same as previously present among the reaction products. The non-volatile component remaining in the reaction flask contained no n-hexane, hex-1-ene, or 2,3-dimethylbutane. Clearly, therefore, the monomeric hydrocarbons originally produced were not formed in the gas chromatograph, and the residue in the reaction flask was not able, by a pyrolysis during chromatographic analysis, to produce any further low boiling hydrocarbons.

A similar reaction (Table III) was carried out and the reaction mixture evacuated in the same way as above (0.5mm.) until a residue of approximately 10 ml. was left in the reaction flask. The mother liquors were then transferred under nitrogen, in an all-glass syringe, to a small vacuum distillation apparatus, with a receiver cooled at -80°, and distilled under nitrogen at high vacuum (0.1 mm.). The temperature of the distillation flask

Table III

Evacuation of the Reaction Flask after the Oxidation of Tri-n-hexylborane using Aqueous Hydrogen Peroxide

	Yield of Products (mmoles)						Tri-n-hexylborane (mmole)	Hydrogen Peroxide (mmole)
	n-hexane	hex-1-ene	n-dodecane	5-methylundecane	n-hexanol	Hexan-2-ol		
Experiment 1								
Reaction mixture before evacuation	5.10	2.12					11.80	12.10
Reaction mixture after evacuation	0.0	0.0						
Vacuum Trap	4.6	1.9						
Experiment 2								
Reaction mixture	4.4	1.5	5.1	1.5	3.4	-	12.84	16.6
Non-volatile fraction after the distillation	0.0	0.0	0.2	0.0	5.9	0.3		
Volatile Fraction obtained from the distillation	3.6	0.6	5.1	1.5	1.0	0		
Oxidation of the Non-volatile fraction with alkaline hydrogen peroxide	0.0	0.0	0.18	0.0	13.5	0.8		16.0

Table IVA

The Reaction of Aqueous Hydrogen Peroxide (30% w/v.) with Tri-n-hexylborane in T.H.F. Solution (0.5 M.) at Various Temperatures

Temperature °C	Percentage Yield of Hydrocarbons[a]				Tri-n-hexylborane (mmole)	Hydrogen Peroxide (mmole)
	n-hexane	Hex-1-ene	n-Dodecane	5-Methylundecane		
-20	10.0	5.2	24.3	5.2	12.97	36.0
0	11.9	2.5	28.0	7.2	11.66	35.0
25	11.8	3.9	27.1	8.2	17.20	38.5
66	17.7	2.8	29.4	9.2	11.26	29.4

[a] Percentage calculated from the amount of C-B bond present initially.

was raised slowly from 0° to 50°, and held there until distillation ceased. The apparatus was then brought to atmospheric pressure, under nitrogen, and the cooled receivers warmed to ice temperature. The contents of the two cooled receivers were then combined and analysed. The residue in the distillation flask contained both n-pentanol (internal standard), and n-hexanol, but only a small amount of n-dodecane, and no 5-methylundecane. The presence of boric acid residues in the distillation flask may have caused the drop in volatility of the alcohols through complex formation, or esterification, thus allowing the normally higher boiling n-dodecane to distil at a lower temperature than the alcohols (Table III). The contents of the distillation flask were treated with excess alkaline hydrogen peroxide solution at 0°, and re-analysed for n-hexanol produced. The yield of n-hexanol increased by an amount corresponding approximately to one equivalent of C-B bond. n-Dodecane was therefore produced independently of the gas chromatograph, and any pyrolysis which occurs in the g.l.c. must also take place under reaction conditions below 50°.

Table IVA summarises the yields of hydrocarbons obtained when a series of samples of tri-n-hexylborane, in T.H.F. solution at different temperatures, was treated with aqueous H_2O_2. It was concluded that the reaction shows little sensitivity to temperature over the range studied. For convenience therefore, ice temperature was chosen as the standard temperature for further work, the strongly exothermic reaction being more readily controlled at 0^o.

An earlier experiment (see Table II), where the presence of an excess of hydrogen peroxide led to the slow cleavage of the third C-B bond, producing n-hexanol, suggested the possible importance of two different reaction mechanisms. Further experiments were carried out to attempt to obtain confirmatory evidence. The reaction of disiamylborinic acid with aqueous hydrogen peroxide produced the corresponding monomeric and dimeric hydrocarbons rapidly, and also a larger yield of the alcohol than was observed for tri-n-hexylborane (within 0.17 hr.) as shown in Table IVB. Within 2.5 hr. the yield of 2-methylbutan-3-ol had increased by a further 24.2% leaving only 10% of the alkyl group originally bound to boron unaccounted for. The reaction of

Table IVB

The Reaction of Aqueous Hydrogen Peroxide (30% w/v.) with Thexylboronic Acid (0.5 M.) and Disiamylborinic Acid (0.5 M.) in T.H.F. Solution at 25°.

Organoborane	H_2O_2 (mmoles)	RH %[c]	R(-H) %[c]	RR %[c]	ROH %[c]	Time (hr.)
$RB(OH)_2$[a] (14.7 mmoles)	18.0	-	-	-	59.5	0.2
		-	-	-	77.0	0.7
		-	-	-	93.4	3.0
		<0.1	<0.1	-	95.5	5.0
R_2BOH[b] (12.7 mmoles)	27.0	31.4	1.3	2.9	27.5	0.17
		34.6	1.3	2.9	51.7	2.5

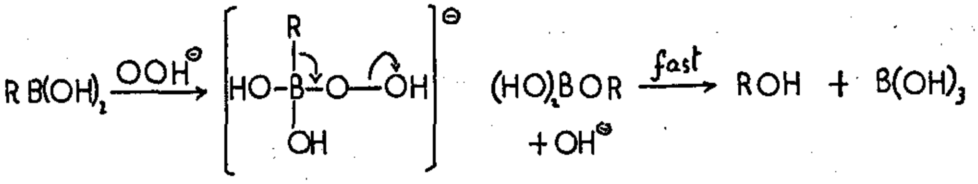
[a] Thexylboronic acid

[b] Disiamylborinic acid

[c] Percentages calculated from the total C-B bond initially present.

thexylboronic acid with one equivalent of aqueous hydrogen peroxide produced 2,3-dimethylbutan-2-ol rapidly and smoothly, accounting for 95.5% of the alkyl group bound originally to boron, within 5.0 hr. Hydrocarbons were produced only in trace quantities.

The latter result is in accordance with the results of T. G. Traylor *et al.*[48] who explained the reaction on the basis of an ionic mechanism similar to that proposed previously for a related study by Kuivila[40,43] (see Scheme 1).



1.

With disiamylborinic acid, the production of alcohol is more important (relative to hydrocarbon formation) than with tri-n-hexylborane where a 7:1 preference for hydrocarbon formation is found (Table II). Alcohol production is slow in comparison with hydrocarbon formation for both the alkyl boron acids, however, and is more comparable to the later slow reaction of tri-n-hexylborane in the presence of an excess of aqueous hydrogen peroxide.

It seems very probable therefore that neutral hydrogen peroxide solution can attack an organoborane by two alternative mechanisms. The slow alcohol producing reaction is favoured by the replacement of alkyl groups at boron by hydroxyl groups, while the fast, hydrocarbon forming reaction is more important for a trialkylborane.

The production of hydrocarbons, and in particular the relative proportions of the monomeric and dimeric compounds, suggests a free-radical mechanism. The production of free n-hexyl radicals in solution would be expected to lead to the formation of n-dodecane, and 5-methylundecane through a radical combination reaction between the n-hexyl and hex-2-yl radicals, as in reaction (i) below. The yield of n-hexane and hex-1-ene could be accounted for by a radical disproportionation reaction (ii), or by abstraction of a hydrogen atom (iii) from the solvent, reagent, etc.

$$2R\cdot \longrightarrow RR \qquad \text{(i)}$$

$$2R\cdot \longrightarrow RH + R(-H) \qquad \text{(ii)}$$

$$HX + R\cdot \longrightarrow RH + X\cdot \qquad \text{(iii)}$$

($HX = H_2O, H_2O_2$, T.H.F., etc.)

The possibility of a free alkyl radical intermediate is strengthened by consideration of the relative proportions of the monomeric to dimeric hydrocarbons produced from tri-n-hexylborane and disiamylborinic acid. With the former borane an n-hexyl radical would be produced, and here a radical coupling reaction yielding n-dodecane is favoured over a hydrogen abstraction reaction by the low energy of activation, and consequently high collisional efficiency, between the primary alkyl radicals.[26] For the secondary (1,2-dimethylpropyl) radical the energy of activation for the coupling reaction is higher owing to the difficulty of approach between the two secondary radicals and therefore a hydrogen abstraction reaction with the solvent would be expected to compete more favourably. In general the ratio of coupled to monomeric hydrocarbons is in agreement with that found by Verbrugge in the free-radical coupling reaction induced under alkaline conditions with silver nitrate.[39,45]

Discussion is complicated by the production of n-hexane by more than one possible route. n-Hexane may be produced from the disproportionation reaction (ii, above), but this should be accompanied by an equimolar amount of hex-1-ene.[26] Hex-1-ene was produced in smaller amounts than the n-hexane, however, on all occasions, and so the disproportionation reaction cannot be very important in this study. The excess of alkane may be accounted for either by a small amount of disproportionation (ii) of R•, accompanied by a more important alternative reaction, such as hydrogen abstraction (iii) producing n-hexane but not hex-1-ene, or possibly by reaction (ii) alone, but with subsequent oxidation of some of the olefin by a further reaction with H_2O_2. It is possible, therefore, that the olefin yields recorded are unreliable owing to instability under the reaction conditions. Before the importante of a free radical reaction was realised, many experiments were invalidated owing to loss of the internal standard, 2,3-dimethylbutane, through its instability to free radical attack.[37]

Tables V and VI show the results obtained when the peroxidation conditions were altered in order to attempt to demonstrate the presence of alkyl radicals in solution. When one equivalent of aqueous hydrogen peroxide was added to a very dilute solution of tri-n-hexylborane (0.0625 M.), the yield of dodecanes decreased (Table V) while the yield of n-hexane increased.

In the much more dilute solution a combination reaction between the alkyl radicals (R•) might be expected, on statistical grounds, to decrease in importance compared with hydrogen abstraction from the solvent, where the probability of a successful reaction is increased. The small change in yields found in this experiment may indicate that R•, free in solution, is not important in the production of dodecane. The possibility remains, however, that the very high relative speed of the combination reaction, over an abstraction reaction, still leads to the preferential formation of n-dodecane. The second experiment (Table V) was the inverse addition of a solution of the organoborane to three mole equivalents of aqueous H_2O_2, but this led to only a small change in the relative yields of monomeric and dimeric hydrocarbons. The solvent here was substantially an aqueous T.H.F. system during the earlier part of the addition.

In a third experiment, the presence of a large amount (1.0 mol.) of 1,4-dihydroquinone (Table V) led only to a very small change in the yields of hydrocarbons obtained. If the products were obtained from a radical chain reaction, as in the autoxidation of

Table V

Variation of Concentration of the Reactants, and of the Solvent in the Reaction of Hydrogen Peroxide Solution with Tri-n-hexylborane

	Concentration of Organoborane. M.	Solvent	Percentage Yield of Hydrocarbon Products[a]				Tri-n-Hexylborane (mmole)	Hydrogen Peroxide (mmole)
			n-hexane	Hex-1-ene	n-Dodecane	5-Methylundecane		
Diluted Organoborane	0.063	T.H.F.	16.9	4.6	24.8	5.1	1.25	3.01
Inverse Addition	0.58	T.H.F., aqueous	13.3	4.5	24.0	4.8	7.6	22.8
Presence of hydroquinone (13.6 mmole)	0.52	T.H.F.	12.4	4.25	24.6	5.13	12.5	14.3
-	0.51	Diglyme	10.6	5.1	27.1	5.6	13.3	31.0
-	0.51	Methanol	11.7	0.7	27.2	6.4	13.5	34.2

Table VI

Addition of Water to the Reaction Mixture

	Percentage Yields of Products[a]					Tri-n-hexylborane (mmole)	Hydrogen Peroxide (mmole)
	n-Hexane	Hex-1-ene	n-Dodecane	5-methylundecane	n-hexanol		
H_2O added after the oxidation	-	-	27.7	7.5	4.5	14.19	15.0
H_2O_2, 5% w/v.	9.3	5.9	24.8	7.3	10.4	12.77	14.0

[a] Calculated from initial amount of C-B bond.

alkanes, phenols, etc.,[27,28] the addition of hydroquinone should quench the reaction until the antioxidant was largely spent.[29] No induction period before reaction started, or a yellow colour due to benzoquinone formation was observed, however. It seemed probable therefore that a chain reaction was not important under the conditions of this study.

The peroxidations in T.H.F. solution showed that n-hexanol was produced with the dodecanes in a fast reaction, or reactions. To exclude the possibility of hexanol production by autoxidation, owing to the possible presence of a small amount of oxygen in the reaction flask, a sample of the organoborane in T.H.F. solution was analysed by g.l.c. before the addition of H_2O_2. No n-hexanol fraction was observed in the chromatogram, however. Further experiments were made in order to find out whether n-hexanol was produced by a reaction involving the water present in the oxidising agent.

Addition of oxygen-free water after the peroxidation in T.H.F. did not cause an increase in n-hexanol yield (Table VI). Hydrolysis of n-hexylborinic, boronic, or borate, esters after the peroxidation was probably not therefore important. The second result in Table VI was obtained when the oxidation was carried out with aqueous H_2O_2 solution which had been diluted from 30% (w/v), to 5% (w/v). The oxidation at 0° was still vigorous and gave similar yields to those obtained in the experiments with T.H.F. as solvent, although sufficient water was now present after the oxidation for an aqueous phase to separate when stirring was discontinued. The course of the reaction was therefore substantially unaltered under these conditions. The small changes in the yields of products indicates that an increase of 3-5% in the n-hexanol yield occurred at the expense of n-dodecane, and n-hexane. Unless, therefore, the attack of a primary alkyl radical (R•), or of an alkoxy radical (RO•), on H_2O is unfavoured, it must be concluded that the presence of free radicals in solution is unimportant in this study. The silver nitrate induced coupling reaction of tri-n-hexylborane, in an aqueous mixture, suggests that attack on water is not favoured.[45]

To obtain further information on the importance of the solvent, additional peroxidations were carried out in diglyme, and methanol solutions (Table V). In both solvents, however, the product yields were substantially unaltered. This supported the conclusion, drawn from the experiments using, in turn, very diluted solutions of the organoborane, and H_2O_2, that the role of an organic, or aqueous solvent in the reaction is unimportant.

Both homolytic reactions, and multicentre reactions show much less dependence on the polarity of the solvent than reactions which proceed through an ionic mechanism. Three possible courses of reaction, then, are suggested by the results above. n-Dodecane may be produced by an intramolecular reaction at the boron atom, breaking two C-B bonds, without any intervention by the solvent.[23] Alternatively the homolytic fission of a C-B bond, after H_2O_2 attack, may produce free alkyl radicals in solution which subsequently combine to produce n-dodecane. Thirdly, the attack of an oxidised organoborane molecule on an unoxidised C-B bond, as proposed in the autoxidation of tribenzylborane, may produce the dimeric hydrocarbon.[30] The following three experiments were carried out in an attempt to find which, if any, of the reaction courses above is followed.

In the first experiment, an excess of H_2O_2 solution was added to a mixture of tri-n-hexylborane (12.81 mmole), and tri-n-pentylborane (13.0 mmole), in T.H.F. solution (0.5 M.) at 0°. When, after 12 hours, the mixture was finally treated with excess alkaline hydrogen peroxide solution, to oxidise residual C-B bonds, and then extracted into ether, g.l.c. analysis showed the following products to have been formed:-

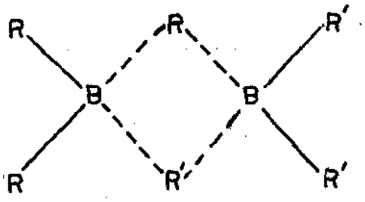
n-pentane 4.56 mmole
n-hexane 4.18 mmole
pent-1-ene 0.98 mmole
hex-1-ene 1.15 mmole

n-decane 2.75 mmole, 7.1%, 1.03 mol.
n-undecane 5.33 mmole, 13.73%, 2.0 mol.
n-dodecane 2.56 mmole, 6.56%, 0.96 mol.
n-pentanol 13.58 mmole
n-hexanol 14.08 mmole

(The isomeric dimeric hydrocarbons were not estimated).

In addition to the products which would be expected from separate oxidations of the two organoboranes, a substantial yield of n-undecane was found. The yields of the dimeric hydrocarbons produced were also calculated as a percentage of the total amount of C-B bond present in the original mixture of organoboranes. The percentage yields of the three dimeric hydrocarbons were then normalised to n-undecane as 2.0 mol. The yield of n-decane was then 1.03 mol., and of n-dodecane 0.96 mol. The production of n-undecane demonstrates that an intramolecular process, involving only one molecule of the organoborane, or an unstable intermediate formed by its reaction with H_2O_2, to produce the dimeric hydrocarbons, does not occur. The close correspondence of the ratio between the normalised dimer yields (n-decane: n-undecane: n-dodecane) to (1:2:1) indicates that the coupling reaction shows no discrimination in reactivity between the n-hexyl-, and n-pentyl-, groups. The experimental ratio of 1.03:2.0:0.96 (n-decane:n-undecane:n-dodecane), differs slightly from unity in the direction of the small excess, from the preparation, of tri-n-pentylborane (1.01 mol.) over tri-n-hexylborane (1.00 mol.), and to a similar extent. It seems certain therefore, that the oxidation in T.H.F. solution depends either on an intermolecular or a bimolecular reaction, to form the dimeric products.

The conclusion drawn from this experiment would be invalid if, before the oxidation, the boranes had suffered a disproportionation reaction to give a random mixture of pentyl-, and hexyl-, groups at each boron atom. Previous studies of the disproportionation reaction of trialkylboranes, however, have used unsymmetrical boranes as starting compounds.[31-33] Disproportionation was then studied using a technique, such as distillation, which would allow the equilibrium formation of the most volatile possible borane from the mixture present, and its subsequent removal.[31,33] Unless the activation energy of the intermediate leading to disproportionation, generally described as a bridged dimer,[31,32] is so low as to allow rapid randomisation at ice temperature, it is unlikely that



disproportionation should be important in the experiment above. Here, the two organoboranes were prepared separately, and oxidised within 15 mins. of mixing. The system was not put under any external constraint likely to produce disproportionation.

In the second experiment, a sample of tri-n-hexylborane in carbon tetrachloride (CCl_4) solution, was oxidised with aqueous hydrogen peroxide (Table VII). In the third experiment, excess iodine (I_2) was added to a sample of tri-n-hexylborane in T.H.F. solution, before treatment with an excess of aqueous H_2O_2 (Table VII). The oxidation in CCl_4 solution gave a small yield of n-hexane, hex-1-ene, n-dodecane, and 5-methylundecane, but gave an increased yield of n-hexanol (24.0%). A substantial yield of 1-chlorohexane

(27.3%) was also produced, together with hexachloroethane (C_2Cl_6). Another compound was eluted as a sharp peak in the g.l.c., but later than n-dodecane. The compound may be 1,1,1-trichloroheptane formed by the combination of the trichloromethyl and n-hexyl radicals. Further identification was not pursued, however.

In the presence of iodine, the oxidation in T.H.F. solution gave a very small yield of the dimeric hydrocarbons, together with an increased yield of n-hexanol (20.5%). In addition, 1-iodohexane (25.8%) was obtained in a yield similar to that of 1-chlorohexane from the second experiment.

The yield of the alkyl halides in the reactions above is similar to the yield of n-dodecane obtained from the oxidation in T.H.F. solution. It is probable, therefore, that the reaction intermediate which leads to n-dodecane formation, may also be responsible for the production of the alkyl halides. C_2Cl_6 is readily produced by the combination reaction between two trichloromethyl radicals (v),[34] and its production during a reaction in CCl_4 solution suggests that the reaction produces free radicals which can attack the solvent as in reaction (v).

Table VII

The Reaction of Aqueous Hydrogen Peroxide (30% w/v) with Tri-n-hexylborane (0.5 M.) (a) in Carbon Tetrachloride Solution, and (b) in T.H.F. Solution in the Presence of Excess Iodine.

