^{13}C Labelled Barbaralyl† Cation: a Non-classical, Totally Degenerate Carbocation

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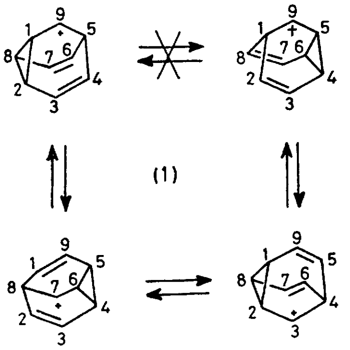
Summary The pulse Fourier transform ^{13}C n.m.r. spectra at −135·5 and −150 °C of the ^{13}C-labelled barbaralyl cation in superacid show that it has a rapidly rearranging 9-barbaralyl cation structure and/or one with D_{3h} symmetry.

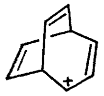
Several studies of barbaralyl cations under solvolytic conditions as well as in superacid have revealed partial and total degenerate rearrangements of these elusive ions, and a number of novel mechanisms and structures have been proposed. However there is controversy about the structure and rearrangements of the parent barbaralyl† cation. Structures (**1**), (**2**), and (**3**) have been suggested for this $C_9H_9^+$ ion but conclusive evidence has not been obtained.[1]



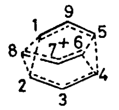
(1)

Scheme

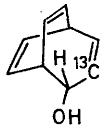
The ^{1}H n.m.r. spectrum at −125 °C of the parent ion in superacid showed a sharp singlet indicating total degeneracy of the ion. The rearrangement barrier was estimated to be < 6 kcal mol^{-1}.[1a,b]‡ The ^{13}C n.m.r. spectrum at −135 °C, on the other hand, showed a broad band, almost concealed by noise. After longer observation times, a large fraction of the ion had reacted to the 1,4-bishomotropylium ion (**5**).[1f]



(2)



(3)



(4)

(5)

In order to settle some of the mechanistic and structural questions, the ^{13}C-labelled parent barbaralyl cation has been synthesized in superacid and studied by ^{13}C n.m.r. spectroscopy. The ion precursor, [3-^{13}C]bicyclo[3.2.2]nona-3,6,8-trien-2-ol (**4**), was prepared by minor modifications of the procedure used for the non-labelled compound using [2-^{13}C]malonic acid containing 90% ^{13}C.[2] *Ca.* 7·5 mg of (**4**) dissolved in 120 mg of CD_2Cl_2 was added to 0·4 ml of FSO_3H–SO_2ClF–SO_2F_2 (1 : 5 : 2, v/v/v) at −135 °C in a 5 mm n.m.r.-tube and the solutions were rapidly mixed in an apparatus previously described.[3] However, to obtain reasonably well resolved spectra at the very low temperatures required, the alcohol (**4**) was instead dissolved in 140 mg of $CHCl_2F$ and added to a solution of FSO_3H–SO_2ClF–SO_2F_2–$CHCl_2F$ (2 : 7 : 7 : 1, v/v/v/v).

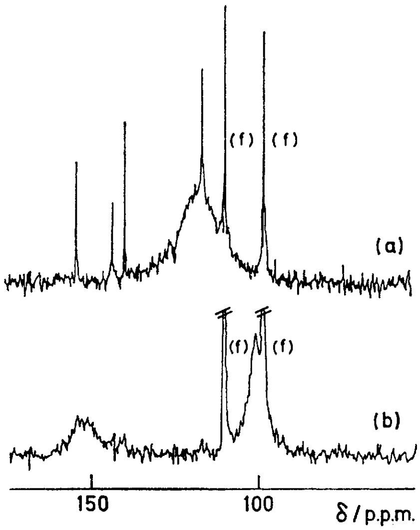


Figure. ^{13}C N.m.r. spectra of the ^{13}C labelled barbaralyl cation. The two peaks (f) (δ 98·6 and 110·3 p.p.m.) are due to the internal reference $CHCl_2F$. (a) Spectrum at −135·5 °C. The barbaralyl cation appears as a broad signal. The other sharp signals are due to the 1,4-bishomotropylium ion (**5**). (b) Spectrum at −150 °C.

