formation, one arising from the rotation (C–H bending) of the methylene group, and one arising from changes in the MO structure at the methylene group affecting the C–H stretching and bending deformations. The extent of the contribution of each of these will depend on the relative extents of bond formation and rotation of the methylene group which need not be the same. There is currently no adequate experimental data available which allow for an estimation of the magnitude of the last two isotope effects. Experimental and theoretical studies are currently under way in our laboratories to evaluate these effects.

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(35) In the STO-3G calculations on allene the degenerate HOMO's and the LUMO's are extensively mixed whereas in the 4-31G calculations this mixing is less extensive.
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(39) The optical purity of the 1,3-dimethylallene and the optical purity and ratio of the products **56–59** were not reported (ref 11).
(40) A product distribution of **43** > **44** > **45** > **42** can be derived with a selectivity of 70:30 between the $[_\pi 2_s + (_\pi 2_s + _\pi 2_s)]$ and $(_\pi 2_s + _\pi 2_a)$ processes and selectivities of 80:20 between **35** > **34** and 70:30 between **38** > **39.**
(41) In the case of the cyclodimerization of partially resolved 1,3-dimethylallene, the optical purity of the allene was ~15%. As a result the product distributions derived from racemic and the partially resolved allene are very similar.

Theoretical Evidence for Nonplanar Cyclopropylcarbinyl Cations. Effect of Orbital Distortion on Endo and Exo Solvolytic Product Ratios

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Abstract: Theoretical evidence based upon ab initio molecular orbital calculations is described which provides an explanation for the predominant formation of endo tricyclic solvolytic products derived from the tricyclo[3.3.0.0^{2,8}]octan-3-yl cation and related carbenium ions. A theoretical rationale is presented which invokes angular distortion and a nonplanar cationic center in the carbenium ion intermediate. The above arguments are based upon a comparison of the relative energies involved in the calculated rotational barrier and sp^2 to sp^3 rehybridization of methylcyclopropylcarbinyl cation.

Introduction

Early evidence for the planarity of carbenium ions was based upon solvolysis studies of optically active substances which led to racemic products.[1,2] Strongly suppressed rates of carbenium ion formation at a bridgehead have also been cited as evidence for the planarity of carbocations. More recently, Raman, infrared,[3a] and ^{13}C nuclear resonance studies[3b] have provided direct evidence for the planarity of the $^+CC_3$ carbon skeleton. Theoretical investigations have also demonstrated the planarity or near planarity of carbenium ion intermediates in the absence of solvent or symmetry influences. For example,

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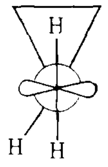
molecular orbital calculations suggest that ethyl cation and propyl cation have cationic centers that deviate from planarity by 2.9 and 5.4°, respectively.[4]

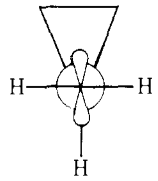
Despite the large body of evidence for the planarity of carbenium ions, several investigators have proposed the existence of nonplanar carbenium ion intermediates.[5a–c] This suggestion was prompted by the fact that carbenium ions, contained within rigid carbon frameworks, often undergo solvolysis reactions with retention of configuration or give products on solvent capture which are inconsistent with predictions based upon steric interactions.[5] The cyclopropylcarbinyl cation contained in a rigid bicyclic carbon framework has been particularly implicated in this anomalous behavior.[5c,e,6]

The parent cyclopropylcarbinyl cation has been the target of numerous theoretical investigations.[7a–f] These studies indicated a clear energetic preference for the bisected conformation (**1**) when compared to the perpendicular form (**2**). The inherent stability of **1** is due to the delocalization of positive charge through the interaction of the antisymmetric Walsh orbitals of the cyclopropane ring with the empty p orbital at C_1 as depicted in **3**.[8] The barrier hindering rotation about the carbenium ion center in dimethylcyclopropylcarbinyl cation has been measured by NMR to be 13.7 kcal/mol.[9] The calculated rotational barrier for cyclopropylcarbinyl cation (i.e., **1** → **2**) has been reported to be 25.7 kcal/mol.[10] In systems where a rigid carbon framework prohibits rotation, a cyclopropylcarbinyl cation may be constrained to an energetically less favorable conformation. The diminished delocalization of positive charge due to diminished C_1–C_2 bonding interaction, as in **3**, is often reflected in slower rates of solvolysis.[11]



