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Methods of Synthesis and Properties of Allylboranes

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The methods of synthesis and chemical properties of allyl derivatives of boron of different types and their applications in organic chemistry, including their use for the synthesis of 1-bora-adamantane and adamantane compounds, are discussed. The bibliography includes 148 references

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I. INTRODUCTION

Studies on the chemical properties of organic boron compounds in recent years have led to the discovery of an increasing number of new fields of application of these substances in organic syntheses. Methods of synthesis based on organoboranes have greatly extended the scope of the applications of organometallic reagents in preparative chemistry, usefully supplementing the available synthetic procedures involving organic derivatives of magnesium, zinc, and alkali metals.

Allyl derivatives of boron, which are highly reactive and exhibit a specific behaviour in relation to different classes of organic compounds, are particularly promising as synthetic reagents. A characteristic feature of triallylborane and some of its analogues is their ability to exist in a state of permanent allyl rearrangement, which takes place at different rates, depending on the nature of the compound and temperature. The high reactivity of allylboranes is manifested in their reactions with water, alcohols, and amines, which occur even at room temperature; this distinguishes them sharply from trialkylboranes, which react with the same substances only at elevated temperatures. Allylboranes react with aldehydes, ketones, quinones, and nitriles like organometallic compounds, their use for synthetic purposes having in many instances considerable advantages compared with magnesium and other metal compounds[1].

A specific feature of allylboranes is their tendency to react with unsaturated compounds. Their reactions with acetylenic and allenic compounds lead to 3-borabicyclo-[3,3,1]nonene and 3-borabicyclo[3,3,1]nonane systems, on the basis of which it proved possible to develop a stereospecific method for the synthesis of compounds of the cyclohexene and cyclohexane series, to synthesise unique 1-bora-adamantane systems, and to devise a novel method for the synthesis of adamantane derivatives.

II. METHODS OF SYNTHESIS

Triallylborane was obtained for the first time in 33% yield by the reaction of triallyl borate and allylmagnesium bromide[2]. Triallylborane is also formed from allylmagnesium bromide and n-butyl metaborate[3]. The reaction between allylmagnesium bromide and boron trifluoride-ether constitutes a preparative method for the synthesis of triallylborane[3]:

$$3\,C_3H_5MgBr + BF_3 \rightarrow (C_3H_5)_3B + 3\,MgBrF.$$

The reaction can be carried out in a single stage by adding a mixture of allyl bromide and boron trifluoride-ether to magnesium in an ethereal medium[4,5].

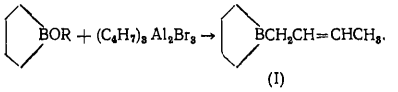
When allylmagnesium chloride and boron trifluoride-ether are used, the yield of triallylborane is 10–47%.[4,6] Allylmagnesium chloride and methyl borate may be used to synthesise triallylborane[7]. Triallylborane can be obtained most conveniently from allylaluminium sesquibromide and n-butyl borate or boron trifluoride-ether[8]:

$$(C_3H_5)_3Al_2Br_3 + BF_3 \underset{78\%}{\rightarrow} (C_3H_5)_3B + AlF_3 + AlBr_3\ .$$

Tricrotylborane in 75% yield[9] and tri-(2-methylallyl)-borane[10] have been synthesised by the last method.

Mixed organoboranes containing one or two allyl groups are obtained by treating the corresponding acid esters with allyl derivatives of magnesium or aluminium.

1-Crotylboracyclopentane (I) has been synthesised from 1-n-butoxyboracyclopentane[11] or 1-methoxyboracyclopentane[12] and crotylaluminium sesquibromide:



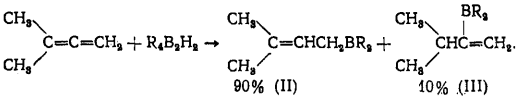
(I)

1-Allylboracyclopentane has been obtained by treating 1-alkoxyboracyclopentane with allylmagnesium bromide or allylaluminium sesquibromide[13]. Dialkylallylboranes[14], alkyldiallylboranes[14], and allyldiarylboranes[15] can be synthesised by this method from dialkylborinic, alkylboronic, or diarylborinic acid esters.

Dialkylallylboranes are also formed when esters of dialkylthioborinic acids are treated with triallylborane[16]:

$$(C_2H_5)_2BSC_6H_{13} \xrightarrow{(CH_2=CHCH_2)_3B} (C_2H_5)_2BCH_2CH=CH_2.$$

Mixed dialkylallyl compounds of boron can be likewise obtained by adding tetra-alkyldiboranes to allenic hydrocarbons. Dialkyl-(3-methylbut-2-en-1-yl)boranes (II) with an admixture of about 10% of the isomeric compounds (III) have been synthesised by this method[17]:



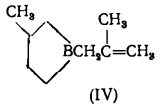
90% (II) 10% (III)

A number of acylic[18] and cyclic[19,20] allenic hydrocarbons have been hydroborated with tetra-(3-methylbut-2-yl)-diborane; the reaction products, containing a mixture of the corresponding substituted dialkylallylboranes and dialkylvinylboranes, were oxidised with hydrogen peroxide.

Alkyldiallylboranes can be obtained by the symmetrisation of dialkylallylboranes. Thus, on being heated above 100°C, diethyl-(3-methylbut-2-en-1-yl)borane is converted into a mixture of triethylborane, ethyldi-(3-methyl-but-2-en-1-yl)borane, and tri-(3-methylbut-2-en-1-yl)borane, which can be separated by fractional distillation[17].

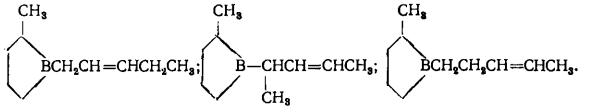
When a 5 : 1 mixture of buta-1,4-diene and diborane reacts in an ethereal medium, a low yield is obtained of a mixture of unsaturated compounds having the composition $C_8H_{15}B$ [together with di-(1-boracyclopentylbutanes)], which consists almost entirely of 1-crotylboracyclopentane[12,21].

The hydroboration of isoprene (using the ratio hydrocarbon : B_2H_6 = 6 : 1) leads to a mixture of 1-alkenyl-3-methylboracyclopentanes [together with di-(3-methylboracyclopentyl)pentanes], which consists to the extent of about 60% of 3-methyl-1-(2-methylbut-2-en-1-yl)boracyclopentane (IV):[22]



(IV)

Hydroboration of piperylene yields a mixture of 1-alkenyl-2-methylboracyclopentanes containing about 35% of 2-methyl-1-(pent-2-en-1-yl)boracyclopentane (V), 15% of 2-methyl-1-(pent-3-en-2-yl)boracyclopentane (VI), and 50% of 2-methyl-1-(pent-3-en-1-yl)boracyclopentane (VII):[22]



(V) (VI) (VII)

Allyl derivatives of boron with oxygen-containing and other functional groups at the boron atom can be obtained by various methods. A general and preparatively convenient method of synthesis of compounds of this type is based on reactions of triallylboranes, which are highly reactive in relation to different reagents. Allylboronic acids and their esters are formed when allylboranes are treated with water or alcohols at room temperature. Thus triallylborane reacts with water to form allylboronic acid, which is isolated as its anhydride on distillation[3]. Studies on reactions of 1-crotylboracyclopentane[11] and tricrotylborane[9] with water, which lead to the formation of but-1-ene and respectively to 1-hydroxyboracyclopentane and crotylboronic acid established that the protonolysis of the boron–carbon bond takes place with allyl rearrangement. The n-butyl ester of diallylborinic acid can be obtained from triallylborane by treating it with one equivalent of n-butyl alcohol. n-Butyl diallylborinate reacts with n-butyl alcohol to form di-n-butyl allylboronate[3].

When methyl alcohol reacts with diallylborane, the reactants being in proportions of 1 : 1, the dimethyl ester of allylboronic acid is obtained, and not the methyl ester of diallylborinic acid, part of the initial triallylborane being recovered unchanged. This can be explained by the fact that the $(C_3H_5)_2BOCH_3$ formed initially undergoes rapid symmetrisation to $(C_3H_5)B(OCH_3)_2$ and $(C_3H_5)_3B$.[3]

Diethyl[23], di-n-propyl[24,25], di-n-butyl, diallyl, dibenzyl, and diphenyl[24] esters of allylboronic acid have been obtained by treating triallylborane with the corresponding alcohols. Tricrotylborane reacts vigorously with methanol at room temperature to form the methyl ester of dicrotylborinic acid and but-1-ene (98%) with a small admixture of but-2-ene (2%) when the initial reactants are taken in equimolar proportions[9]. Thus the alcoholysis of the B–C bond in allyl derivatives of boron takes place with allyl rearrangement.

In order to convert tricrotylborane into the dimethyl ester of crotylboronic acid, the borane must be heated with methanol[9]. The dimethyl ester of allylboronic acid has been synthesised by treating trimethyl borate with allylzinc or allylaluminium compounds[26]. The reaction of crotylmagnesium bromide and methyl borate with subsequent hydrolysis and transesterification of reaction products with n-hexyl alcohol leads to a mixture of di-n-hexyl esters of 1-methylallylboronic and crotylboronic acids in proportions of 77 : 23, with a 44% overall yield[27]. When crotyl-lithium is used, only the ester of crotylboronic acid is obtained (36%). On standing (for several weeks) or in the presence of magnesium bromide (for 18 h at 55°C), the ester of 1-methylallylboronic acid is slowly converted into the ester of crotylboronic acid. The reaction of hex-2-en-1-ylmagnesium bromide with methyl borate leads to the esters of hex-1-en-3-ylboronic and hex-2-en-1-ylboronic acids in proportions of 86 : 14.[27]

According to patent data[28], the dipentyl ester of allylboronic acid is formed when triallyl borate, allyl bromide, and sodium react with subsequent esterification by pentyl alcohol. A mixture of cyclic esters of allylboronic and isopropenylboronic acids in proportions of 66 : 14 is obtained when allene is heated for a long time at 130°C with 4,4,6-trimethyl-1,3,2-dioxaborinane[29].

A simple method for the synthesis of dimethyl allylboronate involves heating a 1 : 2 mixture of triallylborane with methyl borate[30]. It has been established by ^{1}H NMR that a 4 : 1 equilibrium mixture of allylboronic and diallylborinic acid esters is obtained from an equimolar mixture of triallylborate and methyl borate, while the proportions of the esters obtained from an initial 2 : 1 mixture are 1 : 2.3.[31] When triallylborane is heated with triisobutyl borate, di-isobutyl allylboronate is obtained[8].

