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THE BEHAVIOR OF TRISHOMOCYCLOPROPENYL CATIONS[1]

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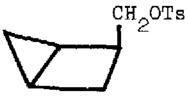
The nature and stability of the trishomocyclopropenyl cation (**1**) have been provocative topics.[3] Apparently, the species is the key intermediate in the solvolyses of the <u>cis</u> tosylates **2**-OTs[4] and **3**[5] which are converted to **2**-OAc and **2**-OH, respectively, in greater than 90% yield. **1** has also been directly observed by NMR during solvolysis of **2**-Cl in superacid at -120°.[6]

1

2



3

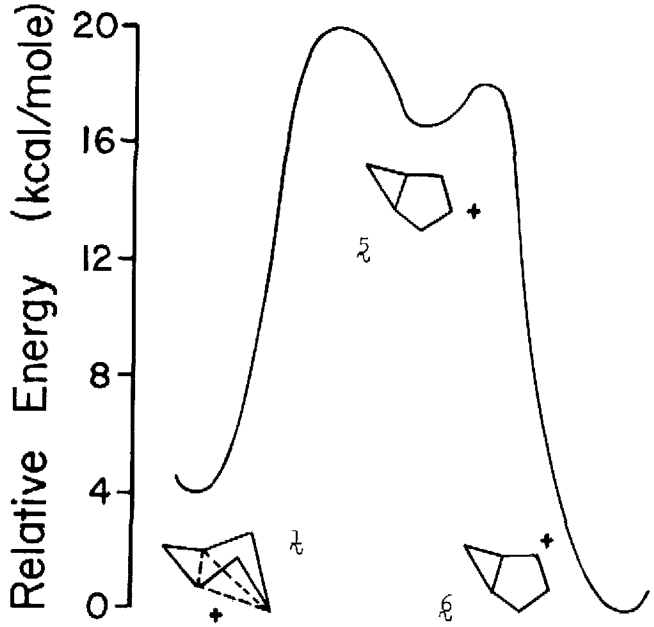
4

Despite these successful preparations, **1** has proven to be an elusive target. Notable failures to generate **1**[7] were via deamination of **2**-NH_2 and **4**-NH_2,[7a] via protonation of bicyclo[3.1.0]hex-2-ene[7b] and via solvolysis of **4**-OTs.[4] In these cases the complex product distributions could be rationalized by the intermediacy of the classical, bicyclo[3.1.0]hex-3-yl (**5**) and bicyclo-[3.1.0]hex-2-yl (**6**) cations. This led to Winstein's postulate that leakage from **5** to **1** is relatively inefficient.[4] The reclusive nature of **1** certainly contributed to the skepticism about the extent of its homoaromatic stabilization.[3,7]

For the purpose of clarifying the interrelationships of **1**, **5** and **6**, we have performed MINDO/3 calculations to determine the relative energies of the species and the activation energies for the conversion of **5** to **1** and **6**. In addition, the 3-methyl derivatives of **1** (**7**) and **5** (**8**) and their rotational barriers have been studied.

<u>Results for C_6H_9 Cations</u>

The calculated relationships between **1**, **5** and **6** are diagramed in the figure. The relative energies of the species are in kcal/mole: **6**(0.0), **1**(3.9) and **5**(16.5). Consistent with the NMR data[6] and earlier theoretical work,[9] **1** is found to possess C_{3v} symmetry, <u>i.e.</u>, two sets of three equivalent carbons. The activation energies for the conversion of **5** to **1** and **6** are computed to be 3.4 and 1.5 kcal/mole, respectively. The transition state for the first rearrangement was assumed to possess C_s symmetry, <u>i.e.</u>, a plane of symmetry passing through C3, C6 and the midpoint



of the C1C5 bond in **5**. Reducing the symmetry should have minor effect as models suggest little conformational flexibility for the conversion. For the hydride shift, the transition state was determined for migration of the hydrogen at C2 in **5** that is *cis* to the cyclopropyl ring. Since the cyclopentyl ring in **5** is calculated to be essentially planar, migration of the *trans* hydrogen is anticipated to be equally facile.

