putative structure are examined,[63] small differences in their binding sites may become apparent by comparison of spectra obtained with bound paramagnetic lanthanides. Otherwise, the most fruitful use of lanthanides in proteins would be for determining distances from relaxation measurements, sorting complex NMR spectra by enhancing the resolution, and identifying residues at metal-binding sites. Detailed structures obtained from lanthanide measurements alone must be considered with extreme caution.

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Kinetics of Degenerate Rearrangements in Nortricyclyl Cation

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Abstract: Degenerate rearrangements in ^{13}C- and in ^{2}H-labeled nortricyclyl cations are studied with NMR spectroscopy. Label scrambling is detected below 0 °C and results from the combination of three distinct processes. Molecular framework reorganization via the intermediate bicyclo[3.1.1]heptenyl cation, a 3,2-hydride shift (within the norbornenyl cation framework), and a 3,5-hydride shift are the proposed mechanisms responsible for label migration. Changes in the area of NMR signals (^{13}C and ^{2}H) over time at constant temperature are monitored; reaction rates are determined (by the Runge–Kutta method) which accurately simulate these changes. Activation energies of 16.9 ± 1 kcal/mol for the skeletal rearrangement process and 18.4 ± 1 kcal/mol for the 3,2-hydride shift are estimated from the rate data; the activation energy for the 3,5-hydride shift is substantially greater than that of the 3,2-hydride shift. The results from quantum mechanics calculations (MP3/6-31g*//6-31g*) are used to complete the energy profile for the skeletal rearrangement: bicyclo[3.1.1]heptenyl cation is an energy minimum at 5.3 ± 1 kcal/mol, relative to nortricyclyl cation.

The nature of the intermediate carbocation(s) involved in the solvolysis of norbornenyl and nortricyclyl derivatives has been under investigation[1,2] since the early 1950's. Mixtures of norbornenyl and nortricyclyl products are obtained from either type of precursor. Both the symmetric nortricyclyl and asymmetric norbornenyl cations have been postulated[3-7] to explain the observed product distributions. No experimental evidence was found to support the involvement of other proposed intermediates, such as bicyclo[3.1.1]heptenyl cation.[8]

Stable cation solutions have been prepared from both nortricyclyl[9] and norbornenyl[10] halides. Identical NMR spectra are recorded for samples prepared from either alkyl halide, indicating that a common carbocation has been produced. The carbocation appears to be symmetrical on the NMR time scale (^{1}H NMR δ 11.30 (1 H, t), 6.72 (2 H, s), 4.72 (1 H, s), 4.15 (2 H, d), 3.65 (1 H, s), 2.73 (2 H, d); ^{13}C NMR δ 258.5 (d), 111.6 (d), 86.3 (d), 46.6 (t) , 42.4 (d)). Chemical shift additivity[11] is used to identify the compound as the nortricyclyl cation,[9] ruling out the possibility that the observed symmetry is the result of a rapidly equilibrating pair of asymmetric norbornenyl cations. This conclusion is supported by the results[10] obtained from application of the method of isotopic perturbation.[12-14]

Thus, the structure of the common cation produced from nortricyclyl and norbornenyl derivatives is best represented by a single tricyclic species (I) with C_2 symmetry. Theoretical treatments[15] (6-31g//6-31g) and ^{13}C–^{13}C coupling constants[16,17] indicate that the C5–C6 bond (1.36 Å, 59.1 Hz) is shorter (higher % s character) than any other C–C bond (C1–C2 is 1.43 Å), and

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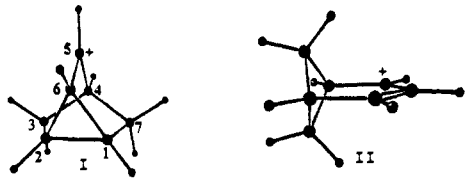
that C1–C6 and C2–C6 (1.67 Å, 11.6 Hz) are the longest (lowest % s character) bonds[18] in nortricyclyl cation; C1–C7/C2–C3, C3–C4/C4–C7, and C4–C5 have more typical sp^3–sp^3 bond characteristics (bond lengths and coupling constants within the range of 1.54 ± 0.01 Å and 32.5 ± 4 Hz, respectively).