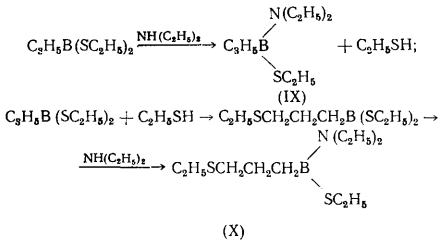
Allylboranes serve as starting materials for the synthesis of allylic thioacids. Triallylborane reacts with ethanethiol at −15°C, the ethyl ester of diallylthioborinic acid and propene being formed from equimolar amounts of the initial reactants[32,33]. When two equivalents of ethanethiol are used, the main reaction product is the diethyl ester of allylthioboronic acid; in addition, the ethyl esters of diallylthioborinic and 3-ethylthio-n-propylthioboronic acids (VIII) are obtained. The latter acid is formed as a result of the addition of ethanethiol to the ester of allylthioboronic acid:

$$(C_3H_5)_3B + C_2H_5SH \xrightarrow[-C_3H_6]{} (C_3H_5)_2BSC_2H_5 \xrightarrow{C_2H_5SH} C_2H_5SCH_2CH_2CH_2B(SC_2H_5)_2. \quad \text{(VIII)}$$

The synthesis of the ethyl esters of diallylthioborinic and allylthioboronic acids has also been described[25].

Like the esters of dialkylthioborinic and alkylthioboronic acids[34–37], those of allylthioboronic acids react readily with various substances. When diethyl allylthioboronate is treated with ammonia, *BBB*-triallylborazole is formed, the reaction with n-butylamine yields allyl-(n-butylamino)-borane, and the reaction with diethylamine leads to the

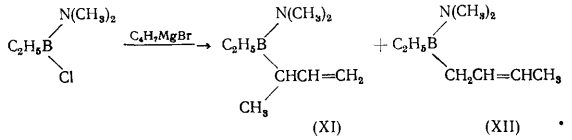
ethyl ester of allyl(diethylamino)thioborinic acid (IX) and to the ethyl ester of (diethylamino)-3-ethylthiopropylthioborinic acid (X):[33]



(IX) (X)

Allyl-containing amino-derivatives of boron can be obtained from allylboranes. Triallylborane reacts with ammonia and primary and secondary amines to form adducts, which are smoothly converted into diallylaminoborane or its *N*-alkyl derivatives on heating to 100–130°C.[3,38] Diallylaminoborane and alkylaminodiallylboranes have been synthesised by this method[25].

When chloro(ethyl)dimethylaminoborane reacts with crotylmagnesium bromide, a mixture of but-1-en-3-yl-(ethyl)dimethylaminoborane (XI) and but-2-en-1-yl(ethyl)-dimethylaminoborane (XII) is obtained in proportions of 65 : 35:[39]



(XI) (XII)

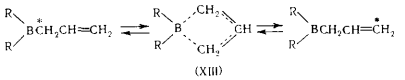
Compound (XI) is comparatively stable at room temperature, but isomerises to compound (XII) at 150°C. The reaction of chlorobis(dimethylamino)borane with crotylmagnesium bromide gives rise to a mixture of but-1-en-3-ylbis(dimethylamino)borane and but-2-en-1-ylbis(dimethylamino)borane (84 : 16).[40]

Allyldichloroborane is formed when BCl_3 is heated with tetra-allyltin[41].

III. THE PERMANENT ALLYL REARRANGEMENT IN ALLYL DERIVATIVES OF BORON

^{1}H NMR studies of triallylborane led to the detection in the latter of a permanent allyl rearrangement[42–44], the activation energy for which proved to be 10 ± 1 kcal mole^{-1}.

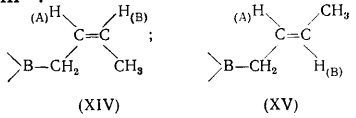
The reversible exchange of CH_2 groups in allyl derivatives of boron proceeds via a transition state (XIII) with symmetrically distributed hydrogen atoms in the CH_2 groups relative to the [boron] atom and equivalent B–C and B–C bonds.



(XIII)

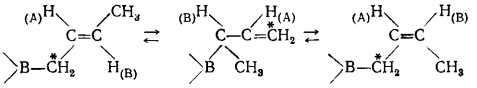
The specific features of the chemical behaviour of triallylborane are undoubtedly associated with the permanent allyl rearrangement occurring in it.

The study of the ^{1}H NMR spectra of tricrotylborane using proton–proton double resonance at frequencies of 60 and 100 HMz shows that this compound exists as a mixture of *cis*- (XIV) and *trans*-isomers (XV) of the but-2-enyl form[45]:



(XIV) (XV)

In contrast to triallylborane, there is no permanent allyl rearrangement in tricrotylborane at room temperature. The proton spectrum of the $-CH_{(A)}=CH_{(B)}$ system, obtained using proton–proton double resonance, shows that *trans*-tricrotylborane predominates in the mixture (J_{AB} = 15.0 Hz), its content at room temperature amounting to 70%. The form of the ^{1}H NMR spectrum of tricrotylborane above 150°C indicates the reversible interconversion of the *cis*- and *trans*-isomers at such a rate that the chemical shift and the spin–spin interaction constants of the $H_{(A)}$ and $H_{(B)}$ protons (J = 14 Hz) are averaged. The observed interconversion evidently proceeds via a stage involving the isomerisation of the but-2-enyl form of tricrotylborane (XV) to the but-1-enyl form (XVI), in which there is free rotation about the $H_{(A)}-C-CH_{(B)}$ bond, ensuring the conversion into the *cis*-form of tricrotylborane (XIV):



(XV) (XVI) (XIV)

The interconversions (XV) ⇌ (XVI) and (XVI) ⇌ (XIV) proceed via a transition state of type (XIII).

The study of the ^{1}H NMR spectra of tri-(2-methylallyl)-borane showed[10] that there is a permanent allyl rearrangement in this compound too, occurring more readily than in triallylborane. Thus, at 100°C the rate of rearrangement is 5709 s^{-1}, while in triallylborane at the same temperature it is 2421 s^{-1}. The activation energy for the rearrangement is 9.8 ± 0.5 kcal mole^{-1}.

The permanent allyl rearrangement in tri-(3-methylbut-2-en-1-yl)borane, 1-allyl-2-(but-2-en-1-yl)5-chloromethylene-4,4-dimethylcyclopentane[46], and 3-allyl derivatives of the 3-borabicyclo[3,3,1]non-6-ene series[47] has been studied by ^{1}H NMR. Permanent intermolecular allyl rearrangements have been detected by ^{11}B and ^{1}H NMR in the exchange reactions of triallylborane, tricrotylborane, and tri-(2-methylallyl)borane with borates[48] and alkyl thioborates[49]. The influence of the permanent allyl rearrangement on the parameters of the NMR spectra of certain allyl derivatives of boron has been studied[50].

IV. CHEMICAL PROPERTIES

1. Capacity for Complex Formation

Triallylborane forms complexes with pyridine[23,51], α-picoline, trimethylamine[51], and diethylamine[38]; a complex of tricrotylborane with pyridine is known[9].

The capacity of triallylborane for complex formation has been studied by ^{1}H and ^{11}B NMR and by boron–proton double resonance[51]. The heats of dissociation of the adducts of triallylborane with trimethylamine, pyridine, 2-methylpyridine, and 3-methylpyridine are respectively 20.6, 25.1, 19.1, and 26.2 kcal mole^{-1}. Reactions involving the substitution of one ligand by another in triallylborane complexes have been investigated by ^{1}H NMR [51] and it has been established that exchange between the free amine and the amine bound in the complex takes place in amine solutions of triallylborane complexes. Tri-(2-methylallyl)borane has a smaller capacity for complex formation than triallylborane[10].

The oxidation of the triethylamine complex of tricrotylborane in an excess of the amine with hydrogen peroxide leads to crotyl alcohol with an admixture of only 2% of

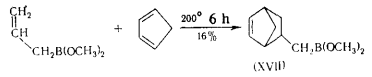
1-methylallyl alcohol, i.e. the oxidative cleavage of the B–C bond takes place without allyl rearrangement[10].

2. Reactions with Organometallic Compounds and Certain Other Reagents

Allyl-lithium adds to triallylborane with formation of lithium tetra-allylborate[52]. Triallylborane, tri-(2-methylallyl)borane, and tricrotylborane enter into exchange reactions with dimethylzinc[53–55] and dimethylcadmium[55,56] with formation of trimethylborane and the corresponding diallyl derivatives of zinc and cadmium. Vanadium tetrachloride forms BCl_3 and allylvanadium trichloride on reaction with triallylborane.

Di-n-butyl allylboronate combines with dichloromethylsilane in the presence of chloroplatinic(II) acid with formation of an ester of 3-methyldichlorosilylpropylboronic acid[58]. In the presence of chloroplatinic(II) acid, triethylsilane adds to the allylboronate ester with much more difficulty. Triethylgermane and triphenylgermane add to dimethyl allylboronate[59] at the double bond of the allyl group linked to $B(OR)_2$ much more readily than to olefinic hydrocarbons and their derivatives having functional groups in the γ-position. The latter substances combine with triethylgermane only in the presence of H_2PtCl_4, while the addition of triethylgermane to the allylboronate ester takes place without catalyst at 110–190°C and leads to the formation of the dimethyl ester of 3-triethylgermylpropylboronic acid in a high yield.

Allylboronate esters are involved in diene condensation with cyclopentadiene and its chloro-derivatives[60]. Dimethyl allylboronate condenses with cyclopentadiene only at a high temperature, forming the ester of *endo*-2-{bicyclo[2,2,1]hept-5-en-1-yl}methylboronic acid (XVII):



(XVII)

The allylboronate ester condenses very readily with hexachlorocyclopentadiene forming the ester of 2-{1,4,5,6,7,7-hexachlorobicyclo[2,2,1]hept-5-en-1-yl}-methylboronic acid. The reaction of the allylboronate ester with 1,2,3,4-tetrachlorocyclopentadiene yields the ester of 2-{1,4,5,6-tetrachlorobicyclo[2,2,1]hept-5-en-1-yl}methylboronic acid.

Triallylborane, tricrotylborane, and tri-(2-methylallyl)borane react with ethyl diazoacetate, forming the esters of $\gamma\delta$-unsaturated acids (XVIII):[61]

$$(RCH{=}CR'CH_2)_3B + N_2CHOOC_2H_5 \xrightarrow[-N_2]{+H_2O} RCH{=}CR'(CH_2)_2COOC_2H_5;$$

(XVIII)

R and R = H or CH_3.

According to some data[23], treatment of triallylborane with bromine at room temperature yields tri-(2,3-dibromopropyl)borane, while according to others[8] the product is 1,2,3-tribromopropane at −35°C. Reaction of di-n-butyl allylboronate with bromine yields the ester of 2,3-dibromopropylboronic acid[62]. In the presence of air, triallylborane forms a polymer containing 25–30% of oxygen[63]. Triallylborane is an active catalyst of the polymerisation of methyl methacrylate[63]. Thermal decomposition of triallylborane leads to the formation of various hydrocarbons and boron-containing products[64,65]. The reaction of triallylborane with tri-isobutylborane at 130–140°C yields butene and a polymer, which are converted on heating with alcohols into 1,5-dialkoxy-1,5-diboracyclo-octanes[66].

