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ORGANOBORON COMPOUNDS

CDXXI *. SYNTHESIS OF BICYCLO[3.3.1]NON-6-ENE AND BICYCLO[3.3.1]NONANE COMPOUNDS USING BORON DERIVATIVES **

Yu.N. BUBNOV*, A.I. GRANDBERG, M.Sh. GRIGORIAN, V.G. KISELEV, M.I. STRUCHKOVA and B.M. MIKHAILOV (deceased)

N.D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the U.S.S.R., Moscow (U.S.S.R.)

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Summary

A convenient method for the synthesis of bicyclo[3.3.1]nonane compounds via allylboron/acetylene condensation has been worked out. The carbonylation-oxidation of 3-methyl-3-borabicyclo[3.3.1]non-6-ene (I) results in the formation of 3α-hydroxy-3β-methylbicyclo[3.3.1]non-6-ene (IVa) and its 3β-hydroxy-3α-methyl isomer (IVb). Similar treatment of 3-methyl-3-borabicyclo[3.3.1]nonane (II) gives 3α-hydroxy-3β-methylbicyclo[3.3.1]nonane (VIIa) and its 3β-hydroxy-3α-methyl isomer (VIIb), having chair–chair and chair–boat conformations, respectively.

The carbinol IVa was converted to 1-methyl-2-oxaadamantane (VI) by the mercuration-reduction reaction, while carbinol VIIa gave compound VI upon the trans-annular oxidation with lead tetraacatate. Dehydration of carbinols IVa and IVb and of a mixture of carbinols VIIa and VIIb led to the formation of 3-methylbicyclo[3.3.1]nona-2,6-diene (VIII), 3-methylbicyclo[3.3.1]nona-2,7-diene (VIIIa) and 3-methylbicyclo[3.3.1]non-2-ene (X), respectively.

Bicyclo[3.3.1]nonane and bicyclo[3.3.1]non-6-ene systems can serve as suitable models to solve a number of problems concerning conformational analysis, dynamic stereochemistry, transannular interaction and transannular reactions [1]. These substances are also starting reagents for the synthesis of adamantane and several of its homologues. However, all known methods for the synthesis of bicyclo[3.3.1]nonane compounds are, as a rule, multistep processes including reactions with low product yields [2].

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* For part CDXX see ref. 21.

** Dedicated to Professor O.A. Reutov on the occasion of his 65th birthday.

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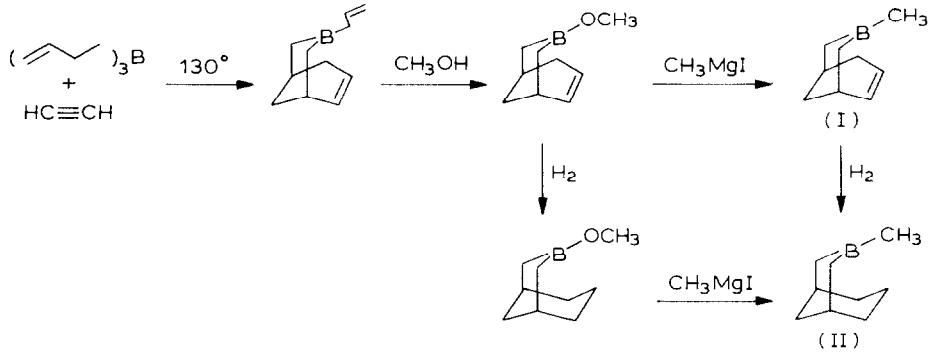
New methods for the synthesis of these proved attractive. Hillman has demonstrated that trialkylboranes convert to trialkylcarbinols upon carbonylation-oxidation [3]. Later the reaction was extended to boracyclanes and cage compounds [4,5].

We have worked out a convenient method for the synthesis of the bicyclo[3.3.1]-nonane compounds from 3-borabicyclo[3.3.1.]nonane derivatives which can easily be prepared from triallylborane and acetylenes RC≡CH using the allylboron-acetylene condensation [4].

