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Preliminary communication

RADICAL ANIONS FROM ORGANOBORANES

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Summary

Radical anions of boranes, which are isoelectronic with tertiary alkyl, allyl and benzyl radicals, have been characterized by ESR spectroscopy. The remarkable sensitivity of boron coupling constants to substituent effects is taken to indicate that boron is more easily pyramidalized than carbon.

While many carbon-centered radicals II [1] and the isoelectronic nitrogen-centered radicals III [2] have been characterized by ESR spectroscopy, only a few special examples [3—6] of the isoelectronic boron-centered radicals I are known. Attempts [3] to identify radicals with R = alkyl have been unsuccessful.

$\dot{B}^{-}R_3$	$\dot{C}R_3$	$\dot{N}^{+}R_3$
(I)	(II)	(III)

We have made use of the power of t-butyl [7—9] and neopentyl [10,11] groups to increase the lifetimes of radicals and present here for the first time ESR coupling constants of radical anions of trialkyl-, dialkylvinyl- and dialkylaryl-boranes, which are isoelectronic with tertiary alkyl, allyl and benzyl radicals.

Synthesis of the boranes followed known routes and will be described in a full paper. Reduction was performed with sodium-potassium alloy in 1,2-dimethoxyethane/THF mixtures. ESR spectra of Ic and Id could be obtained only when the potassium-complexing dicyclohexyl-18-crown-6 was added [5]. The ESR spectrum of Ia is shown in Fig. 1, ESR coupling constants are given in Table 1.

The electronic effect of $B^{\bullet-}$ in delocalized radicals as Ie—Ig is similar to that of $C^{\bullet}$ in corresponding allyl and benzyl radicals. This follows from the

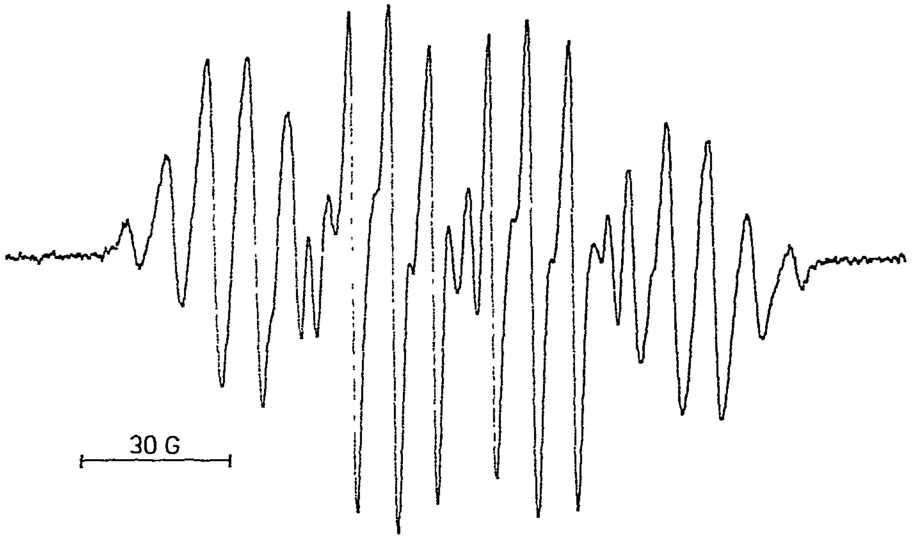


Fig. 1. ESR spectrum of the radical anion from trineopentylborane at −50°C in DME/THF (1/2 v/v).

spin density of ca. 0.5 in the vinyl or aryl part of Ie—Ig, which is calculated from $a(\mathrm{H}) = Q(\mathrm{H}) \times \rho_{\mathrm{C}}$ and $Q(\mathrm{H}) = 20.8$ G [12] and 21.8 G [13]. From the remaining spin density at boron and the experimental $a(^{11}\mathrm{B})$ values for Ie—Ig, the value of the quantity $Q(\mathrm{B})$ in the relation $a(\mathrm{B}) = Q(\mathrm{B}) \times \rho_{\mathrm{B}}$ is calculated to be ca. 15 G.

