Spectroscopic and Product Studies of the Effect of Para Substituents on the Reactivity of Triplet Bis(2,6-dimethylphenyl)carbenes

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A series of diazobis(2,6-dimethylphenyl)methanes (**1**) bearing eight symmetrical para di-substituents have been prepared and photolyzed to generate the corresponding carbenes (**2**). Product analysis studies showed that carbenes (**2**) decay mainly either by dimerization to form tetra(aryl)ethylene (**3**) or by attack at an *o*-methyl group to afford 1,2-dihydrobenzocyclobutenes (**4**) by way of *o*-quinodimethanes (**6**) in solution. The zero-field splitting parameters, *D* and *E*, were measured in matrices of different viscosities and are analyzed in terms of a sigma-dot ($\sigma^{\bullet}$) scale of spin-delocalization substituent constants. Fairly good correlation with $\sigma^{\bullet}$ was found for the *D* values of ^{3}**2** in its minimum energy geometry. Stabilities of ^{3}**2** were estimated either by measuring the temperature at which the triplet carbene signals disappeared upon thawing the matrix or by analyzing the decay kinetics of ^{3}**2** in a degassed solution at room temperature. They are examined in terms of the *D* values in matrix at low temperature and in terms of product distributions in solution at room temperature.

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

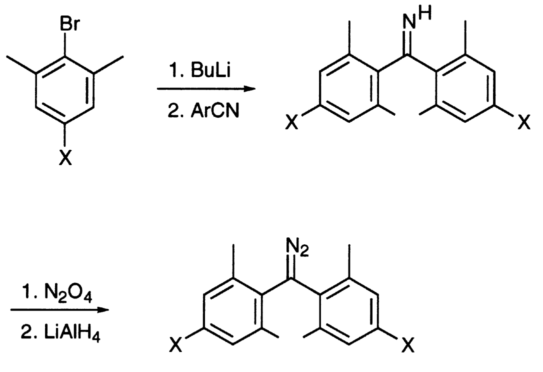
This approach encounters a limitation when diazo compounds are used as precursors since, as bulkier groups are used at the ortho positions, introduction of the diazo group becomes more difficult.[5,6]

The other strategy we have not examined extensively is the electronic (thermodynamic) effect of *para*-substituents on the stability of kinetically protected triplet DPCs. It is well-documented in radical chemistry that the abilities of various substituents to delocalize the spin on a carbon radical play an important role in stabilizing the radical.[7]

In order to explore this effect on the reactivity of triplet diphenylcarbene, we decided to generate bis(2,6-dimethylphenyl)carbenes (2) having eight symmetrical para di-substituents with well-distributed electronic properties by irradiation of the corresponding diazo precursors and to study them not only by product analysis but also by using spectroscopic means. We have found that the kinetically stabilized triplet diphenylcarbenes are further stabilized by strong spin-delocalizing substituents at para positions, but that the correlations between spin-delocalization and stability are not straightforward.[8]

Results

1. Synthesis of Precursor Diazomethanes. All of the diazo compounds **1** used in this study were prepared by either the reduction of the corresponding diaryl *N*-nitroso ketimine with $LiAlH_4$ (Scheme 1) or by the base treatment of the corresponding *N*-nitrosocarbamate (Scheme 2) according to the procedure developed by Zimmerman and Paskovich.[9] The diazomethanes were purified by repeated chromatography on a gel permeation column eluted with $CHCl_3$ immediately before the use.



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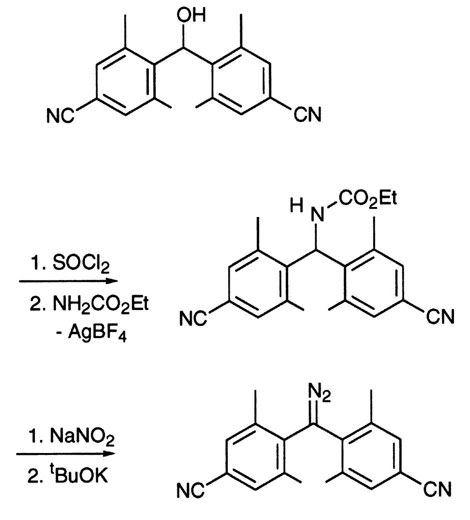
a : X = H, **b** : X = Me, **c** : X = ^{t}Bu, **d** : X = MeO,
e : X = F, **f** : X = Cl, **g** : X = Br

Scheme 1. Preparation of diazobis(2,6-dimethyl-4-X-phenyl)methanes (**1a**–**g**).

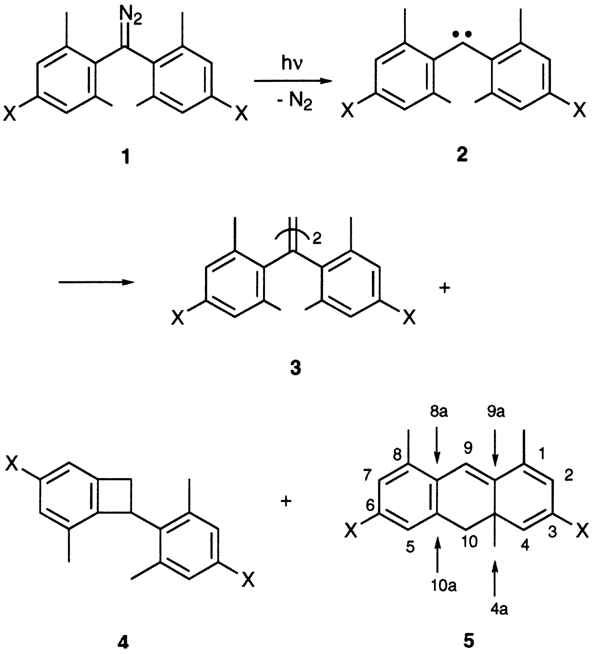
2. Product Analysis Studies. The polymethylated diphenylcarbenes **2** were generated by photolysis ($\lambda > 300$ nm) of a degassed benzene solution of **1** and the products were analyzed by conventional methods.

The reactions observed with all the carbenes studied here



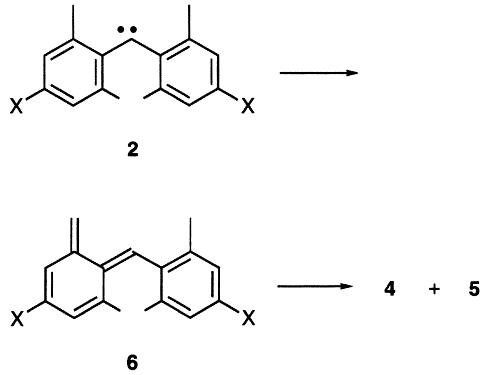
1h

Scheme 2. Preparation of bis(2,6-dimethyl-4-cyanophenyl)diazomethane (**1h**).



Scheme 3. Products obtained by photolysis of diazobis(2,6-dimethyl-4-X-phenyl)methanes (**1a**–**h**) in degassed benzene.

were analogous to those observed with dimesitylcarbene (**2b**).[9,10] Thus, these carbenes did not react with the diazomethane precursors to form ketazines. Instead, they reacted either by dimerization to produce tetra(aryl)ethylene (**3**) or by attack at an *o*-methyl group to afford 1,2-dihydrobenzocyclobutene **4** by way of *o*-quinodimethane **6** (vide infra). An additional product isolated in the photolysis of **1d** (X = OMe) and **1e** (X = F) was assigned to dihydroanthracene derivatives **5** (Scheme 3), presumably formed from *o*-quinodimethanes **6** as a result of intramolecular cyclization (Scheme 4).[11]



Scheme 4. Mechanism for the formation of 1,2-dihydrobezocyclobutenes **4** and dihydroanthracenes **5** from triplet carbenes **2**.

Table 1. Product Distributions in Irradiations of Diazobis(2,6-dimethyl-4-X-phenyl)methanes **1**[a)]

1	X	T/°C	Yield/%[b)]		
			3	**4**	**5**
1a	H	20	60	15	c
		50	32	68	c
1b	Me	20	63	8	c
		50	19	56	c
1c	*t*Bu	20	67	9	c
		50	32	64	c
1d	OMe	20	27	7	27
		50	32	64	c
1e	F	20	70	17	9
		50	14	50	1
1f	Cl	20	87	5	c
		50	47	48	c
1g	Br	20	80	5	c
		50	44	47	c

a) All the irradiations were carried out in a degassed benzene. b) Determined by 500 MHz NMR. c) Less than 1%.

The product distributions were, however, significantly sensitive to the reaction temperatures. For instance, photolysis of **1a** at 20°C resulted in the formation of the ethylene **3a** as main product, but the 1,2-dihydrocyclobutene (**4a**) was increased at the expense of **3a** when the photolysis was carried out at 50°C (Table 1).

Similar trends, i.e., increase in **3**/(**4**+**5**) ratio as a function of increasing temperature of the reaction, were observed in the photolysis of the other diazomethanes **1b**–**1g** (Table 1). This can be explained in terms of activation energy differences between the two processes. Hydrogen abstraction reaction of triplet carbenes requires more energy than the dimerization reaction. Thermolysis of **1a** at 140°C, for instance, gave 1,2-dihydrobenzocyclobutene **4a** almost exclusively at the complete expense of the dimer **3a**.[9]

Comparison of the product distributions observed at the fixed temperatures suggests that the distributions were somewhat sensitive to substituents at the para positions. The ratio of **3**/**4**+**5** at 20°C, for example, increased in the order of *p*-OMe < *p*-F < *p*-H < *p*-^{t}Bu < *p*-Me ≪ *p*-Cl ~ *p*-Br.

