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Triplet Diphenylcarbenes Protected by (Trimethylsilyl)ethynyl Groups

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(2,4,6-Tribromophenyl)(4-*tert*-butyl-2,6-dimethylphenyl)diazomethane (**1a**) was shown to be stable enough to survive Sonogashira coupling reaction conditions at an elevated temperature and gave not only a para-monosubstituted product, (4-trimethylsilylethynyl-2,6-dibromophenyl)(4-*tert*-butyl-2,6-dimethylphenyl)diazomethane (**1b**), but also a disubstituted one, [2,4-bis(trimethylsilylethynyl)-6-bromophenyl](4-*tert*-butyl-2,6-dimethylphenyl)diazomethane (**1c**), and a trisubstituted product, [2,4,6-tris(trimethylsilylethynyl)phenyl](4-*tert*-butyl-2,6-dimethylphenyl)diazomethane (**1d**). Triplet diphenylcarbenes (DPCs) generated by photolysis of those ethynylated diphenyldiazomethanes were characterized by ESR and UV−vis spectroscopies at low temperature and laser flash photolysis techniques in solution at room temperature. Although ESR data indicated that ethynyl groups at the ortho positions are likely to stabilize triplet DPCs both sterically and electronically more effectively than *o*-bromine groups, kinetic studies suggested that the stability of triplet DPCs is not increased by *o*-ethynyl groups, as opposed to *o*-bromine groups. It is likely that triplet DPCs decay by interacting with the *o*-ethynyl groups.

The stabilization of a triplet carbene has emerged as a challenging target[1] since the recent syntheses[2,3] of stable singlet carbenes ruled out the long-standing view that carbenes are not stable enough to be isolated in a macroscopic scale at room temperature. Recent growing interest in triplet carbenes as potential organic ferromagnets[4] adds practical meaning to the project.

To isolate the triplet carbene with its electronic integrity (one centered diradical) intact, steric protection is the ideal method.[1,5] The first step is then to prepare a precursory diazo compound properly functionalized around precarbenic diazo carbon. To this aim, a series of precursor diphenyldiazomethanes bearing various substituents at the ortho positions as kinetic protectors have been prepared. Triplet diphenylcarbenes (DPCs) generated by photolysis of these precursory diazomethanes are actually fairly stable, and some of them can survive a day in solution at room temperature.[1] A species surviving a day is very stable for a triplet carbene but still ephemeral as a real molecule.

This approach has a serious pitfall. Because diazo functional groups are generally labile, these groups should be introduced at the last step of synthesis. Scheme 1 outlines the procedure employed to prepare those sterically congested diphenyldiazomethanes.[6] This indicates that kinetic protectors are introduced in the main framework before diazo groups are constructed. This automatically requires that the kinetic protectors should not be large enough to prevent a subsequent chemical procedure for constructing the diazo group. In other words, the carbene generated from such a diazo precursor should also have a space to be quenched by accepting a reagent externally. This synthetic dilemma needs to be overcome so that a stable triplet carbene can be realized.

We found that a precursory diphenyldiazomethane for a persistent triplet carbene is also persistent for a diazo compound and, hence, can be further modified with the diazo group intact to a more complicated diazo compound. For instance, bis(2,4,6-tribromophenyl)diazomethane survives under Sonogashira coupling reaction[7] conditions and undergoes substitution with trimethylsilylacetylene at the para positions leading to bis(2,6-dibromo-4-trimethylsilylethynylphenyl)diazomethane.[8] This is obvi-

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(1) See for reviews: (a) Tomioka, H. *Acc. Chem. Res.* **1997**, *30*, 315. (b) Tomioka, H. In *Advances in Carbene Chemistry*; Brinker, U., Ed.; JAI Press: Greenwich, CT, 1998; Vol. 2, pp 175−214. (c) Tomioka, H. In *Carbene Chemistry*; Bertrand, G., Ed.; Fontis Media S.A.: Lausanne, 2002; pp 103−152.

(2) Igau, A.; Grützmacher, H.; Baceiredo, A.; Bertrand, M. *J. Am. Chem. Soc.* **1988**, *110*, 6463. See also: Bourissou, D.; Guerret, O.; Gabbai, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39.

(3) Arduengo, A. J., III; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1991**, *113*, 361. See also: Arduengo, A. J., III. *Acc. Chem. Res.* **1999**, *32*, 913.

(4) See for review: (a) Rajca, A. *Chem. Rev.* **1994**, *94*, 871. (b) Iwamura, H. *Adv. Phys. Org. Chem.* **1990**, *26*, 179. (c) *Magnetic Properties of Organic Materials*; Lahti, P. M., Ed.; Marcel Dekker: New York, 1999.

(5) Kirmse, W. *Angew. Chem., Int. Ed.* **2003**, *42*, 2117.

(6) Procedures to prepare sterically congested diphenyldiazomethanes were originally invented by Zimmerman and Paskovich. See: Zimmerman, H. E.; Paskovich, D. H. *J. Am. Chem. Soc.* **1964**, *86*, 2149.

(7) Sonogashira, K. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, U.K., 1991; Vol. 3, pp 521−549.

(8) Tomioka, H.; Hattori, M.; Hirai, K.; Sato, K.; Shiomi, D.; Takui, T.; Itoh, K. *J. Am. Chem. Soc.* **1998**, *120*, 1106.

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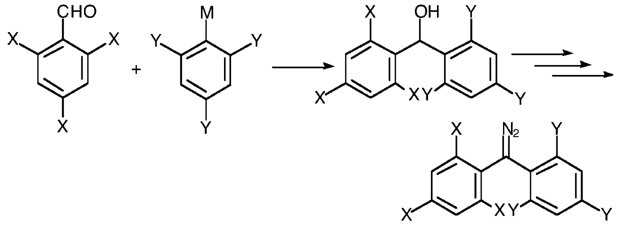
SCHEME 1



ously due to the fact that the kinetic protectors introduced to protect the carbene center from an external reagent are also able to protect the diazo carbon.

