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THE CHEMISTRY OF 1-BORAADAMANTANE

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Abstract - 1-Boraadamantane is a unique compound both in respect of its structure and chemical behaviour. Methods for the synthesis of the 1-boraadamantane compounds, their reactions with carbonyl compounds, aromatic nitriles, nitrogenous and phosphorous ylides, as well as protolysis, halogenation, carbonylation, and amination of the 1-boraadamantane derivatives are described. An application of 1-boraadamantane to organic synthesis is considered, including the preparation of the adamantane, homoadamantane, and 1-azaadamantane compounds.

INTRODUCTION

1-Boraadamantane (1) is one of the most interesting compounds due to both its exotic structure and chemical properties.

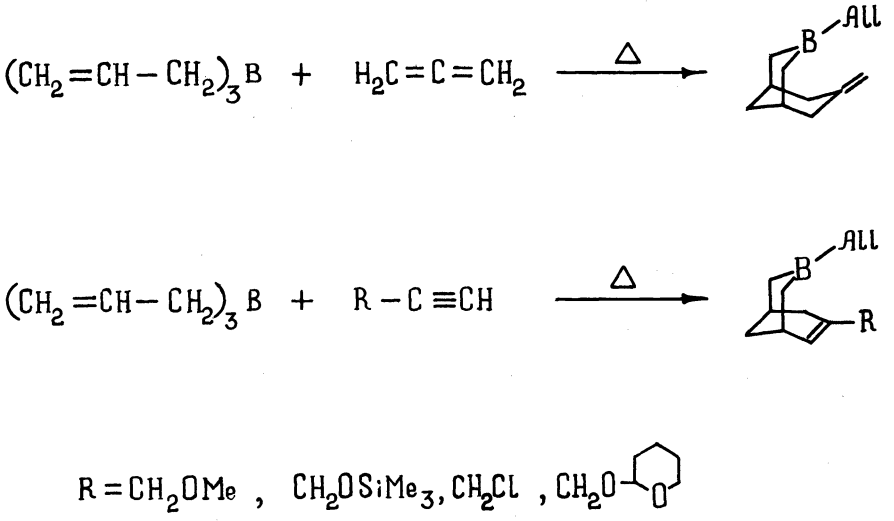
(1)

The uniqueness of the compound is accounted for by the fact that the boron atom in this is not in a trigonal valence state as in all trivalent boron compounds known so far, but in a tetrahedral valence state. This specific feature of 1-boraadamantane is displayed in higher reactivity, as compared with trialkylboranes, particularly, in the high complexing capacity. This compound is of specific interest from the viewpoint of solving those important theoretical problems of organoboron chemistry, which arise from the specifity of its structure. Thus, 1-boraadamantane has served as a unique model of trivalent boron, which allowed estimation of the reorganization energy of a trialkylborane in its transition from a trigonal to a tetrahedral configuration (1,2).
A practical aspect of the 1-boraadamantane usage has an essential significance. On the basis of its reactions, original methods for the synthesis of difficult-to-obtain carbocyclic compounds have been developed. It has also been found that a number of the 1-boraadamantane complex compounds show a pronounced antiviral activity (3).

1. SYNTHETIC METHODS.

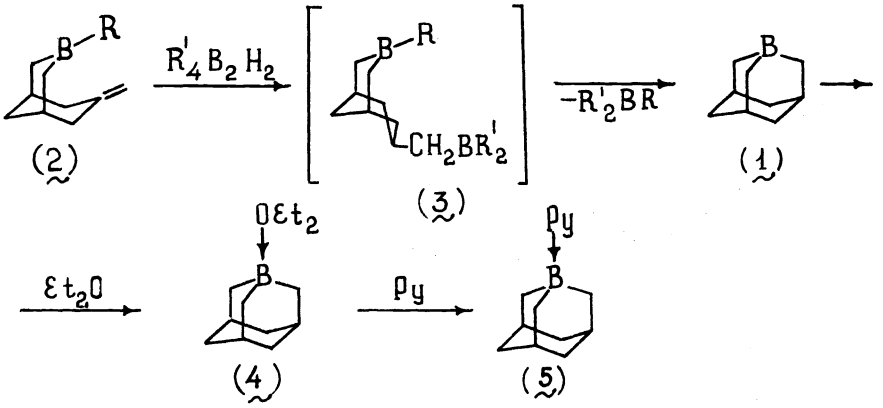
Methods of the synthesis of 1-boraadamantane and its homologues are based on the use of the 7-methylene-3-borabicyclo[3.3.1]nonane and 3-borabicyclo[3.3.1]non-6-ene derivatives, which are obtained by the reaction of triallylborane with allenes and acetylenes (Scheme 1) (1,2,4-7).
For the first time, 1-boraadamantane (1) was obtained by the hydroboration of 7-methylene-3-n-propyl-3-borabicyclo[3.3.1]nonane (2a) with tetrapropyldiborane (Scheme 2) (8).
In the first stage, 3-n-propyl-7-(di-n-propylboryl)methyl-3-borabicyclo-[3.3.1]nonane (3a) formed cyclizes to 1-boraadamantane (1), which gives a stable adduct with pyridine (5) (8-11). In an analogous manner, (1) was synthesized from more accessible 3-methoxy-7-methylene-3-borabicyclo[3.3.1]

Scheme 1.



nonane (2b). A tetraalkyldiborane or diborane may be used as the hydroborating reagent (9,10). If the reaction is carried out in ether, a complex of 1 with ether is formed, which partially dissociates even at room temperature.

Scheme 2.



