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Molecular Addition Compounds. 8. ^{13}C and ^{11}B NMR Examination of B-Substituted Derivatives of 9-Borabicyclo[3.3.1]nonane and Their Pyridine Complexes

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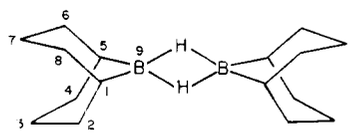
The ^{13}C NMR data for 9-borabicyclo[3.3.1]nonane and 10 representative B-substituted derivatives were examined. For the parent compound and *B*-Cl-, *B*-OMe-, *B*-Et-, *B*-*t*-Bu-, and *B*-$CH_2CH_2SiMe_3$-9-BBN, the ring carbons at positions 2, 4, 6, and 8 of the bicyclic system are identical with a second signal for the ring carbons at positions 3 and 7, confirming the symmetric structure for these derivatives. Larger *B*-alkyl groups containing a chiral center reveal ^{13}C signals for positions 2 and 6 which are different from those for positions 4 and 8, corresponding to the asymmetric environment of the bicyclic structure. The 1:1 pyridine addition compounds of 9-BBN and *B*-Cl-9-BBN exhibit a ^{13}C spectrum corresponding to a nonequivalence of the two halves of the bicyclic ring system. On the other hand, the ^{13}C spectrum for *B*-OMe-9-BBN and pyridine reveals both incomplete formation of a 1:1 complex and full equivalence of the two halves of the bicyclic ring structure. The spectrum for *B*-Et-9-BBN reveals complete formation of the 1:1 complex. However, the ^{13}C spectrum of the bicyclic ring system reveals full equivalence of the two halves, attributed to rapid dissociation and recombination of the complex. With highly bulky alkyl groups at the 9 position, such as *t*-Bu and 1-trimethylsilylethyl, complex formation with pyridine is incomplete, even with excess pyridine.

A variety of methods are now available to prepare B-substituted derivatives of 9-borabicyclo[3.3.1]nonane (9-BBN).[2] The remarkable stability of this bicyclic ring system allows these derivatives to be used for a number of further conversions, with the ring system remaining intact, making such compounds particularly useful synthetic intermediates.[3]

Characterization of these compounds has traditionally been accomplished by using a variety of standard chemical and instrumental methods.[4] However, owing to the complex absorbance of the ring protons, a detailed study of the structural features of such compounds, particularly in the *B*-alkyl case, is not possible using ^1H NMR. Consequently, we chose to investigate the use of ^{13}C NMR in this regard. Further, in conjunction with ^{11}B NMR, we used this technique to investigate the complexation of such compounds with pyridine to obtain more information about the nature of these complexes as the B-substitution is varied.

Results

In $CDCl_3$ solution, 9-BBN (1) itself exists as a dimer, giving a single absorbance at 28.0 ppm in the ^{11}B spectrum.[2b] The proton-decoupled ^{13}C spectrum of 1 is also



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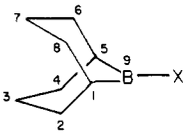
quite simple, giving peaks at 33.4 and 28.9 ppm, in a ratio of approximately 2:1, for the methylene carbons at positions 2, 4, 6, and 8 vs. those at positions 3 and 7.

Carbons bound directly to boron give only very broadened signals in such compounds (positions 1 and 5 in 1) at ca. 30 ppm.

The ^{11}B and ^{13}C absorbances for a series of B-substituted 9-BBN compounds are given in Table I.

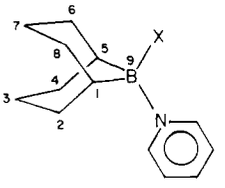


In $CDCl_3$ solvent, the ^{11}B NMR absorbances of these trivalent compounds are all considerably downfield from those of the 9-BBN dimer.

The ^{13}C spectra reveal that the simple B-substituted derivatives give the expected two signals for the ring methylene carbons, as was observed for 1, confirming a symmetrical structure for these derivatives.