	Percentage Yields of Products[a]							C_2Cl_6	Tri-n-hexylborane	Hydrogen Peroxide
	n-Hexane	Hex-1-ene	n-Dodecane	5-Methylundecane	n-Hexanol	1-Chlorohexane	1-Iodohexane	(mmole)	(mmole)	(mmole)
Carbon Tetrachloride Solution	3.1	0.4	7.2	2.4	24.0	27.3		7.0	12.97	35.3
T.H.F./I_2 (60 mmole)	-	-	0.3	0.1	20.5		25.8		13.05	26.4

Table VIII

The Reaction of Fenton's Reagent with Tri-n-hexylborane.[b]

	Percentage Yields of Products[a]						Tri-n-hexylborane	Hydrogen Peroxide
	n-Hexane	Hex-1-ene	n-Dodecane	5-Methyl-undecane	n-Hexanol	Hexan-2-ol	(mmole)	(mmole)
T.H.F. Solution	5.3	-	21.8	7.5	5.4	0.6	12.68	26.45
Aqueous mixture	7.3	1.7	6.2	1.6	9.7	0.7	12.40	26.50
Air Autoxidation in Aqueous Diglyme Solution	7.4	1.1	3.4	-	22.7	-	12.90	0
Addition of excess alkaline hydrogen peroxide solution					59.5			26.50

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[a] Percentages calculated from initial quantity of C-B bond.

[b] Molarities are not quoted as a two-phase system was obtained.

$$R\cdot + CCl_4 \longrightarrow RCl + CCl_3 \qquad \text{(iv)}$$

$$2\cdot CCl_3 \longrightarrow C_2Cl_6 \qquad \text{(v)}$$

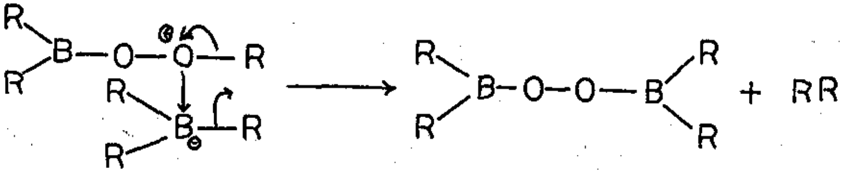
$$R\cdot + I_2 \longrightarrow RI + \cdot I \qquad \text{(vi)}$$

Two isolated reports in the literature refer to the autoxidation of trialkylboranes in CCl_4 solution. Davies and co-workers deduced (from p.m.r. data) the presence of t-butyl chloride in a sample of t-butyldi-isobutylborane in CCl_4 solution which had been treated with oxygen (1.0 mol.)[1]. A small amount of carbonyl chloride ($COCl_2$) was also detected. A second report refers to the autoxidation of tri-n-propylborane in CCl_4 solution.[35] The products isolated here, however, were a mixture of $COCl_2$, propane, and propene, but no alkyl chloride. Neither reference mentions the production of C_2Cl_6, or suggests how the reaction may proceed.

Many studies in free radical chemistry have made use of the low energy of the I-I bond, by using molecular iodine as a radical trapping agent. Walling[36] comments on the efficiency of iodine as a trapping agent, and in a kinetic study of the autoxidation of triethylborane, Hansen and Hamann[23] found iodine to be an effective trapping agent for the ethyl radical.

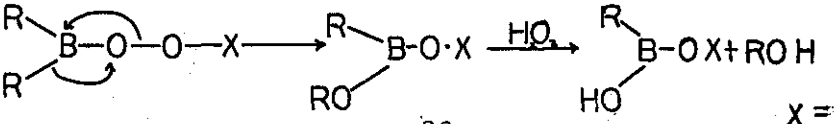
A reasonable explanation of the formation of 1-iodohexane during the experiment above, then, is that the iodine is attacked by hexyl radicals as in equation (vi). The overall reaction between tri-n-hexylborane and neutral H_2O_2 solution may therefore be explained as an initial attack by H_2O_2 on the trialkylborane which leads to the breaking of two C-B bonds. Hydrocarbon products estimated account for the formation of approximately 1.0-1.5 mol. of hexyl radicals. If more than 1.0 mol. of H_2O_2 is added, the third C-B bond is broken slowly as described above (see discussion and Table II), and probably by a different mechanism.[43,48] The fate of the alkyl radicals produced then depends on the solvent system. In T.H.F., diglyme, methanol, and aqueous T.H.F. solutions, the radicals undergo a combination reaction (i) to form n-dodecane and 5-methylundecane, and a hydrogen abstraction reaction with the solvent or oxidising agent to produce n-hexane (iii). The free-radical combination reaction, which has a low activation energy for the primary alkyl radicals, is favoured over hydrogen abstraction from the solvent. Reactions (iv) and (vi) are followed in CCl_4 solution, or the presence of iodine, giving the formation of alkyl halides at the expense of the combination reaction (i). Reactions (iv) and (vi) are related to (iii), as all involve bond breaking during the product forming step. In a recent review, Stirling[37] comments that a 1,2-hydrogen shift has not been reported for alkyl radicals. The amount of 5-methylundecane produced by the oxidation in T.H.F. solution corresponds to the amount of secondary hexyl group formed during the hydroboration of hex-1-ene (approximately 6-8%).[25] The subsequent alkaline H_2O_2 oxidation of the reaction products in T.H.F. solution gives an increase in yield of only 2% of hexan-2-ol, showing that most of the hex-2-yl group was in fact oxidised by the neutral H_2O_2 (Table II).

Both Wilke and Heimbach[30] and Hansen and Hamann,[23] have suggested bimolecular redox reactions between oxidised and unoxidised boron compounds which, if followed in this study, could explain the production of n-dodecane. Wilke and Heimbach obtained bibenzyl in 20% yield from the autoxidation of tribenzylborane, and suggested that it was produced through the nucleophilic attack of the alkylperoxyboron group on an unoxidised borane molecule as in reaction (vii). The maximum possible yield of bibenzyl should therefore be 33%, a yield closely similar to that obtained in the present study. This mechanism only requires 0.5 mol. oxygen to be absorbed, however, to give the maximum yield of dimeric hydrocarbon.


(vii)

A larger amount of H_2O_2 (1.0 mol.) is necessary to obtain the maximum yield of n-dodecane in the oxidation of tri-n-hexylborane, however. The autoxidation of tri-n-alkylboranes was reported by Wilke and Heimbach not to lead to the production of dimeric hydrocarbons in substantial yields. The behaviour of tribenzylborane appears, therefore, to be a special case in the context of the autoxidation studies, and a feasible alternative explanation to that given by Wilke and Heimbach may lie in the ready formation (through heterolytic benzyl-oxygen bond fission) of the benzyl radical, owing to its stabilisation through delocalisation of the unpaired radical electron.[36] The n-alkyl groups studied here were not capable of stabilisation by delocalisation, however. If an intermediate organoperoxyborane were formed during the H_2O_2 oxidation in CCl_4 solution, it is possible that the role of the unoxidised trialkylborane in the non-free radical redox reaction might be taken by the solvent CCl_4 or, similarly, by the iodine molecule. The requirement for

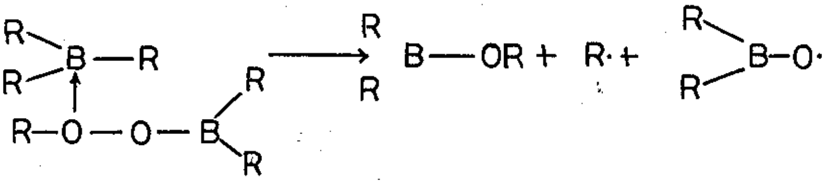
1.0 mol. of H_2O_2 would be met, although the trichloromethyl radical, and hence C_2Cl_6, would not be expected to form. A redox rearrangement (as suggested by Zutty [19]) of the peroxyborane residue would lead to an n-hexylboronic ester which could subsequently hydrolyse to give the increased yield of n-hexanol found, as in reaction (viii).



(viii)

X = CCl_3, I.

Hansen and Hamann [23] found that the organoperoxyboron compound obtained by the oxidation of triethylborane only gave ethyl radicals when in contact with unoxidised triethylborane. This reaction was also explained by a bimolecular redox reaction, (ix),



(ix)

similar to that proposed by Petry,[47] and Zutty,[19] for the intramolecular rearrangement of an organoboron peroxide. Both of these alternative explanations, however, require the hydrogen peroxide as used in this study, to react as oxygen in the presence of

H_2O. Experiments were therefore carried out in order to find out the nature of the attacking species and, if possible, the reaction intermediate responsible for n-dodecane, etc., formation.

A sample of tri-n-hexylborane (12.10 mmole.) in diglyme solution was treated with 2.0 ml. of de-ionised water, and an excess of compressed air bubbled through the solution. The reaction mixture was analysed by g.l.c. after being autoxidised for 24 hr. The gas-liquid chromatogram showed that many products had been formed, but in small yields, as in the air oxidations in dry solution carried out by Mirviss.[22] Table VIII shows the yields of the larger components of the mixture. Although water had been added to the organoborane solution before oxidation so as to allow comparison with the neutral H_2O_2 oxidations, the yield of n-dodecane was reduced to 3.4%, and n-hexanol was now the major product (22.7%). The addition of an excess of aqueous alkaline hydrogen peroxide increased the yields of n-hexanol by 36.8%, showing that one C-B bond had been unaffected during the air oxidation. Although the organoborane was oxidised to the boronic oxidation state, as in the reaction with neutral H_2O_2, the non-boron containing products of the air oxidation were widely different from those in the H_2O_2 study. It was concluded, therefore, that neutral aqueous H_2O_2 does not attack the organoborane as oxygen in the presence of water.

The remaining possible modes of reaction of H_2O_2 in solution are probably either (a) an attack by the hydroxyl radical (HO•), following an initial homolytic dissociation of the oxygen-oxygen bond, or (b) a direct attack of H_2O_2 at the boron atom by co-ordination between the oxygen lone pair electrons and the empty 2p orbital of boron. Ferrous ion promotes the rapid decomposition of H_2O_2 to give the hydroxyl radical, HO•, as in Fenton's reagent.[38] Similarity between the products of an H_2O_2 oxidation using Fenton's reagent, and the normal H_2O_2 oxidation, should indicate that the hydroxyl radical is the active species involved in the attack at boron.

Table VIII shows the yields of products obtained when tri-n-hexylborane (a) in T.H.F. solution, and (b) as an aqueous mixture, is added, with vigorous magnetic stirring, to an aqueous solution of ferrous sulphate, and then treated with aqueous H_2O_2. In T.H.F. solution it was difficult to avoid the separation of the ferrous sulphate solution into a separate aqueous layer, with the attendant possibility that the reaction of the organoborane with H_2O_2 was not affected by the presence of the ferrous ion. Although a brown colour, probably due to the oxidation of the ferrous ion to the ferric state, was observed, the yield of the dodecanes was not significantly different from that obtained in the absence of ferrous sulphate. This result appears to support the importance of the hydroxyl radical in the oxidation. In order to allow the maximum opportunity for the mixing of the hydrogen peroxide solution with the ferrous sulphate, therefore, H_2O_2 was added slowly below the surface of a vigorously stirred mixture of tri-n-hexylborane and aqueous ferrous sulphate. During the addition of the H_2O_2, the reaction mixture became black. The yield of n-dodecane was now greatly reduced. The yields of n-hexane, and n-hexanol, were slightly increased. Although the conditions of the second oxidation were chosen to favour the formation of the hydroxyl radical, the yields of organic products obtained were widely different from those obtained in previous experiments by the action of H_2O_2 on tri-n-hexylborane, both in T.H.F., and in aqueous T.H.F. solutions. It seems likely therefore that if HO• is the attacking species responsible for the coupling reaction, then it is not produced free in solution. Some reservations as to the experimental conditions remain however, as a homogeneous system was not achieved in either experiment.

The rapidity of the hydrogen peroxide oxidation of tri-n-hexylborane tends to obscure the reaction mechanism followed. The products from the oxidation of the borane by molecular oxygen in aqueous diglyme show clearly that hydrogen peroxide does not decompose and react as molecular oxygen (as in x) under the present reaction conditions. It is possible however that the borane catalyses a homolytic fission of hydrogen peroxide to give hydroxyl radicals (as in xi), or hydroperoxide radicals (as in xii).

$$2H_2O_2 \xrightarrow{BR_3} 2H_2O + O_2 \qquad (x)$$

$$H_2O_2 \xrightarrow{BR_3} 2HO\cdot \qquad (xi)$$

$$H_2O_2 \xrightarrow{BR_3} H\cdot + \cdot OOH \qquad (xii)$$

Fenton oxidations are normally carried out in aqueous solution, and consequently the attempted Fenton oxidations in the present study had to be carried out under non-ideal conditions owing to the immiscibility of the reagents. It is possible therefore that the hydroxyl or hydroperoxide radicals are the active species in the hydrocarbon-forming reaction. The enzyme peroxidaze, and silver ion are both known to induce a free radical dissociation of hydrogen peroxide, but with the enzyme there is some uncertainty as to whether the hydroxyl or the hydroperoxide radical, is the species formed.[49]

Production of Alcohols

With tri-n-hexylborane, the small amount of n-hexanol produced during the initial fast reaction may not have been produced by the same mechanism as in the subsequent slower reaction which leads to the breaking of the third C-B bond. The slow, smooth production of an alcohol, with no concurrent hydrocarbon formation, in the oxidation of thexylboronic acid (and also during the slow component of the oxidation of disiamylborinic acid) also suggests two alternative mechanisms which can lead to alcohol formation.

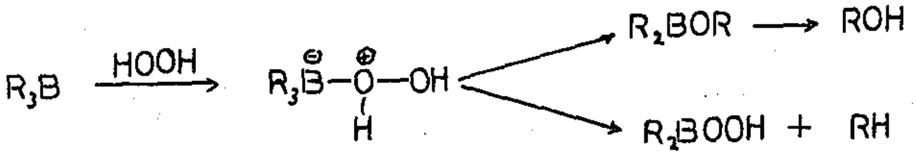
The presence of a borate ester leads to very little if any decomposition of aqueous hydrogen peroxide. This result is expected from the small Lewis acidity of the boron atom in a borate ester, and from the established non-free radical oxidation of a boronic acid. When the stronger Lewis acid tri-n-hexylborane was added in a catalytic amount however, to hydrogen peroxide, a rapid dealkylation occurred. Any catalytic activity of the boron atom cannot therefore be assessed as the borane is unstable in the presence of the products of any free radicals formed.

The ionic mechanism proposed by Kuivila[40,43] and Traylor,[48] as discussed earlier, is compatible with the slow alcohol producing reaction of the third C-B bond. The small amount of alcohol produced during the earlier fast reaction may also be due to the competition of the same mechanism through the very small equilibrium amount of hydroperoxide anion present under the neutral oxidation conditions. The mechanism suggested for the fast reaction (below) may also lead to the production of a small amount of alcohol.

Production of Hydrocarbons

The production of the monomeric and dimeric hydrocarbons (or alkyl halides in the presence of carbon tetrachloride or iodine) suggests the intermediate production of alkyl radicals during the fast reaction. The non-free radical mechanism proposed by Kuivila[43] for boronic acid dealkylation, and extended by Brown[25] to the trialkylboranes probably proceeds through an intermediate similar to those in reactions (xiii) and (xiv). Once the ionic intermediate is formed a subsequent free-radical decomposition leading to dimeric hydrocarbon formation would not be expected.

$$R_3B \xrightarrow{HO\overset{\ominus}{O}} \left[R_3\overset{\ominus}{B}{-}OOH\right] \dashrightarrow \qquad \text{(xiii)}$$

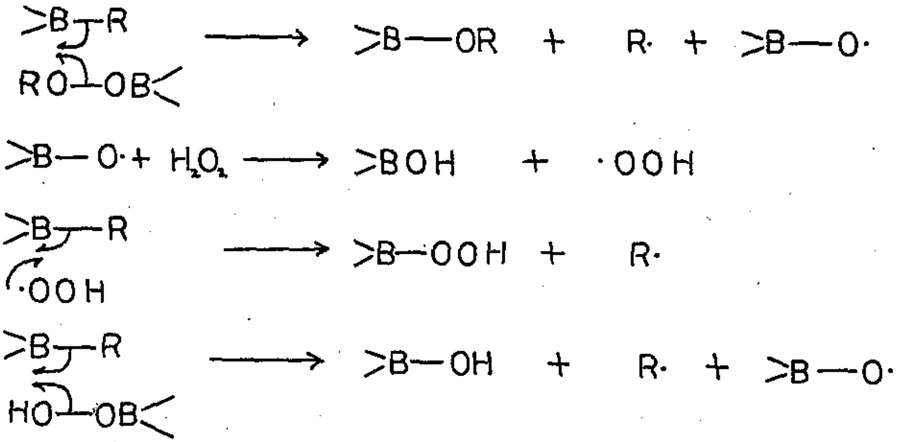


$$R_3B \xrightarrow{HOOH} R_3\overset{\ominus}{B}{-}\underset{H}{\overset{\oplus}{O}}{-}OH \begin{cases} \rightarrow R_2BOR \longrightarrow ROH \\ \rightarrow R_2BOOH + RH \end{cases} \qquad \text{(xiv)}$$

Considering the energy difference between the two alternative reactions in (xiv), the production of an alcohol results in the breaking of an O-O bond (+ 50 kcal.) and the formation of a C-O bond (-90 kcal.), a net stabilisation of approximately 40 kcal.[60] The alternative production of an alkane differs in the breaking of an O-H bond (+110 kcal.) and the formation of a C-H bond (-87.3 kcal.), a net destabilisation of 22.7 kcal. Whatever the energy of the common formation of a B-O bond therefore, the production of an alcohol is favoured energetically by some 63 kcal. Such a mechanism for hydrocarbon formation is probably therefore of little importance.

Even under basic conditions (as used by Brown for alcohol production) where the attacking species is largely the hydroperoxide anion a small yield of hydrocarbons is obtained. The evidence for the alternative mode of attack by un-ionised hydrogen peroxide is therefore very strong. Any alternative mechanism for hydrocarbon formation must take account of the requirement of one equivalent of hydrogen peroxide to break two boron to carbon bonds.

A free radical chain reaction of the type shown in Scheme 2 would satisfy the observed stoicheiometry, and also explain the production of n-undecane during the oxidation of a mixture of tri-n-pentylborane and tri-n-hexylborane. Such a mechanism may require the presence of a trace of alkylperoxyboron group to give initiation, 2a. Small amounts of oxygen in the reaction vessel during the



2a.

2b.

2c.

2d.

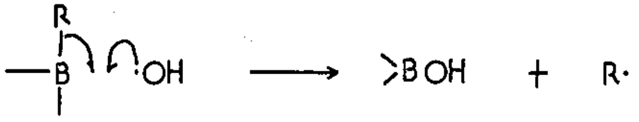
preparation of the borane, or oxygen dissolved in the aqueous hydrogen peroxide reagent, would give the required small amount of peroxide group. Hansen and Hamann[23] have suggested a reaction identical to 2a to explain the production of free radicals during the autoxidation of triethylborane. They did not find evidence for an overall chain oxidation under the action of molecular oxygen. The chain carrier in Scheme 2 would be the boron-oxygen radical in equations 2b and 2d. The mechanism depends on the fission of the H-O bond of hydrogen peroxide (2b) rather than the weaker O-O bond. A similar fission has been proposed as a possibility for the enzyme catalysed homolysis of hydrogen peroxide, however.[49] A further analogy lies in the attack of the t-butoxy radical on t-butyl hydroperoxide which is thought to account for the free radical chain decomposition of the latter compound.[50]

A drawback to this mechanism is the apparent similarity of the oxidation products to those from a Fenton oxidation as carried out under the conditions described above. Here however, a reaction such as (xv) may provide an intermediate in the chain mechanism which would then continue to produce the observed products. It is difficult however to reconcile a chain mechanism with the absence of

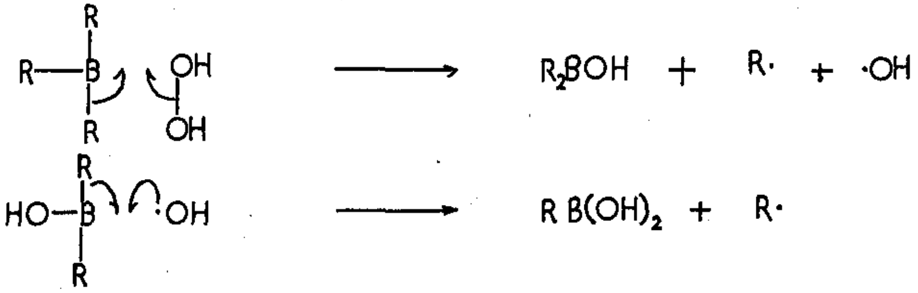
$$HO\cdot + H_2O_2 \longrightarrow H_2O + HOO\cdot \qquad (xv)$$

any inhibition of the reaction in the presence of hydroquinone, a known inhibitor of chain reactions.

