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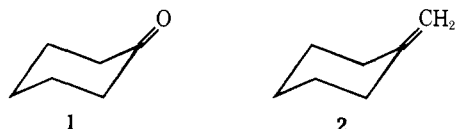
## Conformational Analysis of Tertiary Cycloalkyl ( $C_6$ , $C_7$ , $C_8$ ) Carbocations. Unexpected Preference for the Twist-Boat Conformation in the Cyclohexyl Case

Roger P. Kirchen and Ted S. Sorensen\*

Contribution from the Department of Chemistry, University of Calgary, Calgary, Alberta, Canada T2N 1N4. Received July 22, 1977

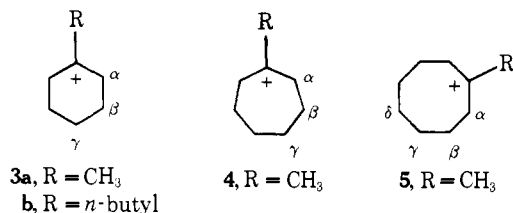
**Abstract:** In carbocations, chair conformations appear to be much less stable than in neutral organic analogues. Thus, tertiary cyclohexyl cations have a twist-boat ground state which is 500 cal/mol more stable than the chair conformation. The equilibrium constant, twist-boat-chair, is slightly solvent dependent, increasing in nonpolar and decreasing in more polar solvents. The tertiary cycloheptyl cation is a fluxionally mobile molecule but the methycyclooctyl cation has an unsymmetrical chair-twist-boat conformation in which the pseudorotational motion can be "frozen out" at low temperatures. The reported 2-methyl-2-bicyclo[3.2.1]octyl cation is instead the 2-methyl-2-bicyclo[2.2.2]octyl cation. At very low temperatures, the former cation can be made but it was not possible to assign a conformation to the six-membered ring. The 9-methyl-9-bicyclo[3.3.1]nonyl cation is postulated to have a chair-boat conformation in contrast to the dichair conformation observed in neutral compounds. Attempts to prepare the observable 2-methyl-2-twistyl cation were unsuccessful.

Virtually all simple neutral cyclohexane, cycloheptane, and cyclooctane ring systems have been subjected to some degree of conformational analysis.<sup>1</sup> However, while cycloalkyl cations, particularly cyclohexyl cation, have been well studied as solvolysis intermediates, virtually nothing is known concerning their conformational ground states. The two closest relatives in the cyclohexyl case (one  $sp^2$  center) are cyclohexanone (1) and methylenecyclohexane (2), both having



ground-state chair conformations.<sup>2</sup>

In observable ion studies, it is impossible at present to prepare secondary cycloalkyl cations, except for the cyclopentyl cation. All higher members collapse "immediately" to smaller ring tertiary ions,<sup>3</sup> even at very low temperatures. However, the tertiary cyclohexyl 3, cycloheptyl 4, and cyclooctyl 5 cat-



ions can be easily prepared. Indeed, ion 3a and many other tertiary cyclohexyl cations have been previously reported.<sup>4</sup>

In this paper, we report NMR spectral evidence from which one can deduce the ground state conformations of 3 and 5 and related spectral evidence giving the  $\Delta G^\ddagger$  activation barrier for conformer interconversions in 5 (and upper limits for 3 and 4). These results are then used to examine the conformations of two fused bicyclo systems containing flexible six-membered ring cations.

### Results

**The Cyclohexyl Case.** The <sup>1</sup>H NMR spectrum of the methylcyclohexyl cation 3a consists of four rather broad lines, assigned to CH<sub>3</sub>,  $\alpha$ CH<sub>2</sub>,  $\beta$ CH<sub>2</sub>, and  $\gamma$ CH<sub>2</sub>.<sup>4a</sup> The spin-spin coupling between these groups is not well resolved so that conventional (Karplus curve) <sup>1</sup>H NMR spectroscopy is not feasible for determining the conformation of 3a, the spectra merely confirming the gross features of this molecule.

At first sight, <sup>13</sup>C NMR spectroscopy looks even less promising since 3a simply shows, with proton decoupling, the expected five lines (Table I). However, one of these lines, assigned to the  $\beta$  carbons, shows a large chemical shift variation with changes in temperature. This variation is shown graphically in Figure 1, and can be contrasted with the  $\alpha$  carbons and the CH<sub>3</sub> carbon, also shown in Figure 1. The chemical shift position of the  $\beta$  carbon also varies with solvent and this is assumed to not be an "intrinsic solvent shift" (see later). Combining variations in temperature and solvent, one is able to "move" the  $\beta$  carbon chemical shift over a range of about 9 ppm. Two near extremes in this regard are shown in Figure 2, together with the experimental conditions used.

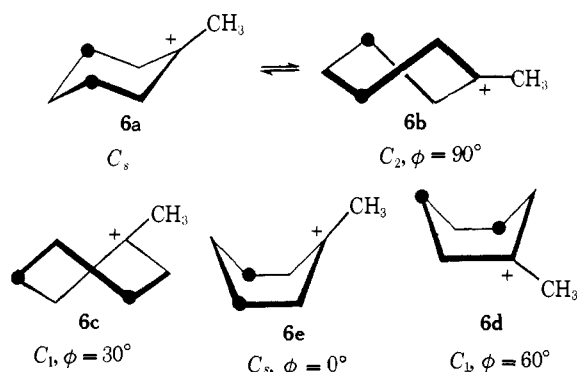
The chemical shift vs. temperature behavior of the  $\beta$  carbons in 3a is very characteristic of an equilibrium situation, involving two or more very rapidly equilibrating structures. In the present case, there is no evidence for any other isomeric ion in rapid equilibrium with 3a, nor would one expect there to be. One must conclude, therefore, that the equilibrium is between different conformers of the cyclohexyl ring. We believe that one conformer is the chair form 6a, while the other must be from the twist-boat (TB) 6b or 6c, or boat (B) 6d or 6e pseudorotation family.<sup>2</sup> Of these, the twist-boat conformers 6b and 6c are expected to be slightly more stable than the boat conformers.<sup>1</sup>

In fact, the results seem to us to be reasonably consistent with the twist-boat conformer 6b as the second populated conformer in the very rapid equilibrium with 6a. This choice of 6a and 6b will seem rather arbitrary at this juncture but the evidence accumulates as other systems are examined.

