Effect of α-Carbomethoxy Group on the Reactivity of Benzyl Cations in Solution

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Abstract: Substituted α-carbomethoxybenzyl cations have been generated upon 248- or 308-nm laser flash photolysis of appropriately substituted methyl phenyldiazoacetates in aqueous solution, 2,2,2-trifluoroethanol (TFE), or 1,1,1,3,3,3-hexafluoroisopropyl alcohol (HFIP). The α-carbomethoxy-4-methoxybenzyl cation, $\lambda_{max} = 235$ nm, is sufficiently unreactive to be observed in aqueous solution. The formation of this carbocation upon photolysis of methyl (4-methoxyphenyl)diazoacetate involves protonation of the transient α-carbomethoxy 4-methoxyphenyl carbene, as shown by the observation that rapid quenching of the carbene with absorption at 355 nm in acetonitrile by the addition of $HClO_4$, $k_{H^+} = 3.5 \times 10^9$ M^{-1} s^{-1}, is accompanied by the formation of the carbocation with absorption at 325 nm. The 4-methyl and unsubstituted α-carbomethoxybenzyl cations are too reactive to be detected in aqueous solution, but could be readily observed in the non-nucleophilic solvent HFIP with absorption maxima at 335 and 330 nm, respectively. The reactions of each of the α-carbomethoxybenzyl cations with solvent and methanol were measured and were found to be considerably slower than the same reactions of the corresponding α-unsubstituted benzyl cations.

Introduction

Carbocations with one or more electron-withdrawing groups, such as CF_3, CN, or CO_2R, attached directly to the cationic center are commonly referred to as "destabilized" carbocations because the electron-withdrawing group is expected to lower the thermodynamic stability of the cation relative to the solvolysis products formed by nucleophilic addition.[1–3] In recent years such carbocations have been subject to considerable theoretical[4,5] and experimental investigation,[6–29] with most experimental work involving studies of the carbocations generated as intermediates in, for example, solvolysis reactions or NMR studies of the structural aspects of the cations produced under strong acid conditions.

One important property of these carbocations that has only recently been examined is their reactivity.[22–25,29] The majority of work in this area has concentrated on the reactivity of α-CF_3 and α-CO_2CH_3 substituted 4-methoxybenzyl cations.[22–25] It was found that the 4-methoxybenzyl cations that have an electron-withdrawing group at the α-position are actually less reactive toward solvent than the α-unsubstituted 4-methoxybenzyl cations,[22–25] a result which is contrary to the expected increase in reactivity due to the thermodynamic destabilization caused by the CF_3 and CO_2CH_3 groups. To explain this result, it was argued that the electron density of the 4-methoxy group is delocalized extensively into the positive charge at the α-position due to the presence of the electron-withdrawing group immediately adjacent to the positive charge,[22–25] and that this enhanced delocalization of charge ultimately results in a significant kinetic barrier that cancels out the expected rate-accelerating thermodynamic effect, bringing the rate constant below that of the α-unsubstituted 4-methoxybenzyl cation.[22–25]

