## The 9-Barbaralyl Cation. Isotopic Perturbation by Eight Deuteriums of a Totally Degenerate $^{13}$C-Labeled C$_9$H$_9^+$ Carbonium Ion

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We report experimental results which resolve the current controversy[1] concerning the structure of the parent barbaralyl cation. Studies by $^{13}$C NMR spectroscopy of this totally degenerate ion perturbed by eight deuteriums now show that it has the 9-barbaralyl (tricyclo[3.3.1.0$^{2,8}$]nona-3,6-dien-9-yl) cationic structure.

The barbaralyl cations have previously been studied solvolytically[2] and theoretically[1c-e] and by NMR spectroscopy in superacid.[1b,f,g,3] These investigations have revealed both partially and totally degenerate rearrangements of these elusive ions, and a number of novel mechanisms and structures have been proposed. Some controversy still remains, however, regarding the parent barbaralyl cation. Structures **1**, **2**, and **3** have been suggested for this C$_9$H$_9^+$ ion, but conclusive evidence has not previously been obtained.

We were recently able to exclude ion **1** as a possible structure for the barbaralyl cation.[1g] The $^{13}$C NMR spectrum of the ion, generated from the precursor **4** in superacid at $-150$ °C, showed two broad signals at 101 and 152 ppm, respectively, with an area ratio of 6:3 (Figure 1b). This result, together with the symmetry of **1**, shows that it is not a possible structure for the totally degenerate ion. The observed ion could be either $^{13}$C-labeled **2** undergoing fast degenerate rearrangements with a barrier <4 kcal mol$^{-1}$ according to Scheme I, or the theoretically interesting **3** which has $D_{3h}$ symmetry.

Inspired by the elegant work of Saunders and co-workers in discriminating between classical and nonclassical carbocations by isotopic perturbation,[4] we have designed the ion precursor **5** with the aim of discriminating between ions **2** and **3**.

The alcohol **5**, which contains eight CD groups and one $^{13}$CH group, has been synthesized by the procedure used to prepare **4**,[1g,2d] but the starting material, cycloheptatriene, was exchanged for its perdeuterated analogue,[5] and the final reduction of the ketone was made with LiAlD$_4$.

About 8 mg of **5**, containing ca. 90 atom % $^{13}$C in the 3 position and about 97 atom % D in each of the deuterium-labeled positions, was dissolved in ca. 0.1 mL of CHCl$_2$F at $-15$ °C. It was then transferred to a 5-mm NMR tube and reacted with a mixture of FSO$_3$H, SO$_2$ClF, SO$_2$F$_2$, and CHCl$_2$F (2:7:7:3, v/v/v/v) at about $-140$ °C by using an ion-generation apparatus. The latter has previously been described in detail.[6] The sealed NMR tube, which now contained a homogeneous pale yellow solution, was then studied by $^{13}$C NMR spectroscopy at temperatures ranging from $-133$ to $-151$ °C.
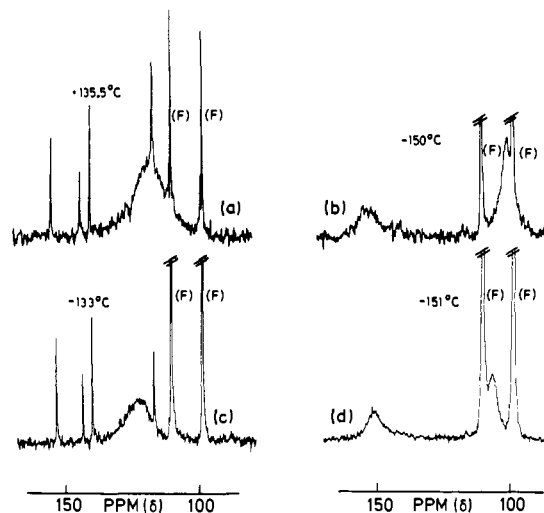


