centrated to 0.5 mL. Water (1 mL) was added followed by ether (2 mL) and 2 M citric acid to bring the mixture to pH 4.0. The ether solution was washed with water (1 × 0.5 mL) and brine (1 × 0.5 mL), dried, and evaporated. The sample of **10** was stored in benzene. HPLC of **10**: t_R = 20.5 min; λ_{max} 235 nm. MS (70 eV, DCI), *m/e* 350 (M^+, 20), 333 (–OH, 65), 315 ($-H_2O$, 100).

The sample of **10** was hydrogenated over 20 mg of Adam's catalyst in methanol for 1 h to give octahydro **10** after filtration and evaporation: MS (70 eV, DCI, TMS derivative), *m/e* 503 (M^+, 8), 471 (–MeOH, 12), 413 (–TMSOH, 77), 381 (fragmentation at C-5, 8), 323 (–2TMSOH, 100), 291 (–2TMSOH, –MeOH, 13), 271 (fragmentation at C-8, 6), 243 (fragmentation at C-8, 29), 203 (fragmentation at C-5, 14).

The Extraordinarily Long Lifetimes and Other Properties of Highly Destabilized Ring-Substituted 1-Phenyl-2,2,2-trifluoroethyl Carbocations[1]

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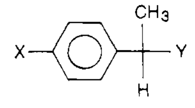
Abstract: A large bromide common ion rate depression is observed for the reactions of 1-(4-methoxyphenyl)- and 1-(4-(methylthio)phenyl)-2,2,2-trifluoroethyl bromides in largely aqueous solutions when the ionic strength is maintained with weakly nucleophilic $NaClO_4$ but not when it is maintained with NaN_3. The rates of the reactions of ring-substituted ($\sigma^+ \leq -0.32$) 1-phenyl-2,2,2-trifluoroethyl tosylates, mesylates, and bromides in 50:50 (v/v) water/trifluoroethanol, at increasing [I^-] or [N_3^-], are independent of nucleophile concentration, but at 0.5 M [Nu] the reactions give yields of the nucleophile adduct which range from 30% to quantitative (≫99%), depending on the ring substituent. These results show that the highly unstable carbocations $XArCH(CF_3)^+$ are readily generated as intermediates of the solvolysis reactions of $XArCH(CF_3)Y$. The rate constant ratios for partitioning of $XArCH(CF_3)^+$ between capture by azide and a solvent of 50:50 (v/v) water/trifluoroethanol (k_{az}/k_s), calculated from product ratios, decrease from 6×10^6 M^{-1} for capture of $4\text{-}N(CH_3)_2ArCH(CF_3)^+$ to 0.8 M^{-1} for capture of $4\text{-}CH_3ArCH(CF_3)^+$ and give k_s values ranging from 800 s^{-1} to 6×10^9 s^{-1}, assuming a diffusion-controlled rate constant of 5×10^9 M^{-1} s^{-1} for k_{az}. There is a modest correlation of log k_s values to σ^+ with a slope $\rho^+_s = 4.8$. The k_s values for the reactions of $XArCH(CF_3)^+$ are nearly identical with k_s values for comparably ring-substituted $XArCH(CH_3)^+$ despite the fact that the former carbocations are at least 8 kcal/mol more unstable relative to a neutral reactant. It is proposed that $XArCH(CF_3)^+$ possess an unusual kinetic stability, which is due to unusually large resonance, electrostatic, or homoconjugative barriers to $XArCH(CF_3)^+$ capture by solvent.

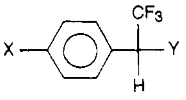
Recently considerable interest has been directed toward the determination and rationalization of the effects of strongly electron-withdrawing α-substituents on the mechanism for solvolysis at saturated carbon and on the stability of the carbocations which may be intermediates in these reactions.[2-5] The studies show that the substitution of an electron-withdrawing group (e.g. cyano,[2a] carbonyl,[2b] or trifluoromethyl[3-5]) for an α-methyl at $XArCH(CH_3)Y$ causes a large decrease in the rate constant for the solvolysis reaction but little change in the structure of the reaction transition state as measured by the structure–reactivity terms ρ^+ and *m*. This suggests, but does not prove, that the solvolysis reactions proceed by the same S_N1 mechanism observed for the parent compounds $XArCH(CH_3)Y$.[6,7]



$XArCH(CH_3)Y$

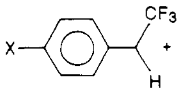
In contrast, aliphatic substitution by highly reactive nucleophiles at substrates with strongly electron-withdrawing α-substituents has been little studied in recent years. A thorough examination of these reactions will complement and greatly extend the results from work on the solvent addition reactions to give a fuller description of the effect of electron-withdrawing groups on the substitution reaction mechanism and on the stability of the putative carbocation reaction intermediates.

First, a determination of the dependence of the rate of substrate reaction on nucleophile concentration could provide kinetic evidence for the formation of a carbocation reaction intermediate; e.g., the observation of nucleophile adduct formation by a reaction zero order in nucleophile concentration or of a common-ion depression of the reaction rate. It is not generally known whether α-CF_3-substituted carbocations form as intermediates of solvolysis reactions. The recent structure–reactivity studies on the solvolysis of $XArCH(CF_3)Y$ provide important information about transi-

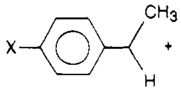


$XArCH(CF_3)Y$

Y = Br, I; Mes = CH_3SO_3;
Tos = $4\text{-}CH_3ArSO_3$;
4-NB = $4\text{-}NO_2ArCO_2$;
3,5-NB = $3,5\text{-di-}NO_2ArCO_2$



$XArCH(CF_3)^+$



$XArCH(CH_3)^+$

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tion-state polarity;[3f] however, they do not directly address the question of whether this transition state leads to the formation of the carbocation intermediate XArCH(CF$_3$)$^+$.[8] Concerted substitution reactions where the transition-state bonding of the nucleophile and leaving group at the central carbon is weak or negligible sometimes show values for structure–reactivity terms which lie in the range observed for stepwise reactions.[8-11] The isolation of racemic products from the solvolysis of optically active 1-phenyl-2,2,2-trifluoroethyl triflate in trifluoroacetic acid and hexafluoroisopropyl alcohol is good evidence that a liberated carbocation intermediate forms in weakly nucleophilic solvents.[3f] Stereochemical studies in more strongly nucleophilic solvents are less informative. Chiral 1-phenyl-2,2,2-trifluoroethyl triflate reacts in methanol or acetic acid to give products with significant inversion of configuration,[3f] a result which is open to a variety of interpretations, not all of which involve a reaction mechanism with a carbocation intermediate.[8,12]

Second, if these reactions proceed via a carbocation intermediate, then it would certainly be trapped by azide ion in a diffusion-limited reaction, which would serve as a "clock" for the rate constant k_s for the solvent addition reaction.[6,7] This allows for the calculation of k_s from the rate constant ratio k_{az}/k_s for carbocation capture by azide and solvent (obtained from product ratios) and a representative diffusional rate constant for k_{az}.[6,7] The k_s values are of considerable interest, because the effect of highly electron-withdrawing substituents on the kinetic reactivity of carbocations with aqueous solvents is not known.

Third, an examination of highly reactive nucleophiles will provide further information about the effect of strongly electron-withdrawing substituents on the barrier to bimolecular substitution reactions.[13-15]

In a preliminary communication, I reported direct kinetic evidence that 4-OCH$_3$ArCH(CF$_3$)Mes, 4-OCH$_3$ArCH(CF$_3$)Br, and 4-OCH$_3$ArCH(CF$_3$)Tos react by S$_N$1 mechanisms through 4-OCH$_3$ArCH(CF$_3$)$^+$.[5a] Surprisingly, the product rate constant ratio k_{az}/k_s for the capture of 4-OCH$_3$ArCH(CF$_3$)$^+$ in 50:50 (v/v) water/trifluoroethanol is nearly the same as for the capture of 4-OCH$_3$ArCH(CH$_3$)$^+$. Since both carbocations are captured by azide with the same diffusion-limited rate constant k_{az}, it was concluded that—despite the large difference in their stabilities relative to a common neutral adduct—the lifetimes ($1/k_s$) for the two carbocations are nearly identical.[5a]

In this paper I report the details of a study of the reactions of 4-OCH$_3$ArCH(CF$_3$)Y and other XArCH(CF$_3$)Y; the lifetimes of the intermediates of these reactions; and the failure to observe bimolecular nucleophilic substitution reactions by the highly reactive nucleophiles N$_3^-$, I$^-$, and Br$^-$. The lifetimes of 4-CH$_3$ArCH(CF$_3$)$^+$, 4-SCH$_3$ArCH(CF$_3$)$^+$, 4-OCH$_3$ArCH(CF$_3$)$^+$, and 4-N(CH$_3$)$_2$ArCH(CF$_3$)$^+$ span a range of $>10^6$ s, yet the lifetime of each carbocation is close to that for the comparably ring-substituted XArCH(CH$_3$)$^+$. It was completely unexpected that the reactivity of XArCH(CH$_3$)$^+$ would be unchanged by the highly electron-withdrawing α-CF$_3$ substituent. Possible explanations for this result are considered.

Experimental Section

Materials. Reagent-grade inorganic salts were used without further purification. Commercially available organic reagents used for syntheses were reagent grade and were not further purified. Trifluoroethanol, Gold Label from Aldrich, and methanol, HPLC grade from Fisher, were used without further purification as solvents for kinetic studies. The water used for kinetic studies was distilled and then passed through a Milli-Q water-purification system.

Syntheses. The substituted 2,2,2-trifluoroacetophenones were synthesized by published procedures[16,17] and were reduced to the phenyltrifluoroethanols by NaBH$_4$.[17] The syntheses of 1-(4-(methylthio)phenyl)-2,2,2-trifluoroethanol and its derivatives are reported here for the first time.

Ring-substituted 1-phenyl-2,2,2-trifluoroethyl tosylates were synthesized from the corresponding phenyltrifluoroethanols and tosyl chloride by the procedure of Tidwell.[3f] Ring-substituted 1-phenyl-2,2,2-trifluoroethyl bromides were synthesized from the corresponding phenyltrifluoroethanols and PBr$_3$ by adaptation of a published procedure.[3e] The esters 4-N(CH$_3$)$_2$ArCH(CF$_3$)-4-NB and 4-N(CH$_3$)$_2$ArCH(CF$_3$)-3,5-NB were synthesized from 1-(4-(dimethylamino)phenyl)-2,2,2-trifluoroethyl alcohol and the appropriate acyl chloride.[3g,i]

1-(4-(Methylthio)phenyl)-2,2,2-trifluoroethanol: mp 43–44 °C; ^{1}H NMR (CDCl$_3$) δ 2.50 (s, 3 H, CH$_3$), 2.64 (d, 1 H, J = 4 Hz, OH), 4.96 (dq, 1 H, J = 5, 4 Hz, CH), 7.26, 7.37 (A$_2$B$_2$, 4 H, J = 8 Hz, C$_6$H$_4$); exact mass calcd for C$_9$H$_9$F$_3$OS 222.0326, found 222.0321. Anal. (C$_9$H$_9$F$_3$OS) C, H.

1-(4-(Methylthio)phenyl)-2,2,2-trifluoroethyl tosylate: mp 82–84 °C; ^{1}H NMR (CDCl$_3$) δ 2.38, 2.43 (each s, 3 H, CH$_3$Ar, CH$_3$SAr), 5.62 (q, 1 H, J = 6 Hz, CH), 7.4 (m, 8 H, aryl H); exact mass calcd for C$_{16}$H$_{15}$F$_3$O$_3$S$_2$ 376.0415, found 376.0413. Anal. (C$_{16}$H$_{15}$F$_3$O$_3$S$_2$) C, H, S.

1-(4-Methoxyphenyl)-2,2,2-trifluoroethyl bromide: bp 86 °C (0.6 mmHg); ^{1}H NMR (CDCl$_3$) δ 3.78 (s, 3 H, CH$_3$), 5.08 (q, 1 H, J = 7 Hz, CH), 6.9, 7.4 (A$_2$B$_2$, 4 H, J = 8 Hz, C$_6$H$_4$); exact mass calcd for C$_9$H$_8$BrF$_3$O 267.9711, found 267.9722. Anal. (C$_9$H$_8$BrF$_3$O) C, H, Br.

