

Cationic Destabilization in a Geometrically Restricted Cyclopropylcarbinyl System

Sir:

The preferred conformation of the cyclopropylcarbinyl cation is bisected (I).¹⁻³ According to molecular orbital calculations⁴ the "perpendicular"⁵ conformation II is less stable than I by a considerable magnitude, variously estimated to be 9 (EHT),^{4a} 19 (ASMO-SCF),^{4b} 26 (CNDO),^{4c} and 22 kcal/mole (NDDO).^{4d}

Direct experimental observations on the dimethylcyclopropylcarbonium ion indicate a high barrier to rotation,⁶ consistent with these theoretical calculations. No other information is available concerning the

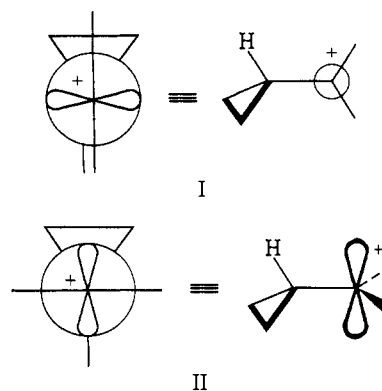


Table I. Solvolysis Rates for 1-Adamantyl Derivatives

Compd	Solvent	Temp, °C	k_1 , sec ⁻¹ ^a	ΔH^\ddagger , kcal/mole	ΔS^\ddagger , eu	k_1 , 25° rel
1-AdCl	50% EtOH	100.6	$(2.44 \pm 0.06) \times 10^{-3}$	22.2	-11.6	
		75.3	$(2.60 \pm 0.02) \times 10^{-4}$			
		25.0	1.00×10^{-6b}			
V	50% EtOH	100.2	$(1.53 \pm 0.05) \times 10^{-5}$	26.2	-10.7	1.0
		76.4	$(1.29 \pm 0.03) \times 10^{-6}$			
		25.0	1.64×10^{-9b}			
VII	50% EtOH	100.6	$(1.79 \pm 0.02) \times 10^{-3}$	23.7	-8.0	1.6×10^{-3}
		76.0	$(1.75 \pm 0.03) \times 10^{-4}$			
		25.0	4.27×10^{-7b}			
VIII	50% EtOH	100.4	$(1.98 \pm 0.04) \times 10^{-3}$	23.1	-9.4	0.4
		76.0	$(2.10 \pm 0.05) \times 10^{-4}$			
		25.0	5.99×10^{-7b}			

^a Rates determined conductometrically. ^b Calculated.

unfavorable perpendicular conformation II.

A few years ago, we attempted to investigate the nature and extent of the interaction between the positive

(1) For a summary of earlier literature references, see G. W. Van Dine and P. von R. Schleyer, *J. Am. Chem. Soc.*, **88**, 2321 (1966). Recent reviews include: (a) M. Hanack and H. J. Schneider, *Fortschr. Chem. Forsch.*, **8**, 554 (1967); *Angew. Chem.*, **79**, 709 (1967); *Angew. Chem. Intern. Ed. Engl.*, **6**, 666 (1967); (b) S. Sarel, J. Yovell, and M. Sarel-Imber, *Angew. Chem.*, **80**, 592 (1968); *Angew. Chem. Intern. Ed. Engl.*, **7**, 577 (1968); (c) H. G. Richey in "Carbonium Ions," Vol. III, G. Olah and P. von R. Schleyer, Eds., Wiley-Interscience, New York, N. Y., 1969; (d) K. B. Wiberg, B. A. Andes, Jr., and A. J. Ashe in ref 1c.

(2) T. Tsuji, I. Moritani, S. Nishida, and G. Tadokoro, *Tetrahedron Letters*, 1207 (1967); *Bull. Chem. Soc. Japan*, **40**, 2344 (1967); T. Tsuji, I. Moritani, and S. Nishida, *ibid.*, **40**, 2338 (1967).

