Table I. Selected Bond Distances and Angles in **5**(I)

	Bond Distances (Å)		
P-N1	2.771(4)	P-N3	1.620(3)
P-N2	1.636(3)	P-N4	1.618(3)
	Bond Angles (deg)		
N2-P-N3	110.8(2)	C3-N1-C6	118.0(3)
N2-P-N4	113.9(2)	C3-N1-C9	117.6(3)
N3-P-N4	115.5(2)	C6-N1-C9	122.5(3)

($N_{ax}C$). MS (FAB) m/z 305.2 (100, $[n\text{-BuSP(NMeCH}_2\text{CH}_2)_3\text{N}]^+$), 737.3 (1.5, $[(n\text{-BuSP(NMeCH}_2\text{CH}_2)_3\text{N})_2\text{I}]^+$).

Reaction of 11 with *i*-PrI. To a solution of **11** (0.050 g, 0.20 mmol) in acetonitrile (5 mL) was added *i*-PrI (0.5 mL). The solution was stirred at 50 °C for 84 h and evaporated in vacuo to give only the starting material **11**, as shown by ^{1}H NMR spectroscopy.

Measurement of Reaction Rates of 4 with RX. To an NMR tube containing **4** (0.063 mmol) and CD_3CN (0.7 mL) was added RX (0.063 mmol). ^{31} NMR spectra of the reaction mixture were recorded every 5 min. The reaction times for reaction completion were <5 min for MeI and $CH_2{=}CHCH_2I$, 20 min for *n*-EtI, 35 min for *n*-PrI, 55 min for *n*-BuI, >6 h for *i*-PrI, and >6 h for *n*-PrBr.

Crystal Structure Analysis of 5(I). A colorless crystal of the title compound was attached to the tip of a glass fiber and mounted on the diffractometer for data collection at -5 ± 1 °C. The cell constants for data collection were determined from a list of reflections found by an automated search routine.

Lorentz and polarization corrections were applied. A correction based on a decay in the standard reflections of 2.0% was applied to the data. An absorption correction based on a series of Ψ-scans was applied. The agreement factor for the averaging of the observed reflections was 1.8% (based on F).

The acentric space group $P2_12_12_1$ was indicated initially by systematic absences and intensity statistics.[19] The positions of the atoms were determined by direct methods.[19] All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were found by the difference Fourier technique and were placed at idealized positions 0.95 Å from the attached atom, with isotropic temperature factors set equal to 1.3 times the isotropic equivalent of that atom. The hydrogen atom positions were not refined. Selected bond distances and angles are given Table I.

Acknowledgment. The authors are grateful to the donors of the Petroleum Research Foundation, administered by the American Chemical Society, for a grant supporting this research. They also thank Dr. Victor G. Young, Jr. of the Iowa State Molecular Structure Laboratory for the solution by X-ray means to the structure of **5**(I) and to the W. R. Grace Company for a research sample of $(H_2NCH_2CH_2)_3N$.

Supplementary Material Available: Tables of complete bond lengths and angles, crystal data, and isotropic thermal parameters (7 pages); listing of observed and calculated structure factors (9 pages). Ordering information is given on any current masthead page.

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Electron-Deficient Carbocations. Direct Observation of α-Carbonylmethyl Cations by Laser Flash Photolysis[†]

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Abstract: The 9-carbomethoxyfluoren-9-yl cation was generated under stable ion conditions and characterized by spectral data (visible/NMR spectroscopy) and product identification of the benzene and toluene trapping reactions. The laser flash excitation of methyl α-bromodiphenylacetate and methyl 9-bromo-9-fluorenylcarboxylate generated both the corresponding cations and radicals. Rate constants for nucleophilic quenching by alcohols and bromide ion were measured for both the α-carbomethoxy cations and the unsubstituted diphenylmethyl and 9-fluorenyl cations. The results indicated an increase in kinetic stability upon replacement of α-hydrogen by α-carbomethoxy. Direct comparison of quenching rate constants in the same solvent showed an increase in reactivity of the 9-fluorenyl cations relative to the diphenylmethyl cations.

Introduction

Over the past decade, there has been wide interest in carbocations that have the positive charge center directly attached to an electron-withdrawing group.[1] Such cations have been considered as "destabilized carbocations" on electrostatic grounds and were believed to be intrinsically unstable so that they would form only with great reluctance under forcing conditions. However, recent studies[2-11] have shown that such cations can be formed, studied, and used for synthetic applications.

The carbonyl group is electron-withdrawing on the basis of the σ^+ values as measured from cumyl chloride solvolysis data, and yet very small rate-retarding and even rate-enhancing effects have been observed in solvolysis when this group is directly substituted on the potential carbocation center.[1] More recent studies have shown that bimolecular quenching rate constants for carbocations substituted by carbomethoxy and other electron-withdrawing groups such as trifluoromethyl do not vary significantly in com-

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[‡] National Research Council of Canada.

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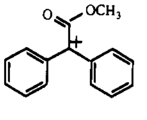
parison with the corresponding parent hydrogen-substituted analogues.[11] These seemingly contradictory observations have been rationalized in terms of π-resonance stabilization provided by the carbonyl group, neighboring group participation of the carbonyl group (oxyranyl cations), increasing resonance stabilization of aryl substituents (in aryl-substituted cations) due to an increase in electron-demand, and steric effects.

