

A Triplet Carbene That Can Almost Be Bottled

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The recent synthesis of stable singlet carbenes^{1–3} seems to upset the long-standing view that carbenes are not stable enough to be isolated on a macroscopic scale at room temperature. However, this view still holds true since those singlet carbenes are strongly stabilized by two heteroatom substituents most likely due to ylidic contributions.⁴ In addition, more importantly, triplet counterparts have not been isolated yet. To isolate a carbene with its electronic integrity (one centered diradical) intact, steric protection is the ideal method. This is especially true for triplet carbene since a protecting group, when introduced near the carbene center, not only blocks the carbene center from external reagents but also results in thermodynamic stabilization by increasing the carbene angle.

Attempts to isolate triplet diphenylcarbene by introducing various substituents at the ortho positions have been made, where triplet carbenes with lifetimes over minutes under normal conditions are realized.^{5,6} This is very long-lived for triplet carbenes but would still be an ephemeral existence for “real” molecules.

The crucial point for realizing stable triplet carbenes is to explore effective kinetic protectors which are bulky yet unreactive toward carbenes, since carbenes have only two modifiable substituents and are reactive enough to attack even very poor sources of electrons such as C–H bonds.

In this respect, the trifluoromethyl (CF₃) group has been regarded as an ideal kinetic protector of carbenes since it is much bigger than methyl and bromine groups and, more importantly, C–F bonds are known to be almost the only type of bond unreactive toward carbenic centers.⁷ However, since it is almost impossible to prepare the precursor diphenyldiazomethane (DDM) bearing four ortho CF₃ groups, we decided to use the sterically less demanding protectors in combination with CF₃ groups. The precursor which we were able to prepare is DDM (**1**) having two ortho bromine groups in addition to two CF₃ groups. The triplet carbene (**2**) generated from this precursor was found to be extremely stable; it is the first carbene that can survive more than 1 h in solution at room temperature and can also be stored in a bottle cooled at –40 °C.

(1) Igau, A.; Grutzmacher, H.; Baceiredo, A.; Bertrand G. *J. Am. Chem. Soc.* **1988**, *110*, 6463. See also: Alcaraz, G.; Wecker, U.; Baceiredo, A.; Dahan, F.; Bertrand, G. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1246 and references therein.

(2) Arduengo, A. J., III; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1991**, *113*, 361. See also: Arduengo, A. J., III; Krafczyk, R. *Chem. Z.* **1998**, *32*, 6, and references therein.

(3) For a recent review, see: Herrmann, W. A.; Köcher, C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2162.

(4) (a) Regitz, M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 674. (b) Dagani, R. *Chem. Eng. News* **1991**, Jan 28, 19. Dagani, R. *Chem. Eng. News* **1994**, May 2, 20. (c) Heinemann, C.; Müller, T.; Apeloig, Y.; Schwarz, H. *J. Am. Chem. Soc.* **1996**, *118*, 2023. (d) Boehme, C.; Frenking, G. *J. Am. Chem. Soc.* **1996**, *118*, 2039.

(5) (a) Tomioka, H.; Hattori, M.; Hirai, K.; Murata, S. *J. Am. Chem. Soc.* **1996**, *118*, 8723. (b) See for a review: Tomioka, H. *Acc. Chem. Res.* **1997**, *30*, 315. Tomioka, H. In *Advances in Carbene Chemistry*; Brinker, U., Ed.; JAI Press: Greenwich, CT, 1998; Vol. 2, pp 175–214.

(6) (a) Tomioka, H.; Nakajima, J.; Mizuno, H.; Sone, T.; Hirai, K. *J. Am. Chem. Soc.* **1995**, *117*, 11355. (b) Tomioka, H.; Hattori, M.; Hirai, K.; Sone, K.; Shiomi, D.; Takui, T.; Ithoh, K. *J. Am. Chem. Soc.* **1998**, *120*, 1106. (c) Tomioka, H.; Mizuno, H.; Itakura, H.; Hirai, K. *J. Chem. Soc., Chem. Commun.* **1997**, 2261.

(7) For instance: Tomioka, H.; Taketsuji, K. *J. Chem. Soc., Chem. Commun.* **1997**, 1745.

