

# Persistent Triplet Carbenes

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Radical chemistry has had a unique and interesting history. During the late 1800's, most chemists felt that free radicals could not exist. This extreme view was upset in 1900 when Moses Gomberg announced the discovery of triphenylmethyl, the first moderately stable free radical.<sup>1</sup> Naturally, Gomberg's interpretation of his product as free triphenylmethyl was not generally accepted at first, and most organic chemists had little general interest in radical chemistry in these early years. This changed in the 1930s when the idea of small free radicals as intermediates in high-temperature gas-phase reactions had considerable development and free radicals had been recognized as important species in ordinary liquid-phase organic chemistry. Therefore, the modern history of radical chemistry is usually considered to date from the 1930s. However, Gomberg is still regarded as the "Moses who had led chemists from the wilderness".<sup>2</sup>

The pioneering work of Staudinger in the 1910s on the decomposition of diazo compounds and ketenes contributed much to the recognition of carbenes as a new reactive species. Since radicals were the intermediates *en vogue* in the following decades,<sup>3</sup> they started by being generally regarded as diradicals. Therefore it might not be very surprising that carbene chemistry developed without the upsetting discovery equivalent to the Gomberg's radicals. However, it is rather surprising to note that stable carbenes have attracted little attention until quite recently when two groups have announced the discovery of these species, i.e., phosphinocarbene as a distillable red oil<sup>4</sup> and imidazol-2-ylidene as a crystalline compound with high melting point<sup>5</sup> in 1988 and 1991, respectively. These carbenes are, however, stabilized by heteroatom substituents connected to the carbenic atom and, thus, have singlet ground states. Their electronic configurations are still a topic of debate.<sup>6</sup> Since triplets resemble radicals in terms of reactivity and electronic properties, one may naturally consider that stable triplet carbenes must be the counterpart of the Gomberg's radicals. It is then extremely surprising to note that almost no paper concerning intentional attempts to generate stable carbenes in triplet states under normal conditions has appeared in the literature, except one by Zimmerman

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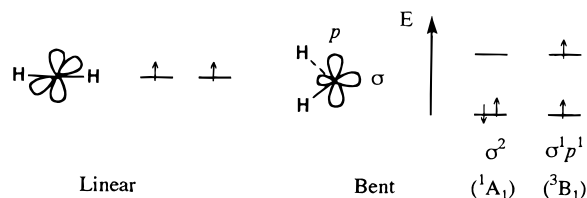


FIGURE 1. Linear methylene with two degenerate p orbitals and bent methylene with  $\sigma$  and p orbitals.

and Paskovich in 1964,<sup>7</sup> at least when we started the work in this field in 1990.

Motivated by this rather naive overview of the historical background, we initiated our study to stabilize triplet carbenes to the extent that they are able to survive under normal conditions. However, as one may easily expect from their highly reactive nature with only two modifiable substituents, it turned out to be a very challenging project. For instance, the lifetime of triplet diphenylcarbene in solution at room temperature is 2 orders of magnitude smaller than that of diphenylmethyl and shorter even than methyl. At present, we are still not able to obtain a triplet carbene which can survive even in a dilute solution for, say, over a period of 1 h. So this is a progress report, not the final summation of our effort to isolate triplet carbenes.

## Relationship between Structure and Ground-State Multiplicities

To design and generate persistent triplet carbenes, we need to know the relationship between structure and stability of both carbene multiplicities. The carbene carbon is linked to two adjacent groups by covalent bonds and possesses two nonbonding electrons which may have antiparallel spins (singlet state) or parallel spins (triplet state). If the carbene unit were linear, it should have two degenerate p orbitals, and Hund's first rule would predict

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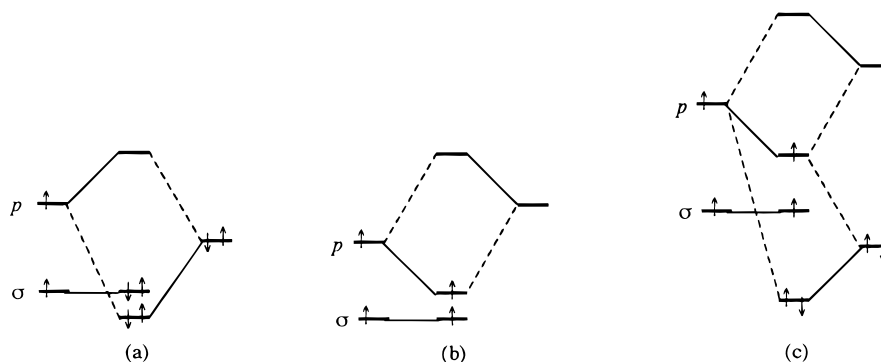