2a R= n-Pr

2b R= OMe

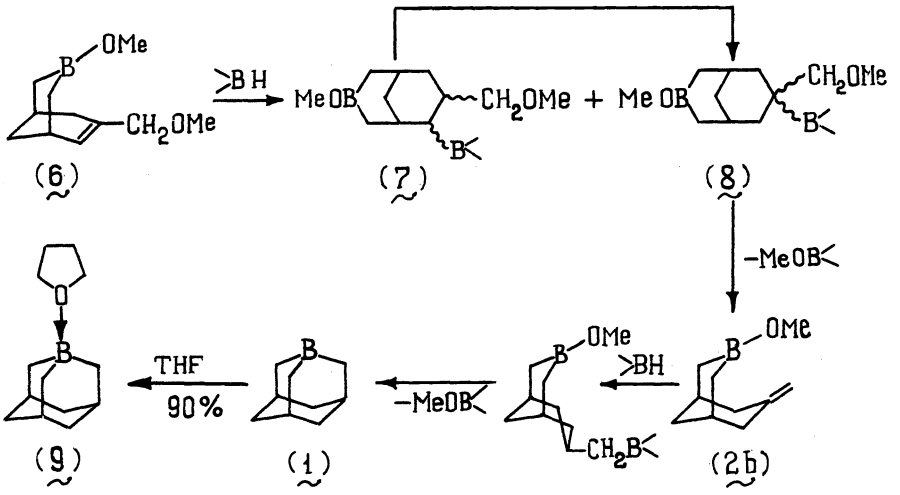
The hydroboration of 3-methoxy-7-methylene-1,5-dimethyl-3-borabicyclo-[3.3.1]nonane afforded 3,5-dimethyl-1-boraadamantane isolated as a complex with pyridine (9,10). Analogously, starting from 3-methoxy-7-methylene-6,6-dimethyl-3-borabicyclo[3.3.1]nonane, 4,4-dimethyl-1-boraadamantane, its etherate and pyridinate were obtained (12).

The most convenient method for the synthesis of 1-boraadamantane is based on the hydroboration of 3-methoxy-7-methoxymethyl-3-borabicyclo[3.3.1]-non-6-ene (6) with the use of B_2H_6, $H_3B.THF$, or $H_3B.NEt_3$ (13,14). In the hydroboration of (9), the boron atom adds both in the 6 and 7 positions to form the compounds (7) and (8). The borane (8) undergoes a β-elimination to produce (2b), which is converted to 1-boraadamantane on further hydroboration. The borane (7) readily isomerizes to (8), and then the whole cycle of conversions of (8) is repeated (Scheme 3).

It should be emphasized that the isomerization of (7) to (8) proceeds rapidly even at 0°C, especially with an excess of THF. Isomerization of organoboron

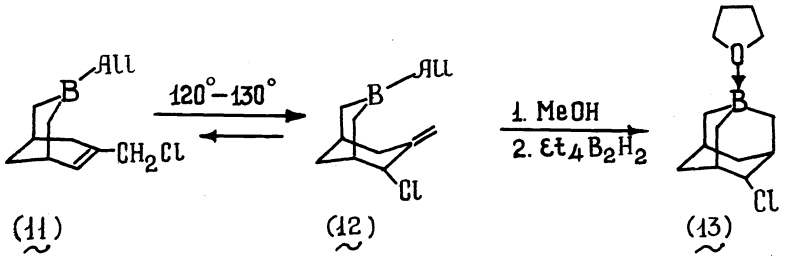
compounds usually takes place at 100-160°C (15), and, only in the series of some steroid type boranes does it proceed under milder conditions (40-60°C) (16).

Scheme 3.



A catalytic effect of compounds with B-H bonds on the rate of isomerization of (7) to (8), which was detected, is in agreement with a "bridge tautomerism" mechanism (17), while it finds no explanation in an "elimination-addition" mechanism (18). 1-Boraadamantane in an individual state is prepared by heating its etherate in vacuum. This synthetic method was expanded to the preparation of the 1-boraadamantane homologues. Hydroboration of 3-methoxy-7-methoxymethyl--1,5-dimethyl-3-borabicyclo[3.3.1]non-6-ene and of 3-methoxy-7-methoxymethyl-8,9-dimethyl-3-borabicyclo[3.3.1]non-6-ene with $H_3B.THF$ yields tetrahydrofuran complexes of 3,5-dimethyl-1-boraadamantane (19) and 4,6-dimethyl-1-boraadamantane, respectively (20). 1-Boraadamantane is also formed in the hydroboration of 3-methoxy-7-trimethylsilyloxymethyl-3-borabicyclo[3.3.1]non-6-ene (21) and a cyclic compound obtained by heating of 7-dipropylboryloxymethyl-3-allyl-3-borabicyclo-[3.3.1]non-6-ene (21). A tetrahydrofuran complex of 1-boraadamantane is obtained by the hydroboration of 3-methoxy-7-tetrahydropyranyloxymethyl-3-borabicyclo[3.3.1]non-6-ene (22) and of 7-chloromethyl-3-methoxy-3-borabicyclo[3.3.1]non-6-ene with $H_3B.THF$ (23,24).
3-Allyl-7-chloromethyl-3-borabicyclo[3.3.1]nonane (11), prepared by condensation of triallylborane with propargyl chloride, isomerizes at 120-130°C to 6-chloro-7-methylene-3-allyl-3-borabicyclo[3.3.1]nonane (12) with a ratio between (11) and (12) of 2:3 in an equilibrium mixture (Scheme 4).

Scheme 4.



Methanolysis of the mixture followed by the hydroboration with tetraethyldiborane makes it possible to obtain a tetrahydrofuran complex of 4-chloro-1-boraadamantane (13) in a satisfactory yield (21).

2. PROPERTIES.

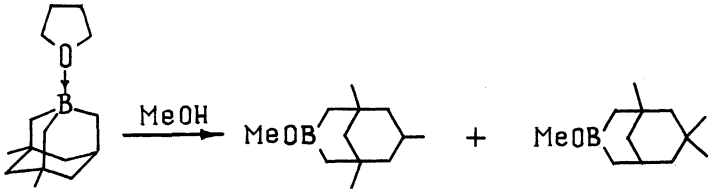
1-Boraadamantane is a highly reactive compound. As a rule, it reacts under milder conditions than trialkylboranes do in analogous conversions. 1-Boraadamantane sublimes in the shape of regular prisms having no accurate melting point. Its ^{11}B NMR chemical shift is equal at 83.5 ppm (11). According to the NMR spectroscopy data (J_{CH}), <<HCαH in (1) are equal 109° 54' and <<CαBCα are close to tetrahedral angles (2).

