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Registry No. Me_2N-*p*-$C_6H_4CH{=}CHNO_2$, 2604-08-2; MeO-*p*-$C_6H_4CH{=}CHNO_2$, 3179-10-0; $PhCH{=}CHNO_2$, 102-96-5; Br-*p*-$C_6H_4CH{=}CHNO_2$, 3156-37-4; Cl-*m*-$C_6H_4CH{=}CHNO_2$, 3156-35-2; NC-*p*-$C_6H_4CH{=}CHNO_2$, 3156-42-1; O_2N-*p*-$C_6H_4CH{=}CHNO_2$, 3156-41-0; piperidine, 110-89-4; morpholine, 110-91-8.

Supplementary Material Available: Kinetic data, Tables S1–S14 (13 pages). Ordering information is given on any current masthead page.

Swain–Scott Correlations for Reactions of Nucleophilic Reagents and Solvents with Secondary Substrates[1]

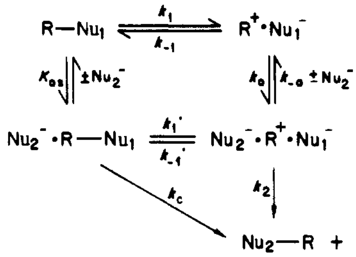
Paul E. Dietze and William P. Jencks*

Contribution No. 1588 from the Graduate Department of Biochemistry, Brandeis University, Waltham, Massachusetts 02254. Received December 13, 1985

Abstract: The reactions of 1-(4-nitrophenyl)-2-propyl derivatives with nucleophilic reagents in 50% trifluoroethanol–water follow Swain–Scott correlations with slopes s = 0.27, 0.34, and 0.43 for tosylate, bromide, and iodide leaving groups, respectively. The rate constants for reaction of this simple secondary system with the solvent components, trifluoroethanol and water, do not show positive deviations from these Swain–Scott correlations. This suggests that the reactions with solvent occur by the same mechanism as the reactions with other nucleophiles. Azide and cyanide ions show positive and negative deviations, respectively. However, linear correlations of log k_n are observed for reactions of nucleophiles, including azide and cyanide, with two compounds that have different leaving groups. These correlations include nucleophiles of both larger and smaller nucleophilic reactivity than the leaving group. The larger sensitivity toward nucleophiles of the iodo compound compared with the tosylate shows that there is an interaction, or "symbiosis", between the attacking and leaving groups in the transition state. It is difficult or impossible to describe a mechanism for these reactions that proceeds through an intermediate between two very similar transition states, with significant barriers for collapse of the intermediate. The results are consistent with a concerted S_N2 or A_ND_N reaction mechanism that proceeds through a single, carbocation-like transition state for the bond-forming and bond-breaking steps.

In spite of extensive investigation, the mechanism of substitution reactions at simple secondary alkyl carbon centers is still not understood. The reactions of secondary substrates exhibit behavior that is characteristic of both the S_N1 and S_N2 mechanisms, or both the $D_N + A_N$ and the A_ND_N mechanisms according to recently proposed nomenclature for reaction mechanisms.[2] The sensitivity of simple secondary substrates toward solvent ionizing power is larger than that of primary and smaller than that of tertiary substrates, while the sensitivity toward solvent nucleophilicity is smaller than that of primary and larger than that of tertiary substrates.[3,4] The solvolysis of 2-butyl tosylate in trifluoroacetic acid occurs with partial racemization,[5] and the 2-propyl and 2-butyl cations have been observed directly in superacid solutions.[6] Substitution reactions of secondary substrates with substituted pyridine leaving groups in solvents of low nucleophilicity at high temperature have been shown to occur by both S_N1 and S_N2 mechanisms.[7] Furthermore, the solvolysis of secondary substrates with labeled oxygen atoms in the leaving sulfonate is accompanied by scrambling of the oxygen atoms in recovered starting material.[8,9] For these and other reasons it has been suggested that the solvolysis of secondary substrates occurs through an intermediate carbocation, possibly through ion-pair intermediates,[10,11] an "S_N2 intermediate",[3,4,9,12,13] or an "ion-sandwich" mechanism.[14]

Scheme I



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[1] Supported in part by grants from the National Institutes of Health (GM 20888) and the National Science Foundation (PCM 81-17816) and a USPHS fellowship to Paul E. Dietze from the National Cancer Institute (1 F32 CA07832-01).

[2] A and D refer to associative and dissociative processes, respectively, and N refers to a nucleophilic or nucleofugic process. A + sign and a * refer to stepwise processes in which the intermediate does or does not exist long enough to become diffusionally equilibrated with the solvent, respectively, while the absence of punctuation refers to a concerted process with no intermediate. Commission on Physical Organic Chemistry, IUPAC, Pure and Applied Chemistry, in press.

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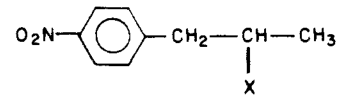
However, there is no conclusive evidence for the existence of an intermediate carbocation during the solvolysis of simple secondary substrates in solvents of moderate nucleophilicity. It is certain that the intermediate, if it exists at all, has an exceedingly short lifetime, and solvolysis in solvents as polar and weakly nucleophilic as formic acid gives only inverted product.[15,16] There is no evidence that there is an activation barrier for collapse of the ion pair at any point along the reaction coordinate for oxygen scrambling of sulfonates; if there is no barrier, there is no intermediate.[17] It has been pointed out that there are significant barriers to collapse that arise from solvent reorganization and other factors when a solvationally equilibrated intermediate is formed,[8b] but this does not mean that there is any chemical barrier to collapse when there is no intermediate. The sensitivity of the solvolysis rate to solvent nucleophilicity could represent nucleophilic assistance to the formation of a carbocation intermediate, if the intermediate exists, but it could also represent a concerted, bimolecular, S_N2 or A_ND_N mechanism. In summary, the available data show that secondary substrates undergo solvolysis through transition states that resemble a carbocation and that secondary cations can be formed in solvents of such low nucleophilicity that the cations have a significant lifetime, but this does not show that solvolysis proceeds through a carbocation intermediate in nucleophilic solvents.

