# Photochemical Behavior of Stable Free Radicals: The Photochemistry of Perchlorodiphenylmethyl Radical

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The excitation of perchlorodiphenylmethyl radical (PDM) at 530 nm leads to the lowest excited doublet,  $D_1$  ( $\tau = 31$  ns), from which emission is observed ( $\Phi = 1 \times 10^{-3} \pm 0.0003$ ). This state is quenched by electron donors and acceptors at a rate at or close to diffusion control and at much slower rates by oxygen and hydrogen atom donors. Fragmentation of PDM ( $\Phi_d = 0.06$ ) occurs from a higher excited doublet ( $D_n, n \ge 2$ ) producing intermediates that are trapped by  $O_2$ , chlorine, or hydrogen donors, yielding products 1–6. Experimental evidence suggests a structure-photoreactivity correlation in the perchlorinated arylmethyl radicals in which the partitioning between photochemical cyclization or fragmentation depends on the twist angle between the appended phenyl rings.

## Introduction

Characterizing the excited-state chemistry of transient arylmethyl radicals poses an intellectual and experimental challenge. These short-lived intermediates have been studied both theoretically and experimentally, in solid matrices at low temperature and in solution at room temperature.<sup>1-7</sup> Their extreme instability, however, usually has permitted only a study of their photophysical characteristics primarily because of the low yield of products resulting from two-photon processes. Their relatively short ground-state lifetimes also make it difficult to study their groundstate intermolecular chemistry and to isolate products. Full reaction characterization would be much easier if, instead, the steady-state irradiation of stable radicals were studied.

The "inert free radicals", first described by Ballester in 1967, are perchlorinated aromatic radicals, so-called because of their exceptional chemical and thermal stability deriving mainly from steric shielding by the bulky halogens.<sup>8,9</sup> They have indefinitely long lifetimes and are essentially chemically inert in the solid state. As such, they are ideal candidates as substrates for studying excited-state radical processes.

Recently we described the photoreactivity of perchlorotriphenylmethyl radical (PTM),<sup>7,10</sup> whose thermal chemistry has previously been investigated by Ballester et al.<sup>11,12</sup> PTM undergoes a photoinduced cyclization to yield the perchloro-9phenylfluorenyl radical (PPF), and a derivative obtained from PPF by H abstraction (from residual hydrocarbon present in the solvent), eq 1. Meisel et al.<sup>2,5,6</sup> have shown that the analogous



hydrocarbon, triphenylmethyl radical, similarly cyclizes upon photoexcitation, to produce the 9-phenylfluorenyl radical. However, they observed that the diphenylmethyl radical behaved quite differently under the same photolysis conditions. Although product analysis is difficult from this transient free radical, no evidence for cyclization could be found, and the excited radical was claimed to suffer initial homolytic bond scission, followed by bimolecular reaction.

To determine whether parallel reactivity holds between other hydrocarbon radicals and their inert perchlorinated analogs, we



Figure 1. Absorption spectrum of PDM in CCl<sub>4</sub>  $(1.25 \times 10^{-4} \text{ M})$  at room temperature. The inset displays an expanded region between 400 and 600 nm showing the 530-nm tailing absorption.

have undertaken the study of the perchlorodiphenylmethyl radical (PDM). Here we report the photochemistry of PDM, a characterization of its photoproducts with a proposed mechanistic pathway for their formation, a study of the photophysical characteristics of its excited doublet states, and a structure-photoreactivity correlation of the contrasting excited states of PDM and PTM radicals that rationalizes the different partitioning between photochemical cyclization and fragmentation.

#### Results

Steady-State Photolysis of PDM. (A) Wavelength-Dependent Photolysis. PDM has an absorption spectrum that tails beyond 530 nm, accounting for its bright orange color, Figure 1. Excitation wavelength dependence in the photodecomposition of PDM was monitored by the disappearance of the 384-nm absorption band, Figure 2. PDM showed rapid degradation upon irradiation at  $\lambda_{ex}$  313 nm, while irradiation at  $\lambda_{ex}$  530 nm produced no photoreaction. At  $\lambda_{ex}$  384 nm, only a very slow photoreaction was seen. The quantum yield of decomposition ( $\Phi_d$ ) of PDM at  $\lambda_{ex} = 313$  nm, measured by following the loss of optical density of a CCl<sub>4</sub> solution of PDM at 384 nm, was 0.06.

(B) Product Studies. Visible light irradiation of an oxygensaturated carbon tetrachloride (CCl<sub>4</sub>) solution of PDM  $(5 \times 10^{-3})$ 

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Figure 2. Disappearance of PDM as monitored by optical density at 395 nm in  $O_2$ -saturated CCl<sub>4</sub> solution at varying excitation wavelengths (O) 313 nm, ( $\bullet$ ) 384 nm, and ( $\Delta$ ) 530 nm.

M) leads to a complex product mixture, Scheme I, containing the cleavage products 1 (30%), 2 (9%), 3 (4%), and oxygenated products 4 (17%), 5 (3%), and 6 (6%). The absolute yields and distribution of these products varies with the concentration of oxygen. When the photolysis solution was rigorously degassed, the major products seen were 1 ( $\sim 25\%$ ) and 2 ( $\sim 8\%$ ). Even with trace amounts of O<sub>2</sub> (in N<sub>2</sub>-purged solutions), small amounts of 4 or 6 ( $\leq 5\%$ ) could still be observed.

