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Excited-State Carbon Acids. Facile Benzylic C–H Bond Heterolysis of Suberene on Photolysis in Aqueous Solution: A Photogenerated Cyclically Conjugated Eight π Electron Carbanion[1]

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The possibility of excited-state carbon acid behavior of the dibenzylic protons of several dibenzannelated systems related to suberene (1) has been investigated in aqueous solution and in several organic solvents. It was found that only suberene (1) displayed observable excited-state carbon acid behavior. Thus photolysis of 1 in D_2O–CH_3CN solutions resulted in facile exchange of the benzylic protons with deuterium from D_2O. Extended photolysis resulted in incorporation of two deuteriums at the benzylic position. Quantum yields for initial deuterium incorporation are in the range 0.02–0.03 for 1 in D_2O–CH_3CN solutions. Deuterium exchange from the benzylic position with solvent protons was also observed on photolysis of 5,5-dideuterio-5*H*-dibenzo[*a*,*d*]cycloheptene (2), where each deuterium atom was exchanged with solvent H_2O in a sequential manner. Fluorescence quenching by water (in CH_3CN solution) of the exchanging suberene systems (1 and 2) gave linear Stern–Volmer plots, with $k_q = (1.68 \pm 0.08) \times 10^8\ M^{-1}\ s^{-1}$ for 1 and $(0.61 \pm 0.06) \times 10^8\ M^{-1}\ s^{-1}$ for 2, which corresponds to an isotope effect for quenching by water, $(k_H/k_D)_q = 2.8 \pm 0.4$. Fluorescence titration of 1 and 11 as a function of medium acidity gave an estimate of $pK(S_1) \approx -1$ for these carbon acids. This compares to their estimated $pK(S_0) \approx 31$–38.

Introduction

Carbanions are ubiquitous and important intermediates in organic chemistry.[2] They are of central importance in organic synthesis because of their facility in forming C–C bonds.[3] In the ground state, the most common way of generating carbanions is via deprotonation of the corresponding carbon acid. This method is in principle capable of generating any carbanion if a suitable base were available.[2,4] Carbanion intermediates can also be *photogenerated*, although the number of examples is limited.[5] The photochemical methods used have all involved heterolytic C–C bond cleavage to generate a carbanion and a carbocation (or equivalent) fragment.[5] Prior to our investigations in this area, there were no examples of neutral excited-state carbon acids. That is, C–H bonds could not be deprotonated in the excited state from any known neutral organic molecule. However, it is well-known that most hydrocarbons (e.g., fluorene (3)) have been predicted to be much more acidic (dibenzylic protons) in the excited singlet state by Förster cycle calculations.[6] A calculation carried out for fluorene (3) gave a $pK(S_1) \approx -9$![6] The failure to observe any proton exchange on excitation of 3 and derivatives may be due to the intrinsically short lifetimes of singlet states (typically 1–10 ns for these compounds), which compete favorably with deprotonation of the C–H bond.[6] Deprotonation rates from C–H acids in the ground state are typically slow[2e] because of the lack of hydrogen bonding to solvent and the substantial geometrical and solvation changes generally required on deprotonation of carbon acids. If true for electronically excited states as well, such intrinsically slow rates for deprotonating C–H bonds would not compete favorably with fast rates of decay generally available to S_1 (or T_1).

We recently reported the first example of an ionizing neutral carbon acid in suberene (1).[1] Since then, two other related systems have been shown by us to undergo C–H bond ionization in S_1.[7,8] In this paper, we report in full our study of the suberene (1) system and related compounds. It is found that of these dibenzannelated systems, only suberene (1)—which can give an incipient cyclically conjugated 8π (4n) electron carbanion on deprotonation of the benzylic proton—undergoes C–H bond ionization in S_1, as monitored by exchange of these protons (deuterons) with solvent. The results give new insights into the mechanistic details of a type of C–H bond cleavage in organic photochemistry about which very little is known.

Results and Discussion

Materials. Dibenzannelated systems 1–8 were chosen for study because of their relatively rigid structures (except for 5 and 6, which were used as less rigid model systems) and also because the methylene protons are doubly activated (i.e., they are *dibenzylic*). In addition, we have already shown[5f,15] that the corresponding benzylic car-

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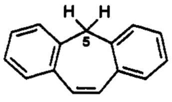
banions of 1, 3, 5, and 7 can be photogenerated relatively efficiently via photodecarboxylation of the corresponding carboxylate ions, although a large range of quantum yields was observed.[5f,15] The dideuterated materials 2, 4, 6, and 8 were studied for possible exchange with solvent protons and also to examine possible isotope effects for photodeprotonation. All of 1–8 were readily made from the corresponding ketones in high yields by reaction with $LiAlH_4$ (or $LiAlD_4$) in the presence of $AlCl_3$. Compounds 2, 4, 6, and 8 were of >98% dideuteration, as shown by mass spectrometry and high field (250- and 360-MHz) ^1H NMR.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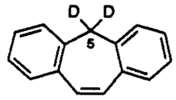
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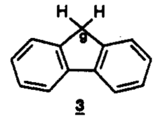
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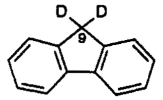
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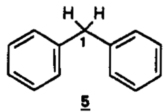
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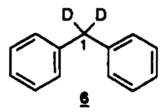
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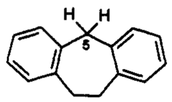
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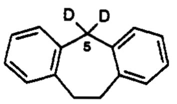
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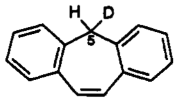
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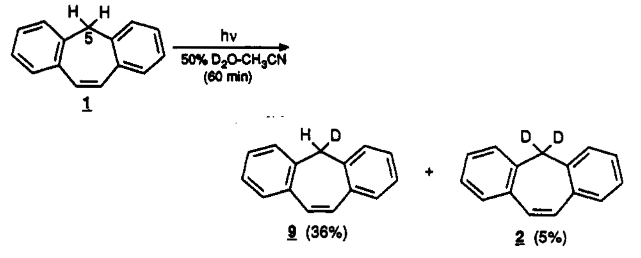
Proton-Exchange Studies. Photolysis of 75–150 mg of 1 dissolved in 50% D_2O–CH_3CN (200–400 mL) for 1–2 h (Rayonet RPR 100 photochemical reactor; 254- or 300-nm lamps; argon purged; ≈12 °C) on workup gave a material which was analyzed by ^1H NMR (250 MHz). The appearance of an unresolved "1:1:1 triplet" at δ 3.75 along with a decrease in relative signal intensity (relative to the vinyl protons) of the methylene signal of 1 at δ 3.78 of the photolyzed sample is consistent with incorporation of deuterium at the 5-position of 1, to give 9. The 1:1:1 triplet ($J \approx 2$ Hz) is due to the monobenzylic proton of 9 coupled to the geminal deuterium. The aromatic proton and vinyl signals remain *unchanged* in the photolyzed sample. The amount of 9 present was calculated to be ≈40%, based on integrated areas. ^1H NMR cannot be used to detect formation of 2. However, mass spectral analysis of the same product mixture shows the presence of 9 (36%) and 2 (5%) (eq 1). In general, good agreements between the calculated percent of monodeuterated product from ^1H NMR and mass spectral data were observed. That deuterium incorporation was predominantly at the 5-position was shown by ^{13}C NMR of the same sample (Figure 1). The methylene carbon (C_5) signal of unreacted 1 appears as a singlet at δ 41.6. After photolysis, the signal intensity of this peak decreased and a "1:1:1 triplet" (J = 24 Hz) appears at δ 41.3, which is consistent with the presence of 9 in the product mixture. The other carbon signals remain essentially unchanged after photolysis.



