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Inert Carbon Free Radicals. 10. Chlorination of Perchlorotriphenylmethyl (PTM) Radical. Synthesis, Structure, and Reactivity of Perchloro(diphenylmethylene)cyclohexa-1,4-diene

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Perchlorotriphenylmethyl radical (PTM$^\bullet$) is the paradigm of the chlorine-shielded "inert free radicals" (IFRs), which owe their unique chemical inertia to the colossal overcrowding about their trivalent carbon. However, they are active in single electron-transfer processes. The present paper reports and describes a remarkable two-step chlorination of PTM$^\bullet$ consisting of a SET, giving the corresponding carbenium ion (PTM$^+$), followed by chloride-ion addition yielding $C_{19}Cl_{16}$. The latter *is not* the would-be conventional, extremely overcrowded perchlorotriphenylmethane (α adduct), but the less-strained perchloro(diphenylmethylene)cycylohexa-1,4-diene (para adduct), as shown by spectral and X-ray data analyses. This and other abnormal reactivity processes and phenomena are described and accounted for in terms of great repulsions among the chlorines. The SET leading to cation PTM$^+$ is conducted by either $SO_2Cl_2/AlCl_3$ or by $CH_2Cl_2/AlCl_3$. The subsequent chloride-ion addition results from chlorine bridging between PTM$^+$ and counter-ion $AlCl_4^-$.

The "inert carbon free radicals" (IFR) are trivalent carbon species provided with astonishingly high thermal stability and chemical inertness.[1] They are completely disassociated even in solid form, and their half-life times in solution in contact with air give half-lives up to the order of 100 years. The paradigm of an IFR is perchlorotriphenylmethyl radical (TPM$^\bullet$), which not only does not react with typical radical reagents, like hydrogen donors, hydroquinone, nitrogen mono and dioxide, etc., but it is inert toward aggressive chemicals such as concentrated sulfuric acid, concentrated nitric acid, chlorine, and bromine as well.[2]

Nevertheless, the IFRs are susceptible to single electron transfers (SET), acting either as donors[1,3,4] or acceptors.[1,5] For example, PTM radical can readily be converted into either perchlorotriphenylcarbenium ion (PTM$^+$) or perchlorotriphenylcarbanion (PTM$^-$).

$$\underset{(PTM^+)}{(C_6Cl_5)_3C^+} \underset{-e}{\overset{+e}{\rightleftharpoons}} \underset{(PTM\cdot)}{(C_6Cl_5)_3C\cdot} \underset{-e}{\overset{+e}{\rightleftharpoons}} \underset{(PTM^-)}{(C_6Cl_5)_3C^-}$$

The chemical inertness of the IFRs is due to steric shielding by the chlorine substituents attached to their molecular carbon backbone. Such a chlorine overcrowding confers not only steric protection to the trivalent carbon atom—where most of the electron *spin* density resides—from attack by chemical species (Figure 2 in ref 2) but also the would-be resulting molecules should be forebiddingly strained and distorted. That shielding is however ineffectual in SET processes since the relevant transition states do not require the reacting centers to become so close as in bond-forming reactions. Furthermore, any site of an IFR π-electron system is in principle a potential SET reaction center.

The chlorination of PTM$^\bullet$ to hypothetical perchlorotriphenylmethane, $(C_4Cl_5)_3CCl$, is the central subject of the research work here described. This has been attempted through a single-electron abstraction to PTM$^+$ by means of oxidizing solutions, such as antimony pentachloride in either active (SO_2Cl_2) or inert (CCl_4) solvents, or aluminum chloride in SO_2Cl_2.[3,4] The PTM$^+$ $SbCl_6^-$ has been isolated.

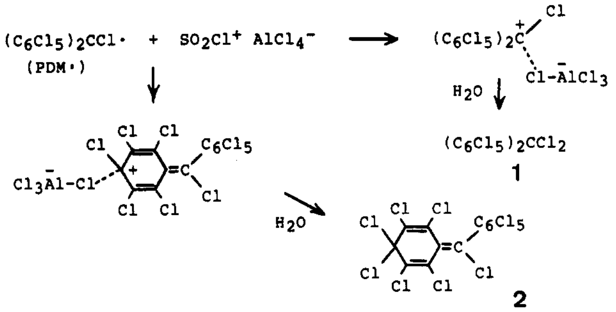
$$(1) \quad PTM\cdot + SbCl_5 \rightleftharpoons PTM^+ SbCl_6^- + SbCl_3$$

