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ORGANOBORON COMPOUNDS

CDXV *. A REGIOSELECTIVE REACTION OF HYDRIDE ABSTRACTION IN THE SERIES OF 3-ALKYL-3-BORABICYCLO[4.3.1]DECANE ATE-COMPLEXES

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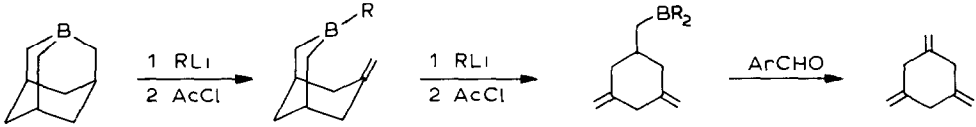
Summary

The ate-complexes of 3,8-dimethyl-, 3,4,8-trimethyl- and 3,4,4,8-tetramethyl-3-borabicyclo[4.3.1]decane react with acetyl chloride to produce the corresponding 2-(3-methylene-5-methylcyclohex-1-yl)alkyl(dimethyl)boranes. The reaction involves the abstraction of a hydride ion from the bridgehead β-carbon atom. The organoboron compounds thus obtained were oxidized with alkaline hydrogen peroxide to the methylene-3-(2-hydroxyalkyl)-5-methylcyclohexanes.

We have shown earlier that the ate-complexes of 1-boraadamantane and of 7-substituted 3-alkyl-3-borabicyclo[3.3.1]nonanes react with acetyl chloride under mild conditions with the abstraction of the β-hydride ion from the bridgehead position to form 7-methylene-3-alkyl-3-borabicyclo[3.3.1]nonanes [1] and 3-methylene-5-alkylcyclohex-1-ylmethyl(dialkyl)boranes [2,3], respectively. The *exo*-methylenic organoboron compounds thereby obtained have been used for the synthesis of substituted methylenecyclohexanes, including 1,3,5-trimethylenecyclohexane [2,3]:



In the chemistry of organoboron compounds, β-hydride ion transfer is usually observed for thermal reactions of trialkylboranes which occur via a cyclic transition state. For example, the reduction reaction of aromatic aldehydes with trial-

* For part CDXIV see ref. 11.
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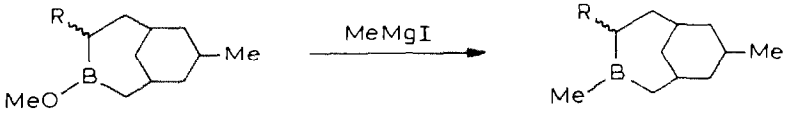
kylboranes accompanied with olefin evolution takes place in such a manner [4,5]. The reaction of trialkylboranes with water, alcohols and amines proceeds along two paths, and it is thought that one of these involves a six-member transition state which leads to an olefin, hydrogen and the corresponding organoboron compound [6,7].

Compounds of tetracoordinated boron, tetraalkylborates, react with electrophiles with the transfer of an α-hydride ion attended by a 1,2-anionotropic alkyl shift [8–10].

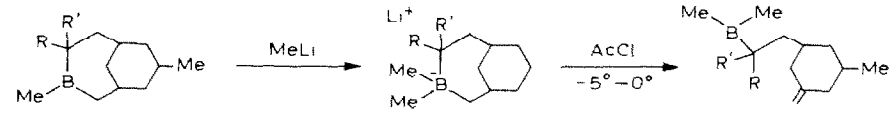
In order to determine to what extent the reaction of β-hydride abstraction has a general character in the case of the interaction between electrophiles and the bridged ate-complexes containing hydrogen atoms on the bridgehead carbon atoms, we have decided to study the conversions of the ate-complexes of 3-alkyl-8-methyl-3-borabicyclo[4.3.1]decane. These compounds are of interest also because of the fact that only one β-hydrogen atom in the compounds occupies the bridgehead position, so one could expect a regioselective hydride abstraction.

