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Abstract: Benzyl (4-MeO, 4-Me, and 4-methoxy-1-naphthylmethyl), phenethyl (4-Me₂N, 4-MeO, 3,4-(MeO)₂, 4-Me, 3-Me, 4-F, 3-MeO, 2,6-Me₂, parent, and 4-methoxy-1-naphthylethyl) and cumyl (4-Me₂N, 4-MeO, 4-Me, parent) cations have been studied by laser flash photolysis (LFP) in 2,2,2-trifluoroethanol (TFE) and 1,1,1,3,3,3hexafluoroisopropanol (HFIP). In most cases styrene or α -methylstyrene precursors were employed for the phenethyl and cumyl ions, the intermediate being obtained by solvent protonation of the excited state. Benzyl cations were generated by photoheterolysis of trimethylammonium and chloride precursors. While a 4-MeO substituent provides sufficient stabilization to permit observation of cations in TFE, cations with less stabilizing substituents usually require the less nucleophilic HFIP. Even in this solvent, the parent benzyl cation is too short-lived (lifetime <20 ns) to be observed. When generated in HFIP, phenethyl cations can be seen to react with unphotolyzed styrene, giving rise to dimer cations that are observed to grow in as the initial phenethyl cation decays. The dimer cations, in common with the oligomer cations seen in cationic styrene polymerization, have a λ_{max} 15–20 nm higher than the monomer and react with both solvent and styrene several orders of magnitude more slowly. This stabilization relative to the phenethyl may reflect an interaction with the aryl group present at the γ -carbon. Cations 4-MeOC₆H₄C⁺(R)-CH₃ (R = Me, Et, i-Pr, t-Bu, cyclopropyl, C_6H_5 , 4-MeOC₆H₄) were generated in TFE via the photoprotonation route. The alkyl series shows that steric effects are important in the decay reaction. The cation with R = cyclopropyl is a factor of 1.5 less reactive than the cation where R = phenyl. Several vinyl cations have also been generated by photoprotonation of phenylacetylenes. ArC⁺=CH₂ has a reactivity very similar to that of its analog ArC⁺H-CH₃, the vinyl cation being slightly (factors of 2-5) shorter-lived. For the various series of cations, including vinyl, substituents in the aryl ring have a consistent effect on the λ_{max} , a shift to higher wavelength relative to hydrogen of 15 nm for 4-Me, 30 nm for 4-MeO, and 50 nm for 4-Me₂N.

Key words: photogenerated carbocations, carbocation lifetime, styrene, photoprotonation.

Résumé : Faisant appel à la photolyse éclair au laser (« LFP »), on a étudié les cations de type benzyles (4-MeO et 4-Me ainsi que 4-méthoxy-1-naphtylméthyle), phénéthyle (4-Me₂N, 4-MeO, 3,4-(MeO)₂, 4-Me, 3-Me, 4-F, 3-MeO, 2,6-Me₂ et le fondamental ainsi que le 4-méthoxy-1-naphtyléthyle) et cumyle (4-Me₂N, 4-MeO, 4-Me et le fondamental) dans le 2,2,2-trifluoroéthanol (TFE) et le 1,1,1,3,3,3-hexafluoroisopropanol (« HFIP »). Dans la plupart des cas, des précurseurs de type styrène ou α -méthylstyrène ont été utilisés pour les ions de type phénéthyle et cumyle, obtenus par solvatation de l'état excité à l'aide d'un solvant. Les cations de type benzylique ont été générés par photohétérolyse de précurseurs triméthylammonium et chlorure. Un substituant 4-MeO fournit assez de stabilisation pour permettre d'observer les cations dans le TFE; toutefois, pour observer des cations portant des substituants moins stabilisants, il faut utiliser le « HFIP » qui est moins nucléophile. Même dans ce solvant, le temps de vie du cation benzyle fondamental est trop court (<20 ns) pour qu'on puisse l'observer. Quand on les génère dans le « HFIP », on peut observer la réaction des cations phénéthyles avec le styrène qui n'a pas réagi; cette réaction donne lieu à la formation de cations dimères dont on observe la croissance avec la décroissance du cation phénéthyle initial. Les cations dimères, comme les cations oligomères observés lors de la polymérisation cationique du styrène, ont un λ_{max} de 15 à 20 nm plus élevé que celui du monomère et leurs vitesses de réaction avec le solvant et le styrène sont de plusieurs ordres de grandeur plus faibles. La stabilisation relative du phénéthyle peut être un reflet d'une interaction avec le groupe aryle

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Received April 19, 1999.

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présent sur le carbone γ . On a généré les cations 4-MeOC₆H₄C⁺(R)-CH₃ (R = Me, Et, i-Pr, *t*-Bu, cyclopropyle, C₆H₅, 4-MeOC₆H₄) dans le TFE par le biais d'une réaction de photoprotonation. Les séries alkyles montrent que les effets stériques sont importants dans la réaction de désactivation. La réactivité du cation avec R = cyclopropyle est 1,5 fois moins grande que celle du cation dans lequel R = phényle. On a aussi généré plusieurs cations vinyliques par photoprotonation de phénylacétylènes. La réactivité d'ion ARC⁺=CH₂ est très semblable à celle de son analogue ArC⁺H-CH₃, le temps de vie du cation vinylique étant légèrement plus court (de 2 à 5 fois plus court). Pour les diverses séries de cations, y compris le cation vinyle, les substituants du cycle aromatique apportent un effet régulier sur le λ_{max} , soit des déplacements d'environ 15 nm (pour le 4-Me), 30 nm (pour le 4-MeO) et de 50 nm (pour le 4-Me₂N) vers une longueur d'onde plus grande par rapport au produit fondamental, portant un hydrogène.

Mots clés : carbocations photogénérés, temps de vie d'un carbocation, styrène, photoprotonation.

[Traduit par la Rédaction]

Laser flash photolysis (LFP) has been employed for a number of years for the observation of reactive intermediates and for the direct measurement of rate constants of their decay reactions. Photolyzing some precursor with a laser pulse initiates a rapid photochemical transformation to the reactive species of interest. This is detected by some method, in most cases absorption spectroscopy, and the decay directly monitored. In recent years, a number of applications involving carbocations have appeared, with the intermediate being generated and directly studied under normal solvolytic conditions, i.e., with water or an alcohol as solvent (1, 2). In this respect, detailed studies have been reported involving species such as xanthylium (3, 4), triarylmethyl (5-8), diarylmethyl (6-11), and fluorenyl cations (12-14). These ions are relatively conjugated, with the formal cationic center bearing at least two aromatic rings. Carbenium ions bearing a single stabilizing aryl ring are inherently more reactive, and thus in principle more difficult to study. In spite of this, such cations are accessible by LFP under appropriate conditions, and in two preliminary communications we have outlined aspects of this work (15, 16). This paper provides the full details, with a discussion of the photochemical methods employed to generate such cations in LFP experiments, and a comparison of the effect of solvent, cation structure, and aryl substituent. Comparisons with analogous vinyl cations are also presented.

Results and discussion

In total, 32 cations have been investigated. Table 1 provides their structure, absorption maxima, and decay rate constants in 2,2,2-trifluoroethanol (TFE) and (or)1,1,1,3,3,3-hexafluoroisopropanol (HFIP). These solvents are necessary with most of the ions in Table 1, since their lifetimes in more nucleophilic solvents such as methanol, ethanol and water are less than 20 ns, the limit of detection with our LFP apparatus. Even then a 4-methoxy substituent (or 4-Me₂N) is usually required for the cation to be observed in TFE, and the less stabilized ones require HFIP. Changing from TFE to HFIP increases the lifetime by a factor of 10^3 – 10⁴. Water, on the other hand, is three orders of magnitude more reactive than TFE.

