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Aqueous Ethanolysis of Unstrained Sterically Congested Homoallylic Halides

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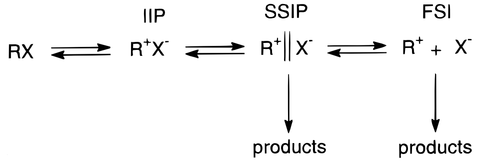
Abstract: The aqueous ethanolysis reactions of the adamantylideneadamantyl halides (**2**-Cl, **2**-Br, and **2**-I) exhibit Grunwald−Winstein sensitivity parameters (*m*) of 0.74 ± 0.06, 0.90 ± 0.01, and 0.88 ± 0.03 for the chloride, bromide, and iodide compounds, respectively. All reaction products are formed with retention of both the ring structure and the stereochemistry of the reaction center. Common-ion rate depressions are observed during the solvolyses of all three of the homoallylic halides, a result that is consistent with these reactions proceeding via a free-solvated homoallylic carbenium ion. The rate of nucleophilic capture of the homoallylic carbenium ion exhibits a Swain−Scott parameter (*s*) of 0.20 ± 0.01, indicating that these reactions show a low sensitivity to the nature of the nucleophile. From the data it is estimated that the lifetime of the homoallylic carbenium ion (**1**) in 60:40 v/v EtOH−H_2O at 25 °C is at least 6.4×10^{-9} s.

Introduction

Solvolysis reactions of aliphatic compounds have been studied for many years to provide mechanistic insight into the reactivity and selectivity of the intermediates formed in S_N1 ($D_N + A_N$)[1] reactions.[2] The observed effects of various salts on solvolytic rates have been interpreted with reference to the Winstein ion-pair mechanism[3] for $D_N + A_N$ reactions (Scheme 1).

Scheme 1



Within the framework of the Winstein ion-pair mechanism[3] (Scheme 1) are three commonly ascribed intermediates, namely (1) the intimate ion-pair (IIP), (2) the solvent separated ion-pair (SSIP), and (3) free-solvated ions (FSIs). During solvolysis reactions the observation of a common-ion rate depression[4] is an indication of the generation of an FSI, and in these cases, the lifetime of the carbenium ion intermediate can be estimated by the "azide-clock" methodology of Jencks and co-workers.[5] A second mechanistic probe for analysis of $D_N + A_N$ reactions involves the use of the Grunwald−Winstein eq 1, where the Y_X parameter is a measure of the solvent's ionizing power.[6]

$$\log(k/k_0) = mY_X \qquad (1)$$

The commonly accepted standard reactions for defining the Grunwald and Winstein *Y* scale involve the solvolysis of either 1-adamantyl or 2-adamantyl derivatives.[7] Furthermore, several different ionizing scales (Y_X, where X = leaving group) have been introduced, due to leaving group dependent variations in the electrophilic assistance by the solvent.[7c,8]

In a third approach, the relative selectivity for the capture of solvolysis intermediates by the components in a binary solvent mixture has been used to infer whether the reaction occurred with the SSIP or the FSI intermediate.[9] Of the many reports in the literature concerning the lifetime of carbenium ion in aqueous solutions, most focus on either oxygen-[10] or phenyl-substituted[2c,5,11] carbenium ions. Consequently, much less is known about the stabilizing interaction of a homoallylic double bond with an electron-deficient center and how this alters the lifetime of a carbenium ion. Recently, it was reported that solvolysis of **2**-OTs in 80% aqueous ethanol occurs with homoallylic participation, and the observed reaction rate is accelerated by a factor of 4×10^5 compared to that with the

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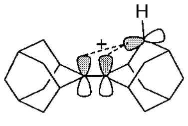
model compound 2-adamantyl tosylate.[12] As a result, the intermediate formed during the solvolysis reactions of the homoallylic tosylate **2**-OTs is proposed to be the free-solvated carbenium ion **1**.[12]



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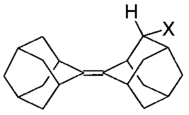

2-X

X = H
X = OTs
X = Cl
X = Br
X = I
X = OH
X = OEt
X = N_3

Accordingly, the present report focuses on the aqueous ethanolysis reactions of the corresponding adamantylideneadamantyl halides **2**-Cl, **2**-Br, and **2**-I (Ad=Ad−X). To probe the reactivity of the presumed intermediate (**1**) in these reactions, the effects of alterations in the solvent composition and salt concentration on reaction rate and product composition were studied.

