tillation of the residue gave 3.2 g (83%) of (V) with bp 140-142.5° (2 mm), n_D^{20} 1.5208. Found: C 48.59; H 2.58%. $C_{16}H_{10}ClF_6NS$. Calculated: C 48.30; H 2.51%. ^{19}F NMR spectrum (in CCl_4): −15.5 s. Infrared spectrum: 1670 cm^{-1} (C=N).

CONCLUSIONS

1. Fluorinated CH acids smoothly react with sulfenyl chlorides in the presence of Et_3N to give either alkyl or aryl polyfluoroalkyl sulfides and polyfluoroalkyl sulfenamides.

2. In a number of reactions the bis(trifluoromethyl)alkyl(aryl)thiomethyl group is effectively leaving as the anion.

3. 2-Ethylthiopentafluoropropylene was synthesized and its transformations during catalysis by fluorine anion were studied.

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ORGANOBORON COMPOUNDS.

376. BROMINATION OF 1-BORAADAMANTANE AND SYNTHESIS OF HETEROBORAHOMOADAMANTANES

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Organoboron compounds easily react with bromine to give brominated organoboranes, which are used successfully in organic synthesis [1].

The bromination of organoboron compounds proceeds by the radical chain mechanism [2, 3]. When the ethylene glycol ester of 1-phenylethylboric acid is brominated in CCl_4, the α-hydrogen is replaced by bromine to give the stable ethylene glycol ester of 1-bromo-1-phenylethylboric acid and HBr [2]. The bromination of triethylborane in the gas phase proceeds in two directions, in which connection $k_1 > k_2$ [3]:

$$\left.\begin{aligned} (CH_3CH_2)_3B + Br^{\cdot} &\xrightarrow{k_1} (CH_3CH_2)_2B\dot{C}HCH_3 + HBr \\ (CH_3CH_2)_2B\dot{C}HCH_3 + Br_2 &\rightarrow (CH_3CH_2)_2BCHBrCH_3 + Br^{\cdot} \end{aligned}\right\} \quad (1)$$

$$\left.\begin{aligned} (CH_3CH_2)_3B + Br^{\cdot} &\xrightarrow{k_2} (CH_3CH_2)_2BBr + C_2H_5^{\cdot} \\ C_2H_5^{\cdot} + Br_2 &\rightarrow C_2H_5Br + Br^{\cdot} \end{aligned}\right\} \quad (2)$$

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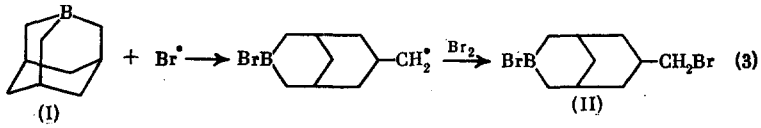
The course of the reactions along directions (1) and (2) is determined by the nature of the organoboron compound and solvent. Thus, the bromination of Bu_3B neat [4] or in benzene [5] proceeds in both directions, whereas in CH_2Cl_2 the Bu_3B reacts with Br_2 according to scheme (1), in which connection the α-bromoorganoborane is cleaved by the formed HBr to R_2BBr and RBr [6]. On the example of the reaction of Et_3B with Br_2 in pentane it was shown that the liberated HBr can be removed from the reaction sphere using a slight vacuum and in this way preventing cleavage of the α-bromoorganoborane [7].

We studied the bromination of 1-boraadamantane (I), which has specific chemical properties when compared with R_3B [8]. The starting (I) was prepared by reacting propargyl methyl ether with triallylborane [9].

It proved that (I) reacts rapidly with Br_2 in hexane at −40 to −50°C, and is smoothly converted to 3-bromo-7-bromomethyl-3-borabicyclo[3.3.1]nonane (II). In practice it is convenient to run this reaction at 0-5°, using hexane, CH_2Cl_2 or benzene as the solvent.

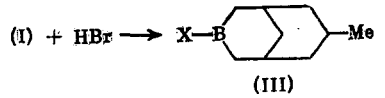
To answer the question of whether HBr is formed in the reaction we ran experiments on the bromination of (I) in hexane, in vacuo (14 mm), at −40 to −50°. Here HBr was not detected* in the trap, containing aqueous NaOH solution and connected to the reaction flask.

On this basis it may be assumed that the reaction of (I) with Br_2 proceeds along direction (2) (Scheme 3).



In the discussed case the attack of Br• on the boron atom finds explanation in the high acceptor ability of (I) when compared with R_3B [8]. However, it can be assumed that the reaction proceeds according to Scheme 1 if it is postulated that the α-bromide reacts so rapidly with the HBr that the latter cannot removed from the reaction sphere, even when the reaction vessel is evacuated.