3. Reactions with Diborane and Tetra-alkyldiboranes

When triallylborane is treated with diborane (in proportions of 1 : 2) in ethereal solution, a solid polymer is obtained[67]. On being heated with n-butyl alcohol, it gives rise to hydrogen, propene, and liquid products, consisting mainly of 1,5-di-n-butoxy-1,5-diboracyclo-octane and the tetra-n-butyl ester of propane-1,3-diboronic acid. On heating with methyl borate, the solid polymer undergoes exchange reactions as a result of which the tetramethyl ester of propane-1,3-diboronic acid and the methyl ester of di-(3-dimethoxyborylpropyl)boronic acid are obtained[68–70]. When the polymer is heated with boron trichloride, 1,3-dichloroborylpropane is formed[71].

The reaction of triallylborane with triethylamine-borane leads to a polymer, whose pyrolysis gives rise to a complex mixture of products, where the main component is 1,5-diborabicyclo[3,3,3]undecane[72].

Hydroboration of dimethyl allylboronate and subsequent oxidation of the products lead to a mixture of diols containing 97% of propane-1,3-diol and 3% of propane-1,2-diol.[30] The main hydroboration product is tri-(3-dimethoxyborylpropyl)borane (XIX):

$$3\,CH_2{=}CHCH_2B(OCH_3)_2 + \frac{1}{2}\,B_2H_2 \rightarrow B[CH_2CH_2CH_2B(OCH_3)_2]_3.$$

(XIX)

On treatment with alcohol in the presence of a catalytic amount of a mercaptan, it is converted into the methyl ester of di-(3-dimethoxyborylpropyl)borinic acid and the dimethyl ester of n-propylboronic acid.

In the reaction of diborane with n-butyl diallylboronate, boron is attached to the extent of 97% to the terminal carbon atom of the allyl group[73]. The hydroboration of the ester with the reactants in proportions of 1 : 2 leads to a complex mixture of products whose treatment with n-butyl alcohol leads to the evolution of hydrogen and distillation of the alcoholysis products yields 1,5-di-n-butoxy-1,5-diboracyclo-octane and 1,3-dibutoxyborylpropane. The reaction of tetra-n-propyldiborane with dimethyl allylboronate results in the formation of the unstable dimethyl ester of 3-di-n-propylborylpropylboronic acid[74], which decomposes on heating into methyl di-n-propylboronate and a polymer. On heating with methyl borate in the presence of a small amount of tetrapropyldiborane, which plays the role of the reaction catalyst[75], the polymer is converted into 1,3-bis(dimethoxyboryl)propane. Allylboronate esters behave similarly in relation to tetraalkylborane [...part of text missing in Russian original (Ed. of Translation)] dimethylester of allylthioboronic acid[74].

4. Reactions with Carbonyl Compounds and Nitriles

It has been reported[23,24] that triallylborane reacts with aldehydes to form the alkyl esters of diallylborinic acid and cyclohexadiene or dialkyl esters of alkylboronic acid, cyclohexadiene, and propene. Subsequently it was shown that the reaction of triallylborane with aldehydes in reality proceeds via the mechanism of organometallic synthesis, i.e. via the addition of allyl groups to the carbon atom and of the BR_2 group to the oxygen atom of the carbonyl group[76]. Depending on the ratio of the initial reactants, the esters of diallylborinic, allylboronic, or boric acids are then obtained. The reaction of triallylborane with ketones stops at the stage involving the formation of allylboronic acid even on heating to 80°C.[76]

Since allylboronate esters and borates are readily hydrolysed and readily undergo transesterification with aminoalcohols, the reaction of triallylborane with aldehydes and ketones can be used to synthesise unsaturated alcohols. The reaction of tricrotylborane with formaldehyde is accompanied by the allyl rearrangement[9]. Triallylborane adds smoothly to $\alpha\beta$-unsaturated aldehydes in the 1,2-positions[77,78]. The reaction of acrolein and triallylborane in 2:1 proportions yields the di(hexa-1,5-dien-3-yl)-ester of allylboronic acid[77,78]. The reaction of triallylborane with α-cyclocitral or β-cyclocitral (in proportions of 1:3) results in the formation of the corresponding borates, which demonstrates the ability of allylboronate esters to add to aldehydes.

The reactions of triallylborane with $\alpha\beta$-unsaturated ketones have also been investigated[77,79]. In contrast to tri-n-butylborane, which adds to methyl vinyl ketone in the 1,4-positions with formation of oct-2-en-2-yl dialkylborinate (XX):[77]

$$(n\text{-}C_4H_9)_3B + CH_2{=}CHC(O)CH_3 \rightarrow CH_3(CH_2)_4CH{=}C(OB(C_4H_9\text{-}n)_2)CH_3, \quad (XX)$$

triallylborane adds to methyl vinyl ketone in the 1,2-positions with formation of the 3-methylhexa-1,5-dien-3-yl ester of diallylborinic acid, whose hydrolysis gives rise to 3-methylhexa-1,5-dien-3-ol. 1-Chloro-3-methylhexa-1,5-dien-3-yl diallylborinate is obtained from triallylborane and β-chlorovinyl ketone (in 1:1 proportions) and its hydrolysis leads to 1-chloro-3-methylhexa-1,5-dien-5-ol.[77]

The reactions of triallylborane with benzylideneacetone, benzylideneacetophone, cinnamylideneacetone, mesitylene oxide, and α- and β-ionones proceed smoothly and lead, after the hydrolysis of the organoboron esters, to the corresponding unsaturated tertiary alcohols. The yield of the latter reaches 77–83% and exceeds in some cases the yields obtained when allylmagnesium bromide is used[79].

The use of allylalkyl compounds, obtained by the alkylhydroboration, of allenes appears to be promising for organic synthesis. When these compounds interact with carbonyl derivatives, the products are the alkyl esters of dialkylborinic acids, whose hydrolysis yields unsaturated alcohols. Thus the esters (XXI) are formed from dialkyl-(3-methylbut-2-en-1-yl)boranes and mesityl oxide, their hydrolysis resulting in the formation of 3,3,4,6-tetramethylhepta-1,5-dien-4-ol (XXII):[17]

$$CH_3{-}C(CH_3){=}CHCH_2BR_2 + (CH_3)_2C{=}CHC(O)CH_3 \xrightarrow[81\%]{} CH_2{=}CH{-}C(CH_3)(OBR_2){-}C(CH_3)_2{-}CH{=}C(CH_3)_2 \xrightarrow[86\%]{-H_2O} \quad (XXI)$$

$$\rightarrow CH_2{=}CH{-}C(CH_3)(OH){-}C(CH_3)_2{-}CH{=}C(CH_3)_2. \quad (XXII)$$

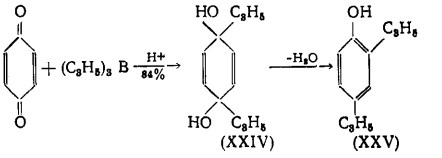
The reactions with acetone, methyl vinyl ketone, and benzaldehyde take place similarly.

Diallyl-(2-ethoxypenta-1,4-dien-1-yl)borane reacts with acetone to form compound (XXIII):[80]

$$(C_3H_5)_2BCH{=}C(OC_2H_5){-}CH_2CH{=}CH_2 + 2(CH_3)_2CO \rightarrow CH_2{=}CHCH_2C(CH_3)(OBCH{=}CCH_2CH{=}CH_2)OCH_2CH_3 \quad (XXIII)$$

Di-n-hexyl crotylboronate reacts with butyraldehyde and cyclohexanone, the products being the corresponding 1-methylallylmethanols[27].

The reactions of triallylborane with various quinones have been investigated[81–83]. When triallylborane is allowed to react with 1,4-benzoquinone in 1:1 proportions and the resulting organoboron compounds are hydrolysed, the *cis*- and *trans*-isomers of 1,4-diallyl-1,5-dihydroxycyclohexa-2,5-diene (XXIV) are obtained in high yield and are converted on steam distillation in the presence of boric acid into 2,4-diallylphenol (XXV):

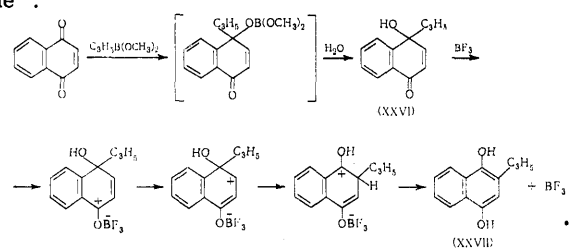


(XXIV) (XXV)

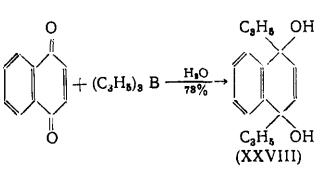
When the reaction ratio is 2:1, the main product (61%) is 2-allyl-1,4-hydroquinone together with 2,4-diallylphenol (26%).[83]

The reactions of triallylborane with substituted 1,4-benzoquinones have been investigated[82]. The interaction of equimolar amounts of 2-allyl-1,4-benzoquinone and triallylborane leads to the formation of 2,4,6-triallylphenol while the interaction of the reactants in proportions of 2:1 leads to the formation of insignificant amounts of 2,4,6-triallylphenol, the main reaction products being 2,5-diallyl- and 2,6-diallyl-1,4-hydroquinones. 2-Butyl-1,4-benzoquinone reacts with trialkylborane (in 1:1 proportions) with formation of 4,6-diallyl-2-butylphenol[83]. The reaction between 9,10-anthraquinone and triallylborane in equimolar proportions leads to 9-allyl-9-hydroxyanthrone and, when two equivalents of triallylborane are used, the main product is *cis*-9,10-diallyl-9,10-dihydroxy-9,10-dihydroanthracene with an admixture of the *trans*-isomer[83].

The esters of allylboronic and diallylborinic acids have proved to be extremely reactive in relation to quinones[82]. Dibutyl allylboronate gives a high yield of 2-allyl-1,4-hydroquinone on reaction with 1,4-benzoquinone. The mechanism of the formation of 2-allyl-1,4-hydroquinone was established in a study of the reaction between dimethyl allylboronate and 1,4-naphthoquinone. In this case it is possible to isolate the intermediate (when the reaction is carried out under mild conditions), namely 1-allyl-1-hydroxy-4-oxo-1,4-dihydronaphthalene (XXVI), which is converted into 2-allyl-1,4-dihydroxynaphthalene (XXVII) on heating with boron trifluoride-ether, as happens in the rearrangement of *p*-tolylquinol into 2-methyl-1,4-hydroquinone[84]:



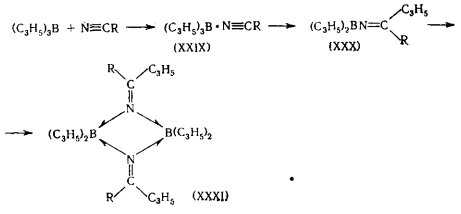
Trialkylboranes react with 1,4-naphthoquinone similarly to dimethyl allylboronate[85], adding to only one carbonyl group, while triallylborane adds readily to two carbonyl groups, forming, after hydrolysis, 1,4-diallyl-1,4-dihydroxy-1,4-dihydronaphthalene (XXVIII):[82]



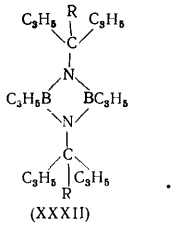
(XXVIII)

The reactions of triallylborane with 1,2-quinones have been investigated[83]. When equimolar amounts of 1,2-naphthoquinone and triallylborane interact, *trans*-1,2-diallyl-1,2-dihydroxy-1,2-dihydronaphthalene is formed after hydrolysis; the same diol is obtained also when 1,2-naphthoquinone is treated with dibutyl allylboronate. 9,10-Phenanthraquinone and acenaphthoquinone react similarly with triallylborane, forming respectively (after hydrolysis) 9,10-diallyl-9,10-dihydroxy-9,10-dihydrophenanthrene and 1,2-diallyl-1,2-dihydroxyacenaphthene (*trans*-configuration).