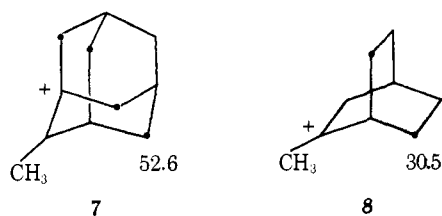
Table I. NMR Chemical Shifts for the Cations<sup>a</sup>

	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	CH <sub>3</sub>	Temp, °C	Remarks
	329.4	58.5	26.9	22.2					44.2	-88.5	
	327.9	55.8	27.4	22.2 or 23.1	59.0	29.0	23.1 or 22.2		13.3	-116	
	327.5	59.2	27.5	24.4					43.5	-128	
	334.3	61.6 or 54.6	46.9 or 29.7	28.3 or 25.8	34.4	28.3 or 25.8	46.9 or 29.7	61.6 or 54.6	43.6	-132	<i>b</i>
	296.1	44.7		33.4			73.6 (4.45, q?)		37.9	-100	<i>c,d</i>
	322.1	58.3	35.3	23.0	30.0	66.0 (4.17)			38.7	-100	<i>e</i>
	325.7	68.8	48.9 (av)	20.5 (av)	48.9 (av)	20.5 (av)			41.5	-133	<i>f</i>

<sup>a</sup>Multiplicities have been confirmed by off-resonance experiments, <sup>13</sup>C shifts in δ ppm, <sup>1</sup>H chemical shifts, in parentheses, in δ ppm relative to external Me<sub>4</sub>Si. The cation numbering system is not systematic and does not correspond to that used in the paper; this system allows the C<sup>+</sup> peak to be compared easily. <sup>b</sup>Broad proton peaks at 3.87 (7 H), 2.60 (2 H), 1.62 (8 H). <sup>c</sup>For C-3, C-5, C-6, C-8, 44.2, 39.1, 34.2, 28.6. <sup>d</sup>Other <sup>1</sup>H peaks at 3.56 (5 H), 2.69 (3 H), 1.80 (6 H). <sup>e</sup>For the first rearrangement cation (-108 °C): 330.5 (C), 80.1 (CH), 60.0 (CH<sub>2</sub>), 48.2 (CH<sub>2</sub>), 42.5 (CH<sub>2</sub>), 31.3 (CH<sub>2</sub>), 30.3 (CH<sub>2</sub>), 27.9 (CH<sub>2</sub>), 23.9 (CH<sub>2</sub>), 19.9 (CH<sub>3</sub>). <sup>f</sup><sup>1</sup>H peak at 1.21, d, *J* = 6.2 Hz; remainder broad and overlapping.



One can analyze the data in Figure 1 if one can estimate  $\beta$  carbon chemical shifts for pure **6a** and **6b**. An estimate of ca. 40–45 ppm can be made for **6a**, based on approximate corrections to the  $\beta$  carbon value in 2-methyl-2-adamantyl cation **7**<sup>5</sup> and the methylcyclooctyl cation (see later section). The best model for **6b** that we could prepare was the 2-methyl-2-bicyclo[2.2.2]octyl cation **8** (see later). Based on this model and



other considerations, an estimate of ca. 20 ppm was used for the  $\beta$  carbon chemical shift in **6b**. This value is actually quite close to the lowest temperature experimental data in Figure 1. The chemical shift averages shown in Figure 1 and the direction in which these averaged chemical shifts move can then

only mean that the TB conformer is the more stable. A standard Boltzmann distribution treatment<sup>8</sup> of the Figure 1 data, for two conformer populations, gives a  $\Delta H$  value of ca. 500–600 cal/mol favoring **6b**, in 1:4 SbF<sub>5</sub>-SO<sub>2</sub>ClF solvent. There is considerable uncertainty in the  $\Delta S$  value but the chair conformer **6a** is favored in all calculations,  $\Delta S$  ca. 1.5–2.5 eu. In 1:1 SbF<sub>5</sub>-FSO<sub>3</sub>H solution, the minimization gives  $\Delta H$  in the above range but  $\Delta S$  is increased to 3.2, i.e., the solvent effect appears to be due to entropy changes. We feel, however, that either  $\Delta H$  or  $\Delta S$  changes could be involved here<sup>9</sup> (note also that the Figure 1 solvent variations are treated as changes in *K* and not as intrinsic  $\delta$  variations).

The temperature-dependent spectrum of the 1-*n*-butylcyclohexyl cation **3b** is very similar to that of **3a**. One now has both ring and side-chain  $\beta$  carbons and two <sup>13</sup>C spectra of this ion (**3b**) are shown in Figure 3 to illustrate that there is no intrinsically large temperature dependence about ordinary  $\beta$  carbon chemical shifts. In these spectra, the peak being "overtaken" by the ring  $\beta$  carbon is assigned to the  $\beta$  carbon of the *n*-butyl side chain. In this same regard, the 2-methyl-2-adamantyl cation **7** was prepared and a <sup>13</sup>C chemical shift vs. temperature study was done. No significant shifts were observed in this conformationally fixed cation.

Proton spectra of **3a** also show temperature-dependent chemical shifts but these were not analyzed since the <sup>13</sup>C results seem more definitive.<sup>10</sup>

In the <sup>13</sup>C spectra of **3a**, there is no sign of "intermediate exchange" line broadening down to -130 °C, at which point viscosity broadening becomes appreciable. This places the chair-TB activation barrier at less than 6 kcal/mol.<sup>11</sup> One can combine the above results into an energy profile, shown in Figure 4.

**The Cycloheptyl Case.** The <sup>13</sup>C NMR spectrum of the methylcycloheptyl cation **4** shows a single peak for both  $\alpha$  carbons, for both  $\beta$  carbons, and for both  $\gamma$  carbons, with no