Much of the controversy about reaction mechanisms for substitution at carbon is semantic and has arisen because mechanisms are frequently characterized according to the *appearance* of the transition state. Many criteria, such as the slopes of structure–reactivity correlations and the magnitudes of secondary isotope effects, provide a quantitative description of the transition state but do not provide a clear distinction between stepwise and concerted mechanisms. Three pathways for bimolecular substitution at carbon that permit a comparatively clear-cut distinction between different mechanisms are shown in Scheme I.[17,18] The upper path involves ionization (k_1) followed by diffusional encounter (k_a) and reaction (k_2) with a nucleophile, as suggested by Sneen.[19] However, if the triple-ion complex $Nu_2^-{\cdot}R^+{\cdot}Nu_1^-$ collapses to reactants (k_{-1}') faster than it separates (k_{-a}), the lowest energy path for both collapse and formation of this intermediate is through a stepwise preassociation mechanism[17,18] (K_{as} and k_1', a $D_N{*}A_N$ mechanism[2]). The "S_N2 intermediate" mechanism is a stepwise preassociation mechanism with nucleophilic assistance to formation of the intermediate. Since secondary substrates undergo solvolysis with inversion in nucleophilic solvents, there is no intermediate with a sufficient lifetime to undergo diffusional steps, and simple secondary substrates must react through either a stepwise or concerted preassociation mechanism in nucleophilic solvents. For the same reason, all Nu_2^- that are stronger nucleophiles than Nu_1^- would react with $R^+{\cdot}Nu_1^-$ at the same diffusion-controlled rate if the reaction proceeded through the k_1 pathway, which is not observed. If there is no barrier for reaction of the carbocation with either Nu_2^- or Nu_1^-, the intermediate $Nu_2^-{\cdot}R^+{\cdot}Nu_1^-$ does not exist, and the reaction must proceed by a concerted preassociation mechanism with a single transition state (k_c, an S_N2 or A_ND_N mechanism).

Reactions of substituted 1-phenylethyl derivatives have been shown to proceed through a series of mechanisms as the lifetime of the carbocation decreases, including the formation of a free carbocation intermediate ($D_N + A_N$), a stepwise preassociation mechanism ($D_N{*}A_N$), and a concerted preassociation mechanism (A_ND_N)[2] when the intermediate has no lifetime in the presence of the nucleophile. No evidence for nucleophilic assistance to ionization by the solvent was found in this system when the intermediate has a significant lifetime.[20-22]

We describe here a search for a carbocation intermediate in the solvolysis of a secondary substrate, by the use of structure–reactivity correlations. An additional mechanism, such as a stepwise reaction through a cation, usually gives a positive deviation from a structure–reactivity correlation. We find no such deviations for reactions of solvent components with 1-(4-nitrophenyl)-2-propyl halides and tosylate, **1–X**. It has been shown that there is no assistance to ionization by the aryl group in this system.[23,24] We conclude that the available data are consistent with a one-step, concerted S_N2 or A_ND_N mechanism for reactions of simple secondary alkyl substrates with solutes and solvents of moderate or high nucleophilicity.



1-X

Experimental Section

Materials. Reagent grade inorganic salts were used without further purification. Trifluoroethanol (99+%, Gold Label grade from Aldrich) was used without further purification. Water was glass distilled. Acetone was purified by refluxing for 30 min over $KMnO_4$ and K_2CO_3, followed by distillation.

1-(4-Nitrophenyl)-2-propyl tosylate (mp 115–117 °C [lit. mp 115.8–117.2 °C]) was prepared according to a published procedure.[24]

1-(4-Nitrophenyl)-2-propyl bromide was prepared by refluxing 2 g of the tosylate with a 4-fold molar excess of lithium bromide in 40 mL of purified acetone. The disappearance of the tosylate was monitored by HPLC analysis. Aliquots of the reaction mixture were dried under a stream of nitrogen, dissolved in 3 mL of 50:50 $CH_3CN–H_2O$, and analyzed by HPLC. When the reaction was complete the solution was filtered and the acetone was removed under reduced pressure. The residue was dissolved in ethyl ether and extracted twice with water. The ether layer was dried over magnesium sulfate, and the solvent was removed under reduced pressure to yield the bromide as a brown oil: NMR ($CDCl_3$) δ 8.15 (d, 2), 7.40 (d, 2), 4.35 (heptet, 1), 3.25 (d, 2), 1.75 (d, 3).

1-(4-Nitrophenyl)-2-propyl iodide was synthesized from the tosylate and lithium iodide by the same procedure to yield a brown solid: mp 36–39 °C; NMR ($CDCl_3$) δ 8.10 (d, 2), 7.25 (d, 2), 4.25 (heptet, 1), 3.15 (m, 2), 1.87 (d, 3).

All solvolysis substrates were shown to be >95% pure by HPLC analysis.

Product Analysis. Products were analyzed by high-pressure liquid chromatography (HPLC) with a Waters Associates reverse-phase 5-μm NOVA PAK C_{18} chromatography column, which was pressurized inside a Waters Radial Compression Module. Separation of the components of the reaction mixture was accomplished by isocratic or gradient elution with mixtures ranging from 50:50 to 80:20 (v/v) $CH_3CN–H_2O$. Peak areas were obtained by electronic integration of their UV absorbance at 266 nm with a Waters Model 730 Data Module. It was shown by UV and HPLC analysis of mixtures containing known concentrations of the compounds that the extinction coefficients of the alcohol, bromide, and iodide at 266 nm are identical. Analysis by HPLC after quantitative conversion of the bromide to the azide or thiocyanate also indicated that these products have the same extinction coefficient at 266 nm. For all other nucleophiles it was assumed that the extinction coefficient of the

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substitution product is the same as for the alcohol. At least two injections of each sample were made for HPLC analyses of product ratios.

Two alkene products were formed that disappeared upon addition of aqueous bromine, as measured by HPLC. Treatment of the iodide with dilute sodium hydroxide gave complete conversion to an alkene product with an extinction coefficient 0.33 times that of the iodide at 266 nm, measured by HPLC and UV. The extinction coefficient for the other alkene product, which was formed in smaller quantities, was estimated to be the same by comparison of the peak areas from HPLC analysis of the tosylate and of the reaction products at 266 nm after complete solvolysis of the tosylate.

