

REACTIONS OF ALLYLBORANES WITH UNSATURATED COMPOUNDS

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ABSTRACT

Allylboranes may react with compounds containing an activated double bond as well as with cyclopropenic hydrocarbons. The reactions of allylboranes with acetylenes yield the substituted diallyl(pentadiene-1,4-yl-1)borane, boracyclohexene, 3-borabicyclo(3,3,1)nonene and 7-methylene-3-borabicyclo(3,3,1)nonane.

The allenic compounds and allylboranes produce substituted 6-methylene- or 7-methylene-3-borabicyclo(3,3,1)nonane. Hydroboration of 7(6)-methylene-3-borabicyclo(3,3,1)nonanes gives 1-boraadamantane and 1-boraprotadamantane systems respectively which may afford adamantane and protadamantane compounds.

In recent years studies in organoboron chemistry have disclosed many new possibilities for organic syntheses. The syntheses involving organoboranes expand essentially the field of application of organometallic reagents in preparative chemistry and supplement successfully the syntheses involving organomagnesium, zinc and alkaline metal compounds.

The allylboron compounds are especially promising as synthetic reagents, being highly reactive and behaving specifically towards a variety of organic compounds. One of the features of triallylborane and some of its analogues is the state of permanent allyl rearrangement whose rate depends on the nature of the compound and temperature¹.

Allylboranes are highly active in reactions with water, alcohols, and amines even at room temperature, unlike trialkylboranes requiring high temperatures.

Allylboranes react with aldehydes, ketones, quinones and nitriles as organometallic compounds but they are more advantageous in many syntheses over magnesium and other metallic compounds¹.

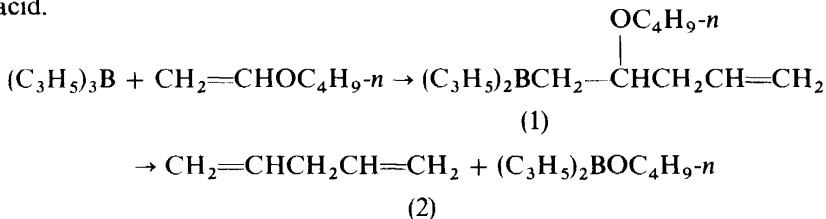
High reactivity is exhibited by allylboranes in their reactions with various unsaturated compounds.

REACTIONS WITH COMPOUNDS CONTAINING AN ACTIVATED DOUBLE BOND

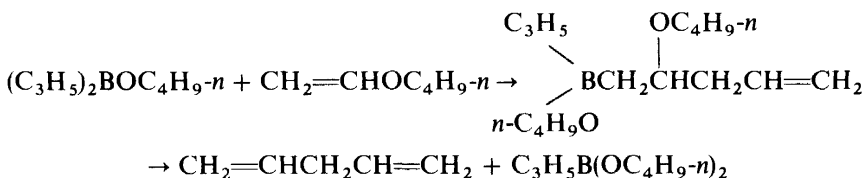
Allylboranes take part in reactions with compounds containing an

activated double bond—vinyl ethers, dihydro(4,5)sylvan and cyclopropenic hydrocarbons.

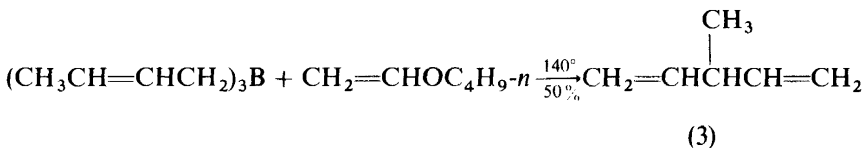
Triallylborane reacts with vinyl-*n*-butyl ether at 110–140° to give penta-1,4-diene (80 per cent)^{2,3}. One may assume that at first allylborane adds at the multiple bond yielding (2-alkoxy-pent-4-ene-1-yl)diallyl-borane (1) which undergoes β-elimination to the diene (2) and *n*-butyl ester of diallylborinic acid.



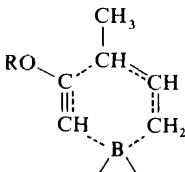
This ester then reacts with another vinyl ether molecule according to the same scheme:



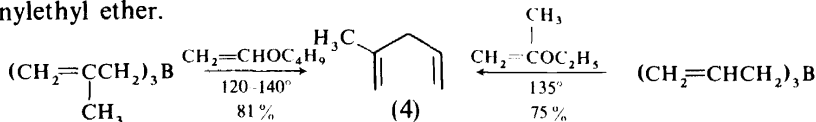
The reaction of tricrotlylborane with vinyl-*n*-butyl ether afforded 3-methyl-penta-1,4-diene (3).



The formation of (3) shows that tricrotlylborane adds at the multiple carbon-carbon bond via an allyl type rearrangement involving the cyclic transition state.



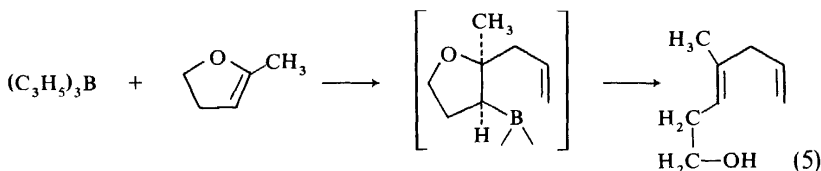
2-Methylpenta-1,4-diene (4) was obtained from *n*-butylvinyl ether and tri(2-methylallyl)borane and by reaction of triallylborane with isoprenylethyl ether.



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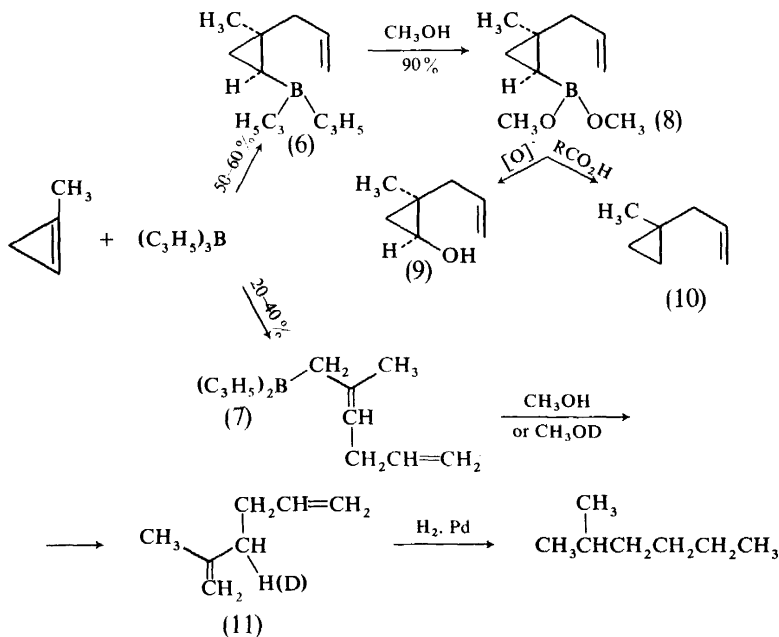
Triallylborane reacts slowly with dihydro(4,5)silylan at room temperature but rapidly (in several minutes) at 80–100°.