Whether even the bromine group at the ortho position can also be replaced by a substituent with the diazo group intact is still questionable. If this were possible, it might be possible to introduce a new (possibly more effective) kinetic protector *after* the diazo group is introduced. To test this idea, we have attempted exhaustive ethynylation of polybrominated diphenyldiazomethane.

Results

Reaction of Brominated Diphenyldiazomethane with Trimethylsilylacetylene. The substrate chosen for the attempt was (2,4,6-tribromophenyl)(4-*tert*-butyl-2,6-dimethylphenyl)diazomethane (**1a**),[9] in which bromine groups on one side of the phenyl ring are replaced with alkyl groups in order to decrease the possible complexity due to multisubstitution. The reaction of the diazomethane with 2 equiv of trimethylsilylacetylene in the presence of $(PPh_3)_2PdCl_2$/CuI in NEt_3 at room temperature gave a para-monosubstituted product, (4-trimethylsilylethynyl-2,6-dibromophenyl)(4-*tert*-butyl-2,6-dimethylphenyl)diazomethane (**1b**), in 90% yield, along with a small amount of a disubstituted one, [2,4-bis(trimethylsilylethynyl)-6-bromophenyl](4-*tert*-butyl-2,6-dimethylphenyl)diazomethane (**1c**), no trisubstituted product being isolated. When **1b** was treated with 7 equiv of the acetylene at 45 °C for 1 day, **1c** was formed in 30% yield along with a small amount of trisubstituted product, [2,4,6-tris(trimethylsilylethynyl)phenyl](4-*tert*-butyl-2,6-dimethylphenyl)diazomethane (**1d**). On the other hand, when **1c** was reacted with 10 equiv of the acetylene at 45 °C for 1 day, **1d** was obtained in 17% yield. Reactions at a temperature higher than this resulted in a significant loss of the diazo functional group.

All of the diazomethanes were purified by alumina column chromatography at −10 °C followed by repeated chromatography on a gel permeation column. They were rather stable for substituted diazomethanes and could be stored in a refrigerator for several months without any appreciable decomposition. The structure of these diazo compounds was characterized by ^1H and ^{13}C NMR and IR.

Spectroscopic Studies. (a) ESR Studies in Rigid Matrix at Low Temperature. The characterization of triplet carbenes generated from these ethynylated diphenyldiazomethanes was then spectroscopically carried out. Irradiation ($\lambda > 300$ nm) of the monosubstituted one (**1b**) in a 2-methyltetrahydrofuran (2-MTHF) glass at 77 K gave rise to ESR spectra (Figure 1a) characteristic of randomly oriented triplet molecules.[10] The zero-field splitting (ZFS) parameters were $D = 0.419$ cm^{-1} and $E = 0.0317$ cm^{-1}, showing unequivocally that triplet signals are due to triplet (4-trimethylsilylethynyl-2,6-dibromophenyl)(4-*tert*-butyl-2,6-dimethylphenyl)carbene (^{3}**2b**) generated by the photodissociation of **1b**.

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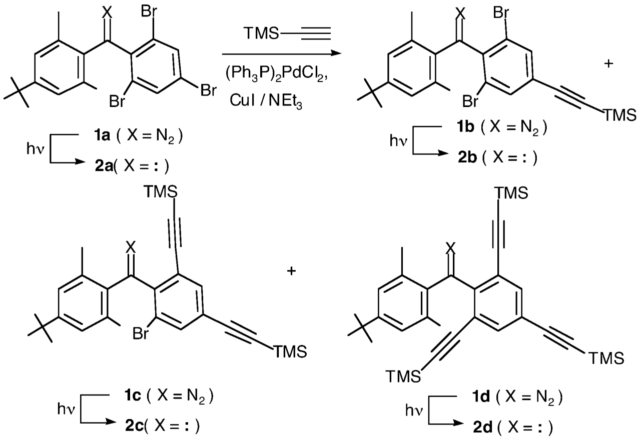

Essentially identical ESR signals attributable to triplet carbenes are observed in the similar photolysis of other precursor diazomethanes (**1c** as well as **1d**).[11] The signals are analyzed in terms of *D* and *E* values, which are reported in Table 1. The parameters of triplet diphenylcarbene (^{3}**2a**)[9] before ethynylation are also included for the sake of comparison.

(b) UV−vis Studies in a Rigid Matrix at Low Temperature. Photolysis ($\lambda > 300$ nm) of **1b** in 2-MTHF glass at 77 K resulted in the appearance of new bands at the expense of the original absorption due to **1b** (Figure 2). The new bands consist of two identifiable features, a strong and sharp maximum at 308 and 330 nm and a broad and weak band tailing from 400 to 500 nm.[10] These features are usually present in the spectrum of triplet diarylcarbenes. The glassy solution did not exhibit any changes for hours when kept at 77 K, but it disappeared completely after a brief thawing to room temperature. On the basis of these observations, coupled with the fact that ESR signals due to triplet diarylcarbene are observed under identical conditions, the absorption spectrum is attributable to the triplet carbene (^{3}**2b**).

The thermal stability is then estimated by raising the sample temperature in 10 K increments to the desired temperature, allowing the sample to stand for 5 min, and

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[9] (a) Tomioka, H.; Watanabe, T.; Hirai, K.; Furukawa, K.; Takui, T.; Itoh, K. *J. Am. Chem. Soc.* **1995**, *117*, 6376. (b) Tomioka, H.; Hattori M.; Hirai, K. *J. Am. Chem. Soc.* **1996**, *118*, 8723. (c) Tomioka, H.; Watanabe, T.; Hattori, M.; Nomura, N.; Hirai, K. *J. Am. Chem. Soc.* **2002**, *124*, 474. (d) Hirai, K.; Iikubo, T.; Tomioka, H. *Chem. Lett.* **2002**, 1226.