[equation 1]

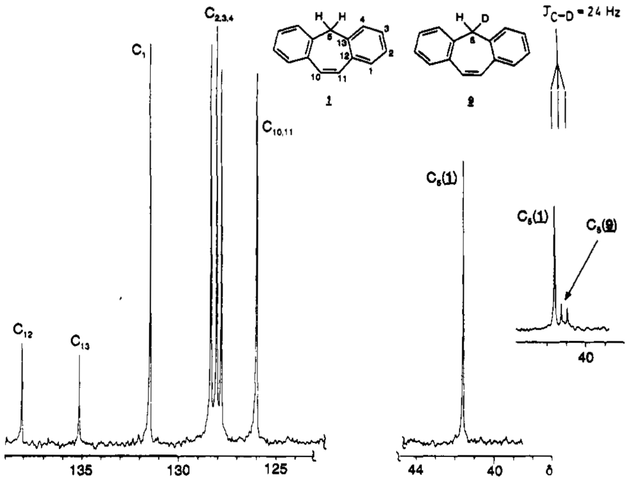


Figure 1. Proton-decoupled ^{13}C NMR spectrum of 1 before and after (inset) photolysis in D_2O–CH_2CN, showing production of monodeuterated suberene (9).

The possibility that a *residual* amount of deuterium might be incorporated into other positions of the molecule (e.g., the vinyl or benzene ring positions) was examined by ^2H NMR. A solution of 1 (as above) was exhaustively irradiated for 2 h and the photolysate examined by ^2H NMR in CH_2Cl_2 with acetone-d_6 as internal standard. The spectrum showed a strong peak at δ ≈3.7, indicative of mono- and dideuteration at the benzylic position, as expected. However, a residual singlet (≈1–2%) was also observed in δ ≈7.05, essentially at the same location as the vinyl proton resonance of 1. A control experiment showed that these peaks were not observed on workup for an identical solution, but without irradiation. As an additional control, photolysis of 2 in H_2O–CH_3CN resulted in no observable deuterium incorporation at the vinyl position in any of the photoexchanged products (1 and 9), thus ruling out the possibility of an *intramolecular* transfer of deuterium from the 5-methylene to the 10-vinyl position. Therefore, the observation of the vinyl ^2H signal on photolysis of 1 in D_2O–CH_3CN indicates that a very small percent of exchange does take place at the vinyl position, which was not detectable by ^1H or ^{13}C NMR. However, the ^2H NMR spectrum showed no detectable exchange in the benzene rings.

Without irradiation, 1 does not undergo observable exchange under the above conditions (at 22 ± 2 °C) or under a variety of other conditions, including use of basic D_2O (pD 7–14). In all cases, quantitative recovery of 1 was possible. In addition, photolysis of 1 in 100% CD_3CN resulted in recovery of only unreacted 1. Photolysis of 3, 5, and 7 under the above conditions and on exhaustive photolysis (2–4 h) also resulted in no observable deuterium incorporation, and in all cases quantitative recovery of the substrates was possible after photolysis.

The kinetics of exchange could be followed by either ^1H NMR or MS using the dideuterated compound 2 as starting material. Thus, photolysis of 2 in 50% H_2O–CH_3CN resulted in initial formation of 9 followed by increasing amounts of 1 on further photolysis (Figure 2). Photolysis of 2 in 100% CH_3CN gave no observable exchange. Photolysis of 4, 6, and 8 in 50% H_2O–CH_3CN gave no exchange of deuterium with solvent, and the substrates could be recovered unchanged. In a separate experiment, a solution of 200 mg of 2 in 50% H_2O–CH_3CN (400 mL)

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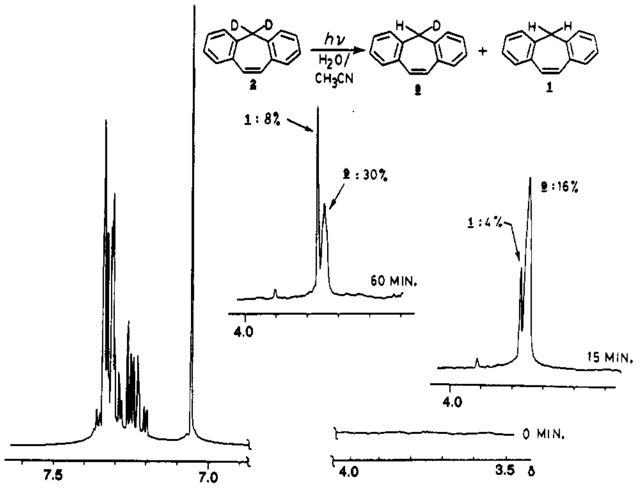


Figure 2. ^{1}H NMR (250 MHz) spectrum of 2 on photolysis in 50% H_2O–CH_3CN, showing production of monodeuterated suberene (9) and the parent suberene (1) with photolysis time.

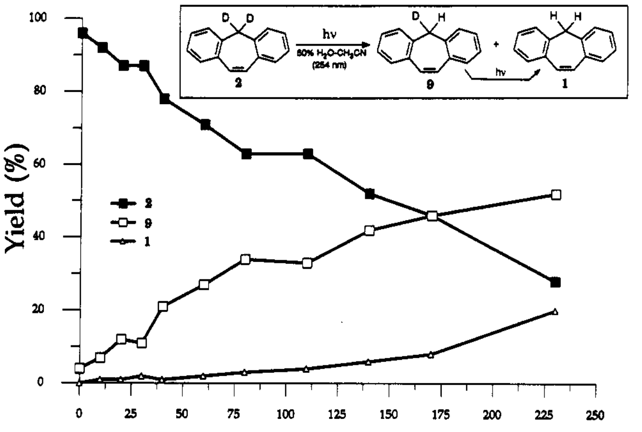


Figure 3. Plot of percent recovered 2 and yields of exchange photoproducts 9 and 1 vs photolysis time in 50% H_2O–CH_3CN.

was irradiated and aliquots removed after set periods of irradiation, and yields of products and starting material were calculated by MS and ^{1}H NMR. The resulting plot is shown in Figure 3. It is clear from this plot that the primary exchange product is 9, which reacts via secondary photoreaction to give 1; that is, the proton exchange (for deuterium) is a sequential process.