The unusually high complexing ability of free 1-boraadamantane is due to the tetrahedral configuration of the borom atom. 1-Boraadamantane forms a large family of coordinate compounds with n-donors. The complexes of (1) with diethyl ether (10), THF (10,13), and triethylamine (12,13) form directly in the synthesis course. These can easily be converted to other complexes by means of exchange reactions with the ligands possessing higher donative ability. In this way, complexes with different aliphatic amines were synthesized (13). A number of the complexes are of great stability, for example - the complexes of (1) with pyridine and triethylamine do not dissociate even at 200°C (6).
On the basis of thermochemical data, a value of the reorganization energy (5.7 kcal/mol) in transition of the boron atom from a trigonal to a tetrahedral configuration (complex formation) has been estimated (2).
With the use of X-ray analysis, geometrical parameters of the complexes of 1-boraadamantane with pyridine and quinoline were determined (25).

2.1 Protolysis

The unusually high reactivity of 1-boraadamantane shows up in an easy protolytic rupture of one B-C bond thus decomposing the 1-boraadamantane structure. 1-Boraadamantane etherate reacts with methanol at room temperature being converted to 3-methoxy-7-methyl-3-borabicyclo[3.3.1]nonane (14) (10). As is known, trialkylboranes react with alcohols at 150-170°C to give esters of dialkylborinic acids together with alkanes, alkenes, and hydrogen (26). Methanolysis of the tetrahydrofuran complex of 3,5-dimethyl-1-boraadamantane (10) affords a mixture of two possible isomers: 3-methoxy-1,5,7-trimethyl-3-borabicyclo[3.3.1]nonane (15) and 3-methoxy-1,7,7-trimethyl-3-borabicyclo[3.3.1]nonane (16) in a ratio of 2:1 (19) (Scheme 5).

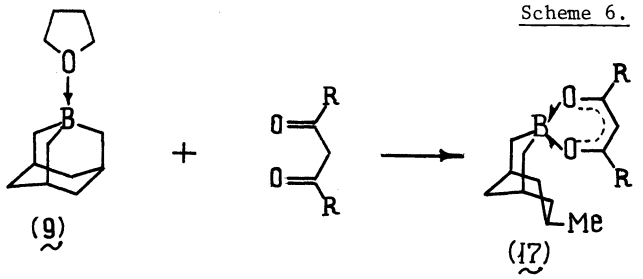
Scheme 5.



(10) (15) (16)

The high sensitivity of the 1-boraadamantane system toward hydrogen halides is demonstrated by the reaction with HBr, which at 20°C produces 3-bromo-7-methyl-3-borabicyclo[3.3.1]nonane (27).
Interaction of tetrahydrofuran-1-boraadamantane (9) with β-diketones takes place with a great ease. As a result of the reaction with acetylacetone and benzoylacetophenone, the β-diketonates of 7-methyl-3-borabicyclo[3.3.1]nonane were obtained (28) (Scheme 6).

Scheme 6.

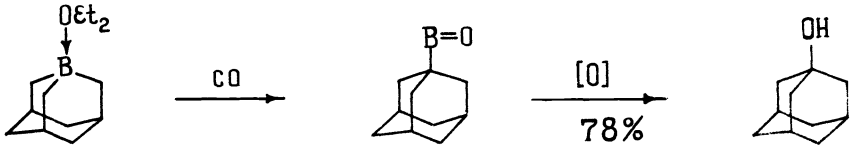


(9) (17) R= Me, Ph

2.2 Carbonylation.

An original method for the synthesis of the adamantane series compounds may serve as an excellent example for the application of 1-boraadamantane in organic synthesis. As was found by Hillman, trialkylboranes react with CO to form, after oxidation of the carbonylation products, trialkylcarbinols (29). 1-Boraadamantane undergoes analogous conversions (10,12) (Scheme 7).

Scheme 7.



(4) (18) (19)

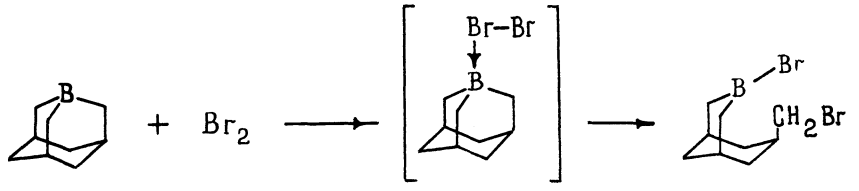
In this way, 1-hydroxy-3,5-dimethyladamantane (10), 1-hydroxy-4,4-dimethyl-adamantane (12), and 1-hydroxy-4-chloroadamantane (23) were obtained.

2.3 Halogenation.

a) Bromination.

1-Boraadamantane readily reacts with bromine even at -40 to -50°C. The reaction proceeds with a rupture of the boron-carbon bond to form 3-bromo-7-bromomethyl-3-borabicyclo[3.3.1]nonane (21) (Scheme 8) (27).

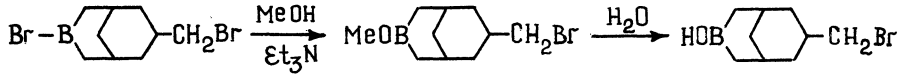
Scheme 8.



(1) (20) (21)

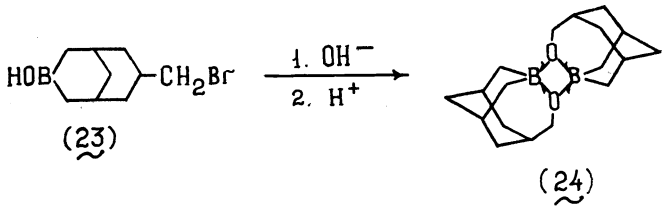
The bromination process of 1 relates to electrophilic halodemetalation reactions (2-isopropyl-2-boraadamantane reacts with bromine under usual laboratory lighting by an analogous mechanism (30)).

Under the action of a mixture of Et_3N and MeOH, (21) is converted to 3-methoxy-7-bromomethyl-3-borabicyclo[3.3.1]nonane (22) with the boron atom possessing a high mobility.



