

PHOTOCHEMICAL TRANSFORMATIONS. 49.* SOLVENT EFFECTS ON SINGLET IONIC AND TRIPLET PHOTOREACTIONS OF SOME BRIDGED POLYCYCLIC CHLORIDES: COMPARISON WITH GROUND-STATE REACTIONS†

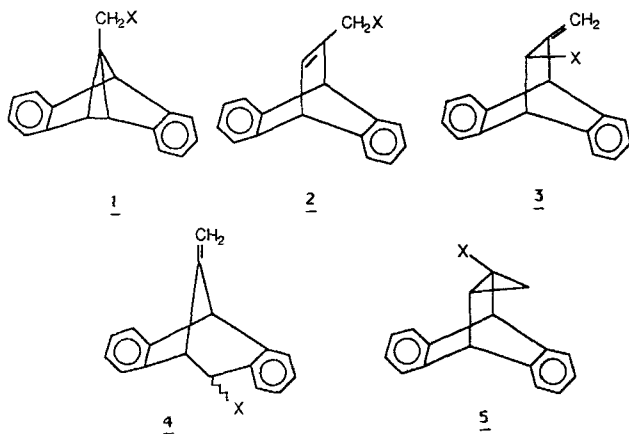
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Direct irradiations of 2-chloro-6,7:8,9-dibenzotricyclo[3.2.2.0^{2,4}]nona-6,8-diene (5-Cl) were conducted in cyclohexane, acetic acid and wet acetonitrile. The products are 1-methylfluoranthene (8) in all three solvents, the allylic chlorides 8-chloro-7-methylene-2,3:5,6-dibenzobicyclo[2.2.2]octa-2,5-diene (3-Cl) and 7-chloromethyl-2,3:5,6-dibenzobicyclo[2.2.2]octa-2,5,7-triene (2-Cl) in acetic acid and acetonitrile and solvolysis product amides in wet acetonitrile. Compound 5-Cl had previously been shown to be the product of triplet sensitization of 2-Cl and 3-Cl, so that the singlet reaction reverses that of the triplet. The formation of 8 from 5-Cl was quenched with piperylene, whereas that of the allylic chlorides was not. Quantum yields of products and singlet lifetimes in the three solvents were measured. The solvent effects are discussed. Deuterium-labeling results on the formation of 5-Cl from 2-Cl and of 8 from 5-Cl are reported.

INTRODUCTION

Some time ago, members of our research group reported photochemical studies² on chlorides and/or bromides of structures 1-5. The ground-state (silver-



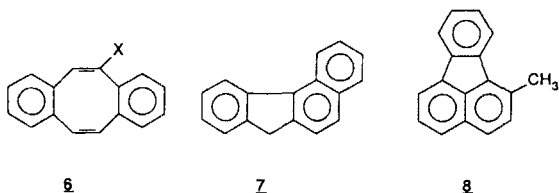
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† Dedicated to Professor Kurt Schaffner on his 60th birthday.

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ion-promoted) acetolyses of similar compounds have also been studied.³ In the earlier photochemical work, we were particularly interested in the differences between triplet-sensitized reactions of the allylic chlorides 2-Cl and 3-Cl and of their bromine analogs 2-Br and 3-Br. It was noted that the chlorides, sensitized by triplet acetone, gave allylic isomerization 2-Cl \rightleftharpoons 3-Cl, accompanied by and ultimately followed by complete allyl to cyclopropyl isomerization to 5-Cl, whereas the bromides gave allylic isomerization, photo-Wagner-Meerwein isomerization to 4-Br epimers and photosolvolysis to 4-OH epimers, but no allyl to cyclopropyl rearrangement. The different results were ascribed² to the more ready electron transfer from photoexcited aromatic rings to carbon-bromine bonds than to less readily reduced carbon-chlorine bonds. The allyl to cyclopropyl isomerization does not require electron transfer, whereas the Wagner-Meerwein isomerization and solvolysis reactions do.⁴