Experimental Section

The homoallylic chloride (**2**-Cl) and bromide (**2**-Br) were synthesized using published procedures.[12,13] The experimental details for the synthesis of **2**-I and **2**-N_3 are included in the Supporting Information.

Kinetics. Solvolysis kinetics were monitored using a Cary-3E UV−vis spectrophotometer equipped with the Cary six-cell Peltier constant-temperature accessory. A stock solution of either **2**-Cl (1−2 μL; 125 mM in THF), **2**-Br (1.5−2 μL; 116 mM in THF), or **2**-I (4−5 μL; 56 mM in CH_2Cl_2) was injected into an equilibrated solvent mixture (3 mL; 30 min), and the change in absorbance was followed at 221, 230, or 250 nm for compounds **2**-Cl, **2**-Br, and **2**-I, respectively. First-order rate constants for the solvolysis reactions were determined by a nonlinear least-squares fit to a standard first-order equation. All kinetic runs exhibited clean, first-order behavior for at least 3 half-lives of reaction.

Product Studies and Azide Trapping. The homoallylic halide **2**-Cl, **2**-Br, or **2**-I was dissolved in acetonitrile (100 mg/mL), and a portion of this solution (≈80 μL) was added to a stirred solution of the required ethanol−water mixture (50 mL) maintained at 25 °C. After the solvolysis reaction was complete (at least 5 half-lives), the solution was concentrated under reduced pressure and the products were extracted with EtOAc (3 × 20 mL). The combined organic extracts were washed with water, dried (Na_2SO_4), and filtered. The filtrate was concentrated to a solid which was dried under vacuum (0.1 mmHg). The resulting residue was dissolved in $CDCl_3$, and the product ratio was determined from the integrated areas of the C*H*N_3 (δ 3.68, **2**-N_3), C*H*OEt (δ 3.29, **2**-OEt), and C*H*OH (δ 3.74, **2**-OH) protons in the ^1H NMR spectrum. Product stereochemistry was determined using ^{13}C NMR spectroscopy using a published methodology.[12]

Results and Discussion

Solvent Polarity. The standard Grunwald−Winstein eq 1 is commonly used to assess the effect of solvent polarity (ionizing power) on solvolysis reaction rates of sterically congested systems such as the homoallylic halides studied in this report. The measured rate constants for the solvolysis reactions of the homoallylic halides **2**-Cl, **2**-Br, and **2**-I in various ethanol−water mixtures are listed in Table 1. Since the solvent ionizing scale (Y_X) depends on the leaving group,[7c,8] the data given in Table 1 were fitted to eq 1 using Y values (Y_{Cl}, Y_{Br}, and Y_I) that were determined for the aqueous ethanolysis of the corresponding 1-adamantyl halide.[14,15] For the reactions of **2**-Cl, **2**-Br, and **2**-I, the derived estimates of the sensitivity parameter (m) are 0.74 ± 0.06, 0.90 ± 0.01,[16,17] and 0.88 ± 0.03,[16,17] respectively. An m value of 0.66 ± 0.02 for the reactions of **2**-OTs has been reported previously.[12] The plot and calculated fit of the data for solvolysis of **2**-Cl, **2**-Br and **2**-I are shown in Figures S1−S3 (Supporting Information).

Table 1. Observed First-Order Rate Constants for the Solvolysis at 25 °C of **2**-Cl, **2**-Br, and **2**-I in Ethanol-Water Mixtures, That Contain No Added Salt[a]

solvent	$k_{obsd} \times 10^5\ s^{-1}$		
($EtOH-H_2O$)	**2**-Cl	2-Br	2-I
100:0		0.26^b	0.35^b
90:10		2.65 ± 0.05	2.83 ± 0.02
80:20	0.70^b	16.0 ± 0.5	14.6 ± 0.1
70:30	3.04 ± 0.03	63.7 ± 0.2	50.0 ± 0.2
60:40	5.7 ± 0.2	200 ± 2	163 ± 2
50:50	24.4 ± 0.6	780 ± 20	594 ± 8

[a] The quoted values are the mean and standard deviation from at least three independent kinetic runs. [b] Extrapolated from data at higher temperatures.