(21) (22) (23)

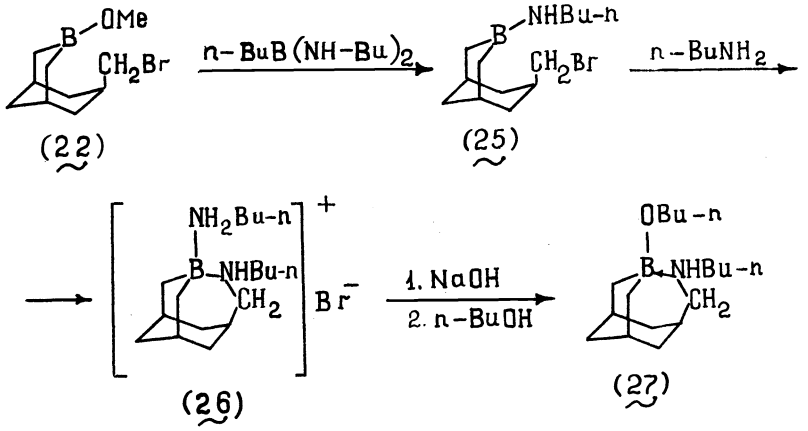
Alkaline hydrolysis of 3-hydroxy-7-bromomethyl-3-borabicyclo[3.3.1]nonane (23) results in the formation of the 4-oxa-3-borahomoadamantane dimer (24) (27), which molecular structure was determined by X-ray analysis. (31).



(23) (24)

An exchange reaction of (22) with di(n-butylamino)butylborane furnished 3-n-butylamino-7-bromomethyl-3-borabicyclo[3.3.1]nonane (25), which was converted to a boronium salt (26) upon heating with n-$BuNH_2$. Treatment of the salt (26) with an aqueous solution of NaOH, followed by esterification with butanol, forms intra-coordinated 3-butoxy-7-n-butylaminomethyl-3-borabicyclo[3.3.1]nonane (27), which is the first representative of organoboron compounds with the azaborahomoadamantane structure (27) (Scheme 9).

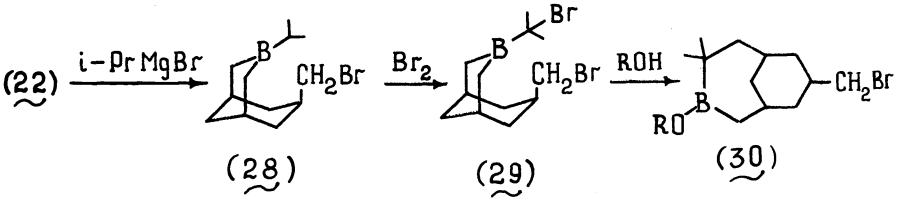
Scheme 9.



(22) (25) (26) (27)

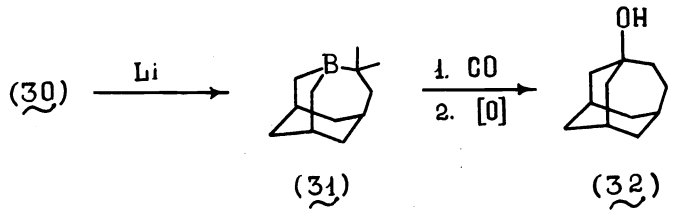
3-Bromo-7-bromomethyl-3-borabicyclo[3.3.1]nonane has served as an initial reagent for the synthesis of 4,4-dimethyl-3-borabicyclo[4.3.1]decane compounds and of 4,4-dimethyl-3-borahomoadamantane (32). An interaction between iso-PrMgBr and (22) produced 3-isopropyl-7-bromomethyl-3-borabicyclo-[3.3.1]nonane (28), bromination of which led to 3-(2-bromo-2-propyl)-7-bromomethyl-3-borabicyclo[3.3.1]nonane (29). Under the action of an alcohol, (29) undergoes a Matteson-Pasto rearrangement (33,34) with the cycle expansion turning to a 3-alkoxy-8-bromomethyl-4,4-dimethyl-3-borabicyclo-[4.3.1]decane (30) (32) (Scheme 10).

Scheme 10.

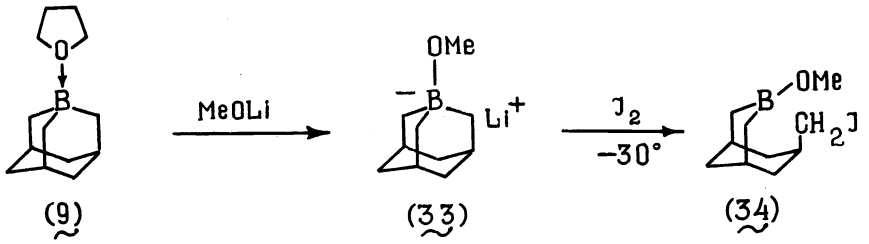


(28) (29) (30)

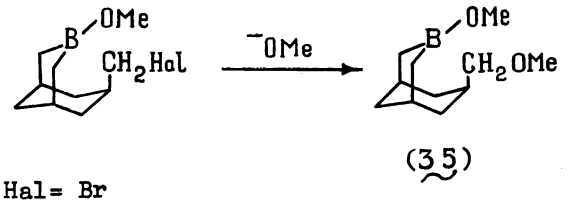
Under the action of lithium in ether, 3-n-butoxy-8-bromomethyl-4.4-dimthyl-3-borabicyclo[4.3.1]decane (30, R=n-Bu) cyclizes to 4,4-dimethyl-3-borahomoadamantane (31), carbonylation of which leads to 4,4-dimethylhomoadamantanol (32) (32).



b) Iodination.
In the presence of alkali metal methoxides, the tetrahydrofuran complex of 1-boraadamantane (9) reacts with iodine at -30°C with the formation of 7-iodomethyl-3-methoxy-3-borabicyclo[3.3.1]nonane (34) (35).