It was also reported that direct irradiation with 254 nm light of 2-Cl in acetic acid led to photosolvolysis to give 2-OAc, 3-OAc and 4-OAc (and their photorearrangement products 1-OAc and 6-OAc), some 3-Cl, when the reaction was interrupted early in its course, about 15% of 3,4-benzofluorene (7) and about 10% of 1-methylfluoranthene (8). As 5-Cl was shown to



give about 50% of **8**, together with about 25% of **2**, **3** and **4** acetates, on direct irradiation in acetic acid, it was suggested that the source of **8** in the direct irradiation of **2-Cl** was probably **5-Cl**, produced by inter-system crossing of the excited singlet state of **2-Cl** (or **3-Cl**) to its triplet. The source of **7** was not speculated upon, although it was noted that **7** was produced^{3a} in the silver-acetate-promoted ground-state acetolysis of **1-Br**. In a more recent paper,⁵ it was shown that **7** is sole product in the direct irradiation of **1-Br** in acetic acid.

RESULTS

We now report further experiments on direct irradiations of **5-Cl**, undertaken in the hope of fathoming the course of the rearrangements observed. Although it had been previously reported that irradiation of **5-Cl** in acetic acid led to a mixture of **8** and acetolysis products, those experiments were conducted under conditions where the allylic chlorides **2-Cl** and **3-Cl** and the benzylic chlorides **4-Cl** are themselves labile, giving acetolysis products and/or further photochemical reactions. More careful studies now show that the initial photoreaction products are 1-methylfluoranthene (**8**) (67%) and 33% of a mixture of **2-Cl** and **3-Cl**. No solvolysis products were seen early in the experiment and the acetates previously reported must therefore have been formed via **2-Cl** and **3-Cl**.

Direct irradiation of **5-Cl** was also carried out in acetonitrile containing 2% water and in cyclohexane. In wet acetonitrile, 1-methylfluoranthene (**8**) was the minor product (about 12% yield), **2-Cl** and **3-Cl** were formed in about 34% yield and, in addition, about a 39% yield of a mixture of amides, resulting from photosolvolysis of **5-Cl**, and not arising from **2-Cl** or **3-Cl**, was observed. In cyclohexane, **8** was the sole product identified; isomeric chlorides were not found.

Quantum yields for **5-Cl** loss and for product formation were determined and are given in Table 1.

When the triplet quencher piperylene was added to solutions of **5-Cl** in acetic acid, which were then irradiated, the formation of **2-Cl** and **3-Cl** was not affected, within experimental error, but the quantum yield for formation of **8** was reduced and that for loss of **5-Cl** was correspondingly decreased. A Stern-Volmer treatment of the data gave a $k_Q^3 \tau$ slope of $110 \pm 10 \text{ l mol}^{-1}$. The results show that the triplet of **5-Cl** was quenched back to ground-state **5-Cl**.

Table 1. Quantum yields and singlet lifetimes of **5-Cl** photo-reactions

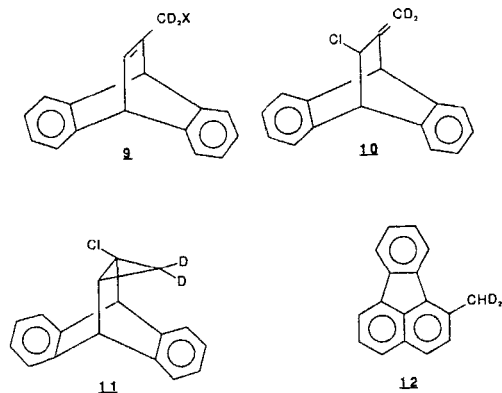
Solvent	Quantum yields				τ_s (ns)
	ϕ_{5-Cl}	$\phi_{2-Cl+3-Cl}$	ϕ_8	$\phi_{\text{solvolysis}}$	
Acetic acid	0.07	0.023	0.047	0.000	7.6
Acetonitrile ^a	0.05	0.020	0.007	0.023 ^b	5.7
Cyclohexane	0.03	0.000	0.015	—	9.1

^a Contains 2% water.