Table 2. Approximate Rate Accelerations for the Solvolysis Reactions at 25 °C of **2**-OTs, **2**-Cl, **2**-Br, and **2**-I in 80:20 v/v Ethanol−Water, Compared To Their Respective 1-Adamantyl Derivatives

	2-OTs[a,b]	**2**-Cl[c]	**2**-Br[d]	**2**-I[e]
k_{obsd}/k_{1-AdX}	2.4	770	570	770

[a] Rate constant for 1-adamantyl tosylate is 4.03 × $10^{-3}\ s^{-1}$, ref 18. [b] Rate acceleration when compared to 2-adamantyl tosylate is 4.0 × 10^5, ref 12. [c] Rate constant for 1-adamantyl chloride is 9.1 × $10^{-9}\ s^{-1}$, ref 14. [d] Rate constant for 1-adamantyl bromide is 2.8 × $10^{-7}\ s^{-1}$, ref 14. [e] Rate constant for 1-adamantyl iodide is 9.0 × $10^{-7}\ s^{-1}$, ref 15.

That anchimeric assistance by the π-electrons of the homoallylic double bond is occurring at the solvolytic transition state for the reactions of **2**-X is supported by the following two observations: (1) the solvolysis rates in 80:20 v/v ethanol−water for the homoallylic compounds **2**-OTs, **2**-Cl, **2**-Br, and **2**-I are accelerated relative to the corresponding 1-adamantyl derivatives (Table 2) and (2) the reaction products are formed with greater than 95% retention of configuration.

Common-Ion Rate Depression. For solvolysis reactions, the observation of a "common-ion" rate depression is indicative of the formation of FSIs. Therefore, rate constant measurements for the solvolyses of **2**-Cl, **2**-Br, and **2**-I were conducted in the presence of the corresponding halide "common-ion". The observed rate constants for reactions measured in 60:40 and 80:20 v/v $EtOH-H_2O$ at 25 °C are presented in Tables S1 and S2 (Supporting Information).

Scheme 2 illustrates the reactions of the free-solvated carbenium ion (R^+), in the presence of added anions, which results in capture of the carbenium ion to generate the phenomenon of "common-ion" rate depression (X^-, Scheme 2) or to give azide product (N_3-, Scheme 2). The constants depicted in Scheme 2 are defined as follows: k_{solv}, the rate constant for the formation of the free-solvated carbenium ion;

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[16] The data for the reactions in 100% ethanol were not included in the fit to the Grunwald−Winstein equation since the Y_{Br} and Y_I values for solvolysis in this solvent were approximated using several long extrapolations.[15]

[17] Using the data in Table 1, extrapolated estimates for Y_{Br} and Y_I values in 100% ethanol are −1.97 and −1.82, respectively.

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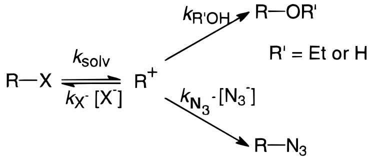
Scheme 2



