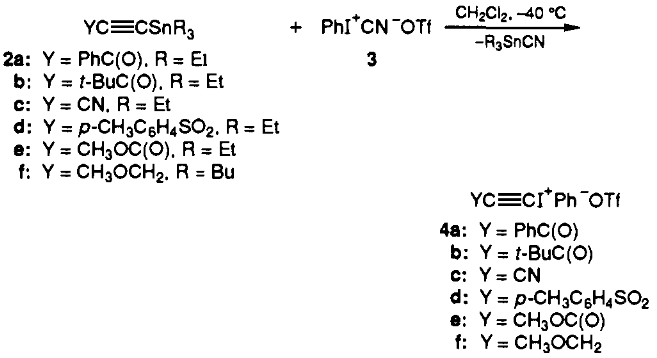
Table I. Physical and Spectral Properties of Alkynyliodonium Triflates **4**

compd	% yield	mp dec, °C	IR, cm^{-1}	^{1}H NMR, δ	^{13}C NMR, δ	^{19}F NMR, δ
4a	77	113–114	(Nujol) 3071, 3067, 2158 (C≡C), 1652 (CO), 1598, 1579, 1294, 1241, 1220, 1180, 1162, 1017	($CDCl_3$) 8.15 (d, 2 H), 8.10 (d, 2 H), 7.70 (t, 1 H), 7.63, (t, 1 H), 7.56 (t, 2 H), 7.47 (t, 2 H)	174.9 (CO), 135.5, 135.0, 134.8, 133.1, 132.7, 130.2, 129.1, 119.6 (q, *J* = 319 Hz), 116.7, 101.5 (βC), 40.6 (αC)	–78.3
4b	82	119	(Nujol) 3085, 2153 (C≡C), 1681 (CO), 1562, 1293, 1234, 1217, 1165, 1024	($CDCl_3$) 8.09 (d, 2 H), 7.67 (t, 1 H), 7.53 (t, 2 H), 1.15 (s, 9 H)	190.6 (CO), 134.5, 132.9, 132.5, 119.4 (q, *J* = 318 Hz), 116.7, 101.0 (βC), 45.2, 40.1 (αC), 25.4 (CH_3)	–77.6
4c	72	100–101	(CCl_4) 3061, 2290 (C≡N), 2149 (C≡C), 1562, 1471, 1447, 1263, 1231, 1175, 1017	(CD_3CN) 8.22 (d, 2 H), 7.78 (t, 1 H), 7.62 (t, 2 H)	136.2, 134.5, 133.5, 120.6, (q, *J* = 319 Hz), 117.8, 104.6 (βC), 75.3 (CN), 38.7 (αC)	–78.9
4d	56	117–118	(CCl_4), 3093, 3056, 2987, 2135 (C≡C), 1596, 1471, 1447, 1331 (Ts), 1313, 1265, 1232, 1207, 1161, 1084, 1020	(CD_3CN) 8.11 (d, 2 H), 7.81 (d, 2 H), 7.77 (t, 1 H), 7.58 (t, 2 H), 7.47 (d, 2 H), 2.47 (s, 3 H)	148.7, 137.0, 136.2, 134.6, 133.8, 131.5, 128.8, 118.1, 99.4 (βC), 45.3 (αC), 21.8 (CH_3)	–78.7
4e	42	48–50	(CCl_4) 3056, 2179 (C≡C), 1722 (CO), 1474, 1444, 1334, 1304, 1255, 1231, 1209, 1180, 1023	(CD_3CN) 8.20 (d, 2 H), 7.79 (t, 1 H), 7.62 (t, 2 H), 3.73 (s, 3 H)	*a*	–79.0
4f	77	72–73	(Nujol) 3091, 2190 (C≡C), 1561, 1274, 1243, 1224, 1177, 1166, 1024	($CDCl_3$) 8.05 (d, 2 H), 7.62 (t, 1 H), 7.51 (t, 2 H), 4.35 (s, 2 H), 3.35 (s, 3 H)	134.1, 132.5, 132.3, 119.6 (q, *J* = 318 Hz), 116.4, 104.8 (βC), 60.6 (CH_2), 58.4 (CH_3), 30.2 (αC)	–77.7

[a] Due to the limited solubility and low stability of **4e**, the ^{13}C NMR spectrum was unobtainable.