The first stage of the reaction of triallylborane with nitriles in isopentane between −70° and −50°C involves the formation of complexes (XXIX) which are completely converted, on gradual heating of the reaction mixture to room temperature, into substituted diallyl(but-3-enylideneamino)boranes (XXX), which dimerise into derivatives of 2,2,4,4-tetra-allyl-1,3-di(but-3-enylidene)cyclodiborazane (XXXI):[86,87]



On heating (100°C), cyclodiborazanes are converted into substituted 2,4-diallyl-1,3-di(hepta-1,6-dien-4-yl)-1,3-diaza-2,4-diboretidines (XXXII), covalent B–N bonds being formed between boron and nitrogen atoms instead of the semicoordinate linkages B ← N, and N=C bonds being converted into single N–C linkages:

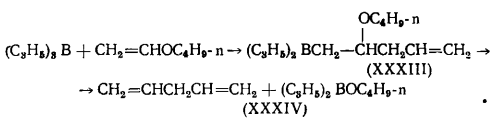


Alcoholysis of diazadiboretidines yields 4-substituted 4-aminohepta-1,6-dienes.

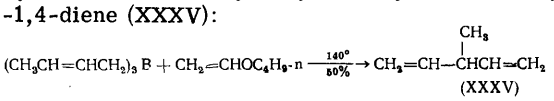
5. Reactions with Compounds Containing an Activated Carbon–Carbon Double Bond

Allylboranes can react with compounds containing an activated double bond—vinyl ethers, 4,5-dihydro-2-methylfuran, and cyclopropene hydrocarbons.

Triallylborane reacts with n-butyl vinyl ether at 110–140°C to form penta-1,4-diene (80% yield)[88,89]. Presumably allylborane initially adds to the double bond with formation of (2-alkoxypent-4-en-1-yl)diallylborane (XXXIII), which is then converted via β-elimination into the diene (XXXIV) and n-butyl diallylboronate:

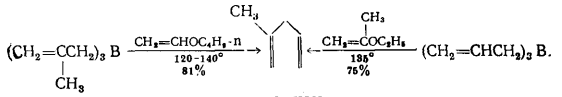


The ether (XXXIII) then reacts with a second molecule of vinyl ether via the same mechanism. The reaction of tricrotylborane with n-butyl vinyl ether yields 3-methylpenta-1,4-diene (XXXV):

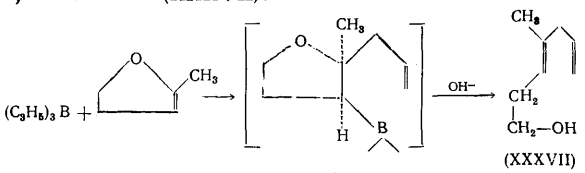


The formation of the diene (XXXV) shows that the addition of tricrotylborane to the carbon–carbon double bond proceeds with allyl rearrangement via a cyclic transition state.

2-Methylpenta-1,4-diene (XXXVI) is obtained from n-butyl vinyl ether and tri-(2-methylallyl)borane and also by the reaction of triallylborane with ethyl isopropenyl ether:



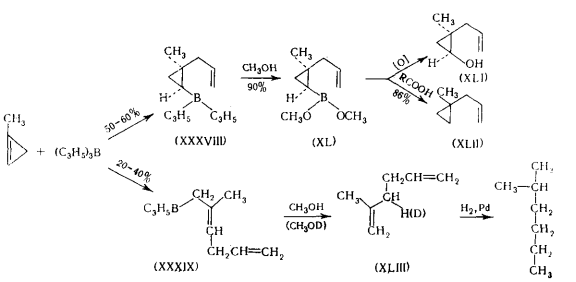
The reaction of triallylborane with 4,5-dihydro-2-methylfuran takes place slowly at room temperature and rapidly (in several minutes) at 80–100°C. Alkaline hydrolysis of the addition product leads to 4-methylhepta-1,4-dien-1-ol (XXXVII):



Thus reactions of allylboranes with acyclic and cyclic vinyl ethers constitute a convenient preparative method for the synthesis of 1,4-diene hydrocarbons and their derivatives with functional groups, which are otherwise difficult to obtain.

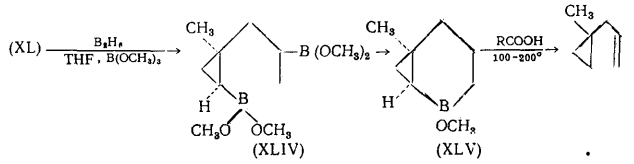
On cooling (to between −70° and 0°C), triallylborane reacts with 1-methylcyclopropene similarly to trialkylboranes[90], namely in two different ways. The preferred pathway involves the *cis*-addition of the organoborane to the double bond of the hydrocarbon with formation of diallyl-(1-allyl-1-methyl-2-cyclopropyl)borane (XXXVIII), but the reaction also takes place partly with rupture of the ring at the $C_{(2)}$–$C_{(3)}$ linkage with formation of diallyl-(2-methylhexa-2,5-dien-1-yl)borane (XXXIX). The methanolysis of compound (XXXVIII) gives rise to (1-allyl-1-methyl-2-cyclopropyl)dimethoxyborane (XL), the oxidation of which leads to 1-allyl-1-methyl-2-cyclopropanol (XLI) and acidolysis yields 1-allyl-1-methylcyclopropane (XLII).

Compound (XXXIX) has not been isolated in a pure state, but its formation has been demonstrated by the isolation of 2-methylhexa-1,5-diene (XLIII) from the products of the methanolysis of the reaction mass:



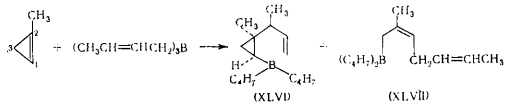
When 1-methyl-2-deuterocyclopropene is treated with triallylborane and the reaction products are subjected to methanolysis, 2-methyl-3-deuterohexa-1,5-diene (30–35%) and (1-allyl-2-deutero-1-methyl-2-cyclopropyl)dimethoxyborane (50–60%) are obtained.

The hydroboration of compound (XL) in tetrahydrofuran (THF) in the presence of methyl borate leads to the diboron compound (XLIV), which is converted on heating (100–200°C) into 5-methoxy-5-methyl-5-borabicyclo[4,1,0]heptane [(5-methoxy-1-methyl-5-boranorcarane)] (XLV) with elimination of methyl borate[92]:



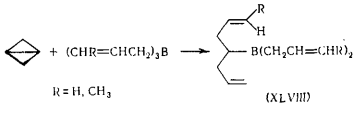
(XLIV) (XLV)

When 1-methylcyclopropene reacts with tricrotylborane, the main product (85–90%) is *cis*-[2-(but-3-en-2-yl)-2-methyl-1-cyclopropyl]di(but-2-enyl)borane (XLVI) together with di(but-2-enyl)-2-methylhepta-2,5-dien-1-ylborane (XLVII) (10–15%) yield); this shows that the addition of the allylborane to the double bond of the three-membered ring takes place with allyl rearrangement, while the insertion in a C–C single bond takes place without such rearrangement[93]:



(XLVI) (XLVII)

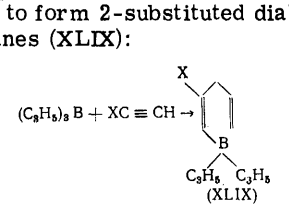
Triallylborane and tricrotylborane react at −70°C with bicyclo[1,1,0]butane to form the unsaturated compounds (XLVIII):[94]



R = H, CH_3 (XLVIII)

6. Reactions with Acetylenic Compounds

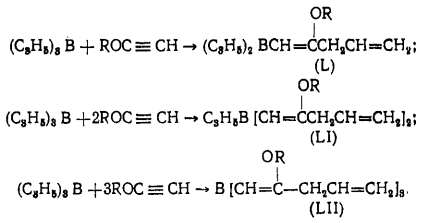
Acetylenic compounds react with triallylborane at room temperature to form 2-substituted diallyl-(2-penta-1,4-dien-1-yl)boranes (XLIX):



(XLIX)

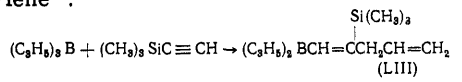
(2-Alkylpenta-1,4-dien-1-yl)diallylboranes (X = CH_3 or C_4H_9), obtained by the reaction of triallylborane with methylacetylene or n-butylacetylene[95–98], cannot be isolated in a pure state, since they are unstable and cyclise to 3-allyl-substituted 1,5-diallyl-1-boracyclohex-2-enes, the reaction being slow at room temperature and rapid on vacuum distillation[98].