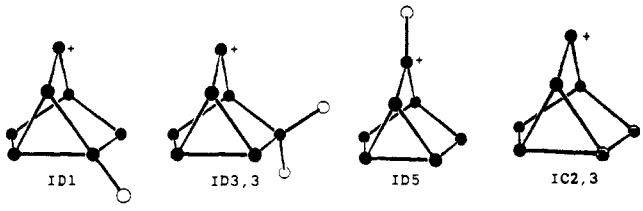


Nortricyclyl cation (I), however, is not static at all temperatures.[10] At least three distinct degenerate rearrangement processes have been detected below 0 °C. These rearrangements are slow on the NMR time scale and do not result in observable line-broadening[19] below 0 °C, but magnetization transfer experiments[20,21] or isotopic labeling[22,23] readily permit their detection. Label migration can first be observed at −70 °C and it is consistent with a carbon skeletal rearrangement where C1,C2 (and associated hydrogen atoms) interchange with C4,C5. Reversible isomerization to bicyclo[3.1.1]heptenyl cation (II)[24] would accomplish this scrambling. At −50 °C, additional spectral changes are observed which indicate that the exo hydrogen atoms of C3,7 interchange with hydrogen of C6, C5, C4, and C1,2. Contribution from a second (slower) scrambling process such as a 3,2-hydride shift[25] (after reversible isomerization to norbornenyl cation), in addition to the skeletal rearrangement, is consistent with these observations. At 0 °C, the intensity of the NMR signal for the endo hydrogen atoms of C3,7 diminish as all other signal intensities increase proportionately. A third (still slower) rearrangement such as a 3,5-hydride shift,[26] now occurring at a sufficiently fast rate so as to effectively contribute (along with the other two mechanisms) to label migration, is consistent with the spectral observations and the conclusion that all atoms are interchanged at 0 °C by a series of scrambling processes.

We present here kinetics of the degenerate rearrangements in nortricyclyl cation. Reaction rate data and the results from quantum mechanics calculations are used to generate an energy profile for the carbon skeletal rearrangement, involving I and II.

Results and Discussions

A variety of isotopically labeled nortricyclyl and norbornenyl halides (**5**, **8**, **11**, and **16**) are prepared and converted to the corresponding nortricyclyl cations (ID3,3, ID1, ID5, and IC2,3,



respectively). The conventional molecular beam method[27] is used to mix the alkyl halide and antimony pentafluoride in sulfuryl chloride fluoride (in the absence of air) and generate stable carbocation solutions below −100 °C; the low temperature is necessary to prevent premature scrambling of the label. The initial proton-decoupled ^{13}C NMR (125.7 and 62.9 MHz, external

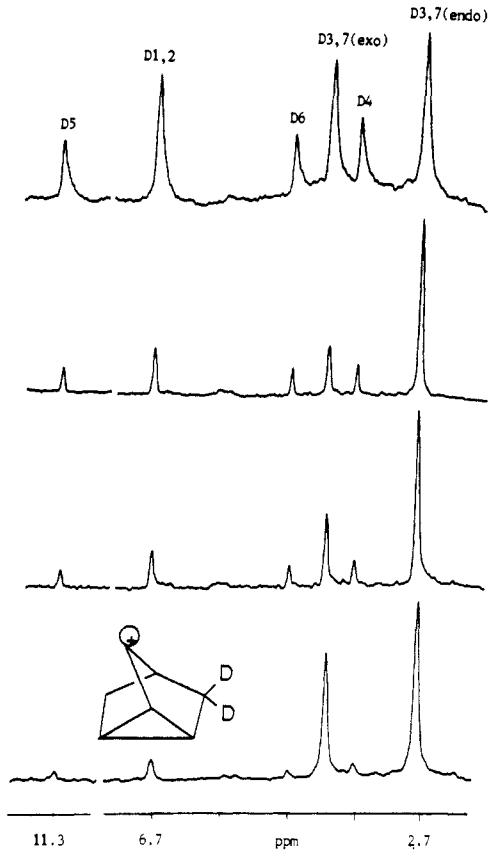


Figure 1. ^2H NMR of 3,3-dideuterionortricycl-5-yl cation as a function of increasing sample temperature: bottom, −80 °C; middle, −45 °C over time (70 min); top, 0 °C.

