

Solvolysis of Substituted Benzylidene Chlorides in Dioxan-Water; an Unusual Role for a Distant Carboxy-group in a Carbonium Ion Reaction

By V. P. VITULLO* and R. J. CAPP

(Laboratory for Chemical Dynamics, Department of Chemistry, University of Maryland Baltimore County, Catonsville, Maryland 21228)

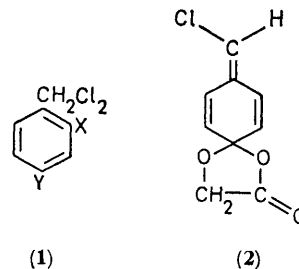
Summary Evidence is presented which points to the existence of a spiro-intermediate in the solvolysis of p -KO₂CCH₂OC₆H₄CHCl₂ in dioxan-water mixtures.

In an effort to obtain additional information concerning the possible catalytic role of a proximate carboxy-group¹ in a carbonium ion reaction we report additional results for a substituted benzylidene chloride which suggests an unusual role for a distant carboxy-residue.

We have previously shown that *o*-carboxybenzylidene chloride is hydrolysed faster than the *para*-isomer in dioxan-water mixtures.² Further investigations using α -deuterium isotope effects^{3,4} showed that the *ortho*-carboxy-group captures the initially formed intimate ion pair in the rate-limiting step and this change in mechanism results in a substantial rate acceleration for a proximate carboxy-group in this reaction.

We have now extended this study to more reactive benzylidene chlorides. For example, (**1a**) in dioxan-water (70:30) is 7×10^4 -fold more reactive than benzylidene chloride and only 15-fold less reactive than *p*-methoxybenzylidene chloride.†

The solvolysis rates of (**1a**) and (**1b**) (Table) can be correlated with the Winstein-Grunwald parameter, Y . The slopes of the plots obtained [$m(\mathbf{1a})$ 1.22, $m(\mathbf{1b})$ 1.32] are similar to that reported for benzylidene chloride.⁵ However, in 70:30 dioxan-water the *para*-isomer reacts faster than the *ortho*-isomer, $k_p/k_o = 186$. In the absence of neighbouring group participation this result is similar to



- (1) a; X=H, Y=OCH₂CO₂Et
 b; X=OCH₂CO₂Et, Y=H
 c; X=H, Y=OCH₂CO₂⁻
 d; X=OCH₂CO₂⁻, Y=H

† This is in marked contrast to *p*-acetoxybenzylidene chloride which is only 4-fold more reactive than benzylidene chloride.

TABLE. Rates of solvolysis of (1a)—(1d) in dioxan-water mixtures at 25 °C

Substrate	$10^4 k_{\text{obs}}/\text{s}^{-1}$	Solvent composition (dioxan:water, v/v)
(1a)	40.0	60:40
"	15.4	65:35
"	5.46	70:30
"	0.50	80:20
(1b)	25.0	35:65
"	10.8	40:60
"	1.78	50:50
(1c)	3590	50:50
"	1950	60:40
"	756	70:30
"	302	75:25
"	214	80:20
"	51.5	90:10
(1d)	385	40:60
"	84.2	50:50
"	4.88	70:30

that reported for a series of benzyl bromides.⁶ The origin of this rate reduction is probably chiefly steric since the smaller acetoxy-substituent gives a reduced ratio, $k_p/k_o = 47$ in water.

Over a large range of solvent compositions (35—70% dioxan in water) the α -deuterium isotope effects for (1a) and

(1b) are limiting[†] *i.e.*, for (1a), $(k_H/k_D) = 1.201 \pm 0.005$; (1b), $(k_H/k_D) = 1.204 \pm 0.013$. Thus, there appears to be nothing unusual about the solvolytic behaviour of the esters (1a) and (1b).

However, while the α -deuterium isotope effects for (1c) and (1d) are limiting as well; for (1c): $(k_H/k_D) = 1.200 \pm 0.014$, (1d): $(k_H/k_D) = 1.188 \pm 0.013$, and m values for the two isomers are very different, $m(1c) 0.52$, $m(1d) 1.07$. The much reduced m value for (1c) would argue for a much less polar transition state, *e.g.*, a transition state in which the charge on the carbonium ion centre has been neutralized.

We suggest that at an early stage in the solvolysis of (1c) (most likely at the intimate ion pair stage) (2) is formed, possibly in the rate-determining step. It should be noted here that an electrostatic shielding of the partial positive charge in the aromatic ring localized somewhat at C-4 would give rise to a similar change in m . In addition, it is important to note here that the same α -deuterium isotope effect would be expected for the rate-determining formation of (2) as would be expected for the formation of the solvent-separated ion pair since for both intermediates the hybridization at the isotopically labelled carbon is trigonal.

We thank the National Institutes of Health for financial support of this work.

(Received, 8th September 1977; Com. 933.)

[†] In this context we use the term *limiting* to mean rate-limiting formation of solvent-separated ion pair (refs. 2 and 3, and V. J. Shiner, Jr., in 'Isotope Effects in Chemical Reactions,' eds. C. J. Collins and N. S. Bowman, Van Nostrand Reinhold (Amsterdam), New York, 1970, pp. 90—159).

¹ For an excellent discussion of the lysozyme literature, see B. M. Dunn and T. C. Bruice, *Adv. Enzymol. Rel. Subj. Biochem.*, 1973 **37**, 1.

² V. P. Vitullo and N. R. Grossman, *J. Org. Chem.*, 1973, **38**, 179.

³ V. P. Vitullo and F. P. Wilgis, *J. Amer. Chem. Soc.*, 1975, **97**, 458.

⁴ V. P. Vitullo and F. P. Wilgis, *J. Amer. Chem. Soc.*, 1975, **97**, 5616.

⁵ B. Colina, M. G. Rotaecche, E. Guerrero, A. M. Alpica, M. Calzadilla, and J. Baumrucker, *J. Org. Chem.*, 1974, **39**, 3918.

⁶ A. Singh, L. J. Andrews, and R. M. Keefer, *J. Amer. Chem. Soc.*, 1962, **84**, 1179; L. Chaffe, L. J. Andrews, and R. M. Keefer, *J. Org. Chem.*, 1966, **31**, 3758.