Nuclear Magnetic Resonance Spectra of *cis*-5,6-Disubstituted Norbornenes. Correlation of Proton Chemical Shifts with the Taft Inductive Substituent Constant

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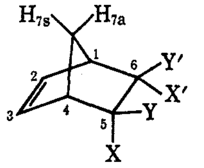
The ^{1}H nmr spectra of *exo,cis*- and *endo,cis*-5,6-dihydroxynorbornene and *exo,cis*- and *endo, cis*- 5,6-diacetoxynorbornene have been analyzed. The chemical shifts of H_{7a} and H_{7s} obtained from these analyses, together with the corresponding chemical shifts of several other *cis*-5,6-disubstituted norbornenes whose spectra have been analyzed and reported in the literature, have been found to be linear functions of the value of the Taft inductive substituent constant for the substituents at C_5 and C_6. These relations show that the nature of the substituents determines whether H_{7a} or H_{7s} is more shielded in *exo,cis*-5,6-disubstituted norbornenes.

Recent reports of work on norbornene[1-3] (1) and substituted norbornenes[4] have served to clear up much of the previous confusion regarding the nmr spectra of these compounds. The synthesis of two additional sets of *exo,cis*- and *endo,cis*-5,6-disubstituted norbornenes and the analysis of their nmr spectra have provided additional insight into the nature of these compounds, and have allowed us to obtain a quantitative measure of the effect of *cis*-5,6-disubstitution on the chemical shifts of norbornene protons. We have found that the chemical shifts of H_{7a} and H_{7s} are linearly related to Taft's[5] σ_I value for the substituents. These correlations are discussed below.



1, $X = X' = Y = Y' = H$
2, $X = X' = H$; $Y = Y' = OH$
3, $X = X' = OH$; $Y = Y' = H$
4, $X = X' = H$; $Y = Y' = OAc$
5, $X = X' = OAc$; $Y = Y' = H$

Experimental Section

Compounds synthesized and used in this study were *exo,cis*-5,6-dihydroxy-2-norbornene (**2**), *endo,cis*-5,6-dihydroxy-2-norbornene (**3**), *exo,cis*-5,6-diacetoxy-2-norbornene (**4**), and *endo, cis*-5,6-diacetoxy-2-norbornene (**5**).[6,7]

The nmr spectra of the four compounds were obtained with a Varian A-60A spectrometer equipped with a Varian V-6058A spin decoupler on solutions in chloroform-*d* ($CDCl_3$). Additional spectra of **2** and **3** were obtained on solutions in dimethylsulfoxide-d_6 (DMSO-d_6). In both solvents, tetramethylsilane (TMS) was used as the internal reference. Chemical shifts for **2** and **3** were determined in both solvents. Coupling constants for these compounds were calculated from the spectra of the DMSO-d_6 solutions; resolution was better than in $CDCl_3$, the chemical shifts of H_{7s} and H_{7a} were more favorable, and coupling with the –OH protons was easily eliminated by exchange with deuterium oxide. Chemical shifts are accurate to within ±0.02 ppm; coupling constants are accurate to within ±0.2 Hz.

Results and Discussion

Assignments of the nmr spectra were made on the basis of spin-decoupling experiments. H_{7a} and H_{7s} were identified by means of the well-established stereospecific long-range couplings[8] between H_{7a} and H_2 (H_3), and between H_{7s} and the *endo* protons at C_5 and C_6. Our assignments are in agreement also with the observation[8] that, for the same substituents, H_5 and H_6 are more shielded in *exo,cis*-5,6-disubstituted norbornenes than in the corresponding *endo*-derivatives.

Analysis of the H_{7s},H_{7a} portion of each spectrum was accomplished by treating it as an AB spectrum on which were superimposed first-order couplings with H_1, H_2, H_3, H_4 (and, in the case of the *exo* derivatives, H_5 and H_6). The H_2,H_3 multiplet was assumed to be one-half of an AA′XX′ spectrum[3] (H_2 and H_3 coupling with both H_1 and H_4) on which was superimposed a first-order coupling with H_{7a}. In the case of compounds **2** and **3**, calculations were made to determine the magnitudes of $J_{1,2}$, $J_{1,3}$, $J_{1,4}$, and $J_{2,3}$ from the H_2,H_3 multiplet. The chemical shift of H_1 (H_4) was taken to be the center of the H_1,H_4 multiplet.

