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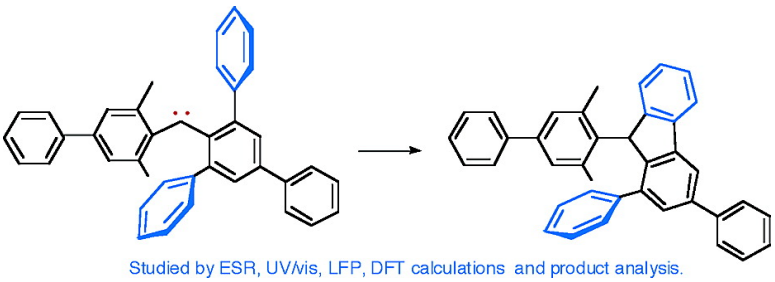

Studied by ESR, UV/vis, LFP, DFT calculations and product analysis.

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Triplet Diphenylcarbenes Protected by *o*-Aryl Groups

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Abstract: Diphenyldiazomethanes (**2a**−N_2) having phenyl groups at the *ortho* positions were prepared and the corresponding diphenylcarbenes (**2a**) photolytically generated from them were characterized not only by the traditional product analysis method but also by ESR and UV/vis spectroscopy in a rigid organic matrix at low temperature and in laser flash photolysis in solution at room temperature. Product analysis indicated that fluorenes **4a** are formed almost exclusively. Fluorene is most likely produced by the attack of singlet carbene ^{1}**2a** on an *ortho* carbon of the phenyl substituent to generate isofluorene, followed by 1,5-H shift. Irradiation of **2a**−N_2 in a 2-methyltetrahydrofuran (2-MTHF) matrix at 77 K gave ESR signals ascribable to triplet carbenes (^{3}**2a**). UV/vis spectra of ^{3}**2a** were obtained by irradiating **2a**−N_2 under identical conditions. However, laser flash photolysis (LFP) of **2a**−N_2 in degassed benzene at room temperature showed transient absorption bands completely different from those observed in photolysis in the 2-MTHF matrix at 77 K. The transient band decayed in first-order with a rate constant of 7.6×10^4 s^{-1}, which was not retarded by deuterium substitution of *o*-phenyl hydrogens. Essentially the same transient band was observed in LFP of fluorene **4a**. The LFP of **2a**−N_2 in nondegassed benzene gave transient absorption bands ascribable to triplet carbene ^{3}**2a** and the corresponding carbonyl oxide. The quenching rate constant of ^{3}**2a** by oxygen and the lifetime of ^{3}**2a** in the absence of oxygen were estimated by plotting the observed pseudo-first-order rate constant of the formation of the carbonyl oxide against the concentration of oxygen. They were 1.9×10^7 $M^{-1}s^{-1}$ and 16 μs, respectively. Similar studies with diphenyldiazomethanes having a series of substituents (4-Ph, 3,5-$(CF_3)_2$, and 2-F) on the *ortho*-phenyl rings gave essentially identical results, indicating that those substituents exhibit little effect on overall reaction pathway. From those studies, it is suggested that triplet carbenes ^{3}**2** are also trapped by the *ortho*-phenyl ring to give eventually fluorenes.

Triplet carbenes are highly reactive organic radicals that are also notoriously difficult to stabilize.[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, the stabilization of a triplet carbene has emerged as a challenging target.[1] 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. Thus, a series of precursor diphenyldiazomethanes bearing various substituents at the ortho positions as kinetic protectors has been prepared and has led to fairly stable triplet diphenylcarbenes, some of which can survive a day in solution at room temperature.[5,6] A species surviving a day is very stable for a triplet carbene, but is still very ephemeral for a real molecule. To realize this, one needs to explore a more effective kinetic protector.

The phenyl group is an attractive protector, although a singlet carbene is known to react with benzene.[7] triplet states are usually unreactive toward benzene. However, it was difficult to prepare the precursor diphenyldiazomethane having a phenyl group at the ortho position. For instance, 2,2′,6,6′-tetraphenylated benzophenones do not form hydrazones, even under rigorous conditions. We found that a diphenyldiazomethane prepared to

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(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) 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.
(6) More recently, a triplet carbene surviving a week has been realized by using anthryl groups that stabilize triplet carbenes both kinetically and thermodynamically. See Tomioka, H.; Iwamoto, E.; Itakura, H.; Hirai, K. *Nature* **2001**, *412*, 626. (e) Iwamoto, E.; Hirai, K.; Tomioka, H. *J. Am. Chem. Soc*. **2003**, *125*, 14664.
(7) For reviews of general reactions of carbenes, see (a) Kirmse, W. *Carbene Chemistry*, 2nd edition; Academic Press: New York, 1971. (b) *Carbenes*; Moss, R. A., Jones, M., Jr., Eds.; Wiley: New York, 1973 and 1975; Vol. 1 and 2. (c) Carbene(oide), Carbine; Regitz, M., Ed.; Thieme; Stuttgart, 1989.

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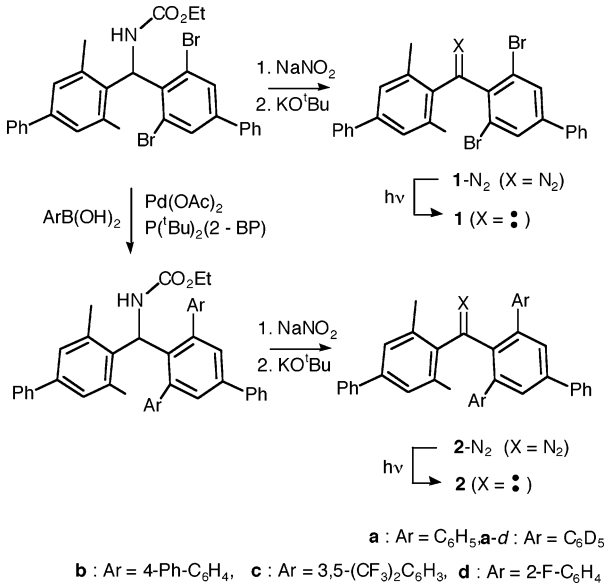
Scheme 1



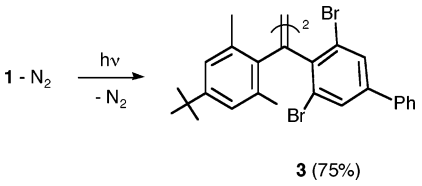
generate a persistent triplet carbene is also relatively stable and hence can be further modified with the diazo group intact to a more complicated diazo compound. For instance, bis(2,4,6-tribromophenyl)diazomethane survives under Sonogashira coupling reaction conditions leading to bis(2,6-dibromo-4-trimethylsilylethynylphenyl)diazomethane.[8] This is obviously due the fact that the kinetic protectors introduced to protect the carbene center from external reagent also are able to protect the diazo carbon. It is potentially possible to prepare the desired precursor by extending this idea.[9] We wish to report here the preparation of *o*-phenylated diphenyldiazomethanes and characterization of carbenes generated from them.

Results

A. Preparation of Precursor Diazomethanes. The diazo compound we chose for this study is (2,6-dibromo-4-phenylphenyl)(2,6-dimethyl-4-phenylphenyl)diazomethane (**1**−N_2). Since we found that bromine groups at the para-position could be replaced with a phenyl group by using Suzuki coupling reaction,[10] we first reacted the diazo compound with benzene boronic acid. However, all attempts to obtain *o*-phenylated diphenyldiazomethane under similar conditions and under more rigorous conditions were unsuccessful. Therefore, we were forced to find a route to introduce *o*-phenyl group at a previous stage. We found that a diarylmethylcarbamate, a precursor for the diaryldiazomethane, was smoothly *o*-phenylated and then the resulting carbamate was converted into the corresponding diazomethane (Scheme 1).

Treatment of (2,6-dibromo-4-phenylphenyl)(2,6-dimethyl-4-phenylphenyl)methylcarbamate with benzene boronic acid in the presence of the $Pd(OAc)_2/P(t\text{-}Bu)_2(2\text{-}BP)$ catalyst system, with KF as the base in tetrahydrofuran (THF)[11] at room-temperature overnight, followed by the usual workup, gave the desired phenylated compound as a yellow solid in ca. 90% yield with the carbamate group intact. Nitrosation of the carbamate with $NaNO_2$, followed by treatment of the resulting *N*-nitrosocarbamate with *t*-BuOK gave [2,4,6-tris(phenyl)phenyl]-(2,6-dimethyl-4-phenylphenyl)diazomethane (**2a**−N_2) as an orange solid.

Scheme 2



Similar arylation using substituted benzene boronic acids, where substituents were 4-phenyl, 3,5-bis(trifluoromethyl), and 2-fluoro groups all resulted in the *o*-arylation although more rigorous conditions were required, and the corresponding diazo compounds were then again obtained as orange solids.

All the diazo compounds were purified by TLC followed by GPC. Appreciable decomposition of the diazo group was not noted in all cases, at least under the conditions employed here. The diazo compounds were fairly stable and could be stored in a refrigerator for several months without any appreciable decomposition.

B. Comparison between [2,4,6-Tris(phenyl)phenyl](2,6-dimethyl-4-phenylphenyl)carbene (2a) and (2,6-Dibromo-4-phenylphenyl)(2,6-dimethyl-4-phenylphenyl)carbene (1). To know the effect of the *o*-phenyl group on the reactivities of triplet diphenylcarbenes (DPCs) as opposed to that of the *o*-bromo group, we first photolyzed [2,4,6-tris(phenyl)phenyl]-(2,6-dimethyl-4-phenylphenyl)diazomethane (**2a**−N_2) and the data are compared with those obtained by irradiation of (2,6-dibromo-4-phenylphenyl)(2,6-dimethyl-4-phenylphenyl)-diazomethane (**1**−N_2).

Product Analysis Studies. Irradiation of **1**−N_2 in a degassed benzene resulted in the formation of tetraarylethylene (**3**) as the main product (Scheme 2). It has been now well documented that sterically congested triplet DPCs undergo coupling at the carbenic center to give a dimer.[5] The formation of the ethylene is thus explained as indicating that the carbene center is well shielded by kinetic protectors and triplet carbene concentration builds up to the point at which dimerization occurs.[12]

In marked contrast, similar irradiation of **2a**−N_2 under identical conditions gave a fluorene derivative (**4a**) as a sole isolable product, neither dimeric products nor anthracene derivatives being detected (Scheme 3). It is very interesting to note that **4a** was obtained when photolysis was carried out even in methanol (vide infra). Methanol is known as an efficient trapping reagent for carbene and is shown to react with both singlet and triplet diarylcarbenes.[13]

A notable difference in the decay pathway between the two carbenes is thus observed.

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(13) For review of O−H insertion reactions of carbenes, see (a) Kirmse, W. In *Advances in Carbene Chemistry*; Brinker, U. H., Ed.; JAI Press: Stamford, 1994; Vol. 1, pp 1−57. (b) Kirmse, W. In *Advances in Carbene Chemistry*; Brinker, U., Ed.; JAI Press: Greenwich, CT, 2001; Vol. 3, pp 1−51.

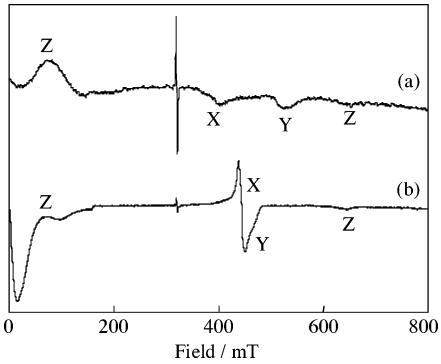
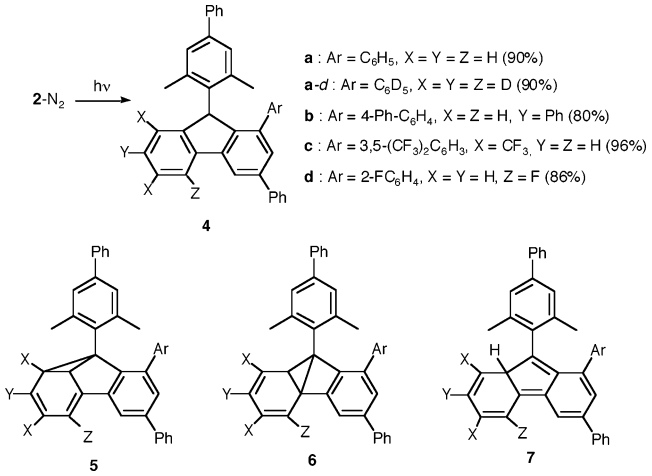


Figure 1. ESR spectra obtained by irradiation of (a) diazo compound **1**−N_2 and (b) **2a**−N_2 in 2-methyltetrahydrofuran at 77 K.

Scheme 3



Spectroscopic Studies. ESR Studies in Rigid Matrixes at Low Temperature. Irradiation (λ > 300 nm) of **1**−N_2 in a 2-methyltetrahydrofuran (2-MTHF) glass at 77 K gave rise to ESR spectra (Figure 1a) characteristic of randomly oriented triplet molecules. The zero field splitting (ZFS) parameters were $D = 0.348$ cm^{-1} and $E = 0.0326$ cm^{-1} ($E/D = 0.0937$), showing unequivocally that triplet signals are due to triplet (2,6-dibromo-4-phenylphenyl)(2,6-dimethyl-4-phenylphenyl)carbene(^{3}**1**) generated by photodissociation of **1**−N_2. Similar irradiation of **2a**−N_2 gave triplet signals ascribable to [2,4,6-tri(phenyl)phenyl](2,6-dimethyl-4-phenylphenyl)carbene(^{3}**2a**) with ZFS parameters of $D = 0.300$ cm^{-1} and $E = 0.00486$ cm^{-1} ($E/D = 0.0162$) (Figure 1b).