In the ground state, 100% exchange of the dibenzylic protons of fluorene (3) with deuterons was accomplished by refluxing 3 in 50% D_2O–dioxane (pD ≈ 13) for 48 h (in refluxing neutral D_2O–dioxane solution, exchange of 3 was not observed). None of 1, 5, and 7 underwent observable exchange under these conditions. These qualitative results are consistent with the known pK_a's of these substrates in the ground state. The most acidic compound is fluorene (3), with a pK_a of about 21–23[9] (in DMSO). The pK_a's of diphenylmethane (5) and dibenzosuberane (7) are 33[10] and 31,[10] respectively. The pK_a of 1 has not been measured to our knowledge. However, the pK_a of other cycloheptatriene derivatives are in the range 31–38,[11] which show that they are much weaker acids than cyclopentadiene derivatives, but not much weaker acids than simple diphenylmethanes. Nevertheless, cycloheptatrienyl carbanions, including the suberenyl carbanion 10, are known to be antiaromatic in the ground state.[11,12]

Quantum Yields. Quantum yields (Φ) for deuterium incorporation in 1 (i.e., formation of 9) and protium incorporation in 2 (i.e., formation of 9) were measured on an optical bench using an Oriel 200-W Hg arc and the monochromator set at λ_{ex} = 280 nm using potassium ferrioxalate actinometry.[13] Conversions were kept <20%, and analyses were carried out using MS and/or GC/MS. Shown in Table I are quantum yields of exchange of 1 in deuterated solvents. It is clear that deuterium cannot be incorporated from a nonhydroxylic deuterium (as in CD_3CN) and that D_2O is better than MeOD in promoting exchange. Shown in Table II are quantum yields for exchange of 2 in a larger variety of solvents. Again, it was found that aqueous CH_3CN was the best solvent mixture for exchange. In addition, quantum yields for exchange in the H_2O–CH_3CN vs D_2O–CH_3CN runs for 1 and 2, respectively (Tables I and II), were essentially the same (i.e., no significant isotope effect), although the initial process required for exchange involves C–H bond breakage in 1 (Table I) vs C–D bond break breakage for 2 (Table II). The significance of the lack of any observable isotope effect will be discussed in a later section.

Table I. Quantum Yields (Φ) for Monodeuterium Incorporation into 1 in Various Solvents[a]

solvent mixture[b]	Φ
100% CD_3CN[c]	0.000
70% D_2O–CH_3CN	0.029 ± 0.004
50% D_2O–CH_3CN	0.030 ± 0.004
20% D_2O–CH_3CN	0.021 ± 0.003
70% MeOD–CH_3CN[d]	0.006 ± 0.001

[a] Determined by mass spectral analyses of 2–3 independent runs. Errors quoted are standard deviations. [b] For solubility reasons, CH_3CN was used as cosolvent. Ratios are v/v. [c] NMR solvent used without further treatment. [d] CH_3CN used here for comparison to 70% H_2O–CH_3CN.

Table II. Quantum Yields (Φ_p) for Protium Incorporation into 2 in Various Solvents[a]

solvent mixture[b]	Φ
CH_3CN[c]	0.000
70% H_2O–CH_3CN	0.045 ± 0.006
50% H_2O–CH_3CN	0.035 ± 0.006
20% H_2O–CH_3CN	0.024 ± 0.003
70% MeOH–CH_3CN	0.012 ± 0.002
70% EtOH–CH_3CN	0.008 ± 0.001
70% 2-PrOH–CH_3CN	0.003
50% $HCONH_2$–H_2O	0.014 ± 0.008
50% $HCONH_2$–CH_3CN	0.010 ± 0.006

[a] Determined by mass spectral analyses of 2–3 independent runs. Errors quoted are standard deviations. [b] CH_3CN was used as cosolvent for solubility. Ratios are v/v. [c] HPLC-grade CH_3CN used without further treatment.

Table III. Quantum Yields (Φ_p) for Protium Incorporation into 2 into Acidic and Basic Solution

solution	Φ_p
70% H_2O–CH_3CN[a]	0.045 ± 0.006
70% 1.25 M H_2SO_4–EtOH	0.012 ± 0.002
70% 2.5 M H_2SO_4–EtOH	0.008 ± 0.001
70% 5.0 M H_2SO_4–EtOH	0.002 ± 0.001
50% H_2O–CH_3CN[a]	0.035 ± 0.006
50% 0.5 M NaOH–EtOH	0.043 ± 0.006
50% 1.0 M NaOH–EtOH	0.048 ± 0.006
50% 2.0 M NaOH–EtOH	0.064 ± 0.008

[a] Used for comparison purposes. Similar quantum yields were observed with EtOH substituting as the cosolvent for CH_3CN.

Quantum yields for exchange of 2 were also measured in aqueous EtOH or CH_3CN where the acidity or basicity of the aqueous portion was varied over a wide range (Table III). The exchange efficiency was reduced in acid and enhanced in strongly basic aqueous NaOH solution.

Steady-State Fluorescence and Lifetime Measurements. Fluorescence emission and excitation spectra

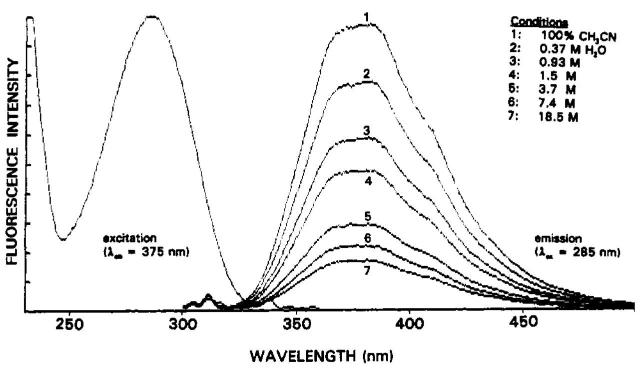


Figure 4. Representative fluorescence excitation and emission spectra in 100% CH$_3$CN, with overlay of fluorescence emission quenching of 1 by added water in CH$_3$CN (λ_{ex} = 285 nm).

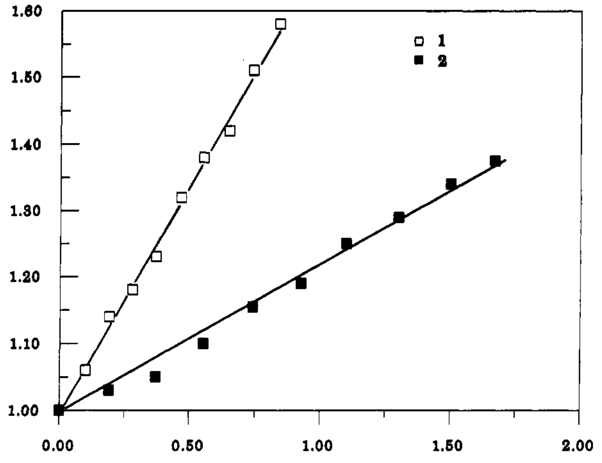


Figure 5. Representative Stern–Volmer plot of fluorescence emission quenching by added water in CH$_3$CN solution for 1 and 2.