FIGURE 2. Carbene center interacting with (a) an X: substituent, (b) a Z substituent, and (c) a C substituent.

a triplet ground state. If the carbene unit is not linear, the two orbitals will become different. The orbital perpendicular to the plane defined by the three atoms is designated as “p”, while that parallel to this plane is called “ $\sigma$ ”. The  $\sigma$  orbital will acquire s character and thereby become stabilized, while the p remains largely unchanged. Actually most carbenes are not linear and the ground-state multiplicity depends upon the relative energy of the singlet and triplet states. The four lowest energy configurations of carbene have electronic configuration described as  $\sigma^1p^1$ ,  $\sigma^2$ , or  $p^2$ . The electron spins in the  $\sigma^1p^1$  configuration may be paired, a singlet, or parallel to form a triplet, while the  $\sigma^2$  and  $p^2$  configurations must be an electron-paired singlet. Thus, the triplet state has  $\sigma^1p^1$  ( $^3B_1$ ) configuration, while  $\sigma^2$  ( $^1A_1$ ) is generally thought to be the lowest energy configuration for the singlet (Figure 1).

In a singlet state  $\sigma^2$  or  $p^2$  carbene, the electron–electron Coulomb repulsion would be severe, since two electrons are constrained to the same small MO. On the other hand, the triplet configuration is stabilized by relief of the Coulomb repulsion and “exchange repulsion”, although one pays a price for separation of the electrons into different MOs. Thus, the magnitude of the energy difference between the triplet and singlet states (the singlet–triplet splitting,  $\Delta G_{ST}$ ) is roughly equal to the electron–electron repulsion minus the energy required to promote an electron from the  $\sigma$  to the p-nonbonding orbital. In other words, as the energy separation between  $\sigma$  and p states increases, the promotion energy becomes large enough to overcome the repulsion energy, while if the spacing is small, the species will still have a triplet ground state.<sup>8</sup> The small difference between the energies of  $S_0$  and  $T_1$  may easily be overturned by the effects of substituents on the carbene center. The factors which influence the spacing can be analyzed in terms of electronic and steric effects.

**Electronic Effects.** Because of more favorable overlap, the interaction of the carbon 2p orbital with substituent p or  $\pi$  orbitals is expected to dominate. The  $\sigma$  ( $sp^n$ ) orbital which lies in the nodal plane of the substituent p or  $\pi$  orbital will not interact, except more weakly with substituent  $\sigma$  orbitals. Its energy is thus mostly unperturbed by the substituent.

According to Fleming, substituents interacting with a  $\pi$  system can be classified into three classes, namely X: ( $\pi$ -electron donors such as  $-NR_2$ ,  $-OR$ ,  $-SR$ ,  $-F$ ,  $-Cl$ ,  $-Br$ , and  $-I$ ), Z ( $\pi$ -electron acceptors such as  $-COR$ ,  $-SOR$ ,  $-SO_2R$ ,  $-NO$ , and  $-NO_2$ ), and C (conjugating such as alkenes, alkynes, or aryl groups).<sup>9</sup>

As shown in Figure 2a, an X: substituent, which has a p orbital, or other suitable doubly occupied orbital which will interact with the  $\pi$  bond, raises the 2p orbital of the carbene, thereby increasing the separation of the 2p and  $sp^n$  ( $\sigma$ ) orbitals. The ground state of an X-substituted carbene becomes singlet. Many carbenes in this class are known. The most familiar are halo carbenes.

Z and C substituents having a p or  $\pi^*$  orbital and evenly spaced  $\pi$  and  $\pi^*$  orbitals, respectively, on the other hand, either lower the 2p– $sp^n$  gap or leave it about the same as shown in Figure 2b,c. In either case, the ground state for these carbenes is expected to be  $T_1$  although the magnitude of  $\Delta G_{ST}$  may vary. It has been demonstrated by EPR studies that most aryl and diarylcarbenes have triplet ground states.<sup>8,10</sup>

**Steric Effects.** The magnitude of  $\Delta G_{ST}$  is expected to be sensitive to the carbene–carbon bond angle. A linear carbene has two degenerate p orbitals, which is calculated to provide the maximum value of  $\Delta G_{ST}$ . Bending the carbene removes the orbital degeneracy and reduces  $\Delta G_{ST}$ . As the carbene–carbon bond angle is further contracted, the  $\sigma$ -orbital picks up more s character and consequently moves even lower in energy. The smaller the bond angle, the more energy it takes to promote an electron from the  $\sigma$  to the p-orbital and the smaller  $\Delta G_{ST}$  becomes.

