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Preparation of Bis(diazo) Compounds Incorporated into Butadiyne and Thiophene Units, and Generation and Characterization of Bis(carbene) From These Compounds

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Received April 9, 2004

[9-{10-(4-*t*-Butyl-2,6-dimethyl)phenyl}anthryl](4-bromo-2,6-dimethylphenyl)diazomethane (**1**−N_2) was found to be stable enough to survive under Sonogashira and Suzuki coupling reaction conditions, and bis(diazo) compounds incorporated into the 1,4-positions of butadiyne (**3**−2N_2) and the 2,5-position of thiophene (**4**−2N_2) were prepared. Irradiation of those bis(diazo) compounds generated bis(carbenes), which were characterized by ESR and UV−vis spectroscopic techniques in a matrix at low temperature, as well as time-resolved UV−vis spectroscopy in solution at room temperature. These studies revealed that both of the bis(carbenes), **3** and **4**, have a singlet quinoidal diradical ground state with a very small singlet−triplet energy gap of less than 1 kcal/mol. A remarkable increase in the lifetime of bis(carbenes) as opposed to that of monocarbene (**1**) was noted and was interpreted to indicate that bis(carbenes) are thermodynamically stabilized as a result of delocalization of unpaired electrons throughout a π-net framework. Despite the stability, both bis(carbenes) are readily trapped by molecular oxygen to afford bis(ketones) as main products.

A diazo compound[1] is an excellent precursor for a carbene and, hence, has been widely employed to generate and study carbenes.[2] Upon either heating or irradiation, it decomposes very efficiently and cleanly to eliminate nitrogen gas and leave only the carbene. Moreover, the reaction occurs even at very low temperatures in the solid phase, which makes the spectroscopic study of a carbene very easy. However, because of the inherent sensitivity of the diazo functional group, not only to heat or light but also to an acid or metal, this group is usually introduced at the last step of synthesis, which sometimes makes the usability of the group rather limited.

We found, more or less by chance, that a diphenyldiazomethane that has been prepared to generate a persistent triplet carbene is also persistent for a diazo compound and, hence, can be further modified into a more complicated diazo compound, leaving the diazo group intact. For instance, bis(2,4,6-tribromophenyl)diazomethane survives under Sonogashira coupling reaction conditions,[3] leading to bis(2,6-dibromo-4-trimethylsilylethynylphenyl)diazomethane.[4] It is both interesting and important to explore the applicability of this method, as it may open a door to a new route to organic magnetic materials. This report shows that the diaryldiazo unit can be connected to a butadiyne unit by an oxidative coupling reaction[5] of acetylene and to the thiophene ring by the Suzuki coupling reaction.[6] The characterization of the bis(carbene) generated from those bis(diazo) compounds is also reported.

Results

Preparation of Bis(diazo) Compounds. The starting diazo compound used in this study was [9-{10-(4-*t*-butyl-2,6-dimethyl)phenyl}anthryl](4-bromo-2,6-dimethylphenyl)diazomethane (**1**−N_2), which was prepared according to the procedure outlined in Scheme 1; this compound can generate a fairly persistent triplet carbene.[7,8] Treatment of **1**−N_2 with trimethylsilylacetylene in the presence of $(Ph_3P)_2PdCl_2$ and CuI at 40 °C for 2 days gave [9-{10-(4-*t*-butyl-2,6-dimethyl)phenyl}anthryl](4-trimethylsilylethynyl-2,6-dimethylphenyl)diazomethane (**2**−N_2) in 74% yield. Deprotection[9] of the TMS

[†] Chemistry Department for Materials.

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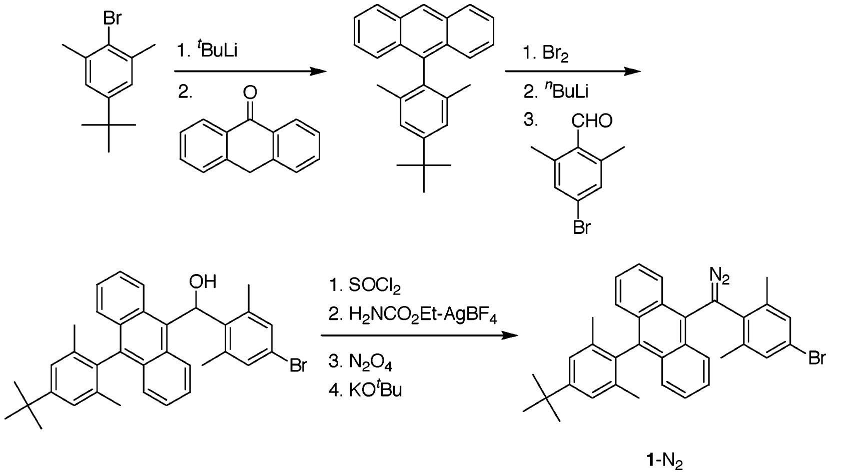
SCHEME 1



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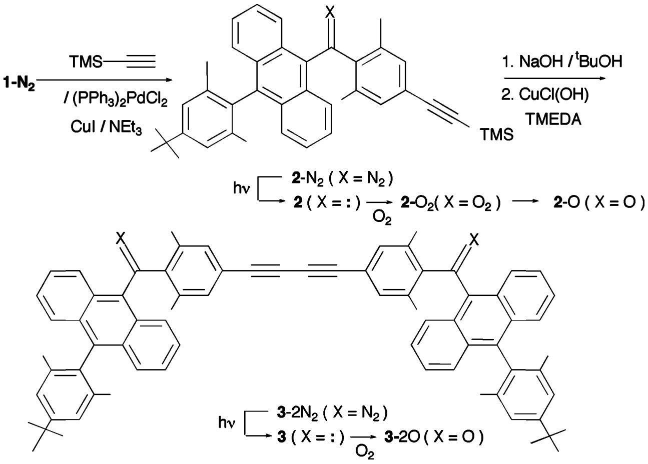

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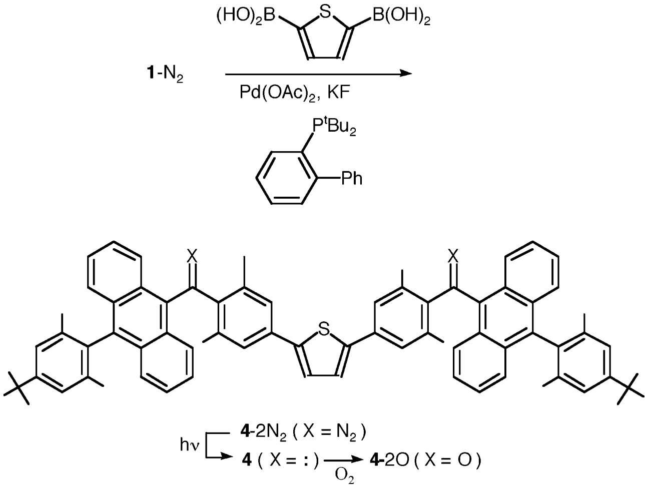

group with NaOH proceeded smoothly to give an ethynyl derivative in 80% yield. Stirring a mixture of ethynylated diazomethane and CuCl(OH)−TMEDA in CH_2Cl_2 under air[5] for 6 h at room temperature gave a bis(diazo) butadiyne compound (**3**−$2N_2$) in 57% yield (Scheme 2). ^{1}H NMR spectra of **3**−$2N_2$ showed no acetylenic protons, and ^{13}C NMR spectra showed the presence of acetylenic carbons at 81.8 and 74.4 ppm, which are shifted from 105.1 and 94.5 ppm in **2**−N_2. This NMR evidence suggests that acetylenic protons are lost while the acetylene bonds remain and are likely connected to carbons. Because diazo functional groups are not persistent enough to survive ionization processes during MS measurements, direct MS measurements were not possible. So, we photolyzed **3**−$2N_2$ in the presence of oxygen and analyzed the products by NMR and MS. From the reaction mixtures, we were able to isolate the diketone (**3**−2O) as the main product.

Attempts to convert the butadiyne portion of **3**−$2N_2$ to the thiophene ring by treatment with $Na_2S{\cdot}9H_2O$[10] in THF at 50 °C for 20 h resulted in the formation of a complex reaction mixture.

