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THE CHEMISTRY OF BORON-CAGE COMPOUNDS

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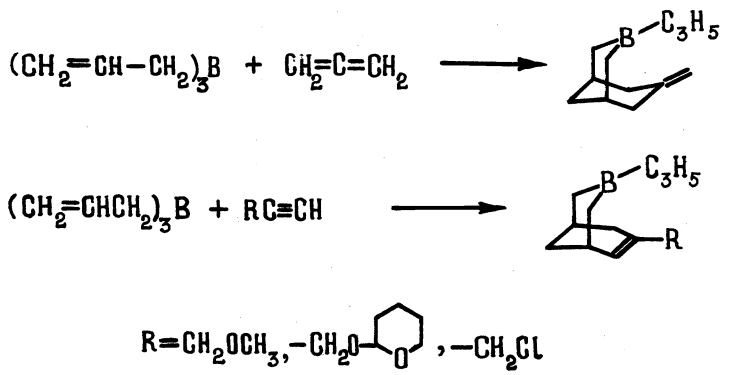
Abstract - Boron-containing polyhedral compounds - 1-boraadamantane and its derivatives - are obtained with the use of 3-borabicyclo-/3,3,1/nonane and 3-borabicyclo/3,3,1/non-6-ene derivatives. On the basis of 1-boraadamantane, a synthesis of 3-borahomoadamantane, its hetero-analogues, and 6-oxa-5-bora-1,1-bihomoadamantane is realized. 2-Boraadamantane is synthesized starting with bicyclo/3,3,1/nona-2,6-diene. 1-Boraadamantane and its analogues are effective reagents in organic synthesis. The complexes of 1-boraadamantane exhibit a significant antiviral activity.

I. Introduction

The chemistry of adamantane, its analogues, and heteroadamantanes have attracted considerable attention. The chemistry of boron-containing polyhedral compounds is of great interest. We have synthesized compounds of this type - 1-boraadamantane and its homologues - using derivatives of 3-borabicyclo/3,3,1/nonane and 3-borabicyclo/3,3,1/non-6-ene. These two compounds are obtained as a result of the reaction of allylboranes with allenes or acetylenes (scheme 1) /1-4/.

Scheme 1



1-Boraadamantane has been the initial compound for the synthesis of 3-borahomoadamantane, 4-oxa-3-borahomoadamantane, 6-oxa-5-bora-1,1-bihomoadamantane. On the basis of bicyclo/3,3,1/nona-2,6-diene, 2-boraadamantane was prepared.

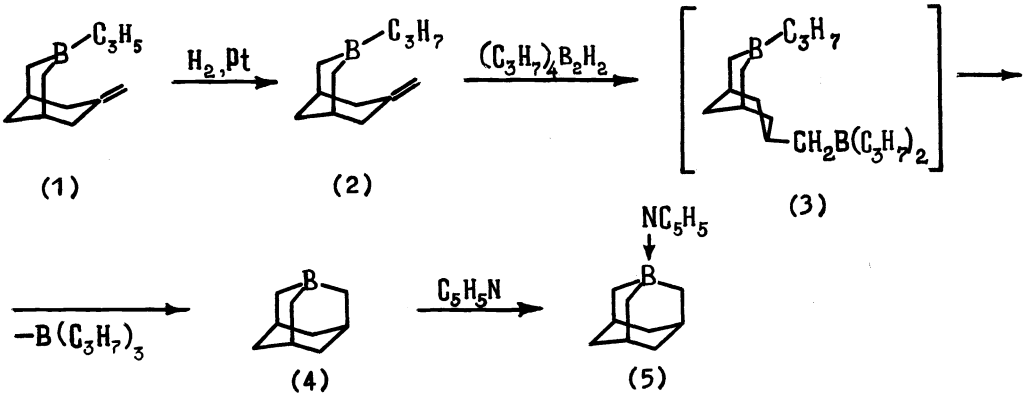
II. 1-Boraadamantane

1. Methods of synthesis

In the earliest method of 1-boraadamantane synthesis, 3-substituted 7-methylene-3-borabicyclo/3,3,1/nonanes were used. The base of various alternatives of this method is the reaction of hydroboration of 7-methylene group with consequent intramolecular cyclization of diboron compounds thus obtained. Cyclization of such type was formerly observed in the series of acyclic diboron systems /5/.

