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UNSATURATED ORGANOBORON COMPOUNDS

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I. INTRODUCTION

The chemistry of organoboron compounds is at present undergoing intensive development. A number of reviews [1-8] dealing with different aspects of this subject have appeared within a comparatively short time interval.

The present review deals with achievements in the field of unsaturated organoboron compounds and covers the literature up to 1962, together with some later papers. It does not deal with alkylboranes containing unsaturated groups; there are two representatives of this class of compound – allyldecaborane [9] and di(allylamino)borane [10]. These compounds are of interest because of a number of unique features in their structure, the possibility of using them as monomers for the production of heat-resistant polymers, and their use as intermediate products in the preparation of a wide variety of boron compounds. Alkenylboronic and dialkenylborinic acids, their esters, and trialkenylborons exhibit more effective insecticidal and fungicidal properties than the analogous boron compounds with saturated radicals. On condensation with polyisocyanates and polyisothiocyanates, alkenylboronic acids give boron-containing polyamides. Polymers based on *p*-vinylphenylboronic acid may be used as materials which are readily shaped and rolled, and the copolymer of this acid with styrene can be formed into threads. The thioesters of chlorovinylboronic acid can be used as plasticisers and also as monomers for the production of film- and fibre-forming materials. The use of octadec-9-enylboronic acid derivatives as additives to poly(vinyl chloride) to improve certain of its properties has been suggested.

B-Allylborazoles can be used as additives to rocket fuels, active ingredients in insecticides, bactericides, and herbicides, and as components of heat-resistant compositions, plasticisers, scintillation indicators, additives to polymers to give neutron-absorbing properties, etc.

II. TRIALKENYLBORONS AND THEIR COMPLEXES

The first alkenylborons – methyldivinylboron, dimethylvinylboron, trivinylboron, dimethylpropenylboron, and methyldipropenylboron – were prepared by the reaction of vinylsodium and propenyllithium with dimethylboron bromide at low temperature [11-13]. An improved method for the preparation of unsymmetrical alkenylmethylboron compounds involves the reaction of chlorodivinylboron or di-

chlorovinylboron with dimethylzinc[14]. Trivinylboron[15] can be obtained in 70% yield by the reaction of vinylmagnesium bromide with boron trifluoride in absolute ethyl ether with a threefold excess of magnesium. Trivinylboron and tripropenylboron were prepared in low yield by the reaction of vinylmagnesium chloride and propenylmagnesium chloride respectively with boron trichloride in tetrahydrofuran[16]. Tripropenylboron can also be obtained from propenylmagnesium chloride and the ether addition compound of boron trifluoride[17]. The same method has been used to prepare tributenylboron, tripentylboron, and trihexenylboron[18].

The first report of a synthesis of triallylboron[19] appeared in the patent literature in 1954. More detailed information on the preparation of triallylboron by the reaction of boron trifluoride or trichloride with allylmagnesium halides appeared in 1958[20,21]. A method has been proposed for the preparation of triallylboron[22] from allylaluminium bromide $(C_3H_5)_3Al_2Br_3$ and butyl borate or the ether addition compound of boron trifluoride.

Tri-2-methallylboron was prepared from the corresponding organomagnesium halide and boron halides or borate in ether at 20–60°.[23]

Tri-*p*-styrylboron[24] and tri-ω-styrylboron[25] were prepared by the reaction of *p*- and ω-styrylmagnesium bromide respectively with boron trifluoride.

Petrov *et al.*[26] reported the preparation of dibutyl(isopropenylethynyl)boron according to the scheme

$$(C_4H_9)_2BCl + BrMgC{\equiv}C{-}C(CH_3){=}CH_2 \xrightarrow{\text{ether}} (C_4H_9)_2BC{\equiv}C{-}C(CH_3){=}CH_2 + MgBrCl.$$

Some acetylenic compounds of boron were prepared from acetylenedimagnesium bromide and dialkylboron iodides[27,28]. Disproportionation of di-(2-chlorovinyl)boron chloride in the liquid phase at 140–190° in the absence of catalyst with the simultaneous distillation of the resulting 2-chlorovinylboron dichloride was used to prepare tri-(2-chlorovinyl)-boron[29,30].

Activated carbon inhibits the disproportionation of di-(2-chlorovinyl)boron chloride to tri-(2-chlorovinyl)boron. Di(chlorovinyl)ethylboron was prepared by the analogous thermal disproportionation of (2-chlorovinyl)ethylboron chloride[30].

An attempt to prepare (2-chlorovinyl)diethylboron by the vinylation of diethylboron chloride and disproportionation of di(chlorovinyl)ethylboron was unsuccessful[30,31]. In the vapour phase the reaction between boron trichloride and acetylene in the presence of typical vinylating catalysts gave, in addition to the halogeno-compounds, a small quantity of tri-(2-chlorovinyl)boron[32]. An attempt to prepare this compound by the reaction of acetylene with di-(2-chlorovinyl)boron chloride at 140–180° was unsuccessful[30].

Tri(perfluorovinyl)boron was prepared in good yield by the reaction of dimethyldi(perfluorovinyl)tin with di(perfluorovinyl)boron chloride in the ratio 1 : 2 at 50°.[33] It is suggested that trialkenylborons are formed as intermediate products in the hydroboration of acetylene derivatives, for example pent-2-yne and hex-2-yne[34]:

$$3R{-}C{\equiv}C{-}R + {}^1/_2(BH_3)_3 \xrightarrow{0^\circ} \begin{pmatrix} R{-}C{-}H \\ \| \\ R{-}C{-} \end{pmatrix}_3 B.$$

The treatment of alkynes with inner multiple bonds, such as hex-3-yne, with hydroborating agents gives the corresponding vinylboron compounds. Under the same conditions, α-alkynes, for example hex-1-yne, undergo chiefly dihydroboration[35]. The hydroboration of but-1-yne, pent-1-yne, and hex-1-yne by *t*-butylborine-trimethylamine proceeds vigorously according to the equation[36]

$$t\text{-}C_4H_9BH_2.N(CH_3)_3 + 2RC{\equiv}CH \rightarrow t\text{-}C_4H_9B(CH{=}CHR)_2 + N(CH_3)_3.$$

The reaction of sodium tetracyclohex-1-enylborate with lead naphthenate gives tricyclohex-1-enylboron and tetracyclohex-1-enyllead[37].

Sodium tetra(phenylethynyl)borate was prepared by the reaction of boron halides with an excess of phenylethynylsodium at -60°. The reaction apparently takes place in two stages; the initial product is $(C_6H_5C{\equiv}C)_3B$, which then adds on a molecule of phenylethynylsodium[38]. The magnesium salt $Mg[B(C{\equiv}C{-}C_6H_5)_4]_2$ was prepared by the reaction of phenylethynylmagnesium bromide and boron trifluoride

$$2BF_3 + 8C_6H_5C{\equiv}C{-}MgBr \rightarrow 3MgF_2 + 4MgBr_2 + Mg[B(C{\equiv}CC_6H_5)_4]_2.$$

The addition of NH_4^+ ions to an aqueous solution of this salt precipitates ammonium tetra(phenylethynyl)borate $NH_4[B(C{\equiv}CC_6H_5)_4]$ quantitatively[39]. Sazonova and Kronrod[40] prepared this compound by the reaction

$$KBF_4 + C_6H_5C{\equiv}CMgBr \rightarrow [KB(C{\equiv}CC_6H_5)_4] \xrightarrow{NH_4Cl} NH_4B(C{\equiv}CC_6H_5)_4.$$

Acidification of the above salts gives tri(phenylethynyl)-boron, which was separated in the form of molecular compounds with tetrahydrofuran, amines, and pyridine[41].