However, treatment of **1**−N_2 with thiophene diboronic acid under Suzuki coupling conditions[6] (i.e., in the presence of $Pd(OAc)_2$ as a catalyst, $P(^tBu)_2$(2-BP) (2-BP = 2-biphenylyl) as a ligand, and KF as a base in THF at 40 °C) gave 2,5-bis(3,5-dimethyl-4-[9-{10-(4-*t*-butyl-2,6-dimethyl)phenyl}anthryl]diazomethylphenyl)thiophene (**4**−$2N_2$) (Scheme 3). Again, irradiation of **4**−$2N_2$ in the presence of oxygen gave bis(ketone) **4**−2O as main product.

All of the procedures were carried out in the dark, and compounds were purified either by silica gel chromatography at ca. 0 °C and/or by repeated chromatography on a gel permeation column. No appreciable decomposition of the diazo group was noted, at least under the conditions employed here.

The results showed that the protected diazo compound is fairly persistent, and it can be used as a building block

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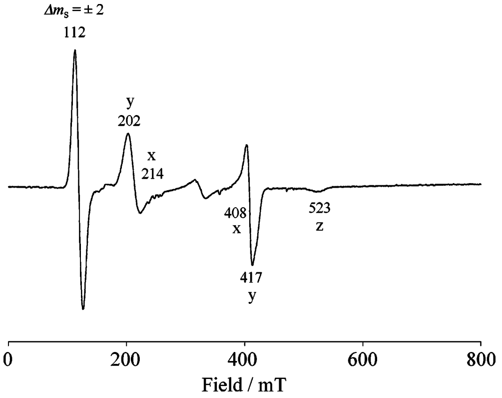

FIGURE 1. ESR spectra obtained by irradiation of monodiazo compound **2**−N_2 in 2-methyltetrahydrofuran at 77 K. The microwave frequency (ν_0) was 9.1327 GHz.

to construct a new poly(diazo) derivative from which a new magnetic system may be derived.

The characterization of the structure of the bis(carbene) expected to be generated upon photolysis of those bis(diazo) precursors is of great importance in view of recent, growing interest in spin molecules.[11,12] Thus, the products obtained by the photolysis of bis(diazo) compounds, **3**−$2\mathrm{N}_2$ and **4**−$2\mathrm{N}_2$, were characterized by ESR and UV−vis spectroscopy and compared with those from the corresponding mono-derivatives, **2**−N_2.

Spectroscopic Studies. ESR Studies. Irradiation of monodiazomethane **2**−N_2 in 2-methyltetrahydrofuran (2-MTHF) at 77 K gave ESR signals with typical fine structure patterns for nonoriented triplet species, i.e., ^{3}**2** (Figure 1).[13] The signals at 202, 214, 408, and 417 mT are assigned to a set of x and y transitions, and the signal at 523 mT is assigned to a high-field z transition from which the zero-field splitting (ZFS) parameters were obtained as $|D/hc| = 0.192$ cm^{-1} and $|E/hc| = 0.002\,75$ cm^{-1}. The values are similar to those observed for a series of triplet anthryl(aryl)carbenes.[7,14] The other signal at 112 mT is assigned to $\Delta m_s = \pm 2$ transitions.

Similar irradiation of a bis(diazo) compound (**3**−$2\mathrm{N}_2$) connected by a butadiyne bond in 2-MTHF at 70 K gave ESR signals (Figure 2a)that are different from those observed for the corresponding monocarbene, ^{3}**2**. The pattern of signals did not change from the initial to the latter stages of irradiation. The signals at 116, 206, and 412 mT are similar to those observed for ^{3}**2** and, hence, are attributable to a monocarbene presumably formed because of incomplete decomposition of **3**−$2\mathrm{N}_2$. The weak signals appearing from 298 to 352 mT are obviously different from those of the monocarbene triplet and are ascribable to bis(carbene), **3**. The major signals are reproduced well by computer simulation,[15,16] as shown in Figure 2g, employing a triplet Hamiltonian with $S = 1$, $g = 2.003$, $|D/hc| = 0.0474$ cm^{-1}, and $|E/hc| \approx 0$ cm^{-1}. Therefore, we assigned the new, fine-structured peaks to a triplet state of bis(carbene), most probably in its quinoidal form. Cooling the sample to 6 K resulted in a marked decrease of the signal (Figure 2c), but the signal was regained when the matrix was warmed. When the 2-MTHF glass was warmed to ~90 K, a new set of triplet

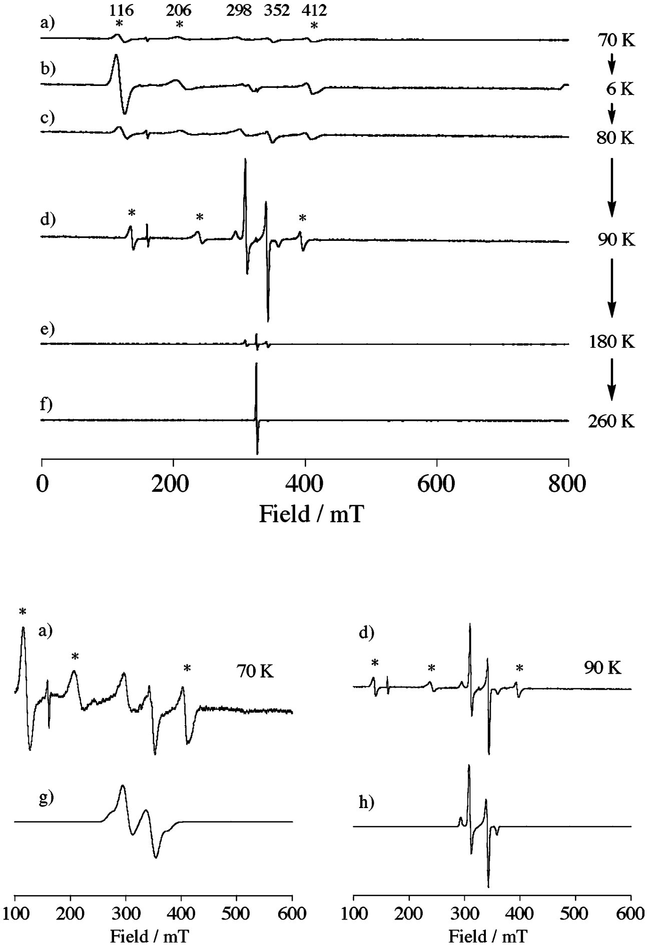

FIGURE 2. (a) ESR spectra obtained by irradiation of bis-(diazo) compound **3**−$2\mathrm{N}_2$ in 2-methyltetrahydrofuran at 70 K ($\nu_0 = 9.1320$ GHz). (b−f) The same spectra observed at 6 (b), 80 (c), 90 (d), 180 (e), and 260 (f) K. (g) Simulated spectra of ^{3}**3** with $S = 1$, $g = 2.003$, $|D/hc| = 0.0474$ cm^{-1}, $|E/hc| = 0$ cm^{-1}, and line width (ΔB) of 68 G. (h) Simulated spectra of ^{3}**3** with $S = 1$, $g = 2.003$, $|D/hc| = 0.0306$ cm^{-1}, $|E/hc| = 0.00$ cm^{-1}, and $\Delta B = 18$ G. Signals marked with asterisks (*) are due to a monocarbene.

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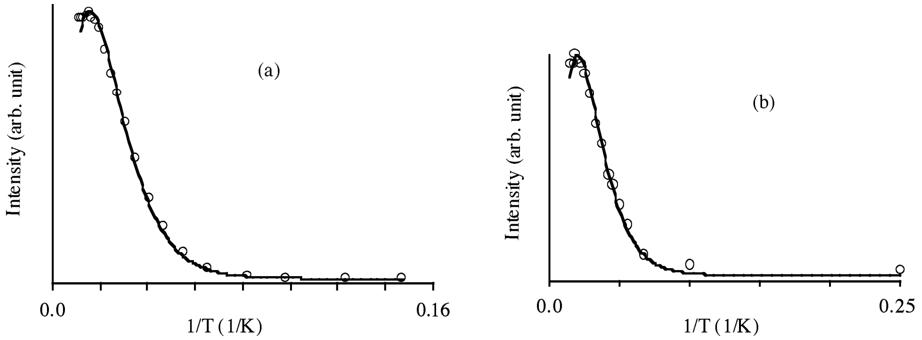

FIGURE 3. Plots of the intensities of the ESR signals (a) at 298 mT due to thermally populated $^{3}\mathbf{3}$ vs reciprocal of temperature (6−75 K), and (b) at 340 mT due to thermally populated $^{3}\mathbf{4}$ vs reciprocal of temperature (4.3−70 K).

peaks ($|D/hc| = 0.0306$ cm^{-1}, $|E/hc| \approx 0$ cm^{-1}) appeared at the expense of the original peaks (Figure 1d). These changes were not reversible: When the sample was cooled to 70 K, no change took place. Changes of this kind have often been observed for sterically congested triplet diarylcarbenes and are usually interpreted in terms of geometrical changes. The intensity of the signals increased up to 90 K and started to decrease above this temperature. The signals continued to decrease until all of the signals disappeared irreversibly when the temperature was raised to 260 K (Figure 2f). No signals attributable to the quintet state were observed during the temperature studies.