[10] See for reviews of the EPR and UV−vis spectra of triplet carbenes: (a) Sander, W.; Bucher, G.; Wierlacher, S. *Chem. Rev.* **1993**, *93*, 1583. (b) Trozzolo, A. M.; Wasserman, E. In *Carbenes*; Jones, M., Jr., Moss, R. A., Eds.; Wiley: New York, 1975; Vol. 2, pp 185−206. (c) Tomioka, H. In *Advances in Strained and Interesting Organic Molecules*; Halton, B., Ed.; JAI Press: Greenwich, CT, 2000; Vol. 8, pp 83−112.

[11] In the ESR spectra obtained by the photolysis of **1c**, the bands not marked with X, Y, and Z could not be assigned properly, except that at 333.6 mT attributable to fortuitous doublet species. As these signals are only observed for **1c**, in which two ortho substituents on one side of the phenyl ring are not same, they may be signals due to a conformer of triplet carbene ^{3}**2c**. However, we could not properly analyze the signals in terms of ZFS parameters.

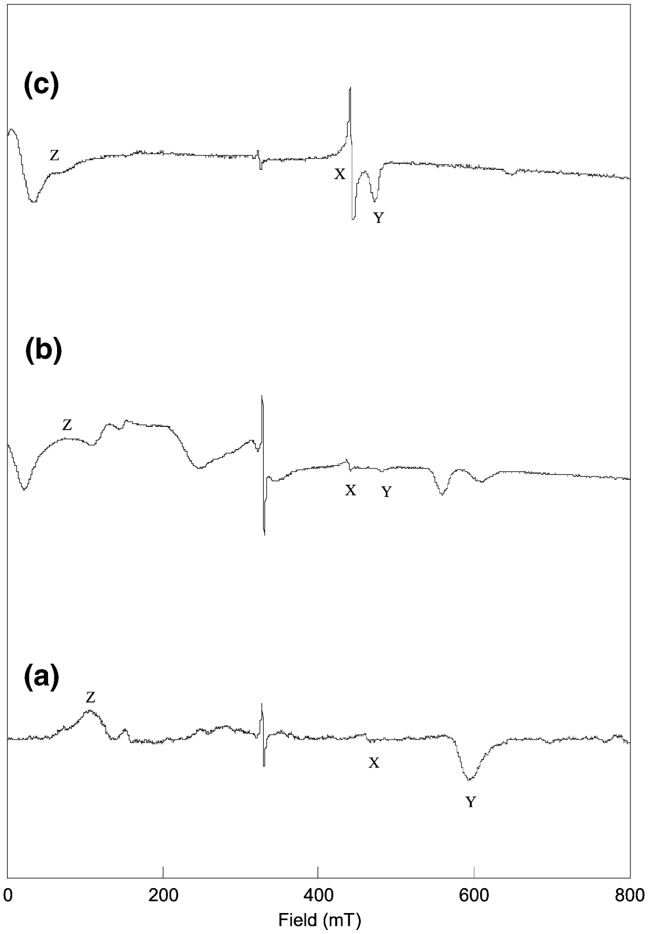

FIGURE 1. EPR spectra obtained after irradiation of (a) **1b**, (b) **1c**, and (c) **1d** in 2-MTHF at 77 K.

TABLE 1. ***D* and *E* Values for Triplet Diarylcarbenes**[a]

carbenes	D (cm^{-1})	E (cm^{-1})	E/D
2a	0.423	0.0326	0.0771
2b	0.419	0.0317	0.0756
2c	0.328	0.0093	0.0285
2d	0.348	0.011	0.0316

[a] Measured in 2-methyltetrahydrofuran at 77 K.

measuring the absorption bands. The characteristic bands due to ^{3}**2b** started to decay slowly at 120 K and decayed rather sharply at 160 K. Similar irradiation of **1c** and **1d** also gave absorption bands ascribable to the corresponding triplet carbenes, ^{3}**2c** and ^{3}**2d**, respectively (Figures S1 and S2, Table 2). The spectrum of ^{3}**2c** and ^{3}**2d** exhibited rather sharp bands at 390 and 405 nm, respectively, in addition to a sharp and strong band at 315 and 416 nm and a weak, broad band in the visible region.

Upon thawing the matrix, those bands for ^{3}**2c** and ^{3}**2d** also disappeared irreversibly at around 160 K, indicating similar thermal stability.

To determine the stability of the present carbenes more accurately, the lifetime is estimated at room temperature in degassed benzene, in which we measured the lifetime of a series of sterically congested diarylcarbenes.[1]

Laser flash photolysis (LFP) of **1b** (1.6×10^{-4} M) in a degassed benzene solution at room temperature with a 10 ns, 10 mJ, and 308 nm pulse from a XeCl laser produced a transient species showing a band with a maximum at 310 and extending to 500 nm, which appeared coincident with the pulse (Figure 3). Because of the overlaps with the absorption maxima of the diazo precursor **1b**, the samples are not sufficiently transparent for adequate monitoring in the 320−360 nm region. Therefore direct comparison of the spectrum with that of ^{3}**2b** observed in the photolysis of **1b** in matrix at low temperature was not possible. It is likely that we are observing the tailing part of the absorption band due to ^{3}**2b**. This assignment was supported by trapping experiments (vide infra). All absorption bands decayed in a similar manner. The inset in Figure 3 shows the decay of ^{3}**2b** in the absence of trapping reagents, which is found to be of the second-order ($2k/\epsilon l = 1.27$ s^{-1}). The rough lifetime of ^{3}**2b** is estimated in the form of half-life, $t_{1/2}$, to be 1.3 ± 0.1s.

Support is lent to this assignment by trapping experiments using oxygen. When LFP was carried out on a nondegassed benzene solution of **1b**, the half-life of ^{3}**2b** decreased dramatically, and a broad absorption band with a maximum at 420 nm appeared at the expense of the absorption due to ^{3}**2b** (Figure 4). The spent solution was found to contain the corresponding benzophenone (**4b**) as the main product. It is well documented[12,13] that diarylcarbenes with triplet ground states are readily trapped by oxygen to generate the corresponding diaryl ketone oxides, which show a broad absorption band centered at 396−450 nm. Thus, the observations can be interpreted as indicating that ^{3}**2b** is trapped by oxygen to form the carbonyl oxide (**3b**), which confirms that the transient absorption quenched by oxygen is due to ^{3}**2b**.