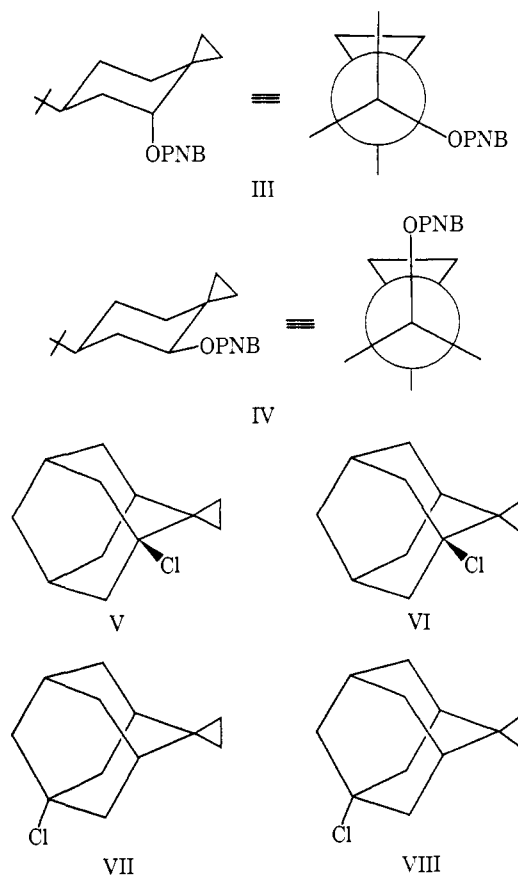
(3) (a) L. Birladeanu, T. Hanafusa, B. Johnson, and S. Winstein, *J. Am. Chem. Soc.*, **88**, 2316 (1966); (b) T. Sharpe and J. C. Martin, *ibid.*, **88**, 1815 (1966); (c) H. C. Brown and J. D. Cleveland, *ibid.*, **88**, 2051 (1966); (d) M. Vogel and J. D. Roberts, *ibid.*, **88**, 2262 (1966); (e) H. G. Richey, Jr., and J. M. Richey, *ibid.*, **88**, 4971 (1966); (f) G. R. DeMare and J. S. Martin, *ibid.*, **88**, 5033 (1966); (g) G. A. Russell and H. Malkus, *ibid.*, **89**, 160 (1967); (h) N. L. Bauld, R. Gordon, and J. Zoeller, Jr., *ibid.*, **89**, 3948 (1967); (i) P. R. Brook, R. M. Ellam, and A. S. Bloss, *Chem. Commun.*, 425 (1968); (j) G. H. Schmid and A. Brown, *Tetrahedron Letters*, 4695 (1968); (k) A. P. Krapcho, R. C. H. Peters, and J. M. Conia, *ibid.*, 4827 (1968); (l) F. A. Carey and H. S. Tremper, *J. Am. Chem. Soc.*, **91**, 2967 (1969); (m) J. K. Kochi, P. J. Krusic, and D. R. Eaton, *ibid.*, **91**, 1877 (1969); (n) J. E. Baldwin and W. D. Foglesong, *ibid.*, **90**, 4303 (1968); (o) J. A. Berson, G. M. Clarke, D. Wege, and R. G. Bergmann, *ibid.*, **90**, 3238 (1968); (p) K. B. Wiberg and G. Szeimies, *ibid.*, **90**, 4195 (1968); (q) G. A. Olah and C. H. Lin, *ibid.*, **90**, 6468 (1968).

(4) (a) R. Hoffmann, *J. Chem. Phys.*, **40**, 2480 (1964); *Tetrahedron Letters*, 3819 (1965); (b) T. Yonezawa, H. Nakatsuji, and H. Kato, *Bull. Chem. Soc. Japan*, **39**, 2788 (1966); (c) K. B. Wiberg, *Tetrahedron*, **24**, 1083 (1968); (d) V. Buss, to be published. For other recent calculations, see J. E. Baldwin and W. D. Foglesong, *J. Am. Chem. Soc.*, **90**, 4311 (1968); K. B. Wiberg and G. Szeimies, *ibid.*, **91**, 4195 (1969); and C. Trindle and O. Sinanoglu, *ibid.*, **91**, 4054 (1969).

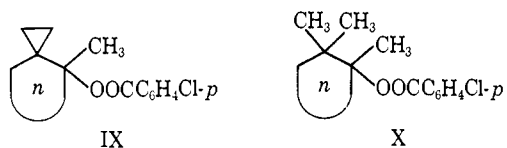
(5) This seems a better descriptive term for II than those used in the past: "crown,"^{3c} "nonbisected,"^{4b} "symmetrical,"^{3h} "out-of-plane,"^{4e} etc.

