monobasic phosphate ion and bicarbonate ion exhibit an unusual catalytic effect in iminolactone hydrolysis, affecting the nature of the products rather than the rate of hydrolysis.[32] The unusual catalytic behavior is explained by the ability of these buffers to promote a concerted cyclic proton shift in the neutral carbinolamine intermediate. If the nitrogen atom of the enamine were protonated, a similar cyclic proton shift might be a possible explanation for the acceleration of β-carbon atom protonation. This, however, is not the case since the pK_a of the morpholine enamine of propiophenone is considerably less than the pH of the regions in which the unusual catalytic effect is observed, and the observation of general acid catalysis by these buffers requires the N-protonated species to be catalyzed by the basic component of the buffer. The basic component of the bicarbonate buffer system is the carbonate ion which is not bifunctional and consequently cannot participate in a concerted cyclic proton shift. It appears that another explanation is required for acceleration of β-carbon atom protonation of enamines by these bifunctional buffers.

Enamine Basicity. There is considerable disagreement in the literature as to whether enamines are stronger or weaker bases than the corresponding saturated amines. This disagreement results from the fact that an enamine has two possible sites for protonation. In all cases where basicity measurements are known to refer to protonation of the nitrogen atom of the enamine, enamines are found to be weaker bases than the corresponding saturated amines.[15,33] The decreased basicity may be attributed to the electron-withdrawing effect of the double bond and delocalization of the free nitrogen electron pair by resonance. Those cases in which enamines have been reported to be stronger bases than the corresponding saturated amines are situations in which C protonation of the enamine is compared with N protonation of the saturated amine.[34] It is evident from the fact that $K_a > 1/K_1$ that the N-protonated enamine is a weaker base than is the C-protonated species (immonium ion). This inequality also indicates that though formed more slowly the C-protonated species is more stable thermodynamically. It is the greater stability of the C-protonated species that is responsible for its eventual buildup during enamine hydrolysis. An nmr investigation of several aliphatic enamines has also shown that the N-protonated enamine is formed more rapidly but the immonium ion is more stable.[35]

Enamines are normally synthesized in hydrocarbon solvents so that inferences regarding the rate-limiting step in the formation reaction must be made with caution. From observations on synthesis rates from cyclic ketones[5,36] and other considerations it appears likely that carbinolamine dehydration (reverse of eq 3) is the rate-limiting step in the synthesis of many enamines.

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Ground States of σ-Bonded Molecules. XI.[1] Conformational Analyses by MINDO/2 Method[2]

Nicolae Bodor[3] and Michael J. S. Dewar

Contribution from the Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712. *Received December 4, 1969*

Abstract: The MINDO/2 method has been used to predict relative stabilities of the conformers of some alicyclic hydrocarbons, including methyl-substituted cyclohexanes, decalins, and steroids. The results seem to agree well with the available evidence.

Recent work in these laboratories[1,4] has led to the development of a semiempirical SCF MO treatment, including all the valence electrons, which provides good estimates both of molecular geometries and heats of formation. This (MINDO/2) is a development of the original MINDO method,[5] using an improved method of parametrization. In its latest[1] form, MINDO/2 has given surprisingly good estimates of the differences in energy between such pairs of conformational isomers as the eclipsed and staggered forms of ethane, the boat and chair forms of cyclohexane, and the *cis* and *trans* forms of 1,3-butadiene; it therefore seems to offer a promising approach to the general problem of conformational isomerism in alicyclic systems. Here we report some preliminary applications of this kind to a number of cycloparaffin derivatives including a few simple steroids; to our knowledge, no all-valence-electron SCF MO treatment has previously been applied to molecules of this size.

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[1] Part X: N. Bodor, M. J. S. Dewar, A. Harget, and E. Haselbach, *J. Amer. Chem. Soc.*, **92**, 3854 (1970).

[2] This work was supported by the Air Force Office of Scientific Research through Grant No. AF-AFOSR-1050-67.

[3] Robert A. Welch Postdoctoral Fellow. On leave of absence from The Chemical-Pharmaceutical Research Institute, Cluj, Romania.