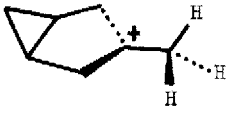
Although the MINDO/3 results formally apply to the gas phase, the correspondence between kinetic and thermodynamic parameters for the interrelationships of isomeric carbonium ions in the gas phase and solution is well documented.[10] The calculated reaction surface is clearly consistent with Winstein's postulate, since **5** is predicted to both kinetically and thermodynamically favor rearrangement to **6** rather than **1**. Thus, if the solvolysis of **4**-OTs and the deaminations of **2**-NH_2 and **4**-NH_2 proceed classically to **5**, little product derived from **1** is anticipated. Furthermore, the protonation of bicyclo[3.1.0]hex-2-ene to yield **6** rather than **1** is thermodynamically justified. Nevertheless, **1** is still computed to gain substantial energetic benefit from homoconjugation. However, the calculated energy difference between **1** and **5** (12.6 kcal/mole) is significantly smaller than earlier estimates (*ca.* 1 eV).[9] The discrepancy may be largely attributed to well known deficiencies in the other computational procedures (EH[11] and MINDO/2[9b]).

Of course, the present method is not above suspicion, however, the results seem reliable for several reasons. (1) The experimental data may be rationalized as discussed. (2) MINDO/3 is apparently accounting well for the strain energies of bicyclo[3.1.0]hexyl systems considering the similarity between the calculated (4.6 kcal/mole) and experimental[12] (9.1 kcal/mole) $\Delta H_f^{298°}$ for bicyclo[3.1.0]hexane. (3) The energy difference between **5** and **6** (16.5 kcal/mole) is a reasonable estimate of the stabilization for a secondary cyclopropylcarbinyl cation. This follows from the experimental value for the rotational barrier in the tertiary, dimethyl-cyclopropylcarbinyl cation (13.7 kcal/mole).[13] The MINDO/3 value for the barrier (10.0 kcal/mole)[8] reveals that the method slightly underestimates the parallel interaction of a cyclopropyl ring and a vacant 2p-orbital. (4) Not surprisingly, the energetic benefit of a perpendicular interaction between a cyclopropyl bond and a vacant 2p-orbital is underestimated using MINDO/3 by a similar amount. This is evident in comparing the calculated (8.8 kcal/mole)[14] and experimental (13.0 kcal/mole)[15] values for the bridge flipping barrier in 9-methyl-9-pentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonyl cation.

These observations lead to the conclusion that the qualitative relationships shown in the diagram are valid; however, quantitatively, the stabilization of both **1** and **6** relative to **5** may be underestimated by ca. 4 kcal/mole.

Results for Methyl Analogs

The classical form of the tertiary cation, **8**, is calculated to be more stable than its nonclassical relative, **7**, by 4.9 kcal/mole. By analogy, this figure may now overestimate the true value by ca. 4 kcal/mole. The qualitative prediction is, however, consistent with the lack of cyclopropyl participation observed in the solvolysis of 3-methyl-**2**-O_2CCCl_3.[3b] The reason for the reduction in the energy difference between the classical and nonclassical ions upon methyl substitution is probably twofold. First, the methyl group aggravates the steric crowding in **1**. Second, the stabilization afforded by a methyl group is much less profound in a nonclassical ion than a classical one, since the positive charge is already highly delocalized in the former species.[14]



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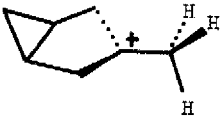
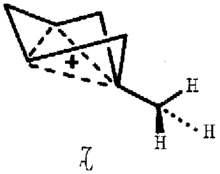


8a



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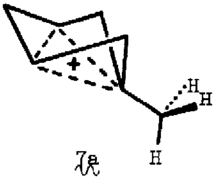
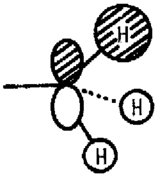
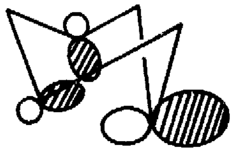


7a

The conformational preference for **8** versus **8a** is found to be negligible due to the planarity of the cyclopentyl ring and, therefore, the similarity between the interaction of the methyl HOMO, π_{CH_3},[16] with the empty 2p-orbital in the two conformations. In contrast, **7** is more stable than **7a** by 0.8 kcal/mole. The preference may be rationalized by greater overlap and stabilization for the interaction of π_{CH_3} and the LUMO of **1**, E_s*,[14] in **7**. This appears to be a general feature of methyl substituted bis- and tris-homoaromatic cations. Thus, analogous preferences are calculated for the 7-methyl-7-norbornadienyl cation (0.4 kcal/mole) and the parent, 3-methyl-bishomocyclopropenyl cation (0.8 kcal/mole).



π_{CH_3}



E_s*

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