Tetrahedron Vol. 44, No. 4, pp 1053 to 1056, 1988
Printed in Great Britain.

0040–4020/88 \$3.00+.00
Pergamon Press plc

1,3-DIHYDRO-1,3,2-DIAZABOROLE- AND 1,3,2-DIAZABOROLIDINE COMPOUNDS FROM ALKALI METAL COMPLEXES OF AROMATIC NITROGEN HETEROCYCLES AND DICHLORO(DIISOPROPYLAMINO)BORANE [1)]

WALTER MARINGGELE, DIETMAR BROMM and ANTON MELLER*

Institut für Anorganische Chemie der Universität Göttingen,
Tammannstraße 4, D-3400 Göttingen, Federal Republic of Germany

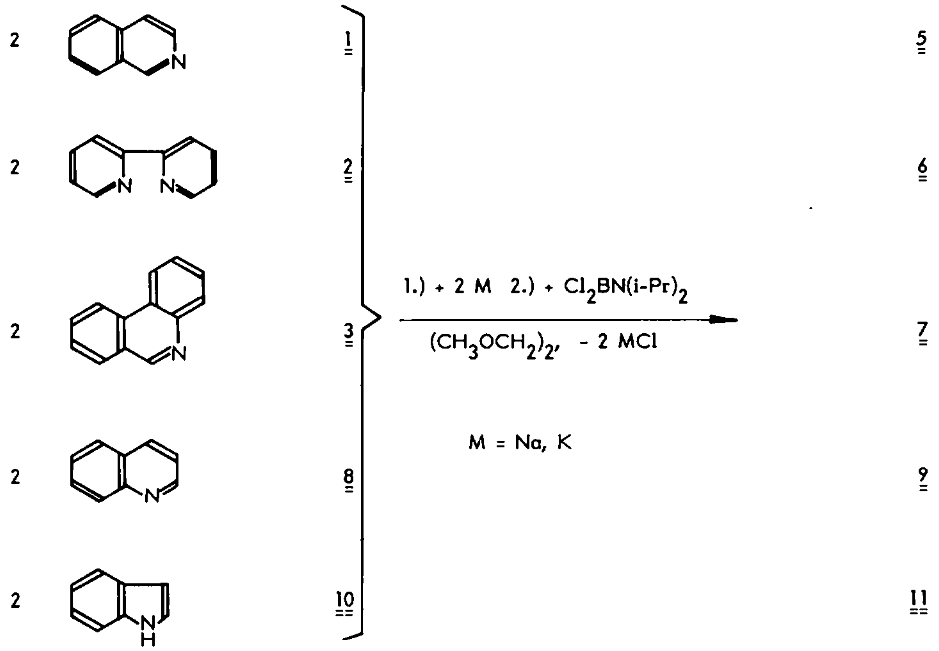
(*Received in Germany* 16 *October* 1987)

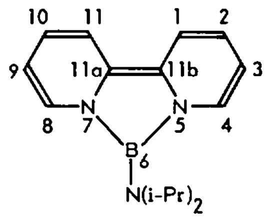
Abstract - Reactions of complexes of isoquinoline, 2,2'-dipyridyl and phenanthridine and sodium or potassium with dichloro(diisopropylamino)borane lead to new heterocycles containing diazaborole and diazaborolidine ring systems. The corresponding reaction starting from quinoline gives bis(1,4-dihydro-quinolinyl-1)diisopropylaminoborane, while with indole bis(1-indolyl)diisopropylaminoborane is the product. The new compounds are characterized by spectroscopic (MS; NMR ^{1}H, ^{11}B, ^{13}C, ^{15}N) data and elemental analyses.