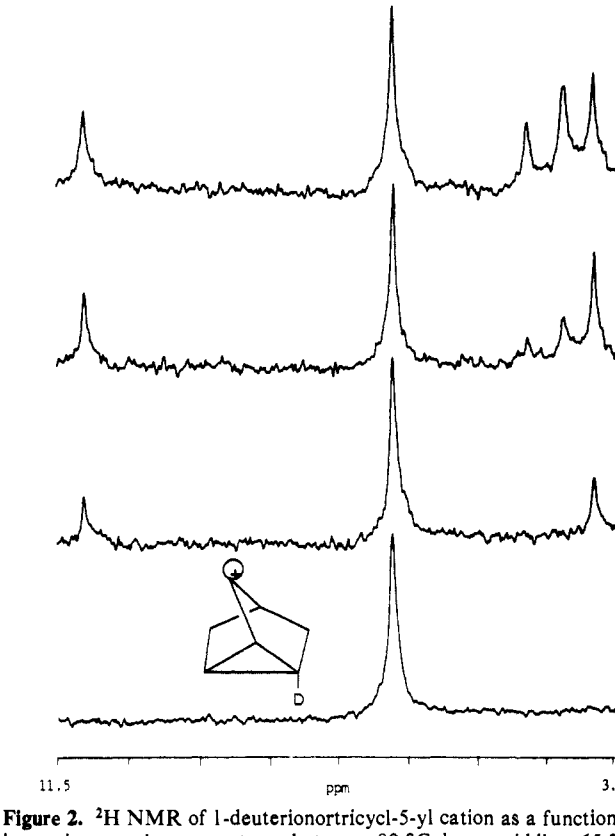


Figure 2. ^2H NMR of 1-deuterionortricycl-5-yl cation as a function of increasing sample temperature: bottom, −80 °C; lower middle, −65 °C; upper middle, −55 °C; top, −45 °C.

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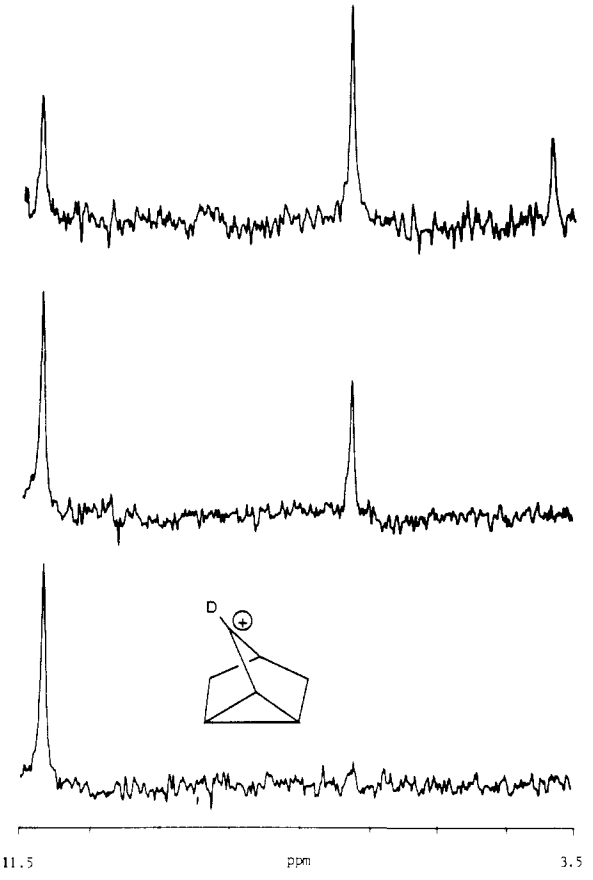


Figure 3. ^2H NMR of 5-deuterionortricycl-5-yl cation as a function of increasing sample temperature: bottom, −80 °C; middle, −65 °C for 30 min; top, −65 °C for 110 min.

