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ORGANOBORON COMPOUNDS

CDIV *. A HYDRIDE TRANSFER REACTION IN THE SERIES OF ATE COMPLEXES OF 7-SUBSTITUTED 3-ALKYL-3-BORABICYCLO[3.3.1]NONANES AND 3-ALKYL-3-BORABICYCLO[3.3.1]NON-6-ENES

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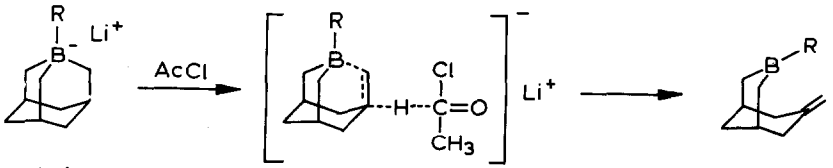
Summary

The ate complexes of 7-substituted 3-alkyl-3-borabicyclo[3.3.1]nonanes and of 3-alkyl-3-borabicyclo[3.3.1]non-6-enes react with acetyl chloride under mild conditions by an intermolecular β-hydride transfer mechanism to form 5-substituted 3-methylenecyclohex-1-ylmethyl(dialkyl)boranes. The latter compounds were converted, by oxidation with alkaline hydrogen peroxide, to 3-substituted 1-methylene-5-hydroxymethylcyclohexanes. The reaction of cycloalkylmethyl(dialkyl)boranes with aromatic aldehydes was applied to the synthesis of 1,3-di- and 1,3,5-tri-methylene derivatives of the cyclohexane series.

Results and discussion

It has been recently found that lithium 1-alkyl-1-boraadamantanates form 7-methylene-3-alkyl-3-borabicyclo[3.3.1]nonanes when treated with acetyl chloride. It has also been shown that elimination of a hydride ion from the β-position of the borate I takes place in this reaction [1]:



(I)

* For part CDIII see ref. 22.

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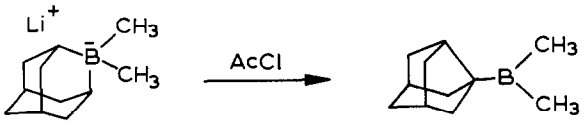
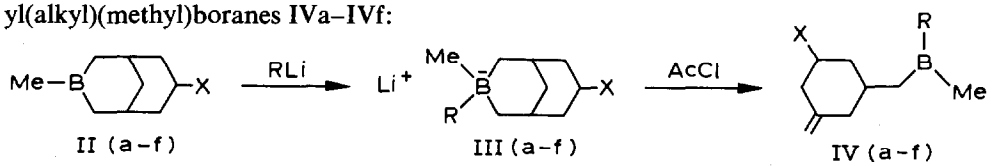
Transformations of this type have not been observed in the reactions of lithium tetraalkylborates with electrophiles.

Lithium tetraalkylborates, $R_3R'BLi$, react with acyl halides either with formation of the corresponding ketones [2,3], or with transfer of an α-hydride ion to the electrophile with simultaneous displacement of a radical from the boron to the α-carbon atom [4–7]. A striking example of reactions of the latter type is the conversion of lithium 2,2-dimethyl-2-boraadamantanate to 3-boradamantyl(dimethyl)borane on treatment of the former with AcCl [7]:



In the light of these reactions, the investigation of bridged structures similar to I (ate complexes of 3-alkyl-3-borabicyclo[3.3.1]nonane, which, like 1-boraadamantane ate complexes, have hydrogen atoms in the β-position to the bridgehead carbon atom [8]) was of interest. The ate complexes of 3-alkyl-3-borabicyclo[3.3.1]nonanes were prepared by the action of lithium alkyls on 7-substituted 3-borabicyclo[3.3.1]nonanes, and were used as their solutions, without being isolated . The presence of the ate complexes in the solutions was determined by ^{11}B NMR spectroscopy. For example, a change in the chemical shift in the spectrum of 7-methylene-3-methyl-3-borabicyclo[3.3.1]nonane (IIa) from 81 to −22 ppm on treatment with MeLi indicates unambiguously the formation of lithium 7-methylene-3,3-dimethyl-3-borabicyclo[3.3.1]nonanate (IIIa).

