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Excited-State Carbon Acids: Photochemical C–H Bond Heterolysis vs Formal Di-π-methane Rearrangement of 5*H*-Dibenzo[*a*,*c*]cycloheptene and Related Compounds

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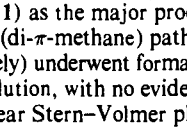
Abstract: The possible excited-state carbon acidity behavior of 5*H*-dibenzo[*a*,*c*]cycloheptene (**2**) and related compounds has been investigated in aqueous CH_3CN solution. In non-basic or aprotic solvents such as CH_3CN or cyclohexane, direct photolysis of **2** gave exclusively dibenzonorcaradiene (**10**) ($\Phi = 0.087$ in CH_3CN), via both singlet (initial 1,7-hydrogen shift of the methylene hydrogen, followed by electrocyclic ring closure) and triplet (di-π-methane) pathways. However, in aqueous CH_3CN or alcohol solutions, the main deactivational pathway from S_1 is C–H bond heterolysis from the methylene 5-position. Thus photolysis of **2** in 70% D_2O–CH_3CN gave 5-deuterio-5*H*-dibenzo[*a*,*c*]cycloheptene (**11**) as the major product ($\Phi = 0.028$), in addition to **10** ($\Phi = 0.010$), which was found to arise exclusively via a residual triplet (di-π-methane) pathway. Two related derivatives that are somewhat less rigid (1,2- and 3,4-benzotropilidenes, **7** and **5**, respectively) underwent formal di-π-methane rearrangement (via initial 1,7-hydrogen shift) exclusively on photolysis, even in aqueous solution, with no evidence for carbon acid behavior. Fluorescence quenching of **2** by added water in CH_3CN solution gave a linear Stern–Volmer plot, with $k_q = 2.05 \times 10^8$ M^{-1} s^{-1}. The fluorescence emissions of **7** and **5** were not quenched to any observable extent on addition of water to CH_3CN solutions of these substrates: quenching of fluorescence by H_2O appears to be a useful experimental criterion for testing the possibility of excited-state carbon acid behavior of these substrates.

The study of carbon acids in the ground state is an area of fundamental interest.[1-3] In contrast, essentially nothing is known with regard to the behavior of carbon acids in electronically excited states, although several examples of Förster cycle calculations[4-7] of a number of hydrocarbons with benzylic protons show that these protons become vastly more acidic in the excited singlet state, by as many as 30 orders of magnitude. Prior to our investigation in this area, there were no known examples of ionizing carbon acids in the excited state. We have reported[7,8] the first example of an ionizing excited state carbon acid in suberene (**1**; also known as dibenzosuberene or 5*H*-dibenzo[*a*,*d*]cycloheptene), in which the methylene protons at the 5-position are readily exchangeable with solvent water on photolysis in aqueous solution. We have noted previously[7,8] the importance of attaining an 8π ($4n$) electron count in the *internal cyclic array* (ICA; defined as the ring system between the two benzene rings) of these carbanion systems, as opposed to $4n + 2$ electrons, or in systems that cannot form a conjugated ICA on reaction. The latter two types of systems failed to display carbon acid behavior on photolysis.[7,8] The importance of the $4n$ electron count for carbanion photogeneration was also evident in our study of relative photodecarboxylation efficiencies of dibenzannelated acetic acids.[9] We now report that 5*H*-dibenzo[*a*,*c*]cycloheptene (**2**), a structural isomer of **1**, is also a very strong carbon acid in S_1. Moreover, the study of this system in particular sheds valuable insight into solvent and structural effects necessary for carbanion photogeneration via C–H bond heterolysis. For example, **2** undergoes formal di-π-methane rearrangement in weakly basic or nonbasic solvents such as CH_3CN and cyclohexane, via distinct singlet and triplet pathways, but upon addition of a sufficient amount of water (to CH_3CN solution), the singlet rearrangement process is essentially completely retarded (as indicated by ^1H NMR studies) and *ionization* of the C–H bond from the 5-position becomes the dominant deactivational pathway from S_1. Such mechanistic behavior is unprecedented in organic photochemistry.

Results and Discussion

Materials. The principal aromatic alkene of interest, 5*H*-dibenzo[*a*,*c*]cycloheptene (**2**, DBC), was made by dehydrating alcohol **3**, which was in turn made from dibenzo[*a*,*c*]cycloheptan-6-one (**4**). Ketone **4** was readily synthesized from the procedure of Tolbert and Ali.[10] The desired DBC (**2**) was identical spectroscopically with data given in the literature for this compound.[11,12]



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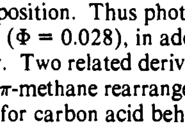

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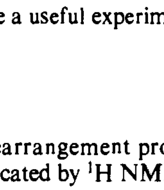

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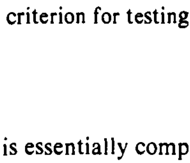

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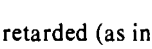

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The 3,4-benzotropilidene (**5**, 3,4-BT) was made from commercially available 1-benzosuberone (**6**) from the procedure of Burdett et al.[13] Conversion of **5** to 1,2-benzotropilidene (**7**, 1,2-BT) was accomplished by simple isomerization with potassium *tert*-butoxide.[14]

Samples of 6-deuterio-5*H*-dibenzo[*a*,*c*]cycloheptene (**8**, 6-*d*-DBC) required in these studies was made via base-catalyzed elimination of bromide **9**, which was in turn made from **4** via

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(13) Burdett, K. A.; Shenton, F. L.; Yates, D. H.; Swenton, J. S. *Tetrahedron* **1974**, *30*, 2057.

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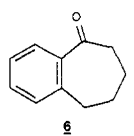

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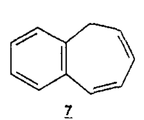

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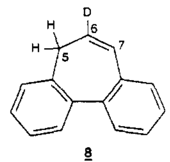

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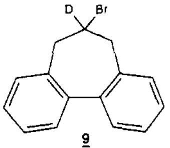
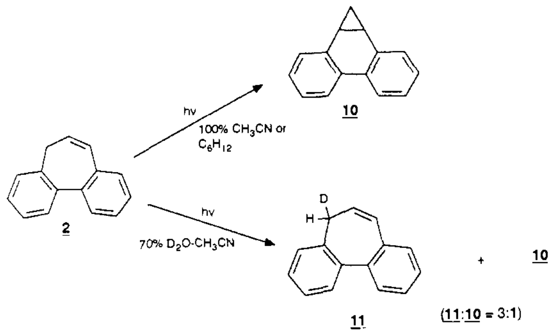


9

standard procedures (see Experimental Section).