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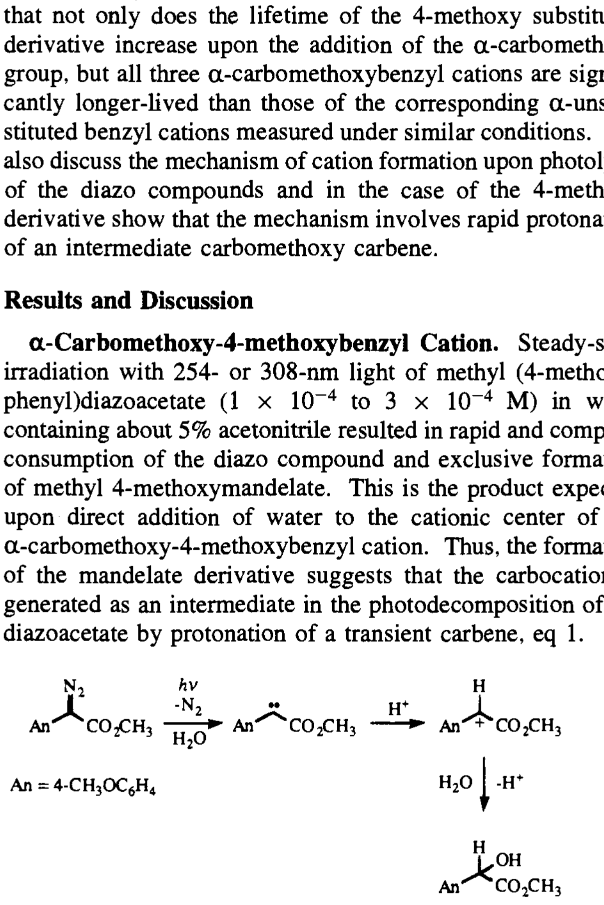
The explanation outlined above suggests that the 4-methoxy group, by virtue of its ability to have a strong resonance interaction with the cationic center, plays a critical role in determining the reactivity of the destabilized benzyl cations. As a result, the effect that an electron-withdrawing substituent such as CO_2CH_3 might have on the reactivity of benzyl cations not bearing a 4-methoxy group remains unclear. We report that we have generated the parent α-carbomethoxybenzyl cation, the 4-methyl derivative, and the 4-methoxy derivative using nanosecond flash photolysis of substituted methyl phenyldiazoacetates and have measured directly the absolute lifetimes of the cations in aqueous and alcoholic solvents. Our results show that not only does the lifetime of the 4-methoxy substituted derivative increase upon the addition of the α-carbomethoxy group, but all three α-carbomethoxybenzyl cations are significantly longer-lived than those of the corresponding α-unsubstituted benzyl cations measured under similar conditions. We also discuss the mechanism of cation formation upon photolysis of the diazo compounds and in the case of the 4-methoxy derivative show that the mechanism involves rapid protonation of an intermediate carbomethoxy carbene.

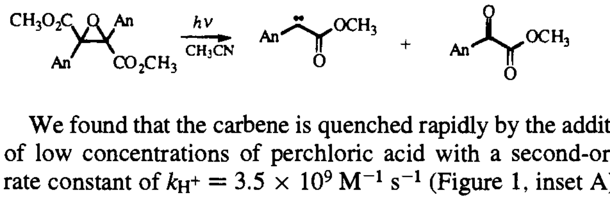
Results and Discussion

α-Carbomethoxy-4-methoxybenzyl Cation. Steady-state irradiation with 254- or 308-nm light of methyl (4-methoxyphenyl)diazoacetate (1×10^{-4} to 3×10^{-4} M) in water containing about 5% acetonitrile resulted in rapid and complete consumption of the diazo compound and exclusive formation of methyl 4-methoxymandelate. This is the product expected upon direct addition of water to the cationic center of the α-carbomethoxy-4-methoxybenzyl cation. Thus, the formation of the mandelate derivative suggests that the carbocation is generated as an intermediate in the photodecomposition of the diazoacetate by protonation of a transient carbene, eq 1.



(1)

Laser flash photolysis of methyl (4-methoxyphenyl)diazoacetate supports the reaction sequence shown in eq 1. In acetonitrile, laser irradiation with either 248- or 308-nm light pulses of 25-ns duration produces a single transient species that is identified as the α-carbomethoxy 4-methoxyphenyl carbene on the basis of the close similarity between its absorption spectrum, $\lambda_{max} = 355$ nm (Figure 1, dashed line), and rate of decay, $k = 8.2 \times 10^4$ s^{-1}, and those for the same carbene generated previously[30] by laser photolysis of *trans*-2,3-bis(carbomethoxy)-4,4′-dimethoxystilbene oxide in the same solvent, eq 2.



(2)

We found that the carbene is quenched rapidly by the addition of low concentrations of perchloric acid with a second-order rate constant of $k_{H^+} = 3.5 \times 10^9$ M^{-1} s^{-1} (Figure 1, inset A) in acetonitrile with 1.0 M water. This is consistent with the carbene undergoing rapid protonation to give the carbocation.