1-(4-(Methylthio)phenyl)-2,2,2-trifluoroethyl bromide: bp 68 °C (0.5 mmHg); ^{1}H NMR (CDCl$_3$) δ 2.47 (s, 3 H, CH$_3$), 5.08 (q, 1 H, J = 7 Hz, CH), 7.22, 7.40 (A$_2$B$_2$, 4 H, J = 8 Hz, C$_6$H$_4$); exact mass calcd for C$_9$H$_8$BrF$_3$S 283.9482, found 283.9477. Anal. (C$_9$H$_8$BrF$_3$S) C, H, S.

1-(4-(Dimethylamino)phenyl)-2,2,2-trifluoroethyl 4-nitrobenzoate: mp 97–99 °C; ^{1}H NMR (CDCl$_3$) δ 2.98 (s, 6 H, CH$_3$), 6.35 (q, 1 H, J = 7 Hz, CH), 6.72, 7.42 (A$_2$B$_2$, 4 H, J = 9 Hz, C$_6$H$_4$N(CH$_3$)$_2$), 8.27, 8.34 (A$_2$B$_2$, 4 H, J = 10 Hz, C$_6$H$_4$NO$_2$); exact mass calcd for C$_{17}$H$_{15}$F$_3$N$_2$O$_4$ 368.0984, found 368.0975. Anal. (C$_{17}$H$_{15}$F$_3$N$_2$O$_4$) C, H, N.

1-(4-(Dimethylamino)phenyl)-2,2,2-trifluoroethyl 3,5-dinitrobenzoate: mp 112–114 °C; ^{1}H NMR (CDCl$_3$) δ 3.00 (s, 6 H, CH$_3$), 6.35 (q, 1 H, J = 7 Hz, CH), 6.75, 7.44 (A$_2$B$_2$, 4 H, J = 9 Hz, C$_6$H$_4$), 9.23 (m, 3 H, C$_6$H$_3$); exact mass calcd for C$_{17}$H$_{14}$F$_3$N$_3$O$_6$ 413.0835, found 413.0847. Anal. (C$_{17}$H$_{14}$F$_3$N$_3$O$_6$) C, H, N.

The 1-phenyl-2,2,2-trifluoroethyl mesylates were synthesized from the corresponding phenyltrifluoroethanols and mesyl chloride by adaptation of the procedures used to synthesize the tosylates and triflates.[3f] The mesylates were obtained as reactive oils, of greater than 90% purity (by NMR and HPLC), and were used directly, without further purification. These compounds were suitable for kinetic studies. However, they were not extensively used in HPLC product studies, because the small amounts of impurities proved difficult to separate from the solvent and nucleophile adducts. The NMR spectra of the mesylates showed characteristic CH(CF$_3$) quartets at δ 5.77, 5.78, and 5.78, respectively, for 4-CH$_3$ArCH(CF$_3$)Mes, 4-SCH$_3$ArCH(CF$_3$)Mes, and 4-OCH$_3$ArCH(CF$_3$)Mes.

1-(4-Methoxyphenyl)-2,2,2-trifluoroethyl Iodide. This compound was obtained by a substitution reaction of iodide anion with 4-OCH$_3$ArCH(CF$_3$)Mes in a synthesis which was carried out in the dark, in order to avoid the light-induced decomposition of 4-OCH$_3$ArCH(CF$_3$)I. 4-OCH$_3$ArCH(CF$_3$)Mes (200 mg) was dissolved in 50 mL of 50:50 (v/v) water/trifluoroethanol containing 0.5 M NaI. After 10 min the trifluoroethanol was rapidly removed at <25 °C, in vacuo, and the iodide adduct was isolated in a fairly pure form by extraction into ethyl ether. In some cases the product was further purified by chromatography on silica gel, with 20% ethyl acetate in hexane as eluant. The product was stored in the dark at −15 °C: ^{1}H NMR (CDCl$_3$) δ 3.83 (s, 3 H, OCH$_3$), 5.33 (q, 1 H, J = 8 Hz, CH), 6.88, 7.44 (A$_2$B$_2$, 4 H, J = 9 Hz, C$_6$H$_4$); exact mass calcd for C$_9$H$_8$F$_3$IO 315.9572, found 315.9571.

1-(4-(Methylthio)phenyl)-2,2,2-trifluoroethyl iodide was synthesized by a similar procedure, but was used without chromatographic purification. The ^{1}H NMR spectrum (CDCl$_3$) showed the CHCF$_3$ quartet at δ 5.28 (J = 8 Hz).

1-(4-Methoxyphenyl)-2,2,2-trifluoroethyl azide was synthesized from 4-OCH$_3$ArCH(CF$_3$)Mes by substituting NaN$_3$ for NaI in the above procedure. The ^{1}H NMR (CDCl$_3$) spectrum of the product isolated by extraction into ether showed the CH(CF$_3$) quartet at δ 4.90 (J = 8 Hz).

Methods. Kinetic Analyses. The kinetic studies were done at 25 °C. The solutions for both the kinetic and product studies were maintained

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at a constant ionic strength ($NaClO_4$) and were prepared by mixing aqueous solutions ($I = 1.0$) with the organic cosolvent. The reactions were initiated by diluting substrate in acetonitrile 100-fold to give a final concentration of between 0.1 and 1 mM, depending on the reaction studied. The reaction progress was followed spectrophotometrically on either a Gilford 2600, a Zeiss PMQ 3, or a Perkin-Elmer λ-4B spectrophotometer, each equipped with a thermostated cell holder.

Pseudo-first-order rate constants were calculated as the slope of linear semilogarithmic plots of reaction progress against time. The reactions were generally followed for ≥3 half-lives. The rate constants are reproducible to ±5%.

Three different methods were used to follow the reaction of $4\text{-}OCH_3ArCH(CF_3)Mes$: (1) The disappearance of the reactant was followed directly by monitoring the absorbance decrease at 247 nm. (2) The appearance of methanesulfonic acid formed in the solvolysis reaction was monitored by following the absorbance decrease at 290 nm resulting from the protonation of a phenolate indicator.[11a] (3) The reactions with iodide or bromide anion were monitored by following the increase in UV absorbance at a fixed wavelength between 280 and 300 nm. Good agreement (±5%) was observed between the rate constants obtained by the three different methods.

The solvolysis reaction of $4\text{-}OCH_3ArCH(CF_3)Tos$ was followed by monitoring the absorbance decrease at 247 nm.[3f]

Only a small absorbance decrease was observed at 247 nm during the solvolysis of $4\text{-}SCH_3ArCH(CF_3)Mes$ and $4\text{-}SCH_3ArCH(CF_3)Tos$ because of the large contribution of the (methylthio)phenyl ring to the extinction coefficient at 247 nm. These reactions were carried out in the presence of 0.01 M NaI, and the formation of $4\text{-}SCH_3ArCH(CF_3)I$ was followed at 290 nm; the formation of the iodide adduct and the disappearance of the substrate occur with the same pseudo-first-order rate constant, k_{obsd},[18] which was found to be independent of the sodium iodide concentration (see the Results section).

The reactions of $4\text{-}OCH_3ArCH(CF_3)Br$, $4\text{-}OCH_3ArCH(CF_3)I$, $4\text{-}SCH_3ArCH(CF_3)Br$, and $4\text{-}SCH_3ArCH(CF_3)I$ were followed by monitoring the absorbance decrease at either 280 or 290 nm; the reaction of $4\text{-}N(CH_3)_2ArCH(CF_3)\text{-}4\text{-}NB$ was followed by monitoring the absorbance decrease at 260 nm; and the reaction of $4\text{-}CH_3ArCH(CF_3)Tos$ was followed by monitoring the reactant disappearance by HPLC.

HPLC Product Analyses. The product studies were carried out at room temperature (22 ± 2 °C). There is no detectable difference between the product ratios at room temperature and 25 °C.

The products of the reactions of $XArCH(CF_3)Y$ with solvent and added nucleophiles were separated by HPLC and detected spectrophotometrically, and the relative yields were recorded as the integrated peak areas from an HPLC chromatogram.[6] The ratios of peak areas from HPLC analysis are reproducible to ±10%. The products of the reaction of $4\text{-}CH_3ArCH(CF_3)Y$, $4\text{-}SCH_3ArCH(CF_3)Y$, or $4\text{-}N(CH_3)_2ArCH(CF_3)Y$ were detected by their absorbance at 254 nm, and the products from $4\text{-}OCH_3ArCH(CF_3)Y$ were detected by their absorbance at 280 nm. The substrate concentrations were generally between 0.1 and 1 mM, except for the reaction of $4\text{-}N(CH_3)_2ArCH(CF_3)Y$ with azide, where the substrate concentration was ca. 5×10^{-6} M. The reactions with nucleophiles were always conducted with the nucleophile present in at least 10-fold excess over the substrate concentration.

HPLC analysis gave the trifluoroethyl ether and azide adduct as a single unresolved peak. The contribution of $XArCH(CF_3)OCH_2CF_3$ to the total peak area was calculated as the product of the observed area for the water adduct ($[area]_{ROH}$) times the ratio of peak area ($[area]_{ROTFE}/[area]_{ROH}$) observed at $[N_3^-] = 0$. This ratio has been shown to be independent of $[N_3^-]$ for a large number of related reactions.[6] The peak area for the azide adduct ($[area]_{RNu}$) is then the total area for the mixture minus the contribution of $[area]_{ROTFE}$.

Product Identification. Two products from the reactions of $XArCH(CF_3)Y$ in mixed water/methanol or water/trifluoroethanol solvents were observed by HPLC, one of which was shown to be the water adduct by comparison with synthetic $XArCH(CF_3)OH$. The second product was identified as the methanol or trifluoroethanol adduct by the increase in its relative area with increasing concentration of the alcohol cosolvent.

The nucleophile adducts were identified by HPLC, and their relative peak areas were shown to increase with increasing nucleophile concentration at the expense of the solvent adducts.

Additional steps were taken to characterize the azide, iodide, and bromide adducts to $4\text{-}OCH_3ArCH(CF_3)^+$. The product of the reaction of $4\text{-}OCH_3ArCH(CF_3)Mes$ with azide was isolated and characterized by ^1H NMR. The product of the reaction of $4\text{-}OCH_3ArCH(CF_3)Mes$ with bromide had a UV spectrum, HPLC retention time, and chemical reactivity identical with that of synthetic $4\text{-}OCH_3ArCH(CF_3)Br$. The product of the reaction of iodide with $4\text{-}OCH_3ArCH(CF_3)Mes$ was isolated and characterized by ^1H NMR and high-resolution mass spectrometry (see above).

Table I. Rate Constants ($k_{obsd}/10^{-4}$ $s^{-1\,a}$) for the Solvolysis of Ring-Substituted 1-Phenyl-2,2,2-trifluoroethyl Derivatives in 50:50 (v/v) Water/Trifluoroethanol[b]

leaving group	ring substituent			
	$4\text{-}N(CH_3)_2$	$4\text{-}OCH_3$	$4\text{-}SCH_3$	$4\text{-}CH_3$
$4\text{-}NO_2ArCO_2^-$	5.4			
I^-		0.73	0.31	
Br^-		6.2	2.6	
$MeSO_3^-$		350	53	
$4\text{-}CH_3ArSO_3^-$		870	145	0.032

[a] The average of values from at least two different experiments. The reactions were followed by a number of different methods which are described in the Experimental Section. [b] The reactions were run at 25 °C and 0.50 M $NaClO_4$. The reactions were initiated by adding substrate in acetonitrile to give a final solvent containing 1% acetonitrile.

Calculation of Nucleophilic Selectivities. When the ratio of the extinction coefficients of two adducts was 1.0, the nucleophilic selectivity was calculated directly from product ratios with eq 1, where $[area]_{RNu1}$ and $[area]_{RNu2}$ are the integrated peak areas for the two adducts.

$$k_{Nu1}/k_{Nu2} = [area]_{RNu1}[Nu_2]/[area]_{RNu2}[Nu_1] \qquad (1)$$

The relative extinction coefficients of the water and nucleophile adducts were determined by comparing the increase in peak area for the nucleophile adduct ($[area]_{RNu}$) with the decrease in the peak area for the solvent adduct ($[area]_{ROH}$) as the nucleophile concentration is increased. The increase in $[area]_{RNu}$ matches the decrease in $[area]_{ROH}$ when the extinction coefficients of the two adducts are the same. This is the case for the methanol, trifluoroethanol, azide, and acetate adducts to $4\text{-}SCH_3ArCH(CF_3)^+$, $4\text{-}OCH_3ArCH(CF_3)^+$, and $4\text{-}N(CH_3)_2ArCH(CF_3)^+$. It was not possible to determine the relative extinction coefficients for alcohol adducts to $CH_3ArCH(CF_3)^+$, because the yields of these adducts were low and the resulting decrease in the peak area for the water adduct was not much greater than the experimental error (±5%). It was assumed that the extinction coefficients for the HOH, CH_3OH, and CF_3CH_2OH adducts to $4\text{-}CH_3ArCH(CF_3)^+$ are the same.