Product Studies of 2. Photolysis of DBC (**2**) (10^{-3} M; Rayonet RPR 100 photochemical reactor with 254-nm lamps; argon purged; ≈15 °C; 5–120 min) in pure CH_3CN or cyclohexane gave dibenzonorcaradiene (**10**)[15] as the only product in low-conversion experiments (<30%) (eq 1). Dibenzonorcaradiene (**10**) may be considered as a formal di-π-methane rearrangement product of **2**, and to our knowledge this reaction has not been reported previously. When **2** was photolyzed in 50% (v/v) H_2O–CH_3CN, the rearrangement yield to **10** was significantly decreased compared to the runs in pure CH_3CN over the same photolysis time (e.g., 40% in pure CH_3CN vs 15% in 50% H_2O-CH_3CN). In other hydroxylic solvents such as 95% EtOH, the rearrangement yield to **10** was also depressed, compared to that in pure CH_3CN. No reactions were observed in the dark under any of these conditions.



(1)

In view of the results of our investigation[7] of the excited-state carbon acidity of suberene (**1**), a possible explanation for the lower *formal* di-π-methane rearrangement yields in hydroxylic solvents of **2** is that a competing C–H bond heterolysis (from the 5-position) pathway was available in **2** when it was photolyzed in polar hydroxylic solvents. Thus, photolysis of **2** in 50% D_2O–CH_3CN (10 min) gave 5-*d*-DBC (**11**) as the major product, along with a lesser amount of **10** (eq 1). Extended photolysis (>20 min) resulted in incorporation of more than one deuterium into **2**, as indicated by mass spectrometry. In addition, phenanthrene and 9-methylphenanthrene were also detected by GC/MS in extended photolysis runs. These two products most likely arise from secondary photolysis of **10**. This is substantiated by work of Richardson et al.,[18] who reported that photolysis of **10** in hydrocarbon solvents gave phenanthrene as the major product. The other fragment produced was believed to be methylene.[18] Although 9-methylphenanthrene was not reported as a photoproduct by these workers, its formation is not unexpected.

No deuterium incorporation was observed in the dark in all solvents, which implies that incorporation of deuterium into substrate is a photochemically initiated process. In addition, no deuterium incorporation into **2** was observed with photolysis in 90% CD_3CN–CH_3CN; only rearrangement to **10**. These observations are consistent with an anionic mechanism for deuterium incorporation, the simplest of which is C–H bond ionization on photolysis, to generate a carbanion intermediate, which on protonation gives back substrate. A hydroxylic solvent is necessary in the exchange process in order to facilitate the formation of the ion pair, as well as assisting the ionization (by functioning as the general base) of what is a weakly polarized C–H bond in the ground state. If a radical mechanism for deuterum incorporation was operative in D_2O, i.e., transfer of a deuterium atom from D_2O to a photogenerated 5*H*-dibenzo[*a*,*c*]cycloheptenyl radical, one would have expected the same mechanism to be operative in pure CD_3CN, noting that the C–H bond in CH_3CN is significantly weaker than the O–H bond of H_2O (86 vs 119 kcal mol^{-1}, respectively).[19] Furthermore, production of any 5*H*-dibenzo[*a*,*c*]cycloheptenyl radical on photolysis would be expected to give some of the corresponding radical coupling product (bis(5*H*-dibenzo[*a*,*c*]cycloheptenyl)), which was not observed under any of the above photolysis runs.

Evidence that *initial* deuterium incorporation from solvent D_2O occurred at the 5-position of **2** was available from ^1H NMR (90 and 250 MHz) spectra of the product mixture on photolysis in 70% D_2O–CH_3CN. The aliphatic region of the spectrum for *unreacted* **2** is as follows: δ 3.1 (d, J = 6 Hz, 2 H, $-CH_2-$), 6.28 (dt, J = 6 and 8 Hz, 1 H, $ArCH_2CH{=}CH$), 6.65 (d, J = 8 Hz, 1 H, $-CH{=}CHAr$). After photolysis in 70% D_2O–CH_3CN, this part of the spectrum changed: δ 3.1 (m, area <2 H), 6.28 (m, 1 H), 6.65 (d, J = 8 Hz, 1 H). The methylene signal at δ 3.1 became a *multiplet* and was decreased in intensity (relative to the vinyl protons) because of deuterium incorporation at this position. The vinyl proton at the 6-position (δ 6.28) also became an unresolved *multiplet* due to increased coupling to the deuterium now at the 5-position. However, its intensity remained unchanged relative to the vinyl proton at the 7-position (δ 6.64), which itself remained as a clean doublet. It should be noted that in these experiments, it is not possible to distinguish whether initial deuterium incorporation is to the *same* carbon from which the proton is lost or to the other equivalent carbon site of the proposed carbanion intermediate. On extended photolysis, which is known to result in incorporation of more than one deuterium into **2** (vide supra), the ^1H NMR spectrum (90 and 250 MHz) of recovered substrate became even more complicated and not readily analyzable, suggesting the incorporation of 2 or more deuteriums *at more than one site*. The determination of where the second (and possibly the third) deuterium atom ends up will require analysis with higher field ^1H and ^{13}C NMR, the results of which will be reported in due course. It is clear, however, that the first deuterium ends up exclusively at the 5-position of the ring system, as far as can be determined by 250-MHz ^1H NMR. It is conceivable that a small fraction of the deuterium content does end up at another position (besides the 5-position) but it is negligible.

Product Studies of 8. Photolyses of **8** were carried out in order to determine the mechanism of the *formal* di-π-methane rearrangement and to delineate the mechanistic relationship between C–H bond heterolysis (carbon acid behavior) and this rearrangement. We were able to prepare **8** in 90–95% purity after purification from preparative LC. The two principal contaminants were 9-methylphenanthrene (≈6%) and **2** (≈4%). The presence of these two contaminants at these levels did not affect the overall aims of the product studies. Deuteration of **2** at the 6-position resulted in a very characteristic change in the aliphatic region of the ^1H NMR (90 MHz) spectrum for this compound. There are now only two broad singlets at δ 3.1 (2 H, $-CH_2-$) and 6.65 (1 H, ArCH), the broadness due to unresolved coupling to deuterium at the 6-position. Mass spectrometry showed >95% monodeuteration.