Kinetics. Reaction mixtures for solvolysis and kinetic measurements in 50% trifluoroethanol–water by volume were prepared by adding 7 mL of a solution of the substrate in trifluoroethanol ($\sim 2.5 \times 10^{-3}$ M), 10 μL of 0.4 M 4-chloronitrobenzene in trifluoroethanol as an internal standard, and 18 mL of trifluoroethanol to a 50-mL volumetric flask. The flask was filled to volume with 1.0 M sodium perchlorate in water. The solution was shaken, and approximately 3 mL was placed into several 4-mL HPLC sample vials. The vials were closed tightly with Teflon-sealed caps and placed in a constant-temperature bath at 75 ± 0.3 °C. After temperature equilibration, samples were removed at intervals, quenched in ice, and analyzed by HPLC, using the internal standard to calibrate injection volumes.

The fraction of alcohol product was found to be 0.63 from solvolysis of the tosylate, 0.72 for the bromide, and 0.60 for the iodide. Errors are estimated to be ±5%.

Pseudo-first-order rate constants for solvolysis, k_{sol}, were determined by monitoring the appearance of alcohol product, P, or the disappearance of the substrate, S, as the function of time. Rate constants were obtained from semilogarithmic plots of [S] or $[P_\infty - P_t]$ against time. The values obtained for k_{sol} are 3.8×10^{-5}, 2.1×10^{-6}, and 1.9×10^{-6} s^{-1} for the tosylate, bromide, and iodide compounds, respectively. Errors are estimated to be ±10%. The pseudo-first-order rate constant for reaction with water, k'_{HOH}, was obtained from the product of k_{sol} and the fraction of alcohol product from HPLC analysis.

The value of k_n for azide was determined by using HPLC to measure the pseudo-first-order rate constants for the disappearance of starting material in the presence of 0.1–0.4 M sodium azide. A plot of k_{obsd} against $[N_3^-]$ gave the second-order rate constant k_n.

The rate constant for thiosulfate as a nucleophile could not be determined by product analysis because the product coeluted with the solvent front. The value of k_n for thiosulfate was determined by measuring the pseudo-first-order rate constant, k_{obsd}, for the disappearance of starting material in the presence of 0.1 M $Na_2S_2O_3$ and by using the formula $k_{obsd} = k_{sol} + k_n[S_2O_3^{2-}]$. All kinetic experiments gave linear pseudo-first-order plots for 2–3 half-lives and contained about 15 data points.

Second-order rate constants for other nucleophiles, k_n, were determined by product analysis. Solutions of nucleophiles were made up to volume at 75 °C. Known volumes of a 1.0 M aqueous solution of the sodium salt of the nucleophile and of 1.0 M sodium perchlorate were placed in a 4-mL HPLC vial to give a total volume of 1.5 mL. To this was added 1.5 mL of a solution of the substrate in trifluoroethanol ($\sim 2.5 \times 10^{-3}$ M). It was shown that solutions prepared in this way have the same solvent composition, within 1%, as solutions that were made up to volume with 1 M sodium perchlorate. The final concentrations of nucleophiles were in the range 0.1–0.4 M, except that the range was 0.01–0.04 M for azide. The vials were sealed, incubated at 75 ± 0.3 °C, and analyzed by HPLC at appropriate time intervals, as described above. Second-order rate constants were obtained from eq 1. Products that

$$\frac{[\text{R-Nu}]}{[\text{R-OH}]} = \frac{k_n[\text{Nu}]}{k'_{HOH}} \tag{1}$$

were unstable under the reaction conditions were analyzed during the early part of the reaction, during which the ratio of nucleophile product to alcohol product was shown to be constant. Solutions containing cyanide became discolored during the reaction but did not give rise to new peaks or changes in product ratios with increasing time of incubation.

Rate constants for alcohol nucleophiles were determined by the same procedure, by mixing 1.5 mL of 1.0 M $NaClO_4$, 0.15 mL of alcohol, and 1.35 mL of a solution of the substrate in trifluoroethanol ($\sim 2.5 \times 10^{-3}$ M) in a 4-mL HPLC vial.

Results

Second-order rate constants, k_n, for the reactions of nucleophilic reagents with the bromide, iodide, and tosylate of **1** in 50% trifluoroethanol–water (v/v) at 75 °C and ionic strength 0.5 M ($NaClO_4$) are reported in Table I. The rate constants for solvolysis, k_{sol}, and for the second-order reactions with azide and thiosulfate ions were determined kinetically as described in the Experimental Section. Rate constants for most nucleophiles were obtained from ratios of k_n/k'_{HOH} that were determined at ⩾4 concentrations of added nucleophile by HPLC analysis of the products, as described in the Experimental Section. The values of k'_{HOH}, the pseudo-first-order rate constants for reaction with water, were obtained from k_{sol} and product analysis. The pseudo-first-order rate constants for reaction with water are 1.5×10^{-6}, 1.2×10^{-6}, and 2.3×10^{-5} s^{-1} for the bromide, iodide, and tosylate, respectively. The rate constant of 3.9×10^{-4} M^{-1} s^{-1} for the reaction of azide ion with **1-Br** that was determined kinetically agrees with the value of 3.5×10^{-4} M^{-1} s^{-1} that was determined by product analysis.

Table I. Rate Constants, k_n, for the Reactions of Nucleophilic Reagents with 1-(4-Nitrophenyl)-2-propyl-X[a]

	10^7k_n (M^{-1} s^{-1}) for leaving group X$^-$			
nucleophile	Br$^-$	OTs$^-$	I$^-$	n_{CH_3I}[b]
$S_2O_3^{2-}$[c]	1200	3400		8.95
I$^-$	440	1300		7.42
SCN$^-$	690	1800	1300	6.70
CN$^-$	59	130		6.70
Br$^-$		620	200	5.79
N_3^-	3500[d]	9200	5700	5.78
OAc$^-$	53	270	57	4.50
Cl$^-$	53	370	98	4.37
F$^-$	5.4	43	6.0	2.70
CH_3OH	1.9	21	1.6	0
H_2O[e]	0.54	8.3	0.46	−0.27[f]
CF_3CH_2OH	0.14	4.0	0.09	−2.8[f]