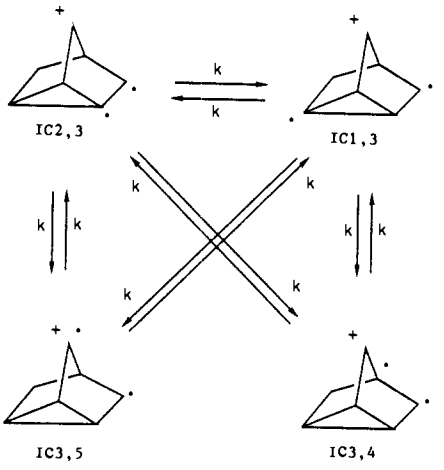
reference Me_2SO-d_6 in sulfuryl chloride fluoride) and ^2H NMR (76.8 MHz) spectra below −80 °C show signals corresponding only to the original labeled positions (see Figures 1–3).

As previously reported [10] (^{13}C NMR) and illustrated in Figures 1–3 (^2H NMR), new signals appear in the NMR spectrum, as the isotopic label scrambles to different locations within the molecule. The fastest scrambling process, which involves C1, C2, C4, and C5, is readily monitored between −70 and −60 °C. Reliable measurements of changes in NMR signal areas, which result solely from the fastest degenerate rearrangement process, can only be obtained over a fairly narrow temperature range. Below −75 °C, the rearrangement process is too slow to effect significant changes in signal intensities during acceptable lengths of time. Above −55 °C, isotopic scrambling occurs before the sample reaches thermal equilibrium in the NMR probe, and the second scrambling process also begins contributing to changes in NMR signal intensities.

At constant temperature, and after thermal equilibration of the sample (up to 20 min), signal integrations are recorded as a function of time. The following typical changes in signal areas are observed at −65 °C: (1) the ratio for D5:D1,2:D4 of ID1 changes from 1:10.5:1 to 1:2.8:1.1 in 95 min; (2) after 30 min, the D5:D1,2:D4 ratio of ID5 is 2.0:1:0, and reaches 0.6:1:0.4 in 100 min; (3) the C2:C4 ratio of IC2,3 decreases from 2.5:1 to 2.0:1 in 85 min.

The recorded changes in signal intensities represent the migration of the isotopic label, in accord with degenerate carbon skeletal reorganization of I via II. This mechanistic scheme establishes an equilibrium between certain isotopically related molecules in a particular manner. For example, Scheme I displays the relationship between the appropriate isomers of IC2,3. Production of the four isotopomers (IC2,3, IC1,3, IC3,4, and IC3,5) in equal amounts is necessary and sufficient to explain spectral observations. Rearrangement via II satisfies this condition and dictates that C2 exchange with C1, C3, and C4 (likewise C1 exchanges with C2, C3, and C4), while C3 (like C4) exchange only with C1,2. Thus there are three direct pathways linking IC2,3 (and IC1,3) to the other isotopomers but only two pathways involving IC3,4 and IC3,5 (there is no direct means for interconversion between IC3,4 and IC3,5).

Scheme I




```
d(IC2,3) = -3ky(IC2,3) + ky(IC1,3) + ky(IC3,5) + ky(IC3,4)
d(IC1,3) = -3ky(IC1,3) + ky(IC2,3) + ky(IC3,5) + ky(IC3,4)
d(IC3,5) = -2ky(IC3,5) + ky(IC2,3) + ky(IC1,3)
d(IC3,4) = -2ky(IC3,4) + ky(IC2,3) + ky(IC1,3)

[C1,2] = (d(IC2,3) + d(IC1,3))/Total
[C3,7] = (d(IC2,3) + d(IC1,3) + d(IC3,5) + d(IC3,4))/Total
[C4]   = d(IC3,4)/Total
[C5]   = d(IC3,5)/Total
Total  = 2(d(IC2,3) + d(IC1,3) + d(IC3,5) + d(IC3,4))
```

where, d(ICn) = rate of appearence of isotopomer ICn; y(ICn) = concentration of isotopomer ICn; k = rate constant for skeletal rearrangement; [Cn] = relative cmr signal intensities.

