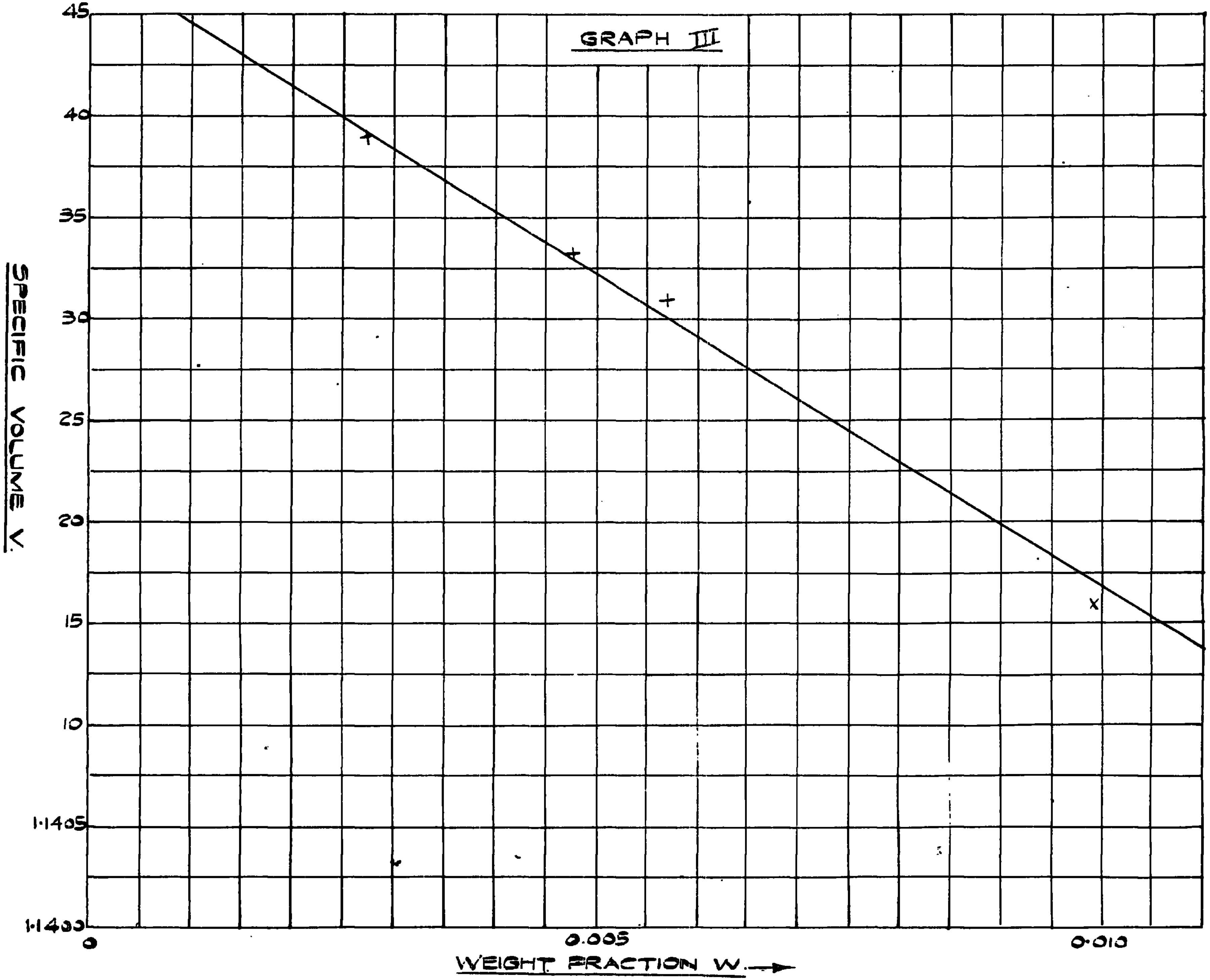
Studies on the organic chemistry of boron

Livingstone, J.G.


GRAPH III
SPECIFIC VOLUME V.
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35
30
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10
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0.005
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WEIGHT FRACTION W.


GRAPH I.
CHANGE IN CAPACITANCE Δ C IN CMS.
1·8
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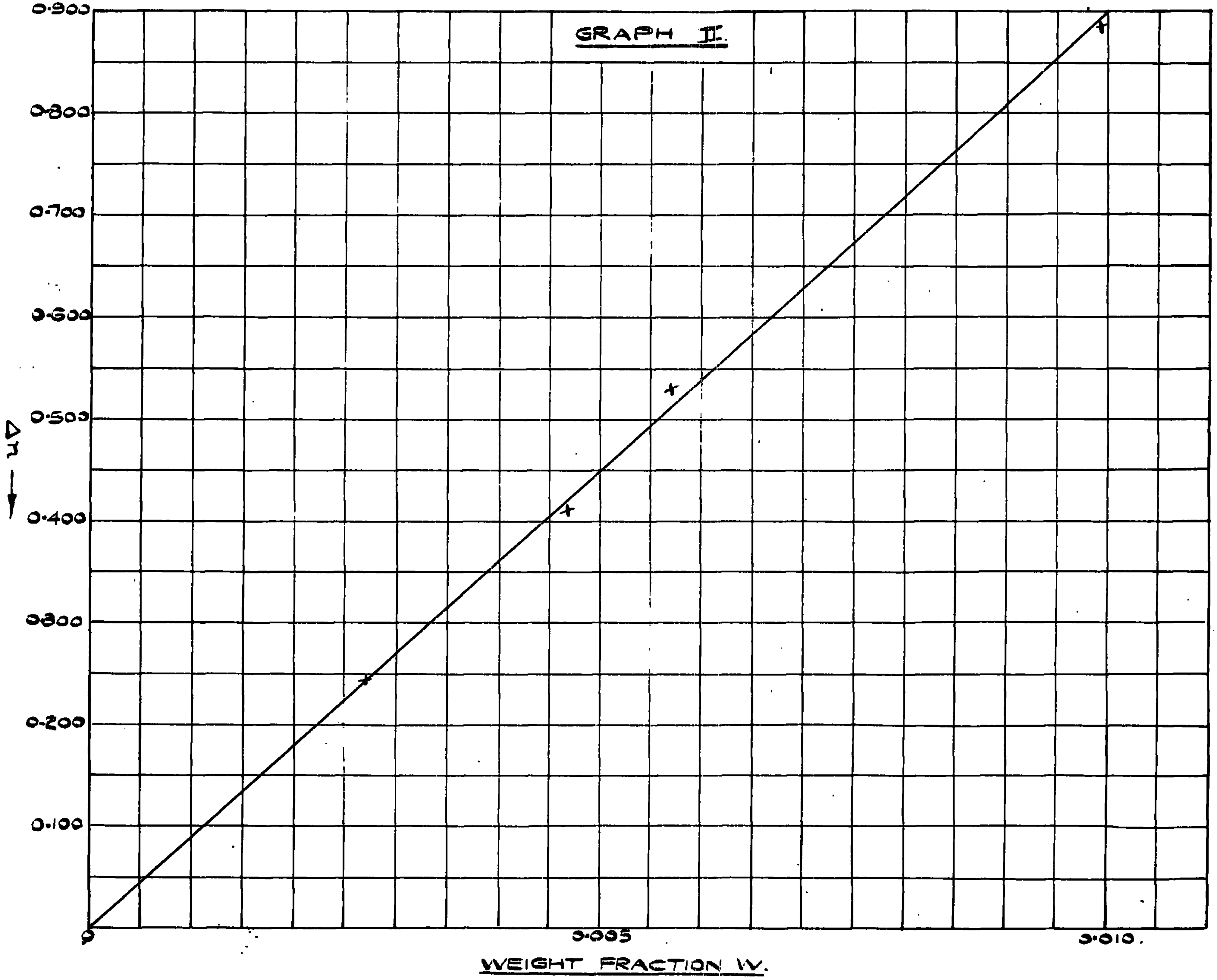
WEIGHT FRACTION W.



GRAPH II.

0·900
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0·100
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WEIGHT FRACTION W.

STUDIES ON
THE ORGANIC CHEMISTRY
OF BORON

BY

J. G. LIVINGSTONE

A dissertation submitted for the Degree of Doctor of
Philosophy in the Durham Colleges of the
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The author wishes to express his most sincere thanks to Professor G. E. Coates, M.A., D.Sc., F.R.I.C., under whose direction this research was carried out, for his constant encouragement and extremely valuable advice, and to Dr. G. Kohnstam and Dr. F. Glockling for their comments.

The author also takes this opportunity to express his thanks to the Senate of Durham University at which laboratories this work was carried out, and to the Department of Scientific and Industrial Research for the award of a grant.

MEMORANDUM

The work included in this thesis was carried out at the Durham Colleges Science Laboratories in the University of Durham between September 1958 and September 1961, and has not been submitted for any other Degree. Part of this work has already been the subject of a publication in the Journal of the Chemical Society.

All the work described is the original work of the author, except that acknowledged by reference.

SUMMARY

Several aminodiarylboranes ($Ar_2B\ NR_2$) have been prepared by the methods:

$$Ar_2BCl + LiNR_2 = Ar_2B{\cdot}NR_2 + LiCl \ \ldots\ldots\ldots\ldots \quad (1)$$

$$Ar_2BCl + R_2NH + Et_3N = Ar_2B\ NR_2 + Et_3NHCl \ \ldots\ldots \quad (2)$$

$$2ArMgBr + Cl_2B\ NR_2 = Ar_2B\ NR_2 + MgCl_2 + MgBr_2 . \quad (3)$$

Aminodiphenylborane (R = H, method 2) is dimeric and non-polar in benzene solution. Experiments with molecular models indicate that larger groups attached to the nitrogen would cause substantial steric interference even with the hydrogen atoms in *ortho*-positions on the aryl groups. Similarly, aminodimesitylborane is monomeric.

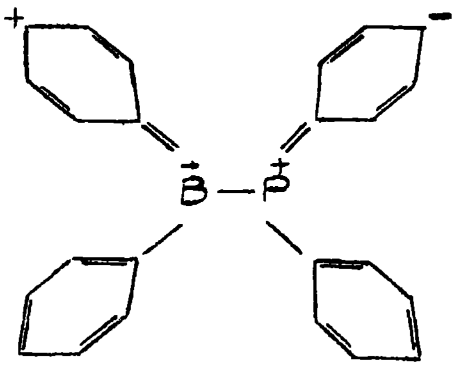
All the other aminodiarylboranes prepared are monomeric in nitrobenzene solution, though often slightly associated in benzene particularly in the more concentrated solutions.

The monomeric aminodiarylboranes have low dipole moments, whose direction is reversed on passing from $Ph_2B{\cdot}NMe_2$ to Ph_2BNPh_2. This reversal of polarity could be due to the electron repelling effect of a methyl group, whereas a phenyl group can act as an electron acceptor in such a system. All the observed moments are consistent with only a small or zero net polarity for the B-N bond.

The rapid and quantitative hydrolysis, by cold water, of the aminoboranes was the basis of a method sometimes used for their analysis, and more important for a most convenient method for the preparation of diarylborinic acids. Some twelve acids have been prepared as the monoethanolamine esters (yields 51-93%) by hydrolysis of the diarylaminoborane obtained from the reaction of a slight excess of the appropriate Grignard reagent with dichlorodiphenylaminoborane. This would appear to be the most convenient preparative method for diarylborinic acids.

Phosphinodiarylboranes are monomeric but unlike the amino compounds they are quite stable to boiling dilute acids and alkalies. However, quantitative oxidation by aqueous alcoholic hydrogen peroxide to boric acid the phosphinic acid and the phenol has sometimes been used as a method for their analysis. Their dipole moments are generally greater than those of the corresponding amino-compounds, and the phosphino-group is at the <u>negative</u> end of the dipole. This surprising result suggests that phosphorus acts as a π donor (to boron) only weakly if at all in these compounds, possibly owing to an unfavourable relation between the "sizes" of boron 2p- and phosphorus 3p- orbitals.

Formula I accounts in a qualitative way not only for the observed dipole moments, but also for the lack of chemical reactivity, since both boron and phosphorus are co-ordinatively saturated (or partly so). Further the indicated charge separation between boron and phosphorus should result in B-P stretching force constants greater than would be expected for B-P single bonds, since the B-P bond would amount to a o-bond possibly with a small π-component but with some electrostatic attraction in addition. In this sense the B-P bond could perhaps be described as a "semi-polar double bond", thus accounting for the rather high frequencies (1400 - 1500 cm^{-1}) associated with the stretching of the B-P bond. The reason for the phosphinodiarylboranes being monomeric, when the series $R_2B\cdot PR'_2$ (R = H, alkyl) form trimers, tetramers, or polymers, thus lies in the boron atom in the diarylborane series being already coordinatively saturated (or nearly so) not by π-bonding with phosphorus but by π-bonding with the aryl groups.



The arsino-derivatives are similar to the phosphino-compounds but they are less polar. Perhaps the most significant difference is that oxidation with aqueous alcoholic hydrogen peroxide affords boric acid, arsenic acid and the appropriate phenols e.g.

$$Ph_2B\ AsAr_2 + H_2O_2 - 2PhOH + 2ArOH + H_3BO_3 + H_3AsO_4$$

The smaller dipole moments of the arsinoboranes is probably due to a smaller degree of electron transfer from arsenic to the aryl groups bound to it.

It now seems evident that though the σ-donor character of nitrogen, phosphorus, and arsenic towards boron diminishes in that order the π-donor character diminishes even more rapidly.

The phosphinoboranes $Ph\ B\ (PPh_2)_2$, $Ph\ P\ (BPh_2)_2$, $(Ph\ B\ PPh)_2$ and $(Ph\ B\ PPh)_x$ have also been prepared. They are all more sensitive to oxidation than the phosphinodiarylboranes mentioned earlier.

PART I

INTRODUCTION

A) ORGANO-DERIVATIVES OF BORIC ACID

1. PREPARATION OF TRIALKYL- & TRIARYL BORATES

The best known and most stable organo derivatives of boric acid are the trialkyl and triaryl borates $(RO)_3B$; unsymmetrical esters $ROB(OR')_2$ are known but they tend to disproportionate to the symmetrical esters. Indeed disproportionation is a common and sometimes troublesome feature of organo-boron chemistry.

Lappert[1] in his review describes several methods of preparation of the borates. Ebelmen and Bouquet[2], the first workers to mention orthoborates, prepared trimethyl, triethyl, and triamyl borates by heating the appropriate alcohol with boron trichloride in a sealed tube, but attempts to prepare triallyl and tribenzyl borates were unsuccessful. Michaelis and Hillringhaus[3] prepared triaryl borates by the sealed tube method at 100° but recently Golclough, Gerrard and Lappert[4] have shown that heating is unnecessary, triaryl borates being obtained in nearly quantitative yield by the addition of boron trichloride (1 mole) to the phenol (3 moles) at - 80°C in methylene chloride. Wiberg and Sutterlin[5] investigated the reaction sequences in the boron trichloride-methanol and boron trichloride-ethanol systems, employing high vacuum apparatus at -80°C, and obtained quantitative yields of the orthoborates when the correct proportion of reagents was used

$$3ROH + BCl_3 \rightarrow B(OR)_3 + 3HCl$$

Later large scale preparations, by this method, in an inert solvent (pentane) afforded the borates almost instantaneously and in nearly quantitative yield. When about 20-100 grams of borate, particularly one of high molecular weight, is required the best method comprises heating boron trioxide with the appropriate alcohol in toluene and allowing the condensed vapours to percolate through anhydrous copper sulphate in a soxhlet extractor to remove the water formed in the reaction. Trimethylborate was obtained in good yield 92% by Schechter[6] when boron trioxide (2 moles) was added to methanol (3 moles) at 35-60° and the mixture digested 1 hour at 25°C. $2B_2O_3 + 3CH_3OH \rightarrow 3HBO_2 + B(OCH_3)_3$.

Pictet and Geleznoff[7] prepared several triaryl and trialkyl borates by warming phenols or alcohols with boron acetate and separating the borate and acetic acid by fractional distillation.

Boric acid was first used to prepare orthoborates by Cohn[8]:- $B(OH)_3 + 3ROH \rightarrow B(OR)_3 + 3H_2O$. The esterification was performed in the presence of hydrogen chloride or concentrated sulphuric acid. Later this method was modified by use of an inert solvent such as benzene, toluene or carbon tetrachloride and removal of the water as a ternary azeotrope[9].

Recently Brown, Mead and Shoaf[10] have found a general synthesis for alkyl borates by the reaction between sodium borohydride and the appropriate alcohol in the presence of one equivalent of acetic acid.

$$3ROH + NaBH_4 + HOAC \rightarrow (RO)_3B + NaOAC + 4H_2$$

With tertiary alcohols higher temperatures are needed to drive off the last mole of hydrogen and yields of about 20% are obtained:- $2ROH + NaBH_4 + HOAC \rightarrow (RO)_2BH + NaOAC + 3H_2$ and at higher temperatures, $ROH + (RO)_2BH \rightarrow (RO)_3B + H_2$.

Brown and co-workers also recommend the transesterification of methyl borate when other methods fail.

Less mention has been made of the metaborates. Schiff[11] observed that the primary reaction between ethanol and boron trioxide was the formation of methyl metaborate, the same compound was also obtained from triethylborate and boron trioxide.

$$C_2H_5OH + B_2O_3 \rightarrow HOBO + C_2H_5OBO$$

$$B(OC_2H_5)_3 + B_2O_3 \rightarrow 3\ C_2H_5OBO$$

Acetyl metaborate has been claimed by Dimroth[12] as a product of the pyrolysis of tetracetyl diborate but no details were given. Goubeau and Keller[13] reported that boron trioxide and trimethyl borate when heated in a sealed tube in equimolar proportions afforded methyl metaborate which was trimeric (cryoscopic) and therefore formulated as a boroxole; it decomposed at 170-220°.

By oxidation of trimeric n-butylboronic anhydride with dry air Grummitt[14] obtained n-butyl metaborate which, contrary to his observations, has been shown by Lappert[15] to be trimeric.

O'Connor and Nace[16] prepared l-menthyl and cyclohexyl metaborates from the appropriate alcohol and orthoboric acid, the water formed was removed by azeotropic distillation with toluene.

$$ROH + H_3BO_3 \rightarrow ROBO + 2H_2O.$$

Recently Lappert[17] has prepared the lower alkyl (Me, Et, Pr^n, Pr^i, Bu^n, Bu^i, Bu^s, but not Bu^t) metaborates $(RO.BO)_3$ by thermal or catalytic decomposition of the corresponding dialkyl chloroboronates, $(RO)_2BCl$, or by heating the orthoborates with boron trioxide. The latter method was also successful for preparing phenyl metaborate.

II. PROPERTIES

(a) PHYSICAL

Parachor and dipole measurements have verified planar structures and electron diffraction measurements on trimethyl borate showed the BO_3 configuration to be planar with angles 120°; bond distances were also measured.[1]

Infra-red spectra of metaborates showed strong absorption bands near 720 and 735 cm^{-1}.[18]

(b) CHEMICAL

The borates are generally easily hydrolysed by water to give orthoboric acid and the appropriate alcohol; their important reaction with organo-metallic compounds will be mentioned in detail later. They are generally very stable and can be heated to quite high temperatures without significant decomposition. They react with acids, typical products being indicated by the following reactions[19]:-

$$B(OC_2H_5)_3 + 2B(OH)_3 \xrightarrow{160-180^\circ C} 3C_2H_5OH + 3HBO_2$$

$$B(OC_2H_5)_3 + H_2SO_4 \xrightarrow{\text{Heat}} C_2H_5HSO_4 + 2C_2H_4 + HBO_2 + H_2O$$

$$B(OC_2H_5)_3 + H_2SO_4 + H_2O \xrightarrow[\text{2 Addition of } H_2O]{\text{1 Heat to } 140-150^\circ} C_2H_5HSO_4 + B(OH)_3 + (C_2H_5)_2O$$

$$B(OC_2H_5)_3 + H_2SO_4 + 2RCOOH \rightarrow C_2H_5HSO_4 + B(OH)_3 + 2RCOOC_2H_5$$

$$R = CH_3, \underline{n} - C_3H_7, \underline{n} - C_4H_9, C_6H_5$$

$$B(OC_2H_5)_3 + 3HNO_3 \rightarrow 3C_2H_5ONO_2 + B(OH)_3$$

$$B(OC_2H_5)_3 + H_3PO_4 \rightarrow BPO_4 + 3C_2H_5OH$$

Rapid dealkylation occurs when borates containing powerful electron releasing groups, e.g. 1 phenylethyl borate, react with hydrogen halides:-

$B(OR)_3 + 3HX \rightarrow 3RX + B(OH)_3$ X = halogen

In contrast to most alkyl borates, the aryl borates being stronger Lewis acids, generally form coordination complexes with ammonia and amines.

B) TRIALKYL- AND TRIARYL BORANES

1. PREPARATION

The rapid development of organo-boron chemistry in the last twenty years is due to three main factors:-

a) The use of the volatile trialkyls in the study of the electronic and steric effects which influence the formation of coordination compounds.

b) The application of trialkyls of boron to the isomerisation of olefins and the preparation of primary alcohols from olefins with either terminal or non-terminal double bonds.

c) The use of the trialkyls of boron as catalysts for the polymerisation of negatively substituted vinyl compounds.

Compounds containing B-C bonds have been prepared by three different types of reaction, these are reactions between

1) another organo-metallic compound and a boron halide or borate ester.

2) an olefin and a boron hydride.

3) a hydrocarbon and a boron halide.

The last of these is generally used to prepare mono- or di-substituted boron halides and will be discussed later.

The first reaction is the most successful and convenient for the preparation of trialkyls and triaryls of boron either on a laboratory or large scale. The boron halides give best yields when used as their ether complexes[20] but alkyl orthoborates appear to be the most generally satisfied reagents:

$$B(OMe)_3 + 3RMgX = R_3B + 3MgXOMe$$

$$3MgXOMe + 3HCl = 1\tfrac{1}{2}MgCl_2 + 1\tfrac{1}{2}MgX_2 + 3MeOH$$

Where quaternary anions (BAr_4^-) may be formed excess of reagent must be avoided and this is particularly important when organo-lithium compounds are used as alkylating agents.

The first trialkyls were prepared by Frankland and Duppa[21] in 1859 by the action of excess dialkyl zinc (methyl and ethyl were used) on triethyl borate.

$$3R_2Zn + 2B(OC_2H_5)_3 = 2BR_3 + 3Zn(OC_2H_5)_3.$$

This reaction has not been much used since, because it is apt to become violent and the yields are not as good as those resulting from Grignard reactions. However careful control of the reaction between dimethyl zinc and boron trichloride has been used by Wiberg and Ruschmann[22] to prepare the unstable methyl boron chlorides; these products readily disproportionate to trimethylborane and boron trichloride. This disproportionation is particularly interesting since McCusker, Ashby and Makowski[23] report that the ethyl and higher dialkylboron chlorides showed no tendency to disproportionate below 170°, even after repeated distillations at atmospheric pressure.

The most satisfactory alkylating agents for the preparation of organo-boron compounds now appear to be the alkyls of aluminium[24]; no quaternary salts are formed and the fact that many of the reactions require no solvent or diluent is a particularly attractive feature for large scale preparations.

Triethylborane was obtained by distillation in 90% yield, relative to boron trifluoride, from the reaction

$$BF_3OEt_2 + Et_3ALOEt_2 \rightarrow Et_3B + EtAlF_2 + OEt_2$$

The use of amine complexes is rather better and yields of over 90% of tripropylborane are obtained when a mixture of tripropylaluminium and triethylamine-boron trifluoride is heated to 150-160°

$$Et_3N.BF_3 + Pr^n_3Al \rightarrow Pr^n_3B + Et_3N + AlF_3$$

Perhaps the most satisfactory method is the reaction between an aluminium alkyl and a borate ester, no solvent being necessary. A mixture of triethyl aluminium and ethyl orthoborate spontaneously heats to over 100° and triethylboron can be distilled off in over 90% yield:

$$B(OEt)_3 + Et_3AL = Et_3B + AL(OEt)_3$$

A useful variation of this method is the preparation of boronic esters by the use of appropriate reactant ratios:

$$Et_3AL + 3B(OBu^n)_3 = 3EtB(OBu^n)_2 + AL(OBu^n)_3.$$

Alkyl metaborates also give good yields of trialkyls of boron when allowed to react with aluminium alkyls or more conveniently in some instances alkylaluminium sesquihalides. The exothermic reaction is conveniently carried out in a mineral oil diluent.[25]

$$3Et_3AL_2Cl_3 + (MeOBO)_3 = 3Et_3B + AL(OMe)_3 + AL_2O_3 + 2ALCl_3.$$

The second general method, the addition of B-H bonds to olefins, is one of the most important developments in boron chemistry. The reaction between diborane and aliphatic olefins[26] and styrene[27] whereby organo-boron compounds are formed was reported some years ago.

The successful development of these reactions as useful laboratory methods resulted from improvements in processes for the preparation of diborane (by adding a solution of sodium borohydride in 2,5,8-trioxanonane $(CH_3OCH_2CH_2)_2O$ - also known as diethyleneglycol dimethyl ether or 'diglyme' to a solution of borontrifluoride-ether complex in the same solvent)[27a] $3NaBH_4 + 4BF_3 \rightarrow 2B_2H_6 + 3NaBF_4$

and from the discovery that the addition of diborane to olefins is strongly catalysed by ethers.