(uncorrected) of 1 in dry CH$_3$CN are shown in Figure 4. Addition of H$_2$O quenches the emission; in 8:2 H$_2$O–CH$_3$CN, the emission (not shown) becomes very weak. Compound 2 also displayed this fluorescence quenching phenomenon. However, all of the nonreacting systems (in exchange) 3–8 did not exhibit this efficient fluorescence quenching by H$_2$O.

Stern–Volmer plots of quenching for 1 and 2 by H$_2$O in the moderate H$_2$O concentration range (up to ≈1.5 M) gave good linear plots (Figure 5). Quenching rate constants were calculated using lifetime data in 100% CH$_3$CN, and gave k_q = (1.68 ± 0.08) × 10^8 M^{-1} s^{-1} for 1 and (0.61 ± 0.06) × 10^8 M^{-1} s^{-1} for 2. This corresponds to an isotope effect for quenching by H$_2$O, $(k_H/k_D)_q$ = 2.8 ± 0.4. These results support the notion that *H$_2$O is the deprotonating base in aqueous solution.*

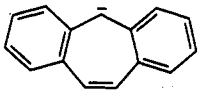
Fluorescence lifetimes (by time-correlated single-photon counting) of 1 and 2 were also measured in different H$_2$O concentrations in CH$_3$CN. Lifetimes decreased with increasing H$_2$O content (Table IV) for both compounds. A Stern–Volmer plot of the inverse of lifetime vs H$_2$O concentration gave good linear plots with k_q = (1.71 ± 0.04) × 10^8 M^{-1} s^{-1} and (0.69 ± 0.05) × 10^8 M^{-1} s^{-1} for 1 and 2, respectively. These rate constants are identical, within experimental error, with those calculated from steady-state fluorescence quenching. These results show unambiguously that fluorescence quenching by H$_2$O of 1 and 2 is a dynamic process.

For comparison, fluorescence lifetimes were also measured at different H$_2$O concentrations for one of the nonexchanging systems, fluorene (3). In 100% CH$_3$CN, τ = 6.7 ± 0.2 ns; in 8:2 H$_2$O–CH$_3$CN, τ = 5.6 ± 0.2 ns (all decays were first-order). Thus the presence of H$_2$O has only a minor effect on the lifetime of 3, as expected from the steady-state fluorescence results. In contrast, the fluorescence lifetime of 1 goes from 5.04 ± 0.04 ns in 100% CH$_3$CN to 0.13 ± 0.2 ns in 8:2 H$_2$O–CH$_3$CN. Due to the very short lifetime of the latter run, a picosecond excitation system had to be used to carry out the measurement since conventional hydrogen flashlamps are limited to lifetimes of >0.2 ns. When both of the dibenzylic positions are blocked, as it is the case of 5-methyl-5-suberenol (11), the fluorescence lifetime (and steady-state emission intensity) of this suberene derivative is essentially *unaffected* by water (τ = 2.1 ± 0.1 ns in 100% CH$_3$CN or 8:2 H$_2$O–CH$_3$CN solution). These observations are again consistent with the proposal that H$_2$O is the deprotonating base of the methylene protons (deuterons) at the 5-position of 1 (and 2).

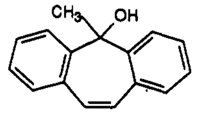
Table IV. Fluorescence Lifetimes of 1 and 2 in Aqueous CH$_3$CN As Measured by Single-Photon Counting[a]

		H$_2$O,[d] M			
compd[b]	100% CH$_3$CN[c]	0.010	0.20	0.56	0.74
1	5.04 ± 0.04	4.63	4.35	3.36	3.07
2	4.72	4.68	4.57	4.23	3.85

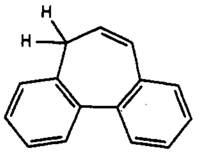
[a] Representative lifetimes; additional data points were used for the Stern–Volmer plots. All decays were good first order, with χ^2 < 1.3. [b] Typical substrate concentration ≈10^{-4} M; λ_{ex} = 265 nm; OD (265 nm) < 0.2. [c] Freshly distilled over CaH$_2$. [d] Water concentration in dry CH$_3$CN.



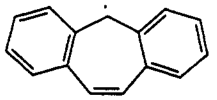
10



11



12



13

Since the fluorescence emissions from the other nonexchanging systems (5 and 7) were substantially weaker, a detailed study of the effect of H$_2$O on their fluorescence lifetimes was not undertaken. However, steady-state fluorescence data show that moderate H$_2$O concentrations do not have a significant effect on their fluorescence emission efficiencies.

The fluorescence emission quantum yield (Φ_f) for 1 in CH$_3$CN was measured relative to two secondary fluorescence standards that have emission in about the same wavelength range, 2-aminopyridine (Φ_f = 0.60 ± 0.05)[14] and anthracene (Φ_f = 0.27 ± 0.03).[14] Use of either standard gave Φ_f = 0.86 ± 0.05 for 1 in 100% CH$_3$CN. Such large fluorescence quantum yields for suberene (5*H*-dibenzo[*a*,*d*]cycloheptene) derivatives in inert solvents have already been observed by us in a related study[15] and are not unexpected since other "locked" stilbenes (of which 1 and 2 are examples) have $\Phi_f \approx 1$.[16]

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(16) Simple stilbenes are very weakly fluorescent (Saltiel, J.; Waller, A.; Sun, Y.-P.; Sears, D. F., Jr. *J. Am. Chem. Soc.* 1990, *112*, 4580). Once these systems are "locked", they become very fluorescent, with Φ_f approaching unity.[17a–c] The "loose bolt" of "free rotor" effect has been used to account for this dramatic effect on fluorescence quantum yield in these and other systems.[17a]

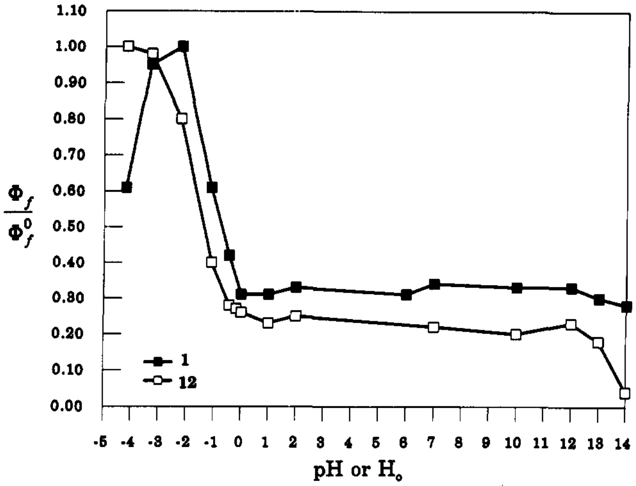

Figure 6. Relative fluorescence emission intensity of 1 and 12 vs pH or H_0 (30% EtOH cosolvent).

