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A SIMPLE ACCESS TO TETRAZABOROL-2-INES

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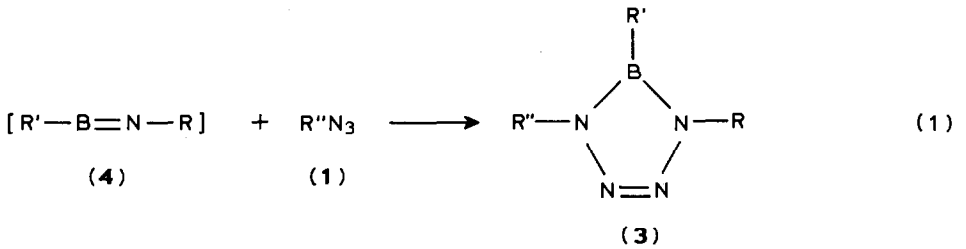
Summary

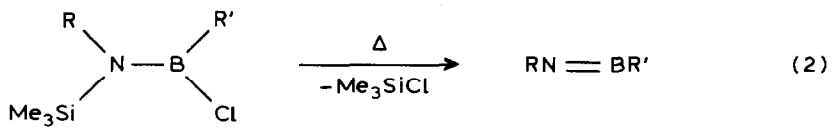
Tetrazaborolines are conveniently prepared by the reaction of organic azides (**1**) with *N*-trimethylsilyl monochloroaminoboranes (**2**) under mild conditions.

Tetrazaborolines (**3**), 5-membered aromatic heterocyclic species with a skeleton involving one boron and four nitrogen atoms, are not too well-documented but have been obtained by a number of routes [1]. Most of these involve the formation of a transient iminoborane [RN=BR′] which then undergoes a 1,3 dipolar cycloaddition with the organic azides $R''N_3$ (eq. 1). Paetzold et al. [2] were the first to devise a



(4) (1) (3) (1)

reliable method for the production of the metastable monomeric iminoboranes (**4**), involving elimination of Me_3SiCl from the *N*-trimethylsilyl monochloroaminoboranes (**2**), in the gas phase at high temperature (eq. 2). It is important to



(2) (4) (2)

note that for kinetic stability, the compounds **2** must contain at least a bulky R group. Paetzold et al. [2] made tetrazaborolines (**3**) (R″ = Ph) by 1,3 dipolar

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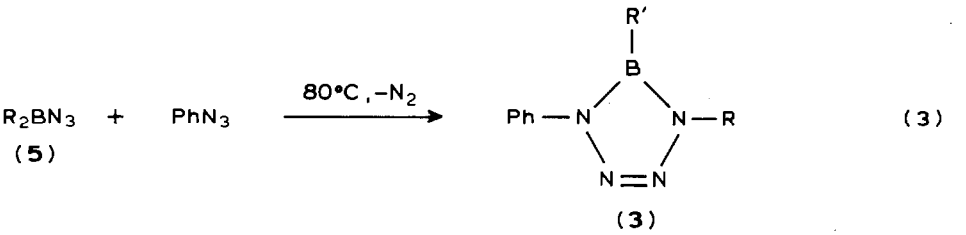
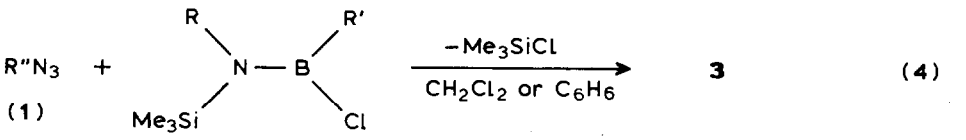
cycloaddition of phenylazide to monomeric **4** at low temperature and in good yields. Compounds **3** are also accessible by thermolysis of dialkylazidoboranes (**5**) in the presence of phenylazide at 80 °C [3] (eq. 3):



These reactions obviously produce tetrazaborolines with identical substituents on the boron and one of the nitrogen atoms of the ring.

We report here a simple and efficient route to various tetrazaborolines (**3**) involving to the following reaction (eq. 4):



The addition of the organic azides (**1**) to a solution of the readily available monochloroboranes (**2**) [4] in anhydrous dichloromethane at room temperature or in benzene at 60 °C gave the tetrazaborolines (**3**), which were isolated in good yields. The results are summarized in Table 1.

The versatility of this method can be seen from this table. Aromatic, aliphatic and functionally-substituted organic azides give equally good results. The substituent R′ on boron may be either aromatic or aliphatic or even chlorine. A wide variety of R groups initially attached to the amino part of the monochloroboranes may be used. Thus, by this method, one can prepare tetrazaborol-2-ines in which R, R′ and R″ are all different. The simplicity of the method, which does not involve the use of the gas phase thermolysis is noteworthy.