Good yields of boron trialkyls are also obtained when triethylamine-borane ($Et_3N.BH_3$) is heated with olefins at 200°.[25]

The preparation of organo-boron compounds by B-H addition to olefins does not necessarily involve the preparation of diborane. One recent method depends on the formation of diborane or some other active B-H compound from sodium borohydride and a little aluminium chloride and its use on situ. For example, tri-n-pentylboron has been prepared by adding 1-pentene (0.5 mole) to a stirred solution of sodium borohydride (0.25 mole) and aluminium chloride (0.084 mole) in diglyme (250 c.c.). When stirring had been continued three hours at room temperature and one hour on a steam bath, solvent was pumped from the cooled reaction mixture, and tri-n-pentylborane collected on 88% yield at 94-95°/2 mm.[27b] More recent work has shown the reaction to work equally well using more easily obtainable ethers (diethyl ether, tetrahydrofuran, and triglyme) different hydride sources and several other Lewis acids.[28a]

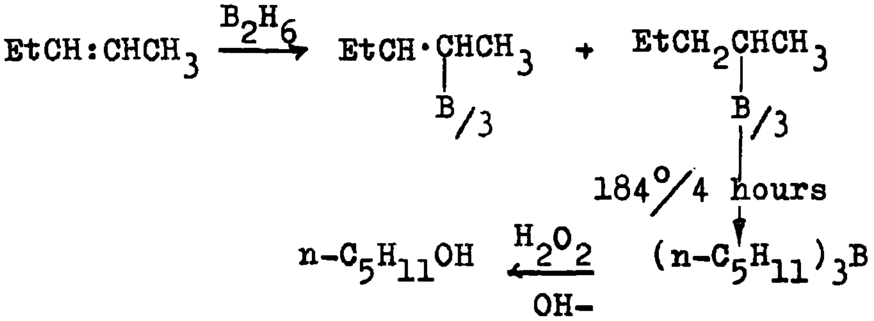
The addition of B-H bonds to terminal olefins is faster than addition to non terminal olefins, and treatment of a mixture of 1- and 2-pentene with a deficiency of diborane results in the selective conversion of the terminal olefin into tri-n-pentylborane. The addition of diborane to 2-pentene gives a mixture of products, since oxidation of the resulting trialkylborane yields a roughly 2:1 mixture of 2-

and 3-pentanol:[28b]

$$Pr^n\ CH{:}CH_2 \xrightarrow{B_2H_6} (C_5H_{11})_3\ B \xrightarrow[OH-]{H_2O_2} 95\%\ n\text{-}C_5H_{11}OH$$

$$EtCH{:}CHCH_3 \xrightarrow{B_2H_6} (C_5H_{11})_3\ B \xrightarrow[OH-]{H_2O_2} 63\%\ Pr^n\ CHOHCH_3 + 37\%\ Et_2CHOH$$

Various attempts at the preparation of mixed trialkylboranes RR^1_2B, have shown that these compounds tend to disproportionate and, more particularly, to isomerise in the sense that compounds are favoured in which chain branching is absent or relatively remote from the boron atom. If the mixed alkylboranes resulting from the reaction of diborane with 2-pentene are boiled in 'diglyme' for four hours, they are converted into tri-n-pentyl boron since oxidation with alkaline hydrogen peroxide affords 1-pentanol:



$$EtCH{:}CHCH_3 \xrightarrow{B_2H_6} EtCH\cdot\underset{B/3}{\underset{|}{C}}HCH_3 + EtCH_2\underset{B/3}{\underset{|}{C}}HCH_3 \xrightarrow{184^\circ/4\ hours} (n\text{-}C_5H_{11})_3B \xrightarrow[OH-]{H_2O_2} n\text{-}C_5H_{11}OH$$

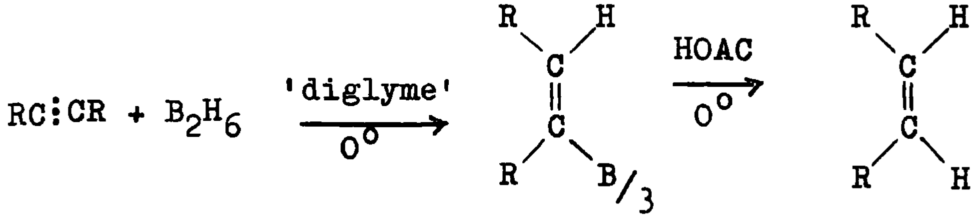
Not only does this reaction provide a method for obtaining primary alcohols from non-terminal olefins, but its scope has been extended by the discovery that the reaction is reversible. A trialkylborane whose alkyl chains are three or more carbon atoms long reversibly dissociates when heated:

$$2(RCH_2CH_2)_3B \rightleftharpoons (RCH_2CH_2)_2BH\cdot BH(CH_2CH_2R)_2 + 2CH_2{:}CHR$$

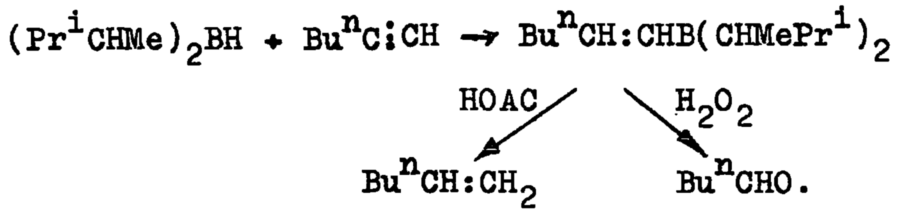
Consequently addition of a less volatile longer chain olefin will displace a more volatile shorter chain olefin.[24,28] (Di-sec-butyl) t-butyl-borane has been prepared by McCusker, Hennion and Rutkowski and was found to be stable to disproportionation or re-arrangement below 60°.[29]

An important distinction between alkylboron and alkylaluminium compounds is that the former react with both terminal and non-terminal olefins (containing $C{:}CH_2$ group). The addition of olefins to trialkylboranes is catalysed by small amounts of trialkylaluminium.[30]

Both boron[31] and aluminium[32] hydrides react with acetylenes by cis addition, and this provides an important route to cis olefins



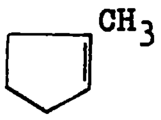
This reaction which has been called the hydroboration reaction, is not satisfactory when applied to terminal acetylenes since complete reduction occurs by addition of two B-H bonds. This difficulty has been overcome by the use of a less reactive B-H compound $(\mathrm{Pr^iCH\ Me})_2$ BH, itself prepared from diborane and 2-methyl-2-butene:

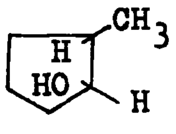


$$(\mathrm{Pr^iCHMe})_2\mathrm{BH} + \mathrm{Bu^nC{:}CH} \rightarrow \mathrm{Bu^nCH{:}CHB(CHMePr^i)_2}$$

$$\mathrm{Bu^nCH{:}CHB(CHMePr^i)_2} \xrightarrow{\mathrm{HOAC}} \mathrm{Bu^nCH{:}CH_2} \qquad \mathrm{Bu^nCH{:}CHB(CHMePr^i)_2} \xrightarrow{\mathrm{H_2O_2}} \mathrm{Bu^nCHO}.$$

The hydroboration of cyclic olefins results in stereospecific cis hydration. For example if diborane is passed into a solution of 1-methylcyclopentene in tetrahydrofaran for two hours at 0° and the reaction mixture hydrolysed and oxidised with alkaline hydrogen peroxide, trans-2-methylcyclopentanol is obtained in 85% yield with only about 2% cis impurity.[33]





The Long and Dollimore[20] modified Grignard method has proved the most successful in preparing the triarylboranes. All of them are air sensitive (requiring work under nitrogen) and this, coupled with their relatively low volatility, can make their separation from reaction mixtures difficult.

$$3C_6H_5MgBr + BF_3.O(C_2H_5)_2 \rightarrow (C_6H_5)_3B + 1\cdot5MgF_2 + 1\cdot5MgBr_2 + (C_2H_5)_2O.$$

Further reaction can occur with excess Grignard to give tetraphenylborate anions.

$$(C_6H_5)_3B + C_6H_5MgBr \rightarrow MgBr^+ \quad B(C_6H_5)_4^{\ -}.$$

This property has proved useful in preparing small amounts of pure triphenylborane. After hydrolysis and removal of magnesium as carbonate, trimethylamine hydrochloride is added to the solution containing tetraphenylborate ions when $(CH_3)_3\overset{+}{N}H \ B(C_6H_5)_4^{\ -}$ is precipitated and this decomposes when heated in a stream of nitrogen at 200°.

$$(CH_3)_3\overset{+}{N}H \quad B(C_6H_5)_4^{\ -} \rightarrow (CH_3)_3N + C_6H_6 + (C_6H_5)_3B$$

The triphenylborane is distilled in vacuum after the benzene and trimethylamine have been swept away: the yield (from tetraphenylborate) is about 90%.

A new method for the preparation of triphenylborane makes use of the reaction between benzene (present in excess) and diethylborane $Et_4 B_2 H_2$ at 180° under pressure.[34]

II. PROPERTIES

(a) PHYSICAL

Molecular weight measurements[35] (cryoscopic in benzene) of several triarylboranes have shown them to be monomeric. Stock and Zeidler[36] showed the methyl and ethyl homologues to be monomeric (vapour density) and Bamford, Levi and Newitt[37] arrived at similar conclusions (methyl, *iso*-propyl, n-propyl) by evaluation of Trouton's constant. The force constants of trimethylborane calculated by Goubeau[38] from Raman and ultra-violet spectra would suggest that resonance of the type found in the boron halides was unlikely, *i.e.* the B-C bonds are essentially single.

(b) CHEMICAL

Generally hydrolytically stable in acid, alkaline, or neutral solution, the trialkylboranes are quite stable except in the presence of oxidising agents, (thus they require an inert atmosphere for their manipulation).

Trimethylborane, though stable to water under ordinary conditions, is slowly (7 hours) hydrolysed at 180° with loss of one methyl group. Still more resistant to hydrogen sulphide it reacts at 280° giving boron sulphide,[39]

$$B_2S_3 + CH_4 \xleftarrow{280^{\circ}} H_2S + Me_3B + H_2O \xrightarrow{180^{\circ}} Me_2BOH + CH_4$$

Triallylborane is most unusual in its ease of hydrolysis and reaction with butanol;[40]

$$(CH_2{:}CH\ CH_2)_3B + H_2O \rightarrow (CH_2{:}CH\ CH_2)B(OH)_2$$

$$(CH_2{:}CH\ CH_2)_3B + Bu^nOH \rightarrow CH_2{:}CH\ CH_2B(OBu^n)_2$$

Triarylboranes are not sensitive to water but triphenylborane reacts with alcohol to give ethyl diphenylborate.

$$(C_6H_5)_3B + EtOH \rightarrow (C_6H_5)_2BOEt + C_6H_6.$$

The chemical reactivity of the trialkyl- and triarylboranes may be accounted for by their very powerful Lewis-acid properties and so as highly reactive electrophiles many of their reactions, at least in the initial stages, probably involve coordination.

(i) OXIDATION

The lower trialkylboranes are spontaneously inflammable, but their pyrophoric character decreases as the size of the hydrocarbon group increases. The triarylboranes are much less easily oxidised, tri-α-naphthylborane being stable in air but this is probably due to slowness of attack by oxygen on account of steric hindrance.

Controlled oxidation[41] of the lower trialkylboranes leads to the formation of esters of alkyl borinic acids, e.g.

$$2\ Bu^n{}_3\ B + O_2 \rightarrow 2\ Bu^n{}_2\ BOBu^n$$

That the primary (or at least an early) step in the reaction is the formation of a peroxide has been confirmed in the case of trimethylborane[42]. At pressures below the explosion limit Me_2BOOMe is obtained; this explosive substance is reduced to methyl dimethylborinate by sodium iodide at -78°C. In a sealed tube at room temperature it rearranges to give about 90% dimethyl methylboronate. $MeB(OMe)_2$.

The oxidation of organo-boron compounds with alkaline (or alcoholic alkaline) hydrogen peroxide smoothly breaks the B-C bonds, with quantitative formation of an alcohol and a boric acid. This is a general reaction of analytical importance.

(ii) REACTIONS WITH HALOGENS AND HYDROGEN HALIDES

The lower trialkyls of boron inflame in chlorine or bromine, but tripropylborane reacts smoothly with iodine at about 150°, giving iododipropylborane:

$$Pr^n_3B + I_2 \rightarrow Pr^n_2BI + Pr^nI$$

The corresponding chloride and bromide have been obtained by the action of antimony trichloride (or $SbBr_3$) on the iodide.[43]

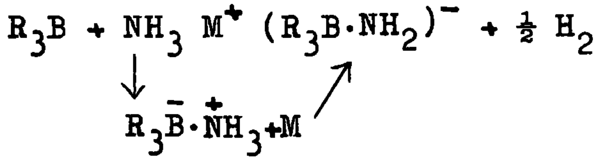
When hydrogen chloride is bubbled into tributylborane at 110° dibutylboron chloride (b.p. 173°) is formed almost quantitatively[44].

$$Bu^n_3B + HCl \rightarrow Bu^n_2\ BCl + C_4H_{10}$$

Further reaction with hydrogen chloride takes place between 180° and 210°, but mixtures of products result.

(iii) REACTIONS WITH ALKALI METALS AND THEIR HYDRIDES

Trialkylboranes react with alkali metals or their amides in liquid ammonia (essentially ammonia coordination compounds are formed):-



$$\begin{tikzcd}[column sep=small] R_3B + NH_3 \arrow[d] & M^{+} (R_3B\cdot NH_2)^{-} + \tfrac{1}{2} H_2 \\ R_3\overset{-}{B}\cdot\overset{+}{N}H_3 + M \arrow[ur] & \end{tikzcd}$$

$$2_3\overset{-}{B}\cdot\overset{+}{N}H_3 + NaNH_2 \rightarrow Na^{+}(R_3BNH_2)^{-} + NH_3$$

These salts can be crystallised from ether, but are only slightly soluble in benzene and are insoluble in light petroleum. Similar compounds are formed in ethylamine solution,[45] e.g.

$$Me_3B\cdot NH_2Et + Li \rightarrow Li^{+} (Me_3B\cdot NHEt)^{-} + \tfrac{1}{2}H_2$$

In the absence of ammonia, tri-n-butylborane in ether solution very slowly develops a colour on standing in contact with liquid sodium/potassium alloy, but no compound has been isolated. In contrast the triarylboranes form well defined adducts with alkali metals.

Although steric effects largely offset the enhanced acceptor properties of the more electronegative aryl groups, strong acceptor properties are still evidenced in their reactions with the alkali metals

$$Ar_3B + Na \rightarrow Ar_3\dot{B}^{\mp} Na^{+}$$

The resulting compounds[46] which are prepared in ether solution with rigorous exclusion of moisture, oxygen and even carbon dioxide, are necessarily radicals (if monomeric). The triphenylborane anion-radical is isoelectronic with the triphenylmethyl neutral radical, and in fact the colours of the two series are similar.

Triphenylborane-sodium reacts with triphenylmethyl with the formation of the triphenylmethyl anion:

$$Ph_3B^{\bullet -}Na^+ + Ph_3C^{\bullet} \rightarrow Ph_3B + Ph_3C^-Na^+.$$

A brilliant red compound results from triphenylmethyl and triphenylborane; this may well be a radical of constitution $(Ph_3B{-}CPh_3)^{\bullet}$. There is some evidence[47] that triphenylborane-sodium is dimeric ($Ph_3B{\cdot}BPh_3{}^{=}\ Na_2{}^{++}$) since it is diamagnetic.

The conductance of these compounds in ether solution is very small, indicating extensive ion-association.

Tri-α-naphthylborane can add successively one atom of sodium to give the brown-yellow compound $(C_{10}H_7)_3B^{\bullet -}Na^+$ (or its dimer) and then a second to give the deep violet $(C_{10}H_7)_3\ B^{=}Na_2{}^{++}$.[48]

Studies on the molecular weights of solutions of the addition compounds, and on their magnetic susceptibilities, have shown a marked dependence of the position of the monomer-dimer equilibria on (a) the aromatic groups bonded to boron, and (b) the solvent.[49] The tendency to form monomeric anions (which, however, exist as ion-pairs) increases with the degree of steric hindrance about the boron, in the order:

phenyl $<$ 1-naphthyl $<$ 2-naphthyl $<$ mesityl

The effect of tetrahydrofaran in dissolving sodium-tri-1-naphthylborane as the green monomeric form, in contrast to diethyl ether dissolving it as the orange dimeric form has been attributed to the stronger donor character of tetrahydrofaran resulting in a B-O covalent bond

$$(1\text{-}C_{10}H_7)_3^{-\bullet}B^{-}-\overset{+}{O}(CH_2)_4\} \quad Na^{+}.$$

The triarylborane-alkali metals compounds are very reactive; iodine in ether is immediately decolorised

$$2\ Ph_3\overset{\bullet -}{B}\ Na^{+} + I_2 = 2\ Ph_3B + 2NaI$$

The reaction with methanol gives a boron hydride derivative:[50]

$$2Ph_3\dot{B}^{-}Na^{+} + MeOH = Na^{+}\left[Ph_3B\cdot OMe\right]^{-} + Na^{+}\left[Ph_3BH\right]^{-}$$

Trimethylborane reacts with lithium aluminium hydride at room temperature (24 hours) to form dimethyl aluminium hydride[51]

$$LiAlH_4 + Me_3B \rightarrow LiBH_3Me + Me_2AlH$$

Recently Wiley and co-workers[52] have shown triethylborane to form an addition compound with sodium hydride.

Sodium (or lithium) triphenylborohydride can be obtained by the direct addition (in ether) of triphenylborane to sodium or lithium hydride, though a better method[53,54] is to add, say, LiH to Ph_3B and heat at 180° until the melt solidifies. They are moderately readily hydrolysed by water, but vigorously evolve hydrogen with acids,

$$Na^+[Ph_3BH]^- + H_3O^+ = Na^+ + Ph_3B + H_2 + H_2O.$$

(iv) REDUCING PROPERTIES

The following examples of reactions with alcohols, aldehydes, ketones and carboxylic acids show the reducing properties of the trialkylboranes.

$$B(C_2H_5)_3 + RCHO \rightarrow (C_2H_5)_2\,BOCH_2\,R + C_2H_4$$

$$B(C_2H_5)_3 + RCH_2OH \rightarrow (C_2H_5)_2\,BOCH_2\,R + C_2H_6$$

$$B(C_2H_5)_3 + RCOOH \rightarrow (C_2H_5)_2\,BOOCR + C_2H_6$$

Using these reactions, Meerwein, Hinz, Majart and Sonke[55] prepared boronous esters and also dialkylboronites.

Triarylboranes react with alcohols to form borinic esters.

$$(C_6H_5)_3\ B + C_2H_5OH \rightarrow (C_6H_5)_2\ BOC_2H_5 + C_6H_6$$

(v) REACTIONS WITH ALKALIS

Triarylboranes react with alkalis to form complexes containing four- covalent boron. A compound which crystallised with water or alcohol was obtained by D. L. Fowler and C. A. Kraus[56] from triphenylborane with tetramethyl ammonium hydroxide in alcoholic solution.

$$Ph_3B + (CH_3)_4\ \overset{+}{N}OH \rightarrow (CH_3)_4\ \overset{+}{N}\ \left[Ph_3BOH\right]$$

Fusion of triphenylborane with alkali-metal hydroxide gives the sodium salt $Na^+\left[Ph_3BOH\right]^-$ which crystallises with solvent of crystallisation from ether. Although soluble in water the salt hydrolyses and acetic acid causes immediate precipitation of triphenylborane. A similar compound, $Na^+\left[Ph_3BCN\right]^-$, prepared by G. Wittig and P. Raff,[57] is more stable to acids and is neutral in aqueous solution. The lithium, sodium, potassium and ammonium salts are soluble in water, the rubidium salt is slightly soluble and the ceasium salt is insoluble. 1:1 Complexes between triphenylborane and sodamide and tetra-n-butyl ammonium hydroxide were confirmed by C. A. Kraus and W. W. Hawes.[58] In the former case, the electrical conductivity and the dissociation constant were measured, and in the latter the polarisation curve. Tri-α-naphthylborane was accurately titrated in alcoholic solution of sodium methoxide, ethoxide, or isopropoxide, using phenolphthalein as indicator.

$$(C_{10}H_7)_3B + Na^+OCH_3^- \rightarrow Na^+\left[(C_{10}H_7)_3BOCH_3 \right]^-$$ [59]

(vi) <u>AMINE COMPLEXES</u>

The volatile trialkylboranes, being Lewis acids, are strongly electrophilic and this property makes them useful in the study of the electronic and steric effects influencing coordination compounds. The most extensively studied compounds are the 1:1 complexes between ammonia or amines and the trialkylboranes (and the triarylboranes). These are prepared by interaction at low temperatures in equimolar proportions or excess base, the excess being pumped off under vacuum. In cases where complex formation has failed steric hindrance has generally been the cause.

Trimethylborane can conveniently be stored and also purified using its solid complex with trimethylamine $(CH_3)_3 B{\cdot}N (CH_3)_3$.

Pure trimethylborane is regenerated with hydrogen chloride after resublimation

$$(CH_3)_3 B{\cdot}N (CH_3)_3 + HCl \rightarrow (CH_3)_3B + (CH_3)_3 NHCl$$

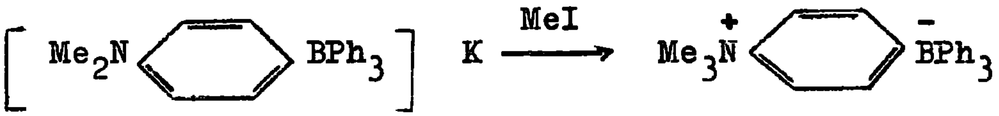
Triethylborane has also been purified by its amine complex by the same workers, H. C. Brown and R. B. Johannesen.[60] Triarylboranes like trialkylboranes do not coordinate to ethers or other oxygen donors but form a number of 1:1 complexes with ammonia and amines. So great is the steric strain in these coordination compounds that ammonia the least sterically hindered donor forms the most stable compounds. With tri-α-naphthylboron, which can exist in two isomeric forms (rotation about B-C bonds) the order of donor strength of the methylamines is $NH_3 > CH_3NH_2 > (CH_3)_2 NH > (CH_3)_3 N$, ammonia forms a stable compound yet trimethylamine does not combine.

(vii) COMPLEXES WITH ORGANO-METALLIC COMPOUNDS

Trimethylborane reacts with ethyl-lithium in benzene solution to form a crystalline compound $LiB(CH_3)_3C_2H_5$, which would normally be regarded as a salt $Li^+ B(CH_3)_3C_2H_5{}^-$

hence its solubility in benzene, a suitable solvent for crystallisation is remarkable. H. I. Schlesinger and H. C. Brown[61] reported that the compound dissolves in water to give a clear solution but within a few seconds a gas is evolved. A similar compound $LiB(CH_3)_4$ was prepared from methyl-lithium and trimethylborane by D. T. Hurd.[62] Lithium tetraphenylborate formed by the reaction of phenyl-lithium with an ether solution of triphenylboron was prepared by G. Wittig, C. Keicher, A. Ruckërt and P. Raff.[63] The salt, more stable than the alkyl salts, is stable to water and is decomposed by acids only at 80° or more. It crystallises from ether as $Li(BPh_4)8Et_2O$, the ether being lost in high vacuum. The sodium salt is best prepared by adding excess sodium chloride to the product of the reaction between boron trifluoride and excess phenyl magnesium bromide (after precipitation of magnesium as carbonate). It is now a valuable analytical reagent particularly for potassium, rubidium, and caesium as the salts of these cations are practically insoluble in water. Several other cations form tetraphenylborates whose insolubility renders them suitable for gravimetric analysis, e.g. $\left[Ph_4P\right]\left[BPh_4\right]$ $\left[C\overset{o}{0}(CO_4)H\right]\left[BPh_4\right]$.

Mixed complexes are well established; the compound $Li[Ph\ C\equiv CB(Ph)_3]$ was prepared by G. Wittig and P. Raff[64] who warmed triphenylborane and lithium phenylacetylide and then cooled to -80°C. The complex generates phenylacetylene with acids and with aqueous iodine gave phenylethinyl iodide. Triphenylborane and p-dimethylaminophenyllithium afforded a complex from which G. Wittig and W. Herwig[65] isolated an interesting "zwitterion" m.p. 337°-339° after conversion to the potassium salt and heating with methyl iodide in acetone.



Prolonged heating of the complexes in aqueous cellosolve resulted in decomposition. G. A. Razuvaev and T. G. Brilkina[66] found that benzene, phenol and diphenylborinic acid were obtained from sodium or potassium tetraphenylboronates. Mixed complexes also reacted.

$$K\left[BPh_4\right] \rightarrow C_6H_6 + C_6H_5OH + Ph_2BOH$$

$$NH_4\left[\alpha\text{-}C_{10}H_7BPh_3\right] \rightarrow C_{10}H_8 + BPh_3NH_3$$

$$K\left[PhB(\alpha\text{-}C_{10}H_7)_3\right] \rightarrow 3C_{10}H_8 + PhB(OH)_2.$$

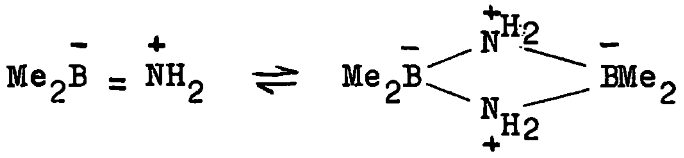
Mixed aralkyl complexes were recently obtained from alkyllithium (methyl, ethyl) compounds and triarylboranes (phenyl, α-naphthyl). Lithium methyltriborane decomposed on exposure to air and fresh aqueous solutions gave no visible evidence of reactions with potassium or ammonium salts; prolonged standing, however, caused precipitation of ammonium tetraphenylborane.