The structure of triplet carbenes is characterized by ESR ZFS parameters D and E.[14] The D value is related to the separation between the unpaired electrons. 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. Since 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.

(14) See for reviews of the ESR 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.

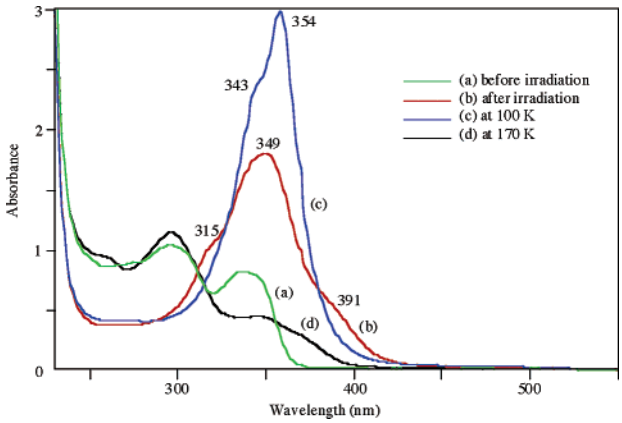


Figure 2. UV/vis spectra obtained by irradiation of diazo compound **1**−N_2. (a) Spectra of **1**−N_2 in 2-methyltetrahydrofuran at 77 K. (b) the same sample after irradiation (λ > 350 nm). (c−d) the same sample after thawing to (c) 100 and (d) 170 K.

A significant decrease in both E and E/D values on going from ^{3}**1** to ^{3}**2a** suggests that, as phenyl groups are introduced at ortho position, the central bond angle is expanded due to increased ortho-interaction induced by the phenyl group. A slight decrease in D values on going from ^{3}**1** to ^{3}**2a** can then be interpreted as indicating that unpaired electrons are delocalized into phenyl groups at the ortho positions not only because of the increasing number of the accepting group but also because of the expansion of the central bond angle. However, the extent of the increase is rather small when taking into account the amount of increase in phenyl rings. This indicates that *o*-phenyl rings are not coplanar with the carbenic phenyl ring (vide infra).

The ESR signals were not only stable at this temperature but disappeared irreversibly when the matrix was thawed to room temperature. The thermal stability of the triplet carbenes could be estimated by thawing the matrix containing triplet carbenes gradually and recooling again to 77 K to measure the signal. This procedure can compensate weakening of signals due to Currie law.[15] The triplet signals of ^{3}**2a** disappeared around 130 K. However, the triplet signals of brominated DPCs are generally weak and broad. The signals of ^{3}**1** were also not strong enough to allow such estimation. Instead, thermal stability of ^{3}**1** was estimated in more accurately by monitoring the UV/vis spectra of ^{3}**1** as a function of temperature.

UV/Vis Studies in Rigid Matrixes at Low Temperature. Photolysis (λ > 300 nm) of **1**−N_2 in 2-MTHF glass at 77 K resulted in the appearance of new bands at the expense of the original absorption due to **1**−N_2 (Figure 2a). The new bands showed rather strong and broad absorption bands centered at 349 nm along with apparent maxima at 315 and 391 nm. Since ESR signals ascribable to triplet carbene are observed under the identical conditions, the absorption spectrum can be attributable to triplet carbene (^{3}**1**). The bands are to be compared with those observed for (2,4,6-tribromophenyl)(2,6-dimethyl-4-*tert*-butylphenyl)carbene,[12c] a nonphenylated analogue of ^{3}**1**, which exhibited rather weak bands at 337 and 349 nm. Rather strong bands at longer wavelength region exhibited by ^{3}**1** clearly showed the role of phenyl groups at para position.

The absorption bands were stable for hours when kept at this low temperature, but upon thawing the matrix, the bands became

(15) Platz, M. S. In *Diradicals*; Borden, W. T., Ed.; Wiley: New York, 1982; pp 195−258. Wasserman, E.; Hutton, R. S. *Acc. Chem. Res.* **1977**, *10*, 27.

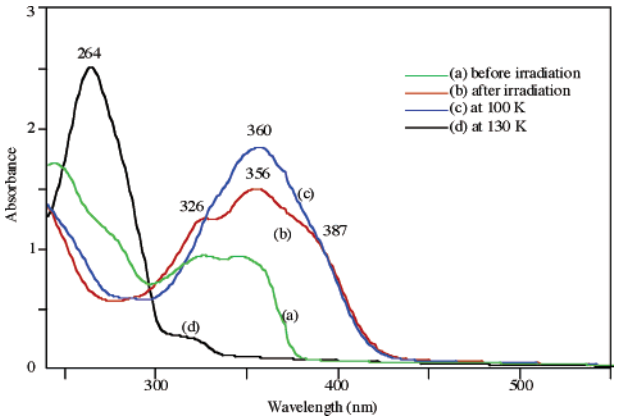


Figure 3. UV/vis spectra obtained by irradiation of diazo compound **2a**−N_2. (a) Spectra of **2a**−N_2 in 2-methyltetrahydrofuran at 77 K. (b) the same sample after irradiation (λ > 350 nm). (c−d) the same sample after thawing to (c) 100 and (d) 130 K.

sharp with an apparent shift of the maximum from 354 to 349 nm at around 100 K (Figure 2b-d). This change was not reversed when the samples were recooled. Changes of this kind have often been observed for sterically congested triplet diarylcarbenes and are usually interpreted in terms of geometrical changes.[14c,16] Thus, when a carbene is generated in rigid matrixes at very low temperature, its initial geometry should be dictated by that of the precursor. Even if the thermodynamically most stable geometry of the carbene is different from the geometry at birth, the rigidity of the matrixes prevents the carbene from achieving its minimum-energy geometry. But, when the matrix is softened by annealing, the carbene is allowed to relax to its preferred geometry probably to gain relief from steric compression. In marked contrast, it has been shown that the ZFS parameters of sterically unperturbed triplet DPCs show little sensitivity toward the temperature of the matrix. The absorption bands due to relaxed carbenes disappeared irreversibly at around 170 K.

Similar irradiation of **2a**−N_2 under identical conditions gave rather strong and broad absorption centered at 356 nm with apparent maxima at 326 and 387 nm (Figure 3a). Again, since ESR signals ascribable to triplet carbene are observed under the identical conditions, the absorption spectrum can be attributable to triplet carbene (^{3}**2a**). The absorption due to ^{3}**2a** is thus very similar but a little bit broader than that of ^{3}**1**. This may be due to the difference of molecular distortion between the two. The bands became sharp with an apparent shift of the maximum from 356 to 360 nm at around 100 K and disappeared irreversibly at around 130 K (Figure 3b-d).

This temperature is to be compared with that observed for ^{3}**1** before *o*-phenylation, which is shown to survive up to 170 K. A marked decrease in the thermal stability upon replacement of *o*-bromine group with phenyl group is thus noted.

Laser Flash Photolysis Studies in Solution at Room Temperature. To know the stability of the present carbenes more accurately, the lifetime is estimated in a degassed benzene at room temperature, in which we have measured the lifetime of a series of sterically congested diarylcarbenes.[5,6]

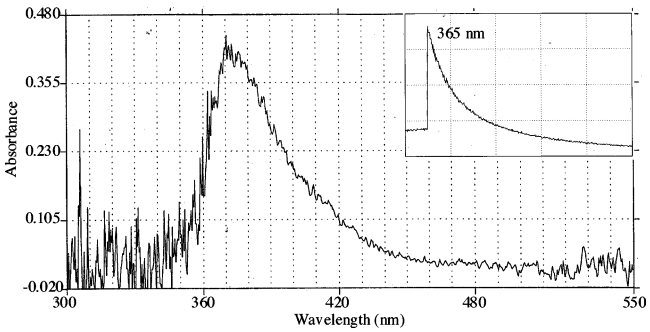


Figure 4. Absorption spectra of the transient products obtained upon 308-nm excitation of **1**−N_2 in degassed benzene recorded after 10 μs. Insets show the decay of the transient products monitored at 365 nm.

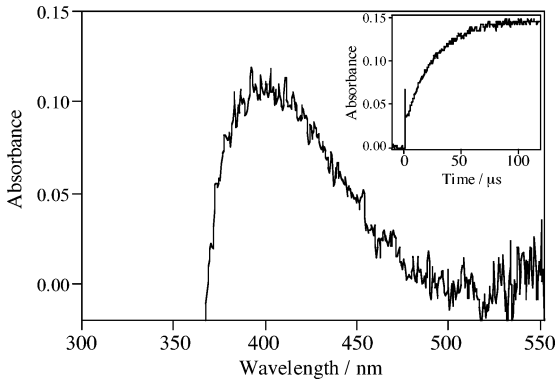


Figure 5. Transient absorption spectra obtained in LFP of **1**−N_2 in nondegassed benzene with a 308-nm excimer laser recorded 200 μs after the pulse. The inset shows the growth of the oxide (**1**−O_2) monitored at 440 nm.

Laser flash photolysis (LFP) of **1**−N_2 in degassed benzene produced transient absorption bands showing maxima at 365 nm (Figure 4), which is essentially identical with that observed in photolysis of **1**−N_2 in a matrix at 77 K. Thus, we assigned the band to triplet carbene ^{3}**1**. The transient band decayed in second-order fashion. This is in accord with the product study indicating that triplet carbene ^{3}**1** mainly decayed by undergoing dimerization to give **3**. The rate constant was estimated to be $2k/\epsilon l = 1.7\ s^{-1}$, where ϵ and l are the extinction coefficient and the optical length, respectively. The lifetime was estimated in the form of a half-life ($t_{1/2}$) to be 0.5 s.

When LFP was carried out on a nondegassed benzene solution of **1**−N_2, the half-life of ^{3}**1** decreased dramatically, and a broad absorption band with a maximum at 410 nm appeared at the expense of the absorption due to ^{3}**1** (Figure 5). The spent solution was found to contain hexabromobenzophenone (**1**−O) as the main product. It is well-documented[17,18] 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. The oxides eventually formed the corresponding ketones (Scheme 4). The spent solution showed the presence of ketone

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

(18) See LFP study of trapping of triplet carbene with oxygen, (a) Sugawara, T.; Iwamura, H.; Hayashi, H.; Sekiguchi, A.; Ando, W.; Liu, M. T. H. *Chem. Lett.* **1983**, 1261. (b) Casal, M. L.; Sugamori, S. E.; Scaiano, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 7623. (c) Casal, H. L.; Tanner, M.; Werstiuk, N. H.; Scaiano, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 4616. (d) Barcus, R. L.; Hadel, L. M.; Johnston, L. J.; Platz, M. L.; Savino, T. G.; Scaiano, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 3928. (e) Fujiwara, Y.; Tanimoto, Y.; Itoh, M.; Hirai, K.; Tomioka, H. *J. Am. Chem. Soc.* **1987**, *109*, 1942.

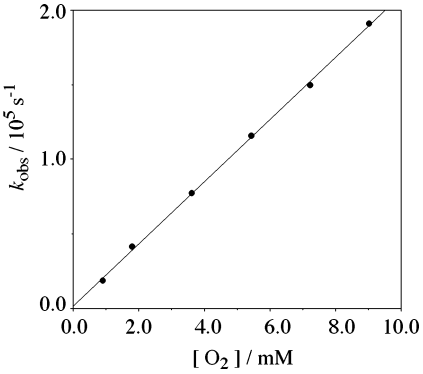
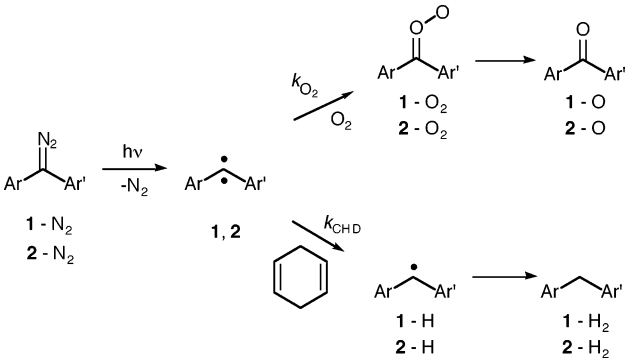


Figure 6. Plot of the growth rate of the oxide (**1**−O_2) monitored at 440 nm as a function of the concentration of oxygen.

Scheme 4



(**1**−O). Thus, the observations can be interpreted as indicating that ^{3}**1** is trapped by oxygen to form the carbonyl oxide (**1**−O_2), which confirms that the transient absorption quenched by oxygen is due to ^{3}**1**.

