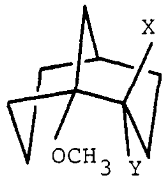
to those of a sample prepared from **1** by hydrogen chloride catalyzed methanolysis.

A similar photochemical experiment using methanol-*O-d* (99% min) as the solvent provided 25% of methyl ether **5nd** after 11 h. The mass spectrum of **5nd** had a molecular ion peak at *m/e* 155 (91% d_1 incorporation) and gave a proton NMR closely similar to that of **5**. Reaction of alkene (*Z*)-**1** with methanol-*O-d* catalyzed by deuterium chloride gave **5xd** quantitatively. Both **5nd** and **5xd** gave identical mass spectra with molecular ions of *m/e* 155 and peaks of nearly equal intensity at *m/e* 111 and 112 (M − 44, 43), consistent with the loss of either one of the three-carbon bridges. The 360-MHz ^{1}H NMR spectra were also quite similar. However, the ^{2}H NMR[11] spectra of the two products were distinctly different. Ether **5nd** produced a single resonance peak at δ 1.78[12] (half-width of 5.01 Hz), whereas **5xd** displayed a single resonance at δ 1.48 (half-width of 5.06 Hz). The spectra showed no cross contamination of epimers.

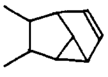


5, X = H; Y = H
5nd, X = H; Y = D
5xd, X = D; Y = H

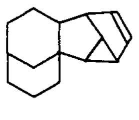
The difference in deuterium chemical shifts of **5nd** and **5xd** arises from incorporation at different loci on C-2. Deuteration on the less hindered (external) face of the double bond of (*Z*)-**1** must give rise to the 2-exo-deuterium ether, **5xd**. The deuterium should be axial in the chair–chair conformer of **5xd**, which is in accord with it having the higher field chemical shift (δ 1.48). It follows that the deuterium in the photochemical product, **5nd**, is endo and equatorial. This marked stereochemical contrast is explained as resulting from deuteration by methanol-*O-d* on the external face of alkene (*E*)-**1**.

Direct photomethanolysis of (*Z*)-**1** in mixtures of CH_3OD and CH_3OH permitted determination of the kinetic isotope effect for protonation of (*E*)-**1** by methanol (k_H/k_D = 8.0). This result indicates that proton transfer is about half completed in the transition state.

Photosensitized methanolysis of alkene (*Z*)-**1** was also accomplished by using molar excesses of benzene and *p*-xylene as photosensitizers, but the yields of ether **5** were lowered due to the formation of alkene–arene adducts. The ^{2}H NMR spectra again showed stereospecific formation of **5nd** when methanol-*O-d* was the solvent. One of the four benzene–alkene adducts (*m/e* 200) was purified by gas chromatography and showed a proton NMR spectrum similar to that of **6**, isolated by Wilzbach and Kaplan in the photoaddition of *cis*-2-butene to benzene. The cycloadducts with benzene are tentatively assigned structures **7** and/or **8**, stereochemistry unknown. Further study of the photochemistry of bridgehead alkenes is in progress.



6



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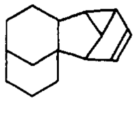

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Registry No. 1Z, 54674-58-7; **1E**, 82509-63-5; **5**, 63160-90-7; deuterium, 7782-39-0.

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[11] Deuterium spectra were obtained at an irradation frequency of 55 MHz. A 1% solution of $CDCl_3$ in carbon tetrachloride served as the solvent.

[12] Measured in reference to δ 7.24 for $CDCl_3$.

[13] Wilzbach, K. E.; Kaplan, J. *J. Am. Chem. Soc.* **1966**, *88*, 2066.

A Simple Relationship between Carbocation Lifetime and Reactivity–Selectivity Relationships for the Solvolysis of Ring-Substituted 1-Phenylethyl Derivatives[1]

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We describe here the experimental demonstration of a predicted[2] V-shaped reactivity–selectivity curve for reactions of 1-phenylethyl derivatives, I (Chart I). The azide–solvent selectivity, k_{az}/k_s, M^{-1} (Figure 1) decreases sharply, crosses a narrow "borderline" region, and increases with increasing σ^+ as the reaction mechanism changes. These changes exhibit a simple correlation with the lifetime of the 1-phenylethyl carbocation.

