

Polymethylated and Poly(*tert*)butylated Diphenylcarbenes. Generation, Reactions, Kinetics, and Deuterium Isotope Effects of Sterically Congested Triplet Carbenes

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Abstract: Dimesitylcarbene (**2a**) was shown to decay by undergoing dimerization and to have a half-life of 160 ms, some 5 orders of magnitude longer-lived than diphenylcarbene. Didurylcarbene (**2b**) was twice as long-lived as **2a**, while decamethyldiphenylcarbene (**2c**) decayed mainly unimolecularly by abstracting H from the *o*-methyl group and became shorter-lived than **2b**. 2,4,6-Tri(*tert*-butyl)diphenylcarbene (**14**) decayed unimolecularly almost exclusively by abstracting H from the *o*-*tert*-butyl group and showed the lifetime of 125 μ s. The Arrhenius plot for H and D abstraction of **2c** and **14** gave data consistent with a classical atom-transfer reaction, although the kinetic parameters are very different between the two systems.

There has been a continued and ever-increasing interest in persistent radicals since Gomberg in the year 1900,¹ and many stable radicals have been synthesized and characterized.¹ In sharp contrast, few efforts have been made concerning persistent carbenes before the isolation of carbenes in the singlet state had been reported very recently.² Phosphinocarbenes³ and imidazol-2-ylidene⁴ have been prepared as “bottle-able” carbenes in 1988 and 1991, respectively. Naturally, however, interpretation of these species as free carbenes has been a topic of debate, especially concerning the possible contribution of the ylidic character as a result of $p\pi-p\pi$ delocalization.⁵ Actually recent theoretical and X-ray crystal studies suggest that the phosphinocarbene is best described as a phosphaacetylene.^{3e} Thus, the stabilization of a triplet carbene hopefully protected by all hydrocarbon substituents emerges as the next challenging target.

The stabilization of a triplet carbene must be better accomplished by steric protection (kinetic stabilization) than thermodynamic methods since the latter strategy seems to result in stabilization of the singlet.⁶ Introduction of sterically bulky groups around the carbenic center may make ΔG_{ST} larger by

increasing the carbene bond angle since theory suggests⁷ that opening of the central angle strongly destabilizes the singlet but requires very little additional energy for the triplet. The first attempts to isolate triplet carbenes using steric protectors were made by Zimmerman and Paskovich⁸ who generated highly hindered diphenylcarbenes, i.e., dimesitylcarbene, in the hope of insulating the highly reactive carbene center from its environment. Although the approach of steric restriction at the divalent carbon did not afford isolable carbenes, the divalent species exhibited unique behavior. For example, in solution at low temperatures, this carbene did not react with the parent diazo compound to give azine, but instead dimerized. The chemistry found for dimesitylcarbene is therefore in sharp contrast with that found for other diarylcarbenes and can be interpreted in terms of steric effects. Thus, the hindered diarylmethylenes do not have accessible singlet counterparts since the singlet would require a smaller aryl–C–aryl angle and incur severe aryl–aryl repulsion. More recent EPR studies showed that dimesitylcarbene had a structure which was significantly less bent than that of diphenylcarbene and in which the aryl groups were orthogonal. This geometry effectively maximizes the triplet–singlet energy gap and hinders the reactive site so that attack on external molecules is disfavored.⁹

In spite of these very promising features of dimesitylcarbene as a potentially isolable triplet carbene, almost no further work has been done to characterize or modify it. In view of the scarcity of the data in this field, despite recent growing interest in triplet carbenes as potential organic ferromagnets,¹⁰ we became interested in designing and generating persistent triplet carbenes.¹¹ Thus, we have generated a series of polymethylated diphenylcarbenes and investigated their reactivities not only by

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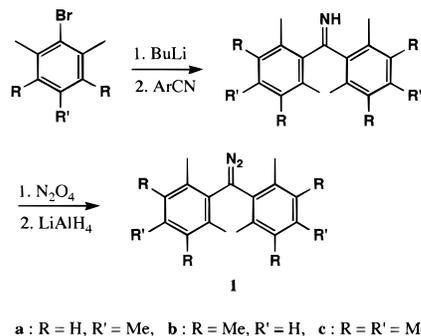
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Scheme 1



product analysis studies but also by flash photolysis techniques.^{12a} We have found that they are exceptionally long-lived for diarylcarbenes with lifetimes on the order of seconds, especially when the CH₃ groups at the ortho positions are replaced with CD₃. We have also studied the effect of the *tert*-butyl group on the reactivities of triplet diphenylcarbene and revealed that this group, although well-known as one of the most effective protecting groups toward a reactive center, is much less effective in stabilizing the divalent center than methyl groups,^{12b} even if all the hydrogens on the *tert*-butyl groups are replaced with deuteriums. We have found, on the other hand, that there is a significant difference in the primary kinetic hydrogen isotope effect for intramolecular H transfer between the methylated and *tert*-butylated diphenylcarbenes.

Results and Discussion

A. Polymethylated Diphenylcarbenes. It is well-known that in 1,2-disubstituted benzene derivatives 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.¹³ One would naturally assume then that protection of the carbenic center by ortho substituents will be greatly strengthened by introduction of another group at the 3-position and that the lifetime of such carbenes must be prolonged.¹⁴ Thus, we investigated the effects of *m*- and *p*-methyl groups on the reactivities of 2,2',6,6'-tetramethyldiphenylcarbenes.

a. Preparation of Precursor Diazomethanes. Diduryl- (**1b**) and decamethyldiphenyldiazomethanes (**1c**) were prepared by essentially the same procedure invented by Zimmerman⁸ for the preparation of dimesityldiazomethane (**1a**), as rather stable orange crystals, although the overall yields tended to decrease as more methyl groups were introduced (Scheme 1). Purification by repeated chromatography on a gel permeation column was found to be very useful to obtain the diazomethanes in a purer form especially for the spectroscopic studies.

b. Product Analysis Studies. The polymethylated diphenylcarbenes (**2**) were generated either by thermolysis at 140 °C in a sealed tube or by photolysis ($\lambda > 300$ nm) at 15 and 35 °C of a benzene solution of the diazomethanes (**1**), and the products were analyzed by conventional methods (Scheme 2, Table 1). Since the product distributions were shown to be significantly sensitive to the temperature, the decomposition tubes were carefully thermostated at the desired temperatures. The reactions

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Scheme 2

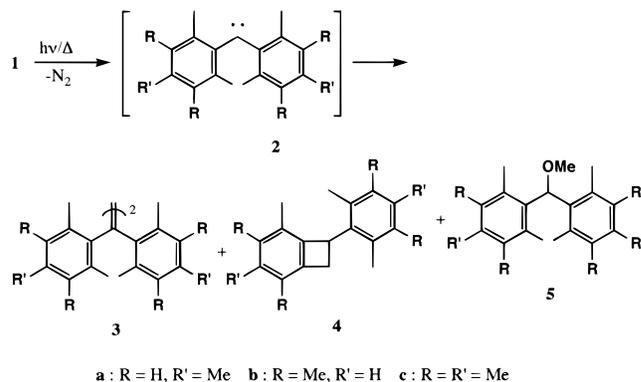


Table 1. Product Distributions in Decomposition of Polymethylated Diphenyldiazomethanes (**1**)^a

diazomethanes	solvent	conditions	3	4	5
1a	PhH	$\Delta/140$ °C	c	70	
1b			c	96	
1c			c	91	
1a	PhH	$h\nu/15$ °C	96	4	
1b			54	46	
1c			4	96	
1a	PhH	$h\nu/30$ °C	60	40	
1b			10	90	
1c			99		
1a	MeOH	$h\nu/10$ °C	c	c	90.0
1b			c	4.2	84.7
1c			c	5.9	76.2

^a Decompositions were carried out on 5 mL of degassed solution of **1** in a sealed Pyrex tube. Irradiations were conducted with a 300 W high-pressure mercury arc. ^b Determined by 500 MHz ¹H NMR. ^c Less than 1%.

observed with didurylcarbene (**2b**) and decamethyldiphenylcarbene (**2c**) were analogous to those observed with dimesitylcarbene (**2a**).⁸ Thus, these carbenes did not react with the diazomethane precursors to give ketazines. Instead they reacted either by dimerization to form tetra(aryl)ethylene (**3**) or by attack at an *o*-methyl group to produce benzocyclobutenes (**4**). The product distributions were, however, significantly different. A key difference is found in the formation of **4**. In the case of **2a**, for instance, while **4a** was produced as main product in the thermolytic run, **2a** underwent mainly dimerization when photolytically generated at 15 °C. On the other hand, in the case of **2b**, **4b** was produced not only by thermolysis but also by photolysis along with the dimer (**3b**). Carbene **2c** produced **4c** as major product at the expense of **3c** even in the photolytic run.

According to the mechanism proposed by Zimmerman and Paskovich⁸ for the reaction of **2a**, the triplet states are responsible for the formation of both products (**3** and **4**). It is reasonable that the dimer is produced from the triplet state since, as a result of the severe steric hindrance and consequent resistance to external attack by solvent, the hindered triplet diarylmethylene concentration builds up to the point where dimerization occurs. Support is lent to this proposal by the fact that triplet carbenes, like radicals, dimerize in a very fast and exothermic reaction.¹⁵ On the other hand, benzocyclobutenes could be produced either from the singlet or from the triplet. Therefore, the significant difference in the product distribution can be interpreted in terms of electronic effects and/or steric factors either on the reactivities of the triplet states or on the singlet–triplet energy gap.