Table I. Rate of Rearrangement via Bicyclo[3.1.1]heptenyl Cation (II) (s^{-1})

cation	nuclei obsd	temp (°C)	rate ($\times 10^4$)	E_a[a] (kcal/mol)
ID1	deuterium	−65	2.0	16.8
ID1	deuterium	−45	80[b]	16.8
ID5	deuterium	−65	3.3	16.6
IC2,3	carbon	−65	0.45	17.5
IC2,3	carbon	−55	5.7[b]	17.2
ID3,3	deuterium	−45	180[b]	16.4

[a] Log A = 14, assumed. [b] Determined in conjunction with rate (r) for the 3,2-hydride shift (Table III).

Based on Scheme I, rate expressions (relating the four isotopomers involved) can be written and numerically integrated, using the Runge–Kutta method,[28] to predict the time dependence of the relative NMR signal intensities for any rate constant. The rate is varied until the best match is found between calculated and measured relative NMR signal intensities, over the same time period (Table I). With only a small temperature window for data collection, an Arrhenius plot is meaningless; however, a value for the activation energy of this scrambling process is estimated to be 16.9 ± 1 kcal/mol, if a typical value[29] for the preexponential term (log A = 14) is assumed.

Although rearrangement via II is completely consistent with the experimental observations, the data cannot be used to make a distinction between its role as intermediate or transition state. Quantum mechanics calculations[15] are performed to provide information on the nature of II. The energy difference between II and I is 5.3 ± 1 kcal/mol (Table II), which is substantially less than the estimated activation energy for the reaction and suggests that II is an energy minimum. This is verified by frequency

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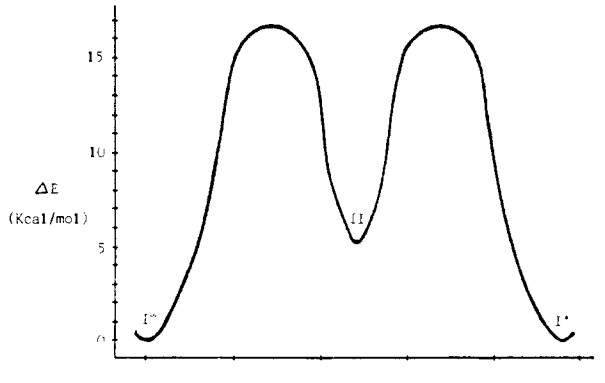
Table II. Relative Energies (kcal/mol)[a]

cation	6-31g*// 6-31g*	MP2/6-31g*// 6-31g*	MP3/6-31g*// 6-31g*
I[b]	0.0	0.0	0.0
II[c]	1.0	7.6	5.7

[a] Does not reflect the vibration zero-point energy difference; II is 0.4 kcal/mol higher in energy than I. [b] With C_2 symmetry imposed. [c] With C_{2v} symmetry imposed.

Scheme II



I*: Nortricyclyl Cation, with an isotopic label at C2.

I'': Nortricyclyl Cation, with the isotopic label at C1 or C4 or C5.

II: Bicyclo[3.1.1]heptenyl Cation.

analysis (at the 6-31g* level), which shows that both I and II are indeed energy minima (no negative eigenvalues).

With an experimentally based estimate of the activation energy for the rearrangement of I via II, and the calculated relative energies of I and II, an energy profile for this overall degenerate reaction is generated (Scheme II). It suggests that there is an activation energy of about 11.6 kcal/mol for rearrangement of bicyclo[3.1.1]heptenyl cation to nortricyclyl cation.

Norpinene was converted to 4-bromobicyclo[3.1.1]hept-2-ene[23,30] and subjected to antimony pentafluoride in sulfuryl chloride fluoride in an attempt to generate a stable solution of II and verify that it is the intermediate involved in the fast scrambling process. The NMR spectrum clearly indicates the formation of I but II was never detected. Thus if II is formed as such, there is a relatively low barrier (less than 12 kcal/mol) for the rearrangement to I.

A second scrambling process (occurring at a slower rate than that of the skeletal rearrangement), which involves H(D)3,7-exo, is readily monitored between −60 and −40 °C. At constant temperature, and after thermal equilibration of the sample (up to 20 min), signal integrations are recorded as a function of time. The following typical changes in signal areas are observed: (1) at −45 °C, the ratio for D5:D1,2:D4:D6:D3,7-exo of ID1 changes from 1:2.9:1.1:0:0 to 1:1.9:1.0:0.4:0.6 in 95 min; (2) the intensity of C6 in IC2,3 doubles after 185 min at −55 °C; (3) at −45 °C, the D5:D1,2:D4:D6:D3,7-exo ratio of ID3,3 goes from 1.5:3.3:1.7:1:9.2 to 2.0:2.1:1.8:1:5.8 in 70 min.