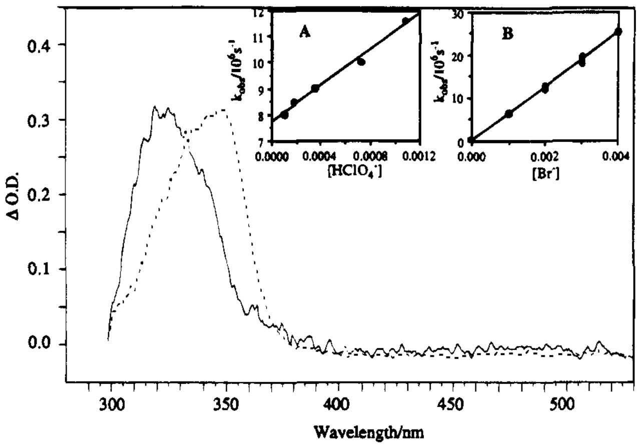


Figure 1. Transient absorption spectra upon 248-nm laser photolysis of methyl (4-methoxyphenyl)diazoacetate (dashed line) in acetonitrile and (solid line) in 0.01 M $HClO_4$ in acetonitrile with 1.0 M H_2O at 20 °C. Inset A shows the relationship between the observed rate constants for the decay of the 355-nm band as a function of the concentration of sodium perchlorate. Inset B shows the relationship between the observed rate constants for the decay of the 325-nm band in TFE as a function of sodium bromide concentration.

Concomitant with the acid quenching is the formation of a second transient with $\lambda_{max} = 325$ nm, and when the concentration of $HClO_4$ exceeds 0.01 M $HClO_4$ in aqueous acetonitrile, the carbene is beyond our time resolution and the 325-nm transient remains the only observed species (Figure 1, solid line).

The same 325-nm transient is observed upon photolysis of either the phenyldiazoacetate or the substituted stilbene oxide in the non-nucleophilic, acidic solvent 2,2,2-trifluoroethanol (TFE), and in this solvent the transient decays in a first-order manner with an observed rate constant $k_{TFE} = 1.7 \times 10^5$ s^{-1} ($\tau_{TFE} = 6.3$ μs). In neat water, the 325-nm transient is again the only species observed, but its decay is considerably faster than in TFE, $k_{H_2O} = 2.0 \times 10^7$ s^{-1} ($\tau_{H_2O} = 50$ ns). In both solvents, the rate of decay is not influenced by the addition or removal of oxygen, but increases rapidly upon the addition of nucleophiles such as methanol and bromide. Linear least squares analysis of observed rate constants for the decay of the transient measured at various concentrations of bromide or methanol in TFE (Figure 1, inset B) gives the second-order rate constants $k_{Br^-} = 6.0 \times 10^9$ M^{-1} s^{-1} and $k_{MeOH} = 3 \times 10^6$ M^{-1} s^{-1}.

The fact that the transient with $\lambda_{max} = 325$ nm is produced upon protonation of the carbene immediately suggests that the transient is the carbocation. It should also be noted that transient carbocations have been produced upon the photolysis of other diazo compounds such as diazodiphenylmethane in protic solvents such as TFE.[31-33] In addition, the absence of an effect of oxygen concentration on the decay rate of the 325-nm transient, the higher decay rate in water relative to TFE, and the increased decay rate in the presence of nucleophiles are properties similar to those or reactive carbocations generated by flash photolysis.[34-38] The absorption maximum at 325 nm

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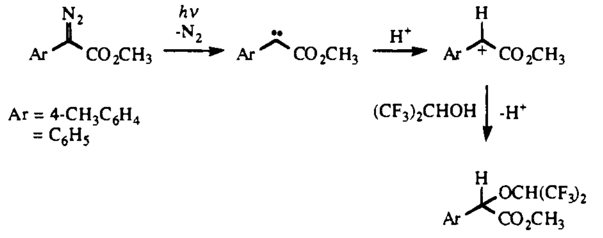
and the magnitude of the second-order rate constant for reaction with bromide also agree well with those determined for benzylic cations such as the 4-methoxybenzyl and α-methyl-4-methoxybenzyl cations.[37,38] On the basis of these observations, together with the formation of methyl 4-methoxymandelate as the sole product upon photolysis of methyl phenyldiazoacetate in water, we identify the 325-nm transient as the α-carbomethoxy-4-methoxybenzyl cation.

