Journal of Organometallic Chemistry, 275 (1984) 19–25
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

ORGANOBORON COMPOUNDS

CDXVI *. SYNTHESIS OF 4,4-DIALKYL-8-METHYL-3-BORABICYCLO[4.3.1]-DECANES USING 7-METHYL-3-BORABICYCLO[3.3.1]NONANE

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(Received May 17th, 1984)

Summary

The dimer of 7-methyl-3-borabicyclo[3.3.1]nonane (I) was prepared by the interaction between 3-methoxy(chloro)-7-methyl-3-borabicyclo[3.3.1]nonane and diborane or the complex of borane with dimethylsulfide. Monohydroboration of symmetrical dialkylacetylenes, e.g. 2-butyne and 4-octyne, with the borane I produced the corresponding B-alkenyl compounds. The latter, under the action of catalytic amounts of inorganic acids (HBr of HCl) in the presence of alcohols, undergo a skeleton rearrangement to 3-alkoxy-4,4-dialkyl-8-methyl-3-borabicyclo[4.3.1]decanes.

Simple methods for the preparation of various 3-borabicyclo[3.3.1]nonane compounds have been developed on the basis of the allylboron-acetylene condensation [1]. However, compounds of this type with a B–H bond, i.e. bicyclic tetraalkyldiboranes, have not been obtained so far. The present paper is devoted to the synthesis of the first representative of this type, namely the dimer of 7-methyl-3-borabicyclo[3.3.1]nonane, and to the preparation of 4,4-dialkyl-8-methyl-3-borabicyclo[4.3.1]decanes from this dimer.

We have earlier demonstrated that tetraalkyldiboranes can be obtained by the treatment of dialkylborinates with diborane [2,3]. This equilibrium reaction is accompanied by an exchange of both the alkoxy and alkyl radicals for hydrogen, leading to a mixture of products. The equilibrium is shifted to the formation of $(R_2BH)_2$ if the latter leaves the reaction zone as a precipitate, which was previously reported [4].

We have investigated the interaction between diborane and 3-methoxy-7-methyl-3-borabicyclo[3.3.1]nonane (II) and found that I is obtained in 45% yield if the

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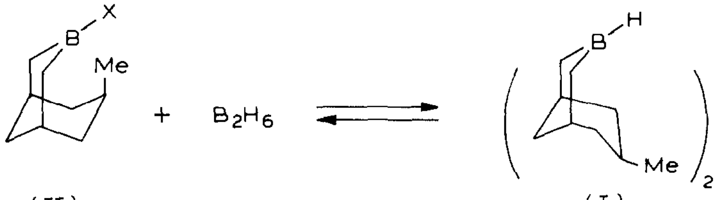
[*] For part CDXV see ref. 19.

[**] Deceased March 1984.

reaction is carried out in an ethereal medium with the ratio II:BH_3 of ~ 1 : 1 and with the sequential removal of the volatile products in a water-jet pump vacuum, addition of isopentane and cooling with dry ice/acetone.



(II) (I)

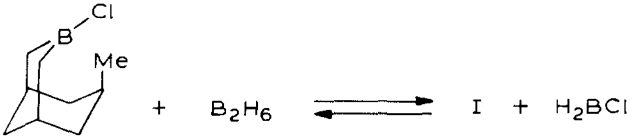
(X = Cl, OMe)

(1)

The yield of I does not change essentially if a solution of diborane in THF or the complex $BH_3 \cdot SMe_2$ are used. The low yield of I is apparently stipulated by the relatively high solubility of I in ether and in isopentane, so that the equilibrium 1 cannot be shifted to the right to a marked extent. In order to increase the yield of I, we used the stepwise isolation of I from the reaction mixture after the equilibrium 1 was achieved. With this end in view, diborane was once again passed through the filtrate after separation of I. This procedure was repeated to give additional 16% of I. Provided this operation is repeated for the third time, the overall yield of I is increased to 72%. A similar result was obtained with the use of a solution of diborane in THF.