Values of k_{az}/k_s (Figure 1, 50:50 trifluoroethanol/water, v/v, μ = 0.5, $NaClO_4$) were determined by product analysis with HPLC.[3] The value of $k_{MeOCOCH_2S^-}/k_s$ instead of k_{az}/k_s was used for ia because the azide adduct is unstable; k_{az}/k_{RS^-} was found to be 1.8 for iic, and ratios of k_{az}/k_{RS^-} = 0.2–0.03 have been reported for triarylmethyl carbocations.[4,5]

The dependence of k_{obsd} on azide concentration for the reactions of substituted 1-phenylethyl chlorides in acetonitrile/water (Figure 2) undergoes a change from zero order for compounds to the left of the selectivity break ($\sigma^+ \leq -0.32$) to first order for compounds to the right of the break ($\sigma^+ \geq -0.08$). The plots are linear for azide concentrations up to 0.6 M. The fraction of azide adduct product was found to agree within experimental error with the fractional rate increase in the presence of azide for all reactions that are first order in azide; i.e., >80% of the azide adduct is formed by the pathway that is first order in azide.

A change in the dependence of selectivity on the leaving group is also observed at the selectivity break. Substrates to the left of the break show constant selectivities for large changes in leaving group (open circles and squares, Figure 1), while substrates to the right of the break exhibit selectivities which are dependent on the leaving group (closed symbols, Figure 1). The right-hand limb in Figure 1 is drawn through points for substituted 1-phenylethyl chlorides.

We account for the decreasing and increasing limbs in Figure 1 as follows. The zero-order dependence of k_{obsd} on azide concentration, through azide concentrations that give at least 40% yield of azide adduct, demonstrates a stepwise mechanism and a carbocation intermediate for substrates to the left of the selectivity break. The decreasing selectivity with increasing carbocation reactivity contrasts with the constant azide selectivity (k_{az}/k_s) of 10^6 M^{-1} observed for the more stable triarylmethyl carbocations.[6,7] The different reactivity–selectivity behavior can be rationalized if the rate constant k_{az} is activation limited for triarylmethyl carbocations and diffusion limited for 1-phenylethyl carbocations.[8-11] A downward selectivity break is expected when

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[1] Supported by grants from the National Science Foundation (PCM-7708369) and the National Institutes of Health (GM20888). Dr. Richard was supported by a grant from the National Institute of Health (AM 07251).

[2] Jencks, W. P. *Acc. Chem. Res.* **1980**, *13*, 161–169.

[3] Products were separated over a reverse-phase octadecylsilane chromatography column (10 μm, Waters Associates) with MeOH/HOH.

[4] A value of k_{az} of 5 × 10^6 M^{-1} s^{-1} for the reaction of the trianisylmethyl carbocation was reported: Bunton, C. A.; Huang, S. K. *J. Am. Chem. Soc.* **1972**, *94*, 3536–3544. A value of k_{RS^-} of 7 × 10^7 for the reaction of $HOCH_2CH_2S^-$ with the same carbocation was reported: Ritchie, C. D.; Gandler, J. *J. Am. Chem. Soc.* **1979**, *101*, 7318–7323.

[5] Ritchie, C. D.; Hofelich, T. C. *J. Am. Chem. Soc.* **1980**, *102*, 7039–7044.

[6] Ritchie, C. D.; Virtanen, P. O. I. *J. Am. Chem. Soc.* **1972**, *94*, 4966–4971.

[7] Ritchie, C. D. *Acc. Chem. Res.* **1972**, *5*, 348–354.

[8] Kemp, D. S.; Casey, M. L. *J. Am. Chem. Soc.* **1973**, *95*, 6670–6680.

[9] Young, P. R.; Jencks, W. P. *J. Am. Chem. Soc.* **1977**, *99*, 8238–8248.

[10] Rappoport, Z. *Tetrahedron Lett.* **1979**, 2559–2562.

