*Journal of Organometallic Chemistry*, 226 (1982) 115—128
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

# ORGANOBORON COMPOUNDS

## CCCXCIX *. THE MATTESON-PASTO REARRANGEMENT IN THE SERIES OF 3-BORABICYCLO[3.3.1]NONANE COMPOUNDS

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(Received August 20th, 1981)

### Summary

Bromination of 3-isopropyl-7-methyl- and 3-isopropyl-7-bromomethyl-3-borabicyclo[3.3.1]nonane leads to corresponding 3-(2-bromo-2-propyl) derivatives, which, on treatment with alcohols or pyridine as well as on heating, undergo the Matteson-Pasto rearrangement to convert into 3-X-4,4,8-trimethyl- and 3-X-4,4-dimethyl-8-bromomethyl-3-borabicyclo[4.3.1]decane (X = Br, OR). Interaction between triethylamine and 3-(2-bromo-2-propyl)-7-methyl-3-borabicyclo[3.3.1]nonane is accompanied by dehydrobromination leading to 3-isopropenyl-7-methyl-3-borabicyclo[3.3.1]nonane. Carbonylation of 3,4,4,8-tetramethyl-3-borabicyclo[4.3.1]decane at 140°C is accompanied by migration of two alkyl groups from the boron to the carbon atom, and subsequent oxidation with $H_2O_2$ produces 1-(2-hydroxy-2-methyl-1-propyl)-3-acetonyl-5-methylcyclohexane. Under more forcing conditions (180—195°C), the third alkyl group also migrates to give, after oxidation, a mixture of isomeric 3,4,4,8-tetramethylbicyclo[4.3.1]decan-3-ols. 3-n-Butoxy-4,4-dimethyl-8-bromomethyl-3-borabicyclo[4.3.1]decane, on treatment with Li, undergoes cyclization to afford 4,4-dimethyl-3-borahomoadamantane, carbonylation and subsequent oxidation of which gave 4,4-dimethylhomoadamantan-3-ol.

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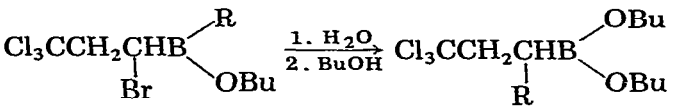
Among the various methods of utilizing organoboron compounds for organic synthesis, the intra-molecular rearrangement of $\alpha$-bromoorganoboranes draws considerable attention. This rearrangement, consisting in migration of the bromine atom to the boron and the reverse transition of the organic radical to the $\alpha$-carbon, was discovered by Matteson and Mah [1] who demonstrated

* For part CCCXCVIII see ref. 27.

0022-328X/82/0000—0000/$02.75 

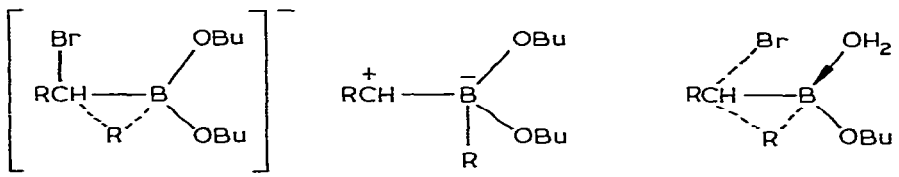
that on treatment with $BuO^-$ or $H_2O$ (in the latter case, after esterification), butyl esters of ethyl- and phenyl-(1-bromo-3,3,3-trichloro-1-propyl)boronic acids (I) exothermally form dibutyl esters of (1-ethyl-3,3,3-trichloro-1-propyl)- and (1-phenyl-3,3,3-trichloro-1-propyl)boronic acids (II) (eq. 1).




(1)

(I) R = Et, Ph (II)

According to Metteson [1,2], the exothermic character of the reaction is in agreement with its proceeding via the transition state III, excluding a mechanism with the zwitterion IV. The rearrangement under the action of water can be symbolized by the transition state V.

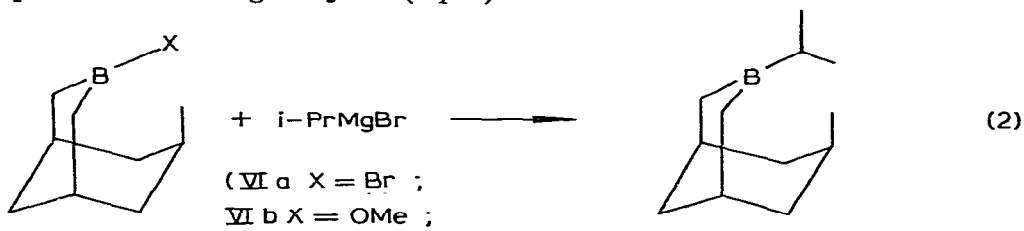



(III) (IV) (V)

Water is able to form adducts with organoboranes, as observed before in the case of diphenylboronic acid [3].

Independently, Pasto and co-workers found that organoboron compounds formed by hydroboration of enethiols [4,5], enols [6], and vinyl halides [7], also undergo rearrangements of such kind. Subsequently, it was found that α-bromoethylborane, which is obtained by brominating triethylborane [8], undergoes the Matteson-Pasto rearrangement under the action of water. According to ref. 9, bromination of 9-isopropyl-9-borabicyclo[3.3.1]nonane gives rise to 9-(2-bromo-2-propyl)-9-borabicyclo[3.3.1]nonane which converts to *cis*-5-(2-hydroxy-2-propyl)cyclooctanol.

We have studied bromination and the Matteson-Pasto rearrangement in the series of 3-borabicyclo[3.3.1]nonane compounds, the objects of investigation were 3-isopropyl-7-methyl-3-borabicyclo[3.3.1]nonane (VIII) and 3-isopropyl-7-bromomethyl-3-borabicyclo[3.3.1]nonane (XXV). As starting compounds for the preparation of VIII, 3-bromo-7-methyl-3-borabicyclo[3.3.1]nonane (VIa), synthesized from HBr and 1-boraadamantane (VII) [10], or 3-alkoxy-7-methyl-3-borabicyclo[3.3.1]nonanes (VIb, c), obtained by reaction of MeOH (BuOH) with VIa [10] or VII [11] were used. Interaction of i-PrMgBr and VI produces VIII in good yield (eq. 2).

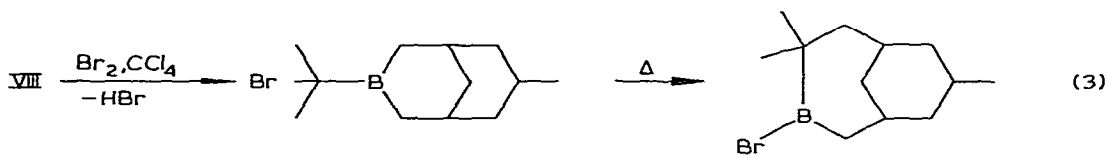



(VI) (VIII ; 80–90%)

(2)

Previously [12], in a work on the conformational analysis of the 3-borabicyclo-[3.3.1]nonane derivatives, it was shown that the value of the C(9) atom chemical shift is characteristic for determining the predominating conformation of the compounds of this series having substituents at the 3 and 7 positions. Since the chemical shifts of C(9) for VIII as well as XIII and XXV (see below) are close to the values found previously for the 3-borabicyclo[3.3.1]nonane compounds with the double chair conformation, this conformation should also be assigned to VIII, XIII, and XXV.