When the dimethylamine addition compound of diethyl ethylboronate was boiled with $C_4H_9C{\equiv}CNa$ for 1 h in ether, the product was the amine complex of ethyldi(hex-1-ynyl)-boron $C_2H_5(C_4H_9C{\equiv}C)_2B.NH(C_2H_5)_2$. In the same way $CH{\equiv}CNa$ and boron trifluoride in pyridine gave a dark red precipitate consisting of the complex compound $(HC{\equiv}C)_3B.NC_5H_5$. The ether addition compound of boron trifluoride under analogous conditions (or a solution of BF_3 in hydrocarbons) at -70° gave $Na[B(C{\equiv}CH)_4]$. Di(methylethynyl)-magnesium $(CH_3C{\equiv}C)_2Mg$ and $Cl_3B.NH(CH_3)_2$ in pyridine at 0° rapidly (15 min) gave $(CH_3C{\equiv}C)_3B.NH(CH_3)_2$.[42] Some complexes of tri(phenylethynyl)boron with Lewis bases were described by Ashby and Foster[43].

When triphenylboron and phenylethynyllithium were heated in ether and then cooled to -70°, the complex $Li[B(C_6H_5)_3(C{\equiv}CC_6H_5)]$ was formed[44]. The reaction of $F_3B.NC_5H_5$ with (phenylethynyl)magnesium bromide at different reagent ratios gives only $Mg[B(C{\equiv}CC_6H_5)_4]_2$.[45] The reaction of $(C_6H_5)_2BOCH_2CH_2NH_2$ with $RC{\equiv}CMgBr$ gave the compounds $(C_6H_5)(RC{\equiv}C)B.NC_5H_5$ (where R = H, CH_3, C_6H_5, *p*-BrC_6H_4, 9-methylanthryl, $(CH_3)_3Si$, $(CH_3)_3SiCH_2$, C_2H_5S, and $(C_6H_5)_2B.NC_5H_5$).[45]

Vinylboron compounds are of interest, since the π electrons of the vinyl group are close to a boron atom with an empty p_π orbital, so that a mesomeric effect is produced:

$$CH_2{=}CH{-}B\langle \longleftrightarrow {}^+CH_2{-}CH{=}\bar{B}\langle .$$

This effect has a considerable influence on the properties of alkenylborons. Thus the presence of the vinyl or propenyl group stabilises the corresponding unsymmetrical compounds. The degree of decomposition of dimethylvinylboron kept for 5 days at room temperature was 33%. The presence of a second vinyl group increases the stability of the compound. Thus methyldivinylboron remained almost unchanged after boiling for 1 h at 100° and only slight decomposition was observed when the compound was heated at 100° for 70 h. The increased stability of these compounds is due to the fact that the phenomenon of mesomerism in alkenylboranes facilitates the production of a

planar configuration in the compounds and hence inhibits their disproportionation[12].

Trivinylboron is monomeric in the gaseous state but in the liquid phase it changes from the monomeric to the dimeric form and compounds of high molecular weight[46]. When heated at 226° for 4 h, tri-(2-chlorovinyl)boron decomposes partly to acetylene, hydrogen chloride, and di-(2-chlorovinyl)boron chloride[30]. Tri(perfluorovinyl)-boron in the gaseous phase does not undergo appreciable decomposition after 7 days at room temperature, but when heated at 100° for 5 h it decomposes completely to perfluorovinylboron difluoride and boron trifluoride[33].

Diallyldiborane and tetraallyldiborane were obtained by boiling triallylboron in an atmosphere of nitrogen[47].

The decomposition temperatures of the complexes of amines with tri(phenylethynyl)boron lie between 210° and 220°.[41]

$$C_6H_5C{\equiv}CB\langle \cdot NH_3 \rightarrow C_6H_5C{\equiv}CH + \rangle B \cdot NH_3 .$$

Unlike saturated compounds of boron, trivinylboron is not oxidised in contact with dry air at 25°. The behaviour of methyldivinylboron towards oxidation is intermediate between that of trivinylboron and that of the readily-oxidised trialkylborons.

Tri-(2-chlorovinyl)boron and (2-chlorovinyl)diethylboron are oxidised rapidly in air with spontaneous ignition[30]. Similar behaviour is shown by triallylboron, tributenylboron, tripentylboron, and trihexenylboron[18,19]. Tri(perfluorovinyl)boron ignites in air and burns with a smoky flame[33]. Organoboron compounds with triple bonds are extremely readily oxidised[27,45,48]. Unsaturated organoboron compounds obtained by hydroboration of the corresponding unsaturated hydrocarbons readily undergo protolysis by glacial acetic acid at 0° to form the corresponding *cis*-olefins[34,35]:

$$\left(\begin{matrix} R{-}C{-}H \\ \| \\ R{-}C{-}- \end{matrix}\right)_3 B + CH_3COOH \xrightarrow{0^\circ} 3\begin{matrix} R{-}C{-}H \\ \| \\ R{-}C{-}H \end{matrix} + B(OCOCH_3)_3 .$$

Tri-(2-chlorovinyl)boron and (2-chlorovinyl)diethylboron are readily hydrolysed in air and acetylene is liberated on treatment with a 10% solution of alkali[30]. The reaction of water with tri(perfluorovinyl)boron at 120° for 15 h gives trifluoroethylene; this reaction does not take place at room temperature[33]. The corresponding dialkylborinic acids R_2BOH are formed by the hydrolysis of the compounds $R_2BC{=}CBR_2$.[27]

Vinyl derivatives of boron, and also tributenylboron, tripentenylboron, and trihexenylboron, are unaffected by water at room temperature[12,18]. The complexes of tri-(phenylethynyl)boron with amines are not decomposed by water; the compound $(C_6H_5C{\equiv}C)_3B.OC_4H_8$ is decomposed slowly by cold water and the reaction with water at 50° leads to complete decomposition:

$$(C_6H_5C{\equiv}C)_3B \cdot OC_4H_8 + 3H_2O \xrightarrow{50^\circ} B(OH)_3 + 3C_6H_5C{\equiv}CH + C_4H_8O .$$

The reaction of the complex of tri(phenylethynyl)boron with alcohols leads to the formation of phenylacetylene and trialkyl borate[41].