The rate constant for the reaction of the same carbocation in 1:1 H_2O/TFE mixtures has been estimated by Richard et al., using the "azide clock" technique, to be 1.4×10^7 s^{-1}.[22] We generated the 325-nm transient in the same solvent mixture and found the rate constant for its decay, $k_{TFE/H_2O} = 1.2 \times 10^7$ s^{-1}, to be very similar to the value determined indirectly. This similarity reinforces our conclusion that the transient at 325 nm is the α-carbomethoxy-4-methoxybenzyl cation.

α-Carbomethoxy-4-methylbenzyl and α-Carbomethoxybenzyl Cations. Aqueous solutions were not used to study the α-carbomethoxybenzyl and α-carbomethoxy-4-methylbenzyl cations that might be formed upon excitation of phenyldiazoacetate and (4-methylphenyl)diazoacetate because these cations would likely be too short-lived to be observed in that medium.[39] The solvent 1,1,1,3,3,3-hexafluoroisopropyl alcohol, HFIP, which has been shown to be a useful solvent for the study of short-lived carbocations,[42] was used instead.

Steady-state irradiation of methyl (4-methylphenyl)diazoacetate and methyl phenyldiazoacetate in HFIP with 254- or 300-nm light resulted in complete conversion of the starting material to the corresponding 1,1,1,3,3,3-hexafluoroethoxy ethers. The reaction shown in eq 3 involves solvent addition to α-carbomethoxybenzyl cation formed by protonation of the intermediate carbene and accounts well for the observed products in both cases.



(3)

Laser excitation of methyl phenyldiazoacetate in HFIP produces a single transient species with an absorption maximum at 330 nm (Figure 2a). This species decays in a first-order manner with the rate constant $k_s = 3 \times 10^6$ s^{-1}. The decay of the transient is insensitive to oxygen concentration, but does increase in the presence of nucleophiles. From observed rate constants measured as a function of bromide and methanol concentration, second-order rate constants for the quenching of the transient were determined and are shown in Table 1.

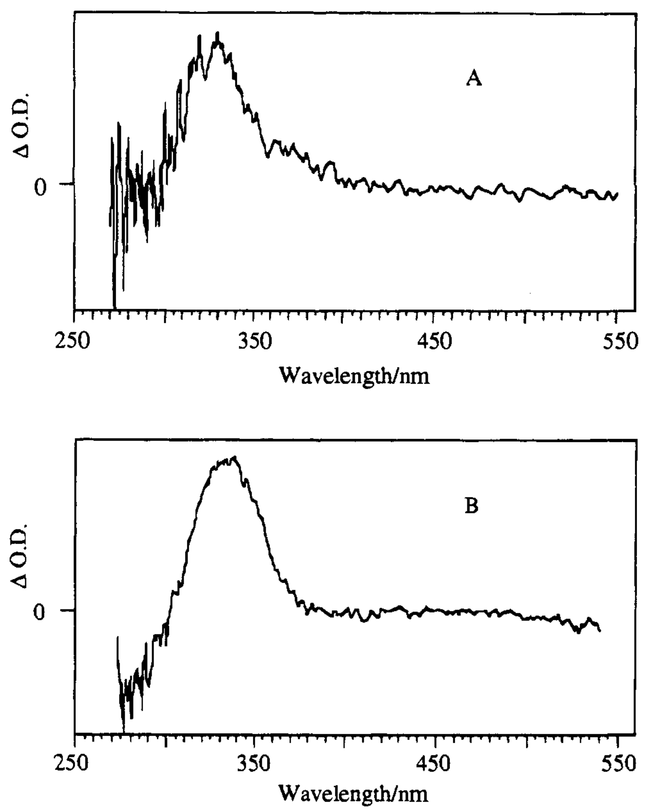


Figure 2. Transient absorption spectra upon 248-nm laser photolysis of (a) methyl phenyldiazoacetate and (b) methyl (4-methylphenyl)-diazoacetate in 1,1,1,3,3,3-hexafluoroisopropyl alcohol at 20 °C.

