The subsequent ring opening of II by the chloride, however, cannot simply be predicted on the basis of the electronic effects underlying the Markovnikov rule. In the case of alkyl substituents apparently little or no partial charge is developed on the carbon atoms involved in intermediate II. Therefore, steric factors control the formation of products III. This is particularly surprising in view of the poor nucleophilicity of the chloride ion. With electronically more biased substrates, such as styrene, electronic effects become increasingly important in II, thus affording Markovnikov products IV.

Further data substantiating the above mechanistic conclusions, defining the scope of this reaction and the nature of the rearrangement, will be presented in a full paper.

Acknowledgment. The authors wish to thank Mr. W. C. Whitlock for excellent technical assistance.

W. H. Mueller, P. E. Butler

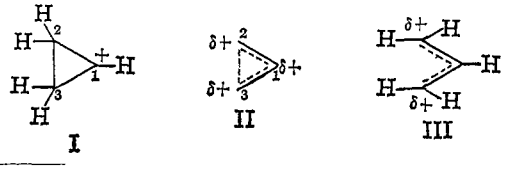
Central Basic Research Laboratory and Analytical Research Division
Esso Research and Engineering Co., Linden, New Jersey

Received March 26, 1966

Steric and Electrocyclic Control of Cyclopropyl Tosylate Solvolysis Rates

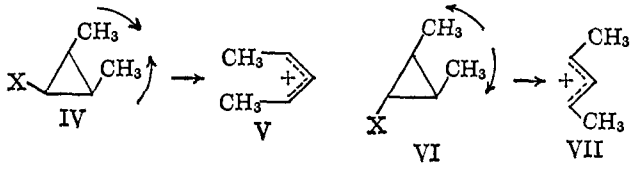
Sir:

Carbonium ion reactions of cyclopropyl derivatives generally lead to allyl rather than to cyclopropyl products.[1,2] The cyclopropyl cation (I) must have a high propensity toward rearrangement to the more stable allyl cation (III). Despite the slow rate of acetolysis of cyclopropyl tosylate,[2] which masks the presence of anchimeric assistance,[3] it appears likely that the ionization and ring-opening processes are concerted.[3-5] The solvolysis transition state resembles II (or III) rather than I, with considerable charge delocalization to C-2 and C-3 and away from C-1.[4-6] Carbonium ion stabilizing substituents produce abnormally small rate enhancements when substituted for hydrogen at C-1 in cyclopropyl derivatives,[5,6] but substantial rate accelerations result from attachment at C-2 or C-3.[4,5]



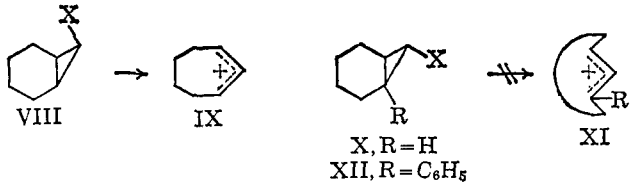
I II III

Woodward and Hoffmann predicted that electrocyclic opening of cyclopropyl cation I to allyl cation III should be stereospecific and "disrotatory," *i.e.*, groups in I *cis* at C-2 and C-3 should rotate *toward* or *away from* one another in proceeding to III.[7] The direction of disrotatory opening should further depend on the stereochemical disposition of the leaving group, in the manner shown below,[7] as also has been suggested by DePuy.[5]



IV V VI VII

The implications of these predictions with regard to solvolysis rates of cyclopropyl derivatives are definite. *If ring opening and ionization are simultaneous*, VI should react faster than IV. In VI the *cis*-methyl groups would move apart, relieving strain, while in IV they would move closer together, increasing strain. *If ionization precedes ring opening and a cyclopropyl cation intermediate intervenes*, then there should be little difference in the solvolysis rates of IV and VI.



VIII IX X, R = H XII, R = C_6H_5 XI

Extension of these ideas to the bicyclic series leads to predictions the reverse of those in monocyclic systems. Compounds with *endo* configurations, as in the norcaryl derivative VIII, should react rapidly by a concerted mechanism because the *cis*-allylic configuration IX is favored in a ring structure. By contrast, *trans* opening (such as X to XI) is impossible, at least with rings with common size, and unassisted solvolysis through classical-type transition states might be anticipated for *exo* isomers X.

Experimental results partially verifying these predictions have been published recently.[5,8] DePuy and co-workers have found *trans*-2-phenylcyclopropyl tosylate to acetolyze 15 times faster than the *cis* isomer.[5] The norcaryl derivative XII was reported qualitatively to be very unreactive under the same conditions.[5] Cristol, Sequeira, and DePuy[8] showed that acetolysis of VIII (X = Cl) was at least 180 times faster than X (X = Cl). The rate of X (X = Cl) was too slow to be measured under these conditions, and no comparison could be made with cyclopropyl itself, for the acetolysis rate of cyclopropyl chloride was not determined.

