Hydroboration of some organometallic systems.

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HYDROBORATION OF SOME ORGANOMETALLIC SYSTEMS

by

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Contents

Hydroboration of some organometallic systems

C. J. Towers

1) Abstract

This thesis contains a review of the literature concerning the hydroboration of multiple bonded organic molecules and the synthetic utility of the organoboranes so formed in these reactions.

Although the reactions of diborane with unsaturated organic molecules are well known, there is little information referring to such reactions with organometallic complexes containing unsaturated ligands. Details are presented herein of complexes which have been synthesized to enable investigation of their reactions with diborane and the results of such subsequent reactions.

Hydroboration of systems which have been studied include those which contain either sigma or pi-interactions between the organic moiety and a metal. 2,4-Pentanedione and related compounds undergo hydroboration and for the former case, reduction of the two carbonyl groups occurs essentially simultaneously giving after hydrolysis a dimeric borate ester of a meso-diol. In contrast the ester produced from the reaction of boric acid and the diol formed from the reduction of the dione with sodium borohydride is a mixture of racemic and meso-forms. In metal 2,4-pentanedionates, where the multiple bonds are delocalised, identifiable products from hydroboration were not obtained. For other systems having localised or delocalised groups pi-bonded to a metal, for example $(\pi\text{-}C_5H_5)_2Fe$ or $(PhC{\equiv}CPh)Pt(Ph_3P)_2$, hydroboration could not be obtained.

In substituted ferrocene derivatives having multiple bonded groups attached to the organic ring system, for example acetylferrocene and vinylferrocene, only hydroboration of the side chain occurred with the mode of addition being essentially the same as if the metal had not been present.

Although indene, (C_9H_7), underwent hydroboration of the 5-membered ring producing 2-indanol on oxidation, when the indene moiety was pi-bonded to iron, the 6-membered ring underwent hydroboration.

2) Statement of objectives

The objectives of the study presented herein were to investigate the hydroboration reactions of systems containing unsaturated organic groups bonded to metal centres to establish whether the presence of the metal affected the overall course of the reaction, as compared to the mode of hydroboration occurring where the organic moiety was not bonded to a metal centre. The types of compound which would be studied include the following categories;

(i) compounds in which the organic group is sigma-bonded to the metal with the multiple bond in a localised or delocalised environment, for example; Schiff's base, pyridylethylene or acetylacetone complexes and $(PhC{\equiv}C)_2Hg$.

(ii) compounds in which the organic group is pi-bonded to the metal, for example; $(PhC{\equiv}CPh)Pt(Ph_3P)_2$, $(\pi\text{-}C_5H_5)_2Fe$ and $(\pi\text{-}C_9H_7)(\pi\text{-}C_5H_5)Fe$.

(iii) compounds in which the organic group is pi-bonded to the metal but contains an unsaturated function in a localised environment, for example; vinylferrocene or acetylferrocene.

3. Acknowledgements

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I am also grateful to my Wife for her patience and endurance during the writing of this thesis.

4. Introduction

4.1) Historical

Following Stock's report[1] of the reaction of diborane with an unsaturated hydrocarbon (acetylene), little else in this area was published until, twenty five years later, the high temperature formation of trialkylboranes by reaction with olefins was reported[2].

At ambient temperatures these reactions were slow and typically were carried out by sealing the reactants in heavy walled glass tubes which were then heated at elevated temperatures for several days.

During studies of the Lewis acid properties of diborane[3] it was noted that ethylene and propylene oxides were polymerized to some extent. Similar reactions with styrene, methyl methacrylate and acrylonitrile resulted in the slow formation of trialkylboranes but not the polymeric products which were then of interest.

The difficulties of preparation of pure diborane and of handling the reactive gas, combined with the slowness of reaction, suggested that such reactions would not be synthetically convenient for the preparation of trialkylboranes.

The synthesis and important reducing properties of lithium aluminium hydride stimulated Brown[4] to institute more research into the properties of sodium borohydride, of which he was co-discoverer[5]. The work concerning the novel synthesis of sodium borohydride had also shown that the reduction of aldehydes and ketones under mild conditions was possible.

The effects of substituents, solvent and the presence of metal ions on the reducing properties of sodium borohydride were investigated[6,7,8]. It was noted that in the presence of aluminium chloride a solution of sodium borohydride reduced an unsaturated ester, ethyl oleate, to a greater extent than the stoichiometry expected for conversion of the ester into the alcohol. Further investigation of this observation showed that olefins reacted to produce a quantitative yield of the corresponding organoborane[9,10].

Although aluminium borohydride in diethylether solution is capable of reducing olefins, the reaction of a 'diglyme' (bis (2-methoxyethylether)) solution of aluminium chloride and sodium borohydride with olefins (1) was not considered to be due to the initial formation of aluminium borohydride because no precipitate of sodium chloride, insoluble in diglyme, was noted until the olefin was added. The conversion of an olefin into the corresponding organoborane via this reaction typically gives an 80-90% yield.

An inherent disadvantage in this otherwise useful reaction is that the reaction products, other than the organoborane, consist of salt and aluminium hydride, as a result of which only three-quarters of the "hydride" actually takes part in the reduction of the olefin (1). The use of an alternative Lewis acid, boron trichloride (2) or boron trifluoride (3), was found to provide a convenient way to utilize all the available hydride in reduction of the olefin.

$$9\,RCH{=}CH_2 + AlCl_3 + 3NaBH_4 \longrightarrow 3(RCH_2CH_2)_3B + 3NaCl + 3AlH_3 \qquad (1)$$

$$12\,RCH{=}CH_2 + 3NaBH_4 + BCl_3 \longrightarrow 4(RCH_2CH_2)_3B + 3NaCl \qquad (2)$$

$$12\,RCH{=}CH_2 + 3NaBH_4 + 4BF_3 \longrightarrow 4(RCH_2CH_2)_3B + 3NaBF_4 \qquad (3)$$

Diborane may be easily generated by the addition of boron trifluoride to an ethereal solution of sodium borohydride. Under conditions similar to those employed in the reactions (1) to (3) such an ethereal solution was found to reduce olefins affording the respective organoborane[11]. Unpublished observations by Brown and Case claim that even small quantities of ether solvents catalysed the addition of diborane to olefins from very slow to extremely fast reactions[12].

The foregoing essentially constitutes the events leading to the basic procedures[13,14] by which olefinic and acetylenic bonds may be reduced by the addition of a boron-hydrogen function across an unsaturated bond to form an organoborane. This reaction, as distinct from the reductions effected by other hydridic reagents, has become known as the "hydroboration" reaction.

4.2) Hydroboration

4.2.1) Initial Importance

The hydroboration reaction provides a convenient and usually efficient synthesis for organoboranes from a wide range of substrates, particularly from alkenes and alkynes. Initial interest in the organoboranes so produced was centred upon the oxidation reactions which produced alcohols. The reactions of organoboranes were subsequently explored and proved to be of great synthetic use.

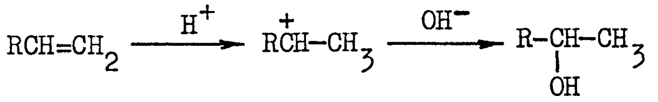
If the organoborane generated by hydroboration of an alkene is subsequently oxidised with a controlled amount of oxygen[15,16](4) or with alkaline hydrogen peroxide[17] (5) the product is an alcohol. The oxidation is essentially quantitative and the alcohol produced is usually the anti-Markovnikov hydration product. More importantly, hydroboration followed by alkaline peroxide oxidation was found to proceed with complete retention of configuration yielding the cis-alcohol product.

$$R_3B + 1\tfrac{1}{2}\, O_2 \xrightarrow[0^{\circ}C]{T.H.F} [RO_2]_{1.5}\, BR_{1.5} \xrightarrow{NaOH/H_2O} 3ROH \qquad (4)$$

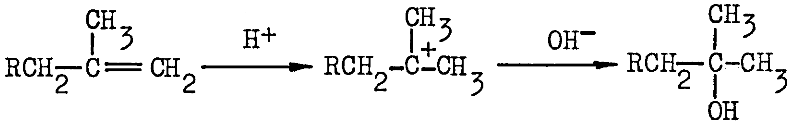
$$R_3B + 3H_2O_2 + NaOH \longrightarrow 3ROH + NaB(OH)_4 \qquad (5)$$

4.2.2) The mechanism of hydroboration

The conversion of alkenes to alcohols may also be accomplished by hydration or via sulphonation. The mechanism of reaction, and the basis of Markovnikov's rule, is the protonation of the alkene in the presence of an acid and the formation of a carbonium ion such that the positive charge is localised on the carbon atom most able to support the charge. Alkenes other than ethylene form secondary (6) or tertiary carbonium ions (7) which subsequently react with the hydroxyl ion to give the desired alcohol.



$$RCH{=}CH_2 \xrightarrow{H^+} R\overset{+}{C}H{-}CH_3 \xrightarrow{OH^-} R{-}\underset{OH}{\underset{|}{C}H}{-}CH_3 \qquad (6)$$

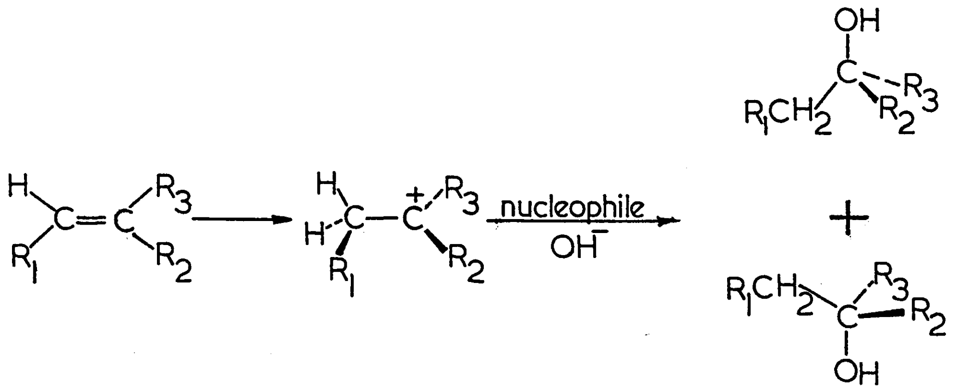


$$RCH_2{-}\overset{CH_3}{\overset{|}{C}}{=}CH_2 \xrightarrow{H^+} RCH_2{-}\overset{CH_3}{\overset{|}{\overset{+}{C}}}{-}CH_3 \xrightarrow{OH^-} RCH_2{-}\underset{OH}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}{-}CH_3 \qquad (7)$$

Consequently the only primary alcohol which can be produced directly is ethanol from ethylene, all other alkenes affording only secondary or tertiary alcohols.

The carbonium ion intermediate produced by the protonation of an alkene is of stereochemical importance. Certain alkenes exhibit cis-trans isomerism which results from hindered rotation about the unsaturated carbon-carbon bond. The configuration of such alkenes is generally fixed by the properties of the unsaturated bond, but some alkenes can undergo isomer interconversion when heated or exposed to ultraviolet light, for example 1,2-diphenylethylene.

The carbonium ion is planar about the positively charged carbon atom. Not only can rotation about the carbon-carbon bonds take place but attack by the nucleophile may take place from either side of the plane of the ion. Thus a mixture of products is assured and the original configuration is lost (8).



(8)

In contrast the retention of configuration during the hydroboration/oxidation of alkenes implies that the reaction does not proceed via a discrete trigonal intermediate involving either carbon atom since it is this step which causes the loss of configuration. The reaction is considered to proceed via a four-centre transition state. Theoretical calculations show that the rate determining step in the hydroboration of alkenes is the formation of a loosely bonded π-complex between the reactants, and that the subsequent rearrangement of the cyclic intermediate to the borane has a very low activation energy[18,19,20]. Experimentally the low activation energy barrier in the formation of both the π-complex and rearrangement to the borane is demonstrated by the high rates of reaction observed. Rates of reaction are controlled by the change in free energy required to form the transition state ($\Delta G^{\ddagger}$) and also by the change in free energy between reactants and products (ΔG). Even when the overall change in ΔG is favourable the reaction will not be fast unless $\Delta G^{\ddagger}$ is relatively small.

4.2.3) Solvent systems for hydroboration

The choice of which ether solvent is used affects the hydroboration reaction mainly because of the varying solubilities of diborane and the reagents used to produce it in ethereal solution. Reactions of suitable substrates may be carried out either by generation of diborane and reaction *in situ*, or by the preparation of an ethereal solution of diborane and addition of this solution to the substrate in either the same or a different, miscible, solvent.

Table I

Solubilities of hydride reagents in ether solvents at 25°C in g/100g solvent.

Reagent	diethylether	tetrahydrofuran	diglyme[a]	monoglyme[b]
B_2H_6	1.1	8.1	0.76	0.66
$LiAlH_4$	35.4	13	3.6	10
$NaBH_4$	0	0.1	6.6	0.8
$LiBH_4$	4.28	28	16.2	12.1

a bis (2-methoxyethyl)ether

b 1,2-dimethoxyethane

Diborane may be conveniently synthesized by the action of a Lewis acid upon sodium borohydride, for example with boron trifluoride (as the diethyletherate) (9).

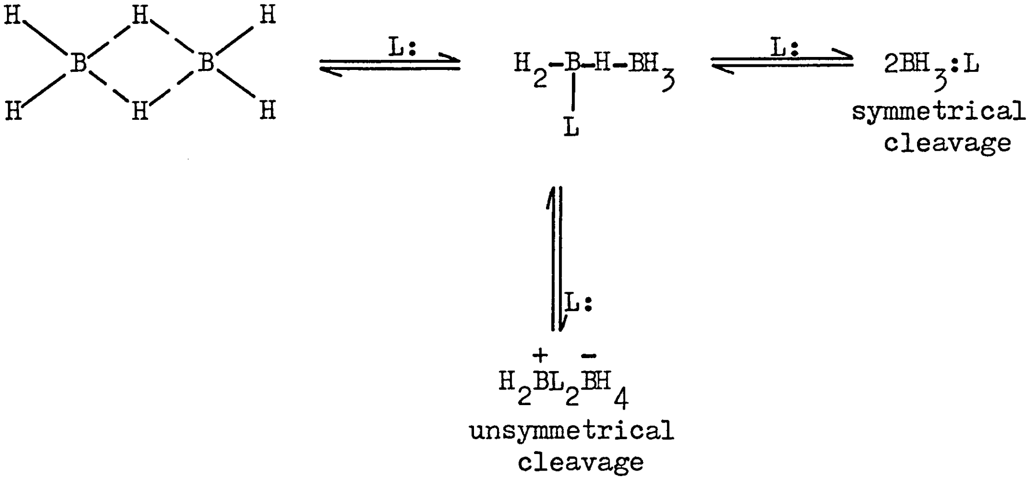
$$3NaBH_4 + 4BF_3.Et_2O \xrightarrow[20^oC]{} 2B_2H_6 + 3NaBF_4 + 4Et_2O \qquad (9)$$

From Table I it can be seen that both diethylether and tetrahydrofuran are poor solvents for sodium borohydride and their use in such a procedure would have practical difficulties. For this reason gaseous diborane is often generated from a reaction solution in diglyme, which is a better solvent for sodium borohydride, and conveyed into tetrahydrofuran by a stream of dry nitrogen. In tetrahydrofuran solution diborane forms a 1:1 complex, BH_3-tetrahydrofuran, which is an active hydroborating species.

During the reaction (9) a complex between sodium borohydride and borane forms, so that diborane is liberated only when an excess of boron trifluoride etherate is added (10).

$$7NaBH_4 + 4BF_3.Et_2O \longrightarrow 4NaBH_4.BH_3 + 3NaBF_4 + 4Et_2O \qquad (10)$$

Diborane exists as a bridged molecule which has two two-electron-three-centre bonds[21]. With various electron-donor ligands diborane will undergo cleavage which is mostly, but not exclusively, symmetrical[22]. A mechanism for the cleavage has been postulated (11).

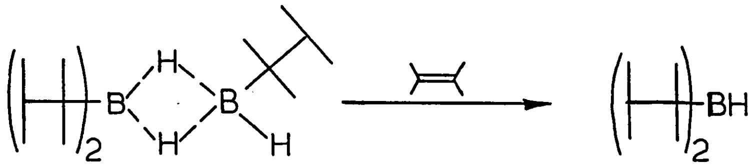


(11)

The symmetrical cleavage of diborane in ethereal solutions produces complexes which with the exception of tetrahydrofuran revert easily to diborane[23]. The hydroborating species present in tetrahydrofuran solutions of diborane is predominantly the BH_3-tetrahydrofuran adduct ("Borane") and the presence of such an adduct is often assumed with other ethereal solvents. The BH_3-tetrahydrofuran adduct, in solution, has been postulated to be in equilibrium with the $B_2H_7^-$ ion[24] which is believed to exist as a singly hydrogen bridged species[25] (12).

$$3BH_3.THF \rightleftharpoons H_2\overset{+}{B}(THF)_2.\overset{-}{B}_2H_7 + THF \qquad (12)$$

The relative intensities of the infrared absorption bands due to B-H-B bridge bonds and terminal B-H bonds at 1500-1600cm^{-1} and approximately 2470cm^{-1} respectively may be used to measure the ratio of dimeric to monomeric organoboranes in solution. Both mono and dialkylboranes tend to dimerise in solution, although not exclusively so, and this is generally attributed to a reduction in Lewis acidity brought about by the steric and polar influences of the alkyl substituents[26]. Even when R_2BH contain sterically large groups dimers are usually formed to some extent. One exception is thexylborane, which exists as a monomer but is formed via dimeric species (13). Di-t-hexylborane may be obtained from the hydroboration of 2,3-dimethylbut-2-ene and the reaction proceeds via a B-H-B bridged species, determined from infrared studies, until on addition of the fourth alkene molecule dissociation occurs. The dissociation of the tetraalkyldiborane is demonstrated by the change from infrared absorption characteristic of B-H-B bonds to that characteristic of terminal B-H bonds following addition of the fourth group.



(13)

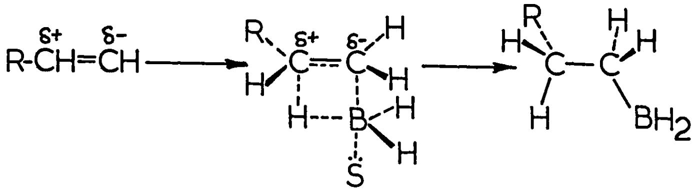
The relative proportions of monomer:dimer for monoalkylthexylboranes increases with the steric size of the alkyl group[27].

It is often assumed that the monoalkyl and dialkylboranes used as hydroborating agents act as monomers; however the presence of the dimeric species in solution is important from a mechanistic viewpoint. In the case of 9-borabicyclo [3.3.1] nonane[28] (9-BBN), in carbon tetrachloride solution, a rate limiting dissociation of the dimer occurs with subsequent fast addition of the monomer to the substrate[28].

The trialkylboranes are not solvated and exist as monomers[29].

4.2.4) Orientation of hydroboration

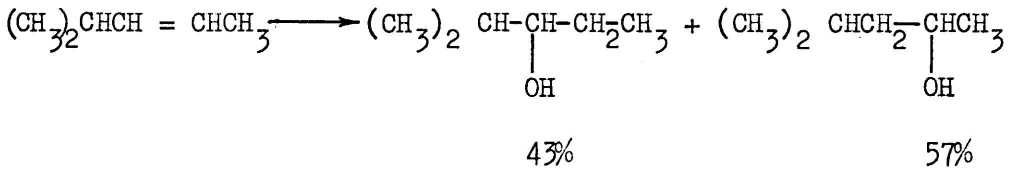
The ether adduct BH_3 acts as a Lewis acid (electron acceptor) and its use as a reagent results in reactions expected of an electrophilic reagent. In contrast to the previously discussed mechanism for the hydration of alkenes, and the reactions of borohydride reagents which involve hydride (H^-) transfer, the BH_3 adduct will react with alkenes to form the four centred intermediate having the boron atom aligned to the carbon atom with highest electron density, and the hydrogen aligned to the adjacent carbon atom. For example when the double bond is situated at the end of the carbon chain the addition of the boron hydride takes place with boron on the terminal carbon (14) since the inductive effect places the highest charge (-ve) on that carbon atom.



(14)

The shift of charge density from the alkene π-bond to boron promotes the transfer of hydride onto the partially positively charged carbon. As previously stated the rearrangement is of low activation energy and affords an organoborane as product. The remaining two hydrides attached to boron subsequently react by the same mechanism to produce a trialkylborane which may be oxidised to produce, in this simple case, a primary alcohol. For some hindered alkenes the hydroboration reaction may not proceed beyond the dialkylborane stage.

Although always cis, the orientation of the electrophilic addition is controlled both by steric and electronic factors. When inductive or electronegativity effects of alkene substituents do not cause a sufficient polarization of the double bond a mixture of products (both cis) may be expected following oxidation (15).



$$\mathrm{(CH_3)_2CHCH=CHCH_3} \longrightarrow \underset{43\%}{\mathrm{(CH_3)_2CH\text{-}\underset{OH}{C}H\text{-}CH_2CH_3}} + \underset{57\%}{\mathrm{(CH_3)_2CHCH_2\text{-}\underset{OH}{C}HCH_3}} \qquad (15)$$

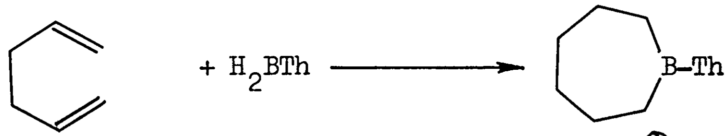
For the reaction of alkenes with borane-tetrahydrofuran the structure of the alkene has been shown to have little effect on the rate of hydroboration[30].

In general borane-tetrahydrofuran will add to an alkene by cis-addition from the least hindered side placing boron predominantly on the least substituted carbon atom. For monosubstituted terminal alkenes the terminal borane is produced, usually in high yield. Disubstituted terminal alkenes tend to give even higher, almost quantitative, yields of the terminal borane. The general term regioselectivity is used in the context of the hydroboration reaction to describe the position at which boron becomes attached during the reaction.

For internal alkenes hydroboration with borane-tetrahydrofuran has low regioselectivity, yielding a mixed product, the distribution of which is little affected by cis-trans isomerism of the alkene[31].

Position at which boron atom is bonded in R_3B.

The hydroboration of acyclic dienes can give rise to cyclic boranes (16), and acetylenes usually proceed past the vinylborane to a diboroalkyl compound (17).



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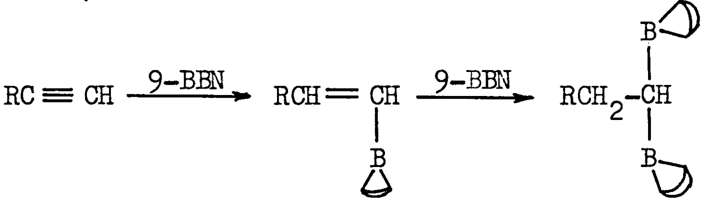


(17)

Although in general the reaction of alkenes with borane-tetrahydrofuran is taken to proceed to the trialkylborane, this is not always the case. Some alkenes react only slowly past the mono or dialkyl borane stage and consequently these boranes are isolable. These boranes themselves have synthetic utility as hydroborating reagents with, in many circumstances, superior properties to borane-tetrahydrofuran.

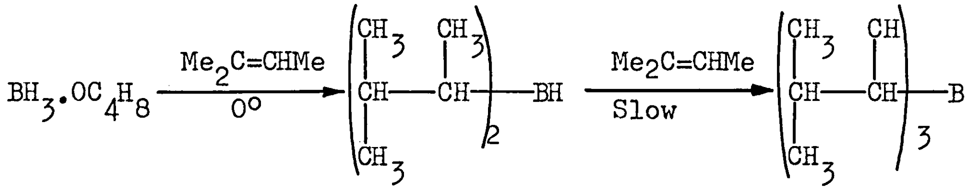
4.3) Hydroborating reagents

4.3.1) Borane-tetrahydrofuran

As previously stated borane-tetrahydrofuran may be conveniently prepared by passing diborane (generated from the reaction of a Lewis acid with a solution of sodium borohydride) into tetrahydrofuran. In this fashion solutions of concentrations up to approximately 2 molar in borane may be prepared.

4.3.2) Disiamylborane

The reaction of borane-tetrahydrofuran with 2-methyl-2-butene proceeds only very slowly past the dialkyl stage so that the monofunctional reagent disiamylborane (Sia_2BH) which has useful properties can readily be isolated[32] (18).



$$BH_3.OC_4H_8 \xrightarrow[0^o]{Me_2C=CHMe} \left(\begin{matrix} CH_3 & CH_3 \\ | & | \\ CH— & —CH— \\ | & \\ CH_3 & \end{matrix}\right)_2 BH \xrightarrow[Slow]{Me_2C=CHMe} \left(\begin{matrix} CH_3 & CH \\ | & | \\ CH— & —CH— \\ | & \\ CH_3 & \end{matrix}\right)_3 B \qquad (18)$$

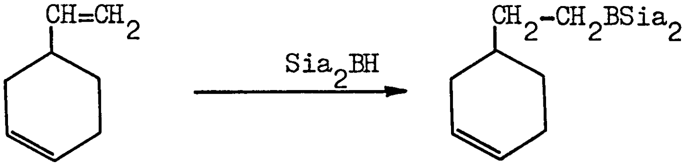
The use of this reagent in the hydroboration of representative alkenes shows higher selectivity for the terminal or least hindered carbon atom than does similar reaction with borane-tetrahydrofuran[32,33].

$$CH_3(CH_2)_3\text{-}\overset{a}{C}H{=}\overset{b}{C}H_2 \qquad ClCH_2\overset{a}{C}H{=}\overset{b}{C}H_2 \qquad \overset{a}{C}H{=}\overset{b}{C}H_2$$

	a	b	a	b	a	b
BH_3.THF	-	-	50%	50%	20%	80%
Sia_2BH	-	99%	-	98%	-	98%

a and b indicate the position of attachment of the boron atom.

The rate of reaction of Sia$_2$BH with alkenes is sensitive to the position of the olefinic bond in the substrate, so that where more than one unsaturated bond is present a degree of selectivity of hydroboration is apparent. Cis-alkenes react faster than trans-alkenes with Sia$_2$BH as do terminal alkenes rather than internal alkenes[32], thus (19)



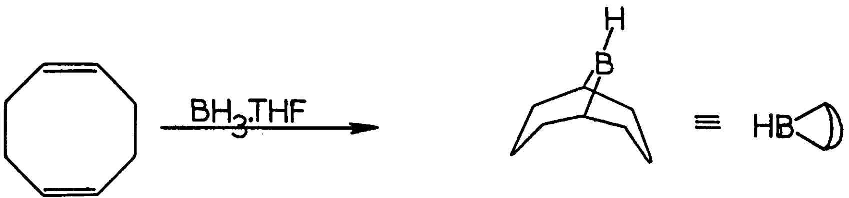
(19)

Due to the monofunctional nature of the reagent the hydroboration of dienes cannot form cyclic products and allows the formation of diols by oxidation of the borane[34]. Also acetylenes may be monohydroborated to give vinylboranes[35], usually the trans-isomer.

A related reagent is that formed by hydroboration of cyclohexene to give dicyclohexylborane which may be broadly used as a substitute for disiamylborane but has a slightly less hindered structure.

4.3.3.) 9-Borabicyclo [3.3.1] nonane

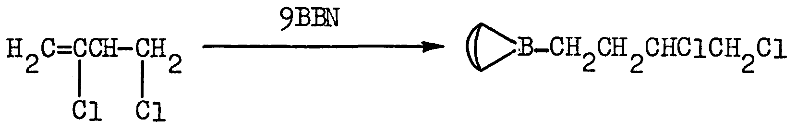
The hydroboration of 1,5-cyclooctadiene can be controlled to yield a bicyclic borane, 9-borabicyclo [3.3.1] nonane[36,37], commonly called 9-BBN (20).



9-BBN

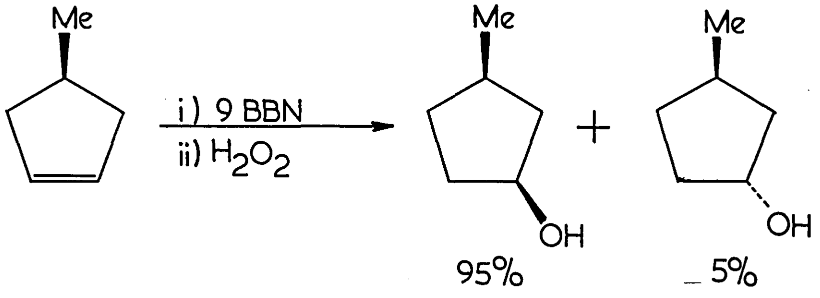
(20)

The reagent is thermally and air stable having convenient handling properties since it is a solid. Although reactions of 9-BBN with other than terminal alkenes are slow at ambient temperatures the simple expedient of conducting the reaction in refluxing tetrahydrofuran affords the alkylborane in a short reaction time and very high regioselectivity[38] (98-100%). Even the powerful directive effects of halogen substituents are less effective with this reagent (21-23).



$$H_2C{=}\underset{\underset{Cl}{|}}{C}H-\underset{\underset{Cl}{|}}{C}H_2 \xrightarrow{\text{9BBN}} \text{B}-CH_2CH_2CHClCH_2Cl$$

(21)



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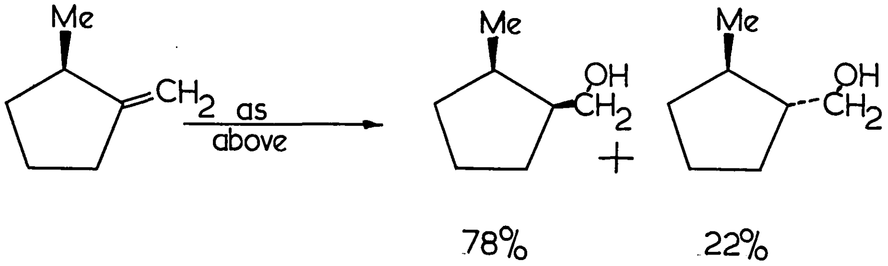
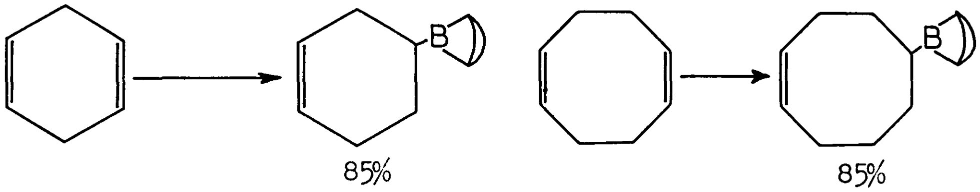


(23)

For non-conjugated dienes where the bonds are well separated and identical e.g. $CH_2{=}CHCH_2CH_2CH{=}CH_2$ the distribution of mono and dihydroborated products closely approximates a statistical distribution. However, where the bonds are in closer proximity or a different degree of substitution exists then a high degree of selectivity is shown [39] (24-27).



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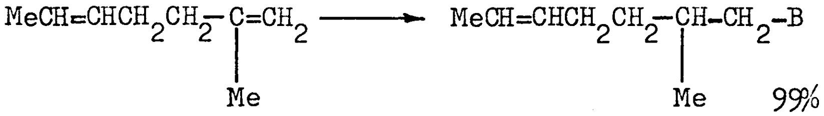
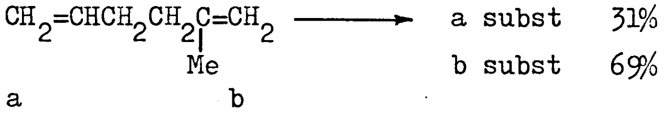


$$MeCH{=}CHCH_2CH_2{-}\underset{Me}{C}{=}CH_2 \longrightarrow MeCH{=}CHCH_2CH_2{-}\underset{Me}{CH}{-}CH_2{-}B \quad 99\%$$

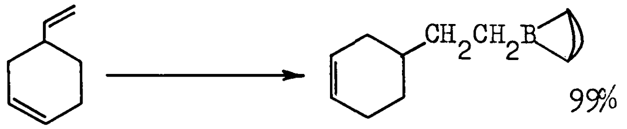
(25)



$$\underset{a}{CH_2}{=}CHCH_2CH_2\underset{\underset{b}{Me}}{C}{=}CH_2 \longrightarrow$$

a subst 31%
b subst 69%

(26)

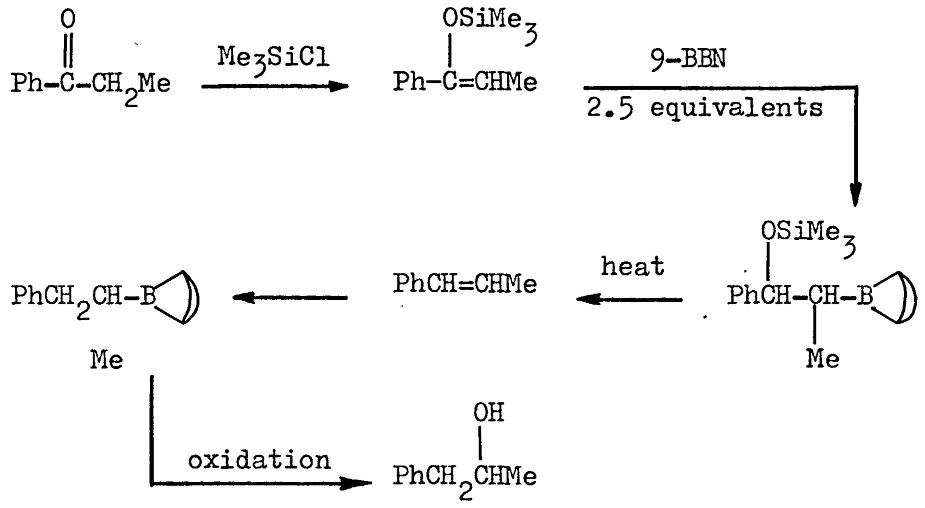


(27)

a and b indicate the position of attachment of the boron atom.

For the hydroboration of internal acetylenes good yields of the monohydroborated product are obtained with 9-BBN whilst terminal acetylenes often yield the 1,1-diboraalkane. Suppression of the dihydroboration of acetylenes may sometime be possible by the use of a molar excess of the substrate[40].

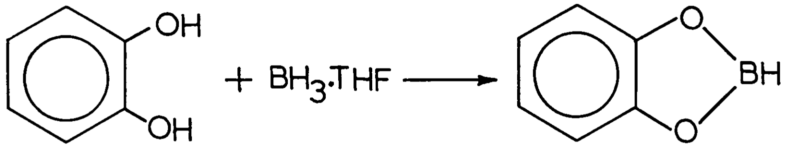
The hydroboration of silyl enol ethers by 9-BBN may be used to effect a reductive 1,2-transposition of ketone[41] groups (28).


(28)

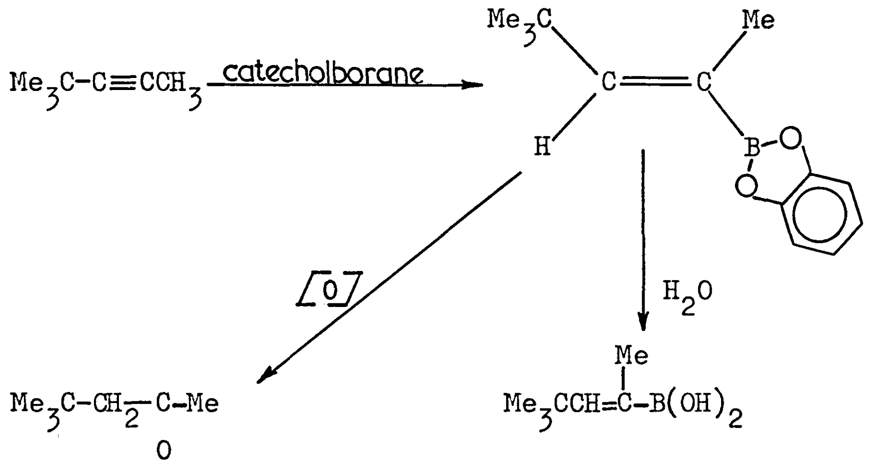
Conversion of 9-BBN into other derivatives is possible[42] and the B-bromo-9-BBN has found use as a selective ether cleavage agent[43].

4.3.4) Catecholborane

The reaction of borane-tetrahydrofuran with glycols has been shown to yield dioxaborolanes, which were considered potential monohydroborating agents but proved to have poor properties in this respect[44]. The similar reaction with 1,2-dihydroxybenzene (Catechol) affords 1,3,2-benzodioxaborolane[45], more commonly called "Catecholborane" (29).


(29)

Catecholborane has much better hydroborating properties than those of reagents formed using other diols but its reactions are slow at ambient temperatures. Alkenes react readily under reflux in tetrahydrofuran[45] and acetylenes react under milder conditions with attack by boron preferentially upon the least hindered carbon atom[46] providing a degree of selectivity compared to "borane"[47]. The boranes thus derived are usually of trans configuration and stable to air allowing the possibility of purification via distillation or recrystallization. Simple hydrolysis of the boranes affords the alkyl or alkenyl boronic acid whilst oxidation affords the corresponding carbonyl compound (30).



(30)

4.3.5) Chloroboranes

The chloroboranes Cl_2BH and $ClBH_2$ can be synthesized but disproportionate to diborane and boron trichloride. If the synthesis is carried out in an ether solvent then the etherate adducts are formed and are much more stable[48] (31,32).

$$B_2H_6 + 4\ BCl_3.Et_2O + 2Et_2O \longrightarrow 6\ Cl_2BH.OEt_2 \qquad (31)$$

$$B_2H_6 + BCl_3.Et_2O + 2Et_2O \longrightarrow 3\ ClBH_2.OEt_2 \qquad (32)$$

Alternatively the reaction between borane-tetrahydrofuran and hydrogen chloride can be utilised[49] (33,34).

$$BH_3.THF + 2HCl \longrightarrow Cl_2BH.THF + 2H_2 \quad (33)$$

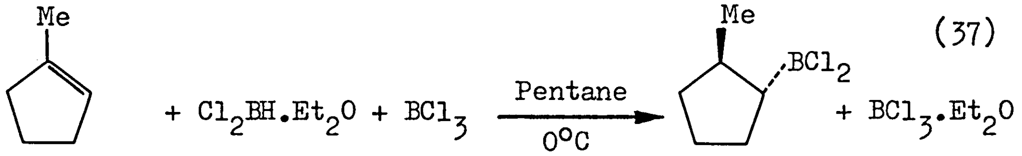
$$BH_3.THF + HCl \longrightarrow ClBH_2.THF + H_2 \quad (34)$$

When utilised for hydroboration the diethyletherates proved to be more reactive than the tetrahydrofuranates because of the relative stabilities of the adducts[49,50,51]. A simpler synthesis of the chloroborane etherates based upon the reaction of lithium borohydride and boron trichloride in diethylether solvent easily affords the required chloroborane diethyletherate[48] and a precipitate of lithium chloride (35, 36).

$$LiBH_4 + 3BCl_3 + 4Et_2O \longrightarrow LiCl + 4\ Cl_2BH.Et_2O \quad (35)$$

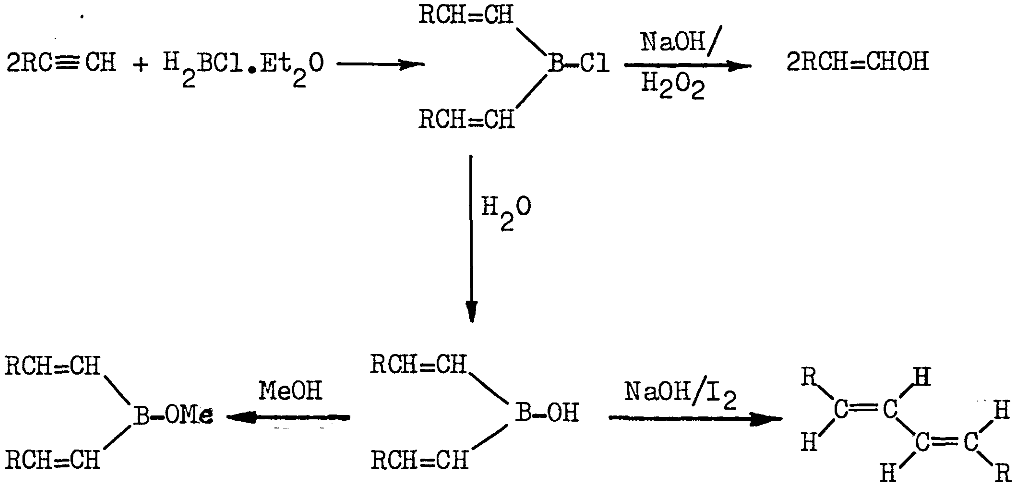
$$LiBH_4 + BCl_3 + 2Et_2O \longrightarrow LiCl + 2\ Cl\ BH_2.Et_2O \quad (36)$$

The electrophilic nature of monochloroborane diethyletherate appears to be much greater than either borane-tetrahydrofuran or 9-BBN. In the hydroboration of alkenes a very high yield of the anti-Markovnikov product is afforded[51]. The use of dichloroborane-diethyletherate for hydroborations requires the addition of boron trichloride to the reaction mixture to displace ether from the complex and enhance the rate of the reaction[52] (37).



(37)

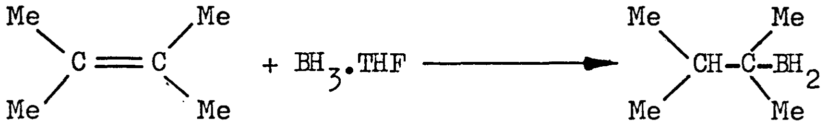
The dialkenylboron chloride afforded by the reaction of an acetylene and monochloroborane diethyletherate can be subjected to normal hydrolytic or oxidative procedures[53], or converted into a diene[54] (38).



a borinic acid (38)

4.3.6) Thexylborane

The treatment of borane-tetrahydrofuran with a molar quantity of 2,3-dimethyl-2-butene readily affords the monoalkylborane[55], commonly called thexylborane (39).



(39)

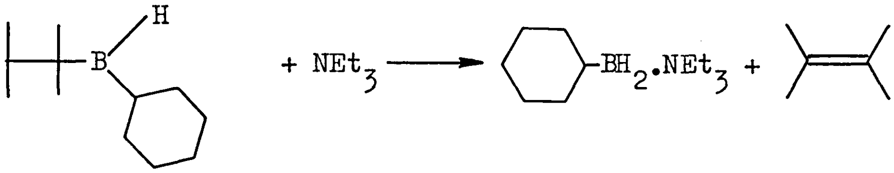
This monoalkylborane has excellent properties as a hydroborating agent[56] especially for dienes, since the cyclic boranes afforded can be converted to cyclic carbonyl compounds by routes discussed later.

In contrast, borane-tetrahydrofuran when allowed to react with dienes often leads to the formation of polymeric products[57]. Exceptions are the reactions with 2,4-dimethyl-1,4-pentadiene and, notably, 1,5-cyclooctadiene[35,36].

The reaction of two equivalents of an alkene with thexylborane leads, simply, to the dialkylthexylborane and similarly for acetylenes to the dialkenylthexylboranes[55]. Except for simple terminal alkenes the hydroboration procedure when carried out at low temperature yields the monoalkylthexylborane almost exclusively. Terminal haloalkynes also yield the monoalkenylthexylboranes[59].