Scheme I



crystallized from CH_2Cl_2/pentane. The pure functionalized iodonium salts, with the exception of **4e**, are stable, white, microcrystalline solids that can be stored at room temperature for several days, whereas salt **4e** turns black at room temperature in a matter of minutes but can be stored at –20 °C for extended periods.

Alkynyliodonium salts **4a–f** were fully characterized[9] by multinuclear NMR and IR as summarized in Table I. Specifically, the infrared spectra display characteristic C≡C signals between 2135 and 2270 cm^{-1} and absorptions due to the triflate as well as the various other functional groups. The ^{1}H NMR spectra display the typical 2:1:2 aromatic resonances between 7.50 and 8.25 ppm characteristic of phenyliodonium species, as well as the appropriate signals for the remaining protons. The ^{13}C NMR spectra are particularly diagnostic of the individual β-functionalized alkynyl(phenyl)iodonium species **4** as summarized in Table I.

Preliminary results indicate that these new functionalized alkynyliodonium salts are highly reactive both toward nucleophiles and in cycloaddition reactions. Hence, we believe that these and related functionalized alkynyl(phenyl)iodonium salts, readily accessible by our newly discovered iodonium-transfer reaction, will greatly extend the already demonstrated synthetic usefulness of these tricoordinate iodine species.

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[9] With the exception of **4e**, all new compounds gave satisfactory (±0.4%) C, H, and S analyses.

Absence of Nucleophilic Assistance by Solvent and Azide Ion to the Reaction of Cumyl Derivatives: Mechanism of Nucleophilic Substitution at Tertiary Carbon

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We report the absence of nucleophilic assistance to the reaction of tertiary cumyl derivatives, $XArC(Me)_2Y$, either by azide ion, 1-propanethiol and methanol, or by a solvent of 50:50 (v/v) trifluoroethanol/water.

The role of solvent in the solvolysis of tertiary substrates has attracted wide attention,[1-9] and the importance of nucleophilic

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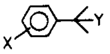
solvent assistance for reaction of *tert*-butyl derivatives has been inferred from the effects of very large changes in solvent on observed rate constants.[3c,d,4,5] The proposed assistance could represent concerted bimolecular substitution, rate-limiting reaction of solvent with a carbocation-leaving group ion pair,[3c,d,10] or nucleophilically assisted ionization to form an intermediate.[4,5,11,12] It has also been concluded that nucleophilic assistance in the solvolysis of tertiary substrates is unimportant or that it is much less important than electrostatic stabilization of the transition state by solvent molecules.[6-9] Nucleophilic assistance in the Ingold sense involves concerted displacement in one stage *without* an intermediate[13] and should lead to increases in both k_{obsd} and the yield of the nucleophile adduct.[14] However, data regarding product yields from solvolysis and nucleophilic substitution in simple tertiary systems are scarce.[14,15] It has been proposed that nucleophilic solvent assistance to *ionization* leads to formation of an "ion sandwich"[2] or "nucleophilically solvated ion pair"[4c,11,12] *intermediate*, but there are almost no data pertaining to the lifetimes of these putative intermediates in hydroxylic solvents.

We have examined nucleophilic substitution by azide ion and solvent at a series of cumyl derivatives, XArC(Me)$_2$Y, in the *single* solvent 50:50 (v/v) trifluoroethanol/water. The stability of the carbocation intermediate was varied by changing the aromatic substituent X from 4-MeO ($\sigma_x^+ = -0.79$)[16] to 3,5-bis-CF$_3$ ($\sigma_x^+ = 0.95$).[17] For all XArC(Me)$_2$Y, k_{obsd} for reaction in 50:50 (v/v) TFE/H$_2$O, at 25 °C and constant $I = 0.50$ maintained with NaClO$_4$, was independent of [N$_3^-$] in the range 0–0.50 M. Figure 1A shows that the *product* selectivity between azide ion and solvent