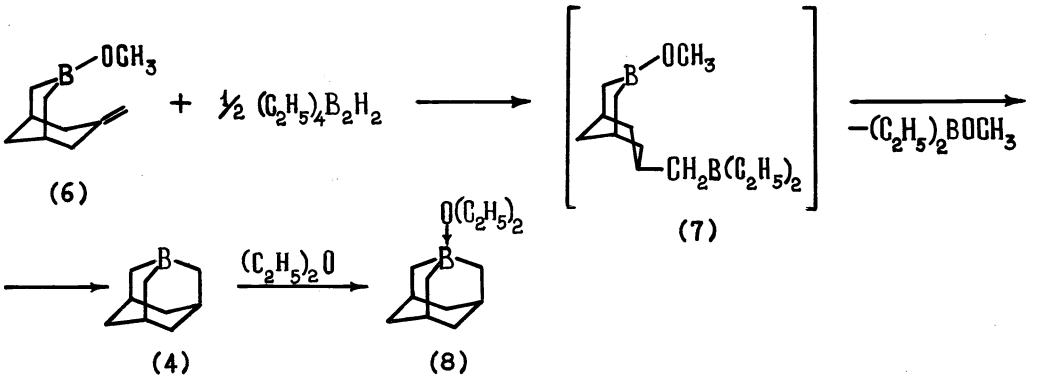
According to one of the versions, 3-allyl-7-methylene-3-borabicyclo-/3,3,1/nonane (1) was partly hydrogenated over Pt-black to give 3-n-propyl-7-methylene-3-borabicyclo/3,3,1/nonane (2) which was then hydroborated with tetra-n-propyldiborane forming 3-n-propyl-7-di-(n-propyl)borylmethyl-3-borabicyclo/3,3,1/nonane (3). Cyclization of the latter (with elimination of tri-n-propylborane) led to 1-boratricyclo/3,3,1,$1^{3,7}$/decane (1-boraadamantane) (4) which gives a stable adduct with pyridine (5) /6-9/ (scheme 2).

Scheme 2



1-Boraadamantane can be more conveniently obtained by hydroboration of 3-methoxy-7-methylene-3-borabicyclo/3,3,1/nonane (6). In the capacity of a hydroborating reagent one can use diborane in etherial medium, or tetraalkyldiborane. Action of tetraethyldiborane on (6) results in 3-methoxy-7-diethylborylmethyl-3-borabicyclo/3,3,1/nonane (7) which eliminates methyl diethylborinate to afford 1-boraadamantane. The latter can be isolated by distillation or as its etherate (8), or pyridinate (5) /7,8/ (scheme 3).

Scheme 3



If compound (6) is hydroborated with diborane in etherial medium, the etherate (8) is isolated, after distilling out the solvent and methylborate formed, as colourless viscous liquid. When hydroboration is carried out with diborane in THF solution, THF-complex of 1-boraadamantane is obtained in high yield.

The etherate of 1-boraadamantane is relatively stable, however it partially dissociates to the components even at room temperature. The etherate (8) was used for synthesizing complexes with some other ligands possessing the greater donor activity. These complexes are obtained merely by mixing the reagents in an inert solvent /7,8/.

3-Methoxy-7-methylene-1,5-dimethyl-3-borabicyclo/3,3,1/nonane, which is prepared from tri-(2-methylallyl)borane and allene, on action of tetraethyldiborane in etherial medium converts smoothly to etherate of 3,5-dimethyl-1-boraadamantane. On action of pyridine the etherate turns to pyridinate of 3,5-dimethyl-1-boraadamantane /7,8/. Similarly, using 3-methoxy-7-methylene-6,6-dimethyl-3-borabicyclo/3,3,1/nonane synthesized from triallylborane and 3-methyl-1,2-butadiene, 4,4-dimethyl-1-boraadamantane, its etherate and pyridinate were prepared /10/.

