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# REGIOSELECTIVE β-HYDRIDE TRANSFER IN REACTIONS OF ATE COMPLEXES OF BORON BICYCLIC AND CAGE COMPOUNDS. SYNTHESIS OF METHYLENECYCLOHEXANE DERIVATIVES(*)

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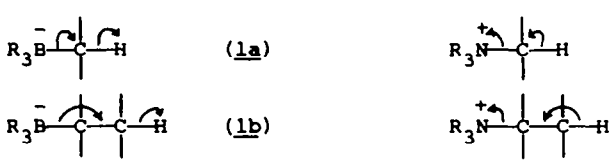
Summary. The reactions of bicyclic and cage boron containing ate complexes with AcCl have been studied, the key stage of which involves β-bridgehead hydride abstraction. The ate complexes of 7-substituted 3-methyl-3-borabicyclo[3.3.1]non-6-ene were converted to the corresponding 5-methylene-3-alkylcyclohex-2(3)-en-1-ylmethyl(dialkyl)boranes 14 and 15. A synthetic application of the reaction is illustrated by conversion of compounds 14 and 15 to 3,5-dimethylene-1-R-cyclohexenes 16, particularly to 3,5-dimethylene-1-isopropenylcyclohexene (16c). The β-hydride transfer in ate complexes of 2-alkyl-1-boraadamantane and of 4-alkyl-3-borahomoadamantane occurs regioselectively, at the unsubstituted bridgehead, to give, respectively, 2-alkyl-7-methylene-3-borabicyclo[3.3.1]nonanes and 8-methylene-3-borabicyclo[4.3.1]decanes.

Boron chemistry has enriched organic synthesis with a series of new, highly effective methods [1-6]. Boron compounds have found wide application as reagents for the reduction of functional groups and multiple bonds [1,6]. Most organic chemists associate the reductive effect of boron derivatives with hydrides only, including boranes, their complexes (with ethers, amines, sulfides), and hydroborates, $[R_3BH]M$.

It is less known that triorganoboranes and tetraorganoborates can, in some cases, be used as hydride sources. Here the hydride is "generated" at the expense of a heterolytic rupture of α-C-H and β-C-H bonds. Such reactions are already used in synthetic practice not only for the reduction of functional groups but also for the preparation of certain types of organic compounds.

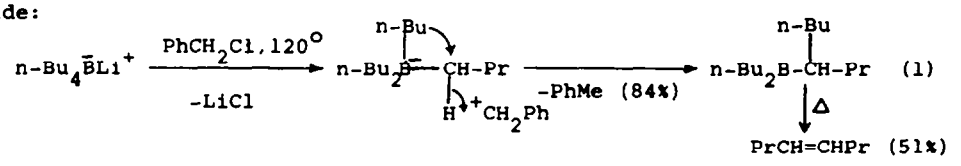
As far back as the 1950's, Wittig [7] compared electronic effects in alkyl borates with those in onium salts and predicted hydride mobility for α- and β-hydrogen in ate complexes (1a,b).



(1a) (1b)

(*) This paper is dedicated to the memory of our teacher Professor B.M.Mikhailov (1906-1984).

Reactions proceeding with hydride abstraction from the α-carbon atom in ate complexes were first performed by Jäger and Hesse [8], who obtained toluene (84%) and 4-octene (51.3%) by heating lithium tetrabutylborate with benzyl chloride:

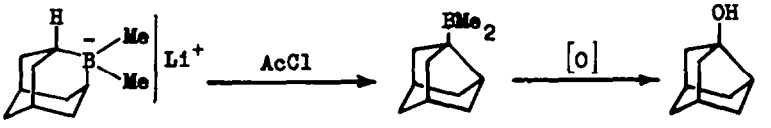


(1)

The principal step of this process consists of the transfer of $H^-$ from α-C-H to the electrophile with simultaneous migration of a butyl group from the negatively charged boron to the neighbouring electron-deficient α-carbon to form a new C-C bond.

Tetraorganoborates with secondary alkyl groups split off α-hydride under milder conditions and can be used for the reduction of various functional groups. Thus, 9-alkyl-BBN ate complexes reduce active halides, oxiranes, and carbonyl compounds.[9,10] In these reactions, the 9-borabicyclo[3.3.1]nonane system rearranges to a bicyclo[3.3.0]octane.

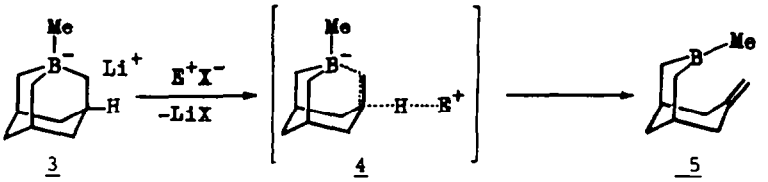
The α-hydride transfer reaction has been used to prepare noradamantane compounds from 2-boraadamantane [11]:



(2)

2

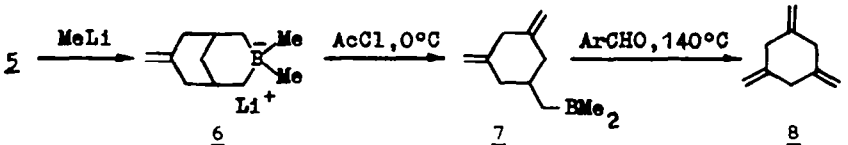
In contrast, the 1-boraadamantane borates react with electrophiles in a fundamentally different way. For example, Mikhailov and co-workers [12] prepared 7-methylene-3-borabicyclo[3.3.1]nonane (5) by treating compound 3 with AcCl in 75% yield:



(3)

3 4 5

Here the electrophile removes $H^-$ from the β-bridgehead carbon atom. The anti-disposition of leaving groups (hydride and boryl fragments) in the hypothetical transition state 4 explains the unusual ease of effecting this specific elimination reaction (3 hours at 0-20°C). A similar reaction of ate complex 6, obtained from 5, with AcCl resulted in the boron dimethylene derivative 7 [13,14]:

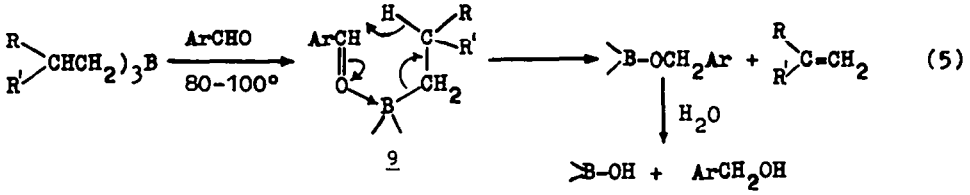


(4)

6 7 8

Heating compound 7 with veratraldehyde produces 1,3,5-trimethylenecyclohexane (8) [13,14].