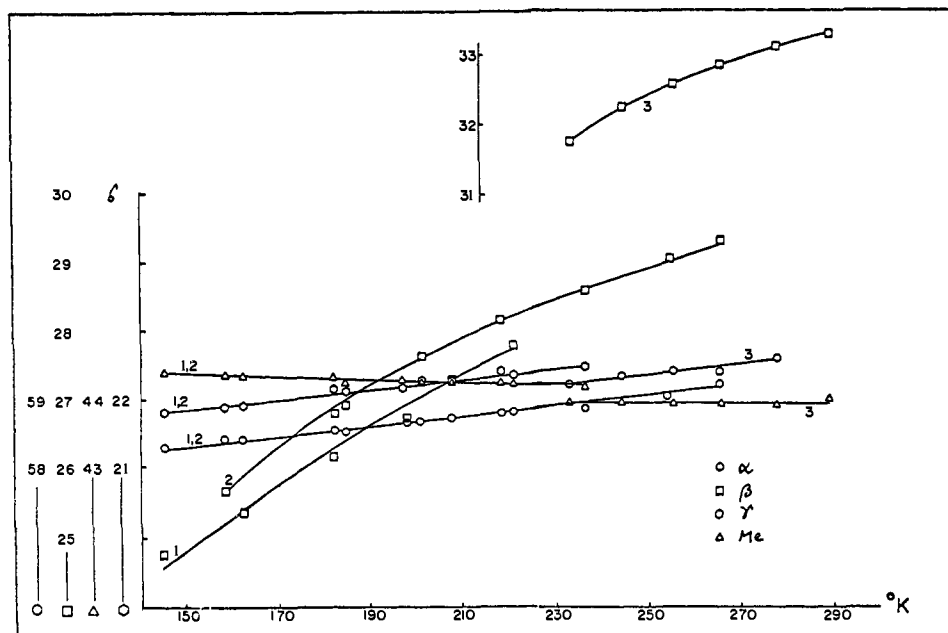


Figure 1.  $^{13}\text{C}$  chemical shift vs. temperature plot for the carbons in the 1-methylcyclohexyl cation **3a** (except  $\text{C}^+$ ). Lines labeled 1 refer to the  $\text{RCl-SbF}_5\text{-SO}_2\text{F}_2\text{-SO}_2\text{ClF}$  solvent system; 2 to the  $\text{RCl-SbF}_5\text{-SO}_2\text{ClF}$  solvent system; and 3 to 1:1  $\text{FSO}_3\text{H-SbF}_5$ . Note the multiple chemical shift scale at the left.



Figure 2. Two extreme decoupled  $^{13}\text{C}$  spectra of **3a**, showing a difference of nearly 9 ppm in the position of the  $\beta$  carbon. The lower spectra were recorded in  $\text{SO}_2\text{F}_2\text{-SO}_2\text{ClF}$  solvent while the upper was in 1:1  $\text{FSO}_3\text{H-SbF}_5$ . The upper spectrum includes peaks due to the 1,2-dimethyl- and 1,3-dimethylcyclopentyl cations, the latter giving the broad baseline absorption. The upper spectrum has been recorded on ions enriched in  $^{13}\text{C}$ .

evidence of NMR line broadening at the lowest temperature ( $-130^\circ\text{C}$ ) (see Table I for peak assignments). Furthermore, none of the peak positions are appreciably temperature dependent. These results are rather similar to those found for cycloheptanone and indicate similar, low, pseudorotational type barriers among conformers of similar energy.<sup>12</sup>

**The Cyclooctyl Case.** The methylcyclooctyl cation **5** is the first<sup>13</sup> of the cycloalkyl cation series, starting from  $n = 5$ , to show  $^{13}\text{C}$  NMR line broadening. This ion is stable only below  $-80^\circ\text{C}$ , and even at this temperature, the averaged  $\beta$  carbon peak is broadened. As one goes to lower temperature, the av-

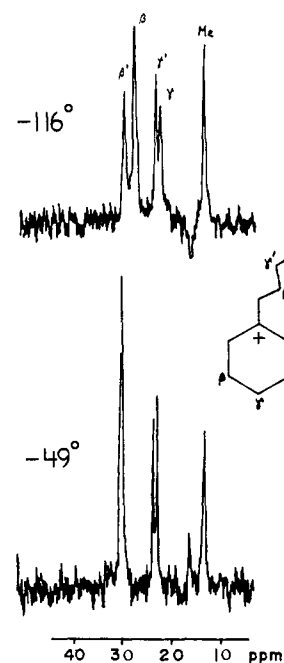


Figure 3. Two decoupled  $^{13}\text{C}$  spectra (partial) of the 1-*n*-butylcyclohexyl cation **3b**, showing that the  $\beta$  carbon chemical shift variation of the ring carbons is not matched by the side-chain  $\beta$  carbon. The  $\gamma$  and  $\gamma'$  carbon assignments may be interchanged. The folded-back  $\text{C}^+$  peak shows up between  $\gamma$  and Me.

eraged  $\alpha$ ,  $\beta$ , and  $\gamma$  carbon peaks broaden, reach coalescence, and finally separate into individual peaks for the  $\alpha$  and  $\alpha'$  carbons, the  $\beta$  and  $\beta'$  carbons, and the  $\gamma$  and  $\gamma'$  carbons. The  $\text{CH}_3$ ,  $\text{C}^+$ , and  $\delta$  carbons on the symmetry line in structure **5a** are unaffected (i.e., not broadened) and this shows that the line broadening is a degenerate process and not one involving two or more different conformations. This single conformation in **5** is of course unsymmetrical. Several representative line-broadened spectra of the cation are shown in Figure 5, together with the matching computer-calculated curves. The activation parameters for the conformational barrier involved in the line broadening were determined in the usual way,  $\Delta G^\ddagger = 7.2 \pm$

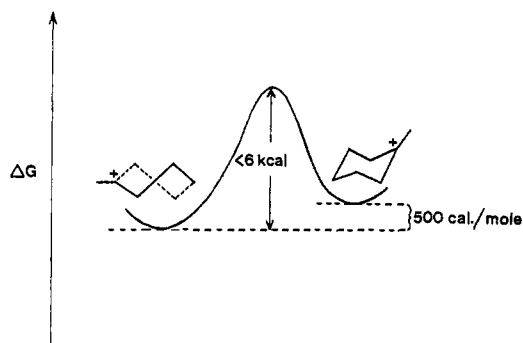


Figure 4. "Reaction coordinate" diagram illustrating the free-energy relationships between the chair, TB, and the transition state interconverting these, for the methylcyclohexyl cation **3a**.

0.1 kcal/mol ( $-105^\circ\text{C}$ ),  $\Delta H^\ddagger = 7.4 \pm 1$  kcal/mol,  $\Delta S^\ddagger = 0 \pm 6$  eu.

A clue to the probable conformation of **5** can be found in the fact that the two  $\beta$  carbons in the "frozen-out"  $^{13}\text{C}$  spectrum are very different. One resonates at 46.9 ppm, appropriate for (and added evidence for) a chair-type orientation in six-membered rings. The second  $\beta$  carbon is found at 29.7 ppm, much closer to the value estimated for TB six-membered rings. The chair-TB conformation **5b** fits these observations well.