This is shown more quantitatively by calculations for methylene. The calculations predict that the energy of singlet methylene will drop below that of the triplet state for carbenes with bond angles less than about  $90^\circ$ . On the other hand, theory also suggests that opening of the central angle strongly destabilizes the singlet state but requires very little additional energy for the triplet, thus making  $\Delta G_{ST}$  larger.<sup>11</sup> In accordance with this prediction, cyclopropenylidene has been shown to have a singlet ground state,<sup>12</sup> while diadamantylidene has a triplet ground state.<sup>13</sup> Although the bond angle effect is not always easily separated from other electronic effects, the

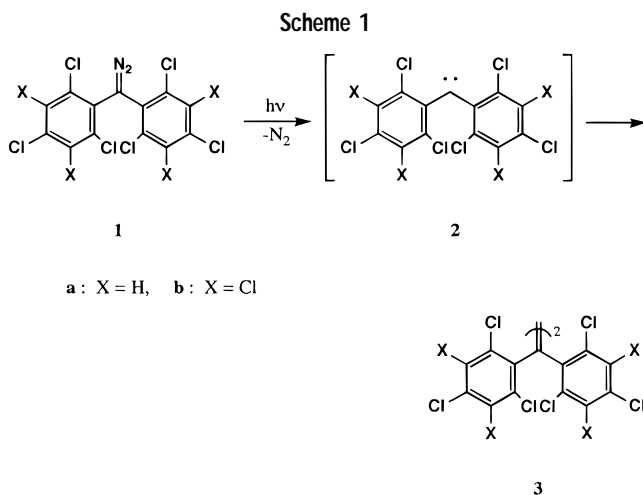
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ground-state multiplicities of these two carbenes are principally determined by the central angle.

### Persistent Triplet Diphenylcarbenes

Examination of the relationship between structure and reactivity thus far reported has shown that electronic effects usually play an important role in stabilizing the singlet state and that the singlet state undergoing thermodynamic stabilization becomes less reactive due to the contribution of ylidic character to such an extent that it can be isolated under ambient conditions. While the triplet states are also stabilized by electronic effects with respect to the singlet state and their reactions through the upper-lying singlet state is suppressed, their intrinsic reactivities are not affected. In this light, kinetic stabilization using steric protectors should be more effective for generating persistent triplet carbenes. Introduction of sterically bulky groups around the carbene center must give an additional important premium for making  $\Delta G_{ST}$  larger by increasing the carbene bond angle. Thus, we have prepared diphenyldiazomethanes bearing a series of substituents primarily at the *ortho* positions and investigated the reactivity of the carbenes generated therefrom.

**Polychlorinated Diphenylcarbenes.** (2,2',4,4',6,6'-Hexachlorodiphenyl)carbene (**2a**) was first generated by Zimmerman and Paskovich in 1964 in their attempts to prepare a hindered divalent species completely unreactive toward external species.<sup>9</sup> Although this carbene was not stable enough to be isolated, it exhibited unusual chemical properties. Thus, in solution at room temperature, this carbene did not react with the parent diazo compound (**1a**) to give azine but dimerized instead to give tetrakis-((2,4,6-trichlorophenyl)ethylene) (**3a**) in 70–80% yield (Scheme 1). The formation of olefinic dimerization products as the main product is rare in the decomposition of diazo compounds, while the formation of ketazine is virtually omnipresent. The authors explained these data by assuming that the hindered diarylmethylenes, having a bent geometry, do not have accessible singlet counterparts since the singlet would require a smaller carbene angle and incur severe aryl–aryl repulsion and that, as a result of severe steric hindrance and consequent resis-

tance to external attack by solvent, the hindered triplet diarylcarbene concentration builds up to the point where dimerization occurs.

While the product analysis studies clearly indicate that the carbene is fairly persistent in its triplet state even in solution at room temperature if not isolated, no further efforts were made to get more quantitative insights into the persistency of the triplet states and/or to extend the lifetime by modification. One would naturally expect that the carbenic center must be more crowded as one introduces four chlorine groups at the *meta* positions which can buttress the four *ortho* chlorine groups.<sup>14,15</sup> Thus, we prepared diphenyldiazomethanes (**1**) having six and 10 chlorine groups and investigated the reactivities of the polychlorinated diphenylcarbenes generated.<sup>16,17</sup>