The conversion of 7 to 8 also occurs via β-hydride abstraction (reductive effect of trialkylboranes). This reaction has previously been used for the preparation of pure olefins [15], counter-thermodynamic isomerisation of methylcyclenes to methylenecyclanes,[16,17] and also for the reduction of carbonyl compounds to the corresponding alcohols,[15,17-21] including chiral carbinols [22-24]. It is quite reasonable to suggest [15,17,19,24] that, unlike reaction (3), organoboranes react with aromatic aldehydes via a cyclic six-member transition state 9.

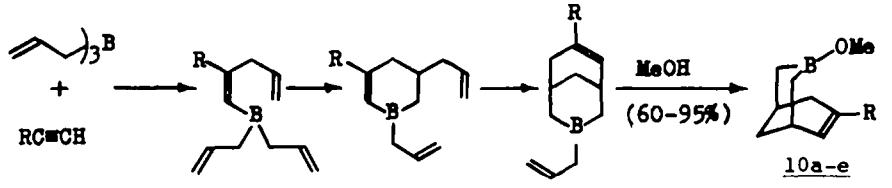



(5)

9

In this paper we report an application of these two reactions of β-hydride transfer to the synthesis of a series of new mono- and dimethylene cyclohexane derivatives starting with 3-borabicyclo[3.3.1]non-6-ene compounds and 2-substituted 1-boraadamantanes.

The 3-borabicyclo[3.3.1]non-6-ene derivatives 10 used in this work were obtained from triallylborane and appropriate acetylenes (the allylboron-acetylene condensation) [5,25,26].

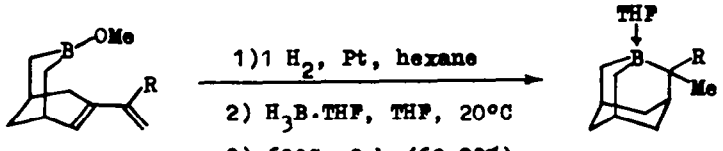



(6)

10a-e

a, R= H
b, R= Me
c, R= $CH_2$=C(Me)-
d, R= $CH_2$=CH-
e, R=

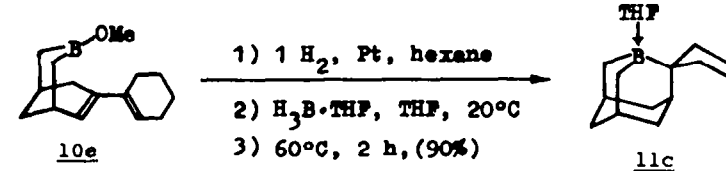
Complexes of 2-susbstituted 1-boraadamantanes with tetrahydrofuran 11a,b,c were synthesized in 60-90% yield from 7-vinyl- (10d), 7-isopropenyl- (10c) and 7-cyclohexenyl-3-methoxy-3-borabicyclo[3.3.1]non-6-ene (10e) in two stages: (1) catalytic monohydrogenation, (2) hydroboration with $H_3B$·THF followed by heating for 2 hours at 60°C:




(7)

10c,d

11a, R= H
b, R= Me



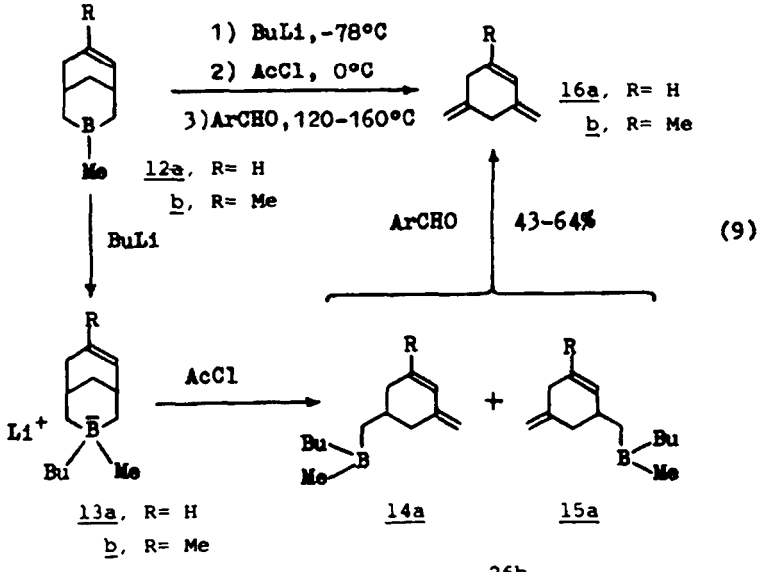

(8)