The introduction of a chiral center at the boron-bound carbon of the alkyl chain leads to a nonequivalence of the ring carbons at positions 2 and 6 vs. 4 and 8, reflecting the asymmetric environment of the bicyclic ring structure. In the case of **5** (X = 2-Bu), this difference is not observed. Evidently, the asymmetric shifts must be too small to be observed under our conditions. However, by making the groups bonded to the chiral center less similar, sufficient separation of these methylene carbons is achieved so as to allow the nonequivalence to be observed (i.e., **6**, **8**, and **10**). Even with the chiral center at the β carbon of the alkyl chain in **11**, this nonequivalence of the ring methylene carbons is observed.

9-BBN is known to form a stable, isolable complex with pyridine (**12**, X = H).[5]



(1) Postdoctoral research associate on Grant CHE 76-20846 of the National Science Foundation.

(2) (a) Scouten, C. G.; Brown, H. C. *J. Org. Chem.* **1973**, *38*, 4092. (b) Brown, H. C.; Knights, E. F.; Scouten, C. G. *J. Am. Chem. Soc.* **1974**, *96*, 7765. (c) Kramer, G. W.; Brown, H. C. *J. Organomet. Chem.* **1974**, *73*, 1. (d) Soderquist, J. A.; Hassner, A. *Ibid.* **1978**, *156*, C9. (e) Brown, H. C.; Kulkarni, S. U. *Ibid.* **1979**, *168*, 281. (f) Soderquist, J. S.; Brown, H. C., manuscript in preparation.

(3) Brown, H. C.; Kramer, G. W.; Levy, A. B.; Midland, M. M. "Organic Syntheses via Boranes"; Wiley-Interscience: New York, 1975.

(4) Brown, H. C.; Kulkarni, S. U. *Inorg. Chem.* **1977**, *16*, 3090.

(5) Trainor, T. M.S. Thesis, Purdue University, 1978.

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Table I. ^{11}B and ^{13}C NMR Spectral Data for B-Substituted Derivatives of 9-BBN[a]

X (compd)	^{11}B	^{13}C C-2,4,6,8	^{13}C C-3,7	^{13}C other[b]
H (1)	28.0	33.4	23.9	
Cl (2)	81.5	34.2	23.0	
OCH_3 (3)	53.2	33.1	23.2	53.3
CH_2CH_3 (4)	88.0	33.2	23.4	8.0
$CH_3CHCH_2CH_3$ (5)	87.3	33.4	23.2	25.3, 13.9
$CH_3CHCH(CH_3)_2$ (6)	88.4	33.8	23.3	30.0, 23.7
		33.6		21.2, 10.9
$C(CH_3)_3$ (7)	85.8	33.6	23.2	25.9
$C_6H_5CHCH_2CH_3$ (8)	83.9	33.9	23.1	131.3, 129.1
		33.7		128.4, 125.7
				14.3, 1.1
$CH_2CH_2Si(CH_3)_3$ (9)	86.4	33.4	23.3	8.6, -2.0
$CH(CH_3)Si(CH_3)_3$ (10)	85.9	33.2	23.2	10.3, -0.9
		32.7		
$CH_2CH(CH_3)Si(CH_3)_3$ (11)	88.9	33.6	23.4	17.9, 15.2
		33.3		-3.6

[a] Spectra were recorded in $CDCl_3$ solvent. No attempt was made to determine the chemical shifts of the very broad signals attributable to boron-bonded carbons. [b] Assignments for the "other" carbons were made based on decoupling experiments. In the order given in the table, they are the following: 3, OCH_3; 4, CH_3; 5, CH_2, CH_3 (coincident signals); 6, CH, 3-CH_3, 3-CH_3, 1-CH_3; 7, CH_3; 8, aromatic (1,3,2,4), CH_2, CH_3; 9, 2-CH_2, $Si(CH_3)_3$; 10, CH_3, $Si(CH_3)_3$; 11, CH_3, CH, $Si(CH_3)_3$.

