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Generation, Reactions, and Kinetics of Di(naphthyl)carbenes: Effects of the Methyl Group

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A series of di(naphthyl)carbenes (DNCs) having methyl groups on aromatic rings were generated by photolysis of the corresponding diazo precursors and studied not only by product analysis, but also by spectroscopic means. "Parent" triplet α-DNC was shown to have a half-life of 70 ms, which is some 30 times larger than that of triplet diphenylcarbene (^{3}DPC), whereas parent triplet *β*-DNC was 2 orders of magnitude shorter-lived than the α-isomer. The lifetimes of triplet DNCs were significantly increased by introducing methyl groups near the carbene center. Thus, ^{3}α-DNC, which has four methyl groups at 2,2′,4,4′-positions, was shown to have a half-life of 100 ms, and the replacement of the two methyl groups at the 2,2′-positions of this carbene with tri(deuterio)methyl groups resulted in an increase of the lifetime by approximately 3 times by quenching the intramolecular H transfer from the methyl groups to the carbene center leading to *o*-quinoid compounds. The results are discussed in terms of the counteracting effects of electronic properties stabilizing the singlet state and steric factors favoring the triplet and compared with similar studies with ^{3}DPCs.

The past decade has witnessed a renaissance in the study of the kinetics and spectroscopy of carbenes as laser flash photolysis (LFP) became a widely used technique in this area.[1] In particular, diarylcarbenes, which are receiving considerable attention as the archetypal triplet ground-state carbene, have been studied in great detail, as they usually exhibit strong absorption bands in a more accessible spectral region than those of other carbenes and are hence readily studied by LFP with UV−vis detection. Thus, diphenylcarbenes and fluorenylidenes bearing various substituents have been extensively studied, and these studies have demonstrated a large dependence of carbene reactivity on the structures.[1−3]

For instance, such studies on cyclic aromatic carbenes bearing a series of aryl substituents have demonstrated that electron-donor groups stabilize the electrophilic singlet carbene more than they do the radical like triplet, whereas electron-withdrawing groups destabilize the singlet and lead to a greater singlet−triplet splitting (ΔG_{ST}).[2] On the other hand, the study of reactivity as a function of the carbene bond angle has revealed that the triplet states are stabilized with respect to the singlet as the angle is increased.[4]

Another basic structural effect on carbene reactivity that should be revealed in a quantitative manner might be the perturbation by the extension of the *π*-system, as in benzo-annelated derivatives. Although several diarylcarbenes with polynuclear aromatic rings such as naphthalene[5−8] and anthracene[9] have been generated, the chemistry of these carbenes has not been systematically studied yet.

The zero-field splitting parameters, *D*/*E* values, of diphenylcarbene, di(1-naphthyl)carbene, and di(9-anthryl)carbene are reported to be 0.4055/0.194, 0.3157/0.0109, and 0.113/0.0011, respectively. This clearly suggests that the triplet states achieve a less bent structure with more extensive delocalization as the number of aromatic rings is increased.[10] These profound structural changes in the rigid matrix should be reflected in the reactivities in the solution phase.

As a part of our project on persistent triplet carbenes,[11−13] we studied the chemistry of di(naphthyl)carbenes bearing a series of methyl groups not only by product analysis but also by means of spectroscopic methods.

Results and Discussion

The diazomethanes that we prepared in this study are listed in Scheme 1. They are di(α-naphthyl)diazomethanes (α-**1**) having a series of methyl groups at the 2- and/or 4-positions and di(*β*-naphthyl)diazomethane (*β*-**1**) having two methyl groups at the 1- and 4-positions. Before going into the details of the effect of methyl groups on the reactivity of di(naphthyl)carbene (DNC), we will first reveal the reactivity difference between "parent" α-(α-**1)** and *β*-DNC (*β*-**1**)systems.

A. Di(α-naphthyl)carbene to Di(*β*-naphthyl)carbene: A Comparison. The chemistry of mono-naphthylcarbenes (NC) has been examined by product analysis[5] and also by spectroscopic means.[6,7] A comparison of the data available on the reactions of α-NC and *β*-NC with hydrocarbons shows that α-NC exhibits lower reactivity and a higher singlet character and possesses a smaller singlet−triplet energy gap (ΔG_{ST}). Two key molecular structural differences are responsible for the observed difference in the reactivity. First, the α-position of the naphthyl moiety has the largest HOMO orbital coefficient (Hückel, 0.425 vs 0.263). This will lead to greater stabilization of the singlet carbene center by a *π*-p overlap, thus making ΔG_{ST} smaller. A second factor that should be taken into account is the interaction between the carbene center and the *peri*-hydrogen, which is clear from matrix-isolation EPR experiments, which show a preference for the syn conformation of α-NC.[6a] It is also evident that similar 1,8-interactions influence the rate of formation of naphthylmethyl anions and cations.[8]

To examine how these two factors influence the reactivity of sterically more congested diaryl systems, we first generated α- and *β*-isomers of DNC (**2a**) and examined their reactivity.

a. Product Analysis Studies. Irradiation ($\lambda > 300$ nm) of **1a** in 2-propanol gave propyl ether **3a** as a major product along with a small amount of di(naphthylmethanes) **4**, the ratio of **3**/**4** being increased on going from α- to *β*-**2a** (Scheme 2, Table 1). These products are apparently derived from photolytically

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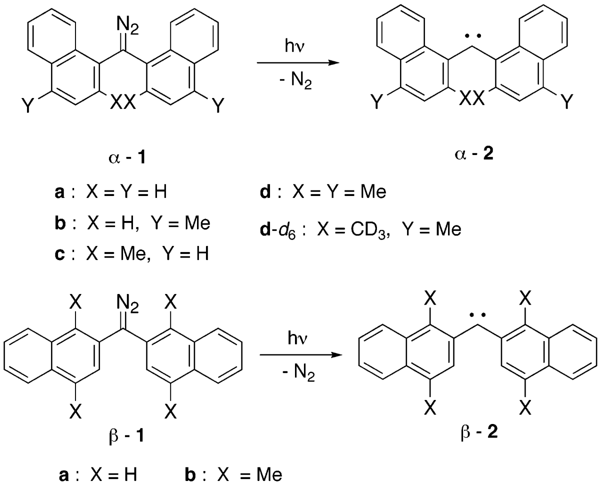
SCHEME 1



SCHEME 2

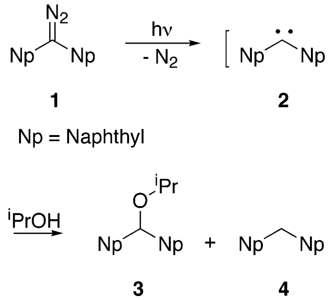


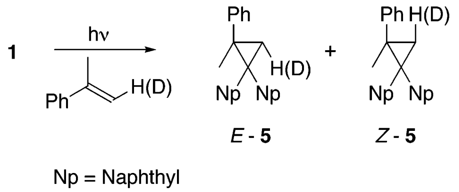
TABLE 1: Product Distributions in Photolysis of Di(naphthyl)diazomethane (1) in 2-Propanol

diazomethanes	**3**	**4**
α-**1a**	88	12
α-**1b**	77	18
α-**1c**	79	15
α-**1d**	49	47
β-**1a**	93	7
β-**1b**	84	12

generated carbenes **2a**, which must react with 2-propanol[14] because the diazomethanes **1a** were completely recovered without change in the dark under otherwise identical conditions. It is generally accepted that the O−H insertion is the characteristic reaction of singlet diarylcarbenes, whereas the triplet carbenes abstract hydrogen from the C−H bond of alcohols to give the corresponding diarylmethyl radicals, which either undergo dimerization to produce tetra(aryl)ethane and/or abstract second hydrogen to form diarylmethane.[14,15] The results indicate that the reaction from the triplet becomes more appreciable in the reaction of α-**2a** than that of *β*-**2a**.

Generation of **2a** in α-methylstyrene, on the other hand, afforded cyclopropane (**5a**) almost exclusively. Addition of a carbene to an olefin to form cyclopropane is the classical way to diagnose the multiplicity of the reacting carbene.[15] The stereochemistry of this reaction was probed by employing *E*-*β*-deuterio-α-methylstyrene.[16] Integration of the NMR absorption of the cyclopropyl hydrogens shows that the two isomeric cyclopropanes are formed in nearly equal amounts regardless of the position of carbene center (Scheme 3, Table 2). The stereochemical outcome of the cyclopropanation depends on the concentration of the styrene if both singlet and triplet states are involved.[16] However, the two cyclopropanes were formed in nearly equal amounts regardless of the initial olefin concentration. The finding suggests that only one spin state of the carbene is responsible for the cyclopropanation of the styrene, and the total loss of stereochemistry implies that this state is the triplet.

SCHEME 3



SCHEME 4

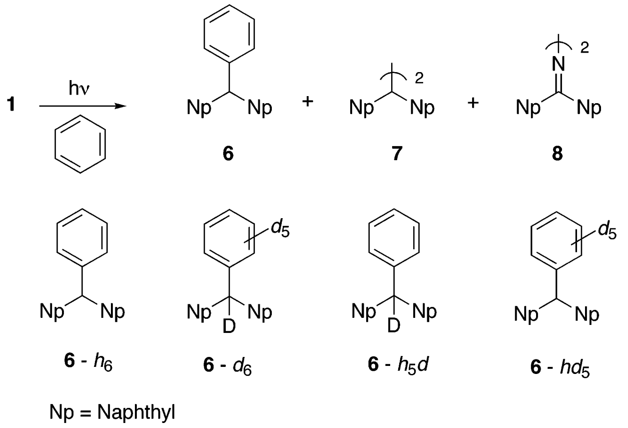


TABLE 2: Product Distributions in Photolysis of Di(naphthyl)diazomethane (1) in the Presence of *E*-***β***-Deuterio-α-methylstyrene

diazomethanes	*E*-**5**	*Z*-**5**
α-**1a**	49	51
α-**1b**	50	50
α-**1c**	0[a]	0[a]
α-**1d**	0[a]	0[a]
β-**1a**	49	51
β-**1b**	49	51

[a] A large amount of intractable materials were formed.

Photolysis in benzene resulted in the formation of products that were much more dramatically affected by the change in the carbene structure. Thus, irradiation of *β*-**1a** in benzene afforded di(2-naphthyl)phenylmethane (*β*-**6a**), formally an insertion product of the carbene *β*-**2a** into the C−H bond of the solvent, as the major product along with a small amount of radical dimer (*β*-**7a**), whereas similar irradiation of α-**1** resulted in the formation of a small amount of the dimer (α-**7a**) and the azine (α-**8a**) along with a large amount of intractable oil, no **6** being detected (Scheme 4, Table 3).

b. Spectroscopic Studies. Irradiation of di(1-naphthyl)diazomethane (α-**1a**) in a 2-methyltetrahydrofuran (2-MTHF) glass at 77 K gave a paramagnetic species shown in Figure 1 readily characterized from its ESR spectrum as triplet di(1-naphthyl)carbene (α-**2a**).[10,17] Essentially, the same spectrum was observed when di(2-naphthyl)diazomethane (*β*-**1a**) was irradiated under the same conditions. Two sets of signals were observed, as in the ESR spectra of other triplet naphthylcarbenes, presumably due to the presence of rotational isomers.[5a,8c−e] Detailed analysis of these spectra will be reported elsewhere. The signals were analyzed in terms of *D* and *E* values and are reported in Table 4. Because *E* measures the difference of the magnetic dipole interaction along the *x* and *y* axes, it allows one to estimate the bond angle at the carbene center, especially when weighted by

TABLE 3: Product Distributions in Photolysis of Di(naphthyl)diazomethane (1) in Benzene

diazomethanes	6	7	8
α-**1a**	<1	19	20
α-**1b**	<1	<1	74
α-**1c**	0[a]	0[a]	0[a]
α-**1d**	0[a]	0[a]	0[a]
β-**1a**	60[b]	<1	11
β-**1b**	0[a]	0[a]	0[a]

[a] A large amount of intractable materials were formed. [b] GC-MS analysis of *β*-**6a** obtained in the photolysis of *β*-**1a** in a 1:1.009 mixture of C_6H_6:C_6D_6 showed peaks at *m/z* 344 (*β*-**6a** -*h*$_6$) and 350 (*β*-**6a**-*d*$_6$) in the ratio of 1:0.98. MS peaks corresponding to *β*-**6a** -*h*$_5$*d* and *β*-**6a**-*hd*$_5$ were negligibly small (<1%).

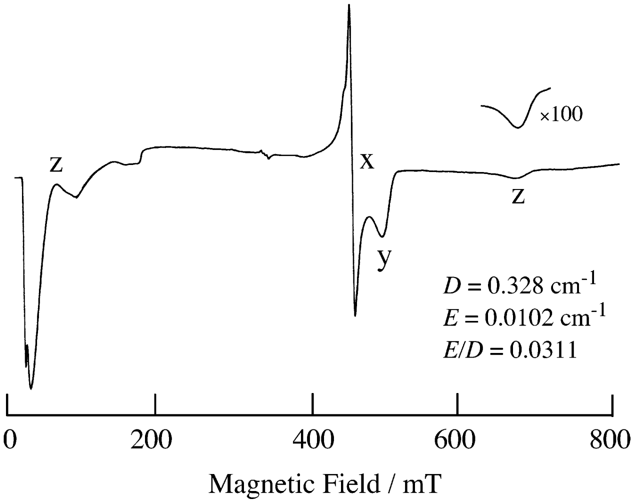


Figure 1. EPR spectrum obtained by irradiation of α-**1a** in 2-methyltetrahydrofuran (2-MTHF) at 77 K.

D. Inspection of the data in the table indicates that *E*/*D* values decrease on going from *β*- to α-isomer of DNC, suggesting that the carbene becomes less bent due to increased steric interaction.