Generally speaking, chloro and bromo derivatives **1f** and **1g** tend to form the corresponding dimer (**3**), while the reverse trends are seen for methoxy and fluoro ones (**1d** and **1e**). On the other hand, alkylated derivatives **1b** and **1c** as well as the parent one **1a** exhibit an intermediate trend. No obvious correlation of the product ratios (**3**/**4**+**5**) was found either with the Hammett substituent parameters (σ, σ^+ etc) or other substituents constants including spin-delocalization ($\sigma^\bullet$).[7]

3. Spectroscopic Studies. In order to obtain more quantitative information on the reactivities of **2**, the following spectroscopic studies were carried out.

(a) EPR Studies in Rigid Matrices at Low Temperature. Irradiation ($\lambda > 300$ nm) of **1c** in 2-methyltetrahydrofuran (2-MTHF) at 77 K gave rise to a paramagnetic species readily characterized from its EPR spectrum as a derivative of triplet carbene (^{3}**2c**). The EPR signals were persistent at this low temperature but disappeared irreversibly when the matrix temperature was raised around 170 K. Similar irradiation of other diazomethanes **1** under identical conditions also gave rise to a similar EPR line shape characteristic of triplet carbene **2**. The EPR signals were analyzed in terms of the zero-field splitting (ZFS) parameters, *D* and *E* values, and are reported in Table 2, which also includes the temperature (*Td*) at which the triplet signal disappeared.

Similar irradiation of **1c** in a more viscous matrix, i.e., 1,2,3-propanetriyl triacetate (PT), at 110 K also gave rise to a typical set of triplet signals due to ^{3}**2** with ZFS parameters similar to those obtained in 2-MTHF at 77 K, as shown in Table 3.

When the PT glass containing carbene **2c** was warmed gradually in 10 K increments, another new set of triplet peaks appeared at the expense of the original peaks, which disappeared rapidly around 180 K (Fig. 1). These changes were not reversible; when the sample was cooled to 110 K, no change took place except that the signal intensity increased according to the Curie law. A signal due to a doublet species also started to appear around 180 K. The triplet signals eventually disappeared around 210 K and were taken over by the signals due to doublet species.

In the new set of triplet peaks, the *x* and *y* lines moved closer together, resulting in a substantial reduction in *E*. Smaller but distinct shifts in the *z* lines were also noted, indicating that *D* has also diminished. The *D* value, which is related to the separation between the unpaired electrons, varies considerably with the nature of the triplet. While the overall magnitude of *D* is

Table 2. Zero-Field Splitting Parameters of Bis(2,6-dimethyl-4-X-phenyl)carbenes **2** in 2-Methyltetrahydrofuran at 77 K

Carbenes (**2**)	X	*D*/hc	*E*/hc	*Td*/K[a)]
		cm^{-1}		
1a	H	0.377	0.0101	140
1b	Me	0.368	0.0117	120
1c	^{t}Bu	0.373	0.0134	170
1d	OMe	0.368	0.0134	120
1e	F	0.377	0.0129	120
1f	Cl	0.354	0.0144	120
1g	Br	0.353	0.0117	120
1h	CN	0.340	0.0093	180

a) Temperature at which the triplet signals disappeared.

Table 3. Zero-Field Splitting Parameters of Bis(2,6-dimethyl-4-X-phenyl)carbenes **2** in 1,2,3-Propanetriyl Triacetate (PT) at 110 K and upon Annealing[a)]

Carbenes (**2**)	X	*D*/hc	*E*/hc	*Td*/K[b)]
		cm^{-1}		
1a	H	0.354	0.0093	240
		(0.335)	(2.8×10^{-6})	
1b	Me	0.381	0.0121	210
		(0.331)	(2.6×10^{-6})	
1c	^{t}Bu	0.371	0.0128	210
		(0.328)	(2.6×10^{-6})	
1d	OMe	0.370	0.0129	200
		(—)[c)]	(—)[c)]	
1e	F	0.377	0.0116	220
		(0.344)	(2.8×10^{-6})	
1f	Cl	0.354	0.0120	220
		(0.326)	(2.5×10^{-6})	
1g	Br	0.348	0.0118	220
		(0.327)	(2.5×10^{-6})	
1h	CN	0.344	0.0093	230
		(0.283)	(2.7×10^{-7})	

a) The values in parantheses refer to those observed upon annealing.

b) Temperature at which the triplet signals disappeared.

c) The triplet signals disappeared before the relaxation.

Fig. 1. ESR spectra of bis(4-*t*-butyl-2,6-dimethylphenyl)carbene (**2c**) in 1,2,3-propanentriyl triacetate (PT). (a) Sample at 110 K. (b) Same sample after annealing to 190 K.

characteristic of a particular class of triplets, smaller variations in this parameter, which reflect structural differences between various triplet carbenes, are seen within a given class.

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 accompanied by a significant reduction in *D*, indicating that the electrons are becoming more delocalized.

Changes of this kind have often been observed for sterically congested triplet diarylcarbenes and are usually interpreted in terms of geometrical changes.[12c,13,14] Thus, when a carbene is generated in rigid matrices at very low temperature, it should have the geometry dictated by that of the precursor. Even if the thermodynamically most stable geometry of the carbene is different from that at birth, the rigidity of the matrices prevents the carbene from achieving its minimum-energy geometry. When matrices are softened by annealing, the carbene undergoes relaxation to the preferred geometry, probably to gain relief from steric compression. It has been shown, on the other hand, that the ZFS parameters of sterically unperturbed DPCs show little sensitivity toward the temperature of the matrix.[12b]

Similar changes in the *D* and *E* values upon annealing were also observed for other carbenes employed in this study, although the temperatures (*Td*) at which the triplet signals of the relaxed species disappeared were somewhat sensitive to the para substituents, as summarized in Table 3.

It is interesting to compare the ZFS parameters of bis(2,6-dimethylphenyl)carbenes (^{3}**2**) with those of the "parent" DPC under identical conditions. As expected, a marked reduction both in the *E* and *D* values is noted as four methyl groups are introduced at all the ortho positions of DPC. Thus, both of these parameters decrease with increasing steric crowding in the carbenes and reflect the steric influence of *o*-methyl groups, which force an expansion of the central angle to some extent even in a rigid matrix. The ZFS parameters of ^{3}**2** undergo further reduction upon annealing the matrix to gain relief from steric congestion.

It is worth examining quantitatively how the para substituents affect the electronic structure of ^{3}**2**. The dominant interaction of the unpaired electron in a *p*-radical is with the electrons paired in the π-bonds. Such interactions are characterized by the delocalization of the spin throughout the *p*-system. To estimate the relative abilities of substituents to delocalize the spin, sigma-dot substituent constants ($\sigma^\bullet$) have been proposed.[7] Among the various approaches to the definition of a $\sigma^\bullet$ scale, Arnold's $\sigma_\alpha^\bullet$ scale[15] is the most suitable for the analysis of the substituent effect on the *D* values of ^{3}**2** since this scale is a non-kinetic measure of radical stabilizing effects based on hyperfine coupling constants in the benzylic radical.[16]

Our attempts to correlate the *D* values of ^{3}**2** with $\sigma_\alpha^\bullet$ show that correlations are sensitive to the geometric structures of the carbenes. Thus, the *D* values observed for carbenes at birth in rigid matrices at low temperature, i.e., those obtained in 2-MTHF at 77 K and in PT at 110 K, where carbenes retain their metastable geometries, give a highly scattered ($r < 0.5$) plot when correlated against $\sigma_\alpha^\bullet$, although a general trend for *D* values to decrease with increasing the power of radical stabilization of a substituent is seen.

Improved correlations are found when the *D* values observed for the carbenes in their minimum-energy geometries, attained upon annealing, are employed. Thus, the *D* values in TA at 200 K correlate relatively well ($\rho = 0.589$, $r = 0.9$) with $\sigma_\alpha^\bullet$ (Fig. 2).

The effect of the para substituents on the thermal stability (*Td*) is to be noted. The data in PT appear to level off to some extent, because *Td* values in PT are close to the limit of the inherent stability of the carbene ^{3}**2**. Inspection of the data in Table 2 indicates that the 4-cyano group exhibits significant stabilizing effects on ^{3}**2**. Taking into account the increased ability of the substituent to delocalize the unpaired electron, one may conclude that triplet carbenes kinetically stabilized by the ortho substituents can be further stabilized thermodynamically by spin-delocalizing para substituents.

The *para-t*-Bu group is found to exert an equally significant effect on *Td*. Since $\sigma^\bullet$ of this group is not large, the effect can not be explained in terms of spin delocalization.

