Charge-induced Change of Rearrangement Mechanism in the Barbaralyl System

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The 9-vinyl- (**3c**) and 9-aryl-9-barbaralyl cations (**3d**) and (**3e**) have been studied by ^{1}H and ^{13}C n.m.r. spectroscopy and found to be in the charge range where the change from the Cope to the divinylcyclopropylmethyl cation mechanism takes place for degenerate rearrangements in the barbaralyl system.

The 9-barbaralyl cations (**3c**)—(**3e**), which have an intermediate amount of positive charge in their barbaralyl systems, fill an important gap in the charge-reactivity correlation (Figure 1) of this intriguing class of compounds.[1] Ions (**3c**)—(**3e**) are found to be in the range where the change between the Cope (Scheme 1) and the divinylcyclopropylmethyl cation mechanism (Scheme 2) takes place for their degenerate rearrangements, whereby C(1) is exchanged with C(5) and C(2), C(8) with C(4), C(6).

Earlier investigations have revealed the retarding influence of positive charge in the barbaralyl system on the Cope rearrangement. Thus, barbaralone (**1b**) rearranges more slowly than barbaralane (**1a**), and in protonated barbaralone (**1c**) the degenerate rearrangement is even slower than in (**1b**).[1] The significance of these results has been questioned[2] but the conclusions also derive some support from theoretical work.[3]

However, a large increase in the amount of positive charge in the barbaralyl system drastically increases the rate of exchange of C(1) with C(5) and C(2), C(8) with C(4), C(6). Thus, the barbaralyl cations (**3a**) and (**3b**) rearrange much faster than (**1b**) and (**1c**). These results forced the introduction of a novel rearrangement mechanism, composed of consecutive divinylcyclopropylmethyl cation–divinylcyclopropylmethyl cation rearrangements shown in Scheme 2 rather than the Cope rearrangement *via* structure (**5**).[1,4]

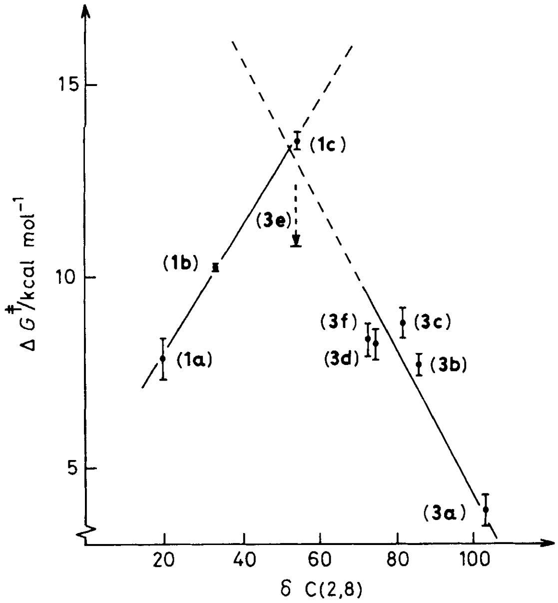
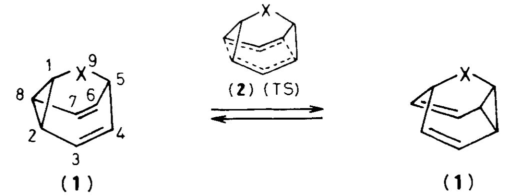


Figure 1. Plot of $\Delta G^{\ddagger}$ (kcal mol^{-1}, 1 kcal = 4.18 kJ) *vs.* δ C(2,8) for degenerate rearrangements of (**1a**)—(**1c**) and 9-barbaralyl cations (**3a**)—(**3f**). Data obtained as follows: (**1a**) $\Delta G^{\ddagger}$ ref. 3a and δ C(2,8) ref. 6, assuming δ C(4,6) as in (**3b**); (**1b**), (**1c**), and (**3b**) ref. 1b; (**3a**) ref. 4, assuming δ C(4,5,6) as in (**3b**) and charge redistribution (**3b**) → (**3a**) proportional to (**1b**) → (**1c**); (**3c**)—(**3e**) this work; (**3f**) ref. 7. The error limits shown are maximal error limits and the present authors have estimated the error limits for (**1a**) ref. 3a and (**3f**) (ref. 7).

