In conclusion, protolytic (electrophilic) activation of onium, carboxonium, and related ions results in doubly electron deficient (dipositive) *superelectrophiles* whose reactivity greatly exceeds that of their parents observed in aprotic or conventional acidic media. The definition of the term *superelectrophile* is arbitrary,[37] as is that of superacids, but it reflects the remarkably enhanced reactivity. Superelectrophiles are highly reactive, energetic, high-lying intermediates and should be differentiated from low-lying, stable intermediates, which are frequently observable (even with relatively slow physical methods) or even isolable, but they are not necessarily the de facto reagents without further activation. The term "reactive intermediate" (used loosely in the past) should be differentiated from "stable intermediate". The discussed onium and carboxonium dications are not considered to be "stable intermediates". They can, however, be present in superacidic solutions in very low equilibrium concentrations, facilitated by protosolvation (clustering). Further related "electrophilic assistance" by superacids, without necessarily forming fully developed dipositive intermediates, must also be considered.

Acknowledgment. Support of our work by the National Science Foundation and the National Institutes of Health is gratefully acknowledged.

Supplementary Material Available: Archive entries of the optimized structures of **1**–**16** (9 pages). Ordering information is given on any current masthead page.

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[37] Olah, G. A. *Angew. Chem.*, in press.

Chemistry, Kinetics, and Spectroscopy of Highly Hindered Diarylcarbenes. The Case of Decachlorodiphenylcarbene

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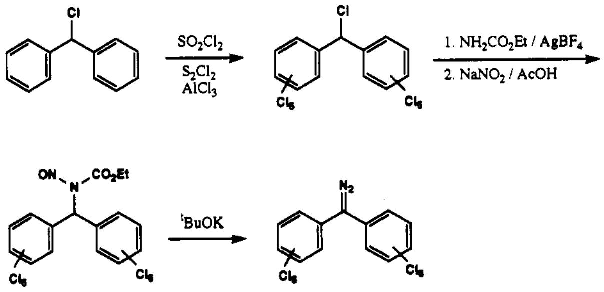
Abstract: Bis(pentachlorophenyl)diazomethane (**1a**) was prepared, and reactivities of perchlorodiphenylcarbene (**2a**) generated by photolysis of **1a** were investigated not only in terms of product analysis but also by using flash photolysis techniques. Although the major reaction found for **2a** was dimerization forming perchlorotetraphenylethylene and was essentially similar to that observed for 2,2′,4,4′,6,6′-hexachlorodiphenylcarbene (**2b**), product distribution clearly indicated that the carbenic center in **2a** is more rigidly protected than that in **2b** by the four ortho chloro substituents which are buttressed by the four meta chloro groups. Irradiation of **1a** in a 2-methyltetrahydrofuran glass at 77 K resulted in the appearance of the absorption due to triplet **2a** at 356, 493, and 525 nm. Flash photolysis of **1a** in benzene solution produced a transient absorption due to **2a** at 357 nm, which decayed in second order in accordance with the product analysis data. The rate constant for dimerization of **2a** was determined to be $2.5 \pm 0.1 \times 10^6$ M^{-1} s^{-1}, 3 orders of magnitude smaller than that of unsubstituted diphenylcarbene. The triplet carbene (**2a**) was trapped by oxygen to generate the perchlorobenzophenone oxide showing its maximum at 390 nm ($t_{1/2} = 510 \pm 9$ ms) and also by 1,4-cyclohexadiene to produce bis(perchlorophenyl)methyl radical (λ_{max} 376 nm) with the rate constant of 6.2×10^3 M^{-1} s^{-1}.

The enormous effect of perchlorophenyl groups on the stability of arylmethyl radicals has been well documented by a series of reports by Ballester and his co-workers.[1] Thus, perchlorotriphenylmethyl has been shown to have its half-life on the order of 100 years in solution at room temperature in contact with air and is therefore termed as an inert free radical. In this light, the perchlorophenyl group is expected to exert a similar stabilizing effect on triplet arylcarbene.

In 1964, Zimmerman and Paskovich[2] generated 2,2′,4,4′,6,6′-hexachlorodiphenylcarbene (HCD) in the hope of insulating the valence-deficient center from its environment. Although the approach did not afford an isolable carbene, the divalent species exhibited unique behavior. In solution, this carbene did not react with the parent diazo compound to give azine but dimerized instead. The chemistry found for HCD is thus in sharp contrast with that found for other diarylcarbenes[3] and is interpreted as reflecting its highly congested divalent center obviously due to the presence of four chlorine groups at the ortho positions. Naturally one would expect that the carbenic center must be more crowded as one introduces four chlorine groups at the meta positions which can buttress the four ortho chlorine groups.[4,5] Thus, we generated decachlorodiphenylcarbene, and its reactivities were investigated not only by product analysis but also by using flash photolysis techniques.