[4] M. J. S. Dewar and E. Haselbach, *J. Amer. Chem. Soc.*, **92**, 590 (1970).

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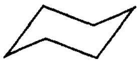
Theoretical Approach

The MINDO/2 method has been fully described in the two previous papers of this series;[1,4] it is a semiempirical SCF MO treatment, including all the valence electrons, based on an approximation equivalent to the EMZDO method of Dixon[6] or the INDO method of Pople, *et al.*[7] Here we used the parameters of part X.[1]

The MINDO/2 method, unlike MINDO/1,[5] leads to good estimates of molecular geometries as well as of heats of formation. In order to make use of this potentiality, one must be able to determine the geometry that minimizes the total energy. Previous calculations of molecular geometries and heats of formation, using empirical potential functions,[8] have been based on prolonged iterative procedures, feasible only because the calculation of the total energy of a given configuration is trivial. This of course is by no means the case when the energy has to be calculated by the MINDO/2 method rather than from simple potential functions; here the calculation of molecular geometry presents an awkward problem. Since no general solution of this was available, we calculated the geometries by brute force, estimating the energies of a large number of configurations near the minimum and interpolating. In order to do this in a reasonable length of time, we were forced to make certain assumptions, as indicated below, in treating the more complex polycyclic systems.

Results and Discussion

Our first objective was to carry out a complete treatment of cyclohexane (I), minimizing the energy with respect to all the molecular parameters; previous MINDO/2 calculations[1,4] had been based on the assumption that the carbon atoms in cyclohexane are tetrahedral, an assumption which is at variance with recent electron diffraction studies.[9] As Table I shows, the present results are in excellent agreement with experiment. The predicted CCC bond angle in particular is close to the measured value and it also lies in the range reported[10] for normal paraffins (*n*-propane,[10a] 111.7°; *n*-pentane,[10b] 112.9 ± 0.2°; *n*-hexane,[10b] 111.9 ± 0.4°; *n*-heptane,[10b] 112.6 ± 0.3°).



I

Table I. Observed and Calculated Geometry and Heat of Formation of Cyclohexane (I)

	Obsd[a]	Calcd
C-C (Å)	1.528 ± 0.005	1.526
C-H (Å)	1.104 ± 0.005; 1.107[b]	1.119[c]
CCC	111.55 ± 0.15	112.11
CCH		110.23
ΔH_f (kcal/mol)	−29.43[d]	−36.25

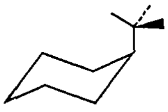
[a] See ref 9. [b] Value given for the C–H bond lengths in 1,4-di-*t*-butylcyclohexane: A. Haaland and L. Schäfer, *Acta Chem. Scand.*, **21**, 2474 (1967). [c] Calculated value reduced by 0.1 Å, according to ref 1 and 4. [d] "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," American Petroleum Institute Research Project 44, Carnegie Press, Pittsburgh, Pa., 1953.

The CCH angle in cyclohexane was not measured. However, the calculated one (110.23°, implying the HCH angle to be 103.5°) is in surprisingly good agreement with the CCH bond angles measured for normal hydrocarbons,[10b] the average value being 110.05 ± 0.42° (for an average CCC angle of 112.45 ± 0.36°).

Next we turned our attention to the other structural element of the steroids, cyclopentane (II), because entropy studies show that its most stable conformation is nonplanar, four carbon atoms lying in a plane with the fifth some 0.4–0.5 Å below.[11,12] Our MINDO/2 calculations confirmed this structure, the deviation of the fifth atom being 0.375 Å and our calculated CC bond length (1.528 Å) agreeing quite well with experiment (1.540 Å[12]). However the calculated difference in energy between this and the planar conformation was only 0.8 kcal/mol, in agreement with the known conformational instability of cyclopentane derivatives due to facile pseudorotation.

II

Next we examined the axial and equatorial conformations of methylcyclohexane, using the CC and CH (ring) bond lengths, and (ring) CCC bond angles, estimated for cyclohexane. The calculated energies and geometries are shown in Table II.



