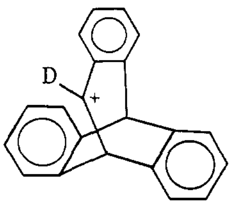
When **2**-Br was irradiated in 95% aqueous acetone (degassed) with a 450-W Hanovia lamp for 9 hr at room temperature in the presence of sodium carbonate, the product mixture (pmr analysis) showed 37% hydrolysis with equal amounts of **2**-OH and **3**-OH and with partial scrambling in the bromide (**2**-Br:**3**-Br = 3:1). A similar experiment (no Na_2CO_3) for 20 hr at 5° gave 50% alcohol (equal quantities of **2**-OH and **3**-OH, analyzed by mass spectral analysis of ketone derived from the alcohol mixture by oxidation[12]) and the recovered bromide was a 2:1 mixture of **2**-Br and **3**-Br (pmr analysis). **1**-Br and **2**-Br were stable to solvolysis and to rearrangement in acetone in the dark for 48 hr at room temperature, and solvolyzed only to the extent of 17% in 90% acetone in 68 hr. Thus, the reactions described above are photoinduced,[13] and clearly proceed *via* cationic intermediates,[14] *viz.*, **4** and **5** or their undeuterated analog, or the corresponding nonclassical ion. The partial deuterium scrambling in the bromide, contrasted with the complete scrambling in the product alcohol, is consistent only with this viewpoint, and also introduces the interesting question of the nature of the return process. We intend to investigate the question of ion-pair intermediates and/or external return in photosolvolysis.



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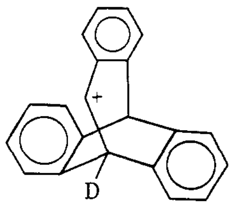

5

It seems to be generally assumed that photosolvolysis occurs from electronically excited states,[2] but our results[10] with triplet sensitizers which can deliver only 70–80 kcal/mol of triplet energy suggest that this is impossible in our examples, unless the triplet energy of a carbenium ion is less than about 50 kcal/mol. We presently prefer the idea that the intermediate immediately preceding the carbenium ion is a vibrationally excited ground state.[9a] Hopefully we will have more precise data in hand in the near future, as well as information on differences, if any, between direct and photosensitized reactions, in this and other systems.

Acknowledgment. The authors are indebted to the National Science Foundation for support of this work.

[12] J. C. Collins, W. W. Hess, and F. J. Frank, *Tetrahedron Lett.*, 3363 (1968).

[13] Work with similar systems[10] has shown that these solvolyses are photosensitized by triplet photosensitizers, and show the typical quenching phenomena for "triplet" reactions.

[14] A small amount of homotriptycene is also produced from 1-Br, presumably *via* radical intermediates.

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The Homoallyl Cation

Sir:

The rapid interconversion of cyclobutyl, cyclopropylcarbinyl, and homoallyl derivatives in solution has come under constant and thorough experimental scrutiny since its discovery several decades ago.[1-3] Although carbocation intermediates were long ago implicated in the mechanism, and although the chemical evidence for them is now overwhelming, it has not been until fairly recently that direct spectroscopic (structural) measurements have been performed.[4] High-resolution proton and carbon-13 magnetic resonance spectroscopy have now provided important information about the symmetry of possible intermediate ions. Such methods, however, cannot yield specific structural data, nor in practice are they normally able to detect several isomeric forms connected by only low-energy barriers.

In this communication we describe the predictions of simple molecular orbital theory on the possible existence of homoallyl-like carbocations, and their relation to the cyclopropylcarbinyl system. Future studies will both further explore the $C_4H_7^+$ potential surface (to include forms of the cyclobutyl cation not considered here), and more deeply probe into the energetics of interaction of carbocationic centers with areas of high electron density.

We employ single determinant *ab initio* molecular orbital theory throughout, utilizing the STO-3G[5] and 4-31G[6] Gaussian basis sets. The STO-3G minimal basis has been shown to be especially suitable for the calculation of molecular equilibrium geometries; it is relatively inexpensive and has on numerous occasions proven its reliability.[7] It is for this purpose that it is employed here. The extended 4-31G functions are more costly to use and only a limited number of calculations have been performed in order to firmly establish the relative energies at selected points on the STO-3G potential surface. All computations have been carried out using the GAUSSIAN 70 series of programs.[8]

It must be cautioned at the outset that the theoretical calculations described herein, as well as those of others,[3] apply rigorously only to isolated molecules. No attempt has been made to account for solvation effects,

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[1] The first report of interconversion between cyclobutyl and cyclopropylcarbinyl derivatives in solution appears to be N. J. Demjanov, *Ber.*, 40, 4393, 4961 (1907). Involvement of homoallyl derivatives was noted some 20 years later, P. Bruylants and A. Dewael, *Bull. Cl. Sci. Acad. Roy. Belg.*, **14**, 140 (1928); *Chem. Zentralbl.*, **99**, 2708 (1928).