Scheme I



1a

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[1] Ballester, M. *Acc. Chem. Res.* **1985**, *18*, 380 and references cited therein. See also: Ballester, M.; Pascual, I.; Riera, J.; Castañer, J. *J. Org. Chem.* **1991**, *56*, 217.

[2] Zimmerman, H. E.; Paskovich, D. H. *J. Am. Chem. Soc.* **1964**, *86*, 2149.

[3] (a) Moss, R. A., Jones, M., Jr., Eds. *Carbenes*; Wiley: New York, 1973, 1975; Vols. 1 and 2. (b) Kirmse, W. *Carbene Chemistry*; Academic Press: New York, 1971. (c) Regitz, M., Ed. *Methoden der Organischen Chemie* (*Houben Weyl*); Thieme: Stuttgart, Germany, 1989; Vol. E19b.

[4] See for example: Newman, M. S. *Steric Effects in Organic Chemistry*; Wiley: New York, 1956; Chapter 11. Ferguson, L. N. *The Modern Structural Theory of Organic Chemistry*; Prentice-Hall: Englewood Cliffs, NJ, 1963; Chapters 3 and 5.

[5] For buttressing effect in carbene chemistry, see: Tomioka, T.; Kimoto, K.; Murata, H.; Izawa, Y. *J. Chem. Soc., Perkin Trans. 1* **1991**, 471.

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Scheme II

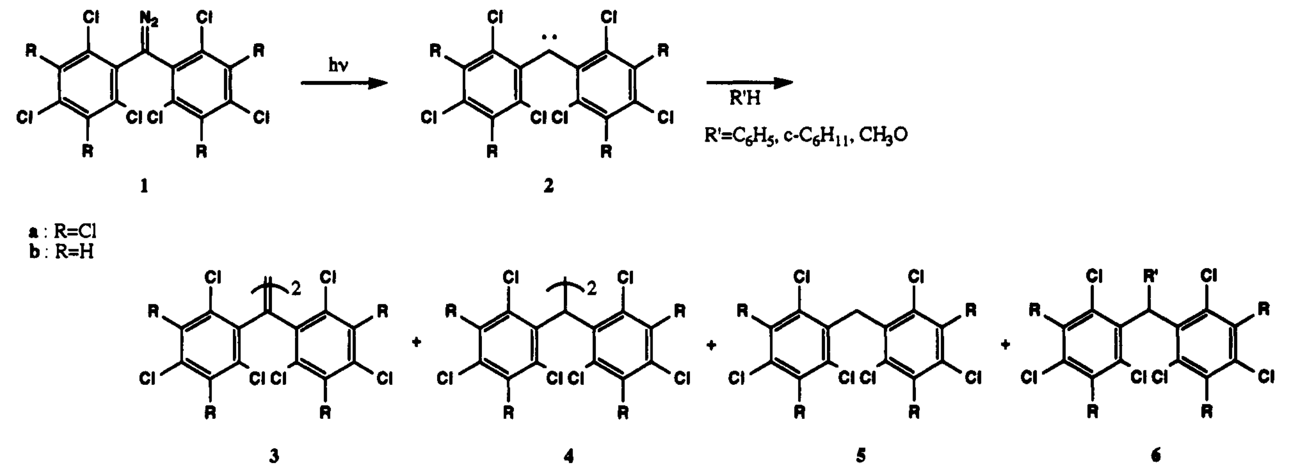

Table I. Photolysis of Chlorinated Diphenyldiazomethane in Fluid Solution at Room Temperature[a]

solvent	precursor	yield,[b] %			
		3	4	5	6
PhH	1a	>99	trace	trace	0
	1b	>99	trace	trace	0
c-C_6H_{12}	1a	80	3	17	0
	1b	26	17	29	28
MeOH-PhH[c]	1a	50	9	20	21
	1b	14	1	24	61

[a] Irradiations were carried out on 5 mL of degassed solution with light of λ > 350 nm from a 300-W high-pressure mercury lamp equipped with a Corning CS-052 filter. [b] Determined by combination of GC and ^{1}H NMR (270 MHz). [c] Benzene was used as cosolvent due to poor solubility of 1 in methanol.

Results and Discussion

Preparation of Bis(pentachlorophenyl)diazomethane (1a). The diazomethane **1a** was prepared by essentially the same procedure reported by Zimmerman[2] for the preparation of the corresponding hexachloro analogues (**1b**) as very stable yellowish crystals (Scheme I), although the overall yield of **1a** was considerably lower than that of **1b**. The crude **1a** containing a small amount of partially chlorinated diphenyldiazomethanes was purified by repeated chromatograph on a Shodex GPC H-2001 column.