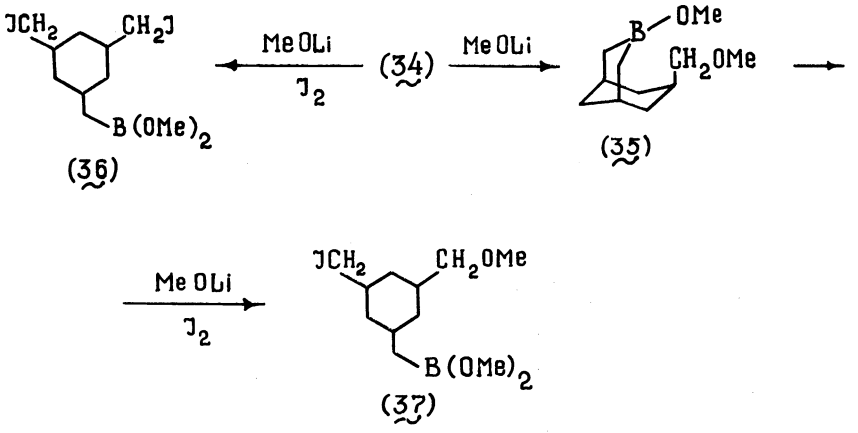
In the compound (22), the active bromine can be exchanged for a methoxy group (27). This property shows up even more in (34) (35).



(22 Hal= Br
34 Hal= I)

Thus, the process of halogen substitution accompanies the iodination reaction in the case of excess alkoxide. This substitution reaction complicates the iodination of compound (34), as a result of which a mixture of products is formed (35) (Scheme 11).

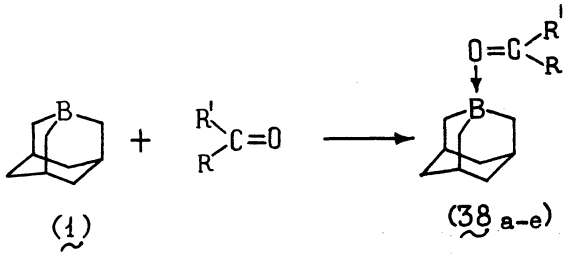
Scheme 11.



The iodination of (9) in the presence of lithiummethyl proceeds at -70°C to give 7-iodomethyl-3-methyl-3-borabicyclo[3.3.1]nonane (35).

2.4 Reactions with carbonyl compounds and aromatic nitriles.

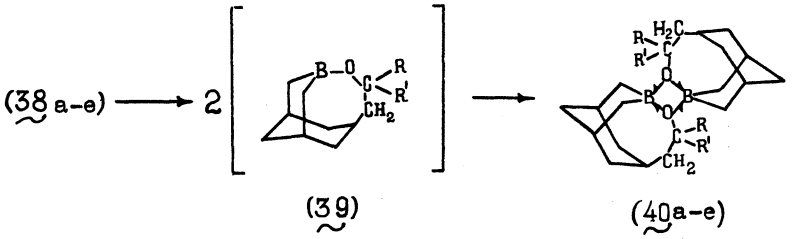
Trialkylboranes do not add to the C=O double bond owing to a low polarity of the B-C bond (7). On the contrary, 1-boraadamantane reacts with aldehydes and acetone just as an organometallic reagent (36). A high complexing capacity of 1 is revealed in an intermediate formation of the adducts (38 a-e) with carbonyl compounds (36).



(1) (38 a-e)

a) R= H, R' = Ph
b) R= H, R' =4-MeOC$_6$H$_4$
c) R= H, R' =3,4-(MeO)$_2$C$_6$H$_3$
d) R= H, R' = iso-Pr
e) R= R' = Me

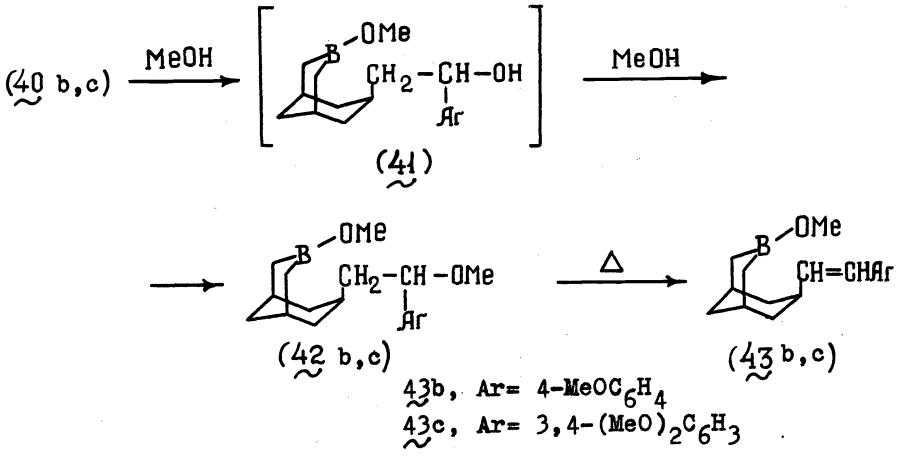
The complexes (38 a-e) are thermally unstable, being converted on heating, with the formation of a new C-C bond, to the dimers of 5-substituted 4-oxa-3-bora-1,1-bihomoadamantanes (40).



(38 a-e) (39) (40a-e)

The compounds (40 a-e) are colourless crystalline substances stable in air. Dimers (40b) and (40c) are converted to 3-methoxy-7-(2-methoxy-2-arylethyl)-3-borabicyclo[3.3.1]nonanes (42) when heated with methanol; the boranes (42) eliminate methanol to form 3-methoxy-7-(2-arylvinyl)-3-borabicyclo[3.3.1]-nonanes (43) (36) (Scheme 12).

Scheme 12.