Steric hindrance is expected to be less effective in boron- than in carbon-centered radicals, since C—B bonds are longer than the corresponding C—C bonds [14]. This expectation is confirmed by (i) the lower barrier to rotation of the neopentyl groups in Ia than in IIa, as indicated by the lower temperature (−50°C, for Ia compared with +47°C for IIa [10]) at which fast rotation leads to similar relative intensities of the ESR lines; and (ii) by the considerably smaller twist angle for Ih (ca. 30°) than for IIh (90° [9]). The twist angle for Ih is deduced from the lower ring proton coupling constants for Ih relative to those for Ig upon the assumption that twisting of radical anions

TABLE 1

ESR COUPLING CONSTANTS (in Gauss 10^{-4} T) OF RADICALS I

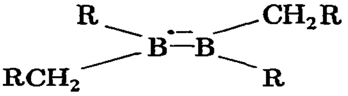
Radical	R^1	R^2	R^3	Temp. (°C)	$a(^{11}\mathrm{B})$	$a(\mathrm{H})$
Ia	CH_2-t-Bu	CH_2-t-Bu	CH_2-t-Bu	−50	28.0	8.0 (6H)[a]
Ib	t-Bu	CH_2-t-Bu	CH_2-t-Bu	−70	33.4[b]	6.3 (4H)
Ic	t-Bu	t-Bu	CH_2-t-Bu	−80	34.6	6.6 (2H)
Id	t-Bu	t-Bu	t-Bu	−100	38.5	—
Ie	CD_2-t-Bu	CD_2-t-Bu	CD=CH-t-Bu	−5	7.5	10.6 (1H); 4.0 (4H)[c]
If	t-Bu	t-Bu	CH=CH-t-Bu	−30	8.4	9.6 (1H)
Ig	CD_2-t-Bu	CD_2-t-Bu	Ar[d]	+40	5.95	3.65 (2H); 6.60 (1H); 0.60 (4D)
Ih	d^9-t-Bu	d^9-t-Bu	Ar[d]	<−60	9.3	3.1 (2H); 5.0 (1H)

[a] Line width alternation effects, especially at lower temperatures. [b] An additional radical of unknown structure with $a(^{11}\mathrm{B})$ 22.3 G was observed. [c] From undeuterated radical. [d] Ar = 3,5-di-t-butylphenyl.

from phenylboranes leads to the same relative decrease in delocalization as in the case of benzyl radicals.

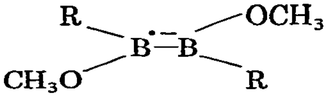
The most interesting result is the strong effect of alkyl substituents on boron coupling constants of radicals from trialkyl-boranes. $a(^{11}B)$ of Ia is 40% larger than $a(^{11}B)$ 19.9 G [6] of $\dot{B}H_3^-$ and 87% larger than to be expected from $Q(B) \sim 15$ G, while the corresponding $a(^{13}C)$ 40.0 G [10] of the more hindered IIa is only 4% larger than $a(^{13}C)$ 38.3 G [17] of $\dot{C}H_3$. Replacement of neopentyl by t-butyl groups increases $a(^{11}B)$ up to additional 38% in Id, while the corresponding increase in $a(^{13}C)$ of the more hindered IId ($a(^{13}C)$ 51.5 G [18]) is only 29%.

A high sensitivity of $a(^{11}B)$ to substituent effects is also apparent in the remarkable increase of $a(^{11}B)$ from < 0.3 G in IV to 8.5 G in V on replacement of neopentyl by methoxy groups.



(IV)

R = t-Bu



(V)

The increase of $a(^{13}C)$ upon introduction of alkoxy groups into carbon-centered radicals II ($a(^{13}C)$ 47.2 G in $H_2\dot{C}{-}OCH_3$ and 97.9 G [19] in $H\dot{C}(OCD_3)_3$ as compared to 38.3 G [17] in $\dot{C}H_3$) is generally accepted to indicate pyramidalization at the radical center. We therefore conclude that boron in radicals I is more easily pyramidalized than carbon in radicals II.

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