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ORGANOBORON COMPOUNDS

CDXIV *. HOMOLOGATION OF 3-METHOXY-7-METHYL-3-BORABICYCLO[3.3.1]NONANE AND 3-METHOXY-7-METHOXYMETHYL-3-BORABICYCLO[3.3.1]NON-6-ENE USING α-HALOALKYLLITHIUM COMPOUNDS. SYNTHESIS OF 3-BORABICYCLO[4.3.1]DECANE AND 3-BORABICYCLO[4.3.1]DEC-7(8)-ENE DERIVATIVES

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Summary

3-Methoxy-7-methyl-3-borabicyclo[3.3.1]nonane (I) and 3-methoxy-7-methoxymethyl-3-borabicyclo[3.3.1]non-6-ene (X) react with α-halomethyllithium compounds at $\leqslant -110\,^{\circ}C$ to yield 3-methoxy-8-methyl-3-borabicyclo[4.3.1]decane and a mixture of 3-methoxy-8-methoxymethyl-3-borabicyclo[4.3.1]dec-7-ene and 3-methoxy-8-methoxymethyl-3-borabicyclo[4.3.1]dec-8-ene. A similar reaction of I or X with α-bromomethyllithium leads to the corresponding *endo*-4- and *exo*-4-methyl derivatives of 3-borabicyclo[4.3.1]decane and of 3-borabicyclo[4.3.1]dec-7(8)-ene.

The 3-borabicyclo[3.3.1]nonane compounds, which are obtained via the allylboration of acetylenes [1], have been used for the synthesis of compounds of the 3-borabicyclo[4.3.1]decane series. The first representatives of this novel series of organoboron compounds, namely 8-substituted 3-methoxy-4,4-dialkyl-3-borabicyclo[4.3.1]decanes, were prepared by the acid-catalysed rearrangement of 7-substituted 3-(2-alkenyl)-3-borabicyclo[3.3.1]nonanes [2] and also by the Matteson-Pasto rearrangement of 7-substituted 3-(2-bromo-2-propyl)-3-borabicyclo[3.3.1]nonane [3].

With the view of workup of the simple methods for the synthesis of 3-borabicyclo[4.3.1]decanes, which have no substituent in position 4 or have one radical in this position, we have investigated the reaction of 3-methoxy-7-methyl-3-borabicyclo[3.3.1]nonane with α-halolithium compounds. The mechanism of such reactions includes the initial formation of borate anions which, either spontaneously

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* For part CDXIII see ref. 16.
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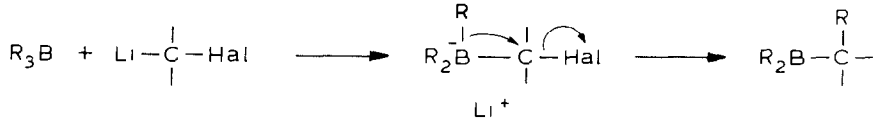
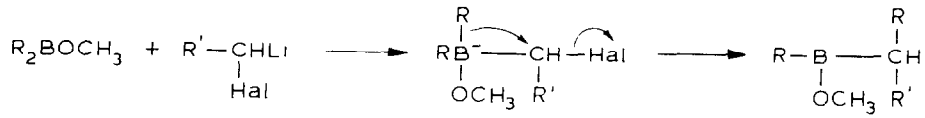
or on treatment with some reagents, undergo 1,2-anionotropic migration to form a new C–C bond:

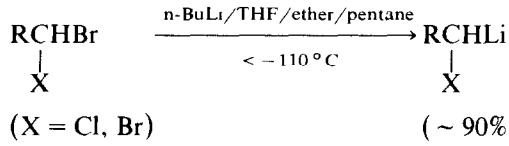


The interaction of trialkylboranes and α-halosubstituted organolithium compounds was first performed by Köbrich and Merkle who conducted the reactions of triphenylborane with dichloromethyllithium, *trans*-1,2-dichlorovinyllithium and with *cis*- and *trans*-β-chloro-α-methylstyrenelithium [4,5]. This method was further used for the metallated derivatives of haloforms, α-halocarbonyl compounds and halonitriles. The organometallic reagent was generated in the course of the reaction from the halo compound and a sterically hindered base in the presence of a trialkylborane [6]. In these reactions, it is possible to realize one, two or three migrations depending on the structure of the organometallic compound formed (i.e. on the number of leaving groups). The organoboranes thus formed were not usually isolated and were converted to the corresponding organic compounds by oxidation or hydrolysis.

