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ORGANOBORON COMPOUNDS

CCCXCV *. AMINATION OF 1-BORAADAMANTANE

B.M. MIKHAILOV *, E.A. SHAGOVA and M.Yu. ETINGER

N.D. Zelinsky Institute of Organic Chemistry of the Academy of Sciences of the U.S.S.R., Leninsky Prosp. 47, Moscow (U.S.S.R.)

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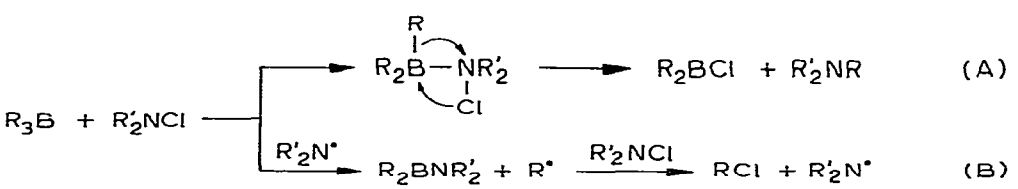
Summary

1-Boraadamantane (I) reacts with Et_2NCl, NH_2OSO_3H or 2,4-$(NO_2)_2C_6H_3ONH_2$ to form the 7-diethylaminomethyl- or 7-aminomethyl derivatives of 3-borabicyclo[3.3.1]nonane containing Cl, SO_3H or 2,4-$(NO_2)_2C_6H_3O$ groups at the 3 position. Oxidation of the 7-aminomethyl derivative affords *cis*-1,3-di(hydroxymethyl)-5-aminomethylcyclohexane. I reacts with $AlkNCl_2$ to form *N*-alkyl-3-azabicyclo[3.3.1]nonanes with the dichloroborylmethyl fragment at the 7 position. Oxidation of the latter compounds gave 3-alkyl-7-hydroxymethyl-3-azabicyclo[3.3.1]nonanes.

Trialkylboranes are able to react with *N*-chloroamines forming alkylamines or alkyl chlorides as well as the compounds having both groups. According to Davies et al. [1], such a dual behaviour of trialkylboranes with respect to *N*-chloroamines is accounted for by these reactions proceeding by two competing mechanisms: polar and radical. According to the first mechanism (A) the reagents form a complex compound which then undergoes an intramolecular rearrangement with a shift of alkyl group from the boron to the nitrogen atom and the reverse transition of the chlorine atom, thus yielding the alkylamines. As a result of the second mechanism (B), involving $R_2N^{\cdot}$ radicals, the alkyl chlorides are formed.



* For part CCCXCIV see ref. 21.

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The ability of the aza-centered radicals to take part in S_H2 reactions was demonstrated by Davies and coworkers [2]: the reaction of tributylborane with dimethylamine radicals generated by photolysis of tetramethyltetrazene leads to the formation of dibutyl(dimethylamino)borane.

A striking instance of a reaction which proceeds according to both the polar and the radical mechanisms is the reaction of tributylborane with *N*-chlorodimethylamine [1]. The interaction of these substances in isopentane affords BuCl and Bu_2BNMe_2 in about equal quantities (in accordance with the radical mechanism) together with $BuNMe_2$ and Bu_2BCl (polar mechanism). The homolitic process is suppressed in the presence of halvinoxyle which is a "trap" for the free radicals, so that the reaction products contain only $BuNMe_2$ and Bu_2BCl.

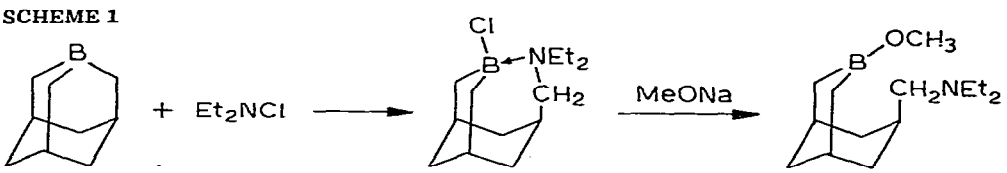
Trialkylboranes react with NH_2Cl in the presence of aqueous NaOH according to only the polar mechanism to give alkylamines [3], whereas reactions of tricyclohexylborane or trioctylborane with *N*-chlorodiethylamine or *N*-chloropiperidine under the same conditions afford alkyl chlorides [4].