It turned out that the ate complexes IIIa–IIIf react with AcCl under mild conditions to form the corresponding 5-substituted 3-methylenecyclohex-1-ylmethyl(alkyl)(methyl)boranes IVa–IVf:



II (a–f) III (a–f) IV (a–f)

(a, R = Me, X = CH_2=;
b, R = Me, X = Me;
c, R = Me, X = CH_2OMe;
d, R = Me, X = Ph;
e, R = n-Bu, X = CH_2=;
f, R = n-Bu, X = Me)

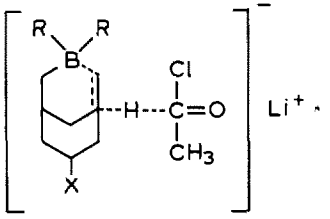
The IR spectra of the compounds IVa–IVf show intense absorption bands in the regions of ~890 ($\delta(CH_2)$), ~1650 ($\nu(C=C)$), ~3080 cm^{-1} ($\nu(C=CH_2)$). In addition, an absorption is observed at 1140 cm^{-1} ($\nu(C-O)$) in the spectrum of 3-methylene-5-methoxymethylcyclohex-1-ylmethyl(dimethyl)borane (IVc) and at 1605, 3040 and 3070 cm^{-1} (Ph) in the spectrum of 3-phenyl-5-methylenecyclohex-1-ylmethyl(dimethyl)borane (IVd).

The ^1H NMR spectra of the compounds IVa–IVf include signals of the olefinic protons of the *exo*-methylene groups at 4.6 ppm and singlets of the methyl protons at 0.6–0.8 ppm ($B-CH_3$). The spectrum of IVc also reveals a singlet at 3.32

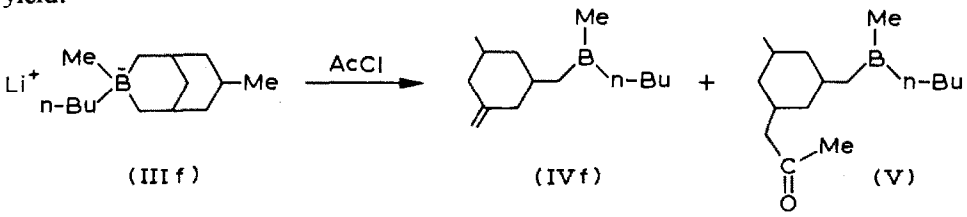
(CH_3–O) and a doublet at 3.21 ppm (O–CH_2), while that of IVd exhibits signals of the aromatic nucleus protons at ~ 7.2 ppm.

The ^{13}C NMR absorptions of the compounds IVa–IVd are shown in Table 1.

The boranes IV are presumably formed accordingly to the scheme suggested for the reaction of 1-boraadamantane ate complexes with AcCl [1], which involves elimination of a hydride ion from the β-position:

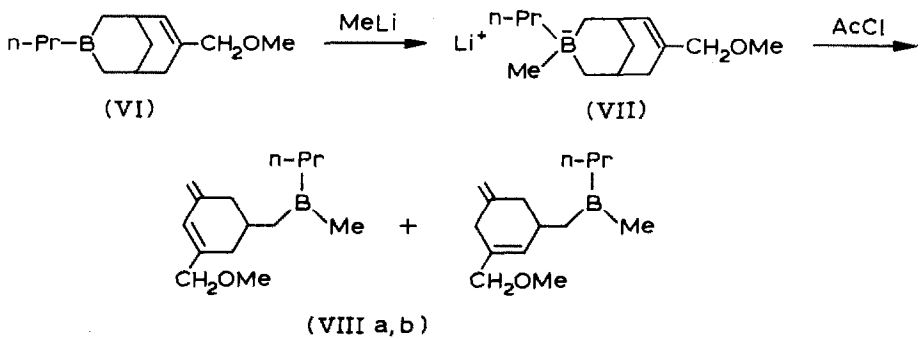


Along with the basic β-hydride-transfer reaction in the interaction of AcCl with the borates III, an intermolecular alkyl transfer of the Grignard reaction type is also observed. The formation of the products of the addition of the acyl group to the cyclic B–C bond was supported by IR spectral data; one of these products was isolated. Thus, the borate IIIf reacts with AcCl to produce IVf (76% yield) along with 3-acetonyl-5-methylenecyclohex-1-ylmethyl(n-butyl)(methyl)borane(V) in a 20% yield:



In the IR spectrum of V an intense absorption band is observed at 1720 cm^{-1} (ν(C=O)). The ^1H NMR spectrum contains a singlet of the acetonyl methyl protons at 2.05 ppm, a doublet of the acetonyl methylene protons at 2.22 ppm and a broadened singlet from the methyl protons of a boron-methyl group at 0.67 ppm.