The photochemical rearrangement of **2** to **10** can proceed via two possible mechanisms. The two routes are as follows: (a) a true di-π-methane (Zimmerman)[20] rearrangement; or (b) initial

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[15] Also known as 1a,9b-dihydro-1*H*-cyclopropa[1]phenanthrene. The ^1H NMR of the product was identical with that previously reported[16,17] for this compound.

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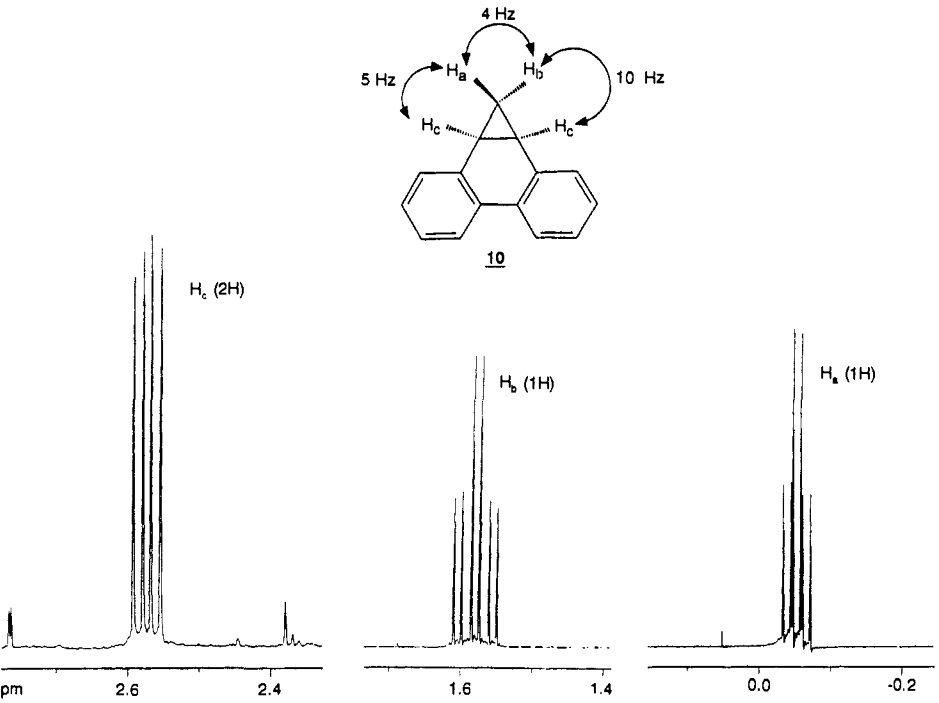
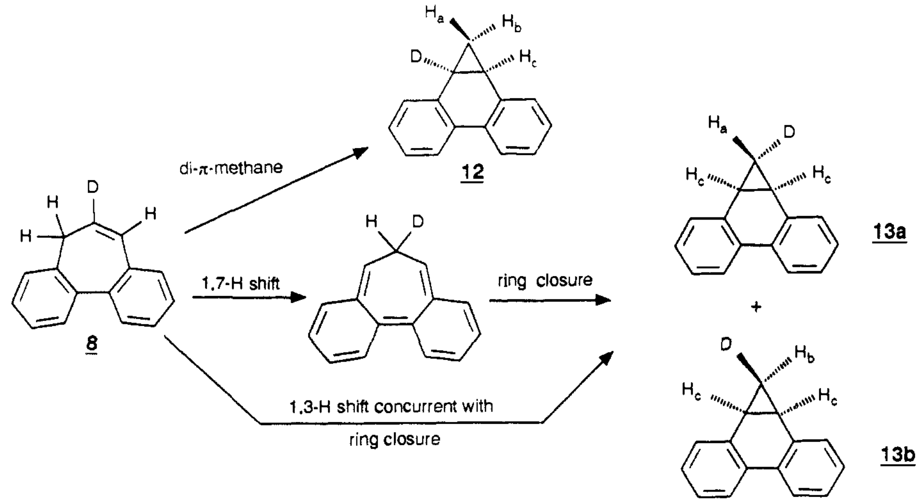


Figure 1. ^1H NMR (360 MHz) spectrum of the cyclopropyl resonance region of **10** formed from direct photolysis of **2** in 100% CH_3CN.

Scheme I



1,7-hydrogen shift followed by electrocyclic ring closure,[21] or the mechanistically indistinguishable alternative (as it applies to **2**) involving a 1,3-hydrogen shift concurrent with formation of the cyclopropane ring[14,22] (Scheme I). In the following analysis, it will be shown that use of **8** can in principle distinguish between these two possible routes, as shown in Scheme I. A true di-π-methane rearrangement of **8** (the Zimmerman[20] route) would give cyclopropane **12** exclusively, where the deuterium would be located at one of the two equivalent methine positions. A mechanism via initial 1,7-hydrogen shift followed by electrocyclic ring closure would give cyclopropanes **13a** and **13b** exclusively, where the deuterium would be located at the methylene position (presumably an equimolar mixture of *exo-d* (**13a**) and *endo-d* (**13b**) isomers). A mechanism in which both routes are operative would give a mixture of **12** and **13a,b**.

For reference, the 360-MHz spectrum of the cyclopropyl proton resonance region of **10** is shown in Figure 1, with the proton resonances assigned and hyperfine couplings indicated. The endo methylene proton (H_a) is at higher field (δ -0.052) than the exo methylene proton (H_b; δ 1.58) because the latter is closer to the deshielding region of the benzene rings. Müller et al.[16,17] and Richardon et al.[18] have made the same assignment for these two protons.

The triplet-sensitized photolysis of **8** was carried out with benzophenone-2-carboxylic acid (BCA; 2-benzoylbenzoic acid) as the triplet sensitizer in 100% CH_3CN solution. The triplet energy of **8** should be about 60 kcal mol^{-1}, using the known triplet of energy of styrene (E_T = 62 kcal mol^{-1})[19] as a guide. The triplet energies of benzophenone derivatives are in the range 68–71 kcal mol^{-1}.[19] Transfer of triplet energy from BCA to **8** should occur. In addition, use of BCA allows irradiation at 350 nm, where **8** does not absorb, as well as ease of separation from the photolysate (by simple extraction with base). Sensitized photolysis with 1.5

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(20) (a) Zimmerman, H. E. In *Rearrangements of Ground and Excited States*; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 3. (b) Hixson, S. S.; Mariano, P. S.; Zimmerman, H. E. *Chem. Rev.* **1973**, 531. (c) Cowan, D. O.; Drisko, R. L. *Elements of Organic Photochemistry*; Plenum Press: New York, 1976; Chapter 8. (d) Turro, N. J. *Modern Molecular Photochemistry*; Benjamin/Cummings: Menlo Park, 1978; p 487.