Recently we reported carbene analogous reactions of the dehalogenation product of dichloro(diisopropylamino)borane with naphthalene, acenaphthylene and 1-methylnaphthalene.[2] In these reactions hydride transfer has also been observed, depending upon the stability of the reaction products (e.g. with formation of 1,2-bis-(diisopropylamino-methoxyboryl)ethyne from the solvent 1,2-dimethoxyethane). Radical intermediates have been established in the formation of 1-dialkylboryl-1,4-dihydropyridines (especially if the pyridine is substituted by an alkyl group in pos. 3) via dehalogenation of pyridine-chlorodiorganylboranes and of a N,N'-diborylated 2,2'-bis(1,2-dihydropyridine)derivative in the reaction of the adduct between 3,5-dimethylpyridine and dichloro(diethyl)borane with lithium in tetrahydrofuran.[3] Furthermore the formation of a substance $(CH_3)_2$-$NBC_{10}H_8N_2$ from dilithium 2,2'-dipyridine and dichloro(dimethylamino)borane has been reported.[4] No actual structural formula was given; however, the structure has been discussed in terms of the 2,2'-dipyridine adduct of dimethylaminoborene.[4] Bis(9-mesityl-9,10-dihydro-9-boraanthryl-10) and 9-mesityl-9,10-dihydro-9-boraanthracene have been observed among the reaction products of 9-mesityl-9,10-dihydro-9-boraanthrylidene with cyclohexane and with isopropanol.[5]

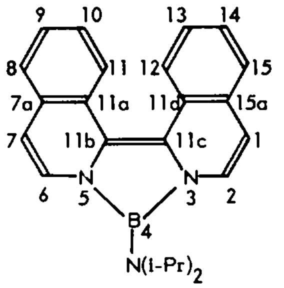
Here we report reactions of the alkali metal complexes of isoquinoline (1), 2,2'-dipyridyl (2) and phenanthridine (3) with dichloro(diisopropylamino)borane (4) in 1,2-dimethoxyethane to give compounds that contain the 1,3-dihydro-1,3,2-diazaborole- or the 1,3,2-diazaborolidine ring system. Apparently one of the factors that influence the formation of the heterocyclic systems is their aromatic stabilization.

In 4-diisopropylamino-[1,3,2]-diazaborolo[5,1-b; 3,4-b']diisoquinoline (5) and in 6-diisopropylamino-[1,3,2]-diazaborolo[5,1-b; 3,4-b']dipyridine (6) the boron atoms form part of an aromatic system, as is documented by the high field shift of $\delta^{11}B$ (at 21.6 and 19.2 ppm) compared to the ^{11}B chemical shift in other tris-(amino)boranes.[6] In contrast, $\delta^{11}B$ in 10-diisopropylamino-19b,19c-dihydro-[1,3,2]-diazaborolo-[5,1-f;3,4-f'] diphenanthridine (7) at 25.6 ppm is as expected. In 7 planarity about the boron atom probably cannot be achieved because of steric interaction of the isopropyl groups with the H-atoms in positions 8 and 12 of the ring system.

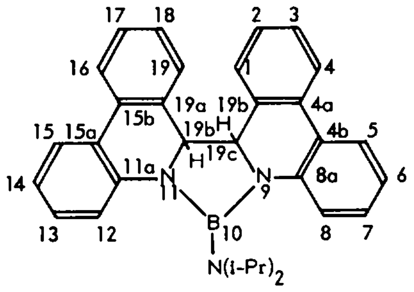

2
1
2
2
2
3
2
8
2
10
1.) + 2 M 2.) + Cl2BN(i-Pr)2
(CH3OCH2)2, - 2 MCl
M = Na, K
5
6
7
9
11


10
11
1
2
9
11a
11b
3
8
7
5
4
6
N(i-Pr)2

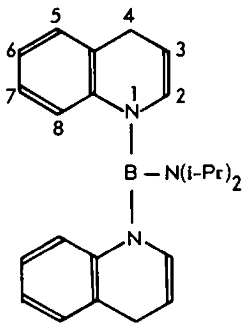
6


9
10
13
14
8
11
12
15
7a
11a
11d
15a
7
11b
11c
1
6
5
3
2
4
N(i-Pr)2

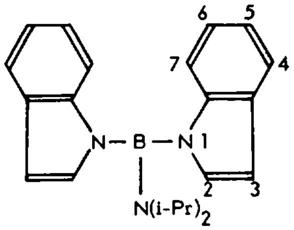
5


17
18
2
3
16
19
1
4
19a
19b
4a
15b
19bH
15
15a
4b
5
11a
H19c
14
11
9
8a
6
13
12
10
8
7
N(i-Pr)2

7


5
4
6
3
7
1
2
8
B – N(i-Pr)2

9


6
5
7
4
N – B – N 1
2
3
N(i-Pr)2

11

Whereas 5 and 7 have been obtained analytically pure, 6 is contaminated with some 2,2'-dipyridyl due to partial decomposition upon distillation. This indicates the additional stabilization from the benzo rings in (5). Upon prolonged heating to 200 °C (7) also shows slow decomposition; phenanthridine and 2,2'-diphenanthridyl are detected (MS, NMR) among the decomposition products.