III

IV

The exocyclic CCC angles (111.83° and 110.3°, respectively) may be compared with those measured for 1,4-*cis*-di-*t*-butylcyclohexanes,[13] where the repulsions are much greater (116.50° for the axial and 115.75° for the equatorial *t*-butyl group).

The calculated C–C and C–H bond lengths, and CCC and CCH angles, were next used in calculations for all the dimethylcyclohexanes, in order to predict the corresponding isomerization energies (Table III). The predicted energies are in surprisingly good agreement with the measured ones except that they are again systematically greater, no doubt for the reasons indicated above.

Next we calculated the *cis*- and *trans*-decalins (XIV, XV) and their 9-methyl-derivatives (XVI, XVII), these being the most common units in many natural products. The calculations were carried out using the bond lengths and angles calculated for cyclohexane and its methyl

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(6) R. N. Dixon, *Mol. Phys.*, **12**, 83 (1967).

(7) J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Chem. Phys.*, **47**, 2026 (1967).

(8) F. H. Westheimer in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley & Sons, Inc., New York, N. Y., 1956, p 523; *cf.* N. L. Allinger, J. A. Hirsch, M. A. Miller, I. J. Tyminski, and F. A. Van-Catledge, *J. Amer. Chem. Soc.*, **90**, 1199 (1968).

(9) M. Davis and O. Hassel, *Acta Chem. Scand.*, **17**, 1181 (1963); **18**, 813 (1964).

(10) (a) D. R. Lide, 134th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1958, Paper 28, Petroleum Chemistry; (b) R. A. Bonham, L. S. Bartell, and D. A. Kohl, *J. Amer. Chem. Soc.*, **81**, 4765 (1959).

(11) C. T. Mortimer, "Reaction Heats and Bond Strengths," Pergamon Press, New York, N. Y., 1962.

(12) L. E. Sutton, "Table of Interatomic Distances and Configurations in Molecules and Ions," Special Publications 11 and 18, The Chemical Society, London, 1958 and 1965.

(13) A. Haaland and L. Schäfer, *Acta Chem. Scand.*, **21**, 2474 (1967).

Table II. MINDO/2 Calculations for Axial and Equatorial Methylcyclohexanes

	ΔH_f(obsd),[a] kcal/mole	ΔH_f(calcd), kcal/mol	Geometry (calcd)
ax-Methylcyclohexane (III)	−35.1	−35.22	C–C(Me): 1.543 Å C–H(Me): 1.116 Å $\widehat{\text{CCC}}$(Me): 111.83° $\widehat{\text{HCH}}$(Me): 106.8°
eq-Methylcyclohexane (IV)	−37.0	−39.25	C–C(Me): 1.536 Å C–H(Me): 1.116 Å $\widehat{\text{CCC}}$(Me): 110.30° $\widehat{\text{HCH}}$(Me): 108°

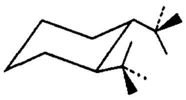
[a] "American Petroleum Institute Project 44," Carnegie Press, Pittsburgh, Pa., 1955.

Table III. MINDO/2 Calculations for Dimethylcyclohexane Isomers

Molecule and geometry	ΔH_f (kcal/mol)		Isomerization energy	
	Obsd[a]	Calcd	Obsd[a]	Calcd
ax-eq-cis (V)	−41.15	−33.80		
			1.87	4.80
eq-eq-trans (VI)	−43.02	−38.60		
ax-ax-trans (VII)		−33.91		
ax-eq-trans (VIII)	−42.20	−37.27		
			1.96	3.95
eq-eq-cis (IX)	−44.16	−41.22		
ax-ax-cis (X)		−27.19		
ax-eq-cis (XI)	−42.22	−37.70		
			1.90	4.16
eq-eq-trans (XII)	−44.12	−41.23		
ax-ax-trans (XIII)		−33.21		

[a] See footnote *a* of Table II.


