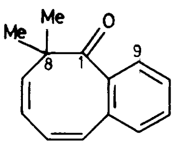
Rearrangements of some 8,8-Dimethylbenzohomotropylium Ions

Ronald F. Childs,* Mailvaganam Mahendran, Manjula Sivapalan, and Placide Nguyen
Department of Chemistry, McMaster University, Hamilton, Ontario, L8S 4M1, Canada

The thermal rearrangement of 2,3-benzo-1-hydroxy-8,8-dimethylhomotropylium cation leads to the formation of a series of products but does not yield the corresponding bridged [11]-annulenium ion.

As 1,6-methano-[11]-annulenium cations are isomeric with benzohomotropylium ions it is possible in principle for these systems to be interconverted by a circumambulatory migration of the 'bridging' methano group. Homotropylium cations containing a C-8 8,8-dimethylmethylene group are known to undergo thermally induced circumambulatory rearrangements.[1] In this report we describe the preparation of 2,3-benzo-1-hydroxy-8,8-dimethylhomotropylium cation (**2**) and an examination of its thermal rearrangements.

Extraction of (**1**)[2] into FSO_3H at −78 °C gave (**2**) whose low temperature n.m.r. spectra (< −60 °C) were fully consistent with the assigned structure. At higher temperatures (**2**)



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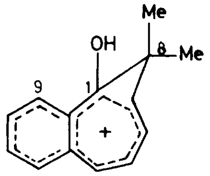

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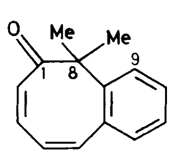

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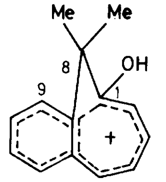

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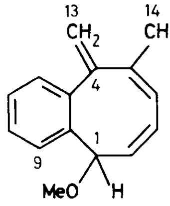

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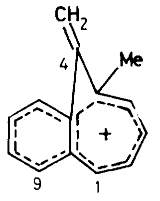

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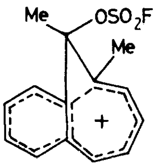

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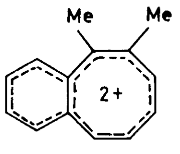

(8)

displayed both reversible and irreversible temperature dependent ^{1}H n.m.r. spectra. At temperatures up to −10 °C a reversible averaging process was observed in which the signals of the two methyl resonances at δ 0.15 and 1.87 broadened, coalesced at −48 °C, and appeared as a sharp singlet at δ 1.10. This averaging can be understood in terms of a ring inversion process involving the bridging carbon that interchanges the *exo* and *endo* C-8 substituents. Such ring inversions of homotropylium cations have previously been detected, however, the present instance is remarkable in the low barrier found for the process ($\Delta G^{\ddagger}$ 9.5 kcal/mol).[1] The existence of this low energy ring inversion process suggests that (**2**) has a very open structure.

An irreversible isomerization of (**2**) occurred at −8 °C to give two ions in a ratio of 2 : 1. No residual amount of (**2**) nor any species corresponding to an annulenium cation could be detected in the acid solutions after isomerization. Neutralization of the acid in MeOH–HCO$_3^-$ led to the recovery of two materials. The major product was identified as (**3**) by its ^{1}H, ^{13}C n.m.r., u.v., i.r., and mass spectra. The formation of this material indicates that the circumambulation of C-8 around the '7-membered' ring of (**2**) to give (**4**) can take place. Heating solutions of (**4**) to temperatures above 0 °C led to a general decomposition without the formation of any characterizable materials.

The minor product of the rearrangement of (**2**) was identified as (**5**). Dissolution of (**5**) in FSO$_3$H led to the formation of (**6**), a unique homotropylium ion bearing a vinyl substituent at C-8. Neutralization of the acid solution of (**6**) in MeOH–HCO$_3^-$ led to reisolation of (**5**). An important point to note is that (**6**) is not present in the initial mixture obtained on rearrangement of (**2**) but rather a different homotropylium cation which reacts to form (**5**) on treatment with base. This precursor to (**5**) is tentatively assigned the structure (**7**). The formation of (**7**) from (**2**) likely involves a combination of a methyl shift and protonation and loss of the hydroxy group to yield a benzocyclo-octatetraene dication, (**8**), which then collapses with FSO$_3^-$ to yield (**7**). Homotropylium cations with similar substituents to those of (**7**) have been reported by Paquette and co-workers.[3] Attempts to generate stable solutions of (**8**) from (**5**) using stronger acid media have thus far failed.

In conclusion, thus far thermal isomerization of either (**2**) or (**4**) to give a bridged annulene has not been detected despite the existence of circumambulatory rearrangement with these systems. It is not clear whether the failure to detect the formation of the annulenium ion results from a large kinetic barrier to its formation or to its relative thermodynamic stability as compared to the 1-benzohomotropylium ions. The isomerization of (**2**) to (**4**) and formation of (**6**) reinforces the earlier suggestion that the 1-benzohomotropylium ions are thermodynamically more stable than other possible isomeric benzohomotropylium cations.[4]

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