Optical spectroscopy in the frozen medium gave analogous but more intriguing results. Irradiation of α-**1a** in 2-MTHF glass at 77 K resulted in the appearance of new absorption bands at the expense of the original absorption due to α-**1a**. As is shown in Figure 2, the new spectrum consists of structured bands in 300−450 nm with a strong and sharp maximum at 375 nm. These features, especially the strong and sharp absorption around 370−380 nm, are also reported for the spectra of α-NC (λ_{max} = 370 nm).[7,8] The glassy solution did not exhibit any changes for several hours when kept at 77 K. However, when it was allowed to warm to room temperature and was then cooled again to 77 K, the characteristic bands disappeared. On the basis of these observations coupled with ESR results, the absorption spectrum can be attributable to triplet di(1-naphthyl)carbene (α-**2a**) generated by the photodissociation of α-**1a**.

Similar irradiation of the *β*-isomer (*β*-**1a**) also gave new absorption bands with strong maxima at 325 and 398 nm, ascribable to triplet carbene (*β*-**2a**) (Table 4). Careful monitoring of the spectral changes as a function of the temperature revealed a significant difference in thermal stability between the two isomers. Thus, no appreciable changes were observed for the absorption bands ascribable to α-2**a** in 2-MTHF up to 100 K, whereas the absorption band observed for *β*-**2a** started to disappear already at 80 K.

To get more quantitative information on the reactivity, flash photolysis was carried out. Laser flash photolysis (LFP) of α-**1a** in a degassed benzene solution at room temperature with a 10 ns, 70−90 mJ, and 308-nm pulse from a XeCl laser produced a transient species showing a strong absorption at 377 nm, which appeared coincident with the pulse and disappeared within 10 ms (Figure 3). On the basis of the low-temperature spectrum, we assigned the transient product to triplet α-**2a**. Support is lent to this assignment by trapping experiments using oxygen and 1,4-cyclohexadiene (vide infra).

The oscillogram trace of the transient absorption due to α-**2a** monitored at 377 nm is shown in the inset of Figure 3. The decay was found to be second-order, and $2k_d/\epsilon l$ was determined to be 7.4×10^4 s^{-1}, where $2k_d$ is the dimerization rate constant, ϵ the extinction coefficient, and *l* the optical path. The rough lifetime of α-**2a** is estimated in the form of half-life, $t_{1/2}$, to be 70 μs (Table 4).

When flash photolysis measurements were carried out on a nondegassed benzene solution of α-**1a**, the half-life of triplet α-**2a** was decreased, and a broad absorption band with a maximum at 440 nm appeared. The rate of increase in the absorbance at 440 nm was practically the same as that of the decay of the peak at 377 nm, showing that triplet α-**2a** was quenched with oxygen to form a new species. Analysis of the spent solution showed the presence of a large amount of di(1-naphthyl)ketone. It is well documented that diarylcarbenes with a triplet ground state are readily trapped by oxygen to give the corresponding diaryl ketone oxides, which are observed directly by either matrix-isolation techniques[18] or flash photolysis.[19] These carbonyl oxides usually show a rather broad absorption band centered around 390−450 nm. Thus, the observation can be interpreted as indicating that the triplet α-**2a** is trapped with oxygen to generate carbonyl oxide (α-**9a**) (Scheme 5). This confirms that the transient absorption quenched by oxygen is due to ^{3}α-**2a**. The decay of the carbonyl oxide was found to be first-order, and the decay rate was estimated to be 2.1×10^2 s^{-1}.

The kinetics of carbonyl oxide formation was studied by monitoring their formation for several concentrations of oxygen in acetonitrile. The build-up of the signal followed pseudo-first-order kinetics (k_{obs}), and the bimolecular rate constant, k_{O_2}, was determined from plots of k_{obs} growth vs [O$_2$] according to eq 1, where *k* represents the rate of decay of α-**2a** in the absence of oxygen and k_{O_2} is the rate constant for the reaction of the carbene with oxygen

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

A plot of k_{obs} against [O$_2$] in the range of 0.5−9 mM is linear, and the slope of this plot yields the absolute rate constant for reaction of α-**2a** with O$_2$, $k_{O_2} = 1.7 \times 10^9$ M^{-1} s^{-1} (Scheme 5, Table 5).

On the other hand, when a solution of α-**1a** in a degassed benzene solution containing 1,4-cyclohexadiene (CHD) was excited, a new species was formed, showing an absorption with λ_{max} = 432 nm as the 377-nm signals of α-**2a** decayed. Figure 4 shows the transient spectrum obtained 50 and 100 μs after the photoexcitation, and the inset shows the decay of α-**2a** at 377 nm and the formation of the new species at 432 nm, indicating that the decay of α-**2a** is kinetically correlated with the growth of the new species. It is now well documented that triplet arylcarbenes generated in good hydrogen donor solvents undergo H abstraction, leading to the corresponding radical.[1] The excellent hydrogen donor properties of 1,4-cyclohexadiene have been recognized in its reaction with triplet benzophenone.[20] Moreover, the diarylmethyl radicals are usually red-shifted with respect to the corresponding triplet carbenes.[1,21] All of the

TABLE 4: Kinetic and Spectroscopic Data for Di(naphthyl)carbene (2)

carbenes	D^a (cm^{-1})	E^a	(E/D)	λ_{max} (nm) 2-MTHF^a	λ_{max} (nm) PhH^b	T_d^c (K)	$t_{1/2}^b$ (μs)	$2k/\epsilon l^b$ (s^{-1})
α-**2a**	0.3232	0.0105	(0.0325)	330, 350, 362, 375, 412	377	100	70	7.4×10^4
β-**2a**	0.3832 0.3971	0.0182 0.0158	(0.0475) (0.0398)	325, 360, 398	390	80	(0.83)^d	(1.2×10^6)^e

[a] In 2-MTHF at 77 K. [b] In degassed PhH at 20 °C. [c] Temperature at which UV absorption bands of ^{3}DNC start to disappear in 2-MTHF matrixes. [d] Lifetime. [e] Unimolecular decay.

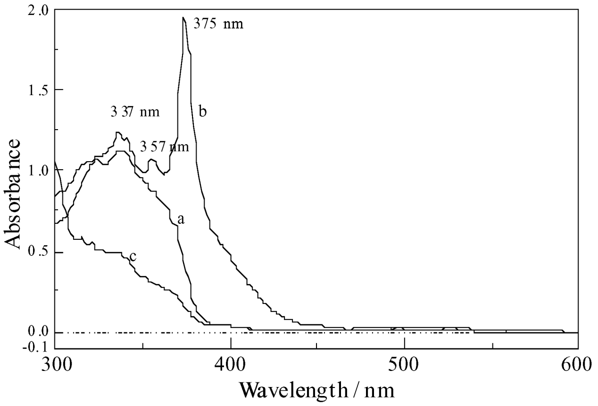


Figure 2. Absorption spectrum obtained by photolysis of di(1-naphthyl)diazomethane (α-**1a**) in 2-methyltetrahydrofuran (2-MTHF) at 77 K. (a) UV−vis spectrum of α-**1a** in 2-MTHF at 77 K. (b) Same sample after 5-min irradiation ($\lambda > 300$ nm). (c) Same sample after warming to room temperature and recooling to 77 K.

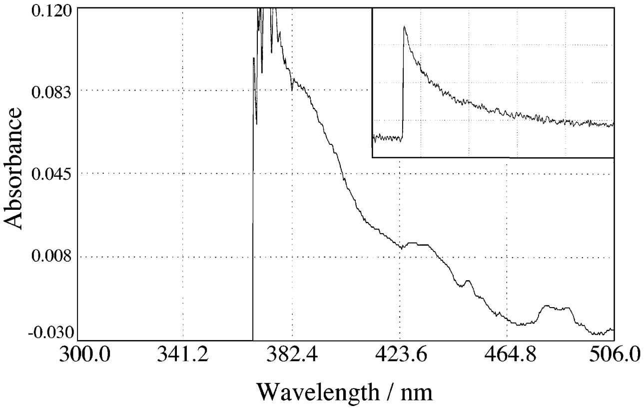


Figure 3. Absorption spectra of the transient products formed by pulsing α-**1a** in degassed benzene with a 308 nm excimer laser recorded after 50 μs. Inset shows oscillogram traces monitored at 377 nm.

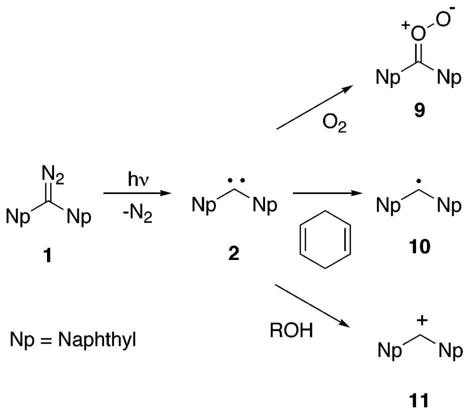
preceding facts suggest that the new signal was attributable to the di(1-naphthyl)methyl radical (α-**10a**) formed as a result of the H abstraction of α-**2a** from the diene (Scheme 5). The apparent build-up rate constant (k_{obs}) of the radical is again expressed in eq 2, where k_{CHD} is a quenching rate constant of α-**2a** by the diene

$$k_{obs} = k + k_{CHD}[CHD] \qquad (2)$$

A plot of the observed pseudo-first-order rate constant of the formation of the radical against [CHD] in the range 0.05−1.0 M is linear, and the slope of this plot yields $k_{CHD} = 1.24 \times 10^4$ M^{-1} s^{-1} (Scheme 5, Table 5).

LFP of α-**1a** in degassed benzene containing methanol formed the same transient species that we had detected in the absence of alcohol. The lifetime of this species decreased as the concentration of alcohol in the solution was increased. The transient decayed following a first-order rate law with a rate constant (k_{obs}) that depends linearly on the alcohol concentration. A plot of k_{obs} against the concentration of methanol is linear, and the slope gives a bimolecular rate constant [k_q(MeOH)] of 3.5×10^5 M^{-1} s^{-1} for the reaction of the carbene (α-**2a**) with the alcohols (Table 5).

SCHEME 5



It is widely believed that singlet carbenes readily undergo insertion into O−H bonds. The reaction of diphenylcarbene (DPC) with methanol has been exhaustively studied by spectroscopic techniques.[1,14] Upon addition of alcohols in the LFP experiments, quenching of both singlet DPC ($k_S = 10^{10}$ M^{-1} s^{-1}) and triplet DPC $k_t \approx 10^7$ M^{-1} s^{-1})[1,22,23] was observed. Preequilibrium and surface-crossing mechanisms have been proposed for the relatively slow reaction of triplet diarylcarbenes with O−H bonds[24] (vide infra).

The LFP of α-**1a** either in acetonitrile-water (1:1) or in 2,2,2-trifluoroethanol-acetonitrile(1.6:1), on the other hand, gave rise to a new transient product showing the maximum at 630 nm (Figure 5). The decay of the transient species was found to be first-order, and the rate constant decreased as solvent nucleophilicity was decreased. It has been demonstrated that most diarylcarbenes undergo protonation in hydroxylic solvents to generate the corresponding diarylcarbocation, which are detected by LFP in the less nucleophilic solvents.[14,25] Therefore, the species showing the maxima at 630 nm was assigned to the di(1-naphthyl)carbocation (α-**11a**).[26] Identification as a cation follows arguments similar to those employed previously, namely the observation of exponential decay kinetics with quenching by a good nucleophile, azide, and no effect of oxygen. In addition, essentially the same transient product was observed in the LFP of di(1-naphthyl)methyl bromide in the same solvent (Scheme 5, Table 5).

Similar measurements were done for the β-isomer of carbene (β-**2a**), and values are summarized in Tables 4 and 5.

As will be discussed in the next section in more detail, β-**2a** was found to be significantly more reactive than α-**2a**, and the rate constant with very efficient reagents, e.g., O_2, was too fast to be determined by our systems.

TABLE 5: Kinetic and Spectroscopic Data for Reactions Involving Di(naphthyl)carbene (2)

		ketone oxide (**10**)[a]			radical (**11**)[b]			cation (**12**)[c]	
carbenes	k_{O_2}[a] (M^{-1} s^{-1})	λ (nm)	k (s^{-1})	k_{CHD}[b] (M^{-1} s^{-1})	λ (nm)	$2k/\epsilon l$ (s^{-1})	k_q (MeOH) (M^{-1} s^{-1})	λ (nm)	k (s^{-1})
α-**2a**	1.7×10^9	440	2.1×10^2	1.2×10^4	432	7.9×10^4	3.1×10^5	630	9.8×10^4 (6.6×10^6)[e]
β-**2a**	$>10^{10}$	425	2.0×10^4[d]	5.0×10^6	406	6.6×10^3	$>10^{10}$	580	(too fast)[e]

[a] In MeCN. [b] In degassed PhH. [c] In CF_3CH_2OH-MeCN (1.6:1). [d] Second-order decay in $2k/\epsilon l$. [e] In MeCN−H_2O (1:1).

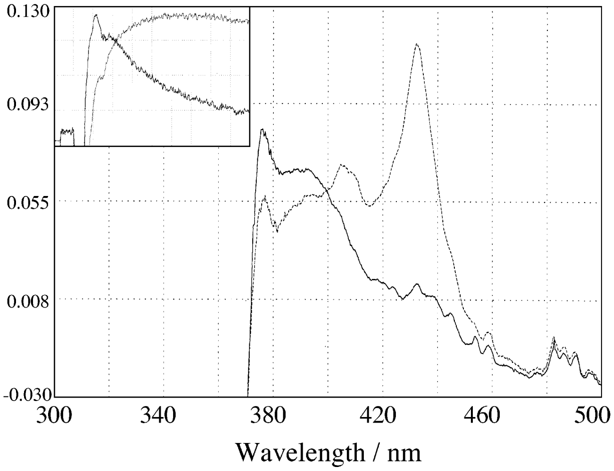


Figure 4. Absorption spectra of the transient products formed during the irradiation of α-**1a** in degassed benzene containing 1,4-cyclohexadiene, recorded after (a) 50 μs and (b) 100 μs. Inset is oscillogram traces monitored at 377 and 432 nm.