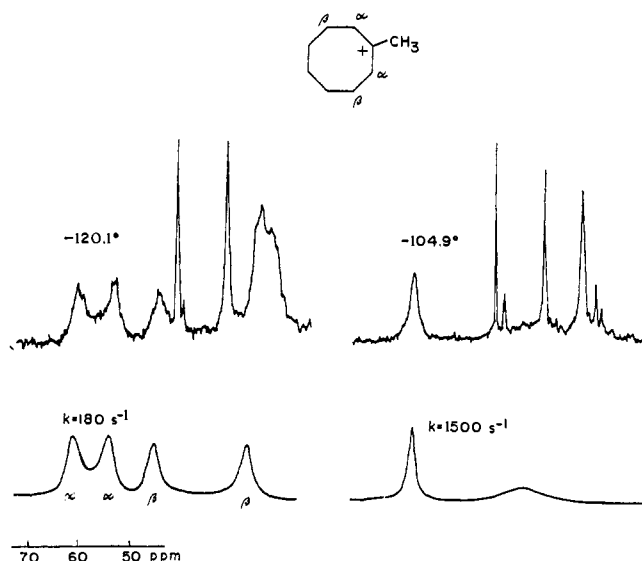
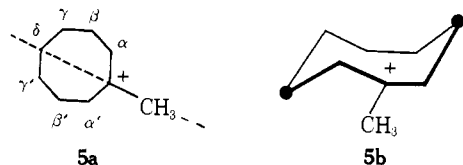
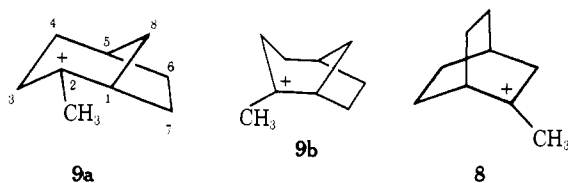


Figure 5. Upper: two representative  $^{13}\text{C}$  spectra (decoupled) of the 1-methylcyclooctyl cation **5**, showing the line broadening which occurs at low temperatures (several impurity peaks are also apparent). At even lower temperatures, all carbons in **5** again sharpen and are all resolved. Lower: computer-generated matching spectra and rate constants for the pseudorotational process in **5**.

Cyclooctanone has the same conformation,<sup>14</sup> although methylenecyclooctane apparently does not.<sup>14</sup>

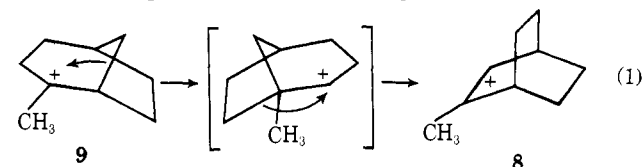
The conformational barrier observed in **5** ( $\Delta G^\ddagger = 7.2$  kcal/mol) can be compared to that found in cyclooctanone ( $\Delta G^\ddagger = 6.3$  kcal/mol).<sup>14</sup> It should be noted that there is another conformational barrier in cyclooctanone which interchanges the nonequivalent geminal  $\text{CH}_2$  hydrogens ( $\Delta G^\ddagger = 7.5$  kcal/mol).<sup>14</sup> However, attempts to observe this same barrier in **5** were unsuccessful since the proton spectrum (Table I) is very complex. Our main objective in this study is to determine ground-state conformations and we feel reasonably confident that this cation has the conformation **5b**.

**The 2-Bicyclo[3.2.1]octyl Case.** Olah and co-workers<sup>15</sup> have suggested that the 2-methyl-2-bicyclo[3.2.1]octyl cation **9** might have a boat structure **9b**. Unfortunately, the ion de-



scribed and published by these authors is instead the 2-methyl-2-bicyclo[2.2.2]octyl cation **8**, so that the boat structure deduction is not surprising. It is possible to prepare cation **9** if one adds the corresponding chloride to  $\text{SbF}_5\text{-SO}_2\text{ClF}$  at  $-135^\circ\text{C}$ . The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectral assignments are given in Table I. At  $-103^\circ\text{C}$ , ion **9** rearranges rapidly into cation **8**,  $k = 5 \times 10^{-4} \text{ s}^{-1}$ ,  $\Delta G^\ddagger = 12.3$  kcal/mol. Ion **8** is easily distinguished in the  $^{13}\text{C}$  NMR by the number and area of the peaks, indicating a plane of symmetry (see Table I for  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts). Conversions of the bicyclo[3.2.1] system into the bicyclo[2.2.2] system have been noted by Farnum and co-workers<sup>16</sup> in phenyl-substituted cations and have also been noted in solvolyses involving secondary cations.<sup>17</sup> This interconversion in tertiary ions occurs by way of

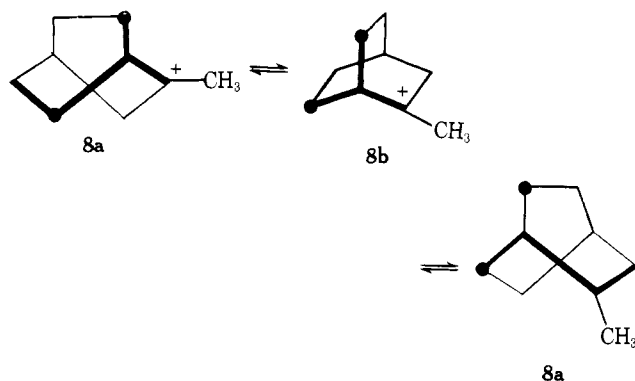
a double Wagner-Meerwein shift (eq 1). In the work of Far-



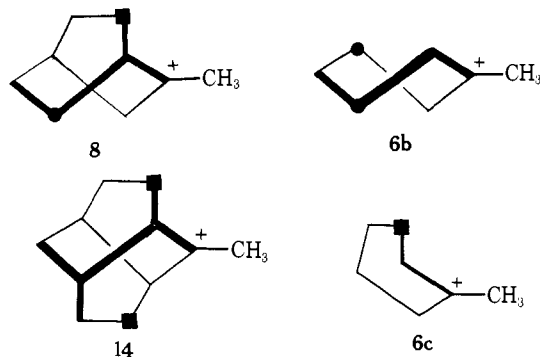
num, ion mixtures containing both ring systems were observed and the surprising observation here is the nearly complete conversion of **9** into **8**; at equilibrium, the concentration of **9** appears to be only about 5–10%. The greater stability of the [2.2.2] system and our cyclohexyl work directly contradict the "fact" statement and its rationalization made in a recent text:<sup>18</sup> "transposition from the bicyclo[2.2.2]octyl cation to the bicyclo[3.2.1]octyl cation represents an increase in thermodynamic stability because the change involves the conversion of a boat conformation of the cyclohexyl cation to a chair conformation".

The  $^{13}\text{C}$  and  $^1\text{H}$  spectra of the 2-methyl-2-bicyclo[3.2.1]octyl cation **9** show several points of similarity to the 2-methyl-2-norbornyl cation, an unusually high field  $\text{C}^+$  peak in the  $^{13}\text{C}$  NMR spectrum (Table I) and an unusually low field  $\text{C}_1$  and  $\text{H}_1$  peak. The conformation of the six-membered ring in **9** might be deduced from the  $^{13}\text{C}$  chemical shift position of the  $\beta$  carbons. Unfortunately, there is no convenient method for definitively assigning or distinguishing the  $\text{C}_4$ ,  $\text{C}_6$ ,  $\text{C}_7$ , and  $\text{C}_8$  carbons.