10e

11c

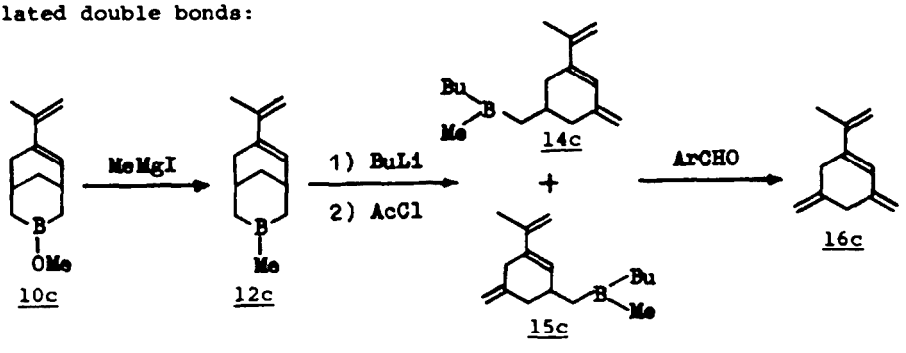
Treatment of borate 13a prepared from butyllithium and 3-methyl-3-borabicyclo[3.3.1]non-6-ene (12a) with AcCl leads to a mixture of two isomeric organoboron dienes 14a and 15a in 68% yield [26a]. Subsequent heating of the mixture with veratraldehyde (120-150°C) gave 3,5-dimethylenecyclohexene (16a) in 64% yield with the overall yield of triene 16a from bicycle 12a equal to 43%.

In a similar manner, 3,5-dimethylene-1-methylcyclohexene (16b) was synthesized in an overall yield of 23% from 3,7-dimethyl-3-borabicyclo[3.3.1]-non-6-ene (12b). Borate 13b reacts with AcCl to afford a mixture of dienes 14b and 15b in a ratio of ~1:1. Hence it follows that there is no decisive difference in the ease of hydride abstraction from the 1 and 5 positions, although one of them is of allylic character.




(9)

Combination of the three consecutive reactions [26b] summarized in Scheme 9 has been used to prepare 1-isopropenyl-3,5-dimethylenecyclohexene (16c), an interesting tetraene hydrocarbon containing a system of both conjugated and isolated double bonds:




(10)

Starting 7-isopropenyl-3-methyl-3-borabicyclo[3.3.1]non-6-ene (12c) was synthesized by treating 3-methoxy-7-isopropenyl-3-borabicyclo[3.3.1]non-6-ene [26] with methylmagnesium iodide.

Polyene compounds 16a,b,c can be used for the synthesis of various organic substances and also for elucidating the mechanism of many types of addition reactions. It is noteworthy that di- and trimethylenecyclohexanes have so far been difficult to obtain. For instance, compound 8 was obtained by a cataly-

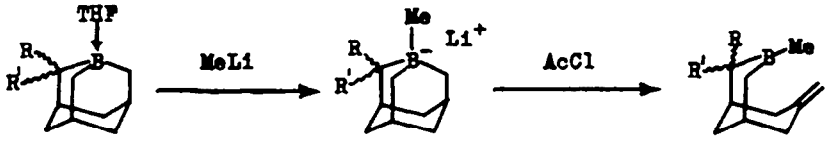
tic oligomerisation of allene in 8% yield, along with its 1,2,4-isomer, tetramers and other compounds [27,28].

We further attempted to apply the β-hydride transfer reactions to the preparation of trienic compounds of the type 17 and 18 using 1-boraadamantane derivatives with one or two substituents in the 2 position:

(11)

11a, R=H; b, R=Me — 17 — 11c — 18 — L= THF

So far, however, our efforts in this direction have been unsuccessful. The action of methyllithium (from MeBr and Li in ether) on complexes of 2-methyl- (11a), 2,2-dimethyl- (11b) and 2,2-pentamethylene-1-boraadamantane (11c) with THF resulted in corresponding ate complexes 19. Their reactions with acetyl chloride proved to proceed in an usual way with a high degree of regioselectivity and to lead, in all cases studied, only to bicyclic compounds with an exo-methylene bond (20a,b,c) [28a], i.e. the hydride transfer involves only the unsubstituted bridge of 1-boraadamantane compounds.

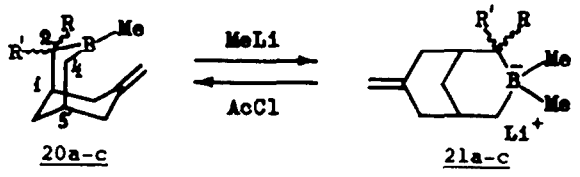


(12)

11a, R=H, R' = Me; b, R= R' = Me; c, R+R' = $(CH_2)_5$ — 20a, R= H, R' = Me; b, R= R' = Me; c, R+R' = $(CH_2)_5$

Thus, alkyl substituents in the α-position with respect to boron in the ate complexes have a deactivating effect on the abstraction of the bridgehead β-hydride.

When reacted with MeLi (from MeBr and Li), bicyclic compounds 20a,b,c produce the corresponding ate complexes 21a,b,c, which is confirmed by $^{11}B$ NMR spectral data: $\delta$ ($^{11}B$)= 18.9 ppm for 21a and 18.6 ppm for 21b. Nevertheless, the action of acetyl chloride on these compounds results not in the expected β-hydride abstraction but in the transfer of a Me group to AcCl (a Grignard type reaction [28b]) and formation of the starting bicycles.



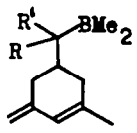
(13)

20a-c — 21a-c

This behaviour of borates 21 is difficult to understand. Formation of the double bond from the $C_1$-$C_2$ fragment can be impeded by purely steric factors, i.e. due to the hampered approach of an AcCl molecule to the hydrogen atom linked to $C_1$ of the bicyclic system (H-$C_1$). But what keeps β-elimination in the unsubstituted fragment $C_4$-$C_5$ from taking place?

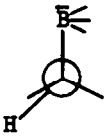
Even more surprising is the fact that borates 21, synthesised using MeLi prepared from MeI and Li, afford the desired compounds of the type 7 when treated with AcCl. The compounds 7, however, isomerise during the reaction to products with conjugated bonds (14d). The double bond shift from the exo-position to the ring may be induced by traces of iodine evolved on workup of the reaction mixture.

