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Photodecarboxylation of Diarylacetic Acids in Aqueous Solution: Enhanced Photogeneration of Cyclically Conjugated Eight π Electron Carbanions[1]

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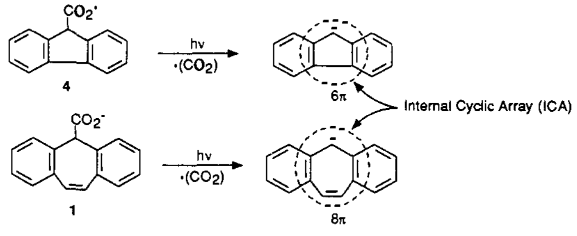
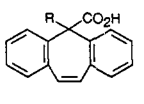
Abstract: The photodecarboxylation of a series of diarylacetic acids **1–6** has been studied in aqueous solution. The mechanism of these photodecarboxylations is shown to involve C–C bond heterolysis from the singlet excited state, giving rise to carbanion intermediates. Quantum yields for photodecarboxylation (Φ_d) are reported at several pH's. Fluorescence quantum yields and lifetimes are reported as a function of pH, and their behavior is consistent with reaction via the carboxylate ions. Rate constants of photodecarboxylation (k_{dc}) are estimated and show a marked dependence on the number of π electrons in the internal cyclic array (ICA). The most reactive compound was suberene-5-carboxylic acid (**1**) ($\Phi_d = 0.60 \pm 0.05$; $k_{dc} \approx 6 \times 10^9$ s^{-1}), which gives a carbanion intermediate of eight π ($4n$) electrons in the ICA. The least reactive system was fluorene-9-carboxylic acid (**4**) ($\Phi_d = 0.042 \pm 0.004$; $k_{dc} = 8.8 \times 10^6$ s^{-1}), which on decarboxylation gives rise to a carbanion with an ICA of six π ($4n + 2$) electrons. The observed reactivity trend in the excited state is the reverse of that observed in the ground state and appears to demonstrate further the utility of the "$4n$ rule" for predicting the relative reactivity of photochemical reactions giving rise to cyclically conjugated, charged intermediates. The possible theoretical significance of these observations is discussed.

Introduction

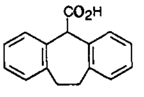
Scheme I



Decarboxylation reactions are relatively common in organic chemistry and are used frequently in organic synthesis, particularly with malonic acid derivatives.[2] Decarboxylation steps are also important in a number of biological systems. For instance, the thiamine-mediated decarboxylation of pyruvate to acetaldehyde and CO_2 and the pyridoxal phosphate-mediated decarboxylation of amino acids have been well-documented.[3-5] Thermal decarboxylations commonly occur from the carboxylate ion and are accelerated by the presence of electron-withdrawing groups, which can stabilize the incipient carbanion.[6-9] Mechanistically, these decarboxylations can be viewed as the reverse of the addition of carbanions to carbon dioxide. One of the first detailed mechanistic studies of *photo*decarboxylation was reported by Margerum and co-workers for *m*- and *p*-nitrophenyl acetates.[10] Over the past two decades a number of additional photodecarboxylation reactions have been reported. The substrates have included pyridyl acetates,[11] alkyl- and phenylglyoxylic acids,[12-15] alkyl- and arylacetic acid derivatives,[16-21] as well as a number of more complex, biologically active carboxylic acids.[22] Although the apparent simplicity of the photochemical process has attracted considerable interest, a variety of mechanisms have been suggested. The mechanisms may be broadly classified as follows: (a) electron transfer induced, (b) homolytic (proceeding through radical intermediates), and (c) heterolytic (proceeding through ionic intermediates). Even for the relatively simple system, phenylacetic acid, there remains some confusion as to the exact nature of the mechanism of photodecarboxylation.[17-20,23,24] The study of this system is, however, encumbered by the low quantum yields observed ($\Phi < 0.03$).[17-20] This diversity in mechanistic behavior has perhaps discouraged systematic approaches to studying structure–reactivity in photodecarboxylation reactions.



1 R=H
5 R=CH3
6 R=D



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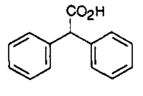

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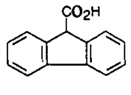

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Our interest in studying the present series of acetic acid derivatives (**1–6**) stems from our work in the photogeneration of cyclically conjugated carbocations.[25] The photosolvolysis of 9-fluorenol and related compounds has led to a means of generating the corresponding carbocations by way of photodehydroxylation.[26,27] 9-Fluorenol and 5-suberenol (5*H*-di-

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Table I. Results of Typical Preparative Photolysis

compd (concn, mM)	solv syst[a]	photoprod	irradiat. time (min)[b]	conversn[c] (%)
1 (2.1)	70% H_2O–CH_3CN	**7**	2.0	75
2 (2.1)	70% H_2O–CH_3CN	**8**	15	60
3 (2.5)	70% H_2O–CH_3CN	**9**	15	55
4 (2.4)	70% H_2O–CH_3CN	**10**	20	70
5 (2.0)	70% H_2O–CH_3CN	**15**	2.0	55
6 (2.1)	70% H_2O–CH_3CN	**11**	1.5	40
16 (2.0)	50% H_2O–CH_3CN	nr[d]	10	
17 (2.2)	50% H_2O–CH_3CN	nr[d]	20	
1 (4.2)	60% D_2O–CH_3CN	**11**	1.5	20
2 (4.2)	60% D_2O–CH_3CN	**12**	15	50
3 (5.0)	60% D_2O–CH_3CN	**13**	15	50
4 (4.8)	60% D_2O–CH_3CN	**14**	20	70

[a] The pH (pD) was adjusted to between 8 and 11 with NaOH(D). [b] Rayonet RPR 100 reactor, λ_{ex} = 254 nm. [c] Determined by ^1H NMR integration; estimated error ±5–10%. [d] nr = no reaction.

benzo[*a*,*d*]cyclohepten-5-ol) were employed as progenitors of 4*n* and 4*n* + 2 π electron carbocation intermediates, respectively. We have discussed the significance of the internal cyclic array (ICA) of π electrons elsewhere and reported that the 4*n* carbocations were much more efficiently photogenerated than their corresponding 4*n* + 2 counterparts.[25] These results prompted us to investigate the possibility of a similar effect for the analogous carbanions (Scheme I). We have investigated a number of methods to photochemically generate carbanions[28] and have found photodecarboxylation an attractive one for our purposes. Firstly, the reactions proceed cleanly, leading to only one product. Secondly, all of the compounds in the series **1–6** show some photoreactivity. Combining the product quantum yields with the lifetime of the reactive state gives a direct comparison of the inherent reactivity of these substrates. A review of the available literature reveals that nothing is known about the influence of a cyclically conjugated π array in the incipient carbanion on the efficiency of *photo*decarboxylation. For the analogous ground-state reactions, application of Hückel's 4*n* + 2 rule to the intermediate carbanions readily predicts the observed reactivity trend.[9,29] We report here the results of a study of the photodecarboxylation of several acetic acid derivatives (**1–6**) to probe the effect of the internal cyclic array (ICA; see Scheme I) on the reaction efficiency. We show that all of the compounds studied react via a simple ionic mechanism to give carbanion intermediates. Moreover, the most reactive system in the series, suberene-5-carboxylic acid (**1**), has one of the largest photodecarboxylation quantum yields (Φ_d = 0.60 ± 0.05) of a carboxylic acid.

