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2,2′,4,4′,6,6′-Hexabromodiphenylcarbene. The First Stable Triplet Carbene in Fluid Solution at Low Temperature and in the Crystal State at Room Temperature

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Since the isolation of carbenes in the singlet state has been realized very recently,[1,2] the stabilization of a triplet carbene emerges as a challenging target. The stabilization of a triplet carbene must be better accomplished by steric protection than thermodynamic effects since the latter strategy seems to result in the stabilization of the singlet state. Attempts have been made along this line whereby triplet diphenylcarbenes (DPC) were stabilized by introducing a series of substituents at the ortho positions.[3,4] Among the protecting groups thus far examined, the methyl group is most effective in protecting the carbenic center; didurylcarbene is shown to be some 5 orders of magnitude longer-lived than the parent DPC.[4e] When two more methyl groups are introduced at the para positions, the carbenic center is more effectively blocked from external reagents due to buttressing effects; however, it is more easily trapped by the ortho methyl groups which are brought closer to the carbene center, The carbene therefore becomes shorter-lived.[4e] Bromine atoms appear to be effective as protecting groups because, while the van der Waals radius is similar to that of methyl, bromine is less reactive in terms of intramolecular insertion and moreover should enhance the intersystem crossing to the triplet. Thus, we generated the title carbene by photolysis of the precursor diazomethane and found that the carbene not only survived for seconds in solution but also existed for months in the crystal state at room temperature.

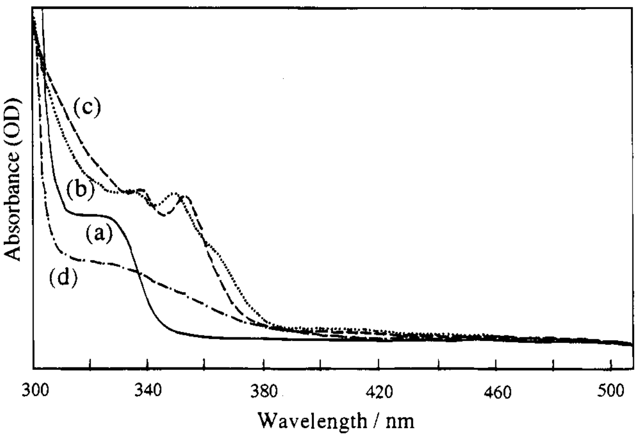
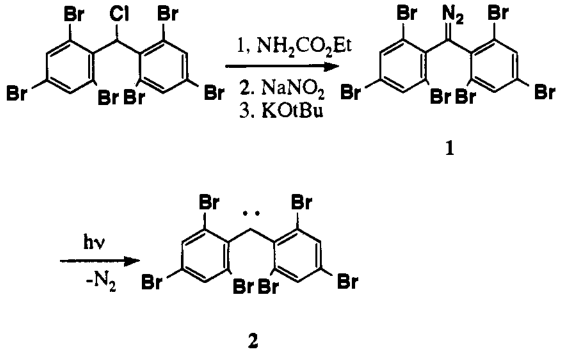


Figure 1. UV/vis spectra obtained by irradiation of **1** in MTHF: (a) spectrum of **1** in MTHF at 77 K; (b) same sample after 1 min irradiation (λ > 300 nm); (c) same sample after warming to 95 K; (d) same sample after warming the matrix to room temperature and refreezing to 77 K.

Scheme 1



The precursor diazomethane (**1**) was obtained by acyl cleavage of the corresponding *N*-alkyl-*N*-nitrosourethane by potassium *tert*-butoxide as a rather stable red crystal (mp 129,0−131.0 °C) which could be purified by repeated chromatography on a Shodex GPC H-2001 column for the spectroscopic studies.

Irradiation (λ > 350 nm) of **1** (1×10^{-4} 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 **1**. As is shown in Figure 1, the new spectrum consists of two identifiable features, two intense UV bands with maxima at 337 and 349 nm and weak and broad bands with apparent maxima around 480 nm. These features are usually present in the spectra of triplet diarylcarbenes in organic matrices at 77 K.[6] The glassy solution did not exhibit any changes for several hours when kept at 77 K. However, when it was allowed to warm to room temperature and then cooled to 77 K, the characteristic bands disappeared. On the basis of these observations coupled with EPR data (vide infra), the absorption spectrum can be attributed to triplet hexabromodiphenylcarbene (**2**) generated by photo-dissociation of **1** (Scheme 1). Monitoring of the spectral changes as a function of temperature shows two interesting features. First, the absorption maxima shifted slightly but distinctly from 337 and 349 nm to 339 and 353 nm when the matrix was warmed from