^b Mixture of **2-**, **3-** and **4-NHCOCH₃**.

Excited singlet lifetimes were measured in the three solvents by Dr J. S. Connolly, and are given in Table 1.

Acetophenone-sensitized irradiation of **10**, the dideuterio analog of **3-Cl**, or of mixtures of **9-Cl** and **10**, resulted in the formation of **11**, in which all of the deuterium was present at C-3. Direct irradiation of **11** in acetic acid led to **12**, in which all of the deuterium initially at C-3 in **11** was present in the methyl side-chain.



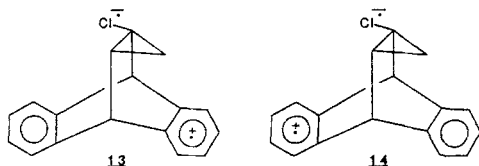
DISCUSSION

Among the interesting results is the reversibility of the **2-Cl** + **3-Cl** and **5-Cl** system, under different conditions. Thus, in acetone as solvent-sensitizer, or in acetonitrile containing acetophenone as sensitizer, **2-Cl** and **3-Cl** are converted into each other and ultimately into **5-Cl** in very high yields.² Reactions of this sort (allyl chlorides to cyclopropyl chlorides) have been shown⁶ to be triplet reactions and to be consistent with the intervention of triplet-biradical intermediates. On the other hand, the photoisomerizations of β -aryl chlorides via Wagner-Meerwein (or other) processes have been shown⁴ to be singlet reactions (except in a few cases), often accompanied by solvolyses, and to involve electron transfer, followed by loss of nucleofuge accompanied by the formation of excited carbocations. Thus, the formation of **2-Cl** and **3-Cl** by direct irradiation of **5-Cl** is

undoubtedly a singlet reaction, and does not follow the same reaction path as its reverse (triplet) reaction, so that the principle of microscopic reversibility does not apply.

One notes that, unlike the formation of 2-Cl and 3-Cl, the formation of **8** from 5-Cl was quenchable with piperylene, indicating that it is a triplet reaction. The intersystem-crossing-produced triplet had a lifetime of about 20 ns, if k_Q is assumed⁷ to be about $5 \times 10^9 \text{ l s}^{-1} \text{ mol}^{-1}$.

Let us next consider the solvent effects on the photo-reactions. Consistent with the idea that the photo-isomerizations of 5-Cl to 2-Cl and 3-Cl and/or the photosolvolyses involve the transformation of the π, π^* state of 5-Cl to the zwitterionic biradical **13** (or its electromer **14** in which the electron-deficient ring is *syn* to the chlorine) and that intersystem crossing to triplet does not require electron transfer, no rearrangement to 2-Cl and 3-Cl is seen in the solvent cyclohexane.



Electron-transfer reactions are generally perceived⁸ to be functions of the dielectric constant of the medium rather than of 'ionizing power' as measured by parameters such as the Winstein-Grunwald Y,⁹ Kosower Z¹⁰ or Dimroth $E_T(30)$ ¹¹ values. Although it might not be predicted that this would be the case where anionic charge is being developed on a halogen atom, where hydrogen bonding might be particularly important, rather than on a delocalized system, as is usually studied in bimolecular electron transfers, we also observe similar behavior. Thus, in acetic acid solvent ($Z = 79.2$,¹⁰ $\epsilon = 6^{12}$) the ratio of ionic products to **8** is 0.5, whereas in wet acetonitrile ($Z_{\text{CH}_3\text{CN}} = 71.3$,¹⁰ $\epsilon = 36^{12}$) this ratio is 6. Clearly, the 'ionizing power' effect, derived initially from ground-state solvolysis rate constants,⁹ is not well reflected in photoinduced intramolecular electron transfer reactions, even in organic chlorine compounds.