(6) C. U. Pittman, Jr., and G. A. Olah, *J. Am. Chem. Soc.*, **87**, 2998 (1965); cf. C. D. Poulter and S. Winstein, *ibid.*, **91**, 3650 (1969).

charge and the cyclopropane ring by determining the solvolysis rates of III and IV.⁷ It was reasoned that



(7) R. Gleiter, unpublished observations.

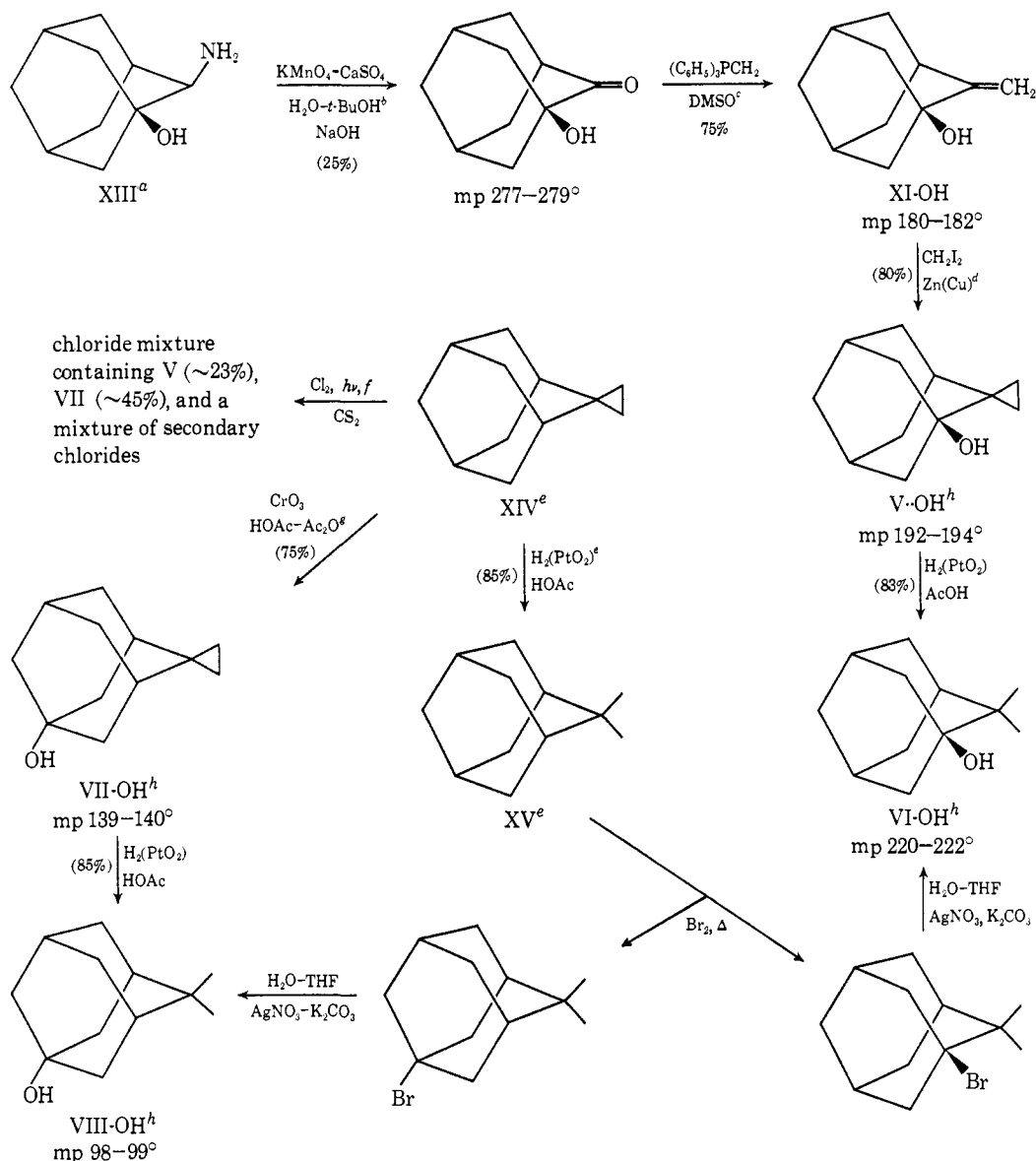


while III should readily give an ion with favorable conformation (I), IV might be unfavorable since the transition state for reaction might resemble II. However,