$$SbCl_3 + SO_2Cl_2 \longrightarrow SbCl_5 + SO_2$$

$$(2) \quad AlCl_3 + SO_2Cl_2 \longrightarrow SO_2Cl^+ AlCl_4^-$$

$$SO_2Cl^+ + PTM\cdot + AlCl_3 \longrightarrow SO_2 + PTM^+ AlCl_4^-$$

In this connection it is mentioned that the reaction of perchlorodiphenylmethyl radical (PDM$^\bullet$) with $AlCl_3$ in SO_2Cl_2, and with $SbCl_5$, gives also the corresponding carbenium ion (PDM$^+$).[4,6] The hexachloroantimonate salt hydrolyzes to perchlorobenzophenone. However, the tetrachloroaluminate does not give a perchloro ketone, as expected, but either perchlorodiphenylmethane (1) (room temperature) or perchlorobenzylidenecyclohexa-1,4-diene (2) (low temperature).[7,8] This abnormal result has been attributed to the formation of two tight chlorine-bridged pairs with the α and a para carbon, respectively.



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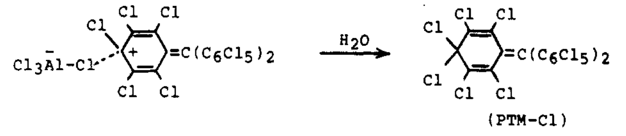
When the two para positions of PDM$^{\bullet}$ are blocked with two pentachlorophenyl groups the hydrolytic treatment gives only the corresponding full aromatic chlorocarbon: $(p\text{-}C_6Cl_5C_6Cl_4)_2CCl_2$. The failure to obtain the para quinonoid chlorocarbon is attributed to both the forbidding steric strain in its would-be chlorine-bridged pair and the loss of biphenyl resonance.[7]

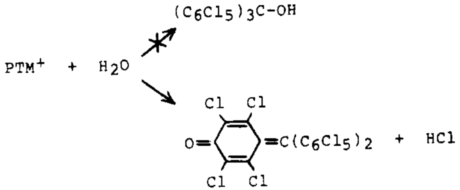
Syntheses of Perchloro(diphenylmethylene)cyclohexa-1,4-diene (PTM-Cl). By hydrolytic treatment of PTM$^+$-$AlCl_4^-$ in SO_2Cl_2, perchlorotriphenylmethane, perchlorotriphenylcarbinol, or perchlorofuchsone (3) are not formed; only perchloro(diphenylmethylene)cyclohexa-1,4-diene (PTM-Cl). Consequently, here a chlorine bridge also occurs but, at variation with PDM$^+$-$AlCl_4^-$, only at a para carbon.



(PTM-Cl)

The lack of chlorine bridging at the α carbon—where most of the positive charge resides—is attributed to a forbidding frontal steric strain in the would-be complex.

When $SbCl_6^-$ is the counter-ion, apparently no tight chlorine bridging exists, and consequently, hydrolytic treatment affords no PTM-Cl. In fact, the product is not the expected perchlorotriphenylcarbinol, but perchlorofuchsone (3). Because the α carbon is shielded by six chlorines and three phenyl groups, the nucleophilic attack occurs at a lesser shielded para position instead.



3

PTM$^+$-$AlCl_4^-$ can be also be obtained by oxidation of PTM$^{\bullet}$ with a mixture of $AlCl_3/CH_2Cl_2$ at room temperature. This mixture is known to be a powerful oxidizing agent.[9] The following mechanism is postulated:

$$CH_2Cl_2 + AlCl_3 \xrightarrow{(1)} CH_2Cl^+\ AlCl_4^-$$

$$CH_2Cl^+ + PTM\cdot \xrightarrow{(2)} CH_2Cl\cdot + PTM^+$$

In the subsequent hydrolysis to PTM-Cl, PTM$^{\bullet}$ is also formed, particularly in diluted solutions. When a substantial amount of *carefully purified* CH_2Cl_2 is added to the carbenium ion solution, quantitative conversion to PTM$^{\bullet}$ might take place, *even before hydrolysis*, showing that the CH_2Cl_2 acts as a single-electron donor. This puzzling, remarkable observation cannot pass unaccounted, and consequently it is tentatively suggested that radical-cation $[CH_2Cl_2]^{+\bullet}$ is formed, the fate of which is obviously a matter of speculation.

$$PTM^+ + CH_2Cl_2 \xrightarrow{(3)} PTM\cdot + [CHCl_2]\cdot^+$$

In this connection it may be mentioned that when the same amount of reagent $AlCl_3/CH_2Cl_2$ is added instead, no PTM$^{\bullet}$ is found, as might be expected.