Alkaline hydrolysis of the adduct gives 4-methylpenta-1,6-diene-1-ol (5).



Thus the reaction of allylboranes with acyclic and cyclic vinyl ethers is a convenient preparative way of synthesis of the hardly available 1,4-dienes and their functional derivatives.

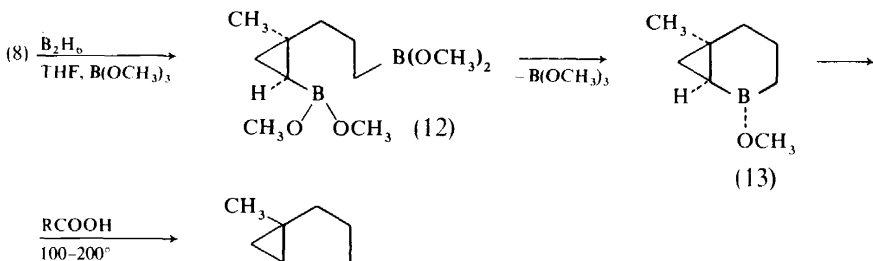
At $-70-0^\circ$ triallylborane reacts with 1-methylcyclopropene along the two lines^{4,5}. *Cis*-addition of organoboranes to the hydrocarbon double bond is predominant and gives diallyl(1-methyl-1-allylcyclopropyl-2)borane (6), the ring partially cleaving along the C_2-C_3 bond to diallyl(2-methylhexa-2,5-diene-1-yl)borane (7). The methanolysis of (6) resulted in dimethoxy(1-methyl-1-allylcyclopropyl-2)borane (8) oxidizing to 1-methyl-1-allylcyclopropanol-2 (9) and acidolysing to 1-methyl-1-allylcyclopropane (10). Compound (7) was not isolated but its formation has been confirmed by isolation of 2-methyl-1,5-hexadiene (11) after methanolysis of the reaction mixture.



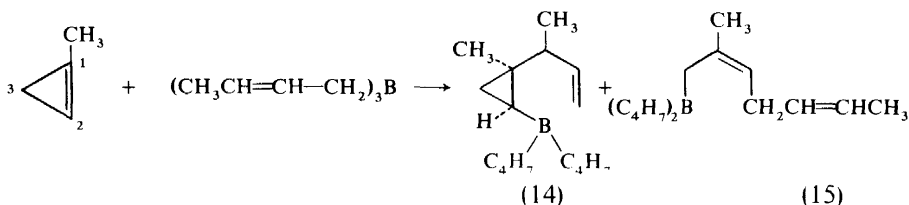
The action of triallylborane on 1-methyl-2-deuterocyclopropene and methanolysis of the reaction products give 2-methyl-3-deuterohexa-1,5-diene

(30–35 per cent) and dimethoxy(1-methyl-1-allyl-2-deuterocyclopropyl-2)-borane (50–60 per cent).

Hydroboration of (8) in THF in the presence of trimethyl borate leads to the diboronic compound (12). This converts at 100–200° to 5-methoxy-1-methyl-5-borabicyclo(4,1,0)heptane (5-methoxy-1-methyl-5-boranocarane) (13)⁵ by elimination of trimethyl borate.



1-Methylcyclopropene and triisobutylborane give predominantly (85–90 per cent) *cis*-2-(but-3-ene-2-yl)2-methylcyclopropyl-1 di-(2-butenyl)borane (14) along with 2-methylhepta-(2,5-diene-1-yl)-di-(2-butenyl)borane (15) (10–15 per cent). Thus allylborane adds at the double bond in the trimembered cycle via allylic rearrangement while no rearrangement occurs on addition to C₂ and C₃ carbons with cleavage of the ordinary C—C bonding.

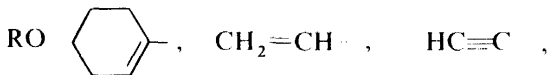


REACTIONS WITH ACETYLENES

The substituted acetylenes react with triallylborane at room temperature giving first 2-substituted diallyl (penta-1,4-diene-1-yl)boranes (16). In general, thermal instability prevented their individual isolation¹.



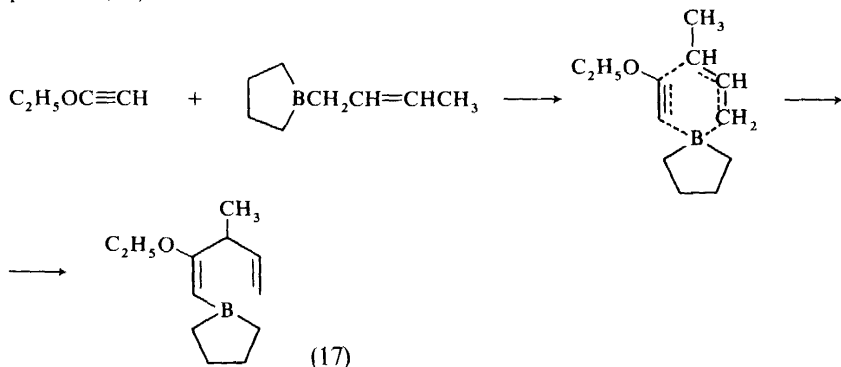
X = CH₃, *n*-C₄H₉, C₆H₅, (CH₃)₃SiCH₂, CH₂Cl, CH₂Br,



However, alkoxyacetylenes and triallylborane produce stable compounds (16, X = OR) which could be isolated by distillation.

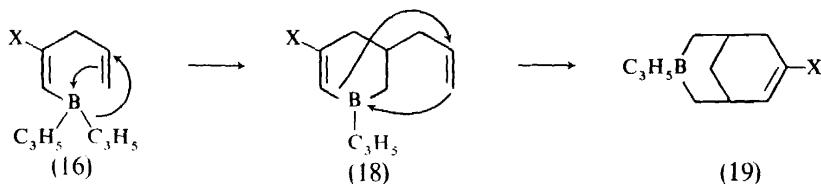
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This reaction is the first step in the allylboron-acetylenic condensation via *cis*-addition of $(C_3H_5)_2B$ and C_3H_5 fragments at the $C=C$ bond. Obviously it may involve a 6-centre transition state with allylic rearrangement and it was confirmed by reaction of 1-crotylboracyclopentane with ethoxyacetylene leading to 1-(2-ethoxy-3-methylpenta-1,4-diene-1-yl)boracyclopentane (17).

