bution to E_0 of approximately 2 kcal/mol would account for the order of magnitude difference in the exchange rates. Gerson[10] has shown that the unpaired electron can move between the two rings in the paracyclophane radical anion on a time scale which is fast compared to the motion of the counterion. In intermolecular electron-transfer processes, the electron-transfer and counterion-transfer processes are assumed to coincide with one another.[11,12] The observations reported in this communication lead to the conclusion that the electron-transfer rate in these more weakly interacting systems is very sensitive to the structure and energetics of the ion pair and is more strongly coupled to internal rearrangements than in the case of the paracyclophanes.

The inability to observe the metal splitting may be related to the preferential association of the ^{39}K cation with the nitrogen position in the carbazole ring. Examination of the Hückel coefficients for the carbazole molecule (calculated using the heteroatom parameters of Streitwieser[13]) reveals a large excess charge density but an extremely small unpaired spin density at the nitrogen. This is fully consistent with the interpretation of the esr spectrum of **1**.

[10] F. Gerson and W. B. Martin, Jr., *J. Amer. Chem. Soc.*, **91**, 1883 (1969).

[11] F. C. Adam and S. I. Weissman, *ibid.*, **80**, 1518 (1958).

[12] N. Hirota, R. Carraway, and W. Schook, *ibid.*, **90**, 3611 (1968).

[13] A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," Interscience, New York, N. Y., 1961.

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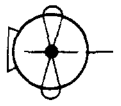
Reactivity of Geometrically Constrained Cyclopropylcarbinyl Systems

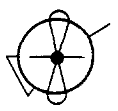
Sir:

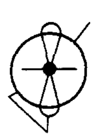
As a result of the many detailed solvolytic studies designed to generate cyclopropylcarbinyl cations,[1-8] numerous structures invoking varying degrees of delocalization have been proposed to account for the specific interactions required or suggested by the various rate enhancements and rearrangements observed in the particular systems studied. Thus, bicyclobutonium,[5] tricyclobutonium,[8] bisected or symmetrical[2] and unsymmetrical[6] homoallylic, and delocalized cyclobutyl[4,7] (symmetrical bicyclobutonium) ions have been proposed.

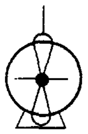
An alternative view arises from consideration of the energy or stabilization of the cyclopropylcarbinyl cation solely (or predominantly) as a function of the angle of rotation of the cyclopropyl group against the planar carbinyl cation; that is, as a function of overlap of a p orbital with the rich in p character exocyclic cyclopropane ring orbitals.

It is generally conceded that the bisected conformation **1** of the cation is the most stable,[9] molecular orbital calculations indicating extremes of stabilization of 9–26 kcal/mol between the bisected (**1**) and perpendicular (**4**) conformations.[2b] Cyclopropylcarbinyl cations in which the bisected conformation is precluded for steric reasons have been observed to have decreased stability.[10,11]


0°
(bisected)
1


30°
2


60°
3


90°
(perpendicular)
4

Recent studies have shown that the perpendicular conformation **4** results in strong *destabilization* of the cation.[2b,d,3a,b] However, there have been no studies of systems in which the ions must be geometrically constrained to conformations in between the bisected (**1**) and the perpendicular (**4**) such as **2** and **3** (30 and 60° off-bisected, respectively). To this end we have synthesized and report preliminary results of studies on the solvolyses of two bridgehead cyclopropylcarbinyl systems, 1-tricyclo[3.2.2.0^{2,4}]nonanyl tosylate (**7-OTs**) and *exo*-1-tricyclo[3.3.1.0^{2,4}]nonanyl 3,5-dinitrobenzoate (**6-ODNB**).

Bridgehead systems were chosen for this study because they are tertiary and hindered from the backside and undergo solvolysis by a limiting mechanism.[12] The bicyclic framework is sufficiently rigid that the carbonium ions formed should have very nearly the same geometry as the initial state. Rearrangements to homoallylic ions[13] or to cyclobutyl derivatives are precluded due to the resultant increase in strain. Rearrangement to another cation can thus have no effect on the reactivity of these cyclopropylcarbinyl compounds.

The tertiary bridgehead alcohol, **7-OH**, was prepared from 1-cyclohexa-1,3-dienyl acetate *via* a Diels–Alder reaction with cyclopropene.[14] Hydrolysis of the adduct followed by hydrogenation on Pd/C gave the alcohol **7-OH**.[15] The tosylate **7-OTs** was prepared according to the method of Coates and Chen.[16] The resulting white crystalline tosylate rapidly turned red at room temperature and became a red oil within a few minutes. Acetolyses were carried out using standard

[1] For reviews see: M. Hanack and H. J. Schneider, *Angew. Chem., Int. Ed. Engl.*, **6**, 666 (1967); R. Breslow in "Molecular Rearrangements," P. deMayo, Ed., Vol. 1, Interscience, New York, N. Y., 1963, Chapter 4; forthcoming reviews by H. G. Richey, Jr., K. B. Wiberg, B. A. Hess, and A. J. Ashe in "Carbonium Ions," Vol. III, G. A. Olah and P. v. R. Schleyer, Ed., Interscience, New York, N. Y., in press.