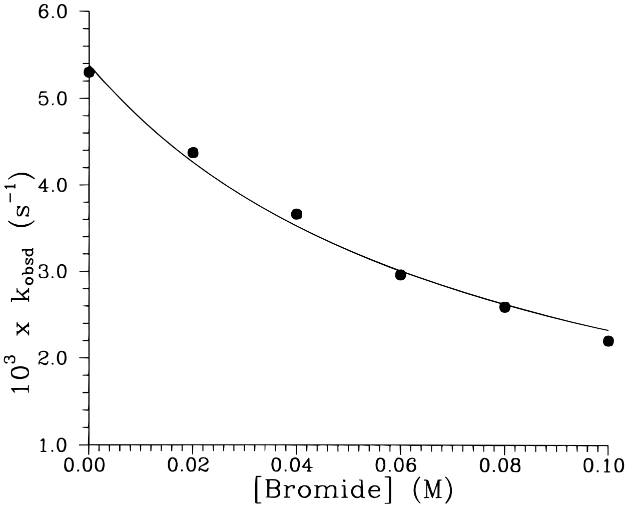


Figure 1. Plot of the observed pseudo-first-order rate constant k_{obsd} versus bromide ion concentration for solvolysis of **2**-Br in 60:40 v/v ethanol−water, $T = 25$ °C, $\mu = 0.5$ M (NaClO$_4$). Error limits are encompassed within the symbol diameter. The line shown is the nonlinear least-squares fit of the data points.

Table 3. Calculated Partition Ratios (k_{X^-}/k_{SOH}) for the Solvolysis of **2**-Cl, **2**-Br, and **2**-I in Ethanol-Water Mixtures, $\mu = 0.5$ (NaClO$_4$), at 25 °C

solvent (EtOH−H$_2$O)	**2**-Cl (M^{-1})	**2**-Br (M^{-1})	**2**-I (M^{-1})
60:40	7.2 ± 0.3	13.2 ± 0.9	31.8 ± 0.4
80:20		14.9 ± 0.6	25.3 ± 0.2

k_{X^-} and $k_{N_3^-}$, the second-order rate constants for capture of the carbenium ion by "common-ion", and azide ion, respectively; $k_{R'OH}$, the pseudo-first-order rate constant for capture of the carbenium ion by the solvent.

Equation 2 which can be derived from Scheme 2, with [N$_3^-$] = 0, accounts for the observed variation in k_{obsd} versus [X$^-$] in solvolysis reactions conducted in the presence of the "common-ion".

$$k_{obsd} = \frac{k_{solv}k_{R'OH}}{(k_{SOH} + k_{X^-}[X^-])} \qquad (2)$$

Figure 1 shows a typical plot of k_{obsd} for solvolysis as a function of "common-ion" concentration (reaction of **2**-Br in 60:40 v/v ethanol−water; $\mu = 0.5$, NaClO$_4$). In addition, Figure 1 shows the calculated nonlinear least-squares fit of the solvolysis data to eq 2. The additional kinetic data given in Tables S1 and S2 (Supporting Information) are plotted accordingly and are shown in Figures S4−S7 (Supporting Information).

Table 3 lists the partition ratios (k_{X^-}/k_{SOH}) that are derived from the nonlinear least-squares fitting to eq 2 of the data given in Tables S1 and S2 (Supporting Information).

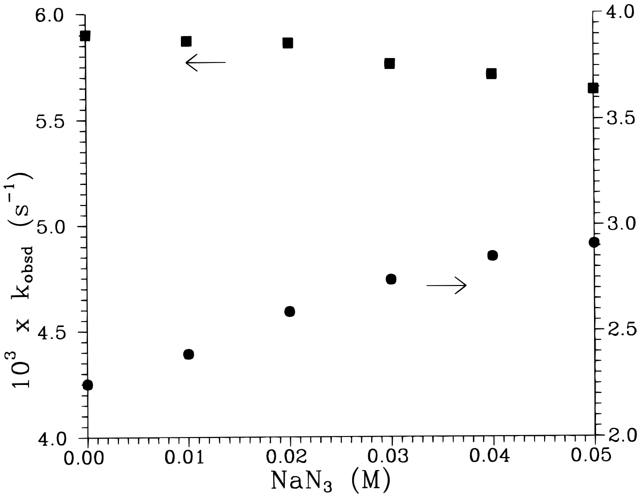


Figure 2. Plot of the observed pseudo-first-order rate constant k_{obsd} versus [NaN$_3$] ($\mu = 0.5$ M, NaClO$_4$) for solvolysis of **2**-I in 60:40 v/v ethanol−water containing [NaI] = 0.05 M (●, right axis scale) or [NaI] = 0.00 M (■, left axis scale), $T = 25$ °C.