As reported by Subramanian, Emerson, and LeBel[4] for dihalonorbornenes, the multiplet due to H_5 and H_6 in compounds **3** and **5** is more complex than might be expected. We found, however, that for **5**, and for **3** in DMSO-d_6, the pattern is that expected for an AA′XX′ spectrum. (The weak outer peaks can be observed at increased gain.) This pattern was not easily recognized in the spectrum of the $CDCl_3$ solution of **3**, but was readily apparent in the spectrum of the DMSO-d_6 solution. From our observations, and from the description of the spectra of *endo,cis*-5,6-dihalonorbornenes by Subramanian, it appears that for *exo*-5,6 protons in the *endo, cis*-5,6-disubstituted norbornenes there is a small but finite coupling between H_1 and H_5, and between H_4 and H_6, which renders H_5 and H_6 magnetically nonequivalent although they are chemical-shift equivalent.

We accordingly treated the H_5,H_6 multiplet as one-half of an AA′XX′ spectrum (H_5 and H_6 coupling with both H_1 and H_4). $J_{5,6}$ and $J_{1,6}$ ($J_{4,5}$) so determined do

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(1) B. Franzus, W. C. Baird, Jr., N. F. Chamberlain, T. Hines, and E. I. Snyder, *J. Amer. Chem. Soc.*, **90**, 3721 (1968).

(2) A. P. Marchand and J. E. Rose, *ibid.*, **90**, 3724 (1968).

(3) E. W. Garbisch, Jr., *Chem. Commun.*, 332 (1968).

(4) P. M. Subramanian, M. T. Emerson, and N. A. LeBel, *J. Org. Chem.*, **30**, 2624 (1965).

(5) P. R. Wells, *Chem. Rev.*, **63**, 171 (1963). In the case of compounds **9** and **10**, in which the substituents at C_5 and C_6 were not the same, the arithmetic mean of the σ_I values for the two substituents was used.

(6) Y. F. Shealy and J. D. Clayton, *J. Amer. Chem. Soc.*, **88**, 3885 (1966). Complete details of the preparation of these compounds are being published separately: Y. F. Shealy and J. D. Clayton, *ibid.*, in press.

(7) The nomenclature and numbering system used here conform to those used in recent descriptions of nmr studies on related compounds.[1,2,4] According to *Chemical Abstracts* practice, the preferred names are *exo,cis*-5-norbornene-2,3-diol (**2**), *endo*,cis-5-norbornene-2,3-diol (**3**), *exo,cis*-5-norbornene-2,3-diol diacetate (**4**), and *endo,cis*-5-norbornene-2,3-diol diacetate (**5**).

(8) Reference 2, and references cited therein.

not differ significantly from values reported by Subramanian, and $J_{1,5}$ ($J_{4,6}$) is shown to be very small. Nevertheless, treatment as half of an AA'XX' spectrum appears to afford a straightforward explanation of the H_5,H_6 multiplet, does not require a difference in chemical shift for H_5 and H_6 as proposed by Subramanian, and produces a value of $J_{5,6}$ in good agreement with comparable values determined by other workers.[4,9,10] By this analysis, $J_{1,4}$ is shown to be nonzero. Additional support for this treatment of the H_5,H_6 multiplet is given by the agreement of the two values obtained for $J_{1,4}$ from the spectrum of **3**, 1.1 and 1.2 Hz. One value is obtained from the analysis of the H_2,H_3 multiplet (when decoupled from H_{7a}) as half of an AA'XX' spectrum, and the other value from the analysis of the H_5,H_6 multiplet as half of an AA'XX' spectrum.