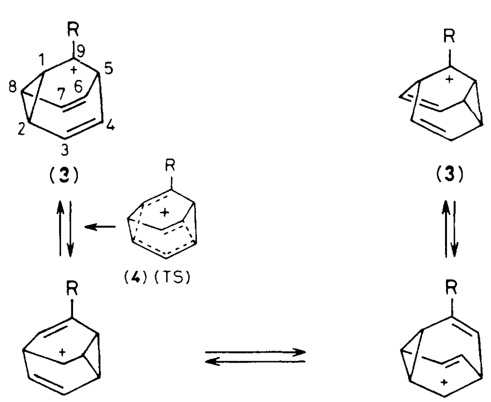


a; X = CH_2
b; X = C=O
c; X = $C{=}\overset{+}{O}H$

Scheme 1

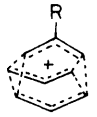
The precursors 9-vinyl-9-barbaralol, 2-phenylbicyclo-[3.2.2]nona-3,6,8-trien-2-ol, and 2-*p*-anisylbicyclo[3.2.2]nona-3,6,8-trien-2-ol were prepared by the standard procedures from the corresponding ketones. The 9-vinyl- (**3c**), 9-phenyl- (**3d**), and 9-*p*-anisyl-9-barbaralyl (**3e**) cations were prepared from these precursors by mixing them into superacid solutions at *ca.* −135 °C in an ion-generation apparatus.[1b]

The structures of ions (**3c**)—(**3e**) were determined using their ^1H and ^{13}C n.m.r. spectra, obtained at −135 °C, and published data.[1] The degenerate rearrangements were studied by the ^1H n.m.r. band shape changes observed in the interval −60 to −140 °C. The cations (**3c**) and (**3d**) both underwent reversible temperature-dependent band changes due to exchange of H(1) with H(5) and H(2), H(8) with H(4), H(6) typical of a Cope or a Cope-mimicking rearrangement.[1] Barriers ($\Delta G^{\ddagger}$) of 8.7 (−87.5 °C) and 8.2 (−97 °C) kcal mol^{-1}† for the degenerate rearrangements of (**3c**) and (**3d**), respectively, were estimated from band widths. The ^1H n.m.r. spectrum of (**3e**), on the other hand, did not change with temperature, apart from improved resolution at higher temperature, until the peaks assigned to (**3e**) disappeared at *ca.* −72 °C. A lower limit for the barrier for a Cope-like rearrangement in (**3e**) was estimated to be 10.7 kcal mol^{-1}.

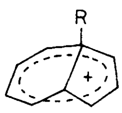


a; R = H
b; R = Me
c; R = $CH{=}CH_2$
d; R = Ph
e; R = *p*-$MeOC_6H_4$
f; R = *p*-FC_6H_4

Scheme 2



(5)



(6)

In Figure 1, barriers ($\Delta G^{\ddagger}$) are correlated with δ C(2,8) for (**1a**)—(**1c**) and the barbaralyl cations (**3a**)—(**3f**). The δ C(2,8) value is used as an indicator of the amount of charge in the barbaralyl system because of the importance of the six basal carbons C(2), C(3), C(4), C(6), C(7), and C(8) which are directly involved in the structural reorganization. Of these positions only C(2,8) varies its chemical shift, δ, substantially over the charge range studied, since cyclopropylmethyl resonance is involved. The remote position of C(2,8) from the substituent at the 9-position avoids direct perturbing interactions with substituents. Factors other than charge are known to affect ^{13}C chemical shifts, but within this series of closely related structures δ C(2,8) is expected to vary uniformly with the amount of positive charge delocalized into the cyclopropane ring.

The behaviour of the 9-barbaralyl cations is opposite to that of (**1a**)—(**1c**) in that a decrease in the amount of charge in the barbaralyl system results in an increased rearrangement barrier. Obviously, there are two reaction mechanisms in operation and these show opposite responses to increased positive charge in the barbaralyl system. We conclude that, in the range containing (**1c**) and (**3e**), both the Cope and the divinylcyclopropylmethyl cation mechanism must be important and be operating parallel to each other in effecting the rearrangements. Transition states or intermediates having structures similar to (**5**)[2b] possibly play a role in this region of mechanism transition.

An explanation of this change of rearrangement mechanism is that the C(2)–C(8) bond in the compounds investigated has increased strength due to increased charge delocalization by cyclopropylmethyl cation resonance, thereby retarding the Cope rearrangement, in which the C(2)–C(8) bond is broken. At the same time, the C(1)–C(2) and C(1)–C(8) bonds are weakened by the resonance and, when the amount of positive

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† 1 kcal = 4.18 kJ.

charge in the barbaralyl system has become large enough, it is possible for the rearrangement to make use of the new route in Scheme 2, *i.e.*, the divinylcyclopropylmethyl cation–divinylcyclopropylmethyl cation rearrangement. Thus, the charge-barrier relationship for (**3a**)—(**3f**) seems to be dominated by the energy difference between the initial tertiary cation (**3b**)—(**3f**) and corresponding secondary cationic intermediates. At higher temperatures, ions (**3a**), (**3b**), and (**3d**) have been found to rearrange to 1,4-bishomoaromatic species like (**6**).[5a—c,e]

Besides theoretical investigations of the parent barbaralyl cation and related compounds,[5c] barbaralyl anions have also been studied.[5d] However, the pattern obtained using rather crude theoretical methods (STO-3G) is not coherent with that presented above for neutral and cation barbaralyl systems.

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