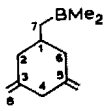
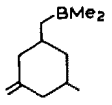
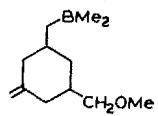
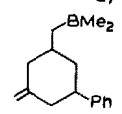
In order to clarify the regioselectivity of the hydride elimination, AcCl was treated with ate complexes of some 7-substituted 3-alkyl-3-borabicyclo[3.3.1]non-6-enes containing non-equivalent β-hydrogen atoms. Thus, as a result of the reaction of lithium 3-propyl-3-methyl-7-methoxymethyl-3-borabicyclo[3.3.1]non-6-enate (VII) ($\delta^{11}B$ NMR 20 ppm) with AcCl, a mixture of the two possible isomers (VIIIa,b) in approximately equal amounts was obtained:

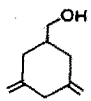
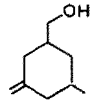
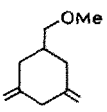


(Continued on p. 134)

TABLE 1

THE ^{13}C NMR CHEMICAL SHIFTS OF THE *exo*-METHYLENECYCLOHEXANE COMPOUNDS (ppm)

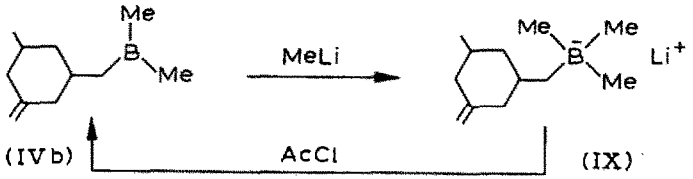
Compound	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	Others
a)  (IVa)	36.2	43.8	146.4	43.9	146.4	43.8	38.8	107.7	14.1 (CH_3–B)
a)  (IVb)	36.7	44.5 [d]	148.2	43.6	34.3	45.2 [d]	40.7	106.9	14.2 (CH_3B) 22.6 (CH_3)
a)  (IVc)	36.3	44.9	148.2	38.2	39.7	39.3	39.2	107.5	13.3 (CH_3B) 58.5 (CH_3O) 78.25 (CH_2O)
a)  (IVd)	36.8	44.3	147.9 [d]	42.5	45.6	43.8	40.3	107.7	14.1 (CH_3B) 125.8 126.4 128.1 146.1 [d] (Ph)

b)  (X)	41.7	37.7	147.0	44.5	147.0	37.7	66.4	103.3	
b)  (XI)	42.3	38.3 [d]	148.7	44.3	34.2	38.5 [d]	67.8	107.6	22.8 (CH_3)
c)  (XII)	145.7	43.3	145.7	43.3	145.7	43.3	107.7	107.7	
a)  (XIII)	33.9	43.1	146.7	44.0	146.7	43.1	21.4	108.0	
a)  (XIV)	38.9	37.7	146.2	44.3	146.2	37.7	76.7	108.1	58.5 (CH_3O)

[a] Neat. [b] In CD_3OD, [c] In $CDCl_3$. [d] These chemical shifts may be interchanged.

The presence of both isomers in the mixture was visible in the ^{1}H NMR spectrum, which exhibited two singlets from the CH_3O protons at 3.21 and 3.12 ppm, as well as in a double set of signals in the ^{13}C NMR spectrum.

It was interesting to apply the reaction under question to a complete dehydroboration of organoboron compounds for the preparation of purely organic derivatives of cyclohexane with two and even three methylene groups. However, the borate IX reacts with AcCl to give the initial borane IVb and acetone, i.e., in this case, another type of transformation, similar to the Grignard reaction, takes place:

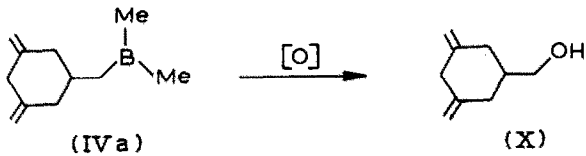


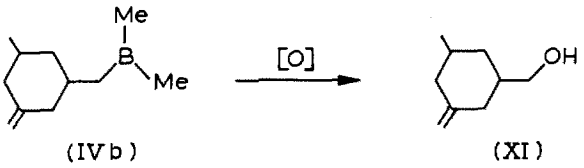
As noted above, other lithium tetraalkylborates can react with acyl halides in an analogous manner [2,3]. Thus, the β-hydride ion transfer in the reactions of the ate complexes of 1-boraadamantane, 7-substituted 3-alkyl-3-borabicyclo[3.3.1]nonanes and 3-alkyl-3-borabicyclo[3.3.1]non-6-enes may be accounted for by structural features of these compounds. One of these features is the anti-parallel disposition of the leaving groups, the hydride ion and the boron atom, in the ate complexes of 1-boraadamantane and of 3-alkyl-3-borabicyclo[3.3.1]nonanes, both in the chair-chair and chair-boat conformations.