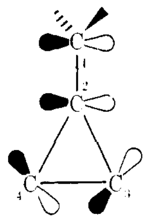
bisected

1



perpendicular

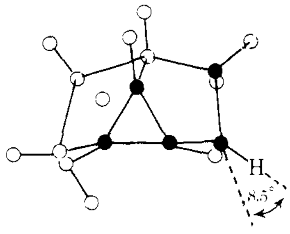
2



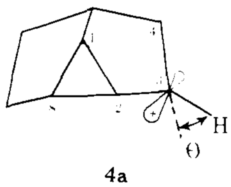
bisected

3

Our previous theoretical investigations[5c,12] of the tricyclo[3.3.0.$0^{2,8}$]octan-3-yl cation (**4**), which contains a methylcyclopropylcarbinyl cationic moiety (indicated by the heavy black circles), presented sound evidence that cation **4** is deformed from the expected sp^2-hybridized planar geometry at C_3. Extended Hückel[13] and INDO[14] molecular-orbital calculations on **4** suggested that the C_3–H bond is bent 13 and 8.5°, respectively, toward the exo side of the molecule. This orbital distortion, as shown in **4a**, predicts the predominant formation of endo tricyclic products, which is in accord with the experimental observations.[5c] If the cationic center of **4** were planar, exo products should be formed preferentially based upon steric considerations.

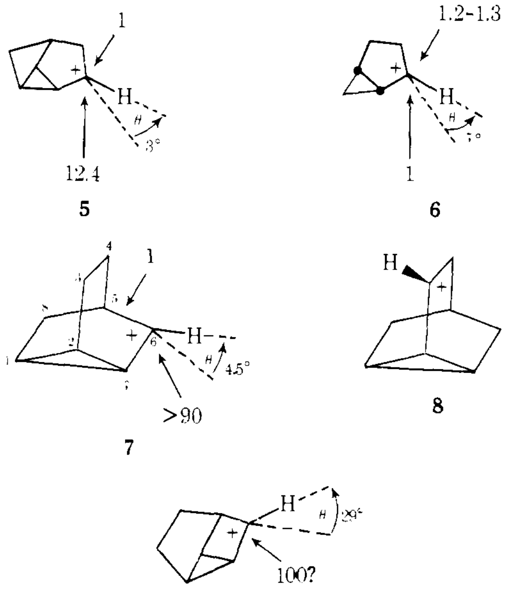


4



4a
tricyclo[3.3.0.$0^{2,8}$]octan-3-yl cation

Chart I. C–H Bond Out of Plane Bending Angles (θ) from INDO Calculations, and Experimental Stereochemical Hydrolysis Results (→) for Some Methylcyclopropylcarbinyl Cations

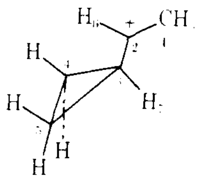


Several other polycyclic cyclopropylcarbinyl cationic intermediates have been described in the literature. A similar theoretical treatment was carried out on cations **5–9**. The calculated angular deviation from planarity together with the reported hydrolysis capture[15] ratios are given in Chart I. The experimental results are in complete accord with the suggestion based upon our theoretical treatment that the anomalous endo solvent capture was a manifestation of stereoelectronic factors arising from nonplanarity at the carbenium ion center. Existing theory accommodates these stereochemical observations as resulting from a blend of steric and (undefined) stereoelectronic factors. We now report the results of a series of ab initio molecular orbital calculations that provide a theoretical rationale for the angular distortion and rehybridization of cyclopropylcarbinyl cations in bicyclic and tricyclic systems.

Method of Calculation

The ab initio calculations were carried out with the GAUSSIAN 70 program using the STO-3G[16] and 4-31G[17] Gaussian basis sets on an IBM 360/67 computer. Relative energies between selected points were calculated at the STO-3G and 4-31G levels of approximation utilizing geometries optimized with an STO-3G basis set.