**The 2-Bicyclo[2.2.2]octyl Case.** Cation **8** should have a relatively rigid conformation; it can oscillate slightly on either side of the symmetrical boat conformation **8b** but this pseudorotational oscillation has undoubtedly a very small barrier. This cation therefore serves as a reasonable model for a cyclohexyl boat conformation of the **6d** type, distorted perhaps toward a di-TB conformation (**6b** and **6c**). It is of interest to examine the  $\beta$  carbon chemical shifts in this system. One of these three  $\beta$  carbons is a bridgehead position but the other two are  $\text{CH}_2$  carbons, which resonate at 29.7 ppm, a considerably lower value than that estimated for the chair cyclohexyl system (40–45 ppm). However, as a model for **6b**, this value should be lowered (as in the adamantyl case) because of the presence of nearby substituents.<sup>19</sup>



It might be thought that the best model for **6b** would be the 2-methyl-2-twistyl cation **14**. The relationship between this

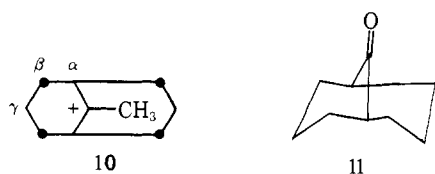


cation and the TB conformers **6b** and **6c** of the cyclohexyl system and the 2-methyl-2-bicyclo[2.2.2]octyl system **8** is shown above. Circles and squares depict  $\text{CH}_2$   $\beta$  carbons having the same orientation relative to the  $\text{C}^+$  center. From this, one sees that the  $\beta$   $\text{CH}_2$  carbons of **14** are actually typical of one of the carbons of TB isomer **6c**. Nevertheless, it would be useful to have a chemical shift estimate for the  $\beta$   $\text{CH}_2$  carbons in **14**.

We have been totally unsuccessful in attempts to prepare the observable 2-methyl-2-twistyl cation, starting from either the tertiary alcohol or chloro compounds, using preparation temperatures of between  $-130$  and  $-140$   $^\circ\text{C}$ . The only product is the 2-methyl-2-adamantyl cation, a result reported originally by Whitlock and Siefkin.<sup>20</sup> In all respects, this cation behaves as a very unstable species.<sup>21</sup>

**The 9-Bicyclo[3.3.1]nonyl Case.** The 9-methyl-9-bicyclo[3.3.1]nonyl cation **10** was originally prepared in this study on the assumption that this ion would serve as another model for a chair cyclohexyl cation. This expectation was reasonable since the 9-keto derivative has the dichair conformation **11**.<sup>22</sup>

The  $^{13}\text{C}$  NMR spectrum of ion **10** (Figure 6 and Table I) could be obtained with some difficulty and proved to be more interesting than expected. At the normal measuring temperature of  $-130$   $^\circ\text{C}$ , the four-carbon  $\beta$  peak was quite broad



(Figure 6) and there was an indication of possible broadening in the  $\gamma$  carbon peak. At higher temperatures, the peak sharpened up, although the ion rearranges before the peak becomes completely sharp. Numerous attempts to obtain "frozen-out" spectra at temperatures as low as  $-150$   $^\circ\text{C}$  were unsuccessful; the peak merely continues to slowly broaden.

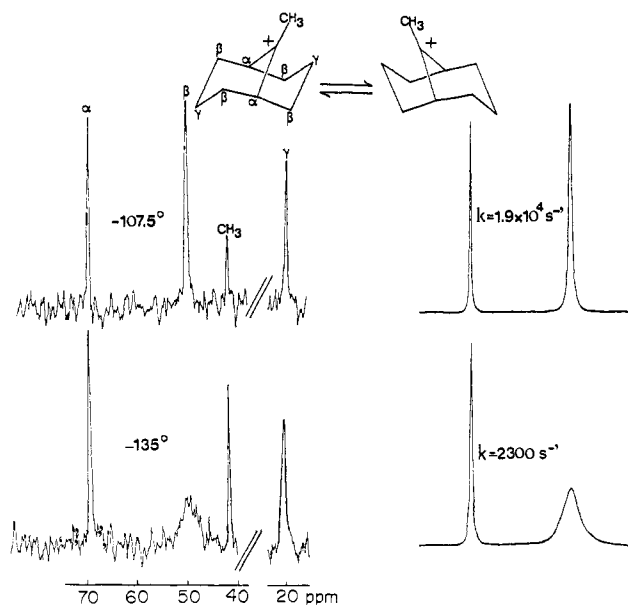
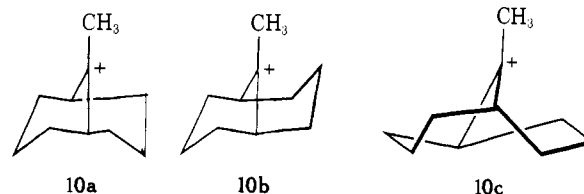


Figure 6. Left: two representative  $^{13}\text{C}$  spectra (decoupled) of the 9-methyl-9-bicyclo[3.3.1]nonyl cation **10**, showing the line broadening which occurs at low temperatures. The higher temperature spectrum represents only 200 scans. Right: computer-generated matching spectra and rate constants for the chair-boat  $\rightleftharpoons$  boat-chair conformational averaging in **10**.

These line-broadening observations rule out the symmetrical dichair conformation **10a** for the cation.<sup>23</sup> The two remaining conformations are a rigid chair-boat **10b** and a di-TB **10c**. In



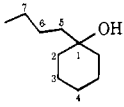
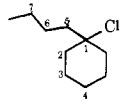
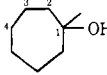
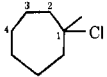
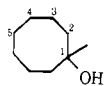
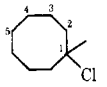
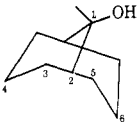
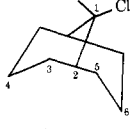
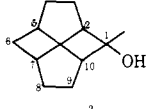
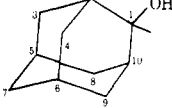
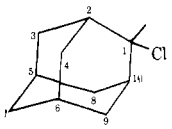


the latter conformation, the molecule is flexible and can oscillate between two equivalent TB forms of the **6c** type via a diboat (**6e**). This averaging motion is pseudorotational and is expected to have a very low barrier. Furthermore, both  $\gamma$  carbons of **10c** are always equivalent in this twisting motion, and hence should not be broadened. The NMR line broadening in **10** therefore fits a chair-boat **10b**  $\rightleftharpoons$  boat-chair **10b'** equilibrium, probably proceeding by way of either the dichair **10a** or diboat **10c** as an intermediate. Assuming that the chair  $\beta$  carbons in **10b** have approximately the same chemical shift as those in the 2-methyl-2-adamantyl cation,<sup>24</sup> one can calculate the following activation parameters, using the usual matching with computer-calculated curves (see Figure 6) and an Arrhenius plot,  $\Delta G^\ddagger = 5.6 \pm 0.2$  kcal/mol ( $-131.5$   $^\circ\text{C}$ ),  $\Delta H^\ddagger = 4 \pm 0.5$  kcal/mol,  $\Delta S^\ddagger = -7$  to  $-15$  eu.

