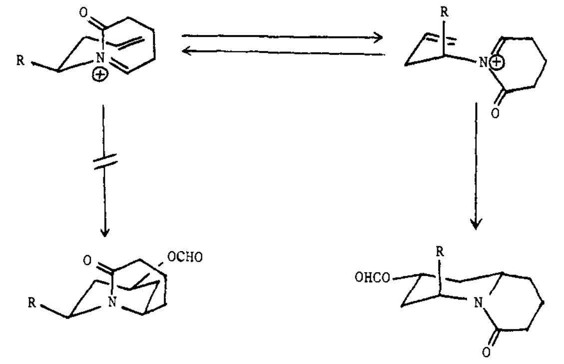
Scheme IV



4 owing to the development of a severe $A^{(1,3)}$ interaction in 7.[10,11]

To evaluate the effect of $A^{(1,3)}$ strain on the stereochemical course of *N*-acyliminium ion cyclizations in a conformationally nonbiased system, carbinolamides **10** and **11** were prepared as outlined in Scheme III.[12] Treatment of **10** and **11** with formic acid (25 °C, 8–10 min) gave quinolizidinones **12** (mp 135–137 °C) and **13** (mp 72–74 °C) in 63 and 71% yields, respectively. Only small amounts (2–5%) of substances stereoisomeric to **12** and **13** were formed in these cyclizations. The stereochemistry of **12** was established by conversion into quinolizidine **14**[13] ($LiAlH_4$, mp 97–99 °C; 72%) and subsequent oxidation to known quinolizidinone **15**[14] (Jones reagent, 70%). The stereochemical assignment for **13** was based on spectral data gathered on the dihydro derivative **16** (H_2, Pd/C; mp 73–75 °C; 95%), aminoacetate **17**, and **13** itself.[15] These results suggest that the *N*-acyliminium ions derived from **10** and **11** cyclize via chair conformations in which the incipient C-4 substituent occupies an axial site (Scheme IV), in contrast to the equatorial orientation of substituents usually observed in olefin cyclizations and other reactions whose transition-state geometries resemble chair cyclohexane.[17-19] This unusual observation can be attributed to the unfavorable development of $A^{(1,3)}$ strain in the transition states leading to C-4 isomers of **12** and **13**.

The results presented here indicate that $A^{(1,3)}$ strain is an important consideration in predicting the stereochemical course of certain *N*-acyliminium ion cyclizations. This and other applications of the $A^{(1,3)}$ strain concept to stereochemical problems in alkaloid synthesis are being explored in these laboratories.[20]

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Stabilities of Carbonium Ions in Solution. 10. A Thermochemical Comparison of the Relative Stabilities of Long-Lived 2-Norbornyl and Butyl Cations in SO_2ClF/SbF_5

Sir:

We report here a calorimetric determination of the heats of isomerization of the secondary 4-methyl-2-norbornyl cation to the tertiary 2-methyl-2-norbornyl ion in SO_2ClF/SbF_5 at low temperatures using methods described previously.[1-3] When compared with the corresponding heat of isomerism of the *sec*-butyl to the *tert*-butyl cation under the same conditions, we find that the rearrangement of the norbornyl system is considerably less exothermic than is that of the acyclic system. We believe that this is the most compelling piece of evidence yet presented in support of the notion that the 2-norbornyl ion enjoys special thermodynamic stability relative to other simple secondary carbonium ions. This in turn confers added significance on the question of the ion's structure—i.e., whether or not it is bridged—for, if, as has been argued,[4] the norbornyl ion has no special degree of stability relative to appropriate models, there is little reason to propose a special structural feature for it.

The reason why the present experiment is particularly illuminating regarding the relative stabilities of the isomeric secondary and tertiary ions is that *no neutral precursor molecules or radicals are involved in the comparison.* We have emphasized recently[3] that initial state contributions render equivocal all interpretations of ionic stabilities in terms of heats of ionization or rates of solvolysis. Very large (e.g., 10 kcal/mol) initial state contributions can confuse comparisons of secondary vs. tertiary halides for such processes.[5] Initial state contributions to the methylnorbornyl systems have also been discussed,[6] and strain in 2-methyl-2-*exo*-norbornyl chloride has been shown to contribute ~2 kcal/mol to its heat of ionization.