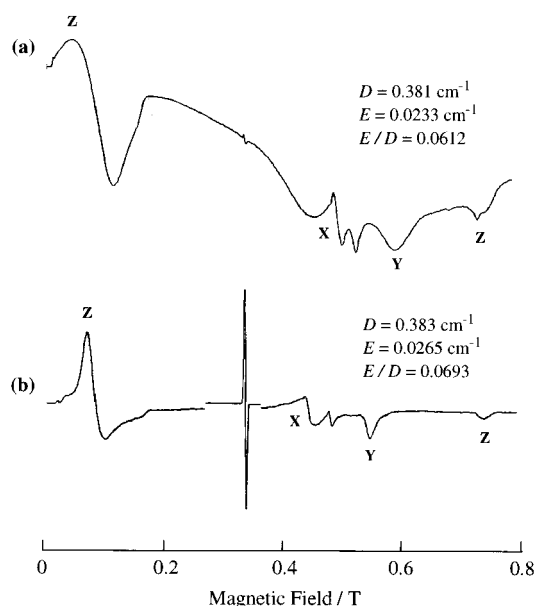


Figure 1. (a) EPR spectra obtained by irradiation of **1** in MTHF at 77 K. (b) Same sample after annealing to 110 K.

Irradiation ($\lambda > 300$ nm) of **1** in a 2-methyltetrahydrofuran (MTHF) glass at 77 K gave a fine-structured EPR line shape (Figure 1). This shape is 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 (**2**). Inspection of the spectrum reveals that there are at least two sets of triplet signals. When the matrix containing the carbene was thawed gradually, another new set of triplet peaks appeared at the expense of the original peaks. These changes were not reversible. These changes of E/D values upon thawing matrices have often been observed in the EPR spectrum of sterically congested triplet diarylcarbenes and are usually interpreted in terms of geometrical changes.^{5,8}

More importantly, the triplet signals were found to be persistent even at a significantly higher temperature. For instance, a significant decay of the triplet signals began only at 210 K in MTHF. In more viscous media, triacetin, no appreciable changes were observed even at 230 K. Measurable decay of the signals was observed only at 273 K (0 °C), where the “first-order” half-life ($t_{1/2}$) was approximately 10 min.

The dramatic stability of **2** was also shown by monitoring the UV/vis spectra of **2** at a low temperature as a function of temperature. Irradiation of **1** in a triacetin matrix at 110 K resulted in the appearance of new bands at the expense of the original absorption due to **1**. As shown in Figure 2, the new spectrum consists of two identifiable features, intense UV bands with maxima at 318, 329, and 343 nm and weak broad bands with apparent maxima at 465 and 489 nm. These features are usually present in the spectra of triplet diarylcarbenes in organic matrices at cryogenic temperatures.⁹ The absorption spectrum can be attributed to triplet carbene (**2**) more unequivocally as triplet EPR signals are observed under the identical conditions. The absorption maxima shifted slightly but distinctly when the matrix was warmed from 225 to 230 K. These observations are again

(8) Wasserman, E.; Kuck, V. J.; Yager, W. A.; Hutton, R. S.; Greene, F. D.; Abegg, V. P.; Weinschenker, N. M. *J. Am. Chem. Soc.* **1971**, *93*, 6335. Tukada, H.; Sugawara, T.; Murata, S.; Iwamura, H. *Tetrahedron Lett.* **1986**, *27*, 235.

(9) See for reviews: (a) Trozzolo, A. M. *Acc. Chem. Res.* **1968**, *1*, 329. (b) Trozzolo, A. M.; Wasserman, E. In *Carbenes*; Moss, R. A., Jones, M., Jr., Eds.; Wiley: New York, 1975; Vol. 2, Chapter 5. (c) Sander, W.; Bacher, G.; Weirlacher, S. *Chem. Rev.* **1993**, *93*, 1593.