An alternative possible mechanism which does not involve a free radical chain is the catalysis of a homolytic fission of the O-O bond by the boron atom. A fast attack by un-ionised hydrogen peroxide on the trialkylborane may be possible as argued earlier because the extent of the fast reaction appears to be dependent on the Lewis acidity of the boron atom (as reflected by the number of oxygen atoms bonded to boron: i.e. $R_3B > R_2BOH \gg RB(OH)_2$). The attack may either be a one-step process via attack at boron by the hydroxyl radical, possibly as in Scheme 3, or a two-step process where the attacking agent is neutral hydrogen peroxide, as in Scheme 4.



3



4a

4b

The hydroxyl radical produced in 4a would then react, probably with the same boron atom, as in 3 or 4b, in accordance with the observed stoicheiometry. A possible objection to reaction 4a is the low yield of alcohol in view of the simultaneous production of hydroxyl and alkyl radicals. A possible explanation may be that only the hydroxyl radical (as in 4b) is likely to react further with the boron atom, through the very favourable energetics of breaking a C-B bond (+ 90 kcal.) and forming an O-B bond (-150 kcal.), a gain in stabilisation of 60 kcal.[60] Attack by the alkyl radical at boron would not be expected to produce any change. A combination between hydroxyl and alkyl radicals during the reactions in Scheme 4 should produce the small amount of alcohols observed.

The subsequent fate of the alkyl radicals was discussed earlier (Reactions i-vi). The high yield of dimeric hydrocarbon could be explained on the basis of a fast reaction of type 4b leading to the production of a second alkyl radical before the first alkyl radical leaves the solvent cage. If the disproportionation of the mixture of pentyl and hexyl boranes is not important however (as discussed earlier), the solvent cage must be assumed to be penetrated very readily by the alkyl radical, as the symmetrical and unsymmetrical dimeric hydrocarbons were produced in the statistical proportions.

The production of hexyl chloride (iv) or iodide (vi) is also readily explained on the basis of reaction Schemes 3 and 4 through the ready attack of an alkyl radical on the weaker C-Cl bond (-66.5 kcal.) or I-I bond (-36.0 kcal.) compared with the stronger C-H bond of an organic solvent (-87.3 kcal.). Previous studies have shown that alkyl radical attack on water is not favoured.[39,45] The formation of alkyl halide may take place either at the walls of the solvent cage, or in the body of solution.

Alkyl chloride formation involves a bond breaking step (reaction iv) while the production of dimeric hydrocarbon does not and has a very small energy of activation, as discussed earlier. The preferential formation of alkyl halide over dimeric hydrocarbons therefore suggests that the former process takes place at the surface of the solvent cage, and adds evidence that the dimerisation reaction occurs in the body of the solvent, as required for n-undecane formation.

Finally the observed blackening and the small yield of compounds normally found with the neutral hydrogen peroxide oxidation, in the attempted Fenton oxidation are in accord with the known indiscriminate attack of the hydroxyl radical on organic compounds.[38] The mechanism in Scheme 4a suggests that this radical, if formed, would react very rapidly at the boron atom. This mechanism can be regarded as a radical displacement reaction at the boron atom. Such reactions have not been suggested commonly in trialkylborane chemistry, although the products obtained in a recent photolytic study on triethylborane suggested the possibility of such a process.[51] Two other reports in the literature suggest a possible displacement of the alkyl group in a boroxine by an attacking free radical.[52,57]

The results obtained in the present study lead therefore to the suggestion of several possible mechanisms. Further experiments are needed however, to draw a more definite conclusion as to the reaction path.

3. The Reaction of Neutral Aqueous Hydrogen Peroxide with Representative Trialkylboranes in Tetrahydrofuran and Carbon Tetrachloride Solution

Results

The trialkylboranes were prepared in tetrahydrofuran (T.H.F.) solution by the Hydroboration method. The molarity of the solutions was similar to that used (0.5 M.) during the oxidation of tri-n-hexylborane (Part 2, above). When the oxidation was to be carried out in carbon tetrachloride or diglyme solution the olefins used in the organoborane preparation were estimated by gas-liquid chromatography (g.l.c.) and then the solvent (and excess olefins from the preparation) was removed by evacuating the solution at 0°/0.5 mm., until distillation ceased. The vacuum trap was warmed to ice temperature and re-analysed for olefins. It was possible in this way to establish that no de-hydroboration had taken place during the evacuation. The evacuated reaction flask was then brought to atmospheric pressure with dry oxygen-free nitrogen before the new solvent was added from a syringe.

The branched boranes reacted more slowly with hydrogen peroxide than did tri-n-hexylborane, in both of the solvents. The reaction mixtures were accordingly analysed at periodic intervals for oxidation products. As the lower boiling products (monomeric hydrocarbons) could not be estimated using the same g.l.c. temperature and stationary phase, the lower and higher boiling products were conveniently estimated at different times during the reaction, and then together after the reaction.

After the oxidation in T.H.F. solution, the reaction mixture was treated with an excess of aqueous alkaline hydrogen peroxide, in order to estimate the amount of unoxidised carbon to boron (C-B) bond. An attempt was made also to estimate the residual C-B bonds after the CCl_4 oxidation of tri-n-hexylborane, but the alkaline hydrogen peroxide oxidation was found to be ineffective in that solvent, and led to a complicated analysis. The final alkaline oxidation was therefore excluded from this part of the study.

Tri-2-hexylborane

Table IX summarises the products, and their yields, obtained from the H_2O_2 oxidation of tri-2-hexylborane. The yields show a considerable departure from those found for tri-n-hexylborane under similar conditions (see Part 2, above). The oxidation in T.H.F. solution at 0° was found to be essentially complete within two hours. The proportion of n-hexane was three times as large as that obtained from tri-n-hexylborane, while the yield of dimeric hydrocarbons was correspondingly reduced. The combined yield of hexan-2-ol, and hexan-3-ol was larger than the yield of n-hexanol from the oxidation of the primary organoborane. The final alkaline oxidation produced only a further 12.6% of mixed hexan-2-ol and hexan-3-ol, confirming that the neutral H_2O_2 oxidation of the third C-B bond in tri-2-hexylborane is more rapid than for tri-n-hexylborane.

To obtain a standard for comparison, a sample of tri-n-hexylborane was oxidised in CCl_4 solution at 25°, using the procedure outlined above. The products obtained from the reaction of a CCl_4 solution of tri-n-hexylborane (12.72 mmole, 0.52 M.), with excess aqueous H_2O_2 (26.4 mmole) in 2.5 hours were:- n-hexane, 3.8%; hex-1-ene, 0.1%; n-dodecane, 6.4%; n-hexanol, 23.0%; 1-chlorohexane, 27.8%; hexachloroethane, 6.80 mmole.

Table IX shows that at 0°, tri-2-hexylborane in carbon tetrachloride solution was incompletely oxidised in 24 hours, while at 78° (refluxing CCl_4) the reaction was very fast and the amount of alkyl chloride obtained tended to decrease slightly after 1.0 hr. An oxidation was therefore carried out at 25°, and analysed for products after 2.0 hr. and 24.0 hr. The reaction was found to be substantially complete within 2.0 hr. n-Hexane, and the isomeric alkyl chlorides, were produced in a slightly higher yield than that obtained from the primary organoborane, while the yield of olefins, and dimeric hydrocarbons was similar, and the two isomeric alcohols were produced in an overall yield smaller than that obtained from tri-n-hexylborane.

Thexyldi-n-hexylborane

The neutral hydrogen peroxide oxidation of thexyldi-n-hexylborane gave a series of products (Table X) in yields similar to those obtained from the tri-2-hexylborane oxidations. The yields of oxidation products

Table IX

The Reaction of Aqueous Hydrogen Peroxide (30% w/v.) with Tri-2-hexylborane in T.H.F. and Carbon Tetrachloride Solution (0.5 M.).

Temperature °C	Time (hr.)	Hydrogen Peroxide (mmole)	Tri-2-hexylborane (mmole)	C_2Cl_6 (mmole)	Percentage Yields of Products[a]						Solvent
					n-Hexane	Hex-1-ene	Hex-2-ene	Isomeric Dodecanes	Hexan-2-ol & Hexan-3-ol	2-Chloro-hexane & 3-Chloro-hexane	
0	2	26.4	13.01		30.2	3.6	7.3	12.6	-		T.H.F.
	24				31.7	2.72	6.4	12.6	24.4		
	(OOH^{θ})								37.0		
0	24	35.2	12.51	1.3						12.3	CCl_4.
78°	1	27.0	12.48							21.5	CCl_4
	3									21.0	
	8			3.41	1.92	<0.1	<0.54	1.5	-	20.5	
25°	2	26.4	13.4		1.99	<0.1	0.92	-	-	-	CCl_4
	24			3.74	4.95	<0.1	0.93	5.62	13.2	33.6	

[a] Percentages based on the amount of C-B bond present initially.

in Table X are expressed as percentagesbased on the amount of the parent alkyl group originally bonded to boron. A measure of the selectivity of the oxidising reagent between the two alkyl groups may therefore be made by direct comparison between the relevant columns of the table. Two samples of the organoborane in T.H.F. solution were oxidised with excess H_2O_2 for 2.0 hr. and 12.0 hr. The results in Table X show that oxidation is essentially complete in 2.0 hr. The two monomeric hydrocarbons, 2,3-dimethylbutane and n-hexane form the main products, followed by the two alcohols, 2,3-dimethylbutan-2-ol and n-hexanol, and a small yield of n-dodecane. Verbrugge found that in the silver nitrate induced coupling reactions of organoboranes, the 1,1,2-trimethylpropyl radical does not readily undergo a coupling reaction.[39] When a sample of thexyldi-n-hexylborane was subjected to silver nitrate coupling conditions three products were obtained in the ratio 1:0.2: 0.2 and the largest component identified as n.-dodecane. G.l.c. comparison between the coupling reaction products from the hydrogen peroxide and the silver nitrate coupling reactions, on several stationary phases, indicated that the two unknown compounds produced in smaller yield in the presence of silver nitrate were not produced during the H_2O_2 oxidation, while n-dodecane was. No evidence was found for the presence of a dimeric hydrocarbon other than n-dodecane, among the neutral oxidation products.

The coupling reactions between two 1,1,2-trimethylpropyl radicals, and between a n-hexyl and a 1,1,2-trimethylpropyl radical, do not therefore appear to take place under neutral H_2O_2 oxidation conditions. Addition of excess alkaline hydrogen peroxide solution to the reaction products at 0° gave an increase in yield of 2,3,-dimethylbutan-2-ol of 5%, and of n-hexanol 15%. From the overall increase in alcohol yield after the alkaline oxidation it is seen that approximately 50% of the organoborane was oxidised to the borate oxidation state during the neutral oxidation.

A preliminary oxidation of thexyldi-n-hexylborane in CCl_4 solution showed that at 0° the production of 1-chlorohexane was very slow (Table X). When the temperature was increased to 25°, the reaction was complete within 12 hours. A subsequent increase in temperature to 50°, however, caused a small decrease in the 1-chlorohexane yield. A second oxidation was therefore carried out during 12.0 hours at 25°, and the mixture analysed for oxidation products (Table X). 2,3-Dimethylbutan-2-ol and n-hexanol were the main products followed by the alkyl halides, 1-chlorohexane and 2,3-dimethyl-2-chlorobutane. Some n-dodecane was produced, but only very small quantities of the two monomeric alkanes.

The change of solvent to CCl_4 therefore causes a change in the pattern of products similar to that found for tri-2-hexylborane, although with the symmetrical borane the proportion of alkyl halide/alcohol produced during the neutral oxidation is larger than for the unsymmetrical borane .

Disiamyl-n-hexylborane

Table XI outlines the conditions used, and the yields of products obtained, when disiamyl-n-hexylborane was oxidised by neutral hydrogen peroxide solution. The yields are expressed as percentages based on each alkyl group (as for thexyldi-n-hexylborane, above). When a sample of disiamyl-n-hexylborane in T.H.F. solution at 25° was oxidised with an excess of aqueous H_2O_2, in a preliminary experiment, it was found that hydrocarbon production was complete within 2 hr. A further sample was therefore oxidised at 25°, and analysed completely for oxidation products after 2 hr., and 24 hr. (Table XI). The highest yield was recorded for n-hexanol, followed by

Table X

The Reaction of Aqueous Hydrogen Peroxide (30% w/v.) with Thexyldi-n-hexylborane in T.H.F., and Carbon Tetrachloride Solution (0.5 M.)

Olefins reacted during preparation (mmoles)		Hydrogen Peroxide (mmoles)	Solvent	Time (hr.)	Temperature °C	C_2Cl_6 (mmoles)	Percentage Yields of Products^a										
Hex-1-ene	2,3-Dimethylbut-2-ene						R^1H^b	$R^1(-H)^b$	RH^c	$R(-H)^c$	R^1R^{1b}	R^1R	RR^c	R^1OH^b	ROH^c	R^1Cl^b	RCl^c
24.5	13.22	26.4	T.H.F.	12.0	25		28.2	<0.1	44.5	0.8	<0.05	<0.05	8.5	-	-		
25.05	13.03	17.6	T.H.F.	2.0	25		31.4	<0.1	42.7	<0.1	-	-	9.9	25.2	30.0		
				$OOH^\ominus$										30.4	46.9		
25.3	13.32	27.6	CCl_4	2.0	0												2.0
				2.0	25												9.0
				13.0	25												34.3
				4.0	50	1.3											32.9
23.90	13.32	28.0	CCl_4	12.0	25	1.56	1.6	<0.1	2.0	<0.1	-	-	4.9	37.2	32.7	19.5	28.3
24.43	13.84	Air	Diglyme (aqueous)	24.0	25		12.7	0.2	15.8	0.6	-	-	2.2	18.1	33.0		
				$OOH^\ominus$										31.4	58.6		
25.0	13.70	Air	Diglyme (dry)	24.0	25		6.7	0.7	8.4	0.3	-	-	0.2	19.1	49.6		
				$OOH^\ominus$										19.7	62.4		

[a] Percentages calculated from amount of R^1-B, or R-B bond present initially.

[b] R^1 = 1,1,2-trimethylpropyl (or thexyl) group

[c] R = n-hexyl group.

2-methylbutane and 2,3,4,5-tetramethylhexane. Smaller yields of 2-methylbutan-3-ol, 2-methylbut-2-ene, and n-hexane were also obtained. The yields of hex-1-ene, and of 2,3-dimethylnonane, and n-dodecane (the other two products obtainable from a possible coupling reaction between the n-hexyl, and the 1,2,-dimethylpropyl, radicals) were very small. The three possible products from combination reactions between the 1,2-dimethylpropyl, and n-hexyl-, radicals therefore were all produced. A mixture of disiamyl-n-hexylborane and sodium hydroxide in methanol solution was treated with an excess of aqueous silver nitrate solution. The organic reaction products were isolated and analysed by g.l.c. Table XI also shows a comparison of the peak areas in the gas-liquid chromatogram of the coupled hydrocarbon products from the H_2O_2 oxidation, and from the silver nitrate induced coupling reaction. The peak areas were normalised to 2,3,4,5-tetramethylhexane as 100, for each reaction. The proportion of n-hexyl group participating in the H_2O_2 induced coupling reaction was far smaller than in the silver nitrate induced coupling reaction.

After analysis of the neutral oxidation reaction mixture, the residual C-B bonds were estimated by treating the reaction mixture with an excess of alkaline hydrogen peroxide solution,

Table XI

The Reaction of Aqueous Hydrogen Peroxide (30% w/v.) with Disiamyl-n-hexylborane in T.H.F. and Carbon Tetrachloride Solution (0.5 M).

Olefins used during the preparation (mmoles)		Hydrogen Peroxide (mmoles)	Solvent	Time (hr.)	Temperature °C	C_2Cl_6 (mmoles)	Percentage Yields of Products [a]										
Hex-1-ene	2-Methyl-but-2-ene						$R^1(H)$ [b]	$R^1(-H)$ [b]	RH [c]	$R(-H)$ [c]	R^1R^1 [b]	R^1R	RR [c]	R^1OH [b]	ROH [c]	R^1Cl [b]	RCl [c]
11.45	25.70	26.40	T.H.F.	2.0	25		43.5	8.0	12.2	<0.1							
				4.0			43.5	8.0	12.2	<0.1							
				12.0			42.8	8.0	12.2	<0.1			<0.3	15.3	57.2		
12.31	25.47	26.15	T.H.F.	3.0	25		37.1	4.0	5.4	1.1	27.0	$0.8/1.65$	0.4	16.3	66.5		
				24.0			37.2	4.0	5.6	1.0	26.9	$0.8/1.68$	0.4	11.5	67.8		
				$HOO^{\ominus}$										14.5	79.2		
12.64	26.10	26.50	CCl_4	24.0	25	3.26	6.5	0.1	0.1	0.1	0.4	$0.15/0.29$	<0.01	22.2	47.1	1.5	3.9
12.00	25.80	Air	Aqueous Diglyme	24.0	25		9.0	0.1	4.0	0.1	<0.5	<0.5	0.5	20.5	21.4		
				$HOO^{\ominus}$										42.0	71.2		
11.49	27.25	Air	Dry Diglyme	24.0	25		14.1	0.9	8.5	0.1	<0.5	<0.5	0.5	15.2	26.2		
				$HOO^{\ominus}$										24.0	67.1		
Silver nitrate induced coupling reaction: normalised g.l.c. peak areas											100	101.5	46.6				
Hydrogen peroxide induced coupling reaction: " " " "											100	10.6	1.5				

[a] Percentages calculated on total amount of each alkyl group present initially.

[b] R' = 1,2-Dimethylpropyl group.

[c] R = n-Hexyl group.

followed by a further g.l.c. analysis for alcohols produced. The increase in yield of 2-methylbutan-3-ol was much smaller than that for n-hexanol (Table XI). Neutral H_2O_2 solution oxidised 40% of the organoborane, therefore, to the borate oxidation state, the remainder being oxidised probably to a boronic acid derivative.

Disiamyl-n-hexylborane in CCl_4 solution at 25° gave a gas-liquid chromatogram which showed the presence only of the solvent, and the organoborane. The formation of oxidation products was not therefore induced by the presence of CCl_4 alone. When excess aqueous H_2O_2 was added, with vigorous magnetic stirring, an induction period of 1.5 hr. was followed by an exothermic reaction. Stirring was continued at 25° for 24 hr. after the addition of the H_2O_2. The reaction mixture was then analysed for oxidation products (Table XI). n-Hexanol was the main product, followed by 3-methylbutan-2-ol. Hexachloroethane was also produced, but only a very small yield of the alkyl halides, 3-chloro-2-methylbutane and 1-chlorohexane. The excess of C_2Cl_6, over the alkyl chlorides produced, showed that not all attack on the solvent was by alkyl radicals leading to the formation of an alkyl chloride, and the trichloromethyl radical. The yields of monomeric, and of coupled hydrocarbons were very much smaller than those from the oxidation in T.H.F. solution.

The Air Autoxidation of Thexyldi-n-hexylborane and Disiamyl-n-hexylborane.