Whether the reactions of R_3B with aminating reagents proceed either in the A or B direction apparently depends upon the donor-acceptor properties of the reagents as well as upon the aptitude of the *N*-chloroalkylamines for radical generation. Trialkylboranes also form alkylamines on treatment with *O*-substituted hydroxylamines, e.g. hydroxylamine-*O*-sulfonic acid [3], *O*-mesitylenesulfonylhydroxylamine [5], and *O*-2,4-dinitrophenylhydroxylamine [6].

In the course of a study on 1-boraadamantane chemistry, we investigated its reaction with the following aminating reagents: *N*-chlorodiethylamine, hydroxylamine-*O*-sulfonic acid, *O*-2,4-dinitrophenylhydroxylamine, *N,N*-dichloromethylamine, *N,N*-dichloro-n-propylamine and *N,N*-dichloro-n-butylamine. These reactions were of interest with regard to the search for novel synthetic approaches to azaborahomoadamantane compounds, aminomethyl derivatives of cyclohexane and 3-azabicyclo[3.3.1]nonanes, which are of importance in the synthesis of azaadamantane.

The reactions of I with aminating reagents containing one functional group at the N atom proceed smoothly in solution at room temperature with heat evolution. Thus, I readily reacts with an equimolar amount of Et_2NCl in hexane to produce 3-chloro-7-diethylaminomethyl-3-borabicyclo[3.3.1]nonane (II) (Scheme 1) which has an intramolecular complex structure as is seen from the value of the ^{11}B chemical shift (9.5 ppm) * (^{11}B chemical shifts of dialkylchloro-

SCHEME 1



(I) (II, 68%) (III, 50%)

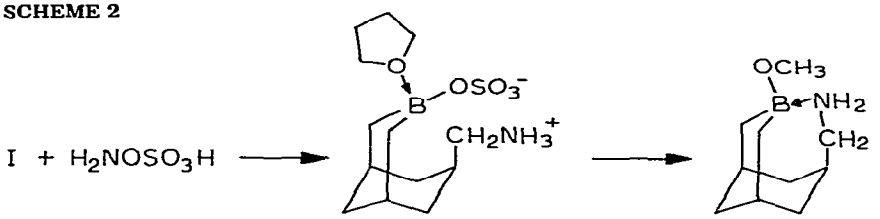
boranes and chloroboracyclanes are in the 70—80 ppm region [8]). Thus the reaction occurs according to the polar mechanism, this fact being explained by the high complexing ability of I [9].

* Here and further, positive values of the chemical shifts are at low field relative to $BF_3 \cdot OEt_2$.

Compound II substitutes chlorine by a methoxy group when treated with sodium methoxide to form 3-methoxy-7-diethylaminomethyl-3-borabicyclo-[3.3.1]nonane (III) which has been obtained previously from Et_2NH and 3-methoxy-7-bromomethyl-3-borabicyclo[3.3.1]nonane [10]. On the basis of the chemical shift value (53 ppm) and the intense absorption (IR) at 1300—1400 cm^{-1} characteristic of a B—O bond, it follows that there is no B—N coordination in compound III. (^{11}B chemical shifts of dialkylborinates are in the 50 ppm region [8].)

Compound I also reacts exothermically with H_2NOSO_3H in THF giving the THF complex of 3-sulfoxy-7-aminomethyl-3-borabicyclo[3.3.1]nonane (IV) (Scheme 2). The latter compound has, most likely, a betaine structure; how-

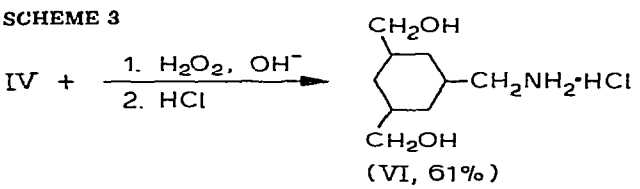
SCHEME 2



ever, this cannot be proven by the spectral method (IR) mainly owing to the broad and gradually increasing absorption in the region of 2300—3300 cm^{-1}, which coincides with the absorption band of the NH_3^+ group. On treatment with MeONa, IV forms 3-methoxy-3-aminomethyl-3-borabicyclo[3.3.1]nonane (V) having a donor-acceptor bond as shown by ^{11}B NMR and IR spectral data. The chemical shift of compound V is 5.1 ppm; its IR spectrum does not reveal the characteristic absorption band of the B—O bond.