To study the effect of medium acidity or basicity on fluorescence efficiency, the fluorescence emission intensity of 1 in aqueous solution (30% EtOH cosolvent) was monitored by varying the aqueous portion of the solution, from 1 M NaOH (pH 14) to ca. 60% H_2SO_4 ($H_0 \approx -4$) (Figure 6). The emission intensity stays relatively constant over the pH 0–13 region, with a modest decrease in the pH 13–14 region. However, most striking is the *enhancement* in fluorescence emission intensity on increasing the acidity, from pH 0 to $H_0 \approx -2$. In stronger acid, the fluorescence intensity drops off. This drop off in stronger acid is probably associated with thermal reaction of the substrate since 1 cannot be recovered unchanged at these acidities. However, the behavior in weaker acids ($-H_0 <$ 3) suggest that we are seeing *fluorescence titration* of the excited-state carbon acid 1. That is, on increasing the solution acidity, the medium basicity is decreased, thus reducing the rate of deprotonation. Corroborating evidence for this interpretation are (i) quantum yields for exchange of 2 decrease in this same acidity region (Table III), and (ii) fluorescence lifetimes in this acid region become *longer* compared to pH 7 (it is 0.41 ± 0.04 ns in $H_0 = -1.08$ and 0.13 ± 0.02 ns in neutral solution). To investigate the generality of this phenomenon, we have also monitored the fluorescence intensity of 5*H*-dibenzo[*a*,*c*]cycloheptene (12), an excited-state carbon acid studied by us recently,[8] and have observed very similar behavior (Figure 6). Aromatic compounds which are not excited-state carbon acids (e.g., fluorene (3)) experience substantial fluorescence *quenching* in this same acidity region, presumably due to photoprotonation of the benzene ring.[18] Therefore, the enhancement in fluorescence intensity shown in Figure 6 is probably a lower limit since there is probably a competing photoprotonation pathway for both of 1 and 12.

The fluorescence of both of 1 and 12 was quenched in basic (pH > 12) solution which suggests base catalysis for deprotonation. This was confirmed by the enhancement of quantum yields for exchange measured for 2 in this same pH region (Table III) although the effects are not large. Since H_2O is itself a very effective quencher (i.e., a deprotonating base), one requires relatively high concentrations of NaOH to compete favorably.

Triplet Sensitization of Exchange. Triplet sensitization of possible deuteron (proton) exchange of 2 (1) (E_T < 57 kcal mol^{-1})[19] was carried out with sodium benzophenone-2-carboxylate ($E_T \approx 70$ kcal mol^{-1})[21] as triplet sensitizer in 50% $D_2O(H_2O)$–CH_3CN. In a typical experiment, 0.5–1 g of sensitizer and 50–80 mg of 2 were dissolved in 50% $H_2O(D_2O)$–CH_3CN solution with the pH(D) adjusted to ≈7–10 with NaOH(OD) solution. The solution was irradiated for 0.5–1 h in a Pyrex vessel at 350 nm where only the sensitizer absorbs. These experiments resulted in no observable exchange in recovered 1 or 2 and shows that the carbon acid behavior is exclusively a singlet-state process.

Mechanism of Proton and Deuteron Exchange. The results presented above argue for an ionic mechanism of exchange from the singlet excited states of 1 and 2. A mechanism involving initial homolysis of the benzylic C–H bond can be ruled out since such a mechanism cannot account for exchange from only hydroxylic protons (or deuterons) of the solvents used. In addition, any photogenerated suberenyl radicals 13 would be expected to dimerize efficiently, to give the corresponding bis(suberenyl), which was not observed.

An ionic mechanism that needs to be addressed is shown on the left-hand side of Scheme I, where the primary photochemical step is photoprotonation of the alkene moiety[22] by H_2O, to generate the corresponding benzylic cation 14. Loss of a proton from the 5-position would give intermediate 15, which may revert back to substrate via a 1,5-sigmatropic shift,[24] resulting in incorporation of a solvent deuteron at the 5-position (to give 9). However, such a mechanism must necessarily also give some alcohol 16 and a significant proportion of deuteration at the vinyl position of 1 (formation of 17), the former was not observed and the latter was formed in only very low yield (vide supra). In addition, such a mechanism would be inconsistent with the observation of fluorescence *enhancement* in acidic medium; the photoprotonation mechanism would result in fluorescence quenching by added acid.[22]

A related possible mechanism is shown in Scheme II where the primary photochemical step from 1 is a 1,5-hydrogen sigmatropic shift[23] from the 5-position to the vinyl position, to generate the *o*-quinone dimethide species 18. Deuteration of the alkene at the 5-position gives cation 19 which can give rise to 9 on loss of a proton. However, such a reaction mechanism must also give some alcohol 20, which was not observed. Alternatively, deuteration of 18 at the 11-position would generate the cation at the 5-position and hence give the corresponding alcohol, which was also not observed. In addition, subsequent reaction of 9 via the mechanism shown in Scheme II must necessarily result in substantial deuterium incorporation at the

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(17) (a) Turro, N. J. *Modern Molecular Photochemistry*; Benjamin: Menlo Park, 1978; p 170. (b) DeBoer, C. D.; Schlessinger, R. H. *J. Am. Chem. Soc.* **1968**, *90*, 803. (c) Saltiel, J.; Zafiriou, O. C.; Megarity, E. D.; Lamola, A. A. *J. Am. Chem. Soc.* **1968**, *90*, 4759.

(18) Fluorescence quenching of aromatic compounds by hydronium ion is a general phenomenon. See, for example: (a) Wan, P.; Wu, P. *J. Chem. Soc., Chem. Commun.* **1990**, 822. (b) Shizuka, H. *Acc. Chem. Res.* **1985**, *18*, 141. (c) Stevens, C. G.; Strickler, S. J. *J. Am. Chem. Soc.* **1973**, *95*, 3922.

(19) Estimated based on the fact that the triplet energy of *cis*-stilbene is <57 kcal mol^{-1}.[20]

(20) Murov, S. L. *Handbook of Photochemistry*; M. Dekker: New York, 1973.