(b) UV/vis Studies in Rigid Matrices at Low Temperatures. Irradiation of **1c** in 2-MTHF matrix at 77 K was monitored by UV/vis spectroscopy, which revealed the rapid appearance of new absorption bands at the expense of the original absorption due to **1c**. As shown in Fig. 3, the new spectrum consists of two identifiable features: a rather sharp UV band with a maximum around 300 nm and a weak broad band with an apparent maximum around 400 nm. These features are usually present in the spectra of triplet diarylcarbenes in organic glasses at 77 K.[12a,17] The glassy solution did not exhibit any changes for several hours when kept at 77 K. However, when it was allowed to warm gradually, the characteristic bands disappeared irreversibly around 150 K. On the basis of these observations, coupled with the fact that EPR signals characteris-

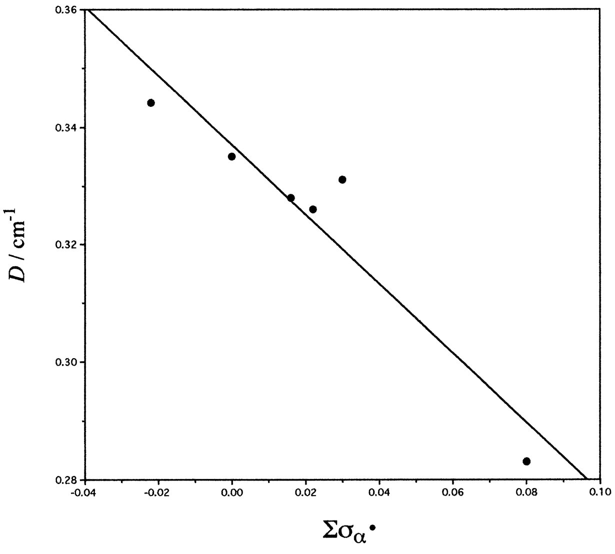


Fig. 2. The plot of the *D* values for bis(2,6-dimethyl-4-X-phenyl)carbenes **2** observed in TA at 200 K against $\sigma_\alpha^\bullet$.

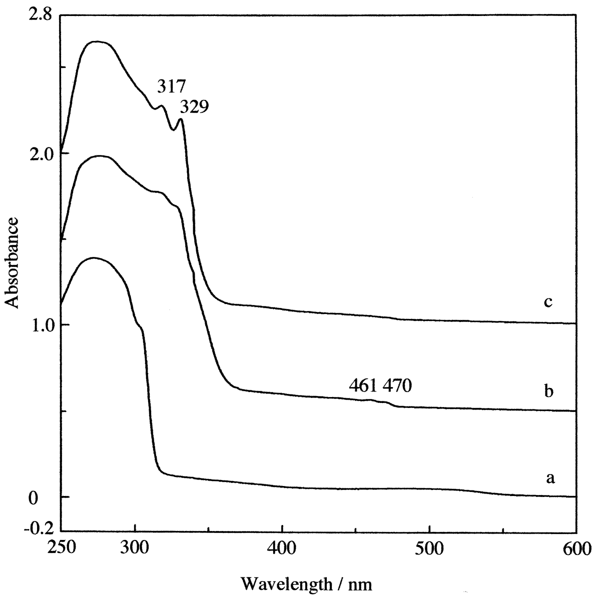


Fig. 3. UV/vis spectral changes observed in the photolysis of diazobis(2,6-dimethyl-4-*tert*-butylphenyl)methane (**1c**). (a) UV/vis spectrum of **1c** in 2-MTHF at 77 K. (b) Same sample after 10- min irradiation (λ > 300 nm). (c) Same sample after thawing the matrix to 110 K.

tic of the triplet carbene were observed under identical conditions, we can safely attribute the absorption spectrum to triplet carbene ^{3}**2c**.

When the spectral changes of the matrix were more carefully monitored as a function of temperature, an interesting feature appeared. At higher temperature around 110 K, a new broad absorption at 355 nm appeared and this band increased as carbene absorption bands decreased. The species responsible for this new absorption showed appreciable thermal stability. Similar species have been observed when the matrix obtained in the photolysis of diazo(dimesityl)methane (**1a**) is thawed gradually and the species are assigned to *o*-quinodimethane (**6a**), which eventually undergoes cyclization to form 1,2-dihydrobenzocyclobutene **4a**.[10]

Table 4. Absprption Maximum of Transient Species Observed in Photolysis of Diazobis(2,6-dimethyl-4-X-phenyl)methane **1** in 2-MTHF

1	X	$\lambda_{\max}$/nm			Td/K$^{a)}$
		2		6	
1a	H	318, 327	435, 446, 472	346	115
1b	Me	317, 330,	460, 470	357	105
1c	^{t}Bu	316, 327,	438, 448, 460, 470	355	150
1d	OMe	321, 333	439, 450, 460, 473	b)	110
1e	F	311, 323	431, 441, 452, 466	b)	110
1f	Cl	330	432, 441, 455, 466	b)	110
1g	Br	341	432, 443, 455, 466	b)	110
1h	CN	331	488	b)	160

a) Temperature at which the absorption due to **2** disappeared.
b) Not observed.

Similar spectra were obtained in the photolysis of other diazo precursors (**1**) in 2-MTHF at 77 K. The absorption maxima observed for ^{3}**2** and the temperature (Td) at which the absorption due to ^{3}**2** disappeared are summarized in Table 4. The absorption bands ascribable to *o*-quinodimethanes (**6**) upon annealing were not observed for the annealing experiments of all the triplet carbenes ^{3}**2** studied, and therefore are shown in Table 4 only when formed. The exact values of Td are not the same as those determined by EPR (Table 2) probably due to the differences in conditions (see Experimental Section), but the general trends are similar. Thus, rather high Td is noted for **2c** and **2h** compared to other carbenes.

(c) Laser Flash Photolysis Studies in Solution at Room Temperature. Laser flash photolysis (LFP) of **1c** (1×10^{-4} M) ($1\ \mathrm{M} = 1\ \mathrm{mol\ cm^{-3}}$) in a degassed benzene solution at room temperature with a 10 ns, 70–90 mJ, 308 nm pulse from a XeCl laser produced a transient species showing a maxima at 328 nm, which appeared coincidentally with the pulse and decayed within several seconds (Fig. 4). The spectrum of the transient species is similar to that measured during the photol-

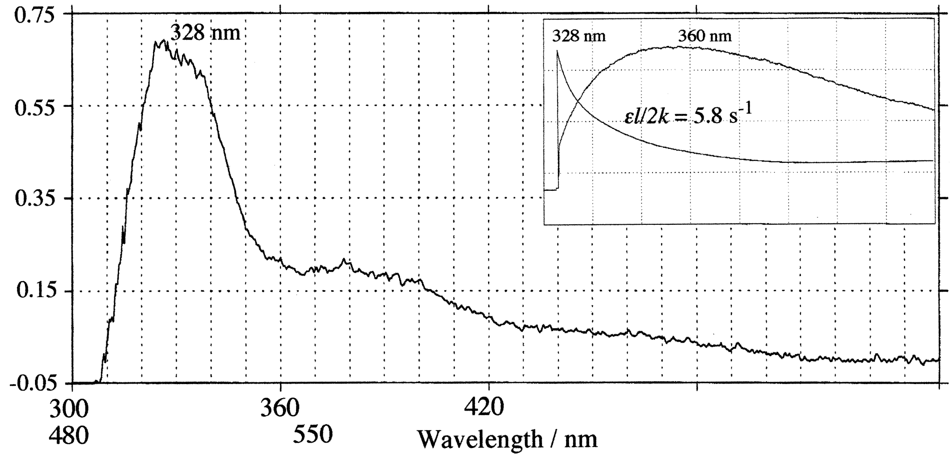
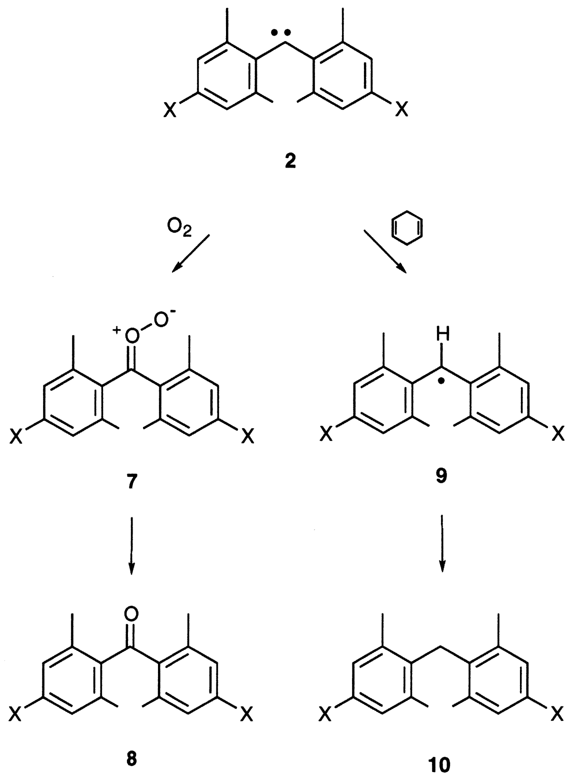


Fig. 4. Transient absorption spectra obtained in LFP of diazobis(2,6-dimethyl-4-*tert*-butylphenyl)methane (**1c**) in degassed benzene with a 308-nm excimer laser recorded 1 µs after the pulse. Inset shows oscillogram traces monitored at 328 and 360 nm.

ysis of **1c** in 2-MTHF glass at 77 K. Moreover, the product analysis of the spent solution showed the presence of the dimer **3c** as the main product, along with **4c**. On the basis of the low temperature spectrum coupled with the chemical analysis, the transient absorption was assigned to triplet carbene (^{3}**2c**).