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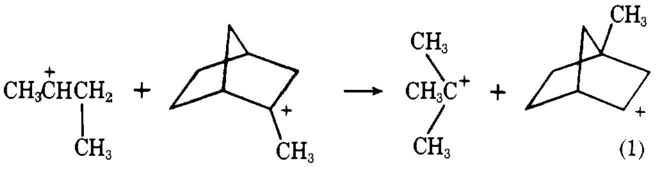
Table I. Heats of Ionization[a] (ΔH_i) at Various Temperatures for Norbornyl Chlorides in SbF_5/SO_2ClF

	ΔH_i, kcal/mol	temp, °C
exo-norbornyl chloride	−23.43 ± 0.72	−55
	−23.16 ± 0.43	−100
2-methyl-2-*exo*-norbornyl chloride	−30.35 ± 0.44	−55
	−30.08 ± 0.81	−100
4-methyl-2-*exo*-norbornyl chloride	−28.77 ± 0.32	−55
	−22.20 ± 0.49	−100

[a] This is defined as the difference between the molar heat of solution of the solute in a 0.2 M solution of SbF_5 in SO_2ClF minus the corresponding value for solution in pure SO_2ClF under the same conditions.[2] The final state of the reaction in this solvent is probably an electrostatically bound but relatively undissociated ion pair.[3] Some values in this table differ slighly from those reported previously.[1-3] The new values were obtained after rebuilding the calorimeter to improve precision.

At −100 °C 2-methyl- and 4-methyl-2-*exo*-norbornyl chlorides are converted quickly and cleanly into their respective carbonium ions by SbF_5 in SO_2ClF without appreciable rearrangement during the period required for measurement of their heats of ionization.[7,8] The results are presented in Table I. At −55 °C both chlorides go instantly and cleanly to the tertiary 2-methylnorbornyl ion. For the secondary chloride the difference between the heat of ionization (ΔH_i) at −100 °C and that at −55 °C is the heat of isomerization of the secondary to the tertiary ion. Rearrangement of the 4-methyl-2-norbornyl cation to the 2-methyl ion releases 6.57 ± 0.41 kcal/mol. In contrast, rearrangement of *sec*-butyl to *tert*-butyl cation releases 14.20 ± 0.60 kcal/mol.[3,10] If this latter value is a normal one for isomerization of saturated secondary to tertiary ions,[11,12] we could use logic applied by Brown and Schleyer[4] to conclude that an added 7.5 kcal/mol of stabilization is available to the norbornyl ions relative to the corresponding butyl ions in exchange reaction 1. These results suggest strongly that the secondary norbornyl ion is stabilized by as much as 7.5 kcal/mol relative to normal saturated secondary ions, assuming that the presence of the 4-methyl group has a negligible stabilizing effect on the charge at the 2 position. The notion that the 4 methyl-2-norbornyl ion is a good model for the unsubstituted ion is supported, but not proved, by the nearly equal heats of ionization of 4-methyl-2-*exo*-norbornyl chloride and unsubstituted 2-*exo*-norbornyl chloride to the respective secondary ions (Table I and Figure 1).



(1)

$\delta\Delta H_i = -7.5$ kcal

A crucial problem in the above argument revolves around the question of a suitable model for a "normal" secondary ion with which to compare the putatively "abnormal" 2-norbornyl ion. The present experiment was possible *precisely because both the secondary butyl and 4-methyl-2-norbornyl ions are abnormal* in the sense that they are long lived enough to permit study by reaction calorimetry at −100 °C. Their unusual *kinetic stability* is the result, in both cases, of special structural features which slow down drastically the rearrangements which normally convert secondary ions into tertiary ones.[11,12] In neither case is there any fundamental reason to relate kinetic stability to thermodynamic stability.