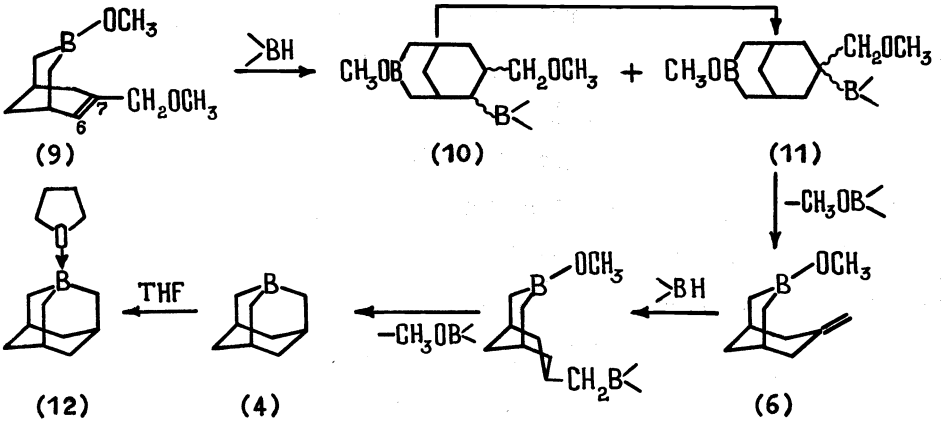
The methods of synthesis 1-boraadamantane from the products of the allylboron-acetylenic condensation were worked out.

A convenient preparative method for synthesis of 1-boraadamantane is based on hydroboration of 3-methoxy-7-methoxymethyl-3-borabicyclo/3,3,1/-non-6-ene (9) which is obtained by methanolysis of 7-methoxymethyl-3-allyl-3-borabicyclo/3,3,1/non-6-ene /11,12/. One can carry out hydroboration of compound (9) with the use of complexes $H_3B{\cdot}THF$ in THF, $H_3B{\cdot}NEt_3$ in a non-polar solvent (e.g. decane), or diborane in ether. The hydroboration of (9)

with $THF \cdot BH_3$ leads to the complex of 1-boraadamantane with THF in 90% yield.

When studying the orientation of adding $THF \cdot BH_3$ to compound (9) by means of oxidation of the hydroboration products, it was found the boron atom to add both to position 6 and 7 to form compounds (10) and (11). The borane (11) undergoes β-elimination to afford methoxyborane (6) which, on further hydroboration, converts to 1-boraadamantane (4) as said above. The borane (10) readily isomerizes giving the compound (11), thereupon the conversion cycle repeats. It should be noted that isomerization of (10) into (11) occurs fast even at 0°C, especially if an excess of $THF \cdot BH_3$ is used. The isomerization of organoboron compounds proceeds usually under hard conditions (100-160°C) /13/,and only in the series of some steroid boranes it occurs under the milder conditions (40-60°C) /14/ (scheme 4).

Scheme 4



The detected catalytic effect of the compounds with B-H bonds on the rate of the isomerization of (10) into (11) is in agreement with "bridge hydrogen tautomerism mechanism" /15/ but cannot be accounted for by "elimination-addition" mechanism /16/.

Hydroboration of the borane (9) with $Et_3N \cdot BH_3$ is carried out in an inert solvent at 130-150°C to give rise to complex of 1-boraadamantane with triethylamine in high yield. In order to prepare the free 1-boraadamantane hydroboration of (9) ought to be performed with diborane in ether with subsequent heating the etherate in vacuum. Under the conditions given the complex dissociates, 1-boraadamantane sublimating as well-formed prisms.

This way of 1-boraadamantane preparation was applied for the synthesis of its homologues. 3-Methoxy-7-methoxymethyl-1,5-dimethyl-3-borabicyclo-/3,3,1/non-6-ene which is obtained from tri-(2-methylallyl)borane and propargylmethyl ether, turns to THF-complex of 3,5-dimethyl-1-boraadamantane

when hydroborating with $THF \cdot BH_3$ in THF /17/.