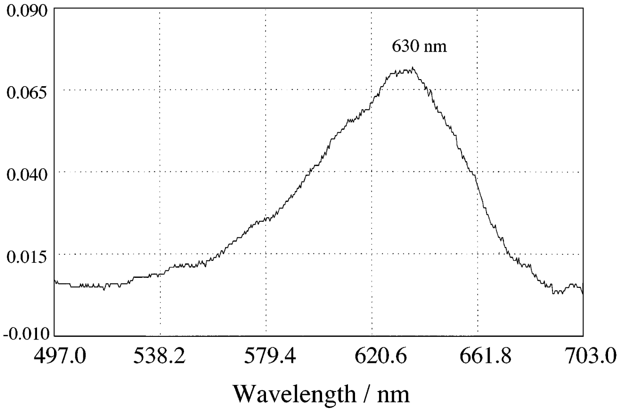


Figure 5. Absorption spectra of the transient products formed during irradiation of α-**1a** in trifluoroethanol−MeCN (1.6:1) recorded after 10 μs.

c. Reactivity Difference between α- and β-DNC. A comparison of the data available on the product distributions in the reaction of α-**2a** and β-**2a** with the substrates shows some interesting differences in the reactivity, which can be explained mostly in terms of steric effects. Thus, in the reaction with efficient trapping reagents for singlet carbene, i.e., alcohols, no significant changes in product distributions were observed. Similarly, essentially the same product ratios were obtained in the reaction with α-methylstyrene, which is believed to react efficiently with the triplet states.

A dramatic difference in the reaction patterns is observed in the reaction with benzene. The formation of a formal insertion product (β-**6a**) into the C−H bonds of benzene in the reaction of β-**2a** is rather unusual because carbenes react with benzene by the initial attack on the π electrons on the aromatic ring in the singlet state to result in the formation of a norcaradiene and/or cycloheptatriene.[15] It may be then that **6a** is produced from the triplet state of **2** by an abstraction-recombination mechanism. To check this possibility, the irradiation of β-**1a** was carried out in a 1:1 mixture of C_6H_6 and C_6D_6, and the deuterium distributions in the product β-**6a** were determined by mass spectrometric analysis, which clearly showed that direct insertion products, i.e., β-**6a**-h_6 and -d_6, were formed almost exclusively (>99%), whereas the yield of scrambled products detected was less than 1%. The kinetic isotope effect (k_H/k_D) for the formation of **6a** was determined to be 0.99 from the product distributions (Scheme 4, Table 3). The results indicate that the C−H insertion product is formed almost exclusively from the singlet carbene β-**2a**.

Olah and co-workers have studied the mechanism of the C−H insertion of methylene (CH_2:) into benzene using kinetic hydrogen isotope effects as well as theoretical calculations and concluded that, while the insertion of the triplet methylene ($k_H/k_D = 12.1 \pm 1.0$) proceeds through a stepwise mechanism which may involve an intermediate, the mechanism for the singlet methylene ($k_H/k_D = 1.34 \pm 0.04$) seems to follow a concerted pathway, although initial formation of π-complexes cannot be excluded.[27] Direct attack of the singlet β-**2a** at the C−H bond of benzene is, however, rather unlikely in the light of the decreased electrophilicity as well as increased steric crowdedness. Presumably, as the carbenic center of β-**2a** approaches the π-electrons on the aromatic ring so as to form norcaradiene, it will experience severe steric hindrance due to the two aromatic rings, and the carbene will thus be forced to follow the pathway to generate a π-complex or a neutral zwitterionic species that will ultimately cascade to **6**. Alternatively, a norcaradiene may be formed and readily undergo rearrangement to give the insertion product owing to steric repulsion either as it is formed or during the workup. However, all attempts to detect the norcaradiene have been unsuccessful to date (vide infra).

The almost complete absence of the solvent adduct (e.g., α-**6a**) in the reaction of α-**2a** is in sharp contrast with that observed for β-**2a** and can be also explained in terms of the steric effect. The approach of the singlet carbene to the π-electrons on the benzene ring so as to a species leading to **6** should experience a much more severe steric hindrance in this case, and carbenes are hence forced to decay by several competing reaction pathways available to form rather complex product mixtures.

Inspection of the kinetic data (Table 5) leads to an analogous but more quantitative conclusion. Unimolecular vs bimolecular decay kinetics for β- and α-isomers in benzene, for instance, must reflect the difference in the reaction patterns between the two carbenes. Unimolecular decay of triplet β-**2a** can be interpreted as indicating that the triplet states are trapped by the solvent benzene. However, the product studies clearly suggest that the singlet state is responsible for the final product (**6**). The fact that the optical density of ^{3}β-**2a** was not decreased significantly compared to that of ^{3}α-**2a** under identical conditions, i.e., in degassed benzene at 20 °C, indicates that not all of **6** is produced from the nascent singlet. Thus, monitored $^3\beta$-**2a** also leads to the final product either by the preequilibrium mechanism, where triplet to singlet intersystem crossing occurs prior to reaction of the singlet carbene, or by surface crossing, where the potential energy surfaces of the singlet and triplet carbene reaction cross after they have begun to interact with the substrate (benzene).

The second-order decay kinetics of $^3\alpha$-**2a**, on the other hand, suggests that the triplet states decay by undergoing dimerization. The product analysis of the mixtures obtained in conventional light irradiation, however, did not completely support the spectroscopic observation, although the absence of the solvent adducts implies that α-**2a** is unreactive toward benzene. It is probable that intense light from the laser can generate a high concentration of α-**2a**. Under such conditions, the carbenes become the most efficient trapping reagent for themselves. Alternatively, the expected dimer, i.e., tetra(1-naphthyl)ethylene, is simply unstable under photolysis conditions.

Comparison of the lifetime in the form of the half-life of the two carbenes in benzene showed that α-**2a** is some 2 orders of magnitude longer-lived than the *β*-isomer. Because the decay processes are not the same for both carbenes, the stability cannot be discussed simply based on the kinetic data. Nevertheless, the stability order is consistent with that of steric congestion.

The kinetic data obtained in typical triplet quenchers should be more informative in order to estimate differences in the reactivity between the two carbenes in the triplet states. Thus, the quenching rate constant of $^3\beta$-**2a** with oxygen is too high to be monitored and significantly higher than that of $^3\alpha$-**2a**. The rate constants for hydrogen abstraction from CHD observed with $^3\beta$-**2a** are 2 orders of magnitude greater than that of $^3\alpha$-**2a**. These results suggest that $^3\alpha$-**2a** is considerably less reactive than $^3\beta$-**2a** and can be interpreted in terms of better steric shielding in $^3\alpha$-**2a** than in the corresponding *β*-isomer.

The stability of intermediates formed from DNC, e.g., **9**−**11**, is also to be noted. Although these intermediates should not be influenced by the same electronic factors, rough trends in stability are more or less similar to that of the precursor DNC. This can be again interpreted as indicating that steric factors play more important roles than electronic effects in the reaction of these polynuclear aromatic systems.

B. Effects of Methyl Groups on the Reactivities of Di(naphthyl)carbenes. The above study reveals that triplet di(naphthyl)carbenes are significantly longer-lived than triplet diphenylcarbene, confirming the expectation from the structural studies based on the ESR measurement in low-temperature matrixes. Thus, triplet di(α-naphthyl)carbene is more than 2 orders of magnitude longer-lived than triplet diphenylcarbene ($t_{1/2} \approx 2\ \mu$s). This suggests that di(naphthyl)carbene can serve as a more promising prototype diarylcarbene for persistent triplet carbene than DPC. Naturally, one would expect that the lifetime of di(naphthyl)carbene could be elongated by introducing appropriate substituents around the carbene centers. Because carbenes react even with very poor sources of electrons, such as C−H bonds, the *tert*-butyl group, which has been successfully employed as one of the most effective protecting groups for many reactive centers in organic chemistry, was found to be ineffective in protecting triplet carbenes.[12f,i] In this respect, methyl groups can serve as an exceptionally good protecting group for triplet carbene in the case of diphenylcarbene; didurylcarbene is shown to have a half-life of 410 ms in solution at room temperature, some **5** orders of magnitude longer-lived than diphenylcarbene under the same conditions.[12d,i] Therefore, we prepared a series of di(naphthyl)diazomethanes (α-**1b**−**d** and *β*-**1b**, Scheme 1) bearing methyl groups on aromatic rings and investigated the effect of methyl groups on the reactivities of di(naphthyl)carbenes (**2**) photolytically generated from them.

a. Product Analysis Studies. Irradiation of methylated **1** in 2-propanol also gave the propyl ether **3** along with dinaphthylmethane **4**. The product distributions are rather sensitive to the substituents, especially in the case of α-isomers. Thus, as methyl groups are introduced at the ortho positions of the carbene center, the product from the triplet carbenes, i.e., **4**, increases rather significantly; in the case of di[1-(2,4-dimethyl)-naphthyl]carbene (α-**2d**), the **3**/**4** ratio is close to 1 (Scheme 2, Table 1).

More dramatic changes in the product distributions are observed in the reactions with other substrates (Tables 2 and 3). Thus, the photolysis of α-**1c** and **d** in α-methylstyrene and benzene resulted in a large amount of intractable oil, almost no meaningful products obtained in the reaction with the “parent” α-**2** being isolated. A similar but less significant change of the product distributions upon the methyl substitution is also observed in the reaction of the *β*-isomers. Thus, in the reaction of *β*-**2b**, significant product formation was not discontinued until the least reactive substrate, i.e., benzene, was used, while essentially the same products were produced in other reagents although the ratio was slightly changed, probably reflecting increased steric factors.

These results are consistent with those observed for analogous reactions with polymethylated diphenylcarbenes[12d,i] and are interpreted similarly in terms of the steric effect on the reaction. Thus, as methyl groups are introduced at the ortho position of di(1-naphthyl)carbene, which is already sterically congested, the carbenic center should be protected more strictly. As a result, the reactions from the singlet side, which are generally more sensitive to the steric factors,[15,28] become energetically less favored, and the singlet state is forced to undergo intersystem crossing to the triplet. The triplet states can react with typical triplet quenchers, e.g., hydrogen donors, but become less reactive toward less efficient triplet quenchers. Steric hindrance is less prominent in the reaction of *β*-**2** because essentially the same products are obtained in the reaction of *β*-**2b** even with less reactive substrates, i.e., styrene, as in the reaction of *β*-**2a**. This confirms the importance of the role of peri-H in the α-isomer.

It should be noted here that, in the case of *o*-methylated diphenylcarbenes, triplet carbenes decay mainly by undergoing intramolecular hydrogen abstraction from the ortho-methyl groups to produce eventually benzocyclobutene derivatives, as more methyl groups are introduced.[12d,i,29]All attempts to isolate expected naphthocyclobutenes were unsuccessful, although the intramolecular H abstraction process is actually observed spectroscopically (vide infra).

b. Spectroscopic Studies. Irradiation of methylated diazomethanes (**1**) in 2-MTHF glass at 77 K gave persistent ESR signals with large *D* values characteristic of triplet DNC. The zero-field splitting parameters, *D* and *E*, are reported in Table 6. Inspection of the data in the table indicates that *E*/*D* values steadily decrease as one introduces more methyl groups on the aromatic rings, suggesting that the carbene becomes less bent due to increased steric interaction between the methyl groups.

Optical spectroscopy in the frozen medium gave essentially the same spectral changes observed with the “parent” carbenes. Irradiation of methylated **1** in 2-MTHF glass at 77 K gave absorption bands ascribable to the corresponding triplet carbenes (**2**). Although the absorption maxima are slightly shifted, the overall shapes of the bands are similar. However, careful monitoring of the spectral changes as a function of the

TABLE 6: Kinetic and Spectroscopic Data for Methylated Di(naphthyl)carbene (2)

carbenes	D^a (cm^{-1})	E^a (cm^{-1})	(E/D)	$\lambda_{\max}$ (nm) MTHF^a	$\lambda_{\max}$ (nm) PhH^b	$T_d{}^c$ (K)	$t_{1/2}{}^b$ (μs)	$2k/\epsilon l^b$ (s^{-1})	$k_i{}^{b,d}$ (s^{-1})
α-**2b**	0.3197	0.0108	(0.0337)	380	380	90	28	1.1×10^5	
α-**2c**	0.3256	0.0089	(0.0273)	379 (435)^e	379 (436)^e	110	1400	1.0×10^4	
α-**2d**	0.2490	0.0053	(0.0215)	384 (454)^e	382 (451)^e	105	100 000		10.5
α-**2d**-d_6	0.3265	0.0099	(0.0303)	383	375		265 000	3.6×10^3	<1
β-**2b**	0.3466	0.0173	(0.0500)	375, 398	375	95	58	5.2×10^4	
	0.3484	0.0141	(0.0405)						

[a] In 2-MTHF at 77 K. [b] In degassed PhH at 20 °C. [c] Temperature at which UV absorption bands of ^{3}DNC start to disappear in 2-MTHF matrixes. [d] Intramolecluar H abstraction rate constant. [e] Absorption maximum for *o*-quinodimethane.

