The Iminoborane $tBuB \equiv NtBu$ as a Dipolarphile in (2+3) Cycloadditions

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Abstract. The iminoborane $tBuB\equiv NtBu$ and the diazomethane $tBuCH=N_2$ give the (2+3) cycloadduct [-HC(tBu)-N=N-N(tBu)=B(tBu)-] in a 1:1 reaction and the seven-membered ring [-C(tBu)=N-NH-N(tBu)=B(tBu)-N(tBu)=B(tBu)-] in a 2:1 reaction. The (2+3) cycloadduct decomposes above 0 °C to give the seven-membered ring, N₂, and HC(tBu)=N-N=CH(tBu) in the ratio 2:1:1. The borane $tBuB\equiv NtBu$ and organic azides R"N₃

yield the (2+3) cycloadducts [-R''N-N=N-N(tBu)=B(tBu)-](R'' = Me, Et, Pr, Bu, *i*Bu, *s*Bu, C₅H₁₁, *c*-C₅H₉, *c*-C₆H₁₁, Bzl, EtOOC).

Keywords: Iminoborane, (2+3) Cycloadducts, Azaboracyclopentadienes, Azaboracycloheptatrienes

We have intensively investigated the synthesis of the shortlived diorganoiminoboranes $RB \equiv NR'$ [1], their stabilization by cyclodi-, -tri-, and -tetramerization or polymerization [1, 2], and their reactions at the BN triple bond: 1,2addtions of polar and unpolar molecules and (2+1), (2+2), and (2+3) cycloadditions with appropriate systems [1]. Partners in the (2+3) cycloaddition were predominantly organic azides R"N₃ [Eq. (1)], explored with 19 different iminoboranes and three azides (R" = Ph, Bzl, *i*Bu) [3]. Azidoboranes R"₂BN₃ do not react according to Eq. (1), but give an azidoboration [Eq. (2)] [4], and the azidosilaten Me₃SiN₃ gives a mixture of cycloaddition and azidosilation products with more of the latter [3c,d]. The nitrone O–NMe=CHPh was explored as a 1,3 dipolar agent with two different iminoboranes [Eq. (3)] [5].

Because of the steric demand of the *tert*-butyl groups, the iminoborane tBuB=NtBu can be more easily handled than other iminoboranes ($t_{1/2}$ ca. 3 d at 50 °C), but it is still rather reactive. It gives the (2+3) cycloadduct with PhN₃ and exclusively the azidoboration product with Me₃SiN₃ [6]. We report here on the (2+3) cycloaddition with *tert*-butyldiazomethane and on further cycloadditions with a series of organic azides.

In pentane at -15 °C, the iminoborane *t*BuB=N*t*Bu and the diazomethane *t*BuCH=N₂, in a 1:1 ratio, give the corresponding 1,2-diaza-3-azonia-4-borata-1,3-cyclopentadiene as a colourless oily liquid, according to Eq. (4). The proposed structure of the product is in accord with the ¹H, ¹¹B, and ¹³C NMR data, proving the presence of three different *t*Bu groups and a CH fragment. The ¹¹B NMR signal of five-membered rings with a C-B(R)=N fragment is expected in the range $\delta = 41-51$ [7], but is observed in our product low field-shifted at $\delta = 53.8$. This is possibly a

+ R''N RB NR' + R",BN (3) -NMe=CH tBu-B=N-tBu (5)(6) + tBuB NtBu 2 tBu—B≣N—tBu HtBuC=N tBu tBu tBu (7) HtBuC: tBu /Bu - 1/2 Ht BuC: - 1/2 N₂ SiMe₃ SiMe₂CI (8)

SiMe.

+ Me₃SiN

CIMe.Si

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consequence of a weakened BN π -bond, since the bulky tBu groups force boron and its three ligands out of planarity. The 2:1 reaction of the same components at 0 °C yields the corresponding 1,2-diaza-3,5-diazonia-4,6-diborata-3,5,7cycloheptatriene, according to Eq (5). This product is also formed, when a second mole of tBuB = NtBu is added to the product of Eq. (4), according to Eq. (6). The colourless, oily heterocycloheptatriene is identified by two characteristic ¹¹B NMR peaks in the ratio 1:1 at $\delta = 29.3$ (B4, adjacent to C, N, N) and 40.3 (B6, adjacent to C, C, N) [7], by a broad ¹H NMR signal at $\delta = 3.73$ (CH_{ring}), by the ¹H and ¹³C NMR signals for five different *t*Bu groups, and by a ¹³C NMR signal at $\delta = 145$ (C7). As a 10 π -electron aromatic system, planarity of the seven-membered ring would be expected, if the sterically demanding tBu group did not press the ring too much out of planarity.