Acetolysis of the corresponding cyclopropyl tosylates[9]

(1) (a) Cyclopropylamine deaminations: N. Kishner, *J. Russ. Phys. Chem. Soc.*, 37, 304 (1905); P. Lipp, J. Buchkremer, and H. Seeles, *Ann.*, 499, 1 (1932); E. J. Corey and R. F. Atkinson, *J. Org. Chem.*, 29, 3703 (1964). Compare D. E. Applequist and G. F. Fanta, *J. Am. Chem. Soc.*, 82, 6393 (1960); J. E. Hodgkins and R. J. Flores, *J. Org. Chem.*, 28, 3356 (1963). Contrast R. Pettit, *J. Am. Chem. Soc.*, 82, 1972 (1960); P. Lipp and C. Padberg, *Ber.*, 54B, 1316 (1921); H. Hart and R. A. Martin, *J. Am. Chem. Soc.*, 82, 6362 (1960). (b) Reviews: R. Breslow in "Molecular Rearrangements," Vol. I, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, pp 256–259; W. Kirmse, "Carbene Chemistry," Academic Press Inc., New York, N. Y., 1964, pp 169–174. Also see references below and papers therein cited.

(2) J. D. Roberts and V. C. Chambers, *J. Am. Chem. Soc.*, 73, 5034 (1951).

(3) P. von R. Schleyer and R. D. Nicholas, *ibid.*, 83, 182 (1961); P. von R. Schleyer, *ibid.*, 86, 1856 (1964).

(4) J. A. Landgrebe and D. E. Applequist, *ibid.*, 86, 1536 (1964).

(5) C. H. DePuy, L. G. Schnack, J. W. Hausser, and W. Wiedemann, *ibid.*, 87, 4006 (1965); acetolysis of 1-methylcyclopropyl tosylate is only 180 times faster than cyclopropyl tosylate at 150°: P. Isele, unpublished observations.

(6) E. F. Cox, M. C. Caserio, M. S. Silver, and J. D. Roberts, *ibid.*, 83, 2719 (1961).

(7) R. B. Woodward and R. Hoffmann, *ibid.*, 87, 395 (1965). Also see H. C. Longuet-Higgins and E. W. Abrahamson, *ibid.*, 87, 2045 (1965).

(8) S. J. Cristol, R. M. Sequeira, and C. H. DePuy, *ibid.*, 87, 4007 (1965); also L. Skattebøl, *J. Org. Chem.*, 31, 1554 (1966); C. W. Jefford and R. Medary, *Tetrahedron Letters*, No. 19, 2069 (1966); J. W. Hausser, N. J. Pinkowski, and J. O. Frohliger, Abstracts, 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966, p124K; Prof. G. Closs, private communication.

(9) Cyclopropanols were prepared by the method of J. Paust and U. Schöllkopf (*Angew. Chem.*, 77, 262 (1965)) and were converted to tosylates by conventional procedure. Stereochemical assignments were made by analysis of the nmr spectra, taking particular advantage of the magnitude of the *CH*–*CH*OTs coupling constants: *cis*, *ca.* 6.5 cps; *trans*, *ca.* 2.5 cps.[5,8]

Table I. Relative Acetolysis Rates of Cyclopropyl Tosylates

	Cyclopropyl tosylates[a]	Rel rate at 100°	Calcd rate[a] at 100°	Rel rate at 150°
1	Parent	1.0[b]	1	1.0[c]
2	*exo*-7-Norcaryl (X, X = OTs)	1.7		0.9
3	*endo*-7-Norcaryl (VIII, X = OTs)	19,000		5,100
4	2-*cis*-3-*cis*-Dimethyl (IV, X = OTs)		1.7	4.0
5	2-*trans*-3-*trans*-Dimethyl (VI, X = OTs)	41,000	22,000	18,000
6	2-*cis*-3-*trans*-Dimethyl	490	570	260
7	2,2-Dimethyl	470	570	330
8	2,2,3-*cis*-Trimethyl		120	80
9	2,2,3-*trans*-Trimethyl	48,000	175,000	
10	2,2,3,3-Tetramethyl	8,050	38,000	5,500

[a] See text. [b] $k_1 = 3.89 \times 10^{-8}$ sec^{-1}. [c] $k_1 = 7.76 \times 10^{-6}$ sec^{-1}. Both these rate constants calculated from data of Roberts and Chambers.

extends these observations; data from ten compounds are summarized in Table I. The *exo* compound X (X = OTs) reacts slowly, about as fast as cyclopropyl tosylate and 11,000 times less rapidly than its *endo* isomer VIII (X = OTs). Nevertheless, we do not regard this result to be necessarily an unambiguous confirmation of the Woodward–Hoffmann predictions for in certain instances bicyclic compounds give anomalous results. For example, 9-*exo*-bicyclo[7.1.0]nonyl tosylate solvolyzes considerably *faster* than its *endo* isomer, behavior opposite that of VIII and X. A full account of these peculiarities and their explanation will be reported subsequently. The monocyclic tosylates (Table I) are free from these difficulties.