Table II. ^{11}B and ^{13}C NMR Spectral Data for Pyridine Complexes of B-Substituted Derivatives of 9-BBN[a]

X (compd)	^{11}B	^{13}C[b] C-2,4,6,8	^{13}C[b] C-3,7	Py[c]
H (12)	-0.7[d]	35.1	25.4	145.9, 138.8, 125.3
		29.0	24.8	
Cl (13)	9.5	31.9	23.9	145.0, 141.7, 126.3
		30.8	23.7	
CH_2CH_3 (14)	1.3	31.6	25.0	146.3, 138.3, 124.8
$CH_3CHCH_2CH_3$ (15)	1.4	31.2	24.7	147.0, 137.9, 124.1
$CH_3CHCH(CH_3)_2$ (16)	-0.1	31.6	24.6	147.1, 138.2, 124.4
		31.2		
$CH_2CH_2Si(CH_3)_3$ (17)	2.1	31.6	25.1	146.1, 138.3, 124.8

[a] See footnote a, Table I. [b] Alkyl carbons were assigned as in Table I. The corresponding signals were observed at 8.5 (14); 24.7, 14.2 (1-CH_3), 12.9 (4-CH_3) (15); 26.3, 26.1, 18.1, 7.8 (16); 9.4, -1.7 (17) ppm. [c] Order follows α, γ, β. [d] Doublet, J = 88 Hz.

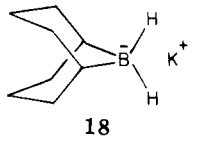
In $CDCl_3$ solution, **12** absorbs at -0.7 ppm in the ^{11}B NMR spectrum as a doublet (J = 88 Hz) owing to the coupled proton (see Table II).

The ^{13}C spectrum of **12** shows that the two halves of the ring system are not equivalent magnetically, giving rise to signals for the carbons at positions 2 and 4 vs. positions 6 and 8, as well as for position 3 vs. position 7.

Taken together, these data indicate that **12** is a nonlabile complex on the ^{11}B and ^{13}C NMR time scale. Excess 9-BBN was added to the mixture to further test this interpretation with no effect on the signals due to **12** in either the ^{11}B or ^{13}C spectrum of the mixture. The signals due to the added 9-BBN were similarly unchanged from those for the pure material. Further, excess pyridine showed no effect on the spectral properties of **12**, and the free pyridine peaks were observed at 149.7, 135.9, and 124.0 ppm in the ^{13}C spectrum of the mixture. These additional findings further support the configurational stability of **12**.

It is desirable to assign the different absorptions for the two halves of the 9-BBN ring system to those which are syn to the pyridine ring and those which are anti. We have achieved this through the following argument.

Nonequivalence of the syn and anti ring carbons has also been observed for the related 2-phenyladamantyl system.[5] Since positions 2 and 4 occupy a γ-gauche relationship to the pyridine, these carbons might be expected to correspond to the upfield signal at 29.0 ppm.[6] To test the validity of this assignment further, we examined the spectrum of the borodihydride **18**.[7]



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This compound gives rise to signals, roughly 2:1 in magnitude, at 36.5 and 27.1 ppm in the ^{13}C spectrum of the solution in deuterated tetrahydrofuran. The similarity of the 36.5-ppm absorbance to the 35.1-ppm absorbance in **12** suggests that this signal is due to the carbons at positions 6 and 8 which are syn to the hydrogen in **12**. If a similar trend holds for a progressive downfield shift for the carbons at position 7 in the series **1**, **12**, **18**, the 25.4-ppm signal in **12** agrees well with this assignment. The 24.8-ppm signal is therefore assigned to position 3 in **12**.

The complex of the *B*-Cl derivative (**13**) also gives separate signals for the syn and anti halves of the 9-BBN ring system. Since a quaternary nitrogen exerts a slightly greater upfield γ effect than chlorine, the methylene

(6) Wehrli, F. W.; Wirthlin, T. "Interpretation of Carbon-13 NMR Spectra"; Heyden: London, 1976; pp 36-40.
(7) Brown, H. C.; Singaram, B.; Mathew, P., manuscript in preparation.