The apparent built-up rate constant, k_{obs}, of the carbonyl oxide (**1**−O_2) is expressed as given in eq 1

$$k_{obs} = k_0 + k_{O2}\,[O_2] \qquad (1)$$

where k_0 represents the rate of decay of ^{3}**1** in the absence of oxygen and k_{O_2} is quenching rate constant of ^{3}**1** by oxygen. A plot of the observed pseudo-first-order rate constant of the formation of the oxide against [O_2] is linear (Figure 6). From the slope of this plot, k_{O_2} was determined to be 2.1×10^7 M^{-1} s^{-1}, which is approximately two orders of magnitude smaller than that observed with the "parent" ^{3}DPC ($k_{O_2} = 5.0 \times 10^9$ M^{-1} s^{-1}).[18b]

When a degassed benzene solution of **1**−N_2 containing 1,4-cyclohexadiene (CHD) was excited, a new species was formed, showing an absorption with $\lambda_{max} = 400$ nm, formed as the 365 nm signal of ^{3}**1** decayed (Figure 7). The decay of ^{3}**1** was again found to be kinetically correlated with the growth of the new species. Thus, this new signal was attributable to the hexabromodiphenylmethyl radical (**1**−H) formed as a result of H abstraction of ^{3}**1** from the diene (Scheme 4), since it is now well-documented[19,20] that triplet arylcarbenes, generated in good hydrogen donor solvents, undergo H abstraction leading to the corresponding radicals that show transient absorptions at longer wavelengths than those of the precursor carbenes. The excellent hydrogen donor properties of CHD have been well recognized.[21] A plot of the observed pseudo-first-order rate constant of the formation of the radical against [CHD] is linear (Inset in Figure 7), and the slope of this plot yields the absolute rate constant for the reaction of ^{3}**1** with the diene, $k_{CHD} = 1.2 \times 10^2$ M^{-1} s^{-1}, which is some five orders of magnitude smaller than that observed with ^{3}DPC ($k_{CHD} = 1 \times 10^7$ M^{-1} s^{-1}).[20b]

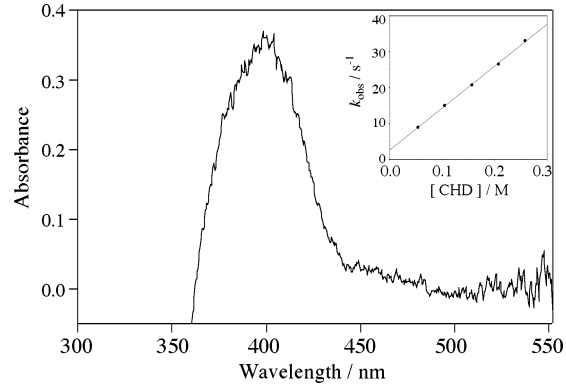


Figure 7. Transient absorption spectra obtained in LFP of **1**−N_2 in degassed benzene in the presence of 1,4-cyclohexadiene (CHD) with a 308-nm excimer laser recorded 100 ms after the pulse. The inset shows a plot of the growth rate of the radical (**1**−H) monitored at 420 nm as a function of the concentration of the diene.

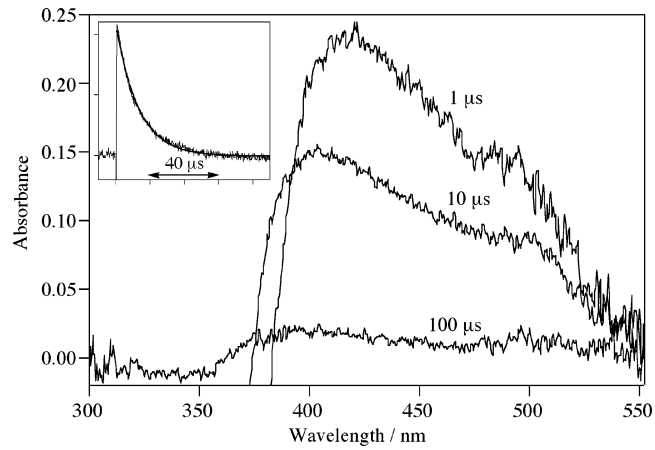


Figure 8. Absorption spectra of the transient products obtained upon 308-nm excitation of **2a**−N_2 in degassed benzene recorded after 1,10, and 100 μs. Insets show the decay of the transient products monitored at 410 nm.

LFP of **2a**−N_2 gave completely different results. Thus, LFP of **2a**−N_2 in a degassed benzene solution at room temperature produced a transient species showing a rather broad band with apparent maxima at 420 and 500 nm extending up 550 nm, which appeared coincident with the pulse (Figure 8). Due to the overlaps with the absorption maxima of the diazo precursor **2a**−N_2, the samples are not sufficiently transparent for adequate

(19) For reviews, see (a) *Kinetics and Spectroscopy of Carbenes and Biradicals*; Platz, M. S., Ed.; 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.

(20) For LFP study of H abstraction by triplet carbenes, see (a) Moritani, I.; Murahashi, S.; Ashitake, H.; Kimura, K.; Tsubomura, H. *J. Am. Chem. Soc.* **1968**, *90*, 5918. (b) Closs, G. L.; Rabinow, B. E. *J. Am. Chem. Soc.* **1976**, *98*, 8190. (c) Grasse, P. G.; Brauer, B.-E.; Zupancic, J. J.; Kaufmann, K. J.; Schuster, G. B. *J. Am. Chem. Soc.* **1983**, *105*, 6833. (d) Sugawara, T.; Iwamura, H.; Hayashi, H.; Sekiguchi, A.; Ando, W.; Liu, M. T. H. *Chem. Lett.* **1983**, 1259. (e) Lapin, S. C.; Brauer, B. E.; Schuster, G. B. *J. Am. Chem. Soc.* **1984**, *106*, 2092. (f) Hadel, L. M.; Platz, M. S.; Scaiano, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 283. (g) Griffin, G. W.; Horn, K. A. *J. Am. Chem. Soc.* **1987**, *109*, 4491. (h) Doss, S. H.; Abdel-Wahab, A. A.; Fruhof, E. M.; Dürr, H.; Gould, I. R.; Turro, N. J. *J. Org. Chem.* **1987**, *52*, 434.

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

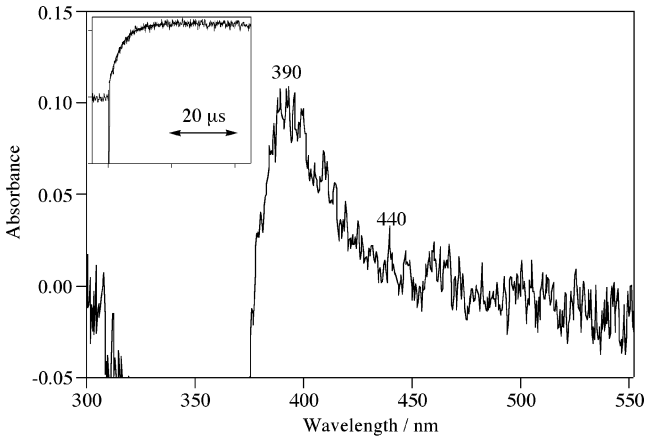


Figure 9. Transient absorption spectra obtained in LFP of **2a**−N_2 in nondegassed benzene with a 308-nm excimer laser recorded 1 μs after the pulse. The inset shows the growth of the oxide (**2a**−O_2) monitored at 440 nm.

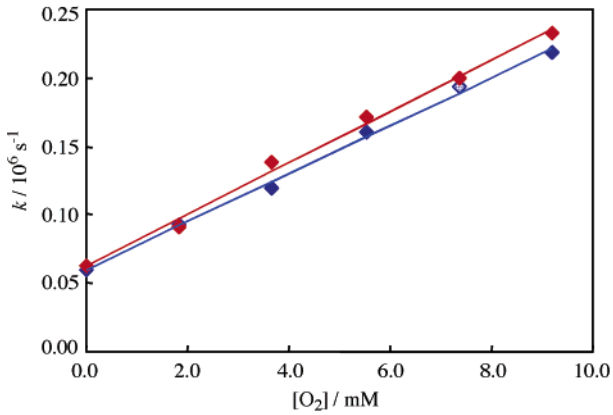


Figure 10. Plot of the growth rate of the oxide (**2a**−O_2) monitored at 440 nm (red) and the decay of triplet carbene (^{3}**2a**) monitored at 390 nm (blue) as a function of the concentration of oxygen.

monitoring in the 300−360 nm region. The two bands decayed in a similar manner. The inset in Figure 8 shows the decay of the transient species in the absence of trapping reagents, which is found to be first order with the rate constant of $k = 7.6 \times 10^4$ s^{-1}, the lifetime being 13 μs. The transient species are significantly different from that observed for ^{3}**2a** in matrix at low temperature (Figure 3a) and hence are not assignable to ^{3}**2a**.

Trapping experiments were carried out to gain more information on the intermediate. When LFP was carried out on a nondegassed benzene solution of **2a**−N_2, transient bands showing apparent maximum at 390 nm that are quite different from that observed in LFP under degassed conditions were observed (Figure 9). Again due to the overlaps with the absorption maximum of the diazo precursor **2a**−N_2, it is not possible to observe whole absorption bands. However, the bands are obviously shifted to a shorter wavelength than that observed in LFP of **2a**−N_2 in degassed benzene and can be regarded as the tail part of the absorption bands due to triplet carbene ^{3}**2a**.

This assignment was actually supported by monitoring the decay of the band more carefully. As the band decayed, a new band appeared at 440 nm. The growth rate of the new band was essentially identical with that of the decay rate (Inset in Figure 10), indicating that the transient product was trapped by oxygen to generate a new transient product, which is most likely carbonyl oxide (**2a**−O_2). Moreover, analysis of the spent solution showed the presence of ketone (**2a**−O) in 10% along with fluorene **4a**.

A plot of the observed pseudo-first-order rate constant of the formation of the oxide against [O_2] is linear (Figure 10). From the slope of this plot, k_{O_2} was determined to be 1.9×10^7 M^{-1} s^{-1}. The intercept gave k_0, the rate of decay of ^{3}**2a** in the absence of oxygen, to be 6.3×10^4 s^{-1} ($\tau = 16$ μs). Essentially the same data are obtained by monitoring the decay of the band at 390 nm ($k_{O_2} = 1.7 \times 10^7$ M^{-1} s^{-1} and $k_0 = 6.0 \times 10^4$ s^{-1}).

LFP of **2a**−N_2 in degassed benzene in the presence of a large excess of CHD, however, resulted in the formation of the same transient bands observed in LFP of **2a**−N_2 in the absence of oxygen, not the other bands being detected. Product analysis studies also indicated that fluorene **4a** was formed almost exclusively even in the presence of large excess of CHD. Triplet carbene ^{3}**2a**, which is efficiently trapped by oxygen, is not trapped by a less efficient trapping reagent, CHD.

Again notable difference in reactivity between the two carbenes is observed.

C. Assignment of Transient Product in LFP of 2a−N_2 in Degassed Solution. The absorption bands observed in LFP of **2a**−N_2 in solution at room temperature are not assigned to ^{3}**2a**. What then is the origin of the absorption? Since the analysis of the spent solution showed the presence of fluorene as an almost exclusive product and since the transient bands decay by first-order kinetics, the band may be ascribable to a species leading to the fluorene from photolytically generated carbene **2a**. A singlet state of ^{1}**2a** is highly unlikely since singlet diarylcarbenes are mostly invisible even in a time resolution in picoseconds.[22] Fluorene (**4a**) is not likely formed directly from carbene ^{1}**2a**, but rather is produced by way of intermediates.

Photochemistry of 2-diazomethylbiphenyl systems has been studied. Photolysis of 2-diazomethylbiphenyl in solution affords fluorene almost exclusively.[23,24] When the irradiation is carried out in methanol, methyl ether, obviously formed as a result of O−H insertion of biphenyl-2-ylcarbene, is obtained competitively.[25] Therefore, the carbene is proposed to be involved in the reaction leading to fluorene. Since the deuterium isotope effect of the formal C−H insertion is very small ($k_H/k_D = 1.12$),[23] rate-controlling cyclization of biphenyl-2-ylcarbene to give a diradical or *o*-quinodimethane (isofluorene) followed by migration of hydrogen is proposed. From the product ratio of fluorene and methyl ether, the rate constants for cyclization are estimated to be 2×10^8 s^{-1} and $\sim 10^{11}$ s^{-1} for triplet and singlet states, respectively.[25] Similar irradiation of (biphenyl-2-yl)-phenyldiazomethane also produces the formal C−H insertion product, 9-phenylfulorene, as the main product. Again, methyl ether is competitively formed when irradiated in methanol.[26]

From these studies on related systems, several intermediates can be assumed. Initial reaction of carbene center with an *o*-phenyl ring will lead to either tetracyclic cyclopropanes (**5**, **6**) or isofluorene (**7**) (vide infra). The former intermediates are

(22) See for instance, Portella-Oberli, M. T.; Jeannin, C.; Soep, B.; Zerza, G.; Chergui, M. *Chem. Phys. Lett.* **1998**, *296*, 323.
(23) Denny, D. B.; Klemchuk, P. P. *J. Am. Chem. Soc.* **1958**, *80*, 3289.
(24) Palik, E. C.; Platz, M. S. *J. Org. Chem.* **1983**, *48*, 963.
(25) Kirmse, W.; Kund, K.; Ritzer, E.; Dorigo, A. E.; Houk, K. N. *J. Am. Chem. Soc.* **1986**, *108*, 6045.
(26) Dorra, M.; Gomann, K.; Guth, M.; Kirmse, W. *J. Phys. Org. Chem.* **1996**, *9*, 598. We thank a referee for notifying us of the relevant works by Kirmse.