Treatment with ammoniacal silver hydroxide solution gives methane and hexa-2,4-diene from methyldipropenylboron, and ethylene and butadiene from trivinylboron[12]. Treatment of the complex $Li[B(C_6H_5)_3(C{\equiv}CC_6H_5)]$ with acids at -30° gives phenylacetylene, and the reaction with aqueous iodine solution gives phenylethynyl iodide[43].

Treatment of tributenylboron with a solution of bromine in carbon tetrachloride at a molar ratio of 1 : 3 apparently leads to the addition of bromine across the double bond. A slight excess of bromine is slowly decolorised with the liberation of HBr.[18] Triallylboron reacts readily with bromine at -35° with rupture of the B–C bond and the formation of 1,2,3-tribromopropane as chief product[22].

On hydrogenation under pressure over Raney nickel as catalyst at room temperature, triallylboron adds on 3 moles of hydrogen with the formation of tripropylboron[22]. Hydrogenation of $(C_6H_5)_2(RC{\equiv}C)B.NC_5H_5$ in the presence of platinum gives $(C_6H_5)_2(RCH_2CH_2)B.NC_5H_5$.[45]

Trivinylboron adds on $HSi(CH_3)_2OSi(CH_3)_3$ under the influence of hydrogen chloroplatinate(II) at 100°[48]:

$$3HSi(CH_3)_2OSi(CH_3)_3 + (CH_2{=}CH)_3B \rightarrow [(CH_3)_3SiOSi(CH_3)_2CH_2CH_2]_3B .$$

Mikhailov and Tutorskaya found that at -15° triallylboron reacts with an equimolar quantitiy of ethanethiol to give propene and ethyl di(allylthio)borinate. The action of 2 moles of ethanethiol gives diethyl allylthioborinate[49].

The reactions of triallylboron with carboxylic acids and alcohols have been studied in detail[20,21,50]. Thus the reaction with glacial acetic acid gives diallylboron acetate and the reactions with ethanol and allyl alcohol give diethyl and diallyl allylboronates respectively.

An alcoholic solution of ammonium tetra(phenylethynyl)-borate is decomposed almost quantitatively by ammoniacal copper(I) chloride solution with the formation of yellow copper phenylacetylide and by mercury(II) iodide with the formation of di(phenylethynyl)mercury[40].

III. ALKENYLBORONIC AND DIALKENYLBORINIC ACIDS AND THEIR ANHYDRIDES

The first representative of this class of compound — 2-chlorovinylboronic acid — was prepared by Arnold in 1946.[32] Later it was found that this acid is formed by the decomposition of 2-chlorovinylboron dichloride with water and is stable in air[52]. Di-(2-chlorovinyl)boronic acid was obtained as a colourless liquid by hydrolysing di-(2-chlorovinyl)boron chloride. This acid readily liberates acetylene when treated with aqueous alkali[52].

A number of alkenylboronic acids — vinylboronic, isopropenylboronic, and 1-methylvinylboronic — were prepared by Normant and Braun[17,53,54] according to the following general scheme

$$\rangle C{=}C{-}MgX + B(OCH_3)_3 \rightarrow \rangle C{=}C{-}B(OCH_3)_2 \xrightarrow{H_2O} \rangle C{-}C{-}B(OH)_2 .$$

The anhydrides of the above acids are formed by azeotropic dehydration or by heating *in vacuo*. The anhydrides add on water and alcohols to give the corresponding boronic acids and their esters. Ammoniacal $AgNo_3$ solution decomposes these acids slowly in the cold and rapidly with heating, to give the corresponding olefins and metallic silver. Hydrogen peroxide and other peroxides break the boron–carbon bond with conversion of the original compounds to the corresponding aldehydes and ketones[54]:

$$\rangle C{=}C{-}B\langle \xrightarrow{H_2O_2} \rangle C{=}C{-}OH \rightarrow \rangle CH{-}C{=}O .$$

Isobutenylboronic acid was prepared in 7% yield by the reaction of isobutenyllithium with trimethyl borate with subsequent hydrolysis of the reaction product[55]. Hydrolysis of n-butyl vinylboronate and n-butyl 1-methylvinylboronate gave the corresponding acids[56].

The action of chlorine on n-butylboronic anhydride gave n-butenylboronic anhydride and hydrogen chloride. Treatment of this anhydride with aluminium chloride gave two products, unstable at room temperature, which were not identified[57].

Allylboronic acid was isolated as its anhydride by the reaction of triallylboron with water:

$$(C_3H_5)_3B + 2H_2O \rightarrow \underset{\downarrow}{[C_3H_5B(OH)_2]} + 2C_3H_6.$$
$$(C_3H_5BO)_3$$

The first stage of the reaction apparently involves the formation of diallylborinic acid, which undergoes further hydrolytic splitting at the boron–carbon bond[21]. The preparation of diallylborinic anhydride by the hydrolysis of methyl diallylborinate was also reported by Rothstein and Saville[58]. This anhydride decomposes slowly in air to boric acid. Allylboronic acid was prepared by Roigh and Erikson[59].

A much more stable product is styrylboronic acid, which can be kept unchanged for a prolonged period. It is prepared from styrylmagnesium bromide and potassium fluoroborate with subsequent hydrolysis and oxidation of the resulting complex salt[37]:

$$C_6H_5CH{=}CHMgBr + KBF_4 \rightarrow [KB(CH{=}CHC_6H_5)_4] \xrightarrow[O_2]{H_2O} C_6H_5CH{=}CHB(OH)_2.$$

Mel'nikov and Rokitskaya[60] prepared this acid from styrylmagnesium bromide and isobutyl borate. When dried, the acid is partly converted to the anhydride. The addition of an ethereal solution of $FeCl_3$ to an ethereal solution of styrylboronic acid leads to rapid formation of the anhydride. Cryoscopic measurements in benzene show that this exists as the dimer. The chemical properties of styrylboronic acid are analogous to those of arylboronic acids. When heated with mercury(II) chloride it readily forms styrylmercury chloride:

$$C_6H_5CH{=}CHB(OH)_2 \xrightarrow{HgCl_2} C_6H_5CH{=}CHHgCl.$$

The action of thallium trichloride gives distyrylthallium chloride[40]:

$$2C_6H_5CH{=}CHB(OH)_2 \xrightarrow{TlCl_3} (C_6H_5CH{=}CH)_2TlCl.$$

The preparation of *p*-vinylphenylboronic acid from *p*-vinylphenylmagnesium bromide and trimethyl borate at -70° with subsequent hydrolysis of the reaction product has been proposed[53,61,62]. The highest yield of acid was obtained by Normant and Braun[53] (80%) and Cazes[61] (75%) using pure reagents. Letsinger and Hamilton[63] used this method to prepare *p*-vinylphenylboronic and *p*-isopropenylphenylboronic acids. They used tributyl borate as starting material. These acids react with *o*-phenylenediamine to form dihydrobenzoboradiazole derivatives[61]. A new method for the preparation of *p*-vinylphenylboronic acid was proposed by Hoffmann and Thomas[64-66]; the acid was prepared by brominating *p*-ethylphenylboronic anhydride with subsequent removal of hydrogen bromide:

$$(CH_3{-}\underset{\underset{Br}{|}}{CH}{-}C_6H_4BO)_3 \xrightarrow{-HBr} (CH_2{=}CHC_6H_4BO)_3 \xrightarrow{H_2O} CH_2{=}CHC_6H_4B(OH)_2.$$

p-Ethylphenylboronic acid was prepared by the reduction of *p*-vinylphenylboronic acid with hydrogen on a platinum catalyst[62].