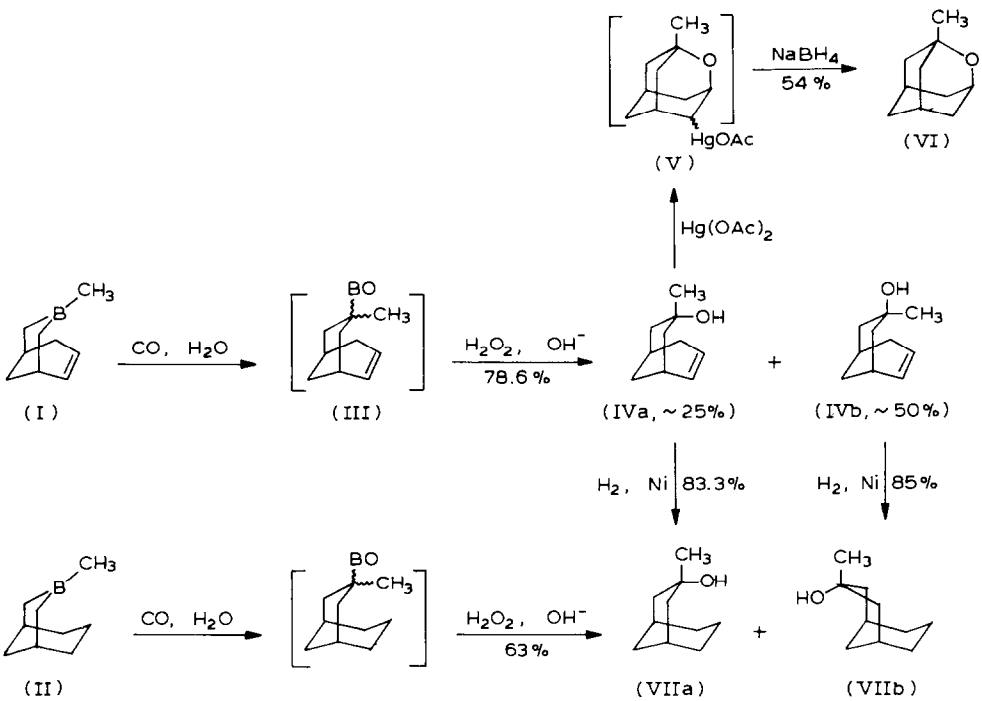
We now report, the preparation of isomeric 3-hydroxy-3-methylbicyclo[3.3.1]non-6-enes (IVa, IVb) and of 3-hydroxy-3-methylbicyclo[3.3.1]nonanes (VIIa, VIIb) by carbonylation-oxidation of 3-methyl-3-borabicyclo[3.3.1]non-6-ene (I) and 3-methyl-3-borabicyclo[3.3.1]nonane (II), the dehydration of the carbinols obtained and the synthesis of 1-methyl-2-oxadamantane.

Compound I was obtained by the reaction of MeMgI with 3-methoxy-3-borabicyclo[3.3.1]non-6-ene [6,7]. Compound II was prepared by the reaction of 3-methoxy-3-borabicyclo[3.3.1]nonane[7] with MeMgI and by catalytic hydrogenation of I.



Carbonylation of compound I in THF in the presence of a minute amount of water (80–100 atm of CO, 150°C, 2–3 h) leads to the formation of a mixture of isomeric boranes III, which, when oxidized with alkaline hydrogen peroxide, produces a mixture of 3α-hydroxy-3β-methylbicyclo[3.3.1]non-6-ene (IVa) and its 3β-hydroxy-3α-methyl isomer (IVb) in a ratio of ~ 1/2 with a total yield of 78.6% based on compound I. The mixture was crystallised from hexane to give carbinol IVb, 30%. The remaining liquid mixture of IVa and IVb (~ 1/1) was separated by column chromatography on Al_2O_3. Carbinol IVa is a liquid while IVb is a solid substance.

The steric arrangement of the hydroxyl and methyl group was determined as follows. Treatment of IVa with mercury(II) acetate in CH_2Cl_2 (20°C, 20 h) with subsequent reduction of the intermediate organomercuric compound V with sodium borohydride gave 1-methyl-2-oxaadamantane in 54% yield. Under the same conditions, IVb does not cyclize to remain unchanged. A similar work-up of a mixture of IVa and IVb (~ 1/1) gave adamantane VI in 40.5% yield (80% of the initial IVb was returned). Mercuration was monitored by GLC; the contents of IVa in the reaction mixture dropped gradually to zero, whereas the concentration of IVb did not undergo essential changes.



The hydrogenation of pure IVa and IVb over Raney nickel in an autoclave gave 3α-hydroxy-3β-methylbicyclo[3.3.1]nonane (VIIa) (m.p. 53–55°C) and its 3β-hydroxy-3α-methyl isomer (VIIb) (m.p. 103–105°C), respectively. GLC data show that compounds VIIa and VIIb are pure, their ^{1}H NMR spectra show signals of methyl groups at 1.26 (VIIa) and 1.22 ppm (VIIb).

Hydrogenation of a mixture IVa and IVb (4/3), that was obtained from the mother liquor after crystallisation of IVa, over Raney nickel led to a mixture of VIIa and VIIb in the same ratio.