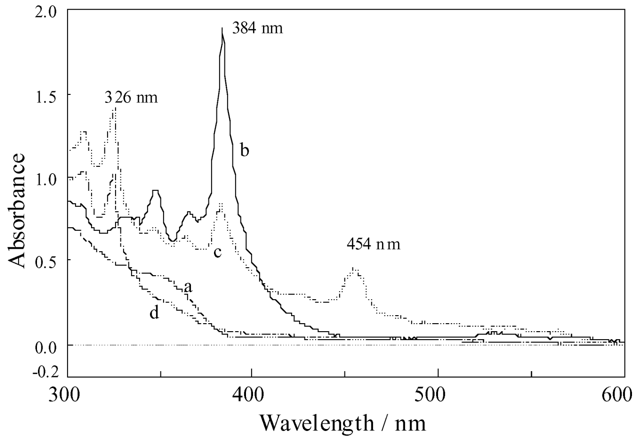
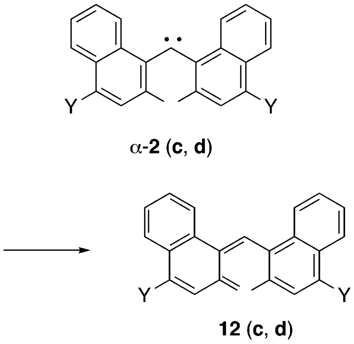


Figure 6. Absorption spectrum obtained by photolysis of di[1-(2,4-dimethyl)naphthyl]diazomethane (α-**1d**) in 2-MTHF at 77 K. (a) UV−vis spectrum of α-**1d** in 2-MTHF at 77 K. (b) Same sample after 5-min irradiation. (c) Same sample after thawing to 110 K. (d) Same sample thawing to room temperature and recooling to 77 K.

temperature showed that the thermal stability and the decay pathway are sensitive to the substitution patterns. First, in the case of α-DNC, the temperature at which the carbene bands start to decay (T_d) increases by about 10 K upon ortho-methyl substitution (compare T_d between α-**2a** and α-**2c** in Table 6). This is obviously due to increased stability by the protecting *o*-methyl groups. On the other hand, this temperature drops to 90 K by *para*-methyl groups (see the T_d difference between α-**2a** and α-**2b** in Table 6). This is interpreted in terms of the electronic effect. It is generally accepted that electron-donating substituents stabilize the electrophilic singlet carbene more than they do the radical-like triplet, thus making ΔG_{ST} smaller.[2] The triplet states then would decay more easily by way of the upper-lying singlet state.

Second, upon thawing the matrix, a new broad absorption appeared around 440−450 nm as carbene absorption bands decreased in the case of the ^{3}α-**2** bearing the methyl group at the ortho position (Figure 6), while all other carbene bands decayed monotonically without showing secondary transient absorption bands. The secondary formed species showed appreciable thermal stability and decayed gradually upon thawing the matrix to room temperature. What is this intermediate? In the analogous spectral monitoring of the decay process of ortho-polymethylated diphenylcarbenes as a function of temperature, we also observed similar broad, secondary transient bands in visible regions, which we assigned as *o*-quinodimethanes generated by the 1,4 H shift from the *o*-methyl to the carbenic center based on the spectral profiles, i.e., broad absorption bands centered around 350−450 nm and appreciable thermal stability.[30] These features are also present in the spectrum obtained in the photolysis of α-**1c** and **d**. In these circumstances, the secondary transient is attributable to *o*-quinodimethanes (**12**) (Scheme 6).

SCHEME 6



α-**2** (**c**, **d**)

12 (**c**, **d**)

The LFP of the methylated **1** in a degassed benzene solution produced similar transient absorption bands with those observed for “parent” **1**, although their decay modes and kinetics are sensitive to the substitution patterns (Tables 6 and 7). Comparison of the data in the tables confirms expectations for the role of steric effects in stabilizing the triplet carbene center more quantitatively. Judging from the half-life in benzene, ^{3}α-**2** becomes destabilized slightly by the *para*-methyl groups ($t_{1/2}$ decreases slightly on going from α-**2a** to α-**2b**) but stabilized significantly by the ortho-methyl groups ($t_{1/2}$ increases significantly on going from α-**2a** to α-**2c**). This can be interpreted in terms of electronic effects, which cause the upper-lying singlet state to be close to the triplet ground states, and steric effects, which stabilize the triplet states kinetically. The introduction of two more methyl groups at the para positions (α-**2c**) resulted in an increase in the lifetime by some 2 orders of magnitude, indicating that para methyl groups in this case stabilize the triplet carbene. The reason for this rather puzzling effect is not clear at present. Benzene is known to be one of the least reactive solvents toward triplet carbenes. Therefore, carbenes usually decay either by undergoing dimerization or by abstracting hydrogen from the *o*-methyl groups. Product analysis showed that large amounts of complex mixtures were formed, little simple carbene dimers being virtually isolated.

It is to be noted that trityl radicals undergo either methyl−para or para−para coupling depending on substitution patterns and that this coupling reactions are suppressed by para substituents.[31] Similar decaying pathways are suggested in the reaction of persistent triplet diarylcarbenes.[12h] Thus, as the carbene center is more sterically congested, simple dimerization at the carbene site must suffer from severe steric repulsion, and the carbene is hence forced to react at the sites where a spin can be delocalized.[3] Increased stability in α-**2d** compared to α-**2c** can then be ascribable to the suppression of this coupling pathway.

However, the reactivities of α-**2** toward typical triplet quenchers, i.e., oxygen and CHD, are also decreased in this order. For example, k_{CHD} decreases by some 2 orders of magnitude on going from α-**2c** to α-**2d**. This suggests that the increased stability of α-**2d** in benzene cannot be simply

TABLE 7: Kinetic and Spectroscopic Data for Reactions Involving Methylated Di(naphthyl)carbene (2)

		ketone oxide (**10**)^a			radical (**11**)^b			cation (**12**)^c	
carbenes	$k_{O_2}{}^a$ (M^{-1} s^{-1})	λ (nm)	k (s^{-1})	$k_{CHD}{}^b$ (M^{-1} s^{-1})	λ (nm)	$2k/\epsilon l$ (s^{-1})	k_{MeOH}/K (M^{-1} s^{-1})	λ (nm)	k (s^{-1})
α-**2b**	1.9×10^9	430	5.6×10^4	6.6×10^4	422	3.6×10^3	$\sim 10^6$	630	6.5×10^5
α-**2c**	6.5×10^8	430	1.8×10^2	2.8×10^3	435	2.2×10^4	1.1×10^4	630	9.2×10^6
α-**2d**	1.0×10^8	415	1.4×10^2	3.6×10	460-470	9.5	12×10^3	645	2.2×10^3
β-**2a**	1.7×10^9	420		1.8×10^5	426	4.1×10^2		610	3.1×10^6

^{a} In MeCN. ^{b} In degassed PhH. ^{c} In CF_3CH_2OH-MeCN (1.6:1).

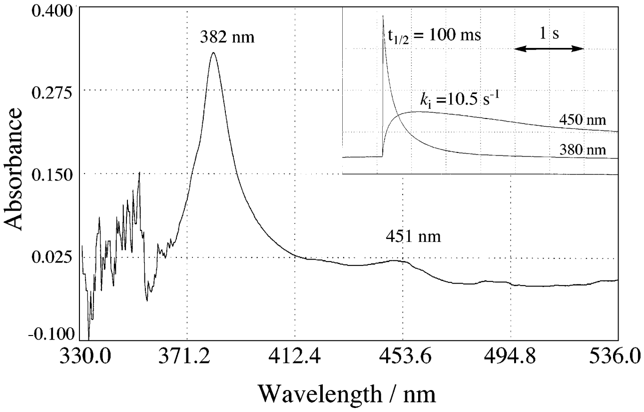


Figure 7. Absorption spectra of the transient products formed during the irradiation of α-**1d** in degassed benzene recorded 50 μs after photoexcitation. Insets are oscillogram traces monitored at 380 and 450 nm.

ascribable to the decrease in the reaction sites in its dimerization reaction but to the inherent decrease of the reactivities of the carbene center. It should be noted here that LFP of α-**1d** in degassed benzene gave a secondary transient species exhibiting a broad band around 451 nm as the 382-nm signal of ^{3}α-**2d** decayed (Figure 7). On the basis of the low-temperature spectrum, the secondary formed transient species is assigned to *o*-quinodimethane (**12d**). It should be noted that the decay of ^{3}α-**2d** was found not to fit the first-order kinetic and to be slower by half than the growth of **12d**. This suggests that not all of ^{3}α-**2d** decays by intramolecular H abstracting. Similar spectroscopic observations were noted in an LFP study of polymethylated diphenylcarbenes, e.g., didurylcarbene, which decays mainly by abstracting hydrogen from the *o*-methyl group to generate *o*-quinodimethane.[12f] The similarity of the absorption band and stability supports the assignment.

In marked contrast, 2,2′-dimethylated carbene (α-**2c**) decays rather monotonically without showing any sign of formation of *o*-quinodimethane (**12c**). These observations suggest that, although both α-**2c** and α-**2d** carry methyl groups at the ortho positions, ^{3}α-**2d** can decay by abstracting hydrogen from the *o*-methyl groups, whereas this process is not involved in the decay pathway for ^{3}α-**2c**.

A simple explanation for this difference is to invoke the distance between the carbene center and hydrogen on the *o*-methyl group. It is well-known that, in 1,2-disubstituted benzene derivatives, the introduction of substituents in the 3-position exerts a very large effect on the rate of appropriate reactions, which are considered in light of the importance of bond bending; the 3-substituents “buttress” the 2-substituents.[33,34] This is a steric effect exerted on a functional group by a more distant substituent through another immediately adjoining substituent. Therefore, 4-substituents are usually expected to exert little steric effect, especially without 3-substituents. However, recent re-estimation of the buttressing effects in methyl-substituted benzoic acid derivatives on the basis of the gas-phase acidities of the acids and the basicities of their methyl esters combined with heat formation by using the principle of isodesmic reaction has revealed that this effect is not zero even in 2,5-dimethyl derivative, suggesting that the interactions between more distant groups cannot be neglected.[35] This effect, if any, should be more significant for the 4-methyl group of naphthalene derivatives than for that in benzenes due to the presence of *peri*-hydrogen in the former case. In this light, the *o*-methyl groups in α-**2d** are brought closer to the carbenic center than those in α-**2c**. Therefore, α-**2d** can decay by abstracting hydrogen from the *o*-methyl group to generate *o*-quinodimethane and, since the carbene center in α-**2d** is more tightly blocked by the *o*-methyl group, it reacts with typical triplet quenchers less efficiently. The fact that α-**2c** decayed without showing any sign of formation of *o*-quinodimethane **12c** but generated **12c** in a low-temperature matrix upon thawing the matrix also suggests that the *o*-methyl groups in α-**2c** are less close to the carbenic center than those in α-**2d**.

Rather significant decrease in the reactivity toward methanol on going from α-**2a** to α-**2d** (Tables 5 and 7) can be interpreted in terms of the change in a singlet−triplet energy gap. Thus, as more methyl groups are introduced at position 2 of α-DNC, the bond angle is increased (as indicated in an decrease in *E*/*D* values), and triplet state is more stabilized with respect to the singlet (vide supra). Similar decrease in the rate as a function of methyl groups is also observed in the reaction of triplet DPC with methanol.[4c]

Similar effects of the methyl groups are also observed for the kinetics of the β-isomer of the carbene. Thus, on going from β-**2a** to β-**2b**, the lifetime increased by 2 orders of magnitude, and k_{CHD} decreased by 1 order of magnitude. The kinetic data for β-**2b** and α-**2c**, both having protecting *o*-methyl groups, should be compared here. Thus, the significantly shorter lifetime in benzene and the larger reactivities toward triplet quenchers of β-**2b** as opposed to α-**2c** again suggest the important steric role of *peri*-hydrogen in the reaction of DNCs.

c. Deuterated Tetramethyldi(1-naphthyl)carbenes (α-2d-*d*$_6$)). Deuterium Isotope Effects. The above study reveals that DNCs are effectively stabilized by methyl groups, especially when they are introduced near the carbene center. These ortho effects are shown to be strengthened even by the distant para methyl groups, and the *o*-methyl groups are more tightly fixed near the carbene center. However, the carbene center comes to be quenched more easily by the *o*-methyl groups in this case, and the lifetime might then not be increased as could have been expected. One of the best ways to hinder this process and to realize more persistent carbene is to replace the hydrogens at the *o*-methyl groups with deuterium. Thus, we prepared di[1-(2-trideuteriomethyl-4-methyl)naphthyl]diazomethane (α-**1d**-*d*$_6$) bearing fully deuterated *o*-methyl groups and studied the kinetic deuterium isotope effects (KDIEs) on the intramolecular H transfer reactions.

Irradiation of α-**1d**-*d*$_6$ in 2-MTHF glass at 77 K gave essentially the same transient absorption bands with those observed in the photolysis of the protio analogue (α-**1d**) ascribable to the triplet carbene (α-**2d**-d_6). A significant difference was seen in the decay profile upon thawing the matrixes. Thus, the bands ascribable to α-**2d**-d_6 decayed monotonically without showing any sign of formation of secondary transient species, i.e., *o*-quinodimethane (**12**). This suggests that there should be rather large KDIEs.

The LFP of α-**1d**-d_6 in degassed benzene also resulted in essentially the same transient absorption bands that were observed for the protio analogue (α-**1d**). Thus, a transient showing a strong absorption at 375 nm due to deuterated triplet carbene (α-**2d**-d_6) appeared coincident with the XeCl pulse.

However, the transient absorption disappeared monotonically in this case. The decay of $^3\alpha$-**2d**-d_6 followed second-order kinetics, and the lifetime of $^3\alpha$-**2d**-d_6 in the form of half-life was estimated to be 265 ms, which is some 3 times greater than that of the protio analogue. No new absorption band ascribable to *o*-quinodimethane was detected to the limit of our LFP time scale and detection. This is partly because the intramolecular H migration pathway is not the exclusive pathway for the decay of the protio analogue ($^3\alpha$-**2d**) (vide supra). Therefore, we could not determine k_i for D transfer in $^3\alpha$-**2d**-d_6, and we could only estimate the highest limit for k_i as <1 s^{-1}. The KDIE on the intramolecular H transfer reaction was then roughly estimated to be $\sim$10 (Table 6). This value is to be compared with 4.8 determined for the similar reaction in triplet decamethyldiphenylcarbene under identical conditions.[12f]

C. Di(naphthyl)carbene to Diphenylcarbene: A Comparison. The present investigation provides some insights into the effect of the benzo-annelation on the reactivity of diarylcarbene. Thus, it is quite important to compare the reactivity difference between ^{3}DNC and ^{3}DPC.