Results

Materials. Compounds **1–4** and the related systems **5** and **6** are ideal for studying the effect of the ICA on the photogeneration of carbanion intermediates. Suberene-5-carboxylic acid (**1**) and fluorene-9-carboxylic acid (**4**) give rise to eight (4*n*) and six π (4*n* + 2) electron intermediates, respectively. On the other hand, the intermediates generated from suberane-5-carboxylic acid (**2**) and diphenylacetic acid (**3**) do not contain a conjugated ICA (on reaction) and thus serve as control systems for comparative purposes. The acids **1–4** and **6** were made by adding CO_2(g) to the corresponding carbanions, which were generated in situ by the addition of *n*-BuLi to THF solutions of the appropriate hydrocarbons. In all cases, good yields (>65%) were obtained, although some care had to be exercised for **1** and **6** since these carbanions are destabilized and considered to be formally antiaromatic in the ground state.[30] Diphenylacetic acid (**3**) was

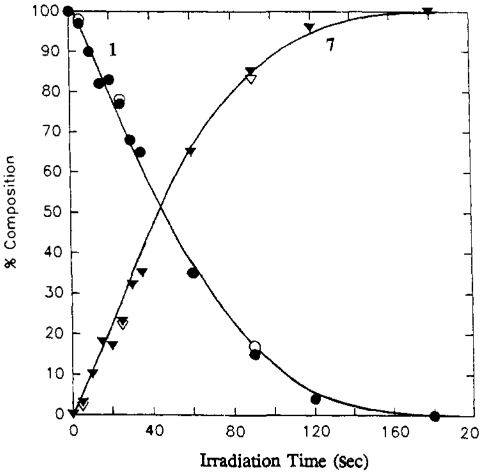
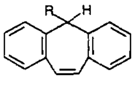
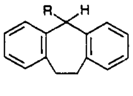


Figure 1. Photolysate composition as a function of irradiation time of **1** (λ_{ex} = 254 nm; argon-saturated aqueous solution; pH 7; 40% CH_3CN cosolvent). Photoproduct 7 is represented by the triangles. The open points are for reactions carried out in an oxygen-saturated solution.

purchased from Aldrich and recrystallized before use. The esters **16** and **17** were prepared from the corresponding carboxylic acids by standard methods. 5-Methylsuberene-5-carboxylic acid (**5**) was prepared by treatment of **1** with excess *n*-BuLi followed by the addition of methyl iodide. Hydrocarbons **7–10** were required for comparison purposes in steady-state and transient fluorescence measurements, as well as for product studies. These were prepared by reducing the corresponding ketones (purchased from Aldrich) with $LiAlH_4/AlCl_3$.



7 R= H
11 R= D
15 R= CH_3
16 R= CO_2CH_3



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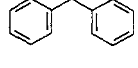

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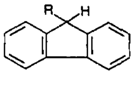
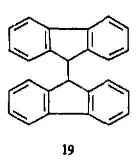
13 R= D



10 R= H
14 R= D
17 R= CO_2CH_3
18 R= CH_2CN



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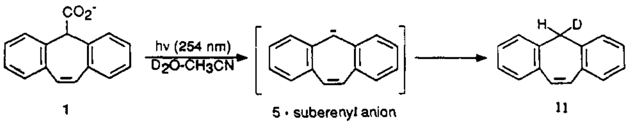
Product Studies. Photolyses were carried out using 200-mL ~10^{-3} M solutions of the substrates dissolved in aqueous CH_3CN (typically 60% (v/v) H_2O–CH_3CN), and the pH was adjusted by adding the appropriate amount of a stock NaOH solution and using a pH meter (Rayonet RPR 100 reactor; 254-nm lamps; quartz vessel; solutions cooled with a cold finger to ~15 °C; argon-purged solutions; photolysis times 1–30 min). On photolysis in deaerated solution, **1–6** all gave high yields of the corresponding hydrocarbon as the exclusive photoproduct (Table I). Photolysis in D_2O–CH_3CN solution resulted in the exclusive formation of the corresponding monodeuterated hydrocarbons **11–14** (e.g., eq 1).[31] Photolysis in CH_3CN[32] resulted in no observable yield of



(1)

the decarboxylation product, except for **1** which gave low yields (~10%) of suberene (**7**, 5*H*-dibenzo[*a*,*d*]cycloheptene). Compounds **2–4** were completely nonreactive in aqueous CH_3CN

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(31) We have checked the isolated photoproduct from the photolysis of **1** in D_2O–CH_3CN for deuterium incorporation at the vinylic 10,11-positions by ^2H NMR. The ^2H spectrum reveals that deuterium has been incorporated solely at the 5-position as indicated by structure **11**.

(32) No efforts were made to exclude trace amounts of water from the CH_3CN used.

Table II. Products Observed on Photolysis of **1–4** in 70% H_2O–CH_3CN in the Presence of Oxygen[a]

compd	% hydrocarbon	% ketone[b]	compd	% hydrocarbon	% ketone[b]
1	>99	<1	**3**	72	28
2	95	5	**4**	62	38

[a] 100 mg of substrate in 200 mL of O_2-saturated solution. Conversions were between 40 and 50%. [b] Based on the integration of GC peaks.

solutions at pH's < pK_a, whereas **1**, the most reactive compound in the series, displayed no measurable pH effect. Furthermore, the methyl esters **16** and **17** were nonreactive toward decarboxylation in either aqueous or CH_3CN solvents[33] (Table I). The loss of **1** and simultaneous growth of **7** were followed as a function of irradiation time and are presented in Figure 1. The reaction can be taken to 100% conversion. Note that in this case oxygen has no effect on the nature or the yield of the product.

Photolysis in the Presence of Oxygen. Photolysis of **1–4** under the conditions outlined above, except with oxygen- rather than argon-saturated solutions, resulted in the formation of the corresponding ketone products in addition to the expected hydrocarbons. Photolysis of these carboxylic acids in oxygenated CH_3CN or of the hydrocarbons **8–10** in oxygenated aqueous CH_3CN gave none or only trace quantities of the corresponding ketones. This suggests that the photogenerated carbanion intermediates are trapped by molecular oxygen, initially forming the corresponding hydroperoxides. Secondary hydroperoxides are known to readily eliminate H_2O to yield the corresponding ketones.[36] The relative amounts of ketone vs hydrocarbon product varied with the different substrates (Table II, all runs were taken to similar (40–50%) overall conversions, although the hydrocarbon to ketone ratio displayed little or no dependence on the conversion). The least photochemically reactive substrate, **4**, gave rise to the highest proportion of ketone (9-fluorenone) relative to the hydrocarbon (1:1.7). Photolysis of compounds **2** and **3** gave modest yields of suberone (5*H*-dibenzo[*a,d*]cycloheptanone) and benzophenone, respectively, whereas suberene-5-carboxylic acid (**1**) showed only trace amounts (<1%) of suberenone (5*H*-dibenzo[*a,d*]cycloheptenone) at conversions of >60%. The data in Table II indicate that the amount of oxygen-trapped product is correlated with the ground-state stability of the corresponding carbanions and *not* the efficiency of their photogeneration. Thus suberenone, which would arise from the reaction of the destabilized 5-suberenyl anion (antiaromatic in the ground state; see Scheme I) with oxygen, was not observed. Conversely, the photolysis of **4**, which generates the 9-fluorenyl anion (aromatic in the ground state), produced the largest amount of the ketone, in this case 9-fluorenone.

Product Quantum Yields. Quantum yields for photodecarboxylation (Φ_d) were measured in aqueous solution using 20% (v/v) CH_3CN as the cosolvent. The measurements for compounds **1**, **4**, and **5** were carried out at $\lambda_{ex} = 280$ nm on the optical bench under a fine stream of argon, which served to deaerate and stir the solutions (ca. 1×10^{-3} M). Potassium ferrioxalate was used to monitor the light intensity. Deaerated solutions of **2** and **3** (ca. 5×10^{-3} M) were photolyzed in a Rayonet reactor ($\lambda_{ex} = 254$ nm) using a merry-go-round apparatus with fluorene-9-carboxylic acid (**4**) as a secondary actinometer, $\Phi_d = 0.042 \pm 0.004$. The conversions were determined by GC analysis using an external standard. The quantum yields for photodecarboxylation are presented in Table III. The esters **16** and **17** showed no tendency to photodecarboxylate under the conditions employed, and an upper limit of $\Phi_d < 0.01$ has been estimated. The quantum yields were also measured in D_2O (pD > 8), CH_3CN, and H_2O (pH 1) (Table III).