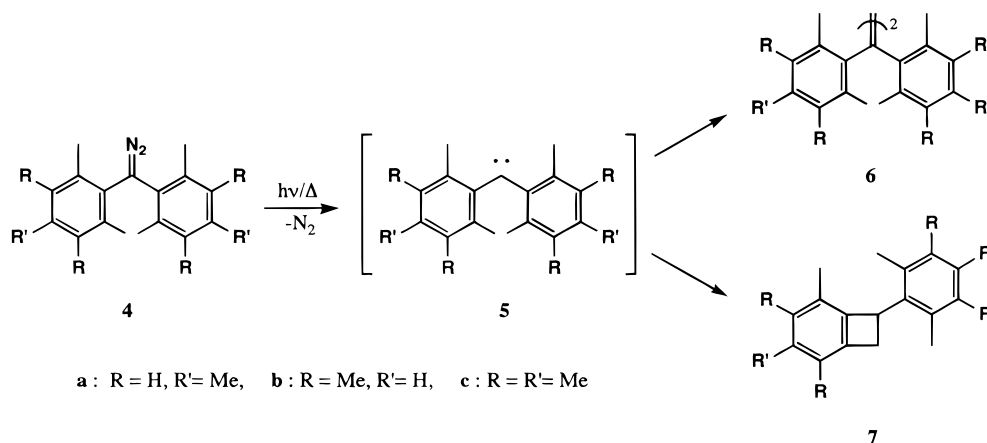
Flash photolysis of a degassed benzene solution of (2,2',4,4',6,6'-hexachlorodiphenyl)diazomethane (**1a**) at room temperature with the output of a xenon flash lamp produced a transient species absorbing at 344 nm which appeared coincident with the xenon pulse and disappeared within ca. 50 ms. The final stable products formed from irradiation of **1a** under these conditions consist mainly of the carbene dimer (**3a**). The transient absorption spectrum is similar to that measured during the photolysis of **1a** in a 2-methyltetrahydrofuran (MTHF) glass at 77 K. The spectrum consists of two identifiable features, a sharp, relatively intense UV band with a maximum at 338 nm and a broad, weak absorption extending from 450 to 500 nm. These absorption bands are stable for hours at 77 K, but warming the sample to room temperature leads to their disappearance. The product analysis of the spent solution again showed the presence of the dimer as the major product. The optical absorption spectra of several triplet aromatic carbenes in frozen media have been assigned. Typically, they consist of an intense UV absorption and a weak visible transition.<sup>10,18</sup> These features are present in the spectrum obtained from the photolysis of **1a**. Moreover, photolysis of **1a** in MTHF at 77 K exhibited EPR signals characteristic of randomly oriented triplet molecules attributable to triplet (hexachlorodiphenyl)carbene (**3a**). On the basis of the low-temperature spectrum and the chemical analysis, the transient product showing an absorption maximum at 344 nm from the photolysis of **1a** in benzene was assigned to triplet (hexachlorodiphenyl)carbene (**3a**).

The decay of the transient absorption due to **3a** was found to be second order, in accordance with the product analysis data, showing that dimerization is the main pathway for **3a** under these conditions. Second-order fitting of the transient absorption data yields  $2k_d/\epsilon I$  values to be  $8.9 \times 10^2 \text{ s}^{-1}$ , where  $k_d$  is the dimerization reaction rate constant,  $\epsilon$  the extinction coefficient, and  $I$  the optical path. The half-life was estimated to be roughly 18 ms

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Scheme 2

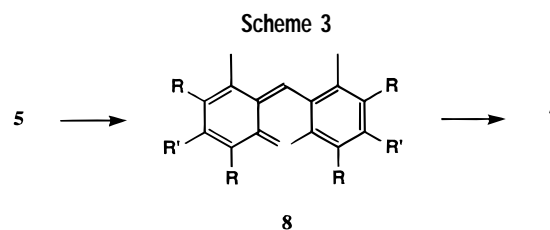
Table 1. Kinetic Data for Polymethylated Diphenylcarbenes Ar<sub>2</sub>C: (5)

carbene	Ar in Ar <sub>2</sub> C:	<i>D</i> (cm <sup>-1</sup> )	<i>E</i> (cm <sup>-1</sup> )	<i>k<sub>i</sub></i> (s <sup>-1</sup> )	<i>t</i> <sub>1/2</sub> (ms)
DPC	C <sub>6</sub> H <sub>5</sub>	0.4053	0.0190		0.002
<b>5a</b>	2,4,6-Me <sub>3</sub> C <sub>6</sub> H <sub>2</sub>	0.3551	0.0116	1.5	160
<b>5b</b>	2,3,5,6-Me <sub>4</sub> C <sub>6</sub> H	0.3805	0.0106	2.2	410
<b>5c</b>	2,3,4,5,6-Me <sub>5</sub> C <sub>6</sub>	0.3636	0.0095	4.1	180