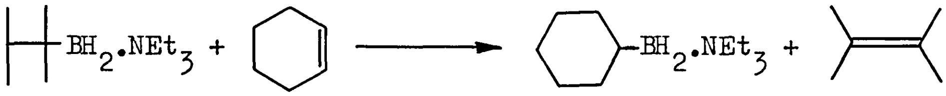
The monoalkyl or monoalkenylthexylboranes may subsequently be treated with alkenes or alkynes to yield the trialkylborane or trialkenylborane respectively.

Of general importance in the preparation of monoalkylboranes is the displacement of the thexyl group from an alkylthexylborane by triethylamine. The reaction is typified by cyclohexylthexylborane (40).



(40)

It has also been shown that moderately hindered alkenes will displace the thexyl group from thexylborane-triethylamine adduct yielding the monoalkylborane-adduct[60] (41).

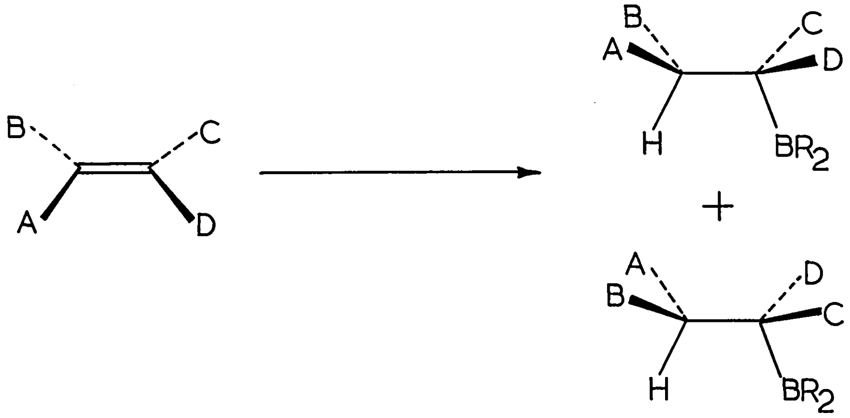


(41)

The adduct of thexylborane and N,N-diethylaniline has also been shown to be a useful hydroborating agent[61].

4.3.7) Optical activity resulting from hydroboration

All the hydroborating reagents discussed thus far have the property of cis-addition to the substrate. Oxidation of the resultant organoboranes proceeds with retention of configuration. The products although of known stereochemistry are usually enantiomeric mixtures since the initial addition may be from either side of the substrate molecule (42).

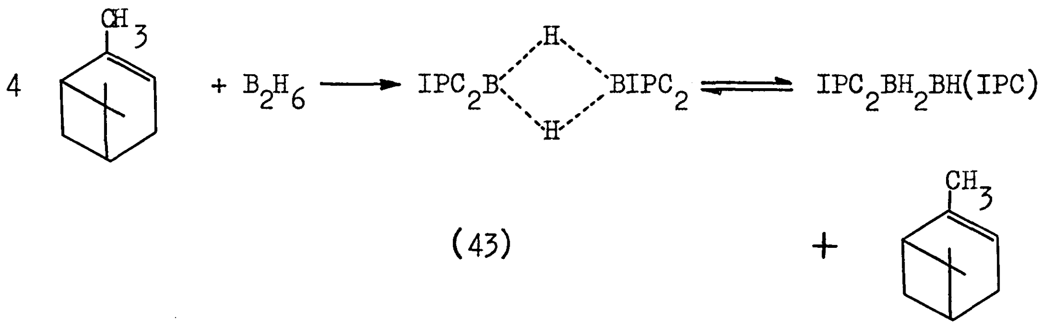


(42)

The ability to control the stereochemical effects of the hydroboration reaction is of obvious synthetic value. The previously discussed reagents go some way towards this goal in that the regioselectivity of reaction can be tailored to a degree by proper selection of the hydroborating reagent. Except for circumstances where the steric requirements of the substrate force a reaction to be mainly from one side of the molecule, optically active products of high enantiomeric purity are not usual. The reverse argument is employed in the utilisation of hindered reagents to obtain optically active products.

4.3.8) Diisopinocampheylborane

The hydroboration of α-pinene with borane-tetrahydrofuran readily yields diisopinocampheylborane (IPC_2BH) which exists in solution as a dimer. In the absence of an excess of α-pinene the dimeric tetraalkyl species is in equilibrium with a trialkyl diborane via elimination of α-pinene (43).

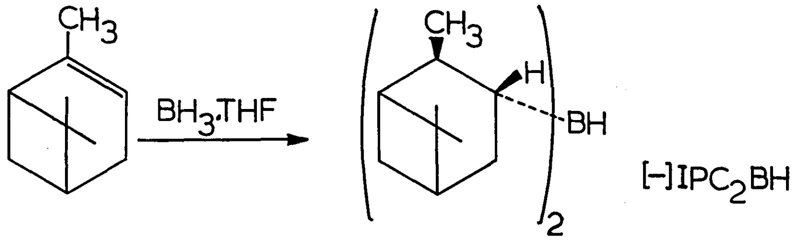


(43)

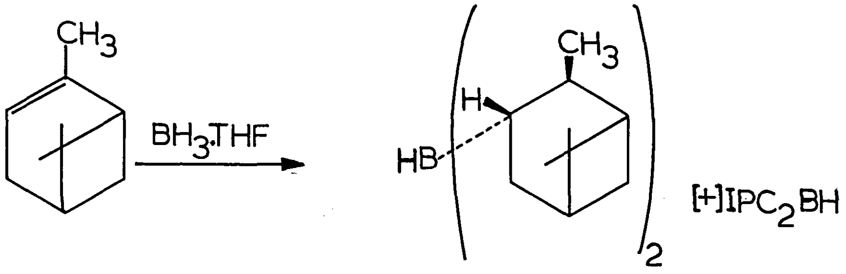
In tetrahydrofuran solvent an equilibrium value of approximately 10% α-pinene remains present under stoichiometric reaction conditions, whilst in diglyme the tetraalkyldimer is much less soluble[17] resulting in only 4% α-pinene present unreacted[62,63].

α-Pinene exists naturally as a mixture of optical isomers. Diisopinocampheylborane may be synthesized from both of the optical isomers of α-pinene (44, 45) and use of the resultant dialkylborane as a hydroborating reagent results in boranes, oxidation of which yields products which are of a high optical purity[62, 63].

The tetraalkylborane formed from optically impure α-pinene can be used as a hydroborating reagent, but following oxidation the products are found also to be of low optical purity. This is because the orientation of hydroboration is controlled by the stereochemistry of the reagent and substrate molecules.



(44)



(45)

Diisopinocampheylborane reacts readily with unhindered cis-alkenes. When the alkene is sterically hindered the displacement of α-pinene from the reagent may result in a consequently lower yield of the desired optically active product. Hindered alkenes have been found to react more predictably with monoisopinocampheylborane, which may be isolated as the tetramethylethylenediamine (TMED) adduct which is a stable solid[64]. Regeneration of the active reagent is achieved by treatment of the adduct with a stronger Lewis acid (boron trifluoride diethyletherate).

4.3.9) Borane-amine adducts

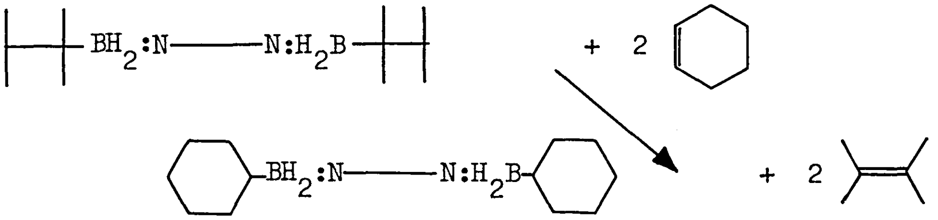
Because of the nature of the addition and the ability to control the orientation of addition by selection of a reagent, the reagents discussed have undoubted value in the synthesis of organoboranes.

The general disadvantage however is the requirement to prepare and use the reagents under an inert atmosphere in moisture free conditions. The availability of many of the reagents commercially has made the syntheses somewhat simpler. Adducts of borane with amines have the advantage of being stable solids at ambient temperatures and, generally, in the presence of dry air.

The borane-amines are generally less reactive than borane-tetrahydrofuran and require more vigorous reaction conditions than those employed with the latter reagent; for example refluxing in toluene solution compared with reaction temperatures of ambient, or more commonly 0°C.

The rate of reaction of borane-amines is believed to be limited by the dissociation of the adduct, and the addition of mineral or Lewis acids increases the rate of reaction. The choice of amine affects the adduct bond strength and faster reactions are apparent when the adduct is easily dissociated. A disadvantage of the reagents is the possibility of isomerization of the organoborane produced as a result of the necessary vigorous reaction conditions[14].

The adducts of monoalkylboranes[65] and dialkylboranes with tetramethylethylenediamine (TMED) are generally air stable and contain one or two moles of the borane. Regeneration of the monoalkylborane is readily achieved by addition of boron trifluoride[65] which is a stronger acceptor than the organoborane. Monoalkylboranes are generally not easy to synthesize unless a hindered borane, say 9-BBN, is utilised but complexes of TMED with thexylborane will allow displacement of tetramethylethylene by a less hindered alkene[67] (46).



(46)

$:N\text{-}N: \; = \; Me_2NCH_2CH_2NMe_2$

4.3.10) Borane-dimethylsulphide

The adduct of borane and dimethylsulphide has proven to be a good hydroborating reagent. The complex has a reactivity which parallels that of borane-tetrahydrofuran. Good solubility of the adduct in a range of solvents and solutions of a higher molar concentration limit than those possible for borane-tetrahydrofuran are combined with a long shelf life[68].

The dibromoborane-dimethylsulphide adduct is a useful reagent in the preparation of boronic acids and esters[69] (47).

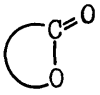
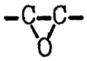
$$\begin{tikzcd} RCH{=}CH_2 + HBBr_2.SMe_2 \arrow[r] & RCH_2CH_2BBr_2.SMe_2 \arrow[d, "OH^-"] \\ & RCH_2CH_2B(OH)_2 \end{tikzcd} \qquad (47)$$

Similarly the chloroborane-dimethylsulphide adducts have reactivity paralleling those of the ether adducts[70] and they are commonly synthesized by the reaction of borane-dimethylsulphide and the appropriate trihaloborane-dimethylsulphide[71]. The use of haloborane-dimethylsulphide adducts as hydroborating reagents has been reported[72] as have procedures for the preparation of many of the alkylborane hydroborating reagents from borane-dimethylsulphide[73].

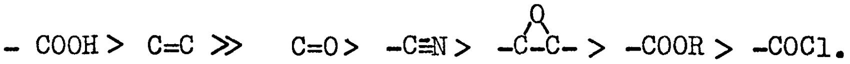
4.3.11) Reduction of functional groups

The reducing properties of borane-tetrahydrofuran are not solely confined to alkenes and alkynes. The reduction of many functional groups is possible with results as shown in Table 2. In general the use of borane-dimethylsulphide instead of borane-tetrahydrofuran gives the same outcome.

Table 2 Hydroboration-oxidation of common functional groups

Substrate		Product
$>C=C<$	alkene	alcohol
$-C\equiv C-$	alkyne	
$-C\begin{smallmatrix}=O\\ -H\end{smallmatrix}$	aldehyde	
$-C=O$	ketone	
$-C\begin{smallmatrix}=O\\ -Cl\end{smallmatrix}$	acid chloride	
$-C\begin{smallmatrix}=O\\ -OR\end{smallmatrix}$	ester	
	lactone	diol with ring cleavage
$-C\equiv N$	nitrile	amine
$-C\begin{smallmatrix}=O\\ -NR_2\end{smallmatrix}$	amide	amine
$>C=N-OH$	oxime	hydroxylamine
$>C=N-OR$	alkoxime	amine
$-CH=NR$	imine	amine
	epoxide	alcohol
$\begin{matrix}-C=O\\ \vert\\ O\\ \vert\\ -C=O\end{matrix}$	acid anhydride	alcohol with cleavage

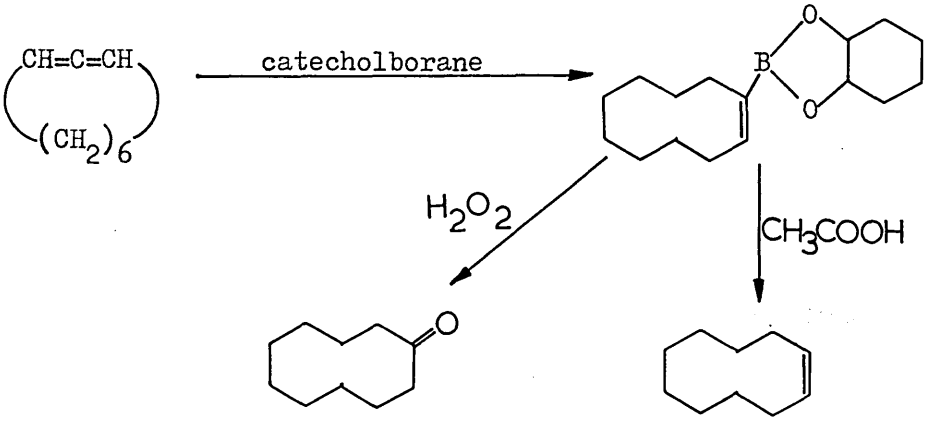
For borane-tetrahydrofuran the general order of reactivity[74] is



$$-\mathrm{COOH} > \mathrm{C{=}C} \gg \mathrm{C{=}O} > -\mathrm{C{\equiv}N} > -\overset{O}{\mathrm{C{-}C}}- > -\mathrm{COOR} > -\mathrm{COCl}.$$

The hydroboration of allenes with 9-BBN, which has a high selectivity for the least hindered terminal carbon, does not cleanly result in monohydroboration and a mixture of products occurs[75].

The use of catecholborane with cyclic allenes results in attack on the centre carbon affording a *Z*-cycloalkenylboronic ester, which by protonolysis or oxidation affords an alkene or ketone respectively[76] (48).



(48)

At this point is is of interest to note that for the reduction of functional groups a number of other reagents with useful properties are available.

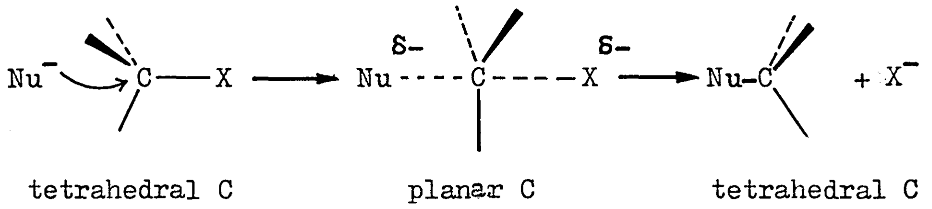
The amine-boranes of which a reasonable number are commercially available (Aldrich Chemical Co.) are capable of reducing ketones, aldehydes and acid chlorides. The ability to use as a reaction solvent water or an alcohol, which would react with borane-tetrahydrofuran, is of great advantage in some instances. The reduction of Schiff-bases is possible with these reagents[77].

Sodium bis(2-methoxyethoxy) aluminium hydride has a high reactivity similar to that of lithium aluminium hydride but is much more easily handled because of its higher solubility in hydrocarbon solvents. The reagent will reduce ketones, aldehydes, acids, acid chlorides and esters to alcohols, nitriles and oximes to amines and alkyl/aryl halides to hydrocarbons. A particular advantage of this reagent is the ability to reduce α, β-unsaturated carbonyl compounds to alcohols without reduction of the alkene function (49).

$$R-C=CH-\overset{\overset{O}{\|}}{C}-R \longrightarrow R-CH=CH-CH(OH)R$$

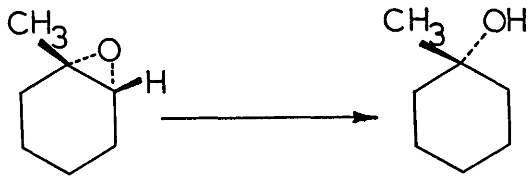
(49)

A related reagent, lithium triethylborohydride has been found to be a powerful nucleophile for the S_N2 displacement of halides. The S_N2 reaction is bimolecular substitution and involves backside attack of the nucleophile on the substrate giving a complete inversion of configuration (50). The rate law for such reactions involves the concentrations of both reactants. The stereochemical implications are that the



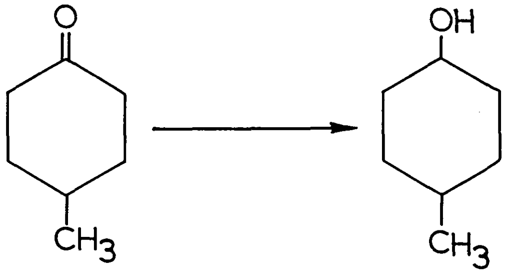
(50)

reaction will result in a change of enantiomeric form of the substrate. The reagent will not displace aryl halides but is known to give stereoselective ring opening of epoxides[78,79] (51).



(51)

Lithium and potassium tri-sec-butylborohydrides are capable of stereoselective reductions, giving mainly cis-products in high yield (52) and have found use in the synthesis of prostaglandins[80,81]. Both reagents are air and moisture sensitive.



(52)

$LiBH(CH\ CH_3.CH_2CH_3)_3$	80.5% cis
$K\ BH(CH\ CH_3.CH_2CH_3)_3$	88% cis
$NaBH_4$	18% cis

Sodium cyanoborohydride will reduce aldehydes and unhindered ketones whilst not reducing other functional groups[82,83]. Tetrabutylammonium cyanoborohydride is even more selective, allowing the reduction of aldehydes in the presence of almost all other functional groups[84]. When used in the reduction of the iminium group ($\rangle C=\overset{+}{N}\langle$) reaction is faster than with carbonyl groups and effects reductive ammination in high yield under mild acid conditions.

The organoboranes available by use of the hydroborating reagents described have come to be recognized as a starting point for further synthetic procedures rather than an end product. The reactions of organoboranes allow synthesis of many compounds which would be available only with difficulty by other synthetic routes.

4.4) Reactions of organoboranes

Organoboranes are easily synthesised using the reagents previously described. One of the factors which has stimulated development of such reagents is the synthetic utility of the organoboranes themselves. Discussion of the hydroboration reaction in many general texts is confined to the products obtainable solely by oxidation. This view does not emphasise the wide range of reactions possible with organoboranes which are described briefly below.

4.4.1) Isomerization

Numerous isomerization reactions occurring at ambient temperature have been reported[89,90,91] but in general heating is required, usually to moderate temperatures (70°-200°C).

Terminal carbon-boron bonds are most thermodynamically favourable and consequently the isomerization of internal alkenes results in the formation of terminal alkylboranes, for example (53).

$$\mathrm{Et_2C{=}CHMe} \xrightarrow[\text{2) heat}]{\text{1) } \mathrm{BH_3.THF}} \mathrm{(Et_2CHCH_2CH_2)_3B} \qquad (53)$$

Following isomerization, boron-tertiary carbon bonds are not present and the distribution of reaction products indicates that primary carbon-boron bonds are more strongly preferred than secondary carbon-boron bonds[29,85].

Experimental observation shows that upon isomerization a distribution of possible organoboranes is achieved with a preponderance of the least hindered borane, excepting that isomerization does not proceed past tertiary carbon atoms (54).

$$\mathrm{Pr^i_3{-}B} \xrightarrow[\text{8 hrs.}]{160^\circ\mathrm{C}} \underset{83\%}{\mathrm{Pr^n_3{-}B}} + \underset{16\%}{\mathrm{Pr^n_2{-}B{-}Pr^i}} + \underset{1\%}{\mathrm{Pr^n{-}B{-}Pr^i_2}} \qquad (54)$$

Originally the mechanism of reaction was considered to involve a rapid cis-elimination followed by re-addition which would be consistent with the reverse mechanism of hydroboration proposed.

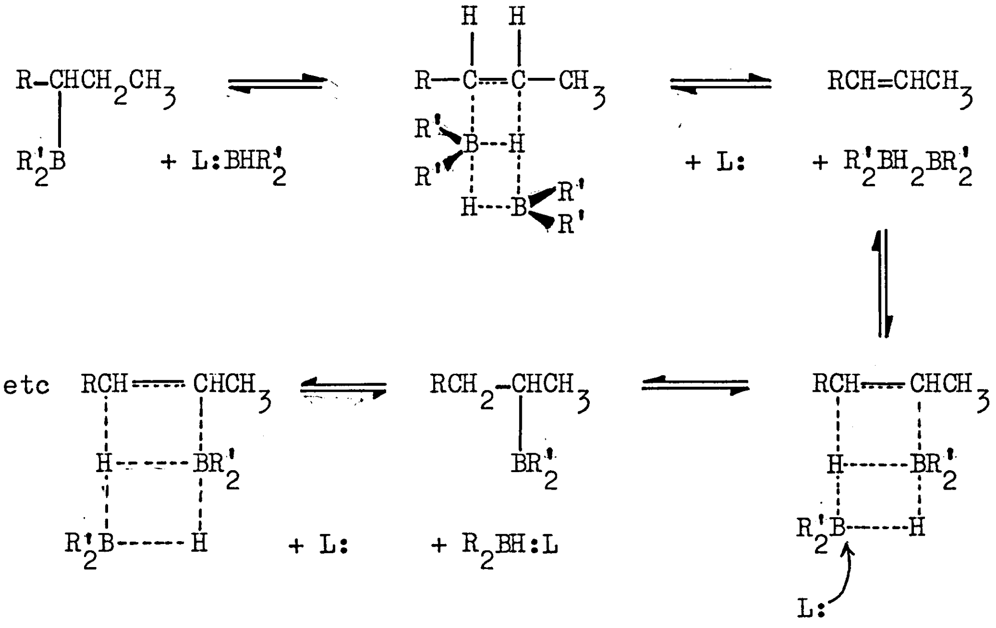
However, such a mechanism does not explain the experimental observations. In the presence of catalytic quantities of a borane-ether adduct or compounds containing B-H bonds the isomerization proceeds at an enhanced rate[86] and converselythe presence of an excess of the alkene reduces the reaction rate.

For example, isomerization of the alkylborane produced from 1-hexene carried out in the presence of a slight excess of the hydroborating reagent affords after oxidation, primary, secondary and γ-alcohols in the ratio 94:4:2. However the corresponding reaction of the organoborane from 2-hexene affords the alcohols in the ratio 13:64:23 when the alkene is in excess[86].

The production of secondary and γ-alcohols in the first case indicates the existence of an equilibrium between the possible products. The second example indicates that the isomerization from one of the possible organoboranes (in the first example) is prevented from occurringby an excess of the alkene even though the predominant organoborane present is not that most favoured under isomerization conditions. In particular this observation cannot be explained by the mechanism initially suggested.

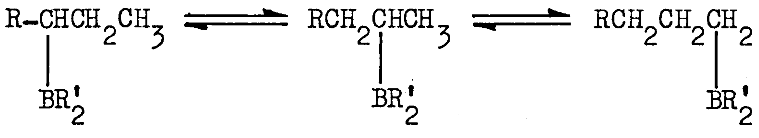
The presence of an excess of the hydroborating reagent or compounds containing B-H bonds implies that the reaction to form trialkylboranes will not go to completion and that tetraalkyldiboranes may be present in solution.

The mechanism postulated to explain the experimental observations involves the formation of a transition state which contains a tetraalkyldiborane coordinated to the alkene molecule which is undergoing isomerization. Subsequent equilibria exist between the possible alkenes and tetraalkyldiboranes via the suggested transition state. The formation of the trialkylboranes from the transition state probably involves the coordination of the solvent with a dialkylborane moeity and loss of this adduct. Coordination of the alkene to form the transition state is aligned so as to produce the thermodynamically most favoured borane (55, 56).



(55)

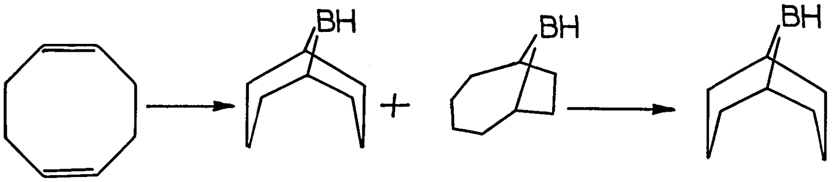
so that the equilibria correspond to:-



$$\underset{BR'_2}{R\text{-}CH}CH_2CH_3 \rightleftharpoons RCH_2\underset{BR'_2}{CH}CH_3 \rightleftharpoons RCH_2CH_2\underset{BR'_2}{CH_2}$$

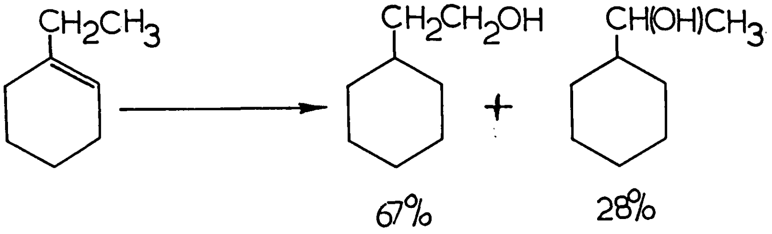
(56)

The isomerization of cyclic alkenes is also possible and of special value in the synthesis of 9-BBN. The hydroboration of 1,5-cyclooctadiene yields a mixture of 1,5 and 1,6-addition products which on heating are isomerized exclusively to the 1,5 product which is 9-borabicyclo [3.3.1] nonane (9-BBN) (57).



(57)

When the cyclic alkene contains alkyl sidechains, migration of the boron atom takes place towards the terminal position. The exact products depend upon the sidechain length and its nature[87] (58).

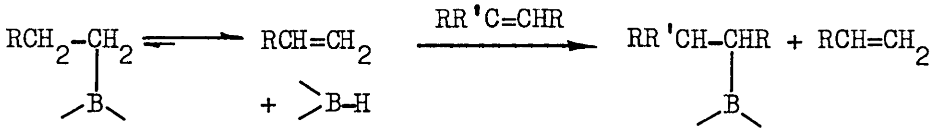


(58)

Cyclic organoboranes resulting from the hydroboration of dienes undergo isomerization giving products, the nature of which are controlled by the thermodynamic stability of the ring system involving the boron atom. In general six-membered rings are most favoured[29,88]. As a consequence of the proposed reaction mechanism, isomerization of optically active organoboranes which have an asymmetric carbon atom as a result of hydroboration involves the possibility of racemization[92].

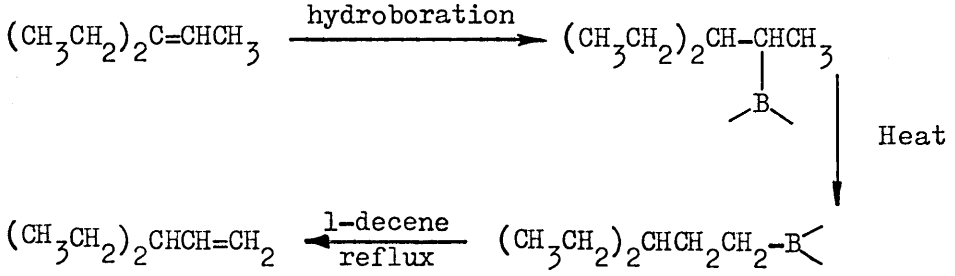
4.4.2) Displacement

The mechanism of reaction by which isomerization is considered to occur, as previously discussed, is considered to involve the formation of a tetraalkyldiborane. The deliberate introduction of an alkene of higher reactivity than the original hydroborated alkene into the reaction causes a competitive reaction resulting in the cis-displacement of the alkyl groups originally attached to boron[13,93]. The higher the thermodynamic stability of the liberated alkene, the higher the rate of displacement. From this the choice of less stable alkenes and displacement agents follows. In addition the displacing alkene should be of lower volatility than that being displaced, allowing the recovery by distillation of the more volatile alkene from the reaction mixture. Following from the law of mass action, an excess of displacing agent is used in the displacement reaction and, generally, no isomerization of the alkylborane occurs[94] implying a very low rate of reverse addition to the original alkene (59).

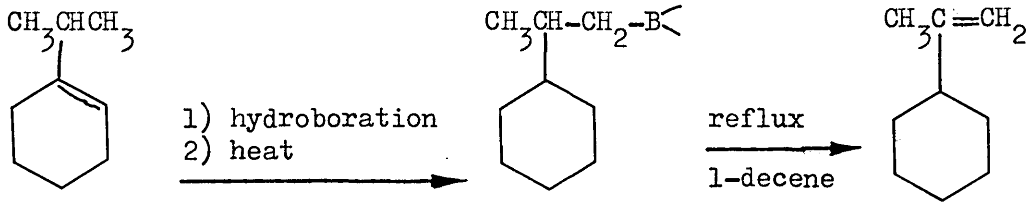


$$RCH_2\text{-}\underset{\diagup B \diagdown}{\underset{|}{CH_2}} \rightleftharpoons \begin{matrix} RCH{=}CH_2 \\ + >B\text{-}H \end{matrix} \xrightarrow{RR'C{=}CHR} RR'CH\text{-}\underset{\diagup B \diagdown}{\underset{|}{CHR}} + RCH{=}CH_2 \qquad (59)$$

By carrying out the isomerization and displacement reactions consecutively, a carbon-carbon double bond may be moved to the terminal position even from within a cyclic alkene to a side chain (60, 61).



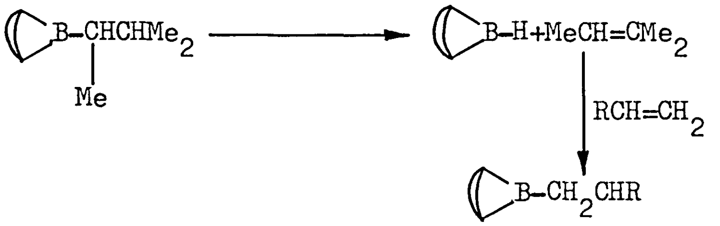
$$\begin{matrix} (CH_3CH_2)_2C{=}CHCH_3 & \xrightarrow{\text{hydroboration}} & (CH_3CH_2)_2CH\text{-}\underset{\diagup B \diagdown}{\underset{|}{CHCH_3}} \\ & & \Big\downarrow \text{Heat} \\ (CH_3CH_2)_2CHCH{=}CH_2 & \xleftarrow[\text{reflux}]{\text{1-decene}} & (CH_3CH_2)_2CHCH_2CH_2\text{-}B< \end{matrix} \qquad (60)$$



(61)

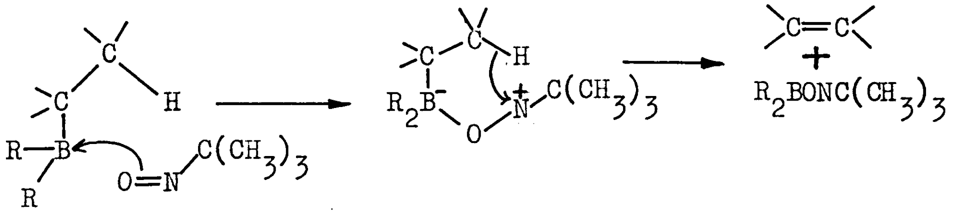
Since terminal alkenes are thermodynamically less stable than internal alkenes, which are stabilized by inductive effects, this reaction sequence is known as contrathermodynamic isomerization[94,95].

B-alkyl-9-BBN derivatives undergo exchange reactions of the alkyl group with olefins, without the occurrence of isomerization[96] (62).



(62)

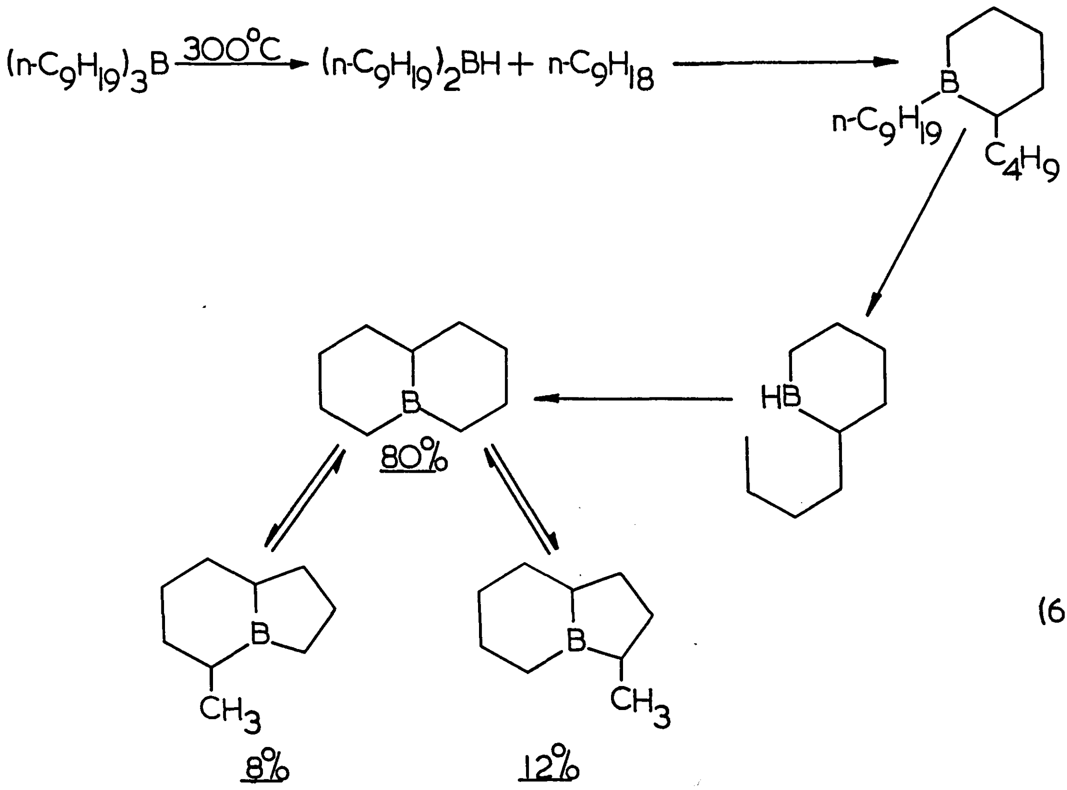
The cis-elimination of alkenes from organoboranes may also be effected by 2-methyl-2-nitrosopropane but does not readily proceed past the elimination of one alkyl group[97] (63).



(63)

4.4.3) Cyclization

The mechanism of isomerization of organoboranes, as discussed previously, involves the formation of B-H bonds and a resultant dialkylborane. When the alkyl groups have carbon chain lengths of four or more, the possibility of elimination of hydrogen and the formation of a cyclic organoborane (a boracyclane) occurs. The efficiency of this reaction is poor since it involves discarding at least one-third of the original alkene during formation of the dialkylborane even though overall conversion of trialkylborane to boracyclane is usually high. The formation of six-membered rings is most favoured thermodynamically and results, where the carbon-chain length is greater than five, in rings having side chains. Subsequently where the side chain is of sufficient length a further elimination and cyclization may occur yielding a bicyclic compound. Such reactions can only achieve a maximum of 33% efficiency if conducted from a uniform trialkylborane[28]. Furthermore in the case of branched alkyl substituents the ease of cyclization is generally decreased as the degree of substitution of the 5-position carbon increases. Although the six-membered rings are most thermodynamically favoured an equilibrium is found to exist with less favoured products (64).

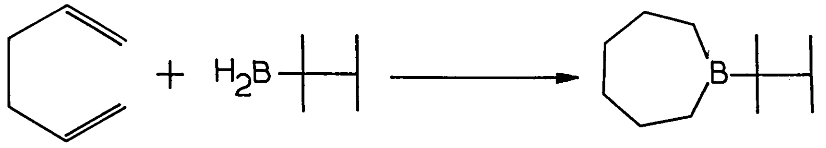


(64)

The cyclic products can arise either as a result of ring formation or via isomerization under the conditions of reaction.

The availability of dialkylboranes via thexylborane allows the more efficient synthesis of boracyclanes. The thexyl group is of too short a carbon chain length to take part in cyclization and all of the original alkene is available for cyclization, none having been lost in formation of a dialkylborane (i.e. from R_3B).

An alternative route to boracyclanes via hydroboration of dienes or trienes offers some advantages over the high temperature route discussed above[98], for example (65, 66).



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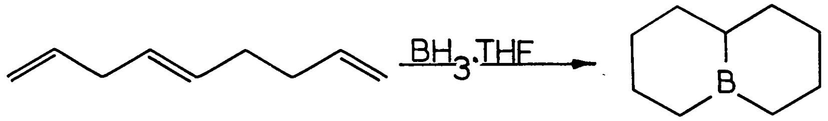
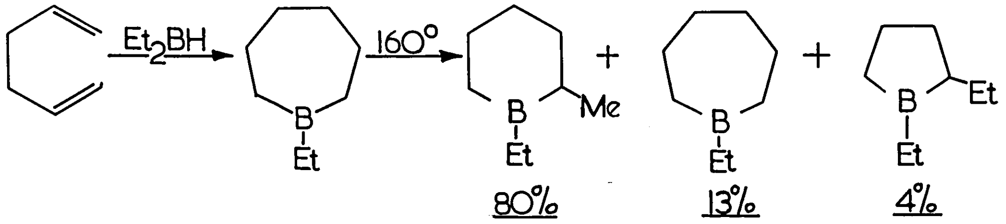


(66)

Although the formation of six-membered rings is most favoured, it may be thermodynamically more favourable to form rings of other sizes where bonding to substituted carbon-atoms is involved[28,88] (67, 68).



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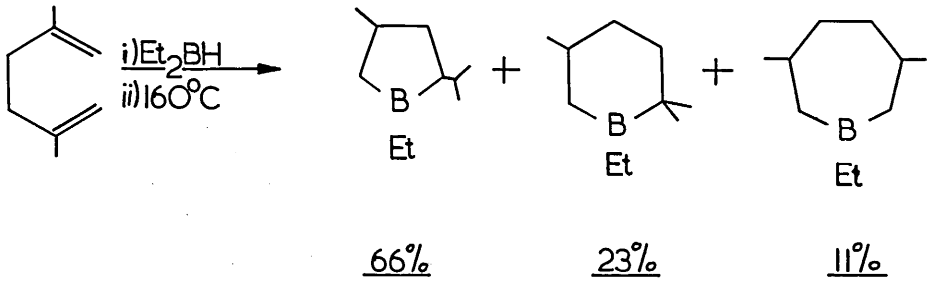
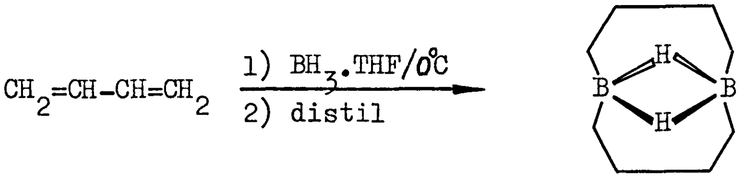
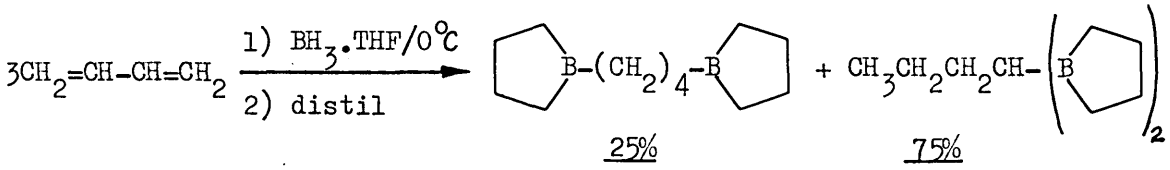


(68)

The use of borane-ether adducts in the formation of boracyclanes can lead to complex products depending upon the stoichiometric conditions[99,22,100] (69,70).



(69)

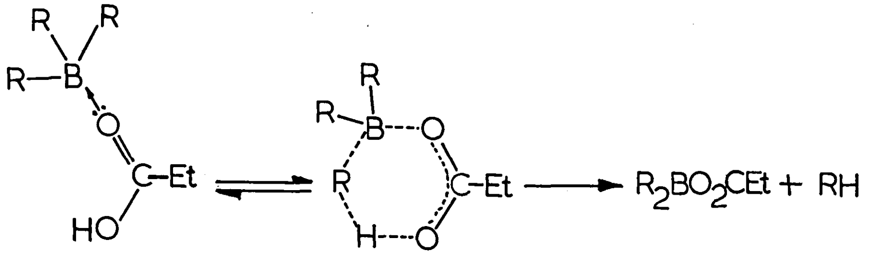


(70)

4.4.4) Protonolysis

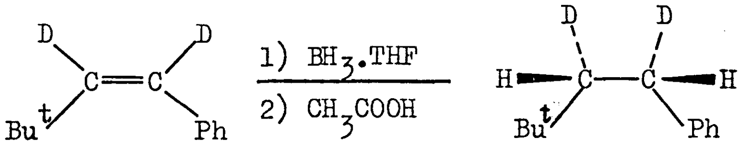
Treatment of organoboranes with propanoic acid under reflux conditions affords the alkane in good yield[101]. The ease of protonolysis of the organic group follows the order primary > secondary > tertiary.

Loss of the first group in R_3B is much faster than for subsequent groups and is attributed to a reduction in Lewis acid character of boron resulting from the boron-oxygen bond formed. The slow protonolysis of tertiary organoboranes is considered to result from steric hindrance of the rate limiting transition state proton transfer required by the proposed mechanism[103,104] (71).



(71)

Although the reaction was considered to proceed with retention of configuration[105,106] this was not definitively shown to be so until recently[107] (72,73). Vinylboranes with acid sensitive substituents may be protonated using silver ammonium nitrate to avoid decomposition[102].



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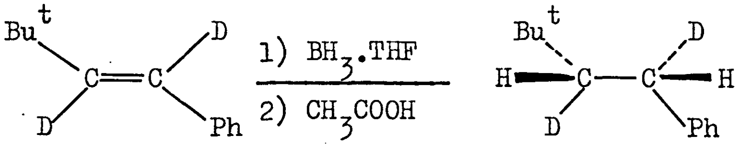


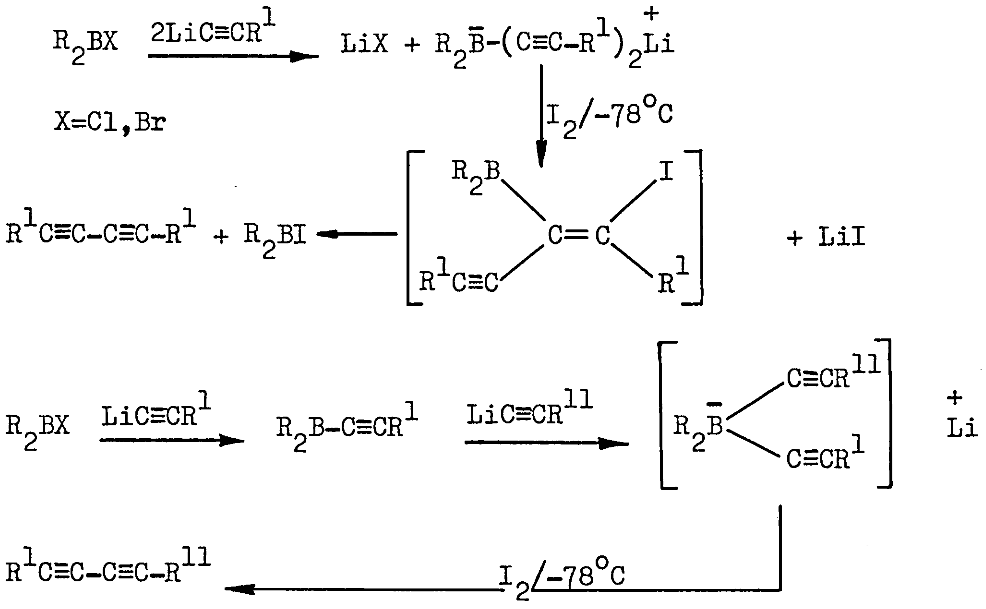
(73)

The protonolysis reaction effectively allows stereospecific cis-hydrogenation via hydroboration without the use of noble metal catalysts, which are often difficult to tailor to specific applications. By means of deuterioacids the stereospecific deuteration of unsaturated compounds may be achieved[105,27].

