

PROTOLYTIC CLEAVAGE OF CYCLOPROPANES:
THE STRUCTURE OF THE TRANSITION STATE,
IN THE PROTONATION OF ARYLCYCLOPROPANES¹

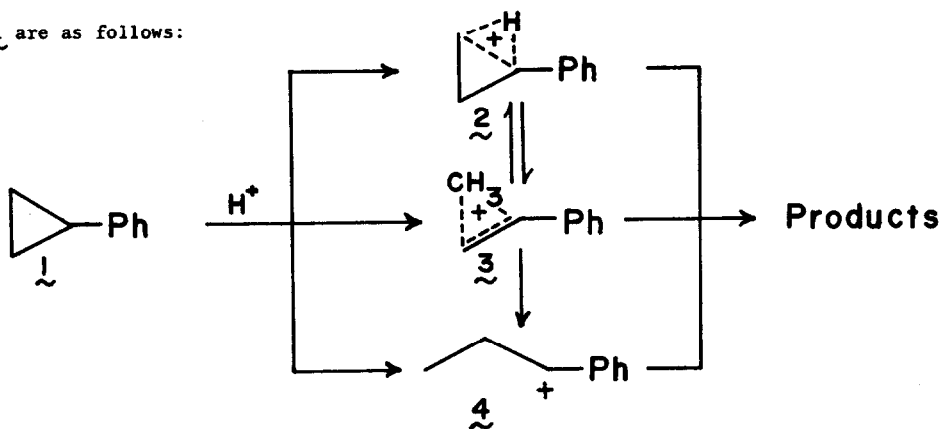
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Electrophilic additions to cyclopropanes have been the subject of many recent investigations². The scope of these investigations has been confined to elucidation of the structures of intermediates^{2b} and the orientation³ and stereochemistry⁴ of the addition. Little has been reported with respect of the kinetics of the reaction and, thus, the nature of its transition state. We wish to report here the results of kinetic studies on the protolytic cleavage of phenylcyclopropane (1) and its derivatives and discuss the interesting mechanistic characteristics of this reaction.





The possible intermediates and/or transition states resulting from proton addition to 1 are as follows:



By analogy to the hydration of styrene⁵ and 2-phenylpropene,⁶ intermediate 4 would appear most reasonable. However, proton addition to cyclopropane⁷ itself leads to intermediates analogous to 2 and 3.

The following results have been obtained (Table I): (1) Values of the first-order rate constants for cleavage, k_{obsd} , in 50-70% sulfuric acid were determined spectrophotometrically for 1 and three arylcyclopropanes (p-CH₃, p-Cl and m-Cl). (2) Plots of $\log k_{\text{obsd}}$ against $-\text{H}_0$ are linear with an average slope of 1.35. (3) A plot of $\log k_{\text{obsd}}$ in 60% sulfuric acid against σ^+ is linear with slope $\rho = -2.48$ and $r = 0.998$. (4) A positive solvent isotope effect of 1.4 was observed for 1 in 9.16M deuteriosulfuric acid.

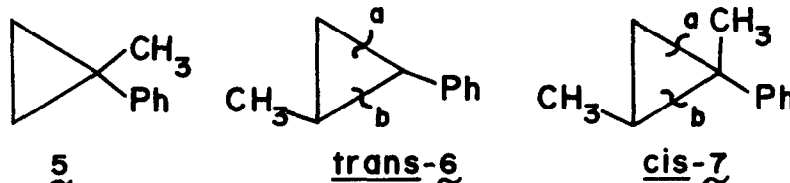
Table I
Rates of Arylcyclopropane Cleavage
in Sulfuric Acid at 25°

Compound	wt% H ₂ SO ₄	Rate, sec ⁻¹ ^a	-d log Rate/dH ₀ ^b
C ₆ H ₅ 	60.03	1.96 x 10 ⁻³	1.25
	64.19	8.21 x 10 ⁻³	
<u>p</u> -CH ₃ -C ₆ H ₄ 	48.70	2.02 x 10 ⁻⁴	1.37
	60.03	9.67 x 10 ⁻³	
<u>p</u> -Cl-C ₆ H ₄ 	60.03	7.95 x 10 ⁻⁴	1.31
	67.16	1.31 x 10 ⁻²	
<u>m</u> -Cl-C ₆ H ₄ 	60.03	2.10 x 10 ⁻⁴	1.42
	68.75	8.67 x 10 ⁻³	

a. The rate constants given are the average of at least two determinations. b. The slopes were determined using data at five acid concentrations.