Support is lent to this assignment by the following control experiments using trapping reagents. When LFP was carried out on an oxygen-saturated benzene solution of **1c**, the decay rate of the transient band due to the carbene increased dramatically and a broad absorption band with a maximum at 390 nm appeared at the expense of the absorption due to the carbene. The rate of increase in the band at 390 nm is practically the same as that of the decay of the peak due to ^{3}**2c**, showing that triplet **2c** is quenched with oxygen to form a new species. Subsequent analysis of the spent solution showed the presence of a large amount of bis(4-*t*-butyl-2,6-dimethylphenyl) ketone (**8c**). It is well documented that diarylcarbenes with triplet ground states are readily trapped by oxygen to give the corresponding diarylketone oxides, which usually show a rather broad band centered around 390–450 nm.[18,19] Thus, the observation can be interpreted as indicating that the triplet **2c** is trapped with oxygen to generate a carbonyl oxide **7c** (Scheme 5), confirming that the transient absorption quenched by oxygen is due to ^{3}**2c**. A plot of the observed pseudo-first-order rate of carbonyl oxide formation versus oxygen concentration yields the quenching rate constant $k_{O_2} = 1.8 \times 10^8$ M^{-1} s^{-1}.

On the other hand, when a degassed benzene solution of **1c** containing 1,4-cyclohexadiene (CHD) was excited, a new species showing a strong absorption with $\lambda_{max} = 356$ nm was formed as the 334 nm band of ^{3}**2c** decayed. The decay of ^{3}**2c** was shown to be kinetically correlated with the growth of the new species.



Scheme 5. Reactions of triplet carbenes **2** with oxygen and 1,4-cyclohexadiene.

It is also well-documented that triplet diarylcarbenes, generated in good hydrogen donor solvents such as CHD, undergo H abstraction leading to the corresponding radicals, which show transient absorptions at longer wavelengths than those of the precursor carbenes.[20] Thus, the new band was attributable to the diarylmethyl radical (**9c**) formed as a result of H abstraction of ^{3}**2c** from the diene. A plot of the observed pseudo-first-order rate constant of the formation of the radical against [CHD] is linear, and the slope of this plot yields the absolute rate constant for the reaction of ^{3}**2c** with the diene, $k_{CHD} = 3.0 \times 10^2$ M^{-1} s^{-1}.

When the decay of ^{3}**2c** in a degassed benzene solution was monitored more carefully, a new absorption around 360 nm appeared as the absorption due to ^{3}**2c** decayed; this secondary species also decayed, but very slowly. Again, on the basis of the low-temperature spectrum coupled with chemical analysis, we assign the second species as *o*-quinodimethane **6c**.[11,21]

Although the observation suggests that some of ^{3}**2c** decays by abstracting H from *o*-methyl group intramolecularly, product analysis data indicate that main decay pathway of ^{3}**2c** at this temperature is dimerization to produce **3**. Reflecting this kinetic dominance, the decay of the absorption due to ^{3}**2c** can be fit to a second order decay ($2k/\varepsilon l = 5.8$ s^{-1}), and a half-life ($t_{1/2}$) was estimated to be ca 500 ms from the decay curve. On the other hand, the growth rate of *o*-quinodimethane **6c** was determined to be $k_i = 0.62$ s^{-1}.

Similar measurements were done for the carbenes **2a**, **b**, **d**–**h** and kinetic data are reported in Table 5. In accordance with the product analysis data and low temperature UV/vis spectroscopic studies, the growth of *o*-quinodimethane **6** was not observed in LFP of **1f** and **1g**. On the other hand, the half-life of ^{3}**2** ranges from 20 (^{3}**2d**) to 600 ms (^{3}**2h**) depending on the para substituents. Significantly large $t_{1/2}$ is noted for ^{3}**2c** and ^{3}**2h** compared to that of other carbenes. This is in accord with the trend in thermal stability of ^{3}**2** estimated by *Td* upon thawing the matrix containing ^{3}**2**.

Table 5. Kinetic Data Observed for Bis(2,6-dimethyl-4-X-phenyl)carbenes **2**[a)]

1	X	$2k/\varepsilon$[b)]	$t_{1/2}$[c)]	k_i[d)]	k_{O_2}[e)]	k_{CHD}[f)]
		s^{-1}	ms	s^{-1}	M^{-1} s^{-1}	
1a	H	1.4×10	180	3.3	1.5×10^8	9.4×10
1b	Me	1.1×10	160	1.5	2.8×10^8	4.6×10^2
1c	*t*Bu	5.8	500	0.62	1.8×10^8	3.0×10^2
1d	OMe	1.3×10^2	20	—	3.1×10^8	1.2×10^3
1e	F	5.8×10	60	2.1	1.7×10^8	4.4×10^2
1f	Cl	4.0×10	100	—	1.1×10^8	1.8×10^2
1g	Br	2.2×10	50	—	9.7×10^7	1.4×10^2
1h	CN	1.8×10	590	1.0×10	3.1×10^7	1.3×10^2

a) All measurements were carried out in degassed benzene at room temperature except trapping experiments with O_2. b) Second order decay of triplet carbenes **2**. c) Half-life of **2**. d) Growth rate of *o*-quinodimethane. e) Quenching rate constant of **2** with O_2. f) Quenching rate constant of **2** with 1,4-cyclohexadiene.

Discussion

The present observations clearly suggest that the reaction patterns as well as the reactivities of bis(2,6-dimethylphenyl)carbenes (**2**) are significantly influenced by the substituents at the para position. However no correlations are noted between the decay modes, i.e., the ratio of dimerization to H abstraction, and the stability of ^{3}**2**, i.e., *Td* in matrix at low temperature and/or $t_{1/2}$ in solution at room temperature. For instance, product analysis studies show that ^{3}**2f** and ^{3}**2g** mainly decay by dimerization, which may be interpreted as indicating that the carbene concentration builds up in solution due to the increased stability. However, the spectroscopic studies show that both carbenes are not stabilized so much. Also, no clear correlations are found for the reaction patterns and reactivities of ^{3}**2** with either the Hammett substituents parameters (σ, σ^+, etc.) or sigma-dot substituent constant ($\sigma^\bullet$). This is rather surprising in the light of the fact that the *D* values correlate relatively well with $\sigma^\bullet$ (vide supra). It may not be unreasonable to suppose that the decay mode as well as the reactivity of triplet carbenes are likely to be affected by the spin density on the carbene carbon.

The reason for this rather poor correlation with the nature of substituents probably lies partly in the mechanism of the photodecomposition of diazomethanes. Triplet carbenes, like radicals, dimerize in a very fast and exothermic reaction.[22] The combination of two triplets to give a singlet product is spin-allowed. Dimers are also known to be formed by attack of the carbene on the carbene precursor, but this reaction also leads to azines.[23] No azines are detected in the photolysis of **1**. Moreover, taking into account the prolonged lifetime of ^{3}**2** as opposed to ^{3}DPC, the concentration of the carbene in this case is expected to be high enough to undergo dimerization. Therefore, triplet carbene itself is responsible for the dimerization.

The formation of 1,2-dihydrobenzocyclobutenes is probably more complicated. It has been recognized that intramolecular reactions of the excited states of the diazo precursor proceed in concert with nitrogen extrusion to give rise to formally carbenic products.[24] For instance, it is well-appreciated that the photochemical Wolff rearrangement of certain diazo ketones can bypass carbene intermediates in the formation of ketenes.[25] More recently, LFP of alkyl- and alkylaryldiazomethanes indicate that photolysis leads to both carbene formation and direct formation of rearrangement products which do not derive from relaxed carbene intermediates.[26]

Thus, it may be that *o*-quinodimethane **6** is formed in the excited state of the diazo precursor (**1***) as a result of 1,4-hydrogen migration and nitrogen extrusion. Actually it has been demonstrated that LFP of diazomesitylmethane produces the transient spectra of both triplet mesitylcarbene and 3,4-dimethyl-1,2-benzoquinodimethane and that the latter is formed directly by 1,4 hydrogen migration in the excited state of the diazo compound, not from a relaxed carbene intermediate.[27]

However, LFP studies of **1** indicates that the transient absorption bands due to *o*-quinodimethanes **6** are usually formed as the band due to triplet carbenes ^{3}**2** decays, suggesting that *o*-quinodimethanes are formed by way of ^{3}**2**, not directly from the excited state of the precursor **1*** in the present system.

It may be then that some of the cyclobutenes **4** can be also produced in the singlet state of the carbene ^{1}**2** as a result of direct insertion into the C–H bond of the *o*-methyl group without intervention of **6**. It has been shown, however, that, while most intermolecular C–H insertion reactions of phenylcarbene proceed by a concerted singlet mechanism, intramolecular C–H insertion follows a triplet abstraction-recombination mechanism, especially when the transition state (TS) requires a small-membered ring.[28] For instance, in the intramolecular C–H insertion of 2-alkoxyphenylcarbene affording 2,3-dihydrobenzofurans, the concerted insertion of the singlet involving the *p* and σ orbitals which interact with δ-C–H bonds requires the rotation. This results in loss of benzylic stabilization of carbene center and deformation of bond angles, if one assumes that the most stable planar conformer for singlet (σ^2) phenylcarbene is the one with vacant *p* orbital perpendicular to the plane of the benzene ring.[29] In contrast, in the case of triplet (σ_π) phenylcarbene, both in the planar and in the perpendicular conformers, interactions occur between the ring π electrons and the half-filled orbital. Therefore, the transfer of δ-hydrogen to the half-filled, in-plane σ orbital of the triplet (σ_π) carbene can proceed via a favorable six-membered TS in which the benzylic resonance is not disturbed.[28]

If one applies similar TS structure considerations to the C–H insertion reaction of *o*-methylphenylcarbene leading to 1,2-dihydrobenzocyclobutene, the abstraction from the triplet state is expected to be more favorable than the concerted C–H insertion in the singlet manifold. Contrary to this expectation, 1,2-dihydrobenzocyclobutene formation in the photolysis of diazophenylmethanes having various CH_2X groups at the ortho position is demonstrated to arise from the singlet state of the carbene, most probably without intervening *o*-quinodimethane intermediate.[30] Taking into account the fact that the loss of benzylic stabilization is not significant in diphenylcarbenes **2** compared to monophenylcarbene systems, one may suppose that the 1,2-dihydrobenzocyclobutenes **4** can also be produced from the singlet state ^{1}**2**.