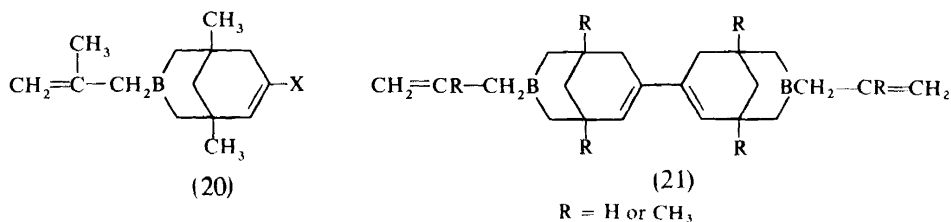


The 2-substituted diallyl(penta-1,4-diene-1-yl)boranes (16) may undergo an intramolecular cyclization to the 3-substituted 1,5-diallyl-1-boracyclohexenes-2 (18). 2-Alkyl-substituted compounds cyclize even at room temperature. The thermally most stable diallyl-(2-alkoxy-penta-1,4-diene-1-yl)boranes convert to the compounds (18) only at 120–130°.

In turn compounds (18) may cyclize at 130–180° to 7-substituted 3-allyl-3-borabicyclo(3,3,1)nonenes-6 (19).



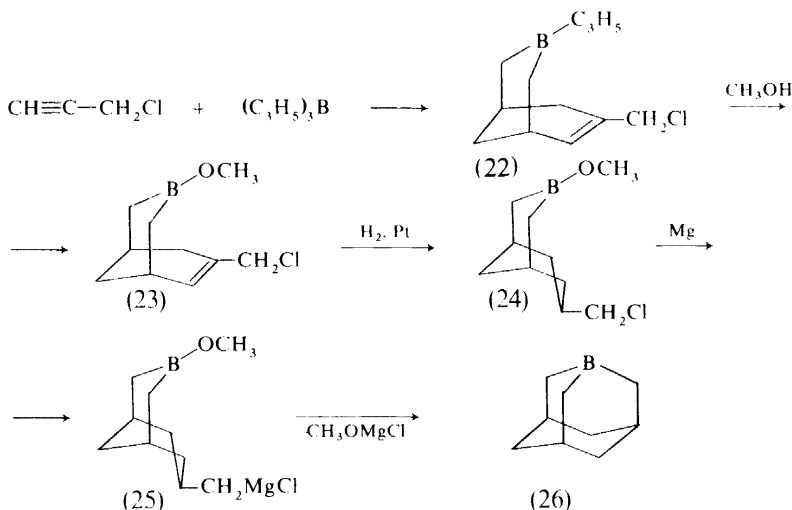
The allylboron-acetylenic condensation may take place with triallylboron homologues, e.g. trimethallylborane may yield the compounds (20)¹. Reactions of triallylborane or trimethallylborane with diacetylene give compounds of type (21)².



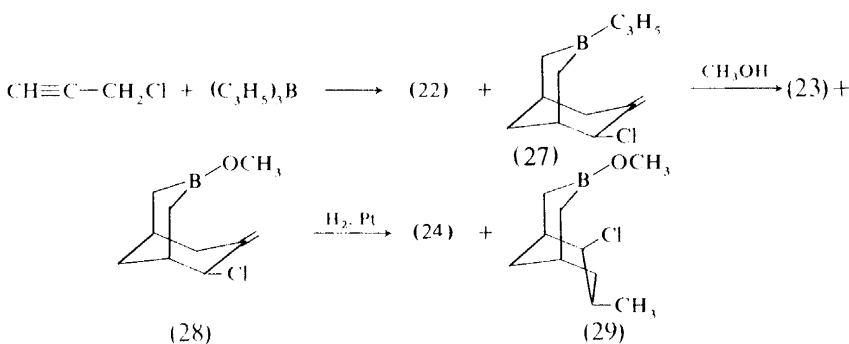
The products of all three steps in the allylboron-acetylenic condensations (16, 18–21) are themselves interesting boron compounds for organoboron chemistry. Moreover from them a variety of acyclic, alicyclic and aromatic compounds could be synthesized.

Allylboron-acetylenic condensation is a stereospecific way of synthesizing alicyclic compounds¹.

One of the most interesting applications of the allylboron-acetylenic condensation could be the synthesis of tricyclic systems with the diamond structure, first of all 1-bora-adamantane. At first sight it seemed that the simplest approach to this compound would be the use of triallylborane-propargyl chloride condensate (22). This scheme may involve the methoxylation of 7-chloromethyl-3-allyl-3-borobicyclo(3,3,1)nonene-6 (22) to the 3-methoxy compound (23) catalytically hydrogenated to 7-chloro-methyl-3-methoxy-3-borabicyclo(3,3,1)nonane (24) with a subsequent closure of the cycle into 1-bora-adamantane (21) via the organomagnesium compound (25).



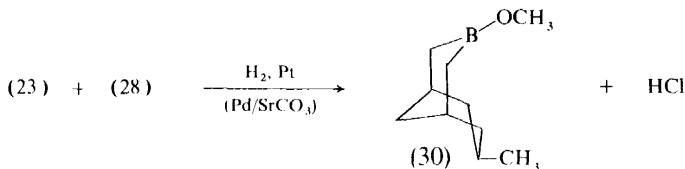
However, in this scheme unexpected complications arose. First of all, it was found that condensation of propargyl chloride and triallylborane yielded (22) with a considerable quantity (4:1) of the isomeric 6-chloro-3-allyl-7-methylene-3-borabicyclo(3,3,1)nonane (27).



Secondly, a catalytic hydrogenation of the mixture of methoxylated compounds (23) and (28) over Adams catalyst or Pd/SrCO_3 gave no compounds

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(24) and (29) but afforded 3-methoxy-7-methyl-3-borabicyclo(3,3,1)nonane (30) as a result of conjugated hydrogenation of the cyclic allylic chlorides which is unsuitable for constructing the 1-bora-adamantane system⁸⁻¹⁰.

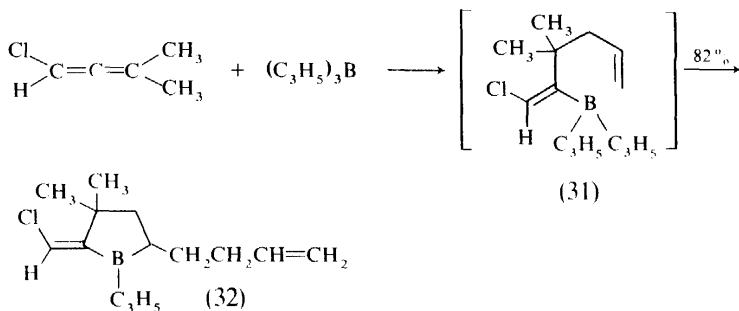


As will be shown further triallylborane condensation with propargyl chloride was used successfully in the synthesis of the 1-bora-adamantane system. But this was preceded by study of the allylborane reaction with allenic compounds which resulted in the first synthesis of the organoboron compounds to have diamond structure.

REACTIONS WITH ALLENES

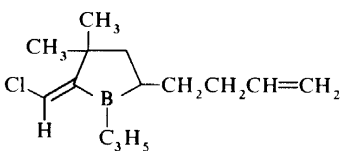
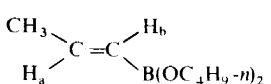
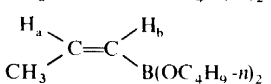
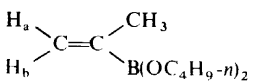
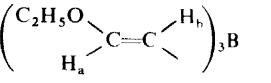
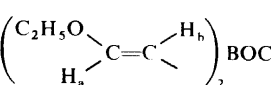
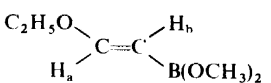
Analogously to acetylenes the allenes may react with allylboranes to give cyclic compounds, the easiness and course of the reactions depending on the nature of the allene.