The presence of PTM$^{\bullet}$ in the product can completely be avoided by adding chlorine to the $AlCl_3/CH_2Cl_2$ mixture, the PTM-Cl being then obtained in an excellent yield. In this connection it is recalled that chlorine forms with $AlCl_3$ a highly polar, "positive chlorine" complex,[10] a most powerful oxidating and chlorinating agent. Therefore, with chlorine, the conversion of PTM$^{\bullet}$ to PTM$^+$ must be caused by this complex, not by CH_2Cl^+.

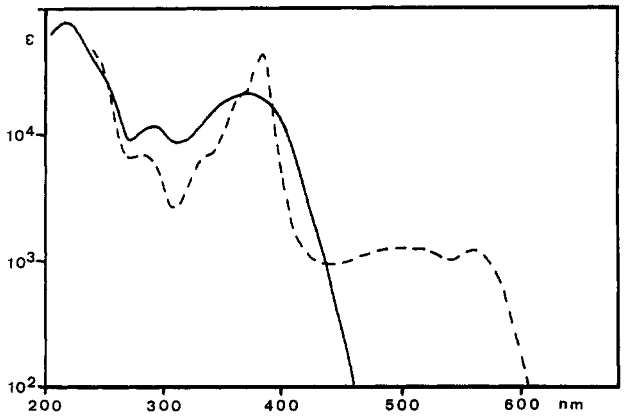


Figure 1. Ultraviolet-visible spectra of PTM$^{\bullet}$ (---) and PTM-Cl (—).

Properties of PTM-Cl. Spectra. The ultraviolet-visible spectra of PTM-Cl and PTM$^{\bullet}$ are shown in Figure 1. The infrared spectrum of the former is reported in the Experimental Section.

Stability. PTM-Cl, at room temperature in air, is perfectly stable toward hexane, cyclohexane, CH_2Cl_2, $CHCl_3$, and CCl_4. In hexane, in contact with activated silica gel, PTM-Cl is rapidly destroyed, giving PTM$^{\bullet}$ and perchlorofuchsone (3) in comparable proportions. The latter process is interpreted as a heterolysis to PTM$^+$ followed by both a SET from hexane and hydrolysis.

The solvolysis of PTM-Cl with concentrated H_2SO_4, at room temperature, gives PTM$^+$ (greenish blue), which by hydrolytic treatment is converted to perchlorofuchsone (3). Treatment of PTM-Cl with $AlCl_3$ in CH_2Cl_2 gives also PTM$^+$, reverting **3** by hydrolytic treatment.

The decomposition of solid PTM-Cl occurs in the interval 200–290 °C, giving PTM$^{\bullet}$. When the thermolysis is conducted in solution (chlorobenzene) under argon at 100 °C (24 h), the product is a mixture of that radical and some starting material. Under the same conditions, in air, the product is a mixture of PTM$^{\bullet}$ and fuchsone **3**. In this connection it is mentioned that PTM$^{\bullet}$ gives **3** under the same reaction conditions.

The kinetics of the homolysis of PTM-Cl in chlorobenzene has been studied at 25.0 and 50.0 °C (Table IV), being monitored by ESR spectrometry. It is first order, the rates being $k(25\ °C) = (1.07 \pm 0.04) \times 10^{-4}\ min^{-1}$ and $k(50\ °C) = (9.3 \pm 0.6) \times 10^{-4}\ min^{-1}$. The Arrhenius activation energy is 15.5 kcal·mol^{-1}.

Since in hexane, cyclohexane, methylene chloride, chloroform, or carbon tetrachloride, at temperatures ranging from 20 to 40 °C, PTM-Cl is stable, being after long standing recovered quantitatively, it is concluded that chlorobenzene assists C–Cl homolysis somehow.