from the decay curve. Similar measurements were done with (perchlorodiphenyl)diazomethane (**1b**), which showed that **32b** also decayed with second-order kinetics with  $2k_i/\epsilon I$  being  $4.2 \times 10^2 \text{ s}^{-1}$  and  $t_{1/2}$  28 ms. The dimerization rate is significantly decreased as four additional chloro groups are introduced at the *meta* position, obviously due to the buttressing effects. Thus **32b** is shown to be 4 orders of magnitude longer-lived than the parent diphenylcarbene. This confirms quantitatively expectations for the role of steric effects in extending the triplet carbene posited in 1964.<sup>7</sup>

**Polymethylated Diphenylcarbenes.** Dimesitylcarbene (DMC, **5a**) was also first generated by Zimmerman and Paskovich in 1964.<sup>9</sup> Although this carbene was also not stable enough to be isolated, the congestion at the carbene center in DMC (**5a**) is again reflected in its unique behavior. Thus, in solution at room temperature, this carbene dimerized to give tetrakis(dimesitylethylene) (**6a**) as the main product and, at high temperature, it decayed by attack at an *o*-methyl group to form benzocyclobutene (**7a**), a reaction that is not observed for (2,2'-dimethyldiphenyl)carbenes under similar conditions (Scheme 2). The chemistry found for **5a** is again in sharp contrast with that found for other diarylcarbenes and is interpreted in terms of steric effects, as described with the hexachloro analogue.

Irradiation of the diazo precursors (**4**) in MTHF glass at 77 K gave a paramagnetic species readily characterized from its EPR spectrum as triplet diphenylcarbenes (**5**). The EPR signals were stable for several hours at this temperature and were analyzed in terms of *E* and *D* values, which are reported in Table 1. Since *E* measures the difference of the magnetic dipole interaction along *x* and *y* axes, it allows estimation of the bond angle at the carbene center, especially when weighted by *D*. Inspection of the data in the table indicates that *E/D* values are considerably smaller than in DPC and steadily decrease as one introduces more methyl groups on the aromatic rings, sug-



gesting that the carbene becomes less bent due to increased steric interaction between the four *o*-methyl groups in going from **5a** to **5b** to **5c**.<sup>19,20</sup>

Optical spectroscopy in the frozen medium gave analogous but more intriguing results. For instance, irradiation of **4b** in MTHF glass at 77 K gave a spectrum consisting of an intense UV band (321 and 335 nm) and a weak visible transition (466 and 495 nm), characteristic of triplet diarylcarbenes. The glassy solution did not exhibit any spectral change for several hours if kept at this temperature, but as the matrix temperature was slowly warmed, a new broad absorption at 375 nm appeared and increased as carbene absorption bands decreased. The species responsible for this new absorption was assigned to *o*-xylylene (**8b**) formed as a result of intramolecular H abstraction of triplet carbene (**5b**). Since the product analysis of the spent solution showed the presence of the dimer (**6b**) and the benzocyclobutene (**7b**), the cyclobutene (**7b**) must be produced from the *o*-xylylene (**8b**) as a result of cyclization.

A similar spectrum was obtained in the photolysis of **4a,c** in MTHF glass at 77 K, where **5a,c** showed two sharp, intense UV bands at 320 and 330 nm and 325 and 338 nm, respectively, and generated the *o*-xylylenes **8a,c**, showing broad absorptions at 390 and 380 nm, respectively.<sup>21</sup>

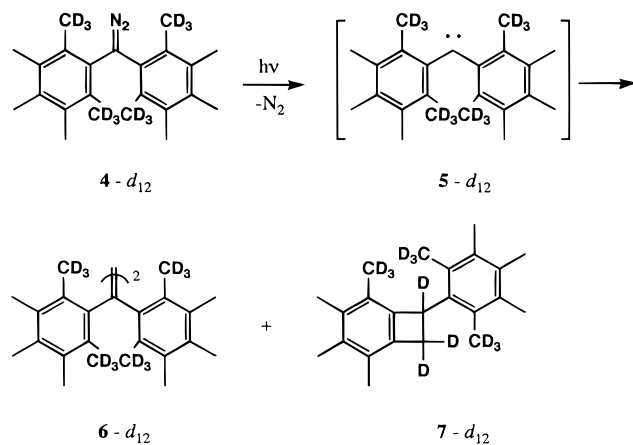
Laser flash photolysis (LFP) of **4b** in a degassed benzene solution at room temperature with a XeCl laser pulse produced a transient species at 320–330 nm coincident with the laser pulse. The decay kinetics of the transients indicate that the absorption at 330 nm decays within 1 s to generate a new species with an absorption

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Scheme 4



maximum around 370 nm, which is too long-lived to be monitored by our system. Product analysis of the spent solution again showed the presence of **6b** and **7b**. On the basis of the low-temperature spectrum coupled with chemical analysis, the initially formed transient with a maximum at 340 nm was assigned to carbene **5b**, while the second to *o*-xylylene **8b**.

