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Hydrolysis of Aryl Orthocarbonates by General Acid Catalyzed and Spontaneous Processes. Characterization of the Water Reaction of $(ArO)_3COAr'$ and $(ArO)_3CN_3$

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Abstract: Twenty-four aryl orthocarbonates of formula $(Aro)_4C$, $(ArO)_2C(OAr')_2$, or $(ArO)_3COAr'$ have been made by coupling of the copper phenoxides with carbon disulfide, and their hydrolyses have been examined in 60% water–40% acetonitrile (I = 1.00 M, KCl) at 70.0 °C. Their hydrolysis by general acid catalyzed and, in the case of $(ArO)_3COAr'$ when Ar′ = *p*-nitrophenyl and *p*-cyanophenyl, spontaneous processes yields aryl carbonates. The initial, rate-determining event for both processes is the cleavage of the bond between the central carbon and the least basic phenoxy group: with mixed orthocarbonates of phenols differing in pK by <1 unit, parallel pathways are observed. The spontaneous reactions of $(X–C_6H_4O)_3C–O–p–C_6H_4NO_2$ and $(X–C_6H_4O)_3C–O–p–C_6H_4CN$ where the σ value of X varies from –0.23 to 0.22 are 4–10 times slower than reactions of *p*-nitrophenyl tetrahydropyrans reported in the literature and give rise to nonlinear Hammett plots. However, plots against the pK_a of $X–C_6H_4OH$ are linear, and the derived β(reaction center) values indicate substantial buildup of positive charge on the central carbon atom. A similar plot is obtained for the spontaneous reactions of five azides $(XC_6H_4O)_3CN_3$ for which common ion inhibition experiments have been performed. The derived selectivities (M^{-1}) of the tris(aryloxy)carbenium ion intermediates between azide ion and water vary from 8.5×10^3 to 6.6×10^3 as the σ value of X changes from –0.28 to 0.06. The lifetime of the tris(aryloxy)carbenium ion intermediates in water is therefore likely to be $>10^{-6}$ s. The slow formation and slow hydrolysis of tris(aryloxy)carbenium ions suggests that (in the formation direction) development of conjugative stabilization lags behind carbon–oxygen bond cleavage and (in the hydrolysis direction) precedes carbon–oxygen bond formation. The stereochemistry of tetraaryl orthocarbonates immediately suggests reasons why this should be so.

Introduction

The hydrolyses of acetals and ortho esters,[1,2] which involve mono-[3] or dioxocarbenium ions as intermediates, have received extensive mechanistic attention because of the biological importance of glycosyl transfer[4] and the bearing of these processes upon the anti-periplanar lone pair hypothesis.[5] The hydrolyses of orthocarbonates ($(RO)_4C$ and $(ArO)_4C$) have been much less studied, even though the general acid catalyzed hydrolysis of $(EtO)_4C$ played an important role in the formulation of the Brønsted catalysis law.[6] Early kinetic work had to use dilatometry to follow the reaction,[6,7] and this technique was uninformative as to whether the simple carbonate accumulated or whether it too was hydrolyzed, although one study from Cordes' lab showed by NMR that methyl carbonate did indeed accumulate during the hydrolysis of methyl orthocarbonate.[8]

More recently, aryl orthocarbonates have become available from a coupling of copper phenolates with carbon disulfide.[9] Hydrolysis of aryl orthocarbonates can give rise to a UV signal, permitting (provided the spectrum of the simple carbonate is known) an unambiguous way of following the reaction. Moreover, as we report below, coupling of CS_2 with mixtures of copper phenolates produces mixed orthocarbonates in an essentially statistical fashion: the method, whilst synthetically unesthetic, nonetheless makes mixed orthocarbonates accessible in quantities adequate for physical organic studies.

We therefore now report an extended study of the hydrolysis of aryl orthocarbonates. The work addresses three questions.

The first concerns the previously remarked[2] lesser reactivity to hydrolysis of orthocarbonates compared to orthoformates. We reasoned that, as a substituent α to a carbocationic center, oxygen should behave qualitatively like fluorine, since both elements withdraw electrons inductively and donate them conjugatively. Fluorine substitution α to a carbocationic center is known to be stabilizing in the case of simple carbocations but destabilizing if the cation already has some stability.[10] We have already presented preliminary data[11] on the general acid catalyzed reactions of tetraphenyl orthocarbonate, tetrakis(*p*-methoxyphenyl) orthocarbonate, and triphenyl orthoformate, from which we argued that the lower rate of hydrolysis of orthocarbonates arises because

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the fourth oxygen of an orthocarbonate destabilizes the rate-limiting transition state for the hydrolysis: additional stabilization of the ground state via cumulative n–σ* interactions[12] or an early transition state[13] appeared not to be important, since very large substituent effects were observed.

The second question concerns the lifetime of trioxocarbenium ions. Steenken et al.[14] used radiation chemistry to generate a series of trialkoxy carbenium ions and found (at room temperature in aqueous solution) lifetimes varying from ~0.2 to ~15 ms, depending on the pattern of alkyl substitution. The rate of reaction of $(MeO)_3C^+$ with hydroxide ion was 7×10^7 s^{-1} M^{-1}. Tris(aryloxy)carbenium ions, which would be destabilized compared to trialkoxy carbenium ions because of the electron-withdrawing effect of the aryl groups, therefore seemed suitably reactive for their lifetimes to be measured by the "Jencks clock".[3a,15] This technique is based upon the finding that carbenium ions in a certain range of reactivity react with good anionic nucleophiles (preeminently azide) at a virtually constant diffusional rate (in the case of azide at 25 °C, 5×10^9 M^{-1} s^{-1}) but undergo activated-limited reaction with the poor nucleophile water. Consequently, since the rate of reaction with water depends upon the structure of the carbenium ion and the rate of reaction with azide ion does not, systems where the "Jencks clock" can be used are characterized by a steep dependence of the selectivity of the ion upon its electronic characteristics. When this can be demonstrated, analysis of the proportions of product arising from capture of the carbenium ion by water and by azide yields the lifetime of the oxocarbenium ion directly.

The third question concerns the characterization of the transition state for general acid catalyzed hydrolysis in terms of the p*K* of the catalyzing acid, the leaving group acidity, and the electron deficiency of the trioxocarbenium ion, using the extensive set of relationships developed to treat two-dimensional free energy diagrams.[16] We have accumulated an extensive set of data which is set out in the following paper and which indicates that third-order terms are required to describe this system. This accords with the conclusion that carbon–oxygen bond cleavage and carbon–oxygen multiple-bond formation in the oxocarbenium ion moiety are not fully coupled, so that three orthogonal axes, not just two, are required for a full description of the movement of the transition state over a free energy surface.

Results and Discussion

General Features of the Hydrolyses. Aryl orthocarbonates contain at least 25 carbon atoms, so it is not possible to study their hydrolyses in purely aqueous solutions for solubility reasons. We found that adequate solubility was achieved by the addition of 40% acetonitrile. This cosolvent had the further advantage that its concentrations were small enough that water structure was still maintained.[18] Because of the inertness of these compounds, it was necessary to work at 70.0 °C. Ionic strength was maintained at 1.00 M using potassium chloride.

As anticipated, the hydrolysis of orthocarbonates is subject to general acid catalysis, as is illustrated for the hydrolysis of tetrakis(*p*-methoxyphenyl) orthocarbonate in Figure 1. The detection of general acid catalysis in aqueous–organic media can be an uncertain undertaking (because the concept of ionic strength breaks down),[19] but the comparatively large changes in rate observed, the low mole fraction of organic cosolvent (0.187), and the well-behaved variation of the buffer catalytic constant with buffer ratio together give confidence that true general acid catalysis is being observed. Additionally, only neutral monobasic acids were used in the study of the general acid catalyzed processes, so that the validity of the concept of ionic strength as $1/2\Sigma c_i z_i^2$ is not essential for the validity of our data, which requires merely that the system is indifferent to the molecular nature of an alkali metal salt of a monobasic acid. Detailed investigations of the buffer-catalyzed process are described in the following paper.

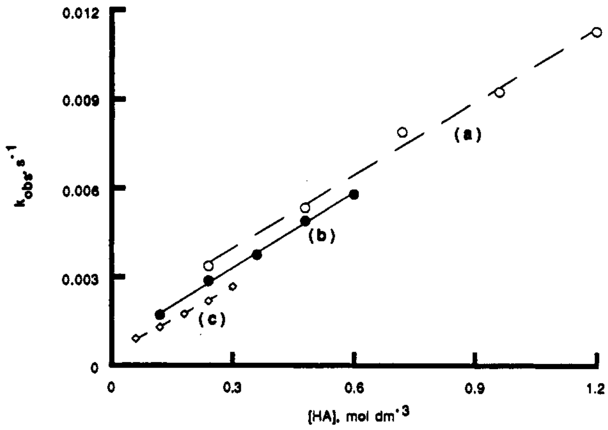

Figure 1. Variation of observed pseudo-first-order rate constants of tetrakis(*p*-methoxyphenyl) orthocarbonate in trichloroacetic acid with the concentration of acid component of the buffer at 70.0 °C in 60% aqueous buffer–40% acetonitrile, *I* = 1.0 M (KCl), at various buffer compositions: (a) $[HA]/[A^-]$ = 2:1, Gra = 0.008 26; (b) $[HA]/[A^-]$ = 1:1, Gra = 0.008 47; (c) $[HA]/[A^-]$ = 1:2, Gra = 0.0074.