A specific trait of the structure of (I), in which the tricoordinated boron atom is found in a tetrahedral valence state, is manifested in a high reactivity of (I) toward nucleophilic reagents [8]. In contrast to Bu_3B, which reacts at 55-60° [4], (I) reacts with HBr at 0° to give 3-bromo-7-methyl-3-borabicyclo[3.3.1]nonane (IIIa).



X = Br (IIIa); OH (IIIb); OBu-*n* (IIIc).

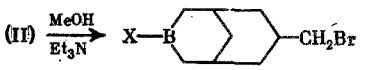
In this connection interesting data were obtained when 1-boraadamantane pyridinate (I·Py) is reacted with dry HBr. It proved that HBr reacts rapidly with (I·Py) in benzene solution, but the thus-formed (I) reacts with HBr at an even faster rate, and as a result, at a reactant ratio of 1:1, (IIIa) is formed, while half of the (I·Py) is recovered from the reaction. With a double amount of HBr, all of the (I·Py) is converted to (IIIa):

$$(I \cdot Py) + 2HBr \rightarrow (IIIa) + Py \cdot HBr$$

In benzene, 49% HBr does not react with (I·Py) at ∿20, but it does react at the boil. The thus-formed 3-hydroxy-7-methyl-3-borabicyclo[3.3.1]nonane (IIIb) is esterified with n-BuOH to 3-n-butoxy-7-methyl-3-borabicyclo[3.3.1]nonane (IIIc). Ester (IIIc) was also obtained by reacting (I) with water at 0° and subsequent esterification with n-BuOH.

Dibromide (II) was used to synthesize 3-borabicyclo[3.3.1]nonane derivatives and heteroborahomoadamantanes, inwhich connection for preparative purposes it was used without prior isolation from the reaction mixture. The treatment of (II) with an equimolar mixture of MeOH and Et_3N gave 3-methoxy-7-bromomethyl-3-borabicyclo[3.3.1]nonane (IVa) in 77% yield.

*Only at the end of reaction, when ∿90% of the Br_2 is consumed, is the liberation of a small amount of HBr observed, in which connection the reaction rate is very slow at this point. This is possibly related to rebromination of the reaction products, when (I) is now practically consumed.

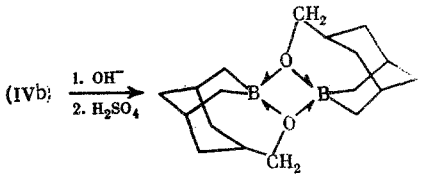


(III)

X = OMe (IVa); OH (IVb)

The hydrolysis of (II) in the presence of Et_3N leads to 3-hydroxy-7-bromomethyl-3-borabicyclo[3.3.1]nonane (IVb).

Previously we had shown that the δ-bromobutyl(alkyl)boric acids, which are similar to (IVb), when heated with aqueous alkali solutions undergo cyclization to 1,2-oxaborinanes [10, 11]. The hydrolysis of (IVb) could be expected to give 4-oxa-3-borahomoadamantane (V). Actually, the reaction of (IVb) with 10% NaOH solution at 20° and subsequent acidification with H_2SO_4 gives (V) as the dimeric form (VI):



(VI)

The dimeric structure of (V) was proposed on the basis of determining the molecular weight by cryoscopic and mass-spectrometric methods. The substantial upfield shift of the ^{11}B chemical shift in (VI) (−17.5 ppm), when compared with the cyclic esters of dialkylboric acids (∿ −50 ppm), testifies to the presence of the B←O coordination bond. The IR spectrum of (VI) lacks the broad band of the B—O bond at 1340-1360 cm^{-1}, which is characteristic for a trigonal B atom. The absence of the indicated bond is also inherent to coordination compounds of boron.

Taking into account the symmetry of compound (VI) and the equivalence of the B—O bonds, it must be assigned a structure with polycoordination B←O bonds. The dimerization of (VI) is explained by the geometric characteristics of this compound, in which the trivalent B atom is found in a tetrahedral valence state, due to which it manifests a high tendency to form complexes, which is accomplished in the given case by its dimerization to (VI).

Ester (IVa), similar to the esters of δ-bromoalkylboric acids [10], smoothly reacts with MeONa to give 3-methoxy-7-methoxymethyl-3-borabicyclo[3.3.1]nonane (VIIa).