(viii) INTERNAL COORDINATION COMPOUNDS

When trivalent boron is bonded to an atom of donor character by trigonal Sp^2 bonds it is possible for the covalency of the boron to increase from three to four by internal coordination. Thus, for example in aminodimethyl borane the boron atom assumes a similar electronic configuration to that of the carbon atoms in ethylene.

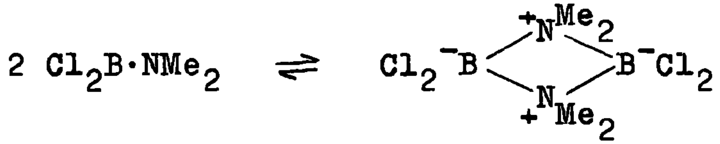
$$Me_2B\text{-}NH_2 \rightarrow Me_2\overset{-}{B} = \overset{+}{N}H_2$$

Coordination saturation can also be achieved by association, usually dimerisation, and J. Goubeau and R. Link[67] have obtained the above compound in two different forms a monomeric gas (b.p. 1^{o}) and colourless crystals (m.p. 9^{o}).



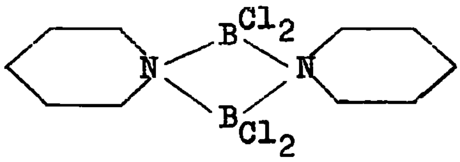
a reversible equilibrium is observed in the gas phase at room temperature. The nature of the atoms or groups attached to the boron or nitrogen determine which form of coordination saturation occurs. When relatively electropositive groups are bound to boron double bonding is favoured, e.g. Me_2BNMe_2 is monomeric[68,69] and the B-N force constant (from its Raman spectrum[70]) indicates a $B = N$ double bond. Similarly trisdimethylaminoboron, $(Me_2N)_3B$,[71] methoxy dimethylboron (Me_2BOMe)[69,72] and methyl borate $(MeO)_3B$ are all monomeric. The degree of coordinative saturation is naturally greatest in the trioxy- or amino- compounds, and this is reflected in a considerable dimunition of reactivity.

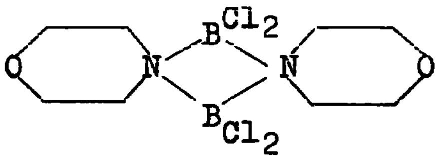
In compounds like $Cl_2B\text{-}NMe_2$[71] coordinative saturation is achieved by dimerisation. Double bonding ($B = N$) is evidently much weakened by the B-Cl, and this substance can be obtained in two forms; the very <u>reactive liquid monomer</u> slowly changes into a remarkable, <u>unreactive solid dimer</u>. The dimer stable to hot acids, is converted back to the monomer on vaporisation. The monomer is violently hydrolysed by cold water



Reactions between boron trichloride (or BBr_3) and secondary amines with relatively bulky alkyl or cycloalkyl groups give aminoboron halides which remain monomeric, e.g. $\mathrm{Pr}^{n}_{2}\mathrm{NBCl}_2$, $\mathrm{Bu}^{n}_{2}\mathrm{NBCl}_2$.

In contrast, piperidino- and morpholino- boron dichloride gradually form dimers:[73]

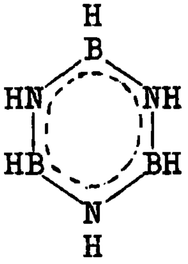




The Borazines, another series of cyclic internal coordination compounds, have been the subject of a recent review.[74] Since the preparation of the parent compound borazine, $B_3N_3H_6$, b.p.53° by A. Stock[75] in 1926 the chemistry of this class of compounds has been greatly extended. The compound was originally obtained by the thermal decomposition of the diborane-diammonia complex

$B_2H_6.2NH_3$ (now formulated as $NH_3^+ \cdot BH_2^- \cdot NH_3^+ BH_4^-$).

The planar essentially aromatic structure of borazine has been confirmed by various electron diffraction and spectroscopic studies.[76] The main distinction from the usual aromatic ring is the alternating electron density resulting from the different electronegativities of the boron and nitrogen atoms. Though borazine itself slowly decomposes at room temperature, many of its derivatives with aryl or alkyl groups substituted for hydrogen (either on the boron or nitrogen atoms) are stable when kept at room temperature and some derivatives have been studied as part of research programmes aimed at materials resistant to high temperatures.



Several new methods have been devised for the preparation of borazine, one of which is the reaction[77]

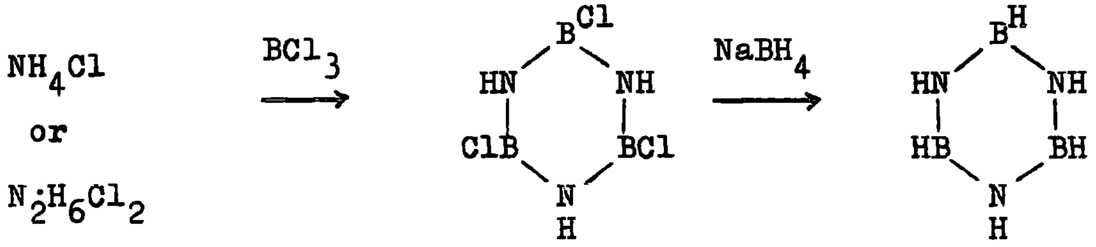
$$3\ LiBH_4 + 3\ NH_4Cl = (NH \cdot BH)_3 + 9\ H_2 + 3\ LiCl.$$

Reaction of lithium borohydride with methylammonium chloride similarly affords N-trimethylborazine:

$$3\ LiBH_4 + 3\ MeNH_3Cl = (MeN \cdot BH)_3 + 9\ H_2 + 3\ LiCl$$

Another method for the preparation of borazine is the reduction of B-trichloroborazine with sodium borohydride in triethylene glycol dimethyl ether (2,3,8,11-tetraoxadecane).[78]

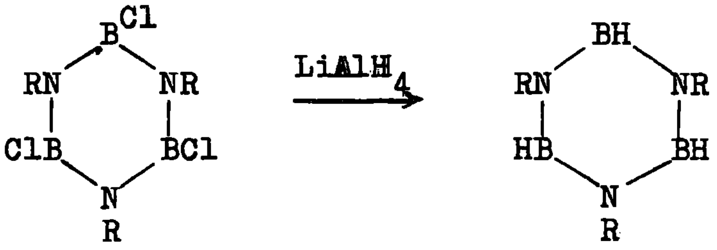
B-trichloroborazine is now relatively easily prepared from ammonium chloride and boron trichloride mixed with pumice soaked in cobalt nitrate solution, dried and reduced.[79]



B-trialkyborazines are best prepared by the pyrolysis of trialkylborane-ammine complexes:[80]

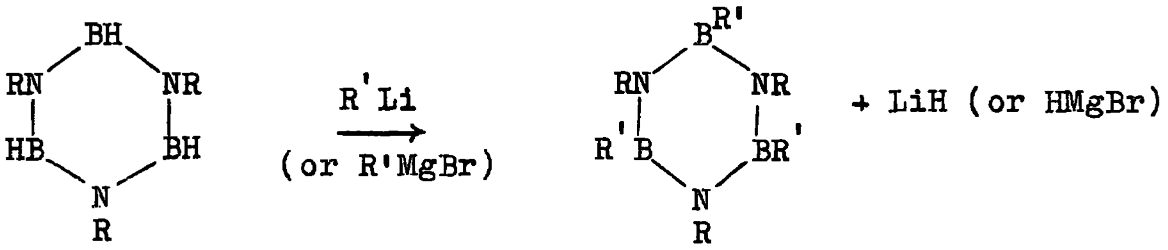
$$Me_3B{\cdot}NH_3 \xrightarrow[20atm.]{330^{o}} (MeB{\cdot}NH)_3 + CH_4$$

N-substituted borazines already mentioned above can also be obtained by the reduction of the B-trichloro-N-trialkyl (or aryl) borazines with lithium aluminium hydride.[81]



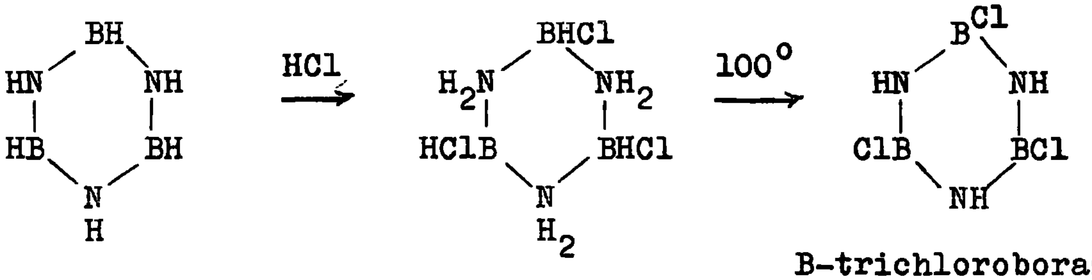
Since the B-trichloro-N-substituted borazines are fairly readily accessible from boron trichloride and the appropriate amine hydrochloride B-N substituted borazines are also readily prepared from the B-trichloro compounds and Grignard or organo lithium reagents,[82] or by Friedel-Craft arylation.[83]

A somewhat remarkable development has been the preparation B-N substituted borazines by the action of Grignard and organo-lithium reagents, not on BCl compounds but on the B-H compounds.[81]



It is possible to prepare borazines with one, two, or all three B-H groups substituted.

Borazines are much more chemically reactive than analogous benzene compounds. Borazine itself adds water, methanol, alkyl iodides and hydrogen halides, the negative parts of these reagents becoming attached to boron.



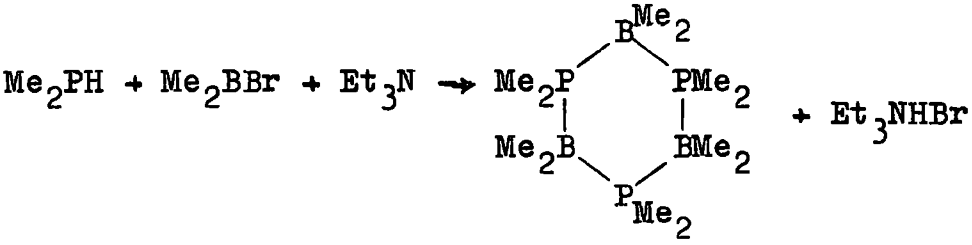
B-trichloroborazine.

The hydrolytic sensitivity is considerably affected by the substituents e.g. B-tripheny-N-trimethylborazine is relatively easily hydrolysed whilst B-trimethyl-N-triphenyl borazine is resistant.

The highly substituted borazines, e.g. hexamethylborazine m.p.99, b.p.221°, are generally substances of fairly high thermal stability.

Rapidly developing is the chemistry of a series of internal cyclic coordination compounds in which each boron atom is bonded to two phosphorus (or arsenic) atoms or *vice versa*. These compounds are generally thermally stable and resistant to chemical attack and these properties have directed attention to the possible development of *linear* polymers of these general types.

Reaction between dimethylphosphine and bromodimethylborane in the presence of 1 mol. triethylamine gives the fully methylated phosphinoborane:



This compound m.p. 333-334°, is resistant to acid hydrolysis below 300°. In contrast, H_2PBMe_2 is rather unstable, but Me_2PBH_2 from $Me_2PH \cdot BH_3$ at 150°, forms exceptionally stable cyclic trimers and tetramers.[84]

Dimethylphosphinoborane polymers $(Me_2PH \cdot BH_2)_n$ have been obtained with n about 80 by the pyrolysis of $Me_2PH \cdot BH_3$ in the presence of an amine (e.g. triethylamine) as a chain end blocking group. These polymers melt at ca., 170° but at this temperature sometimes rearrange to form the thermodynamically more stable cyclic trimers and tetramers.[85]

The only arsenic analogues so far described,[86] $(Me_2AsBH_2)_3$, m.p. 49.7 - 50.6°, and $(Me_2AsBH_2)_4$ m.p. 149.5 - 150.5°, are decidedly less stable both thermally and to hydrolysis. The sulphur compound,[87] $MeSBMe_2$, from MeSH and $Me_4B_2H_2$, is monomeric and easily hydrolysed (c.f. Me_2BOMe).

Several phosphinoboranes have recently been prepared by two general methods,[88, 89] by reduction of dialkyl (or diaryl) chlorophosphines or oxychlorides in ethylene glycol dimethyl ether or 'diglyme' with sodium borohydride

e.g. $$Ph_2PCl + NaBH_4 \rightarrow (Ph_2PBH_2)_3$$

$$Me_2POCl + NaBH_4 \rightarrow (Me_2PBH_2)_2$$

$(PhHP \cdot BH_2)_3$ and $(Et_2PBH_2)_3$ have also been mentioned.

C) MIXED TRIALKYL AND ARYL-ALKYLBORANES

Di-isobutyl-t-butylborane has been prepared from di-isobutylfluoroborane (Bu^i_2BF) and t-butylmagnesium bromide and by four other methods.[90] As already mentioned it may be distilled without disproportionation or rearrangement provided the boiling point does not exceed 60°, otherwise Bu^i_3B is formed. It seems that not more than two t-butyl groups may be attached to the same boron atom, and then only when the remaining group is unbranched. n-Butyl-di-t-butylborane, b.p. 47·7°/1·7 mm and n-pentyl-di-t-butylborane, b.p. 42·5 - 42·7°/0 5 mm., have been prepared, the first from boron trifluoride and t-butylmagnesium chloride in ether containing a large excess of 1-butene; both compounds rearrange rapidly when heated, $(n\text{-}C_5H_{11})Bu^t_2B$ giving a 2:1 mixture of Bu^i_3B and $(n\text{-}C_5H_{11})_3B$.[91]

It has also been possible to prepare n-amyl-isobutyl-t-butylborane, b.p. 43·5 - 44°/0·5 mm., with three different alkyl groups; it gave the correct alcohols in equal amounts when oxidised with alkaline hydrogen peroxide.[92]

Mikhailov and Shchegoleva[93] have prepared mixed trialkylboranes by the addition of organo-lithium compounds in ether to n-butyl-di-n-butylboronite in the same solvent at -70°C, e.g.

$$Pr^{n}Li + (Bu^{n})_{2}BOBu^{n} \longrightarrow Bu^{n}_{2}BPr^{n} \text{ b.p. } 76\text{-}80^{\circ}/9 \text{ mm.}$$

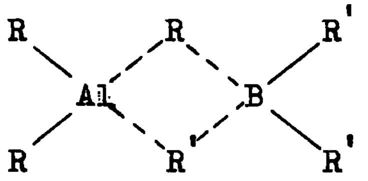
The discovery that the coordination complex t-butylborane-trimethylamine reacts unusually rapidly with olefins at 50-60° has provided an improved route to t-butyldialkylboranes[94]

$$Bu^{t}BH_{2}NMe_{3} + 2CH_{2}\!:\!CHEt = Bu^{t}Bu^{n}_{2}B + NMe_{3}$$

The exchange of radicals

$$R_{3}B + R'_{3}B \rightleftharpoons R_{2}R'B + RR'_{2}B$$

does not take place at an appreciable rate below 100°, unless R is α-branched (e.g. Pr^{i}, Bu^{s}). The exchange is, however, strongly catalysed by traces of trialkylaluminium through the formation of bridged intermediates:[95]

$R'_{3}B + R_{3}Al \rightleftharpoons$  $\rightleftharpoons R_{2}R'Al + RR'_{2}B.$

Dimethylbromoborane[96] reacts with vinyl sodium and propenyllithium to form two mixed trialkylboranes which readily disproportionate e.g.

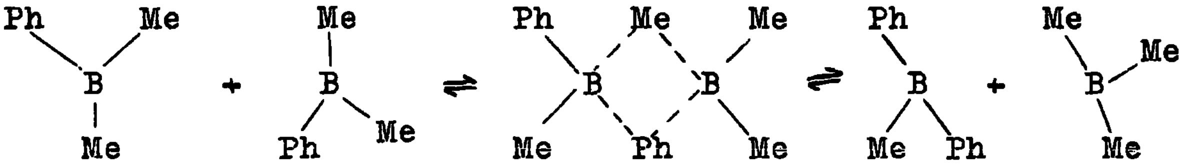
$$2\ Me_2B\ CH{:}CHR \rightarrow Me_3B + MeB(CH{:}CHR)_2$$

Mixed triarylboranes have only recently been prepared. Disproportionation is suppressed by working with amine (usually pyridine) complexes but once prepared the mixed arylboranes are relatively stable to disproportionation. There is evidence that organo-lithium, Grignard reagents and other electron dificient compounds catalyse this kind of disproportionation, so the essential point would appear to be coordinative saturation of the boron during the preparative stages involving such reagents. p-Tolyllithium and the pyridine complex Bu^iOBPh_2py yields $p\text{-}CH_3C_6H_4BPh_2py$ m.p. 156-158°. The pyridine can be removed by the action of aqueous acid, ethereal hydrogen chloride, or picric acid in benzene. These methods have yielded the mixed aryls $p\text{-}CH_3C_6H_4BPh_2$, b.p. 170-173°/3 mm., $(1\text{-}C_{10}H_7)_2BPh$, m.p. 146-148°, b.p. 230-240°/2 mm., and $(1\text{-}C_{10}H_7)_2BC_6H_4OCH_3$, b.p. 197-199°/0·08 mm.,[97]

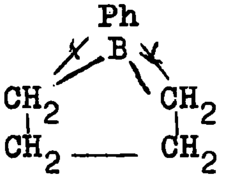
Torsell[98] obtained $O\text{-}CH_3C_6H_4BPh_2$ b.p. 167-9°/3 mm., and $(O\text{-}CH_3C_6H_4)_2BPh$ from diphenylchloroborane and phenyldifluoroborane respectively with the correct proportions of o-tolylmagnesium bromide.

CYCLIC-BORANES

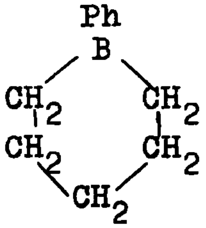
Attempts to prepare aralkylboranes such as $PhBMe_2$ have given only disproportionation products, in this case $Ph_3B + Me_3B$. This ready disproportionation has been ascribed to the formation of relatively low energy bridged dimers similar to those formed by aluminium alkyls:



Alicyclic boranes should therefore be stable to disproportionation and this was confirmed by the preparation of (a) and (b) from phenyldifluoroborane and 1,4-dilithiobutane and 1,5-dilithiopentane:[99]



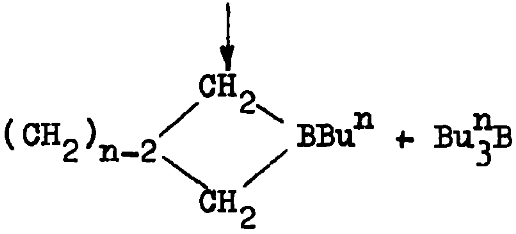
(a)



(b)

Butyl analogues were unexpectedly obtained in attempts to prepare $Bu^n_2B(CH_2)_nB\ Bu^n_2$ ($n = 4$ or 5) from di-n-butylchloroborane and tetramethylene - (and pentamethylene-) dimagnesium bromide:[100]

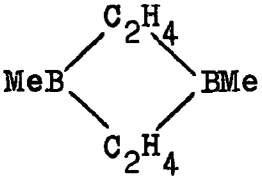
$$2Bu^n_2BCl + BrMg(CH_2)_nMgBr \rightarrow Bu^n_2B(CH_2)_nBBu^n_2 + 2MgBrCl$$

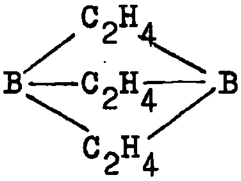


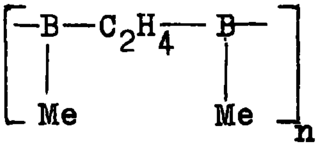
Diboron tetrachloride and ethylene form the compound $Cl_2B\ CH_2\ CH_2BCl_2$, which adds two moles of triethylamine,[101] and whose structure has been confirmed by x-ray diffraction.[102] The chlorine atoms in this have been replaced by methoxy (by methanol) or by methyl.

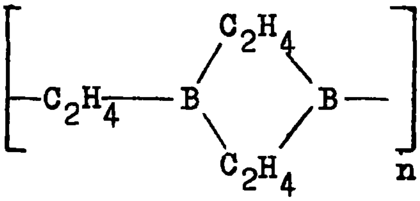
$$Cl_2BCH_2CH_2BCl_2 + 2Me_2Zn \rightarrow Me_2BCH_2CH_2BMe_2 + 2ZnCl_2$$

Slow pyrolysis of $Me_2BCH_2CH_2BMe_2$ at 100° results in the formation of much trimethylborane and of various volatile and polymeric products to which the following structures were assigned:[103]

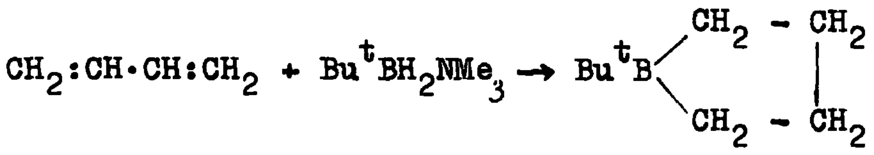








The reaction, already mentioned,[94] between t-butylborane-trimethylamine and olefins provides a neat method of preparing cyclic boranes:



(60%).

These compounds appear to deserve further study.

BORONIC ACIDS AND ESTERS

1. PREPARATION

Until very recently the main use of the esters was as precursors to the acids and so attention will be concentrated on the acids, special methods for the esters being mentioned in a final sub-section.

The more important methods for the preparation of boronic acids and esters have depended on one of the following procedures: (1) the oxidation of a trialkylborane to a boronic ester followed by hydrolysis to obtain the acid; (2) the addition of a metallic alkyl or aryl to a trialkyl borate and the hydrolysis of the boronic ester thus formed; (3) the addition of a metallic alkyl or aryl to a boron trihalide to obtain the alkyl- or arylboron dihalide which on hydrolysis gives the boronic acid or on alcoholysis the ester.

(a) OXIDATION OF TRIALKYLBORONS

Several alkylboronic acids have been prepared by allowing trialkylboranes to stand in loosely stoppered flasks and then hydrolysing the products.[104] Frankland and Duppa[105] obtained diethyl ethylboronate by the controlled oxidation of triethylborane; hydrolysis of the ester afforded ethylboronic acid.

$$B(C_2H_5)_3 + O_2 \rightarrow C_2H_5B(OC_2H_5)_2 \xrightarrow{2H_2O} C_2H_5B(OH)_2 + 2C_2H_5OH$$

(b) METAL ALKYLS OR ARYLS ON TRIALKYL BORATES

Phenyl- and m-tolylboronic acids and some of their alkyl esters were prepared when Khotinsky and Melamed[106] added ethereal solutions of trialkyl borates (methyl, ethyl, n-propyl, iso-butyl, iso-amyl) to the arylmagnesium bromides at 0°C.

$$B(OR)_3 + ArMgBr \rightarrow ArB(OR)_2 \xrightarrow{2H_2O} ArB(OH)_2$$

Addition of the appropriate Grignard reagent to an ethereal solution of tri-n-butyl borate cooled to - 60°C has been used extensively to prepare arylboronic acids[107] as well as aliphatic (primary, secondary, and tertiary) alkyl acids.[108] P. B. Brindley, W. Gerrard and M. F. Lappert[109] have shown for di-n-butyl n-butylboronate that employing n-butyllithium instead of the Grignard reagent improved the yield by some 50 per cent, but using phenyllithium in place of phenylmagnesium bromide decreased the yield, only about 36 per cent of phenylboronic acid being obtained.

(c) METAL ALKYLS OR ARYLS ON BORON HALIDES

Michaelis and Becker[110] heated boron trichloride and diphenylmercury in a sealed tube for 1 hour at 180°- 200°C and thus obtained phenylboron dichloride which hydrolysed or alcoholysed with vigour to give phenylboronic acid and diethyl phenylboronate, respectively. Several arylboronic acids have been prepared using this method.[111]

$$Hg(Ar)_2 + 2BCl_3 \rightarrow 2ArBCl_2 \xrightarrow{4H_2O} 2ArB(OH)_2$$

Boron tribromide has advantages over the trichloride in that reflux conditions can be used, instead of the pressure vessel, and the reaction is more rapid.[112] The most successful modification involved the addition of the diethyl etherate of boron tribromide to the alkyl-[113] or aryl-[114] Grignard reagent in ether at 0°C, and hydrolysis of the alkyl- or arylboron difluorides to afford the boronic acids.

(d) OTHER METHODS FOR BORONIC ACIDS

Schlesinger, Flodin and Burg[115] have prepared methylboronic acid by the hydrolysis of symmetrical dimethyldiborane.

$$(CH_3BH_2)_2 + 2H_2O \rightarrow 2CH_3\ B(OH)_2 + 2H_2.$$

Ethyl- and _n_-propylboronic acids were formed when monoalkyldiboranes, RB_2H_5, were hydrolysed.[116]

Amino-boronic acids have been obtained by reduction of the corresponding nitro acids, using either hydrogenation in the presence of platinum[117] or freshly precipitated ferrous hydroxide.[118] By oxidation of di-n-propylborinic acid, formed by the hydrolysis of di-n-propylboron oxide, some n-propylboronic acid was obtained.[119] The oxidation of diarylborinic acids by halogens (chlorine, bromine) afforded the corresponding boronic acids.[120]

$$Ar_2BOH + H_2O + X_2 \rightarrow 2ArB(OH)_2 + HX + ArX$$

Paraphenylene diboronic acid, $(OH)_2BC_6H_4B(OH)_2$, and several esters have been prepared from methyl or butyl borate and paraphenylenedimagnesium bromide in tetrahydrofuran or by the use of paraphenylene dilithium.[121]

(e) SPECIAL METHODS FOR BORONIC ESTERS

A number of alkyl esters of arylboronic acids have been prepared in nearly quantitative yields from the appropriate boronic acid and alcohol, the water of esterification being removed by refluxing through a Soxhlet extractor of anhydrous copper sulphate (methyl esters), or by azeotropic distillation with excess of the alcohol (n-propyl and n-butyl esters), or by azeotropic distillation with excess of the alcohol and benzene (ethyl esters).[122] Many other esters of phenylboronic acid have also been prepared by this method.[123] A modification was to use the phenylboronic anhydride instead of the acid.[124]

$$ArB(OH)_2 + 2ROH \rightleftharpoons ArB(OR)_2 + 2H_2O$$

$$(C_6H_5BO)_3 + 6ROH \rightleftharpoons 3C_6H_5B(OR)_2 + 3H_2O.$$

Good yields (60-90 per cent) of esters of arylboronic acids with certain polyhydric alcohols have been prepared by simply mixing the two components, whereupon the esters precipitated.[125] This method is limited in its application to those compounds where the esters are less soluble than either of their parent acids or alcohols.