The decreasing intensity of the signals at <30 K and the recovery of the signals upon warming of the matrix clearly indicate that the signals are due to a thermally populated excited state. Actually, the plot of intensity of the signals at 298 mT versus the temperature from 6 to 75 K deviated from the Curie−Weiss law (Figure 3a).

The temperature dependence of the ESR signal intensity for **3** indicates that the quinoidal form of bis(carbene) has a singlet ground state. To determine the singlet−triplet energy gap ($\Delta E_{\mathrm{T-S}} = 2J$) of quinoidal bis(carbene), the observed data were analyzed in terms of the Bleaney−Bowers-type thermal distribution[17]

$$I = \frac{C}{T}\,\frac{3\,\exp(-2J/kT)}{1 + 3\,\exp(-2J/kT)} \tag{1}$$

where I is the intensity of the ESR active triplet state and T, k, and C are the absolute temperature, Boltzman constant, and an arbitrary constant, respectively. Fitting the observed intensity data for thermally populated triplets to eq 1 in the temperature range 6−75 K, where the biscarbenes were chemically intact, gave an exchange integral (J/k) value of −65 K ($\Delta E_{\mathrm{T-S}} = 266$ cal/mol).

A similar irradiation of the bis(diazo) compound (**4**−$2N_2$) connected by a thiophene ring in 2-MTHF at 77 K gave ESR spectra consisting of rather sharp and strong signals at 320 and 340 mT (Figure 4a), along with weak signals attributable to a monocarbene presumably formed by incomplete decomposition of **4**−$2N_2$. The main signals are reproduced well by computer simulation,[15,16] as shown in Figure 4g, employing a triplet Hamiltonian with $S = 1$, $g = 2.003$, $|D/hc| = 0.013$ cm^{-1}, and $|E/hc| \approx 0$ cm^{-1}.

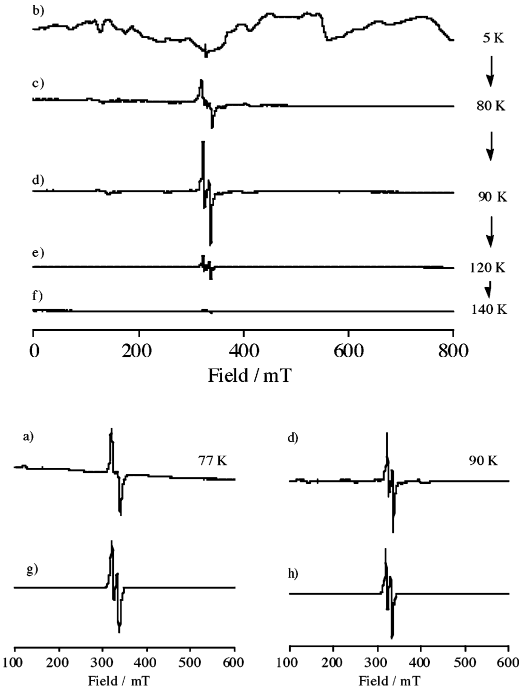

FIGURE 4. (a) ESR spectra obtained by irradiation of bis(diazo) compound **4**−$2N_2$ in 2-methyltetrahydrofuran at 77 K ($\nu_0 = 9.2152$ GHz). (b−f) The same spectra observed at 5 (b), 80 (c), 90 (d), 120 (e), and 140 (f) K. (g) Simulated spectra of $^{3}\mathbf{4}$ with $S = 1$, $g = 2.003$, $|D/hc| = 0.0130$ cm^{-1}, $|E/hc| = 0.00$ cm^{-1}, and $\Delta B = 25$ G. (h) Simulated spectra of $^{3}\mathbf{4}$ with $S = 1$, $g = 2.003$, $|D/hc| = 0.0115$ cm^{-1}, $|E/hc| = 0.00$ cm^{-1}, and $\Delta B = 17$ G.

Therefore, we assigned the new, fine-structured peaks to a quinoidal diradical triplet state of bis(carbene), $^{3}\mathbf{4}$. Cooling the sample to 5 K resulted in a marked decrease of the signal (Figure 4b), but the signal was regained when the matrix was warmed. The intensity of the signals increased rather monotonically up to 80 K. The signals become sharp ($|D/hc| = 0.0115$ cm^{-1}, $|E/hc| \approx 0$ cm^{-1}) at around 90 K (Figure 4d), presumably because of geometrical changes accompanied by softening of the matrix.[14] The intensity continued to increase up to 100 K but started to decrease above this temperature, and it irreversibly disappeared completely at 140 K (Figure 4f). The plot of intensity of the signal at 340 mT versus the temperature from 4.3 to 70 K, where the shape of the signals is unchanged, deviated from the Curie−Weiss law

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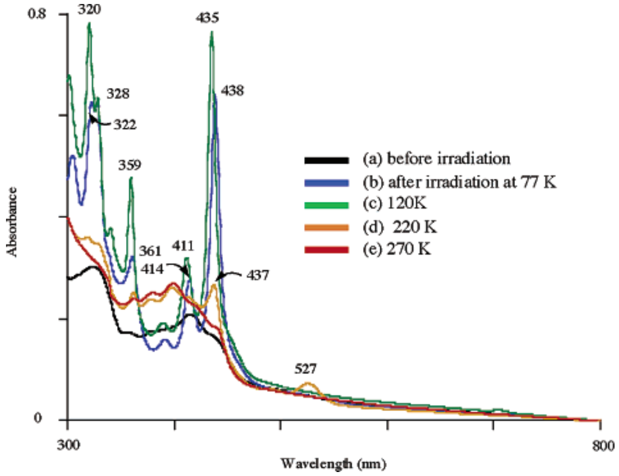

FIGURE 5. UV−vis spectra obtained by irradiation of monodiazo compound **2**−N_2. (a) Spectra of **2**−N_2 in 2-methyltetrahydrofuran at 77 K. (b) Sample from part a after irradiation (λ > 350 nm). (c−e) Sample from parts a,b after thawing to 120 (c), 220 (d), and 270 (e) K.

(Figure 3b), again confirming that the diradical was a singlet ground state having a low-lying excited triplet state. A nonlinear least-squares curve fitting the data in Figure 3b to eq 1 yields the J/k value of −42 K (ΔE_{T-S} = 167 cal/mol).

UV−Vis Spectroscopic Study in a Matrix at Low Temperature. Irradiation of **2**−N_2 in a 2-MTHF matrix at 77 K resulted in rapid disappearance of the original absorption due to **2**−N_2 and concurrent growth of sharp and strong absorption bands at 322, 328, 361, 414, and 438 nm with weak broad bands extending to ca. 700 nm. Similar absorption bands have been observed for a series of triplet anthrylcarbenes[7] and anthryl radicals.[18] Moreover, because ESR signals ascribable to triplet carbene ^{3}**2** are observed under identical conditions, the absorption spectrum can be safely assigned to ^{3}**2**. When the matrix was gradually warmed, the bands became sharper and slightly shifted to a shorter wavelength to 320, 328, 359, 411, and 435 nm. These changes are often observed for sterically congested triplet diarylcarbenes and are attributable to geometrical changes of the species as the matrix softens.[14] Upon further warming, the band started to disappear at ∼125 K and completely vanished at ∼270 K (Figure 5e).

Similar irradiation of **3**−$2N_2$ in a 2-MTHF matrix at 77 K resulted in rapid disappearance of the original absorption due to **3**−$2N_2$ and concurrent growth of sharp and strong absorption bands at 600 nm along with sharp but weak bands at 362, 442, and 543 nm (Figure 6b), which are completely different from those observed in the photolysis of **2**−N_2. The matrix took on a distinct green color. Because ESR signals attributable to a triplet state of bis(carbene) ^{3}**3** are observed under identical conditions, the bands were assigned to ^{3}**3**. The bands were found to be quite stable thermally. Thus, when the matrix was gradually warmed, the bands became sharper and shifted slightly to 362, 543, and 595 nm at around 95 K (Figure 6c). This is presumably related to the geometrical changes associated with softening of the matrix.[14] Upon further warming, the band started to disappear at around 150 K but did not completely disappear until 300 K (Figure 6d). The anomalous thermal stability of ^{3}**3** is noted here.