Previously, $J_{1,4}$ has generally been reported to be zero,[2,9,10] although Subramanian[4] estimated it to be approximately 1 Hz for 5,6-dihalonorbornenes. Recently, analysis by Garbisch[3] has shown $J_{1,4}$ to be nonzero in norbornene. Our findings with regard to $J_{1,4}$ for *cis*-5,6-disubstituted norbornenes with hydroxyl and acetoxy substituents are in agreement with those of Garbisch[3] and Subramanian,[4] but appear to be in conflict with those of Davis and Van Auken,[9] Marchand and Rose,[2] and Laszlo and Schleyer.[10] It now appears likely that, in general, $J_{1,4}$ is not zero. Thus, it is difficult to understand the failure of Davis and Van Auken[9] to observe coupling between H_1 and H_4 in the 5-monosubstituted norbornenes, where H_1 and H_4 have different chemical shifts, unless $J_{1,4}$ is much smaller in those compounds than it is in norbornene and in *cis*-5,6-disubstituted norbornenes.

Chemical shifts from our analyses of compounds **2**, **3**, **4**, and **5** are shown in Table I; coupling constants are listed in Table II.

In seeking a quantitative measure of substituent effects on the chemical shifts of H_{7s} and H_{7a}, chemical shift data from our analyses of the spectra of **2**, **3**, **4**, and **5** in $CDCl_3$ were used, together with data on additional compounds from the literature. The additional compounds are shown in Table III.

Although the chemical shift of H_{7s} was reported by Subramanian[4] to be nearly constant for 5,6-dihalonorbornenes, we find that this is not true for all substituents. The chemical shifts of both H_{7s} and H_{7a} are dependent on the nature of substituents at C_5 and C_6. The chemical shift of H_{7a} is highly dependent on the orientation of such substituents, whereas the chemical shift of H_{7a} has little or no dependence on orientation. As pointed out by Wells,[5] Taft based his list of inductive σ-values on data from 4-substituted bicyclo[2.2.2]octane-1-derivatives. The saturated portion of the norbornenes considered in our investigation is sufficiently similar structurally to such bicyclooctanes that it appeared reasonable to test whether the chemical shifts of H_{7s} and H_{7a} might be represented as functions of the σ_I values of substituents at C_5 and C_6. Linear regression analysis confirms that this is indeed the case, and that the chemical shift of either H_{7s} or H_{7a} may be expressed as a function of the value of the Taft[5] σ_I for the 5,6 substituents. These Taft constants are regarded as measures of the electron-withdrawing power of substituents in compounds where resonance effects are not expected to be important, as in these norbornene derivatives. In fact, Swain and Lupton[11] have recently shown that the effect measured by σ_I is >96% "field effect." Their term "field effect" lumps together both inductive effects through σ bonds and effects through space. The former should be of negligible importance through two or more intervening carbons.[12]

TABLE I

CHEMICAL SHIFTS (PARTS PER MILLION DOWNFIELD FROM TMS)

Compound	Solvent	H_1,H_4	H_2,H_3	H_5,H_6	H_{7a}	H_{7s}
2	$CDCl_3$	2.69	6.03	3.69	1.88	1.62
2	DMSO-d_6	~2.5[a]	5.99	3.46	1.79	1.41
3	$CDCl_3$	2.99	6.23	4.14	1.20	1.49
3	DMSO-d_6	2.81	6.06	~4.0[b]	1.11	1.24
4	$CDCl_3$	2.82	6.16	4.73	2.03	1.72
5	$CDCl_3$	3.12	6.20	5.22	1.36	1.58

[a] Multiplet superimposed on solvent peak. [b] H_5, H_6 and $(OH)_5$, $(OH)_6$ were superimposed. Analysis of H_5, H_6 multiplet performed on spectrum obtained after exchanging OH by addition of D_2O.

TABLE II

COUPLING CONSTANTS (HERTZ)