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The reactions of carbenes are shown to be sensitive to electronic perturbation, probably due to the fact that a small shift in energy may invert the energy difference between the singlet and triplet states (ΔG_{ST}).⁶ Generally speaking, electron-donor groups stabilize the electrophilic singlet carbene more than they do the radical-like triplet and lead to smaller ΔG_{ST} . The two phenyl rings in the triplet diphenylcarbene do not lie in the same plane in the solid state and probably not in solution due to unfavorable steric interactions.¹⁶ This is most likely true for singlet diphenylcarbene as well. Therefore the electronic effects on the diphenylcarbene reactivities are not straightforward.¹⁷ Actually, the electronic effect on the triplet carbene reactivities is not well-characterized. The sum of regular Hammett σ constants¹⁸ ($\sigma_m = \sigma_m^+ = -0.07$, $\sigma_p = -0.17$, $\sigma_p^+ = -0.31$) decreases in the order of **2b** > **2a** > **2c**. This is not reconciled with the observed trends in the product distribution changes regardless of whether the electronic effects are exerted on the ΔG_{ST} or on the reactivity of the triplet states.

The difference in the product distribution can be better interpreted as reflecting the difference in the extent of steric crowdedness around the carbene centers between these three carbenes. Thus, in **2b**, each of the four *o*-methyl groups around the carbene center is buttressed by four additional *m*-methyl groups. Therefore the carbene center in **2b** is surrounded by the *o*-methyl groups more tightly than in **2a**. The *o*-methyl groups in **2c** must be buttressed more effectively since four *m*-methyl groups are buttressed by the two *p*-methyl groups in this case. Therefore, the carbenic center in **2c** is most effectively blocked by the *o*-methyl groups from external reagents. Thus, carbene is forced to undergo C-H insertion to afford **4**. Alternatively, it is possible to assume that, as the ortho methyl groups are buttressed more effectively, they are brought much closer to the carbene, and hence carbene is more easily trapped by the methyl groups before it undergoes dimerization. The two possibilities cannot be discriminated simply by product analysis but will be differentiated by the rate measurement (*vide infra*). On the other hand, photolysis of **1** in methanol resulted in almost exclusive formation of methyl ether **5** obviously produced as a result of insertion of **2** into OH bond of the solvent regardless of the substituent patterns. These results suggest that the carbenic center in **2** is not protected so completely that it is not attacked by a very reactive trapping reagent, e.g., methanol.

c. Spectroscopic Studies. In order to get more quantitative information on the reactivities of **2**, the following spectroscopic studies were carried out. Irradiation ($\lambda > 300$ nm) of **1b** in a 2-methyltetrahydrofuran (MTHF) glass at 77 K gave a paramagnetic species readily characterized from its EPR spectrum as triplet didurylcarbene **2b**. The EPR signals from **2b** were stable for at least several hours at this temperature and survived even at 110 K. These observations established the triplet as the ground state of this carbene. The signals were analyzed in terms of *D* and *E* values, which are 0.3551 and 0.0116 cm^{-1} for **2a**, 0.3805 and 0.0106 cm^{-1} for **2b**, and 0.3636 and 0.0095 cm^{-1} for **2c**. Since *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 *D*.¹⁹ Inspection of the data indicates that *E/D* values steadily decrease as one introduces more methyl groups on the aromatic rings, suggesting that the carbene becomes less

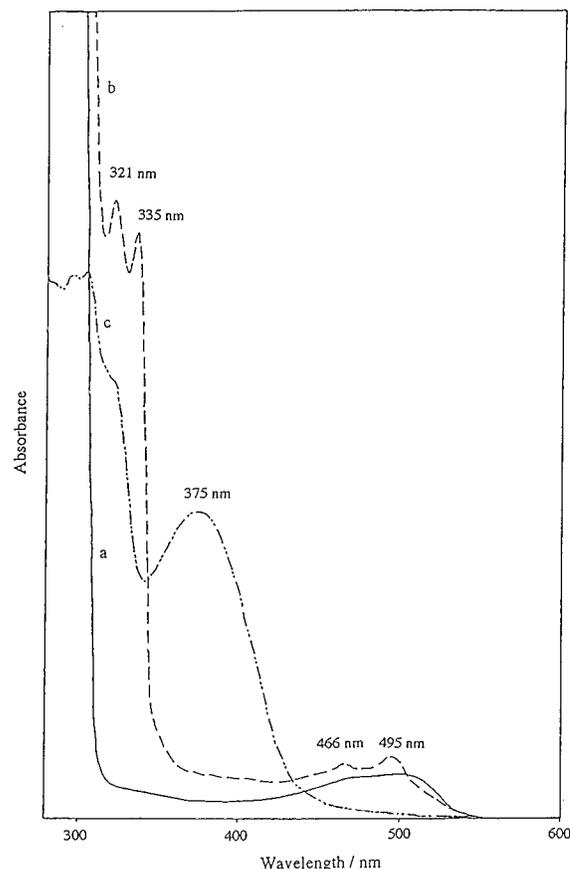


Figure 1. (a) UV/vis spectrum of **1b** in MTHF at 77 K. (b) Same sample after 10-min irradiation ($\lambda > 300$ nm). (c) Same sample after thawing the matrix to 110 K.

benzene due to increased steric interaction between the four *o*-methyl groups in going from **2a** to **2b** to **2c**.²⁰

Optical spectroscopy in the frozen medium gave analogous but more intriguing results. Figure 1b shows the absorption spectrum obtained after irradiation of **1b** in a MTHF glass at 77 K. The spectrum displays two identifiable features: two sharp, intense UV bands centered at 321 and 335 nm, and in the visible portion of the spectrum two weak and broad overlapping bands with apparent maximum at 466 and 495 nm. The glassy solution did not exhibit any spectral change for several hours if kept at 77 K. However, when it was allowed to warm to room temperature and then cooled to 77 K, the characteristic absorption bands disappeared (*vide infra*). The optical absorption spectra of several aromatic carbenes in frozen media have been assigned.²¹ Typically, they consist of an intense UV band and a weak visible transition. These features are present in the spectrum obtained in the photolysis of **1b**. Moreover, the product analysis of the spent solution showed the presence of the carbenic dimer **3b** as well as the benzocyclobutene **4b**. In these circumstances, the absorption spectrum is attributable to didurylcarbene (**2b**) generated by the photodissociation of **1b**.

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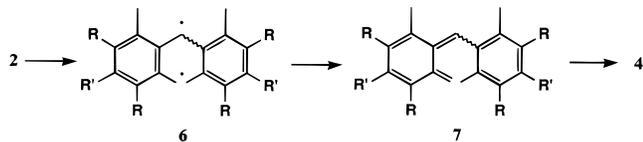
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Scheme 3



When the spectral changes of the matrix were more carefully monitored as a function of temperature, an interesting feature appeared. At higher temperatures, a new broad absorption at 375 nm appeared and increased as carbene absorption bands decreased (Figure 1c). The species responsible for this new absorption showed appreciable thermal stability; even at room temperature it persisted for a few seconds before decaying. These observations suggest that the absorption at 375 nm must be due to an intermediate formed from the initially generated triplet carbene that leads to the final products.

A plausible candidate for the intermediate is one which explains the formation of the benzocyclobutene and must be either the diradical (**6b**) generated by intramolecular 1,4 H shift from the *o*-methyl to the carbene center of **2b** or *o*-xylylene (**7b**) formed from the diradical (Scheme 3). *o*-Xylylenes have been generated by photodecarbonylation of the corresponding 2-indanones²² or by intramolecular H abstraction in photoexcited *o*-alkylaromatic ketones.²³ In both reactions, 1,4-biradical precursor is postulated. While the *o*-xylylenes exhibit broad absorption bands centered around 350–450 nm and show appreciable thermal stability, surviving up to a few seconds to minutes even at room temperature depending on the structure, the 1,4-biradical precursors to the xylylenes show rather sharp absorption in UV region and are much shorter-lived (approximately nanoseconds, *vide infra*). Thus, the biradical precursors are often not detected. The characteristics of the second intermediate, i.e., broad absorption band in a visible region and appreciable thermal stability, are thus in better agreement with *o*-xylylenes (**7**) than with the biradical (**6**).

In order to get more insight into the nature of the intermediate, we prepared 1-phenyl-2-indanone (**8**), expected to generate "parent" 7-phenyl-*o*-xylylene (**9**) upon irradiation, and investigated the intermediate generated by its photolysis. Irradiation of **8** in a MTHF glass at 77 K resulted in a formation of a new species showing a broad absorption band centered around 410 nm as an initial product, with no other transient absorption being detected (Figure 2b). The transient absorption did not decay appreciably upon thawing of the matrix and gradually disappeared at room temperature. Analysis of the spent solution revealed the presence of 3,7-diphenyl-1,2,5,6-dibenzocycloocta-1,5-dienes (**10**), dimers of **9**, as major products. Thus, the transient product obviously assignable to **9** was detected as an initial product without showing the intervention of the precursor biradical and showed appreciable thermal stability (Scheme 4). Coincidentally, the formation of *o*-xylylene from *o*-tolylmethylene within inert gas matrices at low temperature either upon photolysis or by thawing the matrix and its subsequent cyclization forming benzocyclobutene has been demonstrated by the matrix-isolation spectroscopy.^{24,25}

Similar spectra were obtained in the photolysis of **1a** and **1c** in 2-MTHF at 77 K, where **2a** and **2c** showed two sharp, intense

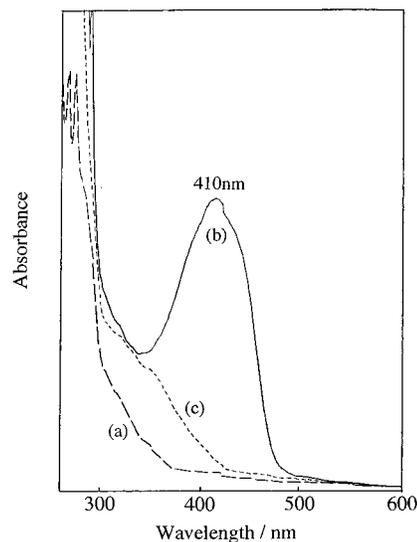
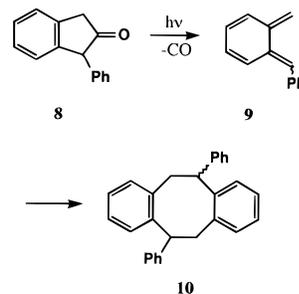


Figure 2. (a) UV/vis spectrum of **8** in MTHF at 77 K. (b) Same sample after 10-min irradiation ($\lambda > 300$ nm). (c) Same sample after warming to room temperature and recooling to 77 K.