2-Substituted diallyl(penta-1,4-dien-1-yl)boranes, formed in the first stage of the reaction of triallylborane with trimethylpropargyloxysilane[99], phenylacetylene[100], cyclohexenylacetylene[101], or propargyl chloride[102,103] are altogether unstable. However, alkoxyacetylenes react with triallylborane to form fairly stable addition products, which can be isolated in a pure state. The exothermic reaction of triallylborane with alkoxyacetylenes proceeds between −70° and −50°C and, depending on the reactant ratio, leads to (2-alkoxypenta-1,4-dien-1-yl)diallylboranes (L), di-(2-alkoxypenta-1,4-dien-1-yl)allylboranes (LI), or tri-(2-alkoxypenta-1,4-dien-1-yl)boranes (LII):[84,95]



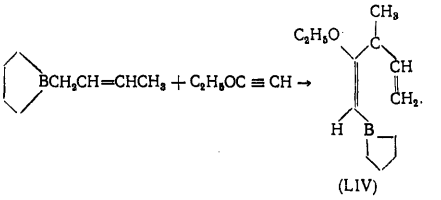
(L) (LI) (LII)

Diallyl-(2-trimethylsilylpenta-1,4-dien-1-yl)borane (LIII) has been obtained from triallylborane and trimethylsilylacetylene[95]:



(LIII)

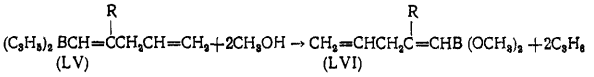
The first condensation stage, leading to compounds (XLIX), involves the *cis*-addition of $(C_3H_5)_2B$ and C_3H_5 fragments to the C≡C bond. The reaction probably proceeds via a six-centre transition state and is accompanied by the allyl rearrangement [as shown in a study of the reaction of 1-crotylboracyclopentane with ethoxyacetylene, which leads to the formation of 1-(2-ethoxy-3-methylpenta-1,4-dien-1-yl)boracyclopentane (LIV)[104,105]



(LIV)

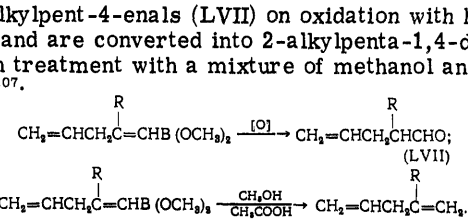
Tri-(2-methylallyl)borane reacts with alkoxyacetylenes like triallylborane. Depending on the reactant ratio, (2-alkoxy-4-methylpenta-1,4-dien-1-yl)di-(2-methylallyl)-boranes, di-(2-alkoxy-4-methylpenta-1,4-dien-1-yl)-2-methylallylboranes, or tri-(2-alkoxy-4-methylpenta-1,4-dien-1-yl)boranes are formed at temperatures between −70° and −20°C.[106]

On treatment with methanol, (2-alkylpenta-1,4-dien-1-yl)diallylboranes (LV) readily exchange their allyl groups for methoxy-groups[95–97,104]. The resulting dimethyl esters of 2-alkylpenta-1,4-dien-1-ylboronic acids (LVI),



(LV) (LVI)

yield 2-alkylpent-4-enals (LVII) on oxidation with hydrogen peroxide and are converted into 2-alkylpenta-1,4-dienes (LVIII) on treatment with a mixture of methanol and acetic acid[96,97,107].

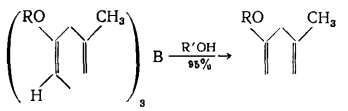


(LVII) (LVIII)

On treatment with alcohols, not only boron–allyl but also boron-vinyl bonds are ruptured in (2-alkoxypenta-1,4-dien-1-yl)diallylboranes and di-(2-alkoxypenta-1,4-dien-1-yl)allylboranes with formation, depending on

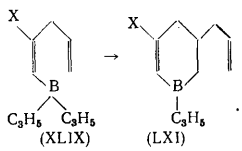
the reactant ratio and the duration of heating, of 2-alkoxypenta-1,4-dienes or allyl methyl ketone ketals[104,107]. Tri-(2-alkoxypenta-1,4-dien-1-yl)boranes behave similarly with respect to alcohols.

Experiments on the alcoholysis of compounds (L)–(LII) by different alcohols have shown that the boron–vinyl bond dissociates via direct attack on the B–C linkage, which has been confirmed by studies on the reactions of tri-(2-methoxypenta-1,4-dien-1-yl)borane with methyl alcohol containing a labelled carbon atom[108]. The alcoholysis of tri-(2-alkoxy-4-methylpenta-1,4-dien-1-yl)-boranes (LIX) leads to 2-alkoxy-4-methylpenta-1,4-dienes (LX):[106]



(LIX) (LX)

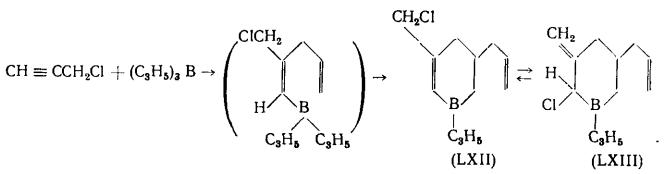
2-Substituted diallyl(penta-1,4-dien-1-yl)boranes (XLIX) can undergo intramolecular cyclisation to 3-substituted 1,5-diallyl-1-boracyclohex-2-enes (LXI):



(XLIX) (LXI)

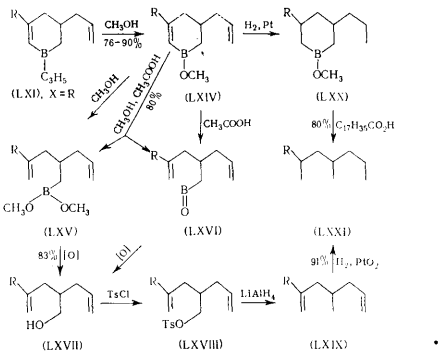
2-Alkyl-substituted compounds (XLIX, X = R) cyclise slowly at room temperature and rapidly on moderate heating (to 40–100°C).[96–98,109,110] 2-Alkoxy-substituted compounds (XLIX, X = OR) are converted into derivatives of type (LXI) at 120–130°C.[109,111] Compounds of type (LXI) are obtained by the reaction of triallylborane with trimethylpropargyloxysilane[99], phenylacetylene[100], and cyclohexylacetylene[101].

Propargyl chloride reacts slowly with triallylborane at room temperature, forming 1,5-diallyl-3-chloromethyl-1-boracyclohex-2-ene (LXII), which isomerises slowly to 1,5-diallyl-2-chloro-3-methylene-1-boracyclohexane (LXIII); after 20 days, the reaction mixture contains approximately 80% of compound (LXII) and 20% of compound (LXIII):[102,103]



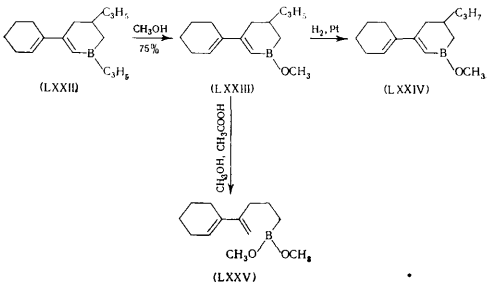
(LXII) (LXIII)

When 3-alkyl-1,5-diallyl-1-boracyclohex-2-enes (LXI) are treated with methanol at 20–30°C, propene is evolved and 3-alkyl-5-allyl-1-methoxy-1-boracyclohex-2-ene (LXIV) is formed[96,97,110]. When compound (LXIV) is refluxed for a long time with an excess of methanol, the B–vinyl bond is cleaved protolytically and (4-alkyl-2-allylpent-4-en-1-yl)dimethoxyborane (LXV) is formed. The ring opening in compound (LXIV) takes place much more rapidly when it is heated (to 80°C) with a mixture of methanol and acetic acid. Under these conditions, the products are the ester (LXV) and the trimer of the anhydride of (4-alkyl-2-allylpent-4-en-1-yl)boronic acid (LXVI) or the trimer (LXVI) alone when the reaction mixture is kept at room temperature for 24 h:

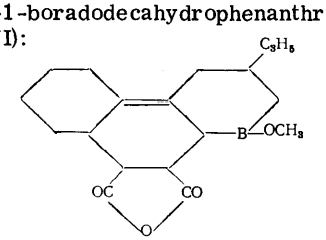


The oxidation of the esters (LXV) or the anhydrides (LXVI) with hydrogen peroxide in an alkaline medium gives an 80–90% yield of 4-alkyl-2-allylpent-4-en-1-ols (LXVII). By reducing the tosylates (LXVIII) with lithium aluminium hydride, it is possible to obtain 2,4-dimethylhepta-1,6-diene (LXIX, R = CH_3) or 2-n-butyl-4-methylhepta-1,6-diene (LXIX, R = n-C_4H_9). Hydrogenation of the methoxy-derivatives (LXIV) over platinum black leads to 3-alkyl-1-methoxy-5-n-propyl-1-boracyclohexenes (LXX). 1-Methoxy-3-methyl-5-n-propyl-1-boracyclohexane can be converted by acidolysis into 2,4-dimethylheptane (LXXI, R = CH_3). 5-Allyl-1-methoxy-3-phenyl-1-boracyclohex-2-ene, obtained by the methanolysis of 1,5-diallyl-3-phenyl-1-boracyclohex-2-ene, is hydrogenated in steps to 1-methoxy-3-phenyl-5-n-propyl-1-boracyclohex-2-ene (over platinum black) and 1-methoxy-3-phenyl-5-n-propyl-1-boracyclohexane (over $Pd/SrCO_3$).[100]

On treatment with methanol, 1,5-diallyl-3-cyclohexenyl-1-boracyclohex-2-ene (LXXII) is converted into 5-allyl-3-cyclohexenyl-1-methoxy-1-boracyclohex-2-ene (LXXIII), which gives rise to 3-cyclohexenyl-1-methoxy-5-n-propyl-1-boracyclohex-2-ene (LXXIV) on hydrogenation over Pt black and (2-allyl-4-cyclohexenylpent-4-en-1-yl)-dimethoxyborane (LXXV) on treatment with a mixture of methanol and acetic acid[101]:

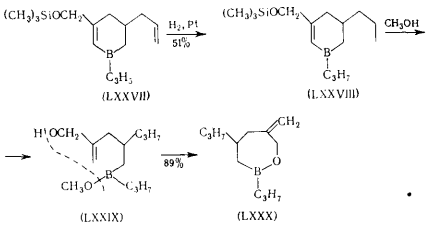


Compound (LXXIV) undergoes the diene condensation with maleic anhydride, forming the anhydride of 3-allyl-1-methoxy-1-boradodecahydrophenanthrenedicarboxylic acid (LXXVI):



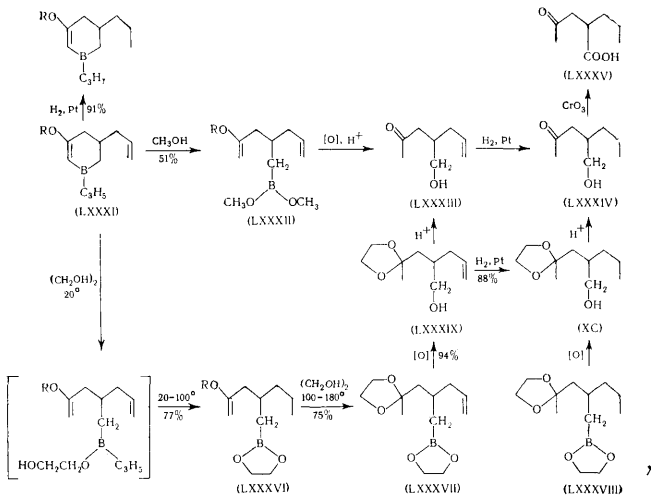
(LXXVI)

1,5-Diallyl-3-trimethylsiloxymethyl-1-boracyclohex-2-ene (LXXVII) is hydrogenated over the Adams catalyst to 1,5-di-n-propyl-3-trimethylsiloxymethyl-1-boracyclohex-2-ene (LXXVIII), which is smoothly converted on brief heating with methanol [with cleavage of the Si–O– and B–C= bonds and subsequent intramolecular condensation of compound (LXXIX)] into 6-methylene-2,4-di-n-propyl-1-2-oxaborepan (LXXX):[99]



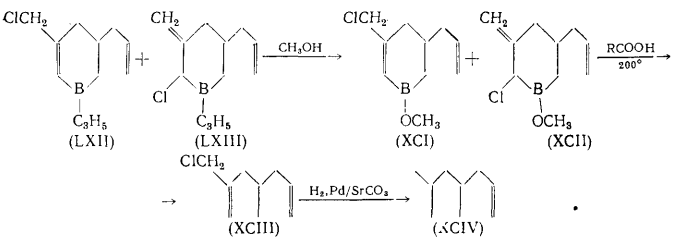
2,4-Dimethylheptan can be obtained from compound (LXXX) by a series of consecutive operations.