The heterocyclopentadiene is not stable in pentane above 0 °C and decomposes into the heterocycloheptatriene, nitrogen, and the 2,3-diaza-1,3-butadiene HtBuC=N-N= CHtBu, according to Eq. (7). Obviously, half of the cyclopentadiene is decomposed under reversion of the formation, Eq. (4), the hereby formed iminoborane reacts with the undecomposed portion of the cyclopentadiene to give the cycloheptatriene, Eq. (6), and the diazomethane component decomposes in a well known manner [8] to give nitrogen and the diazabutadiene. A complete reversion of reaction (4) can be achieved, when the heterocyclopentadiene is heated up to 50 °C without a solvent, but then a part of the products, $tBuB\equiv NtBu$ and $HtBuC=N_2$, is transformed into unidentified polymers.

The formation of the heterocycloheptatriene includes the 1,3-migration of a proton from carbon to nitrogen, allowing the aromatization of the seven-membered ring. We wonder,

why such a 1,3-proton shift does not occur with the heterocyclopentadiene, though this shift would transform the diene-type ring into an aromatic 6π -electron system. We had observed a comparable 1,3-shift of a Me₃Si group at the same cyclopentadiene ring system, when we performed a (2+3) cycloaddition of the methyleneborane MeB= C(SiMe₃)₂ and Me₃SiN₃ [Eq. (8)] [9].

The addition of a slight excess of the azides $R''N_3$ to the iminoborane tBuB=NtBu yields the corresponding triazaazoniaboratacyclopentadienes, according to Eq. (1) (R'' = Me, Et, Pr, Bu, *i*Bu, *s*Bu, C₅H₁₁, *c*-C₅H₉, *c*-C₆H₁₁, Bzl, EtOOC). The products were characterized by their ¹H and ¹¹B NMR data and by elemental analysis (Table 1). The ¹¹B NMR signals are found in the typical range of $\delta = 26-30$ [3].

Experimental

NMR: Bruker WP 80 PFT (¹H), Jeol JNM-PS-100 (¹¹B), Bruker WH 270 (¹³C); standards: tms (intern; ¹H, ¹³C), BF₃(OEt₂) (extern; ¹¹B); in CDCl₃.

3,4,5-*Tri-tert-butyl-1,2-diaza-3-azonia-4-borata-1,3-cyclopentadiene*: An equimolar mixture (10.8 mmol) of $tBuB\equiv NtBu$ [6] and $tBuCHN_2$ [10] in pentane (20 ml) is stirred at $-15 \text{ }^{\circ}\text{C}$ (3 h). Diethyl ether is added until the solution is clear. The product crystallizes over night at $-70 \text{ }^{\circ}\text{C}$. It is filtrated at low temperature (in order to avoid melting) and again recrystallized from pentane/diethyl ether (74 %). The solid can be stored at $-70 \text{ }^{\circ}\text{C}$.

¹**H** NMR: $\delta = 1.07$, 1.16, 1.58, 3.83 (4 s; 9:9:9:1). – ¹¹**B** NMR (-30 °C): $\delta = 53.8$. – ¹³**C** NMR (-30 °C): $\delta = 19$ (broad) 37.2, 56.3 (3 s; *t*Bu), 30.0, 30.4, 31.2 (3 q; *t*Bu), 91.2 (d; $b_{1/2} = 27$ Hz).

3,4,5,6,7-Penta-tert-butyl-1,2-diaza-3,5-diazonia-4,6-diborata-3,5,7cycloheptatriene: A mixture of $tBuB\equiv NtBu$ (25.2 mmol) and

Table 1 Synthesis and characterization of the triazazoniaboratacyclopentadienes [-R''N-N=N-N(tBu)=B(tBu)-]: amounts of tBuBNtBu (n_1) and $R''N_3$ (n_2) (mmol), boiling points (°C) at reduced pressure (Pa) (in the case of $R = c-C_6H_{11}$: sublimation point), yields (%), ¹H and ¹¹B NMR shifts (ppm), and analytical data for C, H, N (%).