4-Methoxyphenethyl cation

Two general photochemical routes were employed, styrene photoprotonation and photoheterolysis, and the results with the 4-methoxyphenethyl cation are typical. PhotoproScheme 1.



tonation, where it can be used, is the better method. This possibility was suggested through the observation of Markovnikov hydration upon irradiation of styrenes in aqueous acid, with the proposed mechanism involving protonation of the excited styrene to give intermediate phenethyl cations (17–19). With TFE (and HFIP) as solvent, addition proceeds smoothly without added acid, as illustrated in Scheme 1 for 4-methoxystyrene **1** where the ether **3** is the only product (Scheme 1). The protonation must be occurring with the solvent OH proton. This is perhaps not surprising, since the protonation of excited styrenes is general-acid catalyzed with a relatively small Bronsted α value (19).

LFP of 4-methoxystyrene in TFE reveals a relatively strong transient with λ_{max} at 340 nm, coupled with significant negative optical density below 300 nm (Fig. 1A). The bleaching signal is the negative of the spectrum of 4-methoxystyrene and arises from use of the precursor solution as the optical density reference. The absorbance changes measured immediately after the laser pulse at both 340 and 255 nm are linear in laser intensity, indicating the occurrence of a monophotonic process. The absorbance above 300 nm decays to essentially zero at all wavelengths with the same rate constant of $(3.9 \pm 0.3) \times 10^5$ s⁻¹. This implies a single transient, and we assign this to the 1-(4-methoxy-

Table 1. Absorption maxima and rate constants (20°C) for cumyl, phenethyl, benzyl and 1-phenylvinyl cations obtained by 248 nm laser flash photolysis.

Ar-subst.	R ₁ , R ₂	λ_{\max}^{a} (nm)	$k_{\rm TFE}~({\rm s}^{-1})$	$k_{\rm HFIP}~({\rm s}^{-1})$	$k_{\rm nuc} \ ({ m M}^{-1} \ { m s}^{-1})$
Cumyl and phen	ethyl cations ArC ⁺ (R ₁)-	·CH ₃ ^b			
$4-\text{Me}_2\text{N}^c$	Me	380	$(1.5 \times 10^2)^d$	$< 10^{2}$	$2.4 \times 10^7 (N_3)^d$
$4 - Me_2N$	Н	360	$(4.0 \times 10^{1})^{e}$	$< 10^{2}$	$1.6 \times 10^7 (N_3^{-})^e$
4-MeO	$4-MeOC_6H_4$	330 (w), 490	1.3×10^2	$< 10^{2}$	$8.2 \times 10^8 (N_3^{-})^f$
4-MeO	cycPr ^g	380	3.3×10^2	$< 10^{2}$	$2.5 \times 10^9 (N_3^{-})^f$
4-MeO	C ₆ H ₅	320 (w), 440	5.1×10^2	$< 10^{2}$	$2.7 \times 10^9 (N_3^{-})^f$
4-MeO	i-Pr	365	3.0×10^3	$< 10^{2}$	$5.0 \times 10^7 (\text{Br}^{-})^{h,i}$
4-MeO	Et	365	9.0×10^3	$< 10^{2}$	$1.2 \times 10^8 (\text{Br}^{-})^{h,i}$
4-MeONap ^j	Н	320, 420	$7.5 imes 10^3$	$< 10^{2}$	$5.1 \times 10^9 (N_3^{-})^f$
4-MeO	Me	360	$1.6 imes 10^4$	$< 10^{2}$	$1.1 \times 10^8 ~({\rm Br}^{-})^{h,i}$
			$(4 \times 10^7)^{d,k}$		
4-MeO	t-Bu	370	1.6×10^{4}	$< 10^{2}$	$2.2 \times 10^8 (\text{Br}^-)^{h,i}$
Н	Ph	310 (w), 420	$1.5 imes 10^5$	3×10^2	$2.1 \times 10^9 (\text{Br}^-)^h$
3,4-(MeO) ₂	Н	345, 430 (w)	2.1×10^{5}	2×10^2	$2.5 \times 10^9 (\text{Br}^{-})^h$
4-MeO	Н	340	3.9×10^5	2×10^2	$4.5 \times 10^9 (\text{Br}^{-})^h$
4-Me	Me	340, 380 (sh)	1.0×10^7	6×10^2	$1.3 \times 10^9 (\text{Br})^l$
Н	Me	325, 400 (w)	$>5 \times 10^{7}$	9×10^{3}	$6.7 \times 10^9 \; (\mathrm{Br}^{-})^l$
2,6-Me ₂	Н	315, 475 (w)	$>5 \times 10^{7}$	3×10^4	$9.8 \times 10^9 (\text{Br}^{-})^l$
4-Me	Н	325, 390 (w)	$>5 \times 10^{7}$	$7 \times 10^{4^{m}}$	$7.1 \times 10^9 (\text{Br}^{-})^l$
4-F	Н	320	$>5 \times 10^{7}$	$2 \times 10^{5^{m}}$	$8.9 \times 10^9 (\text{Br}^{-})^l$
3-Me	Н	320, 430 (w)	$>5 \times 10^{7}$	$2 \times 10^{5^{m}}$	$9.7 \times 10^9 \; (\mathrm{Br}^{-})^l$
Н	Н	315, 410 (w)	$>5 \times 10^{7}$	$4 \times 10^{5^{m}}$	$8.2 \times 10^9 (\text{Br}^{-})^l$
3-MeO	Н	335, 390 (sh)	$>5 \times 10^{7}$	5×10^5	$5.8 \times 10^9 (\text{Br}^{-})^l$
Benzyl cations A	ArCH ₂ ⁺				
4-MeONap ^{j,n}	-	305, 400	$1.8 imes 10^5$	0	$4.9 \times 10^9 (N_3)^{f}$
$4-\text{MeO}^n$		320, 360 (sh)	4.3×10^{6}	3×10^2	$4.8 \times 10^9 (\text{Br}^{-})^l$
$4-Me^p$		310, 410 (w)	$>5 \times 10^{7}$	2×10^{6}	$1.0 \times 10^{10} (\text{Br})^{l}$
1-Phenylvinyl cat	tions ArC ⁺ =CR ₁ R ₂				
$4-\text{MeO}^q$	Ph, Ph	340	$1.4 imes 10^4$	$<1 \times 10^2$	$6 \times 10^6 (\text{Br}^-)^h$
$4-MeO^q$	Me, Me	330	2.3×10^{5}	$<1 \times 10^{2}$	$2.2 \times 10^8 (\text{Br}^{-})^h$
$4-\text{MeO}^r$	Н, Н	335	$1.3 imes 10^6$	3×10^2	$2.3 \times 10^9 (\text{Br}^{-})^h$
H^q	Ph, Ph	310, 410 (w)	$>5 \times 10^{7}$	2×10^4	$8.2 \times 10^8 \ ({\rm Br}^{-})^l$
$2,4,6-\text{Me}_3^{r,s}$	Н, Н	305, 420 (w)	$>5 \times 10^{7}$	4×10^4	$4.8 \times 10^9 (\text{Br}^{-})^l$
4-Me ^r	Н, Н	315, 350 (sh)	$>5 \times 10^7$	3×10^5	$9.2 \times 10^9 (\text{Br}^{-})^l$
\mathbf{H}^{r}	H, Ph	310, 390 (w)	$>5 \times 10^7$	6×10^5	$1.1 \times 10^{10} (\text{Br})^{l}$
\mathbf{H}^{r}	Н, Н	295, 360 (w)	$>5 \times 10^7$	2×10^{6}	$1.0 \times 10^{10} (\mathrm{Br}^{-})^{l}$

 a w = weak; sh = shoulder.