(VII)

X = CH_2OMe (VIIa); CH_2NEt_2 (VIIb); CH_2 (VIIc)

Ester (VIIa) has a ^{11}B chemical shift of −53 ppm, which testifies to the absence of coordination interaction between the B and O of the methoxymethyl group.

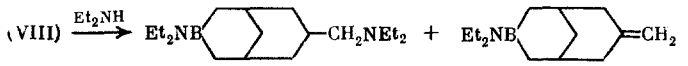
The reaction of (IVa) with Et_2NH is substantially slower and more complex, and here, together with the main aminolysis product, namely 3-methoxy-7-diethylaminomethyl-3-borabicyclo[3.3.1]nonane (VIIb), are formed two by-products, and specifically 3-methoxy-7-methylene-3-borabicyclo[3.3.1]nonane (VIIc) and ester (VIIa). To separate this mixture the reaction products are treated with an ether solution of HCl, the formed salt (VIIb·HCl) is filtered, and a mixture of (VIIa) and (VIIc) is isolated from the filtrate by distillation.

$$(IVa)\xrightarrow[2.MeOH]{1.Et_2NH}\underset{13\%}{(VIIa)}+\underset{42\%}{(VIIb)}+\underset{12\%}{(VIIc)}$$

Replacement of the bromine in compound (IVa) by MeO to give (VIIa) apparently proceeds via the step of the Et_2NH forming a complex with the B atom, similar to what occurs in the esters of δ-bromobutylboric acids when treated with bases [11]. The formation of ester (VIIa) can be avoided if the MeO group in (IVa) is replaced by Et_2N. Such replacement is easily accomplished using the exchange reaction [12] of (IVa) with $(Et_2N)_3B$, followed by vacuum distillation of the formed methyl borate, in which connection 3-diethylamino-7-bromomethyl-3-borabicyclo[3.3.1]nonane (VIII) is obtained in 79% yield.

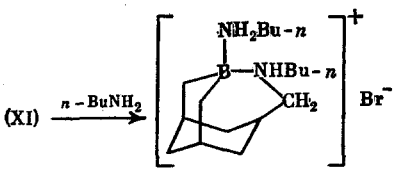
(VIII)

When compared with (IVa), compound (VIII) reacts more smoothly with Et_2NH to give 3-diethylamino-7-diethylaminomethyl-3-borabicyclo[3.3.1]nonane (IX) in 58% yield and unsaturated compound (X) in 15% yield.



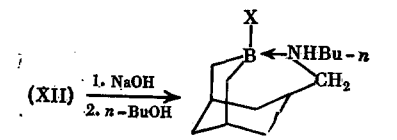
(IX) (X)

The exchange reaction of (IVa) with $(n\text{-BuNH})_2B\text{-Bu-}n$ gave 3-n-butylamino-7-bromomethyl-3-borabicyclo[3.3.1]nonane (XI) in 77% yield. When heated with $n\text{-BuNH}_2$, (XI) forms the boronium salt (XII), which, in contrast to the analogous boronium salts with δ-bromobutylboranes [13, 14], is much more heat stable and does not decompose at 200° in vacuo.



(XII)

The treatment of salt (XII) with aqueous NaOH solution and subsequent esterification with n-BuOH gave the inner coordination 3-n-butoxy-7-n-butylaminomethyl-3-borabicyclo[3.3.1]-nonane (XIIIa) in 85% yield.



(XIII)

X = OBu (XIIIa); OMe (XIIIb).

Compound (XIIIa) has a ^{11}B chemical shift of −6.5 ppm, which testifies to the presence of a coordination bond between the B and N atoms. The IR spectrum lacks the braod absorption band of the B—O bond at 1340-1360 cm^{-1}, which is characteristic for a trivalent B atom, while the band of the N—H stretching vibrations (3270 cm^{-1}) is strongly shifted toward the long-wave region, which is also characteristic for organoboron compounds with a coordination B←N bond. If MeONa in MeOH is used instead of aqueous NaOH solution, then the inner coordination 3-methoxy-7-n-butylaminomethyl-3-borabicyclo[3.3.1]nonane (XIIIb) is formed.

Compounds (XIIIa) and (XIIIb) are the first members of the organoboron compounds with an azaborahomoadamantane structure. In contrast to the related esters of ω-alkylaminoalkylboric acids, which easily cleave alcohol in vacuo to give 1,2-azaboracyclanes [13-15], compounds (XIIIa) and (XIIIb) are much more stable and can be vacuum distilled without decomposition. Only when heated in vacuo at ∿250° do they gradually cleave alcohol, but here, instead of the expected 4-n-butylamino-3-borahomoadamantane, a polymeric product is formed, which is insoluble in hexane and benzene, and which is converted to the starting (XIIIb) when refluxed in MeOH. The oxidation of (I) with H_2O_2 in alkaline medium at 0 to −10° gave 1,3,5-tri(hydroxymethyl)cyclohexane (XIV) in 81% yield. On the basis of the ^{13}C NMR data, and also starting with the structure of (I), triol (XIV) must be assigned a structure with a cis arrangement of all of the hydroxymethyl groups.