For the preparation of 3-borabicyclo[4.3.1]decane compounds, we have chosen a simple scheme involving the reaction of 3-methoxy-3-borabicyclo[3.3.1]nonanes with α-haloalkyllithiums:

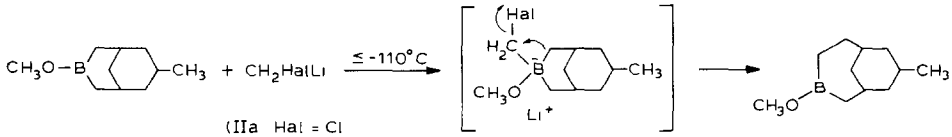


The use of dialkylborinate and 1-haloalkyllithium enables one migration of only the B–C cyclic bond accompanied with expansion of the boron-containing ring by one carbon atom with no introduction into the bicyclic molecule of functional groups or heteroatoms (S, Si, etc.) to be carried out. It should be noted that the reaction of α-haloalkyllithiums with trialkylboranes, which is possibly conditioned by their extreme lability as compared with di- and tri-haloalkyllithiums, has not previously been performed. At the same time, methods for the preparation of these compounds at low temperatures have been elaborated, so they are successfully used in organic synthesis. α-Bromoalkyllithium and α-chloroalkyllithium are obtained by the action of n-BuLi on 1,1-dibromo- and 1-bromo-1-chloroalkenes, respectively, at temperatures $< -110\,^{\circ}C$:



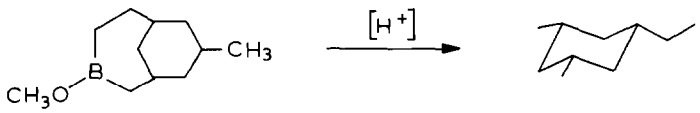
To the α-chloromethyllithium (II) obtained by this scheme [7] was quickly added 3-methoxy-7-methyl-3-borabicyclo[3.3.1]nonane (I) at a temperature $< -110\,^{\circ}C$, whereupon the mixture was stirred for a time at this temperature and was then

allowed to warm to room temperature:



(I) (IIa Hal = Cl, IIb Hal = Br) (III) (IV)

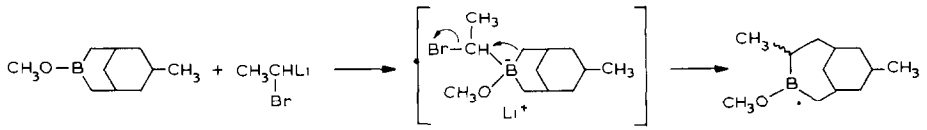
Compound IV was isolated from the reaction mixture by distillation and purified by fractionation on a Hempel column. Both the yield and purity of the 3-borabicyclo[4.3.1]decane derivatives obtained by this method depend to a considerable extent on the care with which the Li/Hal exchange reaction is conducted. The structure of bicycle IV is substantiated by elemental analysis and by its ^{13}C NMR spectrum. Acidolysis of IV with stearic acid affords 1-ethyl-*cis*-3,5-dimethylcyclohexane with an impurity of *cis*-1,3,5-trimethylcyclohexane (2%):



(IV) (V)

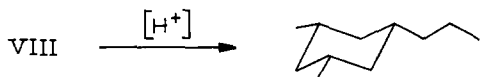
According to the reported data [7], the reagent prepared from CH_2ClBr contains, together with chloromethyllithium, an admixture of bromochloromethyllithium (10%). Therefore we attempted to prepare bromomethyllithium (IIb) from methylene bromide and n-BuLi at a temperature $< -115\,^{\circ}C$ (compound IIb is even less stable than IIa [7,8]). In this case, it is also possible to obtain IV in a satisfactory yield by means of careful fractionation of the reaction mixture.