^bPrecursor unless otherwise noted is ArC(R)=CH₂.

^cPrecursor is 4-Me₂NC₆H₄CMe₂CMe₂C₆H₅.

^dSolvent is 2:1 (v:v) water: acetonitrile. Note that a similar value for k_s is expected in pure water, since k_{decay} in water: acetonitrile does not vary a great deal with solvent composition (ref. 6).

^eSolvent is 50:50 water:TFE.

^fSolvent is 10:90 water:TFE.

^gCyclopropyl.

^hIn TFE.

^{*i*}Addition of bromide is reversible.

^{*j*}4-Methoxy-1-naphthyl.

^kPrecursor is (4-MeOC₆H₄CMe₂)₂.

¹In HFIP.

^mBased on extrapolation to zero styrene concentration.

"Precursor is trimethylammonium BF₄⁻ salt.

"Not examined.

^{*p*}Precursor is 4-MeC₆H₄CH₂Cl.

^qPrecursor is ArC(Br)C=CH₂.

^rPrecursor is ArC=CR₁.

^sIdentical behavior from ArC=CH and ArC(Cl)C=CH₂.

Fig 1. Transient spectra following 248 nm laser irradiation of 0.1 mM 4-methoxystyrene (A) and 1 mM 1-(4-methoxyphenyl)ethyl acetate (B – D) in TFE. Spectra B – D were obtained on the same solution; B, at a laser dose of 6 mJ and with oxygen saturation, C, 6 mJ and with argon, and D, 75 mJ and with oxygen saturation. Spectrum A was obtained at 25 mJ and with argon saturation. This spectra was unchanged on saturating with oxygen. The spectra in C and D, and the initial spectra in A and B were obtained at 50–100 ns after the laser pulse. The final spectra in A and B were obtained at 25–30 μ s.



Scheme 2.



phenyl)ethyl cation 2 implicated by the Markovnikov ether photo-product 3. The transient does exhibit kinetic behavior

characteristic of carbocations (2), being quenched by nucleophiles such as bromide and azide, while oxygen has no effect.

Additional evidence is the observation of the same intermediate from a different precursor, 1-(4-methoxyphenyl)ethyl acetate 5 (Scheme 2). The photochemical reaction here is a photoheterolysis, and, as is typical of this route (2, 6), there are competing photo-reactions. Thus, as shown in Fig. 1C, irradiation of the ester results in two transients, the one with λ_{max} at 340 nm and a second at 275 nm. The former is the same as the transient from the styrene precursor. It has an identical spectrum, decays in TFE alone with the same rate constant, $(4.2 \pm 0.4) \times 10^5$ s⁻¹, and is quenched in an identical manner by bromide and azide ions. The 275 nm transient does not decay by exponential kinetics in argon-saturated solution and, while nucleophiles have no effect, oxygen is a very effective quencher. In fact, in the experiment in oxygen-saturated TFE, the 275 nm signal is no longer seen (Fig. 1B). This intermediate can be assigned as the 1-4methoxyphenethyl radical 6, the result of a competing photohomolysis. At higher laser doses additional absorbances appear: a band with λ_{max} near 295 nm and a second smaller broad peak at 400-500 nm. The 295 signal overlaps that of the radical but can be seen clearly in experiments with oxygen saturation (Fig. 1D). The two new bands appear to represent the same intermediate, since they decay with the same rate constant, with $k \sim 1 \times 10^5 \text{ s}^{-1}$. A clue to the identity is the square dependence on the laser dose of the

%(v/v) TFE	k_{decay} (s ⁻¹)	% Ether product	Initial OD (340 nm) ^a
100	4.0×10^5	100	1.00
95	$1.5 imes 10^6$	90	0.85
90	$3.6 imes 10^6$	80	0.70
80	6.3×10^{6}	40	0.60
70	$9.6 imes 10^6$	Trace	0.50
60	1.3×10^7	0	0.40

Table 2. Effect of water on the irradiation of 4-methoxystyrene.

"Relative to 100% TFE. This is equivalent to a relative quantum yield, since the measurements involve solutions of the same concentration of styrene being irradiated at 248 nm under identical conditions.

optical densities measured at 420 nm. This points to a biphotonic process, and suggests that this intermediate is the cation radical **7**, the result of a two-photon ionization. In fact the spectrum is that expected for the cation radical of an anisole derivative (20). The 340 nm transient on the other hand follows a linear dependence on laser intensity. Thus, as summarized in Scheme 2, the initial excited state, presumably the singlet, reacts to produce the cation and radical and, in competition, is further excited resulting in electron ejection. These experiments do not distinguish mechanisms for the formation of the cation and radical. There is the suggestion with benzyl carboxylates, including 4-methoxybenzyl acetate, that the primary event is photohomolysis with the cation being subsequently produced by electron transfer within the so-formed radical pair (21, 22).

A important feature with the styrene precursor is that there is no return of the absorbance below 300 nm as the cation decays back to the baseline above 300 nm. This is consistent with studies of thermal alkene additions that show that protonation in general is irreversible (23). In other words, the cation reacts predominantly by solvent addition, with little styrene being regenerated by elimination of a proton at the β -position.

As expected, addition of water significantly increases the rate constant for the decay of the cation. In addition, the alcohol **4** is produced at the expense of the ether (Table 2). Interestingly, the initial increase in rate constant is much greater than predicted on the basis of the amount of alcohol product. For example, 10% water results in only 20% of the alcohol product, but the rate constant for the decay of the cation is increased by almost 10-fold. This is consistent with a mechanism where, in addition to its direct nucleophilic combination, water accelerates the decay of the cation by acting as a general base to assist the TFE addition (24). Water also decreases the quantum yield for photoprotonation, as shown in the last column of Table 2. Coupled with the rate accelerating effect, this makes it increasingly difficult to study the cation in highly aqueous mixtures.

Substituted phenethyl cations by styrene protonation

In the same way, other phenethyl and cumyl cations are observed upon irradiation of the appropriate substituted styrene in TFE and (or) HFIP. Spectra of three cumyl cations and a naphthalene derivative are shown in Figs. 2 and 3A respectively. The other examples are available as supplementary material.² These show the same features discussed above for 4-methoxystyrene — a positive absorbance above 300 nm representing a single intermediate as shown by common decay kinetics across the entire spectrum,³ effective quenching by bromide⁴ and (or) azide ion, and bleaching due to depletion of the precursor. Spectra under stable ion conditions are available for the cumyl cation, $\lambda_{max} = 326$ and 390 nm ($\epsilon = 11\,000$ and 1400 respectively) and the 1,1diphenylethyl cation, $\lambda_{max} = 312$ and 422 nm, ($\epsilon = 11\ 050$ and 37 000 respectively) (25). The essentially identical spectra obtained here provide further confidence in the assignment of cation intermediates (see the spectrum for the cumyl ion in Fig. 2).

