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Supplementary Material Available: Experimental details for the synthesis of **1** and **2**, computer-generated drawing of **1b**, summary of data collection and refinement, and tables of atom coordinates and thermal parameters, bond distances and angles, and hydrogen coordinates (18 pages). Ordering information is given on any current masthead page.

Surprisingly Small Effect of an α-CF_3 for α-CH_3 Substitution on 1-(4-Methoxyphenyl)ethyl Cation Reactivity[1]

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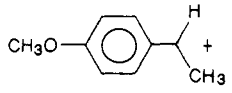
Experimental studies on the effect of the strongly electron withdrawing α-CF_3 group on carbocation stability have been restricted to documenting the large rate-retarding effect on the rate constants for solvolysis by rate-determining carbocation formation.[2,3] Little is known about the effect on the reverse reaction of carbocation with nucleophiles; however, chemical intuition suggests that a highly destabilized α-CF_3-substituted cation will be more reactive than the α-CH_3 counterpart. I wish to report that, contrary to intuition, an α-CF_3 for α-CH_3 substitution at **1** has little effect on the rate constant for the reaction



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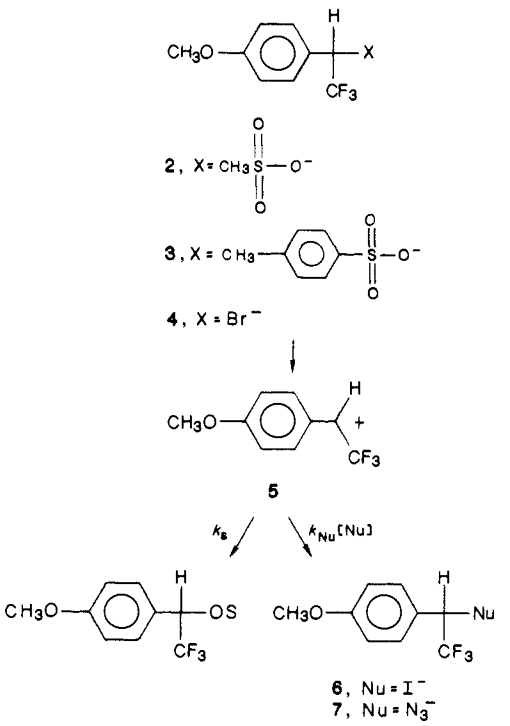
of the 1-(4-methoxyphenyl)ethyl cation with aqueous trifluoroethanol.

Scheme I



The absorbance at 290 nm is constant during the solvolysis reaction of **2**[4,5] but increases during reaction of **2** in the presence of NaI due to the formation of **6**.[5] This reaction is S_N1 because the pseudo-first-order rate constants for **6** formation change only slightly from 3.5×10^{-2} s^{-1} at low [NaI] to 3.2×10^{-2} s^{-1} at 0.5 M NaI where 98% of the product is **6**. The amount of **6** formed is proportional to $(A_f - A_0)$ where A_0 and A_f are the initial and final absorbances at 290 nm, respectively. The data obtained show a good fit to eq 1. The rate constant ratio for iodide and solvent

$$1/(A_f - A_0) = [1/(A_f - A_0)_{max}](1 + k_s/k_I[I^-]) \qquad (1)$$

reaction with **5**, $k_I/k_s = 85 \pm 6$ M^{-1}, is calculated from the slope and the intercept of a plot of $1/(A_f - A_0)$ against $1/[I^-]$. The amount of **6** (as measured by $A_f - A_0$ at 290 nm) formed at a constant NaI and **2** concentration decreases with increasing $[NaN_3]$ due to the formation of **7**. The azide reaction is also S_N1 because the pseudo-first-order rate constants for **6** formation are independent of $[N_3^-]$.[6]

The relative concentrations of the adducts formed from the reaction of **2**, **3**,[2b] and **4**[7] with nucleophiles were determined from their absorbance at 254 nm, after separation by HPLC.[8] The following nucleophilic selectivities were calculated from product concentration data:[9] $k_I/k_s = 90$ M^{-1} for the reactions of **2** and **3**; $k_{Br}/k_s = 37$ M^{-1} for the reaction of **3**; $k_{az}/k_s = 95$ M^{-1} for the reactions of **3** and **4**.

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(1) Part of this work was completed during the author's tenure as the Herchel Smith Fellow at Cambridge University. Address correspondence to the University of Kentucky.