The irradiation of PDM in H-donating solvents likewise led to cleavage products. In degassed cyclohexane, the major products were 1 (47%), 2 (16%), and dicyclohexyl (9%), the latter arising from the dimerization of the  $C_6H_{11}$  radical. (Cyclohexene, a presumed product of cyclohexyl radical dismutation, was not separated from solvent under the analytical conditions employed.) When the irradiation was done in a 1:1 mixture of  $Ccl_4:C_6H_{12}$ , yields of 2 and 3 increased slightly (12% and 6%, respectively) compared with those observed in  $Ccl_4$ . Water saturation of  $Ccl_4$  had no effect on the relative yields of the photoproducts. A dark control experiment under identical conditions showed that no PDM fragmentation occurred in the absence of excitation.

(C) Absence of Ring-Closure Product. Neither the lightinduced ring closure product, perchloro-9-fluorenyl radical (PF), nor perchlorofluorene (7) nor 9H-nonachlorofluorene (8), which might have been expected as final products deriving from the trapping of PF (eq 2), could be detected under these conditions. Subjecting authentic samples of 7 and 8 to the reaction conditions did not lead to skeletal decomposition, allowing us to confirm the absence of such cyclization products in appreciable yields in the photolysis mixture.

Intermediate formation of PF could not be excluded by these steady state experiments, since the possibility of rapid decomposition of the initially formed radical under the photolysis



conditions still remained. The radical PF has been reported to be unstable itself but it does exist as the dimer, 9H-heptadecachloro-9,9'-bifluorenyl (9).<sup>13</sup> Since 9 cleaves to give radical PF at 90 °C in C<sub>6</sub>Cl<sub>5</sub>H, the dimer was subjected to photolysis at elevated temperature, anticipating its homolytic cleavage to produce PF. Irradiation of 9 in Ar- and O<sub>2</sub>-saturated CHCl<sub>3</sub> (4 h) afforded only 7, 8, and 10, the corresponding H<sup>•</sup> and Cl<sup>•</sup> trapped fluorenyl radicals, in 32%, 30%, and 22% relative yield (eq 3). Photolysis of PDM under these same conditions gave the corresponding fragmentation products 1–6, Scheme I.



**Emission Spectra.** PDM has an emission band at  $\lambda_{max} = 670$  nm, with a fluorescence efficiency that depended on the excitation wavelength, Figure 3. Excitation of PDM in the ultraviolet region ( $\lambda \leq 386$  nm) in N<sub>2</sub>-saturated CCl<sub>4</sub> and pentane solutions showed no emission at room temperature. Excitation at longer wavelengths ( $\lambda = 530$  nm) gave a reproducible weak emission band ( $\Phi_f = 0.0010 \pm 0.0003$ ). The possibility that this band is an excimer emission was eliminated by a relative fluorescence quantum yield study (by integrating the emission band at different concentration independent in the range of absorption optical densities from 0.02 to 0.2 at  $\lambda_{ex}$  530 nm. The excitation spectrum shows that a species with  $\lambda_{max} \sim 505$  nm is responsible for the observed emission.

PTM also shows wavelength-dependent fluorescence. The bright red PTM radical has its absorption maximum tailing beyond 600 nm and an emission band at  $\lambda_{em} = 606$  nm, Figure 4. The fluorescence intensity of PTM depended on the excitation wavelength, with the emission intensity observed at  $\lambda_{ex}$  530 nm







Figure 3. Fluorescence spectrum of PDM in CCl<sub>4</sub> at room temperature.



Wavelength (nm)

**Figure 4.** Absorption spectrum of PTM in  $CCl_4$  (5 × 10<sup>-5</sup> M) at room temperature. The inset displays an expanded region between 400 and 700 nm showing the 600-nm tailing band.



Figure 5. Fluorescence spectrum of PTM in CCl<sub>4</sub> at room temperature.

 $(\Phi_f = 0.015 \pm 0.005)^7$  being about an order of magnitude greater than that at  $\lambda_{ex}$  386 nm ( $\Phi_f = 0.0025 \pm 0.0005$ ), Figure 5. The excitation spectrum of PTM indicated a larger contribution at 530 nm than at 386 nm for the observed emission.

Fluorescence Quenching and Lifetimes. Single-photon-counting measurements gave a fluorescence lifetime  $(\tau_f)$  for PDM of 31 ns, somewhat longer than that for PTM (7 ns). Emission observed in PTM at both excitation wavelengths (386 and 530 nm) gave  $\tau_f = 7$  ns, indicating that one excited state is responsible for the observed emission.

Quenching for the emissive states ( $\lambda_{ex}$  530 nm) of PDM and PTM in CCl<sub>4</sub> (10<sup>-3</sup> M) by molecular oxygen, H-donating solvents, and both electron acceptors and donors was monitored by integrating the emission band from 570 to 800 nm, Table I. The ground states of both radicals were unaffected by these quenchers,

TABLE I: Rate Constants  $k_q$  (M<sup>-1</sup> s<sup>-1</sup>) for Fluorescence Quenching of <sup>2</sup>PDM<sup>\*</sup> ( $\tau_f = 31$  ns) and <sup>2</sup>PTM<sup>\*</sup> ( $\tau_f$ ) = 6 ns)<sup>s</sup> by Electron-Transfer Quenchers

quencher	PDM (M <sup>-1</sup> s <sup>-1</sup> )	PTM (M <sup>-1</sup> s <sup>-1</sup> )
triphenylamine	1.01 × 10 <sup>10</sup>	$1.03 \times 10^{10,b}$
chloranil	$2.18 \times 10^{9}$	$1.89 \times 10^{10}$
cyclohexene	<107	<108
oxygen	$1.57 \times 10^{8}$	$1.02 \times 10^{9}$

<sup>a</sup> Measured in carbon tetrachloride at room temperature calculated from Stern-Volmer equation. <sup>b</sup> See ref 7.