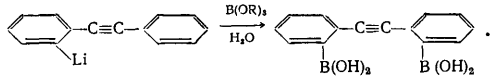
A convenient method for the dehydration of the acid to the anhydride is by drying *in vacuo* over phosphorus pentoxide[60]. When *p*-vinylphenylboronic acid was heated at 100° in a solvent (benzene, xylene, or carbon tetrachloride) until the liberation of water stopped, the anhydride was obtained in yields of more than 95%.[67,68]

Di-(*p*-vinylphenyl)boronic acid $(CH_2{=}CHC_6H_4)_2BOH$ was prepared by the reaction of 2 moles of *p*-vinylphenylmagnesium chloride with butyl borate, followed by hydrolysis; the acid was isolated as the aminoethyl ester in 38% yield[63].

Attempts to prepare *p*-vinylphenylboronic acid from *p*-vinylphenyllithium and tributyl borate were unsuccessful. *p*-Isopropenylphenylboronic acid was prepared from *p*-isopropenylphenyllithium and butyl borate[63].

Two methods for the preparation of *o*-vinylphenylboronic acid have been proposed: the reaction of *o*-vinylphenylmagnesium chloride with tributyl borate, followed by hydrolysis, and the dehydrobromination of 2-(1-bromoethyl)phenylboronic anhydride with quinoline at 130–135°.[65,66,69] *m*-Vinylphenylboronic acid was prepared in analogous fashion[66]. On condensation with nitromethane and acetone, *p*-formylphenylboronic acid formed *p*-(β-nitrovinyl)phenylboronic and *p*-(β-acetylvinyl)phenyl boronic acids respectively[70].

Letsinger and Nazy[71] described a new type of diboronic acid — 2,2′-tolandiboronic acid — obtained in 86% yield by the reaction of the corresponding lithium derivatives with tributyl borate and water:



In alkaline media this acid readily forms heterocyclic compounds; the reaction with *o*-phenylenediamine gives bis(dihydrobenzo)boradiazole and the reaction with hydrogen peroxide gives 2-(*o*-hydroxyphenyl)benzofuran. The action of water at 200° lead to the formation of deoxybenzoin.

2-Tolanboronic acid is analogous to 2,2′-tolandiboronic acid, but it is not isomerised in alkaline media and is oxidised by hydrogen peroxide to hydroxytolan. This acid, and also 2,2′-stilbenediboronic acid, were prepared from the corresponding lithium derivatives and tributyl borate, with subsequent hydrolysis of the reaction mixture[67]. Compounds with hydrophilic groups, intended for use in cancer therapy, include the acid $HOOCCH{=}CHCONHC_6H_4B.(OH)_2$, prepared by acylating aminophenylboronic acid with maleic anhydride[72]. The double bond in this acid is hydrogenated in the presence of PtO_2.

Maitlis[73,74] reported the preparation of *o*-(4-phenylbuta-1,3-dienyl)phenylboronic anhydride from *o*-bromophenyl-4-phenylbuta-1,3-diene, butyllithium, and butyl metaborate. This anhydride has the *trans,trans*-configuration.

IV. ESTERS OF ALKENYLBORONIC AND DIALKENYLBORINIC ACIDS

The methods for preparing esters of unsaturated acids involve the alcoholysis of various organoboron compounds.

a. Alcoholysis of halogeno-compounds of boron. Lazier and Salzberg[75] used the reaction of methanol, with chlorovinylboron dichloride to prepare a number of esters of unsaturated acids, for example dimethyl chlorovinylboronate:

$$ClCH{=}CHBCl_2 + CH_3OH \rightarrow ClCH{=}CHB(OCH_3)_2.$$

A cyclic ester of this acid, $ClCH{=}CHBOCH_2{-}CH_2$ (O), was prepared from chlorovinylboronic acid and ethylene glycol. In analogous fashion, ethanolysis of di(chlorovinyl)boron chloride gave ethyl di(chlorovinyl)borinate[52]:

$$(ClCH{=}CH)_2\,BCl + C_2H_5OH \rightarrow (ClCH{=}CH)_2\,BOC_2H_5 + HCl.$$

b. Alcoholysis of alkenylboronic acids and their anhydrides. Several esters of vinylboronic and propenylboronic acids are known. These were synthesised by the action of alcohol on benzene solutions of the corresponding acids[53]. Later the yield of n-butyl propenylboronate was increased to 95% by using the anhydride of the acid[17].

Di-n-butyl and di-n-hexyl isopropenylboronates and the cyclic ester

$$(CH_3)_2C{=}CHBOCH_2CH_2$$
$$\qquad\qquad\quad O$$

are known[17,53]. This method has been used to prepare several esters of n-propenylboronic acid[17,53].

When *p*-vinylphenylboronic acid is heated in toluene solution with diethanolamine, the product is aminodiethyl *p*-vinylphenylboronate. The analogous reaction with butanol gave di-n-butyl *p*-vinylphenylboronate and that with allyl alcohol gave diallyl *p*-vinylphenylboronate[61,66]. With ethyl tartrate, *p*-vinylphenylboronic acid forms the corresponding ester[63].

An ester of a saturated organoboronic acid with unsaturated ester groups has also been prepared. The addition of an excess of allyl alcohol to di-n-butylborinic anhydride and removal of water gave allyl di-n-butyl borinate[76].

c. Hydrolysis and subsequent esterification of the products of the reaction of a borate with an alkenylmagnesium halide. This method is essentially a variation of the second method, since hydrolysis of the reaction products gives the corresponding acid. The borates used included trimethyl borate, triethyl borate, tributyl borate, and esters of metaboric acid:

$$RMgCl + B(OR')_3 \xrightarrow{HCl+H_2O} RB(OH)_2 \xrightarrow{R'OH} RB(OR')_2.$$

Mikhailov and Tutorskaya[77] prepared n-butyl vinylboronate by the action of vinylmagnesium bromide on trimethyl borate with subsequent hydrolysis and esterification of the reaction products. This ester was obtained by a similar method, but in lower yields, by Normant[17].

Diallyl allylboronate[20,21], dibutyl ethynylboronate, dibutyl butylethynylboronate[78], and 2-aminoethyl di-(*p*-vinylphenyl)borinate[63] were prepared in analogous fashion. An ester of metaboric acid can be used instead of the borate. Di-n-butyl allylboronate was prepared from allylmagnesium bromide and an ester of metaboric acid with subsequent decomposition of the reaction products with water and esterification with n-butanol[21]. Methyl and ethyl diallylborinates were prepared by Rothstein and Saville[58].

