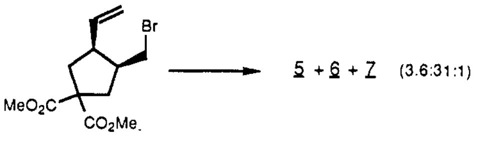
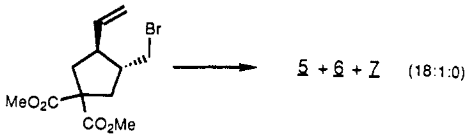


22 (20.1)



23 (14.1)

major product (9:1 cis to trans). Significantly, however, a small amount (2.2%) of the cyclohexyl isomer **7** was produced. As expected, the stereochemistry of bromomethylcyclopentane **23** (14:1 trans to cis) was not significantly altered upon reaction with stannane to give **5** as the major product (18:1 trans to cis). We conclude that there is a real, but small, intrusion of reversibility in allylic radical cyclizations, but that it does not appear sufficient to explain the difference in stereochemical results observed when germanes rather than stannanes are used to bring about cyclization.

Nanosecond Laser Flash Photolytic Generation and Lifetimes in Solvolytic Media of Diarylmethyl and *p*-Methoxyphenethyl Cations

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Although carbocations are intermediates of a number of photochemical reactions,[3] there has been only limited evidence[4] from flash photolysis for their presence, and the potential of this technique for directly studying this important class has not been exploited. We report here experiments showing that the title secondary cations can be observed in aqueous and alcohol solvents, and the rates of their reactions with solvent and azide ion directly measured. We also demonstrate that, at least in the examples reported here, ground-state cations are intermediates of both photosolvolyses and alkene photoprotonations.

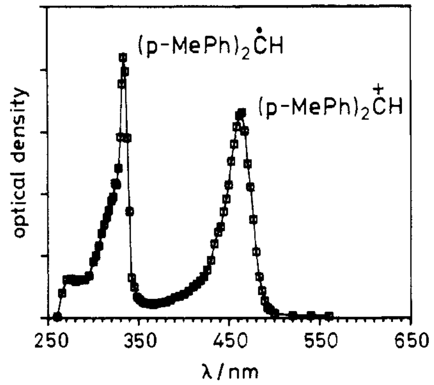

Figure 1. Transient absorption spectrum[5] measured 30–35 ns after the pulse on photolyzing $(4\text{-MeC}_6\text{H}_4)_2\text{CHOAr}$ in argon-saturated TFE. The band at 330 nm is due to $(4\text{-MeC}_6\text{H})_2\text{CH}^\bullet$, that at 465 nm to $(4\text{-MeC}_6\text{H}_4)_2\text{C}^+\text{H}$.

The diarylmethyl cations were produced by photoheterolysis,[5] with acetates and *p*-cyanophenyl ethers as precursors. Standard solvents were 20% by volume acetonitrile:water (1:4 AN:W) and trifluoroethanol (TFE). As illustrated in Figure 1, signals due to both cation and radical were typically observed. The cations, with λ_{max} at 400–500 nm, were identified by the match of these portions of the spectra with those obtained for stable cation solutions in 90% H_2SO_4. The decays of these transients were first-order, unaffected by O_2, and accelerated by azide. In addition, experiments with time-resolved conductivity detection exhibited characteristic[4d] increases in conductance in acid (release of H^+) and decreases in base (neutralization of OH^-), occurring with the same rate constants as those obtained with optical detection. The radicals were identified by their spectra[6] as well as by their second-order decay under argon with efficient scavenging by O_2. Mixtures of heterolysis and homolysis products are frequently encountered upon RX photolysis,[3a,b] and the two types of intermediate were observed with the majority of substrates we investigated (Table I). Not unexpectedly, a polar solvent was necessary for cation production. In pure AN, cations could still be observed, but the cation:radical OD ratios were only 0.1–0.2, considerably smaller than in the aqueous mixture. In CH_2Cl_2 only radical was seen. In all cases the cations were completely formed within the 20 ns laser pulse, which means that their rates of production from the precursors (including electronically excited cation) are $\geq 5 \times 10^7$ s^{-1}.