Spatial isomers of 3-methoxy-4,8-dimethyl-3-borabicyclo[4.3.1]decane (VIII) were synthesized by treating I with 1-bromoethyllithium (VI) at a temperature $< -115\,^{\circ}C$. Highly unstable VI was obtained from 1,1-dibromoethane and n-BuLi as described previously [9]:



(I) (VI) (VII) (VIII)

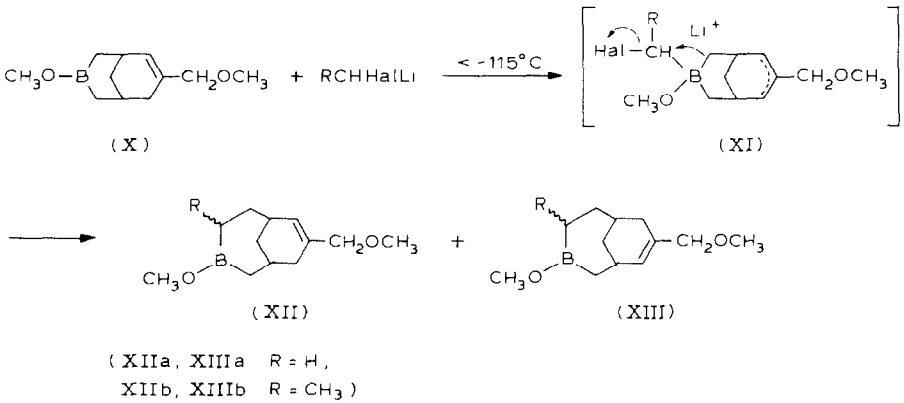
Acidolysis of VIII afforded 1-propyl-*cis*-3,5-dimethylcyclohexane (IX) with an impurity of *cis*-1,3,5-trimethylcyclohexane ($< 0.25\%$).



(IX)

It was essential that this method of broadening of the boron-containing ring turned out to be applicable to the 3-borabicyclo[3.3.1]non-6-ene compounds. Thus, the interaction between CH_2HalLi and 3-methoxy-7-methoxymethyl-3-borabicyclo[3.3.1]non-6-ene (X) produced 3-methoxy-8-methoxymethyl-3-borabicyclo[4.3.1]dec-7-ene (XIIa) and 3-methoxy-8-methoxymethyl-3-borabicyclo[4.3.1]dec-

8-ene, while the reaction of $CH_3CHBrLi$ with X resulted in the formation of 3-methoxy-8-methoxymethyl,*endo*-4-methyl- and 3-methoxy-8-methoxymethyl,*exo*-4-methyl-3-borabicyclo[4.3.1]decenes (XIIb and XIIIb):



(X) (XI)

(XII) (XIII)

(XIIa, XIIIa R = H,
XIIb, XIIIb R = CH_3)

Experimental

All manipulations with organoboron compounds were performed in a dry argon atmosphere. Chlorobromomethane was obtained by a known method [10]; 1,1-dibromoethane was prepared according to ref. 11, and 3-methoxy-7-methoxymethyl-3-borabicyclo[3.3.1]non-6-ene according to ref. 12.

^1H and ^{13}C NMR spectra were recorded on a Bruker WM-250 spectrometer (68.69 MHz for carbon; 250 MHz for hydrogen). Mass spectra were obtained on a Varian CH-6 instrument. GLC analyses were performed on a Chrom-4 apparatus using a 2.4 m column packed with Carbowax 15,000 on Chromaton.

3-Methoxy-7-methyl-3-borabicyclo[3.3.1]nonane (I)

To a solution of 27.5 g (133 mmol) of THF · 1-boraadamantane [12] was added 10 ml (247 mmol) of abs. MeOH. The solution was refluxed for 50 h. The solvents were removed, and subsequent distillation gave 18.3 g (83%) of I, b.p. 58–60 °C (2 mmHg), n_D^{20} 1.4775 [13].

3-Methoxy-8-methyl-3-borabicyclo[4.3.1]decane (IV)