A further feature in common with 4-methoxystyrene is the lack of return of the bleaching as the absorbance of the cation decays. Thus the cations in general react by solvent addition. One exception is the 2,6-dimethylphenethyl cation where a competing deprotonation is indicated by the significant return of the precursor absorbance at the same rate constant as that obtained for cation decay. This aspect of 2,6-dimethyl systems has been recently demonstrated in a study of solvolysis of cumyl derivatives (26). While solvent addition is retarded by the steric effect of the *ortho* substituents, the rate constants for elimination are actually increased relative to analogs without the 2,6-dimethyl groups (26).

Styrene dimerization

The other exception occurs in HFIP with styrene and its 3- and 4-substituted derivatives. One indication of the difference is that the rate constants depend on the precursor concentration. This dependence is linear (eq. [1]), implicating a reaction of unphotolyzed precursor with the cation. With the

²Supplementary material may be purchased from: The Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, Ontario, Canada, K1A 0S2.

³ The one exception is α -*tert*-butyl-4-methoxystyrene, where the decay requires fitting to a double exponential, with rate constants of 7×10^5 and 1.6×10^4 s⁻¹. The spectrum of the intermediate responsible for the slow decay, obtained at longer times when the faster one is complete, shows a λ_{max} of 370 nm. This is assigned to the α -*tert*-butyl-4-methoxyphenethyl cation on the basis of the close similarity with the spectra of the other α -alkyl-4-methoxyphenethyl derivatives. The faster decaying transient has its λ_{max} between 330 and 340 nm and has not been identified.

⁴With some of the cations, bromide addition shows reversible behavior. This has been seen previously (5) and occurs when the ionization of the bromide product has a rate constant similar to the quenching rate constant. With the very stable cations where ionization of the C—Br bond becomes faster than nucleophile–cation combination, bromide does not react at all. These cations are still quenched by azide ion.



Table 3. Rate constants (20°C) for the reaction of phenethyl cations $X-C_6H_4CH^+-CH_3$ with the styrene $X-C_6H_4CH=CH_2$ in HFIP.

X	$k^{1}_{\text{sty}} (\mathbf{M}^{-1} \mathbf{s}^{-1})$
Н	1.0×10^{9}
3-Me	$9.4 imes 10^8$
4-F	$4.3 imes 10^8$
4-Me	3.4×10^8
4-MeO	$1.3 imes 10^{6}$

assumption (see Experimental) that the concentration of styrene is effectively unchanged in the laser pulse, the slopes of these plots (Table 3) are the second-order rate constants for the dimerization. The intercepts are the rate constants for the solvent reaction (the numbers in Table 1 for these cations).

[1]
$$k_{obs}/s^{-1} = k_{HFIP} + k_{stv}^1[ArCH=CH_2]$$

Spectral changes provide further evidence. Figure 4 shows an example where dimerization dominates and a high laser intensity is employed to provide strong signals. After the initial "prompt" bleaching at 240 nm, there is a further exponential decay occurring at the same rate as at the higher wavelengths. Thus additional styrene is reacting. Moreover as the cation decays, a new species appears. There is considerable overlap, but it is clear that this absorbs at a slightly higher wavelength, with a λ_{max} around 345 nm for the product in Fig. 4. Similar observations are made with the other ArCH=CH₂, with a shift of ~20–30 nm in each case. The new absorbance is much more stable than the original one but there is decay at very long times, for example, with styrene (at 340 nm) with a rate constant of ~0.1 s⁻¹. (This is

Fig. 3. Transient spectra following 248 nm irradiation of ~0.0001 M 4-methoxy-1-vinylnaphthalene (A) and 4-methoxy-1-napthylmethylammonium acetate (B) in argon-saturated TFE. Data points were obtained immediately after the laser pulse and at the completion of the exponential decay.



only approximate because of detector instability at very long times).

A similar situation has been observed for cations generated in strong acid solution. For example, when styrene is added to 98–100% sulfuric acid, the species observed is the bis-styryl cation, not the initially-formed phenethyl cation (27, 28). With α -methylstyrene, the cumyl cation is sufficiently stable to be seen, but it is not stable, reacting to give a new, long-lived, species with a higher λ_{max} identified as the bis-cumyl cation (27, 28). In a similar manner, we propose that phenethyl cations **9**, when generated by styrene photoprotonation in HFIP, react in part with residual styrene forming much more stable bis-styryl cations **10** (Scheme 3).

The dimerization is obviously the first step in the propagation sequence of the acid-initiated polymerization of styrenes. The dimer ions **10** in fact appear similar to the oligomeric **11** that have been detected during polymerization. With styrene, for example, the propagating cation has a λ_{max} of 340 nm (29, 30), the same as the cation **10** (X = H) observed in this work. One interesting observation is that the monomer ions **9** have a slightly slower λ_{max} . A possible explanation is that

Fig. 4. Transient spectra following 248 nm irradiation of 0.0004 M 4-methylstyrene in HFIP. The open circles were obtained immediately after the laser pulse and the closed circles at the completion (40 μ s) of the exponential process. The other two traces were obtained at intermediate times. The Inset shows the absorbance change at the three indicated wavelengths. The rate constants (s⁻¹) are 1.6×10^5 (240 nm), 2.0×10^5 (320 nm) and 1.85×10^5 (360 nm).



in **10** and **11** there is an interaction of the aryl group at the γ carbon with the positive charge at the α -carbon, as shown in structures in Scheme 3. Another interesting feature is that the dimer cation is much more stable than the monomer. This is also true of the oligomer. The rate constant for styrene propagation (k_{sty}^{pr} of Scheme 3) is ~10⁵ M⁻¹ s⁻¹ at 20°C (29, 30), four orders of magnitude slower than the rate constant k_{sty}^1 for the phenethyl cation reacting with styrene. It is interesting that the difference in stability between phenethyl and dimer/oligomer cations was suggested in 1968, and the interaction with the adjacent phenyl group in the latter proposed as the explanation (27).

We can be confident that it is the dimer cation **10** being observed at the end of the exponential process in the LFP experiments, and not an oligomer. One argument is based on the observation (Fig. 4) that the "slow" decay of styrene follows clean exponential kinetics, moreover reaching a stable absorbance at the completion of the change. If styrene were continually adding to a growing oligomeric cation, one would have expected a downward drifting absorbance. The other argument is that subsequent reactions with styrene are much slower than the first one, as discussed above. In other words, the reaction of the dimer cation with further styrene occurs on a much longer time scale than the initial reaction. Experimental limitations unfortunately preclude observation at long times at the lower wavelengths, i.e., where further depletion of styrene would be observed.

Cumyl cations do not show any sign of reacting with the residual α -methylstyrene in HFIP. This would appear to be a

Scheme 3.



steric effect, since the reactivities of both the cation and the nucleophile are not that different from the those in the $ArCH=CH_2$ series. There is no dimerization with any of the cations in TFE. Here the more nucleophilic solvent can successfully compete with the low concentrations of precursor.