Cation **10** is one of the more unstable cations we have encountered. Above  $-115$   $^\circ\text{C}$ , it rearranges rapidly and cleanly into an as yet unidentified product ion. This product ion has ten separate carbon atoms and hence no symmetry. It also has the same component of C, CH,  $\text{CH}_2$ , and  $\text{CH}_3$  carbons as **10** (Table I). Furthermore the  $^1\text{H}$  NMR spectrum shows a high-field methyl doublet, indicating that the cation must be a bridgehead species. Two possible structures are **12** and **13**, although we find it difficult to rationalize why either would be



Table II.  $^{13}\text{C}$  Chemical Shifts of the Cation Precursors<sup>a</sup>

	C-1	C-2	C-3	C-4	C-5	C-6	Me	Solvent	Remarks
	69.7	39.4	22.6	25.5			29.4	$\text{CDCl}_3$	<i>b</i>
	71.6	41.3	22.4	25.4			34.8	$\text{CFCl}_3$	
	71.7	37.7	22.6		42.4		14.4	$\text{CFCl}_3$	<i>c</i>
	74.6	39.8	22.3		45.8		14.2	$\text{CDCl}_3$	<i>d</i>
	73.5	43.2	22.9	30.3			31.3	$\text{CFCl}_3$	
	74.4	45.4	23.2	29.7			34.3	$\text{CFCl}_3$	
	73.6	38.3	22.9	28.5	27.1		30.1	$\text{CDCl}_3$	
	75.0	40.2	23.8	28.3	24.7		32.5	$\text{CFCl}_3$	
	71.6	39.0	29.9 or 27.4	21.2	27.4 or 29.9	21.2	27.8	$\text{CFCl}_3$	
	78.6	40.3	29.6 or 28.7	20.8 or 20.4	28.7 or 29.6	20.4 or 20.8	30.7	$\text{CFCl}_3$	
	75.1	41.0 also C-10					31.2	$\text{CFCl}_3$	<i>e</i>
	73.7						32.8	$\text{CDCl}_3$	<i>f</i>
	79.8							$\text{CFCl}_3$	<i>g</i>

<sup>a</sup> Multiplicities have been confirmed, where possible, by off-resonance experiments,  $^{13}\text{C}$  shifts in  $\delta$  ppm, relative to  $\text{Me}_2\text{Si}$ . The numbering system is *not* systematic, but is meant to facilitate comparisons of similarly oriented carbons. The numbering in the text of the paper is systematic. The 2-methyl-2-bicyclo[3.2.1]octanol and chloride are mixtures of the exo and endo isomers and the spectra are complex. These are available on request. <sup>b</sup> J. D. Roberts, I. J. Weigert, J. I. Kroschwitz, and A. J. Reich, *J. Am. Chem. Soc.*, **92**, 1338 (1970); Y. Sende, J. Ishiyama, and S. Imazumi, *Tetrahedron*, **31**, 1601 (1975). <sup>c</sup> For C-4, C-6, C-7: 26.1, 25.4, 23.6. <sup>d</sup> For C-4, C-6, C-7: 26.0, 25.8, 23.2. <sup>e</sup> For C-3, C-4, C-5, C-6, C-7, C-8, C-9: 32.3, 31.9, 31.2 (double), 28.6, 27.6, 23.2, 23.0. <sup>f</sup> For C-2, C-3, C-4, C-5, C-6, C-7, C-8, C-9, C-10: 38.9 (double), 38.2, 35.0 (double), 32.8, 27.4, 27.3, 26.9. <sup>g</sup> For C-2, C-3, C-4, C-5, C-6, C-7, C-8, C-9, C-10, Me: 41.0 (double?), 39.0, 34.9 (double), 34.3 (double), 30.5, 27.3, 27.3.

more stable than **10**. Both can be derived from **10** by reasonable mechanisms. This product cation is itself unstable and, by  $-70^\circ\text{C}$ , one has a very complex  $^{13}\text{C}$  NMR spectrum, indicating a mixture of ions.<sup>25</sup>

The bicyclononyl cation studies conclude our experimental results. Taken as a whole, the results emphasize that chair cyclohexyl cations<sup>26</sup> are not as stable as in neutral analogues

and that  $\beta$ -carbon chemical shifts in carbocations have the potential to become very useful in conformational studies.

### Experimental Section

The ions were prepared from either the tertiary alcohol or the corresponding chloride. The alcohol (150–200 mg) was dissolved in  $\text{CFCl}_3$  (0.4 mL) and added, with stirring, slowly to a solution of 1:1

SbF<sub>5</sub>-FSO<sub>3</sub>H (0.8 mL) in SO<sub>2</sub>ClF (1.5 mL) cooled to -115 °C in the NMR tube. For ions where a lower temperature was desired, the chloride (150–200 mg) was dissolved in 0.4 mL of CFCl<sub>3</sub>. This solution was added slowly, with stirring, to a solution of SbF<sub>5</sub> (0.7 mL) in SO<sub>2</sub>ClF-SO<sub>2</sub>F<sub>2</sub> (1.5 mL/0.5–1 mL) at a temperature of -140 °C (methylcyclopentane-liquid N<sub>2</sub> slush bath). For higher temperature measurements, the ions were prepared by mixing a solution of the alcohol (150–200 mg) in 0.4 mL of CFCl<sub>3</sub> with 2.5 mL of 1:1 SbF<sub>5</sub>-FSO<sub>3</sub>H, at -20 °C.