Scheme 4



UV bands at 318, 330, 449, and 461 nm, and 325, 338, 458, and 485 nm, respectively, and generated the corresponding *o*-xylylenes **7a** and **7c**, showing broad absorptions at 380 and 370 nm, respectively, upon thawing.

Laser flash photolysis of **1b** (1.0×10^{-4} M) in a degassed benzene solution at room temperature with a 10 ns, 70–90 mJ, 308 nm pulse from a XeCl laser produced a transient species absorbing at 320–330 nm; the apparent maximum around 330 nm was coincident with the laser pulse (Figure 3). The decay kinetics of the transients indicate that the absorption at 330 nm decays within 1 s to generate a new species with an absorption maximum around 370 nm, which is too long-lived to be monitored by our system. Product analysis of the spent solution showed the presence of **3b** and **4b**. Thus, on the basis of the low-temperature spectrum coupled with chemical analysis, we assign the initially formed transient with a maximum at 330 nm to carbene **2b** and the second to *o*-quinodimethane **7b**. Again we were not able to detect the possible precursor biradical, i.e., **6b** for **7b**. Porter and Tchir have shown that the 1,4-biradical generated as a result of H abstraction by the n,π^* triplet state of 2,4-dimethylbenzophenone exhibits its transient absorption maximum around 330 nm and has a lifetime of less than 70 ns in cyclohexane.²⁶ Thus it is probable that the biradical could not be detected by our system due to its short lifetime and overlapping absorption.

Support is lent to this assignment by the following control experiments using trapping reagents. In the flash photolysis of

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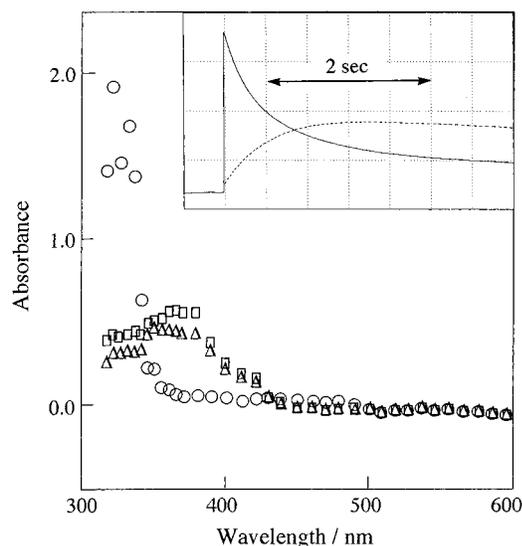
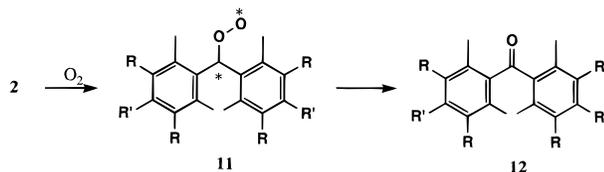


Figure 3. Absorption spectra of the transient products formed by pulsing **1b** in degassed benzene with a 308-nm excimer laser recorded 8 ms (○), 1 s (□), and 6 s (△) after the pulse. Inset shows oscillogram traces monitored at 330 and 370 nm.

Scheme 5



an oxygen-saturated benzene solution of **1b**, a broad absorption band with a maximum at 390 nm appeared at the expense of the absorption due to the carbene. The spent solution was found to contain octamethylbenzophenone (**12b**) as the main product (Scheme 5). It is well-documented that diarylcarbenes with triplet ground states are readily trapped by oxygen to generate the corresponding diaryl ketone oxides, which are easily observed directly either by matrix isolation or by flash photolysis, and show a broad absorption band centered at 390–450 nm.²⁷ Thus, our observations can be interpreted as indicating that the triplet carbene **2b** is trapped by oxygen to form the carbonyl oxide (**11b**), which confirms that the transient absorption quenched by oxygen is due to **2b**. The apparent built-up rate constant, k_{obs} , of the carbonyl oxide is essentially identical with that of the decay of the carbene, and k_{obs} is expressed as given in eq 1

$$k_{\text{obs}} = k_0 + k_{\text{O}_2}[\text{O}_2] \quad (1)$$

where k_0 represents the rate of decay of **2b** in the absence of oxygen and k_{O_2} is a quenching rate constant of **2b** by oxygen. A plot of the observed pseudo-first-order rate constant of the formation of **11b** against $[\text{O}_2]$ is linear. From the slope of this plot, the rate constant for the quenching of **2b** by oxygen was determined to be $7.1 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$, which is approximately 2 orders of magnitude smaller than that observed with the parent diphenylcarbene, DPC ($k_{\text{O}_2} = 5.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$).^{27b}

When a degassed benzene solution of **1b** containing 1,4-cyclohexadiene (CHD) was excited, a new species was formed, showing a strong absorption with $\lambda_{\text{max}} = 356 \text{ nm}$, formed as

Table 2. Kinetic Data for Polymethylated Diphenylcarbenes (**2**)^a

carbenes	$k_i^{\text{H}}, \text{s}^{-1}$	$\tau(t_{1/2}), \text{ms}$	$k_{\text{O}_2}, \text{M}^{-1} \text{s}^{-1}$	$k_{\text{CHD}}, \text{M}^{-1} \text{s}^{-1}$
diphenylcarbene		0.002	5.0×10^9	1.0×10^7
2a	1.5	160	2.0×10^8	4.6×10^2
2b	2.2	410	7.1×10^7	3.4×10
2c	4.1	180	1.0×10^8	9.8×10

^a All measurements were done in benzene at 20 °C.

the 334 nm signal of **2b** decayed. The decay of **2b** was shown to be kinetically correlated with the growth of the new species. Thus, this new signal was attributable to the didyrylmethyl radical formed as a result of H abstraction of **2b** from the diene, since it is now well-documented that triplet arylcarbenes, generated in good hydrogen donor solvents, undergo H abstractions leading to the corresponding radicals which show transient absorptions at longer wavelengths than those of the precursor carbenes.²⁸ The excellent hydrogen donor properties of CHD have been well recognized.²⁹ A plot of the observed pseudo-first-order rate constant of the formation of the radical against $[\text{CHD}]$ is linear, and the slope of this plot yields the absolute rate constant for the reaction of **2b** with the diene, $k_{\text{CHD}} = 34 \text{ M}^{-1} \text{ s}^{-1}$, which is some 5 orders of magnitude smaller than that observed with DPC ($k_{\text{CHD}} = 1 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$).³⁰

Flash photolysis of the indanone (**8**) in degassed benzene, on the other hand, gave a transient species exhibiting a broad band around 410 nm probably due to *o*-xylylene (**9**). We were not able to detect a shorter-lived intermediate ascribable to a possible precursor to the xylylene, i.e., 1,4-diradical (**6**) or the triplet state of the indanone. The decay of the transient was found to be second order ($2k/\epsilon l = 13.8 \text{ s}^{-1}$), and a rough lifetime was estimated in the form of a half-life, $t_{1/2}$, $6 \pm 0.1 \text{ s}$. The product analysis of the spent solution in this case showed the presence of the dimers (**10**). Thus, the similarity of the absorption band and stability again supports the above assignment. On the other hand, the significant difference in lifetime between **7b** and **9** can be interpreted in terms of steric effects. Parent *o*-quinodimethane is known to undergo dimerization, while a unimolecular reaction pathway involving cyclization to cyclobutene becomes the major pathway for those bearing substituents at the 7- and/or 8-positions, probably due to steric hindrance to dimerization.²² Although the substitution pattern at the 7- and 8-positions of **7b** and **9** is not changed, there should be more severe steric hindrance for **7b** to undergo dimerization caused by the methyl groups near reaction centers. Thus, **7b** is forced to undergo cyclization to form **4b**, and due to steric effects, the lifetime of **7b** is increased compared to that of **9**.

The inset in Figure 3 shows the decay of **2b** and the formation of **7b** over time and indicates that the decay of **2b** is kinetically correlated with the growth of **7b**. The decay rate was determined to be $1.6 \pm 0.1 \text{ s}^{-1}$, while the growth rate was $2.2 \pm 0.2 \text{ s}^{-1}$. From the decay curve, a half-life ($t_{1/2}$) of **2b** was determined to be *ca.* 410 ms, while the lifetime based on k_i was estimated to be 455 ms. Similar measurements were done for the carbenes **2a,c**, and values of k_i and $t_{1/2}$ (τ) are summarized in Table 2. It should be noted here that **2c** decayed unimolecularly, in accordance with the product analysis results.