	Compound			
	2	**3**	**4**	**5**
$\lvert J_{7a,7s}\rvert$	8.8	9.4	9.2	9.9
$\lvert J_{7s,6}\rvert = \lvert J_{7s,5}\rvert$	1.7	0.0	1.8	0.0
$\lvert J_{7s,1}\rvert = \lvert J_{7s,4}\rvert$	1.7	2.0	1.5	2.1
$\lvert J_{7a,1}\rvert = \lvert J_{7a,4}\rvert$	1.5	1.5	1.6	1.5
$\lvert J_{7a,2}\rvert = \lvert J_{7a,3}\rvert$	~0.5	~0.5	~0.6	~0.5
$\lvert J_{1,4}\rvert$	1.6[a]	1.1, 1.2[c,d]	...[f]	1.4
$\lvert J_{2,3}\rvert$	6.0[a]	6.0	...[f]	...[f]
$\lvert J_{1,2}\rvert = \lvert J_{3,4}\rvert$	2.6[b]	2.5[b]		
$\lvert J_{2,4}\rvert = \lvert J_{1,3}\rvert$	1.1[b]	1.4[b]		
$\lvert J_{5,6}\rvert$	...[f]	7.6[d]	...[f]	7.4
$\lvert J_{4,5}\rvert = \lvert J_{1,6}\rvert$	0.0	3.7[e]	0.0	4.0[g]
$\lvert J_{1,5}\rvert = \lvert J_{4,6}\rvert$	0.0	0.1–0.2[e]	0.0	0.2[g]
$\lvert J_{1,2} + J_{1,3}\rvert$			3.4	3.8

[a] $J_{1,4}$ and $J_{2,3}$ have the same sign. It was assumed that $|J_{2,3}| > |J_{1,4}|$. [b] $J_{1,2}$ and $J_{2,4}$ have the same sign. It was assumed that $|J_{1,2}| > |J_{2,4}|$. [c] Values from calculations of two separate AA'-XX' subspectra. [d] $J_{5,6}$ and $J_{1,4}$ are of the same sign. It was assumed that $|J_{5,6}| > |J_{1,4}|$. [e] $J_{1,5}$ and $J_{4,5}$ appear to have the same sign. It was assumed that $|J_{4,5}| > |J_{1,5}|$. [f] Not determined. [g] $J_{1,5}$ and $J_{4,5}$ appear to be of different sign. It was assumed that $|J_{4,5}| > |J_{1,5}|$.

For the *exo,cis*-5,6-disubstituted norbornenes (**1**, **2**, **4**, **8**, and **10**), the equations of the correlations, the standard deviations in δ_H (s), and the correlation coefficients (r), are $\delta_{H_{7a}} = 1.04 + 2.68\,\sigma_I$, $s = 0.04$, $r = 0.997$, and $\delta_{H_{7s}} = 1.31 + 1.08\,\sigma_I$, $s = 0.02$, $r = 0.995$, where $\delta_{H_{7a}}$ and $\delta_{H_{7s}}$ are the chemical shifts of H_{7a} and H_{7s} in ppm downfield from TMS.

These correlations are illustrated in Figure 1. It is especially interesting that the lines representing the equations for the chemical shifts of H_{7a} and H_{7s} intersect. These correlations thus predict the "crossover" of the chemical shifts of H_{7s} and H_{7a} in *exo,cis*-5,6-disubstituted norbornenes observed by Marchand[2] on more

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(9) J. C. Davis, Jr., and T. V. Van Auken, *J. Amer. Chem. Soc.*, **87**, 3900 (1965).

(10) P. Laszlo and P. von R. Schleyer, *ibid.*, **86**, 1166 (1964).

(11) C. G. Swain and E. C. Lupton, Jr., *ibid.*, **90**, 4328 (1968).

(12) K. B. Wiberg, "Physical Organic Chemistry," John Wiley & Sons. Inc., New York, N. Y., 1964, Part II, Chapter 8.

TABLE III

CHEMICAL SHIFTS OF ADDITIONAL COMPOUNDS, TAKEN FROM THE LITERATURE (PARTS PER MILLION DOWNFIELD FROM TMS)

Compound	Substituents	Chemical shift H_{7a}	H_{7s}	H_1 (H_4)	Solvent
1	X = X′ = H, Y = Y′ = H	1.03	1.32	2.80	CCl_4[a]
6	X = X′ = Br, Y = Y′ = H	1.50	1.80	3.28	$CDCl_3$[b]
7	X = X′ = Cl, Y = Y′ = H	1.42	1.77	3.22	CCl_4[b]
8	X = X′ = H, Y = Y′ = Br	2.28	1.83	3.17	CCl_4[b]
9	X = Cl, X′ = Br, Y = Y′ = H	1.45	1.73	3.28	$CDCl_3$[b]
10	X = X′ = H, Y = Cl, Y′ = Br	2.25	1.80	2.98	CCl_4[b]

[a] Ref 1. [b] Ref 4.