3,4′-Dimethoxydiphenylmethyl acetate proved exceptional in so far as a strong cation signal with little radical was seen upon photolysis. This is an example of the "meta" effect, the enhancement of photoheterolysis by a *m*-MeO group.[7] This effect was sufficiently pronounced so that cation was even observed with the alcohol as the precursor, while other diarylmethanols lcking the *m*-MeO gave only a radical signal. 9-Xanthenol also produced a good cation transient. There is evidence from fluorescence spectroscopy of photoheterolysis with this system and that the cation is initially formed in the excited singlet state.[8] The cations we observed must, however, be electronically relaxed. This can be concluded from the correspondence of the transient spectra with those obtained in acid, from the independence of the spectra and decay rates on precursor, from the observation of ground-state nucleophilic selectivity[9] and substituent effects, and, with the xanthylium ion, from the agreement with a ground-state rate constant.[10]

The *p*-methoxyphenethyl cation AnC^+HCH_3 was generated by photoheterolysis of the acetate in TFE, along with a considerable yield of radical. The same cation, however with no radical, was

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(5) Conditions: 20 ns pulses of 248-nm light (5–100 mJ), KrF excimer laser.[4d]

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(9) (a) For $4,4'\text{-(MeO)}_2\text{D}^+$ in MeOH, $k_{az}/k_s = (1.3 \pm 0.4) \times 10^3$ M^{-1}, as determined by product analysis upon solvolysis of the mesitoate.[9b] The directly measured ratio is $(1.1 \pm 0.1) \times 10^3$ (this work). (b) Ritchie, C. D. *J. Am. Chem. Soc.* **1971**, *93*, 7324–7325.

(10) k_s in $W = 1.4 \times 10^4$ s^{-1}, from T-jump spectroscopy. Wadsworth, T. M.S. Thesis, San Francisco State University, 1981. Graw, R. M.S. Thesis, San Francisco State University, 1985. Keeffe, J., personal communication.

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Table I. OD(cation):OD(radical) Ratios and Cation Decay Rate Constants (20 ± 1 °C)

cation[a]	precursor[b]	solvent	λ_{max} R^+, $R^\bullet$	$OD(R^+)/OD(R^\bullet)$[c]	k_s,[d] s^{-1}	k_{az},[e] M^{-1} s^{-1}
4,4′-$(MeO)_2D^+$	–OAc, –OAr	1:4 AN:W	500, 350	0.6[f], 0.6[g]	1.0×10^5[h]	$(4.2 \pm 0.2) \times 10^9$
		MeOH		0.4[g]	8.4×10^6	$(9.0 \pm 0.3) \times 10^9$
		TFE			1.4×10^1	
4-Me, 4′-$MeOD^+$	–OAc, –OAr	1:4 AN:W	475, 345	0.6[f], 0.5[g]	8.2×10^5[h]	$(6.7 \pm 0.4) \times 10^9$
		TFE		0.7[f]	2.8×10^2	
4-$MeOD^+$	–OAc, –OAr	1:4 AN:W	455, 345	0.6[f], 0.4[g]	2.0×10^6[h]	$(6.9 \pm 0.4) \times 10^9$
		TFE		0.5[g]	1.2×10^3	
3,4′$(MeO)_2D^+$	–OAc	1:4 AN:W	440, 345	≥10	2.5×10^6[h]	$(7.1 \pm 0.3) \times 10^9$
	–OH	W	440, 345	2.0	2.1×10^6[h]	$(7.2 \pm 0.5) \times 10^9$
4-CF_3, 4′-$MeOD^+$	–OAr	1:4 AN:W	440, 345	2.0	4.4×10^6	$(6.7 \pm 0.4) \times 10^9$
4,4′-Me_2D^+	–OAr	1:4 AN:W	460, 335	~1.0	3.2×10^7	$(6.5 \pm 1.0) \times 10^9$
		TFE		0.8	2.4×10^4	
4-MeD^+	–OAr	TFE	450, 335	0.6	2.7×10^5[h]	
D^+	–OAr	TFE	440, 330	0.3	3.2×10^6	
9-xanthylium(X^+)	–OH	W	365	>10	1.3×10^4	$(5.7 \pm 0.1) \times 10^9$
AnC^+HCH_3	–OAc	TFE	340, 300	~0.3	3.5×10^5[i]	$(5.6 \pm 0.5) \times 10^9$
	$AnCH{=}CH_2$	TFE	340	>10	3.7×10^5[h]	
$Ph_2C^+CH_3$	$Ph_2C{=}CH_2$	TFE	425	>10	1.6×10^5	

