Table I. ^{13}C Nmr Shifts of Phenyl, Cyclopropyl, and Methylcarbenium Ions[a]

					Phenyl			
Ion	C^+	α-CH	β-CH_2	CH_3	C_i	C_o	C_m	C_p
$(CH_3)_2CH^+$	−125.0[b]			132.8				
$(c\text{-}C_3H_5)_2C^+H$	−59.9	148.1	155.1					
$(C_6H_5)_2CH^+$	−6.9				55.4	44.6 50.3	60.0	42.8
$c\text{-}C_3H_5CH^+C_6H_5$	−32.6	148.6	148.6		56.1	48.5 57.3	61.5	44.7
$c\text{-}C_3H_5CH^+CH_3$	−59.1	126.5	136.3	160				
$C_6H_5\overset{+}{C}HCH_3$	−40							
$(CH_3)_3C^+$	−135.4[b]			145.3				
$(c\text{-}C_3H_5)_3C^+$	−77.8	161.2	162.9					
$(C_6H_5)_3C^+$	−18.1[c]				52.9	49.5	62.5	49.7
$(c\text{-}C_3H_5)_2C^+CH_3$	−81.6	148.6	155.4	155.4				
$(C_6H_5)_2C^+CH_3$	−35.5			162.5	52.2	52.5	62.2	45.6
$C_6H_5(c\text{-}C_3H_5)\overset{+}{C}CH_3$	−52.5	147.9	148.7	170.3	53.9	58.9	62.5	48.2
$(C_6H_5)_2\text{-}c\text{-}C_3H_5\overset{+}{C}$	−41.3	152.8	157.8		51.8 56.4	54.7 59.0	62.3 63.8	43.5 48.5
$C_6H_5(c\text{-}C_3H_5)_2\overset{+}{C}$	−67.3	151.0	156.7		58.4	64.1	65.7	57.2
$C_6H_5\overset{+}{C}(CH_3)_2$	−60.6			158.8	53.7	51.3	60.4	37.8
$c\text{-}C_3H_5\overset{+}{C}(CH_3)_2$	−86.8	133.8	140.4	153.9 162.7				
$(CH_3)_2C^+OH$	−55.7			162.0 163.3				
$(c\text{-}C_3H_5)_2C^+OH$	−43.6	174.0 164.7	166.8 167.4					
Ph_2C^+OH	−15.4				62.3 63.2	53.6 57.1	61.3	48.3 50.4

[a] Recorded in SO_2ClF–SbF_5 or SO_2ClF–FSO_3H–SbF_5 at −60 to −90°. Chemical shifts are in parts per million from $^{13}CS_2$. A positive sign indicates shielding from the reference. [b] G. A. Olah and A. M. White, *J. Amer. Chem. Soc.*, **91**, 5801 (1969). [c] G. A. Olah, E. B. Baker, and M. B. Comisarow, *ibid.*, **86**, 1265 (1964); G. J. Ray, R. J. Kurland, and A. K. Colter, *Tetrahedron*, **27**, 735 (1971).

The fact that cyclopropylcarbin esteylrs solvolyze faster than the related phenyl esters clearly shows that cyclopropyl is a better participating group in solvolysis than phenyl. A contributing factor can be that the significant strain in the bent, electron-rich cyclopropyl groups bound to a tetrahedral carbon in covalent cyclopropylcarbinyl esters is partially relieved upon reaching the carbenium ion like transition state, thus greatly facilitating the reaction. The fact that cyclopropyl is a better participating group than phenyl in these reactions does not necessarily mean that it also delocalizes charge better in the intermediate ion. In other words, phenyl can remove charge further, spreading it out over a larger system without necessarily meaning that the stability of phenylcarbenium ions is greater than that of cyclopropylcarbenium ions. Similar considerations explain the equilibrium data between ions and their alcoholic or olefin precursors. pK_{R^+} values show only the stabilities of the ions relative to their covalent precursors, with which they are in equilibrium. If, for example, cyclopropylcarbinyl esters release more strain upon ionization than related phenylcarbinyl esters this could affect the solvolysis and pK_{R^+} data. Spectroscopic data, particularly the ^{13}C nmr study of related long-lived ions, give information on the structure of the carbenium ion intermediates, but cannot directly indicate their stabilities.

