CHEMISTRY LETTERS, pp. 1199-1200, 1975. Published by the Chemical Society of Japan

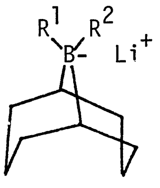
^{1}H AND ^{13}C NMR SPECTRA OF TETRAALKYLBORON ATE COMPLEXES. HYDRIDE CHARACTER OF α-HYDROGENS TO BORON[1)]

Yoshinori YAMAMOTO,* Hiroo TOI, Akio SONODA, and Schun-Ichi MURAHASHI
Department of Chemistry, Faculty of Engineering Science
Osaka University, Toyonaka, Osaka 560

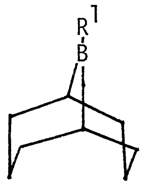
^{1}H and/or ^{13}C NMR spectra of tetraalkylboron ate complexes (1 - 3) reveal that the α-hydrogens and/or α-carbons to boron are shielded in comparison with those of the corresponding trialkylboranes (4 - 6). These results indicate the hydride character of α-hydrogens in 1 - 3.

We recently reported that 9-borabicyclo[3.3.1]nonane (9-BBN) ate complexes (1) enable the selective removal of halo group from tertiary alkyl, benzyl, and allyl halides to afford the corresponding hydrocarbons in excellent yields without a concomitant attack on secondary, primary, and aryl derivatives.[2)] The bridgehead α-hydrogen of the 9-BBN ring acts as the reducing species, and the reducing ability of 1 is the most effective among the ate complexes such as Li^+(sec-Bu)$_3$(n-Bu)B^- (2) and Li^+(n-Bu)$_4B^-$ (3). Although the hydride character of α-hydrogens to boron in tetra-n-alkylboron ate complexes was originally proposed by Wittig,[3)] only a few reports on the spectroscopic study have appeared.[4)] Especially there is no literature on the evidence for the hydride character of α-hydrogens in the sec-alkylboron and bicyclic boron ate complexes. Consequently, both the interesting reducing character of 1 and the lack of evidence provoked us to examine the ^{1}H and ^{13}C NMR spectra of such tetraalkylboron ate complexes.

The ate complexes (1 - 3) were prepared from the reaction of the corresponding trialkylboranes (4 - 6) with n-butyllithium in hexane. The ^{1}H and ^{13}C NMR spectra are summarized in Tables I and II, respectively.



1a, $R^1 = R^2 =$ n-Bu
b, $R^1 = CH_3$; $R^2 =$ n-Bu



4a, $R^1 =$ n-Bu
b, $R^1 = CH_3$

(sec-Bu)$_3$B
5

(n-Bu)$_3$B
6

Table I. ^{1}H Chemical Shifts of the α-Hydrogens to Boron[a]

Ate Complex	CH	CH_2	CH_3	Borane	CH	CH_2	CH_3
1a	0.02	0.08		**4a**	1.16	0.97	
1b	0	-0.16	-0.62	**4b**	1.16		0.90
2	0.12	-0.14		**5**	1.30		
3		0.04		**6**		1.20	

[a] δ_H in C_6D_6. Some resonances have considerable line widths.

Table II. ^{13}C Chemical Shifts of the α-Carbons to Boron[a]

Ate Complex		Borane	
1a	29.2 (CH_2 and CH)[b]	**4a**	33.8 (CH); 28.9 (CH_2)
1b	28.4 (CH_2 and CH)[b]; 5.6 (CH_3)	**4b**	34.0 (CH); 13.6 (CH_3)
2	30.8 (CH_2 and CH)[b]	**5**	31.0 (CH)
3	29.9 (CH_2)	**6**	29.8 (CH_2)

[a] The spectra were measured on a Varian XL-100-15 spectrometer operating in the Fourier transform mode at 25.2 MHz, and were taken in C_6D_6(ca. 50 % concentration) in 12-mm sample tubes. Benzene-d_6 was served as an internal standard and an internal lock, and chemical shifts were converted to δ_C, using $\delta_C^{C_6D_6}$ 128.7; errors were ± 0.1. The resonances of the α-carbons have considerable line widths. [b] The resonances could not be distinguished.

As is apparent from Table I, the α-hydrogens to boron in **1** - **3** are strongly shielded. Table II also demonstrates that the α-carbons to boron are shielded to some extents, suggesting the presence of some negative charge on the α-carbons.$^{5)}$ Consequently, the present spectroscopic data indicate that the bridgehead α-hydrogen of the 9-BBN ring in **1** possesses strong hydride character though they do not shed light on factors which reflect the reactivity difference among **1**, **2**, and **3**.$^{2)}$

References and Notes

1) Spectroscopic Studies of Organoboranes. Part IV. Paper II: Y. Yamamoto and I. Moritani, Chem. Lett., 439 (1975). Paper III: Y. Yamamoto and I. Moritani, J. Org. Chem., in press.
2) Y. Yamamoto, H. Toi, S-I. Murahashi, and I. Moritani, J. Am. Chem. Soc., 97, 2558 (1975).
3) G. Wittig, Angew. Chem., 70, 65 (1958).
4) a) R. Damico, J. Org. Chem., 29, 1971 (1964); b) A. G. Massey, E. W. Randall, and D. Shaw, Spectrochim. Acta, 20, 379 (1964); 21, 263 (1965).
5) As an alternative possibility, the shielding of α-carbons may be due to the steric compression shift. However, we prefer to assume the presence of negative charge because of the results of ^{1}H NMR spectra. See also, J. B. Stothers,Carbon-13 NMR Spectroscopy, Academic, New York, N. Y. (1972). In contrast to the α-carbons, the resonances of the other carbons in **1** - **3** appeared in lower fields than those of the corresponding boranes (**4** - **6**), respectively.

(Received September 22, 1975)