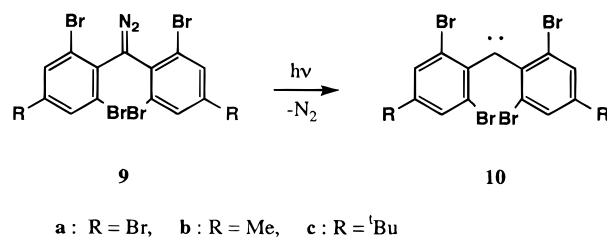
The decay kinetics also shows that the decay of **5b** is kinetically correlated with the growth of **8b**; the decay rate was determined to be  $2.1 \pm 0.1 \text{ s}^{-1}$ , while the growth ( $k_i$ ) was  $2.2 \text{ s}^{-1}$ . From the decay curve, the half-life ( $t_{1/2}$ ) of **5b** was estimated to be ca. 410 ms, while the lifetime based on  $k_i$  was determined to be 455 ms. Similar measurements were done for the carbenes **5a,c**, and values of  $k_i$  and  $t_{1/2}$  are summarized in Table 1.<sup>19</sup>

Thus, triplet dimesitylcarbene (**5a**) is shown to be some 5 orders of magnitude longer-lived than the parent DPC, thus confirming again expectations for the role of a steric effect in persistency of triplet carbenes predicted 30 years ago.<sup>7</sup> As more methyl groups are introduced to the aromatic rings, the carbenic center is more tightly blocked by the four *o*-methyl groups toward external reagents. Thus, didurylcarbene (**5b**) is shown to be longer-lived than **5a**. On the other hand, the steady increase in  $k_i$  in going from **5a** to **5c** clearly suggests that, as the *o*-methyl groups are brought much closer to the carbenic center by the buttressing methyl groups, the carbenic center comes to interact more easily with the *o*-methyl groups. Thus, (decamethyldiphenyl)carbene (**5c**) comes to be trapped by the *o*-methyl groups to generate *o*-quinodimethane (**8**) more efficiently and hence becomes shorter-lived again.

The above study reveals that polymethylated diphenylcarbenes (**5**) are exceptionally long-lived for arylcarbenes, although they are still not persistent enough to be isolated. The buttressing effects are shown to be effective in strengthening the *ortho* effect that protects the reactive center. However, in the case of a methyl group which is potentially reactive toward carbenes, those in the *ortho* position become more efficient intramolecular quenchers of the carbene as a result of the buttressing group, thus making the carbene less persistent again. One of the best ways to quench this process is to replace the hydrogens at the *o*-methyl groups with deuterium.

LFP of **4c-d<sub>12</sub>** in a degassed benzene at 20 °C resulted in essentially the same transient absorption bands as those

Scheme 5



observed for the protio analogue (**4c-d<sub>0</sub>**); a transient showing a strong absorption at 340 nm due to deuterated triplet carbene (**5c-d<sub>12</sub>**) appeared coincident with the XeCl pulse and a second transient at 377 nm due to the deuterated *o*-quinodimethane (**8c-d<sub>12</sub>**) appeared as the initial absorption decayed. However, the kinetic behaviors are distinctly different between these two carbenes. Thus, the growth rate and optical yield of the deuterated quinodimethane were very small compared to those of the protio analogue, and the decay of **5c-d<sub>12</sub>** was found not to be fit by a single exponential, as opposed to the almost completely unimolecular decay of **5c**. This is in accordance with the product analysis data that **5c-d<sub>12</sub>** gave the carbenic dimer as main product, while **5c-d<sub>0</sub>** produced the cyclobutene almost exclusively. The half-life was estimated from the decay curve to be 1.1 s in benzene at 20 °C.<sup>19</sup>