Less expected was the fact that solvolysis (to amides) is a major adjunct accompanying ionic photorearrangements in acetonitrile whereas solvolysis (to acetates) follows, rather than accompanies, ionic photorearrangements in acetic acid. We assume that photorearrangements involve intimate ion-pair return and that photosolvolyses involve solvent-separated ion pairs. One might have expected, from ground-state chemistry, that ease of separation of intimate ion pairs would be a function of 'ionizing power', leading to less ion-pair return in acetic acid than in acetonitrile, but this is not so. Whether this may be, at least in part, an

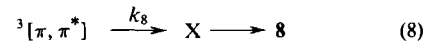
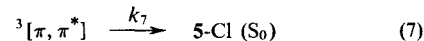
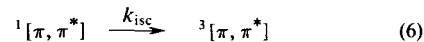
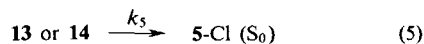
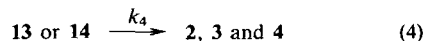
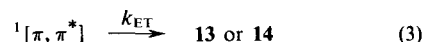
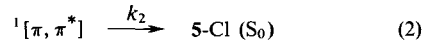
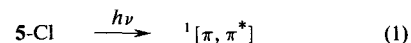
effect of the significantly greater viscosity¹³ of acetic acid (1.15 cP at 25 °C) compared with acetonitrile (0.345 cP at 25 °C), such that ion-pair return is favored by a stronger cage effect in acetic acid, cannot be ignored. The difference between ground-state results and excited-state chemistry is of considerable interest. Clearly, in ground-state reactions, solvent reorganization lifetimes are not dominating in controlling kinetic results. On the other hand, with photoproduct species, solvent reorganization may become the dominant factor. Thus, for acetic acid, which of course is largely dimeric, the cost of separation into monomer and appropriate alignment to give the requisite hydrogen bonding to the chloride ion for conversion to the solvent-separated ion pair seems to be too expensive for it to compete well with ion-pair return to (rearranged) alkyl chloride. For acetonitrile, on the other hand, only dielectric constant (presumably involving a simple rotational restriction) requirements need be met.

Unfortunately, the quantum yields for reaction are small, in the range of 0.03–0.07 in the various solvents. This means, of course, that most of the initially excited singlets of 5-Cl or their descendent excited species revert to ground-state 5-Cl molecules. It is therefore not possible to utilize quantum-yield data and lifetime measurements to extract exact electron-transfer rate constants or intersystem-crossing rate constants. Nonetheless, it is possible to compute the products of these rate constants (k_{ET} or k_{isc}) times the fractions leading to 'ionic' products (F_i) or to **8** (F_8) and to speculate on these values.

The simplest reaction path which can account for the result is shown as Scheme 1. Thus, the quantum yield of ionic products, ϕ_i , can be expressed as

$$\phi_i = \frac{k_{\text{ET}} F_i}{k_2 + k_{\text{ET}} + k_{\text{isc}}}$$

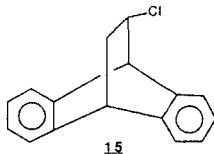
where $F_i = k_4 / (k_4 + k_5)$, and, since $k_2 + k_{\text{ET}} + k_{\text{isc}} = k_d = 1/\tau_s$, $k_{\text{ET}} F_i = \phi_i / \tau_s = \phi_i k_d$. Similarly, $k_{\text{isc}} F_8 = \phi_8 / \tau_s = \phi_8 k_d$.