One may draw a parallel between the reactions of ate complexes of 1-boraadamantane and 7-substituted 3-alkyl-3-borabicyclo[3.3.1]nonanes considered here and some reactions of adamantane and bicyclo[3.3.1]nonane, e.g. bromination, which are considered to proceed with the elimination of a hydride ion from the bridgehead carbon atoms [9,10].

It should be noted that di- and tri-methylene derivatives of cyclohexane are not so readily obtained. A series of methods for the preparation of *exo*-methylene cyclohexane derivatives is known; however, in some cases, especially in the synthesis of di- and tri-methylenecyclohexanes, these methods are very complicated and give low yields of the products. Thus, for example, 1,3,5-trimethylenecyclohexane is obtained by a catalytic oligomerization of allene in a yield of only 8%, along with 1,2,4-isomers and tetramers [11]. The methods known for the synthesis of functional derivatives of *exo*-methylenecyclohexane compounds are much complicated [12].

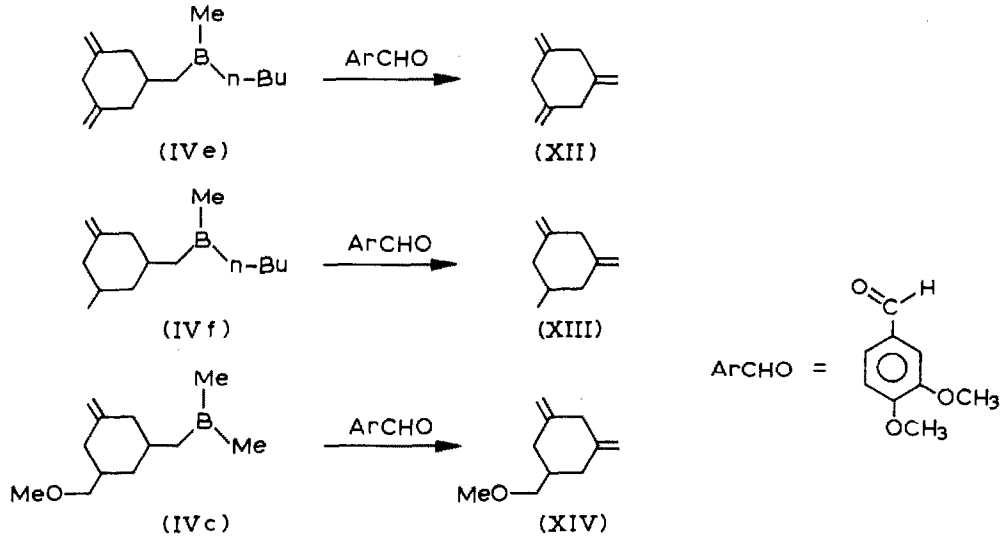
The methylene-substituted cyclohex-1-ylmethyl(dialkyl)boranes, obtained here have been applied to the synthesis of some *exo*-methylene derivatives of cyclohexane. We have obtained 1,3-dimethylene-5-hydroxymethylcyclohexane (X) and 1-methylene-*cis*-3-hydroxymethyl-5-methylcyclohexane (XI) by oxidation of the corresponding boranes, IVa and IVb, with alkaline hydrogen peroxide:



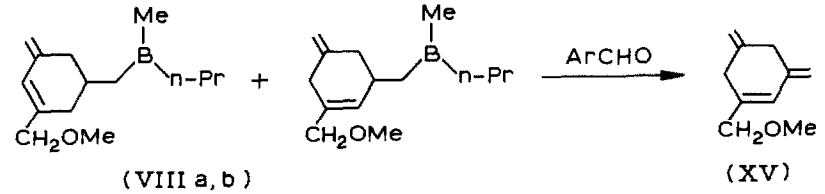


(IVb) (XI)

Cycloalkyl(dialkyl)boranes are known to form methylenecycloalkanes upon heating with aromatic aldehydes. In this way, methylenecyclohexane and methylenecyclopentane were obtained from tri(cyclohexylmethyl)borane and tri(cyclopentylmethyl)borane, respectively [13]. Application of this method to compounds IVc, IVe and IVf made it possible to effect the synthesis of 1,3,5-trimethylenecyclohexane (XII), 1,3-dimethylene-5-methylcyclohexane (XIII), and 1,3-dimethylene-5-methoxymethylcyclohexane (XIV):