Product Analysis Studies. Irradiation (λ > 350 nm[6]) of **1** in various solvents at room temperature produced products apparently derived from the photolytically generated perchlorodiphenylcarbene (**2a**). Thus, photolysis in benzene afforded perchlorotetraphenylethylene (**3a**) almost exclusively, while irradiation in cyclohexane results in the formation of a small amount of perchlorodiphenylmethane (**5a**) and perchlorotetraphenylethane (**4a**) although the carbenic dimer (**3a**) was still the major product. Photolysis in methanol–benzene, on the other hand, produced the OH insertion product (**6a**, R' = OMe) along with **4a**, **5a**, and **3a**, **3a** being a major product. Product distributions are listed in Table I, which includes the data for HCD for comparison purposes. Inspection of the data indicates that, although the reactions observed with **2a** were essentially similar to those observed with hexachlorodiphenylcarbene (**2b**), the product distributions from **2a** were significantly different from those obtained from **2b** (see Table I). A key difference is found in the formation of the dimer **3**. Thus, as more reactive solvents were employed, the yield of **3** was decreased. However, **3a** was always formed as major product, while the formation of **3b** was sharply decreased and the solvent adducts, i.e., **6**, were formed. The difference in reactivities between **2a** and **2b** can be interpreted as reflecting the difference in the extent of steric crowdedness around the carbenic centers between these two carbenes. It is well known[5,6] that, in 1,2-disubstituted benzene derivatives, introduction of substitutents in the 3 position exerts a very large effect on the rate of appropriate reactions and the data are considered in the light of the importance of bond bending; the 3-substituents buttress the 2-substituents. Thus, in **2a**, each of four ortho chlorine groups around the carbene center is buttressed by one of four meta chloro groups, and therefore the carbene center in **2a** is surrounded by the chloro groups more rigidly than that in **2b**. In other words, **2a** is more effectively blocked from external reagents.

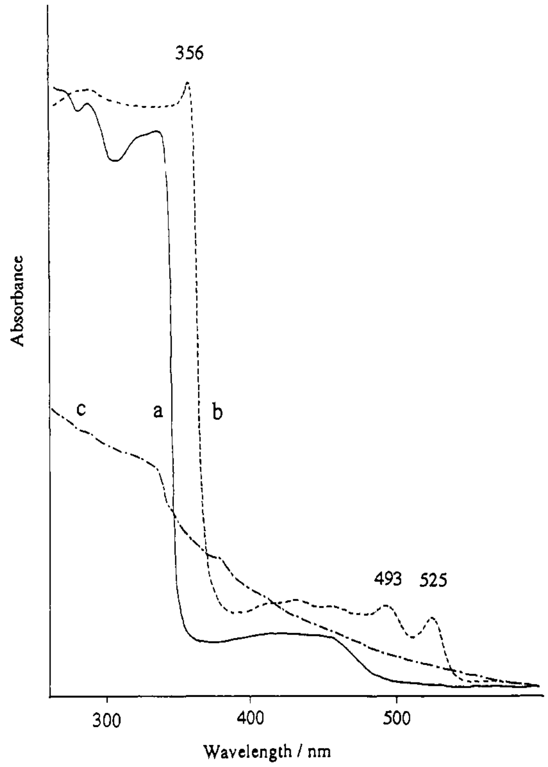

Figure 1. (a) UV/vis spectrum of **1** in MTHF at 77 K. (b) Same sample after 40-min irradiation (λ > 350 nm). (c) Same sample after thawing the matrix.

Steady-State Irradiation of 1 in Frozen Media. Irradiation (λ > 350 nm) of **1a** (0.95 × 10^{-3} M) in a 2-methyltetrahydrofuran (MTHF) glass at 77 K resulted in the appearance of new absorption bands at the expense of the original absorption due to **1a**. As is shown in Figure 1, the new spectrum consisted of two identifiable features. There was a sharp, intense UV band at 356 nm, and the visible portion of the spectrum showed two weak and broad bands with apparent maxima at 493 and 525 nm. The glassy solution did not exhibit any spectral change for several hours if kept at 77 K. However, warming it up to room temperature and refreezing at 77 K led to disappearance of the characteristic absorption bands. Product analysis of the spent solution showed

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(6) Irradiation with the light of λ > 300 nm resulted in the formation of partially dechlorinated products.