Table III. Photodecarboxylation Product Quantum Yields (Φ_d)[a]

compd	H_2O[b] (pH 7)	D_2O[b] (pD ≥8)	H_2O[b] (pH 1)	CH_3CN
1	0.60	0.42	0.62	0.05
2	0.20	0.13	<0.01[c]	<0.01[c]
3	0.19	0.11	<0.01[c]	<0.01[c]
4	0.042	0.035	<0.01[c]	<0.01[c]
5	0.38			
16	<0.01[c]			<0.01[c]
17	<0.01[c]			<0.01[c]

[a] Margins of error ±10% of the value quoted. [b] 20% (v/v) CH_3CN used as a cosolvent. [c] Estimated upper limits based on the recovery of starting material in preparative photolysis.

Table IV. Ground-State pK_a's for **1–5**[a]

compd	H_2O[b]	80% H_2O–CH_3CN[c]	compd	H_2O[b]	80% H_2O–CH_3CN[c]
1	5.2	4.3	**4**	4.3	3.9
2	5.1	4.1	**5**		4.2
3	4.6				

[a] The pK_a's were measured under a nitrogen atmosphere using an automatic titrater. A standard glass electrode was employed for the hydronium ion concentration with a Ag/AgCl reference. End points were determined by a curve-fitting procedure, and the pK_a was taken as the pH at half-neutralization. Errors are estimated to be less than 4% of the quoted values. [b] Substrates (ca. 10^{-4} M) were dissolved in freshly distilled, deionized H_2O. [c] Substrates (ca. 10^{-3} M) were dissolved in 10 mL of CH_3CN and diluted to 50 mL with freshly distilled, deionized H_2O. The titrant, 8.08×10^{-3} M NaOH, contained 20% (v/v) CH_3CN as well.

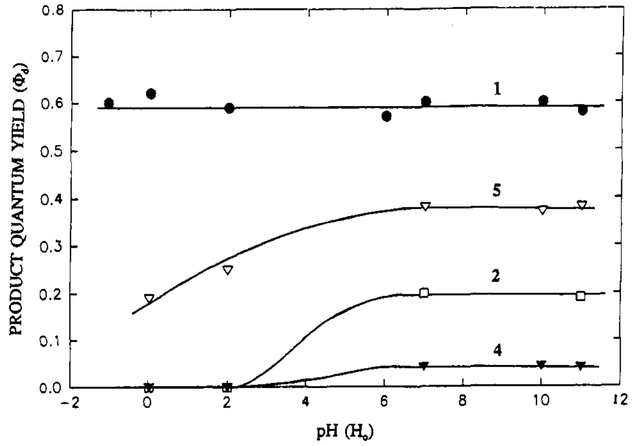

Figure 2. Product quantum yields (Φ_d) as a function of pH for **1**, **2**, **4**, and **5**. Yields based on photolysis of ca. 10^{-3} M solutions (40% CH_3CN) using ^1H NMR integration to measure the conversion; acidity refers to the aqueous portion.

The pH dependence of the product quantum yield is shown in Figure 2. The reduction of reactivity for **2–4** parallels the protonation of the carboxylates (vide infra), which do not photodecarboxylate in aqueous solution at pH 1 or in CH_3CN. This behavior has been observed for other aryl- and diarylacetic acid derivatives and is expected for decarboxylations involving heterolytic cleavage involving the carboxylate ion.[37] The substrates which have only moderate Φ_d's at pH 7 (i.e., **2–4**, Φ_d = 0.04–0.20) do not react at all below pH 2, while **5** showed decreased Φ_d at this pH. However, the photodecarboxylation efficiency of **1** did not display a measurable pH dependence, even in moderately strong acid ($H_0 \approx 0$). To ensure that all of the acids are in fact protonated at pH 1, the ground-state acidity constants have been

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(33) Although it is not directly related to the present series, we have also investigated the possibility of photodecarboxylation for 1,2-diphenylcyclopropene-3-carboxylic acid.[34] However, photolysis of this compound gave 4-hydroxy-3,4-diphenylcrotonic acid γ-lactone (identified by comparison of spectral data with literature values[35]) via a different mechanism. No evidence for the intermediacy of the cyclopropenyl anion has been obtained.

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Table V. Solvent Isotope Effects on Photodecarboxylation Quantum Yields (Φ_{H_2O}/Φ_{D_2O}) for **1**–**4**

compd	Φ_{H_2O}/Φ_{D_2O}	k_{H_2O}/k_{D_2O}	compd	Φ_{H_2O}/Φ_{D_2O}	k_{H_2O}/k_{D_2O}
1	1.4 ± 0.1	≥1.4	**3**	1.7 ± 0.1	1.7
2	1.5 ± 0.1	1.8	**4**	1.2 ± 0.1	1.2

measured (Table IV). The ground-state acid–base behavior of **1**–**4** is unexceptional. The acidity constants are in the expected range, i.e., 10^{-4}–10^{-5}. It is clear that, for **2**–**4**, it is the carboxylate ions that are reactive toward photodecarboxylation, while **1** (and to a lesser extent **5**) continue to decarboxylate in their nonionized forms.

Isotope Effects. It is clear from Table III that substrates **1**–**4** are less reactive (as measured by Φ_d) in D_2O than in H_2O. The solvent isotope effect (Φ_{H_2O}/Φ_{D_2O}) on the photodecarboxylation efficiency was determined by comparing the product quantum yields measured in 80% H_2O–CH_3CN (pH 7) to those obtained in 80% D_2O–CH_3CN (pD > 7). The solvent isotope effects are significant, ranging from 1.2 to 1.7, and are summarized in Table V.

The kinetic solvent isotope effects (k_{H_2O}/k_{D_2O}) were calculated using the fluorescence lifetimes and eq 4 (vide infra). Since the fluorescence lifetime of **1** is <0.15 ns in 20% CH_3CN–H_2O, τ_{D_2O}/τ_{H_2O} could not be determined and the entry for **1** in Table V should be considered a lower limit. The calculated kinetic solvent isotope effects (k_{H_2O}/k_{D_2O}) are relatively large and in the expected range for a mechanism involving a large degree of solvent association in the transition state (Table V).[38]

Triplet Sensitization Studies. To investigate the importance of the triplet pathway in these photodecarboxylations, triplet sensitization experiments were carried out with 2-benzoylbenzoic acid ($E_T \approx 70$ kcal mol^{-1})[39] as the water-soluble triplet sensitizer at pH > 7 ($\lambda_{ex} = 350$ nm). When 50 mg of **4** ($E_T \approx 68$ kcal mol^{-1})[34] was photolyzed through Pyrex at 350 nm in the presence of 2.0 g of 2-benzoylbenzoic acid, under conditions which would otherwise lead to >80% conversion at $\lambda_{ex} = 254$ nm, only trace amounts (~5% conversion) of fluorene (**10**) were detected. Present also in the product mixture were small amounts of 9-fluorenylacetonitrile (**18**) and 9,9′-bifluorene (**19**), as detected by comparison of their GC retention times with authentic materials. The fluorenyl radical is strongly implicated as an intermediate in the triplet-sensitized reaction. Both **18** and **19** have been characterized in earlier photochemical investigations where the fluorenyl radical has been generated in aqueous CH_3CN solvents.[25] Analogous photoproducts were obtained when **1** ($E_T \approx 57$ kcal mol^{-1})[39] was photolyzed under similar conditions. The relative inefficiency of these sensitized reactions and the presence of dimeric and other products dramatically contrasts the results obtained upon direct photolysis. These results suggest that the triplet state may undergo a relatively inefficient homolytic cleavage, thus leading to radical-derived products. It appears, therefore, that the excited *singlet* state is responsible for the clean and efficient photodecarboxylation processes that occur via heterolytic cleavage in aqueous solution on direct excitation. These results are in accord with the photodecarboxylation of other aryl acetates, which proceed via the singlet state.[10,37,40] Further evidence that these photodecarboxylations occur from the excited singlet state comes from the fluorescence data (vide infra).

