

Contrary to statements in the literature [3,9] di-*t*-butylmethoxyborane (V) (b.p.: 75°C/50 mmHg, $^1\text{H-NMR}$ in CDCl_3 : 3.88 (s, 3H), 0.97 (s, 18H), $^{11}\text{B-NMR}$: 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_3 (–10°C) or BBr_3 (–78°C)

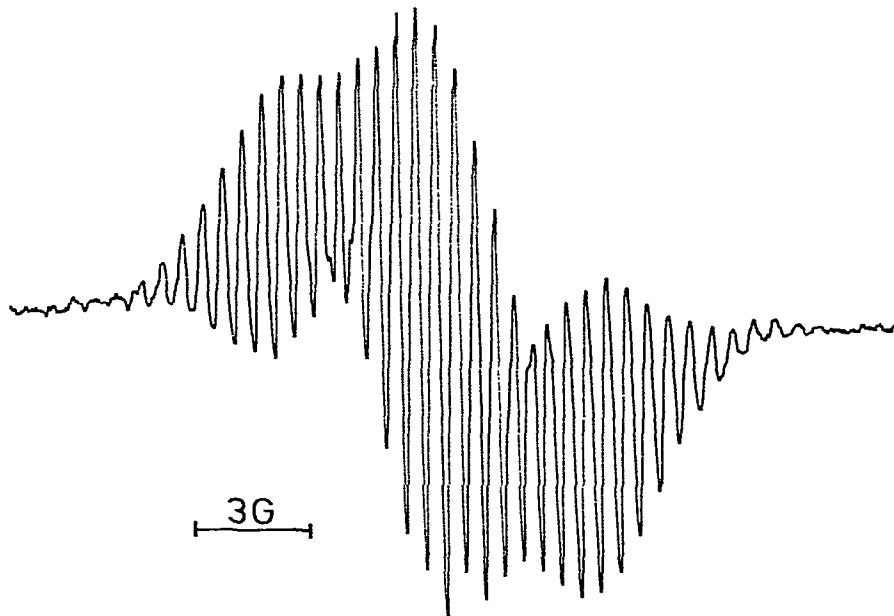


Fig. 1. ESR spectrum of the radical obtained from VIIa or VIIIa and Na/K alloy in THF at 25°C.

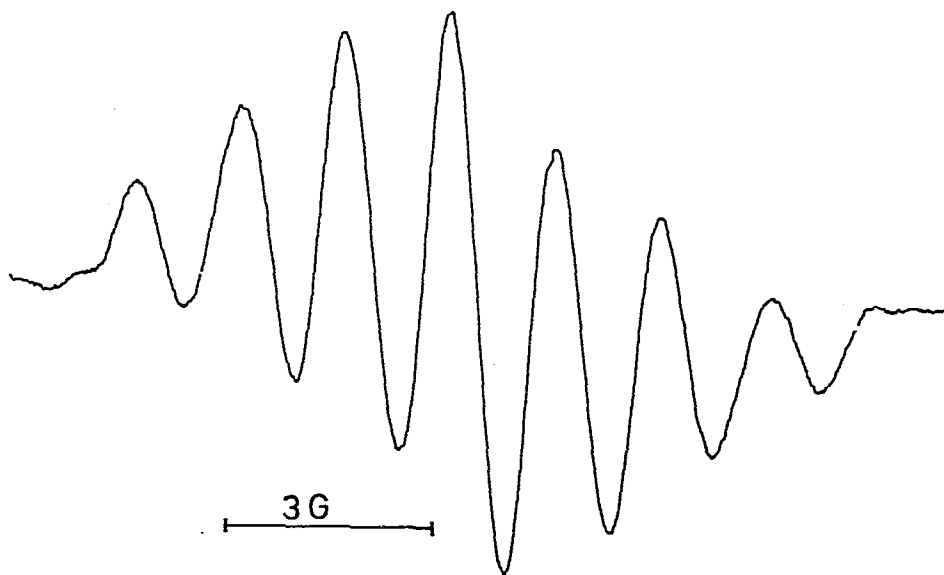


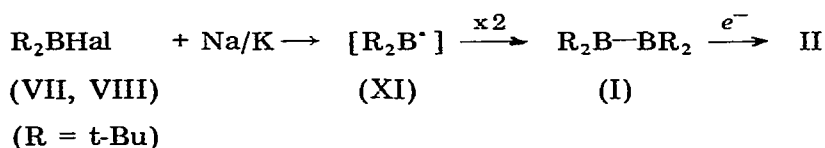
Fig. 2. ESR spectrum of the radical obtained from VIIb or VIIIb and Na/K alloy in THF at 50°C.

easily converts V to VII (b.p.: 60°C/50 mmHg. $^1\text{H-NMR}$ in CDCl_3 : 1.06 (s), $^{11}\text{B-NMR}$: 77.0) or VIII (b.p.: 70–71°C/45 mmHg, $^1\text{H-NMR}$: 1.13 (s), $^{11}\text{B-NMR}$: 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°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 $a(\text{H}) = 0.54$ G for 36 equivalent protons and $a(^{11}\text{B}) = 1.44$ G (2B). This boron coupling constant is of the order of magnitude found for the radical anions of tetraeneopentylidiborane(4) IX (0.8 G [5]) and of di-*t*-butyldineopentylidiborane(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:



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 α -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 α -hydrogen atoms.

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