A much simpler method for the preparation of these esters is by the direct reaction of an alkenylmagnesium halide with borates. Thus the reaction of 1 mole of propenylmagnesium chloride with triethyl borate at -30° in tetrahydrofuran gives diethyl propenylboronate. When the latter is treated with a further mole of $CH_3CH{=}CHMgCl$, the product is ethyl dipropenylborinate[16]. Methyl allylboronate has been synthesised in low yield (6.8%) from allylmagnesium bromide and trimethyl borate[21].

Esters can also be prepared by the alcoholysis of the products of the reaction of borates with alkenylmagnesium halides. At a $(CH_3O)_3B : CH_3CH{=}CHMgBr$ ratio of 1 : 2, treatment of the reaction mixture with n-butanol gave n-butyl dipropenylborinate[17].

Zavgorodnii and Petrov[79] prepared esters of methylethynyl- and vinylethynyl boronic acids by hydrolysing the products of the reaction of methylethynyl- and vinylethynyl-magnesium bromide with tributyl borate at -40°.

d. The reaction of trialkenylborons, trialkenyl borates and esters with alcohols. The action of 1 and 2 moles of methanol on triallylboron at room temperature gives dimethyl allylboronate[21]. The dibutyl ester of this acid was obtained by the action of 2 moles of the alcohol on triallylboron[21,23], and the action of 1 mole of the alcohol gave butyl diallylborinate[21]:

$$(C_3H_5)_3B + C_4H_9OH \rightarrow (C_3H_5)_2B(OC_4H_9) + C_3H_6;$$

$$(C_3H_5)_3B + 2C_4H_9OH \rightarrow C_3H_5B(OC_4H_9)_2 + 2C_3H_6.$$

When 2-aminoethyl di-(*p*-vinylphenyl)borinate was mixed with 1-aminopropan-2-ol, the product was 2-amino-1-methylethyl di-(*p*-vinylphenyl)borinate[63].

e. Other methods. A method for preparing dipentyl allylboronate by the reaction in an autoclave between sodium, a borate, lithium chloride, and allyl bromide with subsequent hydrolysis of the reaction products and esterification with pentanol has been patented[81]. Meerwein and coworkers[82] prepared 2,2-dibromovinyl diethylborinate by the reaction of bromal with triethylboron:

$$B(C_2H_5)_3 + CBr_3CHO \rightarrow (C_2H_5)_2BOCH{=}CBr_2 \xrightarrow{CBr_3CHO} C_2H_5B(OCH_2{=}CBr_2)_2 +$$

$$+ C_2H_5B\begin{matrix}OCH{=}CBr_2\\ OCH_2CBr_3\end{matrix}.$$

Allyl and methallyl diethylborinates were prepared by Rothstein and Saville[58] from diethylzinc and the corresponding borates:

$$Zn(C_2H_5)_2 + B(OR)_3 \rightarrow (C_2H_5)_2BOR + Zn(OR)_2.$$

Johnson *et al.*[83] isolated a small quantity of dibutenyl n-butylboronate as a by-product of the reaction of tributyl borate with t-C_4H_9OCl at -80°.

The esters of alkenylboronic acids are readily hydrolysed by water and this forms the basis of a method for preparing the acids. The action of aqueous solutions of bases or sodium bicarbonate also leads to very rapid hydrolysis in the case of dibutyl ethynylboronate, the ethynyl group being removed as acetylene[78]. On hydrogenation over $Pd/CaCO_3$ dibutyl vinylethynylboronate adds on 2 moles of hydrogen with the formation of dibutyl butenylboronate[79].

In the bromination of dibutyl vinylethynylboronate the first bromine molecule adds chiefly across the double bond[79]. Mikhailov and Aronovich[84] carried out the addition of bromine in the cold to di-n-butyl vinylboronate and allylboronate with the formation of di-n-butyl $\alpha\beta$-dibromoethylboronate and $\beta\gamma$-dibromopropylboronate respectively:

$$CH_2{=}CHB(OC_4H_9)_2 + Br_2 \rightarrow CH_2BrCHBrB(OC_4H_9)_2,$$

$$CH_2{=}CHCH_2B(OC_4H_9)_2 + Br_2 \rightarrow CH_2BrCHBrCH_2B(OC_4H_9)_2.$$

The resulting esters readily undergo β-breakdown under the influence of nucleophilic reagents. The addition of bromine to dibutyl ethynylboronate requires initiation: $BrCH{=}CBrB(OC_4H_9)_2$ is formed in 88% yield. Phosphorus pentachloride readily removes one butoxy-group from dibutyl vinylboronate[77]:

$$CH_2{=}CHB(OC_4H_9)_2 + PCl_5 \rightarrow CH_2{=}CHB(Cl)OC_4H_9 + C_4H_9Cl + POCl_3.$$

In the presence of azobisisobutyronitrile, dibutyl vinylboronate and isopropenylboronate add on CCl_4 with the formation of $CCl_3CH_2CHClB(OC_4H_9)_2$ and $CCl_3CH_2CCl(CH_3).B(OC_4H_9)_2$ respectively. The formation of 1:1 adducts of the above esters takes place much more readily with bromotrichloromethane in the presence of traces of initiator at 80°.[56,85]

Experiments were also carried out on the addition of chloroform and aldehydes to this ester; the former gave a telomer and the latter did not react. Matteson[85] suggests that dibutyl vinylboronate (I) reacts with free radicals ($X^{\cdot}$) to give intermediate radicals (II) which are stabilised by the boron–carbon π bond and subsequently react to give esters (III) containing different functional groups:

$$\underset{(I)}{CH_2{=}CHB(OC_4H_9)_2} \xrightarrow{X^{\cdot}} \underset{(II)}{XCH_2CH\text{------}B(OC_4H_9)_2} \xrightarrow{XY} \underset{(III)}{XCH_2CHYB(OC_4H_9)_2};$$

(III) a: X=CCl_3, Y=Cl;

b: X=CCl_3, Y=Br;

c: X=$HC_6H_{13}S$, Y=H.

In the presence of azobisisobutyronitrile, dibutyl ethynylboronate adds on bromotrichloromethane and hexanethiol to give $CCl_3CH{=}CBrB(OC_4H_9)_2$ and $C_6H_{13}SCH{=}CHB.(OC_4H_9)_2$ respectively. The light-catalysed addition of hexanethiol to dibutyl vinylboronate takes place rapidly even at -70°.[78]

Lazier and Salzberg[75] observed exchange of ester groups when dimethyl chlorovinylboronate was heated to 100° with octanethiol and dodecanethiol:

$$ClCH{=}CHB(OCH_3)_2 + 2C_{12}H_{25}SH \rightarrow ClCH{=}CHB(SC_{12}H_{25})_2 + 2CH_3OH.$$