We cannot recollect, in contrast to Brown, any suggestion that ^{13}C nmr shifts could be used to predict solvolytic rates and stabilities of carbocations or any reason why they should. We maintain our position that ^{13}C nmr shifts, if used with proper consideration of all factors involved, are a very powerful tool in studying the structure of carbocations, including the trend of charge distribution.

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Extended Hückel Calculations on the Electrophilic Ring Opening of Substituted Cyclopropanes. Hyperconjugative Stabilization for a Face-Protonated Cyclopropane

Sir:

The electrophilic ring-opening reactions of cyclopropanes provide the mechanistic challenge of an unusual reaction type (potentially SE2) and the synthetic possibility of simultaneous stereochemical control at three asymmetric carbons.[1] Simple orbital symmetry theory predicts an even number of inversions to be the stereochemical consequence of such a $[_\sigma 2_s + {}_\omega 0_s]$ cycloreaction.[2] Thus, for proton addition, retention of configuration is indicated at the carbon atom receiving the electrophile in a direct one-step reaction;[3]

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(1) For a comprehensive review, see C. H. DePuy, *Fortsch. Chem. Forsch.*, **40**, 74 (1973), and references therein.

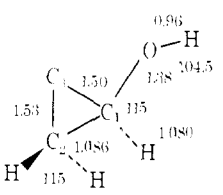
(2) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969); R. R. Schmidt, *ibid.*, **12**, 212 (1973).

(3) This prediction assumes retention of configuration at the departing carbon atom as in the $[_\sigma 2_a + {}_\omega 2_s]$, or SN2, reaction.

however, for addition of an electrophile with a retention–inversion option[4] there is no clear prediction.

Experimental findings on the stereochemistry of acid-catalyzed cyclopropane cleavage reactions have uncovered all three possibilities:[1] complete retention (the most commonly observed stereochemical event),[5–10] complete inversion (three examples in strained systems),[11–13] and mixed retention–inversion (two examples where retention:inversion $\simeq$ 2:1).[14,15] For electrophiles such as Hg^{2+} and Br^+, inversion of configuration is more commonly observed,[1] but the type and arrangement of substituents on the reactant cyclopropane play a major role in determining the stereochemical outcome.[1,16]

The present theoretical study was undertaken to determine what, if any, stereochemical bias is exerted by the substituted cyclopropane during electrophilic attack. Previous molecular orbital calculations have been limited in scope[17] or have only addressed the energies and preferred geometries of the possible intermediate cations.[18,19] The extended Hückel program of Hoffmann[20,21] with modifications by Dugre, Goodisman, and Zumdahl and a CDC-6400 computer were employed here. Bond angles and lengths (given below with distance in ångströms) for cyclopropanol (**1**) and methylcyclopropane (**2**) were fixed at reasonable values[22] in the conformations illustrated below. The Coulomb integrals (H_{ii}) were set equal to the atomic valence-state ionization potential (VSIP) of each orbital in the basis set.[23] Resonance integrals (H_{ij}, $i \neq j$) were calculated within the Mulliken–Wolfsberg–Helmholz approximation[24] with F_x = 1.75. The overlap integrals (S_{ij}) were computed from the atomic coordinates and single Slater function orbital exponents which had been previously optimized by Clementi and Raimondi.[25]



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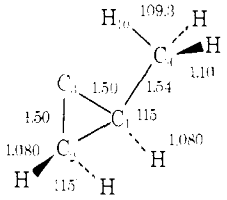

2

To maximize the theoretical return for the time input in our limited exploration of the potential energy surface,[26] five distinct reaction channels for approach of H^+ to substituted cyclopropanes **1** and **2** were examined: (1) edge approach bisecting the C_1–C_2 bond in the plane of the ring, (2) edge approach bisecting the C_2–C_3 bond in the $C_1C_2C_3$ plane, (3) corner approach onto C_2 bisecting the C_1–C_3 bond in the plane of the ring, (4) face approach to the center of the ring syn to OH or CH_3, and (5) face approach anti to OH or CH_3. The first reaction channel leads exclusively to the product of retention in a direct one-step process, the second to the inversion product, and the last three to both products, or mixed retention–inversion.

The calculated energies along each of these approach channels *vs.* the C_2–H^+ separation in ångströms are given in Figures 1 and 2. Overlap populations (OP) confirm the expected bonding to C_2 as reaction progresses along pathways 1, 2, and 3 (*vide supra*). For face approach within pathways 4 and 5, the electrophile experiences weak bonding with all three ring carbons, with C_1 favored over C_2 or C_3 by a factor of two.