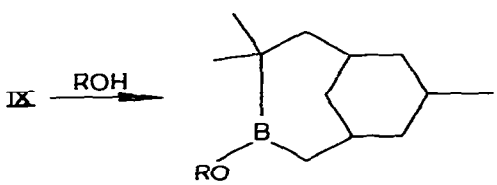
Bromination of VIII occurs readily in usual laboratory lighting conditions; however, it is considerably accelerated by additional irradiation with the help of a 100 W bulb, substitution of the tertiary hydrogen atom in the side chain for bromine occurring to give 3-(2-bromo-2-propyl)-7-methyl-3-borabicyclo-[3.3.1]nonane (IX) and HBr. The latter was removed from the reaction mixture with a 100 Torr vacuum. The $^1$H NMR spectrum of the bromide IX reveals a signal with chemical shift 1.77 ppm ($CH_3CBr$ groups). The bromide IX is thermally unstable and even in the course of the reaction it partially rearranges to form a new bicyclic system: 3-bromo-4,4,8-trimethyl-3-borabicyclo[4.3.1]-decane (X), the process proceeding slowly even at —78°C. For preparing pure X, the reaction mixture, on completion of bromination, is vacuum distilled (eq. 3).




(3)

(IX) (X ; 87%)

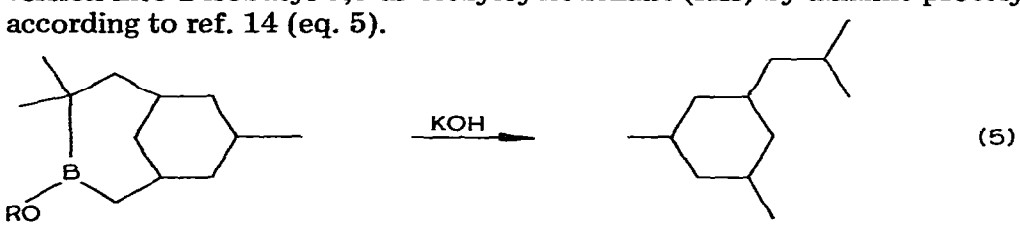
Rearrangement of the bromide IX, leading to the cycle broadening, readily occurs on treatment with alcohols. Thus, on treatment with methanol or butanol, IX exothermally turns into 3-methoxy- (XIa) or 3-n-butoxy-4,4,8-trimethyl-3-borabicyclo[4.3.1]decane (XIb), respectively (eq. 4).




(4)

(XIa R = Me ;
XIb R = Bu )

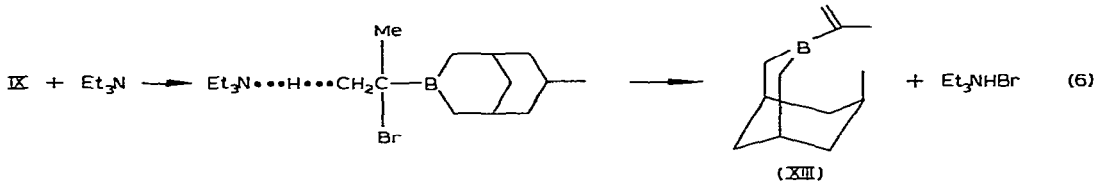
Compound XIb was formerly obtained by a skeletal rearrangement of 3-isopropenyl-7-methyl-3-borabicyclo[3.3.1]nonane, catalyzed by acids [13]. The structure of XI was proved by $^1$H NMR, $^{13}$C NMR, mass-spectra, and its conversion into 1-isobutyl-3,5-dimethylcyclohexane (XII) by alkaline protolysis according to ref. 14 (eq. 5).




(5)

(XI) (XII ; 75%)

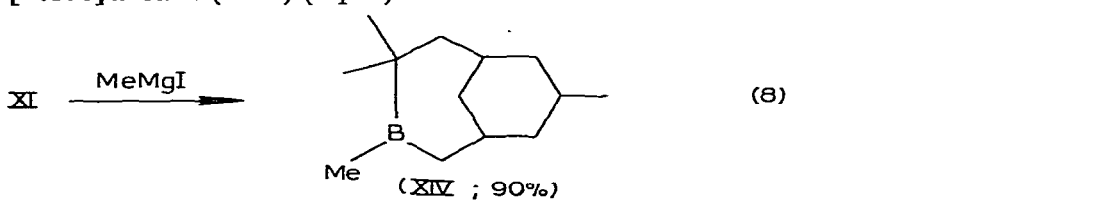
In the course of the study of rearrangement of the bromide IX under the influence of different nucleophilic reagents ($H_2O$, alcohols, pyridine), we unexpectedly found that, instead of the rearrangement, $Et_3N$ gives rise to dehydrobromination of IX to afford 3-isopropenyl-7-methyl-3-borabicyclo-[3.3.1]nonane (XIII). Obviously, in this case the nucleophilic activity of sterically hindered $Et_3N$ with respect to the boron atom is less than its basic affinity to the proton, thus enabling the elimination reaction to proceed according to the E2 mechanism (eq. 6).



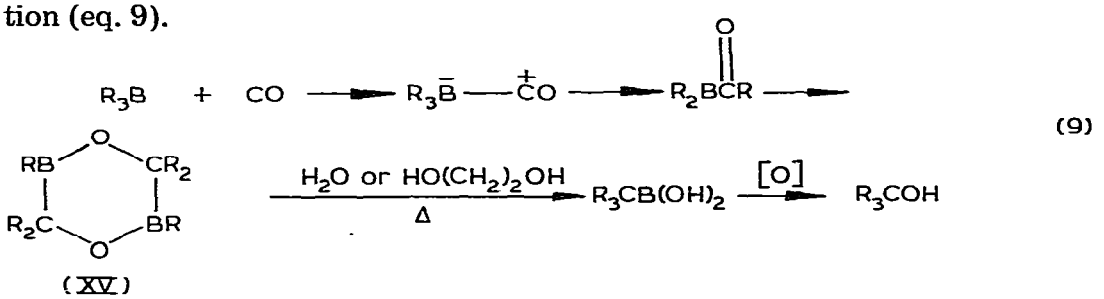

The structure of XIII was evidenced by IR and $^1H$ NMR spectra as well as by comparison with a sample obtained by the action of isopropenylmagnesium bromide on 3-n-butoxy-7-methyl-3-borabicyclo[3.3.1]nonane (VIc) [13] (eq. 7).


It should be noted that after distillation, the compound XIII contained traces of compounds with B—Br bonds (IX or X) which, on alcoholysis, eliminate HBr; the latter catalytically effected conversion of XIII into XI under the action of alcohols [13]. The compound XIII obtained by the use of isopropenylmagnesium bromide and containing no impurities with B—Br bonds, does not react with alcohols up to 100°C.

Interaction of XI and MeMgI produced 3,4,4,8-tetramethyl-3-borabicyclo-[4.3.1]decane (XIV) (eq. 8).