The enhanced yields of **4** from **2d** and **2e** are then interpreted by assuming that a part of **4** arises from the singlet state of **2**. It has been shown that electron-donor groups stabilize the electrophilic singlet carbene more than they do the radical-like triplet.[31] Strong stabilization effects of *p*-donor substituents, i.e., F and MeO, on the singlet state of carbene as a result of conjugative interaction between the formally-vacant *p* orbital of the carbene singlet and a lone pair orbital of a heteroatom are well-appreciated.

Significant increase in the stability is observed for ^{3}**2c** and ^{3}**2h** as evidenced by a significantly higher *Td* value in matrix as well as longer half-life ($t_{1/2}$) in solution at room temperature observed for those two carbenes.

In the case of ^{3}**2h**, a significant decrease in *D* value is also noted, indicating that the unpaired electrons are delocalized more extensively by cyano group at 4-position. Thus, the extended stability can be explained in terms of thermodynamic factors as a result of spin delocalization. This indicates that the kinetically stabilized triplet carbenes can be further stabilized by spin-delocalizing substituents at para positions.

However, the inspection of *Td* and $t_{1/2}$ as a function of *D* value indicates that those data are not correlated to each other. The half-life ($t_{1/2}$) is just a measure of lifetime and cannot be regarded as a quantitative scale for reactivity. *Td* is also not taken as such a scale unless the decay process is demonstrated to be essentially the same over the carbenes studied. In this respect, the rate constant of the triplet carbene with a typical quencher can be employed as a more quantitative measure of the reactivity. However, neither k_{O_2} nor k_{CHD} appreciably correlate with the *D* value.

The reason for this rather unexpectedly poor correlation is not clear at present. Presumably simple linear correlations with spin delocalization factors may not be expected for the reaction of triplet carbenes (diradicals) to form the corresponding radicals since the extents of delocalization of unpaired electrons should be different between the two states. An additional complexity may arise from mixings of the singlet state in the reaction on the triplet energy surface, which have been often pointed out in the reaction of triplet diphenylcarbene systems.[32] Effects of substituents on the energy difference between the singlet and triplet states and spin-orbit coupling efficiencies are taken into account in this case.

Finally, it is interesting to note here that the *para-tert*-Bu group is found to exert a significant effect on *Td* and $t_{1/2}$. Since the $\sigma^{\bullet}$ of this group is not large, the effect can be better explained in terms of a steric factor rather than an electronic one. Sterically congested DPCs usually decay by dimerization at the carbene center to form tetra(aryl)ethylenes in an inert solvent when other intramolecular reaction channels are not available.[1] On the other hand, trityl radicals are known to undergo "head-to-tail" or "tail-to-tail" coupling.[33] It has been suggested that triplet DPCs also decay by undergoing coupling at the para positions, especially when the carbene center is effectively blocked by the ortho substituents.[34] Therefore, the rather large stabilization effect by the *para-t*-Bu group can be explained in terms of steric hindrance on such a coupling reaction.[35]

However, the para, para'-unsubstituted derivative **2a** is not destabilized at all even though hydrogens at the para position have neither a spin-delocalizing effect nor steric protecting ability. Moreover, product analysis studies indicate that not only the product ratios **3/4** but also overall yields of the product are very similar between the two derivatives **2a** and **2c** (Table 1). A possible reason for the increase in the half-life of **2c** in solution may reside in a decrease in diffusion constant due to an increased molecular size,[36] since the main decay pathway in solution at room temperature is dimerization of triplet carbenes. However, this cannot explain the thermal stability in matrix upon thawing, unless the origin of the main decay pathway under these conditions is clarified.

Conclusion

Effect of para-substituents on the structure and reactivities of sterically congested triplet carbenes, bis(2,6-dimethylphenyl)carbenes, have been investigated by using spectroscopic methods in combination with product analysis. It has been revealed that triplet diarylcarbenes, which are kinetically stabilized by ortho substituents, can be further stabilized thermodynamically by introducing a spin-delocalizing para substituent. However the correlations between electronic and molecular structures of triplet diarylcarbenes and their reactivities are found to be poor.

Experimental

General Remarks. ^{1}H-NMR spectra were recorded on a JEOL JNM-AC300FT/NMR spectrometer in $CDCl_3$ with Me_4Si as an internal reference. IR spectra were measured on a JASCO-Herschel FT/IR-600H spectrometer, and UV-vis spectra were recorded on a JASCO CT-560 spectrophotometer. The mass spectra were recorded on a JEOL JMS-600H mass spectrometer. Gel permeation chromatography (GPC) was carried out on a JASCO, Model HLC-01 instrument. The GPC column was a Shodex H-2001. Thin layer chromatography was carried out on a Merck Kieselgel 60 PF_{254}. Column chromatography was performed on silica gel (Fuji Davidson) for column chromatography or on ICN for dry column chromatography.

Diazobis(2,6-dimethylphenyl)methane (1a). To a solution of 2,6-dimethylbromobenzene (1.97 g, 10.6 mmol) in dry ether (10 mL), a hexane solution of butyllithium (1.47 M, 12.3 mL) was added slowly under the atmosphere of Ar, and the mixture was refluxed for 4 hours. After cooling to ambient temperature, the solution of 2,6-dimethylbenzonitrile[37] (1.5 g, 10.6 mmol) in dry Et_2O (20 mL) was added, and the mixture was refluxed for 12 hours. Cooled aqueous-saturated solution of ammonium chloride was added to the reaction mixture and then the reaction mixture was extracted with Et_2O. The ethereal layer was washed with water, dried over anhydrous Na_2SO_4, and the solvent was evaporated by a rotary evaporator and dried under vacuum. Crude product was purified by column chromatography (SiO_2, CH_2Cl_2) to give bis(2,6-dimethylphenyl) ketimine in 54% yield as a light yellow solid: mp 96.1–98.4°C; ^{1}H NMR ($CDCl_3$) δ 7.15 (t, J = 7.59 Hz, 2 H), 7.03 (d, J = 7.59 Hz, 4 H), 2.19 (s, 12 H); MS *m*/*z* (relative intensity) 237 (M^+, 0.6), 236 (1.0), 222 (100), 207 (21.1), 130 (10.5), 103 (9.4). Into a slurry of anhydrous sodium acetate (1.0 g, 12 mmol) and CCl_4 (10 mL) containing dinitrogen tetraoxide (0.5 g, 5.8 mmol) cooled to below 0°C was dropped a solution of the ketimine (0.3 g, 1.2 mmol) in CCl_4 (10 mL) over a period of 20 min. After the reaction was completed, as judged by TLC (CH_2Cl_2), the reaction mixture was poured into a mixture of ice and excess saturated sodium carbonate and then extracted by CCl_4. The organic layer was washed with ice-water, dried over anhydrous Na_2SO_4, and the solvent was evaporated by a rotary evaporator, and dried under vacuum to give bis(2,6-dimethylphenyl) *N*-nitrosoketimine in quantitative yield as a dark-green solid. The crude nitrosoketimine was dissolved in anhydrous Et_2O (10 mL) and cooled to -50°C in a dry ice-methanol bath. A suspension of $LiAlH_4$ (0.13 g, 3.5 mmol) in anhydrous Et_2O (10 mL) was added slowly to the stirred mixture. The temperature was allowed to rise to -10°C for a moment to prevent a build-up of excess $LiAlH_4$. After most of the nitroso ketimine was consumed, as judged by TLC (hexane), a small amount of ethyl acetate was added slowly to destroy excess $LiAlH_4$. After cooling to -50°C, water was added, and then the reaction mixture was returned to ambient temperature naturally and was extracted with Et_2O. The ethereal solution was washed with water, dried over anhydrous Na_2SO_4, and the solvent was evaporated by a rotary evaporator, and then dried under vacuum. The crude diazomethane was purified by column chromatography (ICN alumina/hexane) at 0°C, followed by GPC ($CHCl_3$) to produce diazobis(2,6-dimethylphenyl) methane in 37% yield as a red solid: mp 130.0–132.0°C; ^{1}H-NMR ($CDCl_3$) δ 7.15–7.04 (m, 6 H), 2.11 (s, 12 H); IR ($CHCl_3$) 2032 cm^{-1}.