TABLE II: Rate Constants  $k_q$  (M<sup>-1</sup> s<sup>-1</sup>) for Fluorescence Quenching of <sup>2</sup>PDM<sup>\*</sup> and <sup>2</sup>PTM<sup>\*</sup> by H Donors

quencher	PDM (M <sup>-1</sup> s <sup>-1</sup> )	PTM (M <sup>-1</sup> s <sup>-1</sup> )	Ph <sub>2</sub> HC <sup>•</sup>
cyclohexane	<107	<108	
cyclohexene	<107	<108	
cyclohexadiene	<10 <sup>7,b</sup>	<10 <sup>8,b</sup>	$(1.1 \pm 0.2) \times 10^{6,c}$

<sup>a</sup> Measured in carbon tetrachloride at room temperature. <sup>b</sup> 1,3-Cyclohexadiene; <sup>c</sup> 1,4-Cyclohexadiene; see ref 1.

as evidenced by the intensity of the emission intensity to these compounds (up to 1 day).

Triphenylamine (TPA), a well-known electron donor, has previously been shown to quench the excited state of PTM at an approximately diffusion-controlled rate.<sup>7</sup> Addition of TPA to PDM solutions showed a decrease in the intensity of its emission band with a calculated quenching rate constant  $(k_q)$  from a linear Stern–Volmer plot of  $1.01 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ .

Although we previously<sup>7</sup> reported that the emission of PTM was not quenched by duroquinone, quenching of the excited doublet states of both PTM  $(1.89 \times 10^{10} \,\mathrm{M^{-1}\,s^{-1}})$  and PDM (2.18  $\times 10^9 \,\mathrm{M^{-1}\,s^{-1}})$  by chloranil was efficient. Quenching by oxygen was about 10 (PTM) to 20 (PDM) times slower than the diffusion-controlled rate.

Excited PDM and PTM radicals were poor abstracters of chlorine from carbon tetrachloride and of hydrogen from cyclohexane, cyclohexene, and 1,3-cyclohexadiene at room temperature, Table II. Neither PDM nor PTM showed any change in their emission spectra in the presence of relatively high concentrations of the H donor (0.1-1.5 M). This behavior contrasts with the parent diphenylmethyl radical excited state, where facile chlorine abstraction from CCl<sub>4</sub> was observed.

#### Discussion

**Photolysis Products from PDM.** The photochemical behavior of perchlorinated phenyl radicals parallels that of the analogous hydrocarbons,<sup>2</sup> with the photolysis of PTM and PDM radicals leading, respectively, to cyclization and bond fission. Instead of photochemical cyclization, PDM fragmented to produce a complex product mixture, Scheme I. The yields of products 2 and 3 were unaffected by moisture but were increased by the presence of added hydrogen donors. The additional H atom in these products probably arises from trace quantities of hydrocarbon remaining in the solvent. The absence of oxygenated products in degassed reaction mixtures and the increased yields in O<sub>2</sub>-saturated solution provide evidence that the oxygen in products 4-6 derives from dissolved molecular oxygen rather than adventitious water.

A possible mechanistic sequence for the formation of products 1-6 is proposed in Scheme II. A homolytic fragmentation across bond a in PDM could yield perchlorophenylcarbene and a pentachlorophenyl radical in a process similar to that proposed for the diphenylmethyl radical, eq 4.<sup>2</sup> Abstraction of chlorine or hydrogen from CCl<sub>4</sub> or hydrocarbons by the latter species would yield products 1 and 2 (eq 6 and 7). Product 3 could be formed by sequential chlorine and hydrogen abstraction by the carbene. Alternatively, reaction with molecular oxygen, eq 8, could ultimately yield  $6.^{14-16}$  Cleavage across bond b leading to perchlorodiphenylmethyl carbene (eq 5) and subsequent trapping











by oxygen, similar to that of diphenylmethyl carbene,<sup>17,18</sup> will produce perchlorobenzophenone 4 or ketone 5, eq  $9.1^9$  Oxygenation can occur either at the methyl radical center or at the p position, where a significant fraction of spin density in PDM is located.<sup>22</sup> Alternately, hydrogen abstraction by this carbene<sup>20,21</sup> (eq 10) gives a radical which fragments (by analogy with the hydrogenated analog),<sup>23</sup> producing a radical-carbene pair which leads to products 3 and 1 after the proposed chlorine or hydrogen abstraction.

Our attempts to obtain direct spectroscopic evidence for transient carbene formation from flash photolysis studies in the 300-800-nm region on a  $10^{-9}-10^{-6}$  s time scale in Ar- or O<sub>2</sub>-saturated solutions<sup>14,24</sup> were unsuccessful, presumably because of the very weak absorption of these transients and their low steady state concentrations under these reaction conditions ( $\Phi_d = 0.06$ ).

Lack of Photoinduced Cyclization. As in its thermolysis,<sup>13</sup> dimer 9 undergoes a homolytic bond cleavage upon photolysis to produce the fluorenyl radical which rapidly abstracts either a H or a Cl atom (from solvent CHCl<sub>3</sub>) to give 7, 8, and 10. Thus, if cyclization were a significant pathway for PDM (formation of PF), 7 and 8 would be expected to persist as isolated final products. Because these could not be detected in the reaction mixtures, the possible PDM cyclization followed by fragmentation of the formed PF radical can be eliminated.