The 9-fluorenyl cation is thermodynamically unstable, largely due to its antiaromatic (4n π) character, and attempts to generate the parent ion under stable ion conditions in strong acid have not been successful.[12] With recent detection of transient carbocations generated by laser flash photolysis[13] (LFP), the fluorenyl cation has been observed directly and found to have a lifetime of less than 20 ps in aqueous solution.[14] Our interests in the observation of electron-deficient carbocations under stable ion conditions by low-temperature NMR methods[10] prompted us to investigate the possibility of observing such cations under LFP conditions and to measure their kinetic stabilities in different solvents. In this particular study we report the observation and kinetic stabilities of the diphenylcarbomethoxymethyl cation **1** and the 9-carbomethoxy-9-fluorenyl cation **2** by LFP in neutral solution. We also report the independent generation of cation **2** under strong acid conditions.



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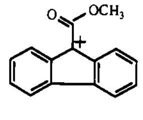

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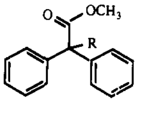
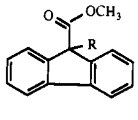
Results and Discussion

Continuous Irradiation and Product Analysis. The precursors to cations **1** and **2** were the corresponding bromides **3a** and **4a**, which were prepared by standard bromination methods (Br_2 in CCl_4 or NBS in CCl_4) from the corresponding esters **3b** and **4b**, respectively.



3a R = Br
b R = H
c R = OCH_3
d R = OH



4a R = Br
b R = H
c R = OCH_3
d R = OH

Table I. Comparison of ^{13}C-NMR Chemical Shifts of the Cation Carbon of Substituted Diphenylmethyl with 9-Substituted Fluoren-9-yl Cations

diphenylmethyl cation	$C^{\delta+}$	9-fluorenyl cation	$C^{\delta+}$
$(C_6H_5)_2C^+CH_3$	217.5[a]	Fl^+CH_3	228.0[a]
$(C_6H_5)_3C^+$	210.9[b]	$Fl^+C_6H_5$	224.2[a]
$(C_6H_5)_2C^+CO_2CH_3$ (**1**)	191.0[c]	$Fl^+CO_2CH_3$ (**2**)	192.0[d]

[a] Reference 12. [b] Reference 17. [c] Reference 10b. [d] This work.

Table II. Comparison of Absorption Maxima Between Diphenylmethyl and Fluoren-9-yl Cation (λ_{max})(solvent)

X	$(C_6H_5)_2C^+X$	9-Fl^+X
CO_2CH_3	489[a] ($CH_2Cl_2/ClSO_3H$)	578 (SbF_5/SO_2)
	465 (CH_3CN)	560 (HFIP)
H	440[b] (H_2SO_4)	515[c] (H_2O/CH_3OH)
	443[d] ($CH_2Cl_2/ClSO_3H$)	
	435[e] (CH_3CN)	
C_6H_5	432[f] (H_2SO_4)	486[g] (CF_3CO_2H)
	410[e] (CH_3CN)	
CH_3	422[b] (H_2SO_4)	485[c] (H_2O/CH_3OH)
	428[d] ($CH_2Cl_2/ClSO_3H$)	488[h] (H_2SO_4)

[a] Reference 10b. [b] Reference 18. [c] Reference 14. [d] Reference 19. [e] Reference 20. [f] Reference 21. [g] Reference 22. [h] Reference 23.

The continuous UV irradiation of bromide **3** in methanol solution (10^{-3} M) for 30 min resulted in complete conversion of starting material to two major products, the reduced ester **3b** and the methanol adduct **3c** in 20 and 30% yields, respectively. The remaining photoproducts were alcohol **3d** and an unidentified dimeric species. Photolysis of **3a** in aqueous acetonitrile solution gave **3b** and **3d** as major products with small amounts of an additional product not found in the methanol photolysis mixture. Under similar conditions the photolysis of **4a** in methanol gave the reduced ester **4b** and ether **4c** as major products (total yield 54%). The use of aqueous acetonitrile resulted in alcohol formation in place of ether **4c**. (All products were found to be photostable during the irradiation period, although some decomposition of **3c**, **3b**, **4c** and **4d** was observed on prolonged irradiation.) The dark reactions of **3a** and **4a** in either methanol or aqueous acetonitrile solutions did not result in any detectable solvolysis products over the same duration. The production of ethers **3c** and **4c** in methanol solution and alcohols **3d** and **4d** in aqueous acetonitrile solution suggests the intermediacy of carbocations **1** and **2**, respectively. The presence of the reduced esters **3b** and **4b** as well as a dimeric species in the photolysis of **3a** suggests the involvement of free radical intermediates; however, carbocations **1** and **2** could, in principle, also be involved and undergo hydride abstraction from the solvent.[15,16]