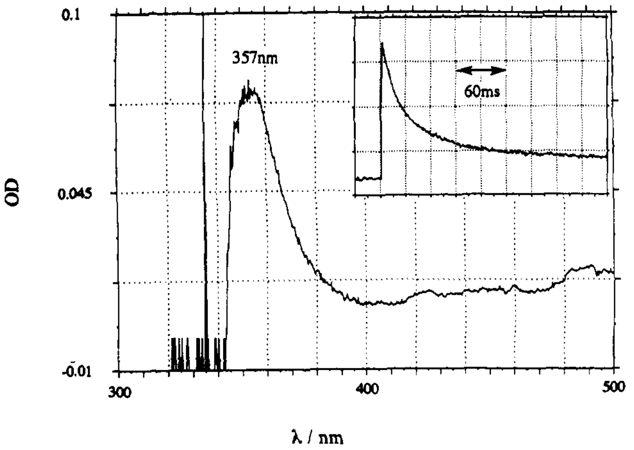
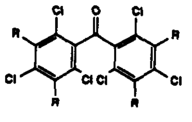


Figure 2. Absorption spectra of the transient products formed during the irradiation of **1** in degassed benzene, recorded after 50 μs. Inset shows oscillogram trace monitored at 357 nm.

the presence of the dimer **3a** as a nearly exclusive product. The optical absorption spectra of several diarylcarbenes in frozen media have been assigned.[7] Typically they consist of an intense UV band and a weak visible transition. These features are present in the spectrum obtained from the photolysis of **1a**. In these circumstances, the transient absorption is attributable to the triplet decachlorodiphenylcarbene (**2a**) generated by the photodissociation of **1a**. Hexachlorodiphenylcarbene also shows an intense absorption at 338 nm along with a broad, weak absorption with an apparent maximum at 482 and 495 nm.[8]

Flash Photolysis of 1 in Fluid Solution. Irradiation of a degassed benzene solution of **1** (1.24×10^{-4} M) at room temperature with the output of a xenon flash lamp (pulse width of 10 μs) produced a transient species showing a strong absorption at 357 nm and a weak absorption extending from 410 to 520 nm, which appeared coincident with the xenon pulse and disappeared within ca. 100 ms (Figure 2). The final stable products formed from irradiation of **1a** under these conditions again consist almost exclusively of carbenic dimer **3a**. On the basis of the low-temperature spectrum coupled with chemical analysis, we assign the transient product from the photolysis of **1a** in benzene at room temperature to triplet decachlorodiphenylcarbene (**2a**). The oscillogram trace of the transient absorption due to **2a** monitored at 357 nm is shown in the inset of Figure 2. The decay was found to be second order in accordance with the product analysis data, showing that dimerization to form **3a** is the main pathway for **2a** under these conditions. Support is lent to this assignment by trapping experiments using oxygen. When flash photolysis measurements were carried out on a non-degassed benzene solution of **1a** ($\sim 10^{-4}$ M), the half-life of triplet **2a** was decreased by about one-third, and a broad absorption band with a maximum at 390 nm appeared. The rate of increase in the absorbance at 390 nm was practically the same as that of the decay of the peak at 357 nm, showing that triplet **2a** was quenched with oxygen to form a new species. Analysis of the spent solution showed the presence of a large amount of perchlorobenzophenone (**7a**) at the expense of the carbenic dimer **3a**. It is now well-documented[8] that diarylcarbenes with triplet ground states are readily trapped by oxygen to give the corresponding diarylketone oxides, which are observed directly either by matrix isolation techniques or by flash photolysis. These carbonyl oxides usually show a rather broad absorption band centered at around 390–450 nm. Thus, the observation can be interpreted as indicating that the triplet **2a** is trapped with oxygen to generate carbonyl oxide **8a**, thus, confirming that the transient absorption quenched by oxygen is due to **2a**.



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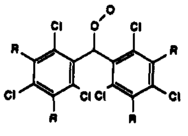

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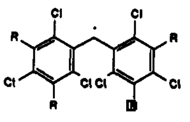

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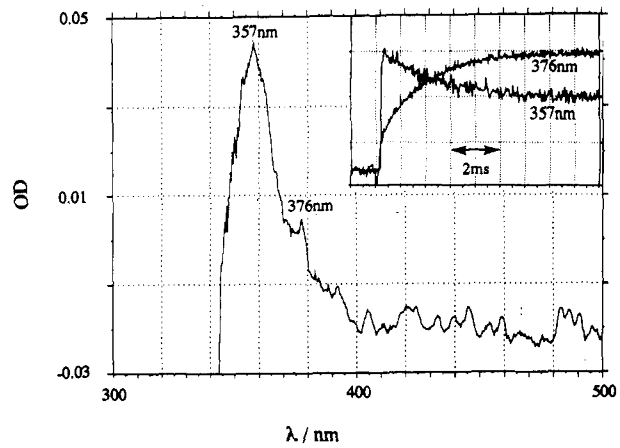

Figure 3. Absorption spectra of the transient products formed during the irradiation of **1a** in degassed benzene containing 1,4-cyclohexadiene, recorded after 50 μs. Inset is oscillogram traces monitored at 357 and 376 nm.