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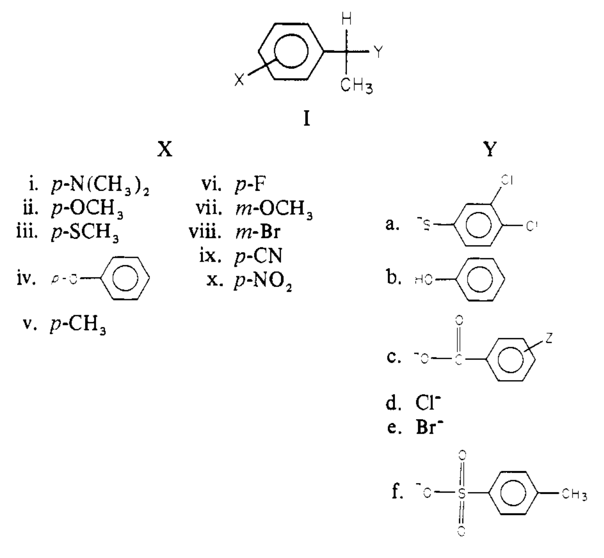
Chart I



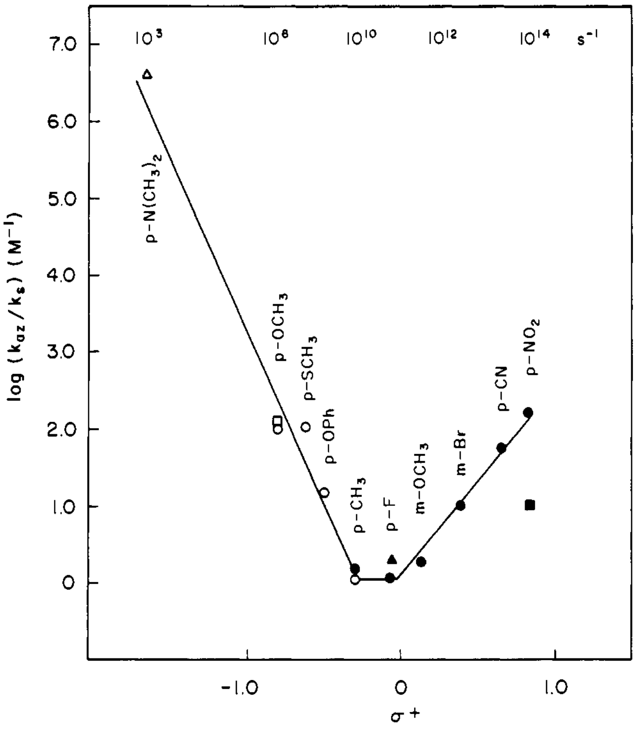


Figure 1. Selectivity values k_{az}/k_s. Reactions were at room temperature for all but the two least reactive 1-phenylethyl chlorides (p-CN and p-NO$_2$), which required a temperature of 70 °C. The latter two values are corrected to 20 °C by dividing by a factor of 2. This correction factor was obtained from a comparison of the selectivities of 1-(m-bromophenyl)ethyl chloride at 20 and 70 °C. Leaving groups: Δ, dichlorothiophenoxide; □, phenol; ○, substituted benzoates; ●, chloride; ▲, bromide; ■, tosylate.

k_{az} reaches an invariant, diffusional value, because the rate constant k_s remains activation limited and continues to increase as the carbocation becomes less stable.

The ratio k_{az}/k_{RSH} of 3 for the reaction of propanethiol with iic in 50:50 water/trifluoroethanol is 10^6 smaller than the azide/thiol selectivity toward triarylmethyl carbocations.[12] The lack of selectivity of the ion formed from iic toward nucleophiles of vastly differing reactivities suggests that both nucleophiles are reacting in encounter-limited processes.[8]