Typical C(sp^3)–Cl bond dissociation energies are 73–84 kcal·mol^{-1}.[11] However, since that bond is much weakened in PTM-Cl by the contribution of the aromatization energy in the homolysis, the activation energy should be dimin-

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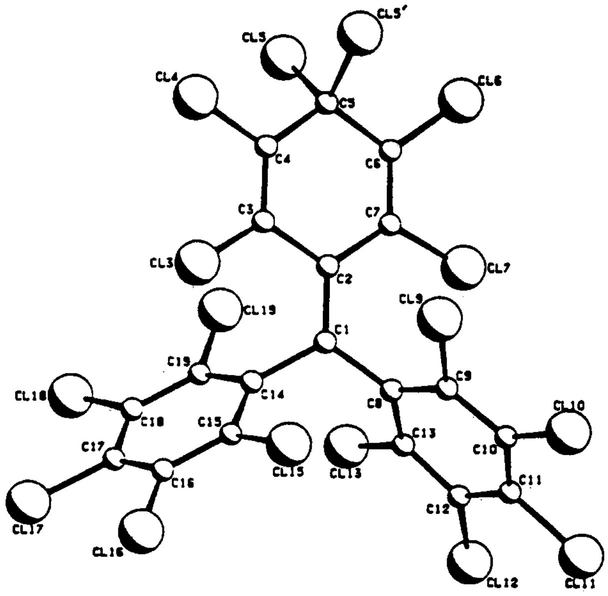
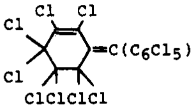


Figure 2. Structure of PTM-Cl.

ished in the resonance energy difference between quinonoid and the benzene structures. Any estimated bond energy should be far from 15.5 kcal·mol^{-1}, the activation energy found. This emphasizes the assistance of chlorobenzene through complexation, as suggested above.

PTM-Cl in CCl_4 under white incandescent light or sunlight, at room temperature, undergoes decomposition presumably giving initially PTM$^•$ and Cl, which evolve to a complex mixture. In this connection it is noted that the photochlorination of PTM$^•$ in CCl_4 saturated with Cl_2, under illumination with white incandescent light, at room temperature, gives a mixture of chlorocarbons, mainly perchloro-3-(diphenylmethylene)cyclohexene (4), PTM-Cl, and perchloro-9-phenylfluorene (5). The structure of 4 has been ascertained by elemental analyses and reduction with $SnCl_2$ in ethyl ether to αH-pentadecachlorotriphenylmethane (6) and PTM$^•$ and with KI in acetic acid (100 °C) to 6. The formation of PTM-Cl indicates that, on account



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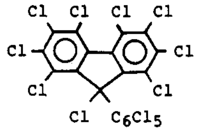
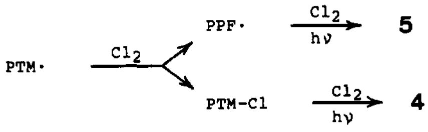


5

$(C_6Cl_5)_3CH$

6

of the prohibitive steric strain of hypothetical perchlorotriphenylmethane, photochlorination of PTM$^•$ takes place again at a para position. The formation of 5 is consistent with the occurrence of photocyclization of PTM$^•$[12,13] to immediate precursor perchloro-9-phenylfluorenyl radical (PPF$^•$).[8] Under the reaction conditions, PTM-Cl adds Cl_2 to 4.



PTM-Cl reacts at room temperature (48 h) with powdered copper in CCl_4, giving PTM$^•$ in an excellent yield.

Table I[a]

Distances (Å) between "Ortho" Chlorines of Different Rings	
Cl15(a)–Cl9(a)	3.509
Cl19(b)–Cl13(b)	3.358
Cl15(a)–Cl13(b)	4.833
Cl19(b)–Cl7(b)	4.485
Cl3(a)–Cl15(a)	3.785
Cl7(b)–Cl13(b)	3.984
Cl3(a)–Cl19(b)	3.958
Cl7(b)–Cl9(a)	3.703
Cl3(a)–Cl9(a)	4.487
Distance (Å) between the Two "Geminal" Chlorines	
Cl5–Cl5′	2.910

[a] a = below the plane C1, C2, C8, C14; b = above.

Table II. Bond Lengths (Å) with Their Esd's (In Parentheses)

C3–Cl3	1.69 (3)	C3–C2	1.52 (3)
C4–Cl4	1.70 (2)	C7–C2	1.44 (4)
C5–Cl5	1.80 (3)	C4–C3	1.37 (3)
C5–Cl5′	1.78 (3)	C5–C4	1.49 (4)
C6–Cl6	1.71 (2)	C6–C5	1.50 (3)
C7–Cl7	1.72 (2)	C7–C6	1.34 (3)
C9–Cl9	1.76 (2)	C9–C8	1.41 (3)
C10–Cl10	1.69 (2)	C13–C8	1.44 (3)
C11–Cl11	1.74 (2)	C10–C9	1.38 (3)
C12–Cl12	1.73 (2)	C11–C10	1.39 (3)
C13–Cl13	1.69 (2)	C12–C11	1.39 (3)
C15–Cl15	1.74 (2)	C13–C12	1.38 (3)
C16–Cl16	1.72 (2)	C15–C14	1.40 (3)
C17–Cl17	1.72 (3)	C19–C14	1.40 (3)
C18–Cl18	1.72 (2)	C16–C15	1.38 (3)
C19–Cl19	1.75 (2)	C17–C16	1.38 (3)
C2—C1	1.38 (3)	C18–C17	1.39 (3)
C8–C1	1.48 (3)	C19–C18	1.37 (3)
C14–C1	1.78 (3)		