V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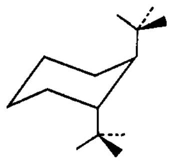
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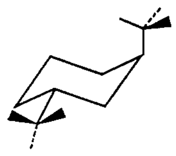
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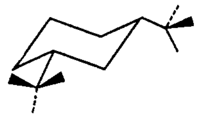
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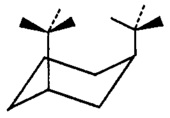
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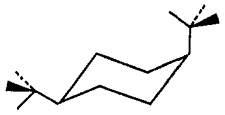
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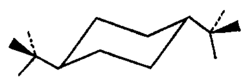
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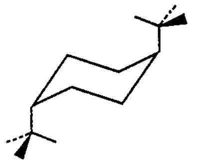
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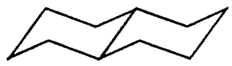
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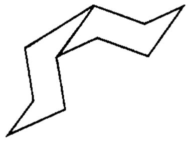
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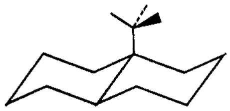
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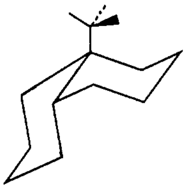
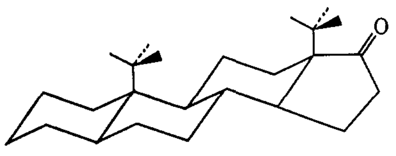

XVII

derivatives, because the measured[9] values for both decalins are closed to those measured and calculated for cyclohexane. The results are shown in Table IV. The calculations again predict too large a difference in energy between the two isomers, due presumably to an overestimate of axial methylene–hydrogen repulsions in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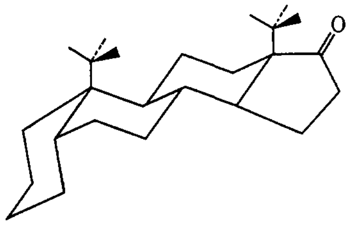
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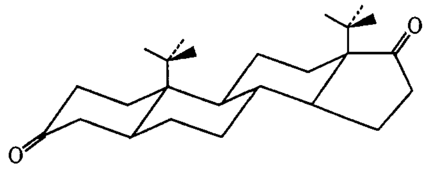
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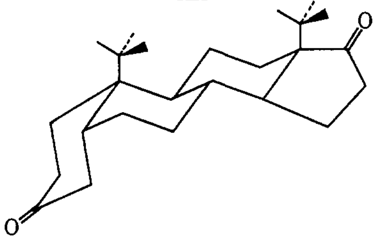

XXI

Table IV. MINDO/2 Calculations on Declains and Steroids

Molecule	ΔH_f (kcal/mol) Obsd	ΔH_f (kcal/mol) Calcd	Isomerization energy Obsd	Isomerization energy Calcd
trans-Decalin (XIV)	−43.57[a]	−45.89		
			3.2	5.4
cis-Decalin (XV)	−40.38[a]	−40.46		
		32.75		
9-Methyl-*trans*-decalin (XVI)			~0.8[b]	
9-Methyl-*cis*-decalin (XVII)		−32.29	1.39 ± 0.64[c]	0.46
5α-Androstan-17-one (XVIII)		−48.13		
				0.46
5β-Androstan-17-one (XIX)		−47.79		
5α-Androstane-3,17-dione (XX)		−79.65		
				0.33
5β-Androstane-3,17-dione (XXI)		−79.32		

[a] T. Miyazawa and K. S. Pitzer, *J. Amer. Chem. Soc.*, **80**, 60 (1958). [b] Estimated value by R. B. Turner, *ibid.*, **74**, 2118 (1952). [c] From the heats of formation measured for liquid isomers, by W. G. Dauben, O. Rohr, A. Labbauf, and F. D. Rossini, *J. Phys. Chem.*, **64**, 283 (1960).