3-Methoxy-7-methoxymethyl-8,9-dimethyl-3-borabicyclo/3,3,1/non-6-ene obtained from tricrotylborane and propargylmethyl ether, on hydroboration with $THF \cdot BH_3$ affords the complex of 4,6-dimethyl-1-boraadamantane with THF which can be converted into the pyridinate. By means of ^{13}C NMR technique it was found that one methyl group occupies axial, and the other - equatorial psition /18/.

The complex (12) is synthesized by hydroboration of 3-methoxy-7-tetrahydropyranyloxymethyl-3-borabicyclo/3,3,1/non-6-ene with $THF \cdot BH_3$ /19/, it is also obtained on hydroboration of 7-chloromethyl-3-methoxy-3-borabicyclo/3,3,1/non-6-ene /20/.

THF-complexes of 1-boraadamantane and 4-chloro-1-boraadamantane are prepared by action of tetraalakyldiborane in THF on the mixture (4:1) of 7-chloromethyl-3-methoxy-3-borabicyclo/3,3,1/non-6-ene and 6-chloro-3-methoxy-7-methylene-3-borabicyclo/3,3,1/nonane /20/.

2. Properties

1-Boraadamantane is a solid colourless substance, sublimates in the shape of well-formed prisms; it begins to melt at 80°C (capillary sealed under nitrogen), further heating to 190-200°C leads to a liquid mass /9/. 4,4-Dimethyl-1-boraadamantane is a liquid, b.p. 78°C/1 mm /10/.

In collaboration with V.N.Smirnov, Yu.A.Ustynjuk, and O.A.Subbotin, we have recorded the NMR ^{13}C spectra of 1-boraadamantane. The NMR ^{13}C chemical shifts and spin-spin interaction constants are listed in table 1.

Table 1

Chem.shifts ^{13}C and J_{CH} in 1-boraadamantane

Carbon atom		Chem.shift ^{13}C	J_{CH}
C_α	(2,8,9)	39.4	127
C_β	(3,5,7)	46.1	135
C_γ	(4,6,10)	38.1	126

It followes from the empiric equation /21/, where λ - coefficient of

$$J_{CH} = \frac{500}{1 + \lambda^2_{CH}}$$

mixing, that orbital S-character of C_α-H bond is equal 3.94, thus $\angle HC_\alpha H = 109^\circ 54'$. Hence it appears that $\angle\angle BC_\alpha C_\beta$ and $\angle\angle C_\alpha BC_\alpha$ approximate to the

tetrahedral angle. In that way 1-boraadamantane is a unique compound in which the boron atom exists in tetrahedral state and not in trigonal one which is characteristic of all the compounds of trivalent boron so far studied.

Complexing ability

The noted above structural feature of 1-boraadamantane reveals in its chemical properties, namely in the higher reactivity in comparison with trialkylboranes, in particular in the higher ability to form complexes.

In complex formation a molecule of boron compound transforms from planar to pyramidal, the B-X bond energy decreasing due to the smaller overlap of sp^3 against sp^2 boron orbitals. A decrease of bond energy on going from sp^3 to sp^2 valence states is called reorganization energy. 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.

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 occured 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.

It is worth of note that an experimental determination of reorganization energy which is an 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 donor-acceptor interaction in 1-boraadamantane pyridinate.

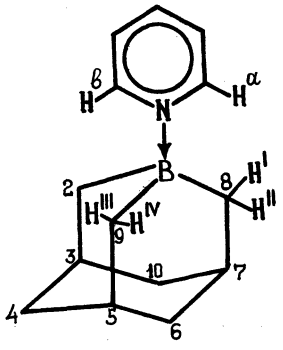
In cooperation with V.N.Smirnov, V.P.Vorob'eva, L.I.Korchetova, E.A. Miroshnichenko, and Yu.A.Lebedev, with the use of microcalorimeter Kalve we have measured enthalpy of pyridine-1-boraadamantane complex formation in pyridine solution (5), enthalpy of dissolving of cristalline (5), and enthalpies of sublimation of 1-boraadamantane and (5). The data thus obtai-

ned allowed to calculate energy of dissociation of (5) which was found to be equal 22.7 ± 0.7 kcal/mole. It results from data on ΔH^{o} for pyridine-trimethylborane complex (17.0 kcal/mole) that the reorganization energy is equal 5.5 kcal/mole. The experimental data evidence the reorganization energy to be a substantial contribution to energetics of the complex formation.