Alcoholysis of boronates was a good method for preparing esters of higher molecular weight from those of lower molecular weight and the n-butyl, sec-butyl, iso-butyl and octan-2-yl esters of phenylboronic acid were prepared from diethyl phenylboronate by reaction with the appropriate alcohol.[126]

$$ArB(OR)_2 + 2R'OH \rightleftharpoons ArB(OR')_2 + 2ROH$$

Tetramethoxysilane and methyldibromoborane afforded dimethyl methylboronate[127]

$$Si(OMe_3)_4 + MeBBr_2 \longrightarrow MeB(OMe)_2 + (MeO)_2SiBr_2$$

II. PROPERTIES

(a) PHYSICAL

Alkyl-[128] and aryl-[129] boronic acids are monomeric (cryoscopic in nitrobenzene) although slight association occurs in benzene solution.

The dissociation constants of many boronic acids, mainly aromatic have been measured and it is interesting to note that phenylboronic acid is three times as strong as boric acid.[130]

(b) CHEMICAL

(i) ACIDIC PROPERTIES

Boronic acids readily form anhydrides and esters. Relatively few salts have been described although phenylboronic acid formed both a sodium and a calcium salt when treated with the appropriate hydroxide.[131] n-Butylboronic acid formed a hydrated sodium salt when treated with very concentrated sodium hydroxide.[132]

Arylboronic acids are easily deboronated with water at elevated temperatures, or more rapidly with acids or (preferably) bases;[133]

$$C_6H_5B(OH)_2 + H_2O \rightarrow C_6H_6 + B(OH)_3.$$

In contrast the deboronation of alkylboronic acids is rather difficult.

(ii) BORON-CARBON CLEAVAGE REACTIONS

Alkylboronic acids are readily autoxidised in dry air to the alcohol and boric acid[134] but the aryl acids are quite stable.

Both alkyl- and aryl-boronic acids are quantitatively oxidised to orthoboric acid by hydrogen peroxide; use has been made of this in estimating the boron content of such compounds.[135]

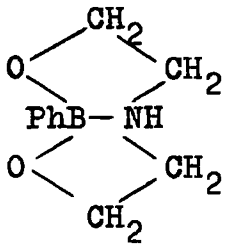
Phenylboronic acid is decomposed by halogens under quite mild conditions, in aqueous solution,[136]

$$PhB(OH)_2 + Br_2 + H_2O = PhBr + HBr + H_3BO_3$$

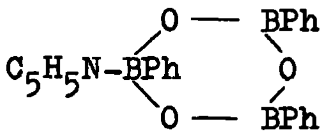
and by mercuric halides conveniently mercuric chloride in sodium chloride solution,

$$PhB(OH)_2 + HgCl_2 + H_2O = PhHgCl + HCl + H_3BO_3.$$

This reaction has also been used in quantitative analytical procedures.[137] Arylboronic acids are best characterised as diethanolamine esters[138] (e.g.a) or as the pyridine complexes of the corresponding boroxines[139] (e.g.b)



(a) m.p. 214-215°



(b) m.p. 154-156°

The boronic esters are generally easily hydrolysed. Cyclic esters are somewhat more stable, but a substantial resistance to hydrolysis only develops when the boron is coordinatively saturated.

F. BORINIC ACIDS AND ESTERS

1. PREPARATION

The borinic acids have generally been prepared by hydrolysis methods using halides, esters, or borines. Diphenylborinic acid, the first borinic acid to be prepared, was obtained by the hydrolysis of diphenylboron chloride which was obtained in low yield from the reaction of diphenyl mercury with phenylboron dichloride.[140,141]

$$(C_6H_5)_2\,Hg + PhBCl_2 \rightarrow Ph_2BCl \xrightarrow{H_2O} Ph_2BOH$$

A number of diarylborinic acids have been prepared by the reaction of 2 moles of aryl Grignard reagent with 1 mole of tri-iso-butylborate,[142] or tri-*n*-butylborate,[143] and yields varied with conditions, particularly temperature and order of addition. Recently Mikhailor and Vaver[144] have prepared several diarylborinic acids (52% yields) by the action of arylmagnesium bromide on tri-iso-butylborate in ether at $-60^\circ C$.

$$ArMgBr + (iso\cdot BuO)_3B \rightarrow Ar_2BOH + (ArBO)_3 + iso\cdot BuOH$$
$$+ H_3BO_3 + MgBr_2.$$

The hydrolysis of borinic esters obtained by various methods has been extensively used to prepare diaryl-[145] dialkyl-[146] and mixed alkylarylborinic acids ($C_6H_5CH_3BOH$)[147]

The hydrolysis of suitable methyldiboranes (di-, tri-, and tetra-), such that two methyl groups were attached to the boron atom gave dimethylborinic acid[148] and similarly the ethyl- and propyl- homologues were obtained.[149]

Recently T. P. Povlock and W. T. Lippincott[150] have reported a new synthesis of arylborinic acids (62% yields) from aromatic Grignard reagents (mole ratio 9:1) and trimethoxyboroxine at 25°C.

The three main methods of preparing borinic esters utilise (1) trialkyl- and triarylboranes, (2) interaction of orthoborates or boronic esters with organometallic compounds or (3) the esterification of borinic acids, anhydrides, or dialkyl- or diarylboron chlorides.

(1) Trialkylboranes and Triarylboranes.

Borinic esters were first prepared by the reaction of triethylborane with certain aldehydes (CCl_3CHO, C_6H_5CHO, p-ClC_6H_4CHO) or with the corresponding alcohols.[151]

$$B(C_2H_5)_3 + RCHO \rightarrow (C_2H_5)_2\ BOCH_2R + C_2H_4$$

$$B(C_2H_5)_3 + RCH_2OH \rightarrow (C_2H_5)_2\ BOCH_2R + C_2H_6$$

Triphenylborane reacted with alcohol to form ethyl diphenylborinate:

$$Ph_3B + EtOH = Ph_2BOEt + C_6H_6$$

The 2-aminoethyl esters of both diphenylborinic and di-α-naphthylborinic acids were prepared in an analogous manner, from the appropriate triarylborane and ethanolamine, by heating in boiling benzene.[152] However with methanol and the triarylborane the reaction was more complex; the α-naphthyl compound afforded naphthalene and trimethyl borate, whilst with triphenylborane and a large excess of methanol phenyl diphenylboronite, $(C_6H_5)_2BOC_6H_5$, was isolated as an ammonia complex.

Triethylborane reacted with carboxylic acids to give aryl diethylboronites.[153]

$$B(C_2H_5)_3 + RCOOH \rightarrow (C_2H_5)_2BOOCR + C_2H_6.$$

Oxidation of trialkylboranes to produce borinates has been mentioned earlier.[154]

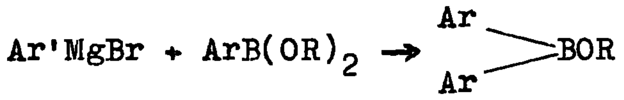
(2) Organometallic Compounds

The addition of 2 moles of allylmagnesium bromide to 1 mole of trimethyl borate afforded methyl diallylboronite;[155] by similar reaction *n*-butyl di-*n*-octylboronite was obtained.[156]

The butyl esters of diphenylborinic acid were also prepared by this method:

$$2\ ArMgBr + B(OC_4H_9\text{-i})_3 \rightarrow Ar_2BOC_4H_9\text{-i}$$

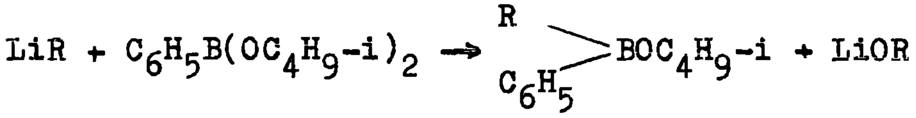
Dialkyl arylboronates react with arylmagnesium bromides to produce mixed boronites[157]



$$Ar'MgBr + ArB(OR)_2 \rightarrow \begin{matrix} Ar \\ Ar \end{matrix} > BOR$$

n-Octyllithium reacted with tri-n-butyl borate to give n-butyl di-n-octylboronite.[158]

Both n-butyl- and n-propyllithium with diisobutyl phenylboronate gave mixed boronites.[159]



$$LiR + C_6H_5B(OC_4H_9\text{-i})_2 \rightarrow \begin{matrix} R \\ C_6H_5 \end{matrix} > BOC_4H_9\text{-i} + LiOR$$

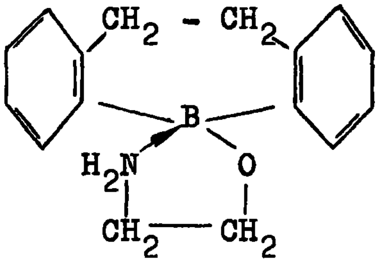
(3) Esterification methods

Di-n-butylborinic anhydride heated with 1-butanol yielded the ester.[160]

$$(C_4H_9)_2B\ _2O + 2C_4H_9OH \rightarrow 2(C_4H_9)_2BOC_4H_9 + H_2O$$

The addition of 2-amino-2-methyl-1-propanol of an aqueous ethanolic solution of the mixed α-naphthyl-phenylborinic acid, obtained by hydrolysis of the 2-aminoethyl ester with a concentrated ethereal solution of hydrogen chloride, gave the appropriate ester.

O;O' - Dibenzyldilithium and tri-n-butyl borate reacted to give a product which on hydrolysis and esterification with ethanolic ethanolamine afforded the ester:[161]



Mixed n-butyl boronites were prepared similarly, using di-n-butyl phenyl- (or α-naphthyl) boronate and α-naphthyl (or phenyl) magnesium bromide.[162,163] Mixed n-propyl diarylboronites were also prepared from mixed diarylborinic acids, obtained in situ, by esterification with 1-propanol, the water produced being removed as an azeotrope with excess of the alcohol.[164] Arylboronic acid dialkyl esters react with alkyl magnesium bromide in mole ratio 1:1 at -65° to -60° to form esters of aryl-alkylborinic acids,[165] if the Grignard reagent is added in mole ratio 2:1 to the boronic ester, disproportionation occurs with formation of tri-alkylboranes and triarylboranes.

II PROPERTIES

(1) PHYSICAL

Few physical properties of the borinic acids have so far been determined and even the reported boiling points may well be those of the anhydrides.

The values for the latent heat of vaporisation and Trouton's constant for methyl dimethyboronite have been obtained, and its molecular weight showed it to be monomeric.[166] Diphenylborinic acid was also shown to be monomeric (cryoscopic in camphor).[167]

(2) CHEMICAL

The dialkyl- and diarylborinic acids are very weak acids, they readily form anhydrides and can easily be esterified. Diphenylborinic acid was said not to form salts with alkalis.[168]

Several borinic acids have been quantitatively oxidised first to boronic acids and subsequently to orthoboric acid,[169] by chlorine, bromine or hydrogen peroxide.

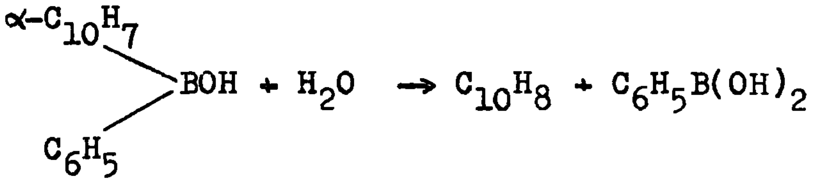
$$Ar_2BOH + Y_2 + H_2O \rightarrow ArB(OH)_2 + ArY + HY$$

$$ArB(OH)_2 + Y_2 + H_2O \rightarrow B(OH)_3 + ArY + HY$$

$Y = Cl$, Br or OH.

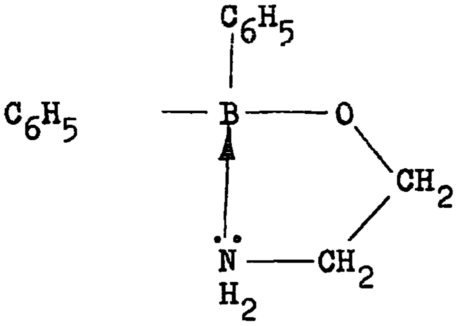
When di-α-naphthylborinic acid was heated for 6 hours at 120-130°C, naphthalene was obtained as a sublimate and a residue of α-naphthylboronic anhydride remained.[170] Similar cleavage was effected by heating the acid with an aqueous ethanolic solution of 2-(dimethylamino) ethanol.[171]

$$3(\alpha\text{-}C_{10}H_7)_2BOH \rightarrow 3C_{10}H_8 + (\alpha\text{-}C_{10}H_7BO)_3$$



$$(\alpha\text{-}C_{10}H_7)(C_6H_5)BOH + H_2O \rightarrow C_{10}H_8 + C_6H_5B(OH)_2$$

Boronic esters are generally easily oxidised (requiring work under nitrogen). Hydrolysis of the borinic esters has already been mentioned. The relative stability of 2-aminoethyl diphenylboronite towards both oxidation and hydrolysis (it can be recrystallised from water) has led to the suggestion that its structure is as shown.[172]



Such chelation has also been suggested to account for the inability for both this ester and its α-naphthyl analog to undergo alcoholysis reactions.[173]

2-Aminoethyl α-naphthyl phenylboronite reacted with ethanolic hydrogen peroxide and with aqueous zinc chloride to give α-naphthol and naphthalene, respectively.[174] Amine complexes of several arylborinic acids have been used as a method for purifying the acids.[175] Methyl dimethylboronite formed a 1:1 complex (m.p. 51-52°C) with dimethylamine. Phenyl diphenylboronite formed a 1:1 complex with ammonia[176] and a similar complex formed from *iso*butyl diphenylboronite slowly evolved ammonia.[177]

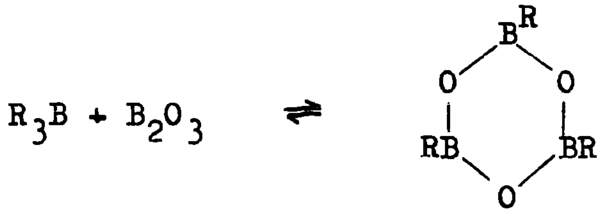
BOROXINES

1. PREPARATION

The cyclic anhydrides of boronic acids are commonly known as boroxines, of empirical formula $(BOR)_3$, R being an aryl or alkyl group.

Until recently the alkyl boroxines were normally prepared by dehydration of alkylboronic acids[178] whilst aryl boroxines were obtained by heating the acids.[179]

Recently an azeotropic distillation process for the dehydration of large amounts of organo-boronic acids has been used to prepare alkylboroxines, some of them hitherto unknown.[180] The most convenient preparative method for normal alkylboroxines is the reaction between trialkylboranes and anhydrous boric oxide.[181]



For example heating equimolar quantities of tri-n-butylborane and boric oxide at reflux (200°) for 40 hours and vacuum distillation of the product gives almost 70% yield of tri-n-butylboroxine. Tri-ethyl, -n-propyl, -isobutyl, -cyclohexyl and -phenylboroxines have been prepared by this method but isomerisation can occur in this reaction. Tri-n-butylboroxine results from tri-s-butylborane and boric oxide.

II. PROPERTIES

(a) PHYSICAL

Molecular weight measurements (cryoscopic in nitrobenzene) on aryl- and alkyl- boroxines[182] show them to be trimeric. Electron diffraction measurements on tri-methylboroxine are in agreement with a planar six-membered ring with methyl groups bonded, in the plane of the ring, to boron. Bond distances and angles were determined.[183]

(b) CHEMICAL

In contrast to dialkyl-silicon oxides the boroxines show no tendency to form higher cyclic or linear polymers. They are readily hydrated to the acids[184] and react with alcohols.[185]

$$(RBO)_3 + 3H_2O = 3RB(OH)_2$$

$$(RBO)_3 + 6R'OH = 3RB(OR')_2 + 3H_2O.$$

Tri-alkyl and -aryl boroxines form 1:1 coordination complexes, those between triarylboroxines and pyridine being suitable for identification purposes.[186] The trialkylboroxines are slowly oxidised by atmospheric oxygen.

Tri-n-butylboroxine yields n-butyldichloroborane and di-n-butylchloroborane on treatment with aluminium chloride[187] and the mixed trialkylborane $BuBMe_2$ is said to be formed with trimethylaluminium or methylaluminium sesqui-iodide[188]

$$BuBCl_2 + BuBCl \xleftarrow{AlCl_3} Bu_3B_3O_3 \xrightarrow{Me_3Al} BuBMe_2$$

ALKYL- AND ARYL- DIHALOBORANES

1. PREPARATION

In view of their importance to the research to be described, the boron halides are reviewed in more detail than the other compounds.

Substituted dihaloboranes are generally prepared by one of the following reactions:

(a) REACTIONS WITH ORGANO-METALLIC COMPOUNDS

Dimethyl zinc was reported to react with boron trichloride to give methyldichloroborane and dimethylchloroborane[189] but the reaction could not be confirmed.[190]

$$2(CH_3)_2Zn + 3BCl_3 \rightarrow (CH_3)_2BCl + 2CH_3BCl_2 + ZnCl_2$$

Reaction between trialkylaluminium compounds and boron halides has been used to prepare several alkyldihaloboranes[191,192].

Several aryldichloroboranes have been obtained from the reaction between boron trichloride and the appropriate di-aryl mercury compound.[193]

$$Ar_2Hg + BCl_3 \rightarrow ArHgCl + ArBCl_2.$$

Phenyldifluoroborane and p-tolyldifluoroborane have been prepared by direct distillation from the reaction between boron trifluoride-ether complex and the Grignard reagent in ether.[194,195]

Boron trichloride heated with 2-chlorovinylmercuric chloride in kerosine in a sealed tube for 2 hours at 50°C (or allowing the mixture to stand for 12 hours at room temperature) gave the dichloride.[196]

Phenyldichloroborane can now be prepared in good yields from boron trichloride and tetraphenyl tin[197] in benzene

$$Ph_4Sn + 4BCl_3 \rightarrow 4PhBCl_2 + SnCl_4.$$

there still appears to be some doubt about the mechanism of the reaction.[198]

The new method for making $PhBCl_2$ from benzene and boron trichloride may make this the most convenient route to phenylboronic acid.[199]

The preparation of boronic (and borinic) esters by reaction between olefins and less than 1 mol. diborane is at present being developed.[200]

(b) TRIALKYLBORANES

Hydrogen chloride bubbled into tri-n-butylborane at 110°, in the presence of aluminium chloride, has been used to prepare n-butyldichloroborane,[201]

$$R_3B + HCl \rightarrow R_2BCl \xrightarrow[AlCl_3]{HCl} RBCl_2 + RH.$$

Trimethylborane reacts with boron trichloride to give methyldichloroborane[202] $Me_3B + 2BCl_3 \rightarrow 3MeBCl_2$

(c) BORONIC AND BORINIC ACIDS AND DERIVATIVES

The rapid reaction, at atmospheric pressure, between trialkylboroxines and boron trichloride is the most convenient method for the preparation of alkyldichloroboranes.[203]

$$(RBO)_3 + 2BCl_3 = 3RBCl_2 + B_2O_3.$$

Slow disproportionation of the dialkylchloroboranes at temperatures above 180° and take off of the more volatile $RBCl_2$ at the top of the column has also been used.[204]

The reaction between tri-organoboroxines and boron trifluoride or trichloride has been claimed as a general method for the preparation of organo substituted dihaloboranes.[205,206] The yields of difluoroboranes are generally much lower than those of dichloroboranes.

Phenyldichloroborane, for example, is best prepared by the dropwise addition of liquid boron trichloride (cooled to -39°C) to triphenylboroxine in methylene chloride cooled to -80°C.[207]

(d) OTHER METHODS

n-Butyldifluoroborane has been prepared by saturating di-n-butylboronate with boron trifluoride.[208] Phenyldichloroborane was similarly prepared, the accompanying dichloroboronite being either unstable (if secondary alkyl) or decomposed by a trace amount of ferric chloride, to facilitate separation.[209]

$$RB(OR')_2 + 2BF_3 \rightarrow RBF_2 + 2R'O\,BF_2.$$

Triphenylboroxine when heated, with phosphorus pentachloride, under reflux (120-130°) for 24 hours gives phenyldichloroborane.[210] Recently aryldifluoroboranes have been obtained by the action of antimony trifluoride and similar fluorinating agents on the corresponding dichloro compounds at low temperatures.[211]

II. PROPERTIES

(a) PHYSICAL

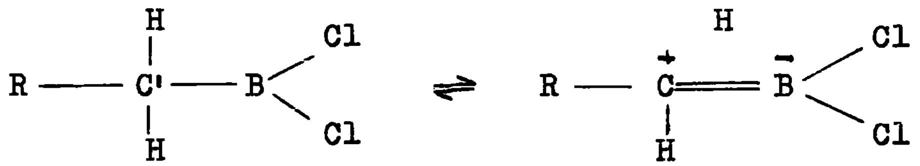
Alkyl- and aryl- dihaloboranes are monomeric (vapour density[212,213,214] and cryoscopic in chloroform[215]).

Electron diffraction measurements[216] on methyldifluoroborane have shown molecule to be planar and similar in configuration to boron trifluoride.

(b) CHEMICAL

Methyldichloroborane is said to disproportionate easily[217] whereas the alkyl- dichloro (and difluoro) boranes (ethyl to hexyl) are quite stable to disproportionation up to 170°.[218]

Alkyldihaloboranes are pyrophoric the chloro compounds being more so than the fluoro compounds. It is interesting to note that the pyrophoric nature is not dependent on volatility since n-butyldifluoroborane can be rapidly poured in air whereas the secondary and tertiary compounds are spontaneously inflammable. It has been suggested that hyperconjugation may account for the unexpectedly reduced electrophilic character of the boron in straight chain compounds,[219]

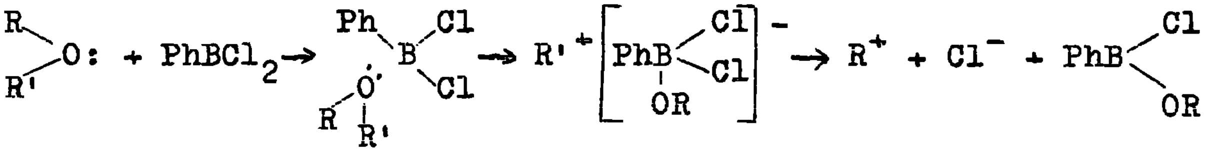


Contributions from quinoid structures may account for the lack of pyrophoric nature in aryldihaloboranes.

Alkyldihaloboranes form 1:1 complexes with ethers the B-O bond being stronger in the chloro- than in the fluoro-compounds. n-Amyldifluoroborane- ether complex completely dissociates on fractional distillation whereas n-butyldichloroborane- ether decomposes,[220]

$$Et_2O - Bu^nBCl_2 \rightarrow EtCl + (EtO)\overset{B}{\cancel{N}}u^nBCl.$$

Phenyldichloroborane reacts with most ethers[221] [Ph_2O and $(ClCH_2CH_2)_2O$ do not react] at high temperatures, alkyl chlorides are produced exclusively from the more electron releasing group in a mixed ether, as well as an alkyl- or aryl- phenylchloroboronite



$RCl + PhBCl(OR)$:

Phenyldichloroborane with hydrogen iodide and iodine gives a phenyldiiodoborane hydrogen iodide complex $PhBI_2.2HI$.[222] Alkyl- and aryl-dihaloboranes form stable 1:1 complexes with amines, those with pyridine (particularly aryls) are useful for identification purposes.[223,224,225]

Reduction of phenyldichloroborane with lithium aluminium hydride in the presence of pyridine gives $PhBH_2py$.[226] If pyridine is absent triphenylborane and diborane are obtained,[227] probably by disproportionation

$$3PhBH_2 \rightarrow Ph_3B + B_2H_6.$$

Diphenyl diborane $(PhBH_2)_2$ m.p. 85° has also been obtained from triphenylborane and diborane at 80° and 2·2 atm., pressure.[228]

DIALKYL AND DIARYL HALOBORANES

1. PREPARATION

The dialkyl- and diaryl- haloboranes have been prepared by methods similar to those used for the dihalides.