Table III. Bond Angles (deg) with Their Esd's (In Parentheses)

C8–C1–C2	124.9 (2.0)	C10–C9–C8	125.5 (1.8)
C14–C1–C2	120.6 (1.9)	C9–C10–Cl10	122.6 (1.5)
C14–C1–C8	114.5 (1.8)	C11–C10–Cl10	121.2 (1.6)
C3–C2–C1	120.9 (2.1)	C11–C10–C9	116.2 (1.9)
C7–C2–C1	123.1 (2.0)	C10–C11–Cl11	118.8 (1.7)
C7–C2–C3	115.9 (2.1)	C12–C11–Cl11	119.3 (1.4)
C2–C3–Cl3	120.0 (1.8)	C12–C11–C10	121.9 (2.1)
C4–C3–Cl3	119.7 (1.7)	C11–C12–Cl12	120.2 (1.4)
C4–C3–C2	119.3 (2.2)	C13–C12–Cl12	119.0 (1.6)
C3–C4–Cl4	118.2 (2.1)	C13–C12–C11	120.6 (1.9)
C5–C4–Cl4	117.1 (1.9)	C8–C13–Cl13	119.0 (1.5)
C5–C4–C3	124.7 (2.1)	C12–C13–Cl13	120.4 (1.6)
Cl5′–C5–Cl5	108.7 (1.4)	C12–C13–C8	120.6 (1.9)
C4–C5–Cl5	107.4 (1.8)	C15–C14–C1	123.6 (1.8)
C4–C5–Cl5	107.7 (1.8)	C19–C14–C1	122.0 (1.9)
C6–C5–Cl5	110.1 (1.7)	C19–C14–C15	114.2 (2.1)
C6–C5–Cl5	110.3 (1.8)	C14–C15–Cl15	118.3 (1.5)
C6–C5–C4	112.5 (2.0)	C16–C15–Cl15	117.3 (1.6)
C5–C6–Cl6	112.5 (1.6)	C16–C15–C14	123.7 (2.1)
C7–C6–Cl6	124.1 (2.0)	C17–C16–C15	118.8 (2.2)
C7–C6–C5	123.3 (2.2)	C16–C17–Cl17	120.1 (2.0)
C2–C7–Cl7	120.8 (2.1)	C18–C17–Cl17	119.7 (2.2)
C6–C7–Cl7	115.0 (2.2)	C18–C17–C16	120.0 (2.7)
C6–C7–C2	123.7 (2.2)	C17–C18–Cl18	119.4 (2.0)
C9–C8–C1	122.9 (1.8)	C19–C18–Cl18	121.7 (1.8)
C13–C8–C1	122.3 (1.8)	C19–C18–C17	118.8 (2.5)
C13–C8–C9	114.7 (1.9)	C14–C19–Cl19	117.8 (1.6)
C8–C9–Cl9	117.5 (1.6)	C18–C19–Cl19	117.9 (1.7)
C10–C9–Cl9	117.0 (1.6)	C18–C19–C14	124.1 (2.3)

Structure of PTM-Cl. The structure of PTM-Cl, which is shown in Figure 2, has been ascertained by X-ray analysis. The atoms are identified by their chemical symbol and a number. In Tables I–III some selected interatomic distances, bond lengths, and bond angles are listed.

The structural parameters of PTM-Cl do not differ significantly from those of other related perchloro com-

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Table IV. Thermolysis of PTM-Cl to PTM Radical. Relative ESR Line Intensities[a]

	time, min									
temp, °C	10	20	30	40	50	60	70	80	90	100
25	0.55	1.25	1.75	2.35	2.85	3.45	4.05			
50	5.7	10.3	15.1	20.5	25.5	29.3	34.9	38.5	42.1	44.9

[a] $k(25\ °C) = (1.07 \pm 0.04) \times 10^{-4}\ min^{-1}$; $k(50\ °C) = (9.3 \pm 0.6) \times 10^{-4}\ min^{-1}$; $E°$(Arrhenius) = 15.5 kcal·mol^{-1}.

pounds, such as perchlorofuchsone[14] and potassium perchlorotriphenylmethide.[15]

Two rings (C8–C13 and C14–C19) are benzenoid, the ring C–C bond (sp^2) lengths being 1.37–1.39 Å, except those of the bridgehead carbons C8 and C14, which are longer (1.40–1.44 Å) on account of the repulsions among "ortho" (central) chlorines Cl3, Cl7, Cl9, Cl13, Cl15, Cl19. The C–Cl bond lengths are 1.69–1.76 Å.