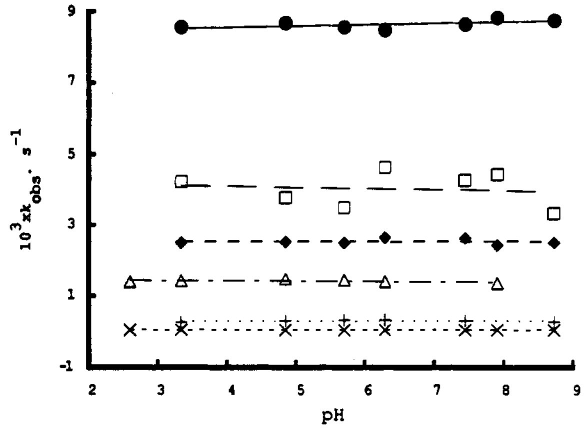

Figure 2. Variation of first-order rate constants for hydrolysis of a series of tris(substituted phenyl) *p*-nitrophenyl orthocarbonates ($(XC_6H_4O)_3CO_pC_6H_4NO_2$) as a function of pH at 70.0 °C in 60% aqueous acetonitrile, *I* = 1.0 M (KCl). The substituent X was varied: *p*-Cl, ×; *p*-F, +; H, △; *m*-Me, ◆; *p*-Me, □; 3,4-diMe, ●.

As would be anticipated from the behavior of acetal systems, a pH-independent water reaction of the tris(substituted phenyl) *p*-nitrophenyl orthocarbonates can be detected (Figure 2). This reaction, uncomplicated by a proton donation step, provides important clues to the origin of the inertness of aryl orthocarbonates.

Nature of the Products and of the Initial Reaction in the Acid-Catalyzed Process. The precedent of acetal hydrolysis[1] suggests that, in the hydrolysis of mixed orthocarbonates, the reaction will be initiated by the departure of the group derived from the most

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Table 1. First-Order Rate Constants (10^4k_{obs} in s^{-1}) for the Hydrolysis of Tris(substituted phenoxy)methyl Derivatives $(ArO)_3CX$ in 1.0 mM Sodium–DIPSO, pH (at Room Temperature) 7.5, I = 1.00 M (KCl) at 70.0 °C in 40% Aqueous Acetonitrile

substituents in Ar	leaving group (X)			
	p-$NO_2(H_2O)$	p-$NO_2(D_2O)$	p-$CN(H_2O)$	azide
p-Cl	0.50	0.376	0.011	
p-F	3.12	2.77	0.100	38.8
none	13.5	11.1	0.741	203
m-Me	26.6	21.1	1.17	320
p-Me	42.7	34.1	2.41	599
3,4-diMe	84	64.6		
p-OMe			2.97	734

acidic phenol, by virtue of electronic effects acting both on leaving group ability and on the stability of the oxocarbenium ion left behind. Electron-withdrawing groups attached to an oxocarbenium ion will destabilize it, but those attached to a leaving group will make its departure easier, since positive β_{lg} values are rarely if ever observed in acetal hydrolysis.

Our data show that the hydrolyses of mixed orthocarbonates are likewise initiated by the departure of the more acidic phenol. In the hydrolysis of $(ArO)_3COAr'$ in 1.0 M sodium dichloroacetate–1.0 M dichloroacetic acid buffer, pH 2.08, where Ar'OH is more acidic than ArOH by more than ~1 p*K* unit, mixed carbonates are not formed. It was shown in the following cases that the only detectable carbonate product was the simple one $(ArO)_2CO$: *p*-chlorophenyl tris(*p*-methoxyphenyl) orthocarbonate, *m*-cyanophenyl triphenyl orthocarbonate, *p*-cyanophenyl triphenyl orthocarbonate, *p*-nitrophenyl triphenyl orthocarbonate, *p*-cyanophenyl tris(*p*-chlorophenyl) orthocarbonate, and *p*-nitrophenyl tris(*p*-chlorophenyl) orthocarbonate. This by itself is circumstantial evidence that orthocarbonates are indeed behaving like acetals, but in strict logic it is a necessary, rather than a sufficient, condition for the reaction to be initiated by the departure of Ar'OH. It is in principle possible that the orthocarbonate first loses the *least* acidic group ArOH to give the triaryl orthocarbonate $(ArO)_2C(OAr')OH$ and that triaryl orthocarbonates decompose by different mechanisms with expulsion of the *most* acidic group to yield exclusively $(ArO)_2CO$. An experiment with the symmetrical mixed orthocarbonate $(PhO)_2C(O\text{–}p\text{-}C_6H_4CN)_2$ in dichloroacetic acid however rules this pattern of selectivities out. Loss of the least acidic phenol would give triaryl orthocarbonate $HO(PhO)C(O\text{–}p\text{-}C_6H_4CN)_2$, whence loss of the most acidic phenol would give the mixed carbonate $PhOCO(O\text{–}p\text{-}C_6H_4CN)$ exclusively. The experimental finding is however that $PhOCO(O\text{–}p\text{-}C_6H_4CN)$ and $(PhO)_2CO$ are formed in a 1:2 ratio. The most acidic phenol therefore cannot be lost exclusively from the triaryl orthocarbonate.

We therefore conclude that, in all cases where mixed orthocarbonates have been studied, the reaction is initiated by departure of the most acidic phenol, where the difference in p*K* values is greater than about 1 unit.

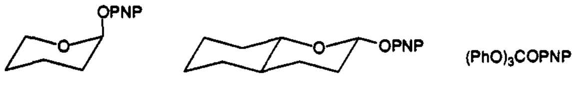
In cases in which the parent phenols of a mixed orthocarbonate are of comparable p*K*, both carbonates are formed. This was observed in the case of *p*-chlorophenyl triphenyl orthocarbonate (1:1). Hydrolyses of orthocarbonates which gave mixtures of carbonate products were not investigated kinetically.

Under all conditions used for kinetic measurements of orthocarbonates, the simple carbonates were stable. As previously noted,[17] this was not the case for the hydrolysis of phenyl orthoformate.

Spontaneous Hydrolysis of Mixed Orthocarbonates. Table 1 gives rates of pH-independent loss of *p*-nitrophenolate, *p*-cyanophenolate, and azide from various tris(aryloxy)methyl groups. The immediately noticeable feature of these reactions is that, considering they are reactions which generate a trioxocarbenium ion, they are remarkably slow. Table 2 gives the activation parameters for $(ArO)_3CO\text{-}p\text{-}C_6H_4NO_2$ and extrapolated rate constants to 39 °C. This is the temperature at which the rates can be compared to rates of liberation of *p*-nitrophenolate from *p*-nitrophenyl tetrahydropyrans reported in the literature.[20,21] The extrapolated relative rates are shown below

Table 2. Activation Parameters for the Spontaneous Hydrolyses of Tris(substituted phenoxy) *p*-Nitrophenyl Orthocarbonates $(ArO)_3C\text{–}O\text{–}p\text{-}C_6H_4NO_2$ in 1.0 mM Sodium-DIPSO, pH 7.5 (at Room Temperature), I = 1.00 M (KCl) in 40% Aqueous Acetonitrile, and First-Order Rate Constants Extrapolated to 39 °C

substituent in Ar	$\Delta H^{\ddagger}$, kJ mol^{-1}	$\Delta S^{\ddagger}$, J mol^{-1} K^{-1}	10^4k (39 °C), s^{-1}
3,4-diMe	93 ± 2	−15 ± 4	3.47_3
p-Me	96 ± 2	−10 ± 6	1.49_4
m-Me	103 ± 2	+4 ± 6	0.73_3
none	105 ± 2	+7 ± 6	0.402
p-F	110 ± 4	+7 ± 9	0.063



k_{rel}	8	3	1
	I	II	III

Therefore, if one estimates the stability of a carbocation from the relative rates of generation by departure of a common leaving group, the data lead to the conclusion that tetrahydropyranyl cations are marginally more stable than tris(aryloxy)carbenium ions. If however one estimates the stability of the cation by its lifetime in water then one is forced to diametrically opposite conclusions. Whereas trialkoxycarbenium ions have lifetimes of milliseconds,[14] simple methoxyalkyl cations have lifetimes of nanoseconds.[15d] Of course, the presence of aryl, rather than alkyl, groups on the oxygen atoms will destabilize the oxocarbenium ion to some extent, both by inductive and by mesomeric effects, in the sense that conjugation of the oxygen lone pairs with substituents in the aromatic ring makes them less able to stabilize a positive charge. Lifetime data on tris(aryloxy)carbenium ions are therefore desirable. It would be surprising, though if the aryl-to-alkyl substitution accounted for the whole of the effect. Lifetimes of dialkoxycarbenium ions[22] are shorter than those of trialkoxycarbenium ions,[14] yet alkyl orthocarbonates are more stable to acids than ortho esters. This paradox can be resolved in two ways: Firstly, single-bond cleavage in the reactions of orthocarbonates may be uncoupled from the development of conjugation so that there is charge imbalance in the transition state. In the reverse sense, reactions of trioxocarbenium ions are anomalously slow because conjugation is destroyed before the transition state is reached. The alternative explanation is that orthocarbonates themselves are stabilized by cumulative n–σ^* interactions of the type that are supposed to be responsible for the progressive shortening of the carbon–halogen bonds of halomethane.[12]

A distinction between these two reasons for the inertness of orthocarbonates can be made on the basis of structure–reactivity relationships in different portions of the molecule: if conjugation lags behind carbon–oxygen cleavage, then clearly reporter groups in different parts of the molecule will give different measures of the progress of the reaction.