The reactivity of carbenes should be examined in terms of the singlet−triplet energy gap (ΔG_{ST}). The factors which influence ΔG_{ST} can be analyzed in terms of electronic and steric effects. It is generally accepted that the triplet state has a σ^1p^1 configuration, whereas σ^2 is thought to be the lowest energy configuration for the singlet. The magnitude of ΔG_{ST} is then roughly equal to electron−electron repulsion terms, caused by confining two electrons to one orbital, minus the energy required to promote an electron from the σ- to the *p*-nonbonding orbital. If carbene substituents have a *p* or π^* orbital that interacts with the 2*p* orbital of the carbene, the separation of the 2*p* and σ (σp^n) orbitals will decrease. This will result in a larger ΔG_{ST} than that of an unperturbed, prototype carbene. If carbene substituents have a doubly occupied orbital that will interact with the carbene 2*p* orbital, the 2*p*-σ gap becomes smaller, thus making ΔG_{ST} smaller.[2] The steric effect, on the other hand, influences the carbene carbon bond angle. The maximum value of ΔG_{ST} occurs when the two carbenic orbitals become degenerate, as they would be for linear methylene. Bending methylene removes the orbital degeneracy and reduces ΔG_{ST}. Thus, as the carbene-carbon bond angle is further contracted, the σ-orbital picks up more *s*-character and consequently becomes even lower in energy. The smaller the bond angle, the more energy it takes to promote an electron from the σ- to the *p*-orbital, and the smaller ΔG_{ST} becomes.[3,4]

One difference between DPC and DNC is the relative energies of the occupied and unoccupied aromatic orbitals that mix with the carbene *p* orbital. In the case of DNC, more than that of DPC, the energy of the singlet is predicted to become lower than that of the triplet by this mixing. This is more significantly so for α-DNC than for the β-isomer, since the coefficient of the occupied π-orbital is greater at the α- than at the β-position.

On the other hand, the *E*/*D* values decrease in the order of ^{3}DPC, $^3\beta$-DNC, and $^3\alpha$-DNC, suggesting that the carbene bond angle increases in that order. Therefore, the electronic and steric factors exert their influence in opposite directions. It is not possible to estimate these two counteracting factors quantitatively; hence, this will be examined rather qualitatively based on experimental observations.

A comparison of the reactivity of ^{3}DPC with that of $^3\beta$-DNC, a sterically less hindered isomer of DNC, will provide an insight into the effect of the extension of the π-system. Two important features, which suggest decreased ΔG_{ST} in DNC, are noted in the reaction of $^3\beta$-DNC with alcohol and benzene forming the singlet product as opposed to that of ^{3}DPC. First, $^3\beta$-DNC reacts considerably faster with methanol than does ^{3}DPC. Similar enhancement on the reactivity toward methanol has been reported for triplet (2-naphthyl)phenylcarbene as opposed to ^{3}DPC.[8] The reaction of the triplet carbenes with the O−H bonds of alcohols is explained either by preequilibrium[24] or by surface-crossing mechanisms.[23] In the preequilibrium mechanism, triplet to singlet interconversion occurs prior to O−H insertion of the singlet carbene, whereas, in the surface-crossing mechanism, triplet states can react with alcohols, with surface crossing occurring after the carbene has begun to interact with the O−H bond. In either of the two mechanisms, the decrease in ΔG_{ST} should result in the increase in the bimolecular rate constants for the reaction of triplet carbene with methanol. Second, the reaction of $^3\beta$-DNC with benzene producing formal C−H insertion product (**6**) is not the usual reaction for diarylcarbenes. DPC, for instance, reacts with the precursor diazo function to form diphenylketazine in benzene.[15] This is interpreted as indicating that DPC has little reactivity toward benzene in either of the multiplicities and that the attack on the terminal nitrogen of the diazo functional group, presumably in its singlet state, thus comes to be the only available major pathway.

These contrasting reactivity patterns are also interpretable in terms of the difference in ΔG_{ST}. Thus, $^3\beta$-DNC can react with benzene through the low-lying singlet state, which is thermally easily accessible. Alternatively and energetically more favorably, $^3\beta$-DNC starts to interact with benzene, and the surface of the triplet reaction crosses with the singlet surface at the lower energy region; this is because, in the preequilibrium mechanism, surface crossing occurs near the energy minimum of ^{3}DNC and, hence, requires more energy than anywhere else on the singlet reaction surface. For ^{3}DPC, on the other hand, the energy required to lead to the final product should not be small enough in order to allow it to react with benzene within the lifetime, most probably because of the larger ΔG_{ST}.

The reaction of β-DNC with α-methylstyrene is shown to occur in its triplet state almost exclusively. This may sound somewhat conflicting with the argument mentioned above. If the reaction in the singlet side were easily accessible for $^3\beta$-DNC, then it would have reacted through the singlet energy surface. Presumably, the reaction of $^3\beta$-DNC with α-methylstyrene should proceed very smoothly with the low energy barrier to form a 1,3-biradical intermediate stabilized by aryl delocalization, and the spin inversion can take place afterward of the process. Therefore, surface crossing is not required at the rate-determining step. On the other hand, the concerted approach of the singlet DNC to the double bond of α-methylstyrene will suffer from steric hindrance due to two canted naphthyl groups and, therefore, becomes kinetically less favorable in this case.

The reactivity of α-DNC is too complicated to be compared with that of DPC. Electronic effects stabilizing the singlet state and steric factors favoring the triplet exert a larger influence for α-DNC than for β-DNC, and it is not easy to estimate its ΔG_{ST}. It is likely that the reactivity of α-DNC is dictated largely by kinetic factors. In this respect, it is interesting to examine α-DNC as a prototype for persistent triplet carbene as opposed to DPC.

"Parent" ^{3}α-DNC has a lifetime of 70 μs, which is some 30 times larger than that of "parent" ^{3}DPC. This is obviously due to the effect of peri-H, which not only stabilizes the triplet state with respect to the singlet but also acts as a kinetic protector toward the carbene center. ESR data suggest that ^{3}α-DNC is significantly less bent than ^{3}DPC. Despite the increased stability of the unsubstituted ^{3}α-DNC compared to ^{3}DPC, the effect of the methyl groups as a kinetic protector on the stability of the triplet state is, disappointingly, rather small. Because the basic skeletons between DNC and DPC are not exactly the same, one cannot find an exact counterpart between the two. However, one can compare the reactivity of ^{3}α-**2d** with that of triplet dimesitylcarbene (DMC) assuming that the peri-hydrogens at the 8 positions are acting as one of the hydrogens of the *o*-methyl groups in ^{3}DMC. Actually, this comparison is fairly valid because the *peri*-Hs are expected to be fixed tightly in the same plane with the carbene carbon, whereas hydrogens on the *o*-methyl groups are rather flexible, even though the van der Waals radius of methyl groups may be estimated to be larger than that of the net C_8 substituent. The E/D values clearly support the idea. This value for ^{3}α-**2d** ($E/D = 0.0215$) is significantly smaller than that for ^{3}DMC ($E/D = 0.033$), suggesting that ^{3}α-**2d** is less bent than ^{3}DMC. Nevertheless, the lifetime of ^{3}α-**2d** ($t_{1/2} = 100$ ms) is not larger than that of ^{3}DMC ($t_{1/2} = 160$ ms).

The reason for this rather puzzling difference is not clear at present. One possible explanation is the larger spin delocalization in ^{3}α-DNC than in ^{3}DPC, as evidenced by decreasing D values on going from ^{3}α-DNC to ^{3}DPC. It has been shown that the variation of D is due to the variation in the π-electron spin density at the divalent carbon, since the dominant interaction is the one-center terms. Consequently, the ratio of that spin density to D should be approximately constant. Thus, the π-electron spin in ^{3}α-DNC systems is largely delocalized into aromatic rings. Therefore, if the carbene center becomes less reactive due to steric hindrance, then the carbene can more easily react at the aromatic rings where spin can be delocalized.

In this respect, it is very interesting to compare the products obtained in the reaction in less reactive solvents, e.g., benzene, between the two carbene systems. In the case of sterically congested ^{3}DPC, tetra(aryl)ethylenes probably formed as a result of ^{3}DPC coupling are the most frequently observed product in benzene.[12f,29] This is explained by assuming that the hindered triplet diphenylcarbene concentration builds up due to decreased reactivities by kinetic protectors, especially in unreactive solvent, and the most reactive counterparts under these conditions must hence be the triplet carbene themselves. Taking into account the increased lifetime, similar reactions are likely decay pathways for sterically more shielded ^{3}DNC. Nevertheless, we isolated almost no simple carbene dimers, i.e., tetra(naphthyl)-ethylene, but mostly intractable oil, from which no assignable products were isolated.

Trityl radicals are known to undergo either methyl−para or para−para couplings depending on the substituent patterns. Thus, it is likely that ^{3}DNCs also undergo similar coupling. The complexity of the products observed in the reaction of DNC must be partly due to the complexity associated with the coupling reactions. The carbene−para coupling of triplet carbenes, for instance, unlike that of trityls, does not lead to a final stable product and gives rise to an intermediate open-shell molecules whose subsequent reactions will be complicated by possible ambient reactivity.

In this light, α-DNC cannot be employed as a promising prototype carbene for constructing persistent triplet carbenes unless substituents can be introduced not only around the carbene centers but also at all possible positions where a spin can be delocalized. This may require tedious synthetic procedures.

Experimental Section

General Methods. IR spectra were measured on a JASCO A-100 recording spectrometer and the mass spectra were recorded on JEOL MS route JMS-600W.

^{1}H and ^{13}C NMR spectra were determined either JEOL JNM-EX 270 or JNM-500 spectrometers. UV−vis spectra were recorded on a JASCO CT-560 Grating Monochromator.

Thin-layer chromatography was done on Merck Kieselgel 60 PF 254. Column chromatography was carried out on silica gel (ICN for dry column chromatography). HPLC and GPC were undertaken with a JASCO 800 chromatograph equipped with a UVIDEC-100-II UV−vis detector using a Fine pack C18-T5 column (4.6 × 25 cm) and a Shodex GPC H-2001 (20 mm × 50 cm) column, respectively, and GLC was carried out with a Yanagimoto G-80 gas chromatograph using an OV-17 on Diasolid L (5.0 mm × 50 cm) column.

Unless otherwise noted, all the reagents employed in this study are commercial products and used after standard purification.

Materials. (a) Preparation of Di(1-naphthyl)diazomethanes (α-1). All α-**1** used in this study were prepared by coupling of naphthylmagnesium bromide with naphthonitrile, followed by hydrazonation of the resulting ketimine and oxidation of the hydrazone with nickel peroxide according to the procedure by Reimlinger and Franzen.[36] Thus, to a solution of Grignard reagent prepared from Mg (1.5 g, 60 mmol) and 1-bromonaphthalene (12.42 g, 60 mmol) in anhydrous Et_2O (20 mL), was added a solution of naphthonitrile (6.13 g, 40 mmol) in anhydrous Et_2O (20 mL), dropwise under vigorous stirring, and the mixture was refluxed overnight. A saturated NH_4Cl aq solution (50 mL) was added carefully to the reaction mixture cooled by ice-bath under vigorous stirring and the mixture was filtered. The filtrate was extracted with Et_2O, and the organic layer was dried and evaporated to leave crude product, which was purified by silica gel column chromatography eluted with pet-ether and Et_2O (2:1) to afford **di(1-naphthyl)ketimine** in 74% yield as viscous oil.

A solution of the ketimine (200 mg, 0.71 mmol) and hydrazine hydrochloride (378 mg, 3.6 mmol) in absolute EtOH (5 mL) was placed in a round-bottom flask, and the whole system was deaerated by repeated cycles of evacuation and purge with nitrogen. Anhydrous N_2H_4 (1.12 g, 36 mmol) was added to the mixture and the resulting solution was refluxed until a TLC monitoring showed that most of the ketimine was consumed. After cooling, the solvent was evaporated, and the mixture was added to Et_2O. The ethereal layer was washed with H_2O, dried (Na_2SO_4), and evaporated to give **di(1-naphthyl)-ketone hydrazone** in 97% yield as yellowish solid (mp 143−147 °C), which was used without further purification for the next step.

To a cooled solution of the hydrazone (600 mg, 2.02 mmol) in dry CH_2Cl_2 (3 mL) was added NiO_2 (1.1 g, 12.1 mmol) at 0 °C under vigorous stirring in the dark over a period of 1 h.

After filtration, the solvent was removed under reduced pressure to afford crude diazo compound, which was chromatographed on a deactivated alumina eluted with CH_2Cl_2-*n*-hexane (1:1) at −10 °C. The diazomethane coming through immediately from the column was fairly pure but was further purified by repeated chromatography on a gel permeation column with $CHCl_3$ to afford pure **di(1-naphthyl)diazomethane** (α-**1a**) as a red solid in 60% yield: mp 72 °C (dec); ^1H NMR ($CDCl_3$) δ 7.35−7.52 (m, 8 H), 7.78−7.92 (m, 6 H); IR (KBr) 2050 cm^{-1}.