Of these substances 6 certainly corresponds to the moiety described earlier,[4] which also shows a deep red colour. The structure of $(CH_3)_2NBC_{10}H_8N_2$ therefore must be analogous to that of 6. The colour now can be ascribed to the aromatic system formed, with the boron atom definitely in oxidation state three.

The reaction between the alkali metal complex of quinoline (8) and 4 however gives bis(1,4-dihydroquinolinyl)diisopropylaminoborane (9). The hydrolysis of 9 leads to quinoline and tetrahydroquinoline. This shows that hydrogen transfer also occurs under the conditions of the hydrolysis (see the experimental part). The formation of the 1,2-dihydro isomer of 9 however has been excluded by selectively decoupled proton NMR spectra.

From indole (10) and 4 merely bis(1-indolyl)diisopropylaminoborane (11) is obtained, as expected.

Experimental

General: All preparative work was performed under N_2 and exclusion of moisture. Mass spectra, E.I. (70 eV) and F.I. have been recorded on a Varian MAT CH5; NMR spectra on Bruker WP 80 SY and AM 250 instruments in $CDCl_3$ solution (conc.: ^1H = 5%, ^{11}B and ^{13}C = 20%, ^{15}N = satur.). Standards: ^1H, ^{13}C: TMS int.; ^{11}B: $F_3B.OEt_2$ ext.; ^{15}N: CH_3NO_2 ext.. Dichloro(diisopropylamino)borane (4) was prepared according to [7].

5 and 6: 55 g (0.425 mol) isoquinoline or 30.7 g (0.197 mol) 2,2'-bipyridyl are dissolved in 600 ml of 1,2-dimethoxyethane and 10.5 g (0.455 mol) finely divided sodium or 8.0 g (0.205 mol) potassium are added. The solution is stirred at 0 °C for 6 h and at 25 °C another 6 h and becomes black or deep violet in colour. At 0 °C, 38.5 g (0.21 mol) or 17.8 g (0.098 mol) $Cl_2BN(i\text{-}Pr)_2$ in 150 ml hexane are added dropwise over 1 h with continous stirring and in due course the reaction mixture is refluxed for 8 h. The solvent is removed under reduced pressure and volatiles distilled into a trap (-196 °C) at 250°/0.001 mbar. From fractional distillation in a 3 bulb tube, 34.5 g (44%) of 5, a highly viscous brown liquid (b.p. 230 °C/0.001 mbar) (air bath temp.) is obtained. The yield of 6, also a viscous brown liquid, b.p. 130 °C/0.001 mbar, is about 22 g, contaminated with about 5% of 2,2'-dipyridyl.

5: $C_{24}H_{26}BN_3$ (367.31). MS (M^+/relat. intens. [base]: E.I. 367/20 [44]; F.I. 367/100. calc. C, 78.78; H, 7.13; B, 2.94; N, 11.44. found C, 78.41; H, 7.18; B, 3.00; N, 11.29.
NMR: $\delta^{11}B$ = 21.6 (h/2 = 730 Hz); $\delta^{15}N$ = -68.1 (pos. 3 + 5), -222.3 ($N(i\text{-}Pr)_2$) INEPT Refok.; δ^1H = 1.10 (d, $^3J_{HH}$= 6.5 Hz, 12 H, 4 x CH_3); 3.45 (sept., 2 H); 7.43 (d, $^3J_{HH}$= 7.3 Hz, 2 H) and 6.24 (d, 2 H) (pos. 1,7 and 2,6); 7.05-7.35 (br, 8 H, pos. 8-11 and 12-15); $\delta^{13}C$ = 24.06 (CH_3); 48.06 (CH, sp^3); 130.86, 127.51, 117.42 (pos. 7a, 15a, 11a, 11d, 11b, 11c); 125.80, 126.00, 126.31, 128.28, 130.45.