The equilibrium 1 may be shifted to the right if $BH_3 \cdot SMe_2$ is slowly passed through II from a capillary with simultaneous removal of methyl borate formed under vacuum. The yield of I in this case amounts to 74%.

In addition, the interaction of 3-chloro-7-methyl-3-borabicyclo[3.3.1]nonane (III) and diborane in an ethereal medium was studied.



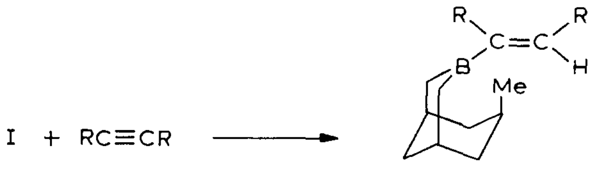
(III)

(2)

It would be expected that the chloroborane formed by reaction 2 will yield more a stable complex with ether than III, thus shifting the equilibrium to the formation of I. However, the yield of I was only equal to 23%. Repeated passing of diborane through the mixture resulted in an increase of the yield to 43%.

The dimer of 7-methyl-3-borabicyclo[3.3.1]nonane is a colourless substance melting at 107–110 °C. Its IR spectrum reveals an intense absorption band at 1580 cm^{-1} characteristic of the bridging B–H bonds and does not contain an absorption band in the region of 2500-2600 cm^{-1} (stretching vibrations of the terminal B–H bonds), which indicates the dimeric structure of I. At the same time, I dissociates under the action of electron impact and, owing to this fact, M^+ of the monomer (135 and 136) are observed in the mass spectrum while $M^{+\cdot}$ of the dimer is utterly absent, which, however, is characteristic of most tetraalkyldiboranes. In the ^{13}C NMR spectrum, the chemical shift of C(9) is equal to 31 ppm, which evidences, in accord with ref. 5, the preferred chair-boat conformation of I.

Compound I reacts slowly with methanol at room temperature to form II, whereas the reaction is markedly accelerated at 40 °C. Monohydroboration of symmetrical acetylenic hydrocarbons (2-butyne and 4-octyne) with the borane I in an ethereal medium proceeds at room temperature leading to B-alkenyl compounds (IVa,b) in ~ 80% yield. To decrease the probability of repeated hydroboration of IV, an excess of the acetylenic hydrocarbon (20–80%) was used.

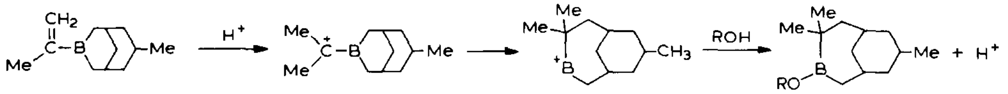


(IVa,b)

(a: R = Me; b. R = n-Pr)

The structure of IV was confirmed by elemental analysis, and also by IR and NMR spectra. In the ^{13}C NMR spectrum, the chemical shift of C(9) is equal to 35.4 ppm, which evidences the double chair conformation. A significant upfield shift of the CH_3 groups signal in IVa (14.2 and 14.8 ppm) as compared with that in V (22.4 ppm) [6] indicates, according to ref. 7, that both CH_3 groups in IVa are in the *cis* position, which is consistent with the mechanism of *cis* addition of the B and H atoms to the triple bond.

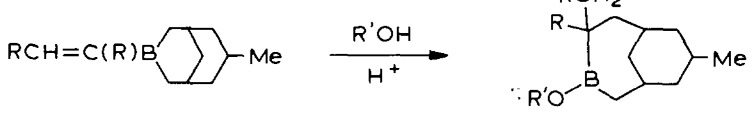
For the example of 3-isopropenyl-7-methyl-3-borabicyclo[3.3.1]nonane, we had formerly discovered a skeleton rearrangement catalysed by inorganic acids * in the presence of alcohols, as a result of which the 3-borabicyclo[4.3.1]decane derivatives VI are formed [8].