Scheme 1

In the solvent cyclohexane, the singlet lifetime (τ_s) is 9.1 ns or, to put it another way, the rate constant for disappearance of the excited singlet (k_d) is $1/\tau_s = 1.1 \times 10^8 \text{ s}^{-1}$. As the quantum yield for **8** formation is 0.015, $k_{isc}F_8 = 1.7 \times 10^6 \text{ s}^{-1}$. As no rearranged chlorides were seen, and as it would have been easily possible to observe 5% of these, $k_{ET}F_i$ must be less than $1 \times 10^5 \text{ s}^{-1}$. In acetic acid, $k_d = 1.3 \times 10^8 \text{ s}^{-1}$, $k_{isc}F_8 = 6.1 \times 10^6 \text{ s}^{-1}$ and $k_{ET}F_i = 3.0 \times 10^6 \text{ s}^{-1}$, and in wet acetonitrile, $k_d = 1.8 \times 10^8 \text{ s}^{-1}$, $k_{isc}F_8 = 1.3 \times 10^6 \text{ s}^{-1}$ and $k_{ET}F_i = 7.7 \times 10^6 \text{ s}^{-1}$.

Compound **15**, the analog of **5-Cl**, but without the cyclopropane ring, has been shown¹⁴ to have a singlet lifetime approximately 50 times greater in cyclohexane than in acetonitrile. This is to be compared with those of **5-Cl**, where the ratio of lifetimes is less than 2. The lifetimes of **5-Cl** and **15** in cyclohexane are about equal, and the significant change must be due to the decreased value of k_{ET} for **5-Cl** in acetonitrile compared with that for **15**.



Our experiments, unfortunately, do not allow us to discriminate as to whether the relative values for $k_{ET}F_i$ reflect, in large part, the effects on the forward electron-transfer rate constant (k_{ET}) or those of the reverse electron transfers to the ground state (k_5). In ground-state reactions,¹⁵ loss of chloride ion from chlorocyclopropanes is accompanied by ring opening to an allyl cation, so that the cyclopropyl cation 5^+ would lead to **2-Cl** and/or **3-Cl** and not to **5-Cl**. Evidence indicates¹⁶ that cleavage of **13** or **14** would not lead to 5^+ directly, but would lead rather to a biradical cation, that is, to an excited state of 5^+ . Whether such a species would react with its counterion (chloride ion) to regenerate **5-Cl** before decay to the allylic cation is unknown, but seems unlikely.

Reverse electron transfer from **13** or **14** to the ground state of **5-Cl** is highly exothermic and may therefore be slow,^{8c} and indeed in contact ion pairs, which may be analogous to our zwitterion, reverse electron transfer has been shown to have rates in the Marcus inverted region.^{8d-f} Clearly, F_i must have a value between $\phi_i/(1 - \phi_8)$ and 1; therefore, maximum and minimum values for k_{ET} can be readily computed. The minimum values, where F_i may be assumed to be 1, are then those given above for $k_{ET}F_i$, and the maximum values are $1.2 \times 10^8 \text{ s}^{-1}$ for acetic acid and $1.7 \times 10^8 \text{ s}^{-1}$ for wet acetonitrile. Similarly, k_{isc} may be computed; minimum values for k_{isc} are those given above for $k_{isc}F_8$, and maximum values are $1.2 \times 10^8 \text{ s}^{-1}$ for acetic acid,

$1.7 \times 10^8 \text{ s}^{-1}$ for acetonitrile and $1.1 \times 10^8 \text{ s}^{-1}$ for cyclohexane. The rather dramatic differences in product ratios with solvent are thus the result of the consequences of very low electron transfer, compared with wet acetonitrile, in cyclohexane (ratio of $k_{ET}F_i$ for $\text{CH}_3\text{CN}:\text{c-C}_6\text{H}_{12} > 75$) and a combination of the consequences of lower electron-transfer (ratio of $k_{ET}F_i$ for $\text{CH}_3\text{CN}:\text{HOAc} = 2.5$) and of higher intersystem crossing (ratio of $k_{isc}F_8$ for $\text{CH}_3\text{CN}:\text{HOAc} = 0.2$) for acetic acid compared with wet acetonitrile.