3,8-Dimethyl- (IIa) and 3,4,8-trimethyl-3-borabicyclo[4.3.1]decanes (IIb) * were synthesized from the corresponding 3-methoxy derivatives [11] by reaction with methylmagnesium iodide:



(Ia R = H, Ib R = Me) (IIa R = H, IIb R = Me)

3,4,4,8-Tetramethyl-3-borabicyclo[4.3.1]decane (IIc), prepared according ref. 12, has also served as an object of the study. The ate-complex solutions of the 3-methyl-3-borabicyclo[4.3.1]decane series (IIIa,b,c) were obtained on treatment of IIa,b,c with lithiummethyl. The reaction of III with the hydride ion acceptor, acetyl chloride, proceeds readily under mild conditions, at -5 to $0\,^{\circ}C$. Thus, a strong warming up together with the immediate formation of LiCl precipitate is observed when AcCl is introduced from a syringe through a septum into the ate-complex ethereal solutions. After the removal of inorganic salts, the 2-(3-methylene-5-methylcyclohex-1-yl)alkyl(dimethyl)boranes (IVa,b,c) formed were isolated by distillation:



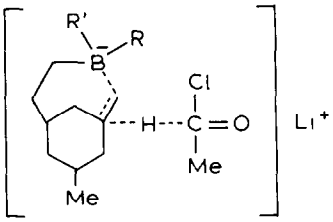
(II) (III) (IV)

(a R = R' = H, b R = H, R' = Me, c R = R' = Me)

Thus, in the series of 3-alkyl-3-borabicyclo[4.3.1]decane ate-complexes, the hydride abstraction reaction takes place; this has previously been observed in the series of 1-boraadamantane and 3-alkyl-3-borabicyclo[3.3.1]nonane ate-complexes. The

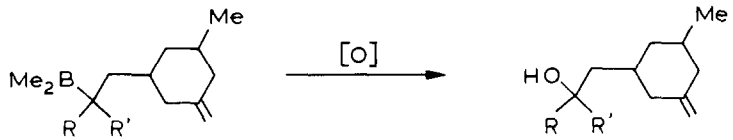
* 3,4,8-Trimethyl-3-borabicyclo[4.3.1]decane is a mixture of *exo*-4-methyl and *endo*-4-methyl isomers

reaction is stereoselective: with cleavage of the β-hydrogen that occupies the bridgehead position of the bicyclo[4.3.1]decane system. As noted earlier [1,3], this fact is apparently connected with the definite activation of hydride mobility of the bridgehead β-hydrogen atoms in the compounds under consideration. It should be suggested, by analogy with the β-hydride abstraction for the 1-boraadamantane and 3-alkyl-3-borabicyclo[3.3.1]nonane ate-complexes [1–3], that in this case a synchronous process also takes place which is similar to the bimolecular elimination reaction and occurs via the transition state V:



(V)

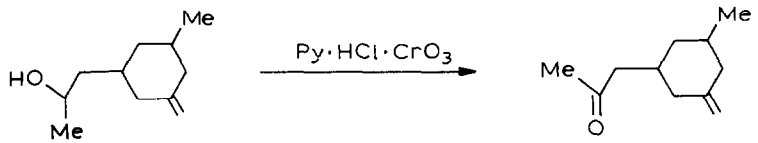
The 2-(3-methylene-5-methylcyclohex-1-yl)alkyl(dimethyl)boranes (IVa–IVc) thereby obtained were oxidized with alkaline hydrogen peroxide to alcohols of the cyclohexane series with an *exo*-methylenic double bond (VIa–VIc). The compounds were purified by distillation in a vacuum (1 mmHg), no isomerisation of the exocyclic double bond to an endocyclic one taking place during the distillation.



(IV) (VI)

(a. R = R' = H; b R = H, R' = Me, c R = R' = Me)

1-Methylene-3-(2-hydroxypropyl)-5-methylcyclohexane (VIb) was oxidized with pyridinechlorochromate to 1-methylene-3-(2-oxopropyl)-5-methylcyclohexane (VII) according to a known method [13]:



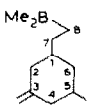
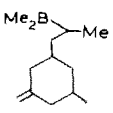
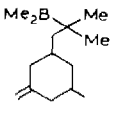
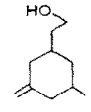
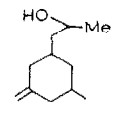
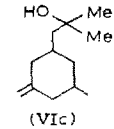
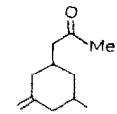
(VIb) (VII)

It is noteworthy that compounds VIc and VII possess a distinctive terpene odour.