On oxidation with hydrogen peroxide in alkaline medium, compound IV gives *cis*-1,3-di(hydroxymethyl)-5-aminomethylcyclohexane, which was isolated as the hydrochloride (VI) (Scheme 3).

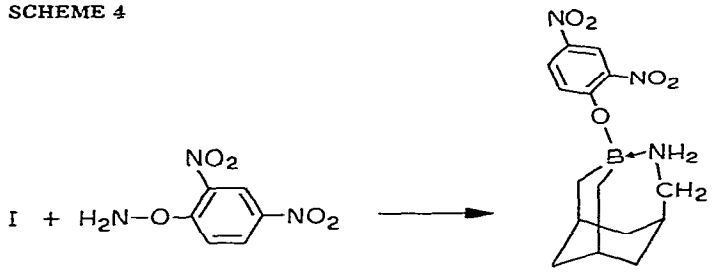
SCHEME 3



The exothermal reaction of I with *O*-2,4-dinitrophenylhydroxylamine in $CHCl_3$ leads to intramolecularly coordinated 3-(2,4-dinitrophenoxy)-7-amino-methyl-3-borabicyclo[3.3.1]nonane (VII) (Scheme 4), in the IR spectrum of which the B—O bond absorption (1300—1400 cm^{-1}) is absent.

It is noteworthy that the ability of the systems under study for intramolecular coordinative interaction between the boron and nitrogen depends on both the nature of the substituent at the boron atom and the number of alkyl radicals at the nitrogen atom. In compound II, containing chlorine at the boron atom, coordination takes place even in the case of a completely alkylated nitrogen,

SCHEME 4



(VII, 73%)

whereas replacement of chlorine by a MeO group breaks the coordination (compound III). However the nitrogen of the 7-aminomethyl group coordinates to the boron in the presence of a RO group at the boron (compounds V and VII). The donor-acceptor interaction is also observed in compounds containing doubly alkylated nitrogen: in 3-alkoxy-7-butylaminomethyl-3-borabicyclo[3.3.1]-nonanes [10].

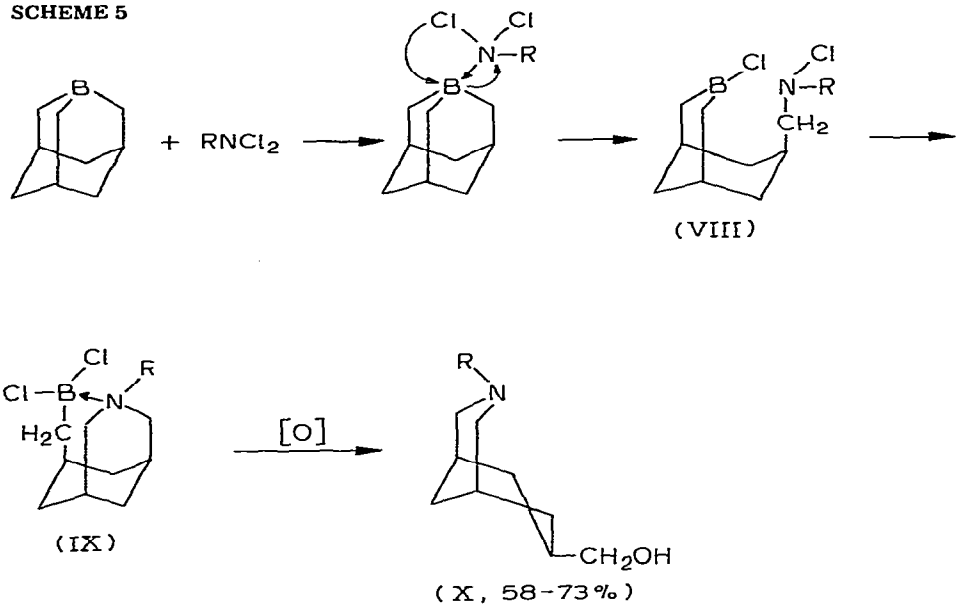
The double chair conformation in compounds II, V and VII is stabilized by the intramolecular donor-acceptor bond between the boron and nitrogen atoms. A comparison of the ^{13}C NMR spectrum of the compound III (uncoordinated) with those of related compounds suggests that III also has a predominant double chair conformation. The characteristic chemical shifts of the C(9) and C(1,5) atoms in III over the temperature range 20 to −50°C are 35.3—36.0 and 27.4—27.5 ppm, i.e. they are close to the values of the chemical shifts of the same atoms in other 3-borabicyclo[3.3.1]nonane derivatives for which this conformation was determined unequivocally [11].