The apparent built-up rate constant, k_{obs}, of the carbonyl oxide (**3b**) is essentially identical with that of the decay of ^{3}**2b** (inset in Figure 4), and k_{obs} is expressed as

$$k_{obs} = k_0 + k_{O_2}[O_2] \qquad (1)$$

where k_0 represents the rate of decay of ^{3}**2b** in the absence of oxygen and k_{O_2} is the quenching rate constant of ^{3}**2b** by oxygen. The plot of the observed pseudo-first-order rate constant of the formation of the oxide against [O$_2$] is linear (Figure 5). From the slope of this plot, k_{O_2} was determined to be 1.8×10^7 M^{-1} s^{-1}, which is approximately 2 orders of magnitude smaller than that observed with the “parent” ^{3}DPC ($k_{O_2} = 5.0 \times 10^9$ M^{-1} s^{-1}).[13]

When a degassed benzene solution of **1b** containing 1,4-cyclohexadiene (CHD) was excited, a new species was formed, showing an absorption with $\lambda_{max} = 390$ nm, which formed as the 310 nm signal of ^{3}**2b** decayed (Figure 6). The decay of ^{3}**2b** was again found to be kinetically correlated with the growth of the new species. Thus, this new signal was attributable to the diphenylmethyl radical (**5b**) formed as a result of the H abstraction of ^{3}**2b** from the diene, since it is now well documented[14,15] that triplet arylcarbenes, generated in good hydrogen-donor solvents, undergo H abstraction leading to the corresponding radicals, which show transient absorptions at

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[12] See for review: Sander, W. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 344. (b) Bunnelle, W. *Chem. Rev.* **1991**, *91*, 336.

[13] Scaiano, J. C.; McGimpsey, W. G.; Casal, H. L. *J. Org. Chem.* **1989**, *54*, 1612.

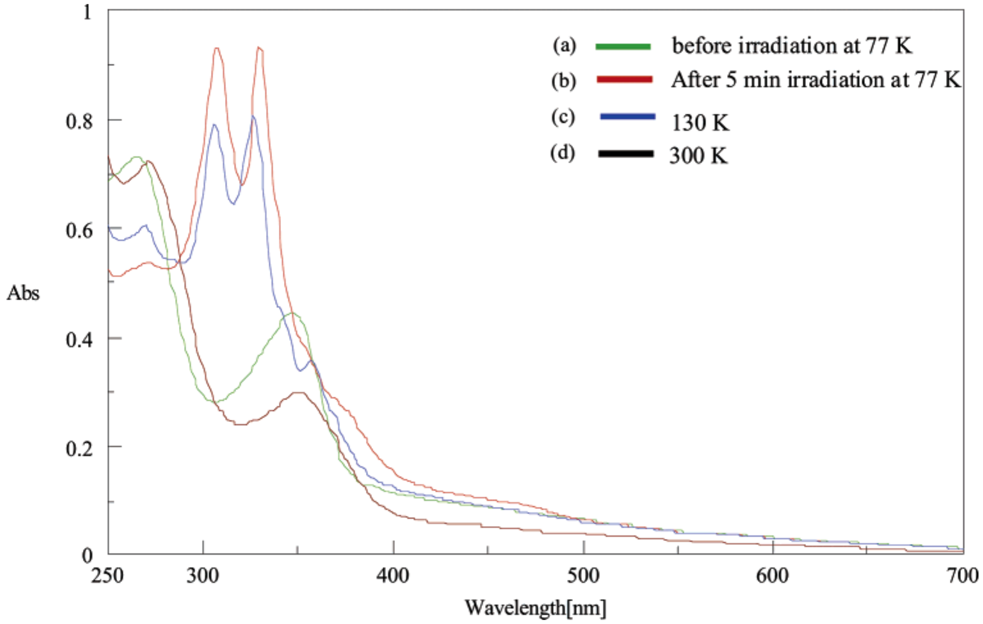

FIGURE 2. UV−vis spectral changes observed in the photolysis of **1b**. (a) UV−vis spectrum of **1b** in 2-MTHF at 77 K. (b) Same sample after 5-min irradiation (λ > 300 nm). (c, d) Same sample after thawing the matrix at 130 (c) and 300 K (d).

TABLE 2. UV−Vis Spectra of Triplet Diarylcarbenes

carbenes	$\lambda_{max}{}^{a}$ (nm)	$T_{d}{}^{b}$ (K)
2a	327, 348	160
2b	308, 330	160
2c	315, 390	160
2d	416, 405	160

[a] Measured in 2-methyltetrahydrofuran at 77 K. [b] Temperature at which the UV−vis spectra of triplet diarylcarbenes disappeared.

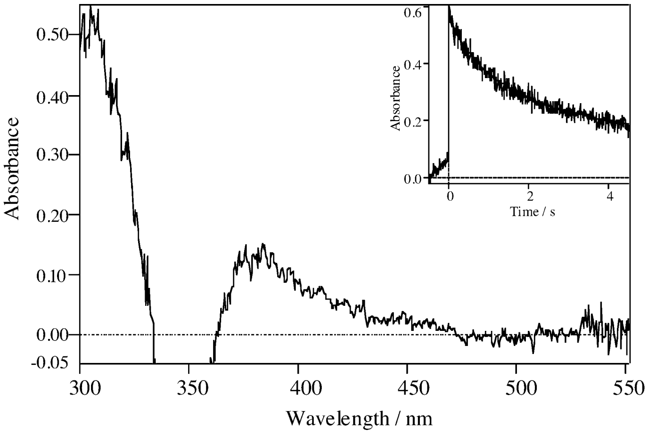

FIGURE 3. Transient absorption spectra obtained in LFP of **1b** in degassed benzene with a 308-nm excimer laser recorded 100 μs after the pulse. Inset shows oscillogram traces monitored at 310 nm.