Y = Cl, ArCO$_2$

for reaction of XArC(Me)$_2$Y decreases sharply for $\sigma_x^+ \le -0.08$ and then levels off to a constant limiting value of $k_{az}/k_s \approx 0.75$ M^{-1} for $\sigma_x^+ \ge 0.12$. Cumyl derivatives with $\sigma_x^+ \le -0.08$ react by an S$_N$1 (or D$_N$ + A$_N$)[18] mechanism, through liberated carbocation intermediates which react with solvent (k_s) or azide ion (k_{az}[N$_3^-$]) (Scheme I). The lifetimes ($1/k_s$) of these carbocations can be estimated from the product selectivities, k_{az}/k_s (M^{-1}), and $k_{az} = 5 \times 10^9$ M^{-1} s^{-1} for the diffusion-limited reaction of N$_3^-$ with α-substituted benzyl carbocations.[19] These and the extrapolated[20] lifetimes of cumyl carbocations with $\sigma_x^+ \ge 0.12$ are given at the top of Figure 1. Very little of the limiting yield of ca. 30% azide adduct at [N$_3^-$] = 0.50 M for cumyl derivatives with electron-withdrawing substituents results from a bimolecular reaction with N$_3^-$ that is masked by a large negative specific salt effect, because 0.50 M N$_3^-$ causes ≤12% decreases in k_{obsd} for cumyl *p*-nitrobenzoates that react through diffusionally equilibrated carbocations. There is no evidence for the onset of a nucleophilically assisted process for the reaction of azide ion with XArC(Me)$_2$Y as the carbocation intermediate is destabilized. The absence of nucleophilic assistance by N$_3^-$ is not related to its negative charge or a requirement for its desolvation[3c,4c] because the product selectivity for reaction of 4-NO$_2$ArC(Me)$_2$Cl with the strong neutral nucleophile 1-propanethiol, $k_{PrSH}/k_s \approx 0.3$ M^{-1}, is no *larger* than that for N$_3^-$.[21]

Scheme I

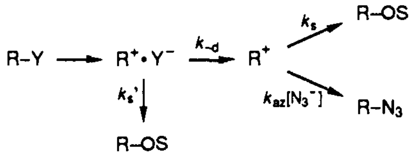


Figure 1B shows that the product selectivity for reaction of XArC(Me)$_2$Y with methanol and trifluoroethanol in a constant solvent of 5:45:50 (v/v/v) MeOH/TFE/H$_2$O, k_{MeOH}/k_{TFE}, decreases with decreasing carbocation stability and then levels off to a constant limiting selectivity of $k_{MeOH}/k_{TFE} \approx 2$ for very electron-withdrawing substituents. There is no evidence for the onset of a nucleophilically assisted solvolysis mechanism that leads to an increase in the yield of the methanol adduct when the carbocation becomes very short-lived.[22] If the strong nucleophiles azide ion, propanethiol, and methanol do not accelerate or assist the reaction of tertiary cumyl derivatives, then we conclude that the rate of these reactions should also be insensitive to variations in the total solvent nucleophilicity and that there is no assistance by the more weakly nucleophilic solvent TFE/H$_2$O.[14]

Our data also exclude nucleophilic assistance by N$_3^-$ or PrSH to *ionization* (k_{asst}, eq 1) i.e., the S$_N$2(intermediate)[4c,11,12] mechanism. This mechanism *cannot* be followed when there is no significant barrier to collapse of the intermediate "ion sandwich". The estimated[23] values of $k_{nuc} \approx 10^{19}$ s^{-1} for collapse of [N$_3^-$•3,5-bis-CF$_3$ArC(Me)$_2^+$•Cl$^-$] and $k_{nuc} \approx 10^{14}$ s^{-1} for collapse

$$\text{Nu}^-\text{•R–X} \xrightarrow{k_{asst}} \text{Nu}^-\text{•R}^+\text{•X}^- \xrightarrow{k_{nuc}} \text{R–Nu} \qquad (1)$$

of [PrSH•3,5-bis-CF$_3$ArC(Me)$_2^+$•Cl$^-$] show that these intermediates have lifetimes much shorter than the time for a single bond vibration (~10^{-13} s), so that they do not exist.[26] We conclude that the reaction of N$_3^-$ is concerted in the sense that it involves only a single step. The absence of nucleophilic assistance suggests that the transition state for this reaction resembles that of the solvolysis reaction but with azide ion present as a *spectator*.[26] The changes in bonding of the nucleophile and the leaving group to the benzylic carbon, which are normally coupled in a concerted reaction, have been uncoupled in the present case. Mechanisms of this type have been termed *uncoupled concerted*.[27]