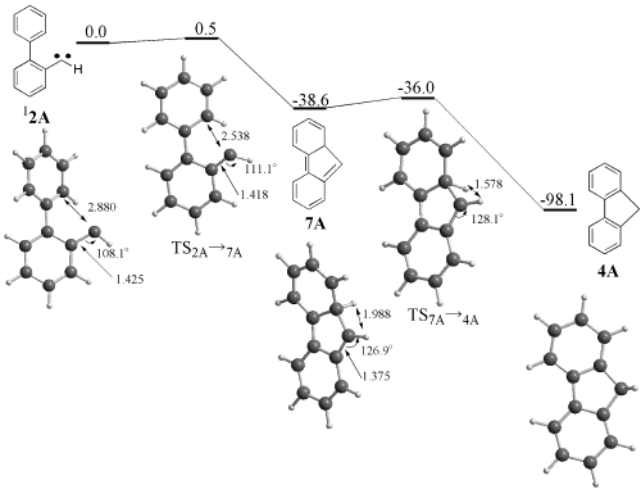
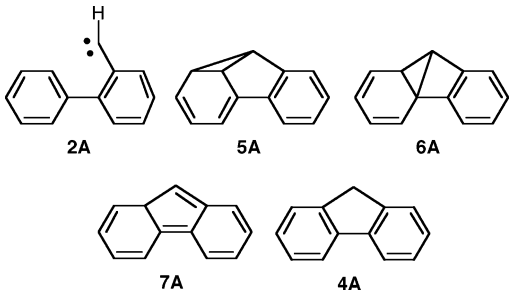


Figure 11. B3LYP/6-31G* relative energies (kcal/mol) of species involved in the reaction of *ortho*-biphenylcarbene **2A** leading to fluorene **4A** by way of isofluorene **7A**.

supposed to be rather very high in energy in the light of ring strain and hence are less likely. Moreover, spectroscopical features of the observed species match with those for quinodimethane structure in isofluorene (**7**) rather than those for the former. For example, *o*-quinodimethanes usually exhibit broad and strong absorption bands centereted around 350−450 nm.[27]

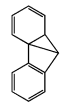
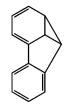
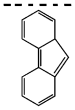
DFT Calculations. To gain some insights into intermediates involved in the present photolysis, we performed DFT calculations[28,29] of potential energy surface for the possible reaction of biphenyl-2-ylcarbene **2A** (Figure 11, Table 1).

The (U)B3LYP calculations predicted carbene **2A** has a triplet ground state with the singlet lying 6.9 kcal/mol higher in energy. The dihedral angles between the two phenyl rings in triplet and singlet states are 41.8 and 35.0 degrees, respectively.



Carbenes can cyclize either by forming σ bonds to two carbons of the phenyl substituent to produce tetracyclic cyclopropanes (**5A** and **6A**) or by attack of carbenic carbon on an ortho carbon of the phenyl substituent to afford isofluorene-(**7A**). B3LYP calculations indicated that isofluorene **7A** is 38.6 kcal/mol lower in energy than singlet carbene. Tetracyclic compounds **5A** and **6A** were calculated to be significantly higher in energy, much higher in energy even than the singlet carbene

Table 1. Energies (ΔE), Relative to **2A**, of Intermediates Calculated Using DFT at the (U)R3BLYP/6-31G(d) Level of Theory

Spiecies	ΔE	λ	f
 **5A**	32.0	383	0.0759
		338	0.0110
		292	0.0867
		277	0.0132
		271	0.0256
		247	0.0544
 **6A**	22.3	338	0.0174
		271	0.0131
		265	0.0415
		253	0.0354
		250	0.0300
		241	0.0176
 **7A**	-38.6	492	0.1460
		312	0.1493
		243	0.0174

Absorption maximum (λ, nm) and oscillator strength (f), computed using time-dependent DFT calculation at the R3LYP/6−31 G(d) level of theory, are also shown.

itself and the transition state for formation of isofluorene **7A**. This suggests that **7A** is, of these three possible cyclization products of the carbene, by far the lowest in energy. Transition state energy leading from singlet carbene ^{1}**1A** to isofluorene **7A** is estimated to be only 0.5 kcal/mol, while that from isofluorene **7A** to fluorene **4A** is 2.6 kcal/mol.

To assist in the experimental identification of the reactive intermediates, the eletronic spectra of tetracyclic intermediates and isofluorene were calculated, using time-dependent (TD) DFT theory.[30] As shown in Table 1, isofluorene **7A** is predicted to have relatively intense absorption bands at 310 and 490 nm, while tetracyclic intermediates **5A** and **6A** are predicted to have a very weak absorption band at 338 and 483 nm at the longest, respectively.

Kinetic Deuterium Isotope Effects. If the transient absorption band is ascribable to isofluorene **7a**, the decay process corresponds to the 1,5-H shift process leading to fluorene **4a**. One may then expect the kinetic deuterium isotope effect (KDIEs) in this process (vide infra). Thus, we prepared desired precursors (**2a**−N_2-*d*) according to the essentially identical procedure employed to prepare the protio analogue by using penta(deutrio)phenylboronic acid.

Irradiation of **2a**−N_2-*d* in degassed benzene again resulted in the formation of fluorene (**4a**-*d*) as the exclusive product, no additional products being detected. Irradiation of **2a**−N_2-*d* in 2-MTHF matrix at 77 K produced ESR signals (having D =

(27) (a) de Fonscka, K. K.; Manning, C.; McCullough, J. J.; Yarwood, A. J. *J. Am. Chem. Soc.* **1977**, *99*, 8257. (b) de Fonscka, K. K.; McCullough, J. J.; Yarwood, A. J. *J. Am. Chem. Soc.* **1979**, *101*, 3277. (c) McCullough, J. J. *Acc. Chem. Res.* **1980**, *13*, 270. (d) Wintgens, V.; Netto-Ferreira, J. C.; H. L. Casal, H. L.; Scaiano, J. C. *J. Am. Chem. Soc.* **1990**, *112*, 2363. (e) Johnston, L. T.; Scaiano, J. C. *Chem. Rev.* **1989**, *89*, 521. (f) Netto-Ferreira, J. C.; Wintgens, V.; Scaiano, J. C. *Can. J. Chem.* **1994**, *72*, 1565.

(28) (a) Lee, C.; Yang, W.; Paar, R. G. *Phys. Rev. B* **1980**, *37*, 785. (b) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098. (c) Becke, A, D. *J. Chem. Phys.* **1993**, *98*, 5648.

(29) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, Foresman, J. B.; K.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. W. M.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. GAUSSIAN 98; Gaussian Inc.: Pittsburgh, PA, 1998.

(30) Casida, M. E.; Jamorski, C.; Casida, K. C.; Salahub, D. R. *J. Chem. Phys.* **1998**, *108*, 4439.

0.304 cm^{-1}, $E = 0.00454$ cm^{-1}) and UV/vis spectra (showing maxima at 323, 353, and 390 nm), which are essentially identical with those observed in the photolysis of the protio analogue, **2a**−N_2. Thermal stability of those signals and absorption bands was also similar to those of ^{3}**2a**. Therefore, those transient species were easily assigned to the corresponding triplet carbene ^{3}**2a**-*d*.

LFP of **2a**−N_2-*d* in degassed benzene produced again transient absorption showing the maxima at 420 and 490 nm, which decayed in essentially the same first-order manner with the rate constant of $k = 7.6 \times 10^4$ s^{-1} ($\tau = 13$ μs), which is almost identical with that observed by LFP of **2a**−N_2. Almost no KDIE was observed.

Kinetics and Thermodynamic of 1,5-Hydrogen Shift. The 1,5-shift in simple cyclic and acyclic compounds is relatively slow as a consequence of substantial activation energies. For instance, the activation energy ($\Delta H^{\ddagger}$) for the 1,5-shift in 1,3-pentadiene is 36 kcal/mol and even higher ($\Delta H^{\ddagger} = 41.7$ kcal/mol, $\Delta G^{\ddagger} = 40.1$ kcal/mol) in 1,3-cyclohexadiene.[31] However it was recently found that the 1,5-shift of isoindene to indene[27a−c,32] and 8a, 9-dihydrophenanthrene to 9, 10-dihydrophenanthrene[33] proceeds rapidly. This indicates that formation of an aromatic ring in the products leading to high exergonicity of the 1,5-shift is responsible for the lowering of the activation energy. The effects of aromatic stabilization on the rates of 1,5-shifts has been estimated and examined by B3LYP/6-31G** computations.[34] The activation barriers $\Delta H^{\ddagger}$ (and $\Delta G^{\ddagger}$) for 1,5-shift of isoindene[27a−c,32] and 8a, 9-dihydrophenanthrene[33] are calculated to be 18.4 (and 17.1) kcal/mol and 14.8 (and 13.8) kcal/mol, respectively. This indicates that formation of an aromatic ring in the products leading to high exergonicity of the 1,5-shift is responsible for the lowering of the activation energy. In the present system, two benzene rings are regenerated in the isomerization of **7a** to **4a** compared with the above two systems. Isofluorene (**7A**)-fluorene(**4A**) conversion is estimated to be the most exothermic (54.5 kcal/mol) and hence to have the smallest barrier ($\Delta H^{\ddagger} = 2.6$ kcal/mol and $\Delta G^{\ddagger} = 3.2$ kcal/mol). This is another example of the Bell-Evans-Polanyi principle. [35]

The rate constant of 7.6×10^4 s^{-1} observed for the present system is more than four and two orders of magnitude larger than that observed for isoindene to indene ($k = 3.1$ s^{-1}) and 9-phenyl-8a, 9-dihydrophenanthrene to 9,10-dihydrophenanthrene processes ($k = 1.6 \times 10^2$ s^{-1}), respectively. However, this rate is very small for the process with $\Delta G^{\ddagger} = 3.2$ kcal/mol, which corresponds to 4×10^{10} s^{-1}. The rate constants observed for 1,5-H shift in isoindene and 9-phenyl-8a, 9-dihydrophenanthrene are in good agreement with those estimated based on $\Delta G^{\ddagger} = 17.1$ (2.1 s^{-1}) and 13.8 kcal/mol (5.5×10^2 s^{-1}), respectively. Moreover, essentially zero kinetic deuterium isotope effect ($k_H/k_D = 1$) observed for the present system is in sharp contrast with k_H/k_D of ca. 5 observed for the 1,5-sigmatropic rearrangement of *cis*-1,3-pentadiene[36] and also with k_H/k_D of 3.7 for the shift of aromaticity-driven isoindene to indene conversion.[27b] It is thus highly unlikely that the transient absorption band is due to isofluorene.

LFP of Fluorene 4a. Kirmse et al.[26] have observed, in LFP of (biphenyl-2-yl)phenyldiazomethane, a transient absorption band with $\lambda_{max} = 370$ nm whose rates of decay are $2.3-3.4 \times 10^5$ s^{-1} and are nearly independent of the solvent. They also noted that the decrease is associated with an increase in the band due to 9-phenylfluorene and that the decay rate is strongly accelerated by the presence of oxygen. They assigned the transient band to triplet 9-phenylfluorene since the same absorption is generated by laser excitation of the fluorene.

LFP of fluorene **4a** in degassed benzene produced a transient band with a sharp band with maxima at 350 nm along with a rather broad band with apparent maxima at 415 and 500 nm extending up to 550 nm. All the bands decayed in first order. The decay rate monitored at 420 nm is found to be 6.37×10^4 s^{-1} ($\tau = 16$ μs). The decacy rate is strongly accelerated by the presence of oxygen with the quenching rate constant of 2.10×10^9 M^{-1} s^{-1}. Although the strong band at 350 nm was not apparent in the transient absorption spectra obtained in LFP of **2a**−N_2 due to the overlap with the absorption maxima of the diazo precursor, the spectroscopic features in the 400 to 550 nm region and decay profile are in good agreement with that observed in LFP of **4a**. It is thus likely that the transient band observed in LFP of diazo compound **2a**−N_2 is ascribable to triplet fluorene **4a**.

It should be noted here that no new band was observed during the quenching reaction of triplet flourene by oxygen. This is to be compared with the observation that the transient band is observed in LFP of **2a**−N_2 in the presence of oxygen (vide supra).

D. [2,6-Bis(aryl)-4-phenylphenyl](2,6-dimethyl-4-phenylphenyl)carbene (2b−d). Effect of Substituents on *ortho*-Phenyl Groups. Observations indicate that singlet carbene ^{1}**2a** is trapped exclusively and very rapidly by the *o*-phenyl group in solution at room temperature to form fluorene before it undergoes intersystem crossing to the triplet. This means that if one can retard the initial trapping reaction of ^{1}**2**, it may be possible to observe a triplet carbene in solution. One way to realize this is to introduce substituents on the *o*-phenyl ring. So, we prepared precursor diphenyldiazomethanes in which *ortho*-phenyl rings carry such substituents as 4-phenyl (**2b**−N_2), 1,3-bis(trifluoromethyl) (**2c**−N_2), and 2-fluoro groups (**2d**−N_2). Trifluoromethyl groups are expected to reduce electron density on the phenyl ring while the 2-fluoro group will increase steric repulsion and hence retard the initial attack of ^{1}**2**.

ESR ZFS parameters and UV/vis absorption maxima of triplet carbenes ^{3}**2b**−**d** observed in the photolysis of the precursory diazomethanes **2**−N_2 in the 2-MTHF matrix as well as *Td* are summarized in Table 2. The data in Table 2 indicate that the structures of triplet carbenes (*D* and *E* values and absorption maxima) and thermal stability (*Td*) are practically unaffected by those substituents.