Control of the stoichiometry of the hydroboration of diynes leads to alkenylboranes which on protonolysis afford cis-enynes or cis, cis-dienes[108] or cis, cis-deuterated alkenes[109]. The availability of symmetrical diynes via oxidative coupling of terminal alkynes[110] (74) and

$$2RC\equiv CH \xrightarrow[\text{Pyridine/acetone}]{O_2/CuCl} RC\equiv C\text{-}C\equiv CR \qquad (74)$$

unsymmetrical diynes via lithiated alkynes $(Li\text{-}C\equiv C\text{-}R)^{111,112}$ allows the synthesis of many derivatives (75).



(75)

4.4.5) Halogenolysis

The direct reaction of organoboranes with halogens is possible only under very vigorous conditions[113] but in the presence of alkali a rapid reaction occurs[114] (76),

$$(RCH_2CH_2)_3B + 2I_2 + 2NaOH \longrightarrow 2RCH_2CH_2I + RCH_2CH_2B(OH)_2 + 2NaI \qquad (76)$$

but this has the disadvantage of low efficiency. For terminal alkenes a high efficiency may be attained by use of the hydroborating agent disiamylborane (77).

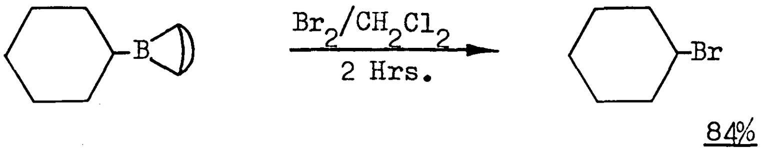
$$RCH_2CH_2BSia_2 + I_2 + NaOH \longrightarrow RCH_2CH_2I + Sia_2BOH + NaI \qquad (77)$$

This reaction can be applied widely to synthesize alkyl halides from alkenes. When bromine is used water must be avoided as, in the presence of alkali, hypobromite is produced and converts the organoboranes to alcohols. To avoid this problem sodium methoxide in methanol is used as base[115].

For primary alkylboranes all the organic groups bonded to boron are converted to primary halides (78).

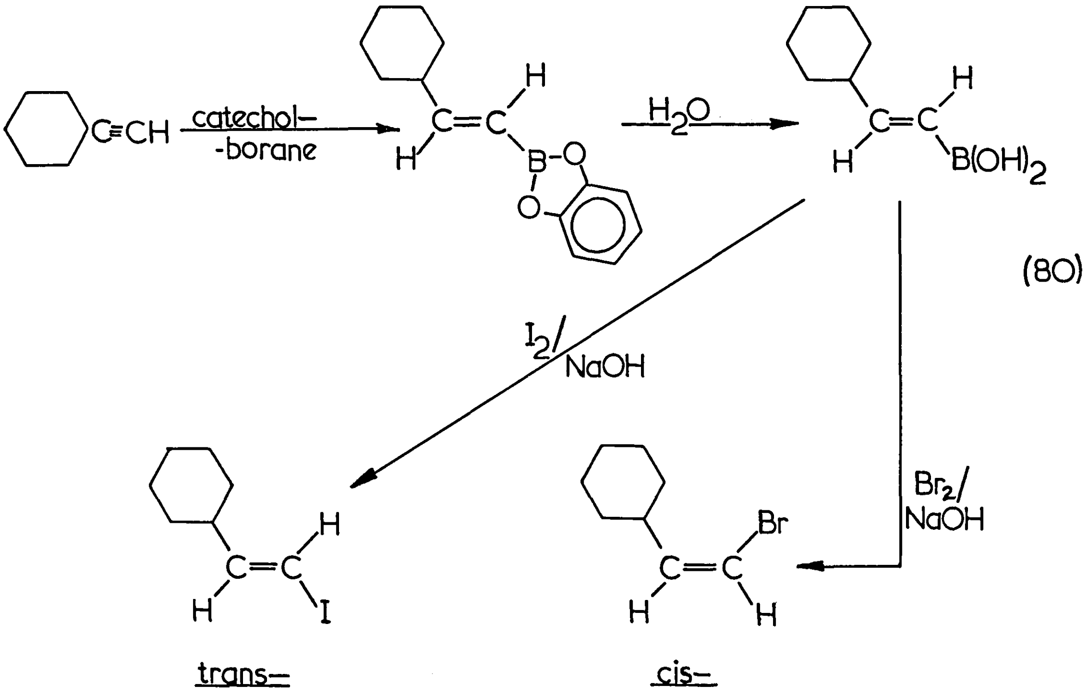
$$R_3B + 3Br_2 + 4\,NaOH \longrightarrow 3RBr + 3NaBr + NaB(OH)_4 \qquad (78)$$

Synthesis of secondary halides may be achieved via hydroboration with 9-BBN and subsequent reaction with bromine[116] (79).



(79)

The stereospecific synthesis of halo alkenes is possible by reaction of iodine or bromine in the presence of a base with an alkenyldialkylborane. The hydroboration of terminal alkynes with catecholborane and subsequent hydrolysis yields the alkylboronic acid which when treated with halogen and base yields the haloalkene[117,118] (80).



(80)

Treatment of an alkenyldialkylborane, as opposed to the boronic acid, with iodine and base affords exclusively the product of cis-alkyl transfer[119], rather than the haloalkene. This reaction has found use in the synthesis of prostaglandin analogues[120]. Conversly treatment with cyanogen bromide affords the product of trans-alkyl transfer[121]. Whilst not strictly halogenolysis these latter related reactions illustrate the importance of the initial choice of hydroborating reagent to the product afforded by the reactions.

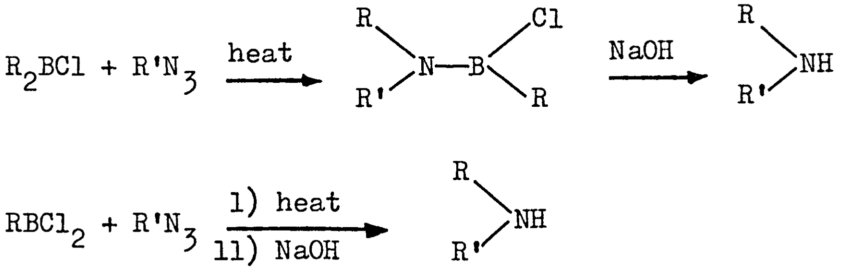
4.4.6) Ammination

Organoboranes will react with chloramine affording primary amines in moderate yield[122] (81).

$$R_3B + 3ClNH_2 \longrightarrow 3RNH_2 + BCl_3 \qquad (81)$$

By use of fresh hydroxylamine-o-sulphonic acid[123] the yield of amine is much improved[122]. The aminations proceed with retention of the configuration of hydroboration.

Reaction of the chloroorganoboranes and trialkylorganoboranes with organic azides afford mixed secondary amines[124,125] with retention of configuration (82).

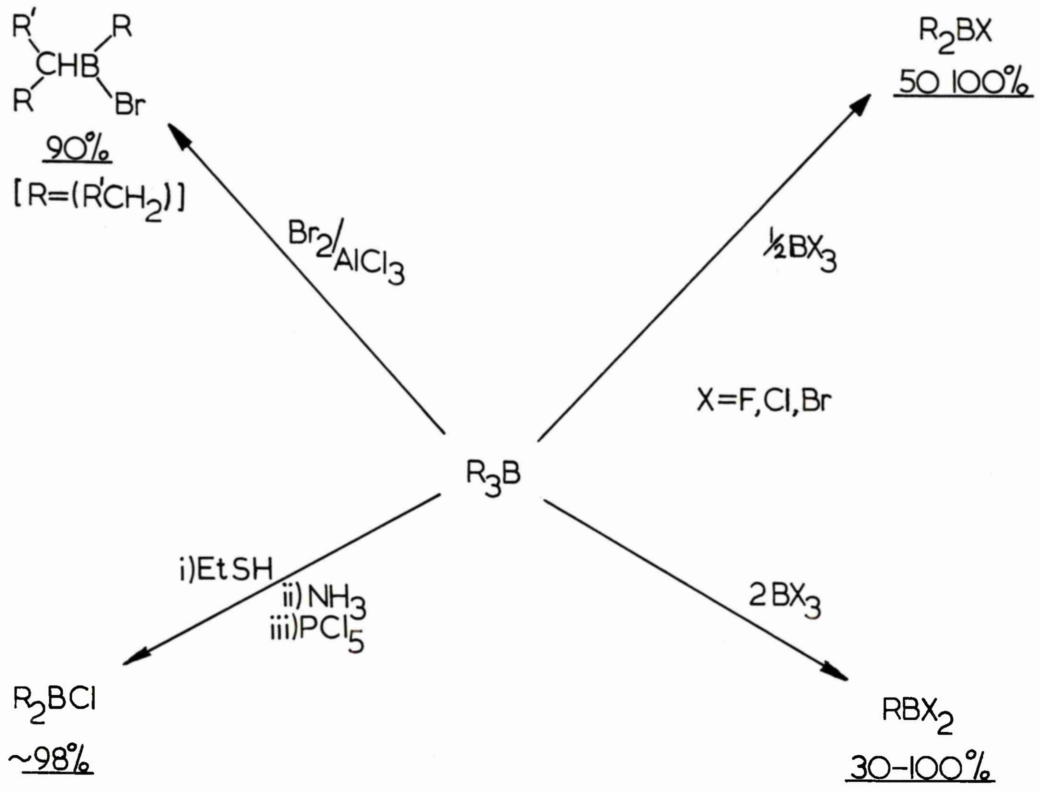


(82)

The use of the dichloroalkylborane is less wasteful in the conversion of alkyl to amine.

Azides formed from alkenes by addition of IN_3 retain their configuration and, upon subsequent reaction with dichlorophenylborane form aziridines, again with retention of configuration[126]. It is therefore possible to predict the stereochemistry of aziridines synthesized by this route.

The haloorganoboranes used in this synthesis are available in moderate to good yield from organoboranes[127,128,129] (83). Alternative routes via tetraalkyltin or boron trichloride are feasible[130,131] (84,85).



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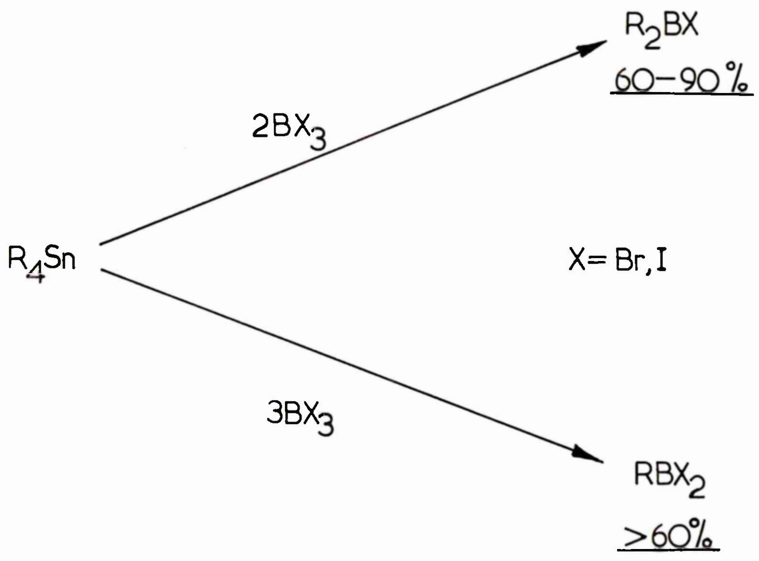


(84)

$$BCl_3 \xrightarrow[Et_2O]{LiBH_4} H_2BCl.Et_2O \xrightarrow{alkene} \underset{\underline{>80\%}}{R_2BCl} \qquad (85)$$

4.4.7) Metallation

Primary organoboranes react quickly and in high yield with mercury (II) acetate[132,133] at ambient temperature affording alkylmercury (II) acetates which may be converted to dialkylmercurials[134] (86).

$$R_3B \xrightarrow{(CH_3COO)_2Hg} RHgOOCCH_3 \xrightarrow[B(OOCCH_3)_3]{Zn} R_2Hg \qquad (86)$$

The mercuration of vinyl derivatives proceeds stereospecifically and a wide range of vinyl substrates are available from the hydroboration of alkynes[135].

Trialkylboranes will react in solution with a suspension of some metal oxides to yield the metal alkyl[132], for example (87).

$$2R_3B + 2PbO \xrightarrow{\bar{OH}/H_2O} R_4Pb + Pb + 2RB(OH)_2 \qquad (87)$$

The coupling of alkyl groups by the reaction of alkaline silver nitrate with trialkylboranes is considered to involve metallation by silver and a subsequent alkyl transfer with deposition of metallic silver. When mixed alkylboranes are used, the ratio of products follows a statistical distribution[136,137].

4.4.8) Oxidation

Hydroboration reactions are usually performed under an inert atmosphere because the organoboranes produced react readily with oxygen, affording after hydrolysis, mixtures of hydroperoxides and alcohols.

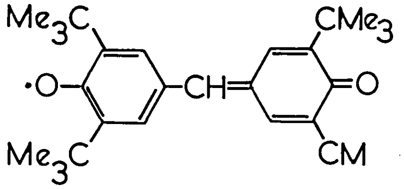
By careful introduction of a known amount of oxygen the oxidation may be controlled to yield predominantly $RB(OOR)_2$ which on alkaline hydrolysis affords the alcohol[16] (88).

$$\begin{tikzcd}
R_3B \arrow[r, "2O_2"] \arrow[dr, "1.5O_2"'] & RB(OOR)_2 \arrow[r, "3H_2O/NaOH"] & 2ROH + ROOH + NaB(OH)_4 \\
& R_{1.5}B(OOR)_{1.5} \arrow[r, "NaOH/H_2O"] & 3ROH
\end{tikzcd} \qquad (88)$$

The reaction proceeds via a free radical mechanism and, as expected, with a loss of stereospecificity[138]. The configuration of the major products is a result largely of thermodynamic constraints.

Studies have shown that although the reaction is initially very fast the three carbon-boron bonds are oxidised with increasing difficulty[16,139].

Although hydroquinone, a radical scavenger, failed to slow the oxidation reaction[140] a better scavenger, galvinoxyl (89), showed a large effect[141,142] and on this basis a homolytic mechanism was proposed[143,144] (90).



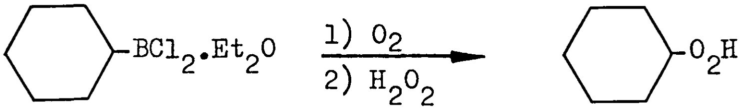
" Galvinoxyl" (89)

$$\begin{aligned}
&R_3B + O_2 \longrightarrow R\cdot \\
&R\cdot + O_2 \longrightarrow RO_2\cdot \\
&RO_2\cdot + R_3B \longrightarrow RO_2\text{-}BR_2 + R\cdot \\
&\left.\begin{aligned}
&2RO_2\cdot \longrightarrow \\
&RO_2\cdot + R\cdot \longrightarrow \\
&2R\cdot \longrightarrow
\end{aligned}\right\} \text{inactive products}
\end{aligned} \qquad (90)$$

As a means of obtaining alcohols this oxidation is inferior to alkaline hydrogen peroxide. By reaction of the intermediate $RB(OOR)_2$ with peroxide in the absence of base a mixture of alcohol and hydroperoxide is obtained. The hydroboration and oxidation are carried out in the normal ethereal solvents, and, following the addition of hexane, the potassium salt of the hydroperoxide can be extracted into strong aqueous alkali[145]. The reaction can only achieve a theoretical maximum yield of 66% based upon the initial alkene hydroborated (91).

$$RB(OOR)_2 + H_2O_2 + 2H_2O \longrightarrow ROH + 2RO_2H + B(OH)_3 \qquad (91)$$

Oxidation of alkyldichloroboranes raisesthe practical yield[118] (92).



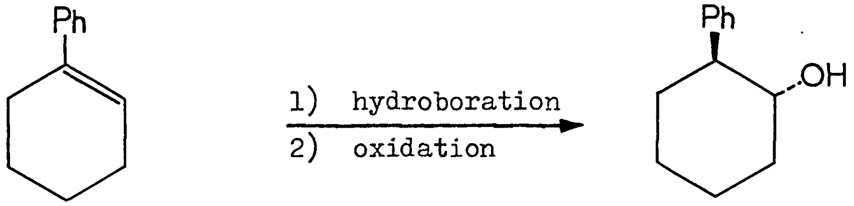
93%

(92)

The use of equimolar amounts of hydrogen peroxide in the oxidation of organoboranes in neutral solution results in the production of a mixture of hydrocarbons and a small amount of the alcohol. The oxidation, as previously, has been considered to follow a free radical mechanism[146] (93).

$$\begin{array}{lll}
R_2BO_2H + R_3B & \longrightarrow & R_2BO\cdot + R\cdot + R_2BOH \\
R_2BO\cdot + HO\text{–}OH & \longrightarrow & R_2BOH + HO_2\cdot \\
 & \searrow & R_2BOOH + \cdot OH \\
R_3B + \cdot O_2H & \longrightarrow & R_2BO_2H + R\cdot \\
R\cdot + \cdot OH & \longrightarrow & ROH
\end{array} \qquad (93)$$

The oxidation of trialkylorganoboranes to alcohols is most commonly achieved with alkaline hydrogen peroxide[147] _in situ_ affording the anti-Markovnikov hydration product of the alkene hydroborated[17] (94,95).



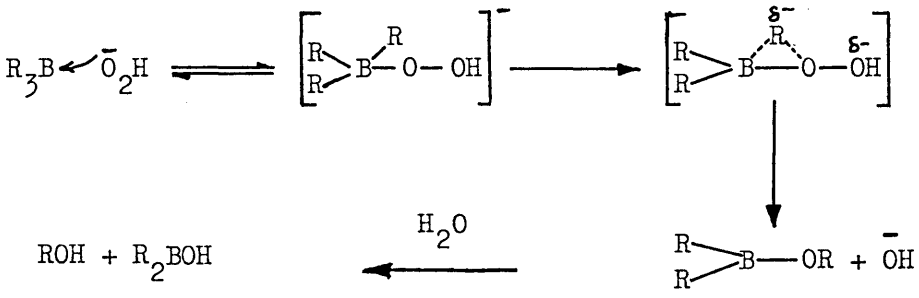
(94)

$$RCH_2CH{=}CH_2 \longrightarrow RCH_2CH_2CH_2OH \qquad (95)$$

Vinylic organoboranes derived from acetylenes also are oxidised to the corresponding ketone[27,46], as are the boronic acids produced by hydrolysis of the catechol-vinyl borane.

The oxidation of the alkylboronic acids is considered to proceed via an S_E2 mechamism which is base catalysed[148] (96).

$$H_2O_2 + \overset{-}{O}H \text{ ——— } H\overset{-}{O}_2 + H_2O$$



(96)

The remaining two boron-carbon bonds are oxidised consecutively by the same mechamism.

The direct production of ketones by treatment of organoboranes with chromic acid provides a route from alkenes via hydroboration[149, 150]. In general the use of diethylether as solvent favours the formation of the ketone. The oxidation of alkylboronic acids at higher pH has been found to lead to alcohol formation[151].

Amine-N-oxides readily oxidise organoboranes containing primary or secondary alkyl, aryl, alkenyl or cycloalkenyl-boron bonds, but not alkynyl-boron bonds[152] (97,98).

$$R_3B + 3\ Me_3NO \longrightarrow (RO)_3B + 3\ Me_3N \qquad (97)$$

$$(RO)_3B + 3MeOH \longrightarrow 3ROH + (MeO)_3B \qquad (98)$$

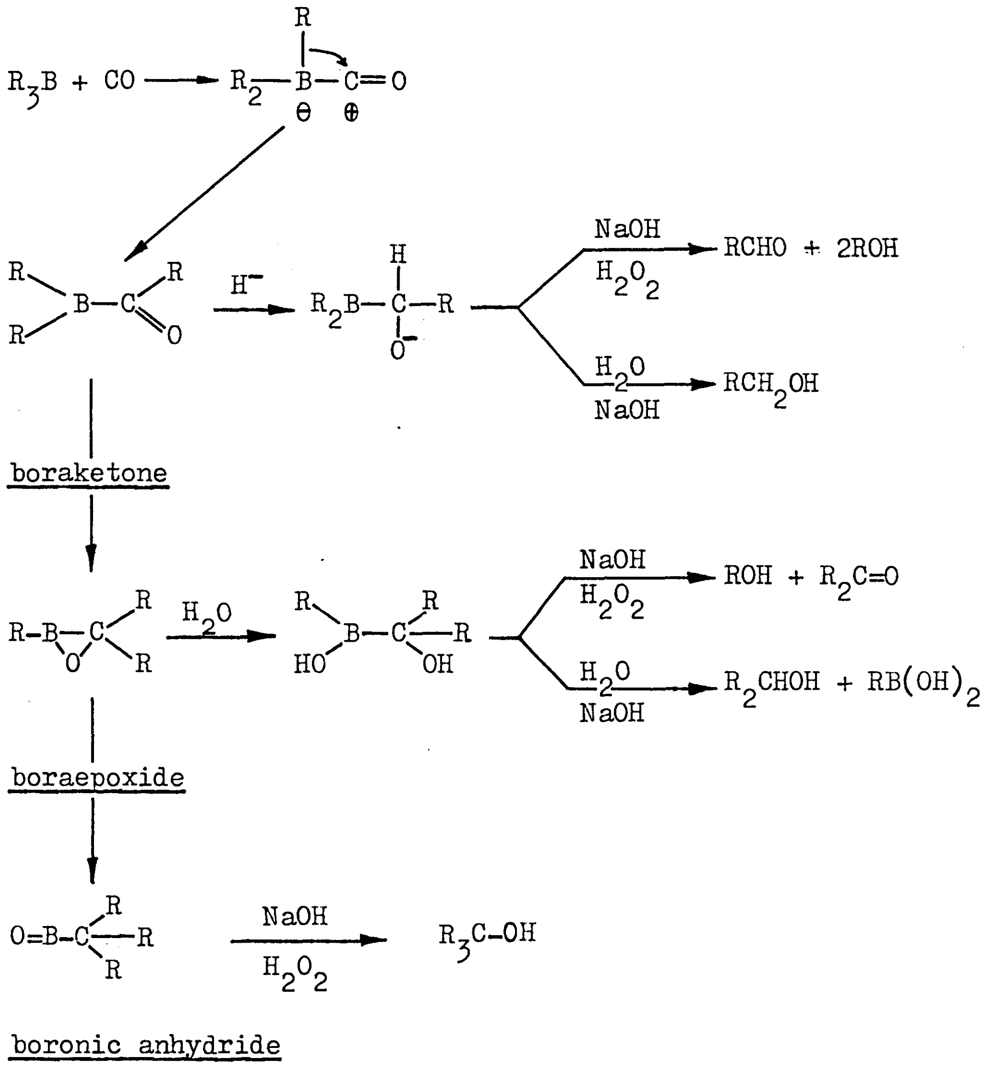
The reaction is essentially quantitative and forms the basis of an analytical procedure[153]. The reaction is considered somewhat milder than alkaline hydrogen peroxide oxidation and proceeds with successively slower oxidation of the three boron-carbon bonds[153].

The use of sodium hypochlorite as an oxidant at ambient temperature leads to the corresponding alcohols in good yield[154].

4.4.9) Carbonylation

Trialkylboranes undergo nucleophilic attack by carbon monoxide and subsequent rearrangement of the intermediate. The initial studies were carried out using very high pressures (ca 700 bar) and moderately high temperatures, up to 150°C[155]. Later work showed that an almost quantitative reaction occurs in diglyme solvent at 100-125°C and atmospheric pressure[156].

The nature of the products is controlled by the extent to which the migration of alkyl groups is permitted[156] (99).



(99)

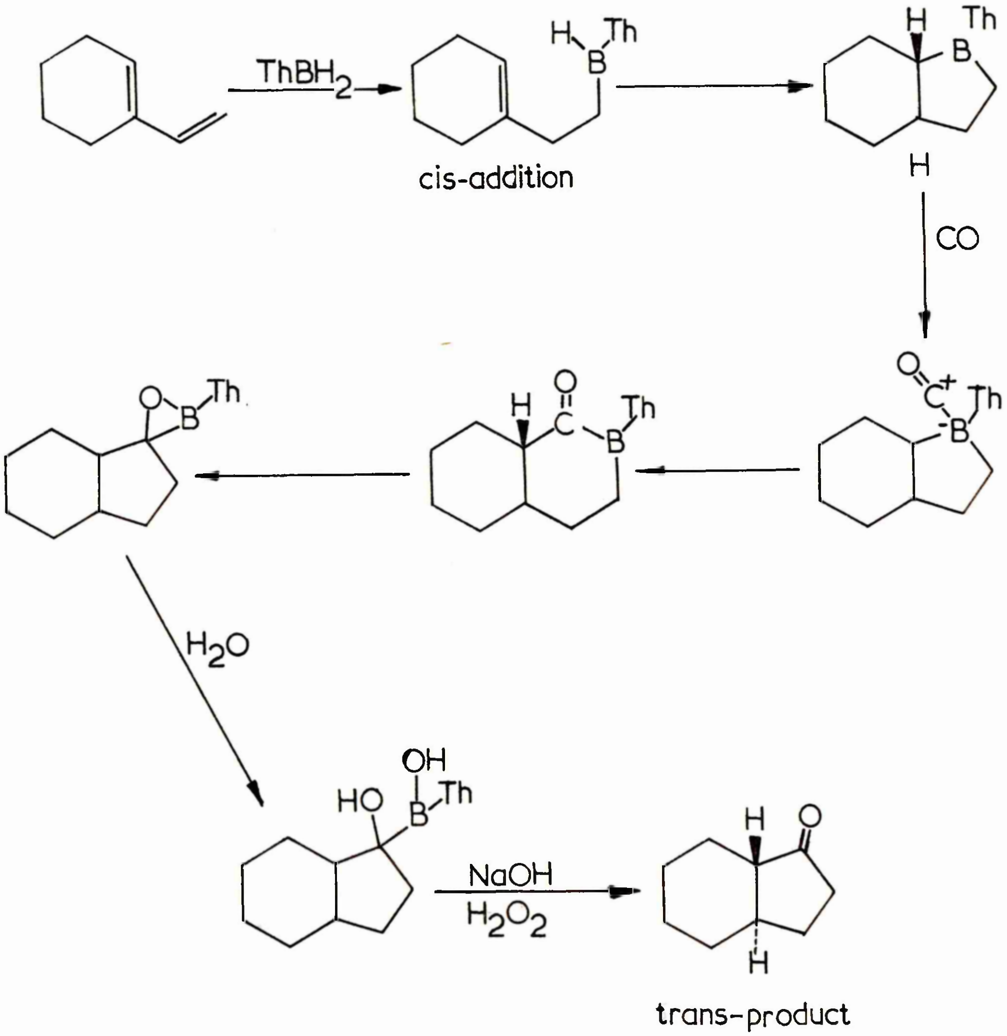
The carbonylation reaction carried out in the presence of a hydridic reagent, such as Li(MeO)$_3$AlH, results in nucleophilic attack on the carbonyl carbon of the boraketone which when followed by oxidation affords a mixture of the aldehyde and alcohol. Alkaline hydrolysis affords the alcohol which has a one carbon atom chain extension[157]. The use of B-alkyl-9-BBN in the reaction improves the yield of aldehyde or homologated alcohol, based on the alkyl group[158]. The use of a milder reducing agent such as Li(Bu^{t}O)$_3$AlH which does not reduce cyano or ester groups allows their presence in thealkyl group which undergoes transfer affording substituted aldehydes or alcohols which have undergone a one-carbon atom extension[159].

In the absence of reducing agents a further alkyl transfer occurs from boron together with epoxide formation affording the boraepoxide which in the presence of water cleaves to form a boraglycol. Oxidation of the boraglycol affords a ketone whilst alkaline hydrolysis results in secondary alcohol formation (99). The use of B-alkyl-9-BBN derivatives is precluded because they cannot form the epoxide. However, the reluctance of the thexyl group to migrate from boron to carbon is of great advantage since it allows the synthesis of either mixed or homogeneous products in respect of alkyl groups from the hydroboration products of thexylborane.

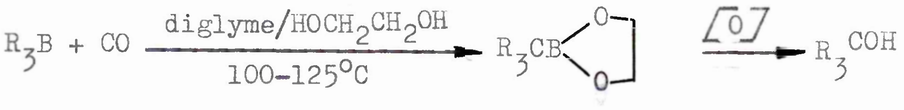
The ability of thexylborane to readily form cyclic boranes from dienes has made possible the direct synthesis of cyclic ketones[160] (100).

A problem with this type of ring synthesis is that the thexyl derivatives require more vigorous conditions (ca 70 bar) for carbonylation which leads to unwanted products. This objection can be overcome via the cyanidation reaction discussed later.

Under dry reaction conditions the boraepoxide suffers a third alkyl transfer to form a boronic anhydride which on oxidation affords the tertiary alcohol (99). The boronic anhydrides can polymerise under the conditions of the reaction and oxidation of the polymeric products (R_3CBO) is difficult. The presence of ethylene glycol in the reaction results in the formation of a cyclic alkoxyborane which prevents polymerization and is more easily oxidised to yield the alcohol[161,162] (101).



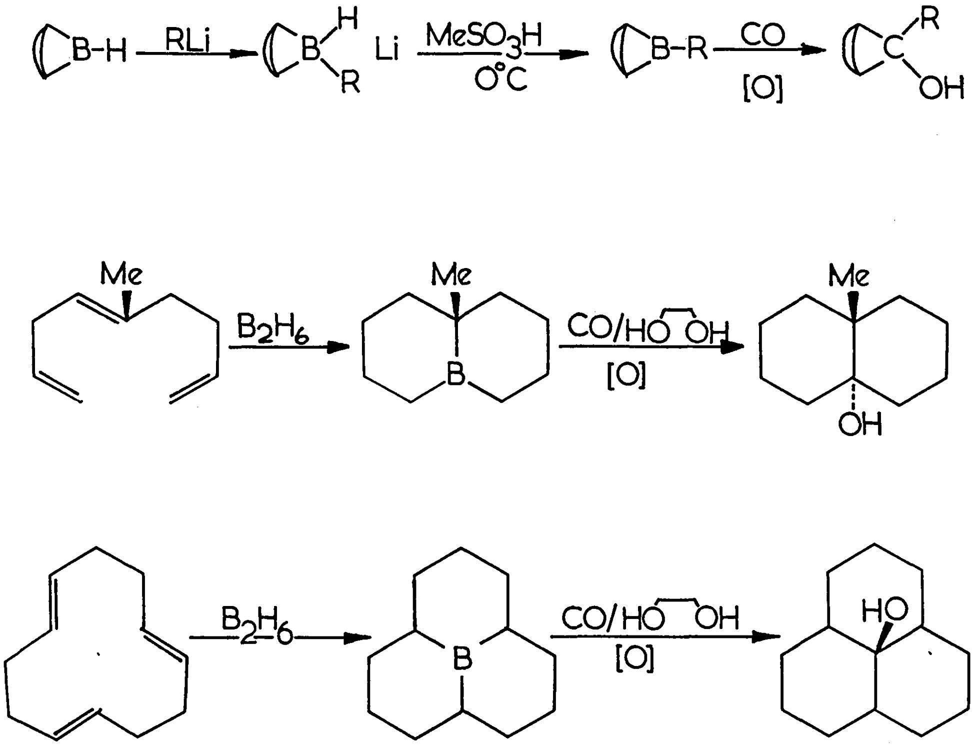
(100)



$$R_3B + CO \xrightarrow[100\text{–}125^{\circ}C]{diglyme/HOCH_2CH_2OH} R_3CB\langle\begin{smallmatrix}O\\O\end{smallmatrix}\rangle \xrightarrow{[O]} R_3COH$$

(101)

The easy replacement of boron by carbon afforded by the carbonylation reaction and the range of products available allow synthesis of structures obtainable with great difficulty by other routes (102).



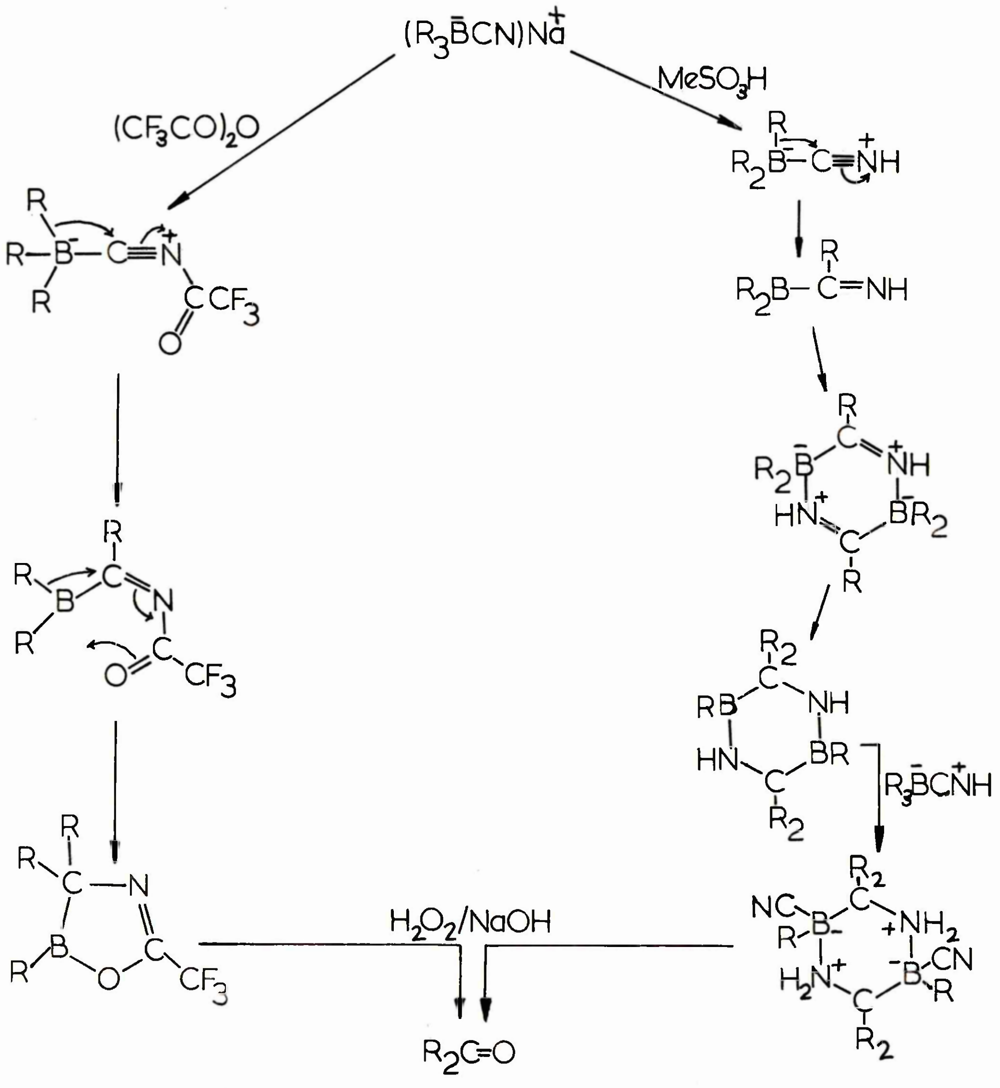
(102)

4.4.10) Cyanidation

The cyanide ion is isoelectronic with carbon monoxide and reacts simply with trialkylboranes to form trialkylcyanoborates[163] (103).

$$R_3B + NaCN \xrightarrow[\text{reflux}]{\text{ether solvent}} \overset{-}{\left[R_3B\text{-}CN\right]} \overset{+}{Na} \qquad (103)$$

Subsequent treatment of the cyanoborate with either methyl sulphonic acid or trifluoroacetic anhydride followed by alkaline peroxide oxidation affords the ketone[164] (104). In the case of chiral alkyl groups the configuration is retained upon migration although the ease of migration decreases with degree of substitution[165].

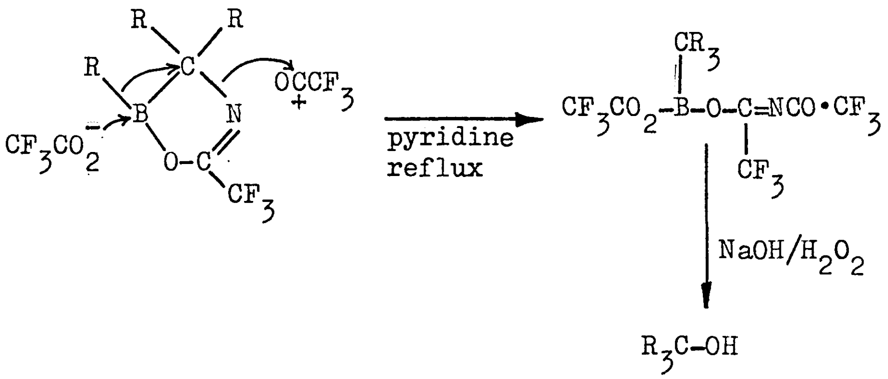


(104)

The use of thexylborane allows the preparation of mixed ketones in high yield as a result of the ease of preparation of the mixed alkylborane and the non-migration of the thexyl group from boron to carbon[166].

The preparation of cyclic or acyclic boranes from thexylborane is convenient and their use affords cyclic or acyclic ketones via the above reaction because in the alkyl transfer to carbon step the thexyl group does not migrate. If in the preparation of an acyclic dialkylthexylborane two different alkyl substituents are introduced (RR'BTh) then the product of reaction will be a mixed ketone (RCOR').

Tertiary alcohols are available by treatment of the reaction intermediate with more trifluoroacetic anhydride in the presence of a base, pyridine, prior to oxidation. A further alkyl transfer and ring opening occurs affording the tertiary alcohol on oxidation[166] (105).



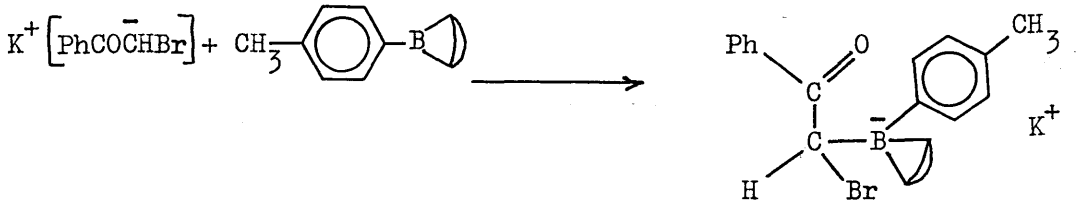
(105)

4.4.11) α-reactions

Organoboranes are capable of undergoing reactions with carbon atoms which are adjacent to boron (α). These reactions are enhanced particularly by the presence of a halogen substituent on the α-carbon.

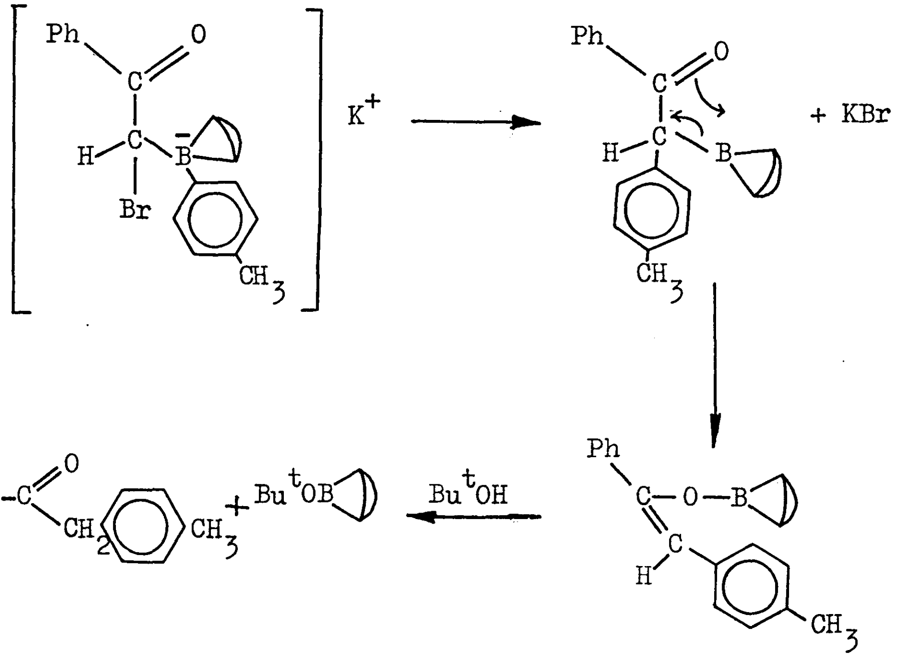
In the presence of a strong base, often potassium t-butoxide or potassium di-2,6-t-butyl phenoxide, α-haloesters, nitriles and ketones form carbanions by abstraction of the α-hydrogen by the base (106). The carbanions thus formed will react as nucleophiles with triorganoboranes[167,168] (107).

$$PhCO.CH_2Br + Bu^tOK \longrightarrow \left[PhCO\bar{C}HBr\right] \; K^+ + Bu^tOH \qquad (106)$$



(107)

The reaction is considered to proceed via rearrangement of the initial product, by an α-transfer from boron, to give an unsaturated dialkylboronate which undergoes protonolysis to give the α-substituted product (108).



(108)

The yield with respect to the transferred group can only be a maximum of 33% when a trialkylborane is used; however, by the use of boranes derived from 9-BBN the theoretical yield is raised to 100% of the desired substituent[169].

The disubstitution of α,α-dihalonitriles is also possible by this route[170] and the two substituents need not necessarily be identical.

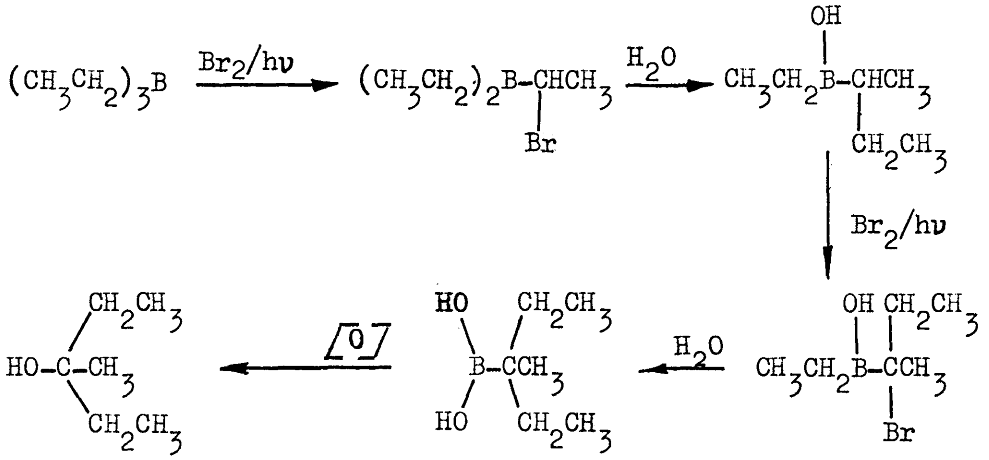
Thus the addition of a borane containing the first substituent desired followed on completion of the reaction by the addition of the second borane allows the synthesis of disubstituted nitriles.