1-Methoxymethyl-3,5-dimethylene-1-cyclohexene (XV) was synthesized from a mixture of isomers VIIIa and VIIIb and veratric aldehyde in an analogous manner:



Experimental

All organoboron compounds were manipulated in a stream of dry argon. ^{1}H NMR spectra were recorded on Tesla BS-497 (100 MHz) and on Bruker WM-250 (250 MHz) spectrometers (relative to TMS). ^{11}B NMR spectra were recorded on a

Bruker SXP/4-100 instrument (relative to $BF_3 \cdot OEt_2$, signals downfield relative to the etherate are positive). ^{13}C NMR spectra were obtained on a Bruker WM-250 spectrometer (effective carbon frequency 68.69 MHz). Assignment of the spectral lines was carried out using the off-resonance method and by comparison of the chemical shifts within a series of similar compounds. Assignment of the CH_2 group for compounds IVb, IVc, IVd and XI was carried out on the basis of additive calculations which were obtained with the use of β-effect increments of $CH_2=$, Me-, Ph-, and CH_2OMe groups as reported [14–17]. IR spectra were recorded on a UR-20 spectrometer and GLC analyses were carried out on a Chrom-3 chromatograph.

Starting organoboron compounds were prepared by known methods: 7-methylene-3-methyl-3-borabicyclo[3.3.1]nonane (IIa) and 7-methylene-3-n-butyl-3-borabicyclo[3.3.1]nonane (IIe) [1], 7-methoxymethyl-3-methyl-3-borabicyclo[3.3.1]nonane (IIc) [18], 3-methoxy-7-phenyl-3-borabicyclo[3.3.1]nonane [19], 7-methoxymethyl-3-allyl-3-borabicyclo[3.3.1]non-6-ene [20].

3,7-Dimethyl-3-borabicyclo[3.3.1]nonane (IIb)

To a solution of 26.4 g (0.13 mol) of tetrahydrofuran-1-boraadamantane (see ref. [21]) in 100 ml of ether were added at −68°C 100.5 ml (0.13 mol) of a 1.26 *M* solution of MeLi in ether. After heating to 20°C, the reaction mixture was stirred for 1 h. Upon cooling to −40°C, to the mixture were added dropwise 34.8 ml (0.13 mol) of a 3.68 *M* solution of ethereal HCl. After stirring for 1.5 h at −40°C, the mixture was heated to 20°C, with 570 ml of CH_4 (19%) being evolved (GLC). After filtering the solution and removing the solvent, the residue was distilled in vacuum to afford: 1) 11.63 g (67%) of IIb, b.p. 70–71°C (14 mmHg), n_D^{18} 1.4775 (lit.data: [18]); 2) 3.73 g (14%) of tetrahydrofuran-1-boraadamantane, m.p. 84–88°C (lit.data: [21]).

3,5-Dimethylenecyclohex-1-ylmethyl(dimethyl)borane (IVa)

To a solution of 11.8 g (80 mmol) of IIa in 30 ml of ether were added 50 ml (80 mmol) of a 1.59 *M* solution of MeLi in ether at −70°C. The mixture was then heated to 20°C and stirred for 1 h. After removing ether, 70 ml of pentane were added to the residue. To the mixture were added from a syringe via a septum inlet 7 ml (80 mmol) of freshly distilled (over CaH_2) AcCl. The resulted mixture was then maintained for 1 h at 0°C, heated to 20°C, and stirred for 1 h more. The solution thus obtained was decanted, and the precipitate was washed with 20 ml of pentane. The decanted layer and the extracts were combined and pentane was removed. Distillation of a residue gave 10.8 g (61%) of IVa, b.p. 62–64°C (8 mmHg), n_D^{19} 1.4708. Found: C, 81.24; H, 11.70; B, 6.80. $C_{11}H_{19}B$ calcd.: C, 81.51; H, 11.82; B, 6.67%. ^1H NMR ($CDCl_3$, δ, ppm): 0.78 s (6 H, CH_3B), 1.23 d (2 H, $J = 6.4$ Hz, CH_2B), 4.61 m (4H, $CH_2=$).