There is a small difference in the extinction coefficients for the azide and solvent adducts to $4\text{-}CH_3ArCH(CF_3)^+$, and the UV spectra for the iodide and bromide adducts are very different from the spectra for the solvent adducts. In these cases the product rate constant ratios were calculated from the slopes and intercepts of plots of $1/[area]_{RNu}$ against $1/[Nu]$ (eq 2)

$$1/[area]_{RNu} = 1/[area]_{max}(1 + k_s/k_{Nu}[Nu]) \qquad (2)$$

$$1/[area]_{RSol} = 1/[area]_{max}(1 + k_{Nu}[Nu]/k_s) \qquad (3)$$

Trapping of $4\text{-}N(CH_3)_2ArCH(CF)_3^+$ by N_3^- was so efficient that the solvent adduct could not be detected when N_3^- was present at 10-fold concentration excess over substrate. Here the nucleophilic selectivity, k_{az}/k_s, was calculated from the ratios k_{AcO}/k_s and k_{az}/k_{AcO} for the reaction of acetate. The latter ratio was determined for the reaction of increasing azide concentrations (5×10^{-5}–2×10^{-4} M) in the presence of 0.48 M acetate.

Results

In general, the compounds $XArCH(CF_3)Y$ were prepared either by known procedures or by simple adaptation of known procedures. The exceptions are the iodide adducts $4\text{-}OCH_3ArCH(CF_3)I$ and $4\text{-}SCH_3ArCH(CF_3)I$, which were prepared by the S_N1 substitution reactions of I^- with the respective mesylates.

The observed first-order rate constants (k_{obsd}) for the solvolysis reactions of $XArCH(CF_3)Y$ in 50:50 (v/v) water/trifluoroethanol at 25 °C ($I = 0.50$, $NaClO_4$) are reported in Table I. The value of 0.061 s^{-1} measured for the reaction of $4\text{-}OCH_3ArCH(CF_3)Tos$ at zero ionic strength is in reasonable agreement with the value of 0.072 s^{-1} reported previously for this compound.[3f]

The effect of added salts on k_{obsd} for the reaction of $4\text{-}OCH_3ArCH(CF_3)Mes$ and $4\text{-}OCH_3ArCH(CF_3)Br$ in 50:50 (v/v) water/trifluoroethanol and 40% methanol in water is shown in Table II. Except for NaBr, which shows a strong common-ion effect on the reaction of $4\text{-}OCH_3ArCH(CF_3)Br$, added salts cause only a small increase in k_{obsd} above the value at zero ionic strength. The largest relative rate increases (ca. 80% for 4-OCH$_3$ArCH-

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(18) Jencks, W. P. *Catalysis in Chemistry and Enzymology*; McGraw-Hill: New York, 1969; p 571.

Table II. Salt Effects on the Solvolysis Rate Constants for the Reactions of 1-(4-Methoxyphenyl)-2,2,2-trifluoroethyl Bromide and Mesylate in 50:50 (v/v) Water/Trifluoroethanol and 40% Methanol in Water[a]

mesylate leaving group		bromide leaving group[e]	
salt (M)	$k_{obsd}/10^{-2}$ s^{-1}	salt (M)	$k_{obsd}/10^{-4}$ s^{-1}
50:50 (v/v) Trifluoroethanol/Water			
none	2.8[b]	none	3.5
$NaClO_4$ (0.50)	3.9[b]	$NaClO_4$ (0.50)	6.2
NaI (0.50)	3.2[c]		
NaBr (0.50)	3.0[c]	NaBr (0.083)	1.3[h]
NaCl (0.50)	3.3[d]	NaCl (0.50)	4.4
NaAcO (0.50)	2.7[d]	NaAcO (0.50)	4.2
$NaCH_3SO_3$ (0.48)	3.0[f]	NaN_3 (0.50)	6.2
40% Methanol in Water			
none	3.4[b]	none	5.4[e]
$NaClO_4$ (0.60)	4.0[b]	$NaClO_4$ (0.60)	8.8[e]
NaI (0.60)	3.7[c]	NaI (0.40)	9.6[c,i]
NaN_3 (0.48)	4.3[g]	NaN_3 (0.60)	9.7[e]
NaCl (0.60)	3.5[d]	NaCl (0.60)	5.7[e]
NaAcO (0.60)	3.0[d]	NaAcO (0.60)	4.3[e]

[a] At 25 °C. The reactions were initiated by adding substrate in acetonitrile to give a final solvent containing 1% acetonitrile. [b] The reaction progress was followed by monitoring the protonation of a phenoxide indicator by the methanesulfonic acid produced during the solvolysis. [c] The reaction progress was followed by monitoring the increase in absorbance at 290 nm resulting from the formation of the nucleophilic adduct. [d] The disappearance of substrate was followed by monitoring the decrease in absorbance at 247 nm. [e] The disappearance of substrate was monitored by following the decrease in absorbance at 280 nm. [f] The reaction was carried out in the presence of 0.02 M NaI and monitored by following the formation of the iodide adduct at 290 nm. [g] The reaction was carried out in the presence of 0.12 M NaI and monitored by following the formation of the iodide adduct at 290 nm. [h] I = 0.50, $NaClO_4$. [i] I = 0.60, $NaClO_4$.

(CF_3)Br) are observed for the nonnucleophilic salt $NaClO_4$ and the nucleophilic salt NaN_3. For reactions at constant ionic strength maintained with $NaClO_4$, k_{obsd} remains constant (±5%) as NaN_3 is substituted for $NaClO_4$.

No S_N2 reaction is expected for the weakly nucleophilic perchlorate ion. Therefore, the rate increase with increasing [$NaClO_4$] is due to a specific-salt effect. It is impossible to rigorously exclude that part of the NaN_3 rate increase over no salt is due to a bimolecular azide reaction; however, the following observations suggest that the rate acceleration is also due to a specific-salt effect.

1. The specific NaN_3 and $NaClO_4$ salt effects for a related reaction are similar; k_{obsd} values for the S_N1 reaction of 1-(4-methylphenyl)ethyl chloride in 50% methanol in water remain constant as 0.50 M $NaClO_4$ is replaced by 0.50 M NaN_3.[11a]

2. If there is a weak S_N2 azide reaction with 4-$OCH_3ArCH(CF_3)Y$, then there should be an even more easily detected S_N2 azide reaction with less reactive 4-$CH_3ArCH(CF_3)Y$.[11a] However, the reaction of 4-$CH_3ArCH(CF_3)Tos$ with azide remains S_N1 (see below).

In conclusion, the data in Table II shows that the reactions of nucleophiles with 4-$OCH_3ArCH(CF_3)Y$ are essentially zero order in nucleophile concentration; the bimolecular substitution reaction does not give a detectable rate increase.

The value of k_{obsd} for the reaction of 4-$CH_3ArCH(CF_3)Tos$ in 50:50 (v/v) water/trifluoroethanol remains constant (3.2 × 10^{-6} s^{-1} (±5%), Table I) as 0.50 M $NaClO_4$ is replaced by 0.50 M NaN_3. HPLC product analysis showed that at 0.50 M NaN_3, the azide adduct constituted 30% of the total substitution reaction products (Table III).

Figure 1A shows the effect of increasing NaI concentrations on the time course for the reaction, in 50:50 (v/v) water/trifluoroethanol (I = 0.5, $NaClO_4$), of a fixed concentration (ca. 0.2 mM) of 4-$OCH_3ArCH(CF_3)Mes$. The absorbance increase is due to the formation of the iodide adduct 4-$OCH_3ArCH(CF_3)I$, which is stable on the time scale for reaction of the mesylate and which is easily resolved by HPLC (see below).

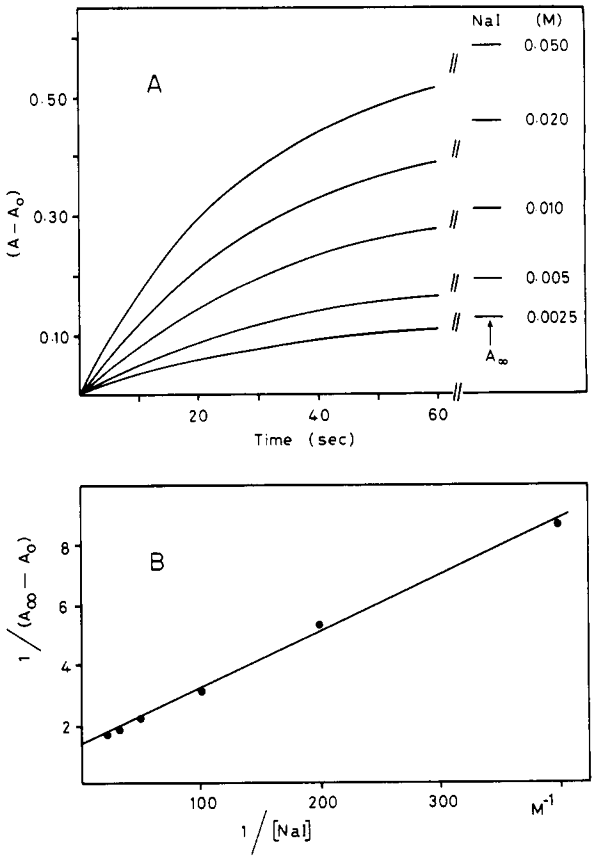


Figure 1. (A) The absorbance change at 290 nm with time for the reaction of 4-$OCH_3ArCH(CF_3)Mes$ with increasing concentrations of NaI in 50:50 (v/v) water/trifluoroethanol (25 °C; I = 0.5, $NaClO_4$). (B) The fit of the data from Figure 1A to eq 4 from the text is shown.

Table III. Nucleophilic Selectivities for the Reaction of Ring-Substituted 1-Phenyl-2,2,2-trifluoroethyl Derivatives in 50:50 (v/v) Trifluoroethanol/Water[a]

ring substit	k_{HOH}/k_{TFE}[b]	k_{MeOH}/k_{TFE}[b,c]	k_{AcO}/k_{TFE}[b]	k_{az}/k_{TFE}[b]	k_{az}/k_s, M^{-1} [d]
4-CH_3[e]	1.4	3.8		37[f]	0.80
4-OCH_3[g]	3.8	80	350[h]	1.1 × 10^4 [f]	95
4-SCH_3[i]	3.9	100	590[h]	4.6 × 10^4 [f]	400
4-$N(Me)_2$[j]	8.4	400	51300[k]	1.4 × 10^8 [l]	6 × 10^6

[a] At 22 ± 2 °C, I = 0.5 $NaClO_4$ and 1% acetonitrile. Nucleophilic selectivities were calculated from product ratios determined by HPLC as described in the Experimental Section. [b] Dimensionless ratio of second-order rate constants. [c] Reaction in a solution containing 50:45:5 (v/v/v) water/trifluoroethanol/methanol. [d] Treating addition by solvent as a pseudo-first-order reaction. [e] Calculated from product data for the reaction of 4-$CH_3ArCH(CF_3)Tos$. [f] Calculated from experimentally determined values for k_{HOH}/k_{TFE} and k_{az}/k_{HOH}. The k_{az}/k_{HOH} values (not reported) are the average for values at a minimum of five azide concentrations. [g] The values obtained for the reactions of 4-$OCH_3ArCH(CF_3)Br$ and 4-$OCH_3ArCH(CF_3)Tos$ agree within the experimental error of ±10%. [h] Reaction in a solution containing 0.1 M acetate buffer (A^-/AH = 9), where acetate catalysis of the trifluoroethanol reaction is not significant. [i] The values obtained for the reactions of 4-$SCH_3ArCH(CF_3)Br$ and 4-$SCH_3ArCH(CF_3)Tos$ agree within the experimental error of ±10%. [j] The values obtained for the reactions of 4-$N(CH_3)_2ArCH(CF_3)$-4-NB and 4-$N(CH_3)_2ArCH(CF_3)$-3,5-NB agree within the experimental error of ±10%. [k] Calculated from k_{HOH}/k_{TFE} and the average of values for k_{AcO}/k_{HOH} obtained at acetate anion concentrations between 0.0025 and 0.05 M and at two different buffer ratios (A^-/AH = 1, 1/4). [l] Calculated from the ratios k_{AcO}/k_s and k_{az}/k_{AcO}. The latter is the average of values obtained at 0.45 M AcO^- and three different azide concentrations between 5 × 10^{-5} and 2 × 10^{-4} M.