The third ring is quinonoid, i.e., C1–C2, C3–C4, and C6–C7 (1.34–1.38 Å) are shorter than C2–C3, C4–C5, C5–C6, C7–C2 (1.44–1.52 Å). The C–Cl bonds (sp^2) lengths are similar to those of the benzenoid ring, except those (sp^3) with the geminal chlorines (1.78, 1.80 Å) which are longer, as expected, and found in perchlorocyclohexa-2,5-dienone[16] (1.79 Å) and perchlorobenzylidenecyclohexa-2,5-diene (1.80 Å).[17]

The bonds of the C1 carbon with the benzenoid rings (C1–C8 and C1–C14) are longer (1.48 Å)—they correspond to sp^2–sp^2 single bonds[18,19] —than that with the quinonoid ring (C1–C2).

The benzene rings are somewhat warped. Mainly on account of steric repulsions between "ortho" chlorine pairs mentioned above, the rings are like the blades of a propeller-like molecule. Since the angles C8–C1–C2, C14–C1–C2, and C14–C1–C8 add 360°, the C1 is on the plane defined by C2, C8, C14; i.e., the C1 is a flat (sp^2) carbon. Referred to this plane, the angles (tilts) with the benzenoid-ring mean planes are about 58.5°. Since, the tilt-angle of the quinonoid-ring mean plane is 27°, the C1–C2 bond is regarded as a twisted formal double bond.

Those steric repulsions between "ortho" chlorine pairs cause molecular distortion at the bridgehead of the rings, as ascertained by the abnormal low values of the angles C7–C2–C3, C13–C8–C9, and C19–C14–C15 (115.9°, 114.7°, and 114.2°, respectively). The unchallenged buttressing of chlorines Cl4 and Cl6 by Cl3 and Cl7, respectively, cause the angles C5–C4–C1 and C5–C6–C16 to become significantly smaller than 120°.

Apparently, the infrared spectrum of PTM-Cl does not show ethylene stretching peaks about 1600 cm^{-1}, as might be expected. In fact, some related compounds of similar structure, such as tetradecachloro-3-alkoxy(diphenylmethylene)cyclohexa-1,4-dienes,[4] 3,3-dimethoxytetradecachloro(diphenylmethylene)cyclohexa-1,4-diene,[4] perchlorofuchsone,[4] *NH*-tetradecachlorofuchsonimine,[4] and perchlorofuchsonimine,[20] do not show such a peak either, while others, such as perchloro(4-phenylbenzylidene)cyclohexa-1,4-diene[7] and perchlorobenzylidenecyclohexa-1,4-diene,[7] do show it at 1608 cm^{-1}, indicating that the absence of such a peak is due to higher symmetry (insignificant transition moment).

Experimental Section

Perchloro(diphenylmethylene)cyclohexa-1,4-diene (PTM-Cl). (a) With Aluminum Chloride in Sulfuryl Chloride. Operating at room temperature, under argon, ground anhydrous $AlCl_3$ (0.217 g) was added to a solution of perchlorotriphenylmethyl radical (PTM$^{\bullet}$) (0.190 g) in SO_2Cl_2 (25 mL). The resulting green-blue mixture was stirred for 22 h and cooled down to −14 °C, and a few water drops were added until the color became orange. Most of the SO_2Cl_2 was eliminated under vacuum and that left in the residue destroyed by treatment with an aqueous solution of $NaHCO_3$. The resulting mass was acidified with aqueous HCl and then extracted with ethyl ether. By evaporation of the ethereal layer perchloro(diphenylmethylene)cyclohexa-1,4-diene (PTM-Cl) was obtained as an orange solid (0.190 g; 95.5%), mp unknown (dec to PTM$^{\bullet}$, mp 305–8 °C): IR (KCl) 1520 (m), 1340 (s), 1311 (m), 1282 (w), 1266 (w), 1246 (m), 1217 (w), 1112 (m), 1036 (m), 819 (m), 778 (w), 757 (s), 705 (m), 679 (w), 644 (m), 536 (w), 524 (s) cm^{-1}; UV–vis (C_6H_{12}) (Figure 1) 217 nm, 245 (sh), 285 (sh), 293, 372 (ϵ 68 800, 32 000, 10 000, 11 100, 19 800). Anal. Calcd for $C_{19}Cl_{16}$: C, 28.7; H, 0.0. Found: C, 28.8; H, 0.3. The product was contaminated with PTM$^{\bullet}$.