(V)

(VI)

We have performed the conversion of IVa,b into the corresponding ethers (VIIa–c) under the action of catalytic quantities of HCl or HBr in the presence of methanol or butanol.



(IVa,b)

(VII a-c)

(a: R = R' = Me
b. R = n-Pr, R' = n-Bu
c R = Me, R' = n-Bu)

10 drops of 49% aqueous HBr or a corresponding amount of ethereal HCl were added to 0.02–0.03 mol of IV. The reaction course was monitored by the disap-

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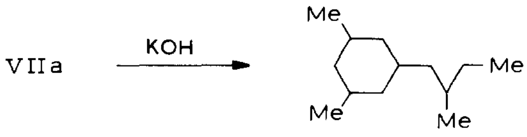
* The ability of alkenylboranes to add HBr was first detected by Matteson and coworkers [9–11].

pearance of the absorption band at 1615 cm^{-1} (B–C=C). The reaction of butanol with IVa, just as with V, occurs with strong warming. If the reaction mixture is cooled so that the reaction may proceed at room temperature, it comes to an end after about 2 h. The reaction with IVb takes place more slowly and is completed in about 24 h. If an ethereal solution of HCl is used instead of hydrobromic acid, the reaction rate decreases. Thus, the reaction of IVa with methanol is completed only after 24 h.

The structure of VII was substantiated by elemental analysis, NMR spectra and by protolysis. The ^{1}H and ^{13}C NMR spectra are complex enough for an interpretation and the number of signals is nearly twice that expected. This fact is accounted for by the presence of two isomers in VII due to the presence of two different substituent on C(4). Protolysis of the mixture of isomeric VII with KOH [12] affords a single hydrocarbon, with the process occurring under more forced conditions than for VI. Thus, the temperature of 235–240 °C is required for the protolysis of VIIa, while 1,3-dimethyl-5-(2-methylbutyl)cyclohexane (VIII) thus formed contains about 9.5% of an impurity (GLC), which is apparently caused by the severe reaction conditions.



(VIII)

Protolysis of VIIb proceeds at higher temperature to lead to a complex mixture of products.

Compounds of the 3-borabicyclo[4.3.1]decane and 3-borabicyclo[4.3.1]dec-7(8)-ene series with no or with one substituent in the 4 position were prepared by the action of α-haloalkyllithiums on 3-methoxy-7-methyl-3-borabicyclo[3.3.1]nonane and 3-methoxy-7-methoxymethyl-3-borabicyclo[3.3.1]non-6-ene, respectively [13].

Experimental

All operations with organoboron compounds were conducted under dry argon. 3-Chloro-7-methyl-3-borabicyclo[3.3.1]nonane (III) was obtained as described [14]. 1-Boraadamantane (IX) was synthesized according as reported [15]. In some experiments, IX was obtained using $H_3B \cdot SMe_2$ as the hydroborating agent by the method cited below. $H_3B \cdot SMe_2$ was prepared by passing diborane through an ethereal solution of Me_2S.

IR spectra were recorded on a UR-20 spectrometer. ^{1}H NMR spectra were obtained on a Varian DA-60-IL (60 MHz) instrument, ^{13}C NMR spectra were recorded on a Bruker WP-60 spectrometer (relative to TMS). The assignment of signals for ^{13}C NMR spectra was carried out using the off-resonance method and also by way of a comparison of spectra of the related compounds. Mass spectra were recorded on a Varian CH-6 spectrometer.

1-Boraadamantane (IX)

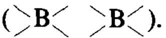
To a solution of 6.66 g (0.0343 mol) of 3-methoxy-7-methoxymethyl-3-borabicyclo[3.3.1]non-6-ene [16] in 20 ml of hexane was added 1 ml of 97.6% solution of

$H_3B \cdot SMe_2$ (0.144 mol) in SMe_2 (warming up was observed). The reaction mixture was then refluxed for 1 h while the temperature was raised gradually to ~ 70 °C. Subsequent sublimation gave 4.32 g (94%) of IX.