Figure 2A shows the effect of increasing azide-ion concentrations on the time course for the reaction (under the same conditions as Figure 1A) of a fixed concentration of 4-$OCH_3ArCH(CF_3)Mes$ at a constant [NaI] of 0.01 M. The decreasing total absorbance change ($A_\infty - A_0$) with increasing [NaN_3] is due to the formation

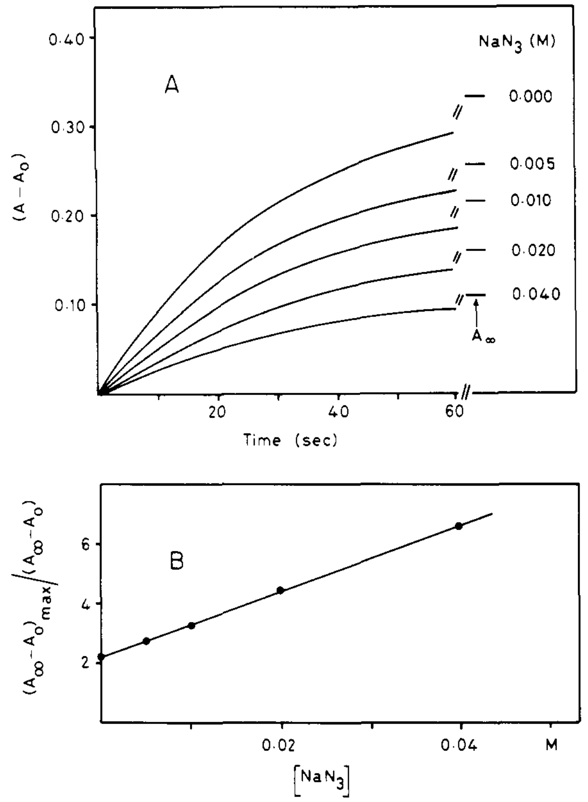
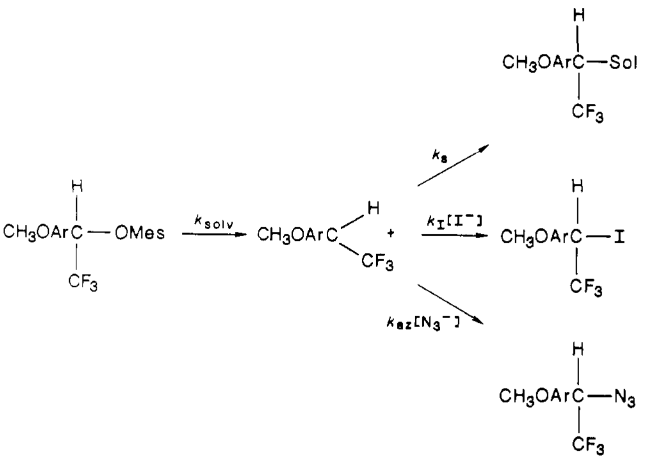


Figure 2. (A) The absorbance change at 290 nm with time for the reaction of 4-$OCH_3ArCH(CF_3)Mes$ in 50:50 (v/v) water/trifluoroethanol (25 °C; I = 0.5, $NaClO_4$). The NaI concentration is held constant at 0.01 M as the concentration of NaN_3 is increased. (B) The fit of the data from Figure 2A to eq 5 from the text is shown.

Scheme I



of the UV-invisible azide adduct at the expense of the iodide adduct.

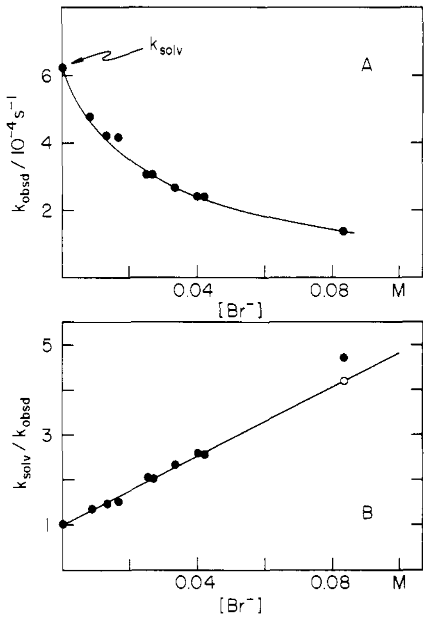


Figure 3. (A) The common-ion rate depression for the reaction of 4-$OCH_3ArCH(CF_3)Br$ in 50:50 (v/v) water/trifluoroethanol (25 °C; I = 0.5, $NaClO_4$). (B) The fit of the data from Figure 3A to eq 6 in the text is shown. The solid circles in this figure are calculated with the k_{solv} value in Figure 3A. The open circle is calculated, as described in the text, from the limiting k_{obsd} value at high [NaN_3] in Figure 4A.

An analysis of the data in Figures 1A and 2A shows that the pseudo-first-order rate constants for substrate reaction are nucleophile-independent under conditions where there is greater than 75% conversion of the substrate to either the iodide or the azide adduct. This demonstrates that there are separate nucleophile-independent rate-determining (k_{solv}) and nucleophile-dependent product-determining (k_s, k_I, and k_{az}) steps (Scheme I). If the reaction is stepwise, then there must be a carbocation intermediate, 4-$OCH_3ArCH(CF_3)^+$. The data in Figures 1A and 2A show a good fit to eq 4 and 5, respectively, where $(A_\infty - A_0)$ is the total

$$1/(A_\infty - A_0) = [1/(A_\infty - A_0)_{max}](1 + k_s/k_I[I^-]) \quad (4)$$

$$(A_\infty - A_0)_{max}/(A_\infty - A_0) = 1 + k_s/k_I[I^-] + k_{az}[N_3^-]/k_I[I^-] \quad (5)$$

absorbance change for the reaction and $(A_\infty - A_0)_{max}$ is the absorbance change observed for quantitative conversion of the substrate to the iodide adduct. Equations 4 and 5 are simply derived for the mechanism in Scheme I by setting the fraction of iodide adduct, $(A_\infty - A_0)/(A_\infty - A_0)_{max}$, equal to the ratio $k_I[I^-]/k_t$, where k_t is the sum of all the pseudo-first-order rate constants for the capture of 4-$OCH_3ArCH(CF_3)^+$.

The fit of data from Figure 1A to eq 4 is shown in Figure 1B. The ratio $k_I/k_s = 85 \pm 6$ M^{-1} is calculated by averaging the value obtained from the slope and intercept of the plot in Figure 1B with values obtained in two further experiments.

Figure 2B shows the fit of data from Figure 2A to eq 5. A rate constant ratio of $k_{az}/k_I = 1.0 \pm 0.1$ was calculated from the slope of the plot in Figure 2B and $[I^-] = 0.01$ M. The same value for k_{az}/k_I is obtained when the reaction is run at 0.02 M NaI.

A similar analysis of data (not shown) for the reaction of 4-$SCH_3ArCH(CF_3)Mes$ with NaI gave $k_I/k_s = 470$ M^{-1} for the capture of 4-$SCH_3ArCH(CF_3)^+$ in 50:50 (v/v) water/trifluoroethanol (I = 0.50, $NaClO_4$).

The reaction of 4-$OCH_3ArCH(CF_3)Mes$ with NaBr gave an increase in absorbance at 290 nm to a maximum value, due to conversion of the substrate to 4-$OCH_3ArCH(CF_3)Br$, followed by a much slower decrease in absorbance as 4-$OCH_3ArCH(CF_3)Br$ solvolyzes. Data (not shown) from an experiment similar to that presented in Figure 1A showed a good fit to eq 4. A rate constant ratio $k_{Br}/k_s = 37$ M^{-1} was calculated from the slope and the intercept of a plot of $1/(A_\infty - A_0)$ against $1/[Br^-]$.

The reaction of 4-$OCH_3ArCH(CF_3)Br$ at 25 °C in 50:50 (v/v) water/trifluoroethanol was subject to a strong common-ion rate depression (Figure 3A).[19] At constant ionic strength (I = 0.50, $NaClO_4$), k_{obsd} for the reaction of 4-$OCH_3ArCH(CF_3)Br$ is zero order in [NaN_3] (squares, Figure 4A), but when the reaction is carried out in the presence of an inhibitory concentration of 0.083 M NaBr, k_{obsd} increases with increasing [N_3^-] to a limiting value slightly smaller than k_{obsd} at zero NaBr (circles, Figure 4A).

The data in Figures 3A and 4A strongly support a mechanism involving a carbocation intermediate (Scheme II). The decrease in k_{obsd} with increasing [NaBr] (Figure 3A) is due to trapping of 4-$OCH_3ArCH(CF_3)^+$ by the bromide anion, regenerating

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(19) Benfrey, O. T.; Hughes, E. D.; Ingold, C. K. *J. Chem. Soc.* **1952**, 2488–2493.

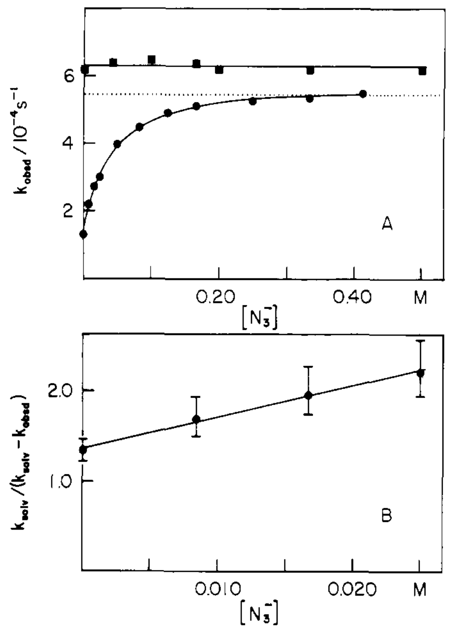
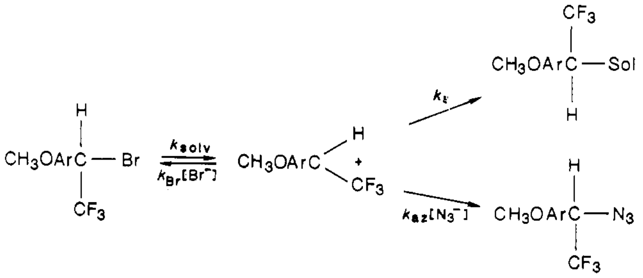


Figure 4. (A) The effect of added azide ion on k_{obsd} for the reaction of 4-$OCH_3ArCH(CF_3)Br$ in 50:50 (v/v) water/trifluoroethanol (25 °C; I = 0.5, $NaClO_4$). The squares are for the reaction in the absence of NaBr, and the circles are for the reaction at a fixed [NaBr] of 0.083 M. (B) The fit of the data from Figure 4A to eq 7 in the text is shown. The error bars are calculated for the estimated error of ±5% in k_{solv} and k_{obsd}.

Scheme II



substrate, and thereby slowing the net rate of its disappearance. The rate-determining step for the reaction of 4-$OCH_3ArCH(CF_3)Br$ at $[Br^-]$ = 0.0 M (k_{solv}) is not affected by the replacement of $NaClO_4$ by NaN_3 (Figure 4A, squares). At 0.083 M NaBr, 4-$OCH_3ArCH(CF_3)^+$ formation is reversible, and capture of this intermediate by nucleophiles is rate limiting. Now the azide anion reacts at the rate-determining step, and k_{obsd} increases with increasing $[N_3^-]$ until 4-$OCH_3ArCH(CF_3)Br$ ionization again becomes irreversible and rate limiting ($k_s + k_{az}[N_3^-] \gg k_{Br}[Br^-]$). At this point k_{obsd} levels off at the limiting value, k_{solv}.