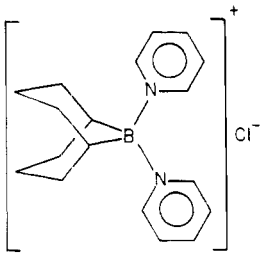
Table III. ^{11}B and ^{13}C NMR Spectral Properties of B-Substituted 9-BBN Derivatives Which Undergo Incomplete Complexation with Pyridine[a]

compd	pyridine equiv	^{11}B	^{13}C C-2,4,6,8	C-3,7	Py	CH_3
3	0	53.2	33.1	23.2		53.3
	1	34.8	32.4	23.6	148.0, 137.1, 124.0	51.1
	2	22.5	32.0	23.7	148.2, 136.7, 123.8	49.1
	3	16.6	31.7	23.8	148.3, 136.4, 123.6	49.1
	4	13.7	31.5	23.8	148.4, 136.1, 123.5	49.8
7	0	85.8	33.6	23.2		25.9
	1	44.8	33.0	23.4	148.6, 137.4, 123.6	28.7
	2	21.8	32.6	23.5	148.8, 136.8, 123.6	30.3
	3	14.5	32.4	23.5	148.9, 136.4, 123.5	30.8
	4	9.0	32.2	23.5	148.9, 136.1, 123.4	31.0
	5	8.2	32.2	23.4	148.9, 136.0, 123.0	31.1

[a] See footnote a, Table I.

carbons at positions 2 and 4 can be assigned to the 30.8-ppm absorbance.[6]

The ^{11}B and ^{13}C spectra of Py·*B*-Cl-9-BBN (**13**) were unchanged with excess *B*-Cl-9-BBN (**2**). The latter exhibits its own characteristic signals. However, addition of pyridine in the stoichiometric amount to **13** resulted in a slow broadening of the ^{11}B absorbance. The ^{13}C spectrum of the mixture showed minor signals due to **13** and a new set of signals at 145.5, 143.2, 127.7, 30.0, and 22.6 ppm. Peaks for free pyridine were not evident. This suggested that pyridine must be reacting with **13** to produce a dipyridyl ionic complex (**19**).



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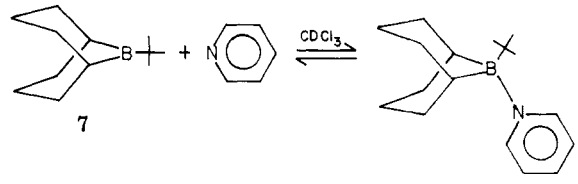
Related reactions and compounds have been reported previously from the action of pyridine on the boron trichloride–pyridine complex.[8]

Unlike the tight complexes observed for **12** and **13**, *B*-alkyl derivatives do not show a nonequivalence for the separate halves of the ring system by ^{13}C NMR. Moreover, addition of excess pyridine causes no effect on the ^{11}B absorbance of such compounds, indicating that complexation is essentially complete.

In the presence of 1 mol equivalent of excess pyridine, Py·*B*-Et-9-BBN (**14**) shows unchanged ring carbon signals, and the pyridine signals are intermediate between those of free pyridine and **14** in the ^{13}C spectrum of the mixture. A 1:1 mixture of *B*-Et-9-BBN and **14** gives intermediate signals for the ring carbons and exhibits pyridine signals as in **14**. The ^{11}B spectrum of this mixture shows very broadened absorbances at 85 and 11 ppm, with an additional peak at 59 ppm. Taken together, these facts suggest that **14** is a labile complex on the ^{13}C NMR time scale, but the equilibration is sufficiently slow to be observed on the faster ^{11}B NMR time scale.[9] The precise nature of the species responsible for the peak at 59 ppm is not yet understood.

With highly bulky *B*-alkyl substitution, such as in *B*-*t*-Bu-9-BBN (**7**), complexation with pyridine is incomplete, and a rapid equilibrium is observed on both the ^{11}B and ^{13}C NMR time scales.



7 20

With progressive amounts of pyridine, the ^{11}B spectrum shows a regular upfield shift for **7** (see Table III). The ^{13}C spectrum also reveals regular incremental shifts for all of the carbons with increasing amounts of pyridine, except for the 9-BBN ring positions 3 and 7, which show a maximum at 2–3 molar equivalents of pyridine.