Tables X and XI also include the results obtained when the unsymmetrical organoboranes were autoxidised with an excess of air during 24 hr. Oxidations were carried out both under aqueous, and anhydrous conditions. In a preliminary experiment when air was bubbled slowly through an aqueous tetrahydrofuran (T.H.F.) solution of thexyldi-n-hexylborane (0.5 M.) at ice temperature, a large proportion of the solvent evaporated into the cold trap. Finally the jet of the air bubbler was exposed above the surface of the reaction mixture. When a similar solution of the borane was opened to an oxygen filled gas burette, however, the reaction was very slow in comparison with the oxidation of di-isobutyl-t-butylborane in dry ether solution.[1] Despite vigorous magnetic stirring only 1.5 mmoles of oxygen were absorbed during 24 hr.

The experimental method chosen, therefore, was to pass air slowly through a diglyme solution of the organoborane (0.5 M.), at ice temperature. After 24 hr. the reaction mixture was analysed by g.l.c. As in the oxidation of tri-n-butylborane under similar conditions, a large number of oxidation products were detected in the gas chromatogram.[22] The infra-red spectrum of the mixed products contained a weak absorption at 1705-1725 cm.$^{-1}$, confirming the production of small amounts of ketones and/or aldehydes.

For convenience, the separation and complete identification of the many oxidation products present in small amounts ($<5.0\%$) was not undertaken, only the larger peaks being identified and estimated by g.l.c. in the presence of an internal standard. In addition, those products obtained in the neutral aqueous hydrogen peroxide oxidations were estimated, even though present in a small yield. The C-5 and C-6 hydrocarbons were found to be swept into the cold trap during the autoxidation, and were analysed separately from the contents of the reaction flask. No low boiling hydrocarbons were found to remain in the reaction flask. The combined results from estimation of the cold trap, and the reaction flask are included in Tables X and XI. The quantities shown are expressed as percentage yields, calculated on the amount of the individual alkyl group present in the parent trialkylborane, as for the hydrogen peroxide oxidations.

The C-10 and C-11 hydrocarbons produced during the neutral hydrogen peroxide oxidation of disiamyl-n-hexylborane were detected only among the reaction flask contents after autoxidation, and in yields smaller than 0.5%. The main products of the autoxidations were alcohols rather than hydrocarbons, in contrast with a neutral hydrogen peroxide oxidation.

The use of a diglycerol forerun on the g.l.c. column (see Appendix) allowed the estimation of alcohols both free in solution, and bound as borinate, boronate, or borate esters. A rapid trans-esterification between a borinate, or boronate ester and a hydroxylic g.l.c. stationary phase has been found to occur readily.[54]

The use of this technique allowed an unambiguous estimation of the unoxidised C-B bonds present by the subsequent addition of an excess of alkaline hydrogen peroxide solution to the reaction mixture. The organic component of the reaction mixture after alkaline oxidation was re-analysed for alcohols present by g.l.c. Tables X and XI include the total yields of alcohols present after the final oxidation. The amount of C-B bond unaffected during the autoxidation was obtained from the difference of the alcohol yields in the two tables, and is included in Table XVII. As expected, the extent of carbon to boron bond breaking was smaller in the presence of water, for each of the boranes.[55]

The gas-liquid chromatogram (diglycerol + polyethylene glycol adipate, 125°) also showed the presence of the corresponding alkylhydroperoxides, but as unsatisfactory flattened peaks. Clearly the decomposition temperature of these compounds had been exceeded under the chromatography conditions.[50,56] When the temperature of a short g.l.c. column (3 ft.) was lowered to 95° however, the alkyl hydroperoxides were not eluted. Estimation of the alkyl hydroperoxides was not therefore continued.

The formation of hydrocarbons during the oxidation, rather than during the analysis, was demonstrated by the collection of the lower boiling compounds in the cold trap. In order to demonstrate the presence of free alcohols in the reaction mixture during autoxidation, the air oxidation of a sample of di-t-butyl-n-hexylborane was carried out in aqueous diglyme solution. The relatively volatile alcohol, t-butanol, was then removed from the reaction mixture, under reduced pressure (0°, 0.05 mm.), thus causing minimal chemical change to the organoboron residue.

The results obtained are shown in Table XII. An aliquot of the reaction mixture was withdrawn after autoxidation for 22.0 hr., and evacuated at 0°, 0.05 mm. During the evacuation t-butanol (4.6%, calculated from the amount of t-butyl group originally bound to boron) was displaced from the reaction mixture and collected in a cold trap (-80°). Thus some of the alcohol produced during the autoxidation was present probably as free alcohol, under aqueous conditions. The amount of t-butanol isolated in this way may not reflect the total amount of free alcohol in the reaction mixture, as the presence of organoboron oxidation residues reduces the volatility of any alcohols present (see Part 2, above: n-pentanol (b.p. = 138°) was less volatile than n-dodecane (b.p. = 216°) in the presence of organoborane oxidation products).

An aliquot was also withdrawn, but after only a short oxidation time (3.3 hr.). Here a g.l.c. estimation was made of the alcohols produced, and then the sample was stirred for 0.5 hr. with aqueous sodium hydroxide, as by Davies et al.[1] G.l.c. analysis of the organic layer after hydrolysis showed only a very small increase in alcohol yields. Thus the trans-esterification between the boronate

Table XII

The Autoxidation of Di-t-butyl-n-hexylborane (12.7 mmole) in Diglyme Solution (0.5 M.) at 25°.

	Time (hr.)	t-Butanol[a]	n-Hexanol[a]
Autoxidation	3.30	5.5	0.7
After basic hydrolysis of an aliquot of reaction mixture		5.6	0.9
Alkaline hydrogen peroxide oxidation of the aliquot		75.5	98.3
Autoxidation	22.0	24.1	7.5
Evacuation of an aliquot of reaction mixture		4.6	
Alkaline hydrogen peroxide oxidation		66.0	96.0

[a] Percentages calculated from the total amount of the individual alkyl group initially bonded to boron.

and/or borinate esters and the diglycerol stationary phase during g.l.c. analysis, gave an accurate estimation of alcohols present, whether esterified or free in solution.

When the hydrolysed sample was treated subsequently with an excess of aqueous alkaline hydrogen peroxide, the yield of t-butanol obtained did not account for all of the t-butyl group bound originally to boron. Subtraction of the total yield of t-butanol obtained from the amount of t-butyl group bound originally to boron shows 20% of the available t-butyl group to have been lost, presumably as t-butylhydroperoxide, isobutane, etc. The yield of n-hexanol produced during the alkaline oxidation showed that the n-hexyl group had not been autoxidised significantly.

Discussion

Table XIII summarises the total yield of products obtained from the neutral hydrogen peroxide oxidation of the series of trialkylboranes in T.H.F. and CCl_4 solutions. The total yield of hydrocarbons and alcohols obtained are tabulated separately. For the unsymmetrical boranes, the table makes no distinction between the two different groups present, and an overall yield is given. A clear trend can be seen in the results. Whereas changing from a less substituted to a more substituted borane causes the yield of alcohols to increase markedly, particularly in T.H.F. solution, the overall yield of hydrocarbons changes only slightly, and the yield of dimeric products falls sharply.

In carbon tetrachloride solution, an increase in branching of the alkyl groups led to a larger increase in the proportion of alcohol obtained, than in T.H.F. solution. In CCl_4 solution, however, the overall yield of organic products was reduced. The increase in alcohol yield was most marked for thexyl-di-n-hexylborane and for disiamyl-n-hexylborane. An explanation of the larger yield of alcohol may lie in the low solubility of H_2O_2 in CCl_4 combined with the larger steric requirements of the unsymmetrical trialkylboranes. Under these conditions, only a reactive hydrogen peroxide species would be able to react with the organoborane.

The hydroperoxide ion, proposed by Brown[25] to be the reagent in the quantitative alkaline hydrogen peroxide oxidation of a trialkylborane to boric acid and the corresponding alcohol, would be present only in a low concentration under the conditions of this study. If the normally fast reaction of un-ionised hydrogen peroxide was inhibited by the change to CCl_4 solution, then attack by the more nucleophilic hydroperoxide ion, which only yields alcohol, may become dominant in spite of the low concentration of that reagent.

The composition of the mixture of hydrocarbon products obtained from the oxidation of a more branched borane gives strong support to the suggestion of free radical intermediates in the fast reaction. Table XIII shows that the yield of monomeric hydrocarbons increases rapidly at the expense of dimeric hydrocarbons, as the branching of the alkyl groups increases. Whereas tri-n-hexylborane gave 35.0% of coupled products, and only 13.3% of monomeric products, tri-2-hexylborane gave 12.5% of coupled products, and 40.9% of monomeric hydrocarbons. The reaction of disiamyl-n-hexylborane with hydrogen peroxide gives 19.1% of coupled hydrocarbons, and 29.6% of monomeric hydrocarbons, while thexyldi-n-hexylborane gives 6.6% of coupled hydrocarbons, and 39.5% of monomeric hydrocarbons.

The suggested free radical formation of n-dodecane, during the oxidation of tri-n-hexylborane (Part 2, above), required the coupling reaction between two n-hexyl radicals to be energetically more favourable than hydrogen abstraction from the solvent. A primary alkyl radical has been calculated[26] to have a very low energy of activation for the combination reaction, owing to its small steric requirements. The secondary alkyl radicals as in the hex-2-yl, or 1,2,-dimethylpropyl radicals, has more stringent steric requirements, and thus probably, therefore, a larger activation energy for the coupling reaction. The coupling reaction would therefore be expected to decrease in importance compared with the hydrogen abstraction reaction. This conclusion is supported by the observation both here, and by Verbrugge,[39] that the tertiary alkyl group, as in thexyldi-n-hexylborane, does not undergo a ready coupling reaction. It is very

Table XIII

Overall Percentage Yields of Hydrocarbons (including Alkyl Chlorides), and Alcohols, Produced in the Neutral Aqueous Hydrogen Peroxide Oxidation of Representative Organoboranes at 25

	T.H.F. Solution				CCl_4 Solution			
	Percentage Yield of Hydrocarbons[a]			Alcohols Produced %	Percentage Yield of Hydrocarbons[a]			Alcohols Produced %
	Monomeric	Dimeric	Total		Monomeric	Dimeric	Total	
Tri-n-hexylborane	13.3	35.0	48.3	10.9	28.8	9.6	38.4	23.0
Tri-2-hexylborane	40.9	12.5	53.4	24.4	39.6	5.6	45.2	33.6
Thexyldi-n-hexylborane	39.5	6.6	46.1	27.6	23.2	5.0	28.2	34.9
Disiamyl-n-hexylborane	29.6	19.1	48.7	30.3	6.1	0.9	7.0	34.7

[a] Percentages based on total C-B bond present before oxidation.

probable therefore, that production of the monomeric and dimeric hydrocarbons is the result of competing radical coupling, and hydrogen abstraction reactions.

The bimolecular reaction,[30] suggested earlier as a possible alternative to the free radical mechanism (Part 2, above), would not be expected to lead to hydrogen abstraction products. H.C. Brown has noted that the silver nitrate induced coupling reaction of trialkylboranes in the presence of CCl_4 yields the corresponding alkyl chloride, and some C_2Cl_6, rather than the coupled product.[46b] This result was interpreted as evidence for a free radical mechanism in the silver nitrate coupling reaction.

The reaction of thexyldi-n-hexylborane in T.H.F. solution, induced by aqueous hydrogen peroxide, yields an anomalously large proportion of n-hexane, compared with n-dodecane. With this borane the behaviour of the n-hexyl group is unlike that of the n-hexyl group in tri-n-hexylborane, where the preferred product is n-dodecane. The oxidation of thexyldi-n-hexylborane was not as vigorous as that of the primary borane, however. The low yield of n-dodecane from the tertiary borane may therefore reflect the necessity for a fast reaction, such as the chain mechanism proposed in Scheme 2 above, giving a high concentration of radicals in solution in order to allow a preference for the coupling reaction.

Alternatively, the low yield of coupled hydrocarbons may support the free radical displacement mechanism suggested in Part 2 of this Section. If such a reaction occurs (as in Scheme 5, below),

Scheme 5

$$H_2O_2 + R'BR_2 \xrightarrow{fast} HO\cdot + HOBR_2 + R' \xrightarrow{fast} (HO)_2BR + R'\cdot + R\cdot \qquad \text{5a}$$

$$\xrightarrow{fast} HO\cdot + HOBR'R + R\cdot \xrightarrow{fast} (HO)_2BR + R'\cdot + R\cdot \qquad \text{5b}$$

$$\xrightarrow{fast} (HO)_2BR' + 2R\cdot \qquad \text{5c}$$

R^1 = 1,1,2-trimethylpropyl (or thexyl) group.

R = n-hexyl group.

then reactions (5a) and (5b) might be expected to predominate, owing to the relief of steric compression at the boron atom following the removal of the bulky 1,1,2-trimethylpropyl group (R^1). Both reactions produce two alkyl radicals which are known not to couple readily.[39] Consequently unless reaction (5c) is followed, the n-hexyl radicals must leave the solvent cage before any n-dodecane formation can follow.

The behaviour of thexyldi-n-hexylborane therefore suggests that if the radical displacement mechanism is important, the formation of dimeric hydrocarbons takes place before the radicals leave the proximity of the boron atom, explaining the low yield of n-dodecane. The argument here appears to be in conflict with the results from the oxidation of a mixture of tri-n-pentylborane and tri-n-hexylborane (see Part 2, above), where the statistical distribution of dimeric hydrocarbon products indicated the random presence of n-hexyl and n-pentyl radicals throughout the system.

Only Davies and his co-workers[1] have reported the oxidation of unsymmetrical trialkylboron compounds under conditions which might lead to the observation of some selectivity in the breaking of C-B bonds. They oxidised t-butyldi-isobutylborane slowly at 0°, using 96% H_2O_2 (1.0 mol.), and found that only t-butanol was produced, the isobutyl groups remaining bound to boron. Surprisingly, no yield of monomeric or dimeric hydrocarbons was reported. Similarly, only t-butyl chloride was detected after the selective autoxidation of t-butyldi-isobutylborane in CCl_4 solution.

When the reaction products from the oxidation of disiamyl-n-hexylborane during the present study were treated with an excess of alkaline hydrogen peroxide solution, the increase in yield of 2-methylbutan-3-ol was 3%, and of n-hexanol, 11.4%. Similar treatment of the products from the oxidation of thexyldi-n-hexylborane yielded a further 5.25% of 2,3-dimethylbutan-2-ol, and 16.9% of n-hexanol. In both of these unsymmetrical boranes, however, the neutral hydrogen peroxide oxidation had broken a larger proportion of secondary, or tertiary C-B bond, than of primary C-B bond. The relative yields of the different alcohols obtained during the neutral hydrogen peroxide oxidation however, showed that a larger proportion of primary C-B bond, than of secondary or tertiary C-B bond, had been broken to form alcohols in each of the two unsymmetrical boranes. This result might be interpreted as showing a selectivity in favour of the breaking of a primary C-B bond under neutral oxidation conditions.

The relative rates of the alcohol and hydrocarbon forming reactions however, show that the alcohols are produced largely after the cessation of hydrocarbon production (Part 2, above). Any selectivity during the breaking of C-B bonds to form hydrocarbons is therefore likely to dominate the overall selectivity observed during the neutral oxidation. Thus selectivity of alcohol production during the neutral hydrogen peroxide oxidation may be only a secondary effect.

Table XIV shows the percentage of each alkyl group spent in hydrocarbon, and alkyl halide formation during the neutral hydrogen peroxide oxidation of disiamyl-n-hexylborane, and thexyldi-n-hexylborane in T.H.F. and CCl_4 solutions. The neutral oxidation of disiamyl-n-hexylborane, containing one primary and two secondary alkyl groups, shows an eight fold selectivity in favour of the breaking of the secondary C-B bond, to form hydrocarbons in T.H.F. solution, but only a two fold preference in CCl_4 solution. The selectivity with thexyldi-n-hexylborane, containing a tertiary, and two primary groups bound to boron, appears to be in the reverse direction, breaking a larger proportion of the primary C-B bond in both T.H.F. and CCl_4 solutions. Although a smaller selectivity between the groups in thexyldi-n-hexylborane was noted during oxidations using the alkaline hydrogen peroxide reagent (Section III, above), the selectivity

Table XIV

Percentage of the Primary, Secondary, and Tertiary Alkyl Groups of Disiamyl-n-hexylborane and Thexyldi-n-hexylborane Present as Hydrocarbons and Alkyl Halides after the Neutral Aqueous Hydrogen Peroxide Oxidation.

	Solvent	Primary C-B bonds[a]	Secondary C-B bonds[a]	Tertiary C-B bonds[a]
Disiamyl-n-hexylborane	T.H.F.	8.7	69.0	
	CCl_4	4.4	8.7	
Thexyldi-n-hexylborane	T.H.F.	52.7		31.5
	CCl_4	35.3		21.2

Table XV

Total Percentage Yields of the Organic Products Obtained from the Neutral and Subsequent Alkaline Hydrogen Peroxide Oxidations of Disiamyl-n-hexylborane and Thexyldi-n-hexylborane in T.H.F. Solution.

	Percentage of C-B bond accounted for[a]		
	Primary	Secondary	Tertiary
Disiamyl-n-hexylborane	87.9	83.5	
Thexyldi-n-hexylborane	99.6		61.9

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[a] Percentages based on the amount of primary, secondary or tertiary C-B bond present before oxidation.

(a preference for oxidation of the more substituted groups) was still in the same direction as for disiamyl-n-hexylborane.

Table XV shows the overall percentage of each alkyl group accounted for in the neutral hydrogen peroxide oxidation of the two unsymmetrical trialkylboranes. In T.H.F. solution, the yield of products from the 1,1,2-trimethylpropyl group is 22% lower than that obtained from the other alkyl groups studied. The results from oxidation in CCl_4 solution are not included in Table XV as a final alkaline oxidation was not carried out in this solvent. A subsidiary experiment was made, accordingly, to ensure that any hydrocarbons produced during the oxidation of the 1,1,2-trimethylpropyl group were stable to oxidation under the reaction conditions.

When a mixture of n-hexane, and 2,3-dimethylbutane under nitrogen, in T.H.F. solution was treated with aqueous hydrogen peroxide (1.0 mol.), g.l.c. analysis showed the amount of the tertiary hydrocarbon present to decrease rapidly. 2,3-Dimethylbutane was therefore unstable under the reaction conditions, and the unexpected selectivity in the oxidation of thexyldi-n-hexylborane is not meaningful. It was not possible to estimate the loss of this product accurately during the organoborane oxidation, but if the proportion of the tertiary group oxidised in thexyldi-n-hexylborane is assumed to be comparable to that of the secondary group in disiamyl-n-hexylborane, then the selectivity of oxidation would indicate a small preference for the oxidation of the tertiary group over the primary group. The overall selectivity in the dealkylation reaction to produce hydrocarbons is probably therefore similar to that found in Section III above, using the aqueous alkaline hydrogen peroxide reagent. Here, also, the 1,2-dimethylpropyl group was removed more selectively than the 1,1,2-trimethylpropyl group, over the n-hexyl group. Similar reasons to those outlined in Section III (from the relief of overall steric strain on removal of the more substituted alkyl group may provide an explanation of the selectivity.

H.C.Brown and co-workers hydroborated mixtures of two olefins of different structure, and treated the resulting mixture of trialkylboranes with the silver nitrate coupling reagent.[39,44,45] They concluded from experiments where an insufficiency of silver nitrate was used, that this reagent broke carbon to boron bonds unselectively, to form an unstable silver alkyl.[45,46] The hydrocarbon products were formed after a homolytic decomposition of the unstable silver alkyl.

The hydroboration and subsequent silver nitrate induced coupling of a 1:1 mixture of pent-1-ene and hex-1-ene, gave C-10, C-11 and C-12 hydrocarbons in a 1.0:2.0:1.0 mixture. The distribution of the primary alkyl groups in the products was therefore controlled by statistical factors only. A similar distribution of hydrocarbon products was found in the hydrogen peroxide oxidation of a similar mixture of boranes in the present study (Part 2, above). When a 1:1 mixture of hex-1-ene, and 2-methylbut-2-ene was hydroborated, and then treated with an excess of the coupling reagent, however, the yield of the C-11 hydrocarbon was smaller than that predicted on a statistical basis.[45]

In the present work, the products of a coupling reaction of the 1,1,2-trimethylpropyl group, either with a similar group, or with the n-hexyl group, could not be detected. In the case of the 1,2-dimethylpropyl, and n-hexyl groups, the molar ratio of products obtained was 66.4: 7.85: 1.0, for the C-10, C-11, and C-12 hydrocarbons, respectively. Reference to Brown's work[45] allows the completion of Table XVI which relates the yields of coupled products to the ratio of alkyl groups involved in hydrocarbon formation.