With a view to obtaining 3-azabicyclo[3.3.1]nonane compounds, we undertook a study of the reaction of I with alkyldichloroamines. The action of bifunctional aminating reagents on trialkylboranes had not yet been investigated. However, perhydroboraphenalene was converted into *trans*-13-azabicyclo-[7.3.1]tridecan-5-ol on treatment with *N*-chloro-*O*-2,4-dinitrophenylhydroxylamine [6].

The reactions of I with alkyldichloroamines were carried out in methylene chloride at −40 to −70°C. Intramolecularly coordinated 3-methyl-7-dichloroboryl-3-azabicyclo[3.3.1]nonane (IX, R = Me) was obtained when $MeNCl_2$ was used. In the case of other alkyldichloroamines, the intermediates IX were not isolated, but instead they were oxidized with hydrogen peroxide in the presence of NaOH to yield 3-alkyl-7-hydroxymethyl-3-azabicyclo[3.3.1]nonanes (X) (Scheme 5). The importance of the order in which the reagents are mixed must be emphasised. Thus X is obtained in 58—73% yield if I is added to *N,N*-dichloroalkylamine, whereas by the reverse order of mixing X is formed only in 15—20% yield. The low yield of X in that case is apparently accounted for by an interaction between VIII and an excess of I that results in the oligomeric products.

3-Methyl-7-dichloroborylmethyl-3-azabicyclo[3.3.1]nonane (IX, R = Me) thus obtained is a white crystalline substance stabilized to a considerable extent by the intramolecular donor-acceptor bond. 3-Alkyl-7-hydroxymethyl-3-azabicyclo-[3.3.1]nonanes (X) are viscous liquids. In the 3-azabicyclo[3.3.1]nonanes syn-

SCHEME 5



(IX)

(X, 58–73%)

Xa, R = Me; Xb, R = n-Pr; Xc, R = n-Bu

thesized the hydroxymethyl group occupies the *endo* position. In accordance with data on the conformational analysis of *exo*- and *endo*-substituted, at the 7-position, 3-azabicyclo[3.3.1]nonanes it is possible to postulate that the 3-alkyl-7-hydroxymethyl-3-azabicyclo[3.3.1]nonanes synthesized by us have the chair-boat conformation as shown in Scheme 5. This conformation is confirmed by the study of the hydrogen bonds in Xb which we carried out. The IR spectrum of Xb contains several bands in the OH group absorption region: a narrow band of free OH (3640 cm^{-1}) and a broad one in the range 3100—3500 cm^{-1} (hydrogen bonded OH). Dilution of the solution by a factor of 500 leads to the broad band of the hydrogen-bonded OH vanishing, which suggest an absence of intramolecular hydrogen bonds characteristic of the double chair conformation.

Thus, from the interaction between 1-boraadamantane and chloroamines it is possible to effect the synthesis of compounds with the intramolecularly complexed azaborahomoadamantane structure, and the synthesis of hydroxymethylaminomethylcyclohexanes or 3-azabicyclo[3.3.1]nonanes.

Experimental

All the organoboron compounds were worked up in a stream of dry argon. Diethylchloroamine was prepared by chlorination of diethylamine hydrochloride with sodium hypochlorite [13]. Hydroxylamine-*O*-sulfonic acid was synthesized as reported [14] by sulfonation of $NH_2OH \cdot H_2SO_4$ with oleum. *O*-2,4-Dinitrophenylhydroxylamine was obtained by hydrolysis of ethyl *O*-(2,4-dinitrophenyl)acetohydroxamate [15—18]. Alkyldichloroamines were prepared by chlorination of aqueous solutions of alkylamines with chlorine as reported [19]. The heavy, oily alkyldichloramines thus formed were separated from the

aqueous layer, dried over K_2CO_3 and used without subsequent purification.

1-Boraadamantane was synthesized as reported [20]. IR spectra were recorded on a UR-20 spectrometer, ^{13}C NMR spectra on a Bruker WP-60 (15.08 MHz with respect to carbon), ^1H NMR spectra on a Tesla BS-497 (100 MHz) and ^{11}B NMR spectra on a Bruker SXP/4-100 instrument (relative to TMS and $BF_3 \cdot OEt_2$, respectively). For IR and ^1H NMR spectra only the values of the characteristic signals are listed.