EXPERIMENTAL

All of the operations with the organoboron compounds were run in a dry argon atmosphere. 1-Boraadamantane (I), obtained as described in [9], was vacuum-sublimed twice using an oil pump. Based on the GLC data, the purity was ∿90%. Bromination of a less pure (I) sharply lowers the yield of the main product and the formation of (IIIa) is observed. Di(n-butylamino)-n-butylborane was synthesized as described in [14].

The IR spectra were obtained on a UR-20 spectrometer, while the ^{11}B NMR spectra were obtained on a Bruker SXP/4-100 instrument, and the chemical shifts were measured relative to $BF_3 \cdot Et_2O$. The PMR spectra were taken on a Varian DA-60-IL instrument, using TMS as the internal standard.

3-Bromo-7-bromomethyl-3-borabicyclo[3.3.1]nonane (II). With stirring, to a solution of 7.0 g (52 mmoles) of (I) in 50 ml of benzene was added in 15 min, at 3-5°, a solution of 8.3 g (52 mmoles) of Br_2 in 10 ml of C_6H_6, gradually raising the temperature to ∿20°, and then the mixture was heated at 60° until decoloration was complete (∿5 min). The C_6H_6 was evaporated in vacuo, while the residue was distilled through a Hempel column filled with glass packing. We obtained 12.1 g (79.2%) of (II), bp 120-121° (1 mm) n_D^{20} 1.5580. Found: C 36.95; H 5.16; B 3.68; Br 54.32%. $C_9H_{15}BBr_2$. Calculated: C 36.78; H 5.15; B 3.68; Br 54.39%. PMR spectrum ($CHCl_3$, δ, ppm): 0.76-2.70 s (∿13H, ring CH), 3.22 d (2H, CH_2Br, J = 7 Hz).

3-Bromo-7-methyl-3-borabicyclo[3.3.1]nonane (IIIa). With stirring and cooling to 0-5°, to a solution of 7.95 g (59 mmoles) of (I) in 70 ml of hexane was added 5.7 g (70 mmoles) of HBr gas in 20 min, after which the mixture was stirred for another 15 min at the same temperature and then the solvent was vacuum distilled. Distillation of the residue gave 11.3 g (89%) of (IIIa), bp 91-92° (8.5 mm), n_D^{20} 1.5175. Found: C 51.00; H 7.72; B 5.07; Br 36.20%. $C_9H_{16}BBr$. Calculated: C 50.28; H 7.50; B 5.03; Br 37.18%.

Reaction of 1-Boraadamantane Pyridinate (I·Py) with HBr. a) At a 1:1 ratio. To a solution of 10 g (47 mmoles) of (I·Py) in 150 ml of C_6H_6 was added 4.2 g (52 mmoles) of dry HBr in 30 min. Here slight heating was observed and the deposition of 4.3 g (57%) of Py·HBr, which was filtered and the filtrate was evaporated in vacuo. The residue was treated with 30 ml of isopentane and the precipitate of 3.8 g (38%) of (I·Py) was filtered. From the filtrate we isolated by distillation 3.0 g (30%) of bromide (IIIa), bp 47-52° (1 mm), n_D^{20} 1.5160.

b) At a 1:2 ratio. To a solution of 8.5 g (40 mmoles) of (I·Py) in 100 ml of C_6H_6 was added 8.5 g (105 mmoles) of HBr gas in 25 min and the mixture was let stand overnight. The Py·HBr precipitate (6.3 g, 98.5%) was filtered. From the filtrate we isolated by distillation 7.2 g (84%) of (IIIa), bp 68-71° (2 mm), n_D^{20} 1.5160.