In Figure 3, Hammett plots for the water reactions of tris(substituted phenyl) *p*-nitrophenyl orthocarbonates and tris(substituted phenyl) *p*-cyanophenyl orthocarbonates are displayed. These data allow us to use substituents in the leaving group and

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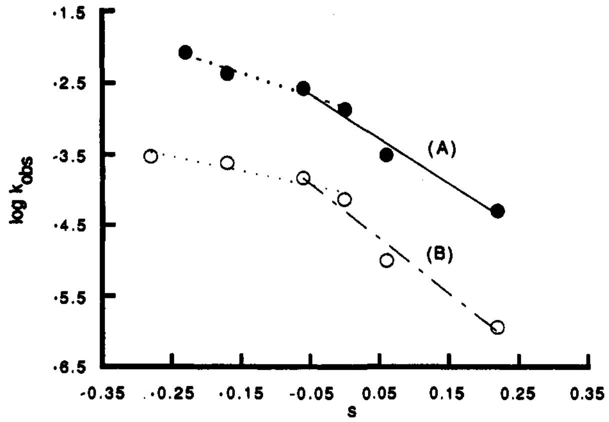


Figure 3. Hammett plots for spontaneous hydrolysis of (●) triaryl *p*-nitrophenyl and (○) triaryl *p*-cyanophenyl orthocarbonates at 70 °C in DIPSO (pH = 7.50).

substituents in the tris(aryloxy)carbenium ion as probes for the progress of the reaction.

The Hammett plots for both systems are nonlinear. The data permit either a gradual curvature or two intersecting linear portions with radically different slopes, one with $\rho \cong -2$ and the other with $\rho \cong -7$. The existence of biphasic Hammett plots could be taken as evidence for a change in rate-determining step, in this case, to a change from rate-determining ionization to rate-determining separation of the ion pair, for which there is ample precedent in acetal chemistry. The requirements for the rate-limiting diffusional separation of the ion pair are that the leaving group must be a good nucleophile and the solvent must react more slowly than diffusion occurs. The rate-determining steps for the pH-independent cleavage reactions of 2-(aryloxy)-tetrahydropyrans and benzaldehyde ethyl aryl thiol acetals have been suggested to be the diffusional separation of the ion pair.[21,23] For such a system

$$(ArO)_3C\text{-}X \underset{k_1}{\overset{k_1}{\rightleftarrows}} (ArO)_3C^+\cdot X^- \xrightarrow{k_2}$$

the observed rate is $k_1k_2/(k_{-1} + k_2)$. The information relayed by the reporter groups in the tris(aryloxy)carbenium ion is consistent with such a scheme: for stable cations, k_{-1} is low, so the observed rate constant is k_1, and there is incomplete charge development at the rate-determining transition state, hence a low value of $-\rho$. For the less stable cations, k_{-1} is high, so the observed rate constant is k_1k_2/k_{-1}, and there is full charge development at the transition state and a high value of $-\rho$. This model however is incompatible with the following observations: (1) The entropies of activation (Table 2) are (given the experimental error) roughly constant and near zero, as would be expected for a simple unimolecular heterolysis; if there is a break, it occurs at a different point in the series to the presumed break in the Hammett plot. (2) The solvent isotope effects (Table 1) are broadly constant across the whole range of compounds.

Conclusions based upon Hammett ρ values in this system should in any event be drawn with caution because the type of substituent constants which should be used in this cross-conjugated system is not obvious (σ^+ would be inappropriate because there is not conjugation between the reaction center and the substituent: the system is cross-conjugated, like the benzoate anion). In Figure 4 the spontaneous rates of $(ArO)_3C\text{-}X$ are plotted against the experimental aqueous pK_a of ArOH: the curvature seen in the plots against Hammett σ disappears, and it is clear that the spontaneous rates being studied do indeed represent only one molecular process, the cleavage of the C–X bond.

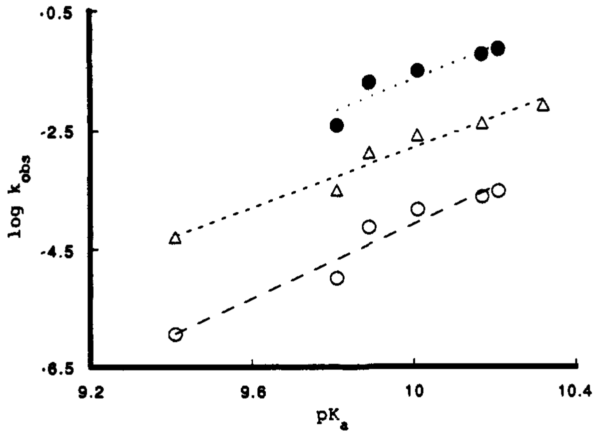


Figure 4. Plots of the spontaneous hydrolysis of $(ArO)_3C\text{–}O\text{–}p\text{-}C_6H_4NO_2$ (△), $(ArO)_3C\text{–}O\text{–}p\text{-}C_6H_4CN$ (●), and $(ArO)_3CN_3$ (○) against the pK_a of ArOH.

The least squares lines in Figure 4 are described by for azide

$$\log k_{obs} = -28.9 + 2.7\text{p}K_a$$

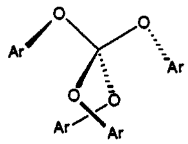
for the *p*-nitrophenyl compound

$$\log k_{obs} = -28.2 + 2.5\text{p}K_a$$

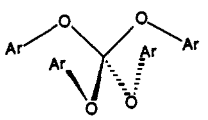
and for the *p*-cyanophenyl compound

$$\log k_{obs} = -35.5 + 3.2\text{p}K_a$$

The large gradients of these plots (which we define as β_{rc} ("rc" for "reaction center")) are far too big to have their origin in ground-state effects. An extensive study of the conformations of aryl orthocarbonates indicated that the S_4 (IV) and D_{2d} (V) conformations were of comparable energy.[24] In both these conformations each aryloxy group experiences anomeric interactions with two other oxygen atoms similar to the interaction of an axial aryloxy group in an (aryloxy)tetrahydropyran with the ring oxygen atom and one such interaction similar to that in an equatorial (aryloxy)tetrahydropyran. From studies of the conformational equilibria of (aryloxy)tetrahydropyrans, it has been estimated that the anomeric effect of a single oxygen atom on an aryloxy group decreases by 0.22 ± 0.08 kJ mol^{-1} per unit increase in pK_a of the parent phenol.[25] On the conservative assumption that the stabilizing anomeric effect experienced from two oxygen atoms is 2 times the size of that experienced from a single oxygen atom, the anomeric effect experienced by a single aryloxy group of an aryl orthocarbonate (in the S_4 or D_{2d} conformation) will decrease by 0.44 ± 0.16 kJ mol^{-1} per unit pK_a increase. Since there are three initially nondeparting aryloxy groups in an orthocarbonate, the maximum β_{rc} value expected from ground-state effects is 0.20 ± 0.07.



IV



V

If crude β_{rc} values are corrected for ground-state effects, the change in charge experienced by each individual oxygen atom of the trioxocarbenium ion moiety on ionization of an orthocarbonate

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(23) Jensen, J. L.; Jencks, W. P. *J. Am. Chem. Soc.* **1979**, *101*, 1476.

(24) Narasimhamurthy, N.; Manohar, H.; Samuelson, A.; Chandrasekhar, J. *J. Am. Chem. Soc.* **1990**, *112*, 2937.

(25) Kirby, A. J.; Williams, N. H. *J. Chem. Soc., Chem. Commun.* **1992**, 1286.

is ~0.7 of that experienced on protonation of a phenolate ion: if the correction is omitted, the charge is higher. Simple resonance theory suggests that each oxygen atom of a trioxocarbenium ion should have a real charge of 0.33. Even though the change in charge on deprotonation of a phenol will be less than a full electrical charge because of hydrogen bond donation to the anion by water and from the phenol to water, the present β_{rc} values are very difficult to reconcile with simple resonance theory and the balanced cleavage of a C–OAr bond and development of conjugation. Substituents in the aryl rings sense more charge at transition state for the generation of the trioxocarbenium ion than exists in the trioxocarbenium ion itself.

The data on the spontaneous reactions of *p*-nitrophenolates and *p*-cyanophenolates enable a β_{lg} value to be determined, admittedly on only two points but in five systems. Although, therefore, the precise value is uninformative, the fact that they are all well below −1 indicates that carbon–oxygen cleavage is essentially complete at the transition state. Large negative values of β_{lg} have been observed for pH-independent hydrolysis of 2-(aryloxy)tetrahydrofurans and 2-(aryloxy)tetrahydropyrans (−1.1 and −1.2, respectively).[21,23]

The differing β_{rc} values obtained with *p*-nitrophenolate and *p*-cyanophenolate (equivalent to a more negative β_{lg} value with the less reactive systems), if real, correspond to a slight Hammond effect (the transition state becomes more oxocarbenium ion-like as the leaving group gets worse).