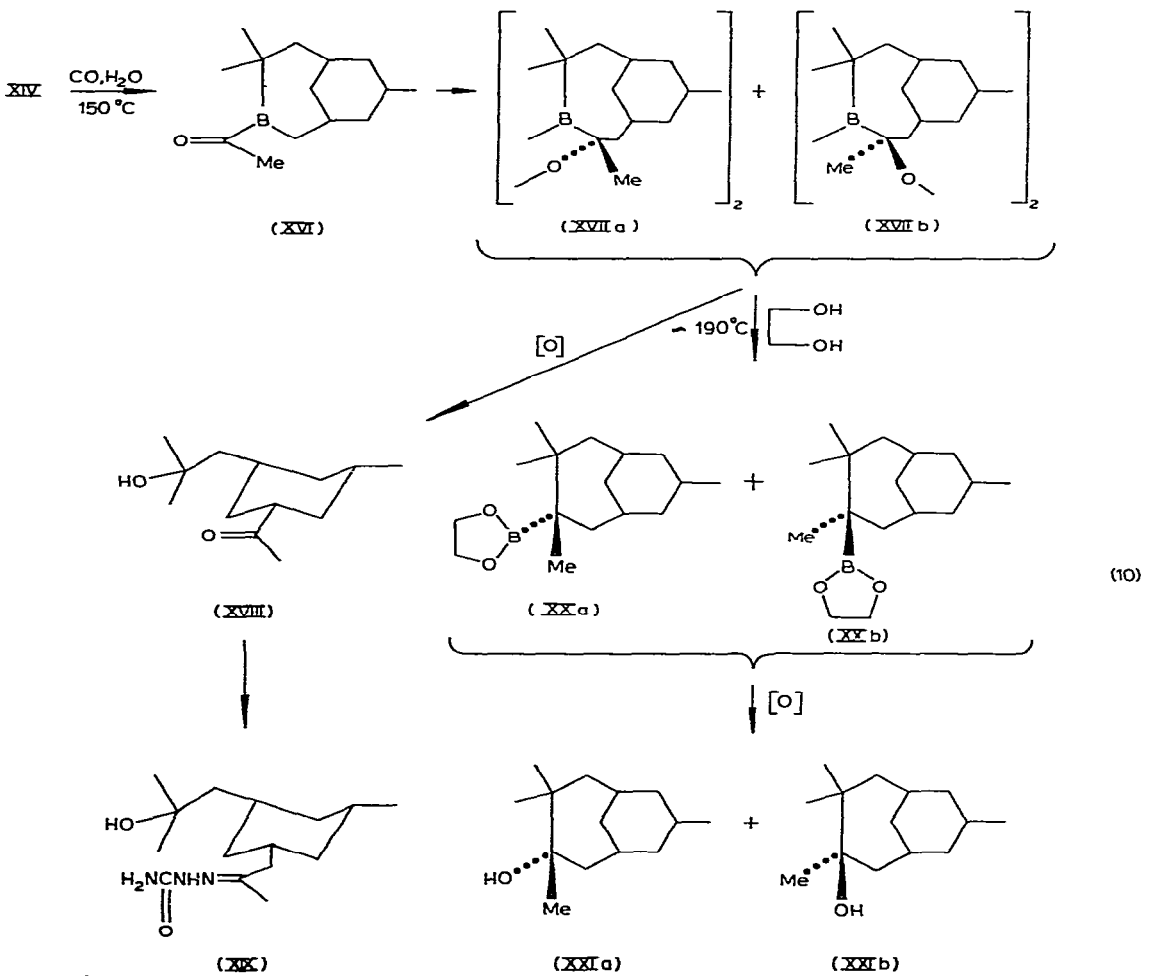

The compound XIV was carbonylated with carbon monoxide according the method of Hillman [15,16]. The Hillman reaction proceeds via the formation of the 2,5-dibora-1,4-dioxane compound (XV) giving, finally, triorganylcarbinylboronic acids or their esters, which afford the tertiary alcohols on oxidation (eq. 9).



Reaction of XIV with CO at 140—150°C and 60 atm in the presence of water with subsequent oxidation gave rise to 1-(2-hydroxy-2-methyl-1-propyl)-3-acetonyl-5-methylcyclohexane (XVIII) characterized also as its semicarbazone (XIX). Formation of XVIII shows that, under the given conditions, only $CH_3$ and cyclic $CH_2$ groups migrate from the boron atom to the carbon of CO to yield XVII (identical with XV), whereas the tertiary cyclic carbon atoms keeps its linkage with the boron.

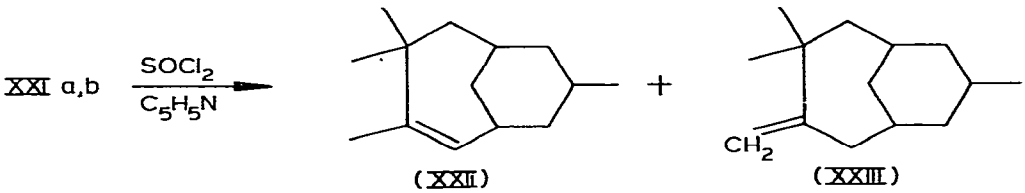
The rearrangement involving all the three B—C bonds was partially realized under more forcing conditions: by heating at 180—195°C in the presence of ethylene glycol. In this way a mixture of isomeric 3,4,4,8-tetramethylbicyclo-[4.3.1]decan-3-ols (XXIa and XXIb, 39% yield) and XVIII (32%, after oxidation with $H_2O_2$) was obtained.

The stereochemical result of carbonylation of XIV demonstrates that the rearrangement at the second stage of the reaction (XVI) proceeds with transition of the $CH_2$ group to the *endo*- and *exo*-positions to form XVIIa and XVIIb. Subsequent migration of the cyclic tertiary alkyl group leads to the esters XXa and XXb, oxidation of which furnishes the isomeric alcohols XXIa and XXIb (eq. 10).




(10)

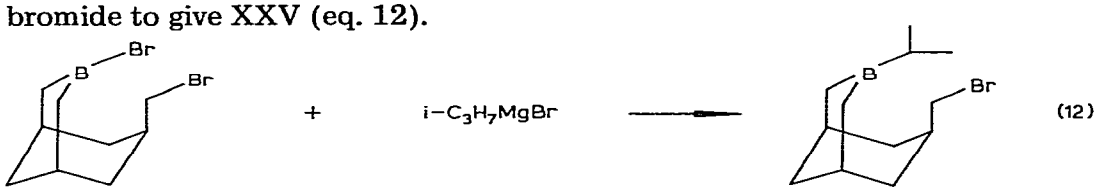
Dehydration of the carbinols XXI with $SOCl_2$ results in a mixture of 3,4,4,8-tetramethylbicyclo[4.3.1]dec-2-ene (XXII) and 3-methylene-4,4,8-trimethylbicyclo[4.3.1]decane (XXIII) with a ratio of ~1 : 3 ($^1$H NMR data) (eq. 11).




(XXII) (XXIII) (11)

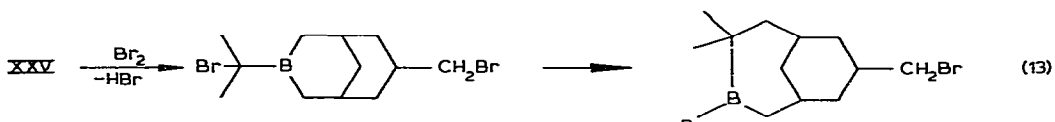
It is noteworthy that recently multistage methods for the preparation of the bicyclo[4.3.1]decane system based on the use of cyclohexanone [17], cycloheptanone [18—21], and bicyclo[3.3.1]nonan-2-one [22] have been developed. Recently the intramolecular cyclization of 3-methylene-1,8-nonadiene and 3-methylene-1,8-nonadien-7-one with formation of the respective bicyclo[4.3.1]-dec-1-(9)-ene derivatives was described [23,24]. However, 4-substituted derivatives of bicyclo[4.3.1]decane have not been obtained so far.