Hydroboration of halosubstituted alkenes allows the direct synthesis of either α or β-halo-substituted boranes depending upon the nature of the alkene substituents. As previously discussed the orientation of hydroboration is controlled both by steric and electronic factors. Halogen substituents favour the formation of α-boranes by stabilizing the negative charge on the α-carbon in the hydroboration transition state.

A different kind of α-transfer occurs with α-halosubstituted boranes, where an alkyl group attached to boron is exchanged with the halosubstituent[171]. The α-transfer process occurs with complete inversion of configuration at carbon and is catalysed by Lewis acids, including an excess of the hydroborating agent[172,173,174,175]. In contrast β-halosubstituted boranes undergo elimination, forming alkenes by loss of the haloborane. The elimination may be catalysed both by acids and bases, and occurs in a trans-fashion, but has been shown to be a cis-process when uncatalysed[176]. The transfer of an alkyl group from boron to the β-carbon and loss of the haloatom (β-transfer) has also been postulated[177].

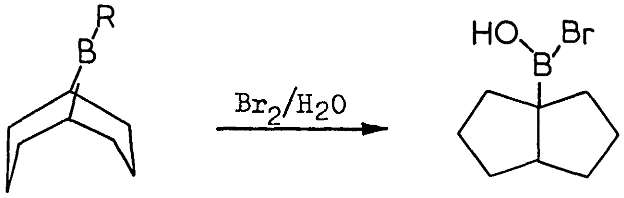
The photochemical bromination of triorganoboranes introduces a bromine atom onto the α-carbon which is very reactive to bromination [178]. In the presence of water the α-brominated compound immediately rearranges by α-transfer and loss of bromine, forming a dialkylborinate. Subsequent bromination takes place in the case of secondary groups on the α-carbon of the remaining untransferred group.

If n-alkyl substituents are present then bromination of the α-carbon of the newly formed group occurs[179] (109).



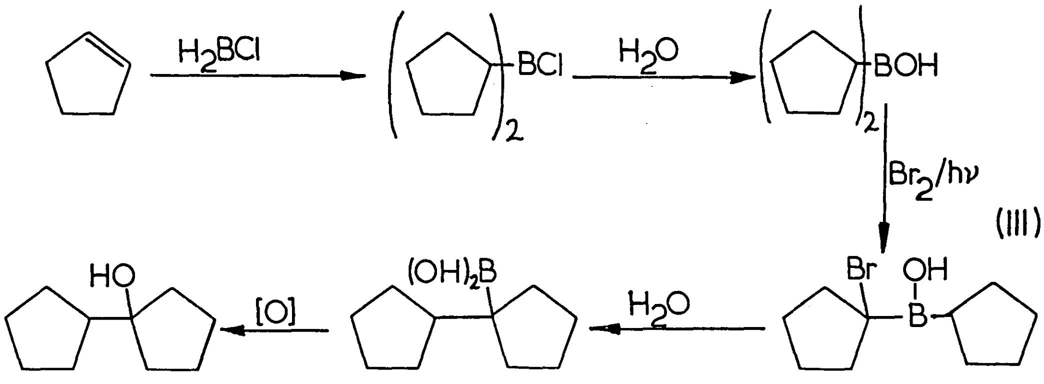
(109)

In contrast B-alkyl-9-BBN when brominated in the presence of water, in the dark affords an alkyl bromoboronate[180] (110).



(110)

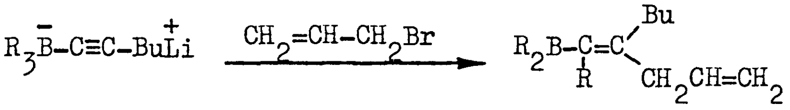
Hydroboration of alkenes with monochloroborane and subsequent hydrolysis of the dialkylchloroborane affords the dialkylborinate which when followed by oxidation provides a route to compounds which are otherwise difficult to prepare, for example[181] (111).



(111)

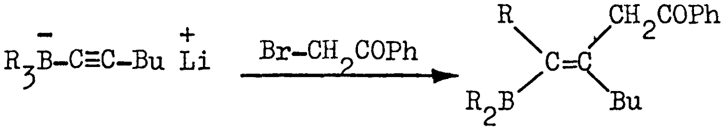
The alkylation of alkynyltrialkylborates by reactive alkylating agents such as methyl sulphate, benzyl or allyl bromide results in both alkyl transfer and alkylation β to boron[182] (112).

The product of the reaction, a dialkylborane, may be subjected to the other possible reactions of boranes.



$$R_3\overset{-}{B}-C\equiv C-Bu\overset{+}{Li} \xrightarrow{CH_2=CH-CH_2Br} R_2B-\underset{R}{C}=C\begin{smallmatrix}Bu\\CH_2CH=CH_2\end{smallmatrix} \qquad (112)$$

The use of electrophiles such as α-bromoketones, iodoacetonitrile, ethyl bromoacetate or propargylbromide results in a stereospecific rearrangement affording, for example an α,δ-enone[183] (113).



(113)

R=n-hexyl,cyclopentyl

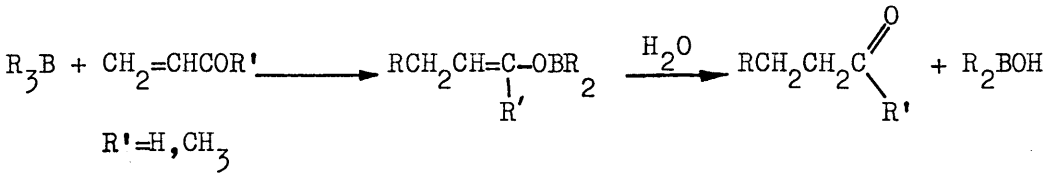
In both cases the cleavage of R_2B by means of carboxylic acids (protonolysis) is stereospecific and provides a useful route to trisubstituted alkenes[184]. Interestingly the protonolysis of the alkynyltrialkylborate results in α-transfer to afford a dialkylalkenylborane[184] (114).

$$R_3\overset{-}{B}-C\equiv C-Bu + H^+ \longrightarrow R_2B-\underset{R}{C}=CH-Bu \qquad (114)$$

When R= phenyl the alkene is cis with respect to the alkyl substituents.

4.4.12) Conjugate additions

Trialkylboranes undergo rapid 1,4-addition reactions with 3-buten-2-one (methylvinyl ketone) and 2-propenal (acrolein) to give vinyloxyboranes which on hydrolysis aford β-substituted ketones [185,186] (115).

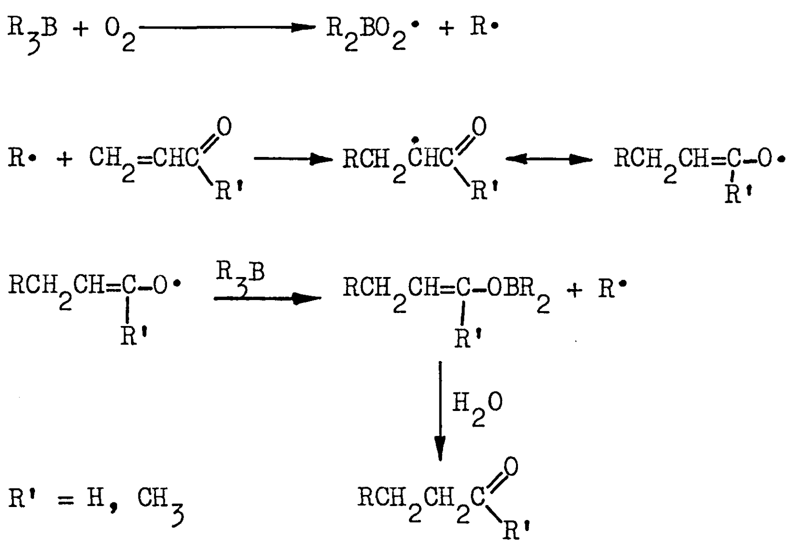


$$R_3B + CH_2{=}CHCOR' \longrightarrow RCH_2CH{=}\underset{R'}{C}{-}OBR_2 \xrightarrow{H_2O} RCH_2CH_2\overset{O}{C}R' + R_2BOH \qquad R'{=}H, CH_3$$

(115)

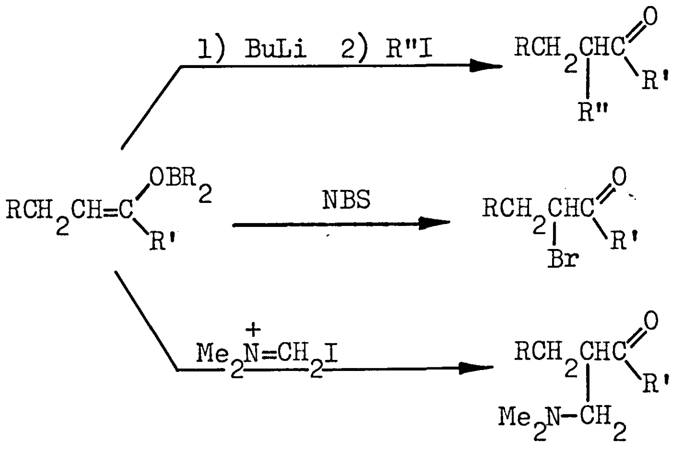
Initially these reactions were thought to proceed via a cyclic transition state[185] but for the reasons below are now considered, with some exceptions, to be free radical reactions. Substituents in the α-position had no effect upon the course of reaction whereas β-substituents prevented reaction, which is inconsistent with the original mechanism.

Free radical reactions have been shown to be inhibited by terminal methyl groups[187] and reactions of methylvinyl ketone and acrolein were inhibited in the presence of a free radical scavenger, galvinoxyl[188]. Conversely, under conditions enhancing the generation of free radicals by addition of air or peroxides or by photochemical means the β-substituted compounds undergo reactions at the β-carbon[189] (116).


(116)

If the vinyloxyborane is hydrolysed with deuterium oxide then the α-deuteroketone is obtained[190] (116).

In the absence of water the vinyloxyborane is stable, to the extent that it may be distilled, and can undergo further reaction[191]. Lithiation followed by treatment with an alkyl halide affords an α-substituted compound (117). Alternatively treatment with N-bromosuccinimide[192] (NBS) (118) or dimethylammonium methylene iodide[193] (119) affords the α-bromo or α-dimethylamino methylene substituted compounds.


(117)

(118)

(119)

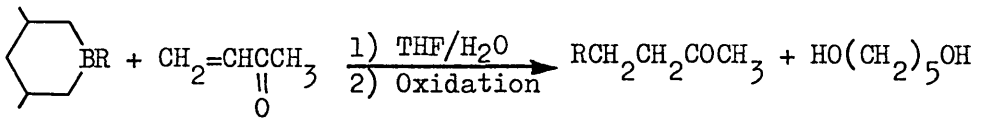
As a result of the free radical nature of the reactions the stereochemistry of the products is solely controlled by the relative thermodynamic stability of the possible products.

The available yield of the transferred alkyl or aryl group can only be a maximum of 33% with respect to the trialkylboranes. This disadvantage is not overcome by the use of B-alkyl-9-BBN derivatives. In the free radical reactions of B-alkyl-9-BBN with conjugated enones the boron-cyclooctyl bond predominantly migrates affording a very different product to that expected. The B-alkenyl-9BBN derivatives will undergo a 1,4-addition with acyclic enones affording γ,δ-unsaturated ketones[194].

The configuration of the original vinylic borane is retained in the substituted product. The reaction is considered to proceed via a cyclic transition state and enones such as 2-cyclohexenone do not react, presumably due to an inability to form the cyclic moiety.

However, the latter disadvantage is overcome by the employment of B-alkyl-3,5-dimethylboracyclohexane and B-alkyl-3,4-dimethylboracycloheptane. Reactions of conjugated enones with the B-alkylboracyclanes afford the products of alkyl transfer as desired by free radical reactions[195,196].

Suitable B-alkylboracyclanes are available from the hydroboration of alkenes by the respective agent or via reaction of alkyl lithium with B-methoxyboracyclanes (120).

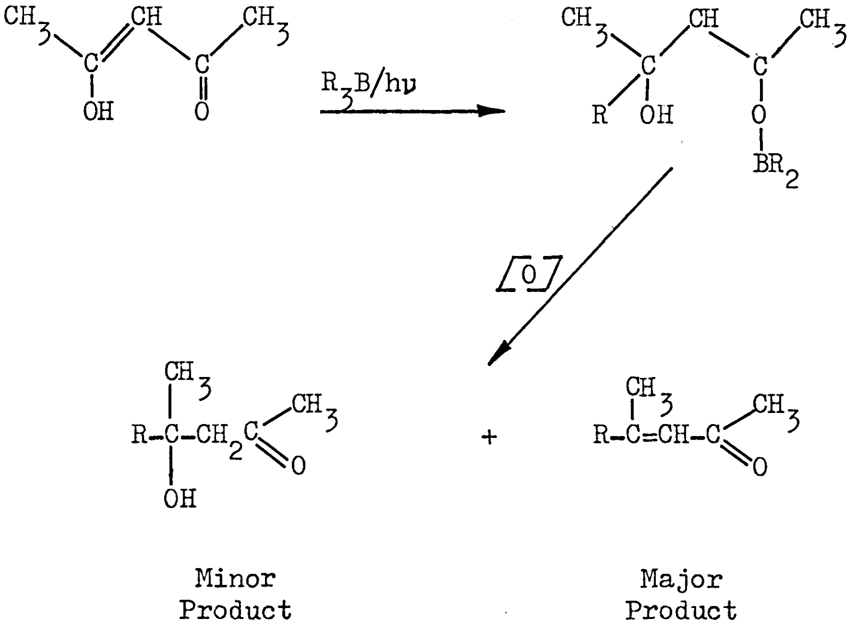


$$\mathrm{BR} + \mathrm{CH_2{=}CH\underset{\underset{O}{\|}}{C}CH_3} \xrightarrow[\text{2) Oxidation}]{\text{1) THF/H}_2\text{O}} \mathrm{RCH_2CH_2COCH_3} + \mathrm{HO(CH_2)_5OH} \qquad (120)$$

Unsaturated epoxides also react by a similar mechanism affording as product an unsaturated alcohol with an effective chain lengthening of four carbon atoms[197].

Addition of triallylborane to enones has been shown to occur only at the carbonyl group[198].

The reaction with the enolic form of β-diketones results in products of addition to both the unsaturated bonds in the enol form and upon oxidation, a mixture of products may be isolated[199] (121).



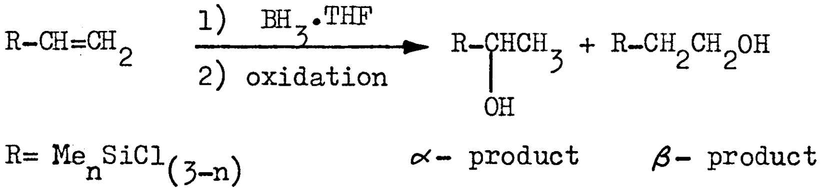
(121)

4.5) Related Work

Initial literature searches showed that most efforts had been directed towards development of hydroborating reagents and the synthetic chemistry of organoboranes. Interest in the possibility of hydroboration of organometallic compounds appeared to be minimal.

However the hydroboration of some organosilanes had been noted and the respective alcohols from oxidation of the organoboranes so produced were isolated.

The hydroboration of allyltrimethylsilane was described as giving the tris (γ-organoborane) exclusively, whilst vinyltrimethyl silane gave the tris (α-organoborane). The orientation of these additions was explained in terms of the relative stabilities of the carbonium ions for the two compounds[200]. In contrast, the attempted reduction of vinyltrichlorosilane with sodium borohydride resulted in the formation of silane[201]. Vinyl and allyl methylchlorosilanes resulting from progressive replacement of the chlorine atoms of the respective alkenyltrichlorosilanes have been hydroborated, and yield alcohols following oxidation[202] (122).

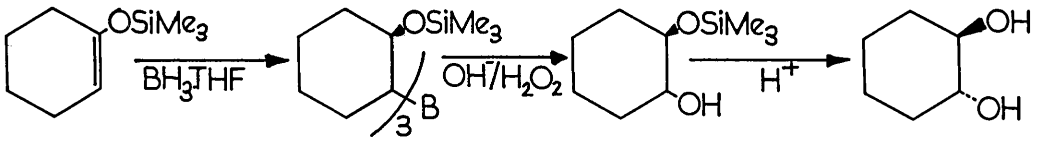


$$R\text{-}CH{=}CH_2 \xrightarrow[\text{2) oxidation}]{\text{1) } BH_3\cdot THF} R\text{-}\underset{\displaystyle OH}{\underset{|}{C}}HCH_3 + R\text{-}CH_2CH_2OH \qquad (122)$$

R= $Me_nSiCl_{(3-n)}$ α- product β- product

The proportions of the alcohols isolated (122) show that the tendency towards α-hydroboration decreases as methyl substitution of the silicon atom increases. The comparable allyl chloromethylsilanes show only γ-hydroboration.

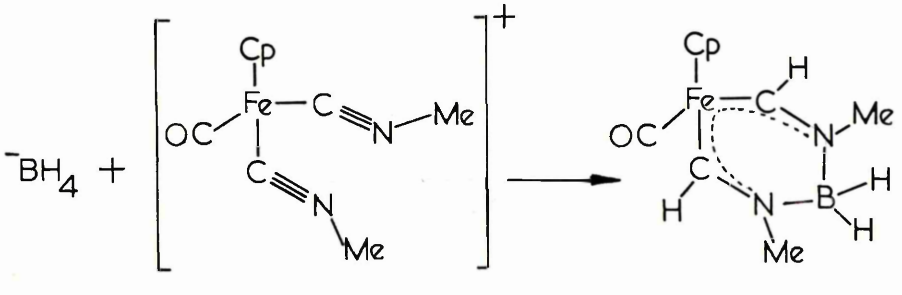
The hydroboration of trimethylsilyl enolethers has been shown to occur with formation of a β-boryl intermediate, which is stable for cyclic systems (123) but undergoes elimination with acyclic systems. Oxidation of cyclic β-boryl intermediates by alkaline peroxide leads to cleavage of the carbon-boron bond and production of an alcohol[203]. The trimethylsilylether group may be converted to an alcohol simply by washing the organoborane oxidation product with aqueous mineral acid.



(123)

Similarly, phenyllithium when formed and hydroborated *in situ* gave, on oxidation, a good yield of phenol. A range of substituted phenols were obtained by the hydroboration of substituted aryl halides in the presence of alkali metals (Li, Ca, K) followed by oxidation[204].

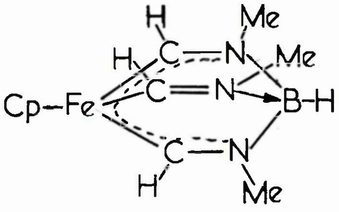
The borohydride reduction of the cationic metal carbonyl complex π-$C_5H_5Fe(CO)(CNMe)_2^+$ with borohydride resulted in reduction of the C≡N bonds, yielding $\pi$$C_5H_5Fe(CO)(CHNMe)_2BH_2$ for which a delocalised structure was proposed[205] (124).



(124)

Cp=π-C_5H_5

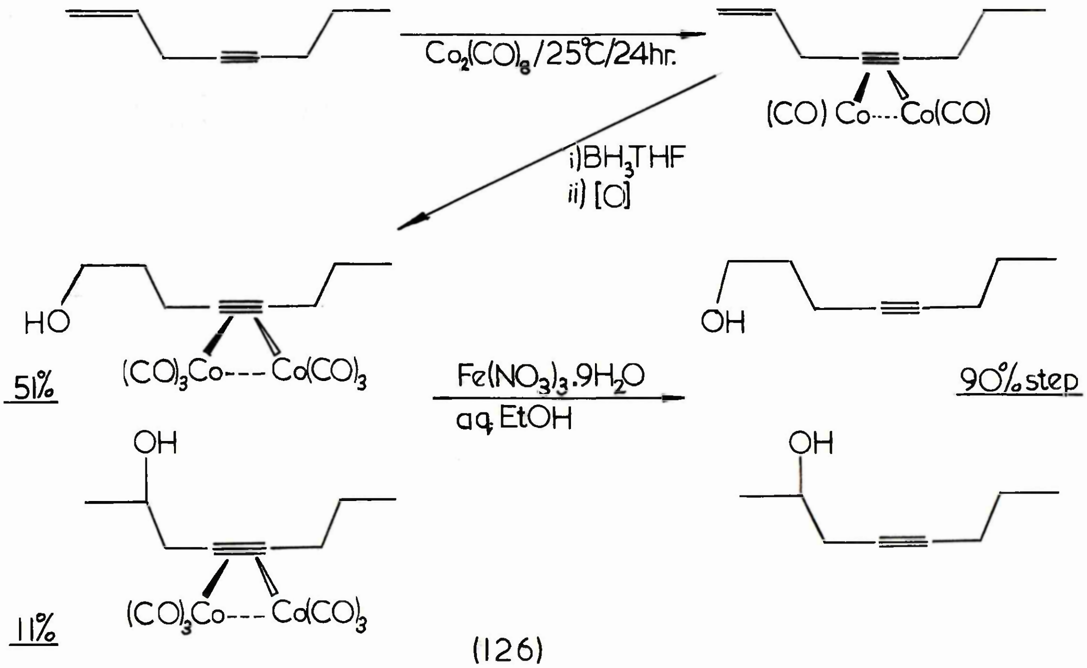
Complexes of molybdenum and manganese containing the same ligands gave similar results. However $\pi$$C_5H_5Fe(CNMe)_3^+$ undergoes reduction of all three C≡N bonds to give a caged structure which is only partially delocalised[206] (125).



(125)

Transition metal complexes formed with the borohydride ion are also known for metals other than iron and can involve hydrogen bridging between the metal centre and boron. In these cases the borohydride ion is acting directly as a ligand and a variety of products can be obtained depending upon the reaction conditions used [207,208,209].

In the context of the aims of this work the borohydride reductions of metal complexes were of interest. However, the major aim was to examine whether via hydroboration of complexed organic moieties a different product could be obtained than with the uncomplexed moeity. Of particular interest was the reported hydroboration of oct-1-en-4-yne in which the $C\equiv C$ bond had been protected by complexation with dicobalt octacarbonyl. Oxidation of the organoborane generated and subsequent degradation of the complex allowed the alkynol to be recovered[210] (126).

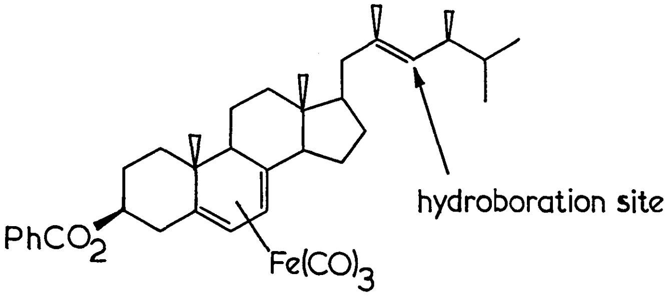


(126)

The acetyl complexes of several metals were shown to be reduced to ethyl complexes by means of hydroboration, and this work prompted investigation of the properties of substituted ferrocenes to ascertain whether alkyl substituents would also result in this case. Following the work on the hydroboration of vinyl ferrocene a thorough literature search indicated that the reaction was not novel[211].

During the course of the work described herein with 2,4-pentanedione, information was published confirming some of the observations of which further details appear in section 6.1.

Recently the complexation of a 1,3-diene with iron tricarbonyl, thus allowing hydroboration of a separate unsaturated part of the molecule, has been reported. The diene was recovered after oxidation of the organoborane by degradation of the complex using iron (III) chloride[213] (127).



(127)

The latter reaction is of interest in context of the work on iron tricarbonyl complexes reported herein.

The possibilities of use of the reactions of compounds involving boron appear to rival those for carbon. Many publications in this area are due to Brown (and co-workers) and it is of note that the Nobel Prize was awarded for his contribution[214].

5) EXPERIMENTAL

5.1) Instruments

5.1.1) Infrared Spectroscopy

Infrared spectra were recorded using either a Pye-Unicam SP1200 or SP800 spectrophotometer. The spectra of liquid samples were recorded using a thin film between sodium chloride plates. The spectra of solid samples were recorded from potassium bromide discs containing 1% - 3% w/w of sample.

5.1.2) Ultraviolet and visible spectroscopy

Ultraviolet and visible wavelength spectroscopy were carried out using a Pye-Unicam SP500 spectrophotometer. All solvents were of spectroscopic grade.

5.1.3) Gas chromatography

Gas chromatography was performed using a Pye 104 with dual flame-ionisation detector and heated injectors (nitrogen carrier gas). Chromatograms were recorded on a Honeywell 10" chart recorder. Preparative scale chromatography was carried out using a Pye 104 preparative gas chromatograph.

5.1.4) Nuclear magnetic resonance spectroscopy

Nuclear magnetic resonance spectra were recorded using a J.E.O.L. 100, 60 MHz spectrometer. Proton magnetic shifts were measured against tetramethylsilane used either as an internal or external standard. Solvents were usually deuterochloroform or deuteroacetone depending upon the sample. Labile protons were identified using deuterated water addition to the sample solution.

5.1.5) Mass spectrometry

Medium resolution mass spectra were measured using an A.E.I. - MS30 mass spectrometer. The spectra of air-stable compounds were obtained using the direct sample insertion inlet. Air-sensitive, volatile, compounds were presented by means of a heated all glass inlet system (AGIS), or by use of a gas chromatograph (Pye 104) linked to the ion-source by a silicone membrane separator.

5.2) Generation of diborane

A magnetically stirred solution of iodine (25.4g, 0.2 mole) in dry bis (2-methoxyethyl)ether (100cm^3) under a nitrogen atmosphere was treated, dropwise, at ambient temperature with a solution of sodium borohydride (7.56g, 0.2 mole) in the same solvent (150cm^3).

$$2\ NaBH_4 + I_2 \longrightarrow B_2H_6 + H_2 + 2NaI$$

The resulting diborane was carried by a slow stream of nitrogen to a reaction flask or via a series of cold traps to a vacuum line apparatus[214].

5.3) Calculation of volumes of gaseous materials

Gaseous compounds were assumed to obey the gas laws. Temperatures were measured by means of mercury in glass thermometers. Gaseous compounds were pumped into a glass vessel of known volume and the pressure in that vessel measured by a mercury manometer. From the volume, temperature and pressure the volume of the material under standard conditions could be calculated. The volume under standard conditions (273.15K and 760mm Hg pressure) was termed 'N'cm^3. The 'N' volume was then related by the molar volume to the mass of the compound being measured.

5.4) Procedure for generating diborane for use on vacuum line

Diborane was generated as previously described from sodium borohydride and iodine under a nitrogen atmosphere. By means of nitrogen the gaseous reaction products were swept into a series of four cold traps (fig. 1). The first trap was maintained at

-60 to -75°C with solid CO_2/acetone slush and served to remove traces of volatilised solvent. The second and third traps were cooled with liquid nitrogen to condense and solidify the diborane. The nitrogen and hydrogen were vented to vacuum via a fourth trap containing acetone maintained at liquid nitrogen temperature. The last trap ensured that no diborane was vented into the pumping system. On completion of reaction the two traps containing diborane were isolated from the reaction flask and evacuated to approximately 0.01mm Hg pressure (rotary oil pump). By means of a three-way tap situated between traps three and four the traps containing diborane were connected to the vacuum line input. By allowing the traps to warm to ambient temperature the trapped diborane was vaporized and re-condensed in a liquid nitrogen cooled trap on the vacuum line. Using a Toepler pump the traps were evacuated onto the vacuum line to below 0.001mm Hg pressure. On completion of the transfer the vacuum line inlet was closed then the traps were reconnected to the fourth isolated evacuated trap. The fourth trap was warmed to ambient temperature and acetone vapour was allowed to fill the entire generation apparatus and react with any remaining diborane, removing the explosion hazard associated with exposure of diborane to air on disassembly of the apparatus. The generation apparatus was then purged with nitrogen several times prior to disassembly. Using the Toepler pump the diborane was pumped from the connecting pipework of the vacuum line to a liquid nitrogen cooled storage vessel leaving a vacuum of better than 0.001mm Hg pressure. After allowing the diborane to condense and solidify in the storage vessel any non-condensable material was pumped away to vacuum. By allowing the diborane to warm to ambient temperature in the isolated storage

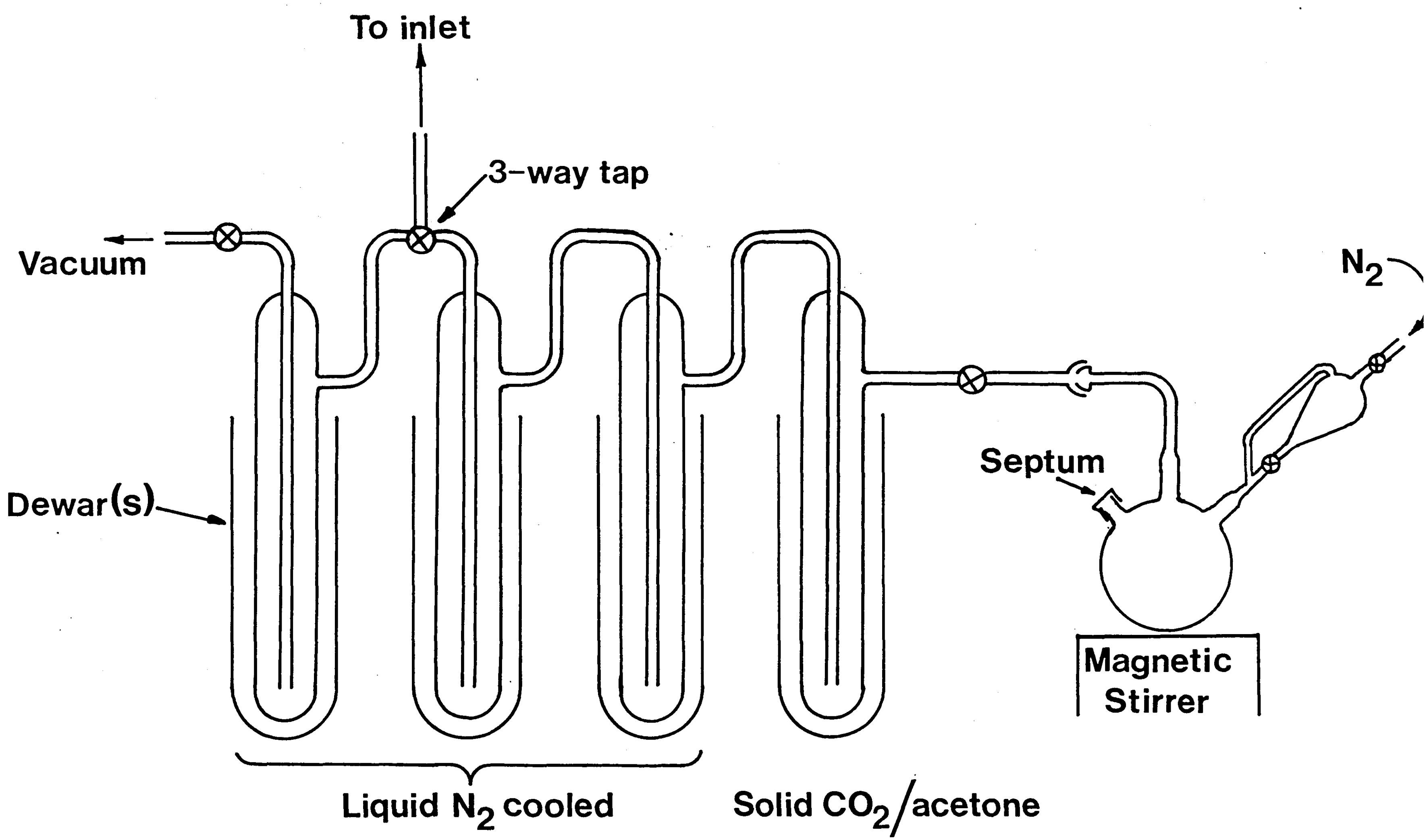


Fig.1

Diborane generation apparatus

vessel of known volume a measurement of pressure (corrected for atmospheric pressure) and temperature allowed calculation of the amount of diborane stored.

5.5) Use of vacuum line apparatus

The apparatus shown in the diagram (fig. 2) was constructed of borosilicate glass. The taps were either glass cone and socket or screw type with a teflon sealing ring and viton o-ring shaft seals, (manufactured by J. Young Limited). Joints within the apparatus were of the clamped hemispherical type with viton o-ring seals, allowing a degree of movement to absorb vibration and thermal expansion. Pressure measurements were made using simple mercury manometers to which a millimetre scale was affixed and mutually calibrated. A Macleod gauge was also fitted to enable more accurate pressure measurements down to 0.001mm Hg pressure. Vacuum was obtained by means of a rotary-vane oil pump and in addition when required a silicone oil diffusion pump. Provision of a Toepler pump within the system allowed gaseous materials to be moved easily within the apparatus and for pressure and volume measurements to be made. The volume of the traps and vessels were measured by weighing the relevant part of the apparatus both empty then filled with pure water; by difference using the density of water the volume of the vessel was calculated. In the case of the Toepler pump calibration, mercury was used in order to obtain a higher degree of accuracy in weighing. Following assembly the apparatus was evacuated and gently warmed with a flame. After outgassing for seventy two hours a stable state was reached and maintained and the apparatus was considered ready for use.

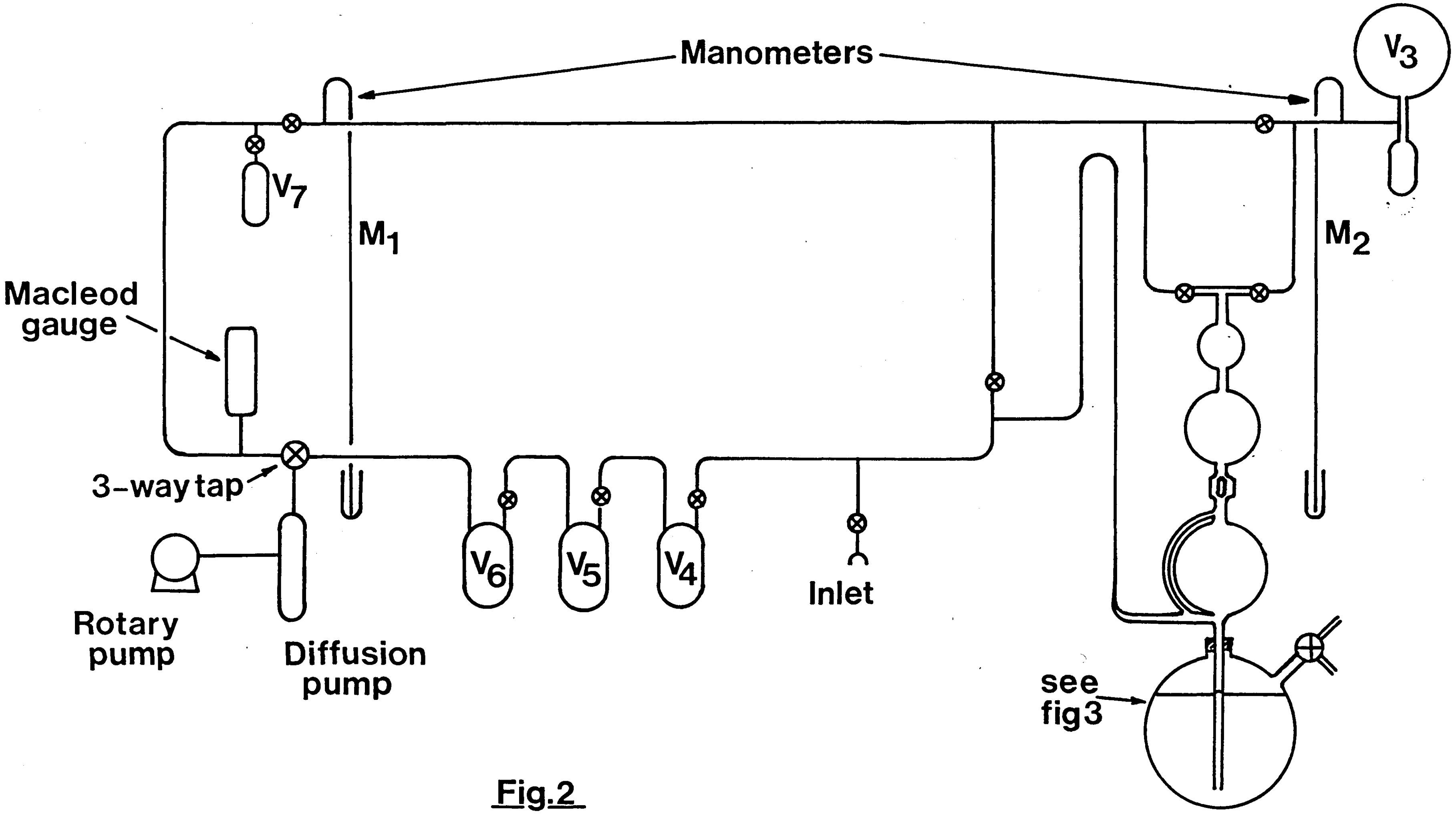


Fig.2
Vacuum line apparatus

5.6) Measurement of gas volumes by Toepler pump

Application of a vacuum to bulb D causes the manometric height of mercury in the side arm to decrease and gas enters bulb C. With taps T_1 and T_2 closed partial atmosphere pressure is restored to bulb D causing the mercury level to rise entrapping a volume of gas in bulb C. As the level of mercury continues to rise the gas is forced past the valve and into bulbs A and B. At this point application of vacuum to bulb D will lower the mercury level again and the valve prevents the gas from leaving bulbs A and B as the level falls. By repeated cycling all the gas can be pumped from the vacuum line into bulbs A and B down to an ultimate pressure equivalent to the vapour pressure of mercury, With the mercury meniscus positioned on either F_1 or F_2 the height of mercury in the side arm can be measured and hence the pressure of the contained gas. The pressure of the gas, corrected for ambient barometric pressure, and measurement of ambient temperature allowed the volume of gas under standard conditions to be calculated. Fig. 3.

5.7) Drying of solvents

5.7.1) Hydrocarbons

Hydrocarbons were dried over sodium wire extruded from oil free sodium directly into the storage bottle containing the solvent. Initially the bottle was fitted with a calcium chloride guard tube and stoppered only when no effervescence could be noted over a long period. Solvents were always examined to ensure that no gross water contamination was present prior to adding sodium.

5.7.2) Alcohols

Methanol and ethanol were dried by refluxing with magnesium and subsequent distillation according to published procedure[215].

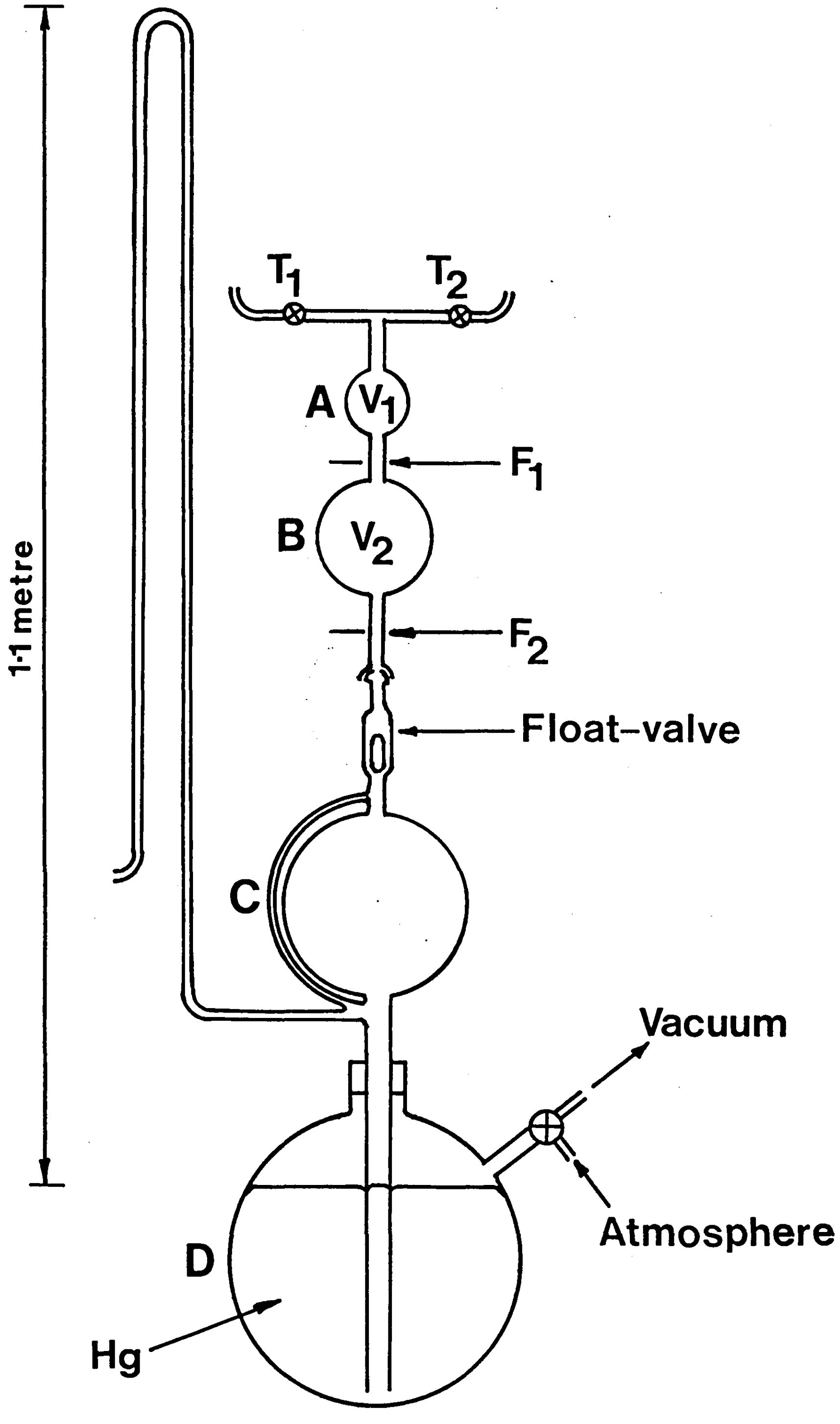


Fig.3
Toepler pump schematic

$$Mg + 2ROH \longrightarrow (RO)_2Mg + H_2$$

$$(RO)_2Mg + 2H_2O \longrightarrow Mg(OH)_2 + 2ROH$$

5.7.3.) Tetrahydrofuran

Tetrahydrofuran (1 litre) under a nitrogen atmosphere was treated with small portions (0.25g) of lithium aluminium hydride. Additions were continued until an aliquot of liquor effervesced when dropped into water, demonstrating the presence of an excess of the hydride. After gently refluxing for thirty minutes, tetrahydrofuran was distilled off into a dry, nitrogen-purged dark glass bottle. A residue of 200cm^3 was allowed to remain in the distillation flask to keep wet unreacted hydride, which was later destroyed by slow addition of an excess of ethyl acetate. Freshly regenerated molecular sieve 4A $^1/16$" pellets were added to the stored solvent to maintain dryness.

$$LiAlH_4 + 4H_2O \longrightarrow Li(OH) + Al(OH)_3 + 4H_2$$

$$LiAlH_4 + 4CH_3COOC_2H_5 \longrightarrow LiOC_2H_5 + Al(OC_2H_5)_3 + 4C_2H_5OH$$

5.7.4.) Bis(methoxyethyl)ether, "diglyme"

Bis(methoxyethyl)ether was dried by storage over molecular sieve 5A $^1/16$" pellets in the volume ratio 10:1 for not less than one week prior to usage. Alternatively the procedure for hydrocarbons was used.