(a) ORGANOMETALLIC COMPOUNDS

Diphenylbromoborane is obtained from diphenyl mercury and boron tribromide[229]

$$2Ph_2Hg + BBr_3 \rightarrow 2PhHgBr + Ph_2BBr$$

Phenyldichloroborane reacts with diphenyl mercury to give diphenylchloroborane.[230]

$$PhBCl_2 + Ph_2Hg \rightarrow PhHgCl + Ph_2BCl$$

Bis(2-chlorovinyl-)mercury and boron trichloride when heated under reflux in benzene give the boron monochloride.[231]

(b) TRIALKYLBORANES AND AMINODIALKYLBORANES

Dialkylchloroboranes are now quite accessible since they are prepared in excellent yield by bubbling boron trichloride into the appropriate trialkylborane at 160°. The equilibrium $2R_2BCl \rightleftharpoons RBCl_2 + R_3B$ lies far to the left, at least at temperatures up to 180°.[232]

The reaction between trialkylboranes and hydrogen halides has been used to prepare several dialkylhaloboranes,[233]

$$R_3B + HX \rightarrow R_2BCl + RH$$

Tri-n-propylborane and iodine at 140° give di-n-propyl iodoborane[234]

$$I_2 + Pr^n_3B \rightarrow Pr^n_3BI + \text{ other products including } Pr^nBI_2$$

Antimony trichloride and tribromide on the iodo- compound give the di-n-propylchloro- and bromo- borane but antimony trifluoride and other fluorinating agents failed to produce the fluoroborane.

$$n\text{-}Pr_2BI + SbCl_3 \xrightarrow[\text{2 hours}]{100^\circ\text{for}} Pr^n_2BCl$$

$$Pr^n_2BI + SbBr_3 \xrightarrow[\text{2 hours}]{100^\circ} Pr^n_2BBr$$

Tri-n-butylborane and bromine give di-n-butylbromoborane.[235] Dimethylchloroborane was obtained from (dimethylamino) dimethylborane and excess hydrogen chloride reacted at 20°C for 2 hours[236]

$$(Me)_2BNHMe + HCl \rightarrow (Me)_2BCl.NH_2Me \overset{HCl}{\rightleftharpoons} Me_2BCl + MeNH_2.HCl$$

(c) BORONIC AND BORINIC ACIDS AND DERIVATIVES

Diphenylchloro (and bromo) borane have recently been prepared by the reaction at -80°C between diphenylborinic anhydride and the appropriate boron halide.[237]

$$(Ph_2B)_2O + BX_3 \rightarrow 2\ Ph_2BX + BOX$$

The reaction between diphenylboronites and phosphorus pentahalides has been used to prepare diphenyl-chloro (and bromo) borane.[238,239]

$$Ph_2BOR + PX_5 \rightarrow Ph_2BX + RX + POX_3$$

Yields from these reactions were rather low due to appreciable dissociation of the pentahalides at the necessarily high temperatures.

II. PROPERTIES

(a) PHYSICAL

Dimethyl-[240] diethyl-[241] and dipropyl-[242] chloroboranes were found to be monomeric in the vapour phase and the Trouton constant for the n-propyl- compound was obtained. Densities, refractive indices and infra-red spectra of many dialkylhaloboranes have been obtained.[243]

(b) CHEMICAL

Dialkylhaloboranes are resistant to disproportionation up to 170°, however at higher temperatures the equilibrium $2R_2BCl \rightleftharpoons RBCl_2 + R_3B$, though far to the left does exist, and careful take off of the more volatile alkyldichloroborane at atmospheric pressure leads to complete disproportionation.[244] It appears that the mechanism for the disproportionation is similar to that of the trialkylboranes, a dimeric intermediate is formed by the overlapping of halogen orbitals with unoccupied boron p-orbitals, the alkyldihaloborane produced rapidly reacts with excess trialkylborane so that the dialkylhaloborane is produced exclusively.

Several dialkyl- and diaryl- haloboranes have been characterised by hydrolysis to the corresponding acids or anhydrides,[245]

$$Ph_2BCl + H_2O \rightarrow [Ph_2B]_2O + 2HCl$$

$$Bu^n_2BCl + H_2O \rightarrow Bu^n_2BOH + HCl$$

The halides readily undergo alcoholysis.

$$Ph_2BBr + Bu^nOH \rightarrow Ph_2BOBu^n + HBr.$$

Reduction of dibutylchloroborane in ether[246] with sodium-potassium alloy, gives a coloured solution containing something equivalent to 'dibutylboron' which disproportionates on evaporation of the ether into tributylborane and a glassy residue $(BuB)_n$ which evolves hydrogen on hydrolysis.

$$Bu^n_2BCl + K \rightarrow [Bu^n_2B] \rightarrow Bu^n_3B + BuB_n$$

Reduction with 2 mols. of metal leads to an alkali metal dibutylboride which forms dibutylmethylborane on treatment with methyl iodide.

$$Bu^n_2BCl + 2K \rightarrow Bu^n_2BK \xrightarrow{MeI} Bu^n_2BMe$$

No reaction was observed when diphenylbromoborane stood over sodium wire in pentane for 50 hours at 20°C.[247]

Diphenylchloroborane and secondary amines[248] react in ether to give solids of the type $Ph_2B - NR_2$

$$Ph_2BCl + Et_2NH \rightarrow Ph_2BNEt_2 + HCl$$

Ph_2BNEt_2 m.p. 36-37°, b.p. 159°-162°/11 mm., and $Ph_2BN(CH_2)_5$ m.p. 65-66° b.p. 200-203°/19 mm., were obtained.

Several diarylhaloboranes have been reacted with pyridine to produce stable complexes.[249]

Compounds of the general type (Ph_2BX) are stable to ethers for as long as 2 hours at 20°C, but experiments at higher temperatures have not yet been attempted.[250]

Diphenylchloroborane undergoes an unusual reaction with aluminium chloride in ethyl methyl ketone, whereby diphenylboronium Ph_2B^-, ions seem to be formed. Addition of silver perchlorate to a solution of diphenylchloroborane in nitrobenzene causes immediate precipitation of silver chloride, and the solution contains diphenylboronium perchlorate.[251]

$$Ph_2BCl + AgClO_4 \rightarrow AgCl + Ph_2B^+ClO_4^-$$

If the reaction is carried out in nitromethane, and bipyridyl added after removal of silver chloride, the crystalline compound 2,2'-bipyridyldiphenylboronium perchlorate crystallises:[252]

$$Ph_2BCl + AgClO_4 \rightarrow Ph_2B^+ClO_4^- \xrightarrow{\text{dipy}} [\text{dipy } BPh_2]^+ ClO_4^-.$$

Although esters of borinic acids are readily hydrolysed,[253] the ester (a) m.p. 74-75° (quantitatively from Ph_2BCl and ethyl aceto-acetate), is very resistant to hydrolysis.

It is both conjugated and coordinatively saturated.[254]

PART II

PREPARATION OF REAGENTS

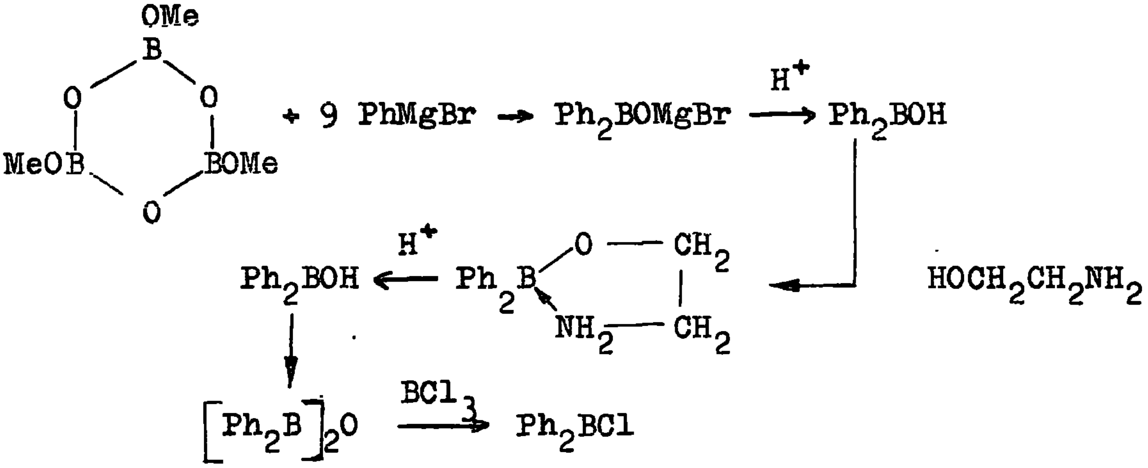
The preparation of chlorodiphenylborane $(C_6H_5)_2$ BCl

Trimethoxyboroxine (87g., 0·5 mole) in dry ether (900 c.c.) was slowly added (2 hours) to phenylmagnesium bromide (4·75 mole) in the same solvent (3000 c.c.) while the temperature was maintained between 24° and 26°. After adding all the boroxine and stirring for a further 2 hours the reaction mixture was hydrolysed with hydrochloric acid (465 c.c. in 1l. of water). The ether layer was then separated, washed three times with water, and distilled to low bulk. The remainder of the ether was evaporated from the yellow oily acid on a water bath.

The acid was heated (20 mins) with 250 c.c. of water on a steam bath to remove any boronic acid, and then separated, dissolved in ether (400 c.c.) and the monoethanolamine ester of the acid (202g., 88% m.p. 188°- 89°) was precipitated on the addition of monoethanolamine (91 c.c.) in water (400 c.c.)[255]

Hydrolysis of the ester in a $^{50}/_{50}$ solution of acetone and methanol with hydrochloric acid (95 c.c.) and sufficient water to separate the layers (500 c.c.) afforded the pure acid which was separated dissolved in ether (400 c.c.) and dried (anhyd. $MgSO_4$). After removal of the ether, the acid was pumped (0·006 mm.) for 3 hours on a water bath at 100°, when it solidified forming the anhydride (crystallised from pentane m.p. 116-116·5°, 110g.,)[256]

Chlorodiphenylborane (m.p. 21·5-22°, b.p. 80°-82°/0·05 mms., 65g., 83·5%) was obtained by the reaction between diphenylborinic anhydride and boron trichloride in methylene chloride, as previously described by Gerrard, Lappert, Dandgoanker and Abel.[257] Better yields than those described were obtained by vacuum distilling directly from the solid gel of boron oxychloride.



<u>Chlorodi-p-tolylborane</u> $(CH_3C_6H_4)_2BCl$ (m.p. 64° b.p. 110°-113°/0·1 mm 18·2g., 76·4%) and <u>Chlorodi-p-bromphenylborane</u> $(BrC_6H_4)_2BCl$, (m.p. 79-80°, b.p. 184°-7°/0·1 mm 23·5g., yield 64%) were similarly prepared from trimethoxyboroxine and the appropriate Grignard reagent.

The preparation of fluorodimesitylborane $(2,4,6,CH_3C_6H_2)_2BF$.

Boron trifluoride-etherate (10·6g., 0·075 mole) was slowly added to mesitylmagnesium bromide (0·24 mole) prepared by the method described by Brown and Dodson.[258] The reaction mixture was refluxed (2 hours) and then left to settle overnight. The yellow-orange upper layer was separated (N_2) and after removal of solvent afforded on vacuum distillation fluorodimesitylborane (m.p. 76°-77° sealed tube, b.p. 130-2°/0·5 mm 16·8g., yield 84%)

The preparation of dimethylamino boron dichloride

Dimethylaminoboron dichloride (b.p. 50-54°/90 mm 94g., 76%) was prepared by the method described by J. F. Brown.[259] It was found by vapour phase chromatography that even after two careful fractionations the final product contained a considerable amount of benzene.

The preparation of diphenylphosphine

The preparation of diphenylphosphine from triphenylphosphine and lithium shot in tetrahydrofuran has already been described.[260] However increased yields of the diphenylphosphine were obtained by using sodium wire instead of lithium shot and deaerated acid for hydrolysis.

$$Ph_3P + 2Na \rightarrow PhNa + Ph_2PNa \xrightarrow[H_2O]{H+} Ph_2PH$$

Freshly cut sodium wire (10g.,) was pressed(N_2) into a solution of triphenylphosphine (52·6g., 0·2 mole) in dry tetrahydrofuran (250 c.c.). The solution rapidly became deep red in colour and it slowly became quite warm. After stirring the reaction mixture (2 hours) it was hydrolysed with dilute hydrochloric acid to pH 7-7·5. Tetrahydrofuran was removed by distillation and vacuum distillation afforded diphenylphosphine (110-112°/2 mm. 26·4g., 71%)

The preparation of di-m-tolylphosphine

Pure di-m-tolylphosphine (b.p. 102°-4°/0.1 mm.) hitherto not described was prepared by the method described by H. Gilman and D. Wittenberg[261] for the preparation of diphenylphosphine. The tri-m-tolylphosphine was prepared as described below.

The infra spectrum of the phosphine a colourless air sensitive liquid showed the strong P-H absorption at 4·33 u. Oxidation with aqueous alcoholic hydrogen peroxide afforded di-m-tolylphosphinic acid (m.p. 169°).

The preparation of tri-m-tolylphosphine

Phosphorus trichloride (65 c.c. 0·73 mole) in dry ether (200 c.c.) was slowly added (N_2) to m-tolyl magnesium bromide (2·9 mole) in the same solvent (1l). After the final addition of halide the solution was refluxed (1 hour) and then carefully hydrolysed with deaerated dilute hydrochloric acid (final pH 7-7·5). The ether layer was separated, dried (anhydrous magnesium sulphate) and distilled to low bulk before finally pumping dry. Crystallisation (charcoal) from ethanol afforded tri-m-tolylphosphine (m.p. 104°, 121g., 49·2%).

The preparation of triphenylarsine

Anhydrous arsenic trichloride (126 c.c., 1·5 mole) in dry ether (350 c.c.) was slowly added (N_2) to phenylmagnesium bromide (5 mole) in the same solvent (3l.). After the final addition of halide the reaction mixture was refluxed (½ hour) and carefully hydrolysed with dilute hydrochloric acid. The ether layer was separated, dried (anhydrous magnesium sulphate) and concentrated before being pumped dry. Crystallisation from ethanol (charcoal) afforded large white crystals of triphenylarsine (m.p. 59-60°, 370g., yield 81%).

The preparation of diphenylarsine

Diphenylarsine (b.p. 120°-22°/1.0 mm, 55·2g., yield 68·2%) was prepared by the method described by W. Kuchen and H. Buchwald[262] from triphenylarsine and lithium shot in tetrahydrofuran. Higher yields of arsine were obtained by using deaerated dilute hydrochloric acid for hydrolysis.

The preparation of phenylphosphine

Phenylphosphine (b.p. 40°/9-10 mms 30·2g., yield 61%) was obtained from phenyldichlorphosphine (80g.,) and lithium aluminium hydride (10g.,) as described by W. Kuchen and H. Buchwald.[263] It was found that increased yields were obtained when the white precipitate formed after hydrolysis was extracted again with hot ether, after decanting off the original solution.

PART III

EXPERIMENTAL RESULTS

Microanalyses (C,H, and halogen) are by Mr. A. Wiper and Miss V. Conway, and infra red spectra are measured by Mr. L. Chadwick and Miss D. A. Chapman of these laboratories.

Combustion analyses often presented the difficulties, familiar with organo-boron compounds, due to the retention of carbon as boron carbide in combustion residues, leading to erratic carbon results. More reproducible results were generally obtained when smaller samples were burnt, and when the residue after combustion was heated with an oxygen enriched flame.

Compounds were in several instances identified by quantitative hydrolysis (for amino-) or oxidation reactions (for phosphino- and arsino- derivatives).

Cryoscopic constants were determined using biphenyl for benzene and p-nitrotoluene for nitrobenzene.

Except in the case of one compound $(Ph_2B\ NH_2)_2$, for which refractivities were measured over a range of wavelengths, refractivities were measured at 6620A^o (Jena interference filter) and atom polarisations were taken as 10% of these refractivities.

Dipole moments were measured in benzene solution, total polarizations being derived by Halverstadt and Kumler's[264] method. In spite of the apparent association of many of the compounds studied, as suggested by cryoscopic measurements, dielectric constant - weight fraction plots were always very nearly linear.

In fra red spectra were measured with a Grubb-Parsons GS2A grating spectrometer.

Aminodiphenylborane $(Ph_2B\ NH_2)_2$

Chlorodiphenylborane (10g., 0·05 mole) in dry ether (100 c.c.) was saturated with ammonia at room temperature and triethylamine (5·1g., 0·05 mole) in ether (50 c.c.) was slowly added. The reaction mixture was boiled with reflux (1 hour), cooled, and filtered under nitrogen from triethylamine hydrochloride. The filtrate was pumped dry and the colourless product crystallised from benzene, m.p. 129-130°(3·6g., 43%) (Found: C, 79·4; H, 6·7 $C_{12}H_{12}BN$ requires C, 79·9; H, 6·6%)

Aminodimesitylborane $(2,4,6,CH_3C_6H_2)_2BNH_2$

Dimesitylfluoroborane (6g., 0·224 mole) in ether was slowly added to excess ammonia in the same solvent (50 c.c.) cooled to -60°C. An immediate precipitate of dimesityl fluoroborane-ammonia complex (m.p. 144°-5°) was observed. The final reaction mixture was refluxed (48 hours) and the precipitate slowly redissolved and ammonium fluoride (0·4g.,) was precipitated. Pumping off solvent afforded aminodimesitylborane (crystallised from pet., ether, m.p. 118°-20° 5·5g., yield 92·6%) Found Ms_2B, 93·4, 93·5%, $NH_2$5·96, 5·92% $C_{18}H_{24}BN$ requires Ms_2B 94·1%, $NH_2$6·0%

Dimethylaminodiphenylborane, $Ph_2B{\cdot}NMe_2$

To a solution of monomeric dimethylamino dichloroborane (3·2g., 0·025 mole) in benzene (50 c.c.) was slowly added phenylmagnesium bromide (0·05 mole) in ether. The reaction mixture was pumped dry, to remove the ether since magnesium halide - ether complexes are soluble in organic solvents, and the organic product was extracted with hot benzene.

Vacuum distillation of the extract yielded a clear colourless, air sensitive liquid product, b.p. 102-104°/ 0·05 mm. (4·1g., 81%) (Found: C, 80·8; H, 8·0. $C_{14}H_{16}BN$ requires C, 80·4; H, 7·6%)

Dimethylamino di-p-tolylborane, $(p\text{-}CH_3C_6H_4)_2B{\cdot}NMe_2$, b.p. 110-112°/0·04-0·05 mm. (4·5g., 76%) Found: C, 80·0; H, 8·6. $C_{16}H_{20}BN$ requires C, 81·1; H, 8·4%. By hydrolysis, found: $(p\text{-}CH_3C_6H_4)_2B$, 81·8; 80·5; Me_2N, 18·8, 18·3. $C_{16}H_{20}BN$ requires $(p\text{-}CH_3C_6H_4)_2B$, 81·5; Me_2N, 18·6%) and

Dimethylamino di-p-bromophenylborane, $(p\text{-}BrC_6H_4)_2B{\cdot}NMe_2$, m.p. 39-40° from benzene-hexane (4·1g 44%) (Found: C, 46·6; H, 3·7; Br 43·9. $C_{14}H_{14}BBr_2N$ requires C, 45·8; H, 3·8; Br, 43·7%) were similarly prepared using p-tolyl- and p-bromphenylmagnesium bromide respectively.

<u>Diphenylaminodiphenylborane</u> $Ph_2B\ NPh_2$ (Method 1.)

Lithium diphenylamide (·051 moles) in dry ether was slowly added to an equivalent quantity of chloro-diphenylborane in the same solvent at -60°C. The reaction mixture was allowed to warm to room temperature, filtered under nitrogen, and the white product which resulted from pumping solvent from the filtrate was crystallised from benzene, 11·9g., m.p. 148-150 (66%) (Found: C, 85·8; H, 6·1; B, 3·14· $C_{24}H_{20}BN$ requires C, 86·4; H, 6·0; B, 3·26%). 0·186g. was warmed with aqueous acetone for a few minutes, and a slight excess of ethanolamine was added. The reaction mixture was poured into water, the solid collected, pumped dry and sublimed in vacuo. The sublimate, 0·093g., m.p. 56°, was identified (infra-red spectrum) as diphenylamine, and the residue 0·132g., m.p. 188°-9°, was similarly identified as the ethanolamine ester of diphenylborinic acid. $C_{24}H_{20}BN$ requires 0·096g, and 0·128g, respectively.

(Method 2.)

Freshly purified diphenylamine (8·5g, 0·05 moles in benzene was added to a solution containing equivalent amounts of triethylamine (9·1 mls.,) and chlorodiphenylborane (10g.) in the same solvent. The reaction mixture was boiled with reflux (30 min.), filtered under nitrogen from triethylamine hydrochloride (6·2g.) m.p. 255-6°, and the filtrate concentrated to crystallisation (11·1g. 61%). The infra spectrum of the product was identical with that of the material prepared by method (1).

Di-p-tolylaminodiphenylborane, [$Ph_2B{\cdot}N(C_6H_4\underline{p}\text{-}CH_3)_2$], m.p. 130-132° (from a benzene-hexane mixture) [Found: C, 85·3; H, 6·5. $C_{26}H_{24}BN$ requires C, 86·3; H, 6·8%. By hydrolysis, found: Ph_2B, 45·9; ($\underline{p}$-$CH_3C_6H_4)_2N$ 54·9. $C_{26}H_{24}BN$ requires Ph_2B, 45·8; ($\underline{p}$-$CH_3C_6H_4)_2N$ 54·2%] was prepared by methods (1) 53% and (2) 57%.

Diphenylaminodi-p-tolylborane [($\underline{p}$-$CH_3C_6H_4)_2B{\cdot}NPh_2$]. - This was prepared by method (2) and the white product was crystallised from benzene-hexane (5·9g., 67%), m.p. 72-73° [Found: C, 89·9; H, 7·0. $C_{26}H_{24}BN$ requires C, 89·1; H, 7·0%. By hydrolysis, found: ($\underline{p}$-$CH_3C_6H_4)_2B$, 53·8, 53·7; Ph_2N, 46·8, 46·4. $C_{26}H_{24}BN$ requires ($\underline{p}$-$CH_3C_6H_4)_2B$, 53·4; Ph_2N, 46·6%].

Aminodi-o-tolylborane, (o-$CH_3C_6H_4)_2B{\cdot}NH_2$ - This was prepared in ether solution by method (2). After filtration (N_2) from triethylamine hydrochloride, the product was obtained by vacuum distillation (67·2% b.p. 86°-88°/10^{-3}mm. [By hydrolysis, found: (o-$CH_3C_6H_4)_2B$, 91·9%; NH_2, 7·6%, 7·4%; $C_{14}H_{16}BN$ requires (o-$CH_3C_6H_4)_2B$, 92·3%; NH_2, 7·7%.]

Diphenyl(diethylphosphine)borane, $Ph_2B{\cdot}PEt_2$

n-Butyllithium (0·025 mole) in dry benzene (50 c.c.) was slowly added to a solution of diethylphosphine (2·3g., 0·025 mole) in the same solvent at room temperature. Sufficient tetrahydrofuran (30 c.c.) was added to dissolve the pale yellow precipitate ($LiPEt_2$), and to the solution was slowly added chlorodiphenylborane (5g., 0·025 mole) in benzene (50 c.c.), and the yellow orange colour slowly disappeared. Water (100 c.c.) was added to the reaction mixture. The benzene layer when separated, dried ($MgSO_4$) and pumped dry, gave a colourless product, m.p. 192° from benzene (5·3g., 84%) (Found: C, 75·8; H, 7·9; B, 4·4; P, 12·0. $C_{16}H_{20}BP$ requires C, 75·6; H, 7·9; B, 4·35; P, 11·8%).

Di-p-bromphenyl(diethylphosphino)borane, $(p\text{-}BrC_6H_4)_2B{\cdot}PEt_2)$

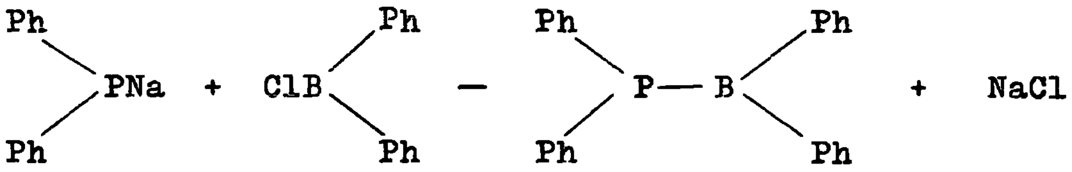
This was similarly prepared from chloro (di-p-bromphenyl)borane, and crystallised from benzene-hexane, m.p. 202°, 4·8g., 49% (Found: C, 45·9; H, 4·3: Br, 38·1. $C_{16}H_{18}BBr_2P$ requires C, 46·5; H, 4·4; B, 38·9%)

Addition of methyl iodide to a solution of the phosphinoborane in benzene gave an immediate white precipitate of methiodide, m.p. 310-312° (decomp.) (Found: I, 23·1, 23·3. $C_{17}H_{21}BBr_2IP$ requires I, 22·9%).

Diphenyl(diphenylphosphino)borane, [$Ph_2B{\cdot}PPh_2$]

Chlorodiphenylborane (5g) in dry benzene (50 c.c.) was added at room temperature to a mixture of diphenylphosphine (4·2g 0·025 mole) and triethylamine (2·5g., 0·025 mole) in benzene (50 c.c.). Part of the resulting thick white precipitate was dissolved by the addition of water, and the rest was separated by filtration, washed several times with ether, pumped dry, and the phosphinoborane collected by sublimation (240°/10^{-3}mm., 5·4g., 61%) [Found: C, 78·9; H, 5·6, $C_{24}H_{20}BP$ requires C, 82·3; H, 5·7% 0·1906g.,] warmed with aqueous alcoholic hydrogen peroxide, phenol separated by steam distillation and converted to the tribromo derivative, yielded tribromophenol, m.p. 95°-6°, 0·348g. $C_{24}H_{20}BP$ requires 0·359g. Diphenyl phosphinic acid (m.p. 195°-6°) was isolated, but not quantitatively from the steam distillation residue.