Diazobis(4-*tert*-butyl-2,6-dimethylphenyl)methane (1c). Bis(4-*tert*-butyl-2,6-dimethylphenyl)ketimine was prepared by the reaction of (4-*tert*-butyl-2,6-dimethylphenyl)lithium (obtained by treating the corresponding bromide[38] (2.6 g, 11 mmol) with *n*-BuLi (1.54 M in *n*-hexane, 18 mL)) with 4-*t*-butyl-2,6-dimethylbenzonitrile[39] in 32% yield as light yellow solid: mp 131.8–134.9°C; ^{1}H NMR ($CDCl_3$) δ 7.02 (s, 4 H), 2.18 (s, 12 H), 1.29 (s, 18 H); MS *m*/*z* (relative intensity) 349 (M^+, 2.1), 334 (100), 318 (4.0), 160 (3.5), 146 (4.7); HRMS calcd for $C_{25}H_{35}N$ *m*/*e* 349.2769, found 349.2708. The ketimine (0.58 g, 1.7 mmol) was treated with N_2O_4, followed by $LiAlH_4$ treatment of the resulting *N*-nitroso compound to produce diazobis(4-*t*-butyl-2,6-dimethylphenyl)methane (1c) in 23% yield as a red adhesive: ^{1}H NMR ($CDCl_3$) δ 7.07 (s, 4 H), 2.11 (s, 12 H), 1.30 (s, 18 H); IR (CHCl3) 2032 cm^{-1}.

Diazobis(4-methoxy-2,6-dimethylphenyl)methane (1d). Bis(4-methoxy-2,6-dimethylphenyl)ketimine was prepared by the reaction of (4-methoxy-2,6-dimethyl-phenyl)lithium (obtained by the reaction of the corresponding bromide[40] (1.4 g, 6.5 mmol) with *n*-BuLi (1.59 N in hexane, 8.2 mL)) with 4-methoxy-2,6-dimethylbenzonitrile,[41] followed by column chromatography in 38% yield as a yellow solid: mp 121.7–125.3°C; ^{1}H NMR ($CDCl_3$) δ 6.56 (s, 4 H), 3.79 (s, 6 H), 2.15 (s, 12 H). The ketimine (0.3 g, 1 mmol) was treated with N_2O_4, followed by $LiAlH_4$ as described above, to afford diazobis(4-methoxy-2,6-dimethylphenyl)methane (**1d**) in 42% yield as a red solid: mp 92.1–92.7°C; ^{1}H-NMR ($CDCl_3$) δ 6.63 (s, 4 H), 3.79 (s, 6 H), 2.10 (s, 12 H); IR ($CHCl_3$) 2032 cm^{-1}.

Diazobis(4-fluoro-2,6-dimethylphenyl)methane (1e). 5-Fluoro-1,3-dimethylbenzene (3.6 g, 29 mmol) was reacted with Br_2 (1.5 mL, 29 mmol) in CCl_4, and the reaction was worked up as usual to obtain 4-fluoro-2,6-dimethylbromobenzene in 62% yield as a light yellow liquid: ^{1}H NMR ($CDCl_3$) δ 6.81 (d, J = 8.91 Hz, 2 H), 2.39 (s, 6 H); MS *m*/*e* (relative intensity) 202 (M^+, 94.3), 123 (100), 103 (14.6), 96 (11.4), 77 (10.3); HRMS calcd for C_8H_8FBr *m*/*e* 201.9793, found 201.9828. A mixture of this bromide (2.2 g, 11 mmol) and CuCN (1 g, 11.5 mmol) in absolute DMF (15 mL) was refluxed overnight and worked up as described above to afford 4-fluoro-2,6-dimethylbenzonitrile in 64% yield as white solid: mp 82.3–85.9°C; ^{1}H NMR ($CDCl_3$) δ 6.84 (d, J = 9.42 Hz, 2 H), 2.53 (s, 6 H); MS *m*/*z* (relative intensity) 149 (M^+, 100), 134 (76.4), 121 (9.1), 107 (5.9), 101 (9.9); HRMS calcd for C_9H_8NF *m*/*e* 149.0641, found 149.0642. Bis(4-fluoro-2,6-dimethylphenyl)ketimine was obtained by the reaction of (4-fluoro-2,6-dimethylphenyl)lithium (prepared from the corresponding bromide (1.4 g, 7 mmol) with *n*-BuLi (1.59 M in hexane, 8.8 mL)) with 4-fluoro-2,6-dimethylbenzonitrile, followed by column chromatography, in 15% yield as a yellow solid: mp 129.5–131.1°C; ^{1}H NMR ($CDCl_3$) δ 6.75 (d, J = 9.57 Hz, 4 H), 2.71 (s, 12 H); MS *m*/*z* (relative intensity) 273(M^+, 1.7), 258(100); HRMS calcd for $C_{17}H_{17}NF_2$ *m*/*z* 273.1329, found 273.1379. The ketimine (0.28 g, 1 mmol) was subjected to nitrosation, followed by $LiAlH_4$ treatment as described above to afford diazobis(4-fluoro-2,6-dimethylphenyl)methane (**1e**) in 19% yield as a red solid: mp 107.0 – 109.7°C; ^{1}H NMR ($CDCl_3$) δ 6.80 (d, J = 9.24 Hz, 4 H), 2.10 (s, 12 H) ; IR ($CHCl_3$) 2048 cm^{-1}.

Diazobis(4-chloro-2,6-dimethylphenyl)methane (1f). To a mixture of concentrated hydrochloric acid (30 mL) and 4-chloro-2,6-xylidine[42] (8.2 g, 52.4 mmol) in H_2O (30 mL) cooled to 0°C was added an aqueous solution of $NaNO_2$ (4.0 g, 57.6 mmol) slowly until an excess of nitrous acid was indicated by starch-iodide paper. KI (8.7 g, 52.4 mmol) in H_2O (20 mL) was added and the mixture was allowed to stand overnight, then refluxed until no more gas was evolved; it was then cooled to ambient temperature, and extracted with CH_2Cl_2. The organic layer was washed with 5% aqueous NaOH, water and dried over sodium sulfate. The solvent was evaporated to dryness in vacuum to give 4-chloro-2,6-dimethyliodobenzene in 50% yield as a brown solid: mp 38.6–39.2°C; ^{1}H NMR ($CDCl_3$) δ 7.06 (s, 2 H), 2.44 (s, 6 H); MS *m*/*z* (relative intensity) 266 (M^+, 100), 231 (6.1), 139 (40.4), 103 (35.7), 77 (21.0); HRMS calcd for C_8H_8ClI *m*/*z* 265.9360, found 265.9402. The iodide (4.6 g, 17 mmol) was treated with CuCN (1.6 g, 18 mmol) in absolute DMF (30mL) to give 4-chloro-2,6-dimethylbenzonitrile in 67% yield as a light yellow solid: mp 57.3–57.9°C; ^{1}H NMR ($CDCl_3$) δ 7.14 (s, 2 H), 2.51 (s, 6 H); MS *m*/*z* (relative intensity) 165 (M^+, 66.9), 150 (10.6), 130 (100), 103 (15.9), 77 (8.8); HRMS calcd for C_9H_8NCl *m*/*z* 165.0345, found 165.0310.. Bis(4-chloro-2,6-dimethylphenyl)ketimine was prepared by the reaction of 4-chloro-2,6-dimethhylphenyllithium (obtained by treating the corresponding iodide (3.2 g, 12 mmol) with *n*-BuLi (1.61 N in hexane, 7.9 mL)) with 4-chloro-2,6-dimethylbenzonitrile, followed by column chromatography, in 15.5% yield as a brown solid: mp 113.5–115.3°C; ^{1}H NMR ($CDCl_3$) δ 10.13 (bs, 1 H), 7.05 (s, 4 H), 2.15 (s, 12 H); MS *m*/*z* (relative intensity) 306 (M^+, 1.2), 291 (63.9), 290 (100), 255 (19.4); HRMS calcd for $C_{17}H_{17}NCl_2$ *m*/*z* 305.0738, found 305.0825. The ketimine (0.24 g, 0.78 mmol) was subjected to nitrosation-$LiAlH_4$ treatment as described above to produce diazobis(4-chloro-2,6-dimethylphenyl)methane (**1f**) in 35.5% yield as red solid: mp136.3–138.6°C; ^{1}H NMR ($CDCl_3$) δ 7.07 (s, 4 H), 2.08 (s, 12 H); IR ($CHCl_3$) 2048 cm^{-1}.

Diazobis(4-bromo-2,6-dimethylphenyl)methane (1g). 4-Bromo-2,6-xylidine[43] (16 g, 80 mmol) was diazotized with HNO_2, followed by KI, to afford 4-bromo-2,6-dimethyliodobenzene in 34% yield as a white solid: mp 32.4–34.1°C; ^{1}H NMR ($CDCl_3$) δ 7.20 (s, 2 H), 2.44 (s, 6 H); MS *m*/*z* (relative intensity) 311 (M^+, 97.9), 310 (100), 185 (29.2), 183 (30.0), 104 (53,5), 103 (28.0), 77 (18.7); HRMS calcd for C_8H_8BrI *m*/*z* 309.8854, found 309.8768. Bis(4-bromo-2,6-dimethylphenyl)ketimine was prepared by the reaction of 4-bromo-2,6-dimethylphenyllithium (obtained by treating the corresponding iodide (2.6 g, 8.5 mmol) with *n*-BuLi (1.61 M in hexane, 5.5 mmol)) with 4-bromo-2,6-dimethylbenzonitrile,[43] followed by column chromatography, in 14% yield as a yellow solid: mp 105.2–108.2°C; ^{1}H NMR ($CDCl_3$) δ 10.17 (bs, 1 H), 7.21 (s, 4 H), 2.15 (s, 12 H); MS *m*/*z* (relative intensity) 395 (M^+, 1.7), 382 (50.9), 380 (100), 378 (50.1), 301 (17.7), 299 (18.1); HRMS calcd for $C_{17}H_{17}NBr_2$ *m*/*z* 392.9727, found 392.9760. The ketimine (0.23 g, 0.58 mmol) was subjected to nitrosation-$LiAlH_4$ treatment to produce diazobis(4-bromo-2,6-dimethylphenyl)methane (**1g**) in 22% yield as a red solid: mp 136.3–137.9°C; ^{1}H NMR ($CDCl_3$) δ 7.24 (s, 4 H), 2.07 (s, 12 H), IR ($CHCl_3$) 2048 cm^{-1}.