Generation of Ions 1 and 2 and Scavenging of Ion 2 under Stable Ion Conditions. In order to assign the UV/visible spectral characteristics of ions **1** and **2** by LFP, these were generated independently in strong acid solution at low temperatures and characterized by ^{13}C-NMR spectroscopy. The ^{13}C-NMR and UV/visible spectral assignments for ion **1** have been reported previously.[10b]

Carbocation **2** was prepared by mixing SO_2 solutions of the bromoester **4a** and SbF_5 at −78 °C. A reddish-brown-colored solution was observed. The ^{13}C-NMR spectrum of cation **2** exhibited two low-field signals at 192 and 187 ppm, which were assigned to the C-9 and carbonyl carbons, respectively, in addition to signals at 147–120 ppm attributable to the six nonequivalent aromatic carbons and a sharp signal at 67 ppm assigned to the methoxyl carbon. The chemical shift of 192 ppm of cation **2** is only slightly more deshielded than the benzylic cation carbon of diphenylcarbomethoxymethyl cation **1** (191 ppm). For the corresponding methyl- and phenyl-substituted derivatives a deshielding of 10–15 ppm is observed (Table I).

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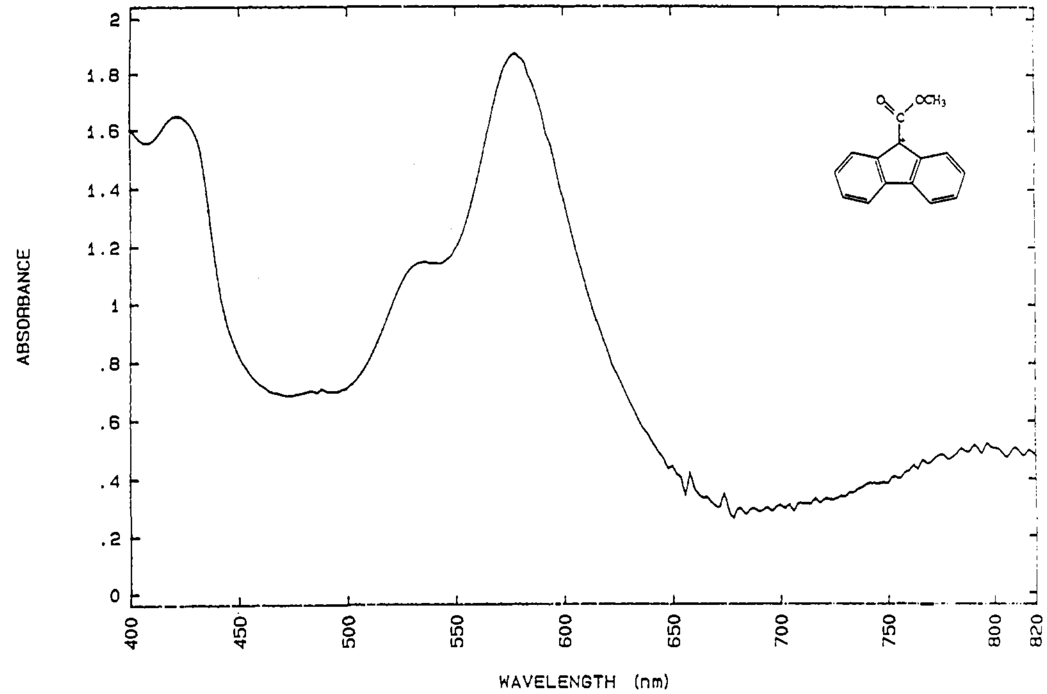


Figure 1. Visible absorption spectrum of cation **2** in SbF_5/SO_2 at −78 °C.

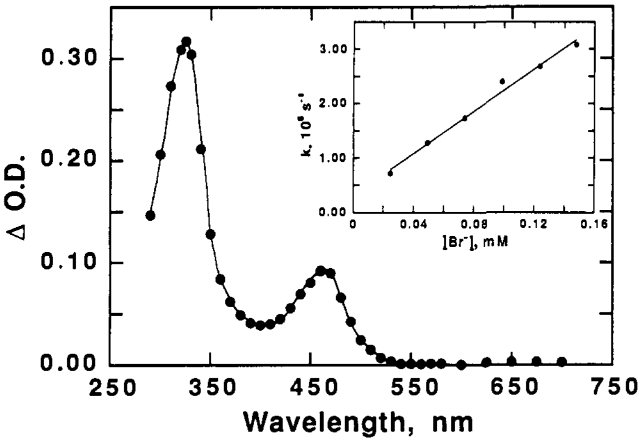


Figure 2. Transient absorption spectrum measured 0.5 μs after 266-nm excitation of bromoester **3a** in aerated acetonitrile. Inset: plot of the observed rate constant for decay of cation **1** at 465 nm as a function of the concentration of added bromide ion.