Table 4. Partition Ratios (k_E/k_W)[a] Observed in the Solvolysis of **2**-OTs, **2**-Cl, **2**-Br, and **2**-I in Aqueous Ethanol at 25 °C

conditions	**2**-OTs[b,c]	**2**-Cl[d]	**2**-Br[d]	**2**-I[d]	ionic strength (M)
80% ethanol[e]	0.41		0.53	0.51	0.0
80% ethanol[f]			0.86		0.5
80% ethanol[g]			0.89		0.5
60% ethanol[e]	0.58	0.69	0.68	0.70	0.0
60% ethanol[f]			1.09		0.5
60% ethanol[g]			1.06		0.5
60% ethanol[h]			1.09		0.5

[a] k_E/k_W is a dimensionless ratio of second-order rate constants (see eq 5). [b] Mean of two determinations. [c] Reference 12. [d] Single determination. [e] No added salt. [f] $\mu = 0.5$ (NaClO$_4$). [g] [NaBr] = 0.1 M; $\mu = 0.5$ (NaClO$_4$). [h] Data from Table S5: [NaN$_3$] ≤ 0.08 M; $\mu = 0.5$ (NaClO$_4$).

Further confirmation that these reactions occur via the FSI **1** comes from an experiment in which the observed first-order rate constants for the solvolysis of **2**-I in 60:40 v/v EtOH−H$_2$O were measured under constant ionic strength as a function of added sodium azide (Figure 2; kinetic data given in Tables S3 and S4 of the Supporting Information).

These results indicate that the ionization of **2**-I is rate-limiting in the absence of iodide ion and that the addition of azide ion to the reaction has only a minor, nonspecific salt effect that results in a small decrease in the solvolysis rate (Table S3). However, in the presence of iodide ion ([NaI] = 0.05 M; Table S4), the reactions of **2**-I involve a significant amount of external return (k_{X^-}, Scheme 2), with capture of the ion **1** being a partially rate-determining event. Under these conditions, addition of azide ion causes a significant increase in the observed reaction rate.

Selectivity of Free-Solvated Bicyclobutenium Ion. Another characteristic of FSIs is that the product ratios obtained in individual solvolysis reactions conducted under identical conditions should be independent of the leaving group. The dimensionless rate ratios (k_E/k_W) were calculated from the measured quantities of the two solvolysis products **2**-OEt and **2**-OH formed from the reactions of **2**-Cl, **2**-Br, and **2**-I in various binary ethanol−water solvent systems. The partition ratios given in Table 4 were calculated according to eq 3, where k_E and k_W are the second-order rate constants for capture of the solvolytic intermediate to form the ether and the alcohol products, respectively. Also listed in Table 4 are the respective data for the solvolysis of **2**-OTs.[12]

$$k_E/k_W = [ROEt][HOH]/[ROH][EtOH] \qquad (3)$$

Since the k_E/k_W ratios are calculated from product ratios measured by integrating peak intensities in ^{1}H NMR spectra, it is expected that the quoted values are only accurate to ±10–15%.[19,20] Nevertheless, for these solvolysis reactions, the invariance of the partition ratios (k_E/k_W), at constant ionic strength, as a function of both the leaving group (tosylate, chloride, bromide, or iodide; Table 4) and added bromide or azide (Table 4) indicates that, of the solvolysis intermediates, only the FSI reacts with the solvent to give the products **2**-OH and **2**-OEt.

Lifetime of Free-Solvated Bicyclobutenium Ion. For many years, the standard approach for estimating the lifetime ($1/k_{SOH}$) of a carbenium ion (R^+) in solution has been the "azide-clock" of Jencks and co-workers,[5] in which the ratio of azide- and solvent-derived products that are formed in the reaction is utilized (Scheme 2). This methodology relies on the assumption that azide ion reacts with a free-solvated carbenium ion at the diffusional rate ($k_{N_3^-} \approx 5 \times 10^9$ M^{-1} s^{-1}; Scheme 2).[5b,10c,21] The validity of this assumption has been affirmed recently by McClelland and co-workers, who utilized laser flash photolysis techniques to measure the diffusion-controlled second-order rate constants for the reactions of (triarylmethyl)-,[22] (diarylmethyl)-,[22,23] and ((*p*-methoxyphenyl)ethyl)carbenium[23] ions with azide ion. In addition, these researchers have shown that the reactions of bromide ion with substituted (phenylethyl)- and benzylcarbenium ions occur at the diffusion limit.[11a] Equation 4 can be derived for the kinetic process shown in Scheme 2 ($[X^-] = 0$), where f_{RN_3} is the mole fraction of azide product (RN_3).[5b]

$$f_{RN_3} = 1 - f_{RN_3}\left(\frac{k_{SOH}}{k_{N_3^-}[N_3^-]}\right) \qquad (4)$$