(a) To a solution of 3.83 g (29.6 mmol) of CH_2ClBr in 76 ml of THF, 47 ml of ether and 35 ml of pentane was added dropwise at < −110 °C 16.1 ml (29.6 mmol) of a 1.84 *M* solution of BuLi in hexane and then, at the same temperature, 4.41 g (26.6 mmol) of I in 12 ml of THF. The mixture was heated to −100 °C for 30 min and then to 20 °C. After solvents had been distilled off, 70 ml of hexane was added to the residue. The resulting sediment was filtered and washed with hexane. The latter was removed, and distillation of the residue afforded 3.57 g of the compound, b.p. 74–76 °C (2 mmHg). The products obtained from two similar runs were combined and fractionated on a Hempel column separating the fraction with b.p. 68–70 °C (1.5 mmHg), the overall yield being 53%, n_D^{19} 1.4800. Found: C, 73.33; H, 11.60; B, 5.96. $C_{11}H_{21}BO$ calcd.: C, 73.35; H, 11.75; B, 6.00%. ^1H NMR spectrum ($CDCl_3$, δ, ppm): 3.61 s (3 H, B–OCH_3), 0.825 d (3 H, C–CH_3, $J = 6$ Hz). ^{13}C

NMR spectrum (δ, ppm): 22.9 (CH_3), 17.1 and 30.2 (CH_2B), 27.0, 27.2, 31.3 (CH), 31.8, 33.3, 35.45, 40.65 (CH_2), 52.56 (OCH_3).

(b) To a solution of 6.06 g (34.8 mmol) of CH_2Br_2 in 77 ml of THF, 48 ml of ether and 36 ml of pentane was added dropwise 20.2 ml (34.8 mmol) of a 1.72 *M* solution of BuLi in hexane at $< -115\,°C$ during 3 min. Whereupon, at the same temperature, a solution of 5.2 g (31.3 mmol) of I in 17 ml of THF was immediately added to the solution during 4 min. The mixture was heated to $-100\,°C$ over a period of 30 min and then to 20 °C. The solvents were distilled off, and 80 ml of hexane was added to the residue. The precipitate was filtered off. The combined filtrates of three identical runs were vacuum-evaporated, and the residue was distilled to yield the compound with b.p. 75–78 °C (2 mmHg). The product was fractionated on a Hempel column separating the fraction with b.p. 64–67 °C (1.5 mmHg) in an overall yield of 61%. n_D^{20} 1.4805. Found: C, 73.44; H, 11.79; B, 5.93. $C_{11}H_{21}BO$ calcd.: C, 73.35; H, 11.75; B, 6.00%.

1-Ethyl-cis-3,cis-5-dimethylcyclohexane (V)

In a distilling apparatus a mixture of 25 g of stearic acid and 3.87 g (12.6 mmol) of IV (prepared from I and CH_2ClLi) was charged and the mixture was heated on an oil bath to 240 °C in a water-jet pump vacuum (~ 93 mmHg). At a bath temperature of 230 °C, the product was distilled into a receiver cooled with solid CO_2. The compound thus obtained was dissolved in 30 ml of ether, washed with 10 ml of 20% NaOH, then with water (2×10 ml), and dried over Na_2SO_4. After the removal of ether, distillation of the residue gave 1.75 g (61%) of V, b.p. 69–70 °C (22 mmHg), n_D^{19} 1.4389 (see also ref. 14). Found: C, 85.79; H, 14.38. $C_{10}H_{20}$ calcd.: C, 85.83; H, 14.37%. Mass spectrum: 140 (M^+). Compound V contained 2% of *cis*-1,3,5-trimethylcyclohexane together with an unidentified, high-boiling impurity (5%, GLC).

An analogous acidolysis of IV obtained from I and CH_2BrLi gave V with an impurity of *cis*-1,3,5-trimethylcyclohexane (9%).

3-Methoxy,exo-4- and 3-methoxy,endo-4,8-dimethyl-3-borabicyclo[4.3.1]decane (VIII)

To a solution of 7.26 g (38.7 mmol) of 1,1-dibromoethane in 92 ml of THF, 62 ml of ether and 47 ml of pentane was added dropwise at $< -117\,°C$ 21.7 ml (38.7 mmol) of a 1.78 *M* solution of BuLi in hexane during 25 min. The reaction mixture was stirred for 5 min at $-115\,°C$ and afterwards a solution of 4.5 g (27.1 mmol) of I in 15 ml of THF was added. The mixture was heated to $-100\,°C$ for 30 min and then to 20 °C. After the solvents had been removed, 15 ml of abs. MeOH was added to the residue. The resulting emulsion was extracted with hexane (3×20 ml). Hexane was removed, and the residue was distilled to afford 3.7 g (71%) of VIII, b.p. 88–89 °C (2 mmHg), n_D^{21} 1.4930. Found: C, 74.27; H, 11.93; B, 5.26. $C_{12}H_{23}BO$ calcd.: C, 74.24; H, 11.94; B, 5.57%. ^1H NMR spectrum ($CDCl_3$, δ, ppm): 3.61 s (3 H, B–OCH_3), 0.86 d and 0.82 d (CH_3).