On treatment with alcohols, the boron–vinyl ring bond is initially broken in 3-alkoxy-1,5-diallyl-1-boracyclohex-2-ene (LXXXI), as shown by infrared spectroscopy, and the boron–allyl bond then undergoes alcoholysis in the resulting acyclic organoboron complex[111]. The final product of the reaction of compound (LXXXI) with methanol is (4-alkoxy-2-allylpent-4-en-1-yl)dimethoxyborane (LXXXII), from which it is possible to obtain 4-hydroxymethylhept-1-en-6-one (LXXXIII), 4-hydroxymethylheptan-6-one (LXXXIV), and 2-n-propyl-levulinic acid (LXXXV). When compound (LXXXI) is heated with ethylene glycol, the resulting product is 2-(4-alkoxy-2-allylpent-4-en-1-yl)-1,3,2-dioxaborolan (LXXXVI), which yields 2-(2-allyl-4,4-ethylenedioxy-1-pentyl)-1,3,2-dioxaborolan (LXXXVII) on further heating (100–180°C) with ethylene glycol. Catalytic hydrogenation and oxidation with hydrogen peroxide of the last product results in its conversion into 2-(4,4-ethylenedioxy-2-n-propyl-1-pentyl)-1,3,2-dioxaborolan (LXXXVIII), 2-allyl-4,4-ethylenedioxypentanol (LXXXIX), and 4,4-ethylenedioxy-2-n-propyl-1-pentanol (XC), from which it is possible to obtain compounds (LXXXIII)–(LXXXV):

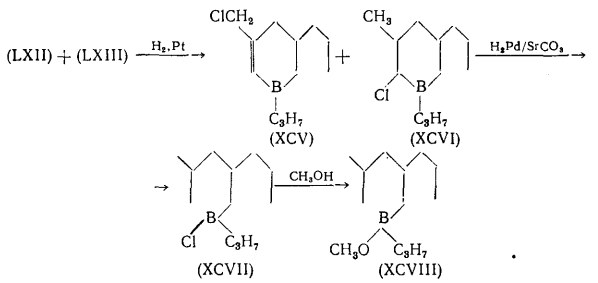


where R = CH_3 or n-C_4H_9.

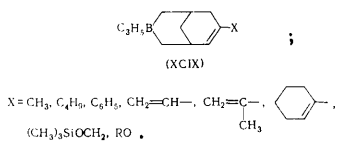
Methanolysis of a mixture of 1,5-diallyl-3-chloromethyl-1-boracyclohex-2-ene (LXII) and 1,5-diallyl-2-chloro-3-methylene-1-boracyclohexane (LXIII) in proportions of 4 : 1 results in a mixture of 5-allyl-3-chloromethyl-1-methoxy-1-boracyclohex-2-ene (XCI) and 5-allyl-1-methoxy-3-methylene-1-boracyclohexane (XCII), which are converted by acidolysis into 2-chloromethyl-4-methylhepta-1,6-diene (XCIII). The last compound is hydrogenated over Pd/$SrCO_3$ to 2,4-dimethylheptane (XCIV):[101]



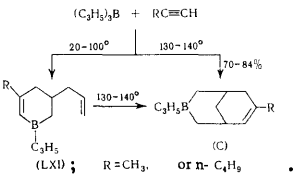
Hydrogenation of a mixture of compounds (LXII) and (LXIII) over platinum yields 3-chloromethyl-1,5-di-n-propyl-1-boracyclohex-2-ene (XCV) and 2-chloro-3-methyl-1-di-n-propyl-1-boracyclohexane (XCVI). On further hydrogenation over Pd/$SrCO_3$, compounds (XCV) and (XCVI) are converted into chloro-n-propyl-(4-methyl-2-n-propyl-1-pentyl)borane (XCVII), which is converted on treatment with methanol into the methyl ester of (4-methyl-2-n-propyl-1-pentyl)-n-propylboronic acid (XCVIII). Acidolysis of the chloride (XCVII) yields 2,4-dimethylheptane (XCIV):



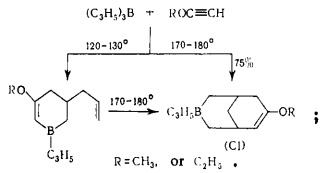
3-Substituted 1,5-diallyl-1-boracyclohex-2-enes (LXI) undergo intramolecular cyclisation on heating (130–180°C) with formation of 7-substituted 3-allyl-3-borabicyclo-[3,3,1]non-6-enes (XCIX):



The reaction of triallylborane with acetylene (at 120–130°C) yields directly 3-allyl-3-borabicyclo[3,3,1]non-6-ene (XCIX, X = H).[112,113] The synthesis of 7-alkyl-3-allyl-3-borabicyclo[3,3,1]non-7-enes (C) requires a temperature of 130–140°C:[113,114]

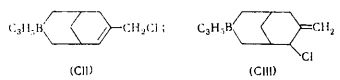


In order to obtain 7-alkoxy-3-allyl-3-borabicyclo-[3,3,1]non-6-enes (CI), the reaction must be carried out at 170–180°C:[115]



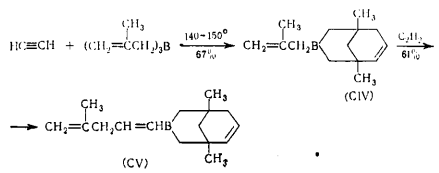
3-Allyl-7-trimethylsiloxymethyl-3-borabicyclo[3,3,1]non-6-ene is formed in 80% yield when triallylborane is heated with trimethylpropargyloxysilane at 140°C;[116] in order to synthesise 3-allyl-7-phenyl-3-borabicyclo[3,3,1]non-6-ene (in 96% yield), a mixture of triallylborane and phenylacetylene is kept for 1 h at 80°C:[100] 3-allyl-7-cyclohexenyl-3-borabicyclo[3,3,1]non-6-ene is formed when 1,5-diallyl-3-cyclohexenyl-1-boracyclohex-1-ene is vacuum-distilled[117].

When propargyl chloride is heated with triallylborane, a mixture of 3-allyl-7-chloromethyl-3-borabicyclo-[3,3,1]non-6-ene (CII) and 3-allyl-6-chloro-7-methylene-3-borabicyclo[3,3,1]nonane (CIII) is formed in proportions of 7 : 3:[102,118]



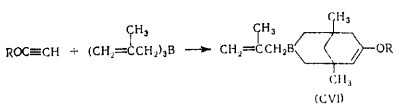
When triallylborane and propargyl bromide are heated, they form a mixture of 3-allyl-7-bromomethyl-3-borabicyclo[3,3,1]non-6-ene and 3-allyl-6-bromo-7-methylene-3-borabicyclo[3,3,1]nonane[119].

When tri-(2-methylallyl)borane is heated in acetylene in an autoclave at 140–150°C, 1,5-dimethyl-3-(2-methylallyl)-3-borabicyclo[3,3,1]non-6-ene (CIV) is formed in 67% yield; it can add to acetylene with formation of compound (CV):[120,121]

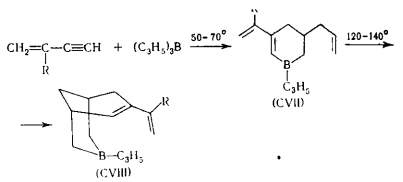


Tri-(2-methylallyl)borane reacts with n-butylacetylene to form 7-n-butyl-1,5-dimethyl-3-(2-methylallyl)-3-borabicyclo[3,3,1]non-6-ene[120].

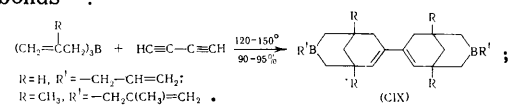
7-Alkoxy-1,5-dimethyl-3-(2-methylallyl)-3-borabicyclo-[3,3,1]non-6-enes (CVI) have been obtained by the condensation of tri-(2-methylallyl)borane with alkoxyacetylenes[120,122]:



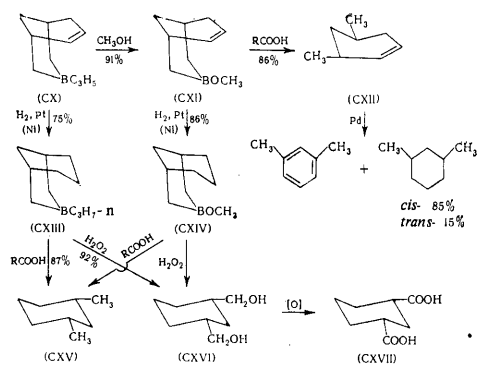
The interaction of triallylborane with vinylacetylene or isopropenylacetylene results in the formation of 1,5-diallyl-3-vinyl-1-boracyclohex-2-ene (CVII, R = H) or 1,5-diallyl-3-isopropenyl-1-boracyclohex-2-ene (CVII, R = CH_3) respectively, which are converted on heating into 3-allyl-7-vinyl-3-borabicyclo[3,3,1]non-6-ene (CVIII, R = H) or 3-allyl-7-isopropenyl-3-borabicyclo[3,3,1]non-6-ene (CVIII, R = CH_3):[123–125]



The reaction of diacetylene with triallylborane or tri-(2-methylallyl)borane at 120–150°C leads to the dibora-compounds (CIX) with a system of conjugated double bonds[126]:

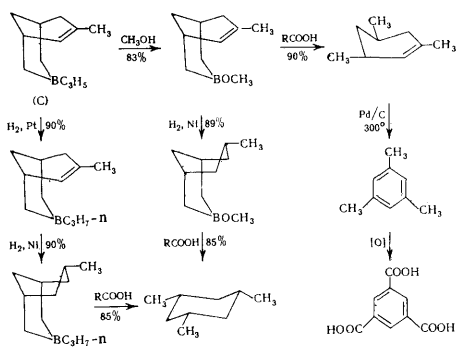


The methanolysis of 3-allyl-3-borabicyclo[3,3,1]non-6-ene (CX) leads to 3-methoxy-3-borabicyclo[3,3,1]non-6-ene (CXI),[113] which is converted into *cis*-3,5-dimethylcyclohexene (CXII) on heating with caproic acid as a result of the cleavage of the B–C bonds. When the THF solution of compound (CXII) is heated with palladium black, a mixture of *m*-xylene and *cis*- and *trans*-1,3-dimethylcyclohexanes is formed. The double bonds in the bicyclic compounds (CX) and (CXI) are readily hydrogenated at 20°C over a platinum catalyst at atmospheric pressure or over Raney nickel in an autoclave, the products being 3-n-propyl-3-borabicyclo[3,3,1]nonane (CXIII) or 3-methoxy-3-borabicyclo[3,3,1]nonane (CXIV) respectively, probably having the chair–chair conformation like bicyclo[3,3,1]nonane. The acidolysis of compounds (CXIII) and (CXIV) leads to *cis*-1,3-dimethylcyclohexane (CXV) with only about 1% of unidentified impurities. The oxidation of compounds (CXIII) and (CXIV) with hydrogen peroxide in an alkaline medium results in the formation of *cis*-1,3-dihydroxymethylcyclohexane (CXVI), which is converted on further oxidation into *cis*-cyclohexane-1,3-dicarboxylic acid (CXVII):



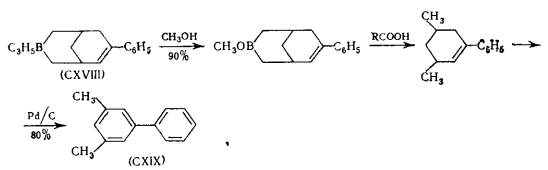
When compound (CX) is heated with n-butylamine, it is converted into 3-n-butylamino-3-borabicyclo[3,3,1]non-6-ene which can be obtained also by the transamination of 3-amino-3-borabicyclo[3,3,1]non-6-ene. The last compound can be obtained by the action of ammonia on 3-n-butylthio-3-borabicyclo[3,3,1]non-6-ene, formed by the reaction of thioborate and 3-methoxy-3-borabicyclo-[3,3,1]non-6-ene[127]. The synthesis of 3-alkylthio- and 3-amino-3-borabicyclo[3,3,1]nonanes has been achieved similarly[127].