Diazobis(4-cyano-2,6-dimethylphenyl)methane. To a solution of 4-bromo-2,6-dimethyliodobenzene (6.2 g, 19.9 mmol) in dry ether (30 mL) cooled to −70°C, hexane solution of *n*-butyllithium (3.02 M, 7.9 mL, 23.9 mmol) was added slowly under the atmosphere of Ar, and the mixture was stirred for 3 hours at this temperature. A solution of 4-bromo-2,6-dimethylbenzaldehyde[44] (4.0 g, 18.8 mmol) in dry ether (20 mL) was added to the mixture, and the mixture was stirred for 12 hours at room temperature. Cooled aqueous saturated solution of ammonium chloride was added to the reaction mixture and then the reaction mixture was extracted with ether. The ethereal layer was washed with water, dried over anhydrous Na_2SO_4, and the solvent was evaporated by a rotary evaporator and dried under vacuum. Crude product was purified by column chromatography (SiO_2, CH_2Cl_2 : hexane =

1:1) to give bis(4-bromo-2,6-dimethylphenyl)methanol in 55% yield as a white solid: mp 159.4–162.2°C; ^{1}H NMR (CDCl$_3$) δ 7.13 (s, 4 H), 6.26 (d, J = 4.95 Hz, 1 H), 2.20 (s, 12 H), 1.80 (d, J = 4.95 Hz, 1 H); MS m/z (relative intensity) 398 (M$^+$, 10.1), 365 (12.5), 284 (18.3), 213 (100), 185 (14.3), 106 (21.6); HRMS calcd for $C_{17}H_{18}OBr_2$ m/z 395.9724, found 395.9724.

Bis(4-bromo-2,6-dimethylphenyl)methanol (3.8 g, 9.6 mmol) was added to a solution of acetic anhydride (40 mL) and pyridine (60 mL) at 0°C, and stirred at room temperature for 12 hours. The reaction mixture was poured into ice-water and extracted with dichloromethane. The dichloromethane layer was washed with 10% aqueous solution of sodium hydroxide and water, and dried over anhydrous Na$_2$SO$_4$. The solvent was evaporated by a rotary evaporator and dried under vacuum to give bis(4-bromo-2,6-dimethylphenyl)methyl acetate in quantitative yield as a light yellowish liquid. The acetate (4.2 g, 9.6 mmol) was treated with CuCN (1.9 g, 21.0 mmol) as described above to give bis(4-cyano-2,6-dimethylphenyl)methyl acetate in 95% yield as brownish solid. The acetate was dissolved in methanol and saturated aqueous solution of potassium carbonate at room temperature to give bis(4-cyano-2,6-dimethylphenyl)methanol in 57% yield as yellowish solid: mp 240.1–242.4°C, ^{1}H NMR (CDCl$_3$) δ 7.30 (s, 4 H), 6.42 (d, J = 4.95 Hz, 1 H), 2.26 (s, 12 H), 1.99 (d, J = 4.95 Hz, 1 H); IR (KBr) 2224 cm^{-1}; MS m/z (relative intensity) 290 (M$^+$, 18.2), 275 (21.5), 257 (42.7), 156 (100), 132 (77.2); HRMS calcd for $C_{19}H_{18}N_2O$ m/z 290.1419, found 290.1350. The methanol (300 mg, 1.0 mmol) was treated with thionyl chloride (5 mL) at room temperature to give chlorobis(4-cyano-2,6-dimethylphenyl) methane in quantitative yield as yellow solid: ^{1}H NMR (CDCl$_3$) δ 7.32 (s, 4 H), 6.58 (s, 1 H), 2.35 (s, 12 H). The chloromethane (304 mg, 1.0 mmol) in dry dioxane (15 mL) was added to a mixture of ethyl carbamate (1.8 g, 19.7 mmol), AgBF$_4$ (0.23 g, 1.2 mmol), and dry dioxane (5 mL) and refluxed until TLC monitoring showed that almost all of the chloride was consumed (12 h). The cooled reaction mixture was extracted with ether, the ethereal layer was washed with water, dried over anhydrous Na$_2$SO$_4$, and the solvent was evaporated by a rotary evaporator. The crude product was purified by column chromatography (SiO$_2$, ethyl ether:hexane–1:1) to give ethyl *N*-[bis(4-cyano-2,6-dimethylphenyl)methyl]carbamate in 45% as yellowish solid: mp 83.3–85.7°C; ^{1}H NMR (CDCl$_3$) δ 7.29 (s, 4 H), 6.40 (d, J = 8.25 Hz, 1 H), 4.97 (d, J = 8.25 Hz, 1 H), 4,19 (q, J = 7.04 Hz, 2 H), 2.20 (s, 12 H), 1.27 (t, J = 7.04 Hz, 3 H); MS m/z (relative intensity) 361(M$^+$, 67.6), 346(28.1), 332(63.2), 288(38.0), 257(100), 157(54.2); HRMS calcd for $C_{22}H_{23}N_3O_2$ m/z 361.1790, found 361.1888.

To a vigorously stirred mixture of the carbamate (160 mg, 0.4 mmol) in acetic acid (5 mL) and acetic anhydride (10 mL) at 0°C was added a portion of NaNO$_2$ (0.7 g, 10.2 mmol) every 5 min for 3 hours . The mixture was stirred overnight at 0°C, then poured into ice-water and extracted with ether. The ethereal layer was washed with a saturated aqueous solution of sodium carbonate and water, dried over anhydrous Na$_2$SO$_4$, and the solvent was evaporated by a rotary evaporator to give ethyl *N*-nitroso-*N*-[bis(4-cyano-2,6-dimethylphenyl)methyl]carbamate in 82% yield as yellowish solid: ^{1}H NMR (CDCl$_3$) δ 7.29 (s, 4 H), 6.83 (s, 1 H), 4.41 (q, J = 7.10 Hz, 2 H), 1.98 (s, 12 H), 1.32 (t, J = 7.10 Hz, 3 H). To a solution of the nitroso carbamate (115 mg, 0.3 mmol) in absolute THF (25 mL) at −10°C was added potassium *t*-butoxide (115 mg, 1.0 mmol) at once under the atmosphere of argon. The mixture was stirred overnight until TLC monitoring showed almost all of the nitroso carbamate was consumed. The mixture was extracted with ether, and the crude diazomethane was purified by column chromatography (ICN alumina/hexane) at −10°C, followed by GPC (CHCl$_3$) to give diazobis(4-cyano-2,6-dimethylphenyl)methane in 2.3% yield as yellow solid: mp 208.9–210.6°C; mp (decomp) 270°C; ^{1}H NMR (CDCl$_3$) δ 7.38 (s, 4 H), 2.11 (s, 12 H); IR (CHCl3) 2048 (C=N$_2$) and 2224 cm^{-1} (CN).

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

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

Tetrakis(2,6-dimethylphenyl)ethylene (3a). ^{1}H NMR (CDCl$_3$) δ 6.93 (t, J = 7.44 Hz, 4 H), 6.79 (d, J = 7.44 Hz, 4 H), 6.72 (d, J = 7.44 Hz, 4 H), 1.93 (s, 12 H), 1.75 (s, 12 H); MS m/z (relative intensity) 444 (M$^+$, 100); HRMS calcd for $C_{34}H_{36}$ m/z 444.2817, found 444.2833.

1-(2,6-Dimethylphenyl)-6-methyl-1,2-dihydrobenzocyclobutene (4a). ^{1}H NMR (CDCl$_3$) δ 7.15 (t, J = 7.44 Hz, 1 H), 7.01-6.92 (m, 5 H), 5.06 (bs, 1 H), 3.61 (dd, J = 5.88, 13.96 Hz, 1 H), 3.77 (dd, J = 3.31, 13.96 Hz, 1 H) 2.47 (bs, 3 H), 1.99 (s, 3 H), 1.88 (bs, 3 H); MS m/z (relative intensity) 222(M$^+$, 4.0), 207(100), 192(82.8); HRMS calcd for $C_{17}H_{18}$ m/z 222.1409, found 222.1396.

Tetrakis(2,6-dimethyl-4-*t*-butylphenyl)ethylene (3c). ^{1}H NMR (CDCl$_3$) δ 6.74 (s, 4 H), 6.63 (s, 4 H), 1.84 (s, 12 H), 1.74 (s, 12 H), 1.20 (s, 36 H); MS m/z (relative intensity) 668 (M$^+$, 100), 278 (16.5), 1.49 (21.3); HRMS calcd for $C_{50}H_{68}$ m/z 668.5321, found 668.5265.