3-Methylene-5-methylcyclohex-1-ylmethyl(dimethyl)borane (IVb)

To a solution of 10.2 g (68.5 mmol) of IIa in 60 ml of ether were added 43 ml (68.6 mmol) of a 1.6 *M* solution of MeLi in ether at −40°C. The mixture was heated to 20°C and then stirred for 1 h. To the reaction mixture were added at 0–5°C 5.0 ml (68.5 mmol) of AcCl from a syringe via a septum inlet. The mixture was then stirred for 15 min at 0°C, heated to 20°C, and stirred for 1 h more. After removing ether, liquid products were distilled off in oil pump vacuum and collected in a

receiver chilled with dry ice. Distillation gave 8.0 g (71%) of IVb, b.p. 83–84°C (22 mmHg), n_D^{19} 1.4510. Found: C, 80.19; H, 12.82; B, 6.64. $C_{11}H_{21}B$ calcd.: C, 80.51; H, 12.90; B, 6.59%. ^1H NMR ($CDCl_3$, δ, ppm): 0.77 s (6 H, CH_3B), 0.91 d (3 H, CH_3C, $J = 6$ Hz), 1.19 d (2 H, CH_2B, $J = 7$ Hz), 4.58 m (2 H, $CH_2=$).

3,5-Dimethylenecyclohex-1-ylmethyl(n-butyl)(methyl)borane (IVe)

As described for IVa, a reaction of 10.5 g (55 mmol) of 7-methylene-3-n-butyl-3-borabicyclo[3.3.1]nonane (IIe) with 36 ml (55 mmol) of 1.54 *M* solution of MeLi and 3.9 ml (55 mmol) of AcCl afforded 6.0 g (55%) of IVe, b.p. 88–89°C (2 mmHg), n_D^{20} 1.4740. Found: C, 82.13; H, 12.30; B, 5.40. $C_{14}H_{25}B$ calcd.: C, 82.35; H, 12.34; B 5.30%. ^1H NMR ($CDCl_3$, δ, ppm): 0.78 s (3 H, CH_3B), 4.63 m (4 H, $CH_2=C$).

3-Methylene-5-methylcyclohex-1-ylmethyl(n-butyl)(methyl)borane (IVf)

To a solution of 11.5 g (77.5 mmol) of IIf in 50 ml of hexane at −65°C were added 37.8 ml (77.5 mmol) of a 2.05 *M* solution of n-butyllithium in hexane. The reaction mixture was heated to 20°C, stirred for 1 h, and cooled to 0°C, whereupon 5.5 ml (77.5 mmol) of AcCl were introduced from a syringe. The mixture was heated to 20°C with subsequent stirring during 1 h. After filtration of a precipitate and removal of the solvent, the residue was distilled to yield: 1) 9.1 g (76%) of IVf, b.p. 72–73°C (1.5 mmHg), n_D^{19} 1.4618. Found: C, 80.19; H, 12.79; B, 6.13. $C_{14}H_{27}B$ calcd.: C, 81.56; H, 13.20; B, 5.25%. ^1H NMR ($CDCl_3$, δ, ppm): 4.60 m (2 H, $CH_2=C$); 2) 3.2 g (20%) of V, b.p. 128–130°C (1.5 mm Hg), n_D^{20} 1.4610. Found: C, 76.27; H, 12.28; B, 4.53. $C_{16}H_{31}BO$ calcd.: C, 76.79; H, 12.49; B, 4.32%. ^1H NMR ($CDCl_3$, δ, ppm): 0.68 s (3 H, CH_3B), 2.05 s (3 H, CH_3CO), 2.22 d (2 H, $CO-CH_2-C$).

IVf contains a small amount of V (by IR spectroscopy).

3-Methoxymethyl-5-methylenecyclohex-1-ylmethyl(dimethyl)borane (IVc)

As described for IVa, from 12.1 g (67 mmol) of IIc, 42 ml (67 mmol) of a 1.6 *M* ethereal solution of MeLi and 4.8 ml (67 mmol) of AcCl were obtained 10.9 g (84%) of IVc, b.p. 69–70°C (1.5 mmHg), n_D^{26} 1.4550. Found: C, 74.12; H, 12.15; B, 5.54. $C_{12}H_{23}BO$ calcd.: C, 74.24; H, 11.94; B, 5.57%. ^1H NMR ($CDCl_3$, δ, ppm): 0.77 s (6 H, CH_3B), 1.22 d (2 H, CH_2B, $J = 7$ Hz), 3.21 d (2 H, CH_2O, $J = 6$ Hz), 3.32 s (3 H, CH_3O), 4.63 m (2 H, $CH_2=C$).

