

Flash Photolysis Studies of Highly Hindered Diarylcarbenes. Optical Absorption Spectrum and Reaction Kinetics of 2,2',4,4',6,6'-Hexachlorodiphenylcarbene

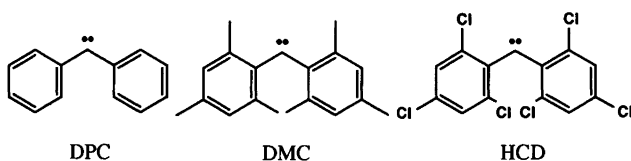
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Dedicated to Professor Lars Skattebøl on the occasion of his 65th birthday.

In 1964, Zimmerman and Paskovich¹ generated two highly hindered diarylcarbenes i.e., dimesityl- (DMC) and 2,2',4,4',6,6'-hexachlorodiphenyl-carbene (HCD), in the hope of insulating this highly reactive, valence-deficient center from its environment. The approach of steric restriction at the divalent carbon did not afford isolable carbenes: the divalent species exhibited unique behavior, for example, proclivity to dimerize and reluctance to attack



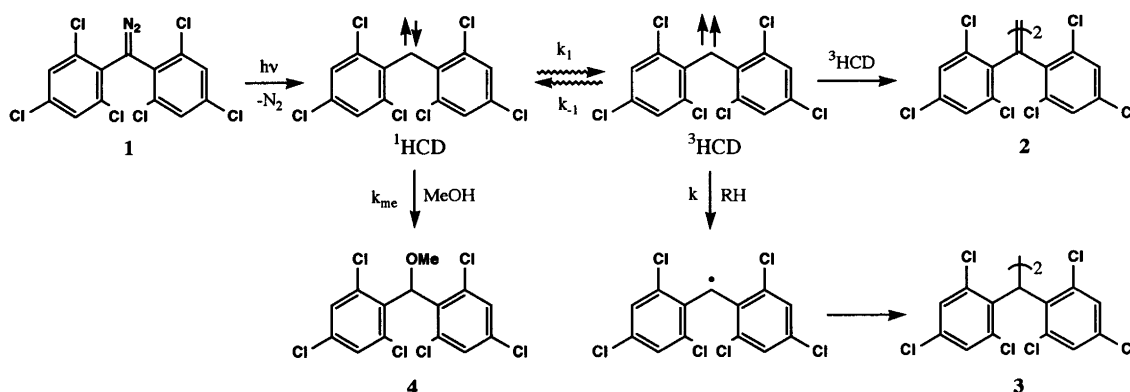
secondary carbon–hydrogen bonds. It was only in 1985, however, that kinetic analysis using laser flash photolytic techniques revealed² that, in benzene at 25 °C, triplet DMC had a lifetime of ca. 200 μ s, *two orders of magnitude greater than those observed for diphenylcarbene* (DPC, 1.7 μ s in cyclopentane), thus confirming expectations for the role of steric effects in carbene chemistry established almost 20 years before. Although one would expect HCD to be even more persistent in the light of the enormous effect of chlorine substituents on the stability of diarylmethyl radicals,³ almost no information is yet available on its lifetime and kinetics. Thus, we carried out time-resolved spectroscopic studies of HCD in solution at room temperature.

Irradiation of a degassed benzene solution of 2,2',4,4',6,6'-hexachlorodiphenyldiazomethane⁴ (**1**, 9.0×10^{-5} M) at room temperature with the output of a xenon flash lamp⁵ (pulse width of 10 μ s) produced a transient species absorbing at 344 nm which appeared coincident with the xenon pulse and disappeared within ca. 50 ms (Scheme 1). The