These spectroscopic studies corroborate the trends observed in the product analysis studies (*vide supra*) which lead to the same but more quantitative conclusion. Thus, triplet dimesitylcarbene is shown to be some 5 orders of magnitude longer-lived than the parent diphenylcarbene ($2 \mu\text{s}$ in cyclohexane),¹⁷ thus confirming expectations for the role of steric effects in

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carbene chemistry posited 30 years ago. As more methyl groups are introduced on the aromatic rings, the carbenic center is more tightly blocked by the four *o*-methyl groups toward external reagents. Thus, didurylcarbene (**2b**) is shown to be longer-lived than **2a**. On the other hand, the steady increase in k_i as going from **2a** to **2c** clearly suggests that the *o*-methyl groups are brought closer to the carbenic center by the buttressing methyl groups and hence the carbenic center comes to interact more easily with the *o*-methyl groups. Thus, decamethyldiphenylcarbene (**2c**) decays unimolecularly by abstracting hydrogen from the *o*-methyl group to generate *o*-quinodimethane (**7c**) and hence is shorter-lived. Support is lent to this explanation by semiempirical calculations. Optimized geometries calculated for a series of polymethylated monophenylcarbenes with the program PM3-ROHF/CI (4×4)³¹ indicate that the distances between a carbenic carbon and *o*-methyl carbon atoms for mesityl-, duryl-, and pentamethylphenylcarbenes are 285, 279, and 278 pm, respectively.

B. Deuterated Decamethyldiphenylcarbenes. Deuterium Isotope Effects. The above study reveals that polymethylated diphenylcarbenes are exceptionally long-lived for arylcarbenes, although they are still not persistent enough to be isolated. The buttressing effects are shown to effectively strengthen the ortho group protection of the reactive center. However, in the case of methyl groups which are potentially reactive toward the carbene, the *o*-methyl groups become more efficient intramolecular quenchers of the carbene as a result of buttressing, thus decreasing carbene persistence. One of the best ways to hinder this process is to replace the hydrogens at the *o*-methyl groups with deuterium. Thus, we prepared a series of decamethyldiphenyldiazomethanes bearing partially and fully deuterated *o*-methyl groups and studied the kinetic deuterium isotope effects (KDIEs) on the intramolecular H transfer reactions.

a. Preparation of Deuterated Decamethyldiphenyldiazomethanes. We prepared two decamethyldiphenyldiazomethanes (**1c-d₁₂** and **1c-d₈**) with different degrees of deuteration on the *o*-methyl groups according to the procedures outlined in the Experimental Section. As di- and trideuteriomethyl groups are successfully prepared³² from carboxy esters by the reduction of the ester groups with LiAlD₄ followed by bromination of the resulting alcohol and subsequent reduction with LiAlH₄(D₄), carboxy groups were introduced at the desired positions of the aromatic ring by the conventional methods starting from 1,2,3-trimethylbenzene. 1,5-Bis(trideuteriomethyl)- and 1,5-bis(di-deuteriomethyl)-2,3,4-trimethylbenzenes thus obtained were converted to the desired diazomethanes by way of the corresponding ketimine prepared by the coupling of pentamethylbenzotrile with (pentamethylphenyl)lithium.

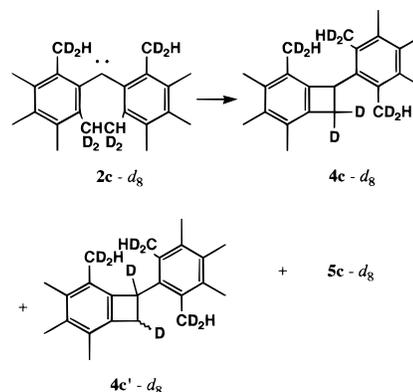
b. Product Analysis Studies. Irradiation of **1c-d_x** in degassed benzene again produced carbenic dimers (**3c-d_x**) and benzocyclobutenes (**4c-d_x**) almost exclusively. Reflecting the KDIEs, however, the product ratios are significantly changed (Table 3). Thus, while **2c-d₁₂** generated by photodissociation of **1c-d₁₂** afforded carbenic dimer (**3c-d₁₂**) as major product at the expense of benzocyclobutenes (**4c-d₁₂**), **2c-d₈** still produced the benzocyclobutenes as the major products although the yields were slightly decreased. The results suggest that there should be large KDIEs in the H atom transfer. Thus, a marked decrease in **4c-d₁₂** in the reaction of **2c-d₁₂** indicates that, in **2c-d₁₂** where all hydrogens on the *o*-methyl groups are replaced with deuterium, the carbenic center becomes less susceptible to the intramolecular quenching due to large KDIEs and therefore has

Table 3. Product Distributions in Irradiation of (Decamethyldiphenyl)diazomethanes (**1c-d₀**) and Its Deuterated Analogues (**1c-d₁₂** and **-d₈**) in Benzene^a

diazomethanes	T, °C	3c-d_x	4c-d_x/4'c-d_x	k_H/k_D^c
1c-d₀	15	4	96	
	35	1	99	
1c-d₁₂	15	73	27	
	35	32	68	
1c-d₈	15	35	58/7	8.0
	35	2	87/11	7.9

^a Irradiations were conducted on 5 mL of degassed solution of **1** with a 300 W high-pressure mercury arc. ^b Determined by 500 MHz ¹H NMR. ^c Calculated on the basis of the product ratio.

Scheme 6



more time to react with a second carbene molecule. On the other hand, the slight decrease in formation of **4c** on going from **2c-d₀** to **2c-d₈** in spite of a significant decrease in the number of H atoms available suggests that the quenching channels through hydrogen atom transfer are rather efficient.

In order to determine the KDIE more quantitatively, we estimated the ratio of benzocyclobutenes formed as a result of C-H and C-D "insertion" by ¹H NMR (500 MHz). Thus, **2c-d₈** gave **4c-d₈** as a result of H abstraction and **4c'-d₈** by D transfer (Scheme 6). The ratio of **4c-d₈/4c'-d₈** was estimated by integrating the protons at C₁ and C₂ and calibrating using the aromatic methyl protons which are fairly well-resolved. The product ratios was determined to be 87/11 at 35 °C, indicating that k_H/k_D is 7.9. The value is fairly large as expected and close to the upper limit set by classical theory.³³ However, we would have to take into account the errors inherent in the ¹H NMR analysis especially with minor components, i.e., **4c'-d₈**, and secondary KDIEs before we discuss the mechanism of this H transfer.

c. Laser Flash Photolysis Studies. In order to obtain more quantitative information on KDIEs, spectroscopic studies were carried out. LFP of **1c-d₁₂** in degassed benzene at 20 °C resulted in essentially the same transient absorption bands that were observed for the protio analogue (**1c-d₀**). Thus, a transient showing a strong absorption at 340 nm due to deuterated triplet carbene (**2c-d₁₂**) appeared coincident with the XeCl pulse, and a second transient exhibiting a broad absorption at 377 nm due to the *o*-quinodimethane (**7c-d₁₂**) appeared as the initial absorption decayed. Figure 4 shows the decay of **2c-d₁₂** and the formation of **7c-d₁₂** as a function of time. The oscillogram traces observed for the protio analogue are also shown in the figure. The kinetic behavior is distinctly different between these two carbenes. Thus, the growth rate and optical yield of the deuterated *o*-quinodimethane **7c-d₁₂** were very small compared

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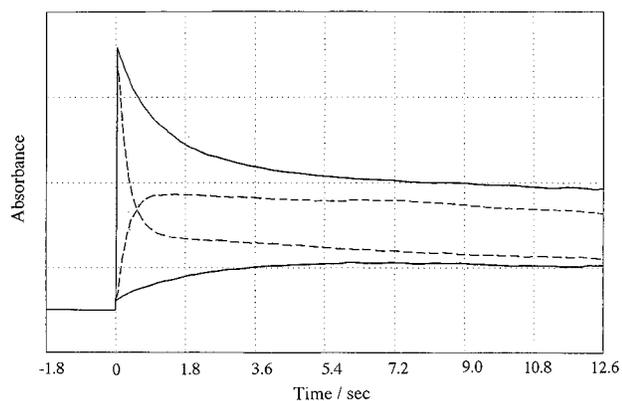


Figure 4. Decay kinetics of carbene **2c-d₁₂** measured at 340 nm and growth kinetics of *o*-quinodimethane **7c-d₁₂** measured at 380 nm in degassed benzene at 20.0 °C. Broken lines indicate the kinetics for the corresponding protio analogues.

Table 4. Arrhenius Parameters for H(D) Transfer in Triplet Decamethyldiphenylcarbenes (**2c**) and Tri-*tert*-butyldiphenylcarbenes (**14**)

carbenes	temp, K	E_a , kcal/mol	A , s ⁻¹	k_H/k_D^a	$[\Delta E_a]_D^H$	A_H/A_D
2c	288–338	9.9	9.8×10^7	4.76	1.0	0.9
2c-d₁₂	290–338	10.9	1.1×10^7			
14	280–298	11.0	1.1×10^{12}	1.16	0.3	0.7
14-d₂₇	280–298	11.3	1.6×10^{12}			

^a Measured at 20 °C.

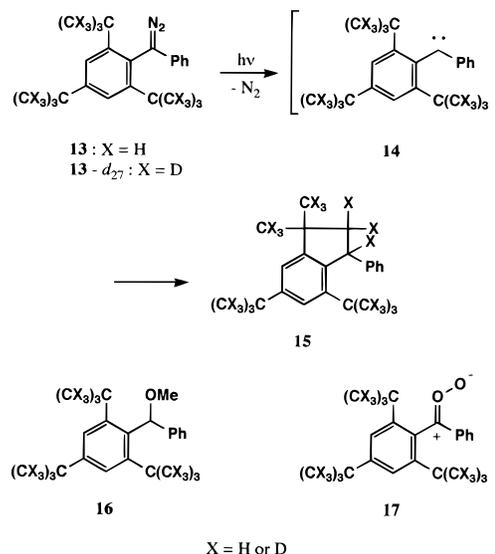
to those of the protio analogue **7c-d₀**, and the decay of **2c-d₁₂** was found not to fit a single exponential. This is in accordance with the product analysis data where **2c-d₁₂** gave the carbenic dimer in a significant amount while **2c-d₀** produced the cyclobutene almost exclusively.