[2] (a) Z. Majerski and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **93**, 665 (1971); (b) P. v. R. Schleyer and V. Buss, *ibid.*, **91**, 5880 (1969); (c) P. v. R. Schleyer and G. W. Van Dine, *ibid.*, **88**, 2321 (1966); (d) V. Buss, G. Gleiter, and P. v. R. Schleyer, *ibid.*, **93**, 3927 (1971).

[3] (a) J. C. Martin and B. R. Ree, *ibid.*, **92**, 1660 (1970); (b) J. C. Martin and B. R. Ree, *ibid.*, **91**, 5882 (1969).

[4] (a) K. B. Wiberg and G. Szeimies, *ibid.*, **92**, 571 (1970); (b) K. B. Wiberg and G. Szeimies, *ibid.*, **90**, 4195 (1968); (c) K. B. Wiberg and J. G. Pfeiffer, *ibid.*, **92**, 553 (1970).

[5] W. B. Kover and J. D. Roberts, *ibid.*, **91**, 3687 (1969).

[6] C. D. Poulter, E. C. Friedrich, and S. Winstein, *ibid.*, **92**, 4274 (1970).

[7] J. E. Baldwin and W. Fogelsong, *ibid.*, **90**, 4304, 4311 (1968).

[8] G. A. Olah, D. P. Kelly, C. J. Jeull, and R. D. Porter, *ibid.*, **92**, 2544 (1970).

[9] C. U. Pittman, Jr., and G. A. Olah, *ibid.*, **87**, 2998, 5123 (1965).

[10] T. Sharpe and J. C. Martin, *ibid.*, **88**, 1817 (1966).

[11] H. C. Brown and J. D. Cleveland, *ibid.*, **88**, 2051 (1966).

[12] P. v. R. Schleyer, J. L. Fry, L. K. M. Lam, and C. J. Lancelot, *ibid.*, **92**, 2942 (1970).

[13] J. R. Wiseman and J. A. Chang, *ibid.*, **91**, 7775 (1969).

[14] (a) G. L. Closs and K. D. Krantz, *J. Org. Chem.*, **31**, 638 (1966); (b) Y. E. Rhodes, P. E. Schueler, and V. G. DiFate, *Tetrahedron Lett.*, 2073 (1970).

[15] All new compounds gave satisfactory microanalyses and had consistent nmr, infrared, and mass spectra.

[16] R. M. Coates and J. P. Chen, *Tetrahedron Lett.*, 2705 (1969).

kinetic and product work-up procedures except that rates for the reactive tosylate **7**-OTs were followed with the titrimetric procedure used by Wiberg and Hess.[17] The only acetolysis product isolated (greater than 85%) was unrearranged bridgehead acetate, identified by comparison with an authentic sample. The rate data are listed in Table I.

Table I. Solvolytic Rate Constants

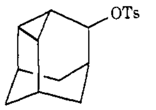
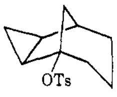
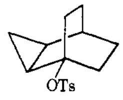
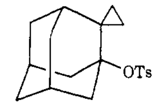
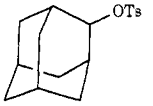
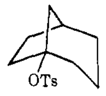
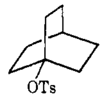
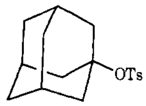
Compd	Solvent	T, °C	$k_1 \times 10^4$, sec^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
7-OTs	HOAc	39.85	19.5 ± 0.1	21.70	−1.71
		45.36	36.8 ± 3.2		
		50.03	59.2 ± 0.7		
		56.03	$115. \pm 1.$		
		25.00[a]	3.25		
11-OTs	HOAc	79.57	0.685 ± 0.010	25.27	−6.26
		87.98	1.68 ± 0.01		
		98.06	4.35 ± 0.06		
		25.00[a]	7.96×10^{-4}		
6-ODNB	49.7% EtOH	92.88	0.124 ± 0.004	28.24	−4.28
		102.07	0.357 ± 0.002		
		132.10	5.99 ± 0.19		
		25.00[a]	1.43×10^{-5}		
t-Bu	49.7% EtOH	25.00[a]	4.84×10^{-4}	26.03	−4.70

[a] Extrapolated from the data at higher temperatures.