LFP of **2b**−N_2-**2d**−N_2 in degassed benzene again produced the transient absorption bands similar to those observed in LFP

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Table 2. *D* and *E* Values and UV/Vis Spectra of Triplet Diarylcarbenes (^{3}**1** and ^{3}**2**)[a]

carbenes	$\|D\|$ (cm^{-1})	$\|E\|$ (cm^{-1})	E/D	λ_{max} (nm)	Td (K)[b]
1	0.348	0.0326	0.0937	315, 349, 391	170
2a	0.300	0.00486	0.0162	326, 356, 387	130
2a-*d*	0.304	0.00454	0.0149	323, 353, 390	130
2b	0.308	0.00557	0.0181	316, 341, 376	140
2c	0.324	0.00873	0.0269	320, 357, 400	130
2d	0.335	0.00586	0.0175	320, 351, 380	140

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

Table 3. Kinetic Data Obtained in LFP of Diazomethanes (**2**−**N$_2$**)[a]

diazomethanes	λ_{max} (nm)	k (s^{-1})	τ (μs)
2a−**N$_2$**	410	7.6×10^4	13
2a−**N$_2$**-***d***	420	7.6×10^4	13
2b−**N$_2$**	480	6.9×10^4	15
2c−**N$_2$**	400	7.1×10^4	14
2d−**N$_2$**	420	8.7×10^4	12

[a] All kinetic measurements were carried out in benzene at 20 °C.

of **2a**−N_2, which decayed in first-order kinetics. No transient bands ascribable to the triplet states were detected. The rate constants summarized in Table 3 apparently indicate that the decay rates change very little by the substituents on *o*-phenyl groups. Finally, product analysis of the spent solution indicated that fluorenes **4** were produced as almost exclusive products in all cases (Scheme 3).

The observations clearly indicate that the substituents on the *o*-phenyl rings exhibit little influence on overall reaction initiated by photoexcitation of **2**−N_2.

Discussion

We have prepared precursor diphenyldiazomethanes **2**−N_2 for DPC having *o*-aryl groups as a potential kinetic protector of carbene center. Carbenes **2** are then generated by irradiating the precursors **2**−N_2.

The observations in the photolysis of **2**−N_2 are different from those in the photolysis of sterically congested diaryldiazomethanes in several respects. First, main products observed in the photolysis of sterically congested diphenyldiazomethanes in benzene solution at room temperature are, as is seen in the photolysis of **1**−N_2, mostly dimers of triplet DPCs. In the present case, however, fluorene **4** is always obtained as the almost exclusive product, no carbenic dimers being detected. It is clear that the nascent singlet state of the carbene is almost exclusively trapped by the *o*-phenyl group to give fluorene **4**. Computational studies suggest that the initial attack of carbene on an ortho carbon of the phenyl group at the ortho position proceeds with a very low activation barrier. It is then likely that the singlet state is almost instantaneously trapped before it undergoes intersystem crossing to the triplet state. This process is not affected by substituents on the ortho phenyl groups. Thus, it is not possible to observe the triplet state in solution at room-temperature directly.

Although isofluorene is likely to be involved in the reaction leading to fluorene, this species is also not detected by LFP with time resolution in nanoseconds. Computational studies predict that the rate for a "double"-aromaticity-driven 1,5-H shift process in isofluorene−fluorene conversion is 4×10^{10} s^{-1} for the model system. These data from calculations for the model system can explain why putative intermediates are not detected in nano-second time resolution.

A crucial difference between the present system and (biphenyl-2-yl)phenylcarbene is found in the reactivity toward methanol. While significant amount of O−H insertion product is formed in the reaction of the latter, the former carbene is not quenched by methanol at all. This suggests that the singlet state is also protected from external reagent in the former carbene.

Second, triplet carbene is observed in matrix photolysis at low temperature although this is not observed in LFP in degassed solution at room temperature. This is somewhat unexpected as, in most cases, the transient bands due to triplet carbene are observed both in matrix photolysis and in LFP. This can be explained by assuming the effect of the matrix on the reaction pathway of the singlet state. If, as is suggested by DFT calculations, *o*-phenyl groups are not coplanar with the carbenic phenyl group, cyclization of the carbenes will require molecular motions. Such motion can be blocked in a rigid matrix to some extent; hence, the decay reaction in the singlet state leading to fluorene is retarded. Thus, the triplet state comes to be observable as the singlet state has enough lifetime to intersystem-cross to the triplet under these conditions. It is interesting to note here that product analysis of the spent solution of the photolysis in the matrix at 77 K showed that fluorene is still formed almost exclusively even under these conditions.[37] This may mean that triplet states also react with the *o*-phenyl group (vide infra).

The effect of oxygen is also interesting. A triplet carbene absorption band is observed in solution only in LFP of **2**−N_2 in the presence of oxygen, along with the band due to carbonyl oxide. This can be interpreted in terms of external perturbation of intersystem crossing by oxygen. It is known that molecular oxygen enhances the overall intersystem crossing.[38] Therefore, the observation of triplet carbene absorption band in the presence of oxygen can be interpreted as indicating that intersystem crossing either in the excited state of diazo compound (S_1 to T_1) and/or in the carbenes (singlet to triplet states) is enhanced by oxygen to the point where detection of the transient bands is possible (vide infra).

However, product analysis indicates that fluorene **4** is still obtained as the major product even in the presence of oxygen while ketone is formed only as a minor product (∼10%), although the triplet carbene band is trapped by oxygen and the band due to the carbonyl oxide is apparent. This suggests that fluorene is still formed as the main product either from the singlet and/or from the triplet. Therefore, a part of the reason that the triplet state **2a** is observable in the presence of oxygen is due to the fact that the bands of triplet fluorene (^{3}**4**) become invisible in the presence of oxygen as a result of efficient quenching and hence the absorption band due to triplet carbene ^{3}**2** becomes apparent under these conditions. However, since the bands due to carbonyl oxide (**2a**−O_2) are also seen only in the presence of oxygen and the oxidation product **2a**−O is formed only in the presence of oxygen, external perturbation

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of ISC by oxygen still plays a role. If the ISC is on a time scale of picoseconds (as with diphenylcarbene), on the other hand, it is not understandable why this should be increased by the presence of triplet oxygen (the increase should be limited by the diffusion of oxygen in solution). It is more reasonable to assume that triplet state ^{3}**2a** is also generated to some extent in the absence of oxygen but undergoes cyclization leading to fluorene, since this is only reaction available to the triplet but that ^{3}**2a** comes to be trapped by oxygen in the presence of oxygen in competition with the intramolecular reaction.

How well is the carbene center in the triplet state protected by the ortho phenyl groups? Since the transient bands due to the triplet state were not seen under ambient conditions, the lifetime was estimated from a Stern−Volmer plot in the oxygen quenching experiments. This value of 16 μs is unexpectedly small. It is interesting to note here that the quenching rate constant of ^{3}**2a** by oxygen is essentially identical with that observed for ^{3}**1** ($k_{O_2} = 1.11 \times 10^7$ M^{-1} s^{-1}), whose lifetime under ambient conditions is ca. 1 s. Moreover, ^{3}**1** was shown to abstract hydrogen from CHD with a rate constant of $k = 7.4 \times 10^2$ M^{-1}s^{-1}, while ^{3}**2a** was not quenched by CHD. This means that the carbenic center in ^{3}**2a** is equally well shielded by the *o*-phenyl groups from external reagents as in ^{3}**1**. Extremely shorter lifetime of ^{3}**2a** ($\tau = 16$ μs) as opposed to ^{3}**1**($\tau = 1$ s) is then interpreted only in terms of reaction of the triplet state with the *o*-phenyl groups. This is in accordance with the product study showing that ketone is produced only in 10% yield even in the irradiation in the presence of oxygen (vide supra).

The reaction of sterically congested triplet carbenes with benzene is usually considered to be very slow. Indeed, almost no products from such reaction have been detected in the photolysis of sterically congested diphenyldiazomethanes. However, methylene is shown to react with benzene both in singlet and triplet states.[39] In the triplet reaction, C−H abstraction is proposed from kinetic studies, but C−C bond formation to generate a diradical intermediate is suggested by theoretical calculations. It is then possible that triplet states can interact with the adjacent ortho carbon of the *o*-phenyl group that is in close vicinity. Such interaction will eventually lead to fluorene by way of isofluorene.

A reaction of triplet carbene leading to a typical singlet product is seen in the reaction with alcohols.[13] Generally, singlet carbenes insert readily into the O−H bond of alcohol while hydrogen abstraction from the C−H bonds of alcohol is a characteristic reaction of the triplet ground state of carbene. The behavior of aryl and diarylcarbenes seemingly violates this simple rule. Upon addition of alcohol in the LFP experiments, for instance, quenching of both singlet ($k_S = 10^{10}$ M^{-1} s^{-1}) and triplet diphenylcarbene($k_T = 10^7$ M^{-1} s^{-1}) is observed.[40]

A reaction from the triplet state to a singlet product must involve surface crossing. Two mechanisms, preequilibrium and surface crossing, are proposed for the relatively slow reaction of triplet diarylcarbenes.[41] According to the preequilibrium mechanism, triplet to singlet interconversion occurs prior to O−H insertion of the singlet, while triplet carbenes can react directly with alcohol with surface crossing occurring after the carbene has begun to interact with the O−H bond in the latter mechanism. In light of the rather large gap between singlet and triplet states calculated for **2A** and also the fact that fluorene **4** is obtained as a main product even in the matrix at low temperature, surface crossing mechanism is likely one in this case.

The present observation is to be compared with the isocarbazole to carbazole conversion, a nitrogen analogue of the present system, observed in LFP of *ortho*-biphenyl azide.[42] The activation and reaction energies for this process are calculated at the B3LYP/6-31G* level of theory to be 7.5 and 53.7 kcal/mol, respectively, suggesting that the activation energy is larger than that of the carbon analogue while the reaction energy is similar. It is pointed out that introduction of heteroatoms significantly increases the activation energy for the hydrogen shift.[34] However, the rate constant observed for isocarbazole to carbazole conversion in pentane is reported to be 1.4×10^7 s^{-1}, more than three orders of magnitude smaller than that predicted on the present system. A considerable kinetic deuterium isotope effect ($k_H/k_D = 3.4$) is observed in this case.

Conclusion

We have explored procedures to prepare precursors for diphenylcarbenes having aryl groups at the ortho position. Diphenylcarbenes generated from those precursors are not stable, but exhibited an interesting chemistry. The finding that the carbenic center is almost completely shielded by an *o*-aryl group from external reagents indicates that once one can introduce an aryl group that can prevent the reaction of carbene at the ortho carbon, one will be able to generate fairly stable triplet carbene. Perfluorophenyl group is an attractive candidate in this respect since C−F bonds are only the bond utterly unreactive toward carbene.

Experimental Section

General Methods. Reagents were obtained commercially and used without further purification unless otherwise noted. Tetrahydrofuran, ethyl ether, toluene, and dioxane were dried over benzophenone ketyl (sodium/benzophenone) and dichloromethane, carbon tetrachloride and triethylamine were dried over calcium hydride. The ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded on a JEOL JNM-AL300FT/NMR spectrometer in $CDCl_3$ with $SiMe_4$ as an internal reference. IR spectra were measured on a JASCO FT/IR-410 spectrometer, and UV/vis spectra were recorded on a JASCO CT-560 spectrophotometer. ESR spectra were measured on a JEOL JES-TE200D ESR spectrometer. The mass spectra were recorded on a JEOL JMS-600H mass spectrometer and AB Voyager-DE PROMALDI-TOF mass spectrometer. Gel permeation chromatography (GPC) was carried out on a JASCO PU-1586 chromatograph with a UV-1570 UV/vis detector using a Shodex GPC H-2001 column (20 mm × 50 cm). Thin-layer chromatography was carried out on a Merck Kieseigel 60 PF 254. Column chromatograph was carried out on a silica gel (Merck for dry column chromatography) or on an aluminum oxide, active neutral (activity I) (ICN for column chromatography).

Preparation of (2,6-Dibromo-4-phenylphenyl)(2,6-dimethyl-4-phenylphenyl)diazomethane (1−N$_2$). A solution of 3,5-dimethylbi-

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phenyl[43] (4.92 g, 27.0 mmol) in CCl_4 was cooled in an ice bath to 0 °C and Br_2 (1.35 mL, 27.0 mmol) was added dropwise under vigorous stirring over a period of 15 min and the mixture was stirred overnight at room temperature. The mixture was neutralized with 10% NaOH aq, and the residue was extracted with CCl_4. The organic layer was washed with H_2O, dried (Na_2SO_4) and evaporated to leave 4-bromo-3,5-dimethylbiphenyl as a white solid in 97% yield, which was used for the next step without further purification: mp 52.2−54.5 °C; ^{1}H NMR ($CDCl_3$) δ 2.48 (s, 6 H), 7.29 (s, 2 H), 7.45−7.32 (m, 3 H), 7.54 (dd, J = 1.65, 6.80 Hz, 2 H).