wavelengths longer than those of the precursor carbenes. The excellent hydrogen-donor properties of CHD have been well recognized.[16] The plot of the observed pseudo-first-order rate constant of the formation of the radical against [CHD] is linear (Figure 7), and the slope of this plot yields the absolute rate constant for the reaction of ^{3}**2b** with the diene, $k_{CHD} = 1.7 \times 10^{2}$ M^{-1} s^{-1}, which is some 5 orders of magnitude smaller than that observed with ^{3}DPC ($k_{CHD} = 1 \times 10^{7}$ M^{-1} s^{-1}).[14c]

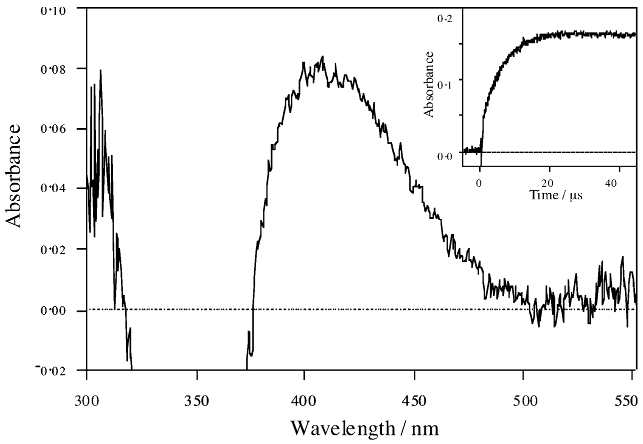

FIGURE 4. Transient absorption spectra obtained in LFP of **1b** in nondegassed benzene with a 308-nm excimer laser recorded 10 μs after the pulse. The inset shows a plot of the growth of the oxide (**3b**) monitored at 440 nm as a function of time.

Again, similar measurements have been done for other carbenes ^{3}**2c** and ^{3}**2d** (Figures S3−S8), and the results are summarized in Table 3, which also includes the data of ^{3}**2a** for the sake of comparison.

Discussion

Effect of *o*-Ethynyl Group on the Structure of Triplet Diphenylcarbenes. The structure of triplet

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(14) For reviews see: (a) Platz, M. S. *Kinetics and Spectroscopy of Carbenes and Biradicals*; Plenum: New York, 1990. (b) Jackson, J. E.; Platz, M. S. In *Advances in Carbene Chemistry*; Brinker, U., Ed.; JAI Press: Greenwich, CT, 1994; Vol. 1, pp 87−160. See also: (c) Closs, G. L.; Rabinow, B. E. *J. Am. Chem. Soc.* **1976**, *98*, 8190.

(15) Hadel, L. M.; Maloney, V. M.; Platz, M. S.; McGimpsey, W. G.; Scaiano, J. C. *J. Phys. Chem.* **1986**, *90*, 2488.

(16) Encinas, M. V.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 6393.

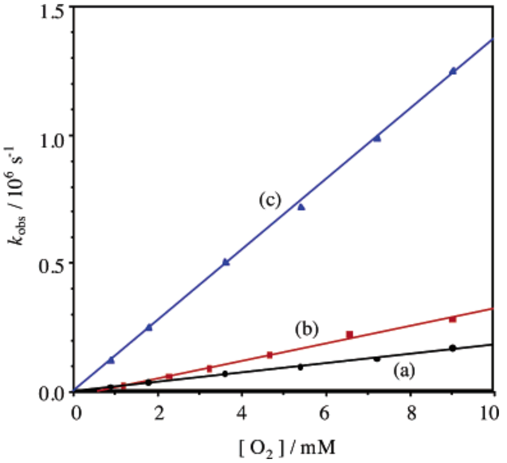
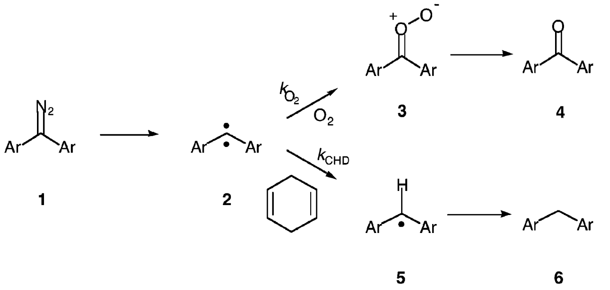


FIGURE 5. Plot of the growth rate of the oxide (**3**) monitored at 440 nm for **3b** (a), **3c** (b), and **3d** (c) as a function of the concentration of oxygen.

SCHEME 3



carbenes is characterized by ESR ZFS parameters *D* and *E*. The *D* value is related to the separation between the unpaired electrons.[10] The *E* value, on the other hand, when weighed by *D*, is a measure of the deviation from axial symmetry. For diarylcarbenes, this value will, thus, depend on the magnitude of the central C−C−C angle. Because the *E* value depends on the magnitude of the central angle, the reduction in *E* indicates that the carbene adopts a structure with an expanded C−C−C angle upon annealing. This interpretation is supported by the observation that the substantial reduction of *E* is usually accompanied by a significant reduction in *D*, indicating that the electrons are becoming more delocalized.

The slight decrease in *D* values on going from ^{3}**2a** to ^{3}**2b** is interpreted as indicating that unpaired electrons are delocalized into the ethynyl group at the para position. A significant decrease in both *D* and *E*/*D* values on going from ^{3}**2b** to ^{3}**2c** then suggests that, as one more ethynyl group is introduced at the ortho position, unpaired electrons are more delocalized into the substituents simply because of the increasing number of the accepting group. This may also indicate that the central bond angle is expanded as a result of an increased ortho interaction induced by the trimethylsilylethynyl group. However, the *D* and *E*/*D* values *increased* slightly on going from ^{3}**2c** to ^{3}**2d**, which was not expected in this interpretation. It is interesting to note here in this connection that significant changes are observed in UV−vis spectra on going from ^{3}**2c** to ^{3}**2d**. It may be, then, that the additional effect of the *o*-ethynyl group is not large enough to affect the ESR ZFS parameters. The spectroscopic features provide no evidence for significant through-space interaction between carbene centers and *o*-ethynyl substituents.

