Effects of *para*-Phenyl Group on the Reactivities of Sterically Congested Triplet Diphenylcarbene

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Bis(2,6-dibromo-4-phenylphenyl)carbene dimerizes to give tetrakis(2,6-dibromo-4-phenylphenyl)ethene, which is further photolyzed to afford 1,8-dibromo-9,10-bis(2,6-dibromo-4-phenylphenyl)-3,6-diphenylphenanthrene.

The stabilization of a triplet carbene has emerged as challenging target[1] since the isolation of carbenes in the singlet state has been realized recently.[2,3] Steric protection is an ideal method for stabilizing the triplet state, since a protecting group when introduced near a carbene center not only blocks the carbene center from external reagents but also results in thermodynamic stabilization by increasing the carbene bond angle. Attempts have been made in this direction whereby triplet diphenylcarbenes were stabilized by introducing a series of substituents at the ortho positions and diphenylcarbenes surviving more than an hour were realized.[4]

This approach encounters a limitation when diazo compounds are used as precursor since, as more bulky groups are used at ortho positions, introduction of the diazo group becomes more difficult.

The other strategy is the electronic (thermodynamic) effect of *para*-substituents on the stability of kinetically protected triplet diphenylcarbenes. We found that kinetically stabilized triplet bis(2,6-dimethylphenyl)carbene is thermodynamically further stabilized by a spin-delocalizing *para*-substituent.[5] In the case of bis(2,6-dibromophenyl)carbene, on the other hand, *tert*-butyl group at the para-positions was found to increase the lifetime by sterically hindering a coupling reaction at para-positions where considerable spins build up.[6] However, effect of *para*-aryl group, which can delocalize a spin,[7] has not been examined. Thus we generated bis(2,6-dibromo-4-phenylphenyl)carbene (**2a**) and studied the reactivities not only by traditional product study but also spectroscopically.

Irradiation of bis(2,6-dibromo-4-phenylphenyl)diazomethane (**1a**)[8] in a 2-methyltetrahydrofuran(MTHF) glass at 77 K gave a fine structured EPR line shape characteristic of randomly oriented triplet molecules with a large D value attributable to one-center $n\pi$ spin-spin interaction at the divalent carbon of diphenylcarbene (Figure 1).[9] The zero field splitting parameters were $|D| = 0.359\,\mathrm{cm}^{-1}$ and $|E| = 0.0301\,\mathrm{cm}^{-1}$, showing unequivocally that the triplet signals are due to diphenylcarbene **2a** generated from **1a** as a result of N_2 elimination upon irradiation. The EPR signals were persistent at this low temperature, but disappeared irreversibly when the matrix was warmed to 170 K. The D value is related to the average separation between the two unpaired electrons. The value of E when weighted by D is a measure of the deviation of the carbene from axial symmetry or, more plainly, it described the extent to which the molecule is bent. Comparison of the D value of **2a** with that observed for bis(2,6-dibromo-4-*tert*-butylphenyl)carbene **2c** ($|D| = 0.397\,\mathrm{cm}^{-1}$, $|E| = 0.0311\,\mathrm{cm}^{-1}$) indicates that an unpaired electron occupying the p-orbital of **2a** delocalize onto phenyl rings at para-positions. This is in accord with the fact that 4-phenyl group is a good spin delocalizing group.[7]

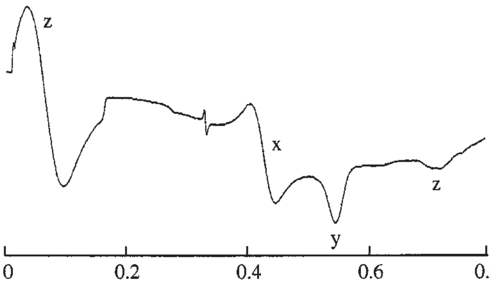


Figure 1. EPR spectrum of triplet bis(2,6-dibromo-4-phenylphenyl)carbene **2a** in MTHF at 77 K.

Irradiation of **1a** in the MTHF glass at 77 K was then monitored by UV-vis spectroscopy, which revealed the rapid appearance of new absorption bands at the expense of the original absorption due to **1a**. The new spectrum consisted of two identifiable features, intense UV band with maximum at 348 nm and weak and broad one with an apparent maximum around 500 nm. These features are usually present in the spectra of triplet diphenylcarbenes in organic glasses at 77 K.[9a,10] The glassy solution did not exhibit any changes for several hours when kept at 77 K. However, when it was allowed to warm to 100 K, the characteristic bands around 350 nm changed to broad bands around 340–360 nm. When it was allowed to warm to 170 K and then cooled to 77 K, the characteristic bands disappeared. On the basis of these observations, coupled with the EPR data, the new absorption spectrum can be attributed to triplet carbene **2a**.

Laser flash photolysis (LFP) of **1a** in a degassed benzene solution at 20 °C with a 10 ns, 180–190 mJ, 308 nm pulse from a XeCl excimer laser produced a transient species showing two strong absorption bands at 338 and 355 nm, which appeared coincident with the pulse (Figure 2). On the basis of the low-temperature spectrum, we assign the transient product to triplet **2a**. The inset in Figure 2 shows the decay of **2a**, which is found to be second-order ($2k/\varepsilon l = 0.35\,\mathrm{s}^{-1}$), suggesting that carbene **2a** decays mainly by undergoing dimerization. The approximate lifetime of **2a** is estimated in the form of half-life, $t_{1/2}$, to be 12 s.