Cumyl carbocations with lifetimes shorter than 10^{-10} s react with solvent before diffusional separation of the carbocation-leaving group ion pair occurs (k_s', Scheme I).[25] If this ion pair were formed reversibly, then the small limiting value of k_{MeOH}/k_{TFE}

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(20) The relationship log $k_s = 2.34[\sigma_n + 1.83(\sigma^+ - \sigma_n)] + 10.23$ was established for $\sigma_x^+ \le -0.08$. Values of σ_n were from ref 16.

(21) The origin of the ~2.5-fold higher limiting selectivity toward N$_3^-$ compared with PrSH is not clear; however, statistical correction of the value for azide ion by a factor of 2 eliminates most of the difference.

(22) There are increasing (5–30%) yields of the α-methylstyrene elimination product for $\sigma_x^+ \ge 0.34$. This will be discussed in a later paper.

(23) $k_{nuc} \approx 10^{19}$ s^{-1} for collapse of [N$_3^-$•3,5-bis-CF$_3$ArC(Me)$_2^+$•Cl$^-$] was estimated from $k_s = 3 \times 10^{12}$ s^{-1}, $k_{az}/k_{HOH} = 10^6$ M^{-1} for carbocations with a chemical barrier to capture by N$_3^-$,[24] $K_{ass} = 0.3$ M^{-1} for formation of a carbocation azide ion pair,[25] and $k_{nuc} = k_{az}/K_{ass}$. Similarly, $k_{nuc} \approx 10^{14}$ s^{-1} for collapse of [PrSH•3,5-bis-CF$_3$ArC(Me)$_2^+$•Cl$^-$] was estimated with k_{PrSH}/k_s = 30 M^{-1} for 4-MeOArCH(Me)$^+$ in 50:50 (v/v) TFE/H$_2$O.[25]

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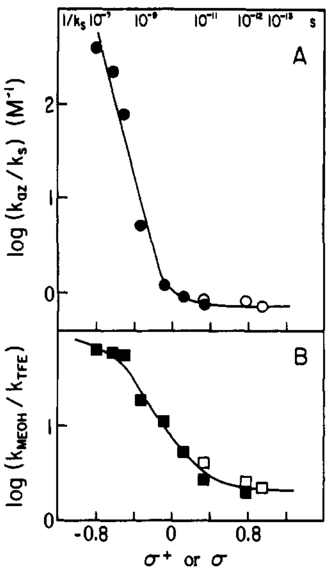

Figure 1. (A) Logarithmic plot of the product selectivity k_{az}/k_s (M^{-1}), determined by HPLC analysis, for reaction of $XArC(Me)_2Y$ in 50:50 (v/v) TFE/H_2O at 25 °C and ionic strength 0.50 ($NaClO_4$) against σ_x^+: (●), Y^- = substituted benzoate leaving groups; (○), Y^- = chloride leaving group. (B) Logarithmic plot of the product selectivity k_{MeOH}/k_{TFE}, determined by HPLC analysis, for reaction of $XArC(Me)_2Y$ in 5:45:50 (v/v/v) $MeOH/TFE/H_2O$ at 25 °C and ionic strength 0.50 ($NaClO_4$) against σ_x^+: (■), Y^- = substituted benzoate leaving groups; (□), Y^- = chloride leaving group.

≈ 2 shows that the nucleophilicity of an associated solvent molecule has little effect on the rates of internal return and reaction to give solvolysis products.