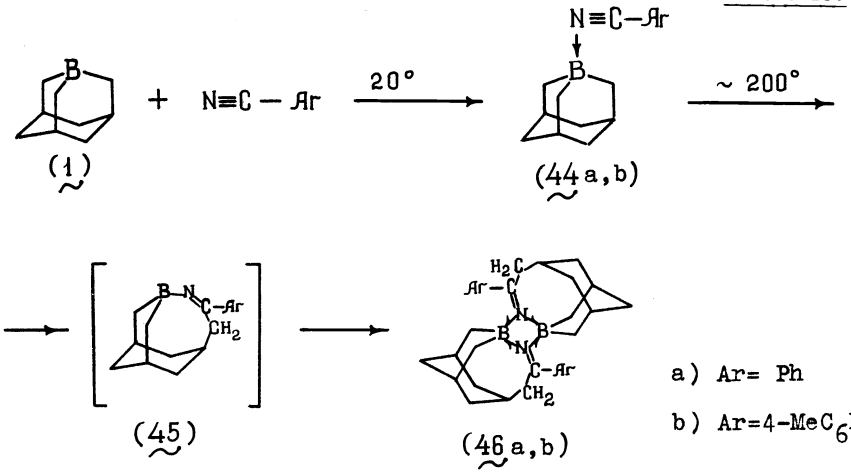


(40 b,c) (41) (42 b,c) (43 b,c)

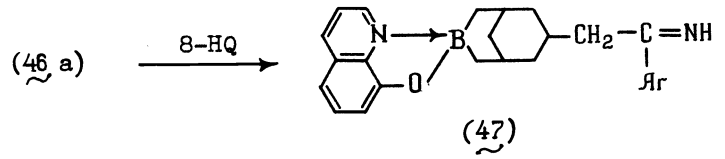
43b, Ar= 4-MeOC$_6$H$_4$
43c, Ar= 3,4-(MeO)$_2$C$_6$H$_3$

Analogously, in accord with a scheme of the organometallic synthesis, proceeds the reaction of (1) with aromatic nitriles (37). Just as in the case of carbonyl compounds, formation of the complexes (44) is observed. Heating these at 200°C leads to the 5-aryl substituted 3-bora-4-aza-1,1-bihomoadamant-4-enes (45), which exist in a dimeric form (46) (37) (Scheme 13).

Scheme 13.



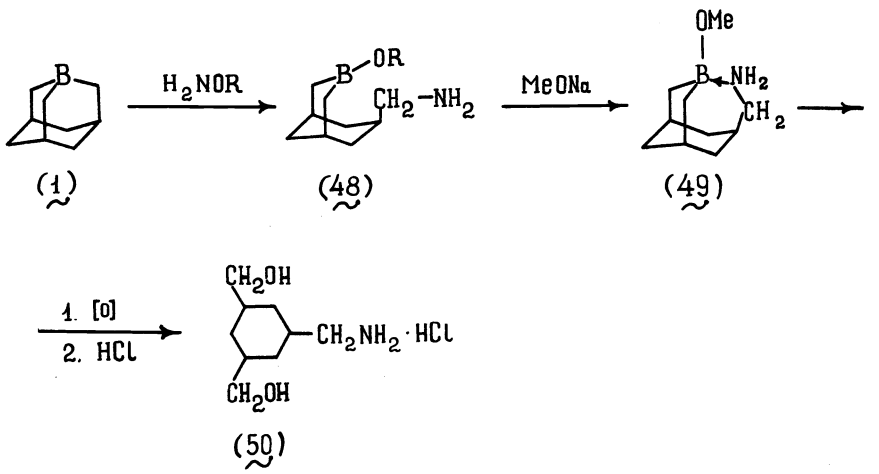
The framework system of (46) is stable toward air and alcohols but it can be broken down with 8-hydroxyquinoline (37).



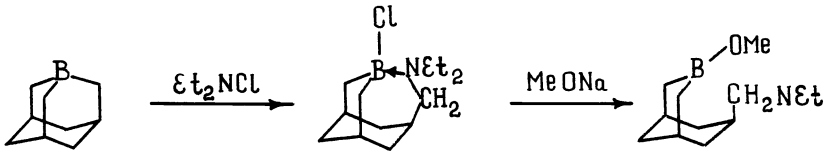
2.5 Amination.

1-Boraadamantane (1) reacts with the hydroxylamine derivatives. An interaction of (1) and hydroxylamine-O-sulfonic acid or 2,4-dinitrophenylhydroxylamine leads to the 3-substituted 7-aminomethyl-3-borabicyclo[3.3.1]nonanes (48), treatment of which with sodium methylate produces intra-complex 3-methoxy-7-aminomethyl-3-borabicyclo[3.3.1]nonane (49). Oxidation of the latter compound affords cis-1,3-di(hydroxymethyl)cyclohexane (50) (33) (Scheme 14).

Scheme 14.



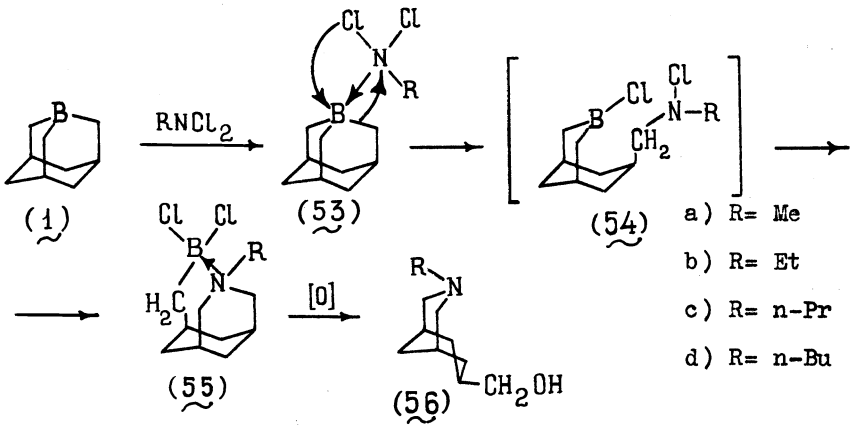
Trialkylboranes react with N-chloramines to form either alkyl amines or alkyl chlorides (7), depending on the mechanism, ionic or radical, by which the reaction occurs (39). 1-Boraadamantane reacts with N-chlorodiethylamine forming 3-chloro-7-diethylaminomethyl-3-borabicyclo[3.3.1]nonane (51), treatment of which with sodium methylate yields 3-methoxy-7-diethylaminomethyl-3-borabicyclo[3.3.1]nonane (52) (38).



(1) (51) (52)

An analysis of the products of the reaction of (1) with the chloramine indicates that the reaction proceeds by a polar mechanism, which is apparently connected with the high complexing capacity of 1-boraadamantane.
An action of N,N-dichloramines on (1) leads to the formation of 3-alkyl-7-dichloroboryl-3-azabicyclo[3.3.1]nonanes (55) oxidation of which affords 3-alkyl-7-hydroxymethyl-3-azabicyclo[3.3.1]nonanes (56) (38,40) Scheme 15).