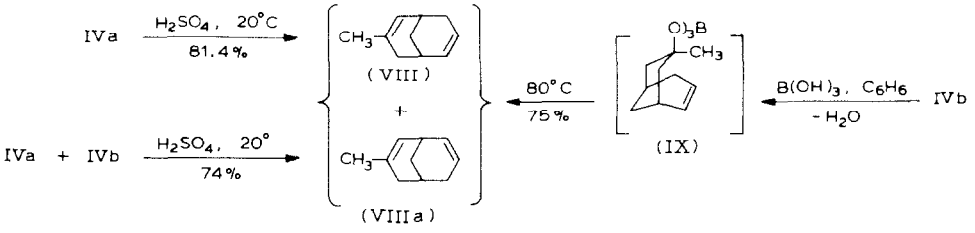
A mixture of carbinols VIIa and VIIb (5/4) was obtained in 63% yield upon carbonylation-oxidation of 3-methyl-3-borabicyclo[3.3.1]nonane (II). Both carbinols were isolated in a pure state by column chromatography on alumina.

Additional support for the relative disposition of 3-OH and 3-Me groups in hydrogenated carbinols VIIa and VIIb was obtained in the study of their reactions with lead tetraacetate, which gave evidence for the disposition of these groups in IVa and IVb. 3α-Hydroxybicyclo[3.3.1]nonane was previously shown to cyclize to 2-oxaadamantane of 89% purity (86% yield) upon oxidation with lead tetraacetate (2-oxaadamantane contained impurities of bicyclo[3.3.1]nonan-3-one (6%) and 3α-acetate of the initial carbinol (4%)) [8]. Under the same conditions 3β-hydroxybicyclo[3.3.1]nonane was not converted to 2-oxaadamantane, 74% of the starting 3β-carbinol being isolated from the oxidation products [8].

We have performed analogous transannular reactions with carbinols VIIa and VIIb, the reaction course was followed by GLC. Both carbinols turned out to react with lead tetraacetate, VIIa producing 1-methyl-2-oxaadamantane (VI) and carbinol VIIb reacting more slowly to turn probably to 1-methylene-3-acetonylcyclohexane [9].

An attempt to cyclize α-carbinol IVa to 1-methyl-2-oxaadamantane (VI) by the

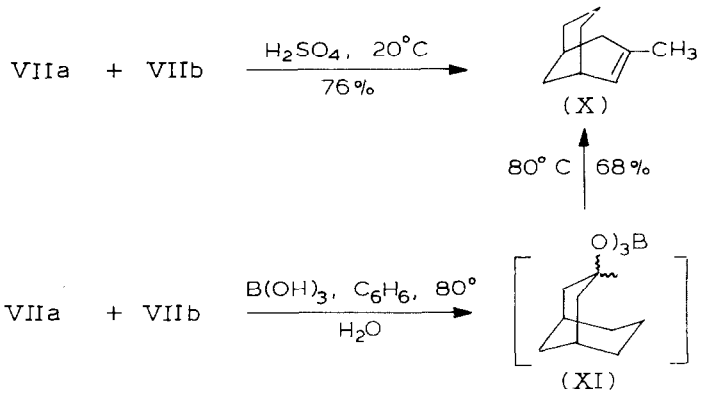
action of 25% H_2SO_4, as with 3α-hydroxy-7-methylenebicyclo[3.3.1]nonane [10], failed because under these conditions both IVa and IVb are dehydrated to form a mixture of dienes VIII and VIIIa in a ratio of ~ 3/1. Compound VI was not detected among the reaction products (GLC).



(VIII)/(VIIIa) = 3/1

A mixture of VIII and VIIIa (~ 3/1) of 99% purity was also obtained in 75% yield by heating IVb with boric acid in benzene (with extraction of water). The borate IX initially formed decomposed already at 80°C to eliminate dienes VIII and VIIIa, but the borates prepared from secondary alcohols eliminate olefin only at 200°C, and at 100°C in the presence of BF_3 etherate [11].

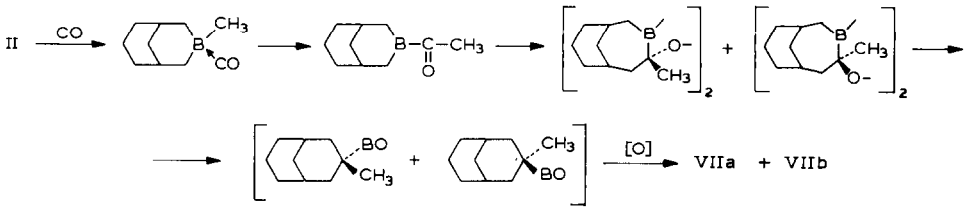
Furthermore, the dehydration of a mixture of carbinols VIIa and VIIb (1/1) afforded 3-methylbicyclo[3.3.1]non-2-ene (X).