An interesting feature of these reactions is that the ionic photorearrangements of **5-Cl** in both acetic acid and acetonitrile give only **2-Cl** and **3-Cl**, whereas solvolysis in the ground state and in photoreactions, where it occurs, also gives substantial amounts of **4** derivatives.^{2,3} Apparently, return from the intimate ion pair does not allow time for the allylic cation $2^+ \leftrightarrow 3^+$ to isomerize to 4^+ . During the period of time involved in solvent-separated ion-pair formation plus its existence, equilibration of the allylic cation with the benzylic cation 4^+ does occur. We have previously noted,¹⁷ in another system, that ion-pair return in photoreactions leads to product mixtures different from ground-state expectations, whereas photosolvolysis, which involves solvent-separated ion pairs, leads to mixtures almost identical with those in ground-state reactions. A similar rationalization was suggested then.

Finally, these results do not allow us to define the reaction path from **5-Cl** to **8**. Clearly, the labelling results (**11** to **12**) suggest that the four carbon atoms in the aromatic ring to which the methyl group is attached arise from the aliphatic carbon atoms in **5-Cl**. Further work may permit the elucidation of other features of this remarkable reaction and we therefore postpone further speculation at this time.

EXPERIMENTAL

General. Melting points were determined with a Thomas-Hoover Unimelt apparatus and were uncorrected. Proton magnetic resonance (¹H NMR) spectra were determined on either a Varian EM-390 (90 MHz) or Bruker WM-250 (Fourier transform, 250 MHz) nuclear magnetic resonance spectrometer. All values reported are in parts per million (ppm) downfield from tetramethylsilane (TMS). Chloroform-*d* was used as solvent. TMS was used as an internal standard with the EM-390 and the residual proton resonance of chloroform-*d* was used as an internal standard on the Fourier transform instrument. Deuterium nuclear magnetic resonance (²H NMR) was conducted by M. Ashley on the Bruker WM-250 instrument using an external deuterium oxide reference and dichloromethane as solvent. Mass spectra were obtained using a VG 7070 mass spectrometer.

7-Chloromethyl-2,3 : 5,6-dibenzobicyclo[2.2.2]octa-2,5,7-triene (2-Cl), *8-chloro-7-methylene-2,3 : 5,6-dibenzobicyclo[2.2.2]octa-2,5-diene (3-Cl)* and *2-chloro-6,7 : 8,9-dibenzotricyclo[3.2.2.0^{2,4}]nona-6,8-diene (5-Cl)*. These compounds were prepared substantially as described earlier.^{3b} In the attempt to repeat the preparation of 2-Cl from 2-OH with thionyl chloride as reported earlier,^{3b} we usually produced a mixture of 2-Cl with its allylic isomer 3-Cl, in which the latter predominated. This was presumably due to thermal rearrangement, as noted earlier.^{3b} The two chlorides were readily separated by crystallization from absolute ethanol.

9,9-Dideuterio-7-hydroxymethyl-2,3 : 5,6-dibenzobicyclo[2.2.2]octa-2,5,7-triene(9-OH). This compound was prepared by the method described earlier^{3a,18} except that lithium aluminium deuteride was used in place of lithium aluminium hydride. The yield was 75%; m.p. 127–129 °C; ¹H NMR, δ 7.3–6.8 (m, 8H, aromatic protons), 6.58 (dd, 1H, H-8, $J_{8,4} = 6$ Hz, $J_{8,1} = 1.5$ Hz), 4.97 (d, 1H, H-1, $J_{8,1} = 1.5$ Hz), 4.94 (d, 1H, H-4, $J_{8,4} = 6$ Hz), 2.31 (bs, 1H, OH).