Second-order fitting of transient absorption data for **2a** yields $2k_d/\epsilon l$ values, where $2k_d$ is the dimerization reaction rate constant, ϵ the extinction coefficient, and l the optical path.[9b] The extinction coefficient of **2a** at 357 nm was conveniently determined in the matrix photolysis in MTHF to be 11 749 ± 160 M^{-1} cm^{-1} on the basis of the assumption that **1a** is completely decomposed and **2a** is not consumed under these conditions. This is shown to be valid by the observations that almost no **1a** was left in the spent solution and that the absorption due to **2a** was not decreased at all if kept at 77 K and even under prolonged irradiation. Thus, k_d was determined to be $(2.5 \pm 0.1) \times 10^6$ M^{-1} s^{-1}. The decay of the carbonyl oxide **8a** was, on the other hand, found to be somewhat difficult to fit with a single exponential presumably due to self-reactions of carbonyl oxides or reactions with other transients likely to be present or generated in the system.[9,10] Therefore the rough lifetime of **8a** is estimated in the form of half-life, $t_{1/2}$, to be 510 ± 9 ms.

When a solution of **1a** in a degassed benzene solution containing 1,4-cyclohexadiene (CHD) was excited, a new species was formed, showing a strong absorption with $\lambda_{max} = 376$ nm, as the 357-nm signals of **2a** decayed. Figure 3 shows the transient spectrum obtained 50 μs after the photoexcitation where decay of **2a** was not complete; the inset shows the decay of **2a** at 357 nm and the formation of the new species at 376 nm, indicating that the decay of **2a** is kinetically correlated with the growth of the new species. Thus, this new signal was attributable to the perchlorodiphenylmethyl radical (**9a**) formed as a result of H abstraction of **2a** from the diene, since it is now well-documented[12] that triplet arylcarbenes generated in good hydrogen donor solvents undergo

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(7) See for reviews: (a) Trozzolo, A. M. *Acc. Chem. Res.* **1968**, *1*, 329. (b) Trozzolo, A. M.; Wasserman, E. In ref 3a, Vol. 2, Chapter 5.

(8) Tomioka, H.; Hirai, K.; Fujii, C. *Acta Chem. Scand.* **1992**, *46*, 680.

(9) (a) See for review: Sander, W. W. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 344. (b) See also: Scaiano, J. C.; McGimpsey, W. G.; Casal, H. L. *J. Org. Chem.* **1989**, *54*, 1612.

(10) Decay of simple benzophenone oxides is shown to be second order while that of dimesityl ketone oxide is found to fit to a first-order decay. See 9b. On the other hand, decay of fluorenone oxide is shown not to fit with a single exponential.[11]

(11) Casal, H. L.; Tanner, M.; Werstiuk, N. H.; Scaiano, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 4616.

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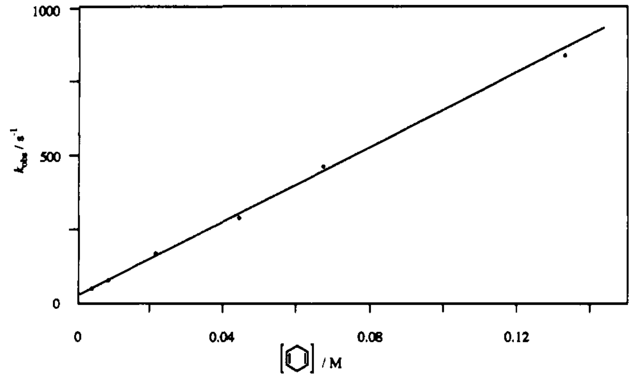

Figure 4. Plots of the growth rate of the perchlorodiphenylmethyl radical (**9a**) in degassed benzene solution containing 1,4-cyclohexadiene.

Table II. Bimolecular Rate Constants for the Reaction of Diarylcarbenes

diarylcarbenes	k_d, M^{-1} s^{-1}	k_{CHD}, M^{-1} s^{-1}
diphenylcarbene	$(5.4 \pm 1.6) \times 10^{9\,a}$	$(1.0 \pm 0.1) \times 10^{7\,b}$
hexachlorodiphenylcarbene (**1b**)	$(1.2 \pm 0.1) \times 10^{7}$	$(3.5 \pm 0.1) \times 10^{3}$
decachlorodiphenylcarbene (**1a**)	$(2.5 \pm 0.1) \times 10^{6}$	$(6.2 \pm 0.1) \times 10^{3}$

[a] Ref 12f. [b] Ref 12b.