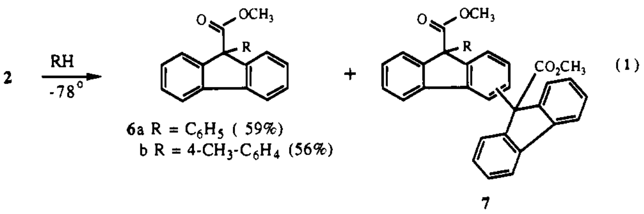
The smaller amount of deshielding on going from the open-form ion **1** to the closed-form **2** is perhaps indicative of a greater charge demand associated with the antiaromatic properties of the latter and the presence of σ-bridged forms **5a** and **5b**. This is also

5a 5b

reflected in the deshielding of the methoxy carbon in the ^{13}C-NMR spectrum of ion **2**. Such structures would suggest that σ-delocalization of charge may be more important than π-conjugation in these species. Such σ-bridged structures are not possible in the case of the methyl- and phenyl-substituted fluoren-9-yl cations.

The visible absorption spectrum of cation **2** (Figure 1) in SbF_5/SO_2 solution at −78 °C shows a maximum at 578 nm with a shoulder at 540 nm. The visible absorption profile of ion **2** is similar to that reported for the parent fluoren-9-yl cation, showing a maximum at 515 nm with a shoulder at 480 nm.[13f] The bathochromic shift of 88 nm in the visible absorption spectrum on going from the open diphenylcarbomethoxymethyl cation **1** to **2** is consistent with similar red shifts reported between the open-form diphenylmethyl cations and fluoren-9-yl cation (see Table II).

Quenching of cation **2** with benzene, toluene, or methanol gave the adducts **6a**, **6b**, and **4c**, respectively.



(1)

6a R = C_6H_5 (59%)
b R = 4-CH_3-C_6H_4 (56%)

7

In a control experiment, no observable methanolysis occurred for bromide **4a** under the same reaction conditions in the absence of SbF_5. This result suggests that bromide **4a** is not ionized in the absence of SbF_5. In addition, small amounts of dimeric adducts **7a** (24%) and **7b** (26%) were also isolated, indicative of incomplete quenching of cation **2** with bimolecular reaction occurring. The regiochemistry of **7** could not be assigned due to the complexity of their NMR spectra.

The ^{13}C-NMR data, the UV/visible spectrum, and the product analysis from quenching of cation **2** with nucleophiles suggest that this species exists as a free ion rather than an intimate ion pair.

Characterization of Ions 1 and 2 by LFP. Excitation (266 nm) of bromoester **3a** in air-saturated acetonitrile produces the transient absorption spectrum shown in Figure 2. There is a visible band with λ_{max} at 465 nm as well as a stronger absorption in the UV region with λ_{max} at 325 nm. There are obviously two transients since the decay kinetics at the two wavelengths are quite different.

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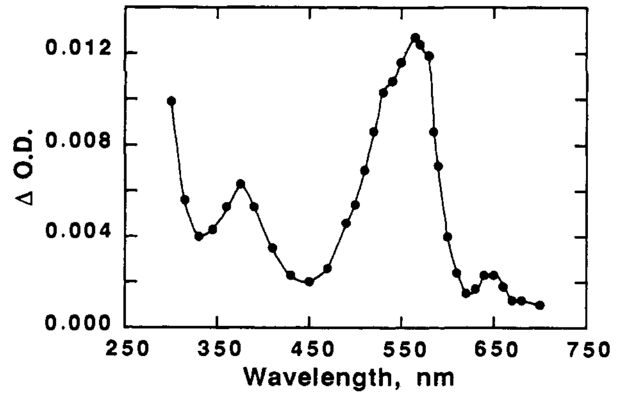


Figure 3. Transient absorption spectrum measured 0.5 μs after 266-nm excitation of bromoester **4a**.

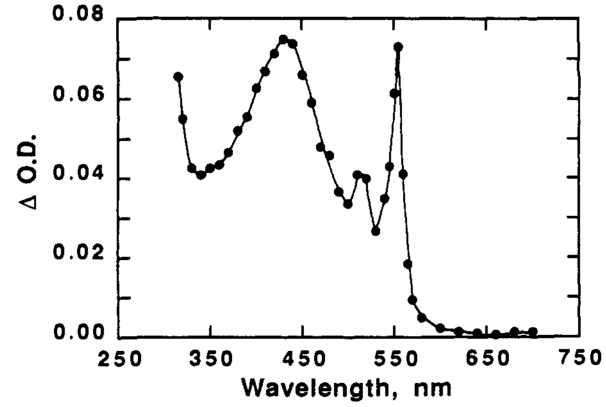


Figure 4. Transient absorption spectrum measured 1 μs after 308-nm excitation of bromoester **4a** in nitrogen-saturated cyclohexane.

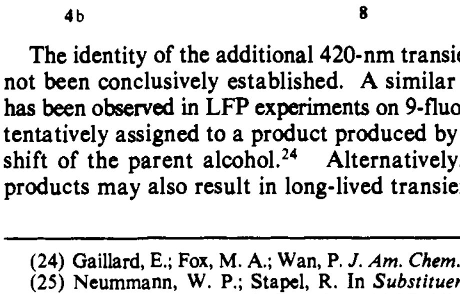
The visible band is assigned to cation **1** on the basis of the similarity to the spectrum for this species recorded in strong acid. Decay kinetics at 465 nm show that the cation decays within 10–20 μs and are reasonably well fit by second-order kinetics, consistent with scavenging of the cation by bromide ions produced by photolysis of the bromoester precursor. This was confirmed by separate quenching studies with external bromide ion (vide infra) in which quenching of the cation occurs with rates close to the diffusion-controlled limit (1.9×10^{10} M^{-1} s^{-1}, see inset in Figure 2).