**Figure 1.** (a) and (b) show $^{13}$C NMR spectra for the $^{13}$C-labeled barbaralyl cation obtained at $-135.5$ and $-150$ °C, respectively, by using a double-pulse sequence to suppress the solvent signal. (c) and (d) show the spectra of the octadeuterated $^{13}$C-labeled barbaralyl cation at $-133$ and $-151$ °C, respectively, recorded by using single pulses. The peaks marked F are due to the solvent and internal standard reference CHCl$_2$F ($\delta_c$ 110.3, 98.6). The other sharp signals originate from labeled 1,4-bis(homotropylium) ions (**6**).
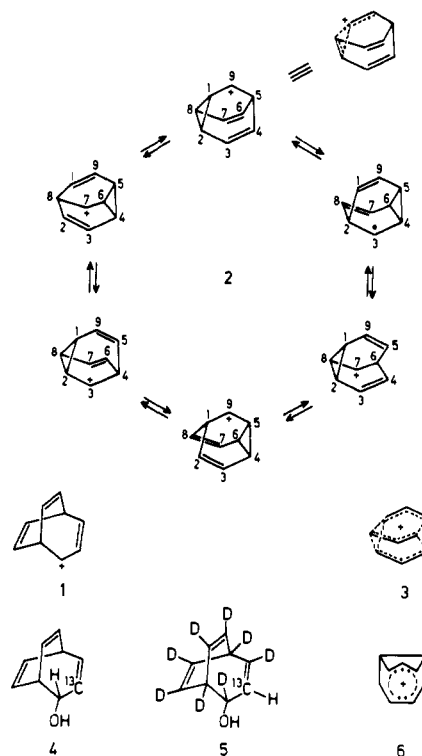
**Scheme I**



Figure 1, c and d, shows the spectra of the ion at $-133$ and $-151$ °C, respectively. All sharp peaks in the figure are due to the $^{13}$C-labeled bis(homotropylium) ion **6**, except those marked F which originate from CHCl$_2$F. In Figure 1c, the broad singlet in the spectrum from the octadeuterated $^{13}$C-labeled barbaralyl cation resembles that from the nondeuterated cation[1g] in Figure 1a. This indicates fast scrambling of all nine carbon atoms. The singlet in Figure 1c has a width $\delta\nu$ of ca. 240 Hz and a chemical shift of 123 ppm, i.e., this singlet has been shifted by about 4.5 ppm downfield relative to that in Figure 1a. The eight deuteriums have clearly perturbed the fast ionic equilibrium which is causing the total degeneracy of the $^{13}$C-labeled barbaralyl cation.

The signal broadened further on lowering the temperature, becoming unsymmetrical and splitting into two new signals at 107

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and 151 ppm, respectively (Figure 1d). The studies were started at ca. −151 °C and the temperature then increased and later decreased. The sharp peaks due to **6** are thus missing from Figure 1d. Relative to the signals in Figure 1b, the upfield signal in Figure 1d is shifted downfield by 6 ppm and the downfield signal shifted upfield by about 1 ppm. This 6-ppm shift motivates our exclusion of ion **3** as the major ion responsible for the spectra. If ion **3** were the major ion showing the total degeneracy, we would expect the $^{13}$CH group to show some preference for one of the two types of positions in this structure because of the difference in zero-point energy between the two types of CH bonds, i.e., the equilibrium constant for the equilibrium between **3a** and **3b** is different from 1. Such a preference would cause a chemical shift in the averaged



3a                                    3b
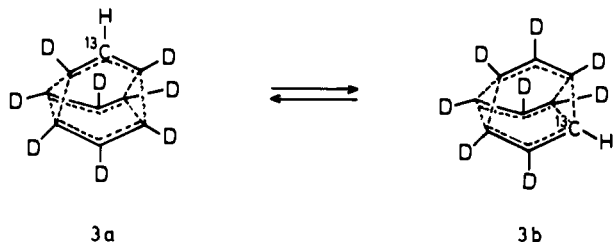
signal (Figure 1c), as was indeed observed (of 4.5 ppm). No shifts are expected, however, in the frozen-out signals (Figure 1d) relative to those of Figure 1b for ion **3**, since the deuteriums are predicted to show negligible influence on the chemical shifts of the $^{13}$C nuclei in the $^{13}$CH groups.[7] However, the area ratio of the two signals might deviate from 6:3 due mainly to the difference in zero-point energy of the two types of $^{13}$CH bonds.