H abstraction leading to the corresponding radical showing transient absorption at longer wavelength than that of the precursor carbene. The excellent hydrogen donor properties of 1,4-cyclohexadiene have been recognized in its reaction with triplet benzophenone.[13] The formation of perchlorodiphenylmethane (**5a**) at the expense of **3a** under these conditions also supports this assignment. The apparent build-up rate constant, k_{obs}, of the radical is essentially identical with that of the decay of the carbene, and k_{obs} is expressed as given in eq 1

$$k_{obs} = k_0 + k_{CHD}[\text{diene}] \qquad (1)$$

where k_0 represents the rate of decay of **2a** in the absence of the diene and k_{CHD} is a quenching rate constant of **2a** by the diene. A plot of the observed pseudo-first-order rate constant of the formation of the radical against [cyclohexadiene] in the range 0.05–0.14 M is linear (Figure 4). The slope of this plot yields the absolute rate constant for reaction of **2a** with the diene, $k_{CHD} = (6.2 \pm 0.1) \times 10^3$ M^{-1} s^{-1}, and the intercept yields $k_0 = 24.1 \pm 8.2$ s^{-1}. Since the product analysis study clearly indicates that dimerization forming **3a** is the sole decay pathway for **2a**, k_0 must be represented as k_d [**2a**]. The concentration of triplet carbene **2a** generated by a pulse of the xenon flash lamp was adequately approximated by using ϵ for **2a** as well as absorbance at 357 nm after photoexcitation in benzene without quencher to be $(8.3 \pm 0.1) \times 10^{-6}$ M^{-1}. This leads to $k_d \sim 2.9 \times 10^6$ M^{-1} s^{-1}, in excellent agreement with that determined by the direct monitoring of **2a** (vide supra).

Essentially similar results were obtained in the flash photolysis of **1b** in benzene, where the absorption due to the carbonyl oxide **8b** appeared at 390 nm ($t_{1/2} = 370 \pm 0.3$ ms) in the presence of oxygen and that ascribable to the hexachlorodiphenylmethyl radical **9b** at 365 nm in the presence of the diene, as the 344-nm triplet **2b** signals decayed. Kinetic data obtained for **2a** as well as **2b** are summarized in Table II, which also includes the data[12] for unsubstituted diphenylcarbene for comparison purposes. Inspection of the data immediately indicates that the dimerization rate is sharply decreased as one simply introduces four chlorine atoms at the ortho positions but is further decreased by 1 order of magnitude as four additional chloro groups are introduced at the meta positions, obviously due to the buttressing effect. This confirms the explanation based on the product analysis (vide supra) and supports the idea that the buttressing effect should play an important "buttressing" role in protecting the reactive center. On the other hand, k_{CHD} is also decreased dramatically in going from Ph_2C: to the hexachlorodiphenylcarbene (**2b**), but it increases albeit slightly as one introduces the four more chlorine atoms. This is somewhat surprising in the light of a marked decrease in the dimerization rate by the four meta buttressing chloro substituents as noted above and is explicable as indicating that electrophilicity of the carbenic center is increased as one introduces more chlorine groups on the phenyl rings. Thus, as more chloro groups are introduced, the carbenic center is more rigidly protected and, on the other hand, becomes more reactive. Thus, the attack of a bulky substrate, e.g., chlorinated diphenylcarbene (**2**), on the carbenic center must be severely restricted while the rate of abstraction of a very small hydrogen atom from a very efficient hydrogen donor is still controlled by electrophilicity of the carbenic center even in these highly hindered carbenes.

Experimental Section

General Methods. IR spectra were measured on a JASCO A-100 recording spectrometer, and the mass spectra were recorded on a Shimadzu QP-1000 mass spectrometer (70 eV). ^{1}H and ^{13}C NMR spectra were determined with JEOL JNM-EX 270 or JNM-MH 100 spectrometer. UV/vis spectra were measured on a Hitachi 220-S spectrophotometer. Thin-layer chromatography was done on a Merck Kieselgel 60 PF$_{254}$. Column chromatography was carried out on silica gel (ICN for dry column chromatography). HPLC and GPC were undertaken with a JASCO 800 chromatography equipped with a UVIDEC-100-II UV/vis detector using a Fine pack C18-T5 column (4.6 × 25 cm) and Shodex GPC H-2001 (20 mm × 50 cm) column, respectively, and GLC was carried out with a Yanagimoto G-80 gas chromatograph using a OV-17 on Diasolid L (5.0 mm × 50 cm).

Preparation of Decachlorodiphenyldiazomethane (1a) and *αH*-Undecachlorodiphenylmethane.[14] To a boiling solution of anhydrous $AlCl_3$ (0.75 g, 5.7 mmol) in SO_2Cl_2 (225 mL) was gradually (20 min) added a solution of diphenylchloromethane (2.64 mL, 14.9 mmol) and S_2Cl_2 (0.90 mL, 11.1 mmol) in SO_2Cl_2 (75 mL). The resulting mixture was then distilled gently until the total volume was down to ca. 60 mL, and then it was refluxed for 2 h to obtain a pure green solution. The solvent was evaporated under reduced pressure to leave a greenish solid, which was added to 5% $NaHCO_3$ aqueous solution (50 mL). The mixture was refluxed for 1 h to give a white precipitate, which was filtered and dried: 9.28 g (99%); mp 230–232 °C; ^{1}H NMR ($CDCl_3$) δ 7.10 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 58.4, 133.4, 133.7, 134.4, 134.5; IR (KBr disk) 1520, 1360, 1340, 1225, 1110 cm^{-1}.