The complex compounds of 1-boraadamantane with ether /8/, THF /8,9/, and triethylamine /9,10/ are obtained directly in the synthesis. These complexes can be readily turn to some other ones by way of exchange reactions with ligands possessing the higher donor ability. In this way adducts of 1-boraadamantane with ethylamine, dipropylamine, octadecylamine /11/, 1-aminoadamantane /11/, as well as pyridinates of 3,5-dimethyl-1-boraadamantane /8,17/, 4,6-dimethyl-1-boraadamantane /18/, and 4,4-dimethyl-1-boraadamantane /10/ were prepared.

With the use of röntgenostructural method the geometrical parameters of 1-boraadamantane complex with pyridine (5) have been determined (L.G.Voronzova, V.N.Smirnov, B.M.Mikhailov).

In the complex (5) the pyridine molecule plane lies in the bisectoral plane of 1-boraadamantane molecule $BC_4C_7C_8$. The bond lengths B-N, $B-C_2$, $B-C_9$, and $B-C_8$ are equal 1.642, 1.616, 1.616, and 1.620 A°, respectively. The C-C bond lengths vary from 1.522 to 1.547 A°. The distances $H^{a}-H^{I}$, $H^{a}-H^{II}$ are equal 2.23 A°, $H^{b}-H^{III}$ = 2.37 A°.



(5)

Angles

$\angle C_2BC_9$	= 110.2°	$\angle C_2C_3C_4$	= 109.5°
$\angle C_2BC_8$	= 108.8	$\angle C_8C_7C_6$	= 110.6
$\angle BC_2C_3$	= 107.1	$\angle C_3C_4C_5$	= 110.1
$\angle BC_8C_7$	= 106.9	$\angle C_4C_3C_{10}$	= 109.5
$\angle NBC_2$	= 109.4	$\angle C_5C_6C_7$	= 110.7
$\angle NBC_9$	= 109.4	$\angle C_6C_7C_{10}$	= 109.6

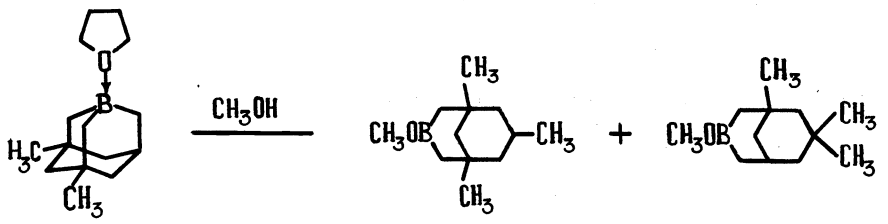
Protolysis

The peculiarity of 1-boraadamantane structure reveals not only in its high complexing ability, but also in the higher activity with respect to a number of other reagents as compared with trialkylboranes.

The etherate of 1-boraadamantane (8) reacts with methanol at room

temperature with the cleavage of B-C bond to turn to 3-methoxy-7-methyl-3-borabicyclo/3,3,1/nonane /8/. It should be noted that trialkylboranes react with alcohols at 150-170°C to give rise to esters of dialkylborinic acids together with a mixture of saturated and unsaturated hydrocarbons and H_2 /22/.

On methanolysis of THF complex of 3,5-dimethyl-1-boraadamantane (13) at 20°C breaking up of the B-C bond occurs along the two possible directions followed by formation of isomeric compounds: 3-methoxy-1,5,7-trimethyl-3-borabicyclo/3,3,1/nonane (14) and 3-methoxy-1,7,7-trimethyl-3-borabicyclo/3,3,1/nonane (15). It was found by NMR ^{13}C method that the ratio (14):(15) = 2:1 /17/.