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(1) Phosphinocarbene and imidazol-2-ylidene were prepared as "bottleable" carbenes in 1988 and 1991, respectively. These carbenes are stabilized not only by bulky protecting groups but also by heteroatom substituents directly connected to the carbenic atoms. Owing to these substitutents, these carbenes have a singlet ground state. See: Igau, A.; Grützmacher, H.; Baceiredo, A.; Bertrand, G. *J. Am. Chem. Soc.* **1988**, *110*, 6463. Igau, A.; Baceiredo, A.; Trinqueir, G.; Bertrand, G. *Angew Chem., Int. Ed. Engl.* **1989**, *28*, 621. Gilette, G. R.; Baceiredo, A.; Bertand, G. *Ibid.* **1990**, *29*, 1429. Dixon, D. A.; Dobss, K. D.; Arduengo, A. J., III; Bertrand, G. *J. Am. Chem. Soc.* **1991**, *113*, 8782. Soleilhavoup, M.; Baceiredo, A.; Treutler, O.; Ahlrichs, R.; Nieger, M.; Bertrand, G. *Ibid.* **1992**, *114*, 10959. Arduengo, A. J., III; Harlow, R. L.; Kline, M. *Ibid.* **1991**, *113*, 361. Arduengo, A. J. III; Kline, M.; Galabrese, J. C.; Davidson, F. *Ibid.* **1991**, *113*, 9704. Arduengo, A. J., III; Rasika Dias, H. V.; Harlow, R. L.; Kline, M. *Ibid.* **1992**, *114*, 5530. Arduengo, A. J., III; Bock, H.; Chen, H.; Denk, M.; Dixon, D. A.; Green, J. C.; Herrman, W. A.; Jones, N. L.; Wagner, M.; West, R. *Ibid.* **1994**, *116*, 6641.

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(5) 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 spectral changes upon thawing were monitored by carefully controlling the matrix temperature with an Oxford Instrument intelligent temperature controller (ITC4).

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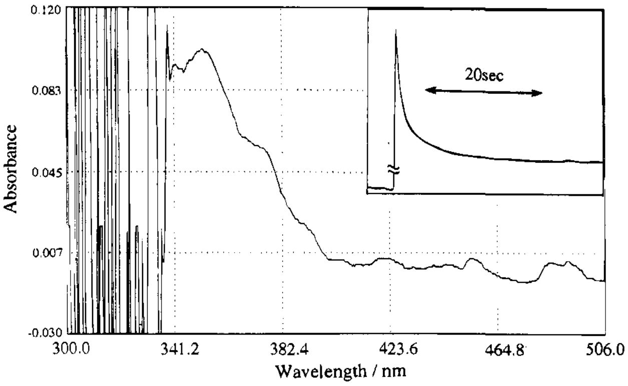

Figure 2. Absorption spectrum of the transient products formed during the irradiation of **1** in degassed benzene, recorded 50 μs after excitation. The inset shows oscillogram trace monitored at 353 nm.

90 to 95 K. This change was not reversed when the samples were cooled, This is interpreted in terms of the geometrical change of carbenes often observed for sterically congested carbenes.[3,7] Thus, when a carbene is formed at low temperature, the rigidity of the matrix prevents it from assuming its minimum energy geometry. However, when the matrix is softened on annealing, the carbene relaxes to a stabler structure. It should be noted here that such a distinct shift in a UV/vis spectrum has not previously been observed for other relatively congested diarylcarbenes undergoing geomerical changes.[4] This suggests that the magnitude of the change must be fairly large (vide infra). Second, while absorption bands of most diarylcarbenes disappear in the temperature range 100–105 K where viscosity of the matrix changes dramatically from 10^7 to 10^3 P,[8] no appreciable changes were observed for the absorption bands ascribable to **2** in MTHF up to 120 K where *the samples were completely fluid.* Significant decomposition began only at 130 K (viscocity is 1,6 P) where the "first-order" half-life ($t_{1/2}$) was approximately 15 min. In more viscous solvents, **2** was able to survive at much higher temperatures; 190 K in dibutylphthalate ($t_{1/2} = 37$ min), and 210 K in triacetine ($t_{1/2} = 33$ min).