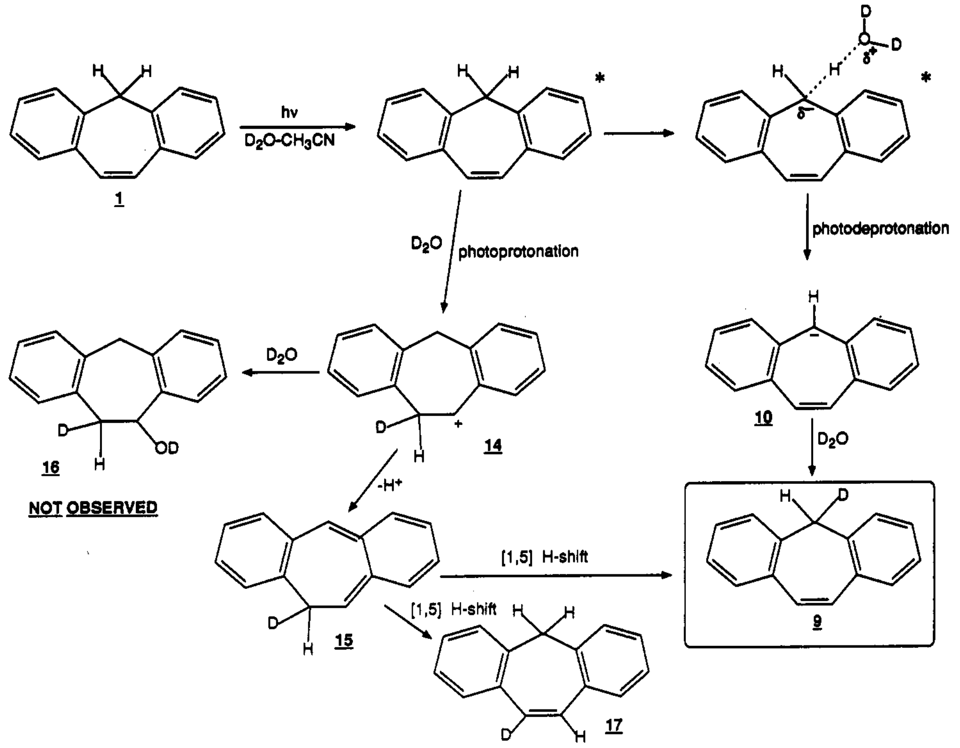
(21) Estimated based on the known triplet energies of benzophenone derivatives,[20] which are in the 68–72 kcal mol^{-1} range.

(22) Photoprotonation of aromatic alkenes at the vinyl position is a well-known reaction but requires moderately strong acid for measurable rates. See, for example: (a) Wan, P.; Culshaw, S.; Yates, K. *J. Am. Chem. Soc.* **1982**, *104*, 2509. (b) Wan, P.; Yates, K. *Rev. Chem. Intermed.* **1984**, *5*, 157.

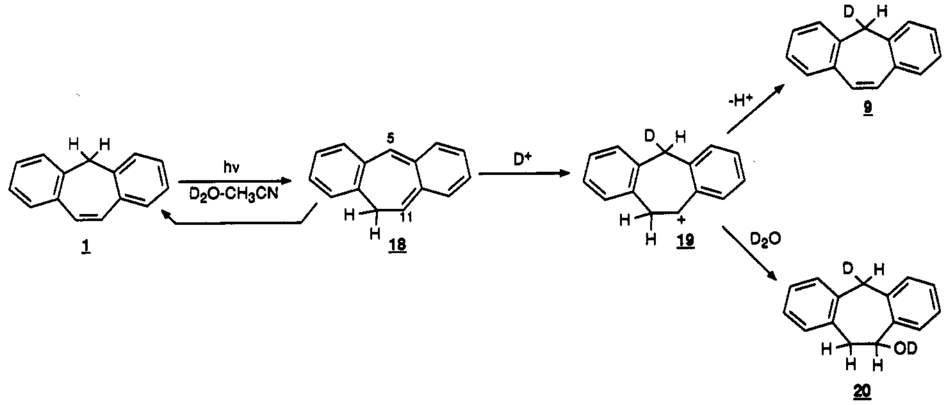
(23) This 1,5-hydrogen sigmatropic shift has been reported to take place under thermal conditions (300 °C);[24] the resulting *o*-quinone dimethide 18 has been trapped with dienophiles. In the absence of such trapping agents, it is believed that 18 quickly reverts back to 1.

(24) Pomerantz, M.; Fink, R. *J. Org. Chem.* **1977**, *42*, 2788.

Scheme I



Scheme II



vinyl position, which was not observed. Furthermore, we have shown (vide supra) that photolysis of 2 in H_2O–CH_3CN does not result in deuterium incorporation at the vinyl position, which is inconsistent with this mechanism. The failure to account for the fluorescence quenching data would also not favor this mechanism.

The proposed mechanism which is consistent with all available data is shown on the right-hand side of Scheme I. In this simple carbon acid mechanism, the singlet excited state is deprotonated by water acting as the base, to give the intermediate suberenyl anion **10** (which is presumed to be hydrogen bonded to the departing hydronium ion). The same proton which was deprotonated may rebond to the carbanion, thus resulting in no net exchange (internal return). However, exchange of the departing proton with deuteron from solvent and subsequent deuteration of the carbanion results in overall exchange at the 5-position. An estimate of the percentage of internal return may be made as follows. The fluorescence quantum yield (Φ_f) of 1 in the nonreactive solvent CH_3CN is 0.86 ± 0.05. In 7:3 D_2O–CH_3CN, Φ_f drops to ≈0.05. The observed exchange quantum yield in this solvent is 0.029 ± 0.004. Assuming that the decrease in Φ_f is mostly due to reaction via deprotonation of the benzylic C–H bond, then out of about 80 deprotonated molecules only 3 exchange. In other words, internal return appears to be by far the major reaction pathway of carbanions photogenerated via C–H ionization by H_2O.

Fluorescence quenching of 1 and 2 by H_2O in CH_3CN shown a significant isotope effect for quenching, $(k_H/k_D)_q = 2.8 \pm 0.4$. However, the corresponding exchange quantum yields in L_2O–CH_3CN (L = H or D) (Tables I and II) indicate only a modest isotope effect ($\Phi_H/\Phi_D = 1.1$–1.6). Assuming the validity of the carbanion mechanism of Scheme I, the primary isotope effect which arises from bond cleavage of C–H vs C–D is not manifested in exchange quantum yields. This is not unexpected since overall exchange requires the carbanion to reprotonate. This second step has associated with it a primary isotope effect (protonation from L_2O) which compensates for the initial isotope effect. That no larger isotope effect was observed in the exchange quantum yields is additional support for significant internal return in these photogenerated carbanions. If every deprotonation resulted in exchange, a large isotope effect (equal to $(k_H/k_D)_q$) would have been observed in the exchange quantum yields. The very minor extent in which deuterium was incorporated at the vinyl position indicates that the photogenerated carbanion probably reverts to the ground state very quickly (diabatic process), where the negative charge would be expected to reside almost exclusively at the 5-position (by virtue of it being an antiaromatic carbanion).[12,25]