6: $C_{16}H_{22}BN_3$ (267.18). MS: E.I. 267/90 [224]; F.I. 267/100.
NMR: $\delta^{11}B$ = 19.2 (h/2 = 230 Hz); δ^1H = 1.10 (d, $^3J_{HH}$= 7 Hz, 12 H, 4 x CH_3), 3.45 (sept., 2 H), 6.06-6.15 (m) + 6.20-6.29 (m) + 7.27-7.32 (m) + 7.61-7.67 (m) (tot. 8 H); $\delta^{13}C$ = 24.02 (CH_3), 48.91 (CH, sp^3), 116.94 (pos. 11a, 11b), 109.43, 113.71, 117.92, 127.38 (CH arom.).

7: 50 g (0.28 mol) Phenanthridine dissolved in 600 ml 1,2-dimethoxyethane are metallated with 11.5 g (0.295 mol) finely divided potassium at 0 °C for 4 h and at 25 °C for 60 h. 25.4 g (0.14 mol) $Cl_2BN(i\text{-}Pr)_2$ in 150 ml hexane are run dropwise (1 h) into the deep red suspension and the mixture is refluxed for 3 h. Filtration at 0 °C leaves on the frit a solid which sublimes at 230 °C/0.001 mbar (air bath. temp.). Yield: 47 g (72%) 7, m.p. 209 °C as a colourless powder.

7: $C_{32}H_{32}BN_3$ (469.44). MS: E.I. 469/60 [426]; F.I. 469/100. calc. C, 81.87; H, 6.87; B, 2.30; N, 8.96. found. C, 82,12; H, 7.01; B, 2.16; N, 8.78.
NMR: $\delta^{11}B$ = 25.6 (h/2 = 580 Hz); δ^1H = 1.06 + 1.18 (both d, $^3J_{HH}$= 6.3 Hz, each 6 H, 2 x CH_3), 3.46 (sept., 2 H), 5.12 (s, 2 H, pos. 19b, 19c), 7.06-7.84 (m, 16 H, CH arom.); $\delta^{13}C$ = 22.32 + 23.38 (CH_3), 46.69 (CH, sp^3), 60.49 (CH, pos. 19b, 19c); 142.11, 137,82, 132.85, 126.41 (quart. C); 128.09, 127.91, 127.41, 124.04, 123.09 (twofold intens.).

9: 32.5 g (0.245 mol) of quinoline dissolved in 700 ml of 1,2-dimethoxyethane are metallated by 0.49 mol Na/K alloy (4 g Na, 12.5 g K) with 5 h stirring at 0 °C, continued for 24 h at 25 °C. At 0°C, 44.5 g (0.245 mol) $Cl_2BN(i\text{-}Pr)_2$ in 100 ml hexane are added dropwise and the reaction mixture is refluxed for 6 h. NaCl/

KCl is filtered off and the solvent removed under reduced pressure. Upon distillation 28 g (62% yield) of 9, b.p. 225 °C/0.01 mbar are obtained. At room temperature 9 is a highly viscous tawny liquid, showing green fluorescence.

Alternatively the synthesis starting from 64.5 g (0.5 mol) quinoline and 12 g (0.52 mol) sodium in 700 ml of 1,2-dimethoxyethane under the same reaction conditions gives a yield of 42 g (45%) of 9.
Hydrolysis: 20 g of 9 in a mixture of 250 ml 1,2-dimethoxyethane, 20 ml H_2O and 5 g KOH were refluxed for 5 h. After separation from the water layer, the organic phase was dried with magnesium sulfate and distilled under reduced pressure. Quinoline and tetrahydroquinoline have been identified by MS and NMR.

9: $C_{24}H_{30}BN_3$ (371.38). MS: E.I. 371/39 [241]; F.I. 371/100. calc. C, 77.62; H, 8.14; B, 2.91; N, 11.32. found C, 77.08; H, 8.99; B, 3.11; N, 10.83.