From the ^{11}B data and assuming a value of 1 ppm for **20**, an equilibrium constant of 0.53 ± 0.14 M^{-1} is calculated for the complexation of **7** with pyridine at 35 °C.[10]

Similar effects on the spectrum of 1-trimethylsilylethyl-9-BBN (**10**) are also observed. Here, 1 mole equiv of pyridine results in a chemical shift in the ^{11}B spectrum from 85.9 to 53 ppm instead of a value of ca. 1 ppm predicted for the fully formed complex. Similarly, the ^{13}C spectrum of this mixture exhibits signals at 32.7, 32.3, and 23.6 ppm for the bicyclic ring carbons and at 10.1 and −0.9 ppm for the alkyl chain, chemical shifts that are intermediate between those of **10** and those anticipated for a fully formed addition compound. Values of 148.4, 137.2, and 124.2 ppm for the pyridine signals are also intermediate between those of free pyridine and those of pyridine in representative complexes.

It is also apparent from the spectral properties of *B*-OMe-9-BBN (**3**)–pyridine mixtures (see Table III) that this derivative also fails to undergo complete complexation, exhibiting, with increasing amounts of pyridine, behavior similar to that shown by *B*-*t*-Bu-9-BBN (**7**). The steric requirements of the methoxy group must be similar to those of the ethyl group. Consequently, the low stability of Py·*B*-OMe-9-BBN, as compared to Py·*B*-Et-9-BBN, must be attributed to the ability of the methoxy group to

(8) Greenwood, N. N.; Wade, K. *J. Chem. Soc.* **1960**, 1130.

(9) For a discussion of the consequences of a dynamic equilibrium process on the ^{13}C spectrum of mixtures, see ref 6, p 198.

(10) The R_3B:R_3B·Py ratio was determined by the ratio of the difference between the observed chemical shift value and that of each of the pure species. By correcting the volume for added pyridine and subtracting the amount of pyridine in the complex form from the total, we calculated the amount and concentration of free pyridine. From these values and the R_3B:R_3B·Py ratio, the K_{eq} was calculated for each pyridine concentration. The reaction temperature should be regarded as ±2 °C.

(11) Minor amounts of the 2-boryl isomer are also formed from the hydroboration of 1-phenylpropene with 9-BBN.[12] However, ^{13}C signals from this minor isomer were insufficiently intense to be detected under our conditions.

release electrons to the boron atom. On the other hand, the lower stability of Py·*B*-*t*-9-BBN or Py·*B*-CH(CH_3)-$SiMe_3$-9-BBN, as compared to the ethyl derivative, must be attributed to the larger steric requirement of the *t*-Bu or the 1-trimethylsilylethyl group. It is clear, therefore, that it is necessary to consider both electronic and steric effects in accounting for the stabilities of these addition compounds.

Thus, by using ^{11}B or ^{13}C NMR, the extent of complexation can be assessed. However, the additional feature of the lability of such complexes can be observed by using ^{13}C NMR, providing a valuable tool for understanding better the nature of such compounds.

Experimental Section

General Procedures. Spectroscopic samples were prepared by literature methods[2-4,7,12] under a nitrogen atmosphere using oven-dried glassware. Compounds were transferred under nitrogen to a septum-sealed NMR tube containing NMR-grade $CDCl_3$. Reagent grade pyridine was predried over potassium hydroxide and distilled from calcium hydride. Spectra were recorded on a Varian FT-80A NMR spectrometer using Me_4Si (δ = 0.00 ppm) as an external standard for the ^{13}C spectra and BF_3·OEt_2 (δ = 0.00 ppm) as an external standard for the ^{11}B spectra. Sweep widths of 4000 and 8000 Hz were used, respectively, for these two nuclei. By use of either 8000 or 16 000 data points for the carbon data and 2000 data points for the boron data, the chemical shifts were reproducible from run to run to ±0.1 ppm for the carbon spectra and ±0.5 ppm for the boron spectra.

(12) (a) Liotta, R. Ph.D. Thesis, Purdue University, 1976. (b) Zee, S.-H., private communication based on unpublished research at Purdue University.

Acknowledgment. The financial support of the National Science Foundation is gratefully acknowledged. We wish to thank Professor John Grutzner for helpful discussions regarding this work.