(b) Di[1-(4-methyl)naphthyl]diazomethane (α-1b). A mixture of 1-bromo-4-methylnaphthalene (4.5 g, 20.4 mmol) and CuCN (2.0 g, 22.4 mmol) in anhydrous DMF (30 mol) was refluxed overnight. The mixture was poured into ice−water (400 mL), and the resulting precipitate was filtered. The solid was transferred to a beaker containing ethylenediamine (115 mL) and H_2O (30 mL), and the precipitate formed was extracted with CH_2Cl_2. The organic layer was washed with a 10% NaCN solution and water, dried and evaporated. The crude product was Kugelrohr-distilled under pressure at 130 °C/3.0 mmHg to give 1-cyano-4-methylnaphthalene in 87% yield as a white solid: mp 49.8−51.1 °C; ^1H NMR ($CDCl_3$) δ 2.78 (s, 3 H), 7.38 (d, J = 7.58 Hz, 1 H), 7.62−7.73 (m, 2 H), 7.82 (d, J = 7.58 Hz, 1 H), 8.07−8.10 (m, 1 H), 8.24−8.28 (m, 1 H). **Di[1-(4-methyl)naphthyl]ketimine** was obtained by the reaction of 4-methylnaphthylmagnesium bromide, prepared from the corresponding bromide (4.0 g, 18.1 mmol) and Mg (440 mg, 18.1 mmol) in Et_2O (20 mL), with 1-cyano-4-methylnaphthalene (3.0 g, 18.1 mmol) in anhydrous Et_2O (15 mL), followed by column chromatography (SiO_2, Et_2O−*n*-hexane 1:1) as a yellow gummy solid in 30% yield: ^1H NMR ($CDCl_3$) δ 2.73 (s, 6 H), 7.24 (d, J = 7.58 Hz, 2 H), 7.34 (d, J = 7.58 Hz, 2 H), 7.45−7.58 (m, 4 H), 8.07 (d, J = 7.92 Hz, 2 H), 8.42 (bs, 2 H). The ketimine (50 mg, 0.16 mmol) was treated with $N_2H_4{\cdot}HCl$ (85 mg, 0.91 mmol) and anhydrous N_2H_4 (0.26 mL, 81 mmol) in absolute EtOH (10 mL) to afford **di[1-(4-methyl)naphthyl]ketone hydrazone** in 96% yield as a yellow gummy solid: ^1H NMR ($CDCl_3$) δ 2.62 (s, 3 H), 2.72 (s, 3 H), 5.49 (bs, 2 H), 7.28 (d, J = 7.26 Hz, 2 H), 7.35 (d, J = 7.26 Hz, 2 H), 7.44−7.57 (m, 4 H), 7.88 (d, J = 7.92 Hz, 1 H), 7.98−8.02 (m, 1 H), 8.07 (d, J = 8.25 Hz, 1 H). The hydrazone (50 mg, 0.15 mmol) was oxidized with NiO_2 (80 mg, 0.88 mmol) in CH_2Cl_2 (2 mL) and the reaction was worked up as described above to give pure **di[1-(4-methyl)naphthyl]diazomethane** (α-**1b**) as a red crystal in 52% yield: mp 71.0−72.1 °C (dec); ^1H NMR ($CDCl_3$) δ 2.72 (s, 6 H), 7.43 (dd, J = 7.92, 7.26 Hz, 2 H) 7.55 (dd, J = 6.93, 8.57 Hz, 2 H), 7.95 (d, J = 8.58 Hz, 2 H); 8.07 (d, J = 8.25 Hz, 2 H); IR (KBr) 2050 cm^{-1}.

(c) Di[1-(2-methyl)naphthyl]diazomethane (α-1c). Di[1-(2-methyl)naphthyl]ketimine was obtained by the reaction of 2-methylnaphthylmagnesium bromide, prepared from the corresponding bromide (3.45 g, 15.6 mL) and Mg (378 mg, 15.6 mmol) in anhydrous Et_2O (15 mL), with 1-cyano-2-methylnaphthalene (2.0 g, 12.0 mmol) in anhydrous Et_2O (10 mL), followed by column chromatography (SiO_2, pet. ether−Et_2O 2:1) as a brownish gummy solid in 17.8% yield: ^1H NMR ($CDCl_3$) δ 2.12 (s, 3 H), 2.40 (s, 3 H), 6.91−7.19 (m, 6 H), 7.46−7.93 (m, 5 H), 8.85 (s, 1 H). The ketimine (56 mg, 0.163 mmol) was treated with $N_2H_4{\cdot}HCl$ (85.7 mg, 0.816 mmol) and anhydrous N_2H_4 (261 mg, 8.51 mmol) in absolute EtOH (3 mL) to give **di[1-(2-methyl)naphthyl]ketone hydrazone** in 93% yield as a yellowish semisolid: ^1H NMR ($CDCl_3$) δ 2.36 (s, 3 H), 2.64 (s, 3 H), 5.51 (bs, 2 H), 7.34−8.35 (m, 12 H). The hydrazone (148.6 mg, 0.46 mmol) was oxidized with NiO_2 (240 mg, 2.6 mmol) in anhydrous CH_2Cl_2 (1 mL) to form **di[1-(2-methyl)naphthyl]diazomethane** (α-**1c**) in 17.8% yield as a red viscous liquid after aluminum column chromatography followed by GPC purification: red liquid; ^1H NMR ($CDCl_3$) δ 2.48 (s, 3 H), 2.55 (s, 3 H), 6.84−6.87 (m, 1 H), 7.19−7.95 (m, 11 H); IR (KBr) 2040 cm^{-1}.

(d) Di[1-(2,4-dimethyl)naphthyl]diazomethane (α-1d). 1,3-Dimethylnaphthalene was transformed to the desired diazomethane by way of the following compounds as described above. **1-Bromo-2,4-dimethylnaphthalene:** 92%; yellow liquid; ^1H NMR ($CDCl_3$) δ 2.57 (s, 3 H), 2.61 (s, 3 H), 7.19 (s, 1 H), 7.46−7.59 (m, 2 H), 7.92 (d, J = 7.26 Hz, 1 H), 8.23 (d, J = 8.25 Hz, 1 H). **1-Cyano-2,4-dimethylnaphthalene:** 90%; white solid; mp 109.7−111.2 °C; ^1H NMR ($CDCl_3$) δ 2.67 (s, 3 H), 2.68 (s, 3 H), 7.21 (s, 1 H), 7.52−7.66 (m, 2 H), 7.97 (d, J = 8.91 Hz, 1 H), 8.17 (d, J = 8.25 Hz, 1 H). **Di[1-(2,4-dimethyl)-naphthyl]ketimine:** 16.7%; yellowish semisolid; ^1H NMR ($CDCl_3$) δ 2.13 (s, 6 H), 2.68 (s, 6 H), 7.10 (s, 2 H), 7.44−7.51 (m, 4 H), 8.02 (d, J = 8.25 Hz, 2 H), 8.30 (bs, 2 H). **Di[1-(2,4-dimethyl)naphthyl]ketone Hydrazone:** 15.3%; yellow gummy solid; ^1H NMR ($CDCl_3$) δ 2.11 (s, 3 H), 2.14 (s, 3 H), 2.61 (s, 3 H), 2.65 (s, 3 H), 7.07 (s, 1 H), 7.15 (s, 1 H), 7.40−7.48 (m, 4 H), 7.91−7.98 (m, 2 H), 8.28 (bs, 1 H), 8.52 (bs, 1 H). **Di[1-(2,4-dimethyl)naphthyl]diazomethane** (α-**1d**): 46.3%; reddish orange solid; mp 130.0−131.2 °C (dec); ^1H NMR ($CDCl_3$) δ 2.32 (s, 6 H), 2.69 (s, 6 H), 7.23 (s, 2 H), 7.35 (dd, J = 8.42, 6.93 Hz, 2 H), 7.44 (dd, J = 7.92, 6.93 Hz, 2 H), 7.93 (d, J = 8.25 Hz, 2 H), 7.98 (d, J = 8.24 Hz, 2 H); IR (KBr) 2051 cm^{-1}.

(e) Di[1-(2-trideuteriomethyl-4-methyl)naphthyl]diazomethane (α-1d-d_6). 3-Bromo-1-methylnaphthalene (8.4 g, 36 mmol) was treated with CuCN (1.5 g, 17 mmol) in DMF (30 mL). The reaction was worked up as usual to provide **1-methyl-3-naphthonitrile** in 96% yield as a yellow solid: mp 57.2−59.8 °C; ^1H NMR ($CDCl_3$) δ 2.71 (s, 3 H), 7.44 (s, 1 H), 7.48−7.72 (m, 2 H), 7.89 (d, J = 8.58 Hz, 1 H), 8.03 (d, J = 8.58 Hz, 1 H), 8.10 (s, 1 H). The nitrile (6.1 g, 36 mmol) was hydrolyzed by refluxing it in H_2O (50 mL) and conc H_2SO_4 (40 mL) overnight. After usual workup, **1-methylnaphthoic acid** was obtained in 88% yield as a white solid: mp 197.6−199.1 °C; ^1H NMR ($CDCl_3$) δ 2.76 (s, 3 H), 7.55−7.69 (m, 2 H), 7.97 (s, 1 H), 7.99 (d, J = 8.57 Hz, 1 H), 8.05 (d, J = 8.25 Hz, 1 H), 8.58 (s, 1 H). **Methyl 1-methyl-3-naphthoate** was obtained by treating the acid with CH_2N_2 in 99% yield as a yellowish liquid: ^1H NMR ($CDCl_3$) δ 2.73 (s, 3 H), 4.03 (s, 3 H), 7.57−7.67 (m, 2 H), 7.91 (s, 1 H), 7.96 (d, J = 7.92 Hz, 1 H), 8.03 (d, J = 8.91 Hz, 1 H), 8.47 (s, 1H). To a stirred solution of the ester (2.75 g, 13.7 mmol) in anhydrous THF (30 mL) was added $LiAlD_4$ (Aldrich, 576 mg, 13.7 mmol) slowly at 0 °C. After usual workup, **3-[hydroxydi(deuterio)-methyl]-1-methylnaphthalene** was obtained as a viscous liquid in 98% yield: ^1H NMR ($CDCl_3$) δ 2.70 (s, 3 H), 3.48 (bs, 1 H), 7.34 (s, 1 H), 7.49−7.55 (m, 2 H), 7.67 (s, 1 H), 7.84 (d, J = 8.90 Hz, 1 H), 7.98 (d, J = 7.58 Hz, 1 H). A solution of the alcohol (2.5 g, 13.7 mmol) in dioxane (50 mL) was added PBr_3 (1.43 mL, 15 mmol) and the mixture was stirred for 2 h at room temperature. After usual workup, **3-[bromodi(deuterio)methyl]-1-methylnaphthalene** was obtained as a brownish solid in 94% yield: mp 48.1−51.7 °C; ^1H NMR ($CDCl_3$) δ 2.69 (s, 3 H), 7.34 (s, 1 H), 7.47−7.56 (m, 2 H), 7.70 (s, 1 H), 7.81 (d, J = 8.91 Hz, 1 H), 7.96 (d, J = 7.57 Hz, 1 H). The bromide was reduced with $LiAlD_4$ as described above to give **1-methyl-3-tri(deuterio)methylnaphthalene** in 93% yield as a colorless liquid: ^1H NMR ($CDCl_3$) δ 2.66 (s, 3 H), 7.16 (s, 1 H), 7.41−7.47 (m, 3 H), 7.92−7.95 (m, 1 H). The tri-

(deuterio)methylated naphthalene was transformed to the desired diazomethane by way of the following compounds as described above. **1-Bromo-2-tri(deuterio)methyl-4-methylnaphthalene:** 95%; yellow liquid; ^{1}H NMR (CDCl$_3$) δ 2.61 (s, 3 H), 7.19 (s, 1 H), 7.46−7.59 (m, 2 H), 7.92 (d, $J = 7.26$ Hz, 1 H), 8.23 (d, $J = 8.25$ Hz, 1 H). **2-Tri(deuterio)methyl-4-methyl-1-naphthonitrile:** 94% brownish solid; mp 110.1−111.4 °C; ^{1}H NMR (CDCl$_3$) δ 2.68 (s, 3 H), 7.21 (s, 1 H), 7.52−7.66 (m, 2 H), 7.97 (d, $J = 8.91$ Hz, 1 H), 8.17 (d, $J = 8.25$ Hz, 1 H). **Di[1-(2-trideuteriomethyl-4-methyl)naphthyl]ketimine:** 31%; yellowish semisolid; ^{1}H NMR (CDCl$_3$) δ 2.68 (s, 6 H), 7.10 (s, 2 H), 7.44−7.51 (m, 4 H), 8.02 (d, $J = 8.25$ Hz, 2 H), 8.30 (bs, 2 H). **Di[1-(2-trideuteriomethyl-4-methyl)naphthyl]ketone Hydrazone:** 18%; pale yellow semisolid; ^{1}H NMR (CDCl$_3$) δ 2.14 (s, 3 H), 2.61 (s, 3 H), 2.65 (s, 3 H), 7.07 (s, 1 H), 7.15 (s, 1 H), 7.40−7.48 (m, 4 H), 7.91−7.98 (m, 2 H), 8.28 (bs, 1 H), 8.52 (bs, 1H). **Di[1-(2-trideuteriomethyl-4-methyl)naphthyl]diazomethane (α-1d-*d*$_6$)**: 3%; orange liquid; ^{1}H NMR (CDCl$_3$) δ 2.69 (s, 6 H), 7.23 (s, 2 H), 7.35 (dd, $J = 8.42$, 6.93 Hz, 2 H), 7.44 (dd, $J = 7.92$, 6.93 Hz, 2 H), 7.93 (d, $J = 8.25$ Hz, 2 H), 7.98 (d, $J = 8.24$ Hz, 2 H); IR (KBr) 2050 cm^{-1}.

(f) Di(2-naphthyl)diazomethane (*β*-2a). A solution of di-(2-naphthyl)ketone (500 mg, 1.77 mmol), N$_2$H$_4$·HCl (931 mg, 8.86 mmol) and anhydrous N$_2$H$_4$ (2.8 mL, 88.6 mmol) in absolute EtOH (10 mL) was refluxed for 3 h. The reaction was worked up as usual, followed by preparative TLC to give **di-(2-naphthyl) ketone hydrazone** in 60% yield as a brownish solid: mp 138.0−141.2 °C; ^{1}H NMR (CDCl$_3$) δ 5.56 (s, 2 H), 7.36−7.45 (m, 2 H), 7.52−7.62 (m, 4 H), 7.78−7.96 (m, 6 H), 8.02−8.07 (m, 2 H). The hydrazone (130 mg, 0.44 mmol) was oxidized with NiO$_2$ (200 mg, 2.2 mmol) in anhydrous CH$_2$Cl$_2$ (10 mL). After usual workup, followed by GPC purification, **di(2-naphthyl)diazomethane (*β*-2a**) was obtained as a reddish purple solid in 80% yield: mp 125.8−127.3 °C (dec); ^{1}H NMR (CDCl$_3$) δ 7.45−7.50 (m, 6 H), 7.72−7.88 (m, 8 H); IR (KBr) 2016 cm^{-1}.