Common Ion Inhibition of Tris(aryloxy)methyl Azides by Added Azide Ions. Since tris(aryloxy)methyl azides react faster than tris(aryloxy)methyl *p*-nitrophenolates (Table 1), it was not possible to study the partitioning between water and azide ion by direct product analysis, since the *p*-nitrophenolates are the most reactive orthocarbonates that we were able to prepare. Where the azides are available, the common ion inhibition technique, pioneered by Amyes and Jencks, provides a simple kinetic method of obtaining the same data.[15d] At the same time, the observation of common ion inhibition is the classic method of demonstrating the real intermediacy of a solvent-equilibrated cationic intermediate.[26] The kinetic scheme is as follows

$$\begin{aligned}&(ArO)_3C{-}N_3 \underset{k_{solv}}{\overset{k_{az}[N_3^-]}{\rightleftharpoons}}\\ &\qquad (ArO)_3C^+ + N_3^- \xrightarrow{k_{HOH}} (ArO)_3COH \xrightarrow{fast} (ArO)_2CO\end{aligned}$$

With small concentrations of substrate and large concentrations of azide, the observed rate law is

$$k_{obs} = k_{solv}k_{HOH}/(k_{HOH} + k_{az}[N_3^-])$$

Consequently, a plot of $1/k_{obs}$ against $[N_3^-]$ should be linear: from the gradient and intercept, the ratio k_{az}/k_{HOH} can be calculated.

Figure 5 shows the common ion inhibition of the hydrolysis of tris(*p*-methoxyphenoxy)methyl azide and tris(fluorophenoxy)-methyl azide by added azide ions. The data fit common ion inhibition rate expressions quite satisfactorily, indicating true common ion inhibition by added azide. Figure 6 shows the effects of other added and presumably inert salts on the k_{solv} of triphenoxymethyl azide and tris(*p*-methylphenoxy)methyl azide by potassium iodide and sodium acetate. The lack of observable added salt effect on the observed solvolytic rate constant supports the validity of common ion inhibition data. The common ion inhibition experiments were done using azide ion concentrations usually ranging from 0 to 0.25 M. But in the case of triphenoxy and tris(*p*-fluorophenoxy)methyl azides a concentration range of 0–0.01 M had to be used because azide ion appeared to react with diphenyl carbonate and bis(*p*-fluorophenyl) carbonate thereby complicating the kinetics of the reaction.

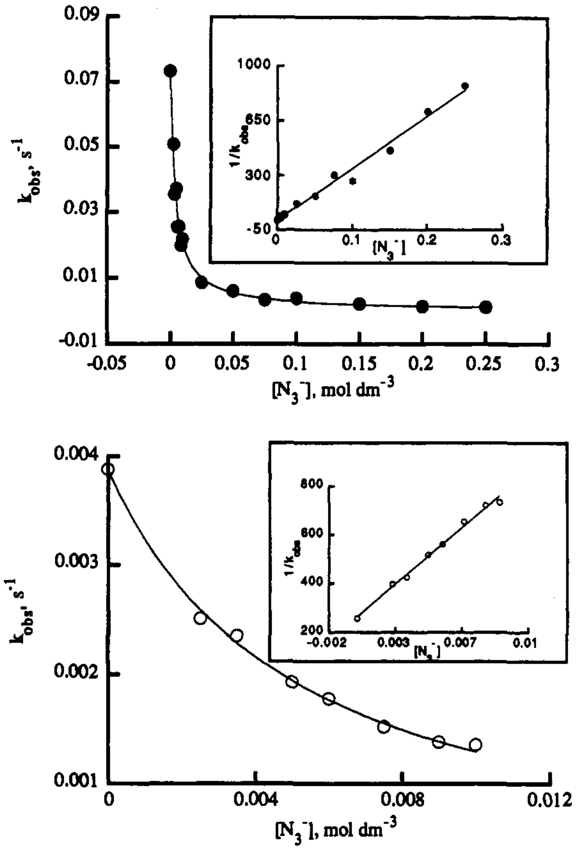

Figure 5. Common ion inhibition of the hydrolysis of (a, top) tris(*p*-methoxyphenoxy)methyl azide and (b, bottom) tris(*p*-fluorophenyl)methyl azide by added azide ions at 70 °C in 60% aqueous acetonitrile at pH 7.50.

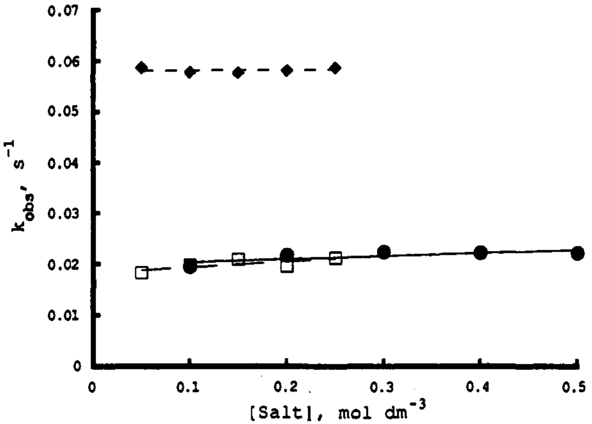

Figure 6. Added salt effects on the observed hydrolytic rate constant for triphenoxymethyl azide by sodium acetate (□) and potassium iodide (●) and for tris(*p*-methylphenoxy)methyl azide by sodium acetate (◆) at 70 °C in 60% aqueous acetonitrile at pH 7.50.

Table 3 shows molar selectivities of tris(aryloxy)carbenium ion between azide and water on the basis of common ion inhibition data and between *p*-nitrophenolate and water on the basis of product analysis experiments in which tris(aryloxy)carbenium ion was generated by the hydrolysis of tris(aryloxy)methyl azides and captured competitively by *p*-nitrophenolate and water. Systems where the "Jencks clock" can be used are usually characterized by a steep dependence of the selectivity of the ion upon its electronic characteristics, but the molar selectivities in Table 3 show only a small dependence on trioxocarbonium ion nature: Figure 7 indicates that the molar selectivities between

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[26] (a) Hughes, E.; Ingold, C. K.; Taher, N. A. *J. Chem. Soc.* **1940**, 949. (b) Church, M. G.; Hughes, E.; Ingold, C. K. *J. Chem. Soc.* **1940**, 966.

Table 3. Lifetimes and Selectivities of Tris(aryloxy)carbonium Ions (70.0 °C, 40% Aqueous Acetonitrile, 1.00 M in KCl)[a]

X	$10^{-3}k_{az}/k_{HOH}$,[a] M^{-1}	$10^{-5}k_{HOH}$,[c] s^{-1}	$10^{-2}k_{PNP}/k_{HOH}$,[b] M^{-1}
p-fluoro	6.57	7.60	6.71
none	7.46	6.70	8.23
m-methyl	7.55	6.61	11.3
p-methyl	8.83	5.65	8.01
p-methoxy	8.52	5.88	

[a] Molar selectivities of tris(aryloxy)carbonium ions of the type $(XC_6H_4O)_3C^+$ between water and (a) azide or ion (b) *p*-nitrophenolate ion, and (c) calculated k_{HOH} values by k_{az}/k_{HOH} assuming $k_{az} = 5 \times 10^9$ M^{-1} s^{-1}.

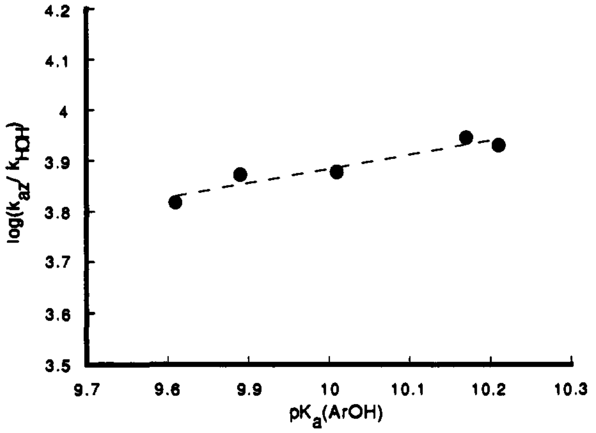


Figure 7. Dependence of molar selectivities of $(ArO)_3C^+$ between azide and water upon the p*K* of ArOH.

azide and water correlate with the pK_a of the parent phenol of the $(ArO)_3C$ moiety with a β_{rc} value of ~0.27. We nonetheless consider that the reaction with azide is diffusion-limited for the following reasons:

(1) The molar selectivities obtained for trioxocarbenium ions (~10^{-4} M^{-1}) are closer to the expected values of 10^1–10^3 M^{-1} rather than approximately 10^6 M^{-1}, which is expected for activation-limited reactions.[27]

(2) The molar selectivities between *p*-nitrophenolate, which is a poorer nucleophile than azide, and water ranged from 600 to 1000 M^{-1}. Therefore, selectivities between azide and *p*-nitrophenolate are around 10. *p*-Nitrophenolate is a poorer nucleophile than azide, so if the reaction of azide ion with trioxocarbenium ions were activation-limited, then that with *p*-nitrophenolate would be so also. The Ritchie N_+ scale is known to apply to the reactions of stable carbocations with nucleophiles. If azide and *p*-nitrophenolate reactivities followed the N_+ scale, then an azide-to-*p*-nitrophenolate selectivity of around 3000 would be observed.[28] The selectivity between azide and *p*-nitrophenolate is even compatible with diffusion-limited reaction of *p*-nitrophenolate as well as azide: Richard and Jencks noted that substituted acetate anions react with the 1-(4-methoxyphenyl)ethyl carbocation with $\beta_{nuc} = 0.13$. The selectivity decreased with increasing cation reactivity as the carboxylate ions approach limiting rate constants of ~5×10^8 M^{-1} s^{-1}. This relatively low limit is attributed to a requirement for desolvation of basic oxygen anions before reaction.[29]

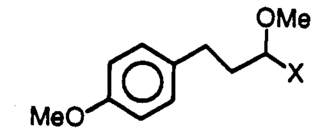
(3) There is precedent for activated rates of reaction of oxocarbenium ions with water being substantially independent of the electronic nature of the cation. Richard and Amyes have also observed selectivities of carbocations between azide and water that are independent of the electronic characteristics of the cationic fragment.[27] They have used the same common ion inhibition technique for α-substituted 4-methoxybenzyl azides and found that a 10^{14}-fold increase in rate of the generation of carbocation is accompanied only by a 2-fold decrease in rate of reaction of the carbocation (4-MeOArCH(R)^+) with the solvent (trifluoroethanol–water 50:50 v/v). This effect is attributed to much greater mesomeric stabilization in the case of the cations with inductively electron-withdrawing substituents.