Table XVI

The Normalised Yields of C-10, C-11, and C-12 Hydrocarbons Obtained from the Coupling Reaction between Varying Proportions of the n-Hexyl- and 1,2-Dimethylpropyl Groups.

Ratio of alkyl groups reacted: 1,2-Dimethylpropyl/n-Hexyl	Normalised Yields of the Coupled Hydrocarbons		
	C-10[b]	C-11[c]	C-12[d]
7.94/1	66.4	78.5	1.00
1.00/1[a]	0.45	1.02	1.00
0.33/1[a]	0.07	0.36	1.00

[a] H.C.Brown, C.Verbrugge, and C.H.Snyder, J.Amer.Chem.Soc. 1961, 83, 1001.

[b] 2,3,4,5-Tetramethylhexane.

[c] 2,3-Dimethylnonane.

[d] n-Dodecane.

Normalisation of the amount of n-hexyl group engaged in coupling to 1.00, and of the C-12 product yields to 1.00 in Brown's work shows a simple numerical relationship between the proportion of 1,2-dimethylpropyl group present and the yield obtained of the C-11 hydrocarbon.

The normalised yield of the C-11 hydrocarbon and the proportion of 1,2-dimethylpropyl group engaged in the coupling reaction in the present study show a similar relationship (Table XVI), suggesting that the two alkyl radicals have a similar aptitude for unsymmetrical coupling when produced by either reagent, and in spite of a difference in solvent. The further implication is that any side reactions of the radicals are similar under the experimental conditions of each study, and that the observed proportions of the primary and secondary alkyl groups present in the dimeric hydrocarbons therefore represent a 7.94 fold preference for the release of a 1,2-dimethylpropyl radical over a n-hexyl radical during the reaction with neutral hydrogen peroxide.

The overall yield of products attributable to free radical intermediates, rather than the ionic intermediates as discussed by Traylor,[48] and Kuivila,[40-43] indicates a clear selectivity towards oxidation of the more branched alkyl group. Allowing for the loss of some 1,1,2-trimethylpropyl group through possible hydroperoxide, etc., formation, the selectivity of removal of the secondary or tertiary, over the primary alkyl group in an unsymmetrical borane is comparable to that found in Section III: The Selective Oxidation of Unsymmetrical Trialkylboranes using Alkaline Hydrogen Peroxide. Owing to the steric, etc., requirements of the subsequent free radical combination reaction in T.H.F. solution, the yield of coupled hydrocarbons was lower than that obtained from the neutral oxidation of tri-n-hexylborane. Each of the unsymmetrical boranes gave a larger yield of the products of hydrogen abstraction from the solvent.

Sharefkin and Banks [24a] treated a trialkylborane with diethyl-N-chloroamine and obtained a 35% yield of the corresponding alkyl chloride. Piperidine was found to catalyse the reaction. A relationship with the present study lies in the formation of approximately 1.0 mole of alkyl chloride from 1.0 mole of the borane. Basic catalysis of the chloro-amine dealkylation suggests a non-free radical reaction whereas the reaction in carbon tetrachloride solution shows the characteristics of a free radical reaction, including an induction period before reaction, and the production of C_2Cl_6.[24b,34] In carbon tetrachloride solution an increase in branching of the trialkylborane caused an increase in the proportion of alcohol formed during the hydrogen peroxide oxidation at the expense of hydrocarbon and alkyl halide production. Thus very little alkyl chloride is produced during the oxidation of disiamyl-n-hexylborane. The selectivity observed with this borane, and with thexyldi-n-hexylborane, however, indicates a reverse in the selectivity between the alkyl groups. The yield of the primary alkyl chloride is higher in each case, and may reflect the greater difficulty of solvent attack by the more substituted free radical.

The promise of the reaction of hydrogen peroxide with tri-n-hexylborane to produce n-dodecane, or 1-chlorohexane, was not therefore fulfilled when an attempt was made to extend the reaction to non-primary trialkylboranes. The coupled hydrocarbon products obtained from the unsymmetrical boranes showed considerable selectivity, however, between the breaking of secondary and primary carbon to boron bonds.

The Autoxidation of Thexyldi-n-hexylborane and Disiamyl-n-hexylborane

Davies examined the air oxidation of di-isobutyl-t-butylborane in dry ether solution using varying amounts of molecular oxygen.[1] Peroxyoctanoic acid was then added to the resulting organoperoxyborane which, after subsequent hydrolysis, yielded a mixture of alcohols and alkylhydroperoxides. The yields of t-butylhydroperoxide and isobutylhydroperoxide indicated ~~tha~~t the selectivity to oxidation between the alkyl groups to be 4.5:1 in favour of oxidation of the t-butyl group (during the uptake of the first mole of oxygen).

Although di-isobutyl-t-butylborane contains one tertiary and two primary alkyl groups bound to boron the boron atom is strongly hindered owing to the presence of twoα- and twoβ- alkyl substituents relative to the boron atom. The steric hindrance at the boron atom is therefore comparable to that in the two unsymmetrical trialkylboranes examined in the present study. A similarity between the autoxidation products of disiamyl-n-hexylborane and thexyldi-n-hexylborane and the autoxidation products of di-isobutyl-t-butylborane should therefore distinguish the established autoxidation mechanism for a trialkylborane (as exemplified by the behaviour of the latter borane) from the neutral hydrogen peroxide reaction mechanism.

The oxidation of a tri-n-alkylborane in the presence of water proceeds readily to oxidise one boron to carbon bond, yielding an alkylperoxyborinate, while under anhydrous conditions a dialkylperoxyboronate is obtained.[55] Addition of an excess of oxygen should not consequently prevent the observation of selectivity through the complete dealkylation of the borane, particularly in the presence of water.

As far as possible, therefore, experimental conditions were chosen to allow a comparison of the results obtained both with those of Davies,[1] and with those in the present study using the aqueous hydrogen peroxide reagent.

The results in Tables X and XI show that the distribution of products obtained from the autoxidation of disiamyl-n-hexylborane and thexyldi-n-hexylborane is widely different from the corresponding oxidation by neutral hydrogen peroxide solution. Thus the production of alcohols occurs in preference to hydrocarbons. The behaviour of the two unsymmetrical boranes therefore parallels that of tri-n-hexylborane during autoxidation under similar conditions (Section IV, Part 2, above).

Treatment of the autoxidation reaction mixtures with an excess of alkaline aqueous hydrogen peroxide allowed the calculation of the overall amount of carbon to boron bond broken during the reaction with oxygen (Table XVII).

During the autoxidation of disiamyl-n-hexylborane in aqueous diglyme, approximately one equivalent of boron to carbon bond remained unaffected, while under anhydrous conditions only 66% of one equivalent of alkyl group remained bound to boron. The autoxidation of thexyldi-n-hexylborane in aqueous diglyme left 66% of one equivalent of C-B bond unoxidised while less than 33% of one equivalent of C-B bond was unoxidised under anhydrous conditions. In both aqueous and dry solutions, therefore, the oxidation continued beyond the predicted extent (i.e. one C-B bond oxidised in the presence of water, and two C-B bonds oxidised under anhydrous conditions).[55]

The large extent of the autoxidation in aqueous solution would be expected to reduce the overall selectivity of carbon to boron bond breaking. Table XVII also includes the quotients of the amounts of the individual alkyl groups oxidised during autoxidation in each of the

Table XVII

The Autoxidation of Solutions (0.5M.) of Disiamyl-n-hexylborane and Thexyldi--n-hexylborane. The Overall Amount of Carbon-Boron Bond Broken During 24 hr.

	Disiamyl-n-hexylborane				Thexyldi-n-hexylborane			
	Aqueous Diglyme		Anhydrous Diglyme		Aqueous Diglyme		Anhydrous Diglyme	
	R-[b]	R'--[c]	R-	R'-	R-[b]	R''-[d]	R-	R''-
Percentage C-B bond broken[a]	50.2	78.5	59.1	90.6	74.4	86.7	86.2	99.4
R'-/R-, R''-/R	1.56		1.53		1.17		1.15	

TABLE XVIII

The Autoxidation of Disiamyl-n-hexylborane and Thexyldi-n-hexylborane. The Production of Alcohols during Autoxidation for 24 hr.

	Disiamyl-n-hexylborane				Thexyldi-n-hexylborane			
	Aqueous Diglyme		Anhydrous Diglyme		Aqueous Diglyme		Anhydrous Diglyme	
Yields:	ROH[b]	R'OH[c]	ROH	R'OH	ROH[b]	R''OH[d]	ROH	R'' OH
1) mmole	2.6	5.3	3.0	4.2	8.1	2.5	12.4	2.6
2) Percentage[a]	21.4	20.5	26.2	15.2	33.0	18.1	49.6	19.1
ROH/R'OH, ROH/R''OH calculated from:								
1) mmole	0.8		0.7		3.2		4.7	
2) Percentage[a]	1.0		1.7		1.8		2.6	

a Percentages calculated from initial amount of C-B bond

b R = n-hexyl

c R' = 1,2-dimethylpropyl

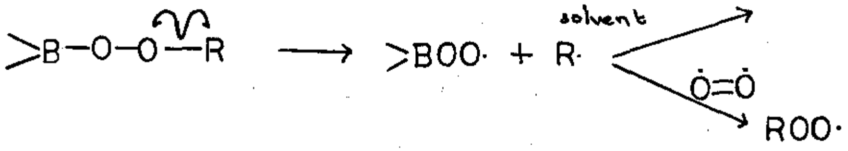
d R'' = 1,1,2-trimethylpropyl.

four experiments (estimated by analysis of the residual C-B bonds). The selectivity of oxidation is small during each experiment and favours the oxidation of the secondary or tertiary carbon to boron bond over the primary carbon to boron bond. Further, the change from aqueous to dry reaction conditions causes a very small change in selectivity in spite of a change in the extent of reaction. It is possible therefore that the large extent of the aqueous autoxidations may not cause a very large change in the observed selectivity of boron to carbon bond breaking.

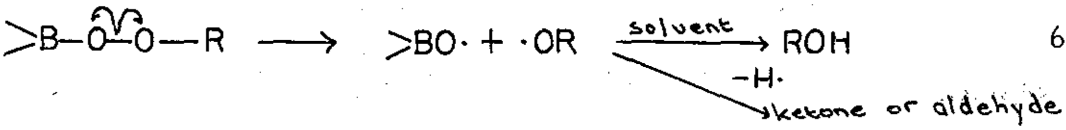
The selectivity and mechanism of formation of the hydrocarbon and alcohol products is conveniently discussed separately.

Alkane Production With both disiamyl-n-hexylborane and thexyldi-n-hexylborane the yields of alkanes obtained are small in comparison with the yields obtained during an oxidation using neutral aqueous hydrogen peroxide. In particular the proportion of dimeric hydrocarbons to monomeric hydrocarbons is small. With hydrogen peroxide the production of hydrocarbons is fast, leading to a large proportion of the coupled hydrocarbon (subject to the steric requirements of the alkyl radical). The smaller proportions of the coupled hydrocarbons obtained under autoxidation conditions suggests that the concentration of alkyl radicals in solution at any given time is very low. The abstraction of a hydrogen atom from the solvent would then be expected to be favoured in comparison with a radical combination reaction.

The formation of monomeric and dimeric hydrocarbons, and also of carbonyl compounds has been explained in terms of a slow free radical fission of the alkylperoxyboron group.[22] The hydrocarbons would arise from an alkyl-oxygen bond fission (Scheme 6a). The carbonyl compounds and some alcohols would result from reactions of the alkoxy radical produced by fission of the oxygen-oxygen bond of the peroxide group (Scheme 6b). In addition the breakdown of an alkylhydroperoxide, formed by hydrolysis of the organoperoxyborane, could account for the products identified. This possibility is not favoured however as the presence of water has a small effect on the

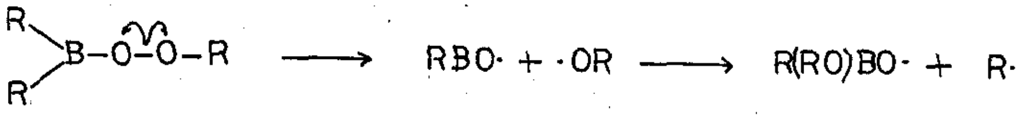


6a



6b

6c



yields of alkanes obtained. Also, the change in alkane yields is irregular, a larger yield being obtained with disiamyl-n-hexylborane in the presence of water, whereas the reverse is the case with thexyldi-n-hexylborane.

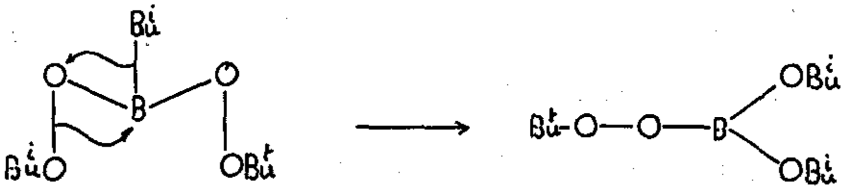
Prediction of the relative yields of n-hexane and the two branched chain monomeric hydrocarbons (2-methylbutane or 2,3-dimethylbutane) is difficult owing to the possibility of more than one subsequent reaction of the intermediate free radicals as shown in Scheme 6a, above. With disiamyl-n-hexylborane , 2-methylbutane is formed in higher yield than n-hexane, while with thexyldi-n-hexylborane, n-hexane is formed in higher yield than 2,3-dimethylbutane. Thus the relative ease of alkyl-oxygen bond fission (Scheme 6a), which should be related to the relative stability of the alkyl radicals formed (tertiary>secondary>primary), does not satisfactorily explain the relative yields of hydrocarbons obtained.

The observed yields are more readily explained on the basis of a free-radical displacement reaction analogous to the two-step reaction proposed for the neutral hydrogen peroxide oxidation of a trialkylborane (Section IV, Part 2, above: Reaction Scheme 4). The second step is a displacement reaction between a hydroxyl radical and an alkyl group bound to boron. The homolytic oxygen-oxygen bond fission proposed to account for carbonyl compound production gives a similar intermediate.[22] Here, therefore, attack of the alkoxy radical at boron could result in the displacement of an alkyl radical, as in Scheme 6c. The net energy difference between the two processes is the breaking of a C-O bond (+ 90 kcal.), as against the breaking of a C-B bond (+ 90 kcal.), and an O-O bond (+ 35 kcal.) together with the formation of a B-O bond (-150 kcal.), a total of -25 kcal. Energetically therefore, the displacement reaction should be preferred.

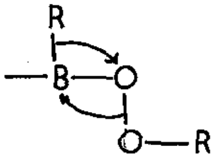
Further the known migratory aptitudes of tertiary, secondary, and primary alkyl groups at boron under autoxidation conditions suggest that the tertiary alkyl group in thexyldi-n-hexylborane will be oxidised in preference to the n-hexyl group. Thus the O-O bond fission of the thexylperoxyboron group would lead to the displacement of a n-hexyl radical, accounting for the observed excess of n-hexane over 2,3-dimethylbutane.

Similar arguments suggest that whereas a smaller preference for the peroxidation of the 1,2-dimethylpropyl (over the n-hexyl) group may apply with disiamyl-n-hexylborane, the subsequent displacement step could produce a free radical at either a primary or secondary carbon atom. On the basis both of the relative stability of alkyl radicals,[36] and of secondary and primary carbon to boron bonds,[33] the latter process is energetically the more favourable. Thus whereas peroxidation of the n-hexyl group must produce the 1,2-dimethylpropyl radical in any subsequent displacement mechanism, peroxidation of the 1,2-dimethylpropyl group should also favour the displacement of this group. The observed excess of 2-methylbutane over n-hexane corresponds with such a process.

Alcohol Production. Two alternative mechanisms have been suggested previously to explain the production of alcohols from an organoperoxyborane. The decomposition of a very dilute ether solution of isobutylisobutylperoxy-t-butylperoxyborane (0.05M.) was explained by a redox mechanism (Scheme 7a) of the generalised type shown in 7b.

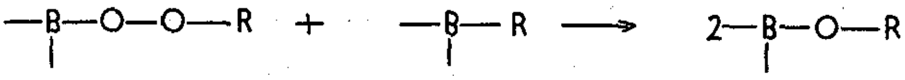


7a



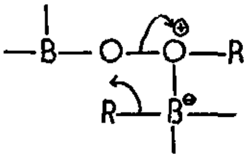
7b

The isobutylperoxy group was reduced more readily than the t-butylperoxy group. The high dilution was thought to favour the intramolecular mechanism proposed. The autoxidation of tri-n-butylborane in much stronger solution (0.5M.) gave the production of n-butanol.[22] Here also the redox rearrangement of an intermediate alkylperoxyboron group was suggested, but as an intermolecular reaction (as in scheme 8a), probably through an intermediate such as 8b.[22,57]



$$-\underset{|}{B}-O-O-R \;+\; -\underset{|}{B}-R \longrightarrow 2-\underset{|}{B}-O-R$$

8a



8b

In the present study an intermolecular redox reaction might be favoured by the high molarity of the organoborane solution (0.5M.). Equally, however, an intramolecular process might be favoured owing to steric hindrance to the approach between the two highly substituted organoboron molecules, The two mechanisms are closely related through the energetically favourable breaking of a C-B bond with concurrent formation of an O-B bond (-54 kcal. overall, approximately).[60] A similarity can be seen also to the oxidative formation of hydrocarbons both in the aqueous hydrogen peroxide reaction (by the two-step free radical displacement mechanism, Scheme 4, above) and the present autoxidation reaction. The main difference from the latter mechanism is that in the alcohol-producing O - O bond fission, the alkoxy group migrates with an electron pair, rather than through a homolytic O - O bond fission. Table XVIII contains a summary of the yields of alcohols obtained during the autoxidations, and also the relative proportions of the two alcohols.

The proportions of the alcohols obtained during the autoxidation of disiamyl-n-hexylborane and thexyldi-n-hexylborane may be explained satisfactorily by either an inter - or intra - molecular rearrangement of the intermediate mono- and diperoxyboranes. Each of the two rearrangement mechanisms suggests several possible intermediates which could allow the formation of the observed yields of the alcohols. In particular the intermolecular rearrangement could allow reaction between a molecule of organoperoxyborane and either an unoxidised organoborane molecule or another peroxyborane molecule depending on the relative rates of the initial autoxidation and the subsequent rearrangement of the organoperoxyborane. A detailed discussion of the alternative reaction paths available is not justified by the present result however, and would require further experiments.

The present results are quite different from those obtained by a neutral aqueous hydrogen peroxide oxidation. Thus the established mechanisms for the air autoxidation of a trialkylborane do not satisfactorily explain the results from a neutral hydrogen peroxide oxidation, and alternative mechanisms similar to the possibilities outlined earlier (Reaction Schemes 2, 3, and 4) provide a more reasonable explanation of the products obtained.

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EXPERIMENTAL SECTION

Purification of Solvents and Olefins used during Hydroborations

Diglyme (diethylene glycol dimethyl ether) and T.H.F. (tetrahydrofuran) were supplied by B.D.H. Ltd. The solvents were refluxed, and then distilled, from sodium wire. Diglyme was then redistilled under reduced pressure (nitrogen) from lithium aluminium hydride (45°-distillation flask /2 mm.). Tetrahydrofuran was redistilled (65°) from lithium aluminium hydride under nitrogen at atmospheric pressure.

The olefins used were supplied by Koch-Light Ltd., and were redistilled at atmospheric pressure (nitrogen) from calcium hydride before use. A central boiling fraction of the olefin was retained for use. The purified olefin was stored over a single lump of calcium hydride. 2,3-Dimethylbut-2-ene, and 2-methylbut-2-ene were prepared as described below, and purified before use as above. A further sample of 2-methylbut-2-ene was supplied by Phillips Hydrocarbons Ltd., and redistilled from calcium hydride before use.