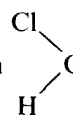
We have studied the reactions of allylboranes with 3-methyl-1-chlorobuta-1,2-diene, allene and 3-methylbuta-1,2-diene. It was shown that 3-methyl-1-chlorobuta-1,2-diene reacts slowly with triallylborane even at room temperature giving 4,4-dimethyl-1-allyl-2-(but-3-ene-1-yl)-5-chloromethyleneboracyclopentane (32)¹¹. Analogously to allylborane-acetylenic condensation the first reaction step may involve triallylborane addition to the allenic system, the diallylboryl group adding to the central carbon while the allyl group adds at the terminal one combined with two methyls. The resulting (1-chloromethylene-2,2-dimethylpent-4-ene-1-yl)diallylborane (31) undergoes an intramolecular cyclization. However, unlike boron pentadienyl compounds of the type (16) it is allyl that adds at the terminal pentenic carbon atom while the boron joins at the central one. It is quite obvious that steric effect plays a role in cyclization: it favours an approach of boron to C₄ closer than to C₅ in a transition state.



The value of the spin-spin coupling constant between boron and hydrogen

Table 1. Coupling constant data. The proton chemical shifts are given in δ scale from TMS.

Compounds	^{11}B	CH_3	H_a	H_b
(32)				
	—	1.10 1.37	7.05	—
(33)				
	-27.2	1.76	6.60	5.49
	-27.2	1.87	6.34	5.37
(34)				
	-27.1	1.80	5.46	5.26
(35)				
	-54.5	—	7.12	5.35
(36)				
	-42.2	3.62	6.95	4.75
(37)				
	-30.1	3.49	6.95	4.39

in  ($J_{\text{BH}} = 3.0 \text{ Hz}$) manifests *cis*-location of the proton with

respect to the boron. This may be evident from a comparison of J_{BH} in compound (32) with J_{BH} and proton chemical shifts in various vinyl boron compounds—(*trans*-2-ethoxyvinyl)boranes^{12,13} and in propenyl- and isopropenyl boronic acid esters prepared by us in collaboration with Drs P. M. Aranovich, Yu. N. Bubnov, V. S. Bogdanov, A. V. Kessenikh and V. V. Negrebetskii.

The values of J_{BH} (Table 1) (geminal and vicinal) were obtained indirectly from the line broadening in the ^1H and ^{11}B n.m.r. spectra by ^{11}B quadrupole relaxation. It can be seen from the table that the values $^3J_{\text{BH}}^{\text{cis}}$ for compounds (33), (36) and (37) are close to $^3J_{\text{BH}} = 3.0 \text{ Hz}$ in (32), while $^3J_{\text{BH}}^{\text{trans}}$ is about 11 Hz.

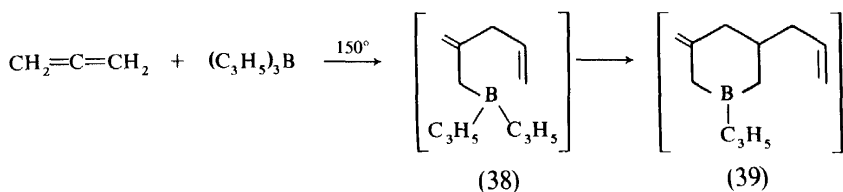
Allene having the less polarized bonds is more inert towards allylboranes in comparison with 1-chloro-3-methylbuta-1,2-diene. It reacts slowly with

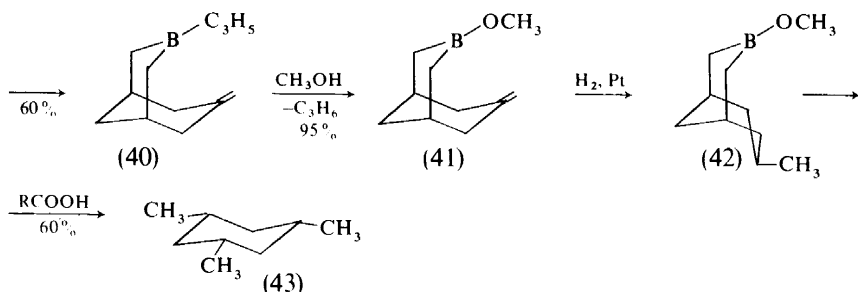
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 The ^{11}B chemical shifts were measured from $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$.

$^2 J_{\text{H-H}}$	$^n J_{\text{H-H}}^{\text{cis}}$	$^3 J_{\text{H-H}}^{\text{vic}}$	$^4 J_{\text{H-H}}^{\text{cis}}$	$^4 J_{\text{H-H}}^{\text{trans}}$	$^2 J_{\text{B-H}}$	$^3 J_{\text{B-H}}^{\text{cis}}$	$^3 J_{\text{B-H}}^{\text{trans}}$	$^3 J_{\text{B-H}}^{\text{vic}}$
—	—	—	—	—	—	3.0	—	—
—	17.80	6.45	1.60	—	3.5	4.3	—	—
—	14.20	6.75	—	1.60	3.5	—	11.5	—
3.40	—	—	1.80	1.34	—	6.0	10.7	3.8
—	14.0	—	—	—	0.0	—	—	—
—	14.00	—	—	—	0.0	2.9	—	2.9
—	14.00	—	—	—	0.0	2.9	—	2.4

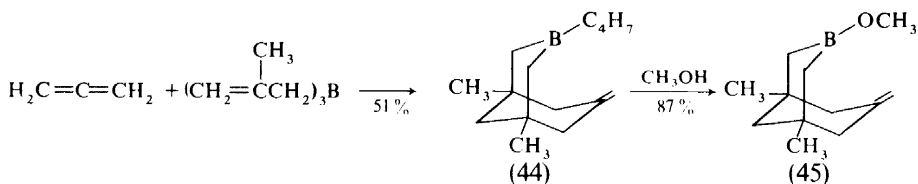
triallylborane at 150° in an autoclave and after five hours it gave 60 per cent of 3-allyl-7-methylene-3-borabicyclo(3,3,1)nonane (40) whose structure was confirmed by the i.r. and n.m.r. spectra and by transformations to known compounds¹⁴. Compound (40) with methanol smoothly gives 3-methoxy-7-methylene-3-borabicyclo(3,3,1)nonane (41) which converted to 3-methoxy-7-methyl-3-borabicyclo(3,3,1)nonane via catalytic hydrogenation (42). Earlier we prepared the last compound from methylacetylene and triallylborane¹⁵, its acidolysis led to the known *cis*-1,3,5-trimethyl-cyclohexane (43). The structure





of compound (40) leads to the conclusion that the first reaction step is an addition of triallylborane to allene so that the boron atom joins the terminal carbon atom while allyl adds to the central carbon atom in allene (38). Analogously to allylboron-acetylenic condensation the subsequent reaction may occur as two consecutive intramolecular cyclizations which finally give compound (40) via 1,5-diallyl-3-methyleneboracyclohexane (39). The cyclization of (39) into (40) includes the cleavage of cyclic boron-allylic ($\text{B}-\text{C}_1$) bond. This is specific for the allylboron-allenic condensation unlike the acetylenic one where the cleavage of boron-vinyl bond (reaction 18-19) yields the boronbicyclic compound.