Table S5 (Supporting Information) lists the percentages of the products that result from the trapping of the FSI **1** that was generated from **2**-Br in 60:40 v/v EtOH–H$_2$O. Data taken from Table S5 are shown in Figure 3 as a plot of f_{RN_3} versus $f_{RN_3}/[N_3^-]$. The calculated values for $k_{SOH}/k_{N_3^-}$ and the intercept are 0.063 ± 0.002 M and 0.97 ± 0.02, respectively.

If the standard assumption is made that the reaction rate constant for capture of the homoallylic carbenium ion **1** with N_3^- is 5.0×10^9 M^{-1} s^{-1}, then the rate at which the cation **1** reacts with solvent is approximately 3.15×10^8 s^{-1} and the corresponding estimate for the lifetime of the homoallylic carbenium ion (**1**) is around 3.17×10^{-9} s. However, when iodide ion is compared with azide ion under identical conditions (60:40 v/v EtOH–H$_2$O; $\mu = 0.5$ M, NaClO$_4$; 25 °C), iodide has an approximate two-fold greater efficiency than azide for trapping the ion **1** ($k_{SOH}/k_{I^-} = 0.0313 \pm 0.0004$ M, Table 3). Hence, if trapping of the cation with iodide occurs at the diffusional rate, the lifetime of the bicyclobutenium ion (**1**) would be approximately 6.4×10^{-9} s. Furthermore, the fact that iodide reacts twice as rapidly with the FSI **1** than does azide indicates that the reaction of **1** with N_3^- occurs with a rate constant of $\leq 2.5 \times 10^9$ s^{-1}.

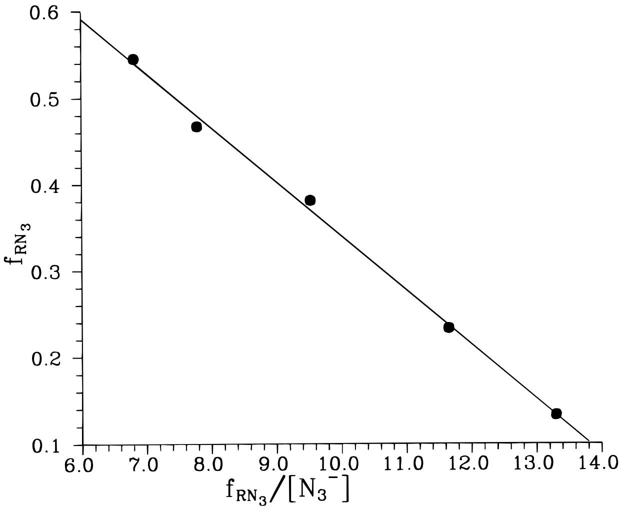


Figure 3. Plot of the fraction of azide product (f_{RN_3}) versus the fraction of azide product divided by $[N_3^-]$ for the reaction of **2**-Br in 60:40 v/v ethanol–water at $T = 25$ °C, $\mu = 0.5$ M (NaClO$_4$). The line shown is the least-squares fit of the data points.

Effect of Homoallylic Double Bond on Carbenium Ion Lifetime. Free-solvated secondary carbenium ions have been estimated to be too unstable to exist in the presence of nucleophilic solvents such as water.[24] This conclusion is in accordance with a recent estimate of 10^{-12} s for the lifetime of the simplest tertiary carbenium ion, the 2-methyl-2-propyl (*tert*-butyl) cation.[21] Clearly, the homoallylic double bond of carbenium ion **1** has caused the cation, which is formally centered on a secondary carbon, to become more stable than a simple tertiary cation and at least as stable as an aryl-substituted secondary carbenium ion. For example, in 50:50 v/v trifluoroethanol:water, the 4-OMe- and 4-OPh-substituted 1-phenylethyl carbenium ions have estimated lifetimes of 2.0×10^{-8} and 3.3×10^{-9} s, respectively.[5b]