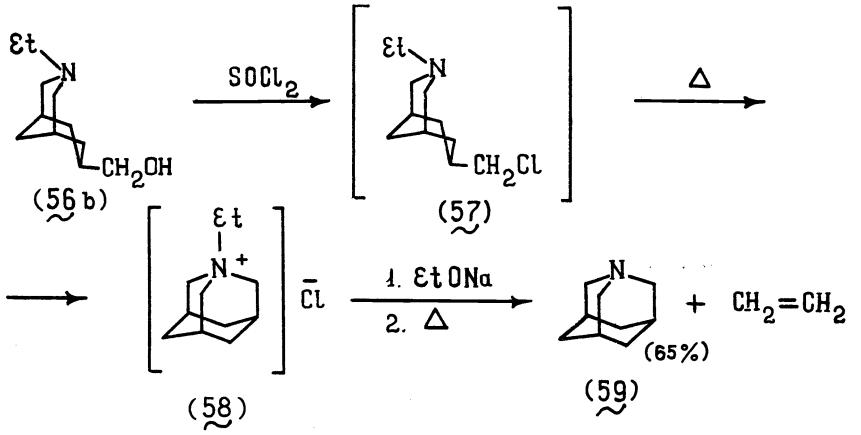
Scheme 15.



(1) (53) (54) (55) (56)

Compounds of the 3-alkyl-7-hydroxymethyl-3-azabicyclo[3.3.1]nonane series (56) have been used for the synthesis of 1-azaadamantane. With this purpose, the following cycle of transformations was effected (40) (Scheme 16).

Scheme 16.

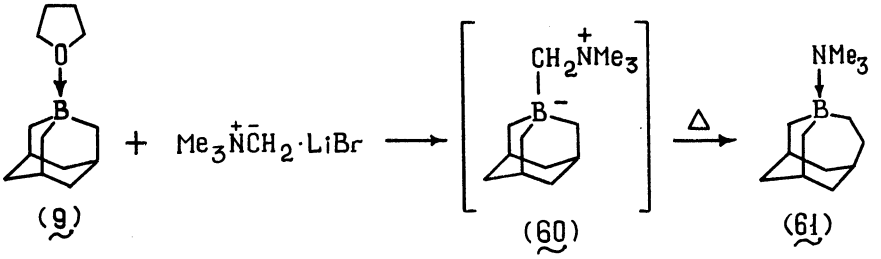


(56b) (57) (58) (59)

In the first stage, the OH group In (56b) was replaced by Cl upon treatment with thionyl chloride with the formation of 3-ethyl-7-chloromethyl-3-aza-bicyclo[3.3.1]nonane (57), which readily cyclizes, without isolation, to N-ethylazoniumadamantane chloride (58). Hoffman's degradation of the ammonium salt obtained results in the formation of 1-azaadamantane (59) (40).

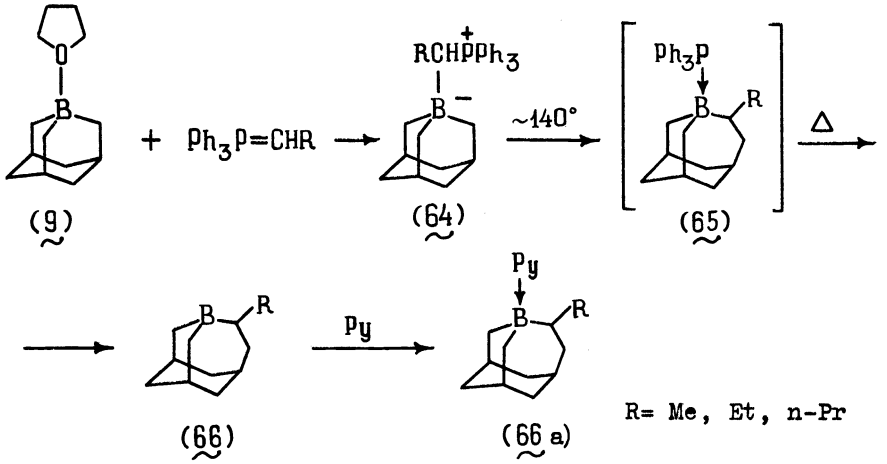
2.6 Reactions with ylides.

In the trialkylborane series, the reaction with ylides finds only very limited preparative application (7). At the same time, this reaction proves to be a very valuable method as applied to 1-boraadamantane, since it permits to realize a selective expansion of one of the cycles by one methylene group thereby transiting to a new type of boron polyhedral compounds, 3-borahomoadamantane derivatives. Thus, in the interaction between trimethylammonium methylide and tetrahydrofuran-1-boraadamantane (9), the initially formed unstable betaine (60) rearranges to trimethylamine-3-borahomoadamantane complex (61).



(9) (60) (61)

Treatment of (61) with BF_3 etherate in tetrahydrofuran results in the formation of the tetrahydrofuran complex of 3-borahomoadamantane (62). The latter was converted to 3-hydroxyhomoadamantane (63) by the carbonylation-oxidation (41). As distinct from trimethylammonium methylide, alkylidenetriphenylphosphoranes form stable adducts of the betaine type (64) with (9).



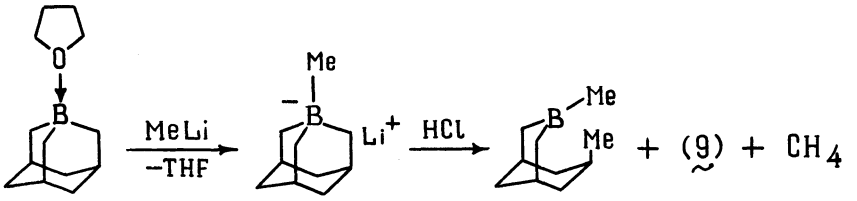
(9) (64) (65) (66) (66a)

The adducts (64) rearrange at 130-140°C to the compounds of the 4-alkyl-3-borahomoadamantane series (66) isolated as colourless readily oxidizible liquids, which form relatively stable complexes with pyridine (66a) (42).