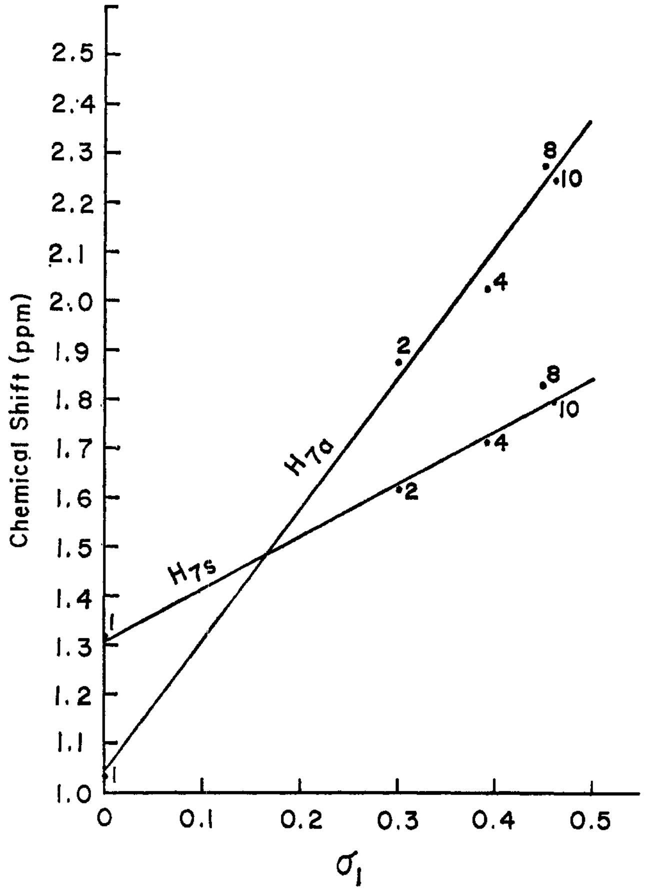

Figure 1.—Chemical shifts of H_{7a} and H_{7s} as functions of the value of σ_I for the substituents in *exo*-5,6-disubstituted norbornenes.

complex compounds, and observed by us in the present series. These correlations thus obviate the need for explanations of the reversal of relative chemical shifts of H_{7a} and H_{7s} based on geometrical considerations other than those implicit in the different slopes of the lines for $\delta_{H_{7a}}$ and $\delta_{H_{7s}}$.

Regression analyses were also performed for the chemical shifts of H_{7a} and H_{7s} in the *endo*-5,6-disubstituted norbornenes (**1**, **3**, **5**, **6**, **7**, and **9**) as functions of the value of σ_I for the substituents.

Equations relating $\delta_{H_{7a}}$ and $\delta_{H_{7s}}$ to the σ_I value of the substituent are $\delta_{H_{7a}} = 1.00 + 0.96\ \sigma_I$, $s = 0.06$, $r = 0.952$, and $\delta_{H_{7s}} = 1.28 + 0.98\ \sigma_I$, $s = 0.08$, $r = 0.934$. These equations are illustrated in Figure 2.

The lines representing $\delta_{H_{7a}}$ and $\delta_{H_{7s}}$ for *endo,cis*-5,6-disubstituted norbornenes and the line representing $\delta_{H_{7s}}$ for *exo,cis*-5,6-disubstituted norbornenes have approximately equal slopes. This indicates that a change in the σ_I value for the substituents at C_5 and C_6 results in nearly equal chemical shift changes for the three cases. The line representing $\delta_{H_{7a}}$ for *exo,cis*-5,6-disubstituted norbornenes has a greater slope, indicative of the larger substituent effect which is observed when the substituents and the affected proton are in spatial proximity. This enhanced effect with decreased distance is to be expected, and supports the view, discussed above, that σ_I is a good measure of the through-space effect.