The reaction of allene with trimethylborane studied by us in collaboration with Drs V. N. Smirnov and V. A. Kasparov occurs in the same manner but under more drastic conditions. Heating of an equimolar mixture of reagents in an autoclave to $160-170^\circ$ for 6.5 h gave 51 per cent of 3-(2-methylprop-2-ene-1-yl)-7-methylene-1,5-dimethyl-3-borabicyclo(3,3,1)nonane (44), b.pt $58-59^\circ/1$ mm Hg, n_D^{20} 1.4903, d_4^{20} 0.8742. The i.r. spectrum of compound (44) shows the band at 1640 cm^{-1} ($-\text{HC}=\text{CH}_2$) along with 1650 cm^{-1} absorption ($\text{C}=\text{CH}_2$).

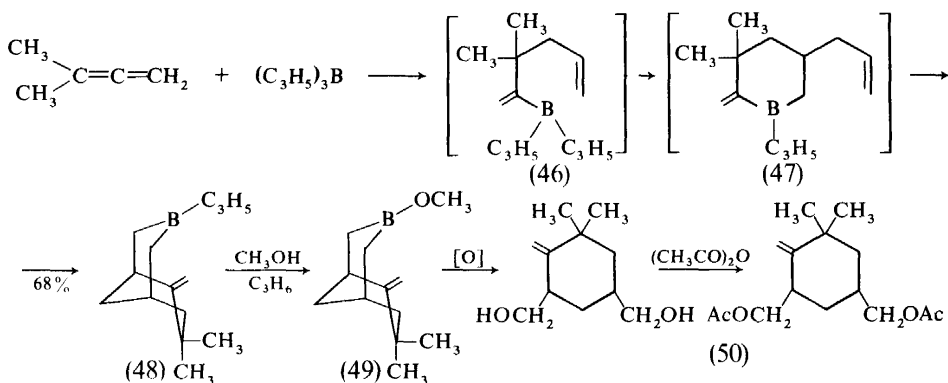


The action of methanol on compound (44) afforded one mole of isobutylene and 87 per cent of 3-methoxy-7-methylene-1,5-dimethyl-3-borabicyclo(3,3,1)nonane (45), b.pt $47-48^\circ/1$ mm Hg, n_D^{20} 1.4755. The p.m.r. spectrum of (45) exhibits a multiplet centred at $\delta = 4.66$ p.p.m. ($=\text{CH}_2$), two singlets at $\delta = 3.44$ p.p.m. (OCH_3) and 0.93 p.p.m. (two methyls) and the broadened singlets at $\delta = 1.75$ p.p.m. [$(\text{CH}_2)_2-\text{C}=\text{}$], 1.24 p.p.m. ($\text{C}-\text{CH}_2-\text{C}$), 0.57 and 0.33 p.p.m. [$\text{B}(\text{CH}_2)_2$]. The ratio of integrated intensities agrees with the theoretical value.

3-Methylbuta-1,2-diene reacts with triallylborane only at elevated temperature. If an equimolar mixture of the components is heated in an autoclave for five hours at 140° then it gives 68 per cent of 3-allyl-6-methylene-7,7-dimethyl-3-borabicyclo(3,3,1)nonane (48) whose structure was confirmed

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by transformation into *cis*-3,5-diacetoxymethyl-1,1-dimethyl-2-methylene-cyclohexane (50)¹⁴.



In this case the triallylborane addition to the allenic bond system is similar to that in 1-chloro-3-methylbuta-1,2-diene. However, an intermediate (46) first transforms into boracyclohexane (47) which then undergoes cyclization to the final reaction product (48).

Methanolysis of (48) gives one mole of propylene and 3-methoxy-6-methylene-7,7-dimethyl-3-borabicyclo(3,3,1)nonane (49).

The reaction of 3-methylbuta-1,2-diene and triallylborane carried out in a flask at 160–170° afforded (48) (37 per cent) and (49) (17 per cent). Formation of the latter compound is due to a realkenylation of triallylborane by 3-methylbuta-1,2-diene. The resultant allene then reacts with triallylborane. Previously substitution of the allyl radical in allylborane by the higher allyl has not been described.

Orientation of the allylborane addition to allenes (the first step in allylborane-allenic condensation) is similar to that of mercury acetate addition¹⁶.

In hydroboration of the allenic compounds the way of addition is determined by the nature of the reagents^{17–23} and it has not been interpreted successfully in terms of ordinary electronic and steric effects.

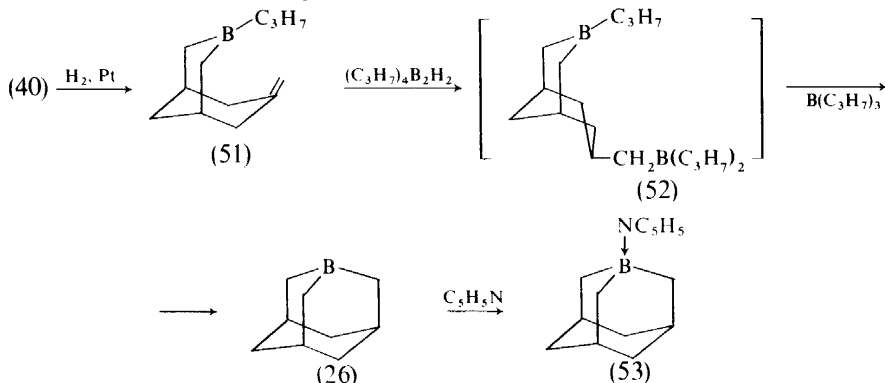
SYNTHESIS OF THE 1-BORA-ADAMANTANE AND 1-BORAPROTOADAMANTANE SYSTEMS

The derivatives of 3-borabicyclo(3,3,1)nonane with the methylene group in position 7 prepared by condensation of allylboranes with allenes were employed in the synthesis of 1-boraadamantane compounds. Different versions of this synthesis are based on the hydroboration of the 7-methylene group followed by an intramolecular cyclization of the generated diboronic compounds observed by us earlier in the series of acyclic diboronic^{24, 25} and triboronic systems²⁶.

In the first version 3-allyl-7-methylene-3-borabicyclo(3,3,1)nonane (40) was partially hydrogenated with hydrogen over platinum black to 3-*n*-propyl-7-methylene-3-borabicyclo(3,3,1)nonane (51). This compound was

hydroborated by tetra-*n*-propyldiborane into 3-*n*-propyl-7-di-*n*-propylboryl-methyl-3-borabicyclo(3.3.1)nonane (52) cyclized to 1-boratricyclo(3.3.1.1^{3,7})-decane (1-boraadamantane) (26) with tri-*n*-propylborane elimination.