[a] Determined from product studies, unless otherwise noted, using the average of at least four different concentrations of nucleophile in 50% aqueous trifluoroethanol (v/v) at 75 °C and ionic strength 0.5 M ($NaClO_4$). [b] From ref 25. [c] Determined by monitoring substrate disappearance as a function of time in the presence of 0.1 M $Na_2S_2O_3$. [d] A value of $k_n = 3.9 \times 10^{-4}$ M^{-1} s^{-1} for azide was determined from pseudo-first-order rate constants obtained at four concentrations of azide. [e] Determined by dividing k'_{HOH} by the concentration of H_2O (27.75 M). [f] Estimated by comparing *N* values for solvolysis with the *N* value for methanol, based on reaction with methyl tosylate.[4]

Table II. Second-Order Rate Constants, k_n, for the Reactions of Alcohols with 1-(4-Nitrophenyl)-2-propyl-X[a]

	10^7k_n (M^{-1} s^{-1}) for leaving group X$^-$		
alcohol	OTs$^-$	I$^-$	pK_a alcohol[b]
CH_3OH	21	1.6	15.5 (10.62)
CH_3CH_2OH	16	0.88	16.0 (10.63)
$CH_3OCH_2CH_2OH$	13	0.58	14.8 (9.2)
$NCCH_2CH_2OH$	5.3	0.28	14.0 (7.7)
CF_3CH_2OH	4.0	0.09	12.4 (5.7)

[a] From product analysis in 50:45:5 (v/v/v) H_2O–TFE–ROH at 75 °C and ionic strength 0.5 M ($NaClO_4$). [b] From ref 26. The pK_a values of the corresponding ammonium ions are shown in parentheses.

Table I also contains Swain–Scott *n* values based on the reactions of methyl iodide in methanol; the second-order rate constant for methanol corresponds to an *n* value of zero by definition.[25] The solvent nucleophilicity scale of Schleyer and co-workers[4] gives estimated values of *n* = −0.27 for water and −2.8 for trifluoroethanol, from the differences between the *N* values of these compounds and methanol.

Rate constants for the reactions of alcohols with **1**-OTs and **1**-I were determined by product analysis and are reported in Table II. These reactions were carried out in 50:45:5 (v/v/v) H_2O–TFE–ROH at 75 °C and ionic strength 0.5 M ($NaClO_4$). The replacement of 5% trifluoroethanol with a second alcohol did not change the ratio of alcohol to trifluoroethyl ether products, within experimental error. The pK_a values of the alcohols and the

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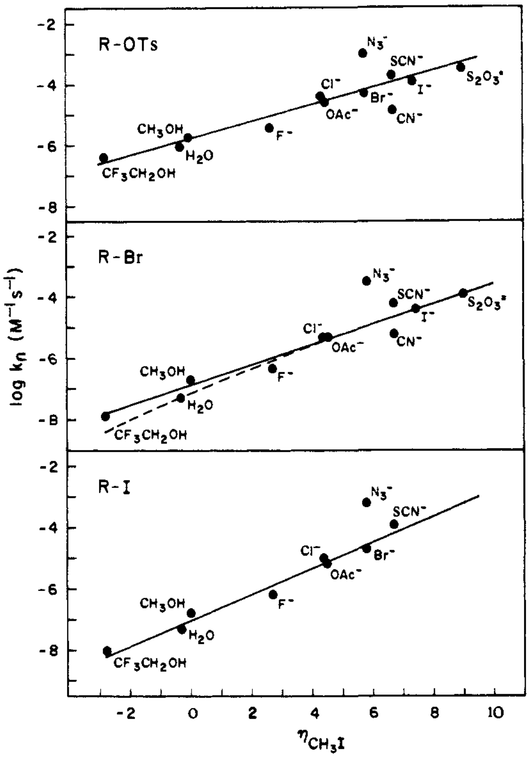

Figure 1. Swain–Scott plots of log k_n against n_{CH_3I} of the nucleophile for the reactions of 1-(4-nitrophenyl)-2-propyl-X (R-X) in 50% trifluoroethanol–water at 75 °C and ionic strength 0.5 M ($NaClO_4$) for X = tosylate, bromide, and iodide. Values of $n = -0.27$ for water and -2.8 for trifluoroethanol were estimated from N values for solvolysis.[4] The dashed line was calculated for a stepwise reaction mechanism, as described in the text.

corresponding ammonium ions in water[26] are also shown.

Discussion

The second-order rate constants for reactions of nucleophilic reagents with 1-(4-nitrophenyl)-2-propyl-X (**1**-X) in 50% trifluoroethanol–water follow Swain–Scott correlations with s values of 0.27, 0.34, and 0.43 for tosylate, bromide, and iodide leaving groups, respectively, as shown in Figure 1. These correlations are based on n values for reactions of methyl iodide in methanol.[25] Correlations with n values for reactions in water, for which fewer n values are available, give s values for the three leaving groups of 0.25, 0.34, and 0.49, based on n values for methyl iodide,[27] and 0.30, 0.41, and 0.63 (four points), based on n values for methyl bromide[28] (not shown). The rate constants for solvent components and for azide and cyanide ions were excluded from the least-squares calculation, because we wish to test the hypothesis that the rate constants for reaction with solvent can be accounted for by the same mechanism as other nucleophiles and because azide and cyanide ions show large deviations from the correlation (see below).

The relatively small sensitivity of the 1-(4-nitrophenyl)-2-propyl derivatives toward the nucleophilicity of the attacking reagent indicates that there is one-quarter to one-half as much bond formation with the nucleophile in the transition states for these compounds as there is with methyl iodide. This also corresponds to a small amount of bonding to the leaving group in the transition state because the reactions are symmetrical. The reaction of Br^- with **1**-Br is symmetrical, and there is little or no change in the structure of the transition state as the nucleophile is changed (Figure 1). The reactions with **1**-Br include nucleophiles of both larger and smaller nucleophilicity compared with Br^-, and there is little or no curvature in the structure–reactivity correlations. This relatively small amount of bonding may be ascribed to steric hindrance and to movement of the transition state perpendicular to the reaction coordinate in secondary compared with primary substrates. Hyperconjugation from neighboring C–H might be expected to stabilize a secondary carbocation and to bring about a change in the nature of the transition state so that it more closely resembles a carbocation; such changes are well-known in other systems.[29,30] The decreases in the rate constants for reactions of isopropyl compared with methyl derivatives by factors of up to 10^3 have been attributed to a steric effect.[31]

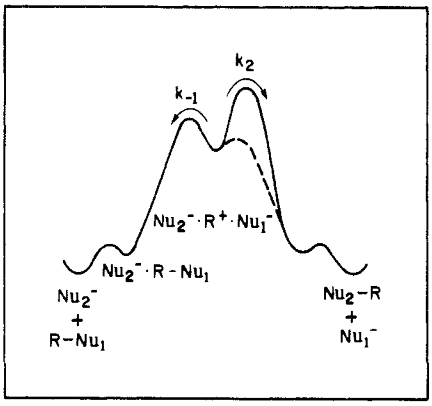

Figure 2. Reaction coordinate diagram for a stepwise preassociation mechanism (D_N*A_N). The reaction is described by the solid line when Nu_2^- is a poorer nucleophile than Nu_1^- and by the dashed line when Nu_2^- is a better nucleophile than Nu_1^-.