The calculations clearly show in-plane C_1–C_2 edge approach to be the preferred reaction pathway (E_a = 0) for both **1** and **2**.[27] In order of increasing activation energy the reaction pathways are as listed above, *i.e.*, $1 < 2 < 3 < 4 < 5$. The relative energetics of these five pathways remained unaffected by charge correction of the electrophile's VSIP,[23] overall charge iteration,[26] and rotation about the substituent–cyclopropane σ bond. Two clear predictions emerge from these findings: (1) direct one-step ring opening should lead exclusively to retention of configuration at the carbon receiving H^+, and (2) formation of corner- or edge-protonated intermediates[18,19,28] should occur through initial C_1–C_2 edge attack.

The unusual stabilization (at least 30 kcal mol^{-1}) affording methylcyclopropane (**2**) plus H^+ within reaction channel 4 (face approach syn to CH_3; see Figure 2) is especially notable. Previous theoretical studies,[18,19] as well as estimates from this work for **2** plus H^+ within reaction channel 5 (face approach anti to CH_3) and cyclopropanol (**1**) plus H^+ within both channels 4 and 5, indicate face protonation to be the least stable configuration. On the other hand, the inference here is that at certain distances beyond chemical bond formation ($R_{C_2-H^+}$ = 2.69–2.23 Å for H^+ 2.5–2.0 Å from the center of the ring while $OP_{C_2-H^+}$ = −0.0069 to −0.0146) a cation syn to an alkyl group may experience significant stabilization by the face of a cyclopropane

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(4) *Cf.* J. A. Berson, *Accounts Chem. Res.*, **5**, 406 (1972).

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(15) A. H. Andrist, C. H. DePuy, and R. H. McGirk, 165th National Meeting of the American Chemical Society, Dallas, Tex., April 1973, Abstract ORGN-10; C. H. DePuy, A. H. Andrist, and P. C. Fünfschilling, *J. Amer. Chem. Soc.*, submitted for publication.

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(22) Tables of Interatomic Distances and Configuration in Molecules and Ions, *Chem. Soc., Spec. Publ.*, **No. 11**, M147, M148, M149, M153 (1958); **No. 18**, M97s, M98s, M107s, M113s (1965).

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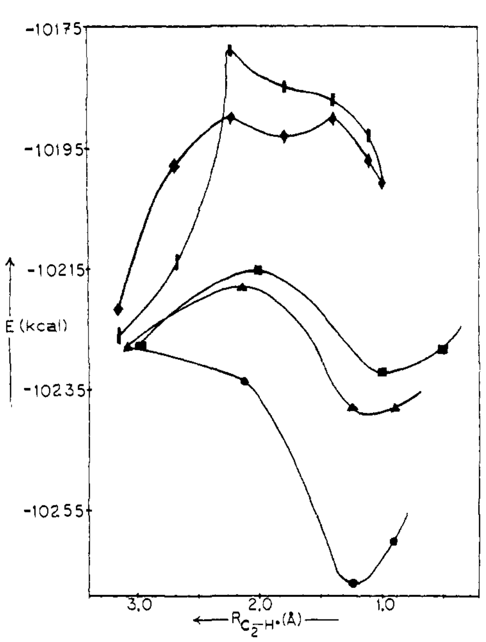


Figure 1. Calculated energies for five H^+ approach channels to cyclopropanol (**1**): (1) 1,2-edge approach (●); (2) 2,3-edge approach (▲); (3) corner approach (■); (4) syn-center face approach (◆); and (5) anti-center face approach (▮).

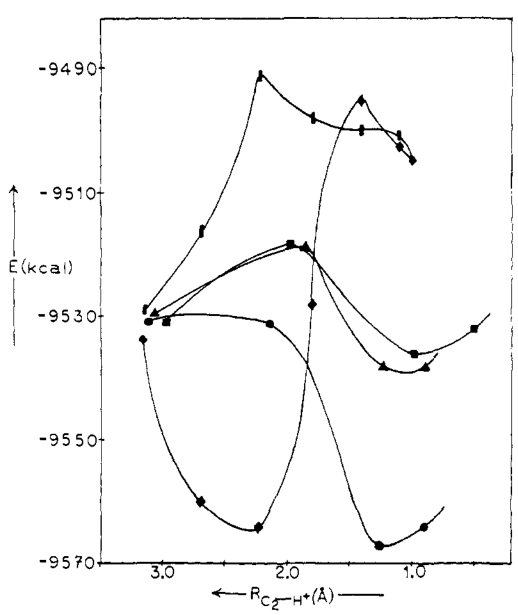
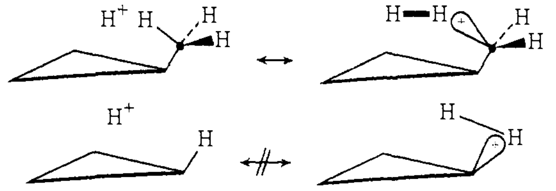