Ethyl *N*-[Bis(pentachlorophenyl)methyl]carbamate. A mixture of 1.44 g (7.4 mmol) of $AgBF_4$, 1.92 g (0.22 mmol) of ethyl carbamate, and 60 mL of dioxane was heated until solution was effected. To this the chloride (3.0 g, 5.48 mmol) in dioxane (240 mL) was added at once at 100 °C. The mixture was refluxed until TLC monitoring showed almost all of the chloride was consumed (18 h). The cooled reaction mixture was extracted with CCl_4 (50 mL) and H_2O (100 mL). After filtering, the organic layer was washed well with water and then dried (Na_2SO_4). After evaporation of the solvent, the resulting white solid was distilled under reduced pressure (60 °C/1.0 Torr) using Kugelrohr to remove excess ethyl carbamate. The residue was chromatographed on silica gel eluted with ethyl ether–*n*-hexane (5:95) to give 950 mg (28.8%) of white crystals: mp 240–245 °C; ^{1}H NMR ($CDCl_3$) δ 1.28 (3 H, t, *J* = 7.0 Hz), 4.20 (2 H, q, *J* = 7.0 Hz), 5.46 (1 H, d, *J* = 10.0 Hz), 7.09 (1 H, d, *J* = 10.0 Hz); IR (KBr disk) 1750, 1520, 1370, 1340, 1130, 1080 cm^{-1}.

Bis(pentachlorophenyl)diazomethane (1a). To a vigorously stirred mixture of the carbamate (0.95 g, 1.58 mmol) in AcOH (30 mL) and Ac_2O (200 mL) at 0 °C was added every 20 min for 5 h a 100-mg portion of $NaNO_2$ (total 3.0 g, 43.5 mmol). The mixture was stirred overnight at 0 °C, poured onto ice–water (100 mL), and extracted with ether. The ethereal layer was washed with water, 5% Na_2CO_3, and water and dried. Evaporation of the solvent afforded ethyl *N*-nitroso-*N*-[bis(pentachlorophenyl)methyl]carbamate as a white solid (663 mg, 66.8%): mp 242–245 °C; ^{1}H NMR ($CDCl_3$) δ 1.38 (3 H, t, *J* = 13.0 Hz), 3.47 (2 H, q, *J* = 13.0 Hz), 7.17 (1 H, s); IR (KBr disk) 1770, 1595, 1530, 1340, 1250, 1130 cm^{-1}.

To a heated solution of potassium *tert*-butoxide (85.3 mg, 0.76 mmol) in *tert*-butyl alcohol (5.0 mL) at 60 °C, was added at once under the atmosphere of argon a solution of the nitrosocarbamate (160 mg, 0.25 mmol) in *tert*-butyl alcohol (100 mL). The mixture was stirred for 2 h at 60 °C and poured onto ice–water to produce an orange solid. The solid

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was dissolved into ether and chromatographed on an alumina column at −10 °C eluted with ether to produce yellowish crystals. Since the ^{1}H NMR spectra of this crystalline product indicated the presence of a small amount of partially chlorinated products, it was further purified by recycling the sample on a gel permeation chromatograph with CHCl$_3$ elution to leave pure sample: 18 mg (3.5%); mp 178–180 °C dec; ^{13}C NMR (CDCl$_3$) δ 29.7, 128.7, 132.8, 133.0, 133.5, IR (KBr disk) 2080, 1350 cm^{-1}. ^{1}H NMR spectra showed no peak.

Bis(2,4,6-trichlorophenyl)diazomethane was prepared by the procedure by Zimmerman.[2] ***αH,αH*-Decachlorodiphenylmethane (5a)** was prepared[14] by the reduction of *αH*-undecachlorodiphenylmethane in diglyme, and ***syn*-tetrakis(pentachlorophenyl)ethane (4a)** was obtained[2] by the treatment of *αH*-undecachlorodiphenylmethane with phenyl lithium.

Irradiation for Product Identification. In a typical run, a solution of the diazo compounds (ca. 30 mg) in solvents was placed in a Pyrex tube and irradiated with a high-pressure, 300-W mercury lamp at room temperature until all the diazo compound was destroyed. The irradiation mixture was then concentrated on a rotary evaporator below 20 °C. Individual components were isolated either by column chromatography or by preparative TLC and identified by NMR and MS.