Table 1. Rate Constants for the Reaction of Substituted Carbomethoxybenzyl Cations, $RC_6H_4C^+HCO_2CH_3$, with Solvent, Methanol, and Bromide at 20 °C

R	k_s/s^{-1} [a]	$k_{MeOH}/M^{-1}\ s^{-1}$ [b]	$k_{Br^-}/M^{-1}\ s^{-1}$ [c]
H	3.0×10^6 [d]	1.3×10^8 [d]	9.1×10^9 [d]
4-Me	3.0×10^5 [d]	3.7×10^7 [d]	8.2×10^9 [d]
4-MeO	1.7×10^5 [e] 2.0×10^7 [f]	3.0×10^6 [e]	6.0×10^9 [e]

[a] Observed rate constant for reaction with solvent. [b] Second-order rate constant for reaction with methanol. [c] Second-order rate constant for reaction with bromide. [d] In HFIP. [e] In TFE. [f] In water.

Similar results were observed upon photolysis of methyl (4-methylphenyl)diazoacetate in HFIP. In this case, a single transient with an absorption maximum at $\lambda_{max} = 335$ nm (Figure 2B) and a first-order decay determined as 3×10^5 s^{-1} was observed. The transient was quenched by nucleophiles with the second-order rate constants shown in Table 1, but was insensitive to oxygen concentration. It should be noted that no transients were observed upon photolysis of either methyl phenyldiazoacetate or methyl (4-methylphenyl)diazoacetate in the more nucleophilic solvent, TFE.

The transients were identified as the α-carbomethoxybenzyl cations for the following reasons. The absorption maxima of the transients near 330 nm are very similar to analogous benzyl cations (λ_{max} (benzyl cation) ≈ 300 nm; λ_{max} (4-methylbenzyl) = 310 nm)[37] and α-methylbenzyl cations (λ_{max} (α-methylbenzyl cation) ≈ 315 nm; λ_{max} (α-methyl-4-methylbenzyl) = 325 nm)[37] in the same solvents. The shift to somewhat higher wavelengths is consistent with recent results showing that absorption spectra of diphenylmethyl and fluorenyl cations are shifted to higher wavelengths when carbomethoxy groups are attached directly to the cationic center.[29] In addition, the transients were

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(39) It is known that enol formation upon nucleophilic attack by water to the carbene center is a significant reaction pathway followed by the carbomethoxy 4-methylphenyl[40] and carbomethoxy phenyl[41] carbenes. The fact that protonation by solvent takes place in HFIP whereas nucleophilic addition of solvent takes place in water is presumably due to the higher acidity and lower nucleophilicity of HFIP relative to the less acidic and more nucleophilic water.

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Table 2. Rate Constants for the Reaction of Substituted Benzyl Cations, 4-$R_1C_6H_4C^+HR_2$ with Solvent and Methanol at 20 °C

	$R_1 = H^a$		$R_1 = 4\text{-}CH_3{}^a$		$R_1 = 4\text{-}OCH_3{}^b$	
R_2	k_s/s^{-1}	$k_{MeOH}/M^{-1}\ s^{-1}$	k_s/s^{-1}	$k_{MeOH}/M^{-1}\ s^{-1}$	k_s/s^{-1}	$k_{MeOH}/M^{-1}\ s^{-1}$
H^c	$>2.0 \times 10^7$		2.0×10^6	6.5×10^7	4.3×10^6	
$CH_3{}^c$	6.0×10^5	4.3×10^7	5.0×10^4	1.1×10^7	3.9×10^5	5.6×10^6
$CO_2CH_3{}^d$	3.0×10^6	1.3×10^8	3.0×10^5	3.7×10^7	1.7×10^5	3.0×10^6

[a] In HFIP. [b] In TFE. [c] Data taken from ref 37. [d] This work.

quenched by the addition of nucleophiles, but remained unaffected by the addition or removal of oxygen. The second-order rate constants for bromide ion quenching are high and are also similar to those for other benzylic carbocations.[34-38]