Benzyl cations

Styrene photoprotonation cannot be applied for the generation of ArCH₂⁺; therefore we were forced to return to photoheterolysis. For 4-methoxybenzyl, both chloride and trimethylammonium (BF4- salt) precursors give a transient that can be assigned to the cation, although the former is limited to TFE solutions containing greater than 50% acetonitrile because of rapid ground state solvolysis. The cation is identified by several criteria. Its λ_{max} (320 nm, Fig. 5A) fits in a comparison with the 4-methoxyphenethyl (340 nm) and 4-methoxycumyl (360 nm) cations. The decay kinetics are typical of cations, a very efficient quenching by bromide, and a large difference between HFIP and TFE (Table 1). The same transient is observed with the two precursors, with the same decay rate constant, 9.0×10^6 s⁻¹ and 8.6 $\times 10^{6} \, \mathrm{s}^{-1}$ for the chloride and ammonium salt respectively in 1:3 TFE:acetonitrile. Finally, product analysis following irradiation of the ammonium salt in TFE shows the presence of 4-methoxybenzyl 2,2,2-trifluoroethyl ether, the product derived from trapping of the cation by solvent. The other product formed in about the same amount is 4-methylanisole. This indicates the presence of a radical intermediate as well (31, 32), and, in argon-saturated solvents, LFP of both precursors shows a large band with λ_{max} at 290 nm, presumably due to the 4-methoxybenzyl radical. With 4-methoxybenzyl acetate in TFE, only the 290 absorbance of the radical is seen at low laser doses, while, like the phenethyl analog, absorbance for a cation radical dominates at higher intensities. Thus, this precursor results in so little cation that the intermediate cannot be detected in competition with the other pathways. In fact, 4-methoxybenzyl acetate is known to result in only low yields of photosolvolysis product when irradiated in alcohol solvents (22, 33).

Fig. 5. Transient spectra following 248 nm irradiation of ~0.001 M 4-methoxybenzyl chloride (A) and 4-methylbenzyl chloride (B) in oxygen-saturated 1:3 TFE: acetonitrile and HFIP respectively. Triangles are the Δ OD immediately after the laser pulse, and squares, Δ OD at the completion of the exponential decay that is observed. The crosses are the difference in the two.



As shown in Fig. 3B, the 4-methoxy-1-naphthylmethyltrimethylammonium ion gives a strong signal that can be assigned to the primary cation. The evidence here is the efficient quenching by nucleophiles and the close similarity with the secondary cation obtained by photoprotonation. There is little indication of the presence of radical intermediate, as shown by very similar spectra being obtained under argon and oxygen.

For the 4-methylbenzyl cation, the chloride could be used as a precursor in HFIP. Spectra in oxygen-saturated solvent are shown in Fig. 5B. Below 300 nm a large non-decaying band of uncertain origin is observed. A shoulder above 300 nm does decay in an exponential fashion. By taking the difference between the initial and final absorbances, this species is found to have a λ_{max} of 310 nm with a weaker absorbance extending out above 400 nm. As will be discussed, this fits the expectation for this cation. The absorbance at 310 is quenched by bromide ion, with the ratio $k_{\rm Br}$: $k_{\rm HFIP}$ equal to $5.0 \times 10^3 {\rm M}^{-1}$. This allows for confirmation that this is due to the cation, through a comparison Scheme 4.



Table 4. Rate constants at 25° C for the solvolysis of 4-methylbenzyl bromide (20 μ M) in HFIP in the presence of tetrabutylammonium bromide.

[Bu ₄ N ⁺ Br ⁻]	$k_{\rm solv}~({\rm s}^{-1})$
0	$2.01 \times 10^{-4^a}$
0.0003	$8.26 imes10^{-5}$
0.0006	$5.15 imes10^{-5}$
0.0009	$3.92 imes 10^{-5}$
0.0012	2.94×10^{-5}
0.0015	2.32×10^{-5}

^aBased on initial rate.

with a ratio obtained from the kinetics of ground state solvolysis of 4-methylbenzyl bromide in HFIP. As shown in Table 4, added bromide results in significant common ion inhibition. By fitting to $k_{solv} = k_{ion}:(1 + k_{Br}:k_{HFIP}[Br])$, $k_{Br}:k_{HFIP}$ is found to be $(4.8 \pm 0.2) \times 10^3$, the same number obtained from the transient spectroscopy.

All attempts to generate detectable amounts of the parent benzyl cation in HFIP failed to provide any evidence of the cation. Precursors of benzyl chloride, benzyl bromide and benzyl acetate were employed. There were transients, but these could be attributed to radicals, or products from the radicals. A comparison of the 4-H and 4-Me derivatives in the phenethyl and cumyl series (Table 1) suggests that the benzyl cation is at least an order of magnitude more short-lived than 4-methylbenzyl. Thus the lifetime of PhCH₂⁺ in HFIP is less than 50 ns. Even if this were the lifetime, the cation would be very difficult to detect unless the photochemical route to it was very efficient.

Radical cation fragmentation

By using photoprotonation, the 4-methoxycumyl cation can be studied in aqueous TFE until about 70% water is **Fig. 6.** Transient spectra following 248 nm irradiation of 4dimethylaminobiscumene **13** in oxygen-saturated 2:1 water:acetonitrile. Closed circles obtained immediately after the laser pulse are attributed to the cation radical **13^{+•}**. Open circles obtained near the end of the completion of the exponential decay are due to the 4-dimethylaminocumyl cation **16**. Rate constants measured at 275, 380 and 500 nm are respectively 8.8×10^4 , 1.12×10^5 , and 1.03×10^5 s⁻¹, respectively.



present. At this point the cation decays with a rate constant of 7.9×10^6 s⁻¹, still below the 20 ns limit. However, the amount of intermediate being produced upon irradiation is so small that further increases in water content are not possible. To obtain a water rate constant, we turned to bis-4methoxycumene **12** as a precursor (Scheme 4). The photochemistry here involves a two photon ionization to the cation radical, which fragments within the laser pulse to cation **14** and radical **15** (34). With 2:1 water:acetonitrile as solvent, the cation can just be detected, with a decay of ~4 × 10^7 s⁻¹. While the acetonitrile is required in this experiment to dissolve the precursor, a similar decay is expected in pure water, because rate constants in water:acetonitrile do not vary a great deal with solvent composition (6).

The very stable 4-dimethylaminocumyl cation is generated from the biscumene **13** in the same water:acetonitrile mixture. In this case the cation radical is much more stable so that it is this species that is present after the laser pulse, and the fragmentation occurs on the microsecond time scale (Fig. 6). This observation has been reported previously (35), although the fragmentation of **13**⁺⁺ in the aqueous solvent of the present study is significantly faster than that for the same cation radical in solvents previously used. The 4-dimethylaminocumyl cation can be observed to grow in as the cation radical decays. This has a λ_{max} at 380 nm (382 nm, ref. 35), and a lifetime in the aqueous solvent of 7 ms.

Fig. 7. Spectra of vinyl cations $4-XC_6H_4C^+=CH_2$ obtained upon 248 nm laser irradiation of ~0.1 mM solutions of $4-XC_6H_4C\equiv CH$ — (A) X = H in HFIP, (B) X = Me in HFIP and (C) X = MeO in TFE. Δ OD values have been adjusted so that the maximum is 0.1 in each case.