Irradiation ($\lambda > 300$ nm) of **1a** in a degassed benzene solution at 20 °C for 1 hour afforded tetrakis(3,5-dibromo-4-phenylphenyl)ethene (**3a**)[11] and 1,8-dibromo-9,10-bis(3,5-dibromo-4-phenylphenyl)-3,6-diphenylphenanthrene (**4a**)[11] in 58 and

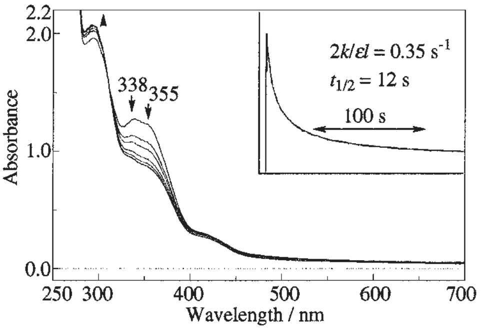
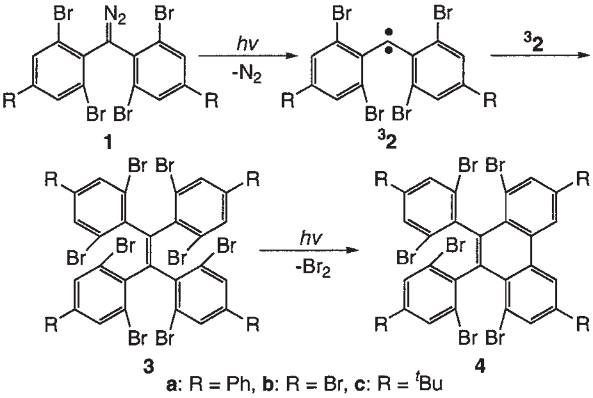


Figure 2. Absorption spectra of the transient products formed during the irradiation of **1a** in a degassed benzene, recorded 1, 10, 20, 30, 60, and 120 s after excitation. Inset shows oscillogram trace monitored at 350 nm.

8% yields, respectively (Scheme 1). A presumable possibility is that triplet carbene (^{3}**2a**) undergoes dimerization to form tetra(aryl)ethene (**3a**), which subsequently cyclizes with loss of two bromine units to lead to phenanthrene derivative (**4a**) upon photoexcitation, since the photocyclization of stilbene derivatives to give the corresponding phenanthrenes has been well-documented.[12] Other persistent triplet diphenylcarbenes, bis(2,4,6-trichlorophenyl)carbene[13] and dimesitylcarbene,[12,13] produced the corresponding tetraarylethenes in fairly good yield ($\approx$80%). On the other hands, photolysis of bis(2,6-dibromophenyl)diazomethanes bearing alkyl or bromo groups at 4 positions under the identical conditions afforded only the corresponding phenanthrene derivatives (**4b** and **4c**) and all attempts to detect or isolate the corresponding ethenes (**3b** and **3c**) were unsuccessful.[6b] The results are interpreted as indicating that the ethenes may be sensitive under these conditions and are consumed to form the phenanthrenes before the ethenes (**3b** and **3c**) accumulate. In this respect, it is rather surprising that carbene **2a** afforded both ethene **3a** and phenanthrene **4a**. When the photolysis of **1a** in a degassed benzene-d_6 solution was monitored by ^{1}H NMR, **3a** was detected as a sole product at the initial stage of the irradiation. Upon further irradiation, **4a** started to form at the expense of **3a**. The observations clearly support our previous view that phenanthrene is derived from initially formed diarylethene as a result of photo-cyclization.



a: R = Ph, **b**: R = Br, **c**: R = ^{t}Bu

Scheme 1.

Thus, the present studies revealed that phenyl groups at para position exerted appreciable effects not only on the stability but also on the reaction pattern of triplet bis(2,6-dibromophenyl)carbene. The smaller D value in **2a** suggested that unpaired electrons are delocalized onto the phenyl ring, which is known as a rather strong spin delocalizer.[7] So, the increased half-life of **2a** compared to **2b**, for instance, can be attributable to thermodynamic stabilization by the phenyl ring. Reasons for this rather dramatic change in the product distributions between **2a** and the other systems are not clear at present. The absorption bands of the precursor diazomethane **1a** are shifted to a longer wavelength and stronger than the other diazomethanes probably because of the perturbation by the 4-phenyl rings. This will increase the efficiency of photodecomposition leading to carbene **2a**, which decays to form ethene **3a**. The ethene, on the other hand, may have decay pathways other than cyclization, such as emission, induced by the phenyl rings.

Further study is in progress in order to reveal other decay pathways and to know more about the effect of aryl groups on the stability of sterically hindered triplet diphenylcarbenes.