Equations 6 and 7, derived for the mechanism in Scheme II, give linear plots for the data in Figures 3A and 4A, respectively. The plot of k_{solv}/k_{obsd} against $1/[Br^-]$ for data in Figure 3A is

$$k_{solv}/k_{obsd} = 1 + k_{Br}[Br^-]/k_s \tag{6}$$

$$k_{solv}/(k_{solv} - k_{obsd}) = 1 + k_s/k_{Br}[Br^-] + k_{az}[N_3^-]/k_{Br}[Br^-] \tag{7}$$

shown in Figure 3B. The dark circles are calculated with $k_{solv} = 6.5 \times 10^{-4}\ s^{-1}$ obtained for the reaction at [NaBr] = 0.0 M. In fact, at 0.083 M NaBr there is a small specific NaBr salt effect on k_{solv}, as shown by the smaller value of $k_{obsd} = k_{solv} = 5.5 \times 10^{-4}\ s^{-1}$ for the reaction at high $[NaN_3]$ (Figure 4A), where the rate-determining step is substrate ionization. The open circle in Figure 3B is calculated with the value of $5.5 \times 10^{-4}\ s^{-1}$ as k_{solv} in eq 6. It shows an overall better fit to eq 6 and is used for the line in Figure 3B, which has a slope $k_{Br}/k_s = 37\ M^{-1}$.

The plot of $k_{solv}/(k_{solv} - k_{obsd})$ against $[N_3^-]$ (eq 7) for the data in Figure 4A is shown in Figure 4B. The error bars in Figure 4B were calculated with an estimated error of ±5% in k_{solv} and k_{obsd}. The slope of the line in Figure 4B times $[Br^-]$ = 0.083 M is the rate constant ratio $k_{az}/k_{Br} = 2.9$. Potentially, rate constant ratios for the reaction of 4-$OCH_3ArCH(CF_3)^+$ with other nucleophiles could have been determined by this method. However, these experiments were not pursued, because the same ratios can be obtained more quickly and with greater accuracy from HPLC product analysis.

A study of the reaction of 4-$SCH_3ArCH(CF_3)Br$ in 20% methanol in water gave results similar to those in Figures 3 and 4 (data not shown; $k_{solv} = 1.6 \times 10^{-3}\ s^{-1}$, $k_{Br}/k_s = 24\ M^{-1}$, $k_{az}/k_{Br} = 5.1$).

The nucleophile adducts from the reactions of $XArCH(CF_3)Y$ were separated by HPLC and quantified by their UV absorbance, and the rate constant ratios for product formation were calculated from product ratios as described in the Experimental Section. The rate constant ratios are for the partitioning of the carbocation reaction intermediates $XArCH(CF_3)^+$.

Product analysis gave the following nucleophilic selectivities for the reaction of 4-$OCH_3ArCH(CF_3)Y$ in 50:50 (v/v) water/trifluoroethanol (I = 0.50, $NaClO_4$): 4-OCH_3-$ArCH(CF_3)Mes$, $k_I/k_s = 90\ M^{-1}$; 4-$OCH_3ArCH(CF_3)Br$, $k_{az}/k_s = 95\ M^{-1}$; and 4-$OCH_3ArCH(CF_3)Tos$, $k_{az}/k_s = 95\ M^{-1}$, $k_I/k_s = 90\ M^{-1}$, $k_{Br}/k_s = 37\ M^{-1}$.

There is good agreement between the rate constant ratios for carbocation partitioning measured by the three methods described here: spectrophotometric analysis (Figures 1 and 2), analysis of the common-ion effect (Figures 3 and 4), and HPLC product analysis. For example, k_{az}/k_{Br} values of 2.3, 2.9, and 2.6 were calculated from spectrophotometric data,[20a] common-ion effect data (slope of Figure 4B), and product data,[20b] respectively; k_I/k_s values of 85 and 90 M^{-1} for the reaction of 4-$OCH_3ArCH(CF_3)Mes$ were calculated from spectrophotometric data and product data, respectively.

Product rate constant ratios for the partitioning of ring-substituted $XArCH(CF_3)^+$ between reaction with solvent (50:50 (v/v) water/trifluoroethanol), methanol, acetate ion, and azide ion are reported in Table III. The selectivities for the reactions of 4-$OCH_3ArCH(CF_3)Y$ (tosylate and bromide leaving groups), 4-$SCH_3ArCH(CF_3)Y$ (tosylate and bromide leaving groups), and 4-$N(CH_3)_2ArCH(CF_3)Y$ (4-nitrobenzoate, and 3,5-dinitrobenzoate leaving groups) are independent of the leaving group. Only one 4-$CH_3ArCH(CF_3)$ derivative (the tosylate) was studied.

As was previously observed for the reaction of $XArCH(CH_3)^+$, acetate ion catalyzed the addition of trifluoroethanol to $XArCH(CF_3)^+$.[21] The k_{ACO}/k_{TFE} values reported in Table III are at low acetate concentrations, where general-base catalysis of trifluoroethanol addition by acetate ion is not significant.

Discussion

Evidence Supporting a Stepwise Mechanism through 1-Phenyl-2,2,2-trifluoroethyl Carbocation Intermediates. The data for the solvolysis reactions of $XArCH(CF_3)Y$ agree well with work previously published by Tidwell et al.[3f] and confirm the large decelerating effect of the α-CF_3 group on the rate of solvolysis. The Hammett $\rho^+ = -9.7$ for the reaction of $XArCH(CF_3)Tos$ in 50:50 (v/v) water/trifluoroethanol, calculated from the rate constants in Table I, is within the range (−6.7 to −11.9) of ρ^+ values reported for the reaction of $XArCH(CF_3)Tos$ in a number of different solvents.[3f] The data also show (as noted elsewhere)[3g] that a second α-CF_3 group has only a small effect on k_{solv}; similar rate constants of $5.4 \times 10^{-4}\ s^{-1}$ and $2.5 \times 10^{-4}\ s^{-1}$, respectively, are observed for the reaction of 4-$N(CH_3)_2ArCH(CF_3)$-4-NB (Table I) and 4-$N(CH_3)_2ArC(CF_3)_2$-4-NB in 50:50 (v/v) water/trifluoroethanol.

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(20) (a) Calculated from the following rate constant ratios obtained in spectrophotometric experiments; $k_{Br}/k_s = 37\ M^{-1}$, $k_I/k_s = 85\ M^{-1}$, and $k_{az}/k_I = 1.0$. (b) Calculated from the following values obtained by HPLC product analysis; $k_{az}/k_s = 95\ M^{-1}$, $k_{Br}/k_s = 37\ M^{-1}$.

(21) Ta-Shma, R.; Jencks, W. P. *J. Am. Chem. Soc.* **1986**, *108*, 8040–8050. Richard, J. P.; Jencks, W. P. *J. Am. Chem. Soc.* **1984**, *106*, 1396–1401.

The following observations, made in the present studies on the reaction of more potent nucleophiles with $XArCH(CF_3)Y$, provide indirect proof for the formation of solvent-equilibrated carbocation intermediates $XArCH(CF_3)^+$ in nucleophilic solvents.

1. The observed rate constants for the solvolysis of 4-$OCH_3ArCH(CF_3)Mes$ and 4-$OCH_3ArCH(CF_3)Br$ are independent of azide ion or iodide ion concentrations, which give up to a 98% yield of the nucleophile adduct (Figures 1, 2, and 4A (squares) and Table II). This is classical evidence for a two-step mechanism and a carbocation intermediate. Similarly, the reactions of 4-$SCH_3ArCH(CF_3)Mes$, 4-$SCH_3ArCH(CF_3)Br$, and 4-$CH_3ArCH(CF_3)Tos$ were found to give nucleophile adducts by reactions zero order in nucleophile concentration.

2. The strong bromide common ion effect observed for the reactions of 4-$OCH_3ArCH(CF_3)Br$ (in 50:50 (v/v) water/trifluoroethanol) and 4-$SCH_3ArCH(CF_3)Br$ (in 20% methanol in water) is classical evidence for the formation of the diffusionally equilibrated carbocation intermediates 4-$OCH_3ArCH(CF_3)^+$ and 4-$SCH_3ArCH(CF_3)^+$, respectively.[19]

3. The biphasic dependence of k_{obsd} on $[NaN_3]$ for the reaction of 4-$OCH_3ArCH(CF_3)Br$ (Figure 4A, circles) is consistent with a two-step mechanism and a change in the rate-limiting step with increasing azide ion concentration (Scheme II).

At 0.083 M NaBr and low azide anion concentrations, 4-$OCH_3ArCH(CF_3)^+$ is reversibly trapped by the bromide common ion, and the capture of this intermediate is the rate-limiting step for the overall reaction. Competitive trapping by the azide anion gives a first-order dependence of k_{obsd} on $[NaN_3]$, because trapping increases the velocity of rate-limiting carbocation capture. At higher $[N_3^-]$ there is a change in the rate-determining step, to substrate ionization (k_{solv}), as the velocity of the N_3^- trapping reaction overtakes the velocity of intermediate return to substrate by Br^- trapping. At still higher $[N_3^-]$, 4-$OCH_3ArCH(CF_3)^+$ is trapped by azide virtually every time it is formed and the values for k_{obsd} level off at k_{solv}.

Figure 4A (circles) is mildly reminiscent of curvature reported by Sneen in plots of k_{obsd} against $[NaN_3]$ for nucleophilic substitution reactions at simple aliphatic and benzyl halides[22] (note that serious questions have been raised about his interpretation of this data[23]). However, there are important differences between the two sets of experiments. (1) In contrast to Sneen's work, the present studies were performed at constant ionic strength, maintained with sodium perchlorate. (2) The curvature in Figure 4A is only observed for reaction in the presence of a moderate concentration of the bromide common ion and is due to the competition between added N_3^- and Br^- for reaction with the *free carbocation intermediate.* The Sneen experiment (squares, Figure 4A) is performed in the absence of the common ion. A curved plot for the Sneen experiment constitutes evidence for azide ion trapping of an *ion-pair intermediate* (4-$OCH_3ArCH(CF_3)^+\cdot Br^-$), which is formed reversibly from reactant, while the observed lack of curvature shows either that the ion-pair intermediate is formed irreversibly from reactant or that it is not trapped by azide ion.

In an expanded S_N1 mechanism, solvent or added nucleophiles may react with the free intermediate $XArCH(CF_3)^+$, the contact ion pair, or the solvent-separated ion-pair intermediates.[24] For the studies reported here, in largely aqueous solutions, solvent addition to the ion pair will not be an important reaction so long as k_{az}/k_s for carbocation partitioning is large, because when this is the case the lifetime of the intermediate is long enough for the ion pair to undergo irreversible dissociation before significant nucleophile reaction can occur.[6] For example, $k_{az}/k_s = 95$ M^{-1} (Table III) for 4-$OCH_3ArCH(CF_3)^+$, showing that k_s is at least 100 times smaller than k_d, the diffusional rate constant for encounter-complex formation between azide and 4-$OCH_3ArCH(CF_3)^+$. Since association constants in water are small ($K_{as} = k_d/k_{-d} \leq 1$ M^{-1})[25a] and the reactivity of the ion pair is similar to that of the free ion,[25b] the rate constant for solvent capture of this ion pair must be at least 100 times smaller than k_{-d}, the rate constant for dissociation of the ion pair to free ions. Thus, dissociation is essentially complete before there is significant ion-pair trapping by solvent or moderate concentrations of added nucleophiles. The identical nucleophilic selectivities observed for the reaction of 4-$OCH_3ArCH(CF_3)Mes$, 4-$OCH_3ArCH(CF_3)Br$, and 4-$OCH_3ArCH(CF_3)Tos$ and for 4-$SCH_3ArCH(CF_3)Br$ and 4-$SCH_3ArCH(CF_3)Tos$ (Table III) are also consistent with nucleophile and solvent trapping of a free carbocation intermediate rather than a species which contains the leaving group.