2,3-Dimethylbut-2-ene was prepared by the method of Schurman and Boord[1a] through the reaction of isopropyl magnesium bromide with acetone in ether solution. The resulting dimethylisopropylcarbinol was dried, redistilled, and then dehydrated by a slow distillation from anhydrous oxalic acid. The isomeric olefins, 2,3-dimethylbut-2-ene (b.p. 72°/747 mm.) and 2,3-dimethylbut-1-ene (56°/750 mm.)

were obtained in a molar ratio of 2·70:1, respectively (estimation by g.l.c. as described in the Appendix). Partial separation, yielding a 9·4:1 (molar) mixture, was achieved by fractionation through a 1 metre screw helix column supplied by Todd Scientific Corp. The residual terminal olefin was then removed completely from the mixture by a selective hydroboration using diborane (generated internally[2] by the reaction of boron trifluoride diglymate with sodium borohydride in diglyme solution at 0°). Diborane was generated in a 15% (mole) excess of B-H bond over the terminal olefin present. After stirring overnight at ice temperature 2,3-dimethylbut-2-ene was removed under reduced pressure (at 0°) and collected in a cooled receiver (-80°). The purified 2,3-dimethylbut-2-ene was then redistilled (b.p. 72°/747 mm.) from calcium hydride and estimated by g.l.c. (at least 97% pure).

Dimethylethylcarbinol was prepared and purified by the same procedure but using ethylmagnesium bromide and acetone.[1b] The carbinol (60·0 ml.) was then dehydrated by refluxing with concentrated sulphuric acid (5·0 ml.) under a vacuum jacketed 12 inch fractionating column. The fraction boiling 30-45° was collected. The isomeric pentenes were purified by washing with aqueous calcium chloride, water, and then dried over potassium carbonate before distillation from calcium hydride. 2-Methylbut-1-ene (b.p. 34·0°/750 mm.) and

2-methylbut-2-ene (b.p.38·4°/750 mm.) were obtained in a molar ratio of 1:4·9 (by g.l.c.). The isomeric olefins had closely similar boiling points and were therefore not fractionated. Purification of the 2-methylbut-2-ene was therefore carried out using the hydroboration technique as described for 2,3-dimethylbut-2-ene, above. Diborane was generated internally at 0° in the presence of the pentene mixture (20·0 g.) to give a 15% (mole) excess of B-H bond over 2-methylbut-1-ene present. After 24 hrs. at 0°, unreacted olefin was removed from the mixture under reduced pressure as described above. G.l.c. analysis showed the 2-methylbut-2-ene 13·5 g., 81% yield) to have been obtained in at least 97% purity.

Reagents

Sodium borohydride (98%) was supplied by B.D.H. Ltd., and used without further purification. Boron trifluoride etherate (from the same supplier) was redistilled under nitrogen from calcium hydride at reduced pressure (60°-distillation flask/14 mm.) and stored in the dark.

A stock solution of diborane in T.H.F. solution was prepared by the method of Brown,[3] and stored at -8°. Boron trifluoride diglymate was prepared by removing diethyl ether under reduced pressure from a magnatically stirred mixture of boron trifluoride etherate, and excess diglyme at 0°. Sodium borohydride in diglyme solution (1·0 M.) was then added at 0°, in the proportions appropriate to the following stoichiometry:

$$3NaBH_4 + 4BF_3 \longrightarrow 2B_2H_6 + 3NaBF_4$$

Diborane generated was passed in a stream of dry, oxygen-free nitrogen through a sodium borohydride/diglyme scrubbing tube, and then through a sintered glass bubbler into T.H.F. in the absorption flask at 0°. A typical generation produced 125 ml. of borane:T.H.F. solution (1·9-2·3 M). The solution was estimated by the hydrolysis of a 10 ml. aliquot using ethylene glycol/water (50% v/v). Hydrogen evolved was measured by a rotating vane gas meter (supplied by Gallenkamp Ltd.).

The Preparation of Disiamylborane

A solution of borane in tetrahydrofuran (8·0 ml., 1·62 M.) at 0° was introduced by means of a dried all-glass syringe into a two-necked 50 ml. flask via a wired Suba-Seal rubber cap. The flask was equipped with a magnetic stirrer and a thermometer well, and a small static head of dry nitrogen was maintained above the solution. Dry T.H.F. (10·0 ml.) was added from a syringe, and then the solution was cooled to -15° with stirring. 2-Methylbut-2-ene in tetrahydrofuran solution (4·40 ml., 6·0 M.) at 0° was then added slowly from a dried all-glass syringe. The flask was brought to ice temperature and the magnetic stirring continued at 0° for a further 8 hrs. The solution was estimated for hydride present by the hydrolysis of a 1·0 ml. aliquot under a gas burette.

SECTION I

The Reaction of Disiamylborane with Enol Acetates

Isopropenyl acetate was supplied by Eastman Organic Chemicals. The ketone enol acetates were prepared by the method of Hagemayer and House;[4], the aldehyde enol acetates and enol pivalates were prepared by the method of Semmler and Bedoukian.[5] All esters were fractionated until at least 97% pure by g.l.c. Since they were mixtures of isomers, physical constants are not quoted. The pairs of isomers in Table XI were separated by preparative g.l.c. as described in the Appendix. The i.r. and p.m.r. spectra were in accord with expectation. The relevant portions serving to differentiate the cis- and trans-isomers are listed in the Table. The C-H out of plane deformation of the cis-acetates and -pivalates (746-750 cm.$^{-1}$) is slightly higher than the corresponding absorption (733 cm.$^{-1}$) reported for cis-but-1-enyl butyl ether.[6] The same absorption of the trans-acetate correlates exactly with the rather low frequency (933 cm.$^{-1}$) reported for the trans ether. These figures, together with the J values of Table XI and the consistently shorter retention times (g.l.c.) of the cis-acetates, leave no doubt as to the correct identification of each isomer.

Table XII

Spectral Data of Enol Acetates and Enol Pivalates

Compound	n_D^{21}		Spectral data (i.r. in CS_2; p.m.r. in CCl_4)
cis-1-Acetoxy-but-1-ene	1·4170	I.r.	3101w*, 3057w*, 1671m, 1220vs, 1044s, 750m
		P.m.r.	C_1-H: Doublet ($J = 6·5$ c./sec.) at 2·93τ; partially resolved triplet structure, $J \sim 1$ c./sec. C_2-H: Two superimposed triplets giving four lines at 5·11τ; $J = 7$ c./sec.
trans-1-Acetoxy-but-1-ene	1·4193	I.r.	3081w*, 3027w*, 1675m, 1220vs, 1104s, 930m
		P.m.r.	C_1-H: Doublet ($J = 12·5$ c./sec.) at 2·80τ; partially resolved triplet structure, $J \sim 1$ c./sec. C_2-H: Two superimposed triplets giving five lines at 4·58τ; $J = 12·5$ and 7 c./sec.

cis-1-Acetoxyhex-1-ene	1·4269	I.r.	3103w*, 3059w*, 1672m, 1220vs, 1044s, 750m
		P.m.r.	C_1-H: Doublet (J = 7 c./sec.) at 2·92τ; partially resolved triplet structure, J∼1 c./sec. C_2-H: Two superimposed triplets giving four lines at 5·16τ; J = 7 c./sec.
trans-1-Acetoxyhex-1-ene	1·4292	I.r.	3084w*, 3030w*, 1675m, 1220vs, 1104s, 934m
		P.m.r.	C_1-H: Doublet (J = 12·5 c./sec.) at 2·82τ; partially resolved structure, J∼1 c./sec. C_2-H: Two superimposed triplets giving five lines at 4·60τ; J = 12·5 and 7 c./sec.
cis-1-Acetoxyoct-1-ene	1·4342	I.r.	3100w*, 3056w*, 1671m, 1220vs, 1060s, 749m
		P.m.r.	C_1-H: Doublet (J = 6·5 c./sec.) at 2·92τ; partially resolved triplet structure, J∼1 c./sec.

trans-1-Acetoxy-oct-1-ene	1·4370	I.r.	3080w*, 3024w*, 1647m, 1220vs, 1102s, 931m
		P.m.r.	C_1-H: Doublet (J = 13 c./sec.) at 2·85τ; partially resolved triplet structure, J∼1 c./sec. C_2-H: Two superimposed triplets giving five lines at 4·61τ; J = 12·5 and 7 c./sec.
cis-1-pivaloyloxy-hex-1-ene		I.r.	3105w*, 3060w*, 1670m*, 1280s*, 1150vs*, 750m*
		P.m.r.	C_1-H: Doublet (J = 6·5 c./sec.) at 2·91τ; partially resolved triplet structure, J∼1·5 c./sec. C_2-H: Two superimposed triplets giving four lines at 5·11τ; J = 7·2 c./sec.

trans-1-pivaloyloxy-hex-1-ene		I.r.	3082w*, 3030w*, 1677m*, 1270s*, 1150vs*, 935m*
		P.m.r.	C_1-H: Doublet (J = 12·8 c./sec.) at 2·80τ; partially resolved triplet structure, J∼1 c./sec. C_2-H: Two superimposed triplets giving five lines at 4·58τ (J = 11·3 and 7·0 c./sec.)

*Liquid-film spectrum

On a polyethelene glycol succinate stationary phase the isomeric enol pivalates of hexaldehyde showed similar g.l.c. retention times to the corresponding enol acetates. When n-hexaldehyde (5·0 g., 50 mmoles) and trifluoroacetic anhydride (25·0 g., 120 mmoles) were refluxed together in the presence of potassium trifluoroacetate (1·52 g.), in an attempt to extend the Bedoukian[5] method to the preparation[5] of enol trifluoroacetates, no enol ester formation could be detected in the reaction mixture during 24 hrs. The reaction mixture slowly polymerised.

Reaction of 1-Acetoxyhex-1-ene with an Excess of Disiamylborane

A solution of disiamylborane in tetrahydrofuran (33·0 ml., 45·0 mmoles) at 0° was introduced by means of a dried all-glass syringe into a 50 ml. flask via a wired Suba-Seal rubber cap. The flask was equipped with a magnetic stirrer and a thermometer well, and a small static head of dry nitrogen was maintained over the solution. The flask was cooled to -10°, and 1-acetoxyhex-1-ene (mixed isomers; 1·54 g., 10·9 mmoles) and chlorobenzene (0·39 g.; internal standard) were injected from syringes. The temperature of the solution was allowed to rise to 0°, and samples (2·0 ml.) were withdrawn at intervals, during 24 hrs., by means of a syringe. Half the sample was hydrolysed under a gas burette to estimate residual disiamylborane and the remainder was quenched with dec-1-ene (0.40 ml.). 1-Acetoxyhex-1-ene in the latter was estimated by g.l.c. (polyethylene glycol succinate on firebrick). After 24 hrs. the reaction mixture was hydrolysed with water (2·0 ml.), the volume of the hydrogen evolved being corrected for material taken as samples. The hydrolysed reaction mixture was oxidised at 0° with a mixture of aqueous sodium hydroxide (3N, 20·2 ml.) and hydrogen peroxide (100 vol., 30%, 20·2 ml.). Glycerol (2·0 ml.) was then added, and the whole saturated with sodium chloride. The organic layer was separated, dried over freshly dried magnesium sulphate, and the n-hexanol was estimated by g.l.c. (polyethylene glycol on Teflon).

Reaction of 1-Acetoxyhex-1-ene with an Equivalent Amount of Di-isopinocampheylborane

To a stirred solution of sodium borohydride in diethylene glycol dimethyl ether (1·0M, 10 ml.) and α-pinene (4·25 ml., 26·8 mmoles) at 0° was added boron trifluoride etherate (1·68 ml., 13·4 mmoles) during 5 min., and the mixture was maintained at 0-5° for 4 hr. At the end of this period a mixture of 1-acetoxyhex-1-ene (1·92 g., 13·5 mmoles) and chlorobenzene (0·42 g.; internal standard) was added by syringe. Samples (1·0 ml.) were withdrawn at intervals, quenched with dec-1-ene (0·40 ml.), and estimated for residual ester by g.l.c. Since the reaction mixture was heterogeneous, the residual active hydrogen of the samples could not be estimated. After 24 hr., hydrolysis of the mixture gave 0·25 mmole of hydrogen. At the time of injection the enol ester mixture consisted of cis, 6·2 mmoles and trans, 7·3 mmoles. After 24 hr. the values were cis, 2·7 mmoles and trans, 5·2 mmoles.

Isomerisation of Disiamylborane

A solution of disiamylborane (17·3 mmoles) in tetrahydrofuran (15·0 ml.) was refluxed under an atmosphere of dry oxygen-free nitrogen. Samples (5·0 ml.) were withdrawn at the time shown (Table II) and oxidised with an excess of hydrogen peroxide and 3N-sodium hydroxide. Gl.c. analysis of the salted-out tetrahydrofuran layer gave the results shown in Table II.

Table II

Time (hr.)	0	3	6
3-Methylbutan-2-ol/ 3-Methylbutan-1-ol . .	100/0	83·7/16·3	77·0/23·0

Preparative Scale Reaction of Disiamylborane with 1-Acetoxyhex-1-ene

1-Acetoxyhex-1-ene (27·5 mmoles) was treated with an excess of disiamylborane in T.H.F. solution (65·4 ml., 1·23 M.) under similar conditions to the smaller scale reaction using excess disiamylborane at 0° (see description above). After 24 hr. the reaction mixture was hydrolysed with water and then treated with an excess of aqueous sodium hydroxide (50·0 ml., 3·0 M.), and hydrogen peroxide (50·0 ml., 100 vol.), added synchronously from all-glass syringes. After stirring at ambient temperature for 0·5 hr. the organic component of the reaction products was extracted into ether solution and then washed successively with aqueous glycerol and water, before drying over anhydrous magnesium sulphate. The solution was filtered and the ether removed by distillation. The residue boiling above 36° was transferred to a small distillation apparatus and fractionated through a vacuum jacketed vigreux column yielding 2-methylbutan-3-ol (b.p. 110-112°, 755 mm.) and n-hexanol : 17·65 mmoles, 65% yield (157-158°, 755 mm.). n-Hexanol was identified by preparation of the phenylurethane derivative which had the same melting point (103°)[7] as a sample prepared from authentic n-hexanol (from B.D.H. Ltd.).

<u>The Stability of Chlorobenzene and Mesitylene (Internal Standards) under Reaction Conditions</u>

Chlorobenzene (1·92 g.) was added to a stirred T.H.F. solution of 1-acetoxybut-1-ene (25·0 ml., 1·1 M.) at 0° in the hydroboration apparatus described above. Aliquots were withdrawn at periodic intervals during 24 hr. and estimated by g.l.c. for enol acetate present (Table XIII). A similar experiment was conducted using mesitylene instead of chlorobenzene (Table XIII). The change in amount of enol acetate present as estimated by g.l.c. was within

Table XIII

1-Acetoxybut-1-ene (a. 27·4 mmoles, b. 23·3 mmoles) in T.H.F. solution in the Presence of Chlorobenzene and Mesitylene (Internal Standards)

Internal Standard	Time (hr.)	Enol Acetate Present (mmole)
a) Chlorobenzene	1·3	27·7
	7·2	27·4
	23·8	28·1
b) Mesitylene	2·5	23·4
	22·7	23·3

the experimental error of the g.l.c. measurements (± 3%). The internal standards were therefore acceptable.

The Reaction of Disiamylborane with Cyclohexenyl Acetate

A sample of disiamylborane (30·0 ml., 1·20 M.) was prepared (as described above) and divided into equal portions in two hydroboration flasks at 0°. Cyclohexenyl acetate (0·7 g., 5·0 mmoles) was added to one flask and then both flasks were maintained at ice temperature with periodic estimations (by hydrolysis of an aliquot of reaction mixture) for residual hydride during 27·4 hr. (Table III).

Table III

The Reaction of Cyclohexenyl Acetate with Excess Disiamylborane in T.H.F. Solution at 0°

Time (hr.):-	0	6·0	27·4
Residual Hydride (mmoles)			
Reaction:	19·0	17·2	12·7
Blank:	19·0	18·4	13·3

The Reaction of Disiamylborane with an Excess of Cis-1-Acetoxyhex-1-ene

Cis-1-acetoxyhex-1-ene (1·03 g., 7·23 mmole), obtained by g.l.c. separation of the mixed isomers (95% cis), was added to a hydroboration flask containing a solution of disiamylborane (1·25 mmole, 0·1 M.) and chlorobenzene (0·52 g., internal standard) in tetrahydrofuran solution at 0°. The extent of reaction was estimated by the periodic withdrawal and quenching (with excess hex-1-ene) of an 0·5 ml. aliquot of reaction mixture and subsequent g.l.c. analysis for residual enol ester. The results are shown in Fig. 2, and Table VIII.

Table VIII (Fig. 2)

The Reaction of Disiamylborane (1·25 mmole, 0·1 M.) with cis-1-Acetoxyhex-1-ene (7·23 mmole) in T.H.F. Solution at 0°

Time (hr.):	0	0·7	3·0	5·0	17·0	24·0
Unreacted Enol Acetate,						
Cis isomer (mmoles):	6.90	6·55	5·95	5·80	5·70	5·65
Trans isomer (mmoles):	0·33	0·33	0·33	0·33	-	0·33

Section II

The Protonolysis of Representative Symmetrical and Unsymmetrical Trialkylboranes

Propionic acid, supplied by B.D.H. Ltd., was redistilled before use. The water content was 0·39% w/v (Fischer determination). A sample of the redistilled acid (200 g.) was shaken briefly with phosphoric oxide (10 g.) in a stoppered flask and then filtered after standing for 24 hr. Fractionation of the filtrate through a vacuum jacketed column packed with Towers multi-turn helices yielded propionic acid (160 g.) boiling at 141°/755 mm., and containing 0·04% H_2O w/v (Fischer).

Di-t-butyl-n-hexylborane was prepared by the method of Hennion and McCusker[9]. A solution of t-butyl magnesium chloride in ether solution (prepared from t-butyl chloride (180 g., 1·83 mole) and magnesium turnings (45 g.) was added to boron trifluoride etherate (0·56 mole) and an excess of hex-1-ene (2·30 mole), also in ether solution at 0°. The preparation was carried out under nitrogen. After stirring overnight at room temperature the reaction mixture was hydrolysed with an excess of oxygen-free water and then filtered under nitrogen to remove insoluble magnesium salts. The organic layer was separated, dried over freshly dried magnesium sulphate, and then excess ether removed at room temperature under reduced pressure. The residue was again filtered to remove ether soluble magnesium salts and then fractionated under nitrogen to give a central boiling fraction (90·0 g., 45% yield) at 40-41·5°/0·57x10^{-3}mm.

The main fraction was redistilled under nitrogen (41-42°/0·57x10^{-3}mm.) and then analysed for n-hexyl and t-butyl groups. An aliquot of the redistilled second fraction (5·558 g.) was weighed from an all-glass syringe into a dried hydroboration flask containing 20·0 ml. dry diglyme and n-pentanol (2·22 g., internal standard), under nitrogen at room temperature. An excess of oxidising agent (aqueous sodium hydroxide (10·0 ml., 3·0 N.) and hydrogen peroxide (10·0 ml., 30%, w/v) was added synchronously from syringes to the magnetically stirred organoborane solution during 0·5 hr. Stirring was continued for a further hour and then the organic products extracted into ether solution, dried over anhydrous magnesium sulphate, and analysed by g.l.c. on a polypropylene glycol column. Alcohols obtained were: n-hexanol, 2·593 g. (25·40 mmoles, 96·0% yield), and t-butanol, 3·800 g. (51·40 mmoles, 97·0%). A second estimation gave similar yields of the two alcohols. The chromatogram showed no peak at the retention time expected for isobutanol. The alcohol yields corresponded to a sample of di-t-butyl-n-hexylborane of not less than 96% purity, allowing for a 94-96% yield in the alkaline oxidation.[13]

t-Butyldi-n-hexylborane was prepared from trimethylamine: t-butylborane and hex-1-ene by the method of M. F. Hawthorne.[10]

t-Butylboronic acid was prepared by the partial alkylation at -75° of trimethylborate (55·0 g., 0·53 mole) in ether solution, using t-butyl magnesium chloride (obtained from magnesium turnings (16·8 g., 0·69 mole) and t-butyl chloride (63·0 g., 0·68 mole). The reaction was carried out under nitrogen as described by P. A. McCusker,[11] yielding 27·9 g. of crude t-butyl boronic acid after hydrolysis of the reaction mixture with water, and removal of excess water and ether. The acid was dried overnight in a dessicator over 65% sulphuric acid and then dehydrated without a further purification stage by the azeotropic removal of water from a solution of the acid in benzene (Dean-Stark apparatus).[12] When the theoretical amount of water (4·97 g.) had been collected, the residual benzene was removed by distillation and then the tri-t-butylboroxine was distilled under reduced pressure. The fraction boiling at 88-91°/17 mm. was collected (15·6 g., 55% yield). The p.m.r. spectrum of this fraction showed one peak, a singlet of high intensity, at $9{\cdot}0\tau$. The tri-t-butylboroxine (15·2 g.) was reduced in ether solution[10] by the addition of excess lithium aluminium hydride (6·94 g.) in ether solution in the presence of excess trimethylamine (10·0 g., 27·5 ml.). The reaction mixture was vigorously stirred under a nitrogen atmosphere and retained by an acetone/solid carbon dioxide condenser. After refluxing with stirring for 1 hr. excess hydride was destroyed by the slow addition of 6·5 ml. water. The resulting slurry was filtered and the ether layer dried over magnesium sulphate. The solvent was then removed under reduced pressure.