To a solution of the bromide (4.47 g, 17.1 mmol) in Et_2O (30 mL) was added *n*BuLi (7.08 mL, 2.66 M in hexane, 18.8 mmol) dropwise at −78 °C. After stirring for 3 h at −78 °C, a solution of DMF (3.97 mL, 51.3 mmol) in Et_2O (7 mL) was added to the solution. The resulting solution was gradually warmed to room temperature and then stirred overnight. Ammonium chloride aq. was added and the resulting mixture was extracted with Et_2O. The ethereal layer was washed with water and brine, dried over Na_2SO_4, and evaporated under reduced pressure. The resulting brownish viscous oil was chromatographed on a silica gel column eluted with CH_2Cl_2-*n*-hexane (1:1). 3,5-Dimethyl-4-formylbiphenyl was obtained as a white solid in 79% yield; mp 41.3−43.9 °C; ^{1}H NMR ($CDCl_3$) δ 2.69 (s, 6 H), 7.31 (s, 2 H), 7.40 (tt, J = 1.65, 7.17 Hz, 1 H), 7.46 (dd, J = 6.98, 7.17 Hz, 2 H), 7.61 (dd, J = 6.98, 1.65 Hz, 2 H), 10.65 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 20.7, 127.2, 128.2, 128.4, 128.9, 131.2, 139.8, 141.8, 145.5, 193.0; IR (NaCl, cm^{-1}) ν 1685; EIMS *m*/*z* (relative intensity) 210 (M$^+$, 100), 209 (88.0); HRMS Calcd for $C_{15}H_{14}O$ 210.1045, Found *m*/*z* 210.1036.

To a solution of the 4-iodo-3,5-dibromobiphenyl[44] (4.75 g, 10.9 mmol) in anhydrous Et_2O (30 mL) was added *n*BuLi (4.53 mL, 2.64 M in hexane, 12.0 mmol) dropwise at −78 °C. After stirring for 5 h at −78 °C, a solution of the aldehyde (2.29 g, 10.9 mmol) in anhydrous Et_2O (15 mL) was added to the solution. The resulting solution was gradually warmed to room temperature and stirred for 1 day. Ammonium chloride aq. was added to the solution and the resulting mixture was extracted with Et_2O. The ethereal layer was washed with water and brine, dried over Na_2SO_4, and evaporated under reduced pressure. The resulting brownish viscous oil was chromatographed on a silica gel column eluted with CH_2Cl_2-*n*-hexane (2:1). **(2,6-Dibromo-4-phenylphenyl)(2,6-dimethyl-4-phenylphenyl)methanol** was obtained as a white solid in 85% yield; mp 103.2−105.1 °C; ^{1}H NMR ($CDCl_3$) δ 2.39 (s, 6 H), 2.73 (d, J = 8.82 Hz, 1 H), 6.61 (d, J = 8.82 Hz, 1 H), 7.24 (s, 2 H), 7.33−7.31 (m, 2 H), 7.47−7.39 (m, 4 H), 7.61−7.54 (m, 4 H), 7.82 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 21.7, 76.3, 124.7, 126.84, 126.87, 127.1, 128.3, 128.4, 128.6, 129.0, 132.1, 136.4, 137.2, 137.7, 138.4, 140.0, 140.4, 142.4; EIMS *m*/*z* (relative intensity) 524 (M+4, 5.7), 523(19.8), 522 (M+2, 11.9), 521(39.2), 520 (M$^+$, 7.2), 519 (19.7), 508 (15.9), 506(31.9), 504(16.6), 183(100); HRMS Calcd for $C_{27}H_{22}Br_2O$ 520.0037, Found *m*/*z* 520.0087.

The methanol (4.39 g, 8.41 mmol) was added to $SOCl_2$ (50 mL) and the mixture was stirred at 35 °C for 1 day. The excess $SOCl_2$ was evaporated to give **(2,6-dibromo-4-phenylphenyl)(2,6-dimethyl-4-phenylphenyl)chloromethane** as a brown solid quantitatively, which was used without further purification; ^{1}H NMR ($CDCl_3$) δ 2.51 (s, 6 H), 7.01 (s, 1 H), 7.25 (s, 2 H), 7.35−7.30 (m, 2 H), 7.48−7.39 (m, 4 H), 7.55 (d, J = 6.80 Hz, 2 H), 7.60 (d, J = 7.17 Hz, 2 H), 7.84 (s, 2 H).

A solution of the chloromethane (4.50 g, 8.41 mmol) in anhydrous dioxane (60 mL) was added slowly to a mixture of ethyl carbamate (18.7 g, 210.2 mmol) and $AgBF_4$ (2.46 g, 12.6 mmol) heated at 60 °C under vigorous stirring and the mixture was stirred at 100 °C for 1 day. The mixture was then filtered and the filtrate was extracted with $CHCl_3$. The organic layer was washed with H_2O to remove dioxane, dried (Na_2SO_4), and evaporated under reduced pressure. The resulting brownish viscous oil was chromatographed on a silica gel column eluted with $CHCl_3$-*n*-hexane (3:1). **Ethyl *N*-(2,6-dibromo-4-phenylphenyl)-(2,6-dimethyl-4-phenylphenyl)methylcarbamate** was obtained as a yellow solid in 63% yield; mp 202.6−204.8 °C; ^{1}H NMR ($CDCl_3$) δ 1.29 (t, J = 7.17 Hz, 3 H), 2.32 (s, 6 H), 4.18−4.24 (m, 2 H), 5.35 (d, J = 8.82 Hz, 1 H), 6.59 (d, J = 8.82 Hz, 1 H), 7.23 (s, 2 H), 7.34−7.29 (m, 2 H), 7.44−7.35 (m, 4 H), 7.58−7.52 (m, 4 H), 7.80 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 14.8, 21.3, 58.1, 61.3, 124.9, 127.0, 127.3, 128.4, 128.5, 128.7, 129.0, 132.6, 135.0, 136.5, 137.5, 137.7, 138.0, 140.3, 140.4, 142.3, 155.0; EIMS *m*/*z* (relative intensity) 595 (M+4, 1.5), 593 (M+2, 2.2), 591 (M$^+$, 1.6), 514 (100), 512 (94.6), 344 (40.9), 183(100); HRMS Calcd for $C_{30}H_{27}Br_2NO_2$ 591.0408, Found *m*/*z* 591.0413.

To a stirred and cooled solution of the carbamate (88.9 mg, 0.15 mmol) in Ac_2O (3 mL) and AcOH (2 mL) was added $NaNO_2$ (207.0 mg, 3.0 mmol) in a small portion at 0 °C over a period of 3 h and the mixture was stirred for 1 day at room temperature after addition was completed. The mixture was poured into H_2O and extracted with Et_2O. The ethereal layer was washed with 5% Na_2CO_3 aq solution, H_2O, dried (Na_2SO_4), and evaporated to dryness. **Ethyl *N*-nitroso-*N*-(2,6-dibromo-4-phenylphenyl)(2,6-dimethyl-4-phenylphenyl)methylcarbamate** was obtained in 50% yield as a yellow solid, which was used without further purification; ^{1}H NMR ($CDCl_3$) δ 1.29 (t, J = 6.62 Hz, 3 H), 2.09 (s, 6 H), 4.40 (q, J = 6.62 Hz, 2 H), 7.08 (s, 1 H), 7.23 (s, 2 H), 7.47−7.39 (m, 6 H), 7.61−7.54 (m, 4 H), 7.79 (s, 2 H).

All the following operations were carried out in a dark room. To a stirred and cooled solution of the nitrosocarbamate (48.5 mg, 0.078 mmol) in anhydrous THF (3 mL) was added *t*-BuOK (17.5 mg, 0.16 mmol) at 0 °C under Ar atmosphere and the mixture was stirred for 1 day at room temperature. The mixture was poured into H_2O and extracted with Et_2O. The ethereal layer was washed with H_2O, dried (Na_2SO_4), and evaporated. The resulting orange solid was chromatographed on a cooled alumina column eluted with *n*-hexane at 0 °C. The diazo compound obtained as a fast-moving fraction from the column was fairly pure but was further purified by repeated chromatography on a gel permeation column with $CHCl_3$. **(2,6-Dibromo-4-phenylphenyl)(2,6-dimethyl-4-phenylphenyl)diazomethane (1−N$_2$)** was obtained as an orange solid in 57% yield; mp 108.5−111.3 °C; ^{1}H NMR ($CDCl_3$) δ 2.27 (s, 6 H), 7.34 (s, 2 H), 7.48−7.38 (m, 6 H), 7.62−7.54 (m, 4 H), 7.84 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 21.2, 47.8, 125.8, 126.9, 127.0, 127.2, 127.6, 128.3, 128.5, 128.7, 129.1, 130.5, 131.7, 137.5, 138.3, 140.4, 140.6, 142.7; IR (NaCl, cm^{-1}) $\nu_{C=N2}$ 2054.

Preparation of (2,4,6-Triphenylphenyl)(2,6-dimethyl-4-phenylphenyl)diazomethane (2a−N$_2$) To a solution of ethyl *N*-(2,6-dibromo-4-phenylphenyl)(2,6-dimethyl-4-phenylphenyl)methylcarbamate (200.0 mg, 0.337 mmol) in THF (10 mL) were added phenylboronic acid (123.3 mg, 1.01 mmol), palladium acetate (7.6 mg, 0.0337 mmol), di-*tert*-butylphosphinobiphenyl (30.2 mg, 0.10 mmol), and potassium fluoride (129.2 mg, 2.22 mmol) under Ar atmosphere and the mixture was stirred at room temperature for 1 day. The mixture was then filtered and the filtrate was evaporated under reduced pressure. The resulting brownish viscous oil was purified by the use of a thin layer chromatograph eluted with CH_2Cl_2-*n*-hexane (1:1). **Ethyl *N*-(2,4,6-triphenylphenyl)(2,6-dimethyl-4-phenylphenyl)methylcarbamate** was obtained as an yellow solid in 90% yield; mp 90.4−92.1 °C; ^{1}H NMR ($CDCl_3$) δ 1.06 (t, J = 7.17 Hz, 3 H), 1.90 (s, 6 H), 3.95−3.74 (m, 2 H), 4.48 (d, J = 9.55 Hz, 1 H), 6.59 (d, J = 9.55 Hz, 1 H), 6.83 (s, 2 H), 7.21 (m, 4 H), 7.32−7.27 (m, 3 H), 7.35 (m, 2 H), 7.47−7.36 (m, 9 H), 7.61 (d, J = 7.17 Hz, 4 H); ^{13}C NMR ($CDCl_3$) δ 14.4, 21.3, 53.6, 60.6, 126.4, 126.8, 126.9, 127.0, 127.5, 127.7, 127.9, 128.6, 128.7, 130.0, 136.5, 136.7, 138.2, 138.6, 139.5, 139.6, 141.0, 142.8, 143.0, 154.7; EIMS *m*/*z* (relative intensity) 587 (M$^+$, 78.3), 558 (47.0), 498 (44.4), 483 (58.5), 376(45.1), 332 (100), 317 (96.0), 208 (48.9); HRMS Calcd for $C_{42}H_{37}NO_2$ 587.2824, Found *m*/*z* 587.2893.

To a stirred and cooled solution of the carbamates (185.7 mg) in Ac_2O (6.0 mL) and AcOH (4.0 mL) was added $NaNO_2$ (436.0 mg,

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6.32 mmol) in small portions at 0 °C over a period of 3 h and the mixture was stirred for 1 day at room temperature after addition was completed. The mixture was poured into H_2O and extracted with Et_2O. The ethereal layer was washed with 5% $NaHCO_3$ aq solution, H_2O, dried (Na_2SO_4) and evaporated to dryness. **Ethyl *N*-nitroso-*N*-(2,4,6-triphenylphenyl)(2,6-dimethyl-4-phenylphenyl)methylcarbamate** was obtained as a mixture in 99% yield as a yellow semisolid, which was used for the next step without isolation.

All the following operations were carried out in a dark room. To a stirred and cooled solution of the nitrosocarbamates (194.9 mg) in anhydrous THF (20 mL) was added *t*-BuOK (70.9 mg, 0.632 mmol) at 0 °C under Ar atmosphere and the mixture was stirred for 1 day at room temperature. The mixture was poured into ice and extracted with Et_2O. The ethereal layer was washed with H_2O, dried (Na_2SO_4), and evaporated. The resulting orange solid was chromatographed on a cooled alumina column eluted with *n*-hexane at 0 °C. The diazo compound obtained as a fast-moving fraction from the column was fairly pure but was further purified by repeated chromatography on a gel permeation column with $CHCl_3$. **(2,4,6-Triphenylphenyl)(2,6-dimethyl-4-phenylphenyl)diazomethane (2a−N_2)** was obtained as an orange solid in 22%: mp 78.2−81.6 °C; ^{1}H NMR ($CDCl_3$) δ 2.10 (s, 6 H), 6.91 (s, 2 H), 7.22−7.16 (m, 5 H), 7.34−7.26 (m, 6 H), 7.43−7.39 (m, 7 H), 7.53 (s, 2 H), 7.66 (d, J = 7.17 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 21.7, 59.4, 126.80, 126.85, 127.0, 127.1, 127.3, 127.5, 127.9, 128.4, 128.6, 128.8, 129.2, 129.4, 129.6, 137.2, 138.5, 139.7, 139.8, 140.8, 141.0, 141.4; IR (NaCl, cm^{-1}) $\nu_{C=N_2}$ 2041.

Preparation of [{2,6-Di(phenyl-*d*$_5$)-4-phenyl}phenyl](2,6-dimethyl-4-phenylphenyl)diazomethane (2a−N_2-*d*) Diazomethane (**1b**-*d*) was prepared by using essentially the same method described above by way of the following compounds.