(b) With Aluminum Chloride and Chlorine in Methylene Chloride. To a solution of PTM$^{\bullet}$ (2.046 g) in CH_2Cl_2 (250 mL) at room temperature was added ground anhydrous $AlCl_3$ (3.9 g), and Cl_2 was bubbled through the mixture until saturation. The suspension was shaken in a ultrasonic water bath for 5 h, preventing the temperature from rising by eventual small additions of cracked ice. The insoluble $AlCl_3$ was filtered off the resulting deep-green mass, ice was added to the filtrate, the organic layer was separated from the colorless mixture, washed with water, and dried over anhydrous sodium sulfate, and the CH_2Cl_2 was evaporated under vacuum at room temperature, leaving pure PTM-Cl behind (1.994 g; 93%).

Photochlorination of PTM Radical. A moderate stream of Cl_2 was passed through a solution of perchlorotriphenylmethyl radical (2.43 g) in CCl_4 (600 mL) at room temperature, while being illuminated with a 500-W incandescent white light lamp situated at 50 cm distance, until the red color of PTM$^{\bullet}$ had disappeared (30 h). By evaporation, a resinous yellow mass (3.05 g) was obtained, which was dissolved in hexane and passed through silica gel to eliminate carbonyl imputities, giving another resin (2.03 g) which by combined column chromatography on silica gel and multiple recrystallization in hexane gave three chlorocarbons in a state of purity: Perchloro-3-(diphenylmethylene)cyclohexene (4) (mp 272–4 °C dec; 0.70 g): IR (KBr) 1575 (vw), 1545 (vw), 1515 (w), 1449 (w), 1351 (s), 1330 (s), 1302 (s), 1235 (m), 1215 (w), 1136 (w), 1111 (w), 990 (w), 939 (w), 889 (w), 873 (w), 820 (m), 808 (m), 788 (m), 760 (w), 742 (s), 717 (m), 684 (m), 678 (m) cm^{-1}; UV–vis (C_6H_{12}) 223 nm, 267 (sh), 285, 310 (ϵ 51 900, 18 900, 13 500, 16 750). Anal. Calcd for $C_{19}Cl_{18}$: C, 26.3; H, 0.0. Found: C, 26.4; H, 0.4. PTM-Cl (0.20 g). Perchloro-9-phenylfluorene[8] (0.04 g).

Hydrolysis of PTM-Cl. A mixture of PTM-Cl (0.107 g) and concentrated H_2SO_4 (20 mL) was shaken at room temperature (24 h). The resulting greenish blue solution was poured onto crushed ice, the yellow precipitate was dissolved in CCl_4, the resulting solution was washed with water, and after drying was passed through silica gel with some additional CCl_4. Evaporation to dryness resulted in perchlorofuchsone[4] (0.086 g; 87% yield).

Reduction of PTM-Cl with Copper. Copper dust (1.5 g) was added to a solution of PTM-Cl (0.051 g) in CCl_4 (10 mL), and the mixture was let stand (48 h) at room temperature. The copper was filtered off and the resulting reddish solution was evaporated to dryness, giving PTM$^{\bullet}$ (90% yield).

Thermolysis of PTM-Cl in Chlorobenzene. Purification of the Solvent. Chlorine was passed extendedly through refluxing chemically pure chlorobenzene, while being illuminated with incandescent white light (500–W bulb). After sweeping off the