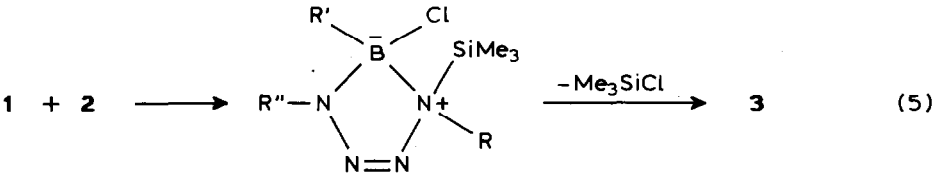
TABLE 1

SYNTHESIS OF 1,4,5-TETRAZABOROL-2-INES (3)

Compound	R	R′	R″	Yield (%) [a]
3a	Me	Ph	Ph	58
3b	Me	Ph	CH_2Ph	70
3c	Me	Cl	Ph	70
3d	t-Bu	Ph	Ph	86
3e	t-Bu	Ph	CH_2Ph	74
3f	t-Bu	Ph	$(CH_2)_4CN$	84
3g	t-Bu	n-C_6H_{13}	CH_2Ph	75

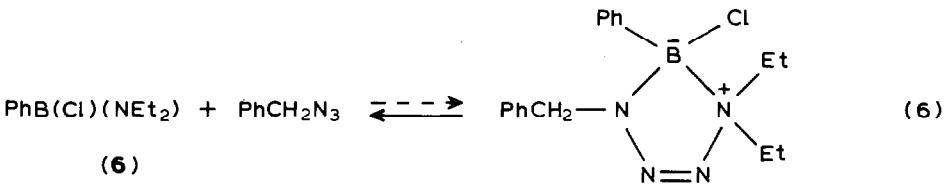
[a] Yields refer to isolated pure products.

As far as the mechanism of this reaction is concerned the following comments are relevant. The boranes (**2**) were recovered unchanged (as revealed by NMR monitoring) after 18 h at 60 °C in benzene under nitrogen. Thus, **3** cannot be formed by a 1,3 dipolar cycloaddition of the azides (**1**) with an initially formed iminoborane (**4**). A possible route might involve the addition, concerted or otherwise, of the azide (**1**) to the B–N bond (isoelectronic with a carbon–carbon double bond) of the aminoborane (**2**) to give an intermediate (**5**), which would give **3** via a Me_3SiCl elimination (eq. 5). Such an addition of an azide to a BN bond leading to a betaine of type **5** has been observed [5]. Furthermore, no reaction could be detected when

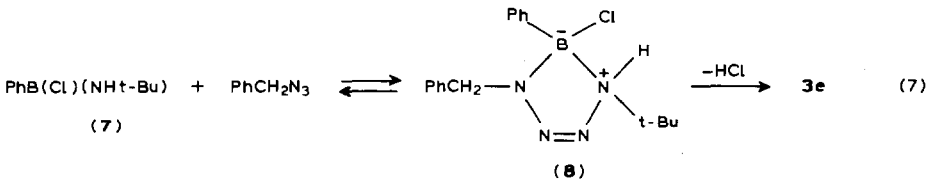


(**5**)

a mixture of the aminoborane (**6**) with benzyl azide in benzene was kept for 12 h at 65 °C (eq. 6). In contrast, the aminoborane (**7**) reacts rapidly at room temperature



with benzylazide to give the tetrazaboroline (**3e**) quantitatively (80% isolated yield) according to reaction 7. Thus, irreversible elimination of Me_3SiCl from **5** or of HCl from **8** seems to be essential for the formation of tetrazaborolines.



(**8**)

Conclusion

The reaction of azides with *N*-trimethylsilyl-aminochloroboranes offers a versatile and simple route to a variety of tetrazaborolines from readily available starting materials. These compounds may act as precursors of the three membered rings (diazaboriridines) by a nitrogen extrusion, but we have so far been unable to produce such rings by thermolysis or photolysis of **3**.

Experimental

All experiments were carried out under dry nitrogen by use of conventional syringe techniques. Methylene chloride and benzene were freshly distilled from calcium hydride and sodium benzophenone ketyl, respectively.

Melting points were determined with a Kofler apparatus. ^1H NMR spectra were recorded on a Bruker WH 80 (80 MHz) spectrometer. Chemical shifts are given in ppm relative to tetramethylsilane as internal standard. Mass spectra were obtained on a Varian Mat 311 spectrometer at 70 eV (Centre de Mesures Physiques de l'Ouest, Rennes). Elemental analyses were performed by the Laboratoire Central de microanalyses du C.N.R.S. (Lyon).

The *N*-trimethylsilylamino monochloroboranes (**2**) were prepared by published procedures [4] and stored under nitrogen at low temperature (−23° C).