(13) (14) (15)

A high sensitiveness of 1-boraadamantane system to action of hydrogen halides was demonstrated by the reaction with HBr. 1-Boraadamantane reacts violently with HBr at 0°C affording 3-bromo-7-methyl-3-borabicyclo/3,3,1/-nonane /23/.

Carbonylation

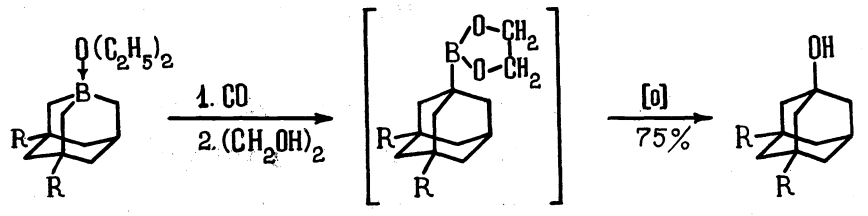
Hillman has discovered that trialkylboranes react with CO in a broad range of temperatures (20-155°C) and pressures (1-1000 atm) to convert, after oxidation of carbonylation products, to trialkylcarbinols /24/.

Analogous conversion undergoes 1-boraadamantane and its derivatives. When heating 1-boraadamantane etherate (16, R=H) with CO at 50-60 atm in the presence of ethylene glycol with subsequent oxidation of ethylene glycol ester of 1-adamantylboronic acid (17, R=H), 1-hydroxyadamantane (18, R=H) is obtained /8,10/.

Carbonylation of 3,5-dimethyl-1-boraadamantane etherate /8/ also proceeds smoothly giving rise to 1-hydroxy-3,5-dimethyladamantane (18, R= CH_3).

4,4-Dimethyl-1-boraadamantane etherate undergoes slow carbonylation at 20°C and atmospheric pressure. However the reaction accelerates at 50-60 atm and 100°C. On oxidation of ethylene glycol ester of 4,4-dimethyl-

1-adamantylboronic acid thus formed, 1-hydroxy-4,4-dimethyladamantane is yielded /8,10/.



(16) (17) (18)

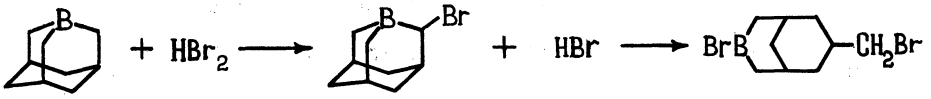
R = H, CH_3

Carbonylation of THF complex of 4-chloro-1-boraadamantane followed by oxidation leads to 1-hydroxy-4-chloroadamantane /20/.

Thus, on the basis of the reaction of acetylenes and allenes with allylboranes an original method of adamantane compounds synthesis was developed.

Bromination

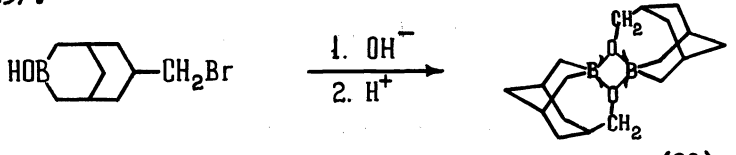
1-Boraadamantane readily reacts with bromine in CH_2Cl_2 at 0°C to give 3-bromo-7-brommethyl-3-borabicyclo/3,3,1/nonane (19) in high yield /23/.



(19)

The dibromide (19) was used for the preparation of various derivatives of 3-borabicyclo/3,3,1/nonane and heteroborahomoadamantanes.

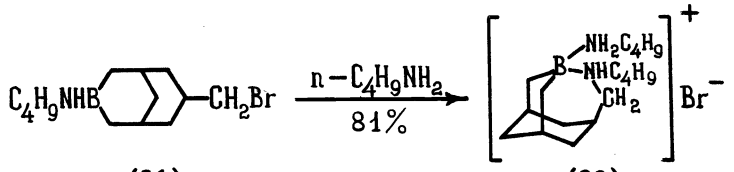
Treatment of dibromide (19) with a mixture of Et_3N and MeOH affords 3-methoxy-7-brommethyl-3-borabicyclo/3,3,1/nonane which in the presence of Et_3N hydrolyses to yield 3-hydroxy-7-brommethyl-3-borabicyclo/3,3,1/nonane. The latter turns to dimeric 4-oxa-3-borahomoadamantane (20) on action of 10% NaOH /23/.