The Figure shows the ^{13}C n.m.r. spectra of the latter ion solution at −135·5 and −150 °C. All sharp peaks in Figure (a) are due to the ion (**5**) except the two marked (f) which originate from $CHCl_2F$. The barbaralyl cation appears as the broad band (δν *ca.* 324 Hz) at 118·5 p.p.m., indicating fast scrambling of all nine carbon atoms. The rate constant and corresponding barrier obtained at −135·5 °C are 4900 s^{-1} and 5·5 kcal mol^{-1}, respectively. Upon lowering the temperature, the signal further broadened, became unsymmetrical, and split into two new

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† Barbaralane = tricyclo[3.3.1.0^{2,8}]nona-3,6-diene.

‡ 1 cal = 4·184 J.

signals at 101 and 152 p.p.m. with an area ratio of 2:1 [Figure (b)]. However, since the studies were actually started at *ca.* −150 °C and the temperature was then increased and later decreased again, the sharp peaks due to (**5**) are missing in Figure (b). The area ratio of 2:1 obtained for symmetry reasons eliminates the ion (**2**) as the ion responsible for the temperature dependence of the band shapes. However, the ratio is consistent with that expected for the ion (**3**) and/or the ion (**1**) rapidly rearranging as shown in the Scheme. The reaction(s) leading to the total degeneracy possibly proceed *via* the ion (**2**) as an intermediate or transition state.[1b]

Further lowering of the temperature to −152 °C made the signals still sharper as expected if ion (**3**) were the rearranging ion.

If on the other hand the ion (**1**) is the ion yielding the spectra it must be rapidly rearranging, possibly according to the Scheme. If the barrier for such a rearrangement had been large enough a lowering of the temperature would have resulted in a broadening of the signals. Such behaviour should first appear in the 152 p.p.m. signal, since C-3, C-7, and C-9 after coalescence are expected at about this chemical shift and the shift difference of these carbon atoms is much larger than that estimated for the other atoms. However, no such significant extra broadening of the downfield signal compared with the upfield one is observed and therefore the barrier for the rearrangement in the Scheme is estimated to be < 4 kcal mol^{-1}. Thus these results do not allow a distinction between structures (**1**) and (**3**).

It is interesting that the average chemical shifts estimated for the barbaralyl cation, assuming rapid rearrangement according to the Scheme and using the chemical shifts of the 9-methyl-9-barbaralyl cation (**6**)[1f] and the shift differences of the carbon atoms in the 3-methyl-3-nortricyclyl and 3-nortricyclyl cations,[4] are 106 and 153 p.p.m., respectively. These values are close to those observed, *i.e.* 101 and 152 p.p.m. respectively, but it cannot be judged if this agreement constitutes support for structure (**1**) rather than (**3**) since estimates of the chemical shifts of (**3**) are not easily accessible.

However extrapolation using the Cope rearrangement barriers of barbaralone and protonated barbaralone, assuming (**3**)-like transition states, predicts structures like (**3**) or 9-methyl-substituted (**3**) to be less stable than (**1**) or (**6**), respectively.[1b,f]

Recent group-theoretical studies of the ions (**1**), (**2**), and (**3**) and their rearrangements have shown that if the ion (**1**) is the most stable, then (**3**) can be neither a transition state nor an intermediate in the degenerate rearrangements.[1e] The observed small barriers (5·5 and < 4 kcal mol^{-1}) and the low temperature indicate that tunnelling between the structures involved may be extensive[1e] and possibly no *single* classical structure can be assigned to the ion.

We thank the Swedish Natural Science Research Council for financial support.

(*Received*, 20*th March* 1979; *Com.* 293.)

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