The dehydration was carried out by two methods: (1) by the action of 25% H_2SO_4 at room temperature with a 76% yield of X (99% purity), and (2) by heating with boric acid in benzene at 80°C, 68% yield of X (99% purity). In the latter case borate XI, like IX, is cleaved with formation of an olefin under very mild conditions (80°C).

The data obtained show that carbonylation of I proceeds stereospecifically resulting in a mixture of boranes III, with the boron isomer in the β-position and the methyl group in the α-position predominating. At the same time the carbonylation of II does not occur stereospecifically yielding a mixture of boranes in about equal amounts.

The formation of the two isomers can easily be explained if the adopted carbonylation mechanism is considered [4] in the case of bicyclic compounds I and II. Although the stereochemistry of some stages is rather vague, this fact does not play an essential role on the course of the process in total.



SCHEME 1

In the first stage of triorganoborane carbonylation the corresponding complexes with carbon monoxide are formed ($\geqslant$B ← CO). Sequential rearrangement of the complexes to give the final products may proceed along different ways, the difference consisting of a sequence of B–C bond ruptures (B–Me, B–C(2) and B–C(4)) and of methyl and methylene fragments migration to the carbonyl carbon (in this mechanism the participation of water or ethylene glycol is not considered though these affect essentially the carbonylation process).

In Scheme 1 a simplified mechanism for the carbonylation of the borane II is presented with the conventional assumption that, in the initially formed complex ($\geqslant$B ← CO), the B–Me bond is the first to be cleaved (the final result would be the same if the B–CH_2 bond in the ring migrated first). The stereochemistry of a newly arising carbon centre (C(3) in the bicyclic compound formed) appears in the course of second group migration.

In borane I, the C(2) and C(4) atoms are different in nature due to the presence of the C(6)–C(7) double bond. This allows three additional possibilities for the migration sequence, only two isomeric products being formed in all cases.

The bicyclic compounds, which are studied in the present work and which are bound genetically with each other, possess conformations as represented in the corresponding schemes. Carbinols VIIa and VIIb have chair–chair and chair–boat conformations, respectively. The conformations of the compounds have been established by ^{13}C NMR and high resolution ^1H NMR spectral methods.

Bicyclo[3.3.1]nonane and its 3β-mono- and 3β,7β-di-substituted derivatives are known to exist in a preferential chair–chair conformation (*CC*), with both rings being flattened appreciably [12,13]. The presence of 3α-substituents in compounds of this series stipulates chair–boat (*CB*) or a boat–chair (*BC*) conformation to be preferred.

An efficient method for determination of the bicyclo[3.3.1]nonane compound conformations is ^{13}C NMR spectroscopy, chemical shifts of the C(9) and C(1,5) carbon atoms being the most informative [12,13]. In the conversion *CC* → *CB* alterations of chemical shifts of C(9) from ~ 34 to ~ 28 ppm and of C(1,5) from ~ 28 to ~ 26 ppm take place (upfield shifts by ~ 5 and ~ 2 ppm, respectively).

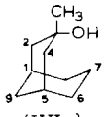
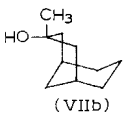
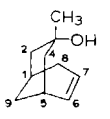
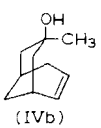
Chemical shifts of the compounds studied are presented in Table 1. The signal assignment was performed taking into account the multiplicity obtained under off-resonance conditions, see the respective literature for chemical shifts of 3-borabicyclo[3.3.1]nonane derivatives [14], 9-thiabicyclo[3.3.1]non-6-ene [15], bicyclo[3.3.1]-nonane and its 3-*endo*, 3-*exo*-hydroxy and -methyl derivatives [13], and 1-hydroxy-1-methylcyclohexane conformers [16].

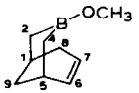
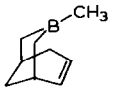
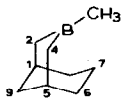
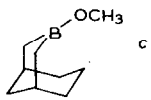
The values of C(9) and C(1,5) chemical shifts (33.0 and 27.7 ppm) (see Table 1) indicate that carbinol VIIa has *CC* conformation. In the spectrum of VIIb, signals of

(Continued on p. 100)

TABLE 1

^{13}C NMR CHEMICAL SHIFTS (δ, ppm) [a]