At this point, however, the question of which systems provide an appropriate thermodynamic norm of stability remains moot because of the lack of well-established systems with which to test it. The experiment reported here at least provides unequivocal evidence that there is a large difference in rearrangement energy between a pair of clearly defined isomeric aliphatic ions in solution and a corresponding pair of norbornyl ones. This test demonstrates further support for the notion that secondary norbornyl ions enjoy a special stabilizing feature.[11-14] We are currently searching for other model secondary ions which may help to settle the question more conclusively. Unfortunately, both the 3-methylcyclopentyl and the 2-adamantyl ions isomerize at once to tertiary ions even at −110 °C.

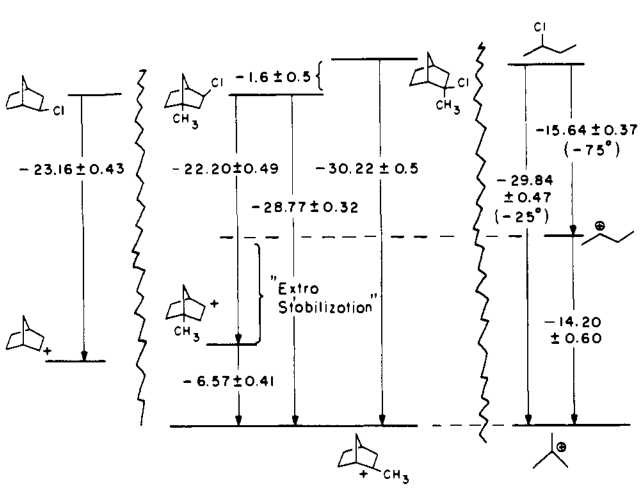


Figure 1. Schematic diagram of ionization and rearrangement processes compared in text. All values represent enthalpies in kilocalories/mole.

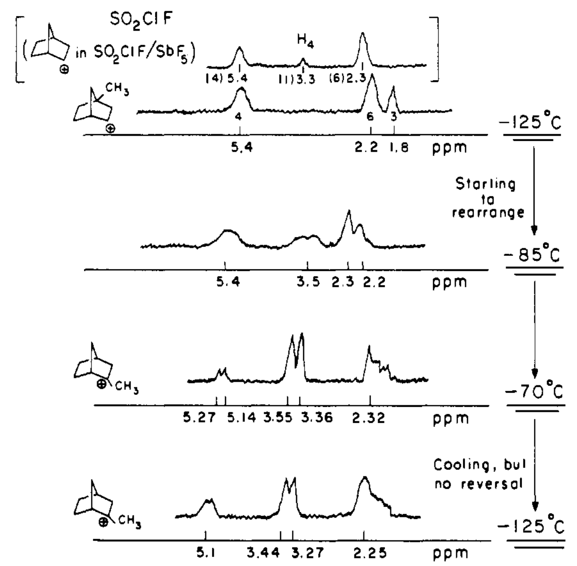


Figure 2. ^1H NMR spectra of 2-norbornyl ion pairs in SO_2ClF at various temperatures.

Preparation of 4-methyl-2-*exo*-norbornyl chloride followed the procedures of Brown and Lui.[15] Careful addition to SbF_5/SO_2ClF at −100 °C[2] produced a solution whose ^1H NMR spectrum was similar to that of the unsubstituted 2-norbornyl ion[9b,16] except for the presence of an added resonance at δ 1.8 ppm, integrating for three protons, and the absence of the single proton peak at 3.3 ppm assigned to the 4-H in the 2-norbornyl ion (Figure 2). Warming the solution to −55 °C changed the spectrum to that of the 2-methyl-2-norbornyl cation.[9b] Detectable rearrangement commenced at about −70 °C which is consistent with the "slow" 3,2 hydride shift being the rate-determining step.[9] The spectrum remained unchanged when the rearranged sample was again cooled to −100 °C.

All ΔH_i values reported here were based on at least two completely independent series of calorimetric measurements using freshly prepared samples of all components. Each such set of measurements included at least five replica determinations of the enthalpy terms reported.

