

Journal of Organometallic Chemistry, 402 (1991) C17–C19
 Elsevier Sequoia S.A., Lausanne
 JOM 21513PC

Preliminary communication

Borylation of dicarbanions: syntheses of new five- and eight-membered boron–carbon rings

G.E. Herberich*, U. Eigendorf and C. Ganter

Institut für Anorganische Chemie der Technischen Hochschule Aachen, Professor-Pirlet-Str. 1, W-5100 Aachen (Germany)

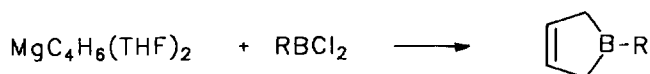
(Received October 18th, 1990)

Abstract

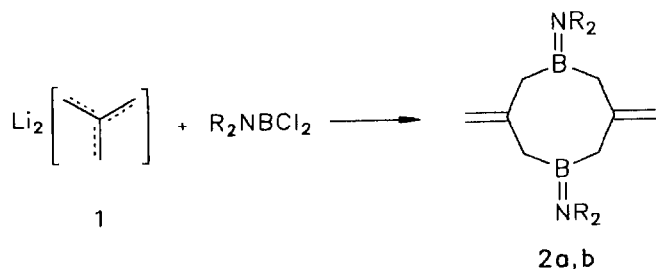
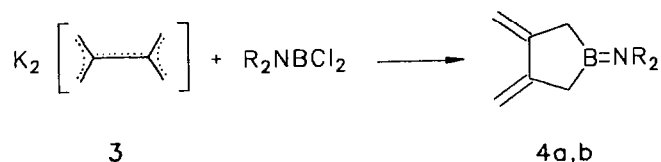
Olefin metallation provides an efficient route to novel unsaturated boracarbocycles. Thus the first 3,7-dimethylene-1,5-diboracyclooctanes $R_2NB(CH_2C(=CH_2)CH_2)_2BNR_2$ ($R = Et, ^iPr$) and the first 3,4-dimethyleneboracyclopentanes $CH_2C(=CH_2)C(=CH_2)CH_2BNR_2$ ($R = Et, ^iPr$) have been made by treatment of dichloro(dialkylamino)boranes with $[Li(TMEDA)]_2[C(CH_2)_3]$ and $K_2[C_2(CH_2)_4]$, respectively.

Borylation of carbanions has been known for a long time [1], but it seems not to have been appreciated that this reaction, when applied to dicarbanions, can provide the most efficient method of synthesis of unsaturated boron–carbon ring systems. We have previously shown that 3-borolenes (2,5-dihydro-1*H*-boroles) [2] can readily be obtained from magnesium-butadiene $MgC_4H_6(THF)_2$ [3] and dihaloboranes (Scheme 1), i.e. in only two steps from butadiene, and a 1,2-dibora-4-cyclohexene was made similarly from magnesium-butadiene and 1,2-dichloro-1,2-bis(dimethylamino)diborane(4) [4].

A wider range of application becomes possible when the dicarbanions used are generated from olefins by metallation and we report here two examples of this type. The lithium derivative $[Li(TMEDA)]_2[C(CH_2)_3]$ (**1**) of the trimethylenemethane dianion is readily accessible by metallation of isobutene with $LiBu/TMEDA$ [5]. When **1** is added dropwise to (dialkylamino)dichloroboranes $(R_2N)BCl_2$ in THF at $-30^\circ C$ the hitherto unknown 1,5-diboracyclooctanes **2a,b** are formed (Scheme 2). In a closely related but more complex synthesis we previously used **1** to build up unsaturated C_3B_2 ring systems with adjacent boron atoms [6].



Scheme 1.

Scheme 2. (a: R = Et; b: R = ⁱPr).Scheme 3. (a: R = Et; b: R = ⁱPr).

The much more reactive dipotassium derivative $\text{K}_2[\text{C}_2(\text{CH}_2)_4]$ (**3**) is obtained from 2,3-dimethylbutadiene and $\text{LiBu}/\text{KO}^t\text{Bu}$ in hexane [7]. After careful removal of the LiO^tBu formed (several washings with hexane), **3** is added to the dihaloboranes $(\text{R}_2\text{N})\text{BCl}_2$ to give the first 3,4-dimethyleneboracyclopentanes **4a,b** (Scheme 3).

It should be noted that for the success of these syntheses it is essential to maintain an excess of the haloborane in the reaction medium. The reaction mixtures were worked up by filtration followed by vacuum distillation. There were severe losses due to polymerization during the distillation, especially in the case of the diethylamino derivatives **2a** and **4a**. Isolated yields were ca. 30%. The compounds **2a** and **4a,b** are colourless liquids whereas **2b** is a colourless solid which crystallizes from hexane at -30°C . They are all highly sensitive to air and moisture.

Similar work with further dicarbanions suitable for the construction of boracyclobutanes is underway.