Me	Et	Pr	Bu	<i>i</i> Bu	sBu ^{a)}
27.3/29.8	18.0/21.1	10.1/15.3	10.1/15.1	20.1/30.3	10.1/15.1
39/0.5/71	42/0.5/66	50/0.8/66	53/0.5/79	52/0.2/73	49/0.3/71
1.25/1.58	1.26/1.59	1.25/1.59	1.25/1.59	1.25/1.60	1.25/1.60
3.72 (s, 3H)	1.36 (t, 3H)	0.94 (t, 3H)	0.95-1.88 (7H)	0.91 (d, 6H)	0.82 (t, 3H)
	4.07 (q, 2H)	1.39-1.92 (2H)	4.00 (t, 2H)	1.81-2.38 (1H)	1.42 (d, 3H)
		3.96(t,2H)		3.83 (d, 2H)	1.66-2.22 (2H)
27.5	26.9	27.3	26.9	27.4	26.7
55.12/55.04	57.16/57.87	58.94/58.96	60.51/60.48	60.51/60.41	60.51/60.69
10.79/10.56	11.03/11.47	11.24/11.56	11.42/11.44	11.42/11.59	11.42/11.24
28.57/28.41	26.66/26.51	24.99/25.07	23.52/23.48	23.52/23.75	23.52/23.69
C ₅ H ₁₁	c-C ₅ H ₉	<i>c</i> -C ₆ H ₁₁	Bzl	EtOOC	
10.1/15.0	10.1/15.3	10.1/15.2	10.1/15.0	10.1/40.0	
66/0.4/82	67/0.5/67	80/0.5/71	100/0.3/62	85/0.5/51	
1.25/1.59	1.26/1.59	1.24/1.59	1.14/1.62	1.30/1.62	
0.77-1.93 (9H)	1.47-2.23 (8H)	1.24-2.00 (10H)	5.29 (s, 2H)	1.43 (t, 3H)	
3.99 (t, 2H)	4.65 (mc, 1H)	4.00 (mc, 1H)	7.20 (mc, 5H)	4.44 (q, 2H)	
26.8	27.3	29.0	26.7	30.3	
61.91/61.63	62.41/62.36	63.64/63.48	66.19/66.34	51.99/51.93	
11.59/11.89	10.88/10.52	11.06/11.31	9.26/9.36	9.12/9.12	
22.21/22.08	22.39/22.25	21.20/20.95	20.58/20.25	22.05/22.20	
	Me 27.3/29.8 39/0.5/71 1.25/1.58 3.72 (s, 3H) 27.5 55.12/55.04 10.79/10.56 28.57/28.41 C ₅ H ₁₁ 10.1/15.0 66/0.4/82 1.25/1.59 0.77-1.93 (9H) 3.99 (t, 2H) 26.8 61.91/61.63 11.59/11.89 22.21/22.08	$\begin{array}{cccc} Me & Et \\ 27,3/29.8 & 18.0/21.1 \\ 39/0.5/71 & 42/0.5/66 \\ 1.25/1.58 & 1.26/1.59 \\ 3.72 (s, 3H) & 1.36 (t, 3H) \\ 4.07 (q, 2H) \\ \end{array}$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$

^{a)} Additional: $\delta(^{1}H) = 4.21$ (pseudo-sext., 1H).

tBuCHN₂ (12.6 mmol) in hexane (20 ml) is stirred at 0 °C (12 h). The yellow colour finally disappears. The product is obtained at 87 °C/0.3 Pa as a colourless oil (71 %).

 $C_{21}H_{46}B_2N_4~(376.2);$ C (found/calc.): 66.85/67.04, H 12.55/12.32, N 14.23/14.89 %.

¹H NMR: δ = 0.85, 1.01, 1.30, 1.38, 1.60, 3.73 (6 s; 9:9:9:9:9:1). - ¹¹B NMR: δ = 29.3, 40.3 (2 s; 1:1). - ¹³C NMR: δ =17.9, 21.4, 37.7, 51.2, 58.7 (5 s; *t*Bu), 29.0, 31.0, 33.3, 34.8, 42.4 (5 q; *t*Bu), 145 (s; $b_{1/2}$ = 81 Hz). - MS (MAT-CH5; 70 eV): m/e = 376 (25 %; M⁺), 361 (3; M-Me), 319 (6; M-C₄H₉), 305 (13; M-Me-C₄H₉), 57 (100; C₄H₉), etc.

4,5-Di-tert-butyl-1-organyl-1,2,3-triaza-4-azonia-5-borata-2,4cyclopentadienes [-R"N-N=N-N(tBu)=B(tBu)-]: The iminoborane tBuB≡NtBu is added to the azide R"N₃ [11], generally without a solvent; in the case of R" = Me, Et, however, each of the components is dissolved in pentane (10 ml). The general starting temperature is -20 °C, but is -78 °C in the case of R" = Me, Et and is 22 °C in the case of R" = EtOOC. The solutions are brought to ambient temperature and stirred for 2 h; in the case R" = Me, Et, stirring is not necessary; in the case of R" = EtOOC, 6 h stirring at 50 °C is necessary. The colourless products are liquids, but are solids in the case of R" = c-C₆H₁₁, Bzl (m.p. 98 and 58 °C, respectively). Further data are presented in Table 1.

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