3-n-Butoxy-7-methyl-3-borabicyclo[3.3.1]nonane (IIIc). a) With stirring, to 8.0 g (38 mmoles) of (I·Py) in 80 ml of C_6H_6 was added at the boil 25 ml of 49% HBr solution and the mixture was refluxed for 4 h. The benzene layer was separated, washed with water, the solvent was vacuum distilled, and the residue was esterified with 5 ml of n-butanol in 150 ml of C_6H_6, using a Dean–Stark column to separate the formed water. By distillation we isolated 6.7 g (85.5%) of (IIIc), bp 85-86° (1 mm), n_D^{20} 1.4705. Found: C 74.57; H 12.06; B 5.23%. $C_{13}H_{25}BO$. Calculated: C 75.01; H 12.11; B 5.20%.

b) To a solution of 5.3 g (40 mmoles) of (I) in 30 ml of CH_2Cl_2 was added at 0° 20 ml of H_2O in 30 min. Slight heating up was observed here and the deposition of a white precipitate. The organic layer was separated, while the aqueous layer was extracted with CH_2Cl_2. The combined organic layer was evaporated in vacuo, the residue (IIIb) was treated with 4.45 g (60 mmoles) of n-butanol and 70 ml of C_6H_6, and the mixture was refluxed using a Dean–Stark trap until all of the water was removed. By distillation we isolated 6.7 g (80%) of ester (IIIc), bp 76-80° (0.5 mm), n_D^{20} 1.4720.

3-Methoxy-7-bromomethyl-3-borabicyclo[3.3.1]nonane (IVa). With stirring, to a solution of 12.5 g (93 mmoles) of (I) in 50 ml of C_6H_6 was added in 1 h, at ∿5°, 14.9 g (93 mmoles) of Br_2 in 10 ml of C_6H_6, and then the mixture was heated for ∿5 min at 60° (until the bromine color had disappeared completely), cooled, and a mixture of 3.2 g (0.1 mole) of MeOH and 9.4 g (93 mmoles) of Et_3N was added in 30 min at ∿20°. The mixture was stirred for another 30 min, the solvent was distilled using a water-jet pump, and the residue was treated with 200 ml of isopentane. The $Et_3N \cdot HBr$ precipitate (16.5 g, 98% yield) was filtered. From the filtrate by distillation through a Hempel column filled with glass packing we isolated 17.6 g (77%) of (IVa), bp 93-94° (1 mm), n_D^{20} 1.5190. Found: C 48.91; H 7.32; B 4.51; Br 32.08%. $C_{10}H_{18}BBrO$. Calculated: C 49.02; H 7.40; B 4.43; Br 32.62%. ^{11}B NMR spectrum (δ, ppm): −51.5. PMR spectrum (CCl_4, δ, ppm): 0.85-2.44 m (∿13H, ring CH); 3.23 d (2H, CH_2Br, J 7.5 Hz), 3.57 s (3H, MeO).

4-Oxa-3-borahomoadamantane Dimer (VI). To 8.43 g (63 mmoles) of (I) in 70 ml of C_6H_6 was added dropwise in 1 h, at ∿5°, a solution of 10.2 g (64 mmoles) of Br_2 in 20 ml of C_6H_6. The mixture was heated at 50° until the color disappeared, and then, with cooling, were added 1 ml of H_2O and 9 ml of Et_3N. The obtained precipitate ($Et_3N \cdot HBr$) was filtered, the solvent was vacuum distilled, and from the residue we obtained 12.95 g of acid (IVb).* To a solution of (IVb) in 50 ml of ether was added 150 g of 10% aqueous NaOH solution. The mixture was stirred for 1 h, and then it was heated at ether reflux for another 1.5 h. The ether layer was separated, while the aqueous layer was acidified with 10% H_2SO_4 solution. Here dimer (VI) is precipitated and it was extracted twice with ether. The ether was evaporated in vacuo, while 8.26 g (87%) of (VI) was obtained from the residue. To obtain the analytically pure compound its solution at ∿20° in the minimum amount of ether was cooled to 0 to −10°. The obtained crystals of (VI) are stable in the air, but are converted to a polymeric mass when heated. Found: C 72.27; H 10.16; B 7.18%; mol. wt. 294 (cryoscopically in C_6H_6). $C_{18}H_{30}B_2O_2$. Calculated: C 72.05; H 10.08; B 7.21%. mol. wt. 300.06. ^{11}B NMR spectrum (C_6H_6, δ, ppm): −17.5. Mass spectrum: M^+ 300 (for ^{11}B). PMR spectrum ($CHCl_3$, δ, ppm): 0.62 m (8H, CH_2B), 1.25-2.80 m (∿18 H, ring CH, 3.54 d (4H, CH_2O, J = 2 Hz). ^{13}C NMR spectrum ($CDCl_3$, δ, ppm): 29.2 ($C^{1,1'}$, $^{8,8'}$), 32.05 ($C^{6,6'}$), 36.85 ($C^{7,7'}$, $^{9,9'}$, $^{10,10'}$), 69.9 (CH_2O).