The C_2–C_3 rotational barrier, **10a** → **10c** (Figure 1), was carried out with partial optimization of pertinent bond distances by STO-3G. The geometry of the cyclopropyl ring for **10a, 10b, 10d,** and **10e** was that reported by Hehre.[18] The numbering system, given in **10a,** was maintained throughout. The parameters minimized in **10c** also included the C_3–C_5 and C_4–C_5 bond distances and the $C_4C_5C_3$ bond angle. The cal-



10a

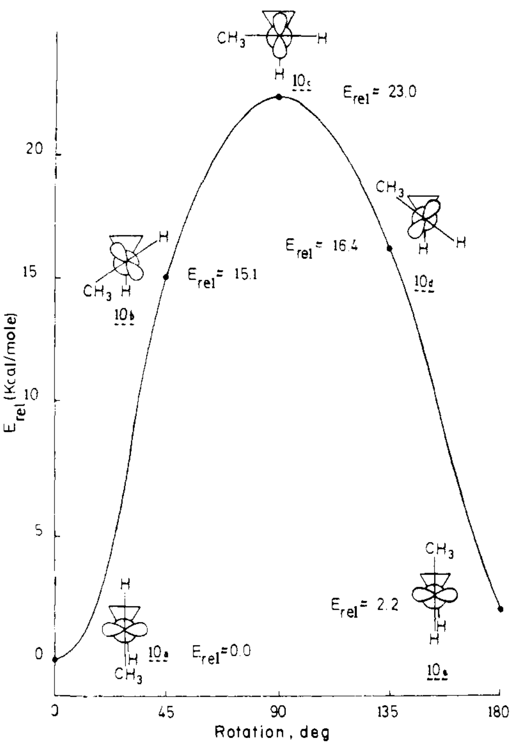


Figure 1. Rotational barrier (STO-3G) of the $C_5H_9^+$ ion. Rotation about the C_2–C_3 bond, deg.

Table I. Optimized Geometry (STO-3G) of Methylcyclopropylcarbinyl Cations

bond distance (r), Å angles (∠), deg	molecule[a]				
	10a	**10b**	**10c**	**10d**	**10e**
rC_1C_2	1.522	1.489	1.513	1.522	1.491
rC_2C_3	1.412	1.439	1.488	1.460	1.423
rC_3C_5	1.609[b]		1.537		
rC_4C_5	1.454[b]		1.482		
$\angle C_1C_2C_3$	122.33	122.00	124.29	124.58	125.13
$\angle H_6C_2C_3$	119.09	119.20	118.88	118.50	118.75
$\angle C_4C_5C_3$	63.15[b]		60.77		
$\angle C_2C_3C_{45}$	120.4[b]		129.49		
$\angle H_7C_3C_{45}$[c]	121.00[b]		123.24		

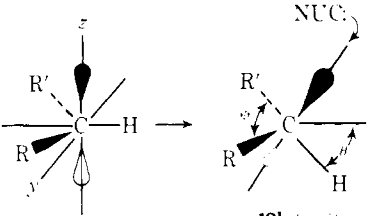
[a] All other bond distances and angles not reported within are identical with those reported by Hehre[18] with the exception of the methyl group, in which standard bond distances and angles were assumed. [b] These values taken from ref 18. [c] C_3C_{45} refers to the line bisecting the plane formed by carbons 3, 4, and 5.

culated bond angles and distances are given in Table I. Five conformers of **10** involving rotation (0–180°) about the C_2–C_3 bond were then calculated to get the difference in energy (2.2 kcal) between the two bisected conformers **10a** and **10e** and the rotational barrier (Figure 1).

Rehybridization at C_2 in **10c–e**, affording **11a–c**, required holding carbons 1, 2, and 3 in the xy plane at selected $C_1C_2C_3$ and $H_6C_2C_3$ bond angles while H_6 was moved out of plane through an angle θ[19] such that the $C_1C_2H_6$ bond angle was identical with both the $C_1C_2C_3$ and $H_6C_2C_3$ bond angles. The energies of the rehybridized cations, **11a–c**, were computed with an STO-3G basis set.

