Tetrahedron Letters No.12, pp. 1431-1434, 1968. Pergamon Press. Printed in Great Britain.

THE IMPORTANCE OF REHYBRIDIZATION ON THE ELECTRONIC EFFECTS OF THE CYCLOPROPYL GROUP[1]

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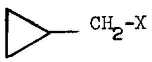
(Received in USA 5 October 1967)

Two major proposals have been advanced to account for the effects of cyclopropyl substituent on the rates of solvolysis reactions of various substrates (e.g., 1). On the one hand, the observed effects have been attributed to neighboring group participation[2] involving overlap of the carbon-carbon σ-orbitals of the cyclopropyl group with the p-orbital of the developing carbonium ion center. On the other, the suggestion has been advanced that the "enhanced rates observed in the solvolysis of these compounds is primarily due to their strained condition"[3]. A change in hybridization of the reacting carbon ($sp^3 \rightarrow sp^2$) during the transformation from reactant to transition state presumably relieves such strain. This latter suggestion is based in part on the observation that a cyclopropyl group has an abnormally large retarding effect on the rate of reduction of cyclopropyl ketones[3] ($sp^2 \rightarrow sp^3$). This rate effect is approximately proportional to the abnormal rate enhancements observed in solvolysis reactions of cyclopropylcarbinyl systems ($sp^3 \rightarrow sp^2$).



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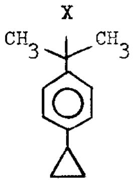

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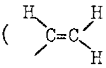
When the cyclopropyl substituent was removed from the immediate vicinity of the reaction site[1,4] but, nevertheless, situated in a position to interact with it by orbital overlap (resonance) (e.g., 2), the substituent still produced a large rate enhancement relative to other alkyl groups implying that steric effects are unimportant. In this communication we report the results of a study which clearly demonstrates that steric effects arising from a hybridization change at the reacting center in solvolysis reactions ($sp^3 \rightarrow sp^2$) are unimportant in determining the overall substituent effect of the cyclopropyl group.

Schubert, Lamm and Keeffe[5] have recently reported a detailed study of the hydration of substituted styrenes. Their data indicate that the mechanism of the acid catalyzed reaction involves the rate determining conversion of the styrene to the corresponding α-phenylethyl carbonium ion followed by reaction of the carbonium ion intermediate with water (fast step) to give products (equation 1). Since a carbonium ion similar to that produced in the solvolysis of $\underset{\sim}{2}$ is generated in the rate limiting step without involving a hybridization change at the benzylic carbon atom, we have utilized this reaction to obtain an independent measure of the $\sigma^{\oplus}$ constant for the p-cyclopropyl substituent. A comparison of this value with that obtained from the solvolysis of p-cyclopropylphenyldimethylcarbinyl chloride[1] ($\sigma^{\oplus}$ = -0.410) should provide a direct measure of the importance of hybridization changes in determining the overall substituent effect of a cyclopropyl group.

$$\text{Ar-CH=CH}_2 + \text{H}_3\text{O}^{\oplus} \xrightarrow{\text{slow}} \text{Ar-}\overset{\oplus}{\text{C}}\text{H-CH}_3 \xrightarrow{\text{fast}} \text{Products} \qquad (1)$$

p-Cyclopropylstyrene was prepared in the following manner. The Grignard reagent of p-bromocyclopropylbenzene[1] was treated with acetaldehyde yielding the corresponding alcohol. In addition, some of the disproportionation product, p-cyclopropylacetophenone, was obtained. This mixture of products was treated with lithium aluminum hydride and then converted to the olefin by acid catalyzed elimination. The structure of the product was confirmed by elemental analysis and spectral data. The nmr spectrum shows absorptions at 0.60-0.97 ppm (four-hydrogen multiplet, cyclopropyl methylene hydrogens), 6.4-6.8 and 5.0-5.8 ppm ( >C=C< group) and 7.28 and 6.98 ppm (two two-hydrogen doublets, aromatic hydrogens). The ultraviolet spectrum in ethanol shows a maximum at 259 mμ (log ϵ 4.26).