Ease of elimination in the bicyclic ate complexes 21 apparently depends to a large extent on their conformations. Elimination readily occurs when boron and β-hydrogen atom are antidisposed and lie at an angle of 180° (22), which exists in a chair-chair conformation. On the other hand, the reaction should be prevented in the case of anti-clinal disposition of leaving groups, when they lie at an angle of 120° in a chair-boat conformation (23).



14d

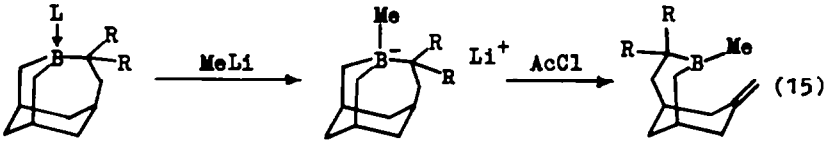
22



23

(14)

β-Hydride transfer in the reaction of acetyl chloride with 3-borahomoadamantane ate complexes 25a,b also proceeds regioselectively, the reaction products being the corresponding 8-methylene-3-borabicyclo[4.3.1]decanes (26).



(15)

24a, R= H, L= $Me_3N$ 25a, R= H 26a, R= H

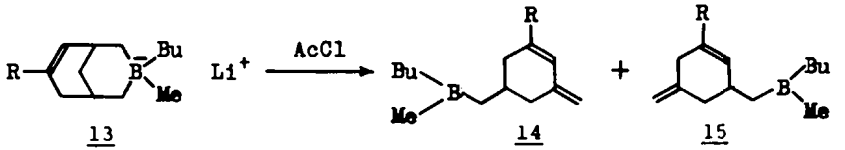
b, R= Me, L= THF b, R= Me b, R= Me

In the case of ate complexes obtained from 26 and methyllithium (from MeBr), again β-abstraction does not occur: when reacted with AcCl, they produce starting bicycles 26.

It should be pointed out that ate complexes of 3-borabicyclo[3.3.1]nonane [13,14] and 3-borabicyclo[4.3.1]decane [29], which have 7-endo-substituents, easily undergo the β-hydride transfer reaction.

This work has therefore demonstrated that β-hydride abstraction from ate complexes of bicyclic and cage boron compounds may be used successfully for

Table 1




13 14 15

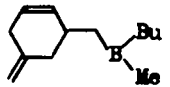
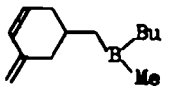
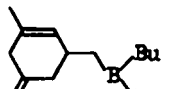
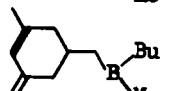
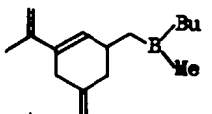
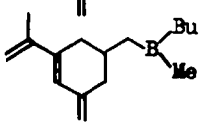
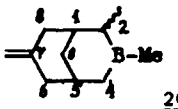
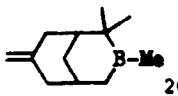
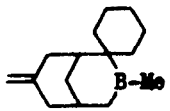
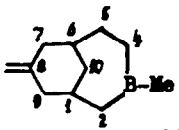
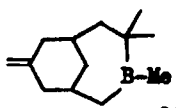
| Compound | | Yield %(g) | B.p. °C/mm | $n_D^{20}$ | IR ν CH=C $CH_2$=C | $^1$H NMR (δ, ppm) |
|---|---|---|---|---|---|---|
|  | 15a | 68(13.08) | 72-74/2 | 1.4775 | 889(δ) 1625sh,1640sh, 1652 3024,3064,3080 | 0.77(3H,$CH_3$-B), 4.59 and 4.65, 4.70 and 4.76(2H,$CH_2$=C), 5.42 and 5.70 (CH=CH) |
|  | 14a | | | | | |
|  | 15b | 55(15.9) | 68-70/1 | 1.4789 | 889(δ) 1612,1630sh, 1643 3030sh,3080 | 0.78(3H,$CH_3$-B), 1.67 and 1.76 ($CH_3$-C=C), 4.62 and 4.67, 4.69 and 4.74(2H,$CH_2$=C), 5.23(CH=C), 5.92(CH=C-C=C) |
|  | 14b | | | | | |
|  | 15c | 70(15.84) | 95-98/0.2 | 1.5095 | 889(δ) 1610,1621sh, 1633,1650 3040,3085sh, 3099 | 4.7-5.13(2H,$CH_2$=C), 5.89(CH=C-C=C), 6.30(C=C-C=CH-C=C) |
|  | 14c | | | | | |

Table 2. Properties of boron bicyclic compounds

| Compound | Yield % (g) | B.p. °C/mm $n_D^{20}$ | IR $\nu$, $cm^{-1}$ | $^1$H NMR ($\delta$, ppm) | $^{13}$C NMR ($\delta$, ppm) |
|---|---|---|---|---|---|
|  20a*) | 80(16.4) | 67-71/7 1.4875 | 895($\delta$) 1648 3078 | 0.62(s,3H,$CH_3$-B), 0.85(d) and 0.99 (d,6H,$CH_3$-C),4.57-4.69(m,2H,$CH_2$=C) | 15.05, 15.2($CH_3$);30.1, 37.3, 37.8, 44.1($CH_2$);34.9, 39.5(C-5);42.0, 42.3 (C-1);44.3, 44.6(C-6);112.8, 113.05 ($\underline{C}H_2$=C);146.9, 147.1(C-7) |
|  20b | 64(11.2) | 86-87/7 m.p.127-130° | 895($\delta$) 1650 3075 | 0.63(s,3H,$CH_3$-B), 4.60 and 4.69(2H, $CH_2$=C) | 24.7, 25.05($CH_3$);32.5, 39.4(C-8,9); 35.6(C-5);44.6(C-6);48.15(C-1); 112.2($\underline{C}H_2$=C);147.1(C-7) |
|  20c | 65(10.8) | 108-110/2 1.5208 | 895($\delta$) 1649 3075 | 0.63(s,3H,$CH_3$-B), 4.59 and 4.71 ($CH_2$=C) | 8.8($CH_3$-B);20.15, 20.2, 27.1, 30.6, 30.7, 31.5, 38.1($CH_2$);32.0(C-4); 35.6(C-5);36.6(C-1);44.7(C-6); 112.7($\underline{C}H_2$=C);147.3(C-7) |
|  26a | 41(4.0) | 84-86/11 1.4958 | 888($\delta$) 1645 3075 | 0.60(3H,$CH_3$-B), 4.6($CH_2$=C) | 13.8($CH_3$-B);28.3, 36.4(C-2,4);32.9 (C-6);33.5(C-10);34.9(C-1);38.4(C-5); 40.1(C-7);42.8(C-9);114.3($\underline{C}H_2$=C); 147.0(C-8) |
|  26b | 77(8.5) | 63-65/1.5 1.4932 | 890($\delta$) 1650 3075 | 0.68(s,3H,$CH_3$-B), 0.72(s) and 0.94 (s,6H,$CH_3$-C), 4.72(2H,$CH_2$=C) | 10.3($CH_3$-B);24.1, 24.25($CH_3$);30.4, 30.8(C-1,6);34.4(C-10);40.7(C-7); 43.5(C-9);44.0(C-5);113.0($\underline{C}H_2$=C); 144.5(C-8) |