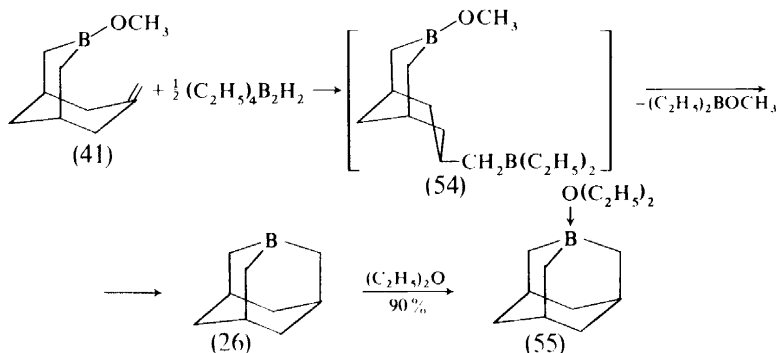
After trialkylborane evaporation *in vacuo* the product (26) is sublimed as well-formed prisms starting to melt at 80° and transforming to a glass-like mass after further heating.



1-Boraadamantane fumes in air²⁷.

If pyridine is added to the mixture of tri-*n*-propylborane and (26) and the greater part of the resulting tri-*n*-propylborane pyridinate is evaporated then one would isolate 40 per cent of 1-boraadamantane pyridinate (53) in the form of colourless crystals, m.pt 160–162°²⁸.

It is more convenient to prepare 1-boraadamantane via hydroboration of 3-methoxy-7-methylene-3-borabicyclo(3.3.1)nonane (41) which could be more readily obtained than (51). Diborane in ether or tetra-alkyldiborane could be used as hydroborating agents. The action of tetra-ethylborane on (41) gives 3-methoxy-7-diethylborylmethyl-3-borabicyclo(3.3.1)nonane (54). Elimination of the methyl ester of diethylborinic acid yields 1-boraadamantane which may be isolated by distillation or in the form of etherate (55) or pyridinate (53). Hydroboration of (41) with diborane in ether gives etherate, which after solvent and trimethyl borate evaporation is a colourless liquid with small quantity of non-identified impurities.



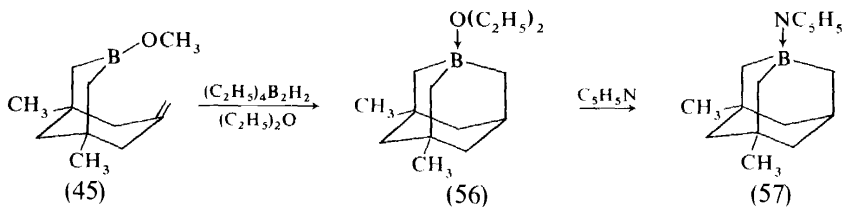
The p.m.r. spectrum of etherate (55) shows a multiplet at $\delta = 0.74$ p.p.m.

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(BCH_2), triplet centred at $\delta = 1.17$ p.p.m. and $J = 7$ Hz ($\text{CH}_3\text{---CH}_2$), multiplet at $\delta = 1.42$ p.p.m. (CH_2), multiplet centred at $\delta = 2.19$ p.p.m. (CH) and the quartet at $\delta = 3.79$ p.p.m. and $J = 7$ Hz (OCH_2). The ^{11}B chemical shift in compound (55) in ether is equal to -15.6 p.p.m. When (41) is hydroborated with diborane in tetrahydrofuran then 72 per cent of the 1-boraadamantane complex is obtained in the form of colourless crystals, m.pt $79\text{--}85^\circ$.

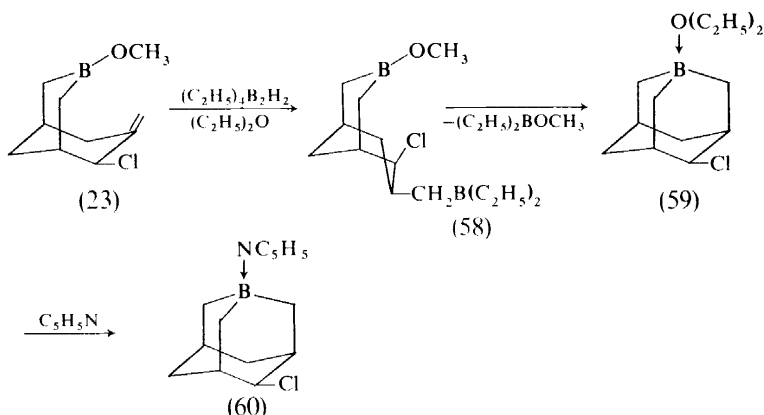
The ethereal complex of 1-boraadamantane is comparatively stable. However, it is subject to partial dissociation into components even at room temperature. The etherate (55) was employed for the syntheses of complexes with other ligands, which are the stronger donors, by direct mixing of the reagents in an inert solvent. Thus a thermally stable complex of 1-boraadamantane with tetrahydrofuran and very stable complexes with pyridine and triethylamine (m.pt $72\text{--}75^\circ$) which do not dissociate even at 200° were prepared. A complex of 1-boraadamantane with ethylacetate was synthesized by direct reaction of these reagents. Its p.m.r. spectrum exhibits multiplets at $\delta = 0.87$ p.p.m. (BCH_2), 1.5 p.p.m. (CH_2), 2.26 p.p.m. (CH), triplet centred at $\delta = 1.22$ p.p.m. and $J = 7$ Hz, singlet at $\delta = 2.07$ p.p.m. ($\text{CH}_3\text{---CO}$) and quartet centred at $\delta = 4.15$ p.p.m. and $J = 7$ Hz (OCH_2). The ^{11}B n.m.r. spectrum of ethylacetate solution of the complex shows the signal at -15.0 p.p.m.

In collaboration with Drs V. N. Smirnov and V. A. Kasparov we have shown that 3-methoxy-7-methylene-1,5-dimethyl-3-borabicyclo(3,3,1)nonane (45) prepared from trimethylallylborane and allene when reacted with tetraethylidiborane in ether smoothly converted to 3,5-dimethyl-1-boraadamantane etherate (56), which with pyridine gives 3,5-dimethyl-1-boraadamantane pyridinate (57), m.pt $51.5\text{--}52^\circ$, b.pt $162\text{--}164^\circ/1$ mm Hg.

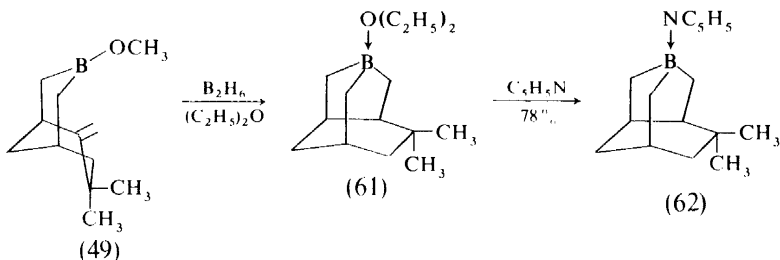


The synthesis of 1-boraadamantane system described was employed for the preparation of substituted 1-boraadamantanes from the products of allylboron-acetylenic condensation.