The recorded changes in signal intensities represents the movement of the isotopic label, in accord with a rearrangement process such as a 3,2-hydride shift (within the norbornenyl cation framework). This scrambling mechanism, in conjunction with the skeletal rearrangement, establishes an equilibrium between isotopically related molecules in a particular manner. Scheme III, for example, displays the relationship between the pertinent deuterated isomers of I. Production of the five isotopomers (ID1, ID3, ID4, ID5, and ID6) in their statistical amounts is necessary and sufficient to explain spectral observations. Rearrangement via a 3,2-hydride shift (and II) satisfies this condition and dictates that D1,2 exchange with D3-exo and D4 by the 3,2-hydride shift

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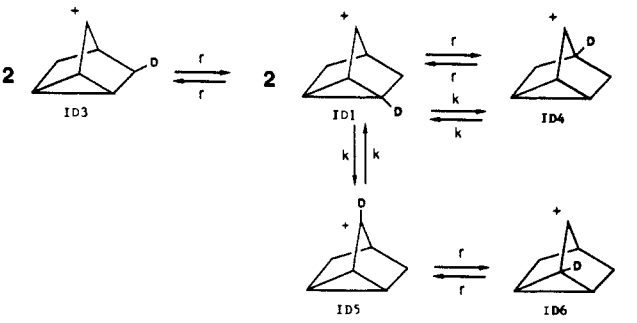
Scheme III




```
d(ID1) = .5ry(ID3) +   ky(ID4) + ky(ID5) -   ry(ID1)
       - ky(ID1) +   ry(ID4)
d(ID3) = .5ry(ID1) - .5ry(ID3)
d(ID4) = .5ky(ID1) -   ky(ID4) - ry(ID4) + .5ry(ID1)
d(ID5) = .5ky(ID1) -   ky(ID5) - ry(ID5) +   ry(ID6)
d(ID6) =   ry(ID5) -   ry(ID6)

(D1,2) = 2d(ID1)/Sum
]D3,7] = 2d(ID3)/Sum
(D4]   = d(ID4)/Sum
(D5]   = d(ID5)/Sum
(D6]   = d(ID6)/Sum
Sum    = 2d(ID1) + 2d(ID3) + d(ID4) + d(ID5) + d(ID6)
```

where, d(IDn) = rate of appearence of isotopomer IDn; y(IDn) = concentration of isotopomer IDn; k = rate constant for skeletal rearrangement; r = rate constant for the 3,2-hydride shift; (Dn) = relative dmr signal intensities.

Table III. Rate of Rearrangement via a 3,2-Hydride Shift (s^{-1})

cation	nuclei	temp (°C)	rate (×10⁴)	E_a[a] (kcal/mol)
ID1	deuterium	−45	1.0	18.8
IC2,3	carbon	−55	0.57	18.2
ID3,3	deuterium	−45	9.0	17.8

[a] Log A = 14, assumed.

and with D4 and D5 via II; D5 and D6 are also interchanged by the 3,2-hydride shift. Thus there are direct pathways which link ID1 with ID4 (two paths), ID3, and ID5; ID5 is directly linked to ID6 as well.

Based on Scheme III, simple rate expressions (relating the five isotopomers involved) are determined and used in conjunction with Runge–Kutta mathematics[28] to calculate isotopomer concentrations and relative NMR signal intensities over time, as a function of the rate constants. The rate for each process is varied until the best match is found between calculated and measured relative NMR signal intensities, over the same time period (Table III). The activation energy for the 3,2-hydride shift is estimated to be 18.4 ± 1 kcal/mol, if a typical value for the preexponential term (log A = 14) is assumed.