*) A mixture of exo-methyl- and endo-methyl-isomers (~1:1)

the synthesis of trienic and tetraenic derivatives of cyclohexene and substituted 7-methylene-3-borabicyclo[3.3.1]nonanes. In the course of the investigation, certain limitations to applicability of the reaction have been revealed.

## Experimental

All operations with organoboron compounds were carried out under dry argon. $^1$H NMR spectra were recorded on TESLA BS-497 (100 MHz) and BRUKER WM-250 instruments relative to TMS. $^{11}$B NMR spectra were obtained on a BRUKER SXP/4-100 spectrometer relative to $BF_3 \cdot Et_2O$. $^{13}$C NMR spectra were recorded on a BRUKER WM-250 spectrometer (68.69 MHz for carbon). Assignment of spectral lines was carried out using the off-resonance method and by comparison of chemical shifts of a series of related compounds on the basis of available data [12,14,29,30].

IR spectra were obtained on a UR-20 instrument from solutions in $CCl_4$.

Methyllithium was prepared from MeBr and lithium in ether or from MeI and lithium in ether. The complex of 3-borahomoadamantane with $Et_3N$ was synthesized by a known method [31] and 4,4-dimethyl-3-borahomoadamantane was prepared as described previously [32].

3-Methyl-3-borabicyclo[3.3.1]non-6-ene (12a)

To a solution of MeMgI (from 6.5 g of magnesium and 15 ml of MeI in 100 ml of ether) was added 28.7 g of 3-methoxy-3-borabicyclo[3.3.1]non-6-ene [33] during 2 hours. The mixture was boiled for 1 hour, the ether layer was then separated and the residue extracted with hexane (4x50 ml). Distillation gave 19 g (74.2%) of 12a, b.p. 56-57°C/13 mm Hg, $n_D^{18}$ 1.4885.

$^1$H NMR ($CCl_4$, $\delta$, ppm) 0.65 (s, $CH_3$), 1.2-1.26 (m, 10 H), 5.5 (m, CH=C). IR: 1645, 3018, 3060 (C=CH) $cm^{-1}$ (Found: C 80.65, H 11.35, B 7.73. Calcd. for $C_9H_{15}B$: C 80.65, H 11.28, B 8.07%).

3,7-Dimethyl-3-borabicyclo[3.3.1]non-6-ene (12b)

This was prepared in an analogous way from 31.3 g of 3-methoxy-7-methyl-3-borabicyclo[3.3.1]non-6-ene (10b) [33] and MeMgI (from 5 g of Mg and 13.5 ml of MeI in 100 ml of ether) in 78.6 % yield (22.17 g), b.p. 49-50°C/6 mm Hg, $n_D^{22}$ 1.4819.

$^1$H NMR ($CDCl_3$, $\delta$, ppm) 0.65 (s, 3 H, B-$CH_3$), 1.57 (s, 3 H, $CH_3$-C=C), 5.42 (m, 1 H, CH=C) (Found: C 80.65, H 11.72, B 7.42. Calcd. for $C_{10}H_{17}B$: C 81.12, H 11.57, B 7.30%).

7-Isopropenyl-3-methyl-3-borabicyclo[3.3.1]non-6-ene (12c)

The compound was obtained (17.4 g, 73%) analogously from 26 g of 3-methoxy-7-isopropenyl-3-borabicyclo[3.3.1]non-6-ene (10c) [26] and MeMgI (from 3.16 g of Mg and 8.2 ml of MeI), b.p. 59-60°C/1 mm Hg, $n_D^{20}$ 1.5155.

$^1$H NMR ($CDCl_3$, $\delta$, ppm) 0.63 (s, 3 H, B-$CH_3$), 1.85 (s, 3 H, $CH_3$-C=C), 4.89 and 4.91 (s, 2 H, $CH_2$=C), 5.89 (d, CH=C) (Found: C 82.83, H 11.19, B 5.99. Calcd. for $C_{12}H_{19}B$: C 82.79, H 11.00, B 6.21%).

Complex of 2-methyl-1-boraadamantane with THF (11a)

22.8 g of 3-methoxy-7-vinyl-3-borabicyclo[3.3.1]non-6-ene (10d) [26] was hydrogenated (1 atm $H_2$, 0.2 g of Pt, 30 ml of hexane) with absorption of 2.9 l of hydrogen. Filtration and subsequent distillation gave 21 g (91%) of a fraction with b.p. 61-62°C/1 mm Hg, $n_D^{20}$ 1.4861, which is a mixture of 3-methoxy-7-ethylidene-3-borabicyclo[3.3.1]nonane and 3-methoxy-7-ethyl-3-borabicyclo-[3.3.1]non-6-ene [34] (NMR). (Found: C 73.93, H 10.75, B 5.96. Calcd. for $C_{11}H_{19}BO$: C 74.19, H 10.75, B 6.07%). 20.6 g of this fraction was dissolved in 40 ml of THF and 50 ml of 1M solution of $H_3B \cdot THF$ was added (heat evolution

took place to 40°C). After boiling for 2 hours the mixture was distilled to afford 20.1 g (82.7%) of complex 11a, b.p. 83-85°C/2 mm Hg, $n_D^{20}$ 1.4996 (Found: C 75.55, H 11.59, B 5.67. Calcd. for $C_{14}H_{25}BO$: C 76.38, H 11.45, B 4.91%).