Ethyl *N*-[{2,6-Di(phenyl-*d*$_5$)-4-phenyl}phenyl](2,6-dimethyl-4-phenylphenyl)methylcarbamate. Yield 74%; yellow solid; mp 103.1−105.0 °C; ^{1}H NMR ($CDCl_3$) δ 1.06 (t, J = 7.17 Hz, 3 H), 1.90 (s, 6 H), 4.00−3.71 (m, 2H), 4.48 (d, J = 9.55 Hz, 1 H), 6.59 (d, J = 9.55 Hz, 1 H), 6.83 (s, 2 H), 7.38 (s, 2 H), 7.31 (tt, J = 1.47, 7.17 Hz, 2 H), 7.35 (s, 2 H), 7.42−7.37 (m, 4 H), 7.46 (dd, J = 1.29, 8.08 Hz, 2 H), 7.61 (dd, J = 1.47, 8.08 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 14.4, 21.3, 53.6, 60.6, 126.85, 126.90, 127.0, 127.5, 127.9, 128.6, 128.7, 129.6, 136.5, 136.7, 138.2, 138.6, 139.5, 139.6, 140.9, 142.7, 142.9, 154.7; EIMS *m*/*z* (relative intensity) 598 (M+1, 47.2), 597 (M$^+$, 100.0), 568 (50.5), 524 (29.0), 508 (34.3); HRMS Calcd for $C_{42}H_{27}D_{10}NO_2$ 597.3442; Found *m*/*z* 597.3446.

Ethyl *N*-Nitroso-*N*-[{2,6-di(phenyl-*d*$_5$)-4-phenyl}phenyl](2,6-dimethyl-4-phenylphenyl)methylcarbamate. Yield 99%; yellow solid; ^{1}H NMR ($CDCl_3$) δ 1.13 (t, J = 7.17 Hz, 3 H), 1.91 (s, 6 H), 4.37−3.95 (m, 2 H), 6.81 (s, 2 H), 7.16 (s, 2 H), 7.30 (s, 2 H), 7.43−7.27 (m, 6 H), 7.47 (dd, J = 1.47, 7.17 Hz, 2 H), 7.60 (dd, J = 1.47, 6.98 Hz, 2 H). **[{2,6-Di(phenyl-*d*$_5$)-4-phenyl}phenyl](2,6-dimethyl-4-phenylphenyl)-diazomethane (2a−N_2-*d*)**. Yield 10%; orange solid; mp 65.3−67.0 °C; ^{1}H NMR ($CDCl_3$) δ 2.10 (s, 6 H), 4.37−3.95 (m, 2 H), 6.92 (s, 2 H), 7.35−7.30 (m, 6 H), 7.46−7.37 (m, 5 H), 7.54 (s, 2 H), 7.67 (dd, J = 2.02, 6.98 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 141.2, 137.2, 127.3, 141.0, 129.4, 127.0 (C14), 140.8, 128.8, 126.9, 139.8, 128.6, 126.8, 139.6, 127.8, 59.7, 138.6, 127.5, 21.8; IR (NaCl, cm^{-1}) $\nu_{C=N_2}$ 2048.

Preparation of [2,6-Bis{2-fluorophenyl}-4-phenylphenyl](2,6-dimethyl-4-phenylphenyl)diazomethane (2d−N_2). To a solution of ethyl *N*-(2,6-dibromo-4-phenylphenyl)(2,6-dimethyl-4-phenylphenyl)-methylcarbamate (300.0 mg, 0.506 mmol) in DME (6 mL) were added 2-fluorophenylboronic acid (426.0 mg, 3.03 mmol), $Pd(PPh_3)_4$ (35.1 mg, 0.0303 mmol), and aqueous sodium carbonate (2 M, 1.0 mL) and the mixture was refluxed under Ar atmosphere for 1 day. The mixture was then filtered and the filtrate was evaporated under reduced pressure. The resulting brownish viscous oil was purified by the use of a thin layer chromatograph eluted with CH_2Cl_2-*n*-hexane (1:1). **Ethyl *N*-[2,6-bis(2-flurophenyl)-4-phenylphenyl](2,6-dimethyl-4-phenylphenyl)-methylcarbamate** was isolated as an yellow solid in 79%: mp 89.1−91.5 °C; ^{1}H NMR ($CDCl_3$) δ 1.17−1.00 (t, J = 7.17 Hz, 3 H), 2.06, 2.02 (s, 6 H), 3.99−3.55 (m, 2 H), 4.92, 4.84, 4.79 (d, J = 9.37 Hz, 1 H), 6.68, 6.57, 6.46 (d, J = 9.37 Hz, 1 H), 6.84, 6.80, 6.78 (s, 2 H), 7.24−7.03 (m, 3 H), 7.35−7.30 (m, 2 H), 7.39 (s, 2 H), 7.44−7.37 (m, 6 H), 7.60 (d, J = 7.17 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 14.3, 14.4, 14.7, 21.4, 21.6, 21.8, 53.2, 53.6, 54.2, 60.59, 60.64, 60.7, 114.7, 115.0, 115.1, 115.3, 115.4, 123.5, 123.6, 123.7, 126.9, 127.0, 127.7, 127.8, 128.2, 128.3, 128.4, 128.6, 128.8, 130.2, 130.4, 130.6, 130.7, 136.2, 136.47, 136.53, 136.8, 137.6, 138.16, 138.24, 138.7, 139.0, 139.2, 139.3, 141.1, 154.7, 154.8; EIMS *m*/*z* (relative intensity) 623 (M$^+$, 69.0), 593 (36.1), 549 (16.3); HRMS Calcd for $C_{42}H_{35}F_2NO_2$ 623.2636; Found *m*/*z* 623.2597. Diazomethane (**2d**−N_2) was prepared by using essentially the same method described above; yield 8%; mp 68.1−71.0 °C; ^{1}H NMR ($CDCl_3$) δ 2.18 (s, 6 H), 6.93 (s, 2 H), 7.09−6.96 (m, 2 H), 7.22−7.13 (m, 2 H), 7.34−7.29 (m, 4 H), 7.47−7.37 (m, 7 H), 7.54 (s, 2 H), 7.66−7.61 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 21.4, 59.2, 115.2, 115.5, 123.7, 126.9, 127.0, 127.2, 127.3, 127.5, 127.8, 128.5, 128.55, 128.63, 128.7, 128.78, 128.81, 129.06, 129.14, 129.24, 130.4, 130.89, 130.93, 1334.5, 138.2, 139.5, 139.9, 141.0, 158.0, 161.2; IR (NaCl, cm^{-1}) $\nu_{C=N_2}$ 2043.

Preparation of [2,6-Bis{3,5-bis(trifluoromethyl)phenyl}-4-phenylphenyl](2,6-dimethyl-4-phenylphenyl)diazomethane (1d-N_2). To a solution of ethyl *N*-(2,6-dibromo-4-phenylphenyl)(2,6-dimethyl-4-phenylphenyl)methylcarbamate (300.0 mg, 0.506 mmol) in toluene (15 mL) were added 3,5-bis(trifluoromethyl)phenylboronic acid (391.2 mg, 1.517 mmol), palladium acetate (11.4 mg, 0.0506 mmol), di-*tert*-butylphosphinobiphenyl (45.3 mg, 0.152 mmol), and potassium fluoride (194.0 mg, 3.340 mmol) under Ar atmosphere and the mixture was refluxed for 1 day. The mixture was then filtered and the filtrate was evaporated under reduced pressure. The resulting brownish viscous oil was purified by the use of a thin layer chromatograph eluted with CH_2Cl_2-*n*-hexane (1:1). **Ethyl *N*-[2,6-bis{3,5-bis(trifluoromethyl)}-4-phenyl]phenyl](2,6-dimethyl-4-phenylphenyl)methylcarbamate (3d)** was isolated as an yellow solid in 59%; mp 108.0−112.0 °C; ^{1}H NMR ($CDCl_3$) δ 0.99 (t, J = 7.17 Hz, 3 H), 1.97 (s, 6 H), 3.92−3.55 (m, 2 H), 4.43 (d, J = 8.82 Hz, 1 H), 6.54 (d, J = 8.82 Hz, 1 H), 6.90 (s, 2 H), 7.45−7.32 (m, 6 H), 7.52 (s, 4 H), 7.59 (m, 4 H), 7.74 (s, 4 H), 7.83 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 13.9, 21.2, 53.2, 61.0, 126.8, 127.0, 127.3, 127.7, 128.1, 128.3, 128.5, 129.0, 130.8, 136.2, 136.7, 137.0, 138.4, 139.6, 139.9, 140.0, 140.8, 144.6, 154.6; MS(MALDI-TOF) 882 (M+Na, 53.5); HRMS Calcd for $C_{46}H_{33}F_{12}NO_2Na$ 882.2212; Found *m*/*z* 882.2233. The carbamate was converted to **ethyl *N*-nitroso-*N*-[2,6-bis{3,5-bis(trifluoromethyl)phenyl}-4-phenylphenyl](2,6-dimethyl-4-phenylphenyl)methylcarbamate;** yield 99%, ^{1}H NMR ($CDCl_3$) δ 1.25 (t, J = 7.17 Hz, 3H), 1.85 (s, 6 H), 4.30−4.19 (m, 2 H), 6.75 (s, 1 H), 6.90 (s, 2 H), 7.44−7.30 (m, 10 H), 7.53 (s, 2 H), 7.79 (s, 4 H), 7.88 (s, 2 H). **Diazomethane (2d−N_2)** was prepared by using essentially the same method described above**;** yield 31%, mp 52.4−54.9 °C; ^{1}H NMR ($CDCl_3$) δ 2.12 (s, 6 H), 6.97 (s, 2 H), 7.48−7.29 (m, 6 H), 7.53 (s, 2 H), 7.71−7.62 (m, 4 H), 7.76 (s, 4 H), 7.79 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 21.1, 67.8, 126.1, 126.9, 127.5, 128.5, 128.6, 128.9, 129.0, 129.1, 129.4, 130.6, 137.5, 140.5, 142.9, 154.7; IR (NaCl, cm^{-1}) $\nu_{C=N_2}$ 2045.

Preparation of (2,6-Bisbiphenyl-4-yl-4-phenylphenyl)(2,6-dimethyl-4-phenylphenyl)diazomethane (1e). Diazomethane **1e** was prepared with using essentially the same method described above by way of the following compounds. **Ethyl *N*-(2,6-bisbiphenyl-4-yl-4-phenylphenyl)(2,6-dimethyl-4-phenylphenyl)methylcarbamate**; yield 21%, mp 120.3−122.5 °C; ^{1}H NMR ($CDCl_3$) δ 0.93 (t, J = 7.17 Hz, 3 H), 1.98 (s, 6 H), 3.93−3.64 (m, 2 H), 4.57 (d, J = 9.37 Hz, 1 H), 6.67 (d, J = 9.37 Hz, 1 H), 6.85 (s, 2 H), 7.46−7.27 (m, 21 H), 7.54 (s, 2 H) 7.56−7.51 (m, 4 H), 7.65−7.62 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 14.3, 21.4, 53.7, 60.7, 126.3, 126.8, 127.0, 127.2, 127.6, 127.8, 128.1, 128.6, 128.8, 129.1, 129.7, 136.3, 136.6, 136.8, 138.4, 138.8, 139.3, 139.5, 139.6, 140.7, 140.9. 142.2, 142.5, 143.7, 154.7; EIMS *m*/*z* (relative intensity)

739 (M^+, 100), 710 (51.1), 666 (38.5), 649 (93.2), 635 (57.6), 557 (36.3), 484 (99.5), 468 (60.9), 208 (41.1); HRMS Calcd for $C_{54}H_{45}NO_2$ 739.3450, Found *m/z* 739.3455. **Ethyl *N*-(2-bromo-4-phenyl-6-biphenyl-4-ylphenyl)(2,6-dimethyl-4-phenylphenyl)methylcarbamate**; yield 75%, mp 105.3−107.0 °C; ^{1}H NMR ($CDCl_3$) δ 1.20 (t, J = 6.98 Hz, 3 H), 2.17, 2.06 (s, 6 H), 4.11 (q, J = 6.98 Hz, 2 H), 5.07 (d, J = 8.82 Hz, 1 H), 6.55 (d, J = 8.82 Hz, 1 H), 7.03 (s, 2 H), 7.44−7.28 (m, 13 H), 7.52−7.49 (m, 4 H), 7.61−7.58 (m, 3 H), 7.89 (d, J = 2.02 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.7, 56.0, 61.1, 124.7, 126.3, 126.9, 126.99, 127.01, 127.2, 127.3, 128.0, 128.7, 128.8, 128.9, 129.5, 131.9, 132.5, 136.6, 137.7, 138.5, 139.8, 139.9, 140.2, 140.5, 140.6, 140.8, 144.4, 155.0; EIMS *m/z* (relative intensity) 667 (M+2, 2.8), 665 (M^+, 2.8), 585 (100), 497 (36.2); HRMS Calcd for $C_{42}H_{36}BrNO_2$ 665.1929; Found *m/z* 665.1935. Diazomethane (**1e**); yield 6%, mp 94.6−96.6 °C; ^{1}H NMR ($CDCl_3$) δ 2.15 (s, 6 H), 6.92 (s, 2 H), 7.57−7.27 (m, 22 H), 7.59 (d, J = 8.08 Hz, 2 H), 7.61 (s, 2 H), 7.69 (d, J = 8.08 Hz, 4 H); ^{13}C NMR ($CDCl_3$) δ 21.9, 68.7, 126.7, 126.8, 126.9, 127.2, 127.3, 127.6, 127.7, 128.6, 128.7, 128.8, 128.9, 129.2, 129.4, 129.7, 137.4, 138.6, 139.8, 139.9, 140.0, 140.5, 140.6, 140.7, 140.8, 140.9; IR (NaCl, cm^{-1}) $\nu_{C=N_2}$ 2045.