The growth rate of *o*-xylylene from **2c-d₁₂**, which is equal to the intramolecular D abstraction rate constant (k^D_i) was then determined to be 0.85 s⁻¹ at 20 °C. The KDIE based on the absolute rate constants, i.e., k^H_i/k^D_i , is calculated to be 4.76. At 30 °C, this value is 5.11. This is smaller than that determined on the product analysis data and is well within the limits predicted by the classical transition-state theory³³ and reported³⁴ for H abstraction by a triplet carbene as well.

In order to get more insight into the nature of the 1,4 H migration, the rate of the migration was measured as a function of temperature over a temperature range 15–75 °C. The Arrhenius plot of the data is almost completely linear ($r = 0.99$) for both **2c-d₀** and **2c-d₁₂** in the temperature range studied. No deviation from linearity at lower temperature is seen. The Arrhenius parameters for H and D migration are summarized in Table 4. Thus, a differential activation energy ($E^D_a - E^H_a = 1.0$ kcal/mol) and a ratio of preexponential factors ($A_H/A_D = 0.9$) are consistent with a classical atom-transfer reaction.^{33,35} The moderate k^H_i/k^D_i , linear Arrhenius plot, and normal differential Arrhenius parameters all suggest that there is no significant contribution of quantum mechanical tunneling (QMT) to the 1,4 H migration in **2c**, at least within the temperature range studied.

C. (2,4,6-Tri-*tert*-butylphenyl)phenylcarbenes. The *tert*-butyl group has been recognized as one of the most effective protecting groups and successfully employed to protect many reactive centers in organic molecules. For instance, the divalent centers of silylenes and germylenes, heavy atom analogues of

Scheme 7



carbenes, are shown to be blocked by *tert*-butyl groups.³⁶ One wonders, however, whether the *o*-*t*-butyl group would act as an equally effective protector of the carbenic center in the light of the affinity of carbenes for electrons since they react even with very weak sources of electrons, e.g., C–H bond σ electrons.² On the other hand, the rather large KDIEs observed for **2c** suggest that the *o*-*tert*-butyl group might be able to exert a larger depressing effect on the reactivities of the carbenic center if it were perdeuterated. Thus, we examined the effect of *o*-*tert*-butyl groups on the reactivities of triplet diphenylcarbene.

a. Preparation of Precursor Diazomethanes. The desired diazo compound (**13**) was obtained by the treatment of the corresponding ketimine with N_2O_4 followed by the reduction of the *N*-nitroso ketimine with $LiAlH_4$. The same procedure was applied to prepare the corresponding deuterated analogue (**13-d₂₇**) without loss of the deuterium content. Again the diazomethanes were purified by repeated gel permeation chromatography.

b. Product Analysis Studies. Irradiation of a degassed benzene solution of **13** at room temperature afforded 4,6-di-*tert*-butyl-1,1-dimethyl-3-phenylindan (**15**) almost exclusively (Scheme 7). It is probable that this indan is produced from the photolytically generated 2,4,6-tri-*tert*-butyldiphenylcarbene (**14**) as a result of insertion into the C–H bonds of *tert*-butyl groups at the ortho position. Similar irradiation of **13** in a more reactive solvent such as cyclohexane and methanol also gave **15** as the main product, no solvent adduct being detected even in methanol. Although it is expected that the carbenic center would be trapped by *tert*-butyl groups at the ortho position, it is rather surprising to note that the carbene is not quenched even by methanol which is known to be an excellent scavenger for most carbenes.^{2,37} This indicates that the carbenic center in **14** is almost completely blocked toward external reagents.

Photolysis of the deuterio compound (**13-d₂₇**) gave essentially the same result. Thus, the indan (**15-d₂₇**) was formed as the main product irrespective of the solvents employed. The only appreciable difference was noted in the reaction carried out in methanol, where only a small amount of the methyl ether (**16**) was detected in the photomixture from **13-d₂₇**. However, the

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(37) For a review on the OH insertion of carbenes, see: Kirmse, W. In *Advances in Carbene Chemistry*, Vol. 1; Brinker, U., Eds.; JAI Press: Greenwich, 1994; pp 1–57.

difference was essentially negligible compared to that observed with decamethyldiphenylcarbenes, where a dramatic decrease in the intramolecular H(D) transfer was noted upon deuterium substitution. This suggests that KDIEs for the intramolecular C–H insertion of **14** could be considerably smaller than those observed for **2c**.

c. Spectroscopic Studies. Flash photolysis studies provided more direct information on the effect of *tert*-butyl groups on the reactivities of diphenylcarbene and the KDIEs of the H abstraction reaction. Laser flash photolysis (LFP) of a degassed cyclohexane or acetonitrile solution of **13** (2.8×10^{-4} M) at room temperature with the fourth harmonic (266 nm) of a Nd/YAG laser (ca. 30 mJ, 4–5 ns pulses) produced no transient species to the limit of time resolution of our LFP system (5 ns). Similar LFP of **13** in the presence of 1,4-cyclohexadiene also produced no transient absorption. Since the cyclohexadiene is known as an excellent hydrogen donor and often used to trap triplet carbenes generating the corresponding radicals, the observation again suggests that the carbenic center is not only sterically blocked toward external reagents but also internally trapped by the butyl group. However, when LFP measurements were carried out in an oxygen-saturated acetonitrile solution of **13**, a weak and broad absorption band with a maximum at 400 nm appeared, and the growth rate of this transient absorption was increased as the concentration of oxygen increased. The observation implies that the triplet carbene (**14**) is trapped with oxygen to generate carbonyl oxide (**17**).²⁷ The bimolecular rate constant for the reaction of **14** with oxygen, k_{O_2} , is readily determined to be $(1.2 \pm 0.2) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ by monitoring the pseudo-first-order growth rate of **17**, k_{obs} , at various oxygen concentrations, using eq 1.

The above observations indicate that the nascent and therefore singlet carbene (**14**) generated by direct irradiation of **13** is trapped almost instantaneously by the *tert*-butyl group before it undergoes intersystem crossing to an extent that the triplet state can be observed directly. In order to generate the triplet state more effectively, a triplet-sensitized photolysis of **13** was carried out.

LFP of a degassed benzene solution of benzophenone (BP, 1.1×10^{-3} M) as a triplet sensitizer at room temperature with the third harmonic (355 nm) of a Nd/YAG laser (ca. 40 mJ, 5–6 ns pulses) produced transient species showing maxima at 340 and 530 nm apparently due to triplet BP.²⁹ When LFP of BP was carried out in the presence of **13**, a similar absorption was observed (Figure 5). However, the absorption band at 530 nm disappeared much faster than that at 340 nm, and the rate of the 530 nm decay increased with increasing concentration of **13**. This suggests that triplet BP is quenched by **13**. The bimolecular rate constant for triplet BP quenching by **13** was obtained from a plot of the rate of decay for triplet BP²⁹ monitored at 530 nm vs concentration of **13** to be $k_{BP} = (4.7 \pm 0.8) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, which is nearly diffusion controlled. This indicates that energy transfer from triplet BP to **13** occurs. The residual spectrum at 340 nm is similar to that obtained during the photolysis of **13** in a 2-methyltetrahydrofuran glass at 77 K. This absorption band was stable for hours at 77 K, but warming of the sample to 110 K led to its disappearance. The product analysis of the spent solution showed the presence of the indan (**15**). On the basis of the low-temperature spectrum and the chemical analysis, we assign the transient product, showing the absorption maximum at 340 nm from the sensitized photolysis of **13** in benzene, to triplet carbene (**14**) generated from the triplet excited state of **13**. The oscillogram trace of the transient absorption due to triplet **14** monitored at 340 nm is shown in the inset of Figure 5. The decay was found to be

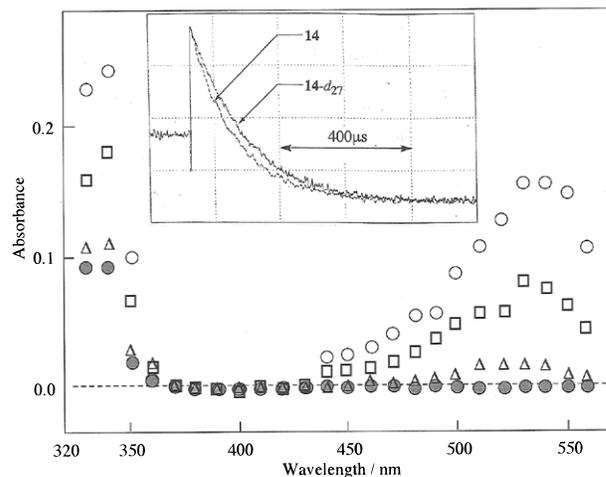


Figure 5. Absorption spectra observed on excitation of benzophenone (1.1×10^{-3} M) with a 355-nm laser pulse in the presence of **13** (6.7×10^{-3} M) in degassed benzene, recorded 0.2 (○), 0.4 (□), 1.0 (△) and 3.0 (●) μs after the pulse. Inset shows decay kinetics measured at 340 nm for **14** and **14-d₂₇** at 20 °C.

first order ($k_i = 7.97 \times 10^3 \text{ s}^{-1}$ at 20 °C), in accordance with the product analysis data, showing that intramolecular CH insertion to form **15** is the main decay pathway for triplet carbene (**14**) under these conditions, and its lifetime was determined to be ca. 125 μs , which is some 60 times longer than that observed for diphenylcarbene.¹⁷

It is probable that the indan is produced from the triplet carbene by a stepwise mechanism by way of the 1,5-biradical. However, no new transient absorption was detected to the limit of our system as the signal due to **14** decayed. Wagner, Scaiano, and co-workers have shown that the 1,5-biradical formed as a result of δ -H abstraction of the *o-tert*-butylbenzophenone triplet state shows a transient absorption with a weak maximum at 465 nm and a strong absorption below 330 nm, and has a lifetime of 43 ns in methanol but only 4 ns in toluene.³⁸ It is known that hydrogen bonding by solvents tends to stabilize this type of radical and leads to longer lifetimes than in nonpolar media.²² Since such stabilizing effects are not expected for less polar biradicals, it may be that the expected 1,5-biradical from **14** is too short-lived to be detected by our system. Therefore we assume that the decay rate of the carbene signal could be equal to the rate of H transfer.