(4) The rate of reaction of the triethoxycarbenium ion with water[22,30] is 27 times faster than the rate of reaction of tri-*p*-anisylcarbenium ion probably due to steric effects in tri-*p*-anisylcarbenium ion, yet the reaction of some triarylcarbenium ions with azide ion is shown to be diffusion-limited.[31]

Tris(aryloxy)carbenium ions which are destabilized by inductive effects of aryl groups appear to be reactive enough to react with azide at a diffusion-limited rate.

Table 3 also shows the calculated k_{HOH} values assuming that k_{az} is diffusion limited. The widely used value of $k_{az} = 5 \times 10^9$ M^{-1} s^{-1}, which is measured at 25 °C in pure water, has been used. McClelland showed that the diffusion-controlled rate of diaryl methyl cations with azide in water and 40% aqueous acetonitrile was the same.[31] Corrections to 70 °C for a diffusional process will be comparatively small:[31] estimates based on the variation of viscosity with temperature suggest a factor of about 2. Even if the reaction of tris(aryloxy)carbenium ions with azide is indeed activation-limited, these values are upper limits, and it is clear that tris(aryloxy)carbenium ions, like trialkoxycarbenium ions, are kinetically stable.

The contrast between the tris(aryloxy)carbenium ions, which are generated in processes that proceed at about the same rate as primary methoxyalkyl cations yet give species that are particularly long-lived, is illustrated by data for compounds **VI** below:[15d]



VI

(i) X = $O\text{–}p\text{-}C_6H_4NO_2$
(ii) X = N_3

VI(i) hydrolyses at a rate of 1.5×10^{-4} s^{-1} at 41 °C (i.e. slower than triphenoxy *p*-nitrophenoxy orthocarbonate), yet the derived oxocarbenium ion reacts with water at a rate of 2×10^{10} s^{-1}.

Origin of the Inertness of Orthocarbonates. Three explanations have been advanced in the literature for the experimentally observed inertness of orthocarbonates: an early transition state in the acid-catalyzed reaction,[13] ground-state stabilization by n–σ* interactions,[12] and the third oxygen of an oxocarbenium ion being destabilizing, in much the same way as α-fluorine.[11] Although the compounds contain a quaternary carbon, approach of a Brønsted acid to the oxygen lone pairs is not sterically hindered.

The first such explanation is clearly inapplicable to the uncatalyzed reactions, which are also slow, and will not be considered further.

Whilst it is difficult to completely rule out the second explanation on the basis of the data on the spontaneous reaction, a number of features are suggestive. Firstly, the substituent effects in the tris(aryloxy)carbenium moiety are very large. They are far too large to be ground-state effects, and yet it is difficult to reconcile them with processes giving rise to species with full

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[27] Amyes, T. L.; Richard, J. P. *J. Chem. Soc., Chem. Commun.* **1991**, 200 and references cited therein.

[28] Ritchie, C. D. *J. Am. Chem. Soc.* **1975**, *97*, 1170.

[29] Richard, J. P.; Jencks, W. P. *J. Am. Chem. Soc.* **1984**, *106*, 1373.

[30] McClelland, R. A.; Ahmad, M. *J. Am. Chem. Soc.* **1978**, *100*, 7031.

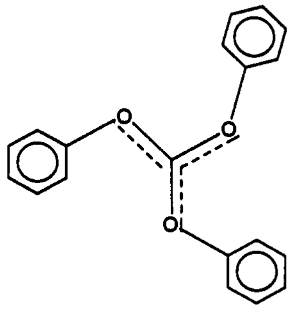
[31] McClelland, R. A.; Kanagasabapathy, V. M.; Banait, N. S.; Steenken, S. *J. Am. Chem. Soc.* **1991**, *113*, 1009.

conjunction, for which "resonance saturation" effects would attenuate mesomeric effects and distance-inductive ones.[32] Secondly, a similar pattern of inertness of $(ArO)_3C$–X is seen when X = azide, for which the anomeric effects will be different than those for aryloxy.[33] Thirdly, if cumulative n–σ^* interactions stabilize ground states, then by the same token ortho esters should be more stable than acetals, yet they are not.[2] Also the basicities of orthocarbonates which should be considerably reduced by double bond–no bond resonance do not support it. In the following paper data on the general acid catalyzed hydrolysis will be presented which require the abandonment of this explanation for the inertness of orthocarbonates or of well-established ways of thinking about transition-state structure.

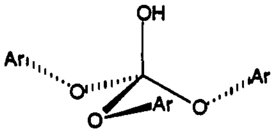
The rates of hydration of tris(aryloxy)carbenium ions which are now available (Table 3) indicate that in a thermodynamic sense tris(aryloxy)carbenium ions are stable, and therefore the idea that, in comparisons of reactions of ortho esters and orthocarbonates, the third oxygen brings about a net destabilization of the intermediate is not really tenable. The destabilization of the transition state leading to it is however incontrovertible.

All our data are compatible with the idea that, because of the necessity for stereochemical changes in the tris(aryloxy)carbenium moiety between the orthocarbonate and the ion, C–O cleavage is in advance of the development of conjugation. Formally, the system can be regarded as the cationic analog of the "nitromethane anomaly": more generally as an example of the "principle of imperfect synchronization"[35] or "transition-state imbalance".[16d] The phenomenon may be particularly marked in this system because the required stereochemical changes are so large: it is pronounced even in systems (such as the deprotonation of nitroalkanes) where all that is required is planarization of the central carbon.

There is only one reasonably stable conformation of a tris(aryloxy)carbonium ion, a planar structure with a three-fold axis of symmetry (**VII**). Other geometrical isomers about the partial C=O double bonds will experience severe steric interactions between the aryl groups, and even **VII** will experience some interaction between the ortho hydrogens and the oxygen atoms which may tilt the aryl groups slightly about the O–Ar bonds. For the tris(aryloxy)methyl moiety to attain conformation **VII** from either the S_4 or D_{2d} conformation requires major changes. In addition to a flattening of the central carbon atom, from both conformations there has to be a rotation of about two of the central C–O bonds of 30° and of one of 90°. (The 30° motions in the case of the S_4 and D_{2d} conformers are in opposite senses). It seems intrinsically reasonable that these changes will require energy. The idea that there is less conjugation at the transition state will also provide some rationalization for the large β_{rc} values, greater than would be expected for equilibrium formation of the tris(aryloxy)carbenium ion. Because of the well-recognized phenomenon of "resonance saturation",[32] it is possible that the effects of substituents will not be a linear function of the charge on oxygen in the trioxocarbenium ion. For the sake of argument, let us assume that, at the transition state, the positive charge is conjugatively stabilized by only one oxygen atom, the stereochemistry with respect to the other two being unfavorable. If the relationship between substituent effect and positive charge is linear, then one substituent sensing a full positive charge will give the same overall effect as three substituents sensing 0.33 of a positive charge. If however the trioxocarbenium ion is "resonance saturated", the three substituents sensing 0.33 of a positive charge will have a *lower* overall effect than one substituent sensing a full positive charge.



VII



VIII

The stereochemical analysis of the hydration reaction is somewhat ambiguous because the least motion path to the triaryl orthocarbonate results in conformation **VIII**.[5d] Such a conformation would be prohibitively sterically hindered in the case of the orthocarbonate itself (and indeed is not observed) but may be permissible when one of the groups attached to the central carbon atom is the small hydroxy group. If indeed the triaryl orthocarbonate does have conformation **VIII**, extension of the principle of microscopic reversibility to argue that hydrolysis of the orthocarbonates and hydration of the cations involves broadly similar transition states becomes of questionable validity. Generation of triaryl orthocarbonates in conformation **VIII** would however result in little change in the positive charge experienced by the aryl groups. The p-type lone pairs on oxygen atoms in the aryloxy groups make a dihedral angle of 30° with the C–OH bond. Since C–O double-bond character varies as the square of the cosine between the p-type lone pair on oxygen and the empty p orbital on the central carbon atom, pyramidalizing **VII** to give **VIII**, even with a C–OH bond order of zero, would still mean that the oxygen atoms carried 0.75 ($\cos^2 30°$) of the charge that they carried in structure **VIII**. Hence formation of triaryl orthocarbonate **VIII** provides a ready rationalization of the low β_{rc} of the hydration reaction.