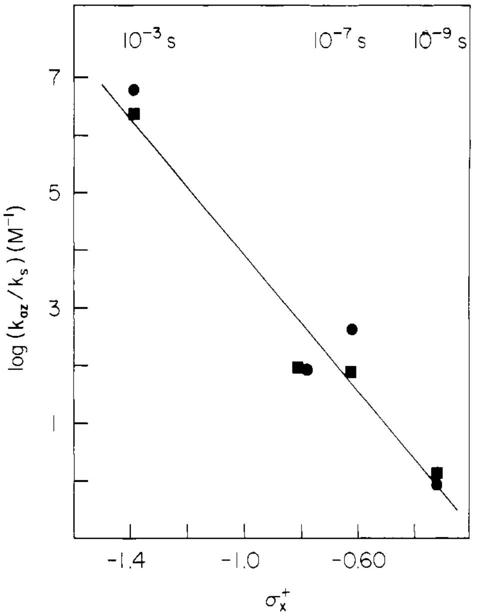

Figure 5. The Hammett plot of azide selectivities (k_{az}/k_s, M^{-1}) for the reaction of $XArCH(CF_3)^+$ (circles, this work) and $XArCH(CH_3)^+$ (squares, data from ref 6). The solid line shows the least-squares fit of the data for the reaction of $XArCH(CF_3)^+$. The values across the top of the figure show the lifetimes of the respective carbocations ($1/k_s$) calculated from the azide selectivity and a diffusional value of 5×10^9 M^{-1} s^{-1} for k_{az}.[34]

The observed k_{az}/k_s value of 0.8 M^{-1} (Table III) for the S_N1 reaction of 4-$CH_3ArCH(CF_3)Tos$ requires that k_s for solvent addition to 4-$CH_3ArCH(CF_3)^+$ be slightly larger than the diffusional value for k_{az} and of the same order of magnitude as the rate constant for diffusional breakdown of the 4-$CH_3ArCH(CF_3)^+\cdot Tos$ ion-pair intermediate. Therefore, this ion pair may react directly with solvent before there is time for it to breakdown by diffusion to free ions.[26]

Ion pairs of the still more unstable carbocation 4-$HArCH(CF_3)^+$ probably react directly with nucleophilic solvents. Racemization of chiral 4-$HArCH(CF_3)Tos$ is 27 and 7 times faster than solvolysis, respectively, for reaction in trifluoroacetic acid and hexafluoroisopropyl alcohol, but the rates are nearly equal in the more nucleophilic solvents acetic acid and ethanol.[3f] Increasing the solvent nucleophilicity also changes the stereochemical course of product formation from racemization to partial inversion of configuration.[3f] These results suggest that in weakly nucleophilic solvents an ion-pair intermediate is formed reversibly from substrate and breaks down to the asymmetric carbocation which is captured by solvent, whereas in solvents more nucleophilic than the tosylate leaving group, the solvent adds directly to an ion-pair intermediate shielded from front-side attack by the tosylate ion.[3f]

1-Phenyl-2,2,2-trifluoroethyl Carbocation Lifetimes and Other Properties. Theoretical calculations predict that a large desta-

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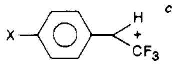
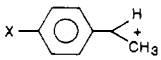
Table IV. Rate Constants for the Capture of Ring-Substituted 1-Phenylethyl and 1-Phenyl-2,2,2-trifluoroethyl Carbocations by Solvent and Added Nucleophiles[a,b]

	 [c]							
para ring substit	k_{TFE}, $M^{-1}\ s^{-1}$	k_{MeOH}, $M^{-1}\ s^{-1}$	k_{AcO}, $M^{-1}\ s^{-1}$	k_s, s^{-1}	k_{TFE},[d] $M^{-1}\ s^{-1}$	k_{MeOH},[e] $M^{-1}\ s^{-1}$	k_{AcO},[e] $M^{-1}\ s^{-1}$	k_s,[d] s^{-1}
$N(Me)_2$	3.6[f]	1400[f]	1.8×10^{5}[f]	800[f]	22	4800		2000
SCH_3	1.1×10^{5}	1.1×10^{7}	6.5×10^{7}	1.2×10^{7}	8×10^{5}	2.9×10^{7}	6.4×10^{7}	4×10^{7}
OCH_3	4.5×10^{5}	3.6×10^{7}	1.6×10^{8}	5×10^{7}	8×10^{5}	3.3×10^{7}	7.6×10^{7}	5×10^{7}
CH_3	1.4×10^{8}[g]	5×10^{8}[g]		6×10^{9}[g]	1.0×10^{8}	7×10^{8}	5×10^{8}	4×10^{9}

[a] In 50:50 (v/v) water/trifluoroethanol at 22 ± 2 °C and $I = 0.50$ ($NaClO_4$). [b] Rate constants were calculated from the product rate constant ratio k_{az}/k_{Nu} and a diffusional value of $5 \times 10^9\ M^{-1}\ s^{-1}$ for k_{az} (ref 33). [c] Calculated from nucleophilic selectivities in Table III. [d] Data from ref 6b. [e] Data from ref 26. [f] An upper limit for the rate constant (see the text). [g] A lower limit for the rate constant (see the text).

bilization will result from the placement of a CF_3 group adjacent to a positively charged carbon,[27] while calculations based on gas-phase data show that an α-CF_3 for α-CH_3 substitution destabilizes $CH_3CH_2^+$ by roughly 50 kcal/mol relative to a common neutral derivative.[28] Conventional attempts to generate highly destabilized secondary α-CF_3-substituted carbocations in superacids have not met with great success.[29,30] Set against these past studies, which emphasize the great instability of α-CF_3-substituted carbocations, the relative ease of the generation of $XArCH(CF_3)^+$ as transient intermediates of solvolysis reactions was met with surprise.

A Hammett plot of log (k_{az}/k_s) against σ_x^+ for the partitioning of $XArCH(CF_3)^+$ between capture by azide and solvent is shown in Figure 5 (circles). The log (k_{az}/k_s) values decrease rapidly as the carbocation is destabilized by changing the ring substituent. This dependence is similar to that observed for $XArCH(CH_3)^+$ (squares Figure 5)[6] and quite different from the reactivity-independent k_{az}/k_s values for a broad series of more stable carbocations.[31] The k_{az}/k_s values are invariant for relatively stable carbocations, because the rate constants k_{az} and k_s are activation limited and free to change with changing carbocation reactivity. The changing k_{az}/k_s ratios observed for the more reactive carbocations $XArCH(CH_3)^+$ and $XArCH(CF_3)^+$ are characteristic of a diffusion-limited azide reaction. The decrease in k_{az}/k_s with increasing carbocation reactivity is due to the increase in k_s for the activation-limited solvent reaction relative to the fixed diffusion-limited value for k_{az}.[6,7,32] It was expected that k_{az} for the capture of $XArCH(CF_3)^+$ would be diffusion limited, because the large thermodynamic destabilization of this carbocation by the electron-withdrawing α-CF_3 substituent could not have caused k_{az} to decrease below the diffusion-limited rate constants observed for the reaction of $XArCH(CH_3)^+$.[6,7]

The first-order rate constants k_s for the reactions of $XArCH(CF_3)^+$ with solvent, estimated from the product rate constant ratios k_{az}/k_s and a diffusional rate constant of $5 \times 10^9\ M^{-1}\ s^{-1}$ for k_{az},[33,34] are listed in Table IV. The carbocation lifetimes $(1/k_s)$ are listed across the top of Figure 5. It is assumed that the diffusion-limited rate constants k_{az} for trapping of $XArCH(CF_3)^+$ and $XArCH(CH_3)^+$ are the same. Charge–dipole interactions between the azide anion and CF_3 substituent will have no more than a small effect on k_{az}, because diffusion-limited rate constants change by only 2–3-fold when the charge at the reactants is changed by a full unit.[33]

Table IV also includes second-order rate constants for the reaction of $XArCH(CF_3)^+$ with trifluoroethanol, methanol, and acetate (likewise calculated from product rate constant ratios k_{az}/k_{Nu} and a diffusional value for k_{az}) and comparable rate constants for the reactions of $XArCH(CH_3)^+$, taken from past work.[6,26]

The diffusion-limited value for k_{az} is an upper limit for the capture of $4\text{-}N(CH_3)_2ArCH(CF_3)^+$, because it is not certain that k_{az} has reached this limit,[35] and a lower limit for the capture of $4\text{-}CH_3ArCHCF_3)^+$, because azide anion probably reacts with this carbocation by both a trapping and a stepwise-preassociation mechanism; i.e., the observed rate constant k_{az} may be the sum of the net rate constants for the two reaction pathways.[26,36] Therefore, the assumption that k_{az} is diffusion limited gives upper and lower limits, respectively, for the rate constants for the reactions of $4\text{-}N(CH_3)_2ArCH(CF_3)^+$ and $4\text{-}CH_3ArCH(CF_3)^+$ (Table IV).

The data in Table IV shows that the kinetic reactivity of $XArCH(CF_3)^+$ with a solvent of 50:50 (v/v) water/trifluoroethanol is nearly the same as the reactivity of comparably ring-substituted $XArCH(CH_3)^+$. That is, the large thermodynamic destabilizing effect of the α-CF_3 substituent is not expressed in the rate constant for $XArCH(CF_3)^+$ capture by solvent.

Similar results are also obtained for the reaction of the charged nucleophile acetate. The rate constants k_{AcO} do not change greatly upon substitution of an α-CF_3 group at $4\text{-}OCH_3ArCH(CH_3)^+$ or $4\text{-}SCH_3ArCH(CH_3)^+$ (Table IV). The k_{AcO} values for the acetate ion reactions are very large and it is possible that the full chemical reactivity of acetate with $XArCH(CF_3)^+$ is not expressed, because the reactions are limited by the rate of encounter-complex formation. The following evidence argues against this and for the proposal that k_{AcO} for acetate capture of $4\text{-}OCH_3ArCH(CF_3)^+$ and $4\text{-}SCH_3ArCH(CF_3)^+$ is limited by the rate of chemical bond formation.

1. When k_{AcO} is limited by the rate of encounter-complex formation, then it takes a constant value that is independent of carbocation reactivity. However, the change from a $4\text{-}OCH_3$ to a $4\text{-}SCH_3$ substituent for $XArCHCF_3^+$ leads to an increase in both k_s (4-fold) and k_{AcO} (2.5-fold, Table IV).

2. Acetate capture of $XArCH(CF_3)^+$ is slower than expected for a simple encounter-limited reaction. The observed k_{AcO} values are up to 8-fold smaller than $5 \times 10^8\ M^{-1}\ s^{-1}$, the previously estimated rate constant for the encounter-limited capture of $XArCH(CH_3)^+$ by acetate.[26]

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(28) Footnote number 58 in ref 4a.

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(34) Footnote 45 in ref 6. A value of $7 \times 10^9\ M^{-1}\ s^{-1}$ has been directly measured for the diffusion-limited reaction of azide with ring-substituted benzhydryl carbocations in mixed water/acetonitrile solvents (R. A. McClelland, submitted for publication).

(35) The observed azide selectivity for the reaction of $4\text{-}N(CH_3)_2ArCH(CF_3)^+$, $k_{az}/k_s = 6 \times 10^6\ M^{-1}$, is close to the values observed for activation-limited reaction of azide with substituted triarylmethyl carbocations.[31] Therefore, any value of k_{az} which is below the diffusion limit or which has just reached the limit is consistent with the observed selectivity.

(36) The observed azide selectivity k_{az}/k_s for the reaction of $CH_3ArCH(CF_3)^+$ is larger than the value for the simple diffusion-limited azide reaction, because of the additional azide adduct formed without diffusion by the reaction of azide present in a preassociation complex with substrate at the time of substrate ionization. Therefore, the k_s value calculated by multiplying k_{az}/k_s times a diffusion-limited value for k_{az} is only a lower limit. A better estimate of $1 \times 10^{10}\ s^{-1}$ for k_s is obtained from eq 11, with the experimental product ratio, $[ROH]/[RN_3]$, $K_{as} = 0.32\ M^{-1} = k_d/k_{-d}$,[25a] and a rate constant of $5 \times 10^9\ M^{-1}\ s^{-1}$ for k_d.[26]

$$k_s = [ROH]K_{as}[N_3^-](k_s + k_{-d})/[RN_3] \qquad (11)$$

The selectivities $k_{\mathrm{MeOH}}/k_{\mathrm{TFE}}$ and $k_{\mathrm{HOH}}/k_{\mathrm{TFE}}$ for addition to comparably ring-substituted $\mathrm{XArCH(CH_3)^+}$ and $\mathrm{XArCH(CF_3)^+}$ (Table III) are significantly larger for the reaction of the thermodynamically more unstable carbocations $\mathrm{XArCH(CF_3)^+}$.[26] This result is contrary to the predictions of simple theory. It will be dealt with in a more extensive report of structure–reactivity effects on the rate constants for nucleophile capture of $\mathrm{XArCH(CF_3)^+}$.