As starting material for the synthesis of 3-isopropyl-7-bromomethyl-3-borabicyclo[3.3.1]nonane (XXV), 3-bromo-7-bromomethyl-3-borabicyclo[3.3.1]-nonane (XXIV) was used, which we previously prepared by bromination of 1-boraadamantane (VII) [10]. XXIV reacts smoothly with isopropylmagnesium bromide to give XXV (eq. 12).



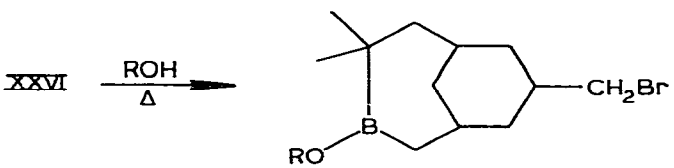

(XXIV) (XXV ; 88 %) (12)

The compound XXV was brominated in benzene solution at 3—5°C in vacuum (100 Torr) to remove the HBr forming in the reaction. 3-(2-Bromo-2-propyl)-7-bromomethyl-3-borabicyclo[3.3.1]nonane thus obtained (XXVI) undergoes, on heating, a fast spontaneous rearrangement to yield 3-bromo-8-bromomethyl-4,4-dimethyl-3-borabicyclo[4.3.1]decane (XXVII) which was isolated in a pure state by distillation of the reaction mixture (eq. 13).




(XXVI) (XXVII; 91%) (13)

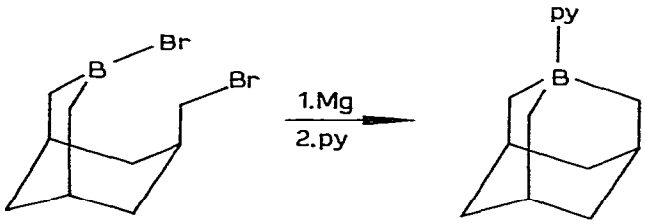
Under the action of alcohols, the dibromide XXVI undergoes the Matteson-Pasto rearrangement accompanied by the cycle broadening to form 3-alkoxy-8-bromomethyl-4,4-dimethyl-3-borabicyclo[4.3.1]decanes (XXVIIIa, b) (eq. 14).




(14)

(XXVIII a , R = Me ; XXVIII b , R = n-Bu)

The compounds XXVIII, containing functional groups at the B and C(8) atoms, were used for the synthesis of 3-borahomoadamantane compounds. Previously, the conditions for transannular cyclization were elaborated using 3-substituted 7-bromomethyl-3-borabicyclo[3.3.1]nonanes. It turned out that the dibromide XXIV, on treatment with metallic Mg in ether, converts smoothly into 1-boraadamantane (VII), isolated as its pyridinate (XXIX) (eq. 15).

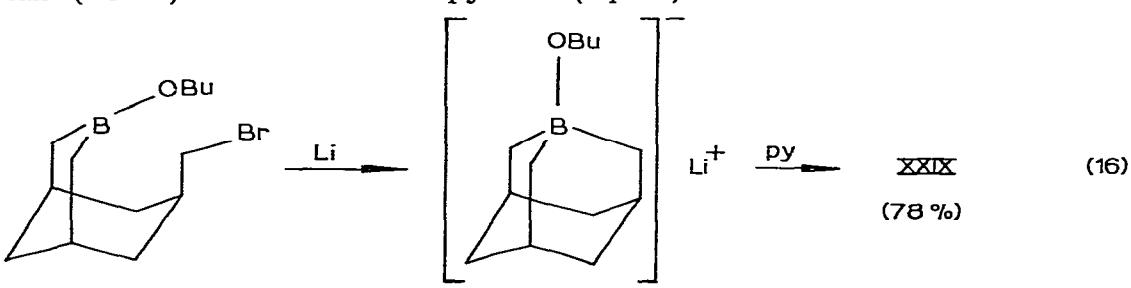



(15)

(XXIV) (XXIX; 67%)

Pure 1-boraadamantane (VII) was obtained by interaction between Mg and 3-n-butoxy-7-bromomethyl-3-borabicyclo[3.3.1]nonane (XXX) prepared from XXIV and n-butanol.

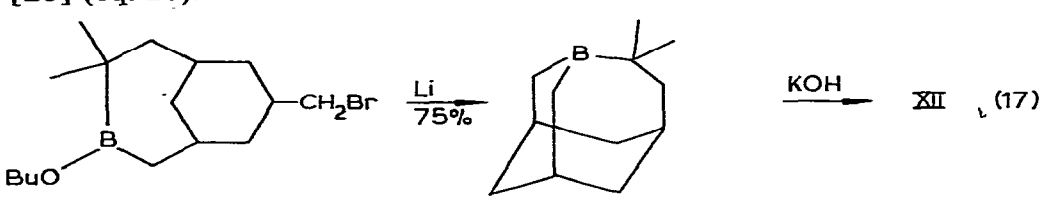
The bromoester XXX reacts violently with metallic lithium in ether; however, in this case the thermally stable boranate XXXI which forms endures heating in vacuum (100°C, 1.5 Torr). The $^1$H NMR spectrum of XXXI contains signals characteristic of the adamantane structure: multiplets of 0.48 ppm ($CH_2$—B), 1.53 ppm ($CH_2$), 2.20 ppm (CH) together with a complex multiplet at 0.77—1.08 ppm ($CH_3CH_2CH_2$ fragment) and a broadened triplet at 3.46 ppm ($CH_2O$) of the butoxy group. The boranate XXXI converts to pyridine-1-boraadamantane (XXIX) on treatment with pyridine (eq. 16).




(16)

(XXX) (XXXI)

3-n-Butoxy-8-bromomethyl-4,4-dimethyl-3-borabicyclo[4.3.1]decane XXVIIIb reacts with lithium in ether to form 4,4-dimethyl-3-borahomoadamantane (XXXII) which is a homologue of 3-borahomoadamantane, synthesized by the interaction between 1-boraadamantane (VII) and trimethylammonium methylide [25] (eq. 17).

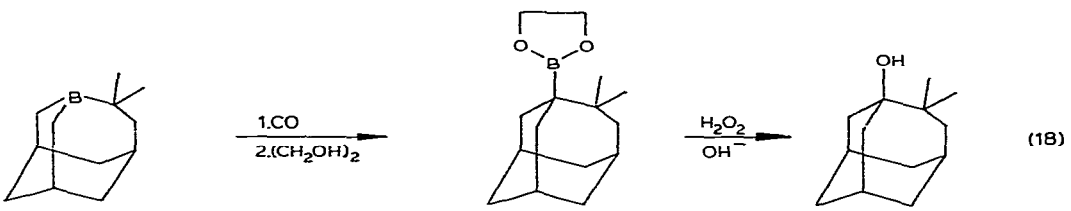



(17)

(XXVIIIb) (XXXII)

Compound XXXII is a colourless liquid, unstable in air. Its structure was proved by elemental analysis, spectral data, and alkaline protolysis, which led to 1-isobutyl-3,5-dimethylcyclohexane (XII). It follows from the $^1H$ and $^{13}C$ NMR data that 4,4-dimethyl-3-borahomoadamantane XXXII has a symmetry plane that passes through the boron atom and C(4), C(5), C(6), C(9) atoms. The compound XXXII forms the pyridinate XXXIII which can be distilled in vacuo without decomposition; it is white crystalline substance, rather stable in air.