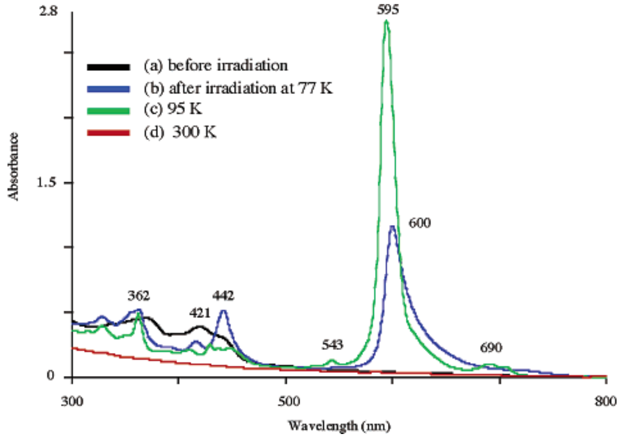

FIGURE 6. UV−vis spectra obtained by irradiation of bis(diazo) compound **3**−$2N_2$. (a) Spectra of **3**−$2N_2$ in 2-methyltetrahydrofuran at 77 K. (b) Sample from part a after irradiation (λ > 350 nm). (c−d) Sample from parts a,b after thawing to 95 (c) and 300 (d) K.

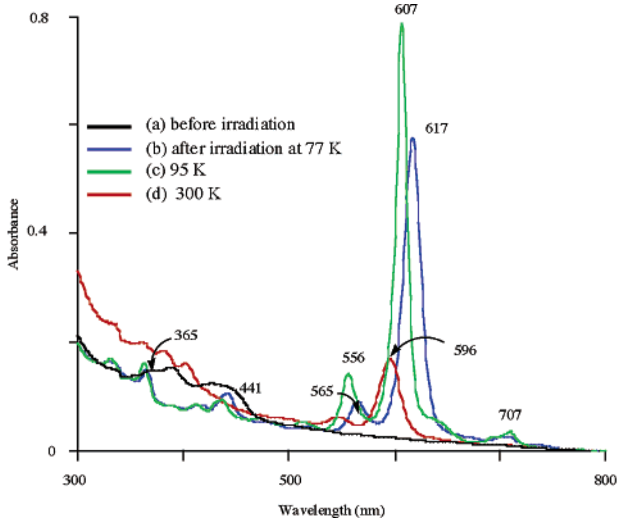

FIGURE 7. UV−vis spectra obtained by irradiation of bis(diazo) compound **4**−$2N_2$. (a) Spectra of **4**−$2N_2$ in 2-methyltetrahydrofuran at 77 K. (b) Sample from part a after irradiation (λ > 350 nm). (c−d) Sample from parts a,b after thawing to 95 (c) and 300 (d) K.

Similar irradiation of the bis(diazo) compound (**4**−$2N_2$) in 2-MTHF at 77 K gave a species showing a sharp and strong band at 617 nm along with weak broad bands at 365, 441, and 565 nm (Figure 7b). Because ESR signals attributable to the triplet state of bis(carbene) ^{3}**4** are observed under identical conditions, the bands are assigned to ^{3}**4**. The bands were found to be quite stable thermally as well. Upon warming of the matrix, the band shifted slightly to 363, 446, 556, and 607 nm at around 95 K and started to disappear at 100 K, but it did not disappear completely even at 300 K (Figure 7c,d).

UV−vis spectral observations indicate that the absorption bands observed for bis(carbene) are completely different from those observed for the corresponding

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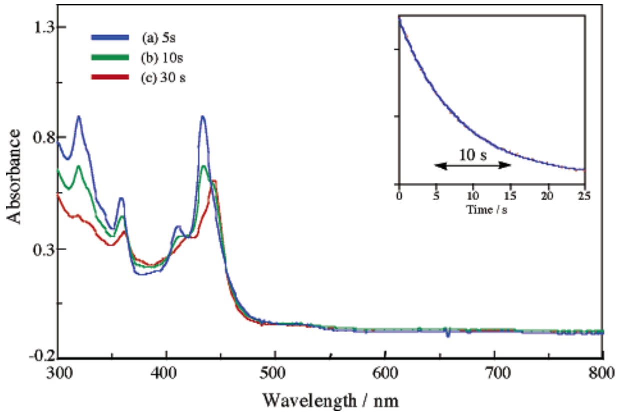

FIGURE 8. Absorption of transient products formed during irradiation of monodiazo compound **2**$-N_2$ in degassed benzene at room temperature, recorded (a) 5, (b) 10, and (c) 30 s after excitation. Inset shows the time course of the absorption at 433 nm (oscillogram trace).

monocarbene. The strong absorption bands in the visible regions that were observed for bis(carbene) systems indicate the presence of an extended π-system[19] and support the idea that bis(carbene) is likely to exist as a fully delocalized quinoidal form rather than a localized one.

It is interesting that the bands ascribable to a monocarbene, whose generation was expected by elimination of one diazo group, were not appreciably detected even at the initial stage of the irradiation, suggesting that the simultaneous elimination of two nitrogen molecules is likely to be a major process under these conditions.[20]

Time-Resolved UV−Vis Spectroscopic Study in Solution at Room Temperature. To determine the stability of the present carbenes more accurately, the lifetime is estimated in degassed benzene at room temperature, in which we measured the lifetime of a series of sterically congested diarylcarbenes.[8]

Laser flash photolysis (LFP) of **2**$-N_2$ 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 absorption bands with a maximum at 320, 359, and 433 nm (Figure 8). The UV−vis spectrum obtained just after irradiation of **2**$-N_2$ in degassed benzene at 20 °C is essentially the same as that observed in the photolysis in 2-MTHF at 77 K and, hence, is attributable to ^{3}**2**. The absorption bands decayed very slowly; the transient bands did not disappear completely even after 1 min under these conditions. The inset in Figure 8 shows the decay of ^{3}**2** in the absence of trapping reagents, which is found to be of the first order ($k = 0.13$ s^{-1}). The lifetime of ^{3}**2** is thus estimated to be 7.7 s.

Support is lent to this assignment by trapping experiments using oxygen. The LFP of **2**$-N_2$ in a nondegassed benzene solution at room temperature with a pulse from a XeCl excimer laser produced a transient species showing a broad absorption band with a maximum at 480 nm that appeared at the expense of the absorption due to ^{3}**2**. The half-life of ^{3}**2** decreased dramatically. The spent solution was found to contain the corresponding ketone (**2**−O) as the main product. It has been well documented[21,22] that diarylcarbenes with triplet ground states are readily trapped by oxygen to generate the corresponding diaryl ketone oxides, which are easily and directly observed by either matrix isolation or flash photolysis and show a broad absorption band centered at 390−450 nm. Thus, the observations can be interpreted to indicate that ^{3}**2** is trapped by oxygen to form carbonyl oxide (**2**$-O_2$), which confirms the fact that the transient absorption quenched by oxygen is due to ^{3}**2**.