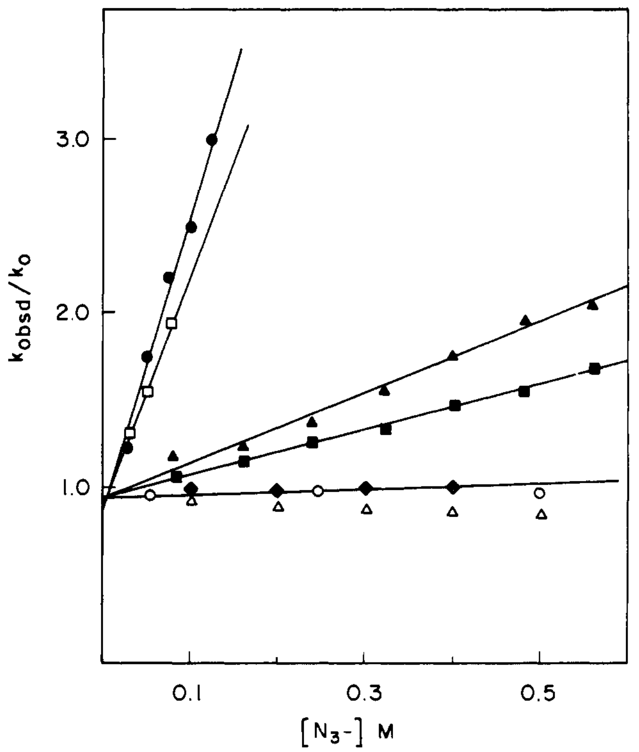


Figure 2. Dependence of substitution rate constants k_{obsd} on azide concentration. Normalized values of k_{obsd}/k_0 give the relative rate change caused by added azide. The following reaction conditions were used: ○, iic; □, xf (in 50:50 trifluoroethanol/water, μ = 0.5, t = 20 °C); Δ, vc (50:50 trifluoroethanol/water, μ = 0.5, t = 25 °C); ♦, vd (50:50 acetonitrile in water, μ = 0.50, t = 25 °C); ■, vid; ▲, viid; ●, viiid (20/80 acetonitrile in water, μ = 0.8, t = 25 °C). Ionic strength was maintained with NaClO$_4$. Reactions in acetonitrile/water were monitored by following the protonation of phenolate ion as an indicator, and reactions in 50:50 trifluoroethanol/water were monitored for substrate disappearance by HPLC.[3]

Estimated values of the first-order rate constants for the reaction of 1-phenylethyl carbocations with solvent (k_s) are shown at the top of Figure 1. Values for carbocations on the left-hand limb were calculated from k_{az}/k_s by assuming a value of 5×10^9 M^{-1} s^{-1} for k_{az}.[13] Estimates of k_s for the more unstable carbocations on the right-hand limb were obtained from an extrapolation of the left-hand limb in Figure 1. The slope of $\rho^+ = -4$ for k_{az}/k_s on the left-hand limb is consistent with $\rho^+ = 0$ for the diffusion-controlled reaction of azide and the unexpectedly large value of $\rho^+ = 4$ for the reaction of solvent with 1-phenylethyl carbocations.

The data in Figure 2 are consistent with a change in the mechanism of the reaction with azide from S$_N$1 to S$_N$2, which is predicted to occur as the stability of the carbocation is decreased.[14] The slope of the right-hand limb in Figure 1, 2.5, is equal to $\rho^+(k_{az}) - \rho^+(k_s)$. Evidence is presented in the following communication that demonstrates a concerted displacement mechanism for the reaction of azide with these 1-phenylethyl chlorides.[15]

In summary, the following reactivity–selectivity relationships may be identified.

(i) $k_{az} < 5 \times 10^9$ M^{-1} s^{-1}: Selectivity is essentially constant, because azide and solvent respond similarly to changes in carbocation stability. This is the region studied by Ritchie in developing the N$^+$ nucleophilicity scale.[6,7] The estimated azide selectivity for ia, 10^6 M^{-1}, is close to the limiting N$^+$ selectivity of $\sim 10^6$ M^{-1}.

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(11) Rappoport, Z.; Apeloig, Y.; Greenblatt, J. *J. Am. Chem. Soc.* **1980**, *102*, 3837–3848.

(12) Based on rate constants of 3.3 M^{-1} s^{-1} for k_{RSH} and the value of k_{az} given in ref 4.

(13) A diffusional rate constant of 5×10^9 M^{-1} s^{-1} estimated by Young and Jencks (footnote 14 in ref 9) is used.

(14) Ingold, C. K. "Structure and Mechanism in Organic Chemistry", 2nd ed.; Cornell University Press: Ithaca, NY, 1969; pp 418–610.