5.7.5) Diethylether

As for hydrocarbons.

5.7.6) Acetonitrile

Analar grade acetonitrile was stored over fresh molecular sieve 5A $^1/16$" pellets with occasional shaking for one week prior to use.

5.7.7) Dry nitrogen gas

Commercial grade compressed nitrogen was reduced in pressure for use by a 2-stage reducing head or by a needle valve control. The gas was passed through a 90cm x 2cm column (glass) of anhydrous calcium chloride granules of size 5mm-10mm supported by a glass frit. A mercury bubbler pressure release was provided in the supply line.

5.7.8) Molecular sieve

Molecular sieve pellets were heated to 350°C in a slow stream of dry nitrogen for several hours then allowed to cool in a desiccator. The sieve was then stored in a tightly capped dry bottle, ready for use.

5.8.1) Reactions with diborane generated in situ

Reactions were carried out in a magnetically stirred 3-necked flask with a condenser and vented dropping funnel at 0°C under a dry nitrogen atmosphere maintained by the use of bubbler traps. The flask was charged with solvent and substrate. Sodium borohydride was added to the resultant solution and the temperature equilibrated. A solution of boron trifluoride-diethylethereate was added slowly during one hour at 0°C. The temperature was maintained at 0-3°C during one hour further and then allowed to rise slowly to ambient. Solvent was removed under vacuum (ca 40°C). The products recovered were then identified as detailed elsewhere.

5.8.2) Reactions with diborane generated externally

$$3NaBH_4 + 4BF_3.Et_2O \longrightarrow 2B_2H_6 + 3NaBF_4 + 4Et_2O$$

Diborane, generated by the action of a solution of boron trifluoride diethyletherate on a stirred solution of sodium borohydride under a nitrogen atmosphere, was passed into a 3-necked flask containing a magnetically stirred solution of the substrate

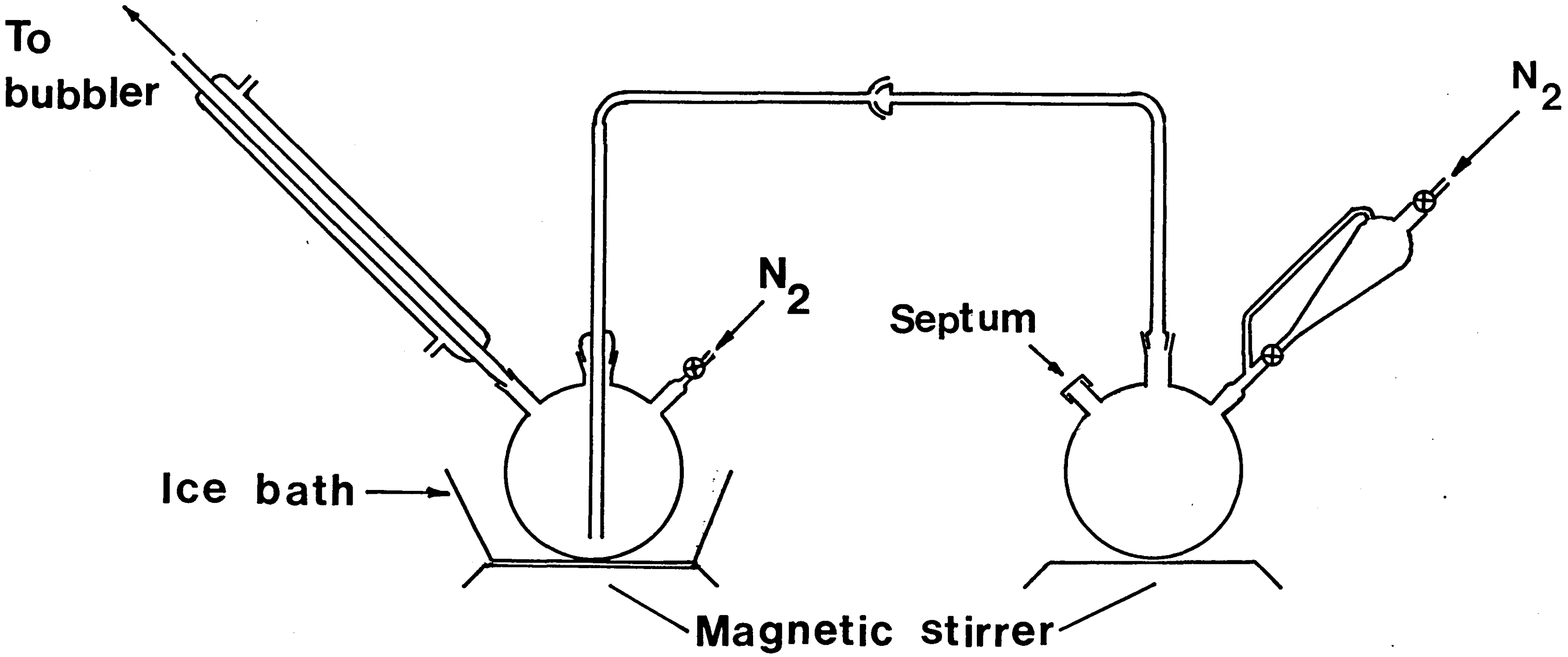


Fig.4

Apparatus using external diborane generation maintained at $0^{\circ}C$. The reaction flask was fitted with a condenser and bubbler trap. The diborane delivery tube was arranged to dip below the surface of the substrate solution. During the course of the reaction a slow flow of nitrogen was used to sweep diborane into the reaction flask. When all the boron trifluoride-diethyletherate solution had been added, the generator flask was warmed gently to $40^{\circ}C$ to complete the reaction and drive off all diborane generated. By manipulation of the nitrogen flow the dip-tube was removed and the neck of the reaction flask stoppered. After a period of reaction the mixture was allowed to warm to ambient temperature and products were isolated and identified. The reaction of boron trifluoride-diethyletherate with sodium borohydride is influenced by the mode of addition. Little diborane is liberated until the ratio of boron trifluoride to sodium borohydride exceeds 0.57. Up to this ratio a complex is formed ($NaBH_4.BH_3$). Therefore to ensure steady liberation ofdiborane, sodium borohydride should be added to a solution of boron trifluoride diethyletherate thus ensuring that the ratio always exceeds the critical value[216] Fig. 4.

5.9 Synthesis of materials

5.9.1) Iron tris(pentane-2,4-dionate)

A warm stirred solution of ferric chloride hexahydrate (5g, 18.5 mmole) dissolved in hydrochloric acid (0.8M, $50cm^3$) was neutralised dropwise with aqueous ammonia (1:1) to the first permanent precipitate, which was just redissolved by the dropwise addition ofhydrochloric acid (2M) and the solution was then cooled. Sodium acetate (8g, 9.75 mmole) was dissolved in the solution followed by slow addition of pentane-2,4-dione (5.9g, 59.0 mmole) depositing a red precipitate. The precipitate was filtered under suction and washed on the filter with water. Recrystallization from aqueous ethanol gave a red product which was filtered off and then dried at 100°C for five minutes, yield 3.9g, (60%).

5.9.2) Diphenylacetylene-bis(triphenylphosphine) platinum (0)

The precursor, cis-bis(triphenylphosphine) platinum dichloride, was prepared by the addition of a hot ethanolic solution ($10cm^3$) of triphenylphosphine (1.25g, 4.77 mmole) to a stirred, hot, aqueous solution ($10cm^3$) of potassium chloroplatinite (1.0g, 2.41 mmole). After shaking the mixture for one hour the product was filtered off (no. 4 sinter) and washed successively with hot water (2 x $5cm^3$), hot ethanol ($5cm^3$), then diethylether ($45cm^3$) and hydrazine hydrate added ($2cm^3$, 100%). The suspension was warmed to 40°C and gently agitated until effervescence ceased. A solution of diphenylacetylene (0.67g, 3.78 mmole) dissolved in absolute ethanol ($5cm^3$) was then added to the yellow reaction mixture. After intermittent shaking over one hour the reaction mixture was allowed to stand overnight at ambient temperature during which time the product precipitated. The product was filtered off and recrystallized from a benzene, methanol mixture giving white plates.

Mpt 161-7°C (yield 1.32g, 78%)

$$K_2PtCl_4 + 2Ph_3P \longrightarrow (Ph_3P)_2PtCl_2 + 2KCl$$

$$2(Ph_3P)_2PtCl_2 + N_2H_4 + 2PhC{\equiv}CPh \longrightarrow 2(Ph_3P)_2PtPhC{\equiv}CPh + N_2 + 4HCl$$

5.9.3) Bis(phenylethynyl)mercury

$$2PhC{\equiv}CH + 2KOH + HgI_2 \longrightarrow (PhC{\equiv}C)_2Hg + 2KI + H_2O$$

A solution of phenylacetylene (1.52g, 15 mmole) in 95% ethanol ($35cm^3$) was added dropwise into an ice cooled, stirred solution of mercuric iodide (3.38g, 7.5 mmole) and potassium hydroxide (1.96g, 35 mmole) dissolved in 95% ethanol (150cm^3). The reaction mixture was allowed to stand for four hours then poured into water (200cm^3) and extracted with diethylether (3 x 100cm^3). The combined diethylether extracts were washed with water (2 x 50cm^3) then dried over anhydrous magnesium sulphate. The dry, filtered diethylether solution was reduced in volume and the products recovered. On recrystallization from 95% ethanol the white product was recovered (yield 2.37g, 80%).

5.9.4) Vanadyl bis(2,4-pentanedionate)

Vanadium pentoxide (5g, 27 mmole) was dissolved in a mixture of conc. sulphuric acid (10cm^3), water (10cm^3) and ethanol (25cm^3). On prolonged boiling (1-2 hours) the solution changed colour from green to blue. The hot solution was filtered and 2,4-pentanedione (12.7g, 126 mmole) was added to the stirred filtrate. The stirred reaction mixture was neutralized with aqueous sodium carbonate (200cm^3, 10% w/v) and the product filtered off then washed on the filter with water. The air dried product was recrystallized from chloroform giving blue-green crystals (yield 5.6g, 78%).

5.9.5) Nickel bis(dimethylglyoximate)

A solution of nickel dichloride (1.3g, 10 mmole) in water (250cm^3) was made acidic with hydrochloric acid (50cm^3, 2M) and heated to boiling then removed from the heat. Dimethylglyoxime (2.5g, 22 mmole) dissolved in ethanol (350cm^3) was added to the hot nickel solution which was then neutralized carefully with dilute ammonia to the first permanent precipitate. The reaction solution was then made alkaline by addition of further dilute ammonia (100cm^3, 2M). The reaction solution was warmed for fifteen minutes then allowed to cool to ambient temperature. Using a sinter funnel the red product was filtered off and washed with water until washings were chloride free (tested by silver nitrate solution). The precipitate was then dried to constant weight at 100 - 120°C, yield 2.5g (86%).

5.9.6) 3-Acetyl-3-penten-2-one ($(CH_3CO)_2C = CH-CH_3$)

2,4-Pentanedione (40g, 0.4 mole) and acetaldehyde (18g, 0.3 mole) were mixed and allowed to stand for 7 days. The reaction mixture was distilled under vacuum (10mm Hg). The fraction collected at 80°C/10mm Hg pressure was identified by 'H.N.M.R. to be the required product, 3-acetyl-3-penten-2-one. A small fraction distilling at 120°C/10mm Hg was considered to be the isomeric 3-acetyl-4-penten-1-one. Analysis of the major fraction by G.L.C. on 10% Apiezon-L at 150°C, 3' x ¼" column showed only trace impurities. Mass spectroscopy showed a molecular ion at 126 m/e., corresponding to the expected product[217].

5.9.7) N-Methylformanilide

Methanoic acid (92g, 1.96 moles) was added with stirring at ambient temperature to a solution of N-methylaniline (107g, 1 mole) in toluene ($200cm^3$). Water was removed by azeotropic distillation, toluene being replaced into the reaction flask, and on completion toluene was distilled from the mixture. The residue was distilled under vacuum bpt 136°C/45mm Hg (cf. lit 114-20°C 0.8mm Hg) yielding 114.9g (85% theory) of the required product[218].

5.9.8) N,N,N',N'-Tetramethyldiaminomethane

Aqueous dimethylamine solution (25%), prepared by the neutralization of a solution of dimethylammonium chloride (40.7g, 0.5 mole) in water ($120cm^3$) with solid sodium hydroxide at 0°C, was added during one hour at 0°C to stirred aqueous formaldehyde (20.3cm^3, 37%, 0.25 mole). The temperature of the water white reaction mixture was maintained below 7°C whilst stirring for a further thirty minutes. Potassium hydroxide solid (ca.15g) was added in portions until the appearance of two layers was noted. Further quantities were added (ca.5g) until no further increase in the amount of the upper layer was noted. The upper layer was then separated and dried over solid potassium hydroxide for two days. Distillation of the colourless liquid gave the required product (16.3g, 0.16 mole, 65.4%) identified by boiling point 82°C/760mm and 'H.N.M.R.[219].

$$2(CH_3)_2NH + HCHO \longrightarrow (CH_3)_2NCH_2N(CH_3)_2 + H_2O$$

5.9.9) N,N-Dimethylaminomethylferrocene (I)

Ferrocene (9.3g, 50 mmole) was added to a warm, stirred mixture of bis(dimethylamino) methane (2.55g, 25 mmole) and paraformaldehyde (0.75g, 25 mmole) dissolved in glacial acetic acid (19.8g, 0.33 mole). The mixture was gently refluxed for four hours, all reactants being fully dissolved within the first hour, then allowed to cool below 100°C when water (50cm^3) was added. The resultant brown slurry was filtered (hot) and the solid washed with dilute acetic acid followed by water. The clear brown filtrate and combined washings were chilled in ice and made strongly alkaline with aqueous sodium hydroxide (50% w/v) then extracted with diethylether (3 x 80cm^3). Water soluble decomposition products were removed by washing the combined ether extracts with water (30cm^3). After drying over anhydrous $MgSO_4$ and filtration the ether was evaporated giving crystals of dark red-brown dimethylaminomethyl ferrocene (I)(5.3g, 21.8 mmole, 43.6%) identified by 'H.N.M.R.[219] Fig. 5.

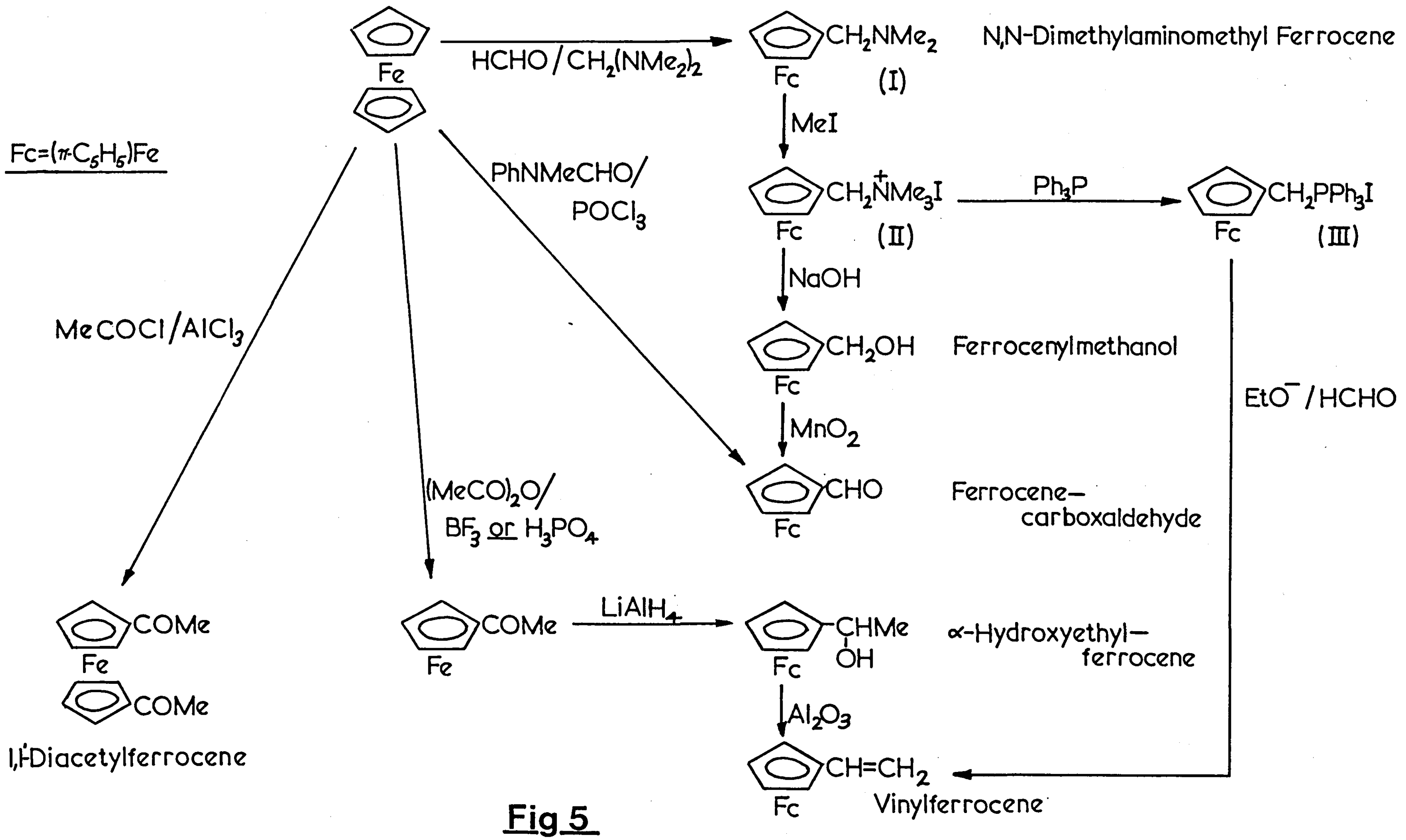
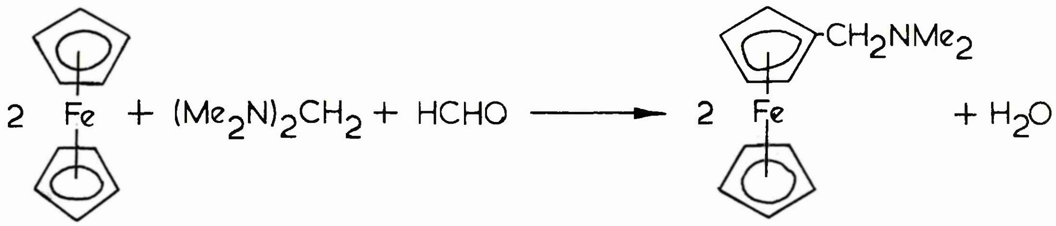


Fig 5

Substituted ferrocenes

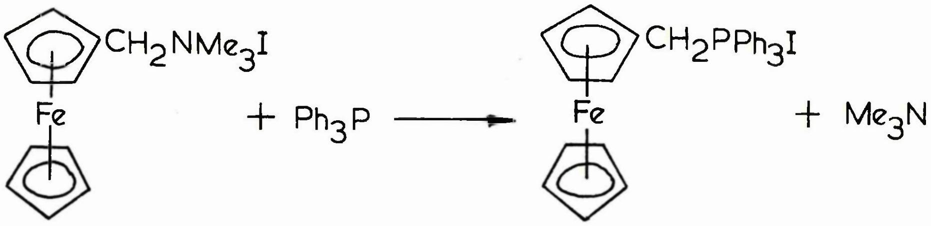


5.9.10) Quaternary methiodide of N,N-dimethylaminomethyl ferrocene (II)

A solution of iodomethane (4.64g, 32.7 mmole) in absolute methanol (5cm^3) was added dropwise to a cold (0°C) solution of N,N-dimethyl ferrocene (4.69g, 21.8 mmole) dissolved in absolute methanol (5cm^3). On completion of the addition, the reaction mixture was refluxed for five minutes, allowed to cool slightly and then diethylether (50cm^3) added. With shaking the reaction mixture dissolved to yield, on cooling, a yellow precipitate. The precipitate was filtered, air dried, then recrystallized from the minimum of absolute ethanol. The filtered product was dried under vacuum at 40°C and identified by infrared spectroscopy as (II) (yield 2.95g, 7.6 mmole, 35.1%)[219] Fig. 5.

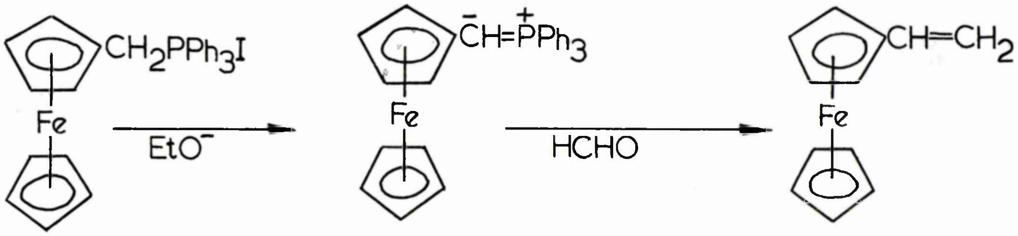
5.9.11) Reaction of N,N-dimethylaminomethylferrocene methiodide (II) with triphenylphosphine

A solution of II (2.95g, 7.6 mmole) dissolved in absolute ethanol (25cm^3) with an equimolar amount of triphenylphosphine (2g) was refluxed for six hours. On allowing to cool, yellow crystals formed on standing during sixteen hours. The crystals were filtered off, then recrystallized from a minimum of absolute ethanol yielding, when dry, ferrocenylmethyl(triphenyl)phosphonium iodide (III), Mpt 215 - 220°C (3.3g, 5.6 mmole, 74%) identified by infrared spectroscopy[219] Fig.5.



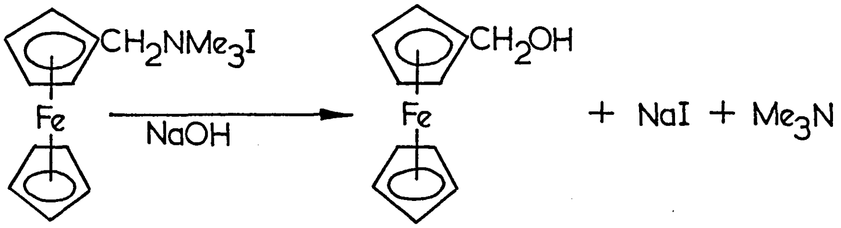
5.9.12) Vinyl ferrocene by Wittig reaction

Ferrocenylmethyl(triphenyl)phosphonium iodide (1.5g, 2.55 mmole) was dissolved in absolute ethanol at reflux followed by the addition of sodium ethoxide solution (1cm^3, 2.73 mmole $NaOC_2H_5$), prepared by dissolution of sodium (1.25g, 54.6 mmole) in ethanol (20cm^3). The solution was refluxed for a further five minutes, during which time darkening occured. Paraformaldehyde (0.12g, 4.0 mmole) was added and reflux continued for thirty minutes at which point the reaction mixture was poured into aqueous hydriodic acid (2M, 40cm^3). The resultant dark solution was extracted with diethylether which was then washed with aqueous sodium chloride solution (10%), aqueous sodium carbonate (10%), and finally aqueous sodium hydroxide solution. The ether solution was dried then evaporated leaving a small amount of dark red-brown product identified as vinyl ferrocene by mass spectrometry.



5.9.13) Hydroxymethyl ferrocene

Aminomethyl ferrocene methiodide (3.29g, 10 mmole) was refluxed in a 10% excess of aqueous sodium hydroxide (1M) for two hours. On cooling the solution was extracted with diethylether which was then water washed until neutral. After drying over anhydrous magnesium sulphate, evaporation of ether gave a yellow solid, yield 1.83g (85%) Mpt 81°C, (Lit 81-2°C), identified as the required product by Mpt and infrared spectroscopy[219].



5.9.14) Active manganese dioxide

A solution of manganese (II) sulphate tetrahydrate (1.04 mole) in water ($312cm^3$) and aqueous sodium hydroxide ($250cm^3$, 40% w/v, 2.5 moles) were simultaneously added to hot stirred aqueous potassium permanganate solution ($1.25dm^3$, 1 mole dm^{-3}) during one hour at 50 - 60°C. The hot mixture was stirred for one hour and then filtered. The precipitated manganese dioxide was washed by dispersion in water($1dm^3$) then filtered off. On drying for sixteen hours at 115°C and grinding to powder a yield of 170g (1.95 moles) was recorded.

5.9.15) Ferrocene carboxaldehyde

A solution of ferrocenyl methanol (10.58g, 49 mmole) in chloroform ($50cm^3$) was cooled in ice (10-15°C) and freshly prepared active manganese dioxide (50g, 0.57 mole) added slowly with stirring and cooling. The slurry was allowed to stand for twenty hours.

The mixture was filtered and the solids washed well, firstly with chloroform, then diethylether until the washings became colourless. The combined washings were evaporated to yield (98% crude) a red solid, identified as the required product by infrared spectroscopy which was stored under nitrogen atmosphere in the dark[220].

5.9.16) Ferrocene carboxaldehyde

Phosphorus oxychloride (4.91g, 32 mmole) was added to N-methylformanilide (4.32g, 32 mmole) and the mixture allowed to stand for one hour at ambient temperature. Ferrocene (2.97g, 16 mmole) was added to the stirred mixture during thirty minutes and, on completion, the flask was purged with nitrogen, stoppered, and stored in the dark for seventy two hours. The dark red reaction mixture was hydrolysed with water for six hours at ambient temperature and the product extracted with chloroform. After drying over anhydrous magnesium sulphate the chloroform was removed and the residue dissolved in dry benzene. Chromatography of the solution on deactivated alumina (2cm x 15cm column) eluted with benzene allowed separation of red-orange ferrocene carboxaldehyde from other reaction products. On removal of benzene the product remained as red-orange light sensitive crystals identified by melting point (120°C) cf. lit 121°C and infrared spectroscopy[221].

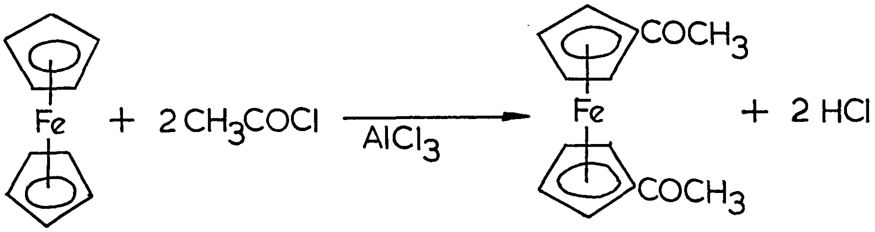
5.9.17) Acetyl ferrocene

A stirred mixture of ferrocene (93.0g, 0.5 mole), acetic anhydride (250cm^3, 2.26 mole) and phosphoric acid (20cm^3, 85%, 0.1 mole) was heated at 100°C for ten minutes. On cooling slightly (85°C) the mixture was poured onto ice and left overnight. The black mass was stirred in a 2 litre beaker and neutralized with a slurry of anhydrous sodium carbonate (170.7g, 1.61 mole) in water

($300cm^3$) added very slowly (six hours) accompanied by vigorous foaming. A further amount of sodium carbonate (29.7g, 0.28 mole) in water ($200cm^3$) was added to achieve neutrality. The brown slurry was filtered and the solid washed with water (2 x $200cm^3$) by distribution in the water and refiltration. The filtrate was dried under vacuum at 45°C (710mm Hg). Purification by sublimation (100°C, 0.1mm - 1mm Hg) gave an orange solid Mpt 74 -78°C. Alternatively, Soxhlet extraction of the mass with dry diethylether, until colourless, gave on evaporation to dryness an orange solid Mpt 74 - 78°C. Overall yield 98.1g (0.43 mole, 85.5%). The crude acetyl ferrocene was recrystallized from n - heptane to yield a product of melting point 84 - 87°C (lit 85 - 86°C)[222].

5.9.18) 1,1'-Diacetyl ferrocene

Anhydrous aluminium chloride (24.03g, 0.18 mole) was added under nitrogen atmosphere to dry, stirred, dichloromethane ($700cm^3$) in a flask equipped with reflux condenser and sidearm dropping funnel. Acetyl chloride (14.13g, 0.18 mole) was added to the reaction mixture, dissolving the aluminium chloride. A solution of ferrocene (19.9g, 0.107 mole) dissolved in dry dichloromethane ($70cm^3$), was added dropwise during two hours with resultant evolution of hydrogen chloride gas from the purple reaction mixture. On completion of addition the reaction mixture was stirred under nitrogen atmosphere at ambient temperature for ninety six hours. The purple/black reaction mixture was then hydrolysed by pouring onto ice (100g) giving a red emulsion. Filtration by suction gave two separate phases (liquid). The organic phase was separated and water washed until the washings were neutral, then dried over anhydrous calcium sulphate for six hours, decanted and further dried for sixteen hours. Evaporation of the solvent under a stream of nitrogen gave a solid residue which, once recrystallized from methanol, had Mpt 123-5°C (Lit 127°C) and was identified by mass spectrometry as 1,1'-diacetyl ferrocene[223].



5.9.19) ∝-Hydroxy ferrocenylethanol

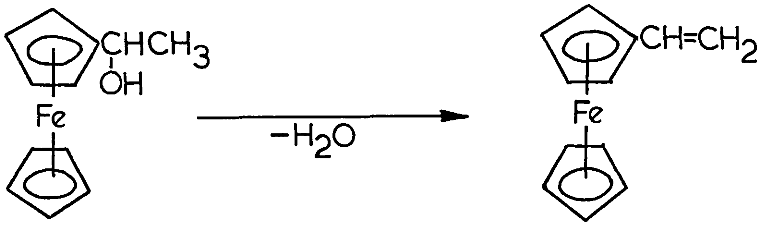
A stirred mixture of acetyl ferrocene (31.9g, 0.14 mole) in dry diethylether (500cm^3) under nitrogen atmosphere was treated dropwise with a solution of lithium aluminium hydride (1.89g, 50 mmole) in dry ether, then refluxed for two hours. Excess lithium aluminium hydride was destroyed by addition of ethylacetate and the resultant mixture was treated with a solution of ammonium chloride (26.75g, 0.5 mole) in water.

$$4\ CH_3COOC_2H_5 + LiAlH_4 \longrightarrow LiOC_2H_5 + Al(OC_2H_5)_3 + 4\ C_2H_5OH$$

The mixture was cooled, with stirring, to 0°C then allowed to stand overnight. After filtration of the whole reaction mixture, the ether layer was separated, then washed with water (2 x 100cm^3). The ether solution was concentrated and allowed to stand (forty-eight hours). Long red needles, found to have formed, were filtered and air dried. The dark red needles were recrystallized from 40 - 60° petroleum to give light red-orange crystals which were air dried, yield 18.2g (79%) Mpt 73 - 75°C (Lit 73 - 75°C) identified by 'H.N.M.R. and mass spectrometry[224].

5.9.20) Dehydration of ∝-hydroxy ferrocenylethanol

∝-Hydroxy ferrocenylethanol (2.2g, 9.6 mmole) was ground together with alumina (Merck neutral grade type T; 10.5g) which had been activated for several days at 350°C. The mixture was charged into a sublimer and covered with an additional layer of alumina. The apparatus was slowly evacuated to 10mm Hg pressure and held at this pressure for one hour before slowly heating to 150°C in an oil bath. During a period of twelve hours at 150°C/10mm Hg pressure an orange solid sublimed onto the cold finger condenser and was found to melt at 47°C. The product was identified by 'H.N.M.R. and mass spectrometry to be vinyl ferrocene. Yield 1.11g, 5.26 mmole, (55%).



5.9.21) Bis(∝-hydroxyethyl-cyclopentadienyl) iron

A stirred solution of diacetyl ferrocene (1.08g, 4 mmole) in dry diethylether (20cm^3) under nitrogen atmosphere was treated dropwise at room temperature with a solution of lithium aluminium hydride (0.18g, 4.75 mmole) dissolved in dry diethylether (25cm^3). (Lithium aluminium hydride solution was prepared by refluxing in dry ether until dissolved-approximately thirty minutes). The reaction mixture was then refluxed for two hours. Excess lithium aluminium hydride was destroyed by the cautious addition of ethyl acetate (1cm^3) to the hot solution. The mixture was cooled to 0°C in an ice bath and treated with a solution of ammonium chloride (0.214g, 4 mmole) in water (10cm^3). The cold solution was stirred for a further thirty minutes then allowed to stand, warming to ambient temperature overnight. The reaction mixture was filtered and the red diethylether layer separated. After washing with water (2 x 5cm^3) the ethereal solution was dried over anhydrous magnesium sulphate. Evaporation of ether gave red crystals of product yield 0.75g (2.73 mmole, 68.3%) identified by 'H.N.M.R and infrared spectroscopy.

5.9.22) Diphenylacetic acid

Red phosphorus was purified by the method previously described.[225] Glacial acetic acid (167cm^3, 2.65 mole) was charged into a flask (500cm^3) together with red phosphorus (10g, 0.32 mole) and iodine (3.3g, 13 mmole). During approximately one and a half hours the iodine was consumed, the mixture being heated to about 35°C after half this time. Water (3cm^3, 166 mole) and benzilic acid (100g, 0.44 mole) were added to the reaction mixture which was then refluxed for three hours and the hot solution filtered to remove excess phosphorus. To remove excess iodine the hot liquor was poured into a well stirred solution of sodium bisulphite (16g, 77 mmole) in water (660cm^3) prepared by dissolution of sodium metabisulphite (14.61g, 77 mmole) thus:-

$$Na_2S_2O_5 + H_2O \longrightarrow 2\ Na\ HSO_3$$

$$Na\ HSO_3 + HI \longrightarrow NaI + SO_2 + H_2O$$

A white precipitate formed which was filtered, washed with cold water then dried under reduced pressure. The product was recrystallized from 50% aqueous ethanol yielding white plates melting at 146°C when dry. The product was identified as diphenylacetic acid by infrared spectroscopy and 'H.N.M.R. yield 56g 0.26 mole, (59%)[225,226].

$$Ph_2C(OH)COOH + I^- \longrightarrow Ph_2C(I)COOH + OH^-$$

$$Ph_2C(I)COOH + H^+ \longrightarrow Ph_2\overset{-}{C}COOH + HI$$

$$Ph_2\overset{-}{C}COOH + H^+ \longrightarrow Ph_2CHCOOH$$

5.9.23) Diphenyl ketene

Thionyl chloride (80cm^3, 1.11 mole) was added during 30 minutes to a stirred solution of diphenylacetic acid (48.8g, 0.23 mole) in dry, thiophen free benzene (150cm^3) at reflux. The solution was then refluxed for a further seven and a half hours. The yellow solution was distilled under reduced pressure with an air bleed. With gentle warming azeotropic benzene/thionyl chloride was removed (214cm^3). A further amount of benzene was added (100cm^3) and distilled off to remove any remaining thionyl chloride, leaving a yellow oil. The yellow oil was poured into refluxing dry hexane (dried by distillation from solid KOH) then treated hot with charcoal. Following filtration the solution was cooled to 0°C in a stoppered flask and maintained at this temperature during six hours with occasional scratching until crystals were seen to form. The flask was maintained at 0°C to allow complete crystallization. On filtration the crystals were washed with a little chilled dry hexane and dried in a desiccator overnight yielding 32.2g melting point 49 - 50°C. The liquors when reduced in volume yielded a further 10g having the same melting point. The whole was recrystallized once more yielding overall 37g, 0.19 mole, (83%) Mpt 49 - 50°C. Identified as diphenylacetyl chloride by ^{1}H.N.M.R.

A stirred ice cold solution of diphenylacetic acid (37g, 0.19 mole) in dry diethylether (300cm^3) was treated dropwise with triethylamine (19.2g, 0.19 mole) during one hour under dry nitrogen atmosphere. The reaction mixture was maintained at 0°C for sixteen hours, then the precipitated triethylamine hydrochloride was filtered off. The filtered solid was washed on the filter with dry ether and the washings and filtrate combined. The diethylether solution was reduced in volume under reduced pressure, leaving a reddish oil. Distillation under reduced pressure of the oil through a 10cm Vigreux column gave a light red oil Bpt 130°C/2mm Hg pressure, which was stored at 0°C. The product was identified as diphenylketene by infrared spectroscopy[224].

$$Ph_2CHCOOH + SOCl_2 \longrightarrow Ph_2CHCOCl + SO_2 + HCl$$

$$Ph_2CHCOCl + N(C_2H_5)_3 \longrightarrow Ph_2C{=}C{=}O + (C_2H_5)_3N\ HCl$$

5.9.24) *Diglyme molybdenum tricarbonyl

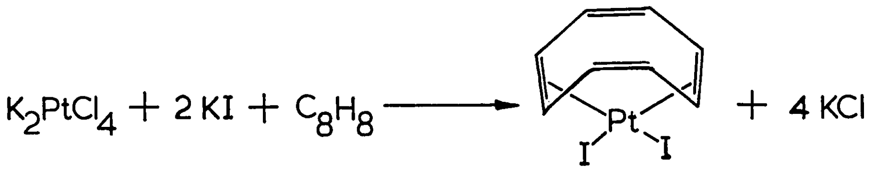
Molybdenum hexacarbonyl (3g, 11.36 mmole) was dissolved in a mixture of dry benzene ($3cm^3$) and diglyme (9.45g, 70 mmole). The yellow-green solution was refluxed under nitrogen atmosphere, gradually darkening in colour, a small amount of black deposit being formed after three hours. The extent of reaction was followed by the evolution of carbon monoxide from the reaction. After ten hours, on cessation of gas evolution, the solution was transferred under nitrogen to a Schlenk tube and warmed to dissolve all soluble material then filtered. On cooling to -20°C the product crystallized. The yellow-green crystals were filtered off then dried under vacuum[228].

*Diglyme: bis(methoxethyl)ether.

$$\begin{array}{c} (CH_3OCH_2CH_2)_2O + Mo(CO)_6 \\ \big\downarrow \\ (CH_3OCH_2CH_2)_2OMo(CO)_3 + 3CO \end{array}$$

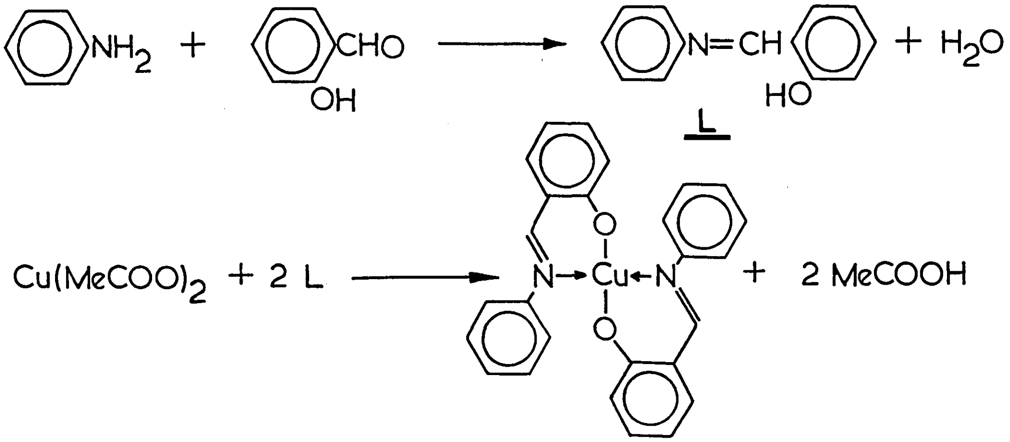
5.9.25) Cyclooctatetraene platinum diiodide

Dipotassium platinum tetrachloride (0.79g, 2.056 mmole) was dissolved in warm water (60°C) to which potassium iodide (1.5g, 9.036 mmole) was added giving a "black" mixture. The solution was filtered and cooled. Cyclooctatetraene (0.5g, 4.8 mmole) was added and the mixture was shaken vigorously at intervals for two hours then allowed to stand for twenty four hours during which time a yellow-brown precipitate formed. The precipitate was filtered and recrystallized from chloroform yielding yellow-orange crystals (0.64g, 1.15 mmole, 56.3%) identified by infrared spectroscopy[229].



5.9.26) Copper bis(salicylidenaniline)

Aniline (0.93g, 10 mmole) and salicylaldehyde (1.22g, 10 mmole) were condensed in absolute ethanol (10cm^3). Following a mildly exothermic reaction a yellow precipitate of the Schiff base formed. A stoichiometric amount of copper (II) acetate monohydrate (1.0g, 5 mmole) was added to the slurry and the reaction mixture was refluxed for fifteen minutes then allowed to cool. A brown crystalline material precipitated from solution and was filtered off, washed on the filter with 40 - 60° petroleum ether, and dried under vacuum. The product was found to melt at 205°C.



5.9.27) <u>Cobalt bis(salicylidenaniline)</u>

Aniline (0.93g, 10 mmole) and salicylaldehyde (1.22g, 10 mmole) were condensed in absolute ethanol (10cm^3) giving a yellow product. Aqueous sodium hydroxide solution (5cm^3/2M = 10 mmole) followed by cobalt (II) acetate hydrate (0.97g, 5 mmole) were added. The red reaction mixture was refluxed for fifteen minutes and gave on cooling a red-brown precipitate. The precipitate was filtered off then reprecipitated from chloroform with 40 - 60° petroleum ether. The red-brown product melted at 186°C.

$$\mathrm{Co(CH_3COO)_2 + 2(PhNCHPh(OH)) \xrightarrow{2NaOH} Co(PhNCHPh(O))_2 + 2\ CH_3COONa + 2H_2O}$$

5.9.28) <u>Nickel bis(salicylidenaniline)</u>

Nickel (II) acetate hydrate (0.97g, 5 mmole) was added to a solution of salicylidenaniline produced by condensation of aniline (0.93g, 10 mmole) and salicylaldehyde (1.22g, 10 mmole) in absolute ethanol (10cm^3) which was then made alkaline by the addition of aqueous sodium hydroxide (5cm^3, 10 mmole). The mixture was refluxed for fifteen minutes then allowed to cool, yielding a green tarry deposit. The supernatant liquor was decanted and the residue dissolved in chloroform ($15cm^3$) and precipitated by the addition of $40^o - 60^o$ petroleum, filtered and air dried, as a yellow-green product of melting point $320 - 322^o$.

5.9.29) Cyclooctatetraene iron tricarbonyl

Triethylamine-N-oxide (3.0g, 40 mmole) and cyclooctatetraene (1.04g, 10 mmole) were stirred together in dry tetrahydrofuran under nitrogen atmosphere at 0^oC (ice bath). Iron pentacarbonyl (3.92g, 20 mmole) was added to the reaction mixture from a disposable plastic syringe via a septum cap during ten minutes. The mixture was stirred at 0^oC for one hour then refluxed for one hour. The dark solution was filtered and the red liquor evaporated to dryness giving a red solid residue. Heating the residue to $70-80^oC$ at 0.1mm Hg pressure in sublimer gave the red product, yield 2.15g, 8.8 mmole (44%)[230].

$$C_8H_8 + Fe(CO)_5 + Me_3NO \longrightarrow (C_8H_8)Fe(CO)_3 + Me_3N + CO_2 + CO$$

5.9.30) π-Cyclopentadienyl-π-indenyliron

All manipulations were carried out under nitrogen atmosphere and freshly dried and distilled tetrahydrofuran was used. Freshly distilled indene (34.9g, 300 mmole) and sodium 6.9g, 300 mmole) were refluxed in tetrahydrofuran ($150cm^3$) until no sodium remained, giving a yellow solution of sodium indenide. Similarly a solution of sodium cyclopentadienide was prepared from cyclopentadiene (16.3g, 250 mmole) and sodium (5.75g, 250 mmole) in tetrahydrofuran ($150cm^3$) giving a rose-pink solution.