3-Methoxy-7-methoxymethyl-3-borabicyclo[3.3.1]nonane (VIIa). To a solution of MeONa, obtained from 0.86 g (37 mmoles) of Na in 60 ml of abs. MeOH, was added 9.0 g (37 mmoles) of ester (IVa) and the mixture was heated for 1.5 h at 50°. The MeOH was vacuum distilled, while the residue was treated with 150 ml of isopentane and the precipitate of 3.7 g (98%) of NaBr was filtered. From the filtrate we isolated by distillation 6.0 g (84%) of (VIIa), bp 69-72° (2 mm). Found: C 67.57; H 10.64; B 5.37%. $C_{11}H_{21}BO_2$. Calculated: C 67.37; H 10.80; B 5.52%. ^{11}B NMR spectrum (δ, ppm): −53.0. PMR spectrum ($CHCl_3$, δ, ppm): 0.83-2.47 m (∿13H, ring CH), 2.98 d (2H, CH_2O, J = 7 Hz), 3.28 s (3H, CH_3OC), 3.64 s (3H, CH_3OB).

Reaction of Ester (IVa) with Et_2NH. A mixture of 9.5 g (39 mmoles) of (IVa) and 17.6 g (242 mmoles) of Et_2NH was heated in a sealed ampul for 80 h at ∿100°. The obtained precipitate of 5.5 g (92%) of $Et_2NH \cdot HBr$ was filtered, the filtrate was treated with 10 ml of MeOH, and the fraction with bp 40-96° (1.5 mm) was isolated by vacuum distillation, which, based on the PMR data, is a mixture of compounds (VIIa), (VIIb), and (VIIc). Treatment of this mixture with an ether solution of HCl gave 4.5 g (42%) of salt (VIIb·HCl), mp 165-170°. Found: C 61.11; H 10.65; B 3.73; Cl 12.22; N 5.42%. $C_{14}H_{29}BClNO$. Calculated: C 61.40; H 10.68; B 3.95; Cl 12.96; N 5.12%. After separating the (VIIb·HCl) from the filtrate we isolated by distillation 1.8 g of a fraction with bp 50-86° (2 mm), n_D^{20} 1.4880, which, based on the PMR data, is a mixture of (VIIa) and (VIIc) in an ∿1.1:1 ratio, which corresponds to an ∿13% yield of (VIIa) and an ∿12% yield of (VIIc). To a methanol solution of 4.2 g of (VIIb·HCl) was added an equimolar amount of MeONa in MeOH, and the deposited NaCl was filtered. Distillation gave 2.5 g of (VIIb), bp 94-95° (2 mm), n_D^{20} 1.4851. Found: C 71.21; H 11.92; B 4.65; N 5.97%. $C_{14}H_{28}BNO$. Calculated: C 70.89; H 11.90; B 4.56; N 5.91%. PMR spectrum (CHC_3, δ, ppm): 0.98 t (MeC, J = 7 Hz), 2.49 q (4H, CH_2N, J = 7 Hz), 3.61 s (3H, MeO).

3-Diethylamino-7-bromomethyl-3-borabicyclo[3.3.1]nonane (VIII). Into a vacuum still, equipped with a Hempel column filled with glass packing, were charged 16.8 g (69 mmoles) of (IVa) and 5.2 g (23 mmoles) of $B(NEt_2)_3$. Then the mixture was heated at 120-140° for 6 h, gradually increasing the vacuum from 150 to 13 mm, to give as distillate 1.7 g (16 mmoles) of $(MeO)_3B$, which was collected in a trap (−80°). The residue was distilled to give 15.44 g (79%) of (VIII), bp 132-134° (2 mm), n_D^{20} 1.5190. Found: C 54.70; H 8.77; B 3.81; Br 28.12; N 5.11%. Mol. wt. 280. $C_{13}H_{25}BBrN$. Calculated: C 54.58; H 8.81; B 3.78; Br 27.93; N 4.90%; mol. wt. 286.076. PMR spectrum ($CHCl_3$, δ, ppm): 1.02 t (MeCNB, J = 7 Hz), 2.98 q (4H, CH_2NB, J = 7 Hz), 3.40 d (2H, CH_2Br, J = 7 Hz).