Complex of 2,2-dimethyl-1-boraadamantane with THF (11b)

29.1 g of 3-methoxy-7-isopropenyl-3-borabicyclo[3.3.1]non-6-ene (10c) [26] in 50 ml of hexane was hydrogenated over 0.5 g of Pt black at 1 atm $H_2$ to take up 3.4 l of hydrogen. Distillation gave a fraction (26.3 g, 89.3%) with b.p. 65-66°C/2 mm Hg, $n_D^{22}$ 1.4875, which is a mixture of 3-methoxy-7-isopropylidene-3-borabicyclo[3.3.1]nonane and 3-methoxy-7-isopropyl-3-borabicyclo[3.3.1]non-6-ene [34]. To 12.74 g of the latter mixture was added 30 ml of a solution of $H_3B$·THF (1.4 M). Boiling the mixture during 2 hours and removal of volatiles under reduced pressure (2 mm Hg) gave 10.15 g (61.8%) of complex 11b, b.p. 62-63°C/2 mm Hg, $n_D^{22}$ 1.5186 (Found: C 76.66, H 11.69, B 4.91. Calcd. for $C_{15}H_{27}BO$: C 76.93, H 11.62, B 4.62%).

Complex of 2,2-pentamethylene-1-boraadamantane with THF (11c)

3-Methoxy-7-(1-cyclohexenyl)-3-borabicyclo[3.3.1]non-6-ene (10e) [35] (40.6 g) was hydrogenated in 60 ml of hexane over 0.5 g of Pt black, 3.9 l of hydrogen was absorbed for 8 hours. The catalyst was filtered off, and distillation produced a fraction with b.p. 98-99°C/2 mm Hg, $n_D^{22}$ 1.5149 (35.6 g, 87%), which is a mixture of 3-methoxy-7-cyclohexyl-3-borabicyclo[3.3.1]non-6-ene and 3-methoxy-7-cyclohexylidene-3-borabicyclo[3.3.1]nonane [34] (Found: C 77.14, H 10.96, B 4.64. Calcd. for $C_{15}H_{25}BO$: C 77.60, H 10.85, B 4.66%).
To a solution of the mixture (34.5 g) in 50 ml of THF was added at 20°C 140 ml of 1.4 M borane solution. After boiling for 2 hours and standing overnight, the precipitate formed was crystallised from THF to yield 36.6 g (89.6%) of complex 11c (decomposes above 80°C) (Found: C 78.36, H 11.37, B 3.96. Calcd. for $C_{18}H_{31}BO$: C 78.83, H 11.39, B 3.96%). Compounds 11a,b,c are oxidised in air.

(5-Methylene-3-methylcyclohex-2-en-1-ylmethyl)butyl(methyl)borane (15b) and (5-methylene-3-methylcyclohex-3-en-1-ylmethyl)butyl(methyl)borane (14b)

A 250 ml three necked flask was charged with 20.9 g of 3,7-dimethyl-3-borabicyclo[3.3.1]non-6-ene (12b) in 50 ml of ether and 65 ml of 2.25 N solution of BuLi in hexane. The mixture was stirred at 20°C for 1 hour. 11.5 ml of AcCl was then added at 0°C from a syringe through rubber septum. After a white precipitate had been formed the mixture was kept at 20°C during 1 hour and the ether was removed in vacuo. The residue was washed with pentane (3x50 ml) and the solvent was removed. Subsequent distillation gave 15.7 g (55%) of a mixture of 14b and 15b (~1:1), b.p. 68-70°C/1 mm Hg, $n_D^{20}$ 1.4789.
$^1$H NMR ($CDCl_3$, $\delta$, ppm) 0.78 (s, $CH_3$-B), 1.76 (s) and 1.67(s) ($CH_3$-C=C), 4.62, 4.67 and 4.69, 4.74 (2 H, $CH_2$=C), 5.23 (CH=C), 5.93 (CH=C-C=C). IR: 889 ($\delta$), 1612, 1630 sh, 1643, 3030 sh, 3080 $cm^{-1}$ (Found: C 81.99, H 12.21, B 5.09. Calcd. for $C_{14}H_{25}B$: C 82.36, H 12.34, B 5.30%).

Compounds 14a, 15a and 14c, 15c were obtained in a similar way from 12a and 12c, respectively (see Table 1).

3,5-Dimethylene-1-methylcyclohexene (16b)

14.4 g of a mixture of 14b and 15b was heated with 14 g of veratraldehyde in a vacuum distillator. The product (6 g) with b.p. 60-75°C/14 mm Hg was distilled off at a bath temperature of 120-150°C during 40 min. The product was redistilled and chromatographed on $SiO_2$ with pentane as the eluent, whereupon it was again distilled to yield 3.7 g (43%) of 16b, b.p. 67-67.5°C/31 mm Hg, $n_D^{20}$ 1.5129.
$^1$H NMR ($CDCl_3$, $\delta$, ppm) 2.78, 2.98 (4 H, $CH_2$), 4.7 (m) and 4.76 (m) (4 H, $CH_2$=C), 5.97 (1 H, CH=C). $^{13}$C NMR ($CDCl_3$, $\delta$, ppm) 23.1 ($CH_3$), 39.0 and 39.5

(C-4,6), 108.2 and 108.4 ($\underline{C}H_2$=C), 125.5 (C-2), 137.2 (C-1), 143.4 and 143.6 (C-3,5). IR: 890 ($\delta$), 1610, 1653, 3019, 3080 $cm^{-1}$ (Found: C 89.75, H 10.22. Calcd. for $C_9H_{12}$: C 89.93, H 10.07%). The compound has >97% purity (GLC). Transfer of the exocyclic double bond to the ring does not take place under the conditions of reaction or isolation.