The apparent built-up rate constant, k_{obs}, of the carbonyl oxide (**2**$-O_2$) is essentially identical to that of the decay of ^{3}**2**, and k_{obs} is expressed as given in eq 2

$$k_{obs} = k_0 + k_{O_2}[O_2] \qquad (2)$$

where k_0 represents the rate of decay of ^{3}**2** in the absence of oxygen and k_{O_2} is the quenching rate constant of ^{3}**2** by oxygen. A plot of the observed pseudo-first-order rate constant of the formation of the oxide against $[O_2]$ is linear (Supporting Information Figure S1). From the slope of this plot, k_{O_2} was determined to be 7.6×10^6 M^{-1} s^{-1}, which is approximately 3 orders of magnitude smaller than that observed with the parent triplet diphenylcarbene ($k_{O_2} = 5.0 \times 10^9$ M^{-1} s^{-1}).[22]

On the other hand, the transient absorption bands observed in the photolysis of bis(diazo) compounds are significantly more stable than those of the corresponding monocarbene. The lifetime of the transient species generated in the photolysis of bis(diazo) compounds was too long to monitor with a laser flash photolysis technique, and in this case, it was more convenient to use the conventional UV−vis spectroscopic method. The photolysis of **3**$-2N_2$ in degassed benzene gave a transient product showing a strong absorption band at 595 nm along with weak bands at 361 and 430 nm (Figure 9). The spectra are very similar to those observed in the photolysis of **3**$-2N_2$ in 2-MTHF at 77 K and, hence, are assigned to ^{3}**3**. The transient bands decayed very slowly. It took more than 2 h for all of the bands to disappear completely. The decay curve was best analyzed by second-order kinetics with $2k/\epsilon l = 0.024$ min^{-1}, $t_{1/2} = 20$ min. Although those transient bands are fairly stable, the decay rate was dramatically accelerated by the presence of oxygen, and the analysis of the spent solution showed the presence of the corresponding diketones (**3**−2O), indicating that they are also quenched by oxygen. Because of the strong absorption band of ^{3}**3**, the bands that are ascribable to the corresponding oxides could not be detected. However, the plot of the decay of ^{3}**3** against $[O_2]$

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[20] It is to be noted here that, in the photolysis of poly(diazo) compounds in 2-MTHF matrix at low temperatures, photo-deazetation processes are sensitive to experimental conditions, such as wavelength and intensity of the light and concentration of the precursor. See: (a) Teki, Y.; Takui, T.; Yagi, H.; Katoh, K.; Iwamura, H. *J. Chem. Phys.* **1985**, *83*, 539. (b) Matsuda, K.; Nakamura, N.; Inoue, K.; Koga, N.; Iwamura, H. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 1483. (c) Nakamura, N.; Inoue, K.; Iwamura, H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 872. (d) Sugawara, T.; Inada, M.; Iwamura, H. *Tetrahedron Lett.* **1983**, *24*, 1723.

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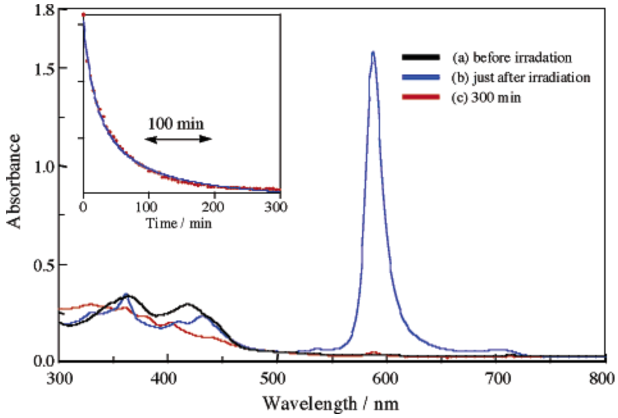

FIGURE 9. Absorption of transient products formed during irradiation of bis(diazo) compound **3**$-2N_2$ in degassed benzene at room temperature, recorded (a) before irradiation, (b) immediately after irradiation, and (c) 300 min after excitation. Inset shows the time course of the absorption at 588 nm.

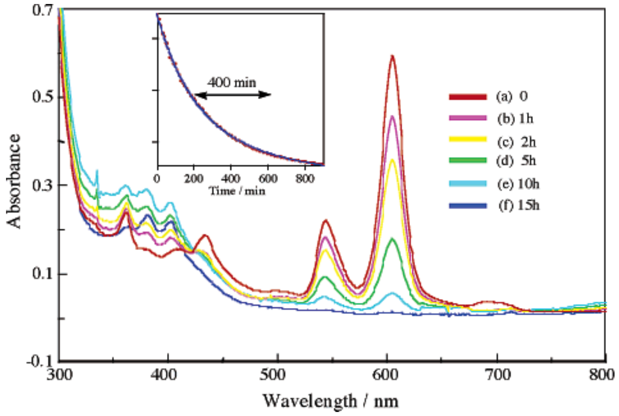

FIGURE 10. Absorption of transient products formed during irradiation of bis(diazo) compound **4**$-2N_2$ in degassed benzene at room temperature, recorded (a) immediately after excitation, and 1 (b), 2 (c), 5 (d), 10 (e), and 15 (f) h after excitation. Inset shows the time course of the absorption at 605 nm.

is linear (Supporting Information Figure S2), and from the slope, the quenching rate constant (k_{O_2}) for ^{3}**3** was determined to be 7.6×10^4 M^{-1} s^{-1}.

Similar photolysis of **4**$-2N_2$ also generated transient bands ascribable to ^{3}**4**, again, by comparison with those observed in the photolysis in 2-MTHF at 77 K. The transient bands due to ^{3}**4** decayed even more slowly; it took more than 10 h for all of the bands to disappear completely (Figure 10). The decay curve was analyzed as a combination of second-order ($2k/\epsilon l = 5.5 \times 10^{-3}$ min^{-1}, $t_{1/2} = 3.5$ h) and first-order kinetics ($k = 3.9 \times 10^{-3}$ min^{-1}, $\tau = 4.2$ h). The decay rate was again dramatically accelerated by the presence of oxygen. The quenching rate constant (k_{O_2}) for ^{3}**4** was determined to be 4.0×10^4 M^{-1} s^{-1} (Supporting Information Figure S3).

Discussion

Numerous studies have been done to construct high-spin systems built around triplet carbene subunits linked across *m*-phenylene.[11b,23,24] In these systems, covalent interaction between the triplet centers is topologically prohibited, but communication via shared π-space is possible, thereby generating high-spin states. Considerably less is known about their conjugated cousins, *p*-phenylene systems, where spin pairing between the triplet carbene units leads to lower-spin states.[23]

For instance, *p*-phenylenebis(methylene) is predicted to have a singlet ground state of A′ symmetry with a delocalized diradical structure.[25] The lower-lying excited state is computed to be the $^3A'$ state about 2 kcal/mol higher in energy, and the $^5A'$ quintet state lies about 27 kcal/mol above the $^1A'$ state. Although the $^3A'$ triplet state was not detected by ESR even at low temperature, probably because of its high reactivity, the species has been generated in an inert gas matrix at 10 K and characterized by a trapping reaction with O_2 and HCl under these conditions.[25] The triplet state of *p*-phenylenebis(phenylmethylene) is detected by ESR and is shown to be a thermally populated state lying about 1 kcal/mol above the ground-state singlet diradical.[26]

A series of *p*-phenylenebis(diradicals), in which the local diradical centers are changed from phenylnitrene, having a triplet ground state with a $\sigma\pi$ singlet lying 18 kcal/mol higher in energy, to phenylchlorocarbene, having a σ^2 singlet ground state with a triplet lying 7−9 kcal/mol higher in energy, has been generated in an inert gas matrix at low temperature and characterized by IR in combination with theoretical calculations.[23,27] These studies reveal that all of the systems have $^1A'$ singlet ground states, with $^3A'$ and $^5A'$ about 2 and 29 kcal/mol higher in energy, respectively, indicating that the relative energies among the three $^1A'$ states change very little regardless of the nature of the local diradical subunits.

The effect of a coupling linker has been extensively studied, not for the systems with bis(carbene) units[28] but for those with bis(nitrene) units. For instance, two nitrene centers introduced into a coupling linker group, such as benzene,[29] biphenyl,[30] stilbene,[31] diphenylbuta-

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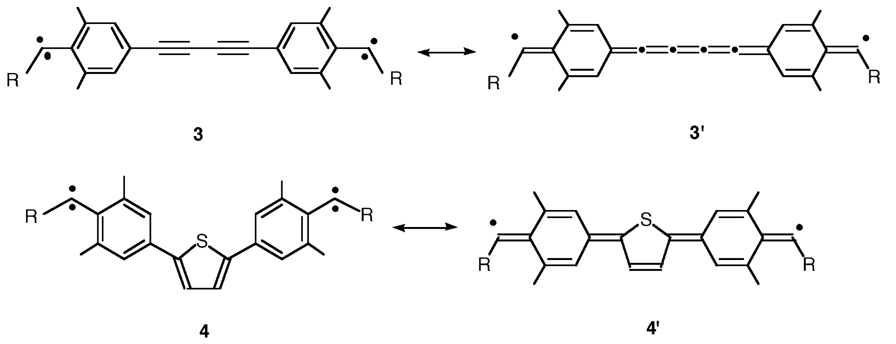
SCHEME 4



diene,[31a,b] diphenyloctatetraene,[31a,b] diphenylacetylene,[32] diphenylbutadiyne,[32] tetraphenylallene,[33] benzophenone,[34] 1,1-diphenylethylene,[34] diphenyl sulfide,[35] azobenzene,[35] and thiophene,[36] have all been generated in a conjugative manner and characterized by ESR, which revealed that all have a singlet ground state with a delocalized diradical structure having a very small singlet−triplet energy gap of 150−600 cal/mol.