The Hammett correlations for the relatively limited set of log $(k_{\mathrm{az}}/k_{\mathrm{s}})$ (Figure 5) or log $(k_{\mathrm{az}}/k_{\mathrm{HOH}})$ values (calculated from the data in Table III, Figure not shown) give identical ρ^+ values of -4.8 (correlation coefficients = 0.98). This corresponds to $\rho^+{}_{\mathrm{w}} = \rho^+{}_{\mathrm{s}} = 4.8$ for k_{HOH} and k_{s}, because $\rho^+{}_{\mathrm{az}} = 0$ for the diffusion-limited reaction of azide. The value of 4.8 for $\rho^+{}_{\mathrm{s}}$ is a lower limit, because of the limiting nature of the k_{s} values estimated for the reactions of $\mathrm{4\text{-}N(CH_3)_2ArCH(CF_3)^+}$ (upper limit) and $\mathrm{4\text{-}CH_3ArCH(CF_3)^+}$ (lower limit).

The large ρ^+ values for $\mathrm{XArCH(CF_3)^+}$ reaction show qualitatively that there is a marked difference between the structure of the ground state for $\mathrm{XArCH(CF_3)^+}$ and the transition state for the solvent-addition reaction. A more quantitative description of the transition state for this reaction is provided by the normalized reaction constant (ρ_{nor}), which expresses the substituent effects on k_{HOH} as a fraction of the total effect on K_{eq} $(\rho^+{}_{\mathrm{w}}/\rho^+{}_{\mathrm{eq}})$, where $\rho^+{}_{\mathrm{eq}} = \rho^+{}_{\mathrm{w}} - \rho^+{}_{\mathrm{H}}$ for eq 8.

$$\mathrm{H_2O + XArCH(CF_3)^+} \underset{k_{\mathrm{H}}}{\overset{k_{\mathrm{HOH}}}{\rightleftharpoons}} \mathrm{XArCH(CF_3)OH + H^+} \qquad (8)$$

The acid-catalyzed conversion of $\mathrm{XArCH(CF_3)OH}$ to $\mathrm{XArCH(CF_3)^+}$ was very slow and $\rho^+{}_{\mathrm{H}}$ was not measured. The value for this reaction is estimated, crudely, to be 0.8 unit less negative than the value of $\rho^+ = -9.7$ for the ionization of $\mathrm{XArCH(CF_3)Tos}$,[37] giving $\rho^+{}_{\mathrm{eq}} = (\rho^+{}_{\mathrm{w}} - \rho^+{}_{\mathrm{H}}) = (4.8 - (-8.9)) = 13.7$ and $\rho^+{}_{\mathrm{nor}} = \rho^+{}_{\mathrm{w}}/\rho^+{}_{\mathrm{eq}} = 0.35$. The values for $\rho^+{}_{\mathrm{eq}}$ and $\rho^+{}_{\mathrm{nor}}$ are lower limits, because they are calculated with a lower limit for $\rho^+{}_{\mathrm{w}}$. These values show that the effect of ring substituents on k_{HOH} is at least 35% of the effect on the equilibrium constant for full bond formation at C-α. The observation that a substantial fraction of the total substituent effect is observed at the transition state for k_{HOH} requires that there be marked progress toward bond formation between water and $\mathrm{XArCH(CF_3)^+}$ at this transition state.

The Hammett constants for $\mathrm{XArCH(CH_3)^+}$ reaction are $\rho^+{}_{\mathrm{w}} = \rho^+{}_{\mathrm{s}} = 4.5$ and $\rho^+{}_{\mathrm{nor}} = 0.53$.[6] The $\rho^+{}_{\mathrm{w}}$ and $\rho^+{}_{\mathrm{s}}$ values are similar to and $\rho^+{}_{\mathrm{nor}}$ somewhat larger than the lower limits set for $\mathrm{XArCH(CF_3)^+}$ reaction. There are insufficient data for a separation of the resonance and inductive contributions to $\rho^+{}_{\mathrm{nor}}$ for the reaction of $\mathrm{XArCH(CF_3)^+}$, as was previously accomplished for the reaction of water with $\mathrm{XArCH(CH_3)^+}$.[6]

The data allows a rough estimate of the α-$\mathrm{CF_3}$ substituent effect on the equilibrium constant for carbocation formation from an acetate ester (eq 9). The effect of an α-$\mathrm{CF_3}$ group on K_{eq} =

$$\mathrm{XArCH(R)OAc} \underset{k_{\mathrm{AcO}}}{\overset{k_{\mathrm{solv}}}{\rightleftharpoons}} \mathrm{XArCH(R)^+ + AcO^-} \qquad (9)$$

$k_{\mathrm{solv}}/k_{\mathrm{AcO}}$ is the effect on k_{solv} times the reciprocal of the effect on k_{AcO}. The ratio of k_{AcO} values for the reaction of comparably ring substituted $\mathrm{XArCH(CH_3)^+}$ and $\mathrm{XArCH(CF_3)^+}$ is close to one (Table IV). Therefore, the entire substituent effect on K_{eq} is expressed as the effect on k_{solv}. There is no data for the solvolysis of $\mathrm{XArCH(CF_3)OAc}$, but the substituent effect on k_{solv} can be estimated from data for the solvolysis of $\mathrm{XArCH(R)Cl}$, with the assumption that the α-$\mathrm{CF_3}$ group has the same effect on the rate constants for the solvolysis of $\mathrm{XArCH(CF_3)OAc}$. The α-$\mathrm{CF_3}$ effect on k_{solv} for the reaction of $\mathrm{4\text{-}OCH_3ArCH(CH_3)Cl}$ is $\sim 4 \times 10^5$.[38] The α-$\mathrm{CF_3}$ substituent effect on k_{solv} for other $\mathrm{XArCH(CH_3)Cl}$, calculated from the ratio for the reaction of $\mathrm{4\text{-}OCH_3ArCH(R)Cl}$ and assuming a 4-unit difference in the ρ^+ values for $\mathrm{XArCH(CH_3)Cl}$ and $\mathrm{XArCH(CF_3)Cl}$,[39] are $\sim 10^7$-fold for $\mathrm{CH_3ArCH(CH_3)Cl}$ and $\sim 10^9$-fold for $\mathrm{HArCH(CH_3)Cl}$. Similarly, the α-$\mathrm{CF_3}$ substituent effects on K_{eq} range from ($\sim 4 \times 10^5$)-fold for the formation of $\mathrm{4\text{-}OCH_3ArCH(R)^+}$ to $\sim 10^9$-fold for the formation of $\mathrm{HArCH(R)^+}$. When expressed as Gibb's free energy, the effect of the α-$\mathrm{CF_3}$ for α-$\mathrm{CH_3}$ substitution at $\mathrm{XArCH(CH_3)^+}$ corresponds to an 8–12 kcal/mol (depending on X) destabilization of the carbocation, relative to the neutral acetate ester.

The Complex Nature of the α-$\mathrm{CF_3}$ Substituent Effect on Benzyl Carbocation Reactivity. In this section the following dichotomy in the data in Table IV will be addressed. *Changing the stability of $\mathrm{XArCH(CH_3)^+}$ by varying the ring substituent X gives large changes in k_{s} and k_{AcO} for carbocation capture, but no change in these rate constants is observed as the stability of the carbocation is decreased 8–12 kcal/mol relative to a neutral reactant by changing the substituent at C-α to a $\mathrm{CF_3}$ group.*

These data cannot be explained by an early transition state for carbocation capture in which there is essentially no bond formation between nucleophile and carbon. Estimates from logarithmic rate–equilibrium relationships of the fractional progress of the transition states for $\mathrm{S_N1}$ solvolysis reactions toward the carbocation intermediate vary greatly (0.47–0.89),[40] but the value of 1.0 required to explain the α-$\mathrm{CF_3}$ substituent effect on the reactivity of $\mathrm{XArCH(CH_3)^+}$ is without precedent. Furthermore, the sensitivity of k_{s} and k_{AcO} to changes in the ring substituent X (Table IV) is direct evidence for bonding between nucleophiles and C-α in the transition state for the reactions of $\mathrm{XArCH(R)^+}$.

Since the transition state for the capture of $\mathrm{XArCH(R)^+}$ by nucleophiles is normal and shows significant carbon–nucleophile bonding, the destabilizing charge–dipole interactions between C-α and the α-$\mathrm{CF_3}$ substituent will be relieved as this transition state is approached from $\mathrm{XArCH(CF_3)^+}$. This will tend to increase the reactivity of $\mathrm{XArCH(CF_3)^+}$ relative to $\mathrm{XArCH(CH_3)^+}$ by an inductive effect. The failure to observe the predicted reactivity increase shows that the α-$\mathrm{CF_3}$ inductive effect is masked by an opposing effect which stabilizes the carbocation to nucleophilic addition. There are several effects which might act to stabilize $\mathrm{XArCH(CF_3)^+}$ to capture by solvent and added nucleophiles.

Resonance. The rate constants for nucleophile capture of $\mathrm{XArCH(R)^+}$ (eq 9 or 10) may be fit to the 4-parameter eq 10, which separates the α-$\mathrm{CF_3}$ substituent effect on the reaction equilibrium constants into resonance and inductive terms [log $(K/K_0)_{\mathrm{I}}$ and log $(K/K_0)_{\mathrm{R}}$, respectively] and assigns individual weights to the fractional expression of these effects in the reaction transition state ($\rho^{\mathrm{I}}{}_{\mathrm{nor}}$ and $\rho^{\mathrm{R}}{}_{\mathrm{nor}}$).[6,41]

$$\log (k/k_0)_{\mathrm{Nu}} = \rho^{\mathrm{I}}{}_{\mathrm{nor}} \log (K/K_0)_{\mathrm{I}} + \rho^{\mathrm{R}}{}_{\mathrm{nor}} \log (K/K_0)_{\mathrm{R}} \qquad (10)$$

There is little or no observed α-$\mathrm{CF_3}$ substituent effect on the rate constants for the solvent and acetate reactions [log $(k/k_0)_{\mathrm{Nu}} \cong 0$, Table IV]. This result is consistent with offsetting inductive-destabilizing and resonance-stabilizing terms in eq 10 [log $(K/K_0)_{\mathrm{R}}$ and log$(K/K_0)_{\mathrm{I}}$ have opposite signs]. However, since the α-$\mathrm{CF_3}$ substituent destabilizes $\mathrm{ArCH(CH_3)^+}$ relative to a neutral derivative, the magnitude of $(K/K_0)_{\mathrm{R}}$ must be smaller than that of $(K/K_0)_{\mathrm{I}}$. In order for the two effects to cancel in $(k/k_0)_{\mathrm{Nu}}$, there must be a marked imbalance in the extent of their expression in the transition state such that the fractional loss of the resonance interactions exceeds that of the inductive interactions ($\rho^{\mathrm{R}}{}_{\mathrm{nor}} > \rho^{\mathrm{I}}{}_{\mathrm{nor}}$, eq 10).

An analysis of the effects of para-resonance-electron-donating substituents and meta-inductive-electron-withdrawing substituents

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[37] The value of 0.8 is an average for the difference in the ρ^+ values for carbocation formation by the specific-acid-catalyzed reactions of ring-substituted 1-phenylethanols (-4.5)[6] and by the solvolysis reactions of ring-substituted 1-phenylethyl chlorides.[39]

[38] Footnote 3 in ref 5a.

[39] The ρ^+ values measured for the reactions of $\mathrm{XArCH(CH_3)Cl}$ range from -5.0[43] to -5.7 (footnote 27 in ref 11a). The ρ^+ value for the reaction of $\mathrm{XArCH(CF_3)Cl}$ is assumed to be equal to the value of -9.7 obtained in this work for the reaction of $\mathrm{XArCH(CF_3)Tos}$.

[40] (a) Arnett, E. M.; Petro, C.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1979**, *101*, 522–526. (b) Arnett, E. M.; Hofelich, T. C. *J. Am. Chem. Soc.* **1983**, *105*, 2889–2895. (c) Forsyth, D. A.; Estes, M. R.; Lucas, P. *J. Org. Chem.* **1982**, *47*, 4379–4380.

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on the rate and equilibrium constants for the capture of $XArCH(CH_3)^+$ by water gives ρ^I_{nor} and ρ^R_{nor} values of 0.42 and 0.53, respectively, consistent with a marked imbalance in the loss of resonance and inductive interactions at the transition state for k_{HOH}.[6] Similar transition-state imbalances have been observed for a number of complex organic reactions and sensible rationalizations have been offered for these imbalances.[42]

If resonance stabilization of $XArCH(CF_3)^+$ is markedly greater than that of $XArCH(CH_3)^+$, then the imbalance will lead to a preferential expression of the resonance effect in the transition state for $XArCH(CF_3)^+$ capture and anomalously slow rate constants for capture. The observations listed below provide good evidence for the existence of a large, stabilizing resonance effect, which opposes the inductive destabilization of $XArCH(CF_3)^+$ by the α-CF_3 group.