Phenylacetylenes as precursors of vinyl cations

Laser flash photolysis of *p*-methoxyphenylacetylene in both TFE and HFIP, and p-methylphenylacetylene, 2,4,6trimethylphenylacetylene, diphenylacetylene, and phenylacetylene itself in HFIP results in transient spectra (see Fig. 7) that can be assigned to vinyl cations produced by photoprotonation (Scheme 5). With each precursor, there is a single intermediate, as shown by the absorbance above 300 nm decaying to near zero with the same rate constant at all wavelengths. Nucleophiles such as bromide ion have a pronounced quenching effect, evidence that these are cations. Vinyl cations, usually with two substituents on the β carbon, have been produced in the past by photoheterolysis of halide precursors (36-39). As seen in Table 1, the 1-(4methoxyphenyl)vinyl cation produced from the acetylene has a similar λ_{max} to that of the 2,2-dimethyl analog produced from the bromide. Even more compelling is the case of the 2,4,6-trimethylphenyl derivative, where the same cation was produced in the two different ways. Like styrenes, substituted phenylacetylenes have been shown to undergo photo**Fig. 8.** Substituent effect on the λ_{max} for benzyl, phenethyl, cumyl, 1-phenylvinyl, and 2,2-diphenyl-1-phenylvinyl cations. See text for explanation of *x* axis. Lines have been drawn with a slope of unity.



hydration in aqueous acids, with the ultimate product an acetophenone (17, 18). Flash photolysis investigations have revealed the presence of the enol intermediate (40–42), the immediate product of the hydration of the vinyl cation. The cations themselves were not detected. As discussed above, they would be too short-lived in water for detection by ns LFP.

Absorption maxima

Substituents affect λ_{max} in the order H < 4-Me < 4-MeO < 4-Me₂N. The effect is essentially the same for a given type of cation with, on average, a shift relative to H of 15 nm for 4-Me, 30 nm for 4-MeO, and 50 nm for 4-Me₂N. This is demonstrated in Fig. 8 where the observed λ_{max} are plotted against these factors. Recognizing that λ_{max} is only determined to ±5 nm, the correlations are excellent. Also apparent from this figure are the similar λ_{max} values for the vinyl and benzylic series. This was previously commented upon in a comparison of the 4-methoxy-substituted ions (15). In an arylvinyl cation, the π systems of the aryl ring and the alkene are orthogonal to one another (43). Thus the aryl ring interacts with the formally empty *p* orbital on the α -carbon in exactly the same way as it does in a benzylic cation.

For the same aryl group, the order of λ_{max} is $ArCH_2^+ < ArCHMe^+ < ArCMe_2^+$, with about a 20 nm difference between each pair. A weaker absorbance at higher wavelength is also apparent with some of the systems. The trend appears to be exactly opposite that of the larger absorbance at lower wavelength, and this is true both in terms of the aryl substituent and the α -methyl substituents. In fact the band at higher wavelength is usually not visible for the 4-MeO and 4-Me₂N substituted cations.

There has been some question as to the spectrum of the parent benzyl cation. An early theoretical calculation showed bands at 400-500 nm and 300 nm, with the latter being significantly stronger (44). This paper also suggested that a report of the benzyl cation in strongly acidic solutions (45) was incorrect. In agreement with the more intense absorbance, a band at 290 nm assigned to the cation was observed in an experiment involving photodissociation in a mass spectrometer (46). A more recent pulse radiolysis experiment in neat benzyl chloride is also in agreement, suggesting a strong band at 303 ± 2 nm and a weak band near 500 nm (47). In contrast, there have been several assignments to the benzyl cation where the λ_{max} is around 360 nm. These are based upon experiments by Dorfmann and coworkers who claimed to have generated the benzyl cation by pulse radiolysis in chlorocarbon solvents (48-50). The basis of this assignment was quenching of the observed transient by nucleophiles, and the fact that the approach does work for the triphenyl- and diphenylmethyl cations. A similar band was then observed and assigned to the benzyl cation following photoionisation of benzyl bromide in an argon matrix (51), and upon photolysis of dibenzyl ketone in vacuum-dried Nafion membranes (52).

While the parent cation has not being observed in this work, the data in Table 1 clearly shows that it must have λ_{max} around 300 nm with a weaker absorbance extending into the visible spectrum. This is in agreement with the first set of results discussed in the previous paragraph. The ~360 nm transient cannot be the benzyl cation. The pulse radiolysis approach requires fragmentation of a cation radical and we suspect that under the conditions employed by Dorfman and coworkers this is not occurring. In fact this is exactly what happens when precursors of the 9-fluorenyl cation are employed; there is no fragmentation and the intermediate that is observed is the cation radical of the precursor (13). Based on estimated pK_R values, the 9-fluorenyl cation is more stable than benzyl (53). Thus, if the approach does not work for 9-fluorenyl it is unlikely to have worked for benzyl. It can also be noted that the nucleophilic reactivities of the 360 nm transient have been criticized as not being appropriate for the benzyl cation (54). As a final comment, we note that even in those cases where the ~300 nm absorbance for the benzyl cation has been observed, this is clearly not the only species present. In other words there has not yet being a study showing a clean spectrum of this cation.

Substituent effects on rate constants

(a) Vinyl vs. phenethyl cations

As was noted previously in the case of the 4-methoxy derivatives (15) there is remarkably little difference in the lifetime of a vinyl cation $ArC^+=CH_2$ relative to that of a phenethyl cation ArC^+H-CH_3 with the same aryl group. The vinyl cation is slightly more reactive, but the differences are only 3.3 (TFE) and 1.4 (HFIP) for Ar = 4-MeOC₆H₄, 4.4 for 4-MeC₆H₄ in HFIP, and 2.5 for C₆H₅ in HFIP. As with the explanation for the similar spectra, this is consistent with the idea that the aryl ring interacts with the *p*-orbital on the α carbon in exactly the same way in the two series. **Fig. 9.** Correlation of log k_{TFE} for 4-MeOC₆H₄C⁺(R)CH₃ vs. $E_{s}(R)$.



(b) α -Alkyl effects

For a given aryl group the rate constant for solvent addition follows the expected order cumyl < phenethyl < benzyl. Interestingly, the second methyl group exerts a greater kinetic stabilization than the first. In the 4-methoxy series in TFE, for example, there is a 11-fold difference between benzyl and phenethyl, but this increases to 24-fold for phenethyl and cumyl. The same comparisons for the 4-Me cations in HFIP lead to ratios of 28 and 120. This suggests that it is unlikely that it is electron donation alone that is important. A steric effect would account for the difference, the second methyl group increasing the steric bulk around the α carbon to such a degree that nucleophilic addition is hindered to an extent greater than that of the first methyl substitution.

While there is insufficient data to perform a detailed breakdown into steric and electronic contributions, steric effects are clearly important. As shown in Fig. 9, there is a good correlation of the data for 4-methoxyphenethyl cations in TFE against the Taft steric parameter E_s , and this includes the point for the secondary cation. The correlation against the polar parameter σ^* is marginally poorer. In particular, this requires a difference in rate constant smaller than the one observed between i-Pr and Et.

An additional steric effect is probably responsible for the deviation of the point for the *tert*-butyl derivative. In this case, unfavorable interactions between the *ortho* hydrogens and the *tert*-butyl group twist the aryl ring, diminishing the resonance interaction with the *p* orbital on the α carbon. In fact MM2 calculations indicate a twist of 80 degrees. This argument is reinforced by the slow rate of solvolysis of 3,3-dimethyl-2-phenyl-2-chlorobutane, which has also been attributed to steric inhibition of resonance (55).

(c) Cyclopropyl versus phenyl

While an α -cyclopropyl group on a carbocation is strongly stabilizing, there has been some dispute whether the effect is greater or less than that of phenyl (56). In terms of the reactivities of fully-formed cations, a series ArCH⁺-R where R = phenyl and cyclopropyl have been compared by

Table 5. Values of ρ^r , ρ^n , and r^+ obtained by fitting rate constants for solvent capture of 1-arylethyl cations to eqs. [2] and [3].

