# The $S_N1$ Hydrolysis of α-Phenylethyl Chloride Proceeding with the Retention of the Configuration in Binary Mixtures of Phenol and Water

By Kunio OKAMOTO, Masayuki HAYASHI and Haruo SHINGU

*Department of Fuel Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto*

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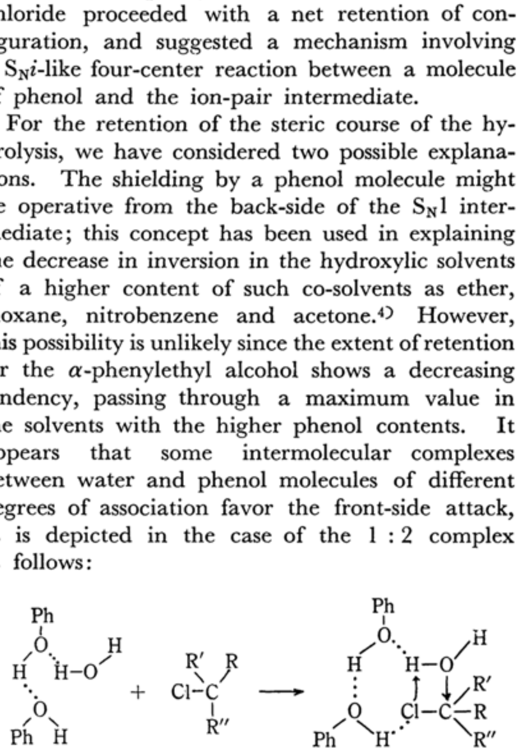
In recent publications, Goering and his collaborators[1] have reported that the $S_N1$ hydrolysis (alkyl-oxygen cleavage) of *p*-chlorobenzhydryl *p*-nitrobenzoate proceeds with an excess retention of the configuration in 80—90% aqueous acetone. Despite extensive investigations of the steric course of $S_N1$ hydrolysis, no other examples which follow the retained steric course are known for such a system without a configuration-retaining group adjacent to the reaction center. The present report is of significance both because it will present another example of hydrolysis with the retention of configuration for a simple secondary carbon system, and because it can throw light on the hitherto elusive nature of the retention mechanism for this system in general.

Solvolyses of optically active α-phenylethyl chloride (0.106 M) were conducted in 75, 80, and 90 wt.% aqueous phenols in the presence of triethylamine (0.114—0.118 M) for ten half-lives at 30.0°C. The products of the competitive phenolysis and hydrolysis were chromatographed over basic alumina and purified by distillation in vacuo. From the rotations of α-phenylethyl alcohol ($\alpha_D$, $-1.58°$, $-1.64°$ and $+1.16°$ (neat, 0.5 dm.) for the respective solvolyses) and α-phenylethyl phenyl ether ($\alpha_D$, $+0.62°$, $+0.76°$ and $-1.97°$, neat, 0.5 dm.) thus obtained, it was found that the configurations of the chlorides ($\alpha_D$, $-27.39°$, $-26.30°$ and $+27.06°$, neat, 0.5 dm.) were retained for both hydrolysis and phenolysis over the entire solvent range examined. The extents of retention[2] were calculated on the basis of the rotaions of the starting chloride to be 16.3, 17.6 and 12.1% for α-phenylethyl alcohol and 6.08, 7.76 and 19.5% for α-phenylethyl phenyl ether for the respective solvolyses. In previous papers,[3] with regard to phenolyses in various mixtures of phenol and organic solvents (e. g.,benzene, cyclohexane, and acetonitrile), we reported that the formation of α-phenylethyl phenyl ether from α-phenylethyl chloride proceeded with a net retention of configuration, and suggested a mechanism involving a $S_Ni$-like four-center reaction between a molecule of phenol and the ion-pair intermediate.

For the retention of the steric course of the hydrolysis, we have considered two possible explanations. The shielding by a phenol molecule might be operative from the back-side of the $S_N1$ intermediate; this concept has been used in explaining the decrease in inversion in the hydroxylic solvents of a higher content of such co-solvents as ether, dioxane, nitrobenzene and acetone.[4] However, this possibility is unlikely since the extent of retention for the α-phenylethyl alcohol shows a decreasing tendency, passing through a maximum value in the solvents with the higher phenol contents. It appears that some intermolecular complexes between water and phenol molecules of different degrees of association favor the front-side attack, as is depicted in the case of the 1 : 2 complex as follows:



This may be regarded as a detailed expression of the "polymolecular"[5] attack of hydroxylic molecules on the halogen atom in the $S_N1$ solvolysis.

The details of this work and descriptions of some further extention experiments with methanolic phenol solvents will be published in the near future.

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[1] a) H. L. Goering, R. G. Briody and J. F. Levy, *J. Am. Chem. Soc.*, **85**, 3059 (1963); b) H. L. Goering and and J. F. Levy, ibid., **86**, 120 (1964).

[2] The maximum rotation of the chloride was taken to be 125° (neat, 1 dm.; H. M. R. Hoffman and E. D. Hughes, *J. Chem. Soc.*,**1964**, 1244), and those of α-phenylethyl alcohol and α-phenylethyl ether, as 44.2° (D. J. Cram, K. R. Kopecky, F. Hauck and A. Langemann, *J. Am. Chem. Soc.*, **81**, 5754 (1959)) and 46.6°, Ref. 3b.

[3] a) K. Okamoto, K. Takeuchi and H. Shingu, This Bulletin, **35**, 525 (1962); b) K. Okamoto, H. Yamada, I. Nitta and H. Shingu, This Bulletin, **39**, 299 (1966).

[4] a) W. v. E. Doering and A. Streitwieser, Jr. Cf. A. Streitwieser, Jr., *Chem. Revs.*, **56**, 571 (1956); b) A. Streitwieser, Jr., and W. D. Schaeffer, *J. Am. Chem. Soc.*, **79**, 6233 (1957); c) A. Streitwieser, Jr., and S. Andreades, ibid., **80**, 6553 (1958); d) H. Weiner and R. A. Sneen, ibid., **87**, 287, 292 (1965).

[5] a) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York (1940), p. 169; b) K. Okamoto and H. Shingu, This Bulletin, **34**, 1131 (1961).