Using Förster cycle calculations, a p$K(S_1)$ of −8.5 for fluorene (3) was reported by Vander Donckt and coworkers.[6a,c] Similar large negative p$K(S_1)$'s have been calculated for other fluorene derivatives.[6a,c] We calculated a p$K(S_1)$ of −4 for this compound. However, it is clear that fluorene (3) shows no evidence for exchange. That is, it is kinetically not an ionizing excited-state carbon acid although it is predicted to be a very strong acid in S_1, based on the assumption that equilibrium can be achieved in S_1. The main difficulty in using Förster calculations for 1 lies in estimating the $E_{0,0}$ energy for the suberenyl anion 10. We have generated this anion in THF using *n*-BuLi and observed a long wavelength absorption band with $\lambda_{max} \approx$ 800 nm. Our best estimate of $E_{0,0}$ for 10 is ≈34 kcal mol^{-1}. Using a p$K(S_0)$ of 32 for 1, we calculate a p$K(S_1)$ = −7 for suberene (1). It is clear that based on Förster cycle calculations, both of 1 and 3 are vastly more acidic in S_1 than in S_0. However, only 1 undergoes proton dissociation. The fluorescence titration of 1 (Figure 6) indicates a p$K(S_1)$ of ≈−1 or less, which is in the general direction of the predicted value. Thus the ΔpK observed on going from S_0 to S_1 for 1 is ≈32 log units! As far as we are aware, this the largest change in acidity relative to the ground state reported for an ionizing excited state acid.

It seems reasonable that the measured k_q's for fluorescence quenching of 1 and 2 by H_2O are equatable to the rates of C–H bond ionization by H_2O acting as the base (i.e., k_H). Since this is the first such rate measurement for this process, it is difficult to comment on the exact magnitude at this time. Suffice it to say that k_H is significantly below the diffusion controlled rate (hence there is the possibility of enhancing the rate) and k_H is not measurable (i.e., <10^5 M^{-1} s^{-1}) for the nonreacting systems.

The results reported here clearly show that there is an enhanced driving force for the photgeneration of cyclically conjugated 8π (4n) carbanions from an excited state precursor, compared to 4n + 2 systems or those which do not give rise to a cyclically conjugated intermediate. The study of photodecarboxylation of several dibenzannelated acetic acids also support this notion.[5f,15] In addition, the study of photosolvolysis of several dibenzannelated systems (in which carbocations are intermediates) again indicate a strong preference for intermediates of 4n (4π) electrons.[27] Although the reactions investigated are not pericyclic reactions in the traditional sense, Woodward–Hoffmann[28] and the Dewar–Zimmerman[29] rules work nicely in predicting the outcome. That is, there appears to be an inherent stabilizing effect of a 4n array of electrons of these compounds (whether negatively or positively charged) on the excited state surface, analogous to the well-known aromatic stabilization associated with 4n + 2 systems in the ground state, where the concept of aromaticity has more solid basis. Since one cannot use the same criteria of aromaticity—which are well-known in the ground state—for excited-state species because of their intrinsically short lifetimes, one encounters a dilemma in trying to offer a simple explanation for the enhanced reactivity observed in this and related work. It is clear, however, that 4n systems appear to have a special inherent stability which is manifested in the ease of photodeprotonation of suberene (1) and the photosolvolysis of 9-fluorenol.[27] If we take the increased *photo*reactivity of the 4n systems to imply a lower activation barrier on the S_1 surface, the extension of the Hammond postulate would indicate that the excited state of 4n charged intermediates are indeed more stabilized than their 4n + 2 counterparts. This interpretation is based on the following assumptions: (i) applicability of the Hammond postulate to the S_1 surface and (ii) adiabaticity of the C–H bond cleavage step. We have no reason to doubt the former, but evidence for an adiabatic first step is at present not available. Additional studies are in progress to better understand the phenomenon of enhanced photoreactivity of 4n vs 4n + 2 systems in ionic reactions.

Experimental Section

General. ^{1}H (250 and 360 MHz), ^{2}H (55.3 MHz), and ^{13}C (62.9 MHz) NMR spectra were taken in $CDCl_3$ or acetone, on Bruker WM 250 or AM 360 instruments. Preparative or semipreparative photolyses were carried out using Rayonet RPR 100 photochemical reactors equipped with 254- or 350-nm lamps. Gas chromatography was carried out on a Varian 3700 instrument with a Hewlett-Packard 3390A integrator and a DB-5 capillary column. Acetonitrile (ACS grade) used for fluorescence quenching studies and lifetime measurements was distilled over calcium hydride overnight and stored over molecular sieves.

Materials. All of 1–9 were readily available via simple $LiAlH_4(LiAlD_4)/AlCl_3$ reduction of the corresponding ketones in dry diethyl ether or THF following a general procedure.[30] The ketones were purchased from Aldrich. Alcohol 11 was made via addition of MeMgCl to 5*H*-dibenzosuberenone. All of the hydrocarbons 1–9 and alcohol 11 had satisfactory ^{1}H NMR and mass spectra and were of >98% purity by GC and ^{1}H NMR.

Proton-Exchange Studies. In general, 50–200 mg of 1–8 was dissolved in the appropriate solvent or solvent mixture (100–400 mL) and irradiated in 100-, 200-, or 600-mL quartz tubes, depending on the scale of the experiment. The tubes were cooled using a cold-finger (tap water) along with continuous purging with a stream of argon via a long fine metal needle. Irradiation was with 16 × 254-nm lamps. Some typical experiments are described below.

Photolysis of 1 in 1:1 D_2O–CH_3CN. A solution of 150 mg of 1 dissolved in 100 mL of CH_3CN and 100 mL of D_2O was irradiated for 2 h. After photolysis, a very fine precipitate could be observed (<2%) which is believed to be the 2 + 2 dimer of 1. The solution was extracted with 2 × 100 mL of CH_2Cl_2. The whole experiment was repeated, and the organic extracts were combined. For improved ^{1}H NMR spectra, the photolysate was purified by prep TLC (silica gel; hexanes), to yield ≈250 mg of a white powder. The ^{1}H and ^{13}C NMR spectra of this material are shown in Figures 1 and 2, respectively. Integration of the ^{1}H NMR spectrum indicate a conversion of 42% compared to a conversion of 40% calculated by MS.

Photolysis of 2 in 1:1 H_2O–CH_3CN. A solution of 30 mg of 2 dissolved in 100 mL of H_2O and 100 mL of CH_3CN was irradiated for 15 min. After extraction, ^{1}H NMR of the photolysate (Figure 2) showed formation of 1 (4%) and 9 (16%). Photolysis of an identical solution for 60 min gave the spectrum also shown in Figure 2, which showed 1 (8%) and 9 (30%). The kinetics plot shown in Figure 3 was obtained by irradiating a solution of 200 mg of 2 dissolved in 200 mL of H_2O and 200 mL of CH_3CN in a 600-mL quartz tube. Aliquots were removed after set intervals of irradiation and worked up by extraction. Conversions to 1 and

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[25] It has been shown[26] that the thermally generated suberenyl anion 10 is protonated exclusively at the 5-position.