The large positive deviations for azide and negative deviations for cyanide from the Swain–Scott correlations in Figure 1 give a reactivity order $N_3^- > CN^-$. This order is opposite to that observed for methyl iodide[25] but is the same as for nucleophilic reactions with carbocations that follow the N^+ scale.[32] It suggests that the transition state resembles a carbocation. Similar deviations have been observed for concerted bimolecular reactions of methoxymethyl and 1-phenylethyl derivatives, which also react through transition states with a large amount of carbocation character.[22,33] A correlation of log k_n for the tosylate of **1** with log k_n for substitution reactions of 1-(4-nitrophenyl)ethyl tosylate gives a good fit with a slope of 0.89, including the points for azide and cyanide ions; however, the rate constant for the reaction of the phenylethyl compound with water is threefold faster than predicted by this correlation (not shown). There is evidence that 1-(4-nitrophenyl)ethyl derivatives undergo concerted bimolecular substitution reactions with a number of nucleophiles (but not water) because the 1-(4-nitrophenyl)ethyl cation does not have a significant lifetime in the presence of these nucleophiles.[22]

If the reactions of **1**-X proceed through an intermediate carbocation, they must proceed through an ion-pair, an S_N2 intermediate, or a stepwise preassociation mechanism, as described in the introduction. If the intermediate exists there must be two transition states, one for bond breaking and another for bond making, and there will be a change in the rate-limiting step from k_2 to k_1' when the attacking reagent becomes a better nucleophile than the leaving group, as shown in Figure 2.[33] Since there must be more bond formation to the nucleophile in the transition state when nucleophilic attack is rate limiting than when bond breaking is rate limiting, one might expect a corresponding break in a structure–reactivity correlation when the nucleophilicity of the

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[33] Knier, B. L.; Jencks, W. P. *J. Am. Chem. Soc.* **1980**, *102*, 6789–6798.

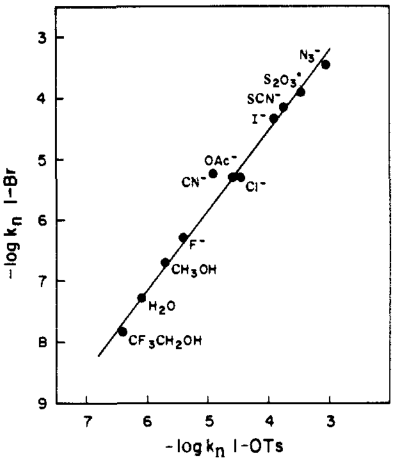

Figure 3. Comparison of nucleophilicity toward 1-(4-nitrophenyl)-2-propyl bromide and 1-(4-nitrophenyl)-2-propyl tosylate for reaction in 50% trifluoroethanol–water at 75 °C and ionic strength 0.5 M ($NaClO_4$).

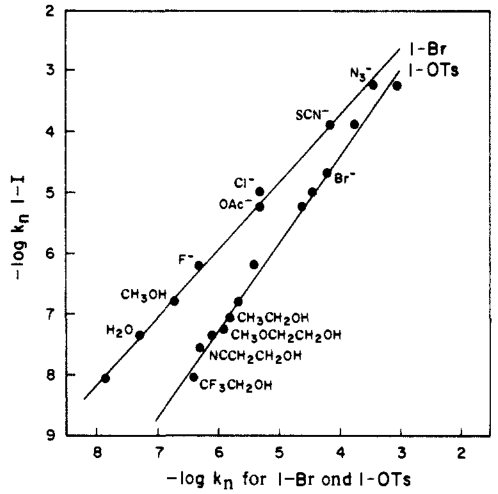

Figure 4. Comparison of nucleophilicity toward 1-(4-nitrophenyl)-2-propyl iodide and 1-(4-nitrophenyl)-2-propyl tosylate or bromide for reactions in 50% trifluoroethanol–water at 75 °C and ionic strength 0.5 M ($NaClO_4$).

attacking group becomes larger than that of the leaving group. The absence of such a break can provide evidence in support of a concerted reaction mechanism with a single transition state, as in the reactions of phosphorylated pyridines and isoquinoline-*N*-sulfonate.[34,35]

The data for reactions of **1**-Br in Figure 1 include rate constants for nucleophiles of both larger and smaller nucleophilicity compared with the leaving bromide ion but show no indication of such a break. Figure 3 shows that there is also no break in a plot of log k_n for **1**-Br against log k_n for **1**-OTs, which shows less scatter. The good fit of the data to this plot and to the other plots of log k_n for two different leaving groups, shown in Figure 4, shows that most of the deviations of the points in the Swain–Scott plots arise from the different reactivity patterns of secondary substrates compared with methyl iodide. These comparisons exclude a stepwise reaction mechanism in which there is much more bond formation to the nucleophile in the bond-making than in the bond-breaking step. They also exclude a Sneen-type mechanism through the upper path in Scheme I because such a mechanism would give a break in the curve to a slope $s = 0$ for a diffusion-controlled reaction with strong nucleophiles; a stepwise mechanism for substitution at the methyl group[36] is excluded for the same reason.