**Polybrominated Diphenylcarbenes.** Among the protecting groups thus far examined, the methyl group is most effective in protecting the carbenic center. However, when more methyl groups are introduced to the *meta* and *para* positions, the carbenic center is more easily trapped by the *o*-methyl groups which are brought closer to the carbene center. The carbene therefore becomes shorter-lived again. To realize a much longer-lived triplet DPC, we needed to explore a new protecting group which must be bigger and less reactive than the methyl group. Bromine atoms appear to be promising as a protecting group toward the triplet carbene center because, while the van der Waals radius is similar to that of methyl (Br, 195 pm; Me, 200 pm), the C–Br bond length (185 pm) is longer than the C–C(Me) (150 pm),<sup>22</sup> suggesting that the *o*-bromo groups must overhang the reactive site more effectively. Moreover, C–halogen bonds are usually reactive toward singlet carbenes to form halonium ylides, but not with the triplet state.<sup>23</sup> In addition, the value of  $\xi_l$ , which gives a measure of the strength of the spin–orbit interaction, is increased dramatically in going from chlorine (370 cm<sup>-1</sup>) to bromine (2460 cm<sup>-1</sup>),<sup>24</sup> suggesting that the intersystem crossing from the nascent singlet carbene to the triplet should be accelerated by introducing a bromine atom.

Irradiation of **9a** in MTHF glass at 4 K gave a fine-structure EPR line shape characteristic of randomly oriented triplet molecules with a large  $D$  value attributable to triplet carbene **10a** ( $D = 0.3598 \text{ cm}^{-1}$ ,  $E = 0.0295 \text{ cm}^{-1}$ ). The EPR signals not only were stable at this temperature but survived even at 130 K. However, as the samples were

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**Table 2. Kinetic Parameters for Polybrominated Diphenylcarbenes Ar<sub>2</sub>C: (10)**

carbene	Ar in Ar <sub>2</sub> C:	<i>D</i> (cm <sup>-1</sup> )	<i>E</i> (cm <sup>-1</sup> )	<i>2k/εI</i> (s <sup>-1</sup> )	<i>t</i> <sub>1/2</sub> (s)	<i>k</i> <sub>q</sub> (M <sup>-1</sup> s <sup>-1</sup> )	
						<i>k</i> <sub>O<sub>2</sub></sub>	<i>k</i> <sub>CHD</sub>
<b>10a</b>	2,4,6-Br <sub>3</sub> C <sub>6</sub> H <sub>2</sub>	0.3958	0.0295	8.9	1.0	1.1 × 10 <sup>7</sup>	7.4 × 10 <sup>2</sup>
<b>10b</b>	2,6-Br <sub>2</sub> -4-MeC <sub>6</sub> H <sub>2</sub>	0.3957	0.0275		0.22	2.3 × 10 <sup>7</sup>	3.7 × 10 <sup>2</sup>
<b>10c</b>	2,6-Br <sub>2</sub> -4 <sup>t</sup> BuC <sub>6</sub> H <sub>2</sub>	0.3966	0.0311	0.35	16	2.1 × 10 <sup>7</sup>	5.3 × 10 <sup>2</sup>

warmed, the *x* and *y* lines of the spectrum moved closer together, resulting in an essentially zero *E* value (*D* = 0.3656 cm<sup>-1</sup>, *E* = 0 cm<sup>-1</sup>). Cooling the sample did not reverse this change. This indicates that, on warming, the carbene relaxes to a structure with an expanded C–C angle, presumably to gain relief from steric compression. Similar geometrical changes upon annealing the matrix have been observed, especially for sterically congested carbenes.<sup>25,26</sup> Thus, when a carbene is formed at low temperature, the rigidity of the matrix prevents it from assuming its minimum energy geometry. However, when the matrix softens on annealing, the carbene relaxes to a more stable structure. Photolysis of single crystals of **9a** at liquid helium temperature also generated a fine-structure EPR spectra due to a typical triplet diarylcarbene with a large *D* value. The signals survived up to room temperature without loss of intensity, considering the effect of the Boltzmann factor, for months. This is the first stable triplet carbene in the crystal state at room temperature.<sup>27</sup>

LFP of **9a** in a degassed benzene solution at room temperature with a 308 nm pulse from a XeCl excimer laser produced a transient species showing a strong absorption at 353 nm and a weak absorption extending from 420 to 500 nm, which is similar to that measured during the photolysis of **9a** in MTHF matrixes at 77 K. The transient signals appeared coincident with the pulse and disappeared rather gradually, persisting for at least 30 s under these conditions. Decay of triplet **10a** is second order (*2k/εI* = 8.9 s<sup>-1</sup>). From the decay curve, the rough half-life of **10a** is estimated to be 1 ± 0.1 s.<sup>27</sup>