The crude trimethylamine:t-butylborane was treated with an excess of hex-1-ene at 50°, under nitrogen without further purification.[10] When the evolution of trimethylamine ceased, residual hex-1-ene and trimethylamine were removed under reduced pressure at 0°, and then the residue fractionated under nitrogen at high vacuum. Two fractions were collected after a small fore-run (2·0 ml.). The first, larger fraction (15·0 ml.) was collected at 57-59°/$6{\cdot}4\times10^{-4}$mm., and the second (5·0 ml.) at 59-63°/$6{\cdot}4\times10^{-4}$mm. The p.m.r. spectrum of the larger fraction showed a sharp singlet at 9·1τ (corresponding to the t-butyl group protons) overlapping with a multiplet which had a maximum at 8·7τ (corresponding to the n-hexyl group protons, by comparison with the spectrum of a known sample of tri-n-hexylborane). The overlap of the two signals was too great to allow a quantitative assessment of the integrated spectrum.

The n-hexyl and t-butyl groups were analysed therefore in the same way as for di-t-butyl-n-hexylborane (above). The alkaline oxidation of an aliquot (1·132 g.) of Fraction 2 with an excess of alkaline hydrogen peroxide solution at room temperature yielded n-hexanol (0·925 g., 9·06 mmoles) and t-butanol (0·339 g., 4·58 mmoles). Estimation was by g.l.c. in the presence of n-pentanol (internal standard). Thus Fraction 2 was t-butyldi-n-hexylborane in at least 96% purity, allowing for a 94-96% yield of the alcohols from the alkaline oxidation.

The Reaction of Di-t-butyl-n-hexylborane with Propionic Acid in Diglyme Solution at 50° with Subsequent Alkaline Hydrogen Peroxide Oxidation of the Reaction Mixture

Di-t-butyl-n-hexylborane (2·50 g., 11·90 mmole) was weighed from an all-glass syringe into a dried two-necked 50 ml. flask containing oxygen-free nitrogen, and equipped with a thermometer pocket, magnetic stirrer and rubber Suba-Seal cap. Dry diglyme (20·0 ml.), and 2,3-dimethylbutane (0·637 g., internal standard) were added from syringes at 25°. Dried propionic acid (2·960 g., 40·0 mmoles) was added from a syringe with vigorous magnetic stirring and the flask transferred at once to a constant temperature bath (from Griffin-Grundy Ltd.) at 50°. Aliquots of the reaction mixture (0·5 ml.) were withdrawn by syringe at periodic intervals, and quenched by injection into an excess of aqueous sodium hydroxide (6·0 M.) at 0°. The organic layer of the resulting mixture was analysed for isobutane and n-hexane by g.l.c. on a tricresyl phosphate stationary phase (see Appendix). The results are included in Fig. 7 and in Table VIa. The residue was neutralised (phenolphthalein end-point, external indicator) with aqueous sodium hydroxide. n-Pentanol (1·535 g., internal standard) was added from a syringe, and the mixture was then treated with sodium hydroxide solution (3·0 ml., 3·0 N.) and aqueous hydrogen peroxide (3.0 ml., 30% w/v) added synchronously from syringes during 0·5 hr. to the stirred solution at room temperature. After stirring for a further hour the organic products were separated into ether solution, dried, and estimated by g.l.c., showing: n-hexanol (0·0 g.) and t-butanol (1·29 g., 17·4 mmoles - 88% yield, calculated on the original amount of t-butyl group present).

Table VIa (Fig. 7)

The Reaction of Propionic acid (40·0 mmoles) with Di-t-butyl-n-hexylborane (11·9 mmoles, 0·65 M.) in Diglyme Solution at 50°

Time (hr.)	0·0	0·25	0·85	1·17	2·80	4·75	9·0	18·15
Isobutane (mmoles)	0·01	0·01	0·04	0·04	0·04	0·04	0·04	0·04
n-hexane (mmoles)	0·1	2·8	7·7	8·9	10·9	11·4	11·7	12·0

Table VIb (Fig. 7)

The Reaction of Propionic Acid (40·2 mmoles) with Di-t-butyl-n-hexylborane (13·38 mmoles, 0·65 M.) in Diglyme Solution at 25°

Time (hr.)	0·0	0·66	2·1	4·0	9·0	17·0	20·33	120
Isobutane (mmoles)	0·0	0·01	0·01	0·01	0·01	0·02	0·03	0·03
n-Hexane (mmoles)	0·0	1·6	4·2	6·3	9·6	11·5	12·4	13·2

The Reaction of Propionic Acid with Tri-n-hexylborane in Diglyme Solution at 0°

Boron trifluoride diglymate, prepared from boron trifluoride etherate (1·891 g., 13·31 mmoles) in excess diglyme (10·0 ml.) as described above, was placed in a pressure-equalised dropping funnel connected to a dried, nitrogen-filled hydroboration flask (50·0 ml. volume). The flask contained sodium borohydride solution in diglyme (10·0 ml., 1·0 M.), hex-1-ene (3·025 g., 36·00 mmoles) and 2,3-dimethylbutane (1·678 g., internal standard). The boron trifluoride diglymate was added dropwise during 0·5 hr. to the magnetically stirred solution. After stirring for a further 0·5 hr. the residual hex-1-ene was estimated by g.l.c. analysis of an 0·5 ml. aliquot of reaction mixture. Dried propionic acid (2·845 g., 38·50 mmoles) was then added from a syringe to the solution at 0°, and the production of n-hexane followed by g.l.c. analysis at periodic intervals as described in the previous experiment.

Table VIIa (Fig. 1)

The Reaction of Propionic Acid (38·50 mmoles) with Tri-n-hexylborane (12·0 mmoles, 0·650 M.) in Diglyme Solution at 0°

Time (hr.)	0·0	0·25	0·50	2·50	16·33	26·75	45·75
Hex-1-ene (mmoles)	0·0	0·0	0·0	0·0	0·0	0·0	0·0
n-Hexane (mmoles)	0·0	3·8	3·1	7·1	11·0	14·	15·1

Table VIIb (Fig. 1)

The Reaction of Propionic Acid (145·0 mmoles) with Tri-n-hexylborane (12·20 mmoles, 0·65 M.) in Diglyme Solution at 0°

Time (hr.)	0·0	0·25	0·63	1·92	3·66	7·00	10·05
Hex-1-ene (mmoles)	2·3	2·3	2·4	2·4	2·4	2·4	2·3
n-Hexane (mmoles)	0·0	7·8	10·0	11·5	12·0	12·2	12·7

The Reaction of an Excess of Dried Propionic Acid with Tri-n-hexylborane in T.H.F. Solution at 25°

Borane: T.H.F. solution (4·6 ml., 2·18 M.) was added from a dried all-glass syringe to a solution of 2,3-dimethylbutane (1·499 g., internal standard) in anhydrous T.H.F. (15·0 ml.) in a dried, nitrogen filled 50 ml. hydroboration flask (description above), at 0°. The magnetically stirred solution was cooled to -15°, and hex-1-ene (2·924 g., 34·8 mmoles) added from a syringe. The temperature was allowed to rise to 0°, and stirring continued for a further 1·0 hr. Excess hex-1-ene present was estimated by g.l.c. Propionic acid (14·725 g., 199 mmoles) was added, with stirring, from a syringe and the reaction flask transferred to a constant temperature bath at 25°. Production of n-hexane was estimated periodically by the g.l.c. analysis of an 0·5 ml. aliquot of reaction mixture withdrawn from the reaction mixture and quenched with an excess of aqueous sodium hydroxide as described above.

Table VIIIa (Fig. 2)

The Reaction of Propionic Acid (199 mmoles) with Tri-n-hexylborane (9·60 mmoles, 0·65 M.) in T.H.F. Solution at 25°

Time (hr.)	0·0	0·22	0·40	1·22	17·20	47·0	110·0
Hex-1-ene (mmoles)	6·0	6·16	5·91	5·95	-	5·68	-
n-Hexane (mmoles)	0·0	9·52	9·32	9·48	12·62	15·68	18·77

Table VIIIb (Fig. 2)

The Reaction of Propionic Acid (234 mmoles) with Tri-n-hexylborane (11·30 mmoles, 0·65 M.) in Diglyme Solution at 25°

Time (hr.)	0·00	0·33	1·60	3·30	17·25	42·2	71·9	92·7
Hex-1-ene (mmoles)	0·0	0·0	0·0	0·0	0·0	0·0	0·0	0·0
n-Hexane (mmoles)	0·0	10·5	10·9	11·0	11·2	11·3	11·2	11·6

After addition of 50·0 ml. diglyme:-

Time (hr.)	3·0	9·0	22·5	31·8	70·8	245
Hex-1-ene (mmoles)	0·0	0·0	0·0	0·0	0·0	0·0
n-Hexane (mmoles)	12·2	12·3	11·9	12·0	12·6	14·3

The Reaction of Propionic Acid with Tri-n-hexylborane in Petrol Ether Solution at 25°

Tri-n-hexylborane (12·4 mmoles) in T.H.F. solution was prepared by the reaction of hex-1-ene with borane: T.H.F. solution at ice temperature as described in the previous experiment. Estimation of the borane was by g.l.c. via 2,3-dimethylbutane (0·515 g., internal standard). The Suba-Seal cap on the reaction flask was then greased, wired onto the flask and the solution stirred magnetically at 0°/0·5 mm., until distillation ceased. Volatile materials were collected in a liquid nitrogen cooled receiver. The receiver was warmed to ice temperature and the contents analysed by g.l.c. The reaction flask was then re-filled with dry oxygen-free nitrogen, and 20·0 ml. of petrol ether (100-120° boiling fraction-dried by distillation from sodium) added from a dry syringe. The solution was analysed by g.l.c. of an 0·5 ml. aliquot. No peaks corresponding to hex-1-ene, n-hexane, or 2,3-dimethylbutane could be detected. 2,3-Dimethylbutane (0·7491 g., internal standard) and dried propionic acid (2·849 g., 39·0 mmoles) were added with stirring from dry syringes and the reaction flask transferred to the bath at 25°. The extent of protonolysis was estimated periodically as in the previous experiment.

Table IXa (Fig. 3)

The Reaction of Propionic Acid (39·0 mmoles) with Tri-n-hexylborane (12·4 mmoles, 0·65 M.) in Petrol Ether Solution at 25°

Time (hr.)	0·0	0·0[a]	0·0[b]	0·1	2·3	3·9	5·17	15·87	23·0
Hex-1-ene (mmoles)	1·02	1·03	0·0	0·0	0·0	0·0	0·0	0·0	0·0
n-Hexane (mmoles)	0·0	0·0	0·0	6·23	11·69	12·23	13·02	16·08	17·7

[a] Analysis of the distillation receiver contents.

[b] Analysis of the reaction flask contents after the addition of 20·0 ml. petrol ether.

Table IXb (Fig. 3)

The Reaction of Propionic Acid (39·5 mmoles) with Tri-n-hexylborane (12·00 mmoles, 0·65 M.) in Diglyme Solution at 25°

Time (hr.)	0·0	1·66	16·00	25·00	41·00	64·00	238·0
Hex-1-ene (mmoles)	0·0	0·0	0·0	0·0	0·0	0·0	0·0
n-Hexane (mmoles)	0·0	11·2	15·5	16·8	18·3	21·8	22·4

Table IXc (Fig. 3)

The Reaction of Propionic Acid (31·00 mmoles) with Tri-n-hexylborane (9·86 mmoles, 0·65 M.) in T.H.F. Solution at 25°

Time (hr.)	0·0	0·30	1·5	4·5	8·8	19·8	25·7	43	71·6	98·0
Hex-1-ene (mmoles)	0·7	0·8	0·9	0·9	1·0	1·1	1·1	1·2	1·3	1·3
n-Hexane	0·0	6·4	8·6	9·8	10·1	11·5	12·1	13·1	13·7	13·7

The Reaction of Disiamyl-n-alkylboranes and Thexyldi-n-alkylboranes with Propionic Acid

The procedure, temperatures, and apparatus used for the preparation of the unsymmetrical boranes follow those outlined for tri-n-hexylborane in diglyme solution. Diborane was generated internally by the dropwise addition of boron trifluoride diglymate to a stirred solution of 2-methylbut-2-ene or 2,3-dimethylbut-2-ene and sodium borohydride in diglyme at 0°. The quantities of boron trifluoride etherate and sodium borohydride solution were identical to those in the tri-n-hexylborane preparation.

A small excess (0·1 equivalent) of 2-methylbut-2-ene was present during the preparation of disiamylborane. The reaction mixture was stirred for eight hours at ice temperature, and then cooled to -10° before addition of a small excess of the second olefin (hex-1-ene, hex-2-ene, or oct-1-ene). 2,3-Dimethylpentane (supplied by Koch-Lights, Ltd., and redistilled from calcium hydride before use) was used as internal standard during the disiamyl-n-alkylborane protonolyses. The trialkylborane was estimated by g.l.c. of the excess olefins from the preparation before the addition of propionic acid.

Thexylborane was prepared by a similar procedure to that for disiamylborane. Diborane was generated (quantities as for tri-n-hexylborane) in the presence of 1·05 mol. of 2,3-dimethylbut-2-ene, at 0°. The reaction mixture was stirred at 0° for 3 hr. to complete the formation of thexylborane. Hex-1-ene or oct-1-ene (2·05 mol.) was added by syringe to the solution (cooled to -10°). The reaction mixture was stirred for 3·0 hr. at 0° and then n-pentane (internal standard) added and the excess olefins from the preparation estimated by g.l.c. (Table Xa, Fig. 5). The borane was protonolysed using the procedure outlined above for tri-n-hexylborane in diglyme solution.

Table Xa (Fig. 5)

The Reaction of Propionic Acid (40·10 mmoles) with Thexyldi-n-hexylborane (10·73 mmoles, 0·65 M.) in Diglyme Solution at 25°

Time (hr.)	0·0	0·1	42·0	97·0	163·0	240·0
RH^a (mmoles)	0·3	0·3	0·4	0·3	0·4	0·5
RH^b (mmoles)	0·0	0·4	1·9	4·0	5·8	7·2

Table Xb (Fig. 5)

The Reaction of Propionic Acid (40·2 mmoles) with Thexyldi-n-hexylborane (10·20 mmoles, 0·65 M.) in Petrol Ether Solution at 25°

Time (hr.)	0·0	1·08	3·50	16·3	69·6	95·3	122·7	146·5	170·0	189·0	240·0
RH^a (mmoles)	0·3	0·3	0·3	0·3	0·4	0·4	0·4	0·4	0·4	0·4	0·4
RH^b (mmoles)	0·0	1·2	1·2	1·9	4·4	5·1	6·2	7·0	8·2	9·5	11·5

[a] R = 1,1,2-trimethylpropyl group

[b] R = n-hexyl group

Attempted Distillation of Thexyldi-n-hexylborane

Thexylborane was prepared in T.H.F. solution at 0°, through the reaction of borane: T.H.F. solution (15·0 ml., 2·61 M.) with 2,3-dimethylbut-2-ene (3·207 g., 38·13 mmoles). A small excess of hex-1-ene (6·964 g., 82·70 mmoles) was added after cooling the thexylborane solution to −15°. The temperature was raised to 0° during 1·0 hr. and then held constant for a further 4·0 hr. before the excess olefins from the preparation were removed under reduced pressure (as described above). Excess olefins were: 2,3-dimethylbut-2-ene, 5·6 mmoles; hex-1-ene, 17·8 mmoles. The trialkylborane (32·5 mmoles) was transferred by syringe to a small distillation apparatus and distilled under nitrogen at high vacuum. A small fraction (0·9 g.) distilled at 63°/$1{\cdot}1\times10^{-1}$ mm., and the main fraction (5·6 g.) distilled at 96°/$1{\cdot}0\times10^{-1}$ mm. Oxidation of each aliquot with an excess of alkaline hydrogen peroxide solution produced only n-hexanol. G.l.c. analysis of the contents of the vacuum trap (-80°) showed the presence of 2,3-dimethylbut-2-ene (2·52 g., 30·0 mmoles).

Attempted Preparation of Thexyldi-2-hexylborane

Thexylborane (12·96 mmoles) was prepared in diglyme solution by the internal generation of diborane in the presence of 2,3-dimethylbut-2-ene as described above. Hex-2-ene (2·275 g., 27·0 mmoles) and n-pentane (0·626 g., internal standard) were added to the stirred solution at -10°, and the mixture brought to 0° during 0·5 hr., and then stirred at constant temperature for a further 6·0 hr. An aliquot of reaction mixture was withdrawn, quenched at 0° by the addition of excess hex-1-ene, and analysed by g.l.c. for hex-2-ene, and 2,3-dimethylbut-2-ene. Hex-2-ene unreacted was 14·04 mmoles. The reaction flask temperature was then raised slowly to 25°, and analysed after a further 3·0 hr. for hex-2-ene and 2,3-dimethylbut-2-ene present. Hex-2-ene unreacted was 0·0 mmoles, while 2,3-dimethylbut-2-ene (12·5 mmoles) had been liberated. Clearly a displacement reaction[14] had occurred rather than the formation of thexyldi-2-hexylborane.