Overall Explanation. The reaction rate for capture of **1** by nucleophiles exhibits a linear correlation with the Swain–Scott nucleophilic parameter *n*. This relationship is illustrated in Figure 4, which shows a plot of $\log(k_{X^-}/k_{SOH})$ versus the Swain–Scott nucleophilic parameter *n* for the data listed in Tables 3 and S5 (60:40 v/v ethanol–water; $\mu = 0.5$, NaClO$_4$; 25 °C).

The partitioning of **1** between the reaction with anionic nucleophiles and water (k_{X^-}/k_{SOH}) is characterized by a small sensitivity to the nucleophilicity of the anion ($s = 0.30 \pm 0.01$, *n* in water;[25] or 0.20 ± 0.01, *n* in methanol[26]). A similar observation has been reported for the reactions of the retinyl carbenium ion with added nucleophiles in aqueous acetonitrile.[27] Specifically, the sensitivity parameter values obtained in these reactions vary from $s = 0.01$, to 0.43, to 0.63 as the concentration of water in the acetonitrile changes from dry CH$_3$CN, to 1 M H$_2$O in CH$_3$CN, to 11 M H$_2$O in CH$_3$CN, respectively (*n* in methanol[26]).[27] The reactions of the retinyl carbenium ion with nucleophiles in dry acetonitrile occur at or close to the

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[19] In 80% v/v EtOH–H$_2$O, a k_E/k_W value of 0.41 is equivalent to 33.5% of the product being the ethyl ether (ROEt), whereas a k_E/k_W value of 0.53 is equivalent to formation of 39.4% ROEt product.

[20] In 80% v/v EtOH–H$_2$O the ratio [ROH]/[H$_2$O] has a value of 1.228, whereas in 78% v/v EtOH–H$_2$O, the ratio [ROH]/[H$_2$O] has a value of 1.089. Therefore, a small difference (2%) in solvent ratio can generate an error of around 13% in the k_E/k_W value.

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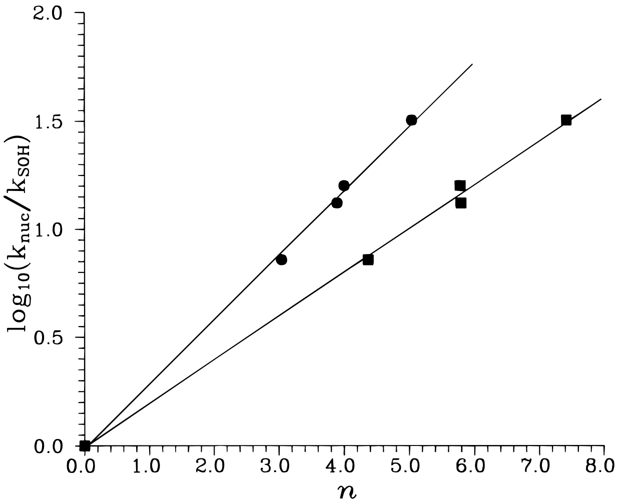
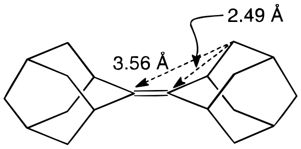


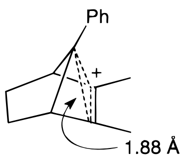
Figure 4. Plot of the Swain−Scott correlation for the selectivity of capture of **1** by added nucleophiles or by the solvent, log (k_{nuc}/k_{SOH}) versus n (●, CH_3Br in H_2O)[27] and n (■, CH_3I in MeOH),[28] $T = 25$ °C, $\mu = 0.5$ M ($NaClO_4$). The lines shown are the least-squares fits through the data points.