1-Propyl-cis-3,cis-5-dimethylcyclohexane (IX)

In a distillation apparatus was placed a mixture of 28 g of stearic acid and 3.6 g (18.5 mmol) of VIII. The mixture was heated in a vacuum (~ 83 mmHg) on an oil bath, with the product being distilled off at 225 °C in the bath. The product was dissolved in 30 ml of ether, washed with 10 ml of 20% NaOH, then with water (2×10 ml), and dried over Na_2SO_4. Ether was evaporated and the residue was

distilled to yield 2.0 g (71%) of IX, b.p. 56–58 °C (8 mmHg), n_D^{20} 1.4355 (see also ref. 15). Found: C, 85.63; H, 14.32. $C_{11}H_{22}$ calcd.: C, 85.68; H, 14.38%. Mass spectrum: 154 (M^+). On the basis of GLC data, the product contained *cis*-1,3,5-trimethylcyclohexane (0.25%) and a high-boiling admixture (2%).

3-Methoxy-8-methoxymethyl-3-borabicyclo[4.3.1]dec-7-ene (XIIa) and 3-methoxy-8-methoxymethyl-3-borabicyclo[4.3.1]dec-8-ene (XIIIa)

To a solution of 4.78 g (36.8 mmol) of CH_2ClBr in 95 ml of THF, 59 ml of ether and 45 ml of pentane was added dropwise 18.8 ml (36.8 mmol) of a 1.96 *M* solution of BuLi in hexane at < −117 °C during 20 min. At the same temperature, a solution of 5.0 g (25.8 mmol) of X in 16 ml of THF was added for 10 min. The mixture was heated to −100 °C for 30 min and then to 20 °C. After the solvents had been evaporated, 50 ml of hexane was added to the residue. The sediment thus formed was filtered off, and hexane was removed from the extract. Distillation of the residue produced 3.9 g (73%) of a mixture of XIIa and XIIIa, b.p. 90–100 °C (1 mmHg), n_D^{21} 1.4920. Found: C, 69.48; H, 10.39; B, 5.10. $C_{12}H_{21}BO_2$ calcd.: C, 69.25; H, 10.17; B, 5.20%. ^{1}H NMR spectrum ($CDCl_3$, δ, ppm): 4.65 d (CH=), 3.76 (CH_2O), 3.57 s ($B-OCH_3$), 3.28 (OCH_3).

3-Methoxy-8-methoxymethyl,exo-4-methyl- and 3-methoxy-8-methoxymethyl,endo-4-methyl-3-borabicyclo[4.3.1]dec-7-ene (XIIb); 3-methoxy-8-methoxymethyl,exo-4-methyl- and 3-methoxy-8-methoxymethyl,endo-4-methyl-3-borabicyclo[4.3.1]dec-8-ene (XIIIb)

To a solution of 7.0 g (37.6 mmol) of 1,1-dibromoethane in 91 ml of THF, 60 ml of ether and 45 ml of pentane was added dropwise 21 ml (37.6 mmol) of a 1.78 *M* solution of BuLi in hexane at < −115 °C. After stirring for 5 min, a solution of 6.6 g (33.8 mmol) of X in 15 ml of THF was added to the mixture with subsequent heating to −100 °C for 30 min and then to 20 °C. The removal of solvents and the addition of 10 ml of MeOH gave an emulsion which was extracted with hexane (2 × 35 ml). Hexane was then removed and the residue distilled to give 5.3 g (71%) of a mixture of XIIb and XIIIb, b.p. 97–99 °C (1 mmHg), n_D^{21} 1.4800. Found: C, 70.17; H, 10.43; B, 4.84. $C_{13}H_{23}BO_2$ calcd.: C, 70.29; H, 10.44; B, 4.87%. ^{1}H NMR spectrum ($CDCl_3$, δ, ppm): 6.3 and 5.7 (CH=C), 3.75 (CH_2O), 3.6 s ($B-OCH_3$), 3.3 s (OCH_3).

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