Recently, 3-homoadamantanol was synthesized by consecutive carbonylation and oxidation of the tetrahydrofuran complex of 3-borahomoadamantane [25]. We have carried out an analogous transformation of the compound XXXII. The carbonylation was effected in two steps. At first, XXXII in tetrahydrofuran solution was heated for 1.5 h at 140°C and 90 atm CO pressure, then ethylene glycol was added and heating continued for 1 h at 140°C. The reaction proceeds via migration of three alkyl substituents from the boron atom to the carbon to produce the ethylene glycol ester of 4,4-dimethyl-3-homoadamantaneboronic acid (XXXIV), oxidation of which with alkaline $H_2O_2$ led to 4,4-dimethylhomoadamantan-3-ol (XXXV) (eq. 18).




(18)

(XXXII) (XXXIV) (XXXV ; 77%)

## Experimental

All the organoboron compounds were handled in a dry argon atmosphere. Bromination of organoboranes was carried out under usual laboratory lighting conditions or with additional irradiation with a 100 W bulb. Bromine was dried by shaking with $H_2SO_4$ and distillation over $P_2O_5$. $^1H$ NMR spectra were recorded on Tesla BS-497 (100 MHz) and Varian DA 60-IL (60 MHz) instruments relative to TMS. $^{13}C$ NMR spectra were recorded on a Bruker WP-60 (15.08 MHz) spectrometer. The method of partially depressing $^{13}C$—$^1H$ coupling was used. Mass spectra were recorded on a Varian CH-6 spectrometer.

*3-Isopropyl-7-methyl-3-borabicyclo[3.3.1]nonane (VIII)*

a) 30 ml of a 1.1 *M* ethereal solution of i-PrMgBr was added with stirring for 40 min to a solution of 7.0 g (33 mmol) of VIa in 30 ml of hexane at —10°C. The precipitate formed was filtered and washed with hexane. The filtrate was vacuum evaporated and distilled to give 4.7 g (80%) of VIII, b.p. 53—56°C (1 Torr), $n_D^{20}$ 1.4792. Found: C, 80.84; H, 12.97; B, 5.93. $C_{12}H_{23}B$ calcd.: C, 80.91; H, 13.01; B, 6.07%. $^1H$ NMR ($CHCl_3$, δ, ppm): 0.75 (d, $J$ = 7.5 Hz, $CH_3$), 0.94 (d, $J$ = 6 Hz, $CH_3CB$). $^{13}C$ NMR ($CH_2Cl_2$, δ, ppm): 18.6 (isopropyl $CH_3$), 24.5 ($CH_3$), 26.3 (C(7)), 27.0 (C(1,5)), 32.5 (C(2,4)) (at —70°C), 35.1 (C(9)), 39.1 (C(6,8)).

b) 80 ml of a 1.32 *M* ethereal solution of i-PrMgBr was added with stirring for 1 h to a solution of 17.3 g (104 mmol) of VIb in 70 ml of isopentane. The precipitate was filtered off and washed with isopentane. After evaporation in vacuum, the residue was distilled to afford 16.8 g (91%) of VIII, b.p. 63—64°C (2.5 Torr), $n_D^{20}$ 1.4795.

c) Similarly, from 19.6 g (95 mmol) of VIc was obtained 15.3 g (90%) of VIII, b.p. 63—64°C (2.5 Torr), $n_D^{20}$ 1.4797.

*3-Bromo-4,4,8-trimethyl-3-borabicyclo[4.3.1]decane (X)*

Bromination of VIII was carried out in a three-necked flask equipped with a magnetic stirrer, condenser, and dropping funnel with the capillary tip in the reaction mixture. The apparatus was connected via a condenser to a trap containing a 10% aqueous solution of NaOH; the trap was joined to a water-jet pump which kept 100 Torr vacuum in the apparatus. To 8 g (45 mmol) of VIII in 35 ml of benzene was added a solution of 8 g (50 mmol) of bromine in 10 ml of benzene for 30 min at 3—5°C. Then the mixture was stirred for 15 min in vacuum (100 Torr) at 3—5°C, a slow stream of argon being supplied through the dropping funnel. (In the trap 49 mmol of HBr was found by titration with $AgNO_3$). After evaporating the solvent in vacuum and distilling the residue, 10.1 g (87%) of X was obtained; b.p. 86—87°C (2 Torr), $n_D^{20}$ 1.5083. Found: C, 56.17; H, 8.62; B, 4.16; Br, 31.04. $C_{12}H_{22}BBr$ calcd.: C, 56.08; H, 8.63; B, 4.20; Br, 31.09%. $^1H$ NMR ($CHCl_3$, $\delta$, ppm): 0.88 (s, $CH_3CB$), 0.90 (d, $J$ = 6 Hz, $CH_3$), 1.03 (s, $CH_3CB$).

*3-Methoxy-4,4,8-trimethyl-3-borabicyclo[4.3.1]decane (XIa)*

To a solution of 7.6 g (42.6 mmol) of VIII in 35 ml of benzene was added a solution of 7.52 g (47 mmol) of $Br_2$ in 10 ml of benzene during 30 min under the conditions described above. After bubbling argon through the reaction mixture for 15 min, 1.6 g (50 mmol) of MeOH was added. Vacuum evaporation and distillation gave 6.7 g (75%) of XIa, b.p. 75—78°C (2 Torr), $n_D^{20}$ 1.4800. Found: C, 74.83; H, 12.03; B, 5.01. $C_{13}H_{25}BO$ calcd.: C, 75.01; H, 12.11; B, 5.19%. $^1H$ NMR ($CHCl_3$, $\delta$, ppm): 0.75 and 0.82 (s, $CH_3CB$), 0.88 (d, $J$ = 6 Hz, $CH_3C$), 3.65 (s, $CH_3O$).

*3-n-Butoxy-4,4,8-trimethyl-3-borabicyclo[4.3.1]decane (XIb)*

Following the above procedure, 17.5 g (109 mmol) of $Br_2$ was added for 1 h to 16.6 g (93 mmol) of VIII, after which 9.6 g (130 mmol) of butanol was added over 10 min at 3—5°C. Evaporation and distillation afforded 18.5 g (79%) of XIb, b.p. 107—110°C (2 Torr), $n_D^{20}$ 1.4730, *m/e* 250 ($M^+$). Found: C, 76.87; H, 12.39; B, 4.29. $C_{16}H_{31}BO$ calcd.: C, 76.80; H, 12.49; B, 4.32%.