3-Allyl-7-methyl-3-borabicyclo[3,3,1]non-6-ene (C, R = CH_3) has been subjected to the following reactions[112]:

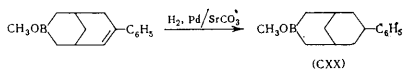


Similar reactions have been achieved with 3-allyl-7-n-butyl-3-borabicyclo[3,3,1]non-6-ene[114].

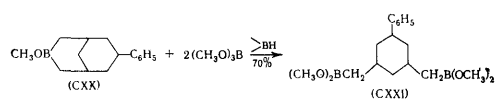
The structure of 3-allyl-7-phenyl-3-borabicyclo-[3,3,1]non-6-ene (CXVIII) has been demonstrated by converting it into 3,5-dimethylbiphenyl (CXIX):[100]



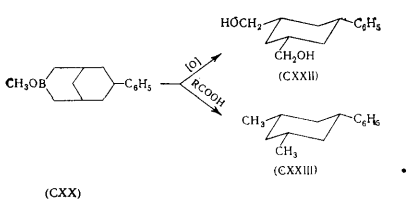
In contrast to 3-methoxy-7-methyl-3-borabicyclo-[3,3,1]non-6-ene, compound (CXVIII) is not hydrogenated in an autoclave over Raney nickel but it can be readily hydrogenated with hydrogen in 7-methoxy-7-phenyl-3-borabicyclo[3,3,1]nonane (CXX) in the presence of $Pd/SrCO_3$ at room temperature[100]:



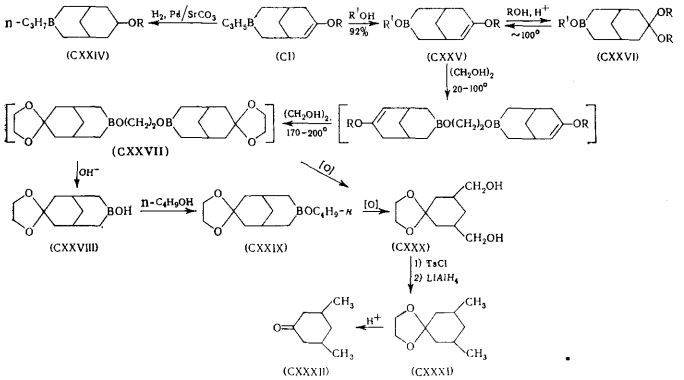
When compound (CXX) is heated with methylborate for a long time in the presence of tetra-n-propyldiborane, the boron-containing ring is cleaved and 1,3-bis(dimethoxyborylmethyl)-5-phenylcyclohexane (CXXI) is formed:



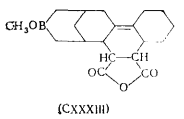
Oxidation of compound (CXX) with hydrogen peroxide leads to the synthesis of 1,3-dihydroxymethyl-5-phenylcyclohexane (CXXII) and, when the latter is heated with stearic acid, it is possible to obtain *cis*-1,3-dimethyl-5-phenylcyclohexane (CXXIII):



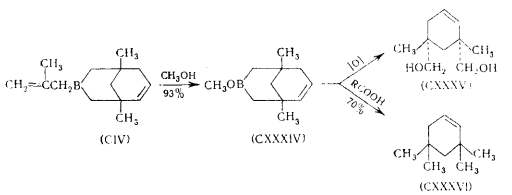
The hydrogenation of 7-alkoxy-3-allyl-3-borabicyclo-[3,3,1]non-6-ene (CI) over $Pd/SrCO_3$ takes place with absorption of two moles of hydrogen and leads to 7-alkoxy-3-n-propyl-3-borabicyclo[3,3,1]nonane (CXXIV).[115] The dialkoxy-derivatives (CXXV) are formed with liberation of propene when compounds (CI) are treated with alcohols. In the presence of acids, the alkoxy-derivative (CXXV), containing the vinyl ether group, readily combines with alcohols to form ketals (CXXVI), which are, however, unstable and split off the alcohol on vacuum distillation (at about 100°C) with reformation of the initial bicyclic compound. Cyclic diboraketals (CXXVII) can be obtained by heating the bicyclic compounds (CI) or (CXXV) with ethylene glycol. The bicyclic acid (CXXVIII) can be obtained by the alkaline hydrolysis of the ethylene ketal (CXXVII) and can be converted by esterification with n-butyl alcohol into 3-n-butoxy-7,7-ethylenedioxy-3-borabicyclo[3,3,1]nonane (CXXIX). The oxidation of the cyclic ketal (CXXIX) or the diketal (CXXVII) with hydrogen peroxide in an alkaline medium led to 1,1-ethylenedioxy-*cis*-3,5-dihydroxymethylcyclohexane (CXXX), the reduction of the di-*p*-tosylate of which with lithium aluminium hydride led to the synthesis of 1,1-ethylenedioxy-*cis*-3,5-dimethylcyclohexane (CXXXI). Under the influence of dilute acid, the last compound was converted into *cis*-3,5-dimethylcyclohexanone (CXXXII):



7-Cyclohexenyl-3-methoxy-3-borabicyclo[3,3,1]non-6-ene undergoes the diene condensation with maleic anhydride, forming compound (CXXXIII):[117]

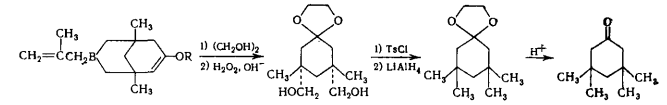


The methanolysis of 1,5-dimethyl-3-(2-methylallyl)-3-borabicyclo[3,3,1]non-6-ene (CIV) leads to 3-methoxy-1,5-dimethyl-3-borabicyclo[3,3,1]non-6-ene (CXXXIV), the oxidation of which with hydrogen peroxide affords *cis*-3,5-di(hydroxymethyl)-3,5-dimethylcyclohex-1-ene (CXXXV) and its acidolysis gives rise to 3,3,5,5-tetramethylcyclohexene (CXXXVI):[120]



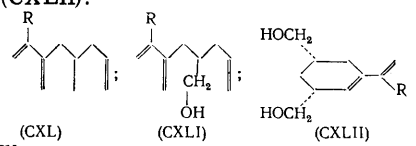
On treatment with ethylene glycol followed by oxidation with hydrogen peroxide in an alkaline medium, 7-alkoxy-1,5-dimethyl-3-(2-methylallyl)-3-borabicyclo[3,3,1]non-6-ene (CVI) can be converted into 1,1-ethylenedioxy-*cis*-3,5-di(hydroxymethyl)-1,3-dimethylcyclohexane (CXXXVII), the reduction of the tosylate of which with lithium

aluminium hydride yields 1,1-ethylenedioxy-3,3,5,5-tetramethylcyclohexane (CXXXVIII). The hydrolysis of the last compound results in the formation of 3,3,5,5-tetramethylcyclohexanone (CXXXIX):[120]



(CVI) (CXXXVII) (CXXXVIII) (CXXXIX)

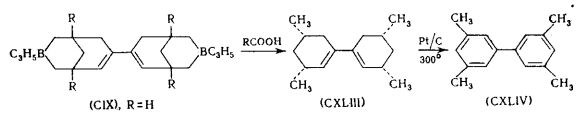
Compounds (CVII) are converted by acidolysis or combined acidolysis and oxidation into the triene hydrocarbons (CXL) or the triene alcohols (CXLI). Oxidation of compounds (CVIII) yields *cis*-di(hydroxymethyl)vinylcyclohexenes (CXLII):[123-125]



(CXL) (CXLI) (CXLII)

R=H,CH$_3$

Compound (CXLIII) and 3,3',5',5'-tetramethylbiphenyl (CXLIV) can be obtained from compound (CIX, R = H) by a series of consecutive chemical reactions[126]:



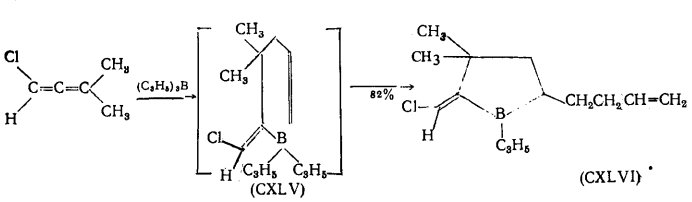
(CIX), R=H (CXLIII) (CXLIV)

Thus a stereospecific method for the synthesis of cyclohexene and cyclohexane derivatives has been developed on the basis of the allylborane–acetylene condensation.

7. Reactions with Allenes

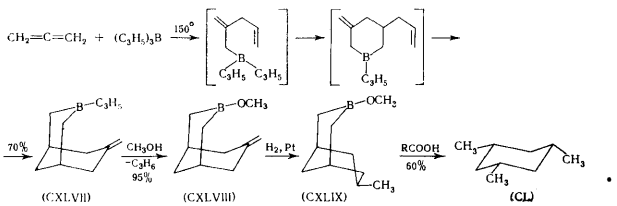
Like acetylenes, allenes can react with allylboranes, forming cyclic compounds, the ease of the reactions and their direction depending on the nature of the allene component.