Thus, photoinduced cyclization parallel to that observed for PTM (eq 1) fails with PDM. This divergent photoreactivity apparently derives from the difference in the degree of twisting of the phenyl groups. Unlike their hydrocarbon analogs, the

perchlorinated radicals, in their ground state, can be rigorously structurally characterized. From X-ray diffraction, twist angles between the pentachlorophenyl rings in PTM and the trigonal plane of the central carbon atom are 48° and 55°<sup>26</sup> and is somewhat larger than in PDM (co-crystal with  $\alpha$ -H-PDM and  $\alpha$ -Br-PDM) which is 47° and 43°.<sup>25</sup> Meisel's proposal that an increase in the twist angle (in Ph<sub>3</sub>C<sup>•</sup>) increases the efficiency of cyclization from the D<sub>1</sub> state, while an increase in coplanarity (in Ph<sub>2</sub>HC<sup>•</sup>) minimizes reactivity, apparently also applies to the perchlorinated analogs.<sup>2</sup> Such twisting in arylmethyl radicals is required to minimize the steric interactions caused by the ortho chlorine groups on the phenyl rings. Even though the difference in the twist angles between Ph<sub>3</sub>C<sup>•</sup> and Ph<sub>2</sub>HC<sup>•</sup> is very small, the conformation of Ph<sub>3</sub>C<sup>•</sup> in the D<sub>1</sub> state allows for a cyclization.<sup>5</sup>

Reactivity of the Doublet Excited States of PDM. The PTM radical has a shorter fluorescence lifetime (7 ns) than PDM (31 ns), presumably because the efficient cyclization of the lowest doublet of PTM that is absent in PDM. Upon long-wavelength irradiation ( $\lambda_{ex} = 530$  nm) of PDM, weak emission is observed ( $\lambda_{em} = 670$  nm). At this wavelength, no photoreactivity was evident. However, the higher excitation energy ( $\leq 313$  nm), no emission could be detected, and instead a rapid degradation of the radical was seen. It is known that lower energy photons provide insufficient energy for the bond scission which is observed at shorter wavelengths.<sup>27</sup> Therefore, ultraviolet excitation of PDM produces an upper excited doublet ( $D_n$ ,  $n \geq 2$ ) with sufficient energy to fragment at a rate at least competitive with relaxation to the lower energy emissive state. Homolytic cleavage occurs in less than 31 ns for PDM, but the quantum efficiencies of both emission ( $\Phi_f \sim 10^{-3}$ ) and decomposition at  $\lambda_{ex} = 313$  nm ( $\Phi_d = 0.06$ ) are low, indicating a facile competing radiationless deactivation.

These results are parallel to that observed for  $Ph_2HC^*$  and seem to be a general phenomenon for diarylmethyl radicals.<sup>2,3</sup> Previous studies have shown  $Ph_2HC^*$  to exhibit practically no photochemistry from the  $D_1$  state, but rather only from the state generated by the absorption of two photons, resulting in homolytic fragmentation from an upper excited state. From the  $D_1$  state, this radical ( $Ph_2HC^*$ ) also exhibits only fluorescence and nonradiative relaxation.<sup>2</sup>

In contrast, the PTM radical undergoes efficient cyclization from its lowest excited energy state  $(D_1)$ . It has been suggested that  $Ph_3C^{\bullet}$  similarly cyclizes from the  $D_1$  state.<sup>2</sup>

Quenching of the Lowest Excited Doublet States. The fluorescence quenching of PDM shows electron transfer rather than collisional quenching to be the major degradation pathway for the doublet excited state. The enhanced redox reactivity of this photoexcited radical derives from its greatly enhanced electrontransfer reactivity in the excited state.<sup>27</sup> In the ground state, PDM exhibits a reversible oxidation (+1.07 V) and reduction (-0.67 V vs Cp<sub>2</sub>Fe) in CH<sub>3</sub>CN,<sup>28</sup> while PTM shows no oxidation between +2 and -2 V, but a reversible reduction at -0.43 V (vs Ag/AgNO<sub>3</sub>).<sup>7</sup>

Electron transfer quenching has been reported in both  $Ph_3C^{**}$ , and  $Ph_2HC^{**}$ , with quenching rate constants in the range  $10^{8}$ –  $10^{10}$  M<sup>-1</sup> s<sup>-1.1</sup> Electron acceptors and donors similarly quench the excited states of PDM and PTM at rates at or close to diffusion control (Table I). Quenching by electron donors, however, is more facile than with acceptors, probably because the electronegativity of the Cl atoms can stabilize the formed anion.<sup>29</sup>

Oxygen quenches  $Ph_2CH^{**}$  at a rate of  $8.7 \times 10^9 M^{-1} s^{-1}$ , and its chlorinated analogue PDM has a quenching rate about 50 times lower  $(1.5 \times 10^8)$ . The rate of reaction of PTM with oxygen closer  $(1.02 \times 10^9)$  to that observed in the analogous hydrocarbon. The perchlorinated radicals apparently show poor hydrogenabstracting ability.

ESR studies have shown that the odd electron density in PDM and PTM radicals reside mainly on the  $\alpha$ -C but with some additional spin density at the p carbons.<sup>30</sup> Although the localization of electron density should enhance reactivity of the radical center, the central carbon is sterically blocked by five chlorine atoms in PDM, and six in PTM, making approach for collisional quenching difficult. Thus, electron transfer dominates the quenching of the D<sub>1</sub> states in PDM and PTM radicals, and oxygen trapping products 4 and 5 are formed only at high concentrations of oxygen. That any of the nonaromatic ketone is 5 observed is further indication of steric blockage at the  $\alpha$ carbon.