This compound was also prepared by method (1)



A deep red solution of the sodium derivative of diphenylphosphine (0·025 mole) in dry 2,5 dioxahexane (50 c.c.)

was slowly added to a solution of chlorodiphenylborane (5g., 0·025 mole) in the same solvent (50 c.c.) at -60°C. The solution was instantly decolourised and a white precipitate was formed. After treatment with de-aerated water (50 c.c.) and several washings with ether, the infra red spectrum of the water-insoluble solid product showed the presence of P-H bonds. Vacuum sublimation of the solid product afforded diphenyl (diphenylphosphino) borane ($240^{o}/10^{-3}$mm., 4·5g., 51%)

<u>Chlorodiphenyl(diphenylphosphine)borane</u>, $BClPh_2$ $PHPh_2$

Diphenylphosphine (4·2g., 0·025 mole) in dry benzene (25 c.c.) was slowly added to chlorodiphenylborane (5g., 0·025 mole) in benzene (20 c.c.). The white crystalline and very hygroscopic <u>adduct</u> (7·3g., 75%), m.p. 83-85°, was collected by filtration. (Found: Cl, 9·04, 9·08, $C_{24}H_{21}$ BCl P requires Cl, 9·18%)

<u>Triethylammonium chlorodiphenyl(diphenylphosphino)borate</u>

Et_3NH^+ $BClPh_2PPh_2^-$ - Diphenylphosphine (42g., 0·025 mole) in dry benzene (25 c.c.) was added dropwise to a mixture of chlorodiphenylborane (5g.,) and triethylamine (2·5g.) in benzene (25 c.c.). The colourless <u>salt</u> immediately precipitated was collected by filtration (9·3g., 77% m.p. 152-3°). (Found: C, 72·4; H, 7·7, B, 3·71, Cl, 6·9, Et_3N, 19·8. $C_{30}H_{36}BClNP$ requires C, 73·5; H, 7·4; B, 3·24; Cl, 7·1; Et_3N, 20·1%).

Diphenyl(di-m-tolylphosphino)borane, $Ph_2B\ P(C_6H_4\underline{m}\text{-}CH_3)_2$

A deep red solution of the sodium derivative of di-m-tolylphosphine (4·2g., 0·02 mole), prepared by adding freshly pressed sodium wire against a current of nitrogen into a solution of the phosphine in tetrahydrofuran (20 c.c.), was added to an equivalent amount of chlorodiphenylborane (4g.) in diethyl ether (20 c.c.) at room temperature. The solution was immediately decolourised and sodium chloride was precipitated. Most of the solvent was then removed by pumping the reaction mixture, and the residue was extracted with hot benzene. Evaporation of the benzene solution gave the colourless *phosphinoborane* (5·1g., 67%), m.p. 123-4°. (Found: C, 81·9; H, 6·3; $C_{26}H_{24}BP$ requires C, 82·4; H, 6·4%)

Di-m-tolylphosphinodi-p-tolylborane, $(\underline{p}\text{-}CH_3C_6H_4)_2B{\cdot}P\ (C_6H_4\text{-}\underline{m}\text{-}CH_3)_2$ m.p. 257-8° (from benzene-hexane, 5·4g., 67%) (Found: C, 80·9; H, 6·9, $C_{28}H_{28}BP$ requires C, 82·8; H, 6·9%) and *Di-p-bromophenyldi-m-tolylphosphinoborane*, $(p\text{-}BrC_6H_4)_2B{\cdot}P\ (C_6H_4\underline{m}\text{-}CH_3)_2$, m.p. 281° (from benzene-hexane 7·05, 66%) (Found: C, 60·2; H, 4·1; Br, 30·1. $C_{26}H_{22}BBr_2P$ requires C, 58·1; H, 4·1; Br, 29-9%) were similarly prepared from the sodium derivative of di-m-tolylphosphine and the appropriate chlorodiarylborane.

Phenyl(bis-diphenylphosphino)borane, $PhB(PPh_2)_2$

Dichlorophenylborane (4g., ca., 0·025 mole m.p. $5{\cdot}1^\circ$-$5{\cdot}5^\circ$ previously described as a liquid b.p. 62/11 mms)[265] in dry benzene (30 c.c.) was slowly added to a mixture of triethylamine (5·1g., 0·05 mole) and diphenylphosphine (9·3g., 0·05 mole) in the same solvent (50 c.c.) at room temperature. The reaction mixture was refluxed (24 hours) to ensure complete dehydrohalogenation before removal of the amine hydrochloride (m.p. 255°-6°) by filtration (N_2). A white solid and a small amount of yellow solid precipitated when the solution was pumped to low bulk. The white solid (m.p. 143-49·2g., yield 78%) was crystallised from benzene/hexane solution. (Found by oxidation PhB 17·5%, Ph_2P 79·8%, $C_{30}H_{25}BP$ requires PhB 18·0%, Ph_2P 80·9%.)

Prolonged heating of the colourless monomer (see Table 2) in benzene afforded more of the yellow involatile polymeric solid (m.p. 120°-32°) (Found by oxidation PhB 16·0%, Ph_2P 79·9% $C_{30}H_{25}BP$ requires PhB 18·0% Ph_2B 80·9%.)

The yellow solid contained no halogen and was insoluble in hydrocarbon, alcoholic, ketonic and ether solvents.

Both solids were unaffected by boiling dilute acids or alkali.

Dichlorophenyl(phenylphosphino)borane, $BCl_2Ph \cdot PH_2Ph$

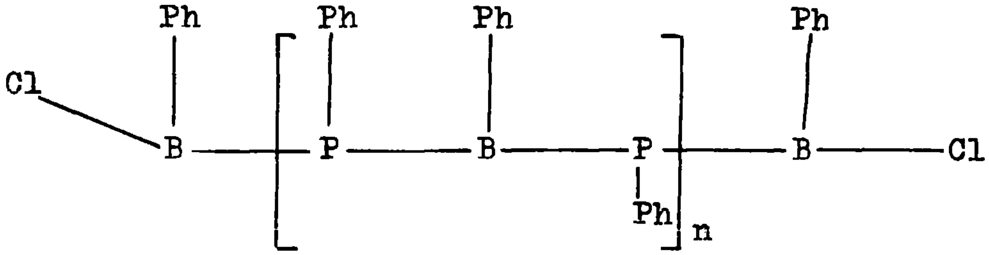
Dichlorophenylborane (4·0g, ca., 0·025 mole) in dry hexane (20 c.c.) was slowly added to an equimolar quantity of phenylphosphine (2·8g.,) in the same solvent. The white crystalline and extremely hygroscopic adduct was collected by filtration (N_2) in a Schlenk tube, washed with solvent and pumped dry (6·4., 74·8% m.p. 62-64° sealed tube)(Found: Cl 26·5, 26·8%, $C_{12}H_{12}BCl_2P$ requires Cl 26·4%).

Phenyl(phenylphosphino)borane, $(PhB \cdot PPh)_2$

Phenylphosphine (11g., 0·1 mole) was heated to reflux (6 hours) with an equimolar quantity of dichlorophenylborane (15·9g.,) until evolution of hydrogen chloride had ceased. Vacuum distillation afforded the colourless fuming liquid PhPH-BClPh (10-11g., b.p. 98-100°/10^{-3}mm) (Found: Cl 15·7, 16·1%, PhB (by hydrolysis) 38·2% $C_{12}H_{11}BClP$ requires Cl 15·4% PhB, 38·1%) and a yellow-red glassy solid residue which was extracted with hot benzene and filtered.)

The benzene solution afforded the white dimer (see Table 2) $(PhB \cdot PPh)_2$ (m.p. 89°-91°, 3·6g.,) (Found by oxidation PhB, 44·7; PhP, 55·6% $C_{12}H_{10}BP$ requires PhB, 44·8; PhP, 55·2%).

The involatile yellowish residue (11-12g., m.p. 168°-175°) was most probably a polymer containing B-Cl end groups. (Found Cl 1·3%, PhP 50·5%, PhB 42·8%)



(The value of n ≡ 15:20)

Di-m-tolylphosphino(di-mesiïtyl)borane $(2,4,6,CH_3C_6H_2)_2BP(pCH_3C_6H_4)_2$. The sodium derivative of di-m-tolylphosphine (0·025 mole) in tetrahydroguran (50 c.c.) was slowly added to dimesitylfluoroborane (6·7g., 0·025 mole) in the same volume of solvent at -30°C. After allowing the reaction mixture to slowly come to room temperature and refluxing (1 hour) it was filtered (N_2) from the white insoluble products. Sodium fluoride was removed by washing the precipitate several times with water and the insoluble compound was washed several times with ether and pumped dry. The tetrahydrofuran solution was pumped dry and afforded a further (1·2g.) of the compound (5·4g., yield 47% m.p. 264-5°). (Found: C, 81·5; H, 8·2; $C_{32}H_{36}BP$ requires C, 82·6; H, 7·9.)

(By oxidation $(2,4,6,CH_3C_6H_2)_2$ B, 55·3%; $(m\text{-}CH_3C_6H_5)_2$ P, 45·2% $C_{32}H_{36}BP$ requires $(2,4,6,CH_3C_6H_2)_2$ B, 55·3%; $(m\text{-}CH_3C_6H_5)_2$ P, 45·7%.)

After oxidation with aqueous alcoholic hydrogen peroxide the mesitol was separated from di-m-tolylphosphinic acid by treatment with sodium carbonate solution and extraction with ether. The compound was insoluble in ethers, hydrocarbons, ketones, alcohols, and chloroform and carbon tetrachloride.

Attempts to prepare the compound by the triethylamine method failed both in boiling benzene and xylene solutions.

Di-m-tolylphosphino(bis-biphenyl)borane, $(4\text{-}C_6H_5C_6H_4)_2BP(m\text{-}CH_3C_6H_4)_2$ (2·84g., 46% yield m.p. 77°-78°) was prepared by the triethylamine method in benzene solution. The insoluble compound was separated from triethylamine hydrochloride by several washings with water, washed with ether and pumped dry. The compound was insoluble in the organic solvents tried above. (Found: C, 85·8 ; H, 5·9 ; $C_{38}H_{32}BP$ requires C, 86·0; H, 6·0. By oxidation $(4\text{-}C_6H_5C_6H_4)_2B$, 58·6%; $(m\text{-}CH_3C_6H_4)_2P$, 39·9%; $C_{38}H_{32}BP$ requires $(4\text{-}C_6H_5C_6H_4)_2B$, 59·9%; $(m\text{-}CH_3C_6H_4)_2P$, 40·1%).

Bis-diphenyl(phenylphosphino)borane $[(Ph_2B)_2PPh]$

Chlorodiphenylborane (10g., 0·05 mole) in dry xylene (50 c.c.) was slowly added to a mixture of triethylamine (6·5 c.c. 0·05 mole) and phenylphosphine (2·6 c.c. 0·025 mole) in the same solvent (50 c.c.). The reaction mixture was refluxed (24 hours) to ensure complete dehydrohalogenation. After filtration (N_2), the solution was pumped to low bulk and afforded a white solid which crystallised from benzene/hexane solution (m.p. 148-50°) [Found: C, 81·8; H, 5·6, $C_{30}H_{25}B_2P$ requires C, 82·2; H, 5·7%, found by oxidation PhP, 24·2%; Ph_2B, 75·1% $C_{30}H_{25}B_2P$ requires PhP, 24·7%; Ph_2B, 75·3%].

Diphenylarsinodiphenylborane, [$Ph_2As{\cdot}BPh_2$]. -

Diphenylarsine (5·8g., 0·025 mole) was converted into its sodium derivative by reaction with excess sodium wire in tetrahydrofuran (50 c.c.) at room temperature. The ruby red solution was decanted (N_2) from excess sodium and was slowly added to chlorodiphenylborane (5g., 0·025 mole) in tetrahydrofuran (50 c.c.) at -60°, the red colour being immediately discharged. The reaction mixture was allowed to warm to room temperature, filtered (N_2) from precipitated sodium chloride, and the filtrate was pumped dry. The residue crystallised from benzene, gave the colourless arsinoborane (5·8g., 57%), m.p. 202-204° [Found: C, 72·6; H, 5·1. $C_{24}H_{20}AsB$ requires C, 73·1; H, 5·1%. 0·0944g. were boiled (10 mins) with aqueous alcoholic hydrogen peroxide. Phenol separated by steam distillation was converted to tribromphenol, 0·2966g.; $C_{24}H_{20}AsB$ requires 0·3190g. The aqueous residue was boiled for a few minutes with a trace of platinum black to remove excess peroxide, filtered, and boric and arsenic acids estimated volumetrically [(Found: B, 3·61; As, 18·6. $C_{24}H_{20}AsB$ requires B, 3·68; As 19·0%)].

The same compound (identical by mixed m.p. and by infra red spectrum) was obtained in 67% yield by the triethylamine method. A small amount of red insoluble material containing boron, arsenic and phenyl groups was also isolated but not identified.

Diphenylarsino(di-p-tolyl)borane, [(p-$CH_3C_6H_4)_2$ B·$AsPh_2$)] (7·3g., 69%), m.p. 224-225° (from benzene-hexane) [Found: C, 73·6; H, 5·6. $C_{26}H_{24}AsB$ requires C, 74·0; H, 5·7%) and diphenylarsino(di-p-bromphenyl)borane, [(p-$BrC_6H_4)_2B$·$AsPh_2$)] (7·5g., 67%), m.p. 244-245°(from benzene-hexane) [Found: C, 52·3; H, 3·4. $C_{24}H_{18}As\ B\ Br_2$ requires C, 52·2; H, 3·3%) were both prepared from the sodium derivative of diphenylarsine and the appropriate chlorodiarylboranes.

Boron Analysis

Boron was determined by the method described by D. E. Fowler and C. A. Kraus.[274]

A quantity of sample (containing 0·02-0·03g., of boron) was completely degraded by warming with concentrated sulphuric acid (5 c.c.,) in a two-necked flask. After cooling, dry (distillation from magnesium) methanol (40 c.c.) was slowly added from a dropping funnel. The reaction mixture was refluxed (15 mins) and then the methylborate was distilled through a short column and the first three 10 c.c., fractions were collected and mixed with an equal volume of water. The boric acid was titrated with $\frac{N}{10}$ sodium hydroxide in the presence of mannitol. [1 c.c. $\frac{N}{10}$ NaOH ≡ 0·0011g B].

Phosphorus Analysis

A weighed amount of sample (containing ca., 0·02g., of phosphorus) was heated at 500° (3-4 hours) with excess sodium peroxide in a bomb. After cooling the solid residue was extracted with boiling water and filtered from carbon. Ammonium nitrate (10g.,) and concentrated nitric acid (5 c.c.) were added to the solution which was warmed to 35° before the ammonium molybdate reagent[275] (50 c.c.,) was added. Phosphorus was then determined by the titrimeric procedure described by Vogel.[276]

DIPOLE MOMENT MEASUREMENTS

1. Theory of Dipole Moment Measurements

It was pointed out by Faraday[266] that the molecules of a dielectric when placed in an electric field become 'polarised' i.e. a separation of charge takes place. One end of the molecule acquires a small positive charge, the other a negative charge of equal magnitude.

Mathematical treatment of this statement led to the derivation of the Clausius and Mosotti law[267,268]

$$\frac{\varepsilon - 1}{\varepsilon - 2} \, \frac{1}{d} = p \qquad \dots\dots\dots\dots\dots\dots\dots \qquad (1)$$

where p is the specific polarisation, d is the density and ε the dielectric constant of the substance.

For a number of materials of low dielectric constant p remains constant despite changes in temperature and pressure, and is almost the same for the liquid or solid states.

It was shown by Maxwell[269] that for such materials the dielectric constant is related to the refractive index n for the same frequency of radiation by

$$n^2 = \varepsilon 0 \qquad \dots\dots\dots\dots\dots\dots\dots \qquad (2)$$

where ϕ is the magnetic permeability of the material.

As ϕ is almost equal to unity for all except ferromagnetic substances then if the values of the refractive index obtained in the visible region of the spectrum are extrapolated to the wavelength at which the dielectric constant is measured (virtually infinite wavelength) then

$$\varepsilon = n^2 \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \qquad (3)$$

For substances of high dielectric constant ε is almost invariably greater than n^2.

It was shown by Lorenz[270] and Lorentz[271] that $\frac{n^2 - 1}{n^2 - 2} \; \frac{1}{d} = r$ where r is a constant, independent of temperature, known as the specific refraction. The product of the molecular weight M and the specific refraction is known as the molecular refraction R.

$$R = \frac{n^2 - 1}{n^2 - 2} \; \frac{M}{d} \qquad \ldots\ldots\ldots\ldots\ldots\ldots \qquad (4)$$

Molecular refractions are additive, within certain limits, and by allocation of certain values to certain atoms and bonds, molecular refractions may be compiled. Molecular polarisation P obtained by multiplying the specific polarisation by the molecular weight would also be expected to be additive. It is found however that P is only additive for compounds of low dielectric constant where $\varepsilon = n^2$.

Debye[272,273] indicated that this behaviour could be explained by assuming that although a molecule as a whole is neutral the centres of positive and negative charge do not usually coincide and the molecule has a permanent doublet or dipole which tends to orientate itself in an electric field of relatively low intensity, (i.e. radio frequency). Thus the molecule shows polarisation by orientation besides charge displacement.

Indeed it would be fortuitous if any molecule other than a symmetrical one did not have some net permanent dipole due to the variation in electronegativity of the atoms of the molecule.

The magnitude of the electronic charge $4 \cdot 8 \times 10^{-10}$ e.s.u. and distances between small atoms 1 to 2×10^{-8} cms. It is found that dipole moments of most molecules lie between 0 and 9×10^{-18} e.s.u. or 0-9 Debye. (1 Debye $= 1 \times 10^{-18}$ e.s.u.) A further contribution to the total polarisation of a molecule is that due to the relative displacement of the atoms of the molecule in an electric field.

If a molecule contains polar bonds so that the atoms carry different effective charges then the nuclei are displaced with respect to one another and this produces an induced dipole the effect of which is superimposed on the permanent dipole if present and the dipole due to the displacement of the electrons with respect to the nucleus.

This type of polarisation is known as atom polarisation and together with orientation polarisation (due to orienting of permanent dipoles) and electron polarisation (that due to displacement of electrons) goes to make up the total polarisation.

Thus Total Polarisation (TP) = Atom Polarisation (AP) + Orientation Polarisation (OP) + Electron Polarisation (EP) .... (5)

For molecules with no permanent dipole and no atom polarisation the total polarisation is the same as the electron polarisation or TP = EP, and is identical with R if the value of n is obtained by extrapolation to infinite wavelength. As the values of R obtained for infinite wavelength usually only differ by 1 or 2 c.c. from those obtained at visible frequencies, often no correction for the difference is made in dipole moment calculations.

The Clausius and Mosotti theory considers each molecule as a sphere of dielectric and assumes that for small displacements of electrons with respect to the nucleus the induced moment m is proportional to the field F.

i.e. $m = \gamma F$ .... (6)

γ is called the polarisability of the molecule and is equal to the moment induced by a field of unit strength.

The treatment gives an equation for the molecular polarisation known as distortion polarisation, $P = \frac{4}{3}\pi N\gamma$ where N is Avogadro's number.

The Debye treatment which is concerned with a molecule with a permanent dipole μ inclined at an angle to an electric field F gives an expression for the molecular orientation polarisation

$$OP = \frac{4}{3} \pi \frac{N\mu^2}{3kT} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (7)$$

where k is Boltzmann's constant and T is the absolute temperature.

Thus the total polarisation is given by

$$TP = \frac{4}{3} \pi N \left(\gamma + \frac{\mu^2}{3kT} \right) \ldots\ldots\ldots\ldots\ldots\ldots \quad (8)$$

$\frac{4}{3}\pi N\gamma$ represents the polarisation a molecule would have in the absence of a permanent dipole and this may be divided up into atom polarisation and electron polarisation. From equation (7):

$$\mu = \sqrt{\frac{9kT}{4\pi N} \text{ O.P.}} \quad = \quad 0{\cdot}012812 \sqrt{\text{OP.T}}$$

As all dipole moment measurements were carried out at 25°, this can be further reduced to

$$\mu = 0{\cdot}2212 \sqrt{\text{OP.}} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (9)$$

II EVALUATION OF RESULTS

The expression for the polarisation of a solution, due to Debye[277,278] is:-

$$P = P_1f_1 + P_2f_2 = \frac{\varepsilon - 1}{\varepsilon - 2} \; \frac{M_1f_1 + M_2f_2}{d} \quad \ldots\ldots. \quad (1)$$

where P_1, P_2, f_1, f_2, are the total polarisations and mole fractions of solvent and solute respectively.

Halverstadt and Kumler[279] used specific volumes instead of densities and weight fractions instead of mole fractions. By assuming that the specific volume and dielectric constant of the solution are linear functions of the weight fraction (i.e. $\varepsilon = a + \alpha w_2$ and $v = b + \beta w_2$ where a and b are the dielectric constant and specific volume of the solvent, w_2 is the weight fraction of the solute), they derived an expression for the total specific polarisation at infinite dilution of the solute $\underline{p}_2$.

$$p_2 = \frac{3\alpha v_1}{(\varepsilon_1+2)^2} + \frac{\varepsilon_1 - 1}{\varepsilon_1 + 2} (v_1 + \beta) \quad \ldots\ldots\ldots\ldots \quad (2)$$

By plotting ε against w_2 and v against w_2, α and β may be evaluated.

In a similar manner the electron polarisation Ep_2

can be expressed as

$$Ep_2 = \frac{6\gamma n_1 v_1}{(n_1^2 + 2)^2} + \frac{n_1^2 - 1}{n^2 + 2}(v_1 + \beta) \ldots\ldots \quad (3)$$

where the assumption is made that $n = n_1 + \gamma w_2$ where n_1 is the refractive index of the solvent.

To obtain dipole moments by measurements on solutions the dielectric constant, refractive index and density of a number of solutions must be determined. By plotting ε, v, and n against w_2, obtaining α, β, and γ from the graphs, and fitting them in the equations then the total polarisation and electron polarisation of the compound being studied may be obtained.

At low concentrations ($w \not< 0{\cdot}02$) the plots are usually close to linear[280] and linear plots of n against w_2 may be obtained at still higher concentrations.

III. PHYSICAL MEASUREMENTS

1. Dielectric Constant Measurements

Benzene was used as solvent in all cases and the dielectric constants of air (ε_1) and benzene (ε_2) were assumed to be 1·0006 and 2·2727 respectively.

The principle used was the measurement of the change in capacitance which occurred when the dielectric of a condenser was charged.

The condenser was a cell[281] the dielectric of which could be changed easily by blowing out with nitrogen and replacing with the required liquids.

If ε_3 is the dielectric constant of the solution and C_1, C_2, and C_3 are the capacitances of the cell filled with air, benzene and solution respectively, then provided the lead capacitances remain constant

$$\frac{C_3 - C_1}{C_2 - C_1} = \frac{\varepsilon_3 - \varepsilon_1}{\varepsilon_2 - \varepsilon_1}$$

$$3 = \left(\frac{C_3 - C_1}{C_2 - C_1}\right) (\varepsilon_2 - \varepsilon_1) + \varepsilon_1$$

$$= \left(\frac{C_3 - C_2}{C_2 - C_1} + 1\right) (\varepsilon_2 - \varepsilon_1) + \varepsilon_1 \ldots\ldots\ldots \quad (1)$$

$C_2 - C_1 = 69{\cdot}05$ pfs, was measured by connecting an N.P.L. calibrated condenser in parallel with the cell and finding the necessary change in capacitance to restore balance when the dielectric was changed from air to benzene. $C_3 - C_2 = C$ was the change in capacitance measured on M, and since l is the reading on the condenser in cms, and the capacitance change per cm was 3·38 pfs, then from equation (1)

$$\varepsilon_3 = \left[\frac{3{\cdot}38\ l}{69{\cdot}05} + 1\right] \quad 1{\cdot}2721 + 1{\cdot}0006$$

$$= \left[\frac{3{\cdot}38\delta l}{69{\cdot}05}\right] \times 1{\cdot}2721$$

$$\alpha = \frac{d\varepsilon}{dw} = \frac{3{\cdot}38 \times 1{\cdot}2721}{69{\cdot}05}\frac{dl}{dw} = 0{\cdot}6227\frac{dl}{dw}$$

$\frac{dl}{dw}$ is the slope of the graph obtained by plotting the reading on the calibrated condenser against weight fraction.

A heterodyne beat capacitance meter similar to that designed by Sutton and Hill[282] was used to measure the capacitance change in the cell. This consisted of two units. The lower one was principally a beat frequency generator made up of two similar radio frequency oscillators one of fixed frequency f_o(approximately 10^5 c.p.s.) and one of variable frequency f_1 incorporating the measuring system. Also in the lower unit were the requisite circuits for mixing, demodulating, and beat frequency amplification. The two oscillators were made as nearly identical as possible so that any disturbances, e.g. fluctuations in temperature or supply voltage, affected both equally.