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(3) A (4×10^5)-fold effect of the α-CF_3 substitution on k_{solv} for the reaction of 1-(4-methoxyphenyl)ethyl chloride in 50:50 water/trifluoroethanol at 25 °C is calculated from k_{solv} values of 20 and 5.6×10^{-5} s^{-1}, respectively, for reaction of the CH_3- and CF_3-substituted compounds. The former rate constant is calculated from the estimated rate constant for reaction in 80% aqueous acetone (Tsuno, Y.; Kusuyama, Y.; Sawada, M.; Fujii, T.; Yukawa, Y. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 3337), a 2.6 unit different in Y values for the two solvents and an m value of 1.0 for S_N1 solvolysis (Shiner, V. J.; Dowd, W.; Fisher, R. D.; Hartshorn, S. R.; Kessick, M. A.; Milakofsky, L.; Rapp, M. W. *J. Am. Chem. Soc.* **1969**, *91*, 4838. Fainberg, A. H.; Winstein, S. *J. Am. Chem. Soc.* **1956**, *78*, 2770), and the latter value from the rate constant reported here for reaction of **4** and an average k_{Br}/k_{Cl} ratio of 11 for the reaction of ring-substituted 1-phenylethyl bromides and chlorides (Richard, J. P.; Jencks, W. P. *J. Am. Chem. Soc.* **1984**, *106*, 1383).

(4) The reactions reported here were at 25 °C in 50:50 (v/v) water/trifluoroethanol and at constant ionic strength of 0.5 ($NaClO_4$).

(5) The mesylate was synthesized by adaptation of the published method for preparation of the tosylate.[2b] The compound was isolated as a highly reactive oil which contained variable small (<10%) amounts of unreacted 1-(4-methoxyphenyl)-2,2,2-trifluoroethanol. The compound showed the expected ^1H NMR spectrum in $CDCl_3$ with a $CHCF_3$ quartet at 5.77 ppm. Compound **6** was isolated by extraction from a solvolysis reaction mixture containing **2** and 0.5 M I^- into ether. The ^1H NMR spectrum in $CDCl_3$ showed a $CHCF_3$ quartet with a chemical shift of 5.34 ppm.

(6) Note that the pseudo-first-order rate constants for **6** and **7** formation and **2** disappearance must all be the same. Jencks, W. P. *Catalysis in Chemistry and Enzymology*; McGraw Hill: New York, 1969; p 571.

(7) Compound **4** was synthesized by bromination of the precursor alcohol with PBr_3[2d] and purified by vacuum distillation. The NMR, IR, and elemental analysis are in agreement with the chemical structure.

(8) Aliquots (50–200 μL) from the reaction mixture (~0.1 mM substrate) were analyzed as described previously.[12]

(9) Nucleophilic selectivities, k_{Nu}/k_s, were calculated from the slope and the intercept of a plot of $1/[area]_{RNu}$ against $1/[Nu]$, where $[area]_{RNu}$ is the integrated area of the HPLC peak for the nucleophilic adduct.

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There is a strong bromide common-ion effect on the reaction of **4**;[10] the pseudo-first-order rate constants for the disappearance of **4** decrease from $k_{solv} = 6.2 \times 10^{-4}$ s^{-1} at zero NaBr to $k_{obsd} = 1.3 \times 10^{-4}$ s^{-1} at 0.083 M NaBr. The addition of 0.083 M NaN_3 or NaCl has no effect on k_{obsd}. A plot of k_{solv}/k_{obsd} against [NaBr] is linear with a slope $k_{Br}/k_s = 38$ M^{-1}.

These results show that 1-(4-methoxyphenyl)-2,2,2-trifluoroethyl derivatives react by an S_N1 mechanism (Scheme I) through a common carbocation intermediate which shows an appreciable selectivity in its reaction with strong nucleophiles and solvent. The azide selectivity $k_{az}/k_s = 95$ M^{-1} for the reaction of **5** is not significantly different than the value of 105 M^{-1} for **1** capture.[11,12] The k_{az} values for the reactions of **1** and **5** must also be similar, since k_{az} for **1** is diffusion-limited and insensitive to further increases in cation reactivity.[11,12] A value of 5×10^7 s^{-1} for both **1** and **5** reaction with solvent can be calculated from the experimental k_{az}/k_s values and an estimated diffusional rate constant of 5×10^9 M^{-1} s^{-1} for k_{az}.[13] Since **1** and **5** show the same reactivity with solvent, it is concluded that the decreased equilibrium stability of **5** compared to **1** is essentially entirely expressed as the difference in the rate constants for the formation of **5** and **1** by S_N1 solvolysis of precursors with the same leaving group.[3]

The absence of an α-CF_3 substituent effect on k_s is surprising, since in a number of other systems carbocation reactivity has been observed to increase substantially with decreasing stability.[12,14] There are at least two explanations for the small substituent effect on k_s.