Experimental

Experiments were carried out under nitrogen by conventional Schlenk techniques. THF was distilled from sodium/benzophenone and hexane from Na/K alloy. Oxygen was removed by repeated distillation under dinitrogen.

1,5-Bis(diethylamino)-3,7-dimethylene-1,5-diboracyclooctane (2a). MS (70 eV): m/z (I_{rel}) 274 (76, M^+). ^1H NMR ($\delta(^1\text{H})$ (ppm), 80 MHz, int. TMS, CDCl_3): 4.56 s ($2\text{CH}_2=$), 1.81 s ($4\text{CH}_2\text{B}$); NEt_2 : 3.09 q (4NCH_2) and 1.01 t (4Me), $^3J = 7.0$ Hz. ^{11}B NMR ($\delta(^{11}\text{B})$, 32 MHz, CDCl_3): 44 ppm, vs. ext. $\text{BF}_3 \cdot \text{OEt}_2$.

1,5-Bis(diisopropylamino)-3,7-dimethylene-1,5-diboracyclooctane (2b). MS (70 eV): m/z (I_{rel}) 330 (63, M^+), 287 (100, $M^+ - ^i\text{Pr}$). ^1H NMR ($\delta(^1\text{H})$ (ppm), 80 MHz, int. TMS, CDCl_3): 4.54 s ($2\text{CH}_2=$), 1.93 s ($4\text{CH}_2\text{B}$); N^iPr_2 : 3.74 sept (4NCH) and 1.14 d (8Me), $^3J = 6.9$ Hz. ^{11}B NMR ($\delta(^{11}\text{B})$, 32 MHz, CDCl_3): 44 ppm, vs. ext. $\text{BF}_3 \cdot \text{OEt}_2$.

1-(Diethylamino)-3,4-dimethyleneboracyclopentane (4a). MS (70 eV): m/z (I_{rel}) 163 (93, M^+), 148 (100, $M^+ - \text{Me}$). ^1H NMR ($\delta(^1\text{H})$) (ppm), 80 MHz, int. TMS, CDCl_3): 5.28 dt and 4.76 dt (2J 2, 4J 2 Hz, $2\text{CH}_2=$), 1.90 "t" br (4J 2 Hz, $2\text{CH}_2\text{B}$); NEt_2 : 3.04 q (2NCH_2) and 1.03 t (2Me), $^3J = 7.1$ Hz. ^{11}B NMR ($\delta(^{11}\text{B})$, 32 MHz, CD_2Cl_2): 49 ppm, vs. ext. $\text{BF}_3 \cdot \text{OEt}_2$.

1-(Diisopropylamino)-3,4-dimethyleneboracyclopentane (4b). MS (70 eV): m/z (I_{rel}) 191 (65, M^+), 176 (100, $M^+ - \text{Me}$). ^1H NMR ($\delta(^1\text{H})$) (ppm), 80 MHz, int. TMS, CDCl_3): 5.28 dt and 4.77 dt (2J 2, 4J 2 Hz, $2\text{CH}_2=$), 2.03 "t" br (4J 2 Hz, $2\text{CH}_2\text{B}$); N^iPr_2 : 3.51 sept (2NCH) and 1.15 d (4Me), $^3J = 6.8$ Hz. ^{11}B NMR ($\delta(^{11}\text{B})$, 32 MHz, CD_2Cl_2): 49 ppm, vs. ext. $\text{BF}_3 \cdot \text{OEt}_2$.

Acknowledgement. This work was generously supported by Deutsche Forschungsgemeinschaft and Fonds der Chemischen Industrie.

References

- 1 J.D. Odom, Non-cyclic three and four coordinated boron compounds, in G. Wilkinson, F.G.A. Stone and E.W. Abel (Eds.), *Comprehensive Organometallic Chemistry*, Vol. 1, Pergamon Press, Oxford, 1982, pp. 253, 272.
- 2 G.E. Herberich, W. Boveleth, B. Heßner, M. Hostalek, D.P.J. Köffer, H. Ohst and D. Söhnen, *Chem. Ber.*, 119 (1986) 420.
- 3 K. Fujita, Y. Ohnuma, H. Yasuda and H. Tani, *J. Organomet. Chem.*, 113 (1976) 201.
- 4 G.E. Herberich, B. Heßner and M. Hostalek, *Angew. Chem.*, 98 (1986) 637; *Angew. Chem., Int. Ed. Engl.*, 25 (1986) 642.
- 5 J. Klein, A. Medlik, *J. Chem. Soc., Chem. Commun.*, (1973) 275.
- 6 G.E. Herberich, C. Ganter, L. Wesemann and R. Boese, *Angew. Chem.*, 102 (1990) 914; *Angew. Chem., Int. Ed. Engl.*, 29 (1990) 912.
- 7 J.J. Bahl, R.B. Bates and B. Gordon III, *J. Org. Chem.*, 44 (1979) 2290; R.B. Bates, B. Gordon III, T.K. Highsmith and J.J. White, *J. Org. Chem.*, 49 (1984) 2981.