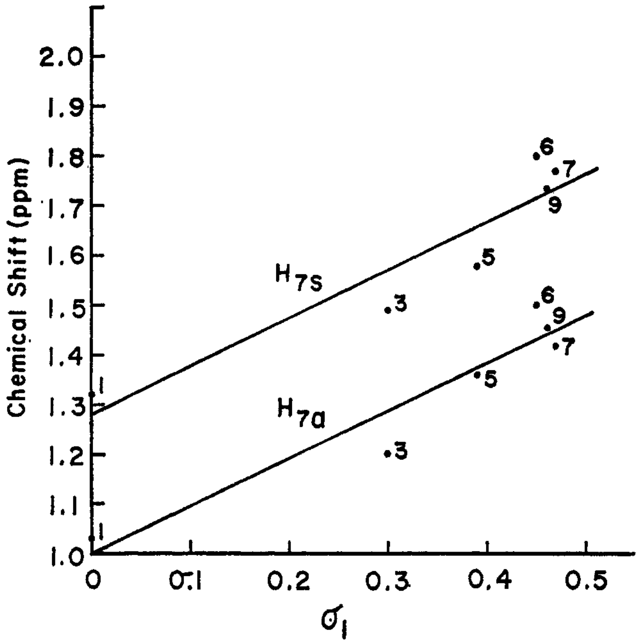

Figure 2.—Chemical shifts of H_{7a} and H_{7s} as functions of the value of σ_I for the substituents in *endo*-5,6-disubstituted norbornenes.

The chemical shift of H_1 (H_4) also appears to increase as the value of σ_I for substituents at C_5 and C_6 increases. The relation does not appear linear, however, if the chemical shift of H_1 (H_4) of norbornene itself is included. Similarly, the chemical shifts of H_5 and H_6 do not appear to correlate in a simple fashion with the nature of the substituents at C_5 and C_6. It is possible that a correlation between δ_{H_5} and δ_{H_6} and the value of σ_I for substituents at C_5 and C_6 may hold if the halogen substituents are omitted from consideration. It has been pointed out by Subramanian[4] that the effects of halogen substitution are complicated at best. Without the halogen-substituted derivatives, however, the available data are too few for more than speculation. As additional compounds are synthesized, doubtless a clearer picture will emerge.

For these *cis*-5,6-disubstituted norbornenes, the chemical shifts of H_{7a} and H_{7s} may also be expressed as linear functions of the group electronegativities of the substituents, calculated by the method of Wilmshurst.[13] Correlations with group electronegativity appear equally as good as those with σ_I, except that in neither case does the equation fit the chemical shift of the appropriate proton of norbornene itself. Therefore, it appears that σ_I is a better measure of the effect of substituents at C_5 and C_6 than is group electronegativity.

Although the same trends are observed if the chemical shifts of H_{7a} and H_{7s} are treated as functions of $\mathcal{F}$, the field substituent constant of Swain and Lupton,[11] the correlations are not so good as those with σ_I.

Registry No.—2, 20224-38-8; 3, 20224-39-9; 4, 20224-40-2; 5, 20224-41-3.

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[13] J. K. Wilmshurst, *J. Chem. Phys.*, **27**, 1129 (1957).

1,3-Diaza-2,4-diborolidines. Isocyanide–Borane Adducts. III[1]

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Evidence is presented supporting a 1,3-diaza-2,4-diborolidine structure for the thermodynamically most stable member of a series of isomers obtained from the reaction of isocyanides with organoboranes. Several compounds possessing that ring system have been prepared, and factors which influence the formation of these compounds are discussed.

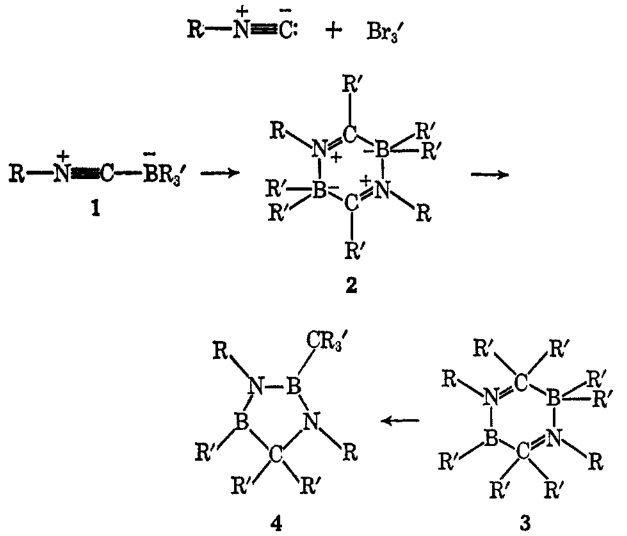
Interest in the chemistry of compounds which contain the >B—N< bond is reflected in the appearance of recent reviews[2] and reference books.[3] Substituted 2,5-dibora-3,6-dihydropyrazines represent an interesting case of this type. From them, 1,3-diaza-2,4-diborolidines may be prepared. The unusual stability of the latter compounds and factors which influence their preparation are the subjects of this paper.