Results and Discussion

The inadequacies of existing theory in providing a satisfactory explanation for the observed preference for endo tricyclic products prompted a theoretical investigation of the bonding mode and the hybridization at the cationic center of ion **4** and related ions **5–9**. Attack of solvent on an $sp^{>2}$-hybridized, nonplanar carbenium ion is expected to occur preferentially from the side of the more directed lobe of the empty p orbital (**12b**). Rehybridization of a trigonal carbocation

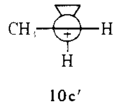
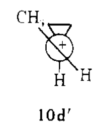
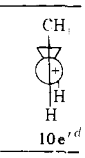


12a (sp^2) **12b** (sp^3)

where RCR′ is held in the xy plane and the RCR′ bond angle (ϕ) is contracted concomitantly with a change in the C–H bond angle (θ = 54.7°) is given below. The rehybridization process is related to the cosine of the angle ϕ subtended by two atomic orbitals.[19] Since rotation is inhibited in these systems, it can be seen that rehybridization at the positive center in **4** involves motion of the C_3–H bond in the exo direction with only a minor distortion of the $C_2C_3C_4$ bond angle being required. With all the bicyclic cations (**4–9**) studied, rotation of the p orbital was in the direction that afforded a more nearly bisected cyclopropylcarbinyl cation. In order for cations **4–9** to be nonplanar, the stabilization provided by nonclassical cyclopropylcarbinyl delocalization must be comparable to or greater than the out of plane deformation energy associated with sp^2-$sp^{>2}$ rehybridization of a cationic center that typically prefers trigonal geometry.

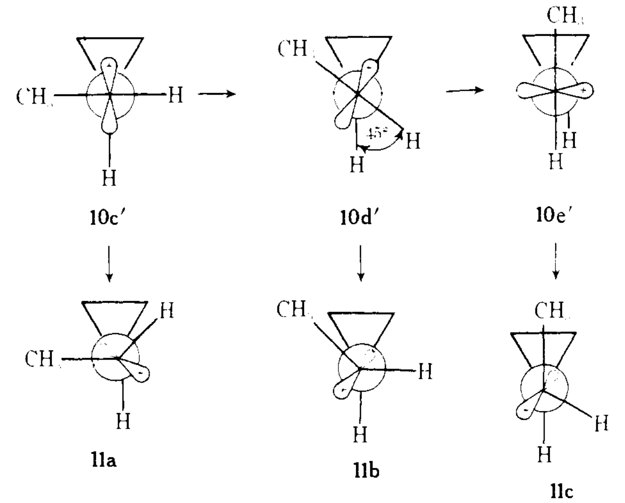
Several significant factors are evident from the results of our rehybridization studies on cations **10c′–e′** (Table II). We elected to use the *s-cis*-methylcyclopropylcarbinyl cation (**10e**) as a model for the corresponding cationic moiety outlined in **4**. Our approach was to calculate the relative energies of rotation and rehybridization in cation **10** to approximate the similar process of **4** rehybridizing to **4a**. It is readily seen in **4a** that the empty p orbital will be distorted toward the endo face of the molecule where solvation and nucleophilic attack would be preferable. Because rehybridization is related to a cosine function, minor changes in RCR′ angle contraction (ϕ) are accompanied by much larger changes in out of plane bend (θ) of H_6. Thus, rehybridization should not be strongly impeded

Table II. Relative Energies (STO-3G) for Rehybridization of Methylcyclopropylcarbinyl Cations[a]

angle ϕ, deg[b]	out of plane bend[c] θ	 **10c′**	 **10d′**	 **10e′**[d]
120.0	0.0	0.0	1.6	0.0
119.7	9.5	0.4	0.0	1.4
119.0	17.2	1.9	0.9	4.6
117.6	26.6	5.5	5.0	11.2
115.9	34.6	10.5	11.6	19.5
113.5	43.4	18.3	23.0	32.1
111.0	40.8	27.4	37.3	46.3
109.5	54.7	33.3	47.0	55.4

[a] Cations **10c′–e′** differ from the energy minimized structure in that the bond angles at C_2 are assumed for the $sp^2 \rightarrow sp^3$ geometries. [b] The $C_1C_2C_3$, $H_6C_2C_3$, and $C_1C_2H_6$ angles are identical. [c] The angle θ through which H_6 is bent along the z axis. [d] The relative energies are given in kcal/mol. The calculated total energy (STO-3G) for **10e′** at a fixed angle of 120.0° was −120 475.9310 kcal/mol. A conversion factor of 627.503 kcal/au was used throughout.