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Two-Dimensional Correlated Nuclear Magnetic Resonance of Spin-Coupled ^{11}B–^{1}H Systems

Sir:

A common problem in the interpretation of ^{11}B NMR spectra of polyhedral boron compounds arises when resonances of similar chemical shift are unresolved owing to the overlap of intrinsically broad peaks whose width is due to unresolved coupling and rapid relaxation.[1] Although the use of higher polarizing magnetic fields certainly mitigates this problem, a powerful new technique which has the potential to circumvent resolution difficulties is two-dimensional (2D) NMR. This method is now commercially available and has been applied to ^{1}H, ^{13}C, and ^{31}P nuclei.[2-11] It is the purpose of this communication to report the successful application of the 2D NMR method to a ^{1}H–^{11}B system, specifically a polyhedral carborane.

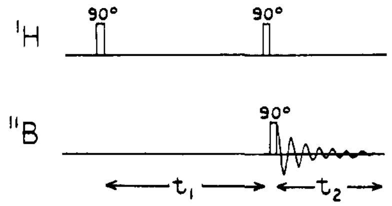

Figure 1. Pulse sequence for the heteronuclear ^{11}B–^{1}H experiment.

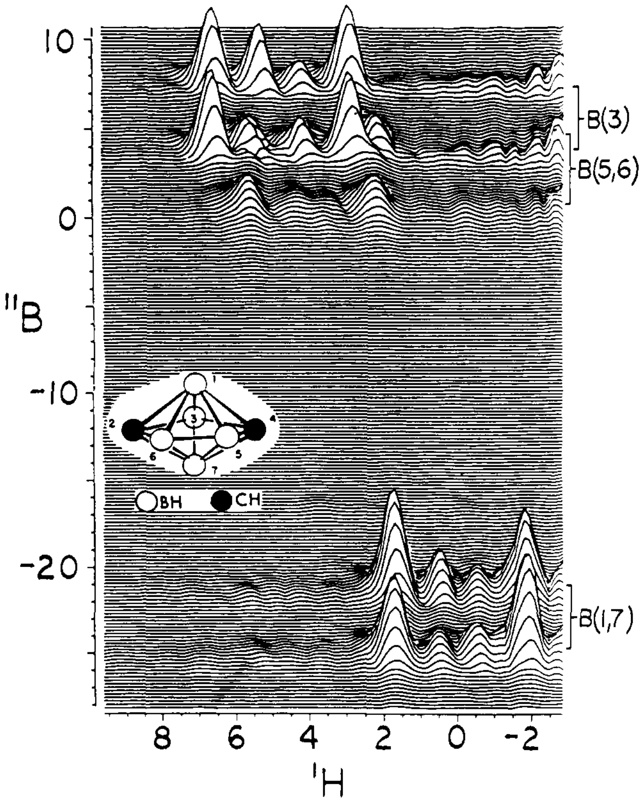

Figure 2. Two-dimensional correlated ^{11}B–^{1}H NMR spectrum of 2,4-$C_2B_5H_7$ obtained on an NT-150 spectrometer. The *x* axis exhibits ^{1}H chemical shift, δ, in parts per million relative to Me_4Si at 150 MHz; the *y* axis shows ^{11}B chemical shift in parts per million relative to $BF_3 \cdot O(C_2H_5)_2$ at 48 MHz. An absolute value spectrum is plotted. The peaks in the upper right are shoulders of unmodulated ^{11}B signals not included in the plot.[5]

The theory of 2D NMR is well established[2] and details of the basic pulse sequence and many variations of it have appeared,[2-6] including chemical applications.[7-11] The experiment that appears to be most useful for the study of polyhedral boron compounds is analogous to those performed on ^{31}P–^{1}H[7] and ^{13}C–^{1}H.[8] The pulse sequence (Figure 1) begins with the application of a 90° pulse to a proton population at thermal equilibrium, thus generating transverse magnetization. After an evolution period t_1, the transverse magnetization vectors of differing frequencies (e.g., the two components of a doublet) will then occupy different orientations in the rotating frame. A second 90° pulse is then applied in order to rotate the dephased vectors out of the x–y plane which produces corresponding vectors of differing M_z values. The second pulse results in selectively "pumping" the spin populations of ^{11}B nuclei that are scalar coupled to protons. Finally, a 90° pulse is applied to the ^{11}B nuclei in order to monitor the ^{11}B free induction decay during t_2. The experiment is repeated many times, systematically varying t_1 and thus establishing a two-dimensional data matrix over t_1 and t_2. A double Fourier transformation

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