(15) Richard, J. P.; Jencks, W. P., following communication in this issue.

(ii) $k_{az} \simeq 5 \times 10^9$ M^{-1} s^{-1} $> k_s$: Selectivity decreases sharply with increasing carbocation reactivity. This behavior is clearly demonstrated in the present communication and has been reported by Young and Jencks for the reaction of X-PhC(OCH$_3$)(CH$_3$)$^+$ with sulfite in water.[9] It is the probable explanation for the correlation between azide selectivity and substrate reactivity for the reaction of a heterogeneous series of alkyl and aryl chlorides.[16-18]

(iii) $k_{az} \simeq 5 \times 10^9$ M^{-1} s^{-1} $\simeq k_s$: Selectivity is constant and close to 1. This corresponds to the borderline region for the azide reaction which is narrow in this system; $-0.32 < \sigma^+ < -0.08$.

(iv) A change to an S$_N$2 mechanism is expected as the intermediate becomes very unstable. This change is enforced if its occurrence coincides with the disappearance of the barrier for the reaction of azide with the carbocation. The S$_N$2 reaction will give an upward break in an appropriate structure-reactivity plot, as for *sec*-octyl chloride in the reactivity-selectivity correlation of alkyl and aryl chlorides.[19]

Registry No. i, 82414-94-6; ii, 18207-33-5; iii, 82414-95-7; iv, 82414-96-8; v, 31042-87-2; vi, 31067-69-3; vii, 82414-97-9; viii, 82414-98-0; ix, 82414-99-1; x, 82415-00-7; N$_3^-$, 14343-69-2.

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[16] Sneen, R. A.; Carter, J. V.; Kay, P. S. *J. Am. Chem. Soc.* **1966**, *88*, 2594-2595.

[17] Raber, D. J.; Harris, J. M.; Hall, R. E.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1971**, *93*, 4821-4828.

[18] Z. Rappoport has independently reached conclusions similar to those reported here upon reexamination of the data of ref 16 and 17 (personal communication).

[19] Raber, D. J.; Harris, J. M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1971**, *93*, 4829-4834.

Concerted S$_N$2 Displacement Reactions of 1-Phenylethyl Chlorides[1]

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In the preceding communication it was reported that the mechanism of the reaction between azide and 1-phenylethyl chlorides changes from a kinetically zero-order, S$_N$1 trapping reaction to a reaction that is first order in azide as the carbocation intermediate is destabilized.[2] We present evidence here that the bimolecular reaction with azide is concerted in the Ingold sense, involving simultaneous covalency changes at the leaving group and nucleophile.[3,4] The concerted mechanism is enforced by the short lifetime of the carbocation-azide encounter complex.[3]

The Hammett plots in Figure 1 show first-order rate constants for the solvolysis reaction and second-order rate constants for reactions of cyanide and azide ions with substituted 1-phenylethyl chlorides in 20% acetonitrile in water (3.8 M CH$_3$CN), $\mu = 0.8$ (maintained with NaClO$_4$).[2] Values of k_{az} and k_{solv} were obtained from the slopes and the intercepts, respectively, of linear plots of k_{obsd} vs. azide concentration.[2] Essentially constant ratios of $k_{CN}/k_{solv} \simeq 0.1$ M^{-1} were obtained from analysis of products by HPLC.[5] These values are too small to give a significant increase of k_{obsd} in the presence of CN$^-$; consequently, the values of k_{CN} in Figure 1 represent upper limits of the second-order rate constants for the reaction with cyanide. The Hammett ρ^+ values for the reactions with solvent, azide, and cyanide are −5.7, −3.3, and −5.7, respectively. A value of $k_{az}/k_{solv} = 130$ M^{-1} was obtained for the reaction of 1-(*p*-nitrophenyl)ethyl chloride in water.