4-*t*-Butyl-1-(4-*t*-butyl-2,6-dimethylphenyl)-6-methyl-1,2-dihydrobenzocyclobutene (4c). ^{1}H NMR (CDCl$_3$) δ 7.00 (s, 2 H), 6.98 (s, 2 H), 4.98 (bs, 1 H), 3.55 (dd, J = 5.70, 13.78 Hz, 1 H), 3.22 (dd, J = 3.31, 13.78 Hz, 1 H), 2.42 (bs, 3 H), 2.00 (s, 3 H), 1.96 (bs, 3 H), 1.32 (s, 9 H), 1.29 (s, 9 H); MS m/z (relative intensity) 334 (M$^+$, 23.3), 319 (100), 207 (68.6), 57 (75.5); HRMS calcd for $C_{25}H_{34}$ m/z 334.2661, found 334.2632.

Tetrakis(4-methoxy-2,6-dimethylphenyl)ethylene (3d). ^{1}H NMR (CDCl$_3$) δ 6.37 (s, 4 H), 6.27 (s, 4 H), 3.70 (s, 12 H), 1.92 (s, 12 H), 1.71 (s, 12 H); MS m/z (relative intensity) 546 (M$^+$, 100), 299 (11.0), 283 (13.6); HRMS calcd for $C_{38}H_{44}O_4$ m/z 564.3239, found 564.3307.

4-Methoxy-1-(4-methoxy-2,6-dimethylphenyl)-6-methyl-1,2-dihydrobenzocyclobutene (4d). ^{1}H NMR (CDCl$_3$) δ 6.55 (s, 2 H), 6.52 (s, 2 H), 4.92 (bs, 1 H), 3.77 (s, 3 H), 3.70 (s, 3 H), 3.53 (dd, J = 5.70, 13.78 Hz, 1 H), 3.15 (dd, J = 3.12, 13.95 Hz, 1 H), 2.43 (bs, 3 H), 1.97 (s, 3 H), 1.88 (s, 3 H); MS m/z (relative intensity) 282 (M$^+$, 15.5), 267 (100), 252 (33.0); HRMS calcd for $C_{19}H_{22}O_2$ m/z 282.1620, found 282.1653.

3,6-Dimethoxy-1,4a,8-trimethyl-4a,10-dihydroanthracene (5d). ^{1}H NMR (CDCl$_3$) δ 6.59 (s, 1 H), 6.56 (s, 2 H), 5.68 (s, 1 H), 4.59 (s, 1 H), 3.80 (s, 3 H), 3.58 (s, 3 H), 3.09 (d, J = 15.43 Hz, 1 H), 2.51 (d, J = 15.43 Hz, 1 H), 2.35 (s, 3 H), 2.02 (s, 3 H), 0.89 (s, 3 H).

Tetrakis(4-fluoro-2,6-dimethylphenyl)ethylene (3e). ^{1}H NMR (CDCl$_3$) δ 6.56 (d, J = 11.94 Hz, 4 H), 6.47 (d, J = 11.94 Hz, 4 H), 1.92 (s, 12 H), 1.73 (s, 12 H); MS m/z (relative intensity) 516 (M$^+$, 100); HRMS calcd for $C_{34}H_{32}F_4$ m/z 516.2440, found 516.2411.

4-Fluoro-1-(4-fluoro-2,6-dimethylphenyl)-6-methyl-1,2-di-

hydrobenzocyclobutene (4e). ^{1}H NMR ($CDCl_3$) δ 6.76 (d, J = 8.27 Hz, 4 H), 4.93 (bs, 1 H), 3.56 (dd, J = 5.80, 14.43 Hz, 1 H), 3.19 (dd, J = 2.57, 14.51 Hz, 1 H), 2.45 (bs, 3 H), 1.97 (s, 3 H), 1.85 (bs, 3 H); MS m/z (relative intensity) 258(M^+, 1.2), 243(100), 228(93.0); HRMS calcd for $C_{17}H_{16}F_2$ m/z 258.1220, found 258.1194.

3,6-Difluoro-1,4a,8-trimethyl-4a,10-dihydroanthracene (5e). ^{1}H NMR ($CDCl_3$) δ 6.74-6.68 (m, 2 H), 6.63 (s, 1 H), 5.76 (d, J = 12.86 Hz, 1 H), 5.12 (d, J = 12.86 Hz, 1 H), 3.13 (d, J = 15.62 Hz, 1 H), 2.53 (d, J = 15.62 Hz, 1 H), 2.36 (s, 3 H), 2.05 (s, 3 H), 0.93 (s, 3 H); MS m/z (relative intensity) 258 (M^+, 1.0), 243 (100), 228 (71.2); HRMS calcd for $C_{17}H_{16}F_2$ m/z 258.1220, found 258.1142.

Tetrakis(4-chlolo-2,6-dimethylphenyl)ethylene (3f). ^{1}H NMR ($CDCl_3$) δ 6.84 (s, 4 H), 6.77 (s, 4 H), 1.90 (s, 12 H), 1.71 (s, 12 H); MS m/z (relative intensity) 586 (M + 6, 13.3), 584 (M + 4, 52.8), 582 (M + 2, 100), 580 (M^+, 28.6); HRMS calcd for $C_{34}H_{32}Cl_4$ m/z 580.1258, found 580.1217.

4-Chloro-1-(4-chloro-2,6-dimethylphenyl)-6-methyl-1,2-dihydrobenzocyclobutene (4f). ^{1}H NMR ($CDCl_3$) δ 6.99 (s, 2 H), 6.95 (s, 2 H), 4.93 (bs, 1 H), 3.58 (dd, J = 5.88, 14.33 Hz, 1 H), 3.21 (dd, J = 3.31, 14.33 Hz, 1 H), 2.43 (bs, 3 H), 1.96 (s, 3 H), 1.84 (bs, 3 H); MS m/z (relative intensity) 292 (M + 2, 9.1), 290 (M^+, 12.0), 275 (60.2), 240 (100); HRMS calcd for $C_{17}H_{16}Cl_2$ m/z 290.0629, found 290.0681.

Tetrakis(4-bromo-2,6-dimethylphenyl)ethylene (3g). ^{1}H NMR ($CDCl_3$) δ 6.99 (s, 4 H), 6.93 (s, 4 H), 1.89 (s, 12 H), 1.70 (s, 12 H); MS m/z (relative intensity) 762 (M + 6, 70.4), 760 (M + 4, 100), 758 (M + 2, 68.1), 756 (M^+,16.1); HRMS calcd for $C_{34}H_{32}Br_4$ m/z 755.9236, found 755.9235.

4-Bromo-1-(4-bromo-2,6-dimethylphenyl)-6-methyl-1,2-dihydrocyclobutene (4g). ^{1}H NMR ($CDCl_3$) δ 7.17 (s, 2 H), 7.09 (s, 2 H), 4.90 (bs, 1 H), 3.60 (dd, J = 5.70, 14.33 Hz, 1 H), 3.23 (dd, J = 3.12, 14.15 Hz, 1 H), 2.43 (bs, 3 H), 1.96 (s, 3 H), 1.84 (bs, 3 H); HRMS calcd for $C_{17}H_{16}Br_2$ m/z 377.9618, found 377.9585.

Irradiation for Analytical Purposes. All irradiations outlined in Table 1 were carried out in a Pyrex tube of 5.0 mL capacity. In order to avoid ambiguity in relative yields due to oxidation, the solution was thoroughly degassed by subjecting the sample to a minimum of three freeze-degas-thaw cycles at a pressure near 10^{-3} Pa before irradiation, and the tube was flame-sealed under reduced pressure. Irradiation was carried out with filtered light from the mercury lamp until all the diazo compound was consumed. Product identities were established by NMR comparisons with "authentic" samples separated as described above, and the product distributions were conveniently determined by NMR using an internal standard.

ESR Measurements. The diazo compound was dissolved in 2-methyltetrahydrofuran (2-MTHF) (5×10^{-4} M), and the solution was degassed in a quartz cell by four 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 lamp using a Pyrex filter. ESR spectra were measured on a JEOL JES TE200 spectrometer (X-band microwave unit, 100 kHz field modulation). The signal positions were read by the use of a gaussmeter.

Low-Temperature UV/Vis Spectra. Low-temperature spectra at 77 K were obtained by using an Oxford variable-temperature liquid-nitrogen cryostat (DN 2704) 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 by four freeze-degas-thaw cycles at a pressure near 10^{-3} Pa. 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 500-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).

Laser Flash Photolysis. All flash photolysis measurements were made on a Unisoku TSP-601 flash spectrometer. The excitation source for the laser flash photolysis was a XeCl excimer laser. A Hamamatsu 150 W xenon short arc lamp (L2195) was used as the probe source, and the monitoring beam guided using an optical fiber scope was arranged in an orientation perpendicular to the excitation source. The probe beam was monitored with a Hamamatsu R2949 photomultiplier tube through a Hamamatsu S3701-512Q linear image sensor (512 photodiodes used). Timing of the laser excitation pulse, the probe beam , and the detection system was achieved through an Iwatsu Model DS-8631 digital synchroscope which was interfaced to an NEC 9801 RX2 computer. This allowed for rapid processing and storage of the data and provided printed graphics capabilities. Each trace was also displayed on an NEC CRT N5913U monitor.

A sample was placed in a long-necked Pyrex tube which had a side arm connected to a quartz fluorescence cuvette and degassed using a minimum of four freeze-degas-thaw cycles at a pressure near 10^{-3} Pa immediately prior to photolysis. The sample system was sealed, and the solution was transferred to the quartz cuvette which was placed in the sample chamber of the flash spectrometer. The concentration of the sample was adjusted so that it absorbed a significant portion of the laser light.

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