Together with Dr K. L. Cherkasova we have hydroborated by tetraethylidiborane in ether 3-methoxy-6-chloro-7-methylene-3-borabicyclo(3,3,1)nonane (28) prepared [along with compound (23)] by methanolysis of the condensation products of triallylborane with propargyl chloride. The resultant 3-methoxy-6-chloro-7-diethylborylmethyl-3-borabicyclo(3,3,1)nonane (58) underwent (via methoxydiethylborane elimination) an intramolecular cyclization into 4-chloro-1-boraadamantane etherate (59). By action of pyridine it led to 4-chloro-1-boraadamantane pyridinate (60) (m.pt $107\text{--}108^\circ$).



It seemed rather attractive to prepare a tricyclic compound isomeric to 1-boraadamantane from 3-methoxy-6-methylene-7,7-dimethyl-3-borabicyclo(3,3,1)nonane (49). It is natural that this system should be essentially more strained than 1-boraadamantane and its synthesis is rather problematical. In the paper with Drs V. N. Smirnov and O. D. Smirnova we have hydroborated compound (49) in ether into 4,4-dimethyl-1-boratri-cyclo(4,3,1,0^{3,8})decane etherate (61) (4,4-dimethyl-1-boraprotadamantane etherate) in the form of an oily liquid. This was reacted with pyridine to give crystalline pyridinate (62), m.pt 87–89° [78 per cent per initial (49)].



The p.m.r. spectrum of etherate (61) has a quartet at $\delta = 3.77$ p.p.m. and $J = 7$ Hz (OCH_2), triplet at $\delta = 1.17$ p.p.m. and $J = 7$ Hz (CH_3CO), two singlets at $\delta = 0.95$ p.p.m. and 0.84 p.p.m. [$\text{C}(\text{CH}_3)_2$] and the multiplet from other protons in the region of 0.34 – 2.45 p.p.m.

The p.m.r. spectrum of pyridinate (61) shows multiplets from protons in pyridine in the region of 7.15 – 8.65 p.p.m. and a singlet at $\delta = 0.96$ p.p.m. [$\text{C}(\text{CH}_3)_2$] imposing on the multiplet from other protons at 0.42 – 2.42 p.p.m.

COMPLEXING ABILITY OF 1-BORAADAMANTANE

1-Boraadamantane is a unique compound in which the boron atom is tetrahedral unlike all known trivalent boron compounds where it is trigonal. This specificity of 1-boraadamantane appears in its chemical properties, in the higher reactivity with respect to trialkylboranes, and in particular in the higher ability to form complexes.

In complex formation a molecule of a boron compound transforms from planar to pyramidal, the B—X bond energy decreasing due to the smaller overlap of sp^3 with respect to sp^2 boron orbitals. A decrease of bond energy on going from sp^2 to sp^3 valence states is called energy reorganization. This energy depends on the nature of the atom bound to boron and probably its value changes in a rather narrow range. This may be evident from the data on purely organic systems. Thus the energies of bonds $C_{sp^3}-C_{sp^3}$ and $C_{sp^3}-C_{sp^2}$ are 84.59 and 89.59 respectively while those of $C_{sp^3}-H$ and $C_{sp^2}-H$ bonds are 97.01 and 100.52 kcal/mole²⁹. The energies of bonds $C_{sp^3}-Cl$ and $C_{sp^2}-Cl$ are equal respectively to 80 and 88 kcal/mole³⁰. The energies of bonds $C_{sp^3}-Br$ and $C_{sp^2}-Br$ differ by 4 kcal/mole³¹. The greater difference was observed (18 kcal/mole) for the energies of $C_{sp^3}-B$ and $C_{sp^2}-B$ bonds³².

The molecule of 1-boraadamantane in which the angle $\angle CBC$ is almost tetrahedral is ready for complex formation because unlike the trialkylboranes its vacant orbital is not purely p but sp^3 type. In other words the energy loss in rehybridization has occurred already in the synthesis of 1-boraadamantane and its potential energy exceeds that of trialkylborane over its reorganization energy. The enthalpy of reaction of 1-boraadamantane with some ligand is a measure of the true energy of the coordination bond. In this case no energy is spent for boron rehybridization as in complex formation from the planar trivalent boron compound.

The energies of complex formation processes have attracted the attention of many theoretical chemists. The first attempt at theoretical estimation of the reorganization energy in boron halides was made by Bauer, Finley and Laubengayer³³. They discussed two factors responsible for the energy change in the boron-halogen bond on going from planar to pyramidal boron trihalide:

- (1) the energy of π -bond cleavage, i.e. resonance energy on passing from a delocalized π -electron model to that with localized π -electrons;
- (2) the change of B—X σ -bond energies in rehybridization of boron orbitals with the change of B—X bond length.

The authors failed to establish the role of the latter factor while a rough estimation of the resonance energy in BF_3 gives the value 21–80 kcal/mole.

Then an attempt was made using quantum chemical methods to estimate the reorganization energy in Cotton and Leto's paper³⁴. Within the formalism of the simple molecular orbital method they computed the resonance energy in BF_3 , BCl_3 and BBr_3 equal to 47.8, 29.8 and 25.7 kcal/mole respectively.

The total reorganization energy, i.e. the change in B-halogen bond energy on going from sp^2 to the sp^3 boron valent state was equal approximately to 48.3, 30.3 and 26.2 kcal/mole in BF_3 , BCl_3 and BBr_3 respectively. That is, it was adopted that the change in σ -energy owing to a rehybridization to a pyramid is rather small: only 0.5 kcal/mole for each boron trihalide. Thus it was assumed that the reorganization energy on the formation of complex boron compounds is determined in practice by the energy of π -conjugation which is now called a vertical reorganization energy.

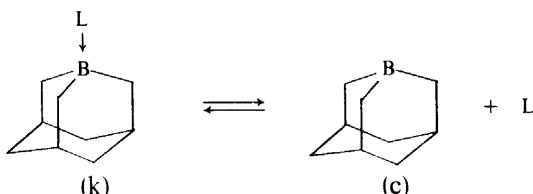
Although possible in principle to estimate the resonance energy (the vertical reorganization energy) in boron trihalides using the methods of quantum chemistry, the case is, however, much more complicated. The range

of the numerical values of the vertical reorganization energies depends essentially on the quantum-chemical computation method. Thus later³⁵⁻³⁸ the computed vertical reorganization energies for BF_3 ranged from 6.7 to 123 kcal/mole, and from 18.2 to 114 kcal/mole for BCl_3 .

Armstrong and Perkins³⁹ have computed the electronic structures and heats of formation of the boron complexes with ammonia and carbon monoxide. From the plotted energy of borane versus the HBH angle it was found that its reorganization energy is equal to 14.5 kcal/mole.

Experimental determination of reorganization energy (a very important factor in the energy balance of complex formation) has not been available up to the present time.