[26] Ceccon, A.; Gambaro, A.; Pizzato, L.; Romanin, A.; Venzo, A. *J. Chem. Soc., Chem. Commun.* 1982, 907.

[27] Wan, P.; Krogh, E. *J. Am. Chem. Soc.* 1989, *111*, 4887.

[28] Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Verlag-Chemie: Weinheim, 1970.

[29] (a) Zimmerman, H. E. *Acc. Chem. Res.* 1971, *4*, 272. (b) Dewar, M. J. S. *Angew. Chem., Int. Ed. Engl.* 1971, *10*, 761.

[30] (a) Nystrom, R. F.; Berger, C. R. A. *J. Am. Chem. Soc.* 1958, *80*, 2896. (b) Ceccon, A.; Gambaro, A. *J. Organomet. Chem.* 1984, *275*, 209.

9 were calculated by ^{1}H NMR and MS.

Photolysis of 4, 6, and 8 in 1:1 H_2O–CH_3CN. Using identical conditions described above for **1** and **2**, photolysis of these compounds resulted in no exchange with H_2O, and complete recovery of the substrate was possible after irradiation.

Photolysis of 3, 5, and 7 in 1:1 D_2O–CH_3CN. Photolysis of these samples in D_2O–CH_3CN resulted in no deuterium incorporation, and the substrates were recovered unchanged.

Thermal Generation of Suberenyl Anion (10). The ground-state suberenyl anion **10** was generated in THF solution by deprotonating suberene (**1**) with excess *n*-BuLi under N_2. The reaction was slow and required heating to reflux for 10–20 min, which gave a deep orange-black solution. That the anion was indeed generated at the 5-position was shown by quenching the solution with CO_2(g), which gave 5-suberenecarboxylic acid in >50% yield. The absorption spectrum of **10** was obtained by transferring a portion (200–400 μL) of the solution to a quartz cuvette containing 2.5 mL of dry THF in a glovebag. The spectrum shows a major absorption band at 455 nm ($\epsilon \approx 8000$ M^{-1} cm^{-1}) and a shoulder at 525 nm ($\epsilon \approx 2000$ M^{-1} cm^{-1}) and a much weaker band at ≈800 nm ($\epsilon \approx 200$ M^{-1} s^{-1}). All of these bands disappear on exposure of the solution to moisture. For comparison, the absorption spectrum of the suberanyl anion (from **7**) was generated in the same manner. This anion showed a band at 430 nm and a shoulder at 475 nm but no longer wavelength absorption band.

Triplet Sensitization of Exchange of 1 and 2. In a typical experiment, a solution of 50 mg of **1** and 1 g of 2-benzoylbenzoic acid dissolved in 50 mL of D_2O and 50 mL of CH_3CN (pH adjusted to ≈7–10 with NaOH) was irradiated for 30–60 min at 350 nm in a Pyrex tube. After photolysis, the solution was extracted with 2 × 100 mL of CH_2Cl_2. The combined organic extract was washed with 0.1 M NaOH to remove residual sensitizer. ^{1}H NMR and MS showed no observable exchange in either **1** or **2**.

Quantum Yields. Quantum yields were measured using 280-nm excitation (10-nm bandwidth) from the output of an Oriel 200-W Hg lamp filtered through an Applied Photophysics monochromator and a Corning 254–400-nm bandpass filter. Solutions (≈10^{-3} M) were prepared in 3.0-mL quartz cuvettes, purged with a stream of argon, and sealed with Teflon stoppers prior to photolysis. Potassium ferrioxalate was used for chemical actinometry.[13] After photolysis, the sample was extracted several times with CH_2Cl_2, and the isotope content was analyzed by GC/MS with a Finnigan 3300 instrument in chemical ionization (CI; methane carrier gas) mode. Blank (unirradiated) samples were also submitted for GC/MS analysis for comparison. Conversions were <25%. The CI mass spectrum of unirradiated **1** (natural abundance material) showed an M + 2 peak intensity of 17–20% (relative to M$^+$ + 1 as parent base peak; recall that in CI, ionization is via protonation of the molecule) which agrees well with the expected theoretical value of 16.4% (due mostly to ^{13}C). After photolysis in D_2O–CH_3CN solution, the M + 2 peak increases, the exact extent depending on irradiation time. Thus the extent of deuterium incorporation can be readily calculated. However, use of CI results in observation of an M$^+$ peak (15–18%) (probably due to formation of suberenyl cation via loss of H_2 or HD in the mass spectrometer) in all runs. This probably results in an inherent error (≈5–10%) associated with all the quantum yield determination using GC/MS since we have no easy method of correcting for this side reaction in the mass spectrometer in the calculations. The overall effect is probably minor since it is partially self-cancelling.

Steady-State Fluorescence and Lifetime Measurements. Steady-state fluorescence spectra (uncorrected, including those used for measuring Φ_f) were taken in 3.0-mL quartz cuvettes at ≈10^{-4} M using a Perkin-Elmer MPF 66 spectrophotometer at ambient temperature (λ_{ex} = 285 nm). Solutions were purged with a stream of argon prior to measurement. Time-correlated single-photon counting fluorescence lifetimes were measured either using a Photon Technology International (PTI) LS-1 instrument with a hydrogen flash lamp or at the Center for Fast Kinetics Research (CFKR) using a picosecond mode-locked, synch-pumped, cavity-dumped dye laser, frequency doubled to provide an excitation source in the UV at 266 nm (Spectra Physics Model 574B dye laser with Spectra Physics series 3000 Nd:YAG at the pump source). All single photon decays were first-order by analysis using software supplied by PTI or CFKR.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. Support was also provided by the Natural Science and Engineering Research Council (NSERC) of Canada. Some single-photon fluorescence lifetime measurements were measured by E. Krogh at the Center for Fast Kinetics Research (CFKR) at the University of Texas at Austin. The CFKR is supported jointly by the Biotechnology Research Program of the Division of Research Resources of NIH (RR00886) and by the University of Texas at Austin. We thank E. Krogh and B. Chak for carrying out some initial experiments.

Note Added In Proof. Excited-state carbon acid behavior of azulenium cations has been reported (Grellmann, K. H.; Heilbronner, E.; Seiler, P.; Weller, A. *J. Am. Chem. Soc.* **1968**, *90*, 4238), but deuterium exchange experiments were not carried for out these systems.

Registry No. **1**, 256-81-5; **2**, 137946-81-7; **3**, 86-73-7; **4**, 778-60-9; **5**, 101-81-5; **6**, 3947-98-6; **7**, 833-48-7; **8**, 88288-96-4; **9**, 137571-37-0; **11**, 219-92-1; **12**, 18259-45-5; D_2O, 7789-20-0; H_2, 1333-74-0; D_2, 7782-39-0.