final stable products formed from irradiation of **1** under these conditions consist mainly of the carbenic dimer (**2**). Shown in Fig. 1 is the absorption spectrum obtained 50 μ s after the excitation. This spectrum is similar to that measured during the photolysis of **1** in a 2-methyltetrahydrofuran (MTHF) glass at 77 K. The spectrum consists of two identifiable features, a sharp, relatively intense UV band with a maximum at 338 nm and a broad, weak absorption extending from 450 to 500 nm. These absorption bands are stable for hours at 77 K, but warming the sample to room temperature leads to their disappearance. The product analysis of the spent solution again showed the presence of the dimer **2** as the major product. The optical absorption spectra of several triplet aromatic carbenes in frozen media have been assigned.⁶ 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 **1**. On the basis of the low-temperature spectrum, the room-temperature transient spectrum, and the chemical analysis, we assign the transient product, showing the absorption maximum at 344 nm from the photolysis of **1** in benzene, to triplet HCD. The oscillogram trace of the transient absorption due to ³HCD monitored at 344 nm is shown in the inset of Fig. 1. The decay was found to be second order, in accordance with the product analysis data, showing that dimerization to form **2** is the main pathway for ³HCD under these conditions, and the half-life was determined to be 18 ms, *four orders of magnitude longer than those observed for DPC*.

When a solution of **1** in a degassed benzene containing 1,4-cyclohexadiene was excited, a new species was formed, showing a strong absorption band with $\lambda_{\text{max}} = 365$ nm, as the 344 nm ³HCD signals decayed. Fig. 2 shows the transient spectrum obtained 1 ms after the excitation where decay of ³HCD was not complete; the inserts show the decay of ³HCD at 334 nm and the formation of the species at 365 nm, indicating that the decay of ³HCD is kinetically correlated with the growth of the new species. Thus, this

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Scheme 1.

new signal was attributable to the hexachlorodiphenylmethyl radical (HCDH) formed as a result of H abstraction of ^3HCD from the diene, since it is now well-documented⁷ that triplet arylcarbenes generated in good hydrogen donor solvents undergo 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 benzophenone triplet.⁸ 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 eqn. (1), where τ_0 is the

$$k_{\text{obs}} = \tau_0^{-1} + k_r[\text{substrate}] \quad (1)$$

lifetime of ^3HCD in the absence of the diene and k_r is a quenching rate constant of ^3HCD by the diene. A plot of the observed pseudo-first-order rate constant for growth of

the radical against [cyclohexadiene] is linear. The slope of this plot yields the absolute rate constant for reaction of ^3HCD with the diene, $k_{\text{CHD}} = 3.5 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ and the intercept yields $\tau_0 = 18 \text{ ms}$. The value of τ_0 is identical with the half-life obtained by direct observation. The excellent agreement between the lifetime measured directly and the extrapolated value based on the transient radical provides further support for the assignment of the transient species as the triplet carbene.

Furthermore, the absolute rate constants, k_r , of the reaction of ^3HCD with several selected substrates were determined. Thus, flash photolysis of **1** in benzene containing hydrogen-donating substrates, e.g., cyclohexene, methylbutene and triethylamine, also resulted in the transient absorption due to the radical. Therefore, kinetic studies were carried out based on the build-up at 365 nm using eqn. (1) since kinetic analysis at this wavelength is more

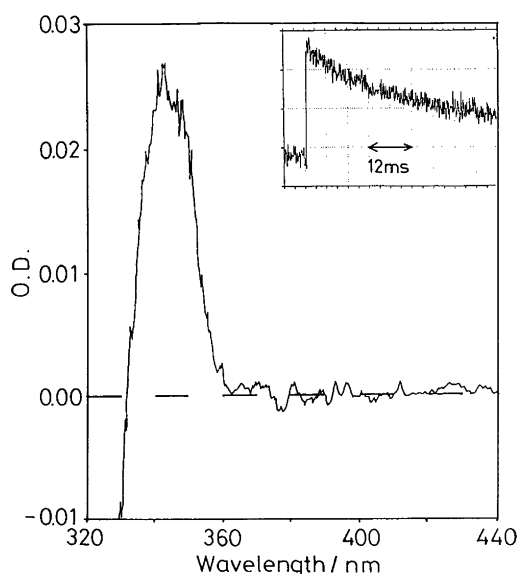


Fig. 1. Absorption spectra of the transient products formed during the irradiation of **1** in degassed benzene, recorded after 50 μs . Insets show an oscillogram trace monitored at 344 nm.