Preparation of tetrazaborolines (3)

A solution of x mmoles of *N*-trimethylsilylamino-chloroborane (**2**) and x mmoles of azide (**1**) in x ml of benzene or dichloromethane was stirred at t° C for n hours. Removal of the solvent provided an oily residue which was purified by column chromatography (silica gel, eluant ether : hexane H = H, 2 : 8).

(3a) 1-methyl-4,5-diphenyltetrazaborol-2-ine. $x = 2.35$, $t = 40$, CH_2Cl_2, $n = 8$, m.p. 103–104° C, yield = 58%. ^1H NMR ($CDCl_3$) δ: 3.76 (s, 3H); 7.25–7.55 (m, 10H). Anal. Found: C, 66.13; H, 5.56; N, 23.72. $C_{13}H_{13}N_4B$ calc: C, 66.14; H, 5.55; N, 23.73%.

(3b) 1-methyl-4-benzyl-5-phenyltetrazaborol-2-ine. $x = 24.9$, $t = 25$, CH_2Cl_2, $n =$ 8, m.p. 41–42° C, yield = 70%. ^1H NMR ($CDCl_3$) δ: 3.77 (s, 3H); 5.20 (s, 2H); 7.26 (br.s, 5H); 7.45 (br.s, 5H). Anal. Found: C, 67.37; H, 6.15; N, 22.44. $C_{14}H_{15}N_4B$ calc: C, 67.23; H, 6.05; N, 22.40%.

(3c) 1-methyl-4-phenyl-5-chlorotetrazaborol-2-ine. $x = 13.2$, $t = 25$, without solvent, $n = 48$, $b.p._{0.01} = 100$° C, yield 70%. ^1H NMR ($CDCl_3$) δ: 3.61 (s, 3H); 7.22–7.75 (m, 5H). Mass spectrum (m/z relative intensity): 194 (93, $M^{\cdot+}$); 165 (46), 137 (100).

(3d) 1-t-butyl-4,5-diphenyltetrazaborol-2-ine. $x = 4.6$, $t = 60$, benzene, $n = 12$, m.p. = 134–135° C, yield 86%. ^1H NMR ($CDCl_3$) δ: 1.55 (s, 9H); 7.20–7.30 (m, 5H); 7.38 (br.s, 5H). Anal. Found: C, 68.95; H, 6.96; N, 20.27. $C_{16}H_{19}N_4B$ calc: C, 69.09; H, 6.89; N, 20.14%.

(3e) 1-t-butyl-4-benzyl-5-phenyltetrazaborol-2-ine. $x = 1.9$, $t = 60$, benzene, $n = 8$, $b.p._{0.01}$ 125° C, yield 74%. ^1H NMR ($CDCl_3$) δ: 1.53 (s, 9H); 4.90 (s, 2H); 7.08–7.25 (m, 5H); 7.33 (s, 5H). Anal. Found: H, 7.14; N, 19.05. $C_{17}H_{21}N_4B$ calc: H, 7.24; N, 19.18%.

(3f) 1-t-butyl-4-(4-cyano butyl)-5-phenyltetrazaborol-2-ine. $x = 4.3$, $t = 25$, CH_2Cl_2, $n = 8$, m.p. 63–64° C, yield 84%. ^1H NMR ($CDCl_3$) δ: 1.51 (s, 9H); 1.65–1.95 (m, 4H); 2.33 (t, 2H, ^3J 6.4 Hz); 3.81 (t, 2H, ^3J 6.3 Hz); 7.40 (s, 5H). IR (Nujol) ν(cm^{-1}): 2240 (C≡N). Anal. Found: C, 63.76; H, 7.79; N, 24.93. $C_{15}H_{22}N_5B$ calc: C, 63.62; H, 7.83; N, 24.73%.

(3g) 1-t-butyl-5-hexyl-4-benzyltetrazaborol-2-ine. $x = 4.7$, $t = 60$, benzene, $n = 8$, $b.p._{0.01}$ 95° C, yield 75%. ^1H NMR ($CDCl_3$) δ: 0.85 to 1.05 (m, 3H); 1.25 to 1.45 (m, 10H); 1.62 (s, 9H); 5.07 (s, 2H); 7.18–7.24 (m, 5H). Mass spectrum (m/z, relative intensity): 250 (100, $M^{\cdot+}$), 221 (21), 193 (11), 117 (17).

Reaction of N-t-butylamino chlorophenylborane with benzylazide

A solution of 5 mmoles of benzylazide and 5 mmoles of (*N*-t-butylamino)(phenyl)chloroborane [6] in 5 ml of benzene was stirred for 18 h at 25° C. After removal of benzene by distillation at reduced pressure, the oily residue

was purified by column chromatography on silica gel (ether/petroleum ether, 1/4). Yield = 80% (identical with **3e** prepared as described above).

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