3-Diethylamino-7-diethylaminomethyl-3-borabicyclo[3.3.1]nonane (IX). A sealed glass ampul, containing 11.8 g (41 mmoles) of (VIII) and 25 ml of Et_2NH, was heated for ∿40 h at 100°. Then the ampul was opened, and the precipitate of Et_2NH_2Br (3.8 g, 60%) was filtered and washed with 10 ml of Et_2NH, which was combined with the filtrate and heated again in an

*An analytically pure sample, obtained by recrystallization from hexane, has mp 91-93°. Found: C 46.76; H 7.04; B 4.64; Br 34.78%. $C_9H_{16}BBrO$. Calculated: C 46.80; H 6.98; B 4.69; Br 34.60%. PMR spectrum ($CHCl_3$, δ, ppm): 0.7-2.60 m (∿13H, ring CH), 3.32 d (2H, CH_2Br, J = 7 Hz), 5.78 s (1H, BOH).

ampul for ∿100 h. Here an additional 2.12 g of the salt was isolated. A total of 5.92 g (98%) of Et_2NH_2Br was obtained. From the filtrate by distillation we isolated: 1) 6.65 g (58%) of (IX), bp 137-140° (2 mm). Found: C 72.71; H 12.41; B 3.92; N 10.05%; mol. wt. 262. $C_{17}H_{35}BN_2$. Calculated: C 73.27; H 12.79; B 3.88; N 10.06%; mol. wt. 278.65. PMR spectrum ($CHCl_3$, δ, ppm): 0.98 t (MeCNC, J = 7 Hz), 1.02 t (MeCNB, J = 7 Hz), 2.40 q (4H, CH_2NC, J = 7 Hz), 2.99 q (4H, CH_2NB, J = 7 Hz); 2) 1.25 g (15%) of (X), bp 81-85° (2 mm), n_D^{20} 1.4933. Found: C 75.76; H 11.78; B 5.39; N 6.20%; mol. wt. 205. $C_{13}H_{24}BN$. Calculated: C 76.11; H 11.79; B 5.27; N 6.83%; mol. wt. 205.15.

3-n-Butylamino-7-bromomethyl-3-borabicyclo[3.3.1]nonane (XI). Using a Hempel column filled with glass packing, from a mixture of 17.1 g (70 mmoles) of (IVa) and 7.98 g (38 mmoles) of n-BuB(NHBu-n)$_2$ we vacuum distilled in 4 h, with gradual elevation of the temperature in the reaction mass from 80 to 130°, and the vacuum from 35 to 3 mm, 4.2 g (92%) of n-BuB(OMe)$_2$. Distillation of the residue gave 15.8 g (77%) of (XI), bp 125-127° (2 mm); n_D^{20} 1.5165. Found: C 54.82; H 8.86; B 3.94; Br 27.94; N 5.20%. $C_{13}H_{25}BBrN$. Calculated: C 54.57; H 8.81; B 3.78; Br 27.94; N 4.90%. PMR spectrum ($CHCl_3$, δ, ppm): 2.93 m (2H, CH_2N), 3.37 d (2H, CH_2Br, J = 7 Hz), 3.81 m (1H, NH).

Boronium Salt (XII). To 10.5 g (37 mmoles) of (XI) was added 14.8 g of N-BuNH_2 (here heat is evolved), the mixture was refluxed for 5 h, 50 ml of isopentane was added, and the precipitate was filtered, washed, and dried to give 10.7 g (81.5%) of (XII), mp 196-202°. Found: C 56.52; H 10.12; B 2.88; Br 22.41; N 8.05%. $C_{17}H_{36}BBrN_2$. Calculated: C 56.84; H 10.10; B 3.01; Br 22.25; N 7.80%. Mass spectrum: M^+ 359 (for ^{11}B). The IR spectrum has a band of the NH_2 deformation vibrations at 1585 cm^{-1} and a broad band, characteristic for boronium salts, of the NH and NH_2 stretching vibrations at 2700-3200 cm^{-1}, which is masked by the band of the CH stretching vibrations.

3-n-Butoxy-7-n-butylaminomethyl-3-borabicyclo[3.3.1]nonane (XIIIa). To a solution of 4.1 g (11 mmoles) of (XII) in 30 ml of MeOH and 10 ml of H_2O was added a solution of 0.46 g (11 mmoles) of NaOH in 10 ml of H_2O. The mixture was refluxed for 30 min, and then it was evaporated to 2/3 volume and the residue was extracted with ether. The ether was distilled off, 1.6 g (22 mmoles) of n-BuOH and 30 ml of C_6H_6 were added to the residue, and the mixture was refluxed using a Dean–Stark trap until the water separation ceased. Distillation gave 2.7 g (85%) of (XIIIa), bp 151-153° (2 mm), bp 65-70°. Found: C 73.45; H 12.34; B 4.11; N 5.01%; mol. wt. 284. $C_{17}H_{34}BNO$. Calculated: C 73.11; H 12.27; B 3.87; N 5.02%; mol. wt. 279.27. Mass spectrum: M^+ 279 (for ^{11}B). ^{11}B NMR spectrum (C_6H_6, δ, ppm): −6.5. PMR spectrum ($CHCl_3$, δ, ppm): 2.98 m (4H, NCH_2), 3.30 t (2H, OCH_2, J = 6.5 Hz).