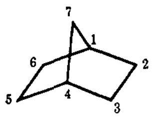
Table V. MINDO/2 Calculations for Norbornane, Bicyclo[2.2.2]octane, and Adamantane

Molecule	ΔH_f (kcal/mol) Lit.	ΔH_f (kcal/mol) Calcd	Geometry Calcd (obsd)
Norbornane (XXII)	−11 ± 2.5[a]	−18.6	C_1–C_2[b] = 1.534 (1.539 ± 0.015) A C_2–C_3 = C_2–C_2 C_1–C_7 = 1.551 (1.568 ± 0.016) Å $\angle C_1C_7C_4$ = 92.84° (93.2 ± 1.5) $\angle\theta$[c] = 114.32° (113.0 ± 1.5)
Bicyclo[2.2.2]octane (XXIII)		−23.8	C–C = 1.534 Å $\angle C_2C_1C_5$ = 108.37° $\angle C_1C_2C_3$ = 110.56°
Adamantane (XXIV)		−34.29	C–C = 1.532 Å $\angle C_2C_1C_4$ = 109.7° $\angle C_1C_2C_3$ = 109.09°

[a] See ref 7. [b] Y. Morino, K. Kuchitsu, and A. Yokozeki, *Bull. Soc. Chim. Jap.*, **40**, 1552 (1967). [c] θ is the angle between the $C_1C_2C_3C_4$ and $C_1C_6C_5C_4$ planes, respectively.

the *cis* isomer, the situation being the same as that in axial methylcyclohexane. Here this interpretation is supported by the good estimate of the *cis–trans* energy difference in 9-methyldecalin; in *trans*-9-methyldecalin, the axial hydrogen–methyl repulsions should be similar to the hydrogen–methylene repulsions in the *cis* isomer. Table IV also lists results for the 5α and 5β isomers of androstan-17-one and androstane-5,17-dione; these predict that the isomers with rings A and B fused *trans* should be the more stable but only by the same narrow margin as in 9-methyldecalin. There is as yet no experimental evidence to test this prediction.

Finally we studied three bicyclic systems of topical interest, namely norbornane (XXII), bicyclo[2.2.2]-octane (XXIII), and adamantane (XXIV). The results are shown in Table V. Note the very good agreement between the calculated and observed geometries for XXII, in particular the values for the CCC bond angle at the 7 position, the small angles in the five-membered rings, and the angle between the 1,2,3,4 and 1,4,5,6 planes. In the case of XXIII and XXIV, the carbon bond angles might have been expected to be close to tetrahedral; the calculated values agree with this intuition. However they lead to the amusing prediction that the CCC bond angles at the bridgeheads in XXIII should be smaller than those of the methylene groups while the reverse should be true for XXIV. While no data are as yet available for XXIII, our prediction is in agreement with recent electron diffraction studies in the case of XXIV.[14]



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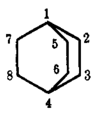

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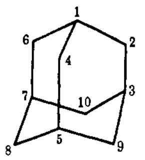

XXIV

Conclusions

The calculations reported here suggest that the MINDO/2 method can give a surprisingly good account of conformational equilibria in cycloparaffins. The results are admittedly less accurate than those derived from purely empirical treatments using empirical potential functions;[8] much even of this difference may well, however, have been due to our inability at the present time to arrive at true equilibrium geometries. The present approach, while obviously more complicated, has the advantage of being applicable to systems of all kinds, including "nonclassical" structures; in this connection we are at present extending it to carbonium ions. If, however, it is to prove generally and genuinely useful, it is essential that some procedure be developed for calculating equilibrium geometries automatically rather than by the shotgun approach we were forced to use here. While such a procedure would be quite impracticable in the case of *ab initio* SCF methods because of the time required for each SCF calculation, the situation is quite different in the case of MINDO/2. Thus the times required (CDC 6600) to calculate a single configuration for some of the molecules listed above were cyclohexane, 14 sec; decalin, 100 sec; androstanedione,

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(14) Personal communication from Dr. I. Hargittai.

10 min. A complete minimization for molecules as large as decalin should not therefore take a prohibitive amount of computer time.[15]

Acknowledgment. The calculations reported here were carried out on the CDC 6600 computer at the University of Texas Computation Center.