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References and Notes

1 See for reviews: a) H. Tomioka, *Acc. Chem. Res.*, **30**, 1315 (1997). b) H. Tomioka, in "Advances in Carbene Chemistry," ed. by U. Brinker, JAI Press, Greenwich, CT (1998), Vol. 2, pp 175–214.

2 Phosphinocarbene and imidazol-2-ylidene were prepared as "bottle-able" singlet carbenes in 1988 and 1991, respectively. See: a) A. Igau, H. Grutzmacher, A. Baceiredo, and G. Bertrand, *J. Am. Chem. Soc.*, **110**, 6463 (1988). b) A. J. Arduengo, III, R. L. Harlow, and M. Kline, *J. Am. Chem. Soc.*, **113**, 361 (1991).

3 D. Bourisson, O. Guerret, F. D. Gabbai, and G. Bertrand, *Chem. Rev.*, **100**, 39 (2000).

4 K. Hirai and H. Tomioka, *J. Am. Chem. Soc.*, **121**, 10123 (1999).

5 a) Y. Hu, K. Hirai, and H. Tomioka, *Can. J. Chem.*, **77**, 1066 (1999). b) Y. Hu, K. Hirai, and H. Tomioka, *Chem. Lett.*, **2000**, 94. c) Y. Hu, Y. Ishikawa, K. Hirai, and H. Tomioka, *Bull. Chem. Soc. Jpn.*, **74**, 2207 (2001).

6 a) H. Tomioka, M. Hattori, K. Hirai, and S. Murata, *J. Am. Chem. Soc.*, **118**, 8723 (1996). b) H. Tomioka, T. Watanabe, M. Hattori, N. Nomura, and K. Hirai, *J. Am. Chem. Soc.*, **124**, 474 (2002).

7 a) J. M. Dust and D. R. Arnold, *J. Am. Chem. Soc.*, **105**, 1221 (1983); J. M. Dust and D. R. Arnold, *J. Am. Chem. Soc.*, **105**, 6531 (1983). b) D. D. M. Wayner and D. R. Arnold, *Can. J. Chem.*, **62**, 1164 (1984). c) D. D. M. Wayner and D. R. Arnold, *Can. J. Chem.*, **63**, 2378 (1985). d) X. Creary, *J. Org. Chem.*, **45**, 280 (1980). e) X. Creary, M. E. Mehrsheik-Mohammadi, and S. McDonald, *J. Org. Chem.*, **52**, 3254 (1987). f) U. Stewen and M. Lehig, *J. Am. Chem. Soc.*, **111**, 5845 (1989).

8 The diazomethane (**1a**) was prepared by the acyl cleavage of the corresponding *N*-alkyl-*N*-nitroso-uretane by potassium *tert*-butoxide. It was purified by gel permeation chromatography to afford an orange solid; mp 153.6–155.0 °C; ^{1}H NMR (CDCl$_3$) δ 7.85 (s, 4H), 7.58–7.55 (m, 4H), 7.45–7.39 (m, 6H); IR (KBr) 2068 cm^{-1}.

9 For reviews of the ESR and UV/vis spectra of triplet carbenes, see: a) W. Sander, G. Bucher, and S. Wierlacher, *Chem. Rev.*, **93**, 1583 (1993). b) A. M. Trozzolo and E. Wasserman, in "Carbenes," ed. by M. Jones, Jr. and R. A. Moss, Wiley, New York (1975), Vol. 2, pp 185–206. c) H. Tomioka, in "Advances in Strained and Interesting Organic Molecules," ed. by B. Halton, JAI Press, Greenwich, CT (2000), Vol. 8, pp 83–112.

10 A. M. Trrozoro, *Acc. Chem. Res.*, **1**, 329 (1968).

11 **3a**: white solid; mp >350 °C; ^{1}H NMR (CDCl$_3$) δ 7.79 (d, J = 2.02 Hz, 4H), 7.64 (d, J = 2.02 Hz, 4H), 7.60–7.57 (m, 8H), 7.45–7.36 (m, 12H). **4a**: pale yellow solid; mp 127.0–128.5 °C; ^{1}H NMR (CDCl$_3$) δ 9.09 (d, J = 1.65 Hz, 2H), 8.30 (d, J = 1.65 Hz, 2H), 7.81–7.79 (m, 4H), 7.65 (s, 4H), 7.59–7.53 (m, 8H), 7.49–7.39 (m, 8H).

12 a) F. B. Mallory and C. W. Mallory, *Org. React.*, **30**, 1 (1984). b) A. Gilbert, in "CRC Handbook of Organic Photochemistry and Photobiology," ed. by W. M. Hprspool and P.-S. Song, CRC Press, Boca Roton, FL (1994), pp 291–300.

13 H. E. Zimmerman and D. H. Pskovich, *J. Am. Chem. Soc.*, **86**, 2149 (1964).

14 a) H. Tomioka, H. Okada, T. Watanabe, and K. Hirai, *Angew. Chem., Int. Ed. Engl.*, **33**, 873 (1994). b) H. Tomioka, H. Okada, T. Watanabe, K. Banno, K. Komatsu, and K. Hirai, *J. Am. Chem. Soc.*, **119**, 1582 (1997).