These results are consistent with a mechanism involving rate determining protonation of 1. The steep acidity dependence of the rates indicates that the transition state is relatively weakly solvated by water⁵ and the small but positive solvent isotope effect is indicative of an unsymmetrical transition state with respect to proton transfer.⁷ The ρ value for the correlation of the cleavage rates with σ^+ is smaller in magnitude than those obtained for the hydration of styrene⁵ ($\rho = -3.4$) or the hydration of α -methylstyrenes⁶ ($\rho = -3.1$), but is in the range found for the reaction of arylcyclopropanes with mercuric acetate, thallium acetate and lead tetraacetate.⁸ Thus, at the transition state for arylcyclopropane cleavage the positive charge is less developed at the benzyl carbon or is more delocalized (structures 2 and 3) than in the analogous styrene hydrations.

In order to determine the extent of charge delocalization at the transition state for cleavage, the rates of cleavage for 5, 6, and 7 were determined spectrophotometrically.



The cleavage reaction leads to an equilibrium mixture of alkenes and alcohols. In the case of trans-6 and cis-7 "a" bond cleavage leads to one alkene-alcohol mixture and "b" cleavage gives a different alkene-alcohol pair. The extent of each type of cleavage was obtained by comparison of the extinction coefficient of the spent reaction mixture after 10 half-lives with the extinction coefficients of authentic alkene-alcohol mixtures in the appropriate acid. The equilibrium mixtures could be attained by starting with authentic alcohol or alkene.

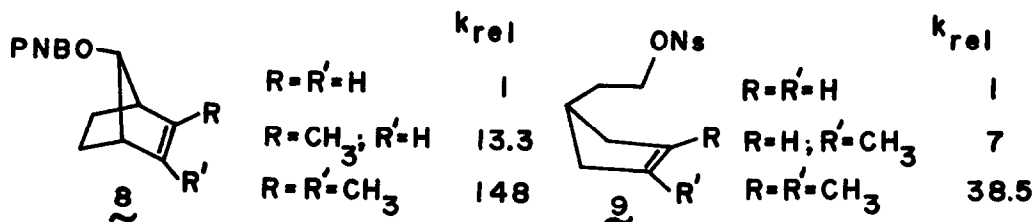
Table II

Compound	Rate, sec ⁻¹	% cleavage		k _{rel} ("a" bond cleavage)
		a	b	
<u>1</u>	1.30 x 10 ⁻⁴			1 ^a
<u>5</u>	1.20 x 10 ⁻³			9.2 ^a
<u>trans-6</u>	4.79 x 10 ⁻⁴	65	35	4.8
<u>cis-7</u>	4.07 x 10 ⁻³	60	40	37

a. Corrected for two equivalent sites of cleavage.

The data of Table II shows that substitution of methyl at C-1 gave a rate acceleration of 9.2 in comparison to the rate of 1. The introduction of a trans-methyl group at C-2 caused a rate increase of 4.8 for trans-6-relative to 1. Finally, substitution of methyl

at C-1 and C-2 caused an overall rate increase of 37 for cis-7 relative to 1 and an acceleration of 4 relative to 5. These rate changes represent a "cumulative" effect of the added methyl groups. This behavior is similar to the effect of methyl substitution on the solvolysis rates of 8⁹ and 9¹⁰. In these systems symmetrically bridged intermediates, analogous to 3, have been postulated.



In marked contrast, the hydrations of aryl olefins,^{5,6} which are believed to occur via the formation of open carbonium ion intermediates, do not show a cumulative effect of methyl substitution on the rate of reaction. Thus, α -methylstyrene undergoes hydration ca. 240 times faster than styrene⁵ and trans- β -methylstyrene undergoes hydration ca. 10 times slower than styrene.¹¹

On the basis of the methyl substituent effects discussed above we feel that our data on the acid catalyzed cleavage of 1, 5, trans-6, and cis-7 are most consistent with a corner protonated structure, 3, for the transition state in these cleavages.

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