1-Boraadamantane was the only structural model of trivalent boron which permitted experimental estimation of the reorganization energy in trialkylborane on passing from its planar to its pyramidal configuration. This problem was solved by quantitative study of the donor-acceptor interaction in 1-boraadamantane complexes using the ^{11}B n.m.r. techniques. It has been found that some 1-boraadamantane complexes, including etherate and ethylacetate, produce an equilibrium mixture of (k) and (c) forms at certain temperature.



adamantane is equal to -82 p.p.m., while those of 1-boraadamantane

The ^{11}B n.m.r. study of the complexes has shown that instead of two signals from forms (k) and (c) the spectrum has only a singlet whose chemical shift is determined by the position of the equilibrium at the given temperature. The signal observed in the ^{11}B n.m.r. spectrum was an average from the (k) and (c) forms, thus one may determine the change in enthalpy from the equilibrium constants at different temperatures found from the following relation^{40, 41}:

$$k = (\delta - \delta_k)^2 / \{(\delta_c - \delta_k)^2 - (\delta - \delta_k)^2\}$$

where δ is an averaged signal chemical shift, δ_k is the chemical shift of form (k), and δ_c is the chemical shift of form (c).

The ^{11}B chemical shift (from boron trifluoride etherate) in 1-boraadamantane is equal to -82 p.p.m., while those of 1-boraadamantane etherate and ethylacetate complexes measured in the donor solutions are equal respectively to -15.6 and -15.0 p.p.m. By determining the ^{11}B chemical shifts in these complexes at various temperatures (40 – 170°) and computing the equilibrium constants we found the enthalpy changes in 1-boraadamantane etherate (5.9 ± 0.5 kcal/mole) and ethylacetate (9.9 ± 1.0 kcal/mole) complexes.

The enthalpy changes obtained in the reaction of 1-boraadamantane with ether and ethylacetate may be used in estimating the reorganization energy of the boron compounds with three alkyl radicals. It is obvious that trimethylborane with the least expressed steric effects may serve as a standard with

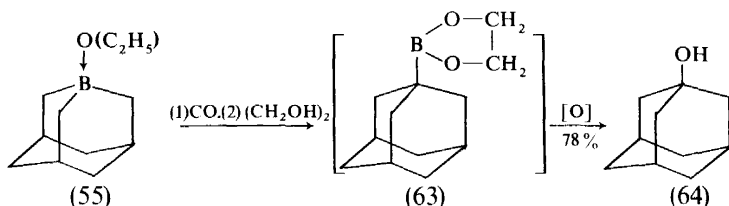
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three alkyl groups at the boron atom. Unfortunately, it gives no complexes with diethyl ether and ethylacetate, thus it is impossible to estimate directly the reactivities of 1-boraadamantane and trimethylborane. However, by thermochemical interpolation one may estimate approximately the enthalpy of formation of trimethylborane complexes with diethyl ether and ethylacetate. It is known that ΔH in BF_3 complexes exceeds that in $\text{B}(\text{CH}_3)_3$ complexes by 10–14 kcal/mole. Since ΔH of boron trifluoride complexes with diethyl ether is equal to 11.9 kcal/mole and 13 kcal/mole for the ethylacetate, the value of ΔH in trimethylborane complexes with diethyl ether and ethylacetate is nearly zero. Thus our changes in the enthalpy in the reaction of 1-boraadamantane with diethyl ether (5.9 kcal/mole) and ethylacetate (9.9 kcal/mole) provide an estimate of the reorganization energy in trialkylboranes (ca. 6–10 kcal/mole).

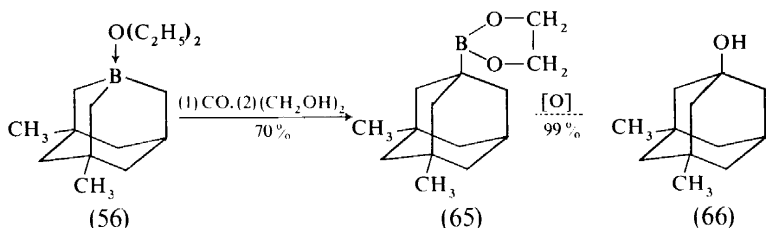
These results demonstrate the invalidity of concluding that the reorganization energy in a boron compound during its complex formation is negligible and makes no essential contribution to ΔH . Actually the reorganization energy contributes sufficiently to the complex formation energy and it is responsible for the existence of boron complexes.

TRANSFORMATION OF 1-BORAADAMANTANE AND 1-BORAPROTOADAMANTANE SYSTEMS INTO ADAMANTANE AND PROTOADAMANTANE SYSTEMS

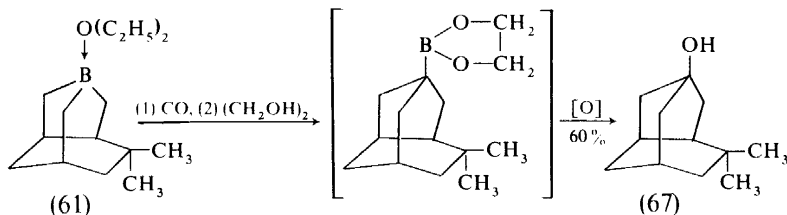
Hillman has shown⁴²⁻⁴⁴ that trialkylboranes may react with carbon monoxide to give trialkylcarbinols. Naturally this study introduced the problem of the transformation of boraadamantane compounds into adamantane systems using Hillman's reaction. It was found that such reactions could be performed. 1-Boraadamantane etherate was heated to 100° with carbon monoxide in an autoclave under 50–60 atm for 3 h, then ethylene glycol was added to the mixture and the latter was heated at 150° for 3 h. Oxidation with hydrogen peroxide alkaline solution transformed the generated ethylene glycol ester of adamantyl-1-boronic acid (63) into 1-hydroxyadamantane (64) (70 per cent). This reaction is direct evidence of the structure of 1-boraadamantane.



Carbonilation of 3,5-dimethyl-1-boraadamantane (56) was also smooth. In this case an intermediate ethylene glycol ester of 3,5-dimethyladamantyl-1-boronic acid (65) (70 per cent) was isolated, b.pt. 86–88°/1 mm Hg, n_D^{20} 1.4911, d_4^{20} 1.0278. Its oxidation with hydrogen peroxide in alkaline medium gave almost quantitatively 3,5-dimethyl-1-hydroxyadamantane (66).



The etherate of 4,4-dimethyl-1-boraprotadamantane (61) was also carbonilated with carbon monoxide into 4,4-dimethyl-1-hydroxyprotadamantane (67).



Tricyclo(4,3,1,0^{3,8}) decane or trivially protoadamantane was first obtained by two methods in 1968. In the first procedure protoadamantane and its 3-substituted derivative were prepared from 3,6-dibromo-adamantane-10,11-dione⁴⁵, in the second method protoadamantane and 2-substituted different syntheses were proposed for protoadamantane compounds which generally started from adamantane derivatives. Mainly they provided 4-substituted protoadamantanes⁴⁷⁻⁵⁷.

No syntheses were known for 1-substituted protoadamantanes, thus our method of protoadamantane preparation with substituents in 1-position is of both theoretical and preparative significance.

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