A suspension of ferrous chloride was prepared by the addition of iron powder (4.7g, 84 mmole) to ferric chloride (27.1g, 167 mmole) suspended in tetrahydrofuran which was then stirred and refluxed for four and a half hours during which time the solution became dark brown with a grey iron residue. The previously prepared solution of sodium indenide and sodium cyclopentadienide were added to the stirred suspension of ferrous chloride simultaneously during twenty minutes, then the black reaction mixture was refluxed for sixteen hours. Tetrahydrofuran was removed under reduced pressure and the residue extracted with dry pentane (5 x 100cm^3) which was then filtered. The pentane solution was reduced in volume by evaporation under a stream of nitrogen to approximately 25cm^3. The solution was chromatographed on alumina H (200 mesh) with pentane eluent (20cm x 1cm column) in several portions. The first band (yellow) was found to contain ferrocene and the second (red-violet) band contained the expected product together with a small amount of ferrocene, as shown by mass spectrometry. The pentane solution containing the required product was reduced in volume to dryness under a stream of nitrogen, allowing recovery of the red-purple product (4.1g, 7.0% yield)[231].

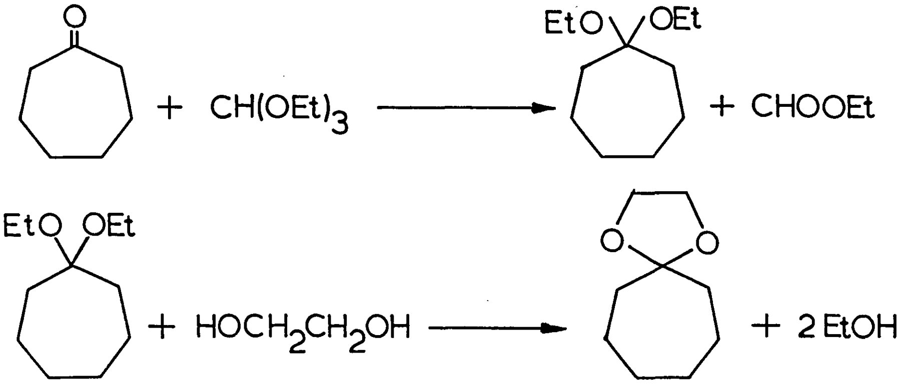
5.9.31) <u>1,3,5-Cycloheptatriene iron tricarbonyl</u>

Trimethylamine-N-oxide (3.0g, 40 mmole) and cycloheptatriene (0.92g, 10 mmole) in dry tetrahydrofuran (25cm^3) were stirred at 0°C (ice bath) under nitrogen atmosphere. Iron pentacarbonyl (3.9g, 2.7cm^3, 20 mmole) was added via a septum cap from a disposable plastic syringe during ten minutes. The reaction mixture became dark red and was stirred at 0°C for a further one hour then refluxed for one hour. The dark red solution was filtered hot and the solution evaporated to dryness leaving a dark red residue identified by mass spectrometry as the required product.

$$C_7H_8 + Fe(CO)_5 + Me_3NO \longrightarrow C_7H_8Fe(CO)_3 + Me_3N + CO_2 + CO$$

5.9.32) 1,3-Dioxaspiro[4,6] undecane

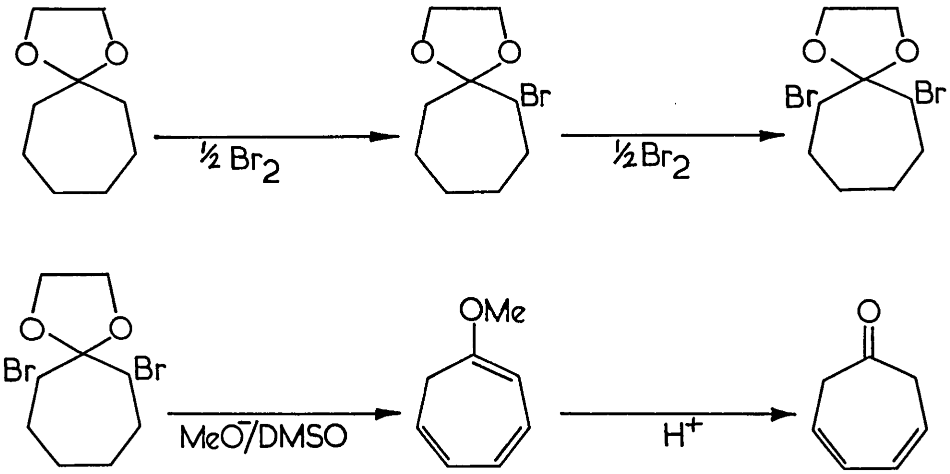
Triethylorthoformate (71.1g, 0.48 mole) was added at room temperature during five minutes to a solution of cycloheptanone (49.4g, 0.44 mole) and p-toluenesulphonic acid (0.19g, 1.1 mmole) in dry diethylene glycol (34.13g, 0.55 mole). The reaction mixture was heated on a steam bath and ethanol distilled from the mixture. After four hours the reaction was complete and the mixture was cooled and dilute aqueous sodium hydroxide (4cm^3, 2M) added and stirred for five minutes. The mixture was extracted with diethylether (2 x 100cm^3) and the combined ether layer dried over anhydrous magnesium sulphate during sixteen hours. The filtered ether layer was reduced in volume by rotary evaporation and the residue distilled under vacuum, the required product boiling at 52-5°C/1.3mm Hg pressure, yield 44.4g, 0.28 mole (64.6%).



5.9.33) 3,4-Cycloheptadienone

1,3-Dioxaspiro[4,6]undecane (31.24g, 0.2 mole) dissolved in absolute methanol (500cm^3) was treated at 25°C whilst continuously stirred, with a small portion (100 drops) of bromine, giving a dark solution. On disappearance of the colouration the remainder was added (32.0g, 0.2 mole, in total) at a rate sufficient to maintain reaction, and leaving a slight excess on completion. The reaction mixture was heated to 40°C and treated again with bromine

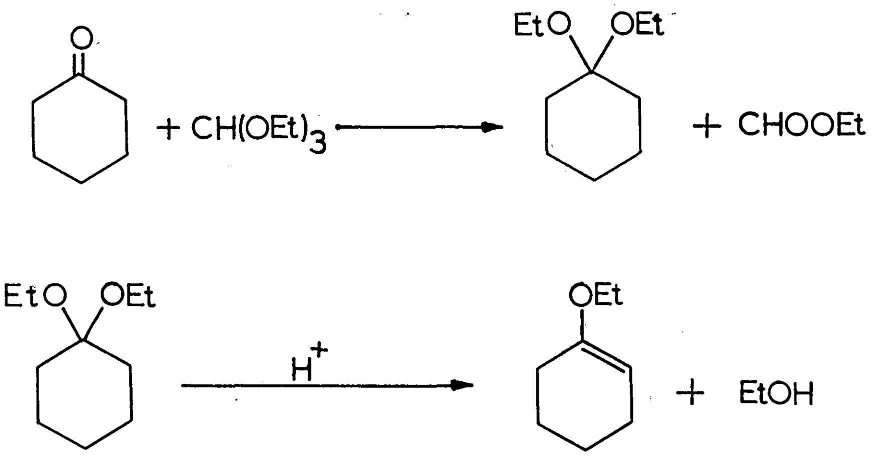
(32.0g, 0.2 mole) as previously. On completion of addition the temperature was maintained for one hour then the reaction mixture was allowed to cool and stand during sixteen hours, at which time a small excess of bromine was still present as indicated by the colour. (An excess of bromine must be present throughout). The yellow reaction mixture was poured into stirred pentane (500cm^3) containing anhydrous sodium carbonate (50g, 0.47 mole), with effervescence, and stirred for five minutes. Following the addition of water (500cm^3), with stirring, the pentane layer was separated and dried over anhydrous magnesium sulphate, then filtered. The volume of the pentane layer was reduced by rotary evaporation at reduced pressure and the temperature raised gradually to 55°C removing all solvent and resulting in a colourless oily pungent liquid. Freshly prepared sodium methoxide (38g, 1 mole) was added to a stirred solution of the oil in dry dimethylsulphoxide (200cm^3) whilst cooling to maintain the temperature below 60°C. After fifteen minutes the temperature of the reaction mixture was stable and cooling was removed. The stirred mixture was allowed to stand for sixteen hours at room temperature. The reaction mixture was poured into saturated brine (200cm^3) and extracted with pentane. The whole mixture was filtered to remove flocculated sodium bromide which was washed on the filter with pentane. The combined liquors were separated and the pentane layer dried over anhydrous magnesium sulphate for four hours. The filtered pentane solution was reduced in volume at atmospheric pressure and the oily product was then distilled under vacuum, boiling at 42°C/o.8mm Hg pressure. The distilled oil was split into 5g portions each of which was stirred at ambient temperature with aqueous sulphuric acid (10%) for sixteen hours. The mixtureswere extracted with pentane and the extracts were washed with aqueous sodium bicarbonate solution then dried over anhydrous magnesium sulphate. Evaporation of the solvent from the combined extracts followed by vacuum distillation gave a colourless oil boiling at 60°C/6mm Hg pressure, yield 5g (23% based on C_7H_8O). During sixteen hours the product darkened and resinified[232].



5.9.34) Cyclohexanonediethylene ketal

Cyclohexanone (40g, 0.41 mole), triethyl orthoformate (185g, 4 mole) were refluxed together with p-toluene sulphonic acid (0.04g, 0.23 mmole) for ten minutes. The reaction mixture was cooled and then neutralised with potassium ethoxide (0.23 mmole). Fractionation under reduced pressure, removing excess alcohol and ethyl formate, allowed recovery of cyclohexanone diethylene ketal boiling at 60°C/9mm Hg pressure in high yield 67g, (95%).

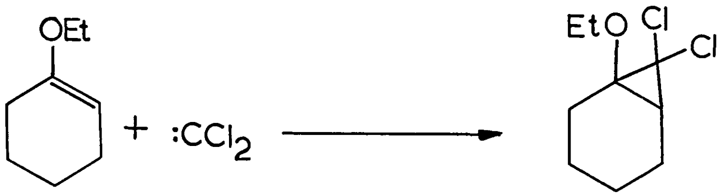
The diethylene ketal (12g, 70 mmole) together with p-toluene sulphonic acid (0.04g) was heated at ambient pressure and ethanol distilled from the mixture. On fractionation under reduced pressure a colourless oil boiling at 47-8°C/10mm Hg pressure was recovered, yield 7.6g (87%), and identified as 1-ethoxycyclohexene by 'H.N.M.R.



5.9.35) 1-Ethoxy-7,7-dichloronorcarane

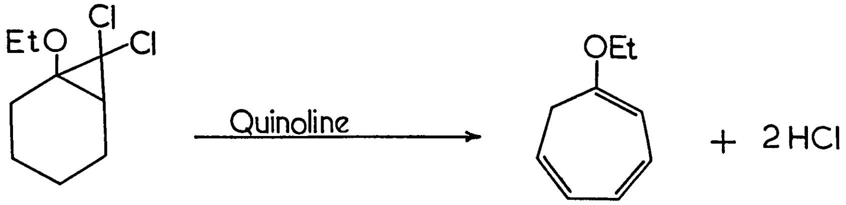
Ethyltrichloroacetate (126.4g, 0.66 mole) was added dropwise to a stirred slurry of sodium ethoxide (44.8g, 0.66M) and 1-ethoxycyclohex-1-ene (80g, 0.63 mole) in sodium dried pentane ($50cm^3$) at 0°C. A vigorous exothermic reaction ensued and after maintaining the reaction at 5°C for one hour after completion of addition the mixture was allowed to warm to room temperature during sixteen hours. The reaction mixture was poured into water ($200cm^3$), extracted with pentane ($2 \times 200cm^3$) and the combined extract dried over anhydrous magnesium sulphate. The filtered dry extract was reduced in volume and the residue distilled under vacuum (bpt 64°C, 1mm Hg) yielding 27.3g, 0.13 mole (21%) of the required product, identified by 'H.N.M.R[233,234].

$$Cl_3COOEt + NaOEt \longrightarrow :CCl_2 + EtOCOOEt + NaCl$$



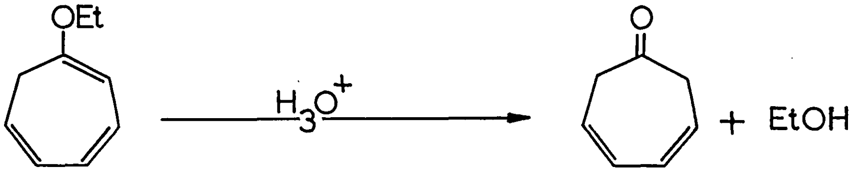
5.9.36) <u>1-Ethoxycyclohepta-1,3,5-triene</u>

1-Ethoxy-7,7-dichloronorcarane (27g, 0.129 mole) was heated under nitrogen atmosphere in dry, redistilled quinoline (100cm^3) to 160^{o}C for two hours, and then at 180^{o}C for one hour. The viscous reaction mixture was then distilled giving a low yield of crude product, redistillation of which yielded 1g, 7.3 mmole (5.7%). The product was identified by infrared spectroscopy and ^{1}H.N.M.R.



5.9.37) <u>3,5-Cycloheptadienone</u>

1-Ethoxycyclohepta-1,3,5-triene (1g, 7.3 mmole) was dissolved in methanol (10cm^3) and water (2cm^3) to which 1 drop of concentrated hydrochloric acid was added. The solution was warmed to reflux for ten minutes then cooled. The acidic solution was neutralised with sodium carbonate then extracted with pentane (3 x 10cm^3). The pentane extract was dried over anhydrous magnesium sulphate then filtered. On evaporation to recover the required product, decomposition was found to have occurred, neither product nor starting material being recoverable. Previous attempts at room temperature had resulted in recovery of the starting material.

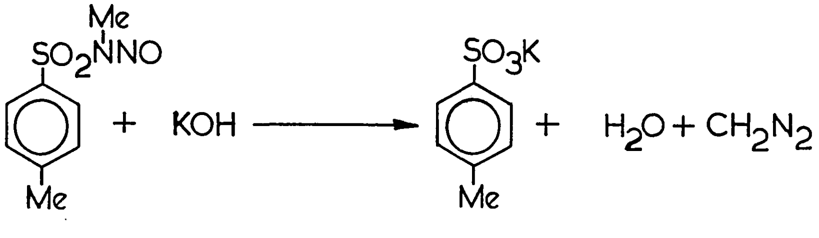


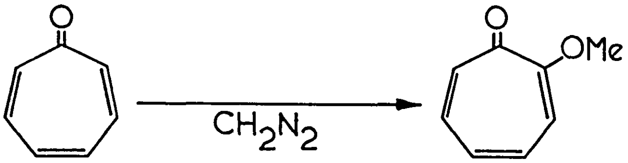
5.9.38) Tropolone methyl ether

A solution of diazomethane was prepared and reacted with tropolone as follows.

A solution of p-tolysulphonyl methyl nitrosamide (4.3g, 0.02 mole) in anhydrous diethylether (60cm^3) was ice cooled to 0^{o}C and to this was added a solution of potassium hydroxide (1.44g, 0.02 mole) dissolved in ethanol. After five minutes the ethereal solution of diazomethane was gently distilled into an ice cooled receiver containing a small amount of chilled diethylether.

Tropolone (2g, 0.0164 mole) dissolved in anhydrous diethylether (100cm^3) was treated with the ethereal diazomethane solution dropwise until a permanent yellow colour appeared. The reaction mixture was allowed to stand for one hour then boiled until all remaining yellow colouration had disappeared. The solution was heated to remove all diethylether by evaporation, leaving the product, identified by 'H.N.M.R yield 1.94g, 0.014 mole, (85.6%)^{235}.





5.9.39) 2,4-Pentanediol

2,4-Pentanedione (10g, 100 mmole) in methanol (40cm^3) was slowly added to sodium borohydride (7.6g, 200 mmole) in aqueous sodium hydroxide (20cm^3, 0.001M) with stirring at 0°C. After two hours the reaction mixture was allowed to warm to room temperature and stand for twenty-four hours. Hydrolysis was carried out by addition of aqueous sodium hydroxide (10cm^3, 2M) followed by water (10cm^3), stirring for one hour. Sodium chloride was added and the saturated solution extracted with diethylether (3 x 30cm^3). After drying the combined extracts over anhydrous magnesium sulphate and filtration, diethylether was removed under reduced pressure yielding a colourless oil. Distillation of the oil at reduced pressure yielded an impure fraction, bpt 80°C/10mm Hg pressure, which when redistilled gave a colourless liquid, yield 1.1g (10.5 mmole) bpt 198°C/760 mm Hg pressure, being identified as 2,4-pentanediol by infrared, 'H.N.M.R and mass spectroscopy.

The required product was found to be readily adsorbed by magnesium sulphate used for drying and all of it could not be recovered.

5.9.40) 1-Phenylbutan-1,3-diol

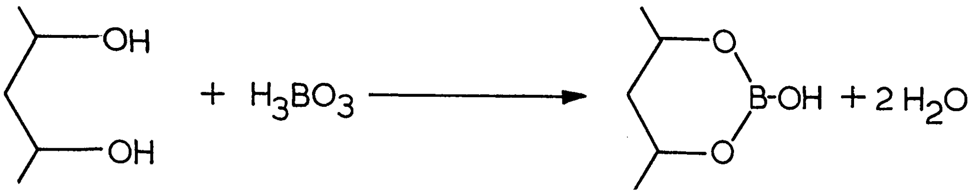
1-Phenylbutan-1,3-dione (6.3g, 38.8 mmole) dissolved in methanol (70cm^3) was added dropwise to sodium borohydride (3.03g, 80.1 mmole) stirred in aqueous sodium hydroxide (10ml, 10^{-3}M) at 0°C under a nitrogen atmosphere during thirty minutes. Stirring under nitrogen was continued during twenty-four hours, the temperature being allowed to rise to ambient during this period. Water (30cm^3) was added to the reaction mixture which was stirred for one hour. Sodium chloride was added and the saturated solution was extracted with diethylether (3 x 30cm^3). The combined extract was dried over anhydrous magnesium sulphate and filtered. Evaporation of ether yielded a colourless viscous oil which was distilled under reduced pressure with a nitrogen bleed giving as major product, 1-phenylbutan-1,3-diol bpt 162°C/3mm Hg pressure, yield 4.33g (67%)

5.9.41) 1,3-Diphenylpropan-1,3-diol

A solution of 1,3-diphenylpropan-1,3-dione (7.02g, 31.3 mmole) dissolved in methanol (180cm^3) was added dropwise to sodium borohydride (2.4g, 63.4 mmole) slurried in aqueous sodium hydroxide (10cm^3, 10^{-3}M) under nitrogen atmosphere at 0°C whilst stirring. On completion of the addition the stirred reaction mixture was allowed to warm to ambient temperature and stand for twenty four hours. Water (25cm^3) was added to hydrolyse the reaction products. Sodium chloride was added and the saturated solution extracted with diethylether (3 x 30cm^3). The combined extracts were dried over anhydrous magnesium sulphate. The filtered dry ethereal solution was reduced in volume and the product, isolated by vacuum distillation, found to be a colourless viscous oil, yield 5.2g (73%).

5.9.42) 2,4-Pentanediol borate ester

2,4-Pentanediol (0.5g, 4.8 mmole) was added to a solution of boric acid (0.297g, 4.8 mmole) in water (10cm^3) and the reaction mixture was warmed then allowed to stand for ten minutes. Sodium chloride was added and the saturated solution extracted with diethylether (3 x 10cm^3). The combined ether extract was dried (anhydrous magnesium sulphate) and filtered. Evaporation of the solution to dryness gave an impure white solid which recrystallized poorly from 40°/60° petroleum ether: diethylether. Sublimation of the impure product gave white crystals mpt 72-4°C yield 0.48g (3.7 mmole: 77%).

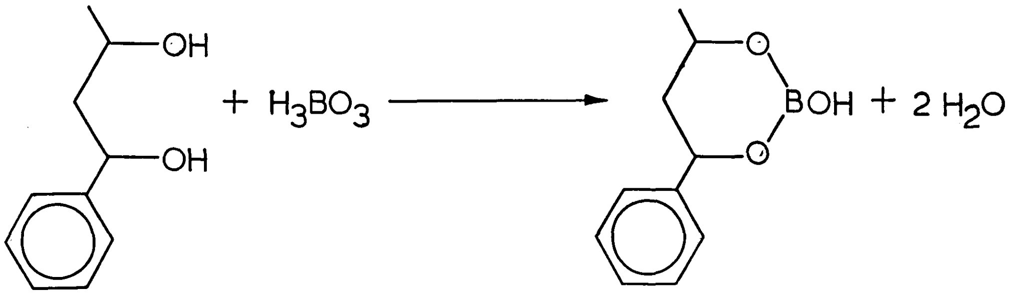


5.9.43) 2,4-Pentanediol from borate ester

2,4-Pentanediol borate ester (016g, 4.62 mmole), derived from reaction of 2,4-pentanedione and diborane, was dissolved in aqueous sodium hydroxide (5cm^3, 2M) and after ten minutes the solution was extracted with chloroform (3 x 4cm^3), the extracts being combined. The alkaline layer was acidified (2M sulphuric acid) and extracted with chloroform (2 x 4cm^3) which was separated and treated with aqueous sodium hydroxide (5cm^3, 2M). The chloroform was then combined with a further 2 x 4cm^3 chloroform and the acidification/ extraction repeated. The combined chloroform extracts were dried over anhydrous magnesium sulphate. Excess chloroform was removed by rotary evaporation then so far as possible all chloroform was removed. A small quantity of a slightly coloured oil was recovered, insufficient for distillation. The material was identified as the meso-diol as detailed elsewhere.

5.9.44) 1-Phenylbutan-1,3-diol borate ester

Boric acid (0.372g, 6.02 mmole) dissolved in hot water (10cm^3) and acetone (5cm^3) was added to 1-phenylbutan-1,3-diol (1g, 6.02 mmole) and the mixture was agitated thoroughly. After two hours the solution was saturated with sodium chloride and extracted with diethylether (3 x 10cm^3). The combined ether extracts were dried over anhydrous magnesium sulphate then filtered. The dry solution was heated to evaporate diethylether and a colourless viscous oil was recovered and identified by 'H.N.M.R as the required product, yield 0.75g, (64.8%).

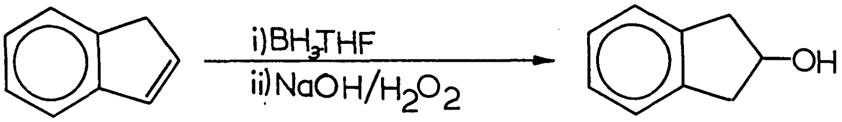


5.10 Reaction of diborane generated in situ

5.10.1) With indene

A stirred solution of indene (5g, 43 mmole) and sodium borohydride (1.22g, 32 mmole) dissolved in dry tetrahydrofuran (30cm^3) under nitrogen atmosphere was treated dropwise at 0°C with boron trifluoride diethyletherate (6.11g, 43 mmole) in dry tetrahydrofuran (10cm^3) during thirty minutes. The reaction mixture was stirred for a further one and a half hours then allowed to slowly warm to room temperature. Aqueous sodium hydroxide (8cm^3, 2M) was added dropwise to the stirred reaction mixture followed by hydrogen peroxide (6cm^3, 30%). The reaction mixture was stirred for twenty minutes then separated. The aqueous layer was extracted with diethylether (4 x 30cm^3) which was combined with the tetrahydrofuran layer. The combined extracts were dried over anhydrous magnesium sulphate then filtered. The diethylether solution was evaporated to dryness and the resulting white mass was recrystallized from

40-60° petroleum ether giving white needles which were air dried. Yield 5g, 37 mmole, (87%). The product melted at 66°C and was identified by infrared spectroscopy and ^{1}H.N.M.R, detailed elsewhere, as the required alcohol.



5.10.2) <u>With ferrocene</u>

A stirred solution of ferrocene (0.37g, 2 mmole) and sodium borohydride (1.36g, 18 mmole) in tetrahydrofuran (25cm^3) under inert atmosphere at 0°C was treated dropwise with a solution of boron trifluoride diethyletherate (0.505g, 6 mmole) in tetrahydrofuran (10cm^3). On completion of the addition the reaction mixture was stirred at 0°C for a further five hours, then allowed to warm to room temperature. The solvent was removed under reduced pressure at 35°C. The starting material, ferrocene was quantitatively recovered together with sodium fluoroborate, identified by infrared spectroscopy and melting point.

5.10.3) <u>With Iron tris(2,4-pentanedionate);-Fe(AcAc)$_3$</u>

a) ratio B_2H_6/Fe(AcAc)$_3$ = 4:1

Iron tris(2,4-pentanedionate) 0.5g, 1.42 mmole) and sodium borohydride (0.32g, 8.46 mmole) were stirred together in dry tetrahydrofuran (30cm^3) under inert atmosphere with cooling to 0°C. A solution of boron trifluoride diethyletherate (1.6g, 11.27 mmole) in dry tetrahydrofuran (10cm^3) was added dropwise and the reaction mixture stirred at $0^{\circ}C$ for a further five hours then slowly allowed to warm to ambient temperature. Removal of solvent allowed isolation of a brown solid which was identified by infrared spectroscopy and melting point as the starting material, iron tris(2,4-pentanedionate).

b) Repetition of above experiment with B_2H_6: $Fe(AcAc)_3$ of 8:1 gave a slow colour change of the reaction mixture from red to yellow/green and a subsequent decolourisation. No identifiable product was recovered from the solution other than sodium fluoroborate and solvent. A small amount of black residue on the flask was identified as iron.

5.10.4) With Vanadyl bis(2,4-pentanedionate):- $VO(AcAc)_2$

Vanadyl bis(2,4-pentanedionate) (0.5g, 1.89 mmole) and sodium borohydride (0.16g, 4.22 mmole) were stirred together, under dry inert atmosphere, in dry tetrahydrofuran ($30cm^3$). A solution of boron trifluoride diethyletherate (0.8g, 5.63 mmole) in dry tetrahydrofuran ($10cm^3$) was added to the reaction mixture, dropwise during ten minutes at a temperature of $0^{\circ}C$. On completion of addition the dark blue-green reaction mixture was stirred at $0^{\circ}C$ for a further two hours, at which point precipitation was noticed. The reaction mixture was allowed to warm to room temperature then filtered under nitrogen into a nitrogen purged vessel. The solvent was evaporated under reduced pressure and the products identified as vanadylacetylacetonate and sodium fluoroborate by infrared spectroscopy and melting point. The precipitated material was found by the same methods to be vanadyl bis(2,4-pentanedionate).

5.11 Reactions of diborane externally generated with complexes

Reactions were carried out using the apparatus shown in Fig. 4 or by means of vacuum line apparatus shown in Fig.2.

5.11.1) With diphenylacetylene - bis(triphenylphosphine) platinum (0)

Diborane (20 mmoles) was passed into a stirred solution of the complex (0.1g, 13.4 mmoles) dissolved in dry tetrahydrofuran (40cm^3) maintained at 0°C under inert atmosphere. During three hours at 0°C no colour change in the reaction solution was noted and the reaction mixture was allowed to warm to room temperature. The reaction flask was isolated, then solvent was removed from the reaction mixture under reduced pressure. A tarry solid was isolated and found to contain no identifiable products.

5.11.2) With bis(phenylethynyl) mercury

Diborane (4 mmoles) was passed into a stirred solution of the mercurial (0.5g, 1.2 mmole) dissolved in dry tetrahydrofuran (40cm^3) and maintained at 0°C under inert atmosphere. During five hours at 0°C no colour change in the reaction solution was noted and the reaction mixture was allowed to warm to room temperature. The reaction flask was isolated, then solvent was removed from the reaction mixture under reduced pressure. The recovered product was identified as starting material by infrared spectroscopy.

5.11.3) With Iron tris(2,4-pentanedionate)

Diborane (4 mmole) was passed into a stirred solution of iron tris(2,4-pentanedionate) (0.5g, 1.28 mmoles) dissolved in dry tetrahydrofuran (40cm^3) under inert atmosphere at 0°C. On completion of addition the stirred reaction mixture was maintained at 0°C for a further five hours then allowed to warm to room temperature.

The reaction flask was isolated, then solvent was removed under reduced pressure. The recovered product was identified by infrared spectroscopy and melting point to correspond with the starting material.

On repetition, a colour change of the reaction solution from red/brown to yellow was noted on addition of diborane. On warming the solution to room temperature the colour reverted to red/brown. Removal of solvent under reduced pressure allowed recovery of the starting material.

On repetition using a ratio of diborane, complex of 10:1 the reaction solution turned green during two hours then decolourised during thirty minutes to give a precipitate. Removal of solvent under reduced pressure allowed recovery of a black insoluble residue which did not melt or change appearance up to 300°C. On repetition using a diborane : complex ratio of 18:1 (large excess) the reaction solution became dark red and on allowing to warm to 10°C promptly decolourised, precipitating a gummy deposit which turned black on removal of solvent. Both infrared spectra and melting point were found to be the same as the previously obtained black residue. The residue was subsequently subjected to elemental analysis. Attempts to obtain samples under inert atmosphere of the reaction mixture for study by N.M.R or M.S. resulted in vigorous effervescence accompanied by the production of boric acid and a black precipitate, the analysis of which is detailed elsewhere.

5.11.4) With vanadyl bis(2,4-pentanedionate)

Diborane (8.6 mmoles) was passed into a stirred solution of the complex (0.5g, 1.73 mmoles) dissolved in dry tetrahydrofuran ($40cm^3$) and maintained at 0°C under inert atmosphere. During two hours at 0°C no colour change was observed and the reaction mixture was allowed to warm to room temperature. The reaction flask was isolated, then solvent was removed under reduced pressure. The recovered solid was identified as starting material by means of infrared spectroscopy and melting point.

On repetition with diborane : complex ratio of 18:1 the recovered product appeared to be a mixture of starting material and a black solid resembling that produced with ferric acetylacetonate (by infrared spectroscopy).

5.11.5) With nickel bis(dimethylglyoximate)

Nickel bis(dimethylglyoximate) (0.5g, 1.73 mmole) and sodium borohydride (0.29g, 7.78 mmole) were stirred together under inert atmosphere in dry tetrahydrofuran (30cm^3) at 0°C. A solution of boron trifluoride diethyletherate (1.47g, 10.38 mmole) dissolved in tetrahydrofuran (10cm^3) was added dropwise to the reaction mixture during thirty minutes. On completion of addition the stirred reaction mixture was maintained at 0°C for a further five hours then allowed to warm to ambient temperature. Following removal of solvent under vacuum at 40°C the solid residue was identified as nickel bis(dimethylglyoximate) together with sodium fluoroborate by means of infrared spectroscopy and melting point.

5.11.6) With Copper complexes - general formula $Cu_2(CH_3COO)_4L$

a) L = 1,2-di(4-pyridyl) ethylene

The complex (0.2g, 0.37 mmole) was stirred in dry tetrahydrofuran (40cm^3) at 0°C together with sodium borohydride (0.012g, 0.32 mmole) under inert atmosphere. A solution ofboron trifluoride diethyletherate (0.061g, 0.43 mmole) in tetrahydrofuran (10cm^3) was added dropwise during fifteen minutes. On completion of addition the reaction mixture was stirred at 0°C for a further five hours at 0°C then allowed to warm to ambient temperature. Evaporation of solvent under reduced pressure left a solid residue which was identified by infrared spectroscopy and melting point as the starting material together with sodium fluoroborate.

b) Complexes where L = 1(2-pyridyl),2(4-pyridyl) ethylene and 1(2-pyridyl), 2(3-pyridyl) ethylene were reacted under the same conditions as above. In both cases the starting material was isolated after reaction and identified as previously[236,237].

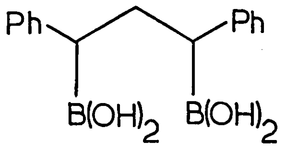
5.12 Reactions of Diborane with β-dicarbonyl compounds

5.12.1) With 2,4-pentanedione

Diborane (50 mmole) generated from iodine (12.69g, 50 mmole) and sodium borohydride (3.78g, 100 mmole) was passed into 2,4-pentanedione (4g, 39 mmole) under inert atmosphere at room temperature during one and a half hours. The exothermic reaction gave rise to a yellow colouration and a temperature of 60°C. After a further one and a half hours the yellow reaction mixture was cautiously hydrolysed by the addition of distilled water (20cm^3). Sodium chloride was added to saturate the aqueous solution which was then extracted with diethylether (3 x 20cm^3) and the combined extracts dried over anhydrous magnesium sulphate. The filtered diethylether solution was reduced to a minimum volume under reduced pressure. The resulting colourless oil when left overnight precipitated colourless crystals which were filtered off, washed with dry 40:60 petroleum ether then air dried. The crystals were found to have Mpt 85°C. Microanalysis showed C,46.4%;H,8.42% calculated C,46.2%; H,8.5% based on molecular formula $C_5H_{11}O_3B$. The product was analysed by mass spectroscopy and 'H.N.M.R.

5.12.2) With 1,3-diphenyl-1,3-propanedione

Diborane (3.8 mmole), generated from iodine (0.96g, 3.8 mmole) and sodium borohydride (0.28g, 7.6 mmole), was passed into a solution of1,3-diphenyl-1,3-propanedione (0.85g, 3.8 mmole) in dry tetrahydrofuran (40cm^3) during thirty minutes at a temperature of 40°C under nitrogen atmosphere. The reaction solution immediately became yellow and the reaction was allowed to continue during two hours. The reaction mixture was hydrolysed by the cautious addition of distilled water (25cm^3). The aqueous solution was saturated with sodium chloride then extracted with diethylether (3 x 100cm^3) and the combined extracts dried over anhydrous magnesium sulphate. The dried ether extract was reduced to a small volume and allowed to stand, whereon a yellow precipitate was obtained which was filtered off, washed with a little hexane and air dried (0.21g, Mpt 250°C dec.). Microanalysis showed C,55.5%; H,5.52% calculated C,57.0%; H,5.74% based on molecular formula $C_{15}H_{18}O_6B_2$.



5.12.3) With 1-phenyl-1,3-butanedione

1-Phenyl-1,3-butanedione was purified by recrystallization from methanol; water (10-15%) to give material melting at 59°C (Lit 59°C)[238].

Diborane (38 mmole) was passed into a solution of 1-phenyl-1,3-butanedione (0.5g, 3.33 mmole) in tetrahydrofuran (5cm^3) under inert atmosphere at a temperature of 45°C during forty minutes. An exothermic reaction occurred accompanied by the reaction mixture turning pale yellow. The reaction mixture was hydrolysed with water (50cm^3) then extracted with diethylether (3 x 30cm^3). The diethylether extract was dried over anhydrous magnesium sulphate then filtered and reduced to a small volume under reduced pressure, resulting in a colourless oil which was identified by mass spectrometry and ^{1}H.N.M.R as the borate ester of 1-phenyl-1,3-butanediol[238].

5.12.4) With 1,3-Trifluoromethylpropane-1,3-dione

Diborane (9.6 mmole) was passed into a solution of 1,3-trifluoromethyl-propane-1,3dione (0.65g, 3.1 mmole) at 0°C during thirty minutes under inert atmosphere. After one hour at 0°C the colourless reaction mixture was cautiously treated with distilled water (70cm^3) then extracted with diethylether (6 x 30cm^3). The ether layer was dried over anhydrous magnesium sulphate and shown to contain only starting material by means of mass spectrometry.

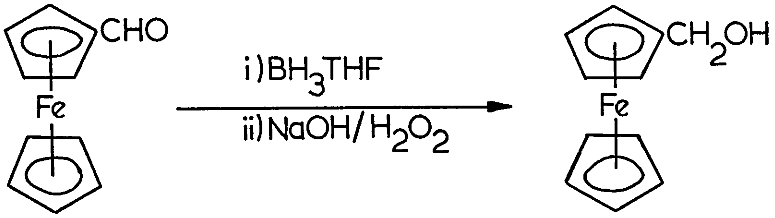
5.13 Reactions of diborane with iron complexes

5.13.1) With vinyl ferrocene

Diborane (3.4 mmole) generated from iodine (0.86g, 3.4 mmole) and sodium borohydride (0.3g, 7.9 mmole) in diglyme was passed into a stirred solution of vinyl ferrocene (0.44g, 2.1 mmole) dissolved in dry tetrahydrofuran (20cm^3) at 0°C and under nitrogen atmosphere during twenty minutes. The reaction mixture was allowed to stand for one hour and was then cautiously hydrolysed with water (10cm^3) followed by sodium hydroxide (5cm^3, 2M) and hydrogen peroxide (2cm^3, 30%). The red-orange product was isolated by extraction into diethylether (20cm^3). The diethylether/tetrahydrofuran layer was separated and dried over anhydrous magnesium sulphate. The dried solution was filtered then evaporated to dryness leaving a dark orange residue which when recrystallized from 40-60° petroleum ether gave red orange needles which were air dried, yield 0.39g, 1.7 mmole (81%) Mpt 74°C (Lit 73-5°C)[239].

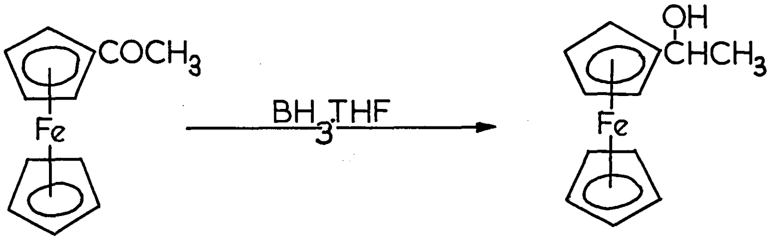
5.13.2) With ferrocene carboxaldehyde

Diborane (10 mmole), generated from iodine (2.54g, 10 mmole) and sodium borohydride (0.8g, 21 mmole) in diglyme solution, was passed into a solution of formylferrocene (2g, 9 mmole) dissolved in dry tetrahydrofuran ($40cm^3$) under nitrogen atmosphere at 0°C during thirty minutes. The red solution diminished in colour, becoming orange, during one and a half hours at 0°C. The reaction mixture was allowed to warm to room temperature and was hydrolysed by the dropwise addition of aqueous sodium hydroxide ($10cm^3$, 2M, 20 mmole) followed by hydrogen peroxide ($4cm^3$, 30%, 40 mmole) giving a yellow solution. The organic/aqueous layers were separated and the aqueous layer was extracted with diethylether (3 x $25cm^3$). The combined tetrahydrofuran and diethylether extracts were dried over anhydrous magnesium sulphate then filtered. Evaporation to dryness of the ethereal solution yielded a yellow product which proved difficult to recrystallize. Air dried yield 1.8g, 8 mmole (89%) Mpt 78°C. The product was identified by infrared spectroscopy and mass spectrometry as ferrocenylmethanol.



5.13.3) Reaction of acetylferrocene with diborane

Diborane (10 mmole), generated from iodine (2.54g, 10 mmole) and sodium borohydride (0.8g, 21 mmole) in diglyme solution, was passed into a solution of acetylferrocene (1g, 4.4 mmole) dissolved in dry tetrahydrofuran (40cm^3) under nitrogen atmosphere at 0°C during thirty minutes. During the course of the addition and a further two hours at 0°C the reaction mixture changed colour from dark red to yellow-orange. The reaction mixture was allowed to warm to room temperature then oxidised by the dropwise addition of aqueous sodium hydroxide (10cm^3, 2M) and hydrogen peroxide (8cm^3, 30%) to the stirred reaction mixture. After one hour, diethylether (10cm^3) was added and the reaction mixture was separated. The aqueous layer was extracted with diethylether (2 x 10cm^3) and the extracts combined with the previously separated ethereal solution, the whole then being dried over anhydrous magnesium sulphate then filtered. Evaporation of the solvent allowed recovery of the product which was recrystallized from 40-60° petroleum ether and then air dried, yield 0.47g, mmole, (46%) melting point 74°C. The product was identified by infrared spectroscopy as α-hydroxy ferrocenylethanol.



5.13.4) <u>With 1,1'diacetylferrocene</u>

Diborane (4 mmole), generated from iodine (1.01g, 4 mmole) and sodium borohydride (0.34g, 9 mmole) in diglyme solution, was passed into a solution of 1,1'diacetylferrocene (1g, 3.7 mmole) dissolved in dry tetrahydrofuran (60cm^3) stirred at 0°C under nitrogen atmosphere during thirty minutes. After stirring at 0°C for a further two hours the reaction mixture was allowed to warm to room temperature. Oxidation of the stirred reaction mixture by the addition of aqueous sodium hydroxide solution ($2cm^3$, 2M = 4 mmole) then hydrogen peroxide ($2.5cm^3$, 30% w/v) was carried out. The reaction mixture was extracted with diethylether ($3 \times 30cm^3$) and the combined extracts dried over anhydrous magnesium sulphate. The filtered diethylether solution was evaporated to dryness and the recovered solid product recrystallized from methanol and identified by 'H.N.M.R and infrared spectroscopy as 1,1'bis(α-hydroxyethyl)-ferrocene.

5.13.5) With (π-indenyl)(π-cyclopentadienyl) iron

A pentane solution of (π-indenyl)(π -cyclopentadienyl) iron (1.0g 4.2 mmole) was added to dry tetrahydrofuran ($20cm^3$) and at $0^{o}C$ was treated with an excess of diborane (10 mmole) under inert atmosphere. After 2 hours the solution was allowed to warm to ambient temperature and was then oxidised by the cautious addition of aqueous sodium hydroxide solution ($4cm^3$, 2M) followed by hydrogen peroxide ($2cm^3$, 37% solution). The reaction mixture was extracted with diethylether and the extract dried over a minimum of anhydrous magnesium sulphate. Mass spectrometry was performed on the dry ethereal solution. A small portion of the ethereal solution was evaporated to dryness with a stream of nitrogen within an N.M.R tube then, following addition of deuteriochloroform, the 'H.N.M.R spectrum was recorded.

5.13.6) With cyclooctatetraenyl iron tricarbonyl

A large excess of diborane (20 mmole) was condensed onto cyclooctatetraenyl iron tricarbonyl (0.5g, 2 mmole) in tetrahydrofuran ($10cm^3$) and the reaction mixture temperature was lowered to just above the freezing point. After two hours the solvent and diborane were distilled off and the residual material treated with water ($2cm^3$). No reaction was visible and the residue was identified as starting material by mass spectrometry.

Cyclooctatetraenyl iron tricarbonyl (0.1g, 0.4 mmole) was dissolved in liquid diborane by the condensation of a large excess of diborane (20 mmole) into the reaction flask. The reaction mixture was cooled to just above the freezing point and maintained at that temperature for six hours. Removal of the diborane onto the vacuum line allowed recovery of the starting material, unchanged.