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(15) It should be added that these times could be greatly reduced in the case of larger molecules by using a matrix diagonalization subroutine of the Givens type. We have tried all these as they appeared, but we have always encountered special cases where they failed. For the sake of reliability we have therefore so far retained the Jacobi method. We are at present trying the latest version of Givens which is now claimed to be completely reliable; we hope that this will prove to be true.

Stereospecific Cationic Rearrangements of *syn*- and *anti*-Bicyclo[6.1.0]nonane Derivatives[1]

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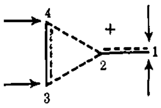
Abstract: Preparations of *syn*- and *anti*-bicyclo[6.1.0]nonan-2-ol (*syn*-**5d**-OH and *anti*-**5d**-OH) are described. Solvolysis of *syn*-**5d**-OPNB in 80% acetone–water gave *syn*-**5d**-OH (61%), *cis*-cyclononen-4-ol (*cis*-**11**-OH) (23%), and *cis*-**11**-OPNB (16%). Under similar conditions, *anti*-**5d**-OPNB gave *anti*-**5d**-OH (96%), *trans*-bicyclo[5.2.0]nonan-*trans*-8-ol (*trans,trans*-**12**-OH) (4%), and *trans,cis*-**12**-OH (trace). Homoallylic brosylate *cis*-**11**-OBs in 80% acetone–water gave *syn*-**5d**-OH (82%) and *cis*-**11**-OH (18%). Hydrolysis of *trans,trans*-**12**-OBs was more complicated. Products in 80% acetone–water were *trans,trans*-**12**-OH, *trans,cis*-**12**-OH, and *trans,cis*-**12**-OBs. At a slightly slower rate, *trans,cis*-**12**-OBs hydrolyzed to a mixture of *trans,trans*- and *trans,cis*-**12**-OH. The stereospecific interconversions of *syn*-**5d**-OH and *cis*-**11**-OH are explained in terms of a nonclassical homoallylic cation (*cis*-**14**). Ionization of *anti*-**5d**-OPNB produces an isomeric homoallylic cation (*trans*-**14**) which can react with solvent to give *anti*-**5d**-OH or isomerize to a nonclassical cyclobutyl cation. The cyclobutyl ion is the precursor of *trans,trans*- and *trans,cis*-**12**-OH.

The cationic interconversions of cyclopropylcarbinyl, homoallylic, and cyclobutyl derivatives are of considerable theoretical and synthetic interest.[3] Early work suggested extensive charge delocalization upon solvolyses of these systems,[4] and subsequent studies, both experimental[5] and theoretical,[6] led to a proliferation of proposed cationic intermediates believed to be important in cyclopropylcarbinyl, homoallylic, and cyclobutyl solvolyses. Both rates and product distributions can be drastically altered by seemingly small changes in substitution or conformation of the parent system. The sensitivity of the parent system to change is partially responsible for the large number of cationic representations. Structures which have enjoyed recent support include the symmetrical homoallylic or bisected ion (**1**),[5d,e,6b–e,7] the homoallylic ion (**2**),[8] the bicyclobutonium ion (**3**),[9] and the symmetrical bicyclobutonium or delocalized cyclobutyl ion (**4**).[6f,10]



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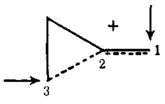

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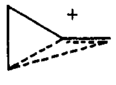

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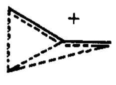

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The solvolytic behavior of many cyclopropylcarbinyl derivatives can best be explained by a symmetrical homoallylic cation (**1**).[5e,7b,7c] Structure **1** is also consistent with the nmr spectra of some cyclopropylcarbinyl cations which were generated in superacid media.[5d,7a,11] However, the results from different systems cannot readily be interpreted in terms of **1**. We

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(1) (a) This research was supported in part by the National Science Foundation. (b) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

(2) (a) This investigation was supported in part by National Institutes of Health Postdoctoral Fellowships 1-F2-GM-29,317-01 and 2-F2-GM-29,317-02 from the Institute of General Medical Sciences. (b) Author to whom inquiries should be addressed at: Department of Chemistry, University of Utah, Salt Lake City, Utah 84112; (c) deceased, November 23, 1969.

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