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Table V. Fractional Atomic Coordinates ($\times 10^4$) with Their Esd's (In Parentheses) and Equivalent Temperature Factors

	x/a	y/b	z/c	B_{eq}, Å^2
Cl3	3111 (3)	−123 (6)	1803 (3)	3.41
Cl4	3352 (3)	898 (7)	395 (4)	4.33
Cl5	4456 (3)	2168 (9)	836 (5)	6.70
Cl5′	3547 (4)	3542 (8)	571 (5)	6.27
Cl6	4378 (3)	4359 (7)	1912 (4)	5.30
Cl7	4224 (3)	3324 (7)	3376 (4)	4.39
Cl9	2856 (3)	2904 (6)	3202 (4)	3.86
Cl10	2726 (3)	3975 (7)	4700 (4)	4.26
Cl11	3414 (3)	3225 (7)	6156 (4)	4.59
Cl12	4274 (3)	1484 (7)	6101 (4)	4.44
Cl13	4443 (2)	499 (6)	4610 (4)	3.58
Cl15	2679 (2)	29 (7)	3656 (4)	3.80
Cl16	2366 (3)	2407 (8)	1174 (5)	5.37
Cl17	3489 (4)	−4119 (8)	3435 (6)	7.40
Cl18	4434 (3)	−3000 (7)	3012 (5)	6.00
Cl19	4503 (2)	−362 (7)	2880 (4)	4.00
C1	3643 (8)	1027 (18)	3255 (11)	1.46
C2	3706 (8)	1548 (20)	2601 (12)	2.05
C3	3515 (9)	986 (21)	1857 (12)	2.22
C4	3598 (9)	1511 (24)	1222 (13)	2.99
C5	3904 (10)	2568 (23)	1199 (14)	3.54
C6	4049 (8)	3112 (21)	1945 (12)	2.42
C7	3955 (9)	2634 (25)	2574 (15)	3.69
C8	3618 (8)	1638 (18)	3956 (12)	1.70
C9	3255 (8)	2481 (22)	4018 (11)	3.13
C10	3181 (9)	2998 (19)	4669 (10)	2.85
C11	3494 (8)	2639 (19)	5311 (12)	3.01
C12	3871 (9)	1840 (20)	5296 (11)	2.84
C13	3952 (8)	1384 (18)	4634 (11)	2.20
C14	3598 (7)	−234 (20)	3298 (12)	3.13
C15	3194 (8)	−790 (16)	3527 (13)	2.39
C16	3147 (9)	−1970 (18)	3557 (13)	2.96
C17	3537 (10)	−2649 (28)	3412 (17)	5.30
C18	3954 (9)	−2145 (18)	3192 (13)	3.14
C19	3981 (9)	−972 (18)	3165 (12)	2.84

dissolved chlorine with a vigorous pure nitrogen stream, the chlorobenzene was fractionated by distillation.

Thermolysis at 100 °C. A solution of PTM-Cl (0.048 g) in dry, purified chlorobenzene (1 mL), under argon, was heated to 100 °C (24 h). By evaporation of the solvent under vacuum a mixture of PTM$^\bullet$ (74%) and some starting material was obtained.

Kinetics. The thermolysis was performed in purified chlorobenzene, under argon, at the temperatures of 25 ± 0.1 °C and 50 ± 0.1 °C. The concentration was 1.0×10^{-3} M. The formation of PTM$^\bullet$ was monitored by ESR spectrometry from 10 to 100 min reaction times. The data are given in Table IV.

X-ray Analysis. Sample: Dark-red crystal of 0.15 × 0.18 × 0.30 mm is monoclinic, space group $C2/c$, a = 27.133 (14), b = 11.664 (14), and c = 18.340 (5) Å, β = 100.0 (5)°, V = 5716 Å^3, Z = 8, D_{calcd} = 1.85 Mg·m^{-3}, μ(M_0 K_α) = 16.2 cm^{-1}, T = 294 K. Data were collected on an Enraf-Nonius CAD 4 diffractometer using graphite-monochromated M_0 K_α radiation. Several spectra were measured from crystals of different crystallizations, since good crystals could not be obtained. Data supplied are those from the best spectrum collected. Lorentz and polarization effects were corrected, not absorption.

The structure was solved by direct methods using MULTAN11/82[21] and successive alternating difference Fourier synthesis and refinement of located atoms. The refinement was carried out with anisotropic full-matrix least-squares methods[22] up to a final accordance factor R of 0.095. From the view of the final difference Fourier map, the residual peaks can probably be attributed to a disordered carbon tetrachloride solvent molecule, but no disordered model could be established. Scattering factors were taken from International Tables for X-Ray Crystallography.[23] Fractional atomic coordinates are listed in Table V. Anisotropic thermal parameters and observed and calculated structure factors are in the supplementary material (Tables 6 and 7).

Supplementary Material Available: Table of anisotropic thermal parameters of PTM-Cl (Table 6) (1 page); table of observed and calculated structure factors of PTM-Cl (9 pages). Ordering information is given on any current masthead page.

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