If ion **2**, on the other hand, is the ion we observe, then shifts in the signals of Figure 1d relative to those of Figure 1b are expected, since each of the peaks originates from an averaging of magnetically nonequivalent carbon atoms in $^{13}$CH groups, whose carbon–hydrogen bonds are likely to have different zero-point energies. The zero-point energy difference between CH bonds involving unsaturated carbons (including C$_9$) and saturated carbons favors in an equilibrium structure like **2a** (in which $^{13}$CH is part of any of the double bonds or is a $^{13}$C$_9$H group) over **2b** (or structures in which the $^{13}$CH occupies any of the other saturated positions). The upfield signal comes from carbons



2a                                    2b
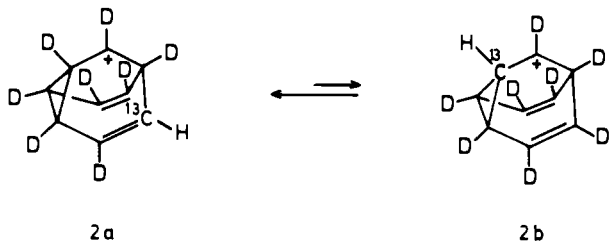
1,2,8,4–6, which exchange rapidly with one another. The downfield signal originates from the group of carbons 3,7, and 9. Since the CD groups probably prefer to occupy certain of the positions within each of the C groups, the $^{13}$CH group is preferentially found at the remaining positions. Shifts will result in the frozen-out signals. The observed behavior of the ion is thus consistent with ion **2** and not **3**.

The average chemical shifts estimated for the barbaralyl cation using the 9-methyl-9-barbaralyl cation (**7**) and the shift differences of the carbon atoms in the 3-methyl-3-nortricyclyl and 3-nortricyclyl cations are 106 and 153 ppm, respectively.[18] The close agreement between these values and those observed for the barbaralyl cation strongly suggest that this ion, like ion **7**, contains a cyclopropylcarbinyl cationic structural element (Scheme I).

A change from 6:3 to 5:3 is observed in the area ratio in Figure 1b upon substitution with the eight deuteriums (Figure 1d). The latter ratio was evaluated by using the chemical shift of the averaged signal in Figure 1c and those of Figure 1d. We therefore

conclude that deuterium substitution increases the preference of the $^{13}$CH group for the 3,7, and 9 positions at the expense of the remaining positions, i.e., the CD groups prefer to occupy non-olefinic positions. A similar behavior has previously been found with deuterium-labeled barbaralone.[8] Furthermore, the small upfield shift (∼1 ppm) indicates a slight preference of the $^{13}$CH group for the olefinic positions (3 and 7) over the 9 position. Amongst the rapidly exchanging carbons 1,2,4–6, and 8 the $^{13}$CH is also concluded to prefer an olefinic position over any of the other types of positions, since a 6-ppm downfield shift is obtained upon labeling with deuterium. The above conclusions are based on the chemical shifts for **2** estimated by using the shifts for the reference ion **7**. As expected, the deuterium isotope effects on the rearrangement rates are found to be small.

That the barbaralyl cation has 9-barbaralyl structure clarifies at least some aspects of the rearrangement mechanisms of **2**. Recent group-theoretical studies of ions **1**, **2**, and **3** and their rearrangements have shown that, if ion **2** is the most stable of these ions, **3** can be neither a transition state nor an intermediate in these rearrangements.[1e] Of the proposed mechanisms we are left with the series of divinylcyclopropylcarbinyldivinylcyclopropyl-carbinyl cationic rearrangements shown in Scheme I. Ion **1** is likely to be a transition state or an intermediate in the totally degenerate rearrangement of **2**. The magnitude of the energy difference between ion **3** and ion **2** remains uncertain from the results obtained so far.

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## On the Question of Ground-State Perpendicular Olefins. Rehybridization of Twisted Olefins[1]

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Investigations centered around the synthesis and reactions of bridgehead olefins[2] have inevitably generated interest in the structure of "anti-Bredt" double bonds. The structural options may be divided into three categories: (a) both trigonal carbons remain sp$^2$ hybridized without distortion of the σ framework, leaving each trigonal carbon and the three attached carbons in a plane and causing greatly diminished π overlap (none at all for **1**); (b) both trigonal carbons retain (partial or complete) ordinary



1              2              3              4
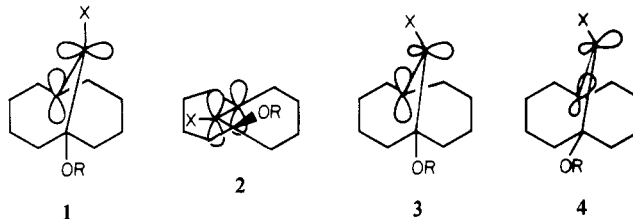
π overlap, necessitating distortion of the σ backbone (**2** shows extreme "bridge leaning" to give full π overlap); (c) the hybridization at the trigonal carbon(s) changes toward sp$^3$ with no (**3**, rehybridization at one carbon) or relatively little (**4**, rehybridization

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