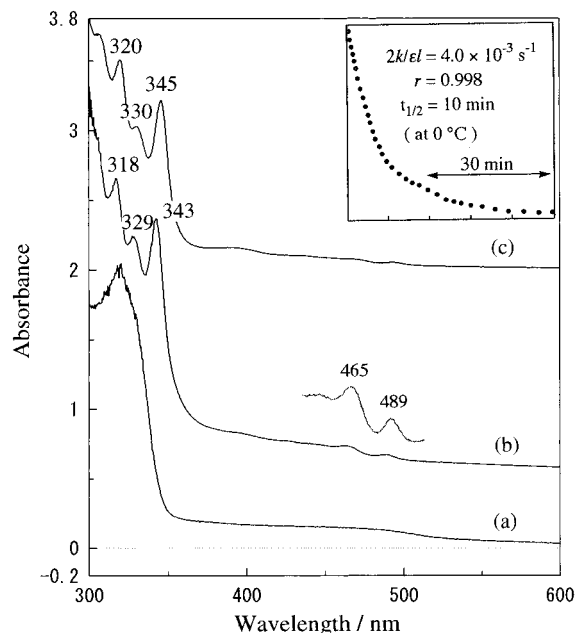


Figure 2. UV/vis spectra obtained by irradiation of **1** in triacetin: (a) spectrum of **1** in triacetin at 110 K; (b) same sample after 15 min irradiation ($\lambda > 350$ nm); and (c) same sample after warming to 273 K. The inset shows a plot of the absorbance at 345 nm as a function of time at 0 °C.

interpreted in terms of the geometrical changes of **2** upon annealing (vide supra). A significant decay of the absorption was not observed until the matrix temperature was raised to 273 K (0 °C), where the half-life ($t_{1/2}$) was estimated to be 10 min. These observations are in excellent agreement with the EPR studies (vide supra).

To estimate the lifetime of triplet carbene **2** under our standard conditions, i.e., in degassed benzene at 20 °C, laser flash photolysis (LFP) of **1** was carried out. However, the lifetime of $^3\mathbf{2}$ was too long to be monitored by the LFP system, and a conventional UV-vis spectroscopic method was more conveniently employed in this case. As shown in Figure 3, the UV-vis spectrum obtained just after photolysis of **1** in benzene at 20 °C exhibits characteristic features of $^3\mathbf{2}$, i.e., an intense absorption in the UV region along with weak, broad bands in visible regions, which decay very slowly. The transient signals did not disappear completely even after 1 h under these conditions. The decay was found to be second order ($2k/el = 1.7 \times 10^{-3} \text{ s}^{-1}$). The approximate half-life ($t_{1/2}$) of $^3\mathbf{2}$ is estimated to be 16 min.

The reactivities of $^3\mathbf{2}$ toward typical triplet quenchers, i.e., oxygen and 1,4-cyclohexadiene (CHD), were then investigated using LFP. Thus, LFP of **1** in a nondegassed benzene solution resulted in a dramatic decrease in the lifetime of $^3\mathbf{2}$ and a concurrent appearance of a new absorption band at 410 nm. The rate of increase in the band at 410 nm is practically the same as that of the peak due to $^3\mathbf{2}$, showing that $^3\mathbf{2}$ is quenched with oxygen to form carbonyl oxide (**3**).¹⁰ The rate constant (k_{O_2}) for the quenching of $^3\mathbf{2}$ by O_2 is determined to be $8.6 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ from a plot of the observed pseudo-first-order growth rate of **3** as a function of $[O_2]$. Similarly, LFP of **2** in degassed benzene in the presence of CHD generated a new signal attributable to the diarylmethyl radical (**4**) as the signals of $^3\mathbf{2}$ decayed, showing that $^3\mathbf{2}$ abstracts H from the diene.¹¹ The rate constant (k_{CHD}) of H abstraction of $^3\mathbf{2}$ from CHD is determined to be $1.0 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ from a plot of the apparent build-up rate constant of the radical vs $[CHD]$.

The kinetic and ESR data for $^3\mathbf{2}$ are to be compared with those observed for the longest-lived triplet carbene thus far known, i.e.,

(10) It is well-documented that diarylcarbenes with triplet ground states are readily trapped by oxygen to generate the corresponding diaryl ketone oxides. For a review, see: Sander W. *Angew. Chem., Int. Ed. Engl.* **1990**, *20*, 344.