The third rearrangement process (occurring at a rate slower than that of the 3,2-hydride shift) is one that scrambles H(D)-3,7-endo and may involve a 3,5-hydride shift, where H(D)3,7-exo migrates to C5 (retaining its identity) and H(D)3,7-endo becomes H(D)5. This process is not readily detected until a sample temperature of 0 °C is obtained. Obviously, the activation energy for this scrambling process is significantly larger than that of the 3,2-hydride shift: 18.4 ± 1 kcal/mol.

Conclusions

A variety of isotopically labeled (^{13}C and ^{2}H) norbornenyl and nortricyclyl halides are coverted to the corresponding nortricyclyl cations. These samples are studied with variable-temperature ^{2}H NMR ^{13}C NMR spectroscopy to determine scrambling rates and provide data for the estimation of activation energies for the three degenerate rearrangement processes responsible for label migration in nortricyclyl cation below 0 °C. All treatments assume involvement of bicyclo[3.1.1]heptenyl cation as a reaction intermediate in the skeletal rearrangement process, as well as a 3,2-hydride shift and a 3,5-hydride shift. Activation energies of 16.9 ± 1 kcal/mol for the skeletal rearrangement process and 18.4 ± 1 kcal/mol for the 3,2-hydride shift (assuming log A = 14) are estimated for the rate data; the activation energy for the 5,3-

hydride shift is significantly greater than that of the 3,2-hydride shift. Quantum mechanics calculations on the related C_7H_9 cations are used to support the assumed cation involvement and complete the energy profile for the skeletal rearrangement process. The difference between energy minima, represented by nortricyclyl cation and bicyclo[3.1.1]heptenyl cation, is calculated to be 5.3 ± 1 kcal/mol. Attempts at observation of bicyclo[3.1.1]heptenyl cation (generated from the corresponding bromide) have thus far been unsuccessful; only nortricyclyl cation is detected. If bicyclo[3.1.1]heptenyl cation is formed as such, the barrier for rearrangement to nortricyclyl cation is less than 12 kcal/mol (in agreement with calculations).

Experimental Section

NMR spectra were recorded on Bruker WM-500 and WM-250 spectrometers. Typical inverse-gated decoupled ^{13}C NMR spectral acquisition parameters include digital resolution of 2.3 Hz/point, 300 (and 4 dummy) scans, a 40° pulse width, 1.6-s delay (four times the acquisition time) to decoupler, and relaxation delays up to 5 s. At the higher magnetic field strength, the broad band decoupler is incapable of complete proton decoupling for signals at both 258.5 and 42.4 ppm, so the ^{13}C NMR spectrum is recorded in two parts. Typical ^2H NMR spectral parameters include digital resolution of 1.2 Hz/point, 32 scans, a 40° pulse width, and relaxation delays up to 5 s.

3,3-Dideuteronorborn-5-en-2-one (3). A mixture of norborn-5-en-2-one (8 g), sodium methoxide (24 g), deuterium oxide (102 mL), and methanol-*d* (25 mL) in a 250-mL container was heated (with stirring) at 100 °C for 16 h. The organic material was extracted with ether, washed with deuterium oxide, filtered through anhydrous sodium sulfate, and distilled to yield **3**[31] (4.8 g, 59%), bp 50–55 °C (10 Torr).

3,3-Dideuteronorborn-5-en-2-ol (4). Methanol (5 mL), **3** (2 g), and acetic acid (0.2 mL) were placed in a 50-mL round-bottom flask and cooled by an ice bath. Sodium borohydride (0.35 g in 5 mL of water) was added slowly, and the mixture was allowed to stir at room temperature for 2 h. The solution was brought to pH 6 by the addition of sulfuric acid (4 N). The product was extracted with ether and dried by sodium sulfate filtration; the solvents were removed by distillation, leaving **4** (1.75 g, 85% yield).

3,3-Dideuteronorborn-5-en-2-yl Chloride (5). Carbon tetrachloride (65 mL), **4** (1.7 g), and triphenylphosphine (14.6 g) were refluxed for 16 h. Pentane was added to the cooled solution until precipitate formation ceased. After filtration, distillation produced 2.8 g (68% yield from the ketone) of a mixture (3:1) of **5** and 3,3-dideuteronortricycl-5-yl chloride (**6**), bp 64–67 °C (10 Torr).[32]

2-Deuteronorborn-5-en-2-yl Chloride (8). The preparation of **8** was the same as that for **5**, except that no H/D exchange was performed on 5-norbornen-2-one; rather, deuterium was introduced through reduction of the carbonyl with sodium borodeuteride (see **4**) to make 2-deuteronorborn-5-en-2-ol (**7**). Compound **7** was converted to a mixture (3:1) of **8** and 2-deuteronortricycl-5-yl chloride (**9**).