*1-Isobutyl-3,5-dimethylcyclohexane (XII)*

To a flask fitted with a condenser were added 2.8 g (13.5 mmol) of XIa and 4.5 g (81 mmol) of powdery KOH. The mixture was heated to 180°C, a homogeneous mass being formed. Thereupon the protolysis products were distilled in vacuum (at first 25, then 8 Torr) during 2.5 h. The products were dissolved in 10 ml of isopentane, dried over $MgSO_4$, and distilled to give 1.7 g (75%) of XII, b.p. 68—69°C (9 Torr), $n_D^{20}$ 1.4383 [14].

*3-Isopropenyl-7-methyl-3-borabicyclo[3.3.1]nonane (XIII)*

a) To 2.9 g (16 mmol) of VIII in 8 ml of $CCl_4$ at —20°C in vacuum (100 Torr) was added during 25 min a solution of 2.87 g (18 mmol) of $Br_2$ in 3 ml of $CCl_4$. The reaction mass was bubbled with a slow stream of argon for 10 min, then a solution of 1.97 g (20 mmol) of $Et_3N$ in 5 ml of $CCl_4$ was added at —20°C, the reaction being exothermal and accompanied by a precipitate formation. The mixture was stirred for 1 h more at —20°C, then 3 h at 25°C. After vacuum evaporation of $CCl_4$ the residue was triturated in 50 ml of isopentane, and the $Et_3N \cdot HBr$ precipitated was filtered off. Vacuum evaporation of the filtrate and subsequent distillation gave 1.5 g (52%) of XIII, b.p. 61—64°C (2.5 Torr), $n_D^{20}$ 1.4969. Found: C, 81.55; H, 12.30; B, 6.00. $C_{12}H_{21}B$ calcd.: C, 81.84; H, 12.02; B, 6.14%. IR spectrum ($cm^{-1}$): 1605, 3060. $^1H$ NMR ($CHCl_3$, δ, ppm): 0.77 (d, $J$ = 7 Hz, $CH_3$), 1.83 (m, $CH_3C{=}C$), 5.61 (m, $H_2C{=}C$). $^{13}C$ NMR ($CH_2Cl_2$, δ, ppm): 22.4 (isopropyl $CH_3$), 25.1 (C(7)), 26.5 ($CH_3$), 27.5 (C(1,5)), 31.8 (C(2,4)) (at —70°C), 35.7 (C(9)), 39.3 (C(6,8)), 128.2 ($CH_2{=}$), 149.9 (BC=).

b) To 26.6 g (126 mmol) of VIc in 200 ml of isopentane 160 ml of 1.01 *M* solution of isopropenylmagnesium bromide in THF was added at 25°C for 1 h and the mixture was allowed to stand overnight. The solvent was vacuum evaporated and to the residue 350 ml of isopentane was added. After filtering off a precipitate and distilling the filtrate in a Hempel column with metal packing, 8.5 g (38.5%) of XIII was obtained, b.p. 54—56.5°C (1.5 Torr), $n_D^{20}$ 1.4965.

*3,4,4,8-Tetramethyl-3-borabicyclo[4.3.1]decane (XIV)*

a) To a solution of 16.5 g (50.5 mmol) of XIa in 35 ml of low-boiling petroleum ether was added with stirring for 1 h 27 ml of a 1.92 *M* ethereal solution of MeMgI. The mixture was stirred for 1 h more at 25°C, the precipitate formed was filtered off, washed with petroleum ether, and the filtrate evaporated in vacuum. Distillation of the residue afforded 8.3 g (90%) of XIV, b.p. 45—48°C (1.5 Torr), $n_D^{20}$ 1.4793. Found: C, 81.29; H, 12.95; B, 5.37. $C_{13}H_{25}B$ calcd.: C, 81.26; H, 13.11; B, 5.63%.

b) 38 ml of a 1.94 *M* ethereal solution of MeMgI was added over 1 h to a stirred solution of 18.5 g (74 mmol) of XIb in 50 ml of low-boiling petroleum ether. After removing the upper layer formed, the lower one was extracted with petroleum ether, vacuum evaporated and distilled to yield 13.1 g (95%) of XIV, b.p. 56—58°C (2.5 Torr), $n_D^{20}$ 1.4795.

*1-(2-Hydroxy-2-methyl-1-propyl)-3-acetonyl-5-methylcyclohexane (XVIII)*

A solution of 8.1 g (42.1 mmol) of XIV in 50 ml of THF and 3 ml of $H_2O$ was heated in an autoclave (0.15 l) with CO (initial pressure 60 atm) during 1.5 h at 140—150°C. After vacuum evaporation, 10 ml of 20% aqueous solution of NaOH was added to the residue and then 6.1 ml of 9 *M* $H_2O_2$ was added dropwise for 1 h at 10—20°C. After standing overnight the mixture was extracted with ether (3 × 50 ml), the ethereal layer washed with water and evaporated in vacuum. Distillation of the residue gave 6.0 g (63%) of XVIII, b.p. 114—118°C (2 Torr), $n_D^{20}$ 1.4748. Found: C, 74.24; H, 11.52. $C_{14}H_{26}O$ calcd.: C, 74.28; H, 11.58%. $^1H$ NMR ($CHCl_3$, δ, ppm): 0.85 (d, $J$ = 8 Hz,

$CH_3C$), 1.21 (s, $CH_3CO$), 2.11 (s, $CH_3C{=}O$), 2.29 (d, $J$ = 7 Hz, $CH_2C{=}O$). IR spectrum ($cm^{-1}$): 1710, 3460.

*Semicarbazone of 1-(2-hydroxy-2-methyl-1-propyl)-3-acetonyl-5-methylcyclohexane (XIX)*

To a solution of 0.9 g (4 mmol) of XVIII in 10 ml of ethanol was added $H_2O$ until a turbidity appeared (~10 ml) and then 0.7 g (6.3 mmol) of semicarbazide hydrochloride and 1.05 g (12.8 mmol) of MeCOONa were added. The mixture thus obtained was stirred for 1 h at 25°C and for a further 1 h at 100°C. The solution was evaporated to dryness and the solid residue triturated with 30 ml of THF, filtered, and the filtrate vacuum evaporated. The residue was crystallized from benzene to afford 0.9 g (79.5%) of XIX, m.p. 135—137.5°C. *m/e* 283 ($M^+$). Found: C, 63.15; H, 10.32; N, 14.97. $C_{15}H_{29}N_3O_2$ calcd.: C, 63.57; H, 10.31; N, 14.83%. $^1H$ NMR ($CD_3OD$, $\delta$, ppm): 0.87 (d, $J$ = 7 Hz, $CH_3C$), 1.16 (s, $CH_3CO$), 1.82 (s, $CH_3C{=}$), 2.11 (d, $J$ = 6 Hz, $CH_2C{=}$).