#### Conclusion

Upon photolysis, the perchlorodiphenylmethyl radical (PDM) fragments from an upper excited state ( $\Phi_d = 0.06$  at  $\lambda_{ex} = 313$ ) producing intermediates which are trapped either by molecular oxygen or by chlorine or hydrogen atom abstration from the solvent, giving a complex product mixture. Wavelength dependences of both fluorescence and steady-state photolysis indicate that PDM reacts from a higher-lying excited state ( $D_1$ ). Emission is observed only from the  $D_1$  state and not from higher lying excited states. Its low fluorescence quantum yield ( $\Phi_f = 0.001 \pm 0.0003$ ) indicates a very efficient nonradiative internal deactivation from  $D_1$ .

The lowest excited doublet state of PDM is longer lived ( $\tau_f = 31 \text{ ns}$ ) than that of PTM ( $\tau_f = 7 \text{ ns}$ ) because of efficient competitive intramolecular ring closure in the latter. This cyclization results from an increase in the appreciable twisting of the phenyl rings from the central molecular plane, a relationship suggested by

Bromberg et al. as significant for the related photocyclization reactivity in  $Ph_3C^*$  and  $Ph_2HC^*$  radicals.<sup>2</sup>

Steric shielding by the substituted chlorine atoms of the sites bearing appreciable odd electron density makes electron transfer, rather than collisional quenching, the major degradation pathway for these excited radicals.

## **Experimental Section**

Instrumentation. Emission and excited spectra were recorded on a SLM-Aminco SPF-500C spectrofluorimeter. Absorption spectra were measured on a HP 8451A diode array spectrophotometer. Steady-state irradiations were conducted through a Pyrex filter with either a 450-W medium-pressure Hg lamp or in a Rayonet photochemical reactor (Southern New England Ultraviolet) equipped with low-pressure Hg lamps blazed at 300 nm. Gas-liquid chromatographic (GC) analyses were obtained on a Hewlett-Packard 5890A instrument equipped with a flame ionization detector and a  $0.5 \text{ mm} \times 10 \text{ m}$  DB-5 capillary column. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a General Electric QE-300 spectrometer. Thin-layer chromatography were performed on plastic sheets precoated with silica gel (Macherey-Nagel Polygram, SIL G/UV<sub>254</sub>) and visualized under a 254-nm UV light. Flash column chromatography was carried out on MN-Kiesel gel 60 silica gel. Gas chromatography/mass spectrometry (GC/MS) analyses were performed on a Varian 3400 GC automated with a Finnigan MAT 700 MS instrument using a 25 m DB-5 capillary column.

Solvents and Materials. Carbon tetrachloride (CCl<sub>4</sub>, Fisher, spectral grade) was distilled from  $P_2O_5$  and was stored over 4-Å molecular sieves. Cyclohexane (Baker, spectra grade) was heated under reflux (24 h) and distilled from CaH<sub>2</sub> immediately before use. Chloroform (spectra grade) was stored over activated 4-Å molecular sieves (at least 24 h). Triphenylamine was recrystallized from EtOH. Hexachlorobenzene (1), pentachlorobenzene (2), dicyclohexyl, chloranil, cyclohexene, 1,3-cyclohexadiene were used as received from Aldrich without further purification. The PTM radical was handled under red safety lights.

Perchlorodiphenylmethane was prepared by the method of Ballester<sup>8</sup> in 96% yield; mp 232-234 °C (lit.<sup>8</sup> mp 231-234 °C).

Perchlorodiphenylmethyl radical (PDM) was prepared by the method of Ballester<sup>8</sup> to give an orange solid in 51% yield. Its ESR spectrum matches with that previously reported.<sup>31</sup>

Pentachloro- $\alpha, \alpha$ -dichlorotoluene (3) was prepared by ring perchlorination of  $\alpha, \alpha$ -dichlorotoluene with reagent-BMC (a mixture of SOCl<sub>2</sub>, S<sub>2</sub>Cl<sub>2</sub>, and AlCl<sub>3</sub>)<sup>32</sup> to give a white solid (CCl<sub>4</sub>) in 67% yield; mp 106–108 °C; MS *m/e* 330 (9, C<sub>7</sub>H<sup>35</sup>Cl<sub>7</sub>), 297 (100%, Cl), 284 (55%, CCl); HRMS *m/z* calcd for C<sub>7</sub>H<sub>35</sub>Cl<sub>7</sub> 329.78 94, found 329.789 802.

*Perchlorobenzophenone* (4) was prepared by the method of Ballester<sup>8</sup> in 33% yield; mp 318–319 °C (lit.<sup>33</sup> mp 318 °C).

Perchloroquinone (5) was solved by an X-ray structure. Fractional sublimation gave clear, yellow crystals. The data crystal was a block of approximate dimensions  $0.10 \times 0.17 \times 0.17$  mm. The data were collected on a Nicolet P3 diffractometer, using a graphite monochromator and Mo K $\alpha$  radiation ( $\lambda = 0.7107$  Å), and equipped with a Nicolet LT-2 low-temperature delivery system (198 K). The crystal system is triclinic and the space group is P1 (No. 2). The lattice parameters were obtained by the least-squares refinement of 38 reflections with 19.3 < 2 $\theta$  M 24.5°; a = 7.7725 (10), b = 8.6893 (10), c = 14.2741 (13) Å,  $\alpha = 84.929$  (8),  $\beta = 84.446$  (9),  $\gamma = 65.732$  (8)°, V = 873.5 (2) Å<sup>3</sup>,  $\rho = 2.27$  g cm<sup>-3</sup> for Z = 2, F(000) = 578. Complete data are included as supplementary material.