Laser flash photolysis[9] of **1** (1.0×10^{-4} M) in a degassed benzene solution at room temperature with a 10 ns, 70–90 mJ, 308 nm pulse from a XeCl excimer laser produced a transient species showing a strong absorption at 353 nm and a weak absorption extending from 420 to 500 nm, which appeared coincident with the pulse. *The transient signals disappeared rather gradually, persisting for at least 30 s under these conditions* (Figure 2), On the basis of the low-temperature spectrum, we assign the transient product to triplet **2**, Support is lent to this assignment by trapping experiments using oxygen. When flash photolysis was carried out on a non-degassed benzene solution of **1**, the half-life of triplet **2** decreased dramatically, and a broad absorption band with a maximum at 410 nm appeared. The rate of increase in the absorbance at 410 nm is practically the same as that of the decay of the peak at 355 nm, showing that triplet **2** is quenched with oxygen to form the carbonyl oxide (**3**).[10] The rate constant for the quenching of **2** by oxygen is determined to be 1.1×10^7 M^{-1} s^{-1}. The inset in Figure 2 shows the decay of **2** in the absence of oxygen, which is found to be second order ($2k/\epsilon l = 8.9$ s^{-1}),[11] The rough lifetime of **2** is estimated in the form of half-life, $t_{1/2}$, to be 1 ± 0.1 s.

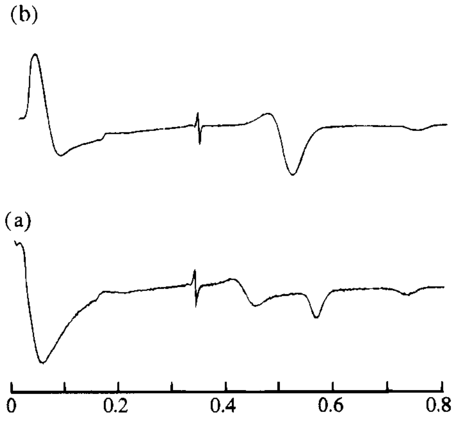

Figure 3. (a) EPR spectrum obtained by irradiation of **1** in MTHF at 4 K before annealing. (b) Same sample after annealing to 130 K and refreezing to 4 K.

Irradiation of **1** in MTHF glass at 4 K gave a fine-structure EPR line shape (Figure 3) characteristic of randomly oriented triplet molecules with a large D value attributable to one-center $n\pi$ spin–spin interaction at a divalent carbon of diarylcarbene.[12] The fine-structure constants were $|D| = 0.3598$ cm^{-1}, $|E| = 0.0295$ cm^{-1}, showing unequivocally that the triplet signals are due to **2**. The EPR signals not only were stable at this temperature but also survived even at 130 K, However, as the samples were warmed, the x and y lines of the spectrum moved closer together, resulting in essentially zero E value. Cooling the samples did not reverse this change, Since the E value, when weighted by D, depends on the magnitude of the central C–C–C angle, it indicates that, on warming, the carbene relaxes to a structure with an expanded C–C–C angle presumably to gain relief from steric compression,[3,7] These observations are in accord with the UV/vis studies (vide supra) showing that **2** is kinetically stable and undergoes substantial geometrical changes upon annealing. Photolyses of single crystals of **1** at liquid helium temperature also generated fine-structure EPR spectra due to typical triplet diarylcarbene with the large D value. *The signals survived up to room temperature without loss of intensity, considering the effect of the Boltzmann factor, for months.* The complete spectral analyses are under way,

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(8) Ling, A. C.; Willard, J. E. *J. Phys. Chem.* **1968**, *72*, 1918.

(9) For a description of our LFP system, see ref 4c.

(10) It is well-documented that diarylcarbenes with triplet ground states are readily trapped by oxygen to give the corresponding diaryl ketone oxides, which are observed directly either by matrix isolation techniques or by flash photolysis. See for reviews: Sander, W. W. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 344. See also: Scaiano, J. C.; McGimpsey, W. G.; Casal, H. L. *J. Org. Chem.* **1989**, *54*, 1612.

(11) Product analysis (500 MHz ^{1}H NMR, HPLC, and GPC) of the spent solution showed the presence of complex mixtures containing small amounts of carbenic dimers and radical dimers. This is in marked contrast with that observed for the corresponding hexachlorodiphenylcarbene, which is shown to decay in the second order under the same conditions and affords carbenic dimer as the major product.[4a,b]

(12) ESR measurements were made on a Bruker ESP 300 spectrometer using magnetic field modulation of 100 kHz. Sample temperatures were controlled by an Oxford ESR 910 helium gas flow system.

(13) It has been reported that 9,9′-dianthrylmethylene is stable up to 160 °C in anthracene.[14a] However, the stability is due to the rigidity of the environment and not to an intrinsic lack of reactivity. For instance, the absorption band of this carbene generated in MTHF glass at 77 K disappeared irreversibly when the matrix was thawed to 95 K.[14a,c] Flash photolysis studies show that it undergoes self-reaction at the diffusion-controlled limit in benzene at room temperature.[14b] The half-life is estimated to be ~100 μs.[14c]

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