(21) To our knowledge, the formal di-π-methane rearrangement of **2** has not been reported. The possibility of this alternative pathway (i.e., path b) is based on what is known about the photochemical rearrangements of benzotropilidenes **5** and **7** studied by Burdett et al.[13] and Pomerantz and Gruber.[14,22]

(22) Pomerantz, M.; Gruber, G. W. *J. Am. Chem. Soc.* **1967**, *89*, 6798.

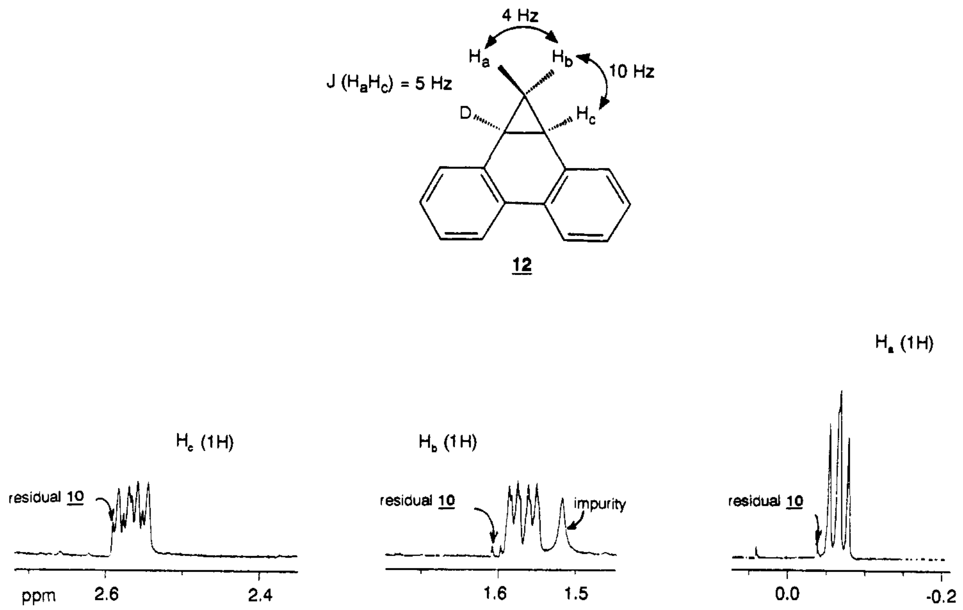


Figure 2. ^{1}H NMR (360 MHz) spectrum of the cyclopropyl resonance region of **12** formed from triplet sensitization of **8** with BCA in 100% CH_3CN.

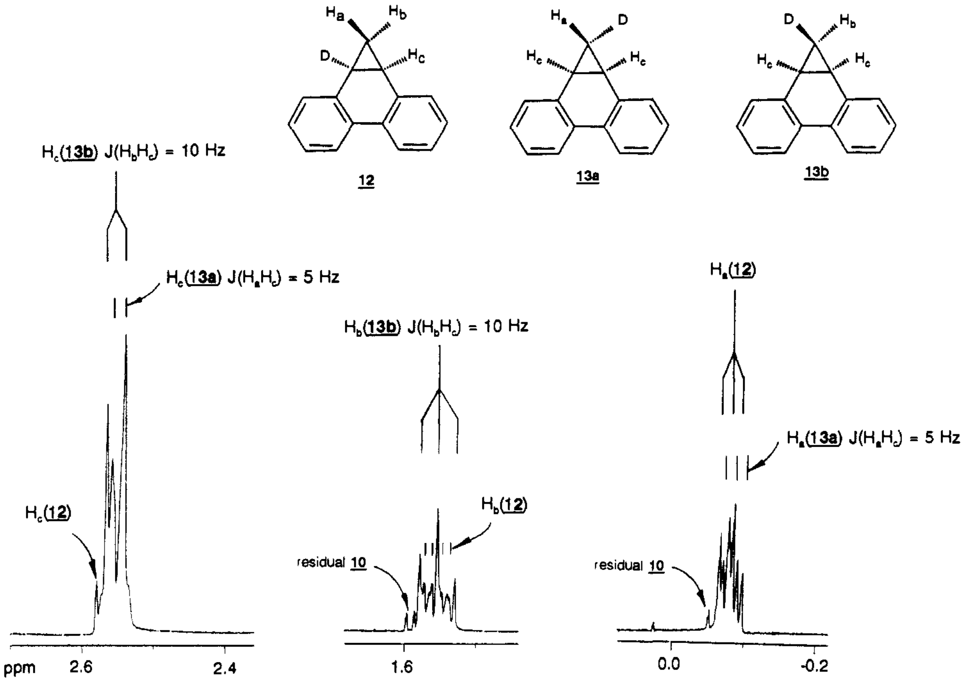


Figure 3. ^{1}H NMR (360 MHz) spectrum of the cyclopropyl resonance region of a ≈1:2 mixture of **12** and **13a,b** formed from direct photolysis of **8** in 100% CH_3CN.

g of BCA and 40 mg of **8** in 100% CH_3CN (λ_{ex} = 350 nm; 60 min) gave (≈29%) a cyclopropane derivative with the ^{1}H NMR (360 MHz) spectrum of the cyclopropyl region shown in Figure 2. The signals are significantly broader than those observed in Figure 1 for **10**, indicative of unresolved coupling to deuterium. Examination of the splitting patterns and integrated areas clearly indicates that the spectrum is that of **12** (with traces of **10** from photoreaction of residual **2**). *That is, the triplet state of **2** undergoes di-π-methane rearrangement exclusively* (in 100% CH_3CN).

Direct photolysis of **8** (40 mg) in 100% CH_3CN (10 min) at 254 nm gave (≈39%) a cyclopropane derivative with the ^{1}H NMR (360 MHz) spectrum of the cyclopropyl resonance region shown in Figure 3. Analysis of the splitting patterns and integrated areas shows that it is a mixture consisting of **12** and **13a,b** in about a 1:2 ratio. Since the triplet state of **2** rearranges to **10** via the di-π-methane mechanism exclusively, the direct photolysis results imply that the singlet state of **2** must rearrange to **10** via mechanism a (i.e., via initial 1,7-hydrogen shift), at least to some extent, although not necessarily exclusively.