1. The 4-OCH_3 ring substituent provides a ~700-fold greater resonance stabilization of the transition state for the solvolysis reaction of 1-phenyl-2,2,2-trifluoroethyl tosylate than for the solvolysis reaction of 1-phenylethyl chloride, on the basis of 4-OCH_3 substituent effects of (4×10^7)-fold[3f] and (6×10^4)-fold,[43] respectively, for the two reactions. If, as the ρ^R_{nor} value of 0.53 for $XArCH(CH_3)^+$ reaction suggests, only 50% of the total resonance stabilization is observed in the transition state for carbocation formation,[6] then the equilibrium resonance stabilization of 4-$HArCH(CF_3)^+$ by a 4-OCH_3 substituent will be 700^2 = (5×10^5)-fold (8 kcal/mol) greater than for 4-$HArCH(CH_3)^+$.

2. The α-CF_3 for α-CH_3 substitution is estimated above to cause only ~8 kcal/mol equilibrium destabilization of 4-$OCH_3ArCH(CH_3)^+$ relative to a neutral adduct. This is much smaller than the ~50 kcal/mol α-CF_3 destabilization of $CH_3CH_2^+$ in the gas phase,[28] but it is similar to the destabilization by a β-CF_3 group of $CH_3CH_2NH_3^+$ (in water) where,[44] relative to 4-$OCH_3ArCH(CF_3)^+$, the formal positive charge is separated by an additional atom from the CF_3 group and is diminished by hydrogen bonding to solvent. The massive attenuation at 4-$OCH_3ArCH(CF_3)^+$ of the α-CF_3 inductive effect is strong evidence for extensive charge delocalization away from the CF_3 group and onto the 4-methoxyphenyl ring.

3. There is a 10^{11}-fold decrease in k_{solv} upon substitution of one α-CF_3 group at $PhC(CH_3)_2Tos$, but only a 10^7-fold further decrease upon substitution of a second α-CF_3 group. These data show that the destabilizing charge–dipole interaction between C-α and the CF_3 substituent decreases when the second substituent at C-α is changed from a CH_3 to a CF_3 group. The trend is consistent with charge movement into the ring upon substitution of the first CF_3 group; this increases the separation between the charge and C-α, thereby decreasing the destabilizing electrostatic interaction between the charge and a second α-CF_3 group. The reactivity of $PhC(CF_3)_2Tos$ might also be increased by transition state release of ground-state strain. However, there is nothing in the bond lengths and bond angles of $Ph(CF_3)_2Tos$ to suggest that the ground-state conformation is strained.[31]

4. Nucleophilic aromatic substitution reactions at the C-4 ring position become increasingly important as more α-CF_3 groups are added to 4-$OCH_3ArCHR_1R_2^+$. Solvent adds exclusively to C-α of 4-$OCH_3ArCH(CF_3)^+$; however, the reaction of $HN(CH_3)_2$ gives low yields of the C-4 adduct 4-$N(CH_3)_2ArCH(CF_3)N(CH_3)_2$.[45] The ring addition reaction is still more pronounced in the ethanolysis of 4-$OCH_3Ar(CF_3)_2Tos$, which gives a 50:50 ratio of 4-$OCH_3Ar(CF_3)_2OCH_2CH_3$ and 4-$CH_3CH_2OArC(CF_3)_2OCH_2CH_3$.[3g] The progressive increase in C-4 electrophilic reactivity with increasing α-CF_3 substituents is direct evidence that these substituents act to move the positive charge away from C-α and onto the aromatic ring.

5. There is good evidence that a 4-SCH_3 group stabilizes, by resonance, a positive charge at C-α more effectively than a 4-OCH_3 group.[46] Therefore, changes in the ratio k_{SMe}/k_{OMe} for solvent addition to $XArCH(R)^+$ are indicative of changing differences between the resonance stabilization of the ground and transition state for carbocation capture. The k_{SMe}/k_{OMe} ratio is one for solvent addition to $XArCH(CH_3)^+$ and four for solvent addition to $XArCH(CF_3)^+$ (this is an unusually large ratio; note in Figure 5 the deviation of log (k_{az}/k_s) for 4-$SCH_3ArCH(CF_3)^+$). The increase in the ratio suggests that the difference between 4-SCH_3 and 4-OCH_3 resonance stabilization of $XArCH(CF_3)^+$ is larger than the difference for $XArCH(CH_3)^+$ and is simply explained by a greater total charge delocalization at $XArCH(CF_3)^+$.

Two factors favor greater resonance charge delocalization at $XArCH(CF_3)^+$ than at $XArCH(CH_3)^+$. First, resonance delocalization from the electron-rich phenyl substituent will increase as the total number of electron-donating substituents at C-α is decreased.[47] Here, the α-CF_3 for α-CH_3 substitution leads to a net loss of electron donation to C-α[48] and a corresponding increase in the availability of the empty orbital at C-α for resonance interaction with the aromatic ring. Second, resonance electron delocalization is favored because movement of the positive charge into the ring reduces the destabilizing electrostatic interaction with the electron-withdrawing α-CF_3 substituent. A driving force for delocalization at $XArCH(CF_3)^+$ necessary to balance the increase in energy associated with the loss of aromaticity may be provided by the reduction in destabilizing charge–dipole interaction, which accompanies the greater separation of the interacting centers.

Other Effects. There is only a partial loss of destabilizing charge–CF_3 interactions upon addition of water or other neutral nucleophiles to $XArCH(CF_3)^+$ (the reaction products, e.g. $XArCH(CF_3)OH_2^+$, are also charged) and the full loss of these interactions upon addition of anionic nucleophiles to give neutral products. Therefore, the inductive α-CF_3 substituent effect on k_{Nu^-} for anionic nucleophiles should be larger than the α-CF_3 effect on k_{Nu} for neutral nucleophiles. For reasons which are unclear, the limited data in Table IV does not show this trend.

The larger steric bulk[49] and dipole moment[50] for the CF_3 than the CH_3 substituent might lead to steric and/or electrostatic repulsion between nucleophiles and the CF_3 group in the transition state for addition to $XArCH(CF_3)^+$. There is evidence that destabilizing electrostatic interactions but not steric interactions of the CF_3 group with the nucleophile and leaving group Y^- are responsible for the extreme resistance of CF_3CH_2Y to S_N2 reactions.[13] The electrostatic effect in the S_N1 case will be less severe, because the distorted tetrahedral transition state for this reaction is less congested than the trigonal-bipyramid S_N2 tran-

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[46] The difference in σ^n for the 4-OCH_3 and 4-SCH_3 substituents is (–0.13 – 0.13 = –0.26). For reactions where resonance interactions develop, the σ^+ scale is used and a much smaller difference in substituent constants (–0.79 – (–0.66) = –0.13) is observed. (Hine, J. *Structural Effects on Equilibria in Organic Chemistry*; Wiley: New York, 1975; pp 72.) The change in the differences is consistent with a more effective resonance stabilization of the positive charge by the SCH_3 group.

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[48] Computational studies show that electron donation from the CF_3 group is small compared to that of the CH_3 group. The calculated electron densities at the cationic carbon of ethyl and 2,2,2-trifluoroethyl carbocations are ~0.15 (different computational methods gave values ranging from 0.12 to 0.18; Dixon, D. A.; Eades, R. A.; Frey, R.; Gassman, P. G.; Hendewerk, M. L.; Paddon-Row, M. N.; Houk, K. N. *J. Am. Chem. Soc.* **1984**, *106*, 3885–3891) and 0.04,[27a] respectively.

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[50] The compound containing both groups, CH_3CF_3, has a dipole moment of 2.28; McClelland, A. L. *Tables of Experimental Dipole Moments*; W. H. Freeman & Co.: San Francisco, 1963.

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sition state. There are insufficient data from this work to evaluate whether or not destabilizing electrostatic interactions contribute to the low reactivity of XArCH(CF$_3$)$^+$.

The results of theoretical calculations show no stabilization of CF$_3$CH$_2$$^+$ by fluorine bridging but some stabilization by homoconjugation of the fluorine lone pair electrons with the cationic center.[27c] The latter effect may contribute to the low reactivity of XArCH(CF$_3$)$^+$.

Bimolecular Substitution Reactions. No S_N2 reactions between XArCH(CF$_3$)Y and the potent nucleophiles N_3^-, I^-, and Br^- were observed in these studies of reactants with electron-donating ring substituents. This is a further example of the extreme resistance of α-CF$_3$-substituted substrates to bimolecular substitution reactions.[13-15] The results reported here support the relationship proposed to exist between the mechanism for nucleophilic substitution at saturated carbon and the lifetimes for the real or hypothetical carbocation intermediates of these reactions.[8,10,11,51] It was previously shown that the addition of electron-withdrawing ring substituents at XArCH(CH$_3$)Y leads to a change from an S_N1 to an S_N2 substitution reaction mechanism for the addition of methanol, acetate, and azide at roughly the point where the ion-sandwich "intermediate" [Nu$^-$·XArCH(CH$_3$)$^+$·X$^-$] ceases to exist for the lifetime of even one bond vibration and is transformed from an intermediate to a transition state.[11] It has been established in the present work that this simple relationship holds for the reactions of XArCH(CF$_3$)Y, since XArCH(CH$_3$)Y and XArCH(CF$_3$)Y with the same ring substituent ($\sigma_x^+ \leq -0.32$) react by the same S_N1 mechanism through intermediates ArCH(CH$_3$)$^+$ and ArCH(CF$_3$)$^+$, respectively, with nearly the same lifetimes. It remains to be determined if there is an enforced change to a coupled-concerted mechanism for bimolecular substitution reactions at XArCH(CF$_3$)Y as the intermediate XArCH(CF$_3$)$^+$ is destabilized by electron-withdrawing ring substituents ($\sigma^+ \gg -0.32$).

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Intramolecular Generation of Oxonium Ylides from Functionalized Arylcarbenes

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Abstract: Arylcarbenes carrying alkoxyalkyl groups in the ortho position have been generated by flash pyrolysis and photolysis of appropriate tosylhydrazone sodium salts. In the gas phase and in aprotic solvents, interaction of the carbenes with the lone electron pairs of oxygen competes efficiently with insertion into C–H bonds. Both five- and six-membered cyclic oxonium ylides have been generated. The ylides **23**, **37**, **61b**, and **74** undergo 1,2 shifts of benzyl groups with ease, even if ring contraction to highly strained benzocyclobutenes is involved (**23**, **74**). The oxonium ylides **37** and **61b** strongly prefer the nonconcerted Stevens rearrangement to the [2.3] sigmatropic Sommelet rearrangement, in contrast to analogous ammonium ylides. Alkyl shifts occur to a very minor extent, if at all. Evidence is presented that alcohols intercept both the carbenes and the oxonium ylides. Protonation of the ylides leads to cyclic oxonium ions, which undergo nucleophilic cleavage of the C–O bonds. Acid-catalyzed decomposition of the appropriate diazo compounds gives rise to six-membered, but not to five-membered, cyclic oxonium ions, thus confirming the different intramolecular reactivities of arylcarbenes and benzyl cations. The efficiency of carbene interception increases with increasing acidity of the medium, suggesting nucleophilic behavior (protonation) of the arylcarbenes.

Ylides may be defined as molecules in which a positively charged heteroatom is connected to a carbon atom carrying an unshared pair of electrons. Two fundamentally different approaches to the generation of ylides exist. The ubiquitous and synthetically useful ylides of phosphorus, sulfur, and nitrogen are commonly prepared by deprotonation of the analogous onium salts. This methodology is less well applicable to oxonium salts, which strongly prefer nucleophilic displacement to deprotonation.[1] Nevertheless, Olah recently generated dimethyloxonium methylide by deprotonation and desilylation of appropriate oxonium ions.[2] The deprotonation route to oxonium ylides is believed to play an important role in the zeolite-catalyzed conversion of methanol to ethylene.[3-5]

The alternative approach to ylides involves the interaction of carbenes with the unshared electron pairs of heteroatoms.[6] The oxygen compounds that have been utilized for the intermolecular trapping of carbenes include 2-phenyl-1,3-dioxolane,[7] styrene

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