(1) The transition state for the reaction of **1** and **5** with solvent is very early. This is unlikely because structure-reactivity studies on the reactions of ring-substituted 1-phenylethyl carbocations show that there is significant bonding between the hydroxylic solvent and the α-carbon in the transition state for solvent addition.[12]

(2) A more likely explanation is that the inductive-destabilizing effect of the α-CF_3 group is partially offset by greater 4-methoxyphenyl stabilization of **5**,[15] and the transition state for cation reaction is unbalanced with respect to the fractional change in ground-state inductive and resonance interactions. The change in k_s is given by eq 2,[16] where $(K/K_o)_I$ is the large equilibrium

$$\log (k/k_o)_s = p_I^n \log (K/K_o)_I + p_R^n \log (K/K_o)_R \qquad (2)$$

inductive effect of the α-CF_3 group, $(K/K_o)_R$ is a measure of the extent to which inductive destabilization is offset by increased resonance delocalization into the 4-methoxyphenyl ring, and p_I^n and p_R^n are the fractional expression of these effects in the reaction transition state. If the transition state is unbalanced ($p_R^n > p_I^n$), then the magnitude of the opposing resonance and inductive effects may be equal, and k_s unchanged.

The results reported here should be added to a diverse list of novel structure-reactivity effects that can be explained by a transition-state imbalance in the progression of two processes.[12,17] Taken as a whole, these novel effects provide good evidence that imperfect transition-state synchronization[17b] often plays an important role in determining the effect of changing reactant structure on reactivity.

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[10] The reaction of **4** was followed by monitoring the decrease in A_{290}.

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[13] Reference 12, footnote 45.

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[15] The observation that a resonance-electron-donating 4-methoxy ring substituent causes a (4×10^7)-fold increase in k_{solv} for 1-phenyltrifluoroethyl tosylate reaction,[2b] but only a (6×10^4)-fold increase in k_{solv} for 1-phenylethyl chloride[3] is good evidence that cation stabilization by resonance is greater in the 1-phenyltrifluoroethyl system.

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Direct Observation of *o*-Xylylene (*o*-Quinodimethane) in Solution. Dimerization Kinetics of Some *o*-Quinodimethanes[1]

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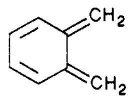
o-Xylylene (**1**), also called *o*-quinodimethane (*o*-QDM), is a reactive molecule that has been extensively studied, both theoretically[2,3] and experimentally.[3,4] Although **1** is very reactive, some direct evident for its existence has been reported. It has been observed directly by UV-visible spectroscopy both in solution[5] and in a low-temperature matrix[3,6] and by IR, Raman, fluorescence, and fluorescence excitation spectroscopy in a low-temperature matrix.[6] The UV-photoelectron spectrum of **1** in the gas phase has also been published.[7] The reported observation of **1** in solution involved the generation of **1** by flash photolysis.[5] Recently, the generation of *o*-QDM's based on the fluoride ion induced 1,4-elimination from [*o*-[α-(trimethylsilyl)alkyl]-benzyl]trimethylammonium halides was reported.[4,8] We now wish to report that we have found this reaction to be very fast, and it provides a simple and efficient method for generating *o*-QDM's under conditions which allow them to be detected by UV-visible spectroscopy.



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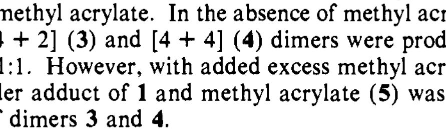
When an acetonitrile solution of [*o*-[(trimethylsilyl)methyl]-benzyl]trimethylammonium iodide (**2**) (10^{-3} M) was treated with an acetonitrile solution of tetrabutylammonium fluoride (TBAF, 10^{-1} M) at room temperature in a UV-visible cell, a species with a λ_{max} of 367 nm was produced which rapidly decayed following second-order kinetics. These observations are consistent with very rapid formation of **1**. The value of the λ_{max} of the reactive species is similar to the reported λ_{max} of **1** in a rigid glass (373 mm)[6] and in benzene (369 nm).[5] Further support for the rapid formation of **1** under the conditions used in the UV-visible spectroscopy experiments was obtained by product studies under these conditions and under conditions which differed only by the presence of an excess of methyl acrylate. In the absence of methyl acrylate, the known[9] [4 + 2] (**3**) and [4 + 4] (**4**) dimers were produced in a ratio of 11:1. However, with added excess methyl acrylate, the Diels-Alder adduct of **1** and methyl acrylate (**5**) was obtained instead of dimers **3** and **4**.



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The very rapid formation of **1** under the conditions used in the UV-visible spectroscopy experiments allows the rate of dimeri-

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[1] (a) Presented in part at the 190th National Meeting of the American Chemical Society, Chicago, IL, Sept, 1985; paper ORGN 152. (b) Based on work by J.R.M. in partial fulfillment of the requirements for the Ph.D. degree at Iowa State University.

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