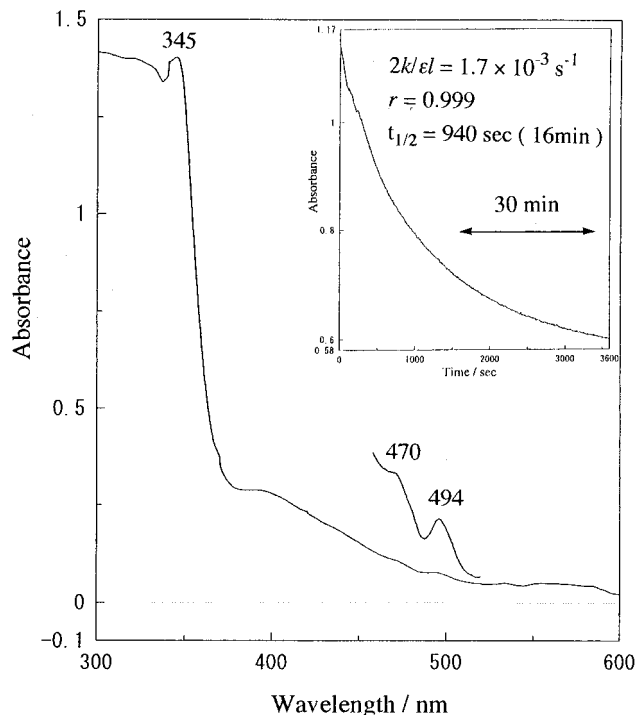
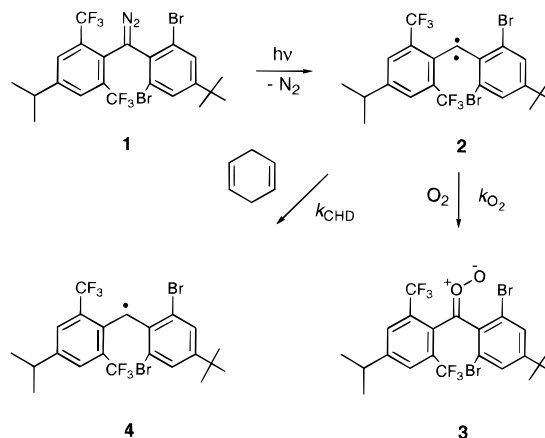


Figure 3. UV/vis spectrum obtained by irradiation of **1** in benzene at 20 °C. Inset shows a plot of the absorbance at 345 nm as a function of time.

Table 1. Kinetics and ESR Data for Triplet Carbene

carbenes	$2k/el^a$ (s^{-1})	$t_{1/2}^a$ (s)	$k_{O_2}^b$ ($\text{M}^{-1} \text{ s}^{-1}$)	k_{CHD}^a ($\text{M}^{-1} \text{ s}^{-1}$)	D^c (cm^{-1})	E^c (cm^{-1})
$^3\mathbf{2}$	1.7×10^{-3}	940	8.6×10^5	1.0×10^6	0.383	0.0247
$^3\mathbf{5}$	3.5×10^{-1}	16	2.1×10^7	5.3×10^2	0.442	~ 0



di(2,4-dibromo-6-*tert*-butylphenyl)carbene ($^3\mathbf{5}$)^{5a} (Table 1). It is clear that reactivities decrease by approximately 2 orders of magnitude as two *o*-bromine groups in $^3\mathbf{5}$ are replaced with two CF_3 groups. CF_3 is thus shown to be an excellent kinetic protector of triplet carbene.

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(11) It is also well-documented that triplet diarylcarbenes generated in the presence of good hydrogen donor undergo H abstraction leading to the corresponding radical showing transient absorption at longer wavelength than the corresponding carbene. For reviews see: Platz, M. S., Ed. *Kinetics and Spectroscopy of Carbenes and Biradicals*; Plenum: New York, 1990. Jackson, J. E.; Platz, M. S. In *Advances in Carbene Chemistry*; Brinker, U., Ed.; JAI Press: Greenwich, CT, 1994; Vol. 1, pp 87–160.