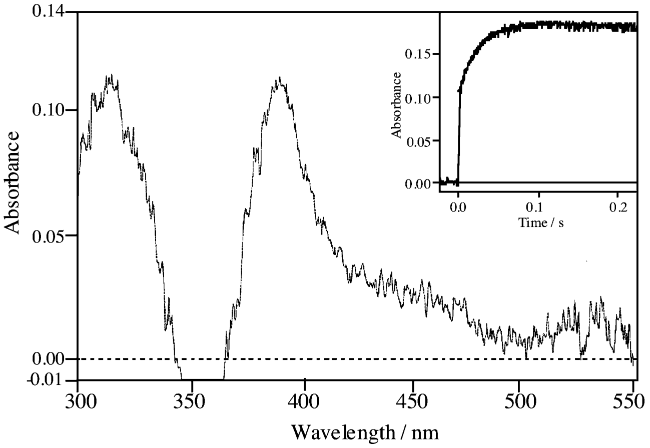


FIGURE 6. Transient absorption spectra obtained in LFP of **1b** in degassed benzene in the presence of 1,4-cyclohexadiene (CHD) with a 308-nm excimer laser recorded 100 ms after the pulse. The inset shows a plot of the growth of the radical (**5b**) monitored at 400 nm as a function of time.

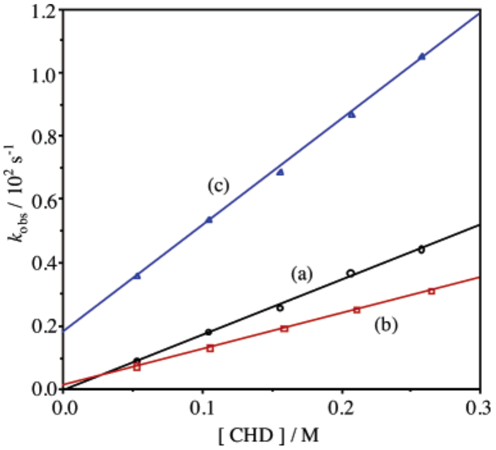


FIGURE 7. Plot of the growth rate of the radicals (**5**) monitored at 400 nm for **5b** (a), at 410 nm for **5c** (b), and at 440 nm for **5d** (c) as a function of the concentration of the diene.

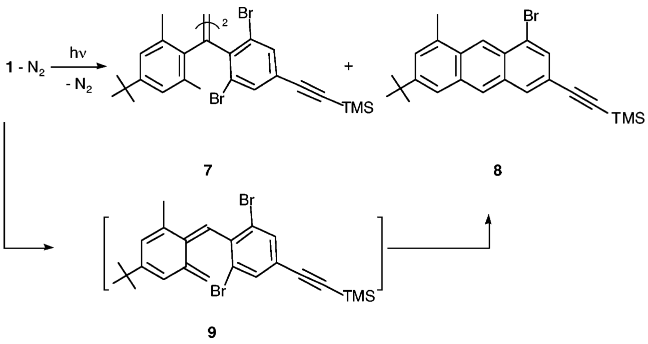
TABLE 3. Kinetic Data for Triplet Diarylcarbenes[a]

carbenes	*k* (s^{-1})	τ (s)	k_{O_2} (M^{-1} s^{-1})	k_{CHD} (M^{-1} s^{-1})
2a	(9.7)[b]	(0.55)[c]	3.1×10^7	3.6×10^2
2b	(1.27)[b]	(1.3)[c]	1.8×10^7	1.7×10^2
2c	0.33	3.0	3.5×10^7	1.0×10^2
2d	3.95	0.25	1.4×10^8	3.4×10^2

[a] All kinetic measurements were carried out in benzene at 20 °C. [b] In $2k/\epsilon l$. [c] Half-life.

Theoretical calculations provided information on the effect of the *o*-ethynyl group on the structure of triplet diphenylcarbenes. Thus, optimized geometries calculated for three model triplet (2-X-6-Y-phenyl)(2,6-dimethylphenyl)carbene systems, where the substituents X/Y are varied from Br/Br (**2a′**) to Br/ethynyl (**2c′**) to ethynyl/ethynyl (**2d′**), by DFT(UB3LYP/6-31G(d)) suggest that the angle of the carbene center (α) *decreases* as the substituents X/Y are changed from Br/Br (α = 171.5°) to

SCHEME 4



Br/ethynyl ($\alpha = 163.2°$) to ethynyl/ethynyl ($\alpha = 160.6°$) (Figures S9−S11). This indicates that the steric interaction decreases as the *o*-bromine group is replaced with the *o*-ethynyl group. The bond distance between the aromatic ortho carbon and the *o*-bromine atom in **2a′** is 1.905−1.906 Å, while that between the ortho carbon and *o*-ethynyl carbon in **2d′** is 1.423−1.424 Å, indicating that the *o*-ethynyl carbon is located closer to the carbenic carbon than the *o*-bromine group. However, the van der Waals radius of Br is larger than that of C. These differences result in the observed difference in the geometrical parameters between **2a′** and **2d′**. It is to be noted here that, although the steric repulsion of the *o*-trimethylsilylethynyl group with the methyl group on the opposite side of the benzene ring may not be as severe in comparison with that of the *o*-bromine groups, the large TMS group located at the end of the ethynyl carbon must overhang the reactive site and would, hence, be expected to prevent external reagents from approaching the carbene center.

Effect of *o*-Ethynyl Groups on the Stability of Triplet Diphenylcarbenes. Inspection of the data in Tables 2 and 3 suggests that replacement of the *o*-bromine group with the TMS ethynyl group would not result in a significant change in the stability of triplet DPCs. Thus, neither the thermal stability in the matrix at low temperature (T_d in Table 2) nor the half-life and/or lifetime in solution at room temperature (τ or $t_{1/2}$ in Table 3) show a particular trend as the bromine substituent is successively replaced with ethynyl groups. It is important to note here that the decay mode of the triplet carbene changed from second order to first order once an ethynyl group was introduced at the ortho position.