3-Chloro-7-diethylaminomethyl-3-borabicyclo[3.3.1]nonane (II)

A hexane solution of 3.44 g of Et_2NCl (32 mmol) was added dropwise to a solution of 4.31 g of I (32 mmol) (exothermal). The colourless precipitate formed on mixing was filtered off, washed with hexane and dried to give 5.59 g (68%) of II, m.p. 140—146°C (decomp.). Found: C, 63.82; H, 10.56; B, 4.34; Cl, 14.90. $C_{13}H_{25}BClN$ calcd.: C, 64.62; H, 10.43; B, 4.49; Cl, 14.67%. ^{13}C NMR (CH_2Cl_2, δ, ppm): 10.3 (CH_3), 26.7 (C(2,4)), 29.5 (C(1,5)), 32.2 (C(7)), 38.3 (C(6,8)), 39.4 (C(9)), 53.9(CH_2N), 66.8 (NCH_2CH_3). ^{11}B NMR ($CHCl_3$, δ, ppm): 9.5.

3-Methoxy-7-diethylaminomethyl-3-borabicyclo[3.3.1]nonane(III)

To 3.06 g (13 mmol) of II were added slowly at first MeOH (45 ml), and thereupon a freshly prepared solution of MeONa (from 0.29 g (13 mmol) of Na in 12 ml of MeOH). After refluxing the mixture for 0.5 h and removing MeOH in vacuo, 10 ml of ether were added to the residue. The NaCl precipitated was filtered off and ether removed in vacuo to afford 1.5 g (50%) of III, b.p. 112—113°C/3 Torr, n_D^{20} 1.4841 (lit. [10]). Found: C, 70.87; H, 11.88; B, 4.23; N 5.90. $C_{14}H_{28}BNO$ calcd.: C, 70.89; H, 11.90; B, 4.56; N 5.91%. ^{11}B NMR (C_6H_6, δ, ppm): 53. ^1H NMR: (see ref. 10). ^{13}C NMR (CH_2Cl_2, δ, ppm): 11.8 (CH_3), 27.4 (C(1,5)), 29.9 (C(7)), 35.3 (C(9)), 35.9 (C(6,8)), 47.2 (CH_2N), 52.4 (OCH_3), 61.6 (NCH_2). IR: 1320—1380 cm^{-1} (B—O).

Complex of 3-sulfoxy-7-aminomethyl-3-borabocyclo[3.3.1]nonane with THF (IV)

5.42 g of NH_2OSO_3H (48 mmol) were added gradually to a solution of 6.43 g of I in 50 ml THF (warming up to 50°C was observed). Then the mixture was refluxed for 1 h and unreacted NH_2OSO_3H was filtered off. After removing THF in vacuo, the colorless precipitate was washed with hexane and kept in vacuo to yield 12.05 g (78.7%) of IV, m.p. 128—130°C. Found: C, 48.68; H, 8.37; B, 3.70; N, 4.36. $C_{13}H_{26}BNO_5S$ calcd.: C, 48.91; H, 8.21; B, 3.38; N, 4.39%. The compound decomposes both in air and on prolonged storage in an argon atmosphere. Heating the compound in vacuo leads to a partial loss of THF. IV does not dissolve in common organic solvents. ^1H NMR ($(CD_3)_2SO$, δ, ppm): 1.72 m, 3.54 m (protons of THF), 6.14 broad s (NH_2).

3-Methoxy-7-aminomethyl-3-borabicyclo[3.3.1]nonane (V)

A solution of MeONa in MeOH, prepared from 0.74 g of Na (32 mmol), was added to 10.26 g of IV (32 mmol) in 95 ml of THF. After filtering off the salt formed and removing the solvent in vacuo, the solid residue was washed with ether and dried to give 4.30 g (74%) of V, m.p. 193—194.5°C. Found: C, 66.34;

H, 11.58; B, 5.83; N, 7.68. $C_{10}H_{20}BNO$ calcd.: C, 66.33; H, 11.13; B, 5.97; N, 7.74%. ^{11}B NMR ($CHCl_3$, δ, ppm): 5.13. ^1H NMR ($CHCl_3$, δ, ppm): 2.88 d (CH_2N), 3.1 s (CH_3O), 4.62 broad s (NH_2). IR (cm^{-1}): $\nu(NH_2)$ 3200—3400 (group of bands), $\delta(NH_2)$ 1620 (1590-(sh)).