Registry No. 1, 280-64-8; 2, 22086-34-6; 3, 38050-71-4; 4, 52102-17-7; 5, 53317-06-9; 6, 63942-78-9; 7, 42928-43-8; 8, 72610-04-9; 9, 72610-05-0; 10, 72610-06-1; 11, 72610-07-2; 12, 64045-95-0; 13, 22086-36-8; 14, 72610-08-3; 15, 72610-09-4; 16, 72610-10-7; 17, 72638-39-2.

Selective Reductions. 27. Reaction of Alkyl Halides with Representative Complex Metal Hydrides and Metal Hydrides. Comparison of Various Hydride Reducing Agents[1]

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The approximate rates and products of the reaction of alkyl halides with representative metal hydrides and complex metal hydrides were examined in order to identify the most promising hydride reducing agents for the hydrogenolysis of alkyl halides. Among the various reagents tested, both lithium triethylborohydride and lithium aluminum hydride exhibit exceptional utility for the hydrodehalogenation reaction. Of the two most promising reagents, lithium triethylborohydride exhibits far greater hydride-transfer ability than does lithium aluminum hydride. Lithium trimethoxyaluminohydride, lithium tri-*tert*-butoxyaluminohydride, sodium borohydride, and lithium borohydride all react with primary alkyl iodides and bromides at a moderate rate; they are essentially inert toward alkyl chlorides. The reaction of alkyl halides with alane is quite slow; borane and dialkylboranes are essentially inert toward alkyl halides. Thus the study has defined those reagents which are most effective for hydrodehalogenation, as well as those reagents which can be utilized for reduction of functional groups with minimum attack on halogen substituents.

The chemistry of complex metal hydrides and metal hydrides has received considerable attention in recent years, especially for the selective reduction of various functional groups in organic molecules.[2] The discovery of sodium borohydride[3] in 1942 and of lithium aluminum hydride[4] in 1945 has revolutionized the procedures utilized for the reduction of organic functional groups. Since their discovery, a number of modified hydride reagents—both nucleophilic and electrophilic—have evolved from time to time. The reducing properties of each of these hydride reducing agents, namely, lithium aluminum hydride, lithium trimethoxyaluminohydride, lithium tri-*tert*-butoxyaluminohydride, sodium borohydride, lithium borohydride, lithium triethylborohydride, alane, borane, thexylborane, disiamylborane, 9-borabicyclo[3.3.1]nonane, are now well characterized.[2a] The reactivity of each of the above-mentioned reagents under standard reaction conditions toward representative organic compounds containing the most common functional groups, for example, aldehydes, ketones, epoxides, carboxylic acids and derivatives, aromatic nitro compounds, organosulfur compounds, etc., has been examined. Unfortunately, the reactivity of these reagents was not tested against alkyl halides. Furthermore, very little attention has been devoted to the hydrogenolysis of carbon–halogen bonds utilizing complex metal hydride and metal hydride as the source of hydrogen. The majority of such reactions reported in the literature were carried out with a slurry of lithium aluminum hydride in ethyl

(1) Partially based upon a thesis submitted by S. Krishnamurthy in partial fulfillment of the requirements for the degree of Doctor of Philosophy, Purdue University. A preliminary communication reporting the exceptionally powerful nucleophilic properties of lithium triethylborohydride in its reaction with alkyl halides appeared earlier: H. C. Brown and S. Krishnamurthy, *J. Am. Chem. Soc.*, **95**, 1669 (1973).

(2) (a) H. C. Brown and S. Krishnamurthy, *Tetrahedron*, **35**, 567 (1979); (b) *Aldrichimica Acta*, **12**, 3 (1979); (c) S. Krishnamurthy, *ibid.*, **7**, 55 (1974).

(3) H. I. Schlesinger, H. C. Brown, H. R. Hoekstra, and L. R. Rapp, *J. Am. Chem. Soc.*, **75**, 199 (1953).

(4) A. E. Finholt, A. C. Bond, Jr., and H. I. Schlesinger, *J. Am. Chem. Soc.*, **69**, 1199 (1947).

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