Scheme I



by the bond angle constraints of a tricyclic system such as **4**. Secondly, substantial deviations from planarity (θ) may be attained with only a modest expenditure of energy. In fact, **10d′**, which has a conformation halfway between a bisected and perpendicular cation, exhibits an energy minimum when it is bent out of plane by 9.5° at C_2.

We have included model substrate **10d′** in our study since a number of the tricyclic cations under consideration have such intermediate cyclopropylcarbinyl geometry. Complete rehybridization (θ = 54.7°) involves considerably higher energies of 33.3, 47.0, and 55.4 kcal/mol for cations **10c′–e′**, respectively. These calculated inversion barriers are depicted graphically in Figure 2. Rehybridization of the bisected conformer **10e′** to **11c** (Scheme I) was calculated by CNDO to require 45.6 kcal/mol.[5c,12]

In general sp^2 to sp^3 rehybridization energies are greater than rotational barriers for simple cyclopropylcarbinyl cations. For example, rotational barriers for the parent cyclopropylcarbinyl and dimethylcyclopropylcarbinyl cations have been calculated to be 25.7[10] (STO-3G) and 15.0 kcal/mol[12,20] (4-31G), respectively. The latter barrier is in good accord with experimental NMR data.[9] We calculate a barrier of 23.0 (STO-3G) and 26.1 kcal/mol (4-31G) for **10a** → **10e** (Figure 1). A lengthening of the C_2–C_3 and C_4–C_5 bond and a shortening of the C_3–C_5 and C_3–C_4 bonds were observed for the STO-3G optimized geometry of **10c**. Our results, which are summarized in Table I, are consistent with previous calculations.[8]

The geometrical distortion of the cyclopropane ring significantly affects the calculated internal rotation barrier. Without optimization of the cyclopropane ring, a rotational barrier of 30.8 kcal/mol was calculated (STO-3G).

The bisected s-anti trans conformer **10a** is 2.2 kcal/mol more stable than the s-cis conformer **10e** (Table III). Our INDO calculation[5c,12] of bisected planar cation **10a** suggest that the rotational barrier for interconversion to the perpendicular form **10c** is 22.2 kcal/mol.

It is evident from a comparison of the calculated rotational barrier (Figure 1) with the inversion barriers that the C_2–C_3 bond rotation represents a relatively steep energy surface relative to the initial stages of rehybridization. Therefore it should be energically favorable to rehybridize tricyclic cations in order to obtain a more bisected cation. For example, rotation of **10d** from its 45° (135°) conformation by 10° toward the bisected conformer results in a net stabilization of 6.3 kcal/mol (Figure 1). In contrast, rehybridization of cations **10c′–10d′** (θ = 9.5°) results in an energy increase of only 0.4, 0.0, and 1.4 kcal/mol, respectively (Table II). When θ = 26.6°, an energy *increase* of only 5.5, 5.0, and 11.2 kcal/mol was calculated for the rehybridization process ($sp^{2.16}$) while C_2–C_3 bond rotation of **10d** by 26° in the direction of a more bisected cation (**10e**) resulted in an energy *decrease* of 11.3 kcal/mol. These results corroborate our earlier INDO results where a 45° C_2–C_3 bond rotation in **10b** was calculated to provide 10.6 kcal/mol of stabilization and rehybridization of **10a** to $sp^{2.16}$ (θ = 26°) demanded a 9.3 kcal/mol energy increase. From these calculated values we conclude that out of plane deformation of a tricyclic cation such as **9** by as much as 29° toward a more bisected cation is energically feasible. Thus, rehybridization occurs until the best balance between the increase in energy accompanying out of plane deformation and the decrease in energy associated with cyclopropylcarbinyl stabilization is attained.