All of the *exo*-methylene cyclohexane derivatives obtained (IV, VI, VII) display intense absorptions in the IR spectra at ~ 890 ($\delta(CH_2)$), ~ 1650 ν(C=C) and ~ 3080 ν(C=CH_2) cm^{-1}). The ^1H NMR spectra are characterized by signals of the CH_2=C group protons in the 4.6 ppm region. The ^{13}C NMR spectral data are presented in Table 1.

TABLE 1

^{13}C NMR SPECTRAL DATA OF 1,3,5-SUBSTITUTED CYCLOHEXANES WITH AN *exo*-METHYLENIC GROUP (δ, ppm) [a]

Compound	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	Me
 (IVa)	41.5	42.0 [b]	148.2	44.1	34.2	41.5 [b]	32.6	28.2	13.7 22.7
 (IVb)	38.48	42.3	148.13	44.0	34.15	42.3	41.4	30.0	12.38 14.97 22.7
 (IVc)	36.9	43.4 [b]	147 9	43.6 [b]	34.10	42.8 [b]	50.3	30.7	11.6 22.6 25.1 25.2
 (VIa)	35.7	41.9 [b]	148.0	43.8	33.9	41.5 [b]	40 1	59.6	22.6
 (VIb)	35.5	42.5 [b]	148.0	43.8	33.9	41.3 [b]	47.1	64.5	22.6 24.1
 (VIc)	35.4	43.6 [b]	148.3	44.0 [b]	34.0	43.30 [b]	51.20	70.8	22.7 30.12 30.03
 (VII)	35.0	41.6 [b]	147.8	43.6	34.0	41.1 [b]	50.7	205.4	22.5 30.0

[a] Without solvent. [b] These chemical shifts may be interchanged.

Experimental

All manipulations with organoboron compounds were performed in dry argon. ^1H NMR spectra were recorded on a Tesla BS-497 (100 MHz) spectrometer and on a Bruker WM-250 (250 MHz) instrument. ^{13}C NMR spectra were obtained on a Bruker WM-250 spectrometer (68.69 MHz for carbon). The assignment of spectral

lines was carried out with the aid of the off-resonance method as well as by comparison of the chemical shifts of the series of related compounds. The chemical shifts are relative to TMS. IR spectra were recorded on a UR-20 spectrometer.

3-Methoxy-8-methyl- and 3-methoxy-4,8-dimethyl-3-borabicyclo[4.3.1]decanes were synthesized according to ref. 11. 3,4,4,8-Tetramethyl-3-borabicyclo[4.3.1]decane was prepared as described in ref. 12.

3,8-Dimethyl-3-borabicyclo[4.3.1]decane (IIa)

To a solution of 10.3 g (57.2 mmol) of Ia in 50 ml of ether was added dropwise a solution of MeMgI prepared from 1.42 g (58.8 mmol) of Mg and 8.4 g (59.0 mmol) of MeI in 40 ml of ether. The mixture was stirred for 1 h, then refluxed for another hour. Ether was removed, and the precipitate was washed with 80 ml of hexane. After the evaporation of hexane, the residue was vacuum-distilled to give 7.9 g (84%) of IIa, b.p. 49–51°C (1.5 mmHg), n_D^{20} 1.4782. Found: C, 80.17; H, 12.77; B, 6.66. $C_{11}H_{21}B$ calcd.: C, 80.51; H, 12.90; B, 6.59%.

3,endo-4,8-Trimethyl- and 3,exo-4,8-trimethyl-3-borabicyclo[4.3.1]decane (IIb)

A solution of MeMgI, prepared from 1.35 g (56.2 mmol) of Mg and 8.0 g (56.2 mmol) of MeI in 40 ml of ether, was added to a solution of 10.6 g (54.6 mmol) of Ib in 50 ml of ether. The reaction mixture was refluxed for 3.5 h, then the ether was distilled off. To the residue was added 35 ml of hexane, the precipitate was filtered off and washed with 50 ml of hexane, whereupon the filtrate was evaporated in a vacuum. Distillation of the residue yielded 7.1 g (73%) of IIb, b.p. 67–70°C (2 mmHg), n_D^{20} 1.4812. Found: C, 81.01; H, 13.21; B, 5.52. $C_{12}H_{23}B$ calcd.: C, 80.91; H, 13.02; B, 6.07%.