Sensitized LFP of **13-d₂₇** also provided transient absorption at 340 nm assignable to **14-d₂₇**. The decay of the absorption was also found to be first-order, again in accordance with the product analysis data, and k^D_i was determined to be $6.87 \times 10^3 \text{ s}^{-1}$ ($\tau = 146 \mu\text{s}$ at 20 °C). The KDIE estimated for intramolecular H abstraction by triplet carbene **14** based on k_i is therefore only 1.16. This is extremely small compared to that observed for the similar H abstraction by triplet carbene **2c**. Consequently, the lifetime of the triplet states is not increased.

In order to gain more insight into the nature of this H migration, the rate measurements were carried out as a function of temperature over a temperature range 7–25 °C. The Arrhenius plot of the data is again almost completely linear ($r = 0.99$) for both **14** and **14-d₂₇** decay in the temperature range studied. The Arrhenius parameters for H and D abstraction are summarized in Table 4. These data again show that there is no contribution of QMT to the H migration in **14**.

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Summarizing Discussion

It is generally observed that the isotope effect for abstraction of hydrogen by a triplet carbene is ca. 4–8 while insertion into a C–H bond by a singlet carbene proceeds with an isotope effect of only ca. 1–2.³⁴ In this light, the large $k_{\text{H}}/k_{\text{D}}$ observed for a H transfer in **2c** suggests that the singlet state of the carbene is not responsible for this process. Support is lent to this interpretation by the sensitized photolysis experiments. Thus, irradiation of **1c-d₈** in the presence of excess benzophenone with light of $\lambda > 350$ nm, where $>98\%$ of the incident light was absorbed by the sensitizer, also resulted in essentially the same **4c-d₈**/**4c'-d₈** ratio which leads to the same $k_{\text{H}}/k_{\text{D}}$ value as that observed in the direct runs. On the other hand, the sensitized LFP of **1c** and **1c-d₈** in the presence of benzophenone with the third harmonic (355 nm) of a Nd/YAG laser also resulted in the quenching of the T–T absorption due to triplet BP and generated the transient absorption bands due to carbene (**2c**) and *o*-quinodimethane (**6c**). The $k^{\text{H}}/k^{\text{D}}$ obtained under these conditions was again in good agreement with that observed in the direct LFP run within experimental error.

One may propose, however, that triplet carbene (**2c**) generated from the triplet excited state of the diazomethane (**1c**) undergoes intersystem crossing to the upper-lying singlet, which then undergoes H migration to produce *o*-quinodimethane (**6c**). It has been demonstrated for dimethylcarbene, however, that triplet–singlet intersystem crossing is not a facile process while the reverse process is extremely efficient.⁹ This is explained by assuming that the carbene has a structure which is almost optimal for the stabilization of the triplet state due to the steric interactions of the methyl groups and that the steric interaction will also disfavor ring rotations and reduction of the central bond angle, which could provide a pathway for intersystem crossing from the triplet to singlet.

On the other hand, the isotope effects for 1,4 H migration in **2c** as determined by the product analysis or LFP are significantly different. There may be several reasons for this, the first and most likely being simple experimental variability in the measurement and imperfect deuteration of the substrates. It has been warned that correction based on the deuterium enrichment of the substrate is essential, especially when intrinsic KIEs are large. For instance, in hydroxylation of adamantane-1,3-*d*₂, the experimental KIE will be increased from 7.0 to 15.6 when the deuterium enrichment of the starting material decreases from 100% to 95%.³⁹

Moreover, there are two intrinsic differences between the two methods which may result in different $k_{\text{H}}/k_{\text{D}}$. First, while LFP measures the “real” absolute rate of H migration from the triplet carbene, since the transient absorptions due to **2** and **7** are shown to be kinetically correlated, the product ratio results from all possible reactions that lead to the benzocyclobutenes (**4**). The most likely possibility which must be taken into account is the involvement of the excited state of the diazo compound, since it has been demonstrated that irradiation of some alkyl(aryl)-diazomethanes produces excited diazo compounds which partition between carbene formation and hydrogen migration directly to 1,2 H migration products.^{40,41} One of the best ways to circumvent the singlet excited state of the diazomethane is to photolyze in the presence of a triplet sensitizer.⁴¹ The fact that sensitized photolysis of **1c-d₈** also gave essentially the same

$k_{\text{H}}/k_{\text{D}}$ value (*vide supra*) suggests then that this state is not responsible for the observed larger KDIE from the product data compared to the direct measurement. Although we are not able to eliminate the possibility of the triplet excited diazo compound, it is unlikely that this state plays a major role in the direct photolytic run. Second, KDIEs should not be exactly same between the two systems if one takes into account the α -secondary isotope effect. Thus KDIEs from LFP using **1c** and **1c-d₈** correspond to $k^{\text{H}}_{\text{H}}/k^{\text{D}}_{\text{D}}$, whereas those estimated from product analysis from **1c-d₈** are equal to $k^{\text{D}}_{\text{H}}/k^{\text{H}}_{\text{D}}$, where k^{H}_{D} , for instance, means D abstraction (subscripts) with one bystander deuterium (superscripts). Maximum resonance stabilization at a benzylic center requires sp² hybridization at the benzylic carbon and a change from sp³ to sp² geometry should generate a normal secondary KDIE of at least 1.15–1.20.^{32,42} However, in the light of the suggestion that the hydrogen to be abstracted by the divalent center in **2** is one nearly coplanar with aromatic ring,⁸ there is little rehybridization toward planarity at the benzylic carbon in the TS. Under these circumstances, α -secondary KDIEs are usually very small.⁴²

Rotational factors should also be taken into account if one assumes that the rate of rotation of an *o*-methyl group is comparable with that of H transfer as well as that of dimerization. Thus, in **2c-d₈**, there might be a small decrease in lifetime in going from the rotamer with in-plane CH bond to the one with an in-plane C–D bond. Consequently, the latter has more opportunity to be trapped by another carbene leading to the dimer before it undergoes 1,4 D transfer forming **4c'-d₈**. This would result in a larger apparent $k_{\text{H}}/k_{\text{D}}$ than the *real* value.

It is very interesting to compare the kinetic parameters for H abstraction reaction between the two carbene systems, **2c** and **14**. First, while the nature of hydrogens being abstracted is very different between the two carbenes, i.e., benzylic hydrogens for **2c** and primary aliphatic ones for **14**, there is only a small difference in their E_{a} values. This can be rationalized again as supporting the earlier suggestion that the transferring hydrogen in **2c** is in-plane with the aromatic ring, where little benzylic stabilization is expected in the TS. On the other hand, a very large A value for **14** over that for **2c** can be easily understood in terms of large difference in number of the transferring hydrogens and distance between the hydrogens and carbenic center, and is responsible for the large difference in k_{H} between the two systems despite nearly equal E_{a} values.

Second, significant difference in $k_{\text{H}}/k_{\text{D}}$ and $[\Delta E_{\text{a}}]^{\text{H}}_{\text{D}}$ should be also noted here. The magnitude of the primary kinetic isotope effect on C–H bond breaking varies depending on the transition state structure. A reasonable explanation for the well-known variation in the magnitude of these effects has been offered by Melander⁴³ and Westheimer⁴⁴ based on a three-center model for the transition state. This model predicts that hydrogen isotope effects will be greatest when the partial bonds holding the hydrogen being transferred to the donor and to the acceptor are of equal strength, i.e., when the hydrogen is half-transferred. Any deviation from this symmetrical situation in either direction will make the isotope effect smaller. Since the strengths of the two partial bonds in a three-center transition state can be expected to vary in a regular way as the energetics of the reaction change, with the symmetrical situation occurring near $\Delta G^{\circ} = 0$, this implies that isotope effects will be small when

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ΔG° is appreciably negative, will pass through a maximum as ΔG° goes through zero, and will diminish again as ΔG° becomes appreciably positive.^{33,45}

Since the H abstraction reaction undergone by the carbenes **2c** and **14** is considered to be exothermic, the smaller k_H/k_D observed with **14** suggests that ΔG° for the reaction of **14** is larger than that of **2c**. According to the Hammond postulate,⁴⁶ activated complexes of strongly exothermic reactions will resemble the reaction substrates more closely than will activated complexes of more nearly thermoneutral systems. The kinetic barrier decreases as the system moves away from thermoneutrality. Thus, it can be suggested that the faster reaction of **14** is more exoergic and has more reactant like transition states than the slower reaction of **2**. This is reasonable again in terms of the difference in the distance between the transferring hydrogens and carbenic center. The closest possible distance calculated (PM3-ROHF/Cl, 4×4)³¹ for triplet 2-methyl- and 2-*tert*-butylphenylcarbenes is, for instance, 243.5 and 166.9 pm, respectively.