Experimental Section

Substrates and Products. A. Orthocarbonates. The known tetraphenyl, tetrakis(*p*-methoxyphenyl), and tetrakis(*p*-methylphenyl) orthocarbonates were made by the coupling of copper phenoxides with carbon disulfide, as described by Narasimhamurthy and Samuelson.[9] A typical procedure for the preparation of mixed orthocarbonates is as follows:

A mixture of sodium aryloxides was prepared by the reaction of phenols (0.005 mol) of the type ArOH and Ar′OH with sodium hydride (0.01 mol) in degassed acetonitrile (50 mL), and cuprous chloride (0.01 mol) was added. Carbon disulfide (0.012 mol) was added to the stirred suspension of copper aryloxides, and the reaction mixture was worked up as described for symmetric orthocarbonates.[9] HPLC analysis of the product showed the presence of five compounds in the ratio of approximately 1:4:6:4:1, and these were separated by medium-pressure liquid chromatography on silica gel using hexane–ethyl acetate or hexane–dichloromethane as eluting solvent. Mixed orthocarbonates were recrystallized by 95% or absolute ethanol. The isolated yields were about 40%–60% of the theoretical yields.

(i) *p*-Cyanophenyl Triphenyl Orthocarbonate: mp 67.5–70.0 °C (95% ethanol); IR ν_{max} (KBr) 3084, 2228, 1589, 1483, 1211, 1103 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.11–7.39 (m, 15H, Ph), 7.40–7.64 (m, 4H, *p*-CN-Ph); ^{13}C NMR (200 MHz, $CDCl_3$) δ 107.3, 119.9, 120.1, 124.6,

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(32) Loudon, J. M.; Berke, C. *J. Am. Chem. Soc.* **1974**, *96*, 4508.

(33) Paulsen, H.; Györgydeák, Z.; Friedmann, M. *Chem. Ber.* **1974**, *107*, 1590.

(34) Pletcher, T.; Cordes, E. H. *J. Org. Chem.* **1967**, *32*, 2294.

(35) Bernasconi, C. F. *Acc. Chem. Res.* **1992**, *25*, 9.

129.5, 133.7, 151.9, 155.7. Anal. Calcd for $C_{26}H_{19}O_4N$: C, 76.27; H, 4.68; N, 3.42. Found: C, 76.25; H, 4.7; N, 3.62.

(ii) *m*-Nitrophenyl Triphenyl Orthocarbonate: mp 99.5–101.0 °C (95% ethanol); IR ν_{max} (KBr) 3069, 1533, 1491, 1205, 1061, 1118 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.08–7.44 (m, 15H, Ph), 7.58–8.20 (m, 4H, *m*-NO_2Ph); ^{13}C NMR (200 MHz, $CDCl_3$) δ 115.1, 118.7, 119.8, 124.4, 125.7, 129.4, 129.8, 151.6. Anal. Calcd for $C_{25}H_{19}O_6N$: C, 69.92; H, 4.45; N, 3.26. Found: C, 69.93; H, 4.50; N, 3.24.

(iii) *m*-Cyanophenyl Triphenyl Orthocarbonate: IR ν_{max} (neat) 3071, 2233, 1589, 1489, 1201, 1074 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.00–7.65 (m); ^{13}C NMR (200 MHz, $CDCl_3$) δ 119.8, 123.3, 124.4, 124.5, 127.6, 129.4, 130.2, 151.9. Anal. Calcd for $C_{26}H_{19}O_4N$: C, 76.27; H, 4.68; N, 3.42. Found: C, 76.15; H, 4.75; N, 3.23.

(iv) *p*-Nitrophenyl Triphenyl Orthocarbonate: mp 65.0 °C dec; IR ν_{max} (KBr) 3074, 1591, 1520, 1489, 1080 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.20–7.40 (m, 15H, Ph), 7.37–8.25 (m, 4H, *p*-NO_2Ph); ^{13}C NMR (200 MHz, $CDCl_3$) δ 118.8, 120.4, 121.5, 125.9, 126.9, 130.0, 144.2, 152.3. Anal. Calcd for $C_{25}H_{19}O_6N$: C, 69.92; H, 4.46; N, 3.26. Found: C, 70.10; H, 4.60; N, 2.99.

(v) *p*-Chlorophenyl Triphenyl Orthocarbonate: IR ν_{max} (neat) 1483, 1215, 1186, 1089 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.1–7.5 (m, 15H, Ph), 6.5–7.0 (m, *p*-ClPh); ^{13}C NMR (200 MHz, $CDCl_3$) δ 119.9, 121.1, 124.0, 129.2, 149.8, 152.2. Anal. Calcd for $C_{25}H_{19}O_4Cl$: C, 71.68; H, 4.57; Cl, 8.46. Found: C, 71.55; H, 4.44; Cl, 8.01.

(vi) Bis(*p*-cyanophenyl)diphenyl Orthocarbonate: mp 98.0–99.0 °C (95% ethanol); IR ν_{max} (KBr) 3083, 2228, 1590, 1485, 1211, 1102 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.9–7.3 (m, 10H, Ph), 7.3–7.6 (m, 8H, *p*-CN-Ph); ^{13}C NMR (200 MHz, $CDCl_3$) δ 107.9, 118.4, 119.8, 123.3, 124.9, 129.6, 133.8, 134.1, 151.4, 155.1. Anal. Calcd for $C_{27}H_{18}O_4N$: C, 74.64; H, 4.17; N, 6.44. Found: C, 74.44; H, 4.10; N, 6.20.

(vii) *p*-Chlorophenyl Tris(*p*-methoxyphenyl) Orthocarbonate: mp 162.0–165.0 °C (95% ethanol); IR ν_{max} (KBr) 3003, 2955, 2837, 1504, 1489, 1248, 1196, 1076 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.77–7.20 (m, 12H, *p*-OMePh), 7.23 (d, 4H, *p*-ClPh), 3.75 (s, 9H, OCH_3); ^{13}C NMR (200 MHz, $CDCl_3$) δ 55.5, 114.2, 121.1, 121.2, 145.8, 156.2. Anal. Calcd for $C_{28}H_{25}O_7Cl$: C, 66.07; H, 4.95; Cl, 6.96. Found: C, 65.85; H, 5.07; Cl, 6.47.

(viii) *m*-Fluorophenyl Tris(*p*-methoxyphenyl) Orthocarbonate: IR ν_{max} (neat) 3003, 2953, 2835, 1610, 1597, 1487, 1248, 1199, 1093 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.76 (s, 9H, OCH_3), 6.76–7.29 (m, 16H, Ar); ^{13}C NMR (200 MHz, $CDCl_3$) δ 55.5, 109.0, 110.7, 114.2, 115.2, 121.2, 129.8, 130.0, 145.8, 156.2. Anal. Calcd for $C_{28}H_{25}O_7F$: C, 68.29; H, 5.11; F, 3.86. Found: C, 68.24; H, 5.11; F, 4.11.

(ix) *m*-Cyanophenyl Tris(*p*-methoxyphenyl) Orthocarbonate: IR ν_{max} (neat) 2953, 2837, 2231, 1637, 1502, 1248, 1196, 1095 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.76 (s, 9H, OCH_3), 6.75–7.25 (m, 12H, *p*-OMePh), 7.20–7.65 (m, 4H, *m*-CN-Ph); ^{13}C NMR (200 MHz, $CDCl_3$) δ 55.5, 114.3, 121.7, 123.1, 124.4, 127.3, 130.1, 145.6, 156.3. Anal. Calcd for $C_{29}H_{25}O_7N$: C, 69.73; H, 5.04; N, 2.80. Found: C, 69.15; H, 5.00; N, 2.65.

(x) *p*-Cyanophenyl Tris(*p*-methoxyphenyl) Orthocarbonate: IR ν_{max} (neat) 2953, 2833, 2226, 1605, 1500, 1248, 1196, 1095 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.76 (s, 9H, OCH_3), 6.78–7.17 (m, 12H, *p*-OMePh), 7.58–7.80 (m, 4H, *p*-CNPh); ^{13}C NMR (400 MHz, $CDCl_3$) δ 55.2, 115.0, 120.6, 121.8, 134.3, 146.2, 157.0. Anal. Calcd for $C_{29}H_{25}O_7N$: C, 69.73; H, 5.04; N, 2.80. Found: C, 69.49; H, 5.04; N, 2.94.

(xi) *p*-Nitrophenyl Tris(*p*-chlorophenyl) Orthocarbonate: mp 115.0–117.0 °C (absolute ethanol); IR ν_{max} (KBr) 3080, 1593, 1520, 1485, 1215, 1113, 1010 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.11–7.31 (m, 12H, *p*-ClPh), 7.32–8.27 (m, 4H, *p*-NO_2Ph); ^{13}C NMR (200 MHz, $CDCl_3$) δ 119.3, 121.1, 125.5, 129.6, 149.9, 157.0. Anal. Calcd for $C_{25}H_{16}O_6Cl_3N$: C, 56.36; H, 3.03; Cl, 19.96; N, 2.63. Found: C, 56.04; H, 2.92; Cl, 19.79; N, 2.50.