2-(3-Methylene-5-methylcyclohex-1-yl)ethyl(dimethyl)borane (IVa)

To a solution of 7.8 g (47.6 mmol) of IIa in 35 ml of ether was added at −65°C 28 ml (47.6 mmol) of a 1.7 *M* solution of MeLi in ether. The mixture was heated to 20°C, then cooled to −10 to 0°C. At this temperature, 3.4 ml of AcCl from a syringe was added to the mixture. The mixture was stirred for 1 h at 0°C, then heated to 20°C. After the removal of ether in a vacuum, 30 ml of hexane was added to the residue. Filtration of the precipitate, evaporation of the filtrate and distillation of the residue gave 5.8 g (70%) of IVa, b.p. 50–52°C (2 mmHg), n_D^{20} 1.4562. Found: C, 80.80; H, 12.95; B, 6.14. $C_{12}H_{23}B$ calcd.: C, 80.91; H, 13.02; B 6.07%. ^1H NMR ($CDCl_3$, δ, ppm): 0.74 s (6 H, CH_3B), 0.92 d (3 H, CH_3–C, *J* 6.4 Hz), 4.59 m (2 H, CH_2=C). IR (CCl_4): 890 δ(CH_2=), 1655 ν(C=C), 3075 ν(C=CH_2) cm^{-1}.

2-(3-Methylene-5-methylcyclohex-1-yl)propyl(dimethyl)borane (IVb)

To a solution of 7.0 g (36.3 mmol) of IIb in 35 ml of ether was added dropwise at −60°C 21.4 ml (36.3 mmol) of a 1.7 *M* solution of MeLi in ether. The mixture was heated to 20°C, then cooled to −10 to 0°C, whereupon 2.85 g (36.3 mmol) of AcCl was added to the mixture. The reaction mixture was stirred for 1 h at 20°C. Ether was distilled off, and 30 ml of pentane was added to the residue. The precipitate was filtered off, and the solvent was removed from the filtrate. Distillation of the residue produced 4.9 g (65%) of IVb, b.p. 55–57°C (2 mmHg), n_D^{20} 1.4588. Found: C, 81.09; H, 13.31; B, 5.63. $C_{13}H_{25}B$ calcd.: C, 81.25; H, 13.11; B, 5.63%. ^1H NMR ($CDCl_3$, δ, ppm): 0.73 s (6 H, CH_3B), 0.83 d (3 H, CH_3–C–B, *J* 6.7 Hz), 0.92 d (3 H, CH_3–C, *J* 5.9 Hz), 4.58 m (2 H, CH_2=C).

2-Methyl-2-(3-methylene-5-methylcyclohex-1-yl)propyl(dimethyl)borane (IVc)

As described above, from 8.26 g (44.0 mmol) of IIc, 25.9 ml (44.0 mmol) of a 1.7 *M* solution of MeLi in ether and 3.2 ml (44 mmol) of AcCl 6.2 g (70%) of IVc was prepared, b.p. 79–81 °C (1.5 mmHg), n_D^{20} 1.4607. Found: C, 81.27; H, 13.15; B, 5.28. $C_{14}H_{27}B$ calcd.: C, 81.55; H, 13.20; B 5.25%. ^1H NMR ($CDCl_3$, δ, ppm): 0.73 s (6 H, CH_3B), 0.84 s (6 H, CH_3–C–CH_3), 0.89 d (3 H, CH_3–C), 4.56 m (2 H, CH_2=C). IR (CCl_4): 892 δ(CH_2=), 1653 ν(C=C), 3078 ν(CH_2=C).