5.14 Analysis of residue from reaction of iron tris(2,4-pentanedionate with diborane

5.14.1) Determination of iron content

A solution of electrolytically pure iron (0.1g) was dissolved in 1:3 nitric acid ($50cm^3$) then the solution was boiled to remove oxides of nitrogen, volume being maintained by the addition of distilled water. The resulting solution was allowed to cool then made up to 1 litre. Ammonium thiocyanate ($20cm^3$, 1.5M) and nitric acid ($5cm^3$, 2M) were added to aliquots of iron stock solution and diluted to $100cm^3$ with distilled water so as to produce solutions of 1,2,3,4 and 5 ppm with respect to iron. One solution was prepared at a time and the absorbance measured at 480nm against a blank containing only ammonium thiocyanate and nitric acid. The time between addition of ammonium thiocyanate to the iron solution and measurement of absorbance was standardized. A graph of absorbance against iron concentration was constructed.

An accurately weighed amount of the black residue (approximately 0.1g) was dissolved in a mixture of concentrated sulphuric acid ($1cm^3$) and concentrated nitric acid ($5cm^3$) and heated to fumes of nitrogen oxides then sulphur trioxide. The volume of the solution was reduced then distilled water was added ($5cm^3$) and the solution again reduced to fumes. On cooling, the solution was made up to $100cm^3$ with nitric acid ($50cm^3$, 2M) and distilled water. An aliquot ($5cm^3$) of the solution was diluted to $250cm^3$ by the addition of ammonium thiocyanate ($50cm^3$) and distilled water. The absorbance of the solution was measured as previously. The iron content of the residue was estimated by comparison with the previously constructed calibration curve.

5.14.2) Determination of boron content

The sample (36.5mg) was dissolved in hydrochloric acid ($5cm^3$, 2M) by gently warming ($\simeq 60^{\circ}C$).

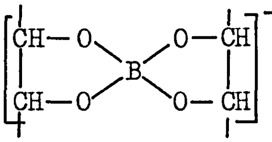
The solution was absorbed onto anhydrous calcium chloride (35g), lumps of about $1cm^3$ being used. The flask was shaken so that the lumps remained separated whilst the solution was absorbed. Absolute methanol was distilled into the reaction flask until the calcium chloride was just immersed. Both flasks were gently heated allowing methanol to distil into the receiver containing distilled water ($25cm^3$) until approximately $200cm^3$ had collected, at which point the receiver was changed and a second aliquot of methanol distilled. The methanolic distillate was made alkaline with aqueous sodium hydroxide solution and the methanol removed under reduced pressure at $40^{\circ}C$. The aqueous residue was cooled then made slightly acidic and p-nitrophenol indicator added (colourless acid/yellow alkaline). The solution was made alkaline to the first faint yellow with aqueous sodium hydroxide (0.1M) then mannitol (2g) together with several drops of phenolpthalein indicator were added. The solution was titrated to the first permanent pink against aqueous sodium hydroxide (0.1M).

The contents of the water traps were added to the second methanolic distillate and the mixture was treated as above. The sum of the titres enabled calculation of the boron content

$$BCl_3 + 2MeOH \longrightarrow (MeO)_3B + 3HCl$$

$$(MeO)_3B + 3NaOH \longrightarrow Na_3BO_3 + 3MeOH$$

$$Na_3BO_3 + 3HCl \longrightarrow H_3BO_3 + 3NaCl$$

H_3BO_3 + 2 Mannitol ⟶  H^+ + $3H_2O$

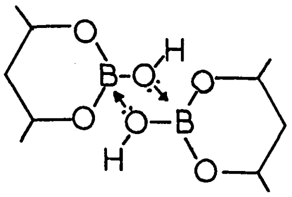
$$NaOH + [B\ Complex]^- H^+ \longrightarrow \overset{+}{Na}\ {}^-[B\ Complex] + H_2O$$

$$Mannitol = (CH_2OH)(CHOH)_4(CH_2OH)$$

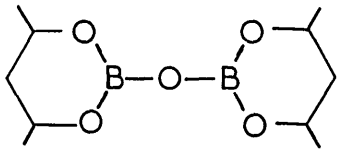
6. Results and discussion

6.1) Derivatives of β-diketones

The reaction between 2,4-pentanedione and diborane, in tetrahydrofuran, produced a yellow solution which decolourised on alkaline peroxide oxidation and then precipitated a white crystalline solid which melted at 85°C. Microanalysis of the solid showed an agreement with the empirical formula $C_5H_{11}O_3B$ (Calc. 46.2%C, 8.50%H; found 46.3%C, 8.55%H) corresponding to the borate ester of the expected product, 2,4-pentanediol. The infrared spectrum showed absence of the carbonyl absorption bands and the presence of hydroxyl bands. The integrated ^{1}H.N.M.R spectrum contained signals assigned thus, 5.5 δ(s,OH); 4.2 δ(m,CH); 1.8 δ(m, CH_2); 1.2 δ(d,CH_3).* The signal at 5.5δ diminished on addition of deuterium oxide and the integrated signals corresponded to the required ratios for the proton assignments as shown. The mass spectrum, measured at 70eV, indicated the possibility of association to form a dimeric species. It is known that borate esters can form anhydrides by loss of water when heated. The supposed anhydride of molecular weight 242 formed by loss of water between two molecules of ester would not satisfy the molecular ion (m/e243) found in the mass spectrum. The possibility of dimer formation would explain the molecular ion and the large ion at m/e 115, the expected molecular weight of the ester whilst also fitting the



Dimer



Anhydride

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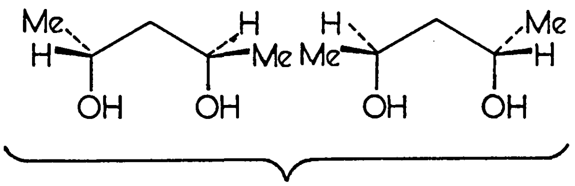
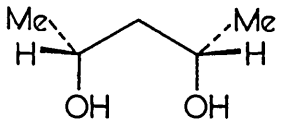
* s = singlet; d = doublet; m = multiplet.

microanalytical data. Measurement of the elevation of boiling point of a solution of the ester gave an ebullioscopic molecular weight of 265, which supports the possibility that the ester exists as a dimer.

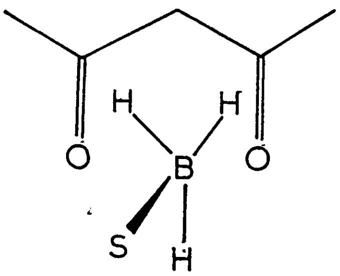
In order to confirm that the previously discussed product was the ester, synthesis by a different route was undertaken. Reduction of 2,4-pentanedione to the diol was accomplished using sodium borohydride. It is worth noting that the use of lithium aluminium hydride for this reduction would have resulted in a very low yield of the diol, the preferred product being either 2,4-dihydroxypent-2-ene or 3-penten-2-one depending upon the reaction temperature[240,241]. The diol was reacted with boric acid and the ester isolated. The ester was found to have a lower melting point (70°C) and an infrared spectrum, containing bands at 770cm^{-1} and 782cm^{-1}. By comparison the previous ester had an infrared band only at 782cm^{-1}. Previous work has shown that the ester, 4,6-dimethyl-1,3,2-dioxaborolane, exists in two forms characterised by melting points of 37°C and 85°C, and an infrared absorption band at 770cm^{-1} and 782cm^{-1} respectively[242]. The two forms have been isolated and the diols recovered by acid hydrolysis. The ester melting at 37°C and having absorption band of 770cm^{-1} has been shown to be that of the racemic diol whilst that melting at 85°C and having absorption band of 782cm^{-1} corresponded to the meso-diol ester[243]. From the evidence the borate ester produced from the reaction of 2,4-penanedione and diborane is of the meso form exclusively and that from the reaction of 2,4-pentanediol and boric acid is a mixture of racemic and meso forms. Figs. 6,7,8,9,10.



Racemate



Meso



Solvated BH_3 sitting over
β-dicarbonyl

In order for the meso form of the ester to be produced exclusively the reduction of both carbonyl groups of the substrate must occur without loss of orientation. The reduction of 2,4-pentanedione might have been expected to proceed via the discrete reduction of each carbonyl group, in which case a mixed product would have occurred. In order to establish the structure of the intermediate borane the reaction between diborane and 2,4-pentanedione was carried out without solvent. By condensing diborane onto frozen 2,4-pentanedione then allowing the two reactants to warm slowly, an exothermic reaction took place eventually giving a pale yellow oil. The oil was found to be air and moisture sensitive. The mass spectrum of the oil showed a molecular ion at m/e 114. The M^+ and (M-1) peaks showed a 4:1 relationship indicating the presence of only one boron atom ($^{11}B:^{10}B \equiv 4:1$). The 'H.N.M.R spectrum was found to be similar to that recorded for the ester with exception of the signal due to the hydroxyl hydrogen at 5.5 δ, the splitting pattern being complex. On hydrolysis with water the oil was found to give a white solid identified, as previously, by melting point and spectroscopy to be the meso-borate ester. From the evidence the oil was considered to be a cyclic borane. Figs. 11, 12. Using the relationship:-

$$\log_{10}\frac{P_2}{P_1} = \frac{\Delta \text{ eh}}{2.303R}\left\{\frac{1}{T_b} - \frac{1}{T}\right\}$$

where P_1 = vapour pressure at boiling point (T_b ^{o}K)

P_2 = vapour pressure at temperature T ^{o}K

and, by Trouton's rule, Δeh is approximated to $88T_b$ joule mol^{-1} the boiling point of the borane was estimated to be 136°C. The exclusive formation of the meso-ester via a cyclic borane intermediate implies that the reduction of both carbonyls occurs either simultaneously or in very rapid succession so that no rotation about CH_2 carbon occurs. The exothermic nature of the reaction can be explained by the relative strength of the B-O bond being created (approximately 500kJ mol^{-1}). In contrast, the reduction with sodium borohydride must be slow with attack on the second carbonyl group being randomly from either side of the molecule.

In both the solution reaction and solvent-free reaction, diborane and 2,4-pentanedione gave the same product when oxidised. It can be inferred that both reactions proceed via the cyclic borane.

The reactions of diborane and β-dicarbonyl compounds ($R_1COCH_2COR_2$) where R_1 and R_2 were phenyl, methyl, trifluoromethyl, or a mixture of these, were carried out.

The reaction product where $R_1 = R_2$ = phenyl was found to be of the same type, as identified by mass spectrometry. The molecular ion (m/e 254) and(M-1) peak, (m/e 254), were found to be in the ratio 4:1 indicating the presence of only one boron atom in the ratio 4:1 indicating the presence of only one boron atom in the molecule. Identification of the meso-racemate ratio was not accomplished by means of infrared spectroscopy. The 'H.N.M.R spectrum showed similar features to that from the borate ester of

2,4-pentanediol. The microanalytical results did not fit the expected empirical formula but could be explained by the presence of a small amount of boric acid in the sample. The procedure previously employed in the formation of the borate esters from the diol and boric acid did not work satisfactorily in the case of 1,3-diphenyl propan-1,3-diol.

Investigation of the reactions of the fluorinated β-diketones with diborane was inconclusive due to the extreme volatility of the substrate compounds and the handling difficulties encountered.

6.2) Derivatives of iron complexes

The reaction of diborane with iron tris(2,4-pentandionate) in tetrahydrofuran solution was found to give no reaction by in-situ generation. Using external generation of diborane a visible change took place and the reaction solution spontaneously effervesced and "blackened". On cessation of the effervescence a black solid was recovered from the reaction mixture together with boric acid. Analysis of the material showed it to contain 34.9%Fe, 19%B, 6.6%C, 2.6%H.

The X-ray powder technique showed the material to be an amorphous solid. The application of other spectroscopic techniques yielded no further information. If the missing mass according to the microanalytical results is assumed to be oxygen then an empirical formula $Fe_2B_5C_2H_8O_8$ can be deduced. The evidence gathered on the black compound do not allow a structure to be assigned although the reaction appeared to proceed to the same material when repeated. The residue from attempted thermogravimetric analysis was analysed and was found not to correspond with the original material, a weight loss of 14.7% having occurred.

Ferrocene was found to be recovered intact from reaction with diborane. In ferrocene the cyclopentadiene ligand is effectively saturated by the complexation with iron. The reactions of substituted ferrocenes were investigated to ascertain whether any novel reactions were made possible by the fact of the ligand being complexed. Vinyl ferrocene was synthesised by two routes. The acylation of ferrocene could be achieved either by the use of phosphoric acid or boron trifluoride as catalyst. Reduction of the acetyl ferrocence by lithium aluminium hydride gave α-hydroxy ferrocenylethanol which by dehydration over alumina yielded vinyl ferrocene. The series of reactions undertaken to synthesise ferrocene carboxaldehyde in good yield involved the synthesis of the quaternary methiodide of N,N'-dimethylaminomethyl ferrocene, cpd (II) Fig. 5. By reaction with triphenylphosphine, involving displacement of trimethylamine, a suitable precursor (III) for a Wittig reaction was synthesised. The reaction of (III) under Wittig conditions with formaldehyde gave vinyl ferrocene as product.

The reaction of vinyl ferrocene with diborane gave, as expected, an alcohol which from 'H.N.M.R evidence appeared to be the β-alcohol. Presumably the π-system of the cyclopentadienyl ligand tends to bias the distribution of electrons within the vinyl side chain π-orbitals away from the ring.

The mass spectroscopic study of the reaction solution before alkaline peroxide oxidation failed to show evidence of a multi substituted borane. Considering the bulk of the vinyl ferrocene substrate it could be considered that the formation of a disubstituted borane would be sterically possible.

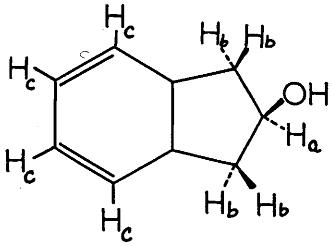
The reactions of acetyl and diacetyl ferrocene with diborane were straight forward and yielded the expected α-hydroxy ferrocenylethanol and bis(α-hydroxyethyl)ferrocene. The recorded mass spectrum showed not only the expected molecular ion but a peak at m/e 299 which can be explained by the formation of an internal borate ester of a similar type to those formed by β-diketones and boric acid. Allowing the alcohol to contact boric acid in the presence of water appeared to enhance the "ester" peak, however it is more likely that heating in the mass spectrometer source was responsible for causing any such condensation reaction to take place.

The effect of the ferrocene substituent appeared to have little effect on the reactions of common groups which might be expected to react with diborane viz alkene and carbonyl functions. The orientation of the reduction of vinyl ferrocene could be explained by reference to the π-electron cloud model.

The reaction of diborane with alkenes and carbonyl groups which formed part of the system directly complexed to the metal was seen as a major objective and for this reason attempts were made to synthesise several molecules. In this context the metal atom was seen as a protecting group, allowing the reduction of a selected part of the ligand molecule in a manner not readily accessible by the hydroboration route.

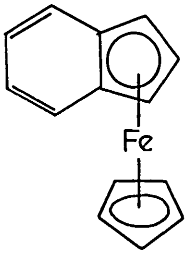
Hydroboration of indene followed by alkaline peroxide oxidation yields 2-indanol, identified by means of infrared, mass spectrometry and ^{1}H.N.M.R. Of particular note is the symmetry of the molecule this being evidenced in the N.M.R splitting pattern.

$2.8\,\delta\,(m,H_b)$, $3.5\,\delta\,(s,OH)$, $4.25\,\delta\,(m,H_a)$, $6.8\,\delta\,(s,H_c)$



The coupling constant of the hydroxyl proton and H_b is very small (ca 1Hz), being just distinguishable. The hydroxyl signal was identified by means of the addition of deuterium oxide to the sample, the hydroxyl signal being removed from the spectrum.

The compound $(\pi\text{-}C_5H_5)$ $(\pi\text{-}C_9H_7)Fe$ has the structure shown. The aromatic character of the 6-membered ring is removed by

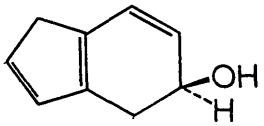


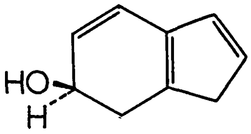
complexation and, potentially, a conjugated diene system is available for reaction.

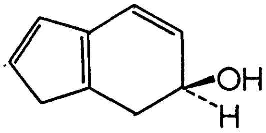
The complex bis$(\pi\text{-}C_9H_7)Fe$ exists and is somewhat simpler to synthesize but suffers the disadvantage of being light sensitive leading to rapid decomposition, in addition to being air-sensitive. The synthesis of the chosen complex, as described, allows the formation of ferrocene to take place if the rate of addition of the sodium cyclopentadienide is not very closely controlled. Although undesirable the presence of a small amount of ferrocene as impurity was unlikely to be detrimental since, as has been discussed, it does not react with diborane. The mass spectrum of the complex was found to contain very few major ions. The molecular ion (m/e 236) was found to decompose by the loss of either one of the ligands giving $C_9H_7Fe^+$(m/e 171) and $C_5H_5Fe^+$ (m/e 121). Both m/e 171 and m/e 121 decomposed by the loss of iron (m/e 56) yielding ions corresponding to the ligand, C_5H_5 (m/e 65) and C_9H_7 (m/e 115) which, by loss of acetylene gives $C_7H_5^+$ (m/e 89).

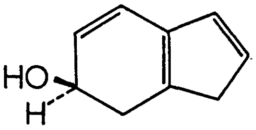
The reaction of a pentane/tetrahydrofuran solution of the complex with diborane occurred with little visible evidence of reaction. Following alkaline peroxide oxidation of the intermediate the product was extracted into diethylether and the solution was analysed by mass spectrometry. The mass spectrum obtained from the ethereal solution indicated an increase in molecular weight of 18 mass units. The fragmentation process was generally similar to that of the substrate and fragments containing the indenyl portion of the molecule were increased in mass by 18 mass units. The 'H.N.M.R spectrum of the product was complex and not of sufficient quality to allow interpretation of the signals other than that recognizably due to the cyclopentadienyl protons by comparison with the unreacted complex. From the data it may be considered that hydroboration of one double bond within the 6-membered ring had occurred. Attempts to release the ligand from the molecule using Ce^{IV} resulted in loss of the sample.

Consideration of the substrate molecule shows that the hydroboration reaction may take place in two orientations on the two conjugated double bonds. Separation of the hydroborated ligand from the metal complex opens the possibility of four isomeric alcohols. The isomerism is due to the restoration of the double bond within the 5-membered ring.







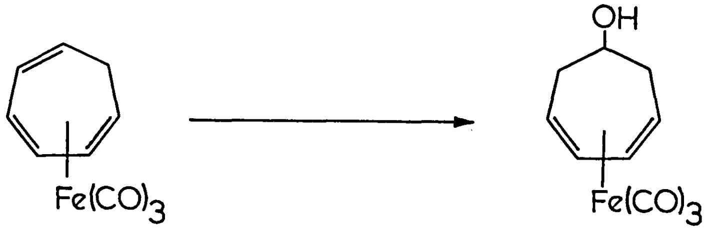


Dependent upon the position of the restored double bond the alcohols produced by attack of diborane from above or below the ring, with respect to the metal centre, are indistinguishable. The position of attachment of the boron, and hence the alcohol, has been assumed to be the 5 or 6 position since, by comparison with the hydroboration of vinyl ferrocene these positions are β to the complexed cyclopentadienyl. The effect of the electron rich π-cloud within the cyclopentadienyl although not available for bonding, as demonstrated with ferrocene, would tend to enhance the electron density at the β-carbons within the attached conjugated system (6-membered ring). Hydrogenation of the complex over a palladium catalyst is known[231] with a hydrogen uptake of 2 moles/mole. It might therefore have been expected that hydroboration would result in a diol. However, although diborane in excess of 2 mole/mole was used the evidence from mass spectrometry indicates that only one of the double bonds was hydroborated.

Cyclooctatetraene iron tricarbonyl has been shown, by 'H.N.M.R, to have the C_8H_8 ring bonded to iron as if it were a 1,3-diene. The iron undergoes a 1,5-shift so that all the ring protons appear to be magnetically equivalent as the iron-ring bonds move around the conjugated double bonds[244,245]. However at room temperature the complex will undergo formylation with $POCl_3$/DMF.

Synthesis of the complex is easily accomplished by use of trimethylamine-N-oxide as described. The complex was isolated and hydroboration was attempted by contacting the complex with ligand diborane. The 'H.N.M.R spectra of the complex at low temperature indicate that below -155°C the protons within the cyclooctatetraene ring are magnetically distinguishable. This implies that the iron 1,5-shift takes place much more slowly. The melting point of diborane (-165.5°C) was sufficiently low to slow the shift and potentially react with the ligand. After several cycles of freezing and warming the products were isolated and found to be indistinguishable from the starting material. It was observed that the complex was poorly dissolved in the liquid diborane. The lack of reaction may have been due to either insufficient energy to form the transition state or simply the presence in solution of too little of the complex for reaction to take place. The use of "normal" solvents for the reaction was precluded by the low temperature requirement, all of the solvents being frozen at the reaction temperature.

The complex cycloheptatriene iron tricarbonyl was reacted in tetrahydrofuran with diborane and gave as expected the alcohol, which was identified by mass spectrometry, after oxidation of the intermediate organoborane.



The inclusion of a carbonyl function within the ring system appeared to be an interesting comparison with the ferrocene compounds already discussed. Therefore attempts were made to synthesise 3,5-cycloheptadienone which was not available commercially. Two routes to the desired compound were attempted. The route involving bromination of the cyclic ketal of cycloheptanone was found not to give the described intermediate. The dibrominated ethylene ketal was found on isolation to have undergone exchange with methanol solvent and elimination, giving 3,6-dibromo-1-methoxycycloheptene. This material was identified by means of 'H.N.M.R and mass spectroscopy. Repetition of the synthesis gave the same result and the route was abandoned in favour of a ring expansion reaction involving the rearrangement of the dichlorocarbene adduct of ethoxycyclohexene. Isolation of the intermediate, 1,-ethoxy-1,3,5-cycloheptatriene, from the quinoline solvent proved difficult and a very low yield was accomplished. Following the rearrangement reaction isolation of the required product would have been better facilitated by pouring into sufficient dilute aqueous hydrochloric acid to convert all the quinoline to the amine hydrochloride then extraction into diethylether and recovery. The acid hydrolysis of the intermediate to 3,5-cycloheptadienone caused all product to be lost, the reportedly mild procedure did not work and slight warming proved disastrous, decomposition being total.

The failure of the synthetic routes to 3,5-cycloheptadienone prevented the direct investigation of hydroboration in a complexed molecule having only one function available for reaction. The only similar commercially available ligands were found to be cycloheptatrienone and 2-hydroxycycloheptatrienone (tropolone).

Since tropolone was more readily available and much cheaper than cycloheptatrienone, complexes of this ligand were decided upon as suitable substrates. In order to prevent reaction of diborane with the acidic hydroxyl group, tropolone was converted to its methyl ether using diazomethane. Using trimethylamine-N-oxide the ligand was reacted with iron pentacarbonyl in benzene solvent by a previously described method. The reaction products suffered decomposition in situ during approximately one hour presumably due to the ingress of air via the septum used for both the addition of iron pentacarbonyl to the reaction solution and the taking of samples for analysis by means of disposable plastic syringes.

6.3) Miscellaneous Complexes

The attempted hydroboration of diphenylacetylene-bis(triphenylphosphine) platinum (0) resulted in the decomposition of the complex with no identifiable products. The complex was chosen to examine whether a complex of this type might yield an adduct to the complexed unsaturated ligand, diphenylacetylene. The ligand in this case was π-bonded to the metal centre. The decomposition of the complex was probably due to interference in the π-bonding between platinum and the ligand. By way of comparison the complex bis(phenylethynyl) mercury has σ-bonds between the ligands and the metal. The hydroboration of acetylenic compounds is well known and proceeds readily. The reaction in tetrahydrofuran failed to change the starting material which was recovered intact. A possible explanation for the unreactive behaviour of the complex may lie in an interaction between the π-electrons of the ligand and the outer d-orbitals of the mercury centre. The extent of such d-π interaction if large enough may confer a pseudo-aromaticity to the molecule enabling extensive delocalisation of the electron density and making addition of diborane unfavourable.

The reaction of vanadyl bis(2,4-pentanedionate) with diborane was investigated in an attempt to gain insight on the formation of a black material by iron tris(2,4-pentanedionate). An unidentifiable product was obtained and the complex was assumed to have decomposed by an unknown mechanism.

Examination of the reactions of diborane with the dipyridylethylene copper complexes, nickel, cobalt and copper - Schiff's base complexes and nickel bis(dimethylglyoximate) were carried out to ascertain whether carbon-carbon or carbon-nitrogen double bonds within ligands could be reduced. In all cases a negative result was obtained. The unsaturated, non-aromatic bonds within the Schiff's base and di-pyridyl ethylene ligands must be considered to have more aromatic (conjugated) character than suggested by the structure of the complexes. In the case of the dimethylglyoxime complex the C=N bonds may have the electron distribution changed by complexation of the nitrogen with nickel.

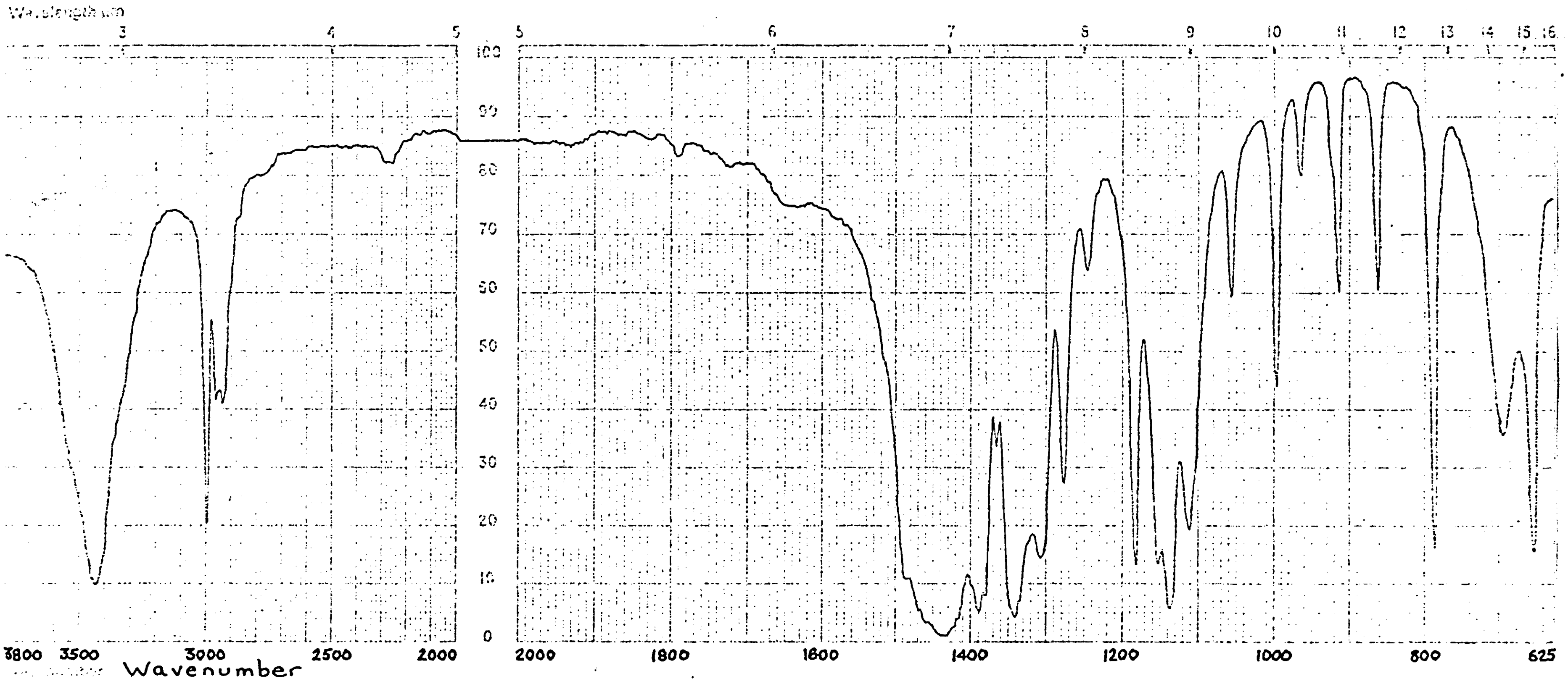


Fig 6

Infrared spectrum of 2,4-pentanedione meso borate ester

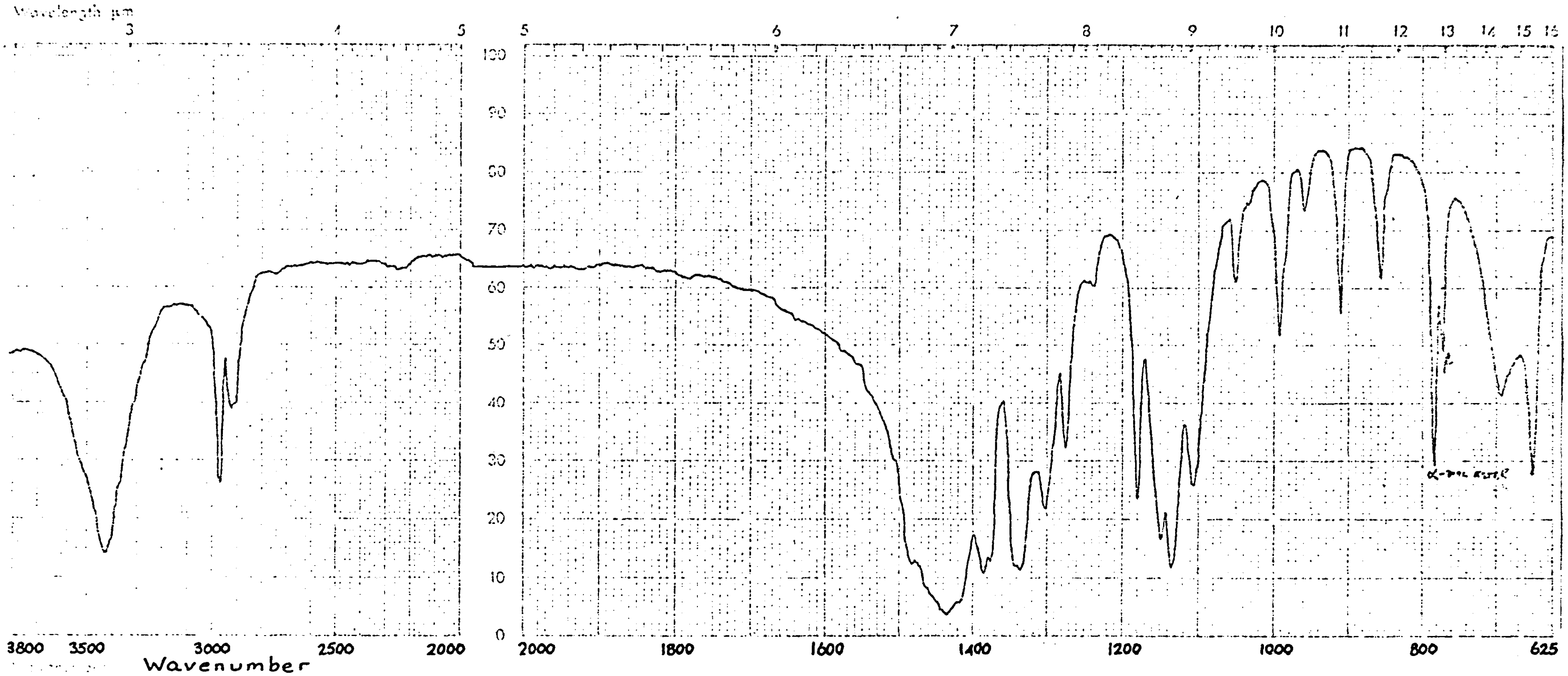


Fig 7

Infrared spectrum of 2,4-pentanedione mixed borate esters

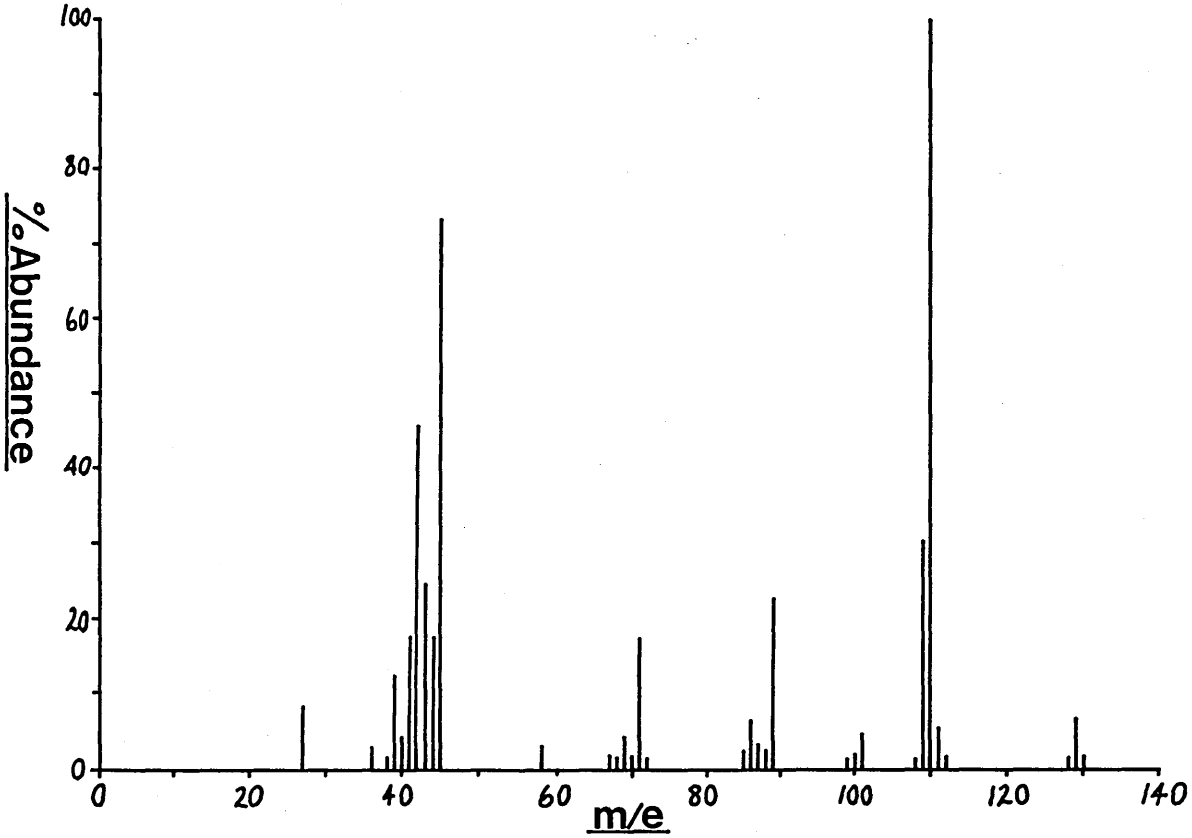


Fig 8

Mass spectrum of borate ester monomer from 2,4-pentanedione

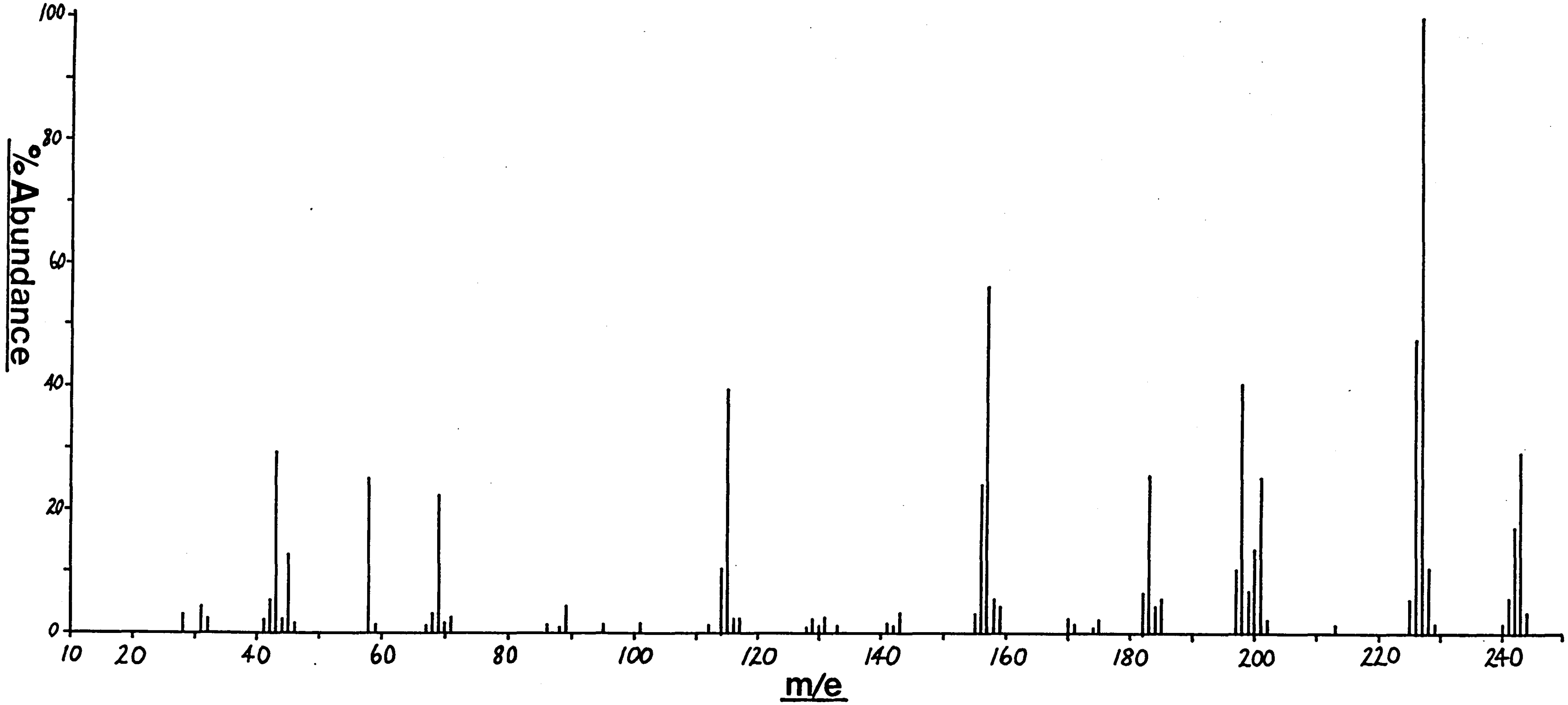


Fig 9
Mass spectrum of borate ester dimer from 2,4-pentanedione

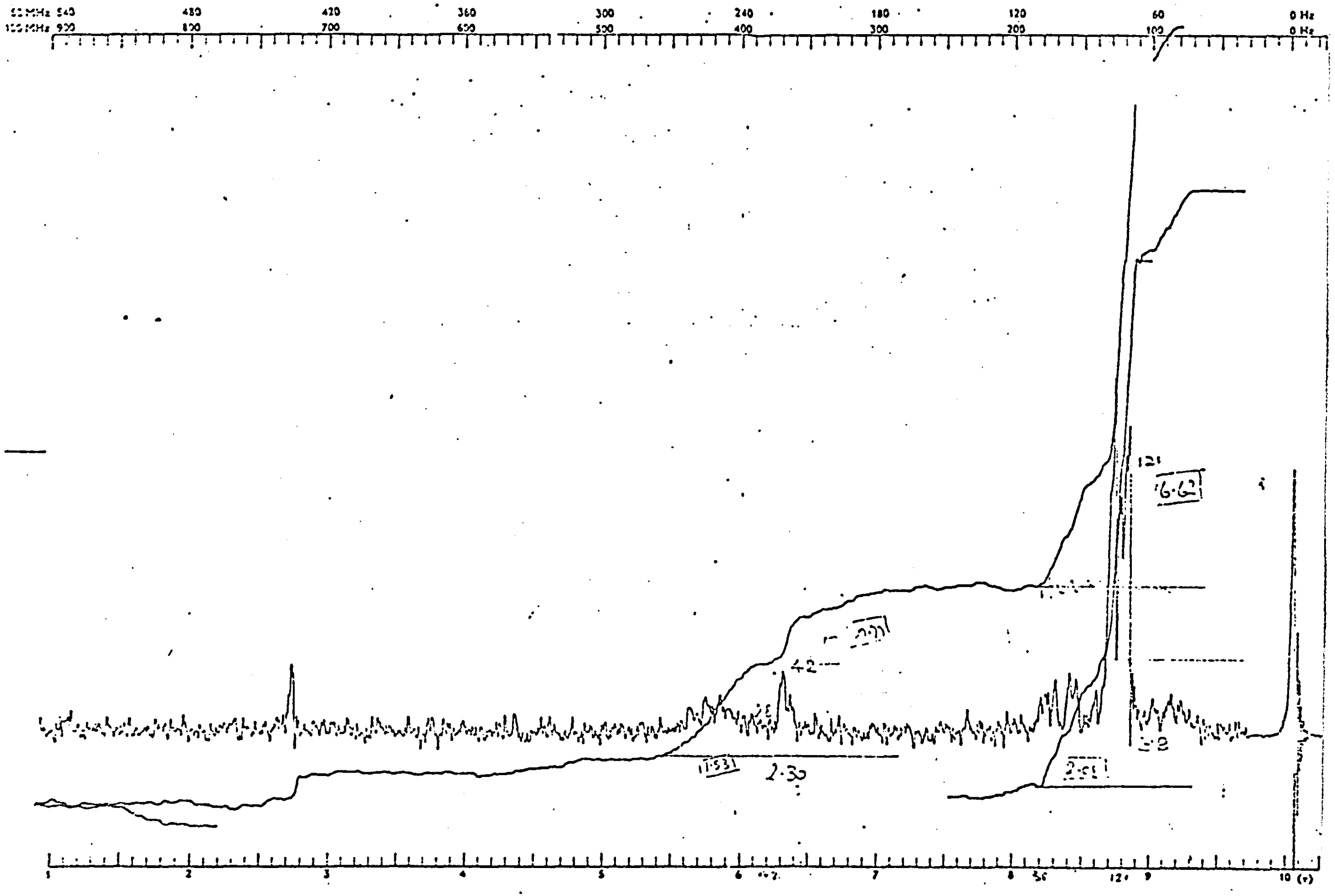


Fig10

N.M.R spectrum of 4,6-dimethyl-1,3,2-dioxaborolane

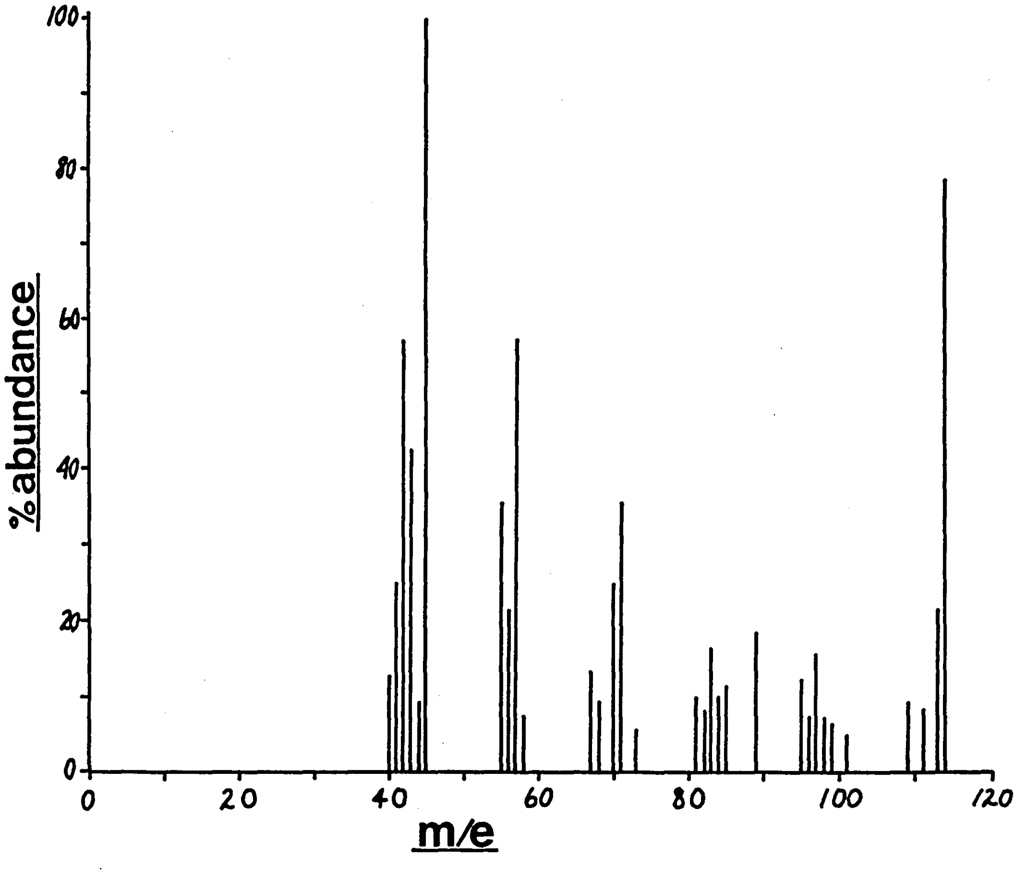


Fig11
Mass spectrum of cyclic borane
4,6-Dimethyl-1,3,2-dioxaborinane

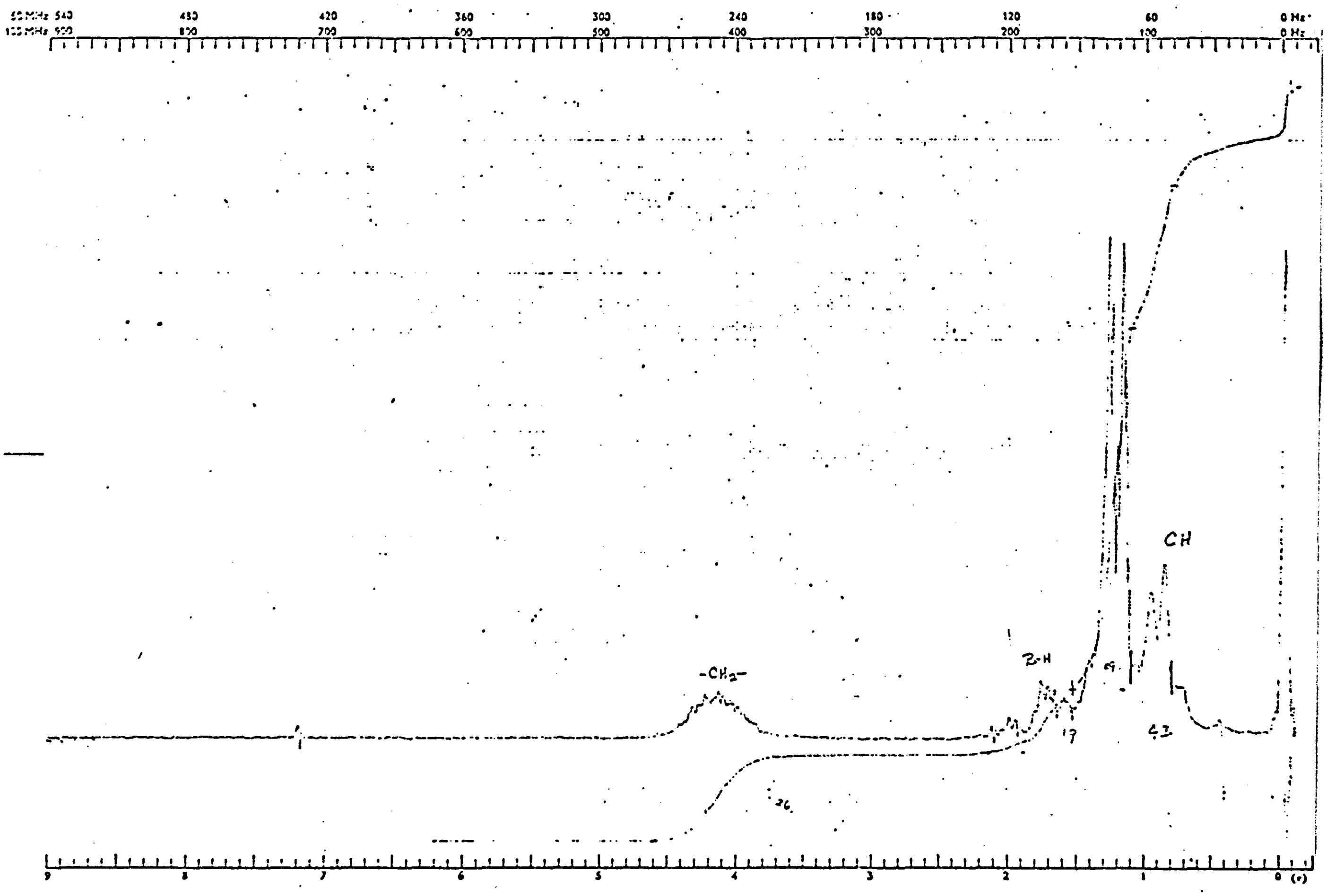


Fig12

N.M.R spectrum of 4,6-dimethyl-1,3,2-dioxaborinane

7.) Conclusions

The reactions of a number of complexes containing ligands both σ and π-bonded to metal centres have been investigated. The most important factor appears to be the extent of conjugation of multiple bonds, particularly with aromatic systems. The overall extension of π-electron density throughout the ligand confers resistance to the hydroboration reaction.

