

with a mixture of Carbowax and KOH, but separation from II was precluded by the inefficiency of the column.

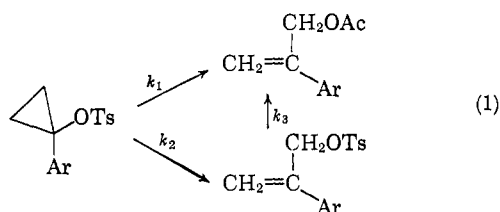
K. E. Wilzbach, Louis Kaplan
Chemistry Division, Argonne National Laboratory
Argonne, Illinois
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Chemistry of Cyclopropanols. III. The Mechanism of the Solvolysis of Cyclopropyl Tosylates

Sir:

Cyclopropyl tosylate undergoes solvolysis reactions at an exceedingly slow rate, 175° being required for its acetolysis.¹ The product of the solvolysis is allyl acetate, resulting from ring opening. In this communication we wish to report on various unusual aspects of this type of transformation.

As expected, 1-arylcyclopropyl tosylates² solvolyze much more rapidly than cyclopropyl tosylate itself, although the reactions are complicated by internal return. The relevant transformations are shown in



eq. 1. At 108° in acetic acid–sodium acetate the first-order rate constants for the unsubstituted case (Ar = C₆H₅) are $k_1 = 1.9 \times 10^{-3} \text{ sec.}^{-1}$, $k_2 = 8.2 \times 10^{-3} \text{ sec.}^{-1}$, and $k_3 = 4.0 \times 10^{-4} \text{ sec.}^{-1}$. The Hammett³ ρ values for the two pertinent reactions are -4.4 ($r = 0.996$)³ for the process corresponding to k_1 and -4.0 ($r = 0.999$)³ for the process corresponding to k_2 .⁴ No 1-phenylcyclopropyl acetate is formed, although it is stable to the reaction conditions.

A more interesting observation is that both *cis*- and *trans*-2-arylcyclopropyl tosylates² solvolyze faster than cyclopropyl tosylate itself, although the inductive effect of the phenyl group might have been expected to decrease the rate. Thus, at 108° the first-order rate constant for acetolysis of *trans*-2-phenylcyclopropyl tosylate is $3.2 \times 10^{-3} \text{ sec.}^{-1}$, and the *cis* isomer reacts at one-fifteenth of this rate. The Hammett ρ value for the solvolysis of a series of *trans*-2-arylcyclopropyl tosylates is -1.8 ($r = 0.95$).⁴ The product of the solvolysis is cinnamyl acetate and no 2-phenylcyclopropyl acetate could be detected, although it was shown to be stable to the reaction conditions. These results indicate that the solvolysis of cyclopropyl tosylates is a concerted process, with ring opening occurring in the transition state of the reaction (eq. 2). The aryl group thus exerts its influence by stabilizing the positive charge being generated on the benzylic carbon.⁵

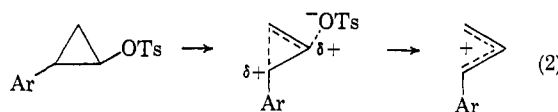
(1) J. D. Roberts and V. C. Chambers, *J. Am. Chem. Soc.*, **73**, 5034 (1951).

(2) C. H. DePuy, G. M. Dappen, K. L. Eilers, and R. A. Klein, *J. Org. Chem.*, **29**, 2813 (1964).

(3) H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).

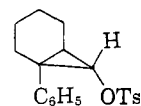
(4) The correlation is with σ^+ .

(5) Cyclopropyl tosylate itself undoubtedly also undergoes ring opening simultaneously with solvolysis since, as slow as its solvolysis rate is, it is appreciably faster than that calculated on the basis of angle



The transformation of a 2-substituted cyclopropyl tosylate into the proposed transition state and thence into the cinnamyl cation involves the rotation of the aryl group through approximately 90°. Woodward and Hoffmann⁶ have recently proposed that groups in the cyclopropyl cation would rotate in opposite directions (both inward or both outward) in going to the allyl cation. Our results indicate that the cyclopropyl cation is not an intermediate in the solvolysis and led us independently to the conclusion that the direction of rotation is dependent upon the stereochemistry of the leaving group. Combined with the theory of Woodward and Hoffmann our results suggest that an R group *trans* to the leaving group rotates outward.⁷ The slower rate of solvolysis of *cis*- than *trans*-2-phenylcyclopropyl tosylate is in agreement with this hypothesis since inward rotation of the *cis*-phenyl group would lead to a less stable, sterically hindered cation.⁸

In agreement with this hypothesis, we have prepared the *exo*-phenylnorcaranyl tosylate shown and find it to be very unreactive under conditions where 2-phenylcyclopropyl tosylate solvolyzes readily. Rotation of the *trans* groups outward in such a system is



obviously impossible. In order for solvolysis to occur a true cyclopropyl cation may have to be formed. The possibility of using this technique to generate these previously unknown ions is currently being explored.⁹

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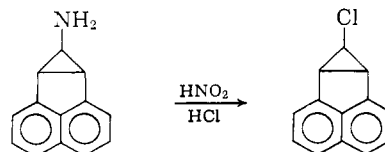
strain. See C. S. Foote, *J. Am. Chem. Soc.*, **86**, 1853 (1964); P. von R. Schleyer, *ibid.*, **86**, 1856 (1964).

(6) R. B. Woodward and R. Hoffmann, *ibid.*, **87**, 395 (1965).

(7) Hoffmann has shown by molecular orbital calculations that such a hypothesis is reasonable.⁵ We are grateful to Dr. Hoffmann for stimulating discussions.

(8) The cinnamyl acetates equilibrate under the reaction conditions: E. A. Braude, D. W. Turner, and E. S. Waight, *J. Chem. Soc.*, 2404 (1958), and earlier papers.

(9) R. Pettit, *J. Am. Chem. Soc.*, **82**, 1972 (1960), has reported one of the very few cases where a cyclopropyl cation was generated without rearrangement. Judging by the method of synthesis, the amine is *trans* to the fused ring. Ring opening cannot be simultaneous with loss of nitrogen and a cyclopropyl cation may be formed, which is captured



by chloride ion. Other examples of the application of this hypothesis are reported in the following communication.

(10) Department of Chemistry, University of Colorado, Boulder, Colo. 80304.

C. H. DePuy,¹⁰ L. G. Schnack
J. W. Hausser, W. Wiedemann

Department of Chemistry, Iowa State University
Ames, Iowa

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