On the other hand, Platz and his co-workers⁴⁷ have studied KDIEs for the benzylic hydrogen atom abstraction of the triplet states of several diarylcarbenes with toluene-*d*₈ in fluid solution in the temperature range -50 to $+100$ °C, and shown that there is a contribution of quantum mechanical tunneling (QMT), especially to the reactions of the sterically hindered carbenes even at this high temperature. This is interpreted as indicating that the decrease in the reactivities of the hindered triplet carbenes results in the relatively slow rate of the classical atom-transfer reaction which allows a QMT pathway to contribute more prominently to the overall hydrogen atom transfer reaction rate.

Ingold and his collaborators⁴⁸ have demonstrated that the intramolecular H transfer in 2,4,6-tri-*tert*-butylphenyl to form 3,5-di-*tert*-butylneophyl at -26 to -160 °C has an exceptionally large KDIE and can be accounted for by QMT through a potential barrier. They have also shown that the analogous isomerization of 2,4,6-trineopentylphenyl is too fast to be monitored even at -160 °C. They suggest that tunneling is enhanced when the reactants are prevented from achieving their optimum separation and orientation in the transition state and that tunneling should be relatively less important in the isomerization of trineopentylphenyl, which occurs via a six-membered cyclic transition state in which the optimum spatial arrangement could be achieved without a large amount of steric strain.

These precedented observations indicate that **2c** is more likely to experience QMT than **14**, since the H atom transfer in **2c** needs a five-membered cyclic TS, achieved with a considerable amount of steric strain, and hence the rate is slowed down, while that in **14** occurs via a six-membered cyclic TS without a large amount of strain and proceeds efficiently. It may be then that the contribution of QMT in **2c** will become important at lower temperature.^{49,50} Unfortunately, however, accurate rate measurement of the H transfer in **2c** becomes difficult at temperatures lower than 10 °C since the competing dimerization

reaction of **2c** becomes the major reaction at lower temperature. It is interesting to note in this connection that the 1,4 H migration of triplet *o*-tolylmethylene to form *o*-quinodimethane at 4.6 K is suggested to proceed with QMT.²⁴

Experimental Section

General Methods. IR spectra were measured on a JASCO A-100 recording spectrometer and the mass spectra were recorded on a Shimadzu QP-1000 mass spectrometer (70 eV). ¹H and ¹³C NMR spectra were determined with either JEOL JNM-EX 270 or JNM-500 spectrometers. UV/vis spectra were recorded on a Hitachi 220-S spectrometer. 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 \times 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 \times 50 cm) column.

Materials. Preparation of Polyalkyldiphenyldiazomethanes (1 and 13). General Procedure. All diazomethanes used in this study were prepared by the reduction of the corresponding *N*-nitrosodiaryl ketimine with LiAlH₄ according to the procedure developed by Zimmerman and Paskovich.⁸ Thus, to a solution of diarylketimine (7.5 mmol) in CCl₄ (15 mL) was added a slurry of CCl₄ (10 mL) containing N₂O₄ (12 mmol) and anhydrous AcONa (2 g) at 5–10 °C. After 1 h of stirring at the same temperature, the mixture was poured into ice and saturated Na₂CO₃ solution and rapidly washed with ice water. The crude *N*-nitrosodiaryl ketimine obtained from the organic layer after the usual workup was dissolved in anhydrous Et₂O (20 mL) and cooled to -30 °C. A solution of LiAlH₄ (1.3 g, 35 mmol) in anhydrous Et₂O (50 mL) was added in small portions to the solution under stirring, and the mixture was occasionally warmed to -10 °C during the addition. After the addition, the solution was cooled to -50 °C and excess EtOAc and water were added. The ethereal layer was washed with H₂O and dried over anhydrous Na₂SO₄. A red-brown solid obtained after concentration of the solution was chromatographed on a silica gel column eluted with Et₂O-*n*-hexane (1:9) 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 CHCl₃.

Diduryldiazomethane (1b). To a solution of bromodurene (2.00 g, 9.4 mmol) in Et₂O (15 mL) was added *n*-BuLi (1.7 M in *n*-hexane, 6.7 mL) at 0 °C under an atmosphere of Ar, and the mixture was refluxed until all the bromide was consumed as judged by GLC. A solution of cyanodurene⁵¹ (1.50 g, 9.4 mmol) in anhydrous Et₂O (10 mL) was added to the lithiated mixture, and the mixture was refluxed overnight. A saturated NH₄Cl solution was added carefully, and the mixture was filtered. The filtrate was extracted with Et₂O, and the organic layer was evaporated to leave crude product, which was purified by silica gel column chromatography eluted with CHCl₃. **Didurylketimine** was obtained in 28% yield as an orange solid: mp 186–189 °C; ¹H NMR (CDCl₃) δ 2.08 (s, 12 H), 2.21 (s, 12 H), 6.97 (s, 2 H). The ketimine (0.76 g, 2.6 mmol) was subjected to nitrosation–LiAlH₄ treatment as described above to afford the diazomethane (**1b**) in 5% yield as an orange solid: mp 157.8–159.6 °C dec; ¹H NMR (CDCl₃) δ 2.03 (s, 12 H), 2.23 (s, 12 H), 6.96 (s, 2 H); IR (KBr) 2038 cm⁻¹.

Decamethyldiphenyldiazomethane (1c-d₆): Decamethyldiphenylketimine was obtained by the reaction of (pentamethylphenyl)lithium prepared from pentamethylbromobenzene⁵² (1.50 g, 6.6 mmol) and *n*-BuLi (1.71 M in *n*-hexane, 4.5 mL) with pentamethylbenzotrile⁵³ (1.14 g, 6.6 mmol) followed by silica gel column chromatography in

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26% yield as yellowish solid: mp 187–189 °C; ¹H NMR (CDCl₃) δ 2.14 (s, 12 H), 2.19 (s, 12H), 2.25 (s, 6 H). The ketimine (0.45 g, 1.4 mmol) was subjected to nitrosation–LiAlH₄ treatment as described above to give the diazomethane (**1c-d₀**) in 16% yield as an orange solid: mp 156–158 °C dec; ¹H NMR (CDCl₃) δ 2.10 (s, 12 H), 2.22 (s, 12 H), 2.26 (s, 6H); IR (KBr) 2032 cm⁻¹.

2,2',6,6'-Tetrakis(trideuteriomethyl)-3,3',4,4',5,5'-hexamethyldiphenyldiazomethane (1c-d₁₂). A mixture of 1,3-dibromo-4,5,6-trimethylbenzene⁵⁴ (34.7 g, 125 mmol) and CuCN (24.5 g, 274 mmol) in anhydrous DMF (150 mL) 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 (40 mL) and H₂O (80 mL) and the precipitate formed was extracted with PhH. The organic layer was washed with a 10% NaCN solution and water, dried, and evaporated. **1,3-Dicyano-4,5,6-trimethylbenzene** was obtained as a brownish solid in 60%: mp 156.2–159.8 °C; ¹H NMR (CDCl₃) δ 2.30 (s, 3 H), 2.57 (s, 6 H), 7.73 (s, 1 H); IR (KBr) 2224 cm⁻¹. A mixture of the dicyanide (14.5 g, 85 mmol), concentrated H₂SO₄ (40 mL), and H₂O (80 mL) was refluxed for 2 days. The usual workup afforded **4,5,6-trimethylisophthalic acid** as a brownish solid in 98% yield, mp 296.0–299.1 °C. A solution of the acid (17.1 g, 82 mmol) and concentrated H₂SO₄ (2 mL) in absolute EtOH (200 mL) was refluxed overnight. Workup, followed by column chromatography on silica gel with CH₂Cl₂–*n*-hexane (1:1), gave **diethyl 4,5,6-trimethylisophthalate** as a yellowish liquid in 40% yield: ¹H NMR (CDCl₃) δ 1.39 (t, *J* = 7.26 Hz, 6 H), 2.27 (s, 3 H), 2.51 (s, 6 H), 4.36 (q, *J* = 7.26 Hz, 4 H), 8.01 (s, 1 H). To a solution of the diester (6.1 g, 23 mmol) in anhydrous THF (30 mL) was added LiAlD₄ (Aldrich, 2.0 g, 47 mmol) at 0 °C with stirring, and the mixture was refluxed overnight. After the usual workup, **1,3-bis(hydroxydideuteriomethyl)-4,5,6-trimethylbenzene** was obtained as white crystals in 90% yield: mp 165.0–167.6 °C; ¹H NMR (CDCl₃) δ 2.24 (s, 3 H), 2.30 (s, 6 H), 3.49 (bs, 2 H), 7.17 (s, 1 H). A solution of the diol (20 mmol) and PBr₃ (7.3 g, 27 mmol) in anhydrous dioxane (20 mL) was stirred overnight at room temperature. The reaction was worked up as usual to obtain **1,3-bis(bromodideuteriomethyl)-4,5,6-trimethylbenzene** in 73% yield as a pale yellow solid: mp 152.8–154.2 °C; ¹H NMR (CDCl₃) δ 2.23 (s, 3 H), 2.32 (s, 6 H), 7.15 (s, 1 H). To a solution of the dibromide (4.7 g, 15 mmol) in anhydrous THF (30 mL) was added LiAlD₄ (0.63 g, 15 mmol) at 0 °C, and the mixture was refluxed overnight. After the usual workup, **1,3-bis(trideuteriomethyl)-4,5,6-trimethylbenzene** was obtained in 99% yield as a white solid: mp 48.3–51.0 °C; ¹H NMR (CDCl₃) δ 2.17 (s, 6 H), 2.21 (s, 3 H), 6.83 (s, 1 H). To a mixture of the hexadeuteriopentamethylbenzene (2.3 g, 15 mmol) and Fe/I₂ (catalytic amount) was added a solution of Br₂ (15 mmol) in CCl₄ (3 mL) at 0 °C, and the mixture was stirred for 1 h at room temperature. The reaction was worked up as usual, and the crude product was Kugelrohr-distilled under reduced pressure at 140–143 °C/2 mmHg to give **1-bromo-2,6-bis(trideuteriomethyl)-3,4,5-trimethylbenzene** in 60% yield as a white solid: mp 125.5–128.0 °C; ¹H NMR (CDCl₃) δ 2.20 (s, 3 H), 2.26 (s, 6 H). A mixture of the 1-bromohexadeuteriopentamethylbenzene (0.46 g, 1.97 mmol) and CuCN (0.54 g, 6 mmol) in anhydrous DMF (5 mL) was refluxed overnight, and the reaction was worked up as described above. The crude product was purified by Kugelrohr distillation at 160–165 °C/3 mmHg to afford **2,6-bis(trideuteriomethyl)-3,4,5-trimethylbenzotrile** in 81% as a white solid: mp 150–152 °C; ¹H NMR (CDCl₃) δ 2.21 (s, 6 H), 2.26 (s, 3 H). **[2,2',6,6'-Tetrakis(trideuteriomethyl)-3,3',4,4',5,5'-hexamethyldiphenyl]ketimine** was obtained by the reaction of [2,6-bis(trideuteriomethyl)-3,4,5-trimethylphenyl]lithium, prepared from the corresponding bromide (0.49 g, 2.1 mmol) with *n*-BuLi (1.7 M in *n*-hexane, 1.59 mL), with 2,6-(CD₃)₂-3,4,5-(CH₃)₃C₆CN followed by column chromatography, in 52% yield as an orange solid: mp 189–192 °C; ¹H NMR (CDCl₃) δ 2.18 (s, 12 H), 2.24 (s, 6 H). The ketimine (0.27 g, 0.81 mmol) was subjected to nitrosation–LiAlH₄ treatment as described above to afford the diazomethane (**1c-d₁₂**) in 11% yield as an orange solid: mp 139–142 °C; ¹H NMR (CDCl₃) δ 2.22 (12 H), 2.26 (6 H); IR (KBr) 2030 cm⁻¹.