*3,4,4,8-Tetramethylbicyclo[4.3.1]decan-3-ols (XXIa, b)*

A solution of 13 g (68 mmol) of XIV in 50 ml of THF and 5 ml of $H_2O$ was heated in an autoclave (0.15 l) with CO (initial pressure 125 atm) for 2 h at 140—150°C. After completing the reaction, THF was removed in vacuum, to the residue 10 ml of ethylene glycol was added, and the mixture was heated for 6 h at 180—195°C. After cooling to 25°C, 50 ml of ether was added to produce two layers. The ethereal layer was removed and ethyleneglycolic one extracted with ether (2 × 30 ml). After evaporation of the extract to the residue was added 16 ml of 20% aqueous NaOH and 7 ml of ethanol, then 13 ml of 9 *M* $H_2O_2$ was added dropwise for 1 h at 10—20°C with stirring. After standing overnight the mixture was extracted with ether (3 × 50 ml), the extract washed with water and vacuum evaporated. Subsequent distillation afforded 12.4 g of a liquid with b.p. 115—140°C (3.5 Torr) consisting of XXIa, XXIb and XVIII (GLC). The latter compound was separated from this mixture by treatment with semicarbazide (XIX was obtained, m.p. 133—135.5°C). The liquid residue (after removing XVIII) was vacuum distilled to give 5.6 g (39.5%) of the mixture XXIa + XXIb, b.p. 85—90°C (2 Torr), $n_D^{20}$ 1.5002. *m/e* 210 ($M^+$). Found: C, 79.67; H, 12.39. $C_{14}H_{26}O$ calcd.: C, 79.94; H, 12.46%. IR spectrum ($cm^{-1}$): 3500, 3625 (OH). The ratio XXIa : XXIb = 3 : 7 (GLC).

*3,4,4,8-Tetramethylbicyclo[4.3.1]dec-2-ene (XXII) and 3-methylene-4,4,8-trimethylbicyclo[4.3.1]decane (XXIII)*

To a solution of 4.0 g (19 mmol) of the mixture XXIa and XXIb as obtained in the preceding run, in 10 ml of pyridine was added 3.32 g (27.9 mmol) of $SOCl_2$ during 15 min at 0°C (the temperature increased to 30°C). After stirring for 1 h more at 25°C, to the mixture were added 70 ml of ether and 40 ml of $H_2O$, the ethereal layer was separated, washed with water (3 × 20 ml), vacuum evaporated, and distilled to yield 2.6 g (71%) of mixture of XXII and XXIII with the ratio 1 : 3 (GLC), b.p. 62—65°C (2 Torr), $n_D^{20}$ 1.4946. *m/e* 192 ($M^+$). Found: C, 87.37; H, 12.50. $C_{14}H_{24}$ calcd.: C, 87.42; H, 12.58%. IR spectrum ($cm^{-1}$): 845w, 890s (shoulder 900), 1638, 3085. $^1$NMR ($CDCl_3$, $\delta$, ppm): 4.74 (m, $CH_2{=}C$) 5.27 (m, —CH=C). The integrated intensity ratio = 6.6 : 1.

*3-Isopropyl-7-bromomethyl-3-borabicyclo[3.3.1]nonane (XXV)*

46 ml of a 1.32 *M* ethereal solution of i-PrMgBr was added at 0°C for 1.5 h to a stirred solution of 17.9 g (61 mmol) of XXIV in 50 ml of isopentane. The precipitate thus formed was filtered off, washed with isopentane, and the filtrate was vacuum evaporated. Distillation of the residue gave 13.8 g (88.3%) of XXV, b.p. 103—104°C (1.5 Torr), $n_D^{20}$ 1.5141. Found: C, 56.18; H, 8.57; B, 4.27; Br, 31.04. $C_{12}H_{22}BBr$ calcd.: C, 56.08; H, 8.63; N, 4.22; Br, 31.09%. $^1H$ NMR ($CHCl_3$, $\delta$, ppm): 0.96 (d, $J$ = 6 Hz, $CH_3CB$), 3.06 (d, $J$ = 7.5 Hz, $CH_2Br$). $^{13}C$ NMR ($CH_2Cl_2$, $\delta$, ppm): 18.4 ($CH_3$ isopropyl), 25.4 (CH isopropyl), 26.3 (C(1,5)), 32.3 (C(2,4)), 34.9 (C(9)), 35.3 (C(7)), 35.9 (C(6,8)), 41.4 ($CH_2Br$) (at —70°C).

*3-Bromo-8-bromomethyl-4,4-dimethyl-3-borabicyclo[4.3.1]decane XXVII)*

Bromination was carried out as described for VIII. To 13.8 g (57.7 mmol) of XXV in 45 ml of benzene was added over 1 h at 3—5°C a solution of 9.1 g (57 mmol) of $Br_2$ in 20 ml of benzene with subsequent bubbling with argon for 15 min. After removing benzene in vacuum, the residue was distilled to afford 15.4 g (91.5%) of XXVII, b.p. 141—144°C (1.5 Torr), $n_D^{20}$ 1.5445. Found: C, 42.83; H, 6.23; B, 3.12; Br, 47.76. $C_{12}H_{21}BBr_2$ calcd.: C, 42.90; H, 6.30; B, 3.22; Br, 47.58%. $^1H$ NMR ($CHCl_3$, $\delta$, ppm): 0.89 and 1.05 (s, $CH_3$), 3.30 (d, $J$ = 6 Hz, $CH_2Br$).

*3-Methoxy-8-bromomethyl-4,4-dimethyl-3-borabicyclo[4.3.1]decane (XXVIIIa)*

To a solution of 6.9 g (26.8 mmol) of XXV in 30 ml of benzene was added in 100 Torr vacuum at 3—5°C over 30 min a solution of 4.65 g (29 mmol) of $Br_2$ in 5 ml of benzene with subsequent bubbling with argon. Then 1.23 g (38.5 mmol) of MeOH was added at 3—5°C, solvent was removed in vacuum, and distillation of the residue gave 5.6 g (75%) of XXVIIIa, b.p. 112—115°C (1.5 Torr), $n_D^{20}$ 1.5151. Found: C, 54.34; H, 8.61; B, 3.74; Br, 28.44. $C_{13}H_{24}BBrO$ calcd.: C, 54.40; H, 8.43; B, 3.76; Br, 27.84%. $^1H$ NMR ($CHCl_3$, $\delta$, ppm): 0.75 (s, $CH_3C$), 0.84 (S, $CH_3C$), 3.30 (d, $J$ = 6.5 Hz, $CH_2Br$), 3.62 (s, $CH_3O$).

*3-n-Butoxy-8-bromomethyl-4,4-dimethyl-3-borabicyclo[4.3.1]decane (XXVIIIb)*

This was obtained by the preceding method in 85% yield, b.p. 151—155°C (2 Torr), $n_D^{20}$ 1.5020. Found: C, 58.19; H, 9.06; B, 3.15; Br, 24.69. $C_{16}H_{30}BBrO$ calcd.: C, 58.39; H, 9.19; B, 3.28; Br, 24.28%. $^1H$ NMR ($CHCl_3$, $\delta$, ppm): 0.75 (s, $CH_3$), 0.82 (s, $CH_3$), 3.28 (d, 2H, $J$ = 6 Hz, $CH_2Br$), 3.88 (t, 2H, $J$ = 7 Hz, $CH_2O$).

*3-n-Butoxy-7-bromomethyl-3-borabicyclo[3.3.1]nonane (XXX)*

To a solution of 5.3 g (18 mmol) of XXIV in 20 ml of hexane, 1.62 g (22 mmol) of n-butanol was added. Distillation of the mixture afforded 4.5 g (87%) of XXX, b.p. 110—113°C (1 Torr), $n_D^{20}$ 1.5039. Found: C, 54.71; H, 8.49; B, 3.71; Br, 27.69. $C_{13}H_{24}BBrO$ calcd.: C, 54.40; H, 8.43; B, 3.76; Br, 27.84%. $^1H$ NMR ($CHCl_3$, $\delta$, ppm): 0.69—2.68 (~20 H), 3.32 (d, 2H, $J$ = 7.5 Hz, $CH_2Br$), 3.85 (t, 2H, $J$ = 6.5 Hz, $CH_2O$).