**NMR Spectroscopy.** <sup>13</sup>C NMR spectra were recorded on a Bruker WH-90 spectrometer equipped with a Nicolet B-NC12 computer. The temperature was measured by inserting a tube filled with 4 mL of silicon oil and containing a thermocouple into the probe. The reported values were obtained by averaging the reading before and after the accumulation of data. Spectra recorded during temperature variations larger than 1 °C were discarded. The field frequency stabilization of the spectrometer was obtained by locking on the <sup>19</sup>F NMR signal of SO<sub>2</sub>ClF, CFCl<sub>3</sub>, or FSO<sub>3</sub>H, or, in those cases involving CDCl<sub>3</sub> solvent, on the <sup>2</sup>D signal. All chemical shifts reported are referenced to external Me<sub>4</sub>Si. Below -100 °C (Me<sub>4</sub>Si freezes) this was accomplished by referencing to CFCl<sub>3</sub> and converting these to a Me<sub>4</sub>Si reference. For the cyclohexyl cations **3a** and **3b**, an internal referencing was used below -100 °C, i.e., the chemical shift vs. *T* line for the α, Me, and C<sup>+</sup> carbons was assumed to continue in a linear way. This method appears to give internally consistent results. Typically 4000 transients were necessary to obtain satisfactory spectra, although for highly unstable species, this was reduced to several hundred. For the chemical shift data for the methylcyclohexyl and *n*-butylcyclohexyl cations, the sweep width was reduced to 4400 Hz; otherwise 8000-Hz sweep widths were used, using 8K data points. The flip angle was 40° (8 μs) and no delay time was used. The <sup>1</sup>H NMR spectra were obtained using the same solvents but with much reduced concentrations. These spectra were referenced to external Me<sub>4</sub>Si.

**Alcohols.** 1-Methylcyclohexanol,<sup>27</sup> [1-<sup>13</sup>C]methylcyclohexanol, 1-methylcycloheptanol,<sup>28</sup> 1-methylcyclooctanol,<sup>29</sup> 1-*n*-butylcyclohexanol,<sup>30</sup> *cis*- and *trans*-2-methyl-2-bicyclo[3.2.1]octanol,<sup>17b</sup> 9-methyl-9-bicyclo[3.3.1]nonanol,<sup>31</sup> and 2-methyl-2-adamantanol<sup>32</sup> were obtained by Grignard reactions on the commercially available ketones. 2-Methyl-2-twistanol<sup>20</sup> was synthesized by the procedure of Whitlock and Siefkin, using methylolithium.<sup>33</sup> The alcohols were checked for purity using <sup>13</sup>C NMR spectroscopy. The data are collected in Table II.

**Chlorides.** The chlorides were obtained by stirring a solution of the corresponding alcohol in CFCl<sub>3</sub> with concentrated hydrochloric acid at 0 °C for several hours. The two layers were then separated and the organic phase was dried over potassium carbonate. Some of the solvent was blown off under a nitrogen stream, maintaining the solution at 0 °C. The resulting chloride solution was analyzed by <sup>13</sup>C NMR spectroscopy, and, if satisfactory, was used in the ion preparation without further purification. The <sup>13</sup>C NMR data are collected together in Table II.

**The Chlorides from 2-Methyl-2-twistanol.** Application of the above procedure to 2-methyl-2-twistanol gave a very complex mixture (by <sup>13</sup>C NMR spectroscopy). The main feature of this mixture was the presence of major peaks at δ 50.8, 50.6, 48.4, and 48.1 ppm and the absence of peaks at ca. δ 70–80 ppm. The former peaks are characteristic of secondary chlorides while the latter region is characteristic for tertiary chlorides (see Table II).

**Boltzmann Distribution Calculation.** The enthalpy-entropy parameters from the temperature-dependent shifts of the alkylcyclohexyl cations were determined by utilizing the Levenberg-Marquardt algorithm, which allows the minimization of a function in several variables, in this case the Boltzmann equation.<sup>8</sup> The program was written in FORTRAN and was run on a Control Data CYBER 170 computer system. In our equation, there are four variables, ν<sub>A</sub>, ν<sub>B</sub>, Δ*H*, and Δ*S*, but the minimization routine does not work in most cases when one allows all four variables to be completely free; the experimental data are essentially reduced to a very small region of the plot because very large positive and negative values are found for ν<sub>A</sub> and ν<sub>B</sub> (chemically impossible values). We therefore fixed (but varied) ν<sub>A</sub> and ν<sub>B</sub> while allowing freedom for Δ*H* and Δ*S*. In some cases, local minima were obtained for chemically reasonable values of ν<sub>A</sub> and ν<sub>B</sub>.

**Line-Broadening Calculations.** The methylcyclooctyl and methylbicyclo[3.3.1]nonyl cation line-broadening results were analyzed by calculating the theoretical line shapes (modified Bloch equation) for

exchanging systems (using a computer and plotter). The off-diagonal matrix elements in the kinetic matrix of the methylbicyclo[3.3.1]nonyl cation were 1/2, since a symmetrical intermediate is expected.

**Use of <sup>13</sup>C-Enriched Material.** At about -40 °C, the methylcyclohexyl cation **3a** equilibrates with the 1,2-dimethyl- and 1,3-dimethylcyclohexyl cations,<sup>4a</sup> with **3a** a slightly minor component. The mechanism of this interconversion is such that a <sup>13</sup>C-methyl label in **3a** will become distributed throughout **3a** (as well as in the cyclopentyl cations, of course). The resulting <sup>13</sup>C concentration at each position in **3a** will be about 14%, and the effective overall intensity will be about 4% when the cyclopentyl isomers are taken into consideration. This increased S/N is very beneficial for obtaining the higher temperature results. The upper limit for obtaining temperature data on the β carbons in **3a** is reached at ca. 10 °C, when a line-broadening process, previously noted by Saunders,<sup>34</sup> starts.

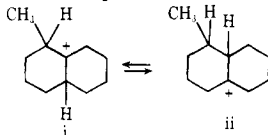
**Acknowledgments.** The authors thank the National Research Council of Canada for generous financial support.

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- At first sight, it appears unusual that the chair form of **3** (**6a**) should have a higher entropy than the TB form **6b**. In cyclohexane itself, the pseudo-rotational TB forms are significantly higher in entropy.<sup>1</sup> In the cations, however, the chair has lost all multiple rotational axes, while the TB isomer **6b** still retains a twofold axis, countered however by an entropy of mixing for *R* and *S* enantiomers. Furthermore, if a single TB isomer were significantly more stable than the other TB and boat forms, then much of the fluxional entropy will be lost. A combination of both effects seems to us to rationalize the entropy changes.
- One would suspect some conformational equilibrium from the proton results but one would be hesitant about describing the conformers involved because neighboring anisotropy effects are so much more dominant in proton spectra, i.e., model system chemical shifts would be more difficult to "correct" or "interpret".
- This estimate is based on line-broadening calculations, assuming the conformer populations derived in this work. The value is actually conservatively high and would still apply even if the equilibrium constant were considerably larger or smaller than the one used.
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- The line-broadening change with temperature is much smaller than we are used to (from numerous other cases) and we were concerned that we might

be seeing either a counterion effect (moving slowly from one side of the molecule to the other) or some more selective and large relaxation effect. However, we have studied the related 2-methyl-2-adamantyl cation **7** at temperatures down to  $-144\text{ }^\circ\text{C}$  and have noted no line broadening analogous to that observed for **10**. We therefore feel that we are seeing a genuine conformational change. This implies that  $\Delta H^\ddagger$  is small, and for this to occur,  $\Delta S^\ddagger$  must be reasonably negative. In considering the conformational process involved, i.e., symmetrical intermediate, this seems reasonable. The Arrhenius plot, although subject to large errors, is consistent with this.