***αH*-Undecachlorodiphenylmethyl methyl ether (6a, R′ = OMe)** was isolated in the photolysis of **1a** in MeOH–PhH as a yellowish oil: ^{1}H NMR (CDCl$_3$) δ 3.49 (3 H, s), 6.32 (1 H, s); MS *m/e* (relative intensity) 548 (4.5), 546 (10.1), 544 (21.1), 542 (24.5), 540 (18.9), 538 (5.7), 513 (25.1), 511 (49.0), 509 (81.9), 507 (100), 505 (74.7), 503 (27.6), 297 (16.1), 295 (46.2), 293 (72.4), 291 (49.3).

***syn*-Tetrakis(pentachlorophenyl)ethene (3a)** was isolated in the photolysis of **1a** in benzene as a yellowish solid: mp > 340 °C; MS *m/e* (relative intensity obs/calcd) 1031.0 (M + 20, 5.8/5.7), 1029.0 (M + 18, 14.1/16.8), 1027.2 (M + 16, 28.8/28.2), 1025.0 (M + 14, 38.3/53.1), 1023.4 (M + 12, 68.8/81.5), 1021.1 (M + 10, 100/100), 1019.3 (M + 8, 77.3/95.9), 1017.4 (M + 6, 60.1/69.2), 1015.4 (M + 4, 21.6/35.4), 1012.9 (M + 2, 12.0/11.4), 1011.4 (M$^+$, 3.2/1.8).

Bis(2,4,6-trichlorophenyl)cyclohexylmethane (6b, R′ = *c*-C$_6$H$_{11}$) was isolated in the photolysis of **1b** in cyclohexane in 15% yield as yellow oil: ^{1}H NMR (CCl$_4$) δ 1.04–1.58 (10 H, m), 3.72 (1 H, b s), 5.32 (1 H, b s), 7.24 (4 H, s); MS *m/e* (relative intensity) 423 (6), 421 (2.3), 4.19 (1.1), 364 (5.3), 193 (2.2), 83 (100).

Bis(2,4,6-trichlorophenyl)methyl methyl ether (6b, R′ = OMe) was isolated in the photolysis of **1b** in methanol as an oil: ^{1}H NMR (CCl$_4$) δ 3.44 (3 H, s), 6.04 (s, 1 H), 7.24 (b s, 4 H); MS *m/e* (relative intensity) 406 (4.5), 404 (5.7), 402 (2.1), 369 (57), 335 (9.6), 207 (100).

Irradiation for Analyses Purposes. The irradiations outlined in Table I were carried out in a Pyrex tube of 5.0-mL capacity at below 10 °C. In order to avoid ambiguity of the yields due to the oxidation, the solution was degassed by subjecting the sample to a minimum of three freeze–degas–thaw cycles at pressure near 10^{-5} Torr before irradiation. Irradiation was carried out with filtered light (λ > 350 nm, Corning CS-052 filter) from the 300-W mercury lamp and was generally continued until all the diazo compound was destroyed. Product identifications were established by GC-MS as well as NMR comparisons with authentic samples, and product yields were conveniently determined by GC and/or NMR using an internal standard.

Low-Temperature UV/vis Spectra. Low-temperature spectra at 77 K were obtained by using an Oxford variable-temperature liquid-nitrogen cryostat (DN1704) equipped with quartz outer windows and sapphire inner windows. The sample was dissolved in dry 2-methyltetrahydrofuran, placed in a long-necked quartz cuvette of 1-mm path length, and degassed by repeated freeze–degas–thaw cycles at pressure near 10^{-5} Torr. The cuvette was placed in the cryostat and cooled to 77 K. After a base line had been recorded, the sample was irradiated for several minutes in the spectrophotometer with a Halos 300-W high-pressure mercury lamp using a Pyrex filter, and the spectral changes were recorded at appropriate time intervals. The spectral changes upon thawing were also monitored by carefully controlling the matrix temperature with an Oxford Instrument Intelligent Temperature Controller (ITC4).

Flash Photolysis. All flash measurements were made on a Unisoku Flash Spectrometer. The sample was dissolved in dry benzene (over benzophenone ketyl), placed in a long-necked 10 × 10 mm or 20 × 10 mm (3–5 mL) quartz fluorescence cuvette, and degassed by a minimum of four freeze–degas–thaw cycles at pressure near 10^{-5} Torr immediately prior to being flashed. An energy input of 100 J/flash was discharged through a cylindrical 150-W Xe flash lamp, which was parallel to the long axis of the photolysis cell. The excitation flash lamp had a half-life of 10 μs. The absorption spectra of the transients were obtained after a predetermined delay. Light from the monitoring flash was dispersed in a multichannel detector and then transferred to a PC9801 RX2 computer which provides data processing, storage, and hard copy graphics capabilities. Decay of the transient absorption was followed quantitatively by a photomultipler.

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