[2] Reviews published in the last decade include R. Breslow in "Molecular Rearrangements," Part I, Interscience, New York, N. Y., 1963, pp 233–294; B. Capon, *Quart. Rev., Chem. Soc.*, **18**, 45 (1964); G. D. Sargent, *ibid.*, **20**, 301 (1966); M. Hanack and H. J. Schneider, *Angew. Chem., Int. Ed. Engl.*, **6**, 666 (1967); K. B. Wiberg, B. A. Hess, Jr., and A. J. Ashe III in "Carbonium Ions," Vol. III, Interscience, New York, N. Y., 1972. We thank Professor Wiberg (Yale) for a copy of this latter manuscript before publication.

[3] Applications of semiempirical molecular orbital methods to the $C_4H_7^+$ potential surface include: C. Trindle and O. Sinanoglu, *J. Amer. Chem. Soc.*, **91**, 4045 (1969); N. S. Issacs, *Tetaahedron*, 3555 (1969); K. B. Wiberg and G. Szeimies, *J. Amer. Chem. Soc.*, **92**, 571 (1970); H. Kollmar and H. O. Smith, *Tetrahedron Lett.*, 3133 (1970). No studies at the *ab initio* level have been reported.

[4] G. A. Olah, C. J. Jeuell, D. P. Kelly, and R. D. Porter, *J. Amer. Chem. Soc.*, **94**, 146 (1972), and references cited therein.

[5] W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969).

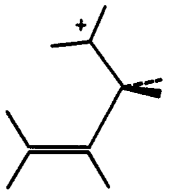
[6] R. Ditchfield, W. J. Hehre, and J. A. Pople, *ibid.*, **54**, 724 (1971).

[7] See, for example: W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, **93**, 808 (1971); L. Radom, W. A. Lathan, W. J. Hehre, and J. A. Pople, *ibid.*, **93**, 5339 (1971); W. A. Lathan, W. J. Hehre, L. A. Curtiss, and J. A. Pople, *ibid.*, **93**, 6377 (1971).

[8] GAUSSIAN 70, a series of programs designed to perform *ab initio* molecular orbital calculations on organic molecules; W. J. Hehre, W. A. Lathan, and J. A. Pople, to be submitted to Quantum Chemistry Program Exchange, University of Indiana, Bloomington, Ind.

but it is hoped that this research may help to lay a foundation for such endeavors.

Initially molecular geometries of the four possible homoallyl cations possessing a plane of symmetry were partially optimized at the STO-3G level.[9] It was found that each of the cis staggered (I), cis perpendicular (II), trans staggered (III), and trans perpendicular (IV) forms was unstable with respect to twisting of the carbon skeleton in the direction of a gauche structure. The molecular symmetry was then relaxed to allow for such geometries but they in turn were found to collapse *without barrier* to the bisected form of cyclopropylcarbinyl (V). Additional calculations at the 4-31G level fully confirmed this behavior. We find that this conversion from cis or trans homoallyl to bisected cyclopropylcarbinyl proceeds with retention at the α carbon and inversion at δ, in agreement with experimental evidence.[10]



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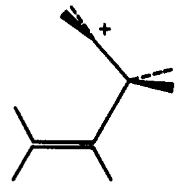

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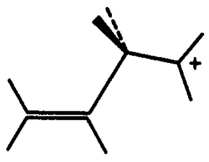

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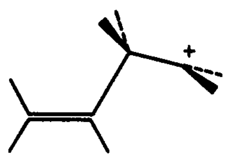
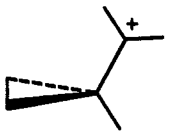
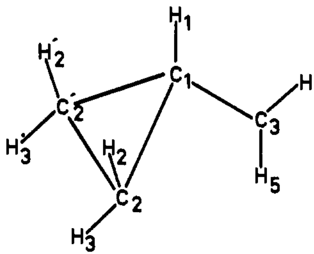