The bridgehead alcohol **6**-OH was prepared by Simmons–Smith[18] cyclopropanation of bicyclo[3.2.1]oct-6-en-1-ol isolated from preparative hydrolysis of 1-bicyclo[2.2.1]hept-2-enylcarbinyl tosylate.[19] Cyclopropanation[18] gave only one isomer, assumed to be exo by analogy to cyclopropanation of norbornene, norbornadiene, and 2-bicyclo[3.2.1]octa-3,6-dienol.[20] In addition the cyclopropyl region of the nmr spectrum of **6**-OH was identical with that of *exo*-tricyclo[3.2.1.0^{2,4}]octane[18] derivatives and very different from that of endo derivatives.

The tosylate of this alcohol, **6**-OTs, proved to be even more reactive than that of **7**. Using the Coates procedure[16] white crystals were obtained which turned black in less than 30 sec and titrated for complete ionization. Thus the dinitrobenzoate **6**-ODNB was prepared in the standard manner and used for solvolysis studies. Product analyses after 10 half-lives for this compound also showed no rearrangement, the product consisting solely of unrearranged alcohol **6**-OH and ethyl ether **6**-OEt.

Table II. Relative Acetolysis Rate Constants at 25°

0°	30°	60°	90°
			
5-OTs $1.47 \times 10^{0\,a}$	**6**-OTs $1.4 \times 10^{-3\,c,d}$	**7**-OTs $3.25 \times 10^{-4\,c}$	**8**-OTs $4.20 \times 10^{-6\,f}$
			
9-OTs $5.94 \times 10^{-9\,b}$	**10**-OTs $3.50 \times 10^{-9\,e}$	**11**-OTs $7.96 \times 10^{-8\,c}$	**12**-OTs $8.37 \times 10^{-4\,f}$
Rate Ratio			
2.5×10^{8}	4.0×10^{5}	4.1×10^{3}	5.0×10^{-3}

[a] Reference 7. [b] Reference 12. [c] This work. [d] Calculated using rate ratios from ref 7. [e] R. C. Bingham and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **91**, 3189 (1971). [f] Reference 3.

As the inductive effect of cyclopropane should be constant and independent of angle of orientation, the only variables remaining in these systems are the strain energy, which may be corrected for by the choice of model compounds (see Table II), and the angle of orientation of the cyclopropane to the developing cation, comparable to the conformations of a freely rotating cyclopropylcarbinyl cation. Inspection of relative rate data as a function of angle for the cyclopropylcarbinyl cations studied, Table II, suggests a smooth continuous function of geometry[21] covering a range of reactivity of eleven powers of ten, rather than the discontinuous function implied by the variety of species proposed to explain cyclopropylcarbinyl reactivity in the past. Of particular importance is the observation that the ion with 60° geometry, approximately the geometry of a bicyclobutonium ion, is considerably less stable than the ion with 30 or 0° geometries. It thus appears that the energy of a cyclopropylcarbinyl cation as a function of geometry may be understood as simply as that of an allyl cation.

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[17] K. B. Wiberg and B. A. Hess, *J. Amer. Chem. Soc.*, **89**, 3015 (1967).

[18] (a) H. E. Simmons and R. D. Smith, *ibid.*, **81**, 1256 (1959); (b) H. E. Simmons, E. P. Blanchard, and R. D. Smith, *ibid.*, **86**, 1347 (1964).

[19] J. W. Wilt, C. T. Parsons, C. A. Schneider, D. G. Schultenover, and W. J. Wagner, *J. Org. Chem.*, 33, 694 (1968).

[20] A. F. Diaz, D. L. Harris, M. Sakai, and S. Winstein, *Tetrahedron Lett.*, 303 (1971).

[21] Preliminary analysis of the data suggests a similarity to a cosine function. Detailed analysis and comparison of rates is deferred to the full paper.

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Optical Activity due to Isotopic Substitution. Circular Dichroism of (1*R*)-[2-^{18}O]-α-Fenchocamphoronequinone

Sir:

During the last 25 years many substances have been synthesized which derive optical activity from deuterium substitution.[1] Only one example of optical activity due to other isotopic substitution has been reported: benzyl *p*-tolyl [^{16}O,^{18}O]sulfone.[2] No Cotton effect has

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[1] For reviews on hydrogen–deuterium asymmetry see: D. Arigoni and E. L. Eliel, *Top. Stereochem.*, **4**, 127 (1969); L. Verbit, *Progr. Phys. Org. Chem.*, 7, 51 (1969).

[2] C. J. M. Stirling, *J. Chem. Soc.*, 5741 (1963).