Silanes are added on to diisobutyl vinylboronate and allylboronate in the presence of hydrogen chloroplatinate(II). The addition of trichlorosilane and methyldichlorosilane to the esters of unsaturated acids takes place under milder conditions than the addition to olefins, due to the activating influence of the boron atom on the double bond. No addition takes place in the absence of catalyst[86]:

$$CH_2{=}CHB(OC_4H_9)_2 + HSiCl_3 \rightarrow Cl_3SiCH_2CH_2B(OC_4H_9)_2;$$

$$CH_2{=}CHB(OC_4H_9)_2 + CH_3SiHCl_2 \rightarrow Cl_2(CH_3)SiCH_2CH_2B(OC_4H_9)_2;$$

$$CH_2{=}CH{-}CH_2B(OC_4H_9)_2 + CH_3SiHCl_2 \rightarrow Cl_2(CH_3)SiCH_2CH_2CH_2B(OC_4H_9)_2.$$

An attempt to replace the butoxy-groups in dibutyl vinylethynylboronate by ethyl groups by the reaction with ethyllithium at -70° gave dibutyl ethylboronate and vinylacetylene[79]:

$$CH_2{=}CH{-}C{\equiv}CB(OC_4H_9)_2 \xrightarrow{C_2H_5Li} [CH_2{=}CH{-}C{\equiv}C{-}B(OC_4H_9)_2(C_2H_5)]Li \rightarrow$$

$$\xrightarrow{HCl} [CH_2{=}CH{-}C{\equiv}CB(OC_4H_9)_2(C_2H_5)]H \rightarrow CH_2{=}CH{-}C{\equiv}CH + C_2H_5B(OC_4H_9)_2.$$

Dibutyl vinylboronate is an active dienophilic reagent and forms an adduct with cyclopentadiene. The ethynylboronate, although a less active dienophilic reagents, also forms an adduct with cyclopentadiene — dibutyl bicyclo-[2,2,1]hepta-2,5-dienylboronate[74].

V. ALKENYL ORTHOBORATES

Alkenyl orthoborates are prepared chiefly by the methods used for alkyl borates[1,2,5]: esterification of boric acid and esterification of alkylboron halides. Esterification of boric acid was used to prepare triallyl borate[87-91], tri-1-methallyl borate[92], tri-2-methallyl borate[93], and tri-3-methallyl borate[92]. Triallyl borate[94-97] was prepared by the esterification of boron trichlorode. A high yield (85%) is achieved by using n-pentane or methylene dichloride as solvents[98,99]. Tri-2-methallyl borate, tripropynyl borate[98], and tributenyl borate[92] were prepared in analogous fashion. Tri-1-methallyl borate can be obtained in 58% yield by the rapid removal of the resulting hydrogen chloride from the reaction sphere[92].

The reaction of phenyl allyl ether with BCl_3 at -80° gives tri-*o*-allylphenyl borate. It is suggested that the first stage in this reaction involves the Claisen rearrangement of the phenyl allyl ether to *o*-allylphenol, catalysed by Lewis acids[100].

Triallyl borate can be prepared from boron acetate and allyl alcohol in 50% yield[90]. Sodium borohydride reacts with allyl alcohol at room temperature in the presence of one equivalent of acetic acid[101]:

$$3C_3H_5OH + NaBH_4 + CH_3COOH \rightarrow (C_3H_5O)_3B + NaOCOCH_3 + 4H_2.$$

The triallyl borate obtained in these experiments has an unusually high refractive index (n_D^{20} = 1.4496).

Thomas proposed a method for the preparation of tri-2-methallyl borate from boric oxide, methallyl alcohol, toluene, and anhydrous copper sulphate with heating up to 110°.[102,103] The transesterification of triallyl borate with 2,6-di-t-butyl-4-methylphenol gave the mixed orthoborate $4\text{-}CH_3\text{-}2,6\text{-}(t\text{-}C_4H_9)_2C_6H_2OB(OCH_2CH{=}CH_2)_2$.[80]

Organoboron and organophosphorus halides have been used to prepare the following borates: diallyl 1-(dimethoxyphosphinyl)-2-trichloroethyl borate, diallyl 1-(ethoxyphenylphosphinyl)propyl borate, and diallyl 1-(diphenylphosphinyl)propyl borate[104]. 2,6-Diallylphenyl borate[105] and octadec-9-enyl borate[106] are also known.

The properties of triallyl borate have been studied in most detail[107,108]. The viscosity of triallyl borate, measured in a Cannon-Fenske-Ostwald viscometer, is 1.25 cS at 7°, 0.902 cS at 23.2°, and 0.747 cS at 37.8°.[80-90] The infrared spectra of triallyl borate were discussed in detail in a review by Washburn *et al.*[80] Alkenyl borates are readily hydrolysed[90,93]. Tri-*o*-allylphenyl borate is hydrolysed by water to *o*-allylphenol[100]. The mixed diallyl $2,6\text{-di-t-butyl-4-methylphenyl borate } 4\text{-}CH_3\text{-}2,6\text{-}(t\text{-}C_4H_9)_2.C_6H_2OB(OC_3H_5)_2$ is stable to hydrolysis[80].

Transesterification of tri-1-methallyl borate with octan-1-ol gives 1-methallyl alcohol and trioctyl borate; analogous treatment of tri-3-methallyl borate gives butenyl alcohol and trioctyl borate[92]:

$$B(OR)_3 + 3C_8H_{17}OH \rightarrow B(OC_8H_{17})_3 + 3ROH.$$

When treated with air at 125°, triallyl borate is converted to poly(triallyl borate)[87]. Triallyl borate reacts with HBr and HI to form both dealkylation and addition products[98]:

$$(CH_2{=}CH{-}CH_2O)_3B + 3HHal \begin{cases} \nearrow 3CH_2{=}CHCH_2Hal + B(OH)_3 \\ \searrow (HalCH_2CH_2CH_2O)_3B. \end{cases}$$

The addition of HHal takes place contrary to Markovnikov's rule. Gerrard *et al.*[98] observed no reaction between

triallyl borate and HCl at 20°. Gaseous HCl does not react at 120° with tri-1-methallyl borate and tri-3-methallyl borate. When these are heated for 4 h at 110° the products are butenyl chloride and boric acid[92]:

$$B(OR)_3 + 3HCl \rightarrow 3RCl + B(OH)_3.$$

The action of a concentrated solution of bromine in carbon tetrachloride on triallyl borate gives tri-(2,3-dibromopropyl)borate[96].

The reaction of boron trichloride with borates in the proportions indicated in the equations gave alkenyloxyboron chlorides only in the case of the but-3-enyl group:

$$2B(OR)_3 + BCl_3 \rightarrow 3BCl(OR)_2;$$

$$B(OR)_3 + 2BCl_3 \rightarrow 3BCl_2OR.$$

In the case of methallyl borates the reaction does not stop at this stage[92]:

$$3BCl(OR)_2 \rightarrow 3RCl + B_2O_3 + B(OR)_3;$$

$$3BCl_2OR \rightarrow 3RCl + B_2O_3 + BCl_3.$$

The intermediate compound di-1-methallyloxyboron chloride could be isolated only as the complex $[H_2C{=}CH{-}CH(CH_3)O]_2BCl.C_5H_5N$.[92]

Aldehydes and ketones are reduced to alcohols more effectively by triallyl borate than by triisopropyl borate[89,109]. Triallyl borate reacts with diethylzinc to form allyl diethylborinate[97]:

$$B(OC_3H_5)_3 + Zn(C_2H_5)_2 \rightarrow C_3H_5OB(C_2H_5)_2.$$

This method can also be used to prepare methallyl esters.