The reaction of iron tris(2,4-pentanedionate) was found to yield an amorphous black solid deduced to have an empirical formula of $C_2H_8O_8B_5Fe_2$ and of indeterminate structure.

Examination of the reaction of diborane with the uncomplexed ligand, to establish the mode of addition to a compound exhibiting keto-enol tautomerism, resulted in the formation of a liquid identified as 4,6-dimethyl-1,3,2-dioxaborinane, the cyclic adduct of BH_3 with the dione. By measurement of the vapour pressure of the liquid the boiling point was calculated to be $136^{\circ}C$. Hydrolysis of the borane yielded the cyclic borate ester which was shown to be exclusively of the meso-form. Comparison with material synthesised by alternative means of reduction of 2,4-pentanedione indicated that simultaneous reduction of both carbonyl groups had occurred. No evidence was found to indicate that diborane could react with the enol form of the diketone. The borate ester is considered to dimerise on storage as indicated by the mass spectroscopic and ebullioscopic measurement of molecular weight. The reactions of substituted β-diketones examined were considered to proceed via an intermediate cyclic borane to give, on hydrolysis, cyclic borate esters.

The unreactivity of ferrocene towards diborane is explained by the aromatic nature of the π-cyclopentadienyl ligand. The reaction of the carbonyl group in substituted ferrocenes has been shown to give the product expected from the reduction of an aldehyde or ketone, namely the primary and secondary alcohols respectively. Disubstituted ferrocenes were reduced to the corresponding di-alcohol.

Conjugation of the π-cyclopentadienyl ligand with the side chain explains the orientation of hydroboration of vinyl ferrocene to give the β-alcohol on oxidation.

The synthesis of vinyl ferrocene by the Wittig reaction of $(\pi\text{-}C_5H_5)Fe(\pi\text{-}C_5H_5.CH_2PPh_3)I$ with formaldehyde has not been discovered in the literature and may constitute a novel route.

The hydroboration of indene yields, on oxidation, 2-indanol. However, complexation with iron allows the reaction to proceed so that a hydroxyl group is introduced into the 6-membered ring. Complexation with iron is via the 5-membered ring and would appear to render the unsaturated portion of the 6-membered ring equivalent to a conjugated diene. The air sensitive nature of the complex made establishing the position of the hydroxyl group difficult. This reaction illustrates the possibility of completely altering the site of addition by complexation.

Although the 'H.N.M.R spectrum of cyclooctatetraene iron tricarbonyl indicates that at low temperature the 1,5-exchange is slowed, reaction with diborane did not occur. The very narrow temperature range over which the slow exchange and the ligand state of diborane coincide (from $-165^{\circ}C$ to $-155^{\circ}C$) and the difficulty in maintaining this temperature over a long period may have contributed. If a suitable solvent could be found the experiment may be worth repeating to establish whether the rate of reaction is $\geqslant 0$.

By way of contrast cycloheptatriene is bonded by a 1,3-diene like unit to iron and undergoes reaction, yielding the alcohol.

The investigation of the reaction of a carbonyl group incorporated in the ring system of the ligand were unable to be carried out due to synthetic difficulties.

The unreactive behaviour of the dipyridylethylene complexes, Schiff's base complexes, mercurial complex and dimethylglyoximate complexes are considered to be a result of the delocalisation of π-electrons. Although the complexes were expected to contain unsaturated ligands which should be capable of undergoing hydroboration such reaction did not occur. In the case of the mercurial,delocalisation involving the metal centre could, effectively, allow an extended π-system to be formed making the molecule less likely to react by hydroboration. Delocalisation of electrons in the other complexes would appear also to be greater than was expected.

The ease with which a complex may be hydrogenated, often using a noble metal catalyst, appears to offer a guide as to the likely reactivity of that molecule to hydroboration. In addition the number of bonds likely to be amenable to hydroboration can be assessed. The lability of the bonds between the metal centre and the ligand, as in cyclooctatetraene iron tricarbonyl, also has a significant bearing on the likelihood that the complexed ligand will undergo hydroboration. Using these criteria several complexes had been selected as interesting and the synthetic routes identified from, mainly, commercially available materials.

The bonding of cyclooctatetraene to several metals gives complexes with non-labile ligand - metal bonds and available unsaturated bonds. The complexes $(C_8H_8)Cr(CO)_3$, $(C_8H_8)W(CO)_3$ and $(C_8H_8)Mo(CO)_3$ are available from the carbonyls via the acetonitrile complex or, in the case of molybdenum, the $(diglyme)Mo(CO)_3$ complex [246,247,248,249,250]. In these complexes the ligand has one available unsaturated bond.

Additionally the complexes $(C_8H_8)Co(\pi-C_5H_5)$ and $(C_8H_8)PtI_2$ contain two available unsaturated bonds[229,251,252,253]. The latter complex has been prepared but the hydroboration reaction has not been fully investigated.

REFERENCES

1) A. STOCK and E. KUSS, Ber., 56, 789 (1923).

2) D. T. HURD, J. Amer. Chem. Soc., 70, 2053 (1948).

3) F. G. A. STONE and H. J. EMELEUS, J. Chem. Soc., 2755 (1950).

4) W. G. BROWN, Organic Reactions, Vol. IV, p469, pubs. J. Wiley, New York, 1951.

5) H. I. SCHLESINGER, H. C. BROWN, B. ABRAHAM, A. C. BOND, N. DAVIDSON, A. E. FINHOLT, J. R. GILBREATH, H. HOEKSTRA, L. HORVITZ, E. K. HYDE, J. J. KATZ, J. KNIGHT, R. A. LAD, D. L. MAYFIELD, L. RAPP, D. M. RITTER, A. M. SCHWARZ, I. SHEFT, L. D. TUCK and A. O. WALKER, J. Amer. Chem. Soc., 75, 186 (1953).

6) H. C. BROWN, E. J. MEAD and B. C. SUBBA RAO, J. Amer. Chem. Soc., 77, 6209 (1955).

7) H. C. BROWN, E. J. MEAD and C. F. SHOAF, J. Amer. Chem. Soc., 78, 3613 (1956).

8) H. C. BROWN and B. C. SUBBA RAO, J. Amer. Chem. Soc., 78, 2582 (1956).

9) H. C. BROWN and B. C. SUBBA RAO, J. Amer. Chem. Soc., 78, 5694 (1956).

10) H. C. BROWN and B. C. SUBBA RAO, J. Amer. Chem. Soc., 81, 6423 (1959).

11) O. P. SHITOV, S. L. IOFFE, V. A. TARTAKOVSKI and S. S. NOVIK, Russ. Chem. Revs., 905 (1970)

12) H. C. BROWN, Hydroboration, pubs. W. A. Benjamin, New York, (1962).

13) H. C. BROWN and B. C. SUBBA RAO, J. Org. Chem., 22, 1136 (1957).

14) H. C. BROWN, K. J. MURRAY, L. J. MURRAY, J. A. SNOVER and G. ZWEIFEL, J. Amer. Chem. Soc., 82, 4233 (1960).

15) C. A. BROWN and H. C. BROWN, J. Amer. Chem. Soc., 84, 2892 (1962).

16) H. C. BROWN, M. M. MIDLAND and G. W. KABALKA, J. Amer. Chem. Soc., 93, 1024 (1971).

17) G. ZWEIFEL and H. C. BROWN, Org. Reactions, 13, 1 (1964).

18) M. J. S. DEWAR and M. L. McKEE, Inorg. Chem., 17, 1075 (1978).

19) M. J. S. DEWAR and M. L. McKEE, *J. Amer. Chem. Soc.*, *100*, 7499 (1978).

20) T. CLARK and P. v. R. SCHLEYLER, *J. Organometal.Chem.*, *156*, 191 (1978).

21) M. F. HAWTHORNE, *The Chemistry of Boron and Its Compounds*, Ch. 5. Ed. E. L. Muetterties, Wiley, New York. (1967).

22) D. E. YOUNG and S. G. SHORE, *J. Amer. Chem. Soc.*, *91*, 3497 (1969).

23) B. RICE, J. A. LIVASY and G. W. SCHAEFFER, *J. Amer. Chem. Soc.*, *77*, 2750 (1955).

24) D. F. GAINES, *Inorg. Chem.*, *2*, 523 (1963).

25) R. E. DICKERSON and W. N. LIPSCOMB, *J. Phys. Chem.*, *27*, 212 (1957).

26) H. C. BROWN and G. J. KLENDER, *Inorg. Chem.*, *1*, 204 (1962).

27) E. NEGISHI, J. KATZ and H. C. BROWN, *J. Amer. Chem. Soc.*, *94*, 4025 (1972).

28) H. C. BROWN, C. G. SCOUTEN and K. K. WANG, *J. Org. Chem.*, *44*, 2589 (1979).

29) R. KÖSTER, *Angew. Chem. Int. Ed.*, *3*, 174 (1964).

30) H. C. BROWN and A. W. MOERIKOFER, *J. Amer. Chem. Soc.*, *85*, 2063 (1963).

31) H. C. BROWN and G. ZWEIFEL, *J. Amer. Chem. Soc.*, *82*, 4708 (1960).

32) H. C. BROWN and G. ZWEIFEL, *J. Amer. Chem. Soc.*, *83*, 1241 (1961).

33) H. C. BROWN and K. A. KEBLYS, *J. Amer. Chem. Soc.*, *86*, 1791 (1964).

34) G. ZWEIFEL, K. NAGASE and H. C. BROWN, *J. Amer. Chem. Soc.*, *84*, 183 (1962).

35) H. C. BROWN and G. ZWEIFEL, *J. Amer. Chem. Soc.*, *83*, 3834 (1961).

36) E. F. KNIGHTS and E. C. BROWN, *J. Amer. Chem. Soc.*, *90*, 5280 (1968).

37) C. G. SCOUTEN and H. C. BROWN, *J. Org. Chem.*, *38*, 4092 (1973).

38) H. C. BROWN, R. LIOTTA and L. BRENER, *J. Amer. Chem. Soc.*, *99*, 3427 (1977).

39) R. LIOTTA and H. C. BROWN, *J. Org. Chem.*, *42*, 2836 (1977).

40) H. C. BROWN, C. G. SCOUTEN and R. LIOTTA, J. Amer. Chem. Soc., 101, 96 (1979).

41) G. L. LARSON and L. M. FUENTES, Synth. Commun., 9, 841 (1979).

42) H. C. BROWN and S. U. KULKARNI, J. Organometal. Chem., 168, 281 (1979).

43) M. V. BHATT, J. Organometal. Chem., 156, 221 (1978).

44) W. G. WOODS and P. L. STRONG, J. Amer. Chem. Soc., 88, 4667 (1966).

45) H. C. BROWN and K. GUPTA, J. Amer. Chem. Soc., 93, 1816 (1971).

46) H. C. BROWN and K. GUPTA, J. Amer. Chem. Soc., 94, 4370 (1972).

47) G. W. KABALKA, J. D. BAKER and G. W. NEAL, J. Org. Chem., 42, 512 (1977).

48) H. C. BROWN and P. A. TIERNEY, J. Inorg. Nucl. Chem., 9, 5 (1959).

49) G. ZWEIFEL, J. Organometal. Chem., 9, 215 (1967).

50) D. J. PASTO and P. BALASUBRAMANIYAN, J. Amer. Chem. Soc., 89, 295 (1967).

51) H. C. BROWN and N. RAVINDRAN, J. Org. Chem., 38, 182 (1973).

52) H. C. BROWN and N. RAVINDRAN, J. Amer. Chem. Soc., 95, 2396 (1973).

53) H. C. BROWN and N. RAVINDRAN, J. Org. Chem., 38, 1617 (1973).

54) G. ZWEIFEL, N. L. POLSTON and C. C. WHITNEY, J. Amer. Chem. Soc., 90, 6243 (1968).

55) G. ZWEIFEL and H. C. BROWN, J. Amer. Chem. Soc., 85, 2066 (1963).

56) E. NEGISHI and H. C. BROWN, Synthesis, 77 (1974).

57) H. C. BROWN and E. NEGISHI, J. Amer. Chem. Soc., 89, 5477 (1967).

58) E. NEGISHI and H. C. BROWN, J. Amer. Chem. Soc., 95, 6757 (1973).

59) E. NEGISHI and T. YOSHIDA, J. Chem. Soc. Chem. Comm., 606 (1973).

60) H. C. BROWN, N. M. YOON and A. K. MANDAL, J. Organometal. Chem., 135, C10 (1977).

61) A. PELTER, P. J. RYDER and J. H. SHEPPARD, Tett. Letts., 4715 (1978).

62) G. ZWEIFEL and H. C. BROWN, J. Amer. Chem. Soc., 86, 393 (1964).

63) H. C. BROWN, N. R. AYYANGAR and G. ZWEIFEL, J. Amer. Chem. Soc., 86, 397 (1964) and 86, 1071 (1964) and 83, 2951 (1961).

64) A. PELTER, P. J. RYDER, J. H. SHEPPARD, C. SUBRAHMANYAM, H. C. BROWN and A. K. MANDAL, Tett. Letts., 49, 4777 (1977).

65) H. C. BROWN, B. SINGARAM and J. R. SCHWIER, Inorg. Chem., 18, 51 (1979).

66) H. C. BROWN and B. SINGARAM, Inorg. Chem., 18, 53 (1979).

67) H. C. BROWN, J. R. SCHWIER and B. SINGARAM, J. Org. Chem., 44, 465 (1979).

68) C. F. LANE, J. Org. Chem., 39, 1437 (1974).

69) H. C. BROWN and N. RAVINDRAN, J. Amer. Chem. Soc., 99, 7097 (1977).

70) H. C. BROWN and N. RAVINDRAN, J. Org. Chem., 42, 2533 (1977).

71) H. C. BROWN and N. RAVINDRAN, Inorg. Chem., 16, 2938 (1977).

72) H. C. BROWN, N. RAVINDRAN and S. U. KULKARNI, J. Org. Chem., 44, 2417 (1979).

73) H. C. BROWN, A. K. MANDAL and S. U. KULKARNI, J. Org. Chem., 42, 1392 (1977).

74) H. C. BROWN and W. KORYTNYK, J. Amer. Chem. Soc., 82, 3866 (1960).

75) H. C. BROWN, R. LIOTTA and G. W. KRAMER, J. Amer. Chem. Soc., 101, 2966 (1979).

76) V. V. R. RAO, S. K. AGARWAL, D. D. DEVAPRABHAKARA and S. CHANDRASEKARAN, Synth. Commun., 9, 437 (1979).

77) J. H. BILLMAN and J. W. McDOWELL, J. Org. Chem., 26, 1437 (1961).

78) H. C. BROWN and S. KRISHNAMURTHY, J. Amer. Chem. Soc., 95, 1669 (1973).

79) S. KRISHNAMURTHY, R. M. SCHUBERT and H. C. BROWN, J. Amer. Chem. Soc., 95, 8486 (1973).

80) H. C. BROWN and S. KRISHNAMURTHY, J. Amer. Chem. Soc., 94, 7159 (1972).

81) E. J. COREY, S. M. ALBONICO, U. KOELLIKER, T. K. SCHAAF and R. K. VARMA, J. Amer. Chem. Soc., 93, 1491 (1971).

82) R. O. HUTCHINS, C. A. MILEWSKI and B. MARYANOFF, J. Amer. Chem. Soc., 95, 3662 (1973).

83) R. F. BORCH, M. D. BERNSTEIN and H. D. HURST, J. Amer. Chem. Soc., 93, 2897 (1971).

84) R. O. HUTCHINS and D. KANDASAMY, J. Amer. Chem. Soc., 95, 6131 (1973).

85) P. A. McCUSKER, F. M. ROSSI, J. H. BRIGHT and G. F. HENNION, J. Org. Chem., 28, 2889 (1963).

86) H. C. BROWN and G. ZWEIFEL, J. Amer. Chem. Soc., 88, 1433 (1966).

87) H. C. BROWN and G. ZWEIFEL, J. Amer. Chem. Soc., 89, 561 (1976).

88) R. KÖSTER, G. GRIASNOW, W. LARBIG and P. BINGER, Annalen, 672, 1 (1964).

89) A. M. KRUBINGER, N. GOTTRIED and E. P. OLIVETO, J. Org. Chem., 33, 1715 (1968).

90) B. RICKBORN and S. E. WOOD, Chem & Ind. (London), 1966, 162.

91) W. HERZ and J. J. SCHMID, J. Org. Chem., 34, 3464 (1969).

92) L. LARDICCI, L. LUCARINI, P. PALAGI and P. PINO, J. Organometal. Chem., 4, 341 (1965)

93) R. KOSTER, Annalen, 618, 31 (1958).

94) H. C. BROWN and M. V. BHATT, J. Amer. Chem. Soc., 88, 1440 (1966).

95) H. C. BROWN, M. V. BHATT, T. MUNEKATA and G. ZWEIFEL, J. Amer. Chem. Soc., 89, 567 (1967).

96) M. M. MIDLAND, J. E. PETRE and S. A. ZDERIC, J. Organometal. Chem., 182, C53 (1979).

97) K. G. FOOT and B. P. ROBERTS, J. Chem. Soc. (A)., 1971, 3475.

98) H. C. BROWN and E. NEGISHI, J. Amer. Chem. Soc., 91, 1224 (1969).

99) R. KOSTER, Angew. Chem., 72, 626 (1960).

100) H. C. BROWN, E. NEGISHI and S. K. GUPTA, J. Amer. Chem. Soc., 92, 2460 (1970).

101) H. C. BROWN and K. J. MURRAY, J. Amer. Chem. Soc., 81, 4108 (1959).

102) E. J. COREY and T. RAVINDRANATHAN, J. Amer. Chem. Soc., 94, 4013 (1972).

103) D. B. BIGLEY and W. PAYLING, J. Inorg. Nucl. Chem., 33, 1157 (1971).

104) L. H. TOPORCER, R. E. DESSY and S. I. E. GREEN, J. Amer. Chem. Soc., 87, 1236 (1965).

105) H. C. BROWN and K. J. MURRAY, J. Org. Chem., 26, 631 (1961).

106) A. G. DAVIES and B. P. ROBERTS, J. Chem. Soc. (C)., 1968, 1474.

107) G. W. KABALKA, R. J. NEWTON and J. J. JACOBUS, J. Org. Chem., 44, 4185 (1979).

108) G. ZWEIFEL and N. L. POLSTON, J. Amer. Chem. Soc., 92, 4068 (1970).

109) G. ZWEIFEL, G. M. CLARK and N. L. POLSTON, J. Amer. Chem. Soc., 93, 3395 (1971).

110) I. D. CAMPBELL and G. EGLINTON, Org. Synth., 45, 39 (1965).

111) A. PELTER, R. HUGHES, K. SMITH and M. TABATA, Tett. Letts., 1976, 4385.

112) J. A. SINCLAIR and H. C. BROWN, J. Org. Chem., 41, 1078 (1976).

113) L. H. LONG and D. DOLLIMORE, J. Chem. Soc., 3902, 3906 (1953).

114) H. C. BROWN, M. W. RATHKE and M. M. ROGIC, J. Amer. Chem. Soc., 90, 5038 (1968).

115) H. C. BROWN and C. F. LANE, J. Amer. Chem. Soc., 92, 6660 (1970).

116) C. F. LANE and H. C. BROWN, J. Organometal. Chem., 26, C51 (1971).

117) A. F. KLUGE, K. G. UNTCH and J. H. FRIED, J. Amer. Chem. Soc., 94, 7827 (1972).

118) H. C. BROWN, T. HAMAOKA and N. RAVINDRAN, J. Amer. Chem. Soc., 95, 5786 (1973) and 95, 6456 (1973).

119) G. ZWEIFEL, H. ARZOUMANIAN and C. C. WHITNEY, J. Amer. Chem. Soc., 89, 3652 (1967).

120) D. A. EVANS, T. C. CRAWFORD, R. C. THOMAS and J. A. WALKER, J. Org. Chem., 41, 3947 (1976).

121) G. ZWEIFEL, R. P. FISHER, J. T. SNOW and C. C. WHITNEY, J. Amer. Chem. Soc., 94, 6560 (1972).

122) H. C. BROWN, W. R. HEYDKAMP, E. BREVER and W. S. MURPHY, J. Amer. Chem. Soc., 86, 3565 (1964).

123) H. J. MATSAGUMA and L. F. AUDRIETH, Inorg. Synth., 5, 122 (1957).

124) A. SUZUKI, S. SONO, M. ITOH, C. BROWN and M. M. MIDLAND, J. Amer. Chem. Soc., 93, 4329 (1971).

125) H. C. BROWN and M. M. MIDLAND, J. Amer. Chem. Soc., 94, 2114 (1972) and 95, 2394 (1973).

126) A. B. LEVY and H. C. BROWN, J. Amer. Chem. Soc., 95, 4067 (1973).

127) L. F. HOHNSTEDT, J. P. BRENNAN and K. A. REYNARD, J. Chem. Soc. (A)., 1970, 2455.

128) H. C. BROWN and Y. YAMOMOTO, J. Chem. Soc. Chem. Comm., 1972, 71.

129) R. KÖSTER and M. GRASSBERGER, Annalen, 719, 169 (1968).

130) H. NOTH and H. VAHRENKAMP, J. Organometal. Chem., 11, 399 (1968).

131) H. C. BROWN and N. RAVINDRAN, J. Amer. Chem. Soc., 94, 2112 (1972).

132) J. B. HONEYCUTT and J. M. RIDDLE, J. Amer. Chem. Soc., 82, 3051 (1960).

133) R. C. LAROCK and H. C. BROWN, J. Amer. Chem. Soc., 92, 2467 (1970).

134) J. D. BUHLER and H. C. BROWN, J. Organometal. Chem., 40, 265 (1972).

135) R. C. LAROCK, S. K. GUPTA and H. C. BROWN, J. Amer. Chem. Soc., 94, 4371 (1972).

136) H. C. BROWN, N. C. HEBERT and C. H. SNYDER, J. Amer. Chem. Soc., 83, 1001 (1961).

137) H. C. BROWN, C. VERBRUGGE and C. H. SNYDER, J. Amer. Chem. Soc., 83, 1002 (1961).

138) A. G. DAVIES and B. P. ROBERTS, J. Chem. Soc. (B)., 1969, 311.

139) S. B. MIRVISS, J. Amer. Chem. Soc., 83, 3051 (1961).

140) M. H. ABRAHAM and A. G. DAVIES, J. Chem. Soc., 1959, 429.

141) P. G. ALLIES and P. B. BRINDLEY, Chem. & Ind. (London), 1967, 319.

142) A. G. DAVIES and B. P. ROBERTS, J. Chem. Soc. (B)., 1967, 17.

143) A. G. DAVIES, K. U. INGOLD, B. P. ROBERTS and R. TURNER, J. Chem. Soc. (B)., 1971, 698.

144) P. B. ALLIES and P. B. BRINDLEY, J. Chem. Soc. (B)., 1969, 1126.

145) H. C. BROWN and M. M. MIDLAND, J. Amer. Chem. Soc., 93, 4078 (1971).

146) D. B. BIGLEY and D. W. PAYLING, J. Chem. Soc. (B)., 1970, 1181.

147) J. R. JOHNSON and M. G. VANCHAMPEN, J. Amer. Chem. Soc., 60, 121 (1938).

148) H. MINATO, J. C. WARE and T. G. TRAYLOR, J. Amer. Chem. Soc., 85, 3024 (1963).

149) H. C. BROWN and C. P. GARG, J. Amer. Chem. Soc., 83, 2951 (1961).

150) H. C. BROWN, I. ROTHBURG and D. L. VANDER JAGT, J. Org. Chem., 37, 4098 (1972).

151) J. C. WARE and T. G. TRAYLOR, J. Amer. Chem. Soc., 85, 3026 (1963).

152) R. KÖSTER and Y. MORITA, Angew. Chem. Int. Ed., 5, 580 (1966).

153) R. KÖSTER and Y. MORITA, Annalen, 704, 70 (1967).

154) H. C. BROWN, U.S. Patent 3, 439, 046 April 15, 1969.

155) M. E. D. HILLMAN, J. Amer. Chem. Soc., 84, 4715 (1962) and 85, 982 and 1626 (1963).

156) H. C. BROWN, Acc. Chem. Res., 2, 65 (1969).

157) H. C. BROWN, R. A. COLEMAN and M. W. RATHKE, J. Amer. Chem. Soc., 90, 499 (1968).

158) H. C. BROWN, E. F. KNIGHTS and R. A. COLEMAN, J. Amer. Chem. Soc., 91, 2144 (1969).

159) H. C. BROWN and R. A. COLEMAN, J. Amer. Chem. Soc., 91, 4606 (1969).

160) H. C. BROWN and E. NEGISHI, J. Chem. Soc. Chem. Comm., 1968, 594.

161) H. C. BROWN and M. W. RATHKE, J. Amer. Chem. Soc., 89, 2737 (1967).

162) E. NEGISHI and H. C. BROWN, Synthesis, 1972, 197.

163) H. WITTE, E. BREHM, and G. HESSE, Z. Naturforsch., 226, 1083 (1967).

164) A. PELTER, M. G. HUTCHINS and K. SMITH, J. Chem. Soc. Chem. Comm., 1970, 1529.

165) A. PELTER, M. G. HUTCHINS and K. SMITH, J. Chem. Soc. Chem. Comm., 1973, 1861.

166) A. PELTER, H. G. HUTCHINS and K. SMITH, J. Chem. Soc. Chem. Comm., 1971, 1048.

167) H. C. BROWN, M. M. ROGIC and M. W. RATHKE, J. Amer. Chem. Soc., 90, 6218 (1968).

168) H. C. BROWN, M. M. ROGIC, M. W. RATHKE and G. W. KABALKA, J. Amer. Chem. Soc., 90, 818 (1968).and 90, 1911 (1968).

169) H. C. BROWN, H. NAMBU and M. M. ROGIC, J. Amer. Chem. Soc., 91, 6852 and 6854 and 6855 (1969).

170) H. NAMBU and H. C. BROWN, J. Amer. Chem. Soc., 92, 5790 (1970).

171) D. J. PASTO and R. SNYDER, J. Org. Chem., 31, 2773 (1966).

172) D. J. PASTO and J. HICKMAN, J. Amer. Chem. Soc., 89, 5608 (1967).

173) A. SUZUKI, K. OHMORI, H. TAKENAKA and M. ITOH, Tett. Letts., 1968, 4937.

174) D. J. PASTO, J. HICKMAN and T. C. CHENG, J. Amer. Chem. Soc., 90, 6259 (1968).

175) D. S. MATTESON, Organometal. Chem. Rev., 5, 42 (1969).

176) D. J. PASTO and R. SNYDER, J. Org. Chem., 31, 2777 (1966).

177) D. J. PASTO and J. L. MIESEL, J. Amer. Chem. Soc., 85, 2118 (1963).

178) H. C. BROWN and N. R. DeLUE, J. Amer. Chem. Soc., 96, 311 (1974).

179) C. F. LANE and H. C. BROWN, J. Amer. Chem. Soc., 93, 1025 (1971).

180) H. C. BROWN and N. R. DeLUE, Tett. Letts., 1977, 3007.

181) H. C. BROWN, Y. YAMAMOTO and C. F. LANE, Synthesis, 303 (1972).

182) A. PELTER, T. W. BENTLEY, C. R. HARRISON, C. SUBRAHMANYAM, and J. R. LAUB, J. Chem. Soc. Perkin Trans., 1, 2419 (1976).

183) A. PELTER, K. J. GOULD and C. R. HARRISON, J. Chem. Soc. Perkin Trans., 1, 2428 (1976).

184) A. PELTER, C. R. HARRISON, C. SUBRAHMANYAM and D. KIRKPATRICK, J. Chem. Soc. Perkin Trans., 1, 2435 (1976).

185) A. SUZUKI, A. ARASE, H. MATSUMOTO, M. ITOH, H. C. BROWN, M. M. ROGIC and M. W. RATHKE, J. Amer. Chem. Soc., 89, 5708 (1967).

186) H. C. BROWN, M. M. ROGIC, M. W. RATHKE and G. W. KABALKA, J. Amer. Chem. Soc., 89, 5709 (1967).

187) R. E. LUTZ and W. G. REVELY, J. Amer. Chem. Soc., 63, 3184 (1941).

188) G. W. KABALKA, H. C. BROWN, A. SUZUKI, S. HONMA, A. ARASE and M. ITOH, J. Amer. Chem. Soc., 92, 710 (1970).

189) H. C. BROWN and G. W. KABALKA, J. Amer. Chem. Soc., 92, 712 (1970) and 92, 714 (1970).

190) J. HOOZ and M. GUNN, J. Amer. Chem. Soc., 91, 6195 (1969).

191) T. MUKAIYANA, K. INOMATA and M. MURAKI, J. Amer. Chem. Soc., 95, 967 (1973).

192) J. HOOZ and J. N. BRIDSON, Canad. J. Chem., 50, 2387 (1972).

193) P. JACOB and H. C. BROWN, J. Amer. Chem. Soc., 98, 7832 (1976).

194) H. C. BROWN and E. NEGISHI, J. Amer. Chem. Soc., 93, 3777 (1971).

195) H. C. BROWN and M. M. MIDLAND, Angew. Chem. Int. Ed. Engl., 11, 693 (1972).

196) A. SUZUKI, S. NOZAWA, M. ITOH, H. C. BROWN, G. W. KABALKA and G. W. HOLLAND, J. Amer. Chem. Soc., 92, 3503 (1970).

197) G. S. TER-SARKISYAN, N. A. NIKOLAEMVA and B. M. MIKHOLIOV, 12v. Akad. Navk. SSSR. Ser. Khim. 1968, 2516 [CA., 70,67808n, (1969).]

198) K. UTIMOTO, T. TANAKA and H. NOZAKI, Tett. Letts., 1972, 1167.

199) D. SEYFERTH, H. YAMAZAKI and Y. SATO, Inorg. Chem., 2, 734 (1963).

200) T. WARTIK and R. K. PEARSON, J. Inorg. Nucl. Chem., 5, 250 (1958).

201) P. R. JONES and J. K. MYERS, J. Organometal. Chem., 34, C9 (1972).

202) G. L. LARSON, D. HERNANDEZ and A. HERNANDEZ, J. Organometal. Chem., 76, 9 (1974).

203) G. M. PICKLES and F. G. THORPE, J. Organometal. Chem., 76, C23 (1974).

204) P. M. TREICHEL and J. P. STENSON, J. Chem. Soc. Chem. Comm., 1969, 423.

205) P. M. TREICHEL, J. P. STENSON and J. J. BENEDICT, Inorg. Chem., 10, 1183 (1971).

206) D. G. HOLAH, A. N. HUGHES, B. C. HUI and K. WRIGHT, Inorg. Nucl. Chem. Letts., 9, 835 (1973).

207) D. G. HOLAH, A. N. HUGHES, B. C. HUI and K. WRIGHT, Canad. J. Chem., 52, 2990 (1974).

208) H. D. EMPSALL, E. MENTZER and B. L. SHAW, J. Chem. Soc. Chem. Comm., 1975, 861.

209) K. M. NICHOLAS and R. PETIT, Tett. Letts., (1971) 3475.

210) T. A. WOODS, T. E. BOYD, E. R. BIEHL and P. C. REEVES, J. Org. Chem., 40, 2416 (1975).

211) R. A. ANDERSON and G. E. COATES, J. Chem. Soc. Dalton., 1440 (1974).

212) A. A. L. GUNATILAKA and A. F. MATEOS, J. Chem. Soc., Perkin Trans., 1, 935 (1979).

213) H. C. BROWN, Nobel Lecture. Science, 210, 485 (1980).

214) G. F. FREEGUARD and L. H. LONG, Chem. and Ind., 471 (1965).

215) A. VOGEL, Practical Organic Chemistry, 4th Edition, Longmans, London (1978).

216) H. C. BROWN and P. A. TIERNEY, J. Amer. Chem. Soc., 80, 1552 (1958).

217) M. E. McENTEE and A. R. PINDER, J. Chem. Soc., 4419 (1957).

218) L. F. FIESER and M. FIESER, Reagents for Organic Synthesis, 680, J. Wiley and Sons Inc., New York, N.Y., (1967).

219) J. K. LINDSAY and C. R. HAUSER, J. Org. Chem.,22, 335 (1957).

220) C. R. HAUSER, J. Org. Chem., 22, 906 (1957).

221) G. D. BROADHEAD, J. M. OSGERBY and P. L. PAUSON, J. Chem. Soc., 650 (1958).

222) P. J. GRAHAM, R. V. LINDSEY, G. W. PARSHALL, M. L. PETERSON and G. M. WHITMAN, J. Amer. Chem. Soc., 79, 3416 (1957).

223) M. VOGEL, M. RAUSCH and H. ROSENBERG, J. Org. Chem., 22, 1016 (1957).

224) F. S. ARIMOTO and A. C. HAVEN, J. Amer. Chem. Soc., 77, 6295 (1955).

225) A. VOGEL, Inorganic Chemistry, 4th Edition, Longmans, London (1954).

226) Organic Syntheses, Collective, 1, 228, 2nd Edition, Wiley (1958).

227) E. C. TAYLOR, A. McKILLOP and G. M. HAWKES, Org. Syntheses, 52, 36 (1972).

228) R. P. M. WERNER and T. H. COFFIELD, Chem. and Ind., 936 (1960).

229) K. A. JENSEN, Acta. Chim. Scand., 7, 868 (1953).

230) Y. SHVO and E. HAZUM, J. Chem. Soc. Chem. Comm., 20, 829 (1975).

231) R. B. KING and M. B. BISNETTE, Inorg. Chem., 3, 796 (1964).

232) E. W. GARBISCH, J. Org. Chem., 30, 2109 (1965).

233) W. E. PARHAM, R. N. SOEDER and R. H. DODSON, J. Amer. Chem. Soc., 84, 1755 (1962).

234) W. E. PARHAM and E. E. SCHWEIZER, J. Org. Chem., 24, 1733 (1959).

235) T. NOZOE, Y. KITAHARA, E. KUNIOKA and T. ANDO, Proc. Jap. Acad., 27, 102 (1951).

236) M. BRIERLEY and W. J. GEARY, J. Chem. Soc., (A)., 963 (1967).

237) M. BRIERLEY and W. J. GEARY, J. Chem. Soc., (A)., 1641 (1968).

238) D. D. PERRIN, A. AMAREGO and D. R. PERRIN, Purification of Organic Compounds, Pergammon, Oxford (1964).

239) T. A. WOODS, T. E. BOYD, E. R. BIEHL and P. C. REEVES, J. Org. Chem., 40, 2416 (1975).

240) J. W. FRANKENFIELD and W. E. TYLER, J. Org. Chem., 36, 2110 (1975).

241) A. DUPIRE, Comp. Rend. Acad. Sci., 278, 1306 (1974).

242) E. NAGAI, S. KURIBAYASHI, M. SHIRAKI and M. UKITA, J. Polymer Sci., 35, 295 (1959).

243) P. B. BRINDLEY, R. G. DAVIS, B. L. HORNER and D. I. RITCHIE, J. Organometal. Chem., 88, 321 (1975).

244) R. GRUBBS, R. BRESLAW, R. HERBER and J. S. LIPPARD, J. Amer. Chem. Soc., 89, 6864 (1967).

245) T. A. MANUEL and F. G. A. STONE, J. Amer. Chem. Soc., 82, 366 (1960).

246) R. B. KING, J. Organometal. Chem., 8, 139 (1967).

247) R. B. KING and A. FRONZAGLIA, J. Chem. Soc. Chem. Comm., 547 (1965).

248) R. B. KING and A. FRONZAGLIA, Inorg. Chem., 5, 1937 (1966).

249) R. B. KING and A. FRONZAGLIA, J. Chem. Soc. Chem., Comm., 274 (1966).

250) D. P. TATE, W. R. KNIPPLE and J. M. AUGL, Inorg. Chem., 1, 433 (1962).

251) T. S. PIPER, F. A. COTTON and G. WILKINSON, J. Inorg. and Nucl. Chem., 1, 165 (1955).

252) A. NAKAMURA, Bull. Chem. Soc. Japan., 33, 425 (1960).

253) A. NAKAMURA, Bull. Chem. Soc. Japan., 34, 452 (1961).

9. Postgraduate Study

The author has attended the following lecture courses and made use of the books listed.

1) Chemical Society annual congress, York (1975).
2) Hydroboration, The University, Sheffield.
3) Catalysis, The University, Sheffield.
4) Metals in organic synthesis, The University, Sheffield.
5) Ionic transport in membranes, The University, Sheffield.
6) Departmental research colloquia.

Books

1) Hydroboration, H. C. Brown, W. A. Benjamin Inc., New York, N.Y., (1962).
2) H. C. Brown, Boranes in organic chemistry, Cornell Univ. Press, Ithaca, N.Y., (1972).
3) T. Onak, Organoborane Chemistry, Academic Press, London (1975).
4) Organoboranes in organic synthesis, G. M. L. Gragg, Dekker Inc., New York, N.Y., (1973).
5) Interpretation of mass spectra, F. W. McLafferty, W. A. Benjamin Inc., New York, N.Y., (1973).
6) Mass spectrometry of inorganic and organometallic compounds, M. R. Litzow and T. R. Spalding, Elsevier, Amsterdam, (1973).
7) G. E. Coates, M. L. H. Green and K. Wade, Organometallic Compounds, 3rd Edition, Vol. I (1967), The main group elements, Vol. II (1968), The transition elements, Methuen, London.
8) Dynamic nuclear magnetic resonance spectroscopy, Editors R. Jackman and F. A. Cotton, Academic Press, (1975).