Direct photolysis of **8** (40 mg) in 70% CH_3CN–H_2O (15 min) gave (≈50%) a cyclopropane derivative with a ^{1}H NMR spectrum of the cyclopropyl region identical with that shown in Figure 2, obtained by triplet sensitization. Thus, in a predominantly aqueous medium, only rearrangement to **12** (via the di-π-methane mechanism) was observed. Since fluorescence studies (vide infra) show that in predominantly aqueous solution (e.g., 70% H_2O–CH_3CN) the fluorescence emission of **2** is almost completely quenched, the observation that photolysis of **8** in 70% H_2O–CH_3CN gave only **12** (via the di-π-methane pathway) argues against the possibility that the S_1 state of **8** reacts via *both* rearrangement mechanisms. The rearrangement that *is* observed therefore comes from reaction of the triplet state obtained from intersystem crossing. However, with the results at hand, it is not possible to completely rule out that the S_1 state of **8** can react via the di-π-methane pathway to a *minor* extent. It is clear, however, the predominant mode of rearrangement of S_1 is via mechanism b. The state-specific route for rearrangement of **2** is not unreasonable

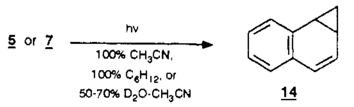
Table I. Quantum Yields for Formal Di-π-methane Rearrangement of **2**, **5**, and **7**

solvent[a]	**2**[b]	**5**[c]	**7**[c]
100% CH_3CN	0.087 ± 0.004 (0.050)[d]	>0.7	
95% EtOH	0.010 ± 0.02	≥0.7	
70% H_2O–CH_3CN	0.010 ± 0.02		
50% H_2O–CH_3CN		≥0.7	≈0.7
C_6H_{12}	0.015 ± 0.001 (0.008)[d]	0.87[e]	0.7 ± 0.1

[a] Aqueous portion at pH 7. Unless otherwise noted, solutions were purged with argon prior to irradiation (at 22 ± 2 °C). [b] Measured with potassium ferrioxalate actinometry[24] and GC for analysis; λ_{ex} = 280 nm. [c] Measured relative to the known quantum yield of **5** in C_6H_{12} (Φ = 0.87);[13] λ_{ex} = 254 nm. [d] Aerated solution. [e] Taken from ref 13.

knowing the state selectively of these types of reactions.[20] As will be demonstrated (vide infra), the quantum efficiency of the rearrangement to **12** in predominantly aqueous solution is much lower than that observed in 100% CH_3CN (by a factor of about 5), suggesting that water not only has quenched the singlet rearrangement process but competes with intersystem crossing as well.

Product Studies of 5 and 7. The related compounds 1,2-BT (**7**) and 3,4-BT (**5**) were studied to explore the possibility of excited-state carbon acid behavior in these less-rigid systems.[23] The mechanism of formal di-π-methane rearrangement of **7** and **5** (to give benzonorcaradiene (**14**)) has been studied in cyclohexane.[13,14,22] The mechanism of the rearrangement has been shown to involve initial 1,7-hydrogen shift followed by electrocyclic ring closure (or equivalently, a 1,3-hydrogen shift concurrent with formation of the cyclopropane ring[14,22]) to give **14**, and hence it is not a true di-π-methane rearrangement.[13,14,22] Photolysis of both **5** and **7** in 100% CH_3CN or 50–70% D_2O–CH_3CN gave **14** as the only product (eq 2), with no evidence for deuterium incorporation in recovered substrate or **14** in the D_2O–CH_3CN run, as determined by GC/MS and ^1H NMR. The rearrangement to **14** is a very efficient process (vide infra) as only short photolysis times were required to convert **5** or **7** to **14**, compared to the photolysis of **2**, which required longer times. Thus it would appear that carbon acid behavior cannot compete with efficient molecular rearrangement (i.e., hydrogen shift) for these more flexible molecular systems, although they possess the correct incipient 8π electron carbanion ring system to undergo C–H bond heterolysis.



(2)

Quantum Yields. Quantum yields for *formal* di-π-methane rearrangement observed on direct photolysis of **2** were measured with use of GC for analysis and potassium ferrioxalate actinometry[24] (λ_{ex} = 280 nm). The results in a number of solvents are shown in Table I. Since product studies with labeled **8** indicate that direct photolysis gives rise to a ≈1:2 ratio of **12** and **13a,b**, which arise from reaction via the triplet and singlet states, respectively, the measured quantum yield of 0.09 from direct photolysis may be thought of as contributions of 0.06 from the singlet state and 0.03 from the triplet state. Therefore, a quantum yield of 0.010 for rearrangement on direct photolysis in 70% H_2O–CH_3CN, in which only the triplet state product **12** was observed, indicates that not only has the singlet state rearrangement pathway been completely quenched by added water but that the efficiency of intersystem crossing was also retarded by added water. This is consistent with the fact that any deactivational process of S_1 must by necessity compete with intersystem crossing.

Table II. Quantum Yields for Deuterium Incorporation to the 5-Position of **2**

solvent[a]	Φ[b]
70% D_2O–CH_3CN	0.028 ± 0.005
35% D_2O–CH_3CN	0.019 ± 0.003
90% CD_3CN–CH_3CN	0.000
70% MeOD–CH_3CN	0.0071 ± 0.0004

[a] Aqueous portion at pH (pD) = 7; argon purged samples; 22 ± 2 °C. [b] Quantum yield for formation of **11** (or deuterium incorporation in recovered **2**). Measured with potassium ferrioxalate actinometry[24] (λ_{ex} = 280 nm) and GC/MS for analysis of deuterium enrichment.

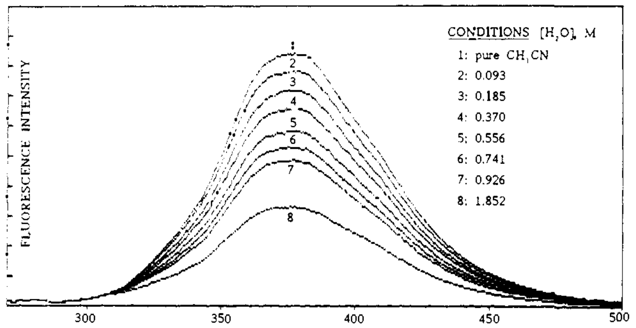


Figure 4. Fluorescence quenching of **2** in CH_3CN by added water (λ_{ex} = 265 nm).