1,3-Dihydroxymethyl-5-aminomethylcyclohexane hydrochloride(VI)

12.1 g of NH_2OSO_3H (107 mmol) were added to a solution of 9.65 g of I, keeping the reaction mixture temperature about 50°C. Then the mixture was refluxed during 1 h and excess NH_2OSO_3H was filtered off. To the residue were added consecutively 48 ml of 3 *N* NaOH and 16.5 ml of H_2O_2. After 24 h the organic layer was separated and dried over K_2CO_3. Removing the solvent in vacuo afforded 9.1 g of a viscous oil that was convert to a solid by trituration. The solid was dissolved in a minimum amount of ethanol, and to the solution thus prepared was added an ethereal solution of HCl. Filtering the precipitate formed, washing and drying in vacuo gave 9.0 g (61%) of VI, m.p. 177—179°C. Found: C, 51.04; H, 9.38; N, 6.68; Cl, 16.91. $C_9H_{20}ClNO_2$ calcd.: C, 51.54; H, 9.61; N, 6.68; Cl, 16.91%. ^1H NMR (CD_3OD, δ, ppm): 2.77 d, J = 7 Hz ($CH_2NH_3^+$), 3.36 d, J = 6 Hz (CH_2OH), 4.85 s (OH, NH_3^+).

3-(2,4-Dinitrophenoxy)-7-aminomethyl-3-borabicyclo[3.3.1]nonane (VII)

A solution of 11 g of *O*-2,4-dinitrophenylhydroxylamine (55.3 mmol) in 200 ml of $CHCl_3$ was added dropwise to a solution of 7.42 g of I (55.3 mmol) in 70 ml of $CHCl_3$, the addition being accompanied by a temperature increase (up to 38°C) and a reddening of the solution. The mixture was allowed to stand overnight, whereupon the yellow crystals that had come to the surface were filtered off, washed with $CHCl_3$, and dried in vacuo to give 6.4 g of VII. After the filtrate had been allowed to stand, it gave 7 g more of VII (total yield 73%), m.p. 187—189.5°C. Found: C, 54.06; H, 6.19; B, 3.41; N, 11.96. $C_{15}H_{20}BN_3O_5$ calcd.: C, 54.07; H, 6.05; B, 3.24; N, 12.61%. ^1H NMR ($(CD_3)_2SO$, δ, ppm): 6.23 broad s (NH_2), 7.61—8.81 (phenyl protons). IR (cm^{-1}): 1340, 1530 (NO_2), 1610, 3000—3100 (arom. C—H), 3280, 3320 (NH_2).

3-Methyl-7-dichloroborylmethyl-3-azabicyclo[3.3.1]nonane (IX R = Me)

A solution of 8 g of I (59.6 mmol) in CH_2Cl_2 was added dropwise to a solution of 5.9 g of $MeNCl_2$ (59.6 mmol), then the mixture was allowed to reach room temperature, and the solution stirred for 2 h at 20°C. After partial evaporation of the solution colourless crystals were obtained. Filtration, washing with pentane, and drying in vacuo yielded 6.74 g of IX (R = Me) melting above 200°C with decomposition. Found: C, 51.44; H, 7.88; B, 4.42; N, 6.15; Cl, 30.12. $C_{10}H_{18}BNCl_2$ calcd.: C, 51.33; H, 7.75; B, 4.62; N, 5.98; Cl, 30.31%. ^1H NMR ($CHCl_3$, δ, ppm): 2.96 s (CH_3N), 4.14 d, J = 13 Hz (CHN). ^{13}C NMR (CH_2Cl_2, δ, ppm): 28.7 (C(1,5)), 29.8 (C(9)), 33.9 (C(7)), 36.2 (C(6,8)), 55.5 (CH_3N), 63.0 (C(2,4)). ^{11}B NMR ($CHCl_3$, δ, ppm): 12.7.