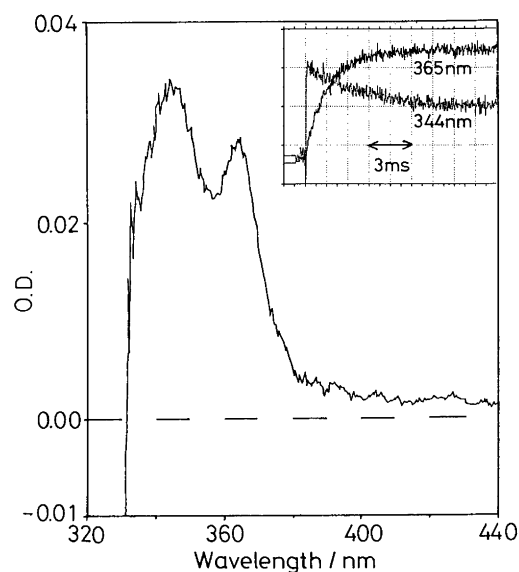


Fig. 2. Absorption spectra of the transient products formed during the irradiation of **1** in degassed benzene containing 1,4-cyclohexadiene, recorded after 1 ms. Insets are oscillogram traces monitored at 344 and 365 nm.

straightforward. Monitoring only the radical growth and the decreased overlap between the radical and carbene absorption facilitates the experiment considerably. The reactions with styrene and methanol where no absorption due to the radical was prominent were analyzed by monitoring directly the absorption due to ^3HCD .

Bimolecular rate constants for the reaction of HCD with several substrates in benzene at room temperature are listed in Table 1 which includes the data for diphenylcarbene (DPC) for comparison. The data indicate that ^3HCD is, at the very least, 4.7×10^3 times less reactive than DPC in H abstraction, 1.6×10^4 times in addition to double bonds, and 2.8×10^6 times in insertion into the OH bond.

The data reported here clearly demonstrate that a chlorine group is at least 100 times more effective than a methyl group in protecting the carbene center. The observed large difference between chloride and methyl groups is rather surprising in the light of the small difference in the van der Waals radii of two groups (Cl, 1.80; Me, 2.0)⁹ and can be interpreted as indicating that, in ^3DMC , the methyl groups at the *ortho* position quench the divalent center by donating

Table 1. Bimolecular rate constants for the reaction of diarylcarbenes.

| Substrate | $k/M^{-1} \text{ s}^{-1}$ | | |
|-----------------------|---------------------------|----------------------------------|--------------------------------|
| | HCD | DPC | |
| 1,4-Cyclohexadiene | 3.5×10^9 | 1.0×10^7 ^a | |
| Cyclohexene | 6.0×10 | 2.8×10^5 ^a | |
| 2-Methyl-2-butene | 5.2×10 | 2.1×10^5 ^{a,b} | |
| Triethylamine | 2.2×10^2 | 3.4×10^5 ^a | |
| Styrene | 8.6×10 | 1.4×10^6 ^a | 3.8×10^5 ^c |
| Methanol ^d | 2.4 | 6.8×10^6 ^c | |

^aRef. 7(f). ^bThis rate constant is observed for reaction of DPC with 2,3-dimethyl-2-butene. ^cRef. 7(b). ^dThis rate corresponds to k_{me}/K , where $K = k_1/k_{-1}$ in terms of Scheme 1 and k_{me} is the second-order rate constant for reaction of singlet carbene with methanol.

ing a hydrogen atom thereby forming benzocyclobutene derivatives, while such an intramolecular leakage pathway is not available for ^3HCD .

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- The diazomethane **1** was prepared according to the literature procedure¹ and purified by GPC.
- A Unisoku Flash Spectrometer with multichannel detectors was used.
- (a) See for example, Trozzolo, A. M. *Acc. Chem. Res.* **1** (1968) 329; (b) The broad, weak absorption extending from 450 to 500 nm observed in the low-temperature spectrum was not detected in the room temperature transient spectrum, presumably due to the inherent weak extinction coefficient as well as the low sensitivity of our flash detectors.
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