Preparation of [(2,4,6-Triphenyl)phenyl][(2,6-dimethyl-4-phenyl)-phenyl]ketone. A solution of (2,6-dibromo-4-phenylphenyl)(2,6-dimethyl-4-phenylphenyl)methanol (50.0 mg, 0.096 mmol) in acetone was stirred, CrO_3 (191.5 mg, 1.91 mmol) in concentrated H_2SO_4 (0.2 mL) and H_2O (0.5 mL)was added dropwise under vigorous stirring over a period of 15 min, and the mixture was stirred for 2 h at room temperature. To the mixture was added *i*PrOH and the residue was extracted with Et_2O. The organic layer was washed with H_2O, dried (Na_2SO_4), and evaporated to leave {(**2,6-bibromo-4-phenyl)phenyl**}-{**(2,6-dimethyl-4-phenyl)phenyl**}**ketone** as a white solid quantitatively, which was used for the next step without further purification: ^{1}H NMR ($CDCl_3$) δ 2.40 (s, 6 H), 7.31 (s, 2 H), 7.51−7.42 (m, 6 H), 7.58 (dd, J = 1.65, 8.27 Hz, 2 H), 7.82 (dd, J = 1.47, 8.45 Hz, 2 H), 7.82 (s, 2 H); IR (KBr, cm^{-1}) $\nu_{C=O}$ 1666. To a solution of the ketone (20.0 mg, 0.0038 mmol) in THF (1.0 mL) were added phenylboronic acid (14.1 mg, 0.115 mmol), palladium acetate (0.9 mg, 0.00384 mmol), di-*tert*-butylphosphinobiphenyl (14.1 mg, 0.0115 mmol), and potassium fluoride (14.7 mg, 0.254 mmol) under Ar atmosphere and the mixture was stirred at 90 °C for 1 day. The mixture was then filtered and the filtrate was evaporated under reduced pressure. The resulting brownish viscous oil was purified by the use of thin layer chromatograph eluted with CH_2Cl_2-*n*-hexane (1:1). **[(2,4,6-Triphenyl)phenyl][(2,6-dimethyl-4-phenyl)phenyl]ketone** was obtained as an white solid in 90% yield; mp 51.0−53.2 °C; ^{1}H NMR ($CDCl_3$) δ 2.09 (s, 6H, −Me), 6.87 (s, 2H), 7.23−7.21 (m, 6H), 7.47−7.29 (m, 12H), 7.59 (s, 2H), 7.70 (dd, J = 1.47, 8.45 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 22.1, 127.0, 127.1, 127.2, 127.5, 127.6, 128.1, 128.7, 128.86, 128.92, 129.0, 129.1, 137.8, 138.2, 138.8, 139.4, 140.4, 141.0, 142.0, 142.2, 142.7, 198.8; EIMS *m/z* (relative intensity) 514 (M^+, 47.1), 437 (100), 361 (21.7), 333 (12.8), 209 (23.3); HRMS Calcd for $C_{39}H_{30}O$ 514.2296; Found *m/z* 514.2296; UV/vis (toluene, nm) λ_{max} 254 (ϵ 25402), 296 (ϵ 19262); IR (NaCl, cm^{-1}) $\nu_{C=O}$ 1658.

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 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.

In this way, the following products were isolated and characterized.

1,2-Bis(2,6-dibromo-4-pheylphenyl)-1,2-bis(2,6-dimethyl-4-phenylphenyl)ethene (3). 75%: yellow solid; mp 238.3−240.8 °C; mixture of cis and trans component (major: minor = 1:0.3); ^{1}H NMR ($CDCl_3$) major: δ 7.79 (d, J = 2.02 Hz, 2 H), 7.68 (d, J = 2.02 Hz, 2 H), 7.54−7.61 (m, 10 H), 7.37−7.44 (m, 10 H), 7.17 (d, J = 2.02 Hz, 2 H), 7.00 (d, J = 2.02 Hz, 2 H), 2.16 (s, 6 H), 2.09 (s, 6 H), minor: 7.17 (d, J = 2.02 Hz,), 7.07 (d, J = 2.02 Hz,), 2.27 (s, 6 H), 2.11 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 22.9, 23.3, 23.7, 24.6, 126.1, 126.4 126.7, 126.8, 127.1, 127.8, 128.5, 128.6, 128.9, 129.1, 129.3, 131.5, 131.8, 132.4, 132.9, 137.1, 138.5, 139.0, 139.7, 140.2, 141.2, 142.5, 142.9; HRMS Calcd for $C_{54}H_{40}Br_4$ 1003.9858; Found *m/z* 1003.9865.

1,3-Diphenyl-9-(2,6-dimethyl-4-phenylphenyl)fluorene (4a). 90%: white solid; mp 80.2−82.0 °C; ^{1}H NMR ($CDCl_3$) δ 1.26 (s, 3H, −Me), 2.30 (s, 3H, −Me), 5.56 (s, 1H,), 6.89 (s, 1H), 7.00 (s, 1H), 7.12−7.03 (m, 5H) 7,25−7.20 (m) 7.34−7.27 (m), 7.38 (d, J = 7.53 Hz, 2H), 7.42 (d, J = 1.65 Hz, 1H), 7.51−7.44 (m, 4H), 7.74 (d, J = 7.72 Hz, 1H), 7.93 (d, J = 7.72 Hz, 1H), 8.09 (d, J = 1.65 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 18.8, 21.5, 49.2, 117.7, 120.0, 124.3, 126.5, 126.7, 126.9, 127.0, 127.3, 127.3, 127.5, 127.8, 128.1, 128.6, 128.8, 136.2, 137.5, 137.8, 139.0, 140.4, 140.5, 140.7, 141.1, 141.2, 142.21, 142.22, 143.9, 147.0; EIMS *m/e* (relative intensity) 498 (M^+, 43.4), 497 (100), 482 (10.5), 420 (7.5), 317 (12.8), 249 (10.6); HRMS Calcd for $C_{39}H_{30}$ 498.2347; Found *m/z* 498.2397.

1-(Phenyl-*d*$_5$)-3-phenyl-5,6,7,8-tetradeuterio-9-(2,6-dimethyl-4-phenylphenyl)fluorene (4a-*d*). 90%; white solid; mp 74.0−76.3 °C; ^{1}H NMR ($CDCl_3$) δ 1.27 (s, 3H, -Me), 2.29 (s, 3H, −Me), 6.89 (s, 1H), 6.99 (s, 1H), 7.34−7.28 (m, 2H), 7.38 (d, J = 7.53 Hz, 2H), 7.42 (d, J = 1.65 Hz, 1H), 7.51−7.44 (m, 4H), 7.75 (dd, J = 1.29, 6.98 Hz, 2H), 8.09 (d, J = 1.65 Hz, 1H); ^{13}C NMR ($CDCl_3$); δ 18.8, 21.5, 117.7, 126.4, 126.9, 127.28, 127.33, 127.8, 128.6, 128.8, 136.2, 137.5, 137.8, 138.9, 140.4, 140.5, 141.2; EIMS *m/z* (relative intensity) 510 (M+2, 10.4), 509 (M+1, 32.5), 508.1 (M^+, 73.0), 493 (12.0), 369 (11.0), 236 (48.1); HRMS Calcd for $C_{39}H_{20}D_{10}$ 508.2965; Found *m/z* 508.2945.

1-Biphenylyl-3,7-diphenyl-9-(2,6-dimethyl-4-phenylphenyl)fluorene (4b). 82%; white solid; mp 98.1−100.2 °C; ^{1}H NMR ($CDCl_3$) δ 1.33 (s, 3 H), 2.37 (s, 3 H), 5.63 (s, 1 H), 6.93 (d, J = 8.82 Hz, 1 H), 7.07 (d, J = 8.08 Hz, 1 H), 7.50−7.26 (m, Ar), 7.58 (d, J = 7.17 Hz, 2 H), 7.78 (d, J = 7.35 Hz, 2 H), 8.01 (d, J = 8.08 Hz, 1 H), 8.13 (d, J = 1.65 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 19.0, 22.6, 51.1, 117.8, 120.5, 123.0, 126.5, 126.9, 127.0, 127.2, 127.3, 127.4, 127.8, 128.2, 128.6, 128.7, 128.9, 129.6, 134.5, 137.7, 138.5, 139.3, 139.9, 140.8, 141.0, 141.3, 142.5, 143.6, 144.9, 147.0; EIMS *m/z* (relative intensity) 650 (M^+, 100), 469 (8.5), 325 (7.5); HRMS Calcd for $C_{51}H_{38}$ 650.2973; Found *m/z* 650.2981.

1-(3,5-Trifluoromethylphenyl)-3-phenyl-6,8-bis(trifluoromethyl)-9-(2,6-dimethyl-4-phenylphenyl)fluorene (4c). 96%; white solid; mp 92.5−95.0 °C; ^{1}H NMR ($CDCl_3$) δ 1.55 (s, 3 H), 2.17 (s, 3 H), 5.58 (s, 1 H), 7.31 (s, 1 H), 7.37 (s, 1 H), 7.43 (d, J = 1.65 Hz, 1 H), 7.75−7.60 (m, Ar), 7.93−7.84 (m, Ar), 8.07 (s, 1 H), 8.14 (d, J = 1.65 Hz, 2 H), 8.26 (s, 1 H), 8.53 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 18.8, 22.4, 51.2, 117.7, 120.2, 120.3, 122.4, 126.9, 127.1, 127.2, 127.9, 128.2, 128.6, 129.0, 130.3, 130.8, 131.7, 132.7, 137.4, 139.1, 139.9, 140.6, 141.1, 142.9, 143.7, 143.9; EIMS *m/z* (relative intensity) 770 (M^+, 48.7), 769 (100), 700 (10.7), 588 (43.8), 181 (30.3); HRMS Calcd for $C_{43}H_{26}F_{12}$ 770.1842; Found *m/z* 770.1809.

1-(2-Fluorophenyl)-3-phenyl-5-fluoro-9-(2,6-dimethyl-4-phenylphenyl)fluorene (4d). 86%; white solid; mp 92.7−94.0 °C; ^{1}H NMR ($CDCl_3$) δ 1.25 (s, 3H, −Me), 2.39 (s, 3H, −Me), 5.63 (s, 1H), 6.82 (d, J = 6.98 Hz, 1H), 6.86 (s, 1H), 6.94 (s, 1H), 7.00 (d, J = 7.35 Hz, 2H), 7.24−7.05 (m, 3H), 7.32−7.27 (m, 2H), 7.43−7.37 (m, 5H), 7.45 (s, 1H), 7.50−7.47 (m, 4H), 7.75 (dd, J = 1.47, 7.17 Hz, 2H,), 8.33 (d, J = 1.65 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 18.8, 21.3, 49.8, 113.9, 114.2, 114.5, 114.9, 122.0, 123.3, 126.4, 126.9, 127.4, 127.7, 127.8, 128.6, 128.7, 128.8, 129.0, 140.8; EIMS *m/z* (relative intensity) 536 (M+2, 10.0), 535 (M+1, 37.0), 534 (M^+, 90.6), 519 (14.3), 368 (16.6), 236 (35.9); HRMS Calcd for $C_{39}H_{28}F_2$ 534.2159; Found *m/z* 534.2152.

ESR 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 ESR cavity at 77 K and irradiated with a Wacom 500 W Xe or Hg lamp using a Pyrex filter. ESR spectra were

measured on a JEOL JES TE 200 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 9650 Microprocessor-based Digital Temperature Indicator/Controller, which provided accuracy of the measurements within ±0.1 K and of 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 an Oxford variable-temperature liquid-nitrogen cryostat (DN 1704) 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 Halos 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 an Oxford Instrument Intelligent Temperature Controller (ITC 4).

Flash Photolysis. All flash measurements were made on a Unisoku TSP-601 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 Quanta-Ray GCR-11 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) Lamda Physik LEXTRA 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 Hamamatsu 150 W xenon short arc lamp (L 2195) was used as the probe source; 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 Hamamatsu R2949 photomultiplier tube through a Hamamatsu S3701-512Q MOS linear image sensor (512 photodiodes used). The timing of the excitation pulse, the probe beam, and the detection system was achieved through an Iwatsu Model DS-8631 digital synchroscope interfaced to an NEC 9801 RX2 computer. This allowed for rapid processing and storage of the data and provided printed graphic capabilities. Each trace was also displayed on an NEC CRT N5913U 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.

Computational Procedures. DFT calculations were carried out using the GAUSSIAN 94,[27] programs. Optimized geometries were obtained at the B3LYP/6-31G(d)[28] levels of theory. Vibrational frequencies obtained at the B3LYP level of theory were scaled by 0.961 and zero-point energies (ZPE) by 0.981.[45] The electronic spectra of tetracyclic intermediates and isofluorene were calculated using time-dependent (TD) DFT theory.[30]

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Supporting Information Available: Variable temperature UV/vis spectra of **2a**−*d*, **2b**, **2c**, and **2d** (Figures S1−S4), time-resolved UV/vis spectra obtained by LFP of **2a**−*d*-N_2, **2b**−N_2, **2c**−N_2, **2d**−N_2 and **4a** (Figures S5−9), optimized geometries of ^{1}**2A**, ^{3}**2A**, **4A**, **5A**, **6A**, and **7A** (Figures S10−S15), and Gaussian archives entries (Table S1). This material is available free of charge via the Internet at http://pubs.acs.org.

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