The upper unit contained a power pack, an audio frequency oscillator, and a cathode ray tube. The audio oscillator with frequency f_2 of about 1,000 c.p.s. could be varied by a coarse and a fine control to allow accurate adjustment. The X plates of the cathode ray tube carried the output from the beat frequency oscillator and the Y plates that of the audio frequency oscillator. Several adjustments were necessary to increase the stability of the system.[283]

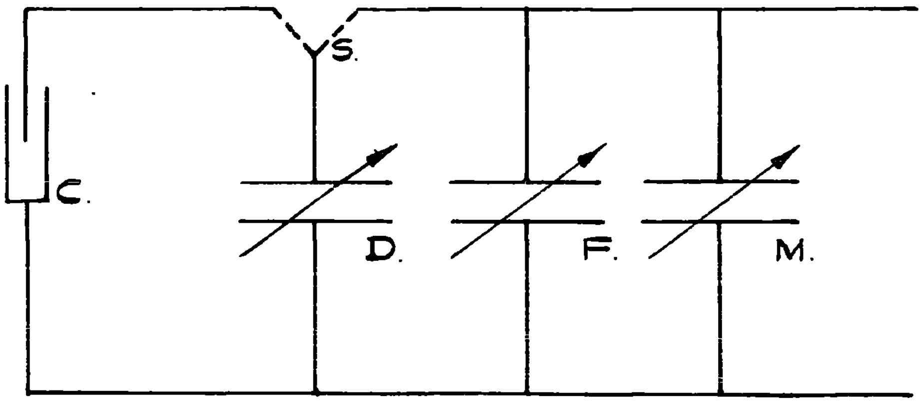
The cell was a modified form of the Sayce Briscoe[284] type with plates of platinum burnt onto the glass instead of deposited silver. This made the cell much more robust and allowed washing out with strong acid if necessary. The capacitance was approximately 50 p.f.s. The 25°C thermostat in which the cell was immersed was filled with transformer oil to reduce stray capacitances.

Procedure

The cathode ray tube was used to obtain the necessary relationship between the output frequency of the beat frequency generator and that of the audio frequency oscillator. As it was possible to obtain two identical beat frequencies, one with $f_o > f_1$ and one with $f_1 > f_o$ care was taken always to work with $f_o > f_1$. By varying F the output from the beat frequency generator was tuned to give a figure eight on the cathode ray tube corresponding to $f_o - f_1 = 2f_2$ this ratio prevented any likelihood of the oscillators pulling and was used as a balance point in all measurements.

The cell was washed out twice and then filled with dry benzene, the benzene used in washing out being expelled by a stream of nitrogen. The cell and contents were allowed to come to thermal equilibrium (10 mins) and F (see fig 1) was adjusted until the figure eight appeared on the cathode ray tube. D and M were then switched in and by adjustment the figure eight was again obtained. These last two operations were repeated since slight variance in the capacitance in the circuit containing F and the cell appeared to cause changes in the frequency of the circuit containing F, D and M, and vice-versa. When a steady figure eight was obtained on both sides of the switch the reading on M was noted.

FIG. I



The benzene was then blown out with dry nitrogen and the cell washed out and filled with the solution under test. The process of adjustment was repeated but this time only F and M were adjusted so that the change in capacitance could be read off on M.

The zero reading (i.e. the reading with the cell filled with benzene) was checked after each solution, as it occasionally showed a tendency to drift during a set of measurements.

(2) Specific Volume Measurements

A Sprengel type pyknometer of approx., 4 c.c. capacity fitted with ground glass caps to prevent evaporation was used. It was calibrated by P. S. Dixon.[284] All measurements were made at 25°C.

$$\text{Volume of pyknometer} = 4{\cdot}1521 \text{ c.c.}$$

$$\text{Specific volume} = \frac{4{\cdot}1521}{Wg} = v$$

where Wg is the weight of solution in the pyknometer

$$v = b + \beta w_2 = \frac{4{\cdot}1521}{Wg}$$

$$\beta = \frac{d\,\dfrac{4{\cdot}1521}{Wg}}{dw_2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

Thus is the slope of the graph of specific volume against weight fraction.

Procedure

The dry pyknometer was filled and placed in a 25°C thermostat (for 15 mins). The meniscus of the liquid was adjusted to the graduation mark by applying a piece of filter paper to the tip of the opposite limb and the pyknometer was removed from the thermostat, dried and the caps put in place. It was hung on the balance (20 mins) to allow to come to hygrometric equilibrium with the atmosphere and then weighed.

(3) Refractive Index Measurements

A Pulfrich refractometer with a divided cell was used, and it was enclosed in a 25°C air thermostat, which consisted of a large box (2'x 2' x 2') fitted with a glove and a terylene window through which one could take readings and see to make adjustments without opening the box.

The box was heated by an electrical sheet heater placed directly in front of a fan. The temperature was controlled by an a/c bridge thermoregulator with a platinum resistance thermometer as the arm of the bridge inside the box, thus giving a quick response to temperature fluctuations.

A 500 watt projector lamp especially set up with a convex lens system to give a strong parallel beam together with six interference filters (Jenear Glasswork Schott and Gen.) was used as a light source. The filters were checked by determining the refractivities of benzene with the red and blue lines of the hydrogen lamp and the sodium D lines. The red filter (λ max = 6620°A) was normally used for the measurements. For the centrosymmetric compound $(Ph_2BNH_2)_2$ refractive indices were measured at several wavelengths to allow an estimation of the electron polarisation at infinite wavelength to be made.

Procedure

The solution was placed in one side of the divided cell and a sample of pure dry benzene in the other. A polythene cap was placed on the cell to prevent evaporation, and the liquids allowed to come to thermal equilibrium (20 mins). The extinction angles were read off from the refractometer and the difference obtained. As differences rather than absolute refractivities were of primary importance, this technique minimised any errors which might be caused by temperature fluctuations. The relationship between the extinction angle and the refractive index of the solution was given by

$$n = \mathrm{Sin}\ A \sqrt{N^2 - \mathrm{Sin}^2 B} + \mathrm{Cos}\ A\ \mathrm{Sin}\ B$$

where A was the refractive angle of the prism

B the angle of emergence and

N the refractive index of the prism.

The graph of extinction angle against refractive index showed a linear relationship making computation of n values relatively simple. It was found that:-

1 min., of arc = 1087×10^{-7} from 7090 to 5893

A plot of Δn against w gave $\frac{dn}{dw}$ which corresponds to γ in equation 11(3).

(4) Total Polarisation

From equation 11(2) i.e. $$P_2 = \frac{3\alpha v_1}{(\varepsilon_1+2)^2} + \frac{\varepsilon_1-1}{\varepsilon_1+2}(v_1+B)$$

$v_1 = 1{\cdot}1447$ $\qquad$ $\varepsilon_1 = 2{\cdot}2727$

Then $P_2 = 0{\cdot}1881\alpha + 0{\cdot}2979\,(1{\cdot}1447+B)$ .... (3)

(5) Electron Polarisation

From equation 11(3) i.e. $$Ep_2 = \frac{6n_1\gamma v_1}{(n_1^2+2)^2} + \frac{n_1^2-1}{(n_1^2+2)}(v_1+B)$$

$v_1 = 1{\cdot}1447$ $\qquad$ $n_1 = 1{\cdot}4979$ (for sodium D line)

Then:

$Ep_2 = 0{\cdot}5712\gamma + 0{\cdot}2932\,(1{\cdot}1447 + \beta)$ [for $\lambda = 5985^{\circ}$A] (4)

For $\lambda = 7090$, $E.p._2 = 0{\cdot}5744\gamma + 0{\cdot}2894\ (1{\cdot}1447 + \beta)$

$\lambda = 6620$, $E.p._2 = 0{\cdot}5734\gamma + 0{\cdot}2906\ (1{\cdot}1447 + \beta)$

$\lambda = 5910$, $E.p._2 = 0{\cdot}5712\gamma + 0{\cdot}2931\ (1{\cdot}1447 + \beta)$

$\lambda = 5440$, $E.p._2 = 0{\cdot}5694\gamma + 0{\cdot}2952\ (1{\cdot}1447 + \beta)$

$\lambda = 4780$, $E.p._2 = 0{\cdot}5656\gamma + 0{\cdot}2997\ (1{\cdot}1447 + \beta)$

$\lambda = 4340$, $E.p._2 = 0{\cdot}5618\gamma + 0{\cdot}3041\ (1{\cdot}1447 + \beta)$

Values of $E.p._2$ at infinite wavelength were obtained by assuming that the values obtained for various values of λ fitted a simple equation of the form

$$E.p._2 = A + \frac{B}{\lambda^2}$$

The $E.p._2$ values were plotted against $\frac{1}{\lambda^2}$ and the curve obtained was extrapolated to $\frac{1}{\lambda^2} = 0$. This gave a value for A which was taken as $E.p._2$ at infinite wavelength.

EXPERIMENTAL

Dipole Moment Measurement for Ph_2BNPh_2

A Typical Series of Results

weight of flask	45·4805	48·7943	34·1301	22·7729
weight of flask + compd	45·5597	48·9070	34·3009	23·0099
Weight of flask + compd + benzene	63·4216	71·1250	57·5594	43·0825
weight of compd	0·0792	0·1077	0·1708	0·2370
weight of compd + benzene	17·8619	22·2180	23·2585	20·0726
weight fraction	0·04434	0·04847	0·07343	0·1178

Density

weight of pyknometer + solution	23·2983	23·2992	23·3008	23·3068
weight of pyknometer	19·6648	19·6648	19·6648	19·6648
weight of solution	3·6335	3·6344	3·6360	3·6420
Specific volume $\left(\frac{4\cdot 1521}{(\text{wt of soln})}\right)$	1·1427	1·1425	1·1420	1·1401

Dielectric

zero cms	2·459	2·459	2·459	2·459
solution reading	2·406	2·387	2·366	2·083
Δc. (cms)	0·053	0·072	0·093	0·476

Refractivity

λ 6620	12·20	13·00	14·20	17·50
change in angle	2·00	2·30	4·00	7·20
$\Delta n \times 10^6$	0·2166	0·2924	0·4332	0·7798

$$\alpha = 0{\cdot}06227 \times \frac{dc}{dw} \text{ (from Graph 1)} = 0{\cdot}06227 \times 10{\cdot}7$$

$$\beta = \frac{dv}{dw} = -\ 0{\cdot}3100 \text{ (from Graph 2)}$$

$$\gamma = \frac{dn}{dw} = 0{\cdot}0816 \text{ (from Graph 3)}$$

$$Tp_2 = 332{\cdot}8\ [0{\cdot}1881\alpha + 0{\cdot}2979(1{\cdot}1447 + \beta)]$$

$$= 332{\cdot}8\ [0{\cdot}1251 + 0{\cdot}2979(0{\cdot}6827)]$$

$$= 108{\cdot}3 \text{ c.c.}$$

$$Ep_2 = 332{\cdot}8\ (0{\cdot}5734 \times 0{\cdot}0816 + {\cdot}2906 \times {\cdot}6827)$$

$$= 84{\cdot}9 \text{ c.c.}$$

$\therefore$ $Ap_2 = 8{\cdot}49$ c.c. $Op_2 = 108{\cdot}3 - 93{\cdot}4 = 14{\cdot}9$ c.c.

$\therefore$ $\mu = 0{\cdot}2212\sqrt{14{\cdot}9} \equiv 0{\cdot}9$ D

$(2,4,6,CH_3C_6H_2)_2BNH_2$

weight fractions	specific vol.	$\Delta n \times 10^6$	ΔC (cms)
0·06764	1·1421	0·3790	0·218
0·11771	1·1417	0·6678	0·342
0·16980	1·1401	0·8664	0·383
0·27334	1·1395	0·9747	0·421

$\alpha = 0{\cdot}9771$, $\beta = -0{\cdot}1264$, $\gamma = 0{\cdot}0799$

$Tp_2 = 119{\cdot}1$ c.c. $Ep_2 = 90{\cdot}5$ c.c. $Ap_2 = 9{\cdot}1$ c.c.

Ph_2BNMe_2

0·06962	1·1479	0·1408	0·101
0·08814	1·1468	0·1507	0·119
0·17861	1·1461	0·6678	0·190
0·27374	1·1457	1·7508	0·260

$\alpha = 4{\cdot}331$, $\beta = -0{\cdot}1225$, $\gamma = 0{\cdot}07810$

$Tp_2 = 233{\cdot}9$ c.c. $Ep_2 = 155{\cdot}7$ c.c. $Ap_2 = 15{\cdot}6$ c.c.

$(p\text{-}BrC_6H_4)_2BNMe_2$

0·05181	1·1419	0·4512	0·452
0·07484	1·1410	0·6859	0·495
0·09573	1·1402	0·8844	0·985
0·10731	1·1393	0·9025	1·153

α = 6·119 β = - 0·393 γ = 0·08031

Tp_2 = 548·3 c.c. Ep_2 = 323·3 c.c. Ap_2 = 32·3 c.c.

$(p\text{-}CH_3C_6H_4)_2BNMe_2$

0·05211	1·1476	0·1444	0·083
0·08586	1·1464	0·3791	0·124
0·14311	1·1454	0·5957	0·192
0·23910	1·1442	0·7942	0·282

α = 0·9762 β = - 0·2901 γ = 0·0785

Tp_2 = 103·9 c.c. Ep_2 = 71·9 c.c. Ap_2 = 7·2 c.c.

$Ph_2BN(C_6H_4p\text{-}CH_3)_2$

0·03171	1·1431	0·2166	0·033
0·07026	1·1426	0·6661	0·071
0·09552	1·1417	1·0462	0·106
0·13774	1·1411	1·3711	0·140

α = 0·9504 β = - 0·5170 γ = 0·04740

Tp_2 = 234·4 c.c. Ep_2 = 165·8 c.c. Ap_2 = 16·6 c.c.

Ph_2BNH_2

0·05010	1·1433	0·3533	0·0310
0·07575	1·1417	0·5448	0·0417
0·11487	1·1405	0·8664	0·0594
0·13667	1·1401	1·1047	0·0602

$\alpha = 2{\cdot}047$ $\beta = -\ 0{\cdot}2298$ $\gamma = 0{\cdot}0552$ (average)

λ	$\frac{1}{\lambda_2}$	γ	Ep_2(c.c.)
4340	5308	0·0596	108·3
4780	4376	0·0588	106·7
5440	3380	0·0574	105·3
5910	2863	0·0594	104·6
6620	2282	0·0557	103·9
7090	1989	0·0527	103·1

Absolute Ep_2 (when $\frac{1}{\lambda_2} = 0, \lambda = o0$) = 100·3 c.c.

∴ Absolute $Ap_2 = Op_2 - Ep_2$ = 119·9 c.c. − 100·3 c.c. = 19·6 c.c.

Ph_2BPEt_2

weight fraction	specific vol.	$\Delta n \times 10^6$	ΔC(cms)
0·05254	1·1427	0·9379	0·030
0·07158	1·1424	1·1187	0·084
0·11536	1·1422	1·2744	0·107
0·18076	1·1418	1·4536	0·131

$\alpha = 0{\cdot}4905$, $\beta = -\ 0{\cdot}3109$ $\gamma = 0{\cdot}0402$

$Tp_2 = 92{\cdot}8$ c.c. $Ep_2 = 68{\cdot}0$ c.c. $Ap_2 = 6{\cdot}8$ c.c.

<u>$(p\text{-}BrC_6H_4)_2B\ PEt_2$</u>

0·03178	1·1433	0·2171	0·041
0·07139	1·1429	0·6709	0·081
0·09566	1·1420	1·0512	0·126
0·14704	1·1416	1·3822	0·158

$\alpha = 0{\cdot}7447$, $\beta = -\ 0{\cdot}2911$ $\gamma = 0{\cdot}0895$

$Tp_2 = 162{\cdot}5$ c.c. $Ep_2 = 132{\cdot}4$ c.c. $Ap_2 = 13{\cdot}2$ c.c

<u>$Ph_2B\ P(C_6H_4m\text{-}CH_3)_2$</u>

0·03689	1·1424	0·2888	0·277
0·06143	1·1420	0·5415	0·307
0·06930	1·1411	0·7761	0·424
0·11759	1·1399	1·3176	0·528

$\alpha = 2{\cdot}7103$, $\beta = -\ 0{\cdot}3244$, $\gamma = 0{\cdot}06221$

$Tp_2 = 472{\cdot}6$ c.c. $Ep_2 = 321{\cdot}7$ c.c. $Ap_2 = 32{\cdot}2$ c.c.

<u>$(\underline{p}\text{-}CH_3C_6H_4)_2B\ P(C_6H_4m\text{-}CH_3)_2$</u>

0·03386	1·1458	0·4657	0·460
0·06214	1·1425	0·5632	0·558

0·07148	1·1407	0·6981	0·609
0·09936	1·1398	0·8113	0·872

$\alpha = 29{\cdot}42$ $\beta = -\ 0{\cdot}4080$ $\gamma = 0{\cdot}1663$

$Tp_2 = 313{\cdot}8$ c.c. $Ep_2 = 125{\cdot}6$ c.c. $Ap_2 = 12{\cdot}6$ c.c.

$\underline{(p\text{-}BrC_6H_4)_2B\ P(C_6H_4m\text{-}CH_3)_2}$

0·08095	1·1427	0·2274	0·106
0·09894	1·1401	0·5848	0·111
0·11742	1·1396	0·6422	0·147
0·13411	1·1382	0·7914	0·199

$\alpha = 4{\cdot}531,$ $\beta = -\ 0{\cdot}3721$ $\gamma = 0{\cdot}0665$

$Tp_2 = 174{\cdot}1$ c.c. $Ep_2 = 144{\cdot}9$ c.c. $Ap_2 = 14{\cdot}5$ c.c.

$Ph_2B \cdot AsPh_2$

0·02687	1·1432	0·1354	0·091
0·04685	1·1425	0·4115	0·111
0·05724	1·1420	0·5307	0·119
0·09996	1·1401	0·8881	0·174

α = 0·9431 β = − 0·3076 γ = 0·0503

Tp_2 = 168·2, Ep_2 = 117·2 c.c. Ap_2 = 11·7 c.c.

$(p\text{-}CH_3C_6H_4)_2B\ AsPh_2$

0·05855	1·1424	0·2383	0·280
0·08084	1·1401	0·4440	0·405
0·12035	1·1396	0·6498	0·508
0·14371	1·1378	0·6972	0·638

α = 2·097 β = − 0·4201 γ = 0·0865

Tp_2 = 257·5 c.c. Ep_2 = 129·7 c.c. Ap_2 = 13·0 c.c.

$(p\text{-}BrC_6H_4)_2BAsPh_2$

0·03195	1·1448	0·0433	0·084
0·05145	1·1424	0·1625	0·097
0·07429	1·1409	0·2709	0·124
0·11322	1·1391	0·3046	0·137

α = 4·327 β = − 0·3649 γ = 0·04907

Tp_2 = 173·1 c.c. Ep_2 = 148·7 c.c. Ap_2 = 14·9 c.c.

DISCUSSION

Compounds in which an atom of acceptor character is covalently bound to one of donor character can achieve co-ordination saturation either by the formation of a double bond or by association. The first situation is exemplified by dimethylamino (dimethyl) borane, $Me_2B = NMe_2$, since the force constant of the B-N bond is appropriate for a double bond.[285] Similarly the force constant of the B-N bonds in trisdimethylaminoborane,[286] $(Me_2N)_3B$ is $5{\cdot}5 \times 10^5$ dyne cm^{-1} which is appropriate for bonds of order $^4/_3$. Valency expansion by the formation of a fourth sigma bond occurs in the dimeric forms of the chlorides, e.g. $(MeNBCl_2)_2$,[287] and in the much studied phosphinoboranes in which cyclic trimers $(Me_2PBMe_2)_3$[288] tetramers $(Me_2PBH_2)_4$ and polymers are found. No monomeric phosphino- or arsinoboranes appear to have been described, with the possible exception of $PH_2{\cdot}BMe_2$[289] and $Ph_3P{\cdot}BH_3$.[290]

The absence of any general rule which might be used to predict whether a compound of this type would be monomeric (and presumably contain a partial double bond) or associated suggested the need to obtain further data concerning (a) circumstances in which aminoboranes are associated and (b) the possible existence of monomeric phosphino- and arsinoboranes.

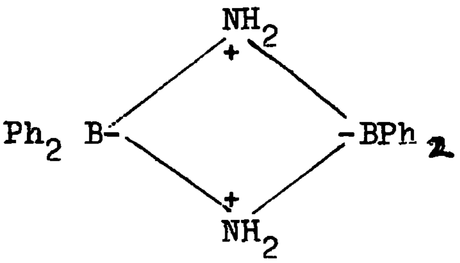
Aminoboranes - Unsubstituted aminoborane[291] appears to be polymeric, $(H_2B\cdot NH_2)_n$, and unstable. The extent of association decreases as hydrogen is substituted by alkyl groups: thus N-methylaminoborane is trimeric $(H_2B\cdot NHMe)_3$,[292] and reversible monomer-dimer equilibria may be realised with $H_2B\cdot NMe_2$,[293] $MeHB\cdot NMe_2$,[294] $Me_2B\cdot NHMe$[295] and $Me_2B\cdot NH_2$.[296] All known tetrasubstituted aminoboranes appear to be monomeric.[297]

Relatively few B-arylaminoboranes have been studied, but methylaminodiphenylborane, $Ph_2B\cdot NHMe$, slowly changes from monomer to dimer at room temperature;[298] all others described are monomeric.

Aminodiphenylborane was prepared from ammonia and chlorodiphenylborane in the presence of triethylamine,

$$Ph_2BCl + NH_3 + NEt_3 = \tfrac{1}{2}\,(Ph_2B\cdot NH_2)_2 + Et_3NHCl$$

and is dimeric (cryoscopically in benzene and nitrobenzene). The most likely structure (I) is centrosymmetric, and the observed electric polarisation is in agreement with this. The total polarisation, measured in benzene solution at 25°, was 119·9 c.c. The electron polarisation, measured at six wavelengths and extrapolated to infinite wavelength, was 100·3 c.c. and the difference, 19·6 c.c., is about the expected value of the atom polarisation in co-ordination compounds containing balanced dipoles (e.g. the atom polarisations of trans $(R_3P)_2$ $PdAr_2$ complexes are usually about 20 c.c.).[299] The dipole moment of (I) is therefore zero.



(I)

Thus the only dimeric aminodiarylboranes are those containing NH_2 or $NHCH_3$ groups. Experiments with molecular models indicate that any larger groups attached to the nitrogen would cause substantial steric interference even with the hydrogen atoms in ortho positions on the aryl groups.

All the other aminodiarylboranes prepared in this investigation were monomeric in nitrobenzene solution, though often slightly associated in benzene particularly in the more concentrated solutions.

The aminodiarylboranes, Ar_2BNR_2, were prepared by three methods:

$Ar_2BCl + LiNR_2 = Ar_2B{\cdot}NR_2 + LiCl$ .... (1)

$Ar_2BCl + R_2NH + Et_3N = Ar_2B{\cdot}NR_2 + Et_3NHCl$ ...... (2)

$2ArMgBr + Cl_2B{\cdot}NR_2 = Ar_2B{\cdot}NR_2 + MgCl_2 + MgBr_2$.... (3)

Method (3) was particularly suitable for the preparation of dimethylaminoboranes.[300]

The ultra-violet spectrum of diphenylaminodiphenylborane is similar in general appearance to that of tetraphenylethylene[301] (both measured in cyclohexane), absorption maxima and extinction coefficients being at 282 mu (18,200) and 312 mu (14,000) respectively.

The infra red spectra of these two compounds are nearly identical, the main differences being the splitting of the C_{ar}- H out-of-plane deformation bands (already reported,[313] and observed in all the diarylboranes used in this investigation) and the very strong band at 1372 cm^{-1} in the region in which B-N absorptions are commonly found.[314] The band due to B-N absorption was always strong and easily recognised in aminoboranes, and its frequency in the various compounds examined is given in Table 1, which also summarizes dipole moments and degrees of association in benzene and in nitrobenzene. The aminoboranes listed in Table 1 are all readily hydrolysed by cold water; this is a general property of aminoboranes and was the basis of a method sometimes used for their analysis.

The B-N frequencies of all but the first compound in Table 1 fall within the range 1330-1530[302] reported for eleven other aminoboranes. A variation in these frequencies has generally been interpreted as mainly due to a change in the multiplicity of the B-N bond, so the high frequency (1552) observed in the case of the dimeric compound (I), in which the B-N bonds must surely be single, may at first sight appear remarkably high. However, vibrational modes due to the stretching of B-N bonds in a ring can scarcely be expected to be closely comparable to those due to an isolated B-N bond in a monomeric compound.

Although the tetramethyl compound $Me_2B\ NMe_2$ contains a double bond, the large dipole moment expected from the formula $Me_2\overset{-}{B} = \overset{+}{N}Me_2$ is evidently very considerably reduced by unsymmetrical electron sharing in the sense $B \leftarrow N$ owing to the electronegativity difference between boron and nitrogen. The observed dipole moment^{303} is only $1{\cdot}40 \pm 0{\cdot}03$D ($1{\cdot}47 \pm 0{\cdot}06$D in $Me_2B{\cdot}NH_2$). Both Ph_2BNMe_2 and $Ph_2B{\cdot}NPh_2$ have such small dipole moments (1·6 and 1·0D) that it is not obvious which end of the molecule is positive. Examination of p-tolyl derivatives shows that the N-methyl compounds have polarities of different sign from those of the N-aryl compounds:

$$Ph_2\overset{\longleftarrow\!+}{B{\cdot}N}Me_2 \quad \text{and} \quad Ph_2\overset{+\!\longrightarrow}{B{\cdot}N}Ph_2$$

This reversal of polarity could be due to the electron repelling effect of a methyl group, whereas a phenyl group can act as an electron attractor in such a system. The change in moment, however, is rather large ($\mu = 2{\cdot}6D$ for the two compounds just mentioned). All the observed moments are consistent with the B-N bond having a small or zero net polarity.

Phosphinoboranes. The only monomeric phosphinoboranes previously mentioned are the not very well characterised compound $Me_2B\ PH_2$, which was described as being sensitive to hydrolysis, methanolysis and slowly forming a polymer in ether solution[304] and more recently triphenylphosphinoborane[305] which was found to be insensitive to water dilute acids or alkalies. In contrast to the tri- tetra- and polymeric phosphinoboranes of the type $R_2B{\cdot}PR'_2$ (R = H or alkyl, R' = alkyl or aryl), all the phosphinodiarylboranes prepared in this investigation are monomeric. Unlike the aminoboranes, the monomeric phosphinodiarylboranes are relatively resistant to hydrolysis. The diarylphosphino compounds are also unaffected by air.