(20)

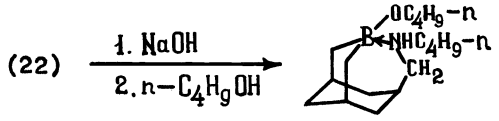
The ready dimerization of 4-oxa-3-borahomoadamantane is accounted for by the geometrical peculiarities of the molecule in which trivalent boron atom is in tetrahedral valence state, therefore it exhibits the higher complexing ability.

An exchange reaction of 3-methoxy-7-brommethyl-3-borabicyclo/3,3,1/-nonane with di(n-butylamino)butylborane affords 3-n-butylamino-7-brommethyl-3-borabicyclo/3,3,1/nonane (21) which on heating with n-butylamine converts to boronium salt (22).



(21) (22)

On treatment with aqueous NaOH solution with subsequent esterification of the reaction products with n-butanol, the salt (22) turns to intracoordinated 3-n-butoxy-7-n-butylaminomethyl-3-borabicyclo/3,3,1/nonane (23) /23/.

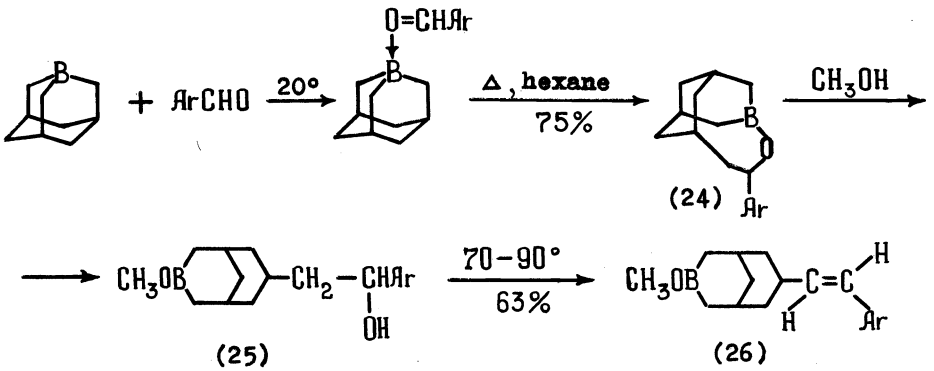


(23)

Reaction with aldehydes

In collaboration with T.K.Baryshnikova, we have found that 1-boraadamantane reacts with aromatic aldehydes according to organo-metal synthesis to give 7-aryl-6-oxa-5-boratricyclo/5,3,1,$1^{3,9}$/dodecane (7-aryl-6-oxa-5-bora-1,1-bihomoadamantane) (24). On heating of benzene solution of compound (24) with MeOH, alcohol (25) is formed which dehydrates on heating in vacuum to give 3-methoxy-7-(2-arylvinyl)-3-borabicyclo/3,3,1/nonane (26) (scheme 5).

Scheme 5

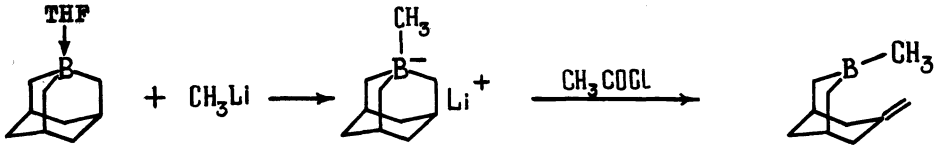


Ar = C_6H_5, CH_3O−C6H4−

Ate-complexes

1-Boraadamantane readily forms ate-complexes with metal alcoholates and alkaline metal hydroxides (B.M.Mikhailov, O.D.Smirnova).