2.7 Ate complexes.

1-Boraadamantane forms the borates with lithium alkyls and alkoxides, their ^{11}B NMr chemical shifts are -20 and -3 ppm, respectively. The action of an ethereal solution of HCl on lithium 1-methyl-1-boraadamantanate (67a) produces 3,7-dimethyl-3-borabicyclo[3.3.1]nonane (68) (70%), tetrahydrofuran-1-boraadamantane (9) (15%), and methane, i.e. there is observed a cleavage of the B-C bonds, which corresponds approximately to a statistical distribution (43).

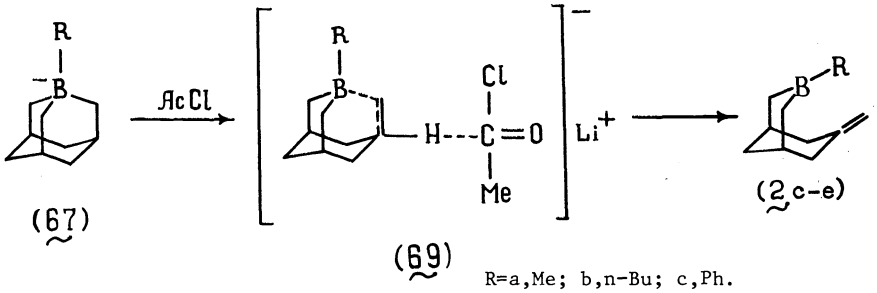
Lithium 1-alkyl-1-boraadamantanes (67) undergo an unusual β-elimination on reaction with acetyl chloride (44).



(9) (67a) (68)

A whole number of reactions of lithium tetraalkylborates is known, which are accompanied by the abstraction of an α-hydride ion with simultaneous shift of an alkyl radical from the boron to α-carbon (see e.g. (45)). On the contrary, in the action of AcCl on (67 a-c,) splitting off a β-hydride ion from a bridgehead position takes place with the formation of 7-methylene-3-alkyl-3-borabicyclo[3.3.1]nonanes (2) (44) (Scheme 17).

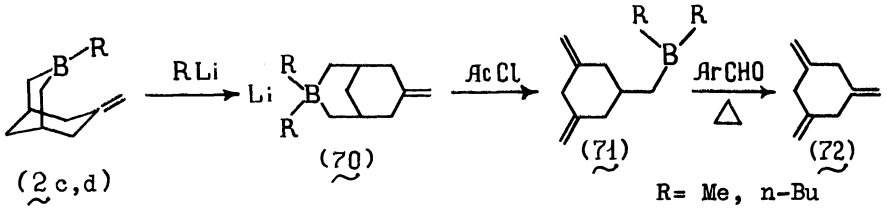
Scheme 17.



(67) (69) (2c-e)

R=a,Me; b,n-Bu; c,Ph.

From the formal standpoint, the dehydroboration process described (Scheme 17) is a reverse reaction with respect to forming the 1-boraadamantane structure by the hydroboration of (2) (Scheme 2).
Analogously, the ate complexes (70) obtained from 7-methylene-3-alkyl-3-borabicyclo[3.3.1]nonanes (2 c,d) react with AcCl to give 3,5-dimethylenecyclohexylmethyl(dialkyl)boranes (71) (43,46).

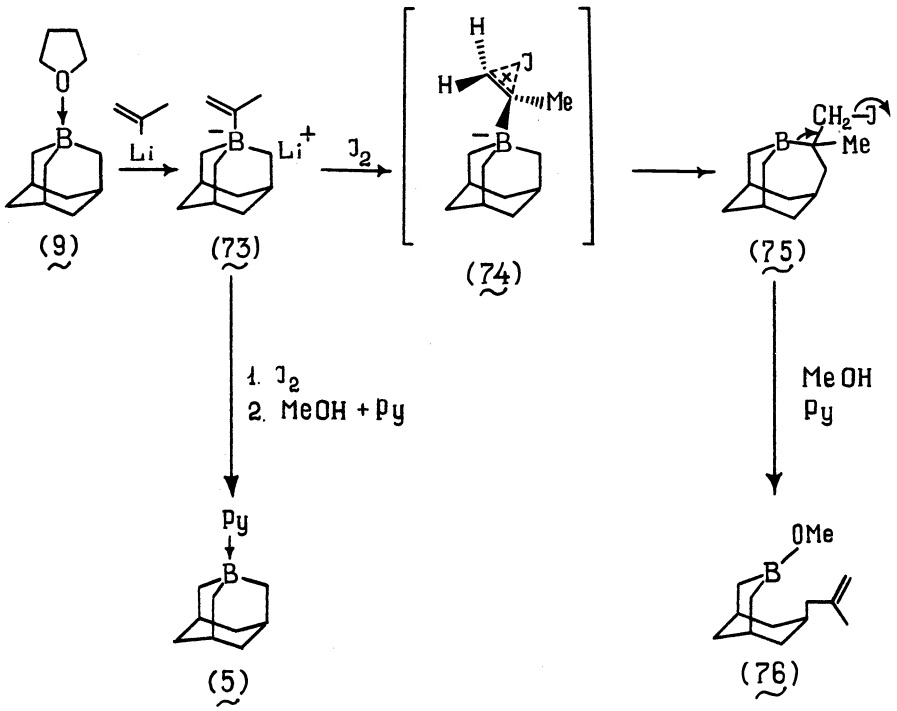


(2c,d) (70) (71) (72)

R= Me, n-Bu

Using a known reaction of trialkylboranes with aromatic aldehydes (47), (71) were converted to difficultly available 1,3,5-trimethylenecyclohexane (72) (43,46).
Iodination of lithium 1-isopropenyl-1-boraadamantanate (73) by Zweifel's method (48) leads, after treatment of the reaction mixture with methanol and pyridine, to a mixture of 3-methoxy-7-isobutenyl-3-borabicyclo[3.3.1]-nonane (79) (45%) and pyridine-1-boraadamantane (5) (35%) (Scheme 18).

Scheme 18.



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