Compound	Solvent (°C)	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	C(9)	CH_3
 (VIIa)	$CDCl_3$ (30)	27.7 D	44.7 T	67.6 S	44.7 T	27.7 D	31.3 T	17.6 T	31.3 T	33.0 T	36.5 Q
 (VIIb)	$CDCl_3$ (30)	25.1 D	40.7 T	70.2 S	40.7 T	25.1 D	34.2 T	16.4 T	34.2 T	28.3 T	33.2 Q
 (IVa)	$CDCl_3$ (30)	26.6 D	42.1 T	70.1 S	45.9 T	28.8 D	135.2 D	129.3 D	31.4 [b] T	32.5 [b] T	32.5 Q
 (IVb)	$CDCl_3$ (30)	27.7 D	43.2 T	70.1 S	47.3 T	29.7 D	132.6 D	128.0 D	30.7 [b] T	32.7 [b] T	32.1 Q

 (XII)	$CDCl_3$	27.3 D	–	–	–	29.3 D	134.4 D	123.4 D	32.7 [b] T	34.5 [b] T	53.1 Q
	(−80)	–	22.4	–	25.7	–	–	–	–	–	–
 (I)	CH_2Cl_2 (−70)	27.4 D	33.1	–	36.5	28.8 D	135.1 D	123.2 D	32.4 [b] T	34.5 [b] T	13.9 Q
 (II)	$CDCl_3$ (30)	30.0	–	–	–	30.0 D	33.7 T	18.6 T	33.7 T	35.4 T	–
	CH_2Cl_2 (−50)	–	33.8	–	33.8	30.2	33.8	18.8	33.8	35.3	11.5
	(−70)	30.1	33.6	–	33.6	30.1	33.6	18.8	33.6	36.3	11.6
	(−90)	30.1	33.6	–	33.6	30.1	33.6	18.8	33.6	35.2	11.7
 [c]	CH_2Cl_2 (−90)	29.3	25.7	–	25.7	29.3	34.0	17.6	34.0	35.2	53.6
 [d]	$CDCl_3$	32.8	30.6	18.0	32.8	33.6	130.3	129.0	35.3	–	–

[a] D, doublet; Q, quartet; S, singlet; T, triplet. [b] Chemical shifts for C(8) and C(9) should possibly be interchanged. [c] See ref. 14; [d] See ref. 15.

C(9), C(1,5) and C(2,4) show upfield shifts of 4.7, 2.6 and 4.0 ppm, respectively, while signals C(6,8) are shifted downfield by 2.9 ppm as compared with the position of the corresponding carbon atom signals in the spectrum of VIIa. The values for C(9) (28.3 ppm) and C(1,5) (25.1 ppm) show that carbinol VIIb has a *CB* conformation.

In order to determine which of the two rings in VIIb is in a boat conformation, their high resolution in ^{1}H NMR spectrum (360 MHz, 15% in $CDCl_3$) were recorded. Chemical shifts and the most characteristic coupling constants are listed in Table 2.

The correctness of the main signal assignment is supported by measuring the spectra in the presence of $Eu(FOD)_3$ and also by the double resonance spectroscopy. With sequential addition of $Eu(FOD)_3$ the highest paramagnetic shift are found for protons H(2β, 4β), H(9*syn*) and those of the Me group, while mean shifts are found for H(2α, 4α), H(9*anti*) and H(1,5).

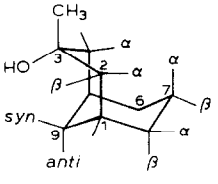
Under the double resonance conditions, two coupling constants, $^2J_{2\alpha 2\beta}$ 15 Hz and $^3J_{12\beta}$ 10.5 Hz, can be determined from the proton H(2β, 4β) multiplet at 1.90 ppm. The latter constant value evidences that the substituted ring has boat conformation (the dihedral angle H(1)–H(2) is close to 0°).

The difference in conformations of carbinols VIIa and VIIb is accounted for by greater conformation energy of the methyl group (1.5–2.12 kcal/mol) [16,17] against the hydroxyl group (0.29–1.48 kcal/mol) [16,18] which causes an equatorial position of the methyl group, boat-shaped form of the substituted ring in VIIb and chair-shaped form in VIIa. This effect does not take place in the unsaturated carbinol IVb, in which the 3,7-transannular interaction is significantly less due to the double bond, as a result of which the substituted ring both in IVa and IVb is in chair conformation.