The present findings, showing that two persistent diarylcarbene units introduced on either thiophene or butadiyne systems have a singlet quinoidal biradical ground state with a very small singlet−triplet energy gap, are in full accordance with previous observations and predictions.

Most studies on those species have been done simply by using ESR because the measurements have been crucial for characterization of those paramagnetic species and have been successfully employed in many systems. However, almost no information is available on the electronic properties and reactivities of those interesting species. In the present study, we have measured UV−vis spectra and have also revealed their reactivity in solution at room temperature.

Both bis(carbenes), **3** and **4**, are characterized by very sharp and strong absorption bands in the visible region. These features are usually noted for some diradical species incorporated into quinoidal cumulated π-conjugating systems (Scheme 4).[19] These observations provide further evidence for the contribution of a fully delocalized diradical structure. The surprising thermal stability of the absorption bands is noted. Thus, the bands due to **4** survive even at room temperature. In accordance with this, **4** survives for hours in solution at room temperature and is stable enough to be observable by the conventional spectroscopic means. A remarkable increase in the lifetime of biscarbenes **3** and **4**, as opposed to the isolated local diradical system, suggests that the biscarbenes are thermodynamically stabilized as a result of delocalization of unpaired electrons throughout the π-net framework. This is further supported by the observation that 1,3-bis[3,5-dimethyl-4-(anthrylcarbeneno)phenyl]benzene, a high-spin analogue of the present system, has essentially identical stability to that of the corresponding monocarbene.[37]

Despite the stability, both bis(carbenes), **3** and **4**, are readily trapped by oxygen, although the quenching rate constants observed for **3** and **4** are 2 orders of magnitude smaller than those of the isolated local carbene unit **2**.

Conclusion

The present investigation revealed that sterically congested diphenyldiazomethanes can be used as building blocks to prepare functionalized bis(diazo) compounds. Fairly stable bis(carbenes) with fully delocalized diradical structures are realized by this method, which enabled us to study the reactivity of those molecules for the first time. Although these molecules are not candidates for practical use in the development of organoferromagnetic materials, they are of considerable importance in understanding the nature of open-shell organic molecules. The present method can easily be extended to construction of precursor poly(diazo) compounds, which can generate high-spin polycarbenes with considerable stability.

Experimental Section

9-(4-*t*-Butyl-2,6-dimethylphenyl)anthracene. To a stirred solution of 4-*t*-butyl-2,6-dimethylbromobenzene[38] (5.0 g, 20.7 mmol) in dry ether (40 mL) was added dropwise a 1.50 M *n*-pentane solution of *t*-butyllithium (30.4 mL, 45.6 mmol) at −78 °C under an argon atmosphere. After stirring for 1 h, the mixture was allowed to warm to room temperature. A solution of anthrone[39] (4.0 g, 20.7 mmol) in dry toluene (80 mL) was added dropwise to the mixture, and the mixture was refluxed overnight. After cooling to room temperature and adding saturated aqueous ammonium chloride (40 mL), the mixture was extracted with ether, and the organic layer was washed with water, dried over anhydrous sodium sulfate, and concentrated under reduced pressure to leave a crude product, which was purified by column chromatography (silica gel, *n*-hexane) followed by short-path distillation (68° C/0.1 Torr) to give 9-(4-*t*-butyl-2,6-dimethylphenyl)anthracene (3.1 g, 44%) as a pale

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yellow solid. Mp 167° C. ^{1}H NMR (300 MHz, CDCl$_3$, ppm): δ ~8.47−7.29 (m, 9H, Anth−H), 7.24 (s, 2H, Ph−H), 1.73 (s, 6H, −Me), 1.44 (s, 9H, −^{t}Bu). ^{13}C NMR (75.5 MHz, CDCl$_3$, ppm): δ 150.3, 137.0, 136.0, 134.4, 131.6, 129.8, 128.6, 126.1, 126.0, 125.5, 125.1, 124.4, 34.5, 31.6, 20.4. EIMS (*m*/*z*): 338 (base, M$^+$), 323 (41.3, M$^+$ − Me). HRMS calcd for $C_{26}H_{26}$, 338.2035; found (*m*/*z*), 338.2034.

9-(4-*t*-Butyl-2,6-dimethylphenyl)-10-bromoanthracene. Bromine (0.5 mL, 9.0 mmol) was added to a stirred solution of phenylanthracene (3.1 g, 9.0 mmol) in carbon tetrachloride (40 mL) at 0 °C. The solution was stirred at room temperature overnight. The reaction mixture was washed with 20% aqueous potassium hydroxide, saturated aqueous sodium thiosulfate, and water, and the organic layer was dried over anhydrous sodium sulfate and concentrated under reduced pressure to leave a residue, which was reprecipitated with *n*-hexane to give 9-(4-*t*-butyl-2,6-dimethylphenyl)-10-bromoanthracene (3.3 g, 89%) as a yellow solid. Mp 180−181 °C. ^{1}H NMR (300 MHz, CDCl$_3$, ppm): δ ~8.60−7.35 (m, 8H, Anth−H), 7.24 (s, 2H, Ph−H), 1.72 (s, 6H, −Me), 1.44 (s, 9H, −^{t}Bu). ^{13}C NMR (75.5 MHz, CDCl$_3$, ppm): δ 150.7, 136.8, 134.0, 130.6, 130.5, 128.0, 127.0, 126.5, 125.8, 124.5, 122.1, 124.4, 34.5, 31.5, 20.4. EIMS (*m*/*z*): 418 (base, M + 2), 416 (98.0, M + 1), 401 (32.3, M$^+$ − Me). HRMS calcd for $C_{26}H_{25}$, 416.1139; found (*m*/*z*), 416.1125.

[9-{10-(4-*t*-Butyl-2,6-dimethyl)phenyl}anthryl](4-bromo-2,6-dimethylphenyl)methanol. A 2.66 M hexane solution of *n*-butyllithium (2.2 mL, 5.8 mmol) under an argon atmosphere was added dropwise to a stirred solution of bromoanthracene (2.0 g, 4.8 mmol) in dry ether (40 mL) at 0 °C. After the mixture stirred for 3 h, a solution of 4-bromo-2,6-dimethylbenzaldehyde[40] (1.0 g, 4.8 mmol) in dry tetrahydrofuran (13 mL) was added dropwise to the mixture, and the mixture was stirred at room temperature overnight. After the addition of saturated aqueous ammonium chloride (30 mL), the mixture was extracted with ether, and the organic layer was washed with water, dried over anhydrous sodium sulfate, and concentrated under reduced pressure to leave a crude product, which was purified by column chromatography (silica gel, hexane/dichloromethane = 2:1) to give [9-{10-(4-*t*-butyl-2,6-dimethyl)phenyl}anthryl](4-bromo-2,6-dimethylphenyl)methanol (2.0 g, 74%) as a yellow solid. Mp 99.5−100.0 °C. ^{1}H NMR (300 MHz, CDCl$_3$, ppm): δ ~8.49−7.25 (m, 8H, Anth−H), 7.48 (d, J = 4.04 Hz, 1H, HO−C−H), 7.24 (s, 2H, Anth−Ph−H), 7.18 (s, 2H, Ph−H), 2.41 (d, J = 4.04 Hz, 1H, −OH), 2.18 (s, 6H, Ph−Me), 1.72 (s, 6H, Anth−Ph−Me), 1.44 (s, 9H, −^{t}Bu). ^{13}C NMR (75.5 MHz, CDCl$_3$, ppm): δ 150.5, 139.3, 139.1, 138.1, 136.7, 134.7, 132.9, 132.7, 129.81, 129.76, 127.1, 125.9, 125.0, 124.7, 124.5, 120.8, 73.1, 34.5, 31.5, 21.8, 20.2. EIMS *m*/*z* (relative intensity): 552 (M + 2, 39.5), 550 (M$^+$, 40.1), 339 (100), 283 (40.9), 213 (69.8), 211 (71.8), 57 (68.4). HRMS calcd for $C_{35}H_{35}BrO$, 550.1871; found (*m*/*z*), 550.1862.