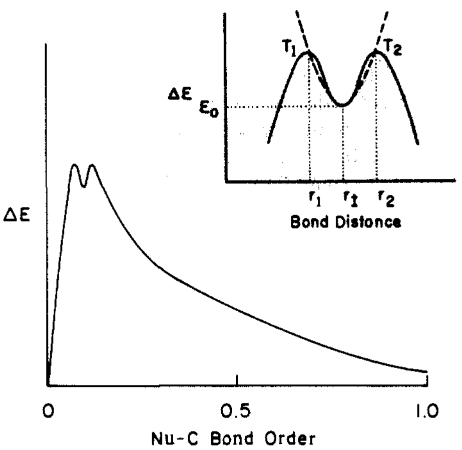

Figure 5. Reaction coordinate diagram of energy vs. bond order to the nucleophile for bond orders of 0.08 and 0.13 for nucleophilic assistance to ionization and nucleophilic attack, respectively, in a stepwise reaction mechanism of **1**-X. The inset shows an enlarged picture of the region around the hypothetical intermediate, with a parabola drawn through the energy minimum and the two transition states, T_1 and T_2, for collapse of the intermediate.

However, the possibility must be considered that there is an intermediate and that the amount of bond formation to the nucleophile in the transition state for the bond-breaking step, in which the intermediate is formed, is very similar to that in the transition state for bond making and collapse of the intermediate. It has been proposed[3,4,9,12] that the bond-breaking step for the formation of a carbocation intermediate occurs with nucleophilic assistance to ionization. If there is an intermediate, the reactions of the tosylate, with $s = 0.27$, represent nucleophilic assistance to ionization and the reactions of the iodide, with $s = 0.43$, represent almost entirely rate-limiting nucleophilic attack on the intermediate, because tosylate is a weak nucleophile (small k_2, Figure 2) and iodide is a strong nucleophile (large k_2). These values of s are not sufficiently different to give sharp curvature in a structure–reactivity correlation. The correlation line for reactions of the bromide was calculated for a two-step mechanism with $s = 0.27$ and 0.43 and is shown as the dashed line in Figure 1.[37] This line is not inconsistent with the observed rate constants.

The problem with this model is that the two transition states, for nucleophilic assistance to ionization and for nucleophilic attack on the carbocation, are so similar to each other that it is difficult to postulate an intermediate in an energy well between them that can exist for longer than a vibration frequency and have a significant barrier for collapse. It is generally believed that there is only a moderate amount of bond formation in the transition state for nucleophilic attack on methyl halides and even less for secondary substrates. Brønsted-type plots for the reactions of substituted pyridines with methyl iodide show that there is approximately 30% as much charge development on the pyridine in the transition state for nucleophilic attack as there is in the product.[38] If this 30% is a measure of bond order to the pyridine in the transition state for nucleophilic attack on methyl iodide,

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[34] Skoog, M. T.; Jencks, W. P. *J. Am. Chem. Soc.* **1983**, *105*, 3356–3357. Bourne, N.; Williams, A. *J. Am. Chem. Soc.* **1983**, *105*, 3357–3358. Hopkins, A.; Bourne, N.; Williams, A. *J. Am. Chem. Soc.* **1983**, *105*, 3358–3359.

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[36] Scott, J. M. W. *Can. J. Chem.* **1970**, *48*, 3807–3818.

[37] The line was calculated as described previously.[35] The rate constant for the symmetrical rection with bromide ion, k_{Br}, was estimated from the n value for bromide by interpolation in Figure 1, and the values of k_1 and k_b at this n value were taken as $2k_{Br}$. A value of $s = 0.45$ for rate-limiting nucleophilic attack on the iodide of **1** (k_b) was estimated for a stepwise mechanism by fitting the observed rate constants to the same equation. The calculated line for the bromide using $s = 0.45$ does not differ significantly from that calculated with $s = 0.43$.

[38] Arnett, E. M.; Reich, R. *J. Am. Chem. Soc.* **1980**, *102*, 5892–5902. Several workers agree with this estimate of approximately 30% bond formation to pyridines in the transition state, although there are differences of opinion regarding the amount of bond breaking (Harris, J. M.; Paley, M. S.; Prasthofer, T. W. *J. Am. Chem. Soc.* **1981**, *103*, 5915–5916. Abraham, M. H.; Nasehzadeh, A. *J. Chem. Soc., Chem. Commun.* **1981**, 905–906).

the Swain–Scott slopes $s = 0.27$ and 0.43 for nucleophilic reactions with **1**-OTs and **1**-I correspond to 8% and 13% bond formation to the nucleophile in the transition state. If there is an intermediate, the bond order to the nucleophile would then be 0.08 in the transition state for formation of the intermediate and 0.13 in the transition state for its collapse; the bond orders to the leaving group would be 0.13 and 0.08, respectively, in the two transition states. A reaction coordinate profile for bond formation to the nucleophile would then have the curious shape shown in Figure 5, and an intermediate between the two transition states, with a bond order of $(0.13 + 0.08)/2 = 0.105$, would have to reach a transition state with a change in bond order of only 0.025.

It is concluded that there is no intermediate with a significant barrier for its collapse in these reactions. We are not aware of any precedent for a significant barrier to collapse of an intermediate that involves such a small change in bonding, and the conclusion is based on the implausibility of such a barrier. We are not qualified to provide a sophisticated quantitative evaluation of this system, but a crude calculation illustrates the problem and suggests that such an intermediate is not likely to exist.[39] If we assume that such an intermediate for a symmetrical reaction is in a parabolic energy well between two transition states with bond orders of 0.08 and 0.13 to the entering and leaving groups, as shown in the inset of Figure 5, a force constant of 0.90 mdyn Å^{-1} is required to give a barrier of $RT = 690$ cal mol^{-1} at 75 °C. The force constant for a carbon–bromine bond[40] is 2.8 mdyn Å^{-1}, so that Badger's rule gives a bond order for the intermediate of $n = 0.90/2.8 = 0.32$, which is larger than the bond orders of the transition states for formation and cleavage of the intermediate. It is difficult to imagine how the attack of a nucleophile on such an intermediate to give product would occur with a decrease rather than an increase in the bond order to the nucleophile as the transition state is reached. The choice of a parabola through the two transition states for the calculation is conservative because a still larger force constant and bond order would be required to fit the actual curvature of the energy well around an intermediate, which is shown by the solid line in the inset of Figure 5. The calculation does not, by itself, exclude an "uncoupled concerted" mechanism[17] with a flat region or even a small dip at the energy maximum, in which there is no significant interaction between the entering and leaving groups. However, the existence of nucleophilic assistance to solvolysis and the similar or identical Swain–Scott slopes for reagents that are better or worse nucleophiles than the leaving groups show that the reactions are not uncoupled; there is significant nucleophilic involvement in all of the reactions, and the increase in this involvement with increasing polarizability of the leaving group suggests that there is also significant coupling between the nucleophile and the leaving group (see below). The data are most easily explained by a concerted mechanism with a single energy maximum.