This suggests that carbenes ^{3}**2c** and ^{3}**2d** most likely decayed by reacting with the *o*-ethynyl group. Product analysis study supports the suggestion. Most persistent triplet DPCs decay by undergoing dimerization at the carbene center to give tetra(aryl)ethene.[1] Photolysis of **1b** (having no *o*-ethynyl groups) in degassed benzene also gave dimer, tetraarylethene (**7**), along with anthracene (**8**) (Scheme 4). The latter product is known to be obviously derived from *o*-quinodimethane derivative (**9**).[9c,d] These observations indicate that the decay pattern is not affected by a change in the substituent at the para position.

In marked contrast, similar irradiation of **1c** and **1d** (having ethynyl gropus at ortho positions) resulted in the formation of a tarry matter, from which no particular products could be isolated. When the photolysis was carried out in a degassed C_6D_6 solution sealed in an NMR tube and was monitored by ^{1}H NMR (300 MHz), new signals appeared at the initial stage of irradiation but did not grow significantly even though the starting compound decomposed. The product signals gradually disappeared when the sample was allowed to stand overnight. More interestingly, an ESR measurement of the mixture showed the presence of paramagnetic species even at room temperature.

It has been reported that triplet carbenes react with a carbon−carbon triple bond quite efficiently. For instance, triplet diphenylcarbene reacts with acetylenes in a stepwise fashion to give a triplet diradical, which eventually results in the formation of indene derivatives.[17] Triplet fluorenylidene reacts with phenylacetylene and other terminal acetylenes even at 77 K to give the corresponding triplet vinylcarbenes.[18] A more electrophilic triplet carbene, e.g., 4-oxo-2,3,5,6-tetrafluorocyclohexa-2,5-dienylidene, reacts with acetylene even at temperatures as low as 35 K.[19]

Therefore, it is likely that the triplet carbene center in ^{3}**2c** and ^{3}**2d** can be trapped by the ethynyl bond at the ortho position to generate a triplet diradical. Probably, the diradical cannot give a stable final product in a simple step, unlike in the case of intermolecular reaction, and hence leads to a complex reaction mixture. 2-(2-Ethynylphenyl)phenylcarbene undergoes intramolecular addition to the ethynyl group to give a cyclopropene derivative.[20] In the present case, an indenylidene in its triplet state may be formed as the cyclopropene from **2c** and **2d** would be highly strained. However, it was not possible to obtain evidence for the indene substructure as NMR signals of the product mixtures were very broad and weak.

As it is clear that there is a significant difference in the decay pathways between DPC having *o*-bromine groups and that having *o*-ethynyl groups, it is more useful to compare the reactivity toward typical triplet quenchers, i.e., oxygen and CHD, to examine the role of a kinetic protector on the reactivity of triplet DPC. Inspection of the data in Table 3 again indicated that there are no clear trends in the quenching rate constant to evaluate the effect of the ethynyl group on the reactivity of triplet DPC, as opposed to the bromine group.

Conclusion

The present investigation revealed that sterically congested diphenyldiazomethanes, precursors for persistent triplet carbenes, are also fairly persistent and can be further modified with the diazo group intact. Although, in the present study, a new kinetic protector introduced by using this method is reactive with the triplet carbene center and hence cannot effectively protect the carbenic center, it will be basically possible to introduce a bulkier

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and less reactive protector so as to generate a more persistent triplet carbene. A study along this line is in progress in this laboratory.

Experimental Section

Preparation of {2,6-Dibromo-4-(trimethylsilyl)ethynylphenyl}(2,6-dimethyl-4-*tert*-butylphenyl)diazomethane (1b). A mixture of (2,4,6-tribromophenyl)(2,6-dimethyl-4-*tert*-butylphenyl)diazomethane (**1a**, 93 mg, 0.18 mmol), $(Ph_3P)_2PdCl_2$ (10 mg, 0.032 mmol), and CuI (5 mg, 0.03 mmol) in anhydrous triethylamine (1 mL) was stirred at room temperature under an Ar atmosphere for 1 h. Trimethylsilylacetylene (50 μL, 0.36 mmol) was added to the mixture, and stirring was continued for 1 day. The solution was evaporated, and the residue was chromatographed on a silica gel column eluted with *n*-hexane. The resulting crude product was purified by repeated chromatography on a gel permeation column with $CHCl_3$. Diazomethane **1b** was obtained as an orange viscous liquid in 89% yield: ^{1}H NMR ($CDCl_3$) δ 7.66 (s, 2H), 7.07 (s, 2H), 2.14 (s, 6H), 1.30 (s, 9H), 0.25 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 151.2, 137.7, 136.4, 132.8, 126.2, 124,9, 124.8, 124.6, 101.8, 98.2, 63.9, 34.6, 31.5, 21.4, 0.0; IR (NaCl) ν 2066 cm^{-1}.

Preparation of [2-Bromo-4,6-bis{(trimethylsilyl)ethynylphenyl}](2,6-dimethyl-4-*tert*-butylphenyl)diazomethane (1c). A mixture of monotrimethylsilylethynylated diazomethane (**1b**, 25 mg, 0.047 mmol), $(Ph_3P)_2PdCl_2$ (3 mg, 0.009 mmol), and CuI (2 mg, 0.01 mmol) in anhydrous triethylamine (300 μL) was stirred at room temperature under an Ar atmosphere for 1 h. Trimethylsilylacetylene (50 μL, 0.36 mmol) was added to the mixture, and stirring was continued at 45 °C for 1 day. The solution was evaporated and purified by repeated chromatography on a gel permeation column with $CHCl_3$. Diazomethane **1c** was obtained as an orange solid in 30% yield: ^{1}H NMR ($CDCl_3$) δ 7.62 (d, J = 1.83 Hz, 2H), 7.56 (d, J = 1.79 Hz, 2H), 2.15 (s, 6H), 1.31 (s, 9H), 0.24 (s, 9H), 0.14 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 151.0, 137.9, 137.1, 136.8, 134.4, 125.8, 125.5, 123.8, 122.9, 122.5, 102.8, 102.5, 100.9, 96.9, 61.9, 34.5, 31.5, 21.3, 0.0; IR (NaCl) ν 2055 cm^{-1}.