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

To a solution of 26.0 g (0.194 mol) of IX in 100 ml of pentane was added, on cooling during 30 min, 9.6 g (0.3 mol) of methanol. Removal of the solvent and distillation of the residue gave 26.8 g (83%) of II, b.p. 45–47 °C (2 mmHg), n_D^{20} 1.4804 (see also ref. 17).

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

(a) From II and diborane in ether. Through a solution of 14.9 g (0.09 mol) of II in 25 ml of ether diborane obtained from 3.2 g of $NaBH_4$ and 16.5 ml of $BF_3 \cdot OEt_2$ was passed for 3.5 h. After standing overnight, the volatiles were distilled off under water-jet pump vacuum and to the residue were added 10 ml of isopentane. The mixture was cooled with dry ice/acetone and filtered (cooling the filter with dry ice/acetone) to give 5.74 g (45%) of I. To the filtrate was then added 5 ml of ether and 5 ml of isopentane and through it was passed diborane (from 1.3 g of $NaBH_4$ and 6 ml of $BF_3 \cdot OEt_2$). 2.6 g of I was isolated additionally be repeating this procedure. Sequential addition of 7 ml of ether to the filtrate and passing diborane through the latter afforded an extra 1.31 g of I. The overall yield of I was equal to 9.11 g (71.7%), m.p. 107–110 °C (from hexane). Found: C, 79.47; H, 12.67; B, 7.82. $C_{18}H_{34}B_2$ calcd.: C, 79.45; H, 12.60; B, 7.95%. IR spectrum (ν, cm^{-1}): 1580 ( $>B\overset{H}{\underset{H}{<\;>}}B<$). Mass spectrum ($m/z$): 135, 136 ($M^+$). ^{13}C NMR spectrum (CH_2Cl_2, δ, ppm): 22.5 (CH_3), 25.1 (C(7)), 26.9 (C(1,5)), 31.0 (C(9)), 38.7 (C(6,8)) (see ref. 5). Treatment of I with pyridine gave the complex I · Py, m.p. 82–85 °C (from hexane). Found: C, 77.57; H, 10.29; B, 5.32. $C_{14}H_{22}BN$ calcd.: C, 78.15; H, 10.31; B, 5.03%.

(b) From II and $BH_3 \cdot THF$. To a solution of 15.4 g (0.099 mol) of II in 15 ml of pentane was added 33 ml of a 1.06 *N* solution of $BH_3 \cdot THF$ (1/3 of the theoretical quantity). After 2 h, the volatiles were distilled off under water pump vacuum. To the residue was again added 33 ml of the $BH_3 \cdot THF$ solution, repeating this operation twice, whereupon to the residue was added 15 ml of pentane and the mixture was allowed to stay overnight at 0–2 °C. The crystals of I thus formed (6.0 g, 50%) were filtered off with cooling. The addition of 5 ml of pentane to the filtrate and keeping it overnight at 0–2 °C gave an additional 1.4 g of I. To the remaining filtrate was added 5 ml of pentane with subsequent cooling to 0–2 °C for 72 h. Decanting produced 1.47 g of I while the overall yield of I amounted to 8.87 g (70%).

(c) From II and $BH_3 \cdot SMe_2$. 6 ml of $BH_3 \cdot SMe_2$ was passed during 6 h from a capillary through 8.97 g (0.05 mol) of II at 36–40 °C in vacuum of 80–90 mmHg, collecting methyl borate and the volatile components in a trap. Next day, to the mixture were added 10 ml of pentane with sequential filtering at ~ −70 °C to yield 4.34 g (59%) of I. The filtrate was evaporated under water pump vacuum, to the residue was then added 5 ml of pentane and the mixture was cooled to −70 °C to afford an additional 1.1 g of I. The overall yield of I was 5.45 g (74%).