The fact that cation **1** decays by reaction with bromide ions produced by photolysis of the precursor indicates that reaction with acetonitrile is substantially slower for **1** than for the parent diphenylmethyl cations.[20] The relative inertness of **1** toward reaction with acetonitrile is consistent with its decreased reactivity with other nucleophiles (vide infra) and attributable to a combination of steric and electronic effects. The assignment of the long wavelength transient to **1** is further supported by its insensitivity to oxygen and its rapid reaction with added nucleophiles, as outlined below. The 325-nm transient is long-lived in nitrogen-saturated solutions but decays much more rapidly in the presence of oxygen. Its lifetime is unaffected by 0.05 M methanol. This transient is assigned to the α-carbomethoxydiphenylmethyl radical formed by heterolytic cleavage of the C–Br bond in ester **3a**, on the basis of the above observations and its spectral similarity to the parent diphenylmethyl radical (λ_{max} at 335 nm).[20] It is also consistent with the radical-derived product **3b** observed in the continuous irradiation mixtures.

Excitation of bromofluorenyl ester **4a** at 266 nm in either acetonitrile or TFE did not give any readily detectable transients that could be assigned to a cation intermediate. In contrast, in hexafluoroisopropyl alcohol (HFIP) there is a species with λ_{max} at 560 nm (Figure 3) which decays with first-order kinetics with a lifetime on the order of 10 μs. The transient is assigned to cation **2** on the basis of its spectral similarity to the same species generated in strong acid and its reactivity with nucleophiles and lack of sensitivity to oxygen. The hypsochromic shift of ~20 nm for ions **1** and **2** in neutral solution relative to the same ions generated in strong acid is consistent with similar observations for diphenylmethyl cations (see Table II).[20] The spectrum in Figure 3 also shows an additional transient with a weak absorption at 650 nm and a stronger band at 370 nm that decays more slowly than the cation. These signals are assigned to the radical cation of **4a**, formed by photoionization, on the basis of the similarity of the results to those obtained previously for fluorene and 9-fluorenol.[13f]

The lifetime of cation **2** in HFIP varies substantially from one sample to the next and most likely reflects different water concentrations in the HFIP. There may also be some contribution due to reaction with bromide ion produced by photolysis of the precursor bromofluorenyl ester. In TFE/HFIP mixtures the lifetime of the cations was substantially reduced (300 ns in 1:1 TFE/HFIP), and in pure TFE it was not observed at all. This is consistent with literature results for the parent fluorenyl cation, which was not observable in TFE on a nanosecond time scale.[13f] It should also be noted that under our experimental conditions lifetimes on the order of 10–15 μs were typical for the 9-fluorenyl cation generated from 9-fluorenol. These are considerably shorter than the literature value of 30 μs and reflect the fact that the HFIP used in these experiments was not dried. As a result of the varying water content and the potential reaction with either bromide or hydroxide counterions (depending on the cation precursor), our observed lifetimes cannot be used as a measure of the stability of the two cations in this particular solvent.

The above results for ester **4a** in HFIP showed only the cation and did not provide any evidence for photohomolysis to form the radical. However, excitation of ester **4a** in nitrogen-saturated cyclohexane at either 266 or 308 nm gave quite different results, as shown in Figure 4. The spectrum shows one species with a sharp maximum at 555 nm which decays within ~30 μs, although the decays do not fit either first- or second-order kinetics. The second species has a broad maximum at 420 nm and does not decay appreciably over 100 μs. Identical results (both in terms of signal intensity and kinetics) are obtained in oxygen-saturated cyclohexane. The 555-nm transient is probably the radical, although the maximum is shifted by ~60 nm from the parent fluorenyl radical, and the lack of reaction with oxygen is somewhat surprising. We were able to confirm this by independent generation of the radical by hydrogen abstraction from the parent hydrocarbon with *tert*-butoxyl radical (reaction 2). Thus, 355-nm excitation of di-*tert*-butyl peroxide (4:1 peroxide/benzene) in the presence of 0.1 M **4b** generated radical **8** with λ_{max} at 555 nm and a second weaker absorption at 500 nm, in good agreement with the spectrum shown in Figure 4. The radical was unaffected by purging the same with oxygen.



+ $t\text{-}C_4H_9OH$ (2)

The identity of the additional 420-nm transient in Figure 4 has not been conclusively established. A similar long-lived species has been observed in LFP experiments on 9-fluorenol and has been tentatively assigned to a product produced by a 1,3-sigmatropic shift of the parent alcohol.[24] Alternatively, radical coupling products may also result in long-lived transients.[28] Formation