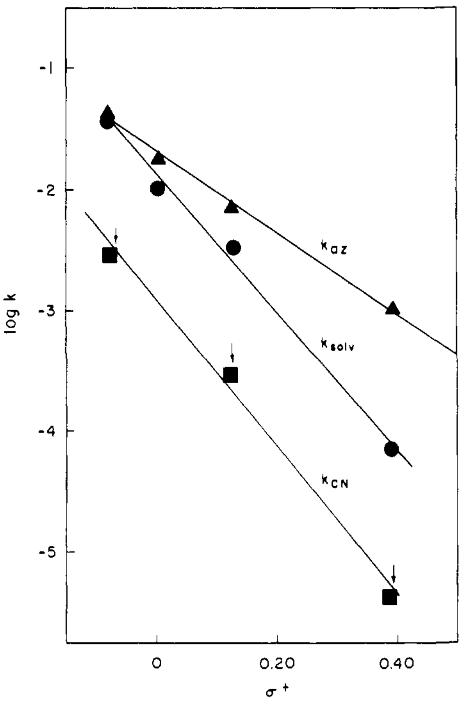
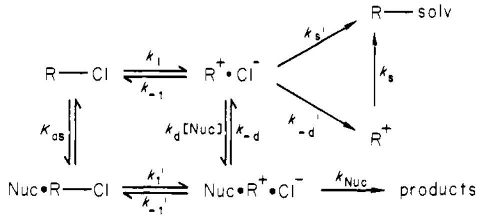


Figure 1. Hammett plots of the first-order rate constants for solvolysis (k_{solv}, ●), the second-order rate constants for azide reaction (k_{az}, ▲), and upper limits for the second-order rate constants for cyanide reaction (k_{CN}, ■) with substituted 1-phenylethyl chlorides in 20% acetonitrile in water.

Scheme I



Similar values of ρ^+ for k_{az} are obtained in 20% acetonitrile and 50:50 trifluoroethanol/water, respectively, based on ρ^+ values of 2.4 and 2.5 for k_{az}/k_{solv}[2] and the observation that ρ^+ values for k_{solv} are only slightly dependent on the solvent.[6]

The reaction that is first order in azide could proceed by a concerted mechanism or by a stepwise mechanism through the ion-pair intermediate [Nuc·R$^+$·Cl$^-$] in Scheme I. In the upper pathway of Scheme I the intermediate reacts competitively with solvent and Nuc by a trapping mechanism.[3,7] The observed reaction rate can be first order in Nuc when k_d is rate determining ($k_{-1} > k_d$[Nuc]). The lower pathway for a preassociation reaction will be preferred when the intermediate is unstable and the low-energy pathway for the formation of Nuc·R$^+$·Cl$^-$ is through k_1' (i.e., when $k_{-1}' > k_{-d}$).[3]

The following observations eliminate these stepwise pathways as viable mechanisms for the reaction that is first order in azide.

(1) The large values obtained for k_{az}/k_{solv} are inconsistent with a trapping pathway. For there to be an observable second-order azide reaction for this pathway k_d must be larger than $k_{-d}' + k_s'$ so that azide can compete effectively with solvent and so that the ion pair has a lifetime long enough for Nuc·R$^+$·Cl$^-$ to form. The

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[1] Supported by grants from the National Science Foundation (PCM-7708369) and the National Institutes of Health (GM20888). Dr. Richard was supported by a grant from the National Institutes of Health (AM-07251).

[2] Richard, J. P.; Jencks, W. P., preceding communication in this issue.

[3] Jencks, W. P. *Chem. Soc. Rev.* **1981**, *10*, 345-375.

[4] Ingold, C. K. "Structure and Mechanism in Organic Chemistry", 2nd ed.; Cornell University Press: Ithaca, NY, 1969; pp 418-610.

[5] Reference 2, footnote 3.

[6] A ρ^+ value of 5.7 for solvolysis in 50:50 ethanol/water (for substituents with $\sigma^+ \leq -0.08$) at 25 °C was calculated from the data of Shiner et al. (Shiner, V. J.; Buddenbaum, W. E.; Murr, B. L.; Lamaty, G. *J. Am. Chem. Soc.* **1968**, *90*, 418-426). A ρ^+ value of 5.0 for solvolysis in 80:20 acetone/water at 45 °C was reported: Tsuno, Y.; Kusuyama, Y.; Sawada, M.; Fujii, T.; Yukawa, Y. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 3337-3346.

[7] Sneen, R. A. *Acc. Chem. Res.* **1973**, *6*, 46-53.

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