Our results (Table I) fully confirm the Woodward–Hoffmann predictions for cyclopropyl cation opening and provide additional evidence for the concerted nature of cyclopropyl solvolyses. The all-*cis* compound IV solvolyzes 4500 times slower than its epimer VI at 150°. Similarly in the 2,2,3-trimethylcyclopropyl series the *cis* isomer is appreciably slower than the *trans*. It is important to realize, however, that the Woodward–Hoffmann predictions do not, in themselves, provide a method for the quantitative analysis of these results. We present here the outline of a possible interpretation based on a consideration of electronic and steric factors in ground and transition states. Among the many assumptions implicit in this rough treatment is that the reaction has proceeded substantially toward the open allyl cation (as III) in the transition state and that the electrocyclic opening process is highly specific.

1. Electronic Factor. The rate enhancements recorded in Table I due to alkyl substitution are chiefly electronic in origin. For the dimethyl compounds **4–7** (Table I) a factor of 5000 rate increase due to the greater stabilization provided the protoallylic transition state during ionization is assumed. This factor, about 70/methyl ($70.7^2 = 5000$), is of reasonable magnitude for the additional stabilization provided by methyl in a highly delocalized transition state.[10]

2. Steric Factors. The extra ground-state strains due to nonbonded interactions between substituents on the same side of a cyclopropane ring are estimated to be the following: two methyls, 1.1 kcal/mole;[11] two methyls and a tosyl group, 1.7 kcal/mole; one methyl and a tosylate, negligible strain. The extra nonbonded strains in the transition states are estimated from the best models available: two methyls in the "interior" of the allyl cation (as in V), 7.6 kcal/mole (model: 1,8-dimethylnaphthalene);[12] one methyl in the "interior" (*e.g.*, V with one methyl replaced by hydrogen), 1.6 kcal/mole (model: 1-methylnaphthalene);[12] no strain in VII.

Using these steric and electronic factors the rates of compounds **4–10** (Table I) can be calculated. At 100°, assuming entropy differences to be negligible, 1.7-kcal/mole strain difference between ground and transition state is equal to a power of ten in rate. The general formula for the calculations is simple: rate relative to cyclopropyl tosylate = electronic factor due to alkyl substituents $\times 10^{[(\text{ground state} - \text{transition state strains, in kcal/mole})/1.7]}$. For **4**, $5000 \times 10^{[(1.7-7.6)/1.7]} = 1.7$; for **5**, $5000 \times 10^{[(1.1-0)/1.7]} = 22{,}000$; for **6** and **7**, $5000 \times 10^{[0-6.6)/1.7]} = 570$. The same scheme is "successful" with **8**, assuming that the third methyl group contributes an additional electronic factor of 70: $5000 \times 70 \times 10^{[(1.7-7.6)/1.7]} = 120$. With **9**, the agreement between calculation and experimental values is poorer than with **4–8**: $5000 \times 70 \times 10^{[(1.1-1.6)/1.7]} = 175{,}000$. With **10**, 5000^2 (four methyls) $\times 10^{[(2.8-7.6)/1.7]} = 38{,}000$, an even larger discrepancy is observed. Perhaps the additional methyl groups do not contribute electronically to a constant extent and a leveling effect is responsible for the deviations of the tri- and tetramethyl derivatives **9** and **10**. Alternatively, a buttressing effect may be operating or the neglect of entropy may be introducing error. The approach is crude, the assumptions are many, but the over-all success (Table I) is surprisingly good.

The importance of the interpretation presented here is not the degree of agreement of calculation with experiment, but the reasonableness of the approach and the verification of the soundness of the basic mechanistic assumptions made. If the degree of Woodward–Hoffmann electrocyclic selectivity were small, and if there were not considerable progress toward the allyl cation in the cyclopropyl tosylate solvolysis transition state, then the wide variations in rate (Table I) would not have been found.

Acknowledgments. We wish to thank the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research at Princeton University, and the Deutschen Forschung-Gemeinschaft and the Fonds der Chemischen Industrie for support of the work at the University of Göttingen.

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(14) American Machine and Foundry Fellow, 1963–1964.

Paul von R. Schleyer,[13] George W. Van Dine[14]
Department of Chemistry, Princeton University
Princeton, New Jersey 08540

Ulrich Schöllkopf, Joachim Paust
Organisch-Chemisches Institut der Universität Göttingen
34 Göttingen, Germany

Received April 6, 1966