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Table III. Rate Constants for Quenching of Cations with Nucleophiles

nucleophile	**1**(CH_3CN)	**9**(CH_3CN)	**2**(HFIP)	**10**(HFIP)
water	9.3×10^6	$1.3 \times 10^{8\,a}$	$2.4 \times 10^{5\,b}$	$1.5 \times 10^{6\,d}$
methanol	7×10^7	8.1×10^8	6.7×10^6	1.8×10^7
TFE			$\sim 2 \times 10^{5\,c}$	$\sim 4.6 \times 10^{6\,c,d}$
ethanol	4.8×10^7	6.9×10^8	4.6×10^6	1.3×10^7
2-propanol	1.4×10^7	3.9×10^8	2.3×10^6	7.9×10^6
bromide	1.9×10^{10} 6.5×10^8(HFIP)		3.5×10^9	9.6×10^9

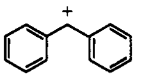
[a] Reference 13d. [b] Plot curved at higher quencher concentrations. [c] Based on one point. [d] Reference 13f.

of radicals in the case of **4a** is seen from the photoproduct **4b** present in the continuous irradiation of **4a** in either methanol or acetonitrile as well as in the transient experiments.

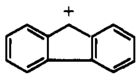
Reactivity of Cations 1 and 2 Toward Nucleophiles. The rate constants for reactions of carbocations **1** and **2** with several nucleophiles (k_q) were determined by measuring the rate constant for decay (k_{obs}) of the signals at 465 and 550 nm, respectively, as a function of quencher concentration. The data were fit according to reaction 3, where k_0 is the lifetime of the cation in the

$$k_{obs} = k_0 + k_q[Q] \qquad (3)$$

absence of quencher. The data are listed in Table III, along with data for the parent cations **9** and **10**.



9



10

The data indicate that in all cases the carbomethoxy-substituted cations are less reactive than the parent hydrogen-substituted analogues, although the effects are considerably more pronounced for the diphenylmethyl series. For example, cation **2** is approximately 3 times less reactive toward quenching by alcohols and bromide ion than the parent ion **10**, whereas **1** is 10–20 times less reactive than **9**. Such decreased reactivity for cations substituted with electron-withdrawing groups has been observed previously from solvolytic studies of specific anisylmethyl cations substituted by carbethoxy or trifluoromethyl groups at the cationic site.[11] For example, the addition of an α-carbethoxy group to the 4-methoxybenzyl cation leads to a 14-fold decrease in reactivity toward solvent (1:1 trifluoroethanol/water), based on the ratio of azide/solvent-derived products.[11a] The observations have been rationalized on the basis of factors such as increasing resonance stabilization of aryl groups resulting from an increase in electron demand caused by the presence of an electrophilic substituent. The present results provide the first example of a detailed comparison of the effects of electron-withdrawing substituents on the reactivity of diphenylmethyl and fluoren-9-yl cations.

The apparently lower reactivity of the fluoren-9-yl cations as compared with the diphenylmethyl cations for both the parent and carbomethoxy cases was initially surprising. However, it has recently been established that cation reactivities in different solvents cannot be compared directly.[13d,g] For example, rate constants for azide ion quenching can vary by almost 1 order of magnitude in TFE and acetonitrile.[13g] In order to test how much of the apparent difference in reactivity for diphenylmethyl and fluoren-9-yl cations (Table III) was due to solvent effects, we attempted to measure the reactivity of **1** in HFIP, since cations **2** and **10** could only be observed in this solvent. However, bromoester **3a** was rapidly solvolyzed by HFIP containing methanol, precluding measurement of the reactivity of **1** toward alcohols. The reactivity of **1** toward bromide ion could be measured in HFIP. The rate constant of 6.5×10^8 M^{-1} s^{-1} is almost 30 times lower than the rate constant of 1.9×10^{10} M^{-1} s^{-1} measured for reaction of bromide with **1** in acetonitrile. *Thus, the diphenylmethyl cation is substantially less reactive than the fluorenyl cation toward bromide quenching when reactivities on the same solvent are compared.* This is consistent with the relative thermodynamic stabilities of these cations as measured by pK_{R^+} values. A difference of 4 pK units is found between 9-phenyl-9-fluorenol (−10.82[26]) and triphenylmethanol (−6.63[27]). Since a phenyl substituent delocalizes the positive charge to a greater extent than either hydrogen or carbomethoxy substituents, the difference in pK_{R^+} values for the cations in this study must be at least as large.

The differences in reactivity of these cations with neutral nucleophiles is noteworthy. The order of reactivity follows methanol > ethanol > isopropyl alcohol > H_2O, TFE and is indicative of the importance of both electronic and steric effects in the nucleophilic quenching of cations.

Conclusions

Diphenylmethyl and fluorenyl cations directly substituted by electron-withdrawing groups have been observed in neutral solutions by LFP for the first time. (The anisylcarbomethoxymethyl cation has been observed by LFP and its lifetime measured: Schepp, N.; Wirz, J. submitted for publication.) Quenching data for reaction of ions, **1**, **2**, **9**, and **10** with nucleophiles point to an increase in kinetic stabilities on replacing a hydrogen for a carbomethoxy group. Such measurements of absolute rate constants provide a more direct method for evaluating substituent effects and avoid the assumptions required in competitive studies of solvolysis reactions. The observation that the 9-carbomethoxyfluoren-9-yl cation **2** can be generated under stable ion conditions and trapped with various nucleophiles whereas the parent ion **9** cannot be produced under the same conditions suggests that the carbomethoxy group contributes to thermodynamic stabilization of the ion. Measurement of pK_{R^+} values for ions **1** and **2** using McClelland's method[28] of LFP and labeled water exchange of the alcohol precursors using mass spectral techniques could not be performed with the carbalkoxy derivatives because of the fast exchange of the carbonyl oxygen with water.