Preparation of [2,4,6-Tris{(trimethylsilyl)ethynylphenyl}]-(2,6-dimethyl-4-*tert*-butyl-phenyl)diazomethane (1d). A mixture of bis(trimethylsilyl)ethynylated diazomethane (**1c**, 12 mg, 0.038 mmol), $(Ph_3P)_2PdCl_2$ (3 mg, 0.009 mmol), and CuI (2 mg, 0.01 mmol) in anhydrous triethylamine (200 μL) was stirred at room temperature under an Ar atmosphere for 1 h. Trimethylsilylacetylene (50 μL, 0.36 mmol) was added to the mixture, and stirring was continued at 45 °C for 1 day. The solution was evaporated and purified by repeated chromatography on a gel permeation column with $CHCl_3$. Diazomethane **1d** was obtained as an orange viscous liquid in 17% yield: ^{1}H NMR ($CDCl_3$) δ 7.52 (s, 2H), 7.07 (s, 2H), 2.17 (s, 6H), 1.31 (s, 9H), 0.23 (s, 9H), 0.11 (s, 18H); ^{13}C NMR ($CDCl_3$) δ 150.7, 138.2, 137.8, 131.2, 125.7, 125.6, 121.9, 120.8, 105.3, 101.2, 95.8, 61.1, 34.5, 31.5, 29.3, 0.0; IR (NaCl) ν 2066 cm^{-1}. Diazomethane **1c** was recovered in 33% yield.

Irradiation for Product Analysis. In a typical run, a solution of the diazo compound (**1**, ca. 10 mg) in solvent was placed in a Pyrex tube and irradiated with a high-pressure, 300-W mercury lamp until all of the diazo compound was destroyed. The irradiation mixture was then concentrated on a rotary evaporator below 20 °C. Individual components were isolated by column chromatography or by preparative TLC and identified by NMR and MS.

EPR Measurements. The diazo compound was dissolved in 2-methyltetrahydrofuran (10^{-3} M), and the solution was degassed in a quartz cell by three freeze-degas-thaw cycles. The sample was cooled in an optical transmission EPR cavity at 77 K and irradiated with a 500-W Xe or Hg lamp using a Pyrex filter. EPR spectra were measured on an ESR spectrometer (X-band microwave unit, 100 kHz field modulation). The signal positions were read by the use of a gaussmeter. The temperature was controlled by a digital temperature indicator/controller, which provided accuracy of the measurements within $\pm$0.1 K and of the control ability within $\pm$0.2 K. Errors in the measurements of component amplitudes did not exceed 5%, and the accuracy of the resonance field determination was within $\pm$0.5 mT.

Low-Temperature UV−vis Spectra. Low-temperature spectra at 77 K were obtained by using a variable-temperature liquid-nitrogen cryostat equipped with a quartz outer window and a sapphire inner window. The sample was dissolved in dry 2-MTHF, placed in a long-necked quartz cuvette of 1-mm path length, and degassed thoroughly by repeated freeze-degas-thaw cycles at a pressure near 10^{-5} Torr. The cuvette was flame-sealed under reduced pressure, placed in the cryostat, and cooled to 77 K. The sample was irradiated for several minutes in the spectrometer with a 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 a temperature controller.

Flash Photolysis. All flash measurements were made on a flash spectrometer. Three excitation light sources were used depending on the precursor absorption bands and lifetime of the transient species. They were (i) a cylindrical 150-W Xe flash lamp (100 J/flash with 10 μs pulse duration), (ii) a Nd:YAG laser (355 nm pulses of up to 40 mJ/pulse and 5−6 ns duration; 266 nm pulses of up to 30 mJ/pulse and 4−5 ns duration), and (iii) a XeCl excimer laser (308 nm pulses of up to 200 mJ/pulse and 17 ns duration). The beam shape and size were controlled by a focal length cylindrical lens.

A 150-W xenon short arc lamp (L 2195) was used as the probe source, and the monitoring beam, guided using an optical fiber scope, was arranged in an orientation perpendicular to the excitation source. The probe beam was monitored with a photomultiplier tube through a linear image sensor (512 photodiodes used). The timing of the excitation pulse, the probe beam, and the detection system was achieved through a digital synchroscope interfaced to a computer. This allowed for rapid processing and storage of the data and provided printed graphic capabilities. Each trace was also displayed on a monitor.

A sample was placed in a long-necked Pyrex tube with a sidearm connected to a quartz fluorescence cuvette and degassed using a minimum of four freeze-degas-thaw cycles at a pressure near 10^{-5} Torr immediately prior to being flashed. The sample system was flame-sealed under reduced pressure, and the solution was transferred to the quartz cuvette that was placed in the sample chamber of the flash spectrometer. A cell holder block of the sample chamber was equipped with a thermostat and allowed to come to thermal equilibrium. The concentration of the sample was adjusted so that it absorbed a significant portion of the excitation light. For experiments in which the rate constant for reaction of oxygen with carbenes was determined, varying concentration of oxygen in nitrogen were bubbled through the solution.[13]

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Supporting Information Available: UV−vis spectra of **2c** and **2d** (Figures S1 and S2), time-resolved UV−vis spectra of **2c** and **2d** in the absence and presence of oxygen or 1,4-cyclohexadiene (Figures S3−S8), optimized geometries of **2a′**, **2c′**, and **2d′** (Figures S9−S11), Gaussian archives entries (Table S1), and NMR spectra of **1a**, **1b**, **1c**, and **1d**. This material is available free of charge via the Internet at http://pubs.acs.org.

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