Interestingly, the lifetime of triplet *ortho*-tetrabrominated diphenylcarbenes in benzene is found to be affected by the substituents at the *para* positions in a striking manner. Thus, the half-life of the triplet state was decreased when the substituents at *para* positions are changed from bromo to methyl groups, but increased rather dramatically when more bulky groups such as *tert*-butyl groups are introduced. Thus, in the case of (2,2',6,6'-tetrabromo-4,4'-di-*tert*-butyldiphenyl)carbene (**10c**), the transient absorption survived over several minutes in degassed benzene at room temperature and the half-life was estimated to be 16 s. Surprisingly, however, the reactivities of these highly long-lived triplet carbenes toward oxygen and 1,4-cyclohexadiene (CHD) were not changed so dramatically (Table 2). To obtain insight into the effect of *para* substituents on the structure of these (tetrabromodiphenyl)carbenes, ESR spectra were mea-

sured. Zero field splitting parameters summarized in Table 2 clearly suggest that changes of substituents at the *para* positions result in almost no measurable change in their structures.<sup>28</sup>

**Summarizing Discussion.** These studies have shown that introduction of four substituents at all the *ortho* positions of diphenylcarbenes is a very effective way to increase the lifetime of the triplet states without resulting in an undesirable decrease in Δ*G*<sub>ST</sub>. The extent of stabilization is, of course, not only dependent upon the van der Waals radius and bond length but also on the reactivity of the substituent. A bromine group is found to be the most effective kinetic stabilizer for the triplet carbene center. In light of the fact that C–F bonds are generally believed to be the least reactive bonds toward carbenes, trifluoromethyl groups look to be the most effective and hence attractive stabilizer for triplet carbene.

Effects of *meta* substituents on the reactivity of 1,2-disubstituted benzenes are usually explained in terms of a steric effect exerted on a functional group by a more distant substituent through another immediately adjoining substituent (buttressing effect). These effects are shown to be effective in strengthening the *ortho* effects.

Substituents at *para* positions are usually considered to exert little steric effects to strengthen the *ortho* effects, although the isodesmic reactions suggest that the interaction with the *ortho* substituents is certainly not zero.<sup>29</sup> Peculiar effects of *p*-alkyl groups on the reactivity of (2,2',6,6'-tetrabromodiphenyl)carbenes (**10**) are especially noteworthy; large effects on the lifetime in benzene contrast with small effects on *k*<sub>CHD</sub> and *k*<sub>O<sub>2</sub></sub>. The fact that the reactions with highly efficient triplet trapping reagents are little affected by *para* substituents can be interpreted to mean that *para* substituents exert little effect on the steric congestion around the carbene center. Since benzene is generally recognized as a very unreactive solvent, especially for triplet carbenes, and hence the hindered triplet diarylcarbene concentration must build up, it is highly likely that the most reactive counterparts under these conditions must be the triplet carbenes themselves. However, the products obtained from the photolysis mixture in benzene consist of a highly complex mixture containing only small amounts of carbene dimers. This is in marked contrast with that observed in the similar reaction of the (hexachlorodiphenyl)carbenes (**2a**) and (hexamethyldiphenyl)carbenes (**5a**), which produce the corresponding dimers as main products. It is then probable that simple dimerization of (hexabromodiphenyl)carbene at the carbenic center must suffer from severe steric repulsion and therefore the carbene is forced to react at the aromatic rings where spin can be delocalized. In this light, it is important to note that trityl radicals are

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known to undergo either "head-to-tail" or methyl-*para*, or "tail-to-tail" or *para-para* couplings depending on the substitution patterns.<sup>30</sup> Thus, it is likely that the brominated diphenylcarbenes also undergo similar couplings. The coupling reactions of trityl radicals are not suppressed by "reactive" *para* substituents. The anomalous reactivity of halogen at the *para* position is noted, for instance; (*p*-bromophenyl)diphenylmethyl undergoes methyl-*para* coupling.<sup>31</sup> On the other hand, tri-*p*-tolylmethyl undergoes rapid disproportionation to yield tris-*p*-tolylmethane and a quinoid structure which rapidly polymerizes.<sup>32</sup> However, the coupling at the *para* position is retarded by

*tert*-butyl groups not only at the *para*<sup>33</sup> but also at *meta* positions.<sup>34</sup> Thus, rather large effects of *tert*-butyl groups at the *para* positions on the lifetime of the brominated diphenylcarbenes compared to that of bromo and methyl groups in benzene are compatible with the effect of substituents observed in the coupling reaction of trityl radicals.

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