7-Phenyl-3-methyl-3-borabicyclo[3.3.1]nonane (IId)

To a solution of 13.4 g (59 mmol) of 7-phenyl-3-methoxy-3-borabicyclo[3.3.1]nonane in 50 ml of hexane were added 68 ml (60 mmol) of MeMgI (from 1.45 g (60 mmol) of Mg and 3.7 ml (60 mmol) of MeI in 60 ml of ether). The mixture was stirred for 1 h and then refluxed during 1 h. Ether was distilled off, and 120 ml of hexane were added to the residue. Filtration of the precipitate, evaporation of hexane and subsequent high-vacuum distillation produced 8.8 g (71%) of IId, b.p. 88–89°C (1.5×10^{-2} mmHg), n_D^{21} 1.5420. Found: C, 84.65; H, 10.15; B, 4.88. $C_{15}H_{21}B$ calcd.: C, 84.94; H, 9.98; B, 5.10%. ^1H NMR ($CDCl_3$, δ, ppm): −0.13 s (3 H, CH_3B), 7.02 m (5 H, phenyl protons).

3-Phenyl-5-methylenecyclohex-1-ylmethyl(dimethyl)borane (IVd)

As described above, from 8.8 g (41 mmol) of IId, 26.6 ml (41 mmol) of 1.55 *M*

ethereal MeLi and 3.0 ml (41 mmol) of AcCl were obtained 5.4 g (59%) of IVd, b.p. 86–87°C (1.5×10^{-2} mmHg), n_D^{19} 1.5177. Found: C, 84.55; H, 10.19; B, 4.61. $C_{16}H_{23}B$ calcd.: C, 84.96; H, 10.25; B, 4.78%. ^{1}H NMR ($CDCl_3$, δ, ppm): 0.78 s (6 H, CH_3B), 1.25 d (2 H, CH_2B, $J = 7$ Hz), 4.68 m (2 H, CH_2=C), 7.2 m (5 H, phenyl protons).

7-Methoxymethyl-3-propyl-3-borabicyclo[3.3.1]non-6-ene (VI)

Into a hydrogenizing apparatus were placed 0.4 g of Pt black and a solution of 32.1 g (156 mmol) of 7-methoxymethyl-3-allyl-3-borabicyclo[3.3.1]non-6-ene in 70 ml of hexane.Vigorous shaking during 5 h was accompanied by absorption of 3605 ml (160 mmol) of hydrogen. The solution was then filtered through a paper filter to remove the catalyst. After removing hexane, the residue was distilled to yield 26.0 g (81%) of VI, b.p. 96–98°C (2 mmHg), n_D^{20} 1.4847. Found: C, 75.38; H, 11.14; B, 5.35. $C_{13}H_{23}BO$ calcd.: C, 75.74; H, 11.25; B, 5.25%. ^{1}H NMR ($CDCl_3$, δ, ppm): 3.12 s (3 H, CH_3O), 3.56 s (2 H, C–CH_2–O), 5.56 d (C=CH).

5-Methylene-3-methoxymethylcyclohex-2-en-1-ylmethyl(propyl)(methyl)borane (VIIIa) and 5-methylene-3-methoxymethylcyclohex-3-en-1-ylmethyl(propyl)(methyl)borane (VIIIb)

As described for IVa, from 14.1 g (68.5 mmol) of VI, 51.5 ml (68.5 mmol) of 1.33 *M* ethereal MeLi and 4.9 ml (68.5 mmol) of AcCl were obtained 10.4 g (69%) of a mixture of VIIIa and VIIIb, b.p. 92–95°C (1.5 mmHg), n_D^{20} 1.4820. Found: C, 76.05; H, 11.77; B, 4.96. $C_{14}H_{25}BO$ calcd.: C, 76.37; H, 11.45; B, 4.91%. ^{1}H NMR ($CDCl_3$, δ, ppm): 3.19 s (3 H, CH_3O), 3.24 s (3 H, CH_3O) (intensity ratio 2 : 3), 3.67–3.76 m (4 H, C–CH_2O), 4.73 m (4 H, CH_2=C), 5.54–5.68 m (2 H, C=CH).