The quantum yield for the formal di-π-methane rearrangement of **5** has been measured by Swenton and co-workers[13] to be ≈0.9 in cyclohexane (λ_{ex} = 330 nm). Using this reaction as the secondary actinometer, quantum yields for rearrangement of **5** and **7** (to **14**) have been measured in a number of additional solvents (Table I). In all cases, the rearrangement quantum yields were very high, with no apparent retarding effect by added water.

Quantum yields for deuterium incorporation (i.e., formation of **11**) into **2** were measured in D_2O–CH_3CN solutions and also in 100% MeOD (Table II). The rearrangement product **10** formed in these runs contained no observable deuterium content since total conversions were kept <20%. The quantum yields for deuterium incorporation are relatively low but substantial for such a process, especially considering that the departing proton (from the 5-position) can return *without* exchange with solvent deuteron. To exchange this proton in the ground state requires use of very strong bases such as *n*-BuLi because of the antiaromatic character of these types of 8π carbanions.[10]

Triplet Sensitization of Proton Exchange. The above triplet state sensitization experiment with **8** and BCA showed that the formal di-π-rearrangement can react via the triplet state. In order to test whether the triplet state of **2** can react via proton exchange (i.e., as a carbon acid), we irradiated **2** with excess BCA (λ_{ex} = 350 nm) in 50% D_2O–CH_3CN (pD ≈ 7). Although rearrangement to **10** took place, no deuterium incorporation in recovered **2** and product **10** was observed.

Steady-State and Transient Fluorescence Studies. The above results indicate that carbon acid behavior of **2** is a singlet state process (as was shown to be the case for **1**).[7] Therefore, studies of fluorescence behavior (both steady-state and time-resolved methods) should provide insight into the mechanism for exchange. The fluorescence emission of **2**, with emission maximum at 375 nm (Figure 4) was relatively strong, with Φ_f = 0.12 ± 0.02 in 100% CH_3CN (measured against 2-aminopyridine as secondary standard; Φ_f = 0.60).[25] The fluorescence emission intensity was

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(23) The compounds **1**, **2**, **5**, and **7** have basically two conformations available, obtained by ring flip of the cycloheptatriene ring. The availability of only two important conformations was confirmed by molecular mechanics calculations (ALCHEMY II and PCMODEL). By using molecular models, it can be shown that introduction of an extra benzene ring to **5** and **7** (to give **2** and **1**) increases the number of peri interactions at the transition state of the ring-flipping process, and hence a higher activation energy for ring flipping. On the basis of this expected difference in relative rates for conformational change, we can describe **1** and **2** as being "more rigid" than **5** and **7**.

(24) Hatchard, C. G.; Parker, C. A. *Proc. R. Soc. London, Ser. A* **1956**, *235*, 518.

(25) (a) Eaton, D. F. *Pure Appl. Chem.* **1988**, *60*, 1107. (b) Rusakowicz, R.; Testa, A. C. *J. Phys. Chem.* **1968**, *72*, 2680.

efficiently quenched by added water (Figure 4). In wholly or predominantly aqueous solution, emission from **2** was very weak ($\Phi_f < 0.01$). Fluorescence lifetimes of **2** were measured with time-correlated single-photon counting. All fluorescence decays were well-fitted to single-exponential decays. In 100% CH_3CN, $\tau = 4.04 \pm 0.03$ ns, whereas in 80% H_2O–CH_3CN, $\tau = 0.36 \pm 0.03$ ns. A Stern–Volmer plot of fluorescence intensity against water concentration gave a good linear plot and the calculated k_q was $(2.05 \pm 0.05) \times 10^8$ M^{-1} s^{-1}. It seems clear from these observations that water deactivates the excited singlet state of **2** by *acting as a base for protons at the 5-position*, resulting in generation of a transient carbanion intermediate. That is, k_q may be taken as a measure of the observed rate in which protons from the 5-position are transferred to solvent water from S_1, if not the rate of deprotonation itself.[26] Compounds **5** and **7** do not display excited-state carbon acid behavior: correspondingly, the fluorescence emissions of **5** and **7** were not quenched by any amount of added H_2O!

Summary and Conclusions. We have further demonstrated that the driving force for C–H bond heterolysis from S_1 is inherent in systems capable of giving rise to a cyclically conjugated 8π carbanion.[27] For the relatively rigid systems (**1** and **2**), excited-state carbon acid behavior can easily be observed in aqueous solution. In the case of **2**, carbon acid behavior (via S_1) competes with both 1,7-hydrogen shift and intersystem crossing. *With respect to singlet-state reactivity, it is interesting to note that the mode of transfer or "flight" of the hydrogen atom at* the *5-position is highly medium dependent: as a proton to solvent base in aqueous solution or formally as a hydrogen shift to the adjacent carbon in CH_3CN or cyclohexane.* Fluorescence quenching of **2** by added water to a CH_3CN solution gave a linear Stern–Volmer plot, with $k_q = 2.05 \times 10^8$ M^{-1} s^{-1}, which may be taken as (or at least a measure of) the rate in which water deactivates S_1 of this compound via C–H heterolysis. For the structurally less rigid systems (**5** and **7**) formal di-π-methane rearrangement dominates, with no evidence for carbon acid behavior in neutral aqueous solution.

Experimental Section

General Procedures. ^1H NMR spectra were recorded on Perkin-Elmer R32 on Bruker WM250 or AM360 instruments in $CDCl_3$ (TMS internal standard). UV spectra were obtained on a Perkin-Elmer Lamda 4B spectrophotometer. GC/MS and mass spectra were taken on a Finnigan 3300 instrument (Cl mode). Gas chromatography was carried out with a Varian 3700 instrument with a Hewlett-Packard 3390A integrator and a SE-54 capillary column. Preparative and semipreparative photolyses were carried out in 100- or 200-mL quartz tubes with use of a Rayonet RPR 100 photochemical reactor (254-, 300-, or 350-nm lamps). Quantum yield runs were carried out in Suprasil quartz cuvettes with an Oriel 200 W Hg arc and an Applied Physics monochromator set at 280 nm.