(d) From 3-chloro-7-methyl-3-borabicyclo[3.3.1]nonane (III) and diborane in ether. Diborane (prepared from 1.6 g of $NaBH_4$ and 8 ml of $BF_3 \cdot OEt_2$) was passed during 3.5 h through a solution of 8.3 g (0.045 mol) of III in 20 ml of ether and the mixture

was allowed to stand overnight. Next day, after distilling off the volatiles under water pump vacuum, to the residue were added 5 ml of hexane and then 5 ml of ether. Filtration afforded 1.8 g (22.9%) of I. The repeated passing of diborane (from 1 g of $NaBH_4$ and 5 ml of $BF_3 \cdot OEt_2$) and subsequent workup as above gave 0.8 g more of I. The overall yield of I was 2.6 g (43.3%).

3-(1-Methylprop-1-enyl)-7-methyl-3-borabicyclo[3.3.1]nonane (IVa)

To a solution of 2.88 g (0.053 mol) of 2-butyne in 20 ml of ether was added during 2 h at 7 – 10 °C a solution of 6.1 g (0.022 mol) of I in 300 ml of ether. Distillation yielded 6.88 g (81%) of IVa, b.p 77–79 °C (1 mmHg), n_D^{20} 1.5055. Found: C, 81.66; H, 12.12; B, 5.64. $C_{13}H_{23}B$ calcd.: C, 82.12; H, 12.19; B, 5.69%. IR spectrum (ν, cm^{-1}): 1615 (B–C=CH).

^1H NMR spectrum (CCl_4, δ, ppm): 0.76 d (CH_3 cycl., $J = 7$ Hz), 1.67 s ($CH_3C{=}CH$), 1.74 d ($CH_3CH{=}C$), 6.33 broad. quadr. ($CH_3C{=}CH$, $^3J(H,CH_3) = 5.5$ Hz). ^{13}C NMR (CH_2Cl_2, δ, ppm): 14.2 and 14.8 (CH_3 at the double bond), 24.8 (CH_3 at C(7)), 26.1 (C(7)), 27.2 (C(1,5)), 32.0 (C(2,4)), 35.6 (C(9)), 38.8 (C(6,8)), 139.8 (CH=), 142.1 (B–C=) (the spectrum was recorded at –10 °C). The signals assignment was performed on the basis of reported data [5].

3-(1-Propylpent-1-enyl)-7-methyl-3-borabicyclo[3.3.1]nonane (IVb)

To a solution 5.5 g (0.05 mol) of 4-octyne in 30 ml of ether was added for an hour at 10 °C a solution of 3.9 g (0.014 mol) of I in 200 ml of ether. Distillation gave 5.38 g (76%) of IVb, b.p. 114–116 °C (1 mmHg), n_D^{20} 1.4980. Found: C, 82.47; H, 12.90; B, 4.32. $C_{17}H_{31}B$ calcd.: C, 82.92; H, 12.69; B, 4.39%. IR spectrum (ν, cm^{-1}): 1605 (B–CH=CH-). Mass spectrum (m/z): 245, 246 ($M^{+\cdot}$).

3-n-Butoxy-4,8-dimethyl-4-ethyl-3-borabicyclo[4.3.1]decane (VIIc)

To stirred 4.9 g (0.026 mol) of IVa were added 5 drops of HBr (here and below 49% aqueous HBr was used), while warming of the reaction mass was observed. Afterwards a mixture of 11 ml of n-butanol and 5 drops of HBr was added. Strong heat evolution took place after about 5 min; the mixture was cooled to ~ 20 °C and kept at this temperature until the reaction was completed (~ 2 h). Distillation gave 4.95 g (71%) of VIIc, b.p. 100–102 °C (1 mmHg), n_D^{20} 1.4742. Found: C, 77.12; H, 12.57; B, 4.32. $C_{17}H_{33}BO$ calcd.: C, 77.26; H, 12.59; B, 4.09%.
Mass spectrum (m/z): 263, 264 (M^{+}).