1-Methylene-3-(2-hydroxyethyl)-5-methylcyclohexane (VIa)

To 5.5 g (31.0 mmol) of IVa in 15 ml of ether was added a solution of 1.25 g of NaOH in 25 ml of water, then 7 ml of 30% H_2O_2 was added dropwise at 0–5 °C. The mixture was stirred for 2 h at 20 °C and for another hour at the temperature of boiling ether. The aqueous layer was extracted three times with ether (3 × 15 ml) and the combined ethereal extracts were dried over Na_2SO_4. Removal of ether in a vacuum and subsequent distillation yielded 3.86 g (81%) of VIa, b.p. 64–65 °C (0.5 mmHg), n_D^{20} 1.4797. Found: C, 77.69; H, 11.80. $C_{10}H_{18}O$ calcd.: C, 77.86; H, 11.76%. ^1H NMR ($CDCl_3$, δ, ppm): 0.92 d (3 H, CH_3, *J* 6.1 Hz), 3.68 t (2 H, CH_2O, *J* 6.5 Hz), 4.6 m (2 H, CH_2=C). IR (CCl_4): 890 δ(CH_2=), 1652 ν(C=C), 3075 ν(CH_2=C), 3340 ν(OH) cm^{-1}.

1-Methylene-3-(2-hydroxypropyl)-5-methylcyclohexane (VIb)

To a solution of 3.85 g (20.4 mmol) of IVb in 20 ml of ether was added at 0 °C 0.81 g of NaOH in 20 ml of H_2O and then, dropwise, 5 ml of 30% H_2O_2. The mixture was stirred for 1 h at 0 °C, then for 2 h at 20 °C, whereupon it was refluxed for 1 h. The mixture was extracted with ether (3 × 20 ml), and the extracts were dried over Na_2SO_4. Removal of ether and distillation of the residue gave 1.83 g (54%) of VIb, b.p. 75–76 °C (0.5 mmHg), n_D^{20} 1.4736. Found: C, 78.79; H, 12.11. $C_{11}H_{20}O$ calcd.: C, 78.51; H, 11.98%. ^1H NMR ($CDCl_3$, δ, ppm): 0.92 d (3 H, CH_2–C, *J* 6 Hz), 1.19 d (3 H, CH_3–C–O, *J* 6 Hz), 3.93 m (1 H, CHO), 4.60 (2 H, CH_2=C). IR (CCl_4): 891 δ(CH_2=), 1651 ν(C=C), 3075 ν(CH_2=C), 3360 ν(OH) cm^{-1}.

1-Methylene-3-(2-hydroxy-2-methylpropyl)-5-methylcyclohexane (VIc)

As described above, 4.73 g of IVc was converted to 3.5 g (84%) of VIc, b.p. 65–68 °C (0.2 mmHg), n_D^{20} 1.4738. Found: C, 78.84; H, 12.16. $C_{12}H_{22}O$ calcd.: C, 79.06; H, 12.16%. ^1H NMR ($CDCl_3$, δ, ppm): 0.91 d (3 H, CH_3–C, *J* 6 Hz), 1.23 s (6 H, CH_3–C–CH_3), 4.6 (2 H, CH_2=C). IR (CCl_4): 890 δ(CH_2=), 1651 ν(C=C), 3076 ν(CH_2=C), 3420 (OH) cm^{-1}.

1-Methylene-3-(2-oxopropyl)-5-methylcyclohexane (VII)

2.8 g (13 mmol) of pyridinechlorochromate and 0.4 g (4.9 mmol) of NaOAc were suspended in 5 ml of CH_2Cl_2. After the addition of 1.44 g (8.6 mmol) of alcohol VIc, the mixture was stirred for 5 h at 20 °C and afterwards allowed to stand overnight. The reaction mixture was diluted with 50 ml of ether, and the ethereal solution was filtered through a thin layer of SiO_2. Ether was removed in a vacuum, and the residue was chromatographed on silica gel using CH_2Cl_2 as the eluant to afford 1.05 g (75%) of VII, b.p. 67–68 °C (1.5 mmHg), n_D^{20} 1.4669. Found: C, 79.47; H, 10.87. $C_{11}H_{18}O$ calcd.: C, 79.46; H, 10.91%. ^1H NMR ($CDCl_3$, δ, ppm): 0.92 d (3

H, CH_3–C, J 6.1 Hz), 2.13 s (CH_3–C=O), 2.35 d (2 H, CH_2–C=O, J 6 Hz), 4.62 m (2 H, CH_2=C). IR (CCl_4): 893 $\delta(CH_2=)$, 1360 $\nu(CH_3)$, 1652 ν(C=C), 1715 ν(C=O), 3078 $\nu(CH_2=C)$ cm^{-1}.

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