## **Preliminary communication**

## THE RADICAL ANION FROM TETRA-t-BUTYLDIBORANE(4)

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## Summary

The title radical has been generated from di-t-butylchloro- or di-t-butylbromo-borane and Na/K alloy and identified by ESR spectroscopy. Formation of a tetraalkyldiborane(4) by reductive dimerization of dialkylhalogenoboranes is thus demonstrated for the first time.

Attempts to synthesize the strongly hindered tetra-t-butyldiborane(4) (I) have been unsuccessful [1-3] as have those to synthesize the related tetra-t-butylethylene (IV) [4]. Since radical anions [5,6] of tetraalkyldiboranes(4) are more persistent than the corresponding diboranes(4), we tried to generate the radical anion II from I and present here the ESR identification of II, which is isoelectronic with the unknown radical cation III from IV.



The precursors of II, di-t-butylchloroborane (VII) or di-t-butylbromoborane (VIII) were synthesized by the following routes:

 $B(OMe)_{3} + 2 RLi \rightarrow R_{2}BOMe \xrightarrow{BX_{3}} (Va, Vb)$   $(a: R = C(CH_{3})_{3}, \land CH_{3}OH$   $b: R = C(CD_{3})_{3}) \land CH_{3}OH$   $Cl_{2}BNMe_{2} + 2 RLi \rightarrow R_{2}BNMe_{2} [8] \xrightarrow{HX} (VIIa, VIIb: X = Cl [7]; VIIIa, VIIIb: X = Br)$  (VIa, VIb)

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Contrary to statements in the literature [3,9] di-t-butylmethoxyborane (V) (b.p.:  $75^{\circ}C/50 \text{ mmHg}$ , <sup>1</sup>H-NMR in CDCl<sub>3</sub>: 3.88 (s, 3H), 0.97 (s, 18H), <sup>11</sup>B-NMR: 50.9) can be prepared from trimethoxyborane and t-BuLi in petroleum ether (b.p. 40–60°C) in 88% yield (50 mmol scale). V is also obtained from VI by heating with methanol. Reaction with BCl<sub>3</sub> (-10°C) or BBr<sub>3</sub> (-78°C)



Fig. 1. ESR spectrum of the radical obtained from VIIa or VIIIa and Na/K alloy in THF at 25°C.



Fig. 2. ESR spectrum of the radical obtained from VIIb or VIIb and Na/K alloy in THF at 50°C.

easily converts V to VII (b.p.: 60°C/50 mmHg. <sup>1</sup>H-NMR in CDCl<sub>3</sub>: 1.06 (s), <sup>11</sup>B-NMR: 77.0) or VIII (b.p.: 70-71°C/45 mmHg, <sup>1</sup>H-NMR: 1.13 (s), <sup>11</sup>B-NMR: 82.4).

On reaction of VIIa or VIIIa with Na/K alloy in ether solvents (THF, DME, diglyme, triglyme) at temperatures not lower than  $-10^{\circ}$ C we obtained the ESR spectrum shown in Fig. 1. A proton splitting of 0.54 G but no boron splitting can be extracted from this spectrum. The ESR spectrum of the radical obtained from the perdeuterated boranes VIIb or VIIIb (Fig. 2), however, clearly shows a 1/2/3/4/3/2/1 septet characteristic for two equivalent boron atoms.

The spectrum of Fig. 1 can be simulated with a(H) = 0.54 G for 36 equivalent protons and  $a(^{11}B) = 1.44$  G (2B). This boron coupling constant is of the order of magnitude found for the radical anions of tetraneopentyldiborane(4) IX (0.8 G [5]) and of di-t-butyldineopentyldiborane(4) (X) (< 0.3 G [6]). The *g*-value of the new radical 2.0024 is the same as those for IX and X. We therefore conclude, that the radical under discussion is the radical anion II from tetra-t-butyldiborane(4).

Generation of II from VII or VIII demands formation of I as an intermediate:

R <sub>2</sub> BHal	+ Na/K $\rightarrow$	$[R_2B^*] \xrightarrow{x2}$	$R_2B - BR_2 \xrightarrow{e^-}$	II
(VII, VIII)		(XI)	(I)	
$(\mathbf{R} = \mathbf{t} - \mathbf{B}\mathbf{u})$				

Earlier attempts to form tetraalkyldiboranes(4) by reductive dimerization of dialkylhalogenoboranes have been unsuccessful [10]. We are unable to observe the very persistent radical anion IX upon reaction of dineopentylbromoborane with Na/K alloy. These results are easily explained by a fast hydrogen atom transfer from the  $\alpha$ -position to the radical center of the primary dialkylboryl radicals, as proposed by Köster [11]. In the case of di-t-butylboryl (XI) there are no  $\alpha$ -hydrogen atoms.

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