9,9-Dideuterio-7-chloromethyl-2,5 : 5,6-dibenzobicyclo[2.2.2]octa-2,5,7-triene (9-Cl) and *9,9-dideuterio-8-chloro-7-methylene-2,3 : 5,6-dibenzobicyclo[2.2.2]octa-2,5-diene (10)*. These compounds were prepared by the method described earlier^{3b} to prepare 2-Cl and 3-Cl. Starting with 200 mg (0.85 mmol) of 9-OH gave an 80% yield of allylic chlorides. Recrystallization from ethanol gave 121 mg (56%) of 10; m.p. 132.5–133 °C; MS, m/z (relative intensity) 257 (2.3%, M + 3), 256 (8.8%, M + 2), 255 (5.7%, m + 1), 254 (26%, M⁺), 217 (21%), 178 (100%), 77 (11%); exact mass = 254.0836 u, calculated = 254.0831 u; ¹H NMR, δ 7.5–7.0 (m, 8H, aromatic protons), 4.70 (s, 1H, H-1), 4.67 (d, 1H, H-4, $J_{4,8} = 2$ Hz), 4.47 (d, 1H, $J_{4,8} = 2$ Hz); ²H NMR, δ 5.41 (bs, 1H, H-9), 5.20 (bs, 1H, H-9). A second crystallization yielded 51 mg (24%) of 9-Cl; m.p. 148–150 °C; ¹H NMR, δ 7.5–6.9 (m, 8H, aromatic protons), 6.74 (dd, 1H, H-8, $J_{8,4} = 6$ Hz, $J_{8,1} = 1.5$ Hz), 5.09 (d, 1H, H-1, $J_{8,1} = 1.5$ Hz), 5.06 (d, 1H, H-4, $J_{8,4} = 6$ Hz).

3,3-Dideuterio-2-chloro-6,7 : 8,9-dibenzotricyclo[3.2.2.0^{2,4}]nona-6,8-diene (11). Compound 11 was prepared as described earlier^{3b} for 5-Cl, except that 10 was used as starting material instead of 3-Cl; m.p. 119–121 °C; MS, m/z (relative intensity), 257 (1.7%, M + 3), 256 (7.1%, M + 2), 255 (4.6%, M + 1), 254 (21%, M⁺), 219 (100%), 217 (38%), 204 (19%), 191 (29%), 178 (21%); exact mass = 254.0853 u, calculated = 254.0831 u; ¹H NMR, δ 7.8–7.0 (m, 8H, aromatic protons), 4.53 (s, 1H, H-1), 4.44 (d, 1H, H-5, $J_{5,4} = 5$ Hz), 1.80 (d, 1H, H-4, $J_{5,4} = 5$ Hz); ²H NMR, δ 1.19 (bs, 1H, H-3_{anti}), 0.55 (bs, 1H, H-3_{syn}).

Direct irradiation of 3,3-dideuterio-2-chloro-6,7 : 8,9-dibenzotricyclo[3.2.2.0^{2,4}]nona-6,8-diene (11). A solution of 68 mg (0.27 mmol) of 11 was dissolved in 50 ml of acetic acid and placed in a quartz tube. This solution was then deoxygenated by bubbling nitrogen through it for 20 min. The solution was irradiated at 254 nm for 3 h in a Rayonet apparatus. The acetic acid was evaporated off in a Rotavapor and 78 mg of a dark oil was isolated. This oil was chromatographed on a column of silica gel (60–200 mesh) with methylene chloride–hexane as eluent to give three fractions. The second fraction was 11 and weighed 11 mg (84% conversion based on recovered 11).

The first fraction contained α,α -dideuterio-1-methylfluoranthene (12). It was identified by its m.p. of 71–72 °C (72–73 °C for the undeuteriated compound¹⁹), its mass spectrum, m/z (relative intensity) 220 (4%, M + 2), 219 (22%, M + 1), 218 (100%, M⁺), 105 (19%), 77 (12%), 57 (22%), 40 (60%), its ¹H NMR spectrum,¹⁹ δ 8.0–7.3 (m, 9H, aromatic protons), 2.86 (pentuplet, 1H, CD₂H, $J_{H,D} = 2.2$ Hz), its ²H NMR spectrum, δ 2.94 (bs, CD₂H), and its exact mass spectrum, 218.1059 u (calculated = 218.1064 u).