[9-{10-(4-*t*-Butyl-2,6-dimethyl)phenyl}anthryl](4-bromo-2,6-dimethylphenyl)chloromethane. Gaseous hydrochloric acid, prepared by adding hydrochloric acid (10 mL) to concentrated sulfuric acid (15 mL), was bubbled into a stirred solution of the methanol (1.5 g, 2.7 mmol) in dry benzene (20 mL) for 1 h at 5 °C while monitoring the reaction by ^{1}H NMR. The reaction mixture was concentrated and dried under reduced pressure to give [9-{10-(4-*t*-butyl-2,6-dimethyl)phenyl}anthryl]-(4-bromo-2,6-dimethylphenyl)chloromethane (1.5 g, 97%) as a yellow solid. ^{1}H NMR (300 MHz, CDCl$_3$, ppm): δ ~8.49−7.26 (m, 8H, Anth−H), 7.78 (s, 1H, Cl−C−H), 7.24 (s, 2H, Anth−Ph−H), 7.21 (s, 2H, Ph−H), 2.31 (s, 6H, Ph−Me), 1.72 (s, 6H, Anth−Ph−Me), 1.44 (s, 9H, −^{t}Bu). ^{13}C NMR (75.5 MHz, CDCl$_3$, ppm): δ 150.6, 139.7, 139.2, 137.1, 136.7, 134.5, 133.0, 129.9, 129.7, 128.3, 127.3, 126.1, 125.0, 124.8, 124.5, 121.6, 59.4, 34.5, 31.5, 22.4, 20.3.

Ethyl *N*-[9-{10-(4-*t*-Butyl-2,6-dimethyl)phenyl}anthryl]-(4-bromo-2,6-dimethylphenyl)methylcarbamate. A mixture of ethyl carbamate (4.6 g, 51.6 mmol) and silver tetrafluoroborate (0.6 g, 2.8 mmol) was heated to 60 °C. A solution of chloromethane (1.5 g, 2.6 mmol) in dry dioxane (13 mL) was added dropwise to this mixture at the same temperature. After refluxing overnight, the reaction mixture was filtered; the filtrate was then extracted with chloroform, and the organic layer was washed with water, dried over anhydrous sodium sulfate, and concentrated under reduced pressure to leave a crude product, which was purified by column chromatography (silica gel, hexane/dichloromethane = 1:1) to give ethyl *N*-[9-{10-(4-*t*-butyl-2,6-dimethyl)phenyl}anthryl]-(4-bromo-2,6-dimethylphenyl)methylcarbamate (1.2 g, 75%) as a pale brown solid. Mp 136.6−137.2 °C. ^{1}H NMR (300 MHz, CDCl$_3$, ppm): δ ~8.31−7.27 (m, 8H, Anth−H), 7.54 (d, J = 9.00 Hz, 1H, N−C−H), 7.24 (s, 2H, Anth−Ph−H), 7.13 (s, 2H, Ph−H), 5.47 (d, J = 8.64 Hz, 1H, −NH), 4.22 (q, J = 7.17 Hz, 2H, −CH$_2$−), 2.17 (s, 6H, Ph−Me), 1.70 (s, 6H, Anth−Ph−Me), 1.43 (s, 9H, −^{t}Bu), 1.26 (t, J = 7.17 Hz, 3H, −CH$_2$−Me). ^{13}C NMR (75.5 MHz, CDCl$_3$, ppm): δ 155.4, 150.5, 138.7, 138.3, 138.2, 136.7, 134.5, 133.1, 129.8, 129.7, 127.3, 126.4, 125.0, 124.5, 123.7, 120.1, 61.4, 53.8, 34.5, 31.5, 22.5, 20.3, 14.7. MS *m*/*z* (relative intensity): 623 (M + 2, 100), 621 (M$^+$, 94.7), 364 (29.2), 339 (30.3), 283 (30.9), 212 (87.4), 210 (86.2), 57 (42.9). HRMS calcd for $C_{38}H_{40}BrNO_2$, 621.2242; found (*m*/*z*), 621.2196.

Ethyl *N*-Nitroso-*N*-[9-{10-(4-*t*-butyl-2,6-dimethyl)phenyl}anthryl](4-bromo-2,6-dimethylphenyl)methylcarbamate. Nitrogen dioxide (5.0 g) was bubbled into dry carbon tetrachloride (20 mL) at −20 °C while stirring. Sodium acetic acid (9.0 g, 0.10 mol) and a solution of the carbamate (1.2 g, 1.9 mmol) in dry carbon tetrachloride (15 mL) were added to the mixture. The mixture was allowed to warm to room temperature for 2 h and poured into ice. This mixture was extracted with chloroform, and the organic layer was washed with water, dried over anhydrous sodium sulfate, concentrated, and dried under reduced pressure to give ethyl *N*-nitroso-*N*-[9-{10-(4-*t*-butyl-2,6-dimethyl)phenyl}anthryl]-(4-bromo-2,6-dimethylphenyl)methylcarbamate (1.4 g, quantitative) as a yellow solid. ^{1}H NMR (300 MHz, CDCl$_3$, ppm): δ 7.89 (s, 1H, N−C−H), ~7.63−7.22 (m, 8H, Anth−H), 7.24 (s, 2H, Anth−Ph−H), 7.16 (s, 2H, Ph−H), 4.11 (q, J = 7.17 Hz, 2H, −CH$_2$−), 1.96 (s, 6H, Ph−Me), 1.70 (s, 6H, Anth−Ph−Me), 1.44 (s, 9H, −^{t}Bu), 0.81 (t, J = 7.17 Hz, 3H, −CH$_2$−Me). ^{13}C NMR (75.5 MHz, CDCl$_3$, ppm): δ 153.6, 150.6, 139.1, 138.3, 136.6, 134.9, 134.5, 133.0, 130.7, 129.6, 127.3, 126.55, 126.45, 125.0, 124.5, 123.5, 121.0, 64.3, 56.4, 34.5, 31.5, 20.9, 20.2, 13.4.

[9-{10-(4-*t*-Butyl-2,6-dimethyl)phenyl}anthryl](4-bromo-2,6-dimethylphenyl)diazomethane (1−N$_2$). Potassium *t*-butoxide (0.5 g, 4.7 mmol) at −20 °C under an argon atmosphere was added to a stirred solution of the nitroso-carbamate (1.4 g, 2.2 mmol) in dry tetrahydrofuran (15 mL). After stirring overnight, the reaction mixture was poured into ice and extracted with ether. The ethereal layer was washed with water, dried over anhydrous sodium sulfate, concentrated, and dried under reduced pressure to leave a crude product, which was purified by column chromatography (alumina, *n*-hexane at −20 °C), followed by GPC (chloroform, monitored at 350 nm) to give **1**−N$_2$ (0.6 g, 48%) as an orange solid. ^{1}H NMR (300 MHz, CDCl$_3$, ppm): δ ~8.00−7.25 (m, 8H, Anth−H), 7.28 (s, 2H, Ph−H), 7.25 (s, 2H, Anth−Ph−H), 2.14 (s, 6H, Ph−Me), 1.73 (s, 6H, Anth−Ph−Me), 1.44 (s, 9H, −^{t}Bu). ^{13}C NMR (75.5 MHz, CDCl$_3$, ppm): δ 150.6, 138.9, 138.1, 136.8, 134.3, 132.0, 130.2, 130.1, 129.9, 127.2, 126.4, 125.4, 125.1, 124.5, 122.7, 120.8, 57.1, 34.5, 31.5, 21.1, 20.3. IR (KBr, cm^{-1}): $\nu_{C=N_2}$ 2041.

[9-{10-(4-*t*-Butyl-2,6-dimethyl)phenyl}anthryl](2,6-dimethyl-4-trimethylsilylethynylphenyl)diazomethane (2−N$_2$). To a stirred mixture of **1**−N$_2$ (135.0 mg, 0.24 mmol), bis(triphenylphosphino)palladium dichloride (catalytic amount), and copper iodide (catalytic amount) in dry triethylamine (4 mL) and dry tetrahydrofuran (2 mL) was added trimethyl-

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[40] Yamakawa, M.; Kubota, T.; Akazawa, H. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 1600.

silylacetylene (100.0 μL, 0.72 mmol) under nitrogen atmosphere. After heating overnight at 35 °C, the reaction mixture was concentrated under reduced pressure, and the residue was dissolved in ether and filtered. The filtrate was then concentrated and dried under reduced pressure to leave a crude product, which was purified by GPC (chloroform, monitored at 350 nm) to afford **2**$-$N$_2$ (2.0 g, 74%) as an orange, viscous liquid. ^{1}H NMR (300 MHz, CDCl$_3$, ppm): δ ~8.00$-$7.28 (m, 10H, Anth$-$H + Anth$-$Ph$-$H), 7.26 (s, 2H, Ph$-$H), 2.11 (s, 6H, Ph$-$Me), 1.73 (s, 6H, Anth$-$Ph$-$Me), 1.44 (s, 9H, $-^t$Bu), 0.25 (s, 9H, $-$TMS). ^{13}C NMR (75.5 MHz, CDCl$_3$, ppm): δ 150.5, 138.1, 136.80, 136.78, 134.3, 132.8, 131.4, 130.3, 130.1, 127.2, 126.3, 125.4, 125.2, 124.5, 123.0, 121.6, 105.1, 94.5, 57.8, 34.5, 31.5, 21.1, 20.3, $-$0.01. IR (NaCl, cm^{-1}): $\nu_{C=N_2}$ 2040, $\nu_{C\equiv C}$ 2153.