Differences between the ^{13}C chemical shifts of IVa and IVb are conditioned by different orientations of the substituents in the 3 position. The chemical shift values

TABLE 2

CHEMICAL SHIFTS AND COUPLING CONSTANTS FOR CARBINOL VIIb (360 MHz, 15% solution in $CDCl_3$, relative to TMS) [a]



(VIIb)

H	C(1)	C(2α)	C(2β)	C(9*anti*)	C(9*syn*)	CH_3	7β	7α
δ(ppm)	2.05	1.36	1.90	2.34	1.12	1.22	1.42	1.56
J	$^2J_{2\alpha 2\beta}$	$^2J_{9syn9anti}$	$^3J_{12\beta}$	$^3J_{12\alpha}$	$^3J_{19anti}$	$^3J_{19syn}$	$^3J_{17\beta}$	
Hz	15	12.5	10.5	< 2 [b]	2.2	3.7	3.4	

[a] The assignment of multiplet signals at 1.32–1.40 and 1.49–1.63 ppm is somewhat difficult. [b] From line width at 50% of signal height.

for C(9) (~ 33 ppm) correspond to those characteristic for a chair conformation of the cyclohexane ring.

The 3-borabicyclo[3.3.1]nonane compounds with a tri-coordinated boron atom exist in a chair–chair conformation [14]. The boracyclohexane ring in the unsaturated compounds I and XII, in which interaction between the hydrogen on C(7) and the substituent on boron does not take place, has a chair form. Therefore chemical shifts of C(9) and C(1,5) in compounds I and XII are 34.5 and 27.3–29.3 ppm.

In Table 1 are listed ^{13}C chemical shifts of compound II which are assigned according to ref. 14. It can be seen that change of the OMe group for Me leads to a downfield shift of C(2,4) signals of ~ 8 ppm. More significant downfield shifts of these signals are observed in the case of substituting the OMe group by Me (10.8 ppm) or Br (13.6 ppm) in 3-methoxy-7α-methyl-3-borabicyclo[3.3.1]nonane [14].

We may conclude that allylboron-acetylene condensation combined with carbonylation-oxidation is a convenient method for the synthesis of a series of bicyclic systems and oxaadamantane derivatives.

Experimental

All organoboron compounds were treated under dry argon or nitrogen. IR spectra were recorded on a UR-20 spectrometer. ^1H NMR spectra were obtained on Varian DA 60-IL, TESLA BS-497 (100 MHz) and Bruker WH-360 (360 MHz) instruments. ^{13}C NMR spectra were recorded on a Bruker WP-60 spectrometer (15.08 MHz for carbon).

3-Methoxy-3-borabicyclo[3.3.1]non-6-ene (XII)

Triallylborane (38.9 g) was placed in a hydrogenator through which acetylene was passed at 130°C until 6.4 l of the gas had been absorbed (10 h). Dry MeOH (35 ml) was added to the reaction mixture at 0–20°C for 30 min with propene evolution. The mixture was then refluxed for 1 h to give 39.2 g (89.8%) of the title compound (b.p. 88–90°C/21 mmHg, n_D^{20} 1.4882, see, for comparison, refs. 6, 7).

3-Methyl-3-borabicyclo[3.3.1]non-6-ene (I)

To a Grignard reagent (from 6.5 g of Mg and 15 ml of CH_3I in 100 ml of ether) was added 3-methoxy-3-borabicyclo[3.3.1]non-6-ene (28.7 g) during 1.5 h. The mixture was refluxed for 1 h, then the ether solution was separated off and the solid residue was extracted with hexane (4 × 50 ml). Removal of the solvent with subsequent distillation gave 19 g (74.2%) of I. B.p. 55–56°C/13 mmHg, n_D^{18} 1.4885. Found: C, 80.65; H, 11.35; B, 7.73. $C_9H_{15}B$ calcd.: C, 80.65; H, 11.28; B 8.07%. IR (ν, cm^{-1}): 1645, 3018 and 3060 (C=C). ^1H NMR (CCl_4, δ, ppm): 0.65 s (CH_3), 1.2–2.6 m (10 H), 5.5 m (CH=CH).

3-Methyl-3-borabicyclo[3.3.1]nonane (II)

(a) As described above, the reaction of 3-methoxy-3-borabicyclo[3.3.1]nonane (32.6 g) [7] with CH_3MgI (from 7 g of Mg, and 20 ml of CH_3I in 170 ml of ether) gave 21 g (72.2%) of II. B.p. 43–44°C/7 mmHg, $n_D^{22.5}$ 1.4753. Found: C, 79.29; H, 12.43; B, 7.63. $C_9H_{17}B$ calcd.: C, 79.45; H, 12.60; B, 7.95%. ^1H NMR ($CDCl_3$, δ, ppm): 0.6–1.8 m (12H) with a marked signal at 0.74 (CH_3), 2.15 m (CH).

(b) Hydrogenation in an autoclave (100 atm H_2, 40°C, 1 h) of 35.5 g of I in 40 ml of hexane over 0.5 g Raney nickel yielded 29.2 g (81.5%) of II. B.p. 47–49°C/9 mmHg, n_D^{20} 1.4756. I and II are readily oxidized in air and soluble in organic solvents.