Symbiosis. The increasing s values for nucleophilic reactions in the series $s = 0.27$, 0.34, and 0.43 for the tosylate, bromide, and iodide of **1**, respectively, show that there is an interaction between the attacking and leaving groups that stabilizes the transition state when both groups are strong, polarizable nucleophiles. A favorable interaction of strong nucleophiles with **1**-I, for example, will increase the s value for this compound. The ratio of 1.3 for the s values of **1**-I and **1**-Br is essentially the same as the ratio of 1.4 for CH_3I and CH_3Br.[41] The increase in s is not related to the leaving group ability or the absolute rate constants of the reactions—the tosylate is the most reactive compound and the iodide is usually intermediate between the tosylate and the bromide (Table I).

The linear correlations in Figures 3 and 4 show that there is no change in the interaction when the incoming group is a better or worse nucleophile compared with the leaving group. Similar behavior has been observed for concerted bimolecular substitution reactions of nucleophiles with methyl bromide and iodide[41] and with 1-(4-nitrophenyl)ethyl tosylate and chloride.[22] The absence of any bimolecular reaction of 1-(4-methylphenyl)ethyl chloride or pentafluorobenzoate with azide ion at concentrations up to 0.5 M and the presence of a clear-cut second-order reaction of azide with the corresponding dimethylsulfonium ion, which has a "soft" dimethyl sulfide leaving group, provide still another example of such an interaction.[22]

This kind of interaction between entering and leaving groups in these and other systems has been called "symbiosis".[41] It is consistent with a fully concerted reaction mechanism in which bond making and bond breaking are coupled; it is difficult to explain by a mechanism in which bond making and bond breaking take place at different times on opposite sides of the central carbon atom.

The linear correlations in Figures 1, 3, and 4 show no indication of changes in transition-state structure as the nucleophile is changed, such as a "Hammond effect" or a significant direct interaction coefficient $p_x = \partial s/\partial n$, in agreement with most previous conclusions for substitution on methyl derivatives.[38,42] Structure–reactivity contour diagrams suggest that changing the strength of the nucleophile can give movements of the transition state parallel and perpendicular to the reaction coordinate that cancels, so as to give little or no change in transition-state structure for bond formation to the nucleophile ($p_x \sim 0$), but reinforce each other with respect to leaving groups so that a cross-interaction coefficient such as $p_{xy} = \partial\beta_{lg}/\partial pK_{nuc} = \partial\beta_{nuc}/\partial pK_{lg}$ is more likely to be significant.[43] The observed changes in s show that there are changes in transition-state structure with different leaving groups in this system. However, these changes are not necessarily the kind of changes predicted by the cross-coefficients because the changes in the energy surface that are introduced by changing the leaving atom are too large to be described by such a simple perturbation treatment.

Reactions with Solvent. The possibility should be considered that the reactions with solvent and nucleophilic solutes occur by different mechanisms, with an S_N1 ($D_N{*}A_N$) mechanism for solvent and an S_N2 (A_ND_N) mechanism for nucleophilic solutes. An additional reaction mechanism is expected to give positive deviations from a structure–reactivity correlation, instead of the downward curvature that occurs with a change in the rate-limiting step of a single, stepwise mechanism. A structure–reactivity correlation for nucleophilic reactivity that includes both mechanisms for secondary substrates is then expected to show upward curvature, with a small or zero slope for solvent components that

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(39) We consider only the stretching frequencies for the symmetrical linear triatomic intermediate $N^{\delta-}$—$R^{\delta+}$—$L^{\delta-}$ and assume that the potential energy for small displacements of the nuclear geometry is described by $E = (f/2)(\Delta r_N)^2 + (f/2)(\Delta r_L)^2 + f_{12}(\Delta r_N)(\Delta r_L) + E_0$, in which f is the force constant of the bonds to the nucleophile (N) and the leaving group (L), r_N and r_L are the bond distances between R and N or L, respectively, and f_{12} is an interaction force constant. Assuming that this harmonic approximation extends all the way to the transition-state geometries and setting $f_{12} = 0$ gives $E^{*} - E_0 = \Delta E = f\,(r_1 - r_2/2)^2$ for a symmetrical reaction in which N = L, such as the reaction of Br^- with **1**-Br. The values of the carbon–bromine distances in the two transition states, r_1 and r_2, were calculated from the bond orders (0.08 and 0.13) and Pauling's rule (Pauling, L. *J. Am. Chem. Soc.* **1947**, *69*, 542–553). A value of $\Delta E = RT = 690$ cal mol^{-1} at 75 °C gives $f = 0.90$ mydn A^{-1}. Inclusion of an interaction force constant f_{12} that is large enough to reduce f to a reasonable value results in an unstable symmetric stretching motion of the intermediate so that there is no force to prevent its disappearance (Huskey, P., personal communication. Melander, L.; Saunders, W. H., Jr. *Reaction Rates of Isotopic Molecules*; Wiley: New York, 1980; pp 64–66). Conversely, the force constant of the intermediate may be estimated from Badger's rule (Melander and Saunders, p 68) to be $f = nf^0 = 0.105 \times 2.8 = 0.29$. This gives an activation energy of $\Delta E = 220$ cal mol^{-1}, which is less than $RT = 690$ cal mol^{-1} at 75 °C. Bond orders of 0.13 and 0.20, from the β_{nuc} values for reactions of alcohols with the tosylate and iodide of **1** (see below), give a barrier of 280 cal mol^{-1}.

(40) Wilson, E. B., Jr.; Decius, J. C.; Cross, P. C. *Molecular Vibrations*; McGraw Hill: New York, 1955; p 175.

(41) Pearson, R. G.; Songstad, J. *J. Am. Chem. Soc.* **1967**, *89*, 1827–1836. Pearson, R. G.; Songstad, J. *J. Org. Chem.* **1967**, *32*, 2899–2900. Lewis, E. S.; Vanderpool, S. J. *J. Am. Chem. Soc.* **1978**, *100*, 6421–6424.

(42) Lewis, E. S.; Kukes, S.; Slater, C. D. *J. Am. Chem. Soc.* **1980**, *102*, 1619.