(g) Di[2-(1,4-dimethyl)naphthyl]diazomethane (α-2b). To a solution of 1,4-dimethylnaphthalene (3.04 g, 19.5 mmol) in CCl$_4$ (30 mL) was added a solution of Br$_2$ (3.12 g, 19.5 mmol) in CCl$_4$ (15 mL) under vigorous stirring slowly so that the temperature did not raise over 5 °C. After stirring overnight at room temperature, the mixture was washed with 10% NaOH−H$_2$O, and the organic layer was washed with H$_2$O, dried (Na$_2$SO$_4$) and evaporated to dryness to give a crude **2-bromo-1,4-dimethylnaphthalene** as yellowish oil which was used without further purification: ^{1}H NMR (CDCl$_3$) δ 2.62 (s, 3 H), 2.76 (s, 3 H), 7.47 (s, 1 H), 7.51−7.56 (m, 2 H), 7.93−7.96 (m, 1 H). To a solution of the bromide (2.3 g, 9.8 mmol) in ahydrous Et$_2$O (20 mL) added *n*-BuLi (1.71 M in *n*-hexane, 5.93 mL, 9.8 mmol) dropwise. After stirring for 1 h, anhydrous DMF (1 mL) was added under vigorous stirring and the mixture was stirred for 2 h. A saturated NH$_4$Cl aq solution was added to the reaction mixture and the mixture was extracted with Et$_2$O. The ethereal phase was washed with H$_2$O, dried (Na$_2$SO$_4$) and evaporated to dryness to give a crude **1,4-dimethyl-2-naphthaldehyde** as a yellowish liquid in 89% yield, which was used to the next step without further purification: ^{1}H NMR (CDCl$_3$) δ 2.67 (s, 3 H), 2.98 (s, 3 H), 7.46−7.68 (m, 2 H), 7.74 (s, 1 H), 8.02 (d, $J = 8.25$ Hz, 1 H), 8.23 (d, $J = 8.91$ Hz, 1 H), 10.62 (s, 1 H). To a solution of 2-(1,4-dimethylnaphthyl)lithium, prepared by treating the corresponding bromide (2.18 g, 9.28 mmol) with *n*-BuLi (1.65 M in *n*-hexane, 5.6 mL, 9.28 mmol) in absolute Et$_2$O (15 mL) was added a solution the aldehyde (1.6 g, 8.72 mmol) in anhydrous Et$_2$O (2 mL) and the mixture was refluxed for 2 h. After the usual workup, **di[2-(1,4-dimethyl)naphthyl]methanol** was obtained as a white crystal in 37% yield: mp 159.0−161.5 °C; ^{1}H NMR (CDCl$_3$) δ 2.11 (d, $J = 4.29$ Hz, 1 H), 2.62 (s, 12 H), 6.69 (d, $J = 4.29$ Hz), 7.40 (s, 2 H), 7.49−7.55 (m, 4 H), 7.98−8.02 (m, 2 H), 8.08−8.12 (m, 2 H). To a solution of the methanol (500 mg, 1.47 mmol) in acetone (20 mL) was added a mixture of CrO$_3$ (222 mg) and concentrated Na$_2$SO$_4$ (0.12 mL) in H$_2$O (1.44 mL) at room temperature under stirring. The reaction was worked up as usual to leave **di[2-(1,4-dimethyl)naphthyl]ketone** in 98% yield as a gummy solid, which was used to the next step without further purification: ^{1}H NMR (CDCl$_3$) δ 2.61 (s, 6 H), 2.75 (s, 6 H), 7.24 (s, 2 H), 7.62−7.64 (m, 4 H), 8.02−8.06 (m, 2 H), 8.20−8.24 (m, 2 H). The crude ketone (498 mg, 1.47 mmol) was refluxed with N$_2$H$_4$·HCl (500 mg, 4.76 mmol) and anhydrous N$_2$H$_4$ (5.0 mL, 158 mmol) in absolute EtOH (10 mL) for 2 days. After usual workup, the crude mixture was purified by preparative TLC eluted with *n*-hexane−Et$_2$O (2:1) to obtain **di[2-(1,4-dimethyl)naphthyl]ketone hydrazone** in 50% yield as a white gummy solid: ^{1}H NMR (CDCl$_3$) δ 2.56 (s, 3 H), 2.61 (s, 3 H), 2.68 (s, 3 H), 2.79 (s, 3 H), 5.53 (bs, 2 H), 6.99 (s, 1 H), 7.15 (s, 1 H), 7.49−7.55 (m, 2 H), 7.57−7.63 (m, 2 H), 7.91−7.98 (m, 1 H), 8.00−8.05 (m, 1 H), 8.10−8.19 (m, 2 H). The hydrazone (100 mg, 0.28 mmol) was oxidized with NiO$_2$ (200 mg, 2.2 mmol) in anhydrous CH$_2$Cl$_2$ (5 mL) at 0 °C. After usual workup, the crude product was purified by column chromatography (Al$_2$O$_3$, CH$_2$Cl$_2$-*n*-hexane 1:15), followed by GPC yield **di[2-(1,4-dimethyl)naphthyl]diazomethane (*β*-2c**) in 61% yield as a reddish purple solid: mp 126.8−127.7 °C (dec); ^{1}H NMR (CDCl$_3$) δ 2.55 (s, 6 H), 2.60 (s, 6 H), 7.06 (s, 2 H), 7.53−7.59 (m, 4 H), 7.99 (d, $J = 6.92$ Hz, 2 H), 8.09 (d, $J = 6.93$ Hz, 2 H); IR (KBr) 2032 cm^{-1}.

Irradiation for Product Identification. In a typical run, a solution of the diazo compounds (1, ca. 10 mg) in solvent was placed in a Pyrex tube and irradiated with a high-pressure, 300-W mercury lamp at room temperature 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/or GPC and identified by NMR and MS. In this way, the following products were isolated and characterized.

Products in Irradiation in ^{i}PrOH. (a) Di(1-naphthyl)-methyl Isopropyl Ether (α-3a). ^{1}H NMR (CDCl$_3$): δ 1.35 (d, $J = 6.27$ Hz, 6 H), 3.93 (sept, $J = 6.29$ Hz, 1 H), 7.05 (s, 1 H), 7.38−7.49 (m, 8 H), 7.80 (d, $J = 7.92$ Hz, 2 H), 7.87−7.90 (m, 2 H), 8.17−8.21 (m, 2 H). HRMS Calcd for C$_{24}$H$_{22}$O: 326.1671. Found: 326.1630.

(b) Di[1-(4-methyl)naphthyl]methyl Isopropyl Ether (α-3b). ^{1}H NMR (CDCl$_3$): δ 1.34 (d, $J = 6.27$ Hz, 6 H), 2.68 (s, 6 H), 3.91 (sept, $J = 6.27$ Hz, 1 H), 7.01 (s, 1 H), 7.24 (d, $J = 7.26$ Hz, 2 H), 7.35 (d, $J = 7.24$ Hz, 2 H), 7.44−7.54 (m, 4 H), 8.04 (d, $J = 7.92$ Hz, 2 H), 8.21 (d, $J = 7.92$ Hz, 2 H). HRMS Calcd for C$_{26}$H$_{26}$O: 354.1984. Found: 354.1978.

(c) Di[1-(2-methyl)naphthyl]methyl Isopropyl Ether (α-3c). ^{1}H NMR (CDCl$_3$): δ 1.48 (d, $J = 6.27$ Hz, 6 H), 2.48 (s, 3 H), 2.61 (s, 3 H), 3.68 (sept, $J = 6.27$ Hz, 1 H), 7.05 (s, 1 H), 7.33−7.45 (m, 6 H), 7.68−7.87 (m, 6 H). HRMS Calcd for C$_{26}$H$_{26}$O: 354.1984. Found: 354.1718.

(d) Di[1-(2,4-dimethyl)naphthyhl]methyl Isopropyl Ether (α-3d). ^{1}H NMR (CDCl$_3$): δ 1.21 (d, $J = 6.27$ Hz, 6 H), 2.15 (s, 6 H), 2.65 (s, 6 H), 3.72 (sept, $J = 6.27$ Hz, 1 H), 7.05 (s, 2 H), 7.12 (s, 1 H), 7.37−7.45 (m, 4 H), 7.98 (d, $J = 8.24$ Hz, 2 H), 8.59 (d, $J = 8.24$ Hz, 2 H). HRMS Calcd for C$_{28}$H$_{30}$O: 382.2295. Found: 382.2365.

(e) Di(2-naphthyl)methyl Isopropyl Ether (*β*-3a). ^{1}H NMR ($CDCl_3$): δ 1.28 (d, $J = 6.27$ Hz, 6 H), 3.77 (sept, $J = 6.27$ Hz, 1 H), 5.81 (s, 1 H), 7.43−7.51 (m, 6 H), 7.77−7.83 (m, 6 H), 7.87 (s, 2 H).

(f) Di[2-(1,4-dimethyl)naphthyl]methyl Isopropyl Ether (*β*-3b). ^{1}H NMR ($CDCl_3$): δ 1.29 (d, $J = 5.93$ Hz, 6 H), 2.62 (s, 3 H), 3.75 (sept. $J = 5.93$ Hz, 1 H), 6.39 (s, 1 H), 7.43 (s, 2 H), 7.47−7.54 (m, 2 H), 7.96−7.99 (m, 2 H), 8.08−8.11 (m, 2 H).

Products in Irradiation with α-Methylstyrene. (a) 1,1-Di-(1-naphthyl)-2-phenyl-2-methylcyclopropane (α-5a). ^{1}H NMR ($CDCl_3$): δ 1.47 (s, 3 H), 2.25 (bs, 1 H), 2.43 (bs, 1 H), 6.89−7.24 (m, 2 H), 7.25−7.59 (m, 12 H), 7.65 (d, $J = 8.25$ Hz, 1 H), 7.77 (d, $J = 7.92$ Hz, 1 H), 8.15 (d, $J = 6.92$ Hz, 1 H), 8.78 (d, $J = 8.25$ Hz, 1 H), 8.95 (d, $J = 7.92$ Hz, 1 H). HRMS Calcd for $C_{30}H_{24}$: 384.1878. Found: 384.1817.

(b) 1,1-Di[1-(4-methyl)naphthyl]-2-phenyl-2-methylcyclopropane (α-5b). ^{1}H NMR ($CDCl_3$): δ 1.45 (s, 3 H), 2.25 (bs, 1 H), 2.42 (s, 3 H), 2.58 (s, 3 H), 2.70 (bs, 1 H), 6.73 (d, $J = 7.59$ Hz, 1 H), 6.95 (d, $J = 8.25$ Hz, 1 H), 7.30−7.63 (m, 10 H), 7.85 (d, $J = 7.91$ Hz, 1 H), 7.91 (d, $J = 8.25$ Hz, 1 H), 8.01 (d, $J = 7.92$ Hz, 1 H), 8.80 (d, $J = 7.92$ Hz, 1 H), 8.99 (d, $J = 7.59$ Hz, 1 H). HRMS Calcd for $C_{32}H_{28}$: 412.2191. Found: 412. 2192.

(c) 1,1-Di(2-naphthyl)-2-phenyl-2-methylcyclopropane (*β*-5a). ^{1}H NMR ($CDCl_3$): δ 1.77 (d, $J = 5.28$ Hz, 1 H), 2.39 (d, $J = 4.95$ Hz, 1 H), 7.02−7.33 (m, 6 H), 7.39−7.67 (m, 6 H), 8.01 (s, 1 H).

(d) 1,1-Di[2-(1,4-dimethyl)naphthyl]-2-phenyl-2-methylcyclopropane (*β*-5b). ^{1}H NMR ($CDCl_3$): δ 1.44 (bs, 3 H), 2.15 (bs, 3 H), 2.35 (s, 3 H), 2.47 (s, 1 H), 2.62 (s, 1 H), 2.72 (s, 3 H), 2.85 (bs, 3 H), 7.18−7.45 (m, 9 H), 7.77−7.98 (m, 4 H).

Products in Irradiation in Benzene. (a) 1,1,2,2-Tetra(1-naphthyl)ethane (α-7a). ^{1}H NMR ($CDCl_3$): δ 6.99−7.05 (m, 4 H), 7.15 (s, 2 H), 7.26−7.45 (m, 12 H), 7.72 (d, $J = 6.60$ Hz, 4 H), 7.82−7.87 (m, 8 H).

(b) Di(1-naphthyl)ketazne (α-8a). ^{1}H NMR ($CDCl_3$): δ 6.75−6.81 (m, 2 H), 7.09−7.17 (m, 4 H), 7.21−7.39 (m, 4 H), 7.45−7.51 (m, 2 H), 7.56−7.71 (m, 10 H), 7.92 (d, $J = 7.92$ Hz, 2 H), 8.02−8.06 (m, 4 H).

(c) Di(2-naphthyl)phenylmethane (*β*-6a). ^{1}H NMR ($CDCl_3$): δ 5.83 (s, 1 H), 7.44−7.51 (m, 7 H), 7.55 (d, $J = 8.25$ Hz, 2 H), 7.75−7.85 (m, 8 H), 7.93 (s, 2 H). HRMS Calcd for $C_{27}H_{20}$: 344.4605. Found: 344.4603.

(d) Di(2-naphthyl)ketazine (*β*-7a). ^{1}H NMR ($CDCl_3$): δ 7.31−7.43 (m, 2 H), 7.46−7.67 (m, 4 H), 7.73−7.83 (m, 5 H), 7.88−8.00 (m, 3 H).

Irradiation for Analytical Purposes. All irradiations outlined in Tables 1−3 were carried out in a Pyrex tube of 5.0 mL capacity. To avoid ambiguity in relative yields due to oxidation, the solution was degassed by subjecting the sample to a minimum of three freeze−degas−thaw cycles at a pressure near 10^{-5} Torr before irradiation, and the tube was flame-sealed under reduced pressure. Irradiation was carried out with filtered light from the mercury lamp through a Pyrex filter and generally continued until all the diazo compound was consumed. Product identities were established either by GC or by GC−MS comparisons with "authentic"samples separated as described above, and the product distributions were conveniently determined by GC and/or NMR using an internal standard.