To this end, we have synthesized the bridgehead adamantanyl derivative V which also possesses conformation IV, along with model compounds VI–VIII. The routes used are summarized in Chart I. The nmr spectra and analytical data are fully in accord with the structures proposed.⁹

The solvolysis rates of V–VIII and of 1-chloroadamantane were determined in 50% ethanol. With the

Chart I. Outline of Synthetic Sequences Employed



^a W. V. Curran and R. B. Angier, *Chem. Commun.*, 563 (1967). ^b Procedure of S. S. Rawalay and H. Shechter, *J. Org. Chem.*, **32**, 3129 (1967). ^c Procedure of R. Greenwald, M. Cheykovsky, and E. J. Corey, *ibid.*, **28**, 1128 (1963). ^d Cf. H. E. Simmons and R. D. Smith, *J. Am. Chem. Soc.*, **81**, 4256 (1959); E. LeGoff, *J. Org. Chem.*, **29**, 2048 (1964). ^e C. W. Woodworth, V. Buss, and P. von R. Schleyer, *Chem. Commun.*, 569 (1968); J. Vais, J. Burkhard, and S. Landa, *Z. Chem.*, **8**, 303 (1968). ^f Cf. G. W. Smith and H. D. Williams, *J. Org. Chem.*, **26**, 2207 (1961). ^g P. von R. Schleyer and R. D. Nicholas, Abstracts, 140th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1961, p 75Q. ^h Treatment with thionyl chloride gave the corresponding chloride.

experimental fact did not verify these hopes, since the III:IV reactivity ratio was only 2!⁸ It was clear that the *t*-butylcyclohexyl system was insufficiently rigid to prevent IV from achieving a conformation in which cyclopropylcarbonyl resonance was possible. A still more rigid system was indicated.

exception of VI, all compounds gave normal first-order rate constants; the appropriate data are given in Table I. The solvolysis of VI will be described separately as the abnormal behavior of this compound is not pertinent to the point of this paper. All solvolysis prod-

(8) For other examples of the lack of appreciable rate and product discrimination in polycyclic cyclopropylcarbonyl systems, see ref 1, 3i,j.

(9) During the course of this work, we became aware of similar studies at the University of Illinois.¹⁰ We thank Professor J. C. Martin for exchanges of information.

(10) J. C. Martin and B. Ree, *J. Am. Chem. Soc.*, **91**, 5882 (1969).

ucts corresponded to unrearranged alcohols and ethers to an extent greater than 90% (by nmr).

The results with V are startling! Instead of the many powers of ten rate enhancement usually associated with cyclopropylcarbinyl systems,¹⁻³ V reacts almost 10³ more slowly than the model compounds. V is held rigidly in conformation IV. During solvolysis, the developing orbital is constrained to be perpendicular to the cyclopropane ring, *i.e.*, as in II, except for the necessary bending down of the bonds in the adamantane ring. The geometry in V is also not favorable for cyclopropylcarbinyl-cyclobutyl ring expansion nor for ring opening to an allylcarbinyl system. These reactions do not take place either. Thus, there should be no assistance to ionization in V at all, and the solvolysis rate of this compound provides a good indication of what is to be expected in "nonconjugated" II. The observed destabilization and rate depression can be attributed to the electron-withdrawing sp² character of the external cyclopropane bonds.¹

The difference in solvolysis rates between IX (fast) and X (slow) is about 10^{4.3} (*n* = 5 and 6).² In V, the deceleration is about 10³. Thus a rough estimate of the energy difference between I and II (in tertiary systems as solvolysis transition states) is 10 kcal/mol, corresponding to a 10⁷ rate ratio. In the free ions themselves, this difference might be much larger.⁶

Thus, the stabilization of even a tertiary ion by an adjacent cyclopropane ring is very large, a stabilization which can best be understood in terms of a resonance-type or C-C hyperconjugative interaction,^{1,3,4,11} which, of course, is highly geometry dependent.

Acknowledgments. This work was supported by grants from the National Science Foundation, the National Institutes of Health (AI-07766), and the Petroleum Research Fund, administered by the American Chemical Society.

(11) The apparently low methyl:hydrogen ratios, used by Japanese authors as evidence against this interpretation,² can be explained in an alternative manner.¹²

(12) J. L. Fry and P. von R. Schleyer, *J. Am. Chem. Soc.*, in press.

(13) Princeton University Fellow, 1968-1969.