Materials. Benzophenone-2-carboxylic acid (BCA) and diphenic anhydride were purchased from Aldrich and used as received.

Dibenzo[*a*,*c*]cycloheptan-6-one (4). This ketone was synthesized according to the procedure of Tolbert and Ali[10] from commercially available diphenic anhydride (Aldrich). The synthesized material was spectroscopically identical with reported data.[10]

Dibenzo[*a*,*c*]cycloheptan-6-ol (3). To 4 g (10 mmol) of ketone **4** dissolved in cold MeOH was added a water solution of 0.36 g (9.5 mmol) of $NaBH_4$ over a 30-min period. After addition, the solution was warmed to 40 °C for 30 min before quenching with ice water. Upon acidification with aqueous HCl, the solution was extracted with CH_2Cl_2 and on evaporation of the solvent gave **3** (3.5 g; 87%) which was used without further purification: ^1H NMR (90 MHz) δ 1.4–1.9 (br, 1 H, OH), 2–3 (m, 4 H, $-CH_2-$), 4.5 (t, J = 7 Hz, 1 H, $-CHOH-$), 7.2–7.6 (m, 8 H, arom.).

Dibenzo[*a*,*c*]cycloheptene (2). To a 200-mL toluene solution of 3.5 g (17 mmol) of **3** was added 50 mL of 80% H_3PO_4 and the whole solution was refluxed with use of a Dean-Stark trap for 15 h. After reflux, the solution was cooled and poured into crushed ice. The toluene layer was separated and the aqueous layer was extracted several times with CH_2Cl_2. The organic layers were combined and evaporated to give 3 g of a brown oil. Kugelrohr distillation (150 °C) gave 1.2 g of a colorless oil identified as **2**: ^1H NMR (90 MHz) δ 3.02 (d, J = 7 Hz, 2 H, $-CH_2-$), 6.20 (dt, J = 11, 7 Hz, 1 H, $-CH{=}CHAr$), 6.55 (d, J = 11 Hz, 1 H, $-CH{=}CHAr$), 7.1–7.8 (m, 8 H, arom.); mass spectrum (Cl), m/z 193 (M^+ + 1) (100%), 194 (16%; natural abundance ^{13}C). The compound was identical in all other respects with the data reported in the literature.[11,12]

6-Deuterio-6-bromodibenzo[*a*,*c*]cycloheptane (9). To 0.9 g (4.3 mmol) of **3** dissolved in 100 mL of CH_3Cl was added 1.7 mL of PBr_3 and the solution refluxed for 5 h. After cooling, the solution was poured onto ice water and the CH_3Cl separated. The aqueous layer was extracted twice with 150 mL of CH_2Cl_2. Evaporation of the combined organic layers gave **9** which was taken onto the next step without any additional treatment.

6-Deuterio-5*H*-dibenzo[*a*,*c*]cycloheptene (8). A solution of 1.4 g of **9** in 50 mL of 3.0 M KOH in MeOH was refluxed for 1 h. It was then poured into water and extracted with 2 × 150 mL of CH_2Cl_2, which on evaporation gave 0.8 g of an oil shown to consist of two components by GC, 60% of which was **8**. After separation on a Waters Model 500A prep. LC (silica gel column; hexanes as elutant), 500 mg of 90–95% pure **8** was obtained: ^1H NMR (90 MHz) 2.95 (br s, 2 H, $-CH_2-$), 6.5 (br s, 1 H, $ArCH{=}CD-$), 7.1–7.8 (m, 8 H, arom.); mass spectrum (Cl), m/z 194 (M^+ + 1) (100%).

3,4-Benzotropilidene (5). This compound was prepared from 1-benzosuberone (6) according to the procedure of Burdett et al.:[13] ^1H NMR (90 MHz) δ 2.5 (t, J = 7 Hz, $-CH_2-$), 5.85 (dt, J = 10, 7 Hz, $ArCH{=}CHCH_2-$), 6.6 (d, J = 10 Hz, $ArCH{=}$), 7.1–7.4 (m, 4 H, arom.).

1,2-Benzotropilidene (7). This compound was prepared by isomerizing **5** with potassium *tert*-butoxide according to the procedure of Pomerantz and Gruber:[14] ^1H NMR (90 MHz) δ 3.05 (d, J = 7 Hz, 2 H, $ArCH_2-$), 5.6–6.2 (m, 2 H, $ArCH{=}CHCH{=}CHCH_2-$), 6.5 (dd, J = 7, 10 Hz, $ArCH{=}CH-$), 7.1 (d, J = 10 Hz, $ArCH{=}$), 7.1–7.5 (m, 4 H, arom.).

Product Studies. In general, 40–70-mg samples were dissolved in the appropriate solvent or solvent mixture (200 mL) and transferred to a 200-mL quartz tube. The solution was then cooled to ≈12 °C with an internal cold finger and purged with a stream of 99.9% pure argon for 10 min before photolysis inside a Rayonet RPR 100 photochemical reactor (254-, 300-, or 350-nm lamps). Continuous cooling and purging were maintained during the course of the photolysis (5–120 min in duration, depending on the run). Photolyzed aqueous solutions were worked up by first saturating the solution with NaCl, extracting several times with CH_2Cl_2, and then evaporating the solvent on an rotary evaporator. The material thus obtained was then analyzed by NMR, GC, and GC/MS.

Photolysis of 2 in 100% CH_3CN. Photolysis of 70 mg (60 min) at 254 nm gave a product mixture that was first analyzed by GC/MS (180 °C isotemp) to consist of unreacted **2** (37%; 6.8 min), phenanthrene (16%; 7.1 min), **10** (40%; 8.3 min), and 9-methylphenanthrene (4%; 9.3 min). The mass spectrum (Cl) of each of these materials showed natural abundance (M^+ + 2) peaks (recall that in Cl, the M^+ + 1 peak is the *protonated* molecular ion). Analysis by ^1H NMR (90 and 360 MHz) indicated that the major product was **10**, as identified by its characteristic cyclopropyl resonances[15] (see Figure 1). Photolysis with shorter irradiation times gave **10** as the only product.

Photolysis of 2 in 50% H_2O–CH_3CN. Photolysis of 70 mg of **2** in this solvent system gave the same product mixture as above but required an irradiation time of 120 min to achieve the same conversions. The mass spectra by GC/MS of each of these materials again showed natural abundance (M^+ + 2) peaks.