The reactions of allylboranes with 1-chloro-3-methylbuta-1,2-diene, allene, and 3-methylbuta-1,2-diene have been investigated. It has been found that 1-chloro-3-methylbuta-1,2-diene reacts slowly with triallylborane even at room temperature, forming 1-allyl-2-(but-3-en-1-yl)-5-chloromethylene-4,4-dimethylboracyclopentane (CXLVI).[128,129] By analogy with the allylborane–acetylene condensation, the first reaction stage evidently consists of the addition of triallylborane to the allene system, the diallylboryl group adding to the central carbon atom and the allyl group to the terminal carbon atom joined to two methyl groups. The resulting diallyl-(1-chloromethylene-2,2-dimethylpent-4-en-1-yl)borane (CXLV) undergoes intramolecular cyclisation at room temperature, but the mode of cyclisation is in this case different from that of the pentadienyl derivatives of boron of type (LXIX), i.e. the allyl group adds to the terminal carbon atom of the pentene system and the boron atom adds to a non-terminal atom:



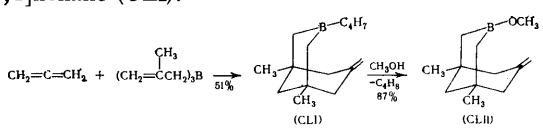
(CXLV) (CXLVI)

Allene, which has less polarised bonds, is more inert with respect to allylboranes than 1-chloro-3-methylbuta-1,2-diene. It reacts slowly with triallylborane on heating (at 150°C) in an autoclave, giving a 60% yield of 3-allyl-7-methylene-3-borabicyclo[3,3,1]nonane (CXLVII), the structure of which has been established by infrared spectroscopy and NMR and also by conversion into known compounds[129-131]. On treatment with methanol, compound (CXLVII) is smoothly converted into 3-methoxy-7-methylene-3-borabicyclo[3,3,1]nonane (CXLVIII), the catalytic hydrogenation of which yields 3-methoxy-7-methyl-3-borabicyclo[3,3,1]nonane (CXLIX). The last compound, which had been obtained previously from methylacetylene and triallylborane[113], is converted on acidolysis into the known *cis*-1,3,5-trimethylcyclohexane (CL):



(CXLVII) (CXLVIII) (CXLIX) (CL)

The reaction of allene with tri-(2-methylallyl)borane proceeds similarly but under more severe conditions[129,131]. When an equimolar mixture of the reactants is heated in an autoclave at 160–170°C, the product is 1,5-dimethyl-7-methylene-3-(2-methylprop-2-en-1-yl)-3-borabicyclo-[3,3,1]nonane (CLI):

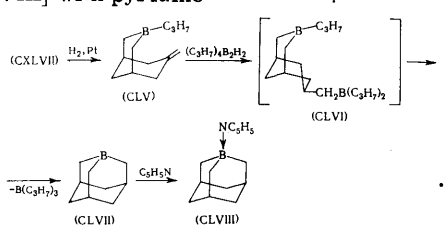


(CLI) (CLII)

8. The Synthesis of 1-Bora-adamantane Derivatives

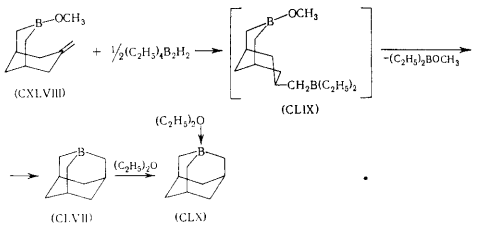
Derivatives of 3-borabicyclo[3,3,1]nonane with a methylene group in the 7-position, obtained by the condensation of allylboranes with allenes, have been used to synthesise 1-bora-adamantanes. Different versions of this synthesis are based on the hydroboration of the 7-methylene group and subsequent intramolecular cyclisation of the resulting dibora-compounds, which had been found previously in a series of acyclic dibora-[132,133], and tri-bora-systems[70].

In the first version, 3-allyl-7-methylene-3-borabicyclo-[3,3,1]nonane (CXLVII) was partly hydrogenated with hydrogen over platinum black to give 7-methylene-3-n-propyl-3-borabicyclo[3,3,1]nonane (CLV), which was then hydroborated by tetra-n-propyldiborane to 3-n-propyl-7-di-n-propylborylmethyl-3-borabicyclo[3,3,1]nonane (CLVI), the latter cyclising to 1-boratricyclo[3,3,1,1^{3,7}]-decane (1-bora-adamantane) (CLVII) with elimination of 3-n-propylborane. The bora-adamantane forms a stable adduct [CLVIII] with pyridine[129,131,134,135]:



(CXLVII) (CLV) (CLVI) (CLVII) (CLVIII)

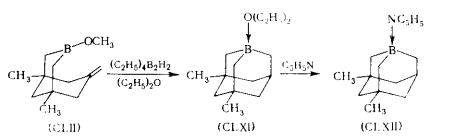
1-Bora-adamantane can be obtained more conveniently by the hydroboration of 3-methoxy-7-methylene-3-bora-bicyclo[3,3,1]nonane (CXLVIII), since the latter compounds can be synthesised more simply than compound (CLV). Diborane in an ethereal medium or a tetra-alkyldiborane may be used as the hydroborating agent. When compound (CXLVIII) is treated with tetraethyldiborane, the product is 7-diethylborylethyl-3-methoxy-3-borabicyclo[3,3,1]nonane (CLIX), which is converted with elimination of methyl diethylborinate into 1-bora-adamantane and the latter can be isolated by distillation or in the form of the ether adduct (CLX) or the pyridine adduct (CLVIII):



In the hydroboration of compound (CXLVIII) with diborane in an ethereal medium, the ether adduct (CLX) formed can be isolated (after the vacuum distillation of the solvent and methyl borate, which is also produced in the reaction) in the form of a colourless viscous liquid. If compound (CXLVIII) is hydroborated with diborane in THF solution, the product is the tetrahydrofuran complex of 1-bora-adamantane in 72% yield.

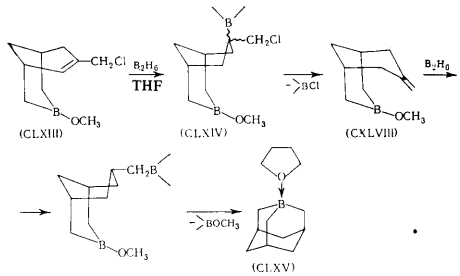
The ether complex of 1-bora-adamantane is comparatively stable, but it partly dissociates into the components even at room temperature. The ether adduct (CLX) has been used to synthesise complexes with other ligands having a more marked electron-donating capacity by simple mixing of the reactants in an inert solvent[129,135]. The thermally stable complex of 1-bora-adamantane with THF and very stable complexes with pyridine and triethylamine, which do not dissociate even at 200°C, have been obtained in this way. A complex of 1-bora-adamantane with ethyl acetate has been synthesised by the interaction of these reactants.

3-Methoxy-1,5-dimethyl-7-methylene-3-borabicyclo-[3,3,1]nonane (CLII) is smoothly converted on treatment with tetraethyldiborane in an ethereal medium into the ether adduct of 3,5-dimethyl-1-bora-adamantane (CLXI). Treatment of compound (CLXI) with pyridine yields the pyridine adduct (CLXII):[129,131]

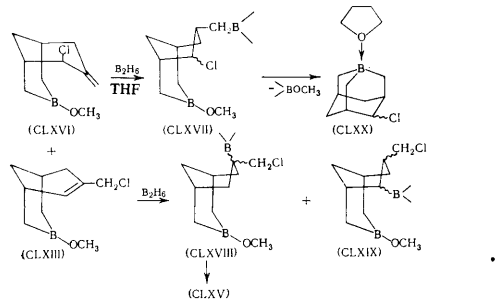


The method of synthesis of the 1-bora-adamantane system described here has been used to obtain 1-bora-adamantane derivatives with functional groups from compounds formed in the allylborane–acetylene condensation.

On treatment with diborane in THF, 7-chloromethyl-3-methoxy-3-borabicyclo[3,3,1]non-6-ene (CLXIII) combines with boron to the extent of 27% in the β-position relative to the CH_2Cl group, forming the borane (CLXIV). The latter eliminates compound (CXLVIII), which is converted as a result of hydroboration and cyclisation into the tetrahydrofuran complex of 1-bora-adamantane (CLXV):[136]



When a 4:1 mixture of compound (CLXIII) and 6-chloro-3-methoxy-7-methylene-3-borabicyclo[3,3,1]nonane (CLXVI) is treated with a tetra-alkyldiborane, a mixture of boranes (CLXVII)–(CLXIX) is formed. The borane (CLXVII) cyclises to 4-chloro-1-bora-adamantane, which can be isolated from the reaction mixture as the adduct (CLXX) with THF. The borane (CLXVIII) is converted by a series of stages into the tetrahydrofuran complex of 1-bora-adamantane (CLXV), which can be isolated from the reaction mixture by vacuum distillation[136].

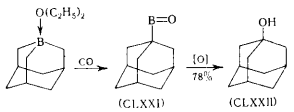


1-Bora-adamantane is a unique compound in which the boron atom is in a tetrahedral state and not in a trigonal valence state as in all the tervalent boron compounds known hitherto. This feature of 1-bora-adamantane is reflected in its chemical properties, in particular in its enhanced tendency towards complex formation. 1-Bora-adamantane forms very stable coordination compounds with pyridine and trimethylamine, which do not dissociate even at 200°C. It also forms complexes with ethyl ether and ethyl acetate, a ^{11}B NMR study of the stability of which made it possible to estimate experimentally the energy of the rearrangement of trialkylborane in its transition during complex formation from the planar to the pyramidal configuration; it proved to be 6–10 kcal mole^{-1}.[129]

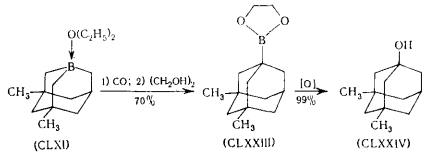
9. Synthesis of Adamantanes

Hillman's studies[137–139] have shown that trialkylboranes are converted into trialkylmethanols on treatment with carbon monoxide and subsequent oxidation of the carbonylation products, 1-Bora-adamantanes undergo similar reactions. The ether adduct of 1-bora-adamantane reacts at room temperature with carbon monoxide, forming the anhydride of 1-adamantylboronic acid (CLXXI). The

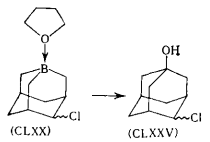
oxidation of the anhydride of the acid or its ester by an alkaline solution of hydrogen peroxide leads to 1-hydroxyadamantane (CLXXII):[129,131]



The carbonylation of the ether adduct (CLXI) to the anhydride of 3,5-dimethyl-1-adamantylboronic acid proceeds just as smoothly; the oxidation of its ethylene glycol ester (CLXXIII) gives an almost quantitative yield of 1-hydroxy-3,5-dimethyladamantane (CLXXIV):[129,131]



The tetrahydrofuran complex of 4-chlorobora-adamantane (CLXX) is converted by carbonylation with carbon monoxide into 4-chloro-1-hydroxyadamantane (CLXXV):[136]



The study of the reactions of allylboranes with acetylenes and allenes has led to the discovery of new methods of synthesising adamantane derivatives, which may be of practical value, since many compounds of the adamantane series possess physiological activity. Compounds with antiviral, antitumour[140], soporific[141], antimalarial[142], insecticidal[143], antidiabetic[144], antibacterial[145], neurotropic[146], curaremimetic[147,148], and other activities have been found in this series.

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