Diphenyl(diphenylphosphino)borane ($Ph_2B{\cdot}PPh_2$) was prepared by method (2), chlorodiphenylborane being added to an equimolar mixture of diphenylphosphine and triethylamine. Addition of diphenylphosphine to the other reactants gives the salt $(Et_3NH)^+\ (Ph_2BCl\ PPh_2)^-$, and diphenylphosphine and chlorodiphenylborane alone give a third compound $Ph_2\overset{-}{B}Cl-\overset{+}{P}HPh_2$. Similar products were obtained from phenylphosphine and dichlorophenylborane. Diphenyl(diphenylphosphino)borane is not only insoluble in and undecomposed by water but is so sparingly soluble in organic solvents that neither its molecular weight nor its dipolemoment was measured. It is presumed to be monomeric or capable of reversible dissociation into monomer since it could be sublimed (240°) in vacuum (dimer or trimer would contain 8 or 12 phenyl groups).

To alter symmetry and obtain more soluble compounds derivatives of di-*m*-tolylphosphine were prepared by a modification of reaction (1) in which the sodium derivative of di-*m*-tolylphosphine in tetrahydrofuran was added to chlorodiphenylborane in the same solvent

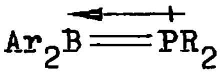
$$(\underline{m}\text{-}CH_3C_6H_4)_2PH + Na \xrightarrow{T.H.F.} Na^+(m\text{-}CH_3C_6H_4)_2P^- + \tfrac{1}{2}\ H_2$$

$$\xrightarrow{Ph_2BCl} Ph_2B{\cdot}P(C_6H_4\underline{m}\text{-}CH_3)_2$$

All the m-tolyl derivatives but two had adequate solubility both for molecular weight measurement in nitrobenzene and dipole moment measurement in benzene (in which they are sparingly soluble.)

The diarylphosphinoboranes prepared are listed in Table 2. The infra red spectra of the phosphorus compounds were very similar to those of their nitrogen analogues, and in all but [the compounds $PhP(BPh_2)_2$, PhBPPh, and $PhB(PPh_2)$ in which several strong bands appeared in the region (1450 - 1550 cm^{-1})] it was easy to distinguish the strong band almost certainly associated with stretching of the B-P bond. Since these bands (1400 - 1500 cm^{-1}) are at higher frequencies than those of the B-N bands in most of the aminoboranes studied, in spite of the mass of a phosphorus being greater than that of a nitrogen atom, the boron-phosphorus bonds in the monomeric phosphinoboranes would appear to have pronounced double bond character.

The monomeric phosphinoboranes might therefore be expected to have pronounced polar character, as indicated by the coordination formula (11)



$$Ar_2\overset{\longleftarrow\!\!+}{B=P}R_2$$

(11)

Moreover, since boron and phosphorus (and arsenic) have much the same electronegativities (in the range 1·9 - 2·1, however computed), the moment indicated in (11) should not be reduced by bond polarisation as in the aminoboranes (the electronegativity of nitrogen being about 3).

In fact, inspection of Table 2, bearing in mind the effect of methyl and bromo substituents on dipole moments, shows that the moments of the phosphinoboranes are larger than those of the corresponding aminoboranes, and that the phosphino group is at the <u>negative</u> end of the dipole (111)

$$Ar_2\overset{\longmapsto}{B - P}R_2$$

(111)

From Table 2 the dipole moment of (111, Ar = R = Ph) must be about 2·5D, that of (111, Ar = Ph, R = Et) being about 1·1D and in the same direction.

This surprising result suggests that phosphorus is acting as a <u>weak</u> π donor (to boron) in these compounds, possibly due to an unfavourable relation between the 'sizes' of B2<u>p</u> and P3<u>p</u> orbitals. In all the diarylboranes some electron flow is to be expected from the aryl group to the vacant boron 2<u>p</u> orbital, and in $Ph_2B{\cdot}PEt_2$ this could account for the greater part of the observed dipole. Good evidence for such effects can be seen by considering the difference (0.64D) between the moments of n-amyl dichloroborane and phenyldichloroborane (see fig., IV). The increased moment of the latter must be due to considerable polarisation of the Ph-B bond $(\overset{+}{Ph}\rightarrow\overset{-}{B})$.

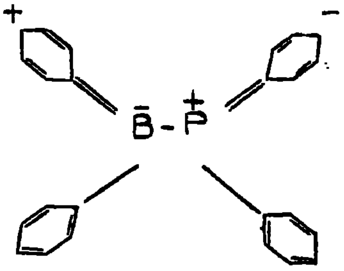
	μ
n-amyldifluoroborane	1·64
n-amyldichloro-	1·55
n-hexyldifluoro-	1·61

n-hexyldichloro-	1·55
phenyldifluoro-	1·90
phenyldichloro-	2·19
p-tolyldifluoro-	2·48
p-tolyldichloro-	2·68

[Fig. IV]

The large moment (1·97D) for chlorodiphenylborane with two such bonds seems to confirm these effects, and the relatively low moment (1·66D) for dimesitylfluoroborane where the aryl groups are almost certainly in different planes makes their presence almost definite. Though the boron atom in a diaryl(diethylphosphino)borane could thus be regarded as coordinatively saturated, or partly so, the phosphorus is not, and in fact the <u>diethyl</u> phosphino compounds add methyl iodide to form phosphonium salts $\left[Ar_2B{\cdot}PEt_2Me\right]^+I^-$.

In $Ph_2B{\cdot}PPh_2$ and related compounds the still larger moments would be due in effect, to conjugation both between boron and aryl and phosphorus and aryl as shown in the resonance formula (IV)



(IV)

Thus formulation accounts in a qualitative way not only for the observed dipole moments, but also for the lack of chemical reactivity since both boron and phosphorus are coordinatively saturated (or partly so). Further, the charge separation between boron and phosphorus indicated in (IV) should result in B-P force constants greater than would be expected for B-P single bonds, since the B-P bond would amount to a σ bond possibly with a small π component but with some electrostatic attraction in addition.

The relative importance of structures analogous to (IV) in the aminoboranes is almost certainly much less since boron and nitrogen achieve co-ordinative saturation by formation of a B = N double bond.

The reason for the phosphinodiarylboranes being monomeric, when the series $R_2B\cdot PR'_2$ (R = H, alkyl) form trimers, tetramers or polymers, thus lies in the boron atom in the diarylborane series being already co-ordinatively saturated (or nearly so) not by π-bonding with phosphorus but by π-bonding with the aryl groups.

Arsinoboranes - These were prepared from the chlorodiarylborane and the sodium salt of the diarylarsine in tetrahydrofuran; they are listed in Table (3). Infra red spectra again resembled those of the nitrogen and phosphorus compounds, but the tetraphenyl compound $Ph_2B\cdot AsPh_2$ was considerably more soluble in organic solvents than its phosphorus analogue. The diarylarsinoboranes resembled the phosphino analogues in their resistance to water and dilute acids or alkalies at 100°, but differed in their quantiative and analytically useful reaction with aqueous alcoholic hydrogen peroxide at room temperature:

$$Ph_2B\ PAr_2 + H_2O_2 - 2PhOH + H_3BO_3 + Ar_2PO_2H$$

$$Ph_2B\ AsAr_2 + H_2O_2 - 2PhOH + 2ArOH + H_3BO_3 + H_3AsO_4$$

The B-As absorption bands are at rather lower frequencies than those of B-P bands in analogues compounds, and in the same region as B-N bands.

The arsino group is, as in the phosphinoboranes, the negative end of the dipole, the moments being rather less. It is concluded that the electronic situation in the arsinoboranes resembles that in the phosphinoboranes, the smaller moments of the former being due to a smaller degree of electron transfer from arsenic to the aryl groups bound to it.

Though the σ-donor character of nitrogen, phosphorus and arsenic towards boron diminishes in the order N P As, it seems that the π-donor character diminishes even more rapidly.

APPENDIX

INTRODUCTION I

Until recently most borinic acids were prepared by the action of a Grignard reagent on an alkyl borate[307 a,b,c,] Letsinger who has recently revived interest in these compounds[308] in addition to preparing solid derivatives has prepared the first mixed borinic acids,[309] and the first tricyclic borinic acid.[310]

Good yields of di-butylborinic acids have recently been reported by Lappert and co-workers[311] from the reaction -

$$(Bu_2B)_2O + BF_3 \rightarrow Bu_2BOH$$

T. P. Povlock and W. T. Lippincott[312] have prepared several borinic acids as their amino-ethyl esters (21-63% yields) by reaction of trimethoxyboroxine and an aromatic Grignard reagent.

The quantitative hydrolysis of aminodiarylboranes to produce the amine and the arylborinic acid (described earlier in this thesis) has led to the investigation of this reaction as a preparative method for diarylborinic acids.

Several acids have been prepared and isolated as their amino-ethyl esters in good yields (51-93%).

EXPERIMENTAL

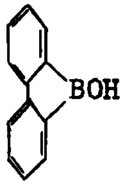
General Procedure

Phenylmagnesium bromide (0.25 mole) in dry ether was slowly added to dichlorodiphenylaminoborane[306] (0·1 mole) in benzene (100 c.c.) and after refluxing (½ hour) the reaction mixture was hydrolysed with dilute hydrochloric acid to pH 6-7, filtered and the layers separated. The organic layer was pumped dry and then extracted with hot water (50 c.c.) on a steam bath to remove any boronic acid. The borinic acid, a yellow oil, was separated dissolved in ether (50 c.c.) and monoethanolamine (22 c.c.) in an equal volume of water was added with vigorous stirring.

The precipitated ester was crystallised free of diphenylamine from ethanol (m.p. 188°-9°).

The ester was dissolved in a solution (100 c.c.) of equal volumes of acetone and methanol and hydrolysed with hydrochloric acid (12·5 c.c. conc. acid in 100 c.c. water). After shaking with ether (100 c.c.), the organic layer was separated, dried (Anhydrous $MgSO_4$) and pumped dry and afforded diphenylborinic acid (16·1g., yield 88%), see Table 4

TABLE 4

R in R_2BOR'		**ESTER** $R' = CH_2CH_2NH_2$						**ACID** $(R' = H)$					
				Found		Required				Found		Required	
		m.p.	yield%	C%	H%	C%	H%	m.p.	yield%	C%	H%	C%	H%
C_6H_5	I	188°–9°	93·4	74·1	7·1	74·6	7·2	216°	88·1	78·9	6·0	79·2	6·1
$o–CH_3C_6H_5$	II	184°	79·6	76·1	7·9	75·9	7·9	78°–9°	74·7	79·9	7·1	80·1	7·2
$p–CH_3C_6H_5$	II	186°	80·1	75·4	7·0	75·9	7·1	105°	71·4	78·9	7·2	80·1	7·2
$o–OCH_3C_6H_5$	IV	164°–5°	58·2	67·4	7·0	67·3	7·0						
$p–ClC_6H_4$	V	226°–7°	81·6	56·8	4·6	57·1	4·8	77°	75·2	57·0	3·5	57·4	3·6
$p–C_6H_5C_6H_4$	VI	219°	56·7	81·9	6·4	82·8	6·4		See note 1.				
$\alpha–C_{10}H_7$	VII	204°	51·4	80·9	6·1	81·2	6·2	117°	44·6	84·7	5·1	85·0	5·3
$C_6H_5C \equiv C$	VIII	172°–4°	58·1	78·8	7·1	79·1	7·4	98°–100°	52·5	83·3	4·6	83·4	4·8
$3,4–CH_3C_6H_3$	IX	204°–6°	72·0	76·1	8·4	76·8	8·6						
$p–BrC_6H_4$	X	236°–7°	56·4	43·3	3·6	43·8	3·7	84°–86°	50·2	42·0	4·6	42·4	4·6
	XI	170°–1°	61·2	75·3	6·2	75·1	6·3						

NOTES

(1) Only when required for further work, or better characterisation were the pure acids isolated.

(2) After difficulty in precipitating the monoethanolamine ester of di-p-tolylborinic acid, it was found that the esters were best precipitated from near neutral solutions.

(3) The esters II, VIII, X and XI were more soluble than normal in ether and pumping the ether solution dry followed by crystallisation from ethanol gave increased yields of these esters.

DISCUSSION

The high yields (51-93%) of esters and the use of only a slight excess (5-10%) of Grignard reagent indicate that the hydrolysis of aminodiarylboranes is the most convenient method of preparing pure diarylborinic acids.

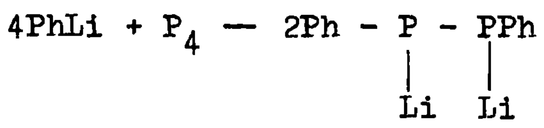
The variation in yields shows no relationship between the electronegativity of the aryl groups and the yield of acid obtained, though the lower yields of compounds IV, VI, VII and VIII suggest the importance of steric factors. Longer refluxing in these latter reactions would probably give better yields of these acids.

INTRODUCTION

If white phosphorus "P_4" has an available lone pair of electrons at each corner of the tetrahedral molecule, it would be expected to behave as a strong donor. This substance is certainly a powerful reducing agent, and it is adequately soluble in dry benzene.

These facts suggest that its reactions with boron trichloride and similar acceptors, and with organo lithium compounds, would be of interest. The only work so far described in the literature is by H. Moissan[313] who reports a vigorous reaction between boron triiodide and yellow phosphorus.

REACTION OF WHITE PHOSPHORUS WITH PHENYLLITHIUM



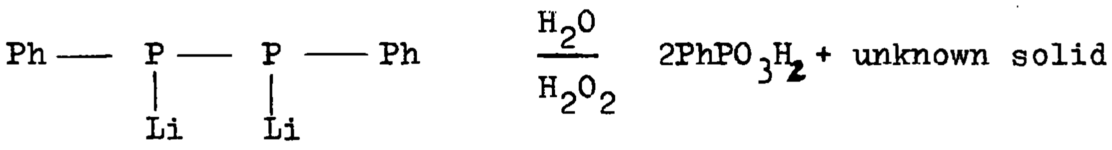
$$4PhLi + P_4 \text{ — } 2Ph - \underset{\displaystyle Li}{\underset{|}{P}} - \underset{\displaystyle Li}{\underset{|}{P}}Ph$$

Phenyllithium (0·32 moles) in ether was added to a solution of freshly distilled white phosphorus (9·9g. 0·32 moles P_4) in benzene (200 c.c.) at a rate sufficient to gently reflux the reaction mixture. The deep red solution was separated into two parts.

Part I

After careful hydrolysis with deaerated dilute hydrochloric acid to pH 6-7, the organic layer was separated (N_2) pumped dry and after boiling with aqueous hydrogen peroxide (3 c.c. of 100 volumes in 50 c.c. of water) afforded on cooling phenylphosphonic acid m.p. 158°-59° (2·8g. yield 55·1%), after filtration of the hot solution from an insoluble white solid (c.a., 4g.). The white solid was not identified although it was shown to contain phosphorus and phenyl groups.

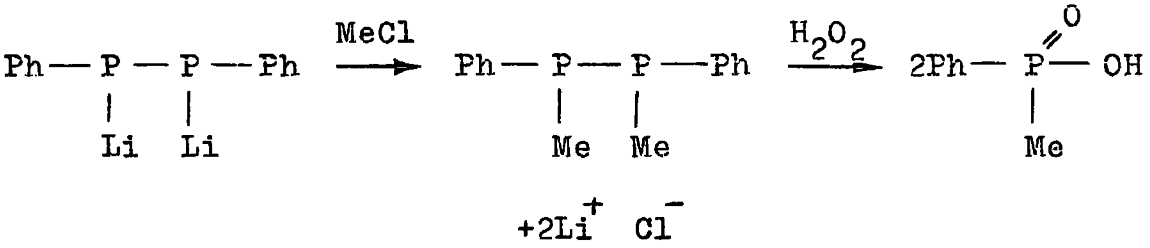
Infra spectroscopy indicated the presence of Ph-P, P = O and P - O - P bonds. The solid was insoluble in organic solvents, water and dilute alkali and soluble in dilute hydrochloric acid.



$$Ph - \underset{\displaystyle Li}{\underset{|}{P}} - \underset{\displaystyle Li}{\underset{|}{P}} - Ph \quad \xrightarrow[H_2O_2]{H_2O} \quad 2PhPO_3H_2 + \text{unknown solid}$$

Part II

Methyl chloride (c.a., 0·32 moles) was slowly bubbled via a flow-meter into the deep red solution (N_2) cooled to c.a., - 10°, until it became colourless. After filtration (N_2) from precipitated lithium chloride the filtrate was pumped dry and then boiled (30 mins.) with aqueous alkaline alcoholic hydrogen peroxide (4 c.c. of 100 volumes in 50 c.c. of 2N NaOH and 50 c.c. of alcohol). Dilute hydrochloric acid was added to adjust the pH 6-7, and the solution was extracted with ether. After pumping dry the ether extract and crystallisation from aqueous alcohol phenylmethylphosphinic acid m.p. 134°-5° was isolated and identified by infra red spectroscopy and mixed melting point. (2·6g. yield 53·1%).



$$\text{Ph}-\underset{\text{Li}}{\underset{|}{\text{P}}}-\underset{\text{Li}}{\underset{|}{\text{P}}}-\text{Ph} \xrightarrow{\text{MeCl}} \underset{+2\text{Li}^{+}\ \ \text{Cl}^{-}}{\text{Ph}-\underset{\text{Me}}{\underset{|}{\text{P}}}-\underset{\text{Me}}{\underset{|}{\text{P}}}-\text{Ph}} \xrightarrow{H_2O_2} 2\text{Ph}-\overset{\text{O}}{\overset{/\!/}{\underset{\text{Me}}{\underset{|}{\text{P}}}}}-\text{OH}$$

REACTION OF WHITE PHOSPHORUS WITH METHYLLITHIUM

Methyllithium (0·2 moles) in dry ether (300 c.c.) was slowly added (room temperature) to a solution of white phosphorus (6·3g., 0·2 moles P_4) in benzene (300 c.c.) and the reaction mixture was stirred (3 hours).

Methyl chloride was then slowly bubbled into the red-brown solution until it just turned white (c.a., 0·2 moles were added). After filtration (N_2), the solution was concentrated and a surprisingly volatile product (b.p. 25°-28°) distilled with the solvent. Addition of methyl iodide to the distillate afforded an immediate white crystalline solid (m.p. 310° decomp.) which was not identified. The infra-red spectrum of this compound showed the presence of CH_3-P and weak P-H absorptions.

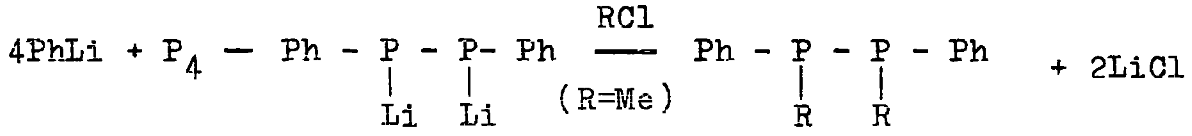
REACTION OF WHITE PHOSPHORUS WITH BORON TRICHLORIDE

Boron trichloride (12g.) in benzene (100 c.c.) at 6° was slowly added (N_2) to a solution of white phosphorus (3·1g., 0·1 mole) in the same volume of solvent at 4°. After stirring the reaction mixture (3 hours), distillation afforded unreacted boron trichloride and white phosphorus (3·0g.).

DISCUSSION

Since white phosphorus did not react with boron trichloride, which is quite a strong acceptor, further reactions were not attempted. It seems possible that hybridisation in phosphorus is such that there are no available lone pairs, a possibility being strained p-bonding with some delocalised bonding.

The reaction with phenyllithium may be a most convenient method of preparing aromatic biphosphines,



$$4PhLi + P_4 \longrightarrow Ph-\underset{Li}{\underset{|}{P}}-\underset{Li}{\underset{|}{P}}-Ph \xrightarrow[(R=Me)]{RCl} Ph-\underset{R}{\underset{|}{P}}-\underset{R}{\underset{|}{P}}-Ph + 2LiCl$$

The oxidation product phenylmethylphosphinic acid was isolated in reasonable yield (53·1%). The reaction with methyllithium was not fully investigated, but further investigation of these and related reactions is now in progress.

TABLE 1

Aminodiarylboranes

Aminodiarylborane	B–N absorption frequency, cm^{-1}	Dipole moment, Debye units	Degree of association			
			Benzene		Nitrobenzene	
			Weight %	n	Weight %	n
$Ph_2B\cdot NH_2$	1552^b (NHν , 3320 and 3362)^b	0	0·38	1·94	1·90	1·97
			0·43	1·97	3·37	1·87
			0·68	2·19	4·44	1·94
					5·27	1·93
$Ph_2B\cdot NMe_2$	1388^b	1·6	3·49	1·08	3·06	0·85
			4·43	1·24	4·41	0·95
			7·59	1·27	5·76	1·06
			9·95	1·17	7·52	1·14
$(p\text{-}CH_3C_6H_4)_2B\cdot NMe_2$	1410^b	1·1	0·63	0·93	2·07	0·98
			1·09	1·02	3·56	0·92
			1·42	1·16	4·66	1·02
			1·71	1·21	5·53	1·06
$(p\text{-}BrC_6H_4)_2B\cdot NMe_2$	1356^b	3·1	0·346	0·96	0·209	1·01
			0·588	0·91	0·479	1·09
			0·894	0·95	0·641	1·11
			1·034	0·99	0·743	1·14
$Ph_2B\cdot NPh_2$	1372^a	1·0	0·774	1·03	0·911	0·97
			1·152	1·31	1·431	0·94
			1·924	1·48	1·827	0·94
			2·259	1·74	2·249	1·10
$Ph_2B\cdot N(C_6H_4p\text{-}CH_2)_2$	1361^a	0·9			0·417	1·04
					1·228	1·09
					1·905	1·14
					2·536	1·25
$(p\text{-}CH_3C_6H_4)_2B\cdot NPh_2$	1385^a	1·7	0·424	1·02	0·579	0·99
			0·763	1·05	1·162	1·04
			1·297	1·14	1·647	1·05
			1·384	1·17	2·06	1·10

Table 1 continued

			Benzene	
$(2,4,6,CH_3C_6H_2)_2BNH_2$	1419[b]	1·0	0·648	1·03
			0·971	1·07
			1·116	0·99
			1·392	1·03
$(o\text{-}CH_3C_6H_4)_2BNH_2$	1450[b]	1·68	0·613	1·03
	(NH v, 3390 and 3490)[c]		0·733	1·03
			0·816	0·98
			1·224	1·10

[a] in KI disc, [b] in benzene solution, [c] contact film.

TABLE 2

Phosphinodiarylboranes

Compound	B–P absorption frequency, cm^{-1}	Dipole moment, Debye units	Degree of association			
			Benzene		Nitrobenzene	
			Weight %	n	Weight %	n
$\mathrm{Ph_2B\cdot PEt_2}$	1440^b	1·2	0·431	1·05	0·223	1·03
			0·801	1·12	0·509	1·12
			1·52	1·22	1·727	1·28
			1·96	1·54	2·466	1·39
$\mathrm{(\underline{p}\text{-}BrC_6H_4)_2B\cdot PEt_2}$	1412^a	0·8	0·172	1·01		
			0·283	1·12		
			0·885	1·16		
			1·571	1·27		
$\mathrm{Ph_2B\cdot PPh_2}$	1445^a	not sufficiently soluble, see text				
$\mathrm{Ph_2B\ P(C_6H_4\underline{m}\text{-}CH_3)_2}$	1482^a	2·3			0·348	1·00
					0·391	1·01
					0·477	0·89
$\mathrm{(\underline{p}\text{-}CH_3C_6H_4)_2B\cdot P(C_6H_4\underline{m}\text{-}CH_3)_2}$	1487^a	3·0			0·472	1·11
					0·943	1·17
					1·266	1·03
$\mathrm{(\underline{p}\text{-}BrC_6H_4)_2B\cdot P(C_6H_4\underline{m}\text{-}CH_3)_2}$	1480^a or 1425^a	0·8			0·421	0·97
					0·987	1·06
					1·19	1·15
$\mathrm{(4\text{-}C_6H_5C_6H_4)_2B\ P(C_6H_4m\text{-}CH_3)_2}$	1497^a	not sufficiently soluble				
$\mathrm{(2,4,6,CH_3C_6H_2)_2B\ P(C_6H_4m\text{-}CH_3)_2}$	1435^a	not sufficiently soluble				
$\mathrm{(PhBPPh)_n}$	1364^a		0·515	1·98		
			0·874	2·00		
			1·164	2·07		
			1·593	2·18		

Table 2 continued

$PhB(PPh_2)_2$			0·733	0·92
			1·101	1·01
			1·124	1·03
$(Ph_2B)_2PPh$	0·125	0·99		
	0·151	1·01		
	0·249	1·04		
	0·317	1·19		

[a] in KI disc, [b] in benzene solution

Table 3

Arsinodiarylboranes

Compound	B-As absorption frequency, cm^{-1} (KI disc)	Dipole moment, Debye units	Degree of association			
			Benzene		Nitrobenzene	
			Weight %	**n**	Weight %	**n**
$Ph_2B\cdot AsPh_2$	1369	1·4	0·333	1·09	0·447	1·04
			0·715	1·26	0·734	1·05
			1·891	1·76	1·802	0·99
			2·891	1·95	2·598	1·06
$(\underline{p}\text{-}CH_3C_6H_4)_2B\cdot AsPh_2$	1439	2·2	0·691	0·94		
			1·23	0·99		
			2·41	1·14		
			3·33	1·37		
$(\underline{p}\text{-}BrC_6H_4)_2B\cdot AsPh_2$	1370	0·5	0·704	1·04		
			1·29	1·12		
			2·44	1·31		
			2·98	1·38		

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