- (24) The "averaged"  $\beta$  peak in **10b** is found at 48.9 ppm. A 10-ppm separation for the "frozen-out" peaks was used in the simulated spectra since this gives the higher field peak a value very close to that in **7**.  
 (25) Peaks ( $^{13}\text{C}$ ) appear in the region characteristic of equilibrating cations.



- The most probable structures are based on the [4.4.0] skeleton, e.g., i and ii. From solvolysis results on the secondary [3.3.1] system, the [4.4.0] skeleton is readily formed: C. S. Foote and R. B. Woodward, *Tetrahedron*, **20**, 687 (1964). It is, in fact, strange that the [4.4.0] skeleton does not seem to be the first-formed rearrangement ion from **10**.  
 (26) It should be possible to determine the effect of substituents on the chair-TB equilibrium in **3**, as long as these substituents are not attacked or protonated by the acid solvent, i.e., alkyl groups. However, the presence of the substituents will change the reference  $\beta$  carbon chemical shifts and require some analysis. It should also be possible to study cyclohexyl cations with other substituents on the cationic center, i.e., phenyl, halogen, OR, etc., but these will probably also require different reference chemical shifts.  
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 (33) We thank Mr. Kim Wagstaff for the synthesis of this compound.  
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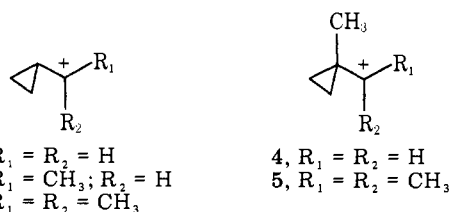
## On the Structure of Cyclopropylcarbinyl and Cyclobutyl Cations. 8,9-Dehydro-2-adamantyl and 2,5-Dehydro-4-protoadamantyl Cations<sup>1,2</sup>

George A. Olah,<sup>3,4</sup> Gao Liang,<sup>4</sup> Kevin A. Babiak,<sup>5</sup> Thomas M. Ford,<sup>5</sup> David L. Goff,<sup>5</sup> Thomas K. Morgan, Jr.,<sup>5</sup> and Roger K. Murray, Jr.<sup>5,6</sup>

Contribution from the Institute of Hydrocarbon Chemistry, Department of Chemistry, University of Southern California, Los Angeles, California 90007, and the Departments of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106, and University of Delaware, Newark, Delaware 19711. Received August 8, 1977

**Abstract:** The parent 8,9-dehydro-2-adamantyl cation (**12**) has been prepared under stable ion conditions from a variety of precursors. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **12** indicate that it is a carbenium ion that is undergoing a threefold degenerate cyclopropylcarbinyl-cyclopropylcarbinyl rearrangement which is fast on the NMR time scale at  $-120\text{ }^\circ\text{C}$ . Warming **12** to  $-78\text{ }^\circ\text{C}$  leads irreversibly to the 2-tricyclo[4.4.0.0<sup>5,9</sup>]dec-3-enyl cation. A series of 2-substituted 8,9-dehydro-2-adamantyl cations has been prepared under stable ion conditions at  $-78\text{ }^\circ\text{C}$ . All of these ions have been shown by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy to be static carbocations with varying degrees of charge delocalization into the cyclopropane ring. In striking contrast, three precursors which potentially could have afforded the 1-methyl-8,9-dehydro-2-adamantyl cation were shown by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy to give the 4-methyl-2,5-dehydro-4-protoadamantyl cation (**32**) under stable ion conditions. Carbocation **32** also undergoes a threefold degenerate rearrangement which is fast on the NMR time scale at  $-120\text{ }^\circ\text{C}$ . By  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy it was determined that under stable ion conditions the 1,2-dimethyl-8,9-dehydro-2-adamantyl cation is a static carbenium ion from  $-95$  to  $-10\text{ }^\circ\text{C}$ . Mechanisms are proposed to account for the degenerate rearrangements of ions **12** and **32** and for the formation of the other observed ions.

The rapid interconversion of cyclopropylcarbinyl, cyclobutyl, and homoallyl derivatives in solvolytic systems has attracted considerable attention.<sup>7</sup> Recently, we have studied by NMR spectroscopy a series of cyclopropylcarbinyl cations under stable ion conditions.<sup>2,8-12</sup> We have concluded from these observations that whereas the primary cyclopropylcarbinyl cation **1** involves degenerate equilibration of rapidly



equilibrating  $\sigma$ -delocalized nonclassical ions in which there is little or no contribution to the NMR parameters by the cyclobutyl cation, the corresponding secondary (**2**) and tertiary (**3**) ions are static classical carbocations with varying degrees of charge delocalization into the cyclopropane ring.<sup>8</sup> Intro-

duction of a methyl substituent at C-1 of the cyclopropyl moiety (ion **4**) does not substantially alter the nature of these ions<sup>12,13</sup>. In contrast, tertiary ion **5** is a static classical carbocation which adopts the bisected geometry characteristic of cyclopropylcarbinyl cations.<sup>12</sup> These studies have now been extended to cyclopropylcarbinyl cations with rigid carbon skeletons.<sup>9-11</sup>

In 1967 Baldwin and Foglesong first reported on the "stability and symmetry" of the 8,9-dehydro-2-adamantyl cation.<sup>14</sup> They observed that solvolysis of 8,9-dehydro-2-adamantyl 3,5-dinitrobenzoate (**6**) occurs with the marked rate acceleration characteristic of cyclopropylcarbinyl systems<sup>7</sup> and that the original C-2, C-8, and C-9 skeletal positions of **6** achieve nearly complete equivalence during solvolysis.<sup>14</sup> In view of these results, Baldwin and Foglesong suggested the bridged nonclassical representation **7** for the charge-delocalized 8,9-dehydro-2-adamantyl cation and proposed that scrambling of the skeletal positions occurred via migration of the C-8 to C-9 bond to give **9**, etc. The ion linking degenerate cyclopropylcarbinyl cations **7** and **9** was represented as bicyclobutonium ion **8**.<sup>14</sup> We now wish to report the direct observation by NMR