Steady-State Fluorescence Studies. The spectral characteristics of **1**–**4** are similar to those of the corresponding hydrocarbon chromophores. Compounds **1** and **4** have strong UV absorption bands at 285 ($\epsilon_{max} = 1.3 \times 10^4$ M^{-1} cm^{-1}) and 265 nm ($\epsilon_{max} = 1.8 \times 10^4$ M^{-1} cm^{-1}), respectively. Compounds **2** and **3**, however, are less conjugated and have weaker absorption bands at 265 nm ($\epsilon_{max} = 6.5 \times 10^2$ and 4.0×10^2 M^{-1} cm^{-1}, respectively).

Table VI. Fluorescence Quantum Yields (Φ_f) of **1**–**5** and **16**–**17** in Various Solvents

	Φ_f[a]			
compd	C_6H_{12}	CH_3CN	pH 7[b]	pH 1[b]
1[c]	0.54	0.53	<0.001	~0.01
2[d]	0.068	0.050	0.023	0.044
3[d]	0.030	0.007	0.010	0.011
4[e]	0.38	0.41	0.27	0.030
5[c]	0.45	0.48	<0.001	0.080
16[c]	0.55	0.53	0.54	0.50
17[e]	0.37	0.36	0.015	0.013

[a] Absolute values are ±10% based on the accuracy of the reported fluorescence quantum yields of the secondary standards employed. The relative values within a set are reproducible to ±5%. [b] Buffered solutions, 20% v/v CH_3CN used as a cosolvent. [c] Reference standard: 2-aminopyridine in 0.1 N H_2SO_4, $\Phi_f = 0.60 \pm 0.06$.[56] [d] Reference standard: benzene in cyclohexane, $\Phi_f = 0.05 \pm 0.02$.[56] [e] Reference standard: fluorene in cyclohexane, $\Phi_f = 0.80$.[38]

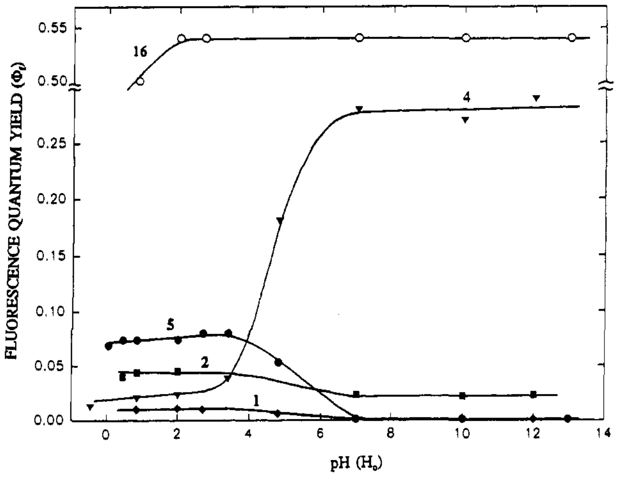

Figure 3. Fluorescence quantum yields (Φ_f) as a function of pH for **1**, **2**, **4**, **5**, and **16**. Emission was measured in argon-saturated aqueous solutions (20% CH_3CN); acidity refers to the aqueous portion.

The fluorescence quantum yields (Φ_f) were measured for **1**–**5**, **16**, and **17** in different solvents and as a function of pH. The results are presented in Table VI. The pH dependence of Φ_f is displayed in Figure 3. The emission intensity of the esters **16** and **17** was essentially unaffected by pH, whereas that of the carboxylic acids varied sharply over the range where deprotonation occurred. In general, it has been observed that the carboxylate forms of aryl-substituted acetic acids are more fluorescent than their protonated counterparts.[37] In the present series, this behavior was observed only for **4**, the least reactive of the substrates. The fluorescence quantum yield drops from 0.27 at pH 7 to 0.030 at pH 1. The methyl ester, **17**, whose fluorescence properties should resemble the acid form of **4**, displays a similarly weak emission in aqueous solution, $\Phi_f \approx 0.014$. Most of the carboxylic acids in the present series were more fluorescent at pH's less than their ground-state pK_a's, following an opposite trend in their photochemical reactivity. The enhanced reactivity of the ionized forms provides an additional deactivational pathway for the carboxylates, which results in the observation that the protonated forms are more strongly fluorescent.

The most striking solvent effect was observed for suberene-5-carboxylic acid (**1**), which has a fluorescence quantum yield of 0.54 in cyclohexane and CH_3CN but is essentially nonfluorescent in H_2O (pH 7), a solvent in which it is very photochemically reactive. We have previously noted a similar fluorescence quenching for suberene (**7**) and have reported on the excited-state carbon acid behavior of this compound.[41] To rule out a similar mechanism for the water quenching of **1** (that is, C_5–H bond

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(38) Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*; Harper and Row: New York, 1987.

(39) These values are based on those given for analogous chromophores as tabulated in Murov, S. L. *Handbook of Photochemistry*; Marcel Dekker: New York, 1973.

(40) Wan, P.; Muralidhuran, S. *J. Am. Chem. Soc.* **1988**, *110*, 4336.

(41) (a) Wan, P.; Krogh, E.; Chak, B. *J. Am. Chem. Soc.* **1989**, *110*, 4073. (b) Wan, P.; Budac, D.; Krogh, E. *J. Chem. Soc., Chem. Commun.* **1989**, 255. (c) Wan, P.; Budac, D. Unpublished results.

Table VII. Fluorescence Lifetimes (τ_f) of **1–5** and **16–17** in Various Solvents

	τ_f (10^{-9} s)[a]				τ_f (10^{-9} s)[a]		
compd	CH_3CN	pH 7[b]	pH 1[b]	compd	CH_3CN	pH 7[b]	pH 1[b]
1	3.7	<0.10[c]	<0.15[c]	**5**	2.6	≪0.5[e]	0.84
2	5.0[d]	1.6[d]	4.0	**16**	4.2	4.5	4.0
3	1.6	1.8	2.6	**17**	9.0	0.4	0.4
4	9.1	4.8	~0.5[d]				

[a] All solutions were exhaustively purged with a stream of argon prior to measurement; values are accurate to ±5%, except those that are less than 1 ns where the uncertainty may be greater. [b] Buffered solutions, 20% (v/v) ACN cosolvent. [c] Picosecond laser pulse excitation source. [d] Biexponential decay; major component is reported. [e] Estimated upper limit using a standard hydrogen spark lamp excitation source.

heterolysis), the 5-methyl-substituted derivative **5** was prepared. The fluorescence quantum yield of **5** drops from 0.48 in CH_3CN, where it is essentially nonreactive, to <0.001 in H_2O, where it efficiently photodecarboxylates. This suggests that it is the tendency of these compounds to efficiently photodecarboxylate from S_1 that results in their diminished fluorescence intensity.