*1-Boraadamantane (VII)*

To 0.8 g (31.4 mmol) of Mg and 25 ml of ether was added with stirring for 40 min a solution of 7.3 g (25.4 mmol) of XXX in 10 ml of ether. The mixture was refluxed for 1 h and evaporated in vacuum. The glassy residue was triturated with hot hexane (50 ml), and the precipitate was filtered off. Vacuum sublimation of the filtrate (2 Torr) gave 2.6 g (76.5%) of VII.

*Pyridine-1-boraadamantane (XXIX)*

a) To 0.3 g (12.5 mmol) of Mg in 10 ml of ether was added with stirring for 30 min a solution of 2.9 g (9.85 mmol) of XXIV in 7 ml of ether. After refluxing for 1 h 1.96 g (24.5 mmol) of pyridine was added, ether removed in vacuo, and the solid residue extracted with boiling hexane. Cooling the extract led to formation of crystalline XXIX, 1.4 g (67%), m.p. 164—166°C (lit. m.p. 160—162°C [26]).

b) To 0.3 g (43 mmol) of Li in 30 ml of ether was added with stirring for 1.5 h a solution of 4.3 g (15 mmol) of XXX in 20 ml of ether (slight boiling was observed). After completing the reaction, 2.1 g (30 mmol) of pyridine in 5 ml of ether was added to the mixture, the solvent was vacuum removed, and to the residue 20 ml of $H_2O$ was added. After neutralization with 10% $H_2SO_4$ the reaction mixture was extracted with ether, the extract was washed with water and evaporated in vacuum. The solid residue was extracted with boiling hexane, cooling of which gave crystals. The latters were filtered and dried in vacuum to yield 2.5 g (78%) of XXIX, m.p, 161—163°C.

*4,4-Dimethyl-3-borahomoadamantane (XXXII)*

To 0.4 g (57 mmol) of Li in 50 ml of ether was added with stirring for 2 h a solution of 6.3 g (22 mmol) of XXVIIIb in 30 ml of ether (slight boiling was observed). The mixture was stirred 1 h more, ether was distilled off, and the solid residue was heated at 100°C in a 2 Torr vacuum with simultaneous distilling of the liquid reaction products, redistillation of which afforded 2.9 g (75%) of XXXII, b.p. 59—61°C (2 Torr), $n_D^{20}$ 1.5154. Found: C, 81.72; H, 12.07; B, 5.98. $C_{12}H_{21}B$ calcd.: C, 81.84; H, 12.02; B, 6.14%. $^1H$ NMR ($CHCl_3$, $\delta$, ppm): 1.10 (s, $CH_3C$). $^{13}C$ NMR ($CCl_4$, $\delta$, ppm): 29.3 ($CH_3$), 31.6 (C(2, 11)) (at —50°C in $CH_2Cl_2$), 32.2 (C(6)), 33.9 (C(1,8)), 37.5 (C(7, 10)), 38.4 (C(9)), 44.5 (C(5)). Protolysis of XXXII with KOH gave XII in 67.2% yield, b.p. 70—71°C (10 Torr), $n_D^{20}$ 1.4373.

*Pyridine-4,4-dimethyl-3-borahomoadamantane (XXXIII)*

To a solution of 0.8 g (4.55 mmol) of XXXII in 5 ml of isopentane was added 0.36 g (4.6 mmol) of pyridine (warming and precipitate formation were observed). After vacuum removal of isopentane the residue was distilled to yield 1.1 g (71%) of XXXIII, b.p. 123—128°C (1 Torr), m.p. 124—125.5°C (hexane). *m/e* 255 ($M^+$). Found: C, 79.79; H, 10.28; B, 4.24; N, 5.64. $C_{17}H_{26}BN$ calcd.: C, 80.00; H, 10.27; B, 4.24; N, 5.49%. $^1H$ NMR ($CH_2Cl_2$, $\delta$, ppm): 0.55 (s, $CH_3$), 7.28—7.59 (m, pyridine, $\beta$-H), 7.67—8.05 (m, pyridine, $\gamma$-H), 8.20—8.33 (m, pyridine, $\alpha$-H). $^{13}C$ NMR ($CDCl_3$, $\delta$, ppm): 29.3 (C(2, 11)) (at —50°C), 30.3 (C(1, 8)), 31.2 ($CH_3$), 33.1 (C(6)), 39.3 (C(7, 10)), 39.9 (C(9)), 53.0 (C(5)), 124.0, 138.8, 145.5 (C-pyridine).

*4,4-Dimethyl-3-homoadamantylboronic acid ethylene glycol ester (XXXIV)*

A solution of 6.0 g (34 mmol) of XXXII in 50 ml of THF was heated with CO in an autoclave (initial pressure 90 atm) at 140°C during 1.5 h. After the mixture was cooled, 2.2 g (36 mmol) of ethylene glycol was added,and heating was continued 1 h more at 140°C and 35 atm. Vacuum evaporation of the solution and distillation of the residue gave 3.8 g (45%) of XXXIV which is a low-melting substance with b.p. 107—110°C (1.5 Torr) $n_D^{20}$ 1.5166. Found: C, 72.95; H, 10.15; B, 4.40. $C_{15}H_{25}BO_2$ calcd.: C, 72.60; H, 10.15; B, 4.36%. $^1$H NMR ($CHCl_3$, δ, ppm): 1.08 (s, 6H, $CH_3$), 1.42—2.25 (m, ~15 H, H cycl.), 4.14 (s, 4H, $CH_2O$). $^{13}$C NMR ($CH_2Cl_2$, δ, ppm): 29.1 (C(1, 8)), 32.0 ($CH_3$), 32.3 (C(6)), 34.5 (C(2, 11)), 38.2 (C(9)), 38.8 (C(7, 10)), 38.9 (C(4)), 53.1 (C(5)), 65.6 ($CH_2O$).

*4,4-Dimethylhomoadamantan-3-ol (XXXV)*

To a suspension of 2.8 g (11.3 mmol) of XXXII in 5.5 g of 10% NaOH and 5 ml of MeOH was added during 20 min at 0—5°C 2 ml of 9 *M* $H_2O_2$. After stirring for 3 h at 25°C, 0.5 ml of $H_2O_2$ was added, and the mixture was allowed to sit overnight. Then the reaction mixture was extracted with ether (3 × 50 ml), the extract was washed with water, and vacuum evaporated. Low-temperature crystallization of the residue from petroleum ether afforded 1.7 g (77%) of XXXV, m.p. 160.5—163°C, *m/e* 194 ($M^+$). Found: C, 80.24; H, 11.34. $C_{13}H_{22}O$ calcd.: C, 80.35; H, 11.41%. $^1$H NMR ($CHCl_3$, δ, ppm): 1.04 (s, $CH_3$), 1.63 (m, $CH_2CO$). $^{13}$C NMR ($CH_2Cl_2$, δ, ppm): 28.9 (C(1, 8)), 29.1 ($CH_3$), 32.1 C(6)), 37.3 (C(7, 10)), 37.6 (C(9)), 41.0 (C(4)), 42.4 (C(2, 11)), 48.3 (C(5)), 75.3 (C(3)).

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