First order rate constants for the hydration of styrene and p-cyclopropylstyrene were determined in 3.83 M. perchloric acid by following the decrease in optical density at 248 and 260 mμ, respectively. These data were obtained using styrene concentrations of 10^{-5}-10^{-4}M. to prevent acid catalyzed polymerization.[5] The data are tabulated in Table I. Since the equilibrium between p-cyclopropylstyrene and the corresponding alcohol was found to be greater than 99% in favor of the alcohol corrections were not applied to the rate data.

Table I. Rates of Hydration of Styrene and
p-Cyclopropylstyrene in 3.83 M. Perchloric Acid

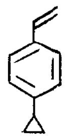
Compound	Temp. °C	$10^4 \times k_1$ (sec^{-1})
Styrene[a]	25.0	0.222 ± 0.003
p-Cyclopropylstyrene	25.0	7.04 ± 0.14
p-Cyclopropylstyrene	9.0	1.08 ± 0.04
p-Cyclopropylstyrene	0.0	0.327 ± 0.006

[a] Agrees with the value reported by Schubert, Lamm and Keeffe[5]

Activation parameters for the hydration reaction of *p*-cyclopropylstyrene in 3.83 M. perchloric acid at 25° were calculated to be $\Delta H^{\ddagger} = 19.3$ kcal/mole and $\Delta S^{\ddagger} = -8.01$ e.s.u. These data when compared with those reported by Schubert[5] for the hydration of styrene indicate that the entropies of activation ($\Delta S^{\ddagger}$) are essentially the same for the two reactions and that the relative rate constants are primarily the result of differences in the heats of activation ($\Delta H^{\ddagger}$).

The $\sigma^{\oplus}$ constant for the *p*-cyclopropyl substituent was calculated to be -0.439 using a rho (ρ) value of -3.42[5] for the hydration reaction. This value is in good agreement with that obtained previously[1] from the solvolysis of p-cyclopropylphenyldimethylcarbinyl chloride (-0.410) and provides compelling evidence that steric strain[3] associated with a hybridization change at the reacting carbon is not an important factor in determining the kinetic effect of a cyclopropyl substituent. The data also provide good evidence that internal return[6] is not a significant factor in the solvolysis of *p*-cyclopropylphenyldimethylcarbinyl chloride in acetone-water solutions.[1]

Product studies were complicated by the facile polymerization of the substituted styrene if concentrations above 10^{-3} M. were employed. U.V. studies, however, indicate that the product of the reaction is the corresponding carbinol. The ultraviolet spectrum of the acid solution of p-cyclopropylstyrene was continuously monitored during the course of the kinetic runs and at no time could any indication of compounds other than **3** and **4** be detected. There was a smooth transition from the spectrum of the former to the latter. The possibility that **3** was transformed into **5** or **6** prior to the hydration reaction can be easily discounted. Compound **6** would show a maximum in the U.V. at approximately 280 mμ. At no time could an absorbance maximum be detected above 260 mμ (i.e., compound **3**).



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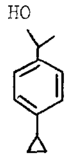

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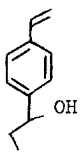

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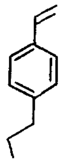

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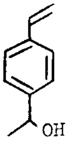

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The substituent effect of the hydroxypropyl group in 5 should be similar to that of the hydroxyethyl group in 7 which has been shown to be considerably smaller[7] than the effect noted for the p-cyclopropyl substituent. As a result, had 3 reacted in perchloric acid to yield 5 prior to the hydration reaction, considerably slower rates would have been observed.

Acknowledgment: Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

References:

1. This is Part II in the series "Electronic Effects in Solvolysis Reactions" For Part I see: L. B. Jones and V. K. Jones, *Tetrahedron Letters*, 1493 (1966).
2. See for example: M. Vogel and J. D. Roberts, *J. Am. Chem. Soc.*, **88**, 2262 (1966) and references cited therein.
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6. J. D. Roberts and K. L. Servis, *Tetrahedron Letters*, 1369 (1967).
7. L. B. Jones and S. S. Eng. unpublished results.