(xii) *p*-Nitrophenyl Tris(*p*-fluorophenyl) Orthocarbonate: mp 90.0–92.0 °C (absolute ethanol); IR ν_{max} (KBr) 3080, 1589, 1500, 1203, 1082 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.89–7.25 (m, 12H, *p*-FPh), 7.40 (d, 2H, J = 8.22 Hz, *p*-NO_2Ph), 8.23 (d, 2H, J = 8.27 Hz, *p*-NO_2Ph); ^{13}C NMR (200 MHz, $CDCl_3$) δ 115.8, 116.3, 119.3, 121.3, 121.5, 125.5, 147.4, 157.1, 162.0. Anal. Calcd $C_{25}H_{16}O_6F_3N$: C, 62.12, H, 3.34; F, 11.79; N, 2.89. Found: C, 62.20; H, 3.29; F, 11.78; N, 2.87.

(xiii) *p*-Cyanophenyl Tris(*p*-fluorophenyl) Orthocarbonate: mp 107.5–109.0 °C (95% ethanol); IR ν_{max} (KBr) 3082, 2228, 1605, 1502, 1203, 1170, 1012 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.94–6.98 (m, 6 H, *p*-FPh), 7.12–7.18 (m, 6H, *p*-FPh), 7.62 (d, 2H, J = 8.21 Hz, *p*-CNPh), 7.35 (d, 2H, J = 8.10, *p*-CNPh); ^{13}C NMR (200 Hz, $CDCl_3$) δ 107.7, 116.3, 121.3, 121.5, 147.5, 157.1, 162.0. Anal. Calcd for $C_{26}H_{16}O_4F_3N$: C, 67.39; H, 3.48; F, 12.29; N, 3.02. Found: C, 67.54; H, 3.45; F, 12.22; N, 3.00.

(xiv) *p*-Cyanophenyl Tris(*p*-chlorophenyl) Orthocarbonate: mp 112.0–113.0 °C (95% ethanol); IR ν_{max} (KBr) 2226, 1605, 1485, 1207, 1132, 1062 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.10–7.30 (m, 12H, *p*-ClPh), 7.31–7.65 (m, 4H, *p*-CNPh); ^{13}C NMR (200 MHz, $CDCl_3$) δ 119.9, 121.1, 129.6, 130.1, 150.0, 155.0. Anal. Calcd for $C_{26}H_{16}O_4Cl_3N$: C, 60.90; H, 3.16; Cl, 19.36; N, 2.84. Found: C, 60.74; H, 3.16; Cl, 19.36; N, 2.84.

(xv) *m*-Cyanophenyl Tris(*p*-methylphenyl) Orthocarbonate: IR ν_{max} (neat) 3036, 2924, 2233, 1608, 1587, 1481, 1207, 1170, 1074 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.33 (s, 9H, CH_3), 7.09–7.63 (m, 16H, Ar); ^{13}C NMR (200 MHz, $CDCl_3$) δ 20.7, 119.7, 123.3, 124.5, 127.4, 129.8, 130.1, 133.8, 149.8, 152.5. Anal. Calcd for $C_{29}H_{25}O_4N$: C, 77.14; H, 5.58; N, 3.10. Found: C, 77.14; H, 5.58; N, 3.10. Found: C, 77.28; H, 5.45; N, 3.03.

(xvi) *p*-Cyanophenyl Tris(*p*-methylphenyl) Orthocarbonate: mp 119.0–120.0 °C (95% ethanol); IR ν_{max} (KBr) 3034, 2924, 2864, 2228, 1506, 1288, 1091, 1018 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.23 (s, 9H, CH_3), 7.07–7.18 (m, 12H, *p*-MePh), 7.38–7.62 (m, 4H, *p*-CNPh); ^{13}C NMR (200 MHz, $CDCl_3$) δ 20.7, 107.0, 119.7, 120.0, 129.8, 133.6, 133.9, 149.7, 155.5. Anal. Calcd for $C_{29}H_{25}O_4N$: C, 77.14; H, 5.58; N, 3.10. Found: C, 77.52; H, 5.69; N, 2.95.

(xvii) *p*-Cyanophenyl Tris(*m*-methylphenyl) Orthocarbonate: IR ν_{max} (neat) 3038, 2922, 2862, 2228, 1606, 1489, 1240, 1080 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.36 (s, 9H, CH_3), 6.95–7.30 (m, 12H, *m*-MePh), 7.41–7.66 (m, 4H, *p*-CNPh); ^{13}C NMR (200 MHz, $CDCl_3$) δ 21.5, 107.2, 116.7, 118.8, 120.1, 120.4, 125.2, 129.5, 133.5, 151.9, 155.8. Anal. Calcd for $C_{29}H_{25}O_4N$: C, 77.14; H, 5.58; N, 3.10. Found: C, 76.95; H, 5.62; N, 3.09.

It was not possible to purify the following orthocarbonates containing nitrophenoxy groups attached to an electron-rich tris(aryloxy)carbenium moiety to analytical purity because of their lability. For kinetic purposes, however, contamination with small amounts of the simple carbonate has no effect, since rate constants were determined for nitrophenol liberation.

(xviii) *p*-Nitrophenyl Tris(*p*-methylphenyl) Orthocarbonate: mp 73.0–74.0 °C dec; IR ν_{max} (KBr) 3034, 2856, 2924, 1593, 1508, 1203, 1109 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.31 (s, 9H, CH_3), 7.08–7.24 (m, 12H, *p*-MePh), 7.49–8.24 (m, 4H, *p*-NO_2Ph); ^{13}C NMR (200 MHz, $CDCl_3$) δ 20.7, 119.3, 119.7, 120.6, 125.3, 129.9, 130.1, 133.9, 149.6, 157.0. Anal. Calcd for $C_{28}H_{25}O_6N$: N, 2.97. Found: N, 2.51.

(xix) *p*-Nitrophenyl Tris(*m*-methylphenyl) Orthocarbonate: mp 75.0–77.0 °C; IR ν_{max} (KBr) 2900, 2850, 1516, 1487, 1232, 1130, 1066 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.29 (s, 9H, *m*-CH_3), 6.89–7.29 (m, 12H, *m*-MePh), 7.36–8.21 (m, 4H, *p*-NO_2Ph); ^{13}C NMR (200 MHz, $CDCl_3$) δ 21.4, 116.7, 119.5, 120.4, 125.2, 129.1, 139.5, 151.8. Anal. Calcd for $C_{28}H_{25}O_6N$: O, 20.35; N, 2.97. Found: O, 20.08; N, 2.71.

(xx) *p*-Nitrophenyl Tris(*p*-*tert*-butylphenyl) Orthocarbonate: mp 112.0 °C dec; IR ν_{max} (KBr) 2855, 1610, 1501, 1462, 1377, 1126, 1078 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.28 (s, 27H, $C(CH_3)_3$), 7.17–7.43 (m, 12H, *p*-*t*-BuPh), 7.42 (d, 2H, J = 9.32 Hz, *p*-NO_2Ph), 8.17 (d, 2H, J = 9.28 Hz, *p*-NO_2Ph); ^{13}C NMR (200 MHz, $CDCl_3$) δ 31.4, 119.2, 119.4, 125.2, 126.1, 147.1, 150.0. Anal. Calcd for $C_{37}H_{43}O_6N$: N, 2.34. Found: N, 2.13.

(xxi) *p*-Nitrophenyl Tris(3,4-dimethylphenyl) Orthocarbonate: mp 86.0–87.0 °C; IR ν_{max} (KBr) 3026, 2922, 1520, 1496, 1230, 1118 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.21 (s, 9H, CH_3), 2.22 (s, 9H, CH_3), 6.97–7.24 (m, 9H, 3,4-diMePh), 7.43 (d, 2H, J = 9.42 Hz, *p*-NO_2Ph), 8.19 (d, 2H, J = 9.38 Hz, *p*-NO_2Ph); ^{13}C NMR (200 MHz, $CDCl_3$) δ 18.9, 19.9, 116.9, 119.5, 120.9, 125.2, 130.1, 137.6, 149.9, 157.0.

B. **Diaryl Carbonates** of the type $(ArO)_2C$ and ArOCOOAr′ were prepared by the reaction of (dichloromethylene)dimethylammonium chloride and phenols according to literature procedures by Viehe and Jannousek.[36]

(i) Phenyl *p*-Cyanophenyl Carbonate: mp 86.0 °C (absolute ethanol); IR ν_{max} (KBr) 3100, 2231, 1770, 1603, 1506, 1496, 1273, 1192 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.15–7.75 (m, Ar); ^{13}C NMR (200 MHz, $CDCl_3$) δ 110.3, 120.7, 122.0, 126.6, 129.7, 133.8, 152.0, 154.0. Anal. Calcd for $C_{14}H_9O_3N$: C, 70.28; H, 3.79; N, 5.85. Found: C, 69.97; H, 3.76; N, 5.51.

(ii) Phenyl *m*-Cyanophenyl Carbonate: mp 73.0–74.0 °C (absolute ethanol); IR ν_{max} (KBr) 3057, 2241, 1774, 1579, 1489, 1269; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.24–7.59 (m Ar); ^{13}C NMR (200 MHz, $CDCl_3$)

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[36] Viehe, H. G.; Jannousek, Z. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 806.

δ 120.7, 124.7, 125.8, 126.6, 129.7, 130.0, 130.6, 150.5. Anal. Calcd for $C_{14}H_9O_3N$: C, 70.28; H, 3.79; N, 5.85. Found: C, 70.14; H, 3.74; N, 5.78.