On the basis of the results described above which show that protonation of the α-carbomethoxy 4-methoxyphenyl carbene gives the α-carbomethoxy-4-methoxybenzyl cation, it is reasonable to suggest that a similar mechanism involving carbene protonation leads to the formation of the 4-methyl substituted and the unsubstituted α-carbomethoxybenzyl cations. The inability to detect the α-carbomethoxy 4-methylphenyl and the α-carbomethoxy phenyl carbenes[43] in our experiments reflects the high acidity of HFIP, which probably protonates the carbene at rate constants greater than those accessible using nanosecond laser photolysis.[31-33] However, since the carbene was not observed, we cannot rule out the possibility that the carbocations are produced by some mechanism not involving the carbene, such as direct protonation of the excited diazo compound.[31-33]

Effect of Carbomethoxy Group on Reactivity of Cations. The rate constants for the reaction of the three "destabilized" carbocations studied in the present work with solvent, bromide, and methanol are summarized in Table 1. The rate constants for reaction with solvent show that the α-carbomethoxybenzyl cation with the electron-donating 4-methoxy group is the only cation that is sufficiently unreactive to be observed in the more nucleophilic solvents such as TFE or aqueous solution. The 4-methyl derivative and the parent α-carbomethoxybenzyl cation are too reactive in TFE and water and therefore were studied only in the non-nucleophilic solvent, HFIP. In this solvent, the 4-methyl derivative is substantially less reactive than the parent cation.

The large magnitude of rate constants of almost 10^{10} M^{-1} s^{-1} for the reaction of the α-carbomethoxybenzyl cations with bromide and the insensitivity of these rate constants to substituent effects suggest that bromide addition takes place at or near the diffusion-controlled limit. On the other hand, the rate constants for the reaction with methanol are considerably smaller and follow the trend expected on the basis of the electron-donating ability of the 4-substituent, with the 4-methoxy derivative being about 100-fold less reactive toward methanol than the 4-methyl derivative, which itself is almost 4-fold less reactive than the parent cation. Thus, the reactivity order for the reactions of the substituted α-carbomethoxybenzyl cations with solvent or methanol is 4-CH_3O < 4-CH_3 < 4-H and is the same as that observed for the reactions of similar carbocations, such as substituted benzyl and α-methylbenzyl cations.[37]

A comparison between the rate constants determined in the present work for the reactions of the α-carbomethoxybenzyl cations with solvent and methanol and the rate constants of the same reactions of structurally similar benzyl and α-methylbenzyl (or phenethyl) cations is given in Table 2. The data in the final two columns of this table show that the α-carbomethoxy substituted 4-methoxybenzyl cation is the least reactive of the three cations in the 4-methoxy cation series, with the α-unsubstituted and the α-methyl derivatives being more reactive toward solvent than the α-carbomethoxy derivative by factors of about 25 and 2, respectively, and the α-methyl-4-methoxybenzyl cation undergoing attack by methanol 2 times more rapidly. These results confirm those reported earlier by Richard and coworkers, who used the "azide clock" technique.[22] To explain the fact that the electron-withdrawing groups actually decrease the reactivity of the 4-methoxybenzyl cation, Richard has suggested[22-24] that destabilizing α-substituents enhance the degree of π-electron donation from the 4-methoxyphenyl group to the cationic center of the fully formed 4-methoxybenzyl cations. As the reaction then proceeds to the transition state, the resonance interaction is lost and the positive charge returns to the benzylic position, while at the same time the destabilizing effect of the inductively electron-withdrawing substituent remains important. According to the principle of nonperfect synchronicity,[45] such an imbalance in which loss of a stabilizing resonance interaction has progressed further than a destabilizing inductive effect will result in an increased activation barrier and a decrease in the reactivity of the destabilized 4-methoxybenzyl cation.