Orthoborates can be used as alkylating agents in Friedel–Crafts alkylations. Alkylation of benzene and toluene with triallyl borate in the presence of aluminium chloride gave 1,2-diphenylpropane[110] and 1,2-ditolylpropane[91] respectively. Replacement of aluminium chloride by ferric chloride in the alkylation of benzene by triallyl borate gives allylbenzene[111].

VI. ALKENYLBORON HALIDES

Borisov[52] proposed two convenient methods for preparing 2-chlorovinyl derivatives of boron: (1) double decomposition of organoantimony compounds with boron trichloride, and (2) the reaction of 2-chlorovinylmercury chloride or di-(2-chlorovinyl)mercury with boron trichloride.

Di-(2-chlorovinyl)boron chloride was prepared by Clark *et al.*[112] by the disproportionation of 2-chlorovinylboron dichloride when heated in the liquid phase at 100–125° in the presence of activated carbon with simultaneous distillation of the resulting boron trichloride:

$$2ClCH{=}CHBCl_2 \rightarrow (ClCH{=}CH)_2BCl + BCl_3.$$

The asymmetric stable chlorovinylethylboron chloride, which is not decomposed under vacuum-distillation conditions, can be prepared by the reaction of ethylboron dichloride with tri-(2-chlorovinyl)boron or by the reaction of ethylboron dichloride with acetylene. Activated carbon was used as catalyst in the second case[31]. Chloromethylvinylboron is formed when a mixture of BCl_3 and methyldivinylboron is kept for 1 h at 25°.[14]

Brinckmann and Stone[113] prepared divinylboron chloride by heating tetravinyltin with boron trichloride. An attempt to prepare divinylboron fluoride by the reaction of tetravinyltin with boron trifluoride or vinylboron difluoride was unsuccessful. This compound can be obtained in good yield by the reaction

$$(CH_2{=}CH)_2BCl \xrightarrow{SbF_3} (CH_2{=}CH)_2BF,$$

carried out at -80° for 35 h.[113] The perfluorovinyl compounds of boron are the first covalent organoboron compounds containing no hydrogen. One such compound — di(perfluorovinyl)boron chloride — was prepared from dimethyldi(perfluorovinyl)tin and boron trifluoride[33]:

$$(CF_2{=}CF)_2Sn(CH_3)_2 + BCl_3 \rightarrow (CF_2{=}CF)_2BCl + Sn(CH_3)_2Cl_2.$$

2-Chlorovinylboron dichloride was prepared by the reaction between boron trichloride and acetylene at 150–300° over a granulated catalyst consisting of $HgCl_2$ deposited on activated carbon[32]:

$$BCl_3 + C_2H_2 \xrightarrow{HgCl_2} ClCH{=}CHBCl_2.$$

This compound was obtained in good yield by Borisov *via* the corresponding organoantimony compound[52]:

$$(ClCH{=}CH)_3Sb + 3BCl_3 \rightarrow 3ClCH{=}CHBCl_2 + SbCl_3.$$

Equivalent quantities of 2-chlorovinylmercury chloride and boron trichloride in kerosene or benzene react as follows[52]:

$$ClCH{=}CHHgCl + BCl_3 \rightarrow ClCH{=}CHBCl_2 + HgCl_2.$$

Vinylboron dichloride was prepared by the reaction of divinylzinc or divinylmercury with boron trichloride. Vinylboron dibromide was prepared in analogous fashion[114]. A method was proposed for the preparation of vinylboron dichloride by the reaction of vinylmagnesium chloride with boron trichloride or an alkyl borate at 0–12°.[16] The same compound was prepared from tetravinyltin and boron trichloride. In the reaction of boron trichloride with alkylvinyltin compounds BCl_3 first adds to the vinyl group, so that compounds such as di-n-butyldivinyltin can be used for the preparation of vinylboron dichloride[113,115].

Organotin compounds can also be used to prepare vinylboron difluoride (yield 52%)[113]. The replacement of the tin compounds in this reaction by divinylmercury of divinylzinc[116,117] decreases the yield of vinylboron difluoride to 30% and 27% respectively. Perfluorovinylboron dichloride was prepared by the reaction of dimethyldi(perfluorovinyl)tin with boron trichloride. Perfluorovinylboron difluoride was prepared in analogous fashion from boron trifluoride, but in lower yield (18%). The best yield (57%) was achieved by the reaction of perfluorovinylboron dichloride with antimony trifluoride[33]:

$$CF_2{=}CFBCl_2 \xrightarrow{SbF_3} CF_2{=}CFBF_2.$$

Allylboron difluoride was prepared by heating boron trifluoride with tetraallyltin[113].

2-Chlorovinyl derivatives of boron fume slightly in air and become dark[52], and the perfluorovinyl compounds ignite (sometimes with detonation)[32].

Different vinylboron halides have different thermal stabilities. Thus vinylboron difluoride can be kept for several months without decomposition and no appreciable decomposition is observed even after heating at 200° for 20 h. Vinylboron dichloride undergoes slight decomposition when distilled at 80–100°. When stored for several months, vinylboron dichloride forms a small quantity of

an apparently polymeric white residue. The degree of decomposition of divinylboron chloride at room temperature after 24 h is not more than 3%, but divinylboron fluoride decomposes appreciably at room temperature after 24 h to form vinylboron difluoride and trivinylboron[113]. The thermal stability of vinylboron halides increases in the order

$$(CH_2=CH)_2BF < (CH_2=CH)_2BCl < CH_2=CHBCl_2 < CH_2=CHBF_2.$$

Allylboron difluoride is much less stable than vinylboron difluoride: the formation of BF_3 is observed after several minutes in the liquid phase at 0°.[113]

Perfluorovinylboron difluoride decomposes in the gaseous phase at room temperature at the rate of 5% per week. Perfluorovinylboron dichloride does not decompose after 5 h at 100° but BCl_3 is liberated when the compound is kept for several days at room temperature.

Di(perfluorovinyl)boron chloride decomposes completely to perfluorovinylboron dichloride and tri(perfluorovinyl)boron in one day at room temperature[32].