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 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.

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-μs 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, 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 MOS linear image sensor (512 photodiodes used). Timing of the excitation pulse, the probe beam, and the detection system was acheived through an Iwatsu Model DS-8631 digital synchro scope which was interfaced to a 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 a NEC CRT N5913U monitor.

A sample was placed in a long-necked Pyrex tube which had 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 which was placed in the sample chamber of the flash spectrometer. A cell holder block of the sample chamber was equipped with a thermostat and allowed to come to thermal equilibrium. The concentration of the sample was adjusted so that it absorbed a significant portion of the excitation light.

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References and Notes

(1) Platz, M. S.; Maloney, V. M. In *Kinetics and Spectroscopy of Carbenes and Biradicals*; Platz, M. S. Ed.; Plenum Press: New York, 1990; pp 239−352.

(2) Schuster, G. B. *Adv. Phys. Org. Chem*. **1986**, *22*, 311; Rak, S. F.; Lapin, S. C.; Falvey, D. E.; Schuster, G. B. *J. Am. Chem. Soc*. **1987**, *109*, 5003.

(3) (a)Geise, C. M.; Hadad, C. M. *J. Org. Chem*. **2000**, *65*, 8348. (b) Sugiyama, M. H.; Celebi, S.; Platz, M. S. *J. Am. Chem. Soc*. **1992**, *114*, 966.

(4) (a) Hoffmann, R.; Zeiss, G. D.; Van Dine, G. W. *J. Am. Chem. Soc*. **1968**, *90*, 1485. (b) Metcalfe, J.; Halevi, E. A. *J. Chem. Soc., Perkin Trans. 2*, **1977**, 634. (c)Alt, R.; Gould, I. R.; Staab, H. A.; Turro. N. J. *J. Am. Chem. Soc*. **1986**, *108*, 6911.

(5) (a) Bailey, R. J.; Card, P. J.; Shecter, H. *J. Am. Chem. Soc*. **1983**, *105*, 6096. (b) Card, P. J.; Friedli, F. E.; Shecter, H. *J. Am. Chem. Soc*. **1983**, *105*, 6104. (c) Engler, T. A.; Shecter, H. *Tetrahedron Lett*. **1982**, *23*, 2715.

(6) For EPR and IR/UV−vis studies at low temperatures, see (a) Trozzolo, A. M.; Wasserman, E.; Yager, W. A. *J. Am. Chem. Soc*. **1965**, *87*, 129. (b) West, P. R.; Mooring, A. M.; McMahon, R. J.; Chapman, O. L. *J. Org. Chem*. **1986**, *51*, 1316. (c) Albrecht S. W.; McMahon, R. J. *J. Am. Chem. Soc*. **1993**, *115*, 855.

(7) For laser flash photolysis studies at room temperatures, see (a) Barcus, R. C.; Wright, B. B.; Platz, M. S.; Scaiano, J. C. *Tetrahedron Lett*. **1983**, *24*, 3955. (b) Hadel, L. M.; Platz, M. S.; Scaiano, J. C. *Chem. Phys. Lett*. **1983**, *97*, 446. (c) Horn, K.; Chateauneuf, J. E. *Tetrahedron* **1985**, *41*, 1465. (d) Barcus, R. C.; Hadel, L. M.; Johnston, L. J.; Platz, M. S.; Savino, T. G.; Scaiano, J. C. *J. Am. Chem. Soc*. **1986**, *108*, 3928. (e) Griffin, G. W.; Horn, K. A. *J. Am. Chem. Soc*. **1987**, *109*, 4919. (f) Clark, K. B.; Bhattacharyya, K.; Das, P. K.; Scaiano, J. C.; Schaap, A. P. *J. Org. Chem*. **1992**, *57*, 3706.

(8) For studies of other naphthylcarbenes, see: (a) Fujiwara, Y.; Sasaki, M.; Tanimoto, Y.; Itoh, M. *Chem. Phys. Lett*. **1988**, *146*, 113. (b) Maloney, V.; Platz, M. S. *J. Phys. Org. Chem*. **1990**, *3*, 135. (c) Despres, A.; Migirdicyan, E.; Haider, K.; Maloney, V.; Platz, M. S. *J. Phys. Chem*. **1990**, *94*, 6632. (d) Kozankiewicz, B.; Despres, A.; Lejeune, V.; Migirdicyan, E.; Olson, D.; Michalak, J.; Platz, M. S. *J. Phys. Chem*. **1994**, *98*, 10 419. (e) Kozankiewicz, B.; Bernard, J.; Migirdicyan, E.; Orrit, M.; Platz, M. S. *Chem. Phys. Lett*. **1995**, *245*, 549. (f) Kozankiewicz, B.; Aloshyna, M.; Gudmundsdottir, A. D.; Platz, M. S.; Orrit, M.; Tamarat, Ph. *J. Phys. Chem*. A **1999**, *103*, 3155. (g) Tomioka, H.; Hirai, K.; Tanimoto, Y. *J. Chem. Soc., Perkin Trans. 2*. **1994**, 633.(h) Chateauneuf, J. E.; Horn, K. A. *Res. Chem. Intermed*. **1999**, *25*, 925.

(9) For studies of anthrylcarbenes, see: (a) Wasserman, E.; Kuck, V. J.; Yager, W. A.; Hutton, R. S.; Greene, F. D.; Abegg, V. P.; Weinshenker, N. M. *J. Am. Chem. Soc*. **1971**, *93*, 6335. (b) Astles, D. J.; Girard, M.; Griller, D.; Kolt, J.; Wayner, D. D. *J. Org. Chem*. **1998**, *53*, 6053. (c) Itakura, H.; Tomioka, H. *Org. Lett*. **2000**, *2*, 2995. (d) Takahashi Y.; Tomura, M.; Yoshida, K.; Murata, S.; Tomioka, H. *Angew. Chem Int. Ed*. **2000**, *39*, 3478. (e) Tomioka, H.; Iwamoto, E.; Itakura, H.; Hirai, K. *Nature* **2001**, *412*, 6847.

(10) Sander, W.; Bucher, G.; Wierlacher, S. *Chem. Rev*. **1993**, *93*, 1583.

(11) For reviews, see (a) Tomioka, H. *Acc. Chem. Res*. **1997**, *30*, 315. (b) Tomioka, H. In *Advances in Carbene Chemistry*; Brinker, U. H., Ed.; JAI Press: Stamford, 1998; Vol. 2, pp 175−214.

(12) For triplet diphenylcarbenes protected by alkyl groups, see: (a) Tomioka, H.; Okada, H.; Watanabe, T.; Hirai, K. *Angew. Chem., Int. Ed. Engl*. **1994**, *33*, 873. (b)Hirai, K.; Komatsu, K.; Tomioka, H. *Chem. Lett.* **1994**, 503. (c) Tomioka, H.; Kawasaki, H.; Kobayashi, N.; Hirai, K. *J. Am. Chem. Soc*. **1995**, *117*, 4483. (d) Tomioka, H.; Okada, H.; Watanabe, T.; Banno, K.; Komatsu, K.; and Hirai, K. *J. Am. Chem. Soc*. **1997**, *119*, 1582. (e) Tomioka, H.; Mizuno, H.; Italkura, H.; Hirai. K. *J. Chem. Soc. Chem. Commun*. **1997**, 2261. (f) Hu, Y.; Hirai, K.; Tomioka, H. *J. Phys. Chem. A*, **1999**, *103*, 9280. (g) Hu, Y.; Hirai, K.; Tomioka, H. *Chem. Lett*. **2000**, 94. (h) Itakura, H.; Mizuno, H.; Hirai, K.; Tomioka, H. *J. Org. Chem*. **2000**, *65*, 8797. (i) Tomioka, H.; Hu, Y.; Ishikawa, Y.; Hirai, K. *Bull. Chem. Soc. Jpn*. **2001**, *74*, 2207.

(13) For triplet diphenylcarbenes protected by halo groups, see (a) Tomioka, H.; Hirai, K.; Fujii, C. *Acta Chem. Scand.* **1992**, *46*, 680. (b) Tomioka, H.; Hirai, K.; Nakayama, T. *J. Am. Chem. Soc.* **1993**, *115*, 1285. (c) Tomioka, H.; Mizutani, K.; Matsumoto, K.; Hirai, K. *J. Org. Chem.* **1993**, *58*, 7128. (d) Tomioka, H.; Watanabe. T.; Hirai, K.; Furukawa, K.; Takui, T.; Itoh, K. *J. Am. Chem. Soc.* **1995**, *117*, 6376. (e) Tomioka, H.; Hattori, M.; Hirai, K.; Mutata, S. *J. Am. Chem. Soc*. **1996**, *118*, 8723. (f) Tomioka, H.; Hattori, M.; Hirai, K.; Sato, K.; Shiomi, D.; Takui, T.; Itoh, K. *J. Am. Chem. Soc*. **1998**, *120*, 1106. (g) Hirai, K.; Tomioka, H. *J. Am. Chem. Soc*. **1999**, *121*, 10213. (h) Tomioka, H.; Watanabe, T.; Hattori, M.; Nomura, N.; Hirai, K. *J. Am. Chem. Soc*. **2002**, *124*, 474.

(14) For review of O−H insertion reactions of carbenes, see: Kirmse, W. In *Advances in Carbene Chemistry*; Brinker, U. H., Ed.; JAI Press: Stamford, 1994; Vol. 1, pp 1−57.

(15) For reviews of general reactions of carbenes, see: (a) Kirmse, W. *Carbene Chemistry, 2nd ed.*; Academic Press: New York, 1971. (b) *Carbenes*; Moss, R. A., Jones, M., Jr., Eds.; Wiley: New York, 1973 and 1975; Vols. 1 and 2. (c) *Carbene(oide), Carbine*; Regitz, M., Ed.; Thieme: Stuttgart, 1989.

(16) See, for example: Grasse, P. B.; Zupancic, J. J.; Lapin, S. C.; Hendrich, M. P.; Schuster, G. B. *J. Org. Chem*. **1985**, *50*, 2352.

(17) Tukada, H.; Sugawara, T.; Murata, S.; Iwamura, H. *Tetrahedron Lett*. **1986**, *27*, 235.

(18) Sander, W. *Angew. Chem., Int. Ed. Engl*. **1990**, *29*, 344.

(19) Scaiano, J. C.; McGimpsey, W. G.; Casal, H. C. *J. Org. Chem*. **1989**, *54*, 1612.

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

(21) See for instance, (a) Griller, D.; Montgomery, C. R.; Scaiano, J. C.; Platz, M. S.; Hadel, L. *J. Am. Chem. Soc*. **1982**, *104*, 6813. (b) Closs, G. L.; Rabinow, B. E. *J. Am. Chem. Soc.* **1976**, *98*, 8190.

(22) Eisental, K. B.; Turro, N. J.; Sitzmann, E. V.; Gould, J. R.; Hefferon, G.; Langan, J.; Chan, Y. *Tetrahedron* **1985**, *41*, 1543.

(23) (a) Griller, D.; Nazran, A. S.; Scaiano, J. C. *J. Am. Chem. Soc*. **1984**, *106*, 198. (b) Griller, D.; Nazran, A. S.; Scaiano, J. C. *Tetrahedron* **1985**, *41*, 1535.

(24) Bethell, D.; Hayes, J.; Newall, A. R. *J. Chem. Soc., Perkin Trans. 2* **1974**, 1307.

(25) Kirmse, W.; Kilian, J.; Steeken, S. *J. Am. Chem. Soc*. **1990**, *112*, 6399.

(26) Naphthyl(phenyl)cations are generated and characterized. Alonso, E. O.; Johnston, L. J.; Scaiano, J. C.; Toscano, V. G. *J. Am. Chem. Soc*. **1990**, *112*, 1270; Alonso, E. O.; Johnston, L. J.; Scaiano, J. C.; Toscano, V. G. *Can. J. Chem*. **1992**, *70*, 1784.

(27) Hartz, N.; Surya-Prakash, G. K.; Olah, G. *J. Am. Chem. Soc*. **1993**, *115*, 901.

(28) See for instances (a) Baer T. A.; Gutsche, C. D. *J. Am. Chem. Soc*. **1971**, *93*, 5180. (b) Kirmse, W.; Homberger, G. *J. Am. Chem. Soc*. **1991**, *113*, 3925. (c) Tomioka, H.; Kawasaki, H.; Kobayashi, N.; Hirai, K. *J. Am. Chem. Soc*. **1995**, *117*, 4483.

(29) Zimmerman, H. E.; Paskovich, D. H. *J. Am. Chem. Soc*. **1964**, *86*, 2149.

(30) (a) Wintgens, V.; Netto-Ferreira, J. C.; Casel, H. L.; Scaiano, J. C. *J. Am. Chem. Soc*. **1990**, *112*, 2363. (b) Netto-Ferreira, J. C.; Wintgens, V.; Scaiano, J. C. *Can. J. Chem*. **1994**, *72*, 1565.

(31) (a) Sholle, V. D.; Rozantsev, E. G. *Russ. Chem. Rev*. **1973**, *42*, 1011. (b) McBride, J. M. *Tetrahedron* **1974**, *30*, 2009.

(32) Actually product as a result of such coupling reaction was isolated in the reaction of di(9-anthryl)carbene. See ref 9d.

(33) Westhermer, F. H. In *Steric Effects in Organic Chemistry*; Newman, M. S., Ed.; Wiley: New York, 1956; pp 523−555.

(34) For buttressing effect in carbene chemistry, see; Tomioka, H.; Kimoto, K.; Murata, H.; Izawa, Y. *J. Chem. Soc., Perkin Trans. 1* **1991**, 471.

(35) Decouzon, M.; Ertl, P.; Exner, O.; Gal, J.-F.; Maria, P.-C. *J. Am. Chem. Soc*. **1993**, *115*, 12 071.

(36) (a) Reimlinger, H. *Chem. Ber*. **1964**, *97*, 3503. (b) Franzen, von V.; Joschek, H.-I. *Justus Liebigs Ann. Chem*. **1960**, *633*, 7.