Quantum yields. Quantum yields were measured in a Rayonet RS photochemical reactor (Southern New England Ultraviolet Co.) equipped with 254-nm lamps (RUL-2537P) and a merry-go-round apparatus, as described earlier,²⁰ using cyclopentanone actinometry.²¹ The data are recorded in Table 1.

For the study of direct irradiation of 5-Cl in various solvents, a typical experiment involved the preparation of six matched quartz tubes. Cyclopentanone was placed in three of the tubes. In the first of the remaining tubes was placed 12 ml of a 1.38×10^{-2} M solution of 5-Cl in glacial acetic acid, in the second tube 12 ml of a 1.48×10^{-2} M solution of 5-Cl in acetonitrile containing 2% water and in the third tube 44.5 mg (0.18 mmol) of 5-Cl in 12 ml of cyclohexane. All six tubes were then sealed using serum stoppers and deoxygenated by bubbling nitrogen through them for 25 min. They were then placed in the merry-go-round apparatus and irradiated for 14 h.

After irradiation each tube containing 5-Cl was opened and the contents were diluted with 100 ml of diethyl ether. The ethereal solutions were extracted with 100 ml of brine and the brine layer was extracted twice with 50 ml of diethyl ether. The ether fractions were then combined and extracted twice with 100 ml of water, twice with 100 ml of brine, three times with 100 ml of aqueous sodium hydrogen carbonate and twice with 100 ml of brine. The solutions were then dried over magnesium sulfate, filtered and the ether was removed under reduced pressure. Each sample was then placed on silica gel (60–200 mesh) and chromatographed with hexanes–10% dichloromethane.

Tube 1 yielded three chromatographic fractions. The

first fraction contained 9.5 mg (0.044 mmol) of 1-methylfluoranthene (**8**), the second 25.5 mg (0.100 mmol) of **5-Cl** and the third 5.6 mg (0.022 mmol) of **2-Cl** with a trace of **3-Cl**. No acetates were formed in this photoreaction. Tube 2 yielded four chromatographic fractions. The first reaction consisted of 1.5 mg (0.005 mmol) of **8**, the second 31.0 mg (0.120 mmol) of **5-Cl**, the third 4.7 mg (0.019 mmol) of **2-Cl** and **3-Cl** and the fourth 5.9 mg (0.022 mmol) of a mixture of amides. The third tube yielded two identifiable fractions (all were identified by ^1H NMR and elution times). The first fraction contained 3.0 mg (0.010 mmol) of compound **8** and the second 34.6 mg (0.140 mmol) of **5-Cl**. About 3.0 mg of as-yet unidentified material was also formed. Tubes 1 and 2 could account for more than 95% of the starting material after chromatography.

For the quenching studies, experiments were conducted as described above for **5-Cl** in acetic acid. Four tubes, each containing 12 ml of a 1.38×10^{-2} M solution of **5-Cl** in glacial acetic acid were prepared. Tube 1 was used as standard to determine ϕ_0 for the Stern-Volmer analysis of the quenching data. Tube 2 has 12 μl of *cis*-pent-1,3-diene added to make a 0.01 M concentration of quencher. Tube three contained 47 μl (0.04 M) and tube four 83 μl (0.07 M) of *cis*-penta-1,3-diene. The tubes were then irradiated for 14 h.

Work-up as described above was followed by analysis as above. The results gave for quantum yields of **8**, tube 1 = 0.047, tube 2 = 0.027, tube 3 = 0.009 and tube 4 = 0.005. The quantum yields of **2-Cl** + **3-Cl** were 0.025 ± 0.002 in all tubes, and those for loss of **5-Cl** were 0.070 in tube 1, 0.049 in tube 2 and 0.038 in both tubes 3 and 4. A plot of the data for **8** formation gives a Stern-Volmer slope of $k_Q^3 \tau = 110 \text{ l mol}^{-1}$.

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