Experimental Section

Infrared (IR) spectra were recorded on a Unicam SP-1000 instrument as thin films or KBr pellets. Ultraviolet (UV) spectra were measured on a Unicam SP800-A spectrometer and Hewlett-Packard 8451 A diode array spectrophotometer. Proton and carbon-13 NMR spectra were recorded on a Bruker AM-300 NMR spectrometer using samples dissolved in $CDCl_3$ or CD_2Cl_2. High-resolution mass spectra were performed at the McMaster University Regional Centre for mass spectrometry using a VG ZAB-E instrument in the EI mode at 70 eV. Elemental analysis was performed by Guelph Chemical Laboratories Limited. The continuous irradiation experiments were performed using a Hanovia 450-W high-pressure mercury arc lamp in a water-cooled quartz immersion well. The quartz sample tube was strapped around this well and immersed in an ice-water bath. Bromoester **3a** was prepared by a literature method[29] and vacuum distilled twice (bp 125 °C, 10^{-3} Torr).

Preparation of Methyl 9-Bromofluorene-9-carboxylate 4a. A solution of 300.0 mg of methyl fluorene-9-carboxylate (**4b**) in 20.0 mL of carbon tetrachloride was prepared. To this solution was added 274.0 mg (1 equiv) of bromine in 10.0 mL of carbon tetrachloride. This solution was irradiated for 30 min. The solvent was removed under reduced pressure. Methyl 9-bromofluorene-9-carboxylate (**4a**) was separated by column chromatography (silica gel/dichloromethane) to give 210 mg (54%) of a solid (R_f 0.86): mp 109–110 °C; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.70 (s, 3 H, OCH_3) 7.36 (m, 4 H, aromatic), 7.60 (d, 2 H, J = 7.2 Hz, aromatic), 7.83 (d, 2 H, J = 7.2 Hz, aromatic); ^{13}C NMR δ 53.6 (OCH_3), 57.9 (CBr), 120.2, 127.3, 128.4, 129.9 (CH, aromatic), 139.2, 143.4 (aromatic, quaternary), 168.6 (C=O); MS, m/e 302 (M^+), 304 (M^+ +

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J. Am. Chem. Soc. 1993, 115, 1669-1676

2). Anal. Calcd for $C_{15}H_{11}O_2Br$: C, 59.41; H, 3.63; Br, 26.40. Found: C, 59.29; H, 3.47; Br, 26.75.

Preparation of Carbocation 2 under Stable Ion Conditions. Methyl 9-bromofluorene-9-carboxylate (**4a**) (100.0 mg) was dissolved in 1.0 mL of SO_2 in a 10-mm NMR tube. This was mixed with SbF_5/SO_2 at -78 °C. A reddish-brown color was observed, ^{13}C NMR: δ 67.4 (OCH_3), 124.5-145.6 (aromatic), 174.2 (C=O), 192.4 (C^+).

Quenching of Carbocation 2 with CH_3OH. A solution of 70.0 mg of methyl 9-bromofluorene-9-carboxylate (**4a**) dissolved in 10.0 mL of dry dichloromethane was prepared. To this solution was added 100.0 mg (1.2 equiv) of silver hexafluoroantimonate in 1.0 mL of dichloromethane. A red color was observed, and silver bromide was formed as a precipitate. The solution was quenched with methanol immediately. The solvent was removed by reduced pressure, and 48.0 mg (83%) of methyl 9-methoxyfluorene-9-carboxylate (**4c**) was obtained (R_f 0.38): ^1H NMR ($CDCl_3$, 300 MHz) δ 2.94 (s, 3 H, OCH_3), 3.68 (s, 3 H, OCH_3); 7.38 (m, 2 H, aromatic), 7.51 (m, 4 H, aromatic), 7.75 (d, 2 H, J = 7.83 Hz, aromatic); ^{13}C NMR δ 51.2 (OCH_3), 53.7 (OCH_3), 87.8 (quaternary), 120.6, 124.1, 128.0, 130.2 (CH, aromatic), 140.5, 141.7 (aromatic, quaternary), 173.7 (C=O): HRMS (M^+) calcd for $C_{16}H_{14}O_3$ 254.0939, found 254.0927. Anal. Calcd for $C_{16}H_{14}O_3$: C, 75.59; H, 5.51. Found: C, 75.27; H, 5.35.