(43) Thornton, E. R. *J. Am. Chem. Soc.* **1967**, *89*, 2915. Thornton, E. K.; Thornton, E. R. In *Transition States of Biochemical Processes*; Gandour, R. D., Schowen, R. L., Eds.; Plenum: New York, 1978; p 3. Jencks, D. A.; Jencks, W. P. *J. Am. Chem. Soc.* **1977**, *99*, 7948. Young, P. R.; Jencks, W. P. *J. Am. Chem. Soc.* **1979**, *101*, 3288. Harris, J. M.; Shafer, S. G.; Moffatt, J. R.; Becher, A. R. *J. Am. Chem. Soc.* **1979**, *101*, 3295.

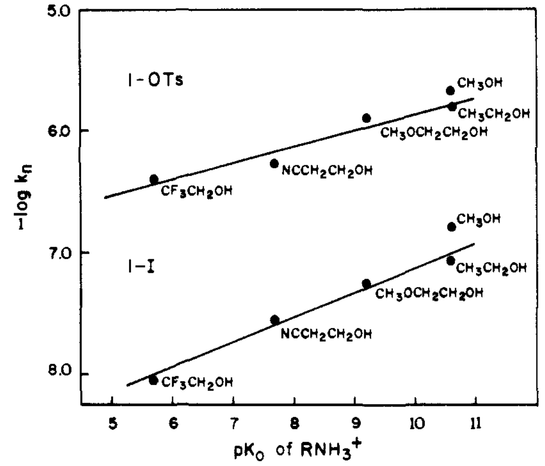

Figure 6. Brønsted-type plots for the reactions of 1-(4-nitrophenyl)-2-propyl tosylate and iodide with alcohols in 50:45:5 (v/v/v) H_2O–TFE–ROH at 75 °C and ionic strength 0.5 M ($NaClO_4$).

react with little or no nucleophilic participation and a larger slope for strong nucleophiles that react in a concerted, bimolecular reaction. There would then be a positive deviation of the rate constants for the solvent components from the correlation line for the strong nucleophiles. The positive deviations of 3–4-fold from Swain–Scott correlations of the rate constants for the reaction of water with 1-(4-nitrophenyl)ethyl chloride and tosylate and 1-(3-methoxyphenyl)ethyl chloride may represent such behavior.[22,44] The rate constants for the reaction of water with the 1-(4-nitrophenyl)ethyl compounds are only 2–3 times smaller than those for fluoride ion, whereas for the derivatives of **1** they are smaller by a factor of 5–13 (Table I). The rate constants for solvolysis of the substituted 1-phenylethyl chlorides show a good fit to a Hammett correlation for reactions that proceed through a carbocation intermediate.[22]

However, the Swain–Scott plots of Figure 1 show that the rate constants for reaction of the solvent components trifluoroethanol, methanol, and water with the tosylate, bromide, and iodide of **1** fall on the same correlation line as solutes that react by concerted nucleophilic substitution. The correlations in Figures 3 and 4 give the same conclusion. Correlations with the more limited series of n values for reactions of methyl bromide[28] and methyl iodide[27] in water show that the second-order rate constant for water has a small *negative* deviation of 2–10-fold from the least-squares lines (not shown). These results are consistent with the hypothesis that water, methanol, and trifluoroethanol react by the same second-order, concerted mechanism for substitution as do other nucleophilic reagents; there is no evidence for a significant contribution to the observed rate constants of any additional, different reaction mechanism.

Brønsted-type plots of log k_n for the reactions of substituted ethanols with the tosylate and iodide of **1** give slopes $\beta_{nuc} = 0.13$ and 0.20, respectively, in a correlation with the pK_a values of the corresponding substituted ethylammonium ions, as shown in Figure 6. This correlation gives a slightly better fit to the data than a correlation with the pK_a values of the substituted alcohols, presumably because the transition state for nucleophilic reaction gives a partial development of positive rather than negative charge on the alcohol.[45] The rate constants for methanol show a small positive deviation. The ratio of the β_{nuc} values for the iodide and tosylate is 1.5, which is essentially the same as the ratio of 1.6 for the s values of the bimolecular substitution reactions for the same compounds. This provides additional evidence that the solvent components and added nucleophilic reagents react by the same mechanism.

Conclusion. The results described here show that the reactions of solvent with **1**-X, a simple secondary substrate, do not show positive deviations from Swain–Scott correlations, which are expected for solvolysis by a mechanism that is different from the bimolecular substitution mechanism followed by stronger nucleophiles, and do not proceed through an ion-pair intermediate that has significant barriers for collapse, which would cause a change in the rate-limiting step with changing nucleophiles and leaving groups. We conclude that the solvolysis of **1**-X in water and trifluoroethanol occurs by simple S_N2 (or A_ND_N) substitution with no carbocation intermediate. The data are consistent with the notion that substitution reactions at carbon will be stepwise if they can be; they will be concerted and may show nucleophilic participation when the carbocation has too short a lifetime to exist in the presence of surrounding nucleophiles, so that the carbocation is a transition state rather than an intermediate.[17]

Acknowledgment. We are grateful to P. Huskey and R. Schowen for their help and advice in calculations.

Registry No. **1**-Br, 102682-78-0; **1**-OTs, 24573-52-2; **1**-I, 102682-79-1; $S_2O_3^{2-}$, 14383-50-7; I^-, 20461-54-5; SCN^-, 302-04-5; CN^-, 57-12-5; Br^-, 24959-67-9; N_3^-, 14343-69-2; OAc^-, 71-50-1; Cl^-, 16887-00-6; F^-, 16984-48-8; MeOH, 67-56-1; CF_3CH_2OH, 75-89-8; EtOH, 64-17-5; $CH_3O(CH_2)_2OH$, 109-86-4; $NC(CH_2)_2OH$, 109-78-4.

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(44) A previously reported positive deviation of ~200-fold[22] is an error. Extrapolated rate constants for reactions of the carbocations with solvent indicate that the 1-(3-methoxyphenyl)ethyl cation has a significant lifetime while that of the 1-(4-nitrophenyl)ethyl cation is borderline.[21]

(45) Richard, J. P.; Jencks, W. P. *J. Am. Chem. Soc.* **1984**, *106*, 1373–1383.