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Supplementary Material Available: Table of the effect of added azide ion on first-order rate constants for reaction of 4-methoxy- and 4-methylcumyl *p*-nitrobenzoates and 4-nitro- and 3,5-bis-(trifluoromethyl)cumyl chlorides in 50:50 (v/v) TFE/H_2O at 25 °C and ionic strength 0.50 ($NaClO_4$) (1 page). Ordering information is given on any current masthead page.

Alternating Current Susceptibility, High Field Magnetization, and Millimeter Band EPR Evidence for a Ground $S = 10$ State in $[Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4]\cdot 2CH_3COOH\cdot 4H_2O$

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Molecular magnetism is passing from the investigation of the paramagnetic properties of isolated molecules to the design and synthesis of materials exhibiting spontaneous magnetization below a critical temperature.[1] In particular clusters of increasing complexity are synthesized, and their magnetic properties have shown unusual features.[2]

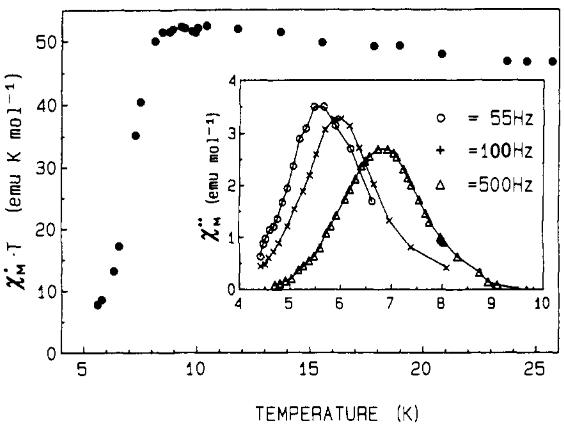

Figure 1. Temperature dependence of the real part of the magnetic susceptibility of a powdered sample of **2** in the form $\chi_M \cdot T$. In the inset is reported the imaginary part of the ac susceptibility at three frequencies.

High nuclearity spin clusters stabilize high-spin ground states. $[Mn(hfac)_2(NITPh)]_6$, which comprises[3] six manganese(II), $S = 5/2$, and six nitronyl nitroxide radicals, $S = 1/2$, has a ground $S = 12$ state, while $[Mn_{12}O_{12}(PhCOO)_{16}(H_2O)_4]$, **1**, which comprises[4] four manganese(IV) and eight manganese(III), has a ground $S = 14$ state.

$[Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4]\cdot 2CH_3COOH\cdot 4H_2O$, **2**, has a structure[5] very similar to **1**; and it is better suited to physical investigations because it has a tetragonal symmetry crystallographically imposed. Also the temperature dependence of the magnetic susceptibility of the two compounds is rather similar, but for the former no indication of the nature of the ground state has been given. Direct evidence of the nature and of the properties of the large spin ground states requires the use of several techniques, such as high field magnetization, high field EPR, and ac susceptibility measurements. The simultaneous use of these magnetic techniques provides evidence of an $S = 10$ ground state for **2** and of a magnetic behavior which resembles that of superparamagnets.

2 was prepared as previously described.[5] Single crystals are indefinitely stable, but when ground they lose 2 mol of acetic acid, as shown by elemental analysis. However the structure of the cluster is preserved, as shown by the similarity of the magnetic data of the crystals and of the powder.

Dc susceptibility measured with a Faraday susceptometer in the range 5–300 K confirmed that previously reported.[5] In order to avoid saturation and/or orientation effects associated with a strong external field, the ac susceptibility was measured in the range 4–25 K in zero applied field. For frequencies in the range 55-500 Hz, the real part of the susceptibility, χ', increases on lowering the temperature to 8 K, and the product χT, which is temperature dependent, reaches a plateau at 52.3 emu K mol^{-1} ($\mu_{eff} = 20.4\mu_b$) below 12 K, Figure 1. On lowering the temperature below 8 K, χ' decreases dramatically, while the imaginary component, χ'', becomes different from zero, reaches a maximum, and goes to zero again. The temperature at which the maximum in χ'' occurs is frequency dependent. These data indicate a frequency-dependent freezing temperature of the magnetization, analogous to that observed in superparamagnets[6] and spin glasses.[7]

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