A close examination of the fluorescence data presented in Figure 3 and Table VI show that both **1** and **5** become slightly *more* fluorescent in their protonated forms. For example, the fluorescence quantum yields of **1** and **5** are both ≤0.001 at pH 7, whereas at pH 1 these values increase to ~0.01 and 0.08, respectively. This observation is significant since it suggests that the carboxylates are indeed more reactive but that the difference is too small to be detected by our product quantum yield (Φ_d) determinations.

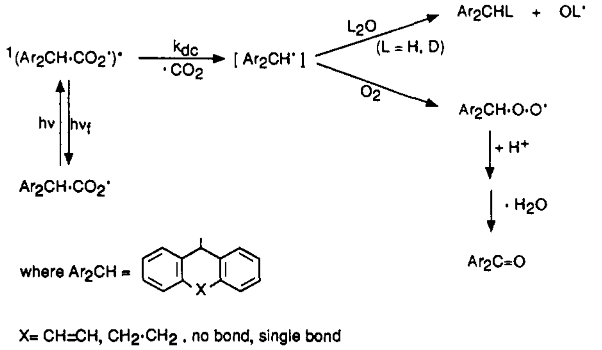
Fluorescence Lifetimes. Fluorescence lifetimes (τ_f) of **1–5**, **16**, and **17** were measured in CH_3CN and H_2O using time-correlated single photon counting (Table VII). The lifetime data follows the same solvent and pH trends that were observed for Φ_f. The fluorescence lifetimes of the acids were typically shorter in aqueous solution, consistent with the added deactivational pathway in this solvent (viz., decarboxylation). The lifetime of the most reactive system, **1**, drops to ~100 ps in H_2O, which is the lower limit of the picosecond single photon counting apparatus that was employed. The substrates **1** and **5** have exceedingly short fluorescence lifetimes in aqueous solution, consistent with a high reactivity in this solvent. Compounds **2–4**, on the other hand, have lifetimes in the nanosecond range ($\tau_f \approx 2–5$ ns). The unusually short fluorescence lifetimes of **4** at pH 1 and **17** at pH's 1 and 7 (as compared to in CH_3CN) are not understood at this time. The fluorescence lifetime of **1** was very sensitive to the presence of H_2O. For instance, the very short lifetime in 100% H_2O (pH 7) steadily increased as the amount of CH_3CN cosolvent was increased.

The solvent isotope effect on the fluorescence lifetime ($\tau_f^{D_2O}/\tau_f^{H_2O}$) has also been calculated for **2–4**. The short lifetime of **1** in aqueous solution prohibited an accurate determination of the solvent isotope effect for this compound. A small solvent isotope effect was observed for **2**, $\tau_{D_2O}/\tau_{H_2O} = 1.2 \pm 0.1$. However, **4**, which was only marginally reactive toward photodecarboxylation ($\Phi_d \approx 0.04$), showed no measurable solvent isotope effect on its fluorescence lifetime, $\tau_{D_2O}/\tau_{H_2O} \approx 1.0$.

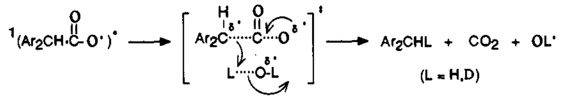
Discussion

Although numerous reports on the photodecarboxylations of carboxylic acids and esters have established the generality of this reaction, a variety of mechanisms have been proposed.[10-24,42] It is important to point out that the photochemical decarboxylations in the present study differ from most of the previous examples in two ways. Firstly, the quantum yields of the diaryl acetates **1–4** are moderate to high, sharply contrasting most of the previously studied substrates, which are considerably less efficient (Φ_p < 0.1). Secondly, we observe the importance of the carboxylate ion in the efficient photodecarboxylation reactions, since neither the esters nor the acidic forms of **2–4** undergo efficient photodecarboxylation.

Scheme II



The following observations support an ionic mechanism involving heterolytic carbon–carbon bond cleavage of the carboxylate ions as the primary photochemical event. (1) The incorporation of deuterium in the photoproducts when the reactions are carried out in D_2O implicates the intermediacy of carbanions. The complete absence of radical coupling products, many of which have been identified in earlier work where radical intermediates reacted with the cosolvent,[25] is inconsistent with radical intermediates in the photodecarboxylation reaction.[43] (2) The steady-state and lifetime fluorescence data, which displayed a strong dependence on the solvent composition in mixed H_2O–CH_3CN solutions, indicate that the solvent polarity has a marked effect on the primary photochemical event. (3) The large normal kinetic isotope effect suggests a heterolytic cleavage step that is associated with strong solvent interactions at the transition state.[38] These observations are consistent with an ionic mechanism and also indicate that the C–C bond cleavage may be concerted with protonation from the solvent (eq 2). The smallest kinetic solvent isotope effect was observed for **4**, which is expected since the carbanion generated in this case is the most stabilized, at least in the ground state. A homolytic fragmentation leading to radical products would be expected to be affected to a much lesser extent.[44]



[2]

A working mechanism that is consistent with our observations is presented in Scheme II. The carbanions produced in the decarboxylation step are many orders of magnitude more basic than solvent H_2O. Therefore, the carbanions will be protonated promptly and, in some cases, this is likely concerted with their formation. The only system which produced appreciable amounts of the ketone in oxygenated solution also had the smallest kinetic solvent isotope effect. Since the 9-fluorenyl anion is stabilized by aromaticity in the ground state, it is expected to have the longest

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[42] Although Miller[20] has outlined 25 possible cleavage modes for the carboxyl function, most of these can be eliminated in the present case on the basis of our product studies.

[43] A mechanism in which the excited-state carboxylate ejects an electron has been proposed in other photodecarboxylation reactions.[23,24] In this sequence, electron ejection is followed by homolytic cleavage to yield the corresponding hydrocarbon radical intermediate. If these radicals are to be converted into the carbanion, as the deuterium incorporation results suggest, they must recapture the initially ejected electrons. We find this mechanism unreasonable since in the present study no radical coupling products are observed in the direct photolysis experiments. It has been shown that similar radicals produced in this mixed solvent system abstract a hydrogen from CH_3CN and generate products of the form R–H, R–CH_2CN, and R–R. It is difficult to imagine that electron capture could compete with these coupling processes so efficiently.

[44] The direct homolytic fragmentation of the carboxylate ion would generate the hydrocarbon radical and the radical anion of carbon dioxide. The initially formed radical–radical anion pair could then generate the carbanion and CO_2 via an electron-transfer step. Although the redox potentials of the various couples are not known, it is not clear why the suberenyl system, which would form an antiaromatic ground-state anion, should be the most favored. In fact, the exact opposite trend would be expected. Furthermore, the complete absence of radical coupling products and the large substrate-dependent solvent isotope effects are inconsistent with this mechanism.

Table VIII. Rate Constants for Photodecarboxylation (k_{dc})

compd	k_{dc} (s^{-1})	rel rates	compd	k_{dc} (s^{-1})	rel rates
1	~6×10^9	680	**4**	8.8×10^6	1
2	1.2×10^8	14	**5**	~4×10^9	450
3	1.0×10^8	11			

lifetime as the "free carbanion".

In ionic ground-state decarboxylations it is recognized that electron-withdrawing groups that can stabilize the departing carbanion, typically β-carbonyl functions, accelerate the reaction. The tendency of **1** and, to a lesser extent, **5** to decarboxylate in their acidic forms would indicate that in the excited state the departing 5-suberenyl anion has an unusual stabilizing property.

Using the mechanism presented in Scheme II, the quantum yield expression for decarboxylation is given by

$$\Phi_d = k_{dc}\tau_f \tag{3}$$

Combining the product quantum yields and the fluorescence lifetimes (measured in 80% H_2O–CH_3CN) according to eq 4 provides rate constants for the heterolytic cleavage step that can be directly compared in the assessment of the intrinsic excited-state reactivity

$$k_{dc} = \Phi_d/\tau_f \tag{4}$$

These rate constants for **1**–**5** are summarized in Table VIII.