Parameter	HFIP	TFE:water ^a
$\overline{\rho^r}$	4.7	6.1
ρ^n	2.7	2.7
<i>r</i> ⁺	1.7	2.3

^aReference 58, as corrected in ref. 14.



LFP in TFE (57). For a given Ar, the reactivities are similar. However the phenyl series shows a greater effect of changing substituents in Ar. The result is that the cyclopropyl cation is slightly more stable (kinetically) when Ar is phenyl, but less stable when Ar is 4-methoxyphenyl.

The difference in the latter comparison is a factor of 10 (21 vs. 22 in Scheme 6). Interestingly, the methylated analogs 23 and 24 studied in this work show a slightly greater stabilization (1.5-fold) for the cyclopropyl system. This can be traced to the substitution of α -hydrogen with methyl resulting only in a threefold rate constant diminution in the diarylmethyl cation, but a 42-fold diminution in the arylcyclopropyl pair. We attribute this to steric inhibition of resonance in the former. In these cations, maximum stabilization occurs when both aromatic rings are fully planar with the plane of the α -carbon. We suspect that methyl substitution results in additional twisting, so that while there is electronic and steric stabilization due to the methyl group, this is compensated by some loss of resonance interaction. The steric problem is not as severe in the cyclopropyl series, since the cyclopropyl is perpendicular to the π system.

(d) Aryl substituent effects

Since the initial studies of Richard et al. (58) it has been known that rate constants for solvent capture of benzylic carbocations do not correlate with σ^+ , as might have been expected. This has been observed now with several systems (2). What occurs is that σ^+ considerably underestimates the stabilizing effect of *para* π -donors like 4-methoxy. This is revealed by fitting to the two parameter Yukawa–Tsumo equation (eq. [2]), where r^+ values significantly greater than 1 result. Fitting to the modified eq. [3] (18), ρ_r is found to be larger than ρ_n .

- [2] $\log (k/k_0) = \rho \{\sigma + r^+(\sigma^+ \sigma)\}$
- [3] $\log (k/k_0) = \rho_n \sigma^n + \rho_r (\sigma^+ \sigma^n)$

The study of Richard et al. (58) actually involved 1-arylethyl cations, with the rate constants being obtained through use of the azide-clock method in 1:1 TFE:water as solvent. Six

such cations were studied directly in HFIP in this work (Table 5). A comparison of the parameters obtained by fitting to the above equations is given in Table 5. Since the two series do not involve the same substituents, and, moreover, since there are a limited number of substituents in each, the two sets of parameters can be regarded as being equivalent. This is perhaps surprising since the cations are 10^{6} -fold less reactive in HFIP.

(e) Styrene dimerization

For the reaction of a substituted phenethyl cation with its precursor styrene, there is a decrease in rate constant with increased electron donation (Table 3). Because of the manner in which this experiment is performed, the substituent is changing in both the electrophile and the nucleophile, and thus there will be compensating effects. Increased electron donation will stabilize the cation but at the same time increase nucleophilicity of the styrene. What the data show is that the former is more important. This is consistent with studies of benzylic-type cations where data are available for the reaction in both the formation and decay directions, in particular the finding that there is imbalance in the reaction coordinate (2, 58). In the direction where the cation is the reagent, the resonance interaction has decreased at the transition state to a greater extent than bond making. The reverse is true in the direction forming the cation, where the developing resonance interaction in the cation lags. In the present case, it can be seen that a benzylic-type cation (9 in Scheme 3) is being replaced by a benzylic-type cation (10) where the positive charge is stabilized by the same aryl group. What we argue is that in the transition state, the resonance interaction in the reagent cation has diminished to a greater extent than the resonance interaction in the product cation that has developed. Thus, in changing from styrene to 4-methoxystyrene, the stabilizing effect of the 4-methoxy group is more important in the starting cation than it is in on the developing cation in the transition state. Thus, the initial state is stabilized more than the transition state and the reaction is slower.

Experimental section

TFE and HFIP were dried over 4 Å molecular sieves and distilled under nitrogen through a 40 cm Vigreux column prior to use. Water was purified with a Millipore-Q system. The nucleophiles tetrabutylammonium bromide and sodium azide were used as received.

Table 6 provides the precursors that were employed and their sources. In most cases the compounds were commercially available or were prepared by a literature method. Where the compounds were solids the mp was in agreement with values in the literature. The ¹H NMR spectra were in all cases fully consistent with the structure.

4-*Methoxy*-1-*vinylnapthalene* was prepared from 4-methoxy-1-napthaldehyde by reacting Tebbe's reagent following standard procedures (77–79). ¹H NMR (CDCl₃) δ (ppm): 3.99 (s, 3H), 5.33–5.39 (dd, 1H), 5.64–5.74 (dd, 1H), 6.79 (dd, 1H), 7.32–7.57 (m, 2H), 8.04–8.32 (m, 4H). HRMS: 184.0886 (calcd.: 184.0888). Anal. calcd.: C 84.75, H 6.56; found: C 84.70, H 6.60.

 α -Isopropyl-4-methoxystyrene was prepared by reacting Tebbe's reagent with 2-methyl-4'-methoxyacetophenone. ¹H NMR (CDCl₃) δ (ppm): 1.10 (d, 6H), 2.82 (sept., 1H), 3.82 (s, 3H), 4.97 (dd, 1H), 5.10 (dd, 1H), 6.86 (d, 2H), 7.31 (d, 2H). Elem. anal. calcd.: C 81.77, H 9.15; found: C 81.44, H 9.02.

4-Methoxybenzyl 2,2,2-trifluoroethyl ether was prepared by adding 4-methoxybenzyl chloride to 2,2,2,-trifluoroethanol containing pyridine. After removal of the solvent, the residue was taken up in ether, washed with water, dilute HCl, and water. The ether was dried over MgSO₄, and after filtering to remove the drying agent, the solvent removed. ¹H NMR (CDCl₃) δ (ppm): 3.75 (q, 2H), 3.79 (s, 3H), 6.90 (d, 2H), 7.28 (d, 2H). EIMS (70 ev), *m*/*z*: 220 (30%, M⁺), 189 (8%, M⁺ – OCH₃), 135 (12%, M⁺ – CH₂CF₃), 121 (100%, M⁺ – OCH₂CF₃).

4-Methoxyphenethyl 2,2,2-trifluoroethyl ether was prepared by irradiating a solution of 4-methoxystyrene in 2,2,2-trifluoroethanol until there was no more styrene left. The ether was isolated as described in the previous paragraph. ¹H NMR (CDCl₃) δ (ppm): 1.45 (d, 3H), 3.65 (q, 2H), 3.81 (s, 3H), 4.56 (q, 1H), 6.90 (d, 2H), 7.28 (d, 2H). EIMS (70 ev), *m*/*z*: 234 (32%, M⁺), 219 (100%, M⁺ – CH₃), 135 (80%, M⁺ – OCH₂CF₃).