Carbonylation of compound I. 3α-Hydroxy-3β-methylbicyclo[3.3.1]non-6-ene (IVa) and 3β-hydroxy-3α-methylbicyclo[3.3.1]non-6-ene (IVb)

A solution of 18.5 g of I in 40 ml of THF and 5 ml of water was placed in an autoclave and CO was introduced (100 atm). After heating with stirring for 2 h at 150°C 3 l of CO had been absorbed. The autoclave content was then transferrred into a four-necked flask fitted with a stirrer, thermometer, dropping funnel and a condenser. 100 ml of 10% NaOH was added dropwise to the reaction mixture with stirring at 0°C then 40 ml of 30% H_2O_2 was added. The mixture was heated at 50°C for 1 h, whereupon the organic layer was separated and the aqueous one was saturated with NaCl and extracted with ether (3 × 50 ml) followed by drying over Na_2SO_4. Removal of the solvent and distillation of the residue furnished 16.7 g (78.6%) of a mixture of IVa and IVb in a ratio of ~ 1/2. B.p. 78–80°C/2 mmHg. Partial crystallisation of the mixture from hexane gave crystalline IVb (4.6 g, pure substance by GLC). The mixture of isomeric carbinols (1/1) remaining in the mother liquor was separated by column chromatography on neutral aluminum oxide using ether as eluent. Carbinol IVa has b.p. 87–88.5°C/12 mmHg, n_D^{23} 1.4940. Found: C, 79.03; H, 10.61. $C_{10}H_{16}O$ calcd.: C, 78.90; H, 10.59%. IR: 1648 (v.weak)sh, 1640, 3020(mean) cm^{-1}. ^1H NMR (20% in $CDCl_3$, δ, ppm): 1.12 s (CH_3), 5.85 m and 6.15 two m (CH=CH), a multiplet of aliphatic protons at 1.35–2.70.

Carbinol IVb has m.p. 125–128°C (from hexane). Found: C, 79.05; H, 10.56. $C_{10}H_{16}O$ calcd.: C, 78.90; H, 10.59%. IR: 1658 (v.weak), 1652 (sh), 3025 cm^{-1} (CH=CH). ^1H NMR (20% in $CDCl_3$, δ, ppm): 1.33s(CH_3) and 2.07s(OH), multiplets at 1.46–2.58 (aliph.protons) and 5.74 (CH=CH).

3α-Hydroxy-3β-methylbicyclo[3.3.1]nonane (VIIa)

A solution of 1.2 g of IVa in 10 ml of hexane was hydrogenated in an autoclave over 0.1 g of Raney nickel (80 atm H_2) at 20°C to take up 180 ml of H_2 during 1 h. Crystallisation from hexane yielded 0.9 g (74%) of VIIa, m.p. 53–55°C. Found: C, 77.91; H, 11.66. $C_{10}H_{18}O$ calcd.: C, 77.87; H, 11.76%. ^1H NMR (20% in $CDCl_3$, δ, ppm): 1.25 s (CH_3), 1.33–2.71 m (aliphatic protons and OH).

3β-Hydroxy-3α-methylbicyclo[3.3.1]nonane (VIIb)

As described above, hydrogenation of 0.6 g of IVb in 5 ml of hexane gave 0.52 g (85%) of VIIb, m.p. 103–105°C (from hexane). Found: C, 77.77; H, 11.65. $C_{10}H_{18}O$ calcd.: C, 77.87; H, 11.76%. ^1H NMR (15% in $CDCl_3$, δ, ppm): 1.22 s (CH_3), 1.3–2.6 m (aliphatic protons and OH).

Carbonylation of compound II. 3α-Hydroxy-3β-methylbicyclo[3.3.1]nonane (VIIa) and 3β-hydroxy-3α-methylbicyclo[3.3.1]nonane (VIIb)

Carbonylation (100 atm of CO, 150°C, 2 h) of 23 g of II in 50 ml of THF with 8 ml of water followed by oxidation (50 ml of 30% H_2O_2 in 120 ml of 10% NaOH) afforded 16.4 g (63%) of a mixture of VIIa and VIIb in a ratio of ~ 5/4, b.p.

71–73°C/2 mmHg. The mixture was separated by column chromatography on neutral Al_2O_3 with ether as the eluent. Carbinol VIIa, m.p. 52.5–54°C; VIIb, m.p. 103–104°C (from hexane). Found: C, 77.95; H, 11.70. $C_{10}H_{18}O$ calcd.: C, 77.87, H, 11.76%. Carbinols VIIa and VIIb are very soluble in organic solvents and insoluble in water.