[a] $D^+ \equiv Ar_2CH^+$. [b] OAc ≡ acetate. OAr = *p*-cyanophenyl ether. [c] Measured 30–35 ns after pulse initiation. In order to calculate from this ratio the concentrations of cation and radical, the extinction coefficients for R^+ and $R^\bullet$ have to be known. [d] First-order rate constant for cation decay. [e] Second-order rate constant for reaction with azide, from slope of plot of *k*(decay) versus [azide] for 4–6 azide concentrations from 0–1 mm. [f] For OAc. [g] For OAr. [h] Optical and conductivity detection. [i] Conductivity detection only. Overlap with radical perturbs optical decay traces.

observed upon photolysis of *p*-methoxystyrene. This is an example of alkene photoprotonation,[3c] with the solvent presumably the proton donor. As a second example, the tertiary $Ph_2C^+CH_3$ was observed on photolyzing $Ph_2C{=}CH_2$ in TFE.

The parent diphenylmethyl cation, its mono 4-Me derivative, and AnC^+HCH_3 were observed on photolysis of the *p*-cyanophenolates or acetate in TFE but not in 1:4 AN:W, though products indicate cation intermediate. Thus, in the aqueous solvent these cations must decay within the 20 ns laser pulse. TFE may be an important solvent for the study of photochemical reactions involving cations, since it is sufficiently polar to support cation production but is significantly less nucleophilic than water. As shown by the one example in Table I, methanol as a solvent is more nucleophilic than water. The Ph_2CH^+ ion and even $PhCH_2^+$ have been seen with the use of pulse radiolysis in halocarbon solvents.[11] Such solvents, however, will make it difficult to photolytically produce cations, while in more polar solvents where they can be formed, cations can be short-lived, as shown with the examples noted above. As a further example, we have observed only $PhCH_2^\bullet$ upon photolysis under a variety of conditions of $PhCH_2OAc$ and $PhCH_2Cl$.

The high reactivity of azide makes it an excellent indicator of cation in time-resolved experiments. This nucleophile has seen extensive study in ground-state solvolysis reactions, with the azide:water ratios k_{az}/k_s as determined by product analyses being a widely cited example of a reactivity–selectivity relationship, in that less stable cations are less selective.[12] A recent interpretation is that for reactive cations the azide combination is diffusion-limited, so that changes in k_{az}/k_s merely reflect changes in k_s.[13,14] The measurements reported here provide a direct proof of this. The k_{az} values for the diarylmethyl cations in 1:4 AN:W are $(7 \pm 0.5) \times 10^9$ M^{-1} s^{-1}, with only the bis-*p*-methoxy derivative slightly below this limit. Azide has recently served as a "clock" for the determination of cation reactivities, the k_{az}/k_s product ratios being converted to absolute k_s values with the assumption that $k_{az} = 5 \times 10^9$ M^{-1} s^{-1}.[14] Our results also establish that this approach is valid, with the recognition that k_{az} limit is not uniformly 5×10^9 M^{-1} s^{-1}.[15]

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(15) This was not intended as a precise value.[14]

Total Synthesis of Both (+)-Compactin and (+)-Mevinolin. A General Strategy Based on the Use of a Special $TiCl_3/C_8K$ Mixture for Dicarbonyl Coupling

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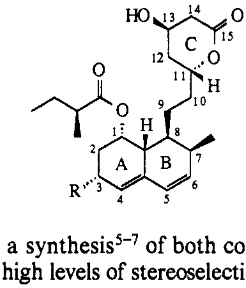
The two fungal metabolites (+)-compactin (**1a**)[2] and the biologically more powerful (+)-mevinolin (**1b**)[3] have been subject to intense scientific examination because of their relevance to the treatment of elevated levels of blood cholesterol.[3a,4]



1a R = H
1b R = Me

We report a synthesis[5–7] of both compounds by reactions that proceed with high levels of stereoselection. Our aim was to develop a method that could provide, without the need for extensive redesign, a variety of substances that differ in the nature of the

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[1] Dedication: To the memory of my father.