3-Methoxy-4,8-dimethyl-4-ethyl-3-borabicyclo[4.3.1]decane (VIIa)

While stirring, to 5.06 g (0.027 mol) of IVa were added 15 drops of a 2.3 *N* ethereal solution of HCl in 5 ml of methanol and, after 18 h, 10 drops more. The reaction was completed at room temperature after about 24 h. Distillation yielded 4.69 g (85%) of VIIa, b.p. 78–81 °C (1 mmHg), n_D^{20} 1.4820. Found: C, 75.46; H, 12.19; B, 4.76. $C_{14}H_{27}BO$ calcd.: C, 75.68; H, 12.25; B, 4.87%.
Mass spectrum (m/z): 221, 222 ($M^{+\cdot}$).

^{13}C NMR spectrum (CH_2Cl_2, δ, ppm): 8.7, 10.4 (CH_3 of ethyl), 21.4, 23.8 (CH_3 at C(8)), 23.8, 25.8 (CH_3 at C(4)), 26.3, 27.4 (C(8)), 27.4 (C × 2)), 29.1, 29.4 (C(1) and C(6)), 29.9, 31.3 (C(10)), 32.1, 34.4 (CH_2 of ethyl), 38.2, 38.8, 41.8 and 42.4 (C(7) and C(9)), 46.5, 47.4 (C(5)), 53.9 (OCH_3). The assignment of signals was in part presumed.

3-Methoxy-4,4,8-trimethyl-3-borabicyclo[4.3.1]decane (VI, R = Me)

See ref. 8. ^{13}C NMR spectrum (CH_2Cl_2, δ, ppm) 21.3 (CH_3 at C(8)), 23.4, 26.5 (two CH_3 at C(4)), 24.8 (C(8)), 27.1, 28.5 (C(1) and C(6)), 30.6 (C(10)), 37.6, 41.4 (C(7) and C(9)), 49.5 (C(5)), 53.4 (OCH_3).

3-n-Butoxy-8-methyl-4-n-butyl-4-n-propyl-3-borabicyclo[4.3.1]decane (VIIb)

To 4.54 g (0.018 mol) of IVb were added 5 drops of HBr and then, during 25 min, a mixture of 10 ml of n-butanol and 5 drops of HBr. At room temperature the reaction required about 24 hours to be completed. Distillation afforded 4.02 g (68%) of VIIb with b.p. 134–135 °C (1 mmHg), n_D^{20} 1.4775. Found: C, 78.78; H, 12.73; B, 3.26. $C_{21}H_{41}BO$ calcd.: C, 78.73; H, 12.90; B, 3.37%.
Mass spectrum (m/z): 319, 320 ($M^{+\cdot}$).

1,3-Ditmethyl-5-(2-methylbutyl)cyclohexane (VIII)

To 6.0 g of powdered KOH were added 5.5 g (0.021 mol) of VIIa and the mixture was gradually heated in a vacuum of 1.5 mmHg to 235–240 °C with simultaneous distillation of the volatiles. Distillation of the residue gave 1.27 g (48.5%) of VIII with b.p. 76–77 °C (7 mmHg), n_D^{20} 1.4450, GLC analysis showed the presence of 9.5% of impurities in VIII. Found: C, 85.82; H, 14.18. $C_{13}H_{26}$ calcd.: C, 85.63; H, 14.37%.
Mass spectrum (m/z): 182 ($M^{+\cdot}$).

^{13}C NMR spectrum (CH_2Cl_2, δ, ppm): 11.6 (C(4)), 19.7 (C(2)), 23.1 (CH_3 at C(3) and C(9)), 30.3 (C(3)), 31.7 (C(2)), 32.9 (C(3,5)), 35.3 (C(1)), 42.2 and 42.3 (C(2,6)), 44.9 (C(4)), 45.4 (C(1)). The signal assignment was carried out taking into account the effect of substituents in the cyclohexane ring in accordance with those reported [18].

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