Figure 2. Calculated energies for five approach channels to methylcyclopropane (**2**): (1) 1,2-edge approach (●); (2) 2,3-edge approach (▲); (3) corner approach (■); (4) syn-center face approach (◆); and (5) anti-center face approach (▮).

ring. The exact nature of this interaction is revealed by the resulting overlap populations and atomic charges. At 2.0 Å from the center of the ring the approaching proton withdraws electron density from the proximate C_4–H_{10} bond ($OP_{C_4-H_{10}}$ = 0.3396 *vs.* 0.8216 in unperturbed **2**, while the atomic charge on C_4 increases to +0.3468 from −0.2545) to achieve strong positive overlap with the methyl hydrogen (H_{10}) lying over the cyclopropane ring ($OP_{H_{10}-H^+}$ = 0.6625). The hyperconjugative interaction illustrated below with its resulting cyclopropylcarbinyl resonance hybrid is, therefore, responsible for this unusual stabilization of a face-protonated cyclopropane.[29] A similar interaction in the parent system should be highly unfavorable.



Experimental work[30] on the solvolysis of 4-tricyclyl-trifluoromethanesulfonate has been carried out to gauge the significance of interaction between a cationic center and the face of a cyclopropane ring. While these studies never claimed to bear on the sort of methyl–H^+ interaction uncovered here, the tricyclyl ring system does appear too constrained to permit the hyperconjugation shown above where an alkyl hydrogen is required directly over the face of the cyclopropane ring. Thus, a valid test case has not yet been examined.

Calculations with other electrophiles as well as appropriate experimentation testing the conclusions reached here are in progress.

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[29] Note that stabilization is achieved in the perpendicular conformation with the tetrahedral configuration at C_4; compare G. A. Olah, C. L. Jeuell, D. P. Kelly, and R. D. Porter, *J. Amer. Chem. Soc.*, **94**, 146 (1972); Y. E. Rhodes and V. G. DiFate, *ibid.*, **94**, 7582 (1972); W. C. Danen, *ibid.*, **94**, 4835, 8647 (1972); and W. J. Hehre and P. C. Hiberty, *ibid.*, **94**, 5917 (1972).

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Long-Lived Benzyl and Tolyl Cations in the Gas Phase[1]

Sir:

The tropylium ion, **1**, has been proposed as the structure of $C_7H_7^+$ ions formed in a wide variety of unimolecular reactions. Following the classic original work of Meyerson and his coworkers, it has been shown by ^2H and ^{13}C labeling studies that the decomposition of $C_7H_7^+$ ions from many $C_6H_5CH_2Y$ (Y = H, CH_3, OH, Cl, $CH_2C_6H_5$) and $CH_3C_6H_4Y$ (Y = *p*-CH_3, *p*-Cl) derivatives is accompanied by complete isotopic scrambling.[2] Conflicting ionization potential evidence[3] has led to the proposal that ionization even of benzyl radicals yields **1** ions. However, in particular cases sub-

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[1] Metastable Ion Characteristics. XXX. For paper XXIX see K. Levsen and F. W. McLafferty, *Org. Mass Spectrom.*, in press.

[2] (a) P. N. Rylander, S. Meyerson, and H. M. Grubb, *J. Amer. Chem. Soc.*, **79**, 842 (1957); (b) J. T. Bursey, M. M. Bursey, and D. G. I. Kingston, *Chem. Rev.*, **73**, 191 (1973); (c) S. Meyerson, H. Hart, and L. C. Leitch, *J. Amer. Chem. Soc.*, **90**, 3419 (1968); (d) A. S. Siegel, *ibid.*, **92**, 5277 (1970); (e) although studies of $C_6H_5CD_2C_6H_5$ indicated the tropylium-*1,2-d₂* ion as the precursor of the $C_5(H,D)_5^+$ product ions,[2c] our measurements on this system are consistent with complete scrambling.

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