Results and Discussion

The reaction between isonitriles and organoboranes to form 1:1 adducts had been reported.[4,5] Compounds of the general structure 1 (Chart I) are thermodynamically unstable with respect to the dimer 2, first observed by Hesse and Witte.[6] Other examples of 2 have been reported by the same[7a] and other[7b–d] workers. Upon being heated, compounds of structure 2 rearrange to isomer 3.

When certain compounds of structure 3 are heated briefly at 300–310°, ring contraction occurs to produce compounds which display the 1,3-diaza-2,4-diborolidine ring system 4. Synthesis of this ring system from a compound of structure 3 using aluminum chloride has been reported previously for one case.[7e] An earlier report from this laboratory[1] suggested, incorrectly, the 1,3-diaza-2,4-diboretidine structure for compounds of structure 4. Conclusive differentiation has now become possible through 32.1-Mc ^{11}B nmr and X-ray crystallographic analysis.[8] Efforts to carry out ring contraction to the 1,3-diaza-2,4-diboretidine nucleus have thus far been without success.

CHART I



a, R = C_6H_5; R′ = C_2H_5
b, R = p-ClC_6H_4; R′ = C_2H_5
c, R = p-$O_2NC_6H_4$; R′ = C_2H_5
d, R = p-$H_2NC_6H_4$; R′ = C_2H_5
e, R = C_6H_5; R′ = CH_3
f, R = C_6H_5; R′ = n-C_4H_9
g, R = p-$CH_3CONHC_6H_5$; R′ = C_2H_5
h, R = p-$Cl^-H_3N^+C_6H_4$; R′ = C_2H_5
i, R = c-C_6H_{11}; R′ = n-C_4H_9

Preparation and Reactions of 4a.—Compound **4a** can be obtained in nearly quantitative yield upon heating **3a** at 305°. A summary of the reactions of **4a** is shown in Chart II. The chemical and thermal stability of **4a** is unusual. The failure of **4a** to react with hydroxide is distinctly apart from observations for

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[1] Paper II: J. Casanova, Jr., H. R. Kiefer, D. Kuwada, and A. H. Boulton, *Tetrahedron Lett.*, 703 (1965).

[2] K. Niedenzu, *Angew. Chem. Intern. Ed. Engl.*, **3**, 86 (1964).

[3] (a) Advances in Chemistry Series, No. 42, K. Niedenzu, Ed., American Chemical Society, Washington, D. C., 1964; (b) K. Niedenzu and J. W. Dawson, "Boron-Nitrogen Compounds," Springer Verlag, New York, N. Y., 1965; (c) M. F. Lappert, *Chem. Rev.*, **56**, 959 (1956); (d) K. Ziegler, *Advan. Organometal. Chem.*, **6**, 1 (1968); (e) D. Seyferth, "Survey of Organometallic Chem," Vol. 3, Elsevier Publishing Co., New York, N. Y., 1967.

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[5] G. Hesse, H. Witte, and G. Bittner, *Ann.*, **687**, 9 (1963).

[6] G. Hesse and H. Witte, *Angew. Chem.*, **75**, 791 (1963).

[7] (a) G. Hesse and H. Witte, *Ann.*, **687**, 1 (1965); (b) S. Bresadola, G. Carraro, C. Pecile, and A. Turro, *Tetrahedron Lett.*, 3185 (1964); (c) J. Tanaka and J. C. Carter, *ibid.*, 329 (1965); (d) S. Bresadola, F. Rosetto, and G. Puosi, *ibid.*, 4775 (1965); (e) H. Witte, *ibid.*, 1127 (1965).

[8] C. Tsai and W. E. Streib, *Tetrahedron Lett.*, 669 (1968).