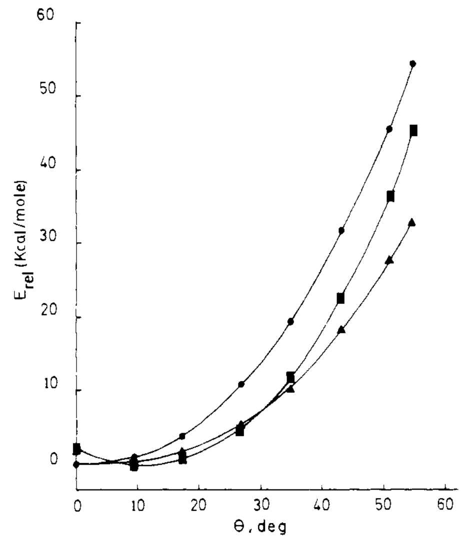


Figure 2. Rehybridization (sp^2 to sp^3) of $C_5H_9^+$ ions **10c′–e′**. Out of plane bend of H_6 (θ), deg. (●) Rehybridization of sp^2 bisected **10e′** to sp^3 **11c**; (▲) rehybridization of perpendicular **10c′** to **11a**; (■) rehybridization of **10d′** to **11b**.

Table III. Calculated Energies for $C_4H_9^+$ Cations

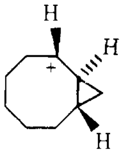
	total hartrees		E_{rel}, kcal/mol[a]	
molecule	STO-3G	4-31G	STO-3G	4-31G
10a	−192.0001	−193.9916	0.0	0.0
10b	−191.9760	−193.9696	15.1	13.8
10c	−191.9634	−193.9500	23.0	26.1
10d	−191.9740	−193.9654	16.4	16.4
10e	−191.9967	−193.9886	2.2	1.9

[a] A conversion factor of 627.503 kcal/au was used throughout.

The above calculations, however, apply only to isolated molecules in the gas phase. Stabilizing interactions of the cationic center with solvent molecules would be expected on the basis of stereoelectronic considerations to occur preferentially from the endo side of the molecule, i.e., in the direction of distortion of the vacant p orbital. Indeed, endo solvation of the partially rehybridized cationic center at C_3 at **4a** may result in further deviation from planarity due to the fact that an increase in θ is accompanied by enhanced cyclopropylcarbinyl stabilization.

The results, shown in Table II, together with reported hydrolysis capture ratios, are in excellent accord with the concept of stereoelectronic control in which extensive rehybridization of the carbenium center has occurred *in the transition state* for solvent capture. Our results also provide a unique explanation for the very high solvolytic rate of *endo*-**9**-OPNB.[15f–h] Solvolysis resulting in formation of a nonplanar cation should not only exhibit enhanced rates but may also result in retention of configuration as a consequence of solvent capture by the stereoelectronically distorted carbenium ion center.

We also invoke these principles in explanation of the kinetic and stereochemical results for *cis*- and *trans*-bicyclo[6.1.0]nonyl derivatives.[21] The *trans*-bicyclo[6.1.0]nonyl cation (**13**) was calculated (INDO) to have a cationic center bent out of the C-C-C plane by 8.5° in the direction cis to the cyclopropyl ring. Significantly, the deviation from planarity occurs in a direction such that the resulting bend of the vacant p orbital occurs in a direction that increases the bisectedness of the cyclopropylcarbinyl system.



13

The report of Rhodes and Difate[22] on the reactivity of geometrically constrained bridgehead cyclopropylcarbinyl systems is consistent with our postulated rehybridization phenomenon. These workers have demonstrated that bridgehead nonplanar cationic centers exhibit markedly enhanced rates of solvolysis if adjacent to a cyclopropyl ring, even if the cyclopropylcarbinyl system is in the approximately 30° geometry conformation which is closely approached by cations **4** and **5**.

Finally, we wish to emphasize that it is becoming increasingly obvious that carbenium ions centers in symmetric environments can deviate from planarity and that stereoelectronic factors can often outweigh steric considerations in such cases.

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