The effect of the ICA in the thermal reactions of **1**–**5** is readily understood on the basis of the Hückel $4n + 2$ rule for aromatic ground states. Thus, those systems that proceed via aromatic intermediates (e.g., the 9-fluorenyl anion (six π)) are several orders of magnitude more reactive than those proceeding through intermediates that are formally antiaromatic (e.g., the 5-suberenyl anion (eight π)).[2b,9,29] Since systems which do not contain an ICA of π electrons, such as **2** and **3**, produce charge intermediates that are neither stabilized nor destabilized by aromaticity, they display reactivities intermediate between these extremes.[2b,9,29]

The relative reactivities for *photo*decarboxylation (Table VIII) indicate that the reactivity trends in the photochemically activated process are the exact opposite of those observed in the thermal decarboxylation reaction. Thus, in the photodecarboxylation series suberene-5-carboxylic acid (**1**), which proceeds through an eight π electron ICA, was the most reactive system. Furthermore, fluorene-9-carboxylic acid (**4**), which is the most reactive system in the ground state, is the least reactive toward decarboxylation in S_1. Using the least reactive system, fluorene-9-carboxylic acid (**4**, $k_{dc} = 8.8 \times 10^6$ s^{-1}), as a base value, the relative reactivity of the other acids can be evaluated (Table VIII). Hence, the suberene systems (**1** and **5**) are considerably more reactive toward photodecarboxylation (680 and 450 times, respectively). The unconjugated systems **2** and **3** ($k_{dc} = 1.2 \times 10^8$ and 1.0×10^8 s^{-1}) are about an order of magnitude more reactive than **4**. That **4** is even less reactive than the systems without a clinically conjugated ICA suggests that the presence of a $4n + 2$ π ICA actually has a retarding effect on the photodecarboxylation rates.

In interpreting the dependence of the excited-state reaction rates on structural features, such as the number of π electrons in the ICA, it is tempting to use the same arguments employed for the ground-state series.[9] These arguments are based on the stability of the various charged intermediates, which are known to be either aromatic or antiaromatic on the basis of electron count. The intuitive principles embodied in the Hammond postulate[37] lead to the conclusion that transformations leading to the highly destabilized $4n$ π intermediates (higher $\Delta G°$) will have considerably larger activation barriers (increased $\Delta G^{\ddagger}$).

If we take the increased *photo*reactivity of the $4n$ systems to imply a lower activation barrier on the S_1 surface, then extension of the Hammond postulate would indicate that the excited-state $4n$ charged intermediates are indeed more stabilized than their $4n + 2$ counterparts. This interpretation is based on two assumptions about the excited-state reactions: (1) applicability of the Hammond postulate to the S_1 surface and (2) some degree of adiabaticity in the C–C bond cleavage step.[45] At present, we have no reason to doubt the former, but the second assumption demands some consideration. If the excited states are "funnelling" down to the ground-state potential energy surface rather than proceeding completely on the S_1 surface, an enhanced stability of the $4n$ systems is not required to explain the observed reactivity trends. Instead, one could envisage the $4n$ systems being more reactive simply on the basis of the higher thermal activation barriers (known for the ground-state reactions), which bring the S_0 and S_1 surfaces much closer together and hence increase the rate of internal conversion. In this case the excited-state reactivity is not a function of the S_1 activation barrier but rather of the S_0–S_1 energy gap at some critical point along the reaction coordinate. However, since the transition state occurs late on the S_0 surface (endothermic reaction[46]) and rather early on the S_1 surface (exothermic reaction), it is unclear why internal conversion should occur prior to the S_1 activated complex. In order for diabatic return to the S_0 surface to be product-forming, it must occur late enough to intercept the S_0 transition state. Thus, as long as internal conversion to S_0 follows the rate-limiting cleavage step, the excited-state reactivity reflects the S_1 potential energy barrier.

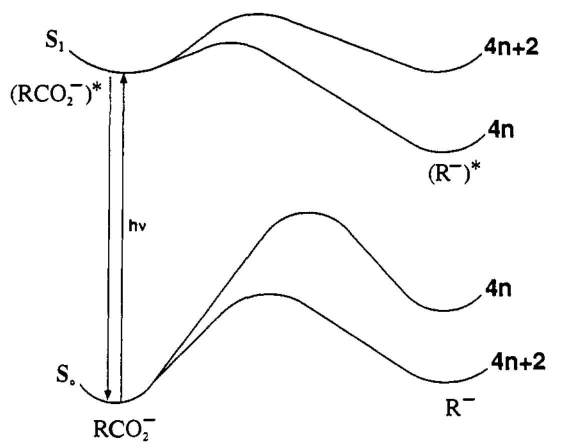

Figure 4. Generalized potential energy diagram for photodecarboxylation in the ground and excited states.

We have attempted to construct a generalized potential energy surface diagram for the thermal and photochemical reactions leading to $4n$ and $4n + 2$ π electron intermediates (Figure 4). Deactivation to the ground-state surface occurs at or near the ionic intermediate stage. Thus, the reactions are adiabatic up to this point. Multiple collisions with the solvent or proton abstraction would almost certainly deactivate the charge intermediates to the ground state. At this point, the reaction can proceed toward completion along the S_0 surface.

The efficient *photo*generation of the eight π electron carbanions in the present study corroborates similar results from our laboratory.[40,47] The results of these studies and those involving the photogeneration of carbocations[25-27] suggest that a "$4n$" stability rule applies in the excited state. The rules for predicting the outcome of pericyclic reactions (Dewar–Zimmermann[48] and Woodward–Hoffmann[49]), which depend in a similar manner on the number of π electrons in a cyclic array, apply to transition states and have not been directly applied to heterolytic bond cleavage reactions. Although at present there is no simple theoretical framework for predicting the stability of cyclically conjugated systems on the excited-state surface, the calculations of

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(45) For a discussion of adiabaticity in organic photoreactions, see: Turro, N. J. *Modern Molecular Photochemistry*; Benjamin/Cumming: Menlo Park, CA, 1978.

(46) Application of Förster cycle type calculations to the photofragmentation of the carbanion intermediates indicates that these transformations are exothermic in the excited state. For a discussion of Förster cycle calculations, see: Weller, A. *Progr. React. Kinet.* **1961**, *1*, 188.

(47) Wan, P.; Budac, D.; Earle, M.; Shukla, D. *J. Am. Chem. Soc.* **1990**, *112*, 8048.

(48) Zimmermann, H. E. *Acc. Chem. Res.* **1971**, *4*, 272.

(49) Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Verlag-Chemie: Weinheim, Germany, 1970.

Jug and others[50] support the notion of "excited-state aromaticity"[51] for 4*n* systems.

Conclusion

The photolysis of **1–5** has led to the photogeneration of carbanions in aqueous solution. These reactions are significant in that they provide a means of studying these important intermediates in highly reactive solvent environments by means of laser flash photolysis. The efficient photogeneration of carbocations and carbanions that contain 4*n* π electrons in a cyclic array of p orbitals has demonstrated a dramatic *reversal of the ground-state structure–reactivity relationships*. The results demonstrate that reactions leading to intermediates with an electron count of 4*n* are enhanced in the excited state. This behavior suggests that species containing a 4*n* ICA are stabilized on the excited singlet state surface.