NMR: $\delta^{11}B = 28.7$; $\delta^{1}H = 1.24$ (d, $^3J_{HH} = 7.0$ Hz, 12 H, 4 x CH_3); 3.43 (d of d of d, $^3J_{HH} = 3.7$ Hz with pos. 3, $^4J_{HH} = 1.6$ Hz with pos. 2 and 0.9 Hz with pos. 5, 4 H, 2 x CH_2); 3.67 (sept., 2 H, CH of i-Pr); 4.71 and 4.74 (d of t, $^3J_{HH} = 7.9$ Hz with pos. 2, 3.9 Hz with pos. 4; 2 H in pos. 3); 6.24 and 6.27 (d of t, $^3J_{HH} = 7.9$ Hz with pos. 3, $^4J_{HH} = 1.6$ Hz with pos. 4; 2 H in pos. 2); 6.83 to 6.95 (m, 8 H, arom.). Selective decoupling from 3.43 gives d (J = 7.9 Hz) at 4.73 and 6.26. By decoupling from the arom. protons the signal of the protons in pos. 4 at 3.43 give d of d. This confirms CH_2 in pos. 4. $\delta^{13}C = 24.22$ (4 x CH_3); 27.26 (2 x CH_2); 47.83 (2 x CH, i-Pr); 100.04, 116.49, 122.08, 126.14, 128.96 and 131.02 (pos. 3, 2, 5-8); 123.82 and 141.76 (quart. C).

11 is prepared as described for 9 from 58.6 g (0.5 mol) indole, 20 g (0.51 mol) K, and 45.3 g (0.25 mol) $Cl_2B=N(i\text{-}Pr)_2$. After filtration from KCl the filtrate is evaporated to a volume of 200 ml. 11 separates in form of pink crystals. The yield is 48 g (56%). The crystals sublime at 135 °C/0.01 mbar (air bath temp.); m.p. 102 °C.

11: $C_{22}H_{26}BN_3$ (343.284). M.S.: E.I. 343/100; F.I. 343/100. calc. C, 76.97; H, 7.63; B, 3.15; N, 12.24. found. C, 76.47; H, 7.99; B, 3.21; N, 12.12.

NMR: $\delta^{11}B = 27.9$; $\delta^{1}H = 1.30$ (d, $^3J_{HH} = 7.0$ Hz, 12 H, 4 x CH_3); 3.87 (sept., 2 H, 2 x CH, i-Pr); 6.40-7.55 (m, 12 H, CH pos. 2, 3, 4-7); $\delta^{13}C = 24.8$ (4 x CH_3); 48.3 (2 x CH, i-Pr); 106.18, 112.97, 120.49, 120.81, 122.46, 131.21 (pos. 2, 3, 4-7); 139.89 and 131.0 (quart. C).

Acknowledgments

We wish to thank the Fonds der Chemischen Industrie for supporting this work and Prof. H. Lackner, Inst. f. Organische Chemie, Göttingen, for providing a NOE spectrum of 7.

References and Notes

[1] Dedicated to Prof. U. Schöllkopf on the occasion of his 60th birthday.

[2] A. Meller, W. Maringgele, G. Elter, D. Bromm, M. Noltemeyer, G.M. Sheldrick, Chem. Ber. 120 (1987) 1437.

[3] R. Köster, H. Bellut, G. Benedikt, E. Ziegler, Liebigs Ann. Chem. 724 (1969) 34.

[4] M.A. Kuck, G. Urry, J. Am. Chem. Soc. 88 (1966) 426; see also: Gmelin Handbook of Inorganic Chemistry, 8th Edition, Boron Compounds Part 4, (1975) p. 123.

[5] St. C. Lapin, B.-E. Brauer, G.B. Schuster, J. Am. Chem. Soc. 106 (1984) 2092.

[6] H. Nöth, B. Wrackmeyer, Nuclear Magnetic Resonance Spectroscopy of Boron Compounds, Springer Verlag, Berlin-Heidelberg-New York (1978).

[7] K. Niedenzu, H. Beyer, J.W. Dawson, H. Jenne, Chem. Ber. 96 (1963) 2653.