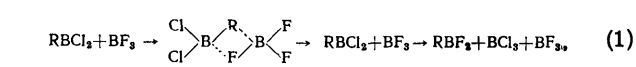
Ethylene is liberated when vinylboron difluoride comes into contact with water at 120°. Under identical conditions vinylboron dichloride and divinylboron chloride give ethylene in 85% and 30% yield respectively. The hydrolysis of vinylboron difluoride at room temperature, however, proceeds without removal of vinyl groups[113]. On treatment with water at room temperature perfluorovinylboron difluoride rapidly loses trifluoroethylene[33]. The sensitivity of various substituted boron halides towards removal of the vinyl groups with water increases in the order

$$C_2H_5BF_2 < (CH_2=CH)_2BCl < CH_2=CHBCl_2 < CH_2=CHBF_2 < CF_2=CFBF_2.$$

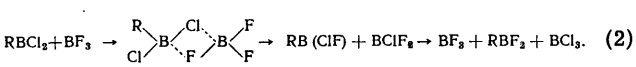
Perfluorovinylboron dichloride and di(perfluorovinyl)boron chloride react with water at low temperatures forming chiefly perfluorovinylboronic acids[33]. 2-Chlorovinyl derivatives of boron split off acetylene when treated with 10% alkali[52]. Vinylboron halides are reduced by ammoniacal silver hydroxide solution at 100°. In the case of divinylboron halides (but not at room temperature) butadiene is formed in addition to ethylene[11,12]. Allylboron difluoride loses only propene[113]. Vinylboron difluoride reacts with boron trichloride according to the equation[113]

$$3CH_2=CHBF_2+2BCl_3 \rightleftarrows 2BF_3+3CH_2=CHBCl_2.$$

Two possible mechanisms for the reactions between boron trifluoride and vinylboron dihalides have been proposed:



$$RBCl_2+BF_3 \rightarrow \text{[Cl, R, F bridged B–B]} \rightarrow RBCl_2+BF_3 \rightarrow RBF_2+BCl_3+BF_3, \quad (1)$$



$$RBCl_2+BF_3 \rightarrow \text{[R, Cl, F bridged B–B]} \rightarrow RB(ClF)+BClF_2 \rightarrow BF_3+RBF_2+BCl_3. \quad (2)$$

The use of labelled boron (^{10}B) in BF_3 shows that no exchange of organic groups takes place in these reactions, so that the second mechanism is more probable[46].

A complex of vinylboron difluoride with trimethylamine has been prepared. The influence of the vinyl group attached to the boron atom on the acidity of these compounds has been compared with the influence of the corresponding saturated groups[118]. Vinylboron difluoride reacts with diethylzinc and trimethylaluminium. The chief product of the reaction with diethylzinc at room temperature is triethylboron and unreacted vinylboron difluoride. Trimethylaluminium reacts with liberation of heat and the formation of trimethylboron in 70% yield[113]. Di-(2-chlorovinyl)boron chloride reacts with thallium trichloride:

$$(ClCH=CH)_2BCl+TlCl_3 \xrightarrow{H_2O} (ClCH=CH)_2TlCl+B(OH)_3.$$

VII. BORON–NITROGEN COMPOUNDS CONTAINING ALKENYL GROUPS

Di-(2-chlorovinyl)boron chloride reacts with piperidine in cooled dry ether to give di-(2-chlorovinyl)boron-piperidine:

$$(ClCH=CH)_2BCl+2C_5H_{11}N \rightarrow (ClCH=CH)_2B \cdot NC_5H_{10}+C_5H_{11}N \cdot HCl.$$

This compound darkens in air and becomes viscous[52]. At room temperature triallylboron reacts readily with n-butylamine; with equimolar quantities of the reagents, diallyl-(n-butylamino)boron is formed[21]. The reaction with aniline takes place equally readily[119]. The first stage of the reaction of triallylboron with ethylamine, diethylamine, and ammonia gives complexes which lose propene when heated[119]:

$$(C_3H_5)_3B+(C_2H_5)_2NH \rightarrow (C_3H_5)_3B \cdot NH(C_2H_5)_2 \xrightarrow{100-130^\circ} (C_3H_5)_2BN(C_2H_5)_2+C_3H_6.$$

When *p*-phenylenediamine is heated with *p*-vinylphenylboronic acid, the product is 2-(4-vinylphenyl)-1,3-dihydrobenzo[2,1,3]boradiazole[63].

Derivatives of bis(dihydrobenzo)boradiazole have been prepared in analogous fashion from *p*-phenylenediamine and 2,2′-tolandiboronic acid[71]. Treatment of 2-chlorovinylboron dichloride with ammonia in dry ether or benzene gave *BBB*-tri-(2-chlorovinyl)borazole[120]. *BBB*-Triallyl-*NNN*-trimethylborazole was prepared from *BBB*-trichloro-*NNN*-trimethylborazole and allylmagnesium bromide[121]. Unsuccessful attempts were made to prepare *BB*-diallyl-*B*-chloro-*NNN*-trimethylborazole and *B*-allyl-*BB*-dichloro-*NNN*-trimethylborazole by this reaction[121]. Groszos and Stafiej[122] prepared *BBB*-triallyl-*NNN*-triphenylborazole from *BBB*-trichloro-*NNN*-triphenylborazole and allylmagnesium bromide. The same compound is obtained using allyllithium[123]. The asymmetric borazole *NNN*-triphenyl-*B*-phenyl-*B*-methyl-*B*-allylborazole, which is stable towards moisture, was recently prepared[123]. By using *NNN*-triphenyl-*BBB*-trialkylborazole (where alkyl represents phenyl or methyl radicals or a hydrogen atom), the alkyl group on the boron atom can be replaced by the allyl group by reaction with allyllithium[124].

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THE PROLONGATION OF THE ACTION OF PHARMACEUTICAL PREPARATIONS BY MIXING OR COMBINING THEM WITH POLYMERS

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In the past decade considerable progess has been made in work on prolonging the action of pharmaceutical preparations. By the use of long-acting compounds, not only can the total amount of a preparation introduced into the body during a course of treatment and the number of doses or injections be reduced, but there are also other substantial advantages. Variations in the blood and tissue concentration of an active compound, which are unavoidable with periodically repeated doses of ordinary preparations, can be reduced or eliminated by the use of long-acting preparations; a constant concentration of the active compound that does not exceed the therapeutic dose, as frequently occurs with ordinary preparations, can be maintained with these long-acting preparations[1-4]. Their use also reduces the probability of unwanted effects, if the patient neglects to take medicine at the right time. Long-acting preparations should rapidly establish the required concentration of active compound in the blood and tissues; if this is not possible an ordinary preparation must be used at the beginning of a course of treatment so as to produce a rapid rise of concentration in blood and tissue. Moreover, the use of long-acting preparations saves much routine time; for example, a single dose or injection may replace four or five; this is of great practical importance in treatment in clinics.

The following methods may be used to prolong the action of pharmaceutical preparations: (1) introduction of various substituents into the molecule to retard the rate of excretion; (2) preparation of complexes or salts of pharmaceutical preparations with low-molecular-weight compounds; (3) use of special compounded preparations; (4) administration as a mixture with polymers; (5) formation of compounds with polymers.

The preparation of special long-acting compounded preparations and the use of these compounded preparations in medical practice have been dealt with in a number of reviews[2-7]. However, there are no systematic reviews on long-acting preparations made by methods (4) and (5). The present review is intended to fill this gap.

In the USSR, work in this field has been initiated by Ushakov and coworkers, who have worked on this problem over a long period, and also by Mokhnach, who has prepared and examined complexes of iodine with various polymers.