Laser flash photolysis experiments were carried out with equipment in Mulheim and in Toronto. The carbocation precursors were photolyzed with 20 nanosecond pulses, typically of 30 mJ, of 248 (KrF*) or 308 nm (XeCl*) monochromatic light. A pulsed Xenon light provided the monitoring beam. This was passed through the cuvette containing the substrate, then through a monochromator onto a photomultiplier tube. The signal was digitized by Tektronix 7612 and 7912 transient recorders, and the digitized signal sent to various computers for data analysis. Stock solutions of the substrates of concentrations 0.1-0.01 M were prepared in acetonitrile or dichloromethane. A small amount of this solution was then added to the appropriate TFE, HFIP, or aqueous solution. This was then introduced into a flow cell apparatus, where, if desired, the solution was saturated with argon or oxygen by bubbling with the appropriate gas for 5-10 min. Absorption spectra were constructed point-bypoint, with the solution being flowed through the cuvette so that there was unreacted substrate of the same concentration at each wavelength. The average optical density over a small time period was then determined at each wavelength and plotted against the latter to generate the spectrum. Rate constants were obtained by fitting the decay data to the exponential equation. five to seven kinetic runs were performed with each solution and the rate constants averaged. Observed rate constants refer to $20 \pm 2^{\circ}C$, and were reproducible to $\pm 2\%$ in TFE and $\pm 10\%$ in HFIP. The nucleophile quenching experiments involved 5-6 solutions of tetrabutylammonium bromide or sodium azide varying in concentration from 5 \times 10⁵ to 0.001 M. Plots of the observed rate constant were linear in the concentration of the added nucleophile. The second-order rate constants were obtained as the least-squares slopes. The rate constants for the styrene quenching in Table 3 were obtained with initial styrene concentrations of 5×10^{-5} to 5×10^{-4} M. A low laser dose (5–10 mJ) was em-

Table 6. Cation precursors.

Cation	Precursor	Reference ^{<i>a</i>}
$\frac{1}{4-Me_2NC_6H_4C^+(CH_3)_2}$	$4-\text{Me}_2\text{NC}_6\text{H}_4\text{C}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{C}_6\text{H}_5$	59
$4-\text{Me}_2\text{NC}_6\text{H}_4\text{CH}^+\text{CH}_3$	$4-\text{Me}_2\text{NC}_6\text{H}_4\text{CH}=\text{CH}_2$	60
$(4-\text{MeOC}_6\text{H}_4)_2\text{C}^+\text{CH}_3$	$(4-\text{MeOC}_6H_4)_2\text{C}=\text{CH}_2$	61
$4-\text{MeOC}_{6}\text{H}_{4}\text{C}^{+}(\text{cycPr})\text{CH}_{3}^{b}$	$4-\text{MeOC}_6\text{H}_4\text{C}^+(\text{cycPr})=\text{CH}_2$	62
$4-\text{MeOC}_6\text{H}_4\text{C}^+(\text{C}_6\text{H}_5)\text{CH}_3$	$4-\text{MeOC}_6\text{H}_4\text{C}^+(\text{C}_6\text{H}_5)=\text{CH}_2$	64
$4-\text{MeOC}_6\text{H}_4\text{C}^+(\text{i-Pr})\text{CH}_3$	$4-MeOC_6H_4C^+(i-Pr)=CH_2$	New
$4-\text{MeOC}_6\text{H}_4\text{C}^+(\text{Et})\text{CH}_3$	$4-\text{MeOC}_6\text{H}_4\text{C}^+(\text{Et})=\text{CH}_2$	65
4-MeONapCH ⁺ CH ₃ ^c	4-MeONapCH=CH ₂	New
$4-\text{MeOC}_6\text{H}_4\text{C}^+(\text{CH}_3)_2$	$4-MeOC_6H_4C(CH_3)=CH_2$	66
	$\{4-\text{MeOC}_6\text{H}_4\text{C}(\text{CH}_3)_2\}_2$	67
$4-\text{MeOC}_6\text{H}_4\text{C}^+(t-\text{Bu})\text{CH}_3$	$4-\text{MeOC}_6\text{H}_4\text{C}^+(t-\text{Bu})=\text{CH}_2$	68
Ph ₂ C ⁺ CH ₃	$Ph_2C=CH_2$	Comm.
$3,4-(MeO)_2C_6H_3CH^+CH_3$	$3,4-(MeO)_2C_6H_3CH=CH_2$	Comm.
4-MeOC ₆ H ₄ CH ⁺ CH ₃	$4-MeOC_6H_4CH=CH_2$	Comm.
	4-MeOC ₆ H ₄ CH(OCOCH ₃)CH ₃	69
$4-MeC_{6}H_{4}C^{+}(CH_{3})_{2}$	$4-\text{MeC}_6\text{H}_4\text{C}(\text{CH}_3)=\text{CH}_2$	Comm.
$C_6H_6C^+(CH_3)_2$	$C_6H_5C(CH_3)=CH_2$	Comm.
2,6-Me ₂ C ₆ H ₃ CH ⁺ CH ₃	$2,6-Me_2C_6H_3CH=CH_2$	Comm.
4-MeC ₆ H ₄ CH ⁺ CH ₃	$4-\text{MeC}_6\text{H}_4\text{CH}=\text{CH}_2$	Comm.
$4-FC_6H_4CH^+CH_3$	$4-FC_6H_4CH=CH_2$	Comm.
3-MeC ₆ H ₄ CH ⁺ CH ₃	$3-MeC_6H_4CH=CH_2$	Comm.
C ₆ H ₅ CH ⁺ CH ₃	$C_6H_5CH=CH_2$	Comm.
4-MeOC ₆ H ₄ CH ⁺ CH ₃	$4-MeOC_6H_4CH=CH_2$	Comm.
4-MeONapCH ₂ ^{+c}	4-MeONapCH ₂ N ⁺ Me ₃ · ⁻ OAc	32
$4-MeOC_6H_4CH_2^+$	$4-MeOC_6H_4CH_2N^+Me_3\cdot BF_4^-$	70
	4-MeOC ₆ H ₄ CH ₂ Cl	Comm.
$4-\text{MeC}_6\text{H}_4\text{CH}_2^+$	$4-MeC_6H_4CH_2Cl$	Comm.
$4-MeOC_6H_4C^+=CPh_2$	4-MeOC ₆ H ₄ CBr=CPh ₂	71
$4-MeOC_6H_4C^+=CMe_2$	$4-MeOC_6H_4CBr=CMe_2$	72
$4-MeOC_6H_4C^+=CH_2$	$4-\text{MeOC}_6\text{H}_4\text{C}\equiv\text{CH}$	73
$C_6H_5C^+=CPh_2$	$C_6H_5CBr=CPh_2$	74
$2,4,6-Me_3C_6H_2C^+=CH_2$	$2,4,6-\text{Me}_3\text{C}_6\text{H}_2\text{C}\equiv\text{CH}$	75
	2,4,6-Me ₃ C ₆ H ₂ CCl=CH ₂	75
$4-\text{MeC}_6\text{H}_4\text{C}^+=\text{CH}_2$	$4-\text{MeC}_6\text{H}_4\text{C}\equiv\text{CH}$	76
C ₆ H ₅ C ⁺ =CHPh	$C_6H_5C \equiv CC_6H_5$	Comm.
$C_{6}H_{5}C^{+}=CH_{2}$	C ₆ H ₅ C≡CH	Comm.

^{*a*}Comm. = commercially available.

^{*b*}cycPr = cyclopropyl.

 c Nap = naphthyl.

ployed to minimize depletion of the precursor. This was verified by observing that the rate constants did not depend significantly on laser dose.

Acknowledgements

Financial support from the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged. We also thank Jim Pincock (4-methoxy-1naphthylmethylammonium acetate) and Joggi Wirz (4dimethylaminostyrene) for initial gifts of compounds.

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