1,3-Dimethylene-5-hydroxymethylcyclohexane (X)

To a solution of 5.7 g (36 mmol) of IVa in 30 ml of ether at −3°C were added 1.4 g (36 mmol) of NaOH in 14 ml of H_2O. To the mixture were then added 17.6 ml (115 mmol) of a 30% solution of H_2O_2. The mixture was stirred for 30 min at 0°C, for 1 h at 20°C, and thereupon refluxed during 30 min. After cooling to 20°C, the mixture was extracted with ether (3 × 20 ml). The combined ethereal extracts were dried over Na_2SO_4. Ether was removed, and distillation of the residue gave 3.0 g (55%) of X, b.p. 80–81°C (2 mmHg), n_D^{19} 1.5018. Found: C, 78.32; H, 10.37. $C_9H_{14}O$ calcd.: C, 78.26; H, 10.27%. ^{1}H NMR ($CDCl_3$, δ, ppm); 3.08 s (1 H, OH), 3.36 d (2 H, C–CH_2O), 4.67 m (4 H, CH_2=C).

1-Methylene-cis-3-hydroxymethyl-5-methylcyclohexane (XI)

As described for X, from 6.5 g (39 mmol) of IVb, 1.6 g (39 mmol) of NaOH in 7.4 ml of H_2O and 21 ml (125 mmol) of 30% H_2O_2 were obtained 4.3 g (77%) of XI, b.p. 74–75°C (2 mmHg), n_D^{19} 1.4788. Found: C, 76.89; H, 11.69. $C_9H_{16}O$ calcd.: C, 77.14; H, 11.51%. ^{1}H NMR ($CDCl_3$, δ, ppm): 0.96 d (3 H, CH_3–C, J 6.75 Hz), 3.20 broad.s (1 H, OH) 3.45 d (2 H, CH_2O, $J = 6$ Hz), 4.63 m (2 H, CH_2=C).

1,3,5-Trimethylenecyclohexane (XII)

In a distillation flask were placed a mixture of 4.5 g (28 mmol) of veratraldehyde and 4.98 g (24 mmol) of IVe. The mixture was heated to 150°C (oil bath). A product was obtained as volatile white needles by distillation at ~ 50°C (30 mmHg).

Sublimation of the product yielded 2.0 g (55%) of XII, m.p. 34–35°C (see [11]). The compound XII contains 0.8–1% of unidentified impurities (GLC). ^{1}H NMR ($CDCl_3$, δ, ppm): 2.92 quintet (6 H, $-CH_2-$), 4.67 quintet (6 H, $CH_2=C$).

1,3-Dimethylene-5-methylcyclohexane (XIII)

As described for XII, from a mixture of 5.2 g (32 mmol) of veratraldehyde and 6.6 g (32 mmol) of IVf were obtained 1.86 g (48%) of XIII, b.p. 55–56°C (39 mm Hg), n_D^{20} 1.4655. Found: C, 88.20; H, 11.65. C_9H_{14} calcd.: C, 88.45; H, 11.55%. ^{1}H NMR ($CDCl_3$, δ, ppm): 0.93 d (3 H, CH_3C, $J = 6.5$ Hz), 4.63 m (4 H, $CH_2=C$). XIII contains less than 2% impurities (GLC).

1,3-Dimethylene-5-methoxymethylcyclohexane (XIV)

Analogously to XII, from 7.0 g (49 mmol) of veratraldehyde and 7.7 g (40 mmol) of IVc were obtained 2.5 g (41%) of XIV, b.p. 84–85°C (23 mmHg), n_D^{20} 1.4740. Found: C, 78.97; H, 10.71. $C_{10}H_{16}O$ calcd.: C, 78.89; H, 10.59%. The compound is of 98% purity (GLC). ^{1}H NMR ($CDCL_3$, δ, ppm): 3.23 d (2 H, CH_2O, $J = 6$ Hz), 3.32 s (3 H, CH_3O), 4.66 m (4 H, $CH_2=C$).

1-Methoxymethyl-3,5-dimethylenecyclohex-1-ene (XV)

Analogously to XII, from 5.7 g (34 mmol) of veratraldehyde and 7.5 g (34 mmol) of a mixture of VIIIa and VIIIb were obtained 1.8 g (35%) of XV, b.p. 92–93°C (22 mmHg), n_D^{19} 1.5141. Found: C, 79.65; H, 9.43. $C_{10}H_{14}O$ calcd.: C, 79.95; H, 9.39% (99% purity by GLC). ^{1}H NMR ($CDCl_3$, δ, ppm): 2.76 and 2.97 ($-CH_2-$), 3.22 s (3 H, CH_3O), 3.80 s (2 H, $C-CH_2-O$), 4.75 m (4 H, $CH_2=C$).

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