Paul von Ragué Schleyer, Volker Buss¹³

Department of Chemistry, Princeton University
Princeton, New Jersey 08540

Received July 7, 1969

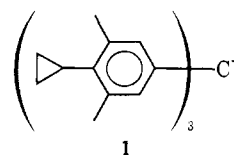
Destabilization of a *t*-Alkyl Cation by an α -Cyclopropyl Substituent. Perpendicularly Twisted Cyclopropylcarbinyl and Allylic Tosylates

Sir:

There is mounting evidence¹⁻⁶ that the maximum interaction between a cyclopropyl ring and an adjacent electron-deficient carbon, as in the cations derived from

cyclopropyl carbinols, occurs when the plane of the three-membered ring is parallel to the adjacent p orbital, *i.e.*, the "bisected"^{1,6} conformation or its equivalent.⁵

This has been shown in equilibrium studies² (*pK_R⁺* of triarylcarbinols) and rate studies³ (cumyl chloride solvolyses) in systems such as 1 in which the flanking *o*-methyls prevent the attainment of the bisected geometry by the cyclopropyl ring, making it even less electron releasing than the isopropyl group. The nmr chemical shift evidence² for a substantial residue of charge delocalization into the cyclopropyl group even in the "twisted" geometry of 1 raised the question of



whether some delocalization is still possible in the unfavored 90°-twist geometry or whether the effect seen in 1 is to be attributed to the failure of the *o*-methyl substituents to constrain the cyclopropyl substituent to a perfect 90°-twist conformation.

We wish to report the results of solvolysis studies on the *p*-toluenesulfonate ester of 1-hydroxyadamantane-2-spirocyclopropane (3c) in which the cyclopropane ring is held rigidly in the twisted conformation. The results of acetolyses of tosylates 2c-5c are shown in Table I.

Table I. Acetolyses of Adamantyl Tosylates at 45°

Tosylate	<i>k</i> , sec ⁻¹ ^a	<i>k_{rel}</i>	ΔH^\ddagger , kcal/mol ^b	ΔS^\ddagger , eu ^b
2c ^c	7.76×10^{-3}	1.1×10^4	20.3	-4.5
3c	5.03×10^{-5}	73	23.3	-5.0
4c	1.81×10^{-2}	2.6×10^4	19.0	-7.0
5c	8.0×10^{-7} ^d	1	26.7	-3.0

^a With 0.02 *M* added NaClO₄. ^b Activation parameters determined over temperature ranges of from 25 to 40°. ^c P. von R. Schleyer and R. D. Nicholas, *J. Am. Chem. Soc.*, **83**, 2700 (1961), report *k*_{25°} = 5.86×10^{-4} compared with our value, 5.15×10^{-4} sec⁻¹. ^d Extrapolated from data at higher temperatures.

In each case, unrearranged acetate is the predominant product.

Carbinol 6a, mp 278-281° (sealed tube), was prepared in 38% yield by the magnesium sulfate buffered potassium permanganate oxidation⁷ of 2-aminoadamantan-1-ol⁸ in *t*-butyl alcohol-water solution at 25°. Treatment of 6a with triphenylphosphine methyldide in DMSO gave 33% of 5a, mp 181-183° (sealed tube). Carbinol 3a, mp 193-195° (sealed tube), was prepared in 83% yield by treating 5a with the Simmons-Smith reagent.⁹ Hydrogenolysis¹⁰ of 3a afforded 4a, mp

(7) S. S. Rawalay and H. Shechter, *J. Org. Chem.*, **32**, 3129 (1967).

(8) W. V. Curran and R. B. Angier, *Chem. Commun.*, 563 (1967).

(9) E. LeGoff, *J. Org. Chem.*, **29**, 2048 (1964).

(10) C. W. Woodworth, V. Buss, and P. von R. Schleyer, *Chem. Commun.*, 569 (1968); J. Vais, J. Barkhardt, and S. Landa, *Z. Chem.*, **8**, 303 (1968).

(1) For a review see H. G. Richey, Jr., in "Carbonium Ions," Vol. 3, G. A. Olah and P. von R. Schleyer, Ed., John Wiley & Sons, Inc., New York, N. Y., 1969.

(2) T. Sharpe and J. C. Martin, *J. Amer. Chem. Soc.*, **88**, 1817 (1966).

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

(4) J. E. Baldwin and W. D. Foglesong, *ibid.*, **90**, 4311 (1968).

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

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