Since the 4-methylphenyl group has less π-electron-donating ability than the 4-methoxyphenyl group, it seems reasonable to predict that the degree of electron-donation from the 4-methylphenyl group to the positively charged carbon, and hence the imbalance in the transition state and the magnitude of the rate reduction, will be less for the α-carbomethoxy-4-methylbenzyl cation than for the corresponding 4-methoxy derivatives. As can be seen in the data from Table 2, this prediction is confirmed, with a smaller, 7-fold reduction in reactivity toward solvent being observed upon the introduction of the carbomethoxy group to the α-position of the 4-methylbenzyl cation, and with the α-carbomethoxy derivative being 3 times more reactive than the α-methyl-4-methylbenzyl cation.

Similarly, replacing the α-hydrogen of the benzyl cation with an α-carbomethoxy group causes a 7-fold reduction in the rate constant for the reaction of the cation with solvent that is considerably smaller than the 25-fold rate reduction observed for the corresponding 4-methoxy derivatives. In addition, a 5-fold increase in reactivity is observed upon replacement of the α-methyl group of the α-methylbenzyl cation with the α-carbomethoxy group, whereas the α-carbomethoxy-4-methoxybenzyl cation is half as reactive as the corresponding α-methyl-4-methoxybenzyl cation. Thus, the results show that the kinetic stability provided by the α-carbomethoxy group decreases as the π-electron-donating ability of the phenyl group becomes weaker, and are consistent with the arguments given above that delocalization into the aryl group provides a significant barrier to the reaction of the carbocations.

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(43) The carbomethoxy phenyl carbene has been observed previously in nonprotic organic solvents such as acetonitrile or Freon 112, in which it is rapidly quenched by alcohols.[44]

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Experimental Section

Materials. *trans*-2,3-Bis(carbomethoxy)-4,4′-dimethoxystilbene oxide,[46] methyl phenyldiazoacetate, methyl (4-methylphenyl)diazoacetate, and methyl (4-methoxyphenyl)diazoacetate[47] were prepared according to literature procedures. TFE and HFIP were commercially available (Aldrich) and were found to be sufficiently pure and dry for use without further treatment.

Flash Photolysis. An excimer laser (Lambda Physik, 248- or 308-nm, ca. 100 mJ per pulse, pulse width ca. 25 ns) was used as a laser excitation source. A detailed description of the laser system has been given elsewhere.[48-50] All experiments were carried out at room temperature, 20 ± 2 °C.

Product Study. A solution of the methyl (4-methoxyphenyl)diazoacetate (0.001 M) in aqueous solution was photolyzed with 254- or 313-nm light from a medium-pressure mercury lamp for 10 min, after which time no absorption due to the diazo compound at 280 nm remained. The samples were then directly analyzed with a Perkin-Elmer 8500 gas chromatograph (Permaphase PVMS/54 column). For GC−MS analysis, the same solution was extracted with a small amount of $CHCl_3$ followed by injection of the $CHCl_3$ layer into a Hewlett-Packard Model 5970 GC−MS. Samples for NMR analysis were prepared in a similar manner, except that the organic material was first extracted from the aqueous layer with diethyl ether. The ether layer was dried and then evaporated under reduced pressure. The residue was dissolved in $CDCl_3$ and the NMR spectrum taken with a Varian VX 300-MHz spectrometer.

GC−MS: 182 (15, M^+), 123 (100, $M^+ - CO_2CH_3$) ^{1}H-NMR, $CDCl_3$, δ ppm: 6.9−7.3 d of d (4 H), 5.1 s (1 H), 3.80 s (3 H), 3.73 s (3 H).

A solution of methyl phenyldiazoacetate (0.001 M) or methyl (4-methylphenyl)diazoacetate (0.001 M) in HFIP was photolyzed with 254-nm light from a low pressure mercury lamp for about 10 min. The samples were then directly analyzed byt GC−MS, which gave mass spectra corresponding to the following hexafluoroisopropoxy ethers.

Methyl (hexafluoroisopropoxy)phenylacetate: *m*/*e* (relative abundance), 316 (5, M^+), 257 (100, $M^+ - CO_2CH_3$), 149 (3, $M^+ - OCH(CF_3)_2$).

Methyl (hexafluoroisopropoxy)(4-methylphenyl)acetate: *m*/*e* (relative abundance), 330 (6, M^+), 271 (100, $M^+ - CO_2CH_3$), 163 (12, $M^+ - OCH(CF_3)_2$).

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