3-Methoxy-7-n-butylaminomethyl-3-borabicyclo[3.3.1]nonane (XIIIb). To 9.1 g (25 mmoles) of (XII) in 20 ml of MeOH was added at ∿20° a solution of MeONa in MeOH (from 0.6 g (26 mmoles) of Na and 20 ml of MeOH), the mixture was refluxed for 30 min, the solvent was vacuum distilled, 30 ml of ether was added, and the NaBr (2.6 g, 99.5%) was filtered and washed with ether. The ether solution was evaporated in vacuo. Recrystallization of the residue gave 4.0 g (66%) of (XIIIb), mp 110-116°. Found: C 71.31; H 12.04; B 4.44; N 5.90%; mol. wt. 237. $C_{14}H_{28}BNO$. Calculated: C 70.89; H 11.90; B 4.56; N 5.91%, mol. wt. 237.19. ^{11}B NMR spectrum (C_6H_6, δ, ppm): −6.0. PMR spectrum ($CHCl_3$, δ, ppm): 0.35-2.22 m (∿20H, ring CH), 2.92 m (4H, NCH_2), 3.17 s (3H, MeO), 3.39 m (1H, NH). ^{13}C NMR spectrum ($CDCl_3$, δ, ppm): 56.0 (ring CH_2N), 50.7 (α-C in BuN), 49.4 (MeO), 38.0 ($C_{6,8}$), 37.3 (C_9), 31.9 (C_7), 29.0 (β-C in BuN), 27.5 ($C_{1,5}$), 20.1 (γ-C in BuN), 13.75 (δ-C in BuN).

Pyrolysis of (XIIIb). Compound (XIIIb) (2.52 g) was heated for 3 h at 220-260°, initially in a vacuum of 56 mm, and then at 2 mm. In the trap (−80°) was condensed 0.26 g (80%) of MeOH, while the (XIIIb) was converted to a polymer, insoluble in C_6H_6 and hexane. To the obtained polymer were added 30 ml of C_6H_6 and 0.6 ml of MeOH and the mixture was refluxed for 1 h, in which connection the polymer dissolved completely. After distilling off the solvents we obtained 2.6 g of crystalline residue, the recrystallization of which from hexane gave 1.5 g (60%) of (XIIIb), mp 108-115°.

Oxidation of 1-Boraadamantane (I). To 7.5 g of 20% aqueous NaOH solution at −5 to −10° was added 4.6 g of (I) in 20 ml of isopentane, in which connection a precipitate of $[C_9H_{16}BO]Na$ deposited. The isopentane was vacuum distilled at −10°, while to the residue at 0 to −10° was added dropwise 15 ml of 29% H_2O_2 solution and the mixture was let stand at 20° overnight. The precipitate was filtered, washed with a little water, while the aqueous layer was acidified with 10% H_2SO_4 solution and evaporated in vacuo to dryness. The residue

was extracted with hot EtOH (2 × 50 ml), and the solvent was distilled off. We obtained 5.0 g of a crystalline residue. Recrystallization from THF gave 4.8 g (81%) of 1,3,5-tri-(hydroxymethyl)cyclohexane (XIV), mp 94-100°, which was identical with that obtained as described in [16]. ^{13}C NMR spectrum (CD_3OD, δ, ppm): 33.6 (CH_2), 40.6 (CH), 68.5 (CH_2OH). After separating the (XIV), the THF solution was shown by GLC to contain 0.15 g of 1.3-di-(hydroxymethyl)-5-methylcyclohexane.

CONCLUSIONS

1. The reaction of bromine with 1-boraadamantane gives 3-bromo-7-bromomethyl-3-borabicyclo[3.3.1]nonane, from which were synthesized derivatives that contain substituents in the 3 and 7 positions.

2. Members of the 4-hetero(O,N)-3-borahomoadamantanes were obtained, and specifically the 4-oxa-3-borahomoadamantane dimer and 3-alkoxy-7-n-butylaminomethyl-3-borabicyclo[3.3.1]-nonanes.

3. A method was developed for the synthesis of cis-1,3,5-tri(hydroxymethyl)cyclohexane by the oxidation of 1-boraadamantane with H_2O_2 in alkaline medium.

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