Experimental Section

General. ^{1}H NMR spectra were recorded on a Perkin-Elmer R32 (90 MHz) or a Bruker AMX (360 MHz) instrument in $CDCl_3$, unless otherwise noted. Mass spectra were taken on a Finnigan 3300 instrument. Melting points were obtained on a Koefler hot stage microscope and are uncorrected. Gas chromatography was performed on a Varian 3700 instrument with a Hewlett-Packard 3390A integrator and a SE-54 capillary column. Acidities in the pH range were measured on a Corning 140 pH meter. Standard buffer solutions (Fisher Scientific), ionic strength 0.05 M unless otherwise noted, were used for product quantum yield experiments and fluorescence work. Solvents for fluorescence studies were of the highest available purity (H.P.L.C or Spectral Grade) and checked for spurious emission before use. Photolyses were carried out in Suprasil quartz cuvettes for 100/200/600 mL quartz tubes using a Rayonet RPR 100 photochemical reactor (254- or 350-nm lamps). An Oriel 200-W Hg light source and an Applied Photophysics monochromator (λ_{ex} = 280 nm) on an optical bench were used for the quantum yield determinations. Fluorescence spectra were taken on a Perkin-Elmer MPF 66 spectrofluorimeter or a Photon Technologies International LS-1 in the steady-state mode. Fluorescence lifetimes were measured using time-correlated single photon counting on a Photon Technologies International LS-1 instrument in the lifetime mode and/or at the Center for Fast Kinetics Research (University of Texas at Austin), using a mode-locked, synch-pumped, cavity-dumped dye laser, frequency-doubled to provide an excitation source at 280 nm (Spectra Physics Model 574B dye laser with Spectra Physics Series 3000 Nd:YAG as the pump source.

Materials. The following compounds were purchased from Aldrich Chemical Co.: 9-fluorenone; suberenone; suberone; fluorene; suberane; diphenylacetic acid; 2-benzoylbenzoic acid; and 2-aminopyridine. The carboxylic acid derivatives were prepared by treating the appropriate hydrocarbons with *n*-BuLi and quenching with CO_2. The esters **16** and **17** were prepared by conventional methods from the corresponding carboxylic acids.

Suberene-5-carboxylic Acid (5*H*-Dibenzo[*a*,*d*]cycloheptene-5-carboxylic Acid) (1). A solution of 1.0 g (5.2 mmol) of suberene (**7**) in 100 mL of dry THF under nitrogen was cooled to 0 °C, and 5.7 mmol of a 2.5 M solution of *n*-BuLi (Aldrich) was added dropwise via syringe. The solution was heated to reflux for 1 h and then cooled to room temperature before purging with dry CO_2(g) via syringe. The reaction was worked up by reducing the THF to 10 mL, diluting with 100 mL of CH_2Cl_2, and then extracting with a 0.1 M NaOH solution (3 × 100 mL). The combined aqueous fractions were acidified, and the cloudy precipitate was extracted into CH_2Cl_2 (2 × 100 mL). The organic layer was dried over $MgSO_4$, filtered, and reduced under vacuum to yield 0.7 g of a white solid (65% yield), which was recrystallized from 1:2 H_2O–ethanol to yield fine white needles: mp 232–238 °C [lit.[52] mp 239–241 °C]; ^{1}H NMR (acetone-d_6) δ 3.8 (br s, 1 H) 5.16 (s, 1 H), 7.05 (s, 2 H), 7.2–7.6 (m, 8 H); mass spectrum (CI) (*m*/*z*) 237 (M^+ + 1).

Suberane-5-carboxylic Acid (5*H*-Dibenzo[*a*,*d*]cycloheptane-5-carboxylic Acid) (2). To a solution of 5.0 g (25 mmol) of suberane (**8**) in 100 mL of dry THF cooled to 0 °C under a nitrogen was added 34 mmol of a 1.7 M solution of *n*-BuLi (Aldrich) via syringe. The reaction was warmed to room temperature and stirred for 1 h before it was poured onto crushed carbon dioxide. The mixture was worked up by diluting with 200 mL of H_2O acidified with 10% HCl and extracting with CH_2Cl_2 (2 × 200 mL). The organic fractions were then extracted with 0.1 M NaOH (2 × 200 mL). The combined aqueous layers were cooled on ice and then acidified. Filtration of the precipitate gave 4 g of a solid material, which was recrystallized from 1:2 H_2O–ethanol to yield white needles: mp 218–220 °C [lit.[53] mp 220–221 °C]; ^{1}H NMR (acetone-d_6) δ 3.6–4.6 (m, 4 H), 4.6 (br s, 1 H), 4.90 (s, 1 H), 7.0–7.5 (m, 8 H); mass spectrum (CI) (*m*/*z*) 239 (M^+ + 1).

Fluorene-9-carboxylic Acid (4). Treatment of fluorene (**10**) with *n*-BuLi and CO_2(s) by the procedure outlined for **2** gave a white solid, which was recrystallized from 95% ethanol: mp 202–210 °C [lit.[54] mp 230–232 °C]; ^{1}H NMR (acetone-d_6) δ 4.2 (br s, 1 H), 4.80 (s, 1 H), 7.2–7.8 (m, 8 H); mass spectrum (CI) (*m*/*z*) 213 (M^+ + 1).

5-Methylsuberene-5-carboxylic Acid (5-Methyl-5*H*-dibenzo[*a*,*d*]cycloheptene-5-carboxylic Acid) (5). To a solution of 0.25 g (1.06 mmol) of suberenecarboxylic acid in 40 mL of dry THF cooled to −78 °C under a nitrogen atmosphere was added 2.6 mmol of a 1.5 M solution of lithium diisopropylamide (Aldrich) via syringe. The solution was stirred for 1 h and warmed to reflux for an additional hour. A solution of 0.30 g (2.1 mmol) of methyl iodide in 20 mL of THF was added slowly via a dropping funnel. After stirring overnight, the reaction mixture was worked up by evaporating the THF to 10 mL, diluting with CH_2Cl_2 (100 mL), and extracting with aqueous sodium hydroxide (3 × 100 mL, 0.01 M NaOH). The aqueous fraction was acidified and extracted with CH_2Cl_2 (3 × 100 mL) to yield 150 mg of a white solid (55% yield), which was recrystallized from 1:2 H_2O–ethanol: mp 224–225 °C; ^{1}H NMR (acetone-d_6) δ 2.24 (s, 3 H), 5.9 (br s, 1 H), 7.06 (s, 2 H), 7.2–7.7 (m, 8 H); mass spectrum (CI) (*m*/*z*) 251 (M^+ + 1); IR (cm^{-1}) 1685. Anal. Calcd for $C_{17}H_{14}O_2$: C, 81.58; H, 5.64. Found: C, 81.16; H, 5.72.

5-Deuteriosuberene-5-carboxylic Acid (5-Deuterio-5*H*-dibenzo[*a*,*d*]cycloheptene-5-carboxylic Acid) (6). A solution of 5,5-dideuteriosuberene was treated with *n*-BuLi and CO_2(g) in the manner outlined for **1** to give white needles after recrystallization from ethanol: mp 226–239 °C; ^{1}H NMR (acetone-d_6) δ 5.8 (br s, 1 H), 7.05 (s, 2 H), 7.2–7.6 (m, 8 H); mass spectrum (CI) (*m*/*z*) 238 (M^+ + 1).

5-Carbomethoxysuberene (5-Carbomethoxy-5*H*-dibenzo[*a*,*d*]cycloheptene) (16). A solution of 100 mg of **1** in 50 mL of methanol was treated with 1 mL of concentrated H_2SO_4 and refluxed for 12 h. After workup, the crude solid was recrystallized from methanol: mp 109–112 °C [lit.[52] mp 111.5–113 °C]; ^{1}H NMR δ 3.45 (s, 3 H), 4.85 (s, 1 H), 7.2–7.4 (m, 8 H).