3-Methyl-7-hydroxymethyl-3-azabicyclo[3.3.1]nonane (Xa)
12.6 ml of a 3 *N* solution of NaOH and 2.9 ml of H_2O_2 were added consecutively to 2.96 g of IX (R = Me) (12.64 mmol) in 40 ml of ether. After standing for 48 h, the ethereal layer was separated and dried over K_2CO_3. Removing ether gave a viscous oil which, on distillation, produced 1.71 g (80%) of Xa, b.p. 104—107°C/1.5 Torr, n_D^{20} 1.5055, *m/e* 169 (M^+). Found: C, 70.76; H, 11.23; N, 8.18. $C_{10}H_{19}NO$ calcd.: C, 70.96; H, 11.32; N, 8.27%. ^{1}H NMR ($CHCl_3$, δ, ppm): 1.85 s (CH_3N), 2.40 d, *J* = 10 Hz (CH_2N), 3.21 broad s (CH_2O), 6.53 (OH). ^{13}C NMR (CH_2Cl_2, δ, ppm): 27.3 (C(1,5)), 28.5 (C(9)), 30.85 (C(6,8)), 31.9 (C(7)), 46.45 (CH_3N), 63.1 (C(2,4)), 69.1 (CH_2O). IR (cm^{-1}): 3640 (free OH), 3100—3500 broad band with maximum at 3400 hydrogen-bonded OH).

3-n-Propyl-7-hydroxymethyl-3-azabicyclo[3.3.1]nonane (Xb)
A solution of 5.77 g of I (43.1 mmol) in 30 ml of CH_2Cl_2 was added dropwise to a stirred solution of 5.48 g of n-$PrNCl_2$ (43.1 mmol), then the mixture was warmed up to 20°C and kept overnight. After removing CH_2Cl_2, to the residue were added consecutively ether, 47.5 ml of 3 N NaOH, and then 13.8 ml of H_2O_2. The mixture was refluxed for 3 h, and the organic layer was separated and dried over K_2CO_3. Removing ether yielded 8.43 g of an oil-like product, distillation of which gave 6.2 g (72.9%) of Xb as a viscous transparent yellowish liquid, b.p. 133—134°C/2 Torr, n_D^{20} 1.4958, *m/e* 197 (M^+). Found: C, 73.16; H, 11.69; N, 7.10. $C_{12}H_{23}NO$ calcd.: C, 73.04; H, 11.75; N, 7.10%. ^{1}H NMR (CCl_4, δ, ppm): 2.67 d, *J* = 10 Hz (NCH_2, heterocycle protons), 3.33 d, *J* = 5 Hz (CH_2O), 5.16 s (OH). ^{13}C NMR (CH_2Cl_2, δ, ppm): 12.1 (CH_3), 19.9 (CH_2CH_3), 27.50 (C(1,5)), 29.4 (C(9)), 30.9 (C(7)), 31.1 (C(6,8)), 61.0 (CH_2N) 61.3 (C(2,4)), 69.4 (CH_2O). IR (cm^{-1}): 3640 (free OH), broad band 3100—3500 with maxima at 3100 and 3400 (hydrogen-bonded OH).

3-n-Butyl-7-hydroxymethyl-3-azabicyclo[3.3.1]nonane (Xc)
The compound was obtained as described above for Xb from 7.98 g of n-$BuNCl_2$ (56 mmol) and 7.54 g of I (56 mmol) with subsequent oxidation with 19 ml of H_2O_2 in 62 ml of 3 *N* NaOH. Distillation gave 6.86 g (58%) of Xc as a transparent oily yellow substance containing only a negligible amount of an admixture. Complete purification was achieved by running an ethereal solution of Xc through a column packed with Al_2O_3. Xc has b.p. 122—123°C/1 Torr, n_D^{20} 1.4945, *m/e* 211 (M^+). Found: C, 73.80; H, 11.88; N, 6.50. $C_{13}H_{25}NO$ calcd.: C, 73.87; H, 11.92; N, 6.63%. ^{1}H NMR (CCl_4, δ, ppm): 2.68 d, *J* = 10 Hz (NCH_2, heterocycle protons), 3.37 d (CH_2O), 4.83 s (OH). IR (cm^{-1}): 3645 (free OH), broad band 3100—3500 with maxima at 3100 and 3390 (hydrogen-bonded OH). Picrate of Xc: m.p. 108—109.5°C. Found: C, 51.60; H, 6.30; N, 12.70. $C_{19}H_{28}N_4O_8$ calcd.: C, 51.80; H, 6.40; N, 12.72%.

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