Quenching of Carbocation 2 with Benzene. To a solution of 30.0 mg of methyl 9-bromofluorene-9-carboxylate (**4a**) in 3.0 mL of SO_2 at -75 °C was added a few drops of SbF_5 in SO_2. The solution was quenched with dry benzene at -75 °C. The mixture was allowed to warm up to -20 °C. The reaction mixture was poured onto ice, saturated sodium bicarbonate was added, and the ice was allowed to melt. The aqueous layer was extracted with benzene (20 mL), and the organic layer was dried by addition of $MgSO_4$. The solvent was removed by reduced pressure. The reaction mixture was applied on preparatory thin-layer chromatography plates (silica gel) and developed in dichloromethane to give compound **6a** (R_f 0.86; 59%): mp 157-159 °C; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.75 (s, 3 H, OCH_3), aromatic protons 7.13 (m, 2 H), 7.23 (m, 3 H), 7.30 (t, 2 H), 7.40 (t, 2 H), 7.59 (d, 2 H, J = 7.6 Hz), 7.75 (d, 2 H, J = 7.49 Hz); ^{13}C NMR δ 52.9 (OCH_3), 67.3 (quaternary), 120.0, 126.7, 127.1, 127.9, 128.4, 128.8 (CH, aromatic), 140.8, 141.9, 146.1 (aromatic, quaternary), 172.5 (C=O); MS, m/e 241, 300 (M^+ base peak); HRMS (M^+) calcd for $C_{21}H_{16}O_2$ 300.1150, found 300.1137. Anal. Calcd for $C_{21}H_{16}O_2$: C, 84.00; H, 5.33. Found: C, 83.71; H, 5.48.

Quenching of Carbocation 2 with Toluene. To a solution of 30.0 mg of methyl 9-bromofluorene-9-carboxylate (**4a**) in 3.0 mL of SO_2 at -78 °C was added a few drops of SbF_5 in SO_2. The solution was quenched with dry toluene at -78 °C. The mixture was allowed to warm up to -20 °C. The reaction mixture was poured onto ice, saturated sodium bicarbonate was added, and the ice was allowed to melt. The aqueous layer was extracted with toluene (20 mL), and the organic layer was dried over $MgSO_4$. The solvent was removed by reduced pressure. The reaction mixture was applied on preparatory thin-layer chromatography plates (silica gel) and developed in dichloromethane to give compound **6b** (R_f 0.90; 56%): mp 128-130 °C; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.75 (s, 3 H, OCH_3), aromatic protons 7.13 (m, 2 H), 7.23 (m, 3 H), 7.30 (t, 2 H), 7.40 (t, 2 H), 7.59 (d, 2 H, J = 7.6 Hz), 7.75 (d, 2 H, J = 7.49 Hz) ^{13}C NMR δ 20.9 (CH_3), 52.8 (OCH_3), 67.3 (quaternary), 120.0, 126.5, 126.9, 127.7, 128.2, 129.3 (CH, aromatic), 137.0, 138.8, 140.6, 146.2 (aromatic, quaternary), 172.6 (C=O); HRMS calcd for $C_{22}H_{18}O_2$ 314.1307, found 314.1295. Anal. Calcd for $C_{22}H_{18}O_2$: C, 84.08; H, 5.73. Found: C, 83.69; H, 5.47.

Continuous Irradiation of Bromides 3a and 4b. A solution containing either **3a** or **4a** (100 mg) in 10 mL of methanol was irradiated for 30 min. The reaction mixture was evaporated to dryness, and the residue was applied on one thin layer chromatography plate and eluted with methylene chloride. A solution of bromide **3a** or **4a** in 50% aqueous acetonitrile was irradiated under identical conditions, and the products were separated as above.

Photoproducts **3b**, **3c**, **3d**, **10b**, **4b**, **4c**, and **4d**,[30] were compared with authentic samples obtained commercially or prepared by literature methods.

Laser Flash Photolysis. Either a Lumonics HY750 Nd:YAG laser (355 or 266 nm; 10-ns pulses; ≤50 mJ/pulse) or a Lumonics EX-510 excimer laser (XeCl, 308 nm, 6-ns pulse, ≤40 mJ/pulse) was used for sample excitation. Solutions were contained in 7 × 7 mm^2 quartz cells (quenching experiments) or in 7 × 7 mm^2 flow-through cells connected with Teflon-brand tubing to a sample reservoir (spectra). For some experiments the samples were deaerated by purging with either nitrogen or oxygen before and during the experiment. The rate constants for reaction of cation **2** with nucleophiles were determined using aerated samples. The rest of the laser system is as described previously,[31] except for the use of a PC-386 computer for data acquisition.

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Novel Cage Molecules from the Reaction of 8,8-Dicyanoheptafulvene with Cyclopentadienide Anion: Structure and Mechanism[1,2]

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Abstract: The reaction of 8,8-dicyanoheptafulvene and sodium cyclopentadienide affords under mild conditions two unusual tetracyclic cage molecules with (dicyanomethylene)tetracyclo[7.2.1.0.0]dodecadiene structures. The structures were elucidated using various modern NMR spectroscopic techniques and deuterium-labeling experiments. The easy formation of the considerably strained molecules is ascribed to a nucleophilic addition, followed by protonation and an intramolecular Diels-Alder reaction with normal electron demand. MNDO-MO calculations suggest a possible reaction mechanism.

In clear contrast to the thermally unstable heptafulvene,[4] 8,8-dicyanoheptafulvene[5] (**1**) is characterized by a relatively large dipole moment (μ = 7.49 D)[6] as well as by considerable π-delocalization, on the basis of an X-ray diffraction study.[7] The

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