Perchlorobenzoic acid was synthesized by the method of Inanaga<sup>34</sup> in 88% yield; mp 197–199 °C (lit.<sup>35</sup> mp 196–198 °C).

Perchlorobenzoylchloride (6) was prepared according to the method of Inanaga<sup>35</sup> by treating perchlorobenzoic acid (300 mg) with thionyl chloride (10 mL) while heating under reflux for 48

h. Recrystallization from hexane gave white needles (61%); mp 86–87 °C; MS m/e 310 (16%, C $_7^{35}$ Cl<sub>6</sub>O), 275 (100%, Cl), 247 (38%, CO); HRMS m/z calcd for C $_7^{35}$ Cl<sub>6</sub>O: 309.808031: found: 309.808751.

9,9-Dichlorofluorene was prepared from fluorenone by the method of Landgrebe<sup>36</sup> in 78% yield; mp 103-104 °C (lit.<sup>36</sup> mp 103-104 °C). The pure product is highly unstable and hydrolyzes back to fluorenone.

Perchlorofluorene (7) was synthesized by ring perchlorination of freshly made 9,9-dichlorofluorene with a modified BMC reagent containing a large excess of AlCl<sub>3</sub> (BMC-P) according to the method of Ballester;<sup>32</sup> isolated yield 35%. We obtained a slightly higher mp (264–266 °C) than reported (256–258 °C)<sup>37</sup>; MS m/e 506 (4%, C<sub>13</sub><sup>35</sup>Cl<sub>10</sub>).

9H-Perchlorofluorene (8) was prepared by the method of Camps<sup>37</sup> in 50% yield; UV 310 nm (lit.<sup>13</sup> UV 306 nm).

9H-Heptadecachloro-9,9'-bifluorenyl (9) was synthesized by the method of Ballester<sup>13</sup> to give white crystals in 98% yield; mp 229-231 °C (lit.<sup>13</sup> mp 227-230 °C).

**Irradiation of PDM.** In photolyses conducted in the absence of  $O_2$ , the solution was degassed by at least three freeze-pumpthaw cycles. For the dark control reactions, a cell prepared identically as the photolyses mixture was covered with aluminum foil while all other experimental conditions were kept constant.

A 50-mL solution of PDM (5  $\times$  10<sup>-3</sup> M) in O<sub>2</sub>-bubbled CCl<sub>4</sub> was irradiated (1 h) with 16 lamps blazed at  $300 \pm 20$  nm in a Rayonet photochemical reactor while being stirred and cooled with chilled water. For bulk-scale photolyses (1 g), irradiations were conducted by using a Pyrex-filtered output ( $\lambda \ge 300 \text{ nm}$ ) of a 450-W medium pressure Hanovia lamp (2 h) in a Pyrex immersion well. The reaction was monitored by disappearance of the 386-nm absorption band. After photolysis was complete, the solvent was removed under reduced pressure and the residue was chromatographically separated into pure products. Flash chromatography (CCl<sub>4</sub>:pentane/7:3 then 1:1) on silica gave 1 (156 mg, 30%). Fractional sublimation at 0.05 mmHg of the remaining residue gave a white solid 4 (164 mg, 17%, recrystalled from dioxane), and fine yellow crystals of 5 (29 mg, 3%). Products 2, 3, and 6 were obtained in 9%, 4%, and 6%, respectively. The reported yields are calculated from GC ratios against an internal standard (naphthalene) compared to their isolated total weight (105 mg). Products 1, 2, 3, and 6 were identified by co-injection on a GCMS with authentic samples and by comparison of fragmentation patterns with those of authentic material. Product 4 was characterized by comparing its mp, MS fragmentation patterns and HRMS with an authentic sample (vide infra for synthesis of 3, 4, and 6). Structure 5 was solved by an X-ray analysis.<sup>31</sup>

A H<sub>2</sub>O-saturated CCl<sub>4</sub> solution (25 mL; achieved by adding an excess of H<sub>2</sub>O (2 mL) and stirring the resulting mixture for 2 h), under the same photolysis conditions gave an identical yield of products.

Irradiation (450-W Hanovia lamp) of PDM (270 mg/100 mL,  $5 \times 10^{-3}$  M) in N<sub>2</sub>-purged C<sub>6</sub>H<sub>12</sub> gave, after separation on a flash column (hexane:CCl<sub>4</sub>/1:1, followed by hexane:EtOAc/7:3): 1 (67 mg, 47%), 2 (20 mg, 16%), and dicyclohexyl (8 mg, 9%), identified by co-injecting on a GCMS with authentic samples.

Photolyses done in a mixture of  $C_6H_{12}$ :CCl<sub>4</sub> (1:1 Rayonet conditions) showed increased yields of products 2 and 3 (12% and 6%), their yields being calculated using an internal standard on a GC. In degassed reaction mixtures of CCl<sub>4</sub>, small amounts of hexachlorobenzene (~25%) were detected, and none of the oxygenated products were present. In the dark, in a 10<sup>-3</sup> M solution PDM in CCl<sub>4</sub> showed gradual decomposition (~10%) only after 3 days.

Flash photolyses experiments were performed on a frequency doubled Q-switched Nd: YAG laser (Quantel YG 481, 8-ns pulse, approximately 100 mJ at 355 nm). Transient absorptions were monitored with a conventional xenon lamp, monochromator, photomultiplier arrangement. Samples were continuously bubbled with either  $N_2$  or  $O_2$ .