3,5-Dimethylenecyclohexene (16a)

This was obtained in an analogous way with a yield of 64% from 14a and 15a, b.p. 62-64°C/62 mm Hg, $n_D^{20}$ 1.5075 (lit.: b.p. 65.5°C/77 mm Hg, $n_D^{20}$ 1.5130, ref. 36).

$^1$H NMR ($CHCl_3$, $\delta$, ppm) 2.88 and 3.09 (4 H, $CH_2$), 4.79 (m, 4 H, $CH_2$=C), 5.8 and 6.18 (d.m, 2 H, CH=CH, J= 9.5 Hz). $^{13}$C NMR ($CDCl_3$, $\delta$, ppm) 33.7 (C-6), 39.8 (C-4), 108.3 ($\underline{C}H_2$=C), 110.5 ($\underline{C}H_2$=C-C=C), 128.3 (C-1), 129.3 (C-2), 142.9 and 143.05 (C-3,5). IR: 890($\delta$), 1600, 1640, 1658, 3032, 3080 $cm^{-1}$ (Found: C 90.45, H 9.65. Calcd. for $C_8H_{10}$: C 90.50, H 9.50%).

1-Isopropenyl-3,5-dimethylenecyclohexene (16c)

The compound was synthesized from 12 g of 14c and 15c in 43% yield (3.25 g) by a similar method, b.p. 77-78°C/7 mm Hg, $n_D^{20}$ 1.5645.

$^1$H NMR ($CDCl_3$, $\delta$, ppm) 1.96 (s, 3 H, $CH_3$), 3.04 (m, 4 H, $CH_2$), 4.81 (m), 4.9 and 4.93, 5.02 and 5.12 (6 H, $CH_2$=C). $^{13}$C NMR ($CDCl_3$, $\delta$, ppm) 20.5 ($CH_3$), 34.5 (C-6), 39.5 (C-4), 108.7 ($\underline{C}H_2$=C), 112.05, 112.65 ($\underline{C}H_2$=C-C=C-C=$\underline{C}H_2$), 126.3 (C-2), 142.6, 143.5, 143.6 (C-1,3,5) (Found: C 90.10, H 9.56. Calcd. for $C_{11}H_{14}$: C 90.35, H 9.65%).

7-Methylene-2,2-pentamethylene-3-methyl-3-borabicyclo[3.3.1]nonane (20c)

74 ml of 1.06 N solution of MeLi in ether was added dropwise at -70 ÷ -60°C to 21 g of complex 11c in 100 ml of ether. The mixture was stirred for 15 min. at -78°C and for 15 min. at 20°C, whereupon 5.9 g of AcCl was added from a syringe through rubber plug, and the mixture was stirred for 1 hour at 20°C. The ether was removed under reduced pressure, and the residue extracted with hot pentane (3x40 ml). Removal of the solvent and distillation furnished 10.82 g (65%) of 20c with b.p. 108-110°C/2 mm Hg, $n_D^{20}$ 1.5208.

$^1$H NMR ($CDCl_3$, $\delta$, ppm) 0.63 (s, 3 H, $CH_3$-B), 4.59 and 4.71 (2 H, $CH_2$=C). IR: 895 ($\delta$), 1649, 3075 $cm^{-1}$ (Found: C 83.38, H 11.61, B 4.71. Calcd. for $C_{15}H_{25}B$: C 83.34, H 11.66, B 5.00%).

Using analogous methods, bicyclic compounds 20a and 20b were obtained from tetrahydrofuran complexes 11a and 11b while 4,4-dimethyl-3-borahomoadamantane (24b) [32] and trimethylamine complex of 3-borahomoadamantane (24a) [31] were converted to 8-methylene-3,4,4-trimethyl-3-borabicyclo[4.3.1]decane (26b) and 8-methylene-3-methyl-3-borabicyclo[4.3.1]decane (26a), respectively (corresponding data are listed in Table 2).

Reaction of a mixture of exo- and endo-isomers (20a) with MeLi and AcCl

To 15.9 g of 20a in 70 ml of ether at -70°C was added 94 ml of 1.09 N solution of MeLi. The mixture was stirred at -70°C for 10 min. and then allowed to heat to r.t. 7.5 ml of AcCl was introduced from a syringe at 0°C while the formation of a precipitate was observed. After stirring the mixture for 1 hour at 20°C, the ether was vacuum evaporated and the residue extracted with hot pentane (3x50 ml). Removal of the solvent and distillation gave 11.45 g (72%) of a substance with b.p. 66-70°C/7 mm Hg, $n_D^{20}$ 1.4875, which is, on the basis of NMR data, a mixture of exo- and endo-isomers (20a) in a ratio of ~1:1. $^{13}$C NMR ($\delta$, ppm) 15.05 and 15.2 ($CH_3$). $^1$H NMR ($\delta$, ppm) 0.85 and 0.99 ($CH_3$).