1,4-Bis(3,5-dimethyl-4-[9-{10-(4-*t*-butyl-2,6-dimethyl)phenyl}anthryl]diazomethylphenyl)butadiyne (3$-$2N$_2$). To a solution of **2**$-$N$_2$ (16.8 mg, 0.03 mmol) in *t*-butyl alcohol (1 mL) was added 10% aqueous sodium hydroxide (0.3 mL). After stirring overnight at room temperature, the reaction mixture was extracted with ether, and the ethereal layer was washed with water, dried over anhydrous sodium sulfate, concentrated, and dried under reduced pressure to leave a crude product, which was purified by GPC (chloroform, monitored at 350 nm) to afford a deprotected diazo compound (11.7 mg, 80%) as an orange, viscous liquid. ^{1}H NMR (300 MHz, CDCl$_3$, ppm): δ ~8.00$-$7.29 (m, 8H, Anth$-$H), 7.27 (s, 2H, Ph$-$H), 7.25 (s, 2H, Anth$-$Ph$-$H), 3.09 (s, 1H, acetylene), 2.13 (s, 6H, Ph$-$Me), 1.74 (s, 6H, Anth$-$Ph$-$Me), 1.44 (s, 9H, $-^t$Bu). IR (NaCl, cm^{-1}): $\nu_{C=N_2}$ 2041.

To a solution of the deprotected diazo compound (10.6 mg, 0.02 mmol) in dichloromethane (2 mL) was added CuCl(OH)·TMEDA (catalytic amount) under an oxygen atmosphere. After stirring overnight at room temperature, the reaction mixture was filtered, and the filtrate was concentrated and dried under reduced pressure to leave a crude product, which was purified by GPC (chloroform, monitored at 350 nm) to give **3**$-$2N$_2$ (6.0 mg, 57%) as an orange, viscous liquid. ^{1}H NMR (300 MHz, CDCl$_3$, ppm): δ ~8.00$-$7.29 (m, 8H, Anth$-$H), 7.27 (s, 2H, Ph$-$H), 7.25 (s, 2H, Anth$-$Ph$-$H), 3.09 (s, 1H, acetylene), 2.13 (s, 6H, Ph$-$Me), 1.74 (s, 6H, Anth$-$Ph$-$Me), 1.44 (s, 9H, $-^t$Bu). ^{13}C NMR (75.5 MHz, CDCl$_3$, ppm): δ 150.6, 138.3, 136.9, 136.8, 134.3, 133.2, 132.3, 130.3, 130.1, 127.2, 126.5, 125.5, 125.1, 124.5, 122.8, 120.2, 81.9, 74.4, 57.9, 34.5, 31.5, 21.1, 20.3. IR (NaCl, cm^{-1}): $\nu_{C=N_2}$ 2041, $\nu_{C\equiv C}$ 2153.

2,5-Bis(3,5-dimethyl-4-[9-{10-(4-*t*-butyl-2,6-dimethyl)phenyl}anthryl]diazomethylphenyl)thiophene (4$-$2N$_2$). Palladium acetate (0.8 mg, 3.6 × 10^{-3} mmol), potassium fluoride (6.2 mg, 0.11 mmol), 2-(di-*t*-butylphosphino)biphenyl (3.2 mg, 1.1 × 10^{-2} mmol), and 2.5-thiophene diboronic acid (3.1 mg, 0.02 mmol) were added to a stirred solution of **1**$-$N$_2$ (20.0 mg, 0.04 mmol) in dry tetrahydrofuran (0.5 mL) under a nitrogen atmosphere. After heating overnight at 35 °C, the reaction mixture was filtered, and the filtrate was concentrated and dried under reduced pressure to leave a crude product, which was purified by GPC (chloroform, monitored at 350 nm) to afford **4**$-$2N$_2$ (1.6 mg, 8%) as an orange, viscous liquid. ^{1}H NMR (300 MHz, CDCl$_3$, ppm): δ ~8.08$-$7.42 (m, 12H, Anth$-$H), 7.42 (s, 2H, thiophene$-$H), ~7.35$-$7.28 (m, 4H, Anth$-$H), 7.31 (s, 4H, Ph$-$H), 7.26 (s, 4H, Anth$-$Ph$-$H), 2.21 (s, 12H, Ph$-$Me), 1.75 (s, 12H, Anth$-$Ph$-$Me), 1.44 (s, 18H, $-^t$Bu). ^{13}C NMR (75.5 MHz, CDCl$_3$, ppm): δ 150.5, 143.0, 138.0, 137.5, 136.8, 134.4, 133.0, 130.3, 130.1, 130.0, 127.2, 126.4, 126.3, 125.4, 125.3, 124.5, 123.9, 123.3, 57.6, 34.5, 31.5, 21.4, 20.3. IR (NaCl, cm^{-1}): $\nu_{C=N_2}$ 2039.

Irradiation for Product Analysis. In a typical run, a solution of the diazo compound (**1**, ca. 5 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 preparative TLC and identified by NMR and MS. The following products were isolated and charatcterized.

Butadiyne$-$diketone (3$-$2O). ^{1}H NMR (300 MHz, CDCl$_3$, ppm): δ 8.05 (d, J = 9.00 Hz, 4H), 7.51 (d, J = 8.64 Hz, 4H), 7.44$-$7.39 (m, 4H), 7.32$-$7.30 (m, 4H), 7.30 (s, 4H), 7.21 (s, 4H), 2.13 (s, 12H), 1.73 (s, 12H), 1.44 (s, 18H). MS (MALDI-TOF) calcd for $C_{74}H_{65}O_2$ (M $-$ H$^+$), 985.4979; found (*m*/*z*), 985.5131.

Thiophene$-$diketone (4$-$2O). ^{1}H NMR (300 MHz, CDCl$_3$, ppm): δ 8.10 (d, J = 8.82 Hz, 4H), 7.51 (d, J = 8.23 Hz, 4H), 7.44$-$7.21 (m, 18H), 2.20 (s, 12H), 1.74 (s, 12H), 1.45 (s, 18H). MS (MALDI-TOF) calcd for $C_{74}H_{67}O_2S$ (M $-$ H$^+$), 1019.4856; found (*m*/*z*), 1019.4973.

EPR Measurements. The diazo compound was dissolved in 2-methyltetrahydrofuran (10^{-3} M), and the solution was degassed in a quartz cell by 3 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 ±0.1 K and the control ability within ±0.2 K. Errors in the measurements of component amplitudes did not exceed 5%, and the accuracy of the resonance field determination was within ±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 of the 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 ms 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 with 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 4 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, which 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 in order to absorb a significant portion of the excitation light. For experiments in which the rate constant for the reaction of oxygen with carbenes was determined, varying concentrations of oxygen in nitrogen were bubbled through the solution.[41]

Acknowledgment. The authors are grateful to the Ministry of Education, Culture, Sports, Science and Technology of Japan for support of this work through a Grant-in-Aid for Scientific Research for Specially Promoted Research (12002007). Support from the Mitsubishi Foundation and the Nagase Science and Technology Foundation is also appreciated.

Supporting Information Available: Plot of the growth rate of the carbonyl oxide from the photoproduct of **2**$-N_2$ (Figure S1), **3**$-2N_2$ (Figure S2), and **4**$-2N_2$ (Figure S3) as a function of oxygen concentration and ^{1}H NMR spectra of **2**$-N_2$ (Figure S4), **3**$-2N_2$ (Figure S5), and **4**$-2N_2$ (Figure S6). This material is available free of charge via the Internet at http://pubs.acs.org.

JO0494026

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