Irradiation of 9*H*-Heptadecachloro-9,9'-bifluorenyl (9). A 2  $\times 10^{-4}$  M solution of 9*H*-heptadecachloro-9,9'-bifluorenyl in Arsaturated CHCl<sub>3</sub> was photolyzed (4 h) by the Pyrex-filtered output of a 450-W medium pressure Hg lamp in a Pyrex immersion well while stirring. Analysis of the reaction mixture by TLC and GC showed the presence of 7 (32%), 8 (30%) and 10 (22%); their yields were calculated from the intensity of the MS molecular ion peaks in the product mixture. Products 7 and 8 were identified by comparing to authentic samples, and MS fragmentation patterns were used to confirm the presence of 10 (M<sup>+</sup> 442). No other products (<5%) were detected. As a control reaction, PDM was photolyzed under similar experimental conditions (in CHCl<sub>3</sub>), producing fragmentation products identical to those seen in the photolysis of CCl<sub>4</sub>.

**Emission Spectra and Quantum Yield Measurements.** The quantum efficiency of decomposition  $(\Phi_d)$  of PDM at  $\lambda_{ex}$  313 nm was measured by UV spectrophotometry by following the loss in optical density at 384 nm. *trans*-Stilbene was used as chemical actinometer for the measurement of incident light intensity.<sup>38</sup> *trans*-Stilbene  $(10^{-2} \text{ M})^{37}$  prepared in a 3.0-mL quartz cuvette was purged with N<sub>2</sub> prior to photolysis at  $\lambda_{ex} = 313$  nm on an optical bench. The trans/cis ratio after photolysis was analyzed by GC according to literature procedures.<sup>40</sup> Under these conditions,  $\Phi_d$  for PDM was found to be 0.06, assuming a  $\Phi_d$  for *trans*-stilbene of  $0.4.^{41,42}$ 

The emission spectra were recorded at room temperature in 1-cm quartz cuvettes for samples with absorption optical densities  $\leq 0.1$  at the excitation maximum. Each measurement was corrected for a background by filling the cell with the appropriate solvent and subtracting it from the recorded sample fluorescence spectra. The output was corrected for instrument response as well.

A solution of rhodamine B in absolute EtOH was used as the standard  $(\Phi_f = 0.97)^{43}$  in the determination of  $\Phi_f$  of PDM in hexane. For PTM, a solution of 9,10-diphenylanthracene in benzene was used as the standard, assuming a  $\Phi_f$  of 0.84.<sup>44</sup> Quantum yields were calculated from the ratios of the integrated fluorescence intensities of sample and standard after having applied a linear correction for the optical density. A refractive index correction was applied,<sup>45</sup>  $\Phi_s(o.d.)_s/\Phi_s(o.d.)_s = A_s(n_s)^2/A_s(n_s)^2$  where A is the integrated area under the fluorescence curve in arbitrary units, s is the sample, S is the standard, n is the refractive index, and o.d. is the solution optical density.

Fluorescence Quenching Studies. To  $10^{-3}$  M PDM and PTM solutions in CCl<sub>4</sub> were added different concentrations (0.02–0.001 M) of quencher (TPA, cyclohexane, cyclohexene, 1,3-cyclohexadiene, chloranil). Emission spectra were recorded at  $\lambda_{ex}$  530 nm at room temperature. Each sample was corrected for the background emission of the corresponding quencher solution. For the oxygen quenching study, solutions of PDM in CCl<sub>4</sub> (10<sup>-3</sup> M) were bubbled with oxygen and nitrogen (30 min) and their emission spectra were recorded. The maximum concentration of O<sub>2</sub> in CCl<sub>4</sub> was  $1.3 \times 10^{-2}$  M.<sup>51</sup>

Single-Photon Counting Experiments. This experimental arrangement, described in detail elsewhere,<sup>47</sup> consists of a Nd: YAG laser mode-locked to yield a continuous train of pulses of 50-ps duration. PDM was excited at 570 nm (against a rhodamine-6G standard), and its emission was monitored at 680 nm. The resulting decay profile gave a  $\tau_f = 31.4818 \pm 0.0410$  ns. For PTM, excitation at 351 nm (against-pyridine-1), with emission monitored at 600 nm, produced an emissive transient with  $\tau_f = 7.015 \pm 0.0222$  ns.

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Supplementary Material Available: For 5, text detailing the X-ray analysis, tables listing fractional coordinates, isotropic and anisotropic thermal parameters, bond lengths and angles, and torsion angles, and figures showing atom labeling and unit cell packing (9 pages); table listing observed and calculated structure factors for 5 (10 pages). Ordering information is given on any current masthead page.

### **References and Notes**

(1) Scaiano, J. C.; Tanner, M.; Weir, D. J. Am. Chem. Soc. 1985, 107, 4396.