(iii) p-Chlorophenyl *p*-Methoxyphenyl Carbonate: mp 114.0–116.0 °C (absolute ethanol); IR ν_{max} (KBr) 3101, 2957, 2833, 1763, 1510, 1487, 1282, 1188; ^1H NMR (200 MHz, $CDCl_3$) δ 3.80 (s, 3H, OCH_3), 6.83–7.39 (m, 8H, Ar); ^{13}C NMR (200 MHz, $CDCl_3$) δ 55.6, 114.6, 121.7, 122.3, 129.6, 157.7, 144.9, 152.0. Anal. Calcd for $C_{14}H_{11}O_4Cl$: C, 60.33; H, 3.97. Found: C, 59.99; H, 3.77.

(iv) Phenyl *p*-Chlorophenyl Carbonate: mp 93.0–94.0 °C (absolute ethanol); IR ν_{max} (KBr) 1761, 1593, 2489, 1296, 1186, 1086; ^1H NMR (200 MHz, $CDCl_3$) δ 7.18–7.46 (m, Ar); ^{13}C NMR (200 MHz, $CDCl_3$) δ 120.8, 122.2, 122.3, 126.4, 129.6, 149.5. Anal. Calcd for $C_{13}H_9O_3Cl$: C, 62.79; H, 3.64. Found: C, 62.53; H, 3.36.

C. Tris(aryloxy)methyl Azides. Sodium azide (500 mg) was dissolved in acetonitrile (25 mL) containing 15 crown ether (1.5 mL), and *p*-nitrophenyl triaryl orthocarbonate was added (*p*-cyanophenyl tris(*p*-methoxyphenyl) orthocarbonate was used in the case of tris(*p*-methoxyphenyl)methyl azide). The reaction mixture was refluxed at 85 °C for 25–30 h, and the progress of the reaction was followed by HPLC. After completion of the reaction the reaction mixture was cooled and diethyl ether (100 mL) was added and washed with three portions of 5% sodium hydroxide (50 mL) solution. The dried ether layer was chromatographed on silica gel using dichloromethane–hexane (3:1) as solvent. Tris(aryloxy)methyl azides were separated as colorless oils, and all attempts to crystallize them failed.

(i) Triphenoxymethyl Azide: IR ν_{max} (neat) 3044, 2133, 1589, 1489, 1205, 1170 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.06–7.40 (m, Ph); ^{13}C NMR (200 MHz, $CDCl_3$) δ 119.9, 120.5, 123.9, 124.7, 129.2, 129.3, 152.0. Anal. Calcd for $C_{19}H_{15}O_3N_3$: C, 68.46; H, 4.54; N, 12.60. Found: C, 68.32; H, 4.50; N, 12.34. Yield 69%.

(ii) Tris(*p*-methylphenoxy)methyl Azide: IR ν_{max} (neat) 3032, 2924, 2133, 1504, 1203, 1091 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 2.33 (s, 9H, CH_3), 7.10–7.24 (m, 12H, *p*-MePh); ^{13}C NMR (200 MHz, $CDCl_3$) δ 20.7, 120.5, 129.8, 134.1, 150.0. Anal. Calcd for $C_{22}H_{21}O_3N_3$: C, 70.38; H, 5.64; N, 11.19. Found: C, 70.65; H, 5.76; N, 10.92. Yield 71%.

(iii) Tris(*p*-fluorophenoxy)methyl Azide: IR ν_{max} (neat) 3003, 2133, 1502. 1246, 1196, 1078 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 6.97–7.52 (m, *p*-FPh); ^{13}C NMR (200 MHz, $CDCl_3$) δ 115.8, 116.2, 122.1, 122.3, 147.8, 157.3. Anal. Calcd for $C_{19}H_{12}O_3F_3N_3$: C, 58.82; H, 3.12; N, 10.85. Found: C, 59.18; H, 3.20; N, 10.59. Yield 66%.

(iv) Tris(*m*-methylphenoxy)methyl Azide: IR ν_{max} (neat) 3036, 2922, 2864, 2135, 1585, 1487, 1244, 1089; ^1H NMR (200 MHz, $CDCl_3$) δ 2.37 (s, 9H, CH_3), 6.98–7.28 (m, 12H, *m*-MePh); ^{13}C NMR (200 MHz, $CDCl_3$) δ 21.4, 117.5, 121.2, 125.4, 129.0, 139.4, 152.2. Anal. Calcd for $C_{22}H_{21}O_3N_3$: C, 70.34; H, 5.64; N, 11.19. Found: C, 70.40; H, 5.60; N, 11.35. Yield 75%.

(v) Tris(*p*-methoxyphenoxy)methyl Azide: IR ν_{max} (neat) 3003, 2932, 2837, 2133, 1502, 1246, 1196, 1078 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 3.78 (s, 9H, OCH_3), 6.79–7.25 (m, 12H, *p*-OMePh); ^{13}C NMR (200 MHz, $CDCl_3$) δ 55.5, 114.3, 122.0, 145.8, 156.5. Yield 43%. This, the most labile of the tris(aryloxy)methyl azides we prepared, was too labile to permit purification to analytical purity.

Kinetic Methods. First-order rate constants were measured by monitoring absorbance changes in tightly stoppered 1 cm path length cells in a Perkin-Elmer Lambda 6 spectrophotometer, fitted with a Peltier-effect temperature-controlled cell block with direct temperature readout. Absorbance changes were fitted directly to $A = A_0 + B(1 - e^{-kt})$ using the nonlinear least squares program *Kaleidagraph* (Synergy, PCS Inc.). Wavelengths used were 350 nm for all compounds having a *p*-nitro- or *m*-nitrophenyl groups, 298 nm for all compounds having a tris(*p*-methoxyphenyl) group, 285 nm for all compounds having a tris(*p*-methylphenyl) group, 278 nm for tetraphenyl orthocarbonate, and 290 nm for *p*-cyano- and *m*-cyanophenyl triphenyl orthocarbonates. It was confirmed in the case of tetraphenyl orthocarbonate that the absorbance change *B* corresponded to the production of two molecules of phenol and one of diphenyl carbonate.

Hydrolysis of triphenoxymethyl azide was followed at 278 nm, that of tris(*p*-methylphenyl)methyl azide at 285 nm, that of tris(*p*-fluorophenoxy)methyl azide at 290 nm, and that of tris(*p*-methoxyphenoxy)methyl azide at 298 nm.

For the determination of the spontaneous hydrolysis rates of mixed orthorcarbonates with nitrophenolate or cyanophenolate leaving groups, the following neutral acid–sodium hydroxide buffer systems were used at a concentration of 0.5–1.0 mM (I = 1.0 M, KCl) between the following pH values as indicated: 2–3, dichloroacetic acid; 3–4, chloroacetic acid; 4–5, acetic acid; 5–6, 2-(*N*-morpholino)ethanesulfonic acid (MES); 6–7, *N*-(2-acetamido)-2-aminoethanesulfonic acid (ACES); 7–8, 3-[*N*,*N*-bis-(2-hydroxyethyl)amino]-2-hydroxypropanesulfonic acid (DIPSO); 8–9, 3-[(1,1-dimethyl-2-hydroxyethyl)amino]-2-hydroxypropanesulfonic acid (AMPSO). The pH values of the ordinate of Figure 2 refer to room temperature: temperature corrections for amine-based buffers will in principle be substantial but not germane, since the reaction of interest is pH-independent.

All first-order rate constants quoted in the text are the mean of at least two independent determinations. Enthalpies and entropies of activation were calculated from determination at minimally five temperatures spanning minimally a 20-deg temperature range.

Analysis of Products. Stock solutions of orthocarbonates were made by dissolving the orthocarbonate (8–10 mg) in acetonitrile (1.00 mL). The appropriate hydrolysis medium was thermostated to 70.0 °C and the reaction monitored by HPLC using a Spectrophysics SP 8800 system, a C18 reversed-phase analytical column, and UV/visible detection. Isocratic elution by 70–80% acetonitrile–30–20% water (depending on the system) was used, and the reaction was followed for about 5 half-lives. Peak positions of potential diaryl carbonate products were determined prior to the product analysis, and solvent systems were selected for good resolution.

Capture of Tris(aryloxy)methyl Cations by Azide Ion. The products from the reaction of $(p\text{-}MeC_6H_4O)_3C\text{–}O\text{–}p\text{-}C_6H_4NO_2$ with varying concentrations of sodium azide in 1.0 mM DIPSO were monitored by HPLC in the system described above. The azide was not stable under the reaction conditions, and so partitioning ratios were measured by common ion inhibition of the hydrolysis of the azide.

Determination of the Selectivities of Tris(aryloxy)methyl Cations between Water and *p*-Nitrophenolate. To sodium DIPSO buffer, pH 7.5, 0.187 mole fraction acetonitrile, containing various concentrations of sodium *p*-nitrophenolate at 70.0 °C, were added portions (50 μL) of a stock solution of tris(aryloxy)methyl azide (10 mg mL^{-1}). The reaction mixture was analyzed by HPLC using a C18 analytical column and isocratic elution with 70% acetonitrile–30% water after 2–3 half-lives. The selectivities k_{PNP}/k_{HOH} were determined from the gradients of four- or five-point plots of $[(ArO)_3COpC_6H_4NO_2]/[(ArO)_2CO]$ against nitrophenolate concentration. Relative molar response factors were determined for $(ArO)_3COpC_6H_4NO_2$ and $(ArO)_2CO$ from analyses of mixtures of known composition.

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