5-Deuteronortricycl-5-yl Chloride (11). Nortricyclan-5-one was converted to 2-deuteronortricyclan-2-ol (**10**) with sodium borodeuteride (see **4**) and **10** was converted to **11** with triphenylphosphine and carbon tetrachloride (see **5**).

[1,2-$^{13}C_2$]Acetylene (12). Barium carbonate-^{13}C (20 g, 98% enriched) and magnesium powder (49.2 g, 70–80 mesh) were mixed and loaded in a quartz tube. After 20 purge/evacuations with argon gas, the tube was heated strongly with a Meker burner until the solid mixture ignited and the quartz tube became incandescent. Once cooled, the tube was attached to a water-filled dropping funnel topped with a supply of helium gas, and separately to a drying tower leading to a bead-filled collection U-tube in liquid nitrogen. Helium was passed through the system as water (20 mL) was allowed to drip onto the barium carbide. After all the water had been added, the solution was brought to boil for 20 min.[33] A vacuum line was used to handle **12**, which was generated in 70% yield: ^{13}C NMR (acetone-d_6) δ 73.4 (d).

[1,2-$^{13}C_2$]Vinyl Acetate (13). Magnesium oxide (0.3 g), phosphorus pentoxide (0.2 g), phosphoric acid (0.2 mL), acetic anhydride (1 mL), and acetic acid (9 mL) were placed in a 1000-mL round-bottom flask and degassed. After **12** (35 mmol) had been added, the reaction vessel was shaken for 20 h. The material was removed, combined with potassium acetate (1 g), and distilled to yield **13** (1.1 g, 80%), bp 72–74 °C: ^{13}C NMR (chloroform-*d*) δ 142.0 (d×d), 96.7 (t×d), *J*(CC) = 82.8 Hz.

[2,3-$^{13}C_2$]Norborn-5-en-2-yl Acetate (14). Cyclopentadiene (4.5 mL) and **13** (4 g) were placed in a sealed tube and heated to 200 °C for 14 h. The contents were distilled and, in addition to recovering about half of the starting amount of **13**, **14** (1.8 g) was isolated, bp 82–83 °C 17 Torr): ^{13}C NMR (chloroform-*d*) δ 74.8 (d×d), 34.8 (t×d), *J*(CC) = 44.1 Hz.

[2,3-$^{13}C_2$]Norborn-5-en-2-ol (15). Sodium metal (0.5 g) and **14** (0.5 g) were added to methanol (30 mL). The reaction mixture was refluxed for 4 h. Methanol was removed by distillation. The remains were taken up in diethyl ether, washed with dilute aqueous acid, and dried. The ether was removed, leaving **15** in 72% yield: ^{13}C NMR (methanol-*d*) δ 55.03 (d×d), 19.4 (t×d), *J*(CC) = 43.6 Hz.

[2,3-$^{13}C_2$]Norborn-5-en-2-yl Chloride (16). Triphenylphosphine in carbon tetrachloride (see **5**) was used to transform **15** into a mixture (3:1) of **16** and [2,3-$^{13}C_2$]nortricycl-5-yl chloride (**17**). Preparative gas chromatography with a UV-101 column at 145 °C allowed for separation of **16** and **17**: ^{13}C NMR (chloroform-*d*) for **16**: δ 58.4 (d×d), 38.2 (t×d), *J*(CC) = 42.7 Hz; for endo/exo **17**: δ 30.1 (d×d), 11.1 (t×d), 31.5 (d×d), 13.7 (t×d), *J*(CC) = 39.5 Hz.

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Supplementary Material Available: Table of Cartesian coordinates for nortricyclyl and bicyclo[3.1.1]heptenyl cations (1 page). Ordering information is given on any current masthead page.

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