[2,2',6,6'-Tetrakis(dideuteriomethyl)-3,3',4,4',5,5'-hexamethyldiphenyldiazomethane (1c-d₈). 1,5-Bis(bromodideuteriomethyl)-

2,3,4-trimethylbenzene (4.7 g, 15 mmol) was treated with LiAlH₄ (0.65 g, 17 mmol) in anhydrous THF (30 mL) as described above to give **1,3-bis(dideuteriomethyl)-4,5,6-trimethylbenzene** in 91% yield as a white solid: mp 47–49 °C; ¹H NMR (CDCl₃) δ 2.17 (s, 6 H), 2.21 (s, 3 H), 2.24 (bs, 2 H), 6.83 (s, 1 H). The bis(dideuteriomethyl)benzene (2.1 g, 14 mmol) was reacted with Br₂ (2.2 g, 14 mmol) in CCl₄ (20 mL) in the presence of Fe/I₂ to afford **1-bromo-2,6-bis(dideuteriomethyl)-2,3,4-trimethylbenzene** in 71% yield as a white solid: mp 142–144 °C; ¹H NMR (CDCl₃) δ 2.20 (s, 3 H), 2.26 (s, 6 H), 2.40 (bs, 2 H). The bromide (1.2 g, 5.2 mmol) was treated with CuCN (0.56 g, 6.3 mmol), and the reaction was worked up as usual to obtain **2,6-bis(dideuteriomethyl)-3,4,5-trimethylbenzotrile** in 74% yield as a white solid: mp 150–153 °C; ¹H NMR (CDCl₃) δ 2.21 (s, 6 H), 2.26 (s, 3 H), 2.44 (bs, 2 H). **[2,2',6,6'-Tetrakis(dideuteriomethyl)-3,3',4,4',5,5'-hexamethyldiphenyl]ketimine** was prepared by the reaction of [2,6-bis(dideuteriomethyl)-3,4,5-trimethylphenyl]lithium, obtained by treating the corresponding bromide (1.11 g, 4.8 mmol) with *n*-BuLi (1.71 M in *n*-hexane, 6.0 mL), with 2,6-(CD₂H)₂-3,4,5-(CH₃)₃C₆CN (0.67 g, 3.8 mmol) followed by column chromatography, in 32% yield as an orange solid: mp 190–193 °C; ¹H NMR (CDCl₃) δ 2.10 (s, 4 H), 2.19 (s, 12 H), 2.25 (s, 6 H). The ketimine (0.40 g, 1.2 mmol) was treated with N₂O₄ followed by LiAlH₄ of the resulting *N*-nitroso compound to produce the diazomethane (**1c-d₈**) in 11% yield as an orange solid: mp 151–153 °C dec; ¹H NMR (CDCl₃) δ 2.06 (s, 4 H), 2.22 (s, 12 H), 2.26 (s, 6 H); IR (KBr) 2034 cm⁻¹.

(2,4,6-Tri-*tert*-butyldiphenyl)diazomethane (13): **(2,4,6-Tri-*tert*-butyldiphenyl)ketimine** was prepared by the reaction of (2,4,6-tri-*tert*-butylphenyl)lithium, obtained by treating the corresponding bromide⁵⁵ (1.00 g, 3.07 mmol) with *n*-butyllithium (1.65 M in *n*-hexane, 2.8 mL), with benzonitrile (0.50 g, 4.9 mmol), followed by column chromatography (silica gel, CHCl₃–*n*-hexane) in 45% yield as a brown solid: ¹H NMR (CDCl₃) δ 1.20 (s, 18 H), 1.36 (s, 9 H), 6.80–7.40 (m, 7 H). The ketimine (0.45 g, 1.3 mmol) was subjected to nitrosation–LiAlH₄ treatment to produce the diazomethane (**13**) in 29% yield as red crystals: mp 80–85 °C; ¹H NMR (CDCl₃) δ 1.34 (s, 18 H), 1.40 (s, 9 H), 6.88–7.60 (m, 7 H); IR (KBr) 2050 cm⁻¹.

[2,4,6-Tris(perdeuterio-*tert*-butyl)diphenyl]diazomethane (13-d₂₇). Treatment of 2,4,6-tris(perdeuterio-*tert*-butyl)benzene (0.90 g, 3.3 mmol) with Br₂ (1.23 g, 7.7 mmol) in P(O)(OMe)₃ (10 mL) in the presence of Fe gave **1-bromo-2,4,6-tris(perdeuterio-*tert*-butyl)benzene** in 70% yield as white prisms: mp 60–63 °C; ¹H NMR (CDCl₃) δ 1.34 (s, 2 H). **[2,4,6-Tris(perdeuterio-*tert*-butyl)diphenyl]ketimine** was prepared by the reaction of [2,4,6-tris(perdeuterio-*tert*-butyl)phenyl]lithium, obtained by the reaction of the corresponding bromide (0.81 g, 2.3 mmol), with *n*-BuLi (1.64 M in *n*-hexane, 2.5 mL), and then with benzonitrile (0.61 g, 5.9 mmol), followed by column chromatography in 25% yield as yellow oil: ¹H NMR (CDCl₃) δ 6.98 (d, *J* = 6.93 Hz, 1 H), 7.19–7.41 (m, 4 H), 7.48 (s, 2 H), 8.47 (d, *J* = 7.92 Hz, 1 H). The ketimine (0.57 mmol) was treated with N₂O₄ followed by LiAlH₄ to afford the diazomethane (**13-d₂₇**) in 21% yield as red crystals: mp 82–83 °C; ¹H NMR (CDCl₃) δ 6.27 (d, *J* = 7.59 Hz, 1 H), 6.90 (d, *J* = 7.26 Hz, 1 H), 6.98 (dd, *J* = 7.26, 7.59 Hz, 1 H), 7.13 (dd, *J* = 7.26, 7.59 Hz, 1 H), 7.36 (dd, *J* = 7.26, 7.59 Hz, 1 H), 7.55 (s, 2 H); IR (KBr) 2042 cm⁻¹.

Irradiation for Product Identification. In a typical run, a solution of the diazo compound (ca. 10 mg) in solvent was placed in a Pyrex tube and irradiated with a high-pressure, 300-W mercury lamp 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 column chromatography or by preparative TLC and identified by NMR and MS. In the irradiation of polymethylated diazomethanes (**1**), the irradiations were conducted at high (~50 °C) and low (~0 °C) temperatures in order to isolate benzocyclobutenes and carbene dimers, respectively.

In this way, products **3b**, **4b**, **5b** (from **1b**), **3c-d₀**, **4c-d₀**, **5c-d₀** (from **1c-d₀**), **3c-d₁₂**, **4c-d₁₂**, **5c-d₁₂** (from **1c-d₁₂**), **3c-d₈**, **4c-d₈**, **4c'-d₈**, **5c-d₈** (from **1c-d₈**), **15** (from **13**), **15-d₂₇** (from **13-d₂₇**), and **10** (from **8**) were isolated and characterized. Spectral data of those compounds are described in the supporting information.

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Irradiation for Analytical Purposes. All irradiations outlined in Tables 1 and 3 were carried out in a Pyrex tube of 5.0 mL capacity. In order to avoid ambiguity in relative yields due to oxidation, the solution was 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- μ s 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 achieved 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 side arm 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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Supporting Information Available: Spectral data for compounds **3b**, **4b**, **5b**, **3c-d₀**, **4c-d₀**, **5c-d₀**, **3c-d₁₂**, **4c-d₁₂**, **5c-d₁₂**, **3c-d₈**, **4c-d₈**, **4c'-d₈**, **5c-d₈**, **15**, **15-d₂₇**, and **10**, and the Arrhenius plots of H/D migration rate constants for **3c-d₀**/**3c-d₁₂** and **13-d₀**/**13-d₂₇** (5 pages). See any current masthead page for ordering and Internet access instructions.

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