- (2) Bromberg, A.; Schmidt, K. H.; Meisel, D. J. Am. Chem. Soc. 1985, 107, 83.
  - (3) Schmidt, J. A.; Hilinski, E. F. J. Am. Chem. Soc. 1988, 110, 4036. (4) Craig, B. B.; Sonnenschein, M. F. J. Lumin. 1989, 43, 227.
  - (5) Bromberg, A.; Meisel, D. J. Phys. Chem. 1985, 89, 2507.
  - (6) Bromberg, A.; Schmidt, K. H.; Meisel, D. J. Am. Chem. Soc. 1984,
- 106. 3056. (7) Fox, M. A.; Gaillard, E.; Chen, C.-C. J. Am. Chem. Soc. 1987, 109,
- 7088 (8) Ballester, M.; Riera, J.; Castañer, J.; Badfa, C.; Monsõ, J. M. J. Am.
- Chem. Soc. 1971, 93, 2215.
  - (9) Ballester, M. Pure Appl. Chem. 1967, 15, 123.
  - (10) Luckhurst, G. R.; Ockwell, J. N. Tetrahedron Lett. 1968, 38, 4123.
  - (11) Ballester, M. Adv. Phys. Org. Chem. 1989, 25, 267. (12) Ballester, M.; Castañer, J.; Riera, J.; Pujadas, J.; Armet, O.; Onrubia,
- C.; Rio, J. A. J. Org. Chem. 1984, 49, 770. (13) Ballester, M.; Castañer, J.; Riera, J.; de la Fuente, G.; Camps, M. J. Org. Chem. 1985, 50, 2287.
- (14) Liu, M. T. H.; Bonneau, R.; Jefford, C. W. J. Chem. Soc., Chem. Commun. 1990, 1482.
- (15) Ganzer, G. A.; Sheridan, R. S.; Liu, M. T. H. J. Am. Chem. Soc. 1986, 108, 1517.
- (16) Turro, N. J.; Butcher, J. A.; Moss, R. A.; Munjal, W. G. R. C.; Fedorynski, M. J. Am. Chem. Soc. 1980, 102, 7576.

(17) Baron, W. J.; De Camp, M. R.; Hendrick, M. E.; Jones, M.; Levin, R. H.; Sohn, M. B. In Carbenes from Diazo Compounds; Jones, M., Moss,

- R. A., Eds.; Wiley: New York, 1973; p 1.
  - (18) Trozzolo, A. M. Acc. Chem. Res. 1968, 1, 329
  - (19) Zayas, J.; Platz, M. S. Tetrahedron Lett. 1985, 26, 2853.
- (20) Hadel, L. M.; Platz, M. S.; Scaiano, J. C. J. Am. Chem. Soc. 1984, 106. 283
- (21) Scaiano, J. C.; Lougnot, D.-J. Chem. Phys. Lett. 1984, 105, 535. (22) Lankamp, H.; Nauta, W. T.; MacLean, C. Tetrahedron Lett. 1968, 2 249
  - (23) Closs, G. Top. Stereochem. 1968, 3, 193.
- (24) Absorption maxima of these carbenes should occur at 300-600 nm,
- if one assumes that Cl substituent shifts the spectrum by about 10 nm. Trozzolo, A. M. Acc. Chem. Res. 1968, 1, 329.
- (25) Silverman, J.; Soltzberg, L. J.; Yannoni, N. F.; Krukonis, A. P. J. Phys. Chem. 1971, 75, 1246.
- (26) Rius, J.; Miravitalles, C.; Molins, E.; Crespo, M.; Veciana, J. Mol. Cryst. Liq. Cryst. 1990, 187, 155
- (27) Scaiano, J. C.; Johnston, L. J.; McGimpsey, W. G.; Weir, D. Acc. Chem. Res. 1988, 21, 22.
  - (28) de la Fuente, G.; Federlin, P. Tetrahedron Lett. 1972, 15, 1497.
  - (29) Lochert, P.; Federlin, P. Tetrahedron Lett. 1973, 13, 1109
- (30) Falle, H. R.; Luckhurst, G. R.; Horsfield, A.; Ballester, M. J. Chem. Phys. 1969, 50, 258.
  - (31) Pujadas, J. University of Barcelona, Ph.D. Dissertation, 1971
  - (32) Ballester, M.; Castañer, J.; Riera, J. Anal. Quim. 1977, 73, 547.
  - (33) Steiner, K.; Monatsh. Chem. 1915, 36, 825.
- (34) Inanaga, J.; Kawanami, Y.; Yamaguchi, M. Bull. Chem. Soc. Jpn. 1986, 59, 1521.
- (35) Ishikawa, M.; Inanaga, J.; Yamaguchi, M. Mem. Fac. Sci., Kyushu Univ. 1987, 16, 47
- (36) Martin, C. W.; Gill, H. S.; Landgrebe, J. A. J. Org. Chem. 1983, 48, 1898
- (37) Camps, M., University of Barcelona, Ph.D. Dissertation, 1979
- (38) Kuhn, H. J.; Braslavsky, S. E.; Schmidt, R. Pure Appl. Chem. 1989, 61, 188.
- (39) Lewis, F. D.; Johnson, D. E. J. Photochem. 1977, 7, 421.
- (40) Ho, T.-I.; Su, T.-M.; Hwang, T.-C. J. Photochem. Photobiol. 1988, 41. 293
- (41) Saltiel, J.; Charlton, J. L. In Rearrangements in Ground and Excited States; de Mayo, P., Ed.; Academic Press, NY, 1980; p 25

  - (42) Gusten, H.; Klasinc, L. Tetrahedron Lett. 1968, 26, 3097.
    (43) Weber, G.; Teale, F. W. J. Trans. Faraday Soc. 1957, 53, 646.
  - (44) Melhuish, W. H. J. Phys. Chem. 1961, 65, 229.
- (45) Parker, C. A. Photoluminescence of Solutions; Elsevier: New York, 1968; p 262.
- (46) Stephan, H.; Stephan, T. Solubilities of Inorganic and Organic Compounds.; Pergammon Press: London, 1963; p 569
- (47) Atherton, S. J.; Beaumont, P. C. J. Chem. 1986, 90, 2252.