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[26] The question arises as to what percentage of deactivated excited singlet states by solvent water (via C–H bond heterolysis) results in overall exchange. In other words, what is the extent of "internal return" of the departing proton. We can estimate this from the following argument. A solution consisting of 70% H_2O–CH_3CN nearly completely quenches the fluorescence emission from **2**, which has $\Phi_f = 0.12$ in pure CH_3CN. In 70% D_2O–CH_3CN, the exchange quantum yield was 0.028. Assuming that other effects are negligible, which is reasonable, the deactivation of about 4 singlet states results in one deuterium-exchanged molecule. Put another way, 3 out of every 4 molecules that are deprotonated (from S_1) undergo internal return. This argument probably gives only a *lower limit* for the degree of internal return because the quantum yield of quenching by water of S_1 is not known exactly, but it should be at least 0.12.

[27] Although the "8π ($4n$) rule" appears to work well for predicting carbanion photogeneration (i.e., it is a *necessary* condition for excited-state carbon acid behavior), we do not as yet have a satisfactory theoretical explanation for this phenomenon, apart from resorting to use of Hückel-Möbius differentiation (Dewar-Zimmerman rules)[28] or the Woodward–Hoffmann rules[29] used in pericyclic reactions. However, it is clear that C–H bond heterolysis is not a pericyclic reaction in the traditional sense and use of the above rules may not be strictly valid. Theoretical calculations using π-SCF methods are underway, which is anticipated to provide a viable theoretical jusitification for these observations.

[28] Zimmerman, H. E. *Acc. Chem. Res.* **1971**, *4*, 272.

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

Photolysis of 2 in 50% D_2O–CH_3CN. Several runs at different photolysis times were carried in this solvent system. Photolysis of 70 mg at 10 min irradiation gave **10** (10%; *no* deuterium incorporated, as shown by GC/MS) and <5% phenanthrene and 9-methylphenanthrene. Recovered **2** had the following mass spectrum (CI) (*m/z*): 193 ($M^+ + 1$) (100%), 194 ($M^+ + 2$) (33%), 195 ($M^+ + 3$) (4%). Taking into account that natural abundance material has a ($M^+ + 2$) peak of 16%, we calculated 14.5% monodeuterium incorporation into **2** (i.e., formation of **11** (vide infra) in 14.5% yield). Evidence that deuterium incorporation occurred at the 5-position was available from ^{1}H NMR (250 MHz) of the recovered **2**, which has already been presented. Additional evidence came from ^{13}C NMR (62.9 MHz; ^{1}H decoupled). The methylene carbon at the 5-position of unreacted **2** appears as an expected singlet at δ 33.2. However, after photolysis (as above conditions), a weak unresolved "1:1:1 triplet" appears at slightly higher field (the two observable peaks of this triplet are at δ 32.6 and 32.9, which calculates to give $J(^{13}C\text{–}D) = 19$ Hz), indicative of a methylene carbon attached to a single deuterium atom.

Photolysis of 70 mg for 120 min gave a mixture consisting (by GC/MS) of **2** (47%), **10** (37%), phenanthrene (13%), and 9-methylphenanthrene (3%). The mass spectrum (CI) of each of these materials indicated extensive deuterium incorporation. Recovered **2**: 39% monodeuteration, 21% dideuteration. **10**: 40% monodeuteration, 20% dideuteration, 4% trideuteration. Phenanthrene: 30% monodeuteration. 9-Methylphenanthrene: 37% monodeuteration, 15% dideuteration, 3% trideuteration. These results indicate that successive incorporation of deuterium into **2** is facile, resulting in enrichment of deuterium in all the photoproducts.

Photolysis of 8. Conditions used for these runs and the results obtained have been presented in a previous section. Product mixtures obtained in these runs were also analyzed by GC/MS and showed that product **10** contained the same percent deuterium content as did **8**.

Photolysis of 5 and 7. Photolysis of 70-mg samples of **5** or **7** in 100% CH_3CN, 50% H_2O–CH_3CN, or 50% D_2O–CH_3CN at 254 nm gave high yields (>50%) of **14** with only short photolysis time (5 min); ^{1}H NMR (90 MHz) of the product mixture assignable to **14**: −0.21 (m, 1 H, *endo*-CH_2–), 1.51 (m, 1 H, *exo*-CH_2–), 1.9 (m, 1 H, CH=CHC*H*–), 2.45 (m, 1 H, ArC*H*–), 6.25 (m, 1 H, ArCH=C*H*), 7.1 (m, 1 H, ArC*H*=). Unlike **2**, the photorearrangement yields of **5** and **7** (to **14**) were not retarded to any observable extent on photolysis in aqueous solution, compared to runs in 100% CH_3CN.

Triplet Sensitization of Proton Exchange. A solution of 700 mg of BCA and 10 mg of **2** in 50 mL of D_2O/50 mL of CH_3CN (pD = 7) contained in a Pyrex tube was irradiated for 30 min at 350 nm. After workup, GC/MS showed 70% conversion to **10** with no deuterium incorporation in unreacted **2** or **10**.

Quantum Yield Measurements. Quantum yields were measured with 3.0-mL solutions of the substrate (10^{-3} M) in the appropriate solvent. The solutions were purged with argon before irradiating on the optical bench at 280 nm. Typical photolysis times were 15–30 min. Photolyzed samples were extracted with CH_2Cl_2 and then analyzed by GC/MS to determine the extent of conversion to **10** and extent of deuterium incorporation to **2**. Potassium ferrioxalate actinometry was used.[24]

Steady-State Fluorescence and Lifetime Measurements. Fluorescence spectra (uncorrected) were measured on a Perkin-Elmer MPF 66 instrument in 1.00-cm Suprasil quartz cuvettes at 10^{-4} M at ambient temperature (22 ± 2 °C). Solutions were purged with argon prior to measurement. Time-correlated single-photon counting (for fluorescence lifetimes) was measured at the Center for Fast Kinetics Research (CFKR) with use of a standard single-photon counting system and as excitation sources either a 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 Nd:YAG as the pump source), or a standard hydrogen spark lamp.

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Registry No. 2, 29564-10-1; **3**, 3594-99-8; **4**, 1139-82-8; **5**, 264-09-5; **7**, 264-08-4; **8**, 129034-90-8; **9**, 129034-89-5; **10**, 949-41-7; **14**, 3463-79-4; H_2O, 7732-18-5.