IV



V

The theoretical equilibrium geometry for the bisected form of the cyclopropylcarbinyl carbocation shows shortening of the C_1C_3 bond to a value midway between normal single and double lengths, indicative of a large rotational barrier.[12] Also a large distortion in the cyclopropane ring (decrease in the $C_2C_1C_2'$ angle and increase in the C_1C_2 and C_1C_2' bond lengths) away from threefold symmetry is noted.[13]



$r(C_1C_2) = 1.609$ Å
$r(C_1H_1) = 1.083$ Å
$r(C_2H_2) = 1.088$ Å
$r(C_3H_4) = 1.104$ Å
$\angle C_2C_1C_2' = 53.7°$
$\angle H_1C_1C_{22}'$[11] $= 121.0°$
$\angle H_2C_2C_1 = 110.9°$
$\angle H_3C_2C_1 = 115.3°$
$\angle H_4C_3C_1 = 122.0°$

$r(C_1C_3) = 1.384$ Å
$r(C_2C_2') = 1.454$ Å
$r(C_2H_3) = 1.087$ Å
$r(C_3H_5) = 1.104$ Å
$\angle C_3C_1C_{22}'$[11] $= 120.4°$
$\angle H_2C_2C_2' = 119.5°$
$\angle H_3C_2C_2' = 120.0°$
$\angle H_5C_3C_1 = 121.6°$

Table I. Energy Data (kcal/mol)

Molecule	4-31G	STO-3G
Bisected cyclopropylcarbinyl (V)	0	0
Trans staggered homoallyl (III)	20.0	33.4
Cis staggered homoallyl (I)	21.4	35.0
Trans perpendicular homoallyl (IV)	22.3	32.7
Cis perpendicular homoallyl (II)	23.2	34.4

Table I presents the STO-3G and 4-31G total energies for the $C_4H_7^+$ isomers considered here, relative to the value of the most stable form, cyclopropylcarbinyl. The energies of all forms of the homoallyl cation are within a few kilocalories of each other and all are significantly higher than that of *bisected* cyclopropylcarbinyl.

In conclusion *we find no stable minimum on the* $C_4H_7^+$ *potential surface corresponding to a homoallyl-like cation; all possible structures seemingly collapse without activation to the bisected form of cyclopropylcarbinyl.* It would seem to us that the appearance of solvolysis products derived from homoallyl cations must be accounted for on the basis of solvation effects, or arrive by the rapid capture of a counterion by a metastable homoallyl species. Although previous theoretical studies[14] on carbocation systems generally support the recent conclusions of Traylor and coworkers[15] regarding the importance of vertical stabilization, the present work demonstrates the need for caution in their application.

Acknowledgments. Rewarding discussions with Professors Lionel Salem (Orsay) and Roald Hoffmann (Cornell) are gratefully acknowledged.

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[9] Optimum values for all carbon–carbon bond lengths and all carbon–carbon–carbon bond angles were determined as well as the deviation of the CH_2^+ group away from planarity in the eclipsed structures (II and IV). CH bond lengths were taken at 1.10 Å, angles HC=C and HC^+H at 120°, and the (methylene) HCH angle at 109.5°. Full details are forthcoming.

[10] M. Gasic, D. Whalen, B. Johnson, and S. Winstein, *J. Amer. Chem. Soc.*, **89**, 6382 (1967); D. Whalen, M. Gasic, B. Johnson, and S. Winstein, *ibid.*, **89**, 6384 (1967).

[11] C_1C_{22}' refers to the line bisecting the plane formed by carbons 1, 2, and 2′.

[12] A recent determination using *ab initio* wave functions, but without geometry optimization and assuming rigid rotation, gives a value of 17.5 kcal/mol: L. Radom, J. A. Pople, V. Buss, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **92** 6380 (1970). Full geometry optimization of both bisected and eclipsed forms using the STO-3G basis leads to a 26.3 kcal/mol barrier.

[13] The consequences of interaction of a π-electron acceptor with the valence orbitals of cyclopropane have been discussed: R. Hoffmann, *Tetrahedron Lett.*, 2709 (1970); H. Günther, *ibid.*, 5173 (1970); W. J. Hehre, *J. Amer. Chem. Soc.*, **94**, 5919 (1972).

[14] See, for example, R. Hoffmann, L. Radom, J. A. Pople, P. v. R. Schleyer, W. J. Hehre, and L. Salem, *J. Amer. Chem. Soc.*, in press.

[15] T. C. Traylor, W. Hanstein, H. J. Berwin, N. A. Clinton, and R. S. Brown, *ibid.*, **93**, 5715 (1971), and references therein.

[16] Also part of the Laboratoire de Physico-Chimie des Rayonnements associated with the CNRS.

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