Table XIa (Fig. 4)

The Reaction of Dried Propionic Acid (186 mmoles) with Tri-n-hexylborane (11·50 mmoles) in Diglyme Solution at 25°, in the Presence of Sodium Borofluoride (12·3 mmoles)

Time (hr.)	0·0	0·63	1·33	5·50	12·0	24·66	29·0	42·5	100
Hex-1-ene (mmoles)	0·0	0·0	0·0	0·0	0·0	0·0	0·0	0·0	0·0
n-Hexane (mmoles)	0·0	11·5	12·2	15·8	19·2	19·6	21·0	23·6	24·4

Table XIb (Fig. 4)

The Reaction of Dried Propionic Acid (208·0 mmoles) with Tri-n-hexylborane (12·27 mmoles) in Diglyme Solution at 25°

Time (hr.)	0·0	0·20	0·58	1·20	3·33	9·53	72·0	81·0
Hex-1-ene (mmoles)	0·0	0·0	0·0	0·0	0·0	0·0	0·0	0·0
n-Hexane (mmoles)	0·0	12·7	14·1	15·2	18·2	21·8	27·8	27·0

Table XIIa (Fig. 6)

The Reaction of Dried Propionic Acid (39·0 mmoles) with t-Butyldi-n-hexylborane (11·12 mmoles) in Diglyme Solution at 25°

Time (hr.)	0·0	1·38	3·43	5·29	21·5	30·0	55·0	72·8	146·0
Isobutane (mmoles)	0·0	0·0	0·0	0·0	0·1	0·1	0·1	0·1	0·1
n-Hexane (mmoles)	0·0	5·5	9·0	10·1	11·0	12·4	13·4	14·3	16·1

Table XIIb (Fig. 6)

The Reaction of Dried Propionic Acid (40·7 mmoles) with t-Butyldi-n-hexylborane (11·15 mmoles, 0·65 M.) in Diglyme Solution at 50°

Time (hr.)	0·0	0·27	0·62	1·0	3·0	5·4	21·1	29·1	54·0	72·0
Isobutane (mmoles)	0·0	0·0	0·0	0·0	0·1	0·1	0·1	0·1	0·1	0·1
n-Hexane (mmoles)	0·0	7·3	9·7	10·4	12·7	14·0	18·9	19·6	20·8	20·8

Table XIII (Fig. 8)

The Reaction of Thexyldi-n-hexylborane (5·87 mmoles, 0·65 M.) in Diglyme Solution with Propionic Acid (20·6 mmoles) at 25°; Comparison with an Identical Solution of the Borane as Control

	Time (hr.)	Hydrocarbons Present (mmoles)			
		2,3-dimethylbutane	2,3-dimethylbut-2-ene	n-hexane	hex-1-ene
	0·0	0·4	2·2	0·0	2·6
Reaction	96·0	0·8	2·8	2·9	2·5
Blank	96·0	0·5	2·2	0·0	2·4
Reaction	144·0	0·7	3·0	3·2	2·4
Blank	144·0	0·4	2·3	0·0	2·4

Table XIV (Fig. 9)

The Reaction of Thexyldi-n-hexylborane (5·96 mmoles, 0·65 M.) in Diglyme Solution with Propionic Acid (20·6 mmoles) at 50°; Comparison with an Identical Solution of the Borane as Control

	Time (hr.)	Hydrocarbons Present (mmoles)			
		2,3-dimethyl-butane	2,3-dimethyl-but-2-ene	n-hexane	hex-1-ene
	0·0	0·5	2·4	0·0	4·8
Blank	1·5	0·4	4·7	0·0	4·1
Reaction	2·0	0·7	2·6	1·1	4·5
Blank	8·85	0·4	4·9	0·0	4·2
Reaction	9·17	0·6	4·4	2·3	4·3
Blank	24·24	0·4	4·3	0·0	3·5
Reaction	26·25	0·8	3·0	4·7	4·2
Blank	72·00	0·5	4·7	0·0	2·6
Reaction	72·25	0·8	3·6	9·1	5·0
Blank	95·25	0·5	7·6	0·0	2·3
Reaction	95·50	0·9	3·2	10·6	4·7
Blank	143·25	-	7·4	0·0	1·7
Reaction	153·00	1·0	3·8	12·2	4·3

Section III

The Selective Oxidation of Unsymmetrical Trialkylboranes using Alkaline Hydrogen Peroxide Solution

Samples of the unsymmetrical trialkylboranes to be oxidised were prepared in quantities (12-13 mmoles) similar to those in Section II (Experimental) above. t-Butyldi-n-hexylborane and di-t-butyl-n-hexylborane were prepared and purified by the methods described in Section II (Experimental) above. The boranes were introduced by weighing from a syringe into the previously described two-necked hydroboration flask (under nitrogen) and then diluted to the required molarity (0·26 M., or 0·52 M.) by the addition of the necessary amount of dried diglyme. The t-butyl boranes were oxidised in diglyme solution owing to the difficulty of g.l.c. analysis of t-butanol in the presence of T.H.F.

Disiamylborane was prepared in T.H.F. solution by the method described in detail in Section I (Experimental) above. The dialkylborane solution was cooled to -10°, before the addition of hex-1-ene or oct-1-ene to form the trialkylborane. The quantity of trialkylborane prepared was estimated by g.l.c. analysis of the residual olefins from the preparation as described in Section II (Experimental) above (n-pentane, internal standard).

Thexylborane was prepared in T.H.F. solution by the procedure described in Section II (Experimental) above.

The mono-alkylborane was cooled to -10° before the addition of hex-1-ene, or oct-1-ene from a weighed all-glass syringe. The trialkylborane was estimated by g.l.c. analysis of the residual olefins after the preparation (2,3-dimethylbutane, internal standard).

The Reaction of Disiamyl-n-hexylborane in T.H.F. Solution with Successive Aliquots of the Alkaline Oxidising Agent

A solution of disiamyl-n-hexylborane (11·30 mmoles) was prepared and estimated in T.H.F. solution (0·26 M.) at 0°, as described above. n-Pentanol (2·201 g., internal standard) was added from a weighed all-glass syringe. Aqueous sodium hydroxide (0·35 ml., 3 N.) and aqueous hydrogen peroxide (0·35 ml., 34·00% w/v) were introduced synchronously below the surface of the rapidly stirred organoborane from two all-glass syringes. The rate of addition of the oxidising agent was controlled to avoid raising the temperature of the reaction mixture above 2·0°. The addition of an 0·35 ml. aliquot took approximately ten minutes and then an 0·5µl. aliquot was withdrawn with a microlitre syringe (Hamilton Co.) and analysed by g.l.c. (on-column injection; Pye 104 Series Chromatograph, see Appendix). A second aliquot of oxidising agent was then added (during ten minutes) below the surface of the reaction mixture, and a further sample analysed as before. The procedure was repeated until the borane was completely oxidised (Table I, Fig. 4).

Table I (Fig. 1)

The Reaction of Disiamyl-n-hexylborane (11·30 mmoles) in T.H.F. Solution (0·26 M.) with Successive Aliquots (3·50 mmoles) of Aqueous Alkaline Hydrogen Peroxide

Hydrogen Peroxide (mmoles)	3·5	7·0	10·5	14·0	17·5	21·0	24·5	28·0	31·5
2-Methylbutan-3-ol (mmoles)	3·3	6·9	10·1	13·1	16·0	18·0	20·8	21·4	23·7
n-Hexanol (mmoles)	0·25	0·63	1·1	1·7	2·6	4·0	5·0	6·5	8·1

Table II (Fig. 2)

The Reaction of Disiamyl-n-hexylborane (12·55 mmoles) in T.H.F. Solution (0·51 M.) with Successive Aliquots (3·50 mmoles) of Alkaline Hydrogen Peroxide Solution

Hydrogen Peroxide (mmoles)	0·0	3·50	7·00	10·5	14·0	17·5	21·0	24·5	28·0
2-Methylbutan-3-ol (mmoles)	0·0	3·8	8·2	12·4	10·8	14·6	17·3	18·9	22·4
n-Hexanol (mmoles)	0·0	0·5	1·3	1·6	2·6	2·5	4·5	3·8	5·1

Table III (Fig. 3)

The Reaction of Disiamyl-n-octylborane (13·11 mmoles) in T.H.F. Solution (0·52 M.) with Successive Aliquots (5·00 mmoles) of Aqueous Alkaline Hydrogen Peroxide

Hydrogen Peroxide (mmoles)	0·00	5·00	10·0	15·0	20·0	25·0	30·0	35·0
2-Methylbutan-3-ol (mmoles)	0·0	4·4	8·3	12·6	17·3	20·4	22·0	23·5
n-Octanol (mmoles)	0·0	1·1	1·8	2·6	3·5	4·2	5·9	7·7

Table IV (Fig. 4)

The Reaction of Thexyldi-n-hexylborane (12·00 mmoles) in T.H.F. Solution (0·26 M.) with Successive Aliquots (2·75 mmoles) of Aqueous Alkaline Hydrogen Peroxide

Hydrogen Peroxide (mmoles)	0·00	2·75	5·50	8·25	11·0	13·7	16·5	19·3	22·0
2,3-Dimethylbutan-2-ol (mmoles)	0·0	1·1	2·6	3·6	4·6	5·7	7·1	8·1	10·5
n-Hexanol (mmoles)	0·0	1·0	2·6	4·2	5·7	7·5	9·2	10·4	11·4

Table V (Fig. 5)

The Reaction of Thexyldi-n-hexylborane (13·00 mmoles) in T.H.F. Solution (0·52 M.) with Successive Aliquots of Aqueous Alkaline Hydrogen Peroxide

Hydrogen Peroxide (mmoles)	0·00	3·25	6·50
2,3-Dimethylbutan-2-ol (mmoles)	0·00	1·30	2·47
n-Hexanol (mmoles)	0·00	1·69	3·72

Table VI (Fig. 5)

The Reaction of Thexyldi-n-octylborane (12·31 mmoles) in T.H.F. Solution with Successive Aliquots of Aqueous Alkaline Hydrogen Peroxide

Hydrogen Peroxide (mmoles)	0·00	2·60	5·20	7·80
2,3-Dimethylbutan-2-ol (mmoles)	0·00	1·13	2·19	2·91
n-Octanol (mmoles)	0·00	1·48	3·18	4·33

Table VII (Fig. 6)

The Reaction of Thexyldi-n-hexylborane (12·40 mmoles) in Diglyme Solution (0·26 M.) with Successive Aliquots of Aqueous Alkaline Hydrogen Peroxide

Hydrogen Peroxide (mmoles)	0·00	3·10	6·20	9·30	12·4	15·5	18·6	21·7
2,3-Dimethylbutan-2-ol	0·0	1·9	3·4	4·6	5·8	7·1	8·0	9·8
n-Hexanol (mmoles)	0·0	1·4	3·3	5·0	6·9	8·8	10·1	11·9

Table VIII (Fig. 7)

The Reaction of t-Butyldi-n-hexylborane (4·30 mmoles) in Diglyme Solution (0·28 M.) with Successive Aliquots of Aqueous Alkaline Hydrogen Peroxide

Hydrogen Peroxide (mmoles)	0·00	2·00	4·00	6·00	8·00	10·00	12·00	14·00
t-Butanol (mmoles)	0·00	0·84	1·58	2·29	3·13	3·75	4·01	4·05
n-Hexanol (mmoles)	0·00	1·14	2·23	3·10	4·19	5·14	6·45	7·40

Table IX (Fig. 8)

The Reaction of Di-t-butyl-n-hexylborane (4·91 mmoles) in Diglyme Solution (0·26 M.) with Successive Aliquots of Aqueous Alkaline Hydrogen Peroxide

Hydrogen Peroxide (mmoles)	0·00	2·00	4·00	6·00	8·00	10·00	12·00	14·00
t-Butanol (mmoles)	0·00	1·56	2·84	4·75	6·35	7·96	8·66	8·96
n-Hexanol (mmoles)	0·00	0·53	1·04	1·42	1·81	2·38	2·96	3·61

Section IV

The Reaction of Neutral Aqueous Hydrogen Peroxide with Representative Trialkylboranes; a New Reaction

Reagents and solvents for the preparation of diborane, and olefins to be hydroborated, were obtained and purified as described previously. n-Dodecane, n-undecane, n-decane, n-hexane, n-pentane, 2-methylbutane and 2,3-dimethylbutane were supplied by Koch-Light Ltd. 5-Methylundecane was supplied by B. Newton Maine Ltd., and 2,3,4,5-tetramethylhexane and 2,3-dimethylnonane were prepared by the method of Brown[15] and purified by preparative g.l.c. All hydrocarbons were fractionated from calcium hydride.

Chloro-compounds required as g.l.c. standards were prepared by standard literature methods. 1-Chlorohexane (b.p. 135-6°, n_D^{20} 1·4236) was prepared by the method of Rydon and Landauer.[16] 2-Chlorohexane (b.p. 123°, n_D^{22} 1·4142), 3-chlorohexane (b.p. 123°, n_D^{20} 1·4163), 2-chloro-2,3-dimethylbutane (b.p. 110°, n_D^{20} 1·4126), and 3-chloro-2-methylbutane (b.p. 93°, n_D^{20} 1·4095) were all prepared and purified as described by Vogel.[17] 1-Iodohexane was also prepared and purified by the method of Vogel. A sample of hexachloroethane was kindly donated by I.C.I. Ltd. Alcohols used as g.l.c. standards (n-hexanol, n-pentanol, hexan-2-ol, hexan-3-ol and 2-methylbutan-3-ol) were supplied by Koch-Light Ltd. and purified by fractionation. 2,3-Dimethylbutan-2-ol was prepared and purified as described earlier.

All organoboranes were prepared in T.H.F. solution in a 50·0 ml. two-necked hydroboration flask by the reaction of borane: T.H.F. solution with the required olefin, as described in Sections I, II and III (Experimental). As in previous Sections the preparation was arranged to give 12-13 mmoles of the organoborane. After the preparation, the borane was estimated by the addition of an internal standard (n-hexane) followed by g.l.c. analysis of the residual olefins. The solvent and excess hydrocarbons were then removed at 0°, 2 mm. as described in Section II (Experimental). The solvent and olefins caught in the liquid-nitrogen cooled receiver were re-analysed to ensure that the organoborane had not undergone any de-hydroboration. The new solvent T.H.F., methanol, diglyme, petrol ether, water, or carbon tetrachloride was then added from a syringe to dilute the organoborane to the required molarity (0·5 M., except in specific cases described in the text). Disiamylborinic acid and thexylboronic acid were prepared in T.H.F. solution by the hydroboration of 2-methylbut-2-ene, and 2,3-dimethylbut-2-ene respectively, using the procedure described above. A small excess of distilled, oxygen-free water was then added slowly from a syringe to the mono- or di-alkylborane to hydrolyse the borane to the required acid. Estimation of excess olefins was then carried out by the same method as for a trialkylborane.

The organoborane solution was cooled to 0° (tri-n-hexylborane), or held at 25° (unsymmetrical trialkylboranes, borinic and boronic acids) and a weighed quantity of n-pentanol (internal standard for the higher boiling products) introduced by syringe. Hydrogen peroxide solution (30% w/v - estimated by permanganate titration) was then added during 10 mins. from an all-glass syringe. The quantities of the reagents and the molarities and temperatures of the solutions to be oxidised are shown in the tables of results. Intermediate estimations of the higher boiling products (alcohols, alkyl halides and dimeric hydrocarbons) was carried out by g.l.c. analysis as in Section III (Experimental) above. Monomeric hydrocarbons were estimated by the addition of an internal standard and g.l.c. analysis after the completion of the oxidation.

For the oxidations using Fenton's reagent 13 mmoles of tri-n-hexylborane was prepared in T.H.F. solution. During the oxidation in the presence of T.H.F., the oxidising agents, ferrous sulphate (7·350 g., 26·0 mmoles, Analar grade heptahydrate, ex B.D.H. Ltd.) in 20·0 ml. de-ionised water, and aqueous hydrogen peroxide (26·4 mmoles, 30% w/v solution) were added synchronously (during 0·5 hr.) from syringes below the surface of the magnetically stirred reaction mixture in a hydroboration flask. A brown aqueous layer separated. After stirring for a further hour the reaction mixture was saturated with sodium chloride, and the organic products extracted into ether solution and analysed by g.l.c. In the second Fenton's reagent oxidation the solvent T.H.F. was removed after the preparation and estimation of the tri-n-hexylborane (as described above) and replaced with 20·0 ml. of distilled, oxygen-free water. The borane was not completely soluble and the resulting mixture was stirred vigorously during the addition of the oxidising agents, as in the previous experiment. During the addition of the oxidising agents the solution became black. The organic products were salted out from the reaction mixture and estimated as above.

For oxidations using molecular oxygen tri-n-hexylborane, disiamyl-n-hexylborane, and thexyldi-n-hexylborane (12-13 mmoles) were prepared in T.H.F. solution as for the neutral hydrogen peroxide oxidations. The solvent was then removed, and the borane diluted to 0·5 M. with diglyme. Distilled, oxygen-free water (2·0 ml.) was added at this stage to the organoborane solutions to be autoxidised under aqueous conditions. Dried compressed air was then passed (approximately 15 ml. $min.^{-1}$) through a fine-jet bubbler into the magnetically stirred solution at 25° for 24 hr. The exhaust gases were passed through a trap cooled to -80° in order to retain low-boiling hydrocarbons, etc. After 24 hr. the cold trap and the reaction flask were analysed by g.l.c. for organic reaction products. The reaction flask contents were then treated with an excess of alkaline hydrogen peroxide solution. After stirring at ambient temperature for 0·5 hr. the salted out organic products were re-analysed for alcohols present.

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Appendix

Gas Liquid Chromatography

The g.l.c.'s of Sections I and II were performed with a Perkin Elmer Model 451 Fractometer (hot-wire detector). In Sections III and IV, Pye Model 104 (flame ionisation detector; on-column injection) chromatographs were used as outlined below, with the exceptions noted.

The following stationary phases and supports were used:-

Section I. Alcohols: 6 ft. polypropylene glycol 15% w/w on firebrick (Ucon Oil, code R), *and 3 ft. polypropylene glycol 15% w/w on Teflon (Code W).* Enol esters: 6 ft. polyethylene glycol succinate 15% w/w on firebrick (code P).*

Section II. Alkanes and alkenes: 12 ft. tricresyl phosphate 30% w/w on 44/60 celite.‡

Isomeric olefins from the dehydration of 2-methylbutan-2-ol, and 2,3-dimethylbutan-2-ol: 3 ft. silver nitrate with polypropylene glycol, 15% w/w on firebrick (code H).*

Sections III, IV. All dimeric hydrocarbons, alcohols and alkyl halides, except hexachloroethane: 6 ft. polypropylene glycol 15% w/w on 60/80 mesh Chromosorb W, or 6 ft. polyethylene glycol adipate 15% w/w on Silocel.§ Hexachloroethane: 3 ft. silicone oil 15% w/w on firebrick (code O).*

*as supplied by Perkin Elmer, Ltd.

‡tricresyl phosphate supplied by Wilkins Scientific Co.: 12 ft. length of dead-soft copper tubing supplied by Z. Onion Co., Derby Road, Loughborough: 44/60 celite from Chromatography Supplies, King's Lynn, Norfolk.

[8]polyethylene glycol adipate on Silocel as supplied by M. E. L. Ltd., London; polypropylene glycol and Chromosorb W supplied by Perkin Elmer, Ltd.

The preparation of column packings followed standard techniques. Column packing was carried out as directed by the manufacturer. Quantitative analysis of a mixture was achieved by one of two methods, as described below.

Where the peaks were symmetrical, the peak areas were calculated from the product of the peak height and the width of the peak at half height. The chromatograph conditions were adjusted as necessary to give no more than 10% overlap of the peak height, measured from the baseline, for two incompletely resolved peaks (as during the relative rate experiments using cis/trans 1-acetoxyoct-1-ene).

Correction factors were calculated before all quantitative estimations. The method used was to inject a sample of an accurately known mixture of the compound (Wc) and the proposed internal standard (Ws) in ether solution, and then to calculate the correcting factor (f) from the following relationship:-

$$\frac{Wc}{Ac} = \frac{Ws}{As} \, .f$$

(where A represents area of the corresponding g.l.c. peak). Wc and Ws were arranged to be as close as possible to the relative proportions expected in the reaction mixture.

When peaks were partially obscured, or of poor triangularity, measurement was made using an All-Brit planimeter.

The peaks obtained for the higher boiling alcohols (n-hexanol, n-octanol) tailed, and were estimated by this method. The g.l.c. correction factor was then recalculated from a standard mixture, again using the planimeter.

The cis and trans isomers of the enol acetates and pivalates were separated by preparative g.l.c. on a Wilkins Autoprep - Model A 700, using a column of Carbowax 20 M (20% w/w) on Chromosorb P (20 ft. x $\frac{1}{4}$ in.). Automatic injection of samples, and fraction collecting was used.

During analysis of the partially oxidised boranes using a polypropylene glycol, or polyethylene glycol adipate, stationary phase the sharpness and resolution of alcohol peaks was found to deteriorate markedly after some 12-20 injections. On-column injection probably allowed boric acid or involatile hydroxylic organoboron residues to accumulate close to the inlet end of the column. Alcohols injected into the system were then able to esterify reversibly with the B-OH groups, giving abnormal elution characteristics. The difficulty was overcome by adding a short (8 in.) forerun of a stationary phase containing a high concentration of hydroxyl groups. Glycerol (30% w/w on 60/80 mesh Chromosorb W) was slowly eluted at the temperatures necessary to analyse the alcohols, but diglycerol (30% w/w on 60/80 mesh Chromosorb W) was found to be useful at temperatures up to 130°. Sharp, well resolved alcohol peaks were obtained for as many as 100-150 injections of 1μl. of reaction mixture before any deterioration in peak sharpness could be detected.