References and Notes

1. A.Pelter, K.Smith, in: Comprehensive Organic Chemistry, vol. 3, ed. B.Barton, W.D.Ollis and D.N.Jones, Pergamon Press, London, 1979, pp. 689-940.
2. E.-I.Negishi, Organometallics in Organic Synthesis, vol. 1, J.Wiley Interscience Publ., N-Y, 1980.
3. R.Köster, Houben-Weyl Methoden der Organischen Chemie, B 13/3c, G.Thieme Verlag, Stuttgart, 1984, S. 215.
4. J.D.Odom, in: Comprehensive Organometallic Chemistry, vol. 1, ed. G.Wilkinson, F.G.A.Stone, E.W.Abel, Pergamon Press, London, 1982, p. 253.
5. B.M.Mikhailov, Yu.N.Bubnov, Organoboron Compounds in Organic Synthesis, Harwood Academic Publ., 1984.
6. E.R.H.Walker, Chem.Soc.Rev., 5, 23 (1976).
7. G.Wittig, Angew.Chem., 70, 65 (1958); Quart.Rev., 20, 191 (1966).
8. H.Jäger, G.Hesse, Chem.Ber., 95, 345 (1962).
9. Y.Yamamoto, H.Toi, S.-I.Murahashi, I.Moritani, J.Amer.Chem.Soc., 97, 2558 (1975); Y.Yamamoto, H.Toi, A.Sonoda, S.-I.Murahashi, J.Amer.Chem.Soc., 98, 1965 (1976); J.Chem.Soc., Chem.Commun., 1976, 672.
10. G.W.Kramer, H.C.Brown, Heterocycles, 7, 487 (1977).
11. T.A.Shchegoleva, E.M.Shashkova, B.M.Mikhailov, Izv.Akad.Nauk SSSR, Ser. Khim., 1980, 2169.
12. B.M.Mikhailov, M.E.Gursky, T.V.Potapova, A.S.Shashkov, J.Organometal.Chem., 201, 81 (1980).
13. M.E.Gurskii, S.V.Baranin, B.M.Mikhailov, Izv.Akad.Nauk SSSR, Ser.Khim., 1980, 2188.
14. M.E.Gurskii, S.V.Baranin, A.S.Shashkov, A.I.Lutsenko, B.M.Mikhailov, J.Organometal.Chem., 246, 129 (1983).
15. B.M.Mikhailov, Yu.N.Bubnov, V.G.Kiselev, Zh.Obshch.Khim., 36, 62 (1966).
16. B.M.Mikhailov, V.G.Kiselev, Yu.N.Bubnov, Izv.Akad.Nauk SSSR, Ser.Khim., 1965, 898.
17. See ref. 5, p. 311.
18. H.Meerwein, G.Hintz, H.Majert, H.Sönke, J.pr.Chem., 147, 226 (1937).
19. M.M.Midland, S.A.Zderic, J.Amer.Chem.Soc., 104, 525 (1982).
20. M.M.Midland, A.Tramontano, S.A.Zderic, J.Organometal.Chem., 156, 203 (1978).
21. M.M.Midland, J.I.McLoughlin, J.Org.Chem., 49, 1316 (1984).
22. M.M.Midland, S.Greer, A.Tramontano, S.A.Zderic, J.Amer.Chem.Soc., 101, 2352 (1980).
23. M.M.Midland, D.C.McDowell, R.L.Hatch, A.Tramontano, J.Amer.Chem.Soc., 102, 867 (1980).
24. M.M.Midland, A.Tramontano, A.Kazubski, R.S.Graham, D.J.S.Tsai, D.B.Gardin, Tetrahedron, 40, 1371 (1984).
25. B.M.Mikhailov, Yu.N.Bubnov, Izv.Akad.Nauk SSSR, Ser.Khim., 1965, 1310.
26. B.M.Mikhailov, Yu.N.Bubnov, S.I.Frolov, Izv.Akad.Nauk SSSR, Ser.Khim., 1981, 2114.
26a. In reactions of hydride transfer of borates with AcCl, the latter converts to ethyl acetate [10,11].
26b. In the preparation of hydrocarbons 16 from boracyclanes, butyllithium was used and not MeLi, which was caused by boranes 14 and 15 having higher boiling points as compared with their dimethyl analogues. When heated with veratraldehyde, dimethyl analogues of 14 and 15 are distilled partially along with 16.
27. R.Benson, R.Lindsey, J.Amer.Chem.Soc., 81, 4247 (1959).

28. R.J.De Pasquale, J.Organometal. Chem., 32, 381 (1971).

28a. Product 20a was isolated as a mixture of exo- and endo-Me-isomers in a ratio of ~1:1.

28b. A Grignard-like reaction of R'COCl with certain lithium tetraorganyl borates was used for the preparation of ketones:

$$R'COCl + [R''BR_3]^-Li^+ \xrightarrow[-LiCl]{} R'COR'' + R_3B$$

(See: E.Negishi, K.W.Chiu, T.Yoshida, J.Org.Chem., 40, 1676 (1975)).

29. M.E.Gurskii, S.V.Baranin, A.I.Lutsenko, B.M.Mikhailov, J.Organometal. Chem., 270, 17 (1984).

30. M.E.Gurskii, A.S.Shashkov, B.M.Mikhailov, J.Organometal.Chem., 199, 171 (1980).

31. B.M.Mikhailov, N.N.Govorov, Ya.A.Angeluk, V.G.Kiselev, M.I.Struchkova, Izv.Akad.Nauk SSSR, Ser.Khim., 1980, 1621.

32. L.S.Vasilyev, V.V.Veselovskii, M.I.Struchkova, B.M.Mikhailov, J.Organometal.Chem., 226, 115 (1982).

33. B.M.Mikhailov, Yu.N.Bubnov, S.I.Frolov, Izv.Akad.Nauk SSSR, Ser.Khim., 1967, 2290.

34. Catalytic hydrogenation of conjugated double bonds in compounds 10c,d,e at 1 atm $H_2$ proceeds simultaneously along two directions: (1) as 1,4-addition of hydrogen leading to respective 7-alkylidene bicyclic derivatives, and (2) as usual 1,2-addition of $H_2$ to the terminal (10c,d) or cyclohexenic (10e) double bond, with the $C_6$-$C_7$ double bond of bicyclic system remaining unchanged. Fortunately, both hydrogenated products formed (1,2- and 1.4-addition of $H_2$) produce only 2-susbstituted 1-boraadamantane (11a,b,c) when hydroborated in THF with subsequent heating.

35. B.M.Mikhailov, K.L.Cherkasova, Zh.Obshch.Khim., 42, 1744 (1972).

36. R.E.Benson, R.V.Lindsey, J.Amer.Chem.Soc., 81, 4250 (1959).