1-Methyl-2-oxaadamantane (VI)

(a) A mixture of 2 g of IVa, 4.3 g of $Hg(OAc)_2$ and 20 ml of CH_2Cl_2 was stirred at room temperature for 20 h and then 20 ml of 15% NaOH was added. After the organic layer had been separated 1.5 g of $NaBH_4$ in 20 ml of 15% NaOH was added to the stirred residue, the mixture was then boiled during 5 h and extracted with hexane (3 × 50 ml). The solvent was removed to yield 1.08 g (54%) of VI, b.p. 49–50.5°C/2 mm Hg, n_D^{20} 1.4886 (lit.: 199–200°C/760 mmHg [10]). Found: C, 79.06; H, 10.68. $C_{10}H_{16}O$ calcd.: C, 78.90; H 10.59%. The IR spectrum is identical with that previously described [19]. ^1H NMR (20% in $CDCl_3$, δ, ppm): 1.10 s (CH_3), 1.26–2.26 m (12 H), 4.06 br, s (1 H) (see [19]).

(b) 2.09 g of a mixture of IVa and IVb in a ratio of 4/3 and 4.25 g of $Hg(OAc)_2$ in 20 ml of abs. CH_2Cl_2 were stirred at 20°C during 12 h, about 75% of IVa are consumed this time, then 1 g of mercury acetate was added, and the mixture was stirred for 4 h (until complete disappearance of IVa in the GLC). Then 10 ml of 15% NaOH was added to the mixture and the organic layer was separated which was evaporated then the residue was crystallised from hexane to produce 0.69 g of IVb (80.2% based on its content in the initial mixture), m.p. 124–127°C (this does not contain any IVa as shown by GLC). An additional 10 ml of 15% NaOH was added to the aqueous layer, a solution of 1.5 g of $NaBH_4$ in 20 ml of 15% NaOH, and the mixture was refluxed for 5 h with subsequent extraction with hexane. The organic extracts were dried over Na_2SO_4 to give 0.48 g (40.5%) of VI, b.p. 48–50°C/2 mmHg, n_D^{21} 1.4882.

3-Methylbicyclo[3.3.1]nona-2,6-diene (VIII) and 3-methylbicyclo[3.3.1]nona-2,7-diene (VIIIa)

(a) A mixture of 2 g of IVa and 40 ml of 25% H_2SO_4 was stirred vigorously at 20°C for 4 h. The reaction mixture was extracted with ether (3 × 30 ml), the extracts were washed with a soda solution and water and dried over Na_2SO_4. Removal of the solvent gave 1.43 g (81.4%) of a mixture of VIII and VIIIa (3/1). B.p. 58–60°C/9 mmHg, n_D^{20} 1.5050. Found: C, 89.61; H, 10.52. $C_{10}H_{14}$ calcd.: C, 89.49; H, 10.51%. IR: 3020, 3000, 1670, 1650 (C=C) cm^{-1}.

(b) Analogously, 2 g of a mixture of IVa and IVb in a ratio of 1/1 was converted to 1.3 g of a mixture of VIII and VIIIa, b.p. 54–55°C/8 mmHg, n_d^{20} 1.5052.

(c) A mixture of 2 g of IVb, 0.4 g of boric acid and 50 ml of benzene was boiled for 3 h in a two-necked flask equipped with a Dean and Stark water separator. A mixture of VIII and VIIIa (1.32 g, 75%) was obtained. B.p. 53–54.5°C/8 mmHg, $n_D^{22.5}$ 1.5041.

(d) As described in (c); From 2 g of a mixture of IVa and IVb (1/1), 0.4 g of boric acid and 50 ml of benzene a mixture of VIII and VIIIa (1.28 g, 72.8%) was obtained. B.p. 53–54°C/8 mmHg, n_D^{20} 1.5048.

3-Methylbicyclo[3.3.1]non-2-ene (X)

(a) Similarly as described above: From 2 g of a mixture of VIIa and VIIb

(~ 1/1), 0.4 g of boric acid and 50 ml of benzene, X (1.36 g, 68%) was obtained. B.p. 51–52°C/7 mmHg, n_D^{20} 1.4903. Found: C, 88.25; H, 11.84. $C_{10}H_{16}$ calcd.: C, 88.16; H, 11.84%. ^{1}H NMR (20% in $CDCl_3$, δ, ppm): 1.65s (CH_3), 1.20–2.50 m (12 H), 5.33 d (HC=C<) [20].

(b) Starting from 2 g of a mixture of VIIa and VIIb (~ 1/1) and 40 ml of 25% H_2SO_4, as described for VIII (see (a)) X (1.34 g, 76%) was obtained. B.p. 50–51°C/7 mmHg, n_D^{23} 1.4890.

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