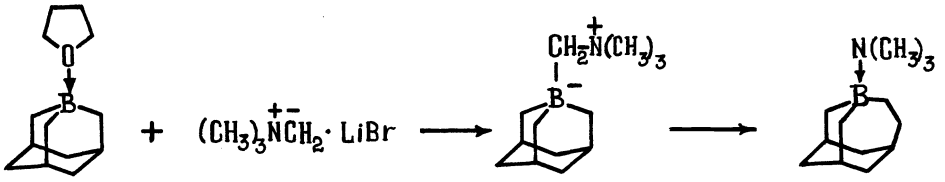
In cooperation with M.E.Gursky, we have demonstrated that lithium 1-methyl-1-boraadamantanate (27), obtained on action of lithium methyl on THF complex of 1-boraadamantane , under the influence of acetyl chloride converts to 3-methyl-7-methylene-3-borabicyclo/3,3,1/nonane. In this reaction elimination of hydride ion occurs probably from the bridged carbon C_3.



(27) (6)

III. 3-Borahomoadamantane

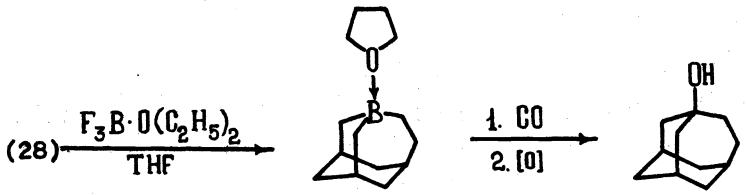
Organoboron compounds are able to react with ylides to give as a result the product of including methylene group into a B-C bond. Thus reaction of trimethylammonium methylide with tri-n-hexyl- or triphenylborane affords, after oxidation, n-heptyl or benzyl alcohol, respectively /25/. We have found THF complex of 1-boraadamantane to convert to trimethylamine complex of 3-borahomoadamantane (28) on action of trimethylammonium methylide /26/.



(28)

The complex (28) was converted to THF complex of 3-borahomoadamantane (29) when treating with boron trifluoride in THF.

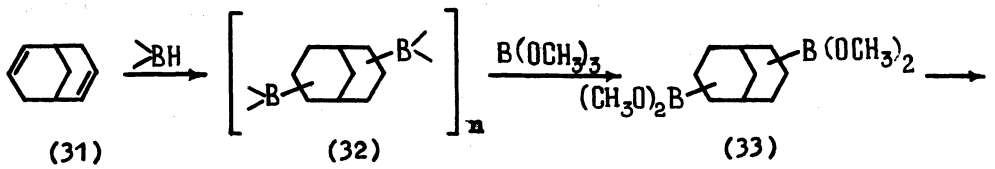
Carbonylation of complex (29) with CO at 120°C and 80 atm followed by oxidation of the reaction products leads to 3-hydroxyhomoadamantane (30).



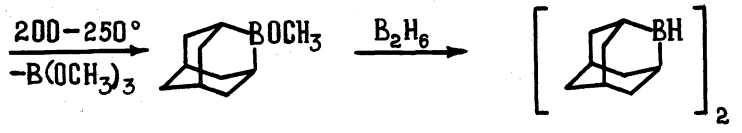
(29) (30)

IV. 2-Boraadamantane

Hydroboration of bicyclo/3,3,1/nona-2,6-diene (31) with diborane, diborane in the presence of trimethylborate, or tetraethyldiborane affords polymer (32). On heating with trimethylborate, compound (32) turns to diboron compound (33) which at 200-250°C affords 2-methoxy-2-boraadamantane (34). On action of diborane on compound (34), dimeric 2-boraadamantane (35) is obtained.



(31) (32) (33)



(34) (35)

2-Boraadamantane possesses a complexing ability characteristic of common trigonal boron compounds.

On oxidation of compound (34) with hydrogen peroxide in alkaline medium, bicyclo/3,3,1/nonane-3,7-doil was obtained which gave 2-oxaadamantane on treatment with concentrated H_2SO_4.

Polyhedral boron compounds are of interest not only from the chemical viewpoint but also from the biological one. It has been found /28/ that various boron complexes reveal significant therapeutical and prophylactic activity against influenza.

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