9-Carbomethoxyfluorene (17). Treatment of **4** as above led to **17**, which was recrystallized from methanol: mp 63–64 °C [lit.[54] mp 63 °C]; ^{1}H NMR δ 3.70 (s, 3 H), 4.85 (s, 1 H), 7.2–7.8 (m, 8 H); mass spectrum (EI) (*m*/*z*) 224 (M^+).

Product Studies. Preparative Photolysis of 1–6, 16, and 17 in H_2O–CH_3CN Mixtures. In a typical preparative study, 100 mg of substrate was dissolved in 30 mL of CH_3CN and then diluted with 70 mL of H_2O. The solution was adjusted to a pH ≥ 8, with the aid of a pH meter, by adding dropwise a stock solution of ~1 M NaOH. (For preparative runs at other pH's, a stock solution of ~1 M HCl was employed. For photolyses carried out at pH < pK_a, 40–50% CH_3CN as cosolvent was employed.) The solution was then irradiated at 254 nm in an RPR 100 Rayonet photochemical reactor. After photolysis the solution was worked up by saturating with NaCl, acidifying to pH ≈ 1 with 10% HCl, and extracting with CH_2Cl_2 (2 × 100 mL). The photolysate was analyzed by ^{1}H NMR, and conversions were determined by the integrated peak areas. These reactions were very clean, giving rise to only one photoproduct. The photoproducts were separated from the carboxylic acid starting material by extracting the crude mixture with a bicarbonate solution. The ^{1}H NMR and mass spectral data were compared with those of authentic materials.

Preparative Photolysis of 1–4 in D_2O–CH_3CN Mixtures. In a typical preparative study, 50 mg of substrate was dissolved in 20 mL of CH_3CN and diluted with 30 mL of D_2O. After the pD was adjusted to ≥8 with ~1 M NaOD, the solutions were photolyzed and worked upo in the usual manner. Conversions were determined by ^{1}H NMR integrations, and the monodeuterated photoproducts were then isolated by extracting the crude mixture with a bicarbonate solution. The ^{1}H NMR and mass spectral data for the isolated monodeuterated products are presented below.

5-Deuteriosuberene (5-deuterio-5*H*-dibenzo[*a*,*d*]cycloheptene) (11): ^{1}H NMR δ 3.73 (br t, *J* = 2 Hz, 1 H), 7.02 (s, 2 H), 7.1–7.5 (m, 8 H);

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(51) The term "excited-state aromaticity" is employed to imply certain features of the electronic distribution and a relative stability on the excited-state potential energy surface. The unusual chemical stability associated with ground-state aromatic molecules does not apply to charged intermediates or excited states which are necessarily unstable with respect to the neutral compounds and ground states.

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mass spectrum (EI) (m/z) 193 (M^+). **5-Deuteriosuberane (5-deuterio-5*H*-dibenzo[*a*,*d*]cycloheptane) (12)**: ^1H NMR δ 4.02 (br s, 1 H), 3.10 (s, 4 H), 7.0 (m, 8 H); mass spectrum (EI) (m/z) 197 (M^+). **Deuteriodiphenylmethane (13)**: ^1H NMR δ 3.96 (br t, J = 1 Hz, 1 H), 7.2–7.3 (m, 10 H); mass spectrum (EI) (m/z) 169 (M^+). **9-Deuteriofluorene (14)**: ^1H NMR δ 3.80 (br t, J = 2 Hz, 1 H), 7.2–7.7 (m, 8 H); mass spectrum (EI) m/z 167 (M^+).

The deuterium NMR spectrum of **11** obtained from the photolysis of **1** in D_2O-CH_3CN as above indicated that there was <1% ^2H incorporation at the 10,11-positions of 5*H*-dibenzo[*a*,*d*]cycloheptatriene.

Preparative Photolysis of 1–4, 10, and 16–17 in Oxygen-Saturated Solution. Photolyses were carried out as before but under a continuous stream of oxygen instead of argon. The conversions were determined by analysis of the crude ^1H NMR signals. The conversions were determined by analysis of the crude ^1H NMR signals. The ketone photoproducts were identified by comparison of their ^1H NMR and GC retention times with those of authentic materials. The ratios of ketone to hydrocarbon were determined by GC.

Triplet Sensitization. Solutions of 2.0 g of 2-benzoylbenzoic acid in 200 mL of 60% H_2O-CH_3CN (pH $\geq$ 8) containing 50 mg of either **1** or 4 were deaerated with argon and photolyzed through Pyrex at 350 nm. The photolysate was saturated with $NaHCO_3$ and extracted with CH_2Cl_2 (5 × 100 mL). The products were analyzed by ^1H NMR and GC and compared to spectra of authentic materials.

Dark Reactions. None of the compounds in this study underwent decarboxylation in the dark under the conditions employed to study the photochemistry. Control experiments were performed by treating 50 mg of each substrate in exactly the same manner as the photolyzed samples, except that they were stirred in the dark for 1 h. The samples were analyzed by ^1H NMR after being worked up in the normal way.

Product Quantum Yields. Quantum yields for the formation of the hydrocarbons for **1**, **4–6**, and **16** were measured in a number of solvents on an optical bench (λ_{ex} = 280 nm). In a typical experiment, 0.6 mL of a stock solution of substrate in CH_3CN (6×10^{-3} M) was transferred to a quartz cuvette and diluted with 2.4 mL of H_2O (pH 7 buffer). The solutions were purged with a stream of argon for 10 min prior to and during the photolysis (usually 1–20 min). Conversions were kept below 10% in all cases. After irradiation, the photolysate was worked up in the normal manner and the conversion determined by GC analysis, using the appropriate correction factors to compensate for differences in the GC detector response. Conversions were determined using an external standard method (9-fluorenol) and by comparison of the starting material and photoproduct GC signals. Both methods compared well, indicating that a good mass balance was obtained. Light intensity measurements were determined by irradiating a 0.006 M aqueous solution of potassium ferrioxalate under identical conditions and working up according to the method of Hatchard and Parker.[55] Quantum yield determinations for **2** and **3** were determined at 254 nm in the Rayonet reactor using a merry-go-round apparatus and fluorene-9-carboxylic acid (4) as a secondary standard (Φ_p = 0.042). In a typical experiment, 0.6 mL of a stock solution of substrate in acetonitrile (ca. 4×10^{-2} M) was transferred into a quartz cuvette and diluted with 2.4 mL of H_2O (pH 7 buffer). Each solution was purged with a stream of argon for 10 min prior to photolysis and placed in a merry-go-round. Solutions were irradiated at 30-s intervals to allow for manual agitation (usual total irradiation time 2–10 min). Solutions were worked up and products analyzed as before. Quantum yields were also determined at various pH's using buffer solutions. Quantum yield determinations in D_2O were basified with 10–80 μL of a ~0.1 M NaOD stock solution.

Steady-State and Transient Fluorescence Behavior. Fluorescence spectra were measured in 1.00-cm Suprasil quartz cuvettes at 10^{-4}–10^{-5} M after 10 min of argon purging. Time-correlated single photon counting was employed to measure the fluorescence lifetimes (τ_f) in argon-saturated solutions with optical densities of 0.03–0.30 at the exciting wavelength. Fluorescence quantum yields (Φ_f) were determined by comparing the integrated corrected emission bands of the substrates with those of secondary standards and correcting for differences in the refractive index.[56] Benzene (spectral grade) was employed for suberane-5-carboxylic acid (**2**) and diphenylacetic acid (**3**), 2-aminopyridine (Aldrich, 99+%) was employed for compounds with the suberene chromophore (**1**, **5**, and **16**), and fluorene (sublimed 2×) was used for substrates with the fluorene chromophore (**4** and **17**). Solutions were absorbance-matched at optical densities less than 0.1 and deaerated with argon for 10 min prior to measurement.

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