diffusional limit. However, as water is added to the solution, the rate of carbenium ion trapping decreases and there is a concomitant increase in the sensitivity of the second-order rate constant to nucleophilicity. Although the factors which cause the nucleophilic capture to show a correlation with the Swain−Scott parameter n are presumably different in the case of the retinyl cation and the FSI **1** in the current report, the observed small sensitivities of both of these cations to nucleophilicity implies that the reaction of **1** with anions proceeds with a small barrier to the cation−nucleophile combination reaction. In contrast, Ritchie's N^+ scale is based on cation−anion combination reactions for long-lived carbenium ions where a sizable barrier exists to the combination reaction,[28] and these carbenium ions display much larger selectivities ($k_{N_3^-}/k_{SOH}$) on the order of 10^6−10^8 M^{-1}.[28]

With respect to the adamantylideneadamantyl carbenium ion **1**, two possible reasons exist for nucleophilic capture to occur at a rate slower than that of the diffusion limit. In the first scenario, extensive heavy atom motion must occur between the free-solvated bicyclobutenium ion **1** and the homoallylic product. The extent of possible motion can be inferred from the measured C−C distance of approximately 1.88 Å for the symmetric bicyclobutenium ion 2,3-dimethyl-7-phenylnorborn-2-en-7-yl carbenium ion (**3**)[29] and the corresponding C−C distances of 2.49 and 3.56 Å found in the parent alkene (**2**-H).[30]



2-H



3

Hence, formation of **1** during the solvolysis reactions of **2**-Cl, **2**-Br, and **2**-I requires extensive movement of the appended adamantylidene group to shorten the distance and thus increase the interaction between the secondary carbenium ion center and the two tertiary carbons of the alkene. This heavy atom motion promotes delocalization of the positive charge onto the two tertiary alkenyl carbon atoms and away from the secondary alkyl carbon atom. However, the development of resonance stabilization that occurs in the formation of both sp^2-hybridized carbocations and carbanions from sp^3-hybridized carbon is not linear with reaction progress, i.e., resonance stabilization lags behind bond cleavage.[31,32] The principle of microscopic reversibility requires that this type of imbalance also occurs between bond formation and loss of resonance stabilization for reactions of carbenium ions. Indeed, this type of imbalance has been proposed to occur during the reactions of α-substituted (4-methoxybenzyl)carbenium ions,[33] (1-phenylethyl)carbenium ions,[10b] and oxocarbenium ions.[10c] Consequently, if the imbalance between π-resonance stabilization and C−N bond formation for the reaction of **1** and azide gives rise to a kinetic barrier greater than that for a diffusion-controlled reaction, this process becomes activation limited. In the second possibility, the approach for attack of a nucleophilic reagent on the bicyclobutenium ion **1** is sterically congested by the adamantyl group. This situation is in contrast to that of benzyl-substituted carbenium ions, in which the approach of a nucleophilic reagent is relatively unhindered by the trigonal-planar ion. In summary, either one or both of these two factors gives rise to the nondiffusional energy barrier for reaction of the FSI **1** with nucleophiles. This energy barrier lowers the reaction rate for azide ion capture to below that of a diffusion-limited process, and consequently, the lifetime of **1** is probably greater than 6.4×10^{-9} s. However, at the present time, it is impossible to resolve whether the rate-limiting step for the reaction of the FSI **1** with azide involves formation of the SSIP, conversion of the SSIP to the IIP, or collapse of the IIP to give azide-substituted product (Scheme 1).

Conclusions. Heavy-atom motion is required for the nucleophilic capture of the homoallylic carbenium ion **1**, leading to product formation during the solvolysis reactions of adamantylideneadamantyl derivatives. This heavy-atom motion is the most likely reason for the capture rate of **1** by azide ion to be reduced to a value below that of the diffusional rate constant. As a result, the bicyclobutenium ion **1** has a lifetime of greater than 6.4×10^{-9} s in 60:40 v/v EtOH−H_2O.

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Supporting Information Available: Text giving experimental details, tables listing observed rate constants for the hydrolysis of **2**-Cl, **2**-Br, and **2**-I as a function of ["common-ion"] and **2**-I versus [NaN_3], Grunwald−Winstein plots for the reactions of **2**-Cl, **2**-Br, and **2